

Light-to-Chemical Energy Conversion with Surface Engineered Quantum Dots

विद्या वाचस्पति की
उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

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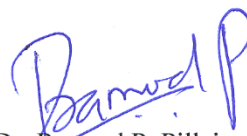
December 2023

Dedicated to,
♣Maa, ♣Baba, Nanu and Jethu

Certificate

Certified that the work incorporated in the thesis entitled '*Light-to-Chemical Energy Conversion with Surface Engineered Quantum Dots*' Submitted by Indra Narayan Chakraborty was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.

Date: 13/12/2023


Dr. Pramod P. Pillai
(Thesis Supervisor)

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Thesis Synopsis

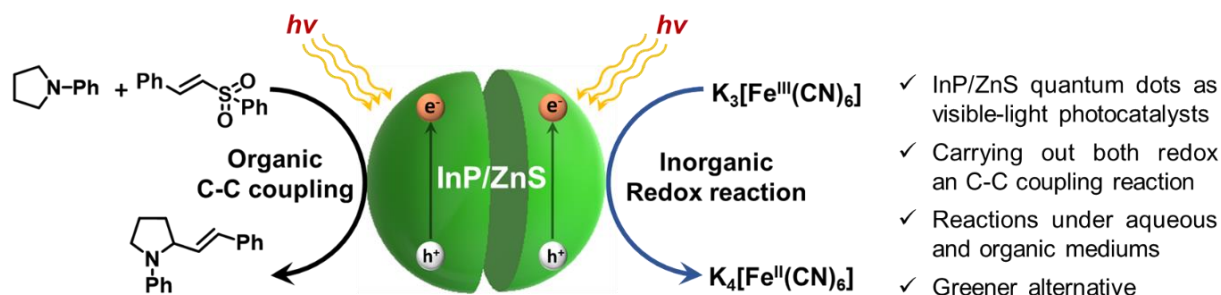
The unique optoelectronic properties of three-dimensionally confined semiconductor nanocrystals or quantum dots (QDs) have rendered them a special place in light harvesting studies, including photocatalysis. As a result, QDs have emerged as potential photocatalysts towards various classes of chemical transformations, such as generation of solar fuels, valorization of biomasses, synthetic organic transformations etc. Interestingly, unlike molecular photocatalysts, along with size-tuneable core optoelectronic properties, QDs exhibit rich and highly modular surface properties as well. By strategically modifying the surface with suitable ligand chemistry, it's possible to fine control the interaction between the QD photocatalysts and the reactant molecules. Such precise regulation of the catalyst-reactant interactions results in the emergence of exceptional and unprecedented behaviours, particularly in terms of the efficiency of the photocatalytic processes. Moreover, besides the traditional photophysical processes, QDs also exhibit exciting non-trivial photophysical processes (such as triplet-triplet annihilation, Auger based recombination, two-photon absorption etc.), which in principle can be advantageous if employed into the field of photocatalysis to perform challenging chemical reactions under milder reaction conditions. However, the aspects of both the surface directed as well as the non-trivial processes still remain elusive in the area of QD photocatalysis, and only dedicated studies in these directions will install the realisation of the vast importance of QDs in photocatalysis in its full potential. Thus, the present thesis focuses on developing a strategy to systematically modulating both the core optoelectronic as well as the surface ligand directed properties of the QDs to carry out a wide variety of chemical transformations under visible-light. Furthermore, efforts were made to investigate the stated objectives with environmentally friendly QDs (e.g. indium phosphide (InP) QDs), wherever possible, thereby enhancing the sustainability aspect of the QD photocatalysis.

The thesis starts with a brief perspective on the rise and the evolution of photocatalysis along with the introduction of the different classes of photocatalyst materials over several decades. This was followed by the rationale behind our choice of QDs as photocatalysts and the superior advantages of QDs arising from the quantum confinement effect. Next, we briefly summarized the development in the area of QD photocatalysis and the design principles that can be adopted to establish QDs as a versatile photocatalyst. Finally, we showcased our idea to systematically modulate both the core as well as the surface ligand directed properties of the QDs to enable a

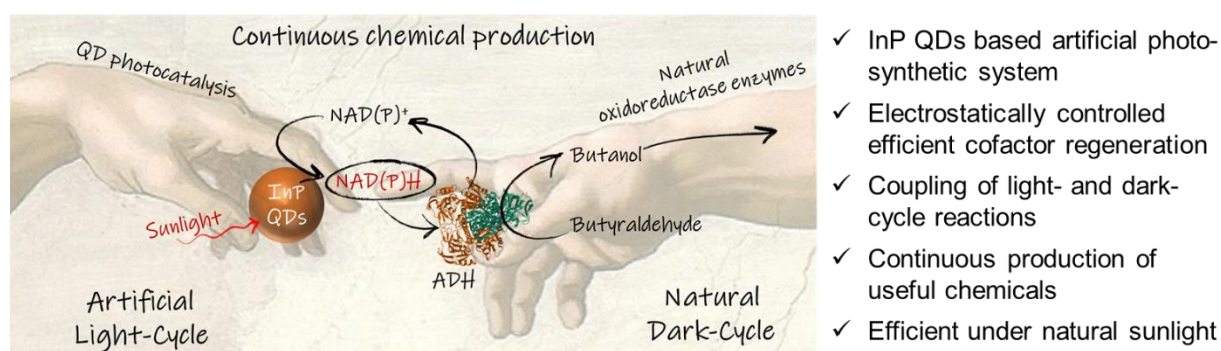
wide variety of photocatalytic as well as photobiocatalytic transformations, including the reactions beyond the redox potential of the QDs, under visible-light excitation.

In the second Chapter, we have mentioned all the chemicals and materials used in the whole thesis, all the experimental procedures as well as the instrumentation techniques used, in detail. We also have thoroughly discussed the synthetic and the surface engineering protocols of all the different QD photocatalysts used in the consecutive Chapters.

The third Chapter, summarizes our efforts in establishing the potency of InP/ZnS QDs towards independently photocatalyzing two important classes of reactions, namely, metal-centred redox and organic C-C coupling reactions. The surface chemistry of the QDs were successfully tuned to stabilize them in polar aqueous medium as well as in non-polar organic solvents. The QD was effective in photocatalyzing the one electron reduction of ferricyanide to ferrocyanide (in water) in presence of a sacrificial reagent, with high photoconversion yield (~70%). We could also address the aspect of catalyst recyclability by introducing a InP/ZnS QD coated dip-catalyst system, achieving the ferricyanide reduction reaction upto 5 cycles of photocatalytic reaction without any appreciable decrease in catalytic efficiency. The ability of InP/ZnS QD was proved to exclusively photocatalyze a C-C coupling reaction (in organic solvent), between 1-phenyl pyrrolidine (PhPyr) and phenyl-trans-styryl sulfone (PhSO₂), with decent yield of ~52% under visible-light, without the aid of any co-catalysts or sacrificial reagents. A good overlap between the action spectra and absorption of QD validates their active participation in these photocatalyzed reactions. Efficient photocatalysis under white-light illumination proves the suitability of InP/ZnS QDs to directly harvest solar radiation as well. An effort was also demonstrated to understand the mechanistic details of the C-C coupling reaction via a set of photophysical quenching experiments with the QDs and the reactants. This was one of the first works which established InP-based QDs as a potential photocatalyst and a ‘greener’ alternative for a variety of chemical transformations.

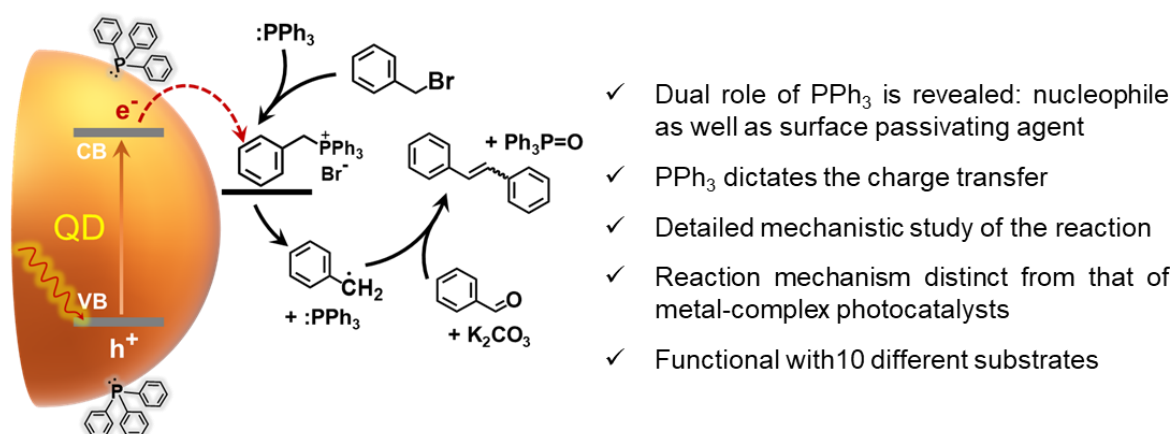


In the fourth Chapter, we could employ our established InP QD photocatalysts to design a complex artificial photosynthetic system, which was efficient in mimicking the photosynthetic light cycle, and upon its successful coupling with enzymatic dark cycle, enabled a continuous synthesis of useful chemicals. For this, a redox shuttling species is necessary to couple the light and the dark cycles. Learning from the nature, we chose the redox-active nicotinamide cofactors that can shuttle between the light and dark cycles to establish an efficient artificial photosynthetic system for the continuous production of useful chemicals. In this direction, we report the design of an artificial photosynthetic system for the continuous production of butanol via the constant photoregeneration and consumption of nicotinamide cofactors, powered by indium phosphide quantum dot (InP QD) photocatalyst and alcohol dehydrogenase (ADH) enzyme, respectively. A strong electrostatic attraction between the oppositely charged InP QDs and electron mediators significantly enhanced the charge extraction and utilization processes, enabling a fast (~ 30 min, with a turn-over-frequency of $\sim 1333\text{ h}^{-1}$), quantitative ($>99\%$), and selective photoregeneration of enzymatically active nicotinamide cofactors in the light cycle. These photoregenerated nicotinamide cofactors were further coupled in the dark cycle to trigger the ADH oxidoreductase enzyme for the production of butanol, via sequential as well as simultaneous light-dark cycles. The amount of butanol produced under simultaneous light-dark cycles was higher than the stoichiometric limit, proving the constant regeneration and consumption of nicotinamide cofactors in the integrated light and dark cycles, respectively, as seen in photosynthesis.



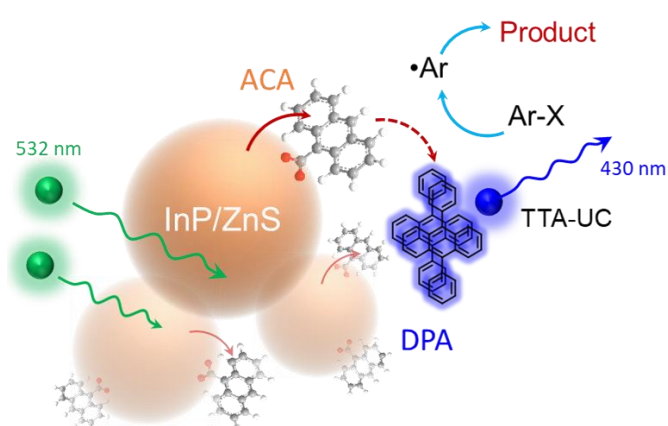
In the fifth Chapter, we have further expanded the scope of the QD photocatalysts towards a different class of photocatalytic organic transformation. In that process, we also focused on understanding the role of surface passivating agents in a photocatalytic transformation, and also studied their effect on the associated charge transfer mechanisms. In that direction, we chose a series of photocatalytic olefination reactions in presence of QDs under visible-light

irradiation at room temperature. Here, we explored the role of triphenylphosphine, present as a reactant in the photocatalytic reaction, in dictating the photoinduced charge transfer pathway using detailed spectroscopic and electrochemical analysis. The dual role of triphenylphosphine – both as surface passivating agent as well as a nucleophile – turned out to be decisive in directing the charge transfer process from the QD to the reactant. The in-situ generated benzyl triphenylphosphonium bromide salt was accepting the electrons from the photoexcited QDs, thereby initiating the catalytic olefination reaction in presence of benzaldehyde. The QD photocatalyzed olefination was demonstrated with formaldehydes as well, resulting in the formation of industrially relevant terminal alkene, such as styrene. Moreover, the environmentally friendly InP QD too photocatalyzed the olefination reaction under mild reaction conditions, which proves the practical suitability of our study. This work presents an attractive and efficient way to introduce double bonds in organic molecules using QDs and visible-light at room temperature.



The sixth Chapter of the thesis summarizes our efforts to find out a sustainable way to carry out photocatalytic transformations with higher redox potentials under visible-light irradiation in presence of InP based QDs. This feat was achieved via a photonic upconversion process based on triplet-triplet annihilation pathway (TTA-UC) sensitized by appropriately designed InP/ZnS QDs. In this process, two low energy photons, via appropriate triplet sensitization and sequential triplet energy transfer process, can get upconverted to a high energy singlet state and eventually emit a higher energy photon as an output. As a result of the annihilation process, the generated high-energy singlet state can directly participate in a charge transfer mechanism to carry out challenging photocatalytic transformations, that are beyond the redox limit of the used QD sensitizer alone. The specific advantages of QDs over the molecular sensitizers comes from the very low energy difference between the singlet and the triplet excited states (<10

meV) of the QDs leading to a greater photonic energy gain for the TTA-UC process. In this work, environmentally friendly InP/ZnS QDs based green-to-blue TTA-UC system was introduced with an excellent upconversion quantum yield of ~5 %, and an achieved apparent anti-Stokes shift (Δ_{as}) of 0.55 eV. The efficient UC process was further introduced to carry out challenging dehalogenation and coupling reactions with excellent yields (~85%) using an aryl bromide as substrate. Upon activation via TTA-UC, the formed aryl radicals were further employed to execute an efficient photo-polymerization reaction, with visible-light. Moreover, thorough photophysical analysis of the reaction mechanism revealed intricate details about the sequence of reductive and oxidative quenching pathways of the TTA-UC driven photoredox transformation.

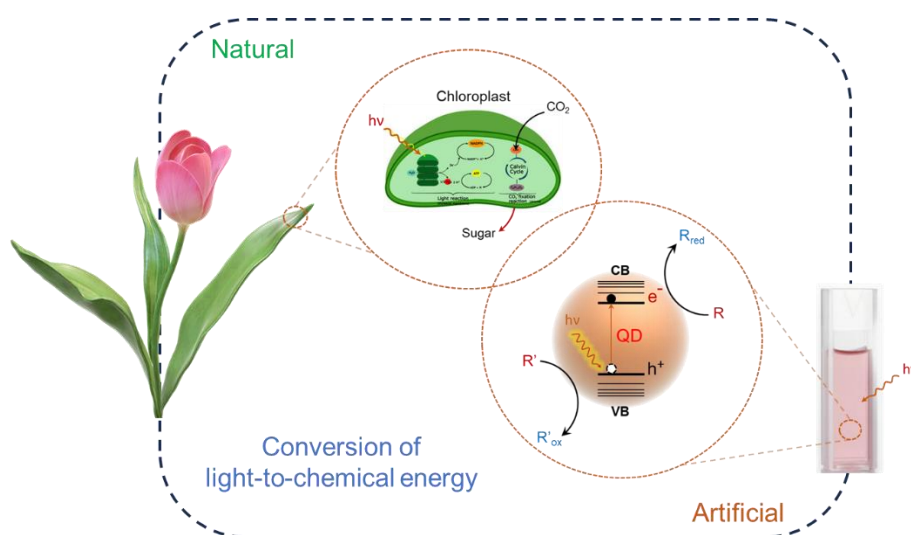


- ✓ A InP/ZnS based versatile photonic upconversion system
- ✓ Application of QD based TTA to photocatalysis
- ✓ Reaction of higher potential with the visible light
- ✓ Photocatalytic transformation as well as photo-polymerization
- ✓ Further extendable to Vis-UV and NIR-Vis ranges

In summary, the present thesis effectively demonstrates a practical design strategy for environmentally friendly QD based photocatalysts. The strategy involves a systematic modulation of both the core and the surface properties, enabling a wide variety of chemical as well as biochemical transformations occurring within, or even beyond the redox potentials of the QDs, under visible-light irradiations.

Chapter – 1

Introduction to Light-Harvesting and Photocatalysis with Surface-Engineered Quantum Dots



Part of this Chapter has been adapted from the following paper with permission. Copyright 2021, Royal Society of Chemistry: Chakraborty, I. N.; Roy, P.; Rao, A.; Devatha, G.; Roy, S.; Pillai, P. P. The Unconventional Role of Surface Ligands in Dictating the Light Harvesting Properties of Quantum Dots. *J. Mater. Chem. A* **2021**, 9, 7422–7457.

1.1. Introduction

Harnessing the solar energy into fuel molecules via chemical transformations represents one of the most promising approaches towards achieving sustainability in the synthesis of molecules and materials.¹⁻⁷ This forms the basis of the area of photocatalysis. However, the underlying inspiration for these processes has consistently been drawn from the natural phenomenon of photosynthesis.¹⁻⁹ In nature, solar energy is harvested and stored in green plants through the ubiquitous process of photosynthesis. In that process, a tandem action of natural light harvesting components along with efficient enzymes carry out the overall solar to biomass conversion.¹⁰⁻¹² The overall process is governed by a series of unidirectional energy and electron transfer processes (as depicted in the Z-scheme of photosynthesis; **Figure 1.1**) that transfers the absorbed photonic energy from the photosystems to the associated reaction centres to generate energy-dense intermediates that trigger the Calvin cycle leading to the continuous formation of carbohydrates.¹³⁻¹⁴ The carbohydrates then get stored in the form of food in the plants and eventually takes the role of the primary source of energy to most of the living creatures.

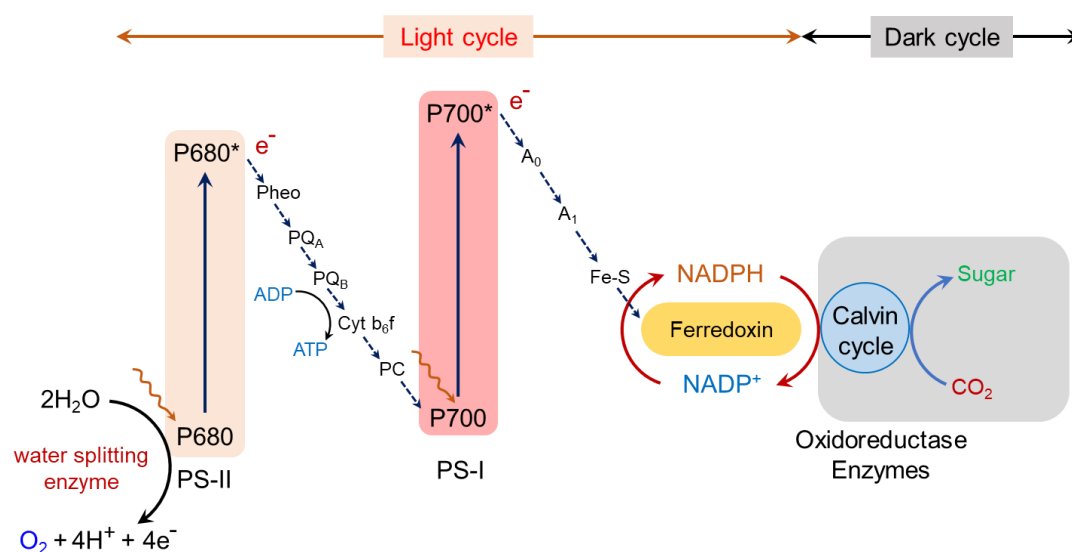


Figure 1.1. Schematic representation of Z-scheme found in natural photosynthesis. The product formed in light cycle triggers the oxidoreductase enzymes to carry out dark cycle reaction finally generating carbohydrates. Redrawn with permission from the ref. 14. Copyright: 2017, Springer Nature.

A successful mimic of such versatile photosynthetic system in a grand scale is highly desirable in terms of effective harvesting and conversion of solar energy in the form of useful chemicals.¹⁻⁹ In other words, the goal is to transform the oblivious solar energy to a more useable form such as, chemical energy. One of the most viable ways to achieve that goal is via

mimicking the fundamental processes and steps of photosynthesis, using an appropriate photocatalyst material.^{7,15-17} In order to design an efficient artificial photosynthetic system, the ideal design should combine the important aspects of both light as well as dark cycles reactions.¹⁸⁻²² Hence, the overall system should both be simultaneously active under sunlight, as well as should be able to carry out specific catalytic transformations in dark. In many of the cases, all these important aspects of photosynthesis might not be easy to achieve using a single system or material, and hence, a multi-component system would be essential to put in place, where different champion systems would be coupled by the means of precise intersystem interactions.²³⁻²⁶ For example, one of the efficient ways to mimic such processes lies in synergistically coupling the working components from both artificial (e.g., light harvesting or photocatalyst molecules/materials), as well as the natural resources (e.g., enzymes or whole cells).²⁷⁻³¹ In that case, under an optimized scenario, the photocatalyst material will conduct the photoinduced electron or energy transfer step under visible-light, generating a reactive intermediate/initiator, which will initiate the biocatalytic transformations leveraging the presence of the natural enzymes. Hence, a thoughtful choice and combination of the photocatalyst, biocatalyst and the initiator is the way forward to efficiently couple the light and the dark cycles of photosynthesis in artificial systems leading to the realisation of artificial photosynthesis.³¹⁻⁴⁴

1.2. Rise and evolution of photocatalysis

The idea of photocatalysis was first introduced more than a hundred years ago (in 1911) in two independent reports by Eibner and Kozak. In the first case, the bleaching of Prussian blue dye was reported in presence of ZnO under photoirradiation,⁴⁵ whereas, the degradation of oxalic acid under irradiation in presence of uranyl (UO_2^+) salts as photocatalyst was reported in the later work.⁴⁶ It is to be noted that the term '*photocatalysis*' was first coined in the title of the later work by Kozak.^{46,47} Following that, in 1921, Baly, Barker and co-workers established the photocatalytic production of formaldehyde from CO_2 and water under visible-light, using colloidal uranium salts and ferric hydroxides as photocatalysts.⁴⁸ Slowly, the metal oxides emerged as a potential photocatalyst material and the process of photocatalysis started to evolve under the diverse topics including the reduction of Ag^+ salts,⁴⁹ degradation of organic dyes,⁵⁰ etc. Later, in the late 1930s, TiO_2 appeared as a promising photocatalyst and was implemented for dye degradation in presence of oxygen and UV irradiation.⁵¹ The introduction of TiO_2

formed the basis of heterogeneous photocatalysis, which followed an exploration, for next couple of decades, majorly limited to the fundamental interests of the process.⁵² Importantly, about this time, the role of electrons and holes in photocatalysis was elucidated as well.⁵³ But the breakthrough in the field of photocatalysis came in 1972 when Fujishima and Honda reported the photo-electrochemical water splitting using a TiO_2 photoanode and platinum cathode under UV irradiation.⁵⁴ The absorption of UV light by the TiO_2 electrode resulted in the flow of electrons from the anode to the platinum cathode, leading to the generation of hydrogen gas (**Figure 1.2**) This work not only opened up an economical way of hydrogen fuel production, but also opened up the avenue for greener photocatalytic pathway applicable to a wider range of chemical transformations. Later, noble metals were introduced into this system resulting in an enchantment in the efficiency as well as removal of requirement of external voltage from the previously designed photoelectrochemical process.⁵⁵

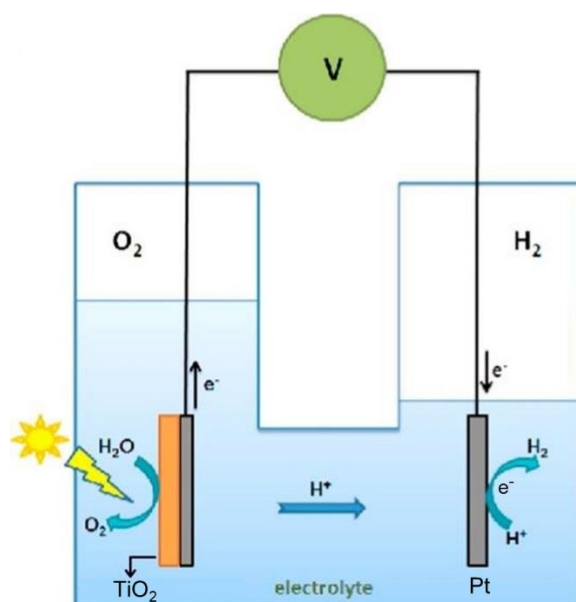


Figure 1.2. A schematic representation of the photoelectrochemical water splitting using TiO_2 photoanode and Pt cathode under photoirradiation. Redrawn with permission from ref. 54. Copyright: 1972, Springer Nature.

1.3. Fundamentals of photocatalysis

1.3.1. Fundamental processes involved in photocatalysis and the parameters defining them

The fundamental process of photocatalysis involves the generation of charge carriers upon appropriate photoexcitation followed by their use to carry out a chemical transformation. A fundamental analysis of the overall process of photocatalysis reveals that it is constituted of three major components:⁵⁷

- Photoexcitation or the generation of the charge carriers
- Separation of the charge carriers in the photocatalyst
- Charge utilization or transfer of the charge carriers out of the photocatalyst

Key steps associated to photocatalysis

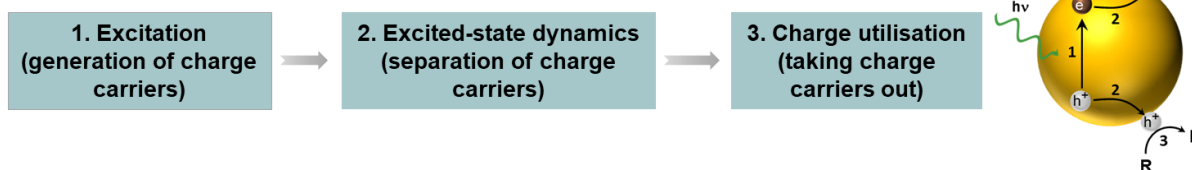


Figure 1.3. Schematics showing the fundamental steps associated to the process of photocatalysis.

With the report by Fujishima and Honda, the general interest in the area of photocatalysis saw a steep surge, and soon the process was expanded to a wider class of photocatalyst materials, including molecular dyes,⁵⁸⁻⁶⁰ and bulk semiconductors^{61,62}. Slowly, with the advancement in nanotechnology, the obvious advantages of using nanoparticles over bulk materials became more evident, resulting in the introduction of metal and semiconductor nanocrystals as potential photocatalysts.⁶³⁻⁷³ As the available photocatalysts now cover a wider variety and specific related advantages, it becomes important to categorize them based on certain fundamental parameters, essential for photocatalytic applications. **Table 1.1** summarizes some of the essential parameters required for photocatalysis (based on the fundamental process mentioned above), with respect to some of the widely explored classes of photocatalysts.⁵⁷

Table 1.1. Summary of the key parameters defining the photocatalytic ability, with respect to some of the widely used classes of photocatalysts.

Photocatalyst	Extinction coefficient ($\text{M}^{-1} \text{cm}^{-1}/\text{cm}^{-1}$)	Carrier concentration ($\text{cm}^{-3}/\text{cm}^{-2}$)	Lifetime of charge carriers	Diffusion length/ Mobility
Molecular systems	10^3 - 10^5	low	A few ns	-
Bulk semiconductors	10^3 - 10^4	10^{12} - 10^{16}	ps to a few ns	10 - few 100's nm/ 10 - $1500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
Quantum dots	10^4-10^6	10^{18}-10^{20}	A few ns to 200 ns	10-100 nm/ 50-$5000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
2-Dimensional	10^5 - 10^6	10^6 - 10^{12}	Few tens of ns	300 - $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
Plasmonic metals	10^8 - 10^{10}	10^{23}	1-100 fs	5-50 nm
Perovskites	10^4 - 10^6	10^{10}	300-500 ns	Few nm-mm/ 1 - $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

The parameters mentioned in **Table 1.1** varies widely with the change in the class of photocatalyst material. In case of an ideal photocatalyst, one would expect a high extinction coefficient for absorption of sufficient number of photons leading to the generation of charge carriers with high concentration. For successful photocatalysis, these charge carriers have to be transferred from the photocatalyst to the reactant molecules, hence a longer lifetime as well as a longer diffusion length for charge carriers in the photocatalyst are essential. Among the widely explored classes of photocatalysts, quantum-confined semiconductor nanoparticles or quantum dots (QDs) satisfy most of these essential parameters for a good photocatalyst and hence has been our choice of material for different photocatalytic applications.^{26,57}

1.4. Introduction to quantum dots and quantum confinement effect

Quantum dots are semiconductor nanocrystals confined at a space comparable to its Bohr excitonic radius (spatial distance between the photoexcited electrons and holes).⁷⁴ Under this confinement, the nanocrystals behave differently than that of their bulk as well as molecular counterparts.⁷⁴⁻⁸⁰ At this size regime, the nanocrystals show fascinating size and shape dependent optoelectronic properties. When the size of the nanocrystal becomes smaller (higher degree of confinement), it increases the band gap of the material, whereas the band gap decreases when the size of the nanocrystals is increased (**Figure 1.4**).⁷⁴⁻⁸⁰ Also, the splitting of the valence and conduction band happens as a result of the quantum confinement leading to the introduction of discreteness into the excitation profile of the quantum dots.⁸¹ Due to this

size tuneable nature of the band gaps, the emission wavelength of the QDs can also be customized accordingly.⁷⁴ Along with these features, the QDs exhibit broad absorption covering the broader part of the solar spectrum, narrow emission, large as well as highly tuneable surface area and, higher photostability with respect to corresponding molecular dyes.⁷⁴⁻⁷⁶

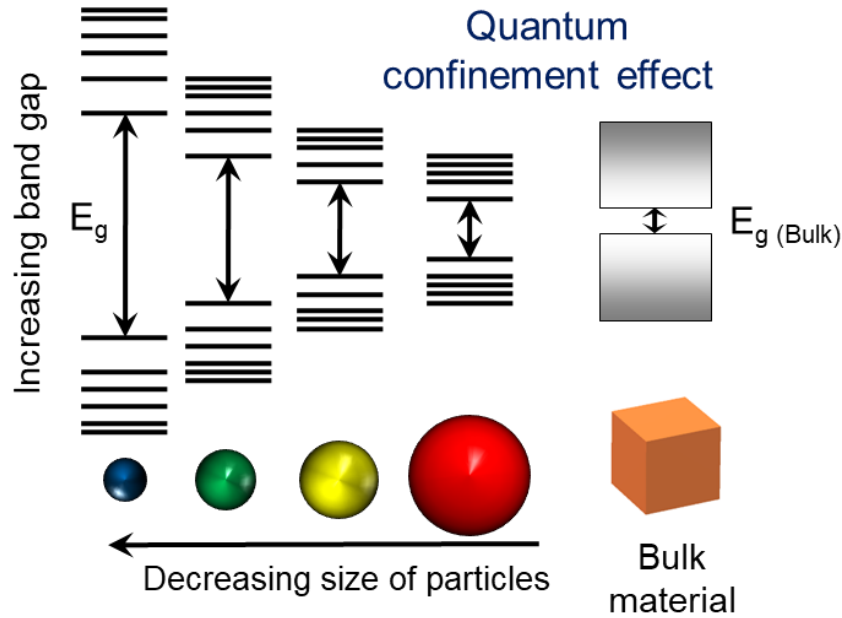


Figure 1.4. Schematics representing the quantum confinement effect, showing the change in band gap with the change in size of the particle. Redrawn with permission from ref. 79. Copyright: 2016, Springer Nature.

The band gap (E_g) of the QDs and its relation with the bulk band gap (E_{bulk}) is generally expressed using the following Brus equation:^{75,78}

$$E_g(QD) = E_{bulk} + \frac{h^2}{8R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.786e^2}{4\pi\epsilon_0\epsilon_r R}$$

Where, h is Plank's constant, R is radius of the QDs, m_e^* and m_h^* are the effective masses of electrons and holes in the QD, ϵ_0 is the permittivity of the vacuum and ϵ_r is the relative permittivity.

1.5. QDs for light-harvesting applications

The exceptional optoelectronic properties of quantum dots (QDs) position them as highly promising candidates for various light-harvesting investigations.²⁶ Upon photoexcitation, QDs can undergo diverse decay pathways, as illustrated in **Figure 1.5**. The efficiencies of these pathways ultimately determine the QDs' role in various light-harvesting applications. One prevalent pathway involves the radiative recombination of excitons, known as photoluminescence (PL; marked as '1' in **Figure 1.5**), and is applied in sensing,⁸² imaging,⁸³⁻⁸⁵ and display technologies.^{86,87} Furthermore, photoexcited charge pairs in QDs can engage in energy and electron transfer processes when coupled with suitable acceptor moieties (marked as '2' and '5' in **Figure 1.5**, respectively).⁸⁸⁻⁹⁶ Additionally, the generated excitons can be extracted from the core of the QDs for both photovoltaic applications,⁹⁷⁻¹⁰¹ as well as the facilitation of various photo-redox transformations (marked as '3' and '4' in **Figure 1.5**, respectively).¹⁰²⁻¹⁰⁹ As per the motivation of the current thesis, we will majorly keep our focus on the application of the QDs as photocatalysts.

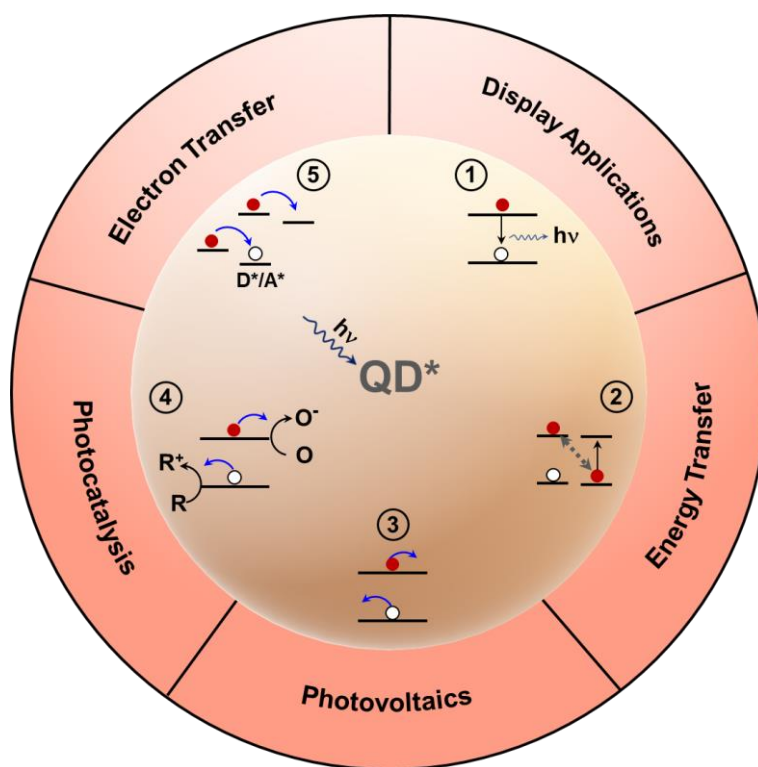


Figure 1.5. Summarizing the primary relaxation pathways in a photoexcited quantum dot (QD*), which serves as the foundation for diverse applications in the area of energy science. Reproduced with permission from ref. 26. Copyright: 2021, Royal Society of Chemistry.

1.6. Photocatalysis with QDs

In a typical photocatalytic cycle, upon visible-light excitation, there is a generation of electrons and holes in conduction and valance bands respectively. These photoexcited electrons and holes are eventually transferred to the corresponding substrates to participate in the desired chemical transformations. For example, in case of a net reduction reaction, only electron transfer from the QD to the substrate is of the interest, but in order to regenerate the QD for further catalytic cycles, the accumulated holes have to be replenished using an appropriate hole scavenger (**Figure 1.6**). On the same note, in case of a net oxidative reaction, the photogenerated holes are used for desired reaction, whereas the accumulated electrons are extracted using appropriate electron scavengers (**Figure 1.6**). Moreover, in another class of reactions known as redox neutral transformations, both the electrons as well as the holes are simultaneously used in the same reaction, leading to an automated regeneration of the QD photocatalyst. Based on the possibilities of these reduction, oxidation or redox neutral reactions, the few major classes of reactions that has come up throughout the years, forming the basis of the field of QD photocatalysis.

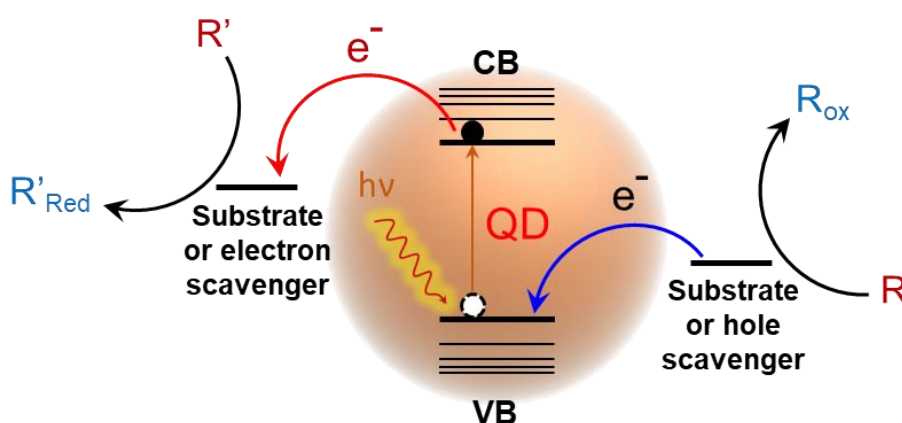


Figure 1.6. General scheme of reduction and oxidation reactions with QDs as photocatalysts under visible-light irradiation.

1.6.1. Generation of solar fuels:

The idea of solar fuel generation is inspired from natural photosynthesis where plants store the solar energy via conversion of glucose from CO_2 and water under sunlight. This motivated the QD photocatalyzed reduction of protons to generate H_2 , and reduction of CO_2 to useful chemicals like CO , CH_4 , CH_3OH etc., that can be further used to generate energy. In one

seminal work by Wu and co-workers, the exceptional photocatalytic H₂ evolution property of cadmium selenide (CdSe) QDs was revealed in absence of any external co-catalysts (**Figure 1.7a**).¹¹⁰ As the electron transfer happened from the conduction band of the photoexcited CdSe QDs to reduce H⁺ to generate H₂, ascorbic acid was used as a hole scavenger to regenerate the catalyst. Interestingly, a partial overcoating (~46%) with ZnS shell helped enhancing the rate as well the overall yield of hydrogen production under photocatalytic condition (**Figure 1.7b**). Under the optimized condition, the reaction could achieve a near constant rate of 306.3 $\mu\text{mol mg}^{-1} \text{h}^{-1}$ for the hydrogen evolution reaction (**Figure 1.7c**). This work has projected the importance of QDs as sole photocatalysts for the generation of useful fuels in absence of any external co-catalyst.

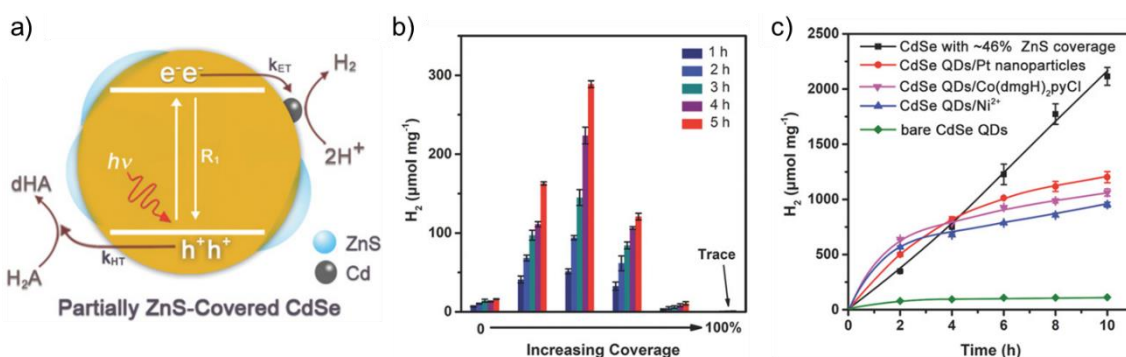


Figure 1.7. a) Schematics showing the photoinduced electron and hole transfer for the proton reduction and ascorbic acid oxidation, respectively, with partially ZnS covered CdSe QDs under photoirradiation. b) Comparison of the yield of photocatalytic H₂ evolution reaction with differently surface modified CdSe QDs with bare CdSe QDs in the presence of external cocatalysts under identical conditions. c) Photocatalytic H₂ evolution of CdSe QDs with different ZnS coverage under different irradiation times. Reproduced with permission from ref. 110. Copyright: 2018, Wiley VCH.

In another work by Weiss and co-workers, CuInS₂ QDs was used as a photocatalyst with *meso*-Tetraphenylporphyrin iron(III) chloride (FeTPP) complex as a co-catalyst to carry out a selective reduction of CO₂ to CO under 450 nm visible-light irradiation (**Figure 1.8a**).¹¹¹ An ultrafast electron transfer (<200 fs) from the QDs to the FeTPP complex was monitored using optical spectroscopy. N,N,N',N'-tetramethyl-p-phenylenediamine was used as a hole scavenger for this photocatalytic reaction. The QD-FeTPP system exhibits a sensitization efficiency (as defined by the number of CO molecules produced per joule of absorbed photon energy per porphyrin catalyst molecule (**Figure 1.8b**)) that is 18 times higher than that of the Ir-based system and 38 times greater than that of the 9-cyanoanthracene (CNA)-based photocatalytic system.

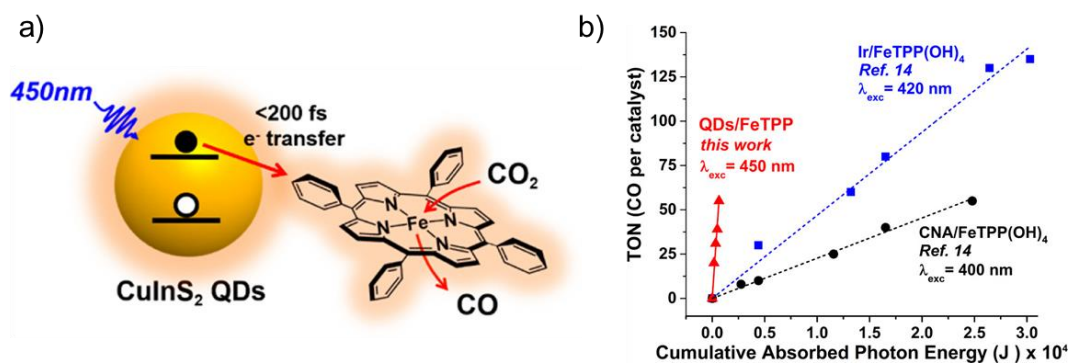


Figure 1.8. Schematic representation of reduction of CO₂ to CO from FeTPP co-catalyst upon electron transfer from the photoexcited CuInS₂ QDs. b) Comparison of the measured turn over number (red triangles being CuInS₂ + FeTPP, blue squares being Ir(ppy)₃ + hydroxylated FeTPP and black circles being CNA + hydroxylated FeTPP under similar photoirradiation conditions). Reproduced with permission from ref. 111. Copyright: 2017, American Chemical Society.

1.6.2. Biomass valorizations

Conversion of biomass to useful chemicals and fuels can be a substantial way-out to simultaneously dealing with both the issues of energy crisis as well as bio-waste treatment. To mitigate this with QD based photocatalytic solution, Reisner and co-workers have designed a cadmium sulfide/cadmium oxide (CdS/CdO_x) based photocatalyst system that can oxidise the lignocellulose from biomass (e.g., grass, paper and wood were used in this work) via the photogenerated holes, whereas the generated electrons can be utilized to carry out a H₂ evolution reaction (**Figure 1.9a**).¹¹² Lignocellulose in other words, takes the role of a hole scavenger and keeps the flow of electrons for the production of H₂ as fuel under photoirradiation (**Figure 1.9b**). Upon optimization, the reaction was found to be most efficient under a strongly alkaline medium (10 M KOH) where the H₂ generation was maximum under irradiation with simulated sunlight of A.M. 1.5 (**Figure 1.9c**). The rate of H₂ generation was found to be consistent even upto 6 consecutive days in presence of cellulose source, whereas the reaction in absence of cellulose ceases after 24 h of irradiation (**Figure 1.9d**). This work proves the versatility as well as demonstrates the real-time applications of the QD photocatalysis under solar irradiation.

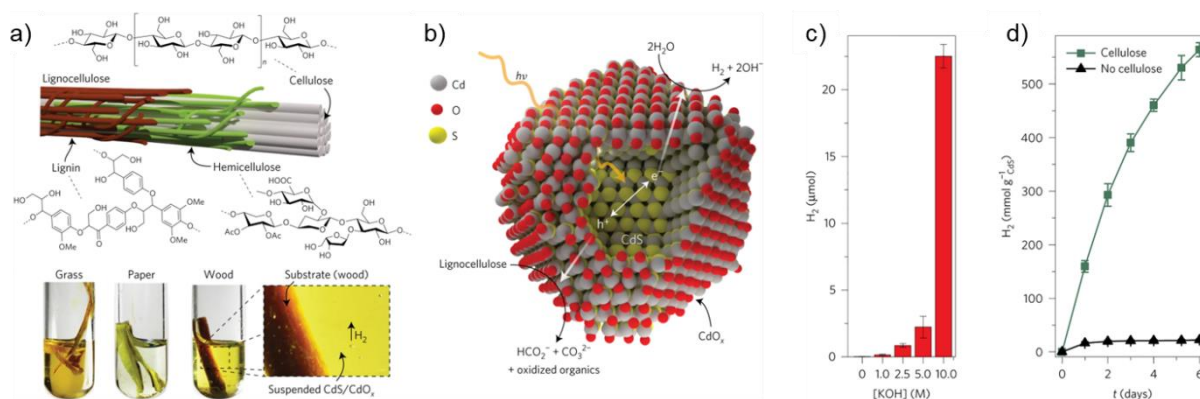


Figure 1.9. a) Lignocellulose is found as microfibrils in plant cell walls and is comprised of cellulose surrounded by the less crystalline polymers hemicellulose and lignin. Some of the natural sources used here are grass, paper and wood. b) These components can be photoreformed into H_2 using semiconducting CdS coated with CdO_x . Light absorption by CdS generates electrons and holes, which travel to the CdO_x surface and participates in proton reduction and lignocellulose oxidation, respectively. c) The pH dependent nature of the photocatalytic H_2 evolution reaction, maximising at a reaction medium with 10 M KOH. d) Long-term efficiency of the photocatalytic H_2 evolution reaction in presence and absence of cellulose. Reproduced with permission from ref. 112. Copyright: 2017, Springer Nature.

1.6.3. Organic photoredox catalysis

In last couple of years, organic photoredox catalysis has flourished as a sustainable way to synthesise complex organic moieties and have also come up as an alternative methodological approach to various high-energy consuming synthetic protocols.¹¹³⁻¹¹⁵ The area has developed majorly using the precious metal-based polypyridyl complexes of Ru(ii), Ir(iii), and Pt(ii) as photocatalysts.¹¹³⁻¹¹⁶ Nevertheless, these classes of molecular photocatalysts based on transition metal complexes pose challenges for widespread industrial use due to their limited availability and elevated expenses.¹¹⁷ QDs come up here not only as a practical and cheaper alternative to these precious-metal based photocatalysts, but also with exciting tuneable optoelectronic properties that are crucial for photoredox applications.^{117,118} In general, the photoredox reactions can be classified into three broad categories based on the types of the associated redox reactions. These are, i) net reduction, ii) net oxidation and, iii) redox neutral reactions (**Figure 1.10a**).¹¹⁷ As an example of the net reduction reaction, Weiss and co-workers reported a reduction of nitrobenzene to aniline using mercaptopropionic acid (MPA) capped cadmium sulfide (CdS) QDs as photocatalysts (**Figure 1.10b**).¹¹⁹ In this case, a six sequential proton-coupled electron transfer reduces nitrobenzene to aniline where MPA and methanol are simultaneously acting as hole scavengers. Another example by Wu and co-workers, have emphasised on the oxidation cycle of the QD photocatalysis by conducting the oxidation of benzylic alcohols to corresponding aldehydes and ketones via assistance from thiolated MPA

that also acts as surface ligands on the CdSe QD photocatalysts (**Figure 1.10c**).¹²⁰ Interestingly, the associated reduction cycle used in this case was to carry out hydrogen evolution reaction. Finally, in the case of redox neutral transformations, various coupling reactions have been reported (including both carbon-carbon as well as carbon-heteroatom couplings) with different classes of QDs.^{105,117,121} Along with coupling reaction where both oxidation as well as reduction cycles are used (i.e., utilization of both electron and holes), cycloaddition type reactions have come up recently based on energy transfer from the associated triplet excited states of the QD photocatalysts. In one such pioneering example, Weiss and co-workers have demonstrated an excellent regio- and diastereoselective intermolecular [2+2] cycloaddition reaction using CdSe QDs as photocatalysts (**Figure 1.10d**).¹²² A selective sensitization of one of the olefin reactants was achieved through the precise control over the triplet energy levels of QDs, leading to the selective heterocoupling between the olefins. This resulted in a high switchable regioselectivity (syn, ~98%) and diastereoselectivity (~98%) in the product formation, which was difficult to achieve with conventional molecular complexes. The binding of olefins on the surface of QDs through carboxylate moieties facilitated the π - π interaction between the reactants, leading to the formation of kinetically disfavoured syn-products.

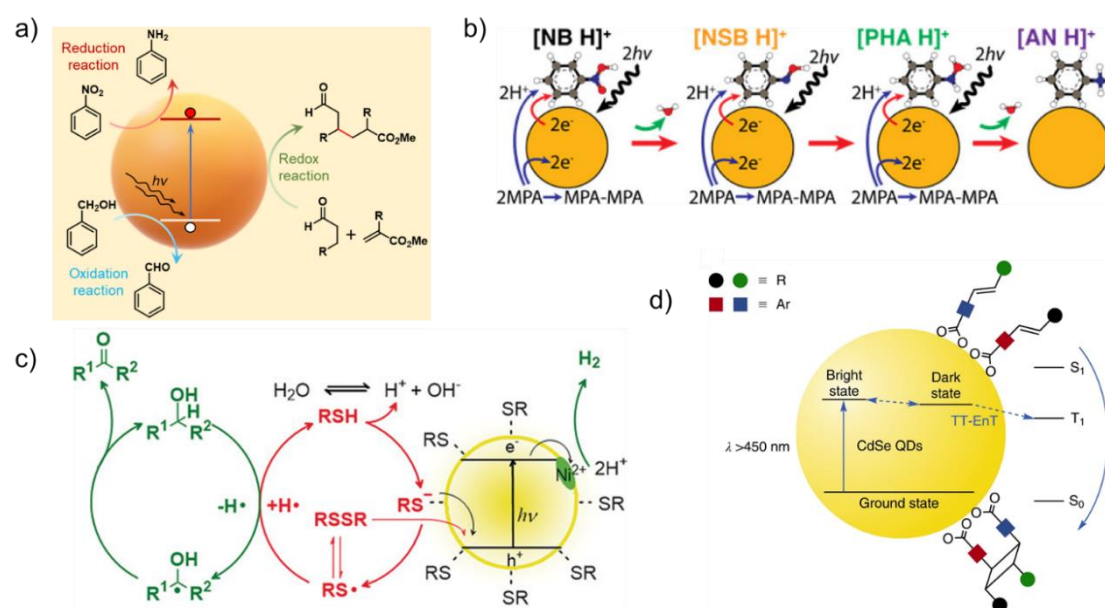


Figure 1.10. a) Schematic representation showing the three major classes of organic photoredox transformations with QDs. b) The sequential $6e^-$, 6H^+ mediated reaction pathway of the photocatalytic reduction of nitrobenzene to aniline with CdS QDs. Reproduced with permission from ref. 119. Copyright: 2016, American Chemical Society. c) Mechanistic diagram of the thiol assisted alcohol oxidation along with hydrogen evolution with CdSe QD and Ni^{2+} photocatalyst-cocatalyst system. Reproduced with permission from ref. 120. Copyright: 2017, Wiley VCH. d) Schematic representation for the regio and diastereoselective [2+2] cycloaddition reaction via triplet sensitization of olefin reactants, through the triplet-triplet energy transfer (TTEnT) from CdSe QDs. Reproduced with permission from ref. 122. Copyright: 2019, Springer Nature.

1.7. Design strategies for QD photocatalysts

A thorough analysis of the anatomy of the QDs reveal two major structural as well as functional components, i.e., core and surface ligands.²⁶ Individual engineering of both the components are essential to achieve the maximum photocatalytic efficiency out of the QDs. The majority of the photophysical characteristics exhibited by quantum dots rely on core parameters (e.g., size, shape, composition, crystallinity, and so on), and thereby determines the nature and the potentials of the photogenerated charge carriers crucial for the process of photocatalysis (**Figure 1.11**).

On the contrary, the surface ligands have been primarily viewed from the perspective of a stabilising or capping agent. It was believed that surface ligands were important mainly in providing stability to a nanoparticle system in a particular medium. However, recent studies have revealed that a rational design of surface ligands can turn out to be critical in deciding the outcome of various optoelectronic properties at the nanoscale, including photocatalysis. In general, a surface ligand has three sub-parts: binding (or head) group, spacer, and terminal group (**Figure 1.11**).^{26,123} The effect of all these individual components were found to be decisive towards charge transfer process thereby determining the overall photocatalytic efficiency of the QDs. A brief discussion about tuning these individual core and surface ligand directed properties towards the photocatalytic efficiency of the QDs are discussed below.

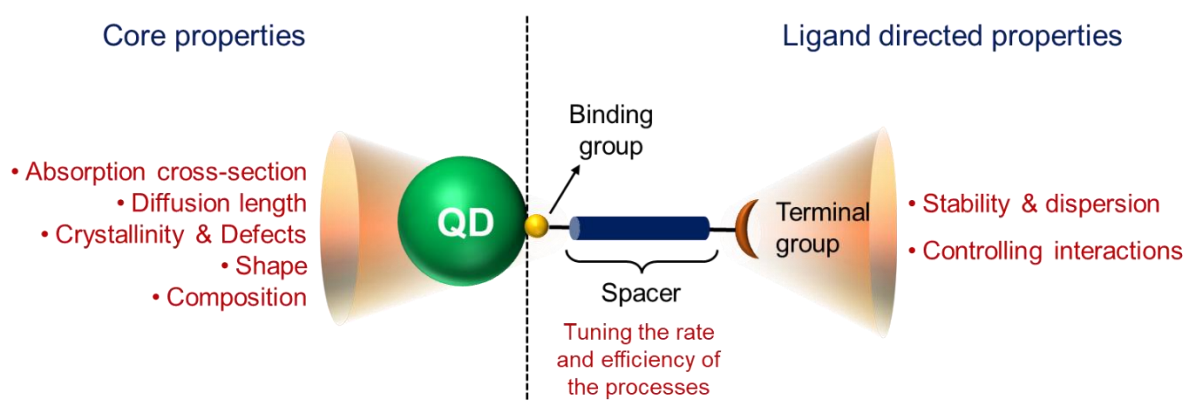


Figure 1.11. Schematic diagram of the anatomy of QDs, with an emphasis on the roles of various components. Reproduced with permission from ref. 26. Copyright: 2021, Royal Society of Chemistry.

1.7.1. Size, shape and composition

As a result of quantum confinement, the band position as well as the band gap of the QDs are variable with respect to the size of the particle.⁷⁵⁻⁸¹ The effect of this exciting feature on the

photocatalytic property has been tested on different classes of QDs in the literature.¹²⁴⁻¹²⁸ In one such example Osterloh and co-workers implemented CdSe QDs of different sizes towards H₂ evolution reaction and measured the size effect through the H₂ production efficiency and rate (**Figure 1.12a**).¹²⁴ As the band gap of the CdSe QDs decreases with the increase in particle size, at the same time, both the conduction as well as valence band positions also drops to lower potentials. This leads to a rapid rise in the $-\Delta G$ values for both electron and hole transfer processes, finally leaving the ΔG positive for the electron transfer process in case of red QDs. The effect of this band alignment is clearly reflected in the normalized H₂ production rate (with respect to absorbed photons) vs QD diameter plot, where the maximum efficiency was obtained with 1.75 nm QDs. Also, the rate decreases exponentially with increase in the size, reaching a negligible value in the presence of 4.81 nm sized QDs (**Figure 1.12b**). This set of observation clearly depicts the importance of the choice of appropriate size of QDs for optimum photocatalytic efficiency.

Keeping the origin and the nature of the generated excitons same, a change in shape of the particle may lead to a significant difference in the charge separation ability, finally resulting in a drastic difference in the overall photocatalytic efficiency. This effect was demonstrated by Alivisatos and co-workers towards H₂ evolution reaction, by using a CdS nanorod photocatalyst decorated with a CdSe seed and a Pt tip for ease of hole and electron transfer processes respectively (**Figure 1.12c**).¹²⁹ Interestingly, keeping the composition constant, when the length of the nanorod was increased from 27 nm to 70 nm, leading to a more spatial distance between CdSe seed and Pt centres, a ~ 4 -fold enhancement in the H₂ evolution efficiency was observed. When the size of the CdSe seed was reduced to 2.3 nm from 3.1 nm, the efficiency of the hole transfer process also enhanced resulting in a drastic increase in the overall H₂ evolution efficiency (**Figure 1.12d**). In this work, the prominent effect of both shape as well as composition of the QD based photocatalytic systems were observed, which can be further implemented as strategies to design any desired QD photocatalysts.

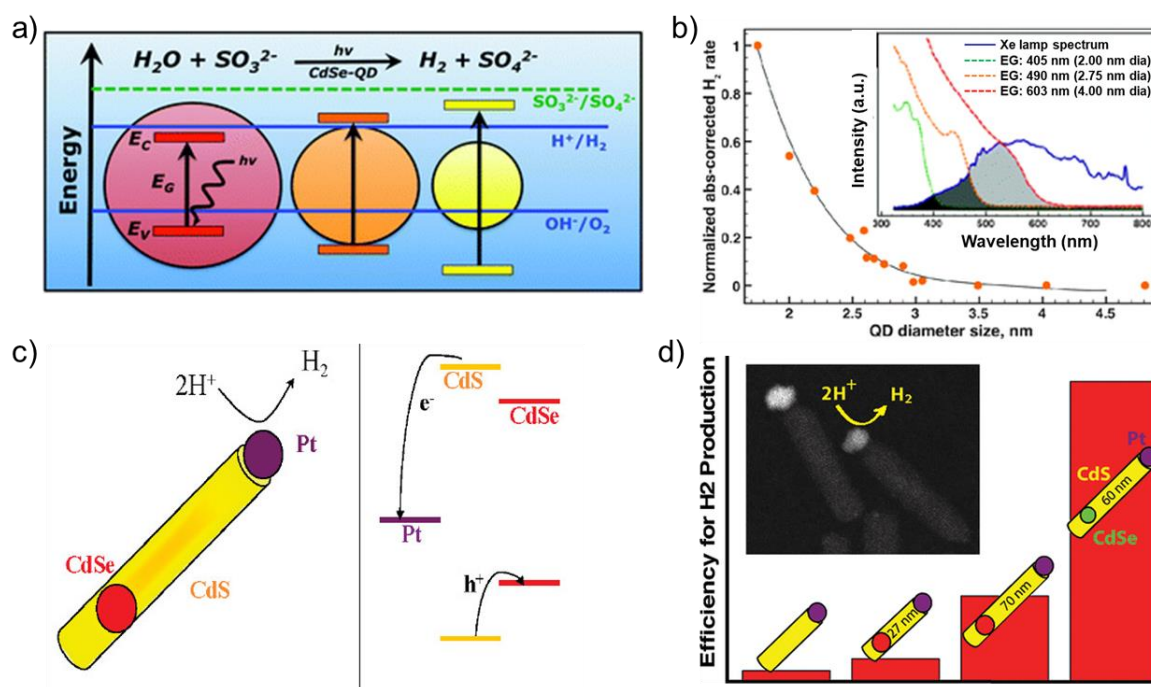


Figure 1.12. a) Schematics showing the band alignment of different sized CdSe QDs with respect to the potentials required for hydrogen evolution reaction. b) Rate of hydrogen generation (moles H_2 /[time $\times$ moles CdSe $\times$ overlap integral area]), *versus* QD size after absorbed photons correction using the overlap integral between irradiance and absorption (shown for three samples in the insert). Reproduced with permission from ref. 124. Copyright: 2011, Royal Society of Chemistry. c) Illustration showing the multicomponent photocatalytic system with CdSe seed, embedded in a CdS nanorod, topped with a Pt nanoparticle. Associated energy level diagram shows that the holes are isolated into CdSe seed, whereas the electrons are transferred to Pt tip for effective separation as well as utilization. d) Relative photocatalytic hydrogen evolution efficiency of the CdS nanorod based system of varied sizes as well as compositions. Reproduced with permission from ref. 129. Copyright: 2021, American Chemical Society.

1.7.2. Surface engineering

As mentioned earlier, the role of surface ligands on QDs are not only to provide colloidal stability, but it also has a significant role in determining the efficiency of the photophysical as well as the photocatalytic processes.²⁶ As we know, the efficiency of the charge transfer processes in catalysis depends on the distance between the catalyst and the reactant, and a close proximity between them can enhance the efficiency of the process many folds. As ligands form the interface between the QD surface and the reactant (or bulk reaction mixture), they can introduce a favourable catalyst-reactant interaction to channelize more reactants closer to the QD surface allowing a better catalytic efficiency.^{26,36,130-134} In one such report, Weiss and co-workers have electrostatically coupled a negatively charged $CuInS_2/ZnS$ QD with a positively charged iron-tetraphenylporphyrin (FeTMA) complex (**Figure 1.13a**).¹³⁵ An ultrafast PET (with components of 3 ps (22%), 40 ps (22%), and 800 ps (56%)) was observed from QDs to

FeTMA in the electrostatically bound nanohybrid assembly, which further resulted in the reduction of CO₂ to CO in aqueous medium under visible-light irradiation (**Figure 1.13a**). A high selectivity (~99%) was achieved in the formation of CO, with a turnover number of 450 after 30 h of irradiation (per FeTMA complex). The photocatalytic performances were superior for electrostatically bound QDs-FeTMA assemblies compared to a mixture of unmodified QDs and FeTMA complex, proving the power of surface ligand directed non-covalent interactions (**Figure 1.13b**).

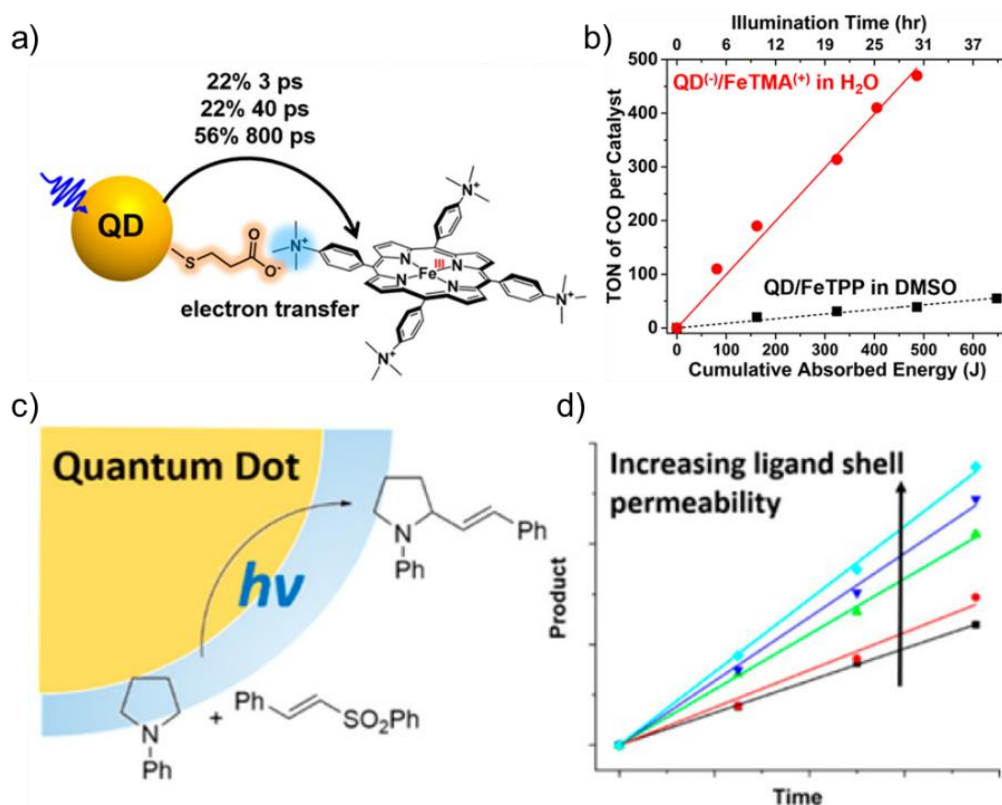


Figure 1.13. Schematics showing the ultrafast electron transfer from the photoexcited QD to the FeTMA moiety in the electrostatically assembled CuInS₂/ZnS QD-FeTMA complex, leading to the selective photoreduction of CO₂ to CO. b) A plot of TON vs cumulative absorbed energy vs illumination time proves that the photocatalytic performances were superior for electrostatically bound QDs-FeTMA assemblies (red circles), compared to a mixture of unmodified QDs and FeTMA complex (black squares). Reproduced with permission from Ref. 135. Copyright 2018 American Chemical Society. c) Schematic representation of the CdS QD photocatalyzed C-C coupling reaction. d) A plot showing the dependence of ligand shell composition on the yield of the product formed in the CdS QD photocatalyzed C-C coupling reaction. More the amount of the shorter OPA ligands, more the permeability, resulting in higher reaction yield. Reproduced with permission from Ref. 121. Copyright 2017 American Chemical Society.

The spacer part of the ligand controls the distance between the QD core and the donor/acceptor species (**Figure 1.11**), which can have a strong impact on QD triggered photocatalytic reactions as well.^{26,121,136,137} The shorter the length of the surface ligands on the QDs, the higher the rate of electron transfer, and hence better the photocatalytic activities.¹²¹ In one of the seminal

works in this direction, Weiss and co-workers have demonstrated the importance of ligand organization on the photocatalytic properties of QDs in a C-C coupling reaction.³¹⁶ CdS QDs, capped with a long chain oleic acid, was used to photocatalyze the C-C coupling reaction between 1-phenyl pyrrolidine and phenyl *trans* styryl sulfone (**Figure 1.13a**). Modification of the QD's surface with shorter octylphosphonate ligands showed a remarkable enhancement in the photocatalytic activity of CdS QDs, because of the disordering of the ligand shell. Specifically, the rate and energy efficiency of the C-C coupling reaction enhanced by a factor of ~ 2.3 and ~ 1.6 , respectively (**Figure 1.13b**). More importantly, the appropriate surface functionalization allowed the use of QDs as a sole-photocatalyst, without the need of any sacrificial reagent or co-catalyst.

1.7.3. Introduction of non-trivial photophysical processes

Majority of the QD based photocatalytic processes discussed so far are associated to the photoexcited charge transfer process and alongside are also bound within the limit of the band positions based on single photon absorption. But, beside all the well-known tuneable optoelectronic properties, QDs also exhibit exciting non-trivial photophysical processes, which in principle can push the boundary of the area of QD photocatalysis to a greater extent.¹³⁸⁻¹⁴⁰ As a representative example, because of very low energy gap between the singlet and triplet excited states, QDs can be directly excited to its triplet states using simple band-edge excitation, unlike molecular chromophores (requiring much higher energy excitation for a transition to the corresponding singlet excited state followed by intersystem crossing to populate the associated low-energy triplet states).¹⁴¹ Now, these excited triplet states can participate in different triplet-triplet energy transfer pathways to either trigger triplet mediated photocatalytic transformations,¹²² or can participate in photonic upconversion processes (e.g., triplet-triplet annihilation; TTA)^{138,139} to attain higher redox potentials (**Figure 1.14a**). Electrons from such high potentials can further be utilized to carry out energetically uphill chemical transformations.¹⁴⁰ On the other hand, the inherent two-photon absorption (TPA) properties of QDs (where two photons of approximately half the energy of the band gap are used to excite the QD to its band edge position) can also be implemented into the process of photocatalysis to achieve specific catalytic transformations with excitation of much lower energy (**Figure 1.14b**). For example, a photocatalytic reaction generally occurring under visible-light can be carried out with NIR excitation using the TPA process of QDs.

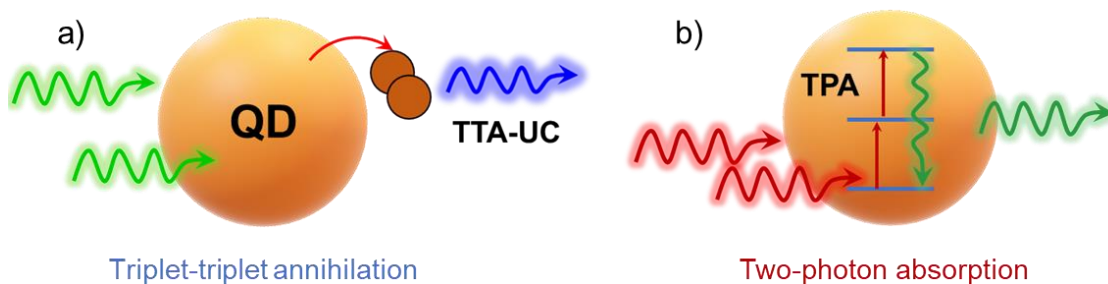


Figure 1.14. Illustrative diagrams of the non-trivial photophysical processes emanating from the photoexcited QDs, a) triplet-triplet annihilation based upconversion, and b) two photon absorption process that can further be coupled to the process of photocatalysis.

1.7.4. Current challenges in QD photocatalysis

Despite the above-mentioned developments in the area of QD based photocatalysis, there are a few associated challenges that are yet to be addressed for the betterment of the field in long run. Some of them are as follows:

- Retention of colloidal, photophysical as well as structural integrity of the QD photocatalysts under prolonged irradiation in reaction medium.
- Recyclability of the QD photocatalysts for higher number of cycles.
- Development of scalable devices and methodologies.
- Incorporation of environmentally friendly QDs and of non-trivial photophysical process in QD based photocatalysis.

1.8. Motivation and objective of the thesis

Primarily, in majority of the examples of QD photocatalysis, we see the involvement of the toxic metal containing chalcogenide QDs (e.g., CdS, CdSe, PbS, etc.). Keeping their environmental impact in mind, along with the increasing restrictions on these classes of toxic metal containing QDs, we were motivated to establish the environmentally friendly alternative, indium phosphide (InP) QDs, as a new class of photocatalysts. Recently, a number of procedures were also developed to synthesize different sizes of InP based core and core shell QDs, covering a broad potential range attainable under visible-light excitation.

With that in mind, the present thesis focuses on precise tuning of both the core as well as the surface ligand directed properties to unravel the exciting photocatalytic ability of QDs for a wider variety of chemical transformations. To design a QD photocatalyst for any specific

chemical transformation, it is essential to precisely synthesise the desired QD core with appropriate size, followed by their surface functionalization with suitable ligands to ensure their colloidal stability in the reaction medium. Moreover, by deliberately choosing surface ligands on QDs with appropriate head groups, we envisage to introduce favourable catalyst-reactant interaction. This in turn will channelize the reactants close to the catalyst surface for better catalytic efficiency, thereby allowing us to tune the efficiency of a catalytic process by simply modulating its surface chemistry (**Figure 1.15**). Furthermore, upon developing such exciting surface ligand directed catalytic process, we would also like to bring out the non-trivial photophysical processes of QDs and couple it into the process of photocatalysis (**Figure 1.15**). In one example, the photonic up-conversion process of triplet-triplet annihilation was used to access the higher redox states with lower energy excitations. This was achieved by the appropriate choice and combination of QDs, surface ligands and annihilator molecules. (**Figure 1.15**). Thus, a successful achievement of these objectives would not only introduce the surface-engineered environmentally friendly QDs as an efficient photocatalysts for various chemical transformations, but also will establish a versatile design strategy to carry out efficient light-to-chemical energy conversion for a wider range of applications.

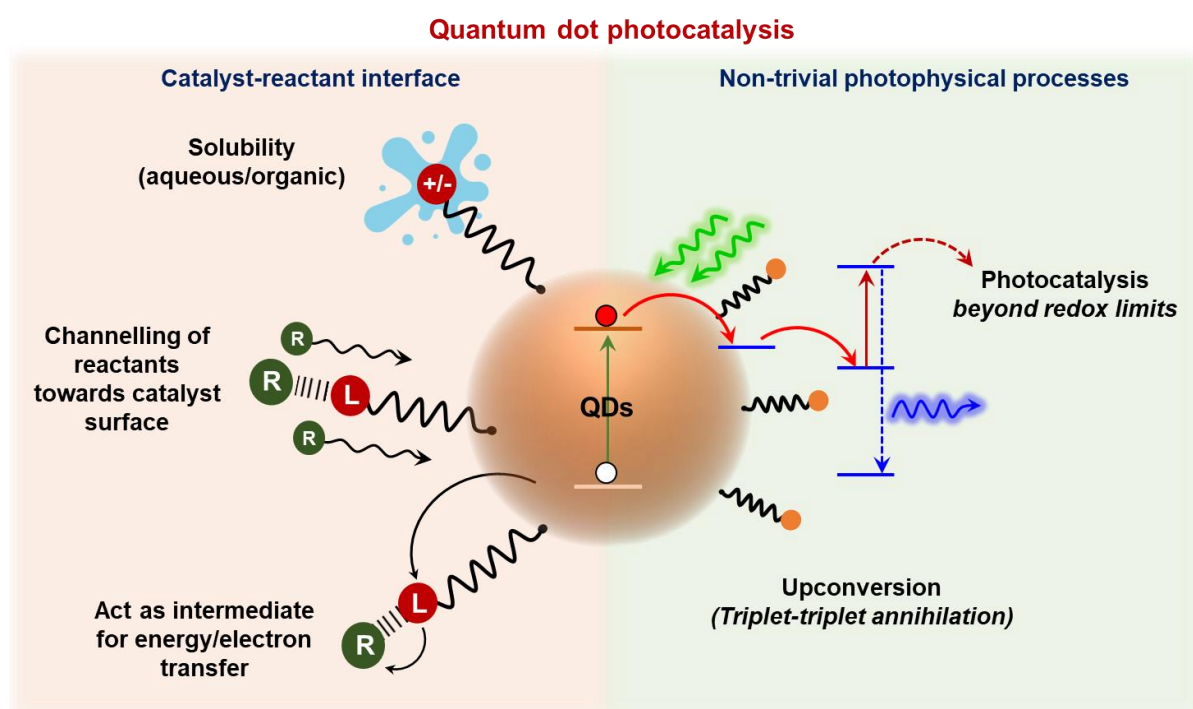


Figure 1.15. A schematic representation of the objective of the thesis, where the main idea is to regulate the QD photocatalysis by modulating both the surface as well as the core properties.

1.8.1. Brief overview of the Chapters

Talking about the progression of the thesis, a brief account of the chemicals used, the synthetic protocols followed and the necessary calculations are described in the second Chapter. In the third Chapter, we went on to establish the potency of InP/ZnS QDs in independently photocatalyzing two important classes of reactions, namely, metal-centred redox and organic C-C coupling reactions. The two types of reactions were carried out in aqueous and organic medium respectively via proper surface engineering of the QDs. This was one of the first works which established InP-based QDs as a potential photocatalyst for two different classes of chemical transformations.

The above work inspired us to reveal the full potential of the InP QDs in devising an artificial photosynthetic system via nicotinamide cofactor regeneration. In Chapter 4, the photosynthetic light and dark cycles reactions were closely mimicked using InP QD-enzyme nanobiohybrid system, finally applying it for the continuous synthesis of useful chemicals under visible-light. Moreover, the catalytic efficiency of the reaction was also enhanced by introducing favourable catalyst-reactant interaction via precise surface engineering of the InP QDs.

In Chapter five, the decisive role of ligand chemistry in directing the charge transfer process from the QD photocatalyst to the reactant was established. Here, we could identify and establish the dual role of triphenylphosphine in acting both as a surface passivating agent as well as a reactant in a series of QD photocatalyzed olefination reactions in organic medium.

Finally, in Chapter six, we could explore the intriguing non-trivial photophysical processes of QDs in developing a triplet-triplet annihilation based upconversion system to carry out energy intensive photocatalytic reactions, that are beyond the redox potentials of the QDs alone.

1.9. References

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Chapter – 2

Chemicals, Methods and Techniques used

2.1. Materials and reagents

Indium acetate ($\text{In}(\text{Ac})_3$), indium chloride (InCl_3), zinc chloride (ZnCl_2), myristic acid (MA), zinc Stearate, 1-dodecanethiol (DDT), 1-octadecene (ODE), Cadmium oxide (CdO), oleic acid (OA), selenium powder, sublimed sulphur, tris-(dimethylamino) phosphine ($\text{P}(\text{DMA})_3$), trioctylphosphine (TOP), oleylamine, 11-mercaptopundecanoic acid (MUA), potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$), cesium acetate (CsOAc), 1,3,5-trimethoxybenzene (1,3,5-TMB), triphenylphosphine (PPh_3), benzyl bromide (PhCH_2Br), benzaldehyde, potassium carbonate (K_2CO_3), paraformaldehyde, 2-nitrobenzaldehyde, 3-bromobenzaldehyde, 2-thiophenecarboxaldehyde, piconaldehyde, 1-(bromomethyl)-4-methylbenzene, 1-(bromomethyl)-4-chlorobenzene, 1-(bromomethyl)-4-nitrobenzene, 4-(bromomethyl)benzonitrile, (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO), β -nicotinamide adenine dinucleotide (NAD^+), β -nicotinamide adenine dinucleotide phosphate (NADP^+), β -nicotinamide adenine dinucleotide reduced sodium salt (NADH), rhodium chloride hydrate ($\text{RhCl}_3 \cdot \text{H}_2\text{O}$), 1,2,3,4,5- pentamethylcyclopentadiene (Cp^*), 2,2-bipyridyl (bpy), butyraldehyde, butanol, alcohol dehydrogenase (ADH) from *Saccharomyces cerevisiae*, albumin from Bovine serum (BSA), ethylenediaminetetraacetic acid tetrasodium salt hydrate (EDTA), diaphorase from *Clostridium kluyveri* (100-UN), 4-bromoacetophenone were purchased from Sigma-Aldrich. Tris(trimethylsilyl phosphine) was purchased from STREM chemicals, phenyl *trans*-styryl sulfone and 1-phenyl pyrrolidine were purchased from Alfa-Aesar. Triethanolamine (TEOA) was purchased from Avra Chemicals. DL-6,8-thioctic acid amide (DL-lipoamide) was purchased from TRC Canada. 9-anthracene carboxylic acid (ACA), 9,10-diphenylanthracene (DPA) and N-methylpyrrole were purchased from TCI Chemicals. All the purchased chemicals were used without any further purification. *N, N, N*-trimethyl (11-mercaptopundecyl) ammonium chloride (TMA) was synthesized according to a reported procedure.¹

2.2. Synthesis of InP/ZnS QDs

2.2.1. Synthesis of ~3.0 nm green emitting MA capped InP/ZnS QDs

The desired InP/ZnS quantum dots were prepared following a reported one-pot synthesis procedure.² In a typical preparation, indium acetate (0.2 mmol, 58 mg), myristic acid (MA; 0.7 mmol, 157 mg) and 6 mL octadecene were taken in a three neck RB and heated to 110 °C under constant N₂ flow with continuous stirring, till a clear solution was obtained. The reaction mixture was degassed for 1h at 110 °C followed by cooling down to room temperature. Now a mixture of tris(trimethylsilyl phosphine) (P(TMS)₃) (0.2 mmol, 580 µL), zinc stearate (0.2 mmol, 125 mg) and DDT (0.2 mmol, 48 µL) were prepared under inert atmosphere and was injected into the reaction mixture, followed by heating at 270 °C for 1h. The color slowly changes from light yellow to dark orange with the increase in temperature indicating the growth of QDs. When the reaction temperature reached ~230 °C, DDT started to decompose leading to the formation of ZnS shell. After keeping for one hour at 270 °C, the reaction was quenched rapidly using a cold-water bath followed by addition of 2 mL of cold toluene to arrest the growth of InP/ZnS QDs. The resultant InP/ZnS QDs were purified two times by precipitation using excess ethanol and re-dispersing back in chloroform and used for further studies. The MA-capped InP/ZnS QDs were used for preparing QD coated Whatman paper and photocatalyzing the C-C coupling reaction.

2.2.2. Synthesis of ~4.2 nm red emitting oleylamine capped InP and InP/ZnS QDs

The synthesis of the desired red emitting InP and InP/ZnS QDs was carried out by following a reported synthetic procedure.³ In a typical synthesis of red-emitting InP/ZnS QDs, indium (III) chloride (0.45 mmol, 100 mg), zinc chloride (2.2 mmol, 300 mg), and oleylamine (15 mmol, 5.0 mL) were taken in a 100 mL three neck RB and heated to ~120 °C under Ar atmosphere with gentle stirring, till a clear solution was formed. The reaction mixture was degassed for ~30 min at ~120 °C and the temperature was raised further to ~200 °C under inert atmosphere. Upon reaching ~200 °C, 350 µL of tris-(dimethylamino) phosphine (1.93 mmol) in 1.0 mL of oleylamine was quickly injected into the reaction mixture, and the temperature was maintained at ~200 °C for 60 min for the growth of InP core QDs. At the end, the reaction mixture was

cooled down to room temperature with a cold-water bath followed by purification via precipitation with ethanol to yield the red-emitting InP core QDs. For further ZnS shell coating, zinc stearate in octadecene (0.05 M, 2 mL) and DDT (0.1 mmol, 24 μ L) were injected into the reaction mixture at room temperature under inert atmosphere, followed by increasing the temperature to ~ 300 $^{\circ}$ C, and kept for 20 min. Finally, the reaction mixture was quenched with water bath followed by addition of 5 mL of hexane. The prepared red-emitting InP/ZnS core/shell QDs were purified by precipitating in ethanol and redispersed back in chloroform, and used for further studies.

2.2.3. Synthesis of ~ 3.5 nm yellow emitting oleylamine capped InP/ZnS QDs

The synthesis of the ~ 3.5 nm yellow emitting InP/ZnS QDs was carried out by following a reported synthetic procedure.³ In a typical synthesis of the ~ 3.5 nm yellow emitting InP/ZnS QDs, indium (III) chloride (0.45 mmol, 100 mg), zinc bromide (2.2 mmol, 496 mg), and oleylamine (15 mmol, 5.0 mL) were taken in a 100 mL three neck RB and heated to ~ 120 $^{\circ}$ C under Ar atmosphere with gentle stirring, till a clear solution was formed. The reaction mixture was degassed for ~ 30 min at ~ 120 $^{\circ}$ C and the temperature was raised further to ~ 180 $^{\circ}$ C under inert atmosphere. Upon reaching ~ 180 $^{\circ}$ C, 327 μ L of tris-(dimethylamino) phosphine (1.8 mmol) in 0.7 mL of oleylamine was quickly injected into the reaction mixture, and the temperature was increased to ~ 200 $^{\circ}$ C and maintained at that temperature for 40 min for the growth of InP core QDs. After 40 min, for further ZnS shell coating, 1 mL of a separately prepared 2.2 M solution of trioctylphosphine-sulfide (TOP-S) was injected dropwise into the reaction mixture at 200 $^{\circ}$ C and kept for 30 min. Next, from another separately prepared octadecene (ODE) solution of Zinc stearate (1.5 g Zinc stearate in 6 mL ODE), 4 mL was added into the reaction mixture. The temperature was increased to 220 $^{\circ}$ C and kept for another 30 min. Next, 0.7 mL of 2.2 M TOP-S was added again followed by increasing the temperature to 240 $^{\circ}$ C. Then, 2 mL of the remaining zinc stearate-ODE solution was added followed by increasing the temperature to 260 $^{\circ}$ C. The reaction was kept at this temperature for next 30 min followed by quenching with 2 mL hexane and bringing down to room temperature. The resulting bright yellow emitting InP/ZnS QDs were purified via precipitation with ethanol and redispersed back in toluene for further studies.

2.3. Synthesis of ~3.6 nm CdSe QDs

The CdSe QDs were synthesised using a modified reported procedure.⁴ In a 100 mL three-neck flask, CdO (2.5 mmol, 318 mg), oleic acid (10 mmol, 3.45 mL) and octadecene (9 mL) were mixed and heated to 110 °C with stirring, under continuous N₂ flow. The reaction was degassed in this condition for 1 h followed by heating up to 270 °C. A solution of 1 M TOP-Se was prepared by mixing Se powder (2 mmol, 136 mg) and TOP (2 mL) inside glove box and was stirred until the solution became clear. After that, 2 mL of 1 M TOP-Se was swiftly injected into the reaction mixture at 270 °C followed by lowering the temperature of the reaction to 220 °C for growth. The reaction was annealed for 30 min to obtain a better quality of QD. Next, the reaction was quenched using water bath followed by addition of 2 mL toluene. The resultant CdSe QDs were purified twice by precipitation using excess ethanol and re-dispersed back in toluene, and used for further studies.

2.4. Ligand exchange reactions of the QDs

2.4.1. Preparation of [-] InP QDs in water:

A ligand exchange protocol was used to prepare MUA capped [-] InP and [-] InP/ZnS QDs dispersed in water (**Figure 2.1**).⁵ In a typical ligand exchange protocol, MUA (~80 mg, 0.36 mmol) was dissolved in 1:4 ratio of water/methanol mixture (300 μ L and 1.2 mL, respectively) and the pH of the solution was adjusted to ~12 using 3N NaOH solution. To the above solution of negatively charged MUA ligands, 1 mL of stock QD solution (~40 μ M) in chloroform was added, and stirred vigorously for ~5 min. Then 2 mL water and 6 mL chloroform were added in the vial followed by stirring for 4 h. The successful ligand exchange was identified via the complete phase transfer of QDs from chloroform layer to the water layer. The aqueous layer was carefully separated and precipitated with acetone to remove excess MUA ligands. The precipitated QD was further redispersed in Milli-Q water and was used for further studies.

2.4.2. Preparation of [+] InP QDs in water:

A similar place exchange procedure was used to prepare [+] InP and [+] InP/ZnS QDs dispersed in water (**Figure 2.1**).⁵ In a typical process, 1 mL stock solution of QDs (~40 μ M) was diluted with 5 mL chloroform followed by mixing with 2 mL aqueous solution of TMA (containing ~50 mg TMA). The bilayer mixture was stirred vigorously for about 4 h leading to a complete

phase transfer of QDs from the organic layer to the aqueous layer. The aqueous phase was carefully separated and precipitated with acetone to remove excess TMA ligands. The precipitated QD was further redispersed in Milli-Q water and was used for further studies.

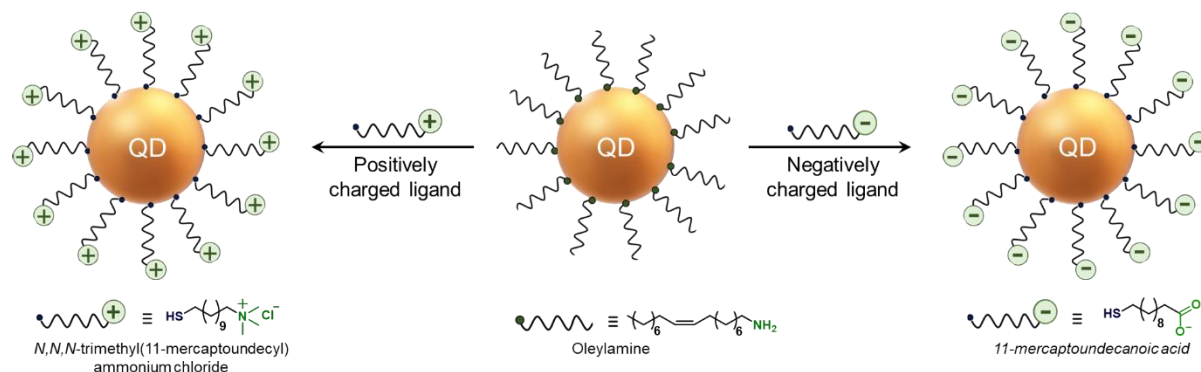


Figure 2.1. A schematic representation of the ligand exchange reaction of InP QDs with MUA and TMA ligands to yield [-] and [+] InP QDs.

2.4.3. Preparation of ACA capped InP/ZnS QDs for triplet-triplet annihilation based upconversion (TTA-UC):

The ACA ligands were functionalized on InP/ZnS QDs using a reported ligand exchange procedure.⁶ In a typical procedure, 6 mg of ACA is mixed in 100 μ L toluene to produce a milky turbid solution. Then, to this ACA solution, 150 μ L of stock oleylamine capped InP/ZnS QD solution was added and both the solutions were mixed thoroughly. Upon proper mixing, the milky solution will slowly turn clear indicating the functionalization of the free carboxylate groups of ACA onto the QD surface (**Figure 2.2**). Next, the mixture was stirred with a stir-bar for ~15 min followed by a high-speed centrifugation to remove any unbound ACA remaining in the solution. The resulting solution is then used as such for the TTA-UC based photocatalytic processes.

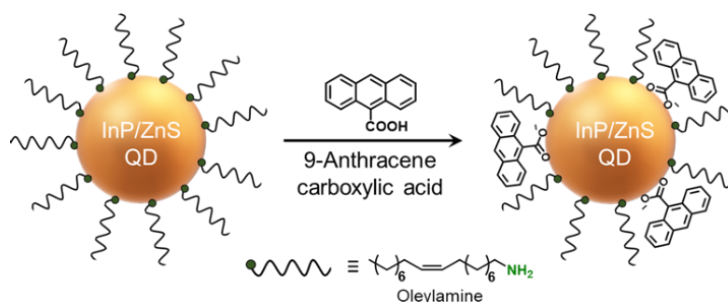


Figure 2.2. A schematic representation of the ligand exchange reaction of InP/ZnS QDs with ACA ligands.

2.5. Instrumentation and techniques used

UV-vis absorption studies: UV-vis absorbance data were recorded on a Shimadzu UV-3600 spectrophotometer and a quartz cuvette of path length 1 cm, over the range of 200-800 nm. The concentration of QD solution was calculated using Beer-Lambert's law:

$$A = \varepsilon \cdot c \cdot l$$

where,

A is the absorbance

ε is the molar extinction coefficient ($M^{-1} \cdot cm^{-1}$)

c is the concentration of the solution (M)

l is the optical path length (cm).

Molar extinction coefficients (ε) for CdSe and InP QDs were calculated using the following equations.⁷

InP QDs:

$$D = (-3.7707 \times 10^{-12})\lambda^5 + (1.0262 \times 10^{-8})\lambda^4 - (1.0781 \times 10^{-5})\lambda^3 \\ + (5.4550 \times 10^{-3})\lambda^2 - (1.3122)\lambda + 119.9$$

$$\varepsilon = 3046.1 (D)^3 - 76532(D)^2 + (5.5137 \times 10^5)(D) - (8.9839 \times 10^5)$$

CdSe QDs:

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda \\ + (41.57)$$

$$\varepsilon = 5857 (D)^{2.65}$$

where,

D is the diameter of QDs (nm),

λ is the wavelength corresponding to the first excitonic peak of the QDs (nm).

Photoluminescence (PL) studies: PL studies were performed using Horiba Jobin Yvon Fluoromax-4 spectrofluorometer (HORIBA Scientific) with xenon lamp as the excitation source. The excitation wavelength used was 400 nm, where all the QDs have appreciable absorption.

Time-resolved photoluminescence (TRPL) lifetime measurements: Time-resolved PL studies were performed using Horiba Deltaflex time-correlated single photon counting (TCSPC) system using a 405 nm delta-diode as the excitation source with a time to amplitude converter (TAC) range of 800 ns for 10,000 counts. The average lifetime (τ_{avg}) was calculated using the following intensity averaged equation.

$$\tau_{\text{avg}} = \sum \alpha_i \tau_i^2 / \sum \alpha_i \tau_i$$

α = relative amplitude and τ = lifetime

Zeta potential measurements: Zeta potential (ζ) was measured to characterize the charge on the surface of InP/ZnS QDs after place exchange with MUA ligands. The measurements were carried out using Zetasizer Nano series, Nano-ZS90 (Malvern Instruments, U.K.) with a 655 laser. The zeta potential is measured in terms of the electrophoretic mobility (U_E) and is calculated from Henry's equation⁸:

$$U_E = \frac{2\varepsilon\zeta f(k_a)}{3\eta}$$

where,

ε is the dielectric constant of the medium,

ζ is the zeta potential (mV)

$f(k_a)$ is Henry's function

η is the viscosity of the medium (Pa.s).

Smoluchowski's approximation was used to measure the zeta potential values.

Nuclear magnetic resonance spectroscopy studies: ¹H NMR data were recorded on Bruker 400 MHz spectrometer.

Transmission electron microscopy (TEM) imaging: The QD sample was drop-casted onto a 400-mesh copper grid and dried under vacuum. The high-resolution transmission electron microscopy (HRTEM) imaging was performed on Jeol JEM2200FS (200 kV) HRTEM instrument.

Cyclic voltammetry (CV) experiments: Metrohm DropSens μ Stat400 electrochemical workstation and Dropview 8400 software of version 2.215B1204 was used to carry out the CV

experiments. Glassy carbon was used as the working electrode, Ag/AgNO₃ as the reference electrode and Pt was used as the counter as well as pseudo-reference electrodes.

Gas chromatography (GC): The gas chromatogram of the reactions/product in organic phase was recorded using Shimadzu GC-2014 using N₂ as a carrier gas. The gas chromatograms of the product butanol formed in the dark cycle (in aqueous phase; Chapter 4) were recorded using Nucon GC equipped with DB624 column and flame ionization detector (FID) with N₂ as the carrier gas.

Gas chromatography-mass spectroscopy (GCMS): The GCMS data was recorded using Shimadzu GCMS-2010 plus using He as a carrier gas.

High Resolution Mass Spectroscopy (HRMS): The HRMS experiments were performed using an ESI-TOF mass analyser.

2.6. Calculation of the photocatalytic parameters

2.6.1. Calculation of turnover number (TON)

The turnover number of QD photocatalyzed reactions were calculated using the following expression:

$$\text{Turnover number (TON)} = \frac{\# \text{ moles of products formed}}{\# \text{ moles of catalyst used}}$$

2.6.2. Calculation of turnover frequency (TOF)

The turnover frequency (TOF) of QD photocatalyzed reactions were calculated using the following expression:

$$\text{Turnover frequency (TOF)} = \frac{\# \text{ moles of products formed}}{\# \text{ moles of catalyst used} \times \text{time of reaction}}$$

2.6.3. Calculation of internal quantum yield (IQY)

The % internal quantum yield (ϕ_{int}) was calculated as per the procedure:⁹

$$\Phi_{int} = \frac{\text{molecules of product formed}}{\text{number of absorbed photons}} \times 100$$

Number of absorbed photons is calculated by multiplying the total number of absorbed photons with the % of light absorbed.

$$\text{number of absorbed photons } (n_{\text{photon}}) = \frac{P_0 \times \lambda \text{ (m)} \times t \text{ (s)}}{hc} \times \% \text{ incident light absorbed}$$

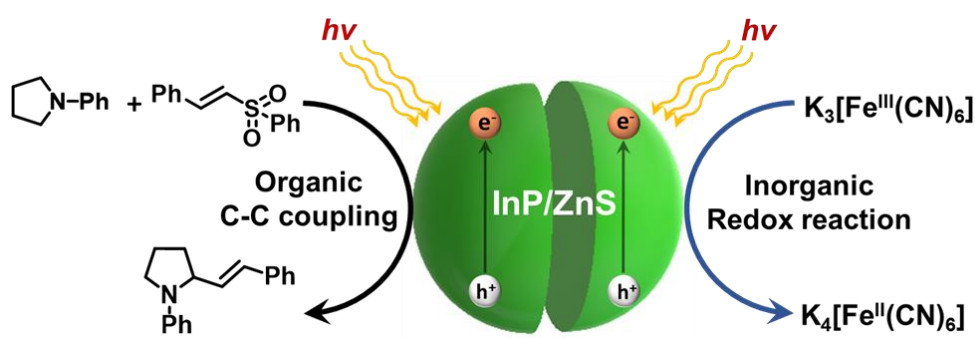
Where P_0 (J/s) is the power of incident light, λ is the wavelength (in meters) of the LED light source, t is the total time of irradiation (in seconds), h is the Plank's constant (J.s), and c is the speed of light (m/s).

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Chapter – 3

Visible-Light Driven Redox and Carbon-Carbon Coupling Reactions using InP/ZnS Quantum Dot Photocatalysts



This Chapter has been adapted from the following paper with permission. Copyright 2019, American Chemical Society: **Chakraborty, I. N.**; Roy, S.; Devatha, G.; Rao, A.; Pillai, P. P. InP/ZnS Quantum Dots as Efficient Visible-Light Photocatalysts for Redox and Carbon–Carbon Coupling Reactions. *Chem. Mater.* **2019**, *31*, 2258– 2262.

3.1. Abstract

Ability to photocatalyze different classes of reactions by a single material is always desirable to meet the growing challenges in solar energy research. In this direction, we have explored the potency of Indium Phosphide/Zinc Sulfide Quantum Dots (InP/ZnS QDs) as an alternate environmentally friendly, visible-light photocatalyst for mimicking the two key classes of chemical transformations found in natural photosynthesis, namely metal-centered redox and carbon-carbon bond forming reactions. As an example, for metal-centered redox reaction, we performed the InP/ZnS QD photocatalyzed reduction of ferricyanide to ferrocyanide with a photoconversion yield of 70% and an internal quantum yield of 0.21%. The recyclability feature of the QD photocatalysts was accomplished by embedding the InP/ZnS QD onto a paper substrate, while retaining its photocatalytic activity. More striking is the ability of InP/ZnS QD to exclusively photocatalyze a C-C coupling reaction between 1-phenyl pyrrolidine and phenyl-*trans*-styryl sulfone, without the aid of any co-catalysts or sacrificial reagents. The catalytic performances of InP/ZnS QD were comparable or superior to that of Ir-complex and CdS QD catalysts reported previously, with an added advantage of being environmentally friendly. A similar photocatalytic performance was observed under white-light illumination as well, which enhances the sustainability aspect of the InP/ZnS QD for the direct solar light harvesting. A good overlap between the internal quantum yield of the reaction with the ground state absorption of InP/ZnS QD confirmed the active participation of QDs in the photocatalyzed metal-center redox and C-C bond forming reactions. In short, our study introduces InP/ZnS QDs as a practical alternative to toxic metal-ion based QDs for efficient visible-light photocatalysis.

3.2. Introduction

Energy research is enormously inspired by one of the most fascinating and elegant phenomena known to mankind called photosynthesis.^{1,2} The efficient harvesting of visible-light and movement of electrons through a number of molecules and redox active metal-centers (leading to new chemical bonds) is the heart of photosynthesis.^{3,4} Understanding and mimicking of such processes in artificial systems is the central idea of solar to chemical energy conversion research, especially photocatalysis.⁵⁻¹³ A diverse pool of catalytic supplies ranging from

organic to inorganic to polymeric materials have been explored for harvesting photons and drive various chemical reactions.⁵⁻¹³ Among them, semiconductor nanoparticles or quantum dots (QDs) have emerged strongly because of their high absorption extinction coefficient ($\sim 10^6 \text{ M}^{-1} \text{ cm}^{-1}$) and electron-hole mobility, size and shape tunable band gap, photostability and flexible surface chemistry.¹⁴⁻²⁵ A thorough literature review reveals that the common practice in the area of QD photocatalysis is to use them in combination with other catalytic materials (like metal ions/complexes, semiconductors, 2D materials etc.).²⁶⁻²⁸ For example, Krauss and co-workers reported the photocatalytic hydrogen generation with CdSe QD as photocatalyst along with Ni^{2+} as cocatalyst.²⁹ The photoexcited electrons from the conduction band of CdSe QDs were transferred to the Ni^{2+} cocatalyst for an efficient reduction of protons, whereas the holes were replenished by ascorbic acid present as a hole scavenger. Moreover, the presence of strongly bound bidentate dihydrolipoic acid (DHLLA) ligands on the surface of QD imparted the desired colloidal stability to the QD photocatalyst, allowing the reaction to proceed for a much longer reaction time. In another notable example, Eisenberg and co-workers used surface-engineered CdSe QDs as a sensitizer for the photocatalytic hydrogen evolution studies in the presence of Fe–dithiolene complexes (**Figure 3.1a, b**).³⁰ The hydrogen evolution activity was dependent on the electronic properties of the Fe–dithiolene catalysts as well as the surface chemistry of the QD sensitizer. The Fe–dithiolene catalyst-2 containing electron-donating dithionate ligands produced the maximum amount of H_2 with the 3-mercapto-2,2-bis(mercaptomethyl)propanoic acid (S3) capped CdSe QD sensitizer (**Figure 3.1b, c**). Notably, an inverse correlation was noted between the surface coverage of the quantum dots and the photocatalytic efficiency. The optimal hydrogen generation occurred at a coverage of 70 units of S3 ligands per quantum dot (**Figure 3.1d**).

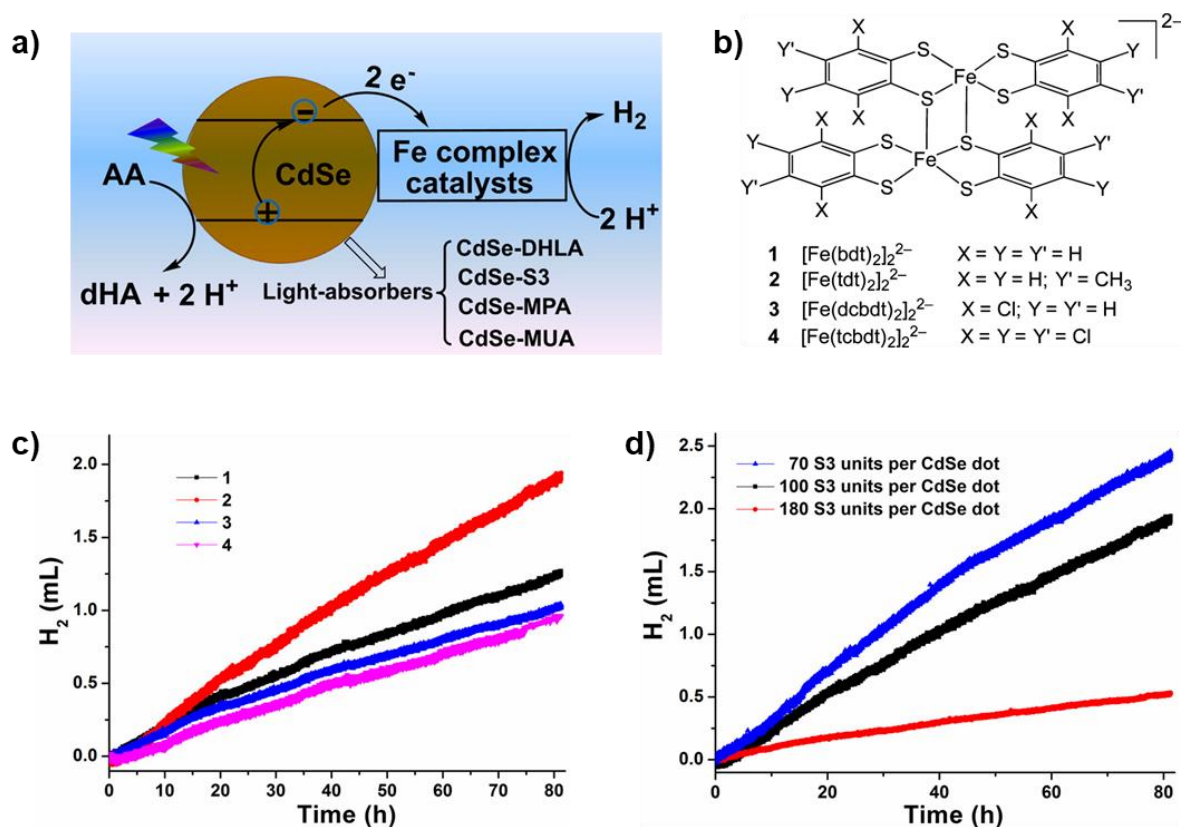


Figure 3.1. a) A schematic representation of surface-engineered CdSe QD-sensitized photocatalytic hydrogen evolution system using Fe-dithiolene complexes as cocatalysts. b) The general molecular structure of Fe-dithiolene complexes with different ligands and substituents. c) The time-dependent hydrogen production was investigated using four distinct Fe-dithiolene complexes in the presence of a CdSe-S3 sensitizer. The ranking of hydrogen production activity among the complexes was found to be $2 > 1 > 3 > 4$. d) Time dependent hydrogen production by Fe-dithiolene complex-2 in presence of CdSe QD sensitizers with different surface coverage of S3 ligands. Reproduced with permission from ref. 30 Copyright: 2016, American Chemical Society.

Interestingly, there have been a few recent reports that have shown the sole use of QDs as photocatalyst for various reactions without the aid of any co-catalysts or sacrificial reagents.³¹⁻³⁶ In one of the pioneering works in this direction, Weiss and co-workers have demonstrated the ability of CdS QDs as a sole photocatalyst to carry out a C-C coupling reaction between 1-phenyl pyrrolidine and phenyl trans styryl sulfone (**Figure 3.2a**).³¹ Also, the effect of surface ligand organization on the photocatalytic properties of the QDs was shown in this work. The photocatalytic efficiency of the CdS QDs was significantly enhanced when the QD's surface was modified by replacing the native long chain ligands with short chain octylphosphonate ligands. This enhancement can be attributed to the disruption of the ligand shell structure allowing better interaction between the reactant and the catalyst surface (**Figure 3.2b**). Almost at the similar time, Weix, Krauss and co-workers have performed five different classes of photoredox transformations (e.g., β -alkylation, β -aminoalkylation, dehalogenation, amine arylation, and decarboxylative radical formation) using CdSe QDs as photocatalysts with

excellent performance (**Figure 3.2c**).³² This work proved that even a single sized QD can match, or in some cases can out-perform, the widely used classes of molecular photocatalysts for organic transformations.

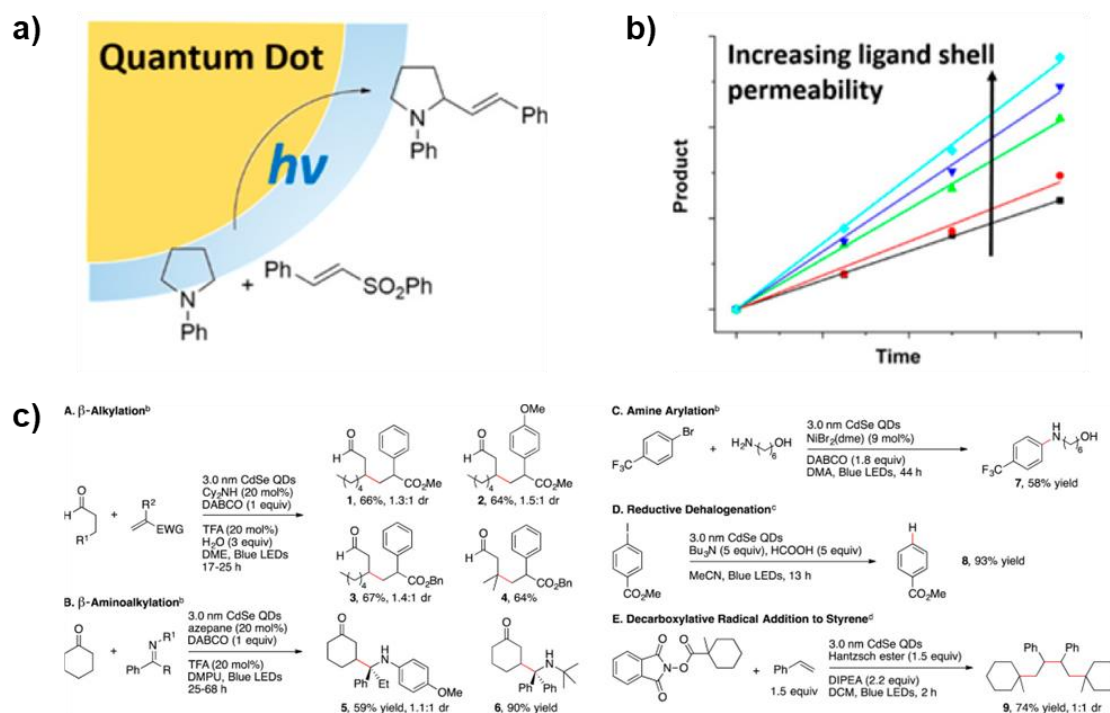


Figure 3.2. a) A schematic diagram of the QD-based photocatalyzed C–C coupling reaction. b) A plot showing the dependence of the yield of the product formed in the CdS-QD-based photocatalyzed C–C coupling reaction on the ligand shell composition; the higher the amount of OPA ligands, the greater the permeability and, hence, the higher the reaction yield. Reproduced with permission from ref. 31. Copyright: 2017, American Chemical Society. c) A series of different classes of organic photoredox transformations depicting the diverse ability of the CdSe QD photocatalysts. Reproduced with permission from ref. 32. Copyright: 2017, American Chemical Society.

In order to hold this promise on a longer perspective, these exciting results with toxic metal ion based QDs should be tested and demonstrated with more environmentally friendly QDs. Even though extensive studies were performed on the fundamental properties of environmentally friendly QDs (synthesis, surface engineering, imaging and biotargeting, energy/charge transfer processes etc.),^{37–44} the photocatalytic aspects of them are still at its infancy. For instance, Weiss and co-workers have used CuInS₂/ZnS QD for carbon dioxide reduction.⁴⁵ In this work, negatively charged CuInS₂/ZnS QDs were electrostatically coupled with a positively charged iron-tetraphenylporphyrin (FeTMA) complex. An ultrafast photoinduced electron transfer (PET) step was observed from QDs to FeTMA in the electrostatically bound nanohybrid assembly, which further resulted in the reduction of CO₂ to CO in aqueous medium under visible-light irradiation (**Figure 3.3a**). A high selectivity (~99%) was achieved in the formation of CO, with a turnover number of 450 after 30 h of irradiation (**Figure 3.3b**). In another work,

Wu, Zhou and Patzke and co-workers have culminated in demonstrating the photocatalytic hydrogen evolution reaction with surface engineered InP/ZnS QDs in presence of Ni^{2+} as a co-catalyst (**Figure 3.3c**).⁴⁶ The native oleylamine ligands on the InP/ZnS QDs were place exchanged with negatively charged ligands of varying lengths (such as sulphide ion, 3-mercaptopropionic acid, and 11-mercaptoundecanoic acid). The maximum H_2 production efficiency was observed with the shortest sulphide ions capped InP/ZnS QDs (**Figure 3.3d**).

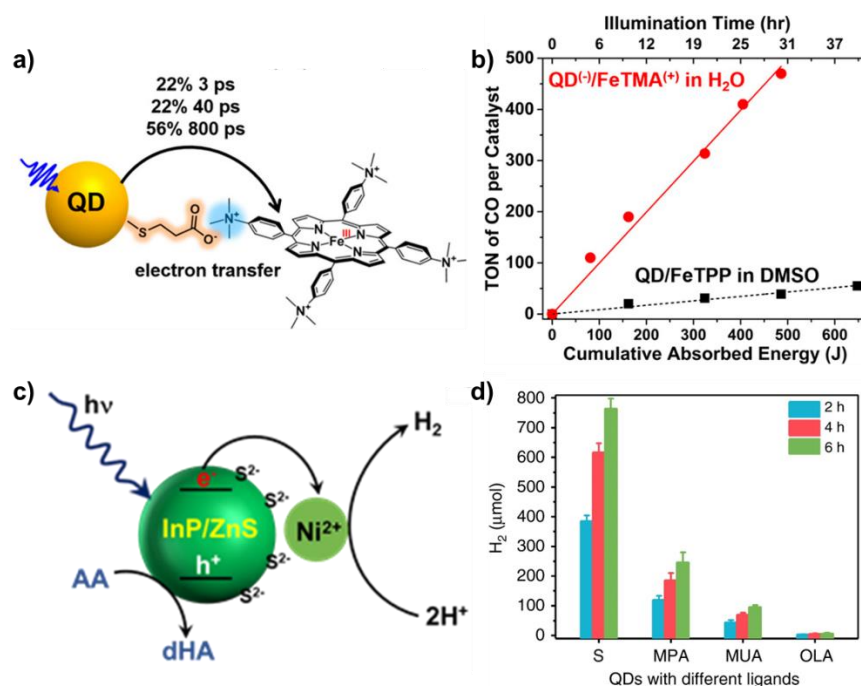


Figure 3.3. a) A schematic representation of the ultrafast photoelectron transfer process from the QD to an FeTMA complex in an electrostatically bound CuInS₂/ZnS QD-FeTMA complex, leading to the selective photoreduction of CO₂ to CO. b) A plot of TON vs. cumulative absorbed energy (with respect to illumination time), proving that the photocatalytic performance of electrostatically bound QD-FeTMA assemblies (red circles) were superior compared to a mixture of unmodified QDs and FeTMA complexes (black squares). Reproduced with permission from ref. 45. Copyright: 2018, American Chemical Society. c) A schematic diagram of photocatalytic hydrogen evolution *via* PET process from S²⁻-capped InP/ZnS QDs to a Ni²⁺ co-catalyst. Ascorbic acid (AA) was used as the hole scavenger. d) The influence of different surface ligands on the photocatalytic hydrogen evolution activity of surface-engineered InP/ZnS QDs. Reproduced with permission from ref. 46. Copyright: 2018, Nature Publishing Group.

To this end, a successful demonstration of environmentally friendly InP/ZnS QDs photocatalyzing different classes of chemical reactions, especially organic transformations, will strengthen their claim of potential ‘greener’ alternatives for toxic metal ion based QDs. In this regard, we have explored the potency of InP/ZnS QD as a visible-light photocatalyst for mimicking the two key classes of reactions in photosynthesis, namely metal-centered redox and carbon-carbon bond forming reactions (**Figure 3.4**). As a representative example for the metal-centered redox reaction, we have performed the InP/ZnS QD photocatalyzed reduction

of ferricyanide to ferrocyanide with a photoconversion yield of ~70% and an internal quantum yield of ~0.21%. The recyclability feature was accomplished by embedding the InP/ZnS QD onto a paper substrate, while retaining its photocatalytic activity over many cycles. In the second example, InP/ZnS QD was used exclusively as an efficient photocatalyst for the C-C coupling reaction between 1-phenyl pyrrolidine (PhPyr) and Phenyl-*trans*-styryl sulfone (PhSO₂), without the aid of any co-catalysts or sacrificial reagents. A photoconversion yield of ~52% and an internal quantum yield of ~1.21% were achieved, under the band-edge excitation of InP/ZnS QD. A similar photocatalytic performance was observed under white-light illumination (similar to A.M. 1.5) as well, which proves the suitability of InP/ZnS QDs in the direct harvesting of solar radiation as well. A good overlap between the action spectra and the ground state absorption of InP/ZnS QD confirmed the active participation of QDs in these photocatalyzed metal-centered redox and carbon-carbon bond forming reactions.

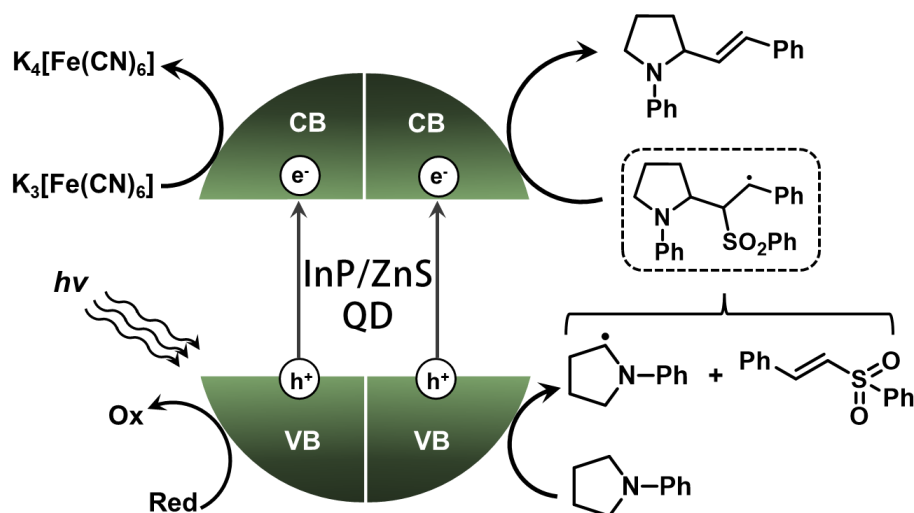


Figure 3.4. Schematics showing the potency of InP/ZnS QD to photocatalyze two distinctly different reactions: metal-centered ferricyanide reduction and C-C bond formation between PhPyr and PhSO₂. InP/ZnS QD photocatalyzed the ferricyanide reduction in the presence of a sacrificial reagent, ethanol, with high photoconversion yield and recyclability (left side). Strikingly, InP/ZnS QD was able to photocatalyze the C-C coupling reaction, exclusively, without the aid of any co-catalysts or sacrificial reagents (right side).

3.3. Experimental section

The materials and reagents used, synthesis of InP/ZnS QDs, their ligand exchange reactions, general techniques, methods and calculations used are described in **Chapter 2**. Some of the other experimental details specific to this Chapter are given below.

3.3.1. Estimation of PL quantum yield of the QD:

The relative quantum yield of [-] InP/ZnS QD was estimated using Coumarin-153 (QY ~ 0.58)⁴⁷ as the reference, using the following equation.⁴⁸

$$\phi_s = \phi_r \left(\frac{F_s A_r}{A_s F_r} \right) \frac{\eta_s^2}{\eta_r^2}$$

where

Φ_s & Φ_r = Quantum yields of QD sample and reference, respectively

F_s & F_r = Integrated fluorescence intensities of QD sample and reference, respectively

A_s & A_r = Absorbance at the excitation wavelength (400 nm) of QD sample and reference, respectively

η_s & η_r = Refractive indices of solvents for QD sample and reference, respectively.

The quantum yield of [-] InP/ZnS was estimated to be 0.30 (30 %).

3.3.2. Electrochemical measurements

Estimation of the band positions of InP/ZnS QD: The positions of conduction and valence bands were estimated by a combination of electrochemical and absorption studies. Only one peak corresponding to the reduction process ($E_{pc} \sim -0.76$ V vs standard hydrogen electrode (SHE)) was observed in cyclic voltammogram study of InP/ZnS QDs (with 50 mM tetra-butyl ammonium perchlorate in chloroform as the electrolyte), which reveals the position of the conduction band to be -0.76 V vs SHE or -3.68 eV vs vacuum (**Figure 3.5**). The measurement was carried out with three-electrode system where glassy carbon was used as the working electrode, Ag/AgNO₃ as the reference electrode and Pt was used as the counter electrode. The position of valence band was calculated from the optical band gap energy (~450 nm or 2.75 eV) obtained from the absorption spectrum of InP/ZnS QD. Accordingly, the energy value of

the valence band was estimated to be +1.99 V vs SHE or -6.43 eV vs vacuum (see appendix Figure 3.16).

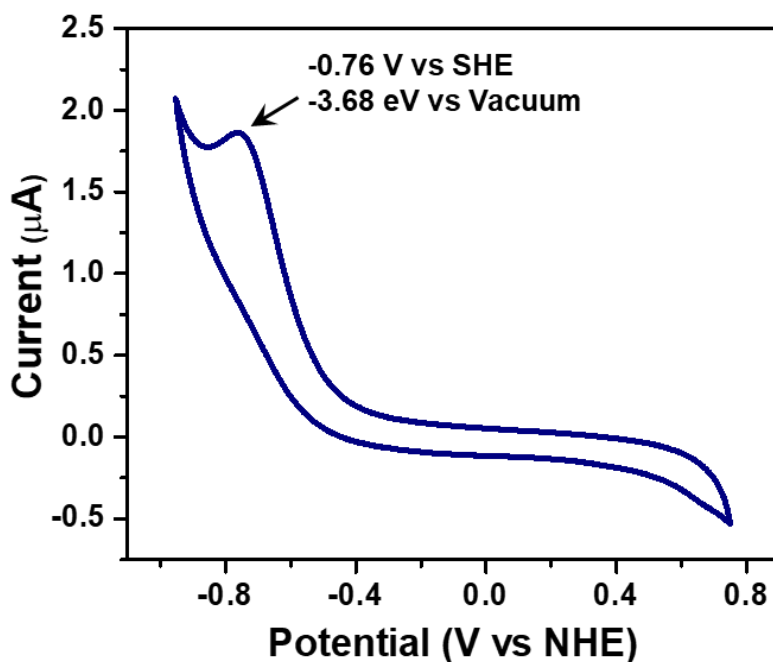


Figure 3.5. Cyclic voltammogram of InP/ZnS QDs dispersed in 50 mM tetra-butyl ammonium perchlorate (TBAP) solution in chloroform, recorded at a scan speed of 50 mV/s. The measurement was carried out with three-electrode system where glassy carbon was used as the working electrode, Ag/AgNO₃ as the reference electrode and Pt was used as the counter electrode.

3.3.3. Photocatalytic studies

3.3.3.1. Light sources used for InP/ZnS QD photocatalyzed reactions

Photocatalytic studies were performed using a single 1W regular blue (~465 nm) LED. The intensity at the wall of the cuvette was measured to be 30 mW.cm⁻² using a Newport optical power meter (model: 842-PE). To generate the action spectra, 1W LEDs of four different wavelengths were used (413 nm, 465 nm, 525 nm and 635 nm), while keeping the incident light intensity same (~30 mW.cm⁻²) throughout the experiments. A broadband white light was generated from a 100 W white light LED source coupled with optical fibre. The incident intensity on the wall of the reaction vial was set to be 100 mW.cm⁻² (equivalent to A.M.= 1.5).⁴⁹

3.3.3.2. InP/ZnS QD photocatalyzed reduction of ferricyanide in solution

In a typical procedure, 300 μ M ferricyanide and 600 nM InP/ZnS QD were added to 3 mL 5 M aqueous ethanol solution in a quartz cuvette. The reaction mixture was purged with Ar for 10 min. The reaction mixture was then irradiated by placing the cuvette in front of one 1W blue LED (465 nm) at a distance of $\sim$ 2 cm (incident intensity = 30 mW.cm⁻²). The reaction was then monitored spectroscopically, and the time-dependent kinetic studies were performed up to 2 h. Longer irradiation did not improve the conversion yield.

3.3.3.3. InP/ZnS QD photocatalyzed C-C coupling reaction

In a stir bar equipped 2 mL GC vial, 20.0 mg phenyl *trans*-styryl sulfone (1 eq.), 13.7 mg 1,3,5-trimethoxybenzene (1 eq.), 13.1 mg 1-phenyl pyrrolidine (2.5 eq.), 47.1 mg CsOAc (3 eq.) and 5 μ M InP/ZnS QDs were taken in 1 mL dry benzene and purged in Ar for 15 min. The vial was then sealed with teflon tape and kept under irradiation for 10 h under 465 nm 1W LED with continuous stirring. At the end of the reaction, the solvent benzene was evaporated under vacuum, and the residue of the crude reaction mixture was dissolved in CDCl₃ to obtain ¹H-NMR spectra. The yield of the product was calculated from ¹H-NMR studies with respect to 1,3,5-trimethoxybenzene present as an internal standard.

3.3.3.4. Purification of the product

After the reaction, solvent benzene was evaporated, and the residue was heated at $\sim$ 100 °C under vacuum to remove the unreacted 1-phenyl pyrrolidine. The product was further purified as a colorless liquid by preparatory TLC with 95:4:1 v/v of hexane:acetone:triethylamine as the eluent.¹⁰

3.3.3.5. Kinetic analysis

The procedure for estimating the rate of reduction was adopted from the literature reports for metal nanoparticle catalysed ferricyanide reduction.^{50,51}

During the reduction, there was a decrease in the absorption of ferricyanide at $\sim$ 420 nm. First, the conversion of ferricyanide to ferrocyanide, in terms of concentration, was calculated by the following formula:

$$Conversion_{420\text{ nm}} = \frac{(A_{t=0\text{ min}} - A_{t=t\text{ min}})}{\epsilon_{K_3[Fe(CN)_6]}}$$

Where A is the absorbance of ferricyanide, which was estimated using Beer-Lambert's law, the molar extinction coefficient of $K_3[Fe(CN)_6]$ was taken as $1050 \text{ M}^{-1} \text{ cm}^{-1}$.^{50,51}

A perfect fit of conversion vs time plot with first order equation confirms that the reduction of ferricyanide follows the first order kinetics. A similar observation was reported previously for metal nanoparticle catalysed ferricyanide reduction.^{50,51} The conversion vs time plot was fitted with the following first order equation:

$$c = c_0(1 - e^{-kt})$$

Where c_0 corresponds to the initial concentration of ferricyanide and k is the first order rate constant. The reaction rate is determined as:

$$\frac{dc}{dt} = c_0 \cdot k \cdot e^{-kt}$$

The rate at $t=0$ is,

$$k' = \frac{dc}{dt}(t = 0) = c_0 \cdot k$$

Hence, the rate constant (k) is determined as,

$$k = k'/c_0$$

Here the initial concentration (c_0) taken is $300 \mu\text{M}$.

3.3.3.6. Calculation of the yield of the photocatalytic reactions

Calculation of the yield of the ferricyanide reduction: The photocatalytic percentage conversion yield was calculated by the following equation.

$$\% \text{ Photoconversion yield}_{420 \text{ nm}} = \frac{(A_{t=0 \text{ min}} - A_{t=t \text{ min}})}{A_{t=0 \text{ min}}} \times 100$$

Where, $A_{t=0 \text{ min}}$ is the initial absorbance of ferricyanide at $\sim 420 \text{ nm}$ in reaction mixture and $A_{t=t \text{ min}}$ indicates the absorbance at $\sim 420 \text{ nm}$ after 2 h of photoirradiation.

Calculation of yield of the C-C coupling reaction: The yield of the C-C coupling reaction was calculated using ^1H NMR spectroscopy with respect to 1,3,5-trimethoxybenzene as an internal standard. The 3H peak (δ 6.12, s) of internal standard and the average of two

distinguishable product peaks (1H, δ 6.25, dd and 1H, δ 6.5, d) were taken as the reference peaks for calculating the reaction yield.

A typical example for the calculation of yield for NMR spectrum shown in **Figure 3.21** is estimated below.

The two distinguishable (1H, δ 6.25, dd and 1H, δ 6.5, d) of the product were integrated with respect to the internal standard.

The average of integrated values of two 1H peaks corresponding to the product = $(0.54 + 0.50)/2 = \underline{\underline{0.52}}$

Moles of internal standard present in the reaction = 81.86 μmol ,

Hence, moles of product formed = $(81.86 \times 0.52) \mu\text{mol} = 42.56 \mu\text{mol}$

The molecular weight of the product = 249.36 g. mol^{-1}

Hence, the weight of the product formed = $42.56 \times 10^{-6} \text{ mole} \times 249.36 \text{ g. mol}^{-1} = \underline{\underline{10.61 \text{ mg}}}$

The theoretical expected yield of the reaction = 20.41 mg

So, the yield of the reaction is = $(10.61/20.41) \times 100 = 52\%$

The same procedure was followed throughout the paper to estimate the yields for C-C coupling reactions under different reaction conditions.

3.4. Results and discussion

3.4.1. Synthesis and characterization of InP/ZnS QD photocatalysts

The motive of the present work was to establish the potency of InP/ZnS QDs toward various photocatalytic transformations in both aqueous as well as organic medium. For that, at first, myristic acid (MA) functionalized InP/ZnS QD was synthesized following a reported procedure (described in **Section 2.2.1 of Chapter 2**).⁵² The aqueous dispersion to QDs was imparted by replacing the MA ligand with anionic 11-mercaptoundecanoic acid (MUA [-]) ligand, through a place exchange protocol (**Figure 3.6a**, see **Section 2.4.1 of Chapter 2** for

details).^{42,43} The average size of the particles was calculated to be 2.9 ± 0.3 nm using TEM analysis (**Figure 3.6b**). Negligible change in absorption, PL as well as PL lifetime confirmed the stability and retention of the photophysical properties of the QDs even after the place exchange reaction (**Figure 3.6c, d**). The ζ -potential of -32.3 ± 0.3 mV of the MUA place exchanged QDs confirms the presence of negatively charged ligands on the surface (**Figure 3.6e**). The relative quantum yield of [-] InP/ZnS QD was estimated to be 0.30, with respect to Coumarin-153 as the reference (see **Experimental Section 3.3.1** for details).

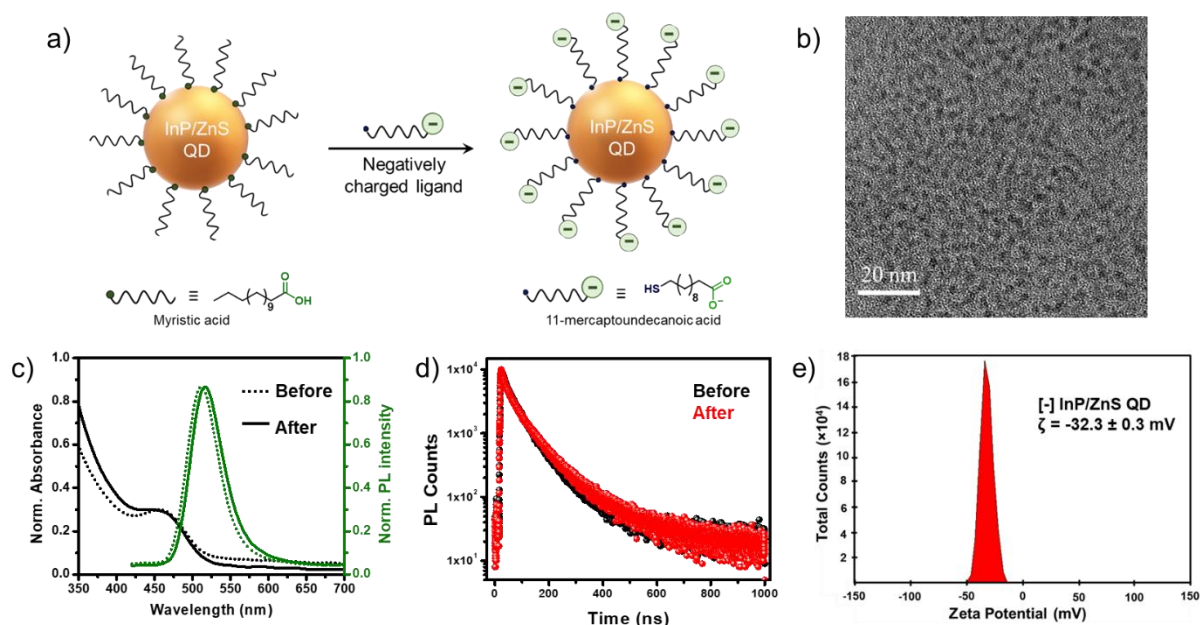


Figure 3.6. Characterization of InP/ZnS QDs. a) Schematic representation of the place exchange reaction of MA capped InP/ZnS QDs with negatively charged MUA ligands, yielding water stable [-] InP/ZnS QDs. b) A representative TEM image of [-] InP/ZnS QDs. The average size was calculated to be 2.9 ± 0.3 nm, from ~ 200 particles. c) Steady-state absorption and PL spectra of InP/ZnS QDs before and after the place exchange with MUA ligands. d) PL lifetime decay profiles of InP/ZnS QDs before and after the place exchange reaction. e) Zeta potential of [-] InP/ZnS QD in water.

3.4.2. InP/ZnS photocatalyzed ferricyanide reduction in aqueous medium

The one-electron reduction of ferricyanide to ferrocyanide, was selected as the model redox reaction to show the potency of InP/ZnS QD photocatalyst in aqueous medium (see **Section 3.3.3.2** for experimental details). The photoirradiation of InP/ZnS QD results in the generation of electrons and holes in the conduction and valence bands, respectively. The favorable energetics between the conduction band of [-] InP/ZnS QD (-0.76 V vs SHE) and the standard

reduction potential of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ couple (0.36 V vs SHE)⁵³ ensured a rapid injection of the photoexcited electrons from QD to ferricyanide (see **Section 3.3.2** for details). On the other hand, ethanol (~5 M, present as a hole scavenger) will extract the holes accumulated in the valence band of InP/ZnS QD photocatalyst to complete the redox cycle (**Figure 3.4**). The main advantage of this redox reaction is that the entire process of ferricyanide reduction to ferrocyanide can be conveniently monitored using UV-vis absorptions studies. One 1W blue light emitting diode (LED) with $\lambda_{\text{max}} \sim 465$ nm, corresponding to QD band edge excitation, was used as the irradiation source. The light intensity on the quartz cuvette wall was measured to be $\sim 30 \text{ mW.cm}^{-2}$. In the presence of $\sim 600 \text{ nM}$ [-] InP/ZnS QD, a drastic decrease in the absorption at $\sim 420 \text{ nm}$ was observed upon $\sim 2 \text{ h}$ irradiation, indicating the reduction of ferricyanide with a photoconversion yield of $\sim 70\%$ (**Figure 3.7a, b**). The internal quantum yield (IQY) of the reaction was calculated to be $\sim 0.21\%$ (see **section 2.6.3 of Chapter 2 for details**). The Prussian blue test further confirmed the formation of the product ferrocyanide (**Figure 3.7c**). However, no noticeable absorption changes were observed upon irradiation of ferricyanide in the absence of InP/ZnS QD, which confirms the photostability of ferricyanide as well (**Figure 3.7a, b**).⁵⁰ Similarly, negligible changes were observed in the absorption of ferricyanide, in the dark, in the presence of InP/ZnS QD. A minimal 20% conversion was observed in absence of hole scavenger ethanol (**Figure 3.7b**). All these experiments together confirm the decisive role of InP/ZnS QD in photocatalysing the reduction of ferricyanide.

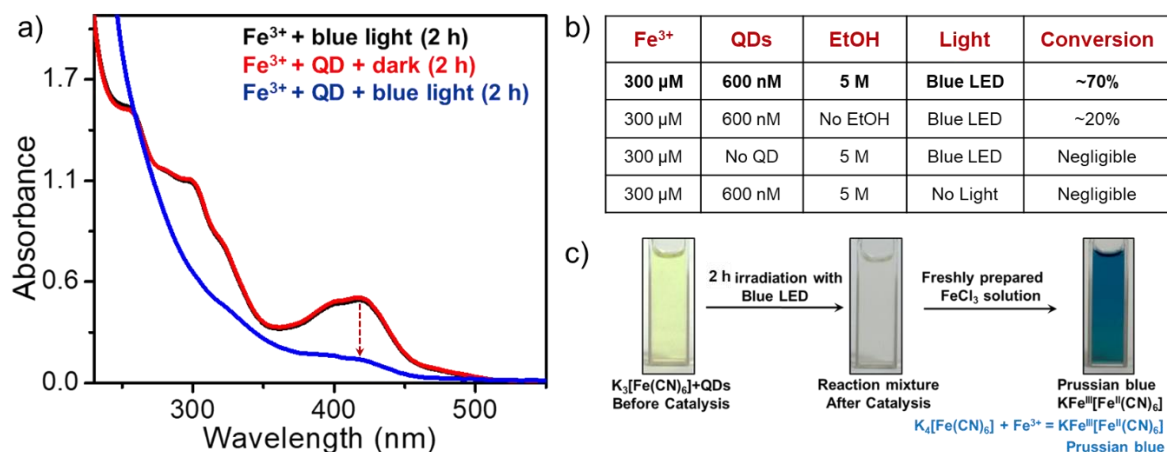


Figure 3.7. Photocatalytic reduction of ferricyanide by InP/ZnS QD. a) Absorption spectra of ferricyanide under different conditions as described in the panel. An appreciable decrease in the ferricyanide absorption was observed only in presence of InP/ZnS QDs and blue light. b) A table summarizing the major control experiments confirming the active and sole involvement of the InP/ZnS QD as photocatalysts. A decent $\sim 70\%$ conversion of ferrocyanide was observed only in the presence of $\sim 600 \text{ nM}$ InP/ZnS QDs, under blue LED irradiation. c) The formation of the product ferrocyanide, was confirmed by the Prussian blue test as seen from the blue colour of the final solution.

Motivated by the initial results, systematic time-dependent absorption studies were performed in the presence of ~ 600 nM of InP/ZnS QDs to gain further insights into the kinetics of the photocatalytic reaction. A gradual and steady decrease in the ferricyanide absorption at ~ 420 nm was observed, with a concomitant increase in the ferrocyanide absorption at ~ 240 nm through an isosbestic point at ~ 265 nm (**Figure 3.8a**). A similar absorption trend has been previously reported for the photocatalytic reduction of ferricyanide with metal nanoparticles.^{50,51,53} Detailed kinetic analysis following the absorbance change at 420 nm reveals that the photoreduction follows first order kinetics with a rate constant of 0.027 min^{-1} and a photoconversion yield of $\sim 70\%$ (**Figure 3.8b** and Experimental Section 3.3.3.5 for details).

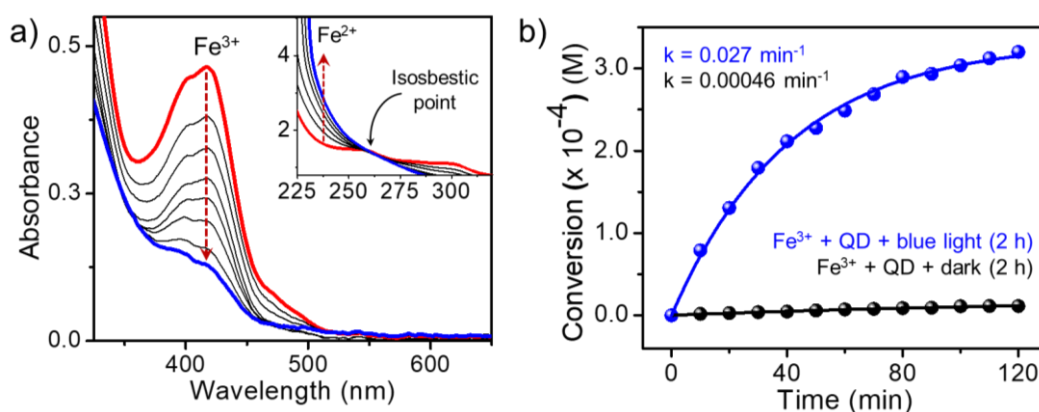


Figure 3.8. Kinetic analysis of the photocatalytic ferricyanide reduction with InP/ZnS QDs. a) Time-dependent absorption spectral changes of ferricyanide in the presence of ~ 600 nM InP/ZnS QDs, under irradiation with 1W blue LED for 2h. b) The exponential first-order fit determining the rate of the reaction following the spectral changes at 420 nm corresponding to panel a. The rate of the reaction in absence of light was negligible compared to the reaction under blue LED.

Constitution of action spectrum: An excellent feature of the QD based photocatalysis is that, the IQY values of the photocatalytic reaction under different excitation wavelengths would follow the ground-state absorption profile of the QDs. These experiments further confirm the participation of the QDs as the active photocatalyst for the chemical transformation. In our case, an excellent overlap between the plot of IQYs of the wavelength dependent reactions and the ground state absorption spectrum of InP/ZnS QD conclusively proved that the photoexcited electron-hole pair from QDs was indeed responsible for the reduction of ferricyanide to ferrocyanide (**Figure 3.9**, Experimental Section 3.3.3.6 and Section 2.6.2 of **Chapter 2** for details).

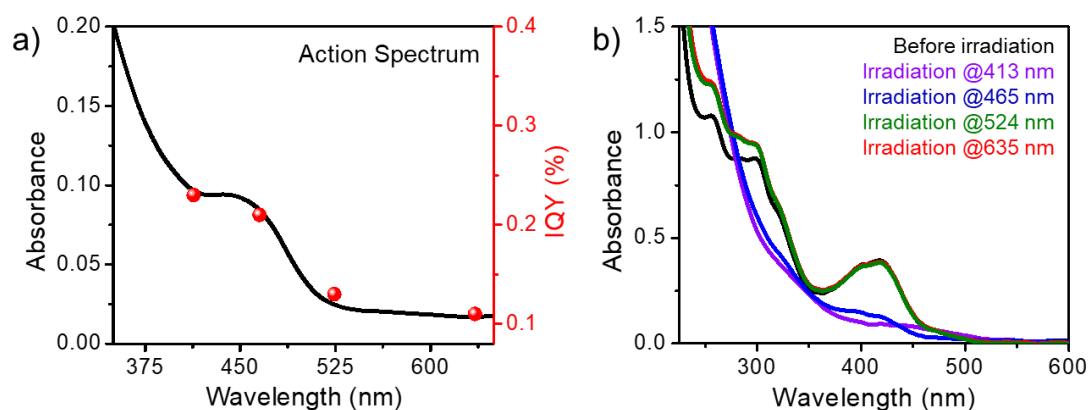


Figure 3.9. Constitution of action spectrum for the photocatalytic ferricyanide reduction with InP/ZnS QDs. a) The action spectrum shows an excellent overlap between the calculated IQY values of the photocatalytic reactions under different excitation wavelengths and the ground state absorption profile of QDs. b) Raw absorption spectra of the photocatalytic reactions used to construct the action spectrum shown in panel a.

3.4.3. Recyclability aspect of the InP/ZnS QD photocatalysts

Our next objective was to study the recyclability aspect of InP/ZnS QD photocatalyst for the ferricyanide reduction reaction. Some of the challenges in homogeneous nano-catalysis are the reusability (because of the NP catalyst instability) and separation of the NP catalyst after the reaction. In the present study as well, a drastic decrease in the photocatalytic activity of InP/ZnS QD was observed after the first cycle of photoreduction (**Figure 3.10**).

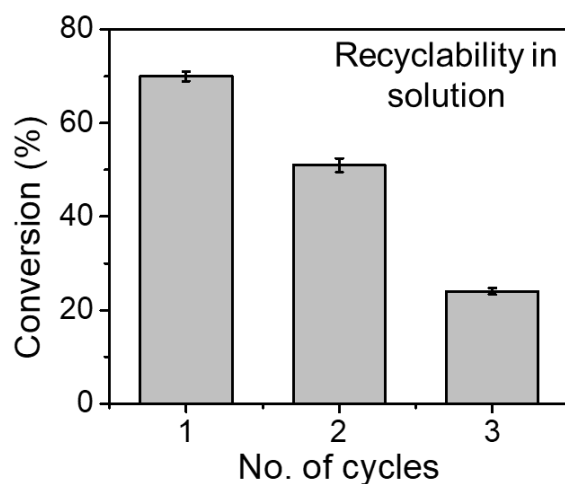


Figure 3.10. Comparison between the percentage photoconversion yields as a function of cycles for photocatalyzed reduction of ferricyanide using colloidal [-] InP/ZnS QDs. A drastic decrease in the photoconversion yield was observed in the consecutive cycles of the reaction.

We have overcome this challenge by successfully embedding the InP/ZnS QD onto a paper substrate. A dip-catalyst system was prepared by the simple dip-coating of Whatman-60 filter paper in the chloroform solution of MA capped InP/ZnS QD, followed by drying under hot air

(**Figure 3.11a**). The successful coating of InP/ZnS QD on Whatman paper was clearly visible from the yellow color on the paper and green emission under UV irradiation (**Figure 3.11a**). The photophysical studies confirmed that the absorption and PL properties of InP/ZnS QD were well preserved on Whatman-60 filter paper (**Figure 3.11b**).

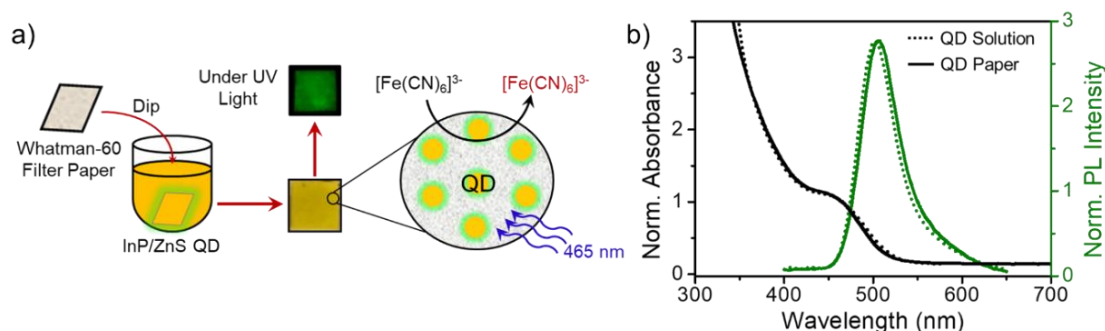


Figure 3.11. Recyclability in the photocatalytic reduction of ferricyanide. a) Schematics showing the preparation of InP/ZnS QD coated Whatman-60 filter paper and its use in the photocatalytic reduction of ferricyanide. b) The comparison of the absorption and steady-state PL profiles of the colloiddally stable InP/ZnS QDs in solution vs the InP/ZnS QDs coated over Whatman-60 filter paper.

An excellent recyclability with negligible loss in the catalytic activity was observed in the ferricyanide reduction (for at least 5 cycles) when InP/ZnS QD coated paper was used as the photocatalyst (**Figure 3.12**). The incorporation of QDs in the Whatman-60 filter paper helped in retaining the stability of InP/ZnS QD during the photoreduction of ferricyanide, leading to the efficient catalyst recyclability over multiple cycles.

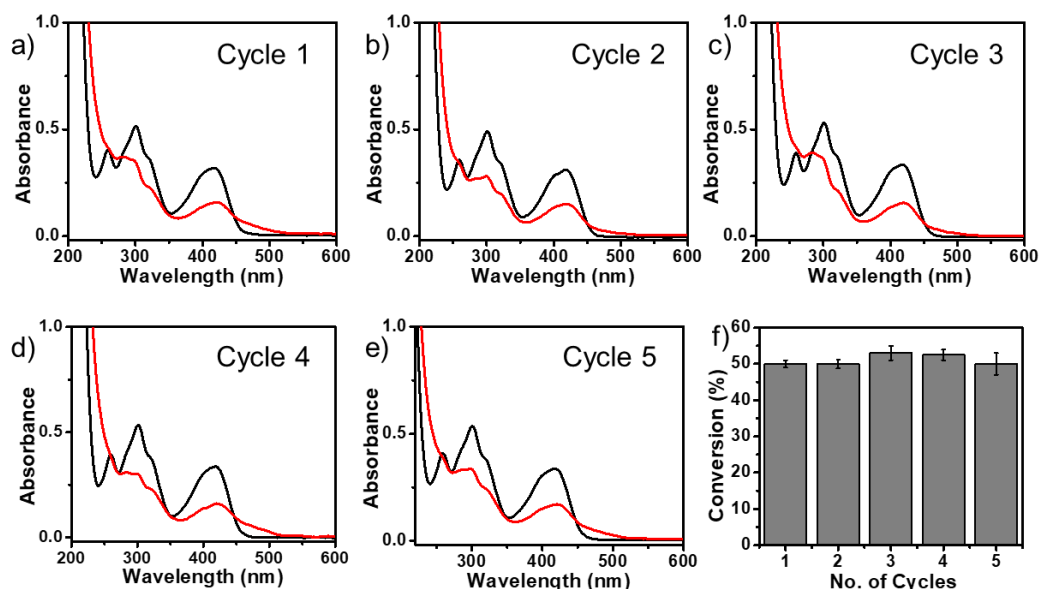


Figure 3.12. Recyclability studies. a-e) Absorption spectral changes of ferricyanide in the absence (black trace) and presence of InP/ZnS QD coated paper catalyst (red trace), for five cycles of photoreduction. f) Bar diagram showing the percentage photoconversion yields for ferricyanide reduction up to five cycles using InP/ZnS QD coated paper catalyst, based on the raw data of panel a-e.

3.4.4. Photocatalytic C-C coupling with InP/ZnS QD photocatalysts in organic medium

After establishing the potential of InP/ZnS QD to photocatalyze a metal-centered redox reaction, our next task was to test a more complex and important C-C bond forming reaction. One of the major limitations in QD based photocatalysis is the necessity to use additional sacrificial reagent (like ethanol in the ferricyanide reduction) or co-catalyst in catalyzing a particular reaction. Addition of sacrificial reagents increases the photocatalytic activity at the cost of undesirable byproduct formation, leading to a ‘partial solar to chemical conversion’.⁵⁴ Now we discuss about the potency of InP/ZnS QD as a sole photocatalyst to catalyze the two redox halves of a C-C coupling reaction, without the aid of any co-catalyst or sacrificial oxidant or reductant. For this, a representative photocatalytic C-C coupling reaction between 1-phenyl pyrrolidine (PhPyr) and phenyl-*trans*-styryl sulfone (PhSO₂) was selected (**Figure 3.13a**). As a common practice in literature, iridium-based polypyridyl complexes are used to photocatalyze these classes of C-C bond forming reactions.¹⁰ Recently Weiss and Co-workers have used CdS QDs to photocatalyze the C-C bond formation between PhPyr and PhSO₂ reactants.³¹ The selection of this particular C-C bond forming reaction as a test reaction in the present work was essential to conclusively compare the photocatalytic performances of InP/ZnS QD with already reported iridium-based metal complexes and CdS QDs. More importantly, performing a well-known C-C bond forming reaction using InP/ZnS QD photocatalysts will ensure a practical ‘greener’ alternative to toxic metal-ion based QDs for future organic and inorganic transformations.

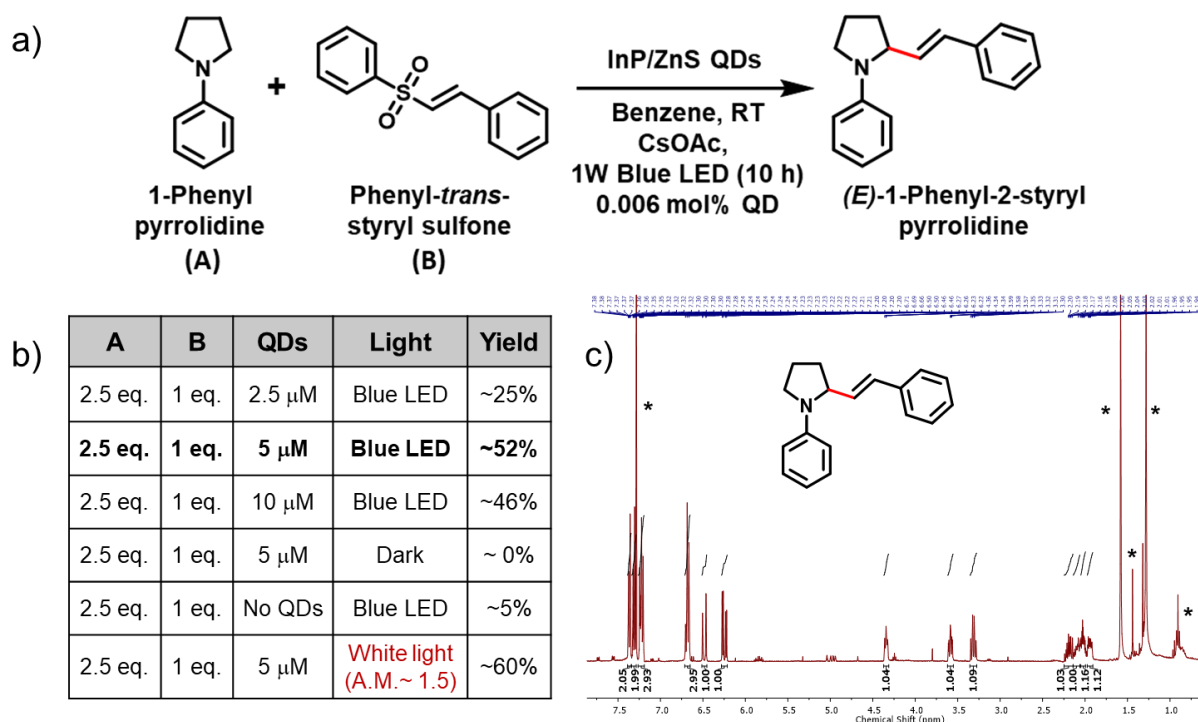


Figure 3.13. Photocatalytic C-C coupling reaction with InP/ZnS QDs. a) Reaction scheme for the C-C bond formation between PhPyr and PhSO₂ in the presence of InP/ZnS QD and blue LED. b) A table summarizing various reaction conditions adopted to optimize the catalyst concentration and prove the exclusivity of InP/ZnS QD to photocatalyze the C-C bond formation. The yields were calculated from ¹H NMR spectroscopy using 1,3,5-trimethoxy benzene as an internal standard (I.S.). c) The ¹H-NMR spectrum of the purified C-C coupled product formed in the photocatalytic reaction.

The photoexcited electrons and holes generated in InP/ZnS QD were effectively used to catalyze the C-C coupling reaction between PhPyr and PhSO₂ to form (*E*) 1-phenyl-2-(2-phenylethenyl) pyrrolidine. For this, a mixture of 2.5 eq. PhPyr, 1 eq. PhSO₂ and 3 eq. cesium acetate (CsOAc) in benzene was irradiated in the presence of ~5 μM MA-capped InP/ZnS QD using a 1W blue LED (see **Experimental Section 3.3.3.3** for details). After 10 h of irradiation, to our delight, we observed the formation of the C-C coupled product (*E*) 1-phenyl-2-(2-phenylethenyl) pyrrolidine (**Figures 3.13a, b**). The product was further purified and thoroughly characterized using ¹H and ¹³C NMR studies (**Figure 3.13c, appendix Figures 3.18 and 3.19**). Optimization of the catalyst concentration showed a maximum product yield of ~52% for an InP/ZnS QD concentration of 5 μM (**Figure 3.13b**). The yield of the product was estimated from NMR studies using 1,3,5 trimethoxy benzene (1,3,5-TMB) as the internal standard (**appendix Figures 3.20-3.25**). The photocatalytic activity of InP/ZnS QD is comparable to that of the Ir based and CdS QD photocatalysts^{10,31} (**appendix Table 3.1**). Negligible conversion yield in the control experiments proves the necessity of InP/ZnS QD to drive the C-C bond formation. Interestingly, a high conversion yield of ~60% of C-C coupled product

was observed under white-light illumination (of A.M. ~ 1.5) with InP/ZnS QDs (**Figure 3.13b and appendix Figure 3.25**). This experiment showcases the sustainability aspect of the InP/ZnS QD photocatalyzed transformations for the direct solar light harvesting.

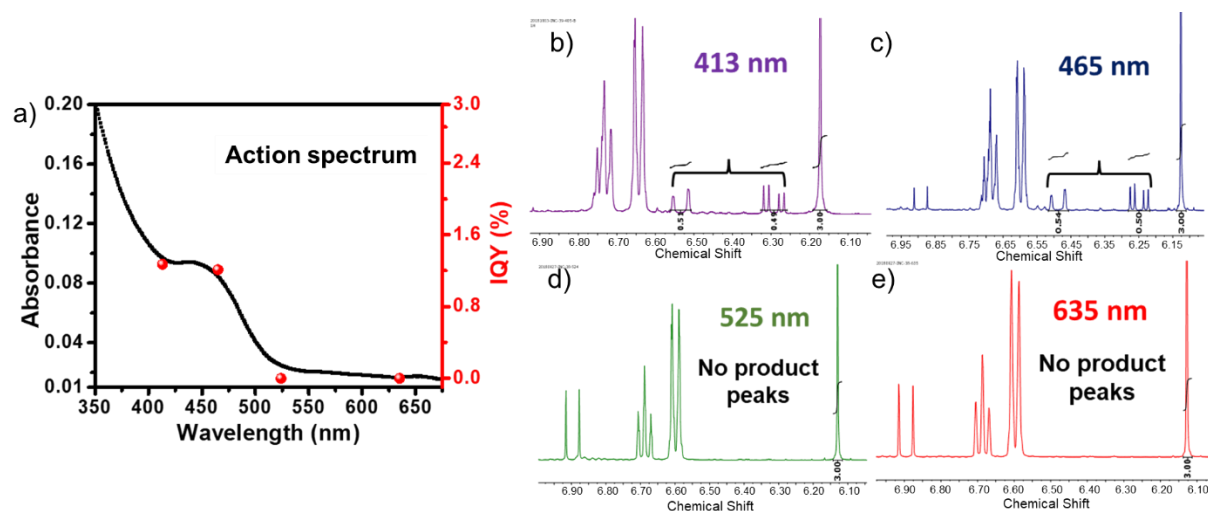


Figure 3.14. Constitution of action spectrum for the photocatalytic C-C coupling reaction with InP/ZnS QDs. a) An excellent overlap between the calculated IQY values of the photocatalytic reactions under different excitation wavelengths and the ground state absorption profile of the QDs, confirms the active involvement of InP/ZnS QDs as the photocatalysts. b) Raw ^1H -NMR spectra used for calculating the yield of the photocatalytic reactions, which was further used to construct the action spectrum shown in panel a.

Again, action spectrum was constructed to confirm the participation of QDs as active photocatalysts. A good overlap between the IQY of the reactions under different excitation wavelengths and ground state absorption profile of InP/ZnS QD further confirmed the active participation of QDs in photocatalyzing the given C-C bond formation reaction (**Figure 3.14**).

3.4.4.1. Mechanistic analysis

The mechanism involved in the InP/ZnS QD photocatalyzed C-C bond formation between PhPyr and PhSO_2 was studied using steady state and time-resolved PL experiments (**Figure 3.15**).¹⁰ To understand the charge transfer steps, PL quenching of the photoexcited InP/ZnS QDs were performed upon sequential addition of both the reagents (PhPyr and PhSO_2) involved in the C-C coupling reaction. When PhPyr was added into the solution of InP/ZnS, a drastic quenching of the PL of InP/ZnS QDs was observed in both steady state as well as time resolved experiments (quenching from black to blue traces in **Figure 3.15a**). Whereas, upon addition of PhSO_2 , the other reagent, negligible quenching was observed in either of the spectrum (black to red traces in **Figure 3.15a**). These photophysical experiments clearly proves the presence of

a charge transfer step between the photoexcited InP/ZnS QDs and the PhPyr moiety during the photocatalytic reaction. With these experiments, along with the support of prior literature reports, we could conclude that after the photoexcitation of the InP/ZnS QD in the first step, there is a hole transfer step happening from the valence band of the QD to PhPyr (reducing the QD to QD⁻; QD acting as an oxidant). This is followed by the abstraction of an α -proton from PhPyr by CsOAc leading to the formation of an α -amino radical. Then the formed radical further reacts with the PhSO₂ to form an intermediate β -sulfonyl radical, which in turn accepts the photoexcited electron from the conduction band of the QD (QD act as a reductant in this step). This step can also be corroborated from the photophysical experiments, where it was clear that PhSO₂ does not undergo any direct charge transfer step with the photoexcited QDs. Then in the final step, an elimination of phenyl sulfone anion yields (*E*) 1-phenyl-2-(2-phenylethenyl) pyrrolidine as the major product (**Figure 3.15b**).

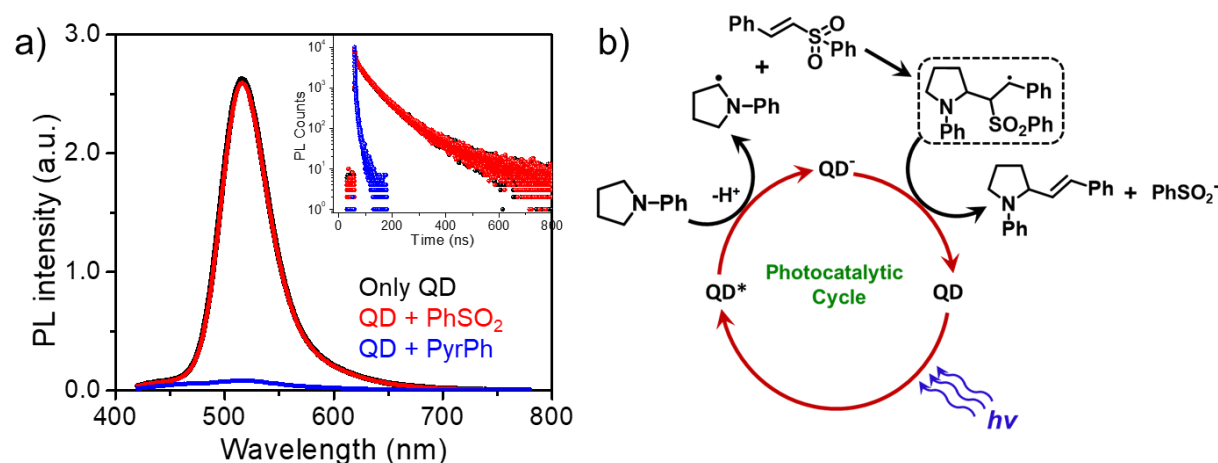


Figure 3.15. Mechanistic understanding of the InP/ZnS QD photocatalyzed C-C coupling reaction. a) Steady-state and lifetime PL quenching experiments to understand the charge transfer mechanism involved in the reaction. b) Plausible mechanism of the photocatalytic C-C coupling reaction as understood with the help of the PL quenching experiments as well as the prior literature reports.

3.5. Conclusions

The potency of InP/ZnS QDs to efficiently photocatalyze two distinctly different classes of redox reactions (metal-centered and C–C bond formation) was successfully demonstrated. The flexibility in tuning the surface chemistry of InP/ZnS QD enabled their use in photocatalyzing the reactions in aqueous as well as organic media. A metal-centered reduction of ferricyanide to ferrocyanide was photocatalyzed by MUA capped [-] InP/ZnS QD with a high

photoconversion yield of ~70% in the presence of ethanol as a sacrificial reagent. A proper deposition of InP/ZnS QD onto a paper substrate helped in retaining the efficient photocatalytic activity of QD over multiple cycles. More importantly, InP/ZnS QD was used as a sole photocatalyst to catalyze a standard C–C coupling reaction without the aid of any cocatalyst or sacrificial oxidant or reductant. InP/ZnS QD was able to exclusively photocatalyze the C–C bond formation between PhPyr and PhSO₂ under the band-edge excitation of QD with an appreciable photoconversion yield of ~52% and internal quantum yield of ~1.21%. A similar photocatalytic performance was observed under white-light illumination, which proves the suitability of InP/ZnS QD for the direct harvesting of solar radiation as well. A good overlap of the action spectra with the ground state absorption of InP/ZnS QD confirmed the active participation of QDs in the photocatalyzed metal-center redox and C–C bond forming reactions. In short, our work projects InP/ZnS QD as a “greener” alternative to the toxic metal-ion-based QDs for future photocatalytic organic and inorganic transformations.

3.6. References

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3.7. Appendix of Chapter 3

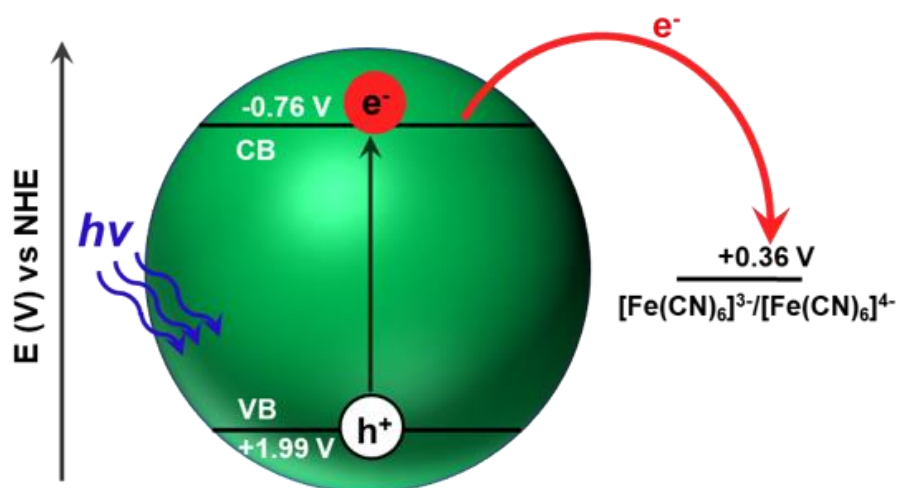


Figure 3.16. Schematics showing the band positions of InP/ZnS QD and the reduction potential of ferricyanide/ferrocyanide redox couple. The ΔG value of -1.12 V for electron transfer confirms that the photoreduction of ferricyanide by InP/ZnS QD is thermodynamically feasible.

NMR characterization of the C-C coupled product

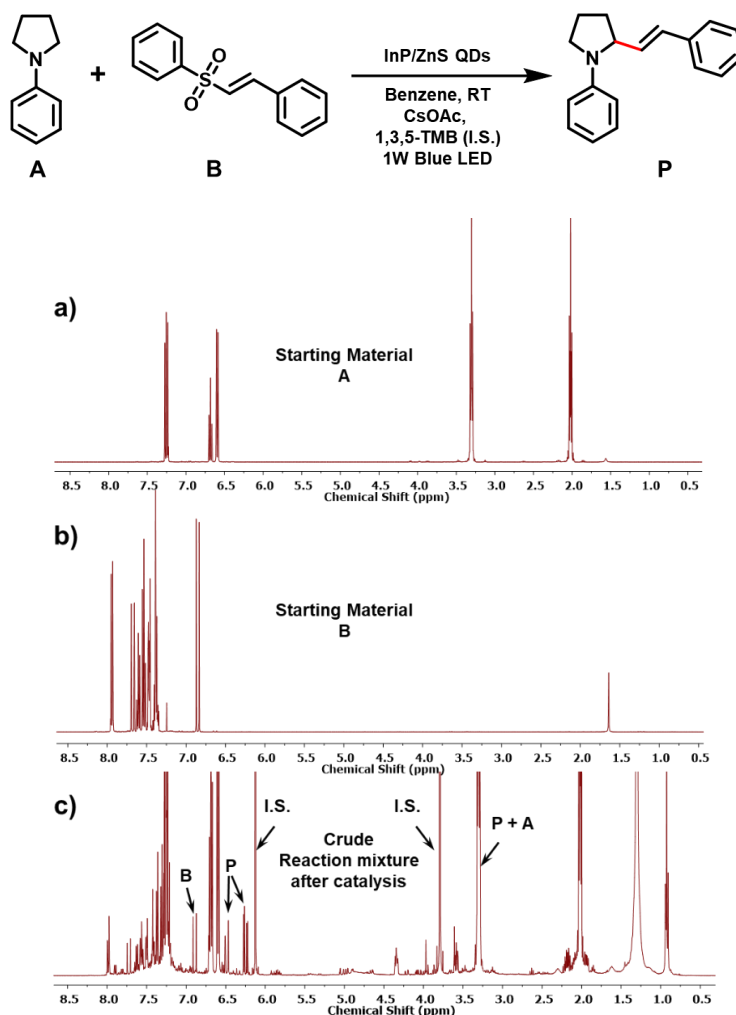
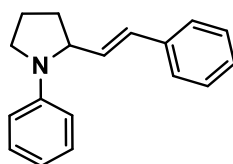


Figure 3.17. Full ¹H NMR spectra of (a) A, (b) B and (c) the crude reaction mixture in CDCl₃ after 10h irradiation with 1W Blue LED. 1,3,5-trimethoxybenzene was used as the internal standard (I.S.). Solvent peaks are marked by with asterisk (*).

Purification and characterization of product



(E) 1-phenyl-2-(2-phenylethenyl) pyrrolidine: ¹H NMR (400MHz, CDCl₃): δ 1.92-2.24 (4H, m), 3.28-3.35 (1H, td), 3.56-3.61 (1H, m), 4.33-4.36 (1H, m), 6.22-6.27 (1H, dd), 6.46-6.56 (1H, d), 6.66-6.71 (3H, m), 7.20-7.25 (3H, m), 7.30-7.33 (2H, m), 7.35-7.38 (2H, m). ¹³C NMR (400 MHz, CDCl₃): δ 23.38, 33.01, 48.74, 60.73, 112.19, 115.72, 126.34, 127.21, 128.48, 129.01, 129.46, 131.67, 137.63, 147.54. The observed values are in good agreement with the literature reports.¹⁰

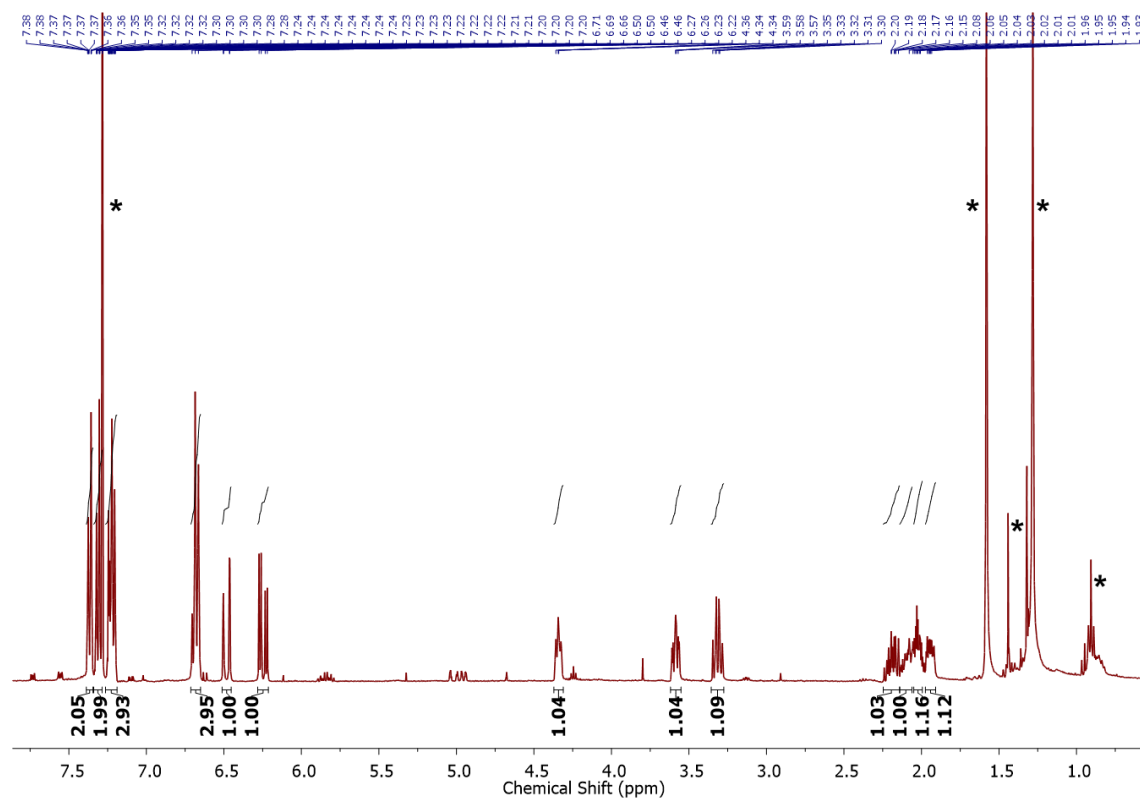


Figure 3.18. Full ^1H NMR spectrum of purified product (*E*) 1-phenyl-2-(2-phenylethenyl) pyrrolidine in CDCl_3 . Solvent peaks are marked with asterisk (*).

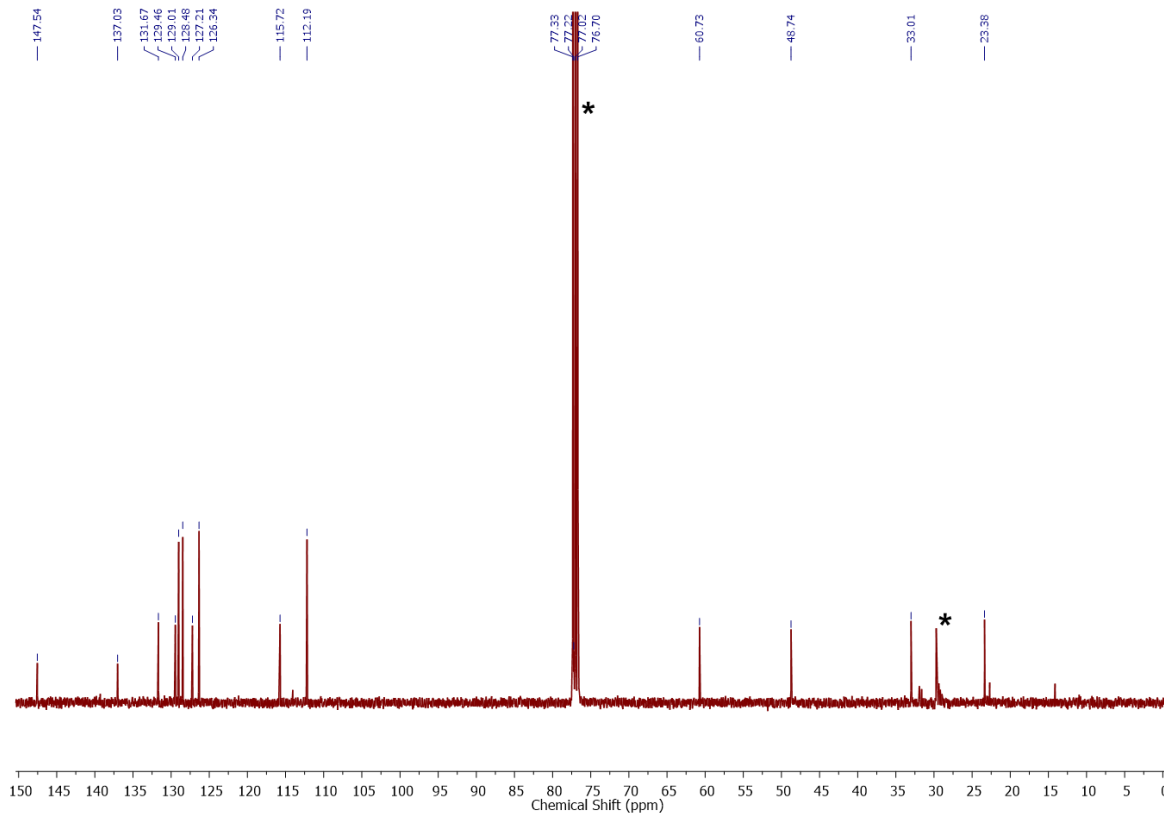
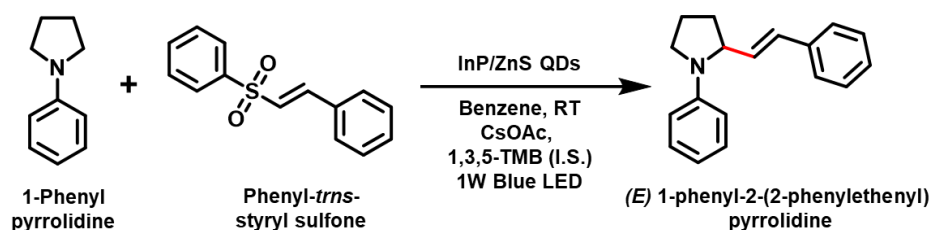


Figure 3.19. Full ^{13}C NMR spectrum of the purified product (*E*) 1-phenyl-2-(2-phenylethenyl) pyrrolidine in CDCl_3 . Solvent peaks are marked with asterisk (*).

Optimization of InP/ZnS QD photocatalyst concentration:



Condition 1: InP/ZnS QD concentration = 2.5 μM

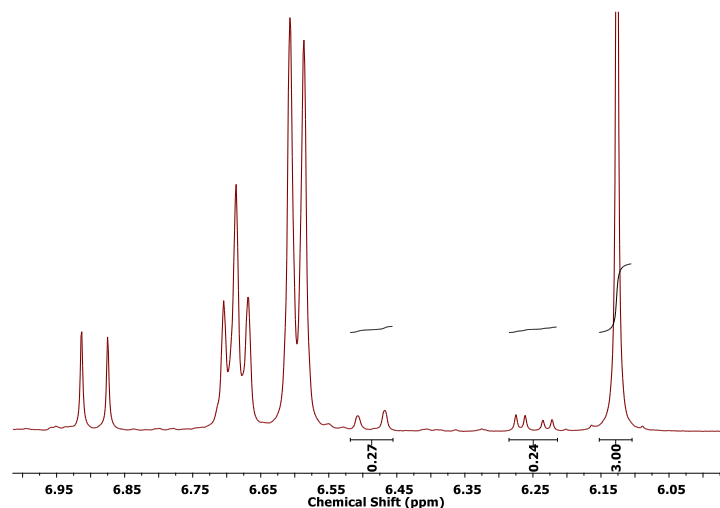


Figure 3.20. Selected area ^1H NMR spectrum of the reaction mixture in CDCl_3 after 10 h of irradiation with 1W blue LED with InP/ZnS QD catalyst concentration of 2.5 μM . The yield of the reaction was estimated to be $\sim 25\%$.

Condition 2: InP/ZnS QD concentration = 5 μM

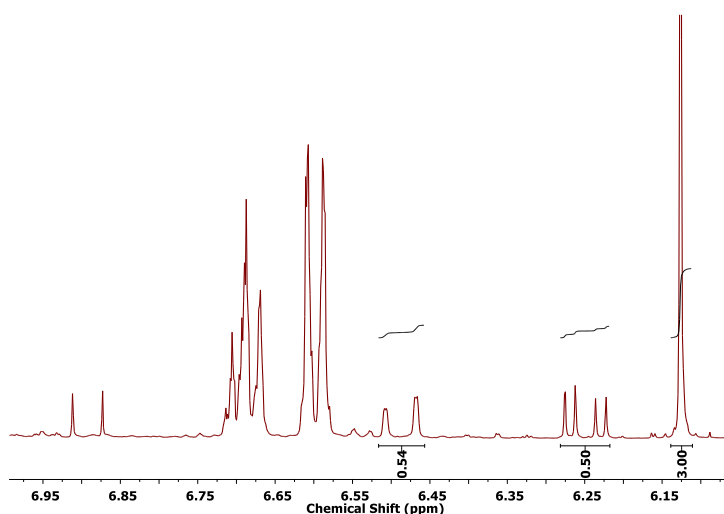


Figure 3.21. Selected area ^1H NMR spectrum of the reaction mixture in CDCl_3 after 10 h of irradiation with 1W blue LED with InP/ZnS QD catalyst concentration of 5 μM . The yield of the reaction was estimated to be $\sim 52\%$.

Condition 3: InP/ZnS QDs concentration = 10 μ M

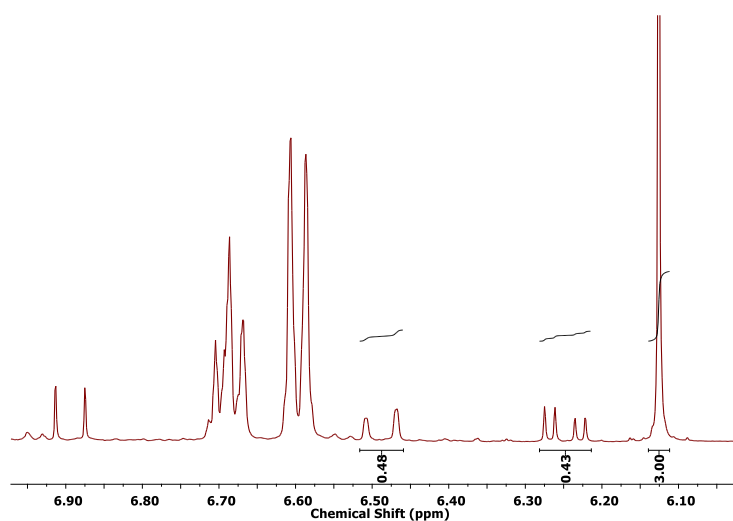


Figure 3.22. Selected area ¹H NMR spectrum of the reaction mixture in CDCl₃ after 10 h of irradiation with 1W blue LED with InP/ZnS QD catalyst concentration of 10 μ M. The yield of the reaction was estimated to be ~46%.

Condition 4: Reaction in dark

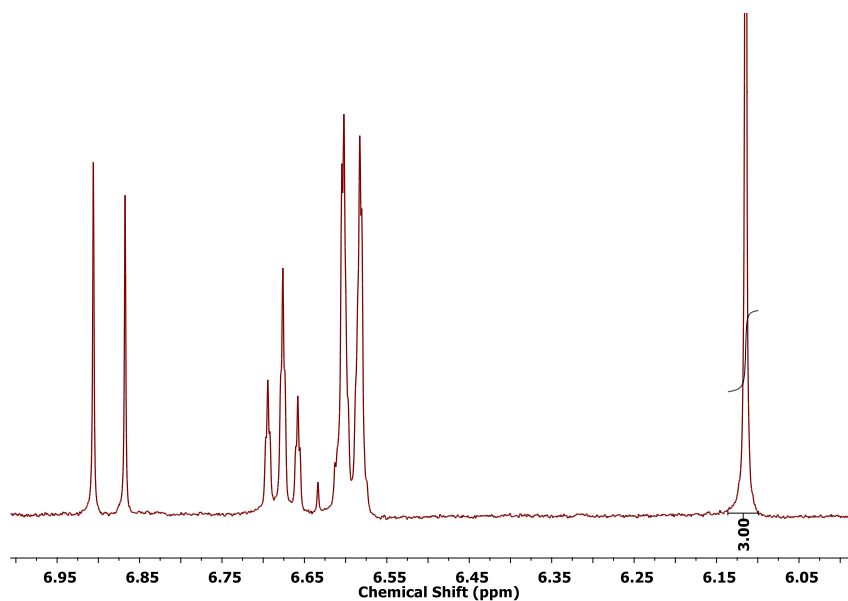


Figure 3.23. Selected area ¹H NMR spectrum of the reaction mixture in CDCl₃ after 10 h in the presence of 5 μ M InP/ZnS QD catalyst in dark. No noticeable signals corresponding to the product was observed (Yield ~ 0%).

Condition 5: Reaction without InP/ZnS QDs

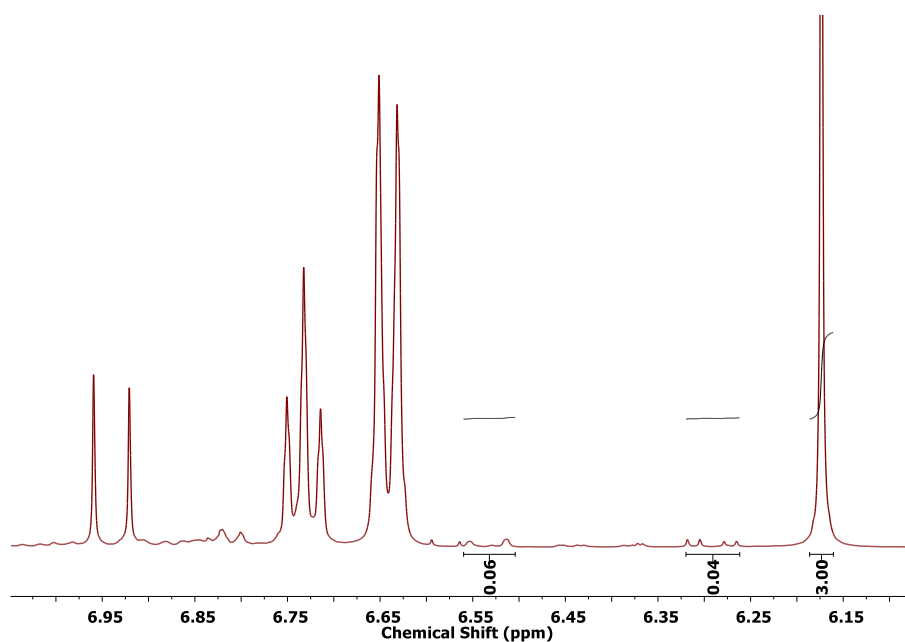


Figure 3.24. Selected area ¹H NMR spectrum of the reaction mixture in CDCl₃ after 10 h of irradiation with 1W blue LED in the absence of InP/ZnS QD. A marginal yield of ~5% was estimated.

Condition 5: Reaction under white-light irradiation

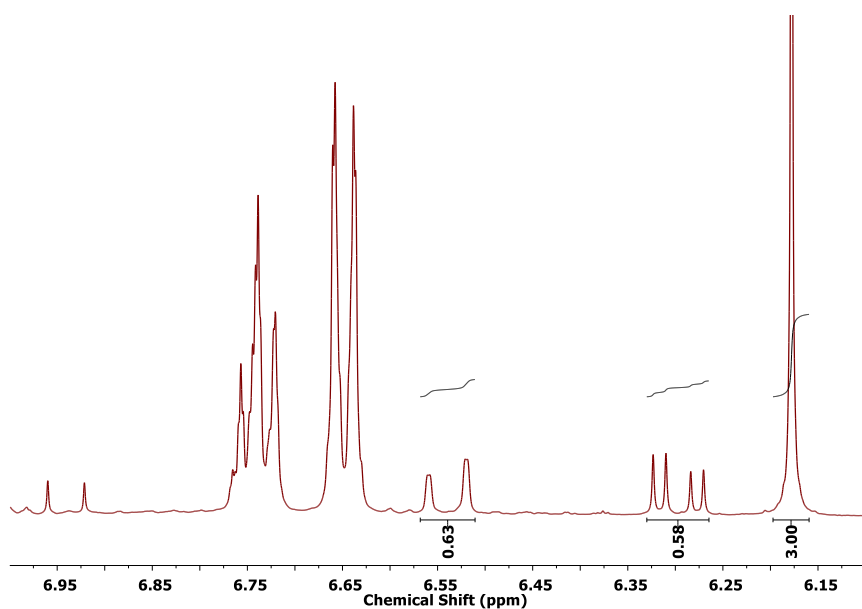


Figure 3.25. Selected area ¹H NMR spectrum of the reaction mixture in CDCl₃ after 10 h of irradiation with white-light (equivalent to A.M.= 1.5) in the presence of 5 μM InP/ZnS QD. The yield of the reaction was estimated to be ~ 60%.

Comparison of conditions for C-C bond formation reaction photocatalyzed by InP/ZnS QD with CdS QD and Ir photocatalysts.

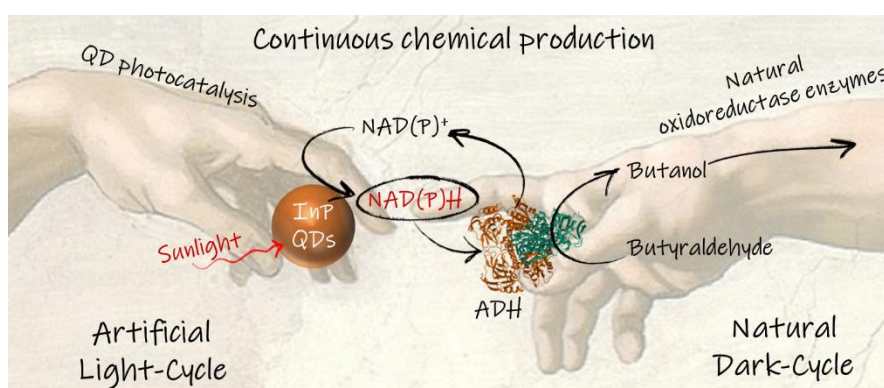
A summary of the reaction conditions for our system and the previous reports for the same C-C coupling reaction performed with Ir and CdS QD based photocatalysts is shown in **Table 3.1**.

Table 3.1. Comparison between Ir-photocatalyst, CdS QD and InP/ZnS QD based photocatalysts for performing the same C-C bond forming reaction.

	Ir catalyst¹⁰	CdS QD catalyst³¹	InP/ZnS QD catalyst
PhPyr added	250 mM	2.5 mM	204.6 mM
PhSO ₂ added	100 mM	1.2 mM	81.8 mM
CsOAc added	3 eq.	2 eq.	3 eq.
Catalyst loading	1 mol%	0.5 mol% QD conc.=5 μ M (with respect to QDs)	(0.006 mol%) QD conc.=5 μ M (with respect to QDs)
Solvent	Toluene	Benzene	Benzene
NMR Yield	81%	60% for CdS QDs treated with 250 eq. OPA	52%
Light Source	Two 26 W compact fluorescence lights	One 13 mW, 405 nm laser	One 1 W blue LED
Reaction time	24 h	5.5 h for CdS QDs treated with 250 eq. OPA	10 h

Chapter – 4

Photoregeneration of Reactive Cofactors with InP Quantum Dots for Continuous Chemical Synthesis



4.1. Abstract

The shuttling of redox-active nicotinamide cofactors between the light and dark cycles is the key to the continuous production of biomass in photosynthesis. Replication of such processes in artificial photosynthetic system demands the fast photoregeneration as well as simultaneous integration of these nicotinamide cofactors into the dark cycle. Here, we report the design of an artificial photosynthetic system for the continuous production of butanol via the constant photoregeneration and consumption of nicotinamide cofactors, powered by indium phosphide quantum dot (InP QD) photocatalyst and alcohol dehydrogenase (ADH) enzyme, respectively. A strong electrostatic attraction between the oppositely charged InP QDs and electron mediators significantly enhanced the charge extraction and utilization processes, enabling a fast (~ 30 min, with a turn-over-frequency of $\sim 1333\text{ h}^{-1}$), quantitative ($>99\%$), and selective photoregeneration of enzymatically active nicotinamide cofactors in the light cycle. These photoregenerated nicotinamide cofactors were further coupled in the dark cycle to trigger the ADH oxidoreductase enzyme for the production of butanol, via sequential as well as simultaneous light-dark cycles. The amount of butanol produced under simultaneous light-dark cycles was higher than the stoichiometric limit, proving the constant regeneration and consumption of nicotinamide cofactors in the integrated light and dark cycles, respectively, as seen in photosynthesis.

4.2. Introduction

A ceaseless and continuous formation of biomass by photosynthetic process offers the best sustainable way for the perpetual synthesis of chemicals using artificial light-harvesting systems.¹⁻⁵ Such desirable outcomes are only possible because of a perfect synergy between light-harvesting components photocatalysing the light phase reactions and enzymes catalysing the dark phase reactions.⁶ Specifically, the reduced nicotinamide cofactor formed in the light cycle (in photosynthetic reaction center) is consumed in the dark cycle (in Calvin cycle) during the enzymatic transformation of carbon dioxide to glucose.⁷ In this process, the nicotinamide cofactors are oxidised back, which further participates in the light cycle to achieve continuous light-dark cycles. A close look at the overall photosynthetic process reveals that the shuttling of the redox cofactors between the light and dark cycles is the key to the ceaseless production of the desired biomolecules.^{8,9} Apart from their participation in the photosynthetic process, the

redox cofactors regulate the functioning of several oxidoreductase enzymes involved in various biomolecular transformations.^{10,11} Inspired by their role in natural processes, nicotinamide (NAD(P)H) and flavin (FADH₂) based redox cofactors have been used as charge shuttling species in the design of artificial photosynthetic systems.¹²⁻²²

In one such notable example, Baeg and co-workers have developed a graphene based visible-light photocatalyst for nicotinamide cofactor regeneration (**Figure 4.1a**).¹⁶ In this work, substituted porphyrin chromophore was covalently bonded with chemically converted graphene, which made the system active under visible-light irradiation. This modified photocatalyst was then coupled to [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator for the regeneration of 1,4-NADH cofactors. A regeneration efficiency of 45.5% was achieved under 2 h of irradiation (**Figure 4.1b**). The enzymatically active 1,4-NADH was further coupled to the function of formate dehydrogenase enzyme for the reduction of CO₂ to formic acid, forming the successful framework of an artificial photosynthetic system. In another recent report, Farha, Li and co-workers have designed an integrated photocatalyst-enzyme biohybrid system by immobilizing an enzyme, formate dehydrogenase, inside a mesoporous metal-organic framework (MOF) scaffold for efficient regeneration of nicotinamide cofactor followed by their utilization for the biocatalytic reduction of CO₂ to formic acid (**Figure 4.1c**).¹⁹ This designed semi-artificial photosynthetic system could regenerate the reduced nicotinamide cofactors with an efficiency of ~28% under 2 h of white-light irradiation (**Figure 4.1d**). These regenerated cofactors were further consumed in-situ, to synthesise formic acid from CO₂ at a turnover frequency of 865 h⁻¹.

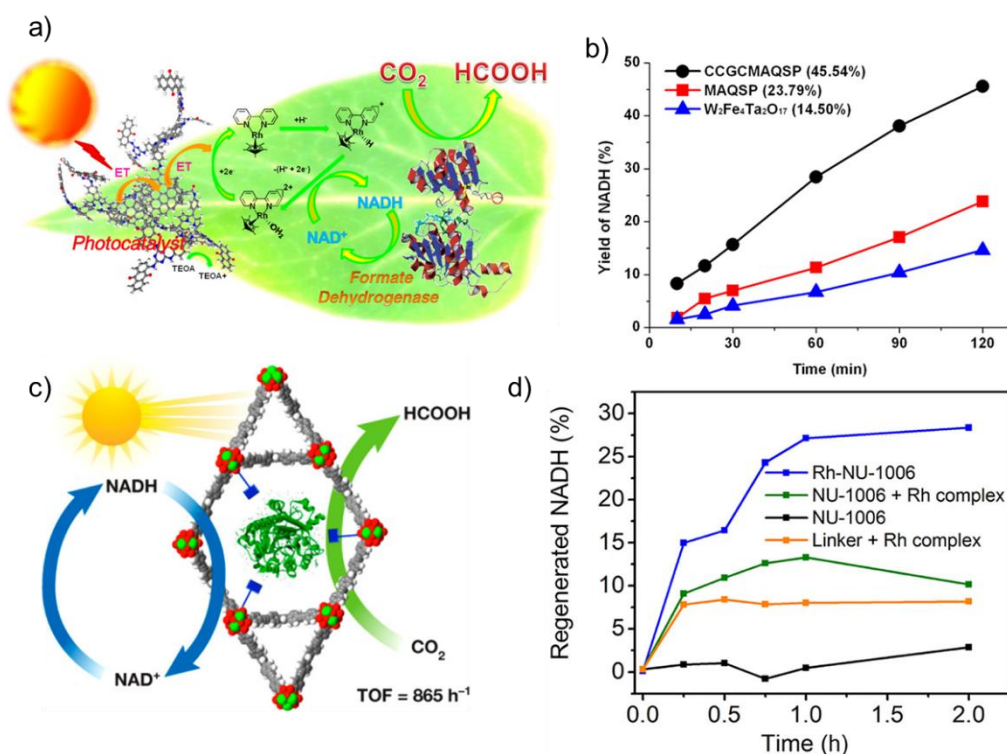


Figure 4.1. a) Schematic representation of the artificial photosynthetic system based on porphyrin bonded chemically converted graphene as photocatalyst. The nicotinamide cofactor regenerated using this photocatalyst is further coupled to formate dehydrogenase for the reduction of CO₂ to formic acid. b) The yield of regenerated NADH with time with respect to the photocatalysts with different compositions. Reproduced with permission from ref. 16 Copyright: 2012, American Chemical Society. c) Schematics of the photocatalytic regeneration of NADH followed by their consumption in an integrated biocatalytic reduction of CO₂ to formic acid with formate dehydrogenase, using a mesoporous MOF photocatalytic scaffold. d) The photocatalytic activity of the system, showing maximum efficiency in presence of the MOF based integrated artificial photosynthetic system, with comparison to the individual components of their physical mixtures. Reproduced with permission from ref. 19 Copyright: 2020, American Chemical Society.

Along with the molecular and polymer based photoregeneration systems, the exploration also expanded to utilize the versatile metal and semiconductor nanoparticle based artificial photosynthetic systems.²³⁻³⁰ In one of the pioneering examples of implementing QDs to regenerate nicotinamide cofactors, Park and co-workers introduced Cd-chalcogenides, e.g., CdS, CdSe and CdTe QDs as photocatalysts (**Figure 4.2a**).²⁴ Interestingly, CdTe QDs were found to be most promising with a highest turnover frequency of 0.540 h⁻¹ followed by CdSe and CdS respectively. In presence of the CdTe QD photocatalyst and [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator complex, a decent regeneration efficiency of ~55% was achieved upon visible-light irradiation for 2 h (**Figure 4.2b**). Moreover, the other CdSe and CdS QDs, followed by the TiO₂ based alternatives showed significant inferiority in terms of catalytic efficiency (**Figure 4.2c**). This work opened up the opportunity of designing artificial photosynthetic systems based of QD based photocatalysts.

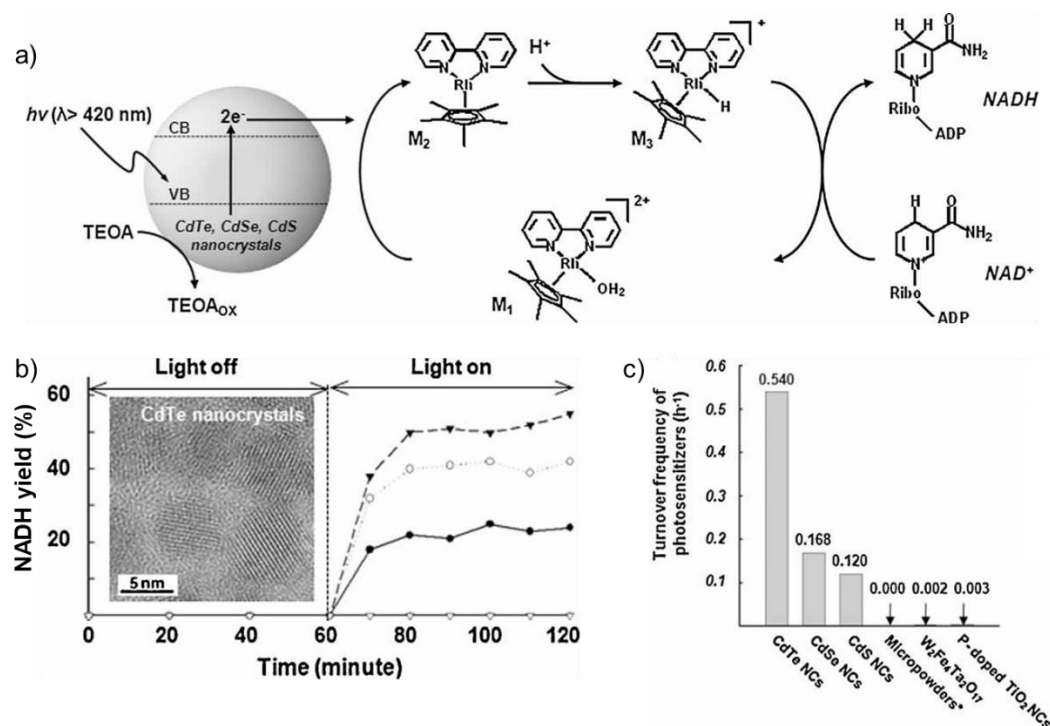
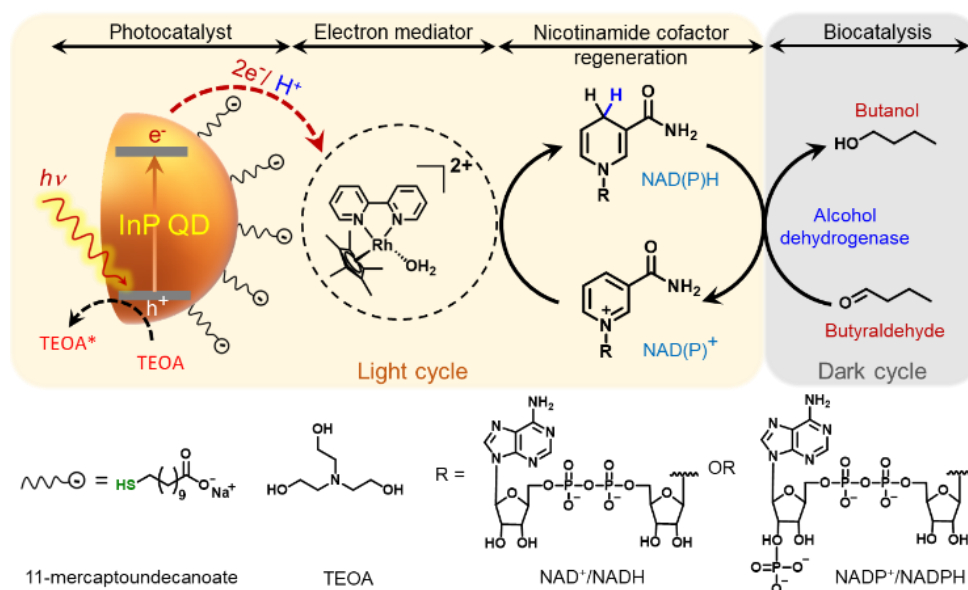


Figure 4.2. a) Schematic representation of the Cd-chalcogenide QD based photocatalytic cofactor regeneration system. b) Photoregeneration activity of different concentrations of CdTe QDs under visible-light excitation. The concentrations used were 2 mM (●), 10 mM (○), and 20 mM (▼) respectively. c) A bar diagram comparing the turnover frequencies of the nicotinamide cofactor regeneration in presence of different photocatalyst moieties under visible-light irradiation. Reproduced with permission from ref. 24 Copyright: 2010, Wiley-VCH.

Comparing the photocatalytic light and enzymatic dark cycle involved in the artificial photosynthetic system, the formation of the desired product in the dark cycle is a relatively easier task, as it is achieved via an enzymatic consumption of the reduced cofactor formed in the light cycle. However, the fast photoregeneration of the reduced cofactors in the light cycle, as well as its integration in the dark cycle, have often been a challenging task to mimic the unidirectional and continuous energy and electron flow seen in the natural process.²³⁻³⁰

Herein, we report a proof-of-concept of an artificial photosynthetic system based on indium phosphide quantum dot (InP QD) photocatalysts for the fast and quantitative photoregeneration of nicotinamide cofactors, and its effective integration in the enzymatically driven dark cycle for the formation of butanol via sequential and simultaneous light-dark cycles. The superior charge separation ability due to inherently lower excitonic binding energy, along with the environmentally friendly nature, made InP QDs a suitable choice as a photocatalyst in the design strategy of an artificial photosynthetic system. Our multicomponent system consists of environmentally friendly InP QDs as the light-harvesting agent, [Cp^{*}Rh(bpy)(H₂O)]²⁺ complex as the electron mediator, NAD(P)⁺ — NAD(P)H as the redox shuttling moiety and

alcohol dehydrogenase (ADH) as the oxidoreductase enzyme for the production of butanol (**Figure 4.3**). The use of an electrostatically bonded $[-] \text{InP QD}:::[+] [\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ complex ensured the efficient generation, separation, extraction, and utilization of charge carriers under visible-light-irradiation, which enabled the fast (within ~ 30 min) and quantitative photoregeneration of NAD(P)H cofactors ($>99\%$) with a turn-over-frequency (TOF) of $\sim 1333 \text{ h}^{-1}$ and an internal quantum efficiency (IQY) of 0.17% . Comparison between the activities of core-only and core-shell InP QDs, as well as wavelength dependent studies, conclusively prove the active participation of the photoexcited electrons from InP QD in the photoregeneration of nicotinamide cofactors. A series of photocatalytic experiments confirmed that hole-transfer process is the limiting step in the photoregeneration of nicotinamide cofactors in the light cycle. The photoregenerated nicotinamide cofactors produced in the light cycle were consumed in the dark cycle to trigger the biocatalytic transformation of butyraldehyde to butanol by ADH enzyme. In this process, the nicotinamide cofactors were oxidised back, which further participated in the next light cycle. In this way, multiple light-dark cycles were achieved in sequential as well as simultaneous fashion. The overall yield of butanol formed was higher than the stoichiometric limit in the simultaneous light-dark cycle experiment, proving the constant photoregeneration and consumption of nicotinamide cofactors in light and dark cycles, respectively. The enhanced photostability and biocompatibility of InP QD photocatalysts, along with the redox shuttling ability of $\text{NAD(P)}^+ \text{---} \text{NAD(P)H}$ cofactors, were the key factors for realising multiple light-dark reaction cycles. In short, a judicious choice of each component in the artificial photosynthetic system enabled the constant regeneration and consumption of nicotinamide cofactors under the photo- and bio-catalytic reaction conditions by InP QDs and ADH enzyme, respectively, leading to the continuous production of butanol.



Scheme 4.3. Schematics showing the role of different components in the effective integration of light and dark cycles in the artificial photosynthetic system based on environmentally friendly InP QDs. The electrostatically bonded $[-]$ InP QD $::[+]$ $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ complex ensures the quantitative and selective photoregeneration of 1,4-NADH cofactors in the light cycle, which further participates in the biocatalytic transformation of butyraldehyde to butanol in the presence of ADH enzyme in the dark cycle.

4.3. Experimental section

The general details of materials and reagents used, synthesis of InP and InP/ZnS QDs, their ligand exchange reactions, general techniques, methods and calculations used are described in **Chapter 2**. Some of the other experimental details specific to this Chapter are given below.

4.3.1. Synthesis of $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator:

$[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ was synthesized using the literature procedure^{31,32} as follows: In a 30 mL glass vial equipped with stir bar, 0.55 mmol of $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ and 3 mL isopropanol (IPA) were added and stirred till solution became deep red in colour. Following this, 0.69 mmol of Cp^* was added to solution and the vial was sealed with Teflon. The resulting mixture was heated at 85 °C for 1 h, resulting in the formation of red-coloured precipitate. The mixture was cooled down to room temperature and then kept at -20 °C for 5-6 h for the complete precipitation. The precipitate was filtered and washed with cold IPA three times, followed by washing with *n*-pentane. The precipitate was dissolved in CHCl_3 and solvent was evaporated under vacuum. This was followed by washing with diethyl ether and finally the solid was dried

under vacuum to yield $[\text{Cp}^*\text{RhCl}_2]_2$ dimer. The dimer was suspended in 5 mL methanol and 2.5 equivalents of 2,2-bipyridyl (bpy) was added to it. A clear orangish-yellow solution was obtained upon bpy addition. Methanol was evaporated under vacuum to concentrate the solution to 1 mL and $[\text{Cp}^*\text{Rh}(\text{bpy})\text{Cl}]\text{Cl}$ was precipitated by addition of diethyl ether. The final product was dried for 12 h at 40 °C under vacuum. Since $[\text{Cp}^*\text{Rh}(\text{bpy})\text{Cl}]\text{Cl}$ immediately hydrolysis to form $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$, a stock solution of 10 mM was prepared in water and stored under dark at 4 °C for further use.

4.3.2. Photocatalytic studies and related calculations:

4.3.2.1. Light sources used for the photocatalytic reactions

Photocatalytic studies were performed using 2×10 W blue (~ 460 nm) LEDs kept at a distance of 1 cm from the reaction cuvette on both sides. The intensity at the wall of the reaction cuvette was measured to be $\sim 100 \text{ mW.cm}^{-2}$ per LED (total $\sim 200 \text{ mW.cm}^{-2}$) using a Newport optical power meter (model: 842-PE). The reactions under other wavelengths of irradiation were performed with two 10 W LEDs of the corresponding wavelength, while maintaining the incident intensity at $\sim 100 \text{ mW.cm}^{-2}$ (total $\sim 200 \text{ mW.cm}^{-2}$).

4.3.2.2. General procedure for the photocatalytic nicotinamide cofactor regeneration

In a typical procedure, NAD(P)^+ (1 mM), TEOA (1 M), $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator (0.25 mM) and [-] InP QDs (1.5 μM) were mixed in 50 mM phosphate buffer keeping the total volume at 3 mL. 50 mM phosphate buffer (PB) was prepared by mixing appropriate amounts of Na_2HPO_4 and NaH_2PO_4 in Milli-Q water. The pH of the reaction mixture was maintained at 8. The mixture was then purged with argon for 15 min followed by irradiation with 2×10 W blue LED (~ 460 nm) for 30 min. After the irradiation, the reaction mixture was half-diluted with 50 mM phosphate buffer and the resulting solution was used for UV-vis absorption measurement as well as for LDH assay.

4.3.2.3. Lipoamide dehydrogenase (LDH) assay

Lipoamide dehydrogenase assay was performed following the Sigma Quality Control Test Procedure (EC 1.8.1.4).^{25,33} All the reagents were prepared fresh before the assay, and the assay was performed at 25 °C. Lipoamide solution (28 mM) was prepared by adding 20 mg of lipoamide in 2 mL of ethanol and 1.5 mL of PB, followed by sonication for 3 min. EDTA (600

mM) with 2% (w/v) BSA was prepared by dissolving 605 mg of EDTA and 100 mg of BSA in 5 mL water, and the pH of the solution was maintained at 7. The enzyme (diaphorase from *Clostridium kluyveri*) stock solution was prepared by dissolving 2 mg of enzyme (5.2 units / mg of protein) in 2 mL of cold PB solution. In a typical enzymatic assay, 100 μ L of lipoamide solution, 100 μ L of EDTA-BSA solution and 100 μ L of enzyme stock solution were added to the half-diluted reaction mixture after irradiation, and the decrease in the absorption at 340 nm was monitored till the decrease got saturated. In presence of enzyme, NAD(P)H will be consumed as per the following reaction resulting in a decrease in the absorbance at 340 nm.^{25,33}



A positive control experiment with the addition of equal amount of NAD(P)H (by making the absorption at 340 nm same to that of the reaction mixture) was also performed to ensure the activity of the enzyme.

4.3.2.4. Calculation of the yield of 1,4-NAD(P)H in the photoregeneration reactions

The concentration of the photogenerated 1,4-NAD(P)H was calculated from the ΔA at ~ 340 nm before and after the ADH assay. The % yield was calculated using the following equation:

$$\% \text{ Yield}_{1,4-\text{NAD(P)H}} = \frac{\text{Concentration}_{1,4-\text{NAD(P)H}}}{\text{Concentration of initial NAD(P)}^+} \times 100$$

Here,

$$\text{Concentration}_{1,4-\text{NAD(P)H}} = \frac{\Delta A_{340 \text{ nm}}}{\epsilon_{1,4-\text{NAD(P)H}}} \times 2$$

And,

$$\epsilon_{1,4-\text{NAD(P)H}} = 6220 \text{ M}^{-1} \text{ cm}^{-1}$$

As the ADH assay was carried out on the half-diluted reaction mixture after irradiation, hence the concentration value was multiplied by a factor of 2.

4.3.2.5. Photoconductivity measurement

The photoconductivity measurements were carried out using a three-electrode electrochemical setup where glassy carbon was used as working electrode, Ag/AgCl as reference and Pt wire

as the counter electrode. At first, 1.5 μM of [-] InP QDs was prepared in 5 mL of 100 mM phosphate buffer and the solution was placed in the electrochemical cell. The amperometric experiment was conducted under a constant potential of 0.2 V. To measure the photoconductivity of the system, 2×10 W blue LEDs were used as light sources. A consecutive series of light-dark cycles were performed on the system with a 60 s light ON followed by 60 sec light-OFF which resulted in the black trace in the **Figure 4.5b**. When 0.25 mM $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator was added into the QD solution, the photocurrent density almost doubled indicating an enhanced charge transfer efficiency (red trace in **Figure 4.5b**).

4.3.2.6. Dark cycle reaction with alcohol dehydrogenase (ADH) enzyme:

Alcohol dehydrogenase (ADH), an oxidoreductase enzyme was selected to carry out the biocatalytic dark cycle reaction utilizing the photoregenerated NADH. For that, the ADH enzyme assay was carried out based on Sigma quality control test procedure (EC 1.1.1.1). The assay was performed at 25 °C and all the reagents were prepared fresh before the assay. The ADH enzyme stock solution was prepared by dissolving 1 mg of the lyophilized ADH powder in 1 mL cold 50 mM phosphate buffer. In a typical assay, 50 μL of the ADH stock solution along with 5 μL of butyraldehyde (29 mM) was added into the 3 mL of photocatalytic reaction mixture after irradiation. To quantify the amount of butanol formed, an appropriate amount of solution was collected and passed through a syringe filter, followed by direct injection into the gas chromatography instrument.

4.4. Results and discussion

4.4.1. Light-cycle: design of InP QD based photocatalytic system and photoregeneration of NAD(P)H cofactor

Core-only InP and core-shell InP/ZnS QDs were prepared in toluene using high-temperature organometallic synthesis, by following modified literature reports.³⁴ The $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ complex was used as the electron mediator to enhance the extraction of charge carriers generated in photoexcited InP QDs, along with facilitating the selective reduction of NAD(P)^+ to NAD(P)H (**Figure 4.4a**).^{24,35,36} The native oleylamine ligands on InP QDs were place

exchanged with negatively charged mercaptoundecanoic acid ligands ([−], MUA) to achieve dispersity in aqueous medium, as well as to install a favourable electrostatic interaction between [−] QD photocatalyst and [+] [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator (**Figures 4.4a-c**). For proving the role of electrostatics (*vide infra*), the surface of as-synthesised InP QDs was functionalised with *N,N,N*-trimethyl(11-mercaptoundecyl)ammonium chloride ligands (TMA, [−]) to install a permanent positive charge on the QD photocatalyst ([+] InP QD).³⁷ Zeta potential studies confirmed the successful functionalization of MUA and TMA ligands on the surface of InP QDs (**Figure 4.4d**). MUA and TMA are bifunctional ligands, wherein the thiol group binds on the surface of InP QDs and the terminal carboxylate/quaternary ammonium group imparts stability to QDs in aqueous medium.³⁷ The size and shape uniformity of InP QDs were preserved even after the surface functionalization with the desired ligands (**Figure 4.4e, f**).

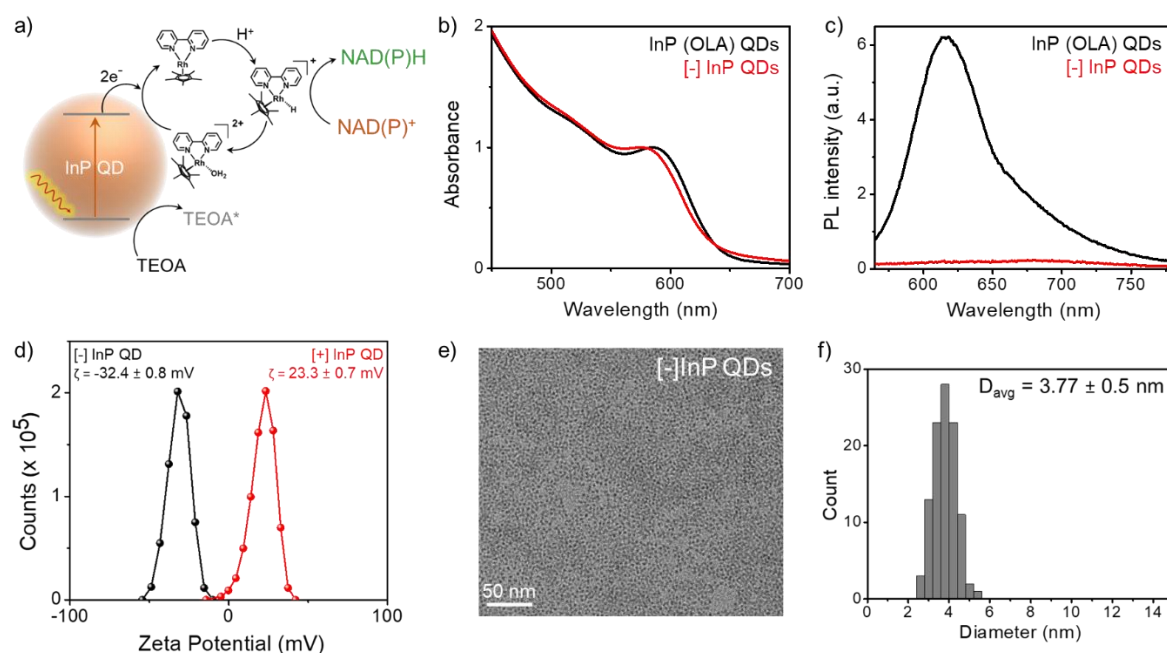


Figure 4.4. a) Schematics showing the reduction and oxidation cycles involved in the photoregeneration of 1,4-NAD(P)H cofactor by electrostatically bonded [−] InP QD::[+] [Cp*Rh(bpy)(H₂O)]²⁺ complex. Spectroscopic characterizations of the InP QDs with b) representative UV-vis absorption profile and, c) steady state PL before and after place exchange reaction with [−] MUA ligands in aqueous medium. d) Zeta potential plot proving the successful functionalization of InP QDs with [+] and [−] thiolated ligands (TMA and MUA). e) A representative TEM image and f) the corresponding size histogram plot showing the shape and size uniformity of [−] InP QDs.

The high molar extinction coefficient and photostability of InP QDs ensured the efficient generation and constant supply of high-energy charge carriers under visible-light irradiation (~460 nm). The main challenge was to optimize the light cycle for the fast and selective photoregeneration of nicotinamide cofactors by [−] QD photocatalyst, under visible-light. This

was achieved by enhancing the charge separation, extraction, and utilization steps in the QD photocatalysed light cycle, with the help of electrostatically bounded $[+]$ $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediators. In a typical optimized light cycle, an argon purged reaction mixture containing $[-]$ InP QD photocatalyst (0.15 mol%), $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator (0.25 mM), NAD^+ (1 mM) and triethanolamine (TEOA, 1 M) in 50 mM phosphate buffer was irradiated with 2×10 W blue LEDs (the total light intensity measured on the walls of the cuvette was $\sim 200 \text{ mW.cm}^{-2}$). Here, TEOA acts as the hole scavenger as well as the proton source.³⁸⁻⁴⁰ The progress of the reaction was monitored using UV-vis spectroscopy, which showed the emergence of a new peak around $\sim 340 \text{ nm}$ indicating the formation of NAD(P)H product.^{17,41} It is worth mentioning that NAD(P)^+ reduction can yield multiple regioisomers of NAD(P)H (1,2-, 1,4- and 1,6- NAD(P)H) as well as the NAD(P)_2 dimer, with most of the by-products having absorption maxima $\sim 340 \text{ nm}$.⁴² Among them, 1,4-isomer alone is the cofactor that is formed in the photosynthetic reaction center, which is enzymatically active to participate in the dark cycle. The use of $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator complex in the present study enables the selective reduction of NAD(P)^+ to 1,4- NAD(P)H , under the photocatalytic condition (see Section 4.3.3.2 for details). This was proved by both lipoamide dehydrogenase (LDH) assay as well as NMR studies. During the LDH assay, only the enzymatically active 1,4- NAD(P)H gets oxidised back to NAD(P)^+ , resulting in a decrease in the $\sim 340 \text{ nm}$ absorption peak.^{25,33} To our delight, a complete decrease of the absorption corresponding to 1,4- NAD(P)H was observed during the LDH assay performed on the photocatalytic reaction mixture (**Figure 4.5a**). This clearly indicates the quantitative as well as selective conversion of NAD(P)^+ to 1,4- NAD(P)H during the photocatalytic reaction with $[-]$ InP QDs. It is important to mention that along with facilitating the product selectivity, the $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator ensures an efficient extraction of the electrons from photoexcited $[-]$ InP QDs, as proved by the photocurrent density studies (**Figure 4.5b**). As a result, a selective and quantitative photoconversion of NAD^+ to 1,4- NADH cofactor was achieved within 30 min of visible-light irradiation, with an excellent TOF of $\sim 1333 \text{ h}^{-1}$ (**Figures 4.5a**). These photocatalytic parameters are one of the best reported so far, even among the QD photocatalysts (**Table 4.1**).

Table 4.1. Comparison of the different parameters associated to the photoregeneration of nicotinamide cofactors with various classes of photocatalysts.

Sr. No.	Photocatalyst material	Electron mediator	Hole scavenger	Light source	Time	Selectivity of 1,4-NADH	Yield of NADH	TOF ^a
1	Diatom templated carbon nitride [31]	[Cp*Rh(bpy)(H ₂ O)] ²⁺	TEOA	>420 nm lamp	2 h	~34%	~100%	0.067 h ⁻¹
2	Carbon-doped TiO ₂ [49]	[Cp*Rh(bpy)(H ₂ O)] ²⁺	Mercapto-ethanol	8W lamp >400 nm	4 h	NA	~74.3%	0.031 h ⁻¹
3	W ₂ Fe ₄ Ta ₂ O ₁₇ [50]	[Cp*Rh(bpy)(H ₂ O)] ²⁺	EDTA	450 W Halogen lamp	24 h	~25%	65%	0.002 h ⁻¹
4	CdTe QDs [24]	[Cp*Rh(bpy)(H ₂ O)] ²⁺	TEOA	450 W Xe lamp (with 420 nm cutoff filter)	2 h	>99%	~55%	0.540 h ⁻¹
	CdSe QDs						~30%	0.168 h ⁻¹
	CdS QDs						~52%	0.120 h ⁻¹
5	CdS-coated SiO ₂ [51]	[Cp*Rh(bpy)(H ₂ O)] ²⁺	TEOA	>420 nm lamp	1 h	~90%	80%	0.278 h ⁻¹
6	CdS-TiO ₂ nanotubular film [12]	[Cp*Rh(bpy)(H ₂ O)] ²⁺	TEOA	>420 nm lamp	2 h	~90%	75%	240 mM cm ⁻² h ⁻¹
7	Quantum Dot-FNR Enzyme Biohybrid Complexes [14]	FNR enzyme used for selective formation of 1,4-NADPH	Ascorbic acid	405 nm LED	3 h	>99%	>99%	1440 h ⁻¹ (with respect to FNR)
8	Amorphous Titania Nanoshell [15]	[Cp*Rh(bpy)(H ₂ O)] ²⁺	TEOA	405 nm LED	10 min	>99%	81.2%	NA
9	Protamine-titania (PTi) microcapsules with CdS quantum dots [27]	[Cp*Rh(bpy)(H ₂ O)] ²⁺	TEOA	405 nm LED	2 h	~70%	93%	NA
10	CdS@p-TiO ₂ Integrated micro-capsule [18]	[Cp*Rh(bpy)(H ₂ O)] ²⁺	TEOA	420 nm	10 min	>90%	~40%	38000 h ⁻¹ (with respect to ADH)
11	InP QDs (this work)	[Cp*Rh(bpy)(H ₂ O)] ²⁺	TEOA	460 nm LED	30 min	>99%	>99%	1333 h ⁻¹

^aAll TOF values are with respect to the photocatalyst used, except for entries 7 and 10.

¹H-NMR studies further corroborated the selective and quantitative formation of the desired nicotinamide cofactor product (**Figure 4.5c**). NAD⁺ molecule shows a signature singlet peak at $\delta \sim 9.2$ ppm for the H-2 proton of the nicotinamide ring; whereas, in 1,4-NADH, the same H-2 proton is more shielded to resonate at $\delta \sim 6.85$ ppm as a singlet.⁴² ¹H-NMR peaks for the other regioisomers and NAD₂ dimer by-products are observed between $\delta \sim 7.01$ -7.13 ppm.⁴² The ¹H-NMR spectrum collected for the photocatalytic reaction mixture after ~30 min irradiation show a singlet peak at ~6.85 ppm, confirming the selective formation of 1,4-NADH (red trace in **Figure 4.5c**). Also, the complete disappearance of the ~9.2 ppm peak of NAD⁺, further ascertains the quantitative photoregeneration of 1,4-NADH by [-] InP QDs. Similarly, a selective and quantitative photoconversion of NADP⁺ to 1,4-NADPH cofactor was achieved within 30 min of visible-light irradiation of the electrostatically bonded [-] InP QD:::[+] [Cp*Rh(bpy)(H₂O)]²⁺ complex (**Figure 4.11 in appendix**). The ability of [-] InP QDs to

photoregenerate both NADH and NADPH cofactors expands the scope of oxidoreductase enzymes that can be used in the dark cycle.

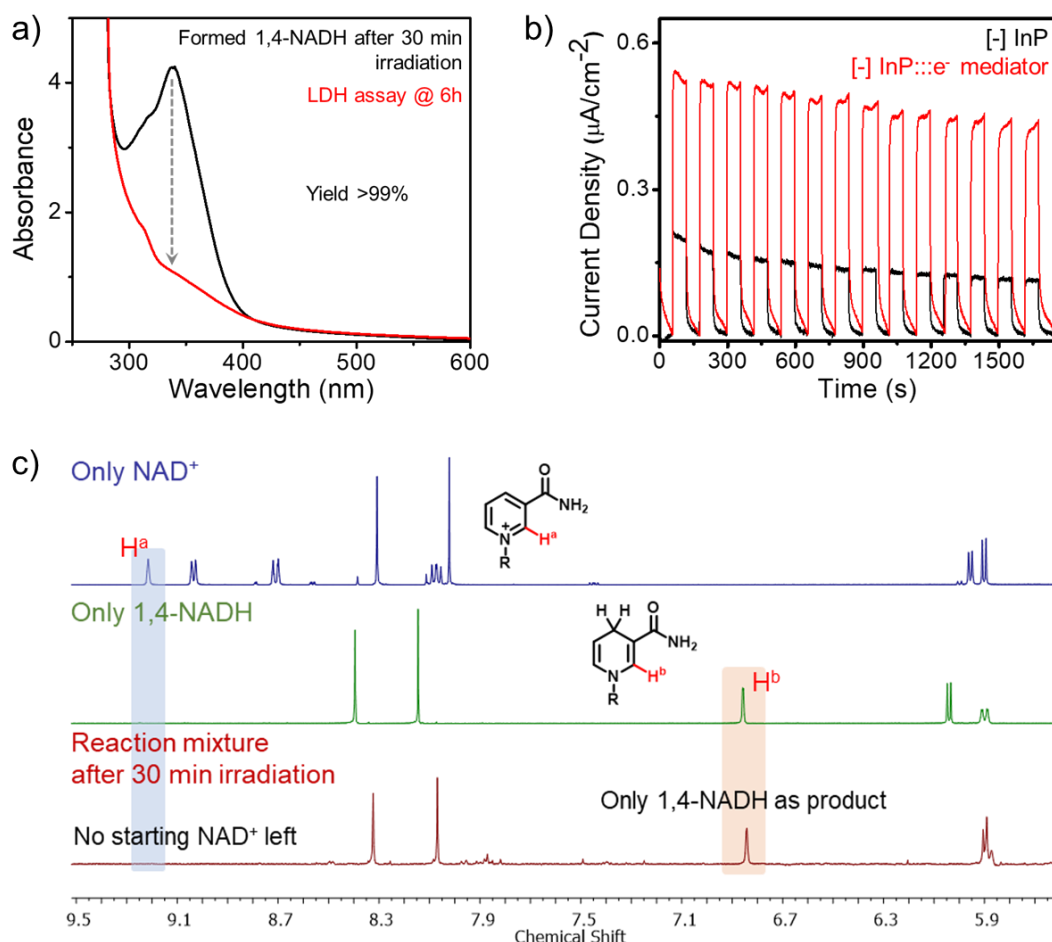


Figure 4.5. a) Characterization of 1,4-NADH cofactor photoregenerated in the light cycle by electrostatically bonded $[-]$ InP QD:::[$+$] $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator complex using UV-vis absorption study. Emergence of a new peak at ~ 340 nm after the photocatalytic cycle (black trace), and its complete disappearance during the LDH assay (red trace) indicate the selective photoregeneration of enzymatically active 1,4-NADH. b) Photocurrent density of $[-]$ InP QDs and $[-]$ InP QD:::[$+$] $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator complex under light ON-OFF conditions. c) Comparative ^1H -NMR studies confirm the formation of 1,4-NADH cofactor as the sole product in the photocatalytic cycle. The photoregeneration reaction mixture contains: NAD^+ (1 mM), TEOA (1 M), $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ (0.25 mM) and $[-]$ InP QDs (1.5 μM) in 50 mM phosphate buffer.

Control experiments performed either in the absence of (i) electron mediator, or (ii) InP QDs, or (iii) light gave negligible yield, confirming the necessity of all these three components in the photoregeneration of NAD(P)H cofactor (**Figures 4.6a** and **4.12 in appendix**). The action spectrum constructed with the reaction yields obtained under different excitation wavelengths conclusively prove the active role of InP QD as the photocatalyst. The trend in reaction yields under different excitation wavelengths followed the ground-state absorption profile of $[-]$ InP QDs, with ~ 460 nm excitation resulting in a quantitative product formation, followed by 532

nm excitation yielding ~65%, ~585 nm excitation yielding ~28% and ~630 nm excitation giving merely ~10% yield (**Figures 4.6b and 4.13 in appendix**). Further, the time-dependent experiments showed that the yield of the photoregenerated 1,4-NADH reached >99% within 30 min of irradiation (**Figures 4.6c and 4.14 in appendix**). In another control experiment, QD photocatalysts coated with a wide band-gap ZnS shell ([–] InP/ZnS QD) gave a lower yield (~67%), compared to core-only [–] InP QD photocatalysts under similar experimental condition (*vide infra*, **Figure 4.7**). The wide band-gap ZnS shell will retard the efficiency of the electron-extraction process by $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ complex, which further proves the active participation of the photoexcited electrons from InP QD in the photoregeneration of nicotinamide cofactor. Further, the photoregeneration of nicotinamide cofactor by InP QDs was found to be efficient even under natural sunlight irradiation ($\sim 95 \text{ mW cm}^{-2}$), with a good yield of ~52% (**Figures 4.6d**). This can be attributed to the excellent overlap between the absorption profile of InP QD and the solar spectrum (**Figure 4.15 in appendix**). The retention of the photocatalytic activity under sunlight proves the sustainability aspect of the cofactor photoregeneration with the environmentally friendly InP QDs.

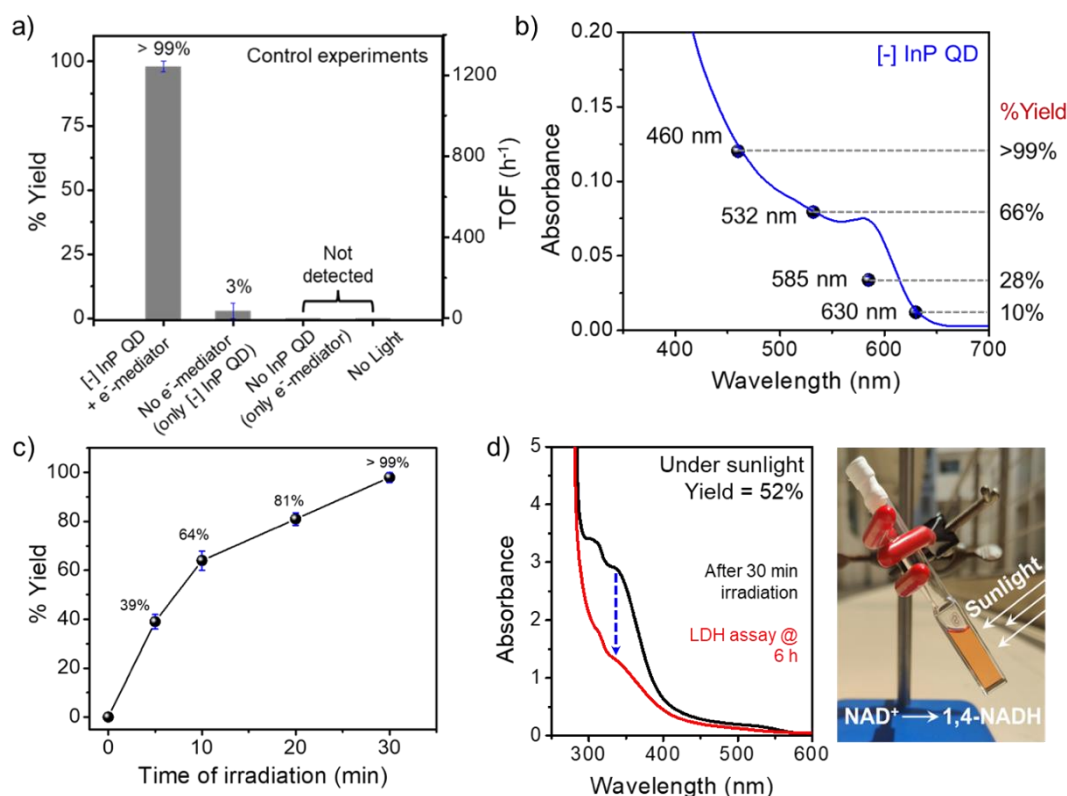


Figure 4.6. a) A summary of photocatalytic experiments performed under different conditions, which confirms the necessity of all three components - QDs, electron mediator, and light - in the quantitative photoregeneration 1,4-NADH. b) An action spectrum constructed with the yield of 1,4-NADH cofactor formed in the photocatalytic cycle under four different irradiations wavelengths, overlapped well with the ground state absorption spectrum of [–] InP QD. c) A plot showing the variation in the yield of 1,4-

NADH cofactor formed in the photocatalytic cycle as a function of irradiation time. d) UV-vis data showing the formation of 1,4-NADH cofactor (black trace) by electrostatically bonded [-] InP QD:::[+] $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ complex under solar irradiation, followed by depletion of the formed 1,4-NADH in the LDH assay (red trace). The corresponding photograph of the photocatalytic reaction set-up is shown on the right.

4.4.2. Electrostatically driven photoregeneration of NAD(P)H cofactors by InP QDs

The favourable electrostatic attraction between oppositely charged [-] InP QD photocatalyst and [+] $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator was anticipated to be the main driving force for the efficient electron-extraction step, which led to the fast and quantitative photoregeneration of nicotinamide cofactors (**Figure 4.7a**). This assumption was proved by comparing the photocatalytic activity of [-] InP QD with [+] InP QD photocatalysts. The yield of the reaction dropped down to ~50%, when [+] InP QD was used as the photocatalyst in the presence of $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator (**Figure 4.7b, 4.16a in appendix**). This drastic decrease in the photoregeneration yield of nicotinamide cofactor was explained with the help of photoluminescence (PL) quenching studies, which is a common way of comparing the charge transfer process in donor-acceptor systems.^{43,44} Here, PL quenching studies were performed with [+] and [-] InP/ZnS core/shell QDs, as the PL was negligible for the respective core-only InP QDs. In our studies, the addition of $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator led to a significantly higher quenching in the steady-state as well as time-resolved PL of [-] InP/ZnS QDs, compared to [+] InP/ZnS QDs (**Figures 4.7c,d and 4.17 in appendix**). A similar trend was observed in the corresponding photocatalytic reactions as well, wherein ~67% and ~34% yields were obtained with [-] InP/ZnS and [+] InP/ZnS QD photocatalysts, respectively (**Figure 4.7b, 4.16b, c in appendix**). Thus, installing a favourable electrostatic attraction enhances the channelling of the oppositely charged electron mediator, which eventually increases their local concentration around the [-] InP/ZnS QD photocatalysts (**Figure 4.7a**). This in turn enhances the probability of the photoinduced electron transfer from [-] InP/ZnS QD to [+] $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ complex, thereby improving the overall efficiency of the nicotinamide cofactor photoregeneration.

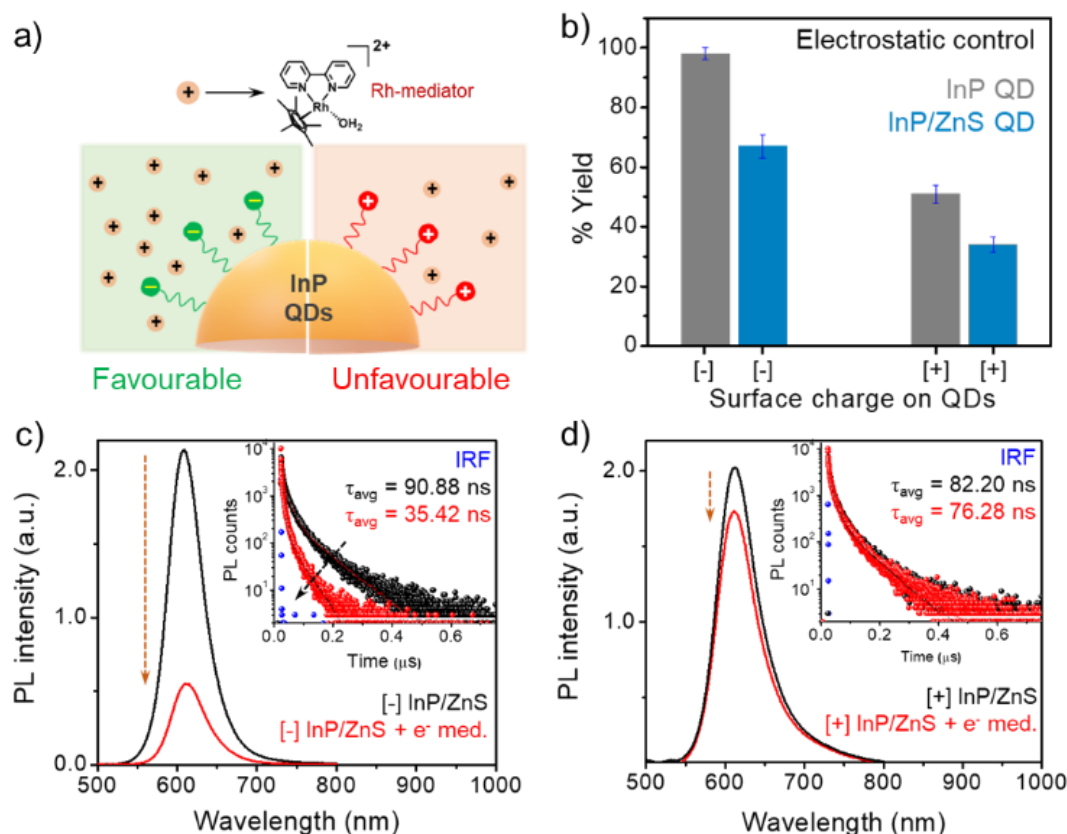


Figure 4.7. a) Schematics showing the influence of favourable and unfavourable electrostatic interactions on the local concentration of $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator around the $[-]$ and $[+]$ InP QDs. b) A bar diagram showing the effect of surface chemistry and ZnS shell-coating of InP QDs on the formation of 1,4-NADH cofactor in the photocatalytic light-cycle. Corresponding emission studies showing the emission quenching of c) $[-]$ InP/ZnS and d) $[+]$ InP/ZnS QDs in the presence of 0.25 mM positively charged $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator. Insets show the corresponding quenching in the emission lifetime decays of $[-]$ InP/ZnS and $[+]$ InP/ZnS QDs. The emission quenching was more for $[-]$ InP/ZnS QDs, confirming the role of electrostatic attraction in the efficient extraction of photoexcited electrons by $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$.

4.4.3. Hole transfer studies

Along with the feasibility of electron transfer step from photocatalyst to reactant, the feasibility of the hole abstraction by the sacrificial agents should also be studied to gain the complete understanding of a photocatalytic cycle. Often, the role of hole scavengers in the photoregeneration of nicotinamide cofactors is not studied to the extent as required. Apart from identifying the hole scavenger and proton source, detailed hole transfer studies will unambiguously confirm the direct involvement of light component and charge carriers in the photoregeneration of nicotinamide cofactors. With this in mind, the photoregeneration of NADH cofactors by $[-]$ InP QDs was studied in the presence of three different hole scavengers: TEOA, EDTA and ethanol. These hole scavengers have different oxidation potentials with respect to the valence band (VB) of InP QDs (Figure 4.8a, 4.18 in appendix), which will

enable the direct correlation between the feasibility of hole transfer step and the overall photocatalytic activity. The highest yield for the photoregeneration of NADH cofactors was obtained in the presence of TEOA (>99%), followed by EDTA (~60%) and ethanol (~37%) (**Figures 4.8b and 4.19 in appendix**). This trend very well matches with the thermodynamic feasibility of the hole transfer step calculated for each hole scavenger: $\Delta G = -191.04$ kJ/mol for TEOA ($E_0 = -3.4$ eV) > -133.15 kJ/mol for EDTA ($E_0 = -4.0$ eV) > -115.78 kJ/mol for ethanol ($E_0 = -4.18$ eV)⁴⁵.

For an ideal artificial photosynthetic system, water should act as the sole scavenging agent to abstract the hole from the photocatalyst and get oxidised to release oxygen. We too checked the possibility of water acting as the hole scavenger in our photocatalytic system. For this, the photoregeneration of NADH cofactors by [-] InP QDs was performed in the absence of any external hole scavengers. Attractive NADH yields of ~70% and ~60% were obtained in phosphate buffer and only-water mediums, respectively, indicating the hole scavenging ability of water in the present study (**Figures 4.8c and 4.20 in appendix**). However, we failed to identify commonly formed oxidation products of water (such as oxygen or hydrogen peroxide) during the reaction. It is worth mentioning that [-] InP QD photocatalysts precipitated after the reaction, when the photocatalysis was performed in buffer or water (i.e., in the absence of any external hole scavengers). This observation strongly points towards the thiol ligands on the QDs to be the potential hole scavengers, in the absence of any external hole scavengers. Alkyl-thiol ligands could oxidise to form dithiols by abstracting the hole from the VB of InP QD photocatalysts, as reported previously for other QD photocatalysed organic transformations.^{46,47} The oxidation of thiols leads to the desorption of the ligands from the QD surface, resulting in the precipitation and sedimentation of QDs from the solution. Interestingly, no signs of QD precipitation were observed when the photocatalytic reaction was performed in the presence of external hole scavengers. This confirms that the hole abstraction ability of thiol ligands is suppressed in the presence of external hole scavengers, which can be attributed to the less-favourable oxidation potential and thermodynamic feasibility of the hole transfer step to thiols, compared to external hole scavengers ($\Delta G = -99.62$ kJ/mol for thiols vs -191.04 kJ/mol for TEOA). As a result, the oxidation of thiols will be suppressed in the presence of external hole scavengers, leaving the thiols intact on the surface of QDs and retaining the colloidal stability of QDs during photocatalysis. These studies helped in identifying and explaining the hole abstraction abilities of different hole scavengers, as well as confirmed that

the hole transfer from the VB of InP QD photocatalyst to the sacrificial agent is the limiting factor in the photoregeneration of nicotinamide cofactors.⁴⁵

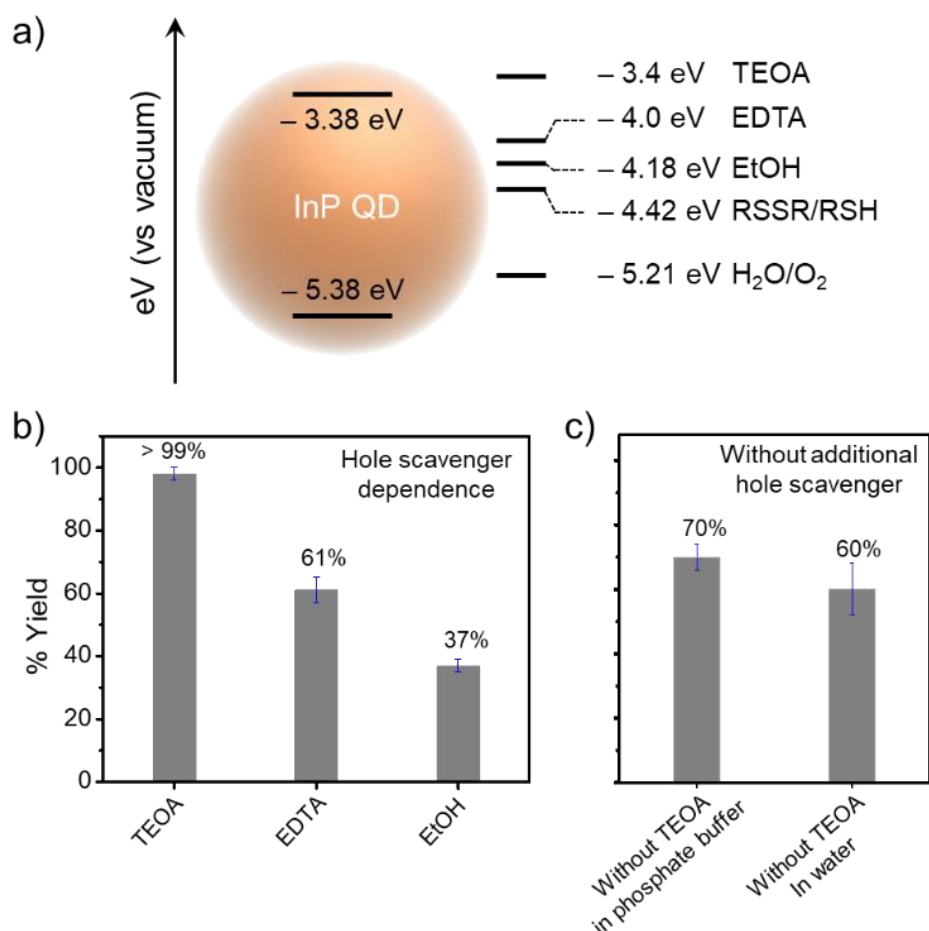


Figure 4.8. a) Schematic representation of oxidation potentials of different hole scavengers with respect to the valence band position of [-] InP QD. Variation in the yields of 1,4-NADH photoregeneration in the presence of b) external hole scavengers, and c) phosphate buffer and water (no additional external hole scavenger was added).

4.4.4. InP QD based artificial photosynthetic system: integration of light and dark cycles

In order to complete the artificial photosynthetic cycle, the nicotinamide generated in the light cycle should be integrated into the dark cycle and trigger the functioning of oxidoreductase enzymes to produce the desired product. As a proof-of-concept, we have chosen the NADH triggered conversion of butyraldehyde to butanol by alcohol dehydrogenase (ADH) enzyme for the dark cycle (**Figure 4.9a**; see Section 4.3.2.6. for details). As mentioned before, a quantitative conversion of NAD⁺ to 1,4-NADH (~1 mM) was achieved within 30 min of irradiation of [-] InP QD photocatalyst in the presence of [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator (**Figure 4.9b**). To check the compatibility between light and dark cycles, a sequential

light-dark cycle was performed wherein ADH enzyme (~30 units) and butyraldehyde (~30 mM) were added to the photocatalytic reaction mixture after 30 min of irradiation. The as-formed 1,4-NADH was completely consumed in the dark cycle by ADH enzyme to produce butanol within 1 h, as it is clear from the complete disappearance of the UV-peak at ~340 nm (Figure 4.9c). Gas chromatography (GC) studies, used for the qualitative as well as quantitative analysis of the product formation, confirmed that butanol was forming in a quantitative amount (~1 mM) with respect to the photoregenerated 1,4-NADH (Figures 4.21 and 4.22 in appendix). Thus, a quantitative photoregeneration of NADH cofactors in the light cycle led to the quantitative formation of butanol in the dark cycle, which further confirms the effective integration of NADH cofactors in the dark cycle.

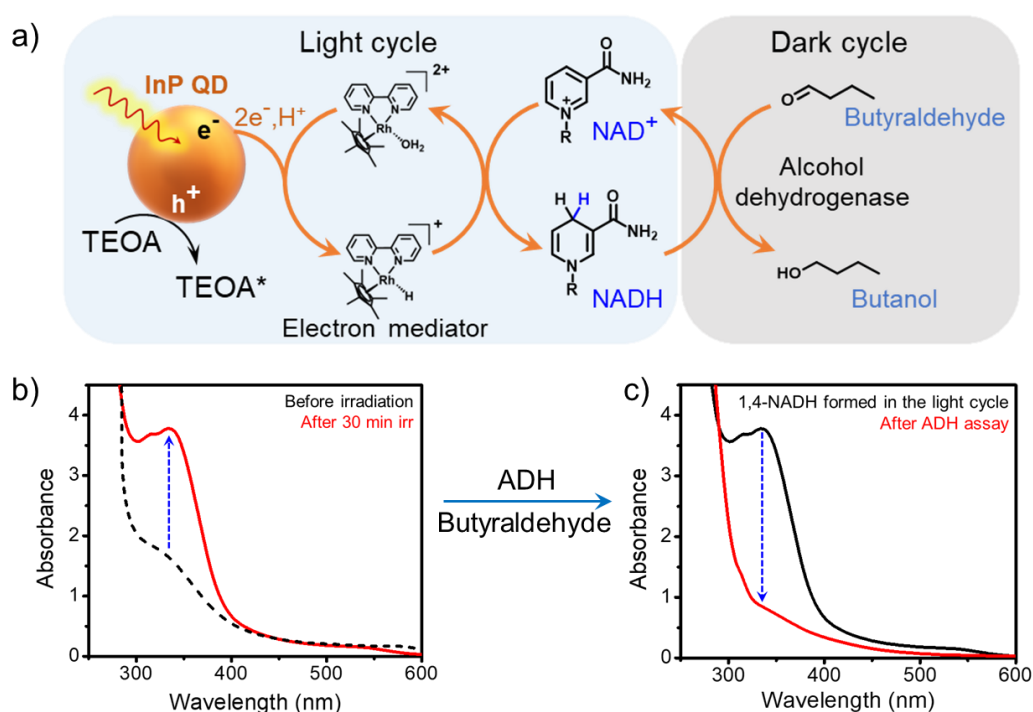


Figure 4.9. a) Schematics of coupling of light and dark cycles for the continuous formation of butanol as the final product. b) Formation of ~340 nm peak in the UV-vis absorption study during the formation of 1,4-NADH in the light cycle, and c) the change in the ~340 nm peak during the ADH assay, in presence of 31.3 units of ADH enzyme and 29 mM butyraldehyde. Black and red spectra correspond to the UV-vis absorption collected before and after the ADH assay. The complete disappearance of the ~340 nm peak confirms the complete consumption of the photoregenerated 1,4-NADH during the ADH assay. **Reaction conditions for light cycle:** NAD⁺ (1 mM), TEOA (1 M), [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator (0.25 mM), [-] InP QDs (1.5 μ M) in 50 mM phosphate buffer + 30 min irradiation. **Reaction conditions for dark cycle:** The above photocatalytic reaction mixture + 31.3 units of ADH enzyme + 29 mM butyraldehyde.

This result motivated us to test the sequential functioning of light and dark cycles by exposing the entire reaction mixture for consecutive 10 min light - 20 min dark cycles (Figure 4.10a). In the first 10 min light cycle, the reaction mixture was irradiated in the absence of ADH

enzyme. As expected, there was no conversion of butyraldehyde to butanol (**Figures 4.10a and 4.23a, b in appendix**). Upon the addition of ADH enzyme after the first light cycle, there was a substantial formation of butanol in the next 20 min dark cycle (**Figures 4.10a and 4.23c in appendix**), confirming the consumption of the 1,4-NADH photoregenerated in the light cycle. In further light-dark cycles, the formation of butanol kept on increasing upto ~0.85 mM over a time span of 150 min (**Figure 4.23d in appendix**). A close look at the sequential light-dark cycles reveals that the rate of butanol formation was always higher in the light cycle compared to the dark cycle (marked with dotted lines in **Figure 4.10a**). This can be attributed to the simultaneous consumption as well as regeneration of the 1,4-NADH in the light cycle, as both QD photocatalyst and ADH enzyme were active. As a result, there is a continuous formation of butanol in the light cycle. However, in the dark cycle, QD photocatalysts are inactive to regenerate the 1,4-NADH cofactors, and the butanol formation ceases after the complete consumption of 1,4-NADH by the ADH enzyme.

Finally, the butanol production was carried out through simultaneous light-dark cycles under continuous irradiation. In this experiment, the photocatalytic reaction mixture (1 mM NAD^+ , 0.15 mol% [-] InP QD, 0.25 mM $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$, and 1 M TEOA in 50 mM phosphate buffer) was continuously irradiated in the presence of butyraldehyde substrate and ADH enzyme (**Figures 4.10b and 4.24 in appendix**). The butanol formation steadily increased with time, yielding ~1.26 mM within ~35 min of irradiation (initial rate of butanol formation was estimated to be 6.12 mM h^{-1}). The overall yield of butanol formation was ~126%, with respect to the initial concentration of NAD^+ cofactors (1 mM). This confirms the constant photoregeneration and consumption of the NADH cofactors in multiple light and dark cycles, respectively, leading to the continuous biocatalytic synthesis of butanol. As a result, the overall yield of butanol formation reaches beyond the stoichiometric limit of the initial NAD^+ concentration (**Figure 4.10b**). Thus, the fast and quantitative photoregeneration of nicotinamide cofactors by [-] InP QDs led to the effective shuttling of charge carriers between the light and dark cycles. These studies closely mimic the simultaneous light-dark cycles seen in natural thylakoid-stroma system, proving the suitability of InP QD based photocatalysts in developing an artificial photosynthetic system for the production of useful chemicals.

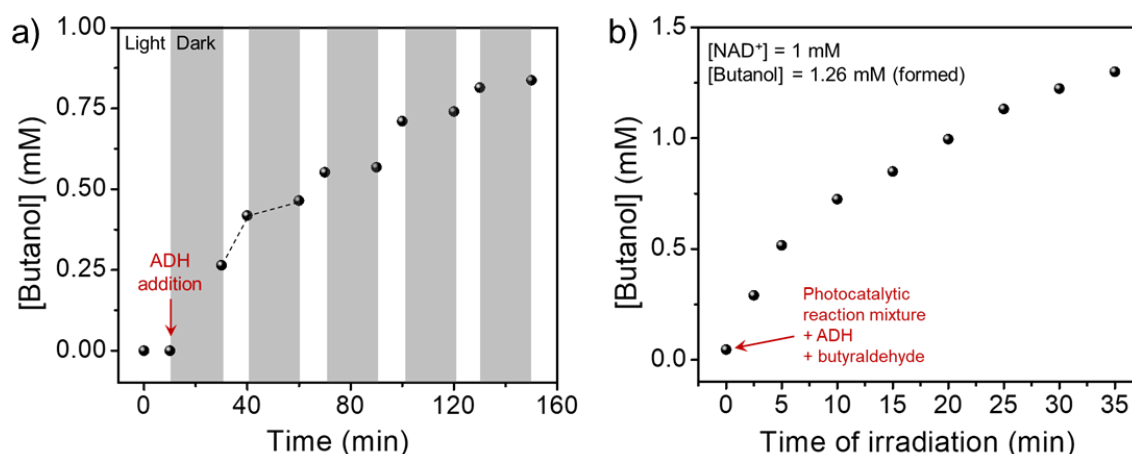


Figure 4.10. a) Artificial photosynthetic system based on [-] InP QDs, operated under sequential light and dark cycles, shows the continuous increase in the butanol formation. The formation of butanol was more in the light cycle compared to the dark cycle (see the slope difference of dotted lines in light and dark cycles). b) Artificial photosynthetic system based on [-] InP QDs, operated under simultaneous light and dark cycles, yields butanol beyond the stoichiometric limit with respect to initial NAD^+ concentration, which proves the constant photoregeneration and consumption of 1,4-NADH cofactors.

4.5. Conclusions

A judicious choice of different components enabled the constant regeneration and consumption of nicotinamide cofactors under photo- and bio-catalytic reactions by InP QDs and ADH enzyme, respectively, leading to the continuous production of butanol. A strong electrostatic attraction between surface engineered [-] InP QD photocatalyst and [+] $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator enhanced the probability of electron extraction and utilization steps under visible-light excitation. This led to the fast (~ 30 min) and quantitative photoregeneration of 1,4-NAD(P)H cofactors ($> 99\%$, with TOF of $\sim 1333 \text{ h}^{-1}$), which further participated in the dark cycle to regulate the functioning of ADH enzyme to produce butanol in a quantitative amount. The environmentally friendly InP QDs retained their ability to photoregenerate nicotinamide cofactors under natural sunlight irradiation as well. The suitability of InP QD based artificial photosynthetic system was successfully tested under sequential as well as simultaneous light-dark cycles. The overall yield of butanol formation surpassed the stoichiometric limit in simultaneous light-dark cycle experiment under continuous irradiation, mimicking the reactions occurring in natural thylakoid-stroma system. The successful integration of the photoregenerated nicotinamide cofactors with the enzymatic catalysis in the dark cycle opens up endless possibilities of coupling a wide variety of oxidoreductase enzymes for the continuous synthesis of desired chemicals using the artificial photosynthetic system built with

InP QD-integrated nano-biohybrid setup. A future study could target the compartmentalization of light and dark cycles to isolate the functioning of photocatalysts and oxidoreductase enzymes, thereby enabling the sustainable and ceaseless production of useful chemicals and materials.

4.6. References

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4.6. Appendix of Chapter 4

4.6.1. Studies related the photoregeneration of nicotinamide cofactors and comparison with existing literature

4.6.1.1 Photoregeneration of NADPH cofactor from NADP⁺ with [-] InP QDs and [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator

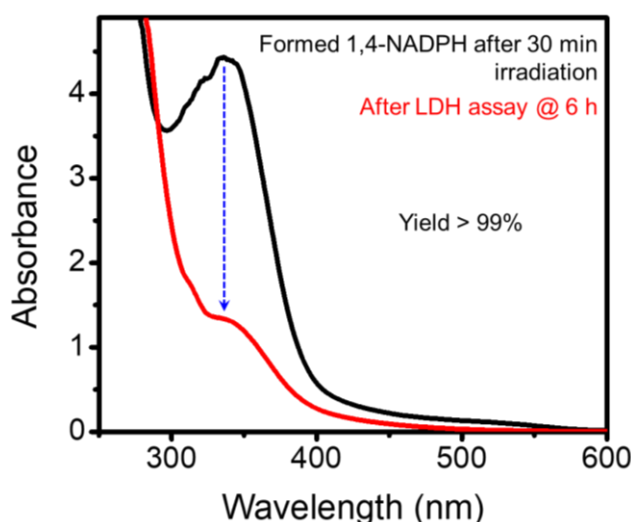


Figure 4.11. Characterization of the photoregenerated 1,4-NADPH cofactor in the light cycle using UV-vis absorption study. Emergence of a new peak at ~340 nm observed after the photocatalytic cycle (black trace), which completely disappeared during the LDH assay (red trace) indicating quantitative as well as selective photoregeneration of enzymatically active 1,4-NADPH. Photocatalytic reaction mixture contains: NADP⁺ (1 mM), TEOA (1 M), [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator (0.25 mM), [-] InP QDs (1.5 μ M) in 50 mM phosphate buffer + 30 min irradiation.

4.6.1.2. Control experiments

Control experiments performed either in the absence of (i) electron mediator, or (ii) InP QDs, or (iii) light gave negligible yield, confirming the necessity of all these three components in the photoregeneration of NAD(P)H cofactor (**Figures 4.6a** and **4.11**).

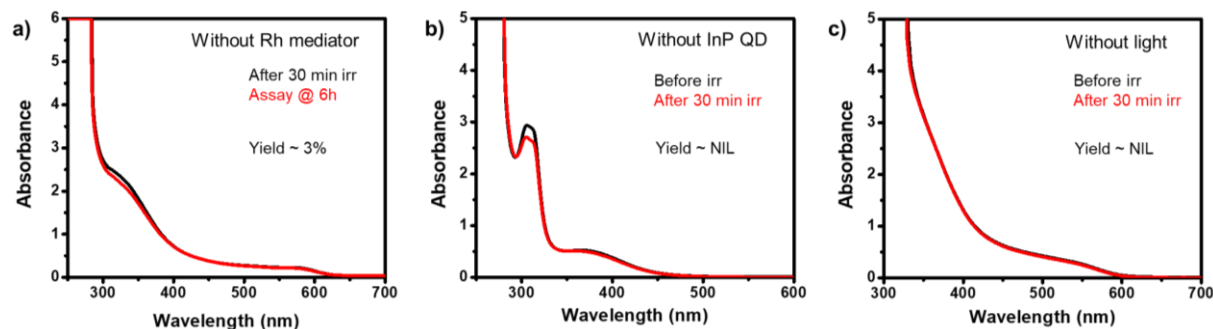


Figure 4.12. Control experiments proving the necessity [-] InP QDs, [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator and light for the photocatalytic regeneration of NADH cofactor. Negligible yields were

obtained when the photocatalytic cycle was performed either in the absence of a) electron mediator, or b) InP QDs, or c) light. Black and red spectra correspond to the UV-vis absorption data collected before and after the LDH assay, confirming negligible formation of 1,4-NADH cofactor in the light cycle in these control experiments.

4.6.1.3. Light cycle under different excitation wavelengths for the construction of the action spectrum

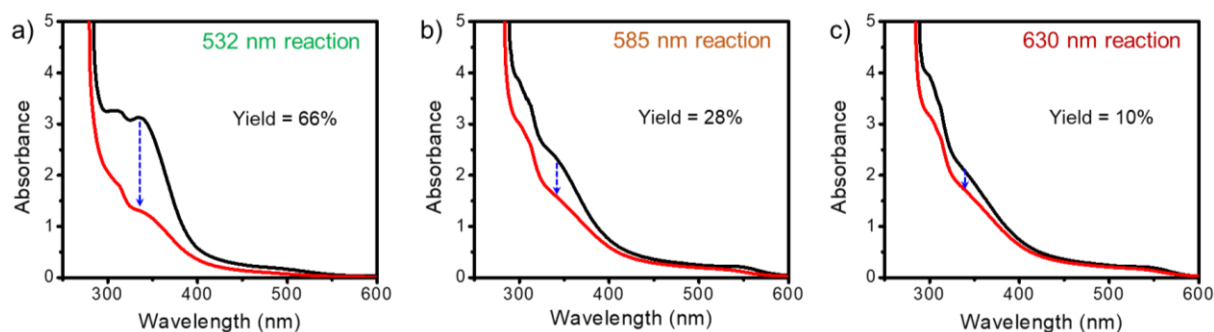


Figure 4.13. Variation in the photocatalytic regeneration of 1,4-NADH cofactor as a function of the excitation wavelength. UV-vis absorption data of the photocatalytic reaction mixture after ~30 min irradiation with a) 532 nm and b) 585 nm and c) 630 nm LEDs. Black and red spectra correspond to the UV-vis absorption collected before and after the LDH assay. Photocatalytic reaction mixture contains: NAD^+ (1 mM), TEOA (1 M), $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator (0.25 mM) and [-] InP QDs (1.5 μM) in 50 mM phosphate buffer.

4.6.1.4. Time-dependent photoregeneration of nicotinamide cofactors with [-] InP QDs

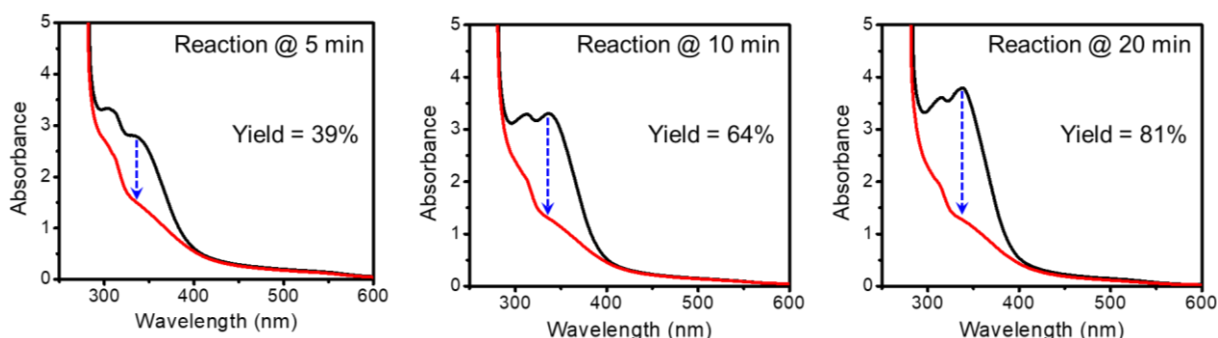


Figure 4.14. Variation in the photocatalytic regeneration of 1,4-NADH cofactor as a function of irradiation time. Black and red spectra correspond to the UV-vis absorption collected before and after the LDH assay. Photocatalytic reaction mixture contains: NAD^+ (1 mM), TEOA (1 M), $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator (0.25 mM) and [-] InP QDs (1.5 μM) in 50 mM phosphate buffer.

4.6.1.5. Spectral overlap between the absorption spectrum of InP QDs and the solar spectrum:

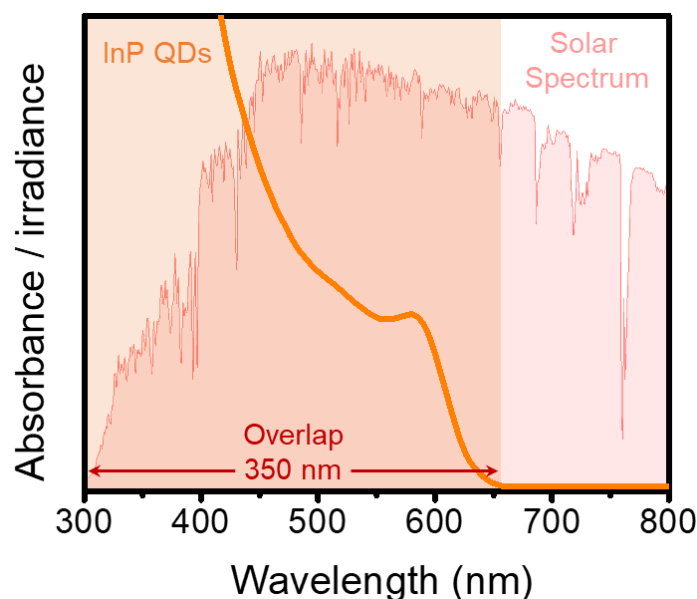


Figure 4.15. Spectral overlap between the absorption of InP QDs and the solar spectrum. The reference solar spectrum was adapted from SMARTS v. 2.9.2 (AM 1.5) for the comparison.

4.6.2. Proof of electrostatically driven photoregeneration of nicotinamide cofactors by InP QDs

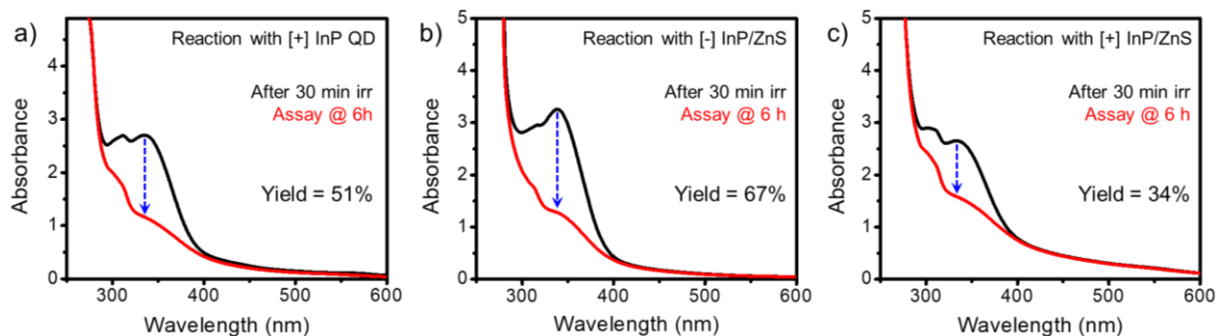


Figure 4.16. Variation in the photocatalytic regeneration of 1,4-NADH cofactor as a function of surface ligands and ZnS shell on InP QDs: a) [+] InP QDs, b) [-] InP/ZnS QDs, and c) [+] InP/ZnS QDs. Black and red spectra correspond to the UV-vis absorption collected before and after the LDH assay. Photocatalytic reaction mixture contains: NAD^+ (1 mM), TEOA (1 M), $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator (0.25 mM) and InP QDs (1.5 μM) in 50 mM phosphate buffer.

4.6.2.1 Effect of electrostatic interactions on the quenching of PL lifetime decay of InP/ZnS QDs

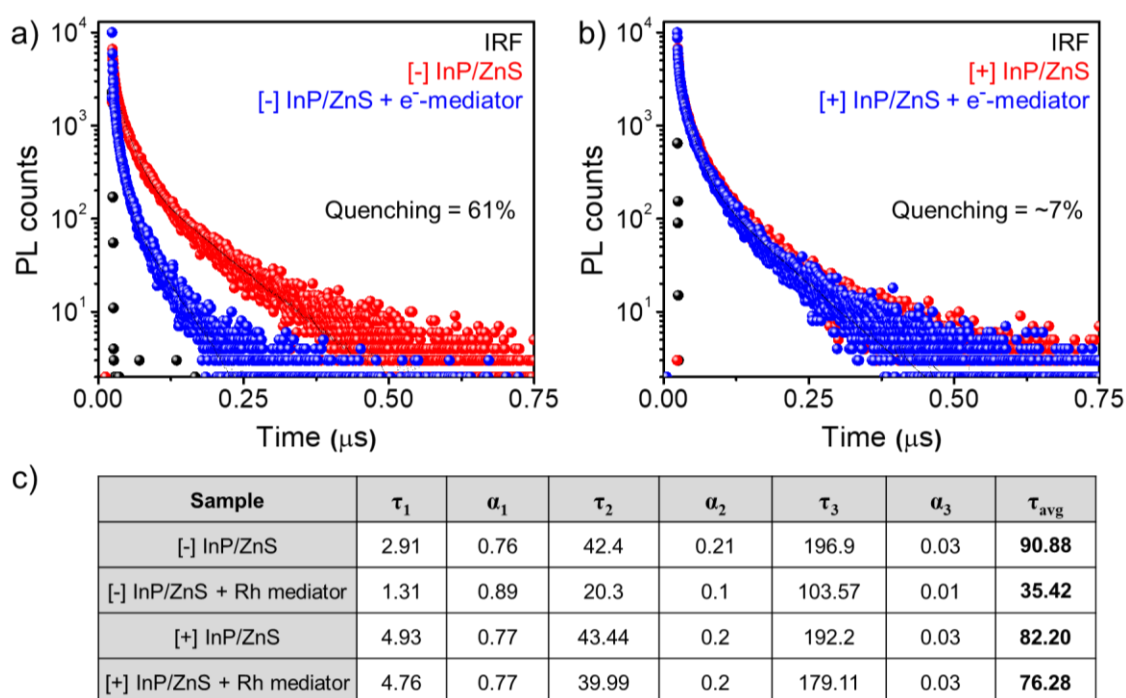


Figure 4.17. Variation in the PL Lifetime a) [-] InP/ZnS QDs and b) [+] InP/ZnS QDs in the presence of 0.25 mM of [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator. A higher quenching was observed in [-] InP/ZnS QDs, confirming the efficient electron extraction by [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator. c) PL decay analysis of [-] InP/ZnS QDs and [+] InP/ZnS QDs in the absence and presence of 0.25 mM of [Cp*Rh(bpy)(H₂O)]²⁺ electron mediator, in a time window of 800 ns. The PL decay was collected at 605 nm.

4.6.3. Estimation of band positions of InP QDs

Absolute energies of valence and conduction bands of InP QDs were calculated using a combination of cyclic voltammetry and UV-vis absorption measurements. All the electrochemical measurements were conducted in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Glassy carbon was used as the working electrode, Ag/AgNO₃ as the reference electrode and Pt was used as the counter electrode.

In case of InP QDs, only the peak corresponding to oxidation was obtained from cyclic voltammogram, located at 0.675 V (vs Ag/Ag⁺ electrode), corresponds to the valence band of InP QDs (**Figure 4.18a**). The relative reference electrode potential (E_{ref}) was calculated to be 4.71 eV, using ferrocene/ferrocenium couple as internal standard. So, the measured valence band energy level was estimated to be -5.38 eV with respect to vacuum. The band gap of the

used InP QDs was calculated to be 2.0 eV from Tauc plot (**Figure 4.18b**). Hence, the position of the conduction band was calculated to be -3.38 eV with respect to vacuum.

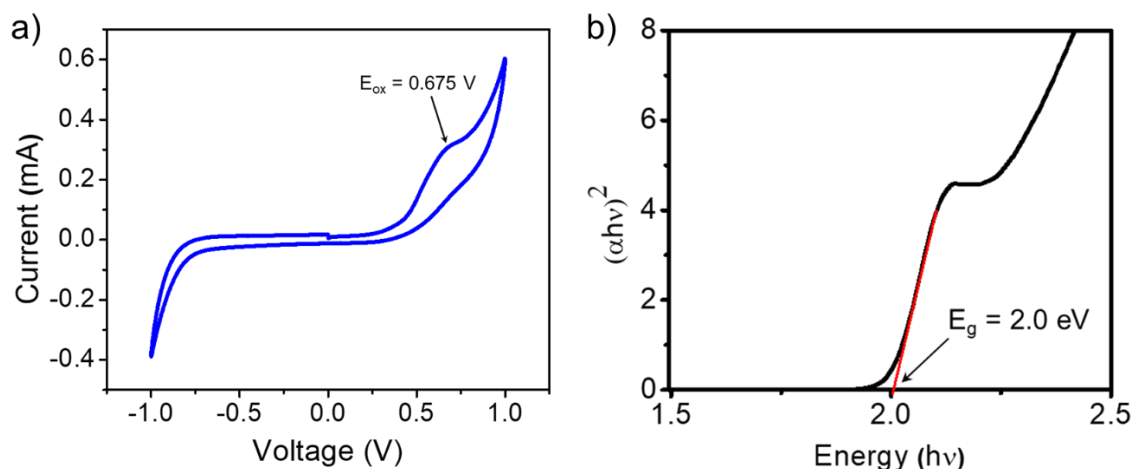


Figure 4.18. a) Cyclic voltammogram of InP QDs measured in acetonitrile solution, at a scan rate of 30 mV/s. b) Construction of Tauc plot for the calculation of band gap of InP QDs. The band gap was calculated to be 2.0 eV.

4.6.4. Photoregeneration of nicotinamide cofactors with [-] InP QDs and $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator in presence of different hole scavengers

4.6.4.1. Photoregeneration of nicotinamide cofactors in the presence of EDTA and ethanol hole scavengers

The photoregeneration reactions with different hole scavengers were carried out following the modified general procedure as mentioned in Section 4.3.2.2. In place of 1 M TEOA as hole scavenger, 1M EDTA and 1M ethanol were added in two different reaction mixtures, keeping all other conditions same. After 30 min of irradiation with $2 \times 10 \text{ W}$ blue LEDs, the reaction mixtures were half diluted individually and were subjected to the LDH assay. The 1,4-NADH photoregeneration yields were estimated to be 61% and 37% for EDTA and ethanol hole scavengers, respectively (**Figure 4.19a, b**).

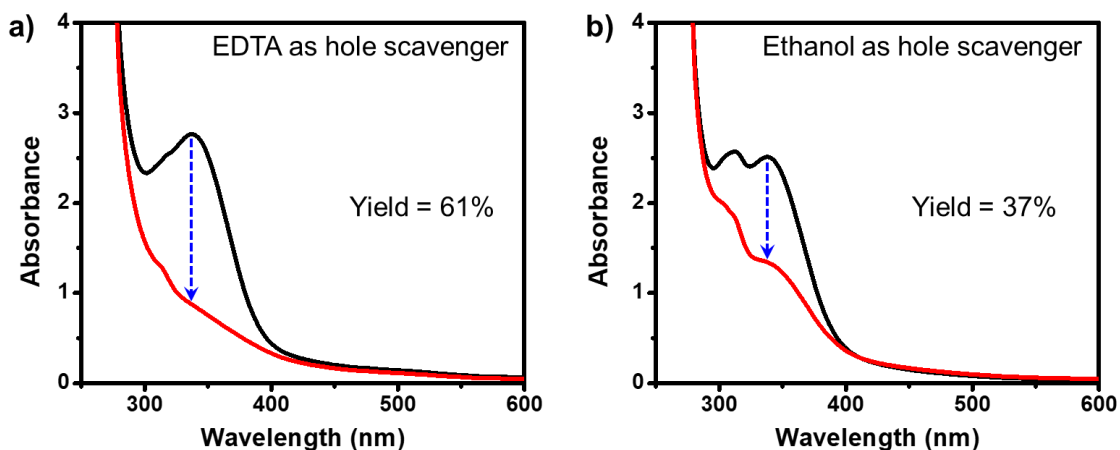


Figure 4.19. Photocatalytic regeneration of nicotinamide cofactors in the presence of a) EDTA and b) ethanol as hole scavengers. Black and red spectra correspond to the UV-vis absorption collected before and after the LDH assay. Both the photocatalytic reactions were carried out in presence of [-] InP QDs and $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator in 50 mM phosphate buffer.

4.6.4.2. Photoregeneration of nicotinamide cofactors in absence of any external hole scavenger

The photoregeneration reaction in absence of external hole scavenger was carried out using the modified general procedure. The reaction mixture was prepared using NAD^+ (1 mM), $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator (0.25 mM), and [-] InP QDs (1.5 μM) in (i) 50 mM phosphate buffer and (ii) pure Milli-Q water. After 30 min of irradiation with 2×10 W blue LEDs, the reaction mixtures were half diluted individually and were subjected to the LDH assay. The 1,4-NADH photoregeneration yields were estimated to be 70% and 60% for experiments in phosphate buffer and water, respectively (**Figure 4.20a, b**).

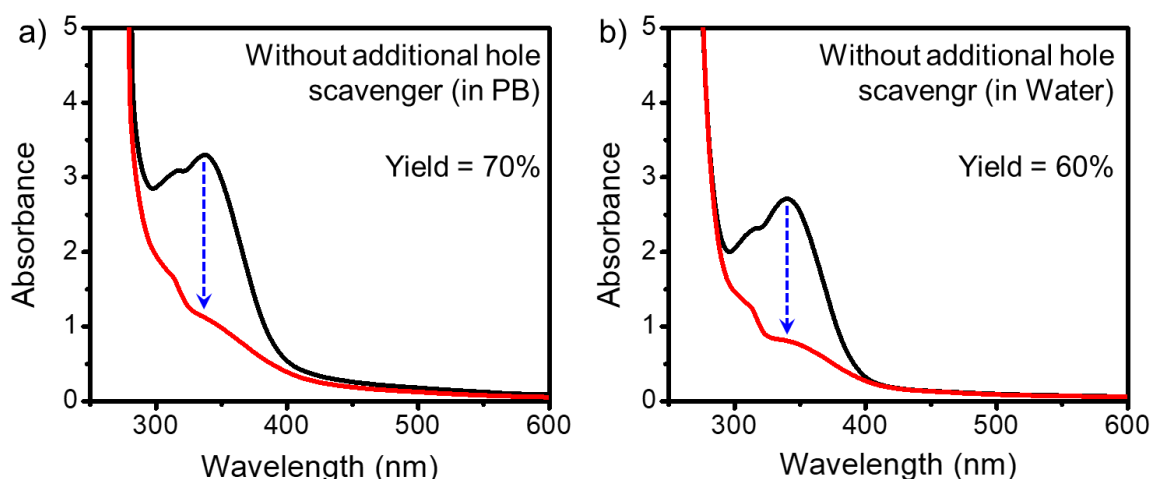


Figure 4.20. Photocatalytic regeneration of nicotinamide cofactors in the a) 50 mM phosphate buffer and b) pure Milli-Q water. Black and red spectra correspond to the UV-vis absorption collected before and after the LDH assay. Both the photocatalytic reactions were carried out in presence of [-] InP QDs and $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator in 50 mM phosphate buffer. No external hole scavenger was added.

4.6.5. Quantification of the butanol produced in the dark cycle

4.6.5.1. GC calibration curve for butanol

Stock solutions of different concentrations of butanol were prepared. A fixed amount (1 μL) from each stock solution was injected into the GC instrument. The area obtained under the peaks corresponding to each concentration of butanol was plotted against the concentration of the stock solutions. The data was fitted with a straight line and the plot was used as a calibration curve for the quantification of the butanol formed in various dark as well as light-dark cycle reactions (**Figure 4.21**).

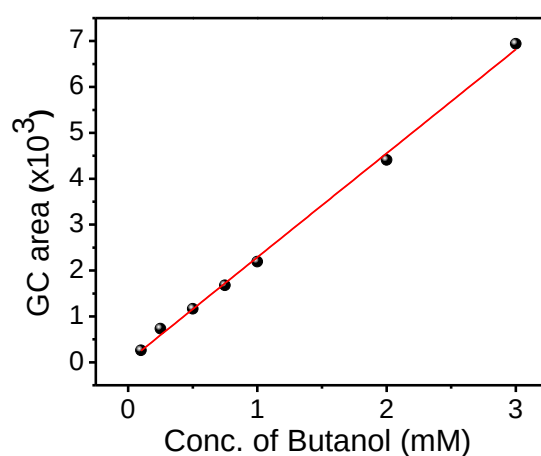


Figure 4.21. GC calibration curve (known concentration vs GC peak area) for butanol.

4.6.5.2. Quantification of the butanol produced in a single dark cycle

The ADH enzymatic assay was carried out as described in Section 4.3.2.6. To quantify the amount of butanol formed with GC analysis, 50 μL of the reaction mixture was passed through a syringe filter and 1 μL of that solution was injected into the GC instrument. The concentration of butanol formed was calculated from the area obtained under the butanol peak, using the above calibration curve.

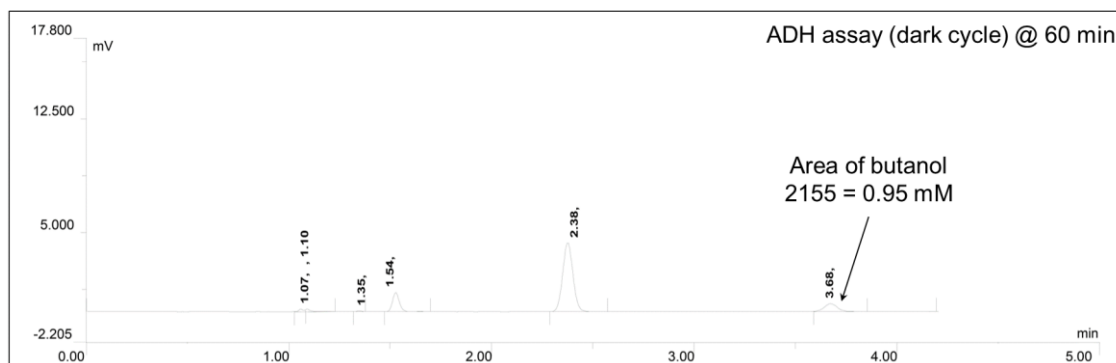


Figure 4.22. A typical GC chromatogram for the dark cycle reaction corresponding to Figure 4.20.

4.6.5.3. Quantification of product butanol formed in sequential light and dark cycles

To carry out the sequential 10 min light and 20 min dark cycle reactions, first, the reaction mixture in presence of NAD^+ (1 mM), TEOA (1 M), $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator (0.25 mM), [-] InP QDs (1.5 μM) and butyraldehyde (29 mM) in 50 mM phosphate buffer was irradiated for 10 min. GC data of either the reaction mixture before irradiation or after the first 10 min does not show any butanol formation (**Figure 4.23, a, b**). Then ADH enzyme (100 μL of 1 mg/mL stock solution; 31.3 units) was added to carry out the 20 min dark cycle. 0.24 mM butanol formation was observed after the dark cycle of reaction (**Figure 4.23c**). Then, the consecutive light and dark cycles were continued till 150 min, where a cumulative formation of butanol was found to be 0.85 mM (**Figure 4.23d**). In each light-dark cycle, amount of butanol produced was quantified using GC. For that, 50 μL of the reaction mixture was passed through a syringe filter and 1 μL of that solution was injected into the GC instrument. The concentration of the butanol was estimated using the calibration curve in **Figure 4.21**.

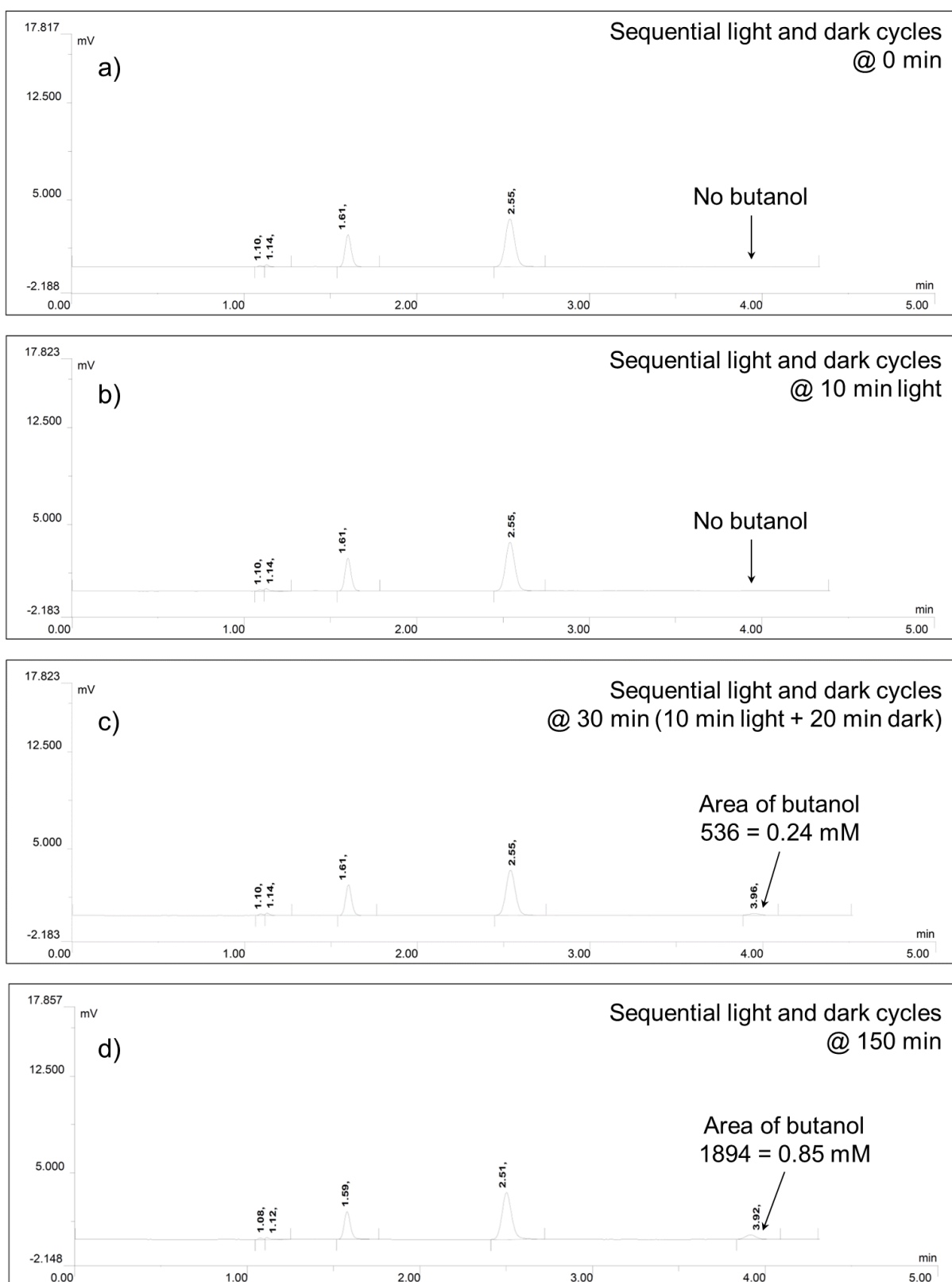


Figure 4.23. GC data for the sequential light-dark cycles. Chromatograms at a) 0 min, b) after 10 min irradiation in absence of ADH enzyme, c) after 20 min dark cycle with ADH enzyme, and d) after 150 min and multiple light-dark cycles. These GC chromatograms corresponds to the data plotted in **Figure 4.10a**.

4.6.5.4. Quantification of butanol formed in simultaneous light-dark cycles

To carry out the simultaneous light-dark cycle experiment, the reaction mixture containing NAD^+ (1 mM), TEOA (1 M), $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ electron mediator (0.25 mM), [-] InP QDs (1.5 μM), butyraldehyde (29 mM) and 50 μL of 1 mg/mL ADH enzyme in 50 mM phosphate buffer was constantly irradiated for 35 min. GC analysis of the reaction at the end of irradiation shows the formation of 1.26 mM butanol (**Figure 4.24**). For GC experiment, 50 μL of the reaction mixture was passed through a syringe filter followed by injection of 1 μL of that solution into the GC instrument. The concentration of the butanol was estimated using the calibration curve in **Figure 4.21**.

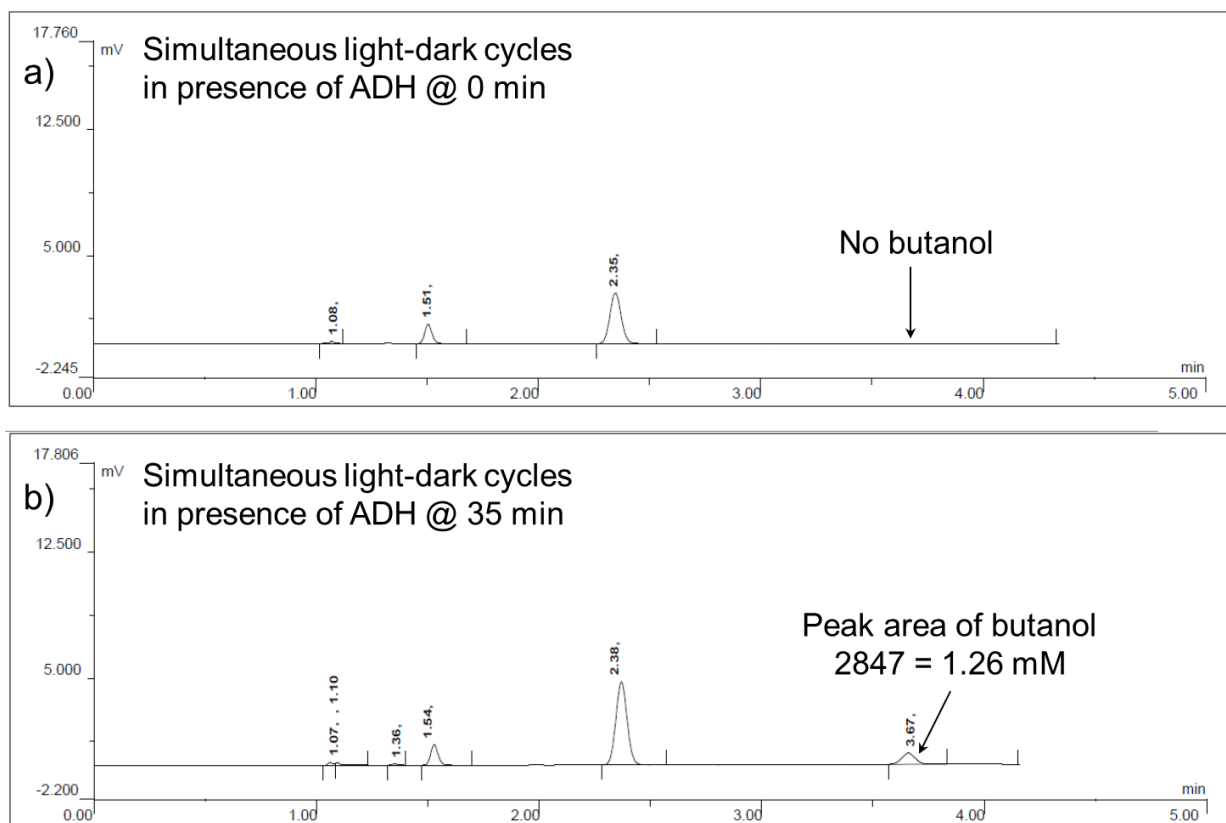
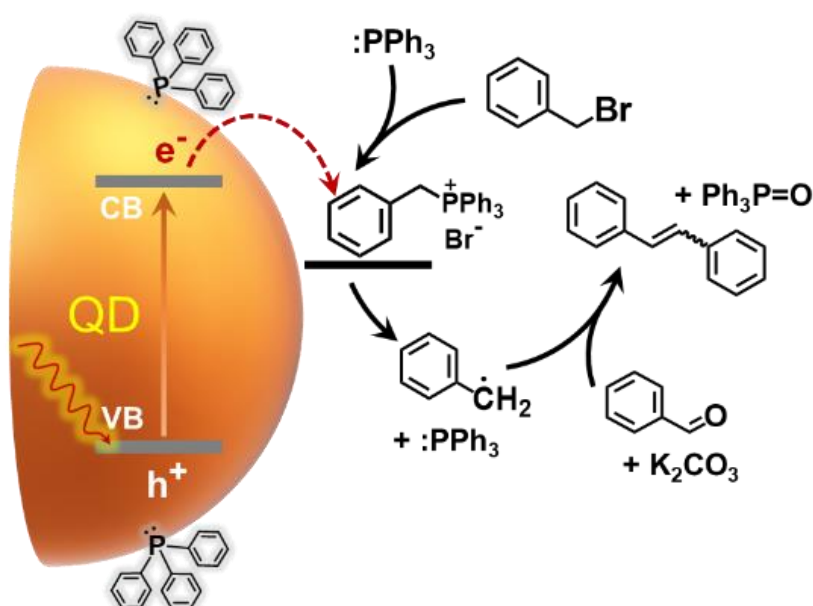


Figure 4.24. GC data for simultaneous light-dark cycles. Chromatogram at a) 0 min of the reaction and b) after 35 min of photoirradiation corresponding to simultaneous light-dark cycles. These GC chromatograms corresponds to the data plotted in **Figure 4.10b**.

Chapter – 5

Introducing Double Bonds in Organic Molecules with Quantum Dots and Visible-Light at Room Temperature



This Chapter has been adapted from the following paper with permission. Copyright 2023, American Chemical Society: **Chakraborty, I. N.**; Roy, P.; Pillai, P. P. Visible Light-Mediated Quantum Dot Photocatalysis Enables Olefination Reactions at Room Temperature. *ACS Catal.* **2023**, *13*, 7331–7338.

5.1. Abstract

The ability of quantum dots (QDs) to photocatalyze organic reactions is gaining attention because of their distinct light harvesting properties over traditional precious-metal and small-molecule based catalysts. However, establishing the potency of QD photocatalysts in diverse and useful organic transformations, as well as deciphering the associated charge transfer mechanisms, is essential to cement their place as an efficient photocatalyst in synthetic organic chemistry. Also, understanding the role of surface ligands in case of organic transformations are not straight forward as in the case of aqueous phase transformations, as discussed in the previous Chapters. In this Chapter, we report the use of QDs in efficiently photocatalyzing a series of olefination reactions under visible-light irradiation at room temperature, and also explored the role of surface ligands in dictating the interesting charge transfer pathway via detailed spectroscopic and electrochemical studies. The dual role of triphenylphosphine – as surface passivating agent as well as a nucleophile – turned out to be decisive in directing the charge transfer process from the QD to the reactant. Benzyl triphenylphosphonium bromide salt was accepting the electrons from the photoexcited QDs, thereby initiating the catalytic olefination reaction. The QD photocatalyzed olefination was demonstrated with formaldehydes as well, resulting in the formation of industrially relevant terminal alkene, such as styrene. Moreover, the environmentally friendly indium phosphide (InP) QD too photocatalyzed the olefination reaction under mild reaction conditions, which proves the practical suitability of our study. This work presents an attractive and efficient way to introduce double bonds in organic molecules using QDs and visible-light at room temperature.

5.2. Introduction

The quest for finding alternatives to precious metal-based photocatalysts has revolutionized the way chemical reactions are performed in recent years. In this direction, semiconductor nanoparticles or quantum dots (QDs) are emerging as attractive visible-light photocatalysts for performing challenging and useful organic transformations.¹⁻¹¹ With respect to traditional transition-metal complex and small-organic molecule based photocatalysts, QDs possess large visible-light absorption cross-section, high charge transfer efficiency, tuneable redox potentials, low catalyst loading, superior photostability and longer shelf-life.¹⁷⁻¹⁹ Apart from

the properties arising from the core, the surface of QDs (in terms of surface atoms and ligands) can be used as multiple binding sites, as well as for controlling the movement of charge carriers.²⁰⁻³³ On top of this, the ease in QD synthesis from readily available precursors is an added advantage in scaling-up their production for industrial level applications.³⁴⁻³⁶ All these unique properties have rendered QD photocatalysts a special place in organic transformations as well.

In a typical QD photocatalysis, the photoexcited electron-hole pairs are extracted from the core to perform net reductive/oxidative and redox neutral reactions (**Figure 5.1a**).¹²⁻¹⁶ For example, in one of the pioneering works, Wu and co-workers carried out a net oxidation reaction (via alcohol oxidation) using cadmium sulfide (CdSe) QDs and visible-light (**Figure 5.1b**).⁵ In another notable work, Weiss and co-workers reported the formation of aniline via 8e- reduction of nitrobenzene using CdS QDs (**Figure 5.1c**).⁶ This forms one of the examples of net reduction reaction with QD photocatalysis. Along with many examples of net oxidation and reduction reactions, there are also a substantial number of reports on redox neutral reactions. In one of the initial reports in that area, Weix and coworkers used CdSe QDs to carry out a series of C-C coupling reactions which consists of involvement of both oxidation as well as reduction reactions as a part of the overall mechanism (**Figure 5.1d**).⁷ Such examples have definitely broadened the applicability as well as the understanding of the QD photocatalyzed reactions for organic transformations.

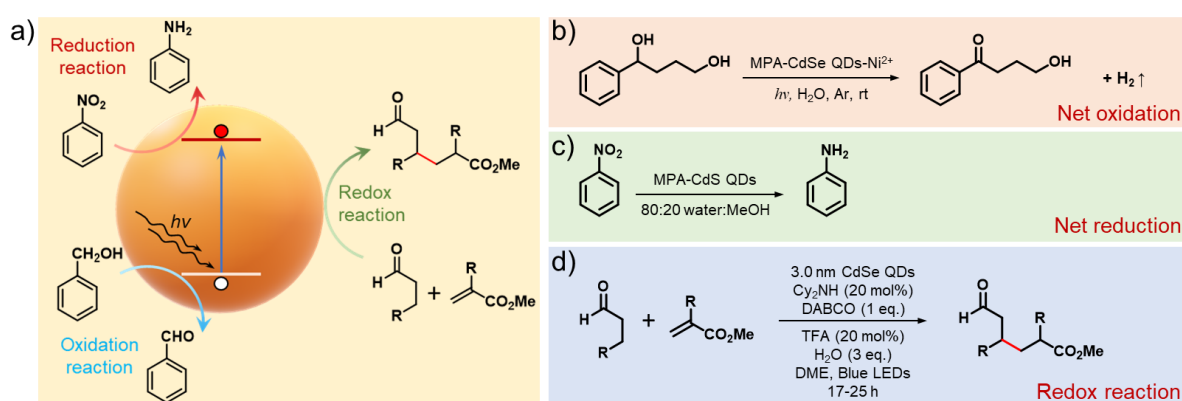


Figure 5.1. Various classes of QD photocatalyzed organic transformations based on redox chemistry. The figure prepared by collating the data from references 5, 6 and 7.

As discussed above, QD photocatalysts have been predominantly used in organic synthesis for carbon-carbon or carbon-heteroatom coupling reactions,^{3,4,6,7,9-12} with limited attempts on industrially relevant olefination reactions. Olefination is an important class of reaction in

synthetic organic chemistry for introducing C-C double bonds in target molecules.³⁷ One of the most popular methods to introduce double bonds in organic molecules was developed by George Wittig in 1953, which consists of a two-step reaction involving the formation of phosphonium ylides and its subsequent reaction with carbonyl moieties to yield the desired alkenes.³⁸ However, the classical Wittig reaction often requires conditions such as usage of high temperature (≥ 100 °C) and strong bases.^{38,39} The wide applicability of Wittig reaction in organic synthesis has led to the development of modified strategies that require milder reaction conditions.⁴⁰⁻⁴⁷ As a result, Wittig reactions have been accomplished at milder bases and low temperature with many stabilized phosphonium ylides, especially for the synthesis of stilbene derivatives.⁴⁸⁻⁵¹ The introduction of visible-light photocatalysis to carry out similar olefination reactions can potentially provide added advantages in terms of sustainability as well as help unraveling newer mechanistic insights of the reaction. In a recent report by Fu and co-workers, the authors reported a series of olefination reactions with Ru-based metal complexes as photocatalysts (**Figure 5.2a**).⁵² The work has revealed a number of mechanistic insights where triphenylphosphine acts as a reductive quencher (or, hole scavenger) which helps the reaction to undergo via a radical mediated pathway, finally yielding the desired alkene product (**Figure 5.2b**).

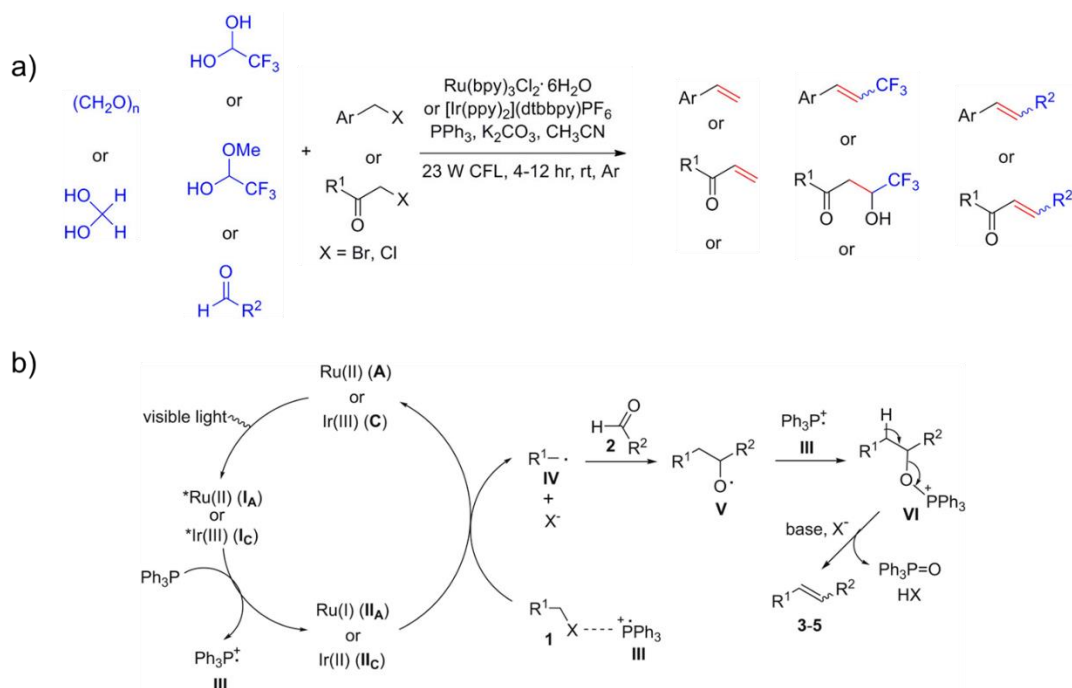


Figure 5.2. Photocatalytic olefination reaction with Ru-based metal complex photocatalysts. a) A schematic showing various classes of olefinations with different substrates under the optimized reaction condition. b) The plausible mechanism of the photocatalytic olefination. Reproduced with permission from ref. 52. Copyright: 2018, *Cell press*.

Here, we report the use of QDs as efficient visible-light photocatalysts at room temperature for performing olefination reactions in one-pot. A series of important olefinations between different substituted aryl aldehydes and benzyl bromides were photocatalyzed using QDs (**Figure 5.3**). The use of visible-light and QD in the olefination reaction gave a mixture of *E* and *Z* alkenes in good to excellent yields. For instance, cadmium selenide (CdSe) QD photocatalyzed olefination between benzaldehyde and benzyl bromide gave an excellent yield of 90%, corresponding to a turnover number (TON) of 3913 and an internal quantum efficiency of 0.1%. Apart from the excellent yield, the use of QD photocatalyst allowed us to conduct the olefination in one-pot using a mild base potassium carbonate (K_2CO_3), and at room temperature. More importantly, crucial insights on the charge transfer mechanism involved in the QD photocatalyzed olefination was obtained using detailed spectroscopic and electrochemical studies. The outcomes were found to be fundamentally different from the traditional metal-complex based photocatalysts. Interestingly, the surface passivating and nucleophilic properties of triphenyl phosphine (PPh_3) turned out to be decisive in directing the light-induced charge transfer process (**Figure 5.3**). Benzyl bromide reactant formed a salt with the PPh_3 (PPh_3 - $PhCH_2Br$ salt) that accepted the photoexcited electrons from the QDs to initiate the photocatalytic olefination. Further, the QD photocatalyzed olefination was extended to synthesise industrially relevant terminal alkenes such as styrene, using formaldehyde as one of the reactants. Although Ru and Ir-based transition metal-complex photocatalysts have been explored for the olefination reactions,⁵² the use of QDs in the present work is fundamentally intriguing with respect to the reaction mechanism and recyclability aspects. Finally, the scope of environmentally benign indium phosphide (InP) QD in photocatalysing the olefination reaction was successfully demonstrated, which proves the practical suitability of our study.

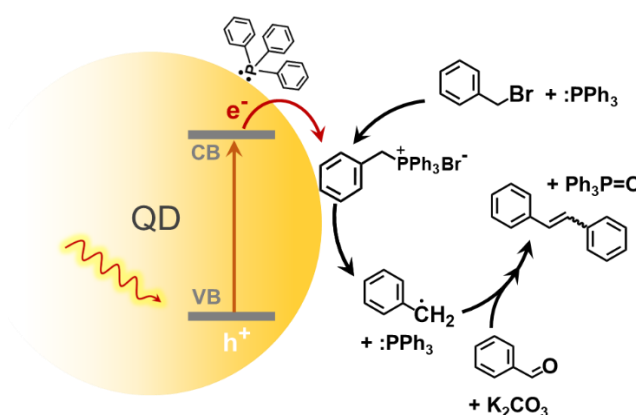


Figure 5.3. A consolidated scheme of the QD photocatalyzed olefination reaction between benzaldehyde and benzyl bromide. The dual role of PPh_3 – as surface passivating agent and nucleophile – was crucial in directing the charge transfer from the QD.

5.3. Experimental section

Materials and reagents, synthesis of CdSe and InP QDs and the instrumentation techniques used are described in **Chapter-2**.

5.3.1. Photocatalytic studies:

5.3.1.1. Light sources used for photocatalytic reactions:

Photocatalytic studies were performed using two 10 W regular blue (~460 nm) LEDs kept at distances of 4 cm from the reaction tube on both sides. The intensity at the wall of the reaction tube was measured to be ~60 mW.cm⁻² using a Newport optical power meter (model: 842-PE). The reactions under other wavelengths of irradiation were performed with two 10 W LEDs of the corresponding wavelength, while maintaining the incident intensity at ~60 mW.cm⁻².

5.3.1.2. Procedure for the photocatalytic olefination reaction:

In a stir bar-equipped 15 mL test tube, 46 µL of 0.50 mM CdSe QDs in toluene were added and the solvent was dried with gentle air flow. Next triphenylphosphine (80 mg, 0.30 mmol), benzaldehyde (11 µL, 0.10 mmol), benzyl bromide (35 µL, 0.29 mmol) and K₂CO₃ (41 mg, 0.29 mmol) were added, followed by the addition of 2 mL dry benzene under inert atmosphere. The mixture was then kept for purging with argon for ~30 min. Then the tube was sealed and kept for irradiation with two 10 W LEDs (at a distance of 4 cm each on the both sides) under stirring for 24 h. After the reaction was completed, the whole reaction mixture was transferred into a centrifuge tube, followed by the addition of ~5 mL MeOH to precipitate the QDs. Next the QDs and the other insoluble by-products were separated via centrifugation (2 min at 8000 rpm). The supernatant was collected and worked up with water-diethyl ether mixture followed by collecting the diethyl ether layer. The solvent was then removed *in vacuo* and the crude residue was purified with silica gel column chromatography using hexane (pentane for styrene) as eluent, to obtain the products.

Different QDs, aromatic aldehydes/formaldehydes, and aromatic bromides were used in different photocatalytic experiments, while maintaining the above-mentioned reaction conditions.

5.3.1.3. Calculation of the yield of the olefination reaction

The yield of the olefination reaction was calculated using ^1H NMR spectroscopy with respect to 1,3,5-trimethoxybenzene as an internal standard. The 3H peak (δ 6.12, s) of internal standard and the two distinguishable peaks for *Z* and *E* stilbene (2H, δ 6.6, s and 2H, δ 7.1, s respectively) were taken as the reference peaks for calculating the reaction yield.

A typical example for the calculation of yield from NMR spectrum shown in Appendix **Figure 5.15** is estimated below.

The two distinguishable peaks (2H, δ 6.55, s and 2H, δ 7.1, s) of the product were integrated with respect to the internal standard.

To normalize the 2H products peaks with 3H internal standard peak, with respect to the number of protons, the 2H product peaks need to be multiplied by a factor of 3/2.

The ratio of *Z*-stilbene peak with respect to internal standard peak = $(1.96 \times 3/2 \times 1) = 2.94$

The ratio of *E*-stilbene peak with respect to internal standard peak = $(1.41 \times 3/2 \times 1) = 2.11$

Moles of internal standard present in the reaction = 17.83 μmol ,

Hence, moles of *Z*-stilbene product formed = $(17.83 \times 2.94) \mu\text{mol} = 52.42 \mu\text{mol}$

Moles of *E*-stilbene product formed = $(17.83 \times 2.11) \mu\text{mol} = 37.62 \mu\text{mol}$

Total moles of product formed = $(52.42 + 37.62) = 90.04 \mu\text{mol}$

The molecular weight of the product = 180.25 g. mol^{-1}

Hence, the weight of the product formed = $90.04 \times 10^{-6} \text{ mole} \times 180.25 \text{ g. mol}^{-1} = \underline{\underline{16.2 \text{ mg}}}$

The theoretical expected yield of the reaction = 18 mg

So, the yield of the reaction is = $(16.2/18) \times 100 = 90\%$

The physical weight of the isolated products (*E* and *Z* combined) was 16.1 mg, which closely matches with the calculated NMR yield. Hence, the isolated yield through weighing was used to calculate the yield of the reactions henceforth.

5.3.1.4. Calculation of internal quantum yield (IQY)

The % internal quantum yield (ϕ_{int}) was calculated below as per the procedure mentioned in **Section 2.6.3 of Chapter 2.**⁵⁶

% Incident light absorbed is calculated from the absorbance of the catalyst at the LED excitation wavelength, using Beer-Lambert law. For the catalyst absorbance of A (O.D.) = 3, at 460 nm, 99.9% incident light is absorbed. Hence the number of absorbed photons for an irradiation with two LEDs is,

$$n_{\text{photon}} = \frac{(0.06 \text{ W} \cdot \text{cm}^{-2} \times 2.25 \text{ cm}^2) \times (460 \times 10^{-9} \text{ m}) \times 86400 \text{ s}}{(3 \times 10^8 \text{ m/s}) \times (6.626 \times 10^{-34} \text{ J} \cdot \text{s})} \times 2 \times 99.9\% = 5.39 \times 10^{22}$$

The moles of product formed during the reaction was 0.09 mmol, which was determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

$$I.Q.Y = \frac{90 \times 10^{-6} \text{ mol} \times 6.023 \times 10^{23}}{5.39 \times 10^{22}} \times 100\% = 0.1\%$$

The internal quantum yield (I.Q.Y.) with CdSe QDs under two 10 W blue LED irradiation was estimated to be **0.1 %**.

5.3.2. Synthesis of Se=PPh₃ complex

In a N₂ filled glove-box, 0.2 mmol of PPh₃ and 2 mmol of Se powder was taken in a 5 mL round bottom flask. The sealed flask was brought out of the glove-box and was heated to ~150 °C till the PPh₃ melted. Upon melting, PPh₃ readily reacts with the Se, forming a blackish liquid. The reaction was kept for 30 min followed by cooling to room temperature, resulting in the solidification of the liquid. Then, the solid residue was dissolved in toluene and the unreacted Se was precipitated via centrifugation. The colorless supernatant (Se=PPh₃) was decanted and used for electrochemical measurements.

5.4. Results and discussion

5.4.1. Synthesis and characterization of the CdSe QD photocatalysts:

To carry out the photocatalytic olefination reaction, we chose the traditional CdSe QDs as the photocatalyst. For this, oleic acid capped 3.6 ± 0.4 nm sized CdSe core QDs were synthesized using a modified reported procedure,⁵³ and dispersed in toluene (**Figure 5.4a, b** and see **Section 2.3 of Chapter 2** for details). The first excitonic and emission peaks of as-synthesized CdSe QDs were centred ~570 nm and ~580 nm, respectively (**Figure 5.4c, d**).

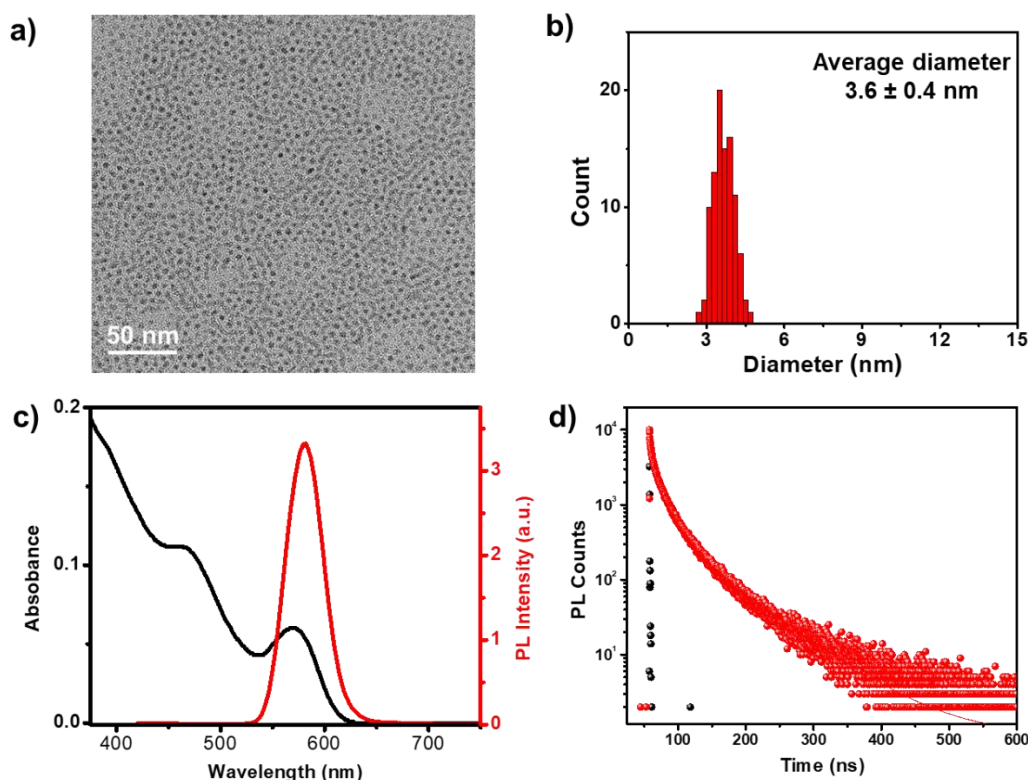


Figure 5.4. Characterization of CdSe QDs. a) A representative HRTEM image of CdSe QDs. b) A histogram showing the size distribution of the QDs. An average diameter was calculated to be 3.6 ± 0.4 nm (from ~ 100 QDs). c) Steady-state absorption and PL spectra of CdSe QDs. d) PL lifetime decay profile of CdSe QDs.

5.4.2. CdSe QD photocatalyzed olefination

In a typical olefination reaction, a mixture of benzaldehyde (0.10 mmol), benzyl bromide (0.29 mmol), PPh_3 (0.30 mmol) and K_2CO_3 (0.29 mmol) in 2 mL dry benzene was irradiated in the presence of 0.023 mol% CdSe QDs (**Figure 5.5a**). The product yield and E:Z ratio were estimated from the weight of isolated product, NMR spectroscopy, and gas chromatography (GC) measurements. The yield estimated from weight of the isolated product well corroborated with the yield calculated using NMR spectroscopy (see **Experimental Section 5.3.1.3** for details). Many photocatalytic experiments were conducted to optimize the wavelength and time of irradiation, as summarized in **Figure 5.5b**. The irradiation of the reaction mixture using 2 x 10 W blue LED ($\lambda_{\text{ex}} \sim 460$ nm, light intensity measured at the reaction tube was $\sim 60 \text{ mW} \cdot \text{cm}^{-2}$) with a catalyst loading of 0.023 mol% for 24 h gave the maximum yield of 90%, with a corresponding turnover number (TON) of 3913 and an internal quantum efficiency of 0.1% (**Figure 5.5b**, entry 1 and **Figure 5.15**; See **Section 2.6** of **Chapter 2** and **Experimental Section 5.3.1.4** for details). The yield obtained using CdSe QDs was comparable with traditional transition metal-complex photocatalyzed olefination reaction,⁵² with an added

advantage associated with the superior optoelectronic properties of QDs (*see below*). As expected, the product stilbene was found to exist in both *E* and *Z* isomers after the photocatalytic reaction (*E* : *Z* = 42 : 58) (**Appendix Figures 5.15 – 5.18**). Further, the linear dependence of the reaction yield on the catalyst loading confirmed the direct participation of QDs as photocatalysts in the olefination reaction (**Figure 5.5b**, entry 2, 3). Other experiments with lower irradiation intensity or time gave inferior yield for the olefination reaction (**Figure 5.5b**, entry 9-11). The active role of QDs in photocatalysing the olefination reaction was confirmed by constructing the action spectra using the yield of the reaction under three different irradiation wavelengths (e.g., 460 nm, 516 nm and 595 nm) under similar conditions, which followed the excitation spectra of CdSe QDs (**Figure 5.5b**, entries 1,7,8 and **Figure 5.5c**). Likewise, control experiments in the absence of (i) QDs and (ii) light gave negligible conversions, which emphasizes the necessity of light and QDs in the olefination reaction (**Figure 5.5b**, entries 4 and 5). The role of the heat generated from LED excitation was overruled by performing a thermal experiment at ~30 °C in the presence of QDs, without irradiation (**Figure 5.5b**, entry 6. Note: the maximum heat generated from the LED sources was measured to be ~27 °C.).

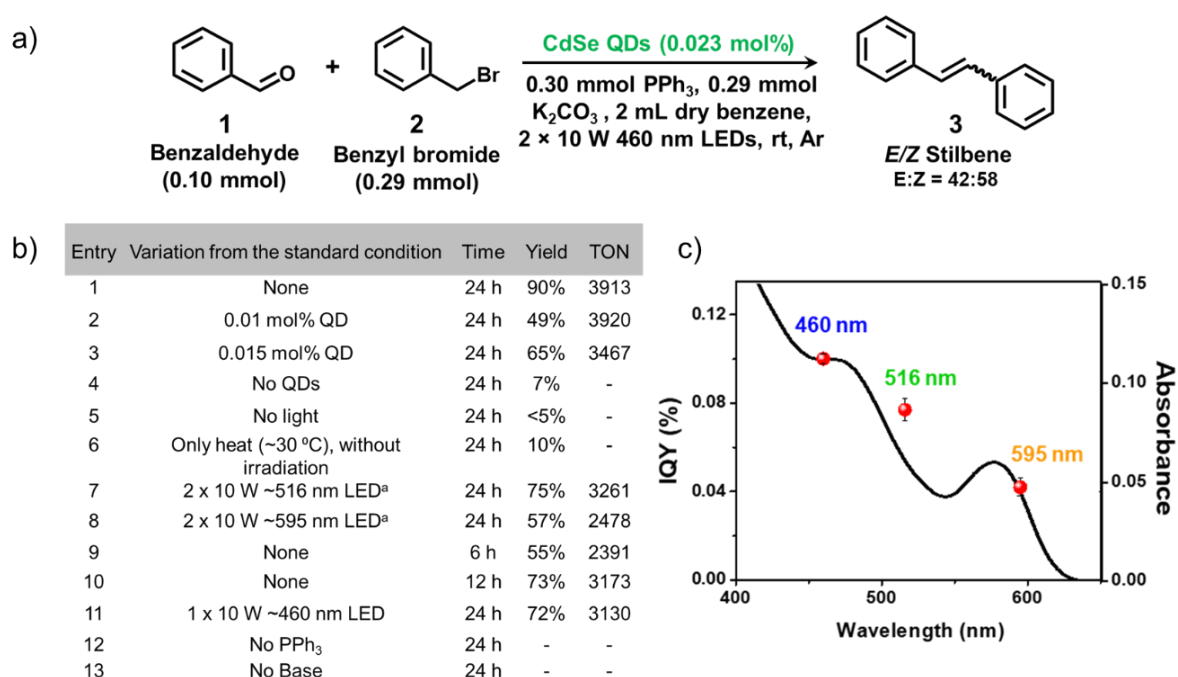


Figure 5.5. Reaction scheme and optimization studies for CdSe QD photocatalyzed olefination reaction. a) Reaction scheme, b) Optimization table for the olefination reaction. ^aThe light intensity measured at the reaction tube was ~60 mW.cm⁻², as in the case of ~460 nm LED. c) The action spectra show an excellent overlap between the calculated IQY values of the photocatalytic reactions under different excitation wavelengths and the ground state absorption profile of the QDs.

The ultimate proof for the active involvement of QD photocatalysts was obtained by performing the olefination reaction under alternate light ON-OFF cycles. As we expected, the reaction occurs only when the light was switched ON, and negligible product was formed once the light source was switched OFF (**Figure 5.6a**). Furthermore, the CdSe QDs retained their photocatalytic activity for at least three cycles, without much compromise in the yield (**Figure 5.6b**).

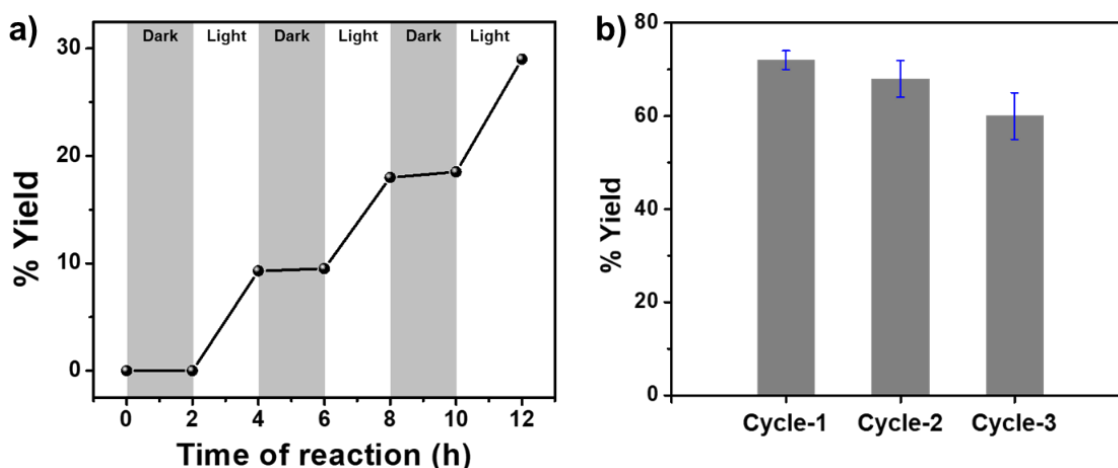


Figure 5.6. a) Progress of the photocatalysed olefination reaction under consecutive ON-OFF irradiation cycles. b) A bar diagram showing the % yields of the reactions carried out for three consecutive cycles by recycling the same CdSe QDs.

5.4.3. Photophysical investigation

Systematic steady-state and time-resolved emission experiments were conducted to gain preliminary understanding on the charge transfer mechanism associated with the QD photocatalyzed olefination (**Figure 5.7 and 5.8**). The strong and stable photoluminescence (PL) of QDs allowed us to follow the charge transfer steps via emission studies, which will result in a drastic quenching in the QD emission. Accordingly, the influence of individual reactants on the PL of QD was monitored. It was well reported in molecular photocatalytic systems that the hole abstraction by PPh_3 is usually the first step in the charge transfer mechanism.^{52,57} As a result, a quenching in the emission of molecular photocatalyst is commonly observed in the presence of PPh_3 . On the contrary, a gradual enhancement in the QD PL was observed in the present study in both steady-state and time-resolved experiments, upon the addition of 0.30 mmol PPh_3 (**Figure 5.7a, b**). PPh_3 is known to bind on the surface selenium sites of the CdSe QDs, resulting in the passivation of the surface trap states (**Figure 5.7a**).⁵⁸⁻⁶⁰ The binding of PPh_3 on the surface of QDs was proved using NMR and IR studies (**Figure 5.7c, d**; see **Appendix Section 5.7.3** for more details). Consequently, the observed

enhancement in the PL lifetime of PPh_3 -treated QDs implies that the photoexcited charge carriers stay longer in the excited state, thereby enhancing the probability of charge transfer process. Also, the thermodynamics does not favour the hole transfer process from QD to surface bound- PPh_3 (*see below*).

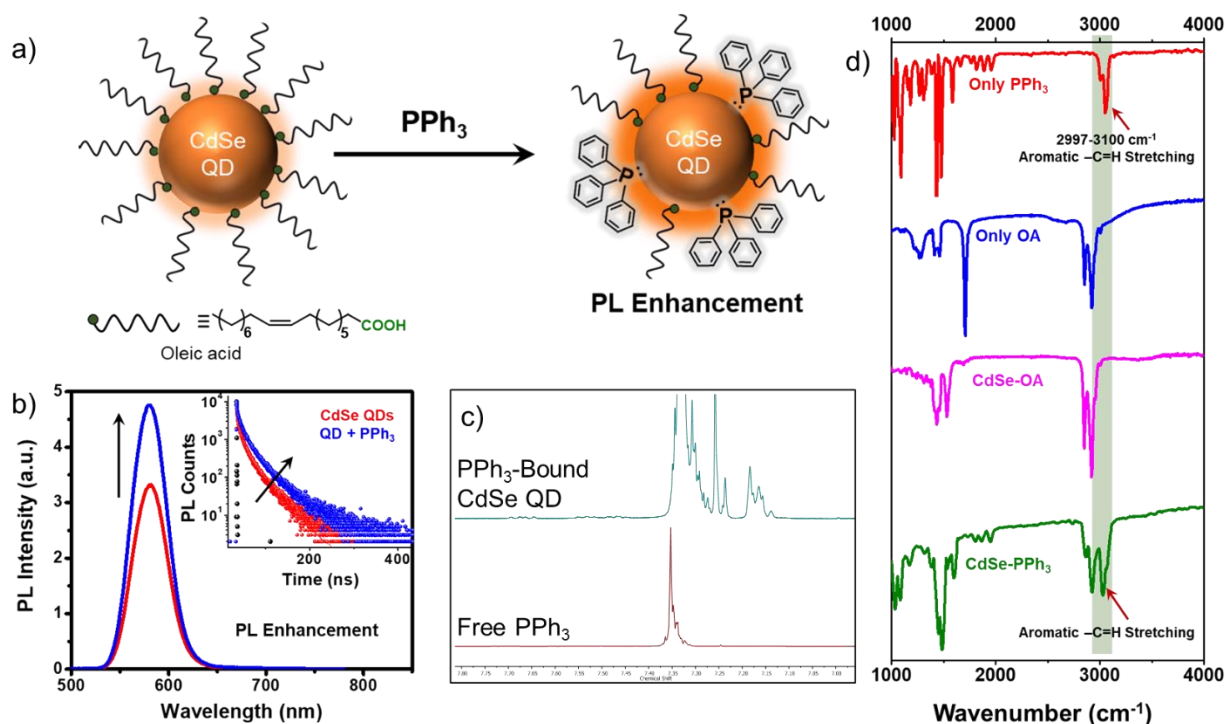


Figure 5.7. Triphenylphosphine as a surface passivating agent on the QDs. a) A schematic representation of the QD surface passivation by PPh_3 followed by PL enhancement. b) A gradual increase in the steady-state (and time-resolved in inset) PL of QDs in the presence of PPh_3 was observed, because of the passivation of the surface defects. c) ^1H NMR spectra (in CDCl_3) of the PPh_3 treated CdSe QDs (purified) and free PPh_3 molecule. The slight broadening of the signature peak of PPh_3 ~ 7.3 ppm indicates the functionalization of PPh_3 on the surface of QDs. d) IR spectroscopic studies confirming the binding of PPh_3 on the surface of CdSe QDs.

Interestingly, the addition of benzyl bromide to this PPh_3 treated QDs resulted in an appreciable quenching in the PL of QDs, as revealed by both steady-state emission and PL lifetime experiments (**Figures 5.8a, b**). Also, the addition of benzyl bromide and benzaldehyde had minimum influence on the PL of QDs, confirming negligible interaction between the QDs and the reactants (**Figure 5.8c**). All the emission studies confirm that the charge transfer from the photoexcited QDs only occurred when both PPh_3 and benzyl bromide were present in the system. This observation can be explained as follows. The nucleophilic character of PPh_3 and the presence of a labile C-Br bond in benzyl bromide can result in the formation of a stable benzyl triphenylphosphonium bromide ($\text{PPh}_3\text{-PhCH}_2\text{Br}$) salt via $\text{S}_{\text{N}}2$ type substitution.³⁸ This dual role of PPh_3 , as surface passivating agent as well as nucleophile, can dictate the charge

transfer pathway of the photocatalytic reaction. In an independent experiment, the direct addition of separately prepared $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt too resulted in the quenching of QD emission (**Figure 5.8d**). Addition of excess PPh_3 with the separately prepared $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt did not result in any further quenching of the QD emission (**Figure 5.8d**). This indicates an operative charge transfer pathway between $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt and QDs (the reduction of $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salts via electron transfer from excited photocatalysts is known.⁶¹). This is further supported by the fact that an excellent yield (87%) was obtained when a freshly prepared $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt was used instead of a physical mixture of triphenylphosphine and benzyl bromide.

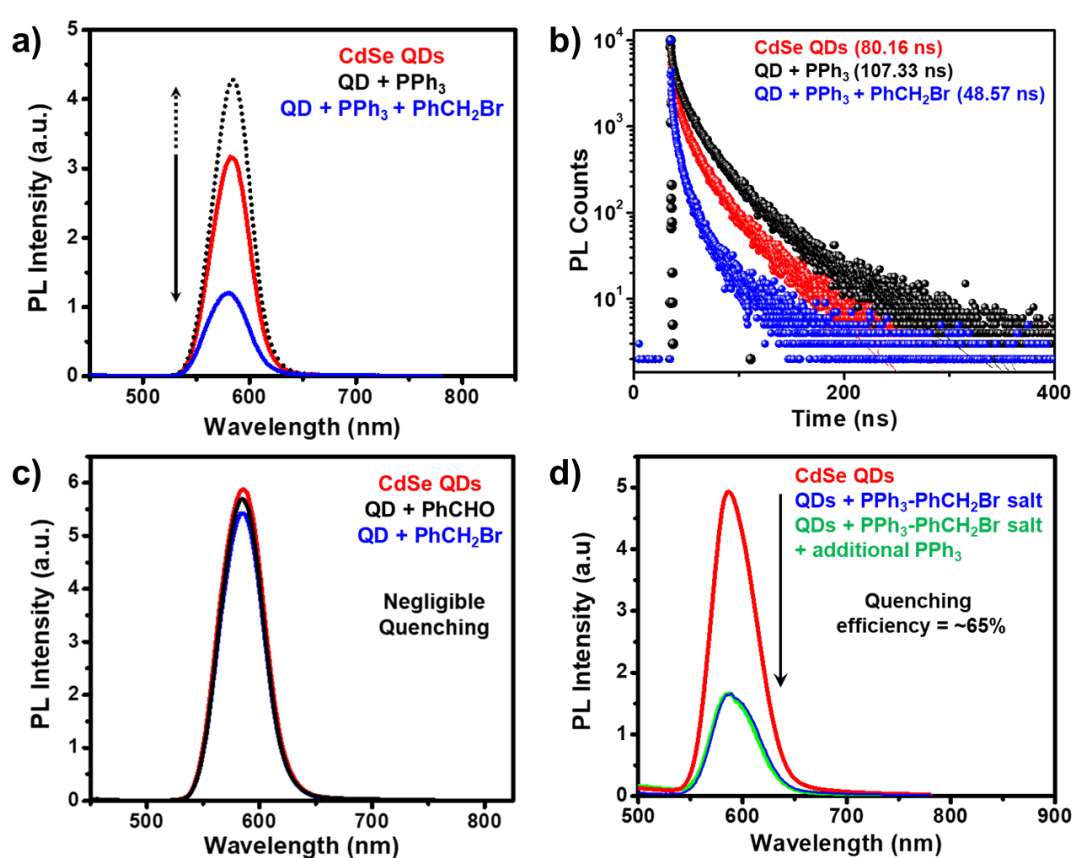


Figure 5.8. Monitoring the charge transfer process in QD photocatalyzed olefination reaction through steady-state and time-resolved PL studies. a) An initial increase and subsequent quenching of QD PL was observed upon addition of PPh_3 and PPh_3 + benzyl bromide, respectively. b) The similar trend of enhancement and subsequent quenching is observed in the corresponding PL lifetime plots as well. c) Control experiments showing negligible quenching in the QD PL upon addition of benzaldehyde and PhCH_2Br separately. d) Quenching in the PL QD upon addition of separately prepared $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt, confirming the charge transfer process. Also, no additional PL quenching was observed upon addition of excess PPh_3 in the solution.

5.4.4. Electrochemical investigation

The thermodynamic feasibility of $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt to participate in the proposed charge transfer pathway was further investigated. For this, detailed electrochemical studies were performed for individual reactants to get a quantitative idea on their energy levels with respect to each other (**Figure 5.9–5.11**). The acquired conduction band (CB) and valence band (VB) values of mention the size if possible CdSe QD were located at -1.37 and $+0.84$ V vs SCE (**Figures 5.9a, b and 5.11**), which are in accordance with previous report.⁶² The oxidation potential of free- PPh_3 was centred at 0.27 V vs SCE, which lies above the VB of QDs, thereby justifying the role of free- PPh_3 as the hole acceptor as reported earlier (**Figure 5.9c**).⁵² However, the PL studies fail to show any signature of a hole transfer process from QDs to PPh_3 , even at higher PPh_3 concentration (**Appendix Figure 5.23**). Rather, an enhancement in the QD PL was observed in the presence of PPh_3 , which confirms the surface passivation effect because of the binding of PPh_3 on the surface of QDs (**Figures 5.7**). As a result, the oxidation potential of the surface bound- PPh_3 ($+1.04$ V vs SCE) is lowered below the VB of QD,⁵⁸ thereby making the hole transfer process from QD thermodynamically unfavourable (**Figure 5.9d, e and 5.11**).

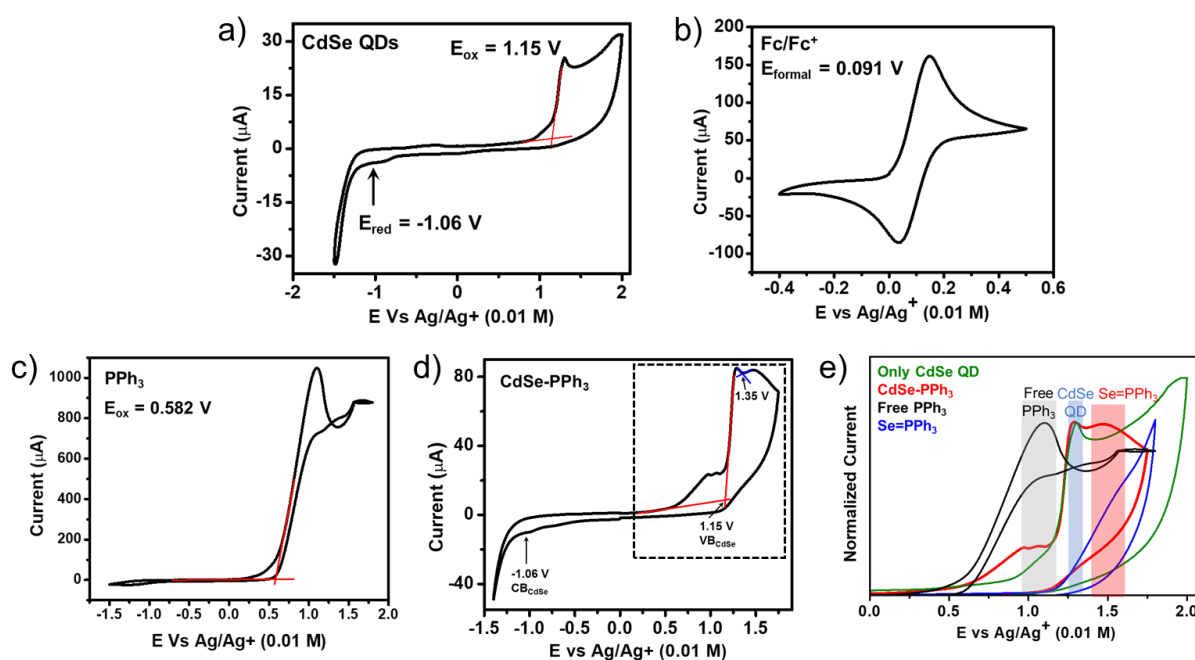


Figure 5.9. a) Cyclic voltammogram of CdSe QDs in acetonitrile solution, at a scan rate of 30 mV/s. The measurement with QDs were performed via dip-coating of QDs over the glassy carbon working electrode. The red lines are drawn for determining the onset redox potentials. b) Calculation of the relative reference electrode potential (E_{ref}) using ferrocene/ferrocenium couple as internal standard. Cyclic voltammograms of c) free PPh_3 and d) surface bound PPh_3 (PPh_3 treated CdSe QDs) in acetonitrile solution. e) Overlap of the selected area voltammogram of PPh_3 treated CdSe QDs (red trace), Se-PPh_3 (blue trace), untreated CdSe QDs (green trace), and free PPh_3 (black trace) in acetonitrile solution. All the spectra were collected at a scan rate of 30 mV/s. The measurement for surface bound PPh_3 was performed via dip-coating of treated QDs over the glassy carbon.

As per the PL studies, the charge transfer occurred only when both PPh_3 and benzyl bromide (or the separately prepared $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt) were added to the QDs. This motivated us to measure the reduction potential of benzyl bromide and separately prepared $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt, which were located at -1.47 V vs SCE and -1.35 V vs SCE respectively (**Figure 5.10a, b and 5.11**).

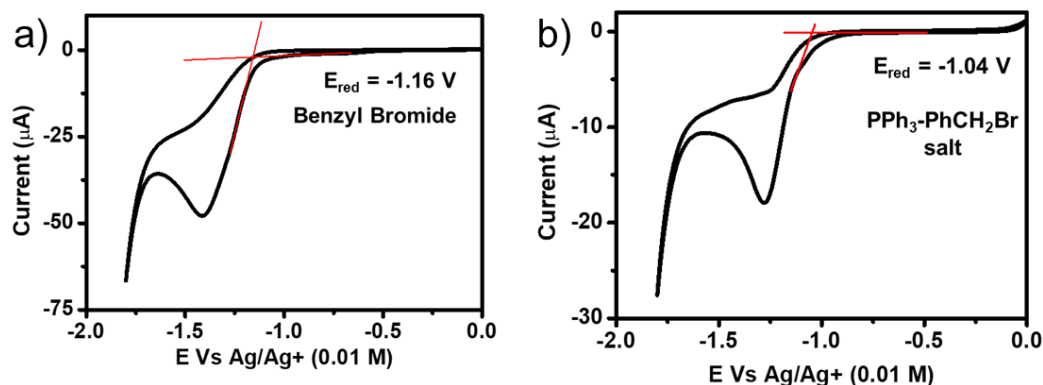


Figure 5.10. Cyclic voltammograms of a) PhCH_2Br , b) $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt dispersed in 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile, recorded at a scan rate of 30 mV/s . The red lines are drawn for determining the onset redox potentials. Ferrocene/ferrocenium couple was used as internal standard.

Thus, an electron transfer from photoexcited QD to $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt was thermodynamically feasible. Following this electron transfer step, the $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt dissociates into neutral PPh_3 and a benzylic radical.⁶¹ The benzylic radical then reacts with benzaldehyde followed by reaction with PPh_3 to form an alkoxyphosphoranyl radical,⁶³ which abstracts the hole from the VB of QDs, thereby regenerating the photocatalyst (*vide infra*). In short, an electron transfer from photoexcited QDs to $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt is the first step, resulting in the formation of a benzylic radical (**Figure 5.11**). This radical then initiates a radical mediated reaction pathway, finally leading to the formation of the desired alkene products. This means that the charge transfer mechanism in the present study is different from transition metal-complex photocatalyzed olefination reaction, where the hole transfer (to PPh_3) was followed by the electron transfer.^{52,57} Having said that, detailed ultrafast transient absorption studies should be conducted to ascertain the above difference in the charge transfer mechanism between the two classes of photocatalysts.

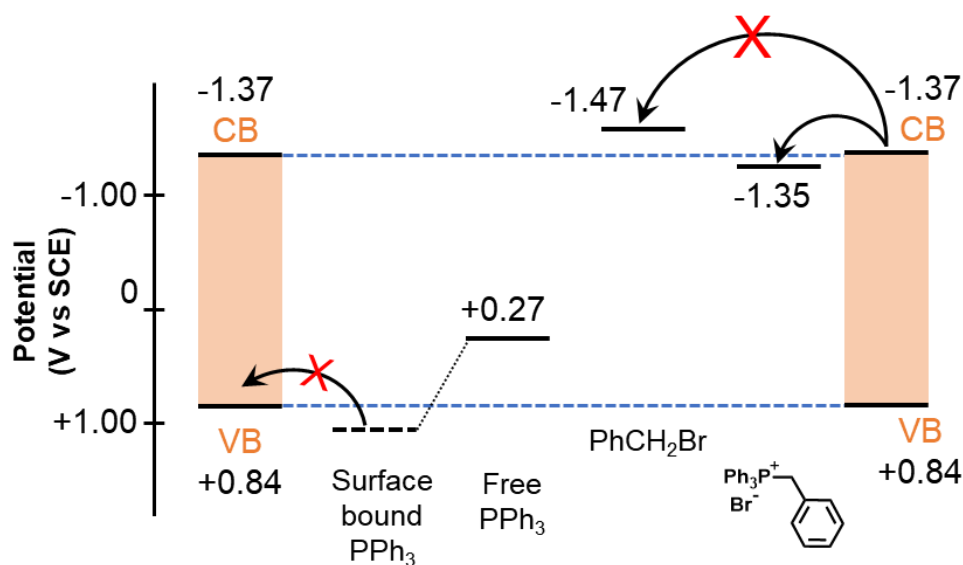


Figure 5.11. Energy level diagram for the QD photocatalyzed olefination reaction. The redox potentials (V vs SCE) (estimated from cyclic voltammetry) of different reactants are shown with respect to CdSe QD, along with the possible charge transfer pathways.

5.4.5. Plausible mechanism

Based on the spectroscopic and electrochemical experiments, the most plausible charge transfer mechanism operating in QD photocatalyzed olefination reaction can be summarized as follows (**Figure 5.12**). The photoexcitation of QD leads to the generation of electron and hole in CB and VB, respectively. At first, $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt is formed by the nucleophilic substitution reaction between benzyl bromide (**2**) and PPh_3 . Next, the $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt (**i**) gets reduced via single electron transfer from photoexcited QD leading to the formation of PPh_3 and benzylic radical (**ii**)⁶¹. The alternate possibility of dissociation of salt (**i**) into PPh_3 radical cation and benzylic anion was overruled as there was no signal of the deuterated product of benzylic anion during a reaction with methanol- D_4 (**Appendix Figure 5.24**). In the next step, the benzylic radical (**ii**) reacts with benzaldehyde (**1**) to form the oxygen centered radical (**iii**)⁶³ that further reacts with the free PPh_3 to form the alkoxyphosphoranyl radical (**iv**)⁶⁴. The formation of the radical **ii** was further confirmed by a radical trapping experiment, using TEMPO as a radical scavenger (see **Appendix Section 5.7.6** and **Figure 5.25**). Also, the negligible formation of the olefine product in presence of TEMPO in the reaction mixture, further confirmed the involvement of photocatalytic radical pathway in the reaction (**Figure 5.26**). This radical **iv** acts as the hole scavenger to regenerate the QD photocatalyst, while forming the alkoxyphosphonium cation (**v**). The cation **v**, in the final stage of the reaction, undergoes

elimination reaction in the presence of K_2CO_3 base, to form the desired stilbene product (**3**), along with triphenylphosphine oxide as the by-product (**Appendix Figure 5.27**). The presence of cation **v** intermediate was confirmed using high-resolution mass spectroscopy on a QD photocatalysed olefination in the absence of the base K_2CO_3 (**Appendix Figure 5.28**. See **Appendix Section 5.7.7** details). No signature of the desired olefine product **3** was observed under this condition (**Appendix Figure 5.29**). Addition of K_2CO_3 to this pre-irradiated reaction mixture gave the desired olefine product **3** in 90% yield, accompanied with a substantial decrease in the amount of cation **v** (**Appendix Figures 5.28, 5.30**). In another set of experiments, the olefination reaction mixture was irradiated for 24 h in the absence of QD photocatalyst and K_2CO_3 . Here, no signature of cation **v** was observed (**Appendix Figure 5.28**). Addition of K_2CO_3 to this pre-irradiated mixture also failed to give any desired olefination product **3**. All these control experiments clearly confirm that the olefination reaction is photocatalysed by QD, and proceeds via radical **ii** and cation **v** intermediates.

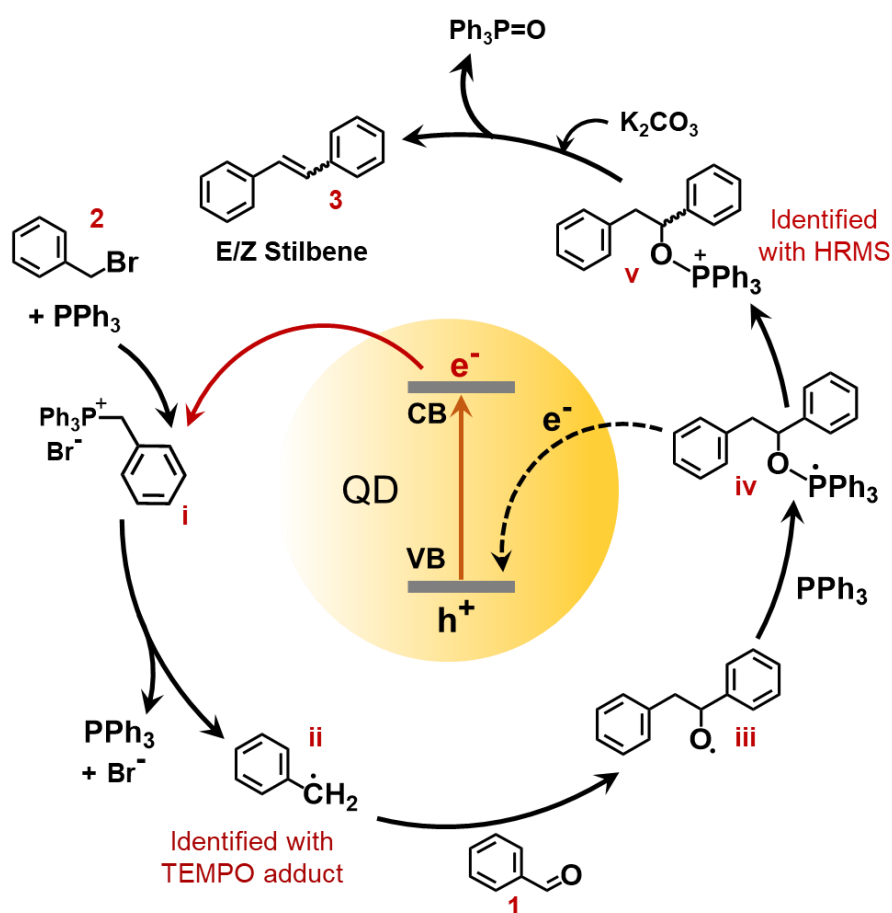


Figure 5.12. The plausible photocatalytic cycle for the olefination reaction in the presence of QDs. The surface passivating and nucleophilic properties of PPh_3 dictate the charge transfer process from the QDs. The formation of benzylic radical and alkoxyphosphonium cation intermediates were confirmed using radical trapping and high-resolution mass spectroscopy (HRMS) experiments, respectively (represented in red highlights).

5.4.6. Exploring the substrate scope of the reaction

The versatility and flexibility of QD photocatalyzed olefination reaction are discussed next. Firstly, the substrate scope was demonstrated with a variety of substituted benzaldehydes and benzyl bromides (**Figures 5.13 and Appendix Figure 5.31 – 5.46**). The substituents were carefully chosen so as to produce olefins containing diverse functional groups and heteroatoms, which can be further used in important organic or biochemical reactions (For instance, styrylpyridines are well-known choline acetyltransferase inhibitors,⁶⁵ and styrylthiophenes are well-established antiradical agents⁶⁶). The reactions of substrate **2** with different substituted benzaldehydes (2-nitro (**1a**), 3-bromo (**1b**), 2-thiophene (**1c**) and 2-pyridyl (**1d**) carboxaldehydes) produced corresponding alkenes (**3a – 3d**) with good to excellent yields (**Figures 5.13, Appendix Figure 5.31-5.38**). Likewise, the reaction of substrate **1** with different substituted benzyl bromides (4-methyl (**2a**), 4-chloro (**2b**), 4-cyano (**2c**) and 4-nitro (**2d**) benzyl bromides) produced corresponding alkenes (**3e – 3h**) with decent to excellent yields (**Figures 5.13, Appendix Figure 5.39-5.46**). Further, the QD photocatalyzed olefination was demonstrated with paraformaldehyde (**1e**) as well, resulting in the formation of industrially relevant terminal alkene, such as styrene (**3i**) (**Figures 5.13, Appendix Figure 5.47**).

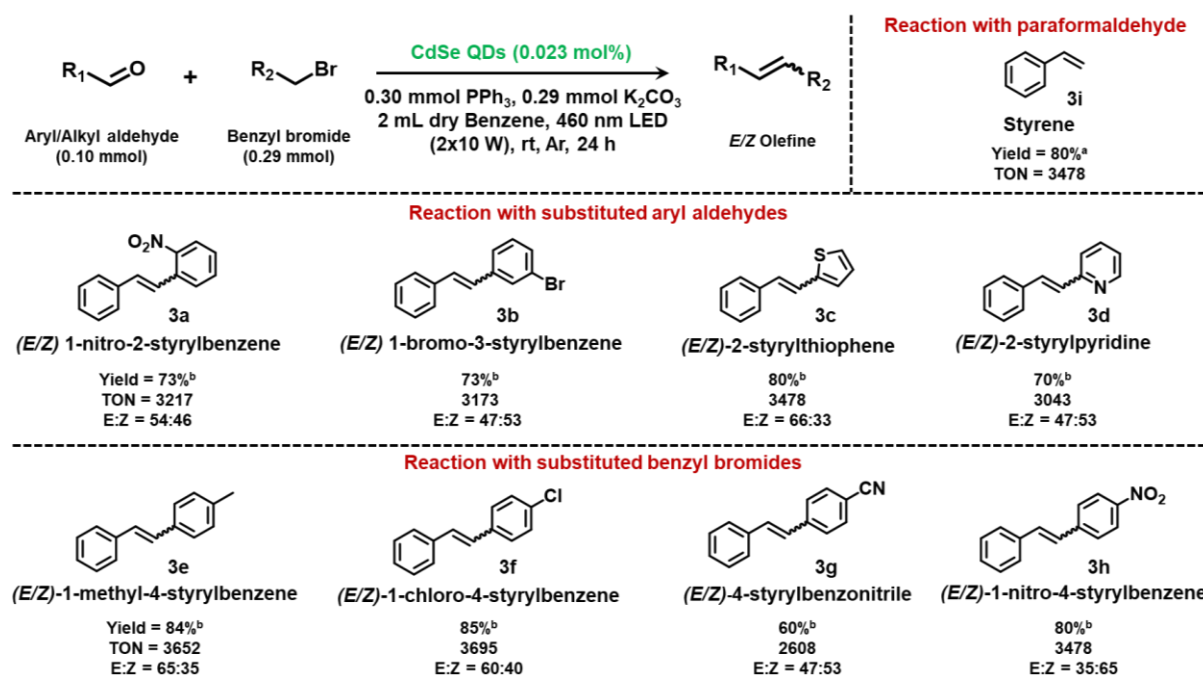


Figure 5.13. Substrate scope of QD photocatalyzed olefination reaction. Synthesis of substituted olefins by systematically varying both aldehyde and benzyl bromide moieties in the presence of QDs and visible-light. ^aIsolated product yield. ^bYields calculated from ¹H-NMR using 1,3,5-trimethoxybenzene as internal standard. All the E:Z ratio were calculated from the corresponding product peaks from ¹H-NMR.

5.4.7. Photocatalytic olefination with ‘Greener’ QDs

Finally, the flexibility with respect to QDs was demonstrated, where the photocatalytic olefination was conducted with environmentally friendly InP QDs (**Appendix Figure 5.48**).⁵⁴ The photocatalytic olefination between **1** and **2** in the presence of 0.023 mol% InP QDs gave a decent yield of 55% (**Figure 5.14a**). Photophysical studies proved that the mechanism of charge transfer in InP QD photocatalyzed olefination was similar to the CdSe QD photocatalyzed olefination (**Figure 5.14b**). It is worth mentioning that no selectivity over the E:Z ratio was achieved in any of the QD photocatalyzed olefination, and close to 1:1 ratio was obtained in most cases. This is understandable as no factors controlling the product selectivity were incorporated into the system. Also, the prolonged light irradiation in presence of QDs can trigger a rapid *E-Z* isomerization in the stilbene derivatives (see details in the **Appendix Section 5.7.11**),⁶⁷⁻⁶⁹ thereby eventually ending up in a mixed ratio of the two isomers (**Appendix Figure 5.49**). Even though there is a room for improvement with respect to product selectivity, the present study demonstrates the potency of QD photocatalyst in creating important substituted olefins at high yields in one-pot at room temperature using visible-light.

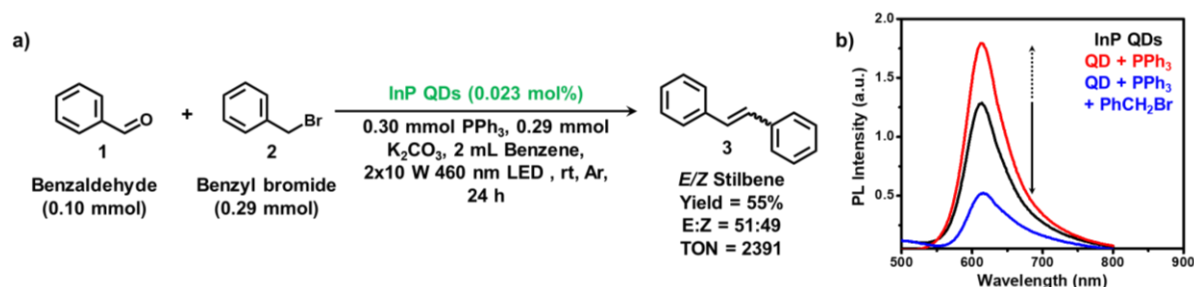


Figure 5.14. A ‘greener’ way of QD photocatalyzed olefination reaction. a) Reaction scheme of the olefination reaction photocatalyzed with InP QDs. b) An initial increase and subsequent quenching of InP QD emission was observed upon addition of PPh₃ and PPh₃ + benzyl bromide, respectively, confirming the charge transfer process.

5.5. Conclusions

The potency of QDs in photocatalysing important class of olefination reactions was successfully demonstrated. Along with the excellent yield, the use of QD photocatalyst enabled the olefination reactions in one-pot under mild reaction conditions, compared to the traditional olefination reactions. A combination of spectroscopic and electrochemical experiments revealed the importance of PPh₃ in directing the charge transfer pathway from QDs to reactants. The versatility of QD photocatalyzed olefination reaction was proved with respect to substrate

scope, as well as ‘green’ QDs. Apart from expanding the scope of QD photocatalysis in synthetic organic chemistry, our work provides an attractive alternative to create double bonds in organic molecules in one-pot at room temperature. Exploring the surface properties of QDs (in terms of surface binding sites and ligands) can be a way forward for achieving a better product selectivity in QD photocatalyzed organic transformations.

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5.7. Appendix of Chapter 5

5.7.1. Characterization of the products and calculation of yields

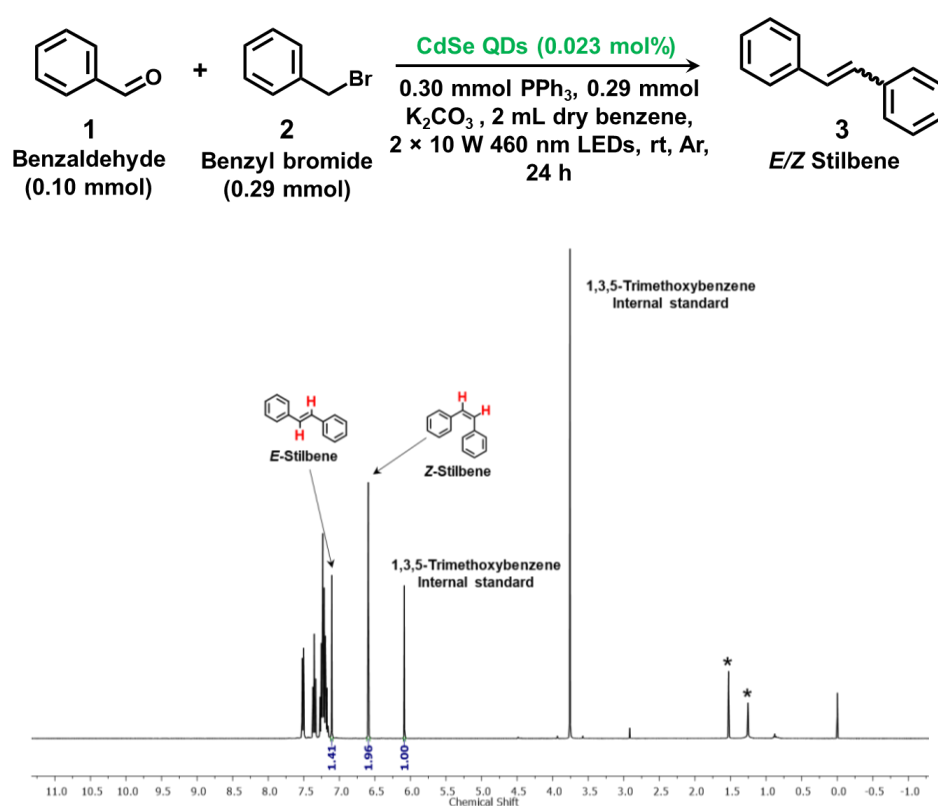


Figure 5.15. ¹H NMR (in CDCl₃) spectrum of a purified mixture of *E* & *Z* stilbene obtained from the QD photocatalyzed olefination reaction between benzyl bromide and benzyl alcohol. The yield of the overall reaction was calculated using 1,3,5-trimethoxybenzene as internal standard. Also, the ratio of *E* and *Z* product was calculated from the relative ratio of the 2H peaks of both stilbenes. Solvent impurity peaks (e.g. water, hexane) are marked with asterisk.

5.7.2. Calculation of the ratio of E and Z products:

The ratio of *Z* and *E* products was calculated from the integrated values of the NMR peaks.

The % of *E* stilbene in the total product formation = $1.41 / (1.96 + 1.41) \times 100 = 42\%$

The % of Z stilbene in the total product formation = $1.96 / (1.96 + 1.41) \times 100 = 58\%$

Hence the ratio of E and Z stilbene would be = 42:58

To cross check the value, the E and Z ratio was also calculated using gas chromatography as shown below.

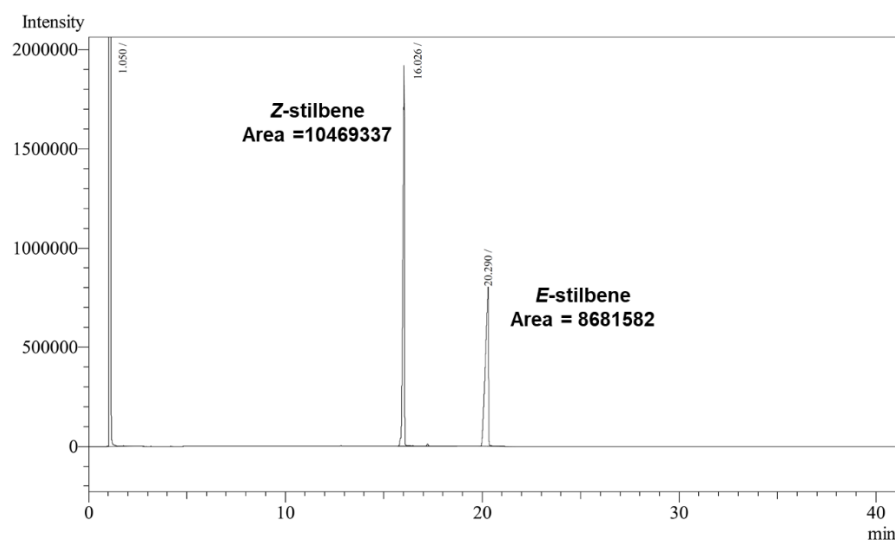


Figure 5.16. Gas chromatography characterization for the estimation of E:Z ratio. The peaks at 16.02 and 20.29 min corresponds to Z and E stilbene, respectively. The ratio between E and Z stilbene product was calculated to be 46:54, from the integrated values of the respective peaks. The value is closely matching with the calculated ratio from ^1H NMR.

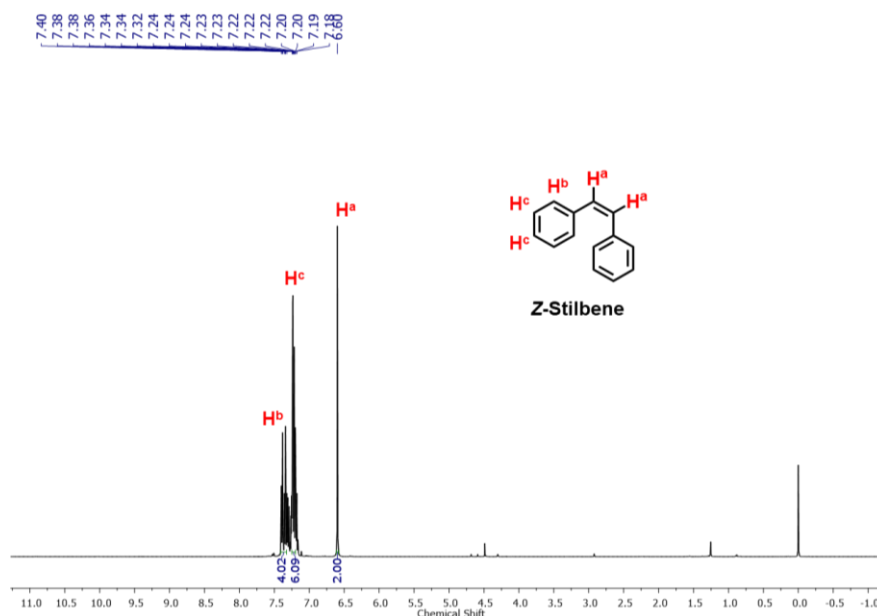


Figure 5.17. ^1H NMR (in CDCl_3) spectrum of Z-stilbene separated after the QD photocatalyzed olefination reaction. The distinguishable proton peaks are labelled accordingly.

(Z)-1,2-diphenylethene: ^1H NMR (400MHz, CDCl_3): δ 6.60 (2H, s), 7.18-7.26 (6H, m), 7.33-7.41 (4H, m).

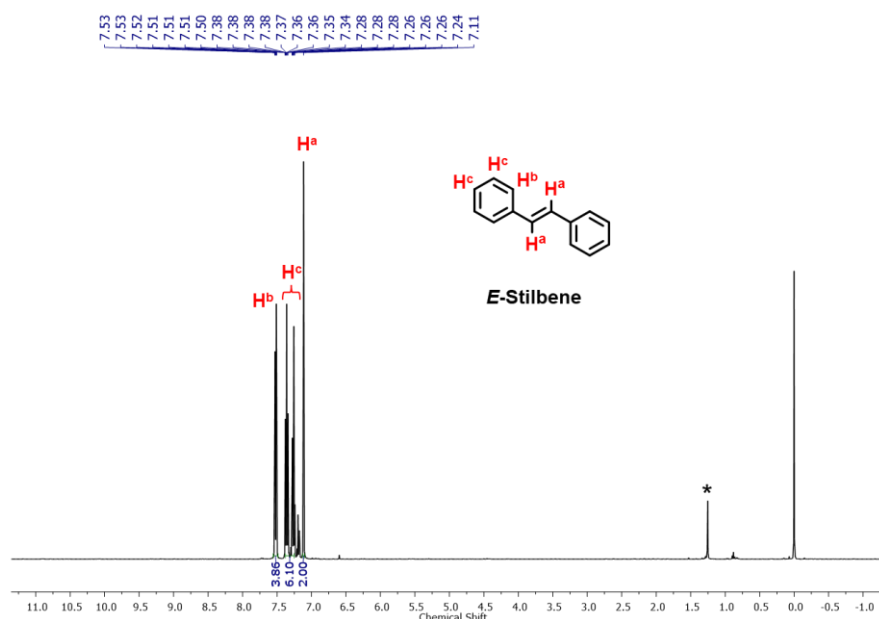


Figure 5.18. ^1H NMR (in CDCl_3) spectrum of *E*-stilbene separated after the QD photocatalyzed olefination. The distinguishable proton peaks are labelled accordingly. Solvent impurity peak (hexane) is marked with asterisk.

(*E*)-1,2-diphenylethene: ^1H NMR (400MHz, CDCl_3): δ 7.11 (2H, s), 7.25-7.39 (6H, m), 7.50-7.53 (4H, m)

5.7.3. Monitoring the surface of the QDs

As per the photophysical experiments, there is an enhancement in the QD PL upon addition of PPh_3 . To relate the actual picture of the phenomena on the QD surface, we performed a set of IR experiments on QDs before and after the treatment of PPh_3 . To treat the QDs with PPh_3 , a QD solution (46 μL of 0.5 mM stock solution) was stirred with PPh_3 (0.9 mmol) for two hours in 2 mL benzene followed by purification of the QDs via precipitation. This helped in the removal of the unbound- PPh_3 . The precipitated QD pellet was used for IR experiment. The signature aromatic C=H stretching of PPh_3 was found between 2997-3110 cm^{-1} in the PPh_3 treated QD sample. (**Figure 5.7d**).

Using the similar process, the purified QD pellet was further redispersed in CDCl_3 to carry out ^1H and ^{31}P NMR experiments (**Figure 5.19, 5.20**).

PPh_3 is well-known to bind weakly on the surface selenium sites of CdSe QDs, leading to only a slight broadening of the ^1H NMR signals.⁶⁰ In our case as well, we observed a slight broadening of the ^1H NMR signals (7.0 – 7.4 ppm) of PPh_3 upon binding on the CdSe QD surface (**Figure 5.19a, b**). As PPh_3 predominantly binds onto the surface Se sites, majority of the oleate ligands (OA) still stay bound on the surface.⁶⁰ This is evident from the broad ^1H NMR signal of the vinylic protons of OA at 5.3 ppm (**Figure 5.19c**).

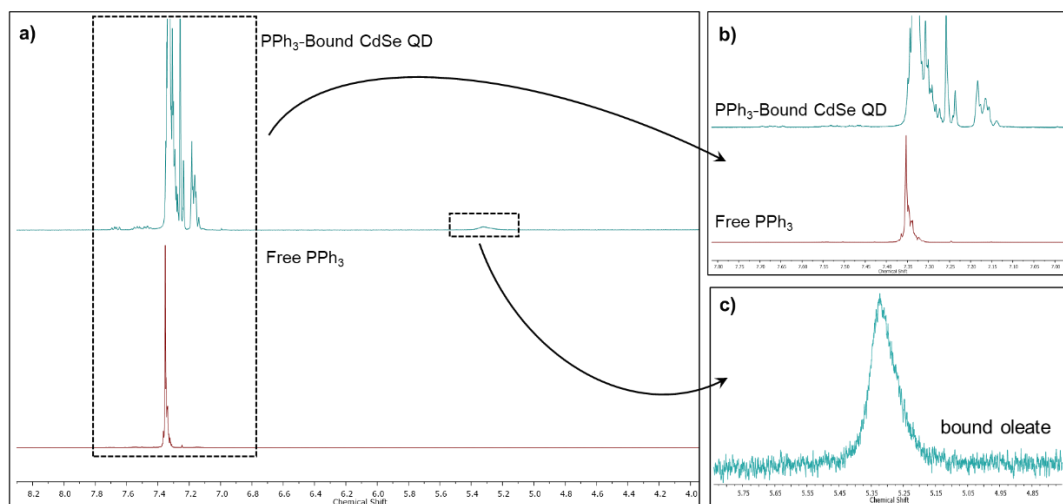


Figure 5.19. a) ^1H NMR spectra (in CDCl_3) of the PPh_3 treated CdSe QDs (purified) and free PPh_3 molecule. b) The dash-framed area is magnified to show the slight broadening of the signature peak of PPh_3 ~ 7.3 ppm, indicating the functionalization of PPh_3 on the surface of QDs. c) The dash-framed area of ~ 5.3 ppm of CdSe- PPh_3 sample is magnified showing the broad signature peak of the vinylic protons of surface bound oleate ligands.

The ^{31}P NMR signals for free PPh_3 molecule as well as for PPh_3 treated QDs are shown in **Figure 5.20**. In both the cases the characteristic peak is observed at ~ -5.5 ppm. As per the prior reports, negligible shift is seen between the ^{31}P NMR signals for bound and free PPh_3 .⁶⁰ The most probable reason for this could be the weak binding of PPh_3 on the surface selenium sites of CdSe QDs.⁶⁰

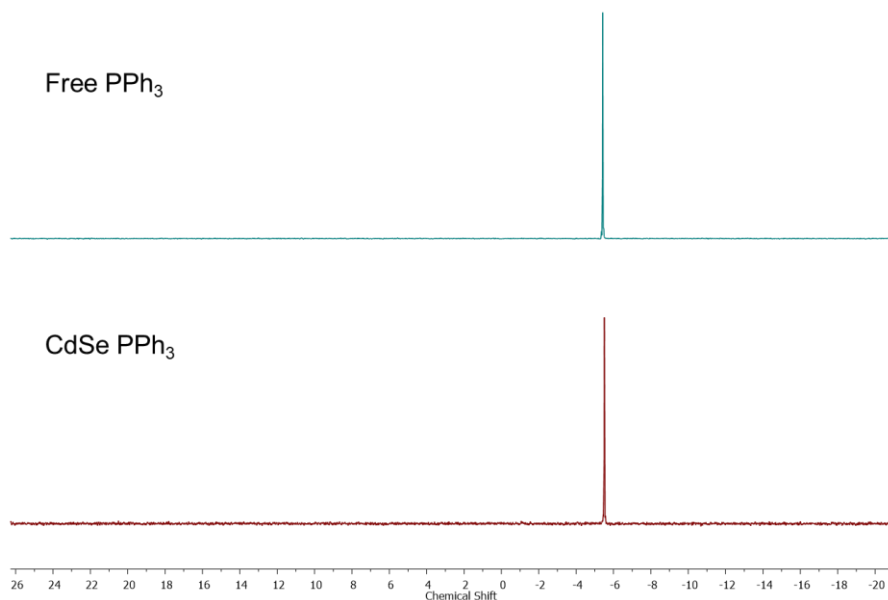


Figure 5.20. ^{31}P NMR (CDCl_3) spectra of free PPh_3 molecule and the PPh_3 treated CdSe QDs (purified). The retention of the signature peak ~ -5.5 ppm indicates the functionalization of PPh_3 on the surface of QDs.

In the case of an incoming L-type ligand displacing the surface bound Z-type oleate ligands, the free oleate species (i.e., Cd-oleates in case of CdSe QDs) shows a sharp NMR signal (at ~ 5.3 ppm) along with the broad signal of bound oleate ligands. This signature of Z-type ligand exchange signifies the successful ligand exchange on the QD surface.⁷⁰ But, as discussed previously, PPh_3 is predominantly known to bind weakly to the surface selenium sites on the CdSe QDs thereby passivating the trap states resulting in the enhancement in the PL QY.⁶⁰ In our case too, we observed the similar binding of PPh_3 on the CdSe surface followed by a PL enhancement. Also, the displacement of a few oleate ligands occur from the QD surface giving a sharp NMR signal at ~ 5.3 ppm corresponding to vinylic protons of the free oleate species. Alongside the sharp peak, a broad peak corresponding to the bound oleates was also observed (**Figure 5.21**). This observation confirms that, during the passivation of selenium sites with PPh_3 , some Cd-oleate gets displaced from the surface, resulting in the formation of the free Cd-oleates in the solution. This once again proves the successful binding of the PPh_3 on the surface of CdSe QDs.

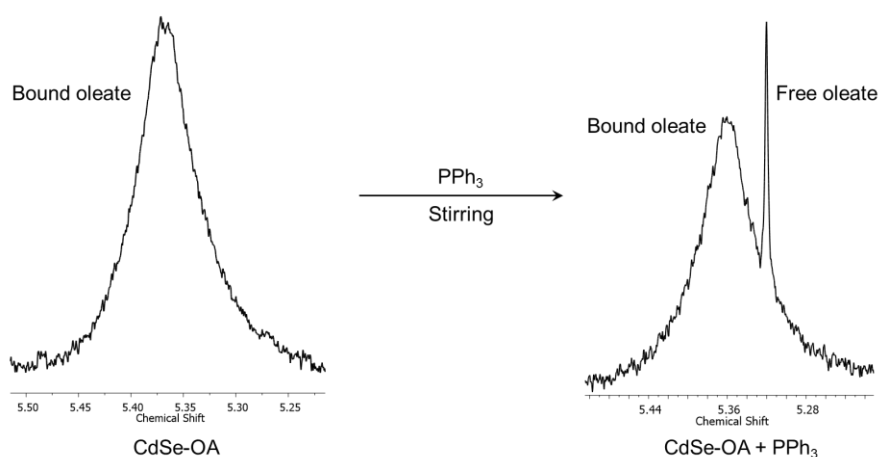
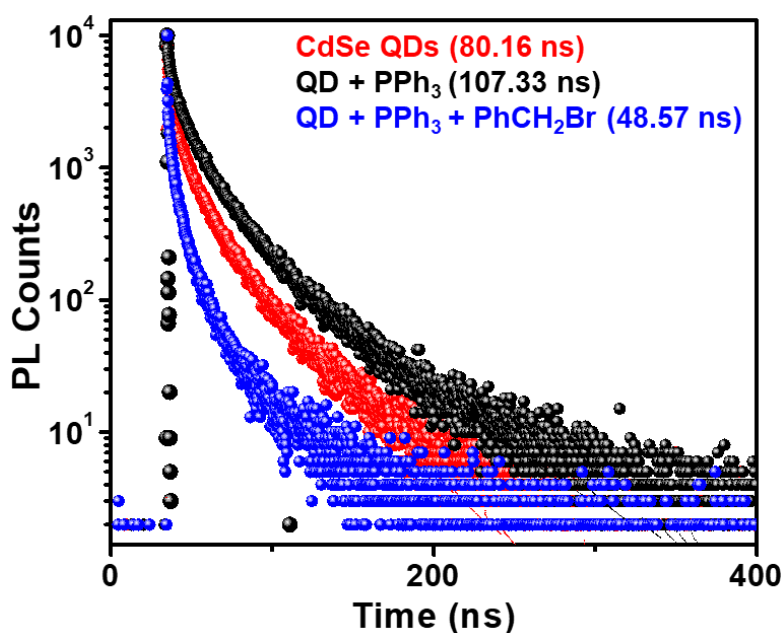


Figure 5.21. Vinyl region of the ^1H NMR spectra of the oleate capped CdSe QDs before and after the place exchange reaction with PPh_3 (without purification). During the place exchange, the displacement of oleate ligands occur from the QD surface giving a sharp NMR signal at ~ 5.3 ppm corresponding to the vinylic protons of the free oleate species. Alongside the sharp peak, a broad peak corresponding to the bound oleates was also observed.

5.7.4. Time-resolved photoluminescence measurements

5.7.4.1. Change in PL lifetime of QDs in presence of PPh₃ and PPh₃ + PhCH₂Br



Sample	τ_1 (ns)	a_1	τ_2 (ns)	a_2	τ_3 (ns)	a_3	τ_{avg} (ns)	χ^2
CdSe QD	3.30	0.71	39.91	0.24	153.75	0.05	80.16	1.18
QD + PPh ₃	7.16	0.55	64.36	0.39	219.32	0.06	107.33	1.22
QD + PPh ₃ + PhCH ₂ Br	0.86	0.93	20.20	0.06	112.93	0.01	48.57	1.01

Figure 5.22. Time-resolved PL (TRPL) lifetime studies show an increase in the lifetime of QDs in the presence of PPh₃ (enhancement from red to black trace), followed by a subsequent quenching of upon addition of benzyl bromide (blue trace). PL decay analysis of CdSe QDs is shown in table, before and after the addition of PPh₃ and PPh₃ + PhCH₂Br, collected in a time window of 400 ns.

5.7.5. Effect of excess PPh₃ on the PL of QDs:

In order to cross-check the possibility of free-PPh₃ to act as an outer sphere electron acceptor, the QD PL was monitored as a function of varying concentrations of PPh₃. An enhancement in the PL of QD was observed as the PPh₃ concentration was increased from 0.15 mmol to 0.30 mmol, which stayed constant upon further increasing the concentration of PPh₃ to 0.45 mmol and 0.60 mmol (**Figure 5.23**). This clearly confirms that the excess free-PPh₃ is not participating as an outer-sphere electron acceptor.

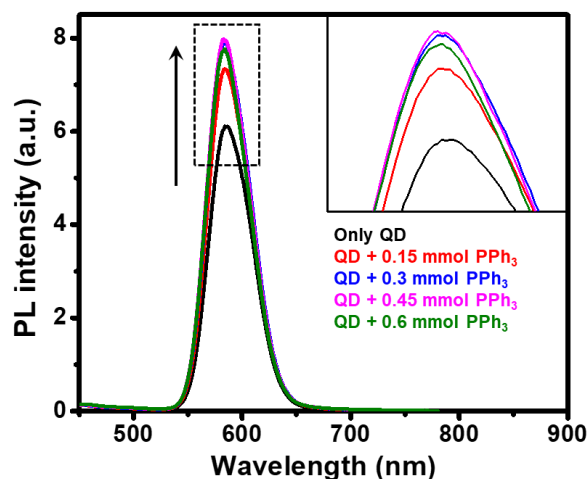


Figure 5.23. PL spectra of QD upon successive addition of PPh_3 . The gradual enhancement in the QD PL was observed till the addition of (0.30 mmol) PPh_3 , which stayed constant even after doubling the amount of PPh_3 (0.60 mmol).

5.7.6. Characterization of the intermediates and by-products

5.7.6.1. Stability study of the benzylic anion intermediate

To check the stability of the benzylic anion in the reaction (whether it can react by itself), we carried out a trapping experiment in the presence of methanol- D_4 , where a formation of toluene- D was anticipated if the anion is stable enough to react. But, no formation of toluene- D was observed (**Figure 5.24**). This experiment disproves the dissociation of $\text{PPh}_3\text{-PhCH}_2\text{Br}$ salt into a benzyl anion species upon the electron transfer from the photoexcited QDs. The experiment was carried out as follows:

In a stir bar-equipped 15 mL test tube, 46 μL of 0.5 mM CdSe QDs in toluene were added and the solvent was dried with gentle air flow. Next triphenylphosphine (80 mg, 0.30 mmol), benzaldehyde (11 μL , 0.1 mmol) and benzyl bromide (35 μL , 0.29 mmol), K_2CO_3 (41 mg, 0.29 mmol) and methanol- D_4 (13 μL , 0.32 mmol) were added, followed by the addition of 2 mL dry benzene under inert atmosphere. The mixture was then kept for purging with argon for ~ 30 min. Then the tube was sealed and was kept for irradiation using two 10 W LEDs (at a distance of 4 cm each on the both sides) under stirring for 24 h. After the reaction was over, the reaction mixture was centrifuged to remove any insoluble parts and 1 μL of the supernatant was directly injected into the Shimadzu GCMS-2010 instrument for analysis.

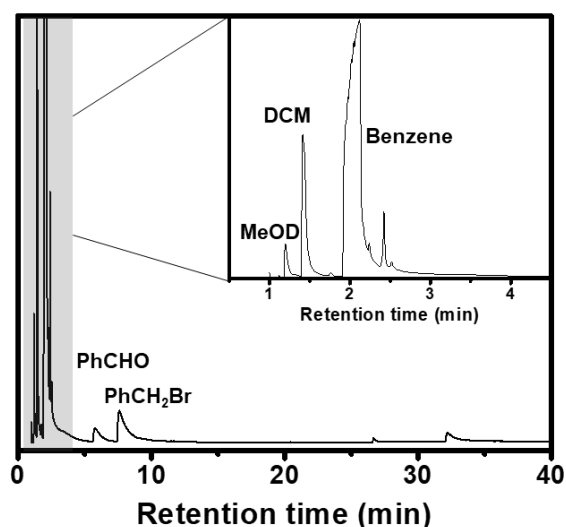


Figure 5.24. GCMS chromatogram of the photocatalytic olefination reaction with QDs in the presence of methanol-D₄.

5.7.6.2. Characterization of the benzyl radical intermediate

As per the proposed mechanism, a benzyl radical should form following the photoinduced charge transfer between QD and PPh₃-PhCH₂Br salt. This benzyl radical then reacts in the further steps to yield the final product. To prove the involvement of benzyl radical in the reaction mechanism, radical trapping experiments were performed using (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO).

A reaction mixture containing 16 mg TEMPO (100 mM in 1mL), 6 μ L benzyl bromide (50 mM), 13 mg PPh₃ (50 mM) and 25 μ L of 0.50 mM CdSe QDs (12.5 μ M) were prepared in 1 mL dry benzene, and was purged with argon for 15 min. The solution was then irradiated with 2 x 10 W blue LEDs for 30 min (**Figure 5.25, a**). After the irradiation, a 1 μ L aliquot of the resulting reaction mixture was directly injected into the Shimadzu GCMS-2010 instrument for analysis. A peak corresponding to the TEMPO-benzylic radical adduct was found at a retention time $\sim$ 20 min (**Figure 5.25, b**). The formation of TEMPO-benzylic radical adduct was confirmed from the corresponding mass spectra, where the molecular ion peak for the adduct was found at m/z 247.1. This experiment conclusively proves that the QD photocatalyzed olefination reaction goes through the formation of benzyl radicals, which again validates our proposed mechanistic pathway. The control experiment was carried out under similar condition in absence of QDs which failed to show any signature of the adduct (blue line in **Figures 5.25 b,c**).

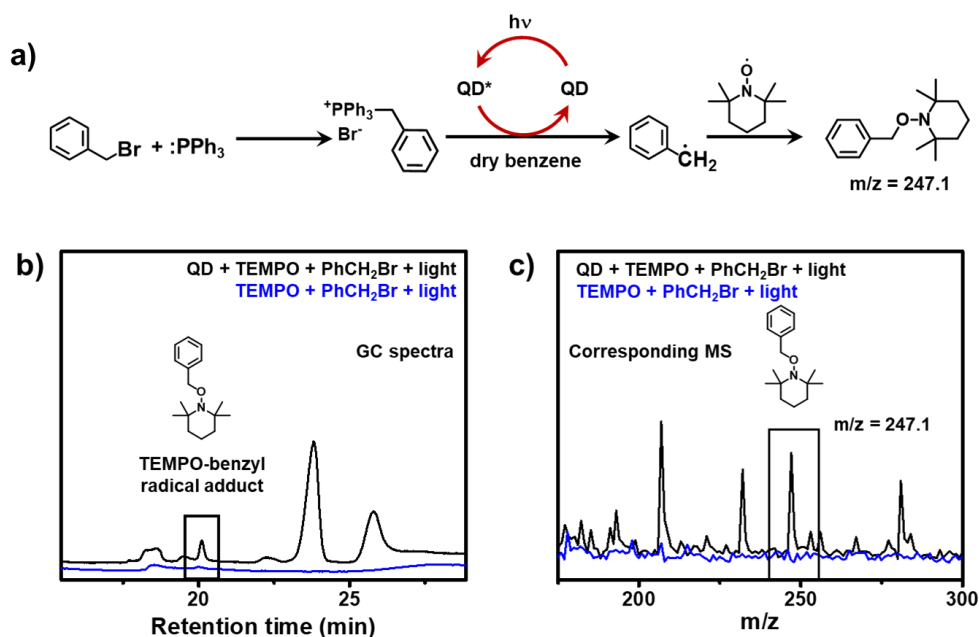


Figure 5.25. a) A schematic representation of the radical trapping pathway using TEMPO. The b) gas chromatography (GC) and, c) mass spectroscopy (MS) data of the trapping experiments in the presence (black) and absence (blue) of QDs.

5.7.6.3. Quantum dot photocatalyzed olefination reaction in presence of TEMPO

In a stir bar-equipped 15 mL test tube, 46 μL of 0.5 mM CdSe QDs in toluene were added and the solvent was dried with gentle air flow. Next TEMPO (78 mg, 0.50 mmol), triphenylphosphine (80 mg, 0.30 mmol), benzaldehyde (11 μL , 0.1 mmol), benzyl bromide (35 μL , 0.29 mmol) and K_2CO_3 (41 mg, 0.29 mmol) were added, followed by addition of 2 mL dry benzene under inert atmosphere. The mixture was then kept for purging with argon for ~ 30 min. Then the tube was sealed, and irradiated with two 10 W LEDs under stirring for 24 h. After the reaction was over, the reaction mixture was centrifuged and 1 μL of the supernatant was directly injected into the Shimadzu GCMS-2010 instrument for analysis (**Figure 5.26**). A prominent peak in the chromatogram was observed with a corresponding mass of 247.2 indicating the formation of TEMPO-benzyl bromide adduct.

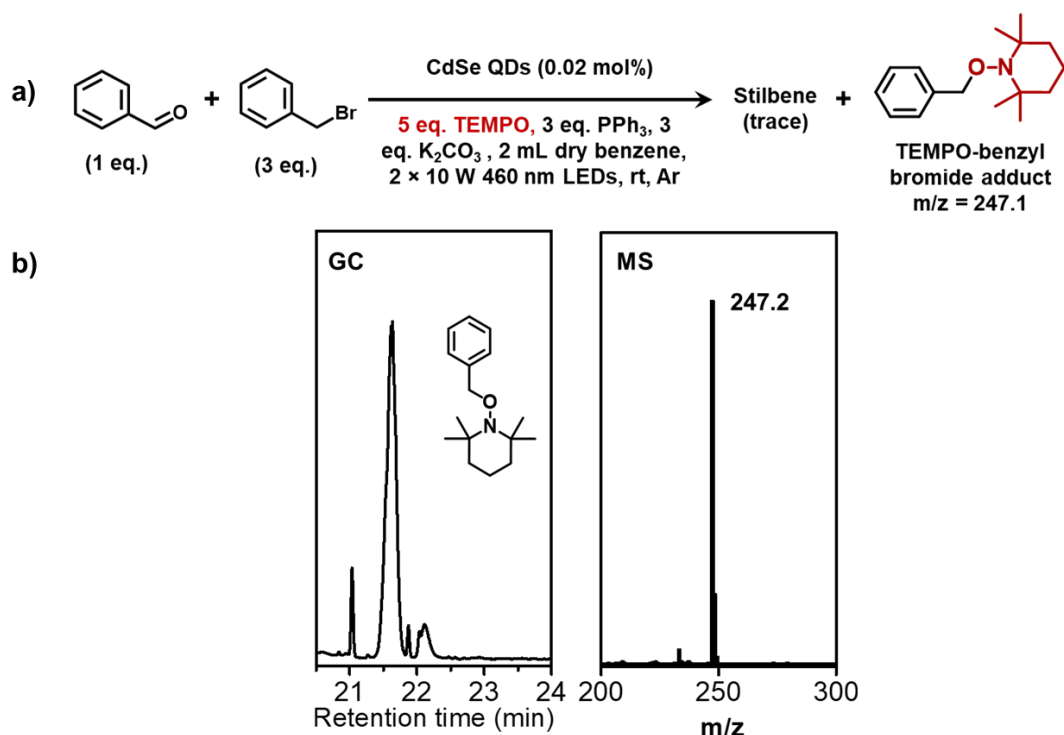


Figure 5.26. QD photocatalysed olefination in the presence of TEMPO. a) Reaction scheme. b) GC-MS characterization shows a prominent peak at ~21.6 min with a corresponding mass of 247.2, which is a characteristic feature for the trapped benzyl radical-TEMPO adduct.

5.7.6.4. Characterization of triphenylphosphine oxide by-product

To characterize the phosphorus containing by-products in the reaction, ^{31}P NMR experiment was carried out with the crude reaction mixture after the QD photocatalyzed olefination reaction. ^{31}P NMR confirms the presence of excess PPh_3 ($\delta \sim -5.35$ ppm), unreacted quaternary phosphonium salt ($\delta \sim 23.2$ ppm) and formed triphenyl phosphine oxide ($\delta \sim 28.94$ ppm) (**Figure 5.27**). This proves the formation of triphenyl phosphine oxide as a by-product.

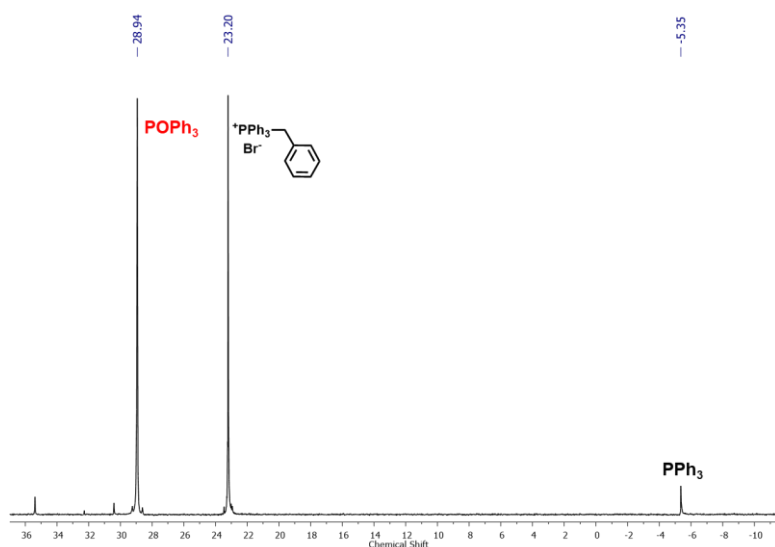


Figure 5.27. ^{31}P NMR of the crude reaction mixture after irradiation.

5.7.7. Role of the base in the reaction

5.7.7.1. Identification of the alkoxyphosphonium cation intermediate

We were successful in identifying the alkoxyphosphonium cation intermediate (**v**) with high resolution mass spectroscopy (HRMS). For this, the QD photocatalysed olefination was carried out in the absence of the base K_2CO_3 (**Figure 5.28**). The HRMS analysis of the reaction mixture, after 24 h of irradiation, revealed the formation of the alkoxyphosphonium cation **v**. No signature of olefine product was observed under this condition. Addition of K_2CO_3 to this pre-irradiated reaction mixture gave the desired olefine product in ~90% yield, accompanied with a substantial decrease in the HRMS peak for the alkoxyphosphonium cation **v**. In another set of experiments, the olefination reaction mixture was irradiated for 24 h in the absence of QD photocatalyst and K_2CO_3 . Here, no signature of alkoxyphosphonium cation was observed. Addition of K_2CO_3 to this pre-irradiated mixture also failed to give any desired olefination product. All these observations clearly confirm that the olefination reaction is photocatalysed by QD, and proceeds via the alkoxyphosphonium cation intermediate **v**.

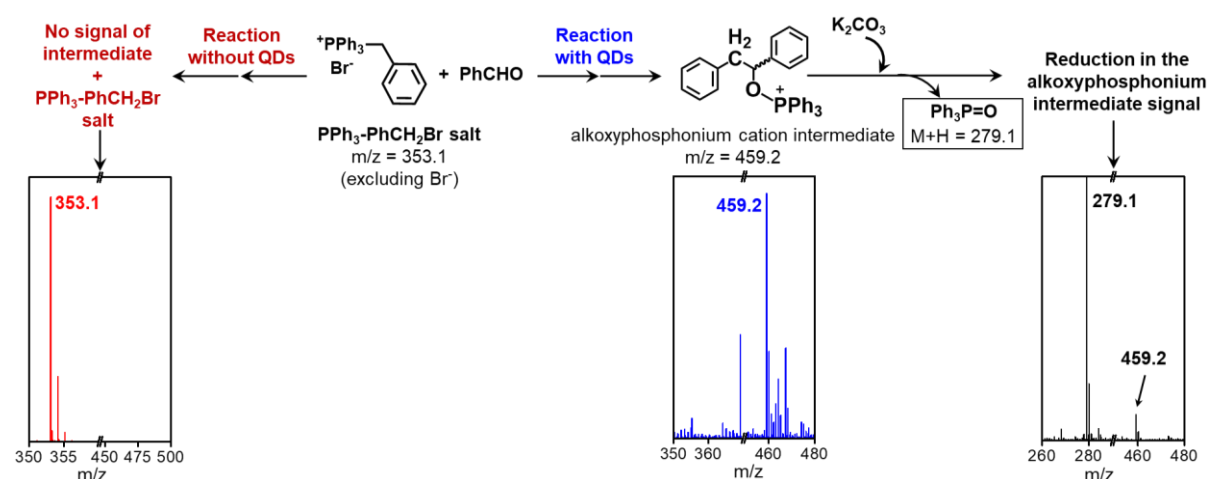


Figure 5.28. Identification of the alkoxyphosphonium cation intermediate **v**. Reaction scheme and HRMS characterization for the identification of alkoxyphosphonium cation intermediate.

To check the role of the base, we carried out a reaction under irradiation for 24 h in the absence of base. As expected, no products were formed. The crude NMR of the reaction mixture is given below (no characteristic Z/E stilbene peaks was found around $\delta = 6.55$ and 7.1 were present) (**Figure 5.29a**). Rather, the signal at $\delta \sim 5.37$ ppm (marked as H_a) can be identified as the signal for the proton adjacent to the O- PPh_3 in the alkoxyphosphonium cation intermediate (**Figure 5.29a**). The HRMS analysis of the corresponding reaction mixture further confirms the formation of the alkoxyphosphonium cation intermediate (**Figure 5.29b**). Next, we added K_2CO_3 to this pre-irradiated reaction mixture, and stirred for 2 h under inert condition in the

absence of irradiation. Interestingly, at the end of 2 h, a product yield of ~90% was obtained (Figure 5.30).

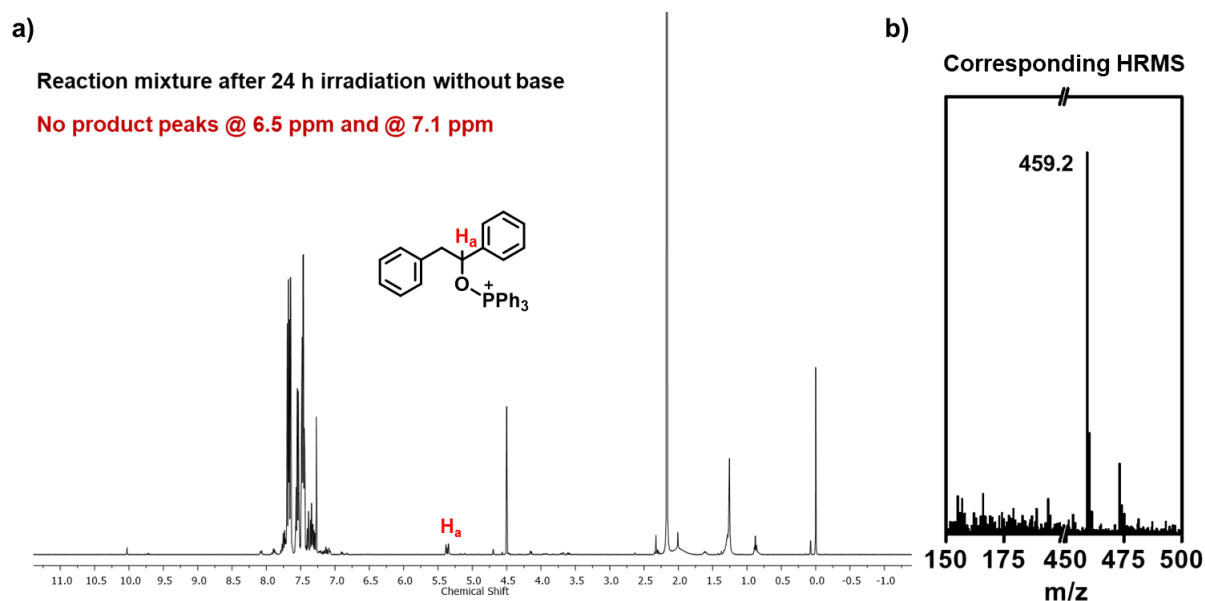


Figure 5.29. a) ^1H NMR (in CDCl_3) spectrum of the crude reaction mixture after 24 h irradiation in the absence of base (K_2CO_3). No signal for the *E/Z* stilbene was observed. The identifiable proton signal of the alkoxyphosphonium cation intermediate is assigned as H_a . b) The corresponding HRMS of the reaction mixture showing the formation of the alkoxyphosphonium cation intermediate.

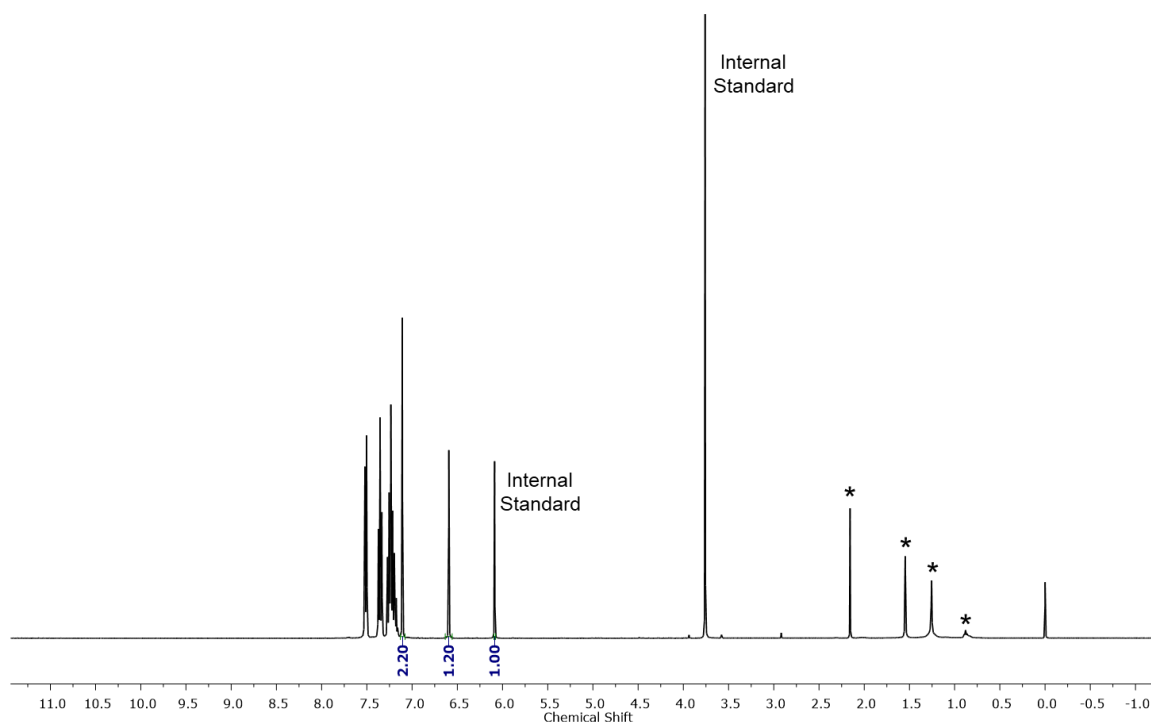


Figure 5.30. ^1H NMR (in CDCl_3) spectrum of a purified mixture of stilbene (*E* and *Z*) (and 1,3,5-trimethoxybenzene as added internal standard) after the addition of base (K_2CO_3) in a pre-irradiated (in absence of base, 24 h) reaction mixture. Solvent impurity peaks (e.g. acetone, water, hexane, heptane) are marked with asterisk.

5.7.8. Characterization of the products formed from different substrates

(*E/Z*) 1-nitro-2-styrylbenzene

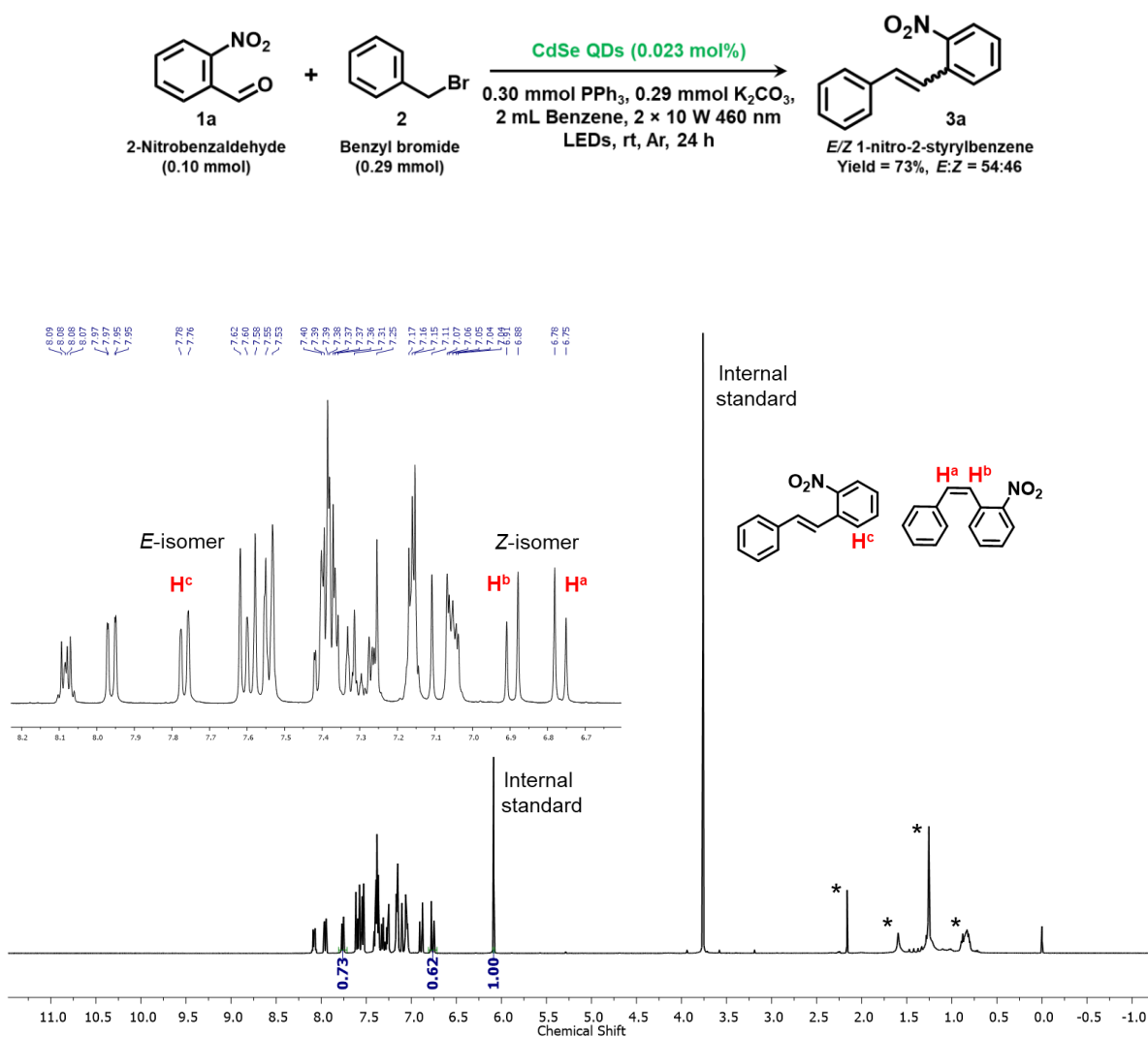


Figure 5.31. ¹H NMR (in CDCl₃) spectrum of purified mixture of *E* and *Z* 1-nitro-2-styrylbenzene products in presence of 1,3,5-trimethoxybenzene as internal standard. The distinguishable ¹H NMR shifts are labelled accordingly. The expansion of the peaks associated to the products are shown in the inset. Solvent impurity peaks (e.g. acetone, water, hexane, heptane) are marked with asterisk.

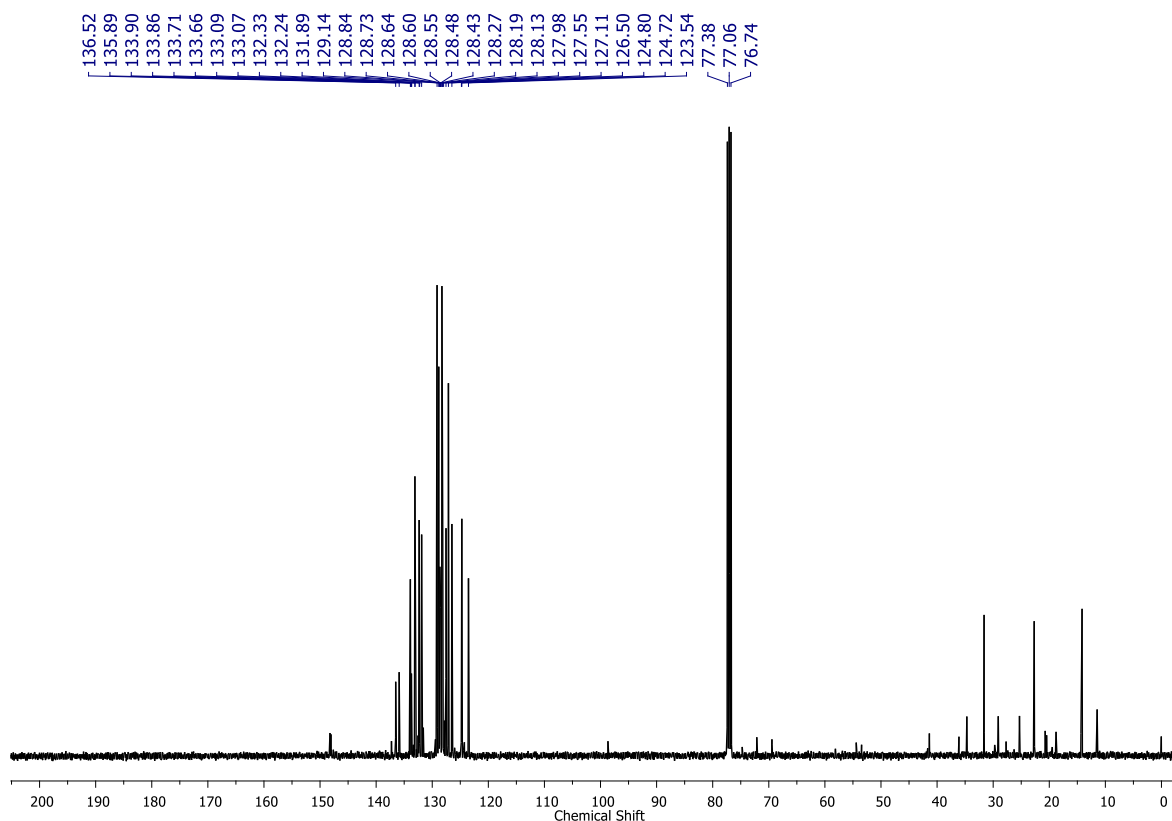


Figure 5.32. ^{13}C NMR (in CDCl_3) spectrum of purified mixture of *E* and *Z*-1-nitro-2-styrylbenzene product.

(*E/Z*)-1-nitro-2-styrylbenzene: Yield: 73%, *E:Z* = 54:46.

^1H NMR (400MHz, CDCl_3): δ 6.77 (d, J = 12.4 Hz, *Z* olefinic protons), 6.90 (d, J = 12.4 Hz, *Z* olefinic protons), 7.10 (m, J = 16.4 Hz, *E* olefinic protons mixed with aromatic protons of *Z* isomer), 7.13 (d, J = 16.4 Hz, *E* olefinic protons mixed with aromatic protons of *Z* isomer), 7.53 – 7.62 (m, aromatic protons of both isomers), 7.77 (m, aromatic protons of *E* isomer), 7.96 (m, aromatic protons of *E* isomer), 8.08 (m, aromatic protons of both isomers).

^{13}C NMR (100 MHz, CDCl_3): 123.5, 124.7, 124.8, 126.5, 127.1, 127.5, 127.9, 128.13, 128.19, 128.2, 128.43, 128.48, 128.5, 128.60, 128.64, 128.7, 128.8, 129.1, 131.8, 132.2, 132.3, 133.07, 133.09, 133.6, 133.7, 133.8, 133.9, 135.8, 136.5.

(*E/Z*) 1-bromo-3-styrylbenzene

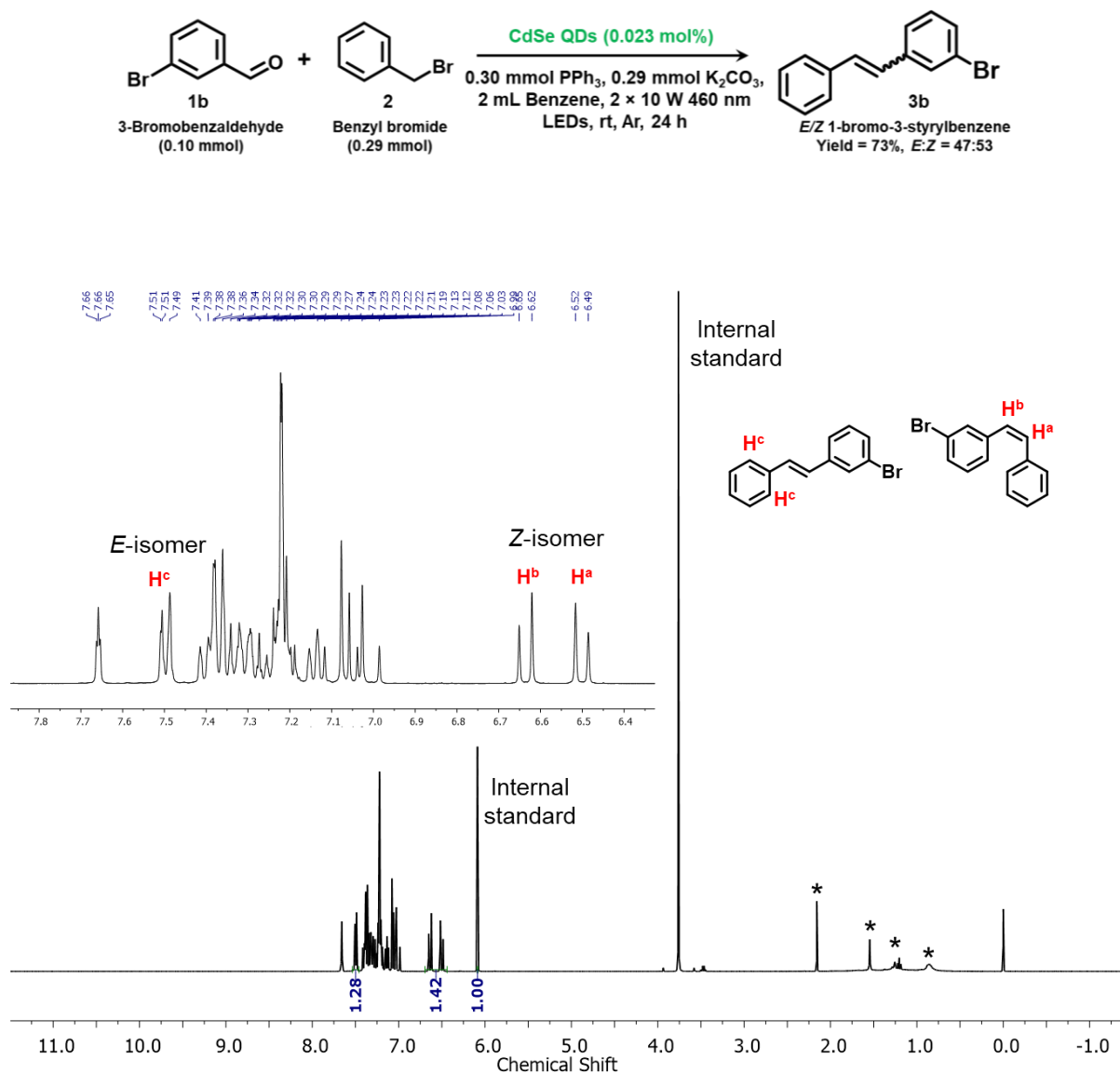


Figure 5.33. ¹H NMR (in CDCl₃) spectrum of purified mixture of *E* and *Z* 1-bromo-3-styrylbenzene products in presence of 1,3,5-trimethoxybenzene as internal standard. The distinguishable ¹H NMR shifts are labelled accordingly. The expansion of the peaks associated to the products are shown in the inset. Solvent impurity peaks (e.g. acetone, water, hexane, heptane) are marked with asterisk.

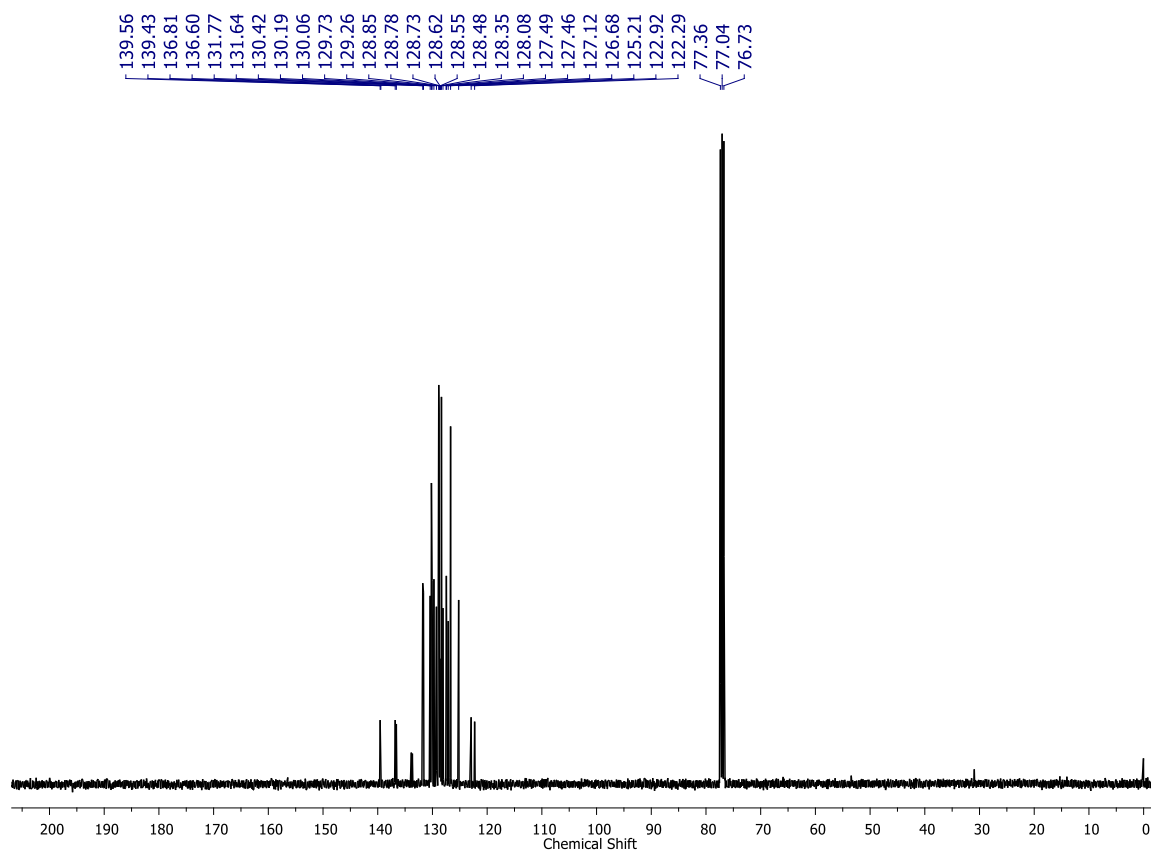


Figure 5.34. ^{13}C NMR (in CDCl_3) spectrum of purified mixture of *E* and *Z*-1-bromo-3-styrylbenzene product.

(*E/Z*)-1-bromo-3-styrylbenzene: Yield: 73%, *E/Z* = 47:53.

^1H NMR (400MHz, CDCl_3): δ 6.51 (d, J = 12.4 Hz, *Z* olefinic protons), 6.64 (d, J = 12.4 Hz, *Z* olefinic protons), 7.01 (d, J = 16.4 Hz, *E* olefinic protons), 7.10 (d, J = 16.4 Hz, *E* olefinic protons), 7.14 – 7.45 (m, aromatic protons of both isomers), 7.50 (m, aromatic protons of *E* isomer), 7.66 (m, aromatic protons of both isomers).

^{13}C NMR (100 MHz, CDCl_3): 122.2, 122.9, 125.2, 126.6, 127.1, 127.46, 127.49, 128.0, 128.3, 128.4, 128.5, 128.6, 128.73, 128.78, 128.8, 129.7, 130.0, 130.1, 130.4, 131.6, 131.7, 136.6, 136.8, 139.4, 139.5.

(*E/Z*)-2-styrylthiophene

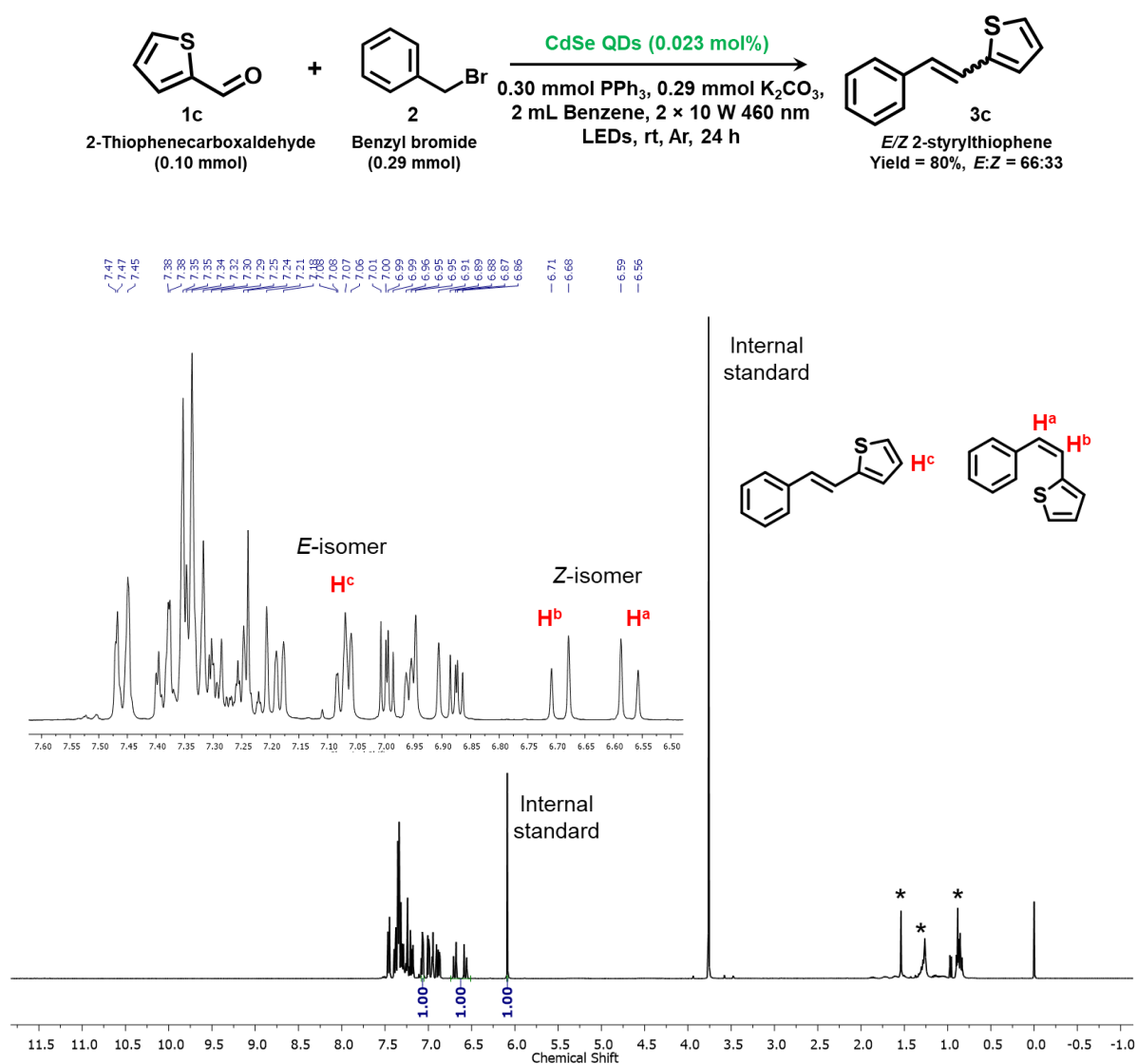


Figure 5.35. ¹H NMR (in CDCl₃) spectrum of purified mixture of *E* and *Z*-2-styrylthiophene products in presence of 1,3,5-trimethoxybenzene as internal standard. The distinguishable ¹H NMR shifts are labelled accordingly. The expansion of the peaks associated to the products are shown in the inset. Solvent impurity peaks (e.g. acetone, water, hexane, heptane) are marked with asterisk.

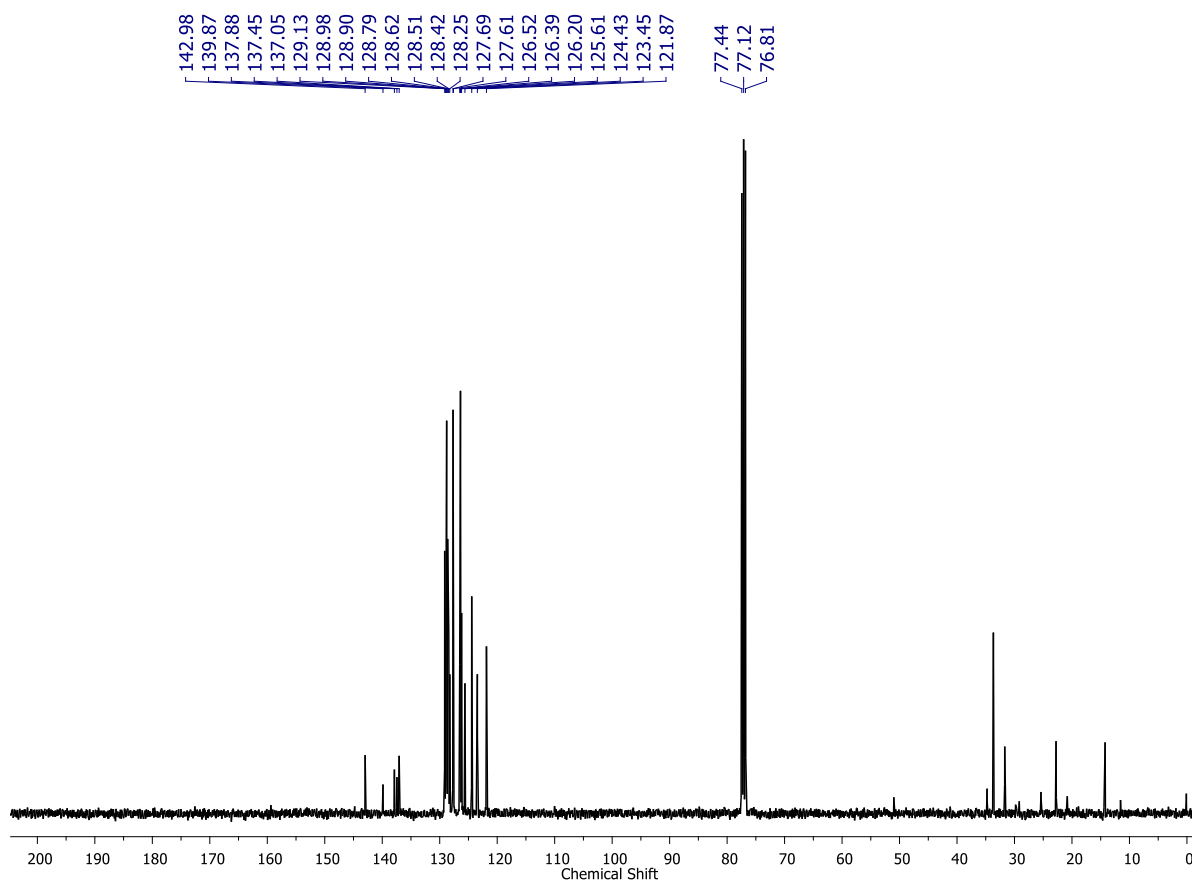


Figure 5.36. ^{13}C NMR (in CDCl_3) spectrum of purified mixture of *E* and *Z*-2-styrylthiophene product.

(*E/Z*)-2-styrylthiophene: Yield: 80%, *E*:*Z* = 66:33.

^1H NMR (400MHz, CDCl_3): δ 6.58 (d, $J = 12.4$ Hz, *Z* olefinic protons), 6.70 (d, $J = 12.4$ Hz, *Z* olefinic protons), 6.87 (m, aromatic protons of both isomers), 6.93 (d, $J = 16.4$ Hz, *E* olefinic protons), 7.00 (m, aromatic protons of both isomers), 7.07 (m, aromatic protons of *E* isomer), 7.18 – 7.47 (m, aromatic protons of both isomers).

^{13}C NMR (100 MHz, CDCl_3): 121.8, 123.4, 124.4, 125.6, 126.2, 126.3, 126.5, 127.61, 127.69, 128.2, 128.4, 128.5, 128.6, 128.7, 128.90, 128.98, 129.1, 137.0, 137.4, 137.8, 139.8, 142.9.

(E/Z)-2-styrylpyridine

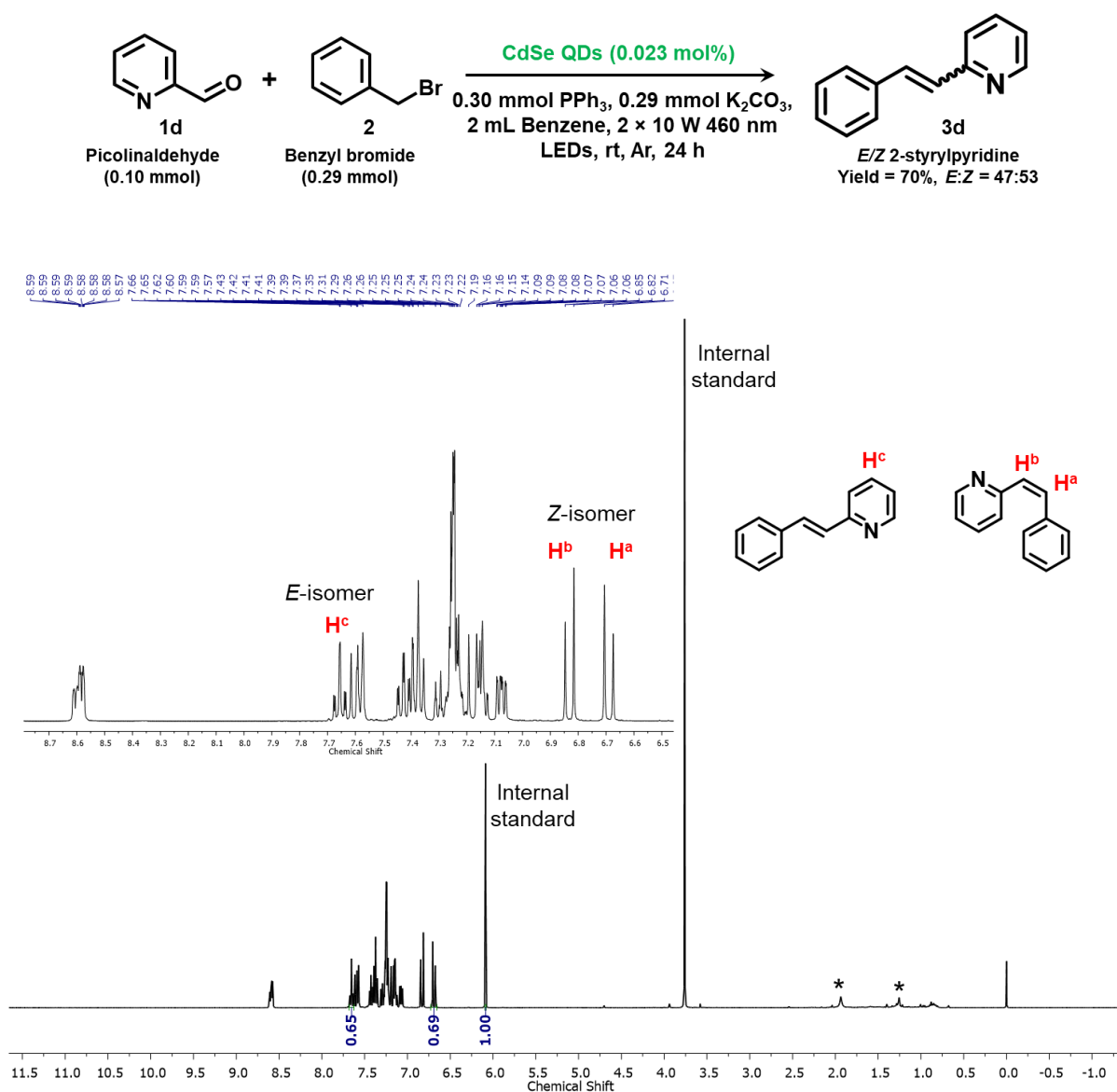


Figure 5.37. ¹H NMR (in CDCl₃) spectrum of purified mixture of *E* and *Z*-2-styrylpyridine products in presence of 1,3,5-trimethoxybenzene as internal standard. The distinguishable ¹H NMR shifts are labelled accordingly. The expansion of the peaks associated to the products are shown in the inset. Solvent impurity peaks (e.g. acetone, water, hexane, heptane) are marked with asterisk.

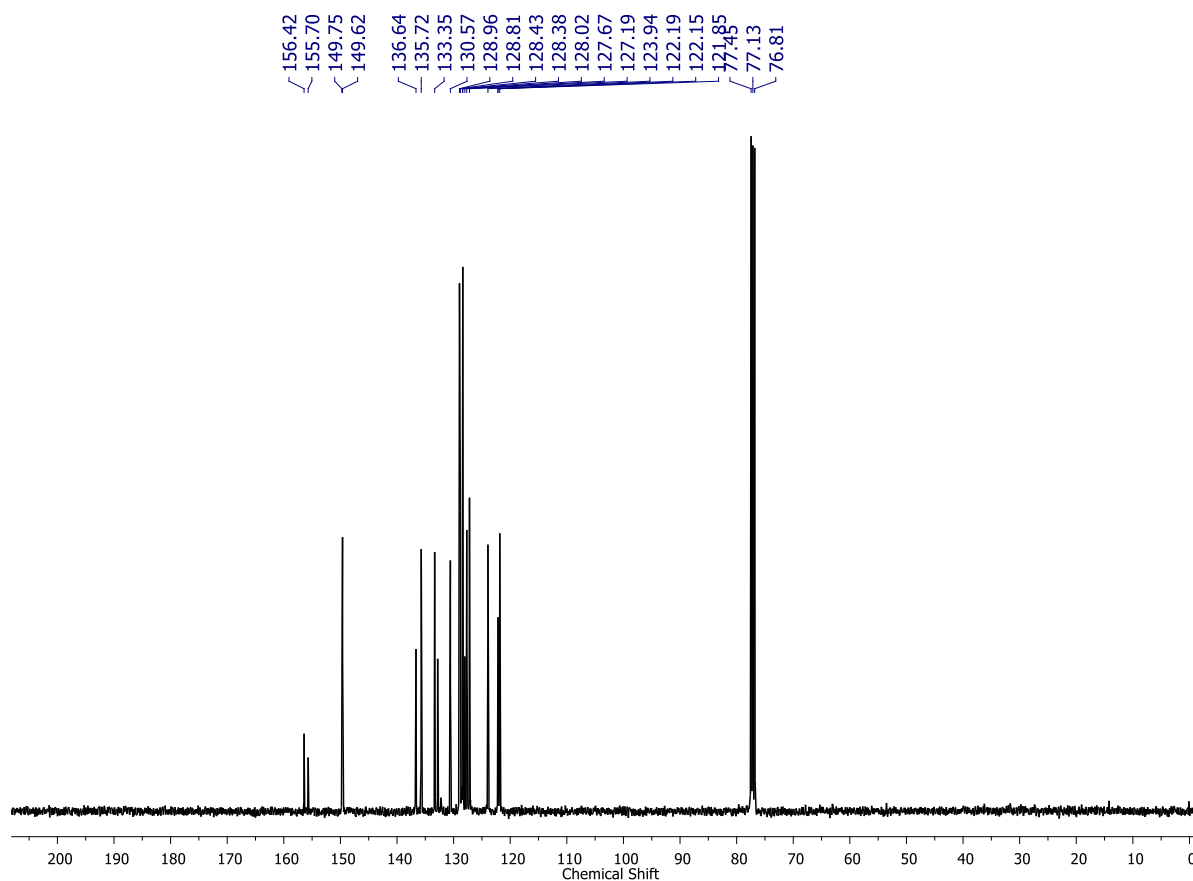


Figure 5.38. ^{13}C NMR (in CDCl_3) spectrum of purified mixture of *E* and *Z*-2-styrylpyridine product.

(*E/Z*)-2-styrylpyridine: Yield: 70%, *E:Z* = 47:53.

^1H NMR (400MHz, CDCl_3): δ 6.69 (d, $J = 12.4$ Hz, *Z* olefinic protons), 6.84 (d, $J = 12.4$ Hz, *Z* olefinic protons), 7.06 – 7.45 (m, aromatic protons of both isomers and signal of *E* olefinic protons merged in it), 7.59 (m, aromatic protons of *Z* isomers), 7.66 (m, aromatic protons of *E* isomers), 8.59 (m, aromatic protons of both isomers).

^{13}C NMR (100 MHz, CDCl_3): 121.8, 122.15, 122.19, 123.9, 127.1, 127.6, 128.0, 128.3, 128.4, 128.8, 128.9, 130.5, 133.3, 135.7, 136.6, 149.6, 149.7, 155.7, 156.4.

(*E/Z*)-1-methyl-4-styrylbenzene

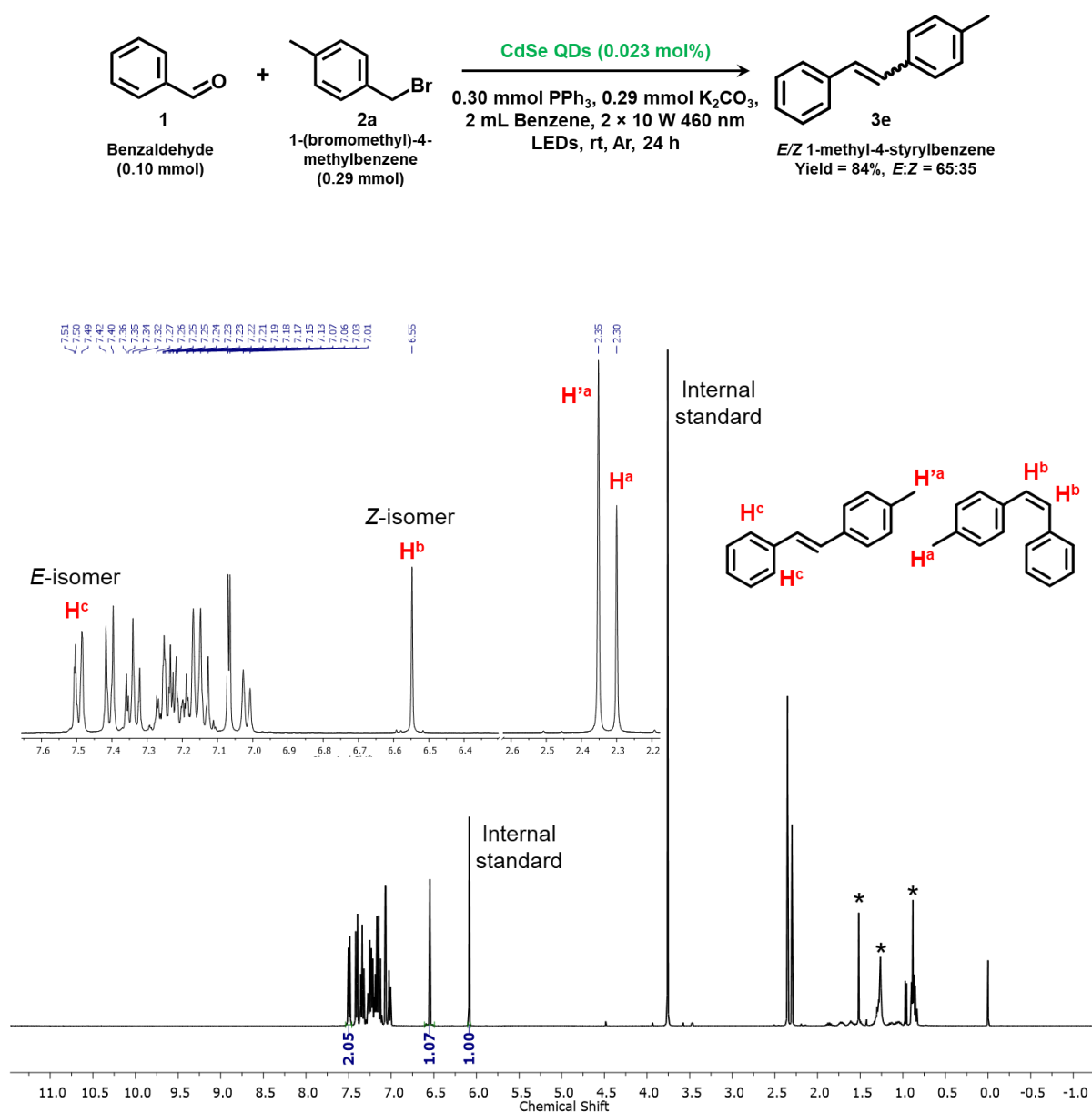


Figure 5.39. ¹H NMR (in CDCl₃) spectrum of purified mixture of *E* and *Z*-1-methyl-4-styrylbenzene products in presence of 1,3,5-trimethoxybenzene as internal standard. The distinguishable ¹H NMR peaks are labelled accordingly. The expansion of the peaks associated to the products are shown in the inset. Solvent impurity peaks (e.g. acetone, water, hexane, heptane) are marked with asterisk.

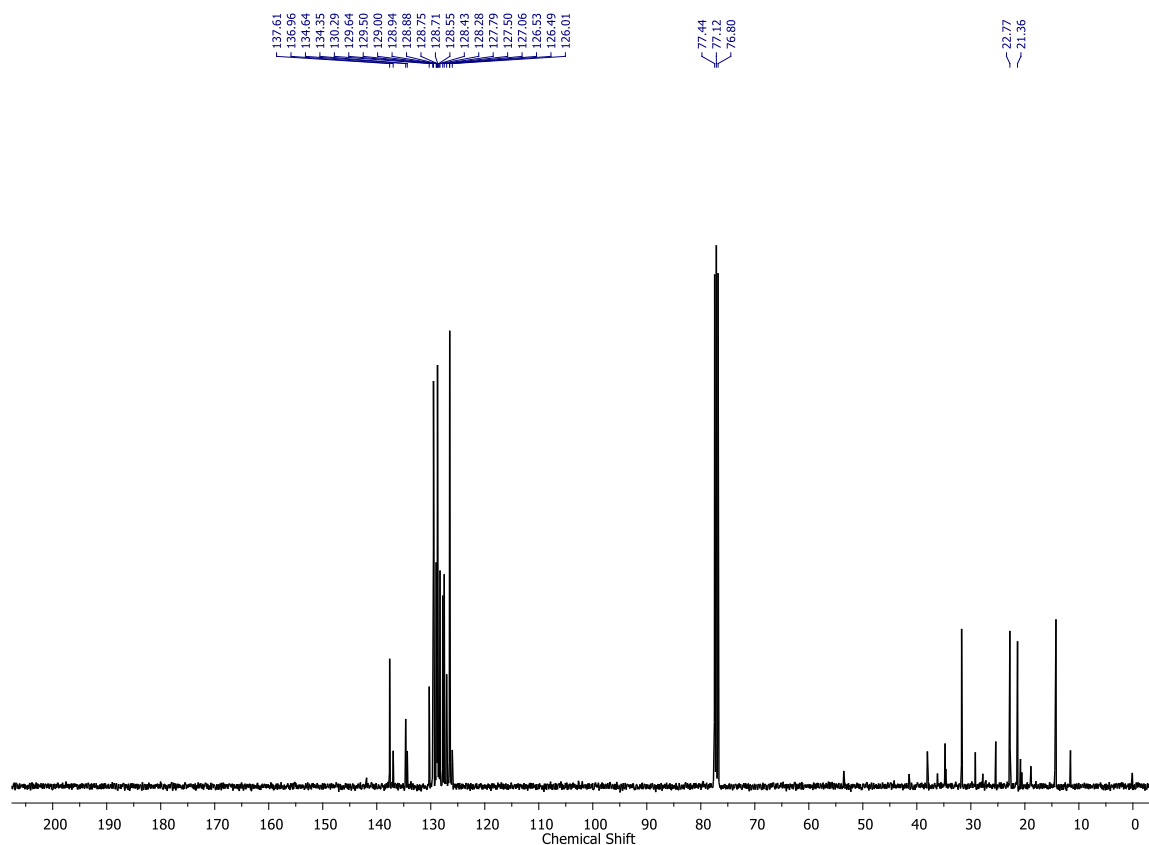


Figure 5.40. ^{13}C NMR (in CDCl_3) spectrum of purified mixture of *E* and *Z*-1-methyl-4-styrylbenzene product.

(*E/Z*)-1-methyl-4-styrylbenzene: Yield: 84%, *E*:*Z* = 65:35.

^1H NMR (400MHz, CDCl_3): δ 2.30 (s, methyl protons of *Z* isomer), 2.35 (s, methyl protons of *E* isomer) 6.55 (s, *Z* olefinic protons), 7.01 – 7.36 (m, aromatic protons of both isomers and signal of *E* olefinic protons merged in it), 7.50 (m, aromatic protons of *E* isomer).

^{13}C NMR (100 MHz, CDCl_3) δ 21.3, 22.7, 126.0, 126.4, 126.5, 127.0, 127.5, 127.7, 128.2, 128.4, 128.5, 128.71, 128.75, 128.8, 128.9, 129.0, 129.5, 129.6, 130.2, 134.3, 134.6, 136.9, 137.6.

(E/Z)-1-chloro-4-styrylbenzene

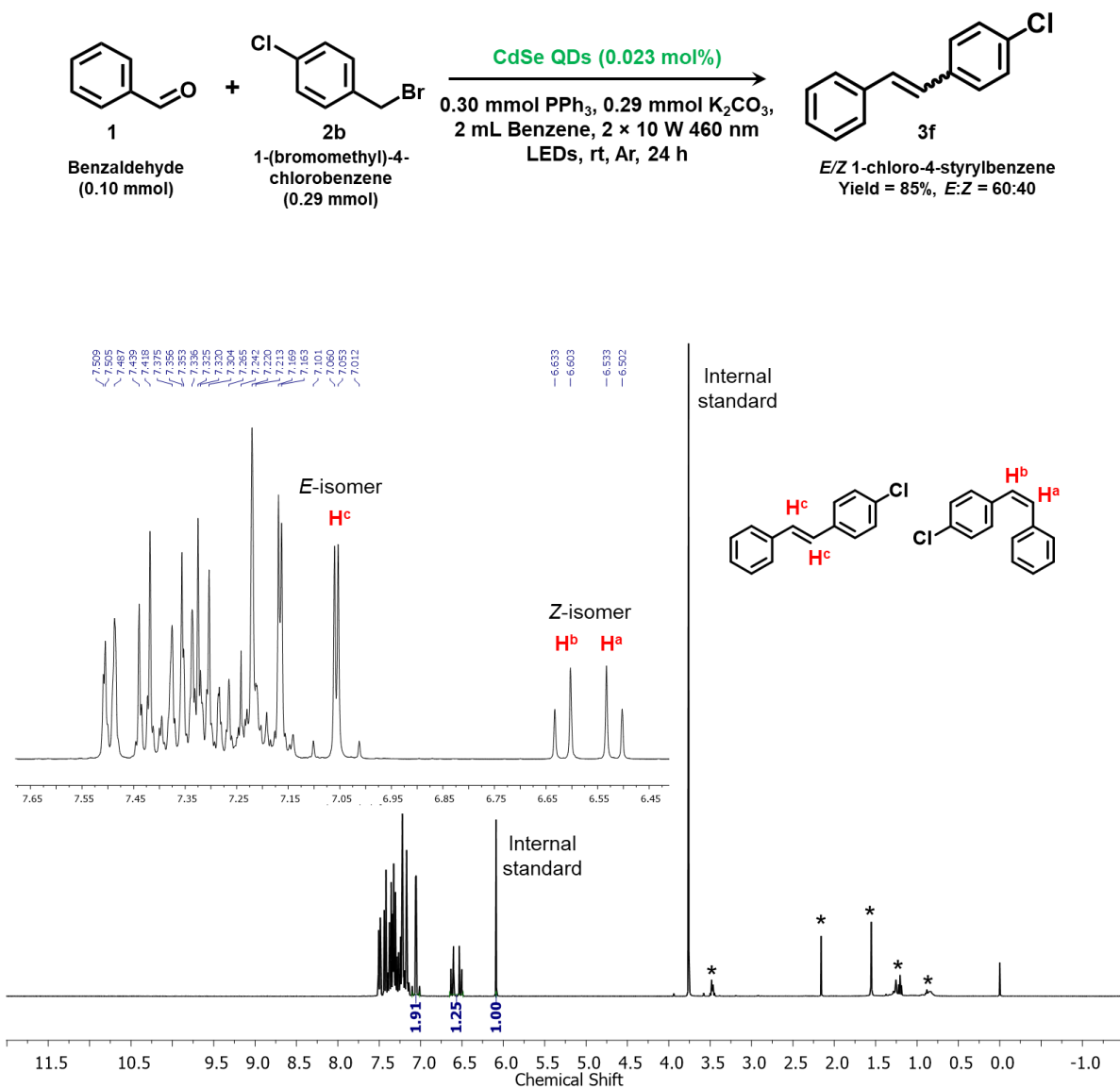


Figure 5.41. ¹H NMR (in CDCl₃) spectrum of the purified mixture of *E* and *Z*-1-chloro-4-styrylbenzene products in presence of 1,3,5-trimethoxybenzene as internal standard. The distinguishable ¹H NMR peaks are labelled accordingly. The expansion of the peaks associated to the products are shown in the inset. Solvent impurity peaks (e.g. acetone, water, hexane, heptane) are marked with asterisk.

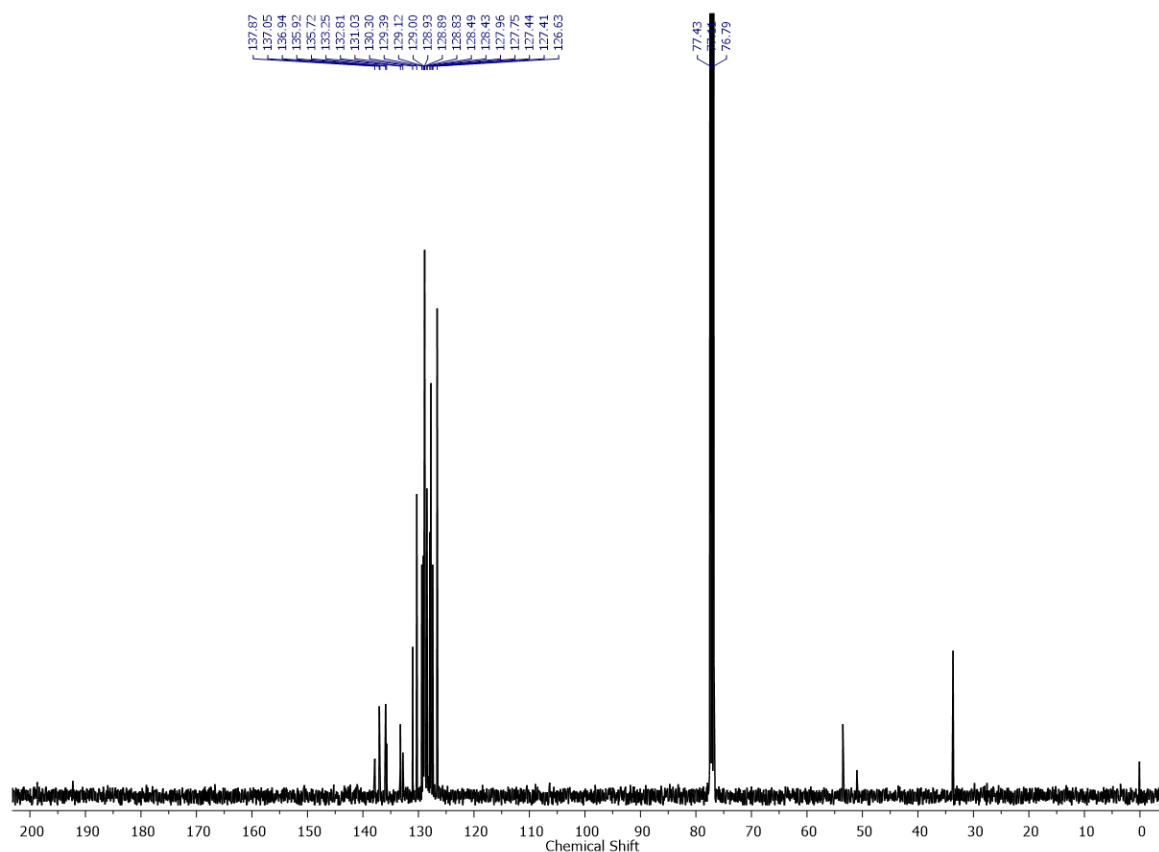


Figure 5.42. ^{13}C NMR (in CDCl_3) spectrum of purified mixture of *E* and *Z*-1-chloro-4-styrylbenzene product.

(*E/Z*)-1-chloro-4-styrylbenzene: Yield: 85%, *E*:*Z* = 60:40.

^1H NMR (400MHz, CDCl_3): δ 6.52 (d, $J = 12.4$ Hz, *Z* olefinic protons), 6.62 (d, $J = 12.4$ Hz, *Z* olefinic protons), 7.03 (d, $J = 16.4$ Hz, *E* olefinic protons), 7.08 (d, $J = 16.4$ Hz, *E* olefinic protons), 7.16 – 7.45 (m, aromatic protons of both isomers), 7.50 (m, aromatic protons of *E* isomer).

^{13}C NMR (100 MHz, CDCl_3): 126.6, 127.41, 127.44, 127.7, 127.9, 128.43, 128.49, 128.83, 128.89, 128.93, 129.0, 129.1, 129.3, 130.3, 131.0, 132.8, 133.2, 135.7, 135.9, 136.9, 137.0, 137.8.

(*E/Z*)-4-styrylbenzonitrile

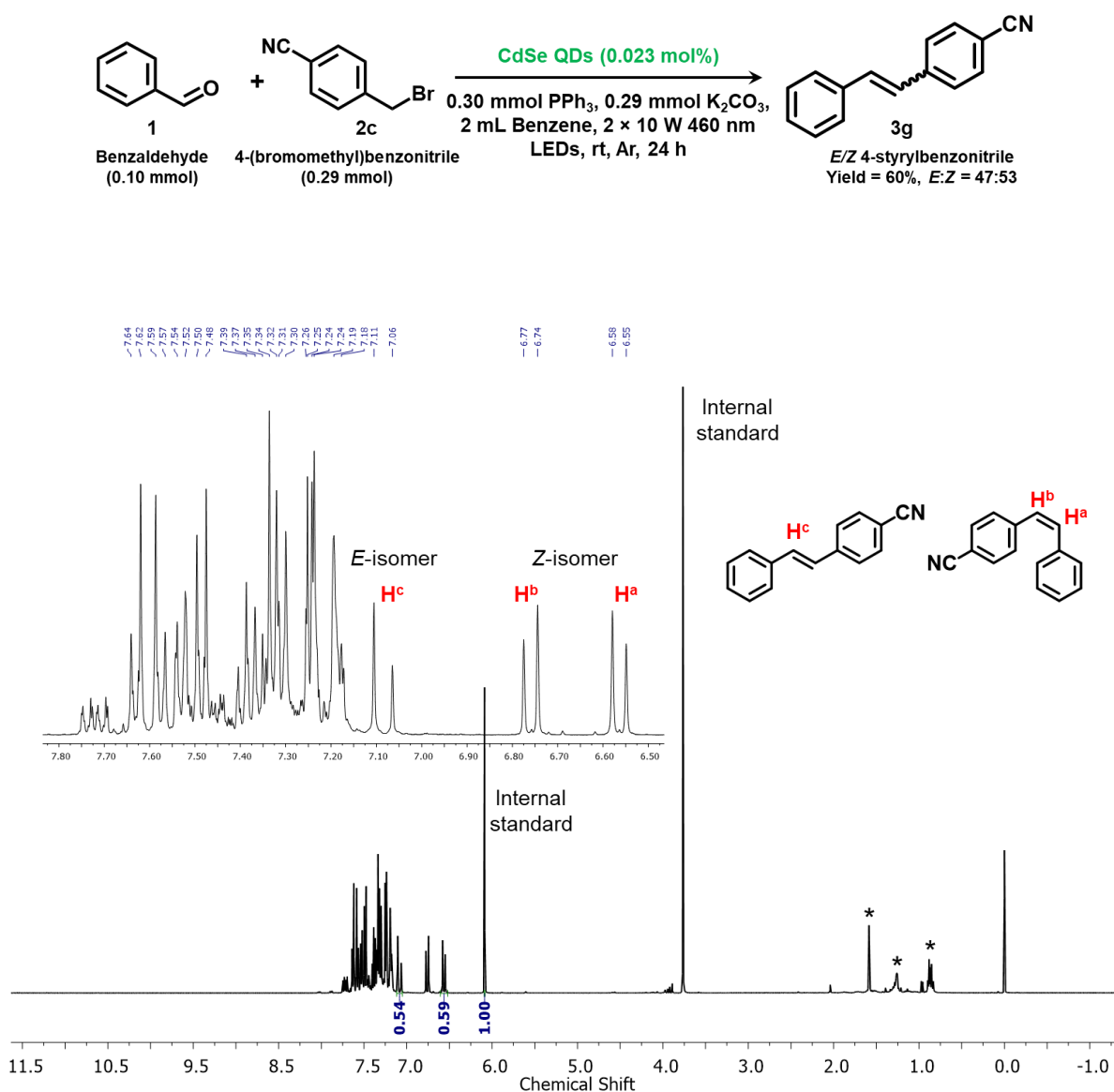


Figure 5.43. ¹H NMR (in CDCl₃) spectrum of purified mixture of *E* and *Z*-4-styrylbenzonitrile products in presence of 1,3,5-trimethoxybenzene as internal standard. The distinguishable ¹H NMR peaks are labelled accordingly. The expansion of the peaks associated to the products are shown in the inset. Solvent impurity peaks (e.g. acetone, water, hexane, heptane) are marked with asterisk.

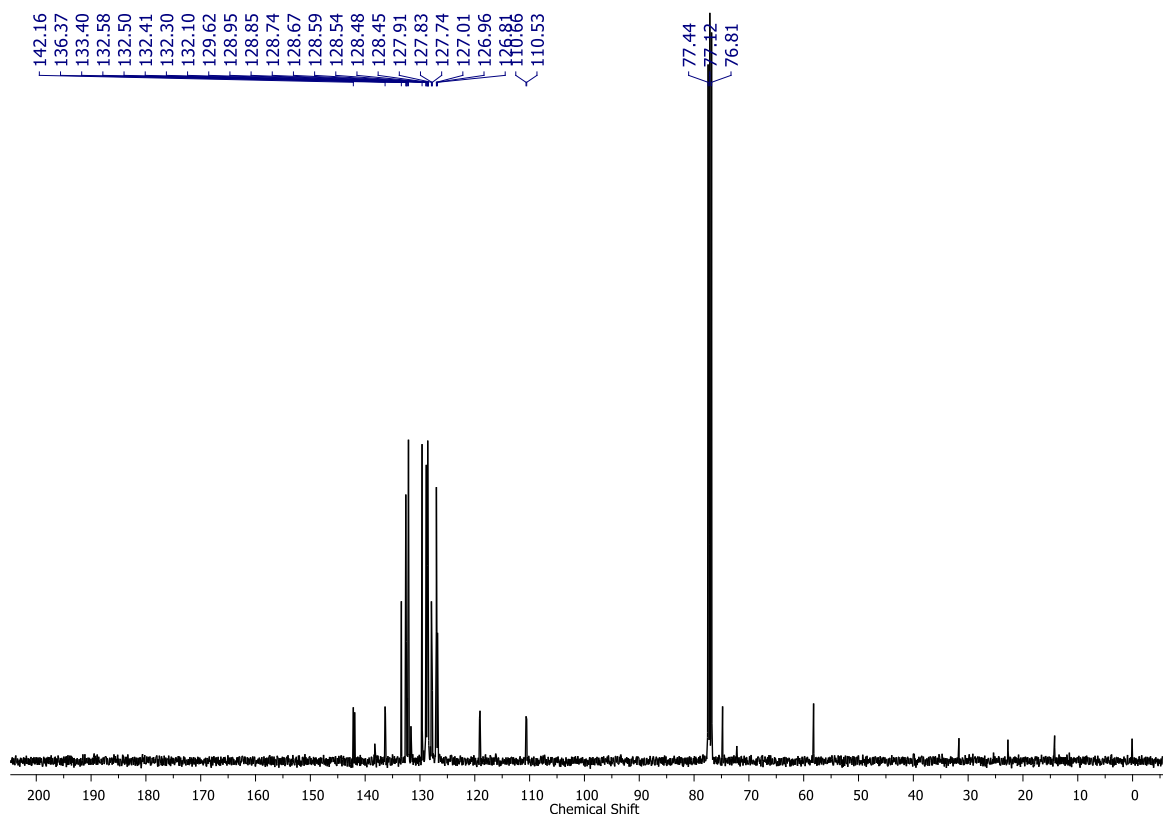


Figure 5.44. ^{13}C NMR (in CDCl_3) spectrum of purified mixture of *E* and *Z*-4-styrylbenzonitrile product.

(*E/Z*)-4-styrylbenzonitrile: Yield: 60%, *E*:*Z* = 47:53.

^1H NMR (400 MHz, CDCl_3): δ 6.56 (d, J = 12 Hz, *Z* olefinic protons), 6.76 (d, J = 12.4 Hz, *Z* olefinic protons), 7.08 (d, J = 16.4 Hz, *E* olefinic protons), 7.17 – 7.25 (m, aromatic protons of both isomers), 7.30 – 7.40 (m, aromatic protons of both isomers), 7.47 – 7.64 (m, aromatic protons of *E* isomer).

^{13}C NMR (100 MHz, CDCl_3): δ 110.5, 110.6, 119.0, 119.1, 126.8, 126.9, 127.0, 127.7, 127.8, 127.9, 128.45, 128.48, 128.54, 128.59, 128.6, 128.7, 128.8, 128.9, 129.6, 131.6, 132.1, 132.3, 132.4, 132.50, 132.58, 133.4, 136.31, 136.37, 138.2, 141.9, 142.1.

(E/Z)-1-nitro-4-styrylbenzene

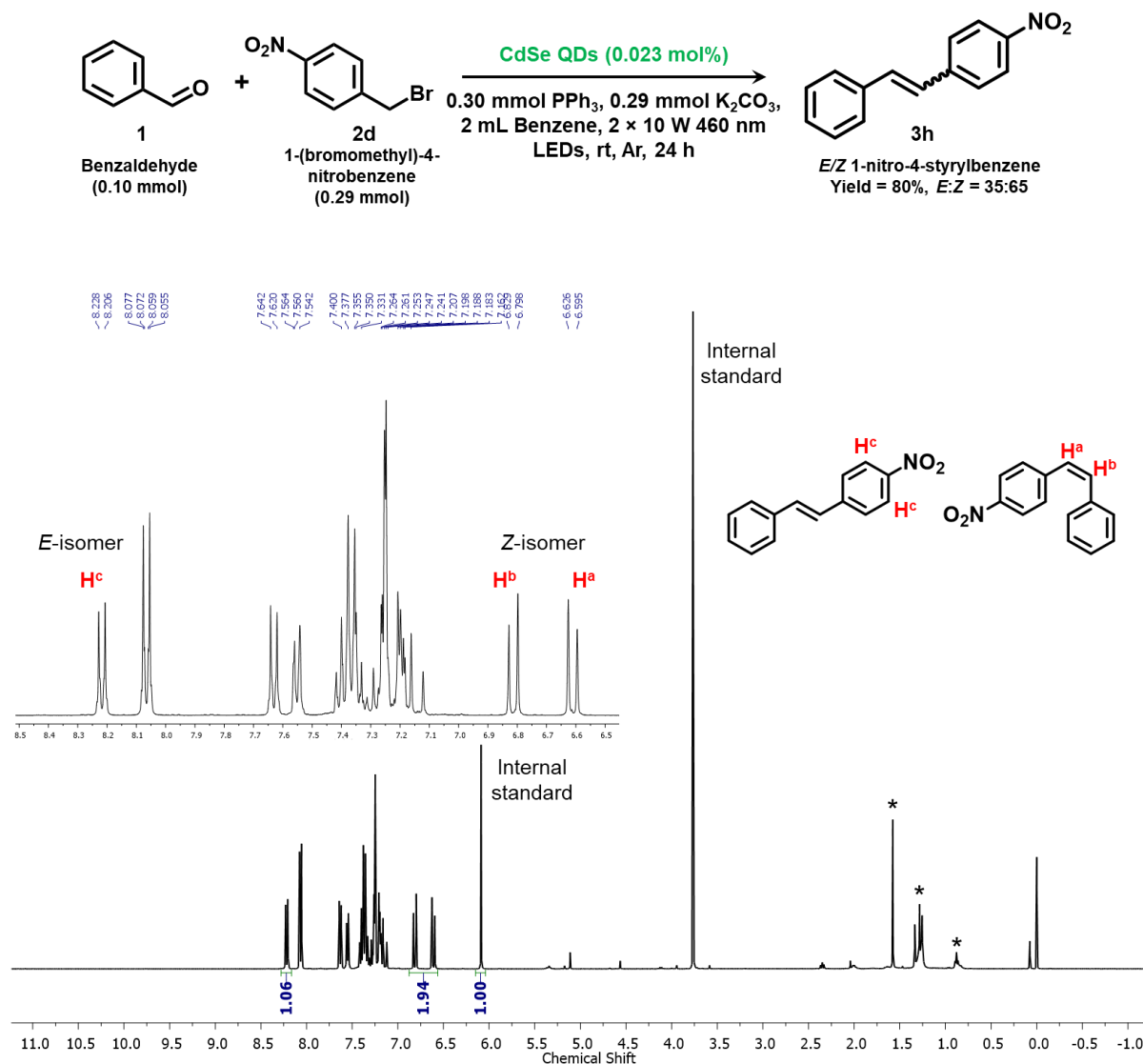


Figure 5.45. ¹H NMR (in CDCl₃) spectrum of purified mixture of *E* and *Z*-1-nitro-4-styrylbenzene products in presence of 1,3,5-trimethoxybenzene as internal standard. The distinguishable ¹H NMR peaks are labelled accordingly. The expansion of the peaks associated to the products are shown in the inset. Solvent impurity peaks (e.g. acetone, water, hexane, heptane) are marked with asterisk.

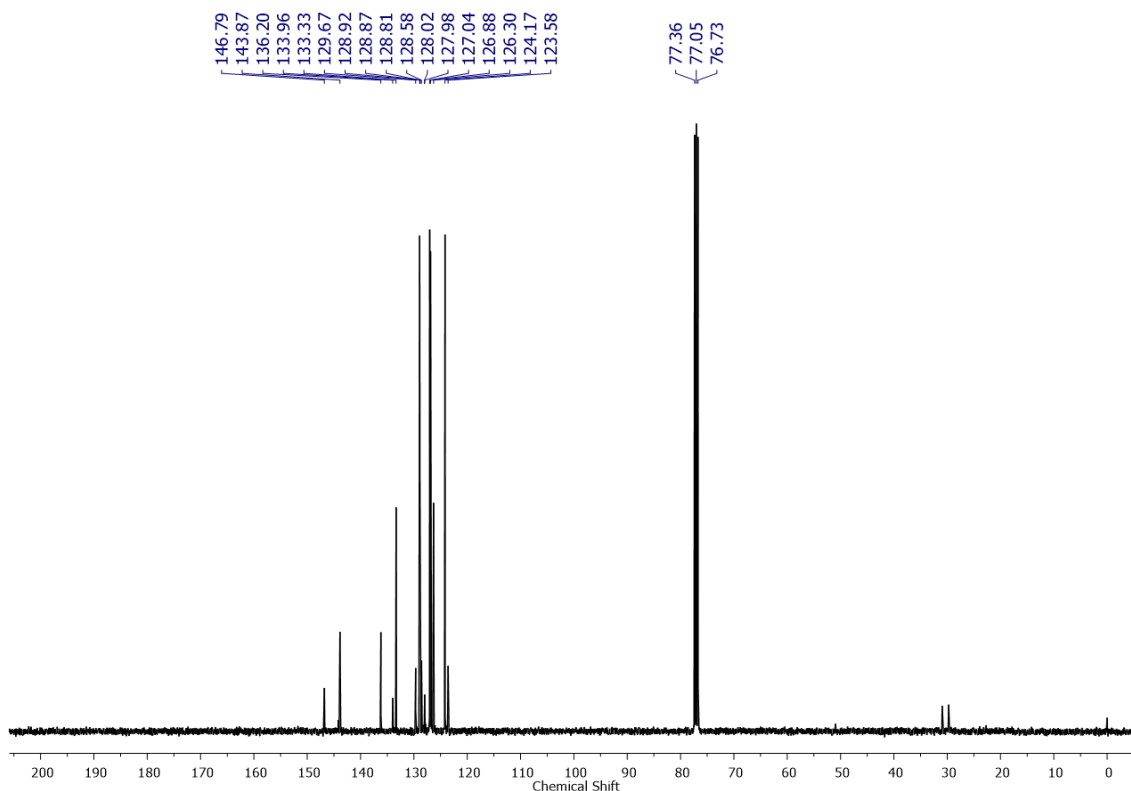


Figure 5.46. ^{13}C NMR (in CDCl_3) spectrum of purified mixture of *E* and *Z* 1-nitro-4-styrylbenzene product.

(*E/Z*)-1-nitro-4-styrylbenzene: Yield: 80%, *E*:*Z* = 35:65.

^1H NMR (400MHz, CDCl_3): 6.62 (d, $J = 12.4$ Hz, *Z* olefinic protons), 6.82 (d, $J = 12.4$ Hz, *Z* olefinic protons), 7.14 (d, $J = 16.4$ Hz, *E* olefinic protons), 7.18 – 7.41 (m, aromatic protons of both isomers and signal of *E* olefinic protons merged in it), 7.55 (d, $J = 8.8$ Hz, aromatic protons of *Z* isomer), 7.63 (d, $J = 8.8$ Hz, aromatic protons of *E* isomer), 8.06 (d, $J = 8.8$ Hz, aromatic protons of *Z* isomer), 8.22 (d, $J = 8.8$ Hz, aromatic protons of *E* isomer).

^{13}C NMR (100 MHz, CDCl_3): 123.5, 124.1, 126.3, 126.8, 127.0, 127.9, 128.0, 128.5, 128.81, 128.87, 128.9, 129.6, 133.3, 133.9, 136.2, 143.8, 146.7.

5.7.9. Reaction with paraformaldehyde and benzyl bromide

In a stir bar-equipped 15 mL test tube, 46 μL of 0.5 mM CdSe QDs in toluene were added and the solvent was dried with gentle air flow. Next, triphenylphosphine (80 mg, 0.30 mmol), paraformaldehyde (10 mg) and benzyl bromide (35 μL , 0.29 mmol) and K_2CO_3 (41 mg, 0.29 mmol) were added, followed by addition of 2 mL dry benzene under inert atmosphere. The mixture was then kept for purging with argon for ~ 30 min. Then the tube was sealed, and irradiated with two 10 W LEDs (at a distance of 4 cm each on the both sides) under stirring for 24 h. After the reaction was over, the whole reaction mixture was transferred in a centrifuge tube, followed by the addition of ~ 5 mL MeOH to precipitate the QDs. Next, the QDs and the insoluble by-products of the reaction were separated via centrifugation (2 min at 8000 rpm). The supernatant was collected and worked up with water-diethyl ether mixture followed by collecting the diethyl ether layer. The solvent was then removed in vacuo in at 0°C in presence of ice, and the crude residue was purified with silica gel column chromatography using pentane as eluent, to obtain the product styrene (**Figure 5.47**).

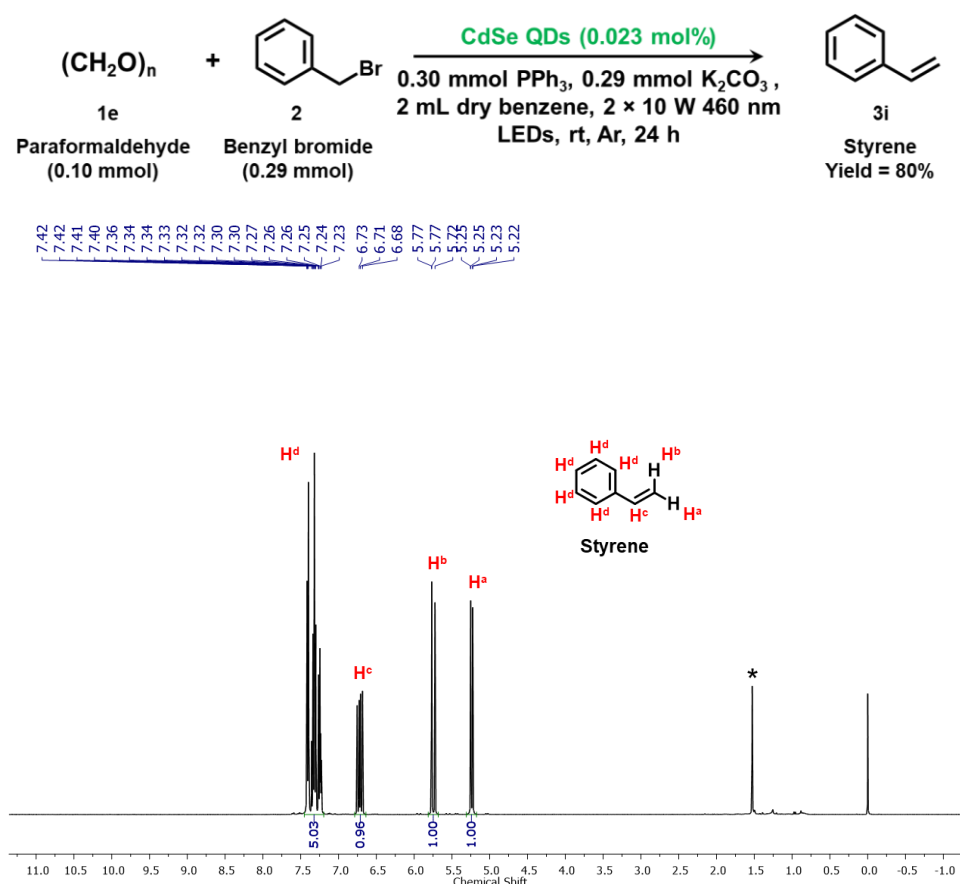


Figure 5.47. ^1H NMR (in CDCl_3) spectrum of purified styrene product obtained from the QD photocatalytic olefination reaction between paraformaldehyde and benzyl bromide. The corresponding proton peaks are labelled accordingly. Solvent impurity peak (water) is marked with asterisk.

5.7.10. Characterization of InP QDs

Photophysical characterization of InP QDs:

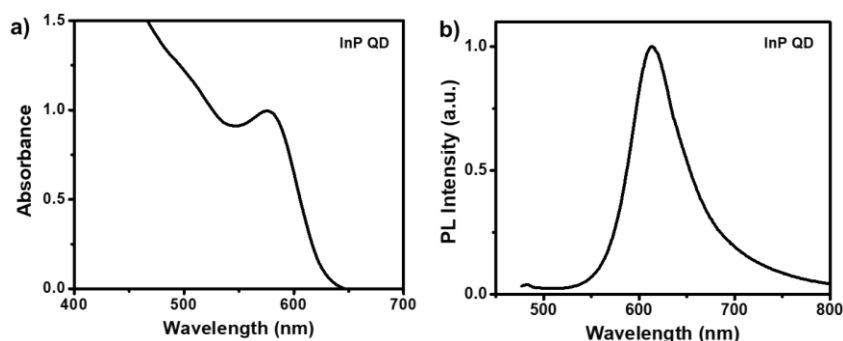


Figure 5.48. Spectroscopic characterization of InP QDs in toluene. a) Absorption and b) steady-state PL spectra of InP QDs.

5.7.11: Photoisomerization of E-Z isomers under irradiation

Interconversion of *E* and *Z* isomers under photocatalytic reaction condition

To check the hypothesis of interconversion of diastereomers under photoirradiation, we have carried out a reaction where pure *E*-stilbene (thermodynamically stable) was taken as the starting material in presence of CdSe QDs in benzene. After irradiation of 24 h with 2 x 10W blue LEDs, the QDs were precipitated with MeOH and the supernatant was dried followed by characterization with ^1H -NMR in CDCl_3 . A new signal at ~ 6.6 ppm appeared which corresponds to the formation of *Z*-stilbene (**Figure 5.49**). The integration of the peaks reveals an interconversion ratio of $E:Z = 75:25$ after the course of photoirradiation. This control experiment clearly indicates a similar possibility of interconversion of diastereomers during the photocatalytic olefination reaction with QDs, eventually reaching to a photostationary state.

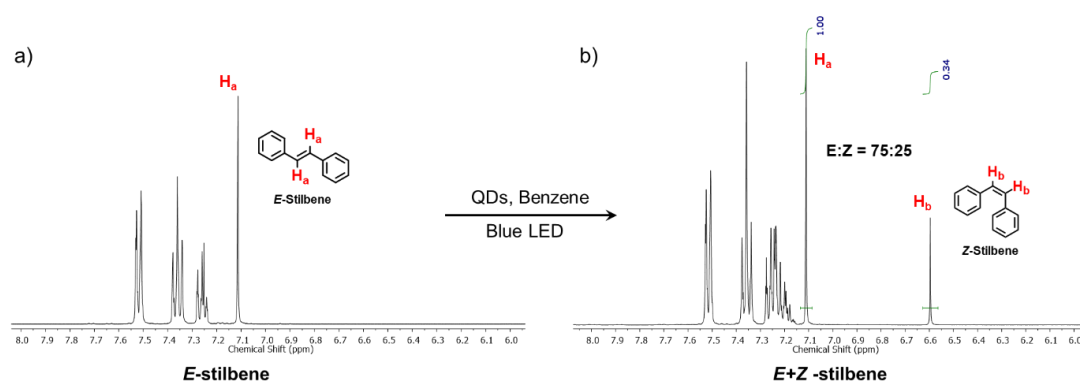
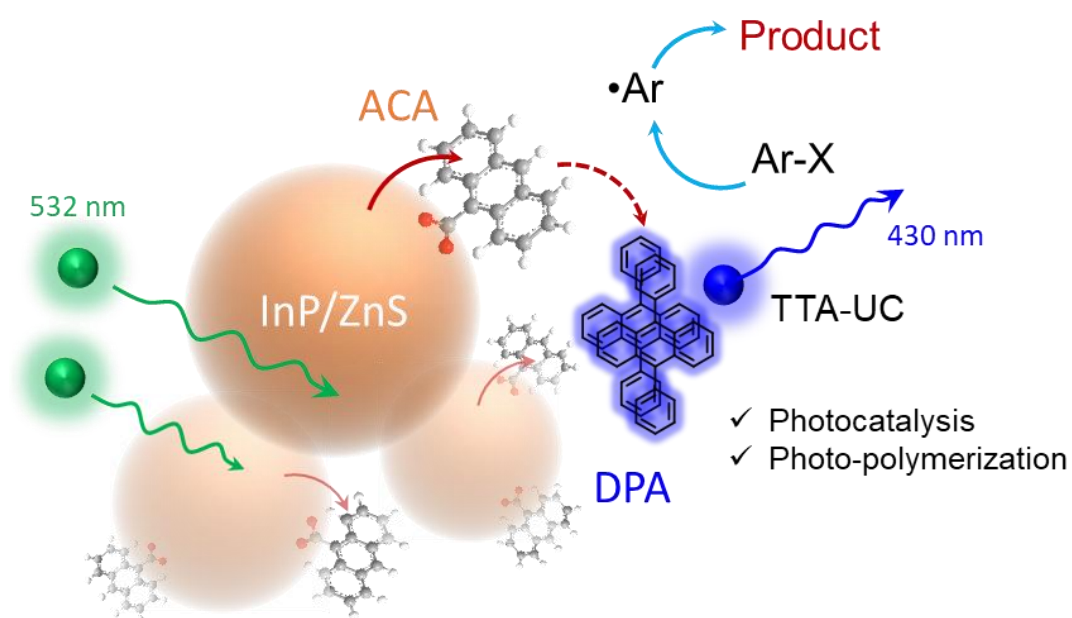


Figure 5.49. ^1H NMR (CDCl_3) spectra of diastereomerically pure *E*-stilbene a) before and b) after photoirradiation in the presence of CdSe QDs, with 2 x 10 W blue LEDs for 24 h. A new signal at ~ 6.6 ppm appeared which corresponds to the formation of *Z*-stilbene. The integration of the peaks reveals an interconversion ratio of $E:Z = 75:25$ after the course of photoirradiation.

Chapter – 6

Triplet-Triplet Annihilation Enables Photocatalysis Beyond the Redox Potential of InP/ZnS Quantum Dots



6.1. Abstract

Ability to carry out photocatalytic transformations with higher redox potentials using visible-light photocatalysts has been a major challenge in the area of light harvesting. One of the promising pathways to achieve so is via triplet-triplet annihilation based photonic upconversion (TTA-UC), where two low energy photons, via appropriate triplet sensitization and sequential triplet energy transfer process, can get upconverted to a high energy singlet state and eventually emit a high energy photon. As a part of this process, the generated high-energy singlet state can directly participate in charge transfer process to carry out challenging photocatalytic processes beyond the redox limit of the used sensitizer. In this direction, quantum dots (QDs) have emerged as a superior sensitizer over traditional molecular systems to execute efficient TTA-UC processes using low energy visible photons, because of very low energy difference between the singlet and the triplet excited states (<10 meV) as well as higher photostability. In this work, we have introduced environmentally friendly InP/ZnS QDs based green-to-blue TTA-UC system with an excellent upconversion quantum yield of $\sim 5\%$, and an achieved apparent anti-Stokes shift (Δ_{as}) of 0.55 eV. The efficient UC process was further introduced to carry out challenging dehalogenation and coupling reactions with excellent yields ($\sim 85\%$) using an aryl bromide as substrate. Upon activation via TTA-UC, the formed aryl radicals were further employed to execute an efficient photo-polymerization reaction, with visible-light. Moreover, thorough photophysical analysis of the reaction mechanism revealed intricate details about the sequence of reductive and oxidative quenching pathways of the TTA based photoredox transformation.

6.2. Introduction

Visible-light photocatalysis has become one of the most prominent ways of harvesting and storage of solar energy into chemical bonds.^{1,2} As the 97% of the solar energy is concentrated into the visible and the NIR parts of the spectrum, it is essential to effectively harvest this range for chemical transformations.³ Although effective, but the visible-light photocatalysts are always limited by their band gap which, by definition, cannot be more than the maximum energy of visible photons, i.e., 3.1 eV. This implies that a photocatalyst can only absorb up to 3.1 eV of energy (corresponding to 400 nm wavelength) and reach the associated redox level.^{4,5} However, the redox potential of many reactions might exceed the maximum achievable redox

level of these visible-light photocatalysts.⁶ This limitation inevitably forced scientists to use UV photocatalysts with higher redox potentials, which is not a sustainable way as only 7% of the solar spectrum consists of UV light.^{7,8} Also, photodamage of the reactants as well as the unwanted side reactions dominates under prolonged UV irradiation.⁹

One of the prominent ways to mitigate this limitation is by incorporating an appropriate photonic upconversion system which can generate higher redox potentials beyond the reach of the native photocatalyst, using low energy visible or NIR irradiation.^{6,10} Triplet-triplet annihilation based upconversion (TTA-UC) is one such practical pathway that can convert non-coherent low-energy photons into higher energy photons.¹⁰⁻¹³ In this process, photosensitizers absorb incoming low-energy photons and subsequently transfer their excited state energy to generate triplet states in the molecular acceptors (or, annihilators). The fusion of two such triplet excited annihilators finally result in the generation of a high energy singlet state, which decays via the emission of a photon of energy corresponding to that energy state (**Figure 6.1**).

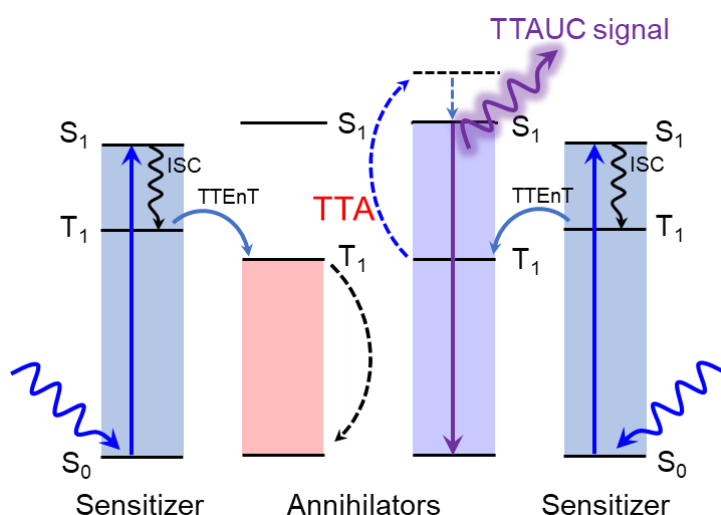


Figure 6.1 A general schematic diagram of the TTA-UC process in molecular systems.

Along with the emission of the high-energy upconverted photons, the generated charge carriers associated to those high-energy excited states can also be used to carry out photoredox transformations with higher required potentials, that are not achievable by the regular visible-light photocatalysts.¹⁴⁻¹⁷ Leveraging the versatility of the process, a variety of molecular TTA-UC systems have been introduced into the field of photoredox catalysis to carry out reactions with higher redox potentials under visible-light excitations.¹⁴⁻¹⁷ In one such pioneering example, Perez-Ruiz, Wangelin and co-workers have implemented the vis-to-UV TTA-UC process to carry out challenging dehalogenation reaction of a series of aryl-bromides (**Figure 6.2a**).¹⁴ The authors chose butane-2,3-dione (BD) as sensitizer and 2,5-diphenyloxazole (PPO)

as annihilator to carry out the TTA process under low-power blue light excitation. The photophysical experiments, accompanied with electrochemical and theoretical calculations, confirms the involvement of TTA process as well as reveals the mechanistic details of the dehalogenation reaction (**Figure 6.2b, c**).

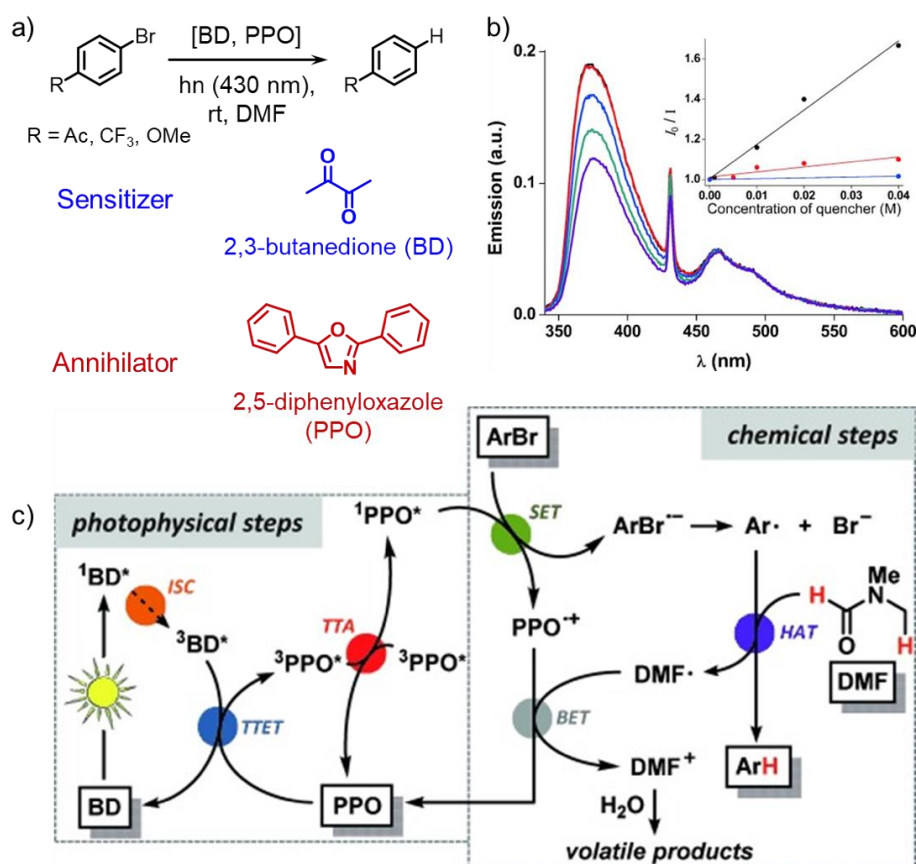


Figure 6.2. a) Schematic representation of the photocatalytic dehalogenation reaction carried out under TTA-UC process using BD as sensitizer and PPO as annihilator. b) The quenching of the TTA-UC signal indicates the charge transfer from the excited singlet state of the annihilator molecule. c) The probable reaction mechanism of the TTA-UC and corresponding the photoredox catalytic reaction. Reproduced with permission from ref. 14 Copyright: 2015, Wiley-VCH.

Although the incorporation of molecular sensitizers has shaped the area of TTA-UC for photoredox catalysis, but the inherent loss of energy due to intersystem crossing (ISC) in the molecular sensitizers makes the system far less efficient both in terms of achievable quantum yield as well as the gain in photonic energy (in terms of anti-stokes shift).¹² Quantum dots (QDs) has come up as a the practical alternative to the molecular sensitizers allowing a superior TTA-UC efficiency as well as a higher photonic energy gain.¹⁸⁻²¹ For example, in one of the seminal works, Tang and co-workers have designed a green-to-blue TTA-UC system with CdSe QDs as sensitizers.¹⁸ The QDs were appropriately surface engineered with 9-anthracene carboxylic acid (ACA) which works as a triplet shuttle ligand and transfers the triplet energy to the annihilator diphenylanthracene (DPA). Upon the TTA process in DPA, the blue

fluorescence (~ 432 nm) comes out as the upconverted signal (**Figure 6.3a**). Interestingly, as a control experiment, when long chain aliphatic octadecyl phosphonic acid ligand capped CdSe QDs (CdSe-ODPA) were incorporated instead of CdSe-ACA QDs, the efficiency of the TTA process turned out to be insignificant (**Figure 6.3b, c**). This experiment emphasised the importance of appropriate surface ligands for effective shuttle of the triplet excitons from QDs to the annihilator for an efficient TTA-UC process. In another notable example by Kimizuka, Yanai and coworkers, CdSe/ZnS core/shell QDs were introduced as an efficient sensitizer for a green-to-blue TTA-UC process.²² In this work, a modified triplet-shuttle ligand 4-(10-phenylanthracene-9-yl)pyridine was used for efficient transfer of triplet-energy from photoexcited QDs to annihilator DPA (**Figure 6.3d**). The pyridyl group in the ligand was introduced for an effective coordination on the QD surface. The TTA-UC signal with a peak at ~ 432 nm was observed upon excitation at 532 nm, with a maximum upconversion quantum yield (UCQY) of $\sim 1.4\%$. The UC signal was found to increase with increase in the excitation power density, proving the process being TTA (**Figure 6.3e**).

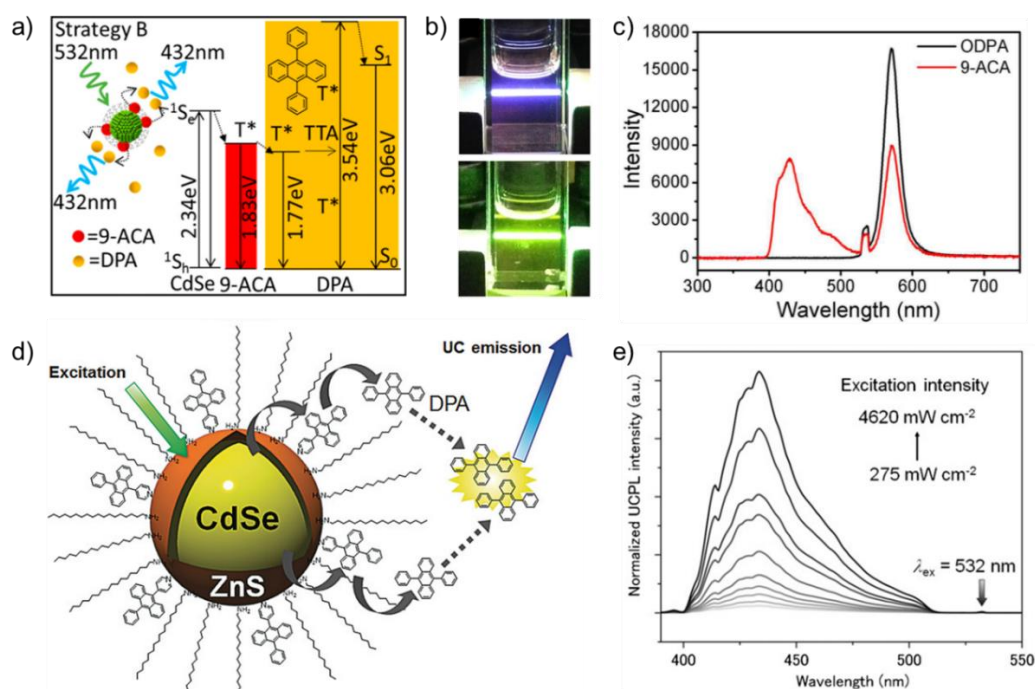


Figure 6.3. TTA-UC using QDs as sensitizers. a) Schematic representation of green-to-blue upconversion using ACA decorated CdSe QDs, along with energy levels of all important components. b) The spectra of the corresponding upconversion signal with ODPA and ACA capped CdSe QDs. The ACA capped QDs show strong upconversion signal at ~ 430 nm, whereas the TTA-UC signal with ODPA capped QD was negligible. Reproduced with permission from ref. 18 Copyright: 2015, American Chemical Society. c) Schematic diagram of TTA-UC process with CdSe/ZnS core/shell QDs. The QDs are decorated with 4-(10-phenylanthracene-9-yl)pyridine ligands for efficient triplet energy transfer to annihilator DPA. e) Spectra showing the upconversion signals and the increasing intensity with increase in the laser excitation density. Reproduced with permission from ref. 22 Copyright: 2016, Wiley-VCH.

Introduction of QD as a sensitizer for the TTA-UC process instead of molecular sensitizers, opened up a wider window of excitation that could be effectively leveraged in the field of photocatalysis.²³ Using the UC process, higher redox potentials can be achieved (with the help of the annihilator) using the lower energy excitations. For example, reactions that are traditionally carried out under high energy UV excitation, can be executed under visible-light using the power of TTA-UC.

In this work, we have introduced a QD sensitized green-to-blue TTA-UC process that was employed to carry out photocatalytic transformations that are beyond the redox potentials of the QDs alone. As a choice of QDs, we have incorporated environmentally friendly indium phosphide/zinc sulfide (InP/ZnS) core/shell QDs which has come up as the most promising alternatives to the traditional toxic Cd and Pb-chalcogenide QDs. The QDs were appropriately surface engineered with 9-anthracene carboxylic acid (ACA) as the triplet-shuttle ligands for efficient transfer of triplet energy from the photoexcited QDs to the annihilator diphenylanthracene (DPA), leading to an efficient TTA-UC process with 4.9% UCQY (**Figure 6.4**). Most importantly, the generated DPA singlets ($^1\text{DPA}^*$) due to the exciting TTA-UC process were utilized in a photoredox catalysis, carrying out a challenging dehalogenation and C-C coupling reaction with substituted aryl halides in excellent yields (85%) (**Figure 6.4**). The proof of TTA-UC as well as the mechanistic detail of the photoredox catalysis was understood using detailed spectroscopic analysis. The versatility of the InP/ZnS QD sensitized TTA-UC driven photocatalysis was further demonstrated through a successful radical polymerization of acrylates in a few-minute time scale, with visible-light.

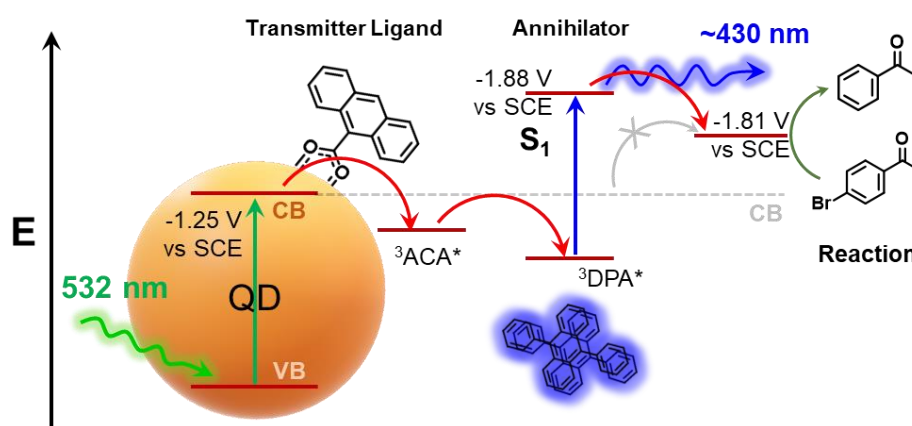


Figure 6.4. Schematic representation of the TTA-UC process with ACA decorated InP/ZnS QDs as sensitizers and DPA as annihilators. The TTA-UC process was utilized for a photoredox catalytic reaction with potentials beyond the redox levels of the associated InP/ZnS QDs.

6.3. Experimental section

Materials and reagents, synthesis and surface functionalization of the InP/ZnS QDs and the associated techniques used are described in Chapter 2.

6.3.1. TTA-UC sensitized by InP/ZnS QDs:

In a typical procedure, a long neck PL cuvette is charged with 0.45 μ M ACA decorated InP/ZnS QDs in 3 mL dry toluene, followed by the addition of 16 mg DPA. The solution is then purged with Ar for 15 min and finally sealed with Teflon tape and parafilm. The sealed tube was then excited with focused 532 nm green laser and the upconverted signal was then collected in an optical fibre coupled Ocean optics spectrometer. A 500 nm short-pass filter was used occasionally to eliminate the source and the PL signals of QDs.

6.3.2. Calculation of TTA-UC QY:

The TTA-UC QY was determined using the relative QY method, following a reported protocol.¹⁸ Rh-6G was used as the reference dye for the calculation. λ_{ex} and λ_{em} were kept at 532 nm and 430 nm respectively. To generate one upconverted photon via TTA requires two incident photons, so the maximum achievable QY would be 50%. To normalize it to 100%, the UCQY is represented after multiplication with a factor 2. In this work, the TTA-UC QY was calculated using the following equation.

$$\varphi_{UC} = 2 \times \varphi_{ref} \times \frac{\frac{\eta^2 \times PL_{sample}}{1 - 10^{-A_{sample}}}}{\frac{\eta_{ref}^2 \times PL_{ref}}{1 - 10^{-A_{ref}}}}$$

Where, φ_{ref} = QY of reference dye (i.e., Rh-6G), PL_{sample} and PL_{ref} are the integrated PL intensity of the TTA sample and Rh-6G dye respectively under identical excitation conditions. A_{sample} and A_{ref} refer to the absorbance of the InP/ZnS QDs and the Rh-6G dye respectively, at 532 nm. η and η_{ref} represent the refractive indices of the respective solvent systems (toluene for TTA-UC system and ethanol for Rh-6G dye).

6.3.3. Procedure of TTA-UC directed dehalogenation and C-C coupling reaction:

In a stir-bar equipped long neck quartz cuvette, 4-bromoacetophenone (50 mg, 0.25 mmol, 1 eq.), N-methylpyrrole (1 mL, 12.5 mmol, 50 eq.) and DIPEA (150 μ L, 0.85 mmol) was mixed

with the separately prepared QD based TTA-UC system containing DPA (16 mg, 0.048 mmol) and 4 μM of InP/ZnS-ACA in a 1:1 dry benzene and dry DMSO solvent system. The total 3 mL of the reaction mixture was thoroughly purged for 15 min with Ar, followed by sealing with Teflon tape and parafilm. The sealed cuvette was then irradiated with 532 nm continuous wave laser with a beam area of $\sim 0.005\text{ cm}^2$ (after focusing) on the cuvette wall. The average power of the laser was kept constant at $\sim 1\text{ W}$ (197 W cm^{-2} upon focusing) throughout all the photocatalytic experiments. After 12 h of irradiation, 3 mL methanol is added into the reaction mixture to precipitate the InP/ZnS QDs via centrifugation. 500 μL of the resulting QD free reaction mixture was then mixed with 5 μL dodecane (internal standard) followed by injection of 1 μL of the resulting solution into the Shimadzu GCMS-2010 instrument for further analysis.

6.3.4. Procedure of TTA-UC triggered photopolymerization reaction:

In a typical TTA-UC triggered radical polymerization procedure, methyl methacrylate monomer (4.7 mmol) was mixed with a cross-linking agent 1,6-hexanediol diacrylate (2.2 mmol) in presence of DIPEA (150 μL , 0.85 mmol) and the radical initiator 4-bromoacetophenone (50 mg, 0.25 mmol). Next, 4.5 μM InP/ZnS-ACA and 16 mg DPA in dry benzene was added. The reaction mixture was then purged with Ar for 15 min followed by irradiation with a focused 532 nm cw laser. Within 10 min, the liquid reaction mixture turned into a solid polymer gel as shown in **Figure 6.12**.

6.4. Results and discussion

6.4.1. Design of InP/ZnS based TTA-UC system

To design the desired green-to-blue TTA-UC system, $\sim 3.5\text{ nm}$ InP/ZnS QDs were synthesised as the sensitizer, using a reported protocol (for experimental details, see Section 2.2.3 of Chapter 2).²⁴ The ZnS overcoating enhanced the photoluminescence quantum yield (PLQY) of the QDs, thereby improving the overall efficiency of the TTA-UC process. Moreover, the overcoating improve the stability of the QDs under various experimental conditions. The synthesised InP/ZnS QDs were dispersed in toluene and showed the first excitonic absorption

peak at ~500 nm, PL emission peak at ~550 nm with an excellent absolute PLQY of 75% (**Figure 6.5**).

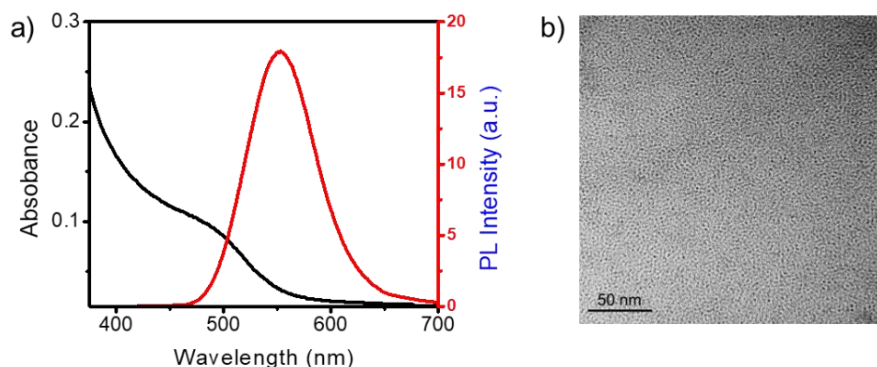


Figure 6.5. Characterization of the InP/ZnS QDs. a) the representative absorption and PL spectra of the as-synthesized InP/ZnS QDs in toluene. b) A representative TEM image of the InP/ZnS QDs.

6.4.2. Triplet-triplet energy transfer (TTEnT) from InP/ZnS QDs

During a TTA-UC process, the triplet excitons from the photoexcited QDs need to sensitize the triplet states of the annihilator molecule leading to the annihilation. For that, an efficient TTEnT must take place from the QDs to the annihilator molecules. Given that the as-synthesized QDs are surrounded by long chain aliphatic ligands (e.g., oleylamine), which does not have any low-lying triplet states, the TTEnT must happen directly from the QDs to the annihilator molecules. As the TTEnT process is known to follow dexter type energy transfer mechanism, a very close (~ 1 Å) proximity of the donor and acceptor are necessary.²⁵ But, the typical length of the long-chain aliphatic ligands is in the order of ~ 1 nm. This severely prevents the annihilators to access the QD surface leading to a minimal efficiency of the TTEnT process.¹⁸ For that, we chose an appropriate ligand with a low-lying triplet state, which upon binding onto the QD surface can act as a transmitter of the efficient TTEnT from the QDs to the annihilators. In this case, our choice of ligand was ACA, which has an $E_T = 1.83$ eV²⁵, intermediate between the triplet energy energies of the InP/ZnS QDs (2.29 eV) and the annihilator molecule, DPA (1.77 eV)²⁰ allowing a favourable transmission of triplet energy from the photoexcited QDs to the DPA molecule.

To achieve the desired system, we functionalized the InP/ZnS QDs with ACA using an appropriate ligand exchange protocol (**Figure 6.6a**; See Section 2.4.3 in Chapter 2 for the detailed procedure).²⁰ The presence of the signature sharp features of ACA below 400 nm, along with the retention of the excitonic peak of the InP/ZnS QDs at 500 nm in the absorption

spectrum of the ligand exchanged QDs confirms the successful functionalization of the ACA on the QD surface (**Figure 6.6b**).²⁰ As expected, upon functionalization of ACA, the PL of the InP/ZnS QDs were quenched by ~80% in steady-state and ~74% in time-resolved experiments (**Figure 6.6c, d**). This indicates an efficient TTEnT from the InP/ZnS QDs to the low-lying triplet state of ACA ligands (**Figure 6.6e**).

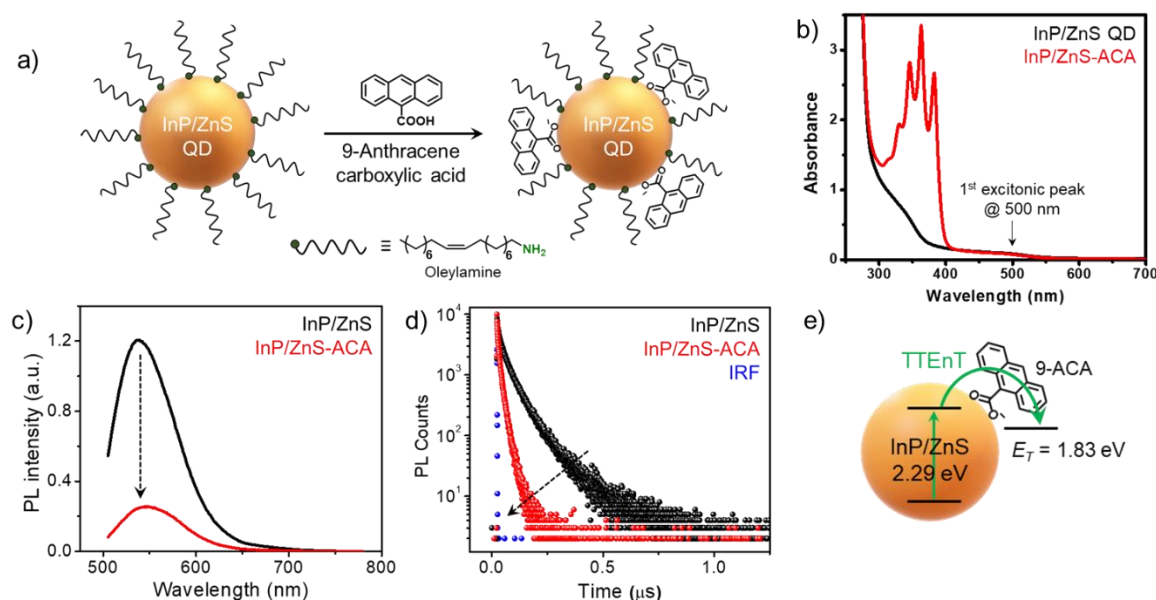


Figure 6.6. a) The schematic representation of the ligand exchange process of ACA on the InP/ZnS QD surface. b) Absorption spectra of the QDs before and after ligand exchange showing the signature feature of ACA on the ligand exchanged QDs below 400 nm. c) The PL spectra of the QDs excited at 500 nm, showing a sharp quenching upon functionalization with ACA. d) The quenching in the time-resolved PL emission of QDs before and after ligand exchange reaction with ACA. e) Schematic showing the successful TTEnT from the photoexcited InP/ZnS QDs to the low-lying triplet state of surface bound ACA.

To confirm that the triplet states are solely associated to the energy transfer step, a similar polyaromatic carboxylate ligand with higher triplet energy, 1-naphthoic acid (NCA) ($E_T = 2.60$ eV),²⁰ was functionalised on the InP/ZnS QD surface, as a control experiment. Interestingly, negligible quenching of the QD PL was observed in both steady-state as well as time-resolved PL experiments upon NCA functionalization (**Figure 6.7a, b**). This result eliminated both the possibilities of introduction of surface trap states upon ligand exchange, as well as the involvement of any alternate energy/charge transfer mechanism leading to the PL quenching (**Figure 6.7c**).

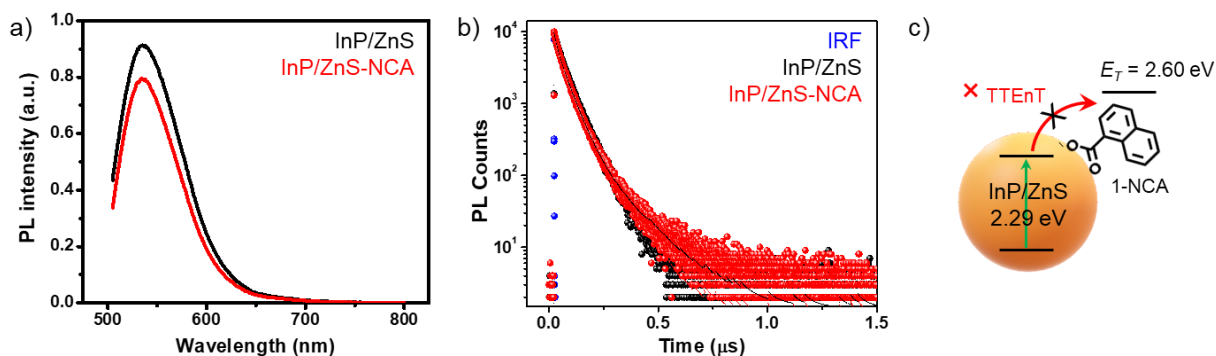


Figure 6.7. Negligible quenching of the QD PL was observed in a) steady state and b) PL lifetime measurements, upon NCA functionalization on InP/ZnS QDs. c) Schematic representation showing that the TTEnt process cannot happen from ~ 3.5 nm InP/ZnS QDs to the surface bound NCA ligands, because of the unfavourable energy level alignment.

6.4.3. Green-to-blue TTA-UC sensitized by InP/ZnS QDs

With the established InP/ZnS-ACA system in hand with efficient triplet sensitization of ACA by InP/ZnS QDs, we went on to introduce the annihilator DPA, into the system to allow the desired TTA-UC process. As depicted in **Figure 6.8a**, the E_T of DPA is 1.77 eV, which is lower than that of ACA ($E_T = 1.83$ eV), allowing a further TTEnt from the sensitized surface bound $^3ACA^*$.

Under a typical experimental condition, 0.45 μM of InP/ZnS-ACA was mixed with 16 mM DPA in Ar-purged toluene followed by excitation with a focused 532 nm continuous-wave (cw) laser with a maximum average power of 1 W. The excitation clearly resulted in a blue emission signal corresponding to the excited singlet states of DPA (captured with a 500 nm short-pass filter as **Figure 6.8b**), indicating a functional TTA-UC process. The recorded spectrum of the overall TTA system (without any filter) showed an apparent anti-Stokes shift (Δ_{as}) of 0.55 eV, considering the energy difference between the λ_{max} of the upconverted emission signal and the excitation wavelength of the laser source (**Figure 6.8c**). The upconverted emission signal also does overlap well with the natural fluorescence spectrum of DPA coming from the singlet state (under direct excitation with $\lambda^{\text{ex}} = 365$ nm), confirming that the final annihilation process is indeed happening from the $^1\text{DPA}^*$ moiety (**Figure 6.8d**).

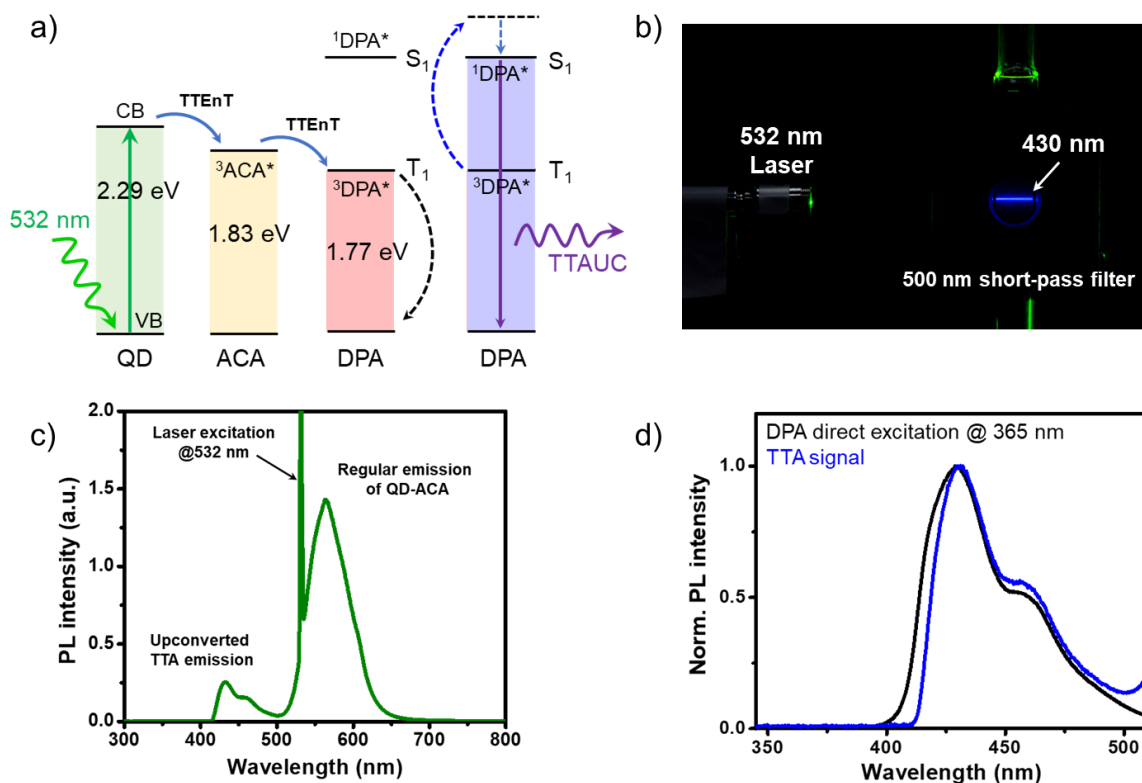


Figure 6.8. Confirmation of the TTA-UC process in InP/ZnS based system. a) A schematic representation of the TTA-UC process containing InP/ZnS QD as sensitizer, ACA as triplet-shuttle ligand and DPA as annihilator. The involved triplet and singlet excited states are shown with the associated triplet energies. b) The optical photograph showing the bright blue upconverted signal from the cuvette (through a 500 nm short-pass filter) containing a solution of InP/ZnS-ACA and DPA, upon excitation with a 532 nm green laser. c) The overall spectrum of the TTA-UC process without any filter, showing the upconverted signal, the laser excitation as well as the direct PL of the InP/ZnS QDs. d) An overlap of the TTA-UC signal with the regular fluorescence of DPA (from the $^1\text{DPA}^*$ state), confirming that the final annihilation happens from DPA.

The intensity of the UC signal was found to increase with the increase in the power density of the laser excitation (**Figure 6.9a**). The integrated values of the UC peak under different laser power density first increased in a quadratic manner which then turned to linearity after a cross-over point defined as the TTA-UC threshold intensity (I_{th}) (**Figure 6.9b**). Below this point, at lower power densities, the concentration of triplet sensitized DPA ($[^3\text{DPA}^*]$) remains low and the TTA-UC intensity increases quadratically with the laser power density. But above the I_{th} value, the $[^3\text{DPA}^*]$ becomes sufficiently high that the TTA becomes the dominant decay pathway leading, and the TTA-UC intensity increases linearly with the excitation power density. This leads to the shift of the slope of double logarithmic plot between the integrated UC PL intensity vs power density from 2 to 1 above I_{th} point. All these observations are in accordance with a classic TTA-UC process.^{10,18,20} Next, the QY of the TTA-UC process was calculated using rhodamine-6G as a reference dye. Interestingly, the QY was found to increase at the lower excitation intensity, finally reaching a plateau of constant QY at higher intensity

values (**Figure 6.9c**). A maximum of QY of $\sim 5\%$ was observed under the optimized experimental conditions (InP/ZnS-ACA $0.45\ \mu\text{M}$, and DPA $16\ \text{mM}$ in Ar purged toluene). Interestingly, the achieved TTA-UC QY was found to be lower at any higher or lower concentrations of InP/ZnS-ACA. This indicates an inefficient TTA process at the lower InP/ZnS-ACA concentration; whereas a dominating self-absorption process occurs at the higher InP/ZnS-ACA concentrations, affecting the radiative quantum efficiency of the TTA-UC process. Moreover, the trends observed in this set of experiments confirms that the observed phenomenon indeed follows the TTA-UC pathway.^{10,18,20}

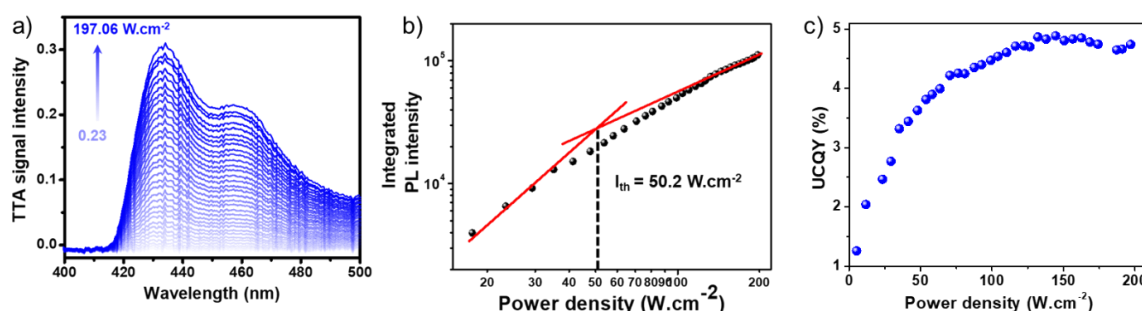


Figure 6.9. Characterization of the TTA-UC process. a) The intensity of the upconverted signal increases with increase in the power density of the laser source. b) Log-log plot of the integrated UC intensity vs laser power density showing the transition from quadratic to linear regime with I_{th} value to be $50\ \text{W cm}^{-2}$. c) The calculated TTA-UC QY plotted as a function of the laser power density. At higher power density, the UCQY saturates at a value of $\sim 5\%$.

6.4.4. Photoredox catalysis using TTA-UC

With the optimized TTA-UC process in hand, we went on to implement it towards challenging photoredox transformations that happens at potentials beyond the redox limit of the QDs. In that direction, we chose the dehalogenation and C-C coupling reactions of aryl bromide substrates as the model reaction (**Figure 6.10a**). The substrate 4-bromoacetophenone ($E_{red} = -1.81\ \text{V vs SCE}$)^{14,15} and the $\sim 3.5\ \text{nm}$ InP/ZnS QDs ($E_{CB} = -1.25\ \text{V vs SCE}$; see **appendix section 6.7.1** for details) were chosen in such a way that the required redox potential of the reaction is beyond that of the redox limit of the QD. In a typical reaction procedure, 4-bromoacetophenone (1 eq., $0.25\ \text{mmol}$), N-methylpyrrole (50 eq., $12.5\ \text{mmol}$) and DIPEA ($150\ \mu\text{L}$, $0.85\ \text{mmol}$) was mixed with the TTA solution containing $16\ \text{mM}$ DPA and $4\ \mu\text{M}$ of InP/ZnS-ACA in 1:1 dry benzene and dry DMSO solvent system in a long-neck cuvette. The system was thoroughly purged for 15 min with Ar, and the sealed cuvette was then irradiated with $532\ \text{nm}$ continuous wave laser with a beam area of $\sim 0.005\ \text{cm}^2$ (after focusing) on the

cuvette wall. The average power of the laser was kept constant at ~ 1 W (197 W cm^{-2} upon focusing) throughout all the photocatalytic experiments. Interestingly, upon 12 h of irradiation, an excellent 85% conversion of the starting 4-bromoacetophenone was observed with the yields of the C-C coupled product and the dehalogenation products to be 34% and 47% respectively (**Figure 6.10**, entry 1). All the products were characterized and the yields were calculated using GC-MS measurements of the reaction mixture after irradiation in presence of dodecane as the internal standard (**Figures 6.14 and 6.15 in appendix**). Additionally, the C-C coupled product was further characterized using ^1H -NMR spectroscopy (**Figure 6.16 in appendix**). Importantly, when the same reaction was conducted under ~ 370 nm UV irradiation in presence of only DPA as the photocatalyst, a staggering $\sim 90\%$ conversion was observed in 12 h (**Figure 6.10**, entry 2 and, **Figure 6.17a in appendix**). This implies that we could achieve a comparable excellence in the reaction yield using TTA-UC process under visible-light excitation, while comparing to the direct UV excitation of DPA photocatalyst. Moreover, a series of other control experiments in absence of QDs, DPA, ACA, and light respectively, shows negligible conversion yield of the reaction, confirming that TTA-UC is solely responsible for the reaction to happen (**Figure 6.10** entries 3-6 and **Figure 6.17 b-e in appendix**).

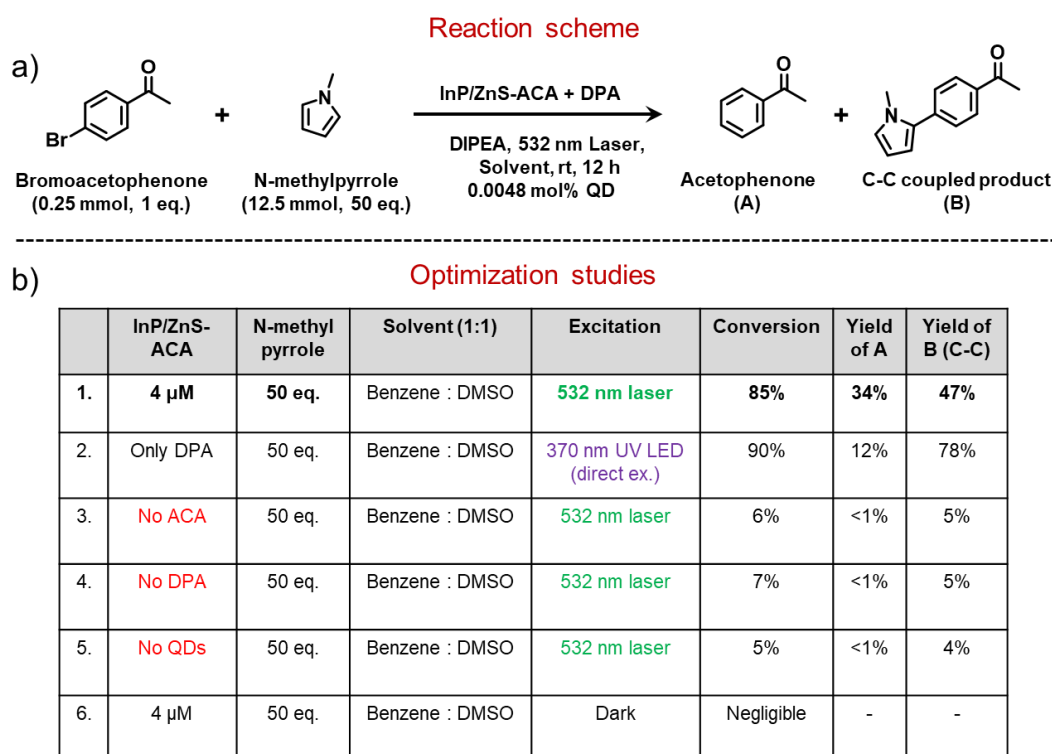


Figure 6.10. Photoredox catalysis using InP/ZnS sensitized TTA-UC process. a) The optimized reaction scheme for the dehalogenation and C-C coupling reaction with 4-bromoacetophenone. b) The table showing the optimization studies as well as other control experiments under different conditions. All these experiments confirm the active involvement of the TTA-UC process in the photoredox catalytic reaction, under visible-light.

The radical driven mechanistic pathway of the dehalogenation and the C-C coupling reaction with aryl halides is well studied in the literature.²⁶ Under our InP/ZnS sensitized TTA-UC system, once the excited $^1\text{DPA}^*$ is generated, the singlet excited $^1\text{DPA}^*$ specie would undergo a sequential reductive and oxidative quenching pathway to activate the C-Br bond on the aryl-bromide substrate. During this process, the DPA is regenerated to take part in the TTA process and eventually carry out the next catalytic cycle (**Figure 6.11a**). To understand the sequence of the oxidative and the reductive cycles of the $^1\text{DPA}^*$ species, we carried out a series of PL quenching experiments. The excited $^1\text{DPA}^*$ state was achieved upon excitation of a dry benzene solution of DPA with 370 nm excitation in a Horiba Fluorolog-3 instrument. Interestingly, there was a minimal quenching of the DPA fluorescence observed upon addition of the substrate, 4-bromoacetophenone into the DPA solution indicating that the electron transfer from $^1\text{DPA}^*$ (i.e., the oxidative quenching) is not the first step (**Figure 6.11b**). Interestingly, upon addition of DIPEA into the DPA solution, a substantial ~80% quenching of the DPA fluorescence was observed, confirming that the reductive quenching is the first step happening with the $^1\text{DPA}^*$ during the catalytic process (**Figure 6.11c**). As a result, the associated radical anion of DPA and the radical cation of DIPEA are generated. The DPA radical anion then undergoes the oxidative quenching process to transfer the electron to 4-bromoacetophenone generating a 4-bromoacetophenone radical anion, which finally dissociates to the aryl radical. This radical then either undergoes a hydrogen atom transfer from the $\text{DIPEA}^{*\cdot+}$ to generate acetophenone, or gets quenched by N-methyl pyrrole present as a coupling agent to yield the C-C coupled product. Overall, we were successful in conducting a reaction with reduction potential (-1.81 V vs SCE) much higher than the sensitizer InP/ZnS QDs (-1.24 V vs SCE) and 532 nm green light excitation, leveraging the exceptional power of the TTA-UC process.

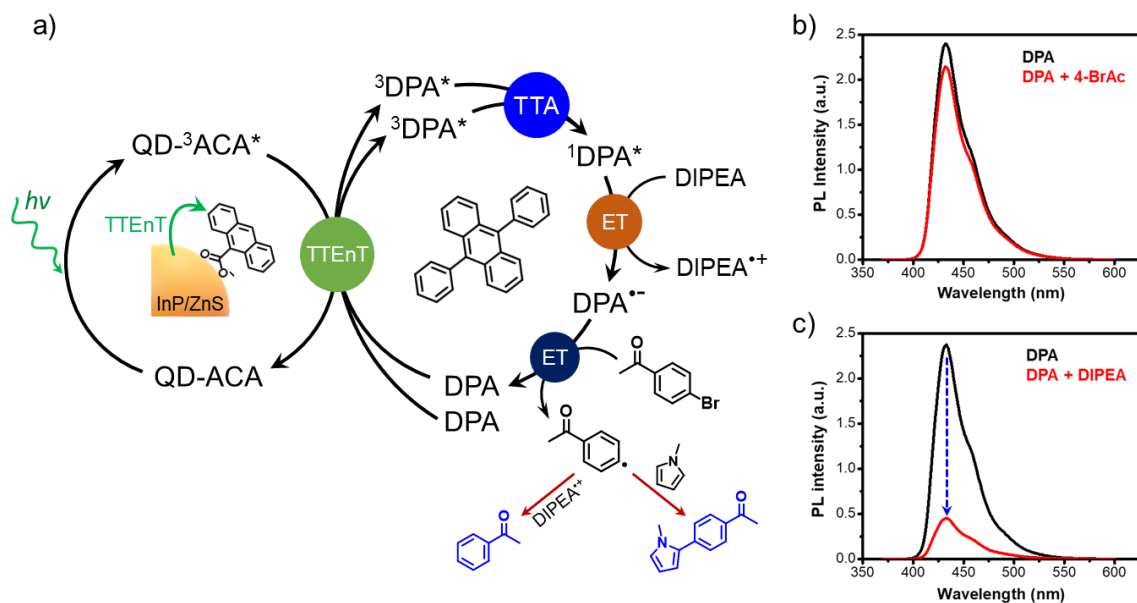


Figure 6.11. a) Schematic representation of the overall reaction mechanism happening under InP/ZnS sensitized TTA-UC process. The photoinduced charge transfer happens sequentially from the annihilator DPA moiety. The photophysical studies show, a) a negligible quenching of $^1\text{DPA}^*$ in presence of 4-bromoacetophenone; whereas, b) a drastic quenching of fluorescence in presence of DIPEA. This indicates that the reductive quenching happens first in presence of DIPEA in the excited $^1\text{DPA}^*$ moiety during the photocatalytic process.

6.4.5. Photopolymerization under TTA-UC

During the dehalogenation reaction of 4-bromoacetophenone, the aryl radical appears as the crucial intermediate essential for the reaction. The ability of our TTA-UC process to generate the radical under visible-light excitation, motivated us to use the radical as an initiator for a photo-polymerization reaction. We chose methyl methacrylate based radical polymerization reaction, which was conventionally carried out in presence of an initiator under UV excitation.²⁷ In a typical TTA-UC triggered radical polymerization procedure, methyl methacrylate monomer (4.7 mmol) was mixed with a cross linking agent 1,6-hexanediol diacrylate (2.2 mmol) in presence of DIPEA (150 μL , 0.85 mmol) and the radical initiator 4-bromoacetophenone. Next, 4.5 μM InP/ZnS-ACA and 16 mg DPA in dry benzene was added. The reaction mixture was then purged with Ar for 15 min followed by irradiation with a focused 532 nm cw laser. Within 10 min, the liquid reaction mixture turned into a solid polymer gel as shown in **Figure 6.12**. The control experiments in absence of DPA or QDs or even either of them shows no signs of polymerization even when the irradiation was carried out for ~ 2 h (table in **Figure 6.12**, entries 2-4). Moreover, no sign of polymerization was observed under continuous heating of the reaction mixture for ~ 2 h at ~ 60 $^\circ\text{C}$, confirming TTA-UC is solely

responsible for the photopolymerization to happen (table in **Figure 6.12, entry 5**). In a positive control experiment, methyl methacrylate monomer (4.7 mmol) along with cross linker hexane-1,6-diacrylate (2.2 mmol) and DIPEA (150 μ L, 0.85 mmol) was irradiated with only DPA (16 mg) under 365 nm UV-LED. Interestingly, here as well, the polymerization occurred within ~10 min, confirming that the efficiency of the TTA-UC based photopolymerization is comparable with the photopolymerization under direct excitation of DPA (table in **Figure 6.12, entry 6**).

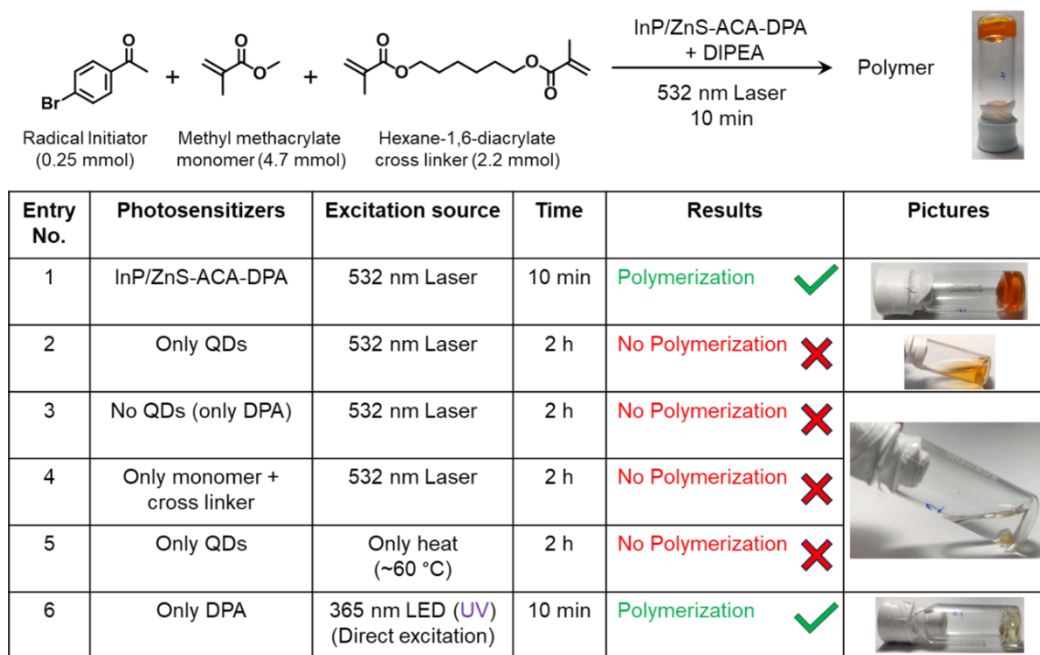


Figure 6.12. Schematic representation of the photopolymerization process under TTA-UC process. The following table summarizes the optimized conditions for the polymerization reaction, as well as the control experiments confirming the sole involvement of the InP/ZnS QD sensitized TTA-UC process.

6.5. Conclusions

A remarkable green-to-blue TTA-UC process was achieved using appropriate InP/ZnS QDs sensitized upconversion system. Thorough photophysical characterization of the TTA-UC process reveals the active involvement of the bimolecular annihilation process, with UC QY of ~5% and an apparent anti-Stokes shift (Δ_{as}) of 0.55 eV. The exceptional potency of the TTA-UC process was utilized to successfully activate substituted aryl-bromides under visible-light excitation. This enabled the accomplishment of both photoredox catalysis as well as the photopolymerization reactions with visible-light, that are traditionally carried out under UV excitation. An excellent yield of the photoredox reaction of ~85% was achieved under 12 h of

excitation. The TTA-UC triggered photopolymerization reaction was completed at a time scale of 10 min, under visible-light. This remarkable introduction of the QD sensitized efficient TTA-UC process into chemical synthesis would open up the possibility to carry out a wider variety of high energy chemical transformations using visible-light excitation. In future, attempts could be dedicated to enhance the efficiency of the TTA-UC process to further enable the upconversion of low energy solar photons, allowing the overall process to be more sustainable as well as economical.

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6.7. Appendix of Chapter 6

6.7.1. Estimation of the band positions of InP/ZnS QDs

Absolute energies of valence and conduction bands of InP/ZnS QDs were calculated using a combination of cyclic voltammetry and UV-vis absorption measurements. All the electrochemical measurements were conducted in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Glassy carbon was used as the working electrode, Ag/AgNO₃ as the reference electrode and Pt was used as the counter electrode.

In case of the used ~3.5 nm InP/ZnS QDs, only the peak corresponding to oxidation was obtained from cyclic voltammogram, located at +1.35 V (vs Ag/Ag⁺ electrode), corresponds to the valence band of the QDs (**Figure 6.13a**). The relative reference electrode potential (E_{ref}) was calculated to be 4.71 eV, using ferrocene/ferrocenium couple as internal standard. So, the measured valence band energy level was estimated to be +1.04 V vs saturated calomel electrode (SCE). The band gap of the used InP QDs was calculated to be 2.29 eV from Tauc plot (**Figure 6.13b**). Hence, the position of the conduction band was calculated to be -1.25 V vs SCE.

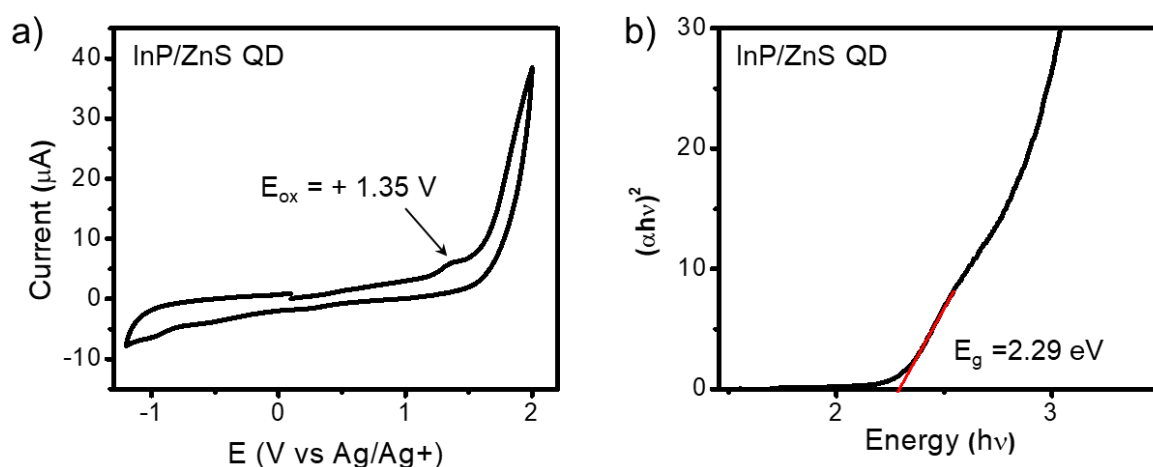


Figure 6.13. a) Cyclic voltammogram of the InP/ZnS QDs measured in acetonitrile solution, at a scan rate of 30 mV/s. b) Construction of Tauc plot for the calculation of band gap of the InP/ZnS QDs. The band gap was calculated to be 2.29 eV.

6.7.2. Characterization and determination of yield of TTA-UC triggered photocatalytic reactions

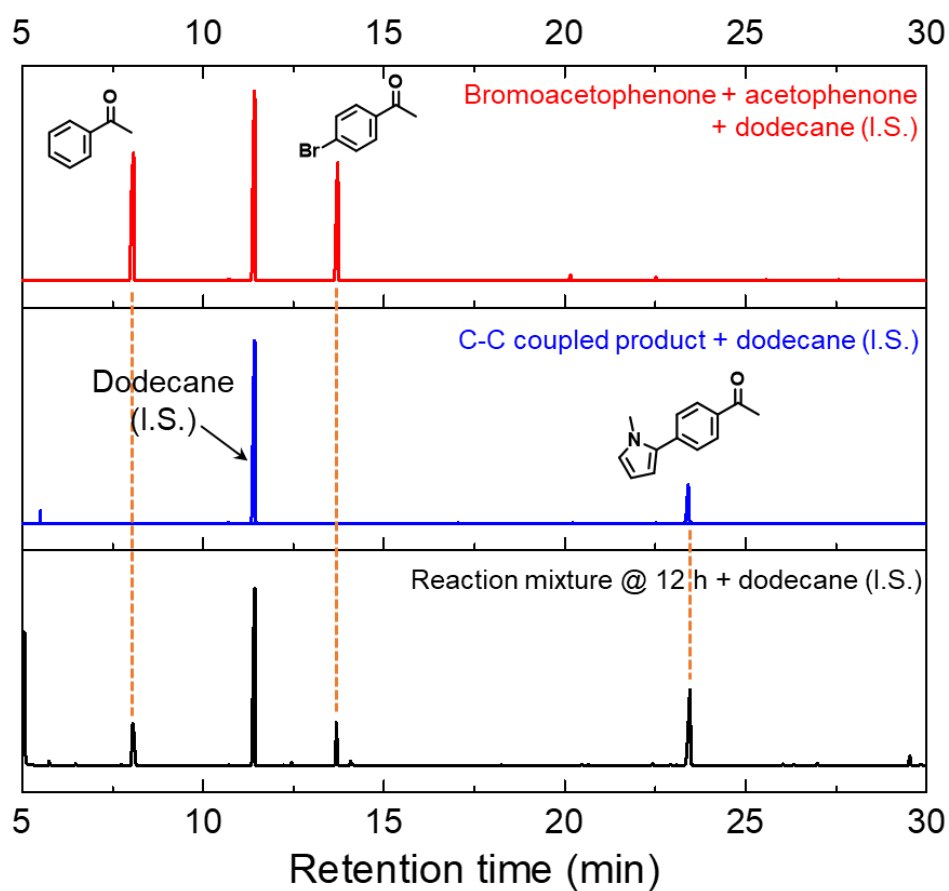


Figure 6.14. Characterization of the dehalogenation and the C-C coupled products formed in the photoredox catalytic reaction under InP/ZnS sensitized TTA-UC process.

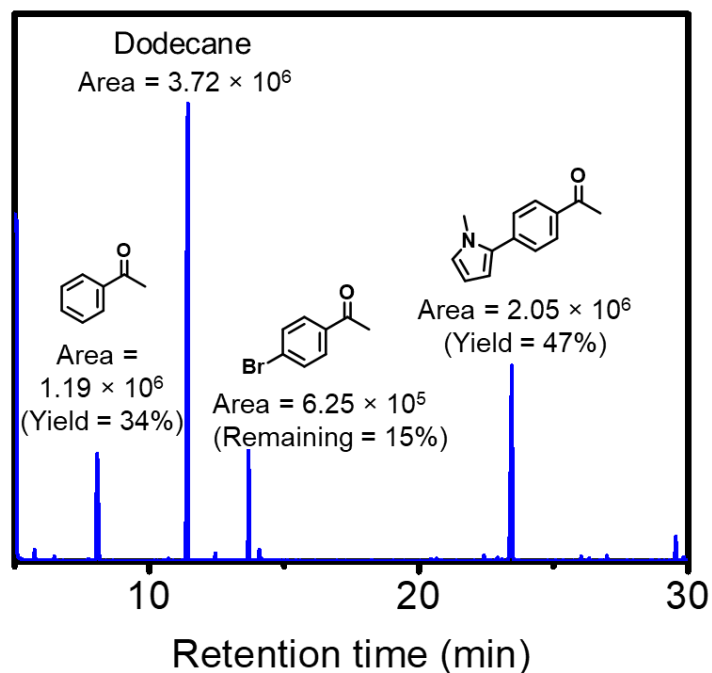


Figure 6.15. The plot of the GCMS measurement of the photoredox reaction with 4-bromoacetophenone under the optimized reaction condition with InP/ZnS QD sensitized TTA-UC process. The corresponding yields were calculated by comparing the area under the curve of the individual peaks with respect to the known amount of the dodecane, present as an internal standard.

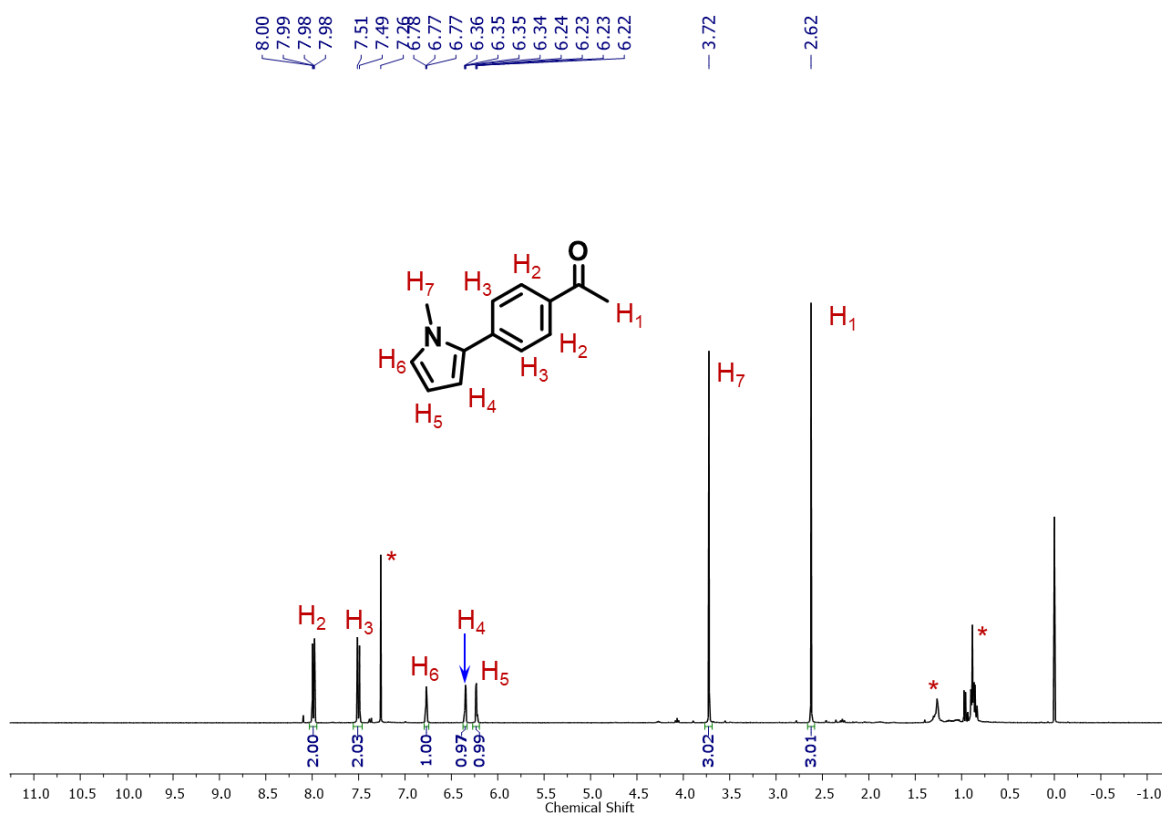


Figure 6.16. ¹H-NMR characterization of the C-C coupled product. All the protons are highlighted with respect to their corresponding peaks. Solvent impurity peaks (e.g. acetone, hexane, chloroform) are marked with asterisk.

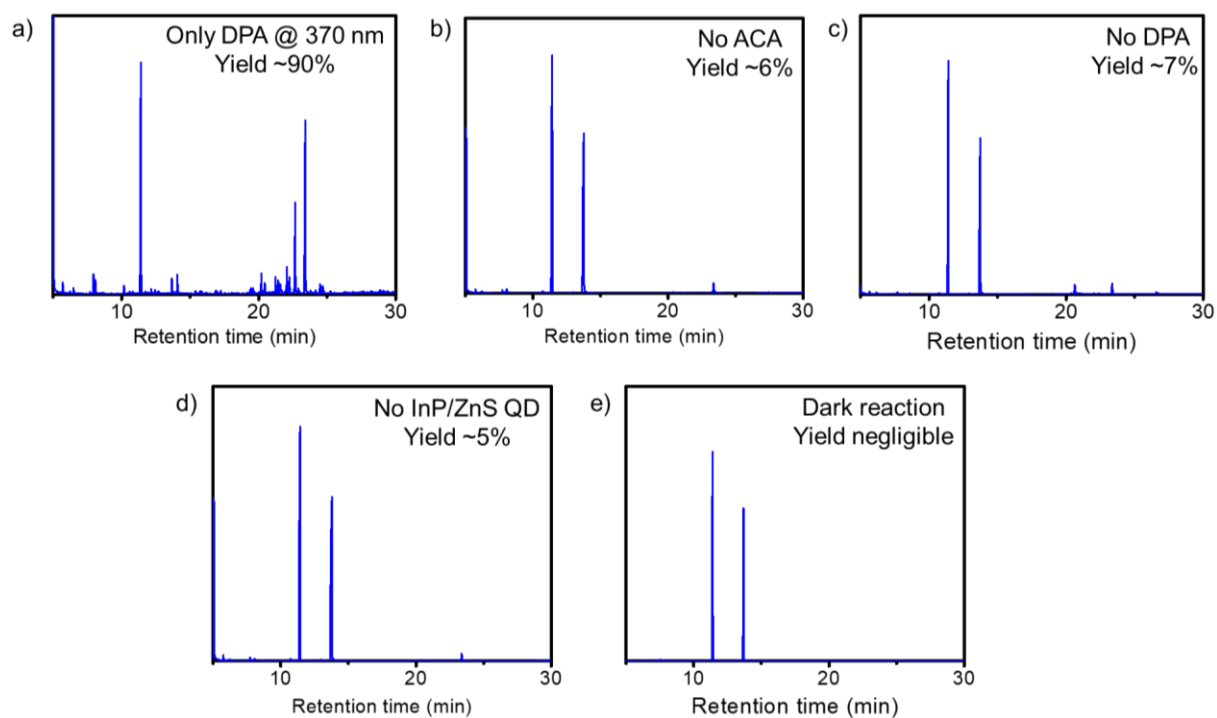


Figure 6.17. a) Reaction under direct excitation of DPA with 370 nm LED. Other control experiments in absence of b) ACA and c) DPA, d) InP/ZnS QDs and, e) photoirradiation shows negligible TTA upconversion as well as product formation. All these control experiments confirm the necessity of the TTA-UC process in performing the photoredox catalytic reaction.

Chapter – 7

Thesis Summary and Future Directions

7.1. Thesis summary

Through the different Chapters of the present thesis, we were able to establish environmentally friendly InP based QDs as efficient photocatalysts. Along with this, we could devise a design strategy to be able to modulate both the core as well as surface properties to carry out a wide variety of chemical transformations under visible-light irradiation. By employing appropriate surface engineering, the QD photocatalysts were stabilised in reaction medium of diverse polarity (both aqueous and organic mediums), as well as favourable catalyst-reactant interaction were introduced to enhance the photocatalytic efficiency. We were successful in designing an InP-QD powered artificial photosynthetic system by systematically coupling both the photosynthetic light and dark cycles connected by efficient photocatalytic cofactor regeneration process. Finally, we could introduce the non-trivial QD sensitized triplet-triplet annihilation process to carry out a high-potential photoredox catalytic transformation that is otherwise not feasible by the QD alone.

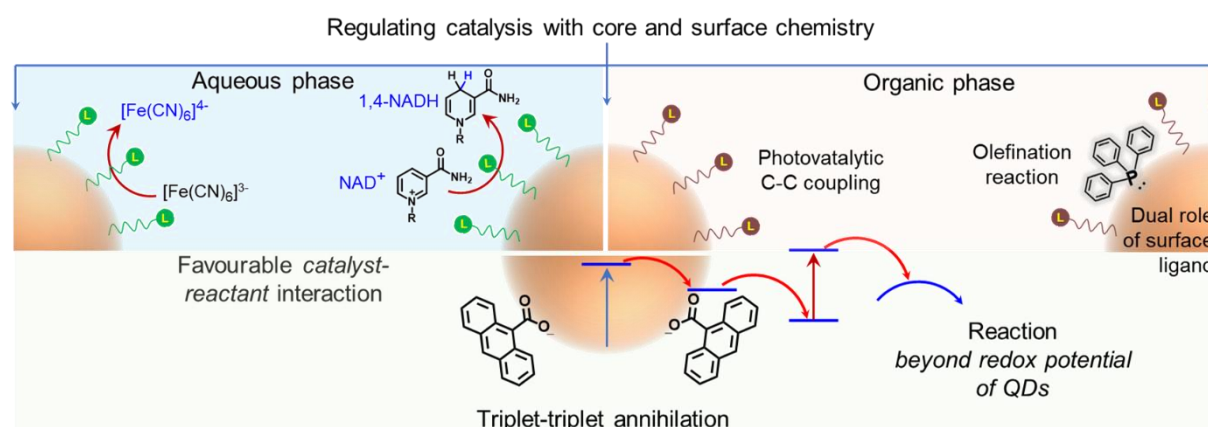


Figure 7.1. A graphical summary of the thesis illustrating the progression of the central motivation to regulate the QD photocatalysis via modulation of both core and surface properties, through the different Chapters (Chapter 3 to 6).

Having a brief go-through of the different Chapters, at first, we went on to establish the potency of InP/ZnS QDs in independently photocatalyzing two important classes of reactions, namely, metal-centred redox and organic C-C coupling reactions (**Figure 7.1**). The two types of reactions were carried out in aqueous and organic medium respectively via proper surface engineering of the QDs. We could also address the recyclability aspect of the QDs towards the multiple cycles of photocatalytic reactions. This was one of the first works which established InP-based QDs as a potential photocatalyst for two different classes of chemical transformations. This work allowed us to reveal the full potential of the InP QDs in devising an artificial photosynthetic system via nicotinamide cofactor regeneration (**Figure 7.1**). We

could closely mimic the photosynthetic light and dark cycles reactions using our devised InP QD-enzyme nanobiohybrid system, finally applying it for the continuous synthesis of useful chemicals under visible-light. We could enhance the catalytic efficiency of the reaction by introducing favourable catalyst-reactant interaction via precise surface engineering of the InP QDs. In another attempt, the decisive role of ligand chemistry in directing the charge transfer process from the QD photocatalyst to the reactant was established. Here, we could identify and establish the dual role of triphenylphosphine in acting both as a surface passivating agent as well as a reactant in a series of QD photocatalyzed olefination reactions (**Figure 7.1**). Finally, we could explore the intriguing non-trivial photophysical processes of QDs in developing a triplet-triplet annihilation based upconversion system to carry out photoredox catalytic reactions (activation of aryl-bromide bond), that are beyond the redox potentials of the QDs alone (**Figure 7.1**).

7.2. Future directions

Careful design of the core and the surface of the environmentally friendly QDs have opened up the applicability of the QD photocatalyst to a wide variety of chemical transformations. But as we can clearly foresee, this can easily be considered as just the very beginning of a versatile field with enormous potential. As a future direction of the current thesis, here are some of the areas where further exploration can be focused on. As the first point, the QD photocatalysis is inherently non-selective in nature. This is a major drawback of the field, which has limited the implementation of QD photocatalysts in reactions requiring high product selectivity. The stereochemical selectivity of reactions can be improved by exploring the highly functional surface of QDs as a template for the photocatalytic transformations (pathway ‘1’ in **Figure 7.2**).¹ Specific chiral ligands can be used to induce stereospecificity for the product formation as well. Next, in order to increase the feasibility of the usage of QD based photocatalysts for large scale applications (e.g., solar fuel generation, biomass valorization), development of photocatalytic device would be crucial (pathway ‘2’ in **Figure 7.2**). Developing leaf-like thin films based on QDs can be a way towards integrating such devices, that are recently being explored in small scales under several reported studies.^{2,3} Moreover, implementation of environmentally friendly InP QD based alternatives to these systems would be highly beneficial for environment, while produced and used as large industrial scales.

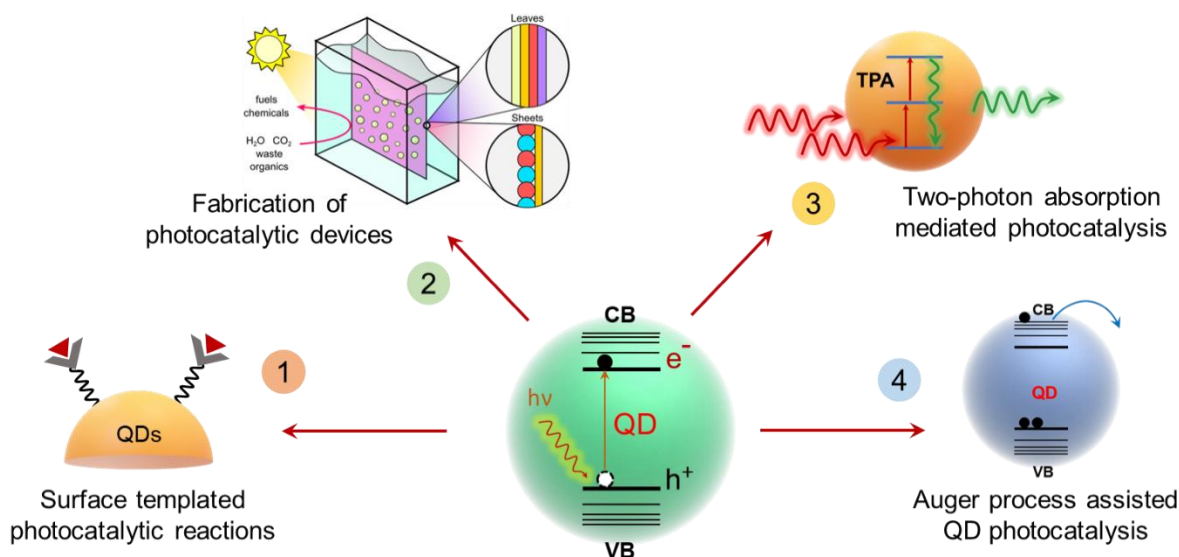


Figure 7.2. Possible future directions in QD photocatalysis. Diagram for process ‘2’ is reproduced with permission from ref 3. Copyright: 2022, American Chemical Society.

In the current thesis, we have introduced the implementation of the TTA-UC based non-trivial photophysical process towards photocatalytic applications. Another prominent way to involve non-trivial phenomena of QDs to photocatalysis is via introducing the two-photon absorption (TPA) property (pathway ‘3’ in **Figure 7.2**). In this process, two low-energy photons can excite the QD to its band edge and allow a photocatalytic process to happen. But, one of the major challenges faced to successfully implement this process is the very low TPA cross section of QDs, which eventually will lead to a lower photocatalytic efficiency. A precise engineering of the QD core and surface has to be undertaken to improve the TPA cross section, leading to an enhanced feasibility of the process. Strategies incorporating the coupling of molecular complexes with high absorption cross section, or, successful funnelling of energy to the QD may help in achieving the goal of increasing the overall TPA cross section of the QD based photocatalytic systems.⁴ Finally, another different type of non-trivial photophysical process can also be exercised with the environmentally friendly QD based photocatalysts (pathway ‘4’ in **Figure 7.2**). Upon regular band edge excitation of the QDs, the photogenerated holes can be replenished using chemical or electrochemical methods. Now, upon a second photoexcitation at this state may generate an excited negative trion state of the associated QD. This negative trion state can undergo an Auger-based pathway to generate a ‘hot electronic’ state of the QD, with reduction potential much higher than the band edge excited QDs.⁵ These highly reducing states can be utilized to carry out photocatalytic transformations with high required potentials, under visible-light irradiation. These discussed possibilities in the QD photocatalysis can be the areas for future exploration and can define a brighter future of the field.

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List of Publications

Included in the thesis

1. **Indra Narayan Chakraborty**, Soumendu Roy, Gayathri Devatha, Anish Rao, Pramod P. Pillai* “InP/ZnS Quantum Dots as Efficient Visible-Light Photocatalysts for Redox and Carbon-Carbon Coupling Reactions” *Chem. Mater.* **2019**, *31*, 72258-2262.
2. **Indra Narayan Chakraborty**, Pradyut Roy, Anish Rao, Gayathri Devatha, Soumendu Roy, Pramod P. Pillai* “The Unconventional Role of Surface Ligands in Dictating the Light-Harvesting Properties of Quantum Dots” *J. Mater. Chem. A*, **2021**, *9*, 7422-7457.
3. **Indra Narayan Chakraborty**, Pradyut Roy, Pramod P. Pillai* “Visible Light-Mediated Quantum Dot Photocatalysis Enables Olefination Reactions at Room Temperature” *ACS Catal.* **2023**, *13*, 7331–7338.
4. **Indra Narayan Chakraborty**, Vanshika Jain, Pradyut Roy, Pramod P. Pillai* “Photoregeneration of Reactive Cofactors with InP Quantum Dots for the Continuous Chemical Synthesis” *Manuscript under peer review*.
5. **Indra Narayan Chakraborty**, Adhra Sury, Aman Chaturvedi, Pankaj Mandal, Pramod P. Pillai* “Triplet-Triplet Annihilation Enables Photocatalysis Beyond the Reduction Potential of InP Quantum Dots” *Manuscript submitted*.

Not included in the thesis

6. Vanshika Jain, **Indra Narayan Chakraborty**, Rohit B. Raj, Pramod P. Pillai* “Deciphering the Role of Light Excitation Attributes in Plasmonic Photocatalysis: The Case of Nicotinamide Cofactor Regeneration” *J. Phys. Chem. C*, **2023**, *127*, 5153-5161.
7. Ankit Dhankhar, Vanshika Jain, **Indra Narayan Chakraborty**, Pramod P. Pillai* “Enhancing the Photocatalytic Regeneration of Nicotinamide Cofactors with Surface Engineered Plasmonic Antenna-Reactor System” *J. Photochem. Photobiol. A Chem.*, **2023**, *437*, 114472.

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1. Figure 3.2c
2. Figure 5.1d
3. Figure 6.3a, b, c
4. Figure 7.2, process 2

Figure 1.1

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Author: Stephen C. Jensen, Stephanie Bettis Homan, Emily A. Weiss

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Feb 1, 2016

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Figure 1.12c, d

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Photocatalytic Hydrogen Production with Tunable Nanorod Heterostructures



Author: Lilac Amirav, A. Paul Alivisatos
Publication: Journal of Physical Chemistry Letters
Publisher: American Chemical Society
Date: Apr 1, 2010

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Photocatalytically Active Superstructures of Quantum Dots and Iron Porphyrins for Reduction of CO₂ to CO in Water



Author: Shichen Lian, Mohamad S. Kodaimati, Emily A. Weiss

Publication: ACS Nano

Publisher: American Chemical Society

Date: Jan 1, 2018

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Enhancing the Rate of Quantum-Dot-Photocatalyzed Carbon-Carbon Coupling by Tuning the Composition of the Dot's Ligand Shell



Author: Zhengyi Zhang, Kedy Edme, Shichen Lian, et al

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Mar 1, 2017

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InP/ZnS Quantum Dots as Efficient Visible-Light Photocatalysts for Redox and Carbon–Carbon Coupling Reactions



Author: Indra Narayan Chakraborty, Soumendu Roy, Gayathri Devatha, et al

Publication: Chemistry of Materials

Publisher: American Chemical Society

Date: Apr 1, 2019

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Catalytic Light-Driven Generation of Hydrogen from Water by Iron Dithiolene Complexes
Author: Hongjin Lv, T. Purnima A. Ruberu, Valerie E. Fleischauer, et al
Publication: Journal of the American Chemical Society
Publisher: American Chemical Society
Date: Sep 1, 2016
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Enhancing the Rate of Quantum-Dot-Photocatalyzed Carbon-Carbon Coupling by Tuning the Composition of the Dot's Ligand Shell



Author: Zhengyi Zhang, Kedy Edme, Shichen Lian, et al

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Mar 1, 2017

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Photocatalytically Active Superstructures of Quantum Dots and Iron Porphyrins for Reduction of CO₂ to CO in Water
Author: Shichen Lian, Mohamad S. Kodaimati, Emily A. Weiss
Publication: ACS Nano
Publisher: American Chemical Society
Date: Jan 1, 2018
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Figure 3.3c, d



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Efficient photocatalytic hydrogen evolution with ligand engineered all-inorganic InP and InP/ZnS colloidal quantum dots

Author: Shan Yu et al

Publication: Nature Communications

Publisher: Springer Nature

Date: Oct 1, 2018

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A Photocatalyst-Enzyme Coupled Artificial Photosynthesis System for Solar Energy in Production of Formic Acid from CO₂
Author: Rajesh K. Yadav, Jin-Ook Baeg, Gyu Hwan Oh, et al
Publication: Journal of the American Chemical Society
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Integration of Enzymes and Photosensitizers in a Hierarchical Mesoporous Metal–Organic Framework for Light-Driven CO₂ Reduction



Author: Yijing Chen, Peng Li, Jiawang Zhou, et al
Publication: Journal of the American Chemical Society
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Institution name	Indian Institute of Science Education and Research Pune
Expected presentation date	Jan 2024
Portions	Scheme 1, figure 1 and figure 2
Requestor Location	IISER Pune Hostel 2, IISER Pune, Dr. Homi Bhabha Road Pashan Pune Pune, Maharashtra 411008 India Attn: IISER Pune
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Visible Light-Mediated Quantum Dot Photocatalysis Enables Olefination Reactions at Room Temperature



Author: Indra Narayan Chakraborty, Pradyut Roy, Pramod P. Pillai

Publication: ACS Catalysis

Publisher: American Chemical Society

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Author: Min Jiang, Haijun Yang, Quentin Lefebvre, Jihu Su, Hua Fu

Publication: iScience

Publisher: Elsevier

Date: 31 August 2018

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Author: Axel Jacobivon Wangelin, Raúl Pérez-Ruiz, Bernhard Dick, et al

Publication: Chemistry - A European Journal

Publisher: John Wiley and Sons

Date: Sep 14, 2015

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Employing Core-Shell Quantum Dots as Triplet Sensitizers for Photon Upconversion

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Publication: Chemistry - A European Journal

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Date: Apr 28, 2016

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