

Synthesis and Studies of Multifunctional Metal-Organic Materials Based on Amino-P(V) Platforms

A Thesis

Submitted in Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

by

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2018

Dedicated to

Babu Ji (My Father)



Mr. Rama Yadav



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IISER Pune

CERTIFICATE

Certified that the work incorporated in the thesis entitled “***Synthesis and studies of multifunctional metal-organic materials based on amino-P(V) platforms***” submitted by **Mr. Ashok Yadav** 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: 12th May 2018
Place: Pune

Dr. R. Boomi Shankar
(Research Supervisor)



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Place: Pune

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Acknowledgements

A protracted and ingenious journey of six years of my Ph.D. is coming to an end. This tenure taught me enough and left an immense impact on my life. I learned a lot, lost and achieved during this period. It gave me an opportunity to interact with various people, who stood with me during my ups and downs and their constant support made it a joyful, pleasant and memorable journey.

I would like to express my sincere gratitude to my thesis supervisor Prof. Dr. R. Boomii Shankar for his excellent guidance, constant encouragement, invaluable suggestions, and supporting this work with ideas and criticisms during my entire Ph.D. I thank him for giving me the freedom to pursue my belief in my way, his faith and motivation which led me to finish my project successfully within the time limitation. I also acknowledge his training for various scientific skills, delivering the project in the right direction and helping to improvise the writing skill. I am very much thankful and appreciate his cooperation and support during my hard days. As a person, I can say he is one of the best supervisors.

I am immensely obliged to Prof. K. N. Ganesh (Former Director) and Prof. Jayant B. Udgaonkar, the Director, IISER-Pune, for providing outstanding research facilities and beautiful research environment. I would like to acknowledge my sincere gratitude to my Research Advisory Committee (RAC) members Dr. P. Hazra (IISER Pune), Dr. K. Krishnamoorthy (NCL Pune) and Dr. B. Praveenkumar (ARDE Pune) for their encouragement, invaluable suggestions, and intellectual support. Many thanks go to all the faculties of the IISER Pune specially faculties of the department of chemistry and the Prof. M. Jayakannan, chair chemistry.

I am grateful to the Dr. B Praveenkumar, Mrs. Divya Pillutla and Mrs. Priyangi Kulkarni for the ferroelectric and dielectric measurements and their fruitful discussions and inputs. I would like to thank Dr. Alexander Steiner (University of Liverpool) for his support to resolve the critical

crystallographic issues. I also appreciate the significant contribution of Dr. Prasenjit Ghosh and Mr. Subrahmanyam Sappati for theoretical calculations. I would like to acknowledge the support of Dr. Sunil Nair, Dr. Surjeet Singh, Mr. Panja, Mr. Ravindranath Bag, Mr. Sarath and Dr. Jitendra Thakur for the dielectric and magnetic measurements. I also thank Dr. T. S. Mahesh, Dr. Jeetender Chugh, Dr. Abhishek Shukla, Mr. Harshad and Mr. Sachin (now my labmate) for recording and processing the NMR data.

I wish to express my thanks to all IISER Pune technical staffs for allowing me access to various instruments: Mrs. Archana (SCXRD), Mr. Parveen Nasa (SCXRD and PXRD), Mr. Prashant Kale (PXRD), Mr. Nilesh Dumbre (PXRD and SEM), Mr. Anil & Mr. Yatish (SEM), Mrs. Megha (AFM), Mrs. Swati M. Dixit (MALDI-TOF and CHN analysis), Mrs. Swati (HRMS), Mrs. Deepali & Mr. N. Dalvi (NMR), Mr. Mahesh Jadhav (TGA), Mr. Suresh Prajapati (UG Chemistry Lab), Mr. Ganesh Dimbar (IR). I would like to acknowledge the consistent support of the staff of Dean Doctoral Studies Office, especially Ms. Dipali Dalvi and Mr. Tushar. I also thank the administrative department of the IISER Pune for their support especially Col. (Retd.) G. Raja Sekhar (Registrar, IISER-Pune), Dr. V. S. Rao, Mr. Prabhash and Mr. Mayuresh. I thank Dr. Umeshreddy Kacherki (Librarian) for support through library services.

My heartfelt gratitude goes to my lab seniors Dr. Arvind Gupta, Dr. Anant, I learnt a lot from them and they supported me always during my initial days and labmates Mahesh, Vijayakanth, Rajashekar, Rishabh, Santosh, Neetu, Sachin, Meghamala, Swati, Atul, Sravan, and Anupriya for their productive discussion about research and support which made it possible. I would like to convey my special thanks to Anant, Mahesh, and Viji for sharing a lot of beautiful moments with me. I also thank Arun, Indra, Saurabh, Kiran, Prashant, and Mehak for working with me and contributing to my research. Gratitude is also extended to some of my seniors in IISER Pune especially Dr. Gopalakrishna, Dr. Santosh Gadekar, Dr. Kiran Reddy, Dr. Panchal, Dr.

Barun Dhara, Dr. Ranguwar Rajendra, Dr. Rajendra Aluri, Dr. K. Narasimha, Dr. Ravi Kiran and Dr. Kishore. I thank all my IISER friends especially, Gurivi, Rajkumar, Subbu, Nanda, Chenna, Bijoyanand, Ashok (Kanti), Mahesh, Plawan, Shammii, Manoharan, Manikannan, Dinesh (Lungi), Aparna, Prabhat, Prahlad and Tushar for their support and to make an enjoyable life in campus as well as outside of institute.

My gratitude goes out to all my M.Sc. Professor especially, Prof. Jagdish (M.Sc. project supervisor), Prof. Prashant Dube, Prof. LDS Yadav, Prof. Jagdamba Singh, Prof. V. Krishna and Prof. Krishna Srivastava for their teaching, motivation, and support. I must also give thanks to all my M.Sc. Friends especially, Devesh, Shashi, Vinod, Ved, Rakesh, Angela, Sujit, Manoj, Sandeep, Ravi, Praveen, Brijesh, Rupam, Ranju, Juhi, Neelam, Shalini, Saurabh, Pankaj, Om Prakash, Ratnesh, and Preeti. I would like to thank my B.Sc. Friends Vikash, Rajesh, Suresh, Sanjeev, Sanjay, and Avinash. I also acknowledge all my Allahabadi friends specially Akhilesh, Nitin, Kamlesh, Anil, Ratnakar, Anup, and Shweta. I would like to admit my school friends Chandan, Pradeep, Vinay (Late), Vivek, Chanchal, Anil, Ravindra, Suraj, Satyendra, and Vinod.

I am deeply indebted to my village (childhood buddies) friends Dinesh, Kamlesh, Vinay, Rajkumar, Sunil, Santosh and Vrijesh for their continuous support and standing behind me anytime and in any condition. In addition, recognition must be given to closest and dearest buddy Dinesh. I don't have enough words to express my feelings about him. He is the person who always saw me as a star in the sky. He put so much effort to keep my chin up and supported me to achieve my goals. He never-ever left me alone in my hardships even when I lost all the hopes. He is the one who always appreciates me for my small and significant achievements. I again thank him for being with me, and hopefully, we will be there to support each other unconditionally.

A debt of gratitude is also owed to Shraddha, a special one without whom this acknowledgment would be incomplete. She has made this

journey a pleasant one with her love, care, and support. She has been a pillar of strength through all my lows and a source of encouragement and inspiration for my highs.

No words can ever convey my sense of gratitude for my parents, who paved the path before me, upon whose shoulders I stand, Babu Ji (Mr. Rama Yadav, Father), Mai (Mrs. Basanti Devi, my lovely mother) and other family members Baba (Late Jai Shree Yadav, Grandfather), Chacha Ji (Mr. Jai Ram Yadav), Chachi Ji (Mrs. Tara Devi), Bhaiya (Mr. Ramashray Yadav), Bhabhi (Mrs. Soni yadav) Anuj (younger brother), Sonu and Golu (cousin brothers), my sweet sisters Anita, Sangita and Saroj (Cousin), and chiller parties Aditi (Pari), Rhiaa (Kuttu), Arnav (Ghanti) and Arsh (Kallu). It is not possible without their support, motivation, patience, and sacrifices. They are central cause and inspiration for all desires which I achieved now or will succeed in future.

I would like to extend my thanks to IISER Pune and CSIR for providing the fellowship to pursue my research. I gratefully acknowledge the DST India for financial support to attend the international TOPOS workshop held in Samara, Russia. I also thank the SCOMM, MTIC, NSC for giving me an opportunity to present my research work. I would like to acknowledge American Chemical Society (ACS), Royal Society of Chemistry (RSC), Elsevier Science Ltd., John Wiley & Sons, Springer, etc. for publishing my research articles as well as for providing the permission and reprinting the materials under copyright.

Finally, I thank Almighty God for his blessings and giving the beautiful life with precious opportunities.

Ashok Yadav

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Synopsis

*The thesis entitled “**Synthesis and Studies of Multifunctional Metal-Organic Materials based on Amino-P(V) Platforms**” is focused on the synthesis of metal-organic cages/polyhedra and coordination polymers based on the amino phosphorus (V) ligands having rigid and flexible backbone and the studies of their host-guest chemistry and physical properties such as luminescence, dielectric and ferroelectric behaviour.*

Chapter 1: Introduction

This chapter provides a brief history of the coordination compounds particularly metal-organic materials (MOMs). Various structural forms of MOMs have been described with a particular focus on the most prevalent types of metal-organic polyhedra (MOPs) and Metal-organic frameworks (MOFs). Especially, the types of metal-organic polyhedra such as Platonic, Archimedean, Faceted and Stellated MOPs and the design principles involved in their construction has been explained in detail. Additionally, this chapter includes a brief discussion about the application of metal-organic polyhedra viz. catalysis, biomedical applications, sensing, molecular recognition, gas adsorption, and their utility as dielectric and ferroelectric materials. Finally, it gives a brief outline and the major objective of the thesis.

Chapter 2: Imido-P(V) Supported Neutral Tetrahedral Cages Showing Selective Encapsulation of o-Xylene and Mesitylene over other Analogues

The energy-efficient separation of chemical feedstocks is major sustainability challenge. Porous extended frameworks such as zeolites or metal-organic frameworks are one of the potential solutions to this problem. Tetrahedral Pd(II) containing cages that are neutral and organic soluble are the recent focus of our laboratory. Spurred by a recent report from our group on tetrahedral $\{[\text{Pd}_3(\text{X})]_4(\text{C}_2\text{O}_4)_6\}$ cage that shows selective encapsulation of benzene over other aromatic compounds, in this chapter we report two porous discrete metal-organic cages for separation of substituted aromatic molecules according to their size and shape. Two tetrahedral cages $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}]_4(\text{L}_\text{A}^-)_6\}$, **1** and $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}]_4(\text{L}_\text{B}^-)_6\}$, **2** were synthesized by the reaction of

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$\{Pd_3[(N^iPr)_3PO](OAc)_2(OH)\}_2 \cdot 2(CH_3)_2SO$ building unit with chloranilate (L_A^-) and 2, 5-dihydroxybenzoquinone (L_B^-) ions respectively. The cage assemblies **1** and **2** show selective encapsulation of o-xylene (OX) and mesitylene (MES) over other aromatic hydrocarbon analogues, respectively (Figure 1). This selective encapsulation was confirmed by the MALDI-TOF mass and 1H -2D-DOSY-NMR spectral analysis. It was also supported by theoretical binding energy calculation which gave highest binding energy for the inclusion compounds of o-xylene and mesitylene with **1** and **2**, respectively.

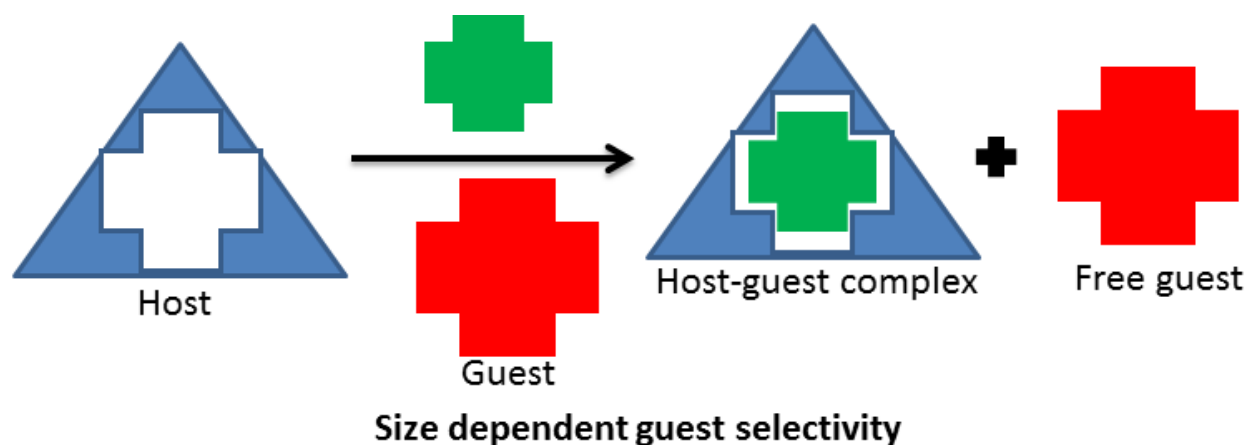


Figure 1: Diagrammatic representation of the size dependent selective host-guest complex formation of the tetrahedral assemblies.

Chapter 3: Mapping the Assembly of Metal-Organic Cages into Complex Coordination Networks

Structural transformations of supramolecular assemblies play an important role in the synthesis of complex metal-organic materials. Nonetheless, more than often little is known of the assembly pathways that lead to the final product. Herein, we describe the conversion of cubic metal-organic polyhedra to connected-cage networks of varying topologies. The neutral cubic cage assembly of formula $\{Pd_3[PO(N^iPr)_3]\}_8(PZDC)_{12}$ has been synthesized from $\{Pd_3[(N^iPr)_3PO](OAc)_2(OH)\}_2 \cdot 2(CH_3)_2SO$ and 2,5-pyrazenedicarboxylic acid (PZDC-2H). This 42-component self-assembly is the largest known among the neutral cages with Pd(II) ions. The cage contains twenty-four vacant

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carboxylate O-sites at the PZDC ligands that are available for further coordination. Post-assembly reactions of the cubic cage with Fe(II) and Zn(II) ions produced cage-connected networks of *dia* and *qtz* topologies, respectively. During these reactions, the discrete cubic cage transforms into a network of tetrahedral cages that are bridged by the 3d metal-ions. The robustness of the $[\text{Pd}_3\{\text{PO}(\text{N}^i\text{Pr})_3\}]^{3+}$ molecular building units made it possible to map the post-assembly reactions in detail, which revealed a variety of intermediate 1D and 2D cage-networks (Figure 2). Such step-by-step mapping of the transformation of discrete cages to cage-connected frameworks is unprecedented in the chemistry of coordination driven assemblies.

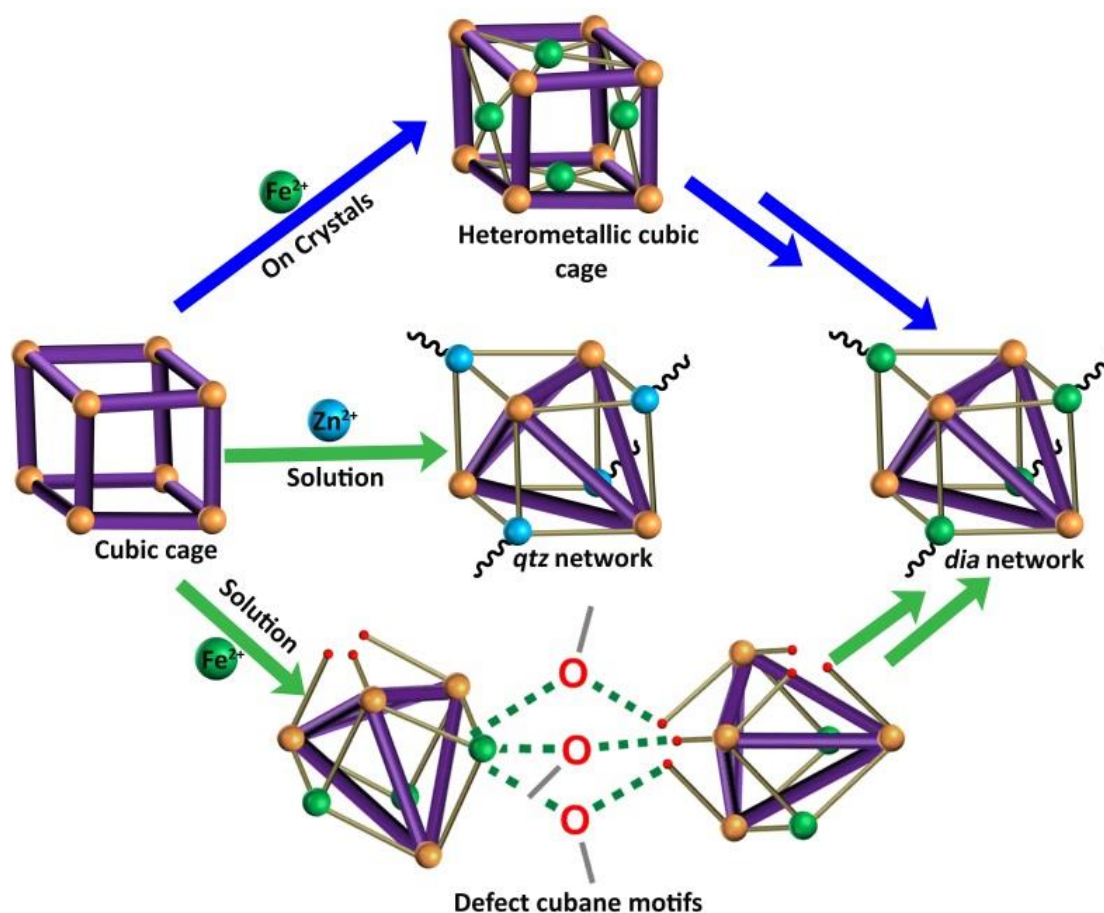


Figure 2: Diagrammatic representation of the post-assembly reaction of cubic cage with Fe(II) and Zn(II) ions in solution as well as in solid state.

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Chapter 4: Anion Induced Ferroelectric Polarization in a Luminescent Metal-Organic Cage Compound

Metal-organic crystalline solids with ferroelectric properties have attracted significant attention recently as materials for high-tech applications. This chapter shows the synthesis of two crystalline assemblies that contain cationic metal-organic cages $\{[\text{Zn}_6(\text{H}_2\text{O})_{12}][\text{TPTA}]_8\}(\text{NO}_3)_{12} \cdot 26\text{H}_2\text{O}$ (**11**) and $\{[\text{Zn}_6(\text{H}_2\text{O})_{12}][\text{TPTA}]_8\}(\text{ClO}_4)_{12} \cdot 18.75\text{H}_2\text{O}$ (**12**) featuring the tripodal ligand $[\text{PS}(\text{NH}^3\text{Py})_3]$ (TPTA).

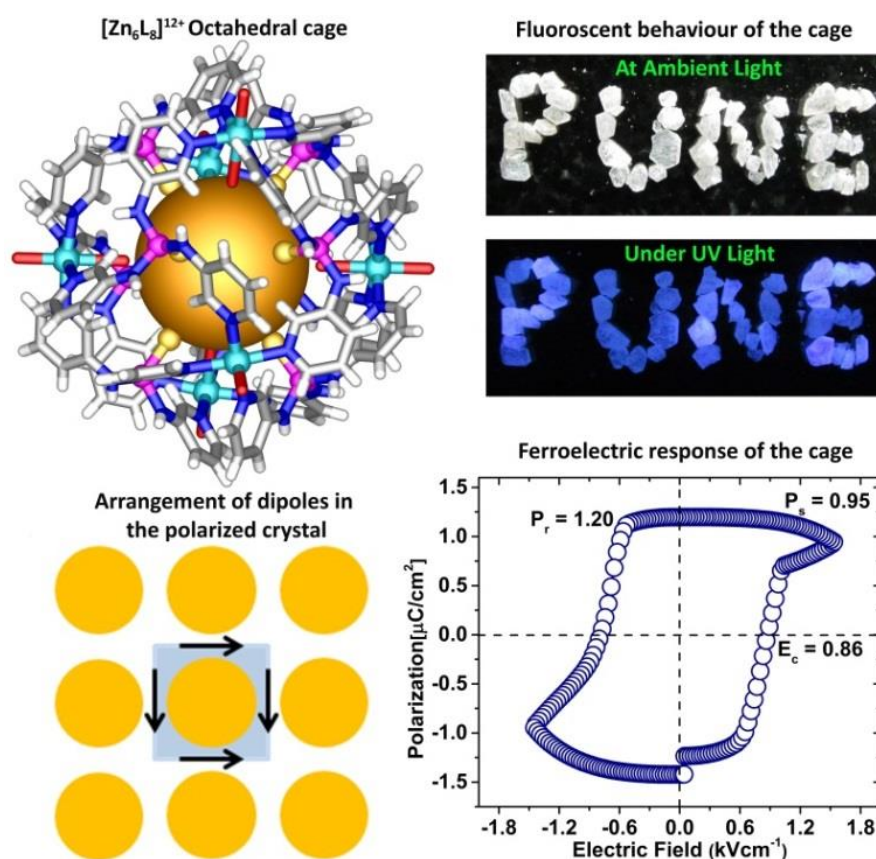


Figure 3: View of the discrete octahedral cage, **11** ordered arrangement of polar nitrate anions in the packing cavity. Colour of the crystals under ambient and UV light and the ferroelectric hysteresis loop of octahedral cage **11**.

Ferroelectric measurement on a single crystal of **11** gave a remnant (P_r) polarization of $1.2 \mu\text{C}/\text{cm}^2$ at room temperature. The ferroelectric response originates from the toggling of nitrate anions and solvate molecules found in pockets between the cages. The

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temperature dependent permittivity of **11** shows an anomalous dielectric peak at 20 °C. This is attributed to the desolvation assisted dielectric relaxation behaviour and signifies the role of solvate molecules in the ferroelectric behaviour of **11**. In addition, this material is highly luminescent exhibiting a bright blue emission under UV-light (Figure 3). This multifunctional behaviour is unique among metal-organic cage frameworks.

Chapter 5: Connected-Cage based Reversible Hierarchical Frameworks Exhibiting Axial Ferroelectric Anisotropy

Recently molecular ferroelectrics are a choice of alternate ferroelectric materials over the conventional ceramics due to nontoxicity, high crystallinity and solution processability. In this report, ferroelectric anisotropy was investigated in a discrete $[\text{Cu}_6\text{L}_8]^{12+}$ octahedral cage and its one dimensional cage connected framework. We have synthesized a octahedral nanocage, **13** $\{[\text{Cu}_6(\text{H}_2\text{O})_{12}][\text{TPTA}]_8\} \cdot (\text{NO}_3)_{12} \cdot 32\text{H}_2\text{O}$, $\{\text{TPTA}, [(\text{NH}^3\text{Py})_3\text{P}=\text{S}]$ (^3Py = 3-Pyridyl)}. Compound **13** gave hierarchical 1D, 2D and 3D cage connected metal-organic frameworks (ccMOFs) **14**, $\{[\text{Cu}_6(\text{H}_2\text{O})_{10}\text{Cl}][\text{TPTA}]_8\} \cdot (\text{NO}_3)_{11} \cdot 12\text{H}_2\text{O}$; **15**, $\{[\text{Cu}_6(\text{H}_2\text{O})_7\text{Cl}_3][\text{TPTA}]_8\} \cdot (\text{NO}_3)_9 \cdot 44\text{H}_2\text{O}$; and **16**, $\{[\text{Cu}_6(\text{H}_2\text{O})_6\text{Cl}_3][\text{TAPP}]_8\} \cdot (\text{NO}_3)_9 \cdot 42\text{H}_2\text{O}$ respectively, by replacing the axial coordinated water (at Cu^{2+}) with chloride ion. Formation of these assemblies are reversible and can be converted back to the lower dimensional ones by using chloride ion acceptors (AgNO_3 or $(^n\text{Bu}_4\text{N})\text{NO}_3$). Ferroelectric (FE) measurements on the respective crystals of **13** and **14** showed anisotropy in ferroelectricity with high remnant polarization values of 20.46 and 28.90 μCcm^{-2} along the polar c-axis compared to other axes which gave a lower remnant polarization values of 1.58 and 6.28 μCcm^{-2} for **13** and **14**, respectively. The difference in the packing arrangement as well as their dimensionality in **13** and **14** causes anisotropy due to the difference in the extent of interactions between the solvents, anions and the metal-organic assembly. Additionally, the twisting in the polyhedra helps to increase in the polarization of these compounds. The temperature dependent dielectric permittivity (ϵ') measurement for all the assemblies gave anomalous peaks in range of 45-50 °C with marked changes in the dielectric constant values. Thus the ferroelectric (in case of **13** and **14**) and dielectric

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behaviour (in case of **13-16**) can easily be tuned as the assemblies can be reversibly converted among each other in a stepwise manner (Figure 4). The combination of high polarization, axial ferroelectricity and the tunable dielectric properties make these materials as a promising candidate for the future applications.

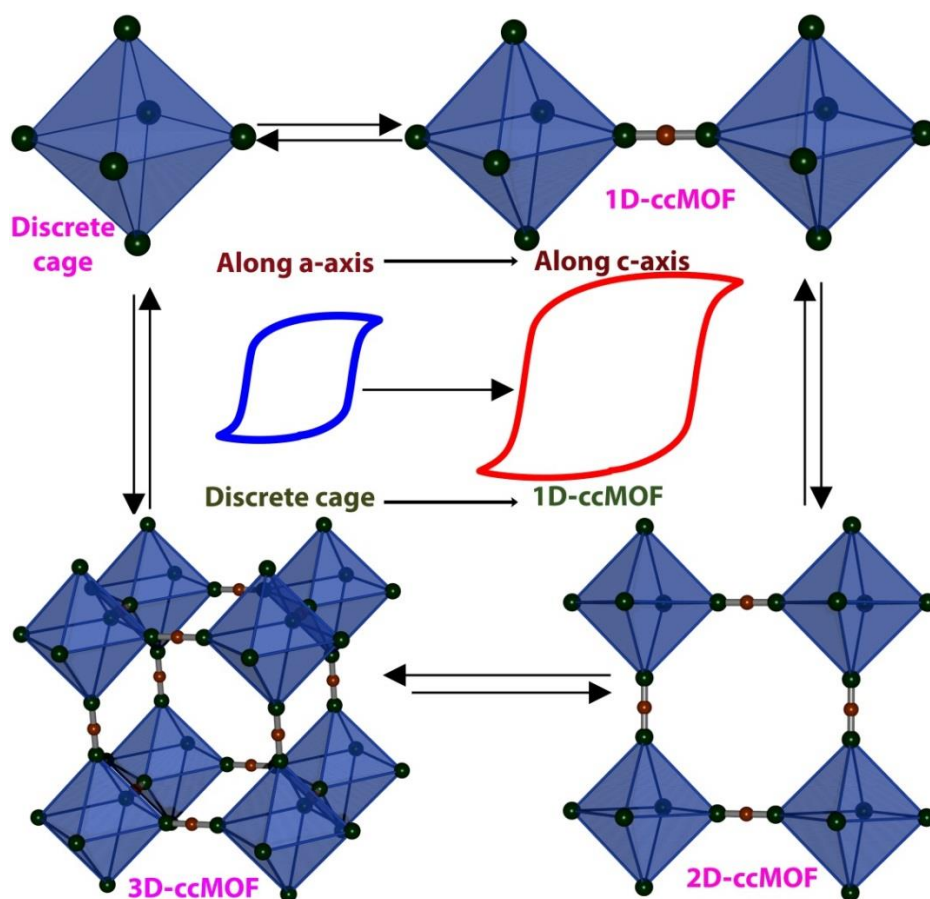


Figure 4: (a) Diagrammatic view of the formation of discrete octahedral cage and its cage connected 1D-, 2D- and 3D-frameworks. Inset imaginary P-E hysteresis loop of discrete and 1D-assembly along a- and c-axis showing increase in polarization on going from discrete to 1D-assembly and suggesting the existence of ferroelectric anisotropy in both molecules.

Chapter 6: Luminescent Cationic Copper Iodide Cluster based Coordination Polymers and their Unusual Thermochromic Behaviour

Employing tridentate thiophosphoramidate ligands, $[(\text{NHR})_3\text{P}=\text{S}]$ (L^1 : R = 3-quinolinyl (AQ); L^2 : R = 3-pyridyl (PY)), two C_3 -symmetric cationic MOFs, **17** $\{[(\text{L}^1)_2(\text{Cu}_6\text{I}_5)](\text{OH})\cdot$

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$3\text{DMF}\cdot 2.5\text{MeOH}\}_n$ and **18** $\{[(\text{L}^2)_2(\text{Cu}_6\text{I}_4)](\text{OH})_2\cdot 3\text{DMF}\}_n$, were synthesized. Photo-physical studies on the 2D-MOF **17** showed an unusual thermochromic luminescent behavior emitting a blue fluorescence at 298K due to the AQ chromophore and a pale-orange phosphorescence at 77K due to the $[\text{Cu}_6\text{I}_5]^+$ unit, while the 3D-MOF **18** exhibited green phosphorescence at both 298K and 77K. The occurrence of the phosphorescence at 77K in **17** is attributed to the intra-molecular energy transfer the T_1 state of the AQ moieties to the ^3CC -excited state of the cluster (Figure 5). Further, the absorption and emission maxima of these MOFs were substantiated by TD-DFT calculations.

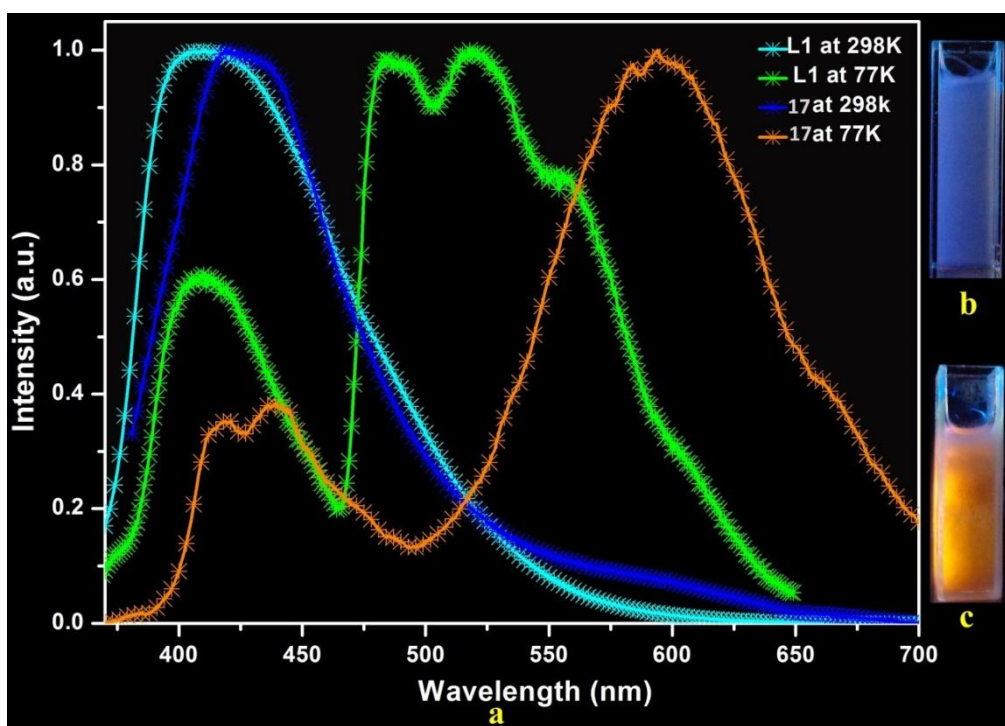


Figure 5: (a) Plot of emission spectra of ligand and the Cu_6I_5 cluster MOF **17** at room temperature as well as 77 K . Solution colour of **17** at RT (b) and 77K (c) in DMF.

Finally, a brief conclusion and future perspectives for the studies described in this thesis has been provided at the end.

Abbreviations

Anal.	Analysis
Calcd.	Calculated
ccMOF	Cage Connected Metal-Organic Framework
CCDC	Cambridge Crystallographic Data Centre
DFT	Density Functional Theory
DMF	N, N-Dimethyl Formamide
DMSO	Dimethyl Sulphoxide
DOSY	Diffusion Ordered Spectroscopy
DSC	Differential Scanning Calorimetry
ESI	Electron Spray Ionization
E _c	Coercive Field
FET	Field-Effect Transistor
FT-IR	Fourier Transform Infrared Spectroscopy
HRMS	High Resolution Mass Spectroscopy
Hz	Hertz
KDP	Potassium Dihydrogen Phosphate
KBr	Potassium Bromide
M.P.	Melting Point
MALDI-TOF	Matrix-Assisted Laser Desorption/Ionization – Time of Flight
MeOH	Methanol
MeCN	Acetonitrile
mg	Milligram
min	Minutes
μL	Microliter
mL	Milliliter
mm	Millimeter
mmol	Millimoles
MOF	Metal-Organic Framework
NMR	Nuclear Magnetic Resonance

Abbreviations

NLO	Non-Linear Optical
RT	Room Temperature
Ph	Phenyl
P _r	Remnant Polarization
P _s	Saturation Polarization
Py	Pyridyl
PZDC	Pyrazene Dicarboxylic Acid
PXRD	Powder X-ray Diffraction
RAM	Random Access Memory
SCXRD	Single Crystal X-ray Diffraction
SCSC	Single Crystal to Single Crystal
SHG	Second Harmonic Generation
T _c	Curie Temperature
TPTA	Tris(3-aminopyridyl)thiophosphoramidate
TGA	Thermogravimetric Analysis
TGS	Triglycine Sulphate
TD-DFT	Time-Dependent Density Functional Theory
VT-PXRD	Variable Temperature Powder X-ray Diffraction

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Chapter 3

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List of Publications

1. Connected-Cage based Reversible Hierarchical Frameworks Exhibiting Ferroelectric Anisotropy

[Ashok Yadav](#), Priyangi Kulkarni, B. Praveenkumar, and Ramamoorthy Boomishankar, Submitted.

2. Mapping the Assembly of Metal-organic Cages into Complex Coordination Networks

[Ashok Yadav](#), Arvind K. Gupta, Alexander Steiner and Ramamoorthy Boomishankar, *Chem. Eur. J.* **2017**, 23, 18296–18302.

3. Anion Induced Ferroelectric Polarization in a Luminescent Metal-Organic Cage Compound

[Ashok Yadav](#), Pillutla Divya, Anant Kumar Srivastava, B. Praveenkumar, Alexander Steiner and Ramamoorthy Boomishankar, *J. Mater. Chem. C*, **2017**, 5, 10624-10629.

4. Cationic and Neutral Copper(I) Iodide Cluster MOFs Derived from Tridentate N-donor Functionalized P(V) Ligands: Synthesis, Structure and Photophysical Properties

[Ashok Yadav](#), Mahesh S. Deshmukh and Ramamoorthy Boomishankar *J. Chem. Sci.*, **2017**, 129, 1093-1103.

5. A Neutral Cluster Cage with a Tetrahedral $[Pd_{12}^{II}L_6]$ Framework: Crystal Structures and Host–Guest Studies

Arvind K. Gupta, [Ashok Yadav](#), Anant Kumar Srivastava, Kormathmadam Raghupathy Ramya, Harshad Paithankar, Shyamapada Nandi, Jeetender Chugh, and Ramamoorthy Boomishankar, *Inorg. Chem.* **2015**, 54, 3196-3202.

6. Thermochromic and Mechanochromic Luminescence Umpolung in Isostructural Metal–Organic Frameworks based on Cu_6I_6 Clusters

Mahesh S. Deshmukh, [Ashok Yadav](#), Rakesh Pant, and Ramamoorthy Boomishankar *Inorg. Chem.* **2015**, 54, 1337–1345.

7. Concentration-Dependent Ratiometric Turn-On Selective Fluorescence Detection of Picric Acid in Aqueous and Non-aqueous Media

[Ashok Yadav](#) and Ramamoorthy Boomishankar, *RSC Adv.*, **2015**, 5, 3903–3907.

List of Publications

8. Cationic Copper(I) Iodide Cluster MOF Exhibiting Unusual Ligand Assisted Thermochromism

[Ashok Yadav](#), Anant Kumar Srivastava, Ayyakkalai Balamurugan and Ramamoorthy Boomishankar, *Dalton Trans.*, **2014**, 43, 8166–8169.

9. Discrete and Polymeric Coordination Assemblies Derived from 3-Pyridyl Attached Flexible Phosphoric Triamide Ligand and Copper Salts

Arvind K. Gupta, [Ashok Yadav](#) and Ramamoorthy Boomishankar, *Proc. Natl. Acad. Sci., India, Sect. A Phys. Sci.* **2014**, 84, 205-212.

10. Tetrahedral $[Pd_{12}L_6]$ Cages Showing Selective Encapsulation of o-Xylene and Mesitylene over other Analogues

[Ashok Yadav](#), Subramannayam Sapati, Atul Chaudhary, and Ramamoorthy Boomishankar, Manuscript under preparation.

11. Magneto-Electric Behaviour in M_6L_8 Discrete Cage and its Cage Connected 2D-Network

[Ashok Yadav](#) and Ramamoorthy Bomishankar, Manuscript under preparation.

Chapter 1

Introduction

1.1 Coordination compounds

The modern coordination chemistry was originated from the work of Alfred Werner in 1893. For the first time, he described the structures of transition metal complexes on the basis of oxidation state, coordination number, and geometry.¹ Soon after, understanding of the coordination geometry of the metal ions and the rational synthetic routes to access metal complexes were achieved. In the past 100 and above years, tremendous growth has been witnessed in the coordination chemistry relevant to structure, synthesis, and reactivity of numerous metal complexes ranging from simple metal-ligand complexes to organometallic catalysts to inorganic and inorganic-hybrid polymers. In recent decades, supramolecular coordination complexes (SCCs) and metal-organic frameworks (MOFs) are the two new areas that have been probed in great detail. The supramolecular coordination complexes are the discrete systems in which the metal center undergoes self-assembly reactions with the multi-site coordinating ligands in a specific angularity to give structurally precise architectures. The metal-organic frameworks (MOFs) encompass an infinite array of networks of the metal centers or the inorganic clusters supported by the organic ligands as a linker involving metal-ligand coordination bonds. These two branches, SSCs and MOFs, share similar design concepts and as such these architectures can be largely defined as the metal-organic materials (MOMs).

Metal-organic materials were not explored much before the early 1990's²⁻⁸ and received more attention due to their facile synthesis appealing structures and their amenable nature to crystal engineering design strategies.⁹⁻¹⁶ Metal-organic materials are largely classified into discrete (e.g., metal-organic polyhedra, spheres, nanoballs or metal-organic polygons) and polymeric assemblies (such as porous coordination polymers, PCPs, metal-organic frameworks, MOFs, or hybrid inorganic-organic materials) (Figure 1.1). In mid of 1950's A. F. Wells first introduced, a particularly useful and simple “node and spacer” model to interpret the inorganic crystals which laid the foundations for today's research activities in the area of metal-organic materials.¹⁷⁻²⁰

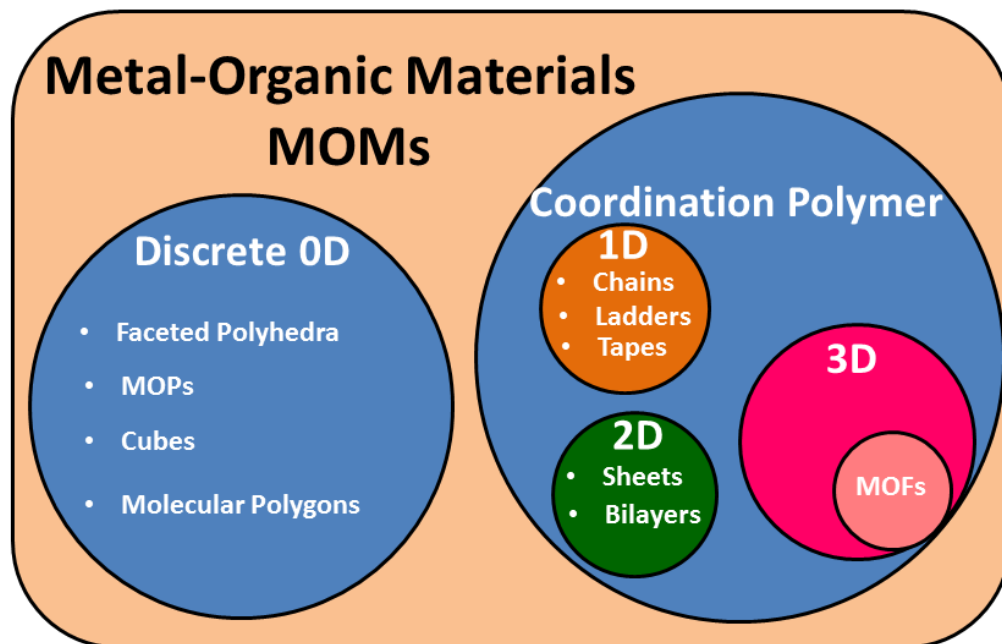


Figure 1.1: Diagrammatic representations of the various forms of the metal-organic materials and the relationship between them.

The inorganic polymer crystal structures were described as a network consisting of nodes (metal ion centers) that are linked together by spacer or edges (bonds). Importantly this gave the subsequent thought about the network topology which is based on the coordination environment and geometry of the nodes, i.e., metal centers. For example, a metal ion adopts tetrahedral geometry with coordination of bi-functional ligand, and it will give a cubic or hexagonal diamondoid network. Similarly, metal with an octahedral geometry can sustain octahedral or square grid nets depending on the metal-ligand stoichiometric ratio.

1.2 Coordination polymers and metal-organic frameworks

The term coordination polymer was used by the J.C. Bailar in 1964, in his review which concerned about the polymeric structures involving ligands and metals.²¹ Coordination polymers are the subset of the inorganic polymers derived from the combination of organic ligands and the metal atoms through metal-ligand bonds. The first synthetic coordination polymer is Prussian blue (Figure 1.2a). The crystal structure determination of Prussian blue in 1977 revealed a mixed-valent Fe(II)/Fe(III) network.²² In 1897,

Hoffman and co-workers synthesized a new coordination polymer $\text{Ni}(\text{CN})_2(\text{NH}_3) \cdot \text{C}_6\text{H}_6$ by the addition of benzene into a solution of $\text{Ni}(\text{CN})_2$ in ammonia (Figure 1.2b).²³

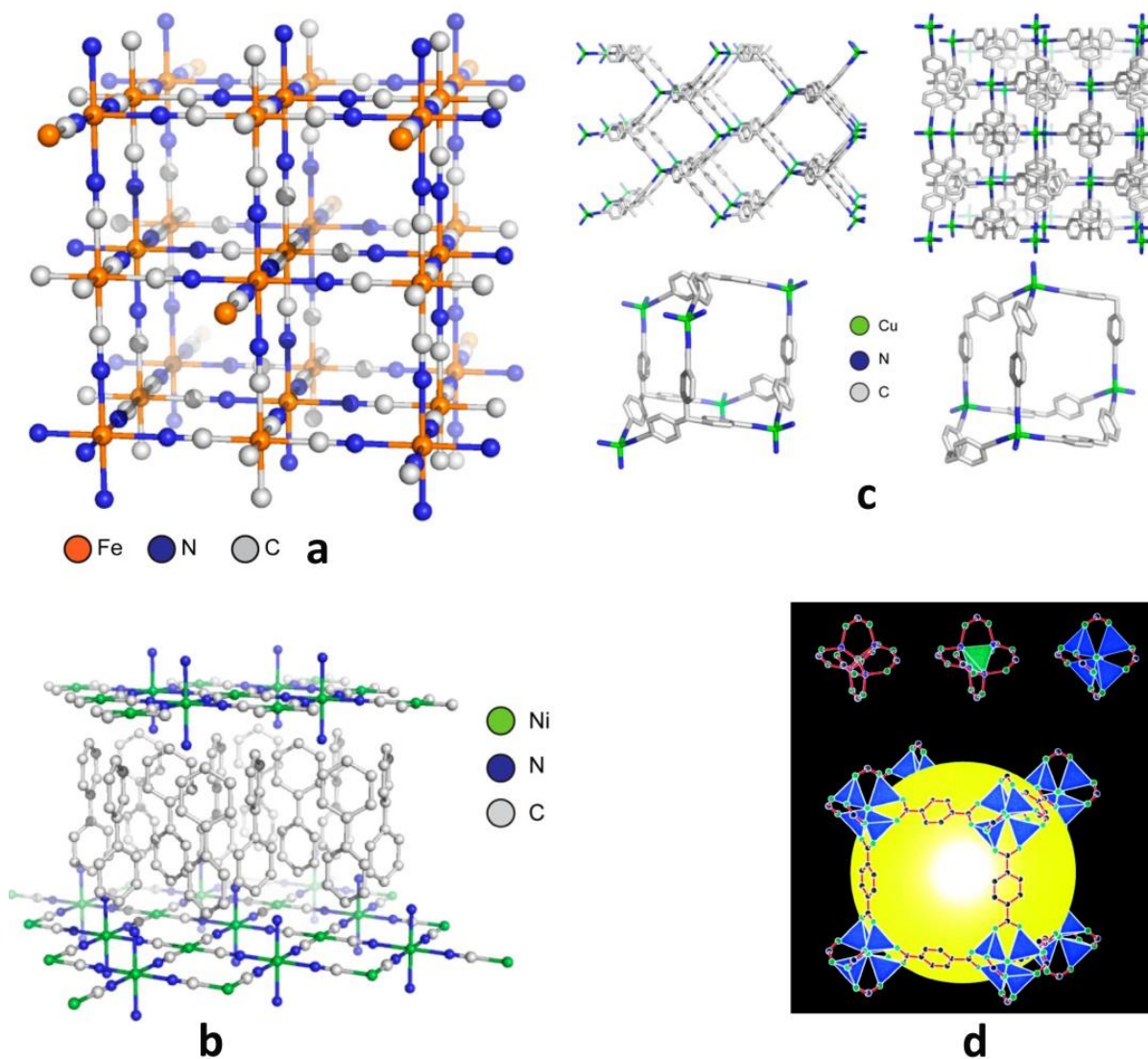


Figure 1.2: Coordination polymers: (a) View of the 3D-network of Prussian blue; (b) the first coordination polymer of Hoffman network; (c) three-dimensional coordination polymer of $\text{Ni}(\text{CN})_2(\text{NH}_3) \cdot \text{C}_6\text{H}_6$ reported by Robson. (c) Three-dimensional view of MOF-5. (Adapted by permission from ACS Publishers Ltd: "Chem. Rev. **2013**, 113, 734" © 2013 and "Science, **2003**, 300, 1127" © 2003)

Due to the lack of structural characterization techniques in that time, the structure of this polymer was not fully understood until Powell and co-workers did the X-ray studies in

1952. They showed that the coordination polymer $\text{Ni}(\text{CN})_2(\text{NH}_3) \cdot \text{C}_6\text{H}_6$ has a similar connection as Prussian blue where the cyanide ligands bridge the metal nodes. However, the coordination polymer grows only in two directions, unlike the Prussian blue which has a three-dimensional network. These results brought attention and motivation to look for the other classes of coordination polymers. As the structure determination techniques become more refined and efficient, syntheses of these materials accelerated after the 1960s. Early coordination polymers have Hoffman-type topologies in which the capping ligands, guests, and metal center were replaced by similar types of species.²⁴ The most significant change came when the cyanide ligand was replaced by the organic ligands which lead to the tremendous growth of coordination polymers.

In 1989, a hallmark discovery of coordination polymer was made by the Robson and co-workers. They have reported a three-dimensional diamondoid network derived from the linkage of Cu(I) ions with 4,4',4'',4'''-tetracanotetraphenylmethane (tctpm) (Figure 1.2c).²⁵ Later, the ligand discovery moved from cyanide to organic nitrile to pyridyl-based N-donor ligands. Fujita and co-workers utilized 4-4'-bipyridyl for the assembly of square complexes.²⁶ A milestone discovery in coordination polymers came in mid of 1990 when Yaghi²⁷ and Kitagawa²⁸ have employed carboxylate ligands for the formation of coordination polymers (Figure 1.2d). These coordination polymers exhibit large porosity and were used for the gas adsorption/desorption studies. These networks were later termed as metal-organic frameworks (MOFs). These metal-organic frameworks were found applications in various fields viz. gas storage and separation, chemical purification, sensing, catalysis, etc.²⁹⁻³⁴

1.3 Discrete metal-organic coordination-driven self-assembly

In 1960's, metal-ligand coordination based supramolecular polygons and polyhedral were reported by Pederson and co-workers, which demonstrate that complementary small molecules can be used for the recognition via non-covalent interaction.³⁵ In early days, crown ethers were the first systems for the molecular identification due to their facile synthesis and ability to accommodate specific simple guest ions. Later, Lehn and

Cram introduced several new host-guest complex systems such as cryptands and spherand as hosts for various small guest molecules (Figure 1.3).³⁶⁻³⁷ In these systems, the non-covalent interactions were playing crucial roles towards the host-guest formation and the construction of the massive structures from tiny molecular components. These tiny constructs were found to aggregate together by various forces such as π - π interactions, van der Waals forces, intra-molecular hydrogen bonding, and other weak interactions forming assemblies that were termed as supramolecules.

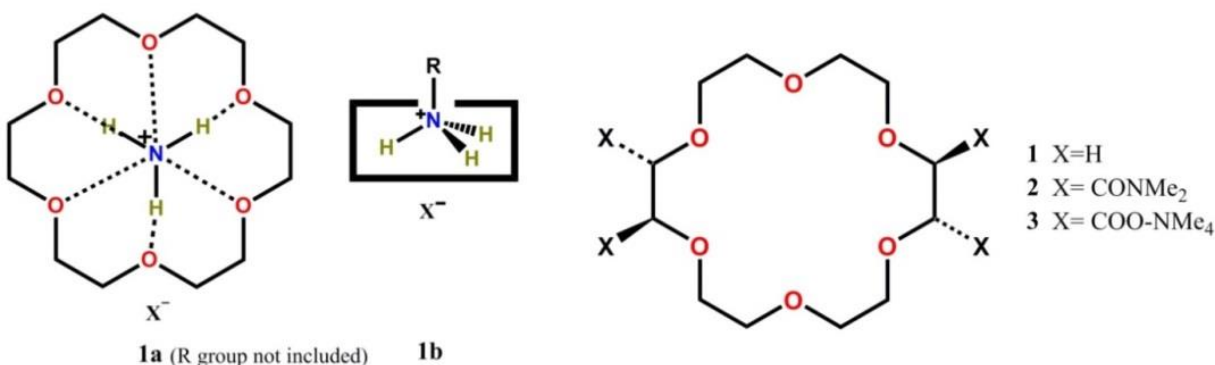


Figure 1.3: Spherand and cryptands reported by Len and Cram.

The supramolecular coordination compounds are discrete constructs derived from the combination of metal ions with organic ligands which forms metal ligands coordination and generate the stable thermodynamic products. This process is called as coordination-driven self-assembly.³⁸⁻⁵⁶ In 1983, Verkade and coworkers introduced a first example of the self-assembly. They showed the formation of the 20-membered macrocycle ring by the reaction of a bridging diphosphine ligand $P(OCH_2)_3P$ with either Cr, Mo, or W carbonyl precursor linked via coordination bonds (Figure 1.4a).⁵⁷

Later, in the early 1990s, Fujita and Stang independently reported various examples of rationally designed supramolecular squares of Pd and Pt using the organic ligands and showed the way to explore the metal-organic discrete supramolecular assemblies (Figure 1.4b).⁵⁸⁻⁵⁹ Further several methodologies have been developed for the rational design of polyhedra, polygons, and prisms by them and also by others Raymond, Mirkin, and Cotton in the past two decades.⁶⁰⁻⁶⁸ Moreover, the higher polygons, triangles, rectangles as well as 3D architectures such as tetrahedra, cubes, octahedral,

cuboctahedra, dodecahedra and others were developed rationally from square motifs. These 3D constructions were known as metal-organic polyhedra (MOPs).⁶⁹⁻⁸⁹ Metal-organic polyhedra are a geometric construct which has been known for eras, and in recent years they have been utilized as a blueprint for the construction of several discrete inorganic, organic, and metal-organic nanoscale structures.⁹⁰⁻¹⁰⁵ Metal-organic polyhedra can be classified into four categories as platonic solids, Archimedean solids, faceted polyhedral and stellated polyhedra.

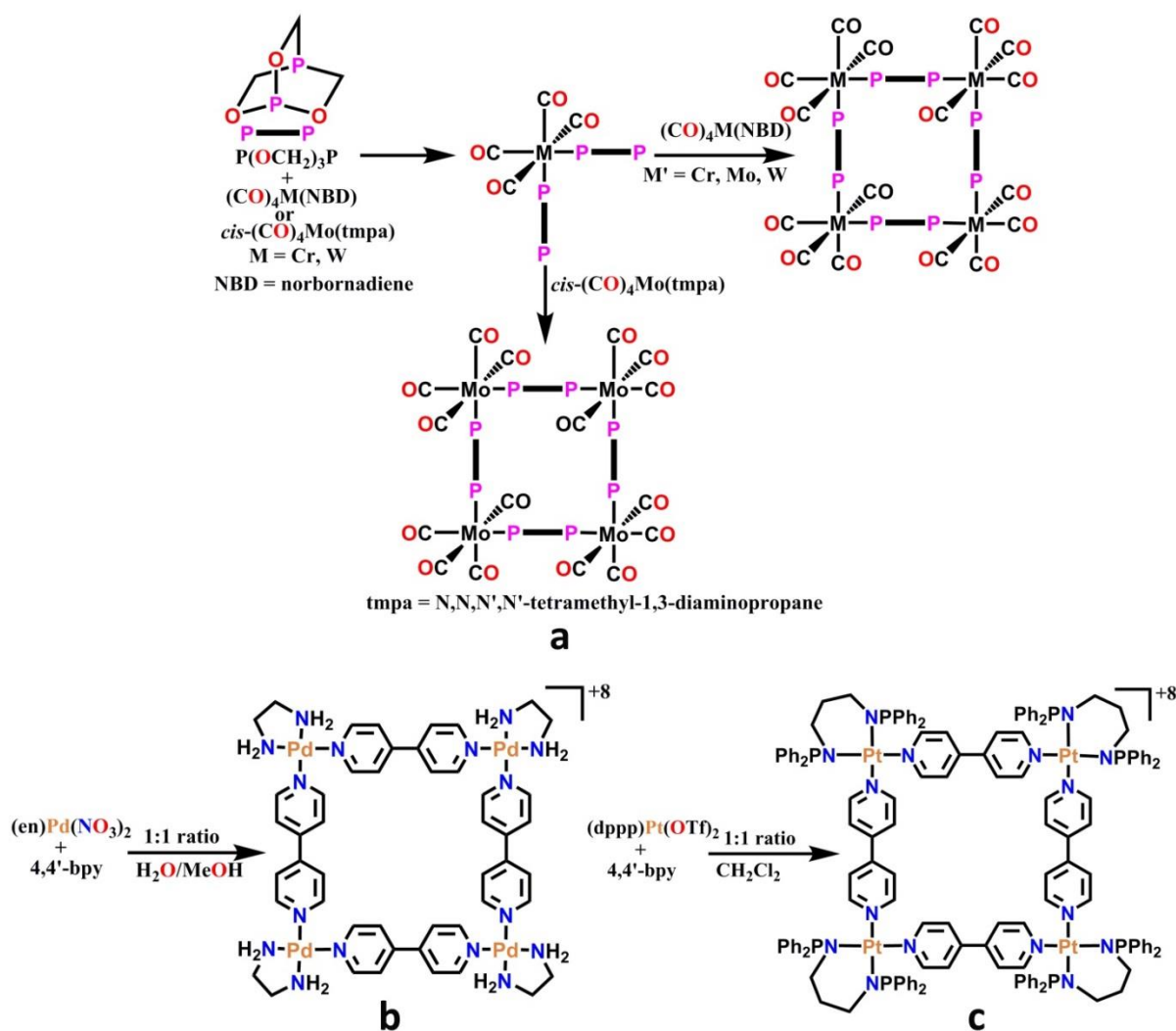


Figure 1.4: (a) Early examples of coordination-driven self-assembly. Square metallacycles formed upon combination of a metal precursor with a linear ligand with two bridgehead phosphorus atoms. The intermediate monomer species is isolable, permitting the construction of

both homo and hetero-tetranuclear squares. Schematic diagram showing the synthesis of earlier examples of square complexes of Pd^{2+} (a) and Pt^{2+} (b) with 4,4'-bipyridine.

1.3.1 Platonic MOPs

Platonic MOPs are simple and most widely known metal-organic polyhedra and derived from one type of regular polygons meeting at similar vertices. These are five types; tetrahedron, hexahedron (cube), octahedron, dodecahedron, and icosahedron (Figure 1.5). These metal-organic polyhedra are highly symmetric in structures and correspond to one of the highly symmetric point groups such as tetrahedral, octahedral or icosahedral.

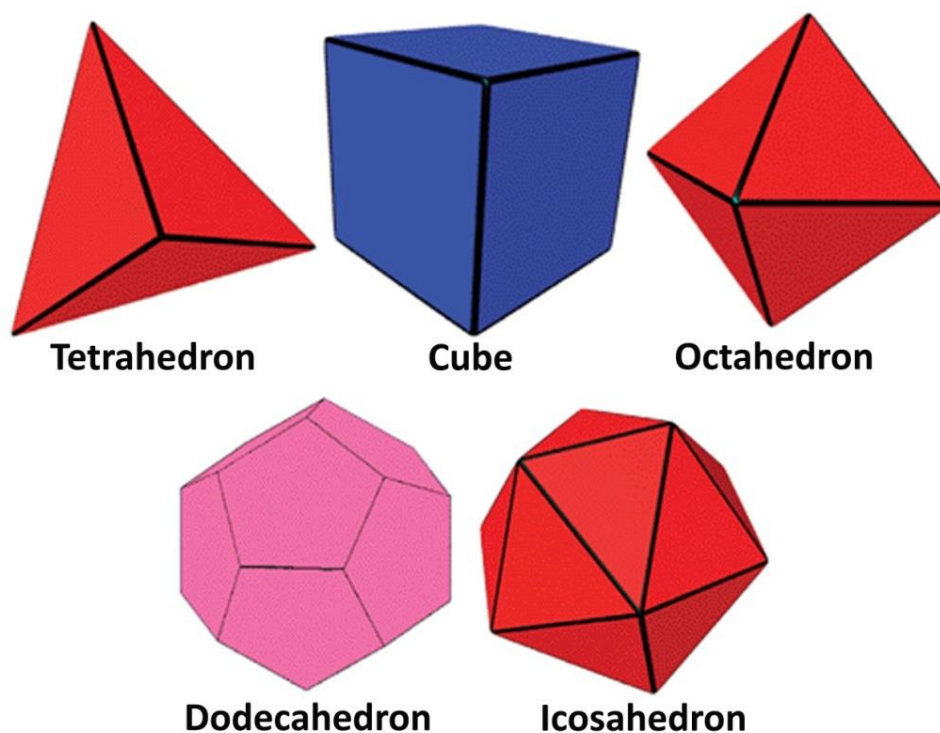


Figure 1.5: Structural view of the five Platonic solids. (Adapted by permission from RSC Publishers Ltd: "Chem. Soc. Rev. **2009**, 38, 1400" © 2009)

Several examples of tetrahedral metal-organic polyhedra have been reported in the literature. Fujita and co-workers have reported various instances of tetrahedral MOPs based on the molecular paneling approach.¹⁰⁶⁻¹⁰⁷ They have designed molecular triangles or panels by coupling of the palladium ions and the organic ligands, and these

panels were self-assembled together in the form of tetrahedral structures. Following the same approaches, another research group, Oppel, and Föcker reported a double walled tetrahedron where they have utilized a C_3 -symmetric ligand having a triaminoguanidinium core and transition metal ions (Zn^{2+} or Cd^{2+}) to form the metal-organic polyhedra/cage. Separately,¹⁰⁸ Yaghi and co-worker have shown a series of isorecticular truncated tetrahedral polyhedra (IRMOP) based on μ_3 -oxo centered $Fe_3O(CO_2)_6$ trimer.¹⁰⁹ These molecular triangles were connected with ditopic organic ligands, for example, 1,4-benzene dicarboxylate, tetrahydropyrene-2,7-dicarboxylate, 4,4'-biphenyl dicarboxylate, or 4,4'-terphenyl dicarboxylate and form the truncated tetrahedral structures.

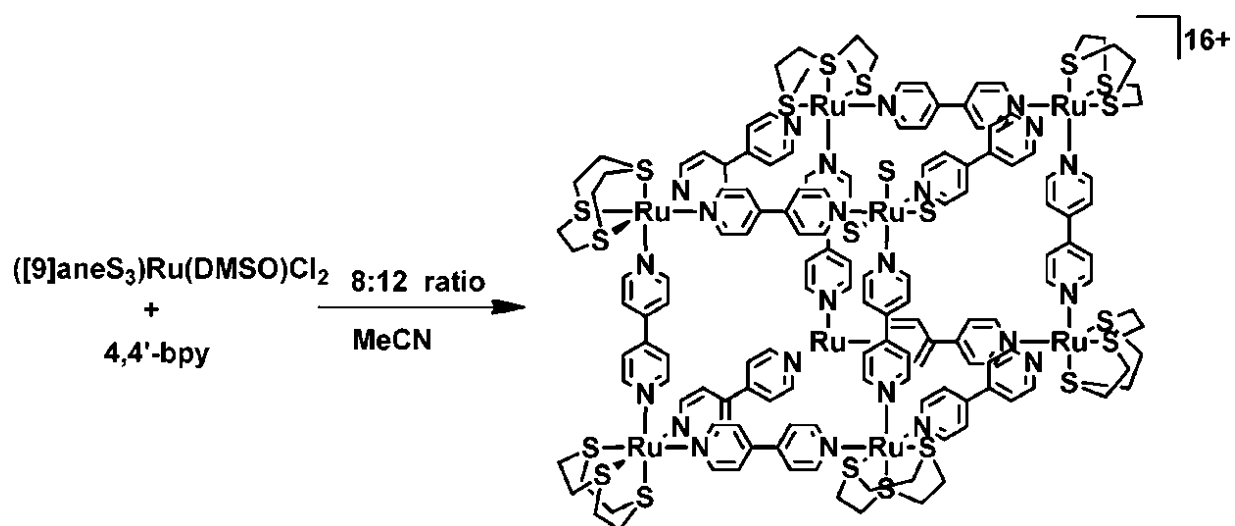


Figure 1.6: Synthesis of a cube complex of ruthenium with $[9]aneS_3$ and 4,4-bipyridine. (Adapted by permission from ACS Publishers Ltd: "Chem. Rev. **2013**, 113, 734" © 2013)

Another interesting platonic solid, hexahedron or cube can be generated by using two distinct strategies. The first method involves an octahedral metal ion with the preinstalled facial ligand as a protecting group which terminates along three exo directions of the metal center. This arrangement transfers a six-coordinated transition metal ion into a three coordinated linker, which are oriented in such a way that it can act as the vertex of a cubic structure. In 1998, Thomas et al. reported cubic cage/polyhedral derived from a ruthenium metal ion coordinated with $[9]aneS_3$ and 4,4-bipyridine moieties (Figure 1.6).⁷⁴

The second strategy was utilized an in-situ approach employed by Eddaoudi and co-workers. In this method, the octahedral nickel metal that is blocked in-situ by 4,4'-trimethylenedipiperidine (TMDP) can further complex with a bidentate bridging moiety such as 4,5-imidazole dicarboxylic acid, with the formation of an anionic metal-organic cube.¹¹⁰ In a different reaction, Chan et al. have shown the formation of another type of a neutral O_h -symmetric cubic cage from the reaction of 2,4,6-tri[(4-pyridyl)sulfanylmethyl]-1,3,5-triazine and Ni^{2+} metal ion. It contains the metal ions, with square planar geometry, lie at the center of each of the cubic faces, the triazine cores at the corners and its pyridyl pendent arms are projected towards the metal centers at the cubic faces.¹¹¹

The octahedron is another well-explored platonic solid among the MOPs. Some examples of the M_6L_8 type of octahedral cages have been reported by several researchers especially by the groups of Fujita, M.-C.Hong. Typically these octahedral cages can be obtained by divalent metal-ions with square-planar and octahedral coordination upon reaction with C_3 -symmetric tridentates N-donor ligands. Eddaoudi and co-workers reported a very interesting example of a neutral octahedron by bridging of the six indium (III) metal ions with twelve 2,5-pyridindicarboxylate ligands that exhibit both bridging and chelating coordination modes.¹¹² The ligand constructs the edges, and metal ions serve as the vertices of the octahedron. The obtained metal-organic polyhedron adopts T_h symmetry.

1.3.2 Archimedean MOPs

Archimedean solids are another class of the MOPs and exhibit structures that closely resemble those of Platonic solids. Nevertheless, unlike the Platonic solids, these metal-organic polyhedra contain at least two different polygons or faces in each polyhedron and are semi-regular. Archimedean MOPs are mostly of 13 types such as a truncated tetrahedron, truncated octahedron, cuboctahedron, truncated cube, rhombicuboctahedron, snub cube, icosidodecahedron, truncated cuboctahedron, truncated dodecahedron, truncated icosahedron, rhombicosidodecahedron, snub dodecahedron, and truncated icosidodecahedron (Figure 1.7).

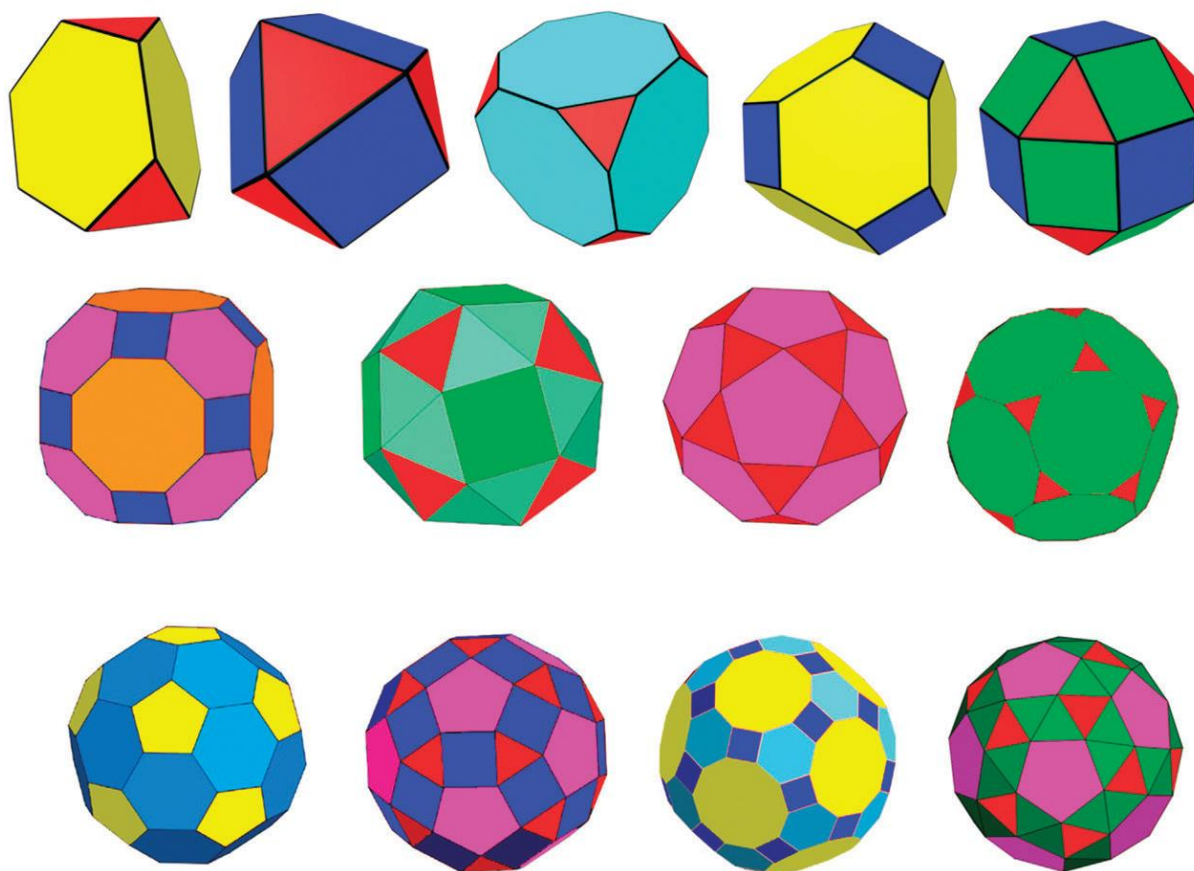


Figure 1.7: Archimedean solids (from left to right); First row: truncated tetrahedron, cuboctahedron, truncated cube, truncated octahedron, and rhombicuboctahedron. Second row: truncated cuboctahedron, snub cube, icosidodecahedron, and truncated dodecahedron. Third row: truncated icosahedron, rhombicosidodecahedron, truncated icosidodecahedron, and snub dodecahedron. (Adapted by permission from RSC Publishers Ltd: "Chem. Soc. Rev. **2009**, 38, 1400" © 2009)

The Stang and co-workers reported the most common and simplest Archimedean MOP of a truncated tetrahedron in 2000.¹¹³ They have synthesized a truncated tetrahedron by adopting a face directed self-assembly of cis-palladium or cis-platinum salts with tritopic ligands, e.g., tris(p-cyanophenylethynyl)benzene or tris(pyridylethynyl)benzene. The obtained polyhedra were confirmed by the NMR experiments and SCXRD analysis. The crystal structure derived from the SCXRD showed that the tritopic ligands built by the triangular (truncated) face and Pd^{2+} and Pt^{2+} act as the vertices of the truncated tetrahedron. At the same time, Yaghi and co-workers have also shown a truncated

octahedron derived from the copper metal ions and dicarboxylate ligands having a bite angle of approximately 90° (Figure 1.8).¹¹⁴

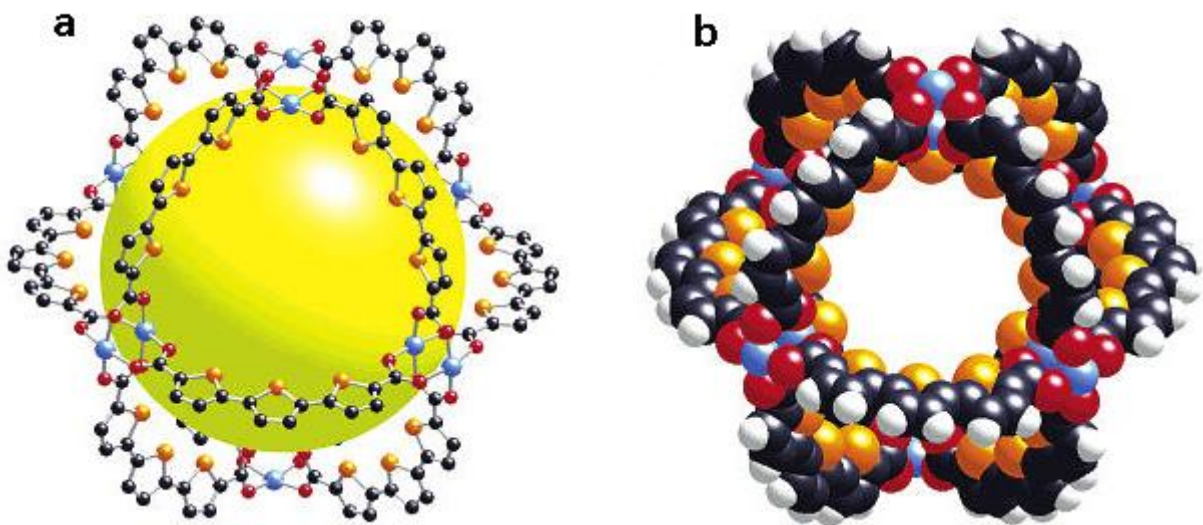


Figure 1.8: The crystal structure of MOP-28. (a) A ball-and-stick model of a MOP-28 molecule viewed approximately down the 3-fold axis, (b) A space-filling model of a MOP-28 molecule viewed down the 3-fold axis, showing the large triangular apertures of $9.0 \text{ \AA}$ in diameter. (For b-c: Cu, blue; O, red; C, black; S, orange; H, light gray. All terminal ligands have been omitted). (Adapted by permission from RSC Publishers Ltd: "J. Am. Chem. Soc., **2005**, 127, 12752" © 2005)

Another example of an Archimedean MOP is cuboctahedron reported by Stang and co-workers, where they have shown the assembly of transition metal ions with twenty tridentate and bidentate subunits.⁷⁷ For example, self-assembly of tridentate triangular 1,3,5-tris(4'-Pt(PPh₃)₂OSO₂CF₃)ethylbenzene with a bidentate ligand 4,4'-bis-pyridylacetal results in a cuboctahedron. Fujita and co-workers have also reported various examples of cuboctahedra based on the self-assembly of palladium and pyridyl donor ligands.¹¹⁵

1.3.3 Faceted MOPs

Faceted metal-organic polyhedra are the third type of MOPs where the polygons share the vertex instead of edge-sharing as in case of Platonic and Archimedean MOPs.

Faceted MOPs are non-convex, different from the convex polyhedra and they have closed as well as an open window to the interior of the spheroid. Faceted MOPs are mostly nine types as shown in figure 1.9. Out of the nine faceted polyhedra three cubohemioctahedron, small rhombihexahedron, and small rhombidodecahedron are formed by the vertex sharing of squares. These three polyhedra differ from each other only in the angles formed by the vertices. Researchers precisely control the angle parameter between the vertices during the linkage of the ligand with square SBUs to form these metal-organic polyhedra.

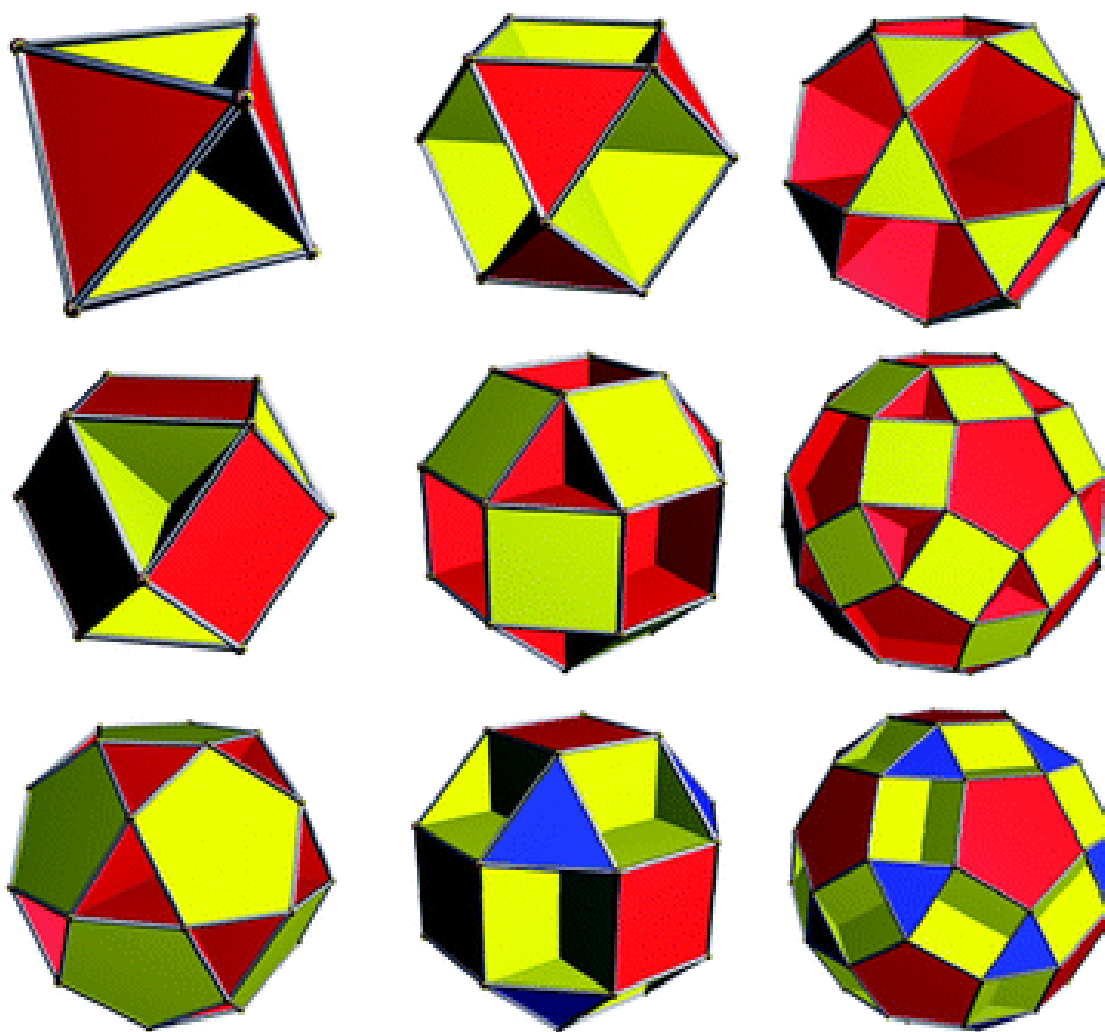


Figure 1.9: Faceted polyhedra. First row (left to right): tetrahemihexahedron, octahemioctahedron, and small icosihemidodecahedron. Second row: cubohemioctahedron, small rhombihexahedron, and small rhombidodecahedron. Third row: small

dodecahemidodecahedron, small cubicuboctahedron, and small dodecicosidodecahedron. (Adapted by permission from RSC Publishers Ltd: "Chem. Soc. Rev. **2009**, 38, 1400" © 2009)

The MOPs cubohemioctahedron, small rhombihexahedron, and small rhombidodecahedron exhibit 12, 24 and 60 vertices respectively. Since the small rhombihexahedron MOP possesses an angle of 120° between the vertices, is also known as nanoball. The small rhombihexahedron MOP which is considered as the prototypal example of a metal-organic faceted polyhedron has been broadly studied by various research groups.¹¹⁶

Zaworotko et al. reported the pioneering instance of a small rhombihexahedron faceted MOP $[(\text{DMSO})(\text{MeOH})\text{Cu}_2(\text{bdc-5-OH})_2]_{12}$. It was derived from the spontaneous reaction of 2,6-dimethylpyridine (2 equivalents) with $\text{Cu}(\text{NO}_3)_2$ (1 equivalent) and $\text{H}_2\text{bdc-5-OH}$ (1 equivalent) in methanol (Figure 1.10).¹¹⁷⁻¹²⁰

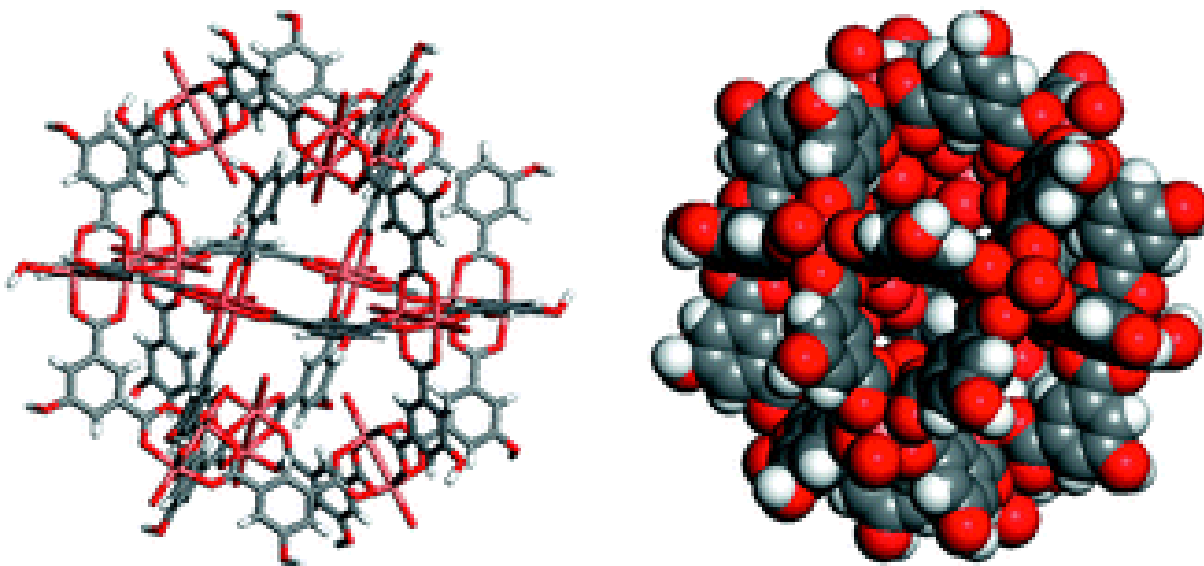


Figure 1.10: Crystal structure of $[(\text{DMSO})(\text{MeOH})\text{Cu}_2(\text{bdc-5-OH})_2]_{12}$ (left). Connectivity of the SBUs is in cage assembly (right). (Adapted by permission from RSC Publishers Ltd: "Chem. Commun, **2001**, 2380" © 2001)

Interestingly, the hydroxylated version of this polyhedron results in polymer composites during the solution studies.¹²¹ Later, different groups have also reported several derivatives of this nanoball. Recently, Mattay et al. reported another example of the

faceted polyhedron. They have shown that the mixing of a cavitand-terpyridine subunit with a zinc salt, $[\text{Zn}(\text{NCMe})_6](\text{tetrakis}(3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl})\text{borate})_2$, in a ratio 2:1 of metal-to-cavitand, it forms a cuboctahedron MOP. In this MOP the six cavitands are bridged through almost linear linkages formed by Zn-terpyridine units. The derived metal-organic polyhedron exhibits an inner cavity of volume $\sim 13.7 \text{ nm}^3$ which is accessible through a large window size of ca. 0.77 nm .¹²²

1.3.4 Stellated MOPs

The fourth class of metal-organic polyhedra is stellated metal-organic polyhedra, and a first example was reported by Hardie et al. which was known as *stella octangulla*. The *stella octangulla* was formed by the self-assembly of Pd^{2+} ions and the derivative of a cyclotrimeratrylene (CTV) macrocyclic core.¹²³ The rigid and the curved structure of the CTV derivative increased the size of the central cavity which was utilized for the molecular recognition studies. In the *stella octangulla*, the curvy part of the CTV occupies the eight faces of octahedron and orient in such a manner where the pyramidal part pointed superficially away from the center. The edge of each face prolonged outward and they encounter at a point away from that face and leads the star-like prismatic structure. Each of this discrete *stella octangulla* is a construct of eight C_3 -symmetric ligands and six Pd^{2+} ions located at the vertices of octahedron and results in a cationic framework. The counter nitrate anions balanced the cationic charge. Each component of the *stella octangulla* is homochiral and the overall structure chiral.

1.4 Methods to synthesize metal-organic polyhedra

Various synthetic approaches have been developed to design metal-organic polyhedra of different shapes and sizes depending on the choice of ligands. The most extensively used methods are directional bonding, symmetry interaction, molecular paneling, weak link, and dimetallic building block approach.

1.4.1 Directional bonding method

This bonding approach is a simple and high yielding method which provides various two- and three-dimensional supramolecular assemblies.¹²⁴⁻¹²⁸ Utilizing this strategy the

earlier square complexes were made by Fujita and Stang's group and later by following similar design principle, they have synthesized a plethora of metallocages and metallamacrocycles.⁵⁸⁻⁵⁹ There are two necessary structural requirements for the construction of supramolecular assemblies based on this method. First, the rigid precursor unit must have predefined bite angle and the second precursor must be used in the appropriate stoichiometric ratio. The organic linkers act as donor building blocks and exhibit two or more binding sites with bite angles in the range of 0 to 180° (Figure 1.11).

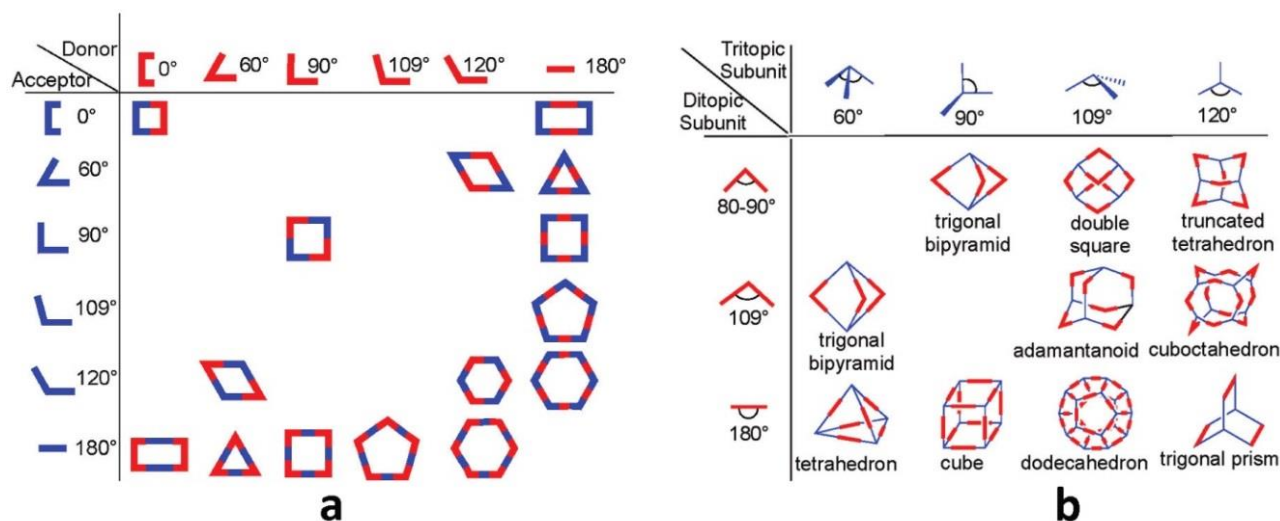


Figure 1.11: Combination of various building units for accessing convex polygons (a) and canonical polyhedra (b). (Adapted by permission from ACS Publishers Ltd: "Chem. Rev. **2011**, 38, 6810" © 2011)

1.4.2 Symmetry interaction method

Symmetry interaction approach utilizes the rational synthetic design of highly symmetric coordination architectures for the formation of metal-ligand bonds that depend on the geometry of the ligand and metal ions used. The driving force to construct the high symmetric architectures originate from the dynamic binding nature and the coordination mode of the ligand together with a metal ion having available coordination sites of inherent symmetry. In general, the multisite rigid ligands are used for the coordination with transition metals. The rigidity of the multisite ligand assists in the selectivity of the precise geometry of complex and avoids the formation of polymer or oligomer. In 1999,

Raymond and coworkers established this design principle and shown the geometric relation between the ligand and the metal ions.¹²⁹⁻¹³⁰ The plane orthogonal to the major symmetry axis at the metal center acts as the chelate plane shown in the figure 1.12. From the orientation of the ligand chelate plane, it will be easy to predict the geometry of the construct, a high symmetric complex or a cluster.

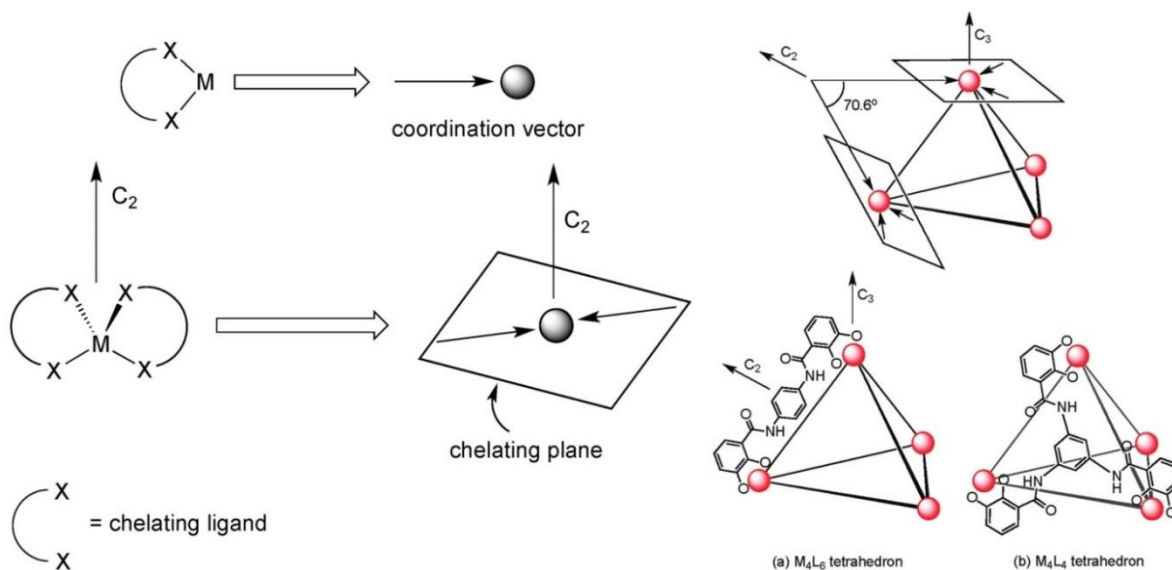


Figure 1.12: Coordinate vector and chelate plane for the symmetry interaction method. A design strategy for preparing (a) M_4L_6 and (b) M_4L_4 tetrahedra by the symmetry interaction approach. (Adapted by permission from ACS Publishers Ltd: "Chem. Rev. **2011**, 38, 6810" © 2011)

1.4.3 Paneling method

This method has been established by the Fujita and co-workers to make 3D supramolecular architectures such platonic solids and also various other assemblies viz equilateral triangles, squares, and pentagons.¹³¹⁻¹³² According to this method, three-dimensional designs can be considered as smaller building units and construction can be fragmented into these building units. For example, a tetrahedral structure can be formed by the assembling of the four triangle planes. Similarly, an octahedron can be designed by stitching together eight such triangular planes. Moreover, a cube can be considered as the result of the assembly of the six squares.

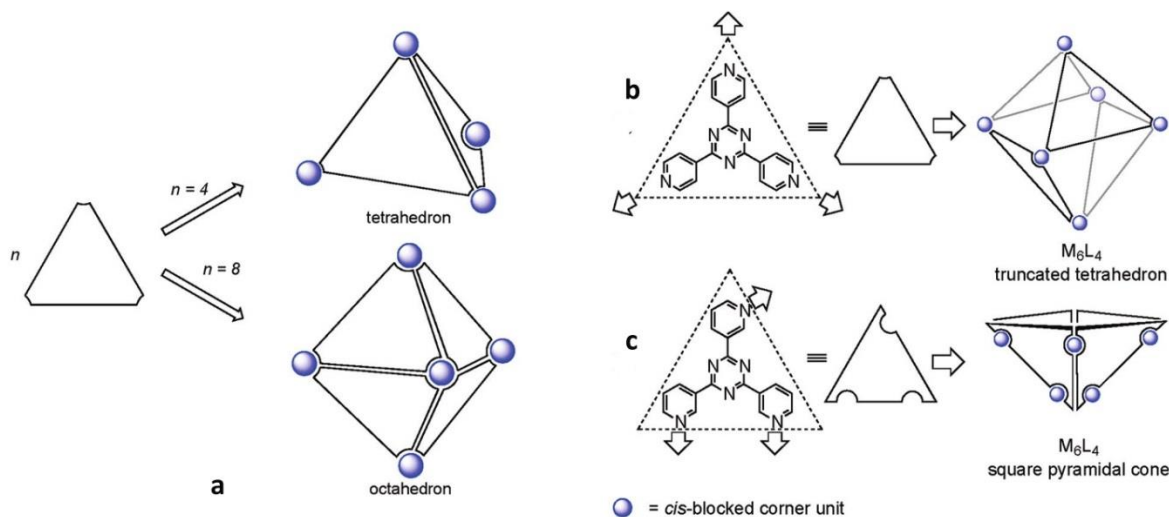


Figure 1.13: (a) Representation for assembling a tetrahedron and an octahedron using triangular panels. (b) An M_6L_4 truncated tetrahedron and (c) an M_6L_4 square-pyramidal cone using triangular panels. (Adapted by permission from ACS Publishers Ltd: “Chem. Rev. **2011**, 38, 6810” © 2011)

In this method, unlike symmetry interaction approach, *cis*-protected metal ions such Pd^{2+} and Pt^{2+} are coordinated with a panel like organic ligands having two or more coordinating sites. A *cis*-blocked metal ion in conjunction with the triangular planes lead to the formation of various structures such as M_6L_4 square pyramidal cone, M_6L_4 truncated tetrahedral cage, M_8L_4 tetrahedra and cone and $M_{18}L_6$ hexahedra. By the assembling of D_{3h} -symmetric triangular panels, an M_6L_4 octahedron is obtained (Figure 1.13a).¹³³ Similarly, the construction of bowl-like M_6L_4 square pyramidal cone is achieved from a combination of ligands as four triangular planes with *cis* protected metal ions as corner units (Figure 1.13b).¹³⁴

1.4.4 Weak link and dimetallic building block method

This method has been demonstrated by Mirkin and co-workers for the construction of both two-dimensional and three-dimensional supramolecular architectures.¹³⁵ In this process they used hemilabile ligands which are coordinated with transition metal ions in such a way that one of the metal-ligand bonds is weaker than others (Figure 1.14, left).

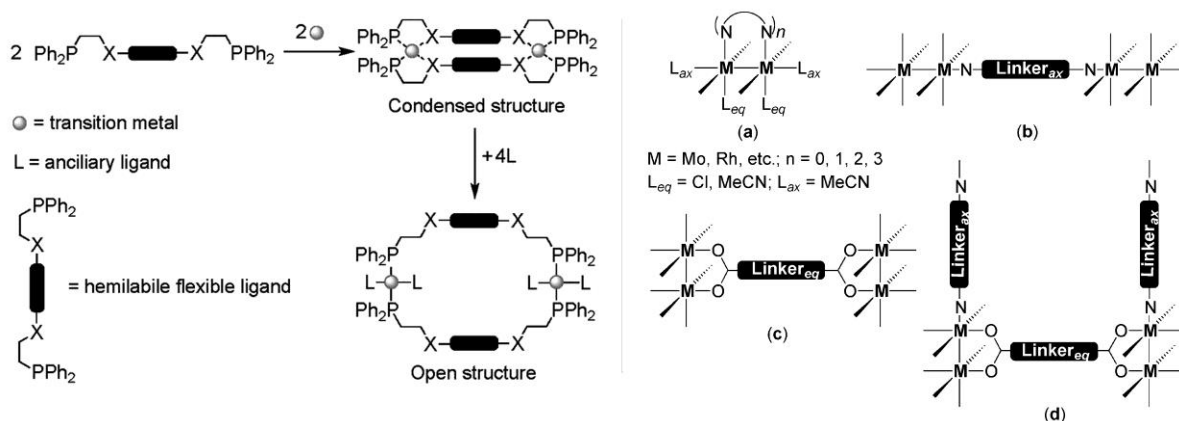


Figure 1.14: Left: Scheme showing the formation of supramolecular architecture by using weak link method. Right: modes of the assembly of dinuclear units in dimetallic building block approach. (Adapted by permission from ACS Publishers Ltd: "Chem. Rev. **2011**, 38, 6810" © 2011)

There are several examples available for the dimetallic building approach such as the formation of paddlewheel or lantern frameworks from these basic units. Cis-protected dimetallic units such as Mo₂⁴⁺ and Rh₂⁴⁺ having one or more edges blocked by non-labile chelating ligands form various supramolecular structure with a combination of a variety of organic linkers (Figure 1.14, right).⁶¹⁻⁶²

1.5 Application of the metal-organic polyhedra

Metal-organic polyhedra have gained more attraction due to the vast application in various field viz. catalysis, sensing, biomedical application, adsorption and separation and as precursors for metal-organic frameworks. Recently, these polyhedral have received prolonged attention for the applications based on physical properties such as dielectric properties, magnetic properties and as proton conducting materials.

1.5.1 Catalysis

Metal-organic polyhedra exhibit central cavity, which can be used for hosting guest molecules. Encapsulation of guest molecules in the cavity of host brings interaction between guests and leads to a change of molecular structure into the desired product. The catalytic activity of the MOP_s depends upon the nature and size of the cavity. The

catalytic activity is also influenced by the stability of the transition state, stability of the guest conformations and concentration of the guest molecules.

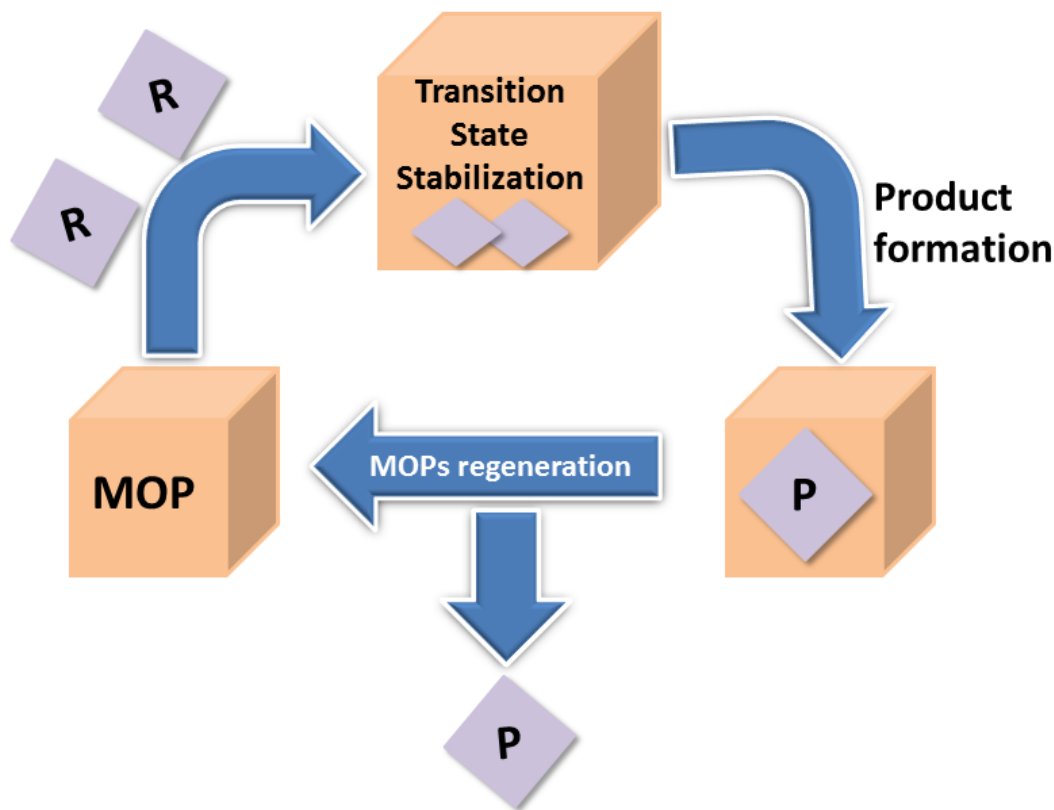


Figure 1.15: Flow chart showing various steps of a catalytic reaction in a “molecular Flask”.

A general schematic MOP assisted catalytic pathway is given in the Figure 1.15. This involves the initial encapsulation of the guest molecules in the pocket of the polyhedron, followed by the reaction between the guest reactants at the cavity of the host. Then, the transition state is stabilized inside, and the subsequent formation of products takes place. Finally, the metal-organic polyhedron is regenerated for further reactions.

Raymond and co-workers have synthesized assembly family of anionic cages of the type $[\text{Ga}_4\text{L}_6]^{12-}$ with large intrinsic cavities of volume of $250\text{--}450 \text{ \AA}^3$. A representative of this cage assembly is $[\text{Ga}_4\text{L}_6]^{12-}$, denoted as **C1**. The cage assembly of **C1** was found to stabilize various sensitive species such as tropylium, diazonium, imminium and phosphonium ions (Figure 1.16).¹³⁶⁻¹³⁹ Further, they have shown that certain reactions that take place inside its cage cavity with high reaction rates of reactivity over those

performed in the bulk solution. Interestingly, they have shown the encapsulation of allyl enammonium cation and a significant increase in the rate of the 3-aza coupling rearrangement reaction by binding a folded conformation of the enammonium cation which looks like the transition state of the reaction.¹⁴⁰

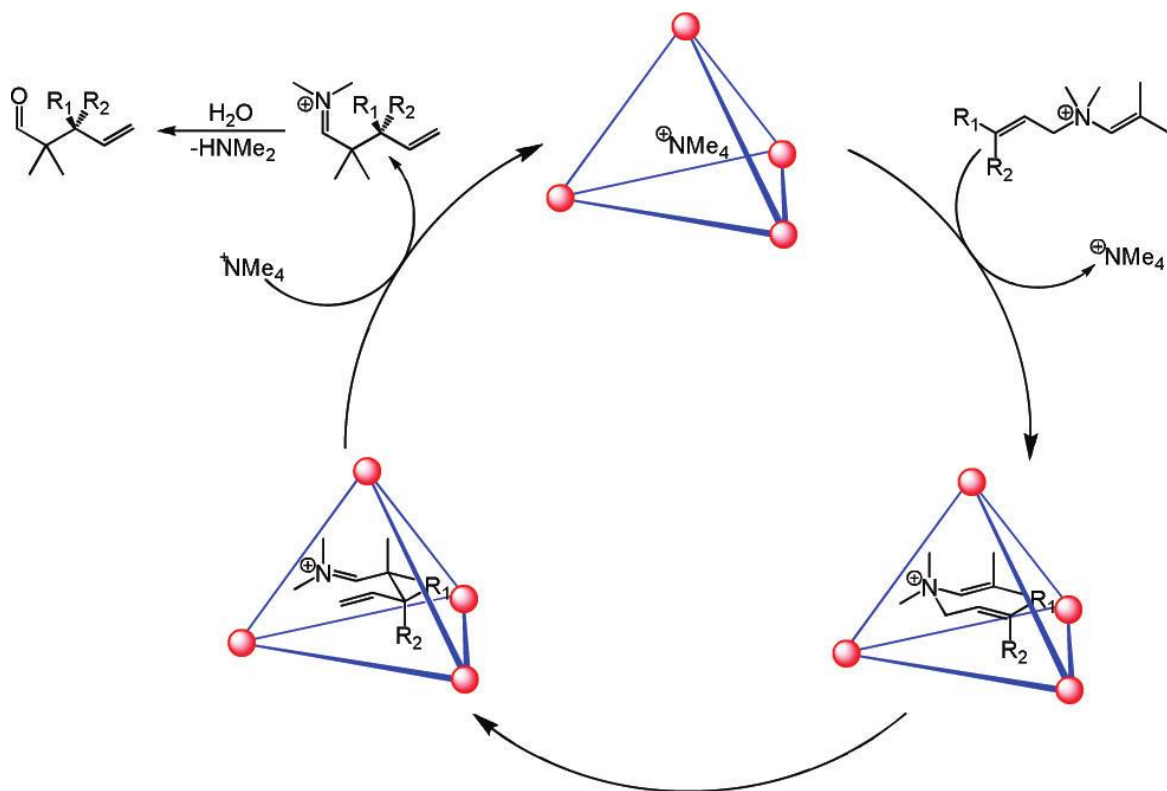


Figure 1.16: Catalytic cycle for the aza-Cope rearrangement within supramolecular assembly C1. (Adapted by permission from ACS Publishers Ltd: “J. Am. Chem. Soc. **2009**, 131, 17531” © 2009).

Utilizing the same cage assembly, they have demonstrated Nazarov cyclization reaction of 3,4,5-trimethylhepta-2,5-dien-4-ol for which the reaction rate is 2100000 times higher as compared to the reaction performed in the absence of the cage catalyst.¹⁴¹

Fujita and co-workers have reported a cationic cage assembly C2 formed by the reaction of palladium (II) ions with pyridine backbone ligand. Utilizing it they have shown several cages catalyzed reactions, such as [2+2] cross photodimerization of acenaphthylene and substituted naphthoquinone, Wacker-type oxidation of styrene and linear alkanols and [2+2] photodimerization of acenaphthalene.¹⁴²⁻¹⁴⁵ By using the same

cage assembly, they have also demonstrated the cage catalyzed Diels-Alder reaction of alkyl substituted naphthalene and the N-cyclohexylmaleimide.¹⁴⁶ Similarly, a Diels-Alder reaction catalyzed by water-soluble construction of furan and maleimide was reported by the Nitschke's group in 2012 employing the cage assembly **1** (Figure 1.17).¹⁴⁷

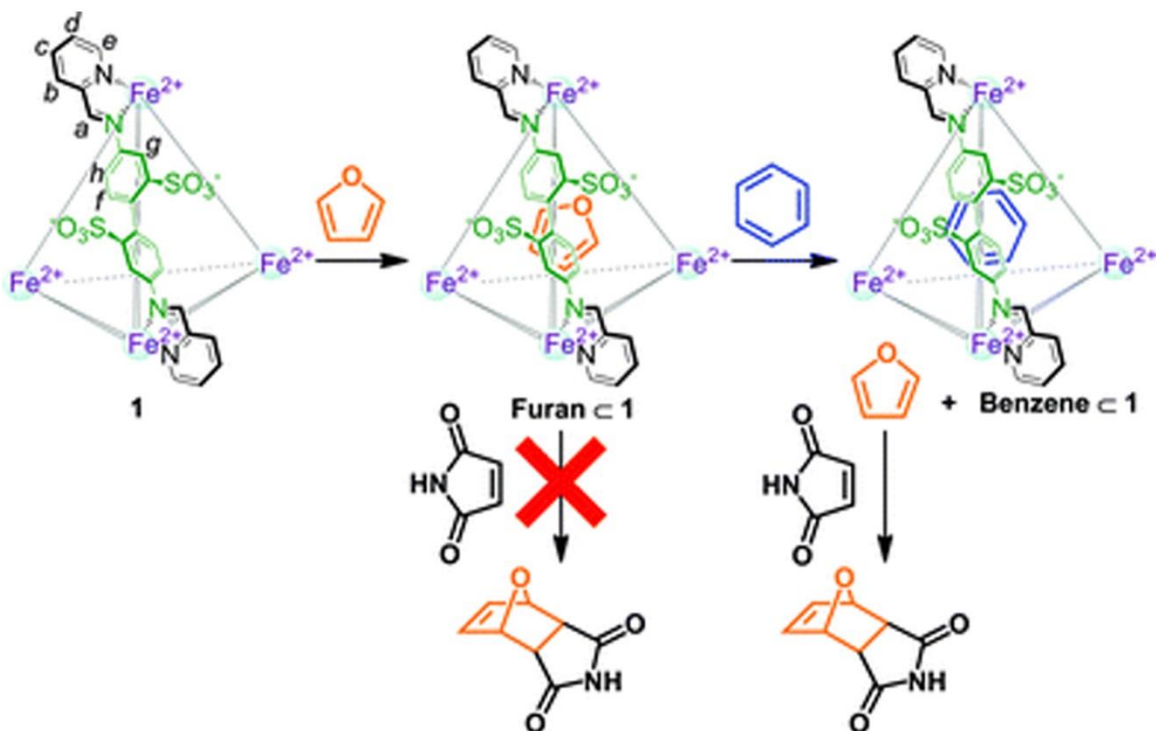


Figure 1.17: A Schematic representation of a capsule mediated Diels-Alder reaction. (Adapted by permission from RSC Publishers Ltd: "Chem. Sci. **2012** 3 785" © 2012)

1.5.2 Sensing

Sensing is the most widely used tool in the past decade(s). Most of the research groups have the interest to develop molecular receptors which show the capability to distinguish or recognize small molecules. Cyclodextrins, crown ethers or amide groups are the most used receptors constructed by associating small recognition sites with their core.¹⁴⁸⁻¹⁵² In recent years fluorescence corroborates as one of the sensitive sensing techniques in chemistry and biology to recognize the molecules of interest. Fluorescent sensors for the recognition of saccharides was synthesized based on the interaction between boronic acid and diol.¹⁵³⁻¹⁵⁴ The metal-organic polyhedral is one of the good

candidates for the sensing of small molecules by non-covalent interactions. In this context, the detection of peptides is essential in biological systems to understand their function in the proteins.¹⁵⁵

Fujita and co-workers reported that cage assembly of **C2** (vide infra) showed the selective recognition of oligopeptides with a highest association constant ($K_a > 10^6$) based on the π - π interaction between the indole and triazine ligands, the CH- π interaction between the triazine ligand and the CH₃ group of alanine.¹⁵⁶ Duan and co-workers have reported two tetrahedral cage TE1 (Ce₄L₆¹) and TE2 (Ce₄L₆²) by the reaction of amide functionalized tridentate ligand with Ce(NO₃)₃.¹⁵⁷ TE1 recognized mannose and glucose selectively, whereas TE2 showed strong affinity towards the disaccharides due to the differences in their cavity size; 300 Å³ for TE1 and 500 Å³ for TE2. Furthermore, some other reports have also been demonstrated the selective recognition of monosaccharides over oligosaccharides based on Ce-derived cages of molecular cubic, octanuclear bicornal prismatic, bicornal trigonal prismatic and tetrahedral topologies.¹⁵⁸⁻¹⁵⁹

Polyfluorinated self-assembly exhibits very exclusive hydrophobic cavity which can be utilized for the recognition of hydrophobic molecules. An M₆L₄ cage (**C2**) was reported by Fujita which displays large hydrophobic intrinsic cavity walled by the four electron deficient triazine core panels. The encapsulated polyfluorinated aliphatic compounds were oriented in such a manner that the hydrophobic parts are pointed towards the cage cavity, and the hydrophilic hydroxyl groups are oriented outside the cage cavity.¹⁶⁰ The driving force for the recognition is the self-aggregation of these polyfluorinated compounds in the cage cavity. Recently, they have prepared an M₆L₃ trigonal pyramid and M₈L₄ tetragonal pyramid by the assembly of the 4,6-di(pyridine-3-yl)-2,5'-bipyrimidine and (en)Pd(NO₃)₂. These precursors gave an M₈L₄ tetragonal pyramid cage exclusively in the presence of calixarene. Nevertheless, self-assembly of tridentate tetragonal ligand 2,4,6-tri(pyridine-3-yl)-1,3,5-triazene with (en)Pd(NO₃)₂ gives two different bowl- and box-shaped conformational isomers. This induced fit architecture houses nitrobenzene and bromocyclopropane.¹⁶¹

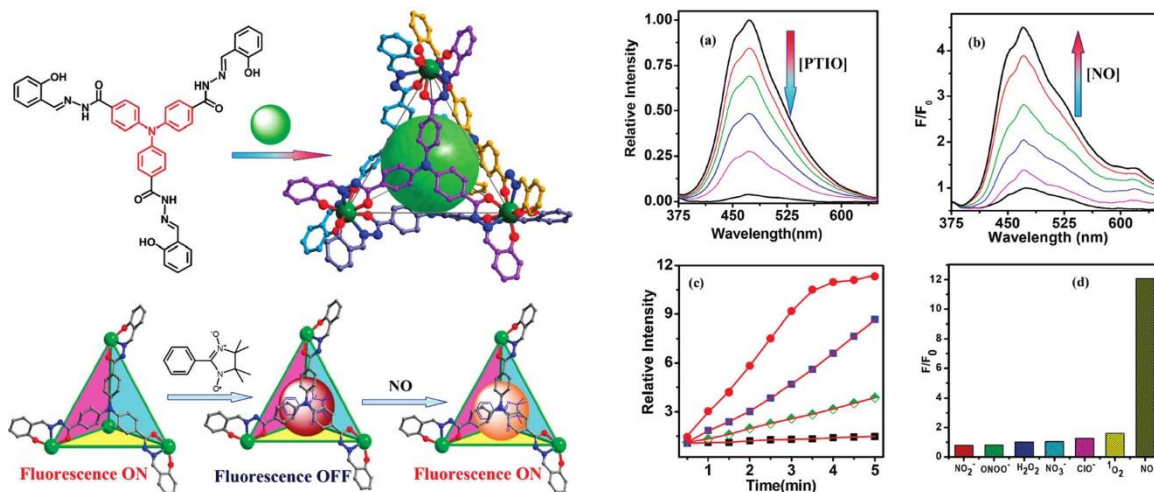


Figure 1.18: Left: Structure of H_6TTS , constitutive/constructional fragments of the functional tetrahedron **1** showing the sequence of fluorescent variation of the tetrahedron **1** upon the addition of PTIO and NO. Right: Change in emission spectra upon addition of the PTIO (a) and NO (b). (c) Time-dependent luminescence variations of cage and PTIO, (d) Luminescence selectivity of cage and PTIO treated with various ROS and RNS. (Adapted by permission from ACS Publishers Ltd: "J. Am. Chem. Soc. **2011**, 133, 12402" © 2011)

The detection of nitric acid is very crucial due to its biological processes in mammals such as vasodilation, neurotransmission, and immune responses.¹⁶² Duan and co-workers have reported its detection by a tetrahedral cage, $Ce_4(H_2TTS)_4$, synthesized by reaction Ce^{3+} ions with H_6TTS ligands (N',N'',N''' -nitritotris-4,4',4''-(2-hydroxybenzylidene)-benzohydrazide). This cage showed an emission at 470, and the intensity of emission gradually decreases with addition of PTIO (2-phenyl-4,4,5,5-tetramethylimidazolineyloxyl-3-oxide) whereas increases many folds with addition of nitric acid (NO) (Figure 1.18).¹⁶³

1.5.3 Biological applications

Given the importance of metal ions in biology, biological applications of MOPs are widely probed and most importantly as synthetic ion channels. The synthetic ion channels have great significance not only due to the understanding the function of natural ion channels but also for their utility in sensing and drug discovery.¹⁶⁴⁻¹⁶⁸ These ion channels were made up of organic molecules such as crown ethers, cyclic peptides,

and rigid-rod β -barrels.¹⁶⁹⁻¹⁷¹ Owing to its discrete structure and presence of hollow cavities, MOPs are looked at as potential materials for ion channel functionalization. One of the potential MOPs for exploring ion channel applications is MOP-18, reported by Yaghi and co-workers.¹⁷² It has a cuboctahedral structure made up of Cu(II) ions and m-benzene dicarboxylate linkers. Kim and co-workers have prepared a derivative of this MOP-18 by replacing the dicarboxylate linker with a lipophilic 5-dodecoxybenzene-1,3-dicarboxylate linker which resulted in a core modified MOP-18 with an overall size of 5 nm. The alkyl chains of the MOP-18, $\text{Cu}_{24}(\text{5-OC}_{12}\text{H}_{25}\text{-mBDC})_{24}$ were located outside the cage and bound to the ion channel span lipid bilayers with a tailored pore.¹⁷³ The ion transport activity of the MOP-18 for the alkali metal cations decreases in the following order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ (Figure 1.19).¹²¹

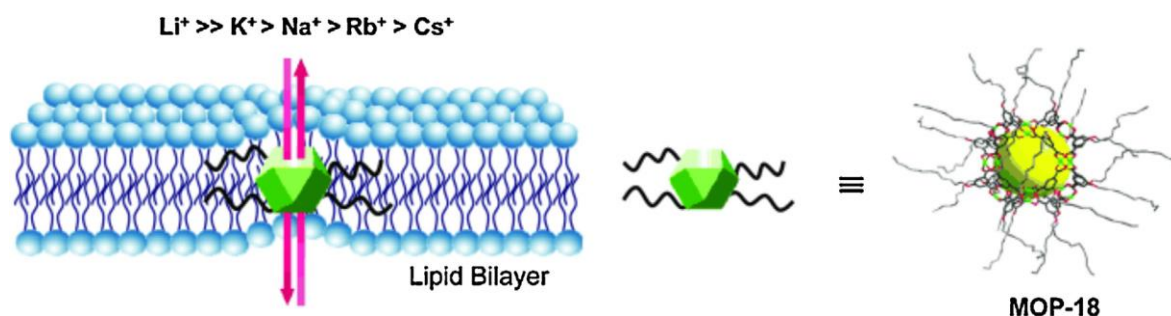


Figure 1.19: Synthetic ion channel formed by a modified MOP-18 in a lipid bilayer. (Adapted by permission from Wiley and Sons Publishers Ltd: “Angew. Chem. Int. Ed. **2008**, 47, 5755” © 2008)

In a recent report, Wang and Zhou have shown a drug release activity by using a polyhedral cage. The cage assembly was synthesized by the reaction of 5-(prop-2-ynyloxy)isophthalic acid (H_2pi) and di-copper paddlewheel cluster. It subsequently undergoes a click reaction in the presence of 2,6-lutidine and gives $\text{Cu}(\text{pi})\text{-PEG5K}$. This cage assembly has been used for the drug release of 5-fluorouracil an anticancer drug.¹⁷⁴ Banerjee et al. have also reported the utility of a Cu-cuboctahedron for the release of encapsulated caffeine (Figure 1.20).¹⁷⁵ Ward and co-workers have shown the reversible pH dependent uptake and the release of aspirin, amantadine, and nicotine using a water-soluble $[\text{Co}(\text{L})_{12}]^{16+}$ cage complex.¹⁷⁶⁻¹⁷⁷

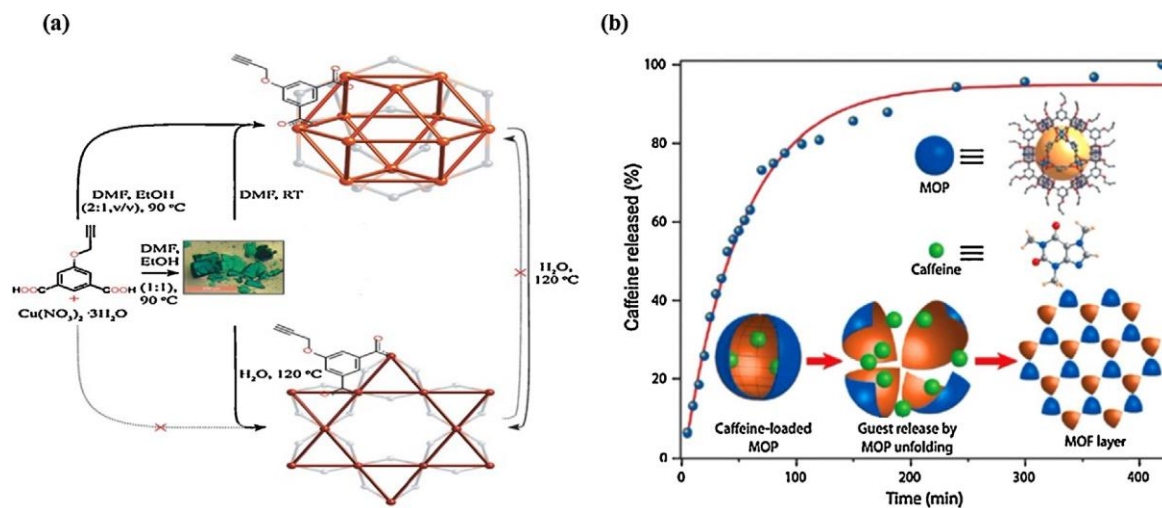


Figure 1.20: (a) Synthesis and conversion of the copper-based materials. (b) The release of encapsulated caffeine molecules from the MOP core and a schematic representation of the release driven by the unfolding event. (Adapted by permission from Wiley and Sons Publishers Ltd: "Angew. Chem. **2013**, 125, 14000" © 2013)

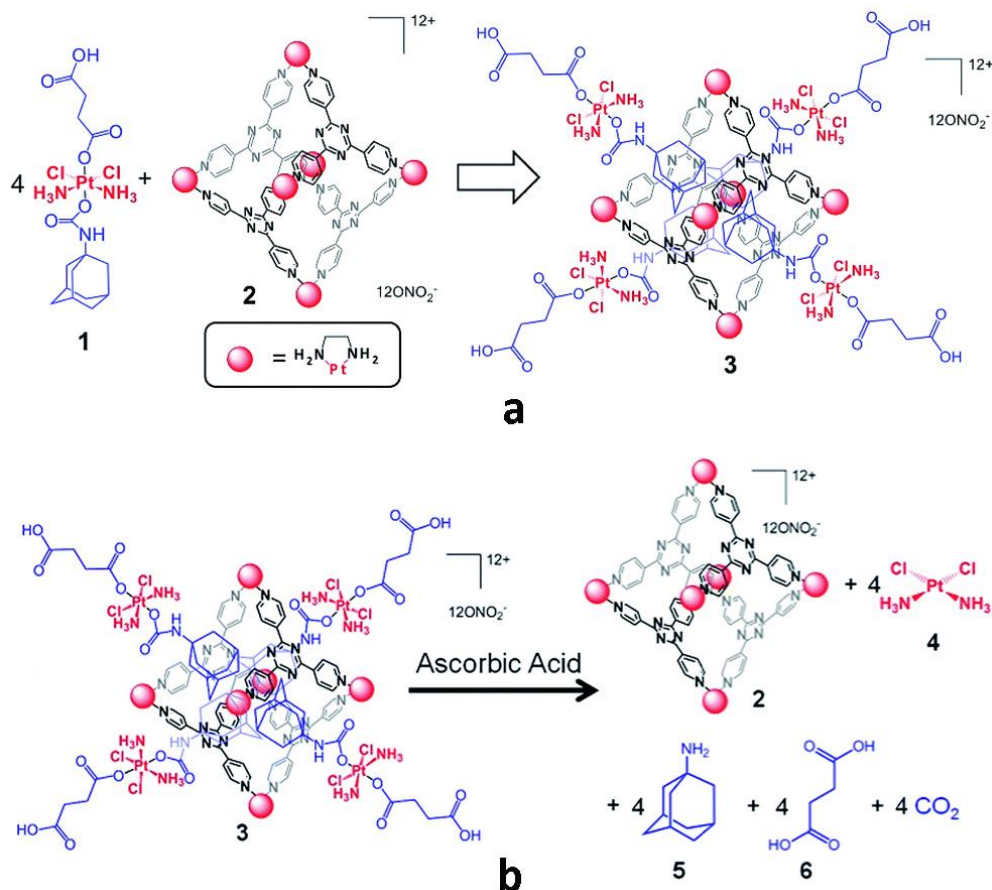


Figure 1.21: (a) Representation of the host-guest complex assembled from the Pt(IV) prodrug and the Pt(II) cage. (b) Chemical representation of the reduction of by ascorbic acid. (Adapted by permission from RSC Publishers Ltd: "Chem. Sci. **2015**, 6, 1189-1193." © 2015)

Lipard and co-workers have reported a host-guest complex, consisting of an adamantyl Pt(IV) prodrug and Pt (II) hexanuclear cage at 80 °C in ratio 4:1. The adamantyl moiety of the prodrug was encapsulated in the hydrophobic cavity of the cage complex. This prodrug is reduced in the presence of ascorbic acid and released cisplatin, 1-adamantylamine, and succinic acid.¹⁷⁸ The *cis*-platin released during the delivery is then covalently bound with guanosine and yields a cationic adduct *cis*-[Pt(NH₃)₂Cl(guanosine)]⁺ which again releases cisplatin (Figure 1.21).

1.5.4 Gas adsorption and separation

Several robust metal-organic polyhedral with a cavity inside the cage frameworks exhibits permanent porosity. The non-covalent interactions rendered by the cavity of the cage makes it a prominent candidate for the adsorption and separation of gas molecules which depends on the cavity size of the cage. If the polyhedron has a large cavity as compared to the size of the gas molecule, then the adsorption will increase, and if the size is small, then selectivity will increase. There are several examples reported for the gas adsorption applications by different research groups.¹⁷⁹⁻¹⁸²

Yaghi and co-workers have reported various metal-organic polyhedra such as truncated tetrahedral and truncated hetrocubane synthesized by the self-assembly of the trinuclear cluster Fe₃O(CO₂)₆ with 1,4-BDC, 4,4'-biphenyl dicarboxylate (BPDC), 4,4"-terphenyl dicarboxylate (TPDC), tetrahydropyrene-2,7-dicarboxylate (HPDC) and tricarboxylic 1,3,5-tris(4-carboxyphenyl)-benzene (BTB) ligands. The obtained polyhedra IRMOP-51, IRMOP-53, IRMOP-54, adsorbed methane molecules 5.6, 5.9 and 7.3 per formula unit, respectively.¹⁸³ Zhou et al. have synthesized two MOPs, SMT-1 and SMT-2, by the reaction of Cu₂(OAc)₄·2H₂O with 3,3'-(naphthalene-2,7-diyl)dibenzoic acid and 3,3'-(1,8-naphyridine-2,7-diyl)dibenzoic acid ligand, respectively. These assemblies showed significant adsorption ability for CO₂ and negligible

adsorption of N_2 and CH_4 . SMT-1 and SMT-2 showed CO_2 uptake of 52 and 25 cm^3g^{-1} respectively at 273K (Figure 1.22).¹⁸⁴

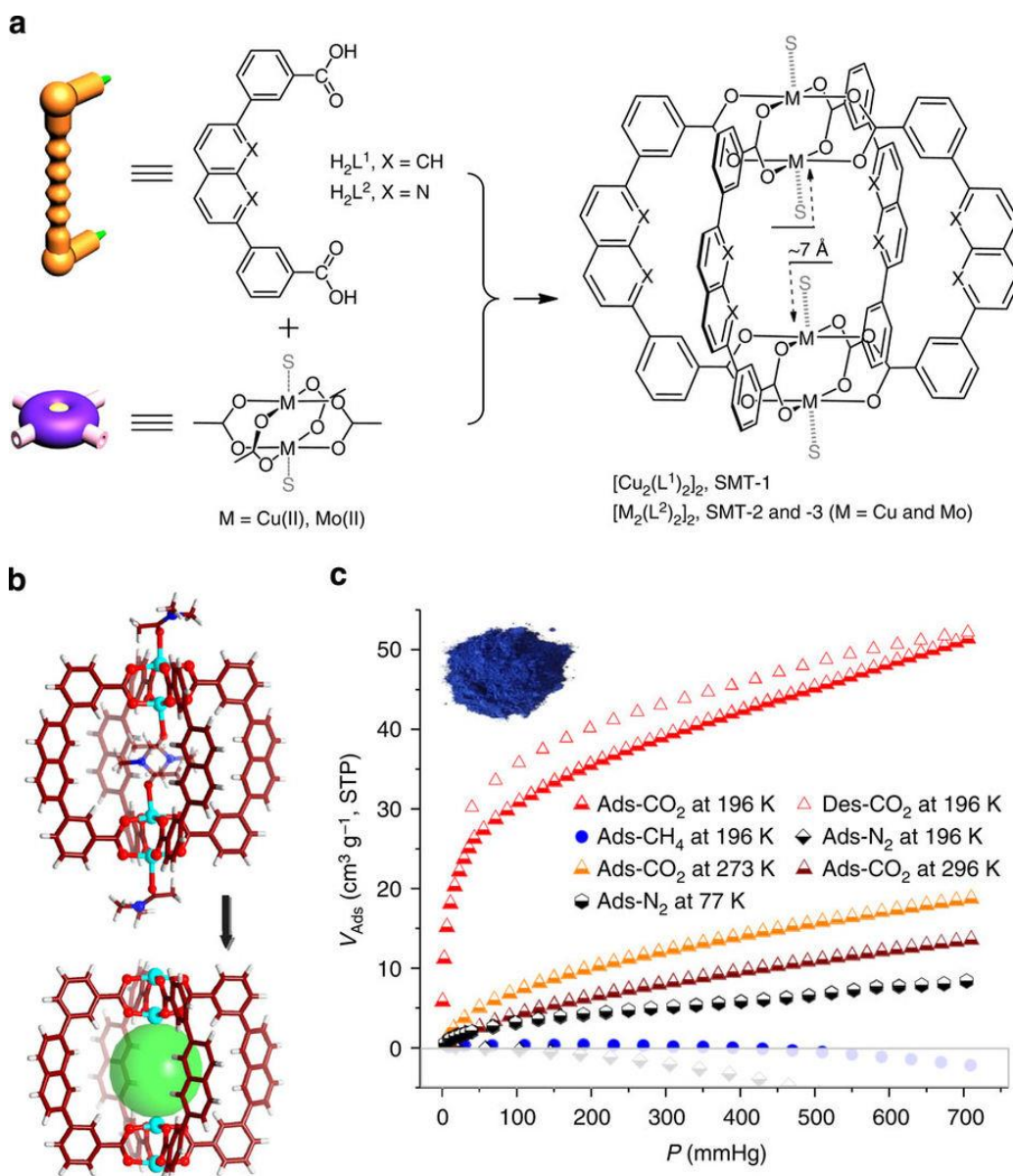


Figure 1.22: (a) Schematic representation of the construction of **SMT-1-3**: S is the coordinated solvent molecule, which can be removed through sample activation to yield an empty molecular cage for gas adsorption. (b) The molecular structure of **SMT-1** with (top) and without (bottom) coordinated solvent molecules. The colour schemes: Cu, cyan; O, red; N, blue; C, brown; and H, light grey. The green sphere represents the free space inside the molecular cage. (c) Gas adsorption isotherms of **SMT-1**, showing selective adsorption of CO_2 over CH_4 and N_2 (inset: a

picture of activated **SMT-1** sample). (Adapted by permission from Macmillan Publishers Ltd: "Nat. Commn. **2013**, 4, 1538." © 2013)

Nitschke and co-workers have demonstrated the encapsulation of the SF₆ by the tetrahedral cage **C4**. Van der Waals forces are responsible for the encapsulation of the SF₆, and the host-guest assembly showed strong binding affinity values of $1.3 \times 10^4 \text{ M}^{-1}$ signifying its preferences over other guest molecules.¹⁸⁵ Yang and Ma have reported the adsorption of dyes by using the rhombic dodecahedron synthesized by the self-assembly of Cu(NO₃)₂·3H₂O and 2,4,6-tris[1-(3-carboxyphenoxy)methyl]mesitylene.¹⁸⁶

1.5.5 Metal-organic frameworks (MOFs) from the MOPs

Metal-organic materials, such as metal-organic polyhedra, metal-organic framework, and metal-organic macrocycles are obtained by the suitable design of ligands and metal ions. Interestingly, the transformation of one type of metal-organic material to another kind is a way to increase the thermal, air/water stability and robustness. The various applications of MOFs are an area not only depends only on the large solvent-accessible void space and the surface area but also on the functionality. It has also been observed that formation of MOPs by incorporating the supramolecular building units increases the robustness. The widely used polyhedra for the establishment of metal-organic frameworks are tetrahedron and hexahedron. In recent years, there are various reports on the design of the MOFs from the MOPs came from the different research groups.¹⁸⁷⁻

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Yaghi and co-workers have shown the synthesis of MOF-500 of SO₂ topology by utilizing the tetrahedral building unit of MOP-51 and MOP-52. To obtain the metal-organic framework, they have substituted the terminal pyridine ligand of MOPs with bridging ditopic ligand, cis-1,2-bis-4-pyridylethane.¹⁹⁵ Furthermore, they have synthesized MOF from the MOP [Ni₈L₁₂]²⁰⁻ using sodium or lithium as the bridging unit.¹¹⁰ Zhou and co-workers have reported the synthesis of the octahedral cage and its metal-organic framework by replacing the axially coordinated DMA (dimethylacetamide) solvent by the DEF (diethylformamide) and further reaction with 4,4'-bipyridine (Figure 1.23c).¹⁹⁶

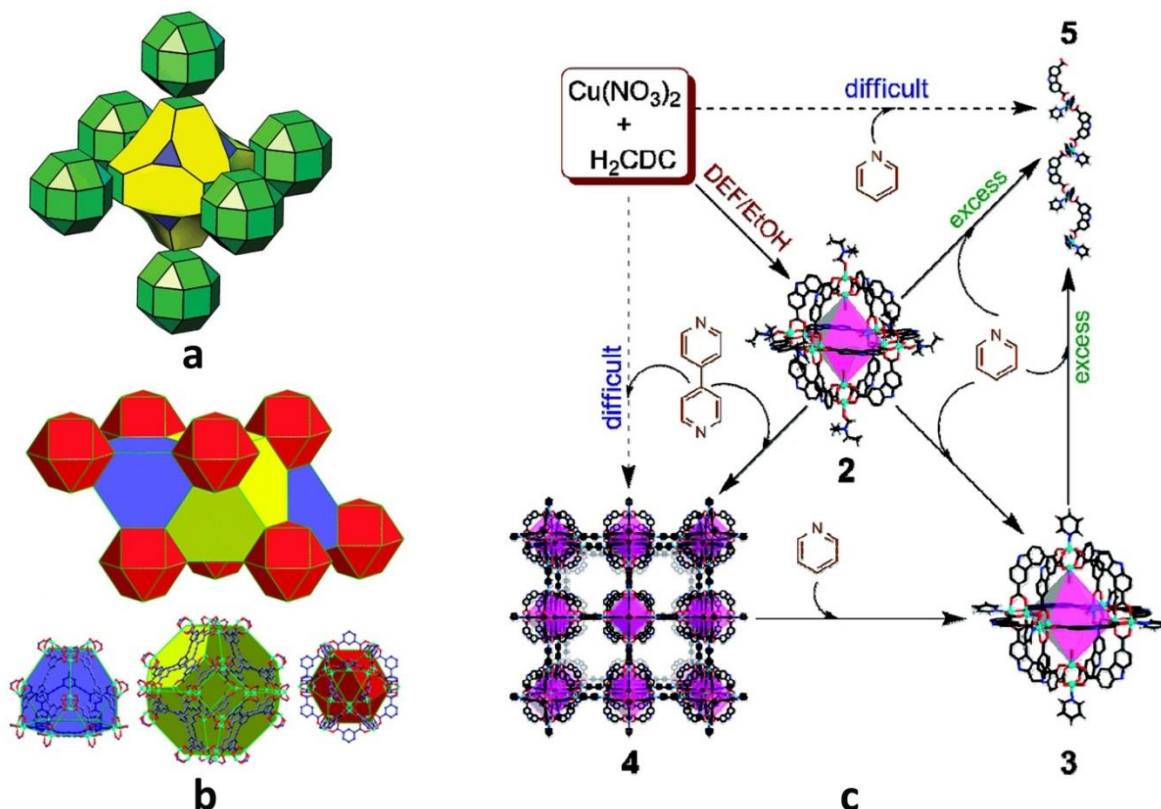


Figure 1.23: (a) Illustration of an rht network, the central tile represents the largest cage formed from six surrounding nanoballs. (b) PMOF-2(Zn), where cuboctahedra (red polyhedra) are interconnected to a cubic close packing arrangement, leads to the generation of superoctahedra cage (yellow polyhedra) and supertetrahedra cage (blue polyhedra). (b) A schematic view of the Inter-conversion of coordination assemblies. (Adapted by permission from Elsevier Publishers Ltd: "Coord. Chem. Rev. **2016**, 306, 171" © 2016)

Eddaoudi and Zaworotko have reported an rht net $[\text{Cu}_6\text{O}(\text{TZI})_3(\text{H}_2\text{O})_9(\text{NO}_3)]_n \cdot (\text{H}_2\text{O})_{15}$ synthesized from the solvothermal reaction of the $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and 5-tetrazolyisophthalic acid (H_3TZI) in DMF/EtOH solution. The MOF contained truncated cuboctahedron, and each cuboctahedron is connected with trigonal $\text{Cu}_3\text{O}(\text{N}_4\text{CR})_3$ cluster via the tetrazolate linker (Figure 1.23a).¹⁹⁷

1.5.6 As ferroelectric and dielectric materials

Metal-organic polyhedral/cages were gained more attention in recent decades due to their several applications in various field such catalysis, molecular recognition and

separation, adsorption and gas storage and sequestration of reactive molecules based on the chemical interaction/properties. But on the aspect of physical properties, the metal-organic polyhedra or cages were still not explored much.

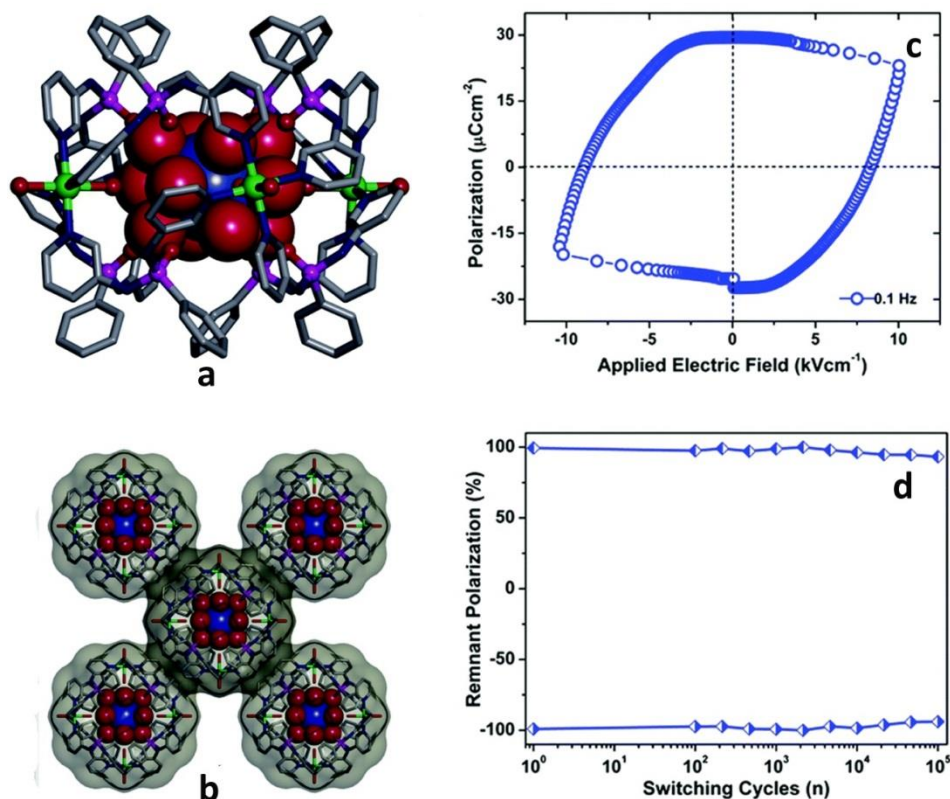


Figure 1.24: (a) Molecular structure of [Hy-K]cNi-Cavitand. (b) The packing view of [Hy-K]c Ni-Cavitand along the c-axis. (c) Ferroelectric hysteresis loop of Ni-Cavitand and (d) its fatigue data up to 10^5 cycles at 1 Hz. (Adapted by permission from RSC Publishers Ltd: "J. Mater. Chem. C **2017**, 5, 7352" © 2017)

Recently, Boomishankar et al. have reported two Ni (II) and Co(II) cavitands based on phosphorus (V) dipodal ligands. The crystal structures of these cavitands were solved in the noncentrosymmetric or polar space group. The cavitand compounds exhibit intrinsic cavity which encapsulates a series of hydrated alkali metals, Li, Na, K, Rb, and Cs.¹⁹⁸ Owing to the polar nature of these compounds; they have investigated the ferroelectric and dielectric properties of the cavitands. Ferroelectric (P-E) hysteresis loop measurements gave high remnant polarization value of $\sim 29 \mu\text{Ccm}^{-2}$. The presence of the guest hydrated alkali metal ions affects the ferroelectric polarization of the host-guest systems (Figure 1.24).

This thesis demonstrated the development metal-organic hybrid materials utilizing the organic ligand based on the phosphorus (V) backbone featuring different N-donor functionality. Next five chapters will discuss the synthesis of the tripodal N-donor functionalized ligands and the metal-organic polyhedral/cages and polymers. Chapter 2 will review the design of the neutral tetrahedral cages and their application in the selective encapsulation of o-xylene and mesitylene from other analogs. Chapter 3 will show the synthesis of a cubic cage assembly and its post assembly reaction to generate cage connected metal-organic frameworks. This post assembly reaction involves various intermediate structures. The chapters 4 and 5 will discuss the synthesis of octahedral cages and their connected cage frameworks. These assemblies exhibit interesting ferroelectric and dielectric properties. Finally, the chapter 6 will deal with the synthesis of CuI based coordination polymer and the studies of their photophysical properties.

Thus the objective of the present thesis is:

- To synthesize tripodal rigid and flexible Phosphorus (V) based N-donor functionalized amino ligands.
- To develop new metal-organic materials such as metal-organic polyhedra/cages and coordination polymers with fascinating structures.
- To investigation various properties of the materials such photophysical, dielectric and ferroelectric.

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Chapter 2

**Imido-P(V) Supported Neutral
Tetrahedral Cages Showing Selective
Encapsulation of o-Xylene and
Mesitylene over other Analogues**

2.1 INTRODUCTION

Polyimido anions of the phosphorus (V) motifs of the type $[\text{PE}(\text{NHR})_x(\text{NR})_{3-x}]^{3-}$ ($\text{E} = \text{O}$ or S or NR) are fascinating because of their isoelectronic relationship with various phosphorus oxo anions and versatile coordination chemistry.¹⁻⁷ These anions were traditionally used for obtaining polynuclear metal clusters based on main group metal ions by the treatment of their amido precursors of the type $[\text{PE}(\text{NHR})_3]$ with strong organometallic bases such as $n\text{-BuLi}$, Et_2Zn , $n\text{-Bu}_2\text{Mg}$, Me_3Al etc.⁸⁻¹⁴ In an effort to obtain the transition metal complexes of these polyimido anions, our group has developed novel protocols which utilize salts of certain soft metal ions as weak bases towards their deprotonation. During these reactions, a facile route to access the tris(imido)phosphate trianions, $[\text{PO}(\text{NR})_3]^{3-}$, (denoted as $(\text{X})^{3-}$, in polar and protic medium was developed by employing the corresponding tris(amido)phosphates, $[\text{PO}(\text{NHR})_3]^{3-}$, in reaction with $\text{Pd}(\text{OAc})_2$.¹⁵ These imido anions were stabilized as tri- or hexanuclear $\text{Pd}(\text{II})$ complexes, in which the trianion was coordinated to the trinuclear $\text{Pd}(\text{II})$ centre in a cisoidal fashion. These Pd -imido complexes can further react with a wide-angle chelating ligand such as oxalic acid giving rise to an interesting charge neutral tetrahedral cage **B** of formula $\{[\text{Pd}_3(\text{X})]_4(\text{C}_2\text{O}_4)_6\}$.¹⁶ This cage assembly exhibits an intrinsic cavity of volume $86 \text{ \AA}^3$, which provides a suitable binding pocket for the selective binding of benzene over other aromatic compounds. The apparent selectivity stems from the charge neutral nature of this cage coupled with the compact interiors of its endohedral void space. Inspired by these observations, we set out to utilize similar such tetrahedral cages which can offer suitable sites for the selective encapsulation of higher aromatic hydrocarbons such as xylenes and mesitylenes. Separation of substituted and isomeric hydrocarbons is one of the most challenging aspects in the pharmaceutical and chemical industries. These are typically purified by fractional distillation which effects these separations based on their boiling points, however, it is an energy intensive process.¹⁷ To overcome this problem it is desired to develop novel strategies for the energy-efficient separation of these molecules.¹⁸ Among all the aromatic hydrocarbons, separation of xylene isomers holds one of the most challenging aspects for the industries not only because of the energy intense distillation methods

but also due to their similar boiling points.¹⁹ The purity of these isomers is essential as they are the main ingredients for some industrial preparations and also useful as solvents and precursors for several organic synthesis. For example, p-xylene (PX, p-C₈H₁₀) is utilised in the polyester industry for the preparation of poly(ethylene terephthalate) derivatives, while o-xylene (OX, o-C₈H₁₀) is employed for the formation of phthalic anhydride, used as plasticisers. The m-xylene (MX, m-C₈H₁₀) is used in the production of derivatives of isophthalic acid that are utilised in PET resin blends.²⁰⁻²² Recently, several rigid MOFs and hydrogen-bonded supramolecular assemblies have successfully been administered for the separation of xylene isomers, essentially by utilizing the molecular sieving phenomena and selective inclusion criteria, respectively.²³⁻³¹ But, until now, neither fractional crystallization, relying on the differences in their freezing points, nor adsorption based on selective host-guest interactions meets the necessary standards of the industrial separation.³²⁻³⁵ Hence, separation of the isomeric mixtures of these C₈-hydrocarbons offers a great challenge and industrial incentive. This chapter describes two iso-structural tetrahedral cage assemblies **1**, {Pd₃[(NⁱPr)₃PO]₄(L_B⁻)₆} and **2**, {Pd₃[(NⁱPr)₃PO]₄(L_C⁻)₆}, built on our [Pd₃(X)]³⁺ motifs and benzoquinone derived anions that show the selective separation of o-xylene and mesitylene, respectively. The cage assemblies were synthesized from the reaction of the PBU precursor {Pd₃[(NⁱPr)₃PO](OAc)₂(OH)}₂·2(CH₃)₂SO, **A**,¹⁵ with the chelating ligands chloranilic acid (L_B-2H) acid and 2, 5- dihydroxy-1,4-benzoquinone (L_C-2H), respectively. Both the cage assemblies exhibit fairly large intrinsic cavity of ~230 Å³, volume. These larger cavity volumes and the quinonate-lined triangular portals of the cage facilitate the encapsulation of bigger aromatic hydrocarbons than benzene. Interestingly, the cage assemblies **1** and **2** show selective encapsulation of o-xylene and mesitylene over other aromatic analogues.

2.2 EXPERIMENTAL SECTION

2.2.1 General remarks

All manipulations involving phosphorus halides were performed under a dry nitrogen atmosphere in standard Schlenk-glassware. Solvents were dried over sodium (toluene).

Isopropylamine and POCl_3 were purchased locally and was distilled before use. Palladium acetate was purchased from the Aldrich and used as received. NMR spectra were recorded on a Jeol or Bruker 400 MHz spectrometer (^1H NMR: 400 MHz, $^{13}\text{C}\{^1\text{H}\}$ NMR: 100 MHz, $^{31}\text{P}\{^1\text{H}\}$ NMR: 161 MHz) at room temperature using SiMe_4 (^1H , ^{13}C) and 85% H_3PO_4 (^{31}P). The mass spectra were obtained on an Applied Biosystem MALDI-TOF spectrometer. The powder X-ray diffraction data were obtained from a Bruker D8 Advance diffractometer. FT-IR spectra were taken on a Perkin Elmer spectrophotometer with samples prepared as KBr pellets. Elemental analyses were performed on a Vario-EL cube elemental analyser.

2.2.2 Synthesis

The ligand $[\text{PO}(\text{N}^i\text{Pr})_3]$ and the PBU precursor $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}](\text{OAc})_2(\text{OH})\}_2 \cdot 2(\text{CH}_3)_2\text{SO}$, **A** were prepared by the earlier reported procedures.¹⁵

2.2.2.1 Synthesis of tetrahedral cage $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}]_4(\text{L}_\text{B}^-)_6\}$ compound 1: To stirred solution of $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}](\text{OAc})_2(\text{OH})\}_2 \cdot 2(\text{CH}_3)_2\text{SO}$, **A** (20 mg, 0.0585 mmol) in MeOH at room temperature, chloranilic acid (10.6 mg, 0.0439 mmol) was added. The resulting solution was heated at 80 °C for 30 min to get a brown coloured precipitate. The obtained precipitate was filtered off and washed with methanol for several times. Dark brown coloured crystals were obtained from its toluene solution after 20 days. Yield: 65%. FT-IR data in KBr pellet (cm^{-1}): 3419, 3131, 1580, 1501, 1384, 1277, 1191, 1112, 1061, 1026, 939, 802, and 699. Anal. calcd. for $\text{C}_{72}\text{H}_{84}\text{N}_{12}\text{O}_{28}\text{P}_4\text{Cl}_{12}\text{Pd}_{12}$: C, 25.50; H, 2.50; N, 4.96. Found: C, 25.45; H, 2.62; N, 5.02.

2.2.2.2 Synthesis of tetrahedral cage $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}]_4(\text{L}_\text{C}^-)_6\}$ compound 2: To stirred solution of $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}](\text{OAc})_2(\text{OH})\}_2 \cdot 2(\text{CH}_3)_2\text{SO}$, **A** (20 mg, 0.0585 mmol) in MeOH at room temperature, 2,5-dihydroxybenzoquinone (6.2 mg, 0.0439 mmol) was added. The resulting solution was heated at 80 °C for 30 min to get a brown coloured precipitate. The obtained precipitate was filtered off and washed with methanol for several times. Dark brown coloured crystals were obtained from its toluene solution after 20 days. Yield: 60%. FT-IR data in KBr pellet (cm^{-1}): 3440, 3149, 1580, 1500,

1277, 1193, 1111, 1064, 1026, 945, 803, and 698. Anal. calcd. for $C_{72}H_{96}N_{12}O_{28}P_4H_{12}Pd_{12}$: C 28.92; H, 3.64; N, 5.62. Found: C, 28.95; H, 3.52; N, 5.55.

2.2.2.3 General Procedure for the host guest assembly formation: To a stirred solution of cage assemblies (20 mg) in DCM (5 ml) the guest (50 μ l) solvent (Toluene, Xylenes, Mesitylene) was added. The resulting solution was stirred further for 30 m. The obtained mixture was diluted in DCM and analyzed by MALDI-TOF mass spectroscopy which revealed the formation of host-guest complexes.

2.2.3 Crystallography

Reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using MoK α radiation ($\lambda = 0.71073$ Å) for **1**, and **2** (Table 2.1). Structures were refined by full-matrix least-squares against F^2 using all data (SHELX97).³⁶ All non-hydrogen atoms were refined anisotropically if not stated otherwise. Hydrogen atoms were constrained in geometric positions to their parent atoms. SHEL command was applied to omit bad reflection for **1** and **2**. The toluene molecules located in the structure of **1** were disordered thus were refined isotropically using similar distances and same U-restraints. The additional solvent molecules at the larger packing cavities were removed by using applying the SQUEEZE routine of the PLATON.³⁷

Table 2.1: Details of the crystallographic data and the structure refinements of the **1 and **2**.**

Compound	1	2
Chemical formula	$C_{164}H_{368}Fe_4N_{48}O_{152}P_8Pd_{24}S_{12}$	$C_{234}H_{288}F_{12}Fe_7N_{72}O_{121}P_{12}Pd_{36}S_4$
Formula weight	8854.54	10994.58
Temperature	100(2) K	100(2) K
Crystal system	Tetragonal	Orthorhombic
Space group	P4/nnc	P2 ₁ 2 ₁ 2
a (Å); α (°)	28.142(8); 90	35.902(11); 90
b (Å); β (°)	28.1421(8); 90	35.914(11); 90
c (Å); γ (°)	25.241(10); 90	22.493(7); 90

V (Å ³); Z	19990(11); 2	29001(15); 2
ρ (calc.) mg m ⁻³	1.471	1.259
μ(Mo K _α) mm ⁻¹	1.363	1.360
2θ _{max} (°)	50	56
R(int)	0.3047	0.1391
Completeness to θ	99.5 %	99.9 %
Data / param.	8804 / 454	73105/1148
GOF	1.045	1.088
R1 [F>4σ(F)]	0.1026	0.0661
wR2 (all data)	0.3747	0.1987
max.peak/hole (e.Å ⁻³)	1.237/-2.050	1.724/-0.824

2.2.4 Theoretical calculation

The binding energies of the host-guest systems were calculated theoretically by using the *Gaussian 03* software. These energies were computed by DFT methods by employing the basis set Lanl2dz with b97d3. The energies of the host cage, guest solvents, and host-guest complex were separately calculated and the binding energy of a given host-guest complex was calculated by using the following equation.

$$\text{Binding energy} = E_{\text{host-guest}} - (E_{\text{host}} + E_{\text{guest}})$$

2.2.5 NMR studies

The ¹H-2D-DOSY NMR experiments were carried out on a Bruker NMR spectrometer operating at a ¹H frequency of 400 MHz, and a constant temperature of 298 K. 2.50 mM solutions of the compounds was prepared in (CD₃)₂SO and allowed to equilibrate for 30 minutes before data acquisition. The standard Bruker protocol using Topspin 2.1 software was used for processing the DOSY data. The fitting of the diffusion dimension in the 2D-DOSY spectra was carried out using a one (monoexponential) or two-parameter biexponential fit (equation 1) that showed better fits when compared with a two-parameter monoexponential fit.³

$$I = I_{0A} \exp \left[-D_A \gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \right] + I_{0B} \exp \left[-D_B \gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \right] \quad (1)$$

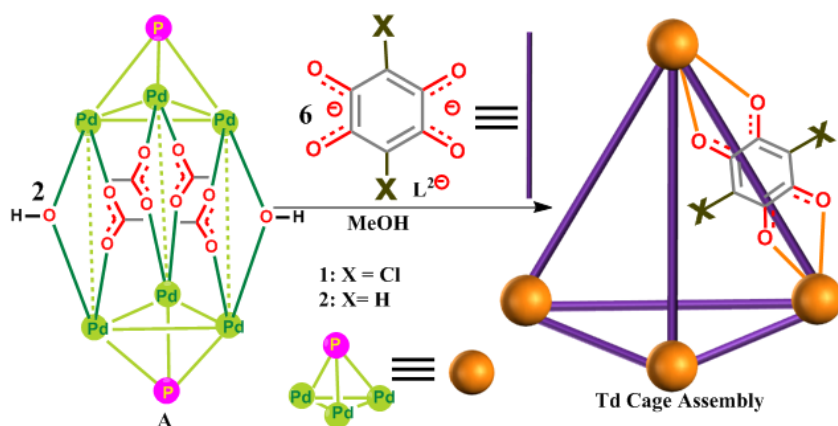
In this equation, I is the observed integral, I_{0A} and I_{0B} the reference integral or unattenuated integrals, D_A and D_B the diffusion coefficients, g the gyromagnetic ratio of the detected nucleus, g the gradient strength, d the length of the gradient, and D the diffusion time.

2.3 RESULTS AND DISCUSSION

2.3.1 Synthesis

The tetrahedral cage assemblies **1**, $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}]_4(\text{L}_B^-)_6\}$ and **2**, $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}]_4(\text{L}_C^-)_6\}$ were synthesized by using the similar process as used for compound **B**. In separate reactions, the hexameric palladium cluster $\{\text{Pd}_3[(\text{N}^i\text{Pr})_3\text{PO}](\text{OAc})_2(\text{OH})\}_2 \cdot 2(\text{CH}_3)_2\text{SO}$, **A** was reacted with chloranilic acid and 2,5-dihydroxybenzoquinone in 1:3 ratio in MeOH and heated to 80 °C for 30 minutes and the resulting solution was precipitate out after heating to yield **1** and **2**, respectively (Scheme 2.1). Formation of cage assemblies was confirmed by NMR, MALDI-TOF mass and single crystal X-ray diffraction (SCXRD) spectroscopic techniques. The ^{31}P -NMR spectra gave a single peak at 72.88 and 70.56 ppm for **1** and **2**, respectively (Figures 2A.1-2A.4, Appendix 2). The mass spectrum gave a peak at $m/z = 3430$ and 3013 corresponding to the mass of **1**+K and **2**+Na respectively (Figures 2A.5-2A-6., Appendix 2). The single crystals of **1** and **2** were grown from their corresponding toluene solutions.

Scheme 2.1: Schematic representation of the formation of cage compounds 1 and 2.



Further, we have studied the competitive formation of the cage assemblies in the presence of all the three linkers. For this experiment, the hexameric building unit **A** was simultaneously treated with all the three linkers, oxalate (L_A^-), chloranilate (L_B^-) and dihydroxybenzoquinone (L_C^-) ions. The MALDI-TOF mass spectrum of the resultant precipitate showed a peak at $m/z = 3430$ which attributes to the mass of the tetrahedral cage **1**+K. Also, ^1H - and ^{31}P -NMR of the product gave signals pertaining to that of **1**.

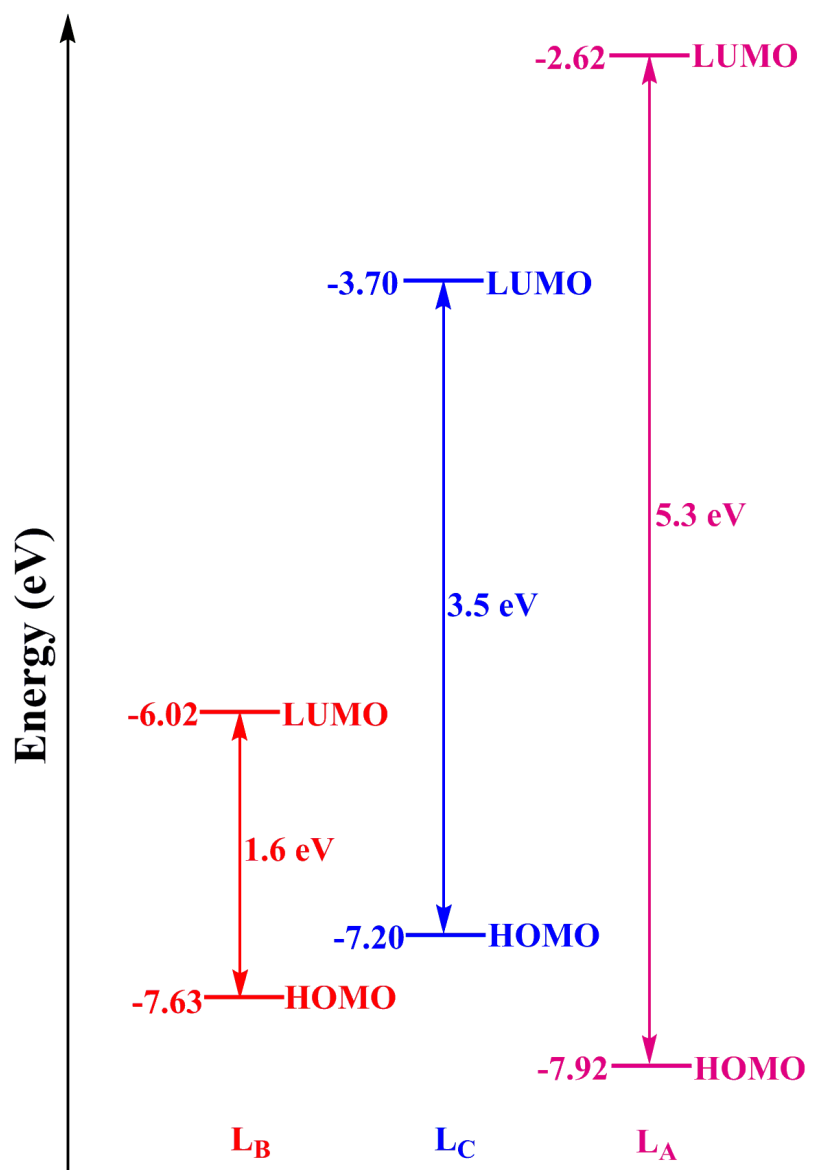


Figure 2.1: Comparative diagram showing the theoretically calculated HOMO-LUMO energy gaps in L_A , L_B and L_C .

The preferential formation of **1** over the other cages can be understood by comparing the energy difference between the HOMO and LUMO orbitals for all the three linkers L_A , L_B and L_C . The HOMO-LUMO energy gaps computed by DFT methods were found to be 5.3 eV, 3.5 eV and 1.6 eV for L_A , L_B and L_C , respectively (Figure 2.1). The observed lowest energy gap of 3.5 eV for L_B implies that, this anionic linker acts as a softer base than the other linkers and is capable of binding stronger to the soft Pd^{2+} ions. Hence, the formation of cage **1** is preferred over the other two cages **B** and **2**.

2.3.2 Crystal structure

The crystal structures of **1** and **2** were solved in the orthorhombic $Pnma$ and monoclinic $P4_2/n$ space group respectively. In addition, one molecule of disordered toluene was located at the intrinsic cavity of **1**. The single crystal X-ray analysis revealed that both molecules are iso-structural and has a similar tetrahedral topology exhibited by the previously reported cage **B**.

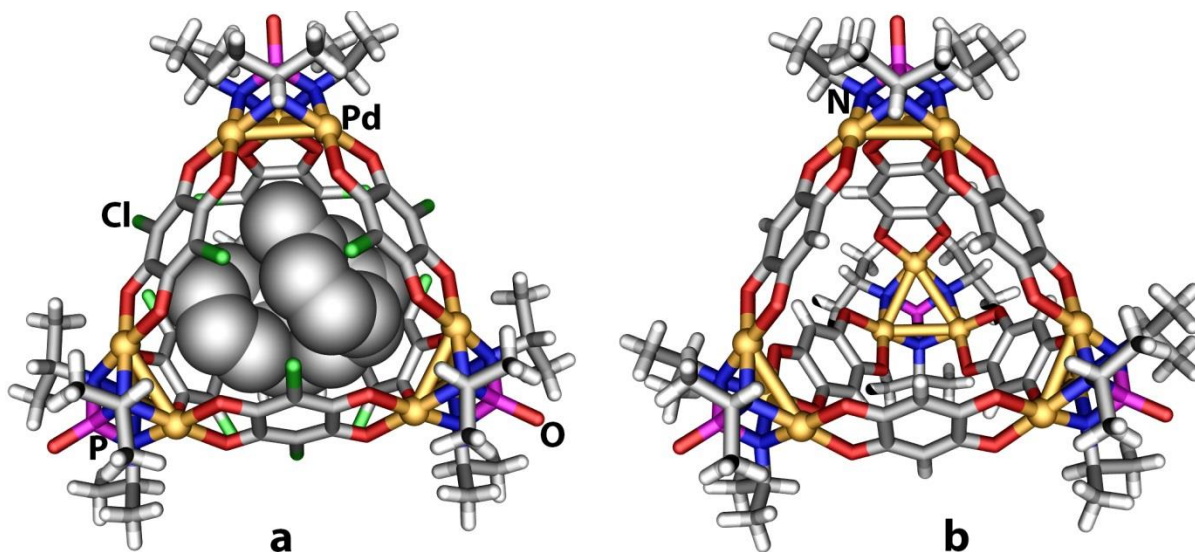


Figure 2.2: Crystal structures of the (a) tetrahedral cages **1** (a) and **2** (b). The encapsulated toluene guest molecule disordered over four positions in **1** is shown in the space fill model in Figure a.

Each vertex of the cage consists of a planar-cluster of three Pd(II) cations which are capped by three chelating N_{imido} sites from $[\text{PO}(\text{N}^i\text{Pr})_3]^{3-}$ (X^{3-}), trianions yielding a

tetrahedral $[\text{Pd}_3\text{X}]^{3+}$ PBU. These PBUs are further connected by bridging interaction of the six chloranilate (L_n^{2-}) and dihydroxybenzoquinone (L_n^{3-}) ions in **1** and **2**, respectively, and complete the tetrahedral cage assembly of composition $[(\text{Pd}_3\text{X})_4(\text{L}_n)_6]$ (Figure 2.2).

The volumes of the central cage cavities in **1** and **2** were determined by MSROLL software calculations with a fixed probe radius of 1.4 Å: 233 Å³ for **1** and 228 Å³ for **2**.³⁸⁻³⁹ These volumes are much larger than that of the previously reported tetrahedral cage **B** which has a cavity volume of ~86 Å³. It suggests that cages **1** and **2** can encapsulate bigger guest molecules as compared to benzene (~100 Å³) which was selectively encapsulated by the cage **B**.

2.3.3 Host-Guest studies

The central cavities in these cages are hydrophobic due to their aromatic portals. Further, the presence of encapsulated toluene molecule in the structure of **1** (Figure 2.2a) prompted us to investigate the ability of these cages for encapsulation of a number of aromatic hydrocarbons such as toluene (C_7H_8), xylenes (C_8H_{10}) and mesitylene (C_9H_{12}). We were able to isolate a number of inclusion compounds for toluene (TOL), o-xylene (OX), m-xylene (MX), p-xylene (PX) and mesitylene (MES) as denoted by $\text{C}_7\text{H}_8\subset\text{C}$, $\text{o-C}_8\text{H}_{10}\subset\text{C}$, $\text{m-C}_8\text{H}_{10}\subset\text{C}$, $\text{p-C}_8\text{H}_{10}\subset\text{C}$ and $\text{C}_9\text{H}_{12}\subset\text{C}$, respectively (C represents the cages **1** or **2**).

The initial MALDI-TOF mass spectral analyses reveal that toluene and o-xylene were successfully encapsulated by the cage assembly of **1**. Thus, in the MALDI-TOF spectra of the toluene and o-xylene treated samples, prominent peaks at $m/z = 3520$ and 3532 were observed which can be assigned to $[\text{C}_7\text{H}_8\subset\text{1}+\text{K}]^+$ (Figures 2A.7, Appendix 2). and $[\text{C}_8\text{H}_{10}\subset\text{1}+\text{K}]^+$ species attributed to respective 1:1 host-guest inclusion solids of toluene and o-xylene (Figures 2.3b and 2A.8, Appendix 2). In contrast, other host-guest complex such as $\text{m-C}_8\text{H}_{10}\subset\text{1}$, $\text{p-C}_8\text{H}_{10}\subset\text{1}$ and $\text{C}_9\text{H}_{12}\subset\text{1}$ were not detected in the MALDI-TOF spectrum of the samples treated with the corresponding solvents MX ($\text{m-C}_8\text{H}_{10}$), PX ($\text{p-C}_8\text{H}_{10}$) and MES (C_9H_{12}) signifying that these guest molecules were unable to access the central cavity of the cage **1**.

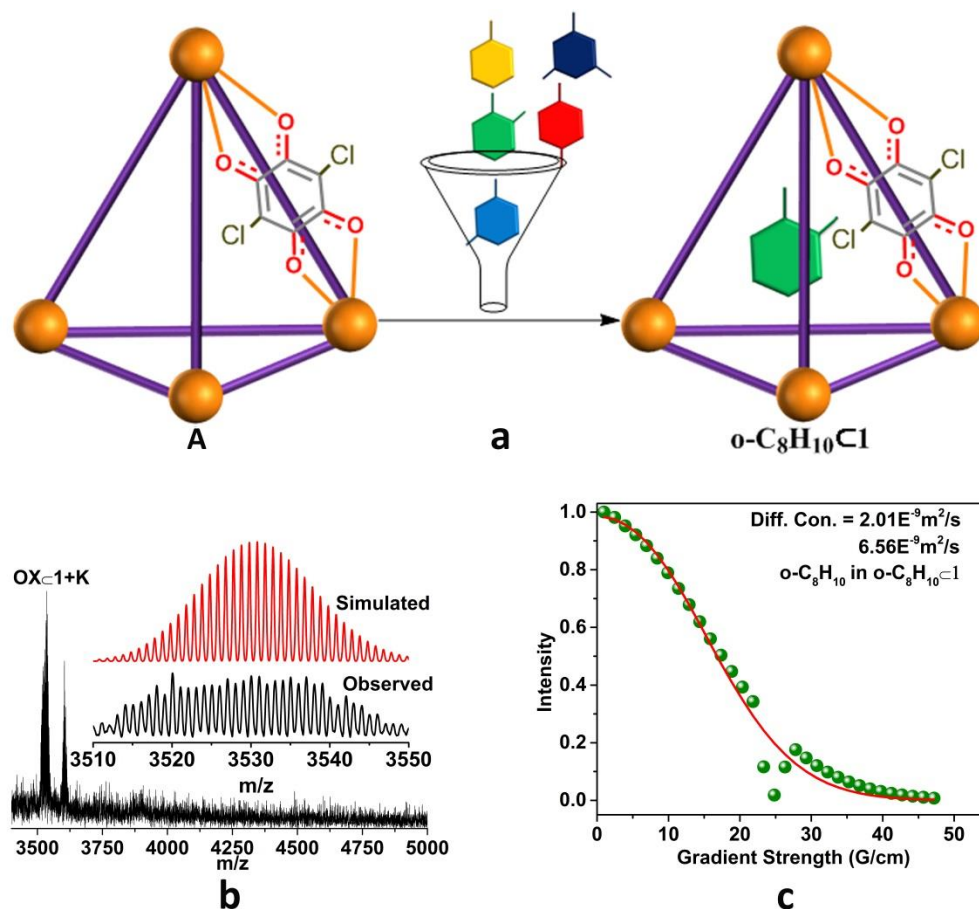


Figure 2.3: (a) Schematic representation of selective encapsulation of o-xylene in **1**. (b) MALDI-TOF mas spectrum of o-C₇H₈<**1**. (c) Plot of the integrated decay profile vs. gradient strength showing the diffusion coefficients of free and bound o-xylene in **1**.

Interestingly, the mass spectra recorded on the toluene, o-xylene, m-xylene, p-xylene and mesitylene treated samples of **2** confirmed the formation of the host-guest inclusion compounds in all the cases. Thus, peaks at $m/z = 3105, 3119, 3119, 3119$ and 3133 have been observed for the C₇H₈<**2**, o-C₈H₁₀<**2**, m-C₈H₁₀<**2**, p-C₈H₁₀<**2** and C₉H₁₂<**2** species in their respective MALDI-TOF mass spectrum (Figures 2.4c and 2A.9-2A.12, Appendix 2).

To further check the existence of these inclusion complexes in solution, NMR spectroscopy of each of the host-guest systems was investigated. The ¹H-NMR spectrum of all these guest treated samples did not give any significant change in the

peak of free and bound guest molecules for the inclusion compounds of both **1** and **2**. Since the protons of the DHBQ anions in **2** are outwardly projected away from the cage cavity, their interaction with the guest protons are very weak or null, while there is no proton in case of the chloranilate anions. Hence, to check the formation of the definite host-guest assemblies, ^1H -2D-DOSY NMR spectroscopy technique was employed. (Figures 2A.13-2A.14, Appendix 2).

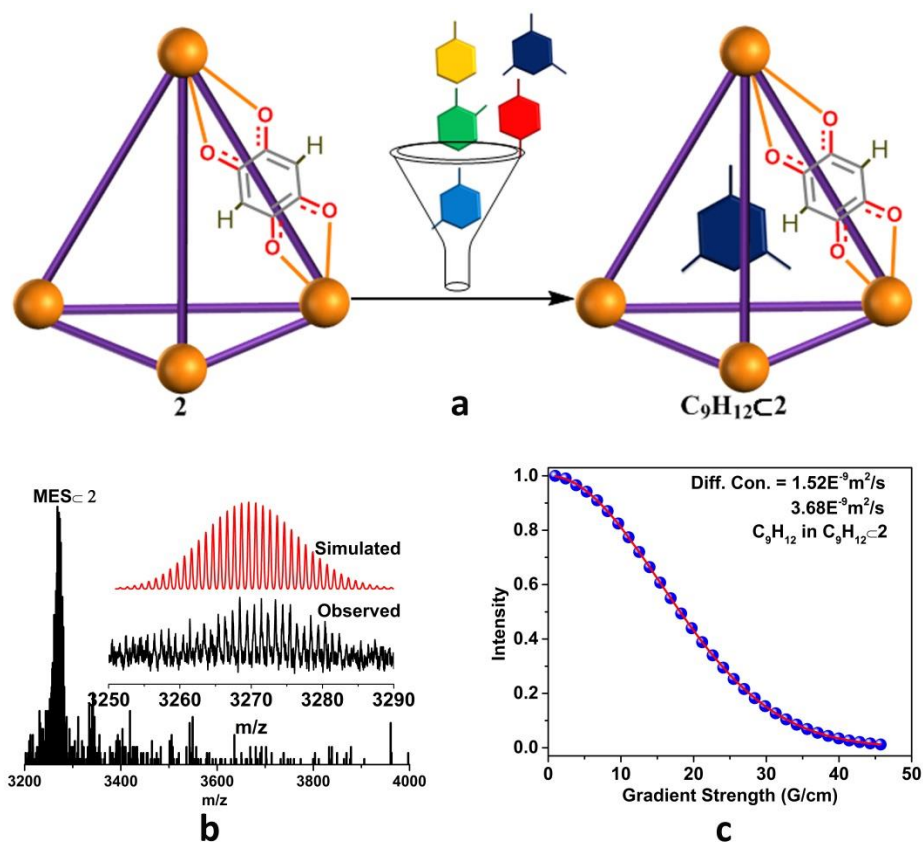


Figure 2.4: (a) Schematic representation of selective encapsulation of mesitylene in **2**. (b) MALDI-TOF mass spectrum of $\text{C}_9\text{H}_{12}\text{C}_2$. (c) The plot of the integrated decay profile vs gradient strength showing the diffusion coefficients of free and bound mesitylene in **2**.

As inferred from the MALDI-TOF spectra, the ^1H -DOSY NMR confirms the formation of host-guest complexes in toluene and o-xylene treated samples of **1**. Each of these two guest molecules gave two diffusion coefficient values: 1.58×10^{-8} (free) $2.42 \times 10^{-9} \text{ m}^2/\text{s}$ (bound) for toluene (C_7H_8) and 6.56×10^{-9} (free) and 2.01×10^{-9} (bound) for o-xylene (C_8H_{10}). For the other aromatic molecules studied, only one D-value pertaining to the

free guests was obtained (Figures 2.4d and 2A.13-2A.14, Appendix 2). This clearly confirms that the cage assembly of **1** can encapsulate only toluene and o-xylene. Similarly, The DOSY NMR spectrums of **2** with guest gave two distinct diffusion coefficients for all the guest molecules and a single diffusion coefficient for the host molecule and suggests that the encapsulation of all the guests in the cage cavity of **2**. However, a single diffusion coefficient value of the order of around 7×10^{-10} and 3×10^{-10} m^2/s was obtained for the host molecules of **1** and **2**, respectively.

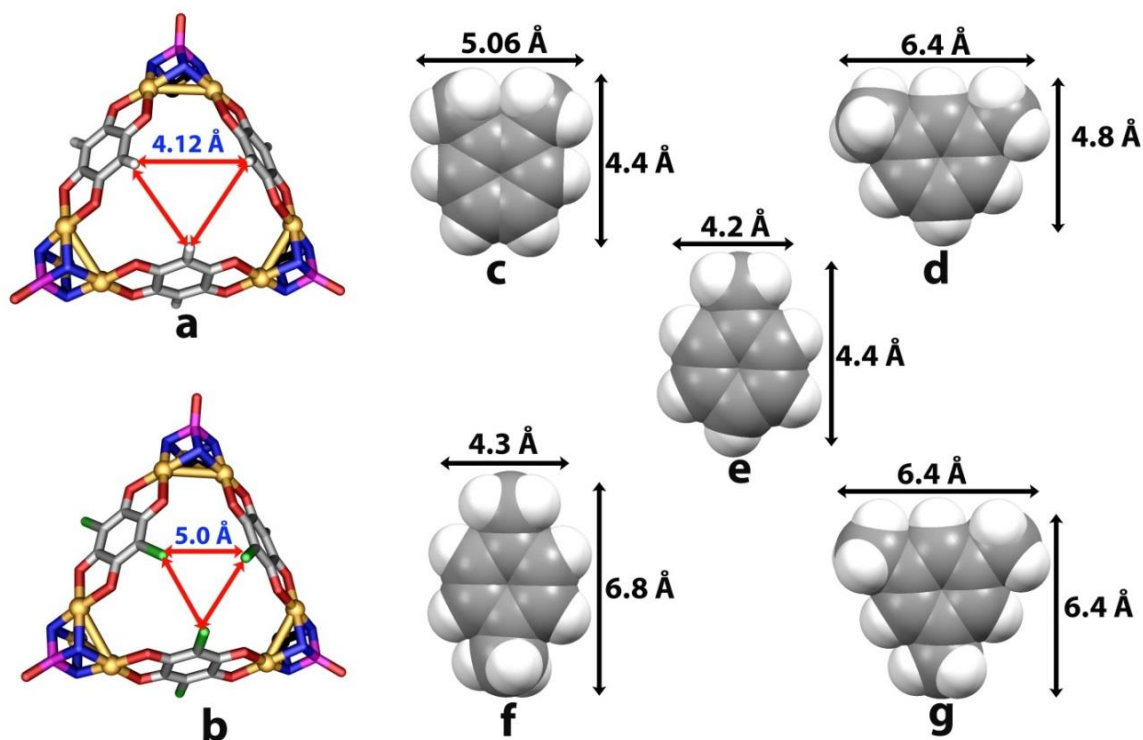


Figure 2.5: View of the portal diameters of the trigonal faces in **1** (a) and **2** (b); Dimensions associated with various guest molecules: o-xylene (c), m-xylene (d), toluene (e), p-xylene (f), and mesitylene (g).

Although, as the MSROLL software calculations on **1** and **2** suggest that both molecules have almost similar cavity sizes, they showed different selectivity towards guest encapsulation. A comparison of the portal diameters of these cages indicate that cage **1** has a relatively smaller window size of (4.2 Å) that of **2** (5.0 Å). The reduced portals in case of **1** were due to the presence of chloride ions that are lined on top of each of the

four windows. The reduced portal diameter in **1** is comparable to the dimensions of toluene and the o-xylene, and therefore suitable for entry of these guest molecules inside the pore. Whereas, for the bigger guests such as m-xylene, p-xylene and mesitylene, the size of the windows is smaller and hence their entry is restricted in cage **1**. The compound **2** has a larger window size as compared to the compound **1** (due to the absence of chloride substituents), and it will enable the entry all the guest molecules inside the cage cavity (Figure 2.5) as observed from the NMR and mass-spectral studies.

Moreover, to see the selective host-guest binding, the all guests were mixed in DCM and added to the individual DCM solutions of **1** and **2**. The MALDI-TOF spectrum of the resulting solution gave peaks at $m/z = 3532$ and 3133 corresponding to the inclusion compounds $[o\text{-C}_8\text{H}_{10}\text{C}\textbf{1}+\text{K}]^+$ and $[\text{C}_9\text{H}_{12}\text{C}\textbf{2}+\text{K}]^+$. This suggests that **1** and **2** exhibits selective encapsulation of o-C₈H₁₀ and C₉H₁₂ respectively, over the other aromatic analogues (Figures 2.3a and 2.4a). The ¹H-DOSY NMR these mixtures also gave the diffusion coefficients corresponding to the $[o\text{-C}_8\text{H}_{10}\text{C}\textbf{1}]$ and $[\text{C}_9\text{H}_{12}\text{C}\textbf{2}]$ which again confirms the selective encapsulation of the OX and MES by **1** and **2**, respectively.

Further support for the selective encapsulation capabilities of **1** and **2** was derived from the computed binding energies of the host-guest complexes. Figure 2.4 shows the pictorial comparisons of the relative binding energies of the various host-guest complexes studied. These calculations yield the highest binding energies of -149.65 kJ/mol and -130.60 kJ/mol for $[o\text{-C}_8\text{H}_{10}\text{C}\textbf{1}]$ and $[\text{C}_9\text{H}_{12}\text{C}\textbf{2}]$, respectively (Figure 2.6 and Table A6.1, Appendix 6). This indicates that cage **1** is selective for o-xylene and cage **2** is selective for mesitylene. These observations are consistent with the selectivity obtained from the mass-spectral and NMR data. Although, the obtained binding energies of m-C₈H₁₀C**1** and o-C₉H₁₂C**1** are relatively lower which suggests their incorporation inside the cage **1**, formation of these host-guest assemblies were not observed in the NMR and mass-spectral experiments. This might be due to the restricted access to these guest molecules through the portals of the cage which contains the bulky chloride substituents. Similarly, incorporation of p-xylene in **1** could

not be experimentally detected (again consistent with the BE data), as it may have smoothly passed through the cage and leached out.

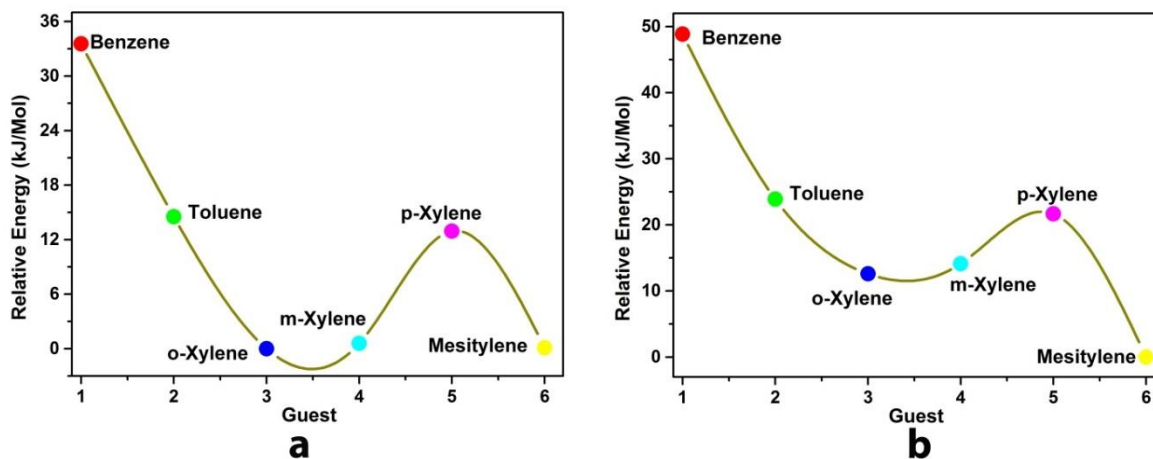


Figure 2.6: Plots depicting the relative energies for the various host-guest complexes studied with **1** (a) and **2** (b).

2.4 CONCLUSION

In conclusion, this chapter describes the synthesis and guest-encapsulation studies of two iso-structural tetrahedral cage assemblies **1** and **2** derived from chloranilate and DHBQ linkers. The structural topology and the bonding arrangements found **1** and **2** are very similar to that found in the reported tetrahedral cage **B** based on oxalate bridges. Competitive experiments showed that the tetrahedral assembly **1** is more favourable as compared to the other similar cages **B** (previous report) and **2** which is attributed to a better interaction between the softer chloranilate ions with soft Pd^{2+} ions. The cage assemblies **1** and **2** exhibit an intrinsic cavity of size 233 and 228 Å³, respectively that were utilized for the selective recognition of aromatic hydrocarbons. While the cage **1** shows the selective binding of o-xylene, the cage **2** is selective for mesitylene among all the other aromatic guest molecules. These host-guest studies were supported by the MALDI-TOF mass spectra, ¹H-2D-DOSY NMR and theoretical binding energy calculations. Charge neutral and tetrahedral cages based on Pd(II) ions are relatively under explored and we believe that this imido-P(V) supported Pd(II) systems would lead to the development of new functional molecules in near future.

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Chapter 3

**Mapping the Assembly of Metal-
Organic Cages into Complex
Coordination Networks**

3.1 INTRODUCTION

Structural rearrangements such as conversions, folding and association play an important role in biological reactions; well-known examples are microbial fission and fusion processes as well as enzyme catalysis.¹⁻³ Over the years, supramolecular self-assemblies in the form of grippers, capsules, cavitands, cages and polymers have been used to mimic such rearrangement processes that can be triggered by various external stimuli.⁴⁻⁹ Several of the supramolecular rearrangement reactions follow assembly-disassembly-reassembly pathways wherein the overall structure of the original construct is maintained.¹⁰⁻¹² Such processes can also play an integral part in the construction of molecular devices.¹³⁻²⁰

Metal-organic polyhedra (MOPs) or cages (MOCs) built from the spontaneous assembly of smaller molecular constituents are an important class of compounds in supramolecular chemistry.²¹⁻³³ Multifunctional MOPs are highly desired for molecular recognition, biological activity, reactive species sequestration, catalysis and gas adsorption and separation.³⁴⁻⁴³ Particularly interesting is the assembly of MOPs to generate hierarchical coordination networks. Utilizing metal-organic squares, cubes and octahedrons, cage-connected frameworks with varying dimensionalities and topologies have been obtained.⁴⁴⁻⁴⁸ Similarly, cage-connected networks with 3D-topologies have been realized by employing carboxylate ligands and certain molecular-building units such as paddle-wheel motifs.⁴⁹⁻⁵³ The construction of MOPs and coordination networks usually involves many assembly and rearrangement steps. Normally, very little is known about the intermediates in these reactions. In some instances they could be studied by NMR, mass spectra and electron microscopy,⁵⁴⁻⁵⁹ whereas obtaining X-ray structures of intermediates are often more challenging.^{60,61} This can be attributed to the complex solution dynamics exhibited by the individual components of the MOPs as well as the unstable nature of the intermediates formed during such transformations.

Chapter three describe the conversions of a cubic metal organic cage $[(\text{Pd}_3\text{X})_8(\text{PZDC})_{12}]$ ($\text{X} = [\text{PO}(\text{N}^i\text{Pr})_3]$) into 3D-frameworks of tetrahedral cages

$[(\text{Pd}_3\text{X})_4(\text{PZDC})_6]$ that are linked via coordination of $\text{M}(\text{II})$ ions ($\text{M} = \text{Fe}, \text{Zn}$) to the vacant carboxylate oxygen sites of the PZDC ligand. The $[\text{Pd}_3\text{X}]^{3+}$ units have shown to be very robust and versatile building blocks.⁶²⁻⁶³ We were able to isolate and characterize intermediates that occur along the pathway to the 3D frameworks. These consisted of discrete cages and one- as well as two-dimensional cage-connected-frameworks. This enabled us to map the process of the conversion reactions and show that they proceed with sequential change of symmetries, which is a rare phenomenon in the chemistry of supramolecular cages.⁶⁴⁻⁶⁷

3.2 EXPERIMENTAL SECTION

3.2.1 General remarks

All manipulations involving phosphorus halides were performed under dry nitrogen atmosphere in standard Schlenk-glassware. Solvents were dried over potassium and sodium (toluene). The primary amines, 2, 5-pyrazinedicarboxylic acid and all metal salts were purchased from Aldrich and used as received. POCl_3 was purchased locally and was distilled prior to use. NMR spectra were recorded on a Jeol 400 MHz or Bruker 400 MHz spectrometer (^1H NMR: 400 MHz, $^{13}\text{C}\{^1\text{H}\}$ NMR: 100 MHz, $^{31}\text{P}\{^1\text{H}\}$ NMR: 161 MHz) at room temperature using SiMe_4 (^1H , ^{13}C) and 85% H_3PO_4 (^{31}P). The mass spectra were obtained on an Applied Biosystem MALDI-TOF/TOF spectrometer. FT-IR spectra were taken on a Perkin Elmer spectrophotometer with samples prepared as KBr pellets. Elemental analyses were performed on a Vario-EL cube elemental analyzer. Melting points were obtained using an Electro Thermal Melting point apparatus and were uncorrected.

3.2.2 Synthesis

3.2.2.1 Synthesis of the cubic cage 3: To a solution of **A**·2DMSO (20 mg, 0.014 mmol) in methanol, 2,5-pyrazinedicarboxylic acid dihydrate (PZDC-2H) $\{\text{C}_6\text{H}_2\text{N}_2(\text{COOH})_2 \cdot 2\text{H}_2\text{O}\}$ (17 mg, 0.084 mmol) in methanol was added. The mixture was stirred for 1 h, filtered and kept for crystallization. Cube like yellow color crystals were

obtained after 10 days. Yield: 80% (20 mg). mp: 216-218 °C. ^1H NMR (400 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 1.26 (d, 18H, CH_3), 2.12 (m, 3H, CH), 9.12 (s, 3H, CH), 9.32 (s, 3H, CH), 11.84 (s, 3H, COOH) : $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 26.90, 53.54, 80.44, 140.09, 142.91, 143.12, 157.24, 174.44. ^{31}P NMR (161 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 73.67. FT-IR data in KBr pellet (cm^{-1}): 527, 555, 633, 707, 893, 902, 950, 1035, 1163, 1288, 1316, 1407, 1437, 1588, 1652 and 3461. Anal.Calcd.for $\text{C}_{157}\text{H}_{275}\text{N}_{48}\text{O}_{84.5}\text{P}_8\text{Pd}_{24}\text{S}_{6.5}$: C, 26.20; H, 3.85; N, 9.34. Found: C, 26.32; H, 3.25; N, 9.71.

3.2.2.2 Procedure for solution based transformation of Fe(II) derivatives

To an *in-situ* generated clear orange solution (5 mL) of 2 in methanol, obtained by treating (PZDC-2H) (8.6 mg, 0.042 mmol) and 1a-2DMSO (20 mg, 0.014 mmol), Iron(II) triflate ($\text{Fe}(\text{OTf})_2$, 7.5 mg, 0.021 mmol) in methanol (2 mL) was slowly added. The progress of the reaction was monitored by an immediate change of colour to green and was further stirred for 1 h. This solution was then filtered on celite pad and kept for crystallization. A first crop of green coloured crystals were extracted from the solution after two days and remaining solution was left again for crystallization. After ten days, the colour of the solution turned into blue from which blue coloured crystals were obtained. Single crystal X-ray diffraction analysis of these green and blue coloured crystals gave the structures of the compound 6 and 7, respectively.

3.2.2.3 Synthesis of iron 3D-ccMOF 4: To an *in-situ* generated clear orange solution (5 mL) of 2 in methanol, Iron (II) triflate ($\text{Fe}(\text{OTf})_2$, 7.5 mg, 0.021 mmol) in methanol (2 mL) was slowly added. The resultant green coloured solution was stirred at 70 °C for 2 h until the solution colour changes to yellow. The solution was then filtered on a cellite pad and kept for crystallization. Yellowish orange coloured crystals were obtained after 5 days. Yield: 60% (15 mg). ^1H NMR (400 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 1.84(d, 18H, CH_3), 3.13 (m, 3H, CH), 8.90 (s, 3H, CH): $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 26.90, 53.54, 80.44, 140.09, 142.91, 143.12, 157.24, 174.44. ^{31}P NMR (161 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 72.27. FT-IR data in KBr pellet (cm^{-1}): 527, 555, 633, 707, 893, 902, 950, 1035, 1163, 1288, 1316,

1407, 1437, 1588, 1652 and 3461. Anal.Calcd.for $C_{80.50}H_{96}F_3Fe_2N_{24}O_{32.50}P_4Pd_{12}S$: C, 27.46; H, 2.75; N, 9.55. Found: C, 27.32; H, 3.10; N, 9.82.

3.2.2.4 Synthesis of hydrogen bonded defect cubane 6: Yield: 75% (45 mg). 1H NMR (400 MHz, $\{(CD_3)_2SO\}$): δ 1.84 (d, 18H, CH_3), 3.13 (m, 3H, CH), 8.90 (s, 3H, CH): $^{13}C\{^1H\}$ (100 MHz, $\{(CD_3)_2SO\}$): δ 26.90, 53.54, 142.91, 149.12, 162.24: ^{31}P NMR (161 MHz, $\{(CD_3)_2SO\}$): δ 72.81, 72.01. FT-IR data in KBr pellet (cm^{-1}): 530, 555, 633, 707, 893, 902, 950, 1035, 1163, 1288, 1316, 1407, 1437, 1588, 1652 and 3461. Anal.Calcd.for $C_{234}H_{288}F_{12}Fe_7N_{72}O_{121}P_{12}Pd_{36}S_4$: C, 25.56; H, 2.64; N, 9.17. Found: C, 25.51; H, 2.72; N, 9.05.

3.2.2.5 Synthesis of trigonal bipyramidal cage 7: Yield: 54% (20 mg). 1H NMR (400 MHz, $\{(CD_3)_2SO\}$): δ 1.82 (d, 18H, CH_3), 3.17 (m, 3H, CH), 8.94 (s, 3H, CH): $^{13}C\{^1H\}$ (100 MHz, $\{(CD_3)_2SO\}$): δ 26.90, 53.54, 80.44, 140.09, 142.91, 143.12, 157.24, 174.44: ^{31}P NMR (161 MHz, $\{(CD_3)_2SO\}$): δ 58.29. FT-IR data in KBr pellet (cm^{-1}): 526, 552, 630, 707, 890, 901, 952, 1034, 1163, 1289, 1314, 1407, 1435, 1588, 1654 and 3460. Anal.Calcd.for $C_{59}H_{92}Fe_3N_{18}O_{40}P_2Pd_6S_2$: C, 26.99; H, 3.53; N, 9.60. Found: C, 26.72; H, 3.25; N, 9.70.

3.2.2.6 General procedure for transformation on single crystals by diffusion

The cubic crystals of **3** (10 mg, 0.001 mmol) were placed in a methanolic (4 mL) solution of iron triflate (1.5 mg, 0.004 mmol). The crystals were analyzed by SCXRD after every one month interval. After one month, the crystal showed the formation of nano-ball shaped assembly of **8**. After two months, formation of a one dimensional helical coordination polymer, **9** was observed. Formation of the 3D- coordination polymer of **4** was observed after six months.

3.2.2.7 Procedure for preparation of Zn(II) derivatives

To an in-situ generated clear orange solution (5 mL) of **3** in methanol, obtained by treating (PZDC-2H) (8.6 mg, 0.042 mmol) and 1a-2DMSO (20 mg, 0.014 mmol), zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$, (4.8 mg, 0.014 mmol) in methanol (2 mL) was slowly added. The

resulting solution was stirred for 4 h, filtered on a cellite pad and was kept for crystallization. A first crop of orange coloured crystals suitable for X-ray analysis were obtained after 6 days. The single crystal X-ray diffraction analysis of these crystals revealed the formation of a three dimensional cage connected framework, **5**. The remaining filtrate was further diluted with methanol (2 mL) and left again for crystallization. A second crop of orange coloured crystals were obtained after 10 days which showed the formation of the discrete hetero-bimetallic cage **10**. Interestingly, when the crushed crystals of **5** were suspended in excess of methanol (4 mL) and left for crystallization it again gave rise to **10**.

3.2.2.8 Synthesis of zinc 3D-ccMOF 5: Yield: 75% (20 mg). ^1H NMR (400 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 1.18 (d, 18H, CH_3), 3.13 (m, 3H, CH), 9.07 (d, 3H, CH): ^{13}C $\{^1\text{H}\}$ (100 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 26.90, 53.54, 80.44, 140.09, 142.91, 143.12, 157.24, 174.44: ^{31}P NMR (161 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 73.83. FT-IR data in KBr pellet (cm^{-1}): 527, 555, 633, 707, 893, 902, 950, 1035, 1163, 1288, 1316, 1407, 1437, 1588, 1652 and 3461. Anal.Calcd.for $\text{C}_{72}\text{H}_{132}\text{N}_{28}\text{O}_{58}\text{P}_4\text{Pd}_{12}\text{Zn}_2$: C, 22.46; H, 3.46; N, 10.19. Found: C, 22.50; H, 3.15; N, 10.35.

3.2.2.9 Synthesis of heterometallic cubic assembly 9: Yield: 85% (12 mg). mp: 216-218 $^\circ\text{C}$. ^1H NMR (400 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 1.26 (d, 18H, CH_3), 2.12 (m, 3H, CH), 9.12 (s, 3H, CH), 9.32 (s, 3H, CH), 11.84 (s, 3H, COOH): ^{13}C $\{^1\text{H}\}$ (100 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 26.90, 53.54, 80.44, 140.09, 142.91, 143.12, 157.24, 174.44: ^{31}P NMR (161 MHz, $\{(\text{CD}_3)_2\text{SO}\}$): δ 72.27. FT-IR data in KBr pellet (cm^{-1}): 526, 556, 632, 705, 890, 902, 952, 1034, 1163, 1289, 1315, 1405, 1435, 1588, 1650 and 3461. Anal.Calcd.for $\text{C}_{164}\text{H}_{368}\text{Fe}_4\text{N}_{48}\text{O}_{152}\text{P}_8\text{Pd}_{24}\text{S}_{12}$: C, 22.25; H, 4.19; N, 7.59. Found: C, 22.48; H, 3.88; N, 7.61.

3.2.3 Crystallography

Reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) (Table 3.1) for **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**. Structures were refined by full-matrix least-squares against F^2 using all data (SHELX97).⁶⁸ All non-

hydrogen atoms were refined anisotropically if not stated otherwise. Hydrogen atoms were constrained in geometric positions to their parent atoms. The diffused solvate molecules were disordered and treated as partially occupied O-atom and refined isotropically. ISOR constrained was applied for the atoms those were not behaving well. The solvent molecules were squeezed using PLATON/ SQUEEZE model⁶⁹ due to their disordered nature in all compounds. For compound **3** The DMSO atoms are thermally unstable therefore the SIMU, SAME and EADP constrained were applied. Similarly, the counter anions in **4**, **5**, **8**, **9**, and **10** were treated isotropically with similar distances and U-restraints (SAME/SIMU) for better refinement of their thermals and occupancies. Also, the bad reflections in these structures were treated with either OMIT or SHEL commands. Compound **6** was showing larger voids in the frameworks due to the extra solvent molecules and we did not squeeze it due to twinning in structures. The largest difference peaks are not due to water but disordered Pd-triangles. However these peaks have a height of only 1.7 e/A which indicates that the presence of the disordered domain is very low and would not allow a reasonable refinement, thus we left them out. Some O-atoms of waters showed up as distinct peaks but others were too diffused and had to be omitted which gives the impression of large solvent-free voids. Compound **4** has combined disorder and twinning along with the disorder of the Pd triangles. These were effectively refined in the *R*3 space group with models that depicts the cages to be racemates. The solvate molecules in **4** were determined by combined TGA and squeeze analysis.

Table 3.1 Crystallographic data of compound 3, 4, 5, 6, 7, 8, 9 and 10.

Compound	3	4
Chemical formula	C ₁₅₇ H ₂₇₅ N ₄₈ O _{84.5} P ₈ Pd ₂₄ S _{6.5}	C ₁₇₂ H ₃₀₀ F ₂₄ Fe ₄ N ₄₈ O ₁₀₃ P ₈ Pd ₂₄ S ₁₈
Formula weight	7169.98	8746.42
Temperature	100(2) K	100(2)
Crystal system	Monoclinic	Tetragonal
Space group	P2 ₁ /c	R3
a (Å); α (°)	23.507(4); 90.	22.274(2): 90
b (Å); β (°)	37.607(7); 97.683(4)	22.274(2): 90
c (Å); γ (°)	42.296(7); 90	56.692(11): 120

V (Å ³); Z	37055(11) ; 4	24357(7);3
ρ (calc.) mg m ⁻³	1.290	1.789
μ(Mo K _α) mm ⁻¹	1.263	1.714
2θ _{max} (°)	50	50
R(int)	0.3677	0.0941
Completeness to θ	99.7 %	99.9%
Data / param.	64711 / 2871	19012/ 978
GOF	0.979	1.040
R1 [F>4σ(F)]	0.1084	0.0736
wR2 (all data)	0.3589	0.2031
max.peak/hole (e.Å ⁻³)	2.068/-1.969	1.392/ -1.313
Compound	5	6
Chemical formula	C ₇₂ H ₁₃₂ N ₂₈ O ₅₈ P ₄ Pd ₁₂ Zn ₂	C ₂₃₄ H ₂₈₈ F ₁₂ Fe ₇ N ₇₂ O ₁₂₁ P ₁₂ Pd ₃₆ S ₄
Formula weight	3849.48	10994.58
Temperature	100(2)	100(2) K
Crystal system	Trigonal	Orthorhombic
Space group	P3 ₁ 21	P2 ₁ 2 ₁ 2
a (Å); α (°)	22.323(5);90	35.902(11); 90
b (Å); β (°)	22.323(5);90	35.914(11); 90
c (Å); γ (°)	23.713(5);120	22.493(7); 90
V (Å ³); Z	10238(4); 3	29001(15); 2
ρ (calc.) mg m ⁻³	1.873	1.259
μ(Mo K _α) mm ⁻¹	2.023	1.360
2θ _{max} (°)	50	56
R(int)	0.1754	0.1391
Completeness to θ	99.4%	99.9%
Data / param.	12014/774	73105/1148
GOF	1.034	1.088
R1 [F>4σ(F)]	0.0745	0.0661
wR2 (all data)	0.2063	0.1987
max.peak/hole (e.Å ⁻³)	1.603/-2.100	1.724/-0.824
Compound	7	8
Chemical formula	C ₅₉ H ₉₂ Fe ₃ N ₁₈ O ₄₀ P ₂ Pd ₆ S ₂	C ₁₆₄ H ₃₆₈ Fe ₄ N ₄₈ O ₁₅₂ P ₈ Pd ₂₄ S ₁₂
Formula weight	2625.52	8854.54
Temperature	100(2)	100(2) K
Crystal system	Monoclinic	Tetragonal
Space group	P2 ₁ /n	P4/nnc
a (Å); α (°)	15.592(3)	28.142(8); 90
b (Å); β (°)	34.241(7)	28.1421(8); 90
c (Å); γ (°)	23.746(5)	25.241(10); 90
V (Å ³); Z	12576(4); 4	19990(11); 2
ρ (calc.) mg m ⁻³	1.387	1.471
μ(Mo K _α) mm ⁻¹	1.301	1.363
2θ _{max} (°)	50	50
R(int)	0.1590	0.3047
Completeness to θ	99.5%	99.5 %
Data / param.	22134 / 1226	8804 / 454

GOF	1.035	1.045
R1 [F>4σ(F)]	0.1123	0.1026
wR2 (all data)	0.3801	0.3747
max.peak/hole (e.Å ⁻³)	1.838/-1.006	1.237/-2.050
Compound	9	10
Chemical formula	C _{75.50} H ₉₆ F _{10.50} Fe _{1.75} N ₂₄ O _{41.50} P ₄ Pd ₁₂ S _{3.50}	C ₇₆ H ₁₂₆ N ₃₀ O ₆₃ P ₄ Pd ₁₂ S ₂ Zn ₃
Formula weight	3813.88	4128.97
Temperature	100(2) K	100(2) K
Crystal system	Orthorhombic	Tetragonal
Space group	C222 ₁	P 4 ₃ 2 ₁ 2
a (Å); α (°)	20.521(3); 90	41.646(5); 90
b (Å); β (°)	51.376(7); 90	41.646(5); 90
c (Å); γ (°)	28.607(4); 90	16.886(2); 90
V (Å ³); Z	30161(8); 8	29287(8); 8
ρ (calc.) mg m ⁻³	1.680	1.873
μ(Mo K _α) mm ⁻¹	1.730	2.081
2θ _{max} (°)	50	45
R(int)	0.1945	0.1876
Completeness to θ	99.4	99.1
Data / param.	26533/1454	19329/1510
GOF	1.012	1.071
R1 [F>4σ(F)]	0.0590	0.0592
wR2 (all data)	0.1727	0.1756
max.peak/hole (e.Å ⁻³)	1.168/-1.247	2.361/-1.080

3.2.4 DOSY-NMR studies

The NMR experiments were carried out on a Bruker NMR spectrometer operating at a ¹H frequency of 500 MHz and at a constant temperature of 298 K. 2.50 mM solution of the compounds were prepared in (CD₃)₂SO and allowed to equilibrate for a period of 30 minutes before data acquisition. The standard Bruker protocol using Topspin 2.1 software was used for processing the DOSY data. The fitting of the diffusion dimension in the 2D-DOSY spectra was carried out using a one (monoexponential) or two-parameter biexponential fit (equation 1) that showed better fits when compared with a two-parameter monoexponential fit.⁷⁰

$$I = I_{0A} \exp \left[-D_A \gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \right] + I_{0B} \exp \left[-D_B \gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \right] \quad (1)$$

In this equation, I is the observed integral, I_{0A} and I_{0B} the reference integral or unattenuated integrals, D_A and D_B the diffusion coefficients, g the gyromagnetic ratio of the observed nucleus, g the gradient strength, d the length of the gradient, and D the diffusion time.

3.3 RESULTS AND DISCUSSION

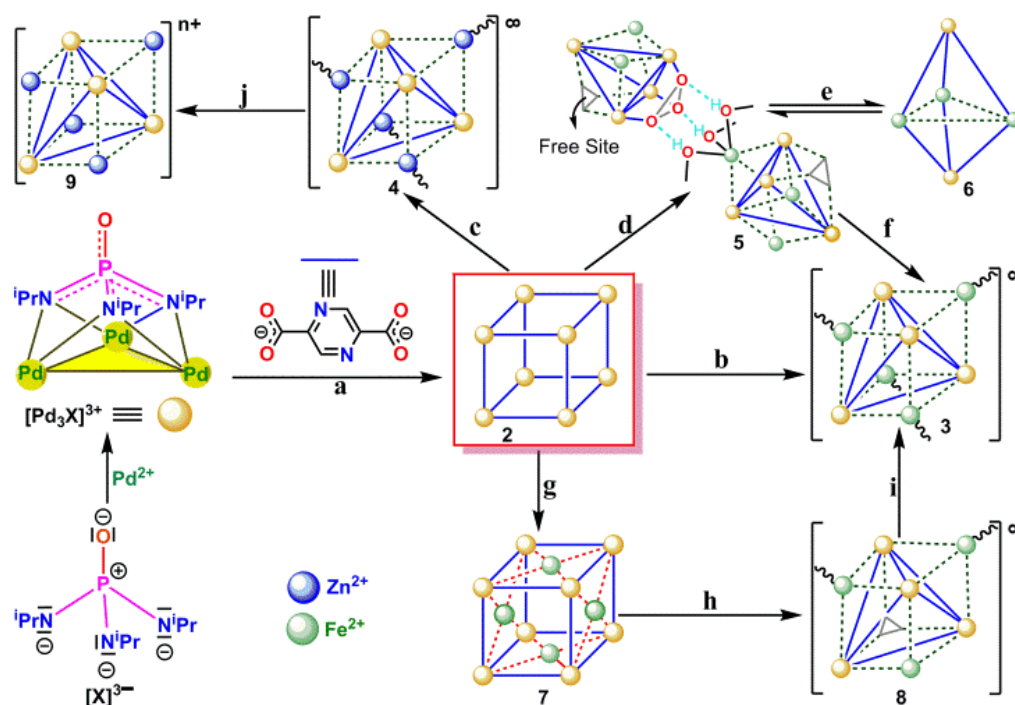
3.3.1 Synthesis and crystal structure

Treatment of $\{\text{Pd}_3\text{X}(\text{OAc})_2(\text{OH})\}_2 \cdot 2(\text{CH}_3)_2\text{SO}$ (**A**)⁶³, which contains tripodal $[\text{Pd}_3\text{X}]^{3+}$ units consisting of a triangular array of Pd(II) ions that is capped by the tripodal ligand $[\text{PO}(\text{N}^i\text{Pr})_3]^{3-}$ ($= \text{X}^{3-}$), with 2,5-pyrazenedicarboxylic acid (PZDC-2H) in a 1:3 ratio in MeOH/DMSO yielded a cubic cage assembly of composition $[(\text{Pd}_3\text{X})_8(\text{PZDC})_{12}]$, **3** (Scheme 3.1). The ^{31}P NMR of **3** recorded in DMSO gave a single peak at $\delta = 73.7$ ppm characteristic of the tris-imido phosphate ligand. The MALDI-TOF spectrum showed a broad signal that is centred at the predicted molecular mass for this cage ($m/z = 6730.23$) (A3.1-A3.2, Appendix 3).

The cubic assembly crystallizes in the form of the solvate **3**·6.5DMSO·22H₂O. The cubic cage comprises eight $[\text{Pd}_3\text{X}]^{3+}$ units (Figure 3.1a). Every Pd(II) ion is coordinated in square planar fashion by a bidentate site of X^{3-} ligand and a bidentate N,O-site of bridging 2,5-pyrazenedicarboxylate anions (PZDC), while in return every PZDC ligand binds two Pd(II) ions in opposite N,O-sites (Figures 3.1b and 3.1c). The result is a cubic cage, in which the eight $[\text{Pd}_3\text{X}]^{3+}$ units occupy the vertices while the twelve PZDC ligands form its edges (Figure 3.1d and Figures A3.3-A3.5, Appendix 3). Altogether the cubic MOP assembly of **3** consists of 42 components. The intrinsic cavity in **3** was determined by MSROLL software calculations^{71,72} with a fixed probe radius of 1.3 Å which gave the cavity volume of 1009.3 Å³. There are a few reports in literature that utilized PZDC ligands as linkers in coordination polymers.⁷³⁻⁷⁵ However, the construction of MOFs/MOPs based on this ligand remained unexplored.

The presence of 24 non-coordinated carboxylate-O-atoms in **3** gave us the idea to populate those sites with metal ions. A summary of the post-assembly reactions showing the formation of the various networks and stable intermediates is shown in scheme 3.1. Treatment of **3** with $\text{Fe}(\text{OTf})_2$ in methanol under reflux conditions and subsequent storage of the solution gave yellowish-green crystals of **4**.

Scheme 3.1. Formation of the cubic assembly of 3 and the schematic representation of its post assembly reactions; the extra framework anions and solvate molecules have been omitted for clarity. Reaction conditions: (a) DMSO/MeOH at RT, (b) $\text{Fe}(\text{OTf})_2/\text{MeOH}$ at 70 °C, (c) $\text{Zn}(\text{NO}_3)_2/\text{MeOH}$ at RT. (d) $\text{Fe}(\text{OTf})_2/\text{MeOH}$ at RT (e) slow evaporation of methanol (f) Heating at 70 °C. Immersion of the crystals of 3 in MeOH/DMSO (g) for one month, (h) after two months and (i) after six months. (j) Suspending the polycrystalline sample of 5 in MeOH for 2 days.



Structural determination of **4** revealed the formation of a 3D cage-connected network of formula $[\text{Fe}_4(\text{Pd}_3\text{X})_8(\text{PZDC})_{12}(\text{H}_2\text{O})_3](\text{OTf})_8 \cdot 10\text{DMSO} \cdot 15\text{H}_2\text{O}$ (Figure 3.2a). The network comprises tetrahedral $[(\text{Pd}_3\text{X})_4(\text{PZDC})_6]$ cages, in which every Pd_3X unit coordinates three PZDC ligands and in return every PZDC ligand bridges between two Pd_3X units,

which corresponds to the primary coordination pattern that was observed in **3**. These tetrahedral cages are fused via Fe(II) ions which occupy the tridentate coordination sites of three carboxylate-O-atoms located on each face of the tetrahedral cage (Figures 3.2c and 3.2d). As such, every $[(\text{Pd}_3\text{X})_4(\text{PZDC})_6]$ cage acts as a tetrahedral 4-connector resulting in a net with a diamond-type topology (*dia* net, Figures 3.2e and A3.6- A3.7, Appendix 3).⁷⁶⁻⁷⁷ The rhombohedral cell (*R3*) contains two crystallographically unique cages and eight unique Fe(II) ions, two of which are octahedrally coordinated by two tridentate cage sites, while the remaining six ions display an unusual seven-coordinated environment consisting of two tridentate cage sites and one water ligand.

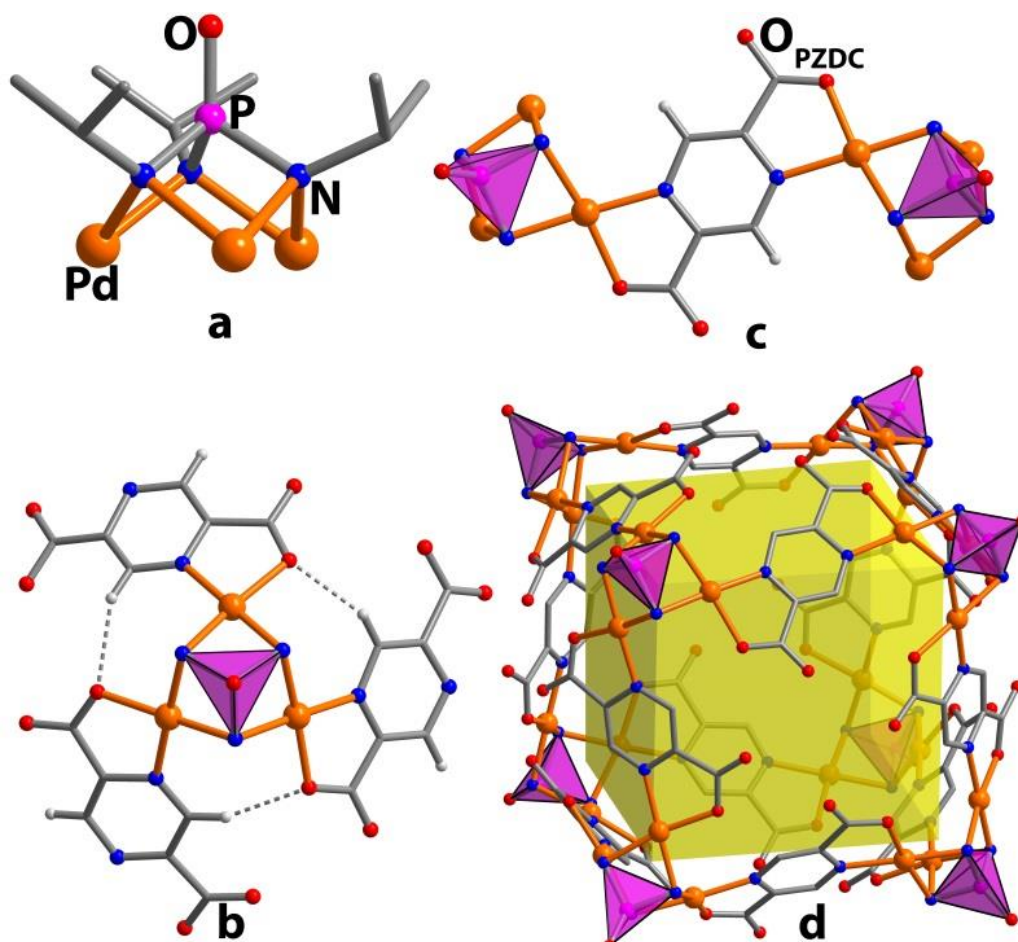


Figure 3.1. Crystal structure of **3**. (a-c) Schematic view of the $[\text{Pd}_3\text{X}]^{3+}$ PBU and its coordination with the PZDC anions leading to the formation of the 42-component cubic cage (d). PON_3 units shown as purple tetrahedra in b-d.

The reaction of **3** with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in methanol at room temperature yielded yellowish-orange crystals, which again consists of a 3D-network that feature tetrahedral $[(\text{Pd}_3\text{X})_4(\text{PZDC})_6]$ cages that are networked via $\text{Zn}(\text{II})$ ions (Figure 3.2b). The crystals of **5** ($P3_121$) are of composition $[\text{Zn}_2(\text{Pd}_3\text{X})_4(\text{PZDC})_6(\text{H}_2\text{O})_4](\text{NO}_3)_4 \cdot 16\text{H}_2\text{O}$. In contrast to the $\text{Fe}(\text{II})$ derivative **4**, they exhibit a chiral network of quartz-type topology (*qtz* net, Figures 3.2f, and A3.8-A3.11, Appendix 3). It is noteworthy that the coordination sphere of Zn ions is even more expanded exhibiting an 8-coordinate square antiprismatic environment of four carboxylate-O-sites and two water molecules.

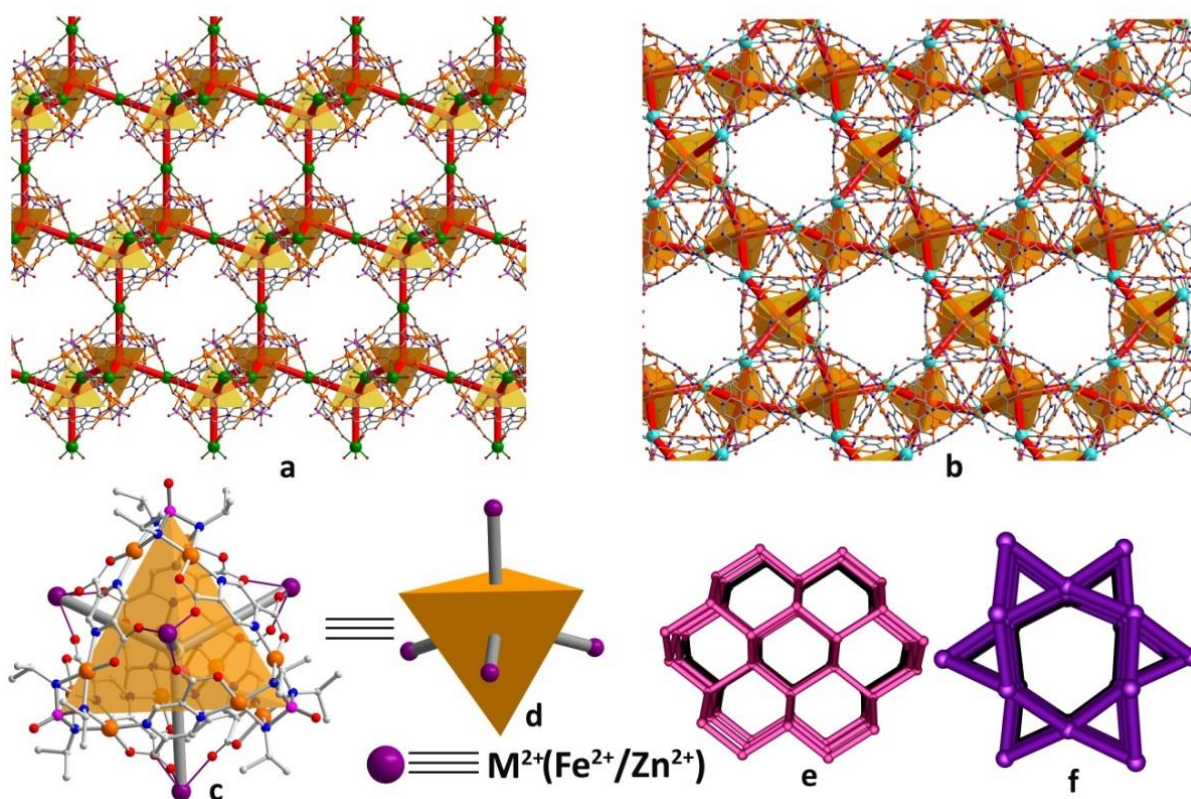


Figure 3.2. Crystal structures of **4** (a) and **5** (b). (c) View of a single isostructural tetrahedral cage of **4** and **5**. (d) Simplified 4-connected representation of the tetrahedral cage; (e) and (f) show the network structures of **4** (dia net) and **5** (qtz net), respectively. Green and cyan coloured spheres represent $\text{Fe}(\text{II})$ and $\text{Zn}(\text{II})$ atoms.

In both **4** and **5**, the basic structural motif is the heterobimetallic cubane of the type $[\text{M}_4(\text{Pd}_3\text{X})_4(\text{PZDC})_6]$ in which the Pd_3X -PBUs form primary tetrahedral nodes that are

connected via Fe(II) and Zn(II) ions. However, the increased coordination spheres around these ions indicate a deviation of linearity of the cage-M-cage axes. The cage(centroid)-M-cage(centroid) angles are 180° for the 6-coordinate Fe(II) and 146° for the 7-coordinate Fe(II) ion in **4**, while it is 145° in **5**. This angle seems to provide for a closer packing of cages; in addition to metal coordination, it also enables Van-der-Waals interactions between the cages.

In return, the deviation from linearity between cages exposes the M(II) ions and thereby expanding the coordination sphere leading to hyper-coordination (Figure A3.12, Appendix 3). TOPOS⁷⁸⁻⁷⁹ analysis was performed on **4** and **5** considering one-unit of the heterometallic $[M_4(Pd_3X)_4(PZDC)_6]$ motif as a node. These analysis gave uni-nodal *dia* net for compound **4**; point symbol (6,6) and vertex symbol $6_2.6_2.6_2.6_2.6_2.6_2$. For compound **5** it gave a uni-nodal *qtz* net; point symbol $\{6^4.8^2\}$ and vertex symbol $6.6.6_2.6_2.8_7$ (Figure-A3.13, Appendix 3).⁸⁰

To understand the formation of these cage-connected 3D-assemblies, we repeated the reactions under milder conditions. The treatment of **3** with Fe(OTf)₂ in methanol at room-temperature resulted in a spontaneous colour change from orange to green. Dark green coloured crystals of **6** of composition $[Fe_7(Pd_3X)_{12}(PZDC)_{18}(CH_3OH)_7(H_2O)_7](OTf)_{14} \cdot 8H_2O$, were recovered from this solution (Figures A3.14-A3.18, Appendix 3). As for **4**, this compound also consists of $[(Pd_3X)_4(PZDC)_6]$ cages. However, in contrast to **4**, not all of the four tridentate carboxylate-O-sites are occupied by connecting Fe(II) ions. There are two crystallographically unique cages present in a 2:1 ratio; these are depicted orange and blue in Figure 3.3a. All four tridentate sites of the 'blue' cage form bridges to neighbouring cages. These bridges consist of an arrangement where one tridentate site accommodates a metal ion, while the opposite site at the other cage forms hydrogen bonds to the methanol/water ligands coordinated to the metal ion that belongs to the first cage. Figure 3.3a shows this arrangement of metal-coordination/hydrogen-bonding linkage. The 'orange' cage, meanwhile, forms three of these bridges while the fourth site is occupied by a terminal, non-bridging Fe(II) ion. Hence, the 'blue' cages act as

tetrahedral 4-connectors, while the 'orange' cages are trigonal pyramidal 3-connectors. The resulting network is a puckered 2D-grid with pentagonal rings (Figure 3.3b).

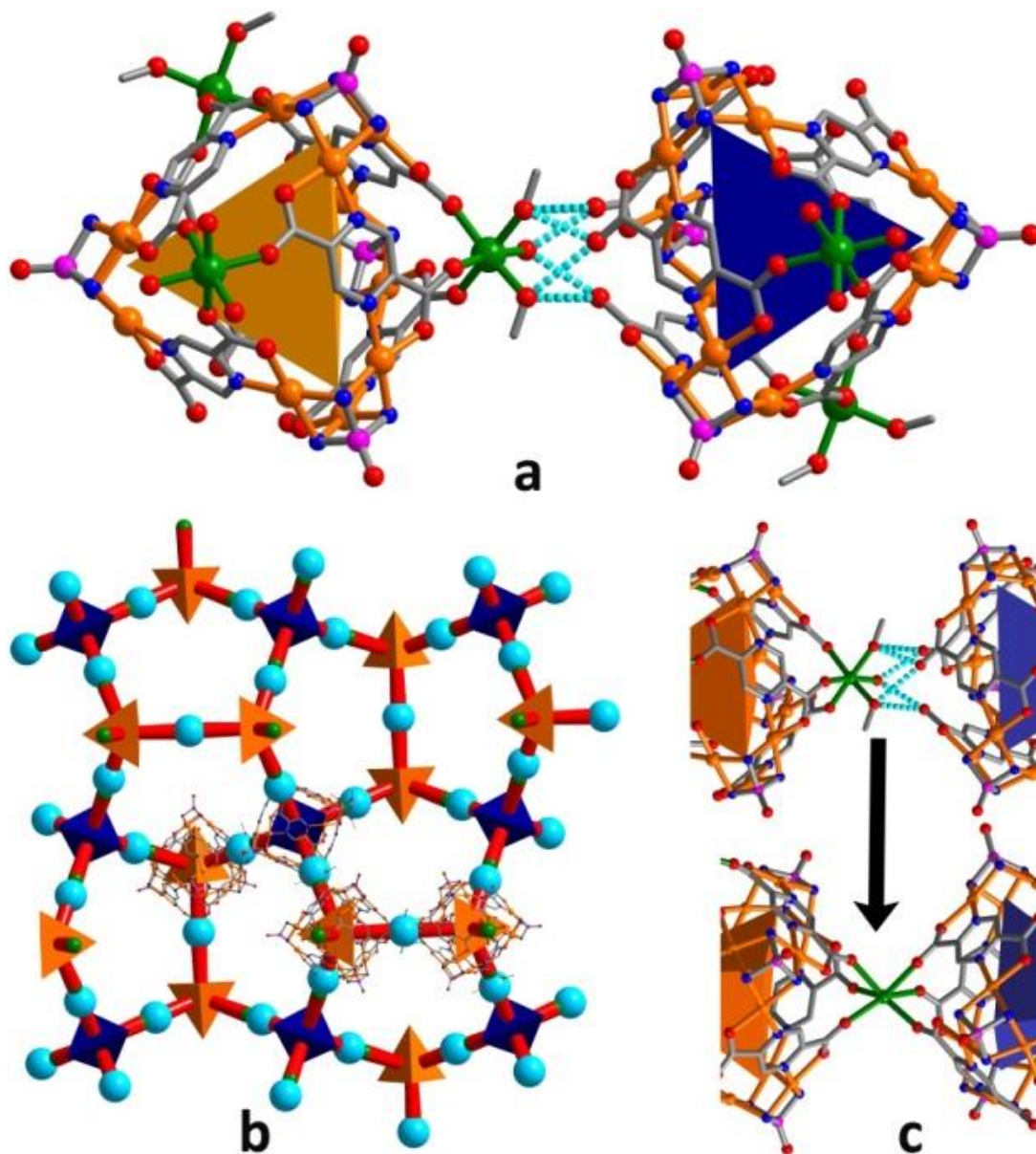


Figure 3.3. (a) Crystal structure of **6** highlighting the metal coordination/hydrogen bonding bridge (H-bonds drawn as dashed lines). (b) The puckered layered network in **6** (metal coordination/hydrogen bonding bridges are shown as cyan spheres). (c) Metal coordination/hydrogen bonding bridge can be regarded as precursor to direct metal coordination link (observed as in **4** and **9**).

When the green crystals of **6** were dissolved and the solution was heated at 70 °C for 4 h, the green solution turns yellow and yellowish green crystals of **4** were again obtained after 3-4 days (Figure A3.19, Appendix 3). It is easy to imagine that elimination of the three water/methanol ligands from the metal-coordination/hydrogen-bonding-bridge generates the more direct all metal-coordination mode between the two cages that is observed in **4** (and in **9**, Figure 3.6). Hence, **6** can be regarded as a kind of intermediate along the pathway toward the coordination network of **4** (Figure 3.3c).

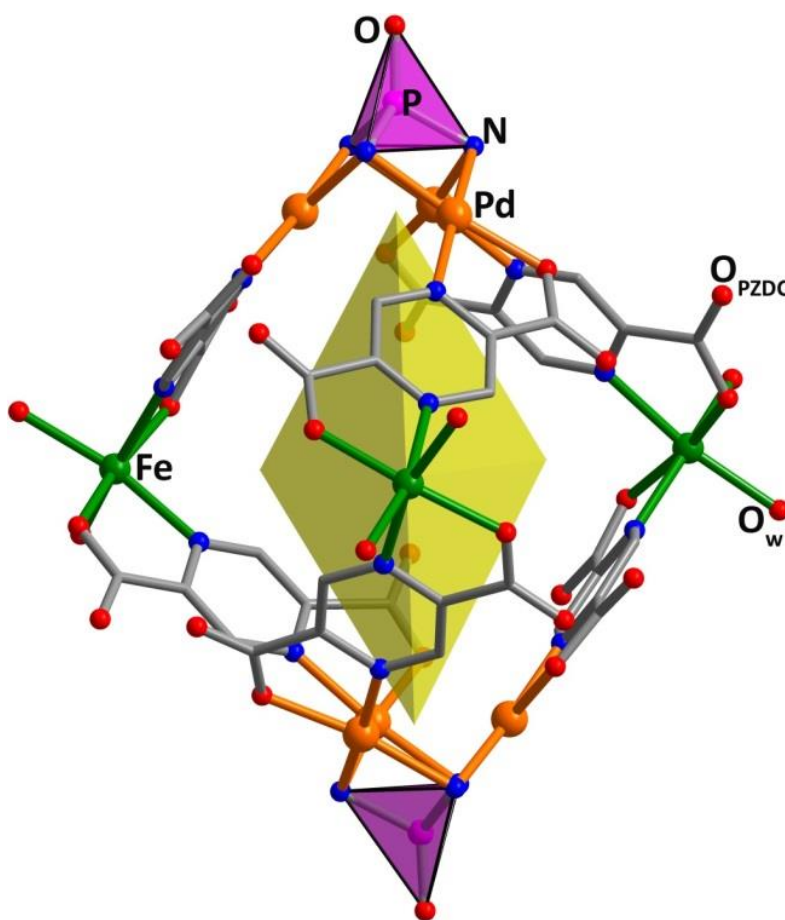


Figure 3.4. Crystal structure of **7**.

3.3.2 Existence of equilibrium in solution

Concentrating the green coloured solution of **6** by half of its original volume and leaving it standing gave blue crystals. The structural determination of these crystals revealed the formation of a compound of formula

$[\text{Fe}_3(\text{Pd}_3\text{X})_2(\text{PZDC})_6(\text{H}_2\text{O})_6] \cdot 2\text{MeOH} \cdot 2\text{DMSO} \cdot 22\text{H}_2\text{O}$ (**7**) (Figure 3.4 and A3.20-A3.24, Appendix 3). This structure consists of trigonal bipyramidal $[\text{Fe}_3(\text{Pd}_3\text{X})_2(\text{PZDC})_6]$ cages where the Fe ions occupy the equatorial and the Pd_3X units at the axial sites. In contrast to the cubic and tetrahedral cages of **3** and **4**, the PZDC ligands in **7** do not act as a bridge between two Pd_3X components. Instead, it can be regarded as an assembly containing two separate $[\text{Pd}_3\text{X}(\text{PZDC})_3]^{3-}$ entities that are linked by Fe(II) ions (Figure 4a). The coordination geometry around the Fe(II) ions can be described as distorted octahedral consisting of the O-sites of four PZDC ligands and two water molecules which are in mutual cis-position (Figure A3.25, Appendix 3).

The conversion of the tetrahedral (in **4**) to the trigonal bipyramidal cage can also be observed in solution. Repeated concentration by solvent evaporation and subsequent replenishment with methanol leads to colour changes to and from green (**6**) to blue (**7**) (Figure 3.5a). Upon heating the green colored solution of **6**, the tetrahedra condense to form the 3D-assembly of **4**. The ^{31}P - and ^1H -NMR spectra recorded on the reaction mixture of **3** and $\text{Fe}(\text{OTf})_2$ in CD_3OD after 24 h gave the signals corresponding to both **6** and **7** (Figures 3.5b and A3.26-A3.27, Appendix 3). These observations were further supported by the ^1H -2D-DOSY NMR spectrum of the reaction mixture which gave two diffusion coefficients (D) at 8.25×10^{-11} and $8.31 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ indicating the presence of **6** and **7**, respectively (Figure A3.28, Appendix 3). Owing to the bigger size of the cages in **6**, it diffuses slower in comparison with the relatively smaller TBP cage **7**. On the other hand, the DOSY data recorded on the freshly prepared sample of **6** fits only to a mono-exponential curve with a D value of $1.36 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ (Figure A3.29, Appendix). Similarly, the DOSY data obtained on the neat sample of **7** fits well to a mono-exponential decay curve with $D = 8.20 \times 10^{-10}$ which signifies the presence of one species in the solution (Figure A3.30, Appendix). The MALDI-TOF mass spectra of the reaction mixture recorded at different intervals show a progressive change of intensities for the peaks due to **6** and **7** (Figures 3.5c-f). The ^{31}P -NMR of a sample of **4** to which methanol was added gave peaks due to both **6** and **7**. These peaks suggest equilibria in solution between the heterometallic assemblies of **4**, **6** and **7**. There are some reports on structural inter-conversions of discrete cage-assemblies in the recent literature.⁸¹

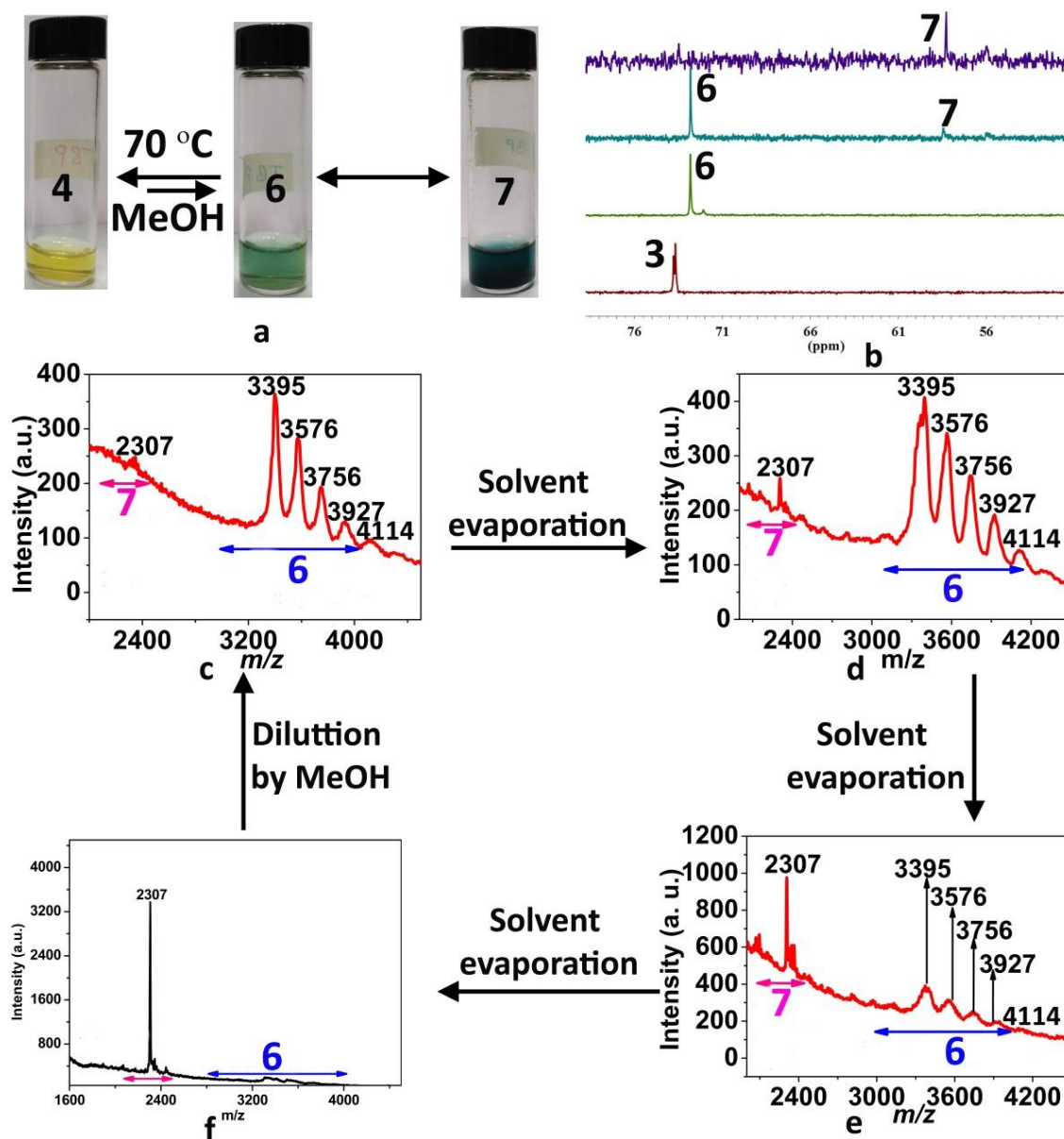


Figure 3.5. (a) Solution color changes involved in the structural transformations. (b) ^{31}P NMR spectra of the reaction mixture of 3 and $\text{Fe}(\text{OTf})_2$ showing the formation of 6 and 7 at various intervals. (c)-(f) MALDI-TOF mass spectra of the reaction mixture of 3 with $\text{Fe}(\text{OTf})_2$ taken at various intervals showing the gradual conversion of 6 to 7; (c) after 1 day, (d) after 3 days, (e) after 6 days and (f) after 8 days. Upon dilution in methanol 7 is converted back to 6 in 1h by a structural rearrangement.

3.3.3 Single crystal to single crystal transformation

In order to stop the process of conversion at an even earlier stage, the crystals of **3** was fully covered with a solution of $\text{Fe}(\text{OTf})_2$ in methanol. After one month the crystals showed a visible change in colour from orange to dark yellow. Structural analysis showed the formation of a heterobimetallic cage assembly **8** of composition $[\text{Fe}_2(\text{Pd}_3\text{X})_8(\text{PZDC})_{12}(\text{H}_2\text{O})_8](\text{OTf})_8 \cdot 8\text{DMSO} \cdot 59\text{H}_2\text{O}$, which features the same cubic cage structure $[(\text{Pd}_3\text{X})_8(\text{PZDC})_{12}]$ as observed in **3** (Figures 3.6a and A3.31, Appendix 3). In contrast to the tetrahedral cage $[(\text{Pd}_3\text{X})_4(\text{PZDC})_6]$ (as in **4** and **5**), which offers four tridentate carboxylate-O-sites, the cubic cage $[(\text{Pd}_3\text{X})_8(\text{PZDC})_{12}]$ provides six tetradentate carboxylate-O-sites of square planar geometry. In **8** four of these sites are occupied by Fe(II) ions. Compared to the non-coordinated cage of **3**, the cage in **8** shows a slight tetragonal distortion, when measured between the centroids of the four carboxylate-O-atoms of the tetradentate coordination site centres. The distance between opposite sites coordinated by Fe(II) ions is 14.8 Å, whereas it is 15.3 Å between the two non-coordinated sites.

The colour of the crystals changed to light-yellow after two months. These consist of tetrahedral cages that are connected via Fe(II) ions into a helical chain (Figure 3.6b). The other two tridentate sites of the cages are partially occupied by Fe(II) ions exhibiting occupancy factors of roughly $\frac{1}{2}$ and $\frac{1}{4}$, respectively, and do not form linkages to other cages. The overall composition of **9** is $[\text{Fe}_{1.75}(\text{Pd}_3\text{X})_4(\text{PZDC})_6(\text{H}_2\text{O})_{3.5}](\text{OTf})_{3.5} \cdot 24\text{H}_2\text{O}$. The bridging Fe(II) ions have distorted octahedral geometry (Figure 3.6b and A3.32, Appendix 3). The pitch of the helical chain contains four cages; its length is 28.6 Å and its width is 30.8 Å. Again, the cage(centroid)-Fe-cage(centroid) angles deviate from linearity; they measure 162 and 176°, respectively. It is noteworthy that such helical chains can also be found as segments in the 3D-network of **4**. Eventually, after six months of storage the diamondoid framework of **4** was formed again (Figure A3.33, Appendix 3).

Similar attempts to trace potential intermediates in the Zn-system remained futile. However, when a suspension of a polycrystalline sample of **5** in methanol was left for crystallization, it gave rise to $[\text{Zn}_3(\text{Pd}_3\text{X})_4(\text{PZDC})_6(\text{H}_2\text{O})_9](\text{NO}_3)_6 \cdot 2\text{DMSO} \cdot 6\text{H}_2\text{O}$, **10**. It

also contains tetrahedral cages and all four tridentate sites are accommodated by Zn(II) ions, albeit with somewhat reduced occupancies (Figure 6c). The cages are not part of coordination network and can be regarded as more or less a discrete assembly with a zeolitic D4R topology (Figure A3.34, Appendix 3).⁸²

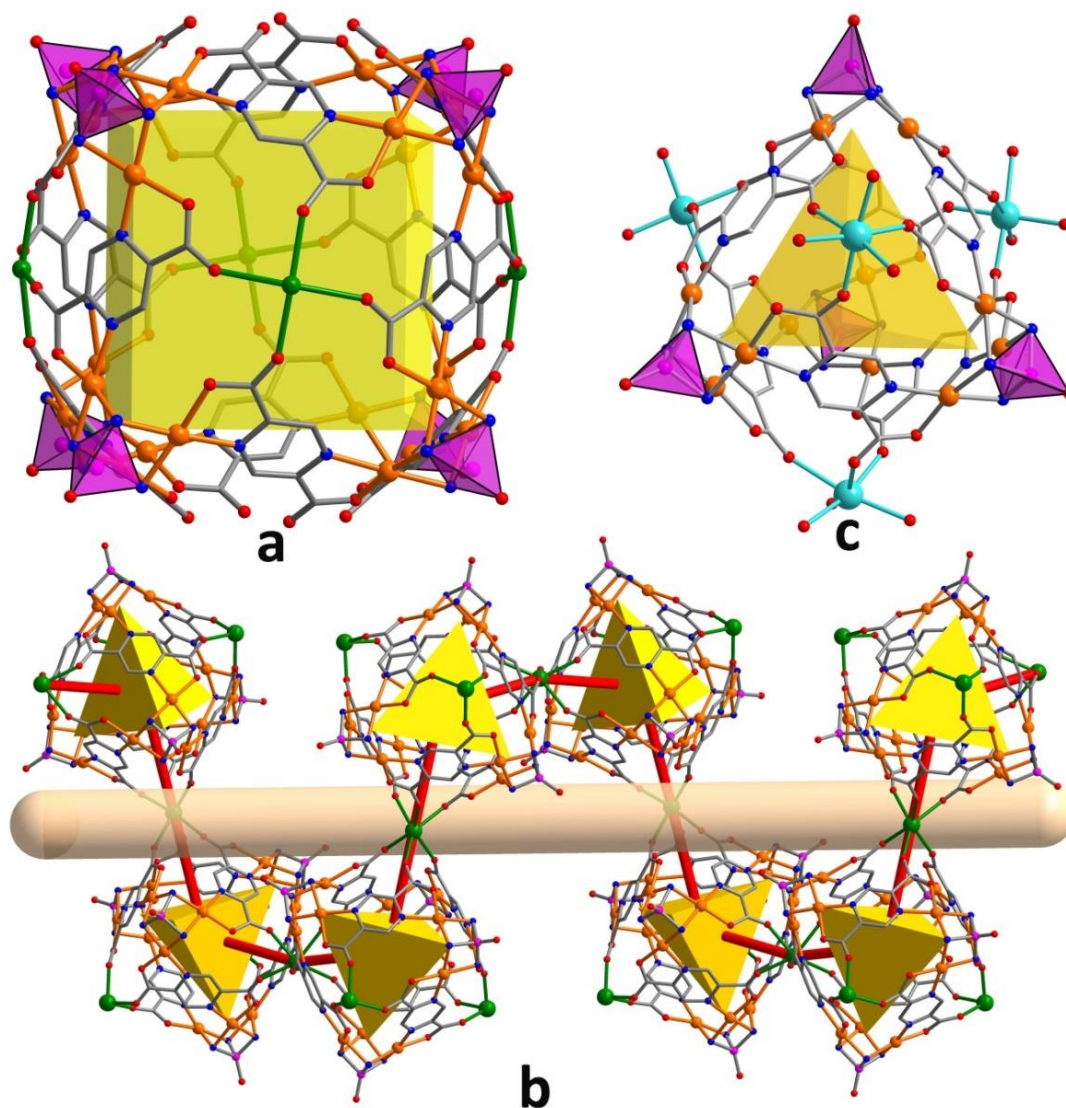


Figure 3.6. (a) Crystal structure of **8**. (b) Helical chain structure of **9**. (c) Molecular structure of **10**.

However, as shown above, fine-tuning of the reaction conditions of the Fe(II)-system allowed us to trap the various stages of the conversions. Treating the system at

elevated temperature in solution ultimately yields the 3D-network, whereas careful submersion of precursor crystals in the solvent enabled the isolation of intermediates. The presence of crystals throughout this process may suggest direct single-crystal-to-single-crystal transformations. However, the accompanying changes to the crystal structures may be too substantial to maintain the integrity of the single crystal. More likely these conversions occur via mass-transport by slow diffusion.⁸³

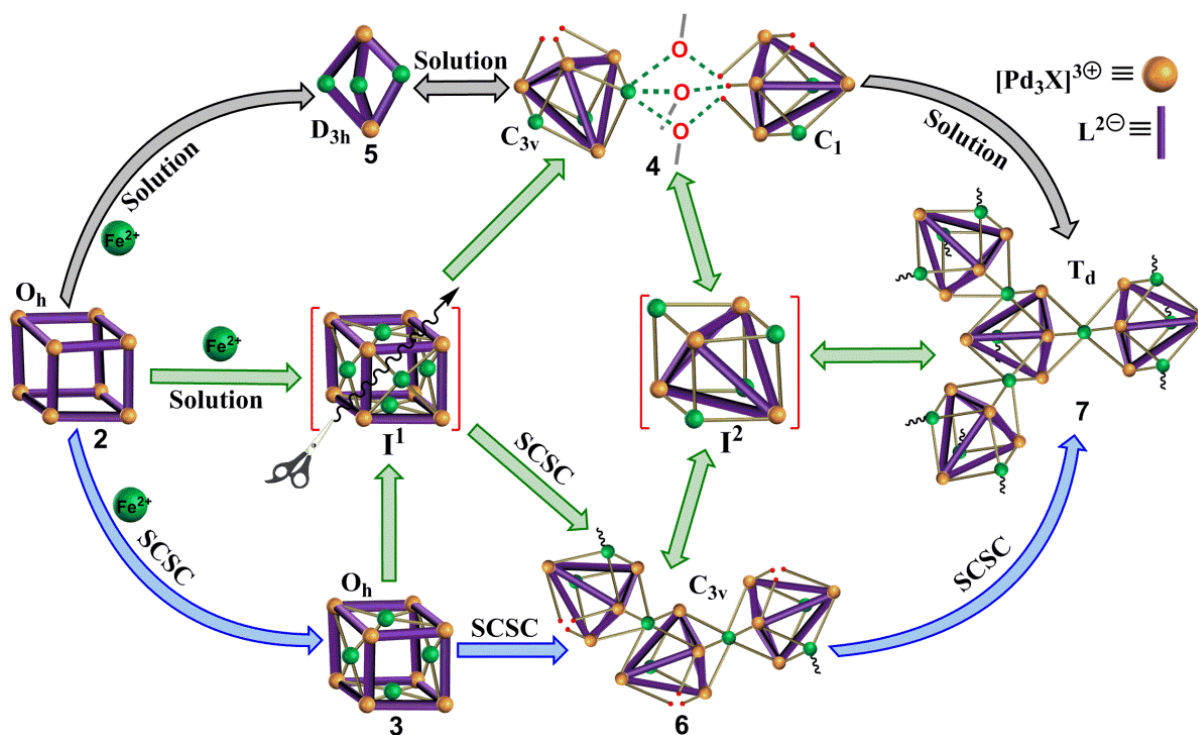
3.3.4 Mapping of the self-assembly conversions

The results suggest that the post-assembly conversion of the cubic cage (**3**) is first initiated by stepwise accommodation of Fe(II) ions into the tetradentate sites of the cubic cage (**8**) (Scheme 3.2). The next step involves rearrangement from a cubic to a tetrahedral cage, which is most likely to be triggered by M(II) coordination. A comparison of the crystal structures of **3** and **8** reveals that the coordination of the Fe(II) ions at the cube-faces leads to tetragonal distortions which may trigger the cleavage of the cubic assembly. Although the stoichiometry of tetrahedral and cubic cages are equivalent ($[(\text{Pd}_3\text{X})_4(\text{PZDC})_6]$ vs. $[(\text{Pd}_3\text{X})_8(\text{PZDC})_{12}]$), which may suggest that simple fission of the cubic cages generates two tetrahedral cages, it remains impossible to formulate a definite mechanism for this re-arrangement from our current data.

Structural comparison between the two cages (cubic and tetrahedral) shows that the primary coordination of Pd_3X and PZDC components is the same for both cages. However, the radius of the canopy that is formed by the arrangement of a Pd_3X unit and its three surrounding PZDC ligands is smaller for the tetrahedral cage (5.5 Å) than for the cubic cage (6.5 Å), which indicates that this arrangement is flexible and therefore able to adapt to various cage geometries. This is also evident from the formation of the trigonal bipyramidal assembly of **7**, which shows the competition of Pd(II) and Fe(II) ions for the coordination with the PZDC ligands.

The pathway of linking the cages can be envisaged via the metal-coordination/hydrogen bonding bridge as observed in **6**. Simple elimination of the three metal-coordinated solvent molecules accomplishes the direct coordination mode, where both cages bind to

the metal ion. Consequently, this will lead to coordination networks of increasing connectivity. The networks with the highest connectivity (**4** and **5**) seem to be the thermodynamically favoured products for both Fe(II) and Zn(II) bridged systems. The choice of metal ion seems to influence the topology of the resulting net. It appears that this is governed by a fine balance between maximising the cage interactions and the coordination requirements of the metal ion. Also, the conversion of the cubic cage to the tetrahedral frameworks involves a series of lower symmetric intermediates. It is interesting to note parallels of these cage conversions that involve polyhedra of different symmetries to developmental biology, where symmetry breaking can be correlated to cellular differentiation in which genome speciation of Zygote leads to a system of complex tissues.⁸⁴⁻⁸⁶



Scheme 3.2. Summary of the step-wise post-assembly reactions involving **3** and Fe^{2+} ions; grey arrows indicate solution conversions and the blue arrows show the SC-SC transformations. Transformations indicated with green arrows show the possible reaction pathways along the proposed intermediates I^1 and I^2 .

3.4 CONCLUSION

This chapter described the utilization of a neutral cubic cage with active coordinating groups for assembling cc-MOFs with *dia* and *qtz* topologies. The neutral cubic cage **3** was obtained in a 42-component self-assembly reaction and is the largest for the neutral homoleptic cage assemblies known for Pd(II) ions. The post-assembly reaction of **3** with Fe(OTf)₂ could be performed in a controlled fashion giving rise to a series of hierarchical heterobimetallic assemblies of discrete, 1D and 2D-architectures, which can be regarded as intermediate stages along the pathway to the final 3D-framework. The topology of the final 3D-framework is governed by the choice of 3d metal-ion; Fe(II) generates a *dia*, Zn(II) a *qtz* net. Mapping the pathways of the conversion reactions revealed that these proceed with sequential change of cage-symmetries. It shows that the stepwise transformation of the discrete cubic cage to the networks of tetrahedral cages is triggered and controlled by the coordination of the 3d metal ions. Such sequential symmetry conversions are rare in metal-organic self-assemblies. They could pave the way for new design strategies towards complex coordination networks and framework structures.

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Chapter 4

**Anion Induced Ferroelectric
Polarization in a Luminescent Metal-
Organic Cage Compound**

4.1 INTRODUCTION

Ferroelectric (FE) materials exhibit switchable spontaneous polarization in response to an external electric field, which led to a wide range of applications in computing devices, capacitors, micro-electro-mechanical systems (MEMS), field-effect transistors (FETs) and off late as enhanced light absorbing layers in FE photovoltaic cells.¹⁻¹¹ Ferroelectric crystals that encompass piezoelectric, pyroelectric, luminescent and nonlinear optical properties have shown potential for energy harvesting and multifunctional optoelectronics.¹²⁻²⁵ Rare-earth doped luminescent ferroelectric perovskites are promising candidates for field emission and vacuum fluorescent displays.²⁶⁻²⁸ Metal-organic materials with ferroelectric, multiferroic and piezoelectric properties have gained immense interest in recent years²⁹⁻³⁸ since they are more amenable for low-temperature fabrication in comparison with traditional ceramic-based materials such as barium titanate and lead zirconate titanate.³⁹⁻⁴⁴ They also offer a broader range of designs and therefore provide a better platform for fine-tuning of material properties. A number of metal tartrates, metal formates, metal sulfates, metal cyanamides and halogenometallates have been screened for ferroelectric and/or multifunctional behaviour.⁴⁵⁻⁴⁸ In some cases hybrid halogenometallates have shown both ferroelectric and luminescent activity.⁴⁹⁻⁵⁰ However, synthetic approaches to access molecular materials with ferroelectric properties are still challenging and often serendipitous.

Recently, our group has embarked on a new family of cationic $[\text{Cu}^{\text{II}}\text{L}_2]_n$, $[\text{Ni}^{\text{II}}\text{L}_2]_4$ and $[\text{Co}^{\text{II}}\text{L}_2]_4$ based discrete or polymeric frameworks derived from dipodal phosphoramidate ligands of the type $[\text{PhPO}(\text{NHPy})_2]$, (Py = 3-pyridyl (³Py) or 4-pyridyl(⁴Py)), which showed tuned ferroelectric responses depending on the counter anions, dimensionality of the framework and guest molecules present in them.⁵¹⁻⁵⁴ Utilizing a similar C_3 -symmetric ligand $[\text{PO}(\text{NH}^3\text{Py})_3]$ (TPPA), Hong and co-workers have synthesized a family of chiral octahedral cages of the type $[\text{M}_6\text{L}_8]^{12+}$ (point group O).⁵⁵⁻⁵⁶ In order to utilize such chiral cages of high symmetry as frameworks that enable FE behaviour, we paid attention to subtly alter the ligand backbone, counter anions and guest molecules.

This chapter reports an octahedral luminescent cage compound $\{[\text{Zn}_6(\text{H}_2\text{O})_{12}][\text{TPTA}]_8\}(\text{NO}_3)_{12} \cdot 26\text{H}_2\text{O}$ **1**, featuring the tripodal tris(3-aminopyridyl)thiophosphoramidate ligand (TPTA),⁵⁷ $[\text{PS}(\text{NH}^3\text{Py})_3]$, which crystallizes in space group *I*4. The ferroelectric measurements on this cage assembly gave a remnant polarization (P_r) value of $\sim 1.2 \mu\text{Ccm}^{-2}$ at room temperature. Polyhedral cages derived from metal-ligand interactions have shown fascinating structures and potential applications in the areas of sorption, sensing, catalysis and host-guest chemistry.⁵⁸⁻⁶⁸ To the best of our knowledge, this is the first report where framework of a polyhedral cage exhibits not only ferroelectric, but a combination of ferroelectric and luminescent behaviour.

4.2 EXPERIMENTAL SECTION

4.2.1 General remarks

All manipulations involving phosphorus halides were performed under a dry nitrogen atmosphere in standard Schlenk-glassware. Solvents were dried over sodium (toluene). 3-aminopyridyl was purchased from Aldrich and used as received. PSCl_3 was purchased locally and was distilled prior to use. NMR spectra were recorded on a Bruker 400 MHz spectrometer (^1H NMR: 400 MHz, $^{13}\text{C}\{^1\text{H}\}$ NMR: 100 MHz, $^{31}\text{P}\{^1\text{H}\}$ NMR: 161 MHz) or on a Bruker 500 MHz (^1H NMR: 500 MHz, $^{13}\text{C}\{^1\text{H}\}$ NMR: 125 MHz, $^{31}\text{P}\{^1\text{H}\}$ NMR: 202 MHz) spectrometer at RT using SiMe_4 (^1H , ^{13}C) and 85% H_3PO_4 (^{31}P). The mass spectra were obtained on an Applied Biosystem MALDI-TOF/TOF spectrometer. The solid-state (CP-MAS) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained on a Bruker 500 MHz spectrometer at a MAS rate of 10.0 KHz. The powder X-ray diffraction data were obtained from a Bruker D8 Advance diffractometer. Thermal analysis data has been obtained from a Perkin-Elmer STA-6000 thermogravimetric analyzer. FT-IR spectra were taken on a Perkin-Elmer spectrophotometer with samples prepared as KBr pellets. Melting points were obtained using an Electrothermal melting point apparatus and were uncorrected. The absorption and emission studies were done by a Perkin-Elmer Lambda 45 UV-Visible spectrophotometer and SPEX Fluorolog HORIBA JOBIN VYON fluorescence spectrophotometer with a double-grating 0.22 m SPEX 1680

monochromator and a 450W Xe lamp as the excitation source. The excitation and emission spectra of the complexes were corrected at instrumental function. The photoluminescence lifetime measurements were carried out using a SPEX Fluorolog HORIBA JOBIN VYON 1934 D phosphorimeter.

4.2.2 Synthesis

4.2.2.1 Synthesis of the [PS(NH³Py)₃] TPTA ligand (L²): PSCl₃ (1mL, 1.67 g, 0.0098 mol) was added dropwise to a stirred solution of 3-aminopyridine (9.3 g, 0.0986 mol) in toluene (250 mL) at 0 °C. The resulting mixture was refluxed for 4 h at 110 °C until a reddish-brown precipitate was formed. The precipitate was collected by filtration and washed three times with water to remove the amine-hydrochloride by-product. The resulting powder was dried in a vacuum desiccator to yield the product. Colourless crystals of TPTA·CH₃OH suitable for X-ray analysis were obtained from its solution in MeOH after 3 days. Yield: 92% (2.3 g) based on P. M.P. 235-340 °C. ¹H-NMR (400 MHz, {(CD₃)₂SO}): δ 7.20 (dd, 3H, CH), 7.55 (d, 3H, CH), 8.06 (d, 3H, CH), 8.44 (s, 3H, CH), 8.56 (d, 3H, NH). ¹³C{¹H}-NMR (100 MHz, {(CD₃)₂SO}): δ 123.98, 125.46, 138.08, 140.74, 142.43. ³¹P NMR (161 MHz, {(CD₃)₂SO}): δ 40.67. FT-IR data in KBr pellet (cm⁻¹): 3117, 1941, 1832, 1596, 1410, 1287, 1156, 947, 775, and 666. Anal. calcd. for C₁₅H₁₅N₆PS: C, 52.62; H, 4.42; N, 24.55; S, 9.37. Found: C, 52.77; H, 4.32; N, 24.81; S, 9.32.

4.2.2.2 Synthesis of the Zn₆L₈ cage 11: To a stirred solution of TPTA (20mg, 0.58 mmol) in MeOH, Zn(NO₃)₂·6H₂O (8 mg, 0.44 mmol) in H₂O was added. The resulting solution was left for 2 h stirring and was filtered through celite pad. The filtrate was left for crystallization. The suitable colourless crystals for X-ray analysis were obtained after 5 days. Yield: 85% (33.7 mg) based on P. M.P. 216-218 °C. FT-IR data on powder (cm⁻¹): 527, 555, 633, 707, 893, 902, 950, 1035, 1163, 1288, 1316, 1407, 1437, 1588, 1652 and 3461. Anal. calcd. For C₁₂₀ H₁₉₆ N₆₀ O₇₄ P₈ S₈ Zn₆: C, 31.61; H, 4.33; N, 18.43; S, 5.62. Found: C, 30.56; H, 4.35; N, 17.67; S, 5.16.

4.2.2.3 Preparation of $\mathbf{11}_{\text{desolvated}}$: This was obtained by heating **11** at 80 °C under high vacuum for 6 h. The formation of desolvated phase was confirmed by the TGA and PXRD analysis.

4.2.2.4 Preparation of $\mathbf{11}_{\text{resolvated}}$: This was obtained by the exposure of $\mathbf{11}_{\text{desolvated}}$ to the H₂O and MeOH mixture in screw capped vial. This conversion has also been observed by adding one drop of mother liquor to $\mathbf{11}_{\text{desolvated}}$.

4.2.2.5 Synthesis of the Zn_6L_8 cage **12:** Compound **12** was prepared by using similar procedure as **1** except $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (22.6 mg, 0.075 mmol) was used instead of the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Yield: 80% (27.9 mg) based on P. M.P. 215-220 °C. FT-IR data on powder (cm^{-1}): 527, 555, 633, 707, 893, 902, 950, 1035, 1163, 1288, 1316, 1407, 1437, 1588, 1652 and 3461. Anal. calcd. for $\text{C}_{120}\text{H}_{149}\text{Cl}_{12}\text{N}_{48}\text{O}_{74.50}\text{P}_8\text{S}_8\text{Zn}_6$: C, 30.17; H, 3.14; N, 14.07; S, 5.37. Found: C, 30.25; H, 3.21; N, 14.05; S, 5.35.

4.2.3 Crystallography

Reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) for all the crystals (Table 4.1). Structures were refined by full matrix least-squares against F^2 using all data (SHELX).⁶⁹ Crystals of **11** and **12** were diffracted weakly at higher angles and hence a $2\theta = 50^\circ$ cut-off was applied. All the non-hydrogen atoms of metal-organic cages were refined anisotropically and hydrogen atoms were constrained in geometric positions to their parent atoms. Hydrogen atoms of water molecules could not be detected in difference maps and were therefore omitted in the refinement due to the high ambiguity of their positions. The crystals structures of **11** and **12** contain disordered nitrate and perchlorate ions which, in both cases, are disordered across symmetry elements. Ions and water molecules that are not disordered were refined anisotropically, while those that are disordered were treated isotropically and given occupancy factors of 0.5 according to the symmetries of disordered sites. SAME restraints were applied to both disordered nitrate and perchlorates ions, RIGU to the ordered ions and SAME to the disordered ions.

Table 4.1: Details of the crystallographic data and the structure refinements of the TPTA, **1 and **2**.**

Compound	TPTA.MeOH	11	12
Chemical formula	C ₁₆ H ₁₉ N ₆ OPS	C ₁₂₀ H ₁₉₆ N ₆₀ O ₇₄ P ₈ S ₈ Zn ₆	C ₁₂₀ H ₁₄₉ Cl ₁₂ N ₄₈ O _{74.50} P ₈ S ₈ Zn ₆
Formula weight	374.40	4559.82	4777.72
Temperature	100(2) K	100(2) K	100(2) K
Crystal system	Triclinic	Tetragonal	Cubic
Space group	P-1	I4	I-43d
a (Å); α (°)	8.937(14); 85.10(3)°	21.096(9); 90	44.497(4); 90
b (Å); β (°)	9.663(15); 84.91(3)°	21.096(9); 90	44.497(4); 90
c (Å); γ (°)	11.854(18); 63.27(3)°	24.031(13); 90	44.497(4); 90
V (Å ³); Z	909.4(2) ; 2	10694.7(11); 2	88103(24); 16
ρ (calc.) mg m ⁻³	1.367	1.416	1.471
μ(Mo K _α) mm ⁻¹	0.283	0.894	1.014
2θ _{max} (°)	56	50	50
R(int)	0.0289	0.0648	0.1268
Completeness to θ	99.7 %	99.8 %	99.4 %
Data / param.	4512 / 228	8788 / 621	12925/849
GOF	1.036	1.051	1.011
R1 [F>4σ(F)]	0.0310	0.0773	0.0887
wR2 (all data)	0.0832	0.2369	0.2870
max.peak/hole (e.Å ⁻³)	0.562/-0.537	1.608 /-0.498	1.229/-1.198

4.2.4 Ferroelectric and dielectric measurements

The powder sample of **11** was compacted in the form of discs (of approximately 10 mm diameter and 1 mm thickness) to measure ferroelectric and dielectric properties. The compacted discs were subsequently electrode using aluminium adhesive foils for both measurements. The dielectric characteristics for **11** were measured using the Novocontrol, Dielectric Spectrometer.

The ferroelectric hysteresis loops in **11** were measured by using Sawyer-Tower circuit. The measurements pertaining to the polarization and fatigue cycles were recorded using hysteresis loop analyser (TF Analyser 2000, aixACCT Germany). Leakage current

was measured dynamically for various voltage steps during the hysteresis loop measurements.

4.2.4.1 Dielectric measurements on the crystals of **11**

The variable (biased) nature of electric dipoles along the different axes of a crystal can be derived from obtaining the information on the dielectric constants at a given direction. A single crystal of **11** electroded with Ag-paint was subjected to capacitance measurements in an LCR meter and the obtained values are given in the table S3. We did not attempt to convert these capacitance values to dielectric constants as crystals were irregular in shape and their dimensions were varying at different ends. Since the value of capacitance is directly proportional to the dielectric constant, the observed capacitance values are the measure of the dipole moments at different directions of the crystals. Notably the values of capacitance, at any given frequency, is very low along the c-axis and are comparably much higher along a- and b-axes confirming the polarization in **11** is operating parallel to the principal axis.

4.2.5 Second harmonic generation

The measurement of the powder second harmonic generation was carried out by using the method of Kurtz and Perry.⁷⁰ The fundamental wavelength is 1064 nm generated by a Q-switched Nd:YAG laser with a frequency doubling at 532 nm. The samples were filled into a capillary tube and a powdered urea sample was used as the reference.

4.2.6 Solid state NMR spectra

The solid-state NMR spectra were measured on a Bruker Advance DSX 500 spectrometer operating at 202.40 MHz for ³¹P. All spectra were collected using a 4 mm triple resonance probe and zirconia rotors. The ³¹P{¹H} MAS NMR spectra were measured at a MAS rate of 10 kHz with ¹H TPPM decoupling during acquisition at an *rf* field of ca. 83 kHz. A ³¹P $\pi/3$ pulse length of 2.1 μ s with a recycle delay of 120.0 s was used.⁷² The solid state CP-MAS ³¹P-NMR spectra of the bulk samples of **11**, **11**_{desolvated} and **11**_{resolvated} gave almost identical peak patterns consisting of a sole signal due to ligand phosphorus atom at 39.13 ppm.

4.2.7 Calculation of dipole moment

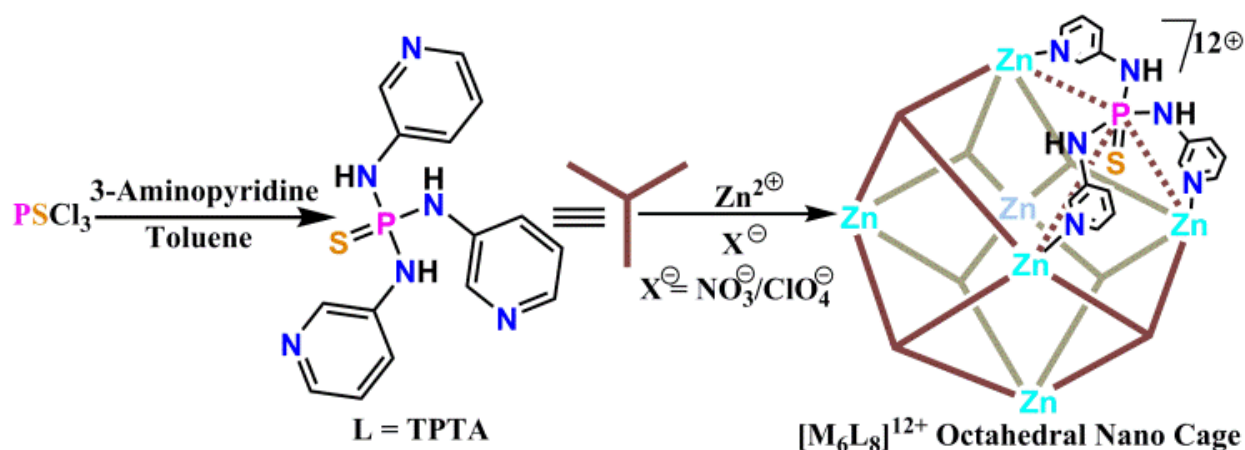
To calculate the polarization of the system we have done the theoretical optimization by using the Gaussian 09 program.⁷¹ The cationic cage segment was considered as low layer and twenty six molecules of H₂O and twelve nitrate anions were selected as high layer to perform ONIOM calculation. The calculation for high layer was done by DFT methods and semi-empirical method (PM₆) was used for the lower layer.

4.3 RESULTS AND DISCUSSION

4.3.1 Synthesis and structure of the octahedral cages

We have found that the solid state assembly of these metal-organic cages is strongly dependent on the choice of counter ions. The treatment of TPTA (Figure 4A.1-4A.4, Appendix 4) with Zn(ClO₄)₄·6H₂O resulted in the formation of {[Zn₆(H₂O)₁₂][TPTA]₈}(ClO₄)₁₂·18.75H₂O, **12**, which crystallizes in the cubic space group *I*-43d as determined from single crystal X-ray diffraction (SCXRD) and features a racemic mixture of cages; its structure corresponds to that of the TPPA derivative reported by Hong and co-workers.⁵⁶

Scheme 4.1: Schematic diagram showing the formation of octahedral cage assemblies 11 and 12.



In contrast, use of the nitrate salt $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ led to the formation of {[Zn₆(H₂O)₁₂][TPTA]₈}(NO₃)₁₂·26H₂O, **11**, which crystallizes in space group *I*4,

consisting of a chiral assembly of cages albeit as part of racemically twinned crystals. The packing of cages in both structures can be described as body-centred; every cage is linked with eight others in a hydrogen-bonded network via water molecules. Both compounds contain partially disordered counter ions (Figure 4.1 and Figure 4A.5-4A.9, Appendix 4). However, the disorder of nitrate ions in **11** can give rise to polar assemblies that facilitate a ferroelectric response (as discussed in detail further below); compound **12** does not show this behavior.

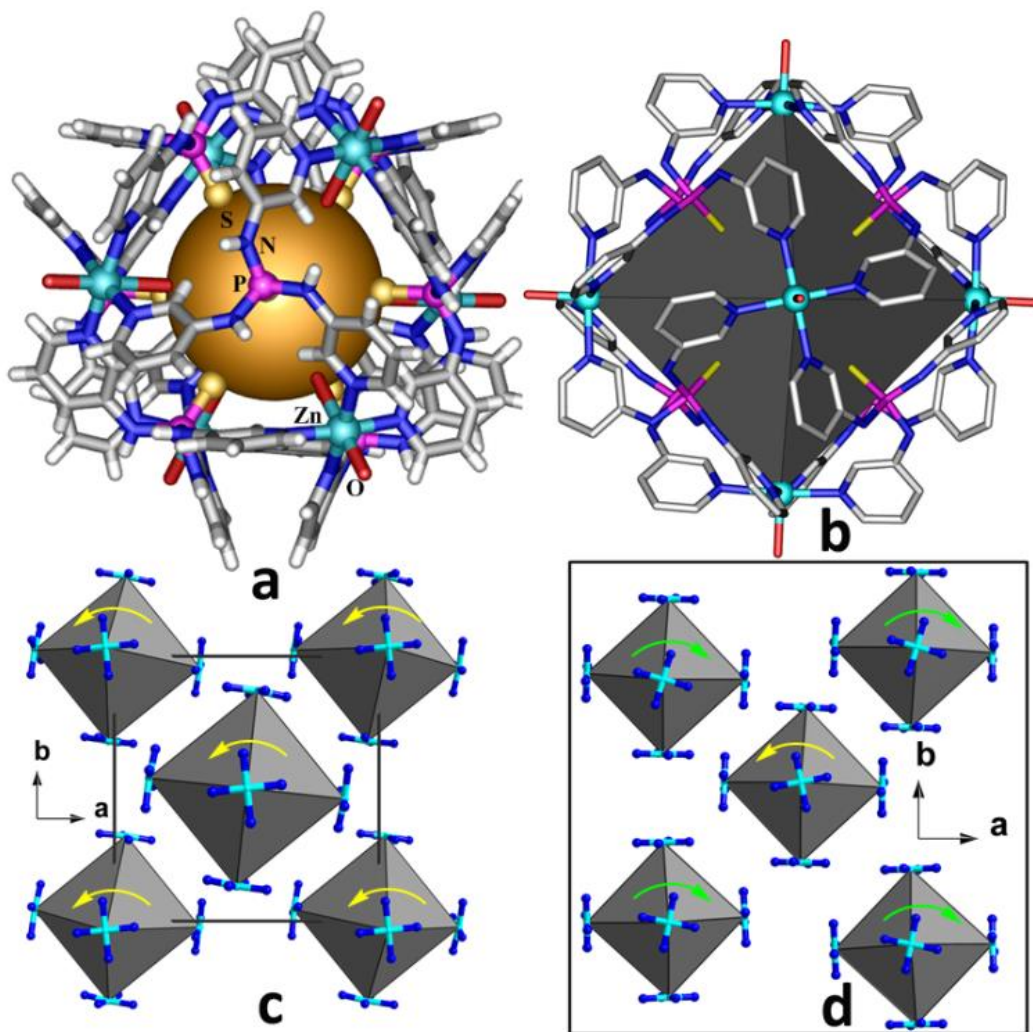


Figure 4.1: View of the $\{[Zn_6(H_2O)_{12}][TPTA]_8\}^{12+}$ cage in **11** and **12**; along the 3-fold (a) and 4-fold axis (b). Packing view of the Zn_6 octahedra in **11** (c) and **12** (d) along with the direction of rotation of the ZnN_4 subunits in them. Only a partial segment of the packing in **12** is given; the organic ligands (except those of $N_{pyridyl}$ atoms), anions and solvates are omitted for clarity.

Each ligand of the cationic cage $\{[\text{Zn}_6(\text{H}_2\text{O})_{12}][\text{TPTA}]_8\}^{12+}$ is connected to three $\text{Zn}(\text{II})$ ions via $\text{N}_{\text{pyridyl}}$ sites and in return, each zinc ion displays an octahedral coordination with four equatorial $\text{N}_{\text{pyridyl}}$ contacts and two water ligands at axial positions (Figure 4.1a and Tables 4.1, A4.1, Appendix 4). All eight TPTA ligands offer a *syn*-mode of coordination to the Zn^{2+} ions in which the $\text{P}=\text{S}$ moieties are oriented towards the cavity of the cage. The cages show local chiral octahedral symmetry (point group O); the six Zn^{2+} ions are located on the three 4-fold axes and the P and S atoms on the four 3-fold axes (Figure 4.1a and 4.1b). The ligands are all twisted in the same direction around the 3-fold axes. Concomitantly, the square planar ZnN_4 arrangements are also twisted the same way when viewed onto the Zn_6 octahedron.

It is interesting to note that mass spectrometry of aqueous solutions of **11** and **12** indicate the existence of complete cages (Figure A4.10, Appendix 4). Variable temperature ^1H and ^{31}P -NMR of **11** and **12** show line broadening at 230 K, which suggest that the cages fluctuate at RT but start to freeze into a static conformation at lower temperature (Figure A4.11-A4.14, Appendix 4). Hence, we assume that the cages also freeze upon crystallization to form either chiral (as in **11**) or racemic crystals (as in **12**). Figures 4.1c and 4.1d emphasize the chiral and racemic structures of **11** and **12**, by highlighting the relative turns of ZnN_4 squares at the corners of the Zn_6 octahedra.

4.3.2 Ferroelectric and dielectric studies of **11**

Ferroelectric measurements of **11** gave a well saturated hysteresis loop for polarization (P) vs electric field (E) at room temperature characteristic of ferroelectric materials. A closer look at the loop indicates remnant (P_r) and saturation polarization (P_s) values of 1.20 and 0.95 μCcm^{-2} , respectively, at 0.1Hz frequency (Figure 4.2a). The slightly higher P_r value as compared to P_s corresponds to the higher relaxation time required for aligning the dipoles created by the weak hydrogen bonding interactions. Such a behaviour has also been observed in several supramolecular ferroelectric systems such as TGS.⁷³ The obtained E_c value of 0.86 kVcm^{-1} is considerably low which indicates the facile switching of the ferroelectric domains in **11**. Recording the data at 1Hz frequency gave an almost similar P-E loop with a P_r of 1.09 μCcm^{-2} and E_c of 1.40 kVcm^{-1} (Figure

A4.15, Appendix 4). The plot of leakage current vs. applied field shows a very low leakage current of the order of 10^{-7} A and exhibits peaks corresponding to the domain switching at the coercive field which confirms the ferroelectric origin of the obtained loop (Figure 4.2b). To further probe its non-conducting behaviour, the crystals of **11** (with contacts) were directly subjected to a DC electric field. The output current measured in this experiment was found to be very low ($47.16 \mu\text{A}$) when 1kV of DC voltage was passed through the crystal. This confirms the resistive nature of the crystal (Table A4.3, Appendix 4).

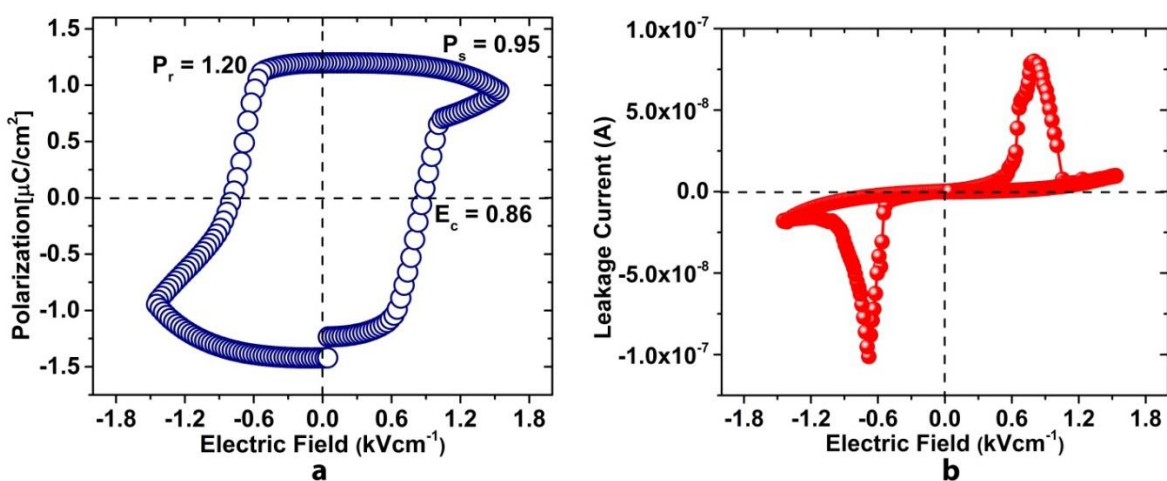


Figure 4.2: (a) Ferroelectric hysteresis loop for **11** and (b) the corresponding plot of the leakage current vs. voltage.

In contrast, a similar P-E loop measurement for **12** gave a negligible polarization (Figure. A4.15, Appendix 4). The obtained P_r values for **11** are in good comparison with several polymeric, organic and molecular ferroelectric materials.⁷⁴ Furthermore, ferroelectric fatigue measurements were performed on **11** (at 1 Hz) to check the loss of remnant polarization during bipolar switching cycles. These measurements showed the retention of nearly 50% of the polarization and rectangularity of the loop after 10^5 switching cycles (Figure A4.16, Appendix 4).

As described earlier, the cages themselves, as well as the framework they build have no dipole moment due to the octahedral symmetry of the cage. The polarization necessary for the ferroelectric response originates from the distribution of nitrate ions

relative to the framework and its interactions with the solvate molecules of water (Figure A4.17-A4.18, Appendix 4).

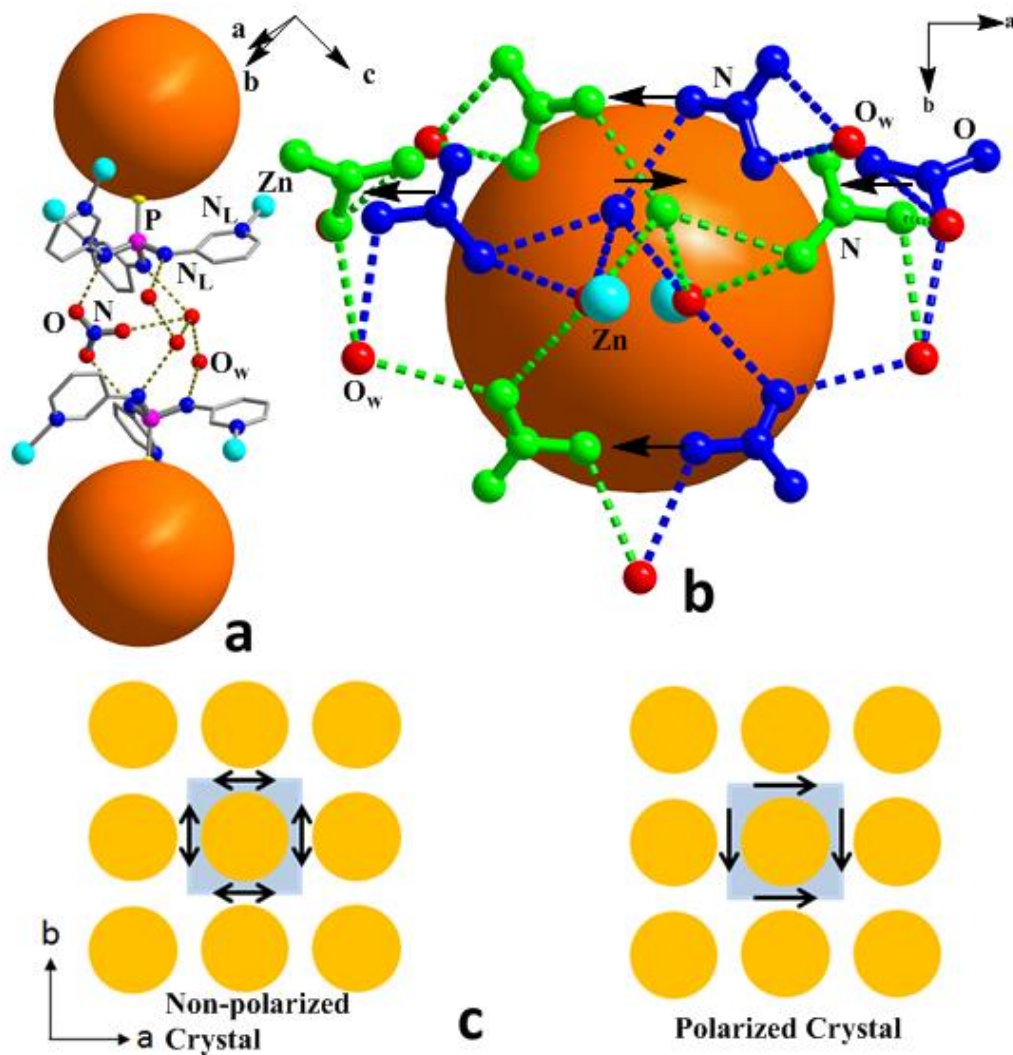


Figure 4.3: Segments of the (a) ordered and (b) disordered parts of the nitrate anions and their H-bonding interactions. The two disordered parts are shown in blue and green colors and the arrows indicate the possible migration pathways. The octahedral cage core is depicted as an orange colored sphere. (c) Schematic diagram showing the overall arrangement of dipoles in the structure of **11** before and after polarization (cages are shown in orange).

The network of nitrate ions and water molecules in **11** consists of both ordered and disordered parts. The ordered part contains one nitrate ion and four water molecules which form bridges between adjacent exogenically facing P(NH)₃ ligand segments

(Figure 4.3a). As such all eight $\text{P}(\text{NH})_3$ units of a given cage are connected in this way to $\text{P}(\text{NH})_3$ units of neighbouring cages. The disordered parts consist of four nitrate ions and water molecules that are located in isolated pockets created by the packing of the cages. These ions are disordered over two positions which are crystallographically related by the 2-fold axis that runs parallel to the *c*-axis (Wyckoff site 4b in space group *I*4). Switching between the two disordered sites would involve a movement of ions along the *a*- and *b*-axis, respectively (Figure 4.3b).

Measurements of capacitance C_p (directly proportional to ϵ) on individual single crystals show that the dipole moments in **11** were dominant along the *a*- and *b*- and weaker along the *c*-axis (Table A4.3, Appendix 4). In a fully polarized state, the location of nitrate ions will be biased towards one of the two positions. A similar bias could also be shown by the disordered solvate molecules perpendicular to the *c*-axis. If the crystal was fully polarized, the space group symmetry would be reduced to *I*1 (*P*1) due to the absence of both 2-fold and 4-fold axes. Refinement of the structure of freshly prepared crystals of **11** in the lower symmetry *I*1 revealed the same disorder as observed for *I*4. This indicates that bulk polarization does not occur prior to the application of an electric field (Figure 4.3c).⁷⁵ Thus, one can assume that the toggling of nitrate anions and water molecules within the isolated pockets of the crystal structure plays a role in the polarization.

To further investigate the polarization attributes of **11**, we performed dielectric permittivity (ϵ) measurements. From the plot of the real part of dielectric permittivity (ϵ') as a function of frequency it can be noted that the maximum room temperature ϵ' value is 39.4 at 100 Hz (Figure A4.19-A4.20, Appendix 4). These values gradually decreased at higher frequencies indicating the contribution of all polarization mechanisms at lower frequencies.⁵¹ The computed dipole moment for **11** gave a value of 59.4 D which is consistent with its observed high-dielectric constant. Next, we studied the temperature dependence of dielectric permittivity at various frequencies between 10^2 and 10^6 Hz. These curves show a broad feature for all measured frequencies with an increase in permittivity up to room temperature (onset at -50 °C), beyond which it gradually

decreases attaining a minimum value of around 8-10 at 60 °C (Figure 4.4a). The maximum ϵ' value of 39.4, which corresponds to an anomalous dielectric peak, is observed at 20 °C at 100 Hz. Furthermore, the intensity of the anomalous peak gradually declined and slightly shifted at higher frequencies suggesting the presence of dielectric relaxation behaviour in **11**. These observations suggest that the dielectric anomaly in **11** is due to desolvation (see also below). Furthermore, the dielectric loss ($\tan \delta$) observed at various frequencies are very low indicating the high dielectric and ferroelectric nature of **11** (Figure 4.4b).

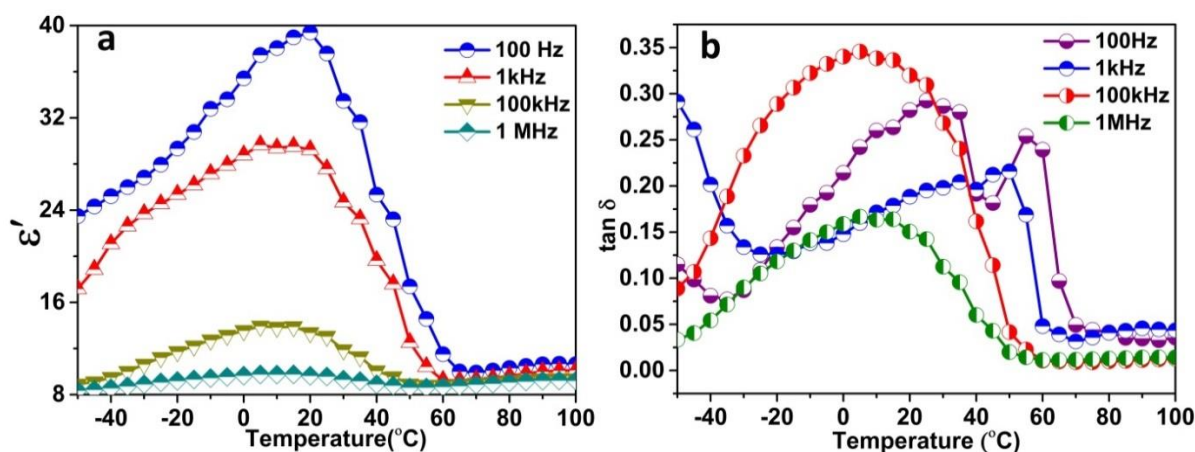


Figure 4.4: Plots of (a) the real part of dielectric permittivity and (b) the dielectric loss as a function of temperature.

The structural integrity of **11** and the desolvation dependant dielectric anomaly has been confirmed by thermogravimetric-differential thermal analysis, infrared spectra recorded in the ATR mode, variable temperature powder X-ray diffraction analysis, SCXRD experiments on **11** at various temperatures between -173 and 100 °C and solid state CP-MAS ^{31}P -NMR spectra. The thermogravimetric-differential thermal analysis of **11** gave an irreversible endothermic peak at 30 °C indicating the onset of desolvation at the transition temperature (Figure A4.23-A4.25, Appendix 4). The Fourier-transform infrared spectra recorded in the ATR mode for the neat samples of **11**, **11**_{desolvated} and **11**_{resolvated} gave almost similar peak patterns except that the –OH stretching frequencies due to the solvate molecules were absent in the case of **11**_{desolvated} (Figure 4.5a).

The variable temperature powder X-ray diffraction (VT-PXRD) analysis showed that the peak patterns begin to change at 30 °C and the profile obtained after 120 °C matched with that of **11**_{desolvated} (Figure A4.26, Appendix 4). However, the PXRD of **11**_{resolvated} exactly matched with that of the as-made **11** confirming the desolvation and resolution processes in **11** are reversible (Figure 4.5b). The SCXRD experiments performed on **11** at various temperatures between -173 and 100 °C are in agreement with the VTPXRD data. Also, a crude model for the structure of **11** at both 273 and 295 K have been obtained that confirms the same packing of cages in *I*4 and even obtained a reflection pattern at 323 K which shows similar unit cell parameters (Figure A4.27, Table A4.4, Appendix 4). This confirms that the integrity of the crystal is retained even after crossing the T_c . The solid state CP-MAS ^{31}P -NMR spectra of the bulk samples of **11**, **11**_{desolvated} and **11**_{resolvated} gave almost identical peak patterns consisting of a sole signal due to ligand phosphorus atom at 39.13 ppm (Figure A4.28, Appendix 4).

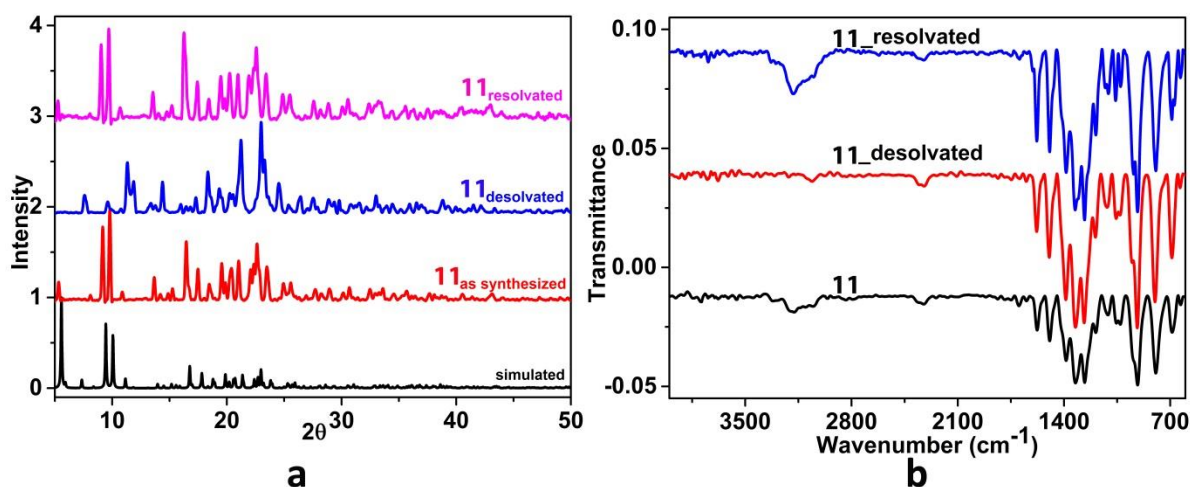


Figure 4.5: (a) IR spectra for **11**, **11**_{desolvated}, and **11**_{resolvated}. (b) PXRD pattern of **11** at various states.

4.3.3 Optical properties of **11**

It is worth noting that the framework of cages in **11**, which can be regarded as static during the ferroelectric response, is polar in itself (space group *I*4). The direction of the ferroelectric response, on the other hand, lies orthogonal to the polar 4-fold axis, leading to an overall reduction in symmetry to *I*1.

Hence, the extra 'permanent' polarity orthogonal to the direction of ferroelectricity implies further interesting properties. Preliminary non-linear optical measurements (NLO) were obtained for **11** in both solvated and desolvated states. The second harmonic generation (SHG) intensities for the bulk un-sieved samples of **11**, **11**_{desolvated} and **11**_{resolvated} were found to be around 30, 20 and 32 %, respectively, with respect to the standard urea sample (Table A4.5, Appendix 4). The cage assembly of **11** was also found to exhibit bright blue luminescence under UV-light in the solid state owing to intra-ligand (π - π^*) transitions (Figure 4.7). The emission spectrum of **11** shows an intense band at $\lambda_{em} = 398$ nm ($\lambda_{ex} = 345$ nm).⁷⁶ The decay profile recorded on **11** gave a lifetime of 6.9 ns for this fluorescence emission (Figure A4.30, Appendix 4). Observation of such dual properties (fluorescence and ferroelectricity) promises interesting applications of metal-organic materials for future electro-optical and energy harvesting applications.

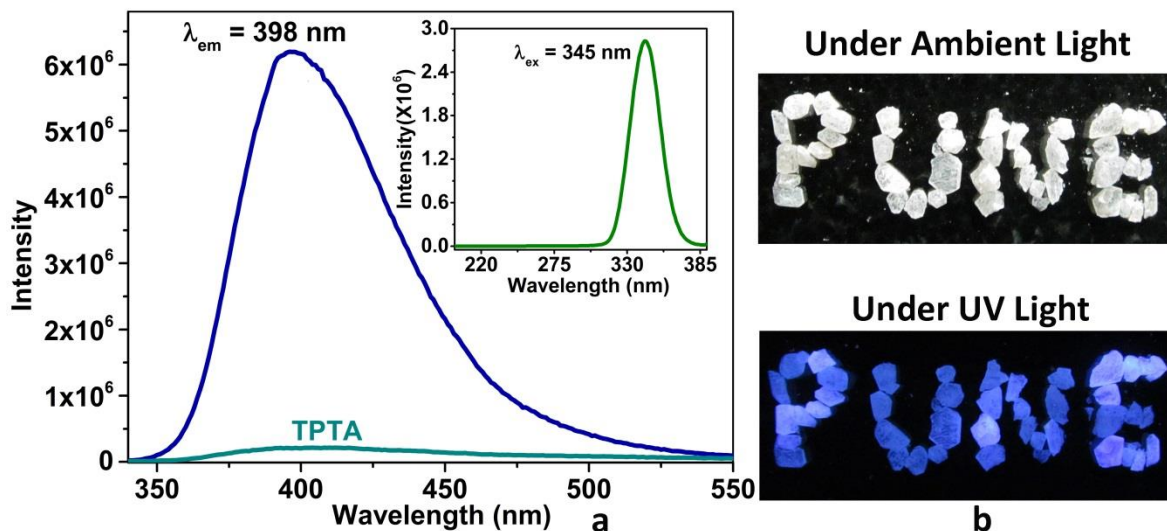


Figure 4.6: (a) Fluorescence profile of **11** and TPTA in the solid state; the inset shows the excitation spectrum of **11**. (b) View of the crystals of **11** at ambient and under UV light.

4.4 CONCLUSION

In conclusion, this work demonstrates that by subtly altering the molecular constituents of a metal-ligand cage assembly, it is possible to derive materials with ferroelectric properties. An assembly of $\{[Zn_6(H_2O)_{12}][TPTA]_8\}^{12+}$ cages and nitrate ions gave a ferroelectric remnant polarization value of 1.2 μCcm^{-2} at room temperature. The

polarization can be attributed to the toggling of anions and water molecules that are located in pockets between the cages. Further, dielectric measurements showed that **11** exhibits a desolvation assisted dielectric transition associated with the release of solvate molecules from the unit cell packing. In addition, crystals of **11** are noncentrosymmetric, which gives rise to NLO activity. Furthermore, the compound **11** is highly luminescent showing a bright blue emission under UV-light. Such multifunctional behaviour is unique among metal-organic cage compounds and may pave the way for new and interesting applications.

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- (76) For **2**, the λ_{em} was found to be 393 nm (Figure A4.29).

Chapter 5

**Connected-Cage based Reversible
Hierarchical Frameworks Exhibiting
Axial Ferroelectric Anisotropy**

5.1 INTRODUCTION

Stepwise assembly of nano-dimensional solids have gained attention in supramolecular chemistry not only for the understanding of molecular phenomena but also to address target oriented applications in the areas of energy, device characteristics, catalysis and biological processes.¹⁻¹⁰ In this effort, use of discrete metal-organic cages offers an attractive route for building well-defined nanostructures particularly in hierarchical architectures.¹¹⁻²³

Ferroelectric materials are a source of large switchable electric fields in low power consumption, non-volatile computing devices, field-effect transistors, electrically controlled magnetic memories, micro-electro-mechanical systems and ferroelectric photovoltaic cells.²⁴⁻³² Ferroelectric systems based on organic, organic-inorganic and metal-organic assemblies are of tremendous interest in recent times due to their simplistic synthetic protocols, tunable structural properties and the amenability for low-temperature and low-cost fabrication.³³⁻⁴¹ Several organic ferroelectrics exhibit polar salt-like structures and are extensively been investigated for their polarization mechanisms.⁴²⁻⁴⁷ The effect of local chemical environment on macroscopic ferroelectricity in these organic salts have precisely been understood as majority of them can be subjected to measurements on crystals. Also, ferroelectric measurements on crystals can give information related to the axial anisotropies in their polarization.⁴⁸⁻⁵¹ But, such level of understanding in metal-ligand based networks is yet to be achieved due to the following reasons. First, these assemblies were mostly obtained by serendipitous synthetic routes followed by difficulties associated with growing regular defect-free crystals.⁵²⁻⁵³ Secondly, as ferroelectricity in most of them is not associated with structure-phase transitions, proper ferroelectric mechanisms in them could not be established.⁵⁴⁻⁵⁵ Thus, one of the ways to systematically understand the physical properties like the ferroelectric and dielectric behaviour in a metal-ligand assembly is to use a bottom-up approach, wherein a discrete moiety can be assembled into a metal-organic framework (MOF) in a stepwise manner, and evaluate their physical properties at various stages of the assembly process. However, such “bottom up” synthesis of 3D-

MOFs from polyhedral precursors is practically difficult to achieve, although a conceptual design can be applied.⁵⁶⁻⁵⁹

This chapter shows the octahedral cage $\{[\text{Cu}_6(\text{H}_2\text{O})_{12}][\text{TPTA}]_8\}$ based on the thiophosphoramidate ligand, $\text{PS}(\text{NH}^3\text{Py})_3$ (TPTA)⁶⁰⁻⁶¹ can be sequentially assembled into higher dimensional 1D, 2D and 3D-cage-connected MOFs by the stoichiometric replacement of outward oriented axially bound aqua ligands with chloride ions. By using stoichiometric quantities of chloride ion acceptors such as AgNO_3 or $(^n\text{Bu}_4\text{N})\text{NO}_3$, these networks can be disassembled into the corresponding lower dimensional frameworks in a stepwise manner. Notably, the C_3 -symmetric nature of the tripodal ligands favoured the formation of axially symmetric assemblies for most of the obtained frameworks. The ferroelectric measurements on the crystals of **13** show anisotropic response with the observed remnant polarizations of 1.48 and 20.46 μCcm^{-2} along a- and c-axes, respectively. This behaviour is retained even in the one-dimensional assembly of **14** which exhibits an improved polarization along the a- and c-axes with the P_r values of 6.28 and 28.90 μCcm^{-2} , respectively. To the best of our knowledge, this is the first report dealing with both the stoichiometry dependant control on the reversible formation of hierarchical cage-connected frameworks and the modulations in their allied polarization and ferroelectric anisotropic behaviour.

5.2 EXPERIMENTAL SECTION

5.2.1 General remarks

All manipulations involving phosphorus halides were performed under dry nitrogen atmosphere in standard Schlenk-glassware. Solvents were dried over sodium (toluene). 3-aminopyridyl was purchased from Aldrich and used as received. PSCl_3 was purchased locally and was distilled prior to use. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was purchased from Aldrich and used as received. The mass spectra were obtained on an Applied Biosystem MALDI-TOF/TOF spectrometer. The powder X-ray diffraction data were obtained from a Bruker D8 Advance diffractometer. Thermal analysis data has been obtained from a Perkin-Elmer STA-6000 thermogravimetric analyzer. FT-IR spectra

were taken on a Perkin Elmer spectrophotometer with samples prepared as KBr pellets. Elemental analyses were performed on a Vario-EL cube elemental analyzer.

5.2.2 Synthesis

5.2.2.1 Synthesis of $\{[\text{Cu}_6(\text{H}_2\text{O})_{12}][\text{TPTA}]_8\} \cdot (\text{NO}_3)_{12}$ octahedral cage **13:** To a stirred solution of TPTA (20 mg, 0.0585 mmol) in MeOH (5 mL) at room temperature, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (10.60 mg, 0.0439 mmol) in H_2O (2 mL) was added drop wise. The resulting blue solution was filtered through cellite and left for crystallization. Block shaped blue crystals suitable for X-ray analyses were obtained after 10 days. Yield: 85%. FT-IR data in KBr pellet (cm^{-1}): 3419, 3131, 1580, 1501, 1384, 1277, 1191, 1112, 1061, 1026, 939, 802, 699. Anal. calcd. for $\text{C}_{120}\text{H}_{208}\text{Cu}_6\text{N}_{60}\text{O}_{80}\text{P}_8\text{S}_8$: C, 30.95; H, 4.50; N, 18.05; S, 5.51. Found: C, 30.91; H, 4.32; N, 17.89; S, 5.39.

5.2.2.2 Synthesis of **1D $\{[\text{Cu}_6(\text{H}_2\text{O})_{10}\text{Cl}][\text{TPTA}]_8\} \cdot (\text{NO}_3)_{11}$ ccMOF **14**:** To a stirred solution of TPTA (20 mg, 0.0585 mmol) in MeOH (5 mL) at room temperature, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (10.60 mg, 0.0439 mmol) in H_2O (2 mL) was added drop wise leading to the formation of a transparent blue solution. After 30 minutes of stirring, an aqueous NaCl (1:1) solution was added to the mixture. The resulting solution was filtered through cellite and left for crystallization. Blue rectangular crystals suitable for X-ray analysis were obtained after 10 days. Yield: 80%. FT-IR data in KBr pellet (cm^{-1}): 3440, 3149, 1580, 1500, 1277, 1193, 1111, 1064, 1026, 945, 803, 698. Anal. calcd. for $\text{C}_{120}\text{H}_{132}\text{ClCu}_6\text{N}_{59}\text{O}_{41}\text{P}_8\text{S}_8$: C, 36.23; H, 3.35; N, 20.78; S, 6.45. Found: C, 36.41; H, 3.02; N, 21.12; S, 6.32.

5.2.2.3 Procedure to preparation of **14**, **15** and **16** from **13**

To the stirred solution of **13** (100 mg, 0.21mmol) in MeOH/ H_2O (5 mL) at room temperature NaCl (1:1 for **14**, 1:3 for **15** and 1:6 for **16**) in H_2O (2 mL) was added slowly (drop wise). After 30 minutes of stirring, the resulting solution was filtered through cellite and left for crystallization. Blue crystals suitable for X-ray analysis were obtained after 10 days.

5.2.2.3.1 Synthesis of 2D $\{[\text{Cu}_6(\text{H}_2\text{O})_7\text{Cl}_3][\text{TPTA}]_8\} \cdot (\text{NO}_3)_9$ ccMOF **15:** Yield: 71%. FT-IR data in KBr pellet (cm^{-1}): 3406, 3139, 1580, 1497, 1273, 1194, 1109, 1063, 1026, 946, 803, 695. Anal. calcd. for $\text{C}_{120}\text{H}_{120}\text{Cl}_3\text{Cu}_6\text{N}_{48}\text{O}_7\text{P}_8\text{S}_8$: C, 43.17; H, 3.62; N, 20.14; S, 7.68. Found: C, 43.35; H, 3.65; N, 20.40; S, 7.12.

5.2.2.3.2 Synthesis of 3D $\{[\text{Cu}_6(\text{H}_2\text{O})_6\text{Cl}_3][\text{TAPP}]_8\} \cdot (\text{NO}_3)_9$ ccMOF **16:** Yield: 80%. FT-IR data in KBr pellet (cm^{-1}): 3433, 3149, 1581, 1500, 1382, 1276, 1119, 1111, 1067, 1026, 946, 800, 700. Anal. calcd. for $\text{C}_{120}\text{H}_{180}\text{Cl}_3\text{Cu}_6\text{N}_{57}\text{O}_{75}\text{P}_8\text{S}_8$: C, 31.24; H, 3.93; N, 17.31; S, 5.56. Found: C, 31.52; H, 4.21; N, 16.97; S, 5.32.

5.2.3 Dielectric and ferroelectric measurements

In order to determine the dielectric measurements, the powdered sample of all the compounds compacted in the form of discs of 10 mm diameter and 1 mm thickness. The compacted discs were subsequently electrode using aluminum adhesive foils. The dielectric properties for all complexes were measured using the Novocontrol Dielectric Spectrometer.

The ferroelectric hysteresis loops in **13** and **14** were measured on single crystal of dimensions 2.5x1.2x1.2 and 2.5x1x0.8 mm respectively by using Sawyer-Tower circuit. The measurements pertaining to the polarization and fatigue cycles were recorded using hysteresis loop analyser (TF Analyser 2000, aixACCT Germany). Leakage current was measured dynamically for various voltage steps during the hysteresis loop measurements.

The room temperature capacitance measurements were done on the same crystals (used for the ferroelectric measurements) of **13** and **14** using LCR meter.

5.2.4 Crystallography

Reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) for **13**, **14**, **15** and **16** (Table 5.1). Structures were refined by full-matrix least-squares against F^2 using all data (SHELX97).⁶² All non-hydrogen atoms were refined anisotropically if not stated otherwise. Hydrogen atoms

were constrained in geometric positions to their parent atoms. The bad reflections were omitted by SHEL and OMIT commands in **13**, **14**, **15** and **16** respectively. In compound **13-16**, some of the nitrate counter anions were not behaving well and thus was fixed by using SAME/SIMU u-restrain. The unbound solvate molecules were refined isotropically in all structures. In compound **15**, one of the copper centers (not participated in bridging) was partially coordinated with chloride anion and water. Partially occupied water molecule was treated isotropically in **13-16**. The solvent and anions which were not behaving well squeezed them out by using SQUEEZE/PLATON model in all structures.⁶³

Table 5.1 Crystallographic data of compound 13, 14, 15 and 16.

Compound	13	14
Chemical formula	C ₁₂₀ H ₂₀₈ Cu ₆ N ₆₀ O ₈₀ P ₈ S ₈	C ₁₂₀ H ₁₃₂ ClCu ₆ N ₅₉ O ₄₁ P ₈ S ₈
Formula weight	4656.93	3977.77
Temperature	100(2)K	100(2) K
Crystal system	Tetragonal	Tetragonal
Space group	I4	I422
a (Å); α (°)	21.163(2) ; 90°	24.1481(19); 90
b (Å); β (°)	21.163(2) ; 90°	24.1481(19); 90
c (Å); γ (°)	24.055(3); 90°	18.2475(16); 90
V (Å ³); Z	10774(3); 2	10640.7(19); 2
ρ (calc.) mg m ⁻³	1.436	1.242
μ(Mo K _α) mm ⁻¹	0.815	0.813
2θ _{max} (°)	56	56
R(int)	0.1191	0.0716
Completeness to θ	100	100 %
Data / param.	23194 / 587	6689 / 218
GOF	1.013	1.730
R1 [F>4σ(F)]	0.0938	0.1376
wR2 (all data)	0.2906	0.4073
max. peak/hole (e.Å ⁻³)	1.714/ -0.975	2.565/-1.493
Compound	15_sq	16
Chemical formula	C ₁₂₀ H ₁₂₀ Cl ₃ Cu ₆ N ₄₈ O ₇ P ₈ S ₈	C ₁₂₀ H ₁₈₀ Cl ₃ Cu ₆ N ₅₇ O ₇₅ P ₈ S ₈
Formula weight	3338.46	4613.03
Temperature	100(2) K	100(2)
Crystal system	Tetragonal	Cubic

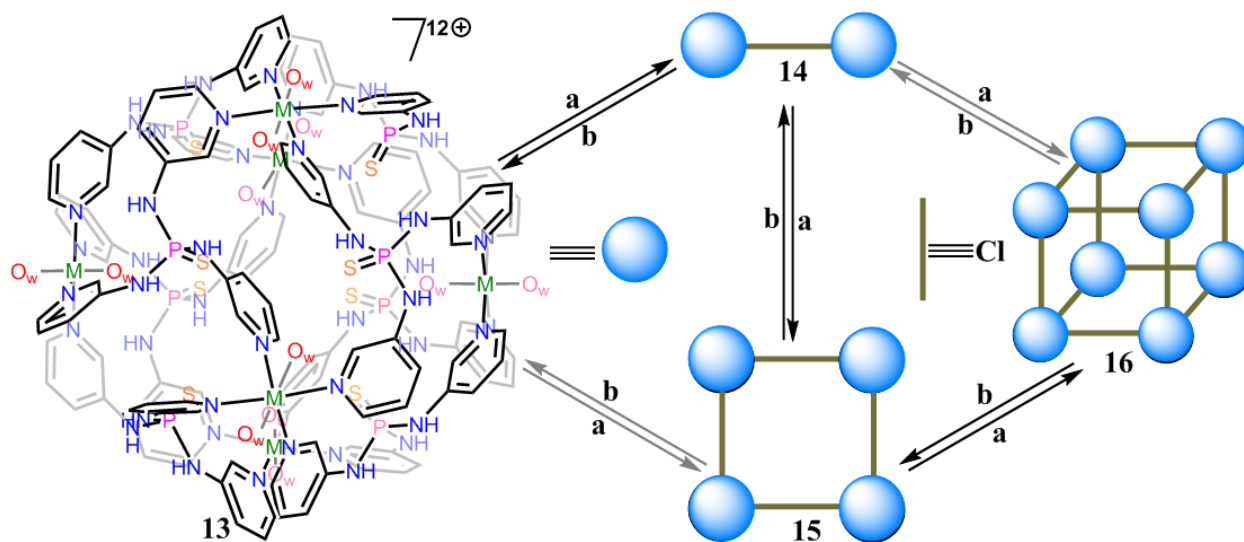
Space group	P 4/nnc	P432
a (Å); α (°)	18.3911(12); 90	18.485(2);90
b (Å); β (°)	18.3911(12); 94.322(8)°	18.485(2);90
c (Å); γ (°)	29.917(8); 90°	18.485(2);90
V (Å ³); Z	9813.4(14); 2	6317(2):1
ρ (calc.) mg m ⁻³	1.130	1.213
μ (Mo K α) mm ⁻¹	3.963	0.723
2 $\theta_{\max}$ (°)	56	56
R(int)	0.05	0.1399
Completeness to θ	99.9 %	99.8
Data / param.	6129 / 232	2675/92
GOF	1.076	1.568
R1 [F>4 σ (F)]	0.0754	0.1176
wR2 (all data)	0.2333	0.3881
max. peak/hole (e.Å ⁻³)	1.466/ -0.738	5.019/-1.179

5.3 RESULTS AND DISCUSSION

5.3.1 Synthesis

Treatment of TPTA with Cu(NO₃)₂·3H₂O in 3:2 ratio gave the expected cage molecule {[Cu₆(H₂O)₁₂][TPTA]₈}·(NO₃)₁₂, **13**. In order to obtain hierarchical cage-connected frameworks, the outer-cage coordinated water molecules in the cage assembly of **13** were sequentially replaced with Cl⁻ ions upon treatment with NaCl in controlled quantities in MeOH/H₂O medium. Thus the 1:1 reaction of **13** with NaCl gave the one-dimensional connected-cage framework {[Cu₆(H₂O)₁₀Cl][TPTA]₈}·(NO₃)₁₁, **14**; 1:3 ratio gave the two dimensional metal organic framework {[Cu₆(H₂O)₇Cl₃][TPTA]₈}·(NO₃)₉, **15** and 1:6 (or excess) ratio gave three dimensional metal organic framework {[Cu₆(H₂O)₆Cl₃][TAPP]₈}·(NO₃)₉, **16**. Notably, direct reaction of TPTA, Cu(NO₃)₂·3H₂O and NaCl in all the ratios (and in excess) leads to the formation **14**, the 1D-assembly, and did not give the other products **15** or **16** (Scheme 5.1). This signifies that formation of the discrete cage assembly of **13** is important to achieve the synthesis of higher dimensional frameworks such as **15** and **16** via the axial ligand substitution pathway. The bulk phase purity of these compounds was confirmed by the powder X-ray diffraction (PXRD) pattern (Figure A5.1- A5.4, Appendix 5).

Scheme 5.1: Schematic diagram for the formation of cage-connected frameworks. Transformations labelled with 'a' and 'b' are for the assembly and disassembly processes, respectively. Black-arrows indicate the stepwise conversions and the gray-arrows indicate some of the cross-conversions.



Similarly, stepwise disassembly of these cage-connected assemblies has been performed in the polar medium of MeOH/H₂O. Treatment of chloride ion acceptors such as AgNO₃ or (nBu₄N)NO₃ have resulted in the hierarchical disassembly of these frameworks starting from the cubic 3D-assembly **16** to until the discrete 0D-assembly **13** (Scheme 5.1). Although there were a few reports on the growth of cage assemblies to three dimensional metal organic frameworks, those reactions were not reversible and not all the intermediate framework structures of their families have been isolated.⁵⁸⁻⁶¹ However, direct experimental evidence for the pathway or mechanism leading to the assembly of cc-MOFs is very limited in literature as (a) these types of MOFs were always synthesized in a one pot reaction and (b) difficulties associated with the solubility of the low-dimensional intermediates that precludes the knowledge about their structures.⁶⁴⁻⁷⁰ As a result a “bottom up” synthesis of MOFs from molecular polyhedral precursors cannot start from bottom, although a conceptual design for the framework construction can be applied.⁷¹⁻⁷⁴ The reversible reactions were confirmed by the single crystal X-ray diffraction (SCXRD) and also by powder X-ray diffraction (PXRD) in bulk phase (Figure A5.5- A5.8, Appendix 5).

5.3.2 Crystal structure

The discrete cage assembly was crystallized as the solvate adduct of formula **13**.32H₂O in the tetragonal space group *I*4. The cage assembly in **13** comprises of a cationic $\{[\text{Cu}_6(\text{H}_2\text{O})_{12}][\text{TPTA}]_8\}^{12+}$ core in which each ligand is connected with three Cu(II) atoms via N_{pyridyl} coordination and each copper atom is in an octahedral coordination with four equatorial N_{pyridyl} contacts and two O_{water} atoms at axial positions. Each of the TPTA ligand offers a syn mode of coordination to the Cu²⁺ ions. As a result all the P=S moieties are oriented towards the inner cavity of the cage. The intrinsic symmetry of the cage in **13** is cubic 432 (*O*) consisting of three 4-fold axes through Cu(II) atoms and four 3-fold axes through P and S atoms (Figure 5.1a and A5.8, Appendix5). The lack of planes of symmetry in the cage assembly is due to the twisting of the tripodal ligands away from additional mirror symmetry (*O_h*) to minimize strain within the complex. Similarly, all the square planar CuN₄ arrangements are also twisted relative to the Cu₆ octahedron. This arrangement thus generates chirality in **13** since all the six CuN₄ squares twist in the same direction in the Cu₆ octahedron (Figures A5.9-A5.10, Appendix 5).

SCXRD analysis of **14**, **15** and **16** confirms the formation of hierarchical cage-connected assemblies while retaining the structural motif of the parent cage in the repeating unit. The outer-cage axial water molecules in the cage motifs were found to be sequentially replaced by chloride ions wherein each Cl[−] ion acts as a linear μ²-bridging ligand between two M₆L₈ fragments. Thus, two chloride bridges at two opposite corners of the M₆L₈ octahedron have been found in case of **14**; four Cl[−] bridges at the four corners of a square plane for **15** and six Cl[−] bridges at all the six-corners of the octahedron in case of **16**. An extra chloride ion, as a terminal ligand, was partially located at the remaining two corners of the octahedron in the crystal structure of **15** and was found to be disordered with a partially occupied molecule of axial water molecule. The intra-cage axial water molecules were found to be unaffected in all these three cage-connected framework molecules (Figures 5.1b-d and A5.11- A5.13, Appendix 5).

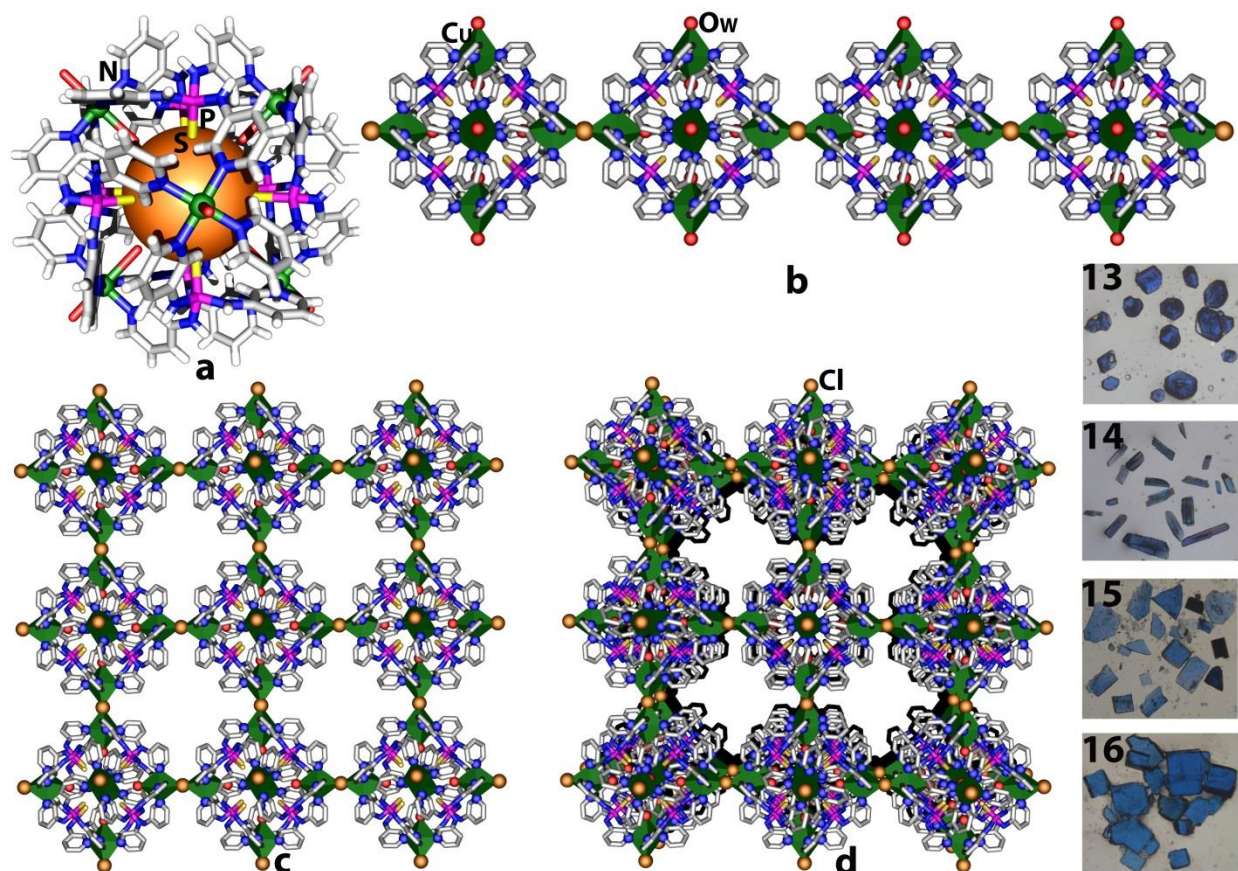


Figure 5.1. Crystal structure: (a) Octahedral view of the **13**, (b) polyhedral view considering the metal center as vertex. (c) cage connected 1D-coordination polymer **14**, (c) view of the 2D-sheet in ccMOF **15**, (d) view of 3D-network in ccMOF **16**. (f) view of distorted octahedral geometry of metal center. Right side images showing the crystals of **13-16**.

The crystal structures of **14** and **15** were solved again in the tetragonal space groups $I422$ and $P4/nnc$, respectively. The crystallographic point group of the cage in both these assemblies is 422 (chiral, D_4); the highest symmetry of the cage. Although both **14** and **15** show a similar tetragonal body centred packing as that of **13**, the 2-D structure shows a primitive lattice due to the cage molecules of the adjacent layers form an enantiomeric pair (vide supra). The 3-D assembly of **16** was crystallized in the rare cubic space group $P432$ which reflects the local symmetry exhibited by the individual cages were exactly mirrored in the 3D-lattice. TOPOS analysis gave a 4-c, uninodal sql net (point symbol $\{4^4.6^2\}$) topology for the cationic assembly $\{[\text{Cu}_6(\text{H}_2\text{O})_7\text{Cl}_3][\text{TPTA}]_8\}^{9+}$ in **15** by considering the Cu_6L_8 cage as a single node. Similar analysis gave, a 6-c

uninodal pcu net (point symbol $4^{12}.6^3$) topology for **16** by adopting the $\{[\text{Cu}_6(\text{H}_2\text{O})_6\text{Cl}_3][\text{TPTA}]_8\}^{9+}$ cage motif as a single node (Figures A5.14- A5.15, Appendix 5).⁷⁵⁻⁷⁶ Furthermore, these framework solids resemble classical inorganic compounds as the cages were firmly locked into positions through the rigid bridging interactions of the chloride ions. For example, the cationic framework $\{[\text{Cu}_6(\text{H}_2\text{O})_{10}\text{Cl}][\text{TPTA}]_8\}^{11+}$ in **14** has a BiF_5 structure, $\{[\text{Cu}_6(\text{H}_2\text{O})_7\text{Cl}_3][\text{TPTA}]_8\}^{9+}$ in **15** adopts the SnF_4 framework and $\{[\text{Cu}_6(\text{H}_2\text{O})_6\text{Cl}_3][\text{TPTA}]_8\}^{9+}$ framework in **16** is analogous to the ReO_3 lattice.⁷⁷⁻⁷⁸

It is interesting to compare the rotational chirality exhibited by these cage connected assemblies to that of the discrete cage **13**. In all the chiral structures (**13**, **14** and **16**), the CuN_4 squares turn only in one direction, albeit a change of direction for **14** and **16** in comparison with **13** (Figure A5.16, Appendix 5). This trend has been observed in circular dichroism (CD) spectra in water where an opposite cotton effect was observed for **14** with respect to **13** (Figures A5.17-A5.19, Appendix 5). However, in the centrosymmetric structure of **15**, the cage molecules in the two adjacent layers exhibit opposite rotations for the CuN_4 squares (Figure A5.16c, Appendix 5). Also it can be noted that cages within the same coordination polymer are always of the same enantiomer; this applies to the centrosymmetric structure of **14** as well where the opposite enantiomer is found only in the other layer. This could be attributed to a slightly staggered arrangement of the Cu_6L_8 cages at the two end of a given Cl^- ion bridge. An eclipsed arrangement of these cage assemblies across the chloride bridge would otherwise have led to opposite enantiomers. This implies that there is an inherent transfer of chirality from the individual cage to the entire polymer.

5.3.3 Ferroelectric and dielectric studies

The presence of axially symmetric cages in all these compounds prompted us to investigate their ferroelectric properties. Hence, ferroelectric hysteresis loop measurements were performed on the crystals of **13** and **14** (Figure A5.20, Appendix 5). These measurements gave well saturated P-E loops similar to those obtained for typical supramolecular ferroelectrics such as TGS (Figure 5.2 and 5.3).⁸⁰⁻⁸² Such ferroelectric

measurements were not performed on the crystals of **15** ($P4/nnc$) and **16** ($P432$) owing to their smaller sizes and higher symmetric (centrosymmetric or cubic) structures.

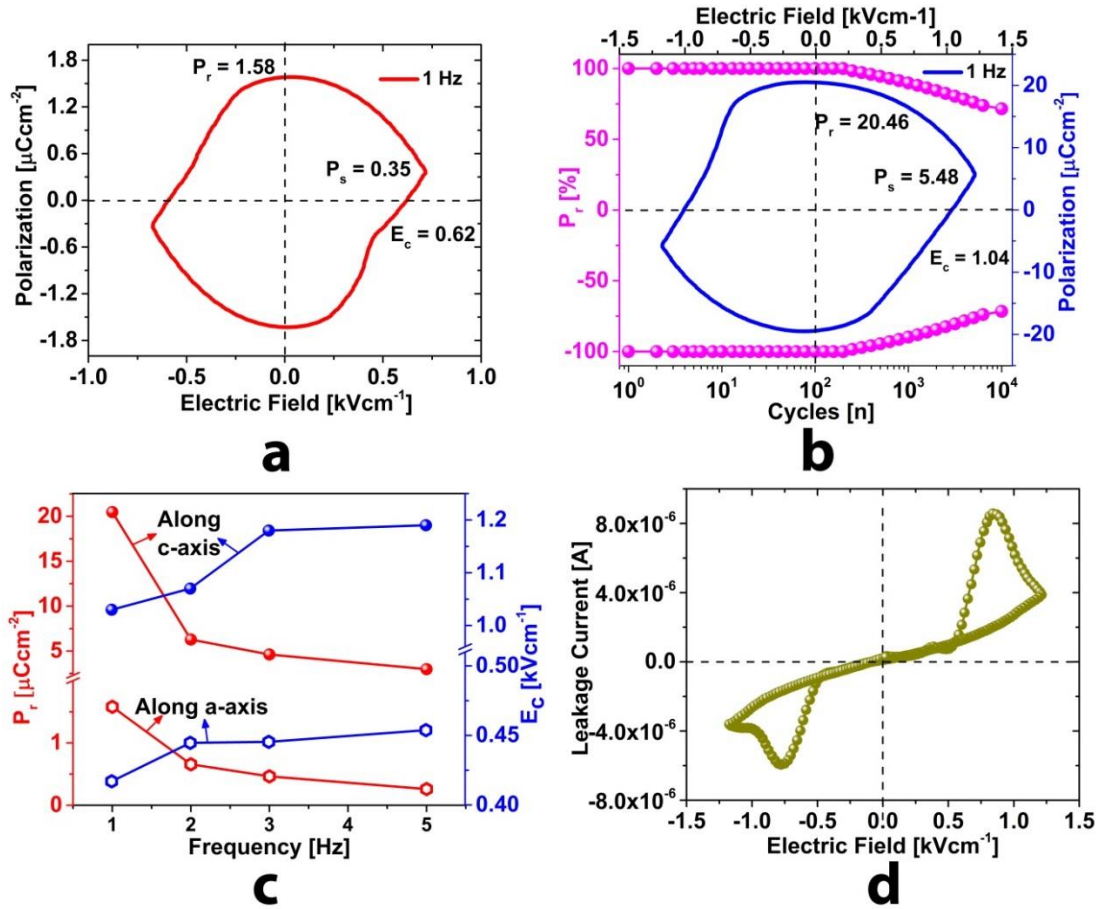


Figure 5.2. Ferroelectric measurement on **13**: P-E hysteresis loop along a-axis (a) and c-axis (b) at 1Hz. (c) Plot showing the values of P_r and E_c at various frequency along a- and c-axis. (d) leakage current vs electric field plot at 1Hz along c-axis.

The P-E loop measurements showed that the crystals of **13** and **14** exhibit axial anisotropy giving distinct polarization values along different axes. The loops obtained in the direction of polar c-axis gave higher remnant polarization (P_r) values of 20.46 μCcm^{-2} (for **13**) and 28.90 μCcm^{-2} (for **14**) as compared to those obtained along the a-axis (1.58 μCcm^{-2} for **13** and 6.28 μCcm^{-2} for **14**) at 1Hz (Figures 5.2a-b and 5.3a-b). The measurements performed at higher frequencies also gave good P-E loops along the c-axis with P_r values of 5.48 (at 3Hz) and 3.0 μCcm^{-2} (at 5Hz) for **13** while the loops for **14** gave P_r values of 8.75 (at 3Hz) and 5.26 μCcm^{-2} (at 5Hz). Similar observations have

been made for the measurements along the a-axis as well, and these values are given in the Figures 5.2c and 5.3c (A5.21- A5.22, Table A5.2, Appendix 5). The lower coercive fields (E_c) of 1.04 (**13**) and 0.86 (**14**) kVcm^{-1} , at 1Hz along c-axis suggest the swift switching of the polarizable domains in both of these crystals. The E_c values obtained for **13** and **14** are found to be lower even at higher frequencies (Table A5.2, Appendix 5). The room temperature capacitance measurements on their single crystals show sizable variations in dielectric constants along a- and c-axes. The observation of higher dielectric constant along the c-axis may be due to long range polar order in comparison with the other two axes strongly supports the existence of ferroelectric anisotropy in both **13** and **14** (Table A5.3, Appendix 5).

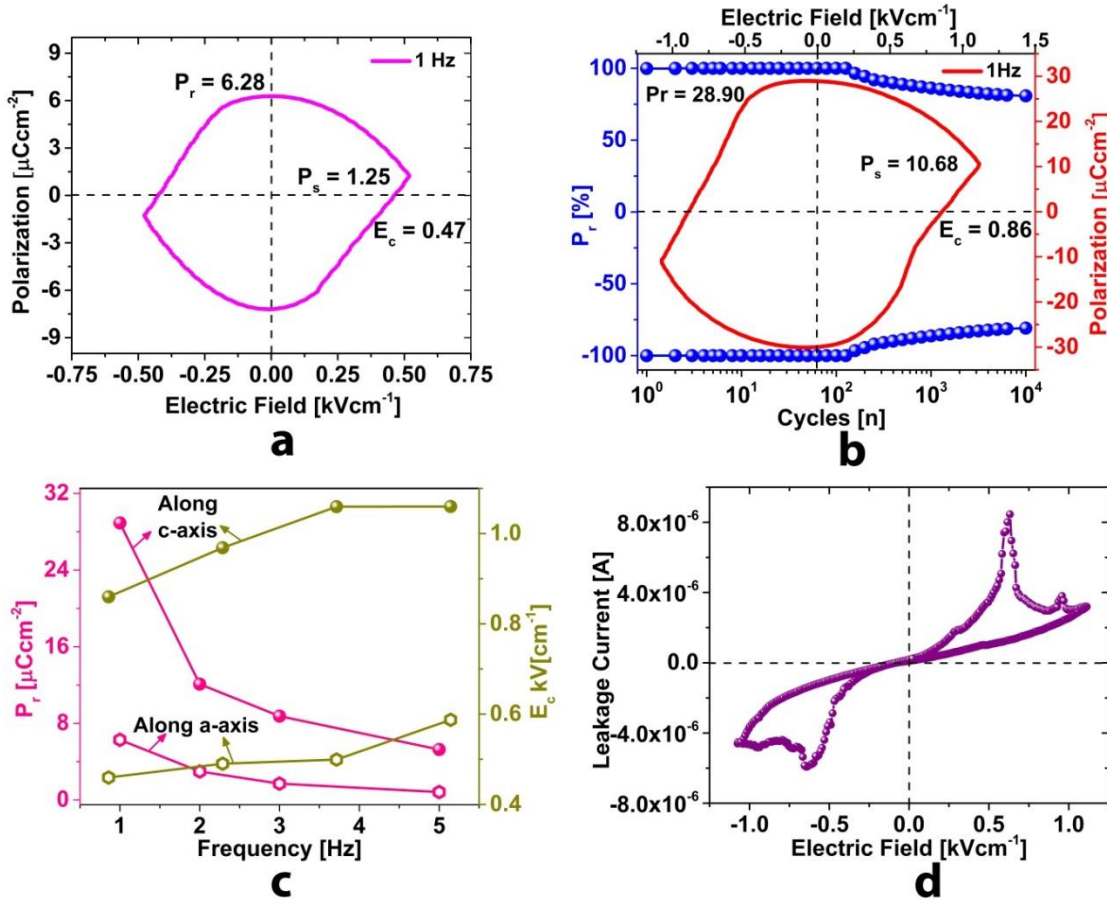


Figure 5.3. Ferroelectric measurement on **14**: P-E hysteresis loop along a-axis (a) and c-axis (b) at 1Hz. (c) Plot showing the values of P_r and E_c at various frequency along a- and c-axis. (d) Leakage current vs electric field plot at 1Hz along c-axis.

The plots of current vs. applied voltage gave very low leakage currents in the range of μA for both **13** and **14** (Figures 5.2d and 5.3d). They also display the peaks associated with the domain switching at the coercive fields which confirm the ferroelectric nature of the obtained loops. Furthermore, cycling measurements were performed on the crystals of **13** and **14** which suggests them to be fatigue resistant, as they retain up to 75% of the original polarization even after 10^4 switching cycles and yet remain higher than those of many traditional ferroelectric materials (Figures 5.2b and 5.3b).¹⁻¹⁸

The octahedral cages in both **13** and **14** exhibit an axial 432 local higher symmetry. However, the presence of un-coordinated solvates and anions (both ordered and disordered) imposes a lower symmetry on them; point group 4 (polar C_4) in case of **13** and 422 (non-polar, D_4) for **14**. The polarization in these assemblies stems from the application of external fields which helps align the polarizable domains in their crystal lattice. This includes ordering of the cationic charges in the Cu_6 -cages and the extra-framework nitrate anions and water molecules located in the channels running parallel to the polar axes. Thus, the crystals of **14** under an external field may exhibit a reduced local symmetry (I_4 or I_1) and eventually show a ferroelectric response.⁵⁵ Such field assisted polarization induction have already been described in certain supramolecular systems based on carbon nanotubes, nanoporous membranes, MOFs, metal-organic cavitands, etc.⁸³⁻⁸⁵

Ferroelectricity in perovskites and other materials such as Aurivillius phases is known to originate from cation displacements and twisting of the octahedra.⁸⁶⁻⁸⁷ Parallels to this can also be drawn for the ferroelectricity in these Cu_6 -based assemblies. The structure of **13** shows a twisted arrangement of the octahedral cages that includes the twisting of the individual Cu_4 squares and the TPTA ligands. It can be visualized that these twisted atomic positions in **13** in the direction of polarization could contribute for its polarization. In contrast, the Cu_6 -octahedra in **14** does not show any twisting in the field-free state as these cages are tightly held in position via the μ_2 -chloride bridges. However, the Cu-Cl-Cu bridges in **14** could be perturbed under the external field, as found in layered halide

perovskites, and can presumably cause twisting of the Cu_6 -octahedra with an eventual dipole induction.⁸⁸

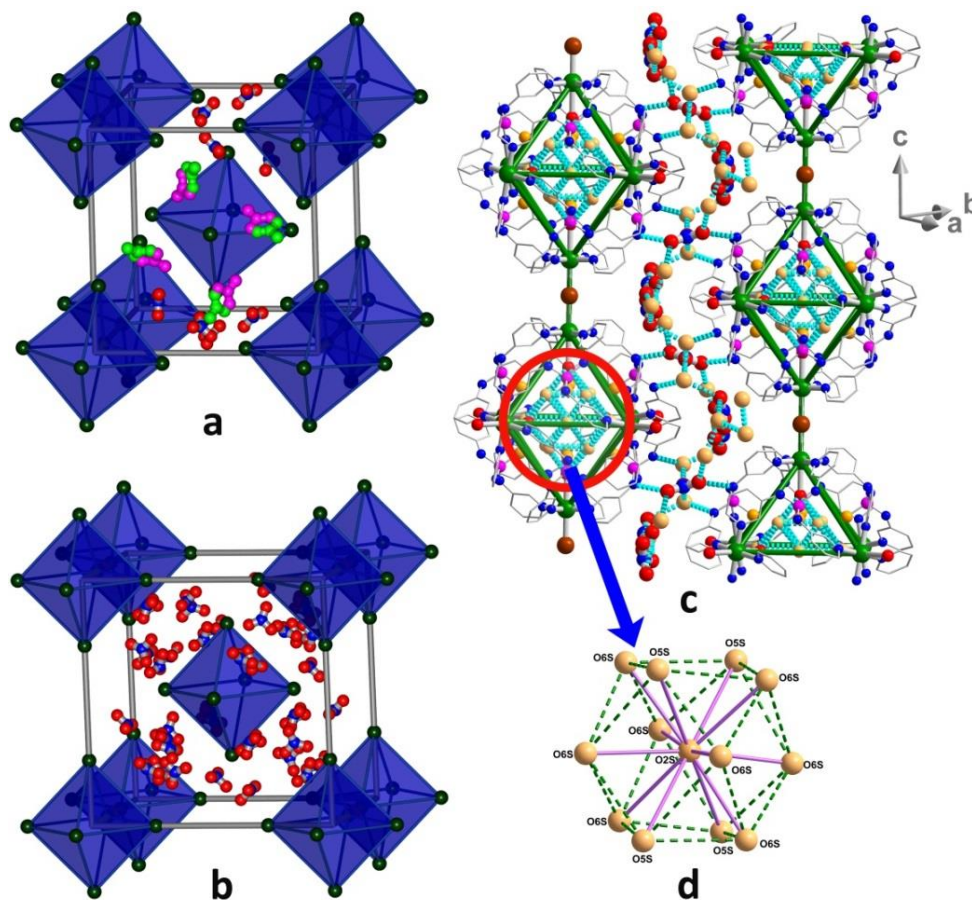


Figure 5.4. View of the nitrate anions arrangement in the unit cell of **13** (a) and **14** (b). View of the hydrogen bonded network of solvent molecules with nitrate anions and frameworks (c). View of the cuboctahedral water cluster encapsulated in the cage cavity of **14**.

A closer look at the packing structures of **13** and **14** along each of their crystal axis provides further structural insights for their polarization. Out of the twelve nitrate anions in **13**, eight are oriented along the c-axis, while the remaining ones are aligned along the other axes (a- and/or b-axis) (Figures 5.4a and A5.23- A5.25, Appendix 5). These are further involved in H-bonding interactions with solvated water molecules in all the three directions. However, these interactions are dominant along the polar c-axis owing to the higher number of nitrate anions in this direction resulting in increase in polarization and domain wall switching. For **14**, all the eleven nitrate anions that belong

to a single cage are predominantly oriented along the c-axis and are stacked in the form of 1D-wires (Figures 5.4b, 5.4c and A5.26- A5.28, Appendix 5). The intrinsic cavity of the Cu₆-cage in **14** contains a cuboctahedral shaped water cluster made up of 3.25 H₂O molecules (Figure 5.4d). These polar water molecules are further connected to the endohedral Cu-bound aqua ligands along the same c-axis. The net effect of these interactions in this direction gives rise to a long range polar order. However, some of the nitrate ions in the 1D-channels form additional H-bonding with the P-NH groups and contribute to the alignment of dipoles along the a,b-plane. Yet, the extent of dynamic orientational ordering of these switchable ferroelectric domains could be different in each of these directions leading to the observation of anisotropy in the P_r values.

The bulk dielectric permittivity (ϵ) measurements were performed on the compacted discs of **13**, **14**, **15**, and **16**. The temperature dependence of real part of dielectric permittivity (ϵ') at various frequencies gave plots with broad anomaly peak in the range of 45-50 °C (Figures 5.5a and A5.29- A5.32, Appendix 5) due to the onset of desolvation in these assemblies. The maximum ϵ' values for **13**, **14**, **15**, and **16** corresponding to their peak maxima at 1 kHz were found to be 98.22, 108.91, 67.68 and 60.84, respectively.

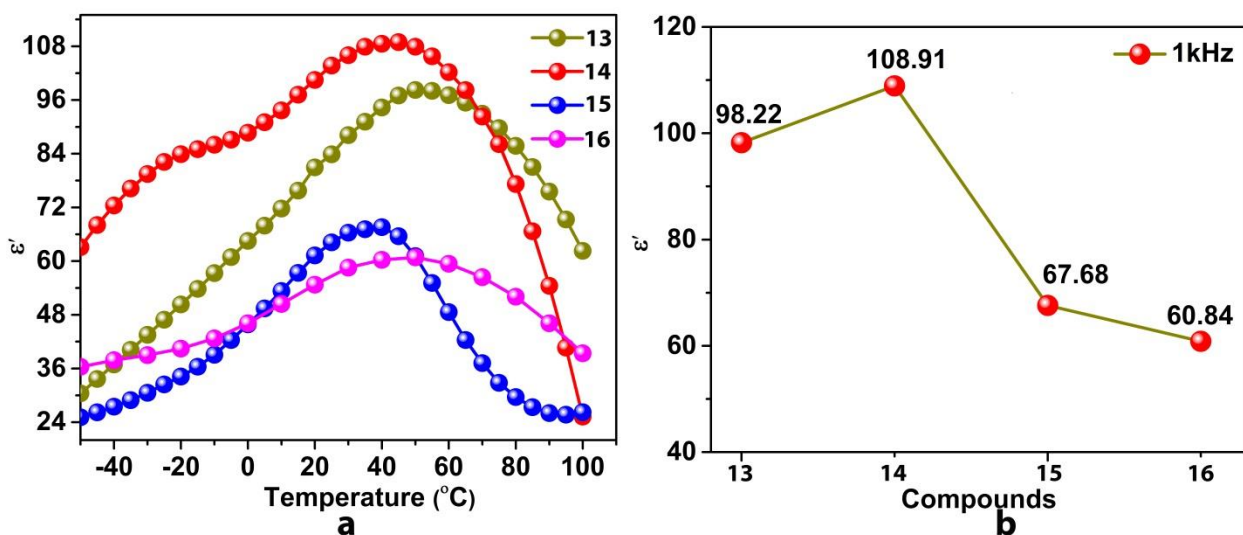


Figure 5.5. (a) Plots of the real part of dielectric permittivity vs. temperature. (b) Comparison of the dielectric peak maxima in **13-16** at 1 kHz.

Figure 5.5b illustrates the variations in the ϵ' values with respect to the dimensionality of the framework. Notably the noncentrosymmetric assemblies of **13** and **14** exhibit higher ϵ' values in comparison with the other two frameworks **15** and **16** which is consistent with the ferroelectric nature of **13** and **14**. As observed before, the broad feature of the dielectric anomaly peaks in these plots corresponds to the desolvation assisted dielectric relaxation phenomenon. The existence of this behaviour is well supported by traditional methods such as TGA-DTA, VT-PXRD and FT-IR measurements (Figures A5.33- A5.39, Appendix 5).

Measurement of dielectric permittivity as a function of frequency for **13**, **14**, **15** and **16** shows that the dielectric constant values gradually decreases with increase in frequencies. The dielectric loss factors measured for all these compounds were found to be very low. The conductivity vs. frequency plot at different temperatures for all the assemblies also gave very low conductivity values. These observations strongly support the high dielectric nature of these materials and again confirm the ferroelectric origin of the obtained P-E loops in **13** and **14** (Figures A5.40- A5.51, Appendix 5).

5.4 CONCLUSION

This chapter described a *de nova* protocol to assemble an octahedral $\text{Cu}_6(\text{TPTA})_8$ cage to cage-connected networks in 1D-, 2D- and 3D-structures in a reversible fashion. Treatment of the parent cage assembly of **13** with stoichiometric amounts of chloride ions yields the hierarchical frameworks **14**, **15** and **16** by sequentially replacing the outer-cage axial aqua ligands. Further, these frameworks undergo step-wise disassembly reactions in the presence of chloride ion acceptors such as $\text{AgNO}_3/(\text{nBu}_4\text{N})\text{NO}_3$. The cage-assemblies of **13** and **14** exhibited axially symmetric tetragonal structures. The ferroelectric P-E hysteresis loop measurement on the crystals of **13** and **14** show anisotropic behaviour for both of them. High remnant polarization (P_r) values of 20.46 and 28.90 μCcm^{-2} were observed along the c-axis, respectively, for **13** and **14**. Whereas, a much lower polarization values of 1.58 and 6.28 μCcm^{-2} were obtained for the respective crystals of **13** and **14**, along the a-axis. The origin of this anisotropic behaviour is due to the preferential location of nitrate anions along the c-axis

and its long-range interactions with the solvate molecules and the cationic framework. Also, these compounds show very high dielectric constants at 50 °C and anomaly peaks associated with desolvation assisted dielectric relaxation behaviour. These observations are rare instances in the family of metal-organic materials where variations in the polarization values are dependent on both the crystallographic axes and the dimensionality of the framework. These results promise the efficacy of new synthetic approaches towards developing metal-ligand assemblies with tunable ferroelectric properties.

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Chapter 6

**Luminescent Cationic Copper Iodide
Cluster based Coordination Polymers
and their Unusual Thermochromic
Behaviour**

6.1 INTRODUCTION

Coordination compounds that possess luminescent properties¹ are well investigated because of their promising applications in the fields of chemical sensors,² biomedical imaging³ and optoelectronic devices.⁴ One of the prominent classes of luminescent coordination compounds are those of copper (I) iodide, $[\text{Cu}_n\text{I}_m]^{(n-m)}$, clusters owing to their diverse structure dependent photo-physical properties.⁵ Studies on metal-organic frameworks (MOFs) featuring copper(I) iodide (CuI) clusters and organic linkers are of major research interest as these clusters can not only provide rigidity to the framework but also can impart the desired photo-physical properties to it.⁶ Thus, it is possible to tune these MOFs for a range of emissions from blue to green to red depending upon the nature of $[\text{Cu}_n\text{I}_m]^{(n-m)}$ clusters, ligand environment and temperature.⁷ These cluster MOFs may typically be obtained in reactions involving CuI and suitable bi- and polydentate linker ligands.⁸ Among several $[\text{Cu}_n\text{I}_m]^{(n-m)}$ type motifs the neutral clusters of Cu_2I_2 and Cu_4I_4 are the readily formed ones in most reactions and are widely studied for structural and photo-physical characteristics,⁹ although there are handful number of reports for other neutral high nuclearity clusters.¹⁰ In contrast, cationic clusters such as $[\text{Cu}_4\text{I}_2]^{2+}$, $[\text{Cu}_4\text{I}_3]^+$, $[\text{Cu}_6\text{I}_2]^{4+}$, $[\text{Cu}_6\text{I}_4]^{2+}$, $[\text{Cu}_6\text{I}_5]^+$, $[\text{Cu}_7\text{I}_4]^{3+}$, $[\text{Cu}_8\text{I}_6]^{2+}$, $[\text{Cu}_{10}\text{I}_4]^{6+}$ and $[\text{Cu}_{24}\text{I}_{10}]^{14+}$ are scarcely reported as they usually involve the unfavorable coordination of charge balancing hard anionic ligands to the soft Cu(I) species.¹¹ As most of these cationic clusters were found to possess a triangular plane of three Cu-atoms, we thought that use of a ligand which offers a C_3 -symmetric ligation,¹² would generate a cationic CuI cluster MOF. Our group has been interested in the chemistry of pyridylamino functionalized P(V) ligands, especially those of tridentate phosphoramidate backbone for obtaining polynuclear compounds with cluster, cage and framework architectures.¹³

Thus, we employed the tridentate thiophosphoramidate ligands of the type $[(\text{NHR})_3\text{P}=\text{S}]$ (L^1 : R = 3-quinoliny (AQ); L^2 : R = 3-pyridyl (PY)) in reactions with CuI with the view of obtaining MOFs with C_3 -symmetric CuI clusters. Chapter six describe the synthesis, structure and photophysical properties of two cationic MOFs **17**

$\{[(L^1)_2(Cu_6I_5)](OH) \cdot 3DMF \cdot 2.5MeOH\}_n$ and **18** $\{[(L^2)_2(Cu_6I_4)](OH)_2 \cdot 3DMF\}_n$. These new MOFs feature a rugby-ball shaped discrete $[Cu_6I_5]^+$ segment in **17** and its structurally related 1D-polymeric $\{[Cu_6I_4]^{2+}\}_n$ chain analogue in **18**.

Photo-physical studies reveal that the 2D-MOF **17** shows an unusual thermochromic luminescent behavior emitting a blue fluorescence at room-temperature due to the AQ chromophore and a pale-orange phosphorescence at 77K from the triplet excited states of $[Cu_6I_5]^+$, while the 3D-MOF **18** emits green phosphorescence at both room-temperature and 77K. A preliminary DFT analysis on discrete model compounds of **17** indicate that population of ligand triplet state is necessary to obtain a cluster based emission that was experimentally observed at 77K.

6.2 EXPERIMENTAL SECTION

6.2.1 General remarks

All manipulations involving phosphorus halides were performed under dry atmosphere in standard Schlenk-glassware. CuI, 3-aminopyridine and 3-aminoquinoline were purchased from Aldrich and used as received. The PCl_3 was purchased locally (SPECTROCHEM, India) and used as received. NMR spectra were recorded on a 400 MHz Jeol FT spectrometer (1H -NMR: 400 MHz, $^{13}C\{^1H\}$ -NMR: 100 MHz, $^{31}P\{^1H\}$ -NMR: 161 MHz) at room temperature using $SiMe_4$ (1H , ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards. The powder X-ray diffraction data were obtained from a Bruker-D8 Advance diffractometer. Thermal analysis data has been obtained from a Perkin-Elmer STA-6000 thermogravimetric analyser. Elemental analyses were performed on a Vario-EL cube elemental analyzer. FT-IR spectra were taken on a Perkin-Elmer spectrophotometer. The absorption and emission studies were done by a Perkin-Elmer Lambda 45 UV-Visible spectrophotometer and SPEX Fluorolog HORIBA JOBIN VYON fluorescence spectrophotometer with a double-grating 0.22 m SPEX 1680 monochromator and a 450W Xe lamp as the excitation source. The excitation and emission spectra of the complexes were corrected at instrumental function. The photoluminescence lifetime measurements were carried out using a SPEX Fluorolog HORIBA JOBIN VYON 1934 D phosphorimeter.

6.2.2 Synthesis

6.2.2.1 Synthesis of tris(3-aminoquinolyl)phosphoramidate ligand (L^1): To a stirred solution of 3-aminoquinoline (2.492 g, 17.2 mmol) and triethylamine (2.75 mL, 1.995 g, 19 mmol) in toluene (150 mL) at 0 °C, $PSCl_3$ (0.5 mL, 0.835 g, 4.92 mmol) was added drop wise over a period of 10 minutes. The resulting mixture was refluxed for 4 h at 110 °C to yield a yellow precipitate. The precipitate was collected by filtration and washed with water and 0.5% aqueous NaOH solution to remove the amine hydrochloride by-product. The resulting powder was washed three times with water and dissolved in methanol/chloroform mixture. This solution was dried with $MgSO_4$, filtered and evaporated to yield L^1 . Yellow crystals of $L^1 \cdot H_2O$ suitable for X-ray analysis were obtained from its solution in MeOH/ $CHCl_3$ after 3 days. Yield: 2.86 g (85%). M.P. 230-233, 1H -NMR (400 MHz, $(CD_3)_2SO$: δ 7.44 (dd, 3H, CH), 7.49 (td, 3H, CH), 7.76 (td, 3H, CH), 8.06 (d, 3H, CH), 8.85 (d, 3H, CH), 9.05 (d, 3H, CH). $^{13}C\{^1H\}$ -NMR (100 MHz, $\{(CD_3)_2SO\}$): δ 120.41, 127.44, 128.45, 128.97, 135.40, 143.62, 145.31, 145.60. ^{31}P -NMR (161 MHz, $\{(CD_3)_2SO\}$): δ 39.89. FT-IR data in powdered sample (cm^{-1}): 3352, 3058, 2359, 1593, 1459, 1334, 1181, 1128, 985, 925, 876, 737, 645. Anal. calcd. for $C_{27}H_{21}N_6PS$: C, 65.84; H, 4.30; N, 17.06; S, 6.51. Found: C, 65.74; H, 4.57; N, 16.98; S, 6.31.

6.2.2.2 Synthesis of tris(3-aminopyridyl)phosphoramidate ligand (L^2): $PSCl_3$ (1mL, 1.67 g, 9.8 mmol) was added drop wise to a stirred solution of 3-aminopyridine (9.28 g, 98.6 mmol) in toluene (250 mL) at 0 °C. The resulting mixture was refluxed for 4 h at 110 °C until a reddish-brown precipitate was formed. The precipitate was collected by filtration and washed three times with water to remove the amine-hydrochloride by-product. The resulting powder was dried in vacuum-desiccator to yield the product. Colourless crystals of $L^2 \cdot CH_3OH$ suitable for X-ray analysis were obtained from its solution in MeOH after 3 days. Yield: 2.25 g (92%). M.P. 235-340, 1H -NMR (400 MHz, $(CD_3)_2SO$: δ 7.21 (dd, 3H, CH), 7.55 (d, 3H, CH), 8.06 (d, 3H, CH), 8.44 (s, 3H, CH). $^{13}C\{^1H\}$ -NMR (100 MHz, $\{(CD_3)_2SO\}$): δ 123.98, 125.46, 138.08, 140.74, 142.43. ^{31}P -NMR (161 MHz, $\{(CD_3)_2SO\}$): δ 40.39. FT-IR data in KBr pellet (cm^{-1}): 3117, 1941,

1832, 1596, 1410, 1287, 1156, 947, 775, and 666. Anal. calcd. for $C_{15}H_{15}N_6PS$: C, 52.62; H, 4.42; N, 24.55; S, 9.37. Found: C, 52.77; H, 4.32; N, 24.81; S, 9.32.

6.2.2.3 Synthesis of cationic $Cu_6I_5^+$ cluster MOF **17:** To a stirred solution of L^1 (49mg, 0.1mmol) in dichloromethane (5ml) and MeOH (2ml), CuI (57mg, 0.3mmol) in CH_3CN (15ml) was added leading to an immediate formation of a yellow precipitate. To this mixture, 2 mL of DMF was added and the mixture was further stirred for 4 h at which point most of the precipitate were dissolved. The solution was then filtered through a thick pad of celite and left for crystallization. Yellow crystals of **17** suitable for X-ray diffraction were obtained after 10 days. Yield: 49 mg (43% based on Cu). FT-IR data in KBr pellet (cm^{-1}): 3521, 3453, 2921, 2852, 1656, 1457, 1344, 1209, 931, 744, and 659. Anal. calcd. for $C_{66}H_{76}Cu_6I_5N_{15}O_7P_2S_2$: C, 33.97; H, 3.28; N, 9.00; S, 2.75. Found: C, 34.28; H, 3.40; N, 9.06; S, 2.92.

6.2.2.4 Synthesis of cationic $Cu_6I_4^{2+}$ cluster MOF **18:** To a stirred solution of L^2 (34mg, 0.1 mmol) in dichloromethane (5 mL) and MeOH (2 mL), CuI (57mg, 0.3 mmol) in CH_3CN (15mL) was added leading to an immediate formation of a white precipitate. To this mixture, 2 mL of DMF was added and the mixture was further stirred for 4 h at which point most of the precipitate were dissolved. The solution was then filtered through a thick pad of celite and left for crystallization. Yield: 73 mg (80% based on Cu). FT-IR data in powdered sample (cm^{-1}): 3550, 3105, 2760, 1573, 1463, 1399, 1261, 1101, 1039, 924, 791, 701, and 655. Anal. calcd. for $C_{39}H_{53}Cu_6I_4N_{15}O_5P_2S_2$: C, 25.64; H, 2.92; N, 11.50; S, 3.51. Found: C, 25.39; H, 2.85; N, 11.31; S, 3.67.

6.2.3 Crystallography

Reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) (Table 6.1). Structures were refined by full-matrix least-squares against F^2 using all data (SHELX97).¹⁴ All non-hydrogen atoms were refined anisotropically if not stated otherwise. Hydrogen atoms were constrained in geometric positions to their parent atoms. Crystals of **17** diffracted weakly at higher angles and hence a $2\theta = 50^\circ$ cut-off was applied. The solvated DMF molecule in **17** was disordered and refined over two positions with SIMU/SAME restraints. The anionic oxygen atom of

17 located in a special position had a bad thermal ellipsoid and hence was refined with partial isotropic displacement parameters. The approximate positions of the two anionic oxygen atoms O1 and O2 in **18** were identified inside the packing cavity with great difficulty. Due to the smaller occupancy factors as well as the strongly absorbing nature of the iodine atoms the thermal ellipsoids of O1 and O2 were big and hence were isotropically refined. The positions of these atoms were merely provided to satisfy the charge balance in **17**. Further evidence for these OH⁻ ions was derived from thermogravimetric and elemental analysis.

Table 6.1: Crystal data of compound L¹, L², 17 and 18

Compound	L ¹ .H ₂ O	L ² .MeOH
Chemical formula	C ₂₇ H ₂₃ N ₆ OPS	C ₁₆ H ₁₉ N ₆ OPS
Formula weight	510.54	374.40
Temperature	100(2)K	100(2)K
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/n	P-1
a (Å); α (°)	12.5293(9); 90°	8.9365(14); 85.097(3)°.
b (Å); β (°)	13.0003(9); 97.7630(10)°	9.6625(15); 84.907(3)°.
c (Å); γ (°)	16.0504(11); 90°	11.8541(18); 63.265(3)°.
V (Å ³); Z	2590.4(3); 4	909.4(2) ; 2
ρ (calc.) mg m ⁻³	1.309	1.367
μ(Mo K _α) mm ⁻¹	0.219	0.283
2θ _{max} (°)	56	56
R(int)	0.0582	0.0289
Completeness to θ	99.4 %	99.7 %
Data / param.	6497 / 333	4512 / 228
GOF	1.021	1.036
R1 [F>4σ(F)]	0.0391	0.0310
wR2 (all data)	0.0994	0.0832
max. peak/hole (e.Å ⁻³)	0.438/-0.584	0.562/-0.537

Compound	17	18
Chemical formula	$C_{67}H_{77}Cu_6I_5N_{15}O_{6.50}P_2S_2$	$C_{39}H_{52}Cu_6I_4N_{15}O_5P_2S_2$
Formula weight	2338.24	1825.86
Temperature	100(2) K	100(2) K
Crystal system	Trigonal	Hexagonal
Space group	P-3	$P6_3/m$
a (Å); α (°)	14.304(4); 90	14.707(3); 90
b (Å); β (°)	14.304(4); 90	14.707(3); 90
c (Å); γ (°)	24.223(7); 120	13.994(3); 120
V (Å ³); Z	4292.0(19); 2	2621.5(11); 2
ρ (calc.) mg m ⁻³	1.830	2.313
μ (Mo K α) mm ⁻¹	3.401	4.945
$2\theta_{max}$ (°)	50	56
R(int)	0.1581	0.1812
Completeness to θ	98.9 %	99.6 %
Data / param.	5002 / 313	2250 / 122
GOF	1.003	1.096
R1 [F > 4 σ (F)]	0.0755	0.0725
wR2 (all data)	0.2207	0.2323
max. peak/hole (e.Å ⁻³)	1.36 / -0.900	2.349 / -3.926

The crystal structure of **17** at room-temperature was solved in the hexagonal space group $P6_3/m$. Due to the diffuse nature of the solvated molecules, the atom positions of the DMF, methanol and hydroxide ion could not be located precisely. Hence, the electron densities due to these groups were removed by the SQUEEZE/PLATON routine. Except the space group difference, the packing diagram of **17** at 298K was exactly matching with that of the 100K structure. The room temperature data was obtained only to compare the Cu...Cu and Cu...I bond differences between the RT and the 100K data as discussed in the main text.

6.2.4 Lifetime and quantum yield

The luminescent lifetime of L^1 , L^2 , **17** and **18** were measured by Time Correlated Single Photon Counting (TCSPC) method at 298K as well as at 77K. The luminescence decay

profiles at 298K were fitted to biexponential / triexponential curves. Similarly, the phosphorescence decay profiles at 77K were fitted to mono- or biexponential equations. The lifetimes were fitted by using the DAS software and average lifetimes were reported for simplicity. Fluorescence quantum yields in solution were determined by using the equation $\phi_s = \phi_r (F_s A_r / F_r A_s) (n_r / n_s)$.¹⁵ In this equation, ϕ is the fluorescent quantum yield, F is the area of the emission, n is the refractive index of the solvent, and A is the absorbance of the solution at the exciting wavelength. The subscripts r and s denote the reference and sample, respectively. Quinine sulfate was employed as the standard.

6.2.5 Computational details

The density functional theory (DFT) calculations have been performed by using Gaussian 03 program package.¹⁶ The B3LYP exchange-correlation functional was used throughout for all calculations.¹⁷ The 6-31g(d,p) basis set was used for geometry optimization and time-dependant (TDDFT) calculation for ligand L^1 . A combination of basis sets i.e., 6-31g(d) for C, H, N, P and S, and LANL2DZ for Cu and I atoms,¹⁸ respectively, were used for the bare $[Cu_6I_5]^+$ cluster as well as on discrete model compounds $\{Cu_6I_5[(AQNH)H_2P=S]_6\}$ (**17a**) and $\{Cu_6I_5[(PYNH)H_2P=S]_6\}$ (**18b**) to obtain the geometry optimization and TDDFT calculations for the excitation energies. The calculated absorption spectra and related MO contributions were obtained from the TDDFT output file and *gausssum* 2.2.6.1.¹⁹ The theoretical emission wavelengths of L^1 , **17a** and **18b** were derived by single point energy calculations on the optimized triplets as the energy difference between the lowest energy triplet state and its corresponding singlet state.

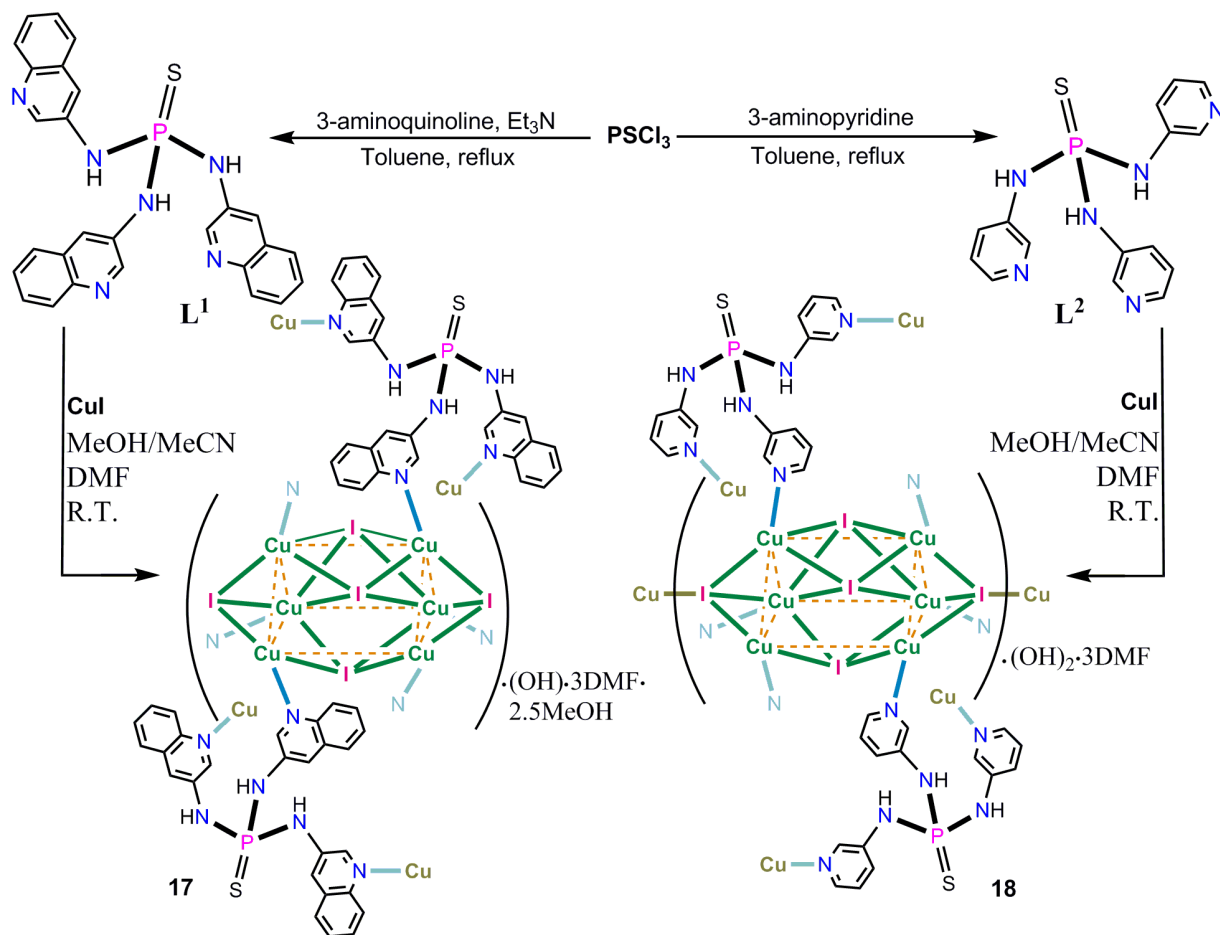
6.3 RESULTS AND DISCUSSION

6.3.1 Synthesis

The thiophosphate ligands L^1 and L^2 were synthesized from the corresponding reaction of 3-aminoquinoline and 3-aminopyridine in refluxing toluene solutions (Scheme 6.1). These ligands were characterized by ^{31}P -NMR, mass spectra and by single crystal X-ray diffraction. Crystals of these ligands were obtained by slow evaporation of their

solution and solved as their solvated adducts as $L^1 \cdot H_2O$ and $L^2 \cdot CH_3OH$ (Figure 6.1). The cluster MOFs **17** and **18** were obtained by the respective reaction of L^1 and L^2 with CuI in DMF/MeOH solvents at room temperature as crystalline solids. The asymmetric units of the cationic segments in these MOFs were given in the figure A6.3 (Appendix 6).

Scheme 6.1: Synthetic routes to access the tridentate thiophosphoramidate ligands and the cationic MOFs.



6.3.2 Crystal structures

The crystal structure of $L^1 \cdot H_2O$ was obtained in the monoclinic space group $P2_1/n$. It consists of three un-symmetrically arranged aminoquinolyl moieties consisting of two chelating N-H moieties and one non-chelating N-H site. Thus, two of the three N-H

groups are H-bonded to the solvated oxygen through a chelating interaction, while the third one is H-bonded to one of the ring N-atom (N23). The remaining ring N-sites are involved in H-bonding interactions with the water hydrogens and leads to the formation of 3D-supramolecular network (Figure A6.1, Appendix 6). The molecular structure of $L^2 \cdot CH_3OH$ was solved in the triclinic space group P-1. Two of its three N-H protons were involved in H-bonding with the two ring N-sites in an infinite fashion and form a zig-zag chain like structure. These chains are further connected by the donor-acceptor interaction of the solvated methanol molecules with the remaining N-H and ring N-sites resulting in a 2D-network (Figure A6.1, Appendix 6).

The crystal structure of **17** was solved in the trigonal space group P-3 (Figure 6.2). The molecular core consists of the cationic cluster $[Cu_6I_5]^+$ and two neutral ligand motifs (L^1), while the charge balance is restored by the presence of a hydroxide anion. The cationic cluster core consists of the trigonal prismatic assembly of six Cu(I) ions that are tethered by three μ_4 -bridging I^- ions. The remaining two I^- ions are located at the two opposite triangular faces of the prism as the μ_3 -capping units (Figure 6.2b). Each Cu(I) center is tetrahedrally coordinated to three I^- ions and one ring N-donor from L^1 . Thus, the prismatic $[Cu_6I_5]^+$ cluster acts as a 6-connected node with each of its triangular face is bound to three thiophosphate ligands. In return each ligand is connected to three Cu(I) centers resulting in the formation of a double sheet 2D-network (Figure 6.2a).

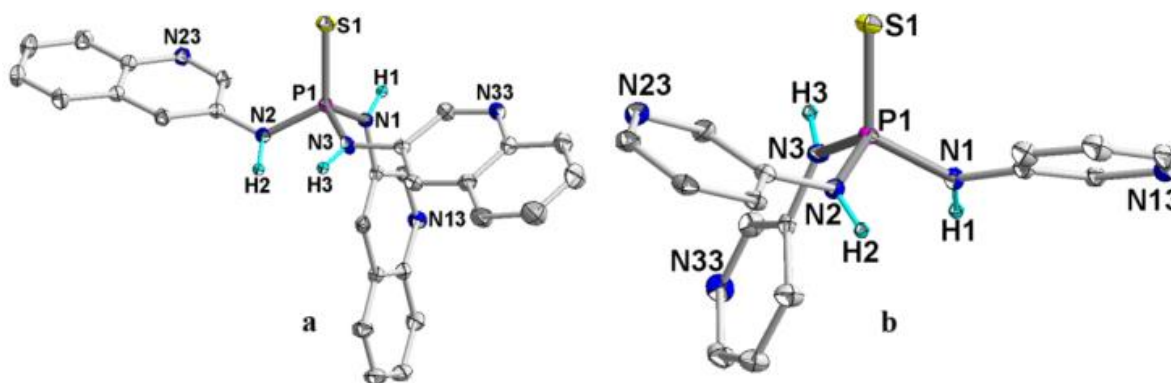


Figure 6.1: Molecular structure of (a) L^1 and (b) L^2 ; aryl-hydrogens and solvated molecules are omitted for clarity

The crystal structure of **18** was solved in the hexagonal space group $P6_3/m$ (Figure 6.3). The molecular core resembles closely to that of **17** in which the rugby-ball shaped $\text{Cu}_6\text{-cationic}$ core was retained and each ligand (L^2) in it is bonded to three cluster motifs in a C_3 -symmetric fashion.

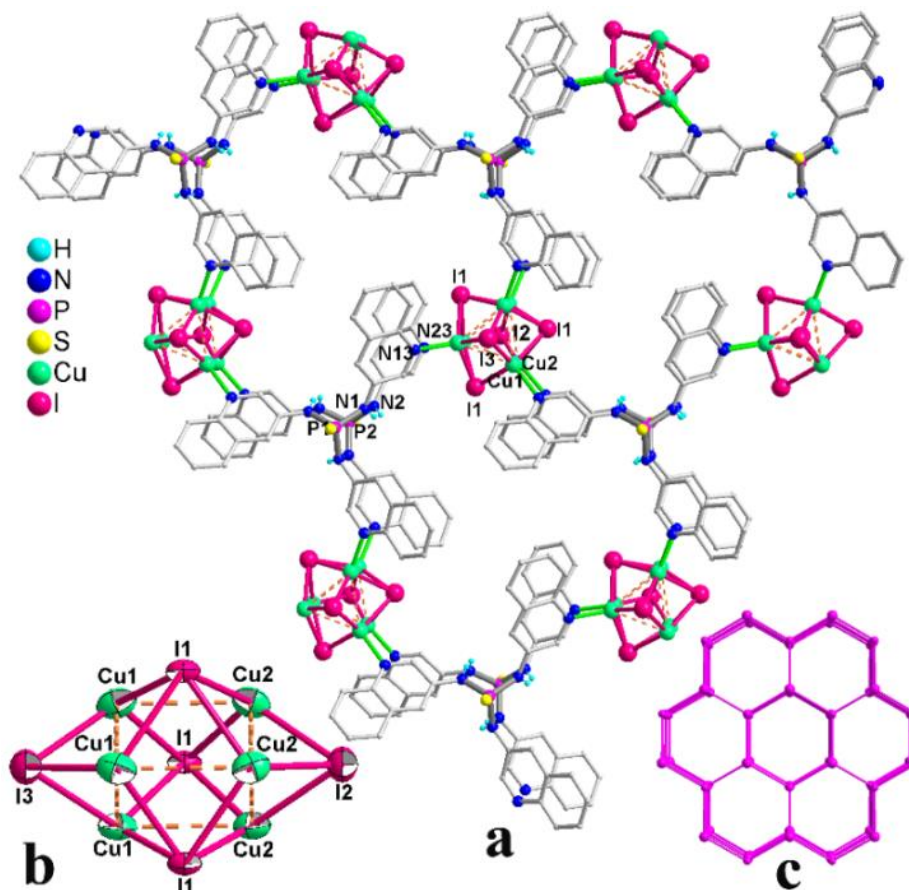


Figure 6.2: The double sheet structure (a) and the $[\text{Cu}_6\text{I}_5]^+$ core (b) of **17**; (c) Packing diagram showing superimposed AAA type of arrangement in **17** along the c-axis. The ligand and the $\text{Cu}_3\text{-}$ plane are depicted as small and big spheres, respectively, as 3-connected nodes.

The charge balance is provided by two OH^- ions located inside the pores. While the three μ_4 -bridging I^- ions in **18** has a similar coordination to those found in **17**, the iodide ions (I2) that are located at the two triangular faces of the prism serve as μ_6 -bridging ligands and tether the neighboring clusters forming a 1D-chain like structure of formula $\{[\text{Cu}_6\text{I}_4]^{2+}\}_n$ (Figure 6.3b). Thus, each $[\text{Cu}_6\text{I}_4]^{2+}$ segment in **18** act as an 8-connected node and the two axial iodide ions in each of them connect the initially formed double

sheets to a 3D-network (Figure 6.3a). A further look at the 1D-chain structure of $\{[\text{Cu}_6\text{I}_4]^{2+}\}_n$ reveal that these μ_6 -bridged iodide ions are at the centers of inversion and bring about the non-superimposing arrangement of the adjoined cluster segments (Figure 6.3b).

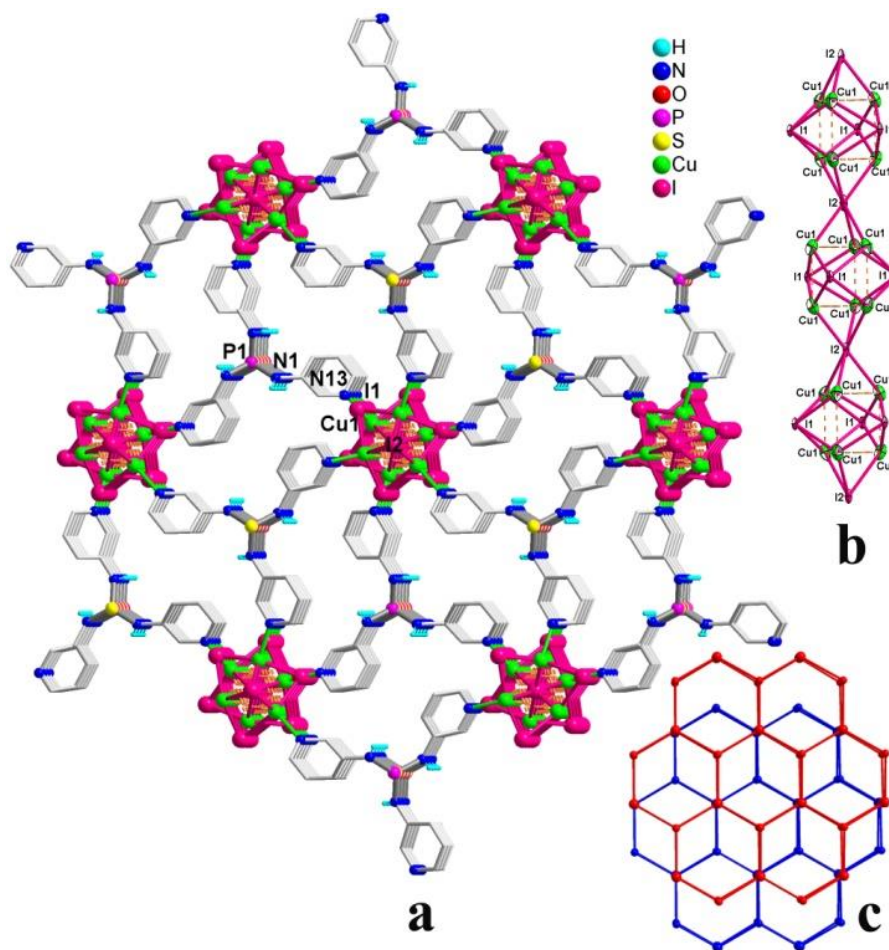


Figure 6.3: (a) View of the 3D-MOF assembly in **18** along the *c*-axis; (b) A small segment of the $\{[\text{Cu}_6\text{I}_4]^{2+}\}_n$ 1D-cluster chain; (c) Crystal packing showing the ABAB type of arrangement of the adjacent double sheets present in **18**.

As a result, the adjacent individual double sheets in **18** are arranged in an ABAB fashion with a topology of a **gra** net, whereas those found in the crystal packing of **17** reveals a superimposing AAA type of arrangement (Figures 6.2c and 6.3c) in a double-layer **hcb** topology.²⁰ Although there was one previous report for a $[\text{Cu}_6\text{I}_5]^+$ cluster along

with $[\text{Cu}_4\text{I}_3]^+$,^{11h} to the best of our knowledge this is the first instance where a CuI-MOF containing rugby-ball shaped $\{[\text{Cu}_6\text{I}_4]^{2+}\}_n$ is constructed via the formation of a Zintl type poly-cationic cluster chain. The solvent accessible void space, excluding the space occupied by the OH^- ions, in **17** and **18** were found to be 1393.89 (32.7%) and 590.92 Å (20.5%), respectively (Figure A6.4-A6.5, Appendix 6). The lower void space found in **18** can be ascribed to the interpenetrating ABAB type of network present in it. Attempts to prepare the guest free samples of **17** and **18** were unsuccessful presumably due to the interaction of the OH^- ions with the solvated molecules.

6.3.3 Photo-physical studies

The absorption and emission spectra of these newly synthesized ligands and MOFs were recorded to establish their photo-physical properties (Table A6.1, Appendix 6). The absorption spectra of all these compounds recorded in DMF show typical values expected of their chromophores ($\text{L}^1 = 330 \text{ nm}$ & $\text{L}^2 = 285 \text{ nm}$ (Figure A6.6, Appendix 6); **17** = 345 nm & **18** = 285 nm (Figure 6.4). In addition, both **17** and **18** shows weak absorptions at 385 and 325 nm, respectively, due to the triplet iodide to ligand charge transfer ($^3\text{XLCT}$) transitions similar to that observed for $\text{Cu}_4\text{I}_4\text{Py}_4$ cluster.^{21a}

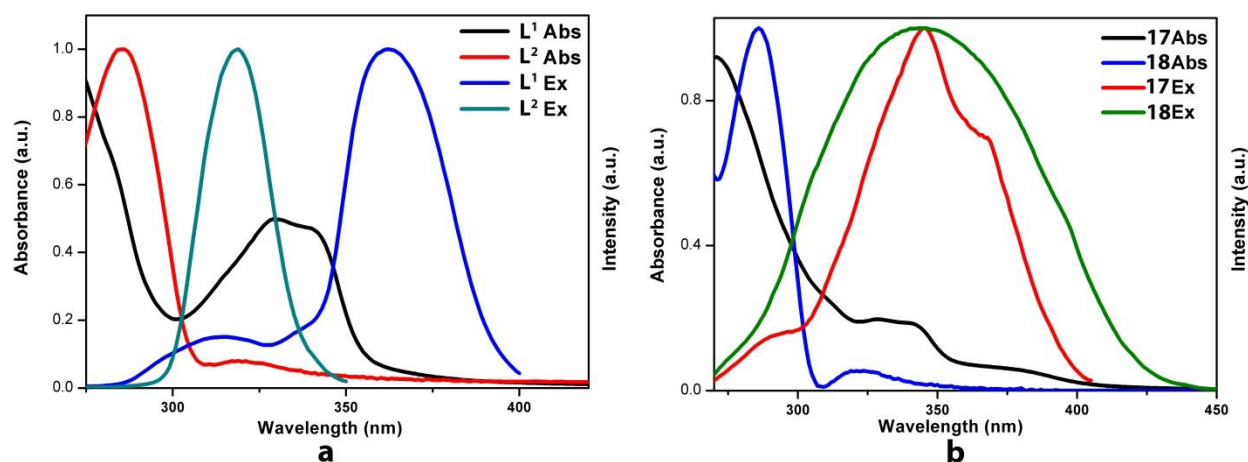


Figure 6.4: Normalized absorption and excitation spectra of **17** and **18** at 298K measured in DMF suspensions.

The solid state emission spectrum of L^1 at room temperature shows a sharp band at $\lambda_{\text{em}} = 411 \text{ nm}$ with a bright blue fluorescent emission (Figure 6.5). Upon lowering the

temperature to 77K, L^1 shows a new band (with shoulders) centred at $\lambda_{em} = 523$ nm in addition to the one at 411 nm and gives rise to a bluish-green emission corresponding to phosphorescence. Thus at 77K, the triplet state of the ligand is partially populated through inter-system crossing (ISC) from $S_1 \rightarrow T_1$ state and the emission occurs from both of these states. The decay time measured at 298K for L^1 fitted to a tri-exponential curve gave $\tau_1 = 0.09$, $\tau_2 = 0.05$ and $\tau_3 = 4.13$ ns characteristic of a fluorescence corresponding to the $S_1 \rightarrow S_0$ transition (Figure 6.7). Whereas the decay profile collected at 532 nm for the low energy (LE) bands for L^1 in DMF gave $\tau_{em} = 986$ μ s confirming the presence of triplet excited state in it (Table A6.1, Appendix 6).

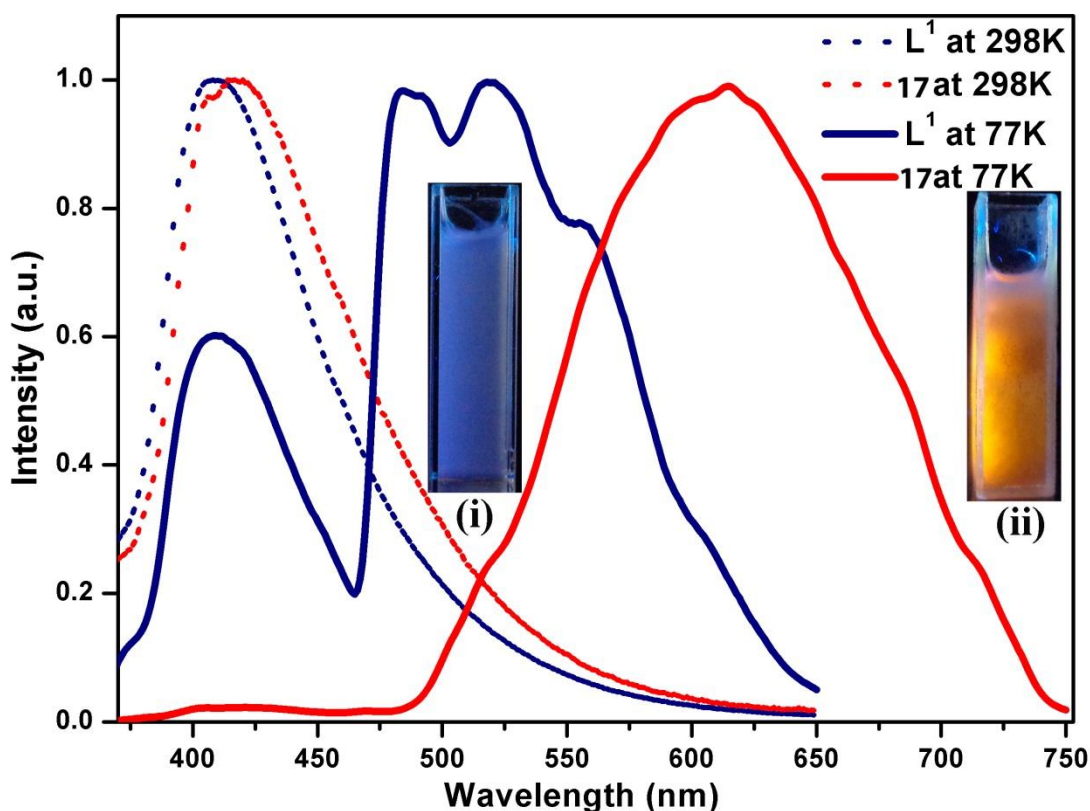


Figure 6.5: (a) Normalized emission spectra for L^1 and **17** ($\lambda_{ex} = 360$ nm) in the solid-state. The emission colour of **17** in DMF suspension at (b) 298 K and (c) 77 K under the UV-lamp ($\lambda = 365$ nm).

The emission spectrum of the crystalline solid-sample of **17** at 298K also shows a similar blue luminescence as that of L^1 in the high energy (HE) region with $\lambda_{em} = 419$ nm

(Figure 6.5). Decay measurement at 298K fitted to a tri-exponential profile gave life-time values of $\tau_1 = 0.07$, $\tau_2 = 0.08$ and $\tau_3 = 4.78$ ns (Figure 6.7). This is attributed to the self-emission of the AQ moieties and rules out the possibility of the cluster based iodide to AQ charge transfer ($^3\text{XLCT}$) transition which has a lifetime in the μs scale. Although **17** is a dual chromophoric system comprising of the AQ segments and the cationic cluster, emission from both of them is forbidden according to Kasha's rule.²² Hence we thought that if the triplet states of **17** are populated at low temperature by an ISC process, it is possible to detect the phosphorescence due to the $[\text{Cu}_6\text{I}_5]^+$ motif. Accordingly, at 77K **17** gave a new orange-yellow emission centred at $\lambda_{\text{em}} = 594$ nm along with the weak HE band at 419 nm. The lifetime for the LE emission at 77K gave $\tau_{\text{em}} = 236.96$ μs (Figure 6.7) characteristic of the emission from the triplet cluster-centred (^3CC) excited state of $[\text{Cu}_6\text{I}_5]^+$ comprising of iodide to Cu charge transfer ($^3\text{XMCT}$) and Cu centred $d \rightarrow s, p$ transitions.²¹

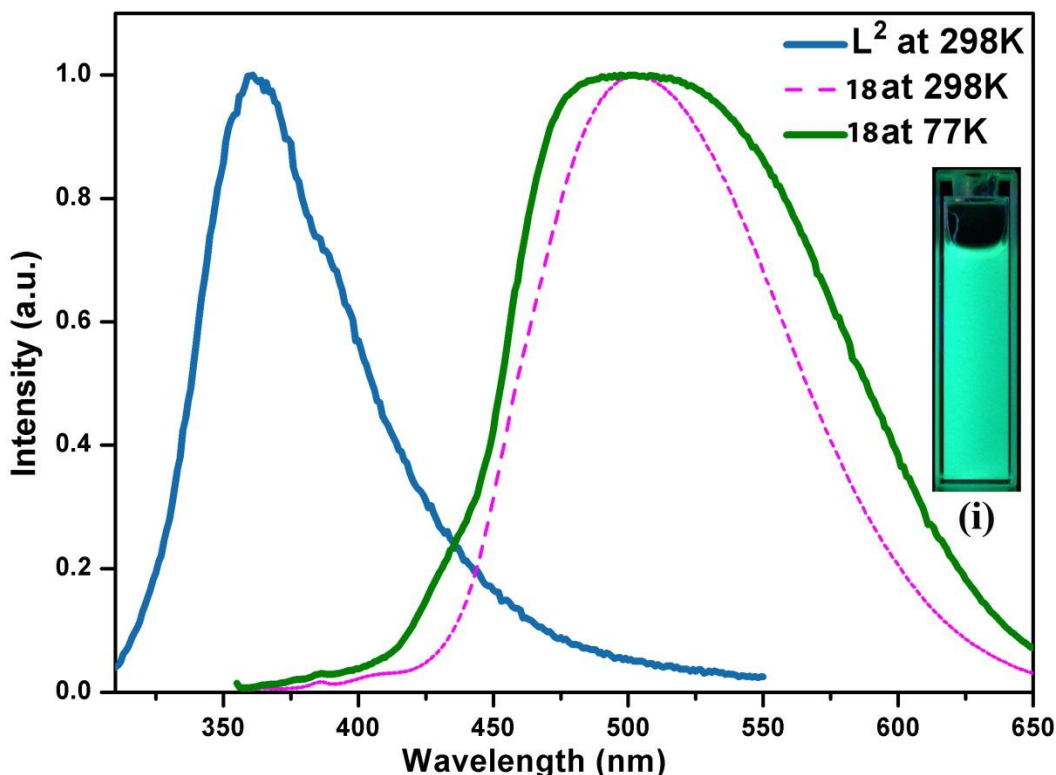


Figure 6.6: (a) Normalized emission spectra of L^2 and **18** in DMF ($\lambda_{\text{ex}} = 360$ nm); inset: the emission color of **18** at (i) 298K and (ii) 77K under the UV-lamp.

Temperature dependant measurements reveal that this ^3CC -emission originates around 189K (Figure A6.11, Appendix 6). It is to be noted that for most $\text{Cu}_4\text{I}_4\text{L}_4$ cubane clusters²¹ the LE ^3CC -band dominates at room temperature and the HE $^3\text{XLCT}$ -bands are observed at low temperatures (sometimes below 10K). In contrast, **17** exhibits an unusual thermochromism that it shows the ligand-centred fluorescence at 298K (HE) and the 3CC phosphorescence at 77K (LE). Thus, the thermochromism in **17** is controlled by the emission characteristics of its ligand moieties. Comparison of the Cu...Cu and Cu...I distances in **17** obtained from the single-crystal X-ray data collected at 298K and 100K reveal that the Cu...Cu distances were notably shortened at 100K. In particular, Cu...Cu bonds between the two Cu_3 -units (3.150(2) (298K) and 3.032(4) Å (100K)) are shortened by about 0.12 Å at 100K (Figure A6.12, Appendix 6). This infers that the cationic cluster might also contribute to the emission shifts in **17**.

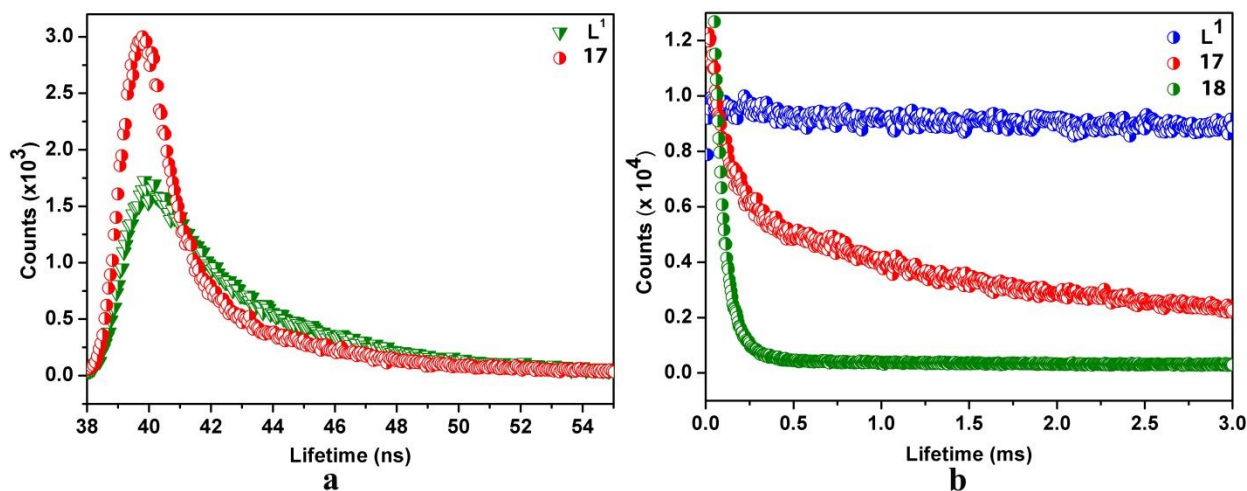


Figure 6.7: TCSPC decay profiles of (a) fluorescence in L^1 and **17** at 298K and (b) phosphorescence in L^1 , **17** and **18** at 77K in DMF.

The emission spectrum of **18** in DMF suspension at room temperature shows a strong band at 506 nm indicating a cluster centered transition typically observed for $\text{Cu}_4\text{I}_4\text{Py}_4$ cubane clusters.^{21a} No appreciable shift in its emission is observed upon lowering the temperature to 77K except for a broadened emission signature. Similar emission signature was also observed when the emission spectrum was recorded in the solid-state (Figure A6.7, Appendix 6). The time decay measurements at 298K and 77K

indicate that the emission at 506 nm is due to phosphorescence with varied τ_{em} values of 0.30 and 67.0 μs , respectively (Figure 6.7 and Figure A6.13, Appendix 6). These values suggest that the origin of this phosphorescent emission is from the triplet cluster-centered (^3CC) excited state of $\{[\text{Cu}_6\text{I}_4]^{2+}\}_n$. Although it can be presumed that both **17** and **18** can give rise to a HE $^3\text{XLCT}$ -band below 77K,^{21b} lack of very low temperature measurement setup (liquid helium cryostat) precludes such an observation.

6.3.4 DFT calculations

To get further insight into the absorption and emission properties of these new MOFs, preliminary DFT calculations were performed by using *Gaussian 03* package.

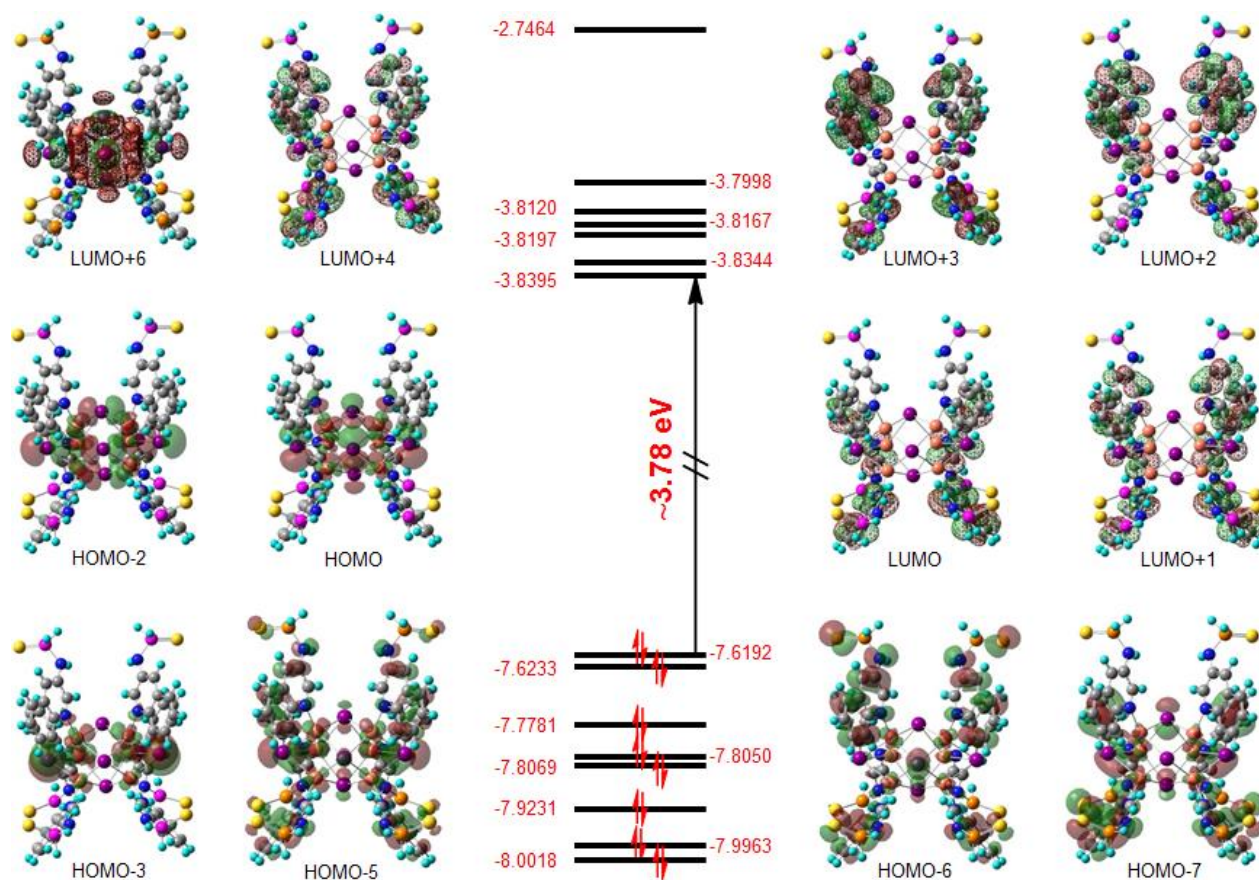


Figure 6.8: DFT derived surface diagrams and energies of some relevant molecular orbitals calculated for singlet ground state at the S_0 optimized geometry for **17a**. Similar data for L^1 and **18b** are available in the supporting information (Figure A6.14-A6.16).

The calculations were done on the bare $[\text{Cu}_6\text{I}_5]^+$ cluster using LANL2DZ basis set as well as on discrete model compounds $\{\text{Cu}_6\text{I}_5[(\text{AQNH})\text{H}_2\text{P}=\text{S}]_6\}$ (**17a**) and $\{\text{Cu}_6\text{I}_5[(\text{PYNH})\text{H}_2\text{P}=\text{S}]_6\}$ (**17b**) using B3LYP exchange correlation functional along with the mixed 6-31g(d)/LANL2DZ basis sets.¹⁸ The calculations on L^1 were performed by B3LYP/6-31g(d,p) basis set. For the purpose of these calculations coordinates from the crystal structures were taken and then optimized for the gas phase structures. A closer look at the frontier orbitals in **17a** indicates that the electronic isodensity surfaces are located on the AQ chromophores as well as on the cluster core. Figure 6.8 shows that the highest occupied molecular orbital (HOMO) in **17a** comprise predominantly of the iodine 5p orbitals and the copper 3d orbitals to some extent. The lower orbitals up to HOMO-4 also feature isodensity surfaces on the cluster; while the further lower ones (HOMO-5, HOMO-6 and HOMO-7) have electron densities primarily located on the AQ chromophores. All these orbitals are separated by a narrow energy gap indicating that the excitations can happen from any one of these orbitals. Similarly, the lowest unoccupied molecular orbitals (LUMOs) up to LUMO+5 are exclusively on the AQ moieties that are spanned over a narrow energy gap whereas the electron densities on the LUMO+6 orbital is located solely on the cluster core.

Further, the optical properties of **17a** were determined by TDDFT calculations on the optimized structures and the first 40 transitions were computed. Thus, the weak band centered at 390 nm in the absorption spectrum of **17** corresponds mainly to the transitions $\text{HOMO}-2 \rightarrow \text{LUMO}+3$ and $\text{HOMO}-2 \rightarrow \text{LUMO}+4$ with each of them exhibiting significant positive oscillator strengths (0.0124) (Table 6.2). It is to be noted that LUMO+6 did not feature in any of these transitions suggesting that this transition must be resulting from the mixture of $^1\text{XLCT}$ and $^1\text{MLCT}$ charge-transfer, as observed for the $\text{Cu}_4\text{I}_4\text{Py}_4$ / $\text{Cu}_4\text{I}_4(\text{PR})_4$ cubane clusters.²³ Whereas, the HE band centered at 345 nm in the absorption spectrum of **17** is due to the ligand centered absorptions corresponding to the transitions $\text{HOMO}-5 \rightarrow \text{LUMO}$, $\text{HOMO}-5 \rightarrow \text{LUMO}+1$, $\text{HOMO}-7 \rightarrow \text{LUMO}+3$ and $\text{HOMO}-6 \rightarrow \text{LUMO}+4$ with each of them showing significantly higher oscillator strengths (Table 6.2). Calculations on bare $[\text{Cu}_6\text{I}_5]^+$ cluster show that the HOMO is mostly on the iodide 5p bonding orbitals and to some extent the Cu-centered 3d-antibonding orbitals,

while the LUMO is the bonding 4s and 4p orbitals from the Cu-centers with some minor contributions from iodide 6s and 6p orbitals (Figure A6.15, Appendix 6). The HOMO-2 and LUMO+6 orbitals in the calculated structure of **17a** matches well with the HOMO and LUMO computed for the bare cluster. This indicates that the energy transfer through ISC process from the triplet states of AQ could populate the Cu-centered LUMOs resulting in a phosphorescent emission from the ^3CC -excited states. A similar set of isodensity surface features has been observed for the analogous pyridyl derivative **17b**, except that the energies of the LUMO orbitals are higher than those of **17a** (~1.0 eV) (Figure A6.16, Appendix 6). Also, the energy separation between the ligand centered LUMO+5 and the metal-centered LUMO+6 in **17a** is 1.05 eV (24.29 kcal/mol) which is much higher than that of **17b** (0.16 eV = 3.74 kcal/mol). Hence, it is highly likely that populating the low-energy ligand π^* orbitals in **17a** would preferably result in the fluorescent emission ($S_1 \rightarrow S_0$ fast radiative decay) than the cluster-centered phosphorescence ($^3\text{CC} \rightarrow S_0$ slow radiative decay), indicating that emission from the AQ chromophore is energetically favored in the absence of the ISC process at 298K.

The calculated emission wavelength of 600 nm from the adiabatic S_0 -T gap obtained from the single-point calculations²⁶ on the optimized triplet geometry of **17a** is in good agreement with the experimental value of 614 nm observed for **17** (Figure A6.17, Appendix 6).

Table 6.2: TDDFT computed transition wavelengths (λ), oscillator strengths (f), and major orbital contributions (%) for singlet-singlet transitions of **17a. (H and L denotes HOMO and LUMO, respectively)**

λ (nm)	(f)	Orbitals involved (%)
413.29	0.0023	H-4 $\rightarrow$ L (16%), H-3 $\rightarrow$ L+1 (12%), H-1 $\rightarrow$ L+3 (37%), H $\rightarrow$ L+4 (27%)
390.76	0.0124	H-2 $\rightarrow$ L+3 (93%)
390.68	0.0124	H-2 $\rightarrow$ L+4 (93%)
380.46	0.0023	H-4 $\rightarrow$ L (33%), H-3 $\rightarrow$ L+1 (29%), H-1 $\rightarrow$ L+3 (17%), H $\rightarrow$ L+4 (15%)

374.48	0.0029	H-4 → L+1 (32%), H-3 → L (35%), H-1 → L+4 (14%), H → L+3 (15%)
363.96	0.005	H-4 → L+4 (17%), H-3 → L+3 (12%), H-3 → L+5 (48%)
363.9	0.005	H-4 → L+3 (12%), H-4 → L+5 (52%), H-3 → L+4 (14%)
353.92	0.0962	H-5 → L (42%)
353.9	0.0963	H-5 → L+1 (42%)
352.6	0.0013	H-7 → L (16%), H-7 → L+1 (16%), H-6 → L (16%), H-6 → L+1 (16%)
351.58	0.0027	H-6 → L+2 (16%), H-5 → L (27%)
351.54	0.0026	H-7 → L+2 (16%), H-5 → L+1 (27%)
350.03	0.0048	H-5 → L+2 (62%)
343.63	0.003	H-5 → L+3 (32%)
343.59	0.0026	H-6 → L+5 (11%), H-5 → L+4 (32%)
343.4	0.0085	H-7 → L (11%), H-7 → L+1 (10%), H-6 → L (12%), H-6 → L+1 (10%), H-5 → L+2 (23%)
343.18	0.0618	H-7 → L+3 (20%), H-6 → L+4 (19%)

Similarly, for L^1 the computed emission wavelength of 548 nm from the S_0 -T gap on the optimized triplet state matches well with the experimentally observed emission signature of 532 nm at 77K. Also, the computed expectation value of S^2 is approximately 2.01 for both L^1 and **17a** from which the presence of triplet states in them could be confirmed. To the best of our knowledge, this is first instance where the optical properties of the cationic $[Cu_6I_5]^+$ cluster has been characterized by experimental as well as by theoretical methods although there were numerous reports on the cubane type $Cu_4I_4L_4$ clusters and rhomboidal $Cu_2I_2L_4$ moieties.

6.4 CONCLUSION

Chapter six has shown that tridentate ligands based on thiophosphoramidate backbone offer C_3 -symmetric platforms for obtaining rugby-ball shaped cationic CuI cluster MOFs. The MOF based on the 3-aminoquinolyl moieties showed unusual thermochromism exhibiting ligand dependent fluorescence at room temperature and the cluster dependent phosphorescence at 77K. The occurrence of the phosphorescence at 77K is attributed to the energy transformation from the T_1 state of the AQ moieties to the 3CC -

excited state of the cluster through ISC process. DFT analysis on the model compound **17a** indicated that emission from the AQ chromophores is favoured at 298K as its π^* orbitals are lower in energy by 24.29 kcal/mol than the cluster based LUMOs in the S0 optimized geometry. However, the ISC process at 77K can populate the cluster based triplet state (L+6 orbitals) for the 3CC-phosphorescence emission. Further, the observed absorption and emission maxima of these MOFs were substantiated by TDDFT calculations.

6.5 REFERENCES

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Thesis Conclusion and Future Perspectives

In summary, this thesis presents the synthesis of interesting examples of metal-organic cages and infinite networks derived from amino phosphorus (V) ligands and their functional studies in the domains of host-guest chemistry, dielectric, ferroelectric and photophysical properties. Two neutral tetrahedral cages of formula $\{Pd_3[(N^iPr)_3PO]_4(L)_6\}$ consisting of imido- Pd_3 clusters and chlorinate and benzoquinone ligands, respectively, were synthesized. Each of these cage assemblies exhibit intrinsic cavity of volume $\sim 233 \text{ \AA}^3$ which are accessible for the encapsulation of various aromatic guest molecules. Interestingly, depending on the substituents on the quinonate backbone, these cage assemblies selectively encapsulated either o-xylene or mesitylene over their other aromatic analogues (Chapter 2). Further, a neutral cubic cage was synthesized by the reaction of Pd_6 -cluster with 2,5-pyrazine dicarboxylic acid with active coordinating groups for assembling cc-MOFs with *dia* and *qtz* topologies. The neutral cubic cage was obtained in a 42-component self-assembly reaction and is the largest for the neutral homoleptic cage assemblies known for $Pd(II)$ ions. The post-assembly reactions of the cubic assembly were performed in a controlled fashion giving rise to a series of hierarchical heterobimetallic assemblies of discrete, 1D and 2D-architectures, which can be regarded as intermediate stages along the pathway to the final 3D-framework. (Chapter 3). Moreover, a distinct octahedral cage compound of Zn^{2+} was prepared based on C_3 -symmetric phosphoramidate ligand which crystallized in non-centrosymmetric space group. The cage compounds exhibit blue luminescent and interesting dielectric and ferroelectric properties. Similarly, another octahedral cage based on Cu^{2+} ion was synthesized which undergoes post-assembly reactions resulting in the formation of 1D-, 2D- and 3D-cage connected frameworks. Interestingly, the discrete cage and its 1D assemblies show anisotropy in ferroelectricity (Chapter 4 and 5). Furthermore, the two rugby-ball shaped cationic CuI cluster MOFs $Cu_6I_5^+$ and $Cu_6I_4^{2+}$ were synthesized based on thiophosphoramidate backbone which offers C_3 -symmetric platforms. These MOFs exhibit interesting photophysical properties and the $Cu_6I_5^+$ cluster MOF shows unusual thermochromic behaviour (Chapter 6). All these findings demonstrate that the amino-P(V) backbone offers an attractive platform for synthesizing versatile ligands where they can be utilized as a rigid or flexible multi-site coordinating ligands to various transition metals. Also, by subtle variations in the reaction conditions,

a number of coordinating groups, the dimensionality of the framework and the allied pores, guest molecules present in them, it is possible to tune the functional properties associated with the obtained complexes. Further work in this area would be to focus on obtaining interesting cage and framework solids having chiral functionalities, which can be used for the asymmetric catalysis and enantiomeric separation. Also, it will be interesting to see if these ligand scaffolds can be utilized for preparing stable metal-organic materials with notable multi-functional behavior exhibiting photophysical and ferroelectric, ferroelectric and ferromagnetic etc. Such materials would lead to applications in solar cells, nanogenerators and memory devices.

Appendix

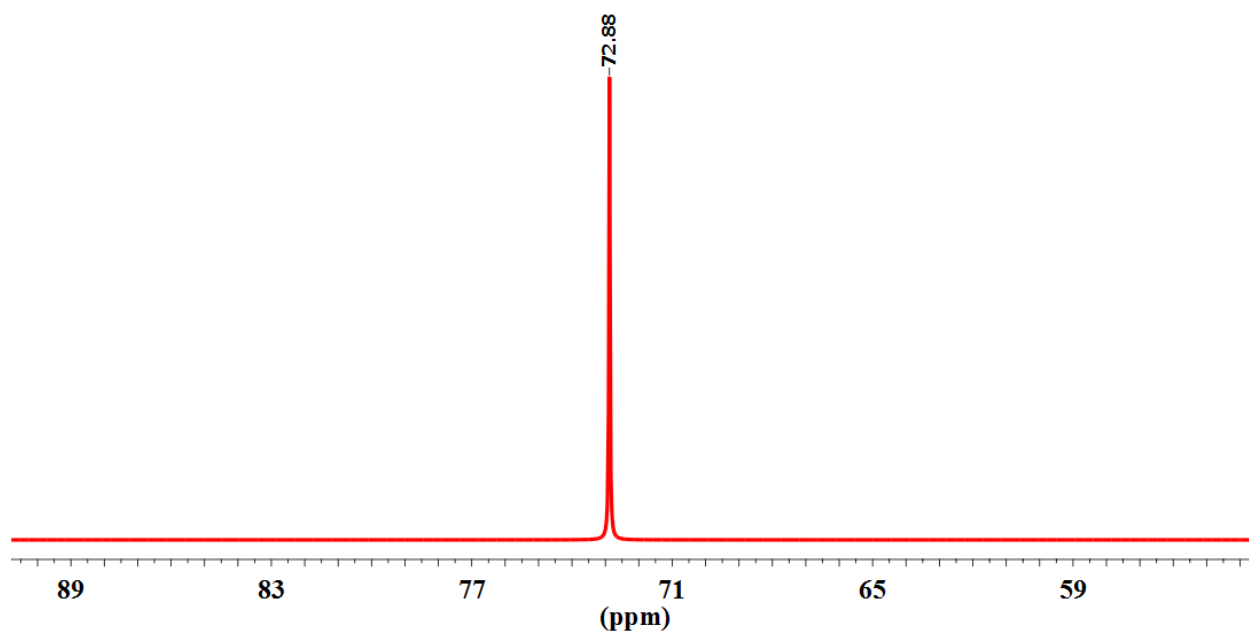


Figure 2A.1: ^{31}P -NMR of compound **1**.

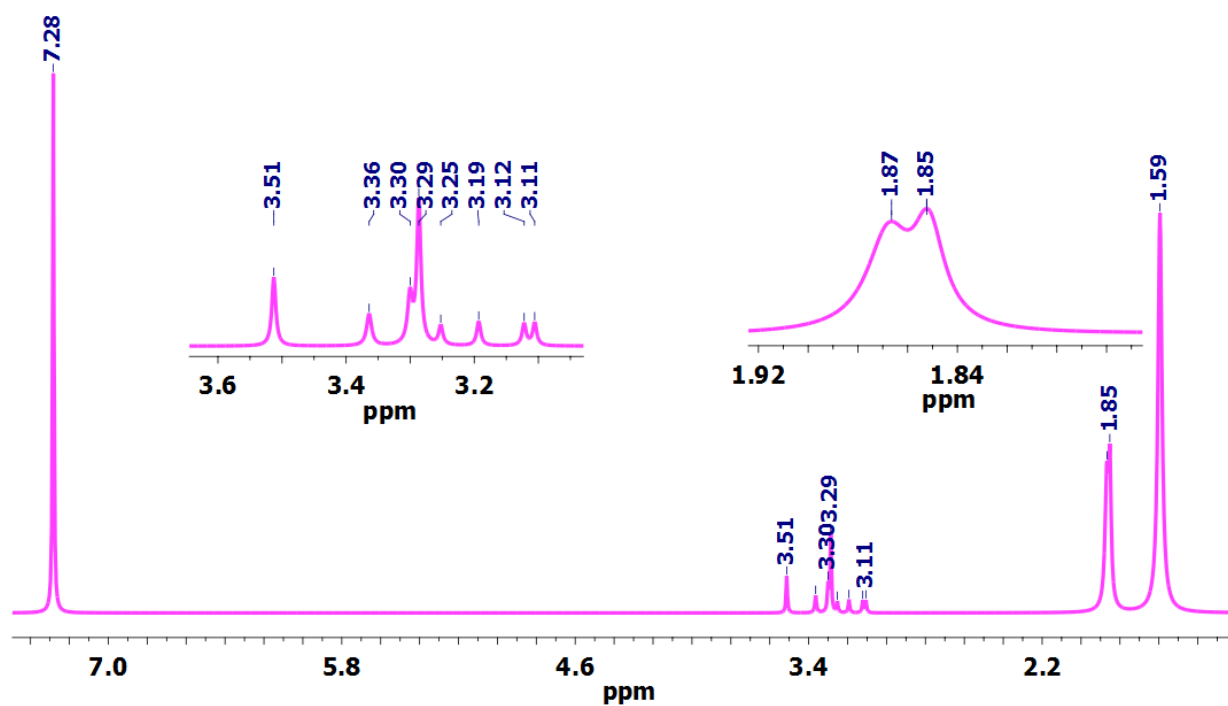


Figure 2A.2: ^1H -NMR of compound **1**.

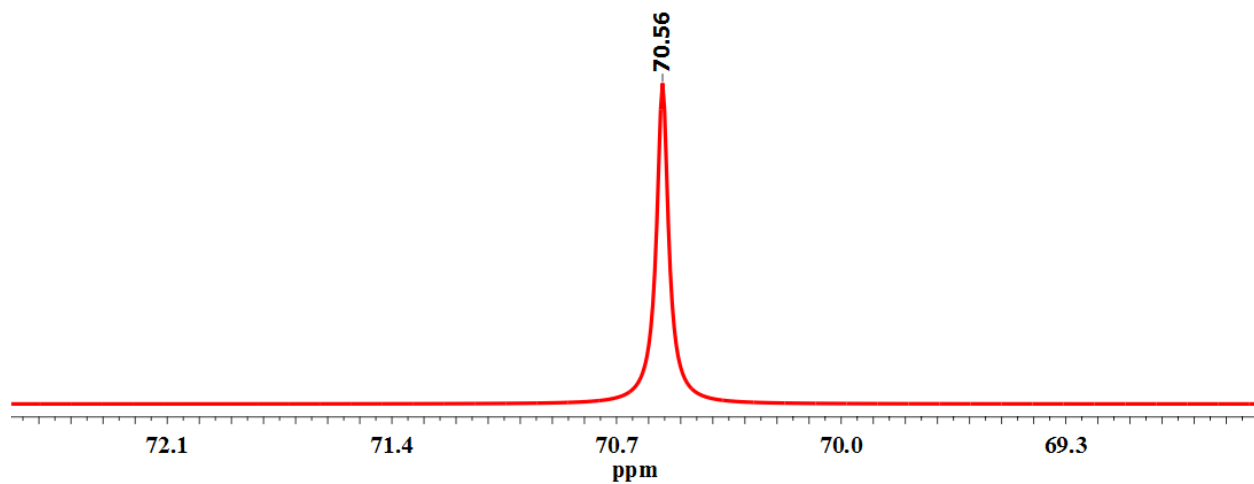


Figure 2A.3: ^{31}P -NMR of compound 2.

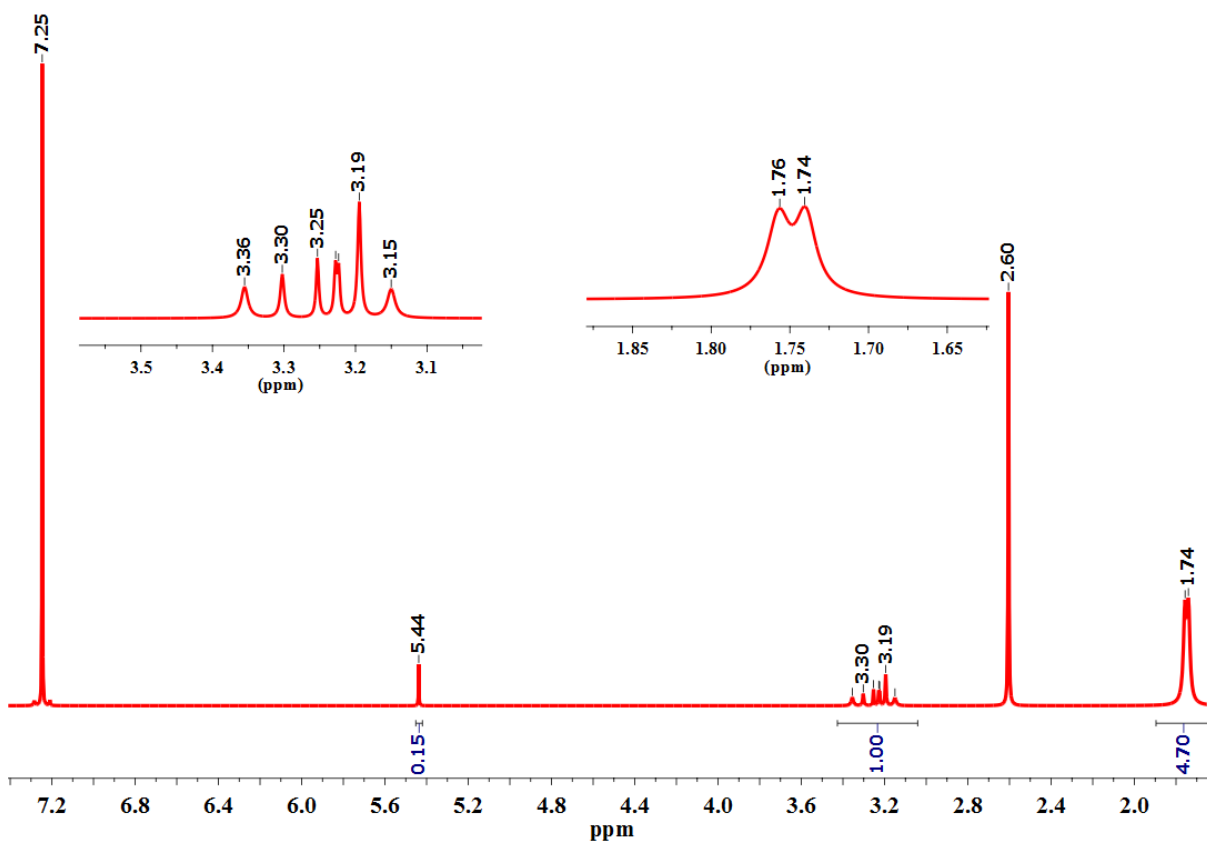


Figure 2A.4: ^1H -NMR of compound 2.

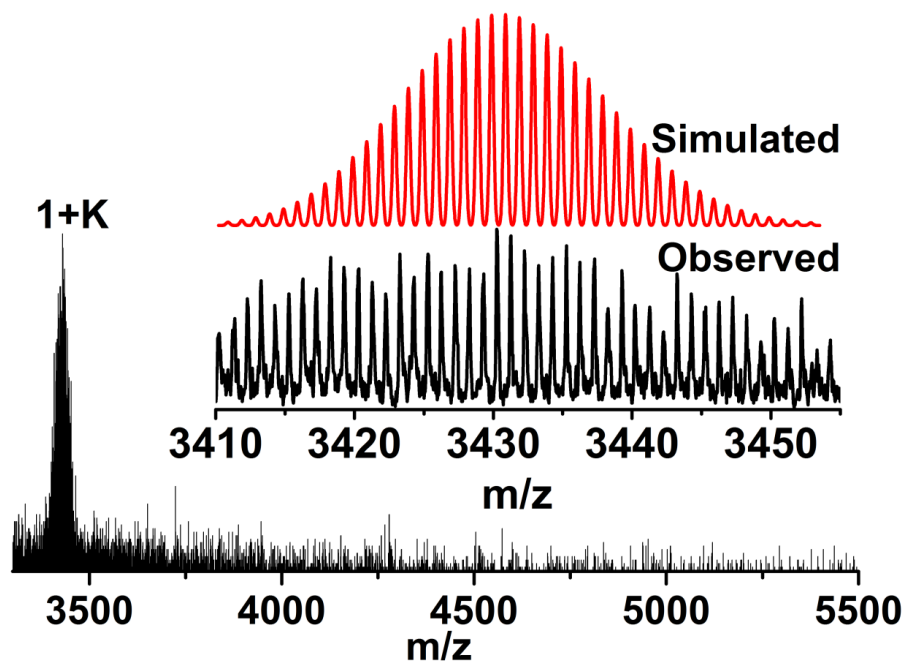


Figure 2A.5: MALDI-TOF mass spectrum of 1.

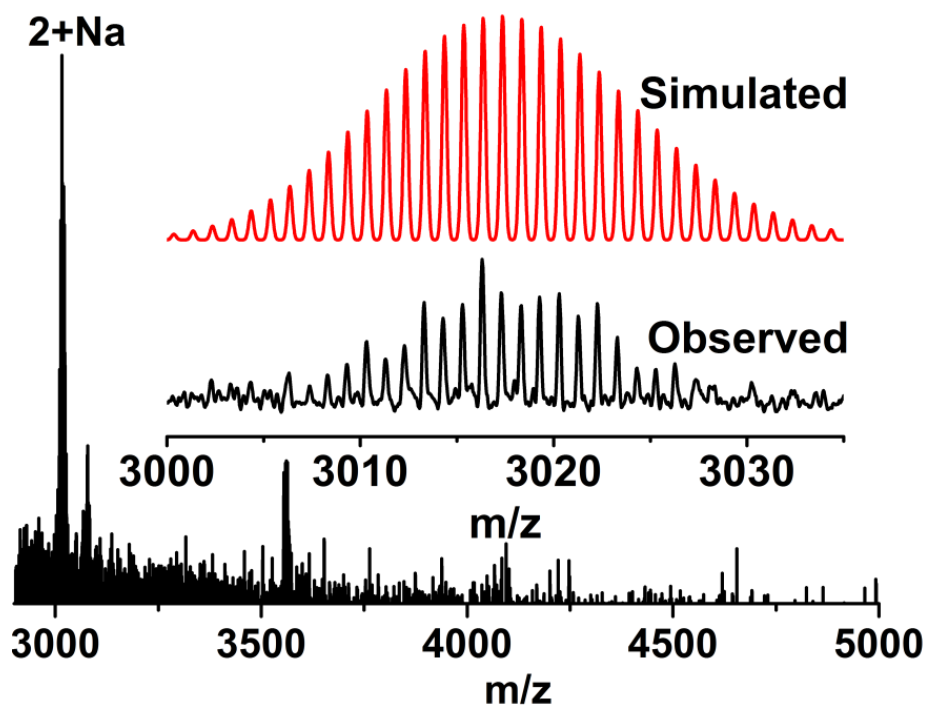


Figure 2A.6: MALDI-TOF spectrum of 2.

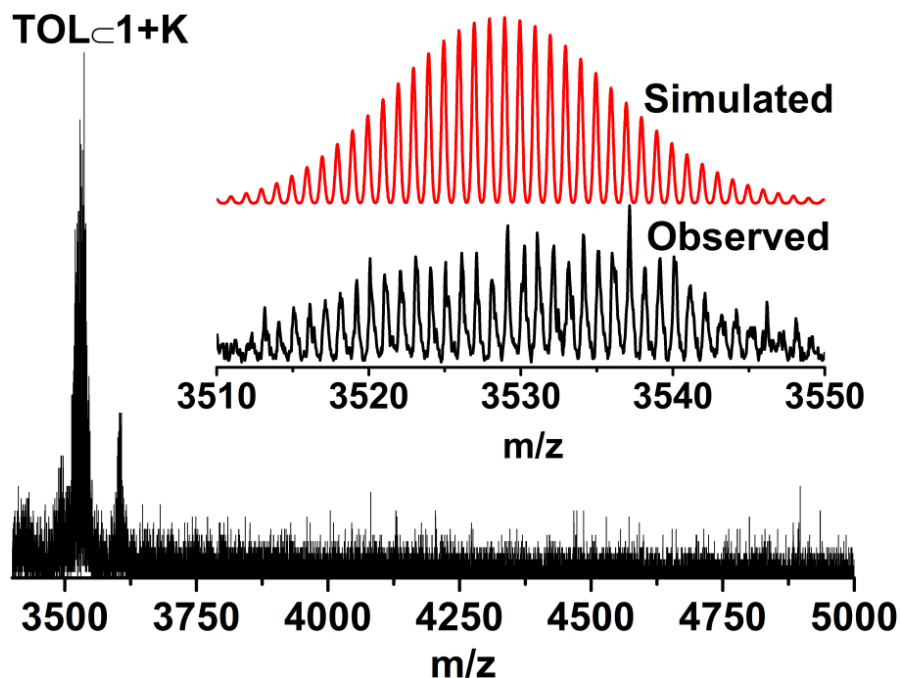


Figure 2A.7: MALDI-TOF spectrum of host-guest complex $\text{C}_7\text{H}_8\text{C1}$ for toluene.

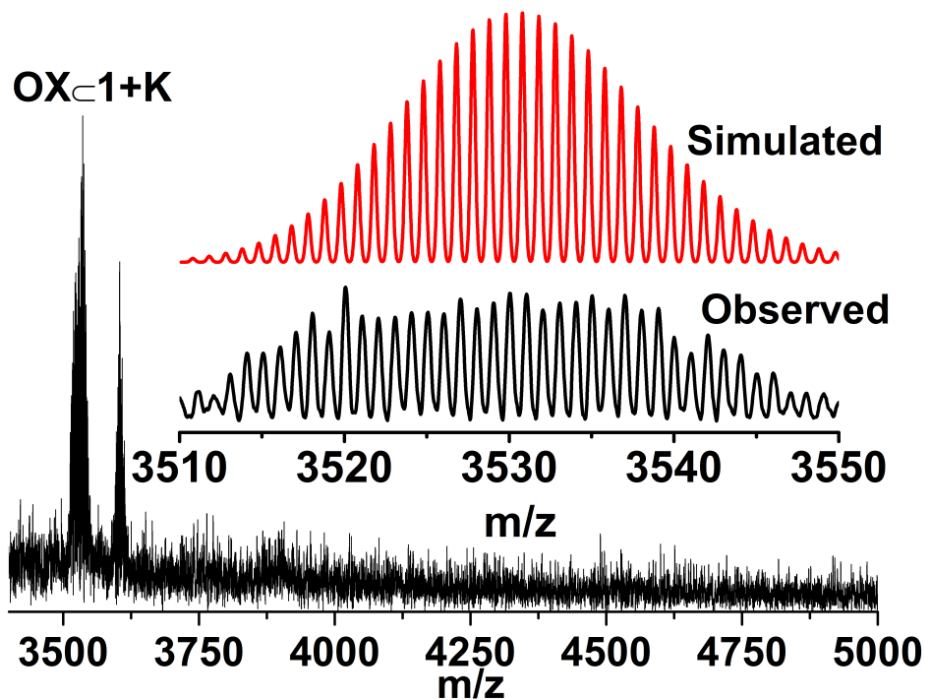


Figure 2A.8: MALDI-TOF spectrum of host-guest complex $\text{o-C}_8\text{H}_{10}\text{C1}$ for o-xylene.

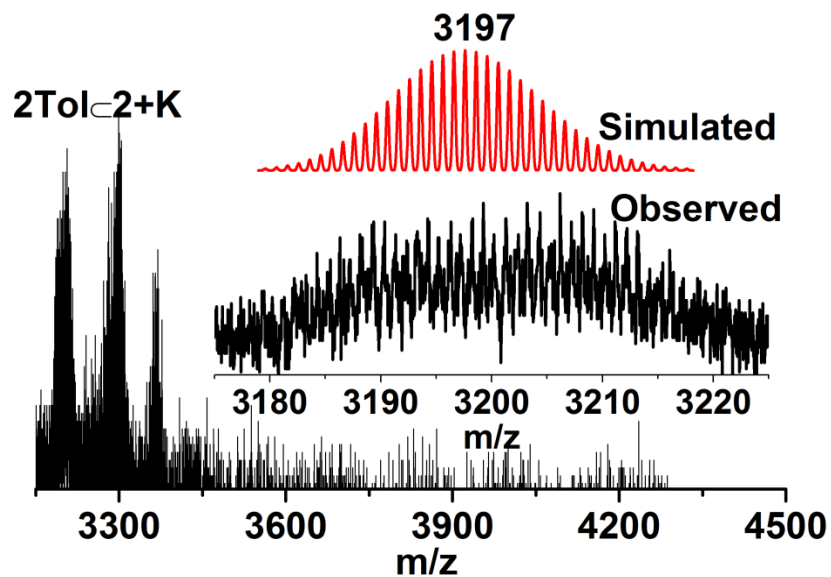


Figure 2A.9: MALDI-TOF mass spectrum of host-guest complex C₇H₈C₂ for toluene.

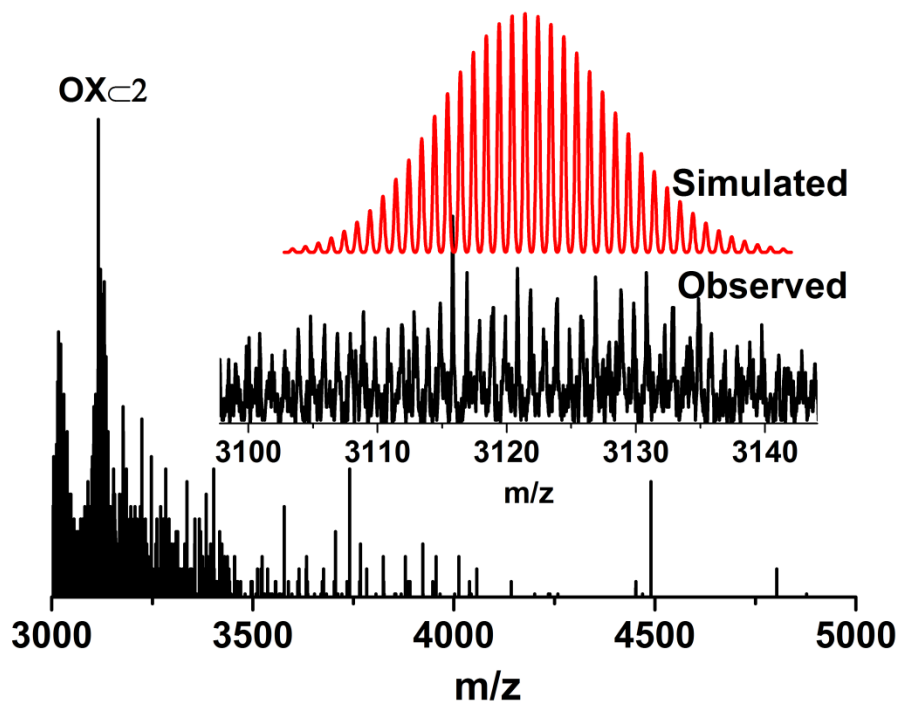


Figure 2A.10: MALDI-TOF mass spectrum of host-guest complex o-C₈H₁₀C₂ for o-xylene.

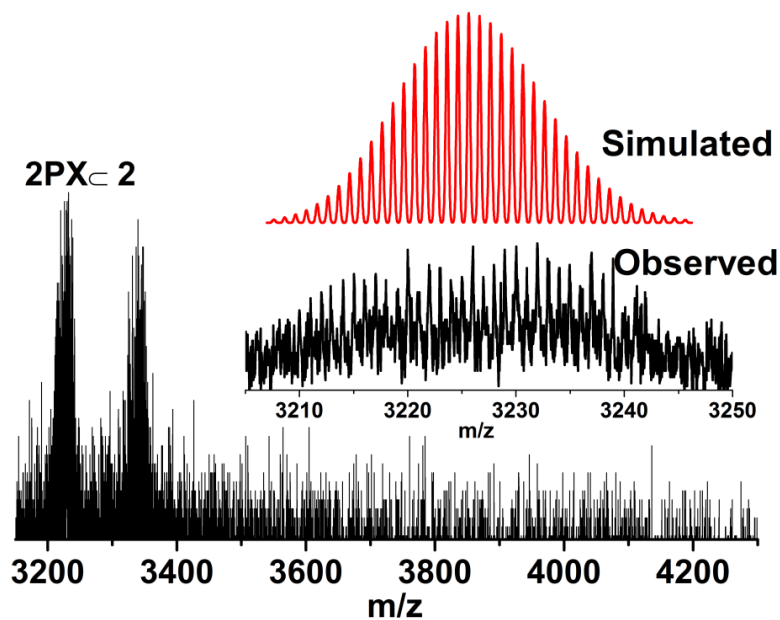


Figure 2A.11: MALDI-TOF mass spectrum of host-guest complex p-C₈H₁₀-C2 for p-xylene.

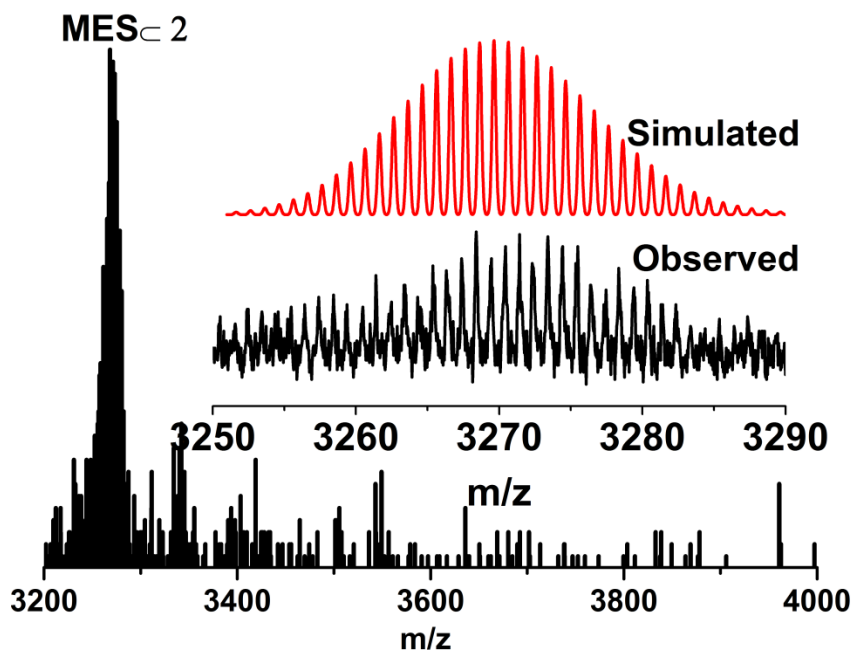


Figure 2A.12: MALDI-TOF mass spectrum of host-guest complex C₉H₁₂-C2 for mesitylene.

Appendix 2

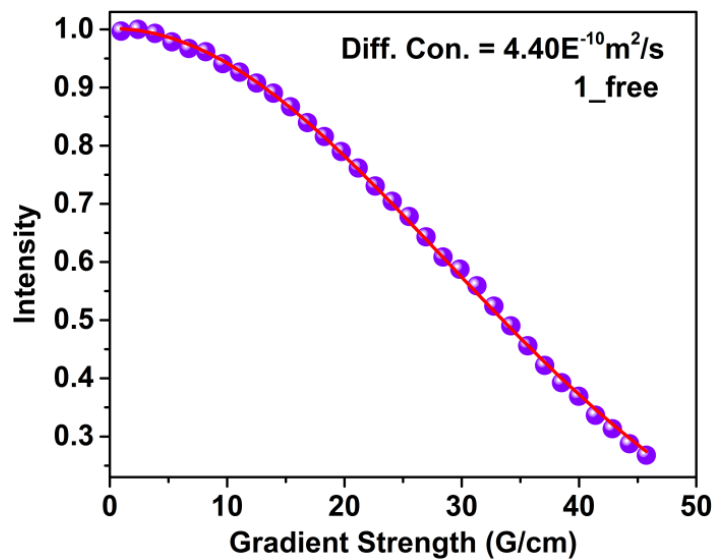
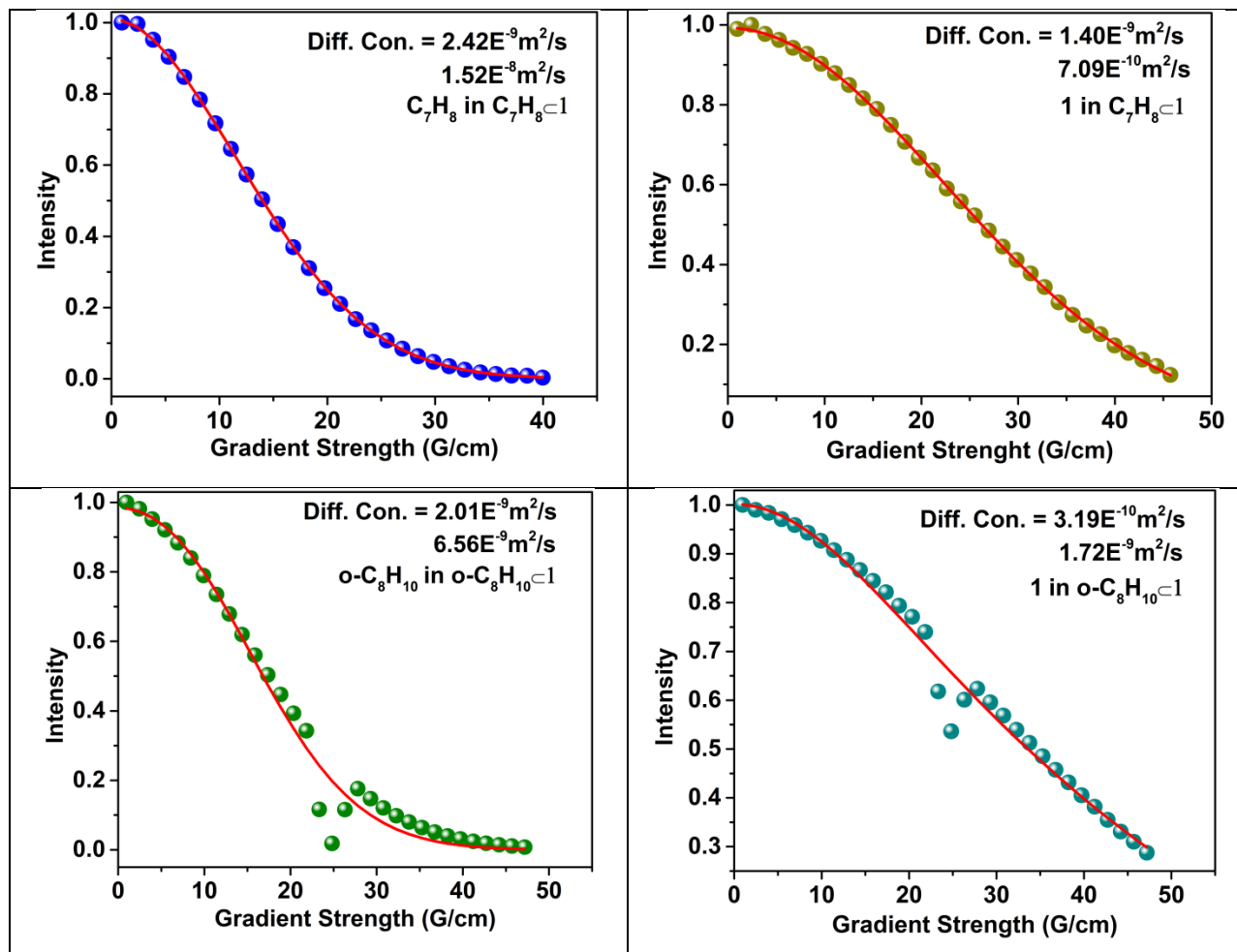


Figure 2A.13: Integral decay profile of host proton without any guest.



Appendix 2

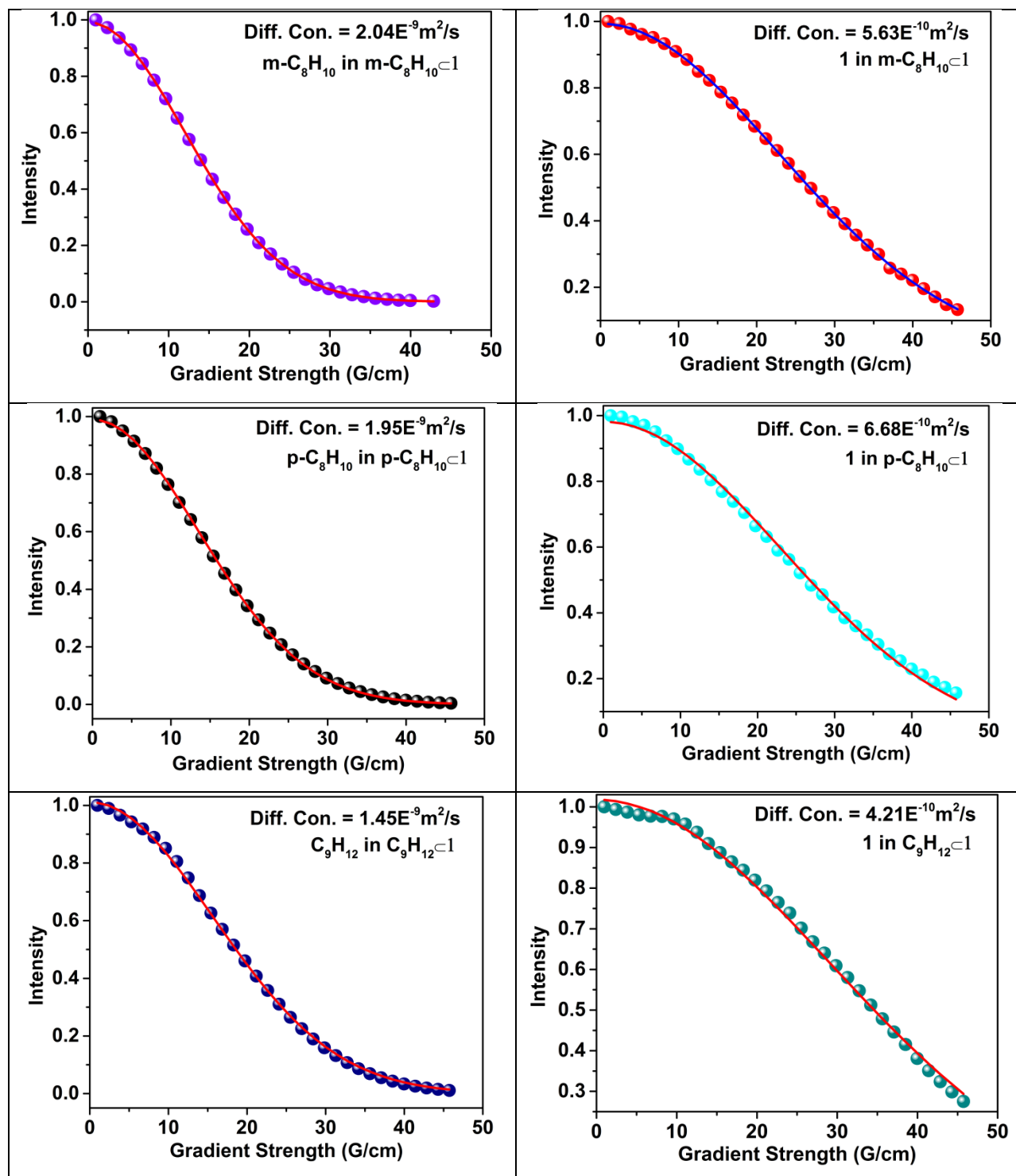


Figure 2A.14: Integral decay profile of guest protons (left), and host protons (right) in the host-guest system plotted as a function of gradient strength. The dots represent experimental data and the red and blue line shows the best fit using the equation 1.

Appendix 2

Name of the guest molecule and the diffusion coefficients obtained for free and bound molecule are shown in the corresponding insets of **1**.

Table 2A.1: Binding energy of the host-guest complex calculated using Lanl2dz with b97d3 basis set by G03 software.

Compound	Complex	binding energy (KJ/mol)	Relative binding energy (KJ/mol)
1	C ₇ H ₈ ⊂ 1	-139.62	10.03
	o-C ₈ H ₁₀ ⊂ 1	-149.65	0
	m-C ₈ H ₆ ⊂ 1	-83.07	66.58
	p-C ₈ H ₆ ⊂ 1	-141.71	7.94
	C ₉ H ₁₂ ⊂ 1	-137.06	12.59
2	C ₇ H ₈ ⊂ 2	-106.70	23.90
	o-C ₈ H ₁₀ ⊂ 2	-118.00	12.60
	m-C ₈ H ₆ ⊂ 2	-116.47	14.13
	p-C ₈ H ₆ ⊂ 2	-108.92	21.68
	C ₉ H ₁₂ ⊂ 2	-130.60	0

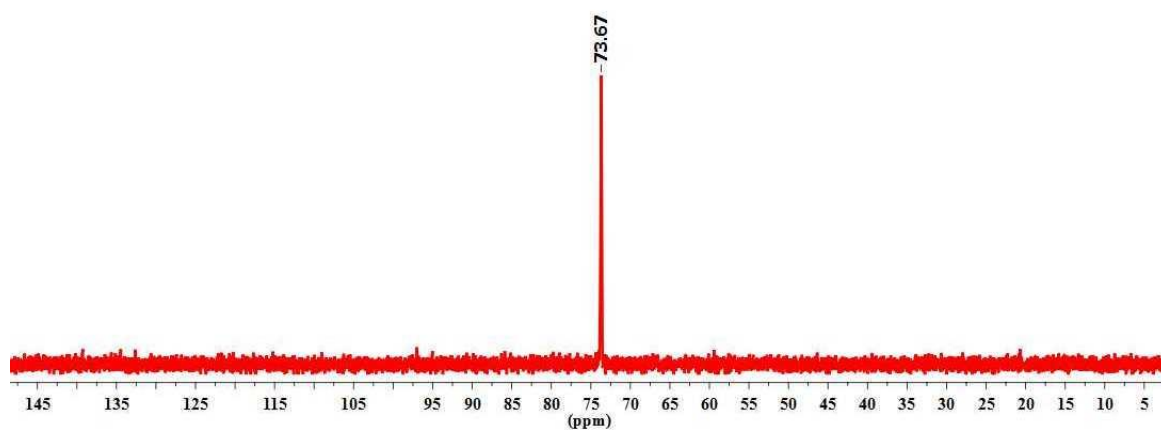


Figure A3.1: ^{31}P NMR spectrum of the cubic assembly **3**.

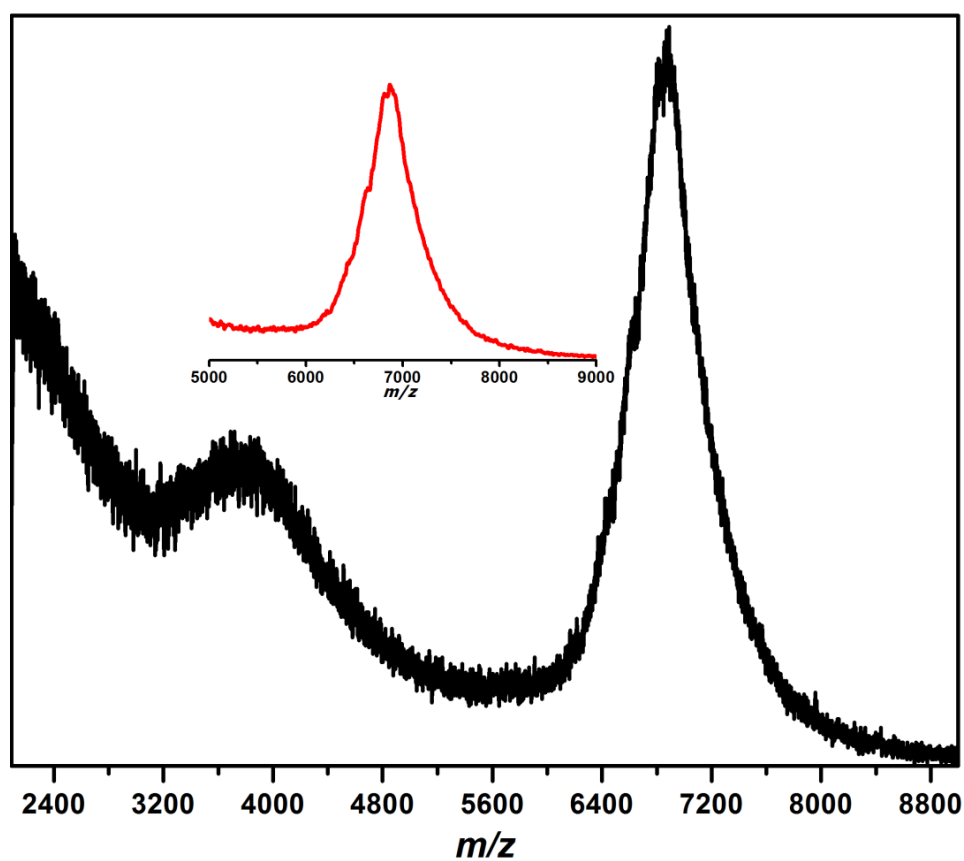


Figure A3.2: MALDI-TOF mass spectrum of **3** in linear mode; inset shows the mass range corresponding to the molecular weight of **3**.

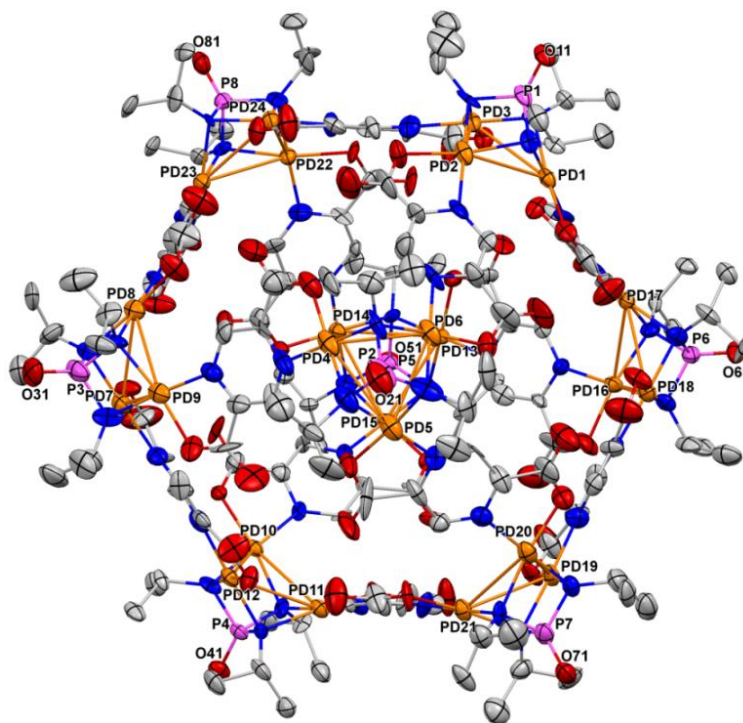


Figure A3.3: ORTEP diagram showing the crystal structure of **3**.

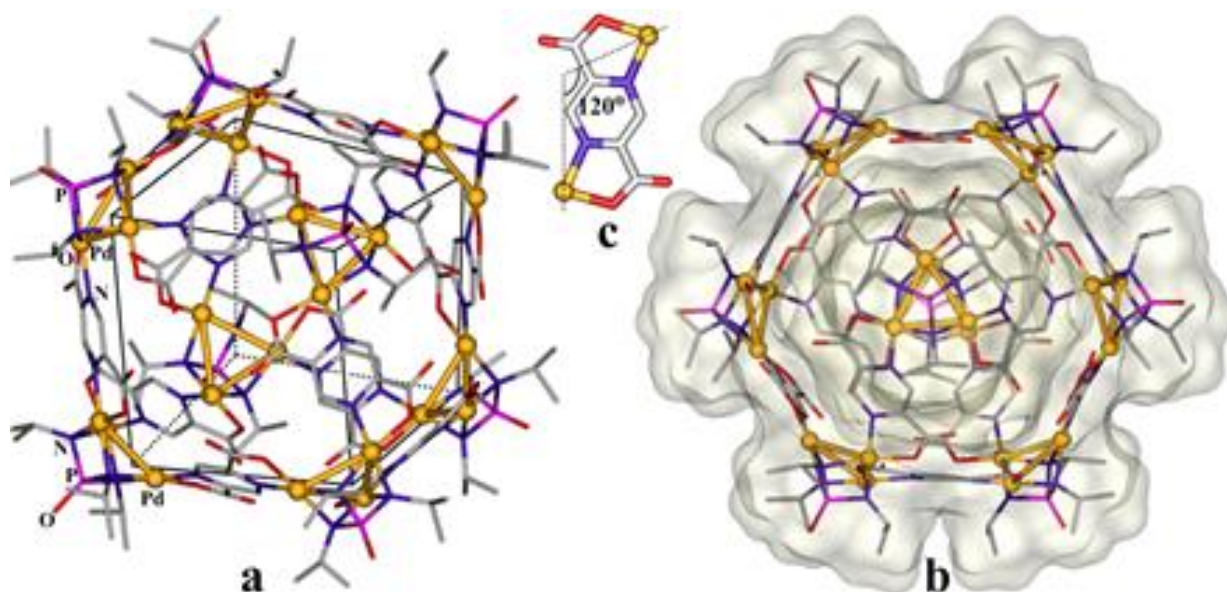


Figure A3.4: Crystal Structure of **3**; (a) view along c-axis, (b) surface view along b-axis, (c) view of chelating 2,5- pyrazinedicarboxylate linker in **3**.

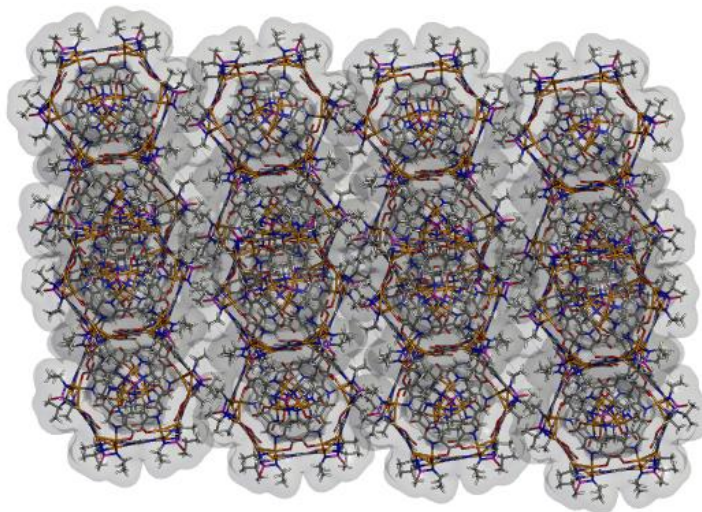


Figure A3.5: Packing diagram of **3**; it shows the presence of intrinsic as well as extrinsic cavities; the solvate DMSO molecules have been located only at the extrinsic pores. The twenty-two solvated water molecules were found to be disordered and located over forty different positions. Among these, about three disordered molecules were located inside the pore, four along the face centres and the remaining ones at the extrinsic pores.

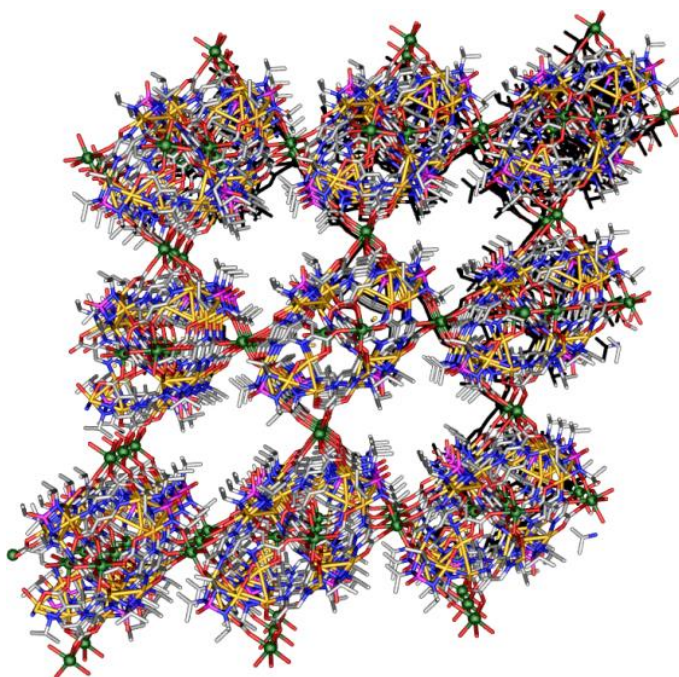


Figure A3.6: View of the cage connected 3D *dia* framework **4**.

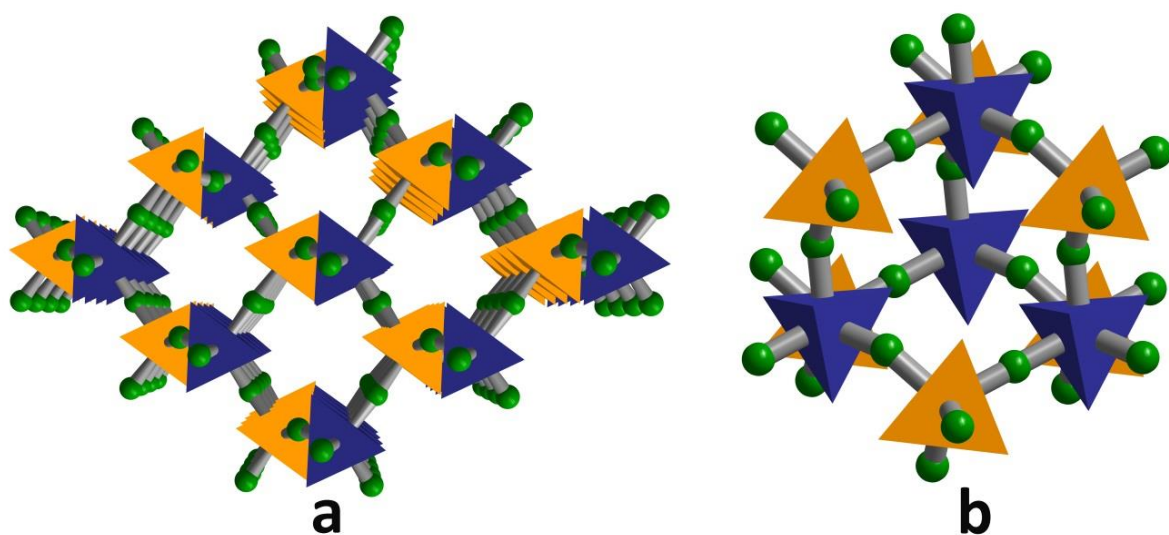


Figure A3.7: View of the 3D *dia* network (a) and adamantoid (b) connection of cages in 4. Cages were represented by the polyhedra and other atoms were omitted for clarity.

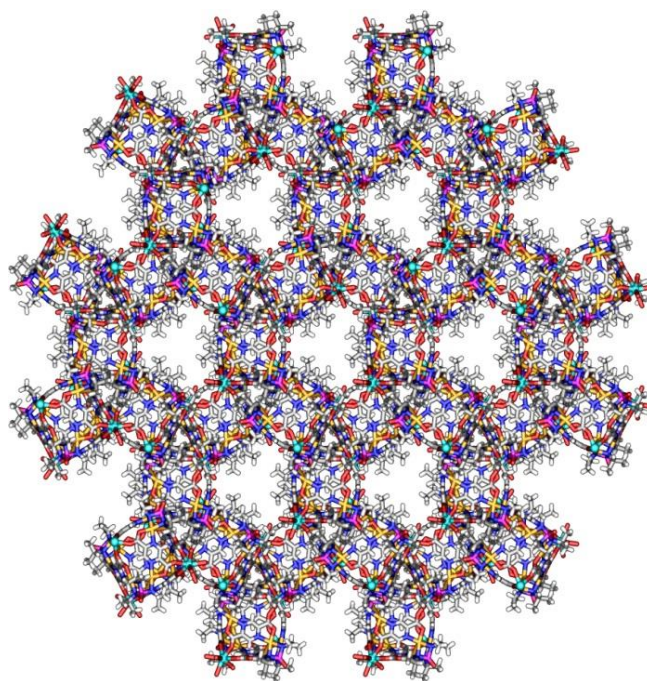


Figure A3.8: View of the cage connected 3D *qtz* framework of 5.

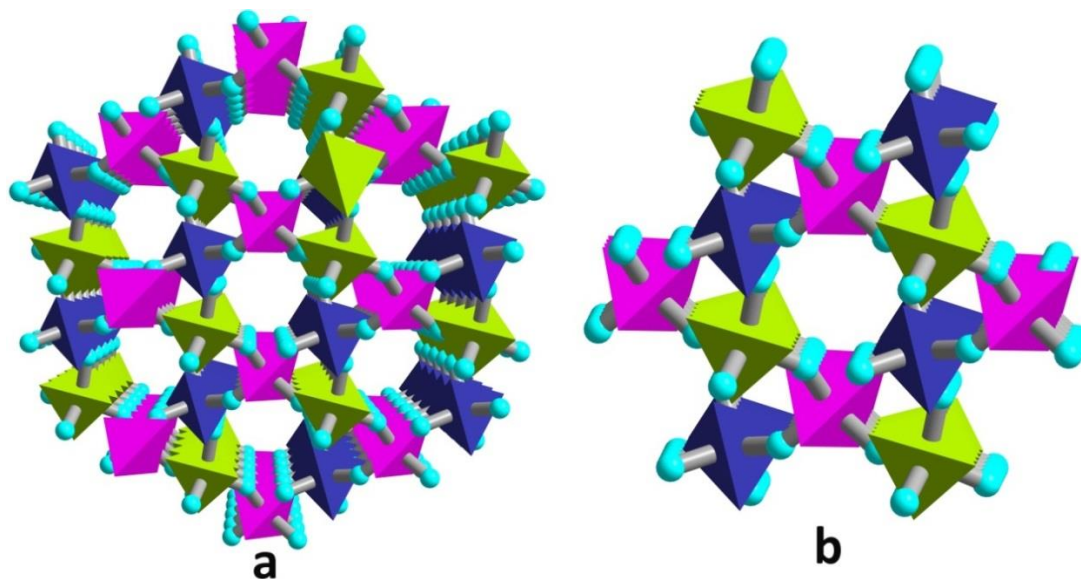


Figure A3.8: View of the 3D *qtz* network (a) and a segment of *qtz* connection (b) of cages in **5**. Cages were represented by the polyhedra and other atoms were omitted for clarity.

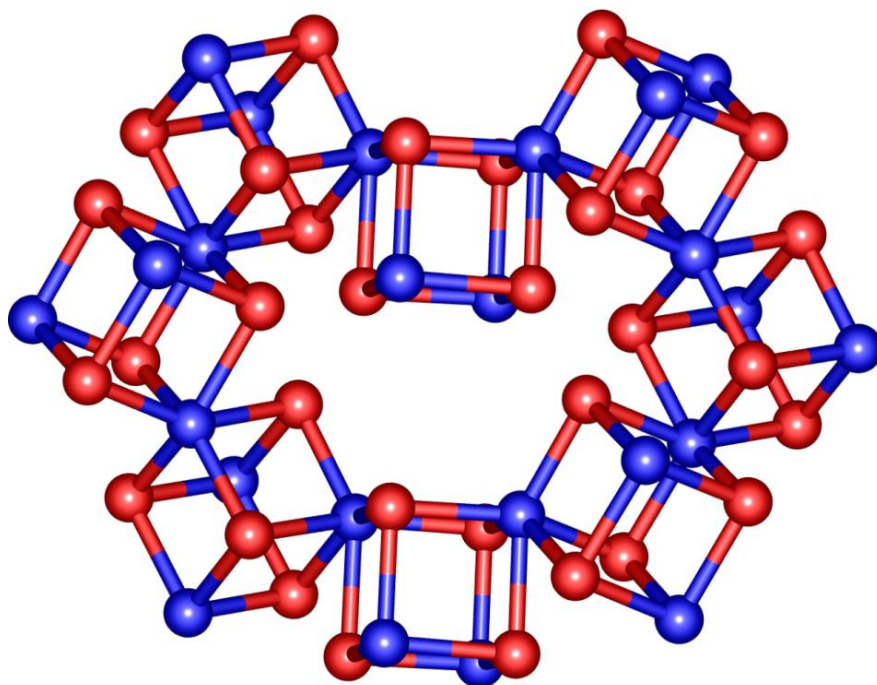


Figure A3.10: View of the *qtz* topology of connected cubic cages in **5** (red and blue spheres represent $[\text{Pd}_3\text{X}]^{3+}$ motifs and zinc atoms, respectively).

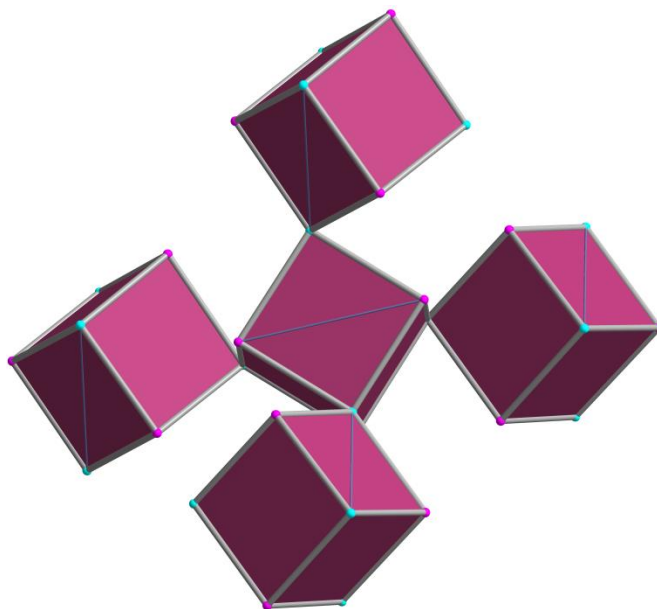


Figure A3.11: View of the four-connected network of the heterocubanes in **5** in a distorted tetrahedral arrangement. The Zn^{2+} ions (cyan dots) and the centroid of the $[\text{Pd}_3\text{X}]^{3+}$ motifs (pink dots) were shown at the alternate corners of the cube.

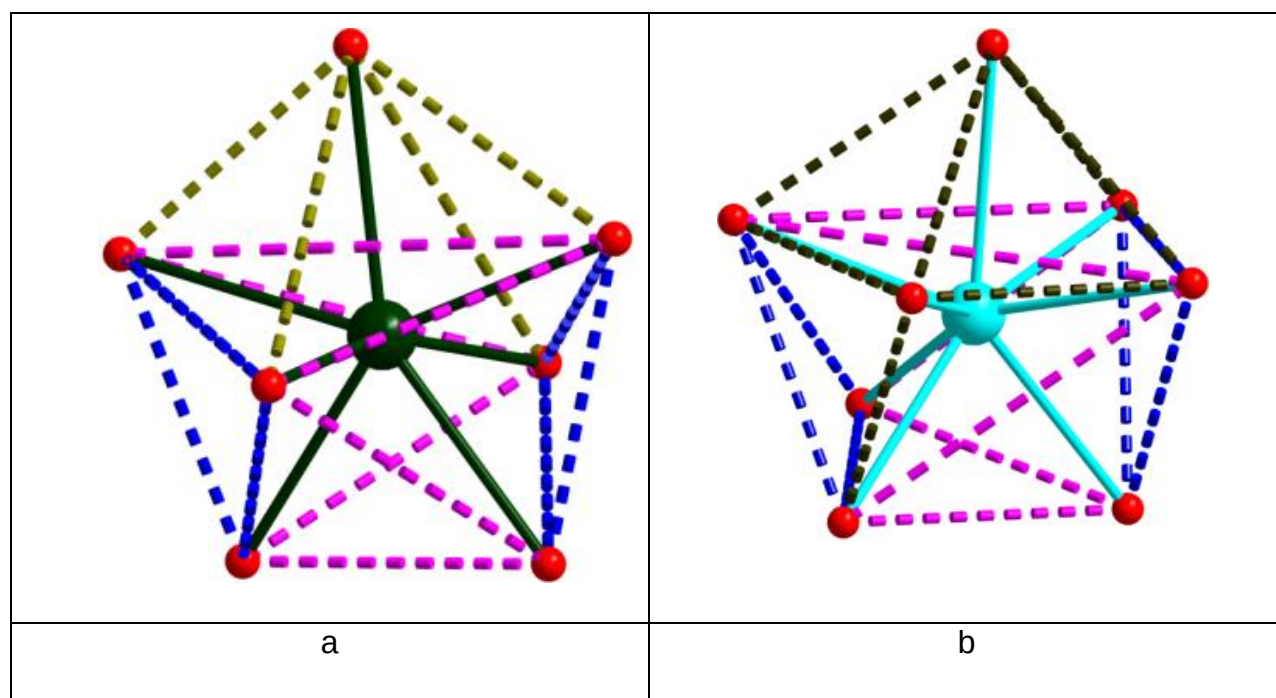


Figure A3.12: Geometry around the metal center: (a) prismatic capped coordination in **4** and (b) bi-capped prismatic coordination of Zn^{2+} in **5**.

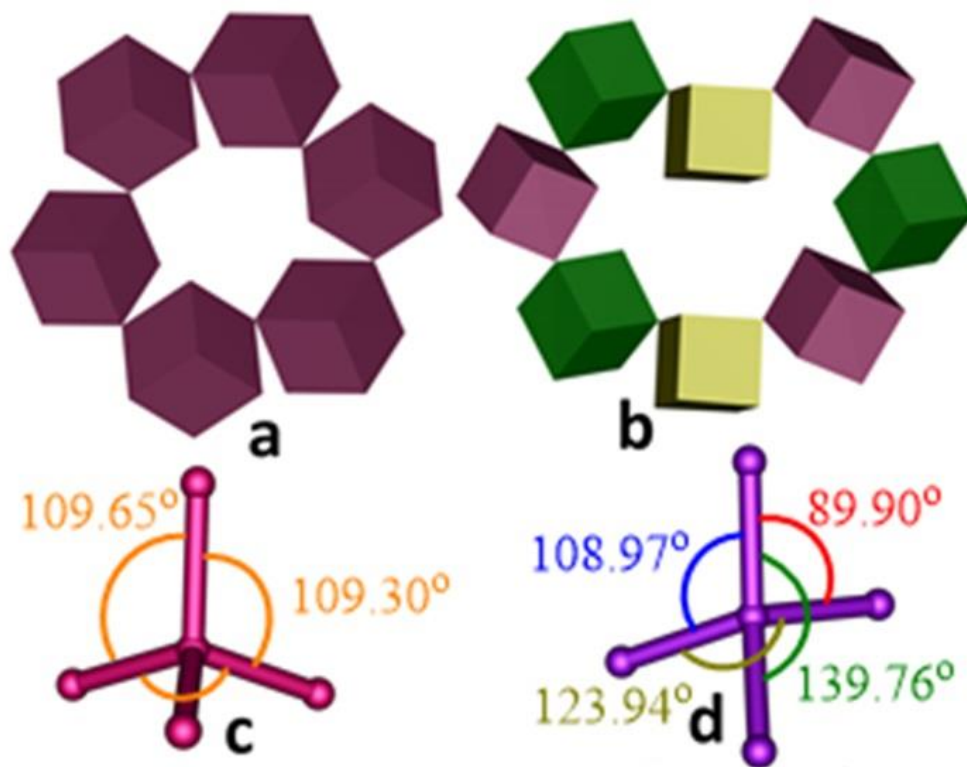


Figure A3.13: (a,b) arrangement of hetrocubanes, (c,d) view of tetrahedral angle, and (e,f) topological view of *dia* and *qtz* net in **4** and **5**, respectively.

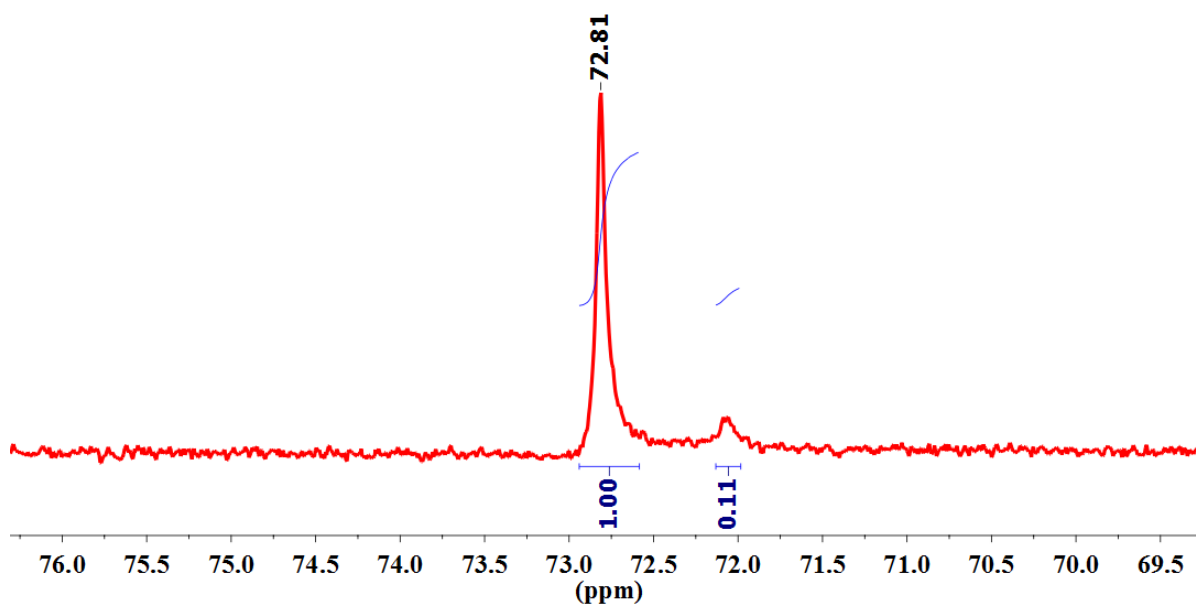


Figure A3.14: ^{31}P NMR spectrum of **6**.

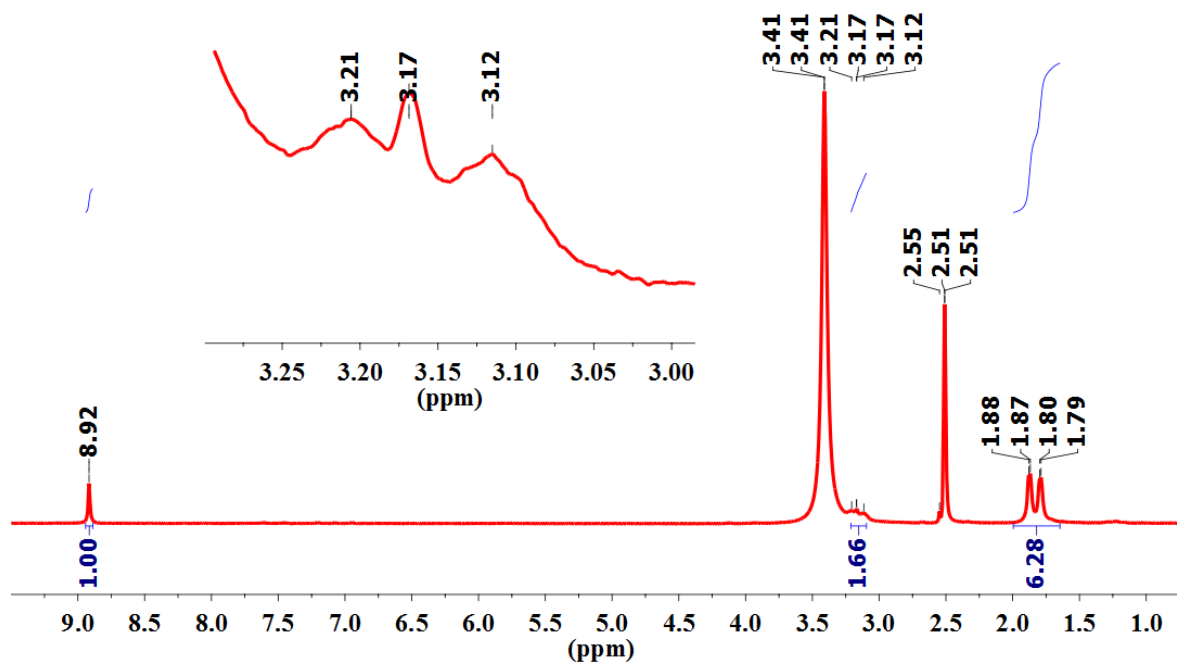


Figure A3.15: ¹H NMR spectrum of 6.

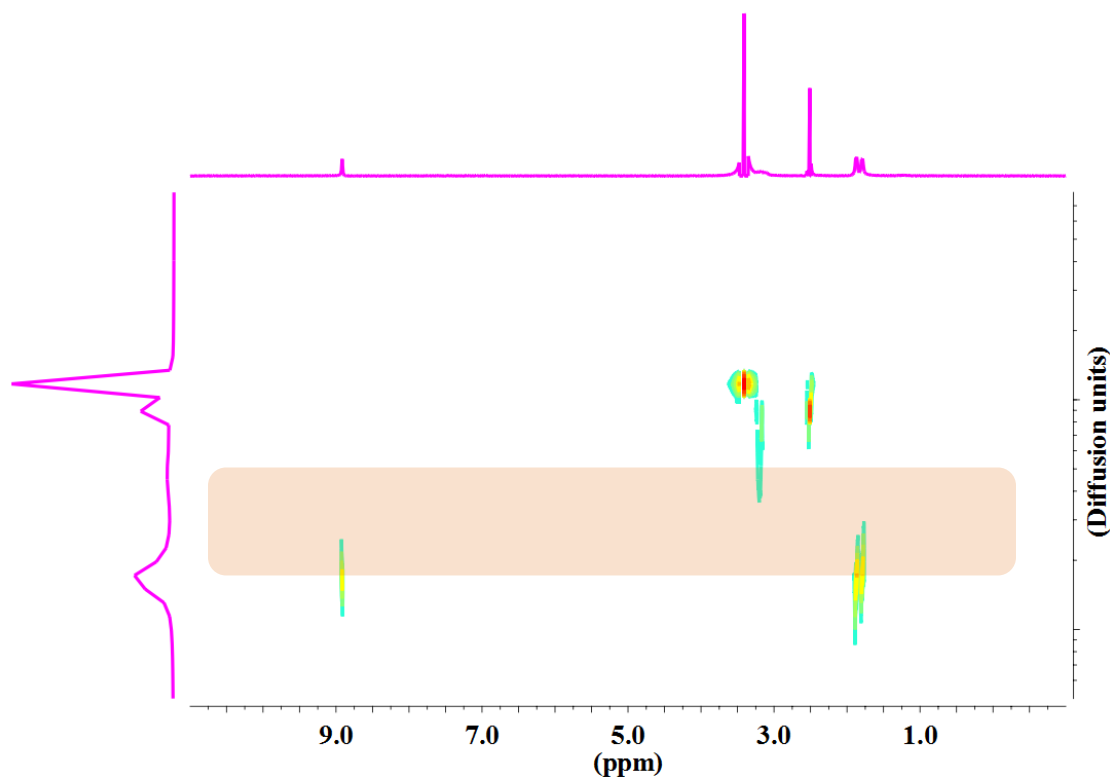


Figure A3.16: ¹H-2D-DOSY NMR spectrum of 6.

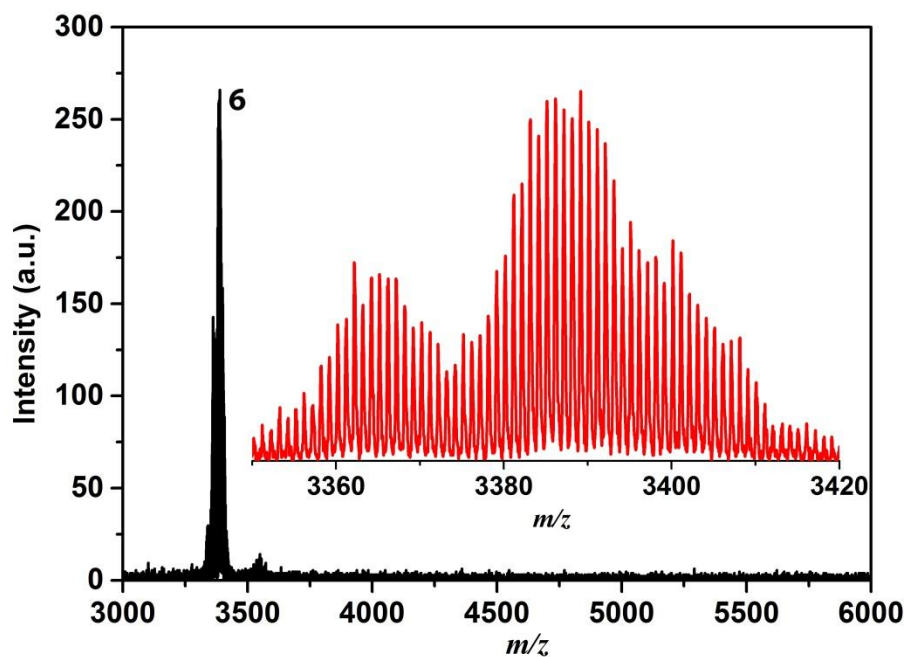


Figure A3.17: MALDI-TOF mass spectrum of **6**.

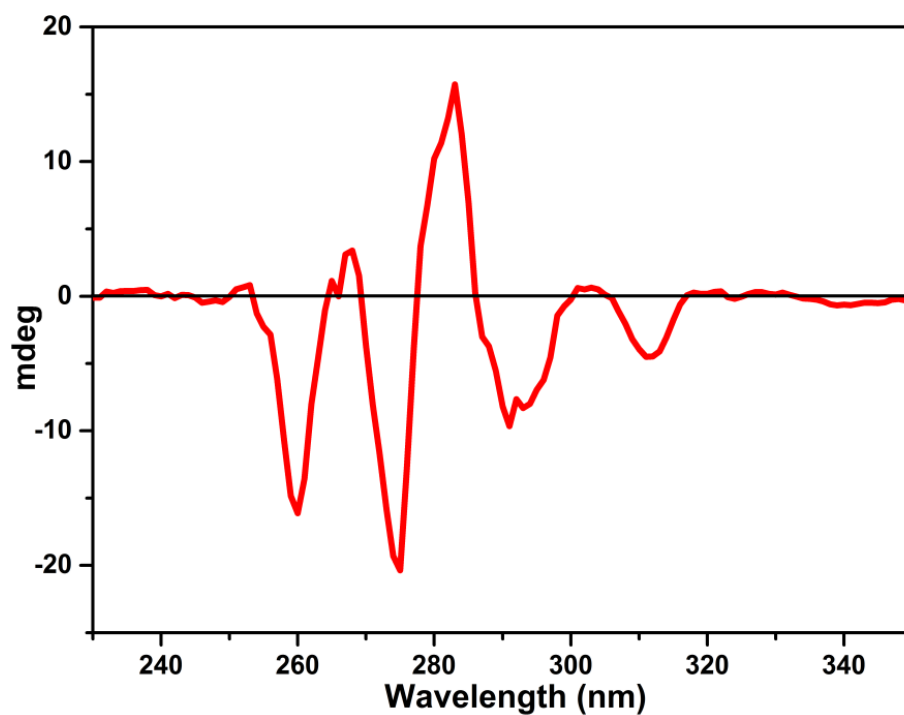


Figure A3.18: CD- spectrum of **6** in solution suggesting the chiral nature of the compound.

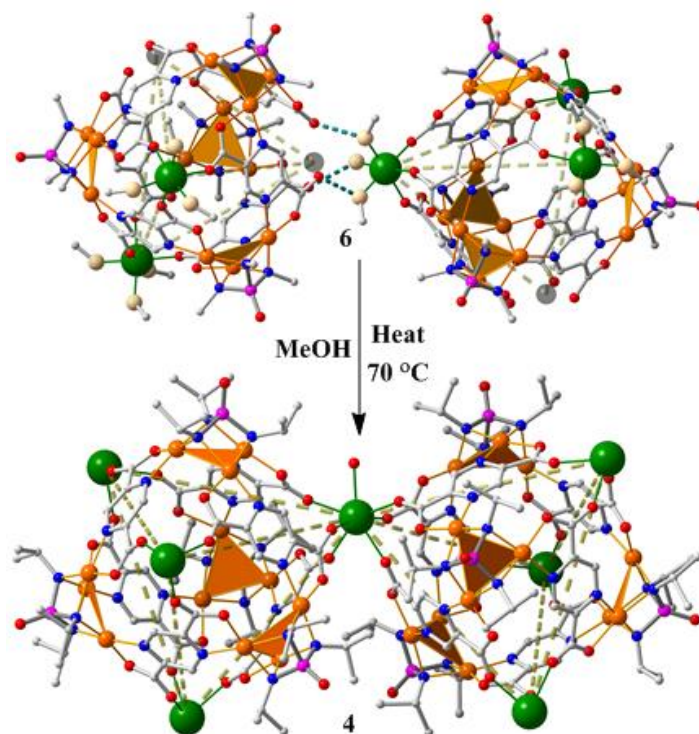


Figure A3.19: Formation of 3D-qtz framework **4** by condensation reaction of **6**. Green spheres represent Fe²⁺ ions.

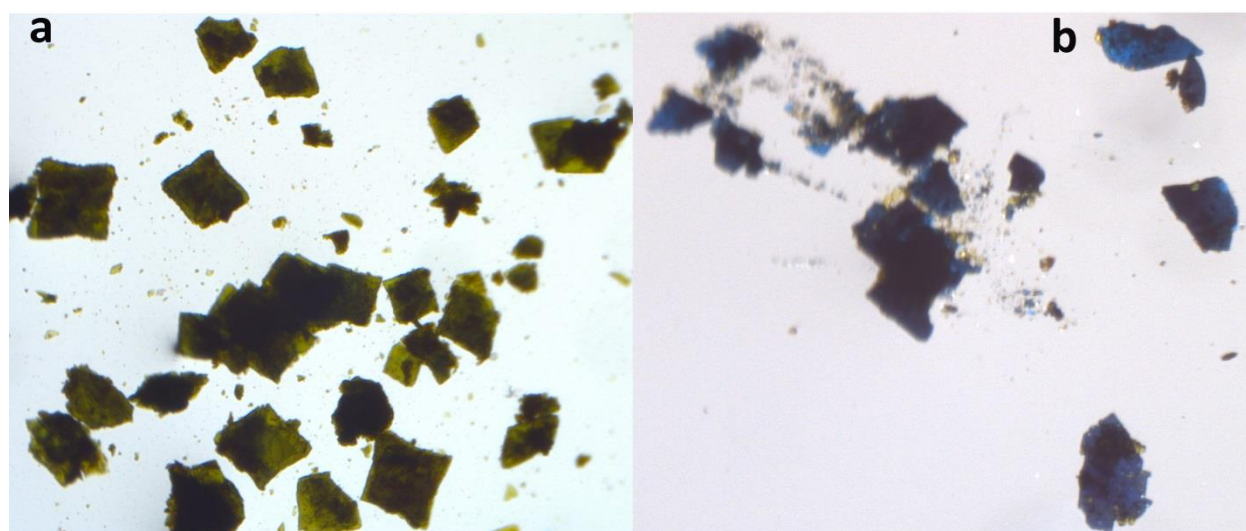


Figure A3.20: View of the single crystals of (a) **6** and (b) **7** obtained after 2 and 12 days of the reaction, respectively.

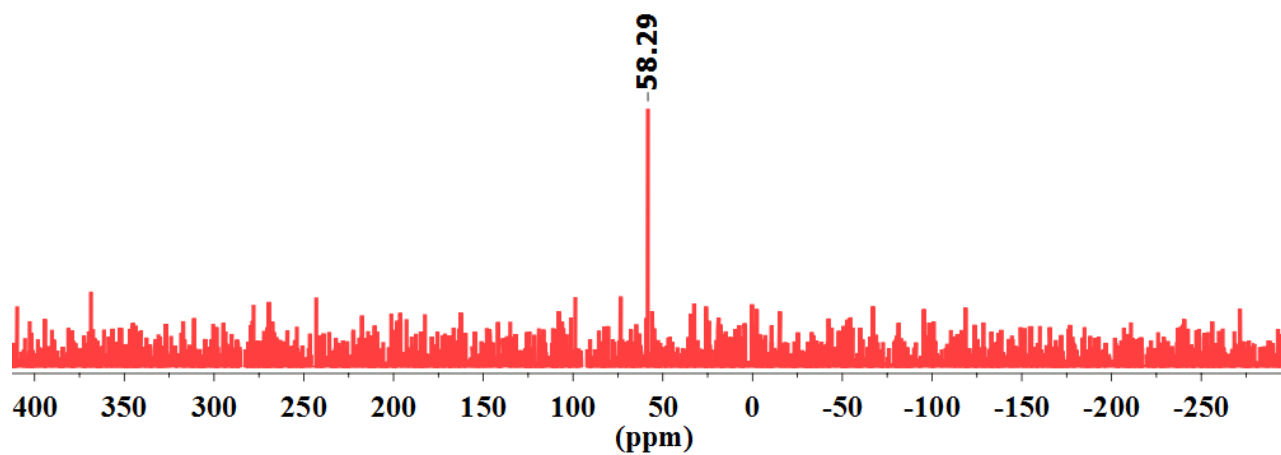


Figure A3.21: ^{31}P NMR spectrum of 7.

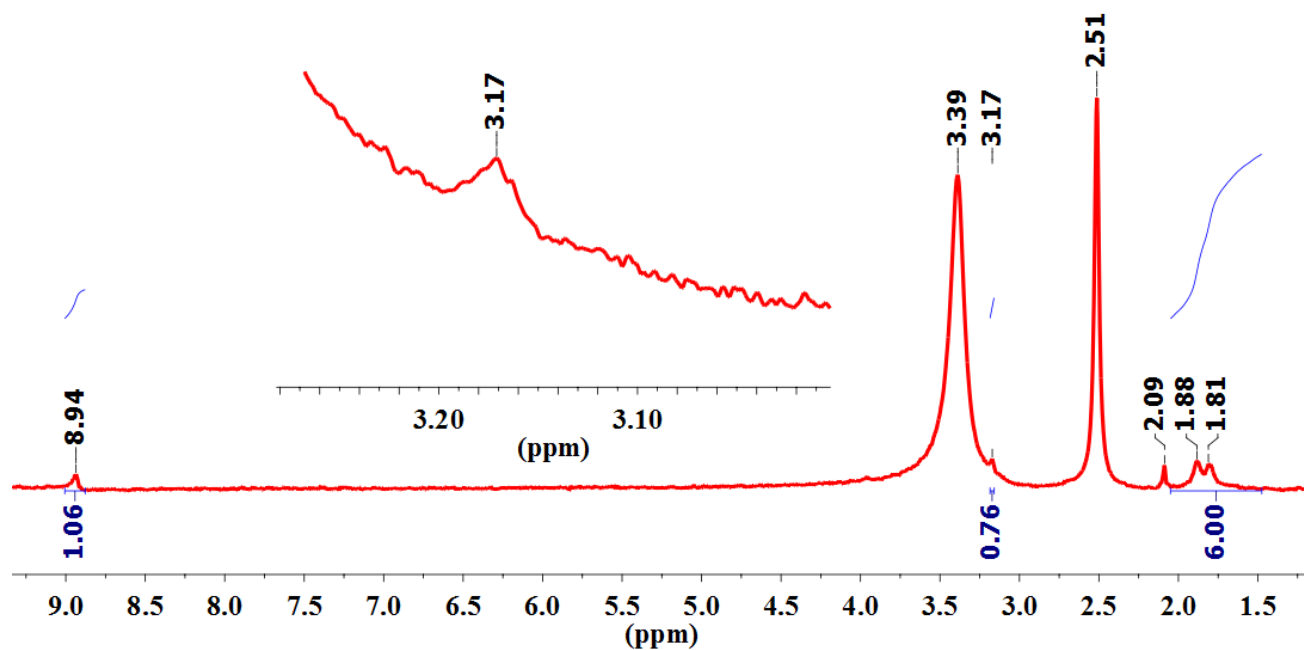


Figure A3.22: ^1H NMR spectrum of 7.

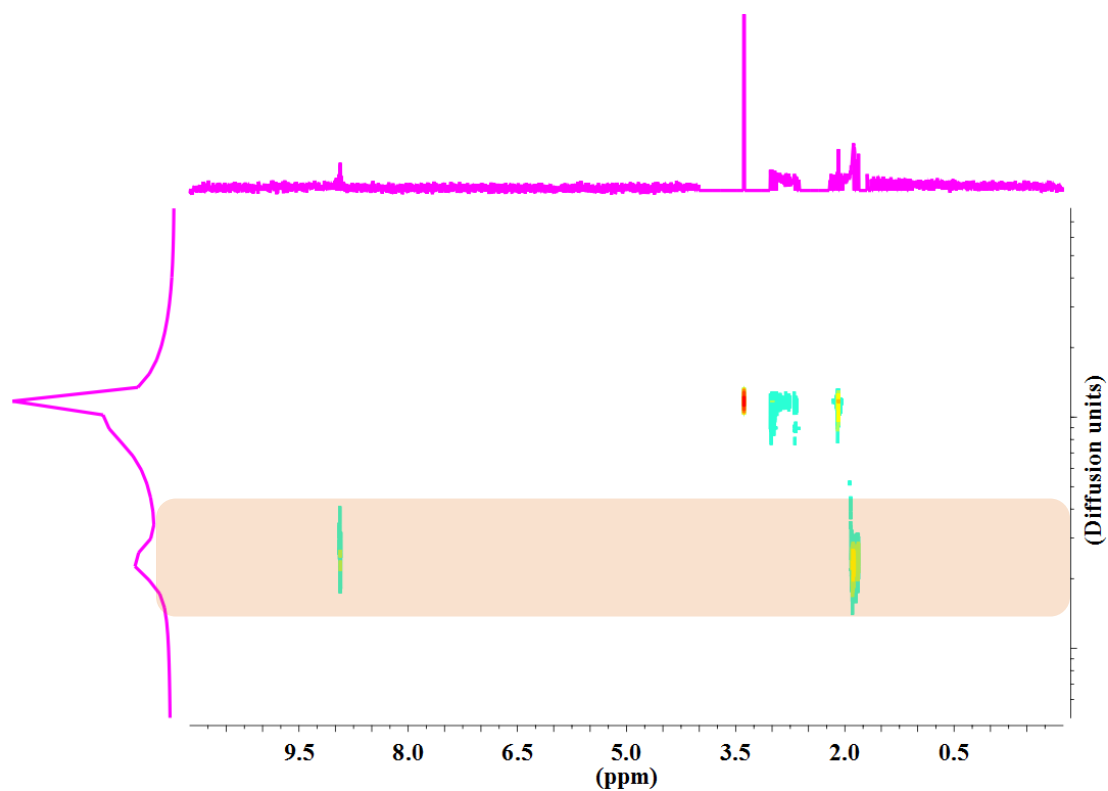


Figure A3.23: ^1H -2D DOSY NMR spectrum of **7**.

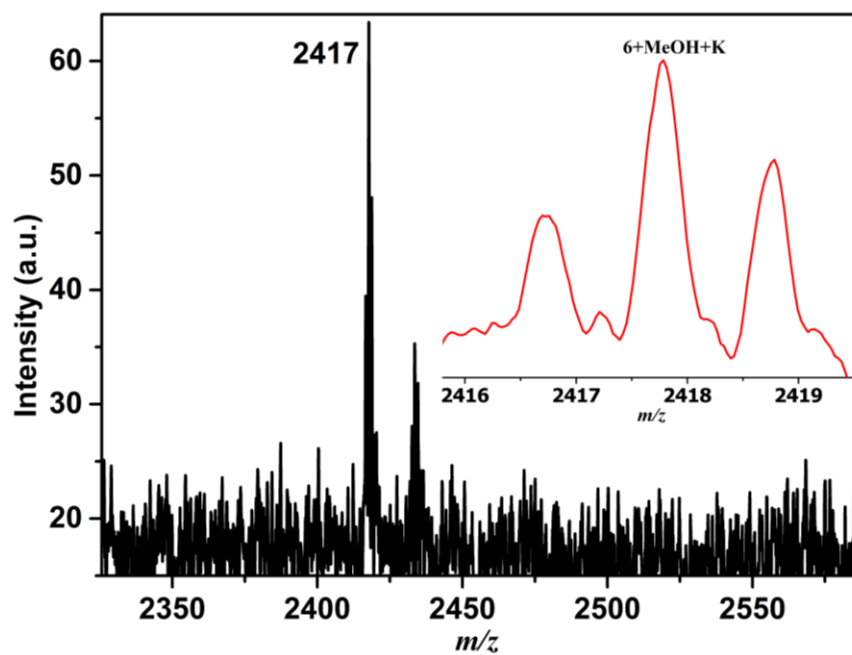


Figure S A3.4: MALDI-TOF (linear mode) mass spectrum of **7**.

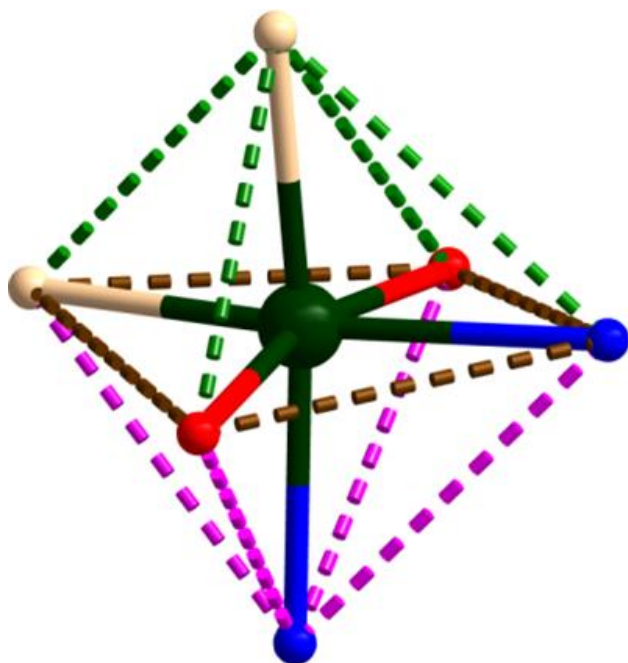


Figure A3.25: View of distorted octahedral geometry at Fe (II) center in **7**.

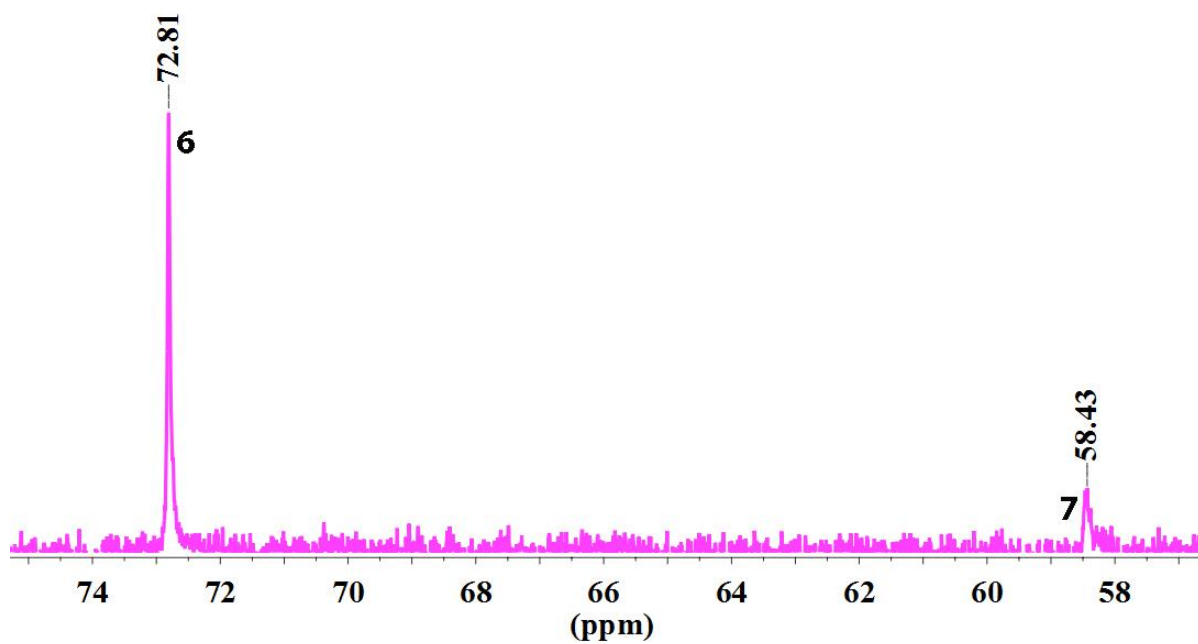


Figure A3.26: ^{31}P -NMR of the reaction mixture of **3** and $\text{Fe}(\text{OTf})_2$ after 4 days showing the peaks corresponding to the phosphorus centers at **6** and **7**.

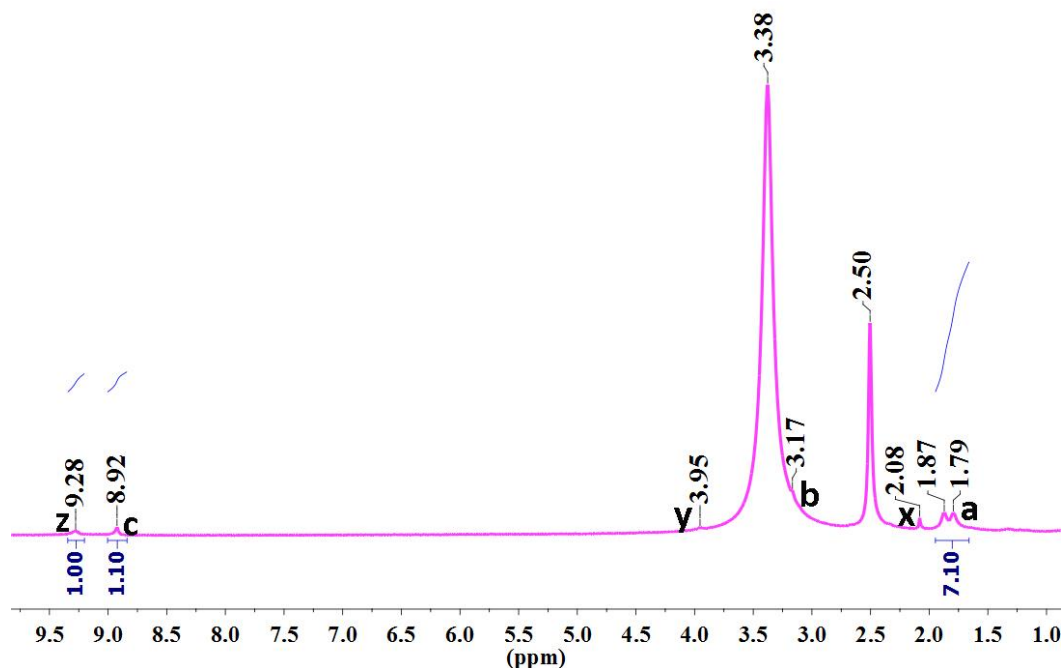


Figure A3.27: ^1H NMR of the reaction mixture of **3** and $\text{Fe}(\text{OTf})_2$ after 4 days showing the peaks corresponding to the protons due to **6** (peaks a, b and c) and **7** (peaks x, y and z).

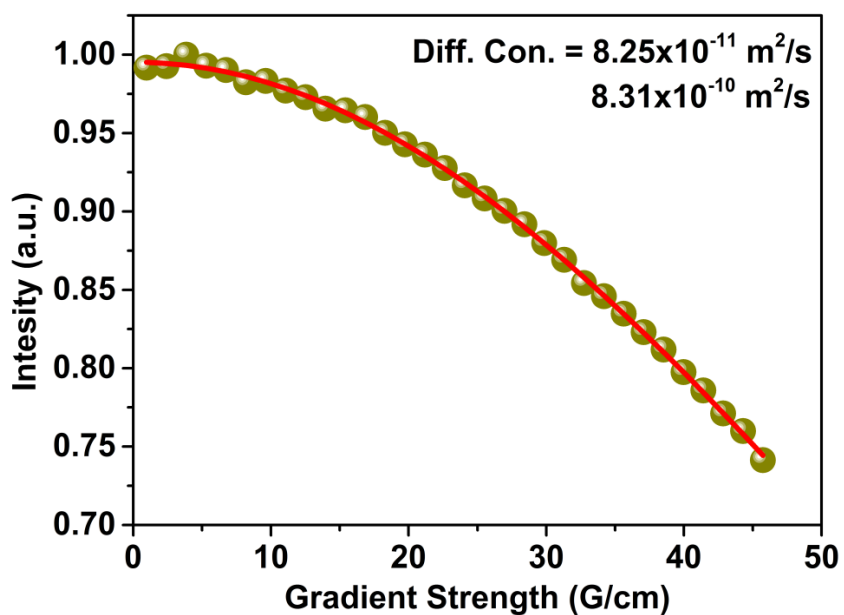


Figure A3.28: Plot of the integrated decay profile vs. gradient strength showing the diffusion coefficients due to **6** and **7** in the reaction mixture.

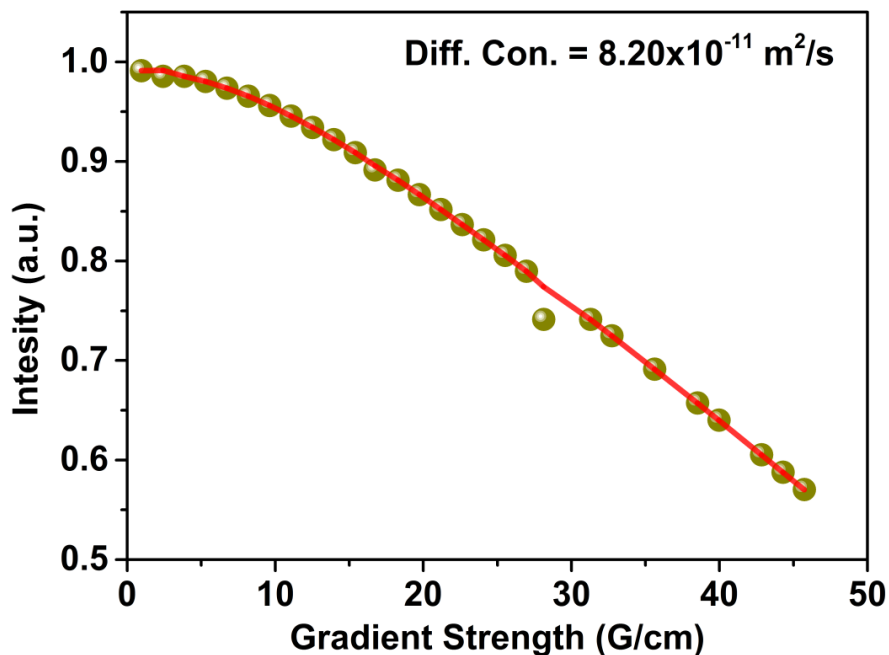


Figure A3.29: Plot of the integrated decay profile vs. gradient strength showing the diffusion coefficients of due to 6.

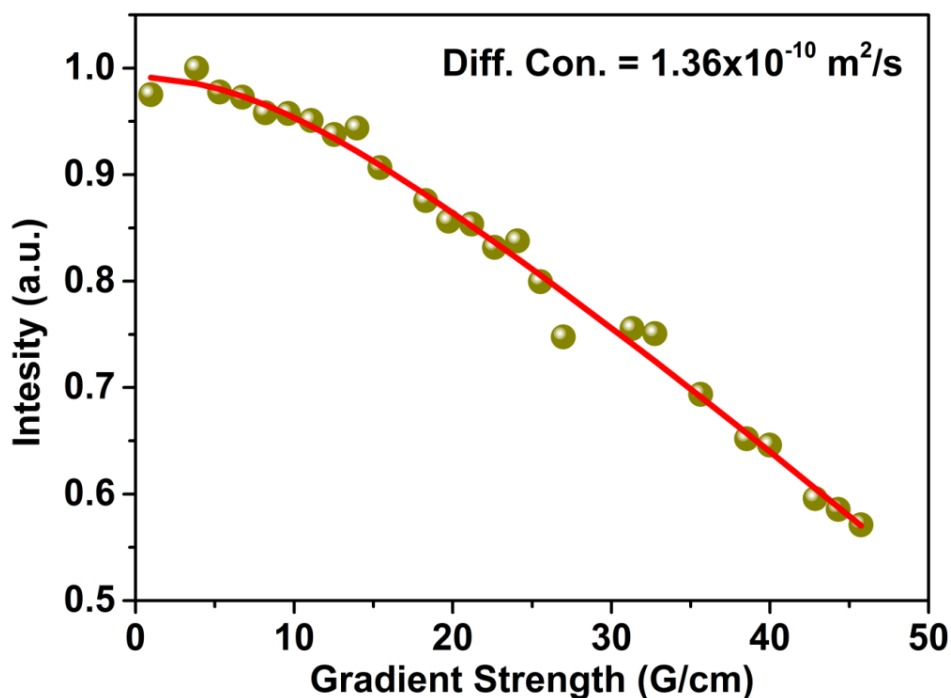


Figure A3.30: Plot of the integrated decay profile vs. gradient strength showing the diffusion coefficients due to 7.

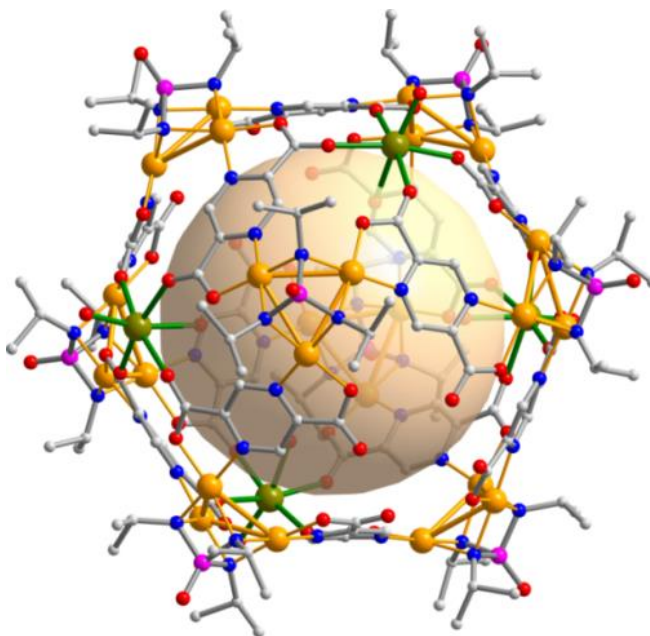


Figure A3.31: Crystal structure of **8**: beige colored sphere represents the intrinsic cavity. The intrinsic cavity of this intermediate complex **8** was found to be 985.379 Å³ which is very close to that found in **3**.

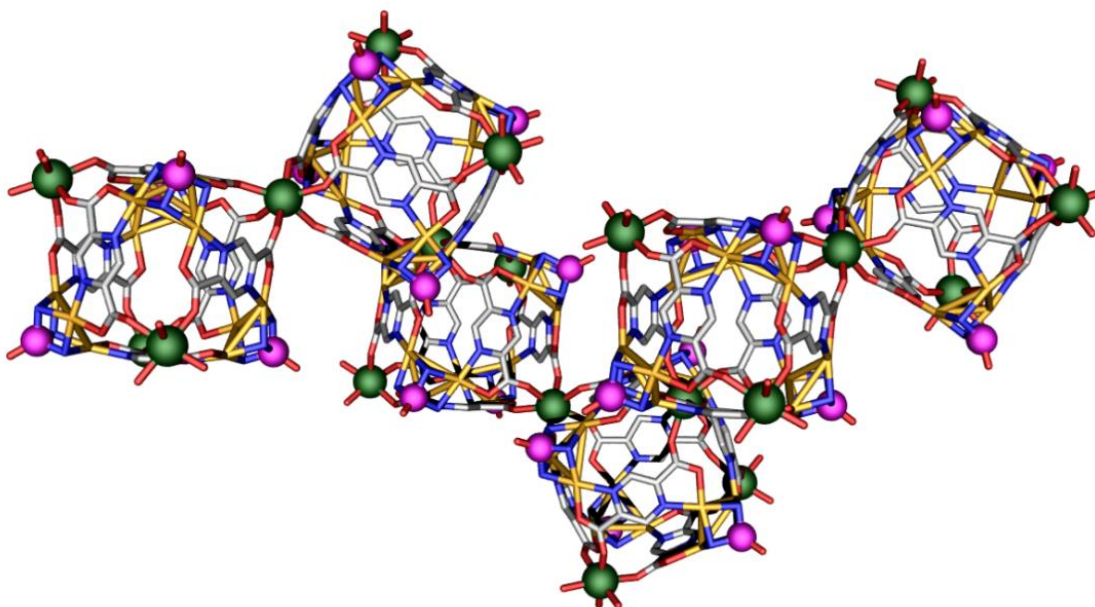


Figure A3.32: Molecular structure of the one dimensional coordination polymer **9** (hydrogens and the isopropyl groups of the tris-imido phosphate trianionic ligands are removed for clarity).

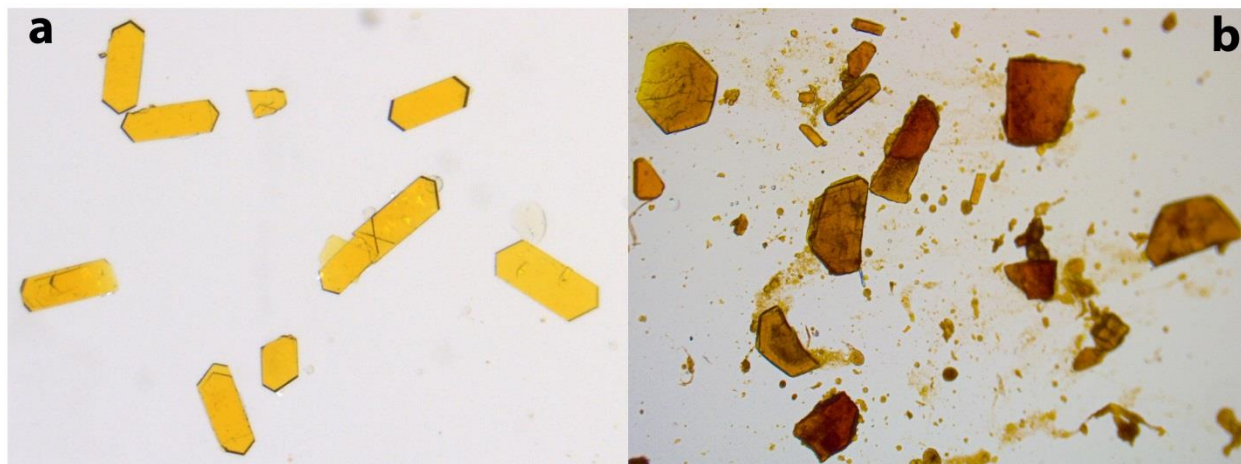


Figure A3.33: Crystal images showing the conversion of the cubic Assembly of **3** (a) to the three dimensional MOF **4**.

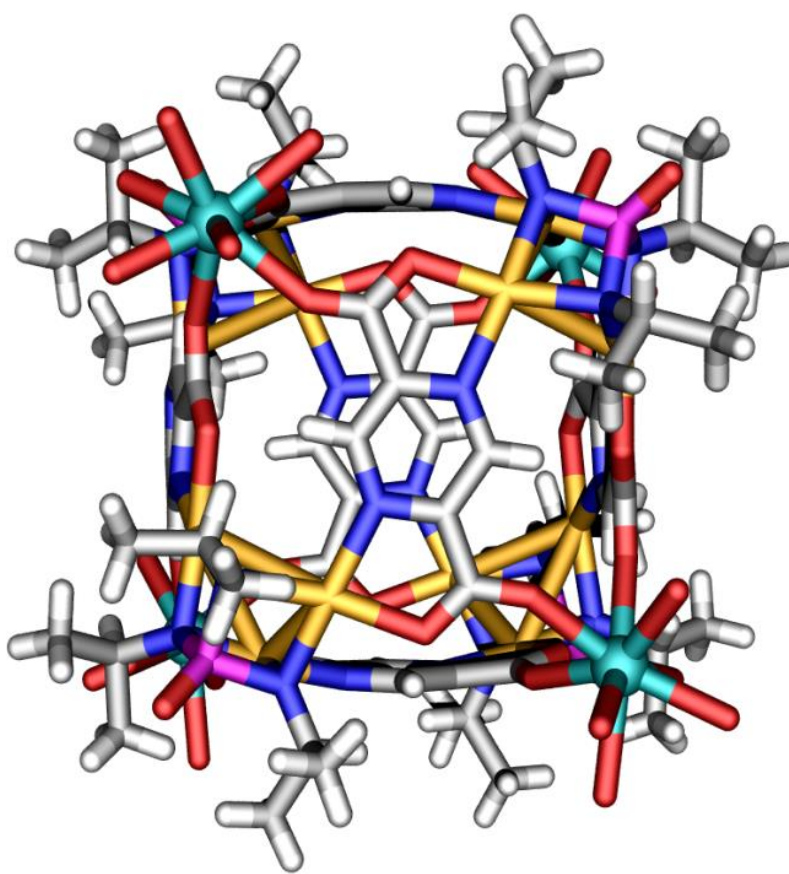


Figure A3.34: Crystal Structure of **10**.

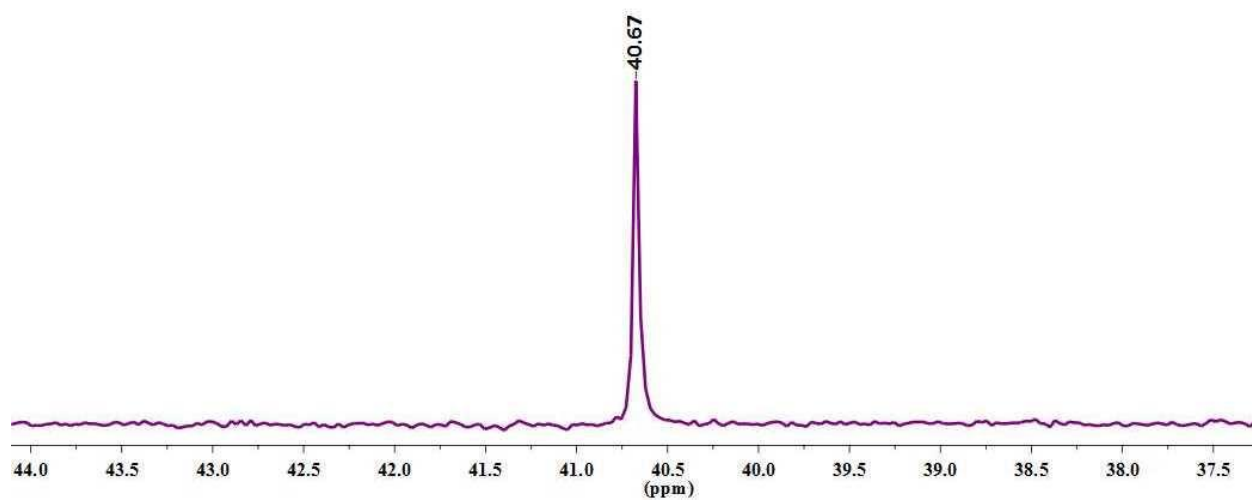


Figure 4A.1: ^{31}P NMR spectrum of ligand TPTA.

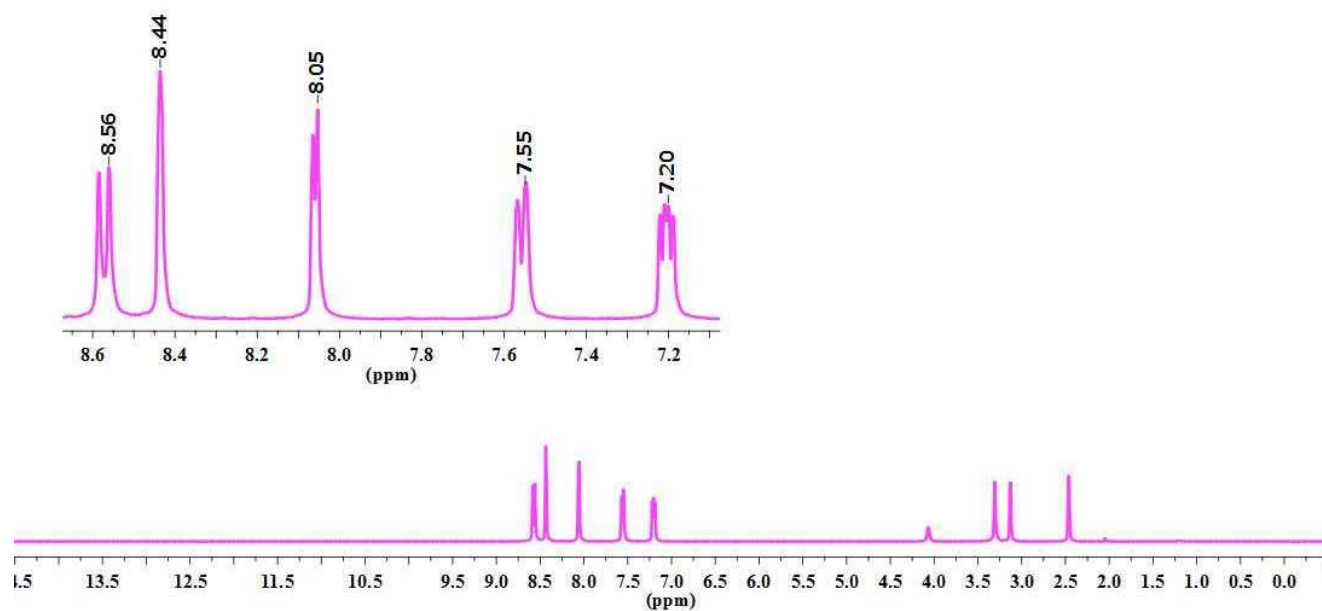


Figure 4A.2: ^1H NMR spectrum of the ligand TPTA.

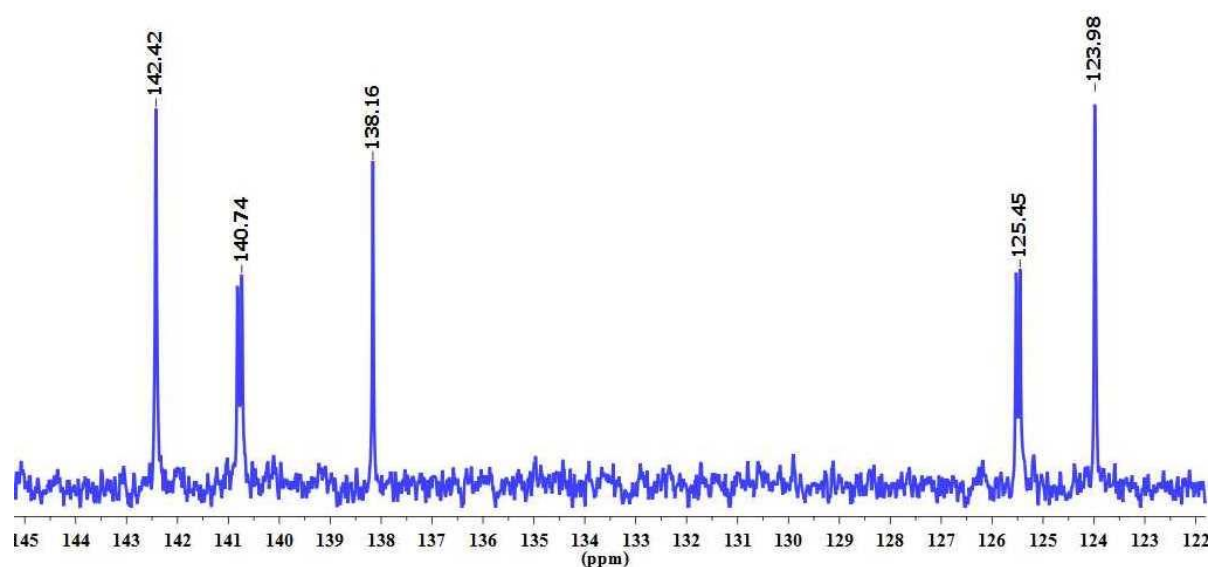


Figure 4A.3: ^{13}C NMR spectrum of ligand TPTA.

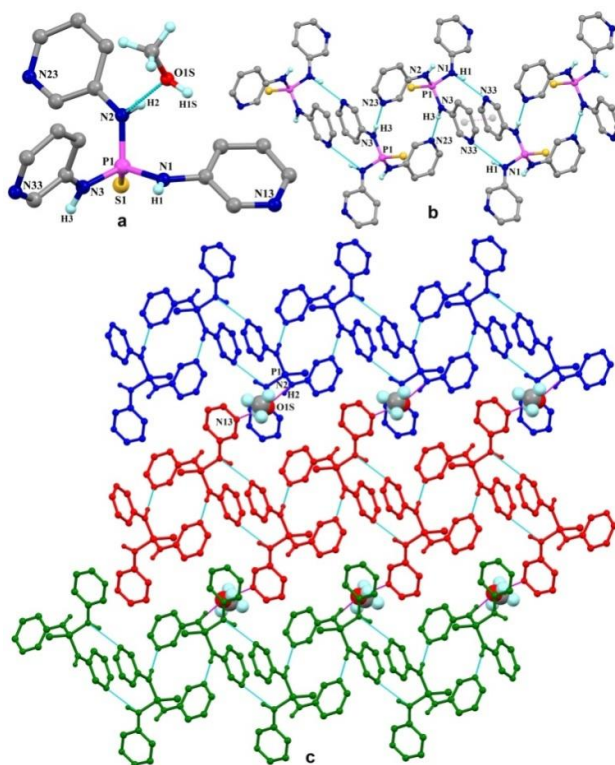


Figure 4A.4: Crystal structure of ligand TPTA: (a) single molecule, (b) showing hydrogen bonding through NH proton and $\text{N}_{\text{pyridyl}}$, (c) two dimensional network formed by the hydrogen bonding.

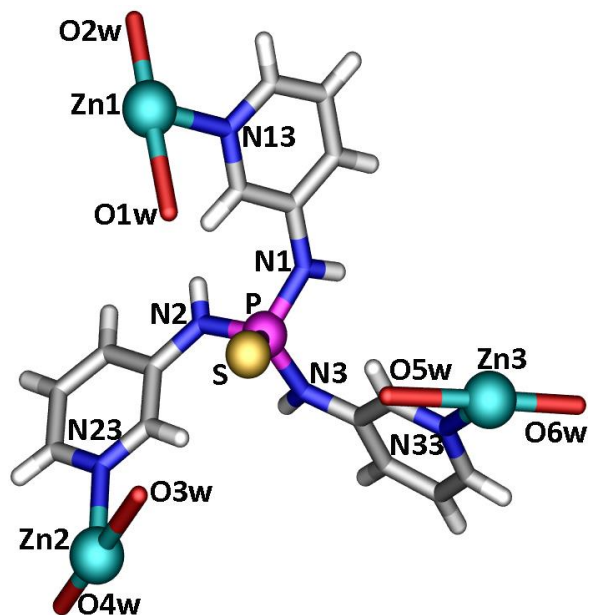


Figure 4A.5: Diagram showing the connection of TPTA ligand with zinc center in **11** and **12**.

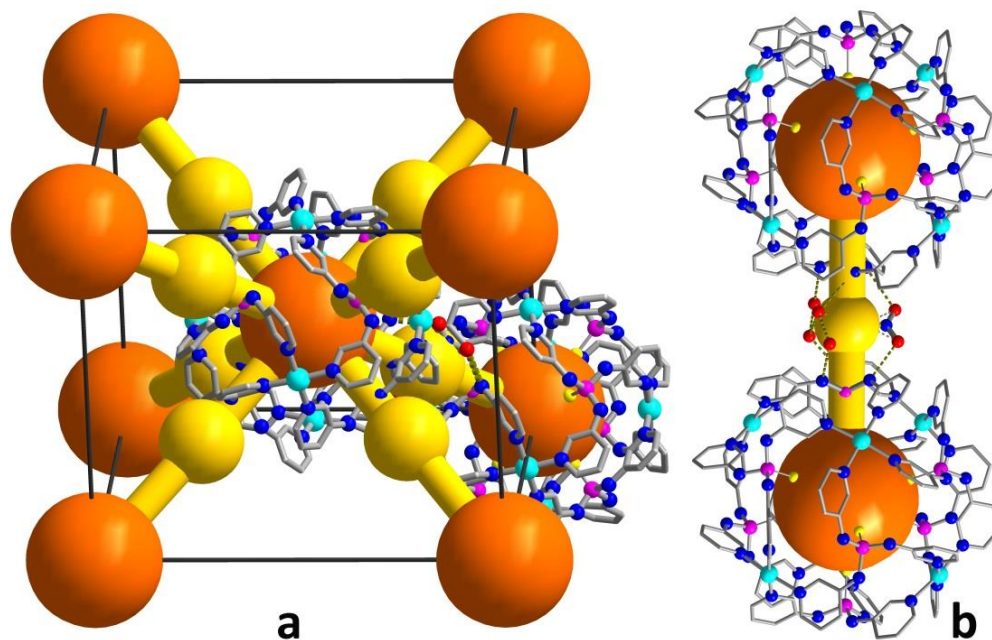


Figure 4A.6: Formation of an interesting H-bonded network in **11** involving the $\text{P}(\text{NH})_3$ units and ordered molecules of solvated water and nitrate ions. These interactions were found at all the eight $\text{P}(\text{NH})_3$ units of the cage.

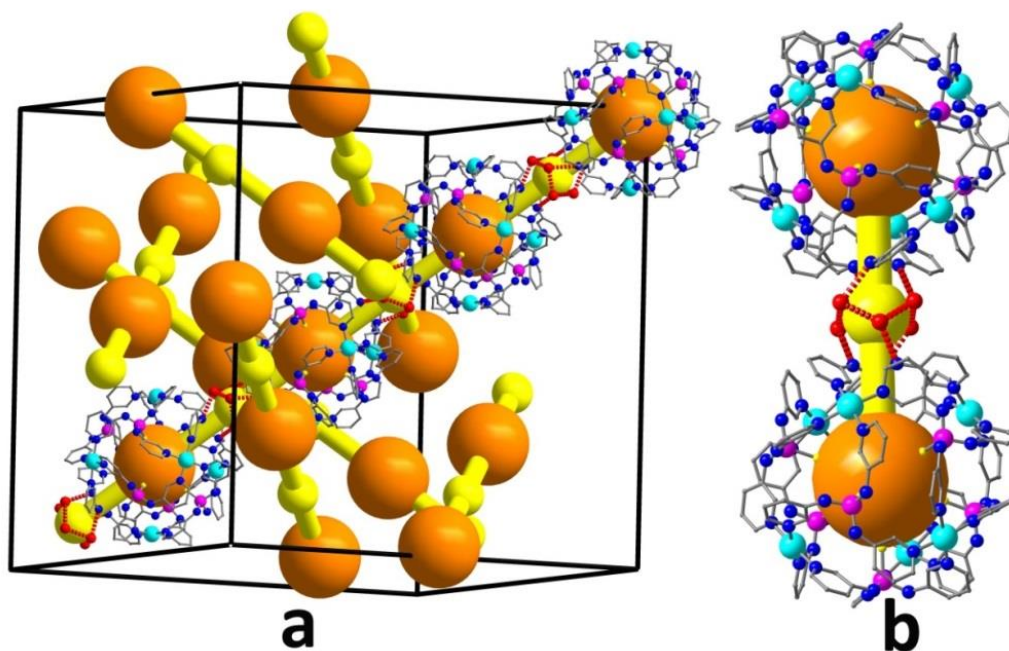


Figure 4A.7: Formation of an interesting water hexamer in **12** that links two cages via $\text{P}(\text{NH})_3$ units, forming linear chains of connected cages throughout the crystal. The other $\text{P}(\text{NH})_3$ groups are linked by disordered perchlorates.

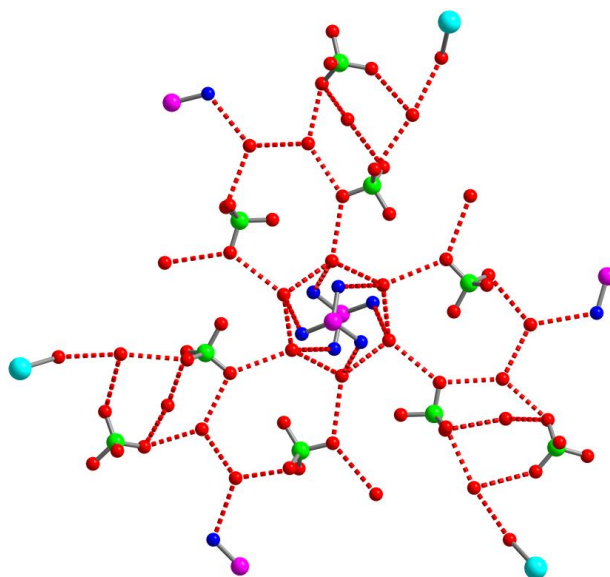


Figure 4A.8: Close view of the H-bonding of the water hexamer in **12** with the two adjacent $\text{P}(\text{NH})_3$ units and ordered part of the perchlorate anions.

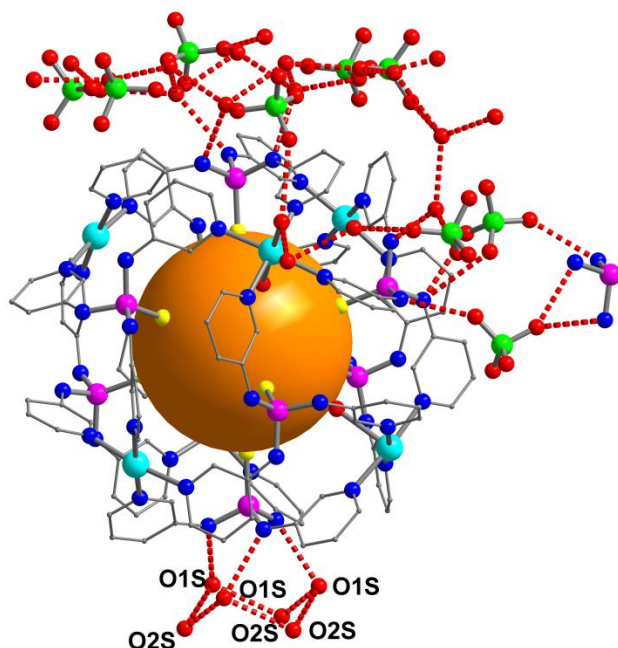


Figure 4A.9: Arrangement of ordered and disordered perchlorate anions around a single cage core in **12** that are H-bonded with six $\text{P}(\text{NH}_3)_3$ units and solvate molecules.

Table 4A.1: Hydrogen bond table for **TPTA**, **11** and **12**

Compound	D-H...A	d(H...A) Å	d(D...A) Å	$\angle(\text{DHA})^\circ$
TPTA	N(1)-H(1)...N(33)#1	2.23	2.9926(16)	144.6
	N(2)-H(2)...O(1S)	1.91	2.7703(15)	164.6
	N(3)-H(3)...N(23)#2	2.09	2.9675(16)	173.4
	O(1S)-H(1S)...N(13)#3	1.92	2.7577(16)	172.4
	#1 -x+2,-y+1,-z+1 #2 -x+1,-y+2,-z+1 #3 -x+2,-y+1,-z+2			
11	N(2)-H(2)...O(103)#1	2.10	2.942(14)	165.5
	N(3)-H(3)...O(11)	2.06	2.885(15)	161.7
	N(4)-H(4)...O(13)#2	2.03	2.890(13)	173.4
	N(5)-H(5)...O(101)#3	2.09	2.925(10)	164.9

Appendix 4

	N(6)-H(6)...O(104)#42.06	2.909(13)	167.3
	#1 -y+3/2,x+1/2,z+1/2 #2 -x+1/2,-y+3/2,z-1/2		
	#3 y-1/2,-x+3/2,z-1/2 #4 y+1/2,-x+3/2,z-1/2		
12	N(1)-H(1)...O(2S)#1 2.05	2.910(12)	163.7
	N(2)-H(2)...O(5S) 2.08	2.938(11)	165.4
	N(3)-H(3)...O(6S) 2.15	2.966(18)	153.9
	N(4)-H(4)...O(9A)#2 2.17	3.045(18)	173.4
	N(4)-H(4)...O(10A)#22.54	3.14(3)	126.6
	N(4)-H(4)...O(10B)#22.03	2.85(3)	154.1
	N(5)-H(5)...O(13A)#32.02	2.88(3)	163.4
	N(5)-H(5)...O(13B)#32.06	2.914(18)	164.2
	N(7)-H(7)...O(14A)#41.92	2.79(2)	169.6
	N(7)-H(7)...O(14B)#4 2.26	3.12(3)	166.0
	N(7)-H(7)...O(15B)#4 2.54	3.24(4)	137.5
	C(56)-H(56)...O(13A)#5 2.56	3.29(3)	133.3
	N(6)-H(6)...O(11A) 2.01	2.886(17)	171.2
	N(6)-H(6)...O(9B) 2.37	3.19(3)	154.4
	N(8)-H(8)...O(8S)#6 2.01	2.87(3)	166.0
	#1 -x+1,y+1/2,-z+3/2 #2 z-3/4,-y+7/4,-x+5/4		
	#3 -x+1/4,z+1/4,-y+7/4 #4 y-1/2,-z+3/2,-x+1		
	#5 z-1/4,y-1/4,x+3/4 #6 -z+5/4,-y+7/4,x+3/4		

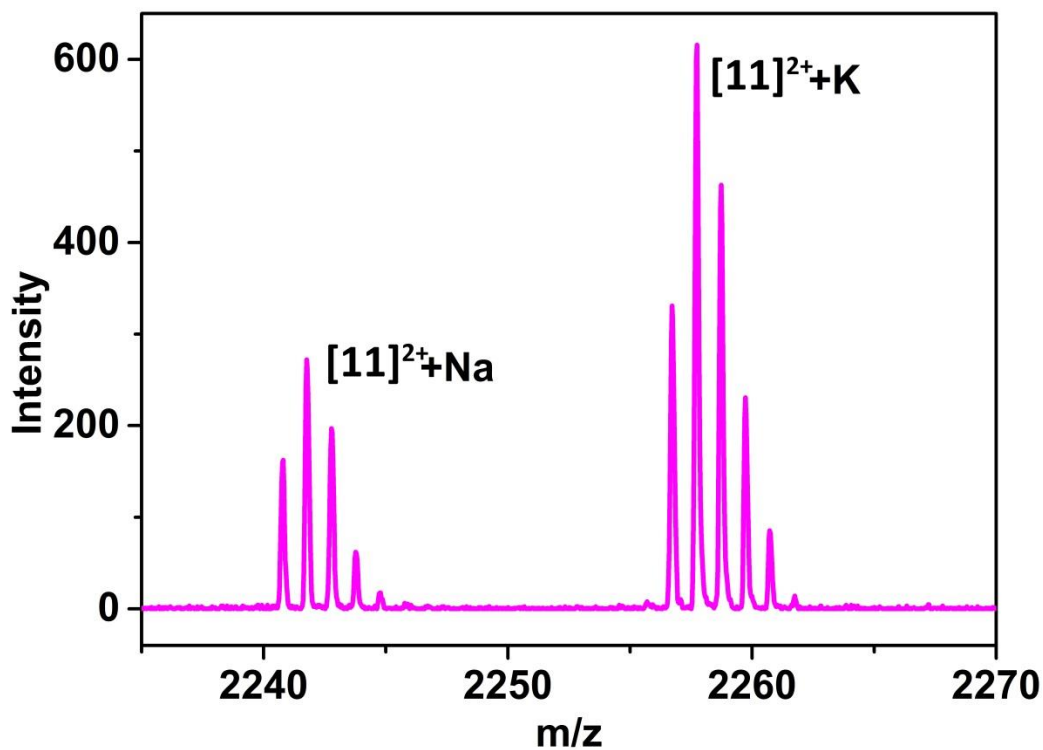


Figure 4A.10: MALDI-TOF mass spectrum of **11**.

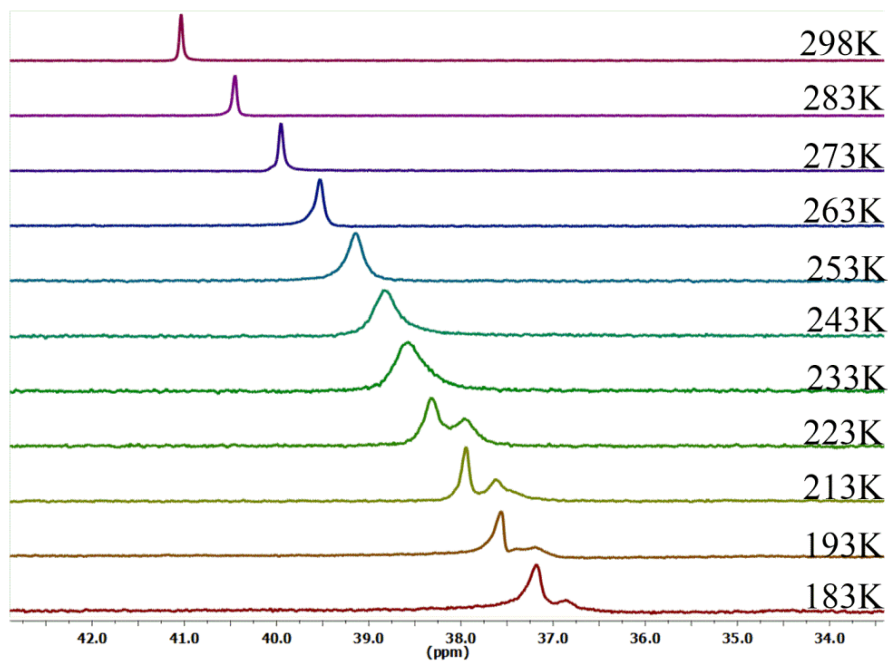


Figure 4A.11: Variable temperature ^{31}P NMR spectrum of **11** suggesting the presence of two enantiomers in the solution.

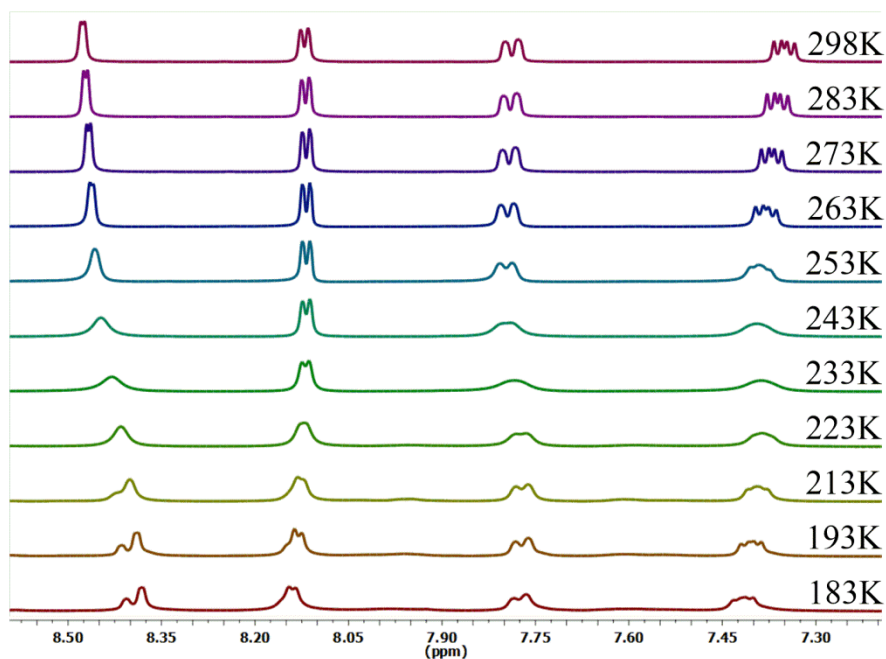


Figure 4A.12: Variable temperature ^1H NMR spectrum of **11**: Broadening in the signals suggesting the presence of two enantiomers in the solution.

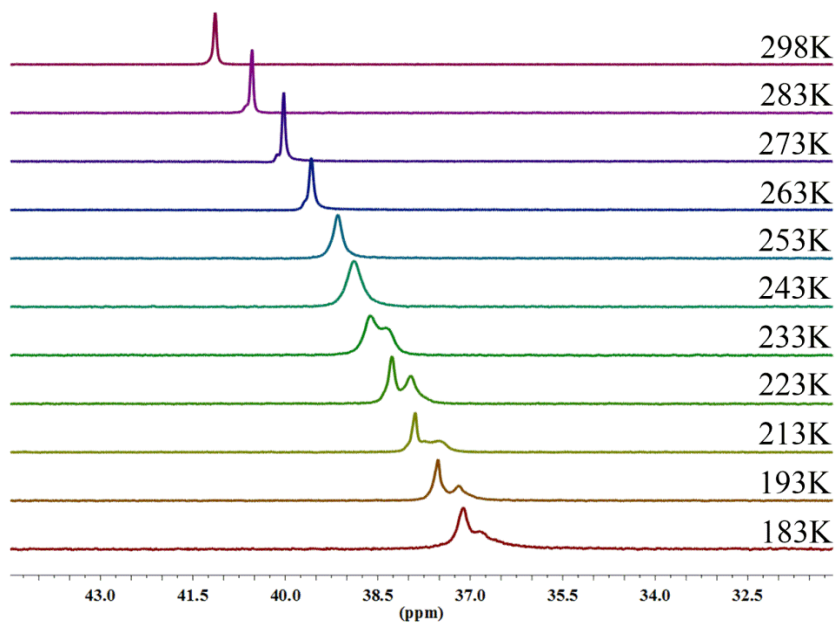


Figure 4A.13: Variable temperature ^{31}P NMR spectrum of **12** suggesting the presence of two enantiomers in the solution.

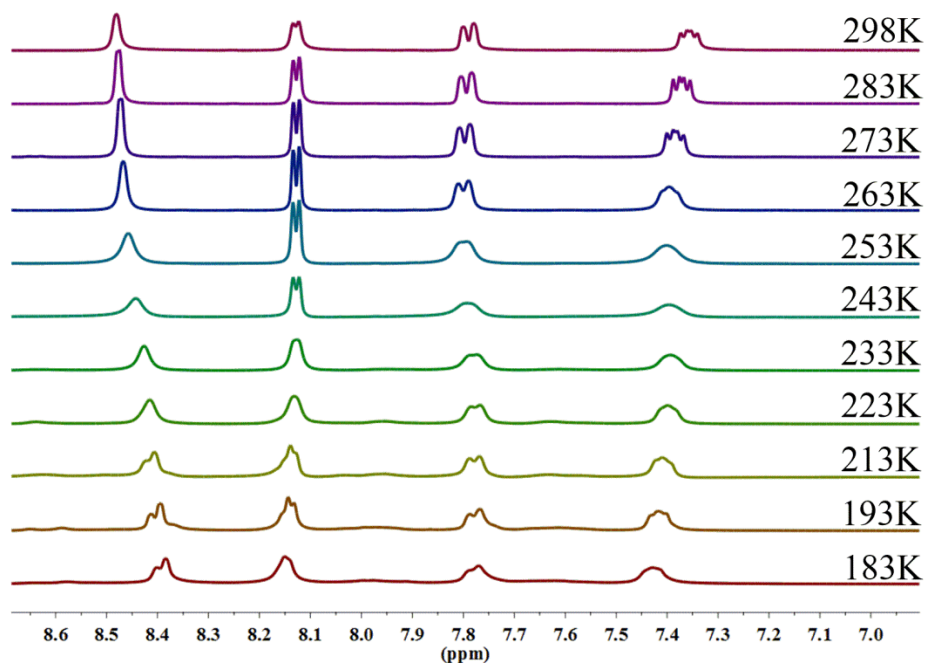


Figure 4A.14: Variable temperature ^1H NMR spectrum of **12**: Broadening in the signals suggesting the presence of two enantiomers in the solution

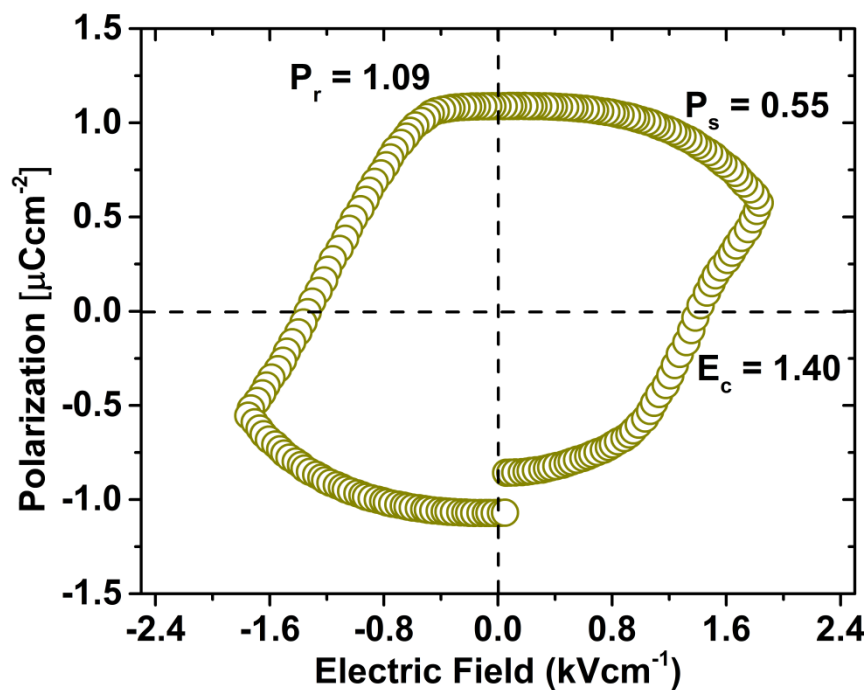


Figure 4A.15: Ferroelectric loop measurements on **11** at 1Hz.

Appendix 4

Table 4A.2: Current data obtained after subjecting the single crystal of **11** to an increasing dc field.

Applied Voltage	Current (μA)
1.5 V	45.69
5 V	46.11
9 V	46.18
15 V	46.27
21 V	46.29
30 V	46.51
45 V	46.64
55 V	46.65
75 V	46.70
85 V	46.75
95 V	46.78
125 V	46.40
225 V	46.56
325 V	46.70
425 V	46.86
525 V	46.90
825 V	47.01
925 V	47.11
1k V	47.16

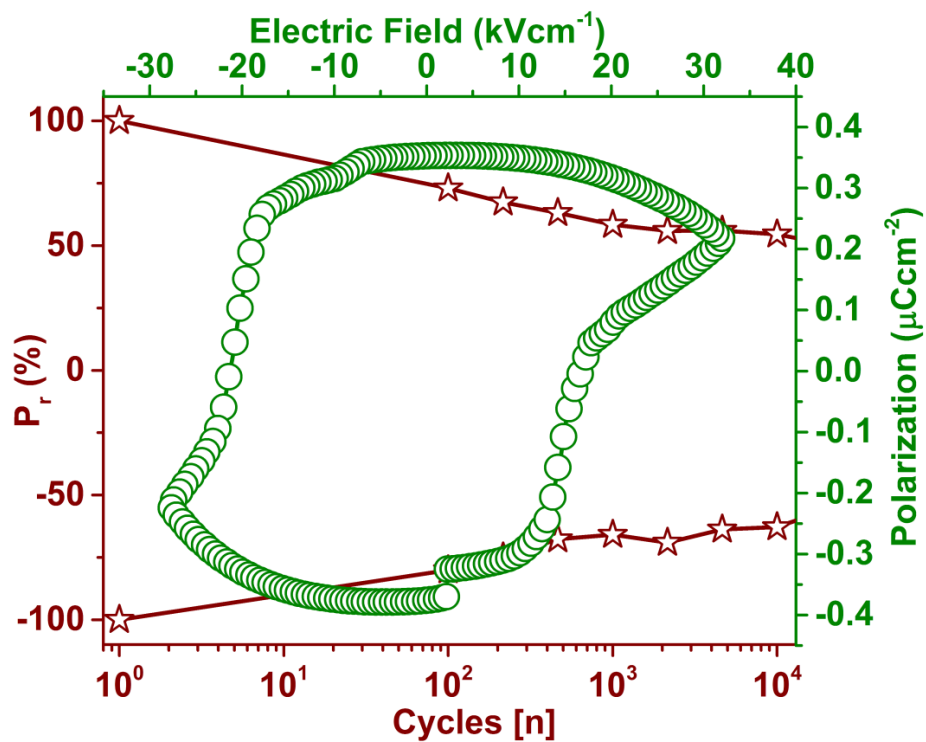
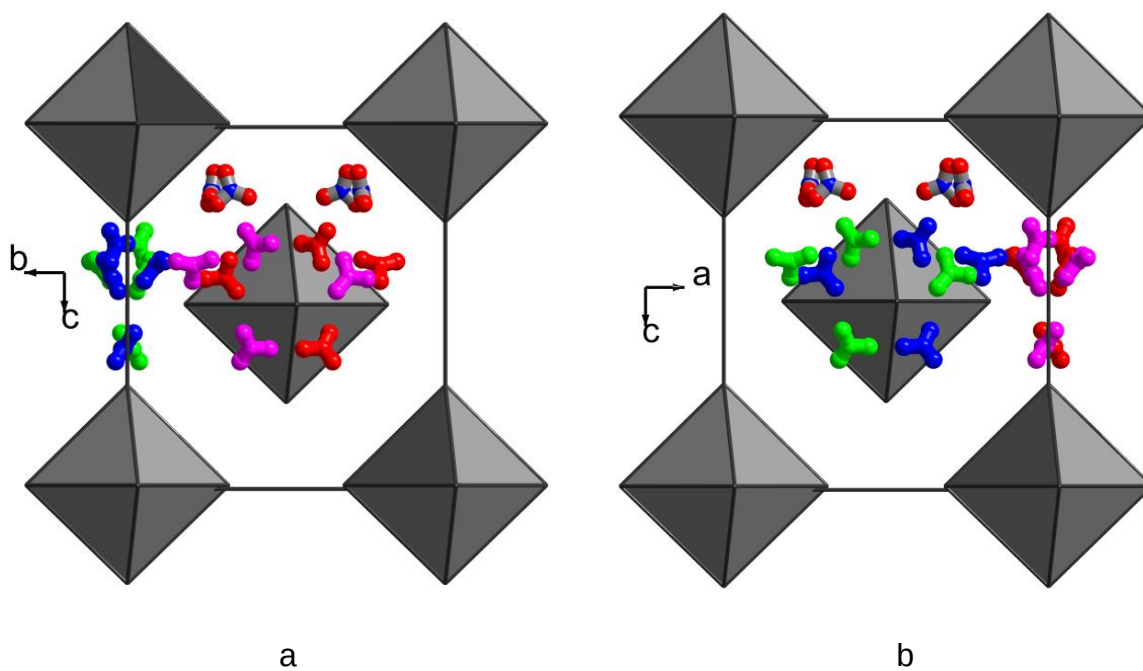


Figure 4A.16: Ferroelectric fatigue measurements on **11** and the corresponding P-E loop at 0.1Hz after 10^5 cycles.



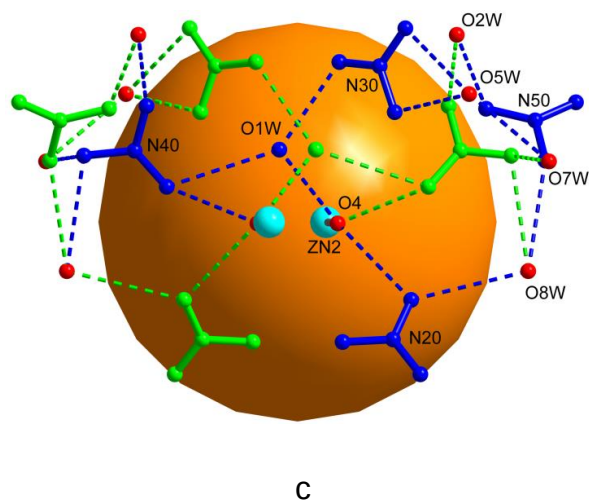


Figure 4A.17: Distribution of nitrate anions in **11** viewed along *a* (figure a) and *b* (figure b) axes within the framework of coordination polyhedra (depicted as grey octahedra, Zn ions mark the corners). The ordered nitrate ions have been shown in regular colours; N: Blue, O: Red, bonds: Grey (along *c* axis), disordered nitrates has been shown in different colours pink and red spheres (along *a*-axis) and blue and green spheres (along *b*-axis). (c) Closer view of the interaction of disordered nitrate ions with solvate water molecules in **11**. The orange sphere depicts the metal-organic cage.

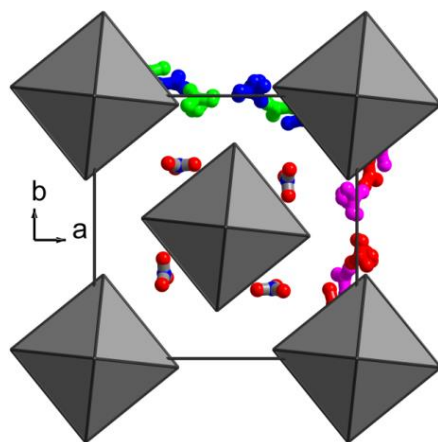


Figure 4A.18: Distribution of nitrate anions in **11** viewed along *c* axis (left) within the framework of coordination polyhedra (depicted as grey octahedra, Zn ions mark the corners). Disordered sets of nitrate ions are depicted in purple/red and blue/green, respectively

Appendix 4

Table 4A.3: Measurement of capacitance values on the single crystals of **11** along different axes at room temperature.

Crystal Dimensions (mm)		Frequency (Hz)	Capacitance (pF)		
			a-axis	b-axis	c-axis
Crystal I	1.54 × 1.88 × 1.48	100	183	269	20
		1000	90	120	11.7
		10000	43	42	8
		100000	15	14	5
		1000000	6	5	4
Crystal II	1.98 × 1.46 × 2.10	100	228	216	33
		1000	145	129	15
		10000	73	69	9
		100000	23	25	5
		1000000	5	5	4
Crystal III	1.26 × 1.03 × 2.62	100	123	104	51
		1000	60	59	25
		10000	28	27	12
		100000	10	10	6
		1000000	5	5	3
Crystal IV	1.56 × 1.00 × 2.10	100	152	104	21
		1000	86	75	9
		10000	58	25	5
		100000	25	17	4
		1000000	7	5	3

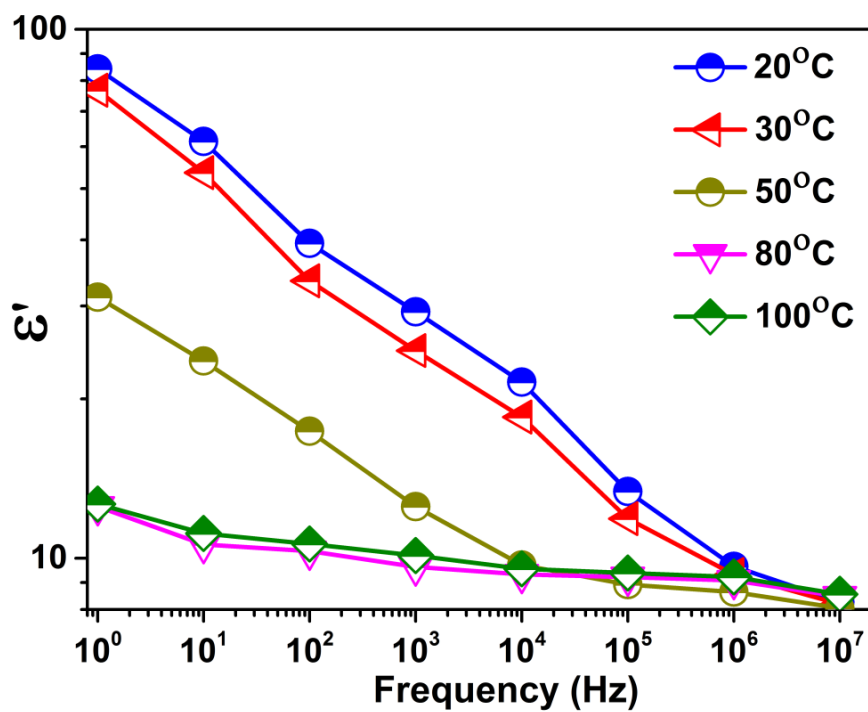


Figure 4A.19: Frequency dependent dielectric constant of **11** at various temperatures.

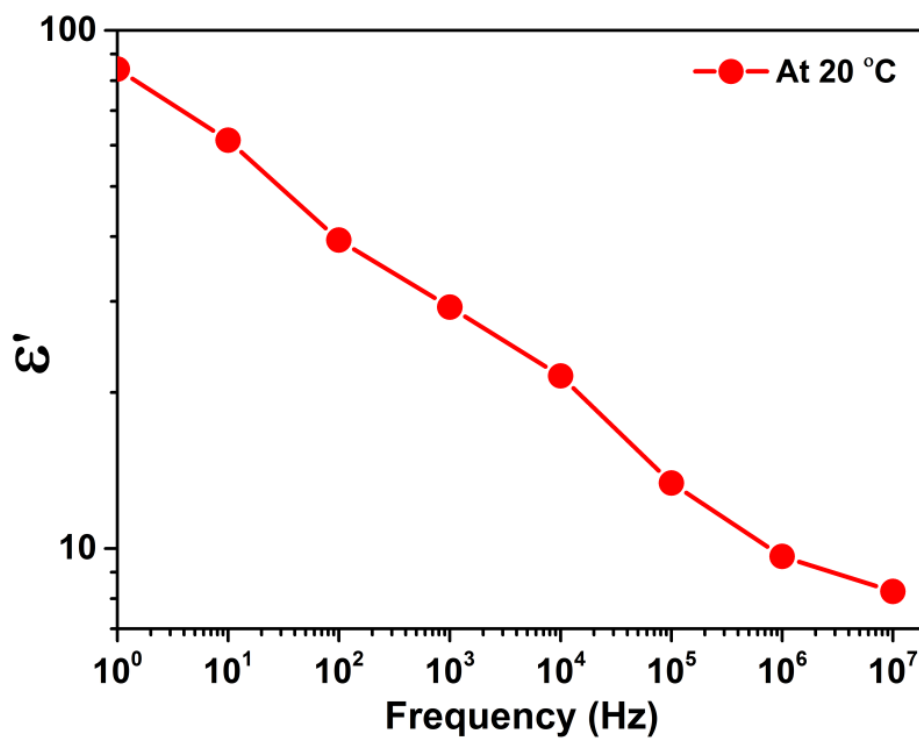


Figure 4A.20: Frequency dependent dielectric constant of **11** at 20 °C.

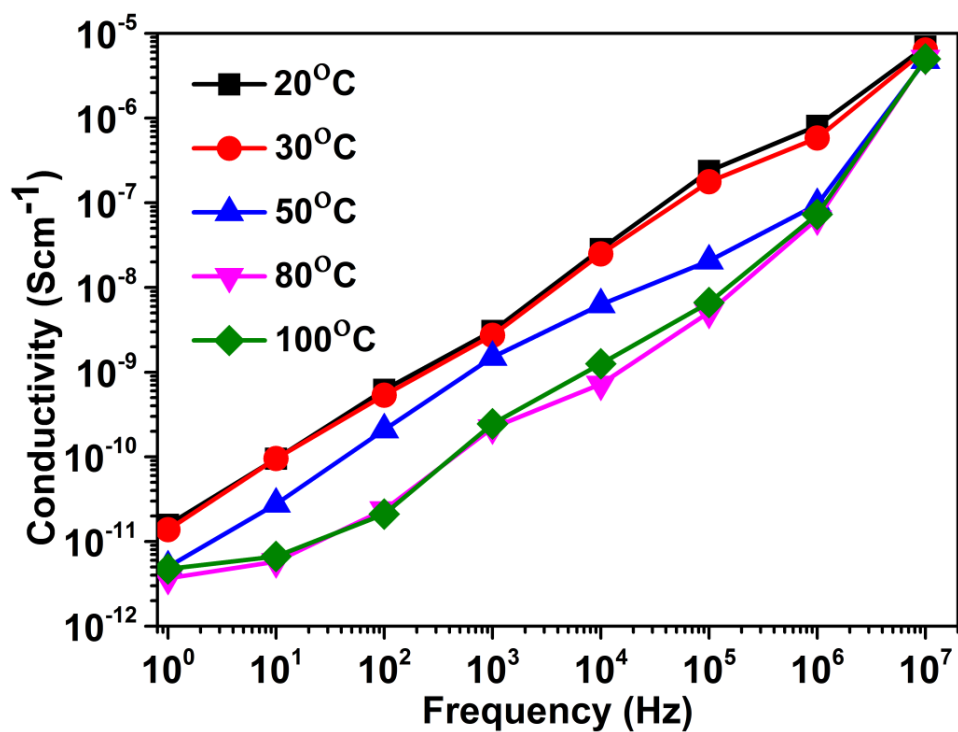


Figure 4A.21: Conductivity vs frequency plot for 11.

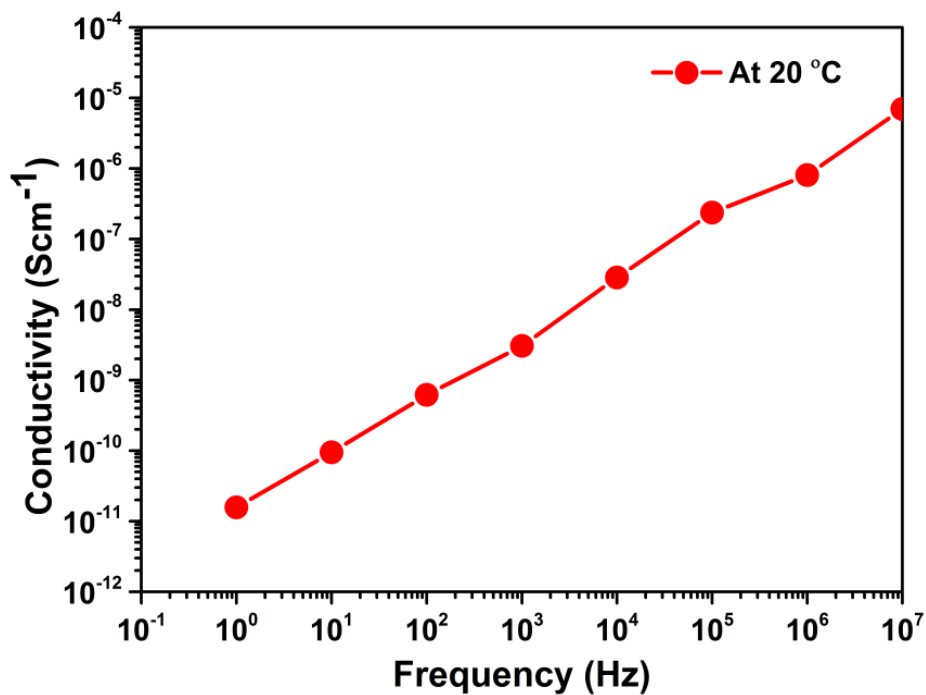


Figure 4A.22: Conductivity vs frequency plot for 11 at 20 °C.

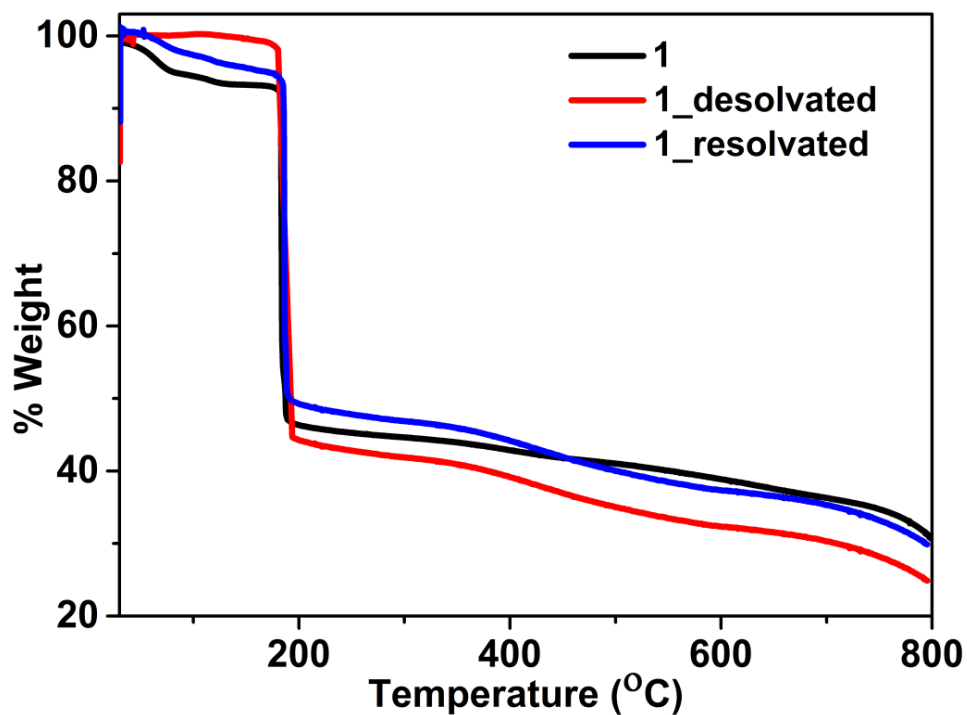


Figure 4A.23: Thermogravimetric analysis (TGA) plot for **11**, **11_{desolvated}** and **11_{resolvated}**.

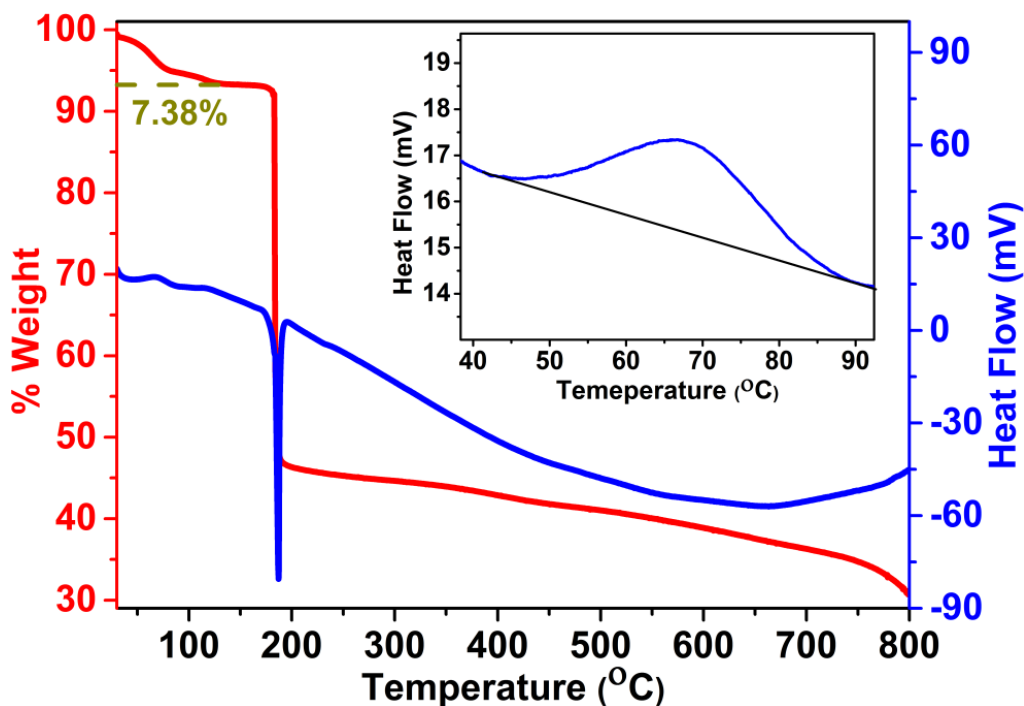


Figure 4A.24: TGA-DTA plot for **11**.

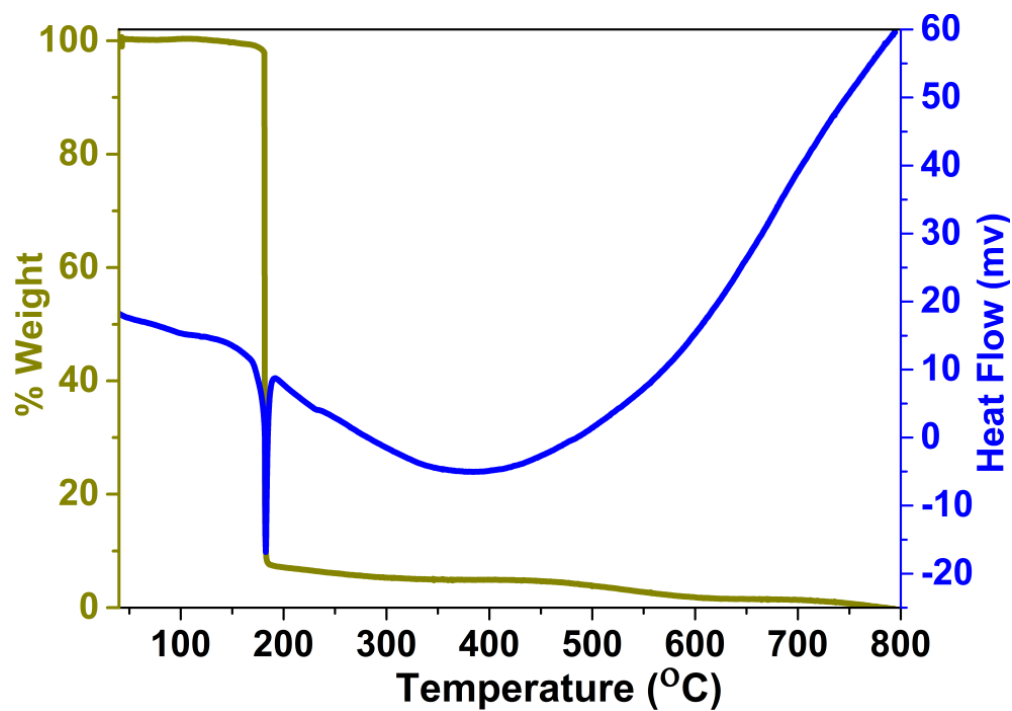


Figure 4A.25: TGA-DTA plot for **11**_{desolvated}.

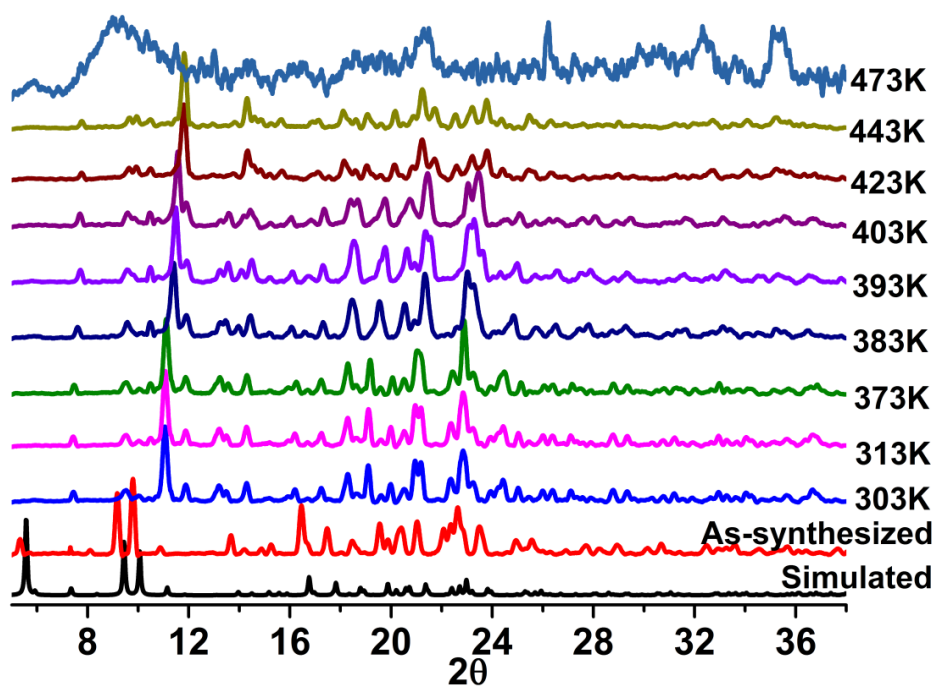


Figure 4A.26: Variable Temperature PXRD pattern of **11**. The crystallinity of the sample was retained up to 120 °C.

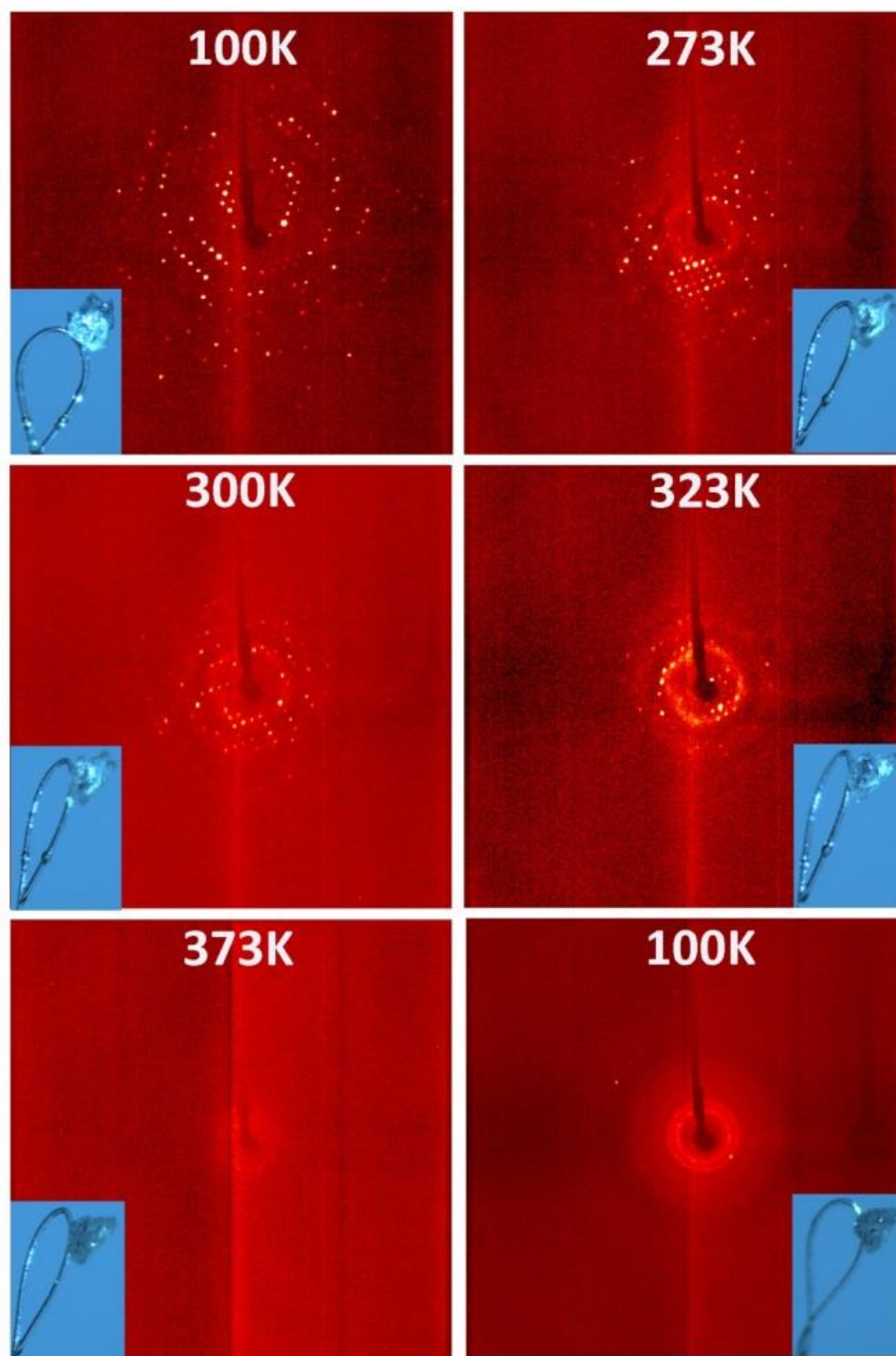


Figure 4A.27: Diffraction spots of the single crystal of **11** during the desolvation and resolution (the frame at the bottom right corner).

Table 4A.4: Unit cell parameter data for **11** at various temperatures

Compound	T (K)	a (Å)	c (Å)	V (Å ³)
11	100	21.12(9)	24.04(13)	11285
	273	21.47(10)	23.74(13)	10946
	298	21.35(7)	23.96(9)	10919
	323	21.37(7)	23.87(8)	10909

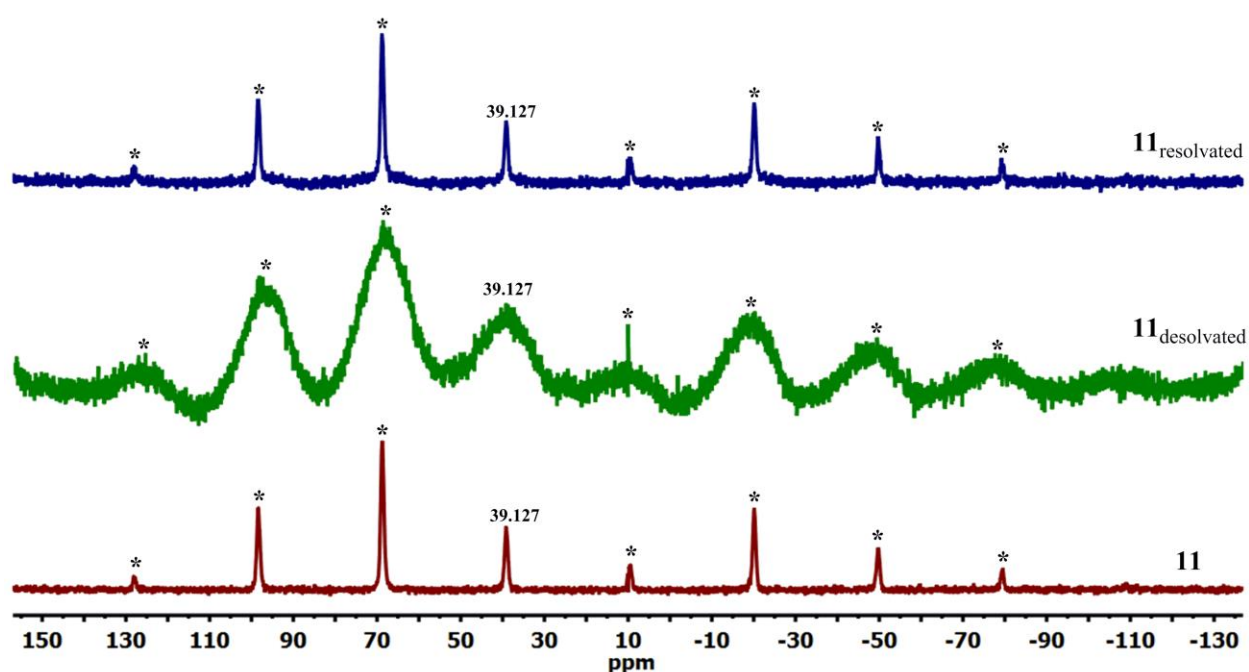


Figure 4A.28: ³¹P-NMR of **11** (brown), **11**_{desolvated} (green), and **11**_{resolvated} (blue). Peaks denoted with asterisks are spinning side bands.

Table 4A.5: Quadratic non-linear optical data.

Compound	SHG Intensity
11	30 mV
11 _{desolvated}	15 mV
11 _{resolvated}	35 mV
Urea	135mV

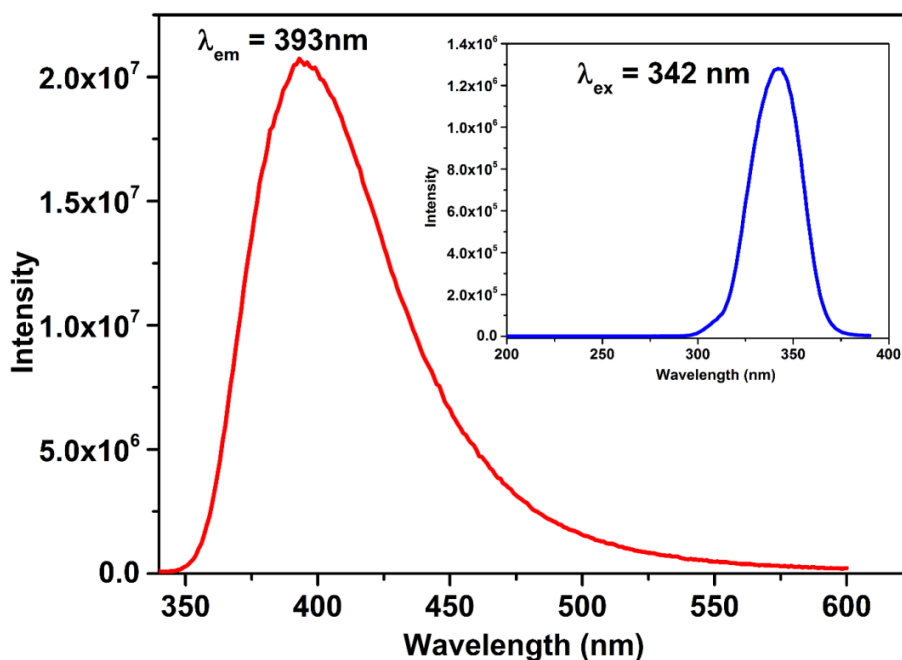


Figure 4A.29: Fluorescence peak profile of **12** in the solid state; the inset shows the excitation spectrum of **12** at 342 nm.

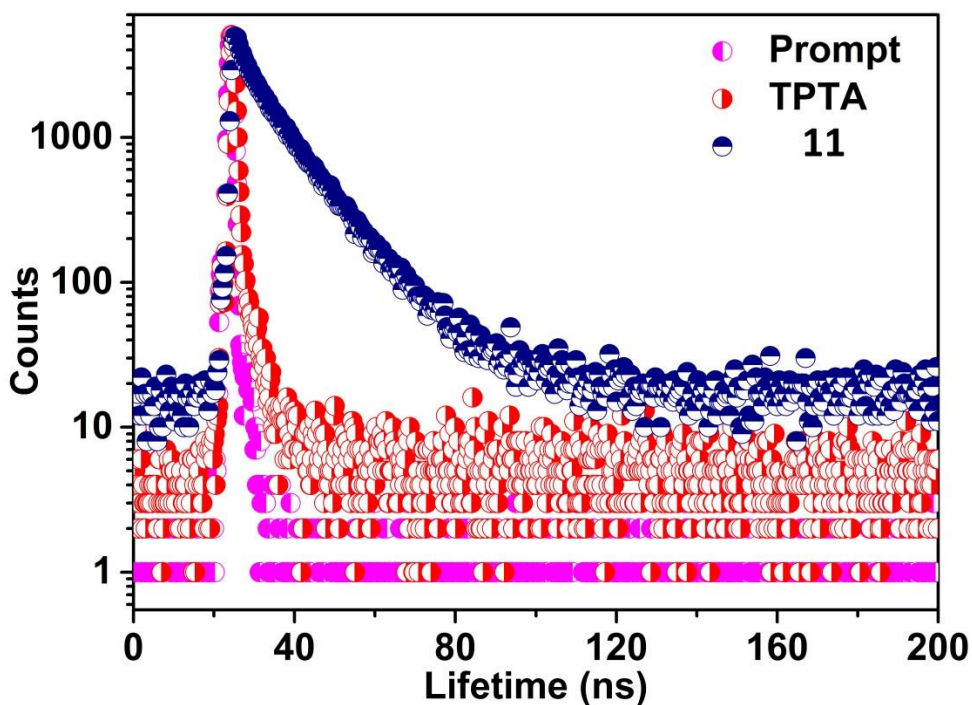


Figure 4A.30: Luminescence decay profile for **11** (navy blue), TPTA (red) and prompt (pink) which gave a lifetime of 6.9 and 0.38 ns for **11** and TPTA respectively.

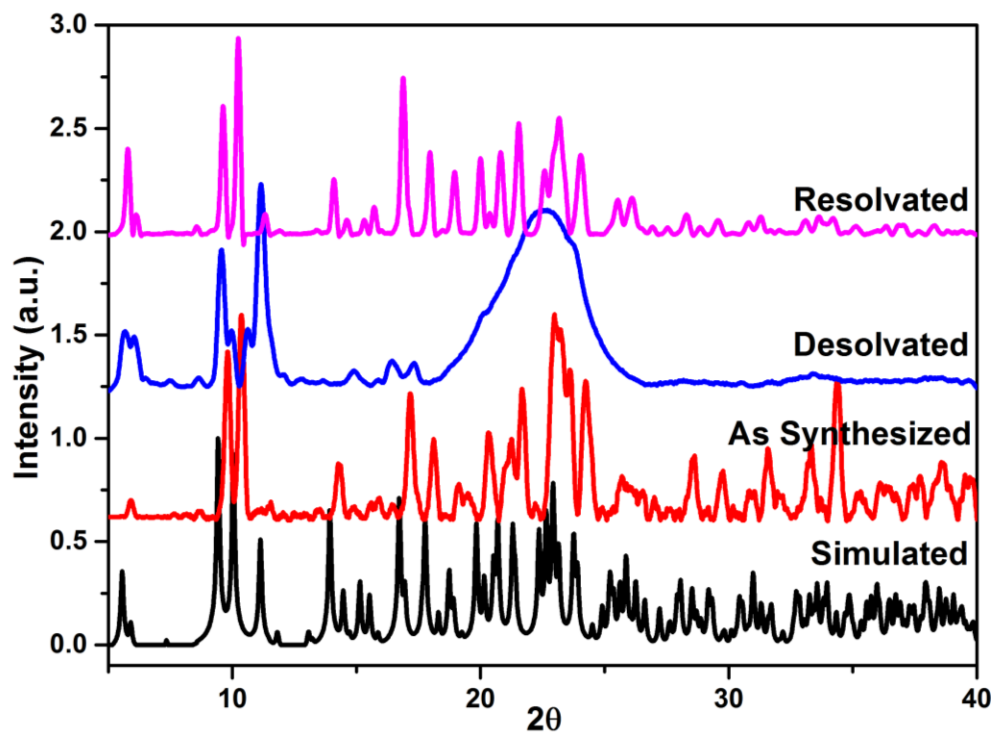


Figure A5.1: Powder X-ray diffraction (PXRD) pattern of the various samples of 13.

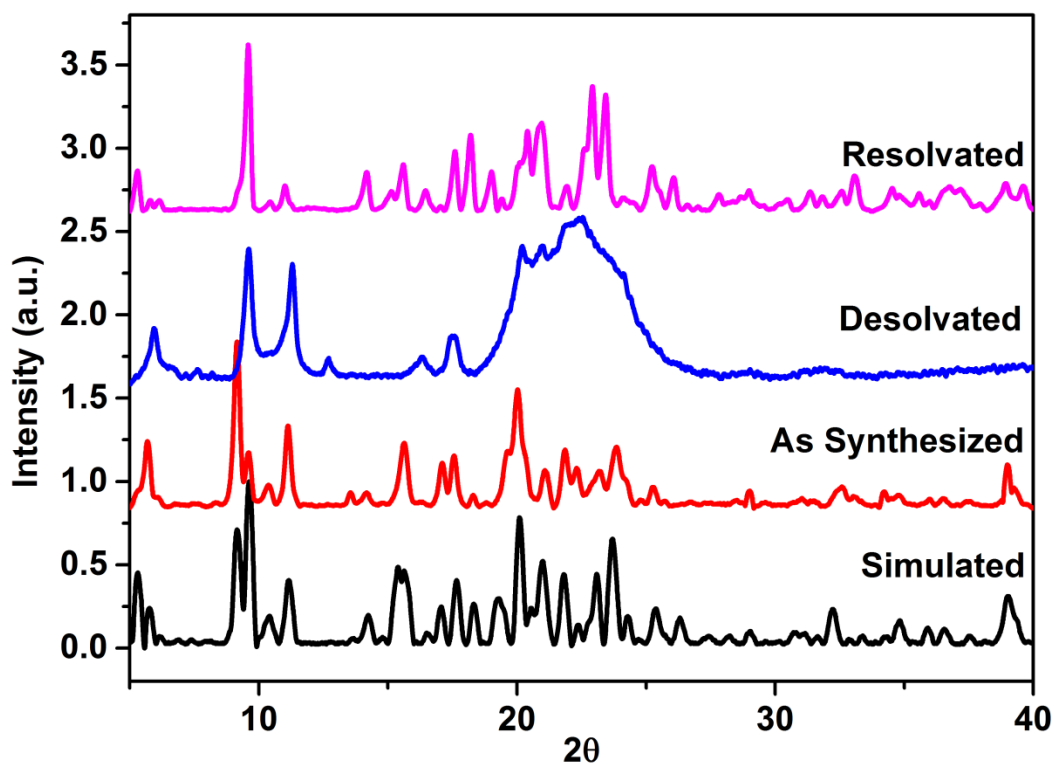


Figure A5.2: Powder X-ray diffraction (PXRD) pattern of the various samples of 14.

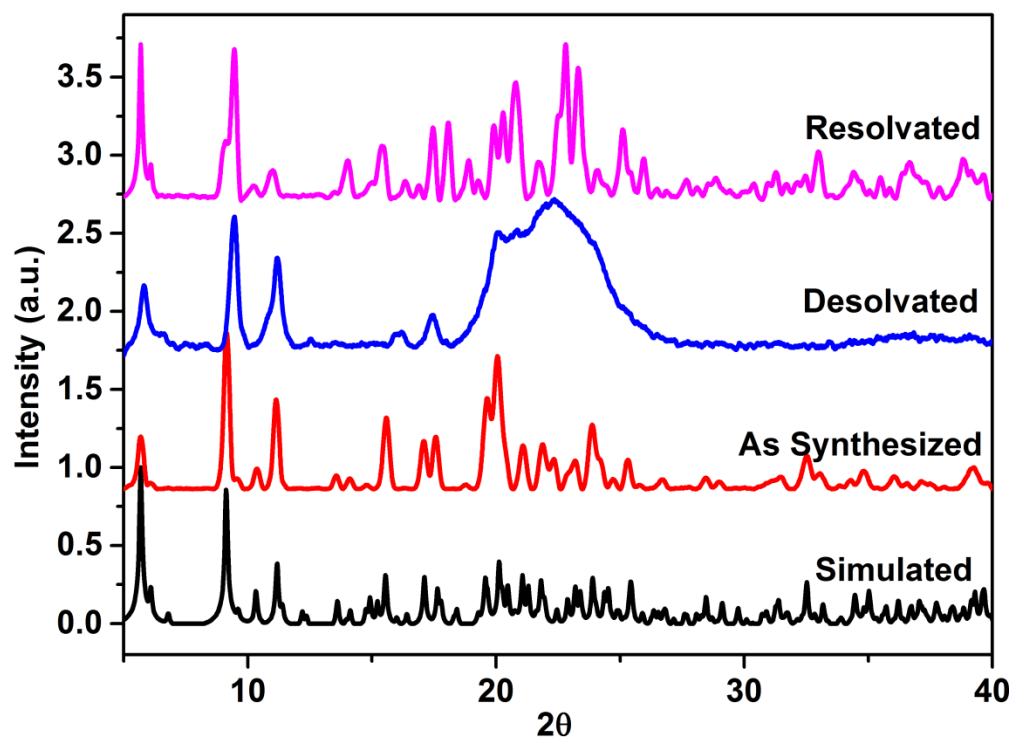


Figure A5.3: Powder X-ray diffraction (PXRD) pattern of the various samples of 15.

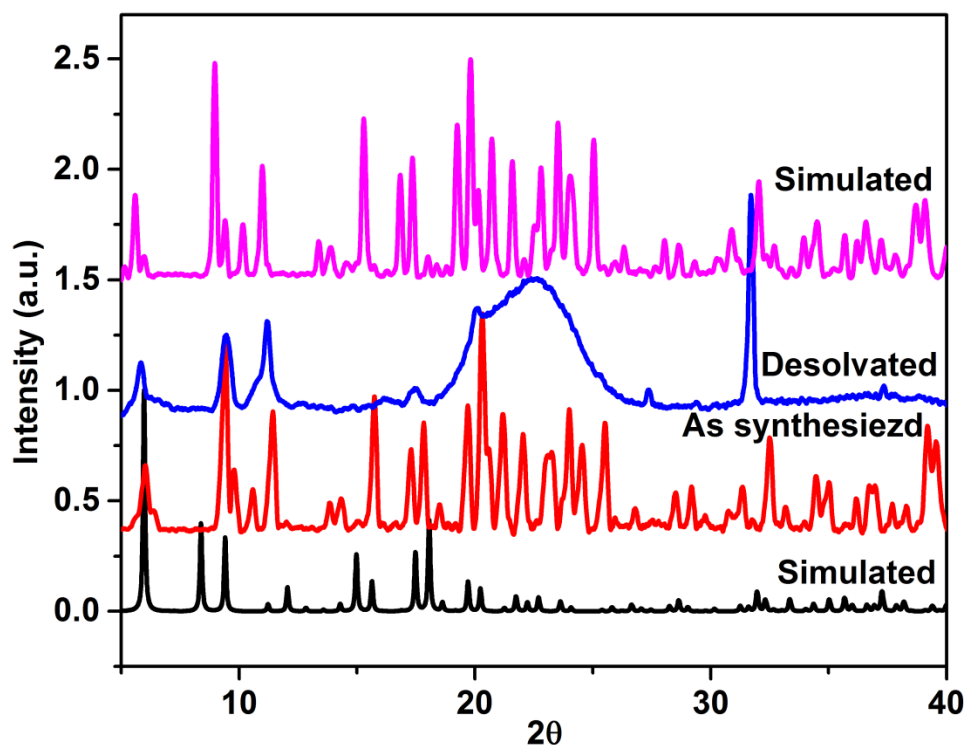


Figure A5.4: Powder X-ray diffraction (PXRD) pattern of the various samples of 16.

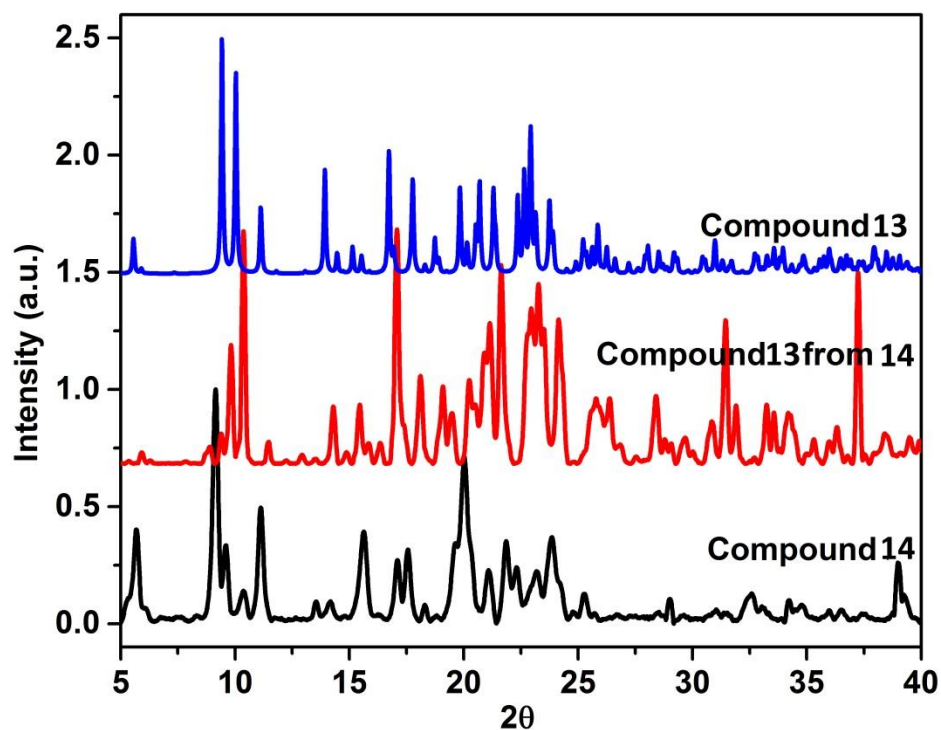


Figure A5.5: PXRD pattern showing the conversion of 14 to 13.

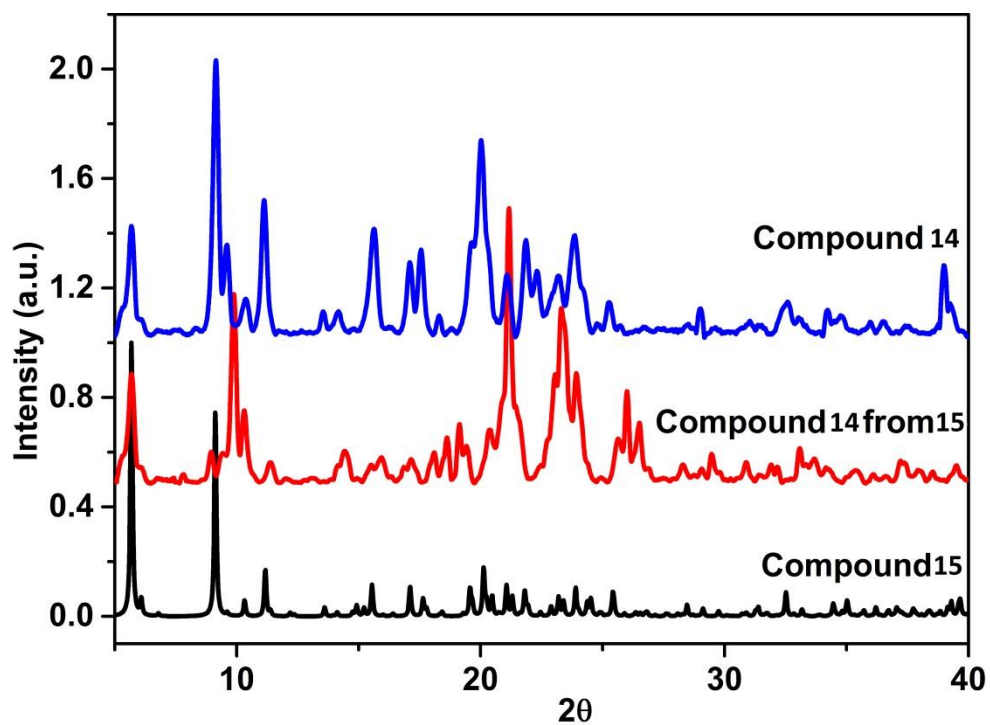


Figure A5.6: PXRD pattern showing the conversion of 15 to 14.

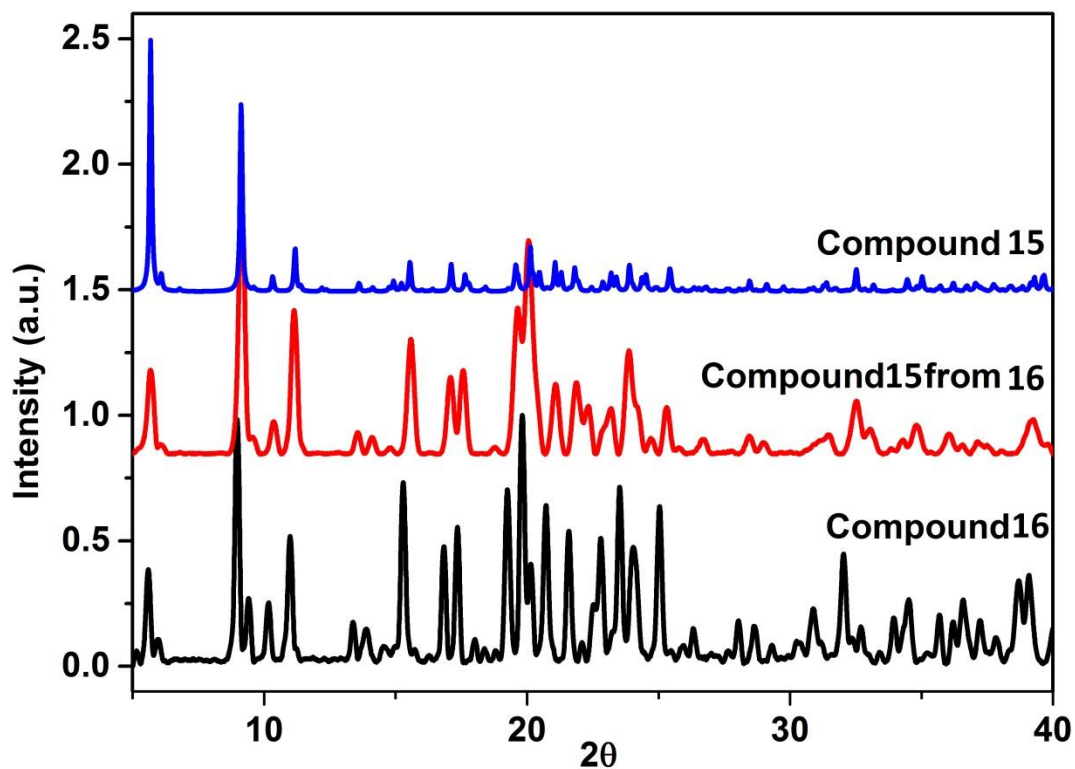


Figure A5.7: PXRD pattern showing the conversion of **16** to **15**.

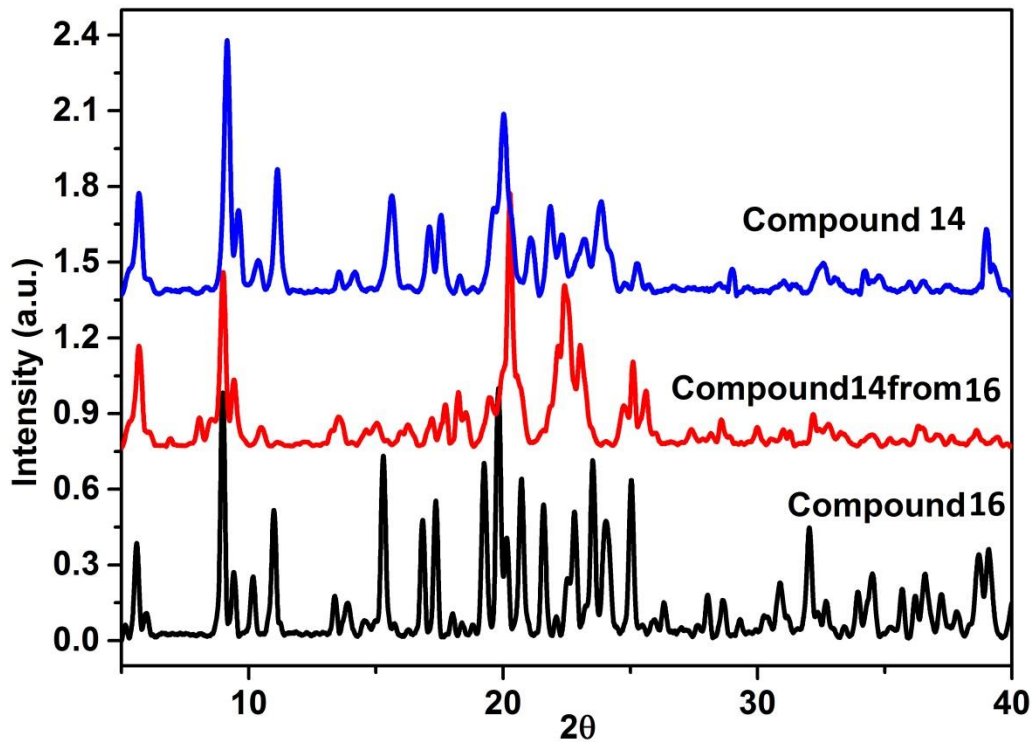


Figure A5.8: Figure S1: PXRD pattern showing the conversion of **16** to **14**.

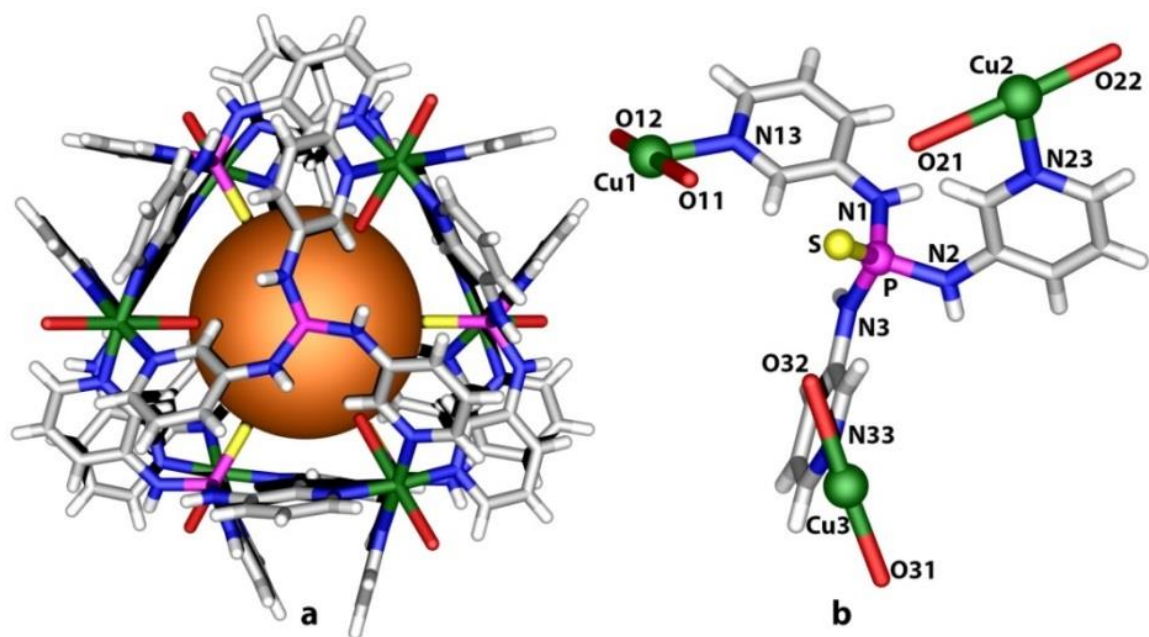


Figure A5.9: Crystal Structure of **13**: (a) View of molecular structure along the C_3 -axis. (b) View of asymmetric unit showing the connection of Cu^{2+} center with TPTA.

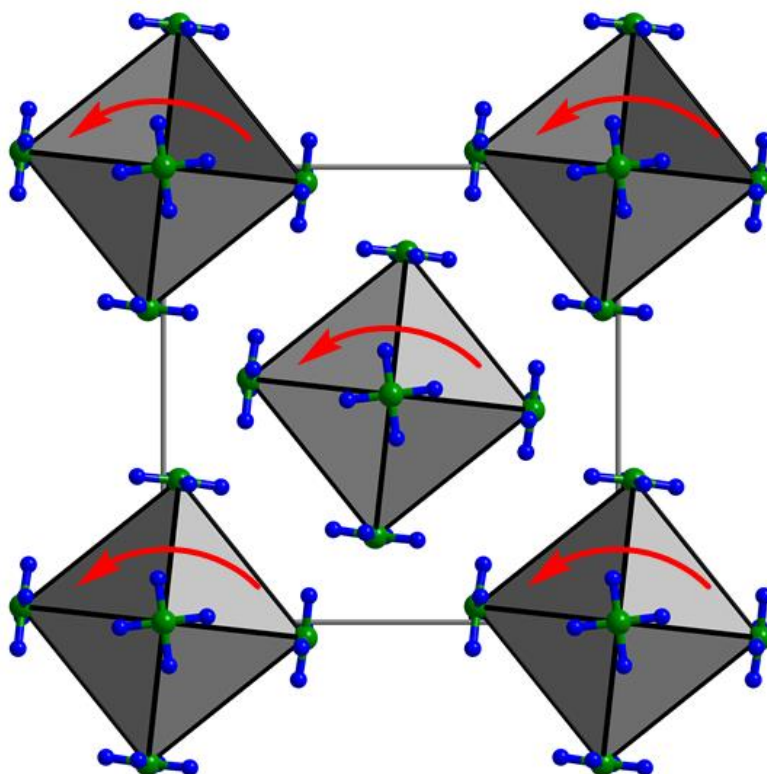


Figure A5.10: Packing view of the Cu_6 octahedra in **13** and along with the direction of rotation of the CuN_4 subunits in them. The organic ligands (except those of $\text{N}_{\text{pyridyl}}$ atoms), anions and solvates are omitted for clarity.

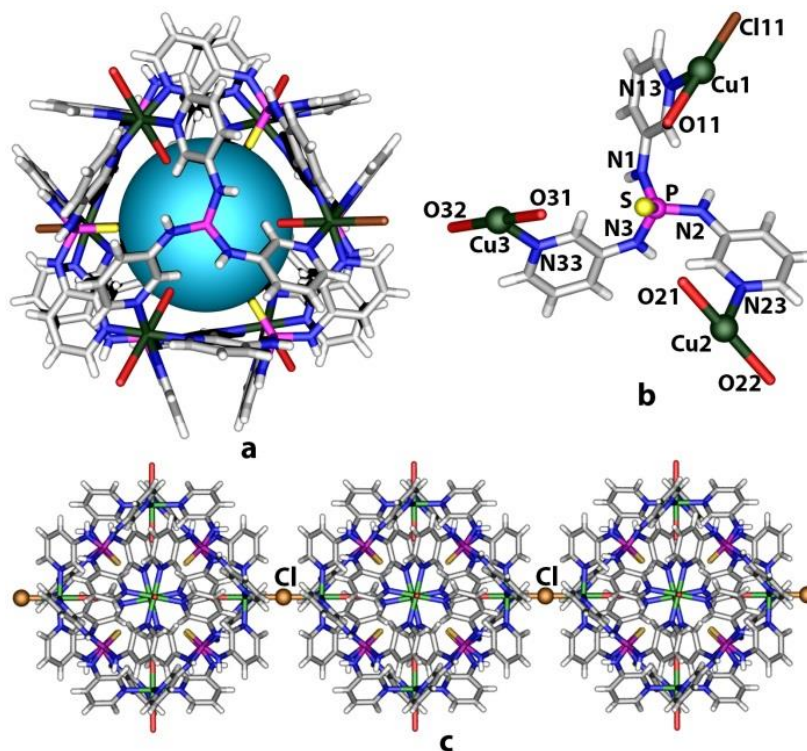


Figure A5.11: Crystal structure of **14**: (a) View of molecular structure along C_3 -axis. (b) View of asymmetric unit. (c) View of the one dimensional network.

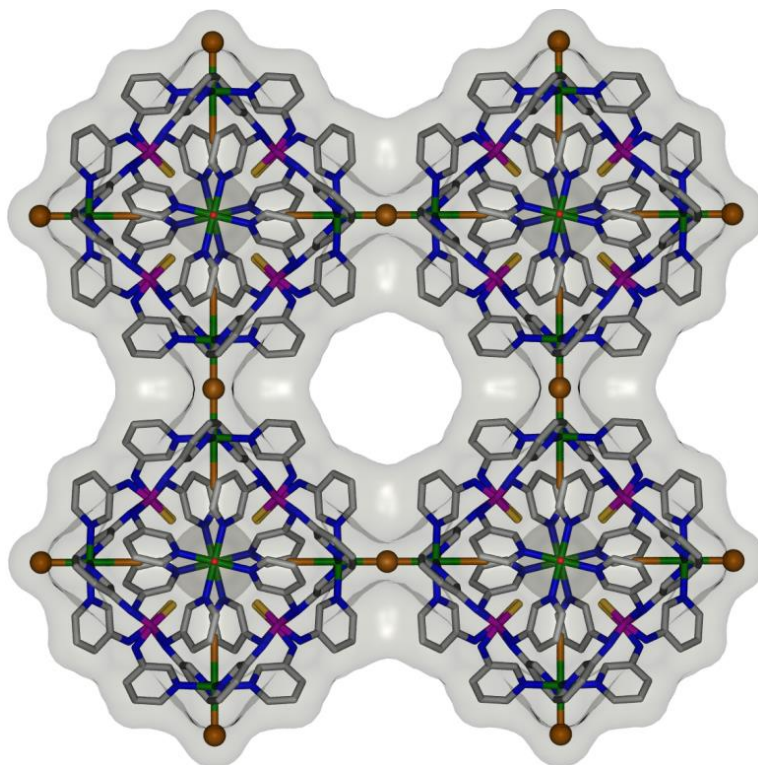


Figure A5.12: Surface view of the two dimensional network of **15**.

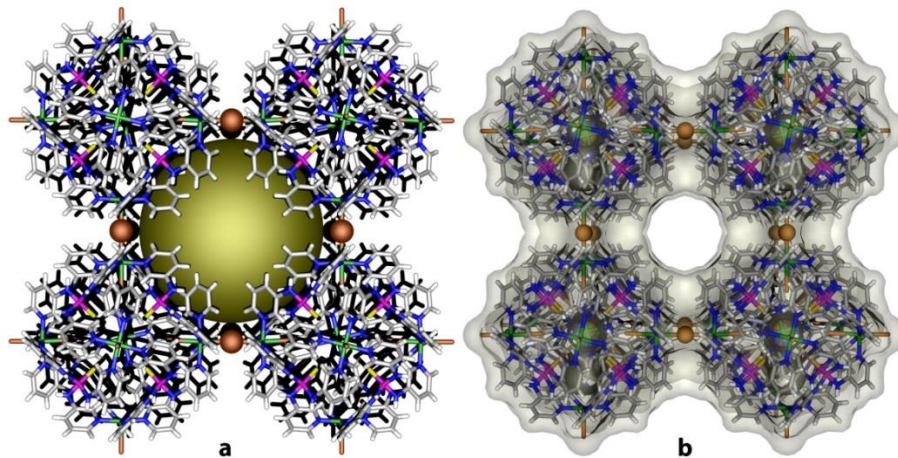


Figure A5.13: Crystal Structure of **16**: (a) view of the three dimensional network of showing the porous cavity inside the framework. (b) Surface view of the three dimensional network.

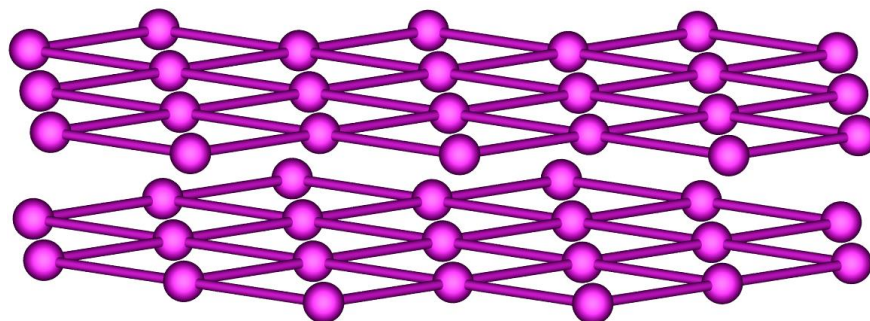


Figure A5.14: Underlying net of **15** showing uni-nodal sql topology.

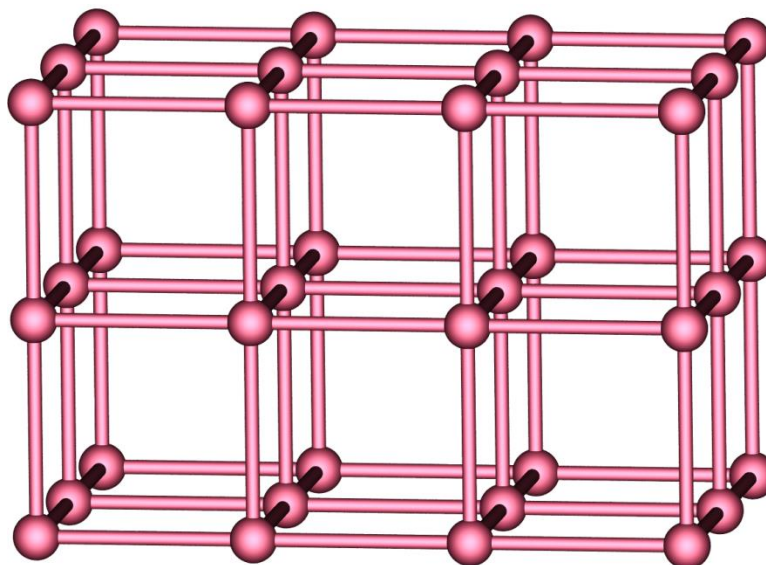


Figure A5.15: Underlying net of **16** showing uni-nodal pcu topology.

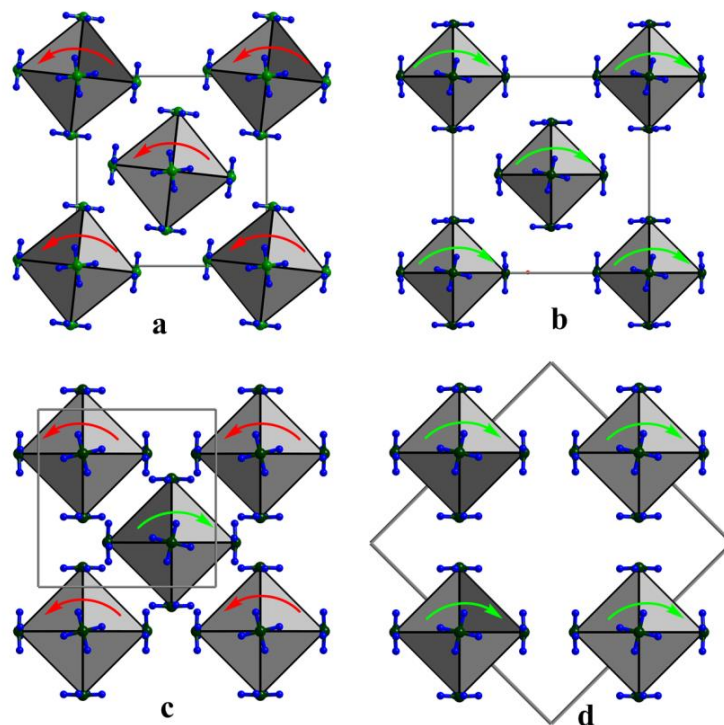


Figure A5.16: Packing view of the Cu₆ octahedra in **13** (a), **14** (b), **15** (c) and **16** (d) and along with the direction of rotation of the CuN₄ subunits in them. The organic ligands (except those of N_{pyridyl} atoms), anions and solvates are omitted for clarity.

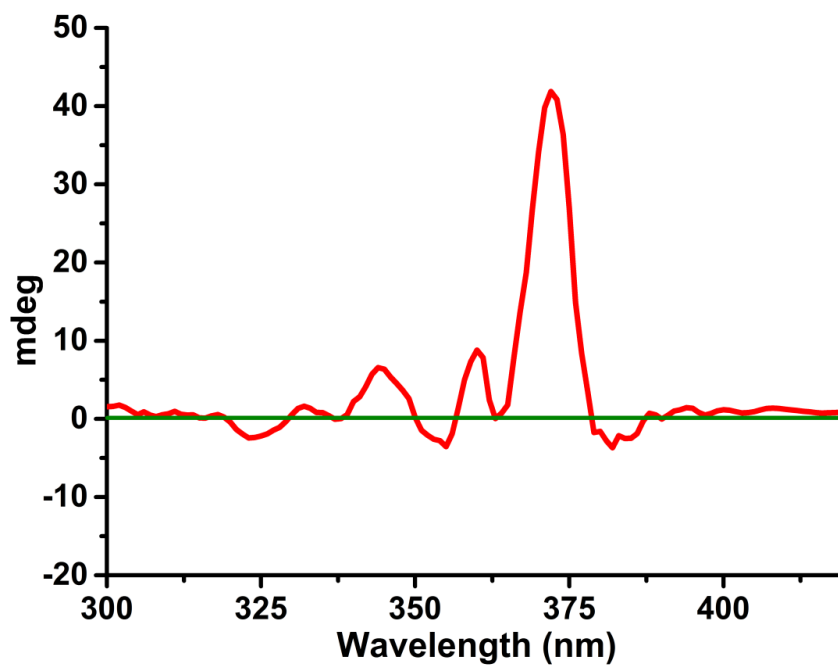


Figure A5.17: CD spectrum of **13** in H₂O suggesting the chiral nature.

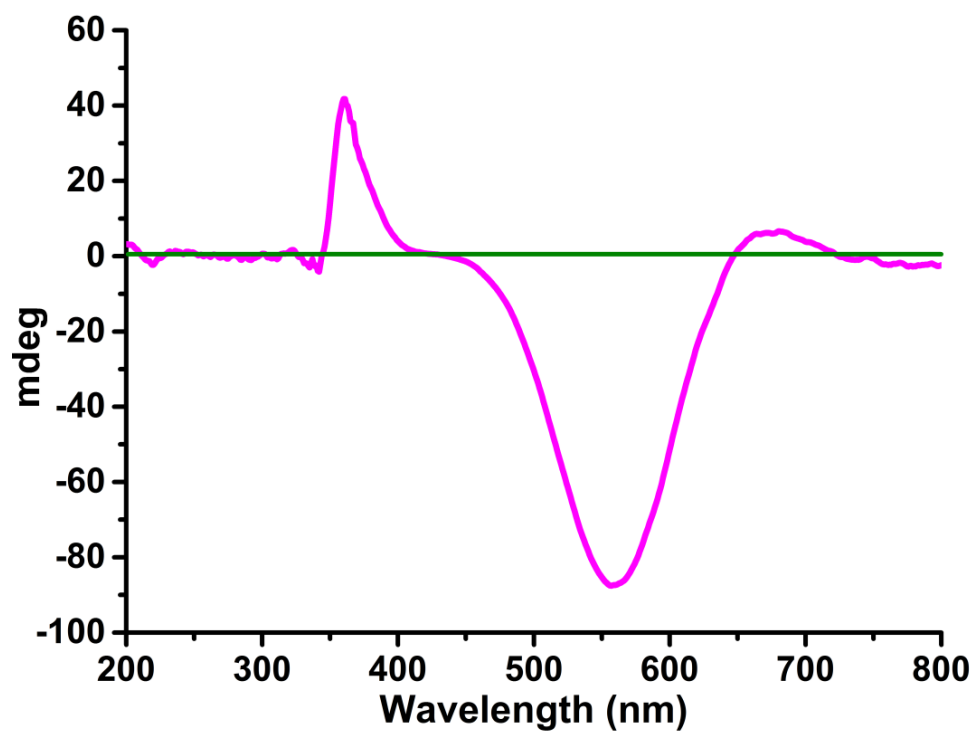


Figure A5.18: CD spectrum of **14** in H₂O suggesting the chiral nature.

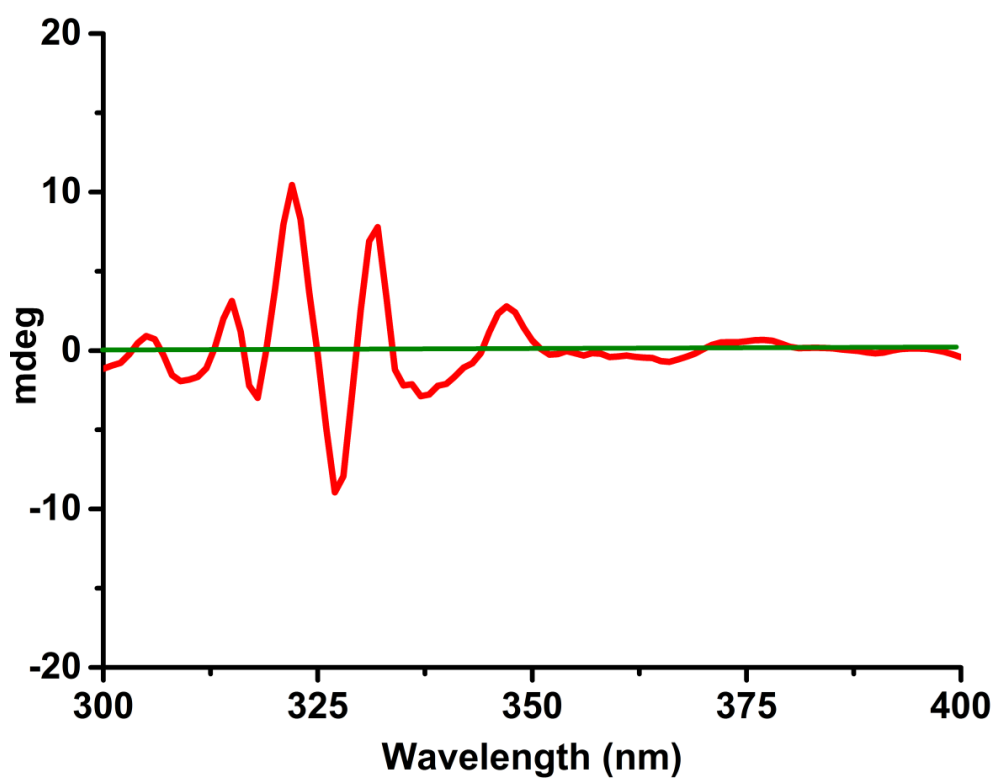


Figure A5.19: CD spectrum of **16** in H₂O suggesting the chiral nature.

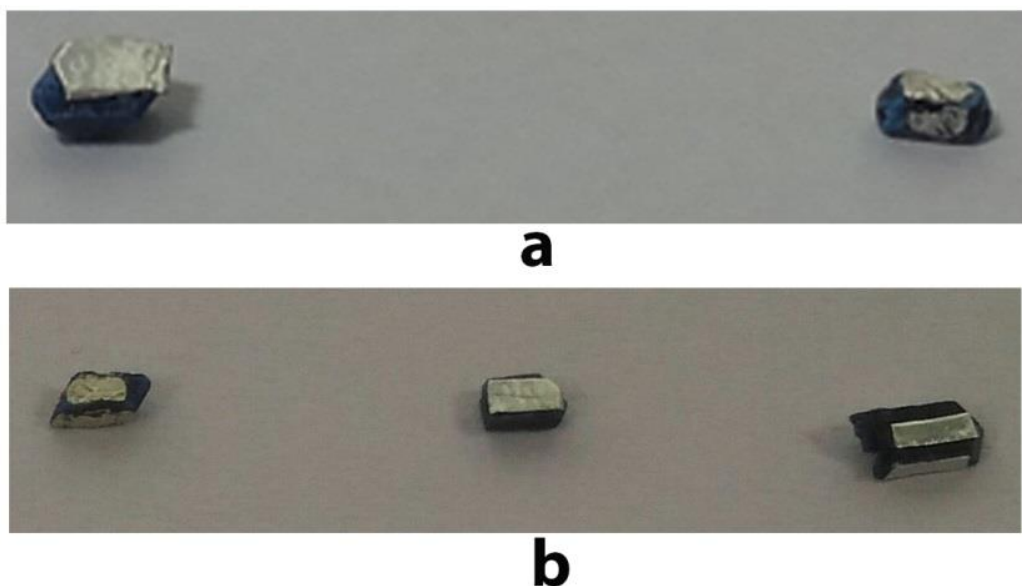


Figure A5.20: View crystal images of **13** (a) and **14** (b) after electroding for the ferroelectric measurements.

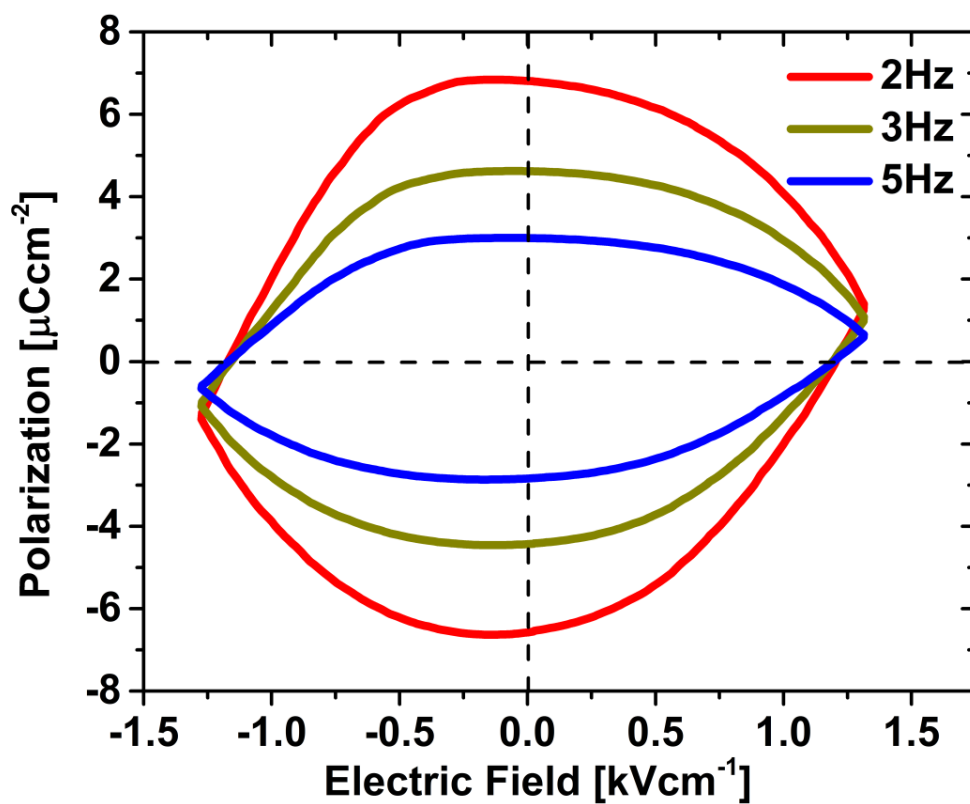


Figure A5.21: P-E hysteresis loop of **13** along c-axis at various frequencies.

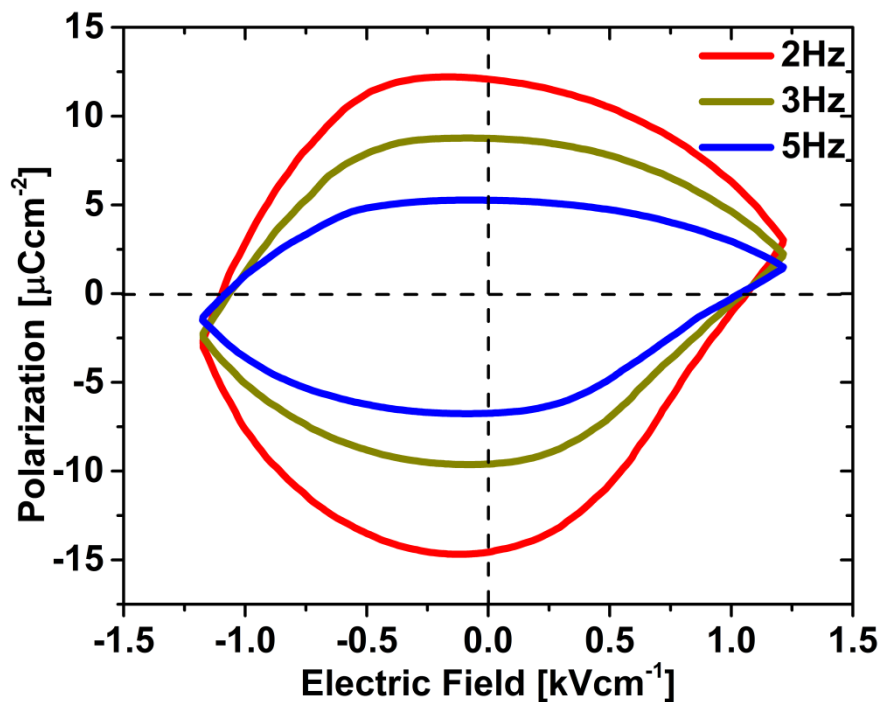


Figure A5.22: P-E hysteresis loop of **14** along c-axis at various frequencies.

Table A5.2: Remnant polarization and coercive field along a- and c-axis at various frequencies in **13** and **14**.

Compound	Frequency (Hz)	Along a-axis		Along c-axis	
		P_r	E_c	P_r	E_c
13	1	1.58	0.417	20.47	1.03
	2	0.6583	0.4447	6.28	1.07
	3	0.4645	0.4454	4.62	1.18
	5	0.2606	0.4538	2.98	1.19
14	1	6.28	0.4597	28.92	0.85979
	2	2.974	0.49027	12.09	0.96858
	3	1.701	0.49949	8.746	1.05947
	5	0.8237	0.5875	5.262	1.0599

Table A5.3: The room temperature measurement of capacitance in **13** and **14** and the corresponding dielectric constants.

Compound	Frequency (Hz)	Capacitance (pF)		Dielectric Constant	
		a-axis	c-axis	a-axis	c-axis
13	1000	607	700	303.5	350
	10000	196.7	319	98.35	159.5
	100000	23.56	34.6	11.78	17.3
	1000000	5.13	5.34	2.565	2.67
14	1000	24.4	204	12.2	65.28
	10000	13	115.2	6.5	36.864
	100000	8.4	25.47	4.2	8.1504
	1000000	5.2	5.4	2.6	1.728

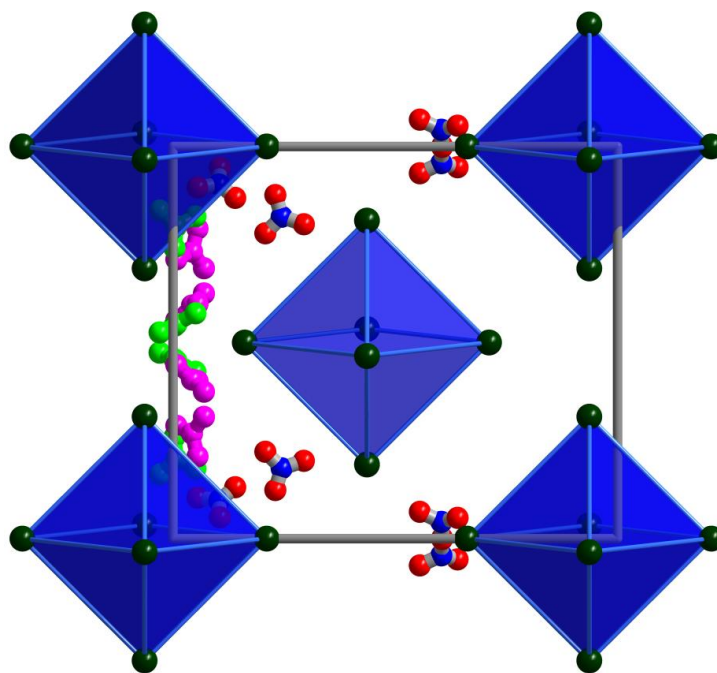


Figure A5.23: Nitrate anions in the unit cell of **13** along a-axis.

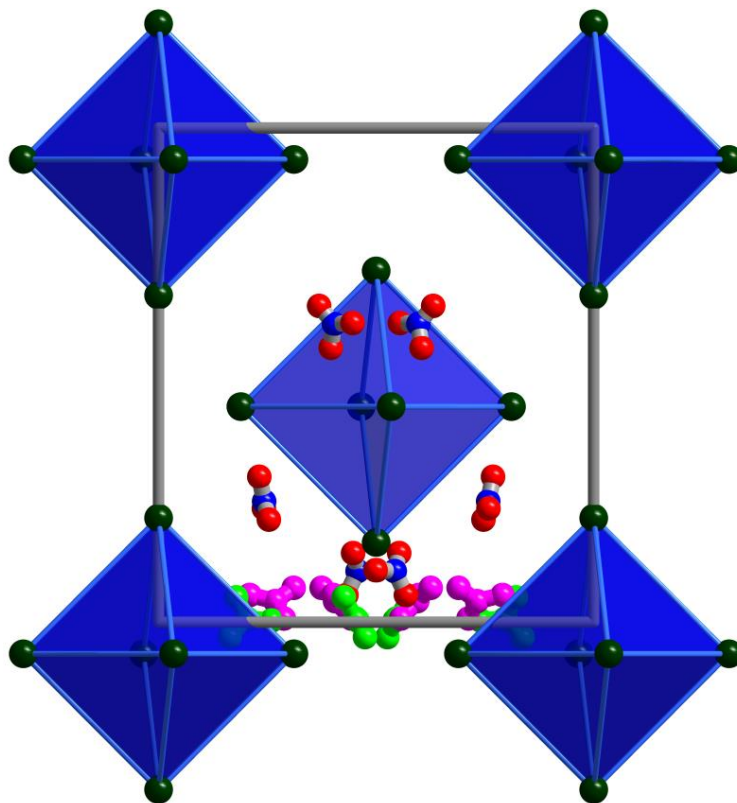


Figure A5.24: Nitrate anions in the unit cell of **13** along b-axis.

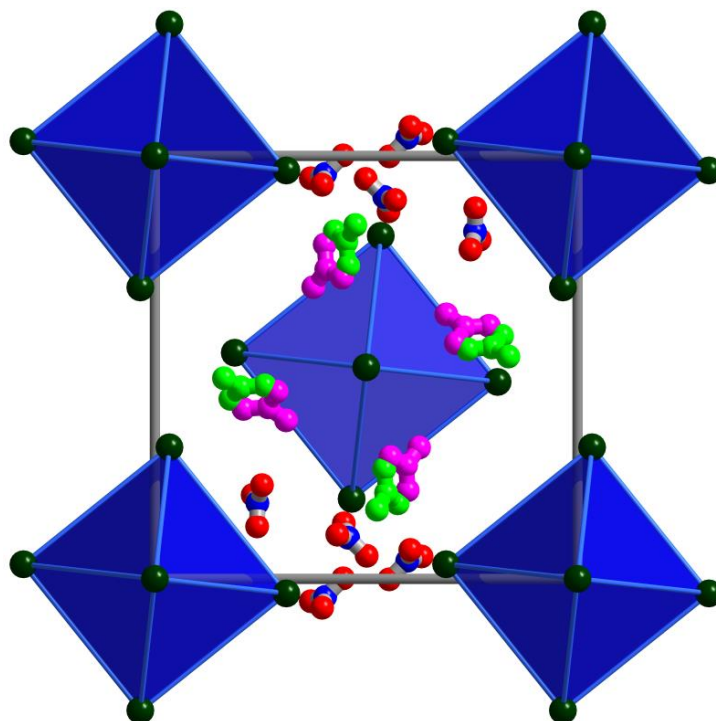


Figure A5.25: Nitrate anions in the unit cell of **13** along c-axis.

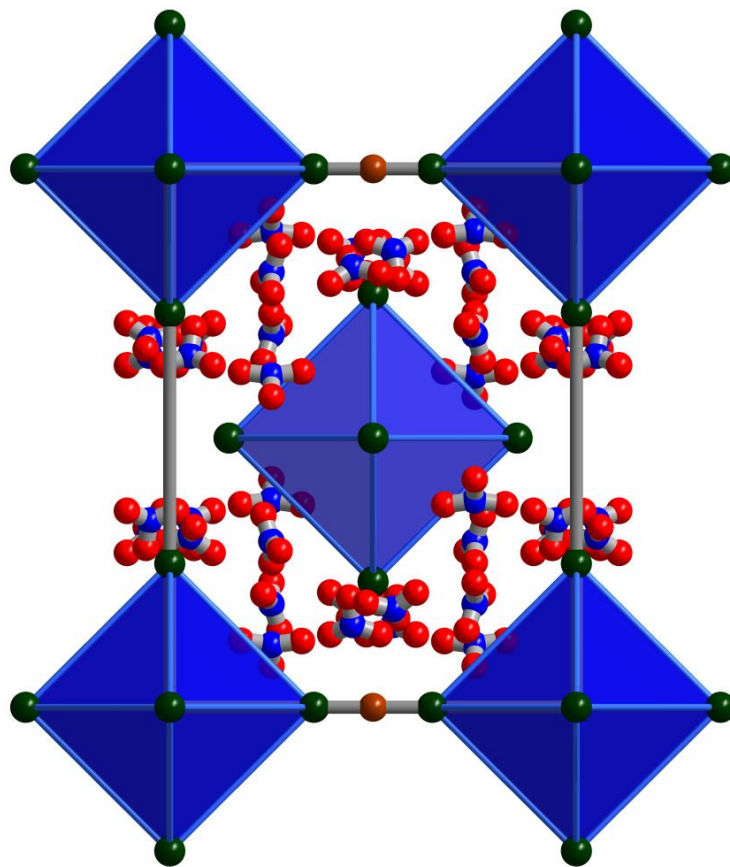


Figure A5.26: Nitrate anions in the unit cell of **14** along a-axis.

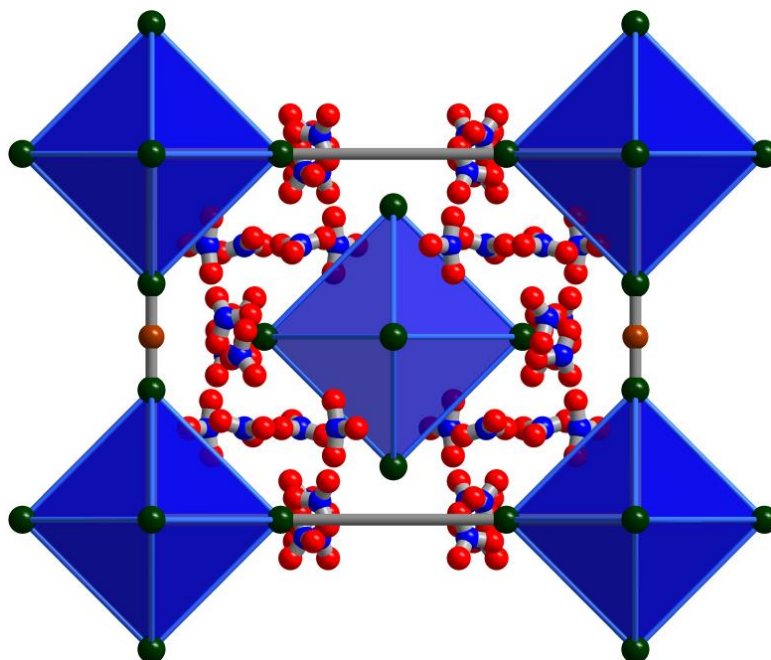


Figure A5.27: Nitrate anions in the unit cell of **14** along b-axis.

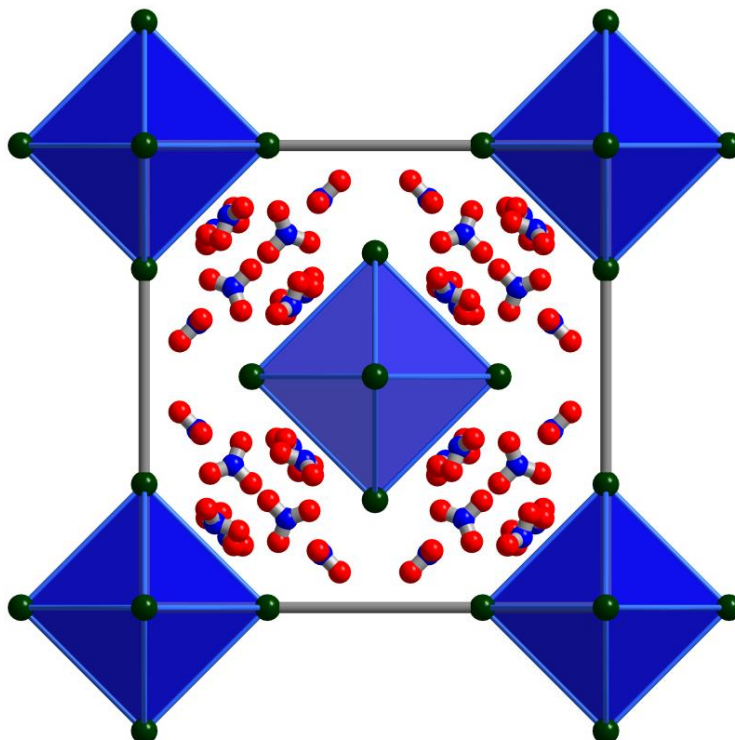


Figure A5.28: Nitrate anions in the unit cell of **14** along c-axis.

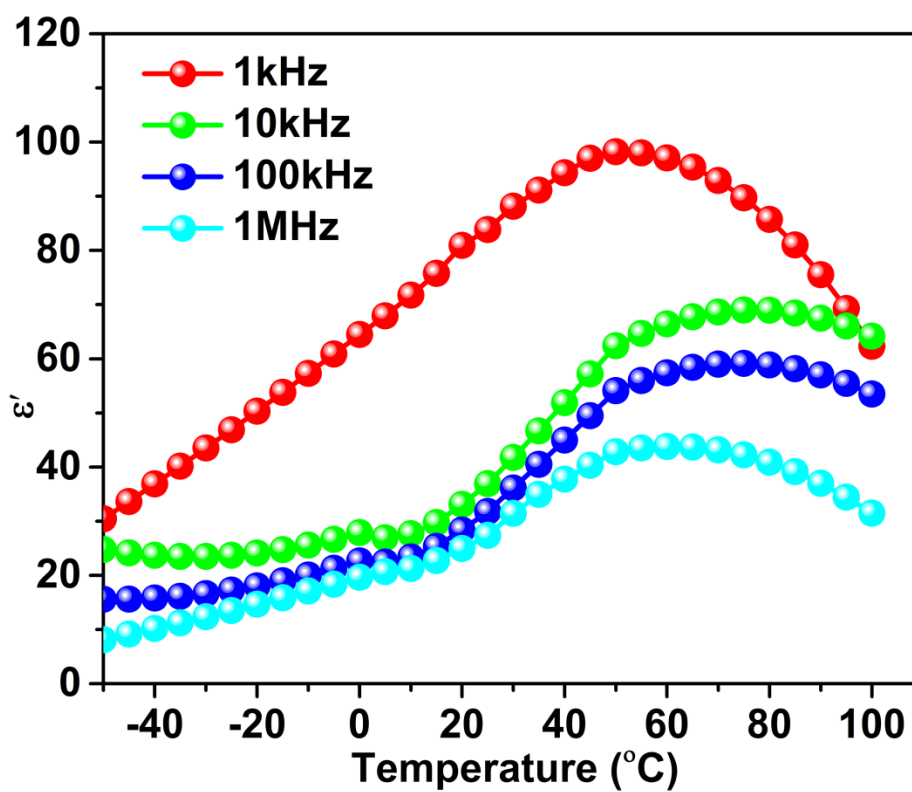


Figure A5.29: Dielectric Permittivity measurement of **13** at various frequencies.

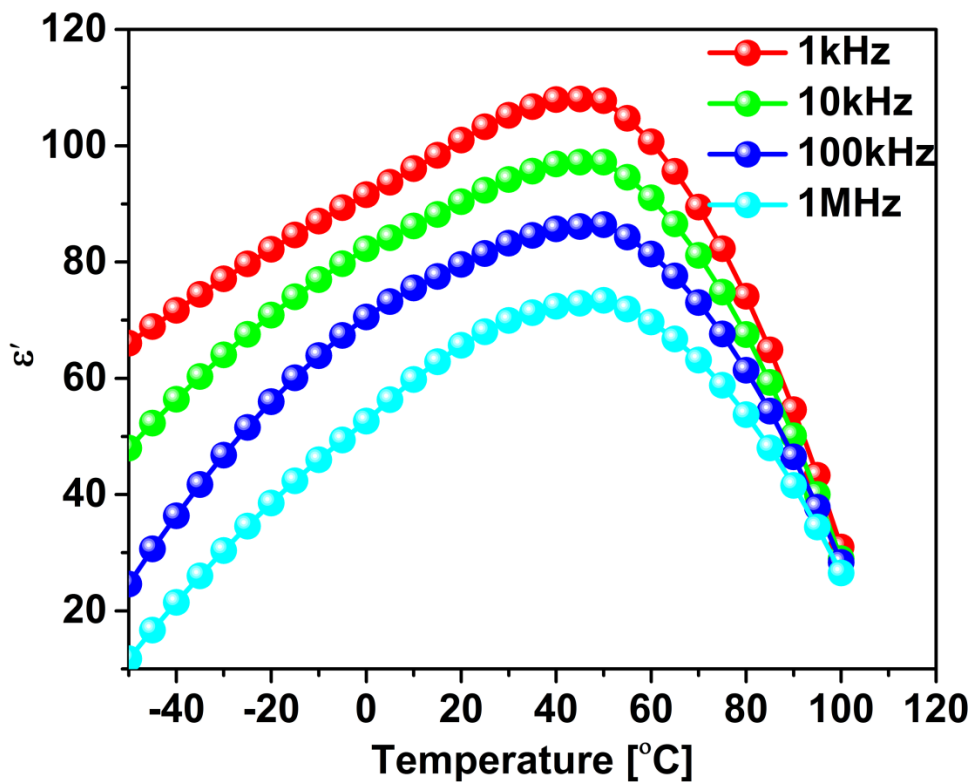


Figure A5.30: Dielectric Permittivity measurement of **14** at various frequencies.

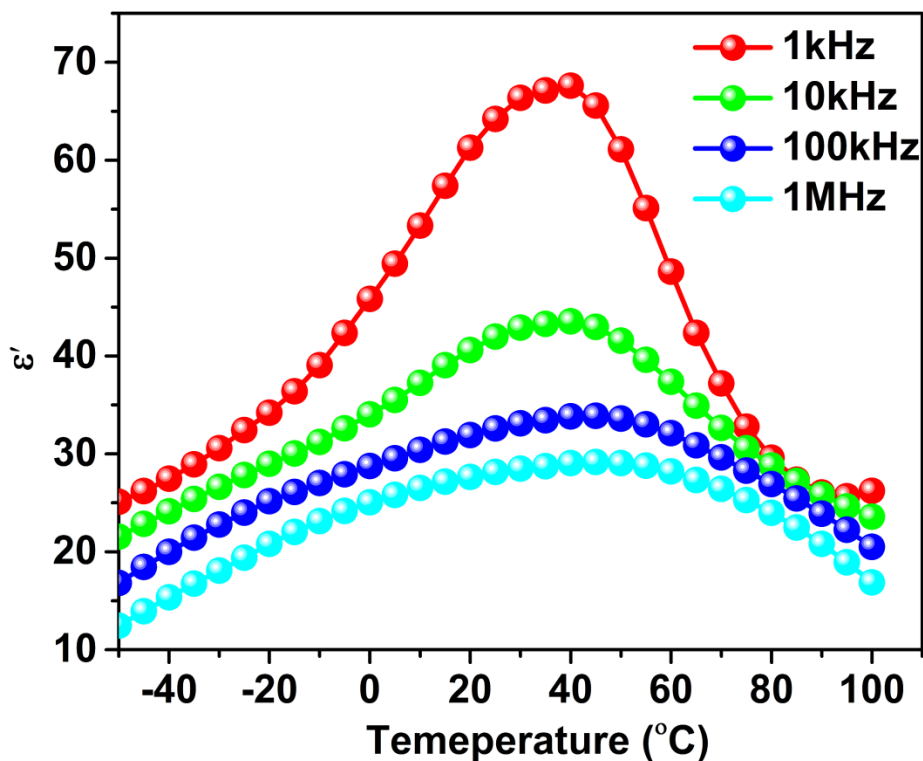


Figure A5.31: Dielectric Permittivity measurement of **15** at various frequencies.

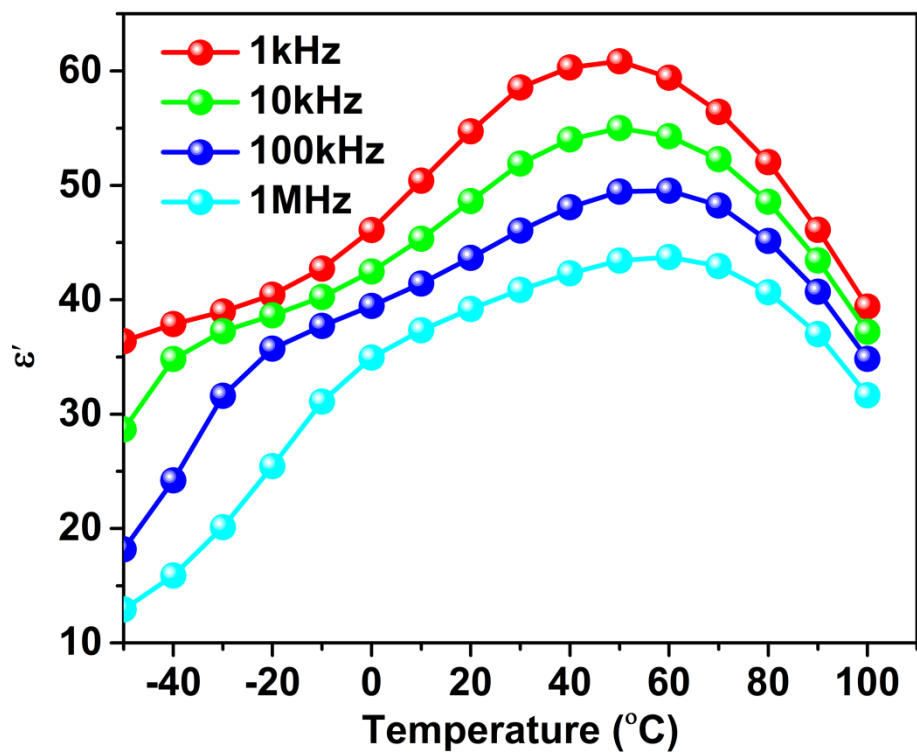


Figure A5.32: Temperature dependent dielectric Permittivity measurement of **16** at various frequencies.

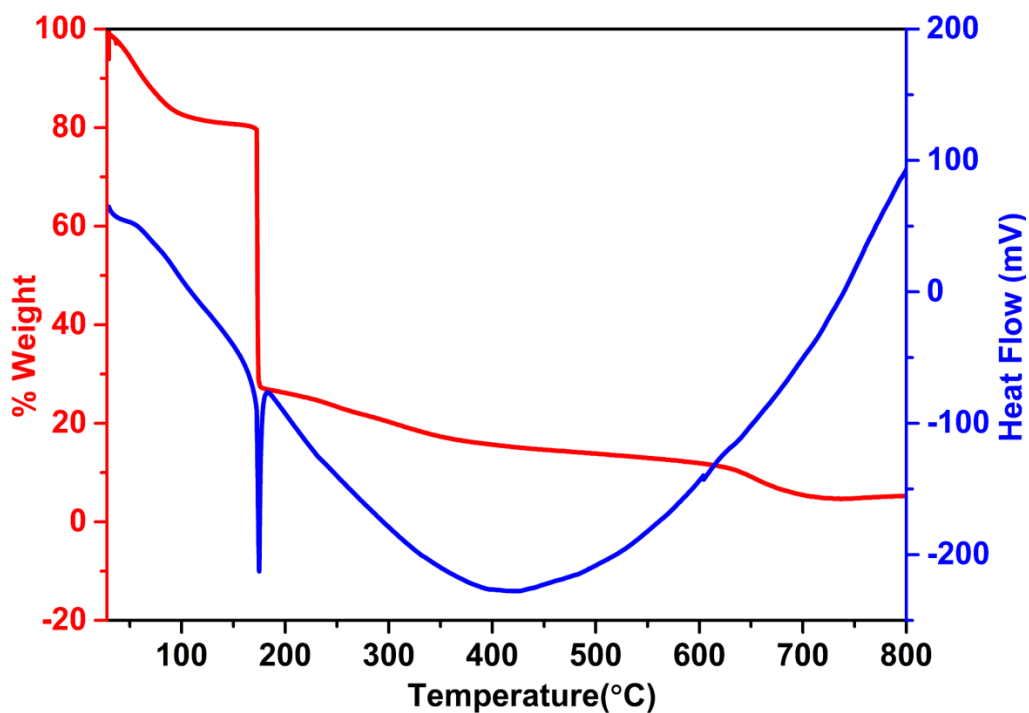


Figure A5.33: Thermo-gravimetric analysis (TGA) differential scanning calorimetric (DSC) plot of **13**.

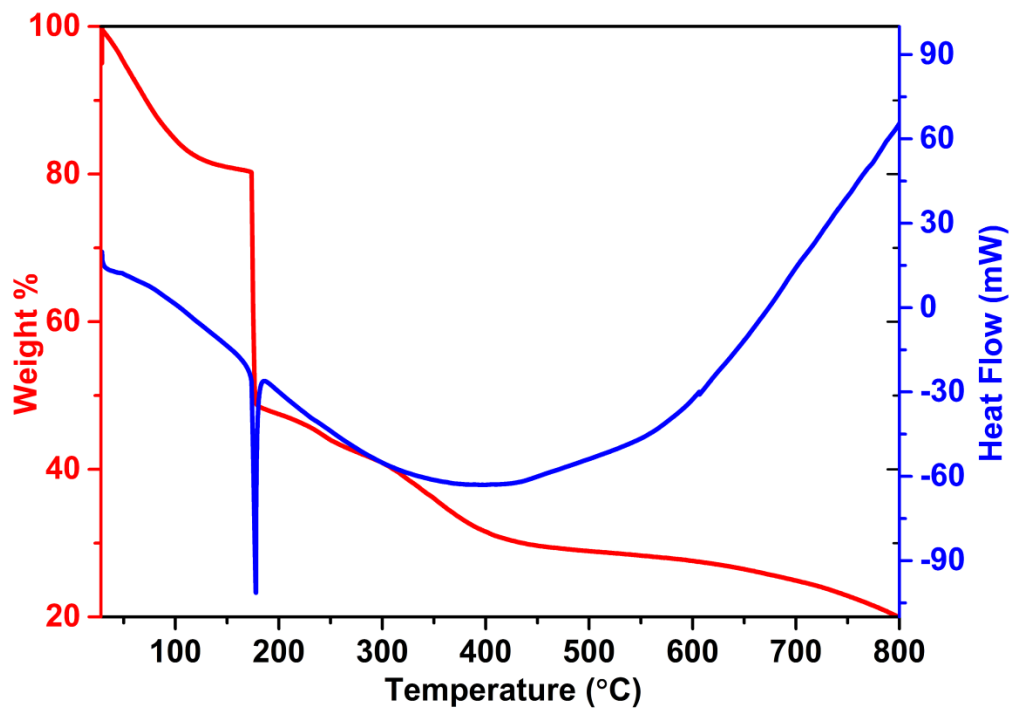


Figure A5.34: Thermo-gravimetric analysis (TGA) differential scanning calorimetric (DSC) plot of 14.

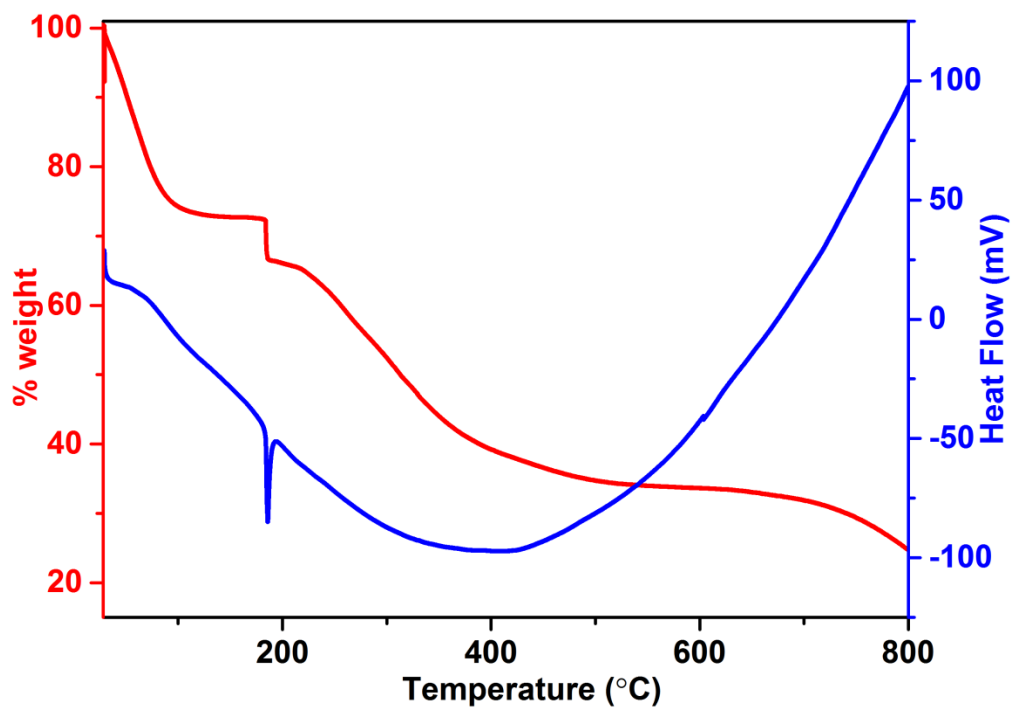


Figure A5.35: Thermo-gravimetric analysis (TGA) differential scanning calorimetric (DSC) plot of 16.

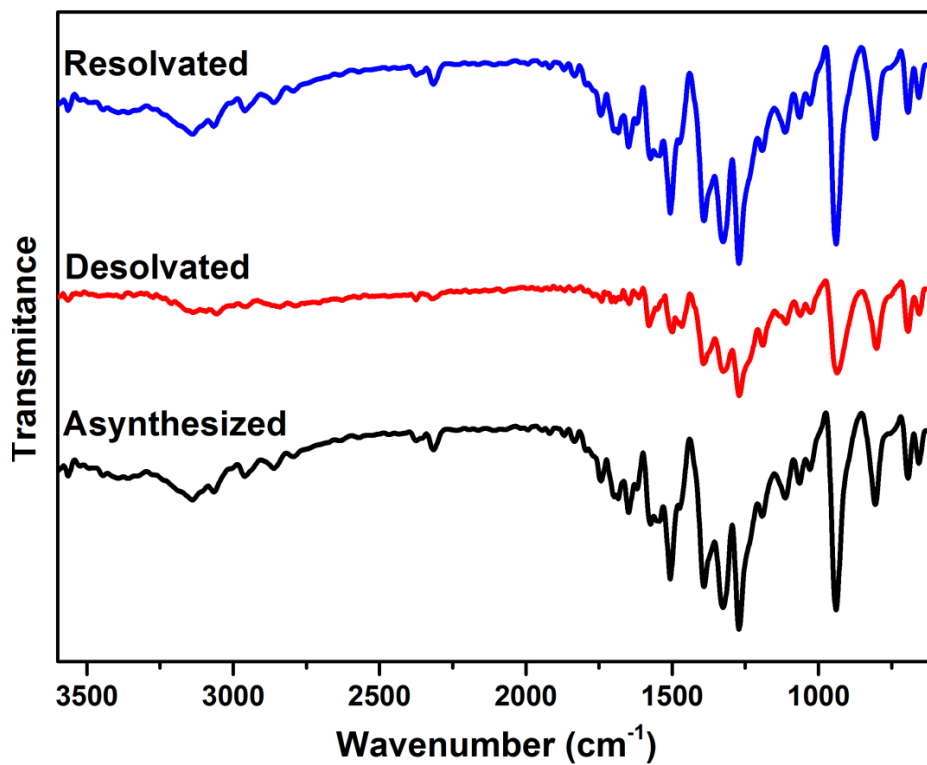


Figure A5.36: IR spectra of synthesized, desolvated and resolvated samples of **13**.

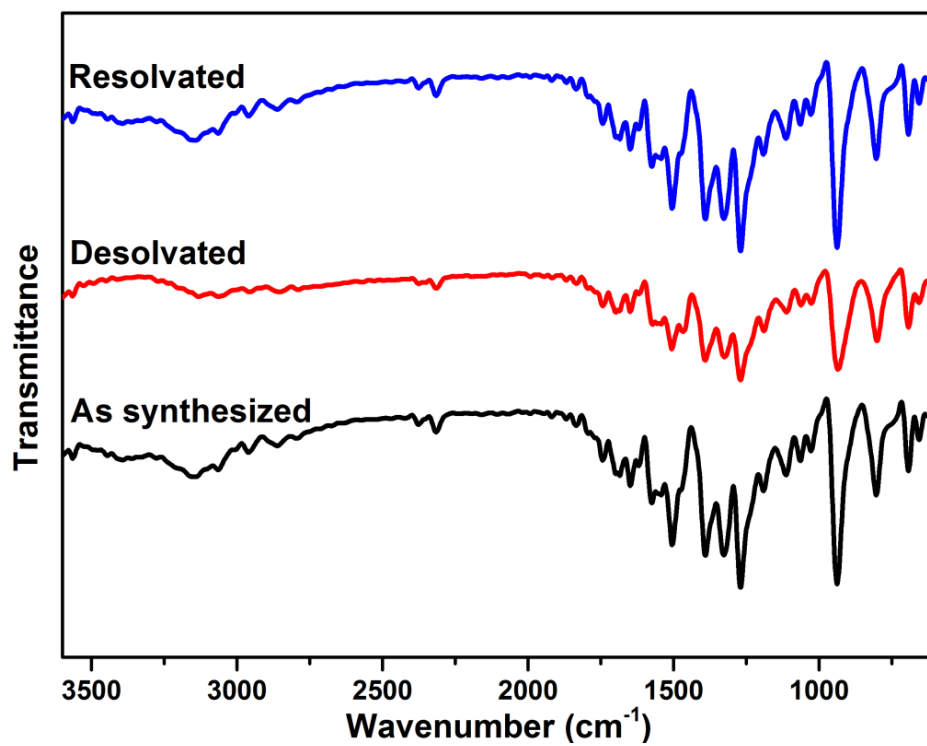


Figure A5.37: IR spectra of synthesized, desolvated and resolvated samples of **14**.

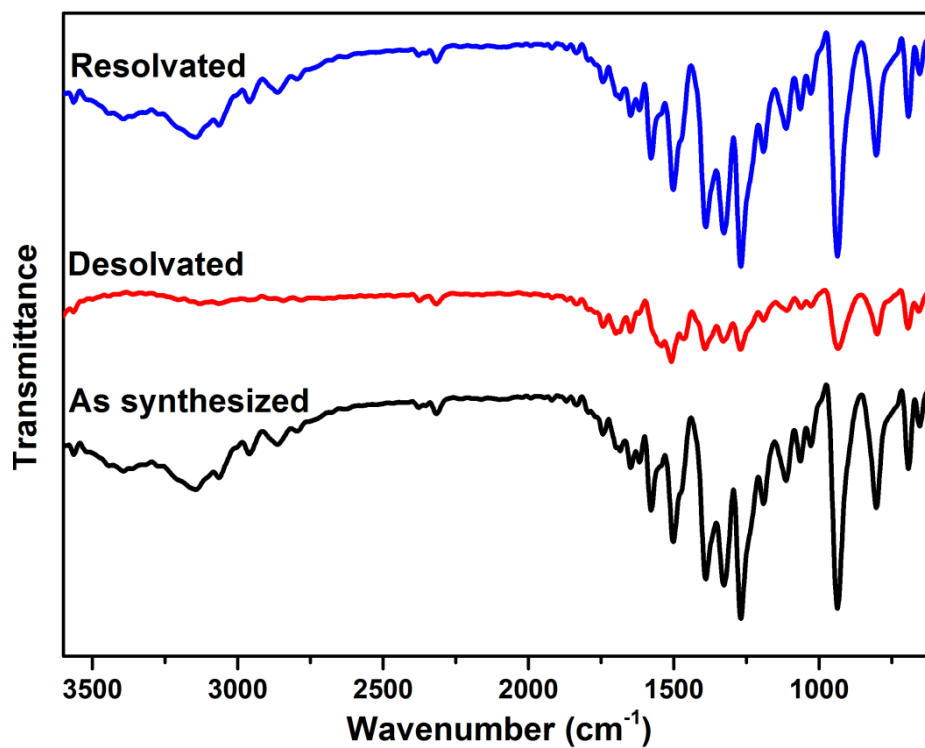


Figure A5.38: IR spectra of synthesized, desolvated and resolvated samples of **15**.

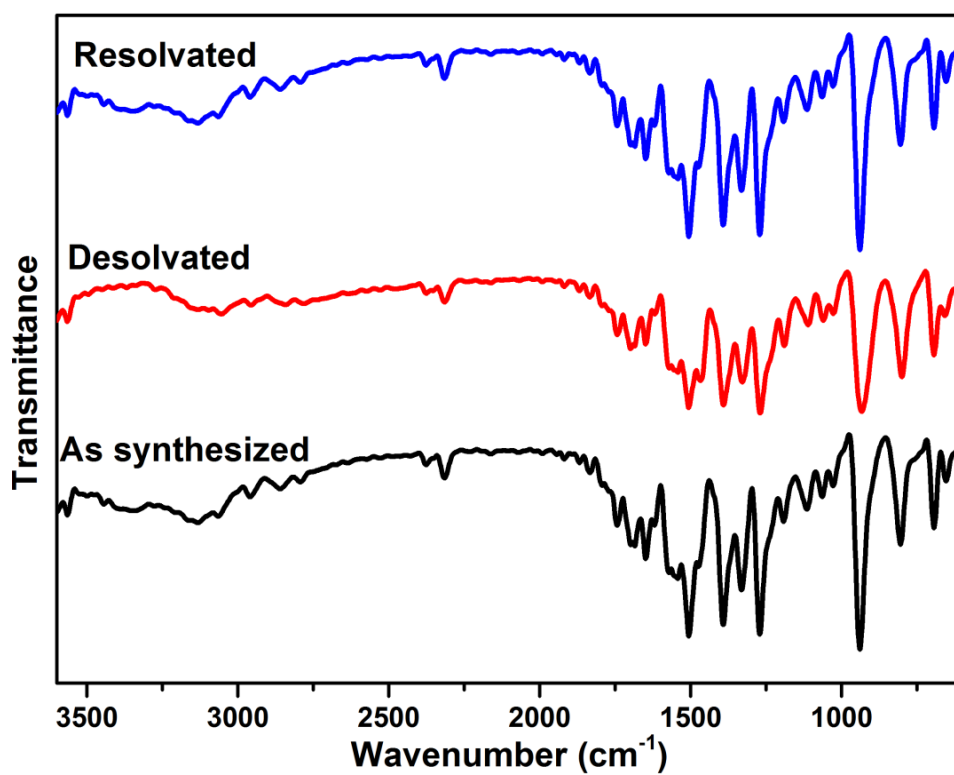


Figure A5.39: IR spectra of synthesized, desolvated and resolvated samples of **16**.

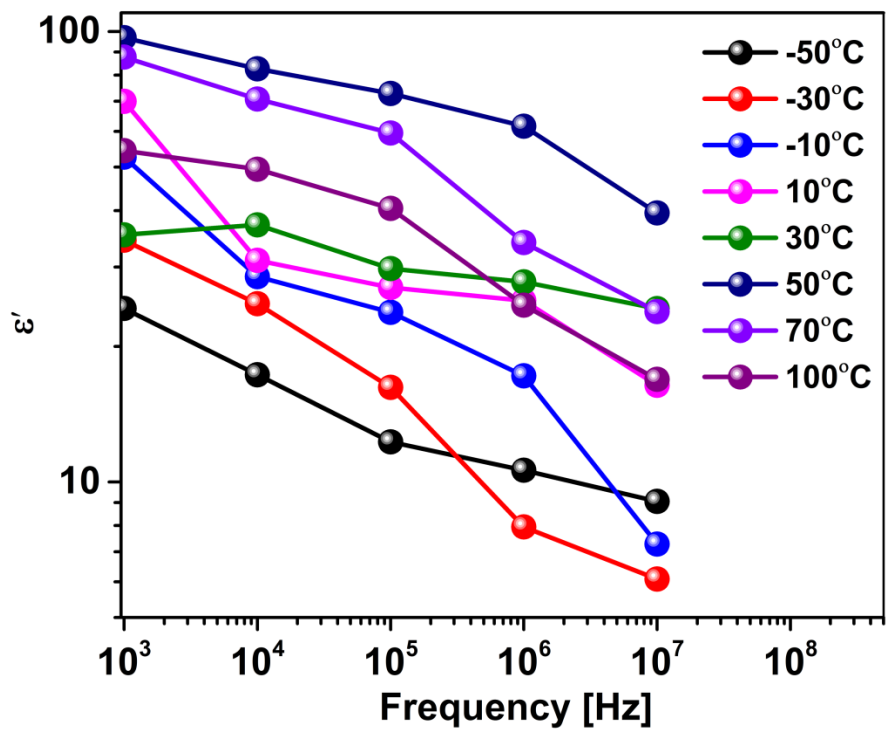


Figure A5.40: Frequency dependent Dielectric Permittivity measurement of **13** at various temperatures.

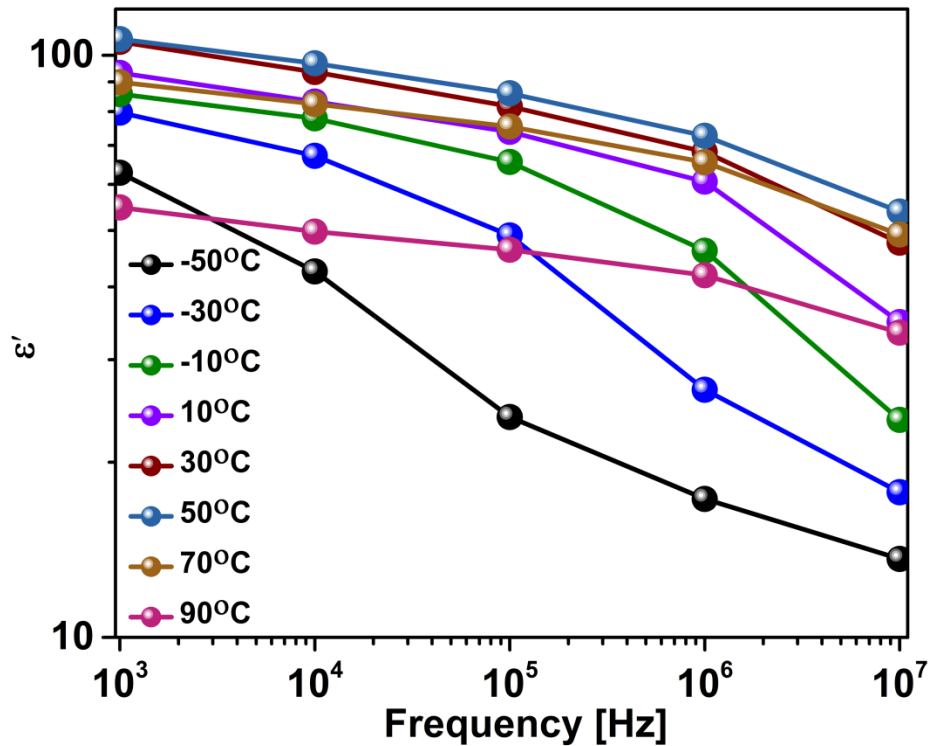


Figure A5.41: Frequency dependent Dielectric Permittivity measurement of **14** at various temperatures.

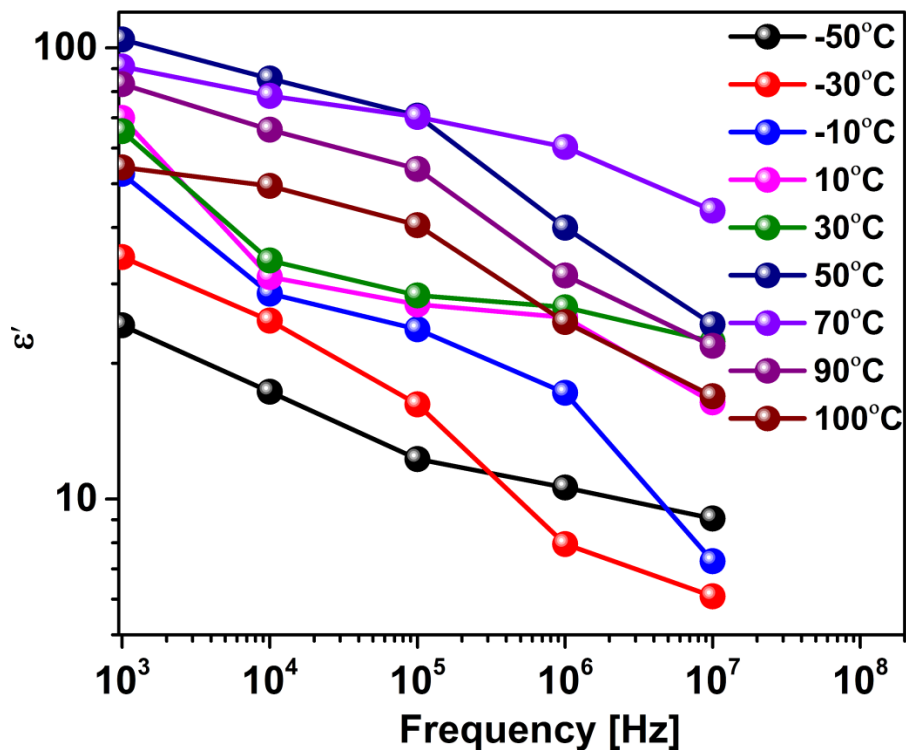


Figure A5.42: Frequency dependent Dielectric Permittivity measurement of **15** at various temperatures.

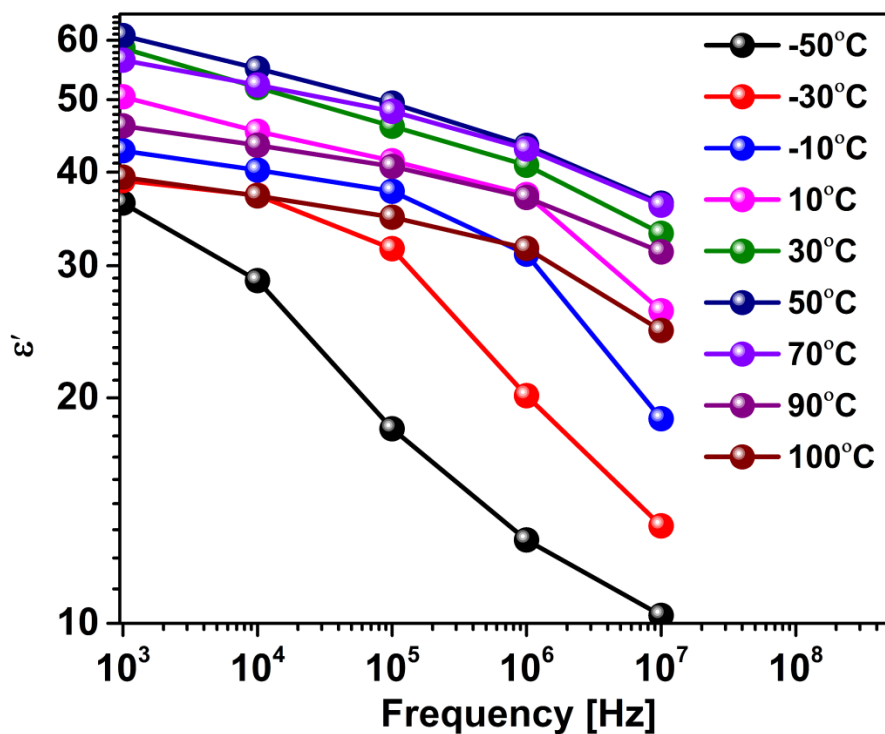


Figure A5.43: Frequency dependent Dielectric Permittivity measurement of **16** at various temperatures.

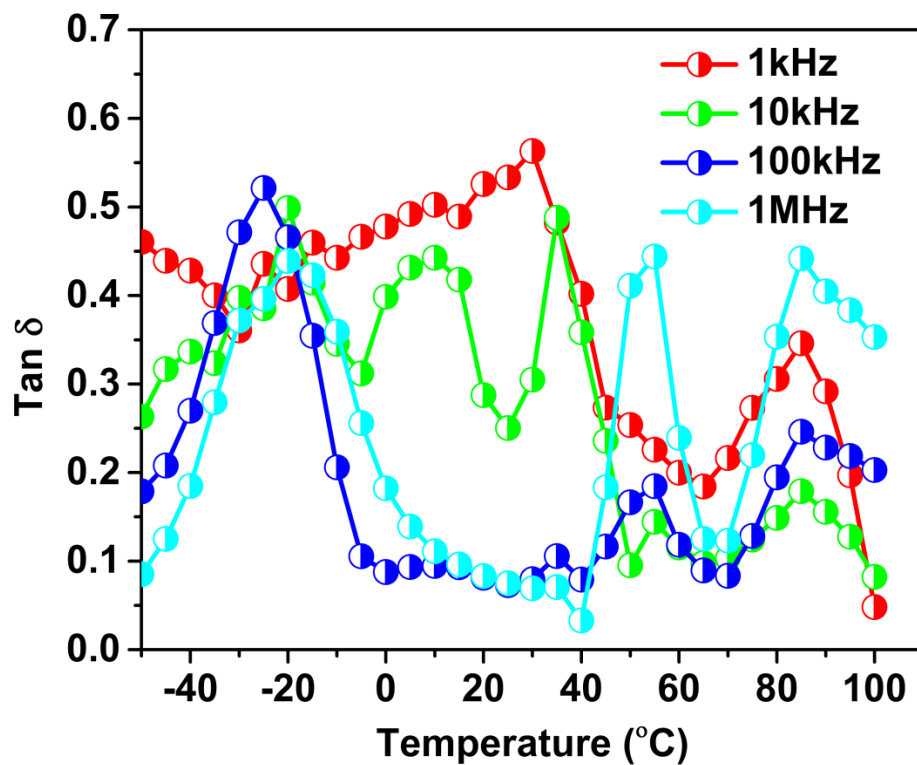


Figure A5.44: Dielectric loss of **13** at different frequencies.

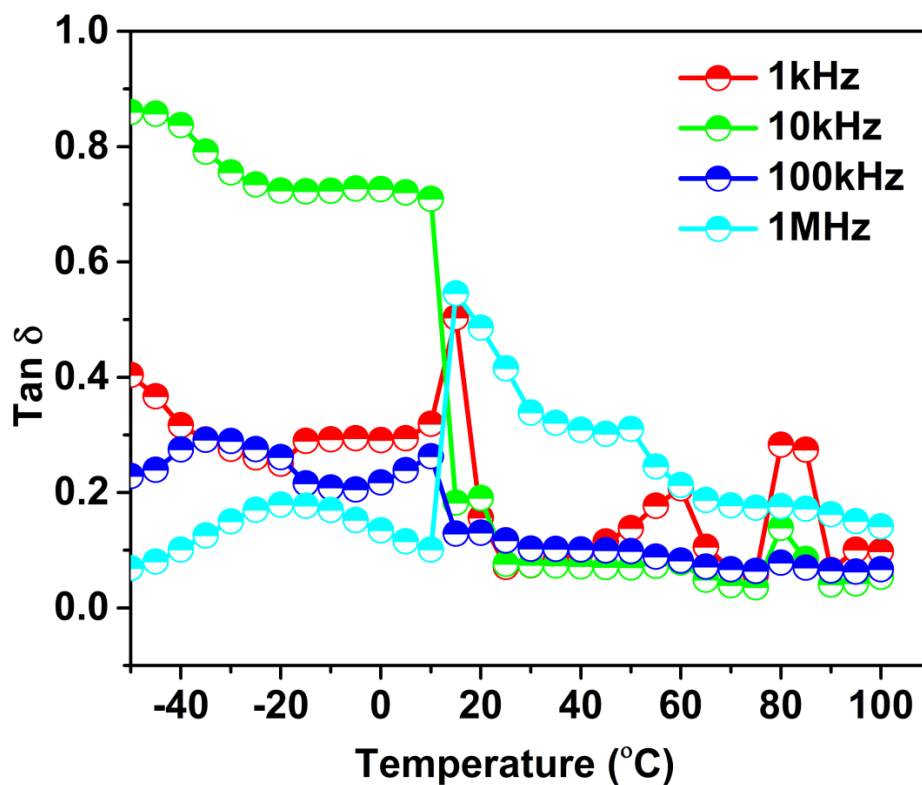


Figure A5.45: Dielectric loss of **14** at different frequencies.

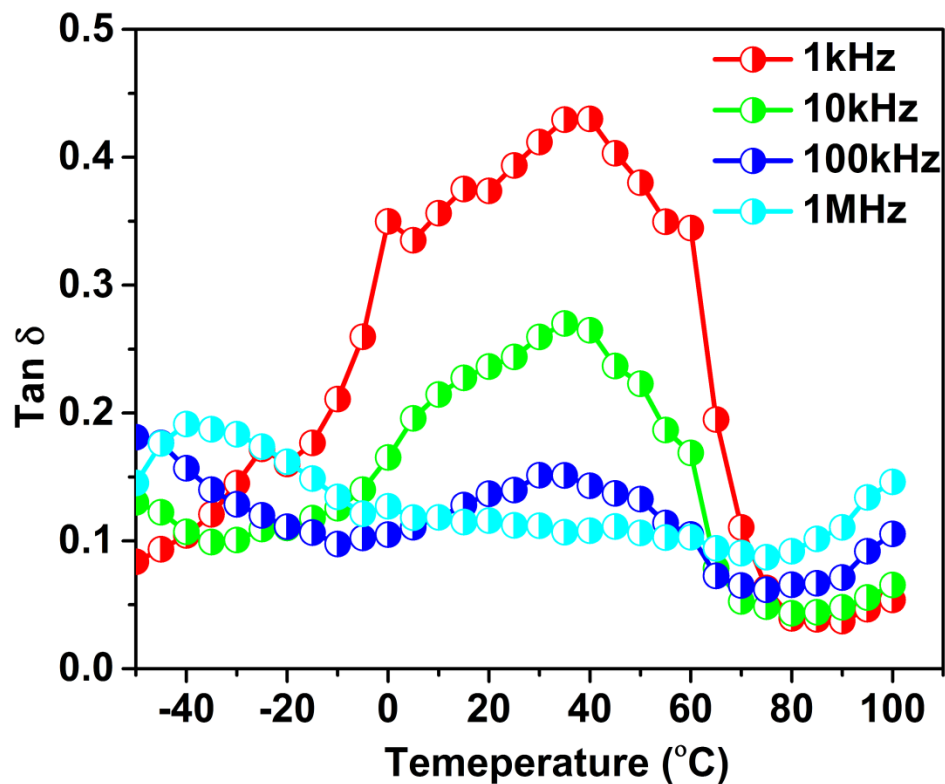


Figure A5.46: Dielectric loss of 15 at different frequencies.

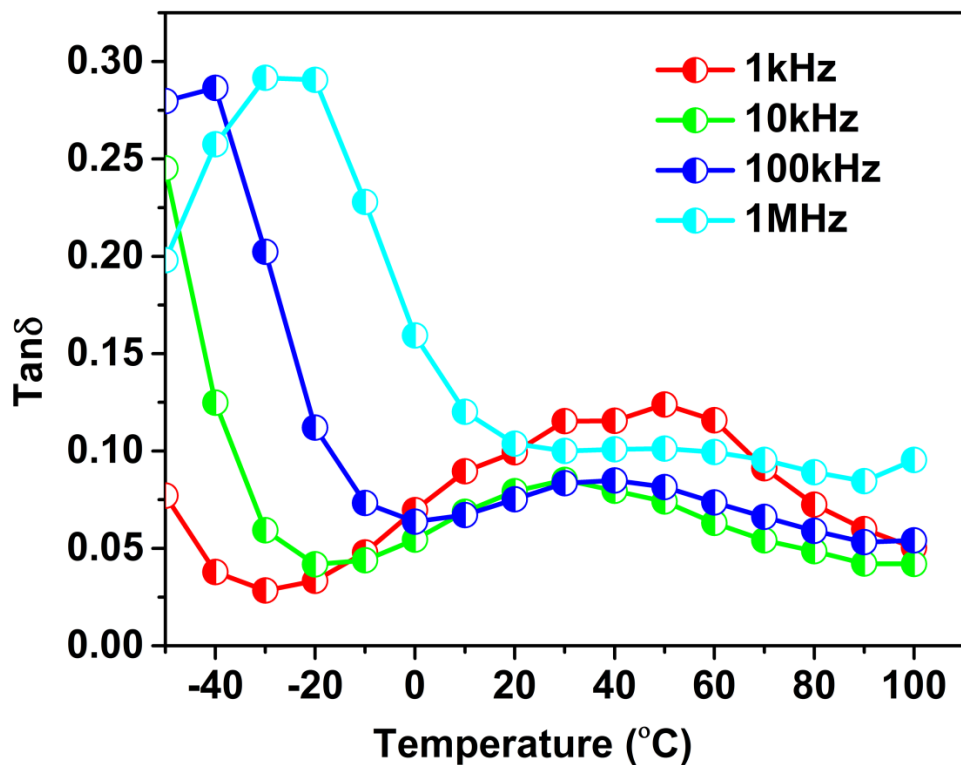


Figure A5.47: Dielectric loss of 16 at different frequencies.

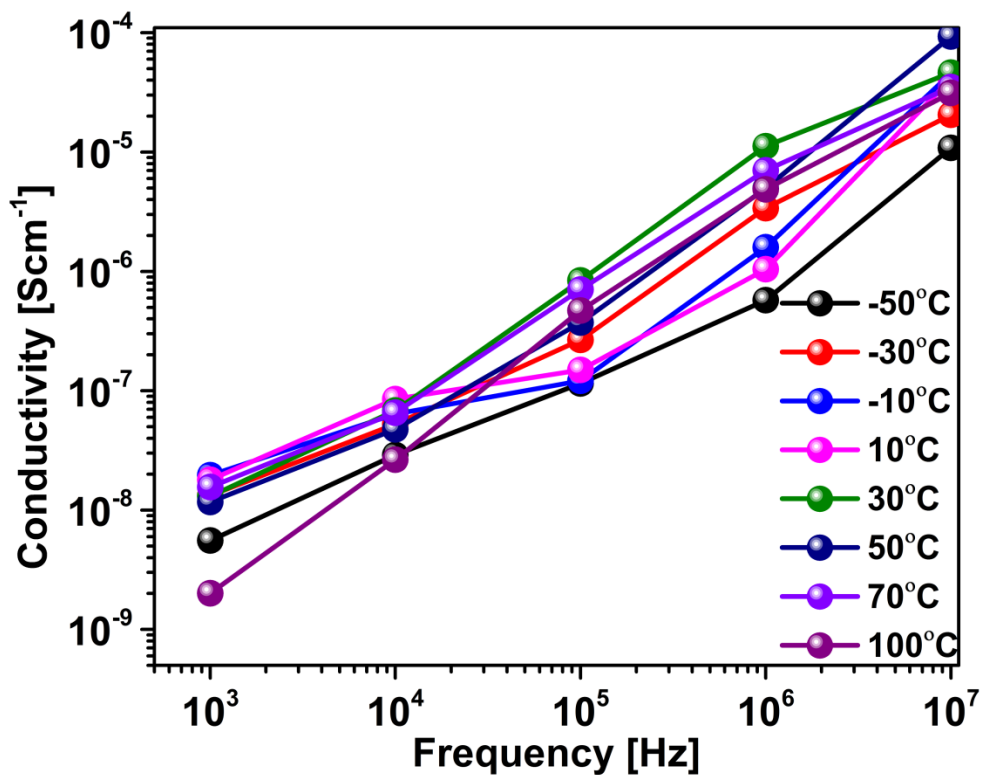


Figure A5.48: Conductivity plot vs. frequency of 13 at various temperatures.

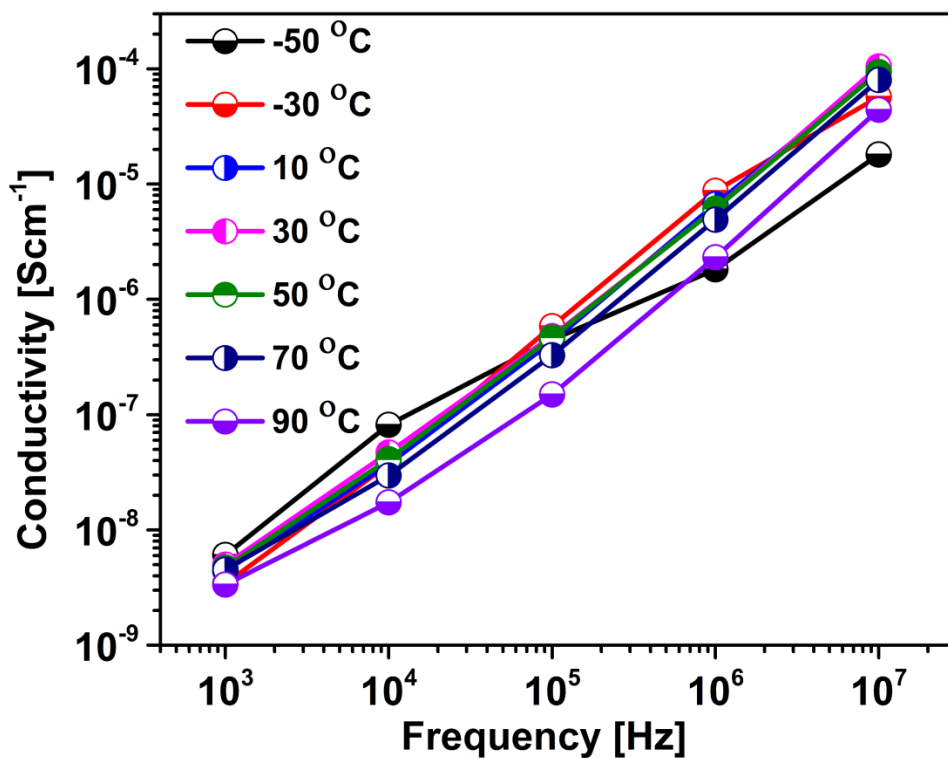


Figure A5.49: Conductivity plot vs. frequency of 14 at various temperatures.

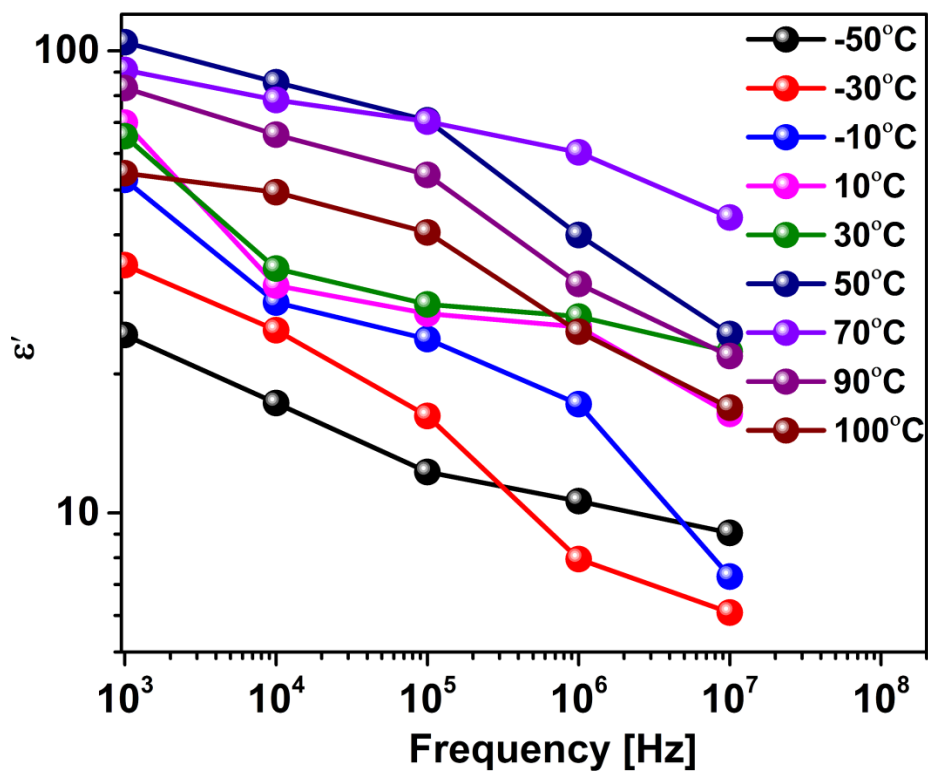


Figure A5.50: Conductivity plot vs. frequency of 15 at various temperatures.

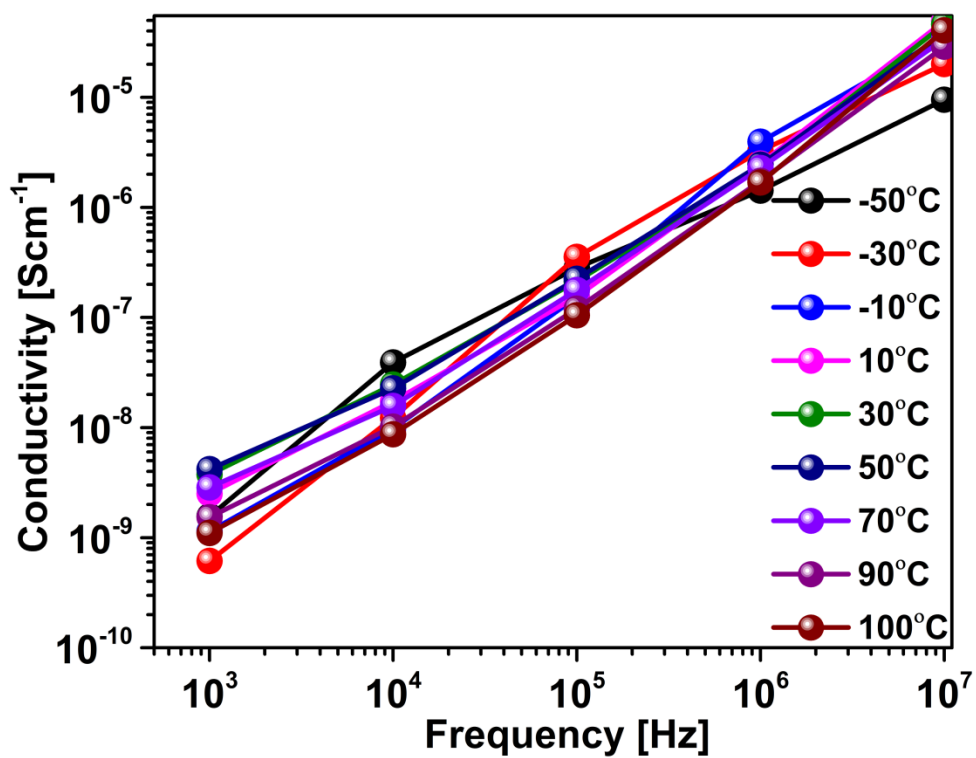


Figure A5.51: Conductivity plot vs. frequency of 16 at various temperatures.

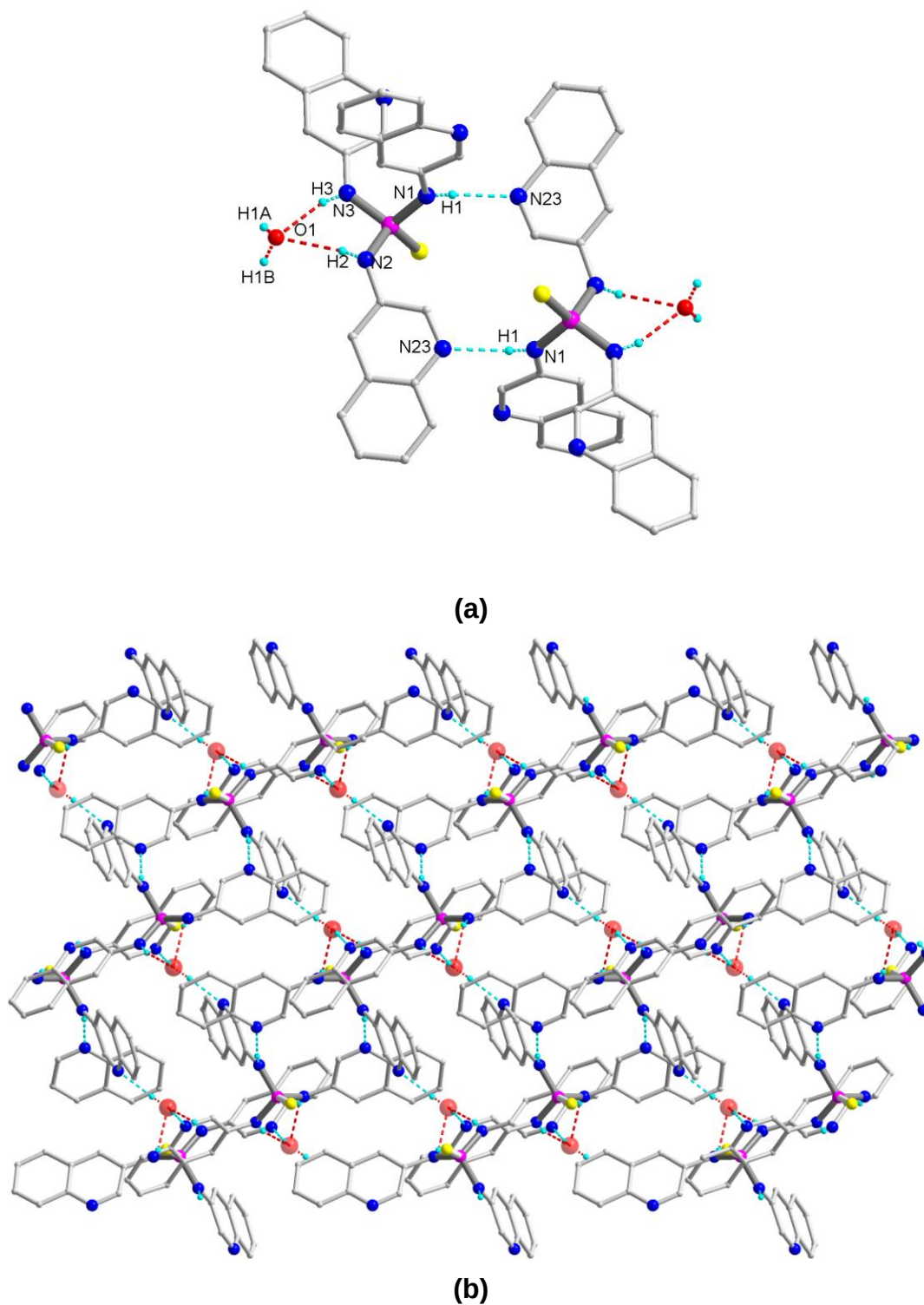


Figure A6.1: Crystal structure of L^1 (a) dimer formation by using N-H hydrogen bonding, (b) 3-dimensional network by using N-H and O-H hydrogen bonding.

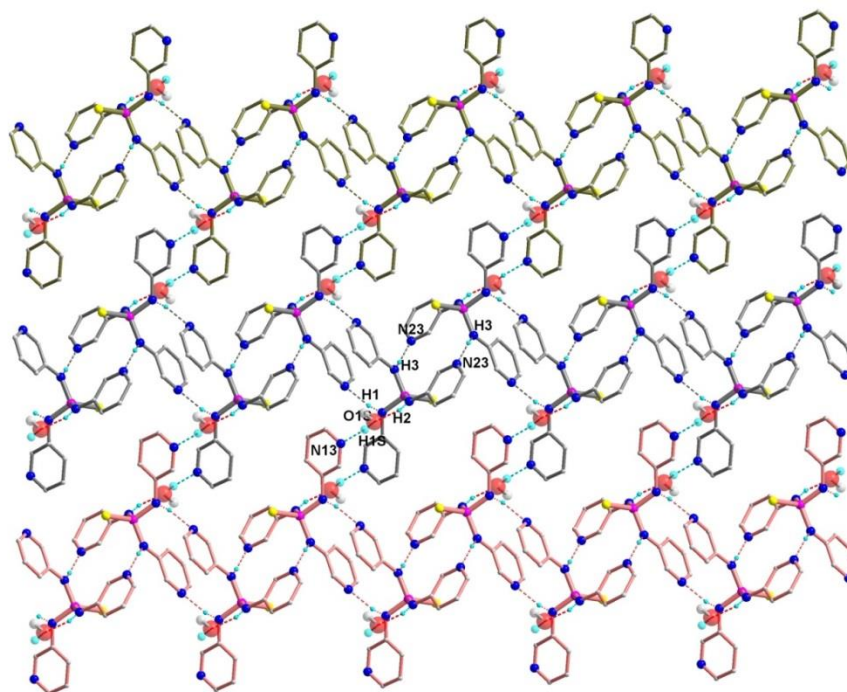
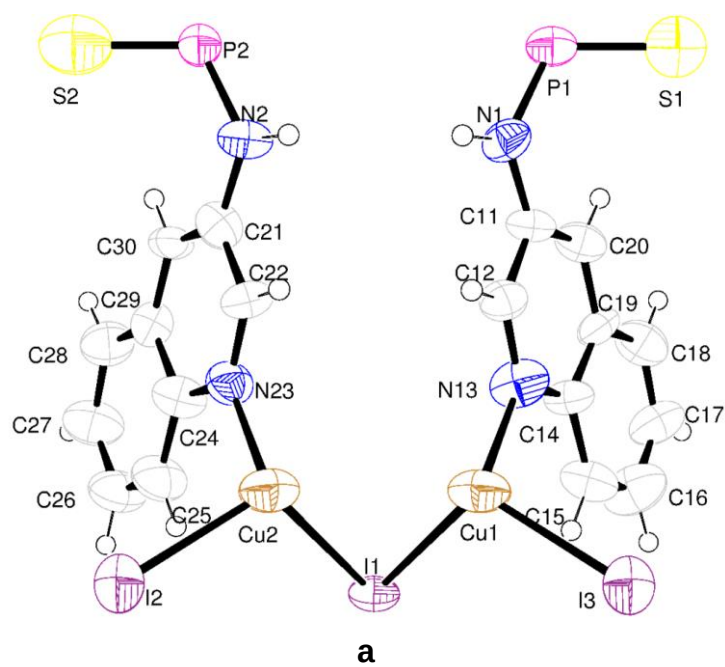


Figure A6.2: 2D-network of L^2 by using N-H and O-H hydrogen bonding.



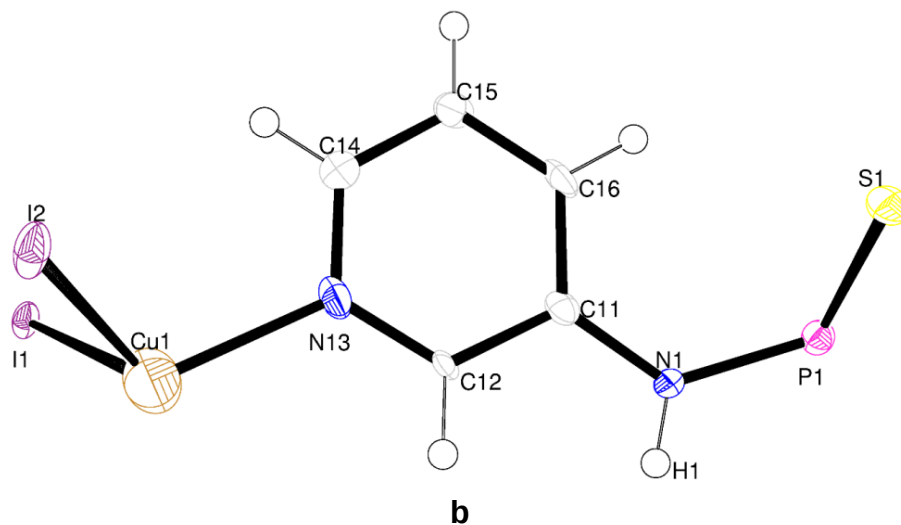


Figure A6.3: Ortep plots at 50% ellipsoid probabilities for the cationic segments of **17** and **18**.

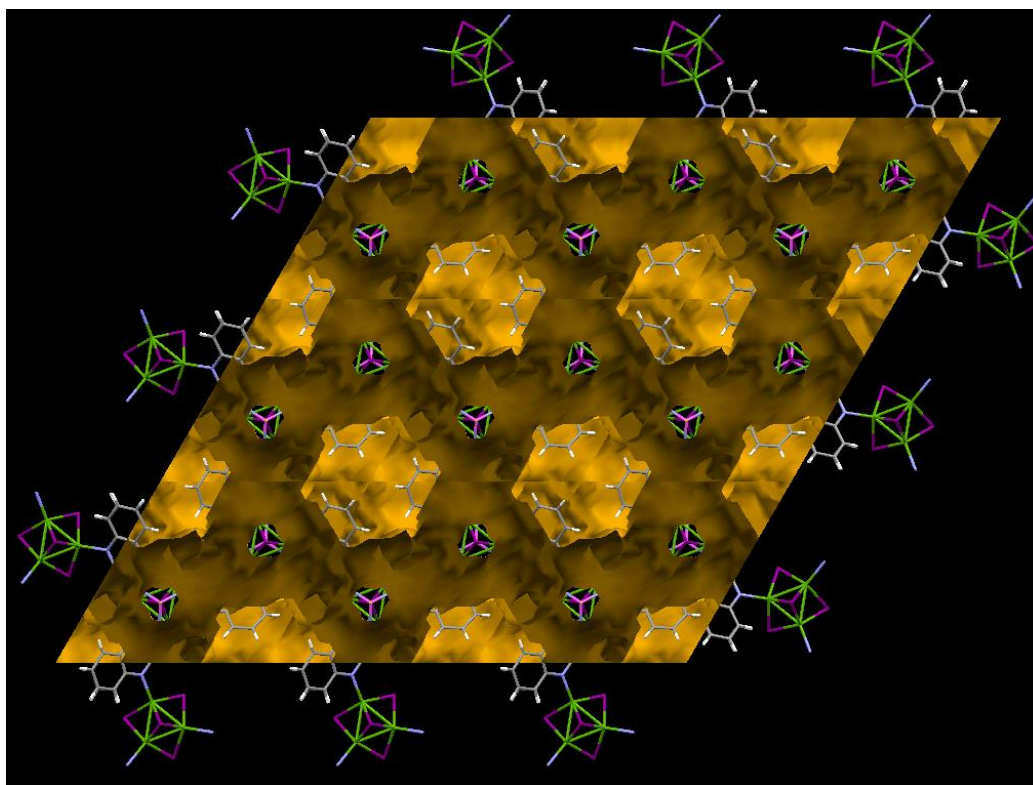


Figure A6.4: Connolly surface view of the packing structure of **17** along the c-axis indicating the solvent accessible voids (generated by Mercury software with a probe radius of 1.2 Å)

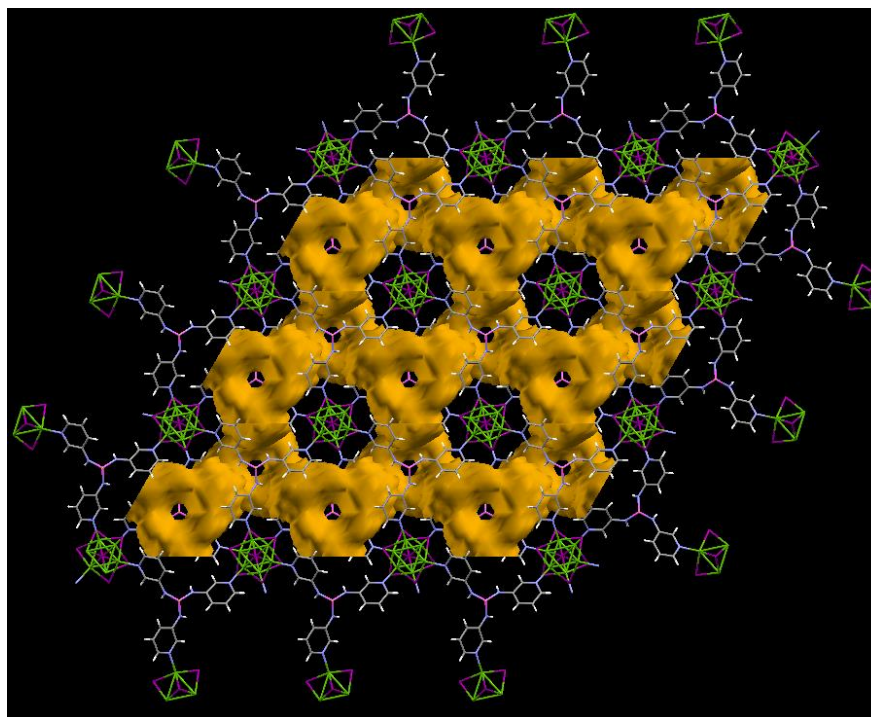


Figure A6.5: Connolly surface view of the packing structure of **18** along the c-axis indicating the solvent accessible voids (generated by Mercury software with a probe radius of 1.2 Å)

Table A6.1: Photophysical Data.

Compound	λ_{abs} (nm)	λ_{ex} (nm)	λ_{em} (nm)	τ_{av}	ϕ
L^1	330	360	408 (298K)	2.877(ns) ^a	0.84
		360	532 (77K)	0.986 (ms)	
L^2	285	319	360 (298K)	1.16(ns) ^b	0.001
17	345	345	370 (298K)	2.14(ns) ^c	0.36
		345	614 (77K)	0.702(ms) ^d	
		360	420 (298K)		
		360	614 (77K)		
18	285	345	506 (298K)	300.56(ns) ^e	0.068
		345	506 (77K)	0.0670(ms) ^f	

a, $\tau_1 = 1.746796$, $\tau_2 = 4.009086$

b, $\tau_1 = 0.234150$, $\tau_2 = 2.07699$

c, $\tau_1 = 0.669887$, $\tau_2 = 3.60644$

d, $\tau_1 = 0.09495$, $\tau_2 = 1.30866$

e, $\tau_1 = 0.796218$, $\tau_2 = 30.79467$, $\tau_3 = 870.0959$

f, $\tau_1 = 0.06698$, $\tau_2 = 0.06698$

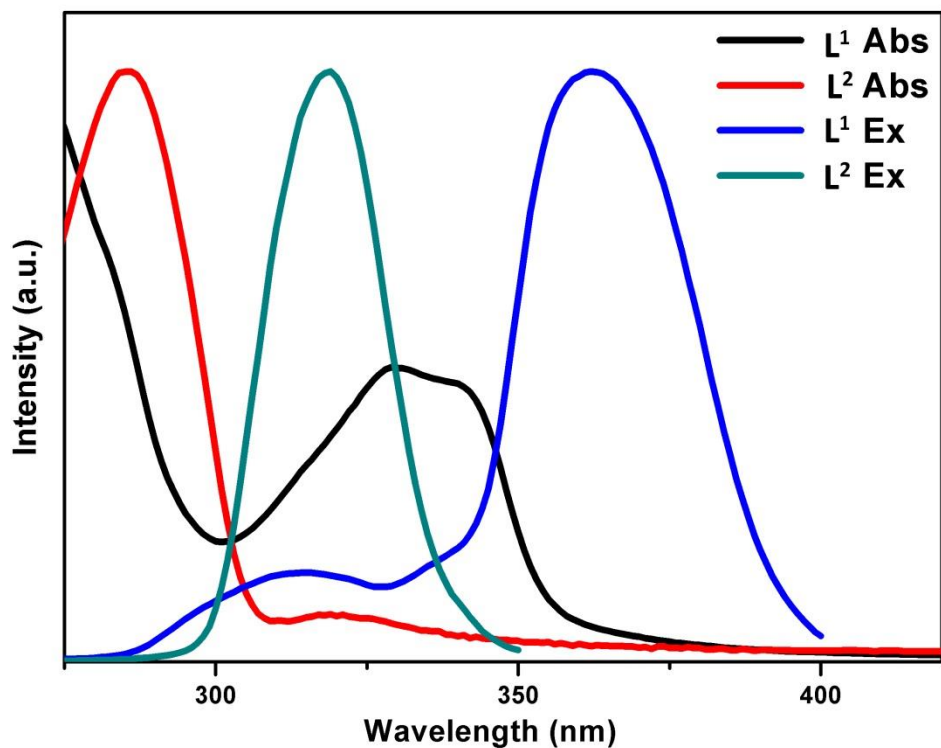


Figure A6.6: Absorbance and Excitation spectra of the ligands

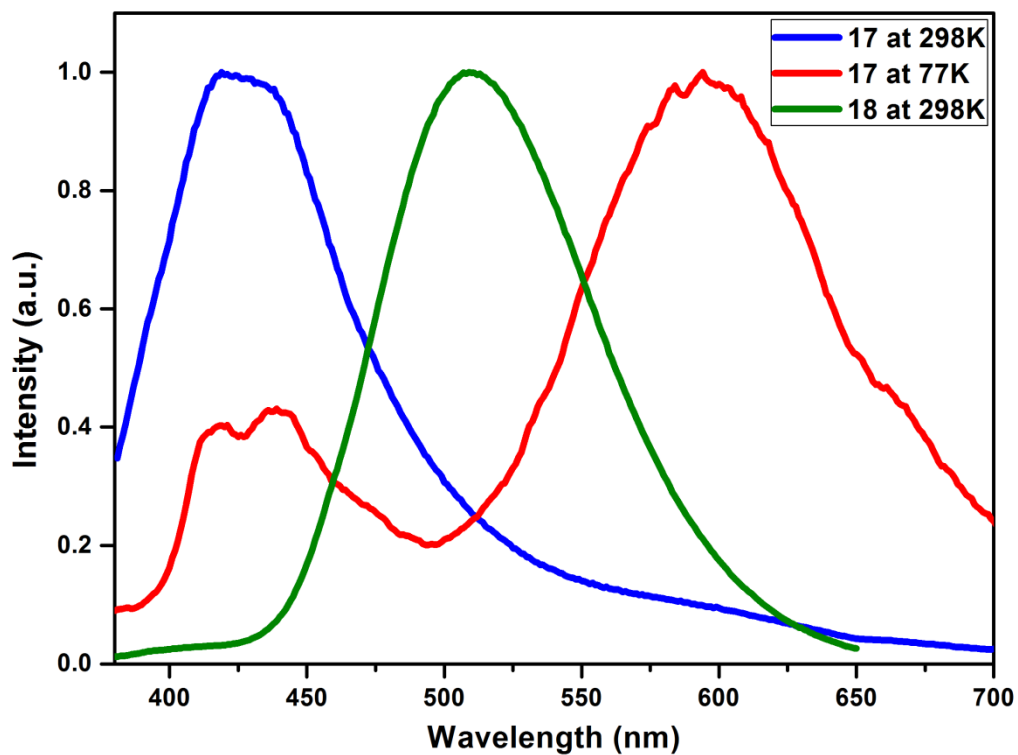


Figure A6.7: Solid-State emission spectra of **17** and **18** ($\lambda_{\text{ex}} = 360$ nm)

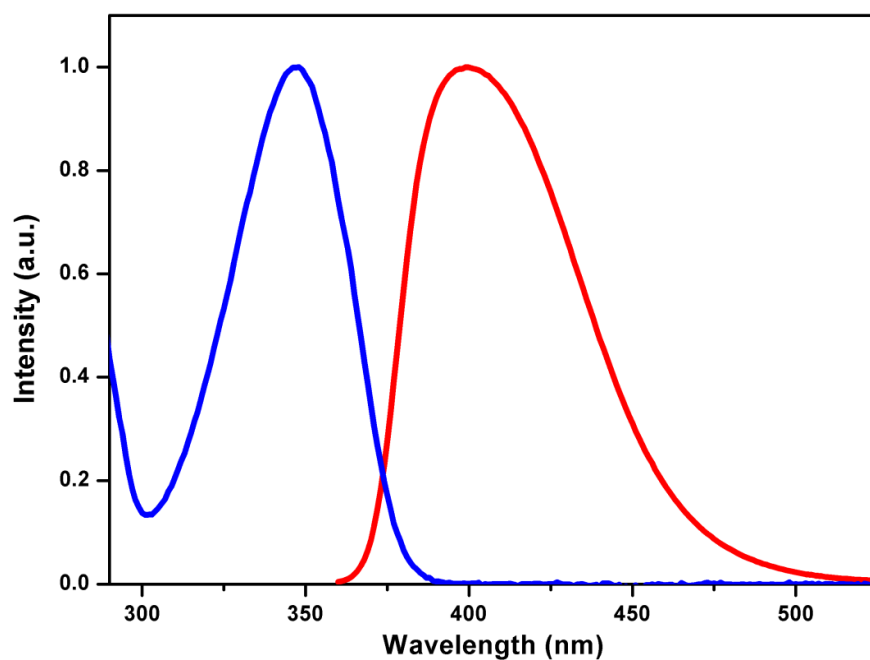
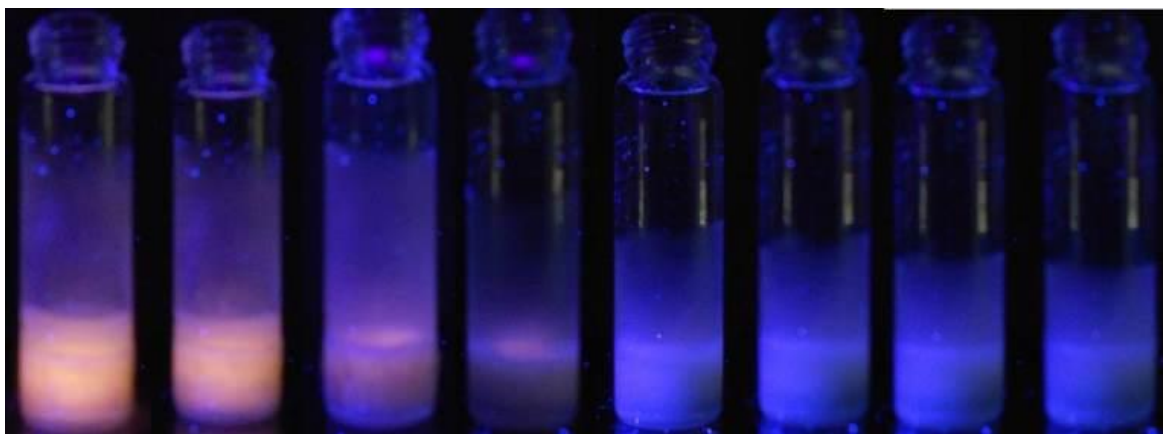


Figure A6.8: Normalised absorbance and emission spectra ($\lambda_{\text{ex}} = 348 \text{ nm}$) of 3-Aminoquinoline (AQH) in acetonitrile.

77K $\xrightarrow{\text{2 minutes}}$ 298K



(a)

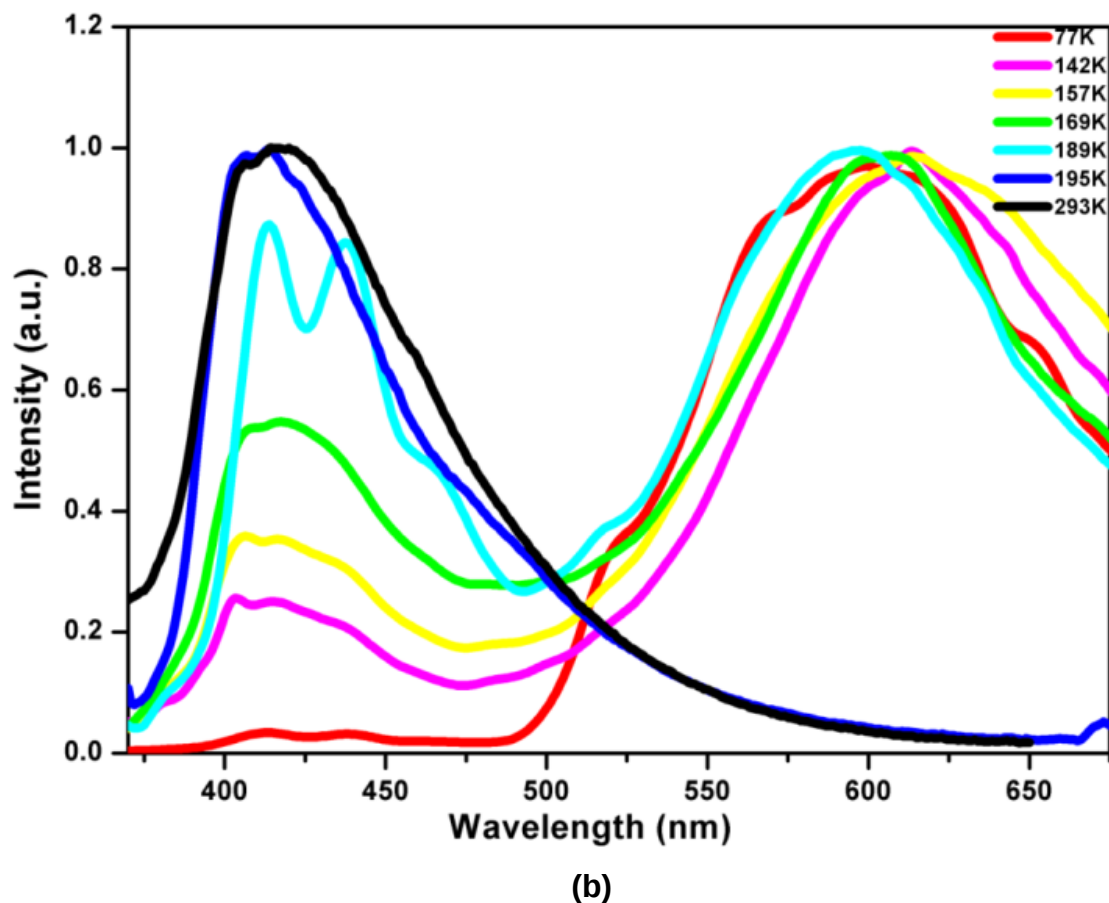


Figure A6.11: (a) Change in emission colours in **17** upon allowing the sample to warm up from 77K to 298K; (b) phosphorescence emission spectra of **17** at various temperatures.

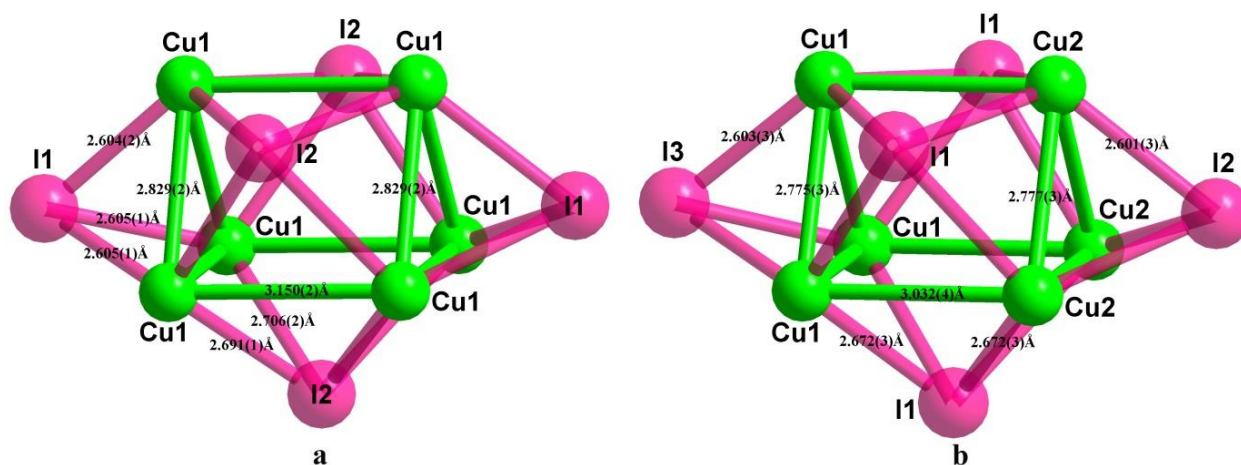


Figure A6.12: Bond distance in $[\text{Cu}_6\text{I}_5]^+$ cluster core in **17**, (a) at 298K and (b) at 100K

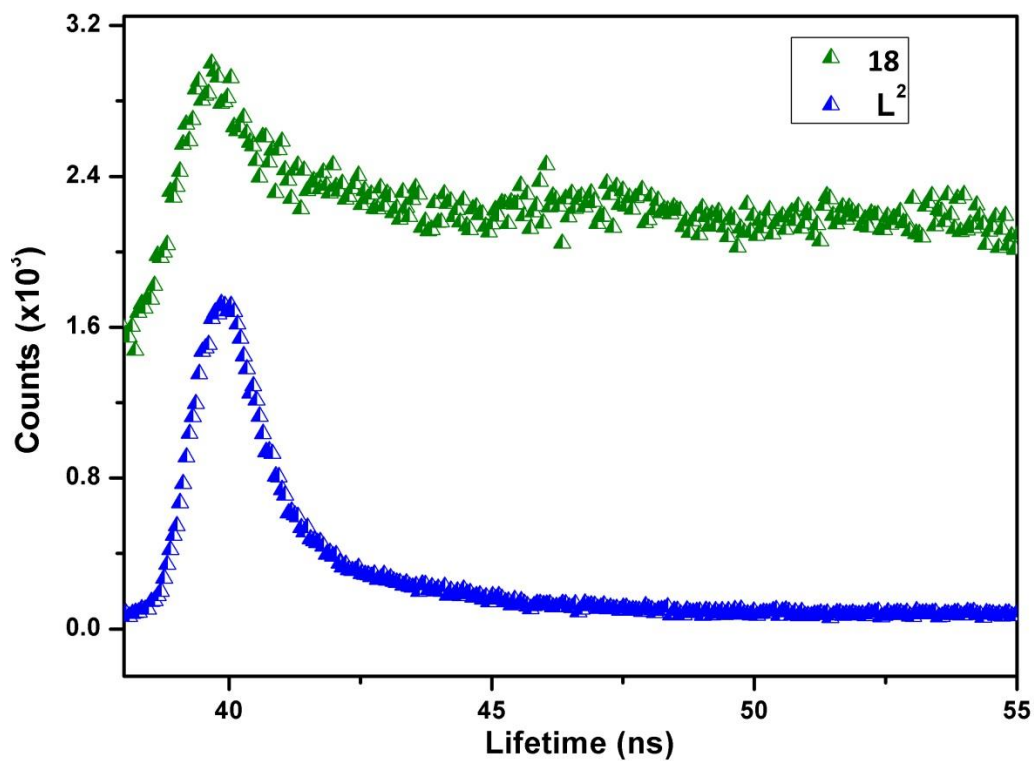


Figure A6.13: TCSPC decay profiles of L^2 and **18** at 298K

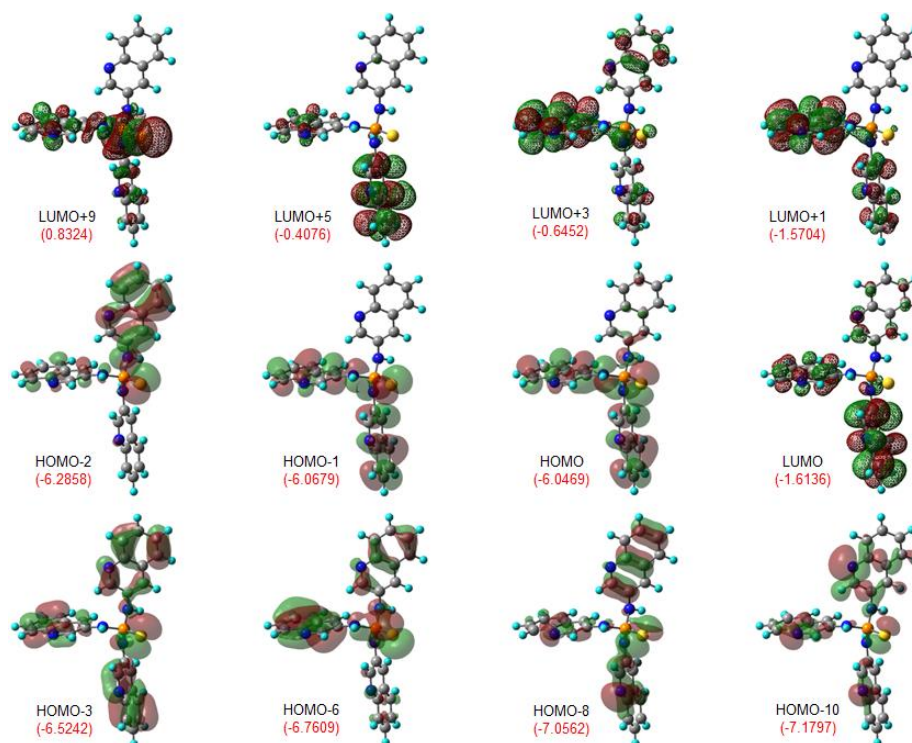


Figure A6.14: DFT derived surface diagrams and energies (in eV) of some relevant MOs calculated for singlet ground state at the S_0 optimized geometry for L^1 .

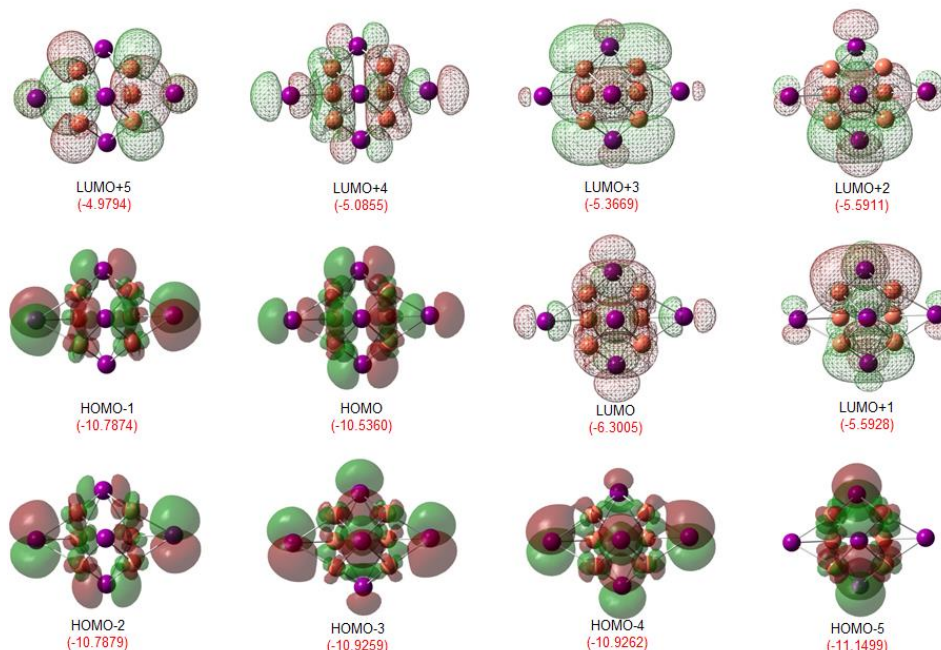


Figure A6.15: DFT derived surface diagrams and energies (in eV) of some relevant MOs calculated for ground state at the S_0 optimized geometry for Bare $[\text{Cu}_6\text{I}_5]^+$ cluster.

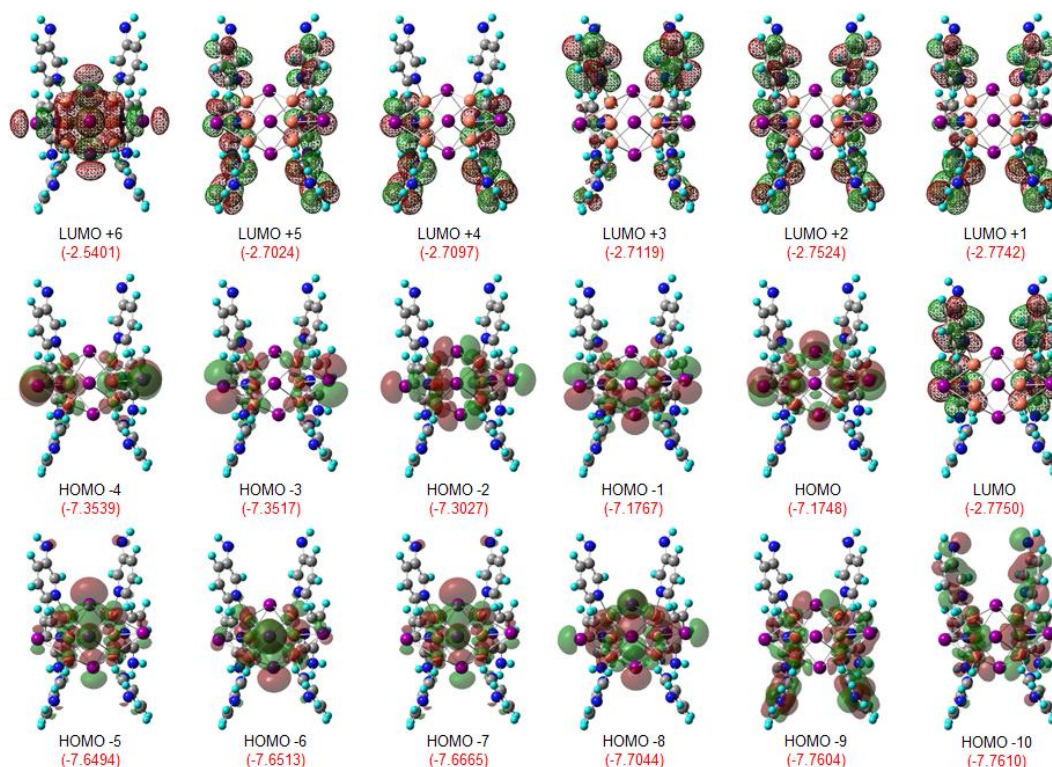


Figure A6.16: DFT derived surface diagrams and energies (in eV) of some relevant MOs calculated for singlet ground state at the S_0 optimized geometry for **17b**.

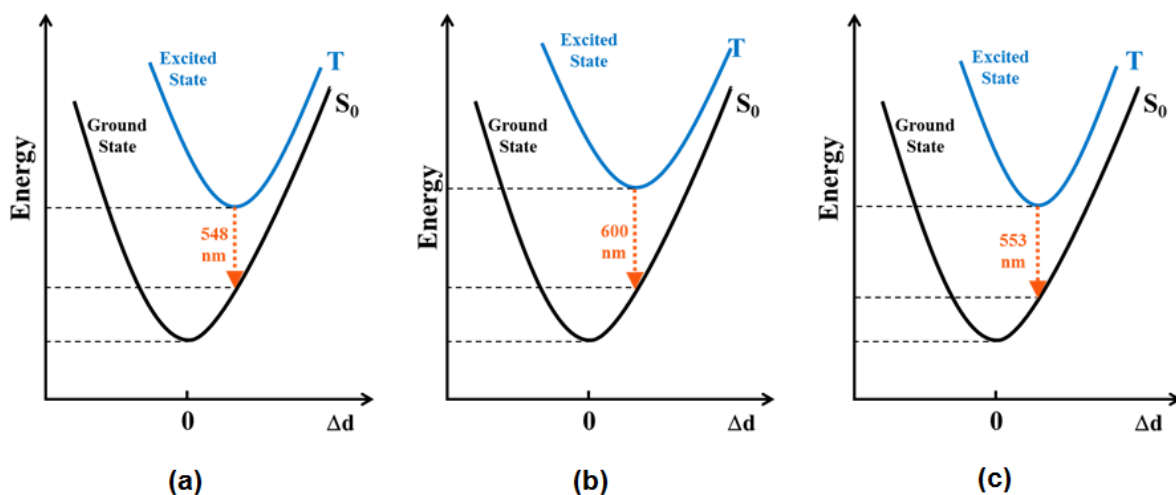


Figure A6.17: Potential Energy Diagram showing S_0 - T gap obtained from Single-point energy calculation on optimized triplet geometry of (a) L^1 , (b) **17a**, and (c) **17b**.

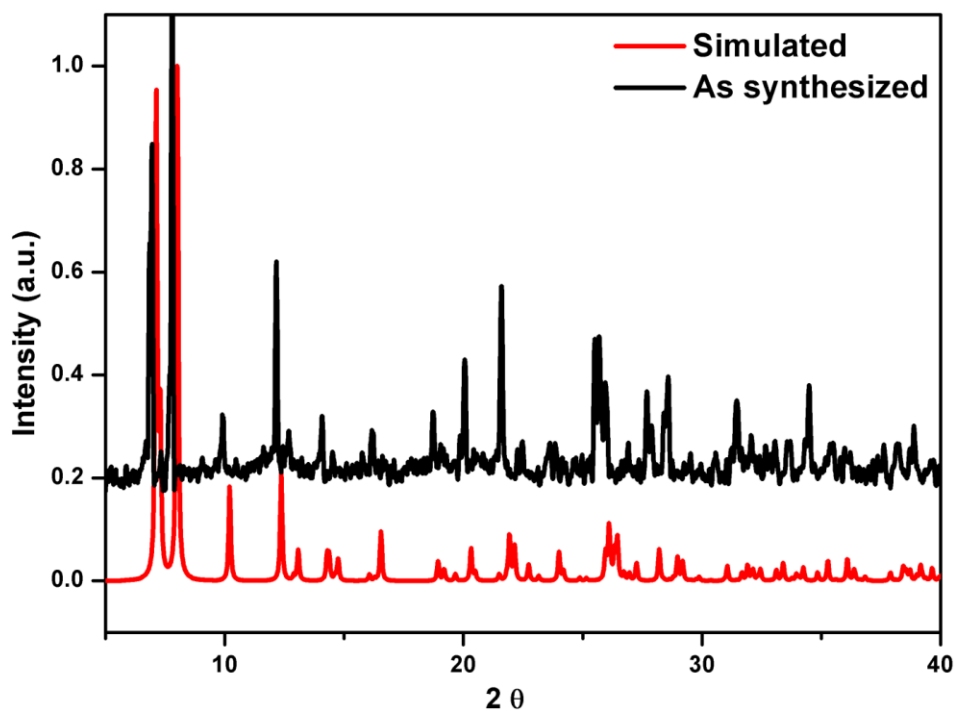


Figure A6.20: PXRD pattern of complex **17**.

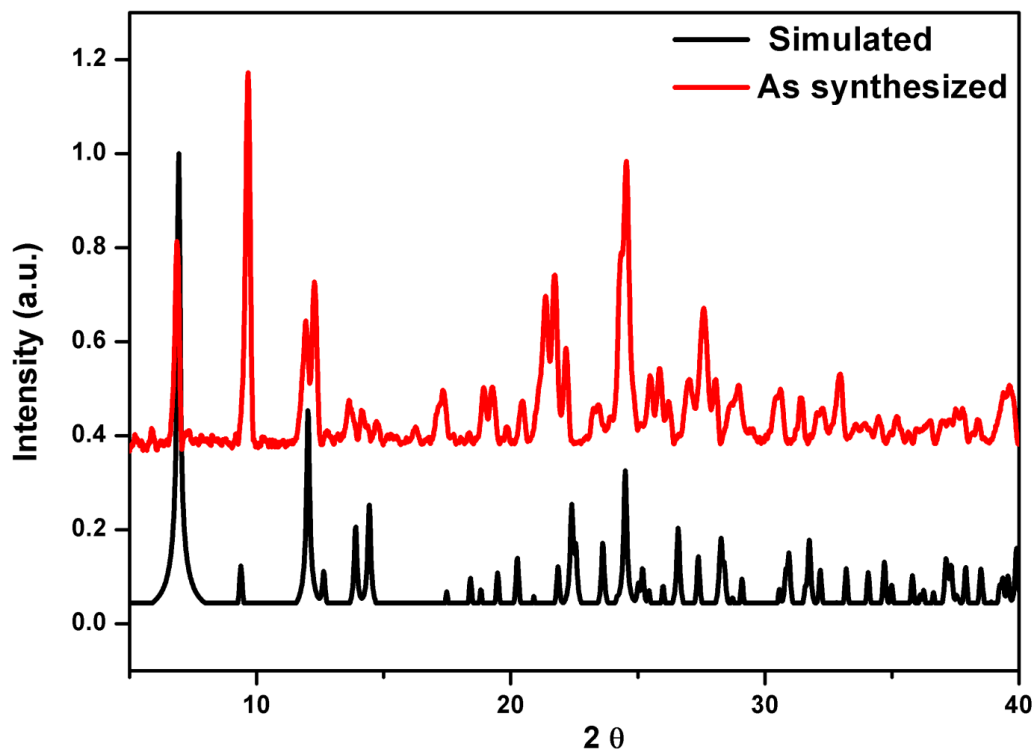


Figure A6.21: PXRD pattern of complex 18.

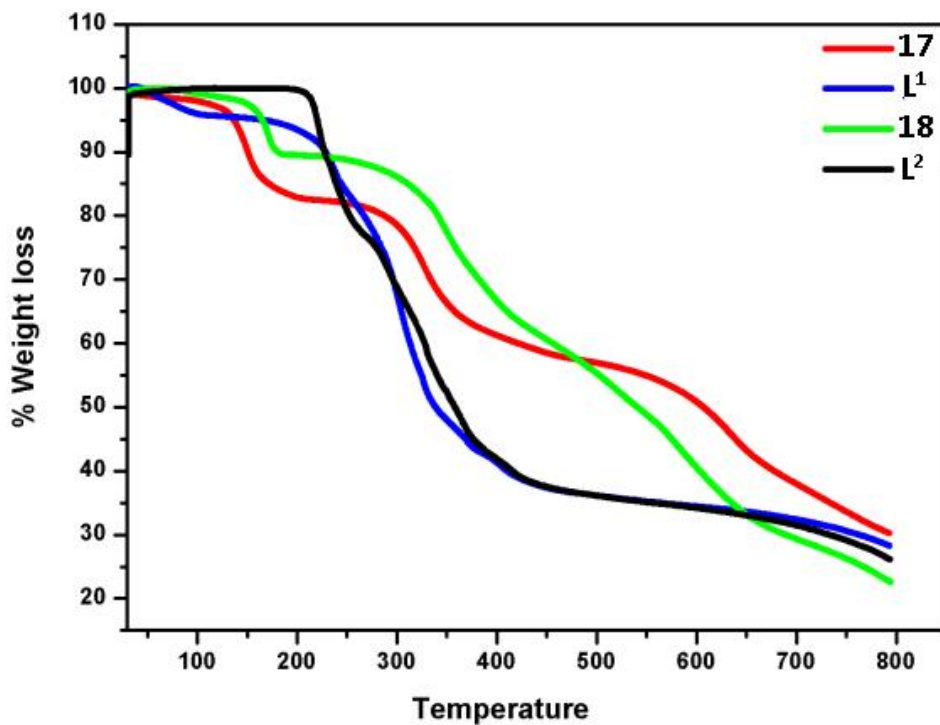


Figure A6.22: Thermogravimetric Plots

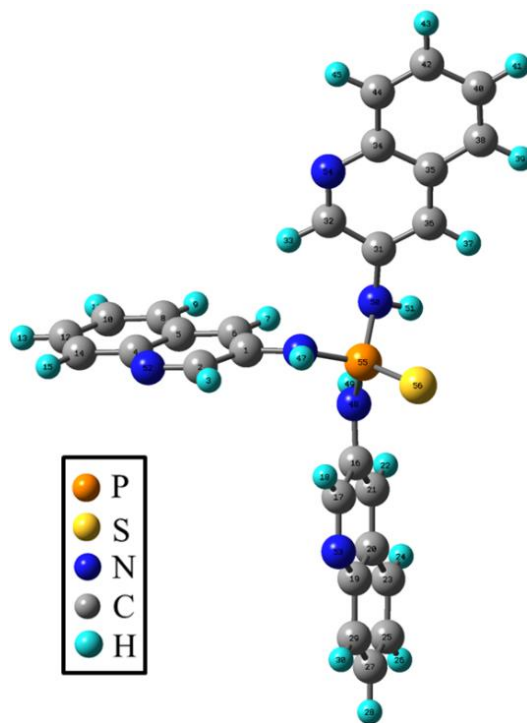


Figure A6.23: Optimized singlet geometry of L^1 .

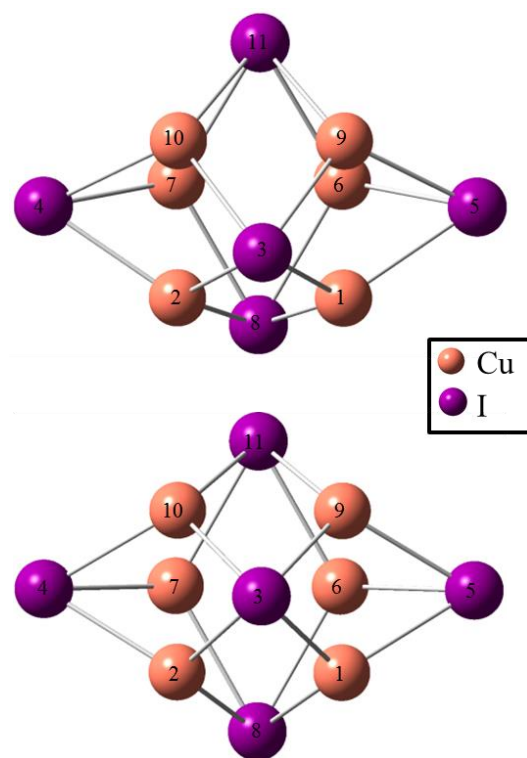


Figure A6.24: Optimized singlet geometry of Bare $[Cu_6I_5]^+$ cluster.

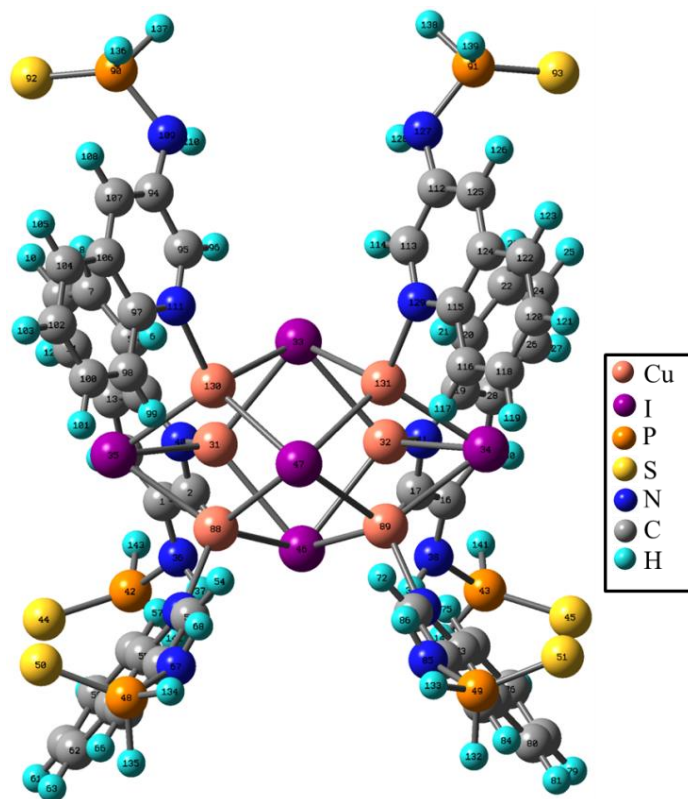


Figure A6.25: Optimized singlet geometry of 17a.

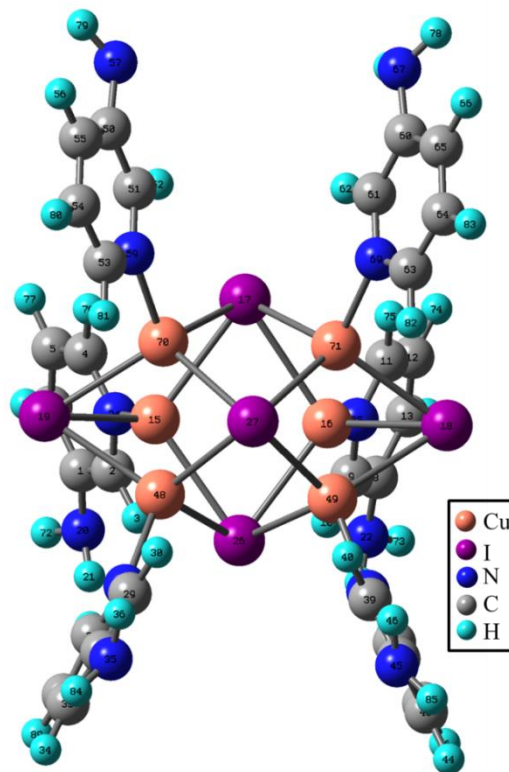


Figure A6.26: Optimized singlet geometry of 17b.

Table A6.2. Averaged Cu...Cu, Cu-I and Cu-N bond lengths from computed data of **17a**.

Parameters	Average Bond Lengths in Å	
	S ₀	T
Cu...Cu within Cu ₃ -triangles	3.0101	3.0350
Cu...Cu along the three rims	3.5750	3.5511
Cu-I distances for μ_4 -iodides	2.8645	2.8667
Cu-I distances for μ_3 -iodides	2.7439	2.7437
Cu-N distances	2.1055	2.0945

Table A6.3. Relevant bond angles from computed data of **17a**.

Atomic centers involved	S ₀	T
Cu(31)-I(33)-Cu(32)	77.31	75.9
Cu(31)-I(33)-Cu(130)	63.23	63.14
Cu(31)-I(33)-Cu(131)	109.37	106.62
Cu(32)-I(33)-Cu(130)	109.33	110.02
Cu(32)-I(33)-Cu(131)	63.26	64.44
Cu(130)-I(33)-Cu(131)	77.44	75.92
Cu(32)-I(34)-Cu(89)	66.62	71.77
Cu(32)-I(34)-Cu(131)	66.36	67.97
Cu(89)-I(34)-Cu(131)	66.66	66.83
Cu(31)-I(35)-Cu(88)	66.58	63.92
Cu(31)-I(35)-Cu(130)	66.37	66.09
Cu(88)-I(35)-Cu(130)	66.56	66.48
Cu(31)-I(46)-Cu(32)	77.59	75.13
Cu(31)-I(46)-Cu(88)	63.45	60.78
Cu(31)-I(46)-Cu(89)	109.36	109.38
Cu(32)-I(46)-Cu(88)	109.29	109.51
Cu(32)-I(46)-Cu(89)	63.47	68.2
Cu(88)-I(46)-Cu(89)	76.72	77.81

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Cu(88)-I(47)-Cu(89)	77.06	77.31
Cu(88)-I(47)-Cu(130)	63.44	63.52
Cu(88)-I(47)-Cu(131)	109.27	107.66
Cu(89)-I(47)-Cu(130)	109.34	111.25
Cu(89)-I(47)-Cu(131)	63.49	63.54
Cu(130)-I(47)-Cu(131)	77.21	77.2

Table A6.4. TDDFT computed transition wavelengths, oscillator strengths, and major orbital contributions for Singlet-Singlet Transitions of L¹. (H and L denotes HOMO and LUMO, respectively)

Transition λ , (nm)	Oscillator Strength (<i>f</i>)	Nature of the Transition (% contribution)
315.37	0.0429	H→L (90%)
309.82	0.0068	H→L+1 (85%)
305.09	0.0267	H→L+2 (80%)
301.46	0.0535	H-2→L (30%), H-2→L+1 (13%)
299.27	0.0473	H-1→L (69%)
293.34	0.0675	H-1→L+1 (59%), H-1→L+2 (12%)
291.97	0.0038	H-9→L+2 (30%), H-7→L+2 (26%)
290.05	0.0075	H-10→L (40%), H-10→L+1 (12%)
289.36	0.0186	H-1→L+1 (16%), H-1→L+2 (53%)
286.42	0.0104	H-8→L+1 (19%), H-2→L+1 (34%)
278.33	0.0321	H-3→L (33%), H-3→L+1 (22%)
276	0.017	H-4→L (44%), H-4→L+1 (13%)

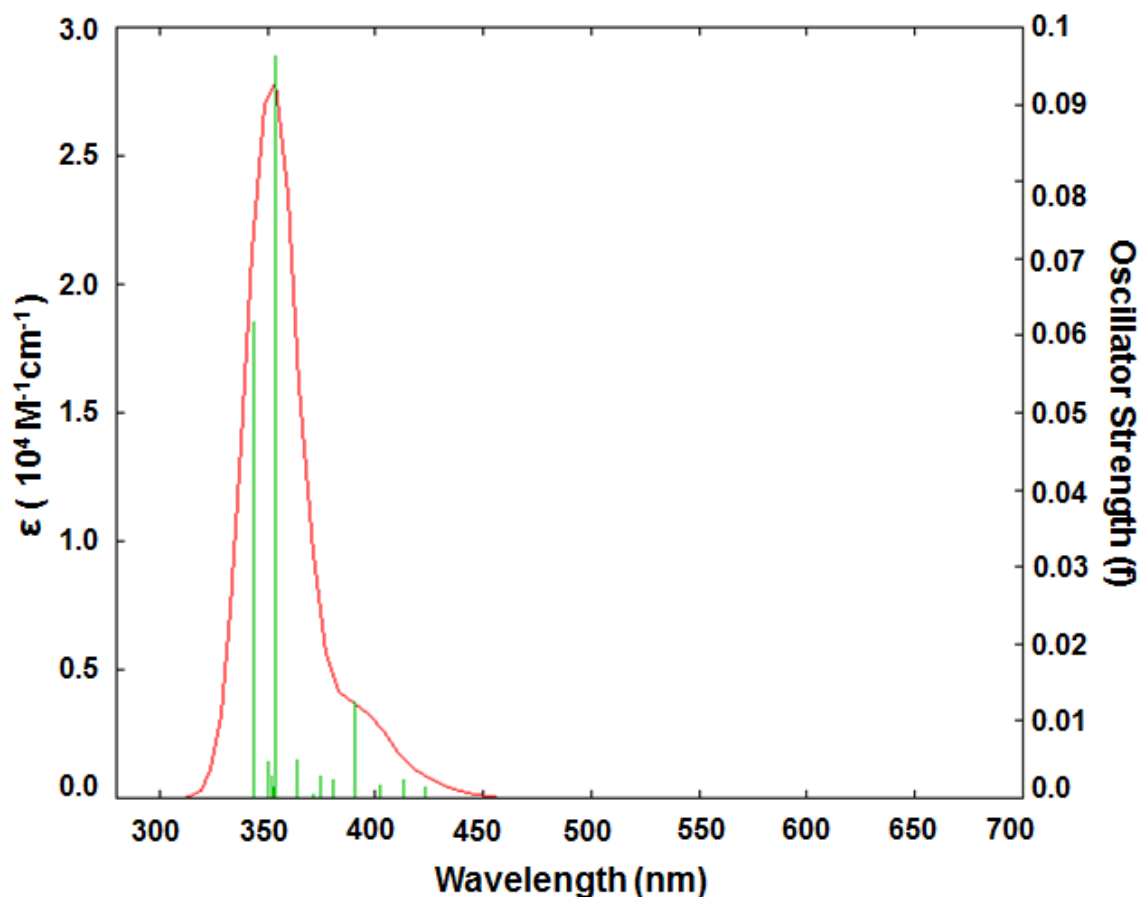


Figure A6.27: TDDFT Calculated transitions (in green) and corresponding absorption spectrum (in red) of **17a**.

Table A6.5: Selected bond-lengths and angles for L^1 , L^2 , **17** and **18**.

Compound	Bond length	Bond angle
L^1	P(1)-S(1) : 1.9297(6) P(1)-N(1) : 1.6511(13) P(1)-N(2) : 1.6634(13) P(1)-N(3) : 1.6590(14)	N(1)-P(1)-N(2) : 109.20(7) N(1)-P(1)-N(3) : 106.42(7) N(3)-P(1)-N(2) : 96.62(7) N(1)-P(1)-S(1) : 107.93(5) N(2)-P(1)-S(1) : 116.67(5) N(3)-P(1)-S(1) : 119.13(5)
L^2	P(1)-S(1) : 1.9392(5) P(1)-N(1) : 1.6665(11)	N(1)-P(1)-N(2) : 101.74(6) N(1)-P(1)-N(3) : 102.75(6)

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	P(1)-N(2) : 1.6558(11) P(1)-N(3) : 1.6592(11)	N(2)-P(1)-N(3) : 109.78(6) N(1)-P(1)-S(1) : 118.26(4) N(2)-P(1)-S(1) : 112.96(4) N(3)-P(1)-S(1) : 110.54(4)
17	P(1)-S(1) : 1.872(14) P(2)-S(2) : 1.875(15) P(1)-N(1) : 1.660(13) P(1)-N(1)#1 : 1.660(13) P(1)-N(1)#2 : 1.660(13) P(2)-N(2) : 1.668(13) P(2)-N(2)#1 : 1.668(13) P(2)-N(2)#2 : 1.668(13) Cu(1)-N(13) : 2.071(13) Cu(1)-I(3) : 2.603(3) Cu(1)-I(1)#3 : 2.672(2) Cu(1)-I(1) : 2.672(2) Cu(1)-Cu(1)#4 : 2.775(3) Cu(1)-Cu(1)#3 : 2.775(3) Cu(1)-Cu(2) : 3.032(4) Cu(2)-N(23) : 2.061(13) Cu(2)-I(2) : 2.601(3) Cu(2)-I(1)#3 : 2.672(2) Cu(2)-I(1) : 2.672(2) Cu(2)-Cu(2)#4 : 2.777(3) Cu(2)-Cu(2)#3 : 2.777(3) I(1)-Cu(2)#4 : 2.671(2) I(1)-Cu(1)#4 : 2.672(2) I(2)-Cu(2)#3 : 2.601(3) I(2)-Cu(2)#4 : 2.601(3) I(3)-Cu(1)#3 : 2.603(3) I(3)-Cu(1)#4 : 2.603(3)	N(1)#1-P(1)-N(1)#2 : 103.4(7) N(1)#1-P(1)-N(1) : 103.4(7) N(1)#2-P(1)-N(1) : 103.4(7) N(1)#1-P(1)-S(1) : 115.0(6) N(1)#2-P(1)-S(1) : 115.0(5) N(1)-P(1)-S(1) : 115.0(6) N(2)-P(2)-N(2)#1 : 102.9(7) N(2)-P(2)-N(2)#2 : 102.9(7) N(2)#1-P(2)-N(2)#2 : 102.9(7) N(2)-P(2)-S(2) : 115.4(6) N(2)#1-P(2)-S(2) : 115.4(6) N(2)#2-P(2)-S(2) : 115.4(6) N(13)-Cu(1)-I(3) : 109.8(5) N(13)-Cu(1)-I(1)#3 : 107.5(4) I(3)-Cu(1)-I(1)#3 : 111.54(8) N(13)-Cu(1)-I(1) : 107.6(4) I(3)-Cu(1)-I(1) : 111.53(7) I(1)#3-Cu(1)-I(1) : 108.78(10) N(13)-Cu(1)-Cu(1)#4 : 145.4(4) I(3)-Cu(1)-Cu(1)#4 : 57.79(5) I(1)#3-Cu(1)-Cu(1)#4 : 107.08(6) I(1)-Cu(1)-Cu(1)#4 : 58.70(7) N(13)-Cu(1)-Cu(1)#3 : 145.3(4) I(3)-Cu(1)-Cu(1)#3 : 57.79(5) I(1)#3-Cu(1)-Cu(1)#3 : 58.72(8) I(1)-Cu(1)-Cu(1)#3 : 107.07(6) Cu(1)#4-Cu(1)-Cu(1)#3 : 60.000(1) N(13)-Cu(1)-Cu(2) : 108.2(4) I(3)-Cu(1)-Cu(2) : 142.03(9)

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		I(1)#3-Cu(1)-Cu(2) : 55.43(7) I(1)-Cu(1)-Cu(2) : 55.43(7) Cu(1)#4-Cu(1)-Cu(2) : 90.02(5) Cu(1)#3-Cu(1)-Cu(2) : 90.02(5) N(23)-Cu(2)-I(2) : 109.5(4) N(23)-Cu(2)-I(1)#3 : 107.8(4) I(2)-Cu(2)-I(1)#3 : 111.48(8) N(23)-Cu(2)-I(1) : 107.7(4) I(2)-Cu(2)-I(1) : 111.47(7) I(1)#3-Cu(2)-I(1) : 108.79(10) N(23)-Cu(2)-Cu(2)#4 : 145.1(4) I(2)-Cu(2)-Cu(2)#4 : 57.74(5) I(1)#3-Cu(2)-Cu(2)#4 : 107.06(6) I(1)-Cu(2)-Cu(2)#4 : 58.68(7) N(23)-Cu(2)-Cu(2)#3 : 145.3(4) I(2)-Cu(2)-Cu(2)#3 : 57.74(5) I(1)#3-Cu(2)-Cu(2)#3 : 58.69(8) I(1)-Cu(2)-Cu(2)#3 : 107.05(6) Cu(2)#4-Cu(2)-Cu(2)#3 : 59.999(1) N(23)-Cu(2)-Cu(1) : 108.6(4) I(2)-Cu(2)-Cu(1) : 141.93(9) I(1)#3-Cu(2)-Cu(1) : 55.43(7) I(1)-Cu(2)-Cu(1) : 55.44(7) Cu(2)#4-Cu(2)-Cu(1) : 89.98(5) Cu(2)#3-Cu(2)-Cu(1) : 89.98(5) Cu(2)#4-I(1)-Cu(1)#4 : 69.14(8) Cu(2)#4-I(1)-Cu(2) : 62.63(9) Cu(1)#4-I(1)-Cu(2) : 100.59(7) Cu(2)#4-I(1)-Cu(1) : 100.58(7) Cu(1)#4-I(1)-Cu(1) : 62.58(9) Cu(2)-I(1)-Cu(1) : 69.13(7) Cu(2)-I(2)-Cu(2)#3 : 64.53(9) Cu(2)-I(2)-Cu(2)#4 : 64.53(9) Cu(2)#3-I(2)-Cu(2)#4 : 64.53(9)
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Appendix 6

		Cu(1)-I(3)-Cu(1)#3 : 64.42(9) Cu(1)-I(3)-Cu(1)#4 : 64.42(9) Cu(1)#3-I(3)-Cu(1)#4 : 64.42(9)
18	P(1)-S(1) : 1.943(7) P(1)-N(1) : 1.664(10) P(1)-N(1)#8 : 1.664(10) P(1)-N(1)#9 : 1.664(9) I(1)-Cu(1)#1 : 2.627(2) I(1)-Cu(1)#2 : 2.627(2) I(1)-Cu(1)#3 : 2.717(2) I(1)-Cu(1) : 2.717(2) I(2)-Cu(1) : 2.637(3) I(2)-Cu(1)#4 : 2.637(3) I(2)-Cu(1)#2 : 2.637(3) I(2)-Cu(1)#5 : 2.637(3) I(2)-Cu(1)#6 : 2.637(3) I(2)-Cu(1)#7 : 2.637(3) Cu(1)-N(13) : 2.095(11) Cu(1)-I(1)#5 : 2.627(2) Cu(1)-Cu(1)#5 : 2.789(4) Cu(1)-Cu(1)#2 : 2.789(4) Cu(1)-Cu(1)#3 : 2.820(5)	N(1)#8-P(1)-S(1) : 115.2(4) N(1)-P(1)-S(1) : 115.2(4) N(1)#9-P(1)-S(1) : 115.2(4) N(1)#8-P(1)-N(1) : 103.2(5) N(1)#8-P(1)-N(1)#9 : 103.2(5) N(1)-P(1)-N(1)#9 : 103.2(5) Cu(1)#1-I(1)-Cu(1)#2 : 64.92(11) Cu(1)#1-I(1)-Cu(1)#3 : 62.89(10) Cu(1)#2-I(1)-Cu(1)#3 : 95.82(9) Cu(1)#1-I(1)-Cu(1) : 95.82(9) Cu(1)#2-I(1)-Cu(1) : 62.89(10) Cu(1)#3-I(1)-Cu(1) : 62.53(11) Cu(1)-I(2)-Cu(1)#4 : 116.16(8) Cu(1)-I(2)-Cu(1)#2 : 63.84(8) Cu(1)#4-I(2)-Cu(1)#2 : 180.0 Cu(1)-I(2)-Cu(1)#5 : 63.84(8) Cu(1)#4-I(2)-Cu(1)#5 : 116.16(8) Cu(1)#2-I(2)-Cu(1)#5 : 63.84(8) Cu(1)-I(2)-Cu(1)#6 : 116.16(8) Cu(1)#4-I(2)-Cu(1)#6 : 63.84(8) Cu(1)#2-I(2)-Cu(1)#6 : 116.16(8) Cu(1)#5-I(2)-Cu(1)#6 : 180.0 Cu(1)-I(2)-Cu(1)#7 : 180.00(10) Cu(1)#4-I(2)-Cu(1)#7 : 63.84(8) Cu(1)#2-I(2)-Cu(1)#7 : 116.16(8) Cu(1)#5-I(2)-Cu(1)#7 : 116.16(8) Cu(1)#6-I(2)-Cu(1)#7 : 63.84(8) N(13)-Cu(1)-I(1)#5 : 109.8(3) N(13)-Cu(1)-I(2) : 108.5(3) I(1)#5-Cu(1)-I(2) : 111.70(8)

Appendix 6

		N(13)-Cu(1)-I(1) : 102.9(3) I(1)#5-Cu(1)-I(1) : 114.55(9) I(2)-Cu(1)-I(1) : 108.90(8) N(13)-Cu(1)-Cu(1)#5 : 149.6(3) I(1)#5-Cu(1)-Cu(1)#5 : 60.13(8) I(2)-Cu(1)-Cu(1)#5 : 58.08(4) I(1)-Cu(1)-Cu(1)#5 : 107.33(7) N(13)-Cu(1)-Cu(1)#2 : 140.2(3) I(1)#5-Cu(1)-Cu(1)#2 : 109.93(7) I(2)-Cu(1)-Cu(1)#2 : 58.08(4) I(1)-Cu(1)-Cu(1)#2 : 56.98(8) Cu(1)#5-Cu(1)-Cu(1)#2 : 60.000(1) N(13)-Cu(1)-Cu(1)#3 : 108.9(3) I(1)#5-Cu(1)-Cu(1)#3 : 57.54(6) I(2)-Cu(1)-Cu(1)#3 : 142.37(5) I(1)-Cu(1)-Cu(1)#3 : 58.74(5) Cu(1)#5-Cu(1)-Cu(1)#3 : 90.0 Cu(1)#2-Cu(1)-Cu(1)#3 : 89.999(1)
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Table A6.6:H-bonding table for L¹, L², **17** and **18**.

Compound	D-H...A	d(H...A)Å	d(D...A)Å	<(DHA)°
L ¹	N(1)-H(1)...N(23)#1	2.05	2.9177(18)	168.2
	N(2)-H(2)...O(1)#2	2.12	2.8278(18)	137.1
	N(3)-H(3)...O(1)#2	1.95	2.8039(17)	164.1
	O(1)-H(1A)...N(33)	1.81(3)	2.7072(18)	170(2)
	O(1)-H(1B)...N(13)#3	1.97(3)	2.8067(19)	169(3)
	#1 -x+2,-y+1,-z #2 -x+3/2,y+1/2,-z+1/2 #3 -x+1,-y+1,-z			
L ²	N(1)-H(1)...N(33)#1	2.23	2.9926(16)	144.6
	N(2)-H(2)...O(1S)	1.91	2.7703(15)	164.6
	N(3)-H(3)...N(23)#22	2.09	2.9675(16)	173.4
	O(1S)-H(1S)...N(13)#3	1.92	2.7577(16)	172.4
	#1 -x+2,-y+1,-z+1 #2 -x+1,-y+2,-z+1 #3 -x+2,-y+1,-z+2			
17	N(1)-H(1)...O(1)#7	1.98	2.83(3)	163.8
	N(1)-H(1)...O(1')#7	2.14	3.01(5)	171.9

Appendix 6

	N(2)-H(2)...O(1')#7 1.84	2.69(5)	163.3
	N(2)-H(2)...O(1)#7 2.06	2.93(3)	168.2
	#1 -y+2,x-y+2,z #2 -x+y,-x+2,z #3 -y+1,x-y+1,z #4 -x+y,-x+1,z #5 -x+1,-y+2,-z+1 #6 -x+1,-y+2,-z+2 #7 x,y+1,z		
18	N(1)-H(1)...O(21) 2.02	2.889(13)	168.7
	#1 -x+y+1,-x+2,-z+3/2 #2 -x+y+1,-x+2,z #3 x,y,-z+3/2 #4 x-y+1,x,-z+1 #5 -y+2,x-y+1,z #6 y,-x+y+1,-z+1 #7 -x+2,-y+2,-z+1 #8 -x+y,-x+1,z #9 -y+1,x-y+1,z		

End of Thesis