

Chapter-VII

Summary and future scope

In this chapter, I summarised all the chapters along with a brief discussion of synthesis, characterization and biomimicking activities with charge transport and aggregation phenomenon. The scope for future works is also delineated. Synthetic coordination complexes including transition metal ions and various polydentate ligands grab a great interest for their exciting structural and physico-chemical properties and smart functionalities. Transition metal-based coordination compounds are also in high demand for their in Biology. Typically, smart coordination-driven functional materials are considered an emerging class of materials applicable for magnetic materials to photo-electronic devices to metallo-therapeutics, and others. In this context, judicious tuning of electronic and geometric parameter of the central metal in combination with suitable polydentate chelators will be treated a central focus for the development of smart molecules. It is well-documented that supramolecular forces like H-bonding, C–H \cdots π and $\pi\cdots\pi$ interactions portray a significant role in rational design of coordination compounds with smart functionality.

In **Chapter I**, the foundation of polydentate ligands and coordination compounds with their promiscuous functional characteristics in the material science have been discussed. **Chapter II**, describes the synthesis, structural and computational characterization, and phosphatase activity of a linkage isomer of complex **1**. In future, deprotonation of the secondary amine in **L¹** may be carried out to examine the ligational diversity of **L¹** towards various metal ions.

Chapter III deals with the synthesis, physicochemical, morphological and supramolecular characterization of a tetraphenylethylene analogue Schiff base, **L²** and study on their aggregation phenomenon. In **Chapter III**, I discussed only the physico-chemical and aggregation properties of the synthetic ligand system, however, there is a lot of room to design the coordination compounds using this synthetic probe. Further, assessment of the aggregation characteristics of **L²** may lead to new insights in molecular aggregation. Furthermore, the bioinspired catalytic applications may also be carried out with the tailor-made complexes.

Chapter IV, demonstrates the synthesis of benzimidazole functionalized Schiff base (**L³**) and its use to develop two isostructural copper(II) complexes, [Cu(**L³**)₂Cl₂]₂ (**2**) and

$[\text{Cu}(\text{L}^3)_2(\text{NO}_3)_2]_2$ (**3**). The synthetic complexes were evaluated as biomimicking catalysts for phenoxazinone synthase like activity in methanol and explored their mechanistic cycles with electro-chemical, spectrophotometric, electron spray ionization mass spectrometry and EPR studies. The compounds exhibited high turn over number. Therefore, the copper complexes may be efficiently allied to the conventional catalytic reactions of industrial significance. It is well-known that benzimidazoles are recommended therapeutics and present many commercially available drugs. Therefore, the cost-effective and water-solubility features of the copper complexes may turn out them an effective therapeutics, although need an extensive trial against various celllines.

Chapter V reports the synthesis, structural characterization, computational calculations and phenoxazinone synthase activity of the tailor-made copper complex, $[\text{Cu}_2(\text{L}^4)_3]\text{ClO}_4$ (**4**). I synthesized this dinuclear copper complex (**4**) having hetero-geometric copper centres bridged via phenolate ions of the synthetic ligand. So, I must make sincere efforts to synthesis some more metal complexes specially zinc, cobalt, nickel, manganese, iron etc. Also, the newly designed complexes may be applied for diffewrent bioinspired oxidation reactions and compare their catalytic activities with the reported copper complex $[\text{Cu}_2(\text{L}^4)_3]\text{ClO}_4$ (**4**).

Chapter VI discusses the unique chelation properties of a polydentate Schiff base for zinc(II) ions in the presence of pseudohalides (thiocyanate and azide) and their charge transport properties of the fabricated solid devices with the zinc complexes in dark and shower photons. The promising charge transport property of **6** envisions a further extension of **6** for future template applications while designing opto-electronic devices according to the needs of the industry.

Synthesis of single crystals of metal complexes bears a serious challenge with promising future scope. It is always a concerning area to design Schiff base ligands and their complexes focusing on the desirable properties of the complexes with suitable modifications. Such challenges always bring an opportunity to discover novel materials with fascinating properties. Further, development of the synthetic analogues for active sites of different metallo-enzymes may lead to novel metallo-catalysts with high selectivity and efficiency of the industrial importance. Truly, the investigations on such bio-inspired catalysis will not only provide valuable information about environmentally sustainable biological oxidation reactions but also offer a strategy to develop an emergent catalyst of future need.

APPENDIX I

List of Publications

- 1. Prafulla Kumar Mudi**, Rajani Kanta Mahato, Mayank Joshi, Suwendu Paul, Angshuman Roy Choudhury, Bhaskar Biswas*, Synthesis and Structural Characterization of a Linkage Isomer to a Mononuclear Nickel(II) Complex: Experimental and Computational Depiction of Phosphoesterase Efficiency, *Journal of Molecular Structure*, **1200 (2019) 114156. (I.F. 3.196).**
- 2. Prafulla Kumar Mudi**, Nilaj Bandopadhyay, Mayank Joshi, Madhusudan Shit, Suwendu Paul, Angshuman Roy Choudhury, Bhaskar Biswas*, Schiff Base Triggering Synthesis of Copper(II) Complex and its Catalytic Fate towards Mimics of Phenoxazinone Synthase Activity, *Inorganica Chimica Acta*, **505 (2020) 119468. (I.F. 2. 545).**
- 3. Prafulla Kumar Mudi**, Rajani Kanta Mahato, Mayank Joshi, Madhusudan Shit, Angshuman Roy Choudhury, Hari Sankar Das, Bhaskar Biswas*, Copper(II) Complexes with a Benzimidazole Functionalized Schiff base: Synthesis, Crystal Structures and Phenoxazinone synthase Activity, *Journal of Applied Organometallic Chemistry*, **(2021) e6211. (I.F. 3.14).**
- 4. Prafulla Kumar Mudi**, Ajit Das, Nagendranath Mahata, Bhaskar Biswas*, Head-to-Tail Interlocking Aromatic Rings of a Hydrazine Functionalized Schiff Base for the development of Nano-aggregates with blue emission: Structural and Spectroscopic Characteristics, *Journal of Molecular Liquids*, **340 (2021) 117193. (I.F. 6.165).**
- 5. Prafulla Kumar Mudi**, Labhini Singla, Anil Chamuah, Sanjib Bhattacharya, Angshuman Roy Choudhury, Bhaskar Biswas,* Schiff Base Driven Denticity-Fluctuated Structural Assortment of Zinc-pseudohalide Complexes: Synthesis, Structures and Electrical Transport Properties, *Crystal Engineering Communications*, **24 (2022) 2418-2428. (I.F. 3.545).**
- 6. Prafulla Kumar Mudi**, Rajani Kanta Mahato, Himanshu Verma, Subhra Jyoti Panda, Chandra Sekhar Purohit, Om Silakari, Bhaskar Biswas,* In Silico Anti-SARS-CoV-2 Activities of Five-membered Heterocycle-substituted Benzimidazoles, *Journal of Molecular Structure*, **1261 (2022) 132869. (I.F. 3.196).**
- 7. Prafulla Kumar Mudi**, Ayan Kumar Mahanty, Muddukrishnaiah Kotakonda, Sunnapu Prasad, Subires Bhattacharyya, **Bhaskar Biswas***, A benzimidazole scaffold

as a promising inhibitor against SARS-CoV-2, *Journal of Biomolecular Structure and Dynamics*, (2021) <https://doi.org/10.1080/07391102.2021.2024448>. (I.F. 3.392).

8. Prafulla Kumar Mudi, Smriti Pradhan, Amrita Sahu, Dipanwita Saha, Bhaskar Biswas*, Synthesis, X-ray Structure and Evaluation of Bactericidal Activity of an o-vanillin Functionalized Schiff Base, *Journal of Applied Microbiology: Theory & Technology*, **2** (2021) 18-28.

9. Prafulla Kumar Mudi, Chanchal Kumar Pal, Bhaskar Biswas*, Synthesis, Supramolecular Architecture and Fluorescence Property of a Mixed Ligand 1D Pb(II) Coordination Polymer, *European Journal of Chemistry*, **10** (2019) 125-130. (I.F. 0.5439).

10. Rajani Kanta Mahato, Prafulla Kumar Mudi, Mayukh Deb, Bhaskar Biswas*, A Direct Metal-free Synthetic Approach for the Efficient Production of Privileged Benzimidazoles in water medium under Aerobic Condition, *Asian Journal of Organic Chemistry*, **10** (2021) 1-11. (I.F. 3.139).

11. Madhusudan Shit, Suvendu Maity, Sachinath Bera, Prafulla Kumar Mudi, Bhaskar Biswas, Thomas Weyhermueller, Prasanta Ghosh*, Nickel(II) di-aqua complex containing water cluster: Synthesis, X-ray structure and catecholase activity, *New Journal of Chemistry*, **45** (2020) 2221-2227. (I.F. 3.591).

12. Nilaj Bandopadhyay, Krishnendu Paramanik, Prafulla Kumar Mudi, Gayetri Sarkar, Muddukrishnaiah Kotakonda, Madhusudan Shit, Bhaskar Biswas*, Hari Sankar Das, A thiomethyl-substituted imidazolyl imine functionalized copper(II) complex: synthesis, structural characterization, phenoxazinone synthase mimics and biological activities, *Polyhedron*, **218** (2022) 115783. (I.F. 3.052).

13. Ajit Das, Anita Sahu, Prafulla Kumar Mudi, Suvendu Paul, Nagendranath Mahata, Bhaskar Biswas*, Synthesis and phenoxazinone synthase activity by a cobalt(II) complex, *Journal of Indian Chemical Society*, **96** (2019) 255-262. (I.F. 0.284).

APPENDIX II

Seminar & Symposium Attended

- **National Seminar on “Frontiers in Chemistry 2020”** Organized by Department of Chemistry, University of North Bengal, Darjeeling, India on 5th March 2020 (**Presented a Poster**).
- **“International Year of the Periodic Table of Chemical Elements- 2019”** Organized by Department of Chemistry, University of North Bengal, India 22nd-23rd November 2019 (**Presented a Poster**).
- **International Seminar on “Frontiers in Chemistry 2019”** Organized by Dept. of Chemistry, University of North Bengal & CRSI North Bengal Local Chapter, Darjeeling, India on 22nd May 2019 (**Presented a Poster**).
- **International Seminar on “Frontiers in Chemistry 2018”** Organized by Dept. of Chemistry, University of North Bengal & CRSI North Bengal Local Chapter, Darjeeling, India on 27th August 2018 (**Presented a Poster**).

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Synthesis and structural characterization of a linkage isomer to a mononuclear Nickel(II) complex: Experimental and computational depiction of phosphoesterase efficiency[☆]

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ABSTRACT

Synthesis and structural characterization of a linkage isomer, bis(2,2'-dipyridylamine)dithiocyanato(*k*-S) nickel(II), [Ni(dpa)₂(*k*-SCN)]₂ (**1**) of a previously reported Ni(II) complex, [Ni(dpa)₂(*k*-NCS)]₂ (dpa = 2,2'-dipyridylamine; SCN = thiocyanate) has been reported herein. X-ray structural analysis of **1** reveals that Ni(II) complex crystallizes in monoclinic system with *P*2₁/*c* space group and exists in *trans* configuration. The coordination geometry for **1** adopts a tetragonal structure. Supramolecular aspects of the Ni(II) complex indicate that N atom of SCN behaves as a donor and H atom of dpa ligand acts as a receptor in growing 1D crystalline structure along *b* axis in solid state. The aromatic rings in **1** prefer to exist in face-centred stacking with interplanar distance of 3.426 Å and supports strongly to form self-assembled 3D crystalline architecture. Hirshfeld surface analysis further recommends this crystalline assembly in solid state. **1** exhibits promising phosphatase activity towards disodium(4-nitrophenyl)phosphate (PNPP) in aqueous-methanolic medium. The hydrolytic phosphatase efficiency for **1** is determined in terms of turnover number (*k*_{cat}) as 3.38 × 10⁴ h⁻¹. Moreover, density functional theoretical computations closely replicate the structural parameters and spectroscopic behaviour of **1**.

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1. Introduction

In this modern era, investigation and exploration of new molecular properties for transition metal based coordination compounds raised the peak of demand in the advancement of functional materials [1–3]. Ligational motif with varying degree of coordination for different ligands may lead to an improvement in morphologies of the coordination compounds and physico-chemical properties as well as structural properties of the compounds may alter in significant manner [4–6]. Nickel(II) compounds with N,N-donor ligand exhibit diverse applications in modern science like fundamental catalysis, magnetism, biomaterials and so on [7–10].

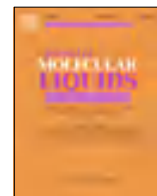
Among the transition metal ions, nickel(II) is very attractive

towards scientific community for its diverse functionality to serve as bio-enzymes like hydrogenase, generator of H₂ gas, etc. Among the available bio-relevant metalloenzymes, alkaline phosphatase enzyme contributes significantly in different biological functions ranging DNA fragmentation to RNA replication to bone metabolism as well as bio-remediation of organophosphate pesticides [11]. Active site of Phosphatase enzyme is surrounded by N or O coordination environment using histidine and aspartate groups [12]. Recently, it is also observed that nickel(II) complexes play key role in phosphatase activity [13] and approved as a well-accepted alternative in pursuing catalyzing hydrolytic reactions. Literature survey indicates that existence of Ni(II) coordination compounds with N,N linkages are well documented [11–14]. L. Dobrzańska et al. [15] have reported same mononuclear Ni(II) complex with dpa ligand having (*k*-N) mode of coordination by NCS ligands. L. Dobrzańska et al. have synthesized this isostructural Ni(II) complex with *k*-N mode of coordination by SCN ligand while we are able to produce its linkage isomer through *k*-S ligational mode in coordination of thiocyanate using a different synthetic approach. The

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Head-to-Tail interlocking aromatic rings of a hydrazine functionalized Schiff base for the development of Nano-aggregates with blue emission: Structural and spectroscopic characteristics

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ABSTRACT

We report the synthesis, physicochemical and morphological characterisation, supramolecular interactions and aggregation-induced blue emission of a newly developed Schiff base, 1,2-bis(phenyl(pyridin-2-yl)methylene)hydrazine (P18). The compound was synthesised through a condensation reaction between hydrazine and 2-benzoylpyridine under reflux in ethanol. The photophysical behaviour of the Schiff base was studied in both monomeric and aggregated forms. Interestingly, the molecular aggregate showed a significant blue shift with ~20 fold higher fluorescence intensity with lifetime, 0.99 ns in the aqueous phase than that of monomeric form, attributed to the development of J-type aggregation. The crystal structure, C–H... π and π ... π interactions, were enumerated to decipher the nature of aggregation. The Schiff base consisting of four aromatic rings (two pyridine and two phenyl rings) displayed a short C–H... π and a long distant π ... π interactions causing a head-to-tail type interlocking of aromatic rings. Energy framework analysis confirmed the predominance of dispersive forces (-192.4 kJ/mol) to the cluster of molecules, thus playing a significant role in the restriction of intramolecular motion of the aromatic rings of P18. A restrain on the rotational probability of =N–N= and Ar–C– bonds leads to an enhancement of an intense fluorescence property of nano-aggregate with blue light emission in solid state. The propagation of the rectangular-shaped monomeric probe in the nano-aggregate with an average hydrodynamic size of 270(\pm 3) nm was established with field emission scanning electron microscopy, dynamic scattering light, and electron dispersive X-ray spectral analysis.

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1. Introduction

The advancement of functional luminophores in light-emitting and light-harvesting processes shows a great promise in bringing novel characteristics and properties to the materials [1,2]. The evolution of light-dependent molecular devices and technologies has triggered a paramount interest to material scientists for the indispensable contribution of molecular devices in scientific and societal advancement [3]. In this context, molecular aggregation beyond the microscopic level is a highly fascinating phenomenon that attributes novel properties to functional materials and the design of high-tech photo-electronic devices [4–6]. Nowadays, the aggregation-induced emission (AIE) phenomenon provides an exciting avenue in scientific research to unveil the properties of

molecular aggregate [1–3]. The advent of newly developed properties endowed by molecular aggregates introduces new characteristics and functionalities in the molecular aggregate compared to single molecules [3,4,7].

AIE deals with a class of molecules having dim or low emission properties in dilute solution. However, the compounds display a pronounced effect on enhancing emission properties in molecular aggregates [8]. A systematic study by Tang *et al.* on different AIE systems summarises that the restriction of active intramolecular motion in the molecular aggregate limits the excited-state non-radiative decay. In contrast, dynamic intramolecular motion increases the non-radiative decay and quenches the molecular emission [9]. Further, the motion-responsive molecular aggregates exhibit strong emission properties in solid state, enabling unique applications in different dimensions, including chemical sensors, fluorescent imaging, photonic drugs, bio-probes, optoelectronics and others [4–7,10].

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Copper(II) complexes with a benzimidazole functionalized Schiff base: Synthesis, crystal structures, and role of ancillary ions in phenoxazinone synthase activity

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This research study reports the synthesis, structural characterization and phenoxazinone synthase-like activity of two structurally similar copper(II) complexes developed with a benzimidazole functionalized Schiff base (**L**). The ligand, **L**, was designed and synthesized in high yield by the reaction of *p*-methoxy benzaldehyde with *o*-phenylenediamine. The reaction of **L** with CuCl₂ and Cu(NO₃)₂ leads to the formation of two isostructural complexes, [Cu(**L**)₂Cl₂]₂ (**1**) and [Cu(**L**)₂(NO₃)₂]₂ (**2**). Single crystal X-ray structural study reveals that both the Cu(II) centre in **1** and **2** adopts a square planar geometry. An attempt has also been made to understand the role of coordinated co-ligands on the catalytic oxidation of 2-aminophenol (2-AP) to 2-amino-3*H*-phenoxazine-3-one (2-APX) in methanol. The presence of coordinated nitrate to Cu(II) ions imparts a more labile character to complex **2**, and the catalytic efficiency (k_{cat}/K_M) for complex **2** (1.50×10^7) was determined almost double compared with that of complex **1** (8.78×10^6). Electro-chemical and electrospray ionization mass spectrometry studies of **1** and **2** with 2-AP suggests that the square planar geometries of the Cu(II) centres remain the driving force to develop enzyme-substrate adducts and excellent catalytic performance of the complexes. Electrochemical and EPR spectral analysis of the reaction mixture confirm the presence of active 2-AP⁻/2-AP^{•-} redox species in the course of catalytic oxidation and suggest the radical driven oxidative coupling of 2-AP in an aerobic environment. Temperature-dependent kinetic measurements were carried out to evaluate the activation parameters (E_a , ΔH^\ddagger , ΔS^\ddagger), which favours the higher rate of catalytic oxidation of 2-AP for complex **2** than complex **1**.

KEYWORDS

copper(II), crystal structure, electrochemical analysis, phenoxazinone synthase activity, Schiff base

Prafullya Kumar Mudi and Rajani Kanta Mahato have equal contributions in this work.



Research paper

Schiff base triggering synthesis of copper(II) complex and its catalytic fate towards mimics of phenoxazinone synthase activity

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ABSTRACT

This research article reports the synthesis, structural characterization and phenoxazinone synthase activity of a new phenoxido-bridged dicopper(II)-Schiff base complex, $[\text{Cu}_2(\text{L})_3]\text{ClO}_4$ (**1**), [HL = (Z)-2-methoxy-6-(((2-methoxyphenyl)imino) methyl)phenol]. X-ray structure of the Cu(II) complex reveals that each of the two Cu(II) centres in **1** adopts different coordination geometries (distorted octahedral and distorted square planar) and phenoxido bridges couple two Cu(II) centres to form a dinuclear copper complex with Cu...Cu distance 3.182 Å. The dicopper(II) complex catalyzes the aerobic oxidation of 2-aminophenol (2-AP) to aminophenoxazinone species in acetonitrile with good turnover number, 78.14 h^{-1} . Electro-chemical and electrospray ionization mass spectrometry analysis of **1** in presence of 2-AP ensure the involvement and key role of the copper(II) centres in formation of enzyme-substrate adduct. Subsequently, electron paramagnetic resonance study confirms the generation of radical species in the course of catalysis. Finally, density functional theoretical calculations well reproduce the experimental geometrical parameters and spectroscopic behaviours of **1** and decisively argue in favour of the proposed catalytic pathways.

1. Introduction

Copper based coordination compounds containing Schiff base ligands have been widely employed in different organic transformations of laboratory and industrial significance [1–3]. In living system, copper ion has played a pivotal role as an essential bio-element. In addition, copper complexes have been widely distributed as the functional sites of various metal dependent enzymes like catechol and galactose oxidase, phenoxazinone synthase, superoxide dismutase, lysine oxidase, N_2O reductase etc [4–7]. Enormous efforts have been made by renowned research groups to mimic structural and functional sites of copper dependent enzymes aiming to develop better catalysts by tuning the electronic and geometric factors associated with the surrounding ligands [8–10]. It has commonly been observed that proper tuning of electronic and steric factors in ligand may lead to improve molecular properties for metal complexes [4–11].

Among the copper(II) complexes of varied nuclearities, dicopper compounds have played significant role in mimicking the functional

activities of type-3 copper proteins with high efficiency [4–7]. Focusing on those structural and functional aspects, synthetic inorganic chemists have actively engrossed in designing and synthesizing coordination compounds aiming to explore the bio-functions of various metal-dependent enzymes [11]. Type-3 copper proteins have a dinuclear copper (II) active site and both the copper(II) centers are antiferromagnetically coupled that makes them EPR silent [12]. The magnetic interactions involving phenoxo-bridged dinuclear copper(II) complexes have been widely investigated in the scientific literature [13,14]. There are lots of examples where dinuclear copper complexes have formed by bridging phenolates and other atomic or molecular bridges (oxides, pyrazoles, phosphates, acetates etc) [15,16].

On the other hand, catalytic oxidative coupling from 2-aminophenol (2-AP) to 2-amino-3H-phenoxazine-3-one (2-APX) by copper(II) based coordination compounds has drawn considerable attention for its important mechanistic insights in the course of oxidative catalysis [17–21]. It has been experimentally observed that a naturally occurring antineoplastic agent, actinomycin D behaves as an inhibitor towards the

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Schiff base driven denticity-fluctuated structural assortment of zinc-pseudohalide complexes: synthesis, structures and electrical transport properties†

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We report the peculiar characteristics of a polydentate Schiff base towards zinc(II) ions in the presence of pseudohalides (thiocyanate and azide) and the charge transport properties of zinc complex mediated devices in the solid state. The designed polydentate chelator, [HL = (Z)-2-methoxy-6-(((2-methoxy phenyl)imino)methyl)phenol], was synthesized by coupling of *o*-anisidine and *o*-vanillin in ethanol under reflux, and the ligand was isolated in a single-crystalline phase in an orthorhombic system with the *Pbca* space group. Interestingly, the ligand bears unique structural features towards the coordination with zinc ions in the presence of thiocyanate and azide ions leading to mononuclear and dinuclear zinc–Schiff base–pseudohalide complexes (ZnP11^{NCS} and ZnP11^{N3}), respectively. In the ZnP11^{NCS} complex, the Schiff base ligand becomes protonated to a zwitterionic form, which causes their monodentate/bidentate behaviour towards Zn(II) ions. In contrast, the ligand, P11, under identical reaction conditions, behaves as a tridentate chelating ligand towards Zn(II) ions in the ZnP11^{N3} complex having a symmetric $\mu_{1,1}$ -phenoxo-bridge. In both complexes, NCS and N₃ ions coordinate with Zn(II) ions in a terminal coordination mode. Crystal engineering approaches and Hirshfeld surface and energy framework analysis of the complexes delineate the dominant contribution of H···S and H···N hydrogen bonding and C–H··· π interactions for a structural assortment of the compounds. Further, the complexes have been employed to construct devices to explore the charge transport properties in the dark and a shower of photons. The ZnP11^{N3} complex exhibits better charge transport properties than ZnP11^{NCS} as evident from high DC conductivity measurement values and relaxation times caused by optical phonon activation under dark and light conditions. This feature might be utilized to explore their template applications in designing electronic devices as per the industry's needs.

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Introduction

Newly designed metal incorporated crystalline materials have been considered an emerging field of research as new structures with promising properties of the solids may

divulge important avenues in science and technology.^{1–4} The development of new metal-based crystalline materials is significant for extrapolating new physicochemical properties and functionalities, leading to the improvement of intelligent molecular devices and applications.^{5–8} In the present context of scientific development, coordination driven materials have emerged as a wealth of advanced functional materials such as novel molecular magnets,⁵ smart optics and electronics,⁶ emerging catalysts,⁷ alloys and composites,⁸ and others.^{9–11}

Nowadays, design and innovation in molecular electronics is an intensive area of scientific and applied research.^{12–14} The foremost applications of molecular electronics include developing innovative materials, logic and memory devices, molecular-scale transistors and energy transduction device sensors, molecular motors, *etc.*^{15–19} In general, molecular electronics may be envisioned as futuristic device miniaturization. The importance of the materials in the development of smart electronic devices stems from their

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† Electronic supplementary information (ESI) available: Supplementary crystallographic data for ZnP11^{N3} and ZnP11^{NCS} are available upon request, quoting deposition numbers CCDC 2120412 and 2120413 respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ce01646f