



Ramakrishna Mission Residential College (Autonomous)
Kolkata 700103, WB, India

Collaborative research in synthetic and structural inorganic chemistry

Number 34

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Period of Investigation: 01-04-2016 to 30-03-2017

Project: Syntheses of oxidovanadium complexes and medicinal activities

Output: The result was published in a journal of international repute

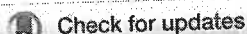
**Publication: Exploring the effect of substituent in the hydrazone ligand of a
family of μ -oxido divanadium(V) hydrazone complexes on structure, DNA
binding and anticancer activity**

Debashis Patra, Subhabrata Paul, Indira Majumder, Nayim Sepay, Sachinath
Bera, Rita Kundu, Michael G. B. Drew and Tapas Ghosh.

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Dr. Tapas Ghosh

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Cite this: *Dalton Trans.*, 2017, 46,
10963Exploring the effect of hydroxylic and
non-hydroxylic solvents on the reaction of
[V^{IV}O(β-diketonate)₂] with 2-aminobenzoyl-
hydrazide in aerobic and anaerobic conditions†Nirmalendu Biswas,^a Debashis Patra,^a Bipul Mondal,^a Sachinath Bera,^b
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Amrita Pal,^f Michael G. B. Drew^g and Tapas Ghosh^h ^{*,a}

Refluxing [V^{IV}O(β-diketonate)₂], namely [V^{IV}O(acetylacetonate)₂] and [V^{IV}O(benzoylacetonate)₂], separately with an equivalent or excess amount of 2-aminobenzoylhydrazide (ah) in laboratory grade (LG) CH₃OH in aerobic conditions afforded non-oxido vanadium(IV) and oxido vanadium(V) complexes of the type [V^{IV}(L¹)₂] (**1**), [V^{IV}O(L¹(OCH₃))₂] (**3**) and [V^{IV}(L²)₂] (**2**), and [V^{IV}O(L²(OCH₃))₂] (**4**), respectively. (L¹)²⁻ and (L²)²⁻ represent the dianionic forms of 2-aminobenzoylhydrazone of acetylacetone (H₂L¹) and benzoylacetone (H₂L²), respectively, (general abbreviation, H₂L), which was formed by the *in situ* condensation of ah with the respective coordinated [β-diketonate] in medium-to-good yield. The yield of different resulting products was dependent upon the ratio of ah to [V^{IV}O(β-diketonate)₂]. For example, the yield of **1** and **2** complexes increased significantly associated with a decrease in the amount of **3** and **4** with an increase in the molar ratio of ah. Upon replacing CH₃OH by a non-hydroxylic solvent, LG CHCl₃, the above reaction yielded only oxido vanadium(V) complexes of the type [V^VO(L¹(OH))₂] (**5**), [V^VO(L²(OH))₂] (**6**) and [V^VO₃(L)₂] (**7**, **8**) whereas, upon replacing CHCl₃ by another non-hydroxylic solvent, namely LG CH₃CN, only the respective [V^VO₃(L)₂] (**7**, **8**) complex was isolated in 72–78% yield. However, upon performing the above reactions in the absence of air using dry CH₃OH or dry CHCl₃, only the respective [V^{IV}(L)₂] complex was obtained, suggesting that aerial oxygen was the oxidising agent and the type of pentavalent product formed was dependent upon the nature of solvent used. Complexes **3** and **4** were converted, respectively, to **7** and **8** on refluxing in LG CHCl₃ via the respective unstable complex **5** and **6**. The DFT calculated change in internal energy (ΔE) for the reactions 2[V^{IV}O(L²(OCH₃))₂] + 2H₂O → 2[V^VO(L²(OH))₂] + 2CH₃OH and 2[V^{IV}O(L²(OH))₂] → [V^VO₃(L²)₂] + H₂O was, respectively, +3.61 and –7.42 kcal mol^{–1}, suggesting that the [V^{IV}O(L²(OH))₂] species was unstable and readily transformed to the stable [V^VO₃(L²)₂] complex. Upon one-electron reduction at an appropriate potential, each of **7** and **8** generated mixed-valence [(L)V^{IV}O–(μ-O)–OV^{IV}(L)][–] species, which showed valence-delocalisation at room temperature and localisation at 77 K. Some of the complexes showed a wide range of toxicity in a dose-dependent manner against lung cancer cells comparable with that observed with *cis*-platin.

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^bDepartment of Chemistry, Ramakrishna Mission Residential College, Narendrapur, Kolkata-700103, India^cHerbert Irving Comprehensive Cancer Centre, Columbia University, 1130 St. Nicholas Avenue, New York, NY 10032, USA^dDepartment of Pathology and Cell Biology, Columbia University, New York, NY, USA^eDepartment of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India^fDepartment of Physical Chemistry, National Chemical Laboratory, Pune, India^gDepartment of Chemistry, The University of Reading, PO Box 224, Whiteknights, Reading, RG6 6AD, UK† Electronic supplementary information (ESI) available: The DFT-optimised structure of complexes **1–8** (Fig. S1), ⁵¹V NMR spectra of complexes **3**, **4**, **7** and **8**(Fig. S2), cyclic voltammogram of **3** and **7** (Fig. S3 and S4, respectively), X-band EPR spectra of complex **1** in CH₂Cl₂ solution at 300 K and 77 K (Fig. S5), X-band EPR spectra of complex **8a** in CH₂Cl₂ solution at 300 K and 77 K (Fig. S6), electronic spectra of **7a** and **8a** in CH₂Cl₂ solution at room temperature (Fig. S7), experimental proof of cell death after treatment with complexes **1–8** (Fig. S8), cytotoxic activity of VOSO₄ at different concentrations (Fig. S9), calculated geometrical parameters for complex **2** (Table S1), calculated geometrical parameters for complexes **3** and **4** (Table S2), calculated geometrical parameters for complex **8** (Table S3), vertical excitation energies (Ecal), oscillator strengths (fcal) and type of excitations of the excited states obtained from TD-DFT calculations of **1–8** (Table S4) and X-ray crystallographic files in CIF format of H₂L² ligand and for compounds **2**, **3**, **4** and **8**. CCDC 1480688–1480691 and 1529620. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt01776f

1. Introduction

Vanadium, the third element of the first-row transition series, is an important trace bioelement.¹ Among the several reported effects of vanadium on organisms, the following are noteworthy: a stimulatory effect on the growth of algae and plants;² the inhibitory action of vanadate(v) on Na, K-ATPase;³ the involvement of vanadate in the regulation of phosphate metabolism in humans;⁴ the presence of vanadium at the active site of certain enzymes, including haloperoxidases in sea algae and lichens⁵ and some nitrogenases in nitrogen-fixing *Azotobacter*.⁶ It has also been demonstrated that many vanadium complexes have therapeutic potential (e.g., insulin-mimicking,⁷ anti-amoebic⁸ and anti-cancer⁹) activities.

Of the eight (−III to +V) available oxidation states of vanadium, the +III, +IV, and +V states are biologically important. In the two higher (+IV and +V) oxidation states, vanadium is oxophilic and forms varieties of oxido species *viz.*, VO²⁺, VO³⁺, (OV-μ-O-VO)^{3+/4+} [*i.e.*, (V₂O₃)^{3+/4+}] and VO₂⁺, that involve extremely strong and inert V≡O bonds (*T*_{1/2} for O-exchange with bulk water is ≈400 min) with unusually high V≡O bond energy^{10,11} (atomization energy = 140 kcal mol^{−1}). In fact, the oxidovanadium ion represents one of the most stable diatomic cations and dominates the chemistry of vanadium.^{12a}

Among the enigmas to be solved with respect to the utilization of vanadium in nature are: the accumulation of V(III) by some sea squirts and fan worms; the presence of the non-oxido V(IV) compound amavadin in fly agaric;¹³ the presence of the non-oxido V(V) compound in the co-factor of an alternative form of nitrogenase, known as VNase, which catalyses the biological conversion of atmospheric dinitrogen to bioavailable ammonia.^{4,14} However, in the abiological domain, the formation of non-oxido or “bare” vanadium(IV) and vanadium(V) complexes is not common because the strong and inert V≡O oxido bond must be removed from the vanadium as a water molecule.

Though this information has encouraged coordination chemists over the last 40 years to synthesize and characterize new non-oxido V(IV) and V(V) complexes, unfortunately, until now, such compounds have been limited in number^{10,12,15–26} due to the strength of the V≡O bond. It has been found that almost all of these compounds have vanadium centres in six-coordinated O/N donor environments^{12,15–21} containing at least one phenolic-O or alcoholic-O moiety, with the exception of a few complexes containing bidentate dithiolenate,²² acetylacetonate²³ and benzoylacetonate²³ ligands. Six-coordinated non-oxido V(IV) complexes with VO₂N₂S₂ coordination have been reported very recently.¹⁰ A few examples of four- and five-coordinated non-oxido V(IV) complexes with VO₄²⁴ and VNO₄²⁵ coordination have been reported. Recently, some eight-coordinated non-oxido V(IV) complexes with VN₄O₄ coordination have been reported together with the structural characterization of one compound.²⁶

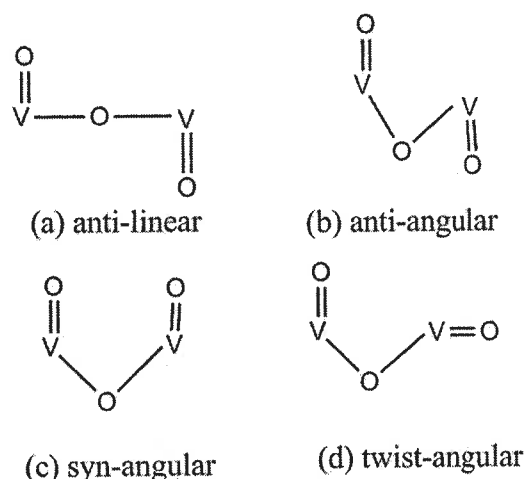
The chemistry of the +V state of vanadium is dominated by VO³⁺, V₂O₃⁴⁺ and VO₂⁺ motifs. Among these three motifs, the

chemistry of μ-oxidodivanadium(V) compounds (*i.e.*, complexes containing the V₂O₃⁴⁺ motif) has attracted considerable attention for coordination chemists for two main reasons. The first reason is the structural diversity of compounds containing identical ligand molecules attached to both the metal centres^{27–32} resulting from different V–O–V bond angles. These angles can range from linear to angular, along with the disposition of terminal oxido atoms from anti-linear,^{31k} to syn-angular,^{30,31a,b} through anti-angular,^{27c,g} and twist angular³² structures (Scheme 1). The second reason is the interesting magnetic behaviour of the mixed-valence species (*i.e.*, containing the V₂O₃³⁺ motif) generated from V₂O₃⁴⁺ species after electro-reduction of one vanadium(V) centre selectively to disclose the location of the electron and hence the state of metal oxidation.

During the formation of non-oxidovanadium(IV) complexes from oxido-V(IV) precursors under aerobic conditions, the formation of oxido-complexes is also thermodynamically feasible (*vide infra*). Unfortunately, until now, almost all reports have focused only on the non-oxidovanadium(IV) species apart from two reports,^{21i,33} which also dealt with the simultaneous formation of non-oxido as well as oxido species. Moreover, reports studying the effects of varying the solvents used (*viz.*, hydroxylic and non-hydroxylic) as well as the presence and absence of air in the course of synthesis are lacking.

Aliphatic/aromatic acid hydrazide-based hydrazone ligands of aliphatic/aromatic carbonyl compounds are versatile ligands and have wide application in analytical³⁴ and medicinal³⁵ chemistry. Hydrazone moieties are important pharmaceutical cores of several anti-cancer, anti-inflammatory and anti-platelet drugs.³⁶

This background prompted us to undertake a scheme to assess four features. First, we explored the feasibility of simultaneous formation of non-oxidovanadium(IV) as well as oxido-



Scheme 1 Possible configurations of the bridging and terminal oxygen atoms in [V₂O₃]^{4+/3+} core.



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Collaborative research in transition metal functional complexes
Number 35

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Period of Investigation: 01-04-2019 to 27-03-2020 June 28, 2017

Project: Coordination polymers and applications

Output: The result was published in a journal of international repute

Publication: Biporous Cd(II) Coordination Polymer via *in Situ* Disulfide
Bond Formation: Self-Healing and Application to Photosensitive
Optoelectronic Device

Kaushik Naskar, Arka Dey, Suwendu Maity, Partha Pratim Ray, Prasanta
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Biporous Cd(II) Coordination Polymer via *in Situ* Disulfide Bond Formation: Self-Healing and Application to Photosensitive Optoelectronic Device

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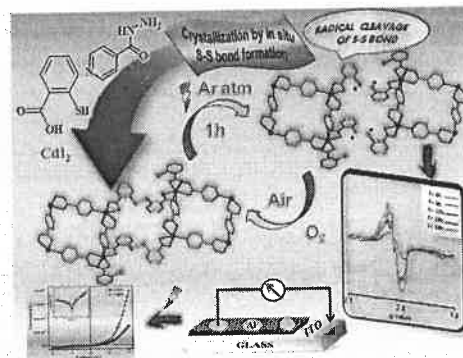


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Supporting Information

ABSTRACT: A heteroporous metal–organic framework, $[\text{Cd}_2(2,2'\text{-DSB})_2(\text{INH})_2(\text{H}_2\text{O})_2]_n$ (**1**), is fabricated by the reaction of CdI_2 , 2-mercaptobenzoic acid (2-MBAH), and isoniazid (INH). The X-ray structure of the compound **1** shows the bridging INH and 2,2'-disulfanediyldibenzoic acid ($\text{H}_22,2'\text{-DSBA}$) around the $\text{Cd}(\text{II})$ ion center. 2-MBAH has been *in situ* dimerized to the formation of $2,2'\text{-DSB}^{2-}$ (S-S -bonded dianion), which has further extended to form the 2D network. However, supramolecular assembly via $\pi\cdots\pi$ and hydrogen bonds strengthens the structural motif within the 3D array. Optical stimulation generated the thiol radical under an argon environment followed by the electron paramagnetic resonance (EPR) study, but upon exposure to air, the EPR signal gradually disappeared by the formation of the S-S bond, which was commonly known as a self-healing property. Again, compound **1** exhibited as a semiconducting material with a band gap of 3.7 eV. The $I-V$ characteristics of **1** show that the conductivity is intensified by an optical response. The Schottky diode property of **1** shows a lower barrier height, a lower resistance, and a higher conductivity upon illumination at 360 nm.



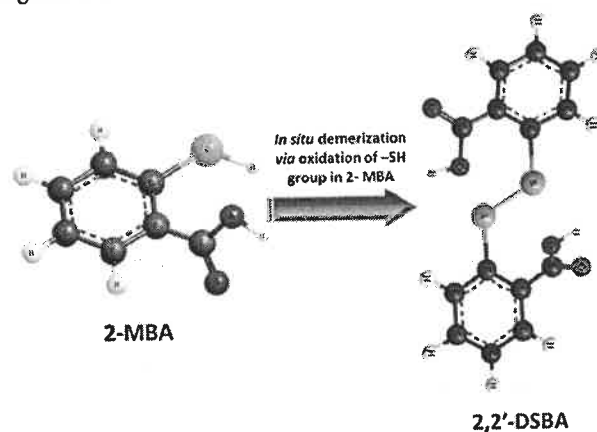
INTRODUCTION

Coordination polymers (CPs) are of intriguing interest due to their wide variety of structure building units and their fascinating potential applications.^{1–13} Smart architecture reversibly changes the molecular structure and the subsequent properties upon exposure to external stimuli such as light, pH, heat, and so on.^{14–19} The CPs are mainly constructed by the support of metal ion nodes and organic linkers.^{1,5} Because of their inexpensive availability, easy synthetic methodology, and various coordinating sites, organic linkers are more appropriate for the design of these organic–inorganic composite materials.

Isoniazid, a recognizable tuberculosis (TB) drug,²⁰ is one of the most attractive coordinating ligands in the club of coordination polymers^{4,21} and has the ability to create a large dimension that depends on the nature of the organic linker and reaction conditions like temperature, solvent, pressure, and so on.

The S-S bond formation of 2-mercaptobenzoic acid (2-MBAH), which is assembled in a long flexible ligand 2,2'-disulfanediyldibenzoic acid (2,2'-DSBA), fabricates a large structural unit in the CPs of $\text{Cd}(\text{II})$ as an ion node.^{22–26} Herein we have employed the “*in situ* ligand generation” technique of 2,2'-DSBA and INH links to construct Cd -based two-dimensional coordination polymer (2D CP) $[\text{Cd}_2(2,2'\text{-DSB})_2(\text{INH})_2(\text{H}_2\text{O})_2]_n$ (**1**) (2,2'-disulfanediyldibenzoic acid (2,2'-DSBA) and isonicotinohydrazide (INH)) (Scheme 1). In

Scheme 1. 2,2'-DSBA Formation through *in Situ* Dimerization (S-S) of the Mercapto Group in 2-MBA via Ligand Oxidation



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recent times, *in situ* ligand generation has grown to be an attractive synthetic pathway to harvest novel coordination polymers. The *in situ* reaction has the ability to construct (oxidative) or cleave (reductive) disulfide bonds (S–S)²⁷ and is also important in the biological process. This innovative disulfide bond formation by oxidation/reduction has the great opportunity to synthesize diverse CPs.^{28,29} The disulfide cross-link^{30–32} executes relatively stable temper to the peptide chains via weak bonding forces, and the stress relaxation of a self-healing elastomeric property has been widely used in the rubber technology.³³ Feng and coworkers reported an exceptional case where the covalent inter-ligand interaction directs the formation of the S–S bond in the ZIF-8 analog, where two 1,2,4-triazole rings are interlinked through disulfide bonds, and this zeolite-type material exhibits high CO₂ uptake and has the potential to separate the mixtures of light hydrocarbons such as ethane/ethylene.³⁴ The reversible disulfide (S–S) bond formation and the S–S bond cleavage have an important role in biological chemistry. Nowadays, food packaging industries widely detect O₂ by the advantage of the disulfide (S–S) bond formation from thiol compounds.³⁵ The disulfide (S–S) bond can be cleaved by the chemical/electrochemical/photochemical reduction.

We have designed CPs of various dicarboxylates and mono- or bidentate N-donor ligands, and the compounds are used in the field of semiconducting devices and the sorption and adsorption of gases.^{4,14,20,36} In this Article, a Cd(II)-bonded zigzag 2D coordination polymer undergoes extensive hydrogen bonding like N–H···O, N–H···S, and $\pi\cdots\pi$ interactions to form the 3D architecture. The presence of a S–S bond may induce flexibility²⁵ in the material due to the twisted conformations of the S–S and C–S single bonds in the H₂DSBA ligand, which further extend the development of self-healed CPs under external stimulus conditions. The S–S bond is cleaved by photoirradiation that appears as a strong electron paramagnetic resonance (EPR) signal. On exposure to air, the thiol radical gradually disappears and self-heals to recover the S–S bond. However, the photosensitive behavior of compound 1 could be used to fabricate a photosensitive electrical device in the future, where the conductivity values would be enhanced from the dark phase ($1.05 \times 10^{-3} \text{ S}\cdot\text{m}^{-1}$) to the light phase ($2.34 \times 10^{-3} \text{ S}\cdot\text{m}^{-1}$). The value of the rectification ratio ($I_{\text{on}}/I_{\text{off}}$) increases from the dark phase (15.11) to the light phase (34.76) for the Schottky diode (SD) device. Thus our synthesized polymeric material 1 has the potential to be utilized for optoelectronic device applications in the future.

EXPERIMENTAL SECTION

Materials and Physical Method. All chemicals were bought from Sigma-Aldrich, and during the experiment, they did not need any essential purification. The CHN analysis of 1 was performed using a PerkinElmer 240C elemental analyzer. Infrared spectra were carried out by a PerkinElmer FT-IR spectrum RX1 spectrometer with a KBr pellet (4500–500 cm⁻¹). Raman spectra were analyzed by a 532 nm laser source with the grating of 1800 grooves/mm by a J-Y Horiba triple Raman spectrometer T64000. The thermogravimetric analyses (TGAs) were recorded by PerkinElmer Pyris Diamond TG-DTA instruments at a temperature range of 24–600 °C and a heating rate of 10 °C/min under a nitrogen atmosphere. The powder X-ray diffraction (PXRD) spectrum was recorded with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in a 2θ range of 5–50° by a Bruker D8 Advance X-ray diffractometer. The solid- and solution-state electronic absorption spectra were verified via a PerkinElmer Lambda 750 UV-vis spectrophotometer. The electroanalytical instrument BASi Epsilon-

EC performed the cyclic voltammetric analyses of 1 with a supporting electrolyte of [N(n-Bu)₄]PF₆ at the concentration of 2 M in DMF solvent. The aqueous Ag/AgCl was chosen as the reference electrode, BASi-platinum was used as the working electrode, and the platinum electrode was preferred as an auxiliary electrode. However, the potential values of the cyclic voltammogram were referenced against the ferrocenium/ferrocene couple (Fc⁺/Fc). The spectroelectrochemistry measurements were carried out by using a spectroelectrochemical cell kit, which was composed of platinum gauze and a block of SEC-C platinum; however, those were used as a working electrode and a counter electrode, respectively. The photoinduced cleavage study was conducted with an ISS P110 lamp as a light source at a wavelength of 360 nm. The X-band EPR data were recorded by a Magnetech mini scope MS400 spectrometer, and the photoreversible polymerization was investigated by using a FESEM imaging study, which was captured by JEOL model JSM-6700F.

Synthesis of [Cd₂(2,2'-DSB)₂(INH)₂(H₂O)₂]_n (1). Compound [Cd₂(2,2'-DSB)₂(INH)₂(H₂O)₂]_n (1) was isolated by the layering method. At first, CdI₂ (0.074 g, 0.2 mmol) was taken in 2 mL of water; then, 2 mL of 1:1 (v/v) DMF–H₂O buffer solution was slowly added. After that, the methanolic solution of isoniazid (0.028 g, 0.2 mmol) (10 mL) was cautiously added; finally, the layering of the neutralized 2-MBA (0.031 g, 0.2 mmol) by Et₃N in a 2 mL of ethanolic solution was carried out. The prism-shaped yellow crystals of [Cd₂(2,2'-DSB)₂(INH)₂(H₂O)₂]_n (1) were developed within 1 week (43 mg, yield 75%). The experiment favors the oxidative addition to generate the disulfide bond *in situ* in the presence of air. Elemental analysis (%) for C₄₀H₃₀Cd₂N₆O₁₂S₄: C, 42.15; H, 2.65; N, 7.37. Found: C, 42.02; H, 2.75; N, 7.16. IR (KBr pellet, cm⁻¹): 1667 $\nu_{\text{as}}(\text{COO}^-)$, 1588 $\nu(\text{C}-\text{N})_{\text{py}}$, 1370 $\nu_{\text{s}}(\text{C}-\text{N})$ amide (Figure S1).

X-ray Crystallography. The Bruker SMART APEX II diffractometer was utilized for the structural analysis of a single crystal of compound 1 (CCDC no. 1920684) with nice shape and size (0.17 × 0.04 × 0.01 mm), which was furnished by graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The least-squares refinements of all reflections were used to solve the unit-cell parameters within the hkl range: $-15 \leq h \leq 15$, $-15 \leq k \leq 15$, and $-22 \leq l \leq 22$ (1). The SAINT program calculated the collected data of ($I > 2\sigma(I)$), and the absorption correction was performed by multiscan. The anisotropic thermal parameter was chosen to refine the non-hydrogen atoms. However, all calculated hydrogen atoms were placed in their structurally ideal positions and forced to remain at the parent atoms. All calculations were further carried out by using SHELXL 2014/7,³⁷ SHELXS 2014/7,³⁸ PLATON 99,³⁹ and ORTEP-3⁴⁰ programs. The crystallographic data are summarized for 1 in Table 1. The structure contains a Level A alert due to the solvent-accessible voids. The highest peak in the final difference map is just 3.81 eÅ⁻³, and no model for any solvent could be found.

Theoretical Calculation. The molecular structure was optimized by density functional theory (DFT) using the Gaussian 09 program package at the B3LYP level, and the theoretical calculations were performed by the GaussView software program. The basis set LanL2DZ was assigned as an effective core potential, and the symmetry constraint was employed for the compound. The optimized structures represent the local minima, and only the positive eigenvalues, which ensure the vibrational frequency calculation, were considered. Time-dependent density functional theory (TD-DFT)^{41–43} was performed to assign the electronic transitions of compound 1, which were obtained from the experimental data. GaussSum⁴⁴ was used to calculate the molecular orbital contribution and the theoretical electronic spectra from groups of atoms.

RESULTS AND DISCUSSION

Structure of [Cd₂(2,2'-DSB)₂(INH)₂(H₂O)₂]_n (1). The binuclear asymmetric unit of [Cd₂(2,2'-DSB)₂(INH)₂(H₂O)₂]_n (1) was authenticated by single-crystal X-ray crystallography, and the polymerization of 2,2'-DSB²⁻ was validated by the construction of the S–S bond from 2-MBA (Figure 1). Compound 1 was crystallized as triclinic



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Collaborative research in transition metal functional complexes
Number 36

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Institute 2: Ramakrishna Mission Residential College (Autonomous)
Concerned Faculty: Dr. Prasanta Ghosh, Dept of Chemistry

Period of Investigation: 20-8-2019 to 15-10-2020

Project: X-ray structures and bio-sensing

Output: The result was published in a journal of international repute

Publication: X-ray structure of two Schiff bases: TURN-ON sensing of
Fe³⁺ and Al³⁺ in the HepG2 cell line

Sunanda Dey, Suvendu Maity, Rakesh Purkait, Kunal Pal Prasanta
Ghosh, Kuladip Jana and Chittaranjan Sinha
Anal. Methods, 2020,12, 5485-5495. DOI: 10.1039/D0AY01090A

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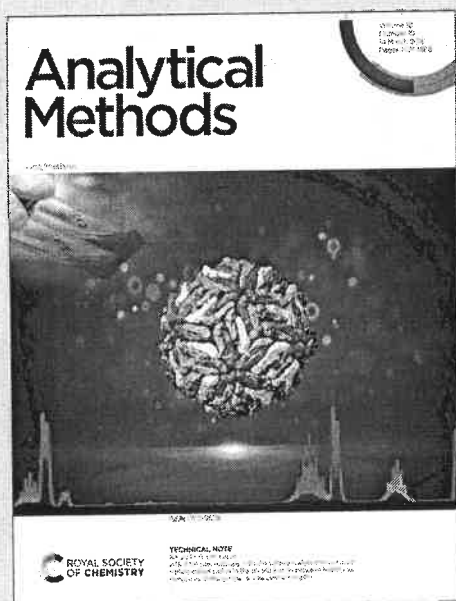
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Analytical Methods

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X-ray structure of two Schiff bases: TURN-ON sensing of Fe³⁺ and Al³⁺ insight the

HepG2 cell line†

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†Electronic supplementary information (ESI)

Abstract: The efficiency of fluorescence sensitivity of a sensor may be tuned by modulation of steric and electronic parameters in the structure. In this work, thiophenyl Schiff base, (E)-N¹-(phenyl(pyridin-2-yl)methyl)-N²-(thiophen-2-ylmethylene)benzene-1,2-diamine (**HL'**) exhibits very high selectivity and sensitive fluorescence enhancement to Fe³⁺ with violet emission (λ_{em} , 385 nm; LOD, 3.8 nM). On the other hand the naphthyl Schiff base, (E)-1-(((2-((phenyl(pyridin-2-yl)methyl)amino)phenyl)imino)methyl)naphthalen-2-ol (**H₂L''**) exhibits fluorescence sensitivity towards Al³⁺ showing blue emission (λ_{em} , 502 nm; LOD, 3.3 nM) in H₂O (HEPES buffer, pH 7.4) medium. The emission enhancement upon binding to Fe³⁺ to **HL'** may be considered by the restriction of intramolecular rotation while probe **H₂L''** selects Al³⁺ showing turn on emission through restriction of ESIPT and introduction of CHEF. Furthermore, DFT computation supports the sensing strategy and the probes have been applied for intracellular detection of Fe³⁺ and Al³⁺ in HepG2 cell lines.



Ramakrishna Mission Residential College (Autonomous)
Kolkata 700103, WB, India

Collaborative research in transition metal functional complexes
Number 37

Institute 1: Ramakrishna Mission Residential College (Autonomous)

Concerned Faculty: Dr. Prasanta Ghosh, Dept of Chemistry
&

Institute 2: Department of Chemistry, Jadavpur University, Kolkata
700032, India

Concerned Faculty: Prof. Chittaranjan Sinha, Department of Chemistry

Period of Investigation: 20-07-2019 to 03-06-2020

Project: Coordination polymers and electrical conductivity

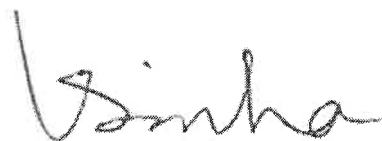
Output: The result was published in a journal of international repute

Publication: Coordination polymers of Ag(i) and Hg(i) ions with 2,2'-azobispyridine: synthesis, characterization and enhancement of conductivity in the presence of Cu(ii) ions

Suvendu Maity, Kaushik Naskar, Tanmay Bhowmik, Amalendu Bera, Thomas Weyhermüller, Chittaranjan Sinha and Prasanta Ghosh
Dalton Trans., 2020,49, 8438-8442. DOI: 10.1039/D0DT01470B


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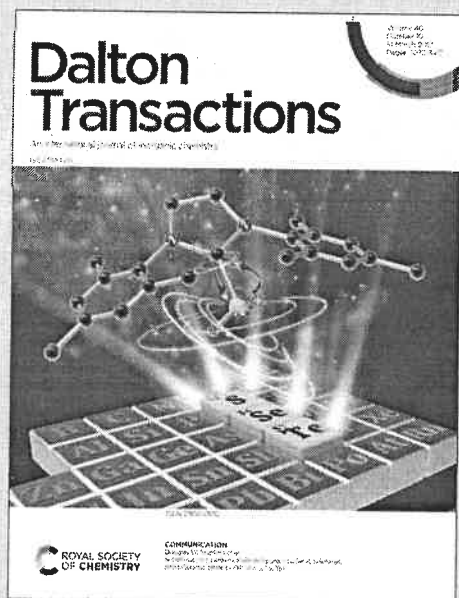
Prof. Chittaranjan Sinha

Dalton Transactions

An international journal of inorganic chemistry

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COMMUNICATION

Coordination polymers of Ag(I) and Hg(I) ions with 2,2'-azobispyridine: synthesis, characterization and enhancement of conductivity in presence of Cu(II) ions

Received 00th January 20xx,
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DOI: 10.1039/x0xx00000x

Suvendu Maity,^{a,b} Kaushik Naskar,^b Tanmay Bhowmik,^a Amalendu Bera,^d Thomas Weyhermüller,^c Chittaranjan Sinha^b and Prasanta Ghosh^{*a}

The cataionic coordination polymers (CP) of the types, $[\text{Hg}_2(\text{abpy})_2]_n[\text{PF}_6]_n$ (1) and $[\text{Ag}(\text{abpy})]_n[\text{PF}_6]_n$ (2) (abpy = 2,2'-azobispyridine) were synthesized and characterized. Experimentation using the crystals confirmed that 1 and 2 are conductors of electricity. The relative conductivity of 1 is 62 times greater than 2. The conductivity of 1 increase 70 fold when it reacts with Cu^{2+} ions.

The design and synthesis of long chain metal organic coordination polymers (CPs) have been a subject of modern research. During the last decades in supra-molecular coordination chemistry and crystal engineering, the utilities of them and their applications were widely explored.¹⁻¹⁰ Due to their different structural features and topologies, CPs can exhibit a wide range of interesting physical and chemical behaviour. The cationic CPs bind anions through non covalent interaction and the conformation and helicity of the polymer structure are controlled by the shape and size of the anions. The another important utility of the cationic CPs is mainly the separation of higher molecular weight anions (like AsO_4 , PO_4 and other radioactive anion species, etc.) from the solution.¹¹⁻¹⁶ The common examples of salts used for this purpose are NaPF_6 , NaBF_4 etc. Anion binding typically involves supra-molecular interactions, such as hydrogen bonding, electrostatic, $\pi \cdots \pi$ stacking, cation $\cdots\pi$, C-H $\cdots\pi$, non-covalent attractive force among anions and π -acidic (or electron-deficient) charge-neutral aromatic rings, namely, the anion- π interaction, and these features have become a topic of interest in the field of crystal engineering for their wide applications in constructing molecular assemblies, new types of material and medicinal chemistry. Depending upon these interactions various types of physical properties developed in the aggregation in supra molecular chemistry.¹⁷⁻²⁰ The 1D/2D

coordination chain or layer can be extended to 2D or 3D coordination polymers in emphasizing structural variation, topologies, dimensionalities and their novel properties. The important properties mainly dimensionality, pore size and surface area of these complexes would be modulated just by changing the linker size, geometry and functionalities.

2,2'-Azobispyridine (abpy) acts as a bridging ligand involving the azo group -N=N- as coordinating π acceptor function and it can form dinuclear complexes with unusual electronic and structural features.²¹⁻²⁴ Particularly abpy can binds in different modes with the transition metal ion particularly exhibiting self and cross binding modes. The coordination polymer of $[\text{Cu}(\text{abpy})]_n$ which was generated after chemical reduction of $[\text{Cu}(\text{abpy})\text{PF}_6]_n$, was used for transformation of NO_2 gas to NO .²⁵ The abpy is easily reducible abpy \cdot^- a radical bridging ligand and this property makes possible the reduction of 1D coordination polymer, $[\text{Cu}(\text{abpy})\text{PF}_6]_n$ to $[\text{Cu}(\text{abpy})]_n$ which is more conductive and porous in nature.²⁶ It was reported that the dinuclear $[\text{Cu}_2(\text{abpy})(\text{CH}_3\text{CN})_8][\text{BF}_4]_4$ complex decomposes to the Cu^I polymer $\{[\text{Cu}(\text{abpy})][\text{BF}_4]_2\}_n$.²⁷ Recently we have reported that the reaction of $[\text{Cu}^{\text{II}}(\text{abpy})_3][\text{PF}_6]_2$ and $[\text{Cu}^{\text{II}}(\text{abpy})_2(\text{bpy})][\text{PF}_6]_2$ with catechol, *o*-aminophenol, *p*-phenylenediamine and diphenylamine (Ph-NH-Ph) in 2:1 molar ratio afford $[\text{Cu}^{\text{I}}(\text{abpy})_2]^+$ and corresponding quinone derivatives.²⁸ So the activities of the copper containing abpy ligand is important in synthetic and material chemistry.

The copper containing MOF $\{[\text{Cu}_2(6\text{-Hmna})(6\text{-mn})]\cdot\text{NH}_4\}_n$ (6-Hmna = 6-mercaptonicotinic acid, 6-mn = 6-mercaptonicotinate), of a 2D (-Cu-S-)n motif was isolated in situ from a S-S bond cleavage reaction under hydrothermal conditions. The complex is found to have a low activation energy (6 meV), small band gap (1.34 eV) and the highest electrical conductivity (10.96 S cm^{-1}) among reported MOFs measured using single crystals.²⁹ The $[\text{Cd}_2(2,2\text{-DSB})_2(\text{INH})_2(\text{H}_2\text{O})_2]_n$ showed a high order of electrical conductivity ($1.05 \times 10^{-3} \text{ S m}^{-1}$) and also exhibited the potential to be ~2.75 times more photosensitive from the dark to light phase.³⁰ In this search, $[\text{Hg}_2(\text{abpy})_2]_n^{2n+}$ (1^{2n+}) and $[\text{Ag}(\text{abpy})]_n^{n+}$ (2^{n+}) complexes were isolated with the heavy metal Hg^{2+} and Ag^+ ions and their cationic polymeric configuration were

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† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



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Collaborative research in synthetic and structural organic chemistry
Number 38

Institute 1: University of Calcutta, 92 APC Road, Kolkata 700009, India

Concerned Faculty: Prof. Chhanda Mukhopadhyay, Department of
Chemistry

&

Institute 2: Ramakrishna Mission Residential College (Autonomous)

Concerned Faculty: Dr. Prasanta Ghosh, Dept of Chemistry

Period of Investigation: 01-04-2019 to 30-01-2020

Project: Nano-SiO₂ Mediated Organic Transformation

Output: The result was published in a journal of international repute

Publication: Nano-SiO₂@[DABCO(CH₂CH₂CO₂H)]+[Br] as an efficient and recyclable SCILL for water mediated facile synthesis of thiol-substituted N-aryl pentasubstituted pyrroles

Priya Mondal, Sauvik Chatterjee, Khondekar Nurjamal, Suwendu Maity,
Asim Bhaumik, Goutam Brahmachari, Prasanta Ghosh and Chhanda
Mukhopadhyay

Catalysis Communications, 2020, 139, 105966-105972. DOI:
10.1016/j.catcom.2020.105966

Chhanda Mukhopadhyay

Prof. Chhanda Mukhopadhyay

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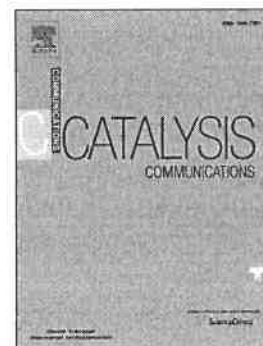
Dr. Prasanta Ghosh

Associate Professor
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Narendrapur, Kolkata-700103

Journal Pre-proof

Nano-SiO₂@[DABCO(CH₂CH₂CO₂H)]+[Br]⁻ as an efficient and recyclable SCILL for water mediated facile synthesis of thiol-substituted N-aryl pentasubstituted pyrroles

Priya Mondal, Sauvik Chatterjee, Khondekar Nurjamal, Suwendu Maity, Asim Bhaumik, Goutam Brahmachari, Prasanta Ghosh, Chhanda Mukhopadhyay



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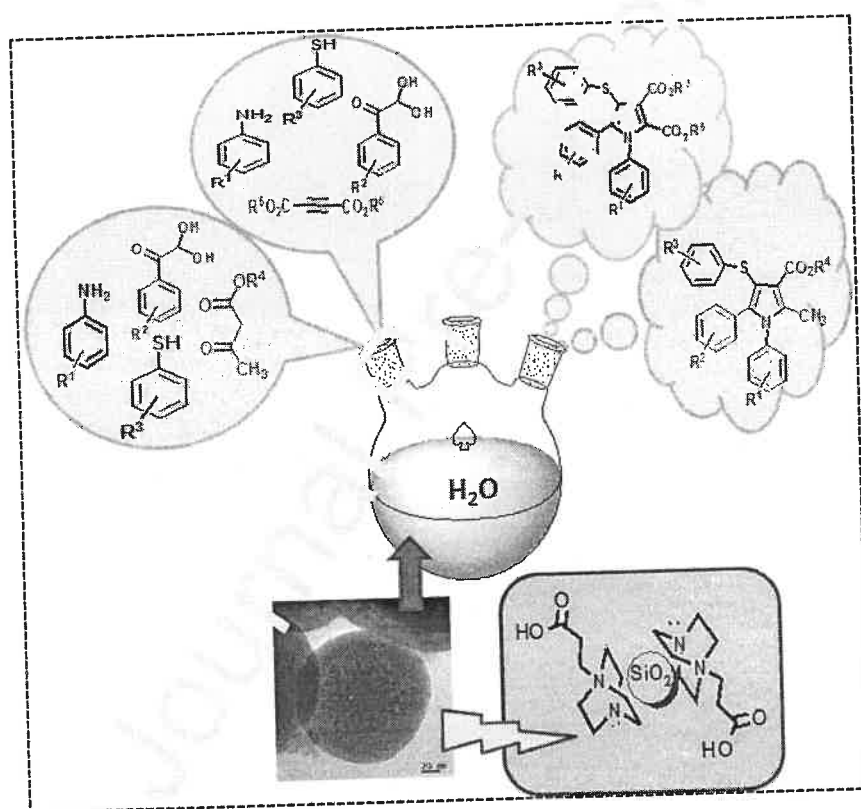
Please cite this article as: P. Mondal, S. Chatterjee, K. Nurjamal, et al., Nano-SiO₂@[DABCO(CH₂CH₂CO₂H)]+[Br]⁻ as an efficient and recyclable SCILL for water mediated facile synthesis of thiol-substituted N-aryl pentasubstituted pyrroles, *Catalysis Communications* (2020), <https://doi.org/10.1016/j.catcom.2020.105966>

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GRAPHICAL ABSTRACT

Nano-SiO₂@[DABCO(CH₂CH₂CO₂H)]⁺[Br]⁻ as an Efficient and Recyclable SCILL for Water Mediated Facile Synthesis of Thiol-Substituted N-aryl Pentasubstituted Pyrroles

Priya Mondal^a, Sauvik Chatterjee^b, Khondekar Nurjama^c, Suwendu Maity^d, Asim Bhaumik^b, Goutam Brahmachari^c, Prasanta Ghosh^d and Chhanda Mukhopadhyay^{a*}



Research Highlights

- Nano-Silica formation using [DABCO(CH₂CH₂CO₂H)]⁺[Br]⁻ as a stabilising agent
- Nano-SiO₂@[DABCO(CH₂CH₂CO₂H)]⁺[Br]⁻ is an Symbiotic catalytic system
- Water-mediated, one pot synthesis of thiol substituted pyrroles using Nano-SiO₂@IL



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Collaborative research in functional transition metal complexes
Number 39

Institute 1: Aliah University, New Town, Kolkata 700 156, India

**Concerned Faculty: Dr. Mohammad Hedayetullah Mir, Department of
Chemistry**

&

Institute 2: Ramakrishna Mission Residential College (Autonomous)

Concerned Faculty: Dr. Prasanta Ghosh, Dept of Chemistry

Period of Investigation: 01-10-2019 to 16-10-2020

Project: Coordination polymers and electrical conductivity

Output: The result was published in a journal of international repute

**Publication: Electrically conductive Cu(ii)-based 1D coordination polymer
with theoretical insight**

Sakhiul Islam, Pubali Das, Saswati Maiti, Samim Khan, Suwendu Maity,
Prasanta Ghosh, Atish Dipankar Jana, Partha Pratim Ray and Mohammad
Hedayetullah Mir

Dalton Trans., 2020, 49, 15323-15331. DOI: 10.1039/D0DT03098H

Md. Hedayetullah Mir

Dr. Mohammad Hedayetullah Mir

Dr. Prasanta Ghosh

Dr. Prasanta Ghosh

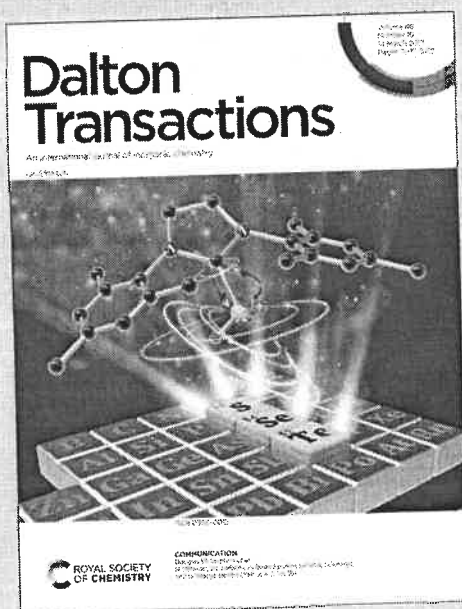
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An international journal of inorganic chemistry

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Journal Name

ARTICLE

Electrically conductive Cu(II)-based 1D coordination polymer with theoretical insight

 Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

 Sakhiul Islam,^a Pubali Das,^b Saswati Maiti,^{c,d} Samim Khan,^a Suvendu Maity,^e Prasanta Ghosh,^f Atish Dipankar Jana,^{*c} Partha Pratim Ray,^{*b} and Mohammad Hedayetullah Mir^{*a}

A nitro functionalized Cu(II) based one-dimensional coordination polymer (1D CP) [Cu(nip)(4-phpy)₂]_n (**1**) (H₂nip = 5-nitroisophthalic acid and 4-phpy = 4-phenylpyridine) has been synthesized and characterized by elemental analysis, powder X-ray diffraction (PXRD) and single crystal X-ray diffraction (SCXRD). In the solid-state self-assembly of **1**, two sets of weak intermolecular forces, CH...π interaction among the axially bound 4-phpy ligands and π...π interaction among bridging nip ligands from adjacent 1D coordination polymeric chains lead to 3D supramolecular packing. Interestingly compound **1** exhibits electrical conductivity in the semiconducting regime and behaves as Schottky barrier diode.

Introduction

Supramolecular Chemistry in recent years have taken a new direction in solid state chemistry due to their great versatility in crystal structures and numerous applications.¹⁻⁴ Investigating the role of supramolecular interaction in the context of crystal engineering i.e. how the different layers in a crystal lattice has been hold together through non-covalent interactions is a part of ongoing research in recent years.⁵ Depending upon the extent of contribution of secondary interactions, various types of molecular assemblies have been generated. These non-covalent weak interactions act as auxiliary linkage forces for the fabrication of higher-dimensional supramolecular aggregate with fascinating structural architectures and desired properties. In this context, coordination polymers (CPs) are assembled through supramolecular interactions with tunable structure and property.⁶⁻⁹ CPs are organic-inorganic solid state hybrid materials, made of metal ions that are bridged together by organic linkers and it can combine two seemingly contradictory properties crystallinity and flexibility. Due to the structural diversity and broad field, CPs are truly attracted towards material scientists.¹⁰⁻¹³ The potential applications of these compounds are also remarkable including gas storage, separation,

catalysis, ion exchange, light harvesting, drug delivery, sensing etc.¹⁴⁻¹⁸ CPs have also been used for the fabrication of electronic and optoelectronic devices. However, it is one of the great challenges in this rapidly expanding field to synthesize CPs that show good charge mobility and conductivity. Due to the presence of hard metal ions and redox-inactive organic ligands, CPs usually do not provide a good conjugation pathway for charge transport. However, during the past few decades, new concepts have been developed for the fabrication of CPs that exhibit high electrical conductivity.¹⁹⁻²¹ Conducting CPs could serve as the basis for new electronic materials²² to solve the difficulty in realizing high performance *n*-type materials that could not be achieved with existing organic materials.

Our team is also devoted to the synthesis of CPs by using mixed-ligand system for tuning the structural architectures.²³⁻²⁴ In these CPs, the mono-donors play important role for assembling the layers via supramolecular interactions such as π...π, C-H...π, hydrogen bonding, halogen bonding, halogen...π and halogen...π(chelate) interactions.²⁵⁻²⁸ The secondary interactions facilitate the charge transport among the layers in the CP revealing semiconducting property. Recently, we have shown the effect of halogen bonding interactions on the charge transport in one-dimensional (1D) CPs by altering *para*-substituent on the halobenzoate ligands.²⁹ Herein, we have synthesized a Cu(II)-based 1D CP [Cu(nip)(4-phpy)₂]_n (H₂nip = 5-nitro isophthalic acid and 4-phpy = 4 phenyl pyridine), which shows interesting electrical conducting property. In the solid state packing of the 1D CPs, a novel mode of π...π interaction among nip ligands act as supramolecular glue between adjacent CPs leading to 2D supramolecular sheets which are further stacked due to the CH...π interaction among the interdigitated 4-phpy ligands from adjacent layers.

Experimental section

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^e Department of Chemistry, Jadavpur University, Jadavpur, Kolkata 700 032, India.

^f Department of Chemistry, R. K. M. Residential College, Narendrapur, Kolkata 700 103, India.

† Electronic Supplementary Information (ESI) available: Table S1-S2, Scheme S1, Figure S1-S4, and X-ray crystallographic data in CIF format for compound **1**. CCDC number 1912597.

For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x



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Collaborative research in functional transition metal complexes

Number 40

Institute 1: Aliah University, New Town, Kolkata 700 156, India

Concerned Faculty: Dr. Mohammad Hedayetullah Mir, Department of Chemistry

&

Institute 2: Ramakrishna Mission Residential College (Autonomous)

Concerned Faculty: Dr. Prasanta Ghosh, Dept of Chemistry

Period of Investigation: 01-10-2019 to 02-09-2020

Project: Coordination polymers and Charge Transfer Properties

Output: The result was published in a journal of international repute

Publication: Fabrication of Cu(ii) based halobenzoate appended ladder polymers with efficient charge transport properties

Sakhiul Islam, Baishakhi Pal, Samim Khan, Suvendu Maity, Sanobar Naaz, Prasanta Ghosh, Partha Pratim Ray, Mohammad Hedayetullah Mir

***CrystEngComm*, 2020, 22, 6720-6726. DOI: 10.1039/D0CE00831A**

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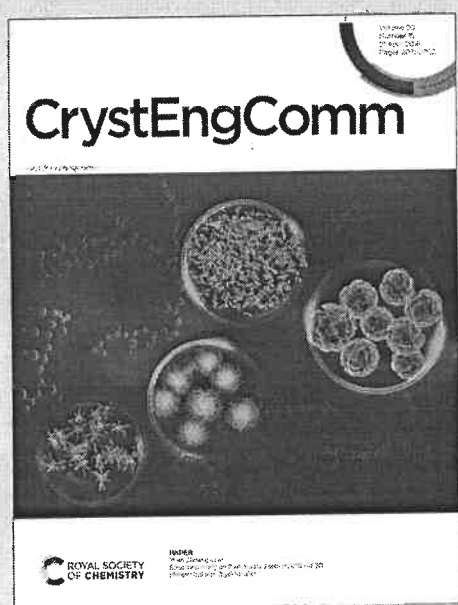
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Journal Name

ARTICLE

Fabrication of Cu(II) based halobenzoate appended ladder polymers with efficient charge transport property

 Received 00th January 20xx,
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DOI: 10.1039/x0xx00000x

www.rsc.org/

 Sakhiul Islam,^a Baishakhi Pal,^b Samim Khan,^a Suvendu Maity,^c Sanobar Naaz,^a Prasanta Ghosh,^d
Partha Pratim Ray,^{*b} and Mohammad Hedayetullah Mir^{*a}

Two isotypical Cu(II) based one-dimensional coordination polymers (1D CPs) $\{[Cu_2(p-clba)_4(bpe)_2]\{Cu(p-clba)_2(bpe)(CH_3OH)\}}_n \cdot 1.25H_2O$ (**1**) and $\{[Cu_2(p-brba)_4(bpe)_2]\{Cu(p-brba)_2(bpe)(CH_3OH)\}}_n \cdot 1.25H_2O$ (**2**) ($H_2p-clba$ = *para*-chlorobenzoic acid, $H_2p-brba$ = *para*-bromobenzoic acid and bpe = 1,2-bis(4-pyridyl)ethylene) have been synthesized and characterized by X-ray structure analysis. In the solid-state structure, both the compounds undergo $X \cdots n$ ($X = Cl$ or Br) interactions to generate two-dimensional (2D) supramolecular architectures. Here, due to the larger size and more polarisability of $Br \cdots n$ interaction is stronger than $Cl \cdots n$, which is accounted for the stronger interchain interactions in **2** as compared to **1**. This is depicted in the observed electrical conductivity of the compounds. The compound **2** with stronger interchain interactions shows better charge transport and hence, increasing conductivity.

Introduction

Supramolecular chemistry has developed huge interest among the synthetic chemists over the last few decades.¹⁻⁵ Noble laureate Prof. Jean-Marie Lehn has defined it as 'chemistry beyond the molecule' and 'chemistry of molecular assemblies and of the intermolecular bond'. It mainly deals with the design and development of novel functional systems by stitching several chemical components through non-covalent interactions. In the context of crystal engineering, Prof. Desiraju has introduced supramolecular synthon approach⁶ i.e. utilisation of intermolecular interactions that may lead to alteration of physicochemical properties of the active compound. These supramolecular interactions are often utilised for the formation of various types of molecular assemblies. In this regard, coordination polymers (CPs) have been developed as special type of organic-inorganic solid state hybrid materials assembled by metal ions and organic ligands connected in an array. The CPs may undergo supramolecular interactions to generate higher dimensional networks, which in turn responsible for structure-property relationship.⁷⁻¹³ Recently, CPs are widely studied for their structural versatility and range of applications from gas storage, separation, ion

exchange, sensing, catalysis, drug delivery, light harvesting to water harvesting.¹⁴⁻²⁶ Implicit of these application, CPs show very low electrical conductivity and thereby limits their applicability in fuel cells, thermoelectrics, resistive sensing, and supercapacitors.²⁷⁻³⁰ In the last two decades, many scientists have been actively involved in the revolutionary development of power semiconductors and power electronic systems.³¹⁻³³ This has been possible due to the excessive drive toward rational use of energy, miniaturization of electrical systems and power management. However, CPs are made of hard metal ions connected by redox-inactive organic ligands and this combination reduces conjugation pathway for charge transport leading to low conductivity. Therefore it is a great challenge to design CPs that exhibit good charge mobility and electrical conductivity. However, only in the last few years new concepts have been realized that allow for the construction of CPs that show high electrical conductivity.³⁴⁻³⁶ Our group is also actively devoted to the synthesis of CPs by using mixed-ligand system with tunable structural architectures that exhibit electrical conductivity and behave as Schottky diode.³⁷⁻⁴¹ We are mainly dedicated to utilise supramolecular interactions for the fabrication of CPs which promotes better charge transport. Herein, we have used a ditopic spacer ligand *trans*-1,2-bis(4-pyridyl)ethylene (bpe), one of the popular choices of ligands for studying topochemical transformations in metal complexes and coordination polymers. In this work, we report the role of halogen $\cdots n$ interactions in supramolecular architecture of one dimensional (1D) CPs in their electrical conductivity. Herein, we have synthesized, two isostructural Cu(II)-based 1D CPs, $\{[Cu_2(p-clba)_4(bpe)_2]\{Cu(p-clba)_2(bpe)(CH_3OH)\}}_n \cdot 1.25H_2O$ (**1**) and $\{[Cu_2(p-brba)_4(bpe)_2]\{Cu(p-brba)_2(bpe)(CH_3OH)\}}_n \cdot 1.25H_2O$ (**2**) ($H_2p-clba$ = *para*-chlorobenzoic acid and $H_2p-brba$ = *para*-bromobenzoic acid), which undergo $X \cdots n$ ($X = Cl$ or Br)

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† Electronic Supplementary Information (ESI) available: Figure S1-S8, Table S1-S4, X-ray crystallographic data in CIF format for compound **1** **2**. CCDC numbers CCDC numbers 1983801 (**1**) and 1881174 (**2**). For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x



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Collaborative research in functional transition metal complexes

Number 41

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Institute 2: Ramakrishna Mission Residential College (Autonomous)

Concerned Faculty: Dr. Prasanta Ghosh, Dept of Chemistry

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Publication: Photodimerization of a 1D Ladder Polymer through Single-Crystal to Single-Crystal Transformation Has an Effect on Electrical Conductivity

Sakhiul Islam, Joydeep Datta, Suwendu Maity, Basudeb Dutta, Samim Khan, Prasanta Ghosh, Partha Pratim Ray, Mohammad Hedayetullah Mir

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Article

Photodimerization of 1D Ladder Polymer Through Single-Crystal to Single-Crystal Transformation has Effect on Electrical Conductivity

Sakhiul Islam, Joydeep Datta, Suwendu Maity, Basudeb Dutta, Samim Khan,
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Photodimerization of 1D Ladder Polymer Through Single-Crystal to Single-Crystal Transformation has Effect on Electrical Conductivity

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ABSTRACT: A one-dimensional coordination polymer (1D CP), [Cd(bpe)(*p*-brba)₂]_n (**1**) has been synthesized by slow diffusion method keeping the mixture of Cd(NO₃)₂·6H₂O and 1,2-bis(4-pyridyl)ethylene (bpe) ligand along with *para*-bromobenzoic acid (*p*-brba) in dark. Interestingly, the compound **1** undergoes single-crystal to single-crystal (SCSC) photochemical [2+2] cycloaddition reaction to generate dimerized 1D CP [Cd(*rctt*-tpcb)_{1/2}(*p*-brba)₂]_n (**2**) [*rctt*-tpcb = *rctt*-tetrakis(4-pyridyl)cyclobutane]. As a result, $\pi \cdots \pi$ stacking interactions among *p*-brba



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Period of Investigation: 01-06-2018 to 25-03-2019

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Publication: Halogen... π Interactions in Supramolecular Architecture of 1D
Coordination Polymers and Their Electrical Conductance

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Inorganic Chemistry

Halogen... π Interactions in Supramolecular Architecture of 1D Coordination Polymers and Their Electrical ConductanceSakhiul Islam,^[a] Joydeep Datta,^[b] Suvendu Maity,^[c] Basudeb Dutta,^[a] Faruk Ahmed,^[a] Prasanta Ghosh,^[d] Partha Pratim Ray,^{*[b]} and Mohammad Hedayetullah Mir^{*[a]}

Two isotypical Cd(II) based one-dimensional coordination polymers (1D CPs) $[\text{Cd}_2(p\text{-clba})_4(\text{bpy})_2] \cdot (\text{C}_2\text{H}_5\text{OH})$ (1) and $[\text{Cd}_2(p\text{-brba})_4(\text{bpy})_2] \cdot (\text{C}_2\text{H}_5\text{OH})$, (2) ($\text{H}_2p\text{-clba}$ = *para*-chlorobenzoic acid, $\text{H}_2p\text{-brba}$ = *para*-bromobenzoic acid and bpy = 4,4'-bipyridine) have been synthesized and characterized by X-ray structure analysis. In the solid-state structure, both the compounds undergo $\text{X} \cdots \text{n}$ ($\text{X} = \text{Cl}$ or Br) interactions to generate two-dimensional (2D) supramolecular architectures. Here, due to the larger size and more polarisability of Br atom, $\text{Br} \cdots \text{n}$

interaction is stronger than $\text{Cl} \cdots \text{n}$, which is accounted for the stronger interchain interactions in 2 as compared to 1. This is depicted in the observed electrical conductivity of the compounds. The compound 2 with stronger interchain interactions shows better charge transport and hence, increasing conductivity. Moreover, band gap of the CPs has been obtained by DFT computation, which also supports the progression of conductivity.

Introduction

Investigating the role of supramolecular interaction in the context of crystal engineering i.e. how the different layers in a crystal lattice has been hold together through non-covalent interactions is a part of ongoing research in recent years.^[1–2] Depending upon the extent of contribution of secondary interactions, various types of molecular assemblies have been generated. In this regard, coordination polymers (CPs) are assembled through supramolecular interactions by which structure and property are tuned.^[3] These are actually organic–inorganic hybrid materials, where metal nodes or metal clusters are interconnected via organic ligands (N-, O-, S- donors). Due to the structural diversity and broad field, CPs are truly attracted towards material scientists.^[4–5] According to the desire application, one can design a particular type of compound. The potential applications of these compounds are also remarkable including gas storage,^[6] separation,^[7] catalysis,^[8] ion exchange,^[9] drug delivery,^[10] sensing^[11] etc. CPs have also been used for the fabrication of electronic and optoelectronic devices. Due to the

presence of long chain carbon containing ligands are not well conducting, however, during the past few decades, new concepts have been developed for the fabrication of CPs that exhibit high electrical conductivity.^[12]

Our group is mainly devoted to the synthesis of CPs by using mixed-ligand system for tuning the structural architectures.^[13] Usually, anionic dicarboxylates are used for polymerization of the monomeric coordination unit and neutral monodentate N-donor ligands hanging from the metal entity to fulfil the coordination sites. In these CPs, the mono-donors play important role for assembling the layers via supramolecular interactions such as $\pi \cdots \pi$, $\text{C} \cdots \pi$, hydrogen bonding, halogen bonding, halogen... π and halogen... π (chelate) interactions.^[14] The secondary interactions facilitate the charge transport among the layers in the CP revealing semiconducting property. Recently, we have shown the effect of halogen bonding interactions on the charge transport in one-dimensional (1D) CPs by altering *para*-substituent on the halobenzoate ligands.^[15] However, utilization of halogen... π interaction in the construction of supramolecular assemblies of CPs is still relatively less explored.

In this work, we report the role of halogen... n interactions in supramolecular architecture of 1D CPs in their electrical conductivity. Here, we have synthesized, two isostructural Cd(II)-based 1D CPs, $[\text{Cd}_2(p\text{-clba})_4(\text{bpy})_2] \cdot (\text{C}_2\text{H}_5\text{OH})$ (1) and $[\text{Cd}_2(p\text{-brba})_4(\text{bpy})_2] \cdot (\text{C}_2\text{H}_5\text{OH})$, (2) ($\text{H}_2p\text{-clba}$ = *para*-chlorobenzoic acid, $\text{H}_2p\text{-brba}$ = *para*-bromobenzoic acid and bpy = 4,4'-bipyridine), which undergo $\text{X} \cdots \text{n}$ ($\text{X} = \text{Cl}$ or Br) interactions to fabricate two-dimensional (2D) supramolecular architecture. It is evident that the $\text{Br} \cdots \text{n}$ interaction is stronger than $\text{Cl} \cdots \text{n}$ as Br atom is larger in size and more polarisable than Cl atom.^[16] Thus, the compound 2 has stronger interchain interactions which lead to the higher conductivity as compared to 1. The increasing conductivity has also been explained by band gap calculation performed by DFT computation.

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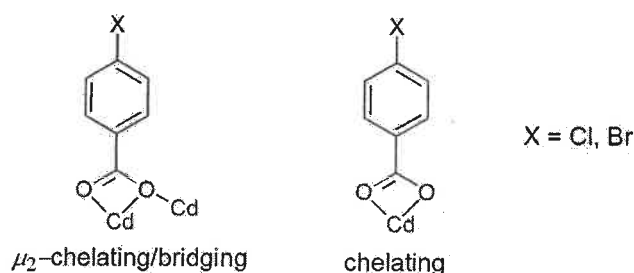
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Results and Discussion

Structural descriptions of $[\text{Cd}_2(p\text{-clba})_4(\text{bpy})_2] \cdot (\text{C}_2\text{H}_5\text{OH})$ (1) and $[\text{Cd}_2(p\text{-brba})_4(\text{bpy})_2] \cdot (\text{C}_2\text{H}_5\text{OH})$, (2)

Single crystal X-ray diffraction analysis reveals that both 1 and 2 are isotypical. Compound 1 crystallizes in the triclinic space group $P\bar{1}$ with $Z=2$. Asymmetric unit contains one Cd(II) ion, two $p\text{-clba}$ and one bpy ligands. The coordination environment of Cd(II) centre is distorted pentagonal bipyramid geometry. The equatorial plane is defined by three oxygen atoms of μ_2 -chelating/bridging carboxylate group from two different $p\text{-clba}$ ligands and two oxygen atoms from a chelating $p\text{-clba}$ ligand (Scheme 1). Two nitrogen atoms from two bpy ligands occupy



Scheme 1. Coordination modes of $p\text{-clba}/p\text{-brba}$.

the axial sites. Here, two Cd(II) ions are equivalently bridged by two μ_2 -chelating/bridging carboxylate groups to form a dinuclear $[\text{Cd}_2(\mu_2\text{-O}_2\text{CC})_2]$ secondary building unit (SBU) as shown in Figure 1a. There is a crystallographic inversion centre at the middle of the $[\text{Cd}_2(\mu_2\text{-O}_2\text{CC})_2]$ core with a Cd...Cd distance of 3.91 Å. The SBUs are connected by a pair of bpy ligands to generate a 1D ladder polymer (Figure 1b). These 1D ladders are further assembled by $\text{Cl}\cdots\pi$ interactions to fabricate a 2D supramolecular network (1c). The distance between the Cl atom to the centroid of pyridine ring of adjacent ladder is 3.72 Å (Figure 2a).

The compound 2 is isostructural with 1 and also forms 2D supramolecular architecture via interchain $\text{Br}\cdots\pi$ interactions. However, the $\text{Br}\cdots\pi$ distance in 2 is slightly shorter (3.65 Å) (Figure 2b), indicating stronger interactions among the adjacent ladders. Therefore, it is anticipated that the ladders are held more tightly in 2 as compared to 1, which reflects in the conductivity properties.

DFT computation and band gap

The energy differences of HOMO and LUMO (ΔE) have been calculated for the compound 1 and 2 by DFT computation. Here, the HOMO-LUMO gap has been obtained for 1 and 2 as 3.83 and 3.82 eV, respectively (Figure 3), which are in good agreement with the band gap derived from experimental Tauc's plot (Figure S3). A little difference of the calculated band gap could be due to the geometry factor that has been ignored during the calculation using single motif of polymeric chain.

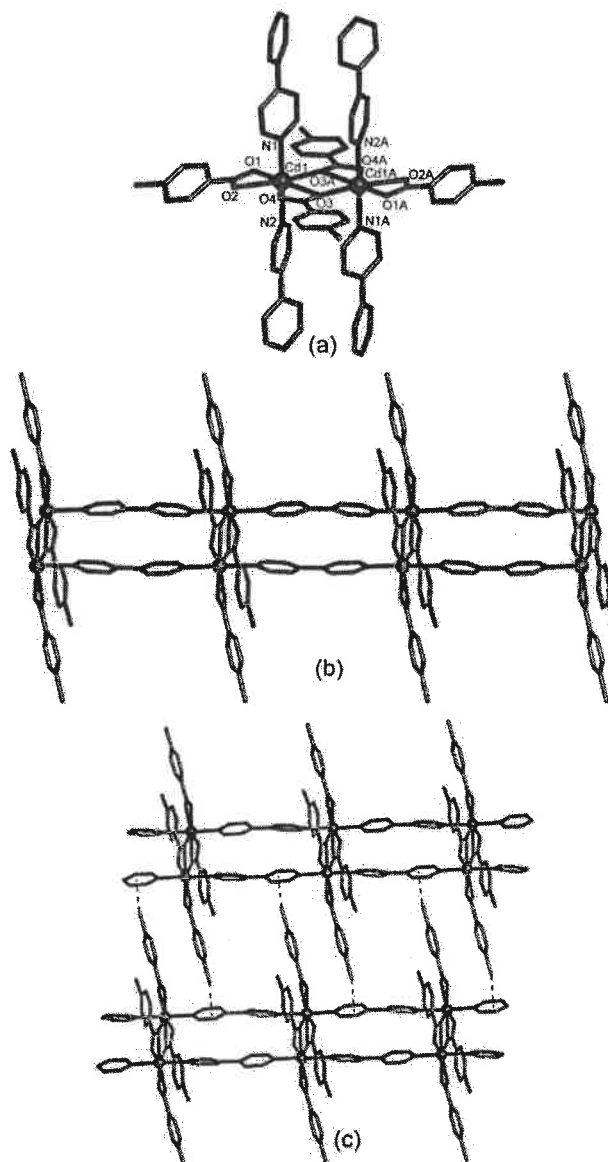


Figure 1. (a) Dimeric repeating unit of 1 showing coordination environment of Cd(II) centre. (b) 1D ladder polymer of 1. (c) 2D supramolecular network of 1 via $\text{Cl}\cdots\pi$ interactions.

Current-voltage analysis

The direct optical band gaps of the compound 1–2 have been calculated as 3.98 and 3.90 eV, respectively using Tauc's plot (Figure S3), which fall within the semiconducting region. This observation prompted us to check further the electrical conductivity of the materials. To reveal the charge transport mechanism of the compound 1–2 through the junction contact, current-voltage (I - V) measurement has been performed, which provides the preliminary idea about the ideality of the diode. The I - V characteristics of both the compounds at room temperature are displayed in Figure 4a. The exponential nature in the forward bias region gives the affirmation of Schottky barrier formation in the diode. From this region, the



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**Publication: Two zinc (ii)-based coordination polymers with flexible
dicarboxylate and pyridine mixed ligands: effect of $\pi \cdots \pi$ interactions on
electrical activity**

**Akhtaruzzaman, Pubali Das, Samim Khan, Suvendu Maity, Sanobar
Naaz, Sakhiul Islam, Prasanta Ghosh, Partha Pratim Ray and
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43, 16071

Two zinc(II)-based coordination polymers with flexible dicarboxylate and pyridine mixed ligands: effect of $\pi \cdots \pi$ interactions on electrical activity†

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Two novel coordination polymers (CPs) $[\text{Zn}(\text{cis-1,4-chdc})(4\text{-phpy})]_n$ (**1**) and $[\text{Zn}(\text{cis-1,4-chdc})(\text{py})]_n$ (**2**) (1,4- H_2chdc = 1,4-cyclohexanedicarboxylic acid, 4-phpy = 4-phenylpyridine and py = pyridine) were synthesized and characterized by elemental analysis, infrared spectroscopy, single-crystal X-ray diffraction, powder X-ray diffraction and thermogravimetric analyses. Both compounds formed a one-dimensional (1D) chain-like structure constructed by $\text{Zn}_2(\text{CO}_2)_4$ paddle-wheel dimers interconnected via double strands of *cis*-1,4-chdc-bridges, whereby pyridine-based ligands were decorated as arms on both sides of Zn_2 dimers. In compound **1**, polymeric 1D chains underwent self-assembly via $\pi \cdots \pi$ stacking interactions among 4-phpy ligands to form a 2D network, whereas this type of interaction was absent in **2**. Interestingly, both compounds exhibited electrical conductivity and revealed Schottky barrier diode behavior. However, compound **1** showed better electrical conductivity ($1.09 \times 10^{-3} \text{ S m}^{-1}$) with respect to compound **2** ($6.01 \times 10^{-5} \text{ S m}^{-1}$) because of $\pi \cdots \pi$ interactions.

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Introduction

Coordination polymers (CPs) are inorganic–organic solid state materials containing metal ion centers or metal clusters linked by organic ligands. They have attracted interest due to their appealing array-forming crystalline structures. Such highly ordered structures with high thermal stability exhibit various topologies. Several novel CPs have been reported.^{1–7} The rational design and synthesis of novel CPs are of immense interest in supramolecular chemistry and crystal engineering because of their potential applications in gas storage,^{8–10} separation,^{11–16} magnetism,^{17–19} catalysis,^{20–23} drug delivery^{24,25} photoactuation^{26,27} and sensing applications.^{28–35} Researchers have been able to choose, quite judiciously, the correct combination of ligands with different lengths and functionalities to synthesize

numerous CPs with desired structures and properties. However, the electrical conductivity of CPs is largely unexplored due to their inherent nature as electrical insulators.³⁶ Recently, new concepts have been developed for the fabrication of CPs that exhibit high electrical conductivity.^{37–40} A useful method for the design of such stable CPs is to utilize O-donor dicarboxylate or polycarboxylate ligands with their various coordination modes and bridging capability with metal centres.^{41–44} It is also possible to “fine tune” and regulate the conductivity by varying the ligand. Much attention has been paid in particular to flexible carboxylic acids and their derivatives.⁴⁵ In this regard, CPs made of the flexible ligand 1,4-cyclohexanedicarboxylic acid (1,4- H_2chdc) have not been explored much.^{46–49} 1,4- H_2chdc containing a chair-type backbone switches between *trans*-1,4- H_2chdc and its isomer *cis*-1,4- H_2chdc (Scheme 1) and displays variable modes of coordination with metal ions.⁵⁰ Optimization of this structure can be achieved by choosing a combination of this flexible dicarboxylic acid with N-donor auxiliary ligands. Our research team has chosen to synthesize CPs from a dicarboxylate ligand along with monodentate pyridyl ligands because of their potential applications in electrical conductivity.^{51–53} Herein, combinations of 4-phenylpyridine (4-phpy)/pyridine (py) with 1,4- H_2chdc have been adopted due to the possibility of forming $\pi \cdots \pi$ stacking interactions. It has been anticipated that Zn(II) metal ions with d^{10} configuration could be employed for synthesizing CPs that show semiconducting properties and could be used as electronic devices.^{54–56} Keeping all of these concepts in mind, we prepared two

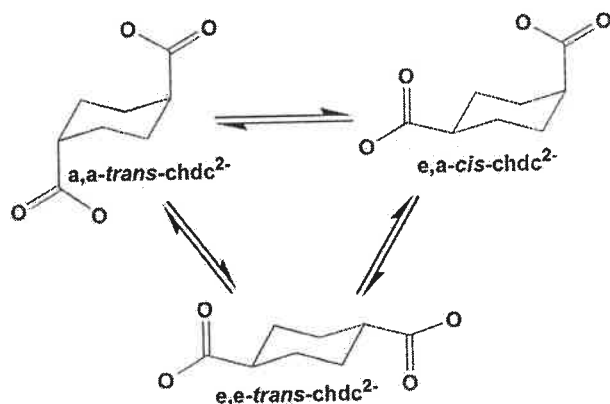
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† Electronic supplementary information (ESI) available: Tables S1–S6, Fig. S1–S7, TGA, PXRD, and X-ray crystallographic data in CIF format for compound **1** and **2**. CCDC 1912778 and 1912779. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9nj03986d

Scheme 1 Three conformations of 1,4-H₂chdc.

isomorphous compounds [Zn(*cis*-1,4-chdc)(4-phpy)]_n (1) and [Zn(*cis*-1,4-chdc)(py)]_n (2) using Zn(NO₃)₂·6H₂O and mixed ligands. Both compounds contained paddle-wheel dinuclear [Zn₂(CO₂)₄] secondary building units (SBUs), which were interconnected by 1,4-chdc to form a one-dimensional (1D) chain structure. However, compound 1 showed $\pi \cdots \pi$ interactions among 4-phpy ligands to form a two-dimensional (2D) sheet, which was absent in 2. Herein, we investigated the electrical conductivity of compound 1 and 2. As expected, both compounds showed substantive electrical conductivity in the range of a semiconductor region. However, in the case of 1, enhanced conductivity was observed compared with 2 due to $\pi \cdots \pi$ interactions in 1.⁵⁷ The charge transport mechanism, effective carrier mobility, transit time, carrier concentration and carrier lifetime were also estimated for both compounds. Data analysis showed that the charge-transport properties for 1 were improved.

Experimental section

Materials and physical method

All chemicals purchased were reagent grade and used without further purification. Elemental analyses (carbon, hydrogen and nitrogen) were done on a PerkinElmer 240C elemental analyzer. Infrared spectra in KBr (4500–500 cm⁻¹) were recorded using a PerkinElmer FT-IR spectrum RX1 spectrometer. Thermogravimetric analyses (TGA) were done on a PerkinElmer Pyris Diamond TGA/differential thermal analyses system in the range 30–900 °C under a nitrogen atmosphere. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation (λ = 1.548 Å) generated at 40 kV and 40 mA. The PXRD spectrum was recorded in a 2θ range of 5–50. Data for electrical properties were recorded from a Keithley 2635B source meter.

Syntheses of compounds 1 and 2

Synthesis of compound 1: a solution of 4-phpy (0.031 g, 0.2 mmol) in MeOH (2 mL) was cautiously layered very slowly to a solution of Zn(NO₃)₂·6H₂O (0.059 g, 0.2 mmol), in H₂O (2 mL) using 2 mL of a 1 : 1 (v/v) buffer solution of MeOH and H₂O. Then, a solution of 1,4-H₂chdc (0.034 g, 0.2 mmol) neutralized with Et₃N (0.021 g, 0.2 mmol) in 2 mL of EtOH

was layered upon it. After a few days, colorless block-shaped crystals of [Zn(*cis*-1,4-chdc)(4-phpy)]_n (1) were obtained (0.046 g, yield 60%). Elemental analysis (%) calcd for C₁₉H₁₉NO₄Zn: C, 58.40; H, 4.90; N, 3.58; found: C, 58.6; H, 4.7; N, 3.4, IR (KBr pellet, cm⁻¹): 1613 $\nu_{as}(\text{COO}^-)$, 1405 $\nu_{ys}(\text{COO}^-)$. Compound 2 was synthesized by a similar procedure as adopted for 1 except that we used py (0.016 g, 0.2 mmol) instead of 4-phpy. Colorless block-shaped crystals [Zn(*cis*-1,4-chdc)(py)]_n (2) were obtained after a few days (0.044 g, yield 70%). Elemental analysis (%) calcd for C₁₃H_{13.36}NO₄Zn: C, 49.84; H, 4.26; N, 4.47; found: C, 49.7, H, 4.4, N, 4.3. IR (KBr pellet, cm⁻¹): 1608 $\nu_{as}(\text{COO}^-)$, 1407 $\nu_{ys}(\text{COO}^-)$.

General X-ray crystallography

Single crystals of compounds 1 and 2 of suitable dimensions were used for data collection using a Bruker SMART APEX II diffractometer equipped with graphite-monochromated MoK α radiation (λ = 0.71073 Å). Molecular structures were solved using the SHELX-97 package.⁵⁸ Least-squares refinements of all reflections within the *hkl* ranges $-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-13 \leq l \leq 13$ (1) and $-10 \leq h \leq 10$, $-25 \leq k \leq 25$, $-20 \leq l \leq 21$ (2) were used to ascertain unit-cell parameters and crystal-orientation matrices. Collected data ($I > 2\sigma(I)$) were integrated using SAINT,⁵⁹ and the absorption correction was done by SADABS.⁶⁰ Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to “ride” on their parent atoms. The crystallographic data for 1 and 2 are summarized in Table S1 (ESI†). Selected bond lengths and bond angles are given in Tables S2–S4 (ESI†).

Fabrication and characterization of the device

To observe the electrical properties of the two synthesized materials, they were applied to thin-film semiconducting devices. In this regard, Schottky diodes were fabricated using synthesized materials and device properties were investigated. Prior to fabrication of devices, indium tin oxide (ITO)-coated glass substrates were cleaned with acetone, ethanol and distilled water sequentially using ultrasonication. Then, at room temperature, the substrates were dried in a N₂ atmosphere. A homogeneous dispersion of synthesized materials in *N,N*-dimethylformamide (DMF) medium (2 mg mL⁻¹) was obtained using an ultrasonicator. Subsequently, to obtain thin films, two dispersions were coated on two different ITO-coated glass substrates using a spin coater. Then, the systems were dried in a vacuum. The thicknesses of the films (*d*) were measured (~ 1 μm) with the help of a surface profiler. Then, at 10⁻⁶ Torr, aluminum (Al) metal was deposited onto the films using vacuum coating unit 12A4D (HINDHIVAC). The effective area of the devices (*A*) was maintained as 7.065×10^{-6} m² using a shadow mask. By recording current–voltage (*I*–*V*) data from a Keithley 2635B source meter (using a two-probe method), characterizations of the electrical properties of the devices were made. All preparations and characterizations were done at room temperature (303 K).

Electrical characterization

To explore the current density–voltage (*J*–*V*) characteristics of 1 and 2, respective devices with configuration ITO/compounds/Al



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Period of Investigation: 01-06-2017 to 18-05-2018

Project: Coordination polymers and electrical conductivity

Output: The result was published in a journal of international repute

Publication: Two isostructural linear coordination polymers: the size of the
metal ion impacts the electrical conductivity

**Basudeb Dutta, Arka Dey, Kaushik Naskar, Suwendu Maity, Faruk Ahmed,
Sakhiul Islam, Chittaranjan Sinha, Prasanta Ghosh, Partha Pratim Ray,
Mohammad Hedayetullah Mir**

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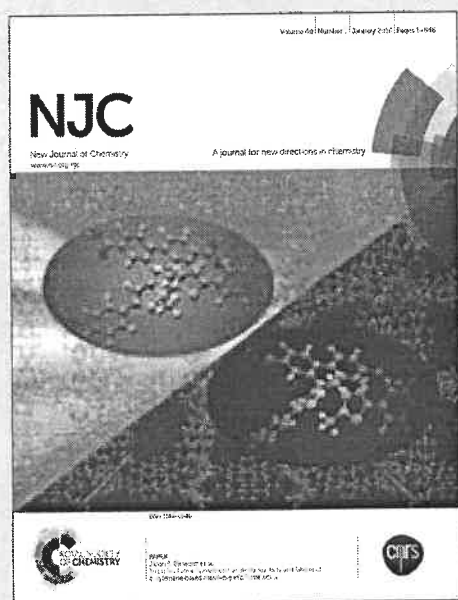
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ARTICLE

Two isostructural linear coordination polymers: Size of metal ion impacts the electrical conductivity

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Two new one-dimensional coordination polymers (1D CPs) {[Zn(adc)(4-spy)₂(H₂O)₂]}_n (**1**) and {[Cd(adc)(4-spy)₂(H₂O)₂]}_n (**2**) (H₂adc = acetylenedicarboxylic acid and 4-spy = 4-styrylpyridine) have been synthesized and well characterized. Single crystal X-ray diffraction data exhibit that the compound **1** and **2** are isostructural and undergo hydrogen bonding and C–H...π interactions to construct 3D supramolecular architectures. Electrical characterization reveals that both the compounds show substantive electrical conductivity and exhibit Schottky diode nature. However, the compound **2** has higher mobility and higher conductivity as compared to **1**. The estimated values of effective carrier mobility, transit time, carrier concentration and diffusion length demonstrate that the charge transport properties have been improved for **2**. Therefore, the compound **2** has better performance in the fabrication of electronic devices.

Introduction

During past few decades organic-inorganic hybrid materials, also called as coordination polymers (CPs)^{1–7} are demanding themselves as the active members in the club of material chemistry. These hybrid materials are composed of metal node (or metal cluster) and organic linkers (O, N, S or P- donors), where metal centres are connected through organic ligands extending in an array. These types of materials are useful in the field of gas storage,^{8–10} separation,^{11–14} magnetism,^{15–17} drug delivery,^{18–20} catalysis^{21–22} and sensing applications.^{23–27} Despite various applications, these materials still lack in charge transport and electrical conductivity owing to their electrical insulator character.²⁸ However, it is possible to fabricate the desire materials by judicious choice of metal ions or organic ligands. In the recent years, successful attempts have been made for the fabrication of CPs that exhibit high electrical conductivity.^{29–33}

A useful method in the design of such stable CPs is to utilize O-donor dicarboxylate or polycarboxylate ligands with their various coordination modes and bridging capability with metal centres.^{34–35} A useful method of synthesizing one-dimensional (1D) CP is to employ linear dicarboxylate, e.g. acetylenedicarboxylate (O₂CCCCO₂[–]) which can bind two

metal ions using either one oxygen atom from each end in η¹ fashion or both the oxygen atoms from both carboxylates in η² manner.^{36–38} It has been found that metal ions with d¹⁰ configuration (e.g. Zn(II), Cd(II) etc.) have been employed for synthesizing CPs that show semiconducting properties and can be used as electronic devices.^{39–41} However, it is possible to fine-tune the conductivity by varying the metal cations.³⁷ Recently, our group reported a series of 1D CPs synthesized from linear dicarboxylate ligands along with monodentate 4-phenylpyridine ligand (4-phpy) for their electrical conductivity and Schottky diode applications.^{42–43} As the ligands with more conjugation are found to exhibit better semiconducting properties, herein, we chose monodentate 4-styrylpyridine (4-spy) as a co-ligand. We have obtained two isostructural linear one-dimensional 1D CP, {[Zn(adc)(4-spy)₂(H₂O)₂]}_n (**1**) and {[Cd(adc)(4-spy)₂(H₂O)₂]}_n (**2**) (H₂adc = acetylenedicarboxylic acid and 4-spy = 4-styrylpyridine) using acetylenedicarboxylate as a linear organic linker. The 1D chains further undergo hydrogen bonding and C–H...π interactions to fabricate three-dimensional (3D) networks. Notably, both the compounds show substantive electrical conductivity in the range of semiconductor and exhibit Schottky diode nature. The conductivity has been improved with those of structurally analogous compounds reported earlier.⁴³ However, compound **2** shows better conductivity as compared to **1**. Here, the enhancement of conductivity of **2** may be due to increase in size of Cd²⁺ as compared to Zn²⁺ in **1**.^{28, 43–44} To get insight into the charge transport mechanism of the compounds, the effective carrier mobility, transit time, carrier concentration and diffusion length have been estimated. The analysis demonstrates that the charge transport properties have been improved for **2**. Therefore, compound **2** will have better

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†Electronic Supplementary Information (ESI) available: Figure S1, Table S1–S6, TGA, PXRD, and X-ray crystallographic data in CIF format for CCDC 1814459 (**2**) and 1814460 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x