



# Mixed ligand coordination polymers with flexible bis-imidazole linker and angular sulfonyldibenzoate: Crystal structure, photoluminescence and photocatalytic activity



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## ABSTRACT

Four ternary coordination polymers (CPs) namely,  $\{[\text{Ni}(\text{SDB})(\text{BITMB})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$  (**CP1**),  $\{[\text{Cd}(\text{SDB})(\text{BITMB})(\text{H}_2\text{O})] \cdot (\text{THF})(\text{H}_2\text{O})\}_n$  (**CP2**),  $\{[\text{Zn}_2(\text{SDB})_2(\text{BITMB})] \cdot (\text{THF})_2\}_n$  (**CP3**) and  $\{[\text{Co}_2(\text{SDB})_2(\text{BITMB})] \cdot (\text{Dioxane})_3\}_n$  (**CP4**) composed of angular dicarboxylate **SDB** (4,4'-sulfonyldibenzoate) and N-donor **BITMB** (1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethyl benzene) have been synthesized by solvothermal reactions and characterized by single crystal X-ray diffraction and other physico-chemical techniques. **CP1** possesses one-dimensional ribbon type metal–organic motifs glued together by H-bonds and  $\pi \cdots \pi$  interactions, whereas **CP2–CP4**, exhibit non-interpenetrated *sql* networks supported by weak supramolecular interactions. Structural diversity of these CPs can be attributed to the coordination geometry adopted by the metal nodes, versatile coordination modes of **SDB** and conformational flexibility of **BITMB**. Solid state luminescence properties of **CP1–CP4** were explored. Photocatalytic performance of all CPs for the decomposition of metanil yellow by dilute hydrogen peroxide in the presence of visible light was also investigated. 25–83% dye removal from aqueous solutions in the presence of **CP1–CP4** was observed.

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## 1. Introduction

Research involving design and construction of new coordination polymers (CPs) or metal organic frameworks (MOFs) has been flourishing for two and a half decades due to their application in the area of molecular recognition, fluorescence, catalysis, gas storage, separation and magnetism etc [1]. Recently considerable research interest has been paid towards the application of CPs as photocatalyst for reactions such as dye degradation and waste water treatment. Generally these photocatalysts work in the presence or absence of oxidants such as  $\text{H}_2\text{O}_2$  [2,3]. Photocatalytic dye degradation generally occurs in the presence of UV radiation as only few systems have been showed activity under visible light [2,4].

Noticeably the relevant literature encompasses a plethora of one- and two-dimensional CPs exhibiting interesting weak molecular interactions in their supramolecular assembly [5]. These weak interactions are not only vital for the self assembly of the super structures but also have been proved as key structural feature for

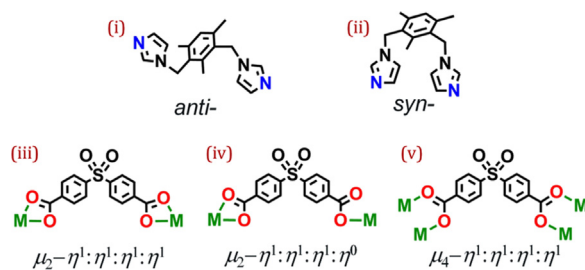
several interesting properties; for instance, electron transfer phenomenon which plays a pivotal role during photocatalysis [1,3].

In a recent review Yaghi and co-workers have underlined the importance of metal–organic materials comprising of more than two components which in turn implies that the assembly of ternary coordination polymers not only result in aesthetic functional materials but also contribute towards the anticipated tailoring of future materials [6]. Angular dicarboxylates, owing to their diverse coordination capability and topological–directional preferences, have secured an obvious space among organic spacers used for the construction of coordination polymers [7]. Recently we have reported ternary CPs derived from angular dicarboxylate **SDB** and N-donor ligands [8]. It was exposed that hydrogen bonding ability of **SDB** through sulfone functionality play vital role to construct the chiral and achiral CPs in addition to other factors. On the other hand bis(imidazol-yl-methyl)benzene linkers, owing to their conformational flexibility, have widen the scope of designing the metal organic supramolecular assemblies [9].

In the present study, we utilized angular dicarboxylate **SDB** and exobidentate N-donor ligand **BITMB** to assemble mixed ligand CPs with different metal centers (Scheme 1). Thus, attempted hydrothermal reactions resulted in  $\{[\text{Ni}(\text{SDB})(\text{BITMB})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$  (**CP1**),

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**Scheme 1.** Depiction of *anti*- and *syn*-conformers of **BITMB** (i, ii) and binding modes of **SDB** observed in present study (iii–v).

$\{[Cd(SDB)(BITMB)(H_2O)] \cdot (THF)(H_2O)_n\}$  (**CP2**),  $\{[Zn_2(SDB)_2(BITMB)] \cdot (THF)_2\}_n$  (**CP3**) and  $\{[Co_2(SDB)_2(BITMB)] \cdot (Dioxane)_3\}_n$  (**CP4**). Crystallographic studies revealed the non-interpenetrated metal–organic motifs in these CPs are stabilized via several weak interactions including inter/intra molecular hydrogen bonding, C–H $\cdots\pi$ , and  $\pi\cdots\pi$  interactions. Moreover, the synthesized materials exhibit promising luminescence and photocatalytic activity. The present investigation shed light on the structural and functional aspects of synthesized CPs which may be endorsed to different metal nodes having divergent coordination geometry besides other discussed factors.

## 2. Experimental section

### 2.1. General

4,4'-Sulfonyldibenzoic acid ( $H_2SDB$ ) and reagents for the synthesis of **BITMB** were purchased from Sigma–Aldrich. Metal salts and organic solvents were obtained from RANBAXY and SD Fine Chemicals, India. Distilled water was used for synthetic manipulations. All the reagents and solvents were used as received without any further purification. Ligand **BITMB** was synthesized by following a reported procedure [10]. CHNS analyses were done using a Perkin–Elmer 2400 CHNS/O analyzer. IR spectra were recorded using KBr pellets on a Perkin–Elmer GX FTIR spectrometer. For each IR spectra 10 scans were recorded at  $4\text{ cm}^{-1}$  resolution. TGA analysis was carried out using Mettler Toledo Star SW 8.10. Solid state UV–vis spectra and luminescence spectra were recorded using Shimadzu UV-3101PC spectrometer and Fluorolog Horiba Jobin Yvon spectrophotometer, respectively. PXRD data were collected using a Philips X-Pert MPD system with  $CuK\alpha$  radiation. Single crystal structures were determined using BRUKER SMART APEX (CCD) diffractometer. Dye decolourization was studied using the Varian CARY 500 Scan UV–vis–NIR spectrophotometer.

### 2.2. Synthesis of $\{[Ni(SDB)(BITMB)(H_2O)] \cdot H_2O\}_n$ (**CP1**)

$H_2SDB$  (70 mg, 0.33 mmol), **BITMB** (75 mg, 0.26 mmol) and  $Ni(NO_3)_2 \cdot 6H_2O$  (100 mg, 0.34 mmol) were dispersed in 10 mL mixed solvent (3 mL water, 3 mL methanol and 4 mL 1,4-dioxane) and then sealed in a 23 mL Teflon-lined autoclave, which was heated at 398 K for 50 h. Yield=45%. Elemental analysis (%), Cal.: C, 54.81; H, 4.75; N, 8.25; S, 4.72; found: C, 54.27; H, 4.87; N, 8.12. IR  $\text{cm}^{-1}$  (KBr): 3435 (br), 2924 (w), 2362 (w), 1616 (s), 1563 (m), 1394 (s), 1298 (m), 1228 (w), 1164 (m), 1103 (m), 1020 (m), 829 (w), 740 (s), 689 (w), 620 (m).

### 2.3. Synthesis of $\{[Cd(SDB)(BITMB)(H_2O)] \cdot (THF) \cdot H_2O\}_n$ (**CP2**)

$H_2SDB$  (60 mg, 0.29 mmol), **BITMB** (100 mg, 0.35 mmol) and  $Cd(NO_3)_2 \cdot 4H_2O$  (300 mg, 0.97 mmol) were dispersed in 10 mL water/tetrahydrofuran (1:1) and then sealed in a 23 mL Teflon-lined autoclave, which was heated at 398 K for 98 h. Yield=67%.

Elemental analysis (%) Cal.: C, 52.21; H, 5.01; N, 6.96; S, 3.98; found: C, 52.48; H, 5.35; N, 6.74; IR  $\text{cm}^{-1}$  (KBr): 3412 (br), 3123 (w), 2961 (w), 2367 (w), 1595 (m), 1553 (s), 1398 (s), 1293 (m), 1223 (w), 1158 (w), 1089 (w), 1019 (w), 856 (w), 745 (s), 619 (m).

### 2.4. Synthesis of $\{[Zn_2(SDB)_2(BITMB)] \cdot (THF)_2\}_n$ (**CP3**)

$H_2SDB$  (75 mg, 0.36 mmol), **BITMB** (70 mg, 0.25 mmol) and  $Zn(NO_3)_2 \cdot 6H_2O$  (100 mg, 0.33 mmol) were dispersed in 12 mL mixed solvent (5 mL water, 5 mL THF and 2 mL methanol) and then sealed in a 23 mL Teflon-lined autoclave, which was heated at 398 K for 50 h. Yield=42%. Elemental analysis (%), Cal.: C, 54.69; H, 4.50; N, 4.81; S, 5.51; found: C, 54.32; H, 4.65; N, 4.68; IR  $\text{cm}^{-1}$  (KBr): 3435 (br), 3142 (w), 2924 (w), 2366 (w), 1657 (s), 1562 (w), 1406 (s), 1293 (w), 1223 (w), 1163 (m), 1098 (m), 1014 (w), 870 (w), 740 (s), 619 (w).

### 2.5. Synthesis of $\{[Co_2(SDB)_2(BITMB)] \cdot (dioxane)_3\}_n$ (**CP4**)

$H_2SDB$  (75 mg, 0.36 mmol), **BITMB** (90 mg, 0.32 mmol) and  $Co(NO_3)_2 \cdot 6H_2O$  (154 mg, 0.52 mmol) were dispersed in a mixture of 3 mL water and 3 mL 1,4-dioxane and then sealed in a 14 mL Teflon-lined autoclave, which was heated at 398 K for 60 h. Yield=36%. Elemental analysis (%), Cal.: C, 53.86; H, 4.76; N, 4.41; S, 5.05; found: C, 53.68; H, 5.02; N, 4.32; IR  $\text{cm}^{-1}$  (KBr): 3425 (br), 3105 (w), 2956 (w), 2850 (w), 2375 (w), 1640 (s), 1562 (w), 1406 (s), 1293 (m), 1163 (m), 1112 (s), 1014 (w), 870 (m), 735 (s), 620 (w).

### 2.6. X-ray crystallography

summary of crystallographic data, detail of hydrogen bonding interactions and selected bond lengths and bond angles for all compounds is given in Table 1, Tables S1 and S2, respectively. Single crystal of the respective compounds with ideal dimensions was transferred rapidly from mother liquor and immersed in paratone oil before being mounted for data collection at 150 K. Intensity data for all the three crystals were collected using  $MoK\alpha$  ( $\lambda=0.71073\text{ \AA}$ ) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector. The data integration and reduction were processed with SAINT software [11]. An empirical absorption correction was applied to the collected reflections with SADABS [12]. The structures were solved by direct methods using SHELXTL and were refined on  $F^2$  by the full-matrix least-squares technique using the program SHELXL-97 [13,14]. In the case of **CP2**, two of the carbon atoms in the imidazole ring of **BITMB** are disordered and the occupancy factors for the disordered positions were determined using FVAR command of SHELXL-97. Contribution to the diffraction data from the highly disordered solvent molecules ( $H_2O$ /THF/Dioxane) present in the lattice of **CP1–CP3** has been removed using the SQUEEZE subroutine as implemented in PLATON [15]. In the case of **CP4** three dioxane molecules present in the lattice were located from the difference Fourier map. Refinement of compounds using the modified reflection data set apparently improved the *R*-factor and GOF. All non-hydrogen atoms were refined anisotropically till convergence is reached. Hydrogen atoms attached to the organic moieties were either located from the difference Fourier map or stereochemically fixed in all the CPs. The accessible void volumes of **CP1**, **CP2**, **CP3** and **CP4** after the complete removal of lattice solvent molecule are 5.6, 20.3, 37.7 and 36.0%, respectively, of the unit cell volumes estimated by PLATON/SOLV.

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