



Temperature dependent structural variation from 2D supramolecular network to 3D interpenetrated metal–organic framework: In situ cleavage of S–S and C–S bonds



Bharat Ugale, Divyendu Singh, C.M. Nagaraja*

Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar, 140001, Punjab, India

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ABSTRACT

Two new Zn(II)–organic compounds, $[\text{Zn}(\text{muco})(\text{dbds})_2(\text{H}_2\text{O})_2]$ (**1**) and $[\text{Zn}(\text{muco})(\text{dbs})]$ (**2**) (where, *muco*=*trans*, *trans*-muconate dianion, *dbds*=4,4'-dipyridyldisulfide and *dbs*=4,4'-dipyridylsulfide) have been synthesized from same precursors but at two different temperatures. Both the compounds have been characterized by single-crystal X-ray diffraction, powder X-ray diffraction, elemental analysis, IR spectroscopy, thermal analysis and photoluminescence studies. Compound **1** prepared at room temperature possesses a molecular structure extended to 2D supramolecular network through (H–O...H) hydrogen-bonding interactions. Compound **2**, obtained at high temperature (100 °C) shows a 3-fold interpenetrating 3D framework constituted by an in situ generated *dbs* linker by the cleavage of S–S and C–S bonds of *dbds* linker. Thus, the influence of reaction temperature on the formation of two structural phases has been demonstrated. Both **1** and **2** exhibit ligand based luminescence emission owing to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions and also high thermal stabilities.

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1. Introduction

In recent years, the design and synthesis of coordination polymers (CPs) or metal–organic frameworks (MOFs) has attracted a great interest due to their fascinating architectures and various functional properties such as gas storage, separation, heterogeneous catalysis, sensing, magnetism and so on [1–16]. A wide range of CPs/MOFs or supramolecular architectures with different dimensionalities (1D/2D/3D) and novel topologies have been developed but however, it is still challenging to obtain CPs/MOFs with desired architectures. It has been observed that the structural dimensionality and the topology of CPs/MOFs can be tuned by several syntheses parameters, such as the solvent type, pH of the reaction, the presence of counter ions, temperature and time of reaction [17–20]. Especially, temperature of the synthesis plays a significant role on the crystal structure dimensionality and the topology of the resulting frameworks. Therefore, systematic investigation on the temperature dependence of framework dimensionalities has gained much attention [21–24]. Generally, higher reaction temperature increases the dimensionality of the framework due to the increased tendencies of M–O–M linkage formation [25]. On the other hand, the shape and connectivity of organic ligand/linker also plays an important role in directing the structure, dimensionality and the topology of the resulting MOFs. In

this context, polycarboxylate ligands are found to be the excellent building blocks to construct MOFs with diverse shape and connectivity [7]. Particularly, long chain, rigid dicarboxylate ligands, such as *trans*, *trans*-muconic acid (*mucoH*₂) has been found to be quite useful for construction of interpenetrated/entangled networks which are attracting much attention due to their intriguing artistic and the structure dependent properties [26–29]. The origin of interpenetration in MOFs has been ascribed due to the presence of large voids in them. However, the factors that influence the resulting degree of interpenetration remain unknown.

Considerable progress has also been made in the construction of functional MOFs by using various bipyridyl spacers along with carboxylate ligands [30,31]. The bipyridyl spacers not only pillar the metal–carboxylate motifs into higher dimensionality but also support diverse structural topologies. Among the various bipyridyl spacers, 4,4'-dipyridyldisulfide (*dpds*) has attracted coordination chemists due to its twisted conformation with a C–S–S–C torsion angle of ca. 90° and its temperature dependent cleavage of disulfide bond [32–37]. Such ligands which under go in situ conversion under solvothermal condition are expected result unusual structures which otherwise are not accessible by direct synthesis [38].

In this regard, we were interested to see the results of the combination of a rigid dicarboxylate ligand, *trans*, *trans*-muconate with flexible *dbds* linker by tuning the temperature. Therefore, herein, we report syntheses of two new Zn(II)–organic compounds, $[\text{Zn}(\text{muco})(\text{dbds})_2(\text{H}_2\text{O})_2]$ (**1**) and $[\text{Zn}(\text{muco})(\text{dbs})]$ (**2**) (where, *muco*=*trans*, *trans*-muconate dianion, *dbds*=4,4'-dipyridyldisulfide and

* Corresponding author. Tel.: +91 1881 242229; fax: +91 1881 223395.

E-mail address: cmnrjaja@iitrpr.ac.in (C.M. Nagaraja).

dbds=4,4'-dipyridylsulfide) by varying the temperature of synthesis. Compound **1**, obtained at room temperature, has a molecular structure extended to two-dimensional (2D) supramolecular network via (H–O...H) H-bonding. Compound **2** synthesized at high temperature (100 °C) possess a 3-fold interpenetrating, 3D framework constituted by an in situ generated dbds linker by the cleavage of S–S and C–S bonds of dbds linker. Hence, the influence of reaction temperature on the formation of two structural phases with different dimensionality and the topology has been demonstrated. Both **1** and **2** exhibit luminescence emission owing to intraligand and/or ligand-to-ligand charge transfer transitions (LLCT).

2. Experimental

2.1. Materials and methods

All the reagents employed were commercially available and used as received without further purification. IR spectra were recorded from KBr pellets on a Thermo Scientific Nicolet iS10 FT-IR Spectrometer in the range 4000–400 cm^{-1} . Thermogravimetric analyses (TGA) were carried out using Mettler Toledo thermogravimetric analyzer in nitrogen atmosphere (flow rate=40 ml min^{-1}) in the temperature range of 25–900 °C (heating rate=10 °C min^{-1}). Powder XRD pattern of the compounds were recorded on a PANalytical's X'PERT PRO diffractometer using $\text{CuK}\alpha$ radiation ($k=1.542 \text{ \AA}$; 40 kV, 20 MA). The photoluminescence measurements were recorded at room temperature on a Perkin Elmer LS55 fluorescence spectrophotometer.

2.2. Synthesis of $[\text{Zn}(\text{muco})(\text{dbds})_2(\text{H}_2\text{O})_2]$ (**1**)

$\text{Zn}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ (0.055 g, 0.25 mmol) was dissolved in 4 ml of deionized water to which an aqueous solution (2 ml) of H_2muco (0.036 g, 0.25 mmol) neutralized with NaOH (0.020 g, 0.5 mmol) was added with constant stirring. To this solution an ethanolic solution (2 ml) of dbds (0.055 g, 0.25 mmol) was added and the contents were stirred for 24 h at room temperature and then the solid obtained was filtered and the filtrate was allowed to evaporate slowly. Orange–yellow block crystals of $[\text{Zn}(\text{muco})(\text{dbds})_2]$ (**1**) were obtained after four weeks (Yield: 70%). Anal. calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_6\text{S}_4\text{Zn} \cdot 3\text{H}_2\text{O}$: C, 42.38; H, 3.21; N, 9.71. Found: C, 42.61; H, 2.70; N, 10.40. FT-IR (KBr, 4000–400 cm^{-1}): 3410–3199(w), 2981(w), 1611(s), 1544(s), 1423–1354(s), 1291–1222(s), 865–713(s).

2.3. Synthesis of $[\text{Zn}(\text{muco})(\text{dbds})]$ (**2**)

Compound **2** was prepared by following the procedure similar to that of **1** except that the reaction mixture was taken in a 30 ml glass vial sealed with parafilm and heated at 100 °C for 4 days. After being cooled to room temperature, orange–yellow block crystals of **2** were isolated (Yield: 40%). Anal. calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2\text{Zn} \cdot 7\text{H}_2\text{O}$: C, 36.82; H, 2.57; N, 6.36. Found: C, 36.40; H, 2.71; N, 6.31. FT-IR (KBr, 4000–400 cm^{-1}): 2932(w), 1593(s), 1533–1478(s), 1421–1377(s), 1223(s), 814–726 (s).

2.4. X-ray crystallography

Single crystal X-ray structural data of compounds **1** and **2** were collected on a Bruker D8 Venture PHOTON 100 CMOS diffractometer equipped with a INCOATEC micro-focus source and graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$). The program, SAINT [39] was used for integration of diffraction profiles and absorption correction was made with SADABS program [40]. Both the structures were solved by SIR 92 [41] and refined by full matrix least square method using 2013 [42] and WinGX system, Ver 2013.3 [43]. In compound **1** a

residual peak of 2.81 e/\AA^3 is appearing near the Zn(II) atom resulting in slightly high value of wR_2 which could be arising due to absorption. All the non-hydrogen atoms were located from the difference Fourier map and refined anisotropically. All the hydrogen atoms were fixed by HFIX and placed in ideal positions and included in the refinement process using riding model with isotropic thermal parameters. Potential solvent accessible area or void space was calculated using the PLATON multipurpose crystallographic software [44]. All the crystallographic and structure refinement data of compounds **1** and **2** are summarized in Table 1. Selected bond lengths and angles are given in Tables S1 and S2, respectively.

3. Results and discussion

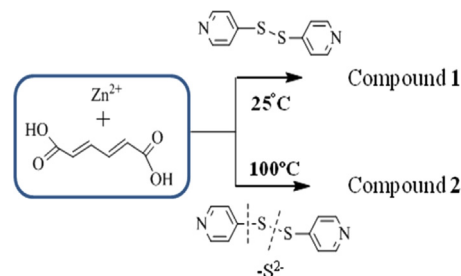
3.1. Formation of **1** and **2**

Compound **1** was obtained by room temperature reaction of Zn(II) ion with muco ligand and dbds linker using water/ethanol combination. At room temperature the formation of extended structure is prevented due to the coordination of water molecules to Zn(II) ion. Increasing the temperature of the reaction to 100 °C resulted in situ generation of dbds linker by the cleavage of C–S and S–S bonds of dbds linker as depicted in Scheme 1. Further, the coordination of dbds linker to $[\text{Zn}(\text{muco})]$ motifs generate the 3D framework of **2**. Hence, the temperature of the reaction plays a crucial role in directing the structure, dimensionality and topology of the resulting frameworks.

Table 1
Crystallographic data for **1** and **2**.

Compound	1	2
Empirical formula	$\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_6\text{S}_4\text{Zn}$	$\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2\text{Zn}$
Formula weight	682.16	393.74
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 13)
<i>a</i> (Å)	11.947(5)	13.400(5)
<i>b</i> (Å)	5.755(5)	8.579(5)
<i>c</i> (Å)	20.465(5)	15.101(5)
β (°)	90.758(5)	91.474(5)
<i>V</i> (Å ³)	1407.0(14)	1735.4(13)
<i>Z</i>	2	4
μ (mm^{-1})	1.219	1.556
Total data	27,063	41,992
Unique data	6932	4331
R_{int}	0.063	0.030
Data [$I > 2\sigma(I)$]	6483	3871
$^a R_1$	0.0929	0.0237
wR_2	0.2472	0.0624
<i>S</i>	1.08	1.04
Flack parameter	0.179(7)	

$$^a R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|, \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$



Scheme 1. Synthesis scheme of compounds **1** and **2**.

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