Journal of Solid State Chemistry 223 (2015) 23–31

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Luminescent MOFs comprising mixed tritopic linkers and Cd(II)/Zn(II) nodes for selective detection of organic nitro compounds and iodine capture

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ARTICLE INFO

Article history:
Received 24 March 2014
Received in revised form
2 May 2014
Accepted 6 May 2014
Available online 21 May 2014

Keywords:
Coordination polymer
Nitro compounds
Explosive detection
Photoluminescence
Tripodal ligands
Iodine encapsulation

ABSTRACT

Two CPs $\{[Cd_3(\mathbf{BTC})_2(\mathbf{TIB})_2(H_2O)_4].(H_2O)_2\}_n$ (**1**) and $\{[Zn_3(\mathbf{BTC})_2(\mathbf{TIB})_2].(H_2O)_6\}_n$ (**2**) composed of tripodal linkers **BTC** (1,3,5-benzenetricarboxylate) and **TIB** (1,3,5-tris(imidazol-1-ylmethyl)benzene) were synthesized via solvothermal route and structurally characterized. Single crystal structural analysis reveals **1** possesses a novel 3D framework structure, whereas **2** represents a previously established compound. Owing to the d^{10} configuration of metal nodes and robust 3D frameworks, **1** and **2** exhibit excellent fluorescence properties which have been exploited to sense organic nitro compounds in vapor phase. Compound **1** demonstrates selective sensing of nitromethane over structurally similar methanol with *ca.* 70 and 43% fluorescence quenching in case of former and later. Similarly, 58% fluorescence quenching was observed in case of nitrobenzene over the structurally resembling toluene for which 30% quenching was observed. Compound **2** did not show any preference for nitro compounds and exhibited comparable fluorescence quenching when exposed to the vapors of nitro or other geometrically resembling organic molecules. Furthermore, adsorption experiments revealed that **1** and **2** can uptake 2.74 and 14.14 wt% molecular iodine respectively in vapor phase which can be released in organic solvents such as hexane and acetonitrile. The maximal iodine uptake in case of **1** and **2** corresponds to 0.15 and 0.80 molecules of iodine per formula unit of respective frameworks. Comprehensive structural description, thermal stability and luminescence behavior for both CPs has also been presented.

1. Introduction

Research involving coordination polymers (CPs) or metal organic frameworks (MOFs) has witnessed enormous growth in designing strategies as well as applications towards molecular recognition, fluorescence, catalysis, gas storage, separation and magnetism [1,2]. Appreciable research interest has been paid towards stimuli triggered structural dynamics of CPs/MOFs and eventual functional responses in recent times owing to the promising applications of such phenomena for selective detection of a variety of analytes [2–13]. Remarkable efforts are being paid to the detection of nitro aromatic explosives and related organic derivatives due to the environmental and security concerns [3–13].

Most of the explosives constitute of highly electron deficient nitro and nitrate functionalities, rendering such species a good electron acceptors. Hence effective vicinity or contact of the explosive materials with electron donor species such as conjugated polymeric systems assists exciton migration resulting in fluorescence quenching. This fluorescence quenching phenomenon has been an efficient route for explosive detection and the methodology has recently been implemented to a few CPs/MOFs. Relevant reports underline the suitability of selective fluorescent CPs/MOFs for quick sensing of electron deficient molecules [3–5]. In this context, report by Li and coworkers on detection of 2,3-dimethyl-2,3-dinitrobutane, a taggant for plastic explosives using a ternary Zn(II) CP is seminal and remarkable [3a]. Reports indicate that Zn(II) and Cd(II) containing MOFs exhibit notable efficiency towards nitroaromatics detection [3–9]. Recently, heterometallic combinations, alkali metals and lanthanides have also been utilized to synthesize MOFs capable of explosive detection [5,10]. Moreover, explosive detection has also been related to textural and

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http://dx.doi.org/10.1016/j.jssc.2014.05.012
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morphological features in case of few metal-organic gels [6,11], nano-MOFs [9,12] and MOF-membranes [7]. A couple of simulation studies are also remarkable in this regard [13].

Controlled capture and release of various analytes in CPs/MOFs has been another major research interest in recent times. Much attention has been paid to the iodine encapsulation due to the momentous effects of iodine on conductivity, magnetism and luminescence properties of MOFs as well as unforeseen hazards associated with use of its radioactive isotope, ^{129}I in nuclear reactors [14,15]. Aptness of CPs/MOFs for iodine capture has recently been demonstrated in few reports focused on zeolitic imidazolate frameworks (ZIFs), HKUST-1 and other coordination polymeric networks.

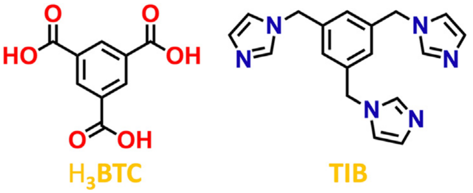
Ternary CPs are highly celebrated solid materials owing to the feasible dual ligand structure modulation which not only provide with esthetic structural assemblies but also multifunctional applications [1c]. So far, a number of judicious combinations of polycarboxylate and N-donor linkers have been utilized to achieve functional ternary CPs; however, reports on CPs comprising both (carboxylate and N-donor) tripodal linkers are still scarce in the literature [16].

Herein, we report on the synthesis and applications of two 3D ternary CPs, $\{[Cd_3(\mathbf{BTC})_2(\mathbf{TIB})_2(H_2O)_4].(H_2O)_2\}_n$ (**1**) and $\{[Zn_3(\mathbf{BTC})_2(\mathbf{TIB})_2].(H_2O)_6\}_n$ (**2**) comprising of tripodal ligands **BTC** and **TIB** (Scheme 1). **1** and **2** were synthesized hydrothermally and characterized by single crystal X-ray crystallography and other physicochemical techniques. Crystallographic studies revealed that **1** possesses an intriguing 3D framework with thorough channels along *a*-axis occupied by water molecules, however, **2** is a previously known CP. Judicious selection of d^{10} metal nodes Cd and Zn provides with noteworthy fluorescence of **1** and **2**, which can selectively be quenched by organic molecules possessing nitro-functionality. Uptake of iodine vapor by these materials at 80 °C and its controlled release in organic solvents has also been systematically studied.

2. Experimental section

2.1. General

H_3**BTC** (1,3,5-benzenetricarboxylic acid; 95%), 1,3,5-tribromomethylbenzene (97%), imidazole (99%) and metal precursors were obtained from Sigma-Aldrich whereas iodine (99.5%) and solvents (analytical grade) were obtained from Alfa Aesar, Fisher Scientific and used without further purification. **TIB** was synthesized by following a reported procedure [17]. CHNS analyses were performed using elementar vario Micro-cube analyzer. IR spectra were recorded using a Perkin-Elmer GX FTIR spectrometer by the KBr pellet method. For each IR spectra 10 scans were recorded at 4 cm^{-1} resolution. ^{1}H NMR spectra for the ligand **TIB** was recorded using Bruker AX 500 spectrometer (500 MHz at temperature 25 °C and was calibrated with respect to internal reference TMS. TGA analysis was carried out using Mettler Toledo Star SW 8.10. X-ray powder diffraction data were collected using a PANalytical Empyrean (PIXcel 3D detector) system with CuKα radiation. Single crystal structural analyses were performed using Bruker SMART APEX (CCD) diffractometer. Solid state UV–vis spectra were recorded using Shimadzu UV-3101PC spectrometer and $BaSO_4$ as a reference. Luminescence spectra were recorded at room temperature utilizing Fluorolog Horiba Jobin Yvon spectrophotometer.



Scheme 1. Molecular structures of the tripodal ligands utilized to prepare **1** and **2**.

2.2. Synthesis of $\{[Cd_3(\mathbf{BTC})_2(\mathbf{TIB})_2(H_2O)_4].(H_2O)_2\}_n$ (1)

H_3**BTC** (75 mg), **TIB** (75 mg) and $Cd(NO_3)_2 \cdot 4\,H_2O$ (150 mg) were dispersed in mixture of 3 mL 1,4-dioxane, 2 mL tetrahydrofuran and 2 mL water when sealed in a Teflon-lined autoclave (15 mL capacity), which was then heated at 408 K for 50 h. After slow cooling to the room temperature colorless single crystal blocks, suitable for single crystal X-ray analysis were obtained with good yield and homogeneity (Yield ~67%). Elemental analysis (%), calculated for $C_{54}H_{54}Cd_3N_{12}O_{18}$: C, 43.35; H, 3.64; N, 11.23; found: C, 40.10; H, 2.677; N, 7.92. IR cm^{-1} (KBr): 3446 (br), 2921 (w), 2366 (m), 1631 (s), 1545 (w), 1444 (w), 1372 (m), 1235 (w), 1098 (m), 1026 (w), 933 (w), 846 (w), 724 (m), 644 (w), 529 (w), 428 (w).

2.3. Synthesis of $\{[Zn_3(\mathbf{BTC})_2(\mathbf{TIB})_2].(H_2O)_6\}_n$ (2)

H_3**BTC** (75 mg), **TIB** (75 mg) and $Zn(NO_3)_2 \cdot 6\,H_2O$ (150 mg) were dispersed in mixture of each 3 mL of 1,4-dioxane, tetrahydrofuran and water when sealed in a Teflon-lined autoclave (23 mL capacity), which was then heated at 408 K for 50 h. After slow cooling to the room temperature white single crystal blocks, suitable for single crystal X-ray analysis were obtained with good yield and homogeneity (Yield ~57%). Elemental analysis (%), Calculated for $C_{54}H_{54}Zn_3N_{12}O_{18}$: C, 47.86; H, 4.02; N, 12.40; found: C, 41.11; H, 4.14; N, 11.07. IR cm^{-1} (KBr): 3431 (br), 3133 (m), 2932 (w), 2367 (m), 1620 (s), 1575 (w), 1439 (m), 1361 (s), 1238 (w), 1101 (s), 1030 (w), 952 (m), 855 (w), 738 (s), 660(m), 458 (w).

2.4. X-ray crystallography

Summary of crystallographic data and details of data collection for **1** and **2** are shown in Table 1 and Table S1. Single crystals with suitable dimensions were chosen under an optical microscope after immersing in paratone oil and mounted on a glass fiber for data collection. Intensity data for both crystals were collected using MoKα (λ=0.71073 Å) radiation using a Bruker SMART APEX diffractometer equipped with CCD area detector at 150 K. The data integration and reduction were processed with SAINT software [18]. An empirical absorption correction was applied to the collected reflections with SADABS [19]. Structures were solved by direct methods using SHELXTL and were refined on F^2 by the full-matrix least-squares method using the program SHELXL-97 [20,21]. All non-hydrogen atoms were refined anisotropically till convergence was reached. Hydrogen atoms attached to the organic moieties present in both CPs are either located from the difference Fourier map or fixed stereochemically. After refining the coordination polymeric networks lattice water molecules were located and anisotropically refined. Hydrogen atoms of the water molecules were located from the difference Fourier map and kept fixed using DFIX card. The void volume in the crystal structure was calculated using the PLATON [22]. Topological analysis of compounds was performed by TOPOS software [23].

2.5. Procedure for determination of sensing selectivity

The fluorescent CPs **1** and **2** were tested to sense vapors of small molecules with or without nitro functionality. For selectivity