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A zeolitic Cd(II) boron imidazolate framework with sensing and catalytic properties

Liyang Liu [a,b], Tian Wen [b,*], Shumei Chen [a,b,*], Jian Zhang [b]

[a] College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China
[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

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ABSTRACT

A zeolitic Cd(II)-boron-imidazolate-framework (**BIF-51**) with **ABW** topology has been successfully synthesized by using pre-synthesized $B(im)_4^-$ ligands (im=imidazole) and $[Cd(CH_3COO)]^-$ building units. Ag nanoparticles (NPs) were loaded in **BIF-51** by the pore confinement effect of BIFs. Sensing property of nitrobenzene on **BIF-51** and catalytic property of 4-nitrophenol (4-NP) on **Ag@BIF-51** were also investigated.

1. Introduction

In recent years, functional porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) continue to attract dramatic interest due to their fascinating structures and potential applications in the areas of gas storage, separation, sensing, biomimicry and catalysis [1–5]. To mimic zeolitic SiO_2 and $AlPO_4$ frameworks, zeolitic imidazolate frameworks (ZIFs) and boron imidazolate frameworks (BIFs) have been developed to be special sub-classes of MOFs [6–8]. In BIFs system, tetrahedral cations (e.g. Li^+ and Cu^+) were often chosen to link variety pre-synthesized boron imidazolate ligands, leading to extended frameworks, just like $AlPO_4$ [8a,b]. However, most of these zeolitic frameworks are neutral. What an important factor to construct this kind of neutral networks is to design charge balancing tetrahedral metal center [8c,d].

In our previous works [8d], we have successfully synthesized two zeolitic BIFs (**BIF-22** and **BIF-23**) by using octahedral divalent metal center. The strategy to form the tetrahedral metal node is reducing six-coordinate to four-connectivity by using acetate as a chelating ligand. Thus, a +1 charged $[M^{2+}(ac)^-]^+$ (M=transition metal; ac=acetate) unit matching to a −1 charged $B(im)_4^-$ unit assembled to 4-connected zeolitic frameworks (Scheme 1). However, this kind of BIFs are still rarely reported. It is necessary for us to synthesize more BIFs through this method.

Herein, we report an **ABW**-type BIF, $[Cd(ac)B(im)_4]$•DMF (**BIF-51**; DMF=N,N-dimethylformamide), which possesses promising luminescent emission and can be a sensor of nitrobenzene.

2. Experimental section

All reagents were purchased commercially and used without further purification. All Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ=1.54056 Å) with a step size of 0.05°. TEM measurements were performed by using a JEOL-2010 TEM equipped with the energy dispersive X-ray spectrum operated at 200 kV. Diffraction data were collected by using a Mercury CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) at 293 K. A summary of crystal data and refinement results are provided in Table 1. The structure was solved by direct methods and refined by the full-matrix least-squares technique by using Olex2 1.1. X-ray photoelectron spectra (XPS) were acquired with a PHI Quantum 2000 XPS system with a monochromatic Al Kasource and a charge neutralizer. Thermal stability study were carried out on a NETSCHZ STA-449 C thermoanalyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. The UV–vis absorption spectra were measured at room temperature with a Perkin-Elmer Lambda 950 UV–vis spectrophotometer. Luminescence spectra were investigated by using Edinbrgh Analytical Instruments M300 Monochromator.

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* Corresponding authors.
E-mail addresses: twen@fjirsm.ac.cn (T. Wen), csm@fzu.edu.cn (S. Chen).

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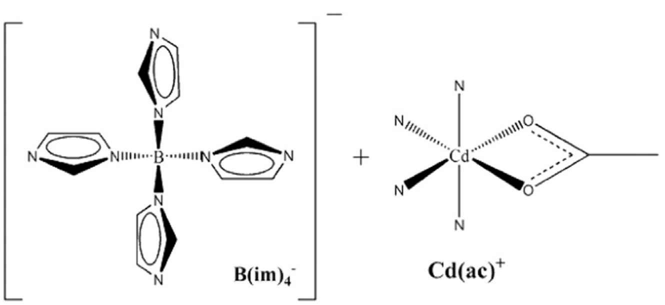

Scheme 1. The tetrahedral building unit: B(im)$_4^-$ and Cd(ac)$^+$.

Table 1
Crystal data and refinement results of **BIF-51**.

Data	**BIF-51**
Empirical formula	$C_{17}H_{22}BCdN_9O_3$
Formula weight	523.65
Temperature (K)	293
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.3944(7)
b (Å)	17.7981(12)
c (Å)	16.6732(15)
β (deg)	112.949(6)
V (Å^3)	2293.9(3)
Z	4
Crystal size(mm^3)	0.10 × 0.15 × 0.20
F (000)	1056
D_c (g cm^{-3})	1.516
μ (mm^{-1})	0.989
Reflections collected	17669
Independent reflections	5229
R_{int}	0.0435
Goodness-of-fit on F^2	1.073
R_1, wR_2 [$I > 2\sigma(I)$]	0.0551, 0.1242
R_1, wR_2 [all data]	0.0774, 0.1380

2.1. Synthesis

2.1.1. Synthesis of [Cd(CH_3COO)B(im)$_4$](**BIF-51**)

A mixture of Cd(CH_3COO)$_2\cdot 2H_2O$ (0.0236 g), KB(im)$_4$ (0.0367 g), DMF 3 ml and tert-butanol 1 ml were sealed in a 20 ml vial and stirred for 15 min. Then heated to 100 °C for 1 day. After cooling to room-temperature, pale yellow crystals were obtained in 60% yield. The phase purity of **BIF-51** has been confirmed by powder X-ray diffraction (PXRD) (Fig. 4e), and the thermogravimetric analysis exhibits its degree of stability (Fig. S1).

2.2. Load Ag NPs in *BIF-51*

Fresh **BIF-51** (96 mg) were immersed in ready-prepared KBH(bim)$_3$ (bim=benzimidazole) DMF solution (3 ml, 20 mg/ml). Then the DMF liquor of $AgNO_3$ (3 ml, 20 mg/ml) was added. During two hours stirring and twenty hours standing, the colorless crystal changed to brown gradually because of the loading of Ag NPs in **BIF-51** (Fig. S2). TEM images and X-ray photoelectron spectra (XPS) of the resulting sample were investigated to prove the formation of Ag NPs. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) demonstrated that the weight percentage of Ag NPs in **BIF-51** is 2.73%. In addition, different concentration of $AgNO_3$ (10 mg/ml, 30 mg/ml) were also tried to prepare **Ag@BIF-51**. Furthermore, higher concentration prepared sample with higher catalytic efficiency was attested by the catalysis experiment (Fig. S3).

2.3. Catalytic reaction

The reduction of 4-NP by KBH_4 was chosen as a model reaction to measure the catalytic activity of the catalysts. Typically, the reaction was conducted under room temperature with string. About 5 mg of sample (**Ag@BIF-51**) and 200 mg of KBH_4 was added into a liquor solution of 4-NP (15 mL, 250 mg/L), respectively. UV–vis spectra were recorded at short intervals to monitor the progress of the reaction. The absorption spectra of the solution were measured in the range of 275–525 nm.

3. Results and discussion

3.1. Description of crystal structures

The structure of **BIF-51** was characterized by X-ray single-crystal diffraction determination and its space group was also confirmed as monoclinic $P2_1/c$. In the structure of **BIF-51**, each Cd^{2+} center is chelated by an acetate to construct as a distorted tetrahedral [Cd(ac)]$^+$ unit. The residue coordination sites of Cd^{2+} are occupied by four different boron imidazolate N-donors, which formed a four-connected node (Fig. 1a). The average length of B–N, Cd–N and Cd–O bond are 1.542 Å, 2.326 Å and 2.364 Å, respectively. Each tetrahedral B(im)$_4^-$ ligand links four Cd^{2+} centers, the distances of Cd…B are ranging from 5.834 Å to 5.909 Å and the Cd-im-B angles are in the range of 140.149(246)–145.515 (300)°. Interestingly, the alternately link of [Cd(ac)]$^+$ units and B(im)$_4^-$ ligands create a three-dimensional (3D) open framework which features zeotype **ABW** topology (Fig. 1b and c). Along the a axis, there are two kinds of channels. The dimension of the large channel is 5.4 × 11.6 Å, and filled with DMF solvent molecules. The free volume of **BIF-51** which removed guest molecules is calculated by PLATON to be 29.1% of its total volume [9].

3.2. Photoluminescent properties

The photoluminescent properties of **BIF-51** in the solid state were investigated at room temperature. Upon irradiation of ultraviolet light at 330 nm, **BIF-51** exhibits a strong emission with maximum wavelength at 374 nm. To better understand its photoluminescence, a fluorogram comparison of KB(im)$_4$ ligand [10] and **BIF-51** was made (Fig. 2). The emission band of the coordination complexes could be assigned to the intraligand charge transfer of the ligands because of the similar emission spectra between **BIF-51** and KB(im)$_4$ [11].

Inspired by our previous work [12], coordination polymers based on d^{10} metal ion may processes potential application on sensing of nitrobenzene. Thus, sensing property of **BIF-51** was explored by using solid-state sample at room temperature. Luckily, significant fluorescence quenching could be observed in the situation of immersing them into nitrobenzene. As nitrobenzene vapor volatilize on end, the intensity of fluorescence increased gradually. By the time nitrobenzene was total removed, the intensity returned to the original (Fig. 3a). Nevertheless, no obvious luminescence change occurred if we place **BIF-51** in some other common solvents, such as methanol, ethanol, acetone, etc. (Fig. 3b). The distinguished fluorescence quenching response of **BIF-51** to nitrobenzene might be attributed to the electrostatic interactions and the electron deficiency [13]. On the basis of the exciting results, **BIF-51** could be regarded as a luminescent probe for testing nitrobenzene.

3.3. *Ag@BIF-51* and its catalytic property

In our previous study for **Au-Pd@BIF-39-Cd** [14], we propose a