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Structures and photocatalytic activities of metal-organic frameworks derived from rigid aromatic dicarboxylate acids and flexible imidazole-based linkers

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ABSTRACT

Three metal-organic frameworks based on the connectivity co-effect between rigid aromatic dicarboxylic acids and flexible linear linkers have been synthesized and characterized. $[Cd(3-NO_2-bdc)(bbi)]_n$ (1) and $[Co(3-NO_2-bdc)(bbi)]_n$ (2) $(3-NO_2-bdcH_2 = 3$ -nitro-1,2-benzenedicarboxylic acid, bbi = 1,1'-(1,4-butanediyl)bis (imidazole)) are isostructural, which exhibit two-dimensional (2D) layer frameworks; $[Co(3,5-pdc)(bbi)]_2H_2O]_n$ (3) $(3,5-pdcH_2 = pyridine-3,5$ -dicarboxylic acid) has 2D 6-connected network with a Schäfli symbol of (3^{44}^{653}) . In addition, compounds 1 and 2 exhibit good photocatalytic activities under visible irradiation, and their different photocatalytic activities have also been analyzed based on the diffuse-reflectance UV/Vis spectra.

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Metal-organic frameworks (MOFs) are a relatively new class of crystalline coordination polymers, which have potential in a myriad of applications, including gas storage, chemical separation, heterogeneous catalysis and optical, electronic, magnetic materials [1–15]. Nowadays, much effort has also been devoted to developing new photocatalytic materials based on metal-organic frameworks, which is motivated largely by a demand for solving pollution problems in view of their potential applications in the green degradation of organic pollutants [16–23].

In this regard, our recent study has been mainly focused on the synthesis and characterization of new MOFs from accessible raw materials, which show rich structural features and encouraging photocatalytic properties [24,25]. As an extension of our work, herein, 3-nitro-1,2-benzenedicarboxylic acid (3-NO₂-bdcH₂) or pyridine-3,5-dicarboxylic acid (3,5-pdcH₂) were chosen as the starting materials together with divalent metal ions, with the aid of flexible bidentate linker 1,1'-(1,4-butanediyl)bis(imidazole) (bbi). Utilizing hydrothermal technique, three new MOFs, [Cd(3-NO₂-bdc)(bbi)]_n (1), [Co(3-NO₂-bdc)(bbi)]_n (2) and [Co(3,5-pdc)(bbi) 2H₂O]_n (3) have been obtained [26,27]. In addition, photocatalytic activities of compounds 1 and 2 under visible irradiation were studied, and their different activities have been analyzed based on the diffuse-reflectance UV/Vis spectra.

Compound 1 crystallizes in the orthorhombic Pbca space group. As shown in Fig. 1a, Cd1(II) is coordinated to three carboxylate oxygen atoms from two inequivalent $3-NO_2-bdc^{2-}$ and two different bbi nitrogen atoms. Furthermore, the Cd1-O2 distance is 2.680 Å, suggesting a non-negligible interaction with the uncoordinated carboxylate oxygen atom, which can be described as a semi-chelating coordination mode [28]. Hence, the coordination environment of Cd1 atom may be also regarded as a distorted trigonal prismatic coordination sphere. The average Cd-O and Cd-N distances are 2.335 and 2.231 Å, respectively, both of which are in the normal range. Each fully deprotonated 3-NO₂-bdc²⁻ ligand coordinates to two Cd atoms, with two carboxylate groups adopting $\mu^1 - \eta^1$: η^1 and $\mu^1 - \eta^1$: η^0 modes. The $3-NO_2$ -bdc²⁻ ligand thus links Cd ions to form a 1D zigzag chain along *b*-axis, as illustrated in Fig. S1. The 1D chain is further stacked with bidentate bbi spacers, thus giving rise to the formation of a 2D layer framework (Fig. 1b). In 1, the bbi spacers adopt cis conformation with imidazole groups twisted by 96°, which establish physical bridge between Cd atoms, imposing Cd···Cd separations of 8.875 Å. It is worth mentioning that compound **1** is a rare MOF in which bbi ligands can adopt cis geometry; in the case of the previously reported coordination framework based on bbi, most bbi spacers exhibit trans geometry [29-31].

The weaker nonclassical hydrogen bonds were observed between C–H moieties and the coordinated carboxylate oxygen atoms (O1, O3, O4) as well as the uncoordinated carboxylate oxygen atom (O2), with the distance varying from 2.996(4) to 3.280(4)Å. The extensive hydrogen bonds may contribute for the stability of the MOF.

Similar cell parameters with the same space group Pbca and the results of crystallographic analysis confirm that **1** and **2** are iso-structural. In compound **2**, the Co(II) ion is in a slightly distorted

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Fig. 1. (a) Coordination environments of Cd atoms with hydrogen atoms omitted for clarity; (b) the 2D layer structure of **1**.

tetrahedral environment, coordinated by two carboxylate oxygen atoms from two different 3-NO₂-bdc²⁻ and two different bbi nitrogen atoms (Fig. S1). The average Co–O and Co–N distances are 2.001 and 2.030 Å, respectively. Each fully deprotonated 3-NO₂-bdc² ligand coordinates to two Co atoms, with both carboxylate groups adopting μ^1 - η^1 : η^0 modes. The 3-NO₂-bdc²⁻ ligand connects Co ions to form a 1D chain, which is further stacked with *cis* bbi bridges, resulting in a 2D layer framework similar to **1**(Fig. S2). The resulting 2D structure is cross-linked by hydrogen-bond interactions between C-H groups from bbi and carboxylate oxygen atoms, thus leading to the formation of a 3D supramolecular architecture.

Compound **3** crystallizes in the monoclinic $P2_1/n$ space group. As displayed in Fig. 2a, the Co(II) metal center in a distorted trigonal bipyramidal coordination sphere, which is defined by two oxygen donors and one nitrogen atom from three distinct 3,5-pdc²⁻ ligands in the equatorial positions while axial positions are furnished by two nitrogen donors from two individual bbi ligands. The average Co-O and Co-N distances are 2.077 and 2.125 Å; both are somewhat longer to those seen in 2, which is consistent with the fact that bond lengths in a tetrahedral geometry are generally shorter than those in other geometries. Each fully deprotonated 3,5-pdc²⁻ anions act as μ_3 -bridge linking three Co centers via two unidentate carboxylate groups and one nitrogen moiety, leading to a 2D porous layer (Fig. S3). In addition, it should be noted that bbi spacers establish physical bridge between Co atoms with Co···Co separations of 7.491 Å, resulting in the formation of a complicated 2D structure with channels along aand *b*- axes, which are occupied by water molecules (Fig. 2b). The effective free volume of 3 was calculated by PLATON analysis as 13.9% of the crystal volume (268.8 out of the 1933.6 Å³ unit cell volume), where water molecules reside as labile ligands [32].

A better insight into the nature of this framework can be acquired by using topological analysis. Each Co node is coordinated by five bridging ligands but linked to six nearest neighbors, ligands 3,5-pdc^{2–} and bbi can be simplified to be connectors; therefore, the combination of nodes and connectors suggests a 6-connected network with a Schäfli symbol of $(3^{4}4^{6}5^{3})$ (Fig. 2c).

Herein, we selected an anionic organic dye X3B (Scheme 1), as a model pollutant in aqueous media to evaluate the photocatalytic effectiveness of compounds 1, 2 and 3, considering that X3B is commonly used as a representative of widespread organic dyes that are very difficult to decompose in waste streams under UV or visiblelight irradiation [33,34]. The photodegradation experiment under visible light irradiation was carried out after the dark adsorption equilibrium achieved according to the previous reported literature [24,25]. In addition, control experiments on the photodegradation of X3B have been carried out. The distinctly shortened degradation time compared with the control experiments indicates that both catalyst 1 and **2** are active for the decomposition of X3B in the presence of visible light irradiation. When pseudo-first-order kinetics was fitted with the experimental data, for **1** and **2**, the rate constant under visible light irradiation was found to be 0.0875 and 0.1137 h^{-1} , respectively (Figs. 3 and 4, Figs.S4 and S5). Obviously, the X3B is degraded about 60 and 80% in the presence of 1 and 2 after 9 h irradiation, which is comparable with those of the reported uranyl-organic assembly compounds [17]. In addition, the number of moles for degradated X3B per gram metal atom in the presence of **1** and **2** is 6.64×10^{-6} and 16.61×10^{-6} mol/g, respectively (Fig. S6).

However, the decomposition rate of X3B under visible light conditions for compound **3** is much slower than those of compounds **1** and **2**, as depicted in Fig. S7. Therefore, only the photoactivities of compounds **1** and **2** were studied in detail.

In order to study the photocatalytic reaction mechanism, the photodegradation of X3B was carried out in the presence of *tert*-butyl alcohol (TBA), a widely used ·OH scavenger [35,36]. The presence of TBA greatly depressed the photodegradation rate of X3B on catalyst 1 (Fig. 3, curve b) and 2 (Fig. 4, curve b), that is, the relevant rate constant for **1** and **2** was sharply individually decreased from 0.0875 to 0.0333 h^{-1} and from 0.1137 to 0.0340 h^{-1} in the presence of TBA under visible light. The \cdot OH quenching experiment result suggests that the photodegradation of X3B on catalyst **1** and **2** is predominately through attack of ·OH radicals, which is similar to the photocatalytic reaction mechanism reported in our previous study. To exclude the possibility that the photocatalytic properties of **1** and **2** result from dissolved molecular or oligomeric fragments of solid catalysis in the photocatalytic process, another control experiments were conducted. The reaction suspensions after 9 h of irradiation were filtered to remove the solid catalyst particles, and fresh X3B was added into the respective filtrates for catalysis testing. Without solid catalyst in the reaction system, the fresh X3B was not degraded during another 9 h of irradiation, which indicates that the solution contains no photocatalytically active fragments. Clearly the photocatalytic activities arise solely from the solid 1 and 2. In addition, the stability of compounds 1 and 2 was monitored using PXRD during the course of photocatalytic reactions (Figs. S8 and S9). After photocatalysis, compounds 1 and 2 display a powder XRD pattern nearly identical to that of the original compounds, implying the stability towards photocatalysis for the complexes is good.

Although **1** and **2** are isostructural, different central metal ions between **1** and **2** may lead to distinct bandgap size, which may give rise to the discrepancy in their photocatalytic activity. The diffusereflectance UV/Vis spectra reveal that solid **1** and **2** have different absorption features (Fig. 5). The main UV absorption bands are around 383(347), 391 (346) nm for **1** and **2**, respectively, which can be assigned to ligand-to-metal charge transfer (LMCT). To obtain the precise values of band gap from the absorption edges, the point of inflection in the first derivatives of the absorption spectrum was used.



Fig. 2. (a) Coordination environments of Co atoms with hydrogen atoms omitted for clarity; (b) the 2D porous structure of 3; (c) The topology structure of 3.

1.0

0.9

The values of the band gap obtained from corresponding transitions are 3.23 and 3.17 eV for **1** and **2**, respectively. In the case of **2**, one clear additional peak was observed at 646 nm, which probably originate from the d-d spin -allowed transition of the d^7 (Co²⁺) ion. Clearly, the



0.8 C/C₀ 0.7 0.6 0.5 0.4 ż 3 Ò 4 5 8 1 6 7 Time/h

Scheme 1. Molecular structure of X3B.

Fig. 3. Control experiments on the photodegradation of X3B. (a) X3B/compound 1/dark; (b) X3B/compound 1/tert-butyl alcohol/visible light; (c) X3B/compound 1/visible light.

c

ģ



Fig. 4. Control experiments on the photodegradation of X3B. (a) X3B/compound 2/dark; (b) X3B/compound 2/tert-butyl alcohol/visible light; (c) X3B/compound 2/visible light.

band gaps of **1** and **2** follow the order **1**>**2** and the degradation rate of X3B follow the reverse order.

As shown in Figs. S10–S12, compounds **1** and **2** exhibit similar thermal decomposition behavior, which are respectively stable up to 240 and 269 °C where the organic groups start to decompose, and consecutive decompositions suggest the total destruction of the framework, then residue of CdO (obsd 27.17%, calcd 25.09%) for **1** and CoO (obsd 17.67%, calcd 16.35%) for **2** remained. For **3**, the weight loss of 8.11% below 85 °C (calcd 7.99%) corresponds to the loss of two free water molecules per formula. A plateau region is observed for **3** from 188 to 317 °C and consecutive decompositions suggest the total destruction of the framework.

The solid-state excitation emission spectra of **1** have been studied at room temperature (Fig. S13). The strongest emission peak for the free ligand 3-NO₂-bdcH₂ is at 420 nm with the excitation peak at 235 nm, which is attributed to the π^* -*n* transitions [37]. The strongest excitation peaks for **1** are at 359 nm and emission spectra mainly show strong peaks at 388 nm. Therefore, it is reasonable to ascribe the luminescence of compound **1** to be an intraligand transition.

In summary, three metal-organic frameworks based on the connectivity co-effect between rigid $3-NO_2$ -bdcH₂ (or 3,5-pdcH₂) and flexible linear ligands bbi have been synthesized and characterized. **1** and **2** are isostructural, which exhibit two-dimensional (2D) layer framework; compound **3** has 2D 6-connected network with a Schäfli symbol of ($3^{4}4^{6}5^{3}$). In addition, compounds **1** and **2** exhibit good photocatalytic activities under visible irradiation, and their



Fig. 5. UV/Vis diffuse-reflectance spectra of compounds 1 and 2 with BaSO₄ as background.

different photocatalytic activities have also been analyzed based on the diffuse-reflectance UV/Vis spectra.

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Appendix A. Supplementary material

Crystallographic data (CIF file) have been deposited at the Cambridge Crystallographic Data Center, CCDC Nos. 765739 for 1, 765738 (for 2), and 765737 (for 3). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *viawww*. ccdc.cam.ac.uk/ data_request/cif. The structure analysis of compound 2, control experiments on the photodegradation of X3B for compound 3, TG curves, fluorescent emission spectra of complex 1 in solid state at room temperature, photocatalytic experiments details, the pseudo-first-order kinetics fitted with the experimental data, and time conversion plots of X3B disappearance per gram metal atom in the presence of 1 and 2 are shown in the supporting information. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.05.017.

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1244 m, 1132w, 1115 s, 1102 s, 1088 m, 1067w, 1032w, 951 m, 926 m, 878 m, 858w, 832 m, 785 m, 761 m, 731 m, 715 m, 696 m, 661 s, 633w, 594w, 574w, 475 m, 435w. Synthesis of [Co(3,5-pdc)(bi) 2H₂O]_n (**3**). Compound **3** was prepared in the same way as **2**, using 3,5-pdcH₂ (0.2 mmol) instead of 3-NO₂-bdcH₂ at 140 °C for 3 days. Purple crystals of **3** were obtained (yield: 42% based on Co). IR (KBr) cm⁻¹: 3426 s, 3143 m, 1628 s, 1606 s, 1567 s, 1525 m, 1449 m, 1435 m, 1412 s, 1373 s, 1300w, 1283 m, 1229 m, 1157w, 1130 m, 1105 m, 1091 m, 1080 m, 1052w, 1031 m, 943 m, 860 m, 832 m, 773 m, 738 s, 697w. 664 m, 626w. 605w. 521w. 455w. 430w.

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