

Short communication

New metal–organic frameworks constructed by 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene and dicarboxylic ligands: Enhanced photocatalytic effect



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ABSTRACT

A series of new metal–organic frameworks (MOFs) composed of a transition-metal organic acid salt and 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene (3-bpdh) was prepared via diffusion in a H₂O–MeOH solvent system. The results illustrated that MOFs self-assembly should be achieved by metal-ion potential and building blocks. The loading of MOF microcrystals with titanium dioxide resulted in the composite photocatalyst TiO₂@ZnMOF, which exhibited excellent photodegradation (64%) of the dye methyl blue. Importantly, this approach provides an innovative way of enhancing the photocatalytic effect of MOFs with potential applications as a catalyst support.

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Metal–organic frameworks (MOFs) are compounds consisting of metal ions linked together by organic bridging ligands. They represent a new field between molecular coordination chemistry and material science and have attracted extensive attention in recent years. Research on MOFs is expanding rapidly because of their novel structural topologies and promising properties related to gas storage [1–4], gas separation [5–8], catalysis [9–12], chemical sensing [13–14], magnetism [15–16], ion exchange [17], fluorescence, and ferroelectricity [18]. The strategies used to synthesize MOFs offer many possibilities for their structural design, enabling the synthesis of complex structures with extensive potential functionalities. The properties of MOFs can be tailored by variation of both inorganic metal centers and organic linkers [19]. Thus far, the most widely studied MOFs are based on pure carboxylate ligands and are constructed from a certain number of distinct building blocks. Apart from carboxylate ligands, those with nitrogen-containing heterocycles such as pyridines, pyrazoles, and tetrazoles have been reported to exhibit promising coordination chemistry for the synthesis of MOFs when combined with carboxylate groups [20–23]. The literature contains numerous reports of MOFs prepared with different metal ions and pyridine ligands [24–30]. As demonstrated in these studies, these long, conjugated, rigid ligands are capable of coordinating transition-metal centers with their terminal pyridyl nitrogen donors to generate

novel MOFs. These building blocks with relative orientations of the nitrogen donors could lead to the construction of a series of new MOFs.

Nanotechnology emerged as a new field in the 1980s and has since been a subject of extensive research interest. Self-assembly is the autonomous organization of components into patterns or structures without human intervention. In the MOF synthesis process, the molecules connect with each other through noncovalent bonds into a structurally stable molecular aggregate. Whitesides and Grzybowski [31] have speculated that such self-assembly will be an essential part of nanotechnology. The application of nanotechnology to the synthesis of MOFs enables the preparation of nanocrystalline materials with superior properties. Liu and Tang [32] have synthesized multifunctional nanoparticle@MOFs, that are core–shell nanostructures in which nanoparticles serve as the core and MOFs as the shell. Dhakshinamoorthy and Garcia's review [33] on catalysis by metal nanoparticles embedded in MOFs was organized according to the embedded metal and included Pd, Au, Ru, Cu, Pt, Ni, and Ag. In their review, they systematically discussed MOF synthesis methodologies and some recent reports related to M NPs/MOFs (M = Pd, Au, Ru, Cu, Pt, Ni, or Ag) catalysts that exhibit excellent performance for various reactions.

In this paper, we describe our isolation of four new two-dimensional (2D) framework structures: Zn(3-bpdh)(HIA) (1Zn), Co(3-bpdh)(HIA) (2Co), Mn(3-bpdh)(HIA) (3Mn), and Zn(3-bpdh)(CHDC) (4Zn) (3-bpdh = 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene, HIA = 5-hydroxyisophthalic acid, CHDC = 1,4-cyclohexanedicarboxylic acid). We also successfully synthesized microcrystals of these four

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compounds and herein discuss the potential applications of these microparticles as the support for several photocatalysts.

The 1Zn crystals were synthesized in a test tube using the slow diffusion method. A mixture of HIA (54.6 mg, 0.3 mmol), NaOH (24 mg, 0.6 mmol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (89.2 mg, 0.3 mmol), and distilled water (10 mL) was stirred to obtain a Zn–HIA aqueous solution, which was subsequently transferred to a test tube. Then, a 4 mL MeOH solution containing 3-bpdh (71.4 mg, 0.3 mmol dissolved in 10 mL MeOH) was carefully layered on top of the Zn–HIA aqueous solution (4 mL) through a 1.5 mL buffer solution consisting of H_2O and MeOH in a volume ratio of 1:1 in the test tube. After one week, pale-yellow block crystals of $[\text{Zn}(\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_5)]_x$ (1Zn) (Fig. S3) suitable for single-crystal X-ray diffraction (XRD) analysis were obtained in the middle of the test tube. The synthesis procedures for the crystals of 2Co, 3Mn, and 4Zn were the same as that for 1Zn, except that $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (87.31 mg, 0.3 mmol) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (59.37 mg, 0.3 mmol) were used instead of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (89.2 mg, 0.3 mmol) to prepare 2Co and 3Mn, respectively, and CHDC (50.46 mg, 0.3 mmol) was added instead of the HIA (54.6 mg, 0.3 mmol) to prepare 4Zn.

Micro/nanocrystalline samples of 1Zn, 2Co, 3Mn, and 4Zn were synthesized under different conditions. The N-ligand 3-bpdh (71.4 mg, 0.3 mmol) was added to an alcohol (10 mL) solution in a 50 mL round-bottom flask to obtain a clear homogeneous solution. The Zn–HIA solution was then continuously injected into the magnetically stirred aforementioned N-ligand alcohol (10 mL) solution at room temperature using an injection pump. The yellow micro/nanocrystals were collected for characterization. The synthesis procedures for the micro/nanocrystals of 2Co, 3Mn, and 4Zn were the same as that for 1Zn. The loaded catalyst $\text{TiO}_2/\text{ZnMOF}$ was synthesized as follows: a certain amount of 1Zn microcrystals was dispersed evenly in 10 mL anhydrous ethanol; tetrabutyl titanate was then added to this mixture while stirring. After approximately 10 min, 10 mL deionized water was added dropwise. The suspension was subsequently placed into an autoclave at 100 °C for 24 h. The loaded crystals were collected by vacuum filtration after the suspension had cooled.

As shown in Fig. 1, 1Zn crystallizes in triclinic space group *P*-1 and exhibits a layered structure. Only one crystallographically independent Zn(II) is located in the six-member coordination environment. Four

oxygen donors provided by carboxyl groups of HIA coordinate with the zinc ions in equatorial positions and two nitrogen atoms from 3-bpdh link to the zinc atom in axial positions. In 1Zn, the Zn–O bond lengths range from 1.984 to 2.008 Å and the Zn–N bond lengths are 2.190 and 2.197 Å. The octahedron around the Zn(II) ion is highly distorted: the N1–Zn1–N4 angle is 177.28° while the O–Zn–O angles vary from 96.29° to 137.63°. Crystallographic data of this complex are listed in Table S1. The carboxyl groups of each HIA coordinate with the zinc ions in bridging- and chelating-mode fashions. The Zn^{2+} ions are chelated by one HIA and bridged by the other HIAs to produce double chains. The 3-bpdhs link to the Zn^{2+} ions of the double chains to construct a 2D double-layer network in the *b*–*c* plane. Interestingly, 2Co and 1Zn are isomorphous. For 2Co, the Co–O bond lengths range from 1.987 to 2.084 Å, the Co–N lengths are 2.166 and 2.176 Å, the N1–Co1–N4 angle is 177.07°, and the O–Co–O angles vary from 93.28° to 147.70°. The structure of 3Mn is very similar to that of 1Zn; it is also six-coordinated and located in the center of a deformed octahedron, where the nitrogen atoms on the pyridine ring of the ligand are coordinated with the ion and four oxygens from two carboxylic group of HIA are chelated with the metal ion. The Mn–O bond lengths range from 2.081(2) to 2.432(2) Å, the Mn–N lengths are 2.286 and 2.294 Å, the N1–Mn1–N4 angle is 174.96°, and the O–Mn–O angles vary from 92.01° to 146.84°. 4Zn is constructed by two Zn(II) ions, two 1,4-CHDC ligands, and one 3-bpdh ligand. Each Zn(II) ion is coordinated in its equatorial positions by four oxygen atoms from 1,4-CHDC ligands and in its axial positions by two nitrogen atoms provided by 3-bpdh. The carboxyl groups of 1,4-CHDC link Zn(II) ions in a bridging manner to form double strands. The 3-bpdh ligand coordinates to one Zn(II) ion as a bridging ligand from layer structures. The Zn–O bond lengths range from 2.0304 to 2.0437 Å, the Zn–Zn bond length is 2.8648 Å, and the Zn–N bond length is 2.046 Å. The O–Zn–O and O–Zn–N angles vary from 88.22 to 161.40° and from 95.34 to 103.22°, respectively, and the N–Zn–Zn angle is 170.42°. $\text{Zn} \cdots \text{Zn}$ metal interactions should occur in the complex because of the short distance among the Zn(II) ions. The MOFs self-assembly should be achieved by metal-ion potential and building-blocks. The outer electronic structures of ions, including those of Mn^{2+} , Co^{2+} , and Zn^{2+} , play an important role in the coordination

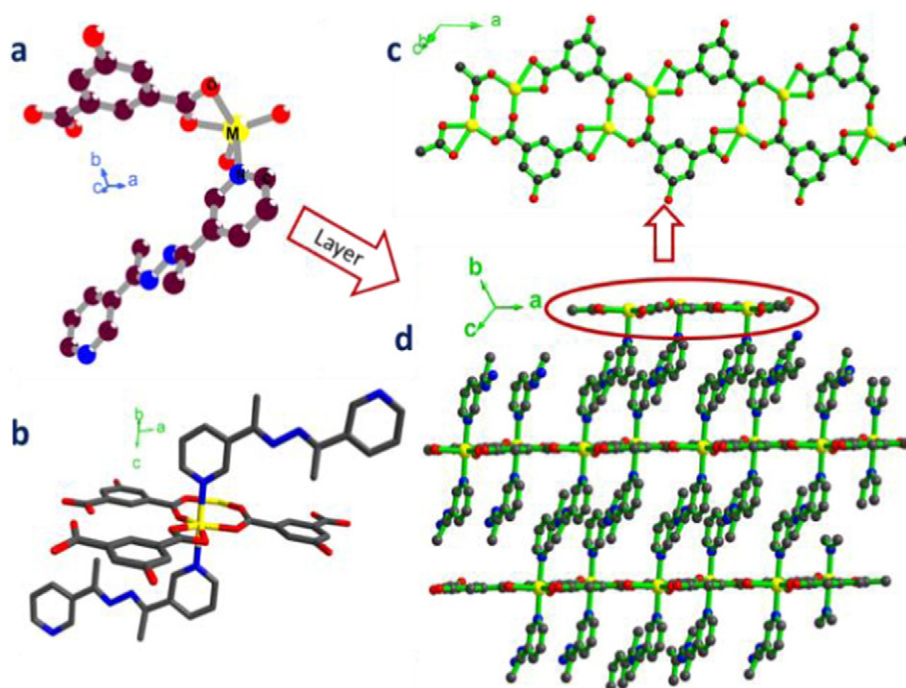


Fig. 1. The coordinate environment of complexes 1Zn, 2Co, and 3Mn. (a and b: ORTEP drawing of the complex, showing the metal M^{2+} ions coordination environment; c and d: perspective views of the complex showing the layer structure).

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