

# Visible-Light-Driven Photocatalysts of Metal–Organic Frameworks Derived from Multi-Carboxylic Acid and Imidazole-Based Spacer

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# **Supporting Information**

**ABSTRACT:** Five new metal-organic frameworks  $[M_{(btc)}_{0.5}(bimb)]_n$  (1) (M = Co (1), Ni (2), Cu (3), Zn (4)) and  $[Cd(btc)_{0.5}(bimb)_{0.5}]_n$  (5), were obtained by reactions of the conjugated 1,2,4,5-benzenetetracarboxylic acid (H<sub>4</sub>btec) and 4,4'-bis(1-imidazolyl)biphenyl (bimb) with corresponding metal salts under hydrothermal conditions, respectively. MOFs 1-5 show different structures and topologies: compounds 1 and 4 are isomorphic, which possess typical PtS 3D nets; compound 2, 3 and 5 exhibit 2D layer structure, NbO 3D network and (4,6)-connected 3D binodal topology, respectively. Notably, compounds 1, 2, and 5 represent the rare example of MOFs-based visible-light-driven photocatalysts and show good stability toward photocatalysis. Furthermore, compound 5 is photo-



catalytically more active than 1 and 2 because of the relatively narrower band gap calculated from LMCT transitions. In addition, the formation rate of  $\bullet$ OH radicals on compound  $5/H_2O$  interface via photocatalytic reactions is much higher than that of 1 and 2, implying that the formation rate of  $\bullet$ OH radicals during photocatalysis is in agreement with photocatalytic activity and the formation rate of  $\bullet$ OH radicals is an important factor influencing photocatalytic performance.

# INTRODUCTION

Photocatalysis is a "green" technology for the treatment of all kinds of contaminants, which has many advantages over other treatment methods, for instance, the use of the environmentally friendly oxidant  $O_{2}$ , the ambient temperature reaction condition, and oxidation of the organics compounds, even at low concentrations.<sup>1</sup> To date, TiO<sub>2</sub> has undoubtedly proven to be the most excellent photocatalyst for the oxidative decomposition of many organic compounds under UV irradiation. However, the relatively wide band gap limits further application of the material in the visible-light region ( $\lambda > 400$ nm).<sup>2</sup> In view of the efficient utilization of visible light, the largest proportion of the solar spectrum and artificial light sources, the development of a photocatalyst with high activity under a wide range of visible-light irradiation is indispensable. Currently, there are two ways to exploit the photocatalysts responsive to visible-light irradiation: the first involves the modification of TiO<sub>2</sub>; the second is the development of new materials. The former has been largely investigated by doping or ion-implanting methods to affect photocatalysis under visible-light irradiation.<sup>3</sup> On the other hand, there have only been a few reports on the development of new materials.<sup>4</sup>

The designed construction of metal-organic frameworks (MOFs) has been of intense interest, due to their intriguing

aesthetic structures and topological features,<sup>5</sup> as well as their promising applications in molecular magnetism, molecular sensor, heterogeneous catalysis, drug delivery, molecular sorption and so on.<sup>6-10</sup> Most recently, considerable attention has been paid to developing new photocatalytic materials based on MOFs. The advantages of MOFs as photocatalyst lie in the fact that the presence of organic linkers and transition metal centers, resulting in different ligand-to-metal charge-transfer (LMCT) transitions, makes MOFs versatile and potentially tunable photocatalysts. Furthermore, MOFs usually exhibit absorption bands in the visible region, which indicate MOFs may undergo photochemical processes and exhibit responses upon visible-light excitation. Chen and co-workers have reported the synthesis and characterization of new uraniumcontaining materials, which show rich structural features and encouraging photophysical properties.<sup>11</sup> Garcia and co-workers have studied MOF-5 as a semiconductor for photodegradation of phenol in aqueous solutions and water stable Zrbenzenedicarboxylate MOF as photocatalysts for hydrogen generation.<sup>12,13</sup> Preliminary ab initio results by Civalleri et al.

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suggest a significant decrease in the band gap of MOF-5 when changing the benzenedicarboxylic acid linker for larger organic molecules. Our recent study has been mainly focused on the syntheses and construction of new MOFs from accessible multicarboxylic acids and imidazole-based spacers.<sup>14</sup> A Cdcontaining MOF, a Gd-containing 3D supramolecular framework and two isostructural trinodal 4-connected 3D frameworks were found to be photocatalytically active, which prompted us to synthesize new water-insoluble MOFs with improved photocatalytic performance, especially visible-lightdriven MOF-based photocatalysts. As an extension of our work, in order to examine the photoactivity of the MOFs by varying the metal centers incorporated in the structures, the conjugated 1,2,4,5-benzenetetracarboxylic acid ( $H_4$ btec) and 4,4'-bis(1imidazolyl)biphenyl (bimb) were chosen as the starting materials together with different divalent metal ions. Utilizing hydrothermal technique, five new MOFs,  $[M(btec)_{0.5}(bimb)]_n$ (1) (M = Co (1), Ni (2), Cu (3), Zn (4)) and  $[Cd(btec)_{0.5}(bimb)_{0.5}]_n$  (5) have been obtained. Interestingly, compounds 1, 2, and 5 represent the rare examples of MOFs with high photocatalytic activity for dye degradation under visible light and good stability toward photocatalysis. Compared to the MOFs constructed from 1,4-benzenedicarboxylate acid and bimb in our previous work,14 the more delocalized  $\pi$  electrons of 1,2,4,5-benzenetetracarboxylic acid may facilitate the LMCT transitions and decrease electronic band gap of the MOFs 1-5, which can be useful for the development of visible-light-driven photocatalysts of MOFs.

#### EXPERIMENTAL SECTION

Materials and Measurements. Reagents and solvents employed were commercially available and used as received. Ligand binb was prepared by literature methods.<sup>15</sup> C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. IR spectra were recorded on KBr discs on a Bruker Vector 22 spectrophotometer in 4000-400 cm<sup>-1</sup> region. Thermogravimetric analyses were performed on a simultaneous SDT 2960 thermal analyzer under flowing N2 with a heating rate of 10 °C/min between ambient temperature and 700 °C. The powder XRD data were collected on a Siemens D5005 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) over the  $2\theta$  range of 5–50° at room temperature. Fluorescence measurements were recorded with a Hitachi 850 fluorescence spectrophotometer. The solid-state diffuse-reflectance UV/vis spectra for powder samples were recorded on a Perkin-Elmer Lambda 35 UV/ vis spectrometer equipped with an integrating sphere by using BaSO<sub>4</sub> as a white standard, whereas the UV-vis spectra for solution samples were obtained on a Shimadzu UV 2450 spectrometer. Photocatalytic experiments: the visible light source was a 500 W halogen lamp with UV cutoff filter (providing visible light with  $\lambda > 420$  nm) and the simulated solar light was a 350 W xenon lamp. A suspension of powdered catalyst (50 mg) in fresh aqueous solution of X3B (50 mL, 6  $\times$  10–6 mol/L) at pH 6 were first sonicated for 5 min, and shaken at a constant rate in the dark overnight (to establish an adsorption/ desorption equilibrium of X3B on the sample surface). At given irradiating intervals, a series of suspension of a certain volume were collected and filtered through a membrane filter (pore size, 0.45  $\mu$ m) to remove suspended catalyst particles, and the filtrate was analyzed on the UV-vis spectrometer. The concentration of the dye was measured by the absorbance at 510 nm, which directly relates to the structure change of its chromophore. The degradation of phenol was carried out by the similar measurements. The initial concentration of phenol was 430 µM, and the filtrate was analyzed on a Dionex P680 HPLC.

Synthesis of  $[Co(btec)_{0.5}(bimb)]_n$  (1). A mixture of Co- $(Ac)_2$ ·4H<sub>2</sub>O (24.9 mg, 0.10 mmol), H<sub>4</sub>btec (21.8 mg, 0.10 mmol), bimb (28.6 mg, 0.10 mmol), and NaOH (0.10 mol/L, 3 mL) was placed in a parr Teflon-lined stainless steel vessel (25 cm<sup>3</sup>), and then

the vessel was sealed and heated at 160 °C for 2 days. After the mixture was slowly cooled to room temperature, purple crystals of **1** were obtained (yield = 42% based on Co). Anal. Calcd For  $C_{23}H_{15}CoN_4O_4$ : C, 58.72; H, 3.22; N, 11.92%. Found: C, 58.75; H, 3.30; N, 11.94%. IR spectrum (cm<sup>-1</sup>): 3425w, 3157w, 2955s, 2925s, 2854s, 1604s, 1567s, 1517s, 1489 m, 1420s, 1374s, 1329 m, 1302s, 1253 m, 1127 m, 1104w, 1070s, 1007w, 961 m, 941w, 873 m, 853 m, 824 m, 765w, 729 m, 688w, 654 m, 626w, 600 m, 543w, 521w, 450w.

**Synthesis of** [Ni(btec)<sub>0.5</sub>(bimb)·(H<sub>2</sub>O)J<sub>n</sub> (2). A mixture of NiCl<sub>2</sub>·6H<sub>2</sub>O (23.8 mg, 0.10 mmol), H<sub>4</sub>btec (21.8 mg, 0.10 mmol), bimb (28.6 mg, 0.10 mmol), and NaOH (0.10 mol/L, 3 mL) was heated at 140 °C for 2 days in an analogous to procedure for 1. Pale green crystals of 2 were obtained (yield = 33% based on Ni). Anal. Calcd For  $C_{23}H_{17}N_4NiO_5$ : C, 56.67; H, 3.52; N, 11.50%. Found: C, 56.70; H, 3.56; N, 11.52%. IR spectrum (cm<sup>-1</sup>): 3421w, 3164w, 3075w, 2925 m, 2855w, 1608s, 1520s, 1483 m, 1413w, 1344s, 1314s, 1256 m, 1198 m, 1151w, 1116 m, 1066s, 962 m, 943 m, 868 m, 820s, 800 m, 696 m, 647 m, 616w, 582 m, 508 m, 462 m, 424w.

**Synthesis of [Cu(btec)**<sub>0.5</sub>(**bimb**)]<sub>n</sub> (**3**). A mixture of CuCl<sub>2</sub>·2H<sub>2</sub>O (17.0 mg, 0.10 mmol), H<sub>4</sub>btec (21.8 mg, 0.1 mmol), bimb (28.6 mg, 0.10 mmol), HCl (6 mol/L, a drop), and deionized water (3 mL) was heated at 160 °C for **2** days in an analogous to procedure for **1**. Purple crystals of **3** were obtained (yield = 19% based on Cu). Anal. Calcd For C<sub>23</sub>H<sub>15</sub>CuN<sub>4</sub>O<sub>4</sub>: C, 58.17; H, 3.18; N, 11.80%. Found: C, 58.15; H, 3.24; N, 11.82%. IR spectrum (cm<sup>-1</sup>): 3434w, 3132 m, 2925 m, 2854w, 1613s, 1586s, 1519s, 1417 m, 1376s, 1350 m, 1310 m, 1296 m, 1249 m, 1128 m, 1101w, 1070 m, 1005w, 962w, 949w, 871 m, 833 m, 822 m, 779w, 743 m, 732w, 688w, 667w, 658w, 615w, 581 m, 536w, 455w, 432w, 406w.

**Synthesis of**  $[Zn(btec)_{0.5}(bimb)]_n$  (4). The synthesis was similar to that described in 1 except using  $Zn(Ac)_2 \cdot 2H_2O$  (0.10 mmol) for 4 instead of  $Co(Ac)_2 \cdot 4H_2O$ . Colorless crystals of 4 were obtained (yield = 36% based on Zn). Anal. Calcd For  $C_{23}H_{15}N_4O_4Zn$ : C, 57.94; H, 3.17; N, 11.75%. Found: C, 57.90; H, 3.23; N, 11.77%. IR spectrum (cm<sup>-1</sup>): 3424 m, 3161w, 3119 m, 2924s, 2854 m, 1624s, 1559w, 1520s, 1488 m, 1368s, 1333s, 1302 m, 1273w, 1186w, 1131s, 1103w, 1066 m, 1004w, 960w, 942w, 850 m, 828w, 813s, 730 m, 685w, 651 m, 554w, 538 m, 465w, 419w.

**Synthesis of**  $[Cd(btec)_{0.5}(bimb)_{0.5}]_n$  (5). A mixture of Cd- $(NO_3)_2$ ·4H<sub>2</sub>O (30.8 mg, 0.10 mmol), H<sub>4</sub>btec (21.8 mg, 0.10 mmol), bimb (28.6 mg, 0.10 mmol), NaOH (0.10 mol/L, 1 mL), and deionized water (3 mL) was heated at 180 °C for 2 days analogous to the procedure for 1. Colorless crystals of 5 were obtained (yield = 33% based on Cd). Anal. Calcd For C<sub>14</sub>H<sub>8</sub>CdN<sub>2</sub>O<sub>4</sub>: C, 44.18; H, 2.12; N, 7.36%; found: C, 44.19; H, 2.14; N, 7.39%. IR spectrum (cm<sup>-1</sup>): 3440w, 3122w, 2923w, 2853w, 1594s, 1557s, 1515 m, 1488 m, 1413 m, 1368s, 1317 m, 1290w, 1262w, 1243w, 1125w, 1105w, 1066 m, 963w, 938w, 865w, 819 m, 768w, 745w, 661w, 584 m, 552w, 453w, 412w.

X-ray Crystallography. Suitable single crystals of 1–5 were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 293 K on a Bruker SMART APEX CCD-based diffractometer with graphite-monochromatic Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data reductions and absorption corrections were performed with the SAINT and SADABS software packages, respectively.<sup>16</sup> All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against  $F^2$  by the full-matrix least-squares technique.<sup>17,18</sup> Anisotropic displacement parameters were refined for all non-hydrogen atoms except for the disordered atoms. The relevant crystallographic data are presented in Table S1, while the selected bond lengths and angles are given in Table S2 in the Supporting Information.

#### RESULTS AND DISCUSSION

**Description of the Crystal Structures.** Similar cell parameters with the same space group *Pbcn* (Supporting Information Table S1), and the results of crystallographic analysis confirm that **1** and **4** are isostructural with each other



Figure 1. (a) Coordination environments of Co atoms with hydrogen atoms omitted for clarity. (b) 2D layer constructed from  $btec^{4-}$  and  $Co^{2+}$ . (c) The complicated 3D structure of 1. (d) A schematic representation of PtS network structure of 1: blue spheres represent Co1 nodes and black spheres represent  $btec^{4-}$  nodes.



Figure 2. (a) Coordination environments of Ni1 atoms with hydrogen atoms omitted for clarity. (b) The 2D layer structure of 2.

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Figure 3. (a) Coordination environments of Cu atoms with hydrogen atoms omitted for clarity. (b) The complicated 3D structure of 3. (c) A schematic representation of NbO network structure of 3: aqua spheres represent Cu nodes and purple spheres represent  $btec^{4-}$  nodes.

though they possess different metal centers; therefore, we analyze the structure of 1 in detail.

In compound 1, each Co(II) ion is in a distorted trigonal bipyramid geometry, coordinated by one carboxylate oxygen atom (O2) and two different bimb nitrogen atoms (N1 and N4#2) at the basal positions, as well as two carboxylate oxygen atoms (O1 and O4#) from two distinct btec<sup>4–</sup> anions at the apical positions (Figure 1a). In 1, each fully deprotonated btec<sup>4–</sup> moiety bridges four Co(II) centers, with two *para*-carboxylate groups in adopting monodentate coordination modes and the other two *para*-carboxylate groups in bidentate chelate fashions, producing 2D square grids (Figure 1b). Meanwhile, the 2D layers are connected via bimb spacers with Co…Co separations of 17.57 Å, resulting in the formation of a final complicated 3D structure (Figure 1c).

A better insight into the nature of this intricate framework can be acquired by using topological analysis. As depicted above, each  $Co^{2+}$  ion is connected by two btec<sup>4</sup> anions and two

bimb ligands in a tetrahedral geometry and can be regarded as a tetrahedral node; each  $btec^4$  anion is linked to four planar Co(II) ions and thus can be considered as a four-connected planar node; both  $btec^4$  and bimb bridges can be simplified to be connectors. In such a case, the framework structure of 1 can be represented to be a cooperite PtS net<sup>19</sup> with the Schläfli symbol of (4<sup>2</sup>8<sup>4</sup>), as displayed in Figure 1d.

In crystal of 4, although the most structural features are similar to those in 1, the distinct difference is that each Zn(II) ion is in a distorted tetrahedron sphere, surrounded by two carboxylate oxygen atoms from two separate btec<sup>4</sup> anions and two bimb nitrogen atoms, as illustrated in Supporting Information Figure S1.

As shown in Figure 2a, the Ni(II) center is in a slightly distorted octahedral environment, the equatorial plane of which comprises three carboxylate oxygen atoms (O1, O3, O3#1) from two inequivalent  $btec^{4-}$  anions and one terminal coordination water (O5); two nitrogen atoms(N1, N3) from



**Figure 4.** (a) Coordination environments of Cd atoms with hydrogen atoms omitted for clarity. (b) 2D layer constructed from  $btec^{4-}$  and  $Cd^{2+}$ . (c) The complicated 3D structure of 5. (d) A schematic representation of (4,6)-connected network structure of 5: green spheres represent Cd1 nodes, purple spheres represent  $btec^{4-}$  nodes and bimb bridges are shown as green bonds.

two different bimb ligands occupying the apical sites. Each btec<sup>4-</sup> anion coordinates to four Ni(II) atoms, with deprotonated carboxylate groups adopting  $\mu^2 - \eta^2 : \eta^0$  and monodentate coordination modes, generating a 1D infinite chain along *b* axis. The 1D chain is further stacked with bidentate bimb spacers acting as double bridges, with Ni…Ni distance of 17.97 Å, therefore, giving rise to the formation of a 2D layer (Figure 2b).

As displayed in Figure 3a, both Cu1 and Cu2 are situated on an inversion center with occupancy of 0.5. The Cu1 and Cu2 atoms are located in the similar distorted square sphere, coordinated to two carboxylate oxygen atoms from inequivalent btec<sup>4–</sup> ligands and two bimb nitrogen atoms. In addition, Cu1– O2 and Cu1–O2#1 distances are 2.936(3) Å, Cu2–O3 and Cu2–O3#2 separations of 2.743(3) Å, suggesting nonnegligible interactions between copper atoms and the carboxylate oxygen atoms, which can be described as a semichelating coordination mode.<sup>20</sup> Consequently, both Cu1 and Cu2 atoms may also be regarded as in a distorted octahedron environment.

In 3, each fully deprotonated  $btec^{4-}$  moiety bridges four Cu(II) centers, with two *para*-carboxylate groups in adopting monodentate coordination modes and the other two *para*-carboxylate groups in bidentate chelate fashions, giving rise to 2D square grids similar to that of compound 1 (Supporting Information Figure S2). Furthermore, the 2D layers are connected via bimb spacers with Cu…Cu separations of 17.57 Å, resulting in the formation of a complicated 3D structure (Figure 3b).

Thus, from the point of view of structural description of the compound, Cu1 and Cu2 were considered as equivalent nodes due to the same coordination configuration; in addition, both the Cu(II) atoms and the  $btec^{4-}$  anions may be considered equivalent to 4-connecting square-planar nodes in the ratio 1:1, precisely equivalent to the NbO network (Figure 3c).<sup>21</sup> Such a

net structure can be characterized by a short vertex symbol of  $(6^4 8^2)$ .

Though the ligands are the same as those in 1–4, the structure of 5 is significantly different from 1–4. Compound 5 is a most remarkable and unique three-dimensional coordination polymer. As shown in Figure 4a, the Cd(II) center is in a severely distorted octahedral environment, the equatorial plane of which comprises three carboxylate oxygen atoms (O2, O1#1, O4#1) from two inequivalent btec<sup>4–</sup> anions and one bimb nitrogen atom (N1); two carboxylate oxygen atoms (O1, O3#2) from two different btec<sup>4–</sup> moieties occupying the apical sites.

Each btec<sup>4–</sup> anion coordinates to six Cd(II) centers, with two para-carboxylate groups in adopting  $\mu^2 - \eta^2 : \eta^1$  coordination modes and another two para-carboxylate groups in  $\mu^2 - \eta^{-1} : \eta^{-1}$ fashions. The btec<sup>4-</sup> ligands thus link Cd ions to form a 2D layer structure in ab plane, as illustrated in Figure 4b. The 2D layers were further stacked with bidentate bimb spacers with Cd…Cd separations of 17.90 Å, giving rise to the formation of a 3D framework. By closer inspection of the structure 5, if the Cd centers act as nodes, btec<sup>4-</sup> anions and bimb bridges serve as linkers, each Cd center can be simply considered as linking three btec<sup>4-</sup> moieties and one Cd atom whereas each of btec<sup>4-</sup> anion acts as connecting six Cd atoms. Remarkably, compound 5 exhibits (4,6)-connected 3D binodal topology, which can be described by the Schläfli symbol of  $(4^3\hat{6}^3)_2(4^6\hat{6}^68^3)$  with the vertex symbols for the 4-connected btec<sup>4-</sup> and 6-connected Cd nodes, as illustrated in Figure 4d.

Obviously, from the crystal structures described above, the different coordination geometry around the central metal atom resulted in the completely different structures of MOFs. The results imply that the metal center has a great impact on the structures of the complexes. The phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD). The PXRD patterns of all as-synthesized products closely match the simulated ones from the single-crystal data, indicating that products are in a pure phase (Supporting Information Figure S9–S13).

**Photocatalytic Activities.** The diffuse-reflectance UV-vis spectra reveal the absorption features of compounds 1, 2, 4, and 5 (Figure 5), and all spectra consist of absorption components



Figure 5. UV–vis diffuse-reflectance spectra of compounds 1, 2, 4, and 5 with  $BaSO_4$  as background.

in the UV and Vis regions. In all cases, the intense absorption peaks at 257, 261, 255, and 262 nm for 1, 2, 4, and 5 can be

ascribed to  $\pi - \pi^*$  transitions of the ligands, whereas the main UV absorption bands at 327, 344(393), 317, and 325 nm for 1, 2, 4, and 5 can be attributed to ligand-to-metal charge transfer (LMCT). It should be noted that the absorption band occurring in the visible region at 476 nm for 5 also could be assigned to LMCT. In the case of 1 and 2, additional clear peaks in the visible region observed at 508(606) and 647 nm, which probably respectively originate from the d-d spin-allowed transition of the  $Co^{2+}$  (d<sup>7</sup>) and Ni<sup>2+</sup> (d<sup>8</sup>) ions. The absorption of 4 in the visible region is not as distinct as that of other samples, which may result from the d-d spin transition of the  $Zn^{2+}$  (d<sup>10</sup>) ion. The presence of visible regions transitions motivated us to explore applications of 1, 2, and 5 in heterogeneous photocatalysis. 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. The values of the band gap for 1, 2, and 5 obtained from corresponding LMCT transitions are 2.68, 2.63, and 2.32 eV, respectively. Clearly, the band gaps of 1, 2, and 5 follow the order  $1 \approx 2 > 5$ .

Herein, we selected an anionic organic dye X3B (Scheme 1), as a target pollutant for degradation experiments to evaluate the

Scheme 1. Molecular Structure of X3B



photocatalytic performance of compounds 1, 2, and 5, 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 visible-light irradiation.<sup>22</sup> It is hard for us to evaluate the photocatalytic performance of compound 3 because of its extremely low yield. The photodegradation experiment under visible irradiation was carried out after the dark adsorption-desorption equilibrium achieved. In addition, control experiments on the photodegradation of X3B have been carried out. Obviously, under dark conditions without light illumination, the concentration of X3B almost does not change for every measurement in the presence of compounds 1, 2, and 5. Illumination in the absence of compounds 1, 2, or 5 does not result in the photocatalytic decolorization of X3B (Supporting Information Figure S3-S5). Therefore, the presence of both illumination and compounds 1, 2 or 5 is necessary for the efficient degradation of X3B. The distinctly shortened degradation time compared with the control experiments indicates that both catalyst 1, 2, and 5 are active for the decomposition of X3B in the presence of visible-light irradiation. Figure 6 presents the comparison of photocatalytic profiles of the samples and commercial  $TiO_2$  (Degussa P-25) under visible irradiation. Apparently, Degussa P-25 showed only slight photocatalytic activity. On the contrary, the asprepared samples of 1, 2, and 5 exhibit higher photocatalytic efficiencies under the same condition. Notably, a very fast degradation of X3B for compound 5 was achieved, but only at the beginning of irradiation. Compound 5 showed the highest photocatalytic activity among all the photocatalysts, with a conversion of more than 80% within 5 h. The kinetic data for the degradation of X3B can be well fitted by the apparent first-



Figure 6. Degradation profiles of X3B under visible light irradiation in the presence of (a) without catalyst, (b) Degussa P-25, (c) 1, (d) 2, and (e) 5.

order rate equation,  $\ln(C/C_0) = kt$ , where k is the rate constant, *C* and *C*<sub>0</sub> are the concentration of X3B at irradiation time t = 0and t, respectively. The rate constant under visible-light irradiation was found to be 0.18, 0.19, 0.30, and 0.04  $h^{-1}$ separately for that of 1, 2, 5, and P-25. The enhanced photocatalytic activity of 5 may be attributed to the combined effects of two factors: first, the band gap of 5 is obviously lower than that of other samples, therefore, the charge transfer for 5, which is from oxygen and (or) nitrogen 2p bonding orbitals (valence band) to empty Cd orbitals (conduction band), easily takes place on photoexcitation. According to CASTEP calculations (Supporting Information Figure S14),<sup>23</sup> the solidstate compound 5 thus shows a semiconducting character with a band gap of 2.96 eV, which is comparable with the experimental value. Second, by careful comparison, it could be noted that the charge-transfer transition of  $\overline{\mathbf{5}}$  could occurs in the visible region (476 nm), whereas that of other samples lie in the UV region, which may give the reasons for the higher visible-light responsive catalytic activities for compound 5. To exclude the possibility that the photocatalytic properties of 1, 2, and 5 result from dissolved molecular or oligomeric fragments of solid catalysts in the photocatalytic process, another control experiments were conducted. The reaction suspensions after 10 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 10 h of irradiation under halogen lamp, which indicates that the solution contains no photocatalytically active fragments. Clearly the photocatalytic activities arise solely from the solid 1, 2, and 5. After photocatalysis, compounds 1, 2, 5 were recycled by filtration and powder XRD for the catalysts were checked to evaluate the stability toward photocatalysis. The patterns were found to be nearly identical to those of the parent compounds, which demonstrate that these complexes are rather stable during photocatalysis (Supporting Information Figure S9-S13).

In our earlier work, the MOFs with photocatalytic activity are constructed from 1,3,5-benzenetricarboxylate acid (btc) and bimb combined with different metal ions. The degradation rate constants under visible light irradiation were 0.073 and 0.13 h<sup>-1</sup> for isostructural compounds  $[Mn_3(btc)_2(bimb)_2\cdot(H_2O)_4]_n$  and  $[Co_3(btc)_2(bimb)_2\cdot(H_2O)_4]_n$ , respectively, which are obviously slowly than those of compounds 1, 2, and 5.<sup>14a</sup> The results

indicate that the more delocalized  $\pi$  electrons of 1,2,4,5benzenetetracarboxylic acid may facilitate the LMCT transitions and decrease electronic band gap of the MOFs, which contribute greatly to the enhanced photocatalytic rate. Therefore, it can be concluded that the semiconductor properties of the obtained MOFs strongly depend on the resonance effects in the organic linker.<sup>13</sup>

To make clear what active species are involved in the photocatalytic process occurring on compound 5, the formation of hydroxyl radicals ( $\bullet$ OH) on the surface of visible-illuminated compound 5 was detected by the photoluminescence (PL) technique using terephthalic acid as a probe molecule (Scheme 2).<sup>24–26</sup> For comparison, compounds 1 and 2 were also

Scheme 2. Formation of 2-Hydroxyterephthalic Acid in the Reaction of Terephthalic Acid with Hydroxyl Radicals



examined under the same conditions (Supporting Information Figure S6–S7). Figure 7a shows the changes in the PL spectra for  $5 \times 10^{-4}$  M terephthalic acid solution in  $2 \times 10^{-3}$  M NaOH with irradiation time in the presence of compound 5. As can be clearly seen from this figure, a gradual increase in the PL intensity of photogenerated 2-hydroxyterephthalic acid at about 425 nm is observed with increasing irradiation time. However, no PL intensity increase is observed in the absence of compound 5, which suggests that the fluorescence is caused by chemical reactions of terephthalic acid with •OH formed at the MOF/water interface via photocatalytic reactions. Figure 7b shows a comparison of the induced PL intensity at 425 nm for different samples with irradiation time. It can be seen that the PL intensity of photogenerated 2-hydroxyterephthalic acid increases linearly with time for all samples. Consequently, it can be inferred that •OH radicals produced at the catalyst surface are proportional to the light irradiation time obeying zero-order reaction rate kinetics.<sup>27</sup> The formation rates of •OH radicals can be expressed by the slope of these lines shown in Figure 7b. Obviously, the formation rate of •OH radicals on compound 5 is much higher than that of 1 and 2, implying that the formation rate of •OH radicals during photocatalysis is in agreement with photocatalytic activity and the formation rate of •OH radicals is an important factor influencing photocatalytic activity.

The photocatalytic degradation kinetics and •OH radical detection experiments provide valuable mechanistic information. Consequently, a simplified model of photocatalytic reaction mechanism was proposed as depicted in Supporting Information Scheme S1. Because the HOMO is mainly contributed by oxygen and (or) nitrogen 2p bonding orbitals (valence band, VB) and the LUMO by empty transition metal orbitals (conduction band, CB). Under visible light irradiation, electrons (e<sup>-</sup>) in the HOMO (VB) of MOF were excited to its LUMO (CB), with same amount of holes  $(h^+)$  left in VB. The HOMO strongly demands one electron to return to its stable state. Therefore, one electron was captured from water molecules, which was oxygenated into •OH active species. Meanwhile, the electrons (e<sup>-</sup>) in LUMO could be combined with the oxygen adsorbed on the surfaces of MOF to form  $\bullet O_2^{-}$ , then they might transform to the hydroxyl radicals



Figure 7. (a) PL spectral changes observed during illumination of compound 5 in a  $5 \times 10^{-4}$  M basic solution of terephthalic acid (excitation at 315 nm). Each fluorescence spectrum was recorded every 30 min of visible illumination. (b) Comparison of the induced PL intensity at 425 nm for compounds 1, 2, and 5.

Wavelength (nm)



Figure 8. Concentration changes of X3B as a function of irradiation time for complexes 1 (a), 2 (b), and 5 (c), respectively. Conditions: (I) H<sub>2</sub>O<sub>2</sub>/ 1(2, 5)/dark, (II) 1(2, 5)/visible light, (III) H<sub>2</sub>O<sub>2</sub>/visible light, (IV) H<sub>2</sub>O<sub>2</sub>/1(2, 5)/visible light.

1610

(•OH). Then the formed •OH radicals could cleave X3B effectively to complete the photocatalytic process. The proposed photocatalytic degradation mechanism was very similar to those of the previously reported MOFs.<sup>14</sup>

Limitation to the rate of photocatalytic degradation had been attributed to the recombination of photogenerated hole– electron pairs.<sup>28–30</sup> The addition of inorganic oxidant, such as  $H_2O_2$ , may play important roles in accelerating the degradation rate of azo dyes. It has been found that H<sub>2</sub>O<sub>2</sub> could increase the rate of hydroxyl radical formation through three ways. First, it could act as an alternative electron acceptor to oxygen (eq 1), which might restrain the recombination of the photogenerated electrons and holes. Second, the reduction of H2O2 at the

conductance band would also produce hydroxyl radical. Even if  $H_2O_2$  was not reduced at the conductance band, it could accept an electron from superoxide to give rise to hydroxyl radical (eq 2). Third, the self-decomposition by illumination would also produce hydroxyl radical (eq 3).

3

Time /h

$$e_{CB}^{-} + H_2 O_2 \to OH^{-} + \bullet OH \tag{1}$$

$$\bullet O_2^- + H_2 O_2 \to OH^- + \bullet OH + O_2$$
(2)

$$H_2O_2 + h\nu \to 2\bullet OH \tag{3}$$

Here, experiments were also conducted to study the synergistic effect of  $H_2O_2$  and MOF on the photodegradation of X3B. Figure 8c shows the degradation of X3B in the presence of  $H_2O_2$  (10 mL) and compound 5 (50 mg) under different conditions. The degradation of X3B is slow in the dark (23.4% of X3B is degraded after 5 h, curve I in Figure 8c). Visible-light irradiation greatly accelerates the photodegradation of X3B (94.1% of X3B is photodegraded after visible irradiation for 5 h, curve II in Figure 8c). It can be seen that, the presence of  $H_2O_2$ can greatly enhance the photodegradation of X3B on 5. The photocatalytic degradation rate constant of X3B was 0.56 h<sup>-1</sup> on 5 in the presence of  $H_2O_2$  (curve IV in Figure 8c), which is 1.8 times higher than that in the absence of  $H_2O_2$  (0.31 h<sup>-1</sup>) under visible illumination. Similar experimental results were also obtained for 1 and 2 photocatalysts after addition of  $H_2O_2$ . The corresponding rate constant for the degradation of X3B on 1 and 2 increased from 0.12 to 0.20  $h^{-1}$  and from 0.13 to 0.39  $h^{-1}$ , respectively.

Considering that the dye can also be degraded through photosensitized pathway, colorless molecule, phenol, was therefore selected to test the photocatalytic activity of compound 5. Figure 9 shows the concentration profiles of



Figure 9. Photocatalytic degradation of phenol in the absence of 5 under simulated solar light.

phenol and the evolution of intermediates as a function of the irradiation time under simulated solar light. Experimental results show that the concentration of phenol decreases, while ortho- and para-intermediates increases with light irradiation time (the conversion of the phenol is 40.13% and the selectivity for the intermediate catechol is 45.32% after 9 h irradiation). Control experiments (without catalyst or in the dark) show that no obvious phenol degradation was observed. Therefore, it can be safe to draw a conclusion that compound 5 is an efficient visible-responsible photocatalyst.<sup>31,32</sup>

# CONCLUSION

Five new metal–organic frameworks with the conjugated 1,2,4,5-benzenetetracarboxylic acid ( $H_4$ btec) and 4,4'-bis(1-Imidazolyl)biphenyl (bimb) have been obtained and found to show different structures and topologies. Compounds 1 and 4 are isomorphic, which possess typical PtS 3D nets; compound 2 is a 2D layer; compound 3 shows the NbO 3D network; compound 5 features a (4,6)-connected 3D binodal topology. Remarkably, the presence of visible regions transitions motivated us to explore applications of 1, 2, and 5 in heterogeneous photocatalysis, which exhibit photocatalytic activities higher than that of commercial TiO<sub>2</sub> (Degussa P-25) under visible irradiation for the degradation of X3B as a

model pollutant which is recognized as being difficult to decompose. Furthermore, compound 5 is photocatalytically more active than 1 and 2 because of the relatively narrower band gap calculated from LMCT transitions. The presence of •OH radicals, which can effectively oxide the dye molecules, have been detected by PL technique. In addition, the formation rate of  $\bullet$ OH radicals on  $5/H_2O$  interface via photocatalytic reactions is much higher than that of 1 and 2, implying that the formation rate of •OH radicals during photocatalysis is in agreement with photocatalytic activity and the formation rate of •OH radicals is an important factor influencing photocatalytic performance. Meanwhile, the synergistic effect of H<sub>2</sub>O<sub>2</sub> and MOF on the photodegradation of X3B has been studied, which could obviously enhance the degradation rate of X3B under visible light. The successful synthesis of 1, 2, and 5 provides access to a promising path in the search for stable new visiblelight-driven photocatalysts.

## ASSOCIATED CONTENT

# **S** Supporting Information

Crystallographic data, selected bond lengths and angles, additional crystal figures, control experiments on the photodegradation of X3B, PL spectral changes observed during illumination of compound 1 or 2 in a basic solution of terephthalic acid, TGA, PXRD, and computational procedures. This information is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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