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# Synthesis of Supramolecular Boron Imidazolate Frameworks for CO<sub>2</sub> Photoreduction

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**ABSTRACT:** Presented here are two novel porous supramolecular boron imidazolate frameworks (BIF-106 and BIF-107), which are stabilized through relatively weak interactions between two-dimensional boron imidazolate layers. Moreover, BIF-107 exhibits efficient CO<sub>2</sub> photoreduction to CO with a remarkable rate of 1186.0  $\mu$ mol·g<sup>-1</sup>·h<sup>-1</sup> under visible-light irradiation.

 ${\rm B}$  ecause of accelerated fossil fuel consumption, excessive emission of carbon dioxide (CO<sub>2</sub>) leads to an undesirable energy crisis and environmental issues.<sup>1-3</sup> Therefore, great efforts have been made in finding new materials for CO<sub>2</sub> capture and conversion. Visible-light-driven photoreduction of CO<sub>2</sub> to renewable fuels is a promising strategy for carbon fixation and solar utilization.<sup>4-9</sup> Metal–organic frameworks (MOFs), composed of tunable metal nodes and organic ligands, have attracted widespread attention as promising candidates for catalysis and  $CO_2$  adsorption.<sup>10–19</sup> Recently, diverse MOFs have been taken as catalysts for CO<sub>2</sub> photoreduction, such as NH2-MIL-101(Fe),<sup>20</sup> NH2-UiO-66(Zr),<sup>21</sup> Co-ZIF-9,<sup>22</sup> and PCN-222.<sup>10</sup> However, the photocatalytic efficiencies of currently developed MOFs are far from desirable levels mainly because of the intrinsic chemical inertness of the CO<sub>2</sub> molecule, low densities of active sites, and sluggish separation of electron-hole pairs. Thus, a new catalyst synthesis is desired for CO<sub>2</sub> photocatalytic reduction to overcome these limitations.

In homogeneous catalysis, tetradentate ligands are the main classes of modules that chelate earth-abundant metals, leading to the most effective molecular catalysts for  $CO_2$  reduction.<sup>23</sup> Boron imidazolate frameworks (BIFs), as a subclass of MOFs that are characterized by zeolitic topological nets based on tetradentate metal centers, are emerging as attractive candidates for heterogeneous catalysis.<sup>24–28</sup> Furthermore, the high density of exposed B–H bonding in BIFs has been proven to be able to facilitate  $CO_2$  adhesion and activation and thus

suppresses electron-hole pair recombination.<sup>29</sup> Up to now, several studies have demonstrated the successful applications of BIFs in photocatalytic CO<sub>2</sub> reduction due to the existence of functional active sites, including tetradentate metal centers and B-H bonding.<sup>30-32</sup> However, the current research is mainly limited to boron imidazolate nanocages and three-dimensional (3D) frameworks, and the application of supramolecular frameworks based on boron imidazolate layers in photocatalysis is rarely reported. The synthesis of supramolecular BIFs, which can withstand the harsh conditions for CO<sub>2</sub> photoreduction, is still a big challenge. Additionally, the porous nature of the catalysts endows them with unique properties for CO<sub>2</sub> capture and activity. Consequently, the construction of porous supramolecular BIFs, with tetradentate metal centers and B-H bonding, is quite desirable for the development of CO<sub>2</sub> photocatalysis.

Herein, we successfully synthesized two novel porous supramolecular BIFs [BIF-106 (CCDC 2032423) and BIF-107 (CCDC 2032424)], which were stabilized through relatively weak interactions between two-dimensional (2D) boron imidazolate layers. Interestingly, BIF-107 exhibits

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efficient CO<sub>2</sub> photoreduction to carbon monoxide (CO) with a remarkable rate of 1186.0  $\mu$ mol·g<sup>-1</sup>·h<sup>-1</sup> under visible-light irradiation. The quenching effects of steady-state photoluminescence (PL), combined with photocurrent responses, confirm that porous BIF-107 can accept photoexcited electrons from a photosensitizer and provide active catalytic sites for CO<sub>2</sub> reduction.

Crystals of BIF-106 and BIF-107 were synthesized by the solvothermal reactions of cobalt salts,  $\text{KBH}(\text{mim})_3$ , and phthalic acid (PA)/isophthalic acid (IPA), respectively. Single-crystal X-ray diffraction analysis revealed that both BIF-106 and BIF-107 possess porous 2D structures, with the interlayer packing motif stabilized by the interdigitation of pendant phthalate/isophthalate. The difference of the carboxylate angles between phthalate and isophthalate resulted in different configurations in the 2D structure. As depicted in Figure 1, in both BIF-106 and BIF-107, the tridentate boron



Figure 1. Coordination environment of the asymmetric unit in (a)  $Co[HBH(mim)_3](PA)$  of BIF-106 and (b)  $Co[HBH(mim)_3](IPA)$  of BIF-107.

imidazolate ligands were protonated during the crystallization process and Co centers adopted a CoN2O2 tetrahedral geometry. BIF-106 crystallizes in a monoclinic crystal system with space group  $P2_1/n$  (Table S1). The asymmetric unit includes one crystallographic Co<sup>2+</sup> ion, one HBH(im)<sub>3</sub> ligand, and one deprotonated phthalic acid (PA<sup>2-</sup>) ligand (Figure 1a). Each Co center is four-coordinated with two N atoms from two different HBH(im)<sub>3</sub> ligands and two O atoms from two different PA<sup>2-</sup> ligands. The carboxylate groups of PA<sup>2-</sup> accepted bis-monodentate coordination modes bridging two  $Co^{2+}$  ions to form  $Co_2$  units (Figure 2a). Then, the HBH(im)<sub>3</sub> ligands served as  $\mu_3$ -bridges to link three Co<sub>2</sub> units, using two N atoms to coordinate to two adjacent Co atoms and the other N atom to link to the third Co atom according to a N-H-O  $[d_{N-O} = 2.8804(2) \text{ Å}]$  hydrogen bond, leading to a 2D planar sheet (Figure 2b,c). For the structure of BIF-107, the Co<sup>2+</sup> ions and HBH(im)<sub>3</sub> ligands showed the same coordination modes as those in BIF-106 (Figure 1b). The alternating linkage between the Co and B nodes via mim results in the typical

double-crankshaft chain with 4-membered rings of  $Co_2B_2$  (Figure 2d). The adjacent chains are further linked by IPA<sup>2–</sup> in a bis-monodentate fashion to produce a 2D layer (Figure 2e,f). Notably, intrinsic tubelike channels were generated along the *b* axis in the layer, and the effective window size of the channel was about 4.3 × 8.2 Å.

In both BIF-106 and BIF-107, the 2D layers as supramolecular building units were blocked to generate 3D frameworks, which were stabilized by the interdigitation of pendant aromatic rings in phthalate/isophthalate (Figure 3a,b). The 2D layers were blocked in parallel in BIF-106, resulting in 1D extrinsic pores in the interstitial spaces (Figure 3c). In BIF-107, tubelike channels of the 2D layer have not been altered by their packing (Figure 3d). Weak C–H… $\pi$ interactions were also observed between the aromatic rings in BIF-107 (Figure 3b). The pore volume ratios were about 18% and 27% for BIF-106 and BIF-107, respectively, as estimated with the *PLATON* program.<sup>33</sup>

The phase purity of these crystals was proven by the wellmatched powder X-ray diffraction (PXRD) patterns between the simulated and as-synthesized ones (Figure S1). The solvent stability was examined by immersion in common solvents, such as water, ethanol, and acetonitrile (Figure S2). In addition, both BIF-106 and BIF-107 exhibited excellent chemical stability when the crystals were immersed in acidic and basic aqueous solutions (pH 2-12; Figure S3). Thermal gravimetric analysis showed that these crystals can be stable up to 300 °C under a N2 atmosphere (Figure S4). CO2 gas-adsorption measurements of BIF-107 exhibit typical type I sorption isotherm behavior, which indicates permanent microporosity (Figure S5). The uptake amounts at 760 Torr are 51.7  $\text{cm}^3 \cdot \text{g}^$ at 273 K and 30.4  $\text{cm}^3 \cdot \text{g}^{-1}$  at 298 K. The corresponding Langmuir and Brunauer–Emmett–Teller surface areas for BIF-107 are 835.0 and 860.4  $m^2 \cdot g^{-1}$ , respectively, calculated from the adsorption data at 195 K (Figure S12). Furthermore, the isosteric heat of adsorption  $(Q_{st})$  for CO<sub>2</sub> was calculated as 21.7 kJ·mol<sup>-1</sup> based on the collected adsorption data at 273 and 298 K (Figure S13).

Solid-state UV/vis spectral and Mott–Schottky measurements were carried out to determine the energy band position and its possibility for subsequent CO<sub>2</sub> photoreduction. As shown in Figure S7, BIF-107 exhibits a broad absorption in the range of 450–680 nm, giving a band-gap energy ( $E_g$ ) of 1.87 eV from the Tauc plot (Figure S8). Mott–Schottky measurement (Figure 4a) showed a positive slope of the obtained C<sup>2–</sup> values (vs the applied potentials), and the conduction-band (CB) position was –0.83 eV (vs the normal hydrogen electrode, NHE), as determined from the intersection point. The energy position of the CB edge of BIF-107 is more negative than the reduction potential of CO<sub>2</sub> to CO (–0.48 eV vs NHE), and it is theoretically feasible for the photoreduction of CO<sub>2</sub> to CO (Figure 4b).

Encouraged by these results, the photocatalytic CO<sub>2</sub> reduction over BIF-107 was carried out in an acetonitrile/ water (4:1, v/v) solvent under visible-light irradiation ( $\lambda > 420$  nm), with [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> as the photosensitizer and triethanolamine (TEOA) as the sacrificial electron donor. Remarkably, BIF-107 exhibited significant activity for CO<sub>2</sub> photoreduction. The main reduction products were CO and H<sub>2</sub>, as detected by gas chromatography. As presented in Figure 4c, the generation of CO and H<sub>2</sub> increased almost linearly with the light illumination time. After 5 h of irradiation, the amounts reached 59.3 µmol for CO and 47.2 µmol for H<sub>2</sub>, with average



**Figure 2.** (a) Co<sub>2</sub> unit bridged by two PA ligands in BIF-106. (b)  $\mu_3$ -bridge link mode of the HBH(im)<sub>3</sub> ligand. (c) 2D planar sheet in BIF-106. (d) Typical double-crankshaft chain in BIF-107. (e) View of the linkage between the IPA<sup>2-</sup> and HBH(im)<sub>3</sub> ligands in BIF-107. (f) Porous 2D layer of BIF-107 with a tubelike channel along the *b* axis.



Figure 3. 2D-layer blocking motifs in (a) BIF-106 and (b) BIF-107, which are stabilized by the interdigitation of pendant aromatic rings in phthalate/isophthalate. 3D frameworks of (c) BIF-106 and (d) BIF-107.

evolution rates of 1186.0 and 944.0  $\mu$ mol·g<sup>-1</sup>·h<sup>-1</sup>, respectively. To confirm the stability, PXRD patterns demonstrated that the structure of BIF-107 was retained after the reaction (Figure S9). The origin of CO was further confirmed by using N<sub>2</sub> instead of CO<sub>2</sub> under the same irradiation. Only H<sub>2</sub> was obtained after 5 h of reaction (Figure 4d). In addition, control experiments were carried out to explore the key roles of BIF-107 and [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in the photocatalytic system. No CO and H<sub>2</sub> products were detected without [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>, suggesting that a photosensitizer was necessary to drive the catalytic reaction. In the absence of BIF-107, only trace amounts of CO and H<sub>2</sub> were detected. It is safe to conclude that BIF-107 can remarkably accelerate the conversion of CO<sub>2</sub> to CO in the presence of a photosensitizer under visible-light irradiation.

The quenching effects on the steady-state PL of  $[Ru-(bpy)_3]Cl_2$  were investigated to unveil photogenerated electron-transfer behavior in the photocatalytic system. As shown in Figures 5a and S10, BIF-107 exhibited an exceptionally stronger quenching effect than TEOA, indicating more photoinduced electron transfer from the photosensitizer  $[Ru(bpy)_3]Cl_2$  to BIF-107 catalysts. Furthermore, the photocurrent responses of BIF-107 and BIF-107/ $[Ru(bpy)_3]Cl_2$  were studied under visible-light irradiation during several on-off cycles. Figure 5b showed that the photocurrent intensity of BIF-107/ $[Ru(bpy)_3]Cl_2$  is dramatically enhanced compared to that of pure BIF-107. In addition, electrochemical impedance spectroscopy performances exhibited that the Nyquist diagram radius of BIF-107/ $[Ru(bpy)_3]Cl_2$  is much smaller than that of pure BIF-107 (Figure S11). On the basis of



**Figure 4.** (a) Mott–Schottky plots of BIF-107. (b) Energy band structure for BIF-107 and  $[Ru(bpy)_3]Cl_2$ . (c) Time-dependent CO and H<sub>2</sub> evolution over BIF-107 (10 mg) under visible-light ( $\lambda > 420$  nm) irradiation in the presence of  $[Ru(bpy)_3]Cl_2$  (75 mg) and TEOA (4.5 mL) in an acetonitrile/water (4:1, v/v) solution (85.4 mL) at pH 9.3. (d) CO and H<sub>2</sub> generation by BIF-107 and control experiments.



**Figure 5.** (a) Quenching effects of BIF-107 on the steady-state PL of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  ( $\lambda_{\text{ex}} = 375 \text{ nm}$ ). (b) Transient photocurrent response for BIF-107 and BIF-107/ $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ .

the above results, we thus propose the following mechanism. Upon irradiation, the photosensitizer  $[Ru(bpy)_3]Cl_2$  adsorbed visible light to its excited state, which then transferred photogenerated electrons to BIF-107 catalysts for the subsequent reduction of CO<sub>2</sub> to CO. During this process, TEOA, acting as sacrificial electron donor, might be oxidized to its aldehyde form.

In summary, two supramolecular BIFs with permanent porosity were successfully synthesized under solvothermal conditions. More importantly, BIF-107 can be used as a catalyst for  $CO_2$  photoreduction under visible-light irradiation with  $[Ru(bpy)_3]Cl_2$  as the photosensitizer and TEOA as the sacrificial electron donor. A combination of PL, photocurrent responses, and electrochemical impedance spectroscopy performances confirmed the enhanced separation of electron-hole pairs in the presence of BIF-107 under the catalytic system. These results open new opportunities on the synthetic design of supramolecular frameworks toward the photocatalyst for  $CO_2$  reduction.

### ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02877.

Experimental details, crystallographic studies, additional figures, and general characterization (PDF)

## **Accession Codes**

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CCDC 2032423 and 2032424 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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