Light-Harvesting Metal−Organic Frameworks (MOFs): Efficient Strut-to-Strut Energy Transfer in Bodipy and Porphyrin-Based MOFs

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S Supporting Information

ABSTRACT: A pillared-paddlewheel type metal−organic framework material featuring bodipy- and porphyrin-based struts, and capable of harvesting light across the entire visible spectrum, has been synthesized. Efficient—essentially quantitative—strut-to-strut energy transfer (antenna behavior) was observed for the well-organized donor−acceptor assembly consituting the ordered MOF structure.

Photon collection and subsequent energy migration from outer antenna chromophores (i.e., carotenoids and chlorophylls) to the reaction centers of photosystems I and II are crucial initial steps in the conversion of sunlight to chemical energy via photosynthesis. Nature employs highly ordered pigment−protein complexes in nanoscopic domains, collectively encompassing scores of chromophores, to achieve these steps with extraordinary efficiency. Indeed, absorbed-light-to-electrical-charge conversion yields (quantum yields) exceed 95% in these natural systems.[1] To mimic such highly optimized natural energy-transfer process, artificial light-harvesting antenna assemblies, including systems based on chromophoric polymers,[2] dendrimers,[3] covalently linked porphyrin arrays,[4] and self-assembled donor−acceptor supramolecular systems,[5] have been devised. Based on studies of artificial and natural light-harvesting arrays, it is clear that energy transfer and antenna behavior are most effectively accomplished by assembling ordered networks of chromophores.[6]

Metal−organic frameworks (MOFs),[7] hybrid materials made from polytopic organic struts and inorganic nodes, constitute a potentially attractive, alternative platform for achieving long-range organization and order. MOFs have already received considerable attention from chemists and materials scientists because of their exceptional chemical and structural diversity, their extraordinary porosity, and their tailorable structures and properties. They have also been explored for numerous potential applications, including gas and chemical storage,[8] chemical separations,[9] sensing,[10] selective catalysis,[11] ion exchange,[12] and drug delivery.[13] Recently, the notion of MOFs as organized light-harvesters has moved to the fore. Most notably, Lin, Meyer and co-workers[14] reported efficient, long-distance energy migration via triplet charge-transfer excited states in a $Ru^{II}(2,2'$-biyridine$)_3$-derived MOF doped with Os^{II}. Similarly, Zhang et al.[15] recently showed that excitation of a UV chromophore constituting the struts of a MOF could be used to sensitize fluorescence from a weakly blue-absorbing secondary linker incorporated as a dopant or phosphorescence from Eu^{III} or Gd^{III} ions employed as nodes.

Scheme 1. Synthesis of the Isostructural BOB MOF and BOP MOF; Images to the Right of the Equations Are Digital Photographs of the Respective MOF Crystals
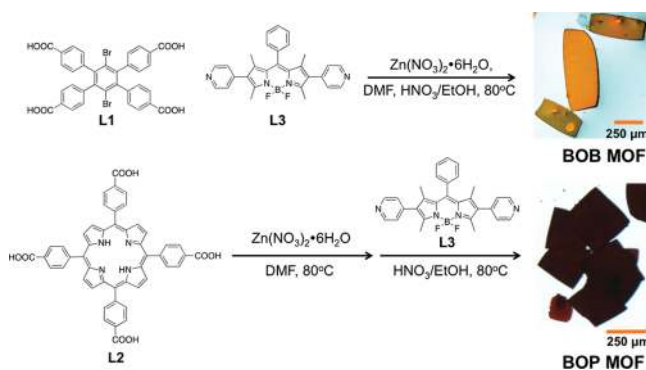
While the aforementioned studies are both interesting and important, they involve the capture of only a fraction of the photons in the visible spectrum. Because our longer-term goal is conversion of solar energy to electrical or chemical energy, we are interested in materials that can absorb essentially all of the visible spectrum. Few structurally simple chromophores are capable of behaving as "black chromophores" and absorbing light with good efficiency across the entire visible spectrum. Consequently, we looked to incorporate a complementary pair of chromophores as struts in a MOF material. Herein, we report the synthesis and structure of a MOF that forms emissive (fluorescent), molecular (i.e., electronically localized) excited states, either via the direct absorption of blue and red photons or through green absorption by an antenna[16] strut, followed by efficient energy transfer to the primary chromophore.

In part because of its structural and chromophoric similarity to various chlorophylls, but also because of our recent experience in assembling catalytic MOFs from this component,[17] we chose a symmetrical porphyrin, **L2** (Scheme 1), as the primary chromophore in our MOF synthesis. Like most other porphyrins, **L2** and its zincated derivative Zn-**L2** are characterized by sizable molar extinction coefficients in the blue and, to a lesser extent, red parts of the visible spectrum. To complete the spectral coverage, we turned to a pyridine-functionalized, boron dipyrromethene (bodipy) molecule, **L3**. Derivatives of bodipy have been employed previously as antenna-type light harvesters[18] with

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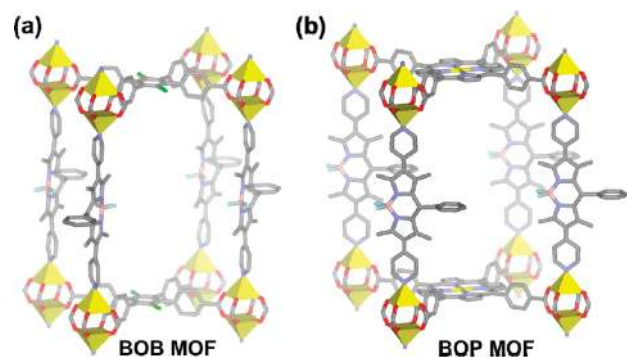dx.doi.org/10.1021/ja206029a | J. Am. Chem. Soc. XXXX, XXX, 000−000

Figure 1. Stick representations of the unit cells for: (a) **BOB** MOF and (b) **BOP** MOF (yellow polyhedral = Zn, red = O, green = Br, blue = N, pink = B, sky blue = F, gray = C). Hydrogen atoms and disordered solvent molecules have been omitted for clarity.

Figure 2. Confocal laser scanning microscopy (CLSM) images of crystals of: (a) **BOB** MOF and (b) **BOP** MOF. For illustrative purposes, when the crystals are shown as black, there is no emission. To denote emission in the "green" and "red" ranges, the remaining crystals are artificially colored green and red, respectively.

numerous favorable properties, including high fluorescence quantum yields, low rates of intersystem crossing, large molar absorption coefficients, relatively long excited-state lifetimes, and excellent photostability.[19]

On account of the good overlap between the emission spectrum of **L3** and the absorption spectrum of Zn-**L2** (inset of Figure S5 in the Supporting Information (SI)), we reasoned that the coassembly of these components with common nodes (pairs of zinc ions) would enable facile energy transfer, such that Zn-**L2** would behave as an antenna chromophore. The resulting **bo**dipy-**p**orphyrin-based MOF, which we have termed **BOP** MOF, is shown in Figure 1. Also assembled as a control material was a MOF featuring a non-chromophoric strut, **L1**, in place of **L2**. This material, based on **bo**dipy and a di**b**rominated strut, was termed **BOB** MOF.

Briefly, **BOB** MOF was synthesized in high yield via standard solvothermal methods in dimethylformamide (DMF) using $Zn(NO_3)_2 \cdot 6H_2O$, 1,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene (**L1**) and dipyridyl boron dipyrromethene (**L3**) in the presence of HNO_3 (Scheme 1, top sequence). **BOP** MOF was synthesized using a recently reported two-step method,[17b] which relies on delaying the addition of the dipyridyl strut until after the tetraacid porphyrin has begun to assemble with zinc ions. Following the same strategy, the tetraacid porphyrin (**L2**) and $Zn(NO_3)_2 \cdot 6H_2O$ were heated in DMF at 80 °C for 2 h, followed by the addition of 0.03 M HNO_3 in ethanol and an excess of **L3**. The resulting suspension was heated at 80 °C for 20 h, which led to the formation of rectangular plate-like crystals (Scheme 1, bottom sequence).

Single-crystal X-ray diffraction revealed that **BOB** MOF and **BOP** MOF are non-interpenetrated, pillared-paddlewheel MOFs with formulas $Zn_2(\mathbf{L1})(\mathbf{L3})$ and $Zn_2(Zn\text{-}\mathbf{L2})(\mathbf{L3})$, respectively. As observed from previous experiments,[17a] the free-base porphyrin **L2** was metalated during the course of the solvothermal synthesis of **BOP** MOF. Both structures are similar, with either **L1** or Zn-**L2** species coordinate pairs of Zn^{II} ions, forming two-dimensional (2D) sheets pillared by **L3** (Figure 1). Powder X-ray diffraction (PXRD) data for the bulk samples of **BOB** and **BOP** MOFs agree well with simulated data (see Figures S1 and S2 in the SI), indicating that phase-pure materials were obtained.

Thermogravimetric analysis (TGA) data for the as-synthesized samples of **BOB** and **BOP** MOFs revealed 45−50% weight loss due to solvent, thus implying substantial porosity (Figure S3 in the SI). CO_2 sorption measurements at 273 K revealed that the
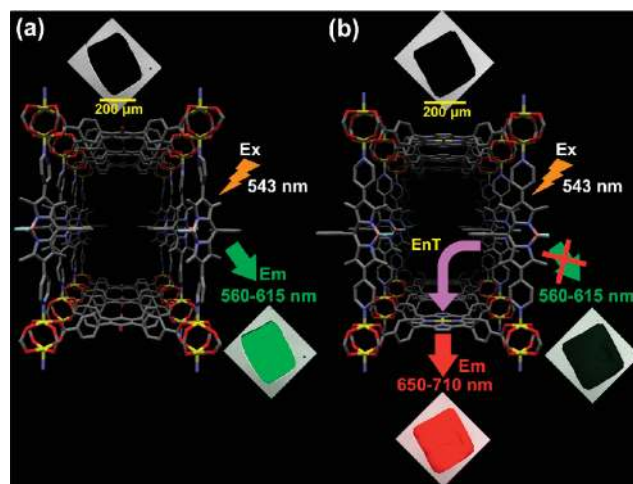
activated (i.e., solvent evacuated) forms of these materials are permanently microporous. Nonlinear density function theory analyses of the CO_2 isotherms showed surface areas of 410 and 540 m^2/g for **BOB** and **BOP** MOFs, respectively (Figure S4 in the SI).

The ground-state absorption spectrum of Zn-**L2** and **L3** ligands in DMF showed the characteristic absorption band for zinc porphyrin (B band: λ_{max} = 428 nm; Q bands: λ_{max} = 559, 599 nm), and boron dipyrromethene (λ_{max} = 522 nm), respectively (Figure S5 in SI). As noted above, there is good overlap of the fluorescence spectrum of **L3** and the absorption spectrum of Zn-**L2**, leading us to expect from Förster theory[20] that singlet−singlet energy transfer from **L3** to Zn-**L2** might readily occur within **BOP** MOF. One concern was that the transition dipole moments of **L3** and Zn-**L2** would be sufficiently geometrically orthogonal that energy transfer would not occur. Fortunately, as shown below, this concern did not materialize experimentally. One possibility is that the root-mean-square value of the angle defined by **L3**−node−Zn-**L2** differs slightly from 90°, even if the simple average value does not.[21]

Confocal laser scanning microscopy (CLSM) was used to investigate the light-harvesting properties of the new **BOB** MOF and **BOP** MOF materials. When irradiated at 543 nm, where **L3** strongly absorbs, emission from **BOB** MOF was readily observed through a 560−615 nm filter (Figure 2a). In contrast, **BOP** MOF was non-emissive over this range; however, luminescence was readily observed through a 650−710 nm filter (Figure 2b). These results can be understood qualitatively by: (a) recognizing that **L3** (bodipy-based strut) is emissive in the 560−615 nm region, (b) recognizing that Zn-**L2** is emissive in the 650−710 nm range covered by the second filter, and (c) assuming that energy is efficiently transferred from within **BOP** MOF from strut **L3** to strut Zn-**L2**.

To obtain more persuasive evidence for strut-to-strut energy transfer within **BOP** MOF, solid-state fluorescence spectra of **BOB** and **BOP** MOFs and the fluorescence excitation spectrum of **BOP** MOF were collected. As anticipated, excitation of **L3** in **BOB** MOF at 520 nm results in typical bodipy fluorescence
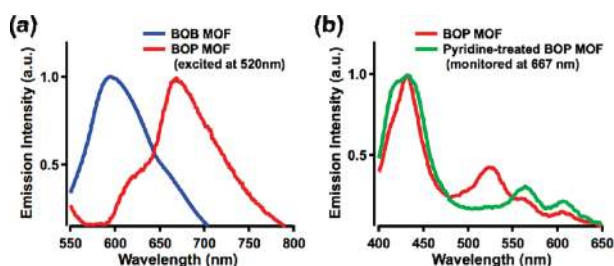
Figure 3. (a) Emission spectra of **BOB** and **BOP** MOFs. Spectra were obtained by excitation at 520 nm. (b) Excitation spectra of **BOP** and pyridine-treated **BOP** MOF. Spectra were obtained by scanning the excitation wavelength from 400 to 650 nm, with fixed emission detection at 667 nm.

behavior with an emission maximum at 596 nm. Excitation of the same strut in **BOP** MOF yields no emission at 596 nm but instead an emission spectrum characteristic of Zn-**L2**, maximizing at 667 nm (Figure 3a). The excitation spectrum of **BOP** MOF, obtained by scanning from 400 to 650 nm with fixed emission at 667 nm (appropriate for observing emission exclusively from Zn-**L2**), showed features attributable to both struts (Figure 3b). These observations confirm that efficient energy transfer from **L3** to Zn-**L2** takes place in **BOP** MOF.

In a final series of experiments, **L3** was selectively removed from **BOP** MOF by exchange reaction with pyridine. This exchange was accomplished simply by immersing as-synthesized crystals of **BOP** MOF in a pyridine-containing solution and allowing the material to soak. After a few hours, the supernatant was decanted and replaced with fresh pyridine-containing solution until soaking yielded a colorless supernatant (Figure S7 in SI). The ^{1}H NMR spectrum of the collected pyridine-treated **BOP** MOF, after being digested in D_2SO_4, showed the absence of the bodipy protons, while porphyrin and pyridine protons were observed (Figure S8 in SI). A comparison of PXRD patterns before and after pyridine treatment revealed that the treated material retains crystallinity, but the diffraction peaks attributable to bodipy spacing of 2D porphyrin layers are lost (Figure S2 in SI). Consistent with selective elimination of the bodipy strut, the initially dark—nearly black—**BOP** (see photograph in Scheme 1) crystals turn purple after repetitive exposure to pyridine (Figure S7 in SI). The excitation spectrum of pyridine-treated **BOP** MOF reveals, as expected, a loss of the peak attributed to Zn-**L2** sensitization by **L3** (Figure 3b).

As one would expect, physical mixing of **BOB** MOF (containing only bodipy struts as chromophores) and pyridine-treated **BOP** MOF (containing only porphyrin struts as chromophores) does not shut down emission from the former (Figure S6 in SI). This observation is consistent with energy-transfer theory, where strut-to-strut (i.e., **L3**-to-Zn-**L2**) energy transfer is expected to occur only between reasonably proximal chromophores.

In conclusion, **BOP** MOF, a highly chromophoric MOF possessing both bodipy and metalloporphyrin struts, was synthesized and found to have cooperative light-harvesting properties where the bodipy struts serve as antenna chromophores for the excitation of porphyrinic struts. Together, the two components contained within the nearly black **BOP** MOF crystals are capable of collecting most of the light constituting the visible spectrum. While energy transfer between differing struts clearly is efficient and rapid, still to be established is the effectiveness of **BOP**-like pillared-paddlewheel materials in moving molecular excitonic

energy between proximal, well-aligned, and chemically *identical* struts/chromophores. We intend to report shortly, however, on the results of experimental studies concerning this interesting, related problem.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Synthesis and characterization data for starting materials and all MOFs, including CIF files for single-crystal XRD data; detailed descriptions of experimental conditions and results of the gas adsorption, UV–vis, and emission experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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