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

Chang Yeon Lee, Omar K. Farha,* Bong Jin Hong, Amy A. Sarjeant, SonBinh T. Nguyen,* and Joseph T. Hupp*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

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 constituting 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. To mimic such highly optimized natural energy-transfer processes, artificial light-harvesting antenna assemblies, including systems based on chromophoric polymers, dendrimers, covalently linked porphyrin arrays, and self-assembled donor–acceptor supramolecular systems, 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.

Metal–organic frameworks (MOFs), 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, chemical separations, selective catalysis, ion exchange, and drug delivery. Recently, the notion of MOFs as organized light-harvesters has moved to the fore. Most notably, Lin, Meyer and co-workers reported efficient, long-distance energy migration via triplet charge-transfer excited states in a Ru(II)(2,2’-bipyridine)₄-derived MOF doped with OsIII. Similarly, Zhang et al. 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 EuIII or GdIII ions employed as nodes.

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 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, we chose a symmetrical porphyrin, L2 (Scheme 1), as the primary chromophore in our MOF synthesis. Like most other porphyrins, L2 and its zincted 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.

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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 bodipy-porphyrin-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, which relies on delaying the addition of the dipirydyl strut until after the tetraacid porphyrin has begun to assemble with zinc ions. Following the same strategy, the tetraacid porphyrin has begun to assemble with zinc ions. The resulting suspension was heated at 80 °C for 2 h, followed by the addition of 0.03 M HNO3 in ethanol and an excess of solvent molecules have been omitted for clarity.

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.

activated (i.e., solvent evacuated) forms of these materials are permanently microporous. Nonlinear density function theory analyses of the CO2 isotherms showed surface areas of 410 and 540 m2/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: λmax = 428 nm; Q bands: λmax = 559, 599 nm), and boron dipyrromethene (λmax = 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 theory20 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 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.
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 exchanging 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, allowing the material to soak. After a few hours, the supernatant was selectively removed from BOP MOF (contain- ed within the nearly black BOP MOF). Spectra were obtained by scanning the excitation wavelength from 400 to 650 nm, with fixed emission detection at 667 nm.

The excitation spectrum of pyridine-treated BOP MOF, after being digested in D$_2$SO$_4$, 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). The $^1$H NMR spectrum of the collected 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 pyridine 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.

**REFERENCE**


