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Metal-organic Framework Materials for Light-Harvesting and Energy Transfer

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A critical review of the emerging field of MOFs for photon collection and subsequent energy transfer is presented. Discussed are examples involving MOFs for (a) light harvesting, using (i) MOF-quantum dots and molecular chromophores, (ii) chromophoric MOFs, and (iii) MOFs with light-harvesting properties, and (b) energy transfer, specifically via the (i) Förster energy transfer and (ii) Dexter exchange mechanism.

1. Introduction

In nature, photosynthesis is facilitated by outer antenna chromophores, such as chlorophylls and carotenoids, which deliver energy from absorbed photons to the reaction centre with efficiencies exceeding 95%.[1] Examples of artificial, yet efficient, light-harvesting systems include covalently linked porphyrins,[2] metal complex polymers,[3] and dendrimers.[4] More recently, chemists have developed hierarchically organized molecular structures, such as metal-organic frameworks (MOFs);[5-7] these have the potential to mimic the hierarchically ordered plant structures found in nature, such as chloroplasts. Just as chloroplasts contain flat discs (thylakoids) stacked tightly together to increase surface area for capturing light, MOFs contain unit cells, which can be assembled together to form high surface area arrays for photon collection. Similarly, just as the membranes of thylakoids contain chlorophyll and carotenoids, which absorb light energy and use it to energize electrons, MOFs can be built with chlorophyll analogues to execute the same process. The analogous structure of MOFs to chloroplasts enables them, in theory, to perform critical steps in photosynthesis—including photon collection and subsequent energy transfer from outer antenna chromophores to chemical-producing reaction centres akin to those of photosystems I and II.

Although MOFs share relevant features of chloroplasts, MOFs differ in important ways. First, MOFs can be built from a plethora of organic linkers and inorganic metal nodes or metal clusters, which make them more chemically diverse than chloroplasts. Second, since the organic linkers vary in dimensions, the resulting MOFs also have structural tunability. Third, MOFs self-assemble into structures that are crystalline, thereby facilitating predictive computational modeling. Due in part to their chemical and structural diversity and their high organization, MOFs have been simultaneously attractive candidate materials for a spectrum of applications, including gas storage[8-10] and separation[11], catalysis,[12-14] sensing,[15] drug delivery,[16] and biomedical imaging.[17, 18]

Despite the plethora of recent developments, from our perspective, the use of MOFs for light harvesting and energy transfer is still in a nascent yet promising stage. For the rest of this report, we have limited ourselves to surveying what has already been accomplished in MOFs for light harvesting and energy transport with an eye towards highlighting criteria for demonstrations of excitonic solar cells. Shown in Figure 1 are the structures of several organic struts used in the synthesis of photoactive MOFs to date, along with abbreviations. Since MOFs for photocatalysis have been thoroughly discussed in excellent reviews by Lin and co-workers,[19-21] we have excluded them, except where they also serve to illustrate an idea not directly related to photocatalysis. For the most part, we have also omitted phenomenological studies of photocurrent or photovoltage generation by MOFs, unless the studies also include substantial emphases on fundamental photophysical behaviour. Finally, we have omitted studies that focus on chemical sensing,[22, 23] or that are solely computational, although these do outline many interesting possibilities.[24] Herein, we examine (a) methods to induce light harvesting in MOFs through sensitization with dyes, or quantum dots involved with photon collection and then (b) metalloporphyrin- and ruthenium-based MOFs used for Dexter exchange and Förster energy transfer studies.

2. MOFs and sensitization

MOFs have been used both as the sensitizer agent to deliver energy to a neighbouring material, or, conversely, as the material to be sensitized. This dual role speaks to the range of building blocks that can be used to construct MOFs, and the range of optical and electronic properties that are possible with MOFs. This dual role also underscores the versatility of MOFs to be integrated with a wide range of materials and to enable a variety of routes to solar light harvesting and energy conversion. We review both sensitizing classes of MOF functionalities here.

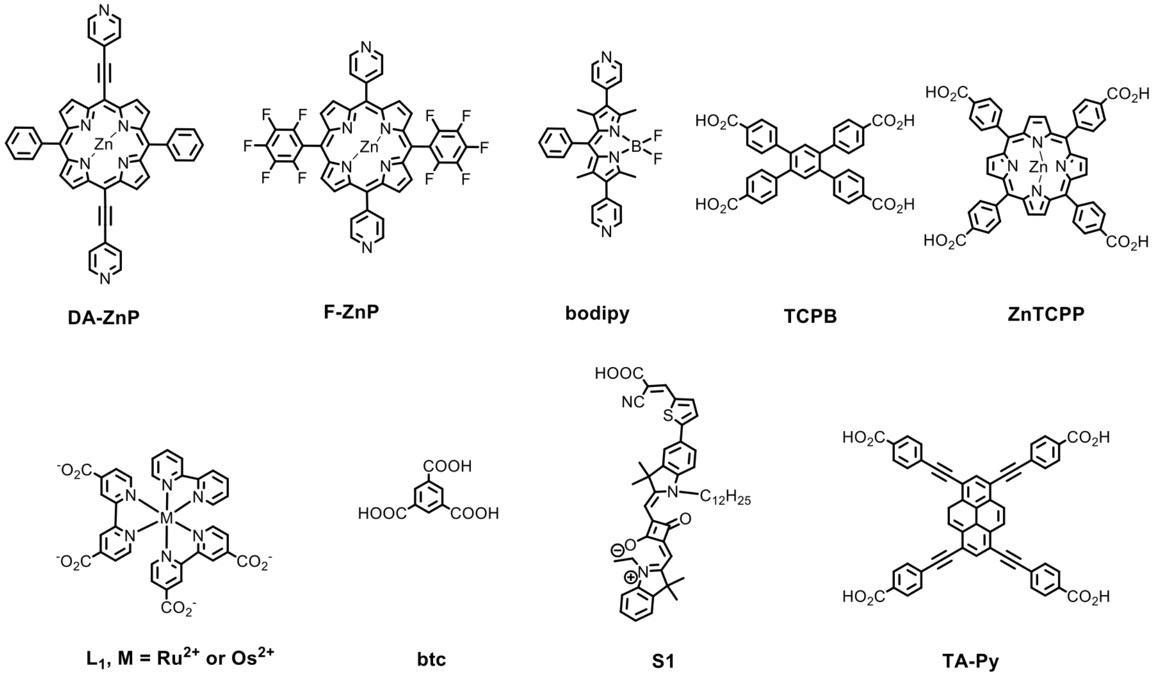

Figure 1. Structures of various molecular struts employed in the synthesis of photoactive MOFs. **TA-Py** has been examined only computationally and not experimentally.

For the cases where the MOF is sensitized by another material, the MOF is usually designed to optimize exciton migration. The chromophores, or struts, that have been shown to produce significant electronic coupling and resonance energy transfer to produce exciton migration do not necessarily also have ideal overlap with the solar spectrum. Thus, the motivation for sensitizing MOFs is grounded in the need to increase solar absorption while maintaining anisotropic and efficient exciton migration, thereby producing an improved material for functional harvesting of solar energy.

A. Molecular chromophores and quantum dots as sensitizers

Porphyrin-containing struts are the primary building blocks used (thus far) in MOFs that target solar light harvesting.[25-27] These porphyrin-based MOFs have proven to have exciton propagation capabilities, displaying anisotropic energy transport over several tens of struts from the initially excited strut. However, the absorption spectra of the porphyrin struts in Figure 2a show that over large regions of the solar spectrum photons are not absorbed. Thus, researchers have sought to enlist secondary chromophores as photo-sensitizers of MOFs. One approach is to functionalize MOF surfaces with quantum dots (QDs) as shown in Figure 2b.[26, 27] QDs have several properties that are advantageous for sensitization, including broad absorption spectra, excellent durability under illumination, the ability to be functionalized to bind to MOFs, and size-tunable exciton energies. This last point is critical for ensuring efficient transfer of energy to the MOF. The QD exciton energy should be chosen so that the emission band has strong overlap with the lowest energy absorption band of the MOF. This ensures a large overlap integral and encourages efficient resonance energy transfer from the QD to the MOF. For the examples in Figure 2, the QDs were chosen to have emission bands that respectively overlap the absorption bands of the F-MOF (QD550) or the DA-MOF (QD620). In both cases, monitoring the change of kinetics of QD emission when the QDs were bound to the surface of the MOF showed that energy transfer from the QD to the MOF occurred with greater than 80% efficiency.

Going forward, the greatest challenge with this approach is to install enough QDs to significantly increase overall absorption of the MOF. In this example, QDs were placed in sub-monolayer density on the surface of a MOF, resulting in an increase of overall absorption by ~5%, assuming a MOF thickness that is similar to a typical exciton diffusion length of approximately 10 layers. (In other words, there is no need to have a MOF with thickness much greater than the exciton propagation length, because the exciton energy will be lost before reaching the surface where it can be utilized in a device.) By the same measures, the use of QDs with a single MOF layer would allow the single layer to harvest ~50% more photons.[26] This provides motivation to find a means to incorporate QDs into MOF structures,[28] perhaps through a layer-by-layer approach.[27] Alternatively, external multilayers of QD might be employed. In either case, however, it is important that the placement of QDs not interrupt the inter-porphyrin electronic coupling, which would preclude exciton transport and eliminate the functional light-harvesting capabilities of the MOF.

Another example of chromophore sensitization is the use of dye molecules doped into porous MOF structures.[29] For example, dye molecules have been adsorbed on the large interior surfaces of porous, anionic zeolitic MOFs to function as solar absorbers. Over a wide range of dyes, the extent of adsorption was found to correlate with the amount of positive charge on the dye molecule, as one might expect for binding within net anionic frameworks. Energy transfer from the MOF to the chromophores was initiated and monitored through continuous wave and time-resolved excitation and luminescence studies.

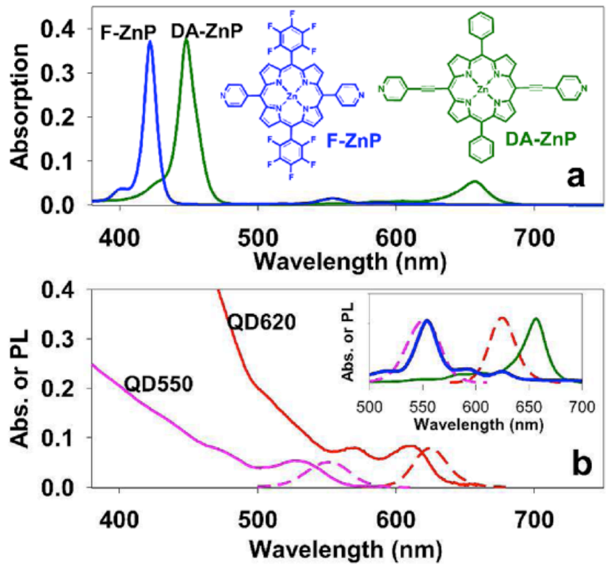

Figure 2. Absorption (solid lines) and emission (dashed lines) spectra of (a) zinc metallated **F-H$_2$P** (**F-ZnP**) and **DA-H$_2$P** (**DA-ZnP**) in DMF and (b) CdSe/ZnS core/shell QDs of different sizes (QD550 and QD620) in water. The inset in (b) compares the normalized emission spectra of the QDs and the Q-band absorptions of **F-ZnP** and **DA-ZnP**. Adapted with permission from ref. 26. Copyright 2013 American Chemical Society.

Closely related, but distinctly different, are very recent studies of Ru(bpy)$_3^{2+}$ (bpy = 2,2'-bipyridine) physically encapsulated by UiO-67.[30, 31] Here, the MOF functions as an otherwise inert, physical scaffold, rather than a framework to be sensitized. Thus, the observed photophysical behaviour is that of the array of incorporated molecular chromophores and not that of the MOF itself. Notably, the photophysical behaviour depends significantly on dye loading, with dye self-quenching or loading-dependent differences in encapsulation environments evidently accounting for the dependence. Complications due to self-quenching (i.e. singlet-singlet or triplet-triplet excited-state annihilation) presumably will be unimportant at typical solar light intensities. Thus, in device applications, systems like Ru(bpy)$_3^{2+}$@UiO-67 may well perform better than anticipated based on transient photophysical studies.

The UiO-67 studies were preceded by studies concerning Ru(bpy)$_3^{2+}$, Os(bpy)$_3^{2+}$, or both, encapsulated in comparatively simple oxalate-derived MOFs.[32] Salient features included: a) long excited-state lifetimes (ca. 0.76 and 1.3 µs for Ru(bpy)$_3^{2+*}$ in different MOFs), b) effective quenching of photo-excited Ru(bpy)$_3^{2+}$ by even small amounts of Os(bpy)$_3^{2+}$ (e.g. ~95% quenching for samples doped with 1% Os(bpy)$_3^{2+}$), and c) substantially shortened excited-state lifetimes in the presence of trace amounts of O$_2$. The Ru/Os quenching behaviour (and concomitant sensitization of Os(bpy)$_3^{2+}$ emission) implies that rates of energy transfer from Ru(bpy)$_3^{2+}$ to Ru(bpy)$_3^{2+}$ and from Ru(bpy)$_3^{2+}$ to Os(bpy)$_3^{2+}$ that are fast to the rate of decay photo-excited Ru(bpy)$_3^{2+}$ in the absence of quenching. Detailed numerical simulations of the coupled rate processes and resulting luminescence transients for both Ru(bpy)$_3^{2+}$ and Os(bpy)$_3^{2+}$, suggest a Ru(bpy)$_3^{2+}$ to Ru(bpy)$_3^{2+}$ exciton-hopping time of ca. 50 ns.[33]

The observed luminescence quenching by O$_2$ is attributed to singlet oxygen formation and underscores that the emissive excited state of Ru(bpy)$_3^{2+}$ is largely triplet in character. In turn, this implies (as discussed further below) that energy transfer is facilitated by Dexter transfer (electronic coupling) rather than by Förster transfer (dipolar coupling). Again, detailed computational studies support this conclusion.[33] Since Dexter transfer is an inherently short-range phenomenon, one likely design consequence is that MOFs featuring Ru-based chromophores will need to configure these chromophores in very close proximity in order to accomplish more than a few energy transfer steps (exciton hopping steps) after photo excitation.

B. Chromophores integrated as MOF building blocks

Another approach to sensitizing porphyrin MOFs is to build the MOF with an additional strut that absorbs in complementary regions of the solar spectrum. Lee and coworkers reported such an approach by building a MOF with both boron dipyrromethene (**bodipy**) and porphyrin struts (**ZnTCPP**).[25] The bodipy absorbs in the green spectral region where the porphyrin absorbs only marginally. Additionally, this study showed that energy absorbed by the **bodipy** struts was efficiently (i.e., essentially quantitatively) transferred to the porphyrin struts. Thus, under green illumination, strong emission from the porphyrin was observed, even though the irradiation directly excited only **bodipy**. The challenge with this approach is that the **bodipy** struts are lengthy enough to produce a relatively large spacing between porphyrins compared to the spacing in MOFs that only use porphyrin struts. This geometrical feature translates into diminished lateral dipolar (porphyrin:porphyrin) coupling and decreased efficiency for extended exciton energy transport.

Others have recently used photoisomerizable and photochromic cyclopentene compounds to link porphyrin struts.[34] The photochromic compounds function as a switch to trap excitonic energy from the porphyrins in the "closed" state, but to have a higher energy "open" state that does not interfere with excitonic energy migration. The open state is reached through UV illumination, while the closed state is reached through visible light illumination prior to monitoring the impact on excitonic energy migration.

C. MOFs as sensitizers

MOFs that function as sensitizers to other materials are equally important to the prospects of using MOF-based materials in energy conversion devices. However, to date, there exist very few reports of photoactive MOFs for this purpose. One recent example reports on the use of MOF films as an apparent sensitizing layer in dye-sensitized solar cells (DSSC).[35] In this work, the MOF essentially replaces the dye molecules that more commonly sensitize TiO$_2$ in a DSSC, and serves to both absorb light and to inject an electron into the TiO$_2$ film. The MOF was constructed from copper(II) benzene-1,3,5-tricarboxylate through layer-by-layer synthesis (Cu-MOF LBL film). Interestingly, iodine doping of the film was explored, which simultaneously showed a large increase in electrical conductivity as well as increased absorption particularly in the blue-green spectral region where iodine absorbs. The reason for the increase in electrical conductivity was stated to be due to an increase in interactions between I$_2$ and the π-electrons of the MOF building blocks. While the overall conversion efficiency of the device was low (0.26%), iodine doping did increase the efficiency of the MOF device by more than an order of magnitude. It is unclear what the identity of the sensitizer is under these conditions, as a photocurrent action spectrum was not reported. I_2 can be photo dissociated with visible light, with the resulting iodine radicals reacting in redox fashion with electrodes to produce photocurrents. It is conceivable that the sensitizer is iodine and that the role of the MOF is to enhance its concentration proximal to the electrode.

Others have discussed the formation of MOF films with porphyrin, benzenetricarboxylate (**btc**), and Cu^{2+} ions on TiO_2-modified indium-tin-oxide electrodes, but these samples also generated low levels (on the order of nanoamperes) of cathodic short-circuit photocurrent.[36]

A report by Leong *et al.*[37] employed MOF-177 as a host for adsorbed fullerene ([6,6']-phenyl-C_{61}-methyl-butyric ester; PCBM) and α,ω-dihexylsexithiophene (**DH6T**) guests. Excitation at 345 nm, which pumps the **btc** linker in MOF-177, yielded efficient Förster energy transfer to **DH6T** and either energy or electron transfer to **PCBM**, as evidenced in part by quenching of framework luminescence and sensitization of **DH6T** luminescence. Note that **PCBM** is not luminescent, so no new luminescence would be expected even if energy transfer does occur. With both guests present, even greater quenching was observed, likely due in part to an energy cascade, *i.e.* sequential MOF-177 → **DH6T** → **PCBM** energy transfer (Figure 3).

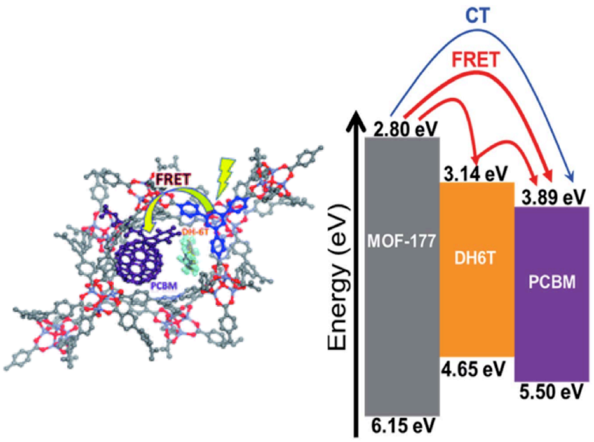

Figure 3. Energy transfer and/or electron transfer from photo-excited linkers of MOF-177 to internally adsorbed fullerene and oligothiophene species. Adapted from ref. 37 with permission from The Royal Society of Chemistry.

Another means for MOFs to function as sensitizers is to deliver their energy to a neighbouring compound with a lower exciton energy, in much the same way that light harvesting complexes in photosynthesis deliver energy from compounds of high exciton energy (such as carotenoids) to those with lower exciton energies and ultimately into the reaction centre.[1] So *et al.* pursued this approach by transferring exciton energy from a porphyrin-based MOF (film grown via layer-by-layer) to a squaraine dye (**S1**). **S1** was chosen, since it absorbs light to the red of the lowest excited state of the MOF.[27] This resulted in the transfer of energy from the MOF to the **S1** layer. In other words, the MOF functions to sensitize the **S1** layer.

One can imagine a MOF acting in both sensitization capacities in a device. The MOF could function as the primary exciton transport medium, while being sensitized by a second film that transfers energy into the MOF in spectral regions where the MOF does not absorb. The MOF could then sensitize another film, such as a lower energy excitonic material (for light harvesting) or an electrode (for direct energy conversion).

3. MOFs and energy transfer

Due to the precise arrangement of donor and acceptor chromophores in MOFs, MOFs act as attractive platforms for studying rapid long-range energy transfer. To date, existing reports focus on examining Förster and Dexter energy transport in metalloporphyrin- and ruthenium-based MOFs. We review both classes of MOFs for energy transfer here.

In supramolecular light harvesting systems with weak coupling between chromophores, the two most relevant models for describing energy transport are those based on the Förster and Dexter energy transfer mechanisms. According to the modified Förster rate expression (**1**),[38] the first-order rate constant (k_{EnT}) for intermolecular energy transfer between a fixed pair of molecules is a function of the overlap integral between normalized emission spectrum of the donor and the normalized absorption spectrum of the acceptor (*OI*), and the exciton coupling constant (*J*) between donor and acceptor chromophores.

$$k_{EnT} = \left(\frac{2\pi}{\hbar}\right) J^2 (OI) \qquad \textbf{(1)}$$

The magnitude of the coupling constant is related to the magnitude of the oscillator strength (integrated absorption intensity) for excitation to the lowest singlet excited state, the fluorescence quantum yield, the separation distance, R, between the donor and acceptor moieties (J^2 **α** $1/r^6$ for point dipoles), and the angle between their transition dipoles.

While the Förster transfer is possible only for symmetry allowed energy-transfer reactions, the Dexter rate expression **(2)**[39] applies to transfers in which the spin state is not conserved. Dexter transfer relies upon electronic coupling and, therefore, donor-acceptor orbital overlap. One important consequence is that the rate of energy transfer via the Dexter mechanism decreases exponentially with the donor-acceptor separation distance:

$$k_{EnT} = \left(\frac{2\pi}{\hbar}\right) K^2 \exp\left(\frac{-2R}{L}\right)(OI) \qquad \textbf{(2)}$$

In the equation, L is the sum of the van der Waals radius, and K is related to the degree of electronic coupling at close contact between the donor and acceptor. Dexter transfer is typically significant only over very short distances relative to those that are viable for Förster transfer.

To date, design strategies to maximize long-range energy transfer in MOFs have not been clearly articulated. However, based on the existing literature, there are two main approaches that have been demonstrated, involving changes in the (a) electronic structure of organic linkers or (b) spatial variations in the supramolecular structure.

A. Metalloporphyrins as conduits for Förster energy transfer

Due to the structural and chromophoric similarity to various chlorophylls, as well as their synthetic tunability, metalloporphyrins can serve an attractive linker for MOFs as not only light harvesting functional struts but for energy transfer. In fact, some of the earliest reports on crystalline MOFs highlighted the promise of porphyrins as building blocks.[40 41, 42]

The first report[25] of porphyrin-strut-based energy transfer involves **BOP MOF**, a pillared paddlewheel MOF featuring dinuclear zinc clusters as nodes, **bodipy** as the pillar, and zinc metallated **H_2TCPP** as the paddlewheel linker. After absorption of red, blue, and green photons, **BOP MOF** exhibited molecular fluorescence, resulting in efficient energy transfer from the antenna pillar to the primary chromophore linker (Figure 4). Despite the geometric orthogonality of its linkers, the slight deviation of their root-mean-square value of the angle from 90° enabled observation of energy transport. Also, the incorporation of Zn(II) of d^{10} configuration as metal nodes prevented the quenching of struts due to any ligand-to-metal charge transfer. The work of Lee *et al.* established that porphyrin-based MOFs can be used as architectures for studying energy transfer behavior.

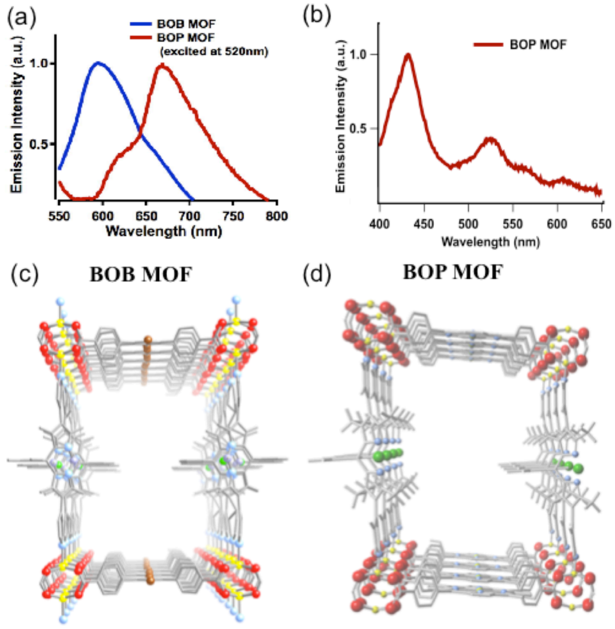

Figure 4. (a) Emission spectra of **BOB** and **BOP** MOFs. Spectra were obtained by excitation at 520 nm. (b) Excitation spectra of **BOP** and pyridine-treated **BOP** MOF. Spectra were obtained by scanning the excitation wavelength from 400 to 650 nm, with fixed emission detection at 667 nm. Crystallographic illustrations of (c) **BOB MOF** and (d) **BOP MOF**. O = red spheres, Zn = yellow spheres, C = grey segment, N = blue spheres, B = green spheres, F = white segment. Adapted with permission from ref. 25. Copyright 2011 American Chemical Society.

Inspired by this notion, Son *et al.*[43] used $Zn(NO_3)_2$•6H2O, the tetratopic ligand **TCPB**, and **DA-ZnP** and **F-ZnP**, to synthesize **DA-MOF** and **F-MOF**, respectively. To study energy transport, they incorporated ferrocene-based quenchers in varying concentrations into the two pillared paddlewheel MOFs. The result was enhanced fluorescence quenching due to exciton diffusion through porphyrin struts was observed. The average number of distinct struts visited by excitons during their lifetimes was 45 struts (2025 hops) and <3 struts (8 hops) for **DA-MOF** and **F-MOF**, respectively.

DA-MOF and **F-MOF** illustrate features relevant to achieving long-range Förster energy transfer. First, due to the presence of two acetylene moieties in **DA-ZnP**, conjugation extends out through the terminal pyridines of the linker. One consequence is a significant reduction in electronic symmetry, such that the transition-dipole moment for excitation to the lowest singlet excited state of the porphyrin is largely aligned with the pyridine-pyridine access. This change sets the stage for enhanced directionality in subsequent exciton hopping. A second consequence of the reduced symmetry is that the nominally forbidden S(0) → S(1) excitation becomes more allowed (see Figure 2). The resulting increase in oscillator strength results in enhanced dipole-dipole coupling and, as promised by Förster theory, faster energy transfer. A third consequence of extending the conjugation of the chromophore is to reduce the Stokes shift for the lowest energy transition, thereby enhancing spectral overlap, and again boosting the rate of energy transfer. The distance covered from exciton hops in the AE direction (Figure 5) results in net displacements of about 60 nm and 3 nm for **DA-MOF** and **F-MOF**, respectively.[43] The rather striking changes in energy transfer efficacy seen in replacing **F-MOF** with **DA-MOF** suggest that a more serious and systematic investigation could yield substantial additional improvements.

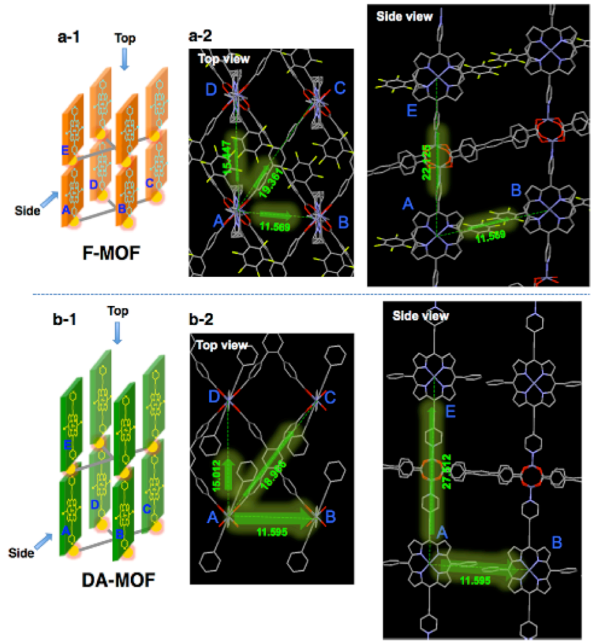

Figure 5. The capped stick representations of the crystal structure of **F-MOF** (a-2) and **DA-MOF** (b-2) with arrows indicating the four energy transfer directions from A to B, C, D and E between the nearest neighboring porphyrin blocks. In structural representations, Zn = yellow spheres, C = grey segments, **F-ZnP** = orange squares, and **DA-ZnP** = green squares. Adapted with permission from ref. 43. Copyright 2013 American Chemical Society.

In a subsequent study, So *et al.*[27] grew **DA-MOF** as thin films using an automated, layer-by-layer assembly technique.[44-47] Upon depositing **S1**, a far-red absorbing squaraine dye exhibiting high overlap integral with the **DA-ZnP**, exclusive emission from **S1** was observed (Figure 6). The work suggested that efficient Förster energy transfer is possible in films of thicknesses, approximately matching that of the expected exciton propagation length.

Since the defining factors for energy transfer directionality were not fully understood in **DA-MOF**, in a follow up theoretical study, Patwardhan *et. al.*[38] replaced the **TCPB** linkers with longer linkers such as **TA-Py** in an effort to increase the directionality of energy transfer. This increases interporphyrin distances in the AB-, AC-, and AD-directions but not the AE-direction (Figure 5). Importantly, the exciton transfer rates reduce by 60% in the ABdirection but remain the same in the AE direction when **TA-Py** is utilized. By changing the spatial variations in the supramolecular structure, the directionality of energy transfer in MOFs can be increased. This is especially relevant for delivering excitons in thin film geometries for solar energy conversion applications.

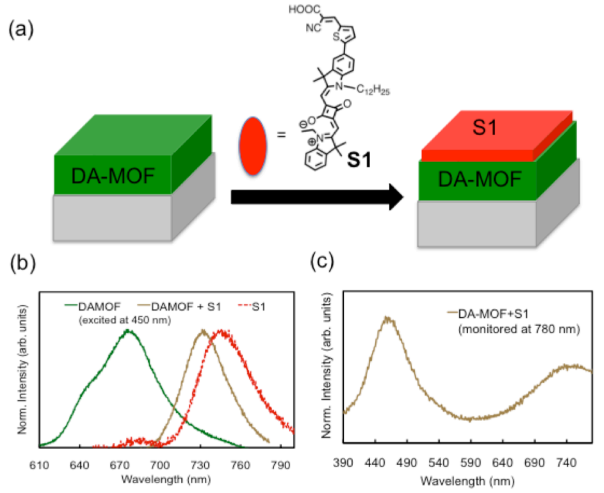

Figure 6. (a) Deposition of **S1** atop **DA-MOF** thin film formed by LbL growth results in (b) exclusive emission from the **S1** upon excitation of the **DA-MOF** film at 450 nm. (c) Contributions from both **DA-MOF** and **S1** are observed when monitored at 780 nm. Adapted with permission from ref. 27. Copyright 2013 from American Chemical Society.

Finally, an additional intriguing element of chromophore design is illustrated in recent studies by two teams.[48, 49] Briefly, by analogy to behavior of fluorophores in rigid environments like solvent glasses, these teams showed the linker rigidification accompanying framework formation can freeze out modes of motion that facilitate nonradiative decay of molecular excited states. As a consequence, linker excited-state lifetimes increase, as do fluorescence intensities. Both, of course, are desirable changes if the goal is to exploit the linkers for light harvesting and subsequent energy transfer.

B. Ruthenium-based complexes as platforms for Dexter energy transfer

Previously, energy transport dynamics have been extensively studied in polypyridyl-based metal-to-ligand chart transfer (MLCT) excited states of Ru(II) to Os(II) in a variety of systems.[50-58] Recognizing the importance of ruthenium-based complexes as photoactive building blocks and as hopping intermediates for energy transfer, Kent *et al.* reported the synthesis of Zn((**L$_1$**•Ru)•2DMF•4H$_2$O) MOF (**1**), constructed from Zn^{2+} as connecting nodes and **L$_1$** as the linker (Figure 7a).[50] Irradiation with visible light yielded triplet MLCT (Ru → bpy) excited states with lifetimes of up to 171 ns. By lightly doping the ruthenium-based MOF with analogous osmium-containing linkers, and photophysical sensitization of the latter via excitonic energy transfer involving the former could be investigated (Figure 7).[50, 59] As demonstrated by time-resolved emission in Figure 7b, the lifetimes of Ru(II) excited states decreased as the doping level of Os(II) increased. An increase in Os(II) emission suggested that Ru-to-Ru excited state migration and Ru-to-Os energy transfer in osmium-doped **1** occurred.

Among the many interesting findings reported were that: a) energy transfer occurs mainly via the Dexter mechanism,[33] b) energy transfer is faster in these materials than in corresponding MOFs that only physically encapsulate Ru(bpy) species,[33] c) faster transfer is due to enhanced (but still comparatively small) electronic coupling through the MOF framework – specifically the carboxylate-zinc connections between chromophores,[33] d) a degree of directionality in exciton transport can be achieved,[33] and e) the photo-excited MOF is capable of engaging in electron transfer with surrounding solution-phase redox species.[50, 60]

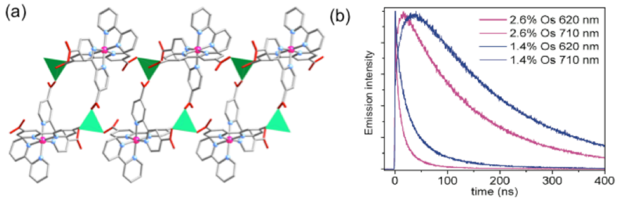

Figure 7. (a) Structure of Zn((**L$_1$**•Ru)•2DMF•4H$_2$O) MOF (**1**). Ru = pink spheres, Zn = green triangles, N = blue spheres, C = grey segments, O = red segments. (b) Transient emission decay profiles for 1.4 and 2.6 mol% Os-doped analog at 620 nm and 710 nm with emission at 620 nm dominated by Ru(II)* and at 710 nm by Os(II)*. Adapted with permission from ref. 50. Copyright 2010 American Chemical Society.

4. Future Outlook

The overall outlook for MOFs as light harvesting and energy transfer materials is promising. Nonetheless, there are important challenges that must be addressed in order to realize their full potential.

Beginning with the efficiency of the initial event of solar light absorption by the MOF, a key challenge is that the spectral overlap of the absorption features of MOFs with that of the solar spectrum must be improved. This can be done by considering new chromophores for the MOF struts with greater spectral overlap; from a synthetic perspective, selection of such chromophores can be done by checking the solution absorption spectra of the linkers of interest. Another more likely approach is through sensitization of MOFs with chromophores or quantum dots that absorb in spectral regions where the MOF struts do not absorb. From a synthetic perspective, solution absorption spectra provide a reasonable starting point for selecting linkers for photon harvesting. Such a sensitization effort has been shown to produce effective energy transfer into MOFs when placed on the MOF surface.[26] However, as we discussed in section 2A, a monolayer or less of sensitizer materials on the planar surface of a MOF does not have enough extinction to produce a significant increase in solar absorption efficiency. An approach to increase the ratio of sensitizer materials to MOF materials still must be found that does not adversely impact the efficiency of either the initial energy transfer event from sensitizer to MOF or the exciton transport itself within the MOF. Thus, simply adding more chromophores to produce more than one monolayer is not effective because the efficiency of energy transfer is much worse for those chromophores/QDs not in direct contact with the surface of the MOF crystals. A possible approach is to utilize the fact that MOFs are inherently porous and can accommodate additional chromophores. However, adding chromophores into these regions without negatively impacting electronic coupling between the struts that support exciton flow is critical. Without such considerations, the material added to the MOF could well increase overall absorption, but dampen energy flow to such a great extent that the materials will be useless as light harvesters. It is also important that the extinction of the struts in the spectral regions where they do absorb be great enough that they absorb most photons over a MOF thickness that is less than or equal to the exciton propagation length (perhaps a few tens of struts, although with close attention to MOF design, considerably larger propagation lengths can be envisioned). If the thickness of the MOF exceeds the exciton transport length, some excitons will not be captured and the quantum efficiency of the MOF in an energy-conversion application will suffer.

A second key challenge is to improve directionality and rate of energy flow. If excitons within a MOF can move with equal efficiency in three dimensions, then the overall energy "transport" distance is proportionally reduced by the cube root of the total number of MOF struts that the exciton reaches. Even in cases where energetic hops of nearly 100 distinct struts is possible, excitonic energy is only displaced over a modest distance from the originally excited strut, if the transport occurs randomly, rather than in a preferred direction.[43] Clearly, maximizing exciton transport distances will require careful attention to chromophore and framework symmetry, as well as properties like fluorescence quantum yield, chromophore oscillator strength, and other parameters that influence the rate of Förster energy transfer. Of course, all of this must be performed without sacrificing the overall integrity of the MOF structure or introducing defects that may unproductively trap excitons.

Recognizing that exciton transport typically is diffusive, one way of boosting transport distances would be to construct chromophore cascades – for example, via layer-by-layer synthesis of MOF films. Cascades of chromophores that each absorb only a portion of the targeted region of the solar spectrum may be attractive for other reasons, such as optimizing overall spectral coverage and light-harvesting efficiency. For 1-dimensional diffusion of excitons within a region of a MOF containing a given (single) chromophore, the net transport distance will scale as the square root of the number of excitonic hops. Thus, a thousand hops will achieve only ca. 3 times the net transport distance as 100 hops. If, however, the light-harvesting MOF contained, for example, five regions of equal thickness, each containing a single chromophore type, and if the regions were arranged appropriately to favour directional energy transport, the resulting cascade type behaviour, under optimized conditions would yield roughly twice the net exciton transport distance as achieved with an otherwise equivalent, single-chromophore MOF.

Closely related to the idea of cascades for light-harvesting is the concept of cascades for charge transport once an exciton has reached its intended destination and engaged in either interfacial electron transfer or hole transfer to a proximal electrode, catalyst, solution species, or other component. To our knowledge, this interesting problem has yet to be experimentally explored, at least in a systematic way. An open question is whether charge transport is best accomplished via site-to-site hopping or by charge-carrier migration or diffusion through a valence or conduction band. The question underscores, however, the close connection of the challenge of MOF photoelectrode development and MOF conductivity. A few reports have appeared for the latter,[61-65] and more can be expected.

The trade-offs between linker extinction, spectral coverage, exciton lifetime, degree of directionality of exciton transport, the degree of “cascading” in both energy and charge flow, and so on, are sufficiently intertwined and extensive to suggest that optimization of trade-offs might benefit greatly from high-throughput computational modelling and subsequent database mining. Indeed, this idea has proven valuable in the context of related, albeit simpler, MOF applications challenges, such as adsorption-based gas storage, and gas-mixture separation.[66-74]

Finally, it is necessary to incorporate the MOFs into devices for their application. By analogy to organic photovoltaic cells, this could mean sandwiching the MOF between electrodes, with a MOF orientation that optimizes directional energy and charge flow to the electrodes. The electrode materials would be chosen to allow electron (hole) injection with the available energy. Or, porous MOFs could be installed on appropriate semiconducting electrodes and then placed in contact with a redox-active electrolyte solution and used as photoelectrochemical energy conversion devices. Again, issues of energy transport, charge transport, and interfacial charge transfer will need to be understood and optimized.

5. Conclusions

Over the past five years, the notion of MOFs as compounds for photon collection and energy transfer, in the service of solar energy conversion, has advanced from a largely hypothetical one, to a nascent field encompassing more than twenty preliminary experimental and theoretical studies. Like chloroplasts in nature, MOFs are highly ordered structures capable of light collection and subsequent energy transport over long distances. However, MOFs have much wider chemical and structural modularity, enabling new and exciting possibilities for harvesting photons and controlling the method by which they transport energy. We suspect simultaneous optimization of linkers and supramolecular structure will be possible through a collaborative effort between synthetic, computational, and materials chemists. Indeed, efficient MOF-based excitonic solar cells may one-day soon become a reality.

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Notes and references

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