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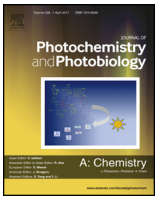

Invited feature article

Light-harvesting and energy transfer in ruthenium(II)-polypyridyl doped zirconium(IV) metal-organic frameworks: A look toward solar cell applications

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ABSTRACT

Metal-organic frameworks (MOFs) as highly ordered, tunable hybrid materials for photon collection, energy transfer and photocatalytic reactions have raised great interest. Understanding the light-harvesting and exciton transport processes within well-defined 3D solid phases will result in the better design of highly efficient biomimetic chromophore arrays for artificial photosynthesis. In this review, we summarize the fundamental principles of energy transfer in the condensed phase and overview a series of studies in light-harvesting, excited state quenching and photo-excited reactivity occurring within ruthenium-polypyridyl-doped zirconium MOFs. The application of MOFs in energy conversion devices such as dye-sensitized solar cells (DSSC) is also discussed.

1. Introduction

With increased consumption of fossil fuels, the demand for finding and using sustainable clean energy sources, such as solar energy, has grown in the past decades. Although the energy which the sun provides is approximately 10,000 times greater than the world's present rate of energy consumption, the current devices for converting solar energy to electrical power/chemical energy suffer from low efficiency, high cost and/or limited scale [1]. Three-dimensional porous coordination polymers, known as metal-organic frameworks (MOFs), constructed by metal ions/clusters and organic bridging molecules, have shown promise for applications in artificial photosynthesis and photocatalysis owing to their rich electronic properties, structural diversity, and synthetic tunability [2,3]. Incorporation of photoactive ligands into MOFs provides an attractive platform to study light harvesting, energy transfer, and photo-excited reactivity within highly ordered and well-defined architectures [4–7].

MOFs as functional materials for solar light-harvesting could be employed as sensitizer agents providing excited state energy to a neighboring material, or, conversely, as the material to be sensitized. Molecular chromophores, such as porphyrins and Ru/Os tris-bipyridine transition metal complexes, have been used as building blocks in MOFs capable of donating and/or accepting excited-state energy or electrons as described above [4,8–12]. For example, Hupp and coworkers have reported two different approaches to modifying porphyrin-based MOFs that display continuous absorption over the majority of the visible spectrum [4,9]. In one approach, they incorporated boron dipyrromethene (bodipy) and porphyrin complexes as complementary pairs of chromophores in the MOF material [13]. The bodipy linkers absorb and emit in the green spectral region and serve as antenna

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chromophores for the excitation of porphyrinic struts via resonance energy transfer. By incorporation of the porphyrin units, the absorption of the bodipy-porphyrin-based (BOP) MOF crystals is extended even further into the visible range so that the MOF crystals appear nearly black compared to just the bodipy-only MOF material [4]. Another strategy demonstrated by the Hupp group is the surface functionalization of porphyrin-based MOFs with quantum dots (QDs), which serves to enhance the light harvesting capability of the hybrid material. The QDs are highly absorbing in the near-UV to the visible region of the spectrum whereas the MOFs have smaller absorption cross-sections but absorb further in the visible to the near-IR region of the spectrum [9]. Together, the light-harvesting efficiency of the hybrid material is, therefore, significantly improved. With CdSe/ZnS core/shell QDs chemically attached to the MOF surface, the QD-MOF hybrids could compensate for the relatively narrow absorption spectra of single-chromophore MOFs [9].

Lin, Meyer and coworkers used $Ru(bpy)_3^{2+}$/$Os(bpy)_3^{2+}$-derivative linkers (bpy = 2,2′-bipyridine) and Zn^{2+}-based connecting nodes to synthesize a phosphorescent MOF [7]. Long excited-state lifetimes ($\tau \sim 375$ ns) were observed in crystals containing only $Ru(bpy)_3^{2+}$. Upon doping the $Ru(bpy)_3^{2+}$-Zn^{2+} MOF crystals with $Os(bpy)_3^{2+}$ analog linkers, rapid quenching of photoexcited $Ru(bpy)_3^{2+}$ due to energy migration to the $Os(bpy)_3^{2+}$ trap sites was observed [7,12]. The sensitization of the $Os(bpy)_3^{2+}$ complexes was proposed to occur via a Ru-to-Ru hopping mechanism to $Os(bpy)_3^{2+}$ trap sites located up to 40 Å from the excited state $Ru(bpy)_3^{2+}$ origin [7].

$Ru(bpy)_3^{2+}$ has also been incorporated into the porous, water stable framework UiO-67 [14]. By simple replacement of bipyridine ligands with 2,2′-bipyridyl-5,5′-dicarboxylic acid, Lin and coworkers doped $Ru(bpy)_3^{2+}$ into UiO-67 MOFs obtaining a solid-state photocatalyst.. The photocatalytic activities of the designed MOF material were investigated in Aza-Henry reactions, oxidative coupling of amines and oxidation of sulfides as model reactions [14]. The dependence of the photophysical behavior on $Ru(bpy)_3^{2+}$ loading was later probed by our group [10,15]. The changes in excited state lifetimes and spectral differences observed with increasing dye concentration were attributed to dipole–dipole homogeneous resonance energy transfer (RET) and loading dependent differences in incorporation/encapsulation environments (vide infra) [10,15].

MOFs have been shown to function as sensitizers for applications in dye-sensitized solar cell (DSSC) devices of differing arrangements. For example, Cu-based MOF thin films prepared by porphyrinic linkers and Cu(II) connecting nodes have been shown to generate photocurrent in TiO_2 based solar cells [16,17]. Although the cell performance of the Cu-MOF thin films was poor compared to conventional porphyrinic dye-based cells, statistically significant trends were observed upon increasing the surface content of the Cu-MOF indicating that MOFs, as highly ordered hybrid materials, afford exciting possibilities for harvesting photons and converting solar energy.

Excellent reviews have been written by Lin, Hupp and coworkers [13,18] discussing MOFs for photocatalysis and energy transfer. Therefore, in this perspective we have limited our focus to the work conducted on energy transfer in $Ru(bpy)_3^{2+}$-doped UiO-67 frameworks with an eye toward highlighting their potential application for sensitized solar cells [10,11,15,19]. For the most part, we discuss (a) different synthetic approaches to doping $Ru(bpy)_3$ into UiO-67 class MOFs; (b) the photophysical properties of the dopant within the MOF matrix and energy transfer mechanism studies performed on these doped MOFs, and (c) the application of these doped materials in photovoltaic devices.

2. Förster and Dexter energy transport in MOFs

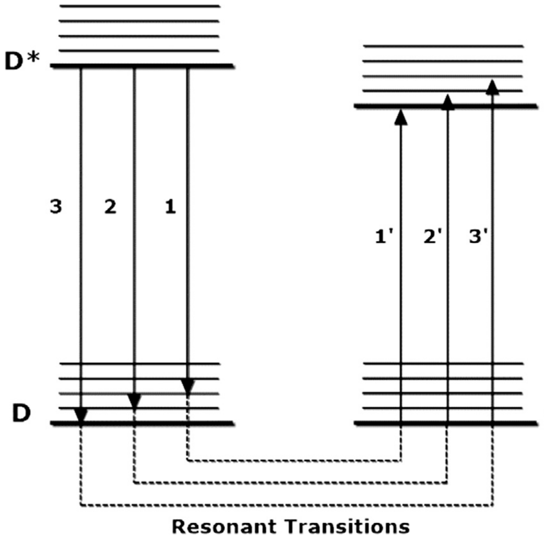
2.1. Resonance energy transfer

Resonance energy transfer (RET) is a non-radiative process in which a portion of the excited state energy of a donor molecule (or sensitizer) is transferred to a neighboring ground-state acceptor molecule, thereby producing an excited-state acceptor and ground-state donor [20–22]. This transfer of energy occurs due to either an exchange mechanism (Dexter) or Coulombic coupling between the transition dipoles of the interacting molecules (Förster, Perrin, etc.) (Scheme 1) [23,24]. Whereas the exchange mechanism occurs over short distances ($r_{DA} < 10$ Å), Coulombic coupling between donor (D) and acceptor (A) can occur over distances up to 100 Å.

There are three Coulombic coupling regimes that have been identified: a strong coupling, weak coupling, and very weak coupling (common referred to as the Förster limit) regimes. The strong and weak coupling regimes are characterized by a r^{-3} dependence on the rate of resonance energy transfer, k_{RET}, whereas Förster resonance energy transfer (or FRET) in the very weak coupling region is characterized by an r^{-6} dependence on k_{RET}.

2.2. Förster and Dexter energy transfer

Understanding the energy transfer processes in supramolecular architectures is an indispensable component to the appropriate design and application of those materials for solar energy conversion devices such as photovoltaics and photoelectrochemical cells. MOFs offer a rich diversity of unique platforms by which to study long-range energy transfer. By judicious choice of ligands and metal nodes, MOFs allow for precise control of distances and angles between chromophores and their alignment via crystal engineering [25]. Förster and Dexter resonance energy transfer mechanisms are the two most studied models for energy transfer in supramolecular light harvesting systems. The Förster model of resonance energy transfer (FRET) is dominated by weak long-range Coulombic dipole–dipole interactions. By contrast, Dexter resonance energy transfer (DRET) relies on stronger intermolecular interactions resulting in electron exchange due to donor-accepter



Scheme 1. Energy diagram depicting coupled transitions in resonance between an excited state energy donor fluorophore, D*, and quenching excited state energy acceptor, A.