# NANO-ORDERING OF DONOR-ACCEPTOR INTERACTIONS USING METAL-ORGANIC FRAMEWORKS AS SCAFFOLDS

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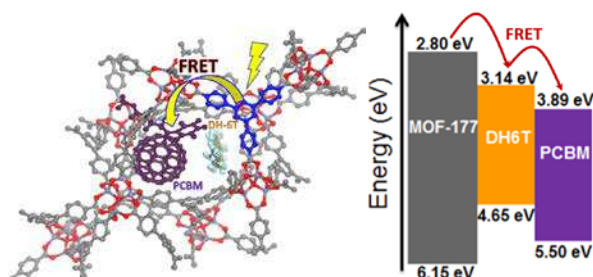
Organic photovoltaics (OPVs) are excitonic devices in which the absorption of light by an organic semiconductor with a low dielectric constant generates bound electron-hole pairs (excitons) that are subsequently dissociated in a charge transfer event at the interface with a second, electron-accepting organic semiconductor. The mechanism of charge separation in polymeric bulk hetero-junction photovoltaic cells is described as electron transfer from the absorbing polymer to an electron acceptor material. Two factors limiting the performance efficiency of OPV devices are the nature of the donor-acceptor (D-A) interface and the exciton diffusion length, which in conjugated polymers is typically < 10 nm before recombination occurs.[1] Much OPV research is directed toward ensuring that the D-A materials form continuous nanoscale networks within the entire photoactive layer, that their interfacial area is maximized, and that they have the proper orientation for efficient exciton splitting.[2] A nanoscale interpenetrating network with crystalline order of both constituents is therefore a desirable architecture for the active layer in photovoltaic devices.[3,3b] Unfortunately, control over both the intermolecular (D-A) and meso (exciton diffusion) length scales is extremely difficult to achieve in conventional bulk heterojunctions due to the inherent disorder of polymeric and/or molecular species in a (typically) amorphous matrix. Further complicating this situation is the need for proper alignment of the D and A electronic bands to enable efficient harvesting of the solar spectrum as well as exciton splitting, which limits the extent to which the chemical structure of D and A can be modified to promote local ordering.

MOFs are a class of hybrid supramolecular materials formed from metal cations or clusters serving as "nodes" connected to multi-topic, electron-donating organic ligands, creating ordered networks with permanent nanoporosity.[4] MOFs possess three critical properties relevant to controlling donor-acceptor interfaces. First, they are crystalline materials, which create a highly ordered and well-defined structure in which the position of all framework atoms is known with sub-angstrom precision. Second, they incorporate both inorganic and organic components, providing an unprecedented ability to tune the electronic structure. This also enables the pore size and chemical environment to be tailored.[5] Third, the rigid MOF structure creates permanent nanoporosity (1–10 nm diameter), which

enables the fabrication of hybrid composites by filling the pores with guest molecules. This suggests that MOFs can serve as passive hosts to maintain close proximity and proper intermolecular alignment between donor and acceptor for efficient energy or charge transfer.

In this presentation, the photo-physical effects of confining an electron donor, α,ω-dihexylsexithiophene (DH-6T), and an electron acceptor, [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), in several MOFs will be discussed. We demonstrate infiltration of both molecules into MOF pores and use luminescence and absorption spectroscopies to characterize the MOF-guest energy transfer processes. Comparisons with density functional theory allow us to determine the energetics and band alignment within the MOF. In addition, MOFs can function as photo-antennas to harvest photons, resulting in an energy transfer cascade to infiltrated molecules. The modification of MOF electrical conductivity will also be discussed. These results demonstrate the utility of MOFs as scaffolds for sub-nanoscale ordering of donor and acceptor species within a highly uniform environment, allowing both the interaction and separation distance to be much more controlled than in the classical bulk heterojunction. A nanoscale interpenetrating network with crystalline order of both constituents is therefore a desirable architecture for the active layer in photovoltaic devices. In addition, this system serves as a prototype for other confined D-A systems that can tuned for other photovoltaic materials.

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