Nanoporous Metal-Organic Frameworks: Promising Elements for Next Generation Hybrid Organic Photovoltaics

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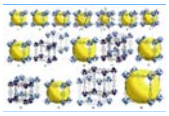
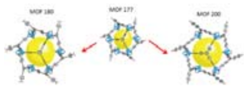
Background and Motivation

- Metal Organic Frameworks (MOFs) are a class of highly ordered, self assembled, supramolecular materials.
- MOFs are created when transition-metal nodes are linked together by synthetically-tunable organic linkers and pillars to form nanoporous crystalline structures.
- By varying the composition of the MOF building blocks, it is possible to tune the chemical, structural, optical, and electronic properties of these versatile materials with sub-nanoscale precision.

Schematic depiction of a crystalline MOF structure comprising metal nodes (M), linkers (L_1) and pillars (L_2). The nanoporous character of the MOF allows incorporation of molecular guests, organized on the nanoscale.

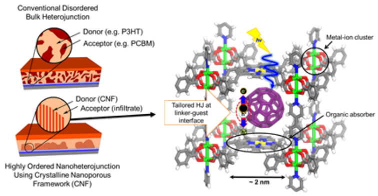


http://yaghi.berkeley.edu/research-MOF.html

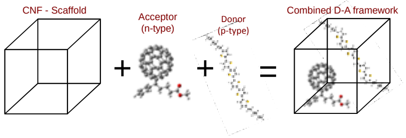


http://www.cchem.berkeley.edu/molsim/teaching/fall2011/CCS/Group7/structure.htm

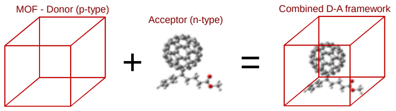
- We are exploring the application of tailored MOFs to direct ordered nanoscale interactions between donors and acceptors in hybrid organic photovoltaics (HOPV).
- MOFs promise highly ordered donor-acceptor interactions on length scales smaller than exciton diffusion lengths, potentially improving carrier recombination and charge transport efficiencies.
- Potential tunability of MOF optoelectronic properties may also lead to desirable optical absorption across a broad excitation spectrum.



Passive Scaffolds - the MOF serves as an inert structural scaffold, ordering donor/acceptor materials.



Active Network – the MOF is designed to play an active role in the PV energy conversion process as a donor, acceptor, charge transport material.



Density Functional Theory Guides MOF-PV Strategy

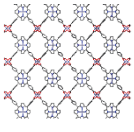
Passive MOFs offer promise coordinating interactions between donors (e.g., thiophenes) or acceptors (e.g., PCBM).

(B6.91: "Nanoscale Phase Segregation of a Molecular System using Metal-Organic Frameworks for Energy Transfer")

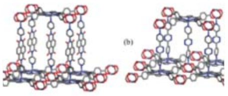
Here, though, we focus on integrating Active Network MOFs into an inverted device configuration, wiring MOFs directly to electron transport layers (e.g., TiO_2).

Consider Pillared Porphyrin Frameworks (PPFs)

In PPF MOFs, transition metal cations coordinate the assembly of photoactive metalloporphyrins into sheets, stacked atop molecular pillars.



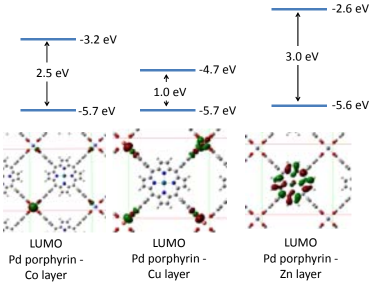
2D porphyrin sheet commonly found in PPF series



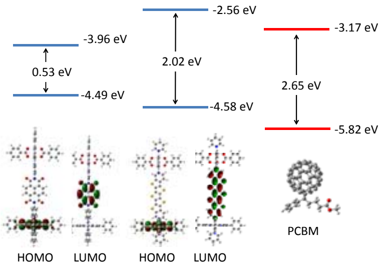
Side view of PPF-18
Chung *et al. Crystal Growth & Design, Vol. 9, No. 7, 2009*

Density Functional Theory (DFT) simulations show that by varying the composition of PPF molecular building blocks, it is possible to tune the electronic band structure of these MOFs.

Varying transition metal ions



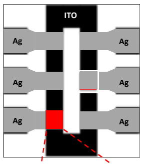
Varying organic pillars



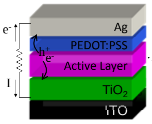
2D periodic optimization - DFT(B3LYP/ CEP-31G)

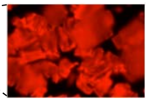
Integrating PPF MOFs into PV Device Structures

***Challenge:** Can we develop the chemistry to integrate these versatile materials into HOPV devices?*



Patterned ITO and Ag define 0.1 cm^2 device areas.



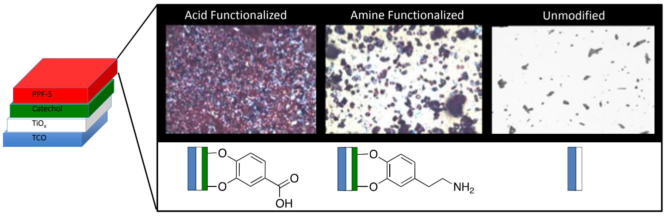


Photoactive PPF-5 MOF incorporated into active layer of "inverted" HOPV device.

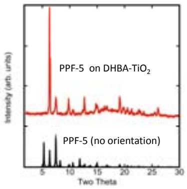
Direct Nucleation of PPF MOFs onto an ETL would provide an excellent interface for charge transfer. Nucleation and growth of PPF-5 crystals onto the electron transport layer.

A TiO_x electron transfer layer was deposited on test substrates with Atomic Layer Deposition and annealed at 300°C.

Substrates were then incubated in aqueous 3,4-dihydroxybenzoic acid or dopamine to provide acid or amine functionalization.



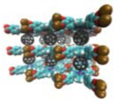
TiO_x was deposited with Atomic Layer Deposition and functionalized with. Acid functionality was found to better promote the nucleation and growth of PPF-5 compared to bare and dopamine-modified TiO_x surfaces.



Grazing Incidence XRD shows growth of PPF-5 with preferential (001) orientation (red).

Ongoing and Future Work

Continue exploring the growth of new PPF materials, rationally designed for optimal molecular ordering and charge transfer.



Explore alternative methods for MOF-thin film growth (e.g., layer by layer).

Angewandte Chemie (2009) 48, 5038-41

Photovoltaic testing of MOF-integrated devices.

Funding Acknowledgement

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