

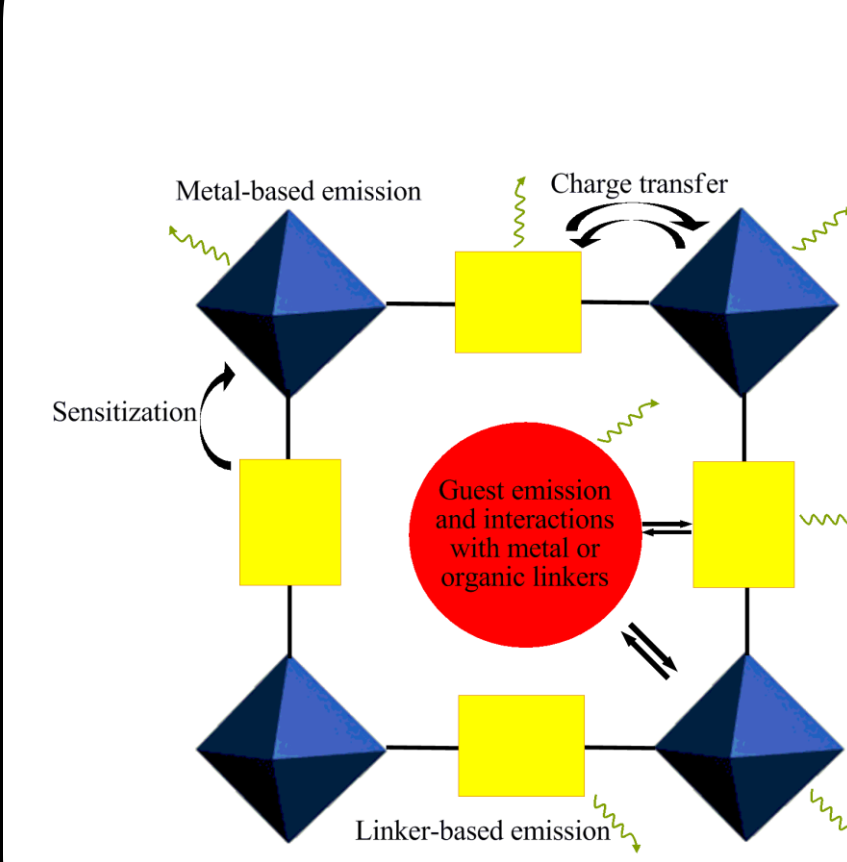
# Highly Ordered Crystalline Nanoporous Frameworks for Nano-heterojunction Photovoltaics

Kirsty Leong<sup>1</sup>, Scott T Meek<sup>1</sup>, Bryan M Wong<sup>1</sup>, Michael E Foster<sup>1</sup>, Erik D Spoerke<sup>2</sup>, Timothy N Lambert<sup>2</sup>, Mark D Allendorf<sup>1</sup>

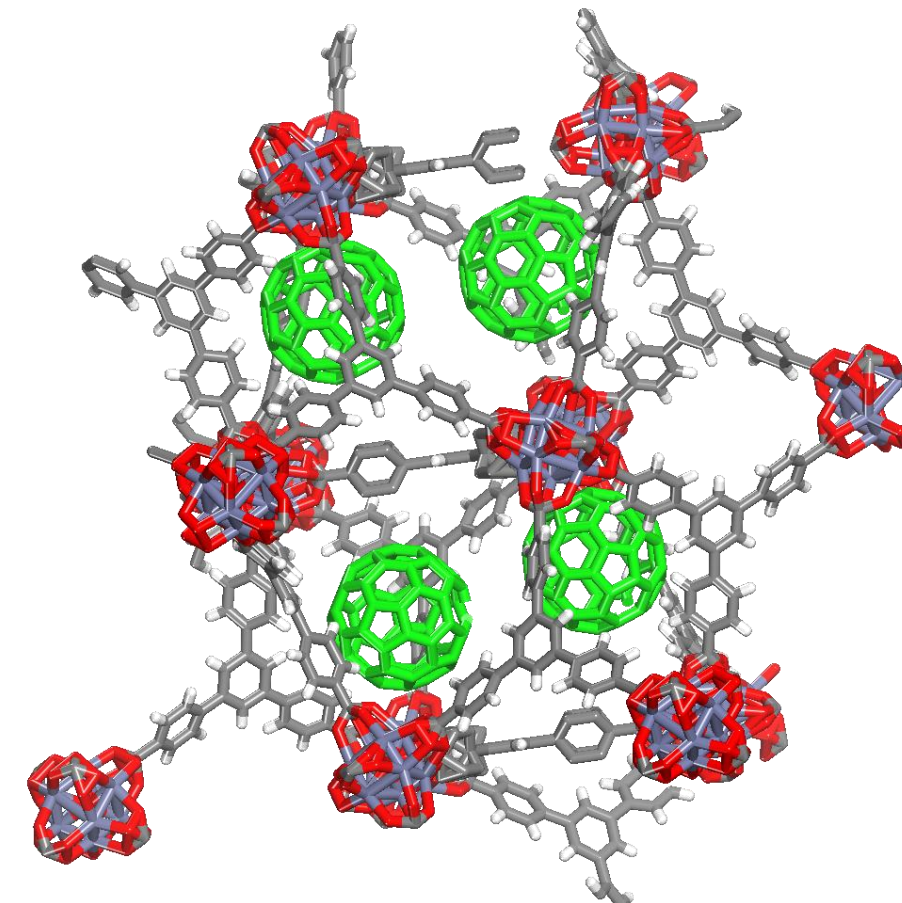
<sup>1</sup>Sandia National Laboratories, Livermore, California, USA;

<sup>2</sup> Sandia National Laboratories, Albuquerque, New Mexico, USA

## Introduction



Crystalline nanoporous frameworks (CNFs) represent a class of hybrid materials composed of ordered networks formed from metal cations or clusters of "nodes" connected by multi-tropic organic linkers. The presence of both inorganic and organic components enables both the pore size and chemical environment to be tailored to achieve specific properties. In addition, these crystalline structures exhibit high surface area, tunable pores sizes, structural flexibility, and can act as hosts for a variety of guest molecules. CNFs display a wide range of luminescent behaviors resulting from the multifaceted nature of their structure. CNF possess an attractive, alternative platform for achieving long-range organization and order. Thus they can be incorporated into light-harvesting devices and in the conversion of solar energy to electrical or chemical energy. These attractive properties make MOF versatile materials that can function as integral, active, and functional components in MOF-based devices. In this study, we probe the nano-confinement of an acceptor molecule (PCBM) in CNF.



## Luminescent Metal-Organic Frameworks

### Motivation

- Crystalline nanoporous frameworks (CNFs), allows for detailed control over key interactions at the nanoscale so that the disorder and limited synthetic control inherent in conventional excitonic heterojunction (HJ) materials can be overcome.
- The aim is to develop novel heterogeneous materials that will serve as platforms for probing both fundamental properties pertaining to PV energy conversion and the electronic and structural interplay at interfaces.

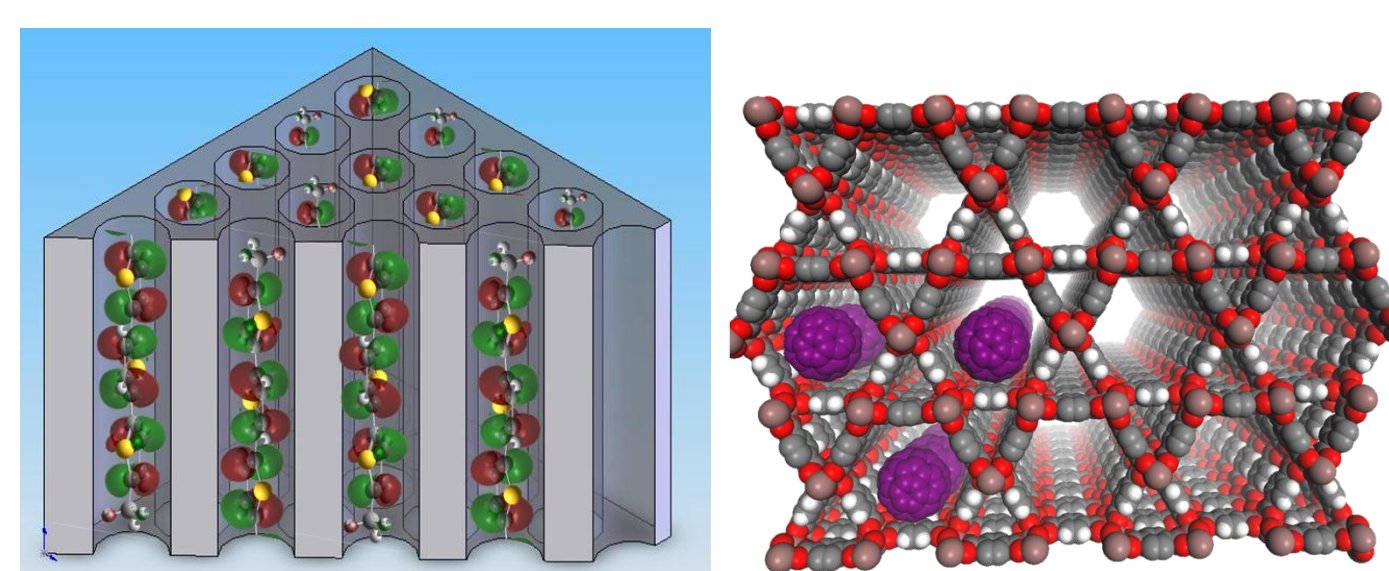


Figure 1. Schematic diagram of a MOF with donor/acceptors in the pores.

- These structural features create many opportunities to tune the interaction between light and the framework and between the framework and constituents in the pores cavities.
- The origins of MOF luminosity include the linker, the coordinated metal ions, antenna effects, excimer and exciplex formation, and guest molecules.



Figure 2. Schematic diagram of a MOF with tunable functionalities.

- Metal-organic frameworks (MOFs) provide many opportunities to tune energy transfer and the associated luminescence spectrum and time dependence.
- Tunable pore sizes using different linkers can result in changes in the LUMO and HOMO levels

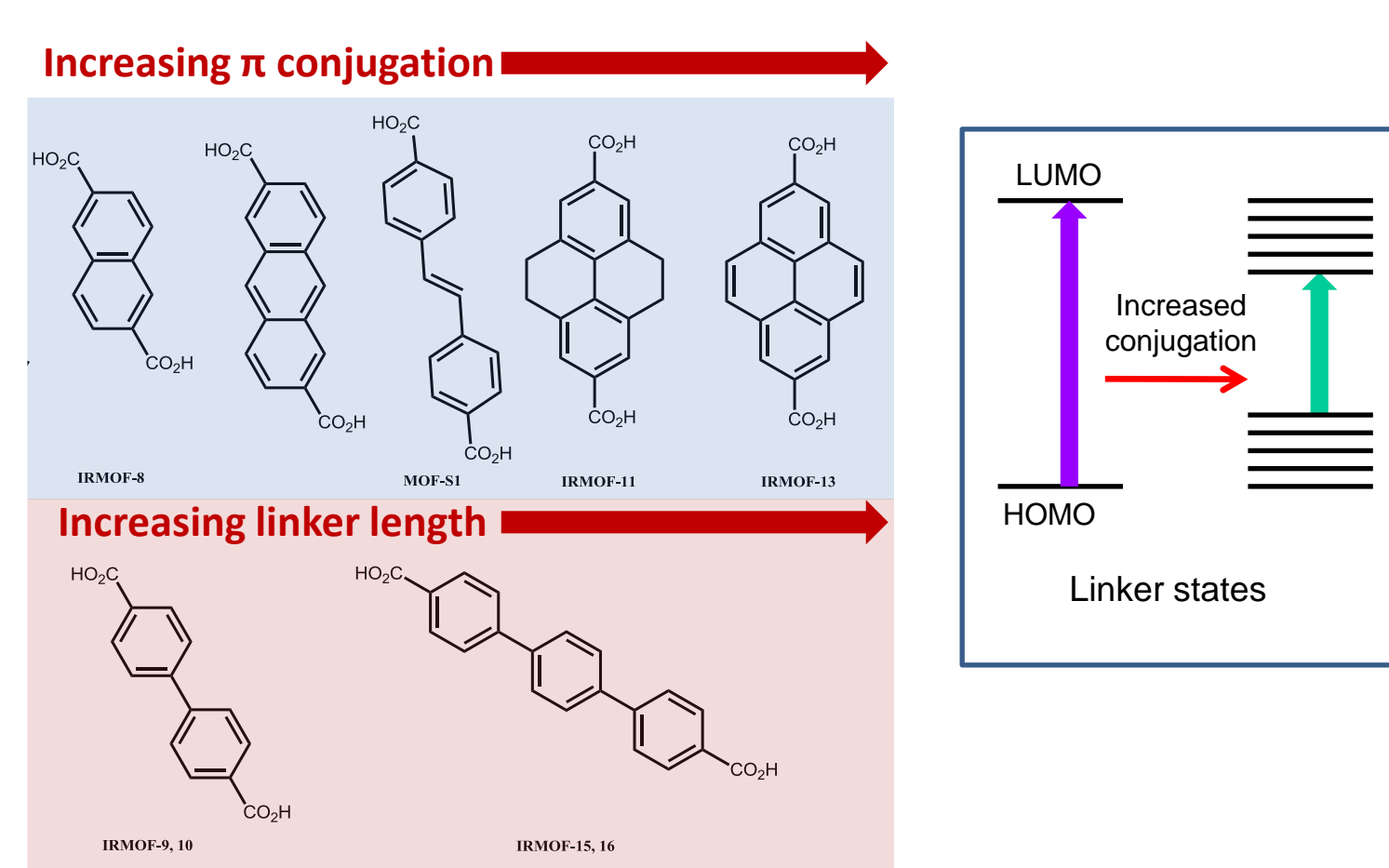


Figure 3. Increasing the conjugation and linker lengths affects the luminescence of MOFs.

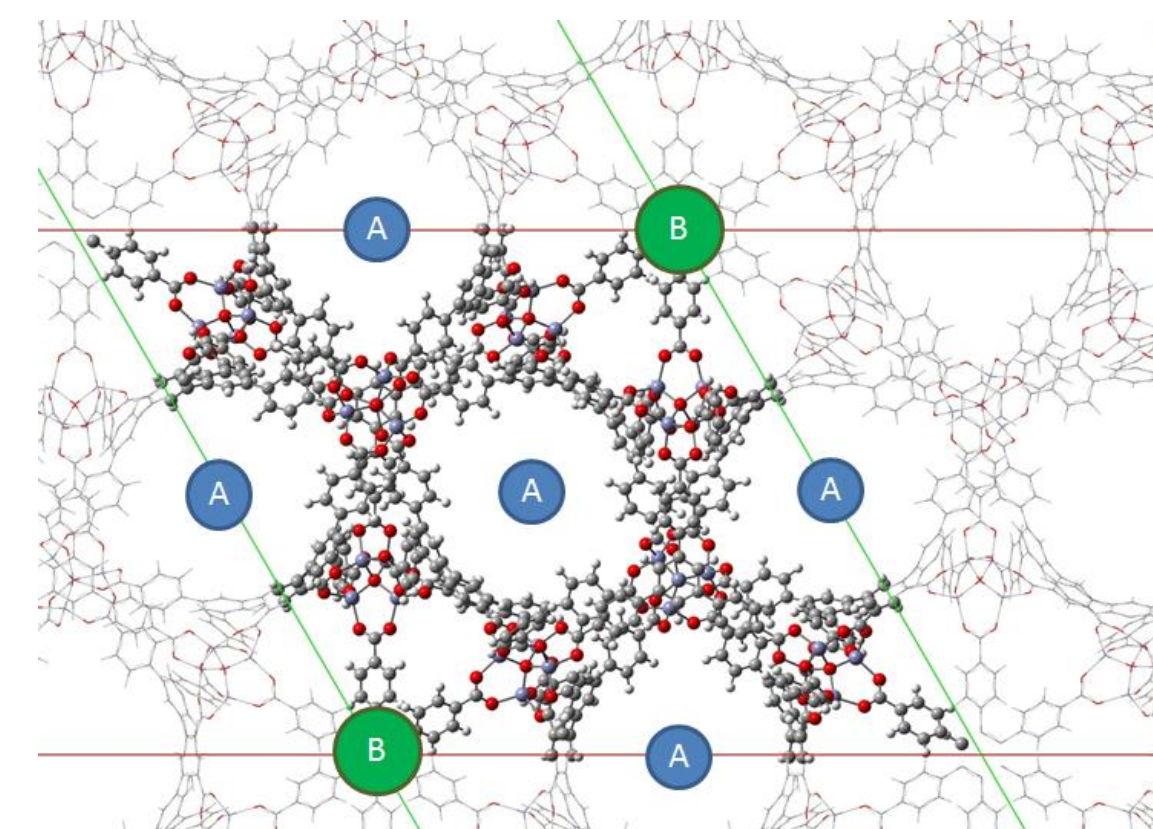
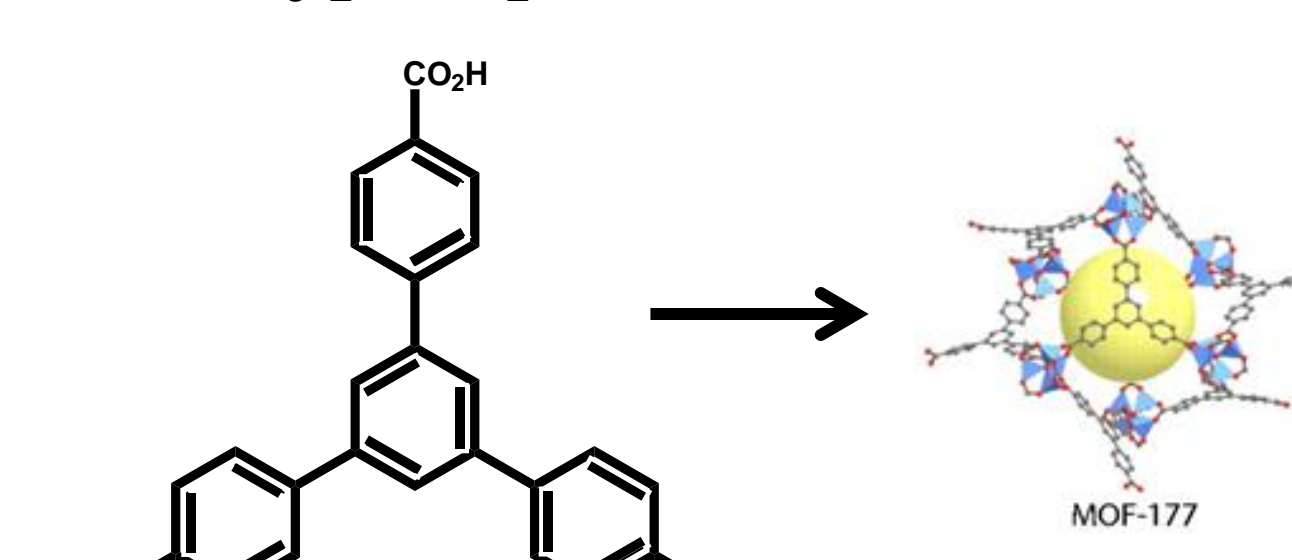
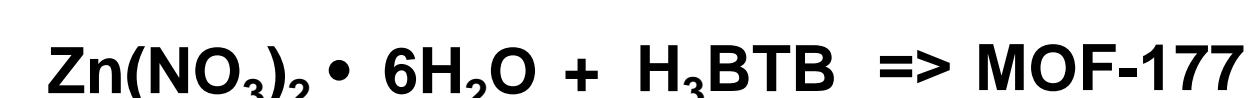


Figure 4. DFTB optimized structure of MOF-177.

### Synthesis and Characterization of MOF-177



- Micron-sized colorless crystals with 6,3-coordinated net: the centre of the octahedral  $\text{OZn}_4(\text{CO}_2)_6$  cluster as the site of 6-coordination and BTB unit site the 3-coordination.

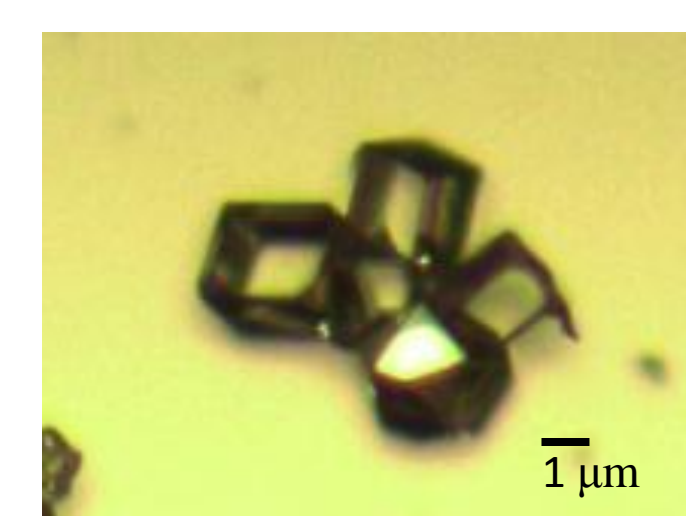


Figure 5. Optical images of MOF-177 crystals.

- DFTB optimized structure shows that MOF-177 has two unique cavities, cavity A and B (9:4 ratio) shown left. The pore diameter is < 20 Å in diameter. The diameter of the cavities are approximately 14 Å and 24 Å.

- Photoluminescence spectra of MOF-177 and its linker reveal the emission originates from the linker itself. The Zn-metal cluster does not play a role in the framework's emission.

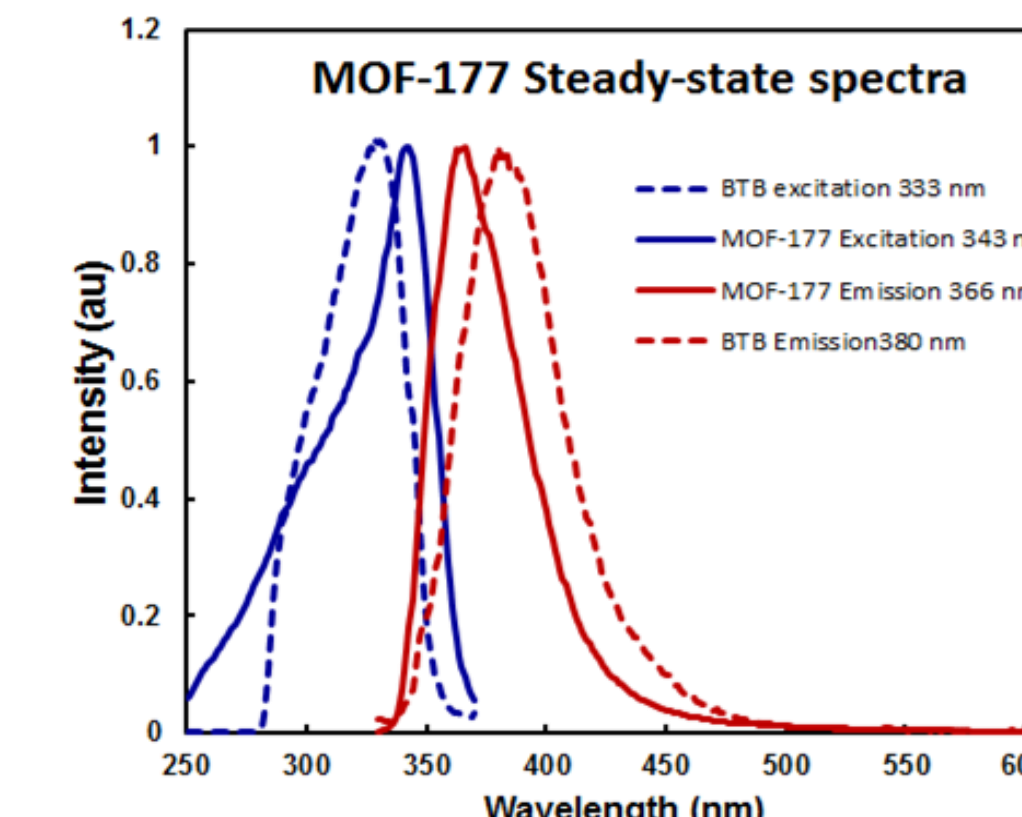


Figure 6. Excitation and Emission spectra of MOF-177 and BTB linker.

- X-ray diffraction shows framework crystallinity and stability. Infiltrating MOF-177 with PCBM does not change the framework orientation.
- There is almost no preferred orientation after sample preparation

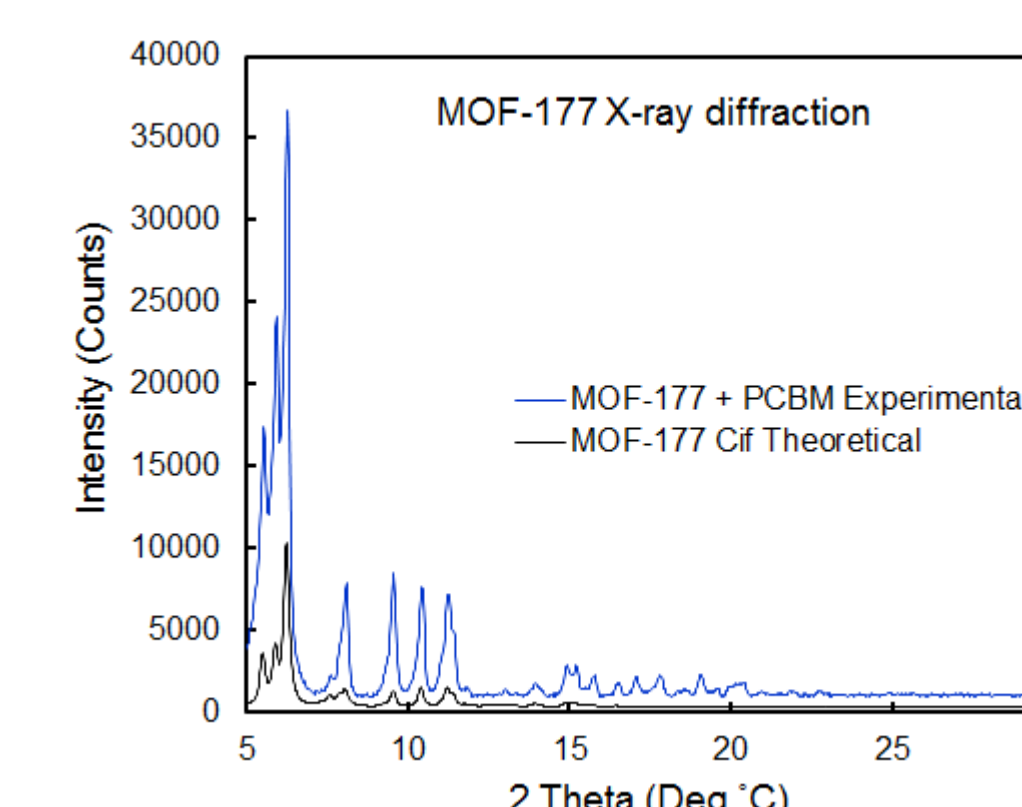


Figure 7. XRD powder pattern of MOF-177-PCBM complex taken in reflection mode.

## Probing the Nano-confinement of PCBM in Metal-Organic Frameworks

### Crystalline Nanoporous Systems

- Create systems that allow manipulation and control of the intimate assembly and communication between the different nanoscale PV components so we can understand and then engineer the system to allow these materials to optimized their functionality.
- These span a range from ionic coordination bonds between positively charged metal ions and negatively charged organic donors to fully covalent bonding. Organic "linkers" serve as both structure-directing elements and as functional groups that impart specialized properties such as luminescence and selective molecular adsorption.
- CNF posses three critical properties: 1) crystallinity, which creates a highly ordered and well-defined structure; 2) permanent nanoporosity (1 – 5 nm diameter), which enables the fabrication of hybrid structures by filling the pores with a second material; and 3) both inorganic and organic components, providing an unprecedented ability to tune the electronic structure.

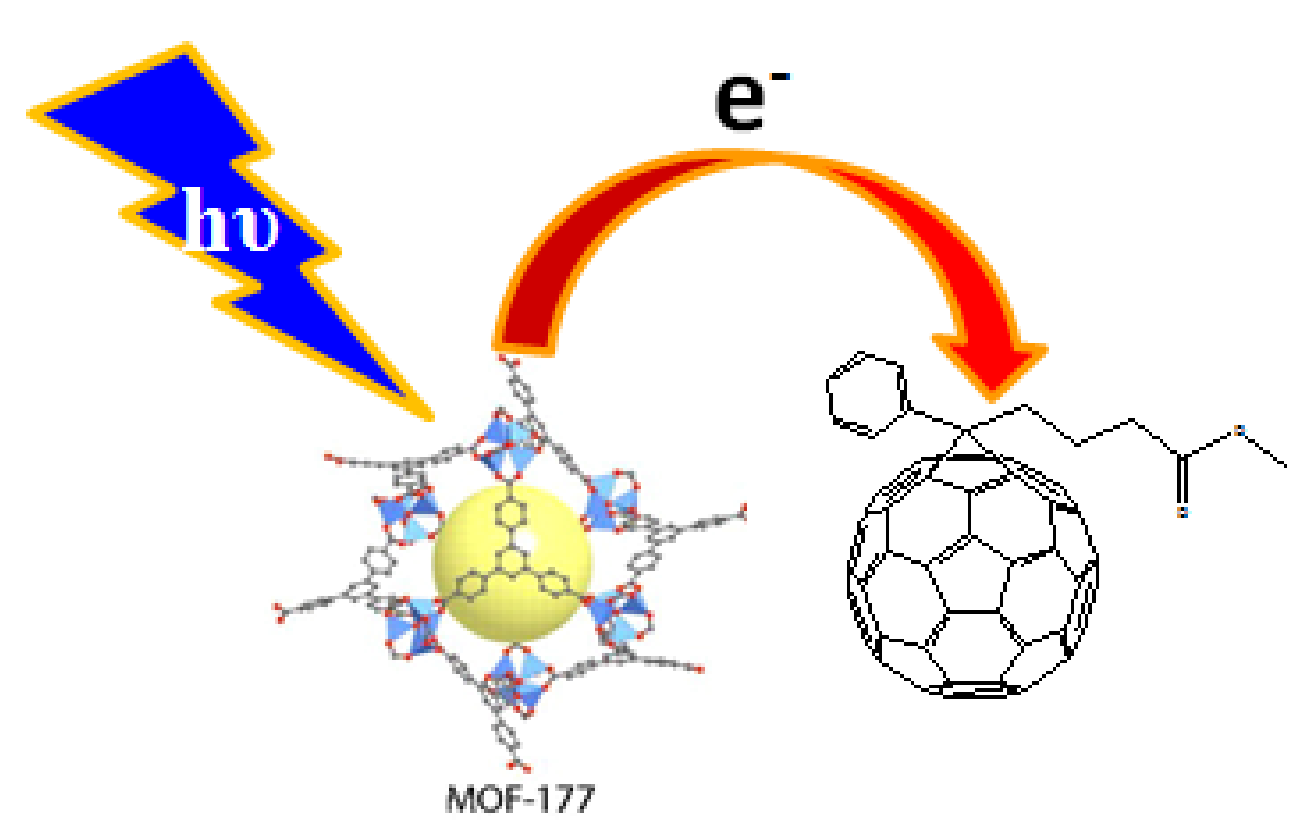


Figure 8. Schematic of charge transfer from MOF-177 to acceptor PCBM.

- DFTB + Optimized Structure: MOF-177 infiltrated with one PCBM per cavity. Modeling calculation predicts only one PCBM molecule can occupy into cavity A and two PCBM molecules per cavity B.

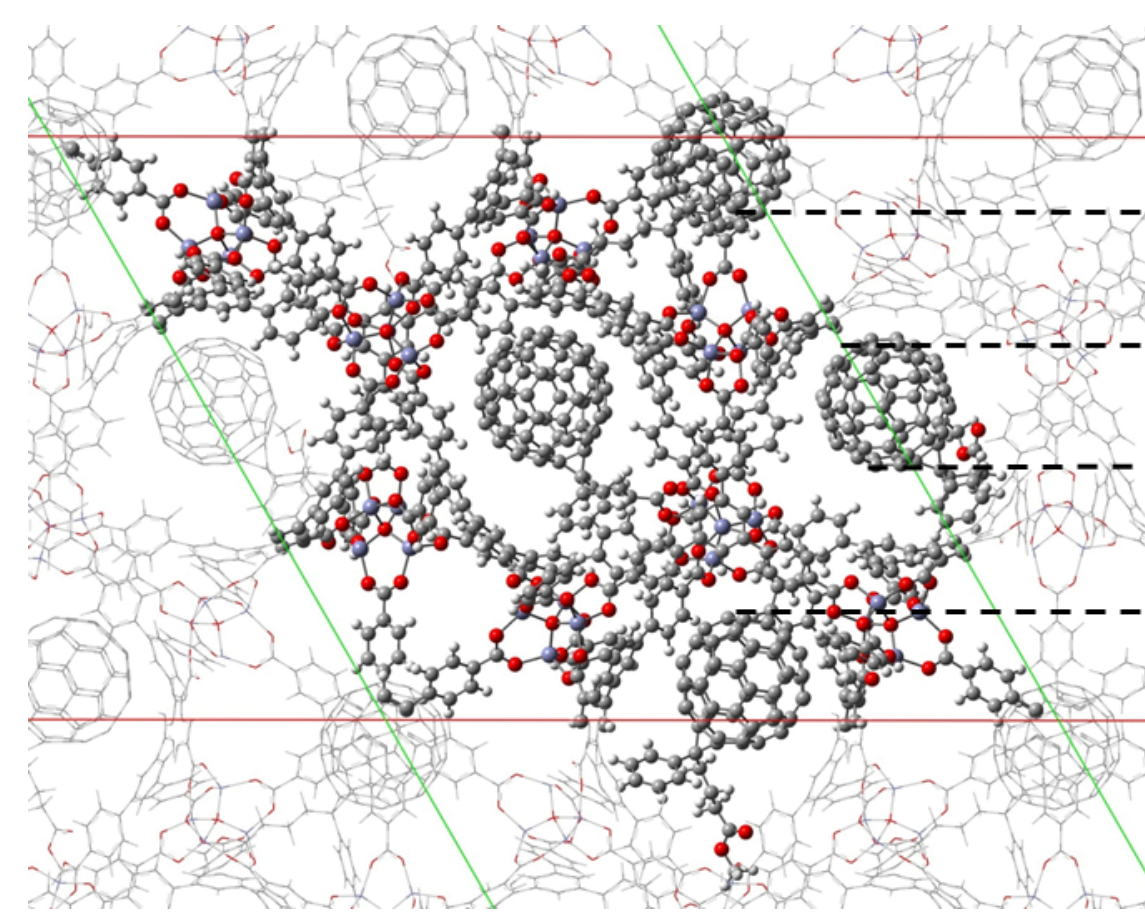


Figure 9. DFTB calculated optimized structure of MOF-177-PCBM complex.

### MOF-177 and PCBM Complex

- Observations of a color change from clear and colorless to a deep purple indicating PCBM pore occupancy in MOF-177.
- Slicing the MOF-177 crystal exposed the inner core of the crystal which shows inclusion of PCBM is not only in the exterior of the crystal, but also in the interior. Evenly colored throughout and uniformity of inclusion.

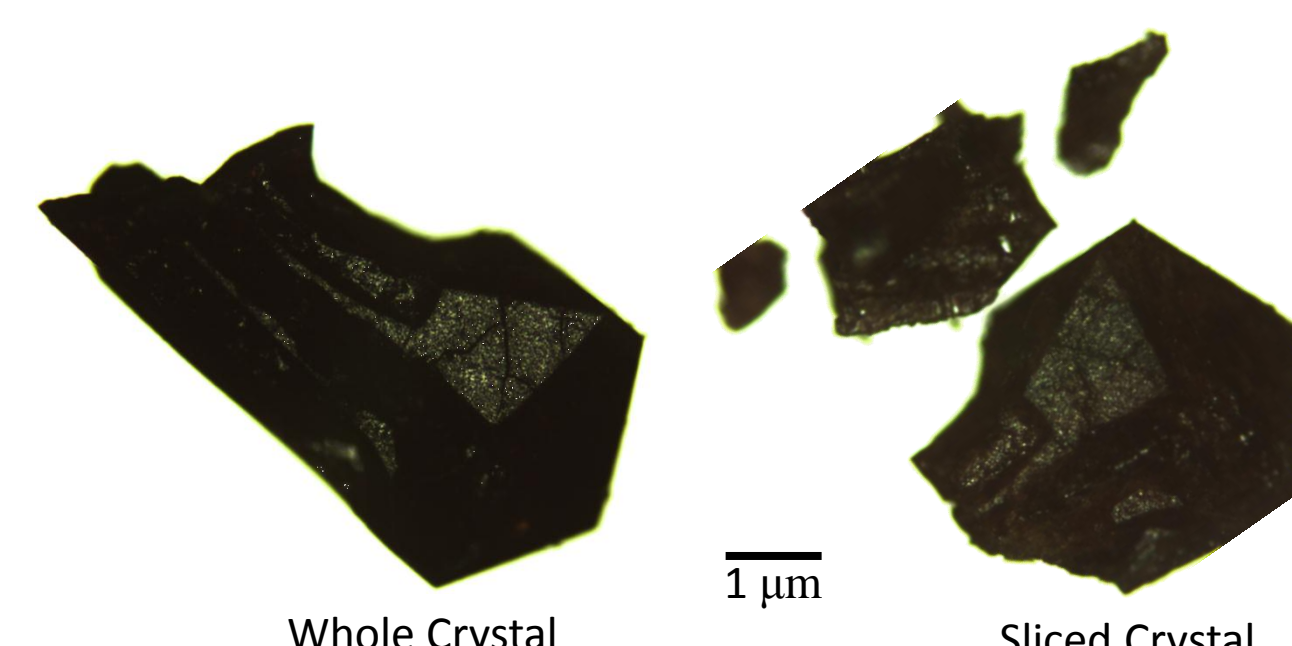


Figure 10. Optical images of a whole (left) and sliced (right) MOF-177-PCBM complex crystal.

- Emission of MOF-177 is quenched when infiltrated with PCBM.

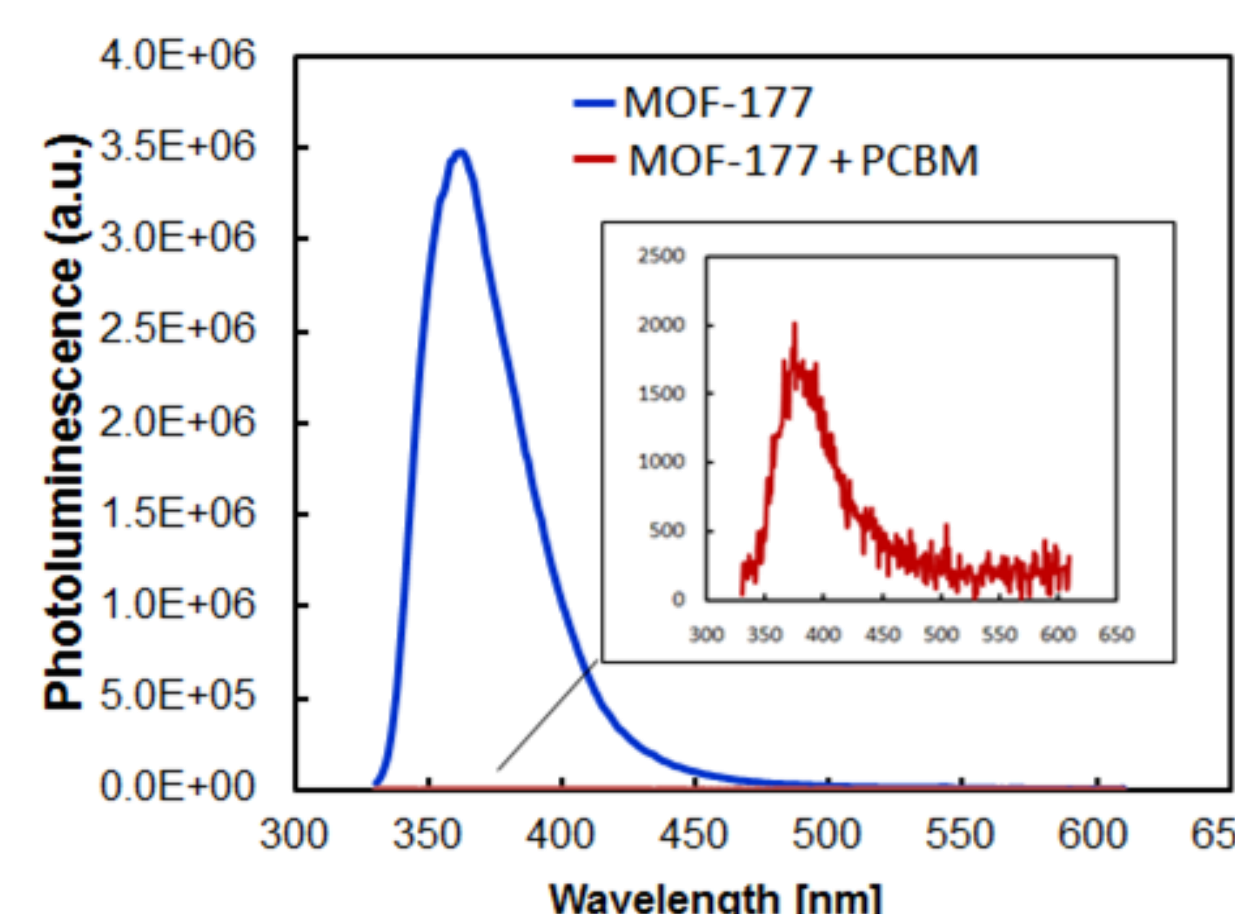


Figure 11. Photoluminescence spectra of MOF-177 (blue) and MOF-177-PCBM complex (insert in red).

- The lifetime of MOF-177 decreases dramatically upon infiltration with PCBM.

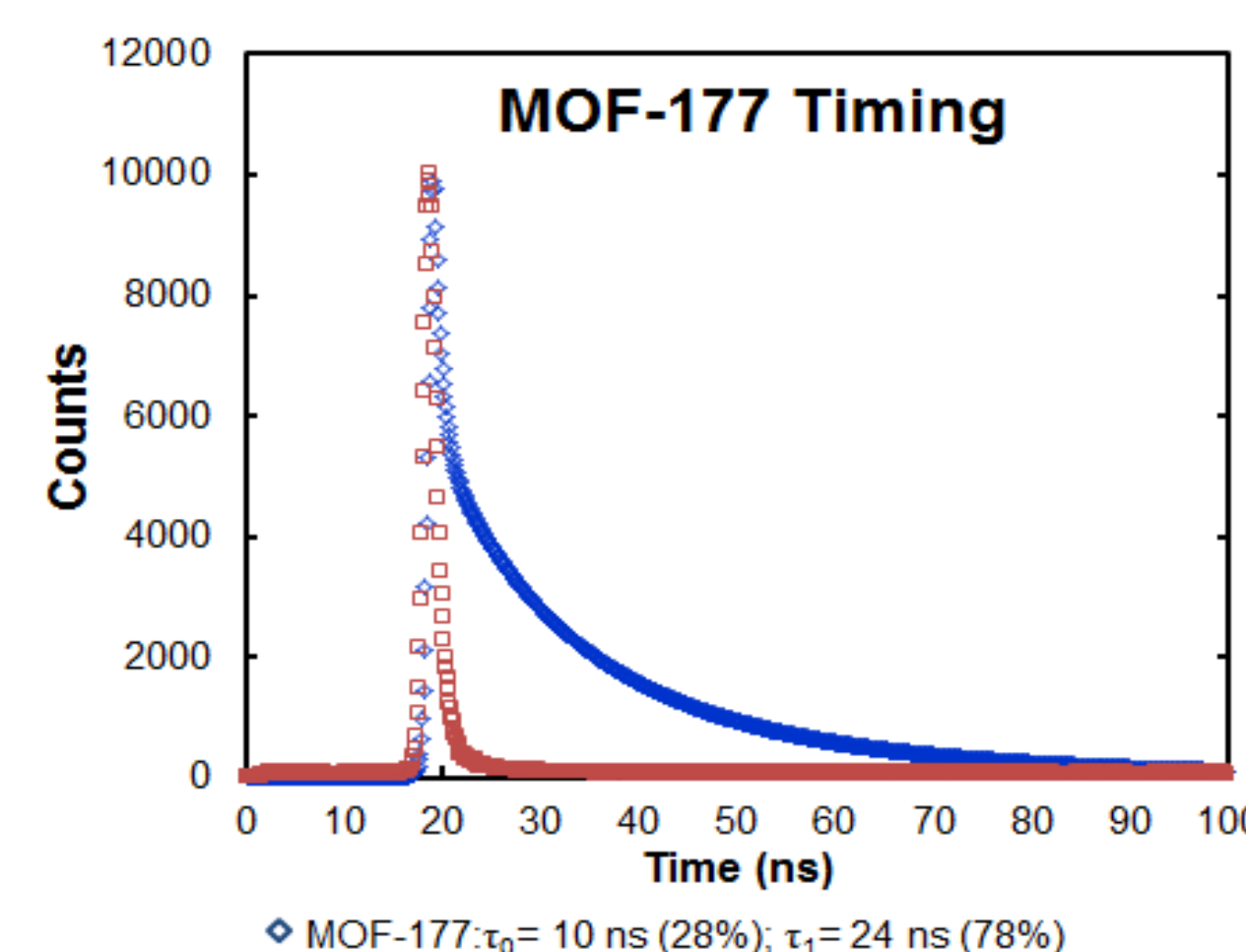


Figure 12. Lifetime measurements of MOF-177 (blue) and MOF-177-PCBM complex (red).

### Quenching Interactions between MOF-177 and PCBM

- Two types of fluorescence quenching can occur: (1) static quenching through the formation of ground state complex; and (2) dynamic quenching due to diffusive collisions between the PL emitter and quencher.
- At low quencher concentrations, the interactions can be described by the Stern-Volmer equation.  $\text{PL}_0/\text{PL} = 1 + K_{\text{SV}}[\text{quencher}]$

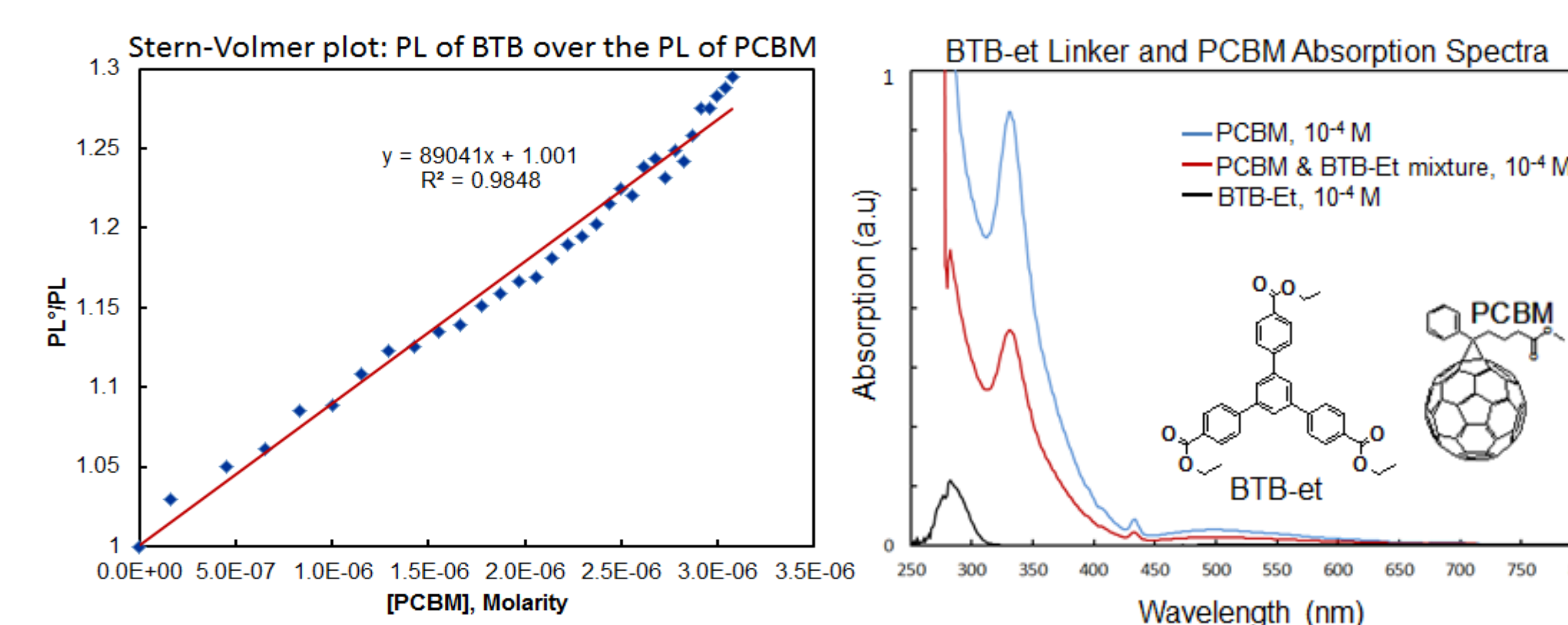


Figure 13. Stern-Volmer plot of PL quenching of BTB by PCBM (left) and UV-vis absorption spectra of BTB (black), PCBM (blue), and BTB-PCBM (red) complex (right)

- The dependence on PCBM quenching concentration is linear with  $K_{\text{SV}} = 8.9 \times 10^4 \text{ M}^{-1}$ .
- In dynamic quenching, the collisions between PCBM and BTB affects the excited state of BTB only. Thus no changes in the absorption spectrum are observed.
- To probe the presence of PCBM, a MOF-177 and PCBM complex was analyzed by Raman spectroscopy.

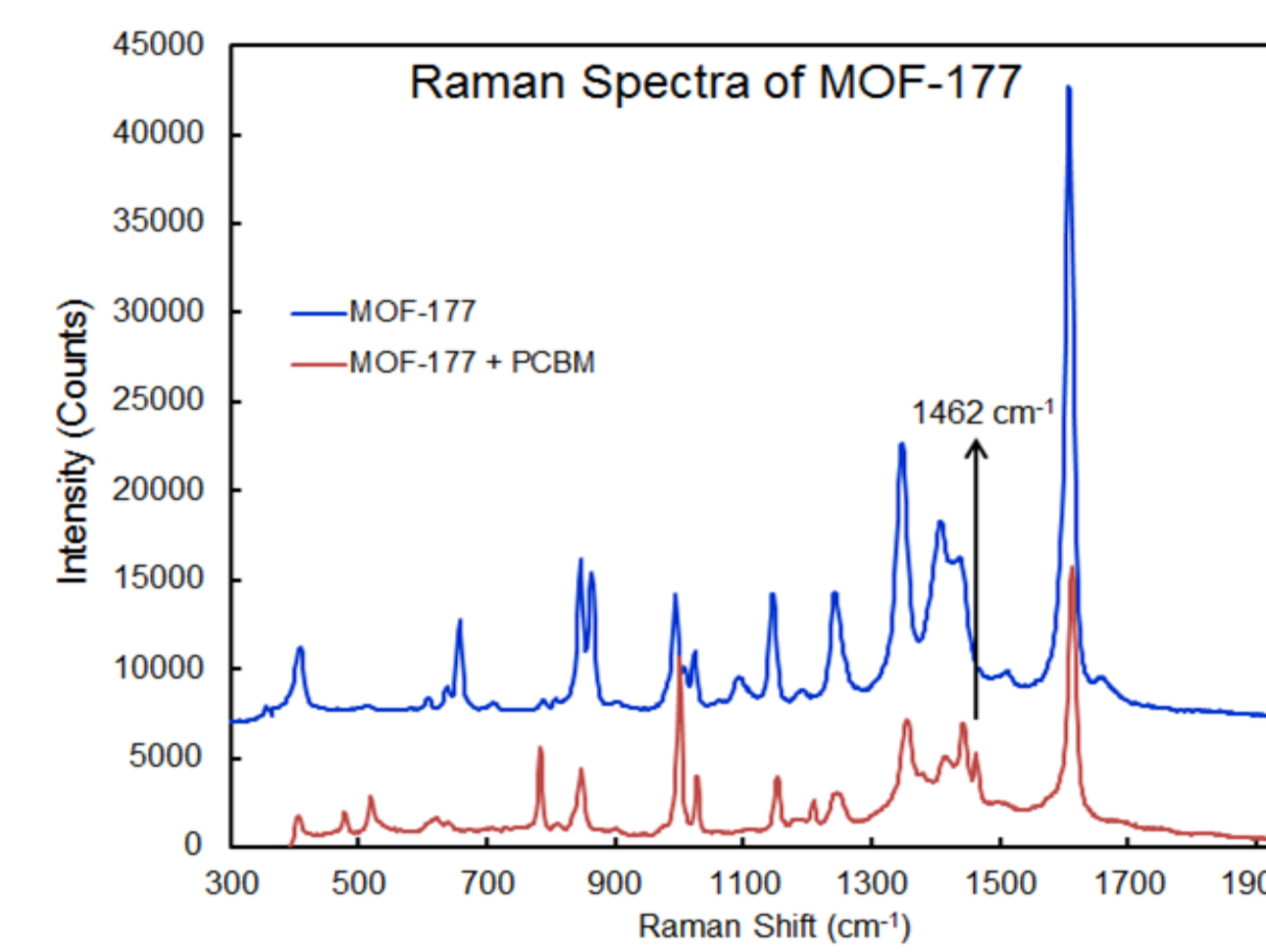


Figure 13. Raman spectra of MOF-177 (blue) and inclusion of PCBM into MOF-177 (red).

- Comparing the vibrational spectra of MOF-177 and MOF-177-PCBM complex, signature peaks corresponding to MOF-177 is slightly red-shifted when infiltrated with PCBM, indicating interaction with the framework.
- A new peak observable in the MOF-177 and PCBM complex at a Raman shift of 1462 cm<sup>-1</sup> corresponds to the C<sub>60</sub> A<sub>g</sub>(2), "pentagonal pinch" mode.<sup>3</sup>

References:  
[1] Chae, H. K., Siberio-Pérez, D. Y., Kim, J., Go, Y. B., Eddaoudi, M., Matzger, A. J., O'Keeffe, M., and Yaghi, O. M., Nature 2003, 427, 523-527.  
[2] Allendorf, M.D., Bauer, C.A., Bhakta, R. A., and Houk, R. J. T., Chem. Soc. Rev., 2009, 38, 1330-1352.  
[3] (a) Yoo et al., Nanoscale Research Letters 2011, 6, 545. (b) Bethune et al. Chem. Phys. Lett. 1990, 174, 219.

### Acknowledgements:

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. With main facilities in Albuquerque, N.M., and Livermore, C.A., Sandia has major R&D responsibilities in national security, energy and environmental technologies, and economic competitiveness. SAND #