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Computational method development to energy and charge transfer within infiltrated metal-organic frameworks

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U.S. DEPARTMENT OF ENERGY

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Organic photovoltaics

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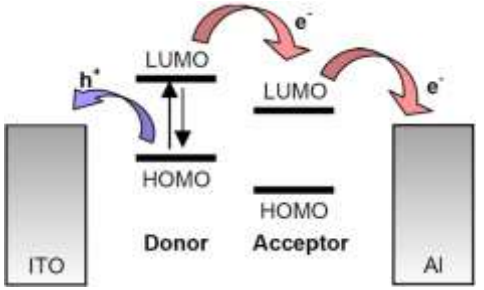
There is a growing interest in converting *clean* solar energy to electricity at low cost.

How can theory/computations aid in experimental design?

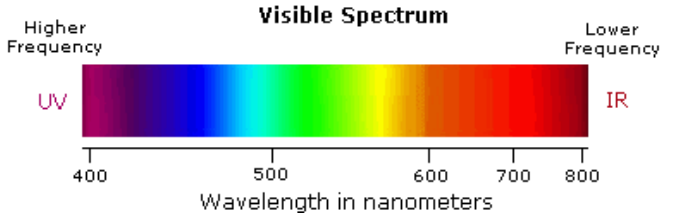
DFT to predict ground-state properties

- Bandgaps
- HOMO/LUMO positions
- Structural properties



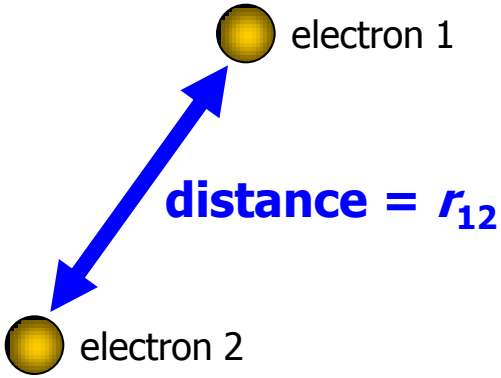
Time-dependent DFT to predict *excited states* properties

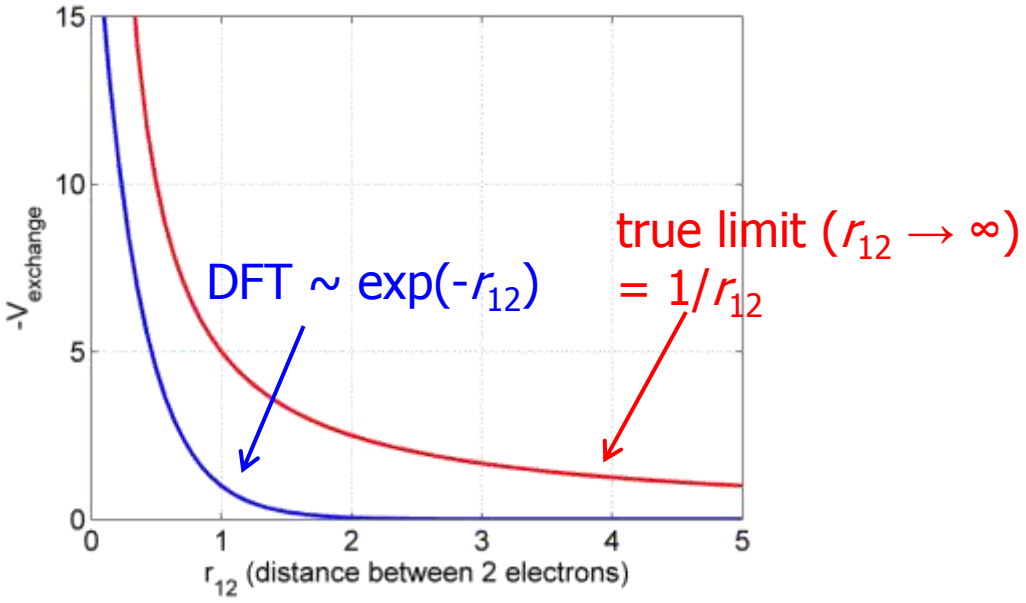
- Absorption / emission spectra
- Energy and charge transfer
- Excitation energies & oscillator strengths



The exchange-correlation functional

- Severe problems in exchange-correlation potential





- Wrong asymptotic behavior → *charge-transfer excitations severely underestimated and poorly predicted molecular orbital energies*

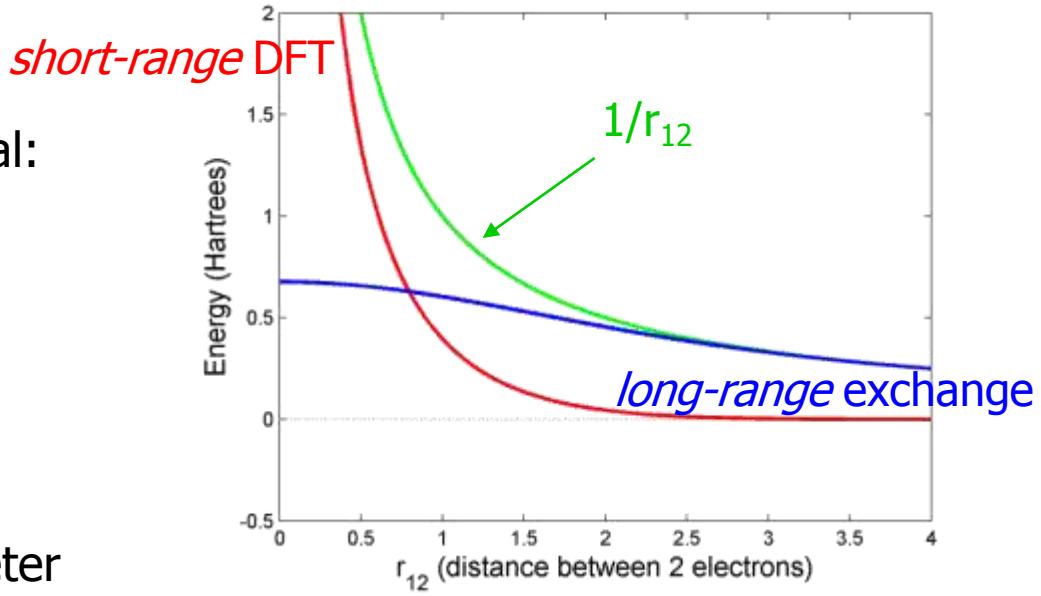
Modifying the exchange functional

- Replace incorrect DFT portion with *long-range nonlocal exchange*

Splitting the Coulomb potential:

$$\frac{1}{\mathbf{r}_{12}} = \frac{1-\mathrm{erf}\left(\mu\cdot\mathbf{r}_{12}\right)}{\mathbf{r}_{12}} + \frac{\mathrm{erf}\left(\mu\cdot\mathbf{r}_{12}\right)}{\mathbf{r}_{12}}$$

short-range **long-range**



μ = range separation parameter
units: 1/Bohr

$$E_{xc}\left[\rho\right] = E_{c,\mathrm{DFT}}\left[\rho\right] + E_{x,\mathrm{DFT}}^{\mathrm{SR}}\left[\rho\right] + E_{x,\mathrm{HF}}^{\mathrm{LR}}\left[\rho\right]$$

Non-empirical tuning

- How do we determine μ?
- *Koopman's (Janak's) Theorem:*

$$IP = -\varepsilon_{HOMO}$$

  - Rigorously obeyed for *"exact"* functional

- Construct objective function J^2 as function of μ

$$J^2(\mu) = [IP(\mu) + \varepsilon_{HOMO}(\mu)]^2$$

  - Minimum of J^2 gives optimal μ for satisfying Janak's Theorem → *non-empirical "tuning" of XC functional*

Quasiparticle/ionization energies

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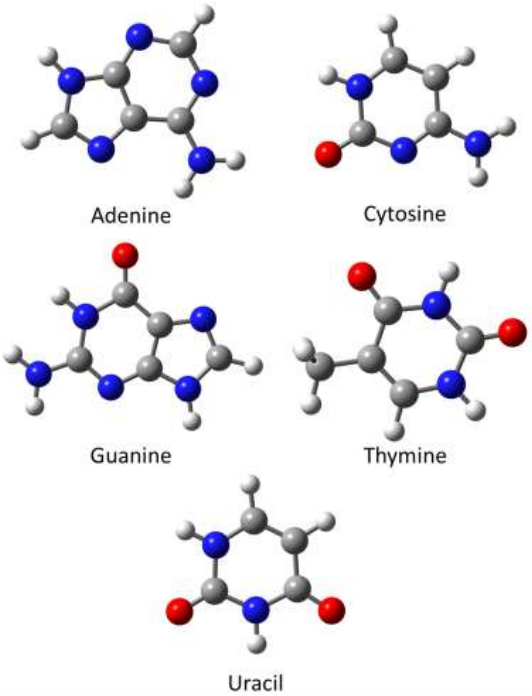
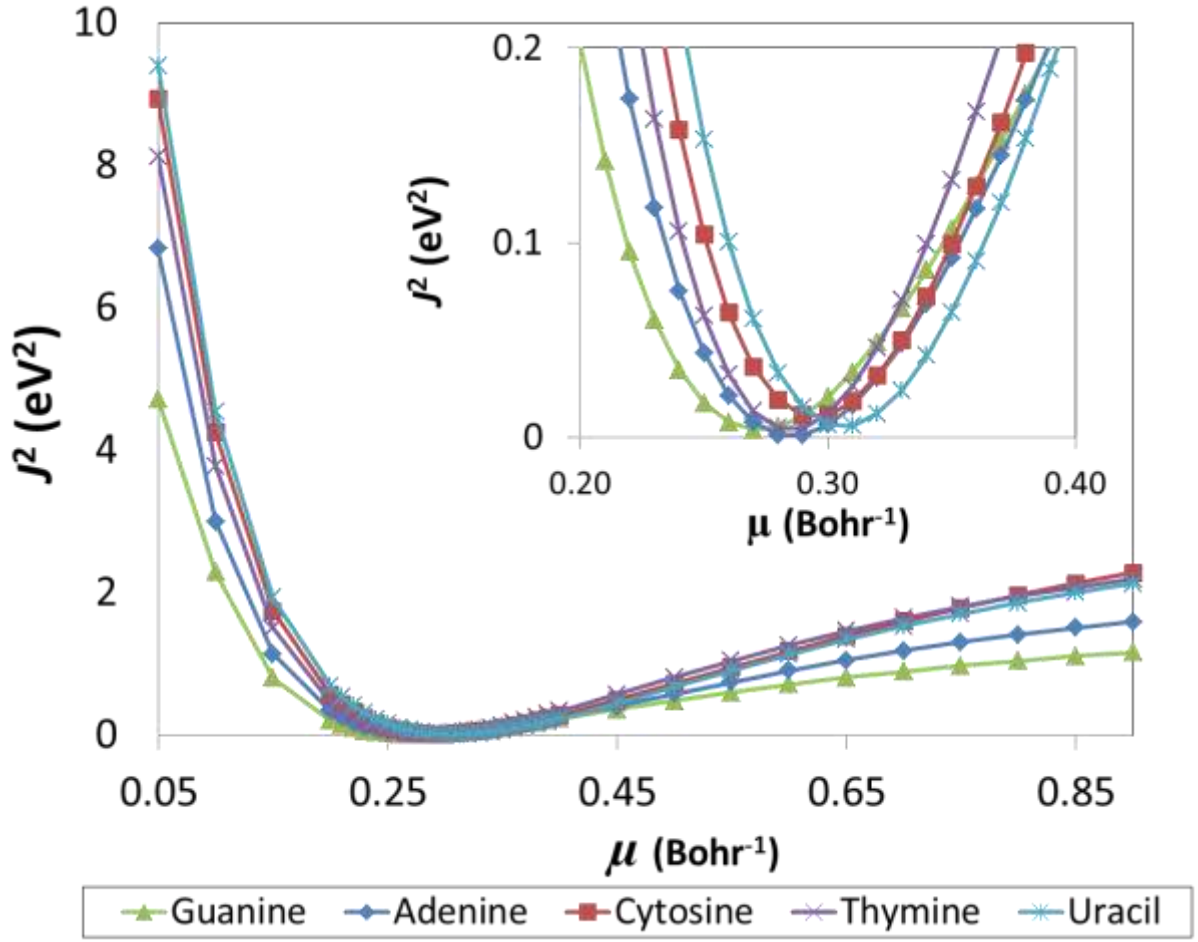
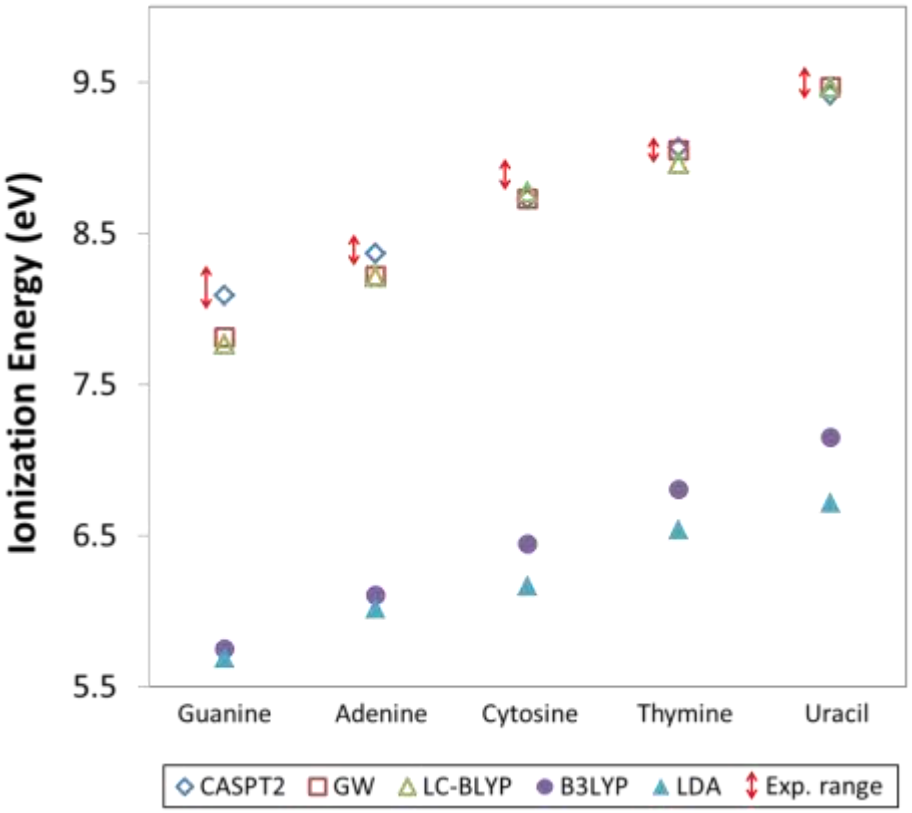
DNA & RNA nucleobases



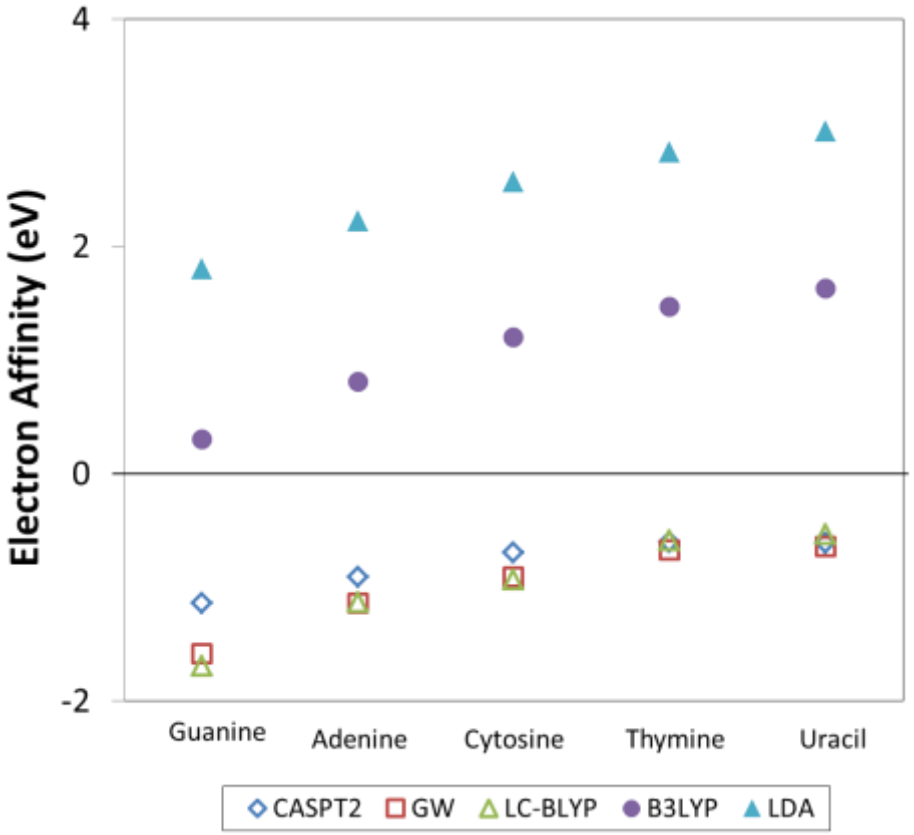
$$J^2(\mu) = [IP(\mu) + \varepsilon_{HOMO}(\mu)]^2$$



Ionization energies / electron affinities



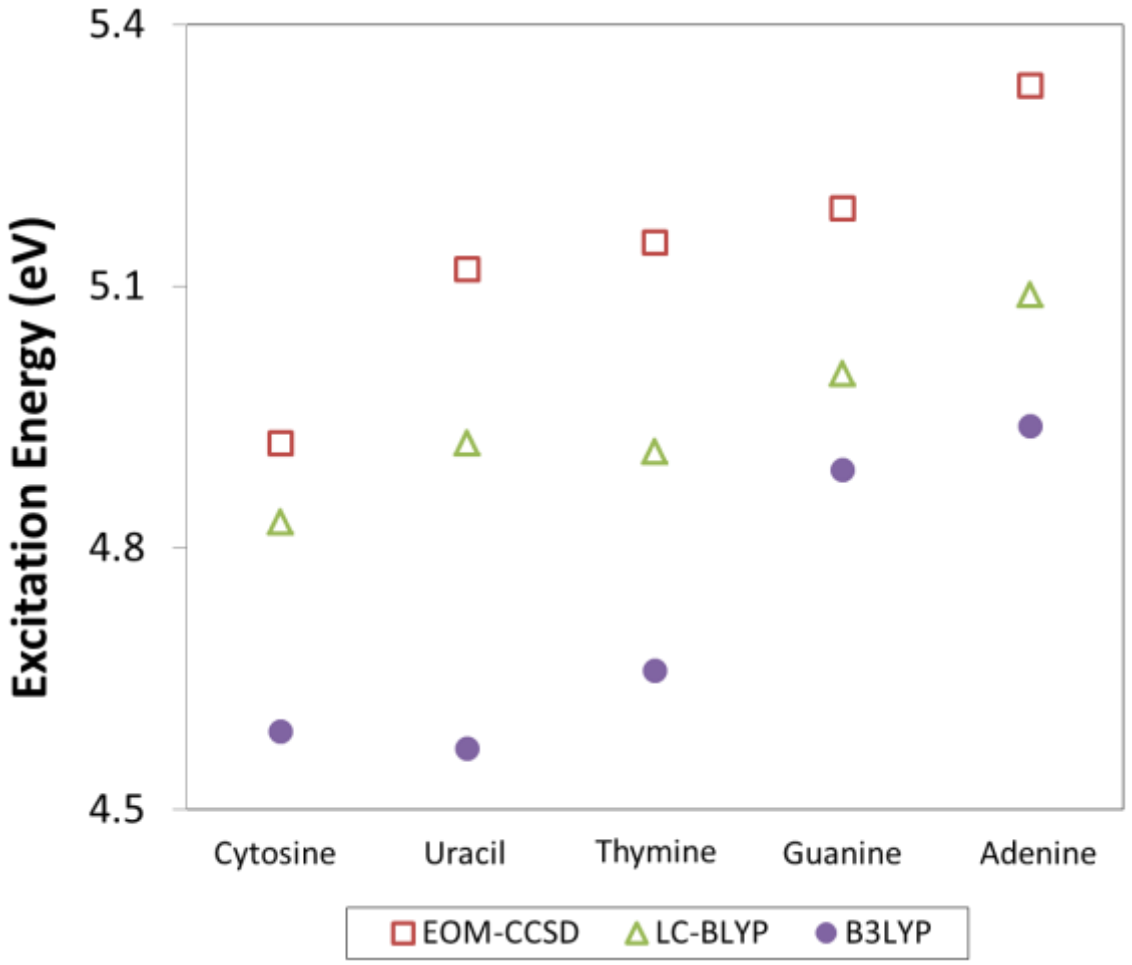
LC formalism matches GW calculations
Other functionals: **errors > 2.0 eV!**



LC formalism matches GW calculations
Other functionals: **qualitatively incorrect**

M.E. Foster, B.M. Wong, *J. Chem. Theory Comput.* **8**, 2682 (2012)

Excitation energies



Mean absolute error (MAE)

LC-BYLP = 0.19 eV

B3LYP = 0.41 eV

MAE is reduced by more than half!

M.E. Foster, B.M. Wong, *J. Chem. Theory Comput.* **8**, 2682 (2012)

Long-range corrected functionals

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- Have the correct *asymptotic* behavior
- Can be *non-empirical tuned*
- Improved *excitation energy*
- Substantial improvements for predicting *ionization energies* and *electron affinities*

M.E. Foster, B.M. Wong, *J. Chem. Theory Comput.* **8**, 2682 (2012)

What are metal-organic Frameworks

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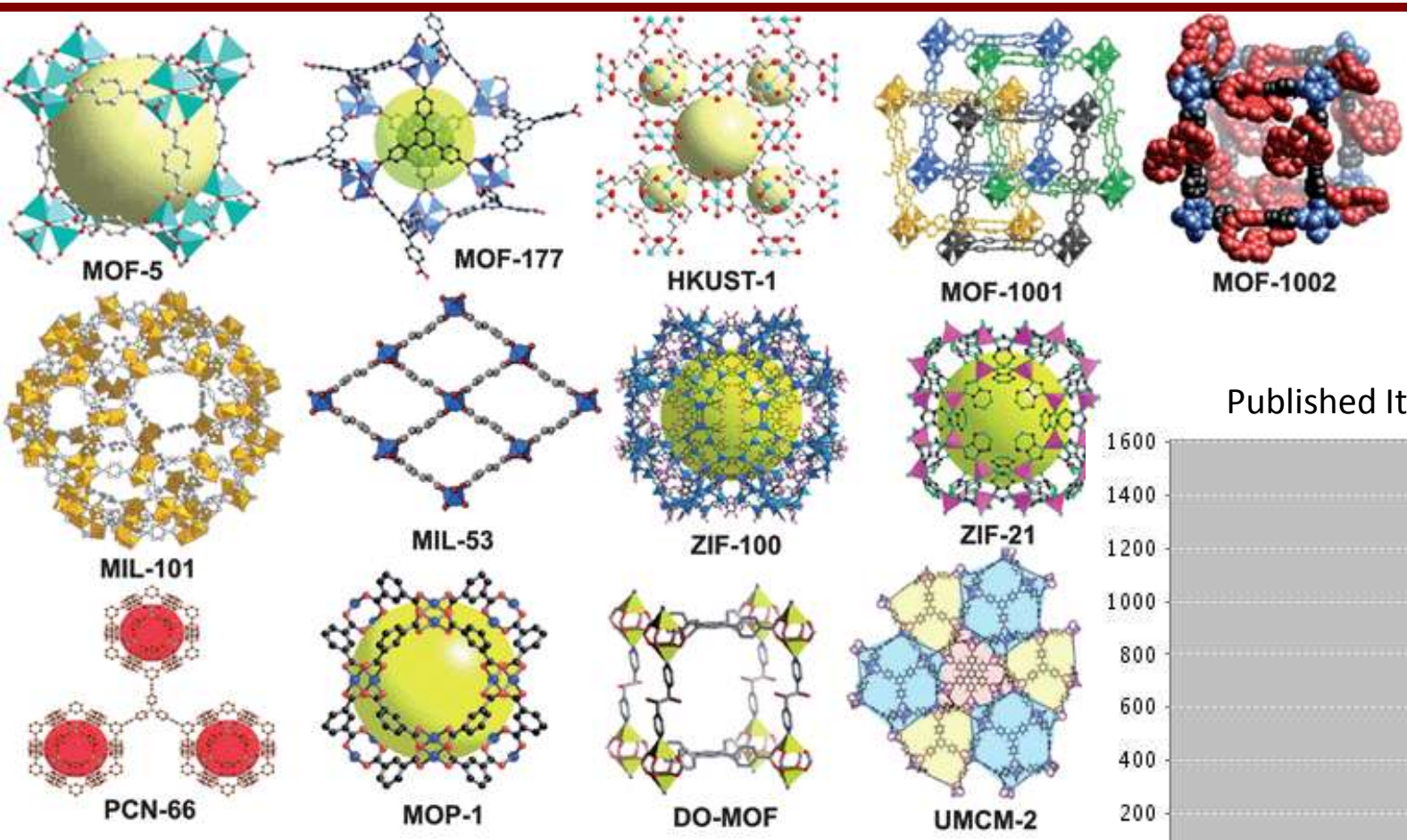
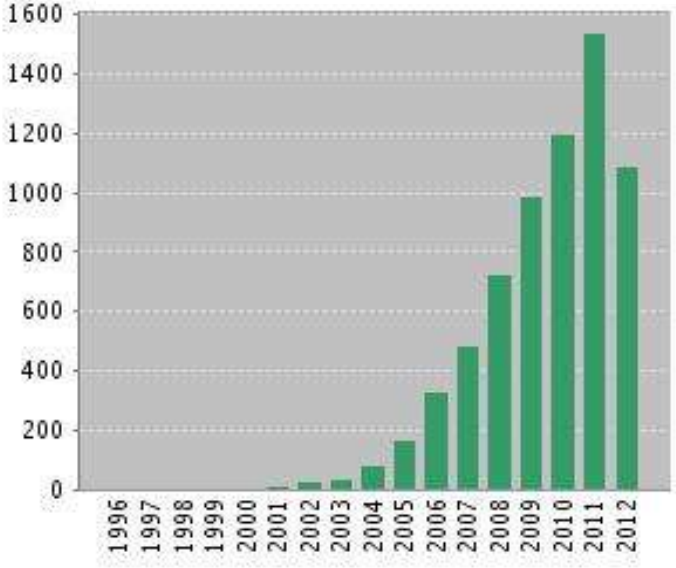


Published Items in Each Year



Metal-organic framework s(MOF) are composed of two major components: a metal ion or cluster of metal ions and an organic molecule called a linker

Ordering donor/acceptor interfaces

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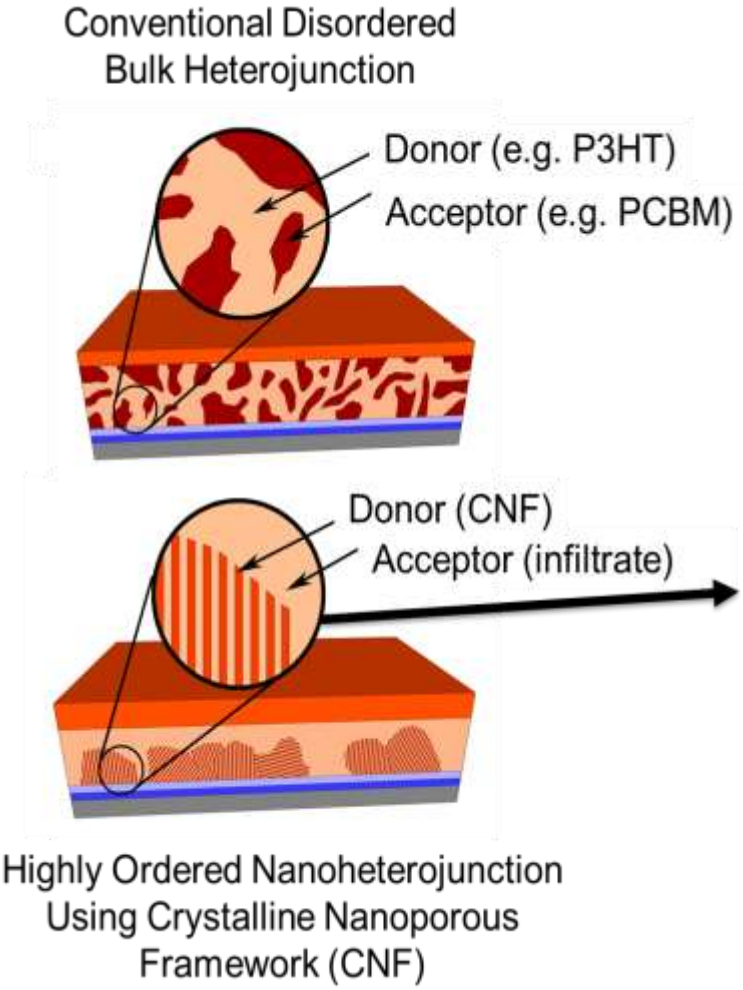

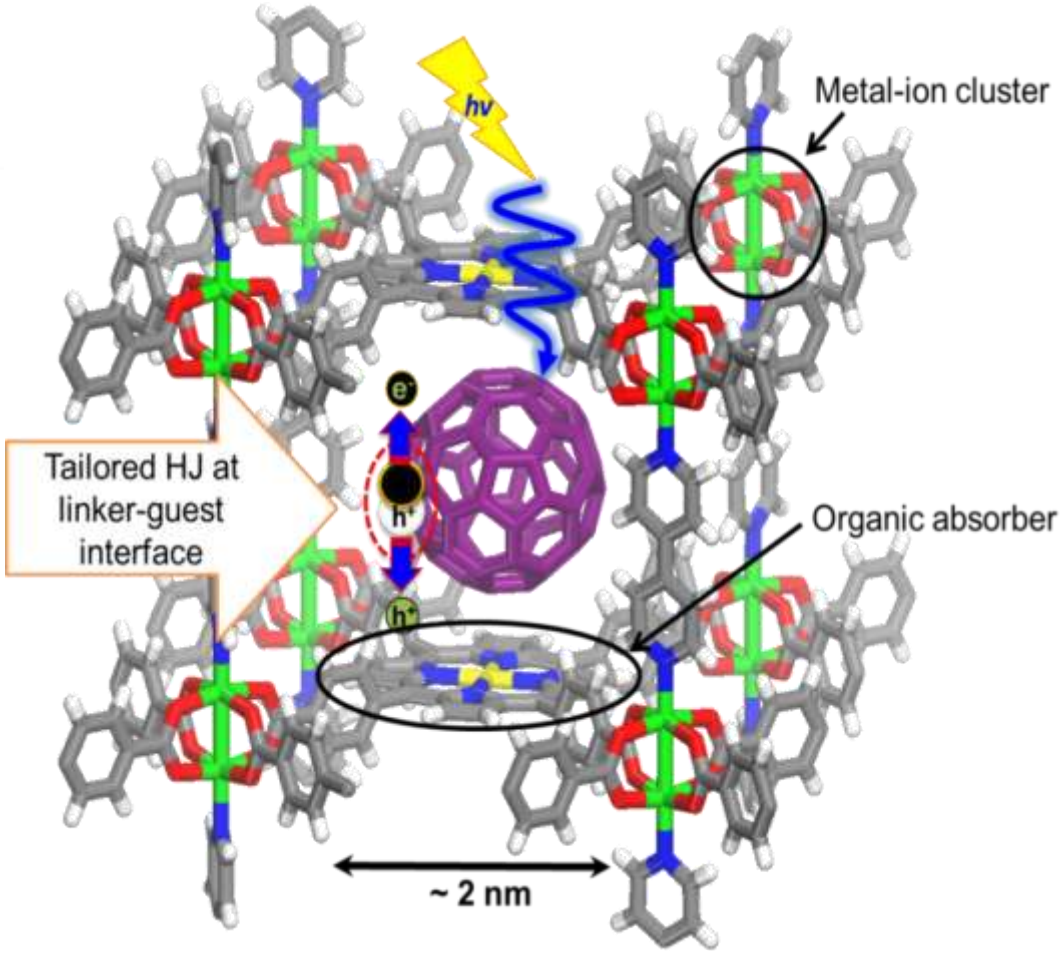

Passive scaffolds and active networks

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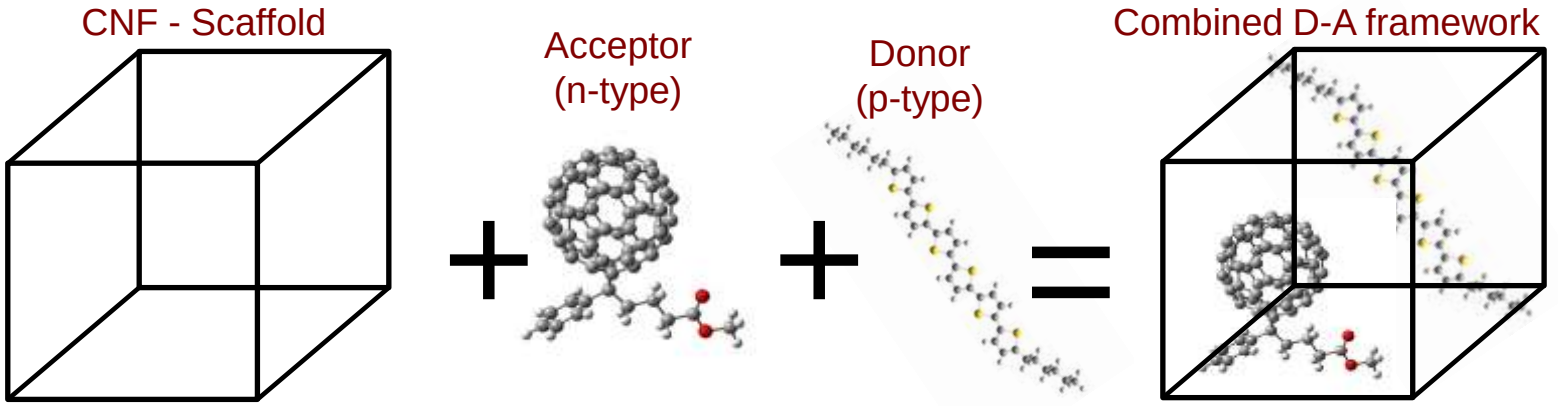
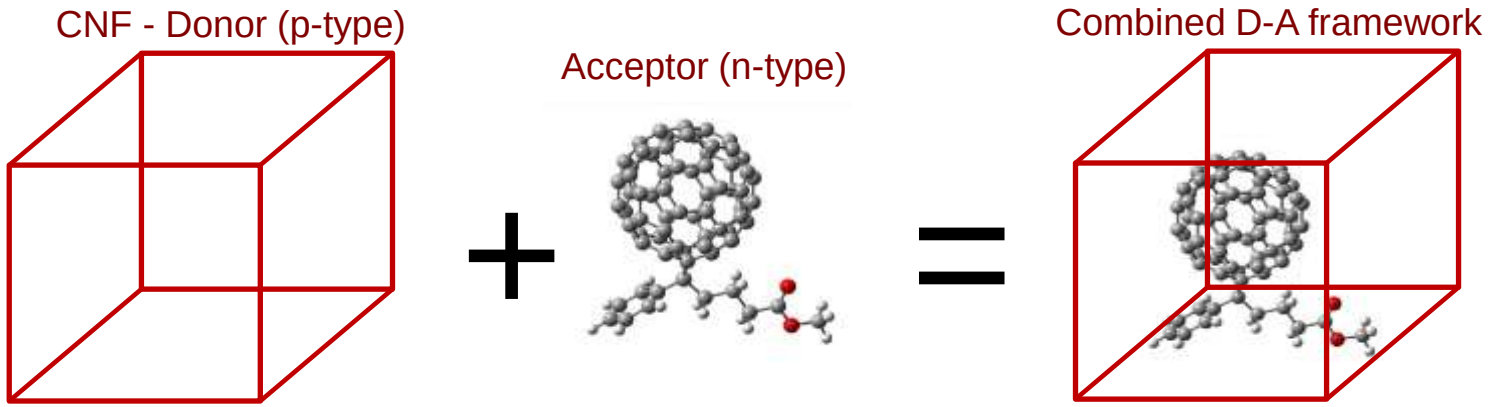
Passive Scaffolds - the CNF simply functions to order the donor/acceptor materials and plays no active role in the PV energy conversion process.

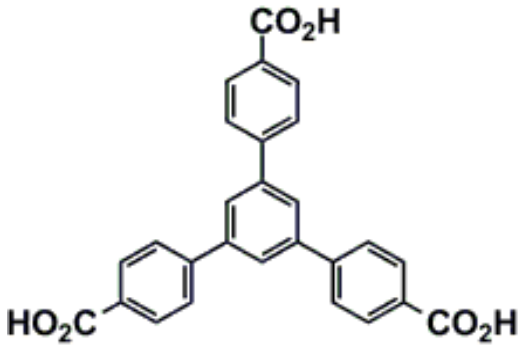


Active Network – the CNF is designed to play an active role in the PV energy conversion process by functioning as the donor or acceptor material.

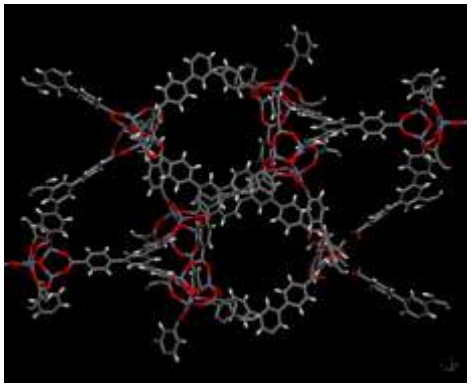


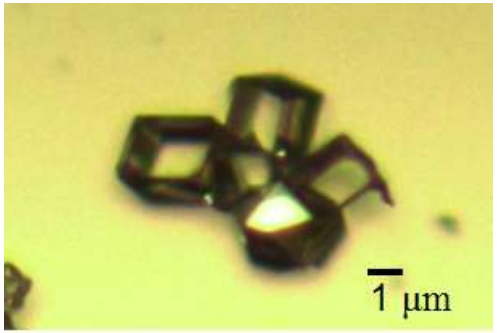
Passive framework infiltration: MOF-177

$Zn(NO_3)_2 \cdot 6H_2O$ + H_3BTB ⟶ MOF-177

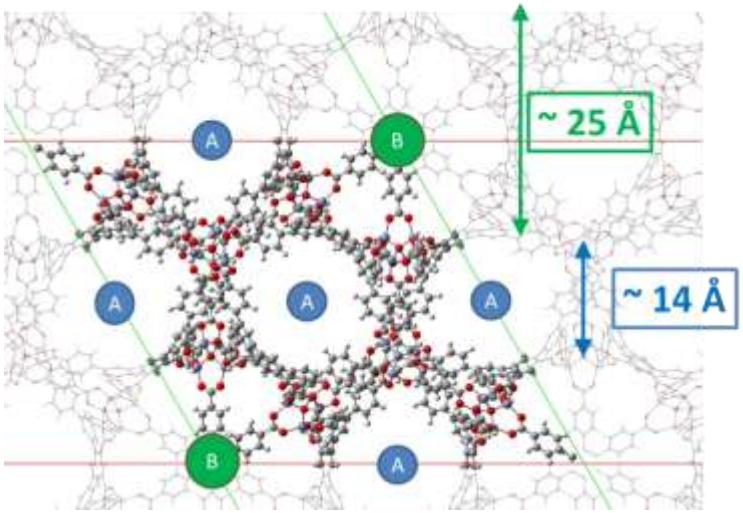


H_3BTB





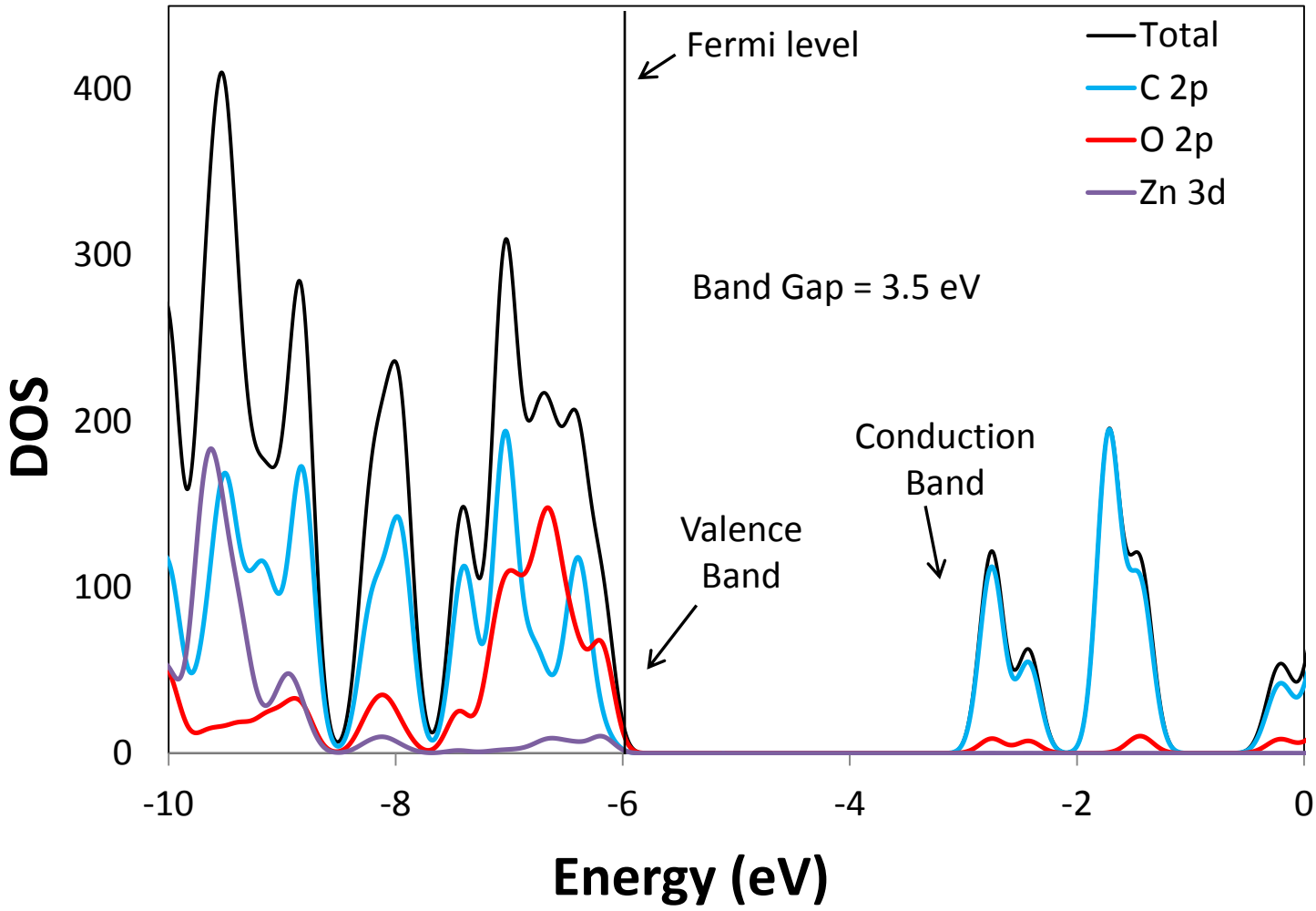
Optical image of MOF-177 crystals



- 808 atoms in the primitive unit cell
- Transparent colorless block shaped crystals
- Open three-dimensional and ordered structure with extra large pores.
- Two unique cavities denoted by “A” and “B”

Optimized Structure - Tight-Binding Density Functional Theory (DFTB)

MOF-177 – Passive scaffold

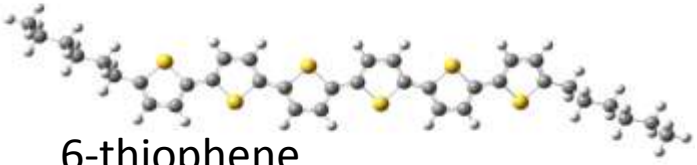


Density of States - Tight-Binding Density Function Theory (DFTB)

MOF Infiltration – Electron Acceptors/Donor

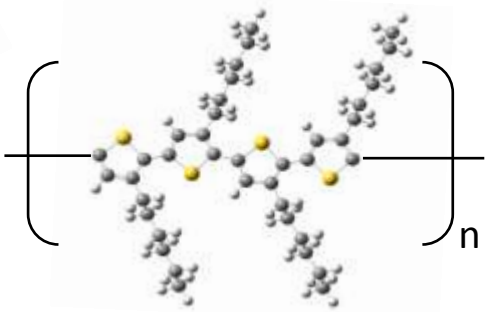
Terthiophene

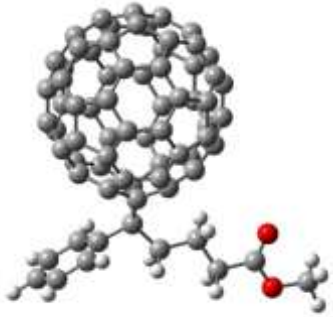
Quaterthiophene



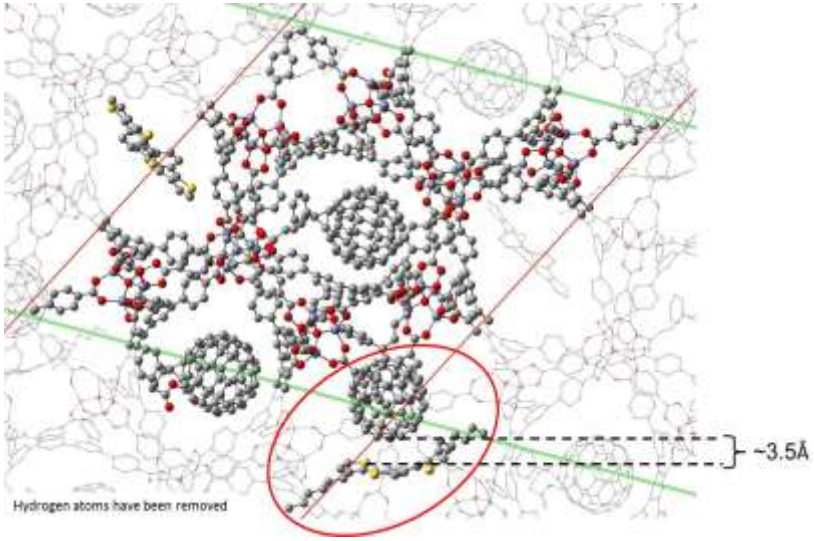
6-thiophene

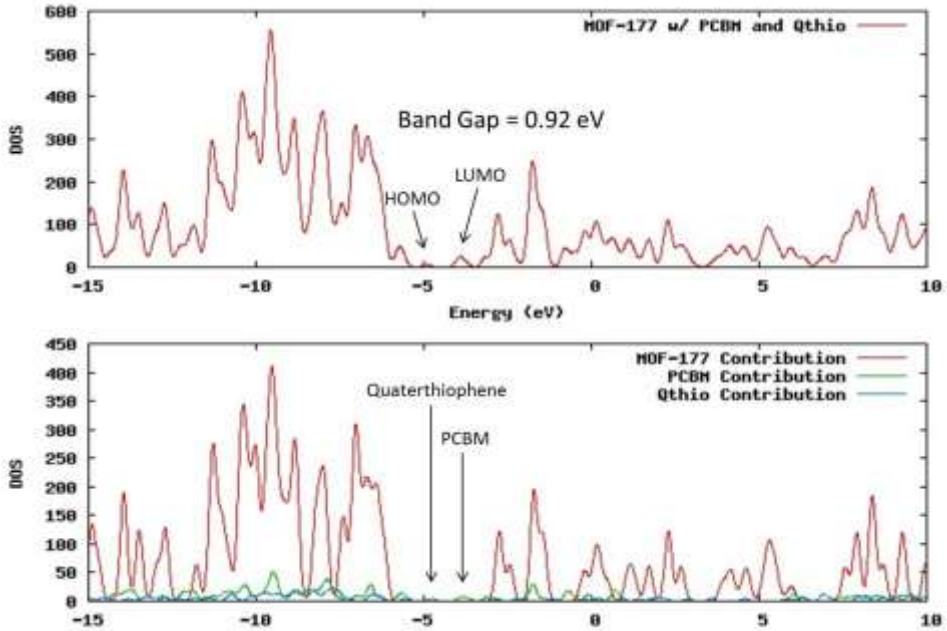
poly(3-hexylthiophene) (P3HT)

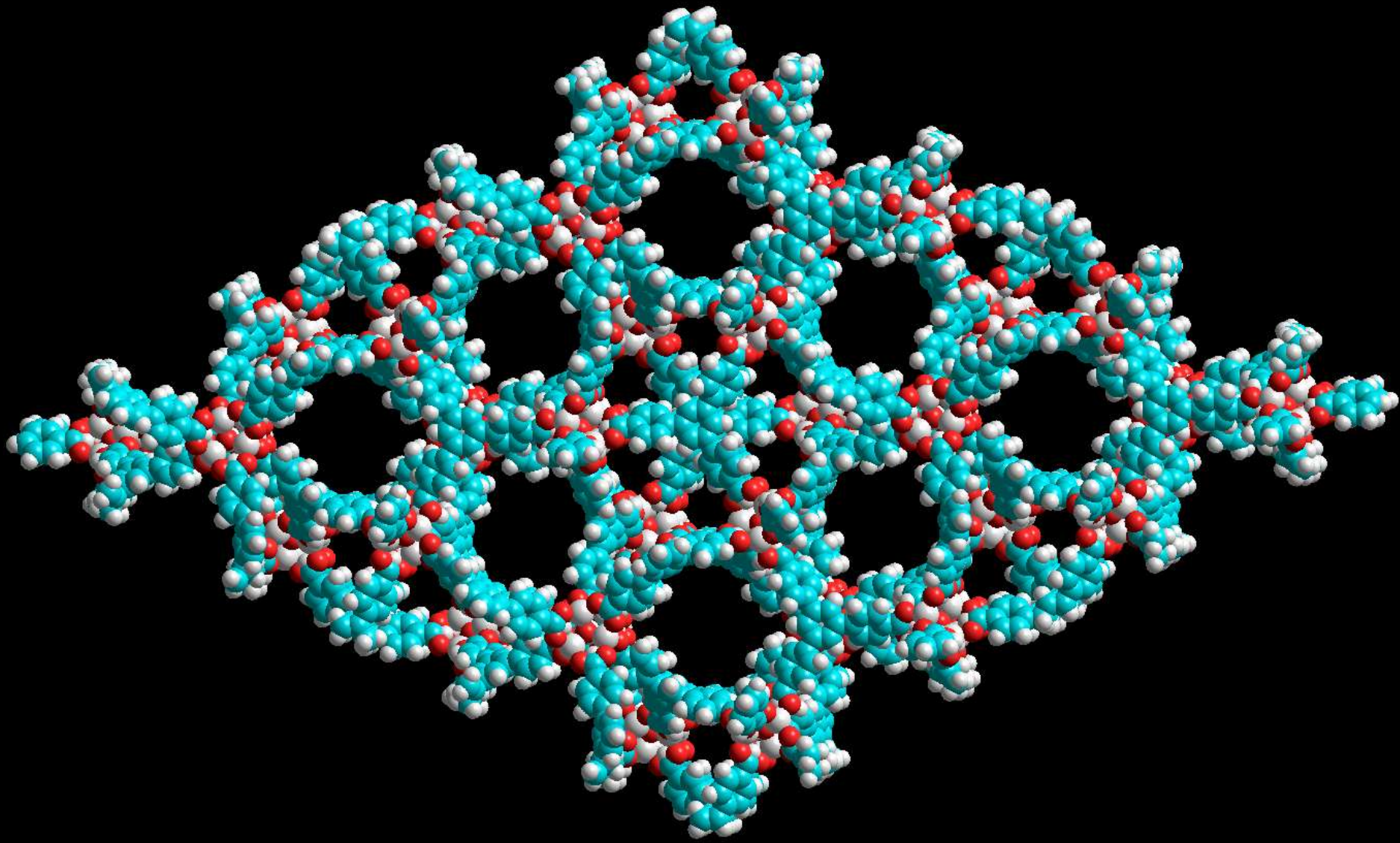




PCBM

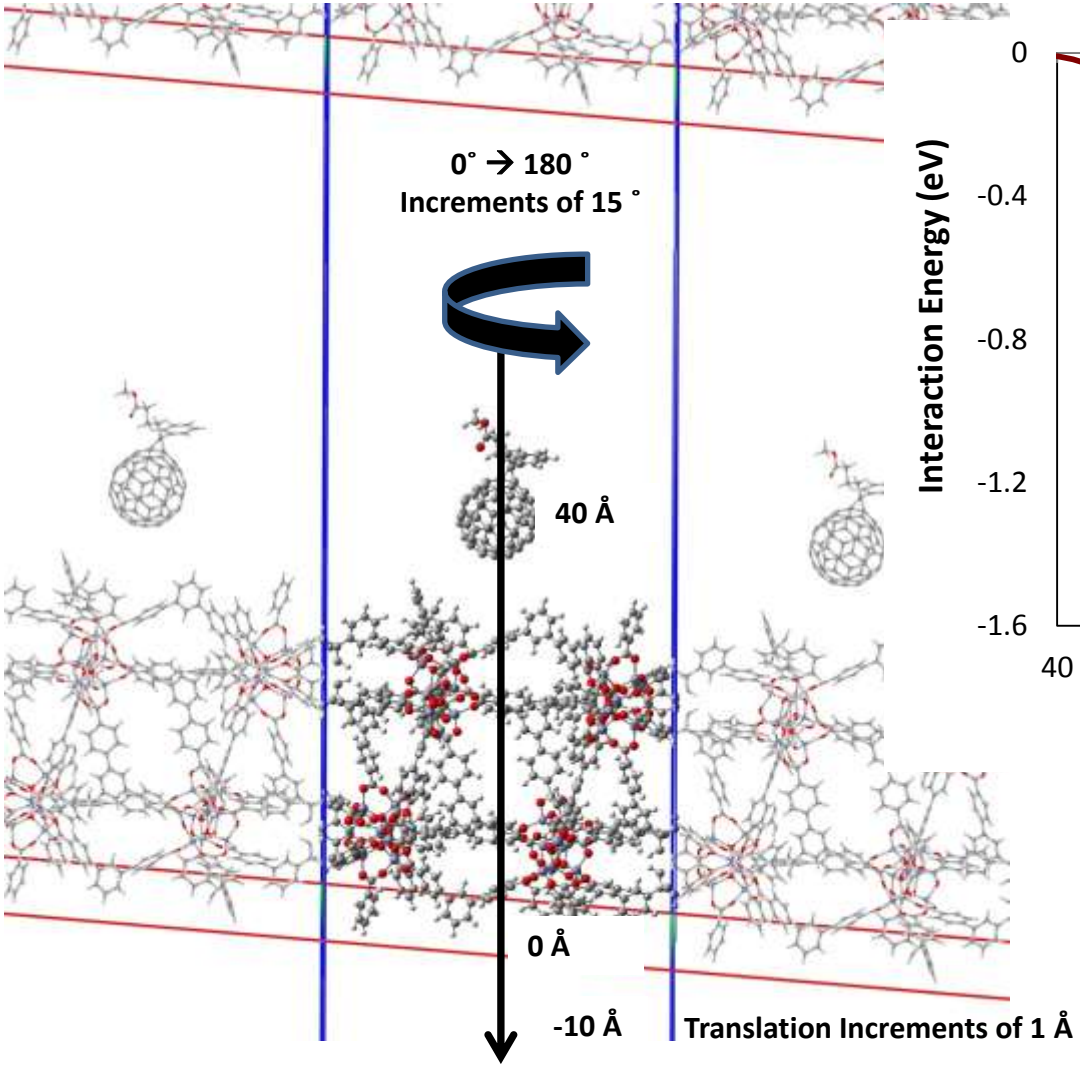


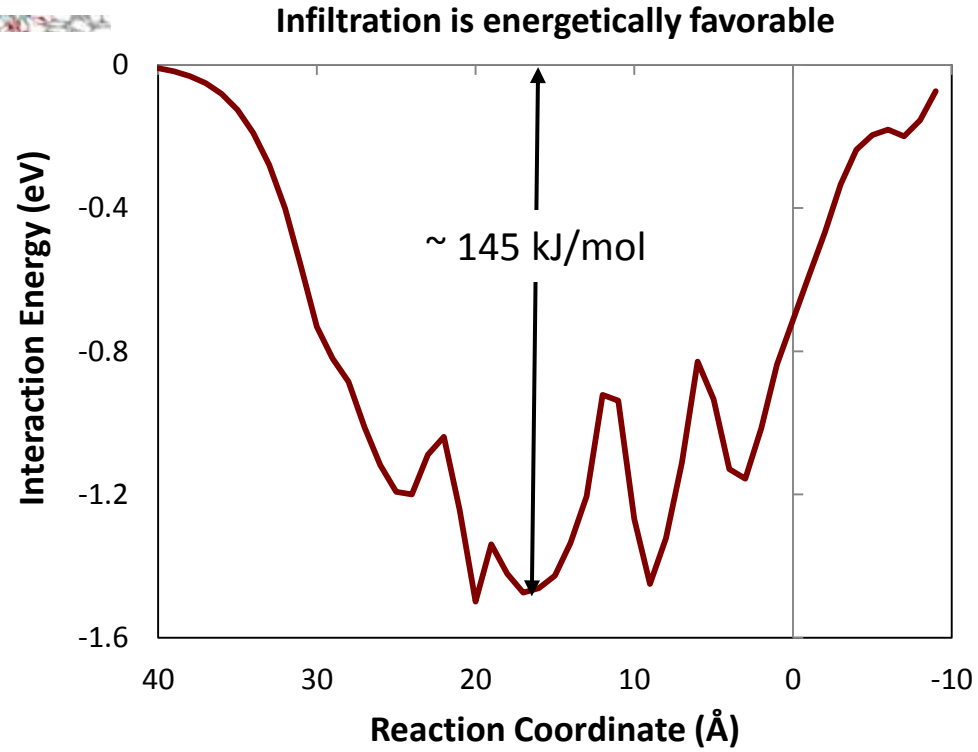




MOF-177

MOF-177 + acceptor molecules: PCBM infiltration





DFT/tight-binding calculations (DFTB):

- 663 Structures generated
- 10-Step optimization to remove close contacts

Characterizing MOF-Infiltration with PCBM through Cross-Sectional Microscopy

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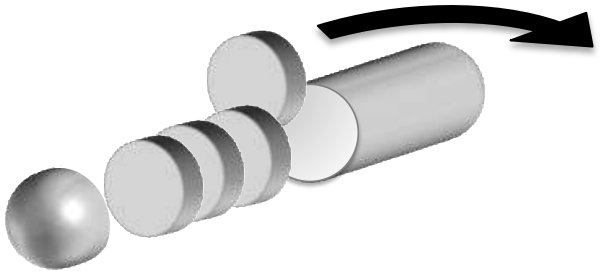
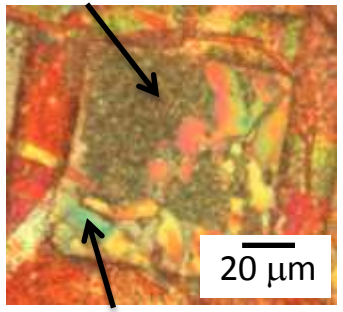
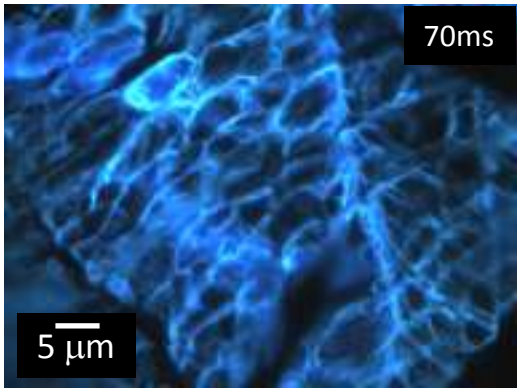
MOF177 particles were embedded in acrylic resin. Microtomed sections from the interior of MOF177 and infiltrated MOF177 particles were examined by microluminescence spectroscopy.





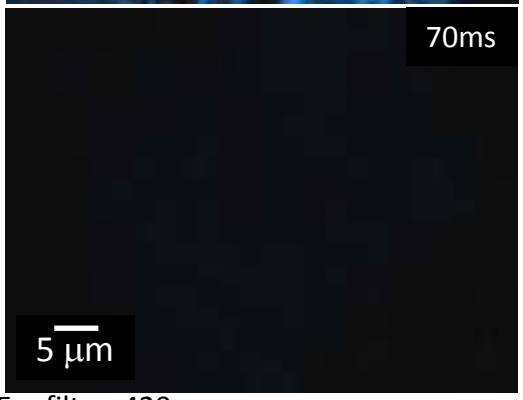
MOF177

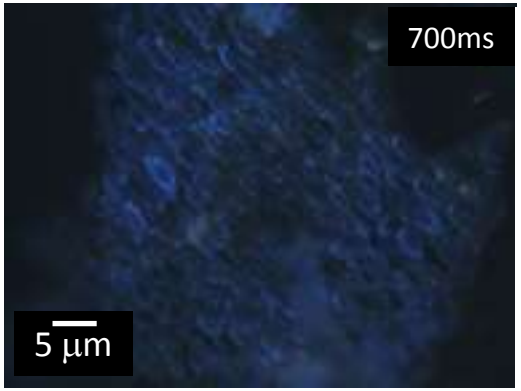


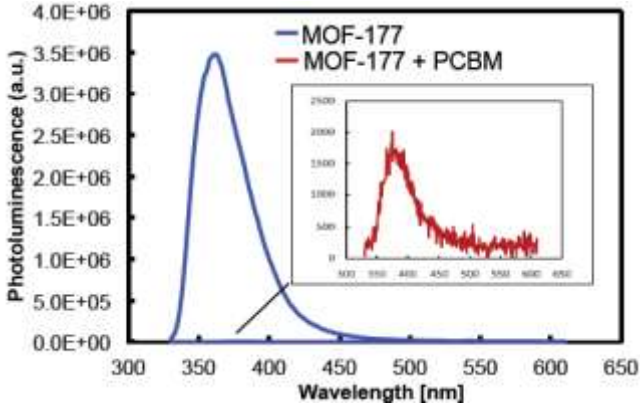
Excited by UV-light, MOF177 fluoresced bright blue.

Infiltrated with PCBM, the local fluorescence was strongly quenched (visible only at long camera exposure times) throughout the section.

MOF177/ PCBM

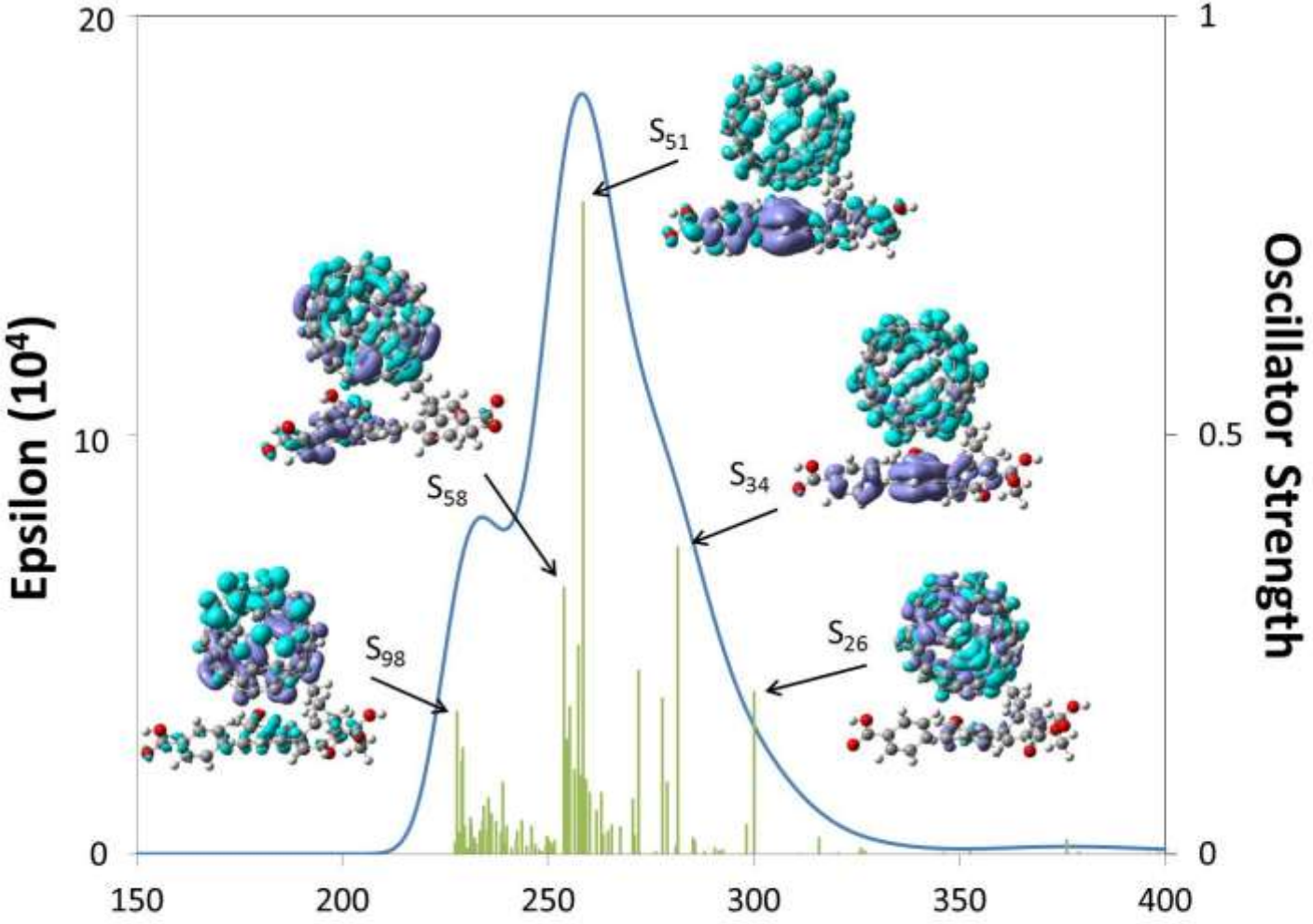






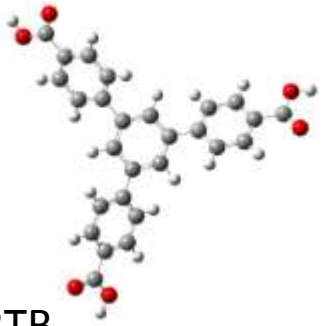
Ex: 330-385nm; Em filter: 420nm

Charge transfer - H_3BTB/PCBM

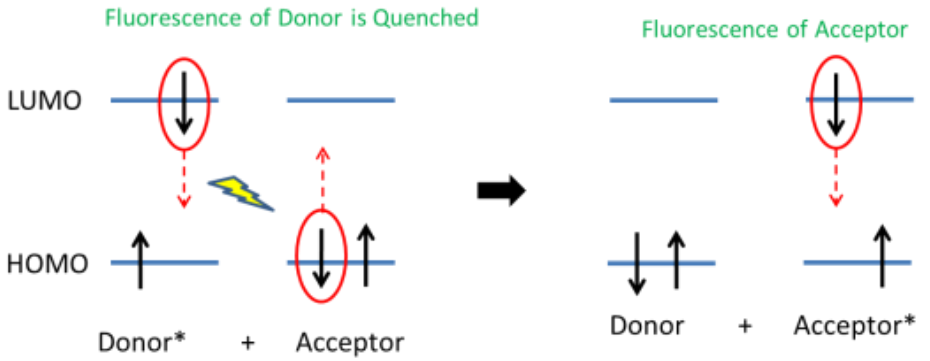


wB97xD/6-31G(d,p)

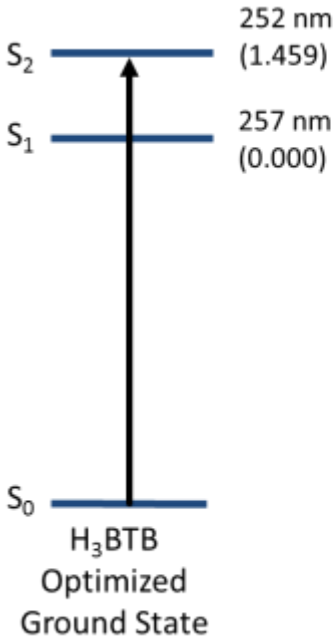
Resonance energy transfer - H_3BTB/PCBM

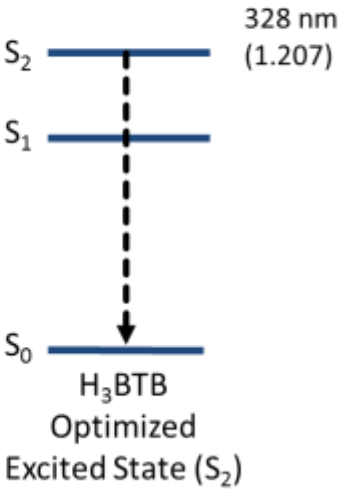


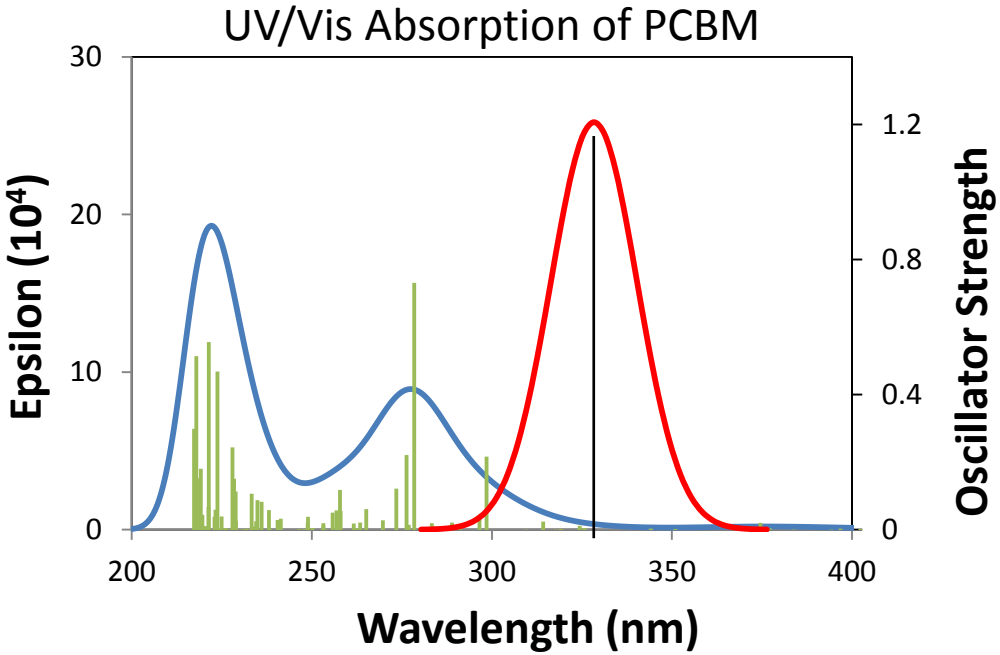
H_3BTB



PCBM

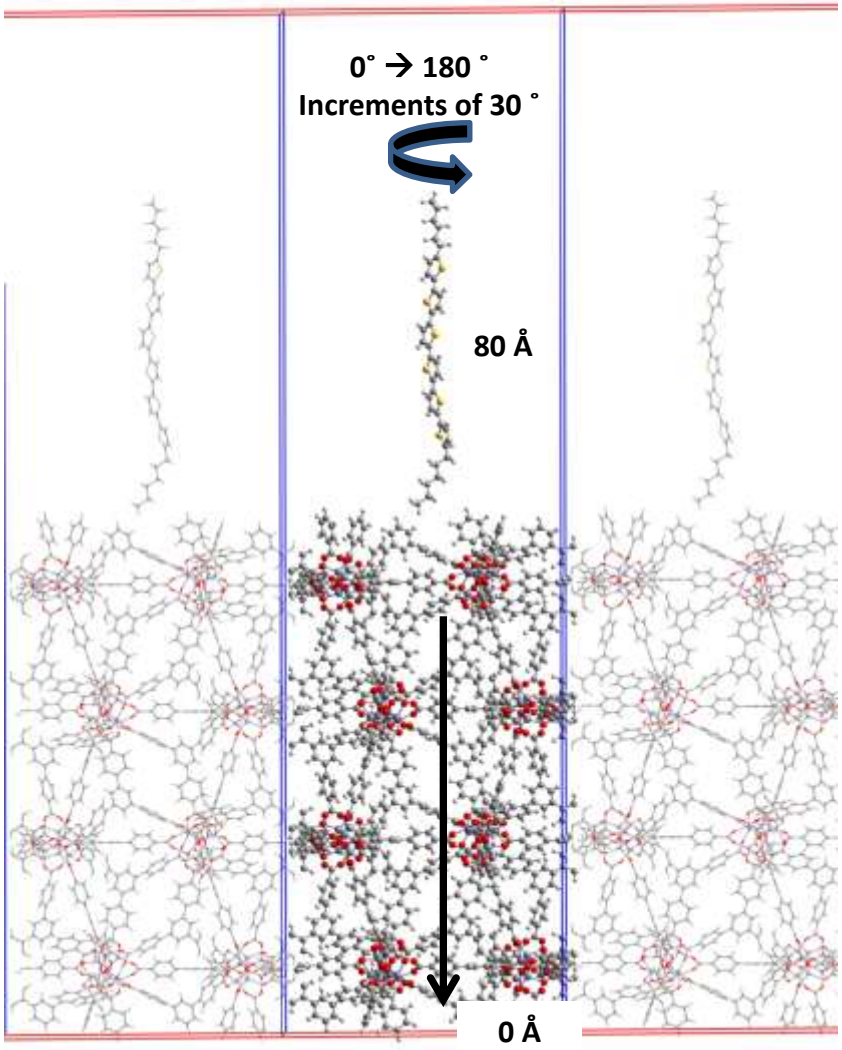


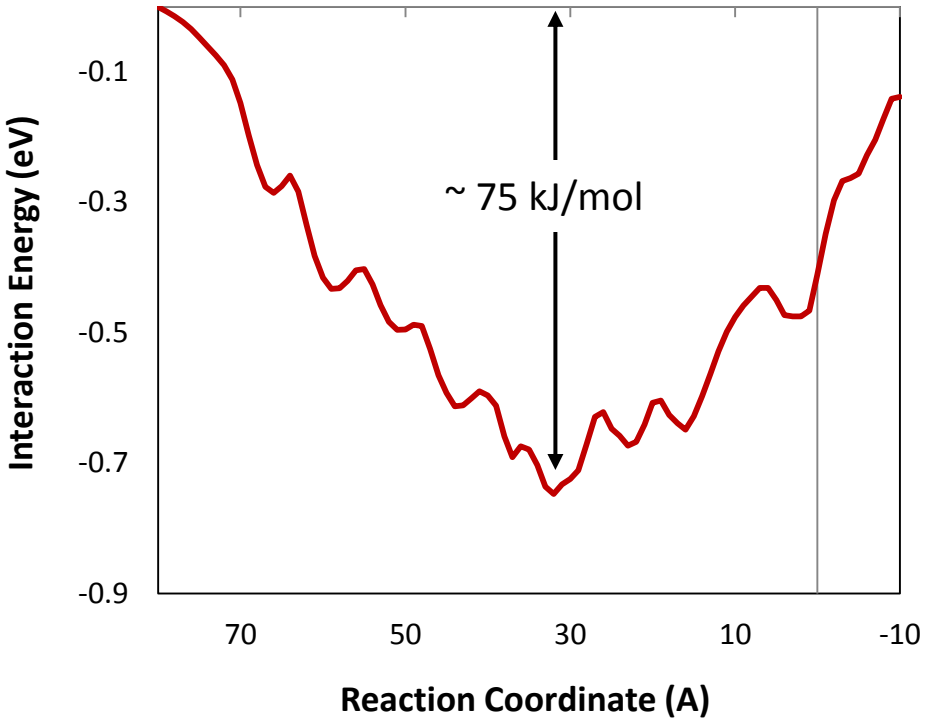




wB97xD/6-31G(d,p)

MOF-177 + donor molecules: thiophene oligomer infiltration is energetically favored





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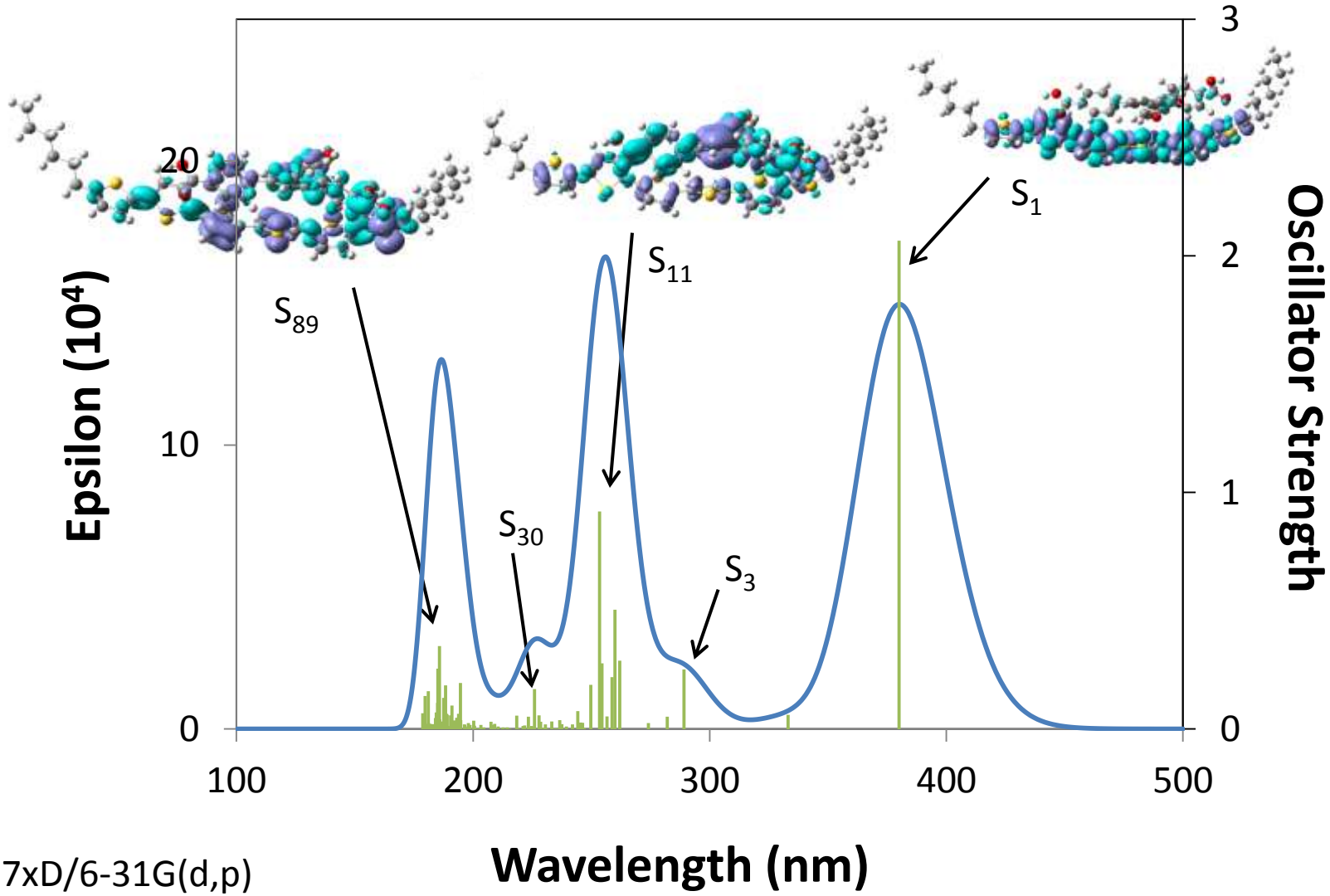
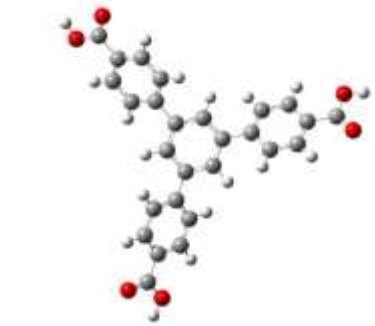
- 1 Å translation increments

Charge transfer - H_3BTB/6-thiophene

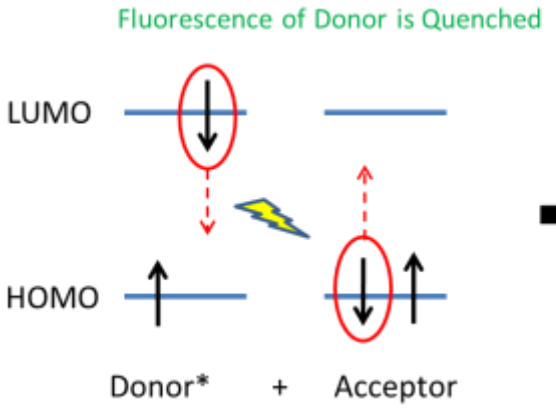


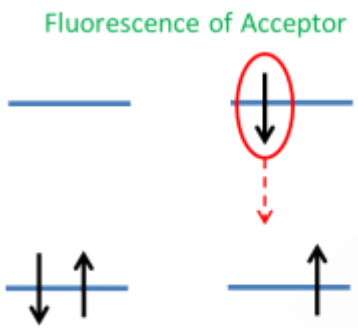
wB97xD/6-31G(d,p)

Resonance Energy Transfer - H_3BTB/6-thiophene

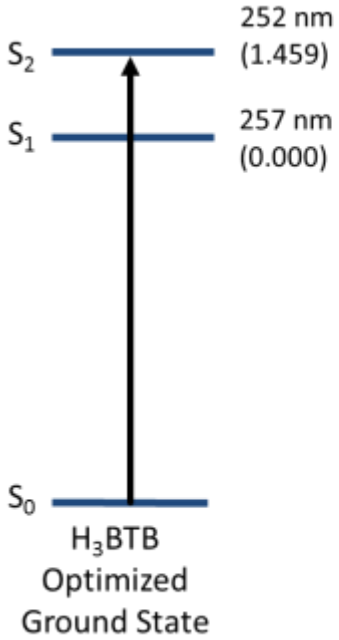


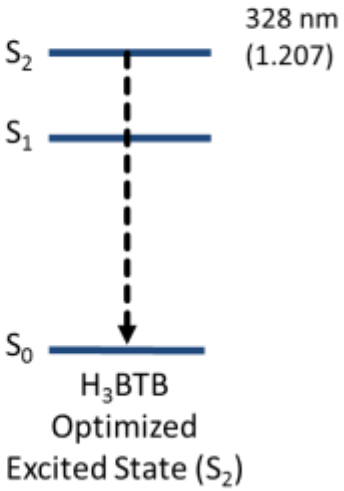
H_3BTB

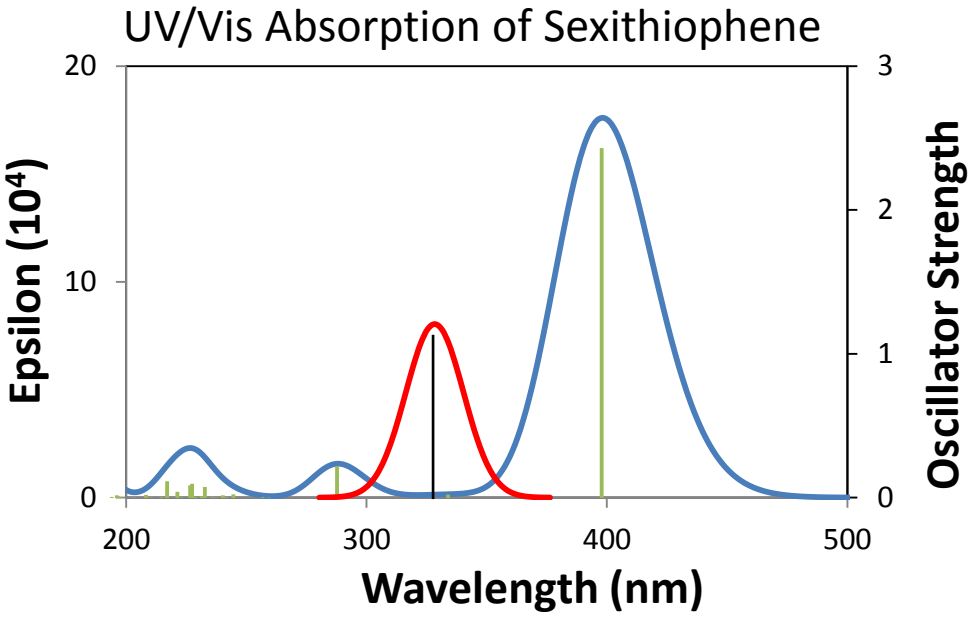




6-Thiophene







Characterizing MOF-Infiltration with 6-thiophene through Cross-Sectional Microscopy

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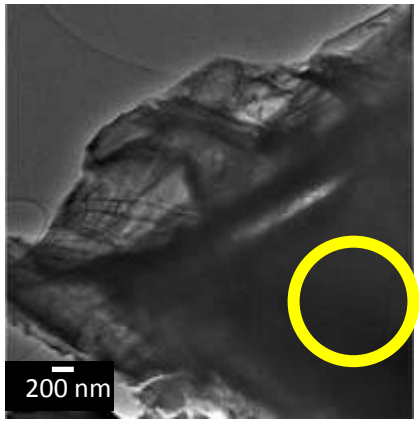
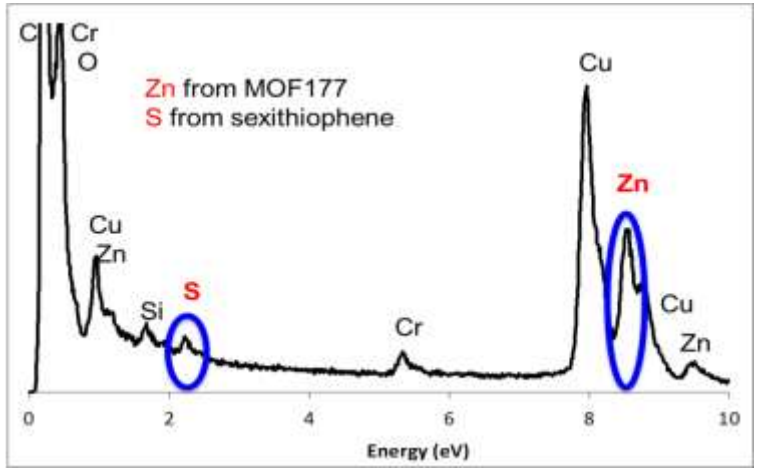
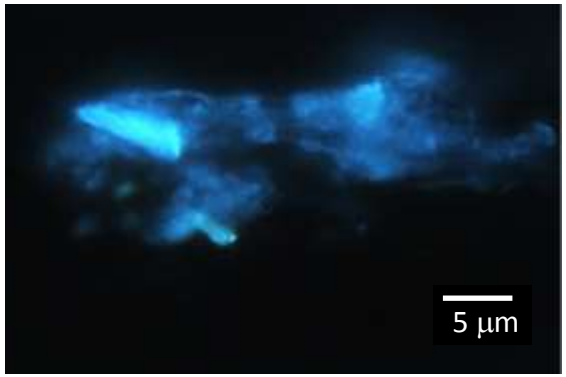


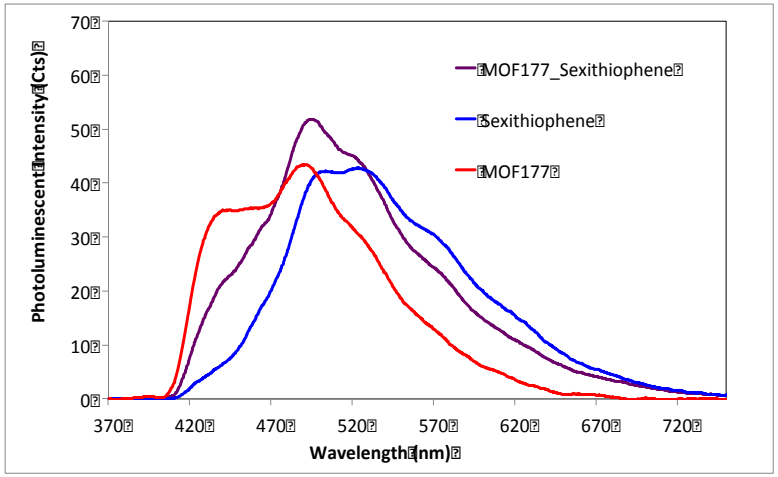
Microtomed sections were used to confirm 6-thiophene infiltration into MOF177.



Energy Dispersive X-Ray Analysis in the TEM identifies sulfur from 6-thiophene in MOF177



Microluminescent image of MOF177 infiltrated with sexithiophene.



Microluminescent spectrum of MOF177/sexithiophene microtomed section shows contributions from MOF177 and sexithiophene.

Conclusions

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- MOF-177 is a *passive network*
- Infiltration of MOF-177 with PCBM and 6-thiophene is *energetically favored*
- *Resonance energy transfer* is responsible for the observed quenching between MOF-177 and PCBM
- MOF have the potential to *order donor/acceptor interfaces*

Thank you

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