SAND2014-3114C

Novel Metal-Organic Framework Linkers for Light Harvesting Applications

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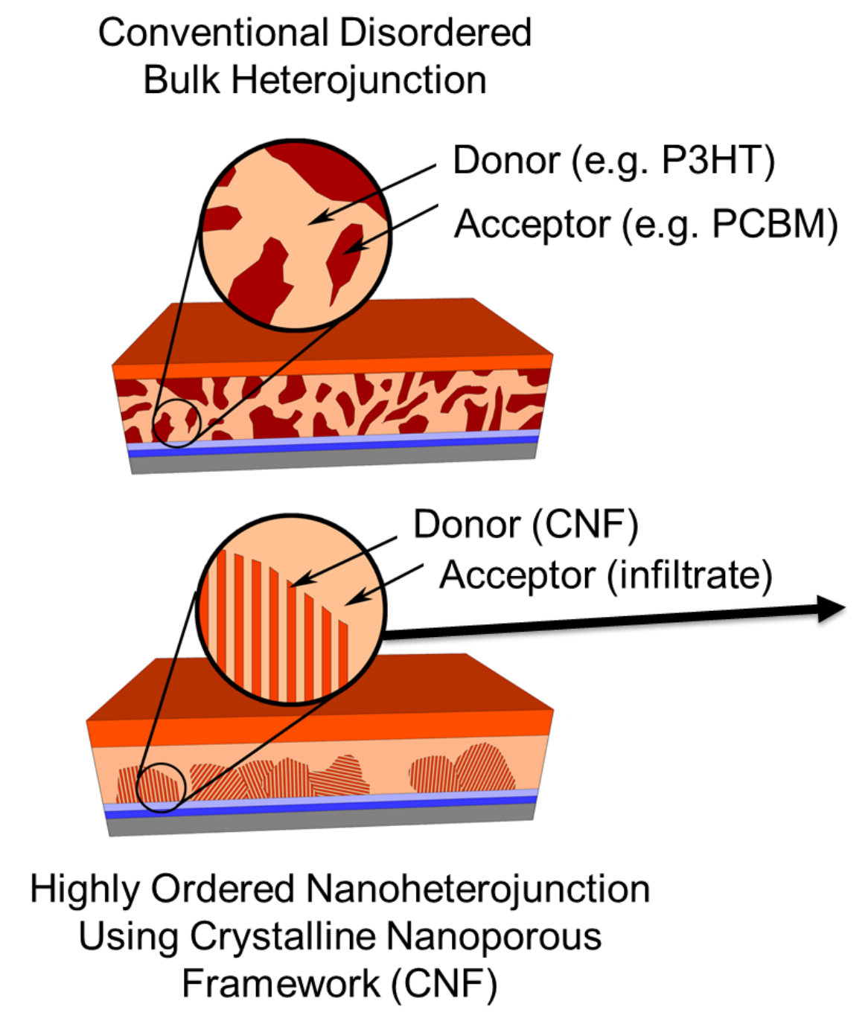
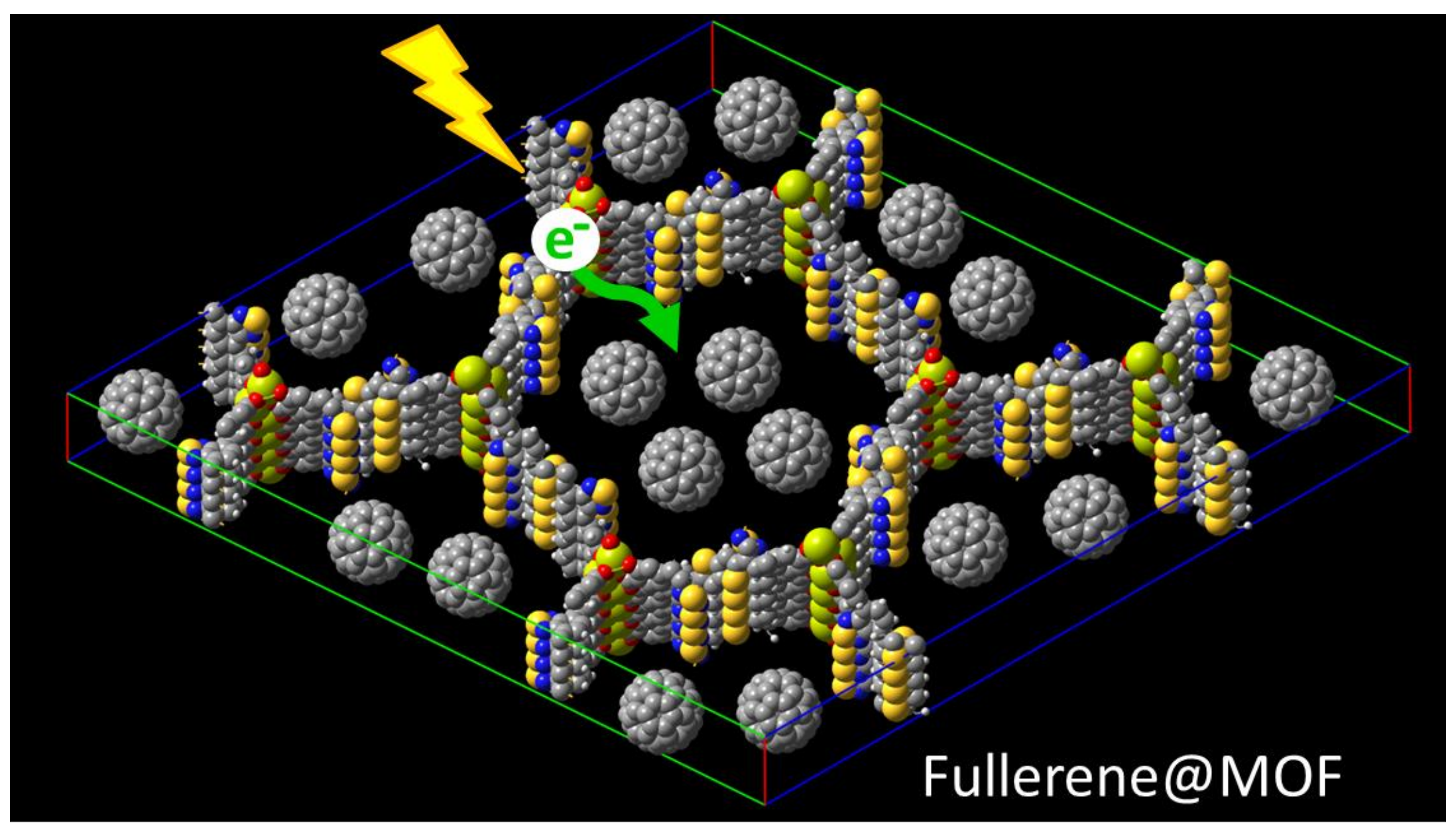
Abstract

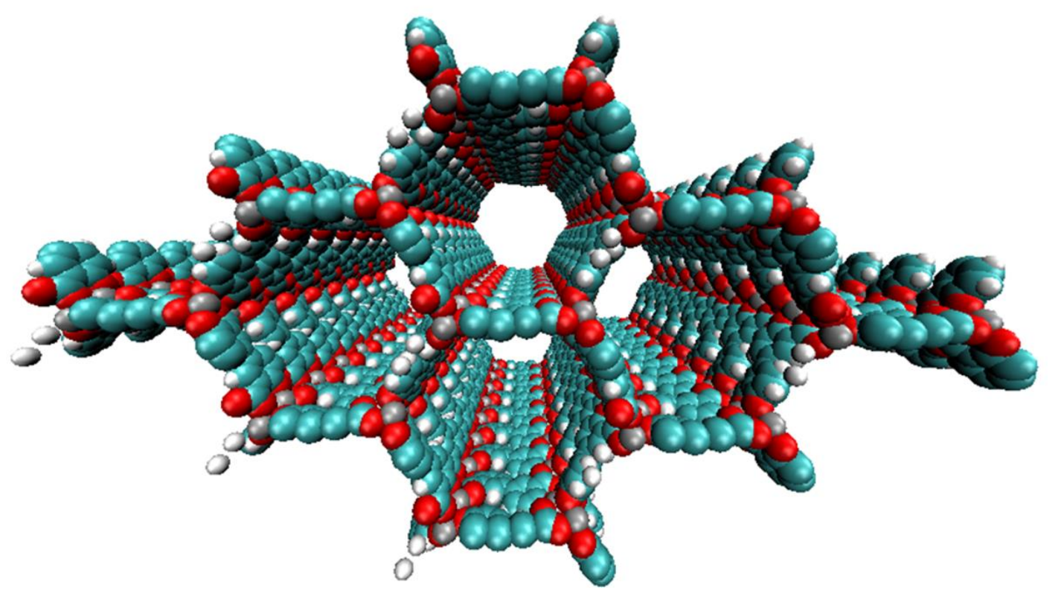
Metal-organic frameworks (MOFs) are composed of organic linkers and coordinating metals that are self-assembled to form a crystalline material with permanent and tunable nanoporosity. Their synthetic modularity along with the inherent structural order of MOFs allows for their utility as new functional electronic materials. Recently, we showed that an electrical insulating MOF can be made conducting through the introduction of guest molecules in the pores (*Science*, 2014, 343, 66-69). However, there has been little attention paid toward identifying and creating semiconducting MOFs by virtue of modification of the organic linker. Herein, we propose a series of new conjugated organic linkers that are capable of forming the same one-dimensional infinite metal-oxide secondary building units (SBUs) as the well-known MOF-74. The SBU allows the linkers to form a continuous π-π stacking network that should enable charge transport in an analogous fashion to organic semiconducting materials while retaining the highly porous nature of the MOF. The structural and electronic properties of the proposed linkers and MOFs have been computationally modeled using a non-empirically tuned range-separated functional. The theoretically motivated tuning of the exchange functional leads to significantly improved results for excitation energies compared to conventional DFT methods. This work demonstrates that the electronic properties of the MOFs (i.e. optical gap) can be readily tuned by modification of the organic linker. Our findings reveal that the proposed systems are capable of harvesting light in the visible spectrum due to their relatively small optical gaps ($E^{TDDFT}_{S_0 \rightarrow S_1}$ < 2.0) and appreciable oscillator strengths (f > 1.0). In addition, we show that these systems have favorable orbital alignments with known electron acceptors to facilitate charge transfer. The predicted properties are in good agreement with experiment (i.e. UV-vis absorption spectra) demonstrating the power of this computational approach for MOF design. This work is published in *Chemical Science*, 2014, **5**, 2081-2090.





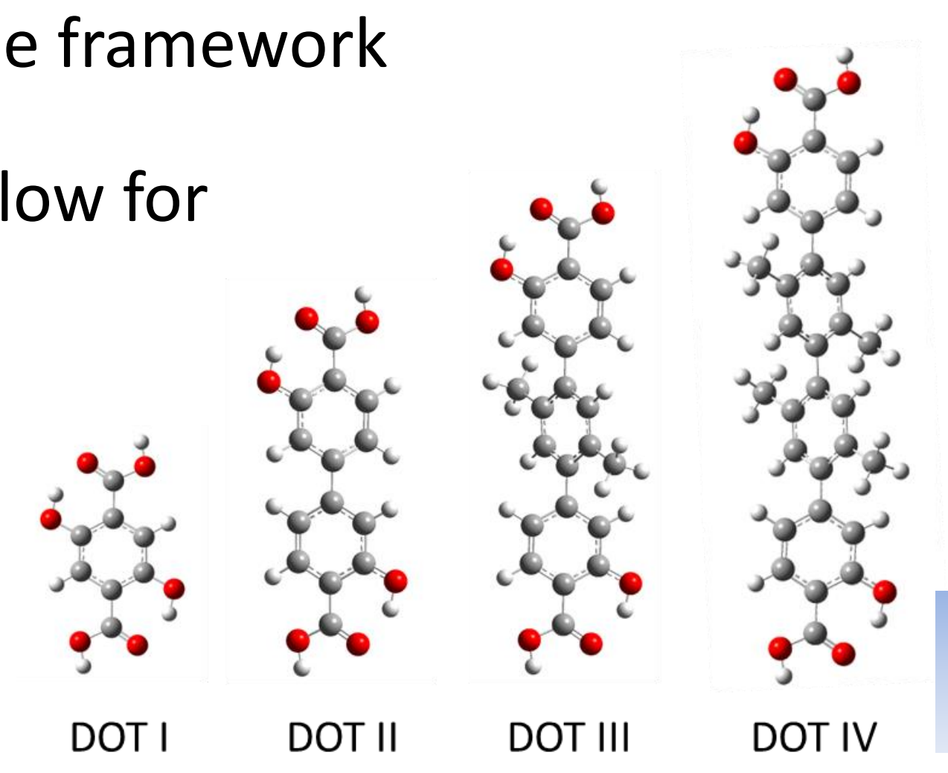
The use of metal organic frameworks (MOFs) is a natural step towards controlling nanoscale donor/acceptor interfaces due to the inherent ordering and self-assembly of these porous crystalline frameworks. The advantage of this configuration is that it confines both the donor and acceptor within a highly ordered chemical environment and drastically minimizes the exciton diffusion length.

MOF-74 - DOT Linkers

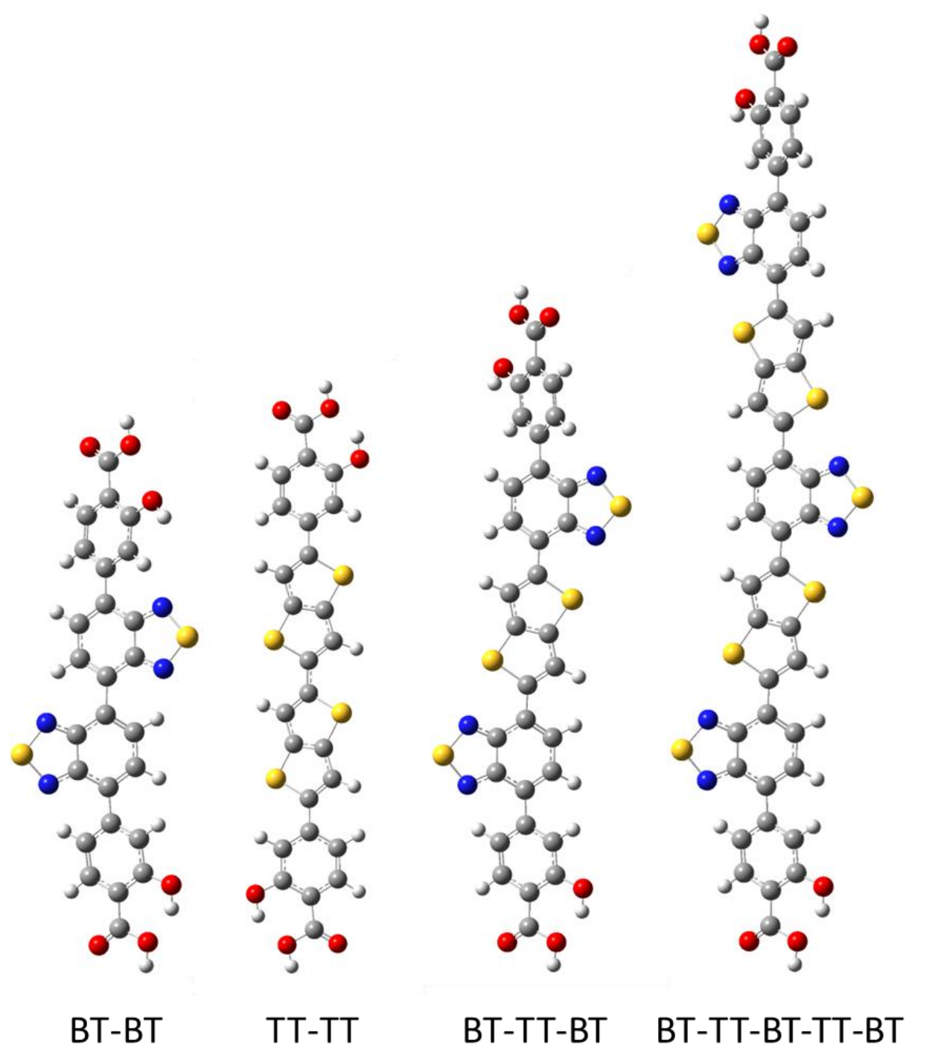


MOF-74-II (Mg)

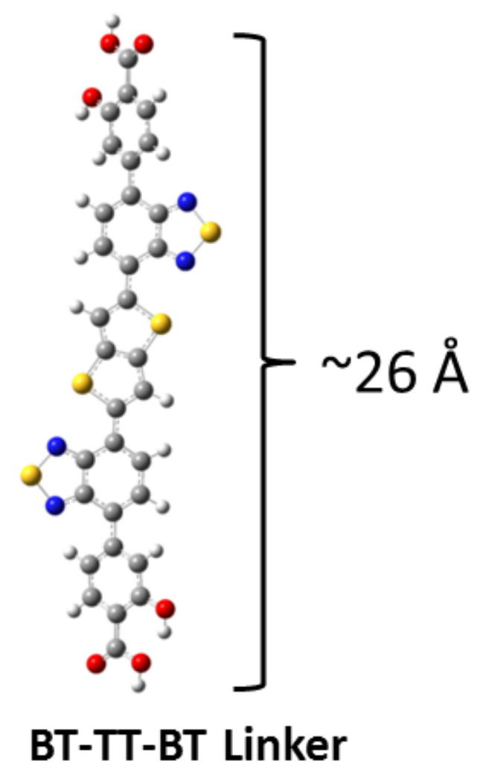
- The linker of MOF-74 can be systematically lengthened to include up to 11 phenylene rings demonstrating the synthetic modularity of the framework
- Large 1D pore channels allow for ample infiltration of guest molecules
- Framework morphology enables interactions between the linkers

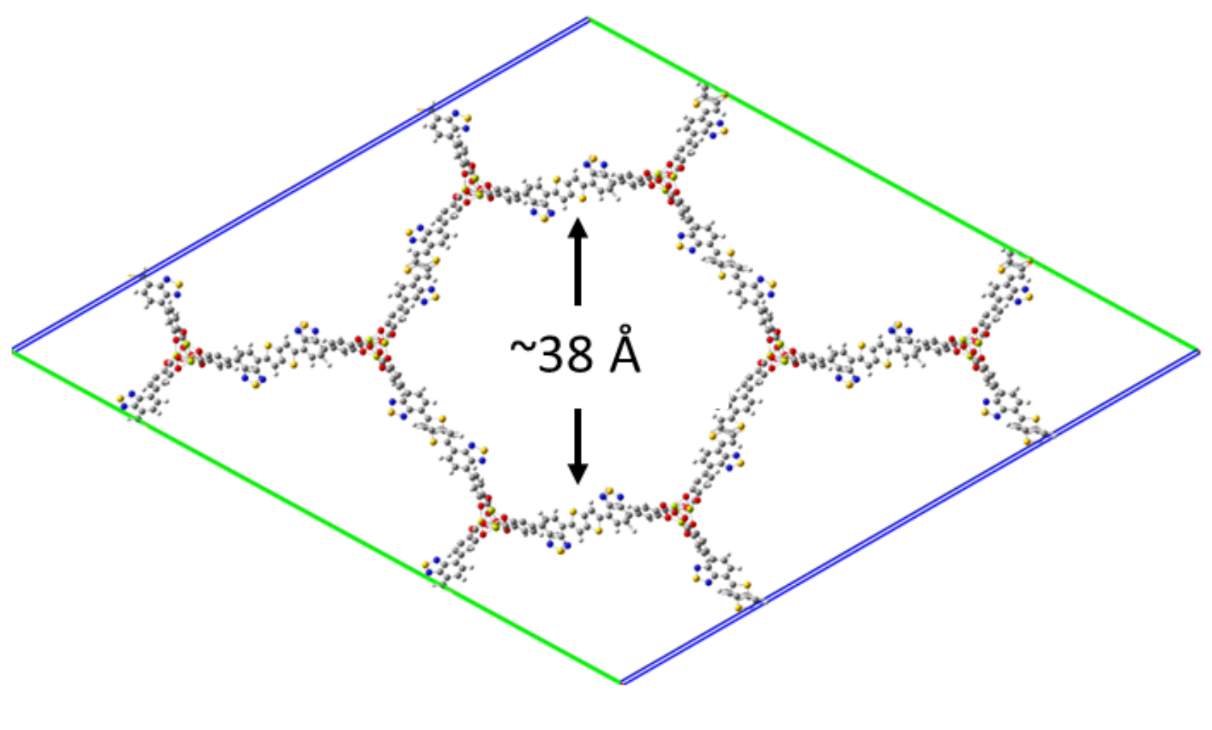


MOF-74 - Proposed Linkers for Light Harvesting

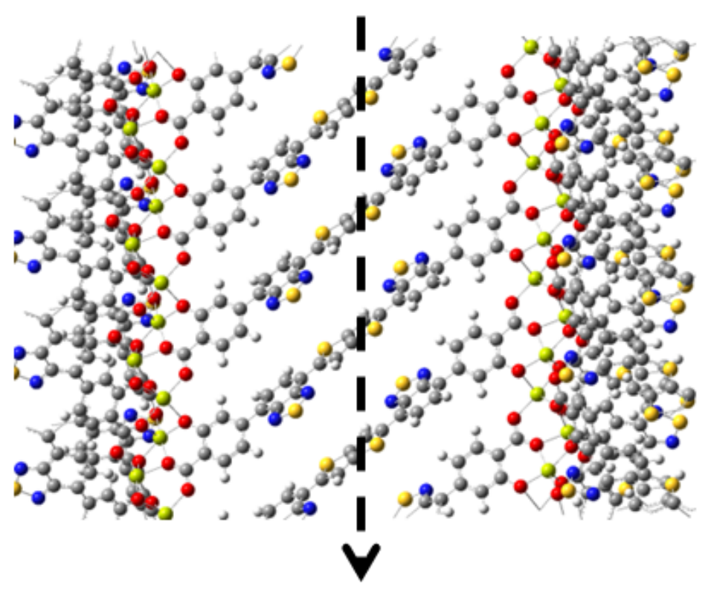


- The proposed linkers have a conjugated backbone allowing visible light to be absorbed
- The orientation of the linkers create a continuous π-π stacking network that should enable charge transport
- Large 1D pore channels are sufficient to accommodate electron acceptor materials (e.g PCBM)



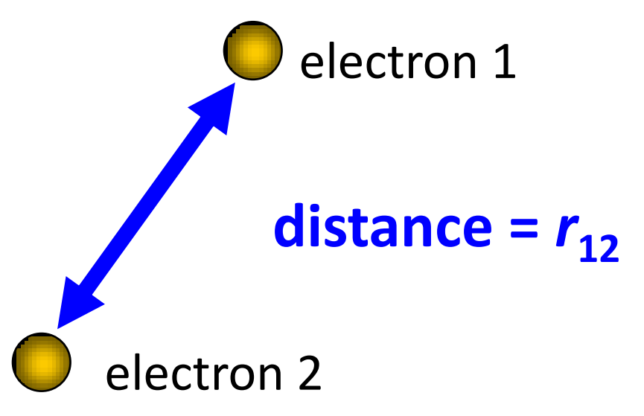


Linker orientation allows for π - π stacking (~5 Å)



Non-empirically Tuned Range-separated Functionals

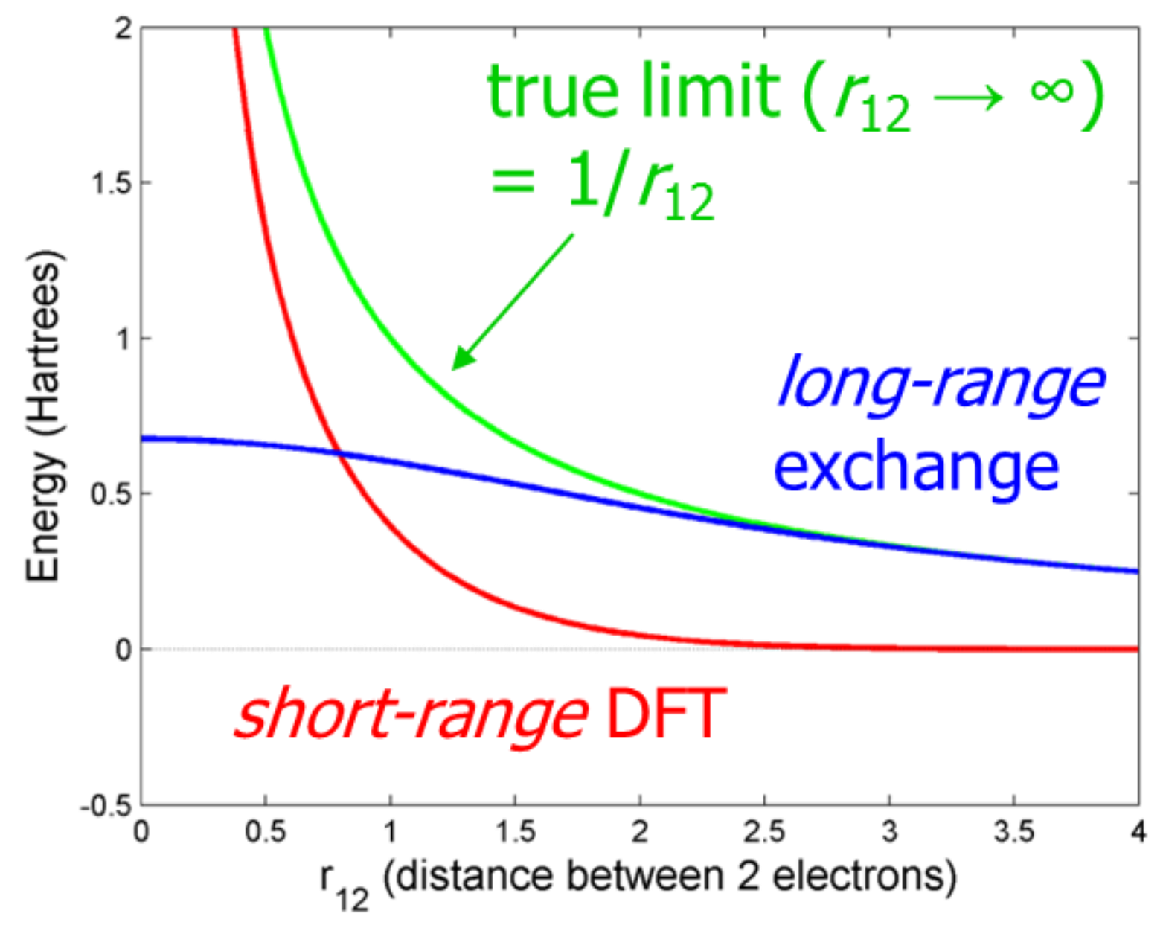
Local DFT exchange potentials have the wrong asymptotic behavior at long-range; as a result, charge-transfer excitations are severely underestimated and molecular orbital energies are poorly predicted.



The range-separated formulism splits the coulomb potential into short-range and long-range terms to recover the correct functional form of electron exchange at long-range.

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

μ = range separation parameter (1/Bohr)



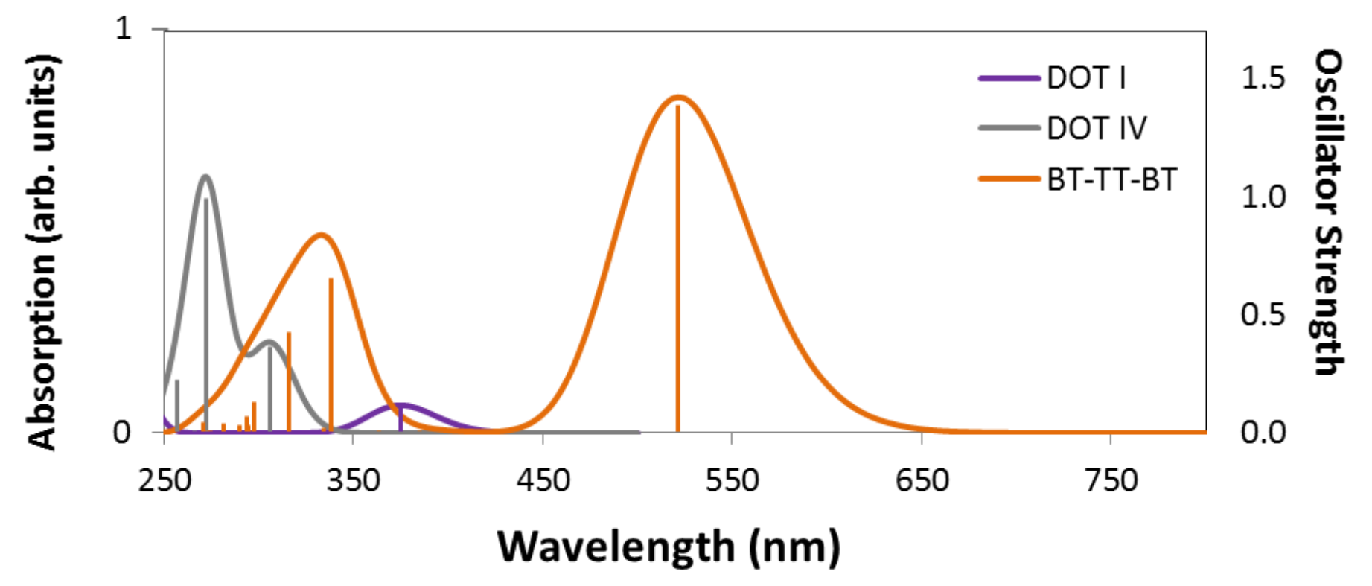
The range separation parameter can be non-empirically tuned for a given system by minimizing the following function:

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

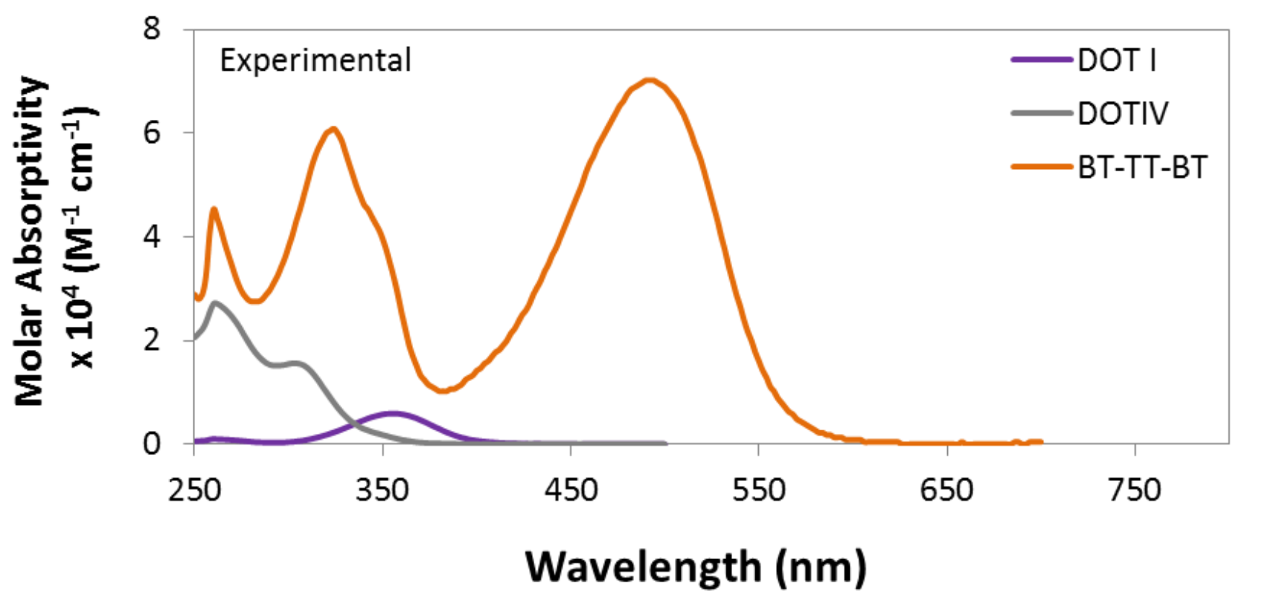
The optimal μ value ensures that the negative of the HOMO energy is equal to the ionization potential. This is a fundamental condition within the Kohn-Sham DFT formalism (i.e., Janak's theorem) justifying the self-consistent tuning of μ.

Optical Properties

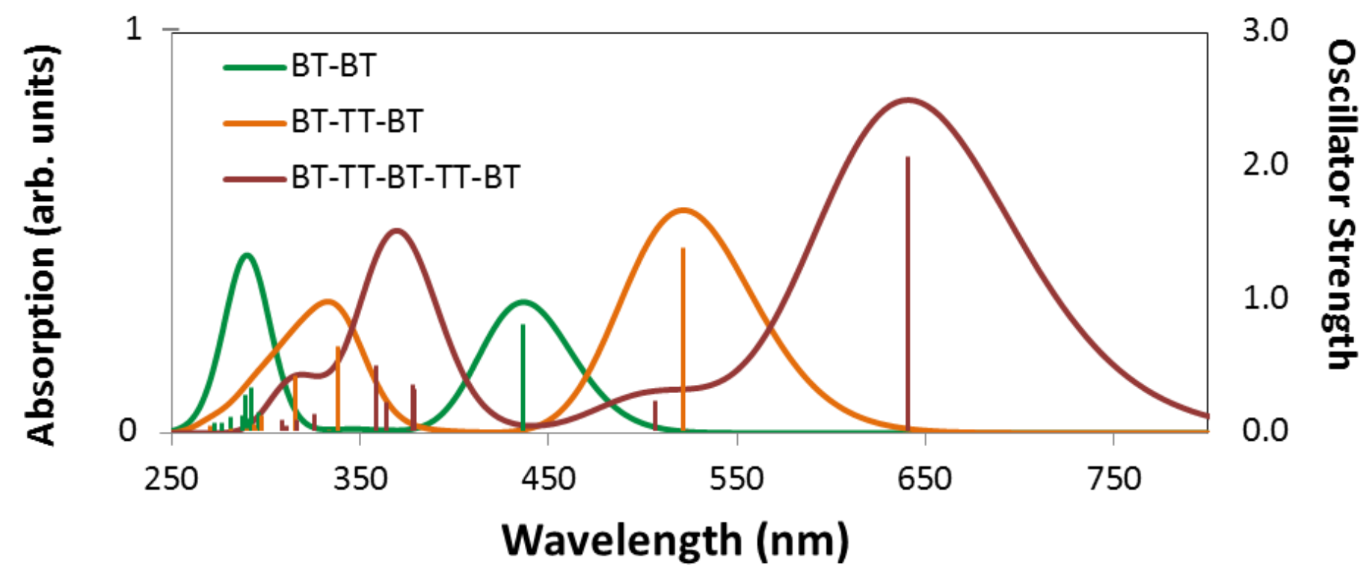
- DOT linkers absorb little, if any, of the visible spectrum, making them of little use for PV applications



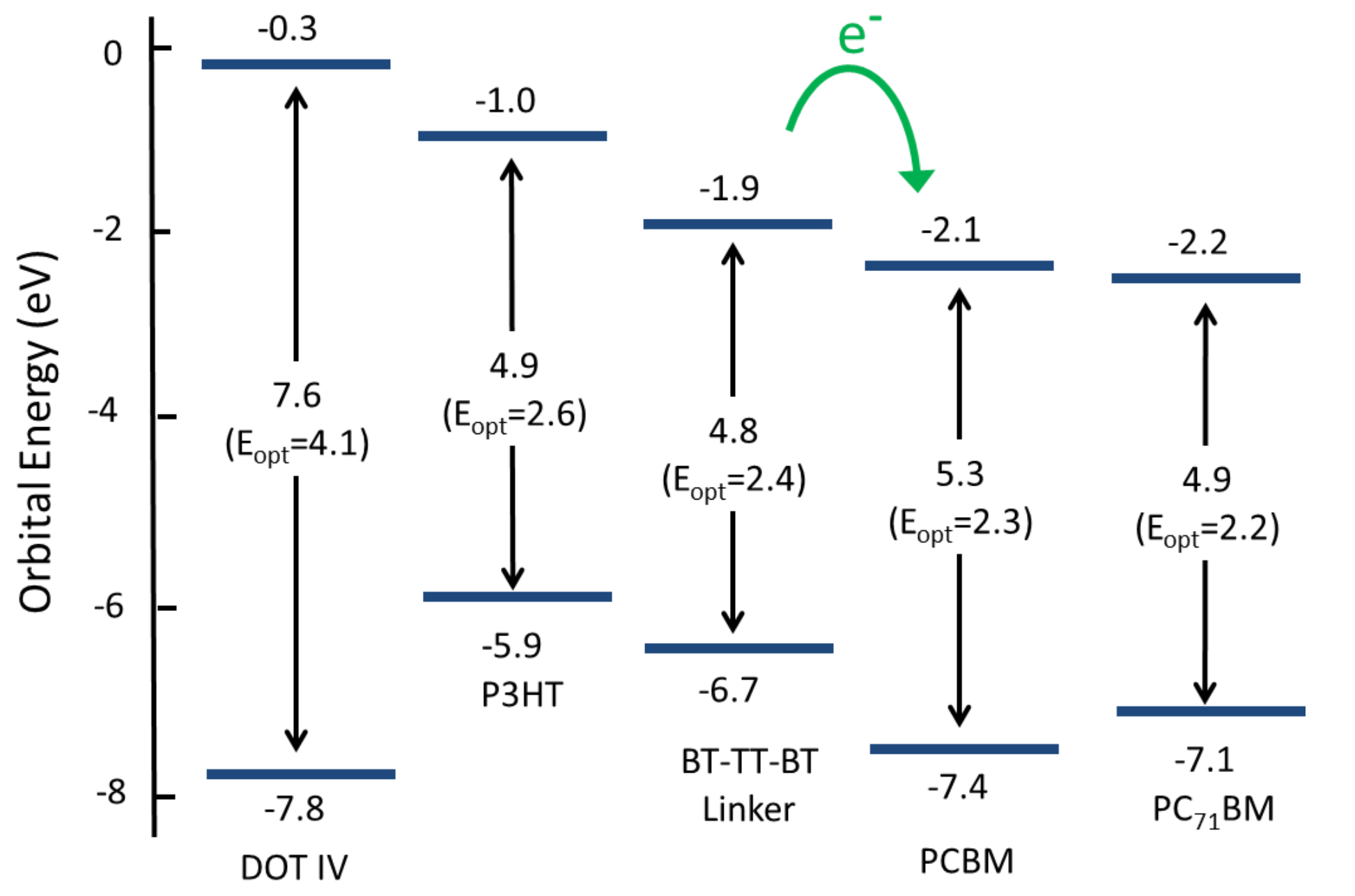
- Excellent correlation between TDDFT predicted (top) and experimental (middle) absorption spectra



- As the BT/TT length increases, the absorption shifts to the red with a concomitant increase in the oscillator strength, equivalent to an increase in molar absorptivity

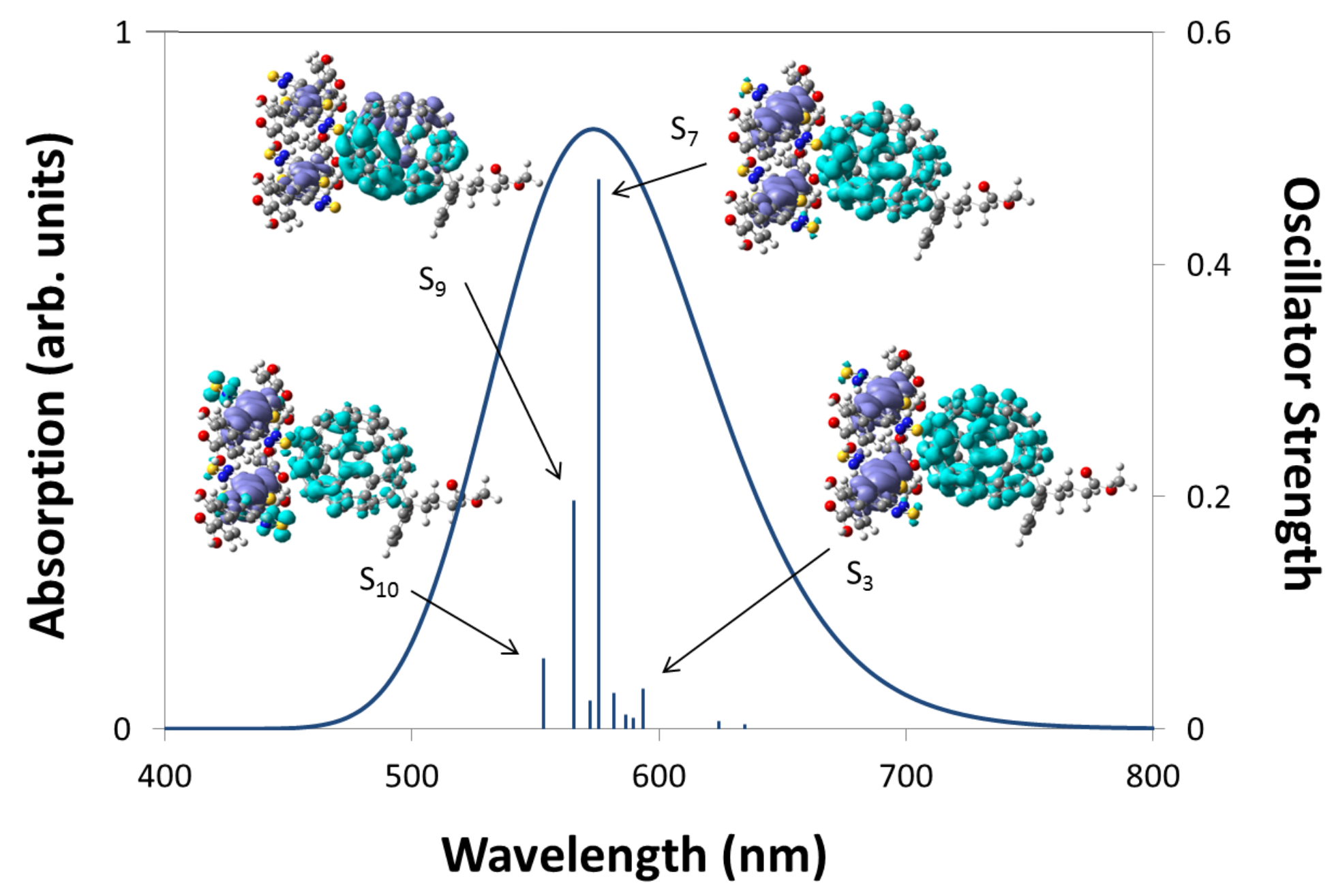


Orbital Alignment and Charge Transfer



- The DOT linkers have improper orbital alignments with known electron acceptors (e.g. PCBM); as a result, lack the ability to transfer charge to PCBM
- The BT/TT linkers have the proper band alignment with respect to PCBM and $PC_{71}BM$

- Upon photoexcitation, electron density is transferred from BT-TT-BT to $PC_{71}BM$ (charge transfer)
- In a MOF based device, the acceptor and donor domains are well ordered and minimum exciton diffusion is required.



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