



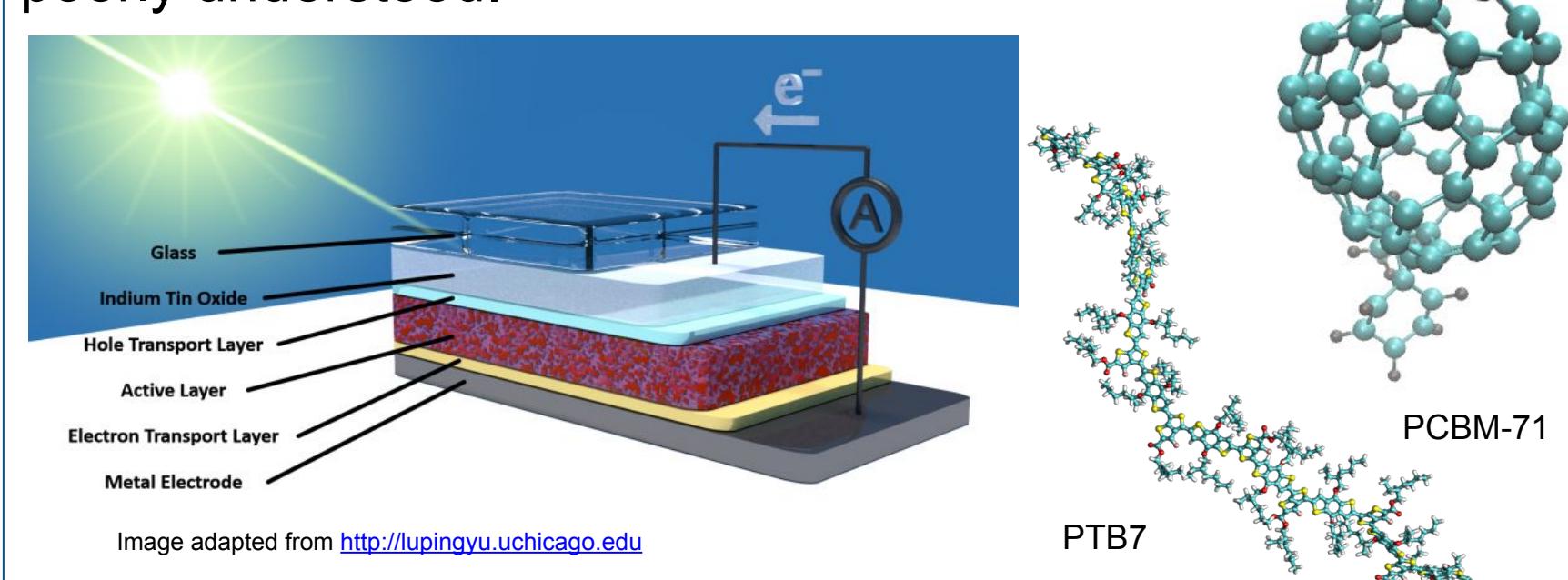
Nanoscale modeling of charge transport

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BACKGROUND

INTRODUCTION

The light absorbing layer in organic photovoltaics (OPVs) consists of a finely interwoven network of two or more types of donor and acceptor molecules. For a device to achieve high efficiency, several challenges must be addressed: First, the donor and acceptor components must microphase separate, providing high interfacial area and conduits for charge transfer. Second, the microphases of donors and acceptors must connect to their respective electrodes. Third, the donor and acceptor must be designed such that they provide a high open-circuit voltage. The complex structures within the bulk heterojunction and the effects of these structures on the efficiency of OPV devices are poorly understood.



To model the electronic structure of polymer blends, we use density functional approximations and many-body theory with a plane-wave basis and periodic boundary conditions.

Quantum dot solids also hold much promise for light harvesting. By splitting one exciton into multiple excitons, the external quantum efficiency can exceed 100%, which has been shown in experiment. However, charge transport in real devices is poorly understood at an atomic scale and better models are needed to understand how defects can effect transport.

We perform calculations using a newly developed implementation of constrained DFT[‡] to study charge transfer and transport properties for these systems.

[‡]M. B. Goldey, N. P. Bawand, M. Vörös, G. Galli, J. Chem. Theory Comput. In Press

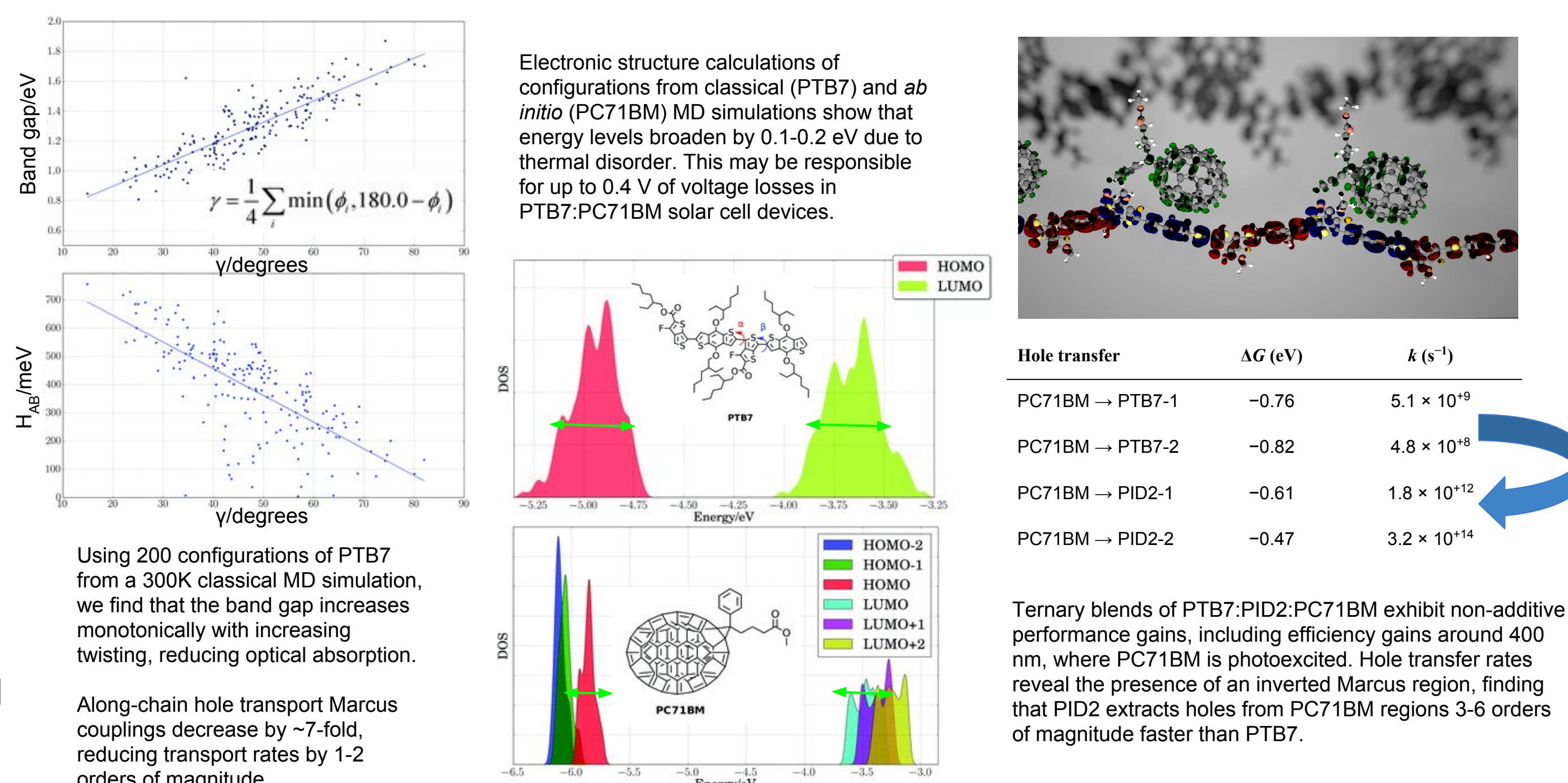
Image adapted from <http://lupinyu.uchicago.edu>

ORGANIC ELECTRONICS

CONDUCTING POLYMER SOLAR CELLS

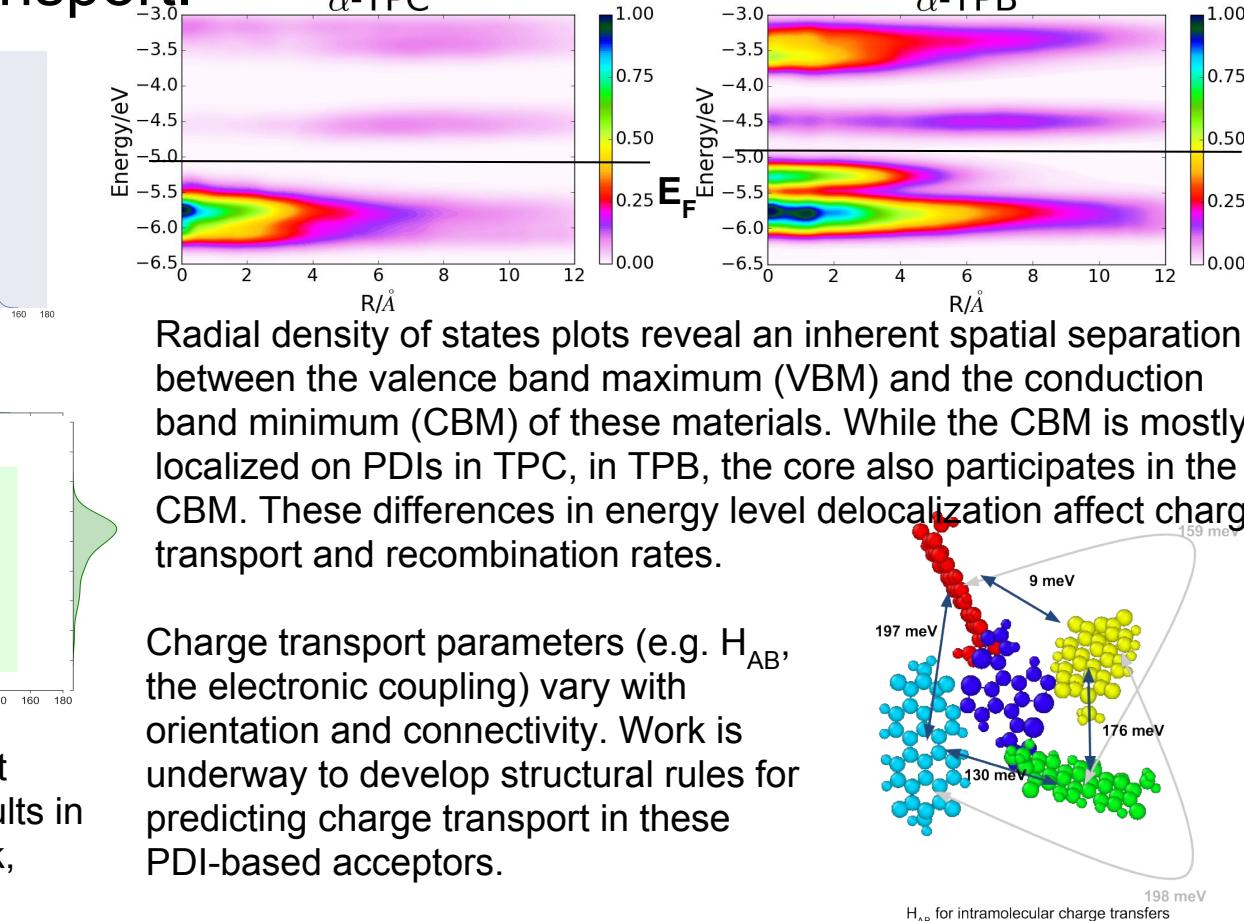
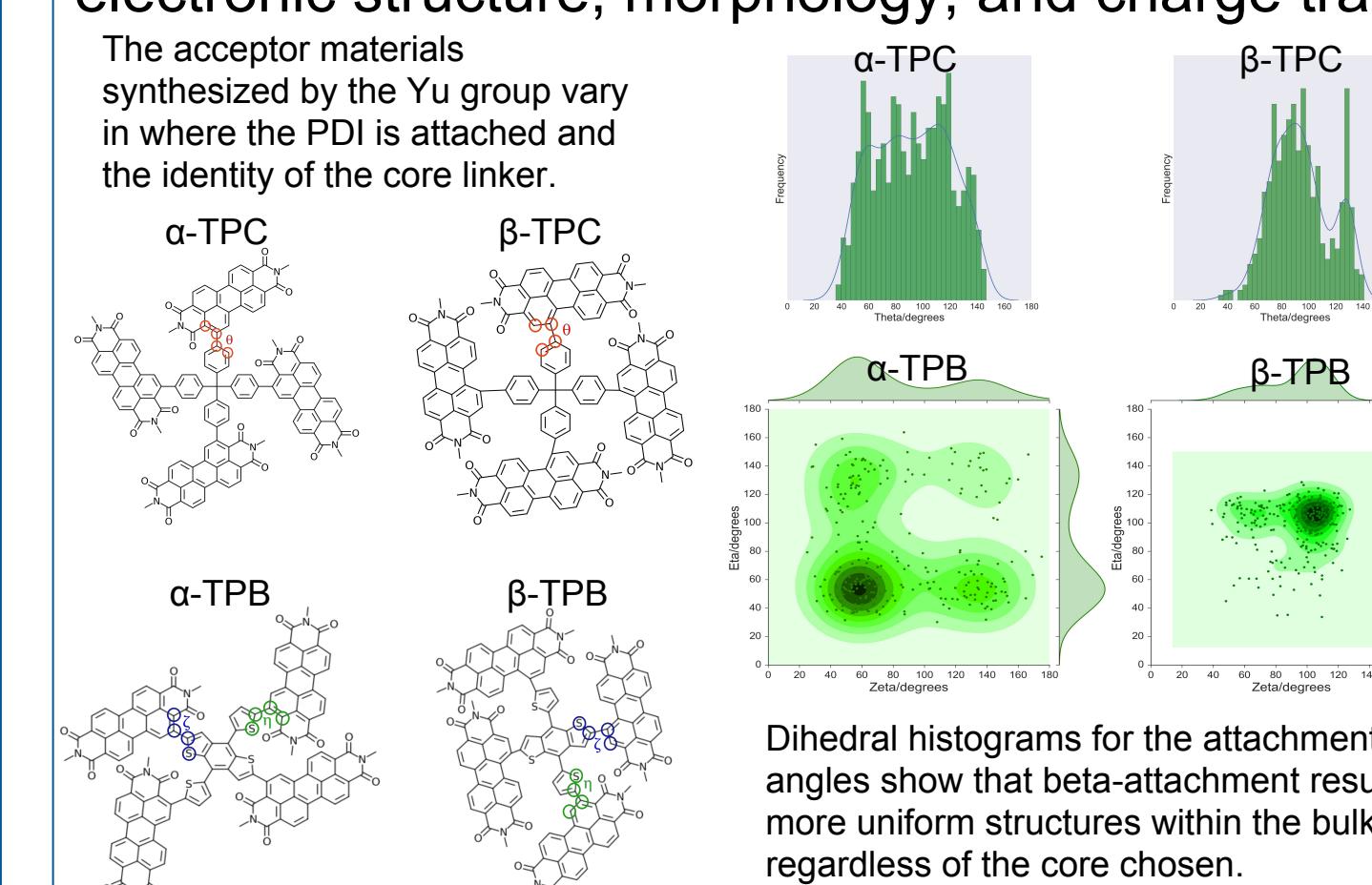
In order to understand how conformation and morphology affect the electronic and transport properties of OPV polymers, we report coupled classical and *ab initio* molecular dynamics simulations showing that polymer linkage twisting significantly reduces optical absorption efficiency, as well as hole transport rates in donor polymers. We predict that blends with components favoring planar geometries contribute to the enhancement of the overall efficiency of ternary OPVs. Furthermore, our electronic structure calculations for the PTB7:PID2:PC71BM system show that hole transfer rates are enhanced in ternary blends with respect to their binary counterpart. Finally, our results point at thermal disorder in the blend as a key reason responsible for device voltage losses and at the need to carry out electronic structure calculations at finite temperature to reliably compare with experiments.

M. B. Goldey, D. Reid, J. de Pablo, and G. Galli, *Phys. Chem. Chem. Phys.*, 2016, **18**, 31388.



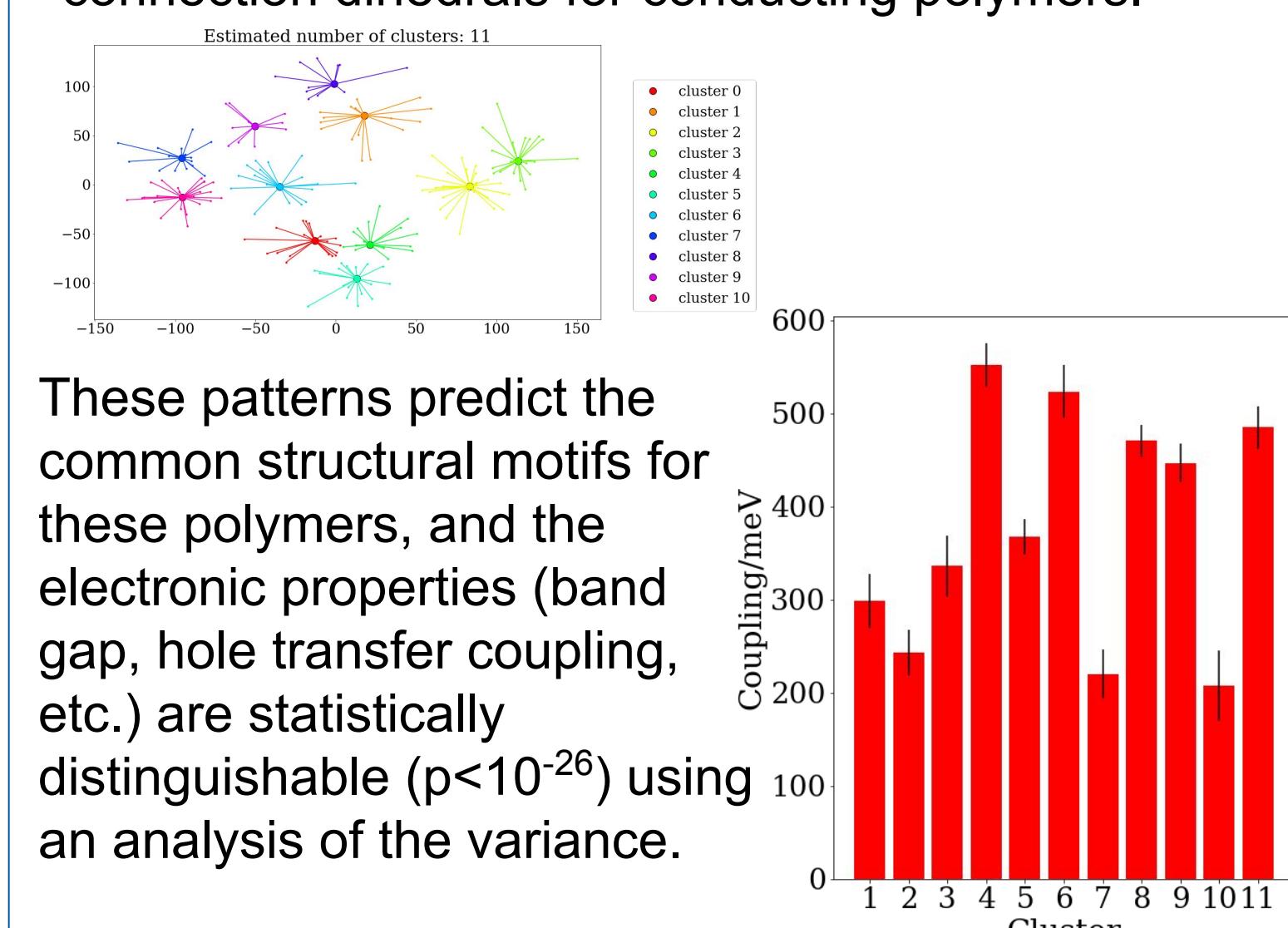
NON-FULLERENE ACCEPTORS

OPV acceptor materials are conventionally made from fullerene derivatives, but poor optical absorption, the instability of bulk morphologies, and high costs limit the potential of fullerene-based solar cells. New developments in the Yu group based on perylene diimide (PDI) molecules (connected via twisted, though pi-conjugated, cores) exhibit promising photoconversion efficiencies. We found that the connectivity to the core drives different electronic structure, morphology, and charge transport.

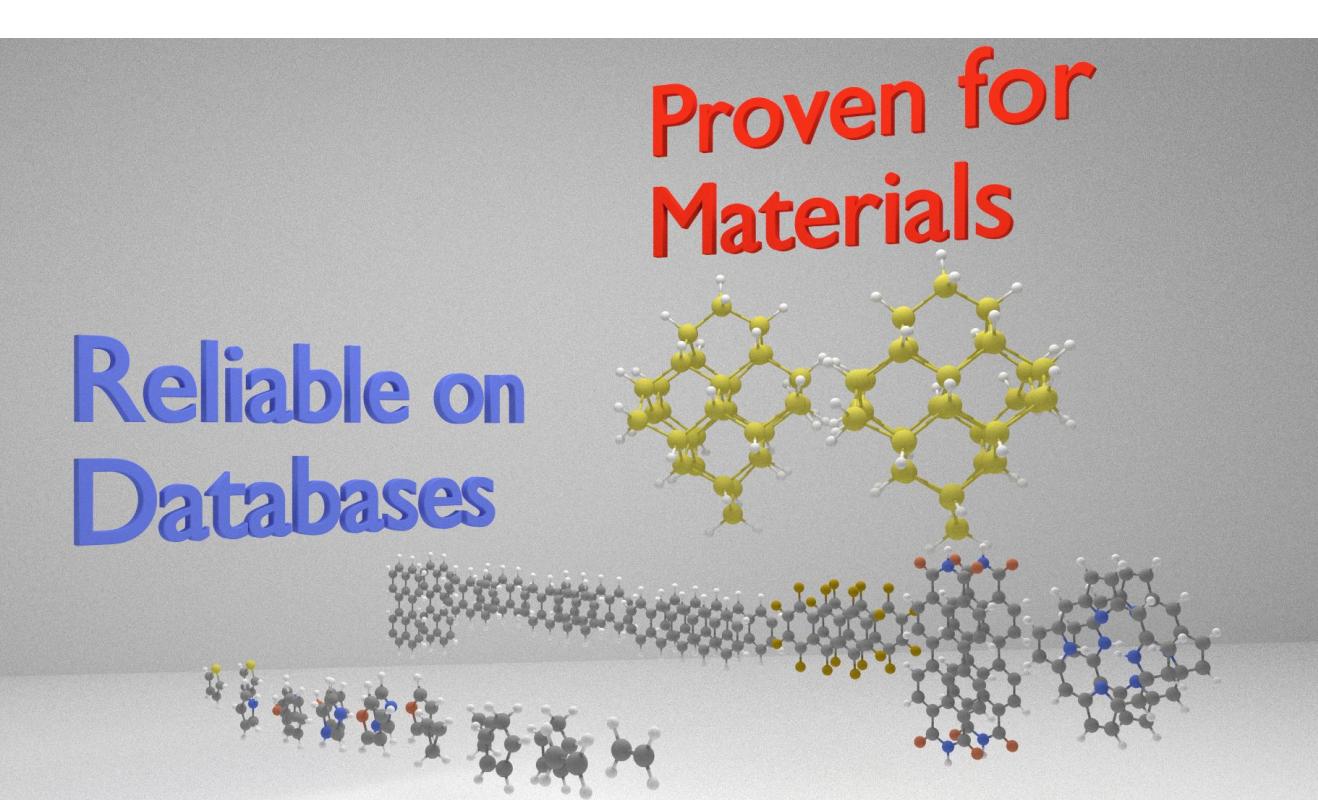


MACHINE LEARNING

Using principal component analysis and affinity propagation, we identified different patterns in the connection dihedrals for conducting polymers.



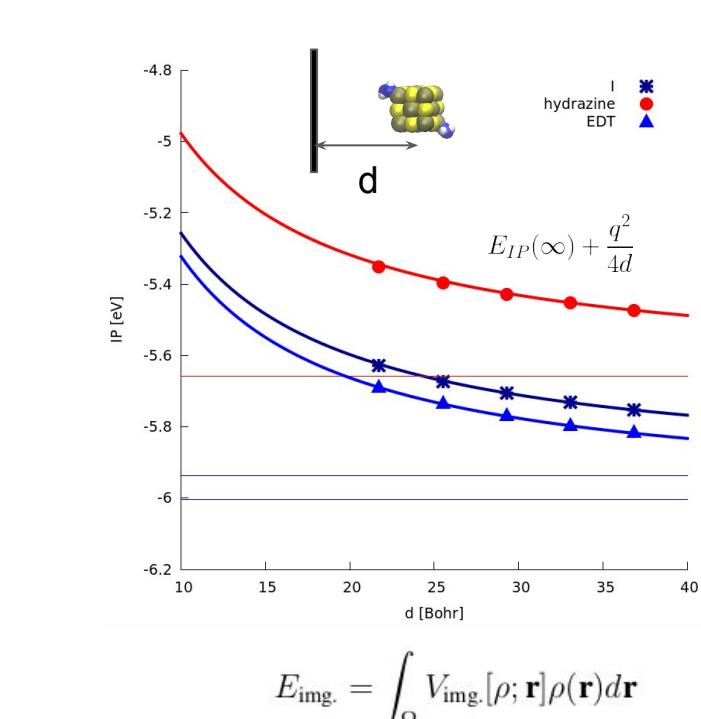
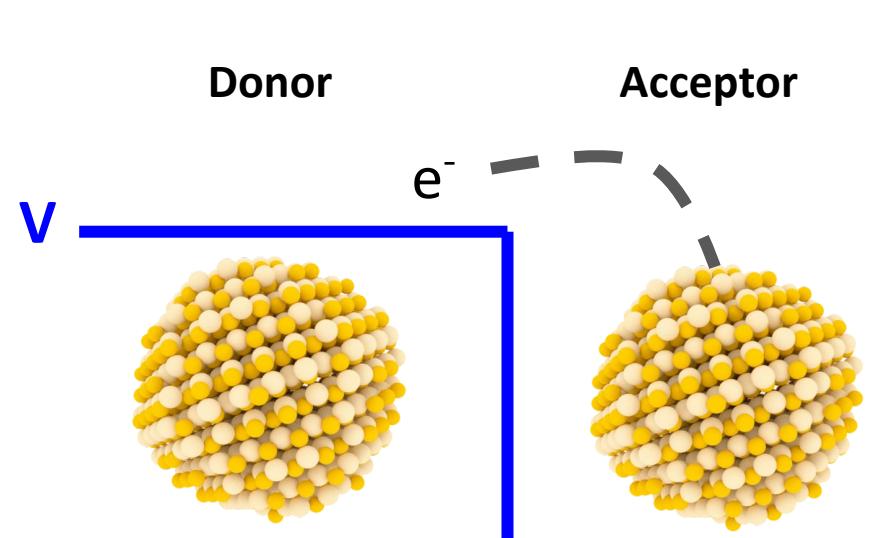
METHODOLOGY



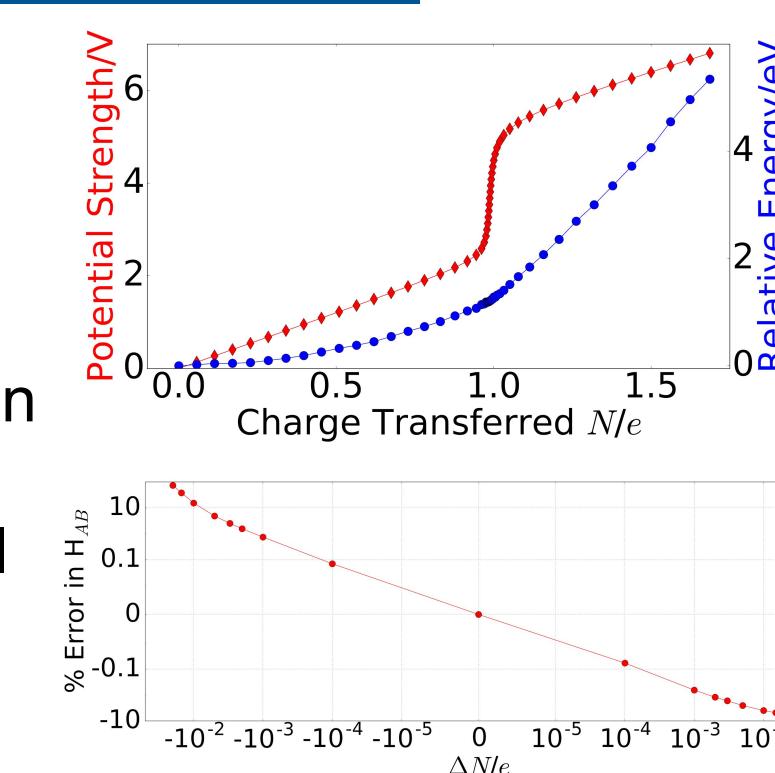
Constrained DFT adds a potential to the Kohn-Sham energy,

$$F[\rho(\mathbf{r})](N) = E[\rho(\mathbf{r})] + V \left(\int_{\Omega} w(\mathbf{r}) \rho(\mathbf{r}) d^3 \mathbf{r} - N_0 \right)$$

self-consistently optimizing the strength to transfer exactly N_0 electrons. Our implementation also adds the option to include the potential from an image charge in order to predict charge transport near electrode and substrate surfaces.

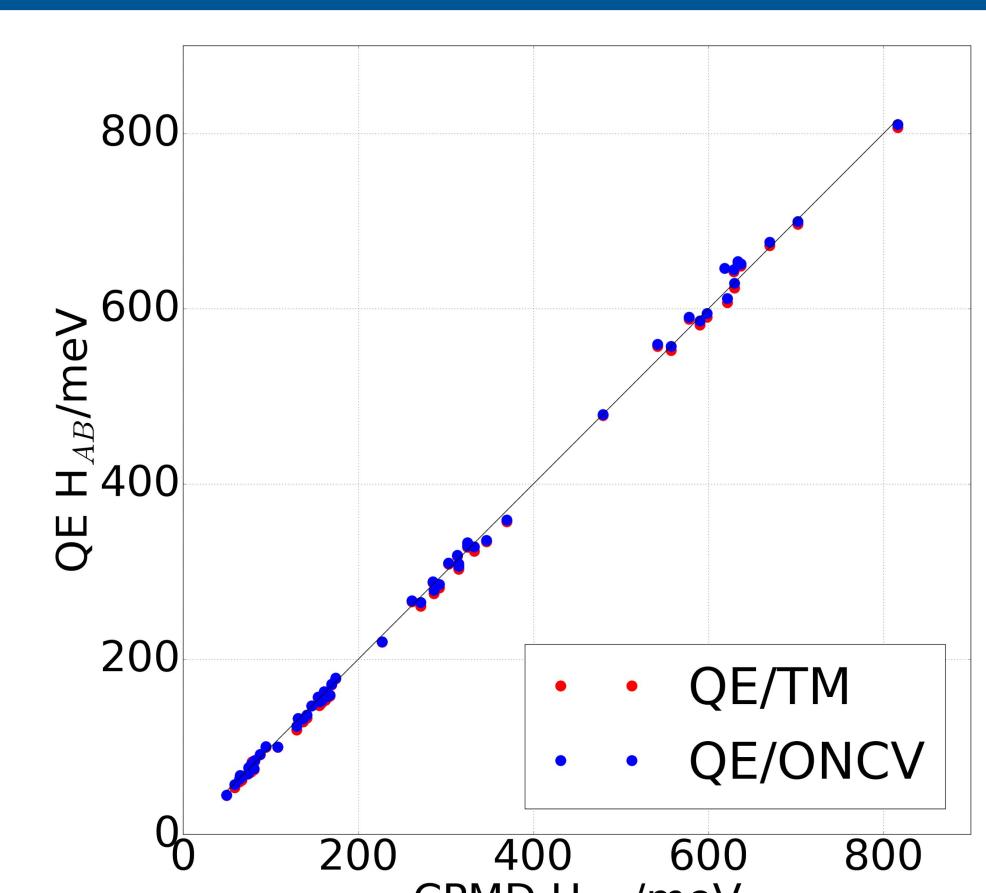


We find that total energies behave nonlinearly with partial charge transfers, indicating self interaction error. Couplings are highly sensitive to small errors in the charges transferred.



Comparing our results against literature values, we find very weak dependence on implementation and choice of pseudopotential, under 2% mean absolute percent error.

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HOW RCC RESOURCES WERE USED

- Prototyped and developed new code for predicting charge transport in nanostructured materials; benchmarked and verified new code using RCC's Midway
- Implemented daily regression testing on Midway during and after development using RCC-hosted git repository
- Employed machine learning algorithms to classify and cluster polymer configurations, data was hosted and processed on Midway
- Used blender software on Midway to illustrate structures and isosurfaces for figures used in publications
- Created jupyter notebook, hosted by RCC, to display results from papers to funding agencies in an interactive format