Modeling Charge-Transport Pathways in Covalent Organic Frameworks

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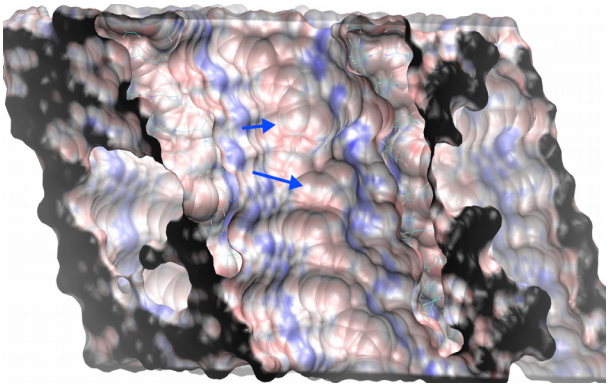
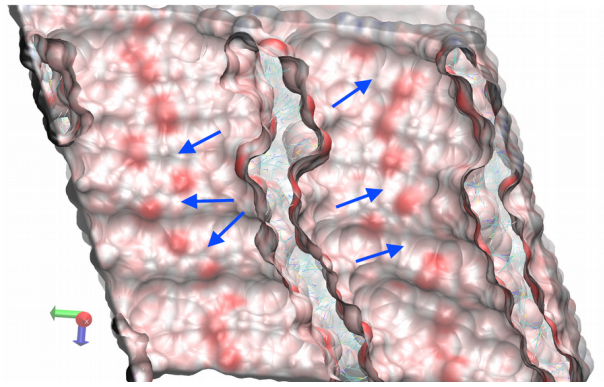
Background Covalent Organic Frameworks (COF) are highly crystalline porous materials. When central metals are inserted in the framework, it produces semiconductor COFs capable of conveying both electrons and holes for use in optoelectronics. Simulating charge transport through the molecular scaffold of the COFs is a challenging Multiscale Problem, because the time scale for the charge transfer is in a range of 10^{-15} sec, while that for the conformational movement is in 10^{-12} sec.

Results We used the co-condensation product of (5,10,15,20-tetra(4-aminophenyl)porphyrin) (TAPP) and thieno[3,2-b]thiophene-2,5-dicarboxaldehyde (TT) for our work. The crystal structure was optimized and MD simulation was done at NPT for 10 nanoseconds. The calculated powder XRD pattern confirmed structure preservation and showed identical high-intensity peaks to those in the experimental one. The electronic structure of the selected ensembles was calculated semiempirically using the AM1* Hamiltonian with *EMPIRE* software. The local electronic properties are then extracted from the wavefunction as Local Electron Affinity ($\boldsymbol{A_L}$) and Local Ionization Energy ($\boldsymbol{I_L}$). We then applied Metropolis Monte Carlo algorithm to track the charge carrier pathways.





Conclusions The PES of $\boldsymbol{A_L}$ and $\boldsymbol{I_L}$ (in the figures below) are color-coded with Red-White-Blue (RWB) gradation; low energy values in **red**, middle values in **white** and high values in **blue**. The arrows point to the energy barriers of the electrons and holes transport pathways. The qualitative results of the search algorithm showed that electrons prefer a pathway through the porphyrin rings and the holes prefer that pathway through the TT linker of the TAPP-TT COF.

[1] Clark T: **Simulating charge transport in flexible systems**. *Perspectives in Science* 2015, **6**:58-65.
[2] Dogru M, Bein T: **On the road towards electroactive covalent organic frameworks**. Chem Commun (Camb) 2014, 50(42):5531-5546.