Charge and Exciton Transport in the Transient Delocalization Regime

Jochen Blumberger, Jan Elsner, Samuele Giannini

University College London, Department of Physics and Astronomy, Gower Street, London, WC1E6BT, UK

Recent computational and experimental studies on ordered organic semiconductors (OS) have shown strong evidence that charge carriers (holes or excess electrons) as well as excitons (bound electron-hole pairs) form partially delocalized quantum objects ``half way" between waves and particles (Fig. 1)[1-7] Strong thermal disorder between the weakly bound molecules in the crystal prevent full wave-like delocalization while sizable electronic couplings and small nuclear reorganization energies prevent full localization. The partially delocalized charge carriers and excitons were found to diffuse through OS via a novel transient delocalization mechanism[1-5,8-9], in a scenario that cannot be described with the standard tools developed for band transport in inorganic semiconductors or hopping transport in aqueous or biological systems. In this talk I will briefly present the quantum dynamical simulation methodology that has led to this picture[10] and I will review design rules extracted from these simulations that pave the way for development of materials with high charge mobilities or exciton diffusion constants. [3,10] I will also give an outlook on our current mechanistic understanding of thermoelectricity in the transient delocalization regime characteristic for ordered OS.

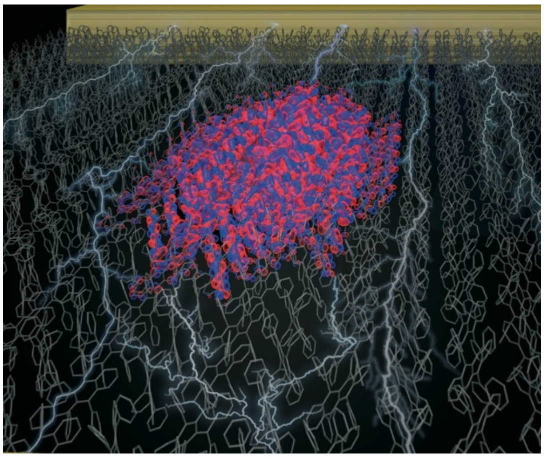

Fig. 1. Snapshot of the hole carrier wavefunction in rubrene at 300 K delocalising over about 5 nm (from Ref. 2).

References

[1] S. Giannini *et al.*, Nat. Commun. **10** (2019) 3843.

[2] S. Giannini *et al.*, Adv. Theory Simul. **3** (2020) 2000093.

[3] S. Giannini *et al.*, Nat. Commun. **13** (2022) 2755.

[4] A. J. Sneyd *et al.*, Sci. Adv. **7** (2021) eabh4232.

[5] A. J. Sneyd, D. Beljonne, and A. Rao, J. Phys. Chem. Lett. **13** (2022) 6820.

[6] D. Balzer *et al.*, Chem. Sci. **12** (2021) 2276.

[7] A. M. Alvertis *et al.*, Phys. Rev. Lett. **130** (2023) 086401.

[8] S. Fratini, D. Mayou, and S. Ciuchi, Adv. Funct. Mater. (2016) 2292.

[9] S. Fratini et al., Nat. Mater. **19** (2020), 491.

[10] S. Giannini *et al.*, Acc. Chem. Res. **55** (2022), 819.