

Short-Range and Long-Range Excitonic Coupling in Molecular Aggregates: Organic Materials Design based on Sub Angstrom Packing Modifications

N.J. Hestand*, R. Tempelaar**, H. Yamagata*, T.L.C. Jansen**, J. Knoester** and F. C. Spano*

*Department of Chemistry, Temple University, Philadelphia, PA 19122

**Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Solid phases of π -conjugated molecules and polymers continue to receive widespread attention as semiconducting materials in field effect transistors, light emitting diodes and solar cells. However, despite the more than five decades of intensive experimental and theoretical research following Kasha's pioneering work on H- and J-aggregates¹ there are still a great many questions regarding the nature of the photo- excitations in molecular assemblies and how their spectral signatures are related to crystal packing and morphology. The theory of Kasha is based on the long-range Coulombic coupling between chromophores. However, in packing morphologies such as the commonly occurring π -stacking motif, the intimate contact between nearest neighbors allows for charge transfer and the creation of a short-range excitonic coupling mechanism due to wave function overlap. In this talk, it is shown how the simultaneous presence of long-range and short-range intermolecular couplings impact photophysical and transport properties in molecular π -stacks. The effect is similar to that recently described in polymer π -stacks.² The analysis is based on a Holstein-style Hamiltonian which includes Coulombic coupling and charge transfer. The interference between short-range and long-range couplings defines four aggregate types: HH, HJ, JH and JJ, based on the sign of the couplings. Each of the four aggregate types possess unique photophysical and transport properties. For example, HH-aggregates have constructively enhanced exciton mobilities and small radiative decay rates, making them excellent candidates for solar cell absorbers. JJ-aggregates can be superradiant at room temperature and therefore serve as good light emitting materials. The photophysical signatures of the four aggregate types include aggregation-induced changes to the vibronic progressions in the absorption and photoluminescence spectra.⁵ The vibronic progression, sourced primarily by the ubiquitous vinyl-stretching mode common to virtually all π -conjugated molecules, therefore serves as a direct probe of the nature of the excitonic coupling, as well as the exciton coherence length and mobility. Specific applications will be made to rylene π -stacks which have been intensively investigated as dye pigments and electron-transporting materials.^{4, 5} A new design paradigm for organic electronic materials is presented based on the extreme sensitivity of the short-range coupling to small (sub Angstrom) intermolecular displacements transverse to the stacking axis.^{6, 7}

References

1. M. Kasha, *Radiation Research* **20** (1), 55-70 (1963).
2. F. C. Spano and C. Silva, *Ann. Rev. Phys. Chem.* **65** (2014).
3. F. C. Spano, *Acc. Chem. Res.* **43** (3), 429-439 (2010).
4. F. Wurthner and M. Stolte, *Chem. Comm.* **47** (18), 5109-5115 (2011).
5. B. A. Jones, A. Facchetti, M. R. Wasielewski and T. J. Marks, *J. Am. Chem. Soc.* **129** (49), 15259-15278 (2007).
6. H. Yamagata, D. S. Maxwell, J. Fan, K. R. Kittilstved, A. L. Briseno, M. D. Barnes and F. C. Spano, *J. Phys. Chem. C* **118** (49), 28842-28854 (2014).
7. N. J. Hestand, R. Tempelaar, J. Knoester, T. L. C. Jansen and F. C. Spano, *Phys. Rev. B* submitted.

