RASEI

RENEWABLE AND SUSTAINABLE ENERGY INSTITUTE

BIG energy seminar series

Addressing global energy challenges in scale and complexity.

Short- and Long-Range Excitonic Coupling in Molecular Aggregates: Introducing a New Paradigm for Designing Organic Optoelectronic Materials

Frank Spano
Temple University

Date: September 22, 2016 9:30am – 10:30am
Location: SERF Auditorium at NREL - 15013 Denver West Parkway, Golden, CO 80401

Abstract:

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-aggregates[1] 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, I show how the simultaneous presence of long-range and short-range intermolecular couplings impact photophysical and transport properties in molecular π-stacks. 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 super radiant 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.[2] 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.[3, 4] 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.[5, 6]

Biography:

Frank Spano got his start at Middlesex County College where in 1980 he received an Associate in Science Degree. He then transferred to Lehigh University majoring in Physics, graduating in 1982 with a BS degree. However, the lure of Chemistry was too strong and in 1982 Spano entered the Graduate Program in Chemistry at Princeton University where he worked with Prof. Warren S. Warren on theory and experimentation in the area of Coherent Transient Spectoscopy. After obtaining a PhD in 1988, Spano went to the University of Rochester as a Post-doctoral Associate with Prof. Shaul Mukamel working on the theory of condensed phase Nonlinear Optics. In 1990 Spano began his academic career at Temple University where he remains to this day.

CAMPUS MAP: http://www.nrel.gov/pv/facilities_serf.html

Sponsored by the Renewable and Sustainable Energy Institute (RASEI) and National Renewable Energy Laboratory

colorado.edu/rasei

Abstract References

1. M. Kasha, Radiation Research 20 (1), 55-70 (1963).

2. F. C. Spano, Acc. Chem. Res. 43 (3), 429-439 (2010).

3. F. Wurthner and M. Stolte, Chem. Comm. 47 (18), 5109-5115 (2011).

4. B. A. Jones, A. Facchetti, M. R. Wasielewski and T. J. Marks, J. Am. Chem. Soc. 129 (49), 15259-15278 (2007).

5. 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).

6. N. J. Hestand, R. Tempelaar, J. Knoester, T. L. C. Jansen and F. C. Spano, Phys. Rev. B 91 (19), 195315 (2015).