

SÉMINAIRE DU DÉPARTEMENT DE GÉNIE PHYSIQUE

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Amphithéâtre du Pavillon J.-A. Bombardier, salle 1035

Prof. Frank C. Spano

Department of Chemistry, Temple University, Philadelphia

The Prospect of Exciton Band Shape Engineering in Organic Materials: Perylene Diimide-Based H_j- and hJ-Aggregates

The aggregated and crystalline phases of π -conjugated molecules and polymers continue to receive widespread attention as semiconducting materials for field effect transistors, light emitting diodes and solar cells. In such materials, the exciton band dispersion is a critical factor in determining the photophysical response and energy transport properties. In this talk the prospect of exciton band-shape engineering in organic materials is explored with applications made to π -stacks of perylene diimide chromophores.[1] In such stacks, the exciton band width and, in particular, the curvature at the band center, is determined by an interference between short-range coupling due to wave function overlap and long-range Coulomb coupling arising from transition dipole-dipole interactions.[2, 3] The interference can be completely destructive, yielding a dispersionless “flat” band resulting in an unusual situation where the aggregate displays monomer-like properties. Coupled chromophores such as these are called “null aggregates” and the perfect balance of interactions that leads to them are referred to as “null points”. The crystal and solution phases of two perylene diimide (PDI) derivatives, *N*-phenyl PDI and tetraphenyl PDI are analyzed in detail.[1] In the crystal phases of both derivatives positive long-range coupling induces H-aggregate behavior, whereas counteracting short-range coupling induces J-aggregate behavior. As such, both derivatives display so-called HJ-aggregate properties but are shown here to straddle a null point. In *N*-phenyl PDI π -stacks, the stronger Coulomb coupling tilts the scales in favor of overall H-like behavior resulting in H_j-aggregates, characterized by a weak 0–0 vibronic photoluminescence (PL) peak, which increases with temperature. By contrast, in tetraphenyl PDI π -stacks, the short-range coupling dominates, resulting in hJ-aggregates, as characterized by dominant 0–0 emission. Identifying the null points in PDI derivatives provides reference geometries for band shape engineering through, for example, chemically induced or pressure- induced changes in molecular packing. Another intriguing possibility is to use the coupling between material and radiation modes in an optical microcavity to control the interference between short- and long-range coupling.

[1] A. Oleson, T. Zhu, I.S. Dunn, D. Bialas, Y. Bai, W.Q. Zhang, M.J. Dai, D.R. Reichman, R. Tempelaar, L.B. Huang, F.C. Spano, Perylene Diimide-Based H_j- and hJ-Aggregates: The Prospect of Exciton Band Shape Engineering in Organic Materials, *Journal of Physical Chemistry C* 123 (2019) 20567-20578.

[2] N.J. Hestand, F.C. Spano, Expanded Theory of H- and J- Molecular Aggregates: The Effects of Vibronic Coupling and Intermolecular Charge Transfer, *Chem. Rev.* 118 (2018) 7069–7163.

[3] N.J. Hestand, F.C. Spano, Molecular Aggregate Photophysics beyond the Kasha Model: Novel Design Principles for Organic Materials, *Acc. Chem. Res.* 50 (2017) 341-350.

Vous êtes tous les bienvenus.

Responsable : Stéphane Kéna-Cohen

Courriel : s.kena-cohen@polymtl.ca

Poste : 2421

