Competitive Pathways in Structurally Dynamic Organic Chromophore Systems

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Organic chromophores provide a broad range of possibilities for developing next generation technologies based on converting light energy to electrical or chemical energy. These materials exhibit high extinction coefficients, ease of synthetic tunability, and desirable semiconducting properties, making them attractive candidates for light-energy conversion applications including photovoltaics and artificial photosynthesis. However, it remains difficult to control photoactive behavior in multichromophore systems, and this presents a critical roadblock to advancing them towards scalable applications.

Multichromophore assemblies exhibit through-space excitonic coupling interactions via the π-electron systems of adjacent chromophores. This is a critical component for driving their photoactive function, as exemplified in natural photosynthesis, which uses excitonic coupling to mediate light-harvesting and charge separation mechanisms. However, these through-space coupling interactions can also result in complex potential energy landscapes, with multiple pathways for excited state energy flow. In synthetic systems, the challenge arises in trying to optimize for desirable processes and minimizing detrimental ones.

Our group is working towards a fundamental understanding of how the interplay between molecular structure, interchromophore coupling and the influence of the surrounding environmental can be used to develop materials with designable and controllable photophysics, mediating processes such as light-harvesting, energy transport, and charge separation. Through-space coupling arises from electronic and vibrational interactions, and particularly depends on the distance and relative orientation of the chromophores. This talk highlights some of our recent work developing structurally dynamic multichromophore systems and elucidating their photophysics.

Delocalized Excited States and Ultrafast Energy Transfer in Self-Assembled Porphyrin Cage Systems

Natural photosynthesis utilizes light-harvesting systems that operate very efficiently under light-limited conditions. Excited-state energy transport is enhanced beyond the Förster rate due to the contribution of delocalized excitonically coupled states, which arise as a result of the relative arrangement of chromophores. In order to emulate photosynthesis and control excited-state energy transport, artificial systems need to achieve similarly precise arrangements of chromophores. We report[1] a series of Pd_nL_{2n} cages, arranging 4 (**Pd_2L_4**) or 24 (**$Pd_{12}L_{24}$** and **$Pd_{12}Lx_{24}$**) porphyrin chromophores around a self-assembled metal-organic cage scaffold. The average inter-porphyrin separation and orientation are controlled by the cage structure. Structural and optical studies indicate magnetic and dipolar interactions between the assembled porphyrins, which vary as function of porphyrin packing density and orientation. The ligands in the **Pd_nL_{2n}** assemblies have some freedom of movement that impacts their relative arrangements. Time resolved optical studies indicate excitation energy transfer between the porphyrins on the cages, which persists within the dynamicity of their through-space coupling interactions. The energy transfer rate and likely mechanism are further dependent on both the inter-porphyrin spacing as well as the topological orientation of the porphyrins. Our results indicate that incoherent Förster-type hopping is insufficient to describe the energy transfer dynamics, and the enhanced excited state hopping rates observed in some of the systems align with the presence of vibronic excitons arising from the through-space chromophore

coupling. The metal-mediated self-assembly approach developed here can act as a stepping stone towards artificial photosynthesis.

Mixed Electronic States and Competitive Pathways in Structurally Dynamic Perylene Diimide Systems

Photoexcited dynamics in through-space coupled chromophore systems are often described as following a sequence of well-defined diabatic electronic states. However, these states are often coherently mixed, with the system rarely in a "pure" Frenkel exciton state but more likely in a mixture of states of varying electronic and spin character. The photoexcited dynamics will therefore depend on how the molecular conformation and surrounding environment tunes the potential energy surface and electronic state mixing. We studied these effects in two different cases of through-space coupled chromophore systems, each of which demonstrate altered molecular conformation, and photophysics, depending on their surrounding environment.

First, we report[2] a conformationally flexible molecular foldamer consisting of two electron accepting perylene diimide chromophores connected via an electron donating diethylaniline bridge. The system adopts either an *open* (chromophores far apart) or *folded* (chromophores within π-stacking distance) form, depending on the solvent environment. This leads to multiple charge separation pathways, the balance of which is mediated by the environmental conditions. In the *open* form, the primary photoproduct is photoinduced charge separation between the electron donating bridge and one of the adjacent electron accepting chromophores. We also find evidence for dynamic conformational change within the *open* form conditions, which leads to a secondary excimer photoproduct in some solvent conditions. In the *folded* configuration, a new charge separation pathway dominates via symmetry breaking charge separation (SBCS) between the π-stacked chromophores, and no evidence of an excimeric state. SBCS is of critical interest to develop artificial photosynthesis and organic photovoltaics, and our work yields insight into how SBCS can be optimized over undesirably photoproducts, such as excimers.

Second, we observe[3] a reversible temperature mediated balance of photoproducts in a polycrystalline perylene diimide thin film. Temperature dependent GIWAXS and single crystal XRD indicate a structural change in the relative geometry of adjacent chromophores. We used time-resolved spectroscopy to identify competitive pathways of symmetry-breaking charge separation and singlet fission, the balance of which is mediated by the temperature. This work demonstrates that an external stimulus, in this case temperature, can be used to control excited state dynamics in this system, offering enticing potential for developing stimuli-responsive materials with programmable photophysics.

1. *T. Keijer, V. Grigorescu, C. Ramanan, J. Reek, submitted.*
2. *K. Thakur, S. Datta, P.W.M. Blom, D. Chaudhuri, C. Ramanan, J. Phys. Chem. B., 2024, 128, 1760-1770. doi.org/10.1021/acs.jpcb.3c07134*
3. *N. Ugur, et al., in preparation*