

NANO HIGHLIGHT

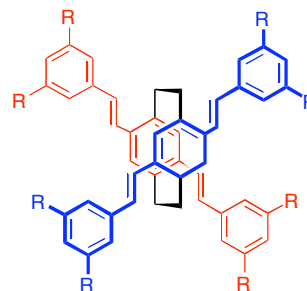
Novel Nanoengineered Chromophore Aggregates with Controlled Electronic and Optical Properties

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This project is focused on the design, synthesis, optical characterization, and modeling of novel materials, with the objective of developing nanoscale control of charge transfer and optical functionality between organic building blocks [1]. The molecular dimer illustrated in Figure 1 contains two chromophores held together in close proximity with a specific orientation by virtue of a paracyclophane (**pc**) core. The chemistry of **pc** allows us to explore electronic delocalization



(communication) between molecular units in a controlled fashion with respect to interchromophore orientation. Water soluble extended conjugated systems are crucial to the study of hydrogen bonding and solvation effects with potential applications to biosensors for proteins and DNA and for self assembly of protein/conjugated polymer complexes. We have developed an improved synthesis of water soluble ionic complexes (**1a** and **2a**) to examine the role of solvent polarity and polarizability on the energies of through-space and through-bond delocalized chromophore states. Solvent effects show that the through-space state is more polarizable and than the through-bond state. Comparative ultrafast pump-probe and simulation studies on another **pc** compound have been carried out to measure the electronic populations and coherences (anisotropy) that are created with optical pulsed excitation [2]. These studies reveal the intermolecular couplings and orientational relationships which often govern the electro-optical properties of bulk organic semiconducting materials. Other femtosecond and photon correlation spectroscopy experiments are designed to further uncover the dynamical correlations which regulate the optical-electronic properties of these aggregates. A new direction of this project involves collaboration with Prof. Wilson Ho's group at the University of California-Irvine. A series of novel single molecule scanning tunneling microscopy (STM) experiments have demonstrated that a single **pc** dimer molecule on a NiAl(110) surface can undergo a reversible switching between a high and a low conductivity state when activated by an external electric field [4]. Inelastic electron tunneling images with sub-molecular resolution reveal how various vibrational modes of the molecular junction are coupled to the tunneling current. Time-dependent density functional techniques for simulating these effects were developed [5].

Fig. 1: water soluble **pc** dimers

1a: R = O(CH₂)₄SO₃⁻N-Bu₄

2a: R = (CH₂)₆N-Me₃Br⁻

References

- [1] For more information link to <http://webfiles.uci.edu/nirt/www/index.html> or email smukamel@uci.edu.
- [2] "Solvatochromism of distyrylbenzene pairs bound together by [2.2]paracyclophane: Evidence for polarizable 'through-space' delocalized state," J. W. Hong, H. Y. Woo, B. Liu, and G. C. Bazan, in press *J. Am. Chem. Soc.* (2004).
- [3] J. Maddox, J. Kim, J. Hong, G. C. Bazan, N. F. Scherer, and S. Mukamel, in preparation.
- [4] C. Silien, N. Liu, W. Ho, B. Liu, G. C. Bazan, J. Maddox, and S. Mukamel, in preparation.

[5] "Superoperator many-body theory of molecular currents: Non-equilibrium Green functions in real time," U. Harbola and S. Mukamel, in press *Phys. Rev. B* (2004).