

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]. Understanding and manipulating through-space electronic communication within aggregates of organic fragments with delocalized bonding structures can impact a range of nanotechnology applications. However, interrogating aggregates of this type has encountered multiple difficulties in the past, ranging from heterogeneity of environments in the solid to the ill-defined geometry of intermolecular contacts in solution. These difficulties are circumvented by designing aggregates which contain [2.2]paracyclophane (**pc**) contacts among molecular units with well-defined architectures and dimensions. These offer excellent control over the distance and relative orientation of the participating units. The synthetic design of these molecular frameworks is coupled to a rigorous spectroscopic and theoretical characterization that interrogates electronic structure.

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 the self assembly of protein/conjugated polymer complexes. The series of compounds shown in Figure 1 were designed and synthesized to examine how through-space and through-bond electron delocalization respond to solvent effects [2]. The general strategy involves the study of the distyrylbenzene chromophore dimers that are held in close proximity by the **pc** core with specific orientation, and a systematic dissection of the chromophores into through-space and through-bond delocalized fragments. Steady-state and time-resolved fluorescence spectroscopies in a range of solvents reveal a red-shift in emission and an increase in the intrinsic fluorescence lifetime for the emitting state of distyrylbenzene dimers in polar solvents when donor substituents are absent. We found that for a given neutral/charged pair, the photoluminescence (PL) properties are identical when in the same solvent, which implies that the ionic groups are not responsible for spectroscopic differences. **pCp-C** shows a solvent induced red-shift in PL and an increased fluorescence lifetime, which does not occur in the parent **DSB-C** chromophore. That information, in conjunction with the solvatochromic effect in **pCp/pCp+** indicates that the through-space state created by electron exchange across the **pc** core is more susceptible to solvent polarity. Analogy to excimer solvatochromism suggests that this solvent

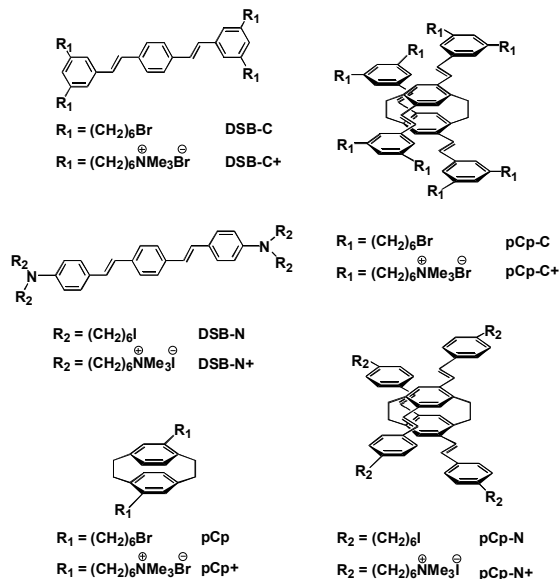


Fig. 1 A family of toluene (neutral) and water (ionic) soluble **pc** compounds.

effect is not due to a charge transfer component in the excited state, but rather to a more polarizable electronic structure as a result of the solvent Stark effect. The solvent Stark effect is further enhanced with increasing conjugation, which is also known to increase polarizability. The lowering of the energy of the through-space state makes its participation in the description of the excited state of **pCp-C** more pronounced, decreasing the oscillator strength and increasing the fluorescence lifetime. In **DSB-N** and **pCp-N** the solvatochromic behavior is dominated by charge transfer from the strongly donating amino components of the distyrylbenzene chromophore, and consequently, similar solvent induced red-shifted PL and lifetimes are observed for the **DSB-N/DSB-N+** vs. **pCp-N/pCp-N+** comparison.

Femtosecond nonlinear optical experiments have been conducted on a five ring oligo(phenylene-vinylene) **pc** dimer complex to measure the electronic populations (pump-probe) and coherences (anisotropy) created with optical pulsed excitation. The pump-probe anisotropy shows a dramatic difference in the decay of electronic coherence between monomer (>100 ps) and dimer species (125 fs). The fast decay in the dimer is due to the strong electronic coupling between single exciton states which has been estimated by numerical simulations to be $\sim 1800 \text{ cm}^{-1}$. The anisotropy exhibits an oscillatory component with frequency $\sim 120\text{-}200 \text{ cm}^{-1}$ and is attributed to the energy difference between vibronic states with different electronic origin in the region of the spectrum where the single exciton vibronic manifolds overlap [3]. Transient grating pump-probe, photon echo, and photon correlation spectroscopy experiments are currently underway. Multi-time photon correlation measurements allow us to correlate different time-dependent properties (e.g., the lifetime) of reporter fluorophores such as **pc** dimer complexes. This new information reveals how long the fluorophore lifetime remains the same or how rapidly this changes in time depending on its environment. Changes in the lifetime may be probed on sub-millisecond to second time scales.

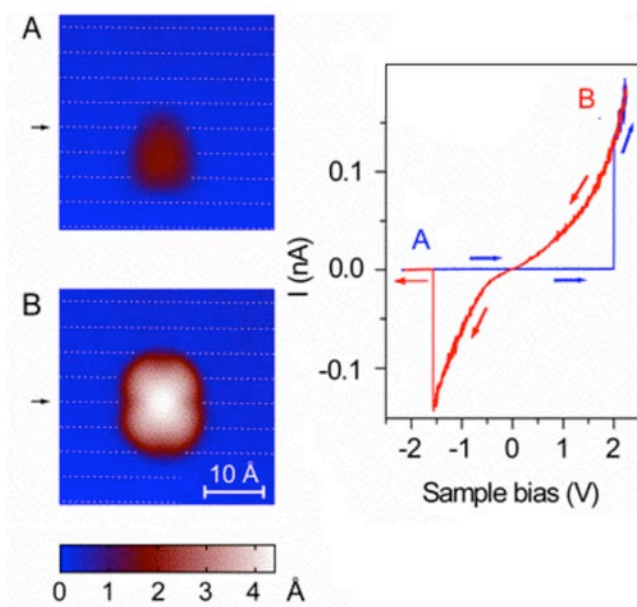


Fig. 2 Switching behavior of DMAS-PCP single molecule on NiAl. (C. Silien, N. Liu, W. Ho, J. Maddox, S. Mukamel, B. Liu, and G. C. Bazan, in preparation)

A new direction of this project involves a series of novel single molecule scanning tunneling microscopy (STM) experiments performed by Professor Wilson Ho's group at the University of California-Irvine. In these studies, single molecules of a **pc** dimer compound (**DMAS-PCP**) were chemisorbed to a NiAl(110) surface. **DMAS-PCP** is similar in structure to **pCp-N** (see Figure 1) except that $R_2 = \text{CH}_3$. For certain orientations of the adsorbed species, it was found that the tunneling current through the molecule exhibits an interesting reproducible hysteric switching behavior with the applied voltage between a high and a low conductivity state, accompanied by a dramatic conformational change. The left panel of Figure 2 shows STM topographies recorded at 0.1 nA and 0.36 V both before (A) and after (B) controlled modification of the molecular conformation induced by the

applied voltage. The dotted lines indicate the Al rows of the surface lattice. The right panel shows the current (I) vs. voltage (V) curves recorded by raising (blue) and decreasing (red) the sample bias with the tip positioned at the center of B (0.1 nA at 1.75 V). The labels indicate the conformation changes when scanning up and down the sample bias. The shape and height of the STM image of the B conformer suggest that the core is positioned over an Al row and oriented with its stacked benzene rings parallel to the surface. Spectral information about an adsorbed species is obtained by monitoring the derivatives of the current as a function of the applied voltage. Spectral peaks in the signal occur when the tunneling electrons are resonant with a vibrational or electronic transition of the adsorbed species. By combining this analysis with topographic imaging, it is possible to obtain spatially resolved spectroscopic information at a sub-molecular level. This is accomplished by scanning the tip across the surface using a closed feedback loop between the tip height and electric current; however, after recording the tip height, the feedback loop is opened and the d^2I/dV^2 intensity is recorded by modulating the electric bias about a value in resonance with a vibrational or electronic transition. The feedback loop is then closed again and the tip is moved in order to analyze an adjacent point on the surface. The

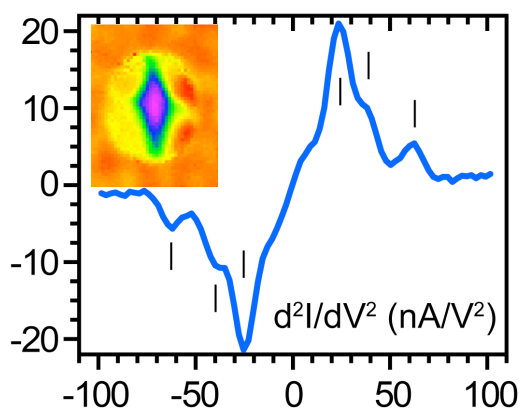


Fig. 3 IETS spectrum of **DMAS-PCP** and an STM image of the resonance at 24 mV. (N. Liu, C. Silien, W. Ho, J. Maddox, S. Mukamel, B. Liu, and G. C. Bazan, in preparation)

d^2I/dV^2 values are then spatially resolved across the molecule and reveal how the various vibrational modes are coupled to the tunneling current. The low frequency inelastic electron tunneling spectrum (IETS) of the B conformer (Figure 3), shows several strong vibrational resonances at 24, 40 and 64 mV. A topographic image of the 24 mV resonance is shown in the inset. Normal mode analysis of the isolated **DMAS-PCP** molecule has been used to identify the vibrations contributing to IETS spectrum and STM images. This analysis predicts several vibrational modes which likely contribute to peak at 24 mV. These involve dihedral angle bending in the **pc** core which causes the top and bottom benzene rings to slide back and forth across one another. Our analysis suggests that this sliding action is responsible for the distinct diamond shape pattern at the center of the

vibrational STM image and further helps to confirm the proposed orientation of the B conformer with respect to the surface lattice. Additional calculations examined electric field effects on the electronic density of states. Simulations of spatially resolved inelastic electronic currents using nonequilibrium many body Green's functions (NEGF) are underway [4,5].

References

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