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Asymmetric Charge Transfer from Pyrene Amide Dyads: Using Amides to Control Photochemistry of Pyrene

Amide bonds are ubiquitous in nature as well in organic chemistry. In biological systems, besides holding together peptide bonds, amide bonds contribute to the dipole moment via hydrogen bonding making alpha helices natural electrets. In aromatic and polyaromatic hydrocarbons (PAH's), amide bonds contribute to the electronic properties as well as means for covalent attachment. We have previously shown that the position of the amide bond on PAH's shifts oxidation or reduction potentials of pyrene by about 100-200 mV, which are in agreement with the Swain-Lupton parameters. Symmetry breaking (SB) charge transfer (CT) processes occurs when symmetrical molecules, upon photoexcitation, undergo a process which makes one molecule an electron donor, and its symmetrical counterpart, an electron acceptor, in the excited state thus creating holes and electrons. Factors such as change in dipole, hydrogen bonding, halogen interactions, etc. have been proven to affect SB in the excited state of D-A-D, A-D-A, quadrupolar, etc. systems. Indeed, for such systems many factors need to be addressed to design an efficient SB CT system. In this presentation I will focus on a pyrene dyad system that is separated by an amide or a methylamide. Tuning of the Pyrene amide dyad HOMO-LUMO energy levels allows, even at ~100-200 mV allows for efficient CT and even a long lived charge separated (CS) state (~1 ns) which is essential for organic electronics.

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