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A Crystallographic and Spectroscopic Investigation of Photo-Induced Electron Transfer in Pyrene-(CH2)2-N,N'-Dimethylaniline: Time-Resolved Studies in Solutions and Polymorphic Crystals.

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Photo-induced electron transfer reactions are crucial for many of the biological and chemical reactions that occur in nature. According to Marcus and others, electronic coupling between an electron donor and acceptor must be nonzero, for a successful electron transfer reaction. [1] Several studies are performed in order to have a better understanding of the photoinduced intramolecular electron transfer, in terms of the rate of transfer and the overall geometry of the donor-bridge-acceptor (D-B-A) system.[2] Pyrene and its derivatives, owing to their high quantum efficiency, high fluorescence lifetimes, prone to form excimers or exciplex in high concentrations and highly sensitive nature of their photophysical properties to microenvironmental changes, are considered extremely useful for photoinduced electron transfer studies.[3] We have designed a mono-substituted pyrene derivative, pyrene-(CH2)2-N, N'-dimethylaniline, where dimethylaniline (DMA) (electron donor) is connected to pyrene (electron acceptor, in this case) through alkane chain. The distance between the donor and acceptor in this molecule is expected to be suitable for electron transfer by tunneling mechanism. A serendipitous occurrence of two polymorphic crystals from two separate batches of crystallization setup, while dissolved in ethanol, provided us a unique opportunity to study these two conformational polymorphs, A and B. While, in A crystal structure pyrene and dimethylaniline are in axial orientation (P-1) with respect to each other, in B they are equatorial (P21/n). Studies on photo-induced intramolecular electron transfer has revealed the importance of conformational parameters of the molecules such as rotation around bonds that affects the distance and relative orientation of donor and acceptor which in turn can proved to be quite decisive in the photo-physical properties of charge transfer states. [4] We have performed time-resolved Laue diffraction experiments with these two polymorphic crystal forms in the ns time domain. Apart from steady-state spectroscopy, we have also measured ultrafast transient absorption with the solution, at different concentrations. A thorough crystallographic and spectroscopic investigation of this particular system, especially with the polymorphic crystals have allowed us to understand the important aspects of photo-induced electron transfer.

Figure 1. Conformation of molecules in single crystals, a) PyDMA1 and b) PyDMA2. c) Molecular superposition of PyDMA1 (black) and PyDMA2 (red) on pyrene ring with RMSD=0.0427Å. The extent of overlap between the pyrene rings belong to the symmetry related/unit translated molecules in PyDMA1/PyDMA2 in single crystals are 67% and 17%, respectively. f) Absorption (blue) and emission (red) spectra of PyDMA1, in toluene, at 0.1mM concentration.

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