

Photo-induced electron transfer in Pyrene-(CH₂)₂-N,N'-Dimethylaniline: Time-resolved pink Laue X-ray diffraction studies on crystalline polymorphs

Krishnayan Basuroy¹, Jose de J. Velazquez-Garcia¹, Darina Storozhuk¹, Robert Henning²,
David J. Gosztola³, Sreevidya Thekku Veedu¹, and Simone Techert^{1,4}

¹Photon Science Division, Deutsches Elektronen-Synchrotron DESY, Hamburg, 22607, Germany.

²Center for Advanced Radiation Sources, The University of Chicago, Chicago, Illinois 60637, US.

³Center for Nanoscale Materials, Argonne National Laboratory, Illinois 60439, US.

⁴Institut für Röntgenphysik, Georg-August-Universität Göttingen, Göttingen, 37077, Germany

Krishnayan.basuroy@desy.de

Photo-induced electron transfer (PET) reactions are crucial for many biological and chemical reactions that occur in nature. Several studies are performed on many donor-bridge-acceptor (D-B-A) systems to have a better understanding of PET in terms of the rate of transfer and the overall geometry.[1] A mono-substituted pyrene derivative, pyrene-(CH₂)₂-N,N'-dimethylaniline, were designed where dimethylaniline (DMA) (electron donor) is connected to pyrene (electron acceptor) through alkane chain. Two polymorphic crystal forms, A and B, were crystallized in two separate crystallization batches in ethanol/ethyl acetate binary mixture. While, in the crystal structure A, pyrene and dimethylaniline are in axial orientation (*P*-1) with respect to each other, in B they are equatorial (*P*2₁/*n*). Studies on intramolecular PET has revealed the importance of conformational parameters of the molecules such as rotation around bonds that affects the distance and relative orientation of the donor and acceptor.[2] We have performed time-resolved (TR) pump-probe pink Laue X-ray diffraction experiments with the polymorphic crystals in *ns* time domain. TR pump-probe data was processed by RATIO[3] method by employing LaueUtil software[4]. The photodifference maps obtained from TR pump-probe diffraction measurements with polymorphic crystals, suggest electron transfer from DMA moiety. A thorough crystallographic and spectroscopic investigation with the polymorphic crystals, have allowed us to understand the important aspects of PET in this particular (D-B-A) system.

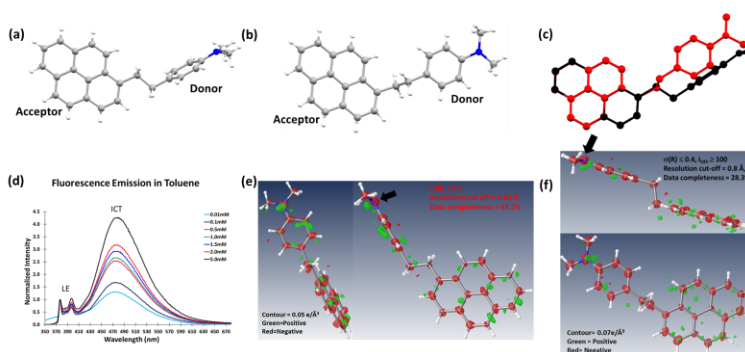


Figure 1. Crystallographic asymmetric unit of (a) PyDMA1 and (b) PyDMA2. (c) Superposition of PyDMA1 and PyDMA2 molecules. (d) Emission spectrum of PyDMA1 in toluene. Photodifference map of (e) PyDMA1 (1ns delay) and (f) PyDMA2 (2ns delay).

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