Oral presentation

Capturing photo-induced structural changes in a donor-bridge-acceptor dyad crystal, that also exhibits elastic bending under mechanical pressure, using pump-probe photocrystallography

K. Basuroy[1], J. Velazquez-Garcia[1], S. Techert[1,2]

[1] Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany, [2]Institute of X-ray Physics, University of Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany.
krishnayan.basuroy@desy.de

Controlling different external stimuli to tune the photophysical properties of purely organic molecular crystals toward designing multifunctional materials remains a challenge. Over the years, pyrene-based fluorophores owing to their high charge carrier mobility, complex photoelectronic characteristics in the excited state, and high fluorescence quantum yield, have come up as an attractive choice for researchers while designing luminescent molecular crystals. Recently, we have employed a pair of polymorphic D-B-A dyad crystals where electron-rich *N,N′*-dimethylaniline (DMA) acts as an electron donor (D) is attached to pyrene (Py) that acts as an acceptor (A), through -CH_2-CH_2- group, to study photo-induced charge transfer (PCT) mechanism by time-resolved pump-probe photocrystallography [1]. These D-B-A dyads sometimes behave like semiconductors and if designed properly can be useful as an efficient means of charge transfer and the creation of long-lived charge-separated states necessary for designing smart optoelectronic materials. The light-driven processes are mostly investigated in the D-B-A dyads due to the obvious reason of the matching of UV-Vis radiation wavelength with the electronic excitations and the need to investigate the excited state electron/hole transfer akin to the one observed in the natural photosynthesis process. For the present study, one such D-B-A molecule with an aromatic ring as the bridging

(B) group has been employed (Fig. 1a). Since, the aromatic ring in the bridging group has the potential to play the role of a hopping station during electron transfer from DMA moiety to pyrene, measurements at different pump-probe delays were employed. The TCSPC measurements show that the photoinduced transient excited state is decaying bi-exponentially with a ~22ns long intramolecular charge transfer (ICT) state and a long-lived excimer state (~85ns) (Fig. 1b). The TDDFT calculations show a spatially separated HOMO and LUMO with a HOMO-LUMO gap of 3.46 eV, suggesting the CT nature of the HOMO-LUMO transition (Fig. 1c). The needle-shaped single crystals were also exhibiting elastic bending up to ~49° upon pressing with a needle (Fig. 1d). These single crystals were employed for time-resolved photocrystallography measurements at the BioCARS beamline at the APS using different pump-probe delays, where a short 35ps laser pump pulse was followed by a ~100ps X-ray probe pulse on the single crystals (Fig. 1e-f). The pump-probe photocrystallography datasets collected at different pump-probe delays show very interesting structural changes directly correlating the photo-chemical processes in solid-state. The photo-difference map from an 18*ns* pump-probe photocrytallography dataset shows how atomic shifts take place in a photo-induced, intramolecular charge-separated state (Fig. 1g). The results will be also useful in accessing the changes in the intermolecular interactions at different pump-probe delays which in turn will help design solid-state, smart materials.

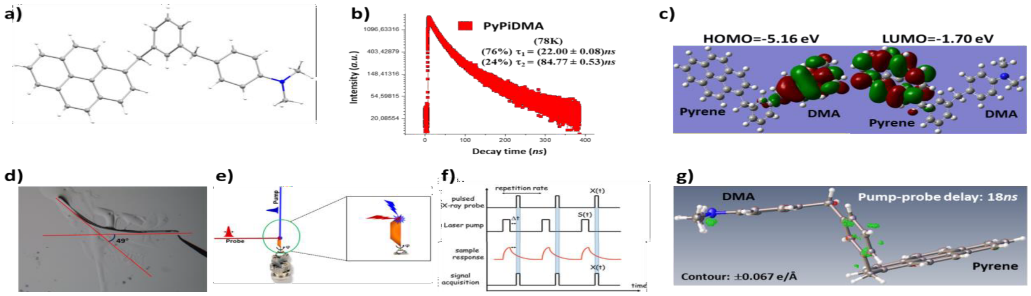

Figure 1. Molecular conformations of Py-CH_2-C_6H_4-CH_2-DMA with 1 molecule in the crystallographic asymmetric unit at 80K. b) The emission decay curve of excited state species at 78K decaying bi-exponentially. λ_{exc}: 375nm. c) TDDFT calculation provided the HOMO and LUMO for the molecule where the HOMO is almost entirely occupying the DMA moiety and the LUMO is entirely occupying the pyrene moiety. d) The needle-shaped single crystal was bent by 49□ under mechanical pressure by a needle. e) Experimental geometry of the TRXRD measurements. The X-ray probe beam is perpendicular to the laser pump beam. On the inset, it is shown that the laser pump beam is bigger than the X-ray probe beam. f) Principle of time-resolved X-ray diffraction pump-probe measurement with an intrinsically pulsed X-ray beam with a scattered signal sampled by a fast-gated detector (only one delay is depicted here). The sample response would be considered as a photo- induced transient state population. g) The photo-difference map for the pump-probe time-resolved photocrystallography data at 18*ns* pump-probe delay.

[1] Basuroy, K., Velazquez-Garcia, J., Storozhuk, D., Henning, R., Gosztola, D. J., Thekku Veedu, S., Techert, S. (2023). *J. Chem. Phys.*, **158**, 054304.