

Crystal engineering pi-ways for enhanced charge transport

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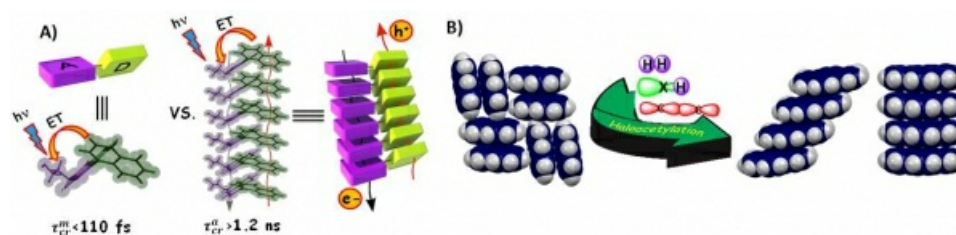
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Molecules that produce charges when excited by light are useful for a variety of (bio-)organic electronic applications. To maximize the utility of these molecules, researchers work to keep the induced charges separate for as long as possible. Stacking the excitable molecules can extend the charge lifetime, but often the donor and acceptor parts of the molecule naturally alternate in the stack, which causes the charges to immediately recombine. Our group aim to minimize charge recombination¹⁻³ by separating the donor and acceptor portions of the molecule on different spatial planes. We have synthesized a naphthalimide-naphthalene dyad where the donor and acceptor units are twisted into different planes. The twisted monomers also assemble into a stacked tower. When illuminated by ultraviolet light, the charge separated state of the stack can last more than 1.2 ns, 10,000 times longer than in the monomeric dyad (Scheme 1). This crystalline assembly could be a novel scaffold for light harvesting, molecular electronics, or new light-induced electronic applications. As opposed to the conventional view of modulating the redox properties and/or distance between donor and acceptor, our results encourage to focus on fine-tuning of spatial organisation of the donor and acceptor chromophores to hop the charges over long distances. Recently, we employed haloacylation for transforming herringbone arrangement to lamellar/columnar arrangement of pyrene.¹ Such organised arrangement of pi-ways show very low resistance when compared to the herringbone equivalent of the same chromophoric system.

[1] Hariharan, M. et al. (2016) Cryst. Growth Des. 16, 4567-4573; 5822-5830; 6327-6336

[2] Hariharan, M. et al. (2015) J. Am. Chem. Soc., 137, 15604-15607.

[3] Hariharan, M. et al. (2014) Energy Environ. Sci., 7, 1661-1669.



Scheme 1. A) Representative strategies adopted in our group to spatially organize electron donors and acceptors for emergent properties; B) Transformation of herringbone to lamellar/columnar arrangement in pyrene via haloacetylation

Keywords: [Double Columnar](#), [Donor Acceptor](#), [Twisted Biaryl](#)