

Unraveling the Photoinduced Symmetry-Breaking Charge Separation (SB-CS) process in a PDI-based Cage

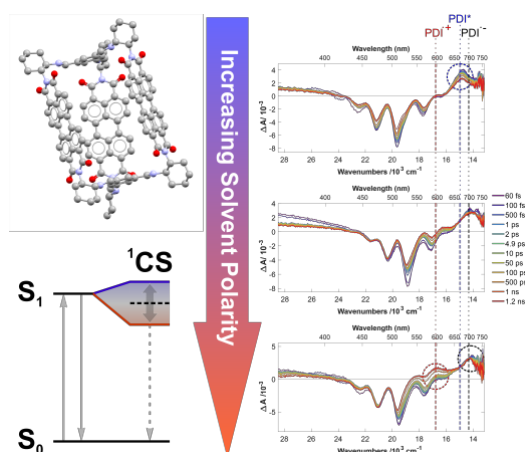
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In a photoinduced symmetry-breaking charge-separation (SB-CS) process, an electron transfer occurs between two identical chromophores, which can be used for applications in harvesting of solar energy. We have previously reported the first example of a rylene cage with delayed fluorescence [1], presumably by a reverse SB-CS process. As a follow-up work, herein we present the transient electronic spectra of the PDI-Cage in increasing polarity toluene/benzonitrile solvent mixtures. As the polarity of the solvent increases, two transient bands centered around 650 and 700 nm can be observed, the last one being overlapped with the excited state absorption (ESA). These bands can be attributed respectively to the radical cation and radical anion of PDI, constituting clear evidence of the SB-CS process.



The TA spectra in pure toluene and 80:20 Tol/BzCN mixture showed no evidence of the presence of the radical species, which appear only at increased polarity mixtures. This is in agreement with a higher stabilization of the ^1CS state in polar environments, that prompts the population of this state after photoexcitation to S_1 in an equilibrium. The backward reaction of this equilibrium re-populates the S_1 state and is then responsible for the previously reported delayed fluorescence of these compounds. Further studies in the NIR-region are being carried out to extend the observable wavelength and collect further evidence of the radical anion spectral signature, preventing its overlap with the ESA transient band.

[1] Huang, Song, Prescimone, Aster, Cohen, Mannancherry, Vauthey, Coskun and Solomek, *Chem. Sci.*, 2021, 12, 5275.