Symmetry Breaking Charge Separation in a PDI-Based Molecular Cage

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The Photoinduced Symmetry Breaking Charge-Separation (SB-CS) process—in which an electron transfer occurs between two identical chromophores —has received a lot of attention lately due to its applications in solar energy conversion. We have previously shown the first example of a perylene diimide (PDI) cage with delayed fluorescence [1], presumably originating from a reverse SB-CS process. Using transient electronic absorption spectroscopy (TAS) in increasing polarity Toluene/PhCN solvent mixtures, we could evidence occurrence of SB-CS through identification of the transient bands of the PDI radical anion and radical cation, which are absent in low polarity media due to the destabilization of the ^{1}CS state.

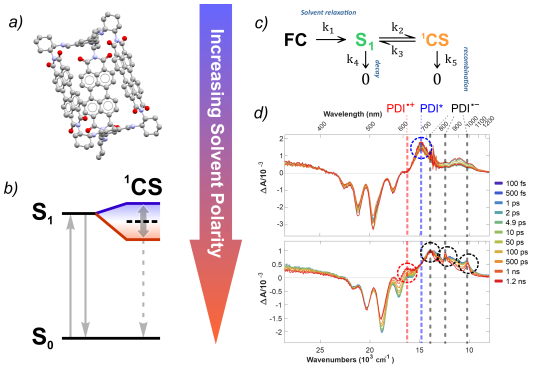


Figure: a) PDI-based cage; b) Stabilization of the ^{1}CS state with increasing solvent polarity; c) Target model ; d) Comparison between toluene (up) and benzonitrile (bottom) transient absorption spectra.

We based our analysis on a five-parameter model that stabilizes the Franck-Condon state, an equilibrium between the S_1 and the ^{1}CS states, and their respective decay and recombination. Due to its intrinsic complexity, we used additional constraints derived from Ware's model of exciplexes [2]. Our new approach allows us not only to extract distinct Species-Associated Spectra (SAS) but also to obtain relevant kinetic constants from such a complicated scheme while ensuring self-consistency between the TAS and time-resolved fluorescence data. Finally, these kinetic constants allowed us to access the equilibrium constant and the driving force for the SB-CS process.

[1] Hsin-Hua Huang, Kyung Seob Song, Alessandro Prescimone, Alexander Aster, Gabriel Cohen, Rajesh Mannancherry, Eric Vauthey, Ali Coskun, and Tomáš Šolomek, *Chem. Sci.*, **2021**, 12, 5275.

[2] Man Him Hui and William R. Ware, *JACS*, **1976**, 98:16, 4718.