ULTRAFAST EMISSION QUENCHING IN PERYLENE DIIMIDES BY STRUCTURE REARRANGEMENT INDUCED ELECTRON TRANSFER FROM THEIR SUBSTITUENTS

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Perylene dyes have attracted great interest for the design of intramolecular energy and charge transfer systems. Chemical substitution of the perylene chromophore can be used as a tool to control its absorption and in particular its emission properties. By choosing an appropriate substituent, the intrinsic high fluorescence yield of the perylene chromophore is effectively turned off due to a photoinduced charge transfer. In order to maximize the persistence of the charge separation for photovoltaic applications we investigate the influence of substitution of two fluorescent perylene diimides on the ultrafast intramolecular dynamics leading to efficient fluorescence quenching by transient spectroscopy and quantum chemical calculations.

The fluorescent systems show no dynamics in the sub-nanosecond time region. For the first, the amino-functionalized molecule the stimulated emission signal decays rapidly on a sub-picosecond timescale, while the excited state absorption decreases with a time constant of several picoseconds. The corresponding excited state energy surfaces are explored on the TDDFT, CC2 and CASPT2 level of theory. Consistently the different quantum chemical methods assign the fast decay of the emission to a charge transfer from the amino substitutient to the perylene diimide chromophore. The transfer is made possible by a planarization of the substituent as the system moves away from the Franck-Condon point. Experiments and theoretical PCM calculations in different solvents demonstrate that the dynamics of this fluorescence quenching correlate with the solvation time. The rapid relaxation from the charge transfer state into the ground state is observed on a picosecond timescale and is attributed to a passage through a conical intersection.

For the second, the phenyl-functionalized perylene diimide a similar charge transfer emission quenching mechanism is observed. An efficient and fast fluorescence quenching still occurs by a charge transfer and is associated with a rotation of the phenyl ring substitutient. But in comparison with the amino-functionalized molecule the lifetime of the charge separation is increased by more than a factor of ten.