Excited state kinetics of anthracene-bridge-aniline intramolecular exciplexes

We report on the synthesis and characterization of fluorescent halogen substituted anthracene-bridge-aniline (ABA) supermolecules that undergo structural reorganization on photoexcitation to form transient complexes. The syntheses were achieved in high yields on a large scale and the molecular structures were confirmed by single crystal X-ray diffraction. The photophysics of the ABA supermolecules were investigated using steady state and time resolved optical spectroscopy. Despite the presence of heavy atoms the series of ABA molecules have high quantum yields of fluorescence from both a locally excited anthracene state (LE) and an excited state complex (exciplex, EP) in non-polar solvents. The kinetics of the excited state processes were established in decalin from the time-resolved emission, and was shown to be strongly influenced by an electron-transfer state (ET). For quantitative studies of the excited state dynamics, the presence of this state required the development of a numerical three-excited-state kinetic model to replace the commonly used two-excited-state model. The experimental results shows that the reaction rates are strongly influenced both by substituents and solvent, illustrating the importance of including all relevant states in the kinetic modeling. Ultimately it is established that the excited state dynamics can conveniently be followed by optical methods, and the applicability of the system as a model system in time-resolved X-ray scattering experiments is discussed.

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