

Photoswitchable and Polar-Dependent Fluorescence of Diarylethenes

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Abstract : Fluorescent photochromic materials collect strong interest due to their possible application in organic photonics such as optical logic systems, optical memory, visualizing sensors, as well as characterization of polymers and biological systems. In photochromic fluorescence switching systems the emission of fluorophore is modulated between 'on' and 'off' via the photoisomerization of photochromic moieties resulting in effective resonance energy transfer (FRET). In current work, we have studied both photochromic and fluorescent properties of several diarylethenes. It was found that coloured forms of these compounds are not fluorescent because of the efficient intramolecular energy transfer. Spectral and photochromic parameters of investigated substances have been measured in five solvents having different polarity. Quantum yields of photochromic transformation $A \rightarrow B$, $\Phi_{A \rightarrow B}$ and $\Phi_{B \rightarrow A}$ as well as B isomer extinction coefficients were determined by kinetic method. It was found that the photocyclization reaction quantum yield of all compounds decreases with the increase of solvent polarity. In addition, the solvent polarity is revealed to affect fluorescence significantly. Increasing of the solvent dielectric constant was found to result in a strong shift of emission band position from 450 nm (n-hexane) to 550 nm (DMSO and ethanol) for all three compounds. Moreover, the emission intensive in polar solvents becomes weak and hardly detectable in n-hexane. The only one exception in the described dependence is abnormally low fluorescence quantum yield in ethanol presumably caused by the loss of electron-donating properties of nitrogen atom due to the protonation. An effect of the protonation was also confirmed by the addition of concentrated HCl in solution resulting in a complete disappearance of the fluorescent band. Excited state dynamics were investigated by ultrafast optical spectroscopy methods. Kinetic curves of excited states absorption and fluorescence decays were measured. Lifetimes of transient states were calculated from the data measured. The mechanism of ring opening reaction was found to be polarity dependent. Comparative analysis of kinetics measured in acetonitrile and hexane reveals differences in relaxation dynamics after the laser pulse. The most important fact is the presence of two decay processes in acetonitrile, whereas only one is present in hexane. This fact supports an assumption made on the basis of steady-state preliminary experiments that in polar solvents occur stabilization of TICT state. Thus, results achieved prove the hypothesis of two channel mechanism of energy relaxation of compounds studied.

Keywords : diarylethenes, fluorescence switching, FRET, photochromism, TICT state

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