

Influence of restricted intramolecular motions on the fluorescence quantum yield

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Fluorescence spectra, fluorescence quantum yields and decay times were measured for aromatic molecules capable of either conformational or rotational mobility in dilute solutions of *n*-heptane and methylmethacrylate and in the rigid polymethylmethacrylate (PMMA) matrix at room temperature. On passing from fluid solutions to the polymeric matrix of PMMA a dramatic increase is obtained for the fluorescence quantum yield of *meso*-substituted anthracenes as well as structurally related molecules of stilbene and 1,3-diphenyl-2-pyrazoline. In some cases fluorescence spectra and quantum yields up to 0.5 can be measured in PMMA matrixes of compounds which do not fluoresce in solution. The rate constants for radiative and radiationless transitions in both media demonstrate that the increases in fluorescence quantum yields are exclusively due to the decreases in the rate constants for radiationless internal conversions. The rigidity of the PMMA matrix slows down the rates of intramolecular motions such as ring inversion or rotation of substituents and lengthens the time interval between excitation and achievement of those conformations that give rise to fast non-radiative decay. In solution these conformations are reached more rapidly and fluorescence is suppressed by the faster non-radiative deactivation of the excited singlet state.

Singlet charge transfer complexes between anthraquinones and electron donors

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Singlet charge transfer complexes between variously substituted anthraquinones and electron donors (E_{ox}° from 0.35 to 1.76 V) were studied in acetonitrile solution by exciting the anthraquinones in their charge transfer absorption band. In each case a linear Stern-Volmer plot was obtained for the quenching of the fluorescence of the anthraquinone by the electron donor. The logarithm of the quenching rate constant, obtained after measurement of the singlet lifetime of the quinone by single-photon counting techniques, was observed to follow the Rehm and Weller equation. No emission of the electron donor-acceptor complex was observed in the present case, nor when ethanol was used as solvent. These results show that quinones behave as good electron acceptors from the singlet