Triplet–Singlet Energy Transfer in Solution

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Summary In contrast to earlier work, no detectable triplet–singlet dipole–dipole energy transfer was found to occur in fluid solution; the reasons are briefly discussed.

TRIPLET–SINGLET energy transfer has been suggested as an intermediate step in some chemiluminescence reactions,[1] and recently a direct measurement of this type of energy transfer in solution was reported by Vaudo and Hercules,[2] who found that, on adding a donor to a solution of an appropriate acceptor, an increase in the acceptor fluorescence (fluorescence enhancement) could be observed. In addition, a deactivation of the donor triplet (observed by flash photolysis) on addition of the acceptor was detected; both of these effects were ascribed to triplet–singlet energy transfer.[2]

In general, on adding a donor D to a solution of an acceptor A, a fluorescence enhancement due to triplet–singlet energy transfer will be observed when the condition

$$10^{-\varepsilon_D c_D x}\,[1 + (\epsilon_D c_D/\epsilon_A c_A) \times \gamma] > 1$$

is fulfilled, where ϵ_D, ϵ_A and c_D, c_A are the extinction coefficients at the exciting wavelength, and the concentrations, of donor and acceptor, respectively; x is the pathlength the exciting light must travel in order to reach the point at which fluorescence is observed, and γ is the overall yield of the donor intersystem crossing and energy transfer steps. We have carried out measurements similar to those of the earlier publication, and the data so obtained are shown in the Table, together with values of $10^{-\varepsilon_D c_D 0.5}$ taken from the absorption spectra, and R, the ratio of acceptor fluorescence with donor to acceptor fluorescence without, measured under degassed conditions. The spectral positions of the donor phosphorescence and acceptor absorption given in the Table show that the spectral overlap required by the dipole–dipole energy transfer mechanism is present in all cases. The aromatics used in this investigation, including benzophenone, were purified by zone-refining; the dyestuffs were purified by column chromatography.

The experimentally determined values of R shown in the Table are all less than unity, showing that in no case is a fluorescence enhancement produced on addition of the donor. This applies also to the system benzophenone–perylene, for which an enhancement of 1·4 had previously been detected under these conditions.[2] Furthermore, these values of R, on being compared with the values of $10^{-\varepsilon_D c_D 0.5}$ (this represents the value of R that would be observed in the

TABLE

System[a]		λ_{ex}[b] (nm)	λ_{Ph} (donor)[c] (nm)	λ_{abs} (acceptor)[d] (nm)	$10^{-\varepsilon_D c_D 0.5}$	R[e]
Triphenylene	(3.4×10^{-5}M)	270	420	435	0·52	0·54[f]
Perylene	(4.4×10^{-6}M)	280	420	435	0·60	0·79[f]
Fluorene	(5.9×10^{-5}M)	290	425	435	0·68	0·79[f]
Perylene	(1.31×10^{-5}M)					
Triphenylene	(3.4×10^{-5}M)	284	420	488	0·66	0·79[f]
Fluorescein	(1.77×10^{-6}M)					
Benzophenone	(2.28×10^{-3}M)	312	450	435	0·52	0·72[f]
Perylene	(1.57×10^{-5}M)					
Phenanthrene	(8.0×10^{-5}M)	270	458	488	0·55	0·58[f]
Fluorescein	(6.1×10^{-6}M)	280	458	488	0·59	0·61[f]
Picene	(1.44×10^{-3}M)	380	497	553	0·30	0·63[f]
Rhodamine B	(2.00×10^{-6}M)					
Benzophenone	(2.07×10^{-3}M	320	450	435	0·80	0·79[g]
Perylene	(1.06×10^{-6}M)	330	450	435	0·74	0·76[g]
		340	450	435	0·73	0·73[g]

[a] The first named compound is the donor, the second the acceptor. [b] Excitation wavelength. [c] Wavelength of the most prominent peak in the donor phosphorescence spectrum. [d] Wavelength of the most prominent peak in the acceptor absorption spectrum. [e] See text. [f] In acetonitrile. [g] In benzene.

absence of any energy transfer) given in the Table, are seen to be consistent with a mechanism by which absorption of the exciting light by the added donor is the only factor influencing the acceptor fluorescence intensity. The use of $10^{-\varepsilon_D c_D 0.5}$ assumes that the observed fluorescence comes entirely from a point in the centre of the cell; in reality an appreciable fraction of the observed fluorescence proceeds from regions which are nearer to the point of incidence of the exciting light, leading to the R values being higher than the corresponding values of $10^{-\varepsilon_D c_D 0.5}$.

The earlier results[2] could be due to traces of impurities which, upon being excited, can give rise to the observed fluorescence enhancement either by direct emission or by singlet–singlet energy transfer to the acceptor. Thus,[2] carbazole is formed photochemically from diphenylamine,[3] and has a fluorescence spectrum which overlaps appreciably with the absorption spectrum of perylene.[4] The uncertainty surrounding the existence of triplet–singlet energy transfer in solution also makes it conceivable that the triplet deactivation observed in the flash experiments[2,5] is due solely to normal triplet–triplet energy transfer.[6]

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