Long-lived Luminescence of Charge-transfer Complexes

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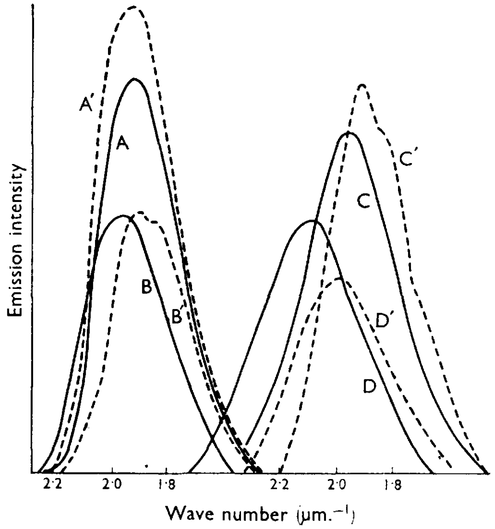
THE possibility that the triplet-state energy of charge-transfer complexes may be close to, or higher than, the energy of the first excited singlet state has been discussed by Mulliken.[1] The long-lived emission observed from rigid solutions of complexes for which the energy of the first charge-transfer transition is lower than the triplet energy of the free donor or acceptor components provides an opportunity to study such charge-transfer triplet states without interference caused by mixing with component transitions. The accompanying Table and Figure show results and spectra for several complexes where the apparent energy-gap between long-lived and prompt emission is either very low or zero, namely hexamethylbenzene–tetrachlorophthalic anhydride (HMB–TCPA), hexamethylbenzene–pyromellitic dianhydride (HMB–PMDA), mesitylene–pyromellitic dianhydride (MES–PMDA), fluorene–tetrachlorophthalic anhydride (FLUOR–TCPA), *N*-phenylcarbazole–tetrachlorophthalic anhydride (NPC–TCPA), and naphthalene–pyromellitic dianhydride (NAP–PMDA). All materials, with the exception of PMDA, were purified by extensive zone refining. Spectra were measured at 90 and 77° K in 1 : 1 ether–isopentane solution, and excitation was in the charge-transfer band so that components were not excited. Delayed emission was proportional to the first power of the exciting-light intensity and the excitation spectrum matched the absorption spectrum of the complex. Such emissions have been attributed to straightforward phosphorescence from a charge-transfer state.[2] However,



FIGURE

Spectra of long-lived and prompt emission of charge-transfer complexes in 1 : 1 *ether–isopentane solution. Long-lived emission: dashed lines, prompt emission: full lines*

A and A′ NPC–TCPA at 77° K, 436 nm., B and B′ NAP–PMDA at 77° *K*, 405 nm., C and C′ FLUOR–TCPA at 90° *K*, 405 nm., D and D′ MES–PMDA at 77° *K*, 366 nm.

Positions of long-lived (ν_e) *and fluorescence* (ν_f) *maxima* (*in* μ*m.*$^{-1}$), *lifetimes* (τ_{CT}) *and approximate ratios of prompt to long-lived emission quantum efficiencies* (ϕ_f/ϕ_e), *measured at* 90° *and* 77° K *for charge-transfer complexes in* 1 : 1 *ether–isopentane solution*

	90° K		77° K					Approx.
	ν_e	ν_f	ν_e	ν_f	τ_{CT} sec.	ΔE μm.$^{-1}$	ν_f 300° K	ϕ_f/ϕ_e 77° K
HMB–TCPA	2·04	2·01	2·02	2·03	0·002	0·03	1·9	2
HMB–TCPA†			2·02		0·004			
HMB–PMDA	1·96	2·0	1·93	1·94	0·004	0·04	1·85	4
HMB–PMDA†			1·98	1·98				
MES–PMDA	1·99	2·14	2·00	2·09	0·30	0·15		15
MES–PMDA†			2·00	2·25				
NPC–TCPA		1·90	1·92	1·92	0·001	0·00	1·81§	5
NAP–PMDA		1·95	1·91	1·95	1·25	0·04		30
FLUOR–TCPA	1·95	1·92	1·92	1·92	0·05 (0·4)	0·03	1·88	3

† Results from reference 2.
§ In cyclohexane solution.[4]

thermal activation from the triplet to the singlet state should occur with reasonable efficiency even at liquid nitrogen temperature in these systems, leading to delayed fluorescence rather than phosphorescence.

It has been suggested that the luminescence is in fact *E*-type delayed fluorescence emitted under conditions approaching those of activation control.[3] Under these conditions the quantum efficiency of delayed fluorescence (ϕ_e) is proportional to ϕ_t, the triplet formation efficiency, where ϕ_t is small and approaches unity when ϕ_t is large ("activation controlled delayed fluorescence").[3] It may be expected therefore that charge-transfer complexes with apparent triplet–singlet gaps *ca.* 0·15 μm.$^{-1}$ may be divided into two groups according to their respective values of ϕ_t. One group with low ϕ_t (and presumably high ϕ_f) will exhibit intense prompt fluorescence and a long-lived emission of relatively long lifetime and low intensity. The other group, with high ϕ_t, would exhibit an intense long-lived emission with a shorter measured lifetime, consisting chiefly of delayed fluorescence. Measurements reported in the Table show that MES–PMDA and NAP–PMDA fall into the first group and HMB–TCPA, HMB–PMDA, and NPC–TCPA into the second group, with FLUOR–TCPA occupying an intermediate classification. While charge-transfer complexes normally show negligible fluorescence in fluid solution, the three complexes in group 2, as well as FLUOR–TCPA, have been found to fluoresce in solution even at room temperature.[4] Fluorescence maxima, red-shifted from those measured in rigid media,[5] are reported in the Table for those complexes found to fluoresce in ether–isopentane at room temperature. The delayed-fluorescence spectra of both HMB–TCPA and NPC–TCPA possess components showing a non-exponential decay extending into an apparent lifetime of 1—2 seconds. Possible explanations based on recombination, annihilation, or triplet–triplet absorption do not account for the observed first-order dependence on exciting-light intensity found throughout the decay period. Delayed emission from FLUOR–TCPA on the other hand shows two differing exponential decay times. In these systems two independent processes leading to light emission must occur.

One further possibility exists, namely, that charge-transfer formation results in a shift in relative energies of the lowest π^*–n and π^*–π triplet states of the acceptor molecule, accompanied by changes in transition probability. An apparently new phosphorescence of long wavelength would then be observed, the actual spectrum varying from complex to complex because of variations in perturbation of the triplet energies. Evidence that a significant increase, due to charge-transfer complex formation, can in fact occur in transition probability for $\pi^* \leftarrow n$ absorption in an acceptor molecule has been reported by Bryce-Smith and his co-workers.[6]

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