# On the Role of Microcrystal Formation in Intermolecular Triplet-Triplet Energy Transfer in Rigid Glasses

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The intermolecular triplet-triplet energy transfer system benzophenone (donor)/naphthalene (acceptor) was studied in various rigid glasses at 77 K. It is shown that energy transfer is much more efficient if the donor is present in the form of microcrystals than in the case where both donor and acceptor compound are in true solution.

Intermolecular singlet-singlet energy transfer from 5-acetyl-5H-benzo[b]-carbazole (donor, $10^{-3}$ M) to 5H-benzo[b]carbazole (acceptor, $2 \cdot 10^{-5}$ M) in a rigid matrix at 77 K has previously been shown to occur in microcrystals of the donor containing small amounts of the acceptor [1]. Related results have now been obtained with the intermolecular triplet-triplet energy transfer system benzophenone (donor)/naphthalene (acceptor) [2].

All experiments were performed at 77 K using $\lambda_{ex} = 380$ nm as the excitation wavelength. Since the uv absorption spectrum of naphthalene lies at wavelengths < 380 nm, the naphthalene phosphorescence cannot be directly excited with 380 nm light. The phosphorescence excitation spectra of benzophenone are almost identical in the solvents used (ethanol, methylcyclohexane/n-pentane (4:1, vol/vol) and EPA).

Curve c in Fig. 1 shows the phosphorescence spectrum of the benzophenone/naphthalene system (concentration of each compound = $10^{-1}$ M) in *ethanol.* The spectrum is identical with that of benzophenone in the absence of naphthalene (curve a in Fig. 1, $10^{-1}$ M) and does not indicate any trace of naphthalene phosphorescence (curve b in Fig. 1, $10^{-1}$ M, $\lambda_{ex} = 320$ nm). A decrease in benzophenone phosphorescence intensity of approx. 8% is observed in the benzophenone/naphthalene system compared to pure benzophenone in ethanol. Analogous results were obtained when either the benzophenone or naphthalene or both concentrations were reduced. Obviously energy transfer is weak under the con-

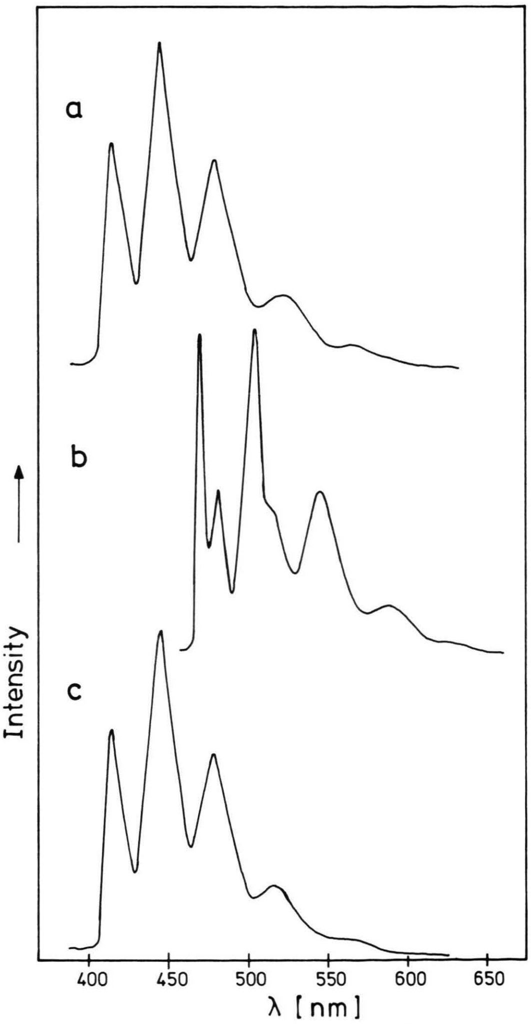

Fig. 1. Phosphorescence spectra of $10^{-1}$ M solutions in ethanol at 77 K of a) benzophenone, b) naphthalene and c) benzophenone/naphthalene 1:1. Spectra are normalized to the intensity of the most intensive band.

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ditions used. Both donor and acceptor molecules can be assumed to be present in true solution.

Quite a different behaviour was observed when *methylcyclohexane/n-pentane* (4:1, vol/vol) was used as a solvent. In contrast to the ethanol solution the $10^{-1}$ M solution of benzophenone in methylcyclohexane/n-pentane is opaque, and the phosphorescence spectrum (curve a in Fig. 2) is slightly different from that in ethanol. Microcrystal formation has already accounted for the phosphorescence behaviour of benzophenone in hydrocarbon glasses at low temperature [3]. Addition of naphthalene ($10^{-1}$ M) causes a decrease in benzophenone phosphorescence intensity of approx. 90% compared to pure benzophenone in methylcyclohexane/n-pentane, and simultaneously the naphthalene phosphorescence appears in the spectrum (curve c in Fig. 2, for comparison see naphthalene spectrum b in Fig. 2, $10^{-1}$ M, $\lambda_{ex} = 320$ nm). There is clear evidence that it is virtually only the phosphorescence of benzophenone microcrystals that is quenched in the presence of naphthalene, while much less energy transfer, or none at all, takes place from the benzophenone molecules present in true solution: (i) The phosphorescence lifetime of the benzophenone measured at the 415 nm band in spectrum c (Fig. 2) is identical with that of benzophenone in the absence of naphthalene in dilute solution (5 msec), (ii) the benzophenone part of spectrum c (Fig. 2) is very similar to that of dissolved benzophenone.

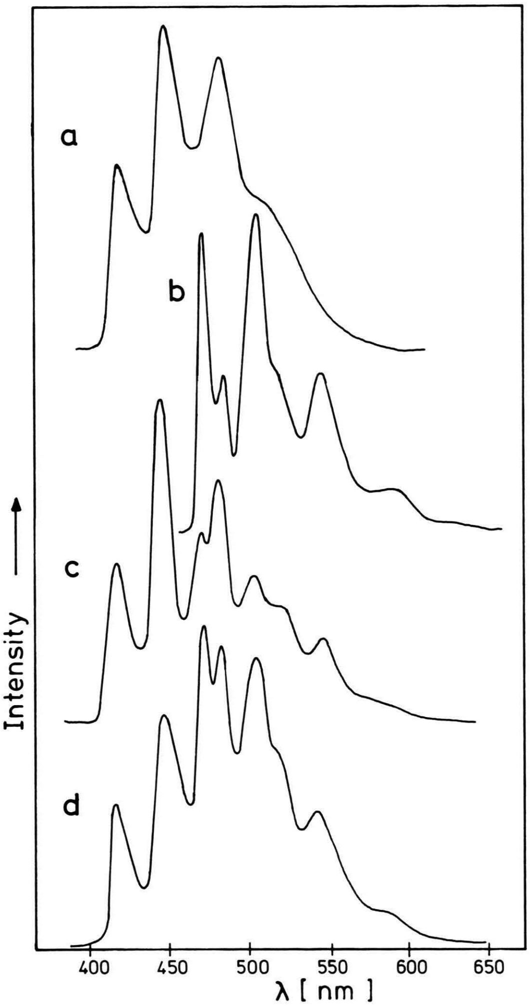

Fig. 2. Phosphorescence spectra in methylcyclohexane/n-pentane (4:1, vol/vol) at 77 K of a) benzophenone ($10^{-1}$ M), b) naphthalene ($10^{-1}$ M), c) benzophenone/naphthalene (each $10^{-1}$ M) and d) benzophenone ($10^{-1}$ M)/naphthalene ($10^{-2}$ M). Spectra are normalized to the intensity of the most intensive band.

Although a drastic decrease in benzophenone phosphorescence intensity in the presence of naphthalene was observed in the hydrocarbon solvent, the intensity of sensitized naphthalene phosphorescence was rather weak in the $10^{-1}$ M solutions (curve c in Figure 2). It was assumed that, although the energy transfer from benzophenone microcrystals to naphthalene is highly effective, the naphthalene triplet state is strongly quenched by intermolecular radiationless interaction due to the high naphthalene concentration. This assumption is supported by the observation that the intensity of sensitized naphthalene phosphorescence increases with decreasing naphthalene concentration (see curve d in Fig. 2, benzophenone: $10^{-1}$ M, naphthalene: $10^{-2}$ M).

EPA solutions of benzophenone/naphthalene (each $10^{-1}$ M) show a decrease of approx. 26% in benzophenone phosphorescence intensity compared to pure benzophenone in EPA, and a weak naphthalene phosphorescence is observed (see curve c in Fig. 3, for comparison curve a: benzophenone, $10^{-1}$ M and b: naphthalene, $10^{-1}$ M). Since EPA has a lower solvent power than ethanol, again it can be assumed that the effects observed are due to microcrystal formation. In contrast to the hydrocarbon solution the EPA solution is transparent. However, it is well known that in some cases small crystallites are not visually observable in rigid matrices [3]. To give an example, a $10^{-3}$ M solution of benzophenone in methylcyclohexane/n-pentane

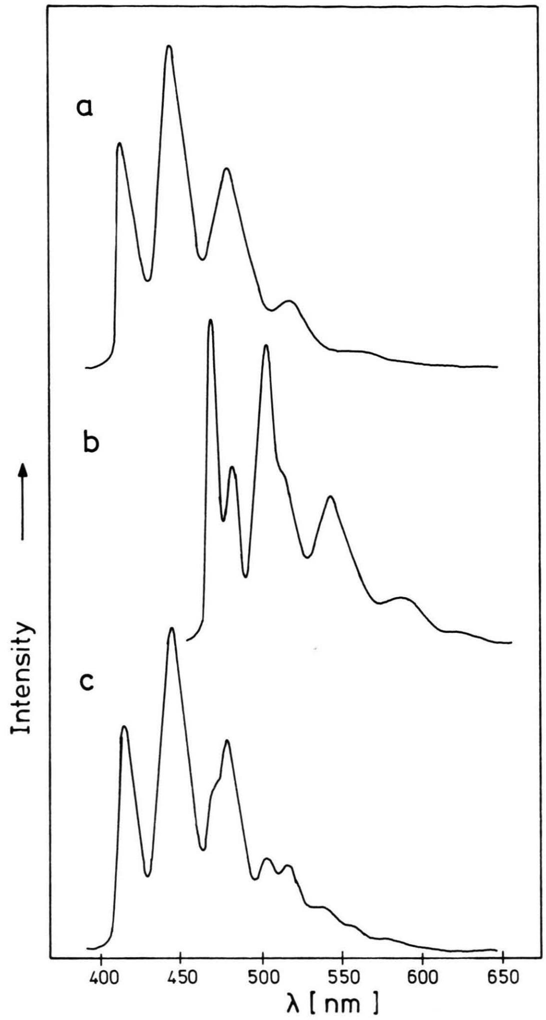

Fig. 3. Phosphorescence spectra of $10^{-1}$ M solutions in EPA at 77 K of a) benzophenone, b) naphthalene and c) benzophenone/naphthalene 1 : 1. Spectra are normalized to the intensity of the most intensive band.

forms a transparent glass at 77 K. In the presence of naphthalene ($10^{-1}$ M) the benzophenone phosphorescence is effectively quenched and sensitized naphthalene phosphorescence appears." Since this has not been observed at these concentrations in solvents of higher solvent power e.g. ethanol, the effect most likely has to be explained by the formation of invisible benzophenone microcrystals in the hydrocarbon solvent.

The findings presented in this Note do not stand in contradiction to the result reached by Siegel and Judeikis [4] that the probability of intermolecular triplet energy transfer in rigid glasses is essentially independent of the solvent used, because microcrystal formation is rather unlikely in the systems studied by these authors.

Although we used high donor and acceptor concentrations in our experiments, it has to be assumed that the concentration of electronically excited donor molecules was rather low due to the low light intensity of the excitation source (xenon lamp, 380 nm). This proved favourable to study the different luminescence behaviour of true solutions and those containing microcrystals.

Although it has been recognized in the literature [5] that formation of microcrystals can obscure "solution" luminescence spectroscopy at low temperature, the phenomenon is possibly much more widespread than is normally realized.

## Experimental

Benzophenone was purified by extensive zone melting. Measurements were performed as described in l.c. [1].

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