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Unusually Strong Delayed Fluorescence of C_{70}

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Abstract: C_{70} (like other fullerenes) is known to have a very weak fluorescence ($\Phi_F \cong 5 \times 10^{-4}$), owing to the high efficiency of triplet formation. In this work we show that, under appropriate conditions, the fluorescence quantum yield increases by one or two orders of magnitude (up to an estimated maximum value $\Phi_F = 0.08$), through the mechanism of delayed thermal fluorescence. We also report a new estimate of the singlet−triplet gap (26 ± 2 kJ mol^{-1}), obtained from the temperature dependence of the delayed thermal fluorescence. This value is shown to be in agreement with the phosphorescence spectrum recorded in the same temperature range. An accurate value of the quantum yield of triplet formation (0.994 ± 0.001) is obtained from a new method of data analysis.

Introduction

Molecular fluorescence is almost always the result of a two-step process: a transition from the ground state to an electronically excited state (absorption) followed by a transition from the same excited state (or another one of lower energy, after fast relaxation) to the ground state (*prompt fluorescence*, PF), see Figure 1. For the common case of closed-shell molecules, the states involved in the last step are S_0 (ground singlet state) and usually S_1 (first excited singlet). However, fluorescence can also occur by a more complicated route, *via* the triplet manifold: after excitation, and once attained S_1, there is an intersystem crossing to the triplet manifold (triplet state T_1), and then, after vibrational thermalization, a second intersystem crossing back to S_1, followed by emission proper (Figure 1). This second type of fluorescence, called *thermally activated delayed fluorescence* (TDF),[1,2] is significant only if the two following conditions are met: (i) reasonably high probability of $S_1 \rightarrow T_1$ intersystem crossing, i.e., high quantum yield of triplet formation Φ_T, where

$$\Phi_T = \frac{k_{ISC}^S}{k_F + k_G^S + k_{ISC}^S} \tag{1}$$

and, (ii) reasonably high probability of subsequent $S_1 \leftarrow T_1$ back intersystem crossing, i.e., high quantum yield of singlet formation, Φ_S, which by analogy with eq 1 we define as

$$\Phi_S = \frac{k_{ISC}^T}{k_P + k_G^T + k_{ISC}^T} \tag{2}$$

In fact, it follows from the kinetic model depicted in Figure 1 that the steady-state intensities ratio of delayed fluorescence (DF) to prompt fluorescence (PF) is given by

$$\frac{I_{DF}}{I_{PF}} = \frac{\Phi_{DF}}{\Phi_{PF}} = \frac{1}{\dfrac{1}{\Phi_S \Phi_T} - 1} \tag{3}$$

From the theory of nonradiative transitions, it is known that high values of k_{ISC}^S are favored by a small ΔE_{ST} (S_1-T_1 gap). The same holds *a fortiori* for k_{ISC}^T, because it is *approximately* given by[2,3]

$$k_{ISC}^T = \bar{k}_{ISC}^T \exp\left(-\frac{\Delta E_{ST}}{RT}\right) \tag{4}$$

where $\bar{k}_{ISC}^T$ is the average rate constant for the adiabatic $S_1 \leftarrow T_1$ intersystem crossing, and the exponential factor is the fraction of triplets whose total internal energy (electronic + vibrational) is equal or larger than the electronic energy of S_1. Therefore, TDF is only possible for molecules with small ΔE_{ST} and even then at not too low temperatures.

Although known for many years,[2] the phenomenon of TDF remains quite rare, with a few unambiguous observations in some dyes[2] and some aromatic ketones[4] and thiones.[5] In most of the cases studied, including the classic one, eosin,[2] it is exceedingly weak, in the sense that $\Phi_{DF} \ll \Phi_{PF}$.

The known photophysical properties of C_{70}, namely the quantum yield of triplet formation close to one,[6−9] the small S_1-T_1 gap,[9−12] and the long intrinsic phosphorescence lifetime,[11−14] make this molecule a likely candidate for TDF.

In this work, we report the observation of a very clear case of *strong* TDF ($\Phi_{DF} \gg \Phi_{PF}$), that of C_{70} dissolved in degassed liquid and solid paraffin, and give revised values of ΔE_{ST} and

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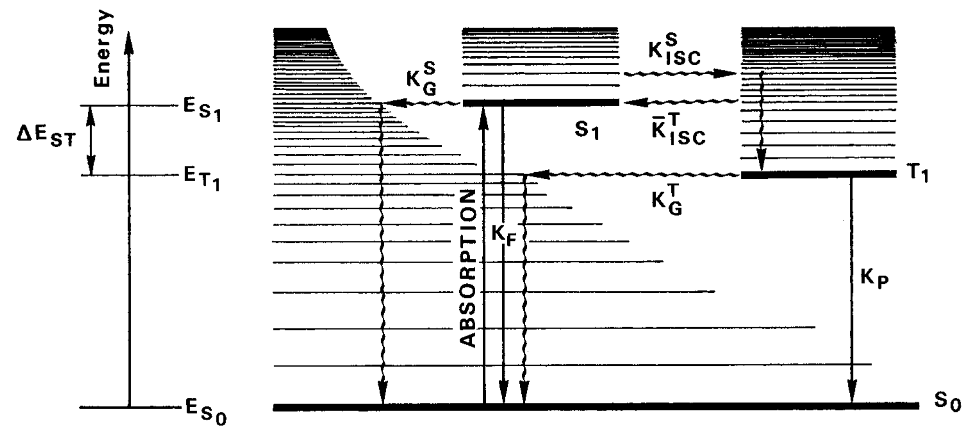

Figure 1. Simplified diagram of the electronic states and kinetic elementary steps after photon absorption. As usual, the radiative processes ($S_1 \leftarrow S_0$ absorption, $S_1 \rightarrow S_0$ fluorescence, and $T_1 \rightarrow S_0$ phosphorescence) are represented by straight lines, while the nonradiative processes ($S_1 \rightarrow S_0$ internal conversion, $S_1 \rightarrow T_1$ intersystem crossing, $S_1 \leftarrow T_1$ intersystem crossing, and $T_1 \rightarrow S_0$ intersystem crossing) are represented by wavy lines. It should be remarked that, owing to the high number of π-electrons (70) of C_{70}, and thus to its high density of electronically excited states, it is possible that one or more higher triplets (T_2, etc.) also lie below S_1, thus participating, as intermediates, in the intersystem crossing process. Definite conclusions cannot be drawn, however, because detailed experimental assignments and calculations of the electronic excited states of C_{70} are lacking.[19] In fluid and nondegassed solutions, collisional quenching of T_1 by dissolved oxygen makes $k_G^T \gg k_{ISC}^T$ and TDF is not observed.

of Φ_T, the last one obtained from a new kinetic analysis. The recorded phosphorescence spectrum supports the ΔE_{ST} obtained from the kinetic analysis.

Experimental Section

Materials. C_{70} (>99%) was purchased from Stefan Kaesdorf (Munich). Liquid paraffin was from Merck (spectroscopic grade). Purity of both materials was checked by UV−vis and luminescence spectroscopies. Taking advantage of the high boiling point (>300 °C) of liquid paraffin, solutions of C_{70} were degassed at room temperature with a turbomolecular pump, under vigorous stirring (final pressure: ca. 3×10^{-8} atm), and the respective cells sealed afterwards.

Instruments. Luminescence spectra were obtained in a Spex Fluorolog F112A fluorimeter, equipped with a specially adapted Aminco rotating can phosphorescence head (used for delayed spectra and for the determination of lifetimes,[2] in the last case coupled to a photodiode and an oscilloscope). Excitation wavelength was usually 470 nm, and an LG530 cutoff filter was used in the emission. Emission spectra were not corrected for the spectral response of the optics and photomultiplier. Viscosity was measured by the falling-ball method with an Haake viscosimeter. Temperature was controlled to within ±0.5 °C.

Results and Discussion

Analysis of Delayed Thermal Fluorescence Kinetics. The standard method of analysis of the delayed thermal fluorescence problem, due to Parker,[2] is to measure the steady-state delayed fluorescence (DF) and the steady-state phosphorescence (P) intensities, as a function of temperature, and then to determine ΔE_{ST} from a plot of $\ln(I_{DF}/I_P)$ vs $1/T$. Indeed, one obtains from the kinetic scheme of Figure 1,

$$\frac{I_{DF}}{I_P} \propto \frac{\Phi_F \Phi_S}{\Phi_P} = \frac{\Phi_F \bar{k}_{ISC}^{T}}{k_P} \exp\left(-\frac{\Delta E_{ST}}{RT}\right) \qquad (5)$$

where Φ_F is the quantum yield of fluorescence and Φ_P is the quantum yield of phosphorescence, and the plot is linear if, as in most cases, neither Φ_F nor k_P is significantly temperature dependent.

An alternative approach is however possible, and ΔE_{ST} can in principle be obtained from the temperature dependence of the ratio I_{DF}/I_{PF}, because eq 3 can be rewritten as,

$$\ln\left[\frac{I_{PF}}{I_{DF}} - \left(\frac{1}{\Phi_T} - 1\right)\right] = \ln\left(\frac{k_P + k_G^T}{\bar{k}_{ISC}^T}\right) + \frac{\Delta E_{ST}}{RT} \qquad (6)$$

Provided ($k_P + k_G^T$), often dominated by k_G^T, is essentially temperature independent, a plot of the left-hand side vs $1/T$ should be linear. However, the correct value of Φ_T (also assumed temperature independent) is required for a linear least-squares fit. In effect, the shape of the plot is a very sensitive function of Φ_T, not being, in general, a straight line. Continuous variation of this parameter in the search for maximum linearity yields its best value and, simultaneously, ΔE_{ST}. The final outcome is of course equivalent to that of a nonlinear fit to the two parameters, but the outlined approach is simpler and clearly demonstrates the extreme sensitivity to Φ_T in the high temperature domain. The method based on eq 6 yields therefore ΔE_{ST} and Φ_T, and, with lesser accuracy, $\bar{k}_{ISC}^T$. Furthermore, as will be shown, the Φ_T recovered in this way may be of high precision.

C_{70} Delayed Fluorescence: Singlet−Triplet Energy Gap. We now describe the application of both methods to C_{70} dissolved in liquid paraffin, a mixture of long-chain alkanes of high viscosity (120 cP at 20 °C, 32 cP at 45 °C, and 14 cP at 66 °C). Firstly, the assumed temperature independence of certain parameters was checked by the following: (i) the measurement of the fluorescence quantum yield of nondegassed solutions (where, owing to quenching of the triplet by molecular oxygen, delayed fluorescence is negligible)—it was temperature independent (spectra were taken at 77 K, 298 K and 343 K), in agreement with a non-thermally activated dominant decay channel ($S_1 \rightarrow T_1$ intersystem crossing); and (ii) the measurement of the phosphorescence lifetime τ_P at two very different temperatures—46 ± 3 ms at 77 K (in agreement with ref 13), and 36 ± 4 ms (measured at 656 nm) at 298 K. Using the kinetic scheme of Figure 1, it can be shown that the phosphorescence lifetime is given by,[15]

$$\frac{1}{\tau_P} = k_P + k_G^T + (1 - \Phi_T) k_{ISC}^T \qquad (7)$$

From the weak temperature dependence observed it follows that

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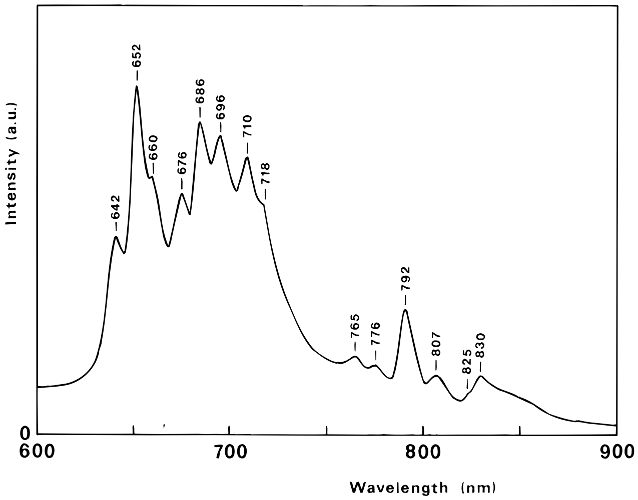

Figure 2. Luminescence spectrum of C_{70} dissolved in paraffin, at −30 °C. $[C_{70}] = 2.5 \times 10^{-5}$ M. Excitation and emission slits were 18 and 2 nm, respectively. The fluorescence spans the range 630−750 nm. The fluorescence band at 642 nm appears to be a hot band. The phosphorescence begins at ca. 750 nm, and extends further to the infrared (not shown). Peak wavelengths have an estimated accuracy of ±1 nm.

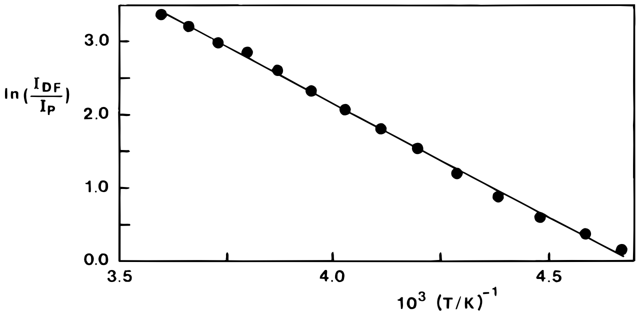

Figure 3. Log plot of the intensity ratio of delayed fluorescence to phosphorescence vs $1/T$, from −59 to 5 °C. Emission wavelengths were 688 (delayed fluorescence) and 832 nm (phosphorescence). $[C_{70}] = 1.1 \times 10^{-5}$ M.

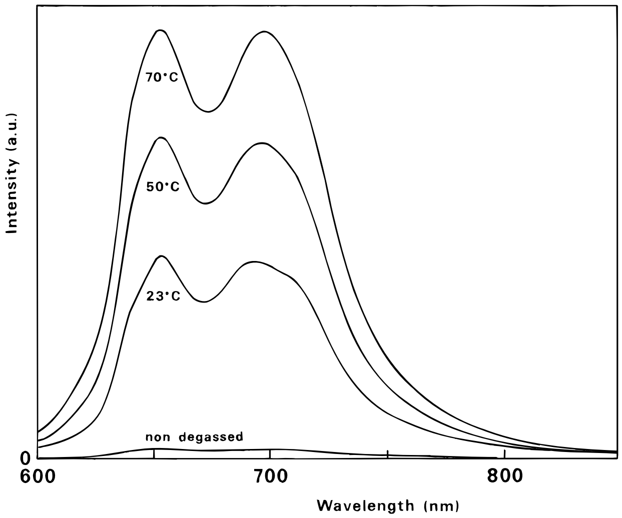

Figure 4. Low-resolution fluorescence spectra of a 1.4×10^{-6} M solution of C_{70} in liquid paraffin. Degassed solution at 23, 50, and 70 °C. The intensity of the nondegassed solution is independent of temperature, and is entirely due to prompt fluorescence. The rise with temperature observed in the degassed solutions results from the increasing contribution of delayed fluorescence to the total intensity. Emission slits were 9 nm.

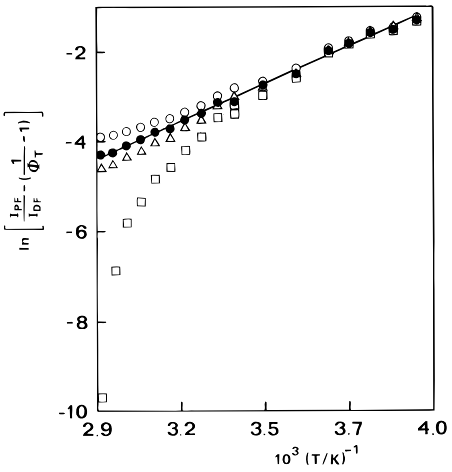

Figure 5. Fit of I_{PF}/I_{DF} vs $1/T$, according to eq 6, for temperatures from −20 to 70 °C. The effect of Φ_T on the linearity is clear: Φ_T =1.000 (○), 0.994 (best value,•), 0.990 (Δ), and 0.980 (□). Excitation and emission slits were 18 and 9 nm, respectively.

$(k_P + k_G^T)$, dominated by k_G^T,[13] is approximately constant for the experimental conditions used.

Secondly, the possibility that the delayed fluorescence is due to triplet−triplet (T−T) annihilation is ruled out by a number of facts: (i) independence on light intensity (checked by use of neutral density filters in the excitation), and (ii) absence of expected concentration effect. The only concentration effect found in the liquid state was ground state quenching,[14] favored by high temperature and low viscosity, but even this was negligible for the concentrations used in the studies above room temperature ($1-2 \times 10^{-6}$ M). As regards the low-temperature studies, no concentration effect was found in the solid solutions (up to 5×10^{-5} M). In this last case, T−T annihilation could only take place in conjunction with solute aggregation, and a concentration effect would thus be expected. In support of the lack of concentration effect is the relatively high room temperature solubility of C_{70} in liquid paraffin ($>10^{-4}$ M).

The luminescence spectrum of C_{70} in paraffin is shown in Figure 2. It consists of a high energy system, fluorescence (630−750 nm), and a low energy system, phosphorescence (>750 nm). A Parker plot (i.e., $\ln(I_{DF}/I_P)$ vs $1/T$) of 10^{-5} M degassed solutions of C_{70}, from −59 to 5 °C, gives a straight line, Figure 3, from whose slope one obtains $\Delta E_{ST} = 26 \pm 1$ kJ/mol. On the other hand, for degassed solutions and temperatures above −20 °C, DF is much stronger than PF (Figure 4; at the highest recorded temperature, 70 °C, it is 50 times stronger). Using the second method described above, for $1-2 \times 10^{-6}$ M solutions and for temperatures from −20 to 70 °C, Figure 5, one obtains a singlet−triplet gap of 25 ± 1 kJ/mol, in good agreement with the value recovered from the Parker plot. From the accepted spectroscopic assignment of 652 nm as the 0−0 band of the fluorescence,[12,16] the determined range of values of ΔE_{ST} (24−27 kJ/mol) places the 0−0 band of the phosphorescence in the range 750−765 nm.

C_{70} Phosphorescence Spectrum. The phosphorescence spectrum recorded at −85 °C (Figure 6), where delayed fluorescence is negligible, has indeed its onset at ca. 750 nm. Exactly the same spectrum is obtained by subtracting the (prompt fluorescence) spectrum of a nondegassed solution at 25 °C from the total luminescence spectrum shown in Figure 2. This shows that the phosphorescence spectrum is constant from at least −30 °C down to −85 °C. Careful examination of the room temperature luminescence spectrum of a degassed solution (dominated by delayed fluorescence) shows again a

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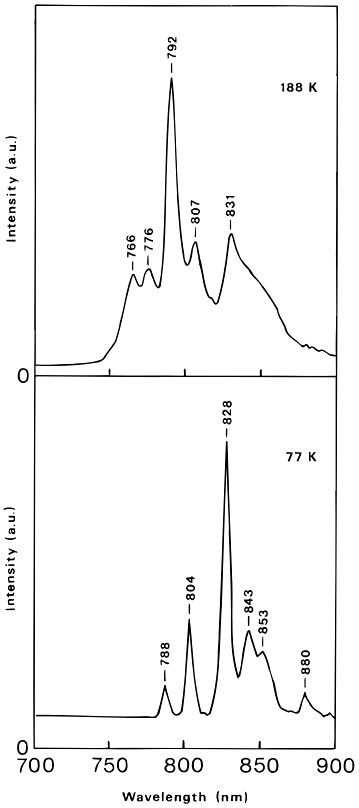

Figure 6. Phosphorescence spectra of C_{70} taken at two different temperatures: 188 (−85 °C) and 77 K. Notice how, on cooling, the high-energy bands at 766 and 776 nm disappear and the other bands simultaneously slightly shift in wavelength and strongly change their relative intensities. $[C_{70}] = 2.5 \times 10^{-5}$ M. Excitation and emission slits were 18 and 2 nm, respectively.

weak shoulder at 776 nm and weak bands at 791 and 830 nm, making it very likely that the room temperature phosphorescence spectrum is identical to that of −85 °C. Because no time delay was employed for taking the luminescence spectrum of Figure 2, in contrast to that used for obtaining the spectra of Figure 6 (5−15 ms), it is clear that all bands have a common lifetime. Previous studies of the phosphorescence spectrum[10−12,17,18] have not explored the temperature region above 77 K and, as a consequence, the high-energy bands were not observed. This occurs because on cooling down to ca. 77 K or less, and thus well below the temperature region where significant TDF is observed, the high-energy system of bands loses intensity, and the first noticeable band of the phosphorescence spectrum appears at 788 nm (77 K), Figure 6, or even at 806 nm (methylcyclohexane at 10 K).[12] This peculiar behavior is probably due to solid matrix effects.[10] In support of this, we have observed that, at 77 K, an aging effect occurs in our samples, the displayed spectrum being attained only after several tens of minutes, the nonequilibrium one being closer to that of −85 °C. Further investigation is nevertheless required for a better understanding of the whole issue.

Intersystem Crossing Rate Constants. The fit according to eq 6 also yields an intercept from which, using the measured phosphorescence lifetime, a value of $\bar{k}_{ISC}^{T} \cong 10^7\ s^{-1}$ is obtained. This value is to be compared with that of the direct intersystem crossing, $k_{ISC}^{S} = 2 \times 10^9\ s^{-1}$, which is simply computed as the inverse of the fluorescence lifetime (ca. 650 ps). The difference between the two rate constants does not appear unreasonable, in view of the much higher density of final states expected for the direct intersystem crossing case.

Quantum Yield of Triplet Formation. A quantum yield of triplet formation $\Phi_T = 0.994 \pm 0.001$ is also obtained. This value is to be compared with the published ones,[6−9] 0.97 ± 0.03, 1 ± 0.15, 0.90 ± 0.15, and 0.76 ± 0.15, and is believed to be substantially more accurate, especially as a lower bound. In this regard, it is interesting to note that direct application of eq 3 to the raw experimental data already allows the estimation of a lower bound for Φ_T. That equation can be rewritten as

$$\Phi_T = \frac{1}{1 + \frac{I_{PF}}{I_{DF}}}\frac{1}{\Phi_S} \tag{8}$$

Because Φ_S is smaller than or equal to unity, a lower bound for Φ_T is

$$\Phi_T^{min} = \frac{1}{1 + \frac{I_{PF}}{I_{DF}}} \tag{9}$$

Φ_T^{min} is the closest to Φ_T, the closest Φ_S is to one, that is, the highest is the temperature. At 70 °C, as mentioned, $I_{DF}/I_{PF} = 50$, and therefore, from eq 9, $\Phi_T^{min} = 0.98$. This simple calculation already puts Φ_T within narrow limits. On the other hand, from the experimental value $\Phi_T = 0.994$ and from eq 3, one obtains for the high-temperature limit ($\Phi_S = 1$), that $(I_{DF}/I_{PF})_{max} = 166$. In this way, the global fluorescence quantum yield ($\Phi_F = \Phi_{PF} + \Phi_{DF}$) of C_{70} can in principle be 167 times higher than that of prompt fluorescence, and thus attain the very respectable value of $167 \times (5 \times 10^{-4}) = 0.08$.

Conclusion

The very weak fluorescence of C_{70} may, under appropriate conditions, increase by one or two orders of magnitude (up to an estimated maximum value $\Phi_F = 0.08$), through the mechanism of delayed thermal fluorescence. A new estimate of the singlet−triplet gap, $\Delta E_{ST} = 26 \pm 2$ kJ mol^{-1}, was obtained from the temperature dependence of the delayed thermal fluorescence, and confirmed by the measurement of the phosphorescence spectrum. An accurate value of the quantum yield of triplet formation, $\Phi_T = 0.994 \pm 0.001$, was obtained from a new method of data analysis.

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