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Fluorescence of fullerene-C₇₀ and its quenching by long-range intermolecular electron transfer

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The fluorescence spectrum and fluorescence quantum yield of C₇₀ were determined in a number of solvents at room temperature. A well resolved fluorescence excitation spectrum, which matches the absorption spectrum, was obtained over a broad wavelength region (250 to 580 nm, in *n*-hexane). The fluorescence lifetime (627 ps in benzene) was determined, thereby settling the uncertainty about the singlet lifetime of C₇₀. It is shown that the quenching of the fluorescence by organic electron donors involves both dynamic and static mechanisms. The contribution of the latter is much more pronounced than can be explained from the degree of ground-state charge transfer complexation. Analysis in terms of a Perrin model indicates that long-range intermolecular electron transfer is important, with a radius of action that increases sharply when the donor oxidation potential is lowered.

1. Introduction

The first detection (by Kroto et al. [1]) and the subsequent bulk preparation (by Krätschmer et al. [2]) of the exceptional spherical polycyclic aromatic carbon compounds C₆₀ and C₇₀, now conveniently named as "fullerenes", has opened a new field of chemistry. Fascinating data are continuously reported now, regarding such topics as fulleride superconductivity [3], organo-metallic and organic fullerene derivatives [4-7] and photophysical properties of fullerenes [8-17].

Although the photophysical properties of C₆₀ are quite established, in the case of C₇₀ they are still a topic of discussion, especially regarding the lifetime of the first singlet excited state. Thus 115 ps was measured by Wasielewski et al. [11], while Tanigaki et al. reported 670 ps [14], both via transient absorption spectroscopy. As reported by our group before [12], and recently confirmed by others [13,17], C₇₀ shows fluorescence in solution at room temperature. From apparent differences between absorption and excitation spectra it has been concluded

[13,17] that UV excitation in higher excited states is significantly less efficient in populating the emissive state. Here we report room-temperature C₇₀ fluorescence spectra, the fluorescence lifetime, fluorescence quantum yields and a fluorescence excitation spectrum from 250 to 580 nm, while we furthermore enhance our earlier [12] study on fluorescence quenching by electron donors.

2. Experimental

HPLC pure C₇₀ was obtained by the courtesy of Professor Dr. R.M. Kellogg (SYNCOM, Groningen University). The absorption spectrum of this material as measured with a Hewlett-Packard 8451A diode array spectrometer is shown in fig. 1 together with a bargraph and numerical data representing the absorption spectrum reported in the literature [8,14,18].

Fluorescence and excitation spectra were recorded on a SPEX Fluorolog 2 instrument equipped with a red-sensitive GaAs photomultiplier (RCA C31034, Peltier cooled) of which the spectral response extends to ≤ 900 nm and is known to be quite flat from the UV to about 860 nm. Fluorescence spectra were measured on dilute solutions (2.08×10^{-5} M in *n*-

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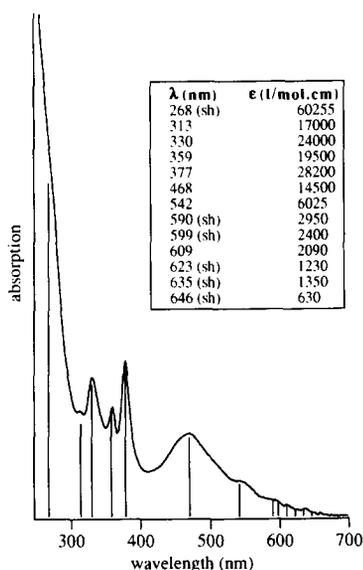


Fig. 1. Absorption spectrum of the C_{70} sample used in the present study together with literature [8,14,18] data (bargraph and numerical values), solvent *n*-hexane.

hexane, 0.99×10^{-5} M in benzene and 2.18×10^{-5} M in dichloromethane) using 455 nm (excitation path) and 570 nm (emission path) cutoff filters. Excitation and emission bandwidths of 9 nm were employed and no corrections were applied to the fluorescence spectra.

For determination of the fluorescence quantum yield meso-tetraphenylporphyrine (5,10,15,20-tetraphenylporphyrine) in non-degassed benzene (2×10^{-4} M, emission maxima at 650 and 719 nm, $\Phi_f = 0.11$ [19]) was used as a standard. Excitation wavelength was 470 nm, and the absorbance of both the reference and sample was adjusted to 0.1 (1 cm) at this wavelength. Bandwidths and cutoff filters used were 2.25, 455 nm (excitation path) and 4.5, 570 nm (emission path).

The fluorescence excitation spectrum in *n*-hexane ($[C_{70}] = 0.5 \times 10^{-5}$ M, bandwidths 9 nm (excitation path) and 28.8 nm (emission path) integration time 5 s) was recorded by monitoring the fluorescence at 770 nm and using a 665 nm cutoff filter. Correction of the excitation spectrum was achieved primarily by ratioing the emission signal and the signal of a rhodamine B quantum counter (effective range 250–590 nm), which is operated by the light

derived from the excitation beam via a quartz-plate beam splitter. Additional correction factors to compensate for the optical path difference between sample and quantum counter were determined by measuring the apparent excitation spectrum of a concentrated rhodamine B solution (in front face geometry).

Fluorescence lifetime determination was performed by the time correlated single photon counting technique, using instrumentation extensively described elsewhere [20]. Excitation pulses of 56 ps fwhm at 566.4 nm from an argon-ion-laser pumped rhodamine 6G dye-laser were employed. Fluorescence was monitored at 660 nm and a 630 nm cutoff filter was used.

3. Results and discussion

Fig. 2 shows the fluorescence excitation spectrum

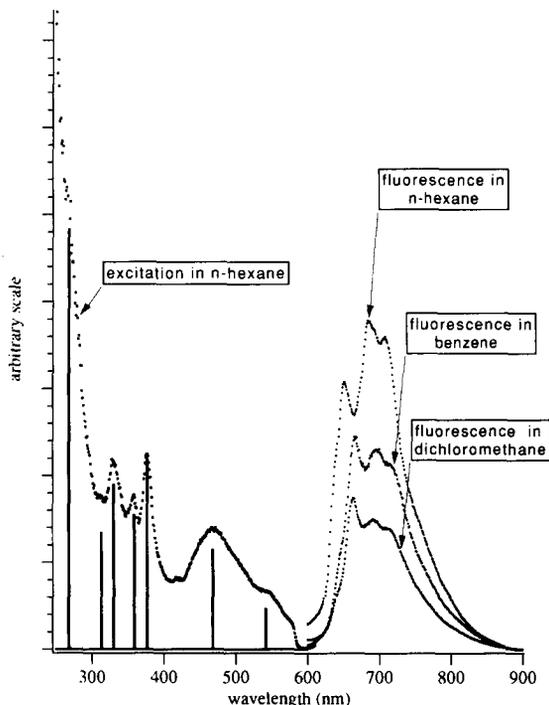


Fig. 2. Fluorescence spectrum of C_{70} in various solvents together with the corrected excitation spectrum as determined in *n*-hexane. For comparison the absorption spectrum (scaled at the 377 nm peak) is also shown in the form of a bargraph.

of C_{70} in *n*-hexane, and the fluorescence in three solvents.

The spectral distribution of the excitation spectrum satisfactorily matches that of the absorption spectrum (see fig. 1) over the spectral region investigated (250–580 nm). This confirms that the fluorescence observed stems from C_{70} and is not due to the presence of highly fluorescent trace impurities, a possibility left open in earlier studies [12,13]. Furthermore, in contrast to earlier reports [13,17], we find that VIS and UV excitation do not show a significant difference in efficiency for producing fluorescence, thus ruling out major dark deactivation of higher excited states bypassing the S_1 state. We have no explanation for this discrepancy, but it appears possible that a combination of incomplete correction of the excitation spectrum and of minor amounts of C_{60} acting as an inner filter^{#1} in the UV contributed to the apparent difference between the absorption and excitation spectra.

Fluorescence quantum yields were determined for 470 nm excitation in argon-degassed benzene ($\Phi_f = 7.0 \times 10^{-4}$), *n*-hexane ($\Phi_f = 5.0 \times 10^{-4}$) and dichloromethane ($\Phi_f = 5.4 \times 10^{-4}$). This is in accordance with the estimate (8.5×10^{-4}) made by Arbogast et al. [13] and agrees reasonably well with the value (2.2×10^{-4}) reported by Wang [17] in methylcyclohexane at 77 K. The latter comparison suggests that the fluorescence quantum yield must be virtually temperature-independent.

The fluorescence spectra show a modest change of vibrational structure and a slight shift upon change of solvent: *n*-hexane: 650, 685, 692(sh), 707 nm; dichloromethane 664, 692, 712 nm; benzene: 667, 696, 715(sh).

Fig. 3 shows the fluorescence decay of C_{70} in argon-degassed benzene solution. The decay can be fitted monoexponentially, leading to a S_1 lifetime of 627 ± 20 ps. From earlier measurements by transient absorption spectroscopy S_1 lifetimes of 115 ps [11] and 670 ps [14] in solution have been reported. Our measurements support the correctness of the latter.

The S_1 lifetime of C_{70} now being established allows for a more complete interpretation of the dynamics of the fluorescence quenching by electron-rich

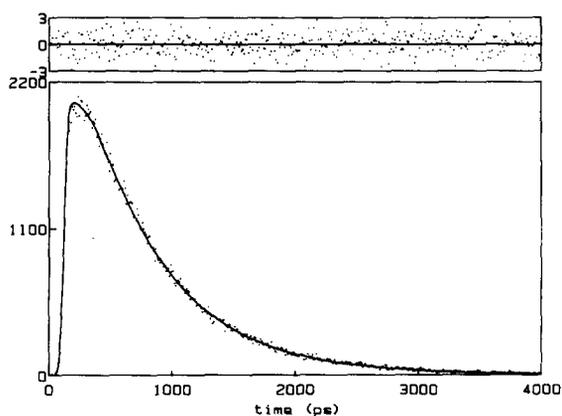


Fig. 3. Fluorescence decay of C_{70} in benzene as measured by time correlated single photon counting (see experimental). The continuous curve is the fit obtained for mono-exponential decay with $\tau = 627$ ps.

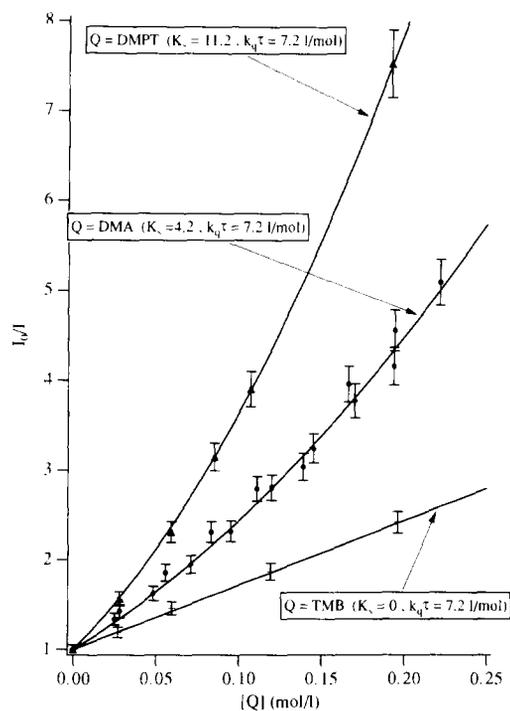


Fig. 4. Dependence of C_{70} fluorescence intensity on quencher concentration ($[Q]$) for $Q = 1,2,4$ -trimethoxy benzene (TMB), N,N -dimethyl aniline (DMA) and N,N -dimethyl-*p*-toluidine (DMPT) in benzene as a solvent. An excitation wavelength of 470 nm was employed. The curves represent best fits obtained with a combined static and dynamic quenching model (eq. (1)) using the parameters indicated.

^{#1} The absorption spectrum of the C_{70} sample shown in ref. [17] in fact indicates contamination by C_{60} .

aromatic species we reported earlier [12]. Fig. 4 shows quenching curves as measured with three such species in benzene as a solvent^{#2}. As noticed earlier a virtually linear Stern–Volmer type behaviour is found when 1,2,4-trimethoxybenzene (TMB) is employed as a quencher. From the slope of this quenching curve a Stern–Volmer constant $k_q\tau=7.2$ l/mol is found. Assuming pure dynamic quenching the rate constant (k_q) of this quenching can now be determined using the S_1 lifetime $\tau=627$ ps established above. The value of $k_q=1.15\times 10^{10}$ s⁻¹ thus found is compatible with a mechanism involving diffusion-limited excited-state electron-transfer quenching. As reported earlier, however, the quenching curves for more powerful electron donors such as N,N-dimethyl-*p*-toluidine (DMPT) and N,N-dimethylaniline (DMA) display an “upward” curvature indicative for a contribution of significant additional static quenching. Since it is known [12,15,17] that the fullerenes form ground-state complexes of the charge-transfer type with strong electron donors, one might assume that such complex formation is responsible for the static quenching. If 1:1 complex formation with an equilibrium constant K_S occurs, and this does not influence significantly the molar extinction at the excitation wavelength, the combined result of static and dynamic quenching on the ratio of the unquenched and quenched fluorescence (I_0/I) is given by

$$I_0/I=(1+K_S[Q])(1+k_q\tau[Q]), \quad (1)$$

where $[Q]$ is the quencher concentration. The latter is assumed to be large in comparison to that of C_{70} (a condition fulfilled here).

It appears likely that for DMPT and DMA the value of k_q will also be close to the diffusion limit, since this is already so for the weaker donor TMB and it is well known [21] that beyond the minimum donor strength where $k_q=k_{diff}$ the value of k_q remains virtually constant. Thus, since τ is now known accurately, the value of K_S can be evaluated from the overall quenching curve measured. As shown in fig. 4 good fits are obtained for $K_S=11.2$ l/mol (DMPT) and $K_S=4.2$ l/mol (DMA).

^{#2} In benzene as a solvent no indication for the formation of emissive exciplexes was found as observed in methylcyclohexane [17].

Interestingly, these K_S values are one to two orders of magnitude larger than the actual formation constants reported [15,17] for ground-state charge-transfer complexes between anilines and fullerenes. Furthermore the sharp decrease of K_S in the series DMPT, DMA, TMB appears incompatible with a change in complexation constant if compared to other charge-transfer complexes containing related electron donors^{#3}. We therefore propose that the major contribution to static quenching derives from photoinduced electron transfer between singlet excited C_{70} and ground-state donor species separated by much longer distances than involved in an actual ground-state complex. Results of studies on the distance dependence of electron-transfer processes in condensed media have amply revealed the possibility of such long-range electron transfer [23]. A useful model for treating such a situation is that provided by a Perrin-type formulation [24], in which all excited species that have a quencher within a distance Δr undergo static quenching, whereas those for which the nearest quencher is beyond that distance do not. Because of their homogeneous surface and (nearly) spherical shape the fullerenes are quite amenable to such a description. If the effective radius of the fullerene is R , the Perrin model implies that for static quenching at least one quencher molecule must be available in an active shell with the volume $(4/3\pi)[(R+\Delta r)^3-R^3]$. For a statistical distribution of the quencher molecules over the total volume of the solution and neglecting the chance that more than one quencher molecule is found within the active shell of a single fullerene, this leads [25] to a quenching behaviour similar to that induced by 1:1 ground-state complexation but with an apparent formation constant K_S given by

$$K_S=(4/3\pi N)[(R+\Delta r)^3-R^3] \\ =0.0025[(R+\Delta r)^3-R^3], \quad (2)$$

where N is the number of molecules in 10^{-27} mol, K_S is in l/mol and R and Δr are in Å.

Assuming that for direct contact ($\Delta r=0$) the minimum nuclear separation is 3.4 Å, the closest dis-

^{#3} For CT complexes between e.g. 1,3,5-trinitrobenzene and alkylated anilines the effect of removing a methyl group at the para position is to decrease the complex formation constant by about 20%, see ref. [22].

tance achievable between the center of C_{70} and that of a small aromatic molecule like DMA is 7 Å along the short axis of C_{70} and 7.4 Å along the long axis (see fig. 5). Substituting the average of this by taking $R=7.2$ Å in eq. (2), the K_S values of 4.2 and 11.2 ℓ/mol found for DMA and DMPT then require Δr values of 5.5 and 9.7 Å, respectively. These distances are sufficiently large to infer that even quencher molecules separated from the fullerene surface by one or two solvent (benzene) molecules can contribute to the quenching. In this context it appears interesting to point out that benzene has been found [26] to be particularly efficient in mediating long-range electron transfer by what is supposed to be a superexchange mechanism. Long-range electron transfer, however, not only requires sufficient electronic coupling (e.g. via superexchange) but also a sufficient driving force to overcome the Coulomb destabilization of the charge-separated state that occurs when the charge separation distance is increased. This factor provides a qualitative rationale for the sharp increase of Δr that occurs when the donor strength of the quencher is increased. Clearly both the efficiency of the superexchange coupling and the electron-transfer thermodynamics may be expected to depend strongly on the nature of the solvent medium, and studies to investigate the solvent dependence of the fluorescence quenching via both continuous and

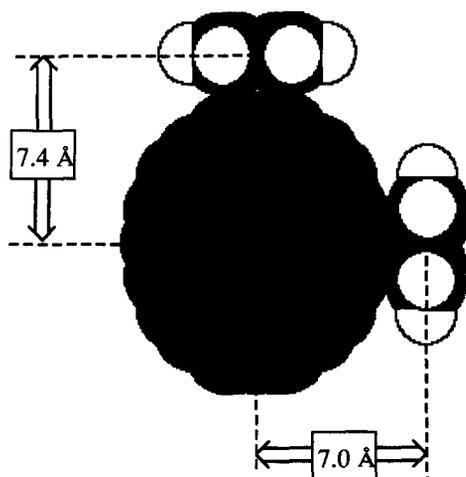


Fig. 5. Space filling model showing the closest center-to-center approach of an aromatic quencher along the long and short axis of C_{70} .

time-resolved spectroscopy are therefore being undertaken.

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References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, *Nature* 318 (1985) 162.
- [2] W. Krätschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature* 347 (1990) 354.
- [3] A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, D.W. Murphy, S.H. Glarum, T.T.M. Palstra, A.P. Ramirez and A.R. Kortan, *Nature* 350 (1991) 600.
- [4] J.M. Hawkins, A. Meyer, T.A. Lewis, S. Loren and F.J. Hollander, *Science* 252 (1991) 312.
- [5] A. Pénicaud, J. Hsu, C.A. Reed, A. Koch, C. Khemani, P.-M. Allemand and F. Wudl, *J. Am. Chem. Soc.* 113 (1991) 6698.
- [6] A.L. Balch, V.J. Catalano, J.W. Lee, M.M. Olmstead and S.R. Parkin, *J. Am. Chem. Soc.* 113 (1991) 8953.
- [7] A. Hirsch, Q. Li and F. Wudl, *Angew. Chem. Intern. Ed. Engl.* 30 (1991) 1309.
- [8] J.P. Hare, H.W. Kroto and R. Taylor, *Chem. Phys. Letters* 177 (1991) 394.
- [9] J.W. Arbogast, A.P. Darmanyan, C.S. Foote, Y. Rubin, F.N. Diederich, M.M. Alvarez, S.J. Anz and R.L. Whetten, *J. Phys. Chem.* 95 (1991) 11.
- [10] C. Reber, L. Yee, J. McKiernan, J.I. Zink, R.S. Williams, W.M. Tong, D.A.A. Ohlberg, R.L. Whetten and F. Diederich, *J. Phys. Chem.* 95 (1991) 2127.
- [11] M.R. Wasielewski, M.P. O'Neil, K.R. Lykke, M.J. Pellin and D.M. Gruen, *J. Am. Chem. Soc.* 113 (1991) 2774.
- [12] J.W. Verhoeven, T. Scherer and D. Heymann, *Rec. Trav. Chim.* 110 (1991) 349.
- [13] J.W. Arbogast and C.S. Foote, *J. Am. Chem. Soc.* 113 (1991) 8886.
- [14] K. Tanigaki, T.W. Ebbesen and S. Kuroshima, *Chem. Phys. Letters* 185 (1991) 189.
- [15] R.J. Sension, A.Z. Szarka, G.R. Smith and R. Hochstrasser, *Chem. Phys. Letters* 185 (1991) 179.
- [16] S.P. Sibley, S.M. Argentine and A.H. Francis, *Chem. Phys. Letters* 188 (1992) 187.
- [17] Y. Wang, *J. Phys. Chem.* 96 (1992) 764.

- [18] P.M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M.M. Alvarez, S.J. Anz and R.L. Whetten, *J. Am. Chem. Soc.* 113 (1991) 1050.
- [19] M. Gouterman, in: *The porphyrins*, Vol. 3, ed. D. Dolphin (Academic Press, New York, 1978) p. 36.
- [20] D. Bebelaar, *Rev. Sci. Instr.* 57 (1986) 1116.
- [21] D. Rehm and A. Weller, *Israel J. Chem.* 8 (1970) 259.
- [22] R. Foster, *Organic charge transfer complexes* (Academic Press, New York, 1969) ch. 7.
- [23] J.R. Miler, J.V. Beitz and R.K. Huddleston, *J. Am. Chem. Soc.* 106 (1984) 5057;
- G.L. Closs and J.R. Miller, *Science* 240 (1988) 440;
- H. Oevering, M.N. Paddon-Row, M. Heppener, A.M. Oliver, E. Cotsaris, J.W. Verhoeven and N.S. Hush, *J. Am. Chem. Soc.* 109 (1987) 3258;
- J.W. Verhoeven, *Pure Appl. Chem.* 62 (1990) 1585.
- [24] F. Perrin, *Ann. Chem. Phys.* 17 (1932) 283.
- [25] J.B. Birks, *Photophysics of aromatic molecules* (Wiley-Interscience, New York, 1970) pp. 441-447.
- [26] A.M. Oliver, D.C. Craig, M.N. Paddon-Row, J. Kroon and J.W. Verhoeven, *Chem. Phys. Letters* 150 (1988) 366.