14 December 2001

ELSEVIER

Chemical Physics Letters 350 (2001) 33–38

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

The fluorescence properties of the phenylated fullerenes $C_{70}Ph_4$, $C_{70}Ph_6$, $C_{70}Ph_8$, and $C_{70}Ph_{10}$ in room temperature solutions

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Received 10 August 2001; in final form 10 October 2001

Abstract

The emission and excitation spectra of four phenylated [70] fullerenes, $C_{70}Ph_4$, $C_{70}Ph_6$, $C_{70}Ph_8$, and $C_{70}Ph_{10}$ in cyclohexane and toluene solutions have been measured. The fluorescence spectra and related excited state properties are found to depend strongly on the number of attached phenyl groups, but with no systematic trends. Quantum yields and fluorescence lifetimes were measured for $C_{70}Ph_6$, $C_{70}Ph_8$, and $C_{70}Ph_{10}$, allowing the determination of $S_1 \rightarrow S_0$ radiative transition rates k_R. It is found that k_R for $C_{70}Ph_{10}$ is about six times larger than for the other compounds. This is consistent with measured absorbtivities for these compounds. The particular character of $C_{70}Ph_{10}$ is also manifested by its higher intersystem crossing rate k_{ISC}.

1. Introduction

The recently reported synthesis of phenylated [70] fullerenes [1] has created speculation about their potential for optoelectronics applications [2,3]. We therefore carried out spectroscopic and photophysical studies on this class of compounds and reported the ground and triplet state absorption spectra as well as the quantum yields of singlet to triplet intersystem crossing (Φ_T) of $C_{70}Ph_4$, $C_{70}Ph_6$, $C_{70}Ph_8$, and $C_{70}Ph_{10}$ [2]. The Φ_T values of these species have been shown to be generally high, similar to the case of C_{60} ($\Phi_T = 0.88$ [4]) and C_{70} ($\Phi_T = 0.76$ [5]). Our study also showed that Φ_T decreases with the number of phenyl rings attached to the C_{70} cage, with the exception of $C_{70}Ph_{10}$ whose triplet yield is close to unity. Its

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0009-2614/01/$ - see front matter
PII: S0009-2614(01)01217-9

behaviour was attributed to the fact that addition of 10 phenyls saturates the same number of carbons and separates the π-electron system of the C_{70} cage into two patches which interact only via σ-bonds. This electron pattern effectively makes this molecule akin to non-planar aromatics rather than to fullerenes. In order to further characterise the pathways subsequent to photoexcitation, we decided to undertake an emission study, the results of which confirm some aspects of the recently reported work of Coheur et al. [3] and provide complementary information due to the following: (1) The dispersed fluorescence spectra have been corrected for the spectral response of the detection system, (2) fluorescence excitation spectra have been recorded and (3) fluorescence lifetimes and quantum yields have been obtained.

2. Experimental

The synthesis of $C_{70}Ph_{10}$ and $C_{70}Ph_8$ is described in detail in [1]. $C_{70}Ph_6$ and $C_{70}Ph_4$ are obtained as by-products during the synthesis [6]. For each compound, the purity was controlled by carefully comparing absorption and fluorescence excitation spectra, described in detail below. Some $C_{70}Ph_8$ samples displayed non-negligible traces of $C_{70}Ph_{10}$. All results presented here are however based on pure samples.

We used an SPEX Fluorolog-2 F111 A1 spectrofluorometer entirely corrected for the spectral response function of both the emission and the excitation. The excitation source is a 150 W Xenon lamp, the excitation grating is blazed at 250 nm, the emission grating at 500 nm and the photomultiplier is a red-sensitive Hamamatsu R928. The entrance and exit slits were 0.5 mm wide giving a ~2 nm spectral bandwidth. The fluorescence quantum yields were measured using two fluorescence standards, quinine bisulphate in perchloric acid (0.1 M) solution and rhodamine 6G in ethanol solution [7].

The fluorescence lifetimes were recorded by using the time-correlated single photon counting (TCSPC) method. The laser source used was a cavity-dumped rhodamine 6G dye laser synchronously pumped by a mode-locked Nd:YAG laser. The fundamental output was frequency doubled in a KDP crystal, providing the 295 nm excitation pulses of a few picoseconds width at a repetition rate of 3.8 MHz. Fluorescence was detected by a Hamamatsu R1564 U microchannel plate, characterised by a 120 ps FWHM response function.

3. Results and discussion

3.1. General description of fluorescence spectra

Fig. 1 shows the fluorescence spectra of $C_{70}Ph_4$, $C_{70}Ph_6$, $C_{70}Ph_8$, and $C_{70}Ph_{10}$ in cyclohexane solution upon photoexcitation at $\lambda = 360$ nm ($C_{70}Ph_8$ and $C_{70}Ph_{10}$) or $\lambda = 355$ nm ($C_{70}Ph_4$ and $C_{70}Ph_6$). The spectra are recorded at room temperature. As can be seen, the positions and shapes of the fluorescence bands depend strongly on the number of phenyl groups. Red-shifts of the fluorescence band, as compared to C_{70} [8], are observed for $C_{70}Ph_4$ and $C_{70}Ph_6$, while they are blue-shifted for $C_{70}Ph_8$ and $C_{70}Ph_{10}$, as already reported elsewhere [2]. This is, as will be discussed more in detail below, due to the modification of the π-system by the presence of saturated carbon atoms. For $C_{70}Ph_6$, $C_{70}Ph_8$, and $C_{70}Ph_{10}$, the emission bands are

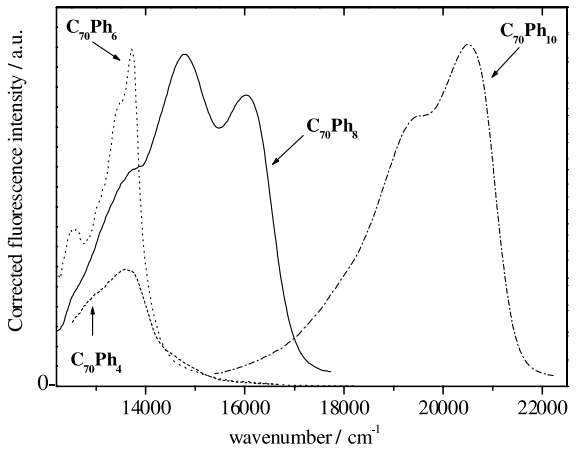

Fig. 1. Fluorescence spectra of phenylated [70] fullerenes in cyclohexane solution at room temperature. The excitation wavelengths used were: $C_{70}Ph_{10}$, $C_{70}Ph_8$: 360 nm; $C_{70}Ph_6$, $C_{70}Ph_4$: 355 nm. The spectra are entirely corrected for the spectral response of the detection system but each spectrum has a different scaling.

structured due to vibrational features as in the case of C_{70} [9,10]. We also examined the band shape and the fluorescence quantum yield for $C_{70}Ph_6$ and $C_{70}Ph_{10}$ in toluene and found that they are unchanged, within experimental precision, with respect to cyclohexane solutions.

For every compound under investigation, the emission is assumed to take place from the first singlet excited state S_1, as inferred from a comparison with absorption spectra [2]. Indeed, for each compound the first fluorescence band is always situated close to the first absorption band, only slightly shifted to the red. This is shown more in detail in Fig. 2, where the fluorescence band is shown together with the red wing of the absorption. For clarity, the first fluorescence and absorption peaks are given equal height. The Stokes shifts $\Delta\nu$, taken as the difference between the first peaks of the fluorescence and absorption bands, are rather small (see Table 1). The Stokes shift is estimated to be 100 cm^{-1} for $C_{70}Ph_6$ and 750 cm^{-1} for $C_{70}Ph_{10}$. The case of $C_{70}Ph_8$ is somewhat special, due to the presence of a first very weak absorption band around 15000 cm^{-1}, and the very broad fluorescence band. Using the first weak absorption band and the second fluorescence peak gives a Stokes shift of 350 cm^{-1}. While using the shoulder of the absorption band at 17050 cm^{-1} and the first fluorescence band gives a value of $\sim$1000 cm^{-1}.

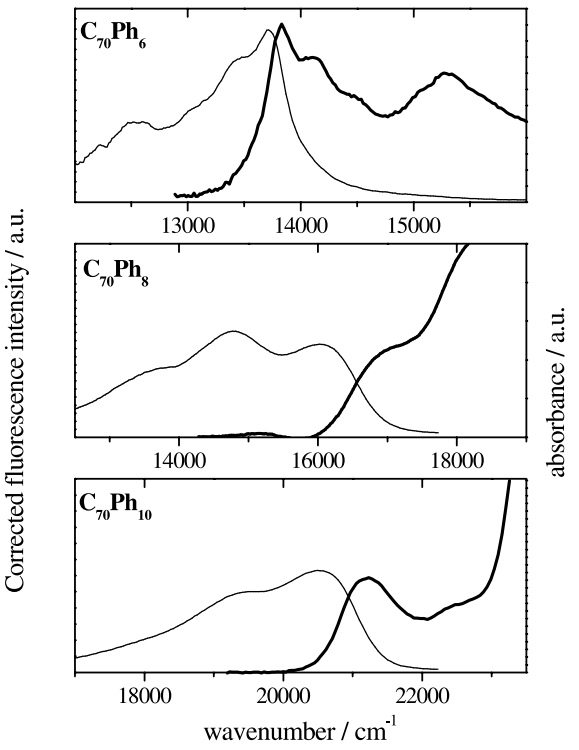

Fig. 2. Fluorescence (thin lines) and absorption spectra (thick lines) of $C_{70}Ph_6$, $C_{70}Ph_8$ and $C_{70}Ph_{10}$. For the absorption spectra only the red edge is shown in a blown-up scale in order to allow a comparison with the fluorescence band.

For $C_{70}Ph_4$, $C_{70}Ph_8$ and $C_{70}Ph_{10}$, the fluorescence spectrum cannot be judged to be a mirror image of the absorption spectrum. This is similar to what is found for C_{70} [11], for which the S_1–S_0 transition is only weakly allowed. The molar extinction coefficients are not known for all compounds treated here, but it is known that the absorptivity of the lowest lying electronic states of $C_{70}Ph_{10}$ is about 10 times stronger as compared to C_{70} [2]. In spite of this, the mirror relation is far from respected (Fig. 2). It should be noted, though, that the fluorescence and the absorption spectrum of $C_{70}Ph_6$ are closer to a mirror image, but it is difficult to draw any further conclusions lacking the absolute value of its absorptivity. The existence of close-lying electronic states in these compounds can also contribute to the absence of mirror image relation between fluorescence and absorption features and can play a role in determining the value of the observed Stokes-shift.

3.2. Fluorescence quantum yields (Φ_F)

Fluorescence quantum yields were calculated by a comparative method following [12]:

$$\Phi_{\mathrm{ref}} = \Phi_{\mathrm{s}}\left(\frac{A_{\mathrm{ref}}^{\lambda_{\mathrm{abs}}}\cdot F_{\mathrm{s}}\cdot n_{\mathrm{s}}^2}{A_{\mathrm{s}}^{\lambda_{\mathrm{abs}}}\cdot F_{\mathrm{ref}}\cdot n_{\mathrm{ref}}^2}\right). \tag{1}$$

In Eq. (1), Φ_{ref} and Φ_{s} are the fluorescence quantum yields, $A_{\mathrm{ref}}^{\lambda_{\mathrm{abs}}}$ and $A_{\mathrm{s}}^{\lambda_{\mathrm{abs}}}$ the number of photons absorbed in the sample ($A^{\lambda_{\mathrm{abs}}} = A_0^{\lambda_{\mathrm{abs}}}(1-10^{-\mathrm{OD}(\lambda_{\mathrm{abs}})})$, where A_0^{λ} is the number of incoming photons and $\mathrm{OD}(\lambda)$ is the optical density at wavelength λ), F_{ref} and F_{s} the total areas of the fluorescence spectra and n_{ref} and n_{s} the refraction indices of the reference and the fullerene samples, respectively.

Table 1
Fluorescence properties of the fullerene derivatives $C_{70}Ph_{2n}$ ($n = 3$–5) in cyclohexane (chx)

	$C_{70}Ph_6$	$C_{70}Ph_8$	$C_{70}Ph_{10}$
$\Delta\nu$ (cm^{-1})	100 ± 50	1000 ± 50	750 ± 50
Φ_F (in tol)	$(2.1 \pm 0.5)\%$ (355 nm)		$(2.0 \pm 0.5)\%$ (360 nm)
(λ_{exc})			$(2.5 \pm 0.5)\%$ (469 nm)
Φ_F (in chx)	$(2.2 \pm 0.5)\%$ (355 nm)	$(1.3 \pm 0.5)\%$ (520 nm)	$(2.3 \pm 0.5)\%$ (355 nm)
(λ_{exc})			$(1.8 \pm 0.5)\%$ (469 nm)
τ_F (in chx)	(6.62 ± 0.05) ns	(4.83 ± 0.05) ns	(1.12 ± 0.05) ns
$\lambda_{exc} = 295$ nm	($\lambda_{obs} = 720$ nm)	($\lambda_{obs} = 620$ nm)	($\lambda_{obs} = 520$ nm)
k_R (in chx)	$(3.3 \pm 0.8) \times 10^6$ s^{-1}	$(2.7 \pm 1.1) \times 10^6$ s^{-1}	$(1.8 \pm 0.5) \times 10^7$ s^{-1}
k_{NR} (in chx)	$(1.5 \pm 0.4) \times 10^8$ s^{-1}	$(2.0 \pm 0.8) \times 10^8$ s^{-1}	$(8.7 \pm 2.4) \times 10^8$ s^{-1}
Φ_T (in chx)	0.5 ± 0.1	0.18 ± 0.04	1.0 ± 0.2
k_{ISC} (in chx)	$(7.6 \pm 1.5) \times 10^7$ s^{-1}	$(3.7 \pm 0.8) \times 10^7$ s^{-1}	$(8.7 \pm 1.9) \times 10^8$ s^{-1}
k_{IC} (#in chx)	$(7.4 \pm 2.3) \times 10^7$ s^{-1}	$(1.6 \pm 0.7) \times 10^8$ s^{-1}	($<10^8$ s^{-1})[a]

Stokes shifts $\Delta\nu$, quantum yields Φ_F (also in toluene (tol)), singlet state life times τ_F, radiative transition rates k_R. Also given are non-radiative transition rates k_{NR}, intersystem crossing rates k_{ISC} and internal conversion rates k_{IC} determined from the experimental data. The triplet quantum yields Φ_T were taken from [2].

[a] Undetermined.

The quantum yields of fluorescence, Φ_F (Table 1), are fairly low for $C_{70}Ph_6$, $C_{70}Ph_8$, and $C_{70}Ph_{10}$, ranging mainly between 1% and 2.5%. The small variation of the Φ_F values between these three compounds should be taken with some care, though, since the experimental uncertainties of the Φ_F values are about 25%. For $C_{70}Ph_{10}$, Φ_F has been measured at two different excitation wavelengths, giving equal values within the experimental error limits. $C_{70}Ph_4$ is somewhat exceptional because of its significantly lower quantum yield (0.13%).

The generally low Φ_F values are in accordance with the high singlet to triplet intersystem crossing efficiencies that were measured for these molecules [2]. However, the Φ_F values are much higher than those of unsubstituted fullerenes such as C_{60} ($\Phi_F = 2.6 \times 10^{-4}$) and C_{70} ($\Phi_F = 5.4 \times 10^{-4}$) [11]. This indicates that internal conversion towards the S_0 ground state is relatively less important in the series of phenylated C_{70} molecules than in C_{70}. In other words, it points towards a more allowed nature of the $S_1 \rightarrow S_0$ transition than in the pristine molecule. No consistent trend concerning Φ_F was observed within the $C_{70}Ph_{2n}$ series (see Table 1).

3.3. Fluorescence excitation (FEX) spectra

FEX spectra have been recorded for each compound and found to be very similar to the

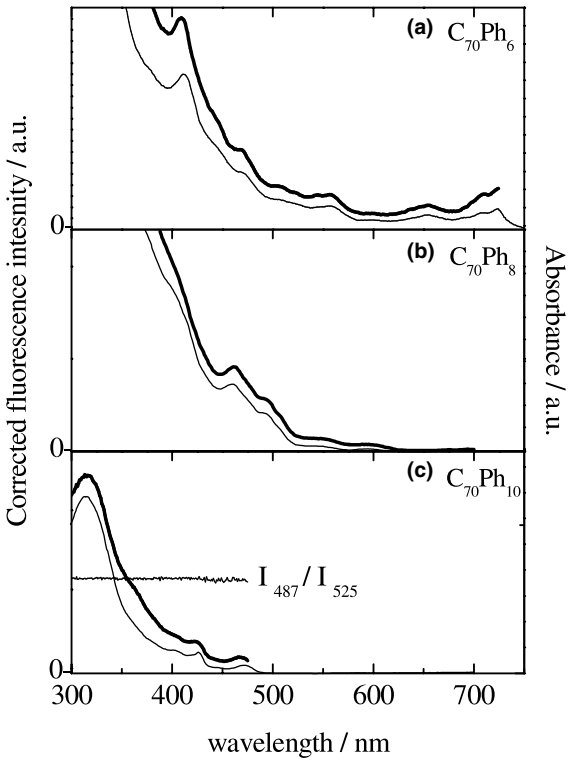

Fig. 3. Absorption (thin line) and fluorescence excitation (thick line) spectra for $C_{70}Ph_6$ ($\lambda_{obs} = 728$ nm), $C_{70}Ph_8$ ($\lambda_{obs} = 619$ nm) and $C_{70}Ph_{10}$ ($\lambda_{obs} = 525$ nm). For $C_{70}Ph_{10}$ is also shown the ratio of the fluorescence excitation spectra with $\lambda_{obs} = 487$ and $\lambda_{obs} = 525$ nm.

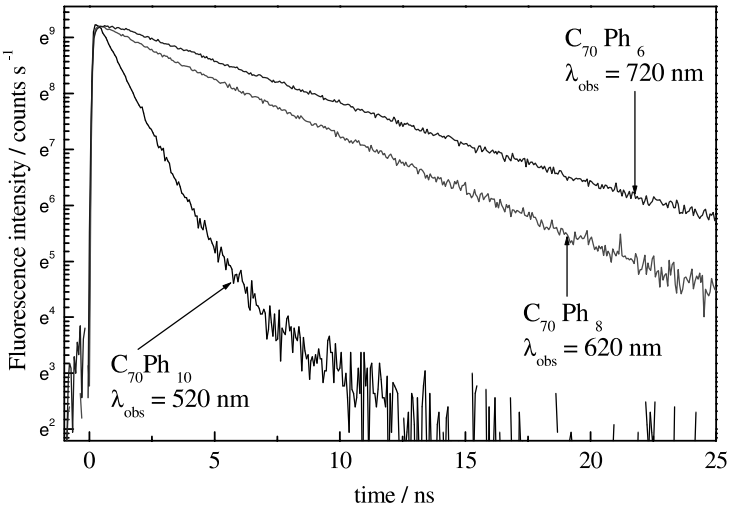

Fig. 4. Fluorescence decay for $C_{70}Ph_6$, $C_{70}Ph_8$ and $C_{70}Ph_{10}$ after photoexcitation at $\lambda = 295$ nm.

absorption spectra. Fig. 3 shows the FEX spectra of $C_{70}Ph_6$ ($\lambda_{obs} = 728$ nm), $C_{70}Ph_8$ ($\lambda_{obs} = 619$ nm) and $C_{70}Ph_{10}$ ($\lambda_{obs} = 525$ nm) together with their ground state absorption spectra (taken from [2]), both of them being recorded in cyclohexane. The excitation spectrum follows the absorption spectrum, reproducing every feature of the latter. This behaviour indicates that on increasing the energy of excitation no new channels for internal conversion are opened. Similarly, for $C_{70}Ph_{10}$, the FEX detected at 487 and 525 nm, near the maxima of the two fluorescence bands, do not show any differences between 300 and 500 nm as illustrated by the intensity ratio I_{487}/I_{525} in Fig. 3c. This fact further supports the assumption that the two fluorescence bands at $\lambda = 487$ and $\lambda = 525$ nm are vibronic bands emitted with the same probability when exciting to the S_1 state or to higher S_n states. In other words, the intersystem crossing and the internal conversion occur from the S_1 state. Similar conclusions were drawn regarding C_{70} [8].

3.4. Fluorescence lifetimes and radiative rate constants

Fig. 4 shows the observed time-resolved fluorescence decay of $C_{70}Ph_6$, $C_{70}Ph_8$ and $C_{70}Ph_{10}$. On the nanosecond time-scale, we observe almost purely exponential decays over three orders of magnitude for each compound studied. The observed fluorescence lifetimes, τ_F, are given in Table 1. Radiative decay rates (k_R) can be obtained by using Eq. (2):

$$k_R = \Phi_F/\tau_F. \quad (2)$$

These values are also shown in Table 1. The ratio of the radiative rates for $C_{70}Ph_{10}$ and $C_{70}Ph_8$, about seven, compare well with the ratio of the molar extinction coefficients of their respective lowest absorption bands [2]. A ratio of this order of magnitude is obtained on introducing the integrated S_1–S_0 absorption and fluorescence spectra of these compounds into the Strickler–Berg equation [13]. The high radiative rate k_R of $C_{70}Ph_{10}$ is noteworthy since this compound also has the highest triplet yield Φ_T, close to unity [2], thus suggesting a very efficient singlet to triplet intersystem crossing pathway. This behaviour further underlines the peculiar chromophore character of $C_{70}Ph_{10}$ as compared to the other phenylated compounds. The radiative rate k_R of $C_{70}Ph_6$ is 20% larger than that of $C_{70}Ph_8$. In general, the greater radiative rates of phenylated C_{70} as compared to C_{70} ($k_R = 8.8 \times 10^5$ s^{-1} [11]) are readily rationalised by the stronger absorption to their lowest-lying singlet states.

3.5. Non-radiative rate constants k_{IC} and k_{ISC}

From the radiative rates k_R together with measured quantum yields for triplet state formation Φ_T [2], the rate constants for $S_1 \rightarrow T_1$ intersystem crossing, k_{ISC}, and $S_1 \rightarrow S_0$ internal conversion, k_{IC}, can be calculated according to the following Eqs. (3)–(5):

$$k_{ISC} = \frac{\Phi_T}{\tau_F}, \tag{3}$$

$$k_{NR} = \frac{1}{\tau_F} - k_R, \tag{4}$$

$$k_{IC} = k_{NR} - k_{ISC}. \tag{5}$$

The resulting values are given in Table 1. Since the Φ_T values were given with 20% relative uncertainties, and our Φ_F values have relative uncertainties on the order of 25%, it is evident that these values of k_{ISC} and k_{IC} are only crude estimates. One may, however, once again note the particularly high k_{ISC} and k_R values for $C_{70}Ph_{10}$ in line with the much shorter fluorescence lifetime observed.

4. Conclusion

We have performed a systematic study of the fluorescence properties of four phenylated [70] fullerenes, $C_{70}Ph_4$, $C_{70}Ph_6$, $C_{70}Ph_8$, and $C_{70}Ph_{10}$ in non-polar (cyclohexane) and weakly polar (toluene) solvents. These fluorescence data are compatible with the singlet–triplet yields, already known from an earlier study. However, we observe no systematic trends of the fluorescence properties as a function of the number of attached phenyl groups. In fact, the data imply that the excited state electronic properties are very specific for each compound.

Acknowledgements

This work was carried out with partial support from the European Union, TMR Network 'USEFULL', contract FRMX-CT97-0126. The authors express their thanks to Francesco Zerbetto for many helpful discussions. PRB acknowledges the EPSRC for the award of an Advanced Fellowship.

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