Fluorescence spectra and quantum yields of [60]fullerene and [70]fullerene under different solvent conditions. A quantitative examination using a near-infrared-sensitive emission spectrometer

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Absorption and emission properties of [60]fullerene and [70]fullerene in solutions of ten different solvents were studied. With the use of a near-infrared-sensitive detector, the complete fluorescence spectra of [60]fullerene and [70]fullerene were determined. The spectra extend well into the near-infrared region. The correct fluorescence quantum yields of [60]fullerene and [70]fullerene in toluene are 3.2×10^{-4} and 5.7×10^{-4}, respectively, and the yields are slightly different in other solvents. For most applications, the fluorescence quantum yield ratio $\Phi_{F,C70}/\Phi_{F,C60}$ of 1.8 can be used as a solvent independent constant. The discrepancies between the experimentally determined transition probabilities and those calculated from observed absorption and fluorescence spectra of both [60]fullerene and [70]fullerene in terms of the Strickler–Berg equation are discussed.

Introduction

Since large quantities of [60]fullerene (C_{60}) and [70]fullerene (C_{70}) became readily available, there has been great interest in the understanding of the electronic properties of the fullerene materials.[1-3] C_{60} (I_h) and C_{70} (D_{5h}) are highly symmetric molecules. Because of the high degree of symmetry in the closed-shell electronic configuration, a number of theoretical calculations have predicted that low-lying electronic transitions in C_{60} are only weakly allowed.[4] The prediction has been confirmed experimentally. The observed first absorption band of C_{60} is indeed very weak, with the molar absorptivity at the band maximum of only ~ 950 dm^3 mol^{-1} cm^{-1} in solution.[5,6] For C_{70}, the symmetry-related forbidden selection is somewhat relaxed, and transition probabilities of low-lying excited states become much higher ($\sim 21\,000$ dm^3 mol^{-1} cm^{-1} at the observed first absorption band maximum).[7,8]

The current understanding of fullerene excited state properties is largely from studies in fluid and glassy solutions.[5-18] C_{60} is only weakly fluorescent, regardless of experimental conditions. The low fluorescence yield is not only due to rapid intersystem crossing to the formation of excited triplet state, but also attributable to a small fluorescence radiative rate constant as a result of weak electronic transition. However, despite a significant increase in transition probabilities from C_{60} to C_{70}, the fluorescence yield of C_{70} is only slightly higher than that of C_{60}.[2,3,5-8,15,18]

Fluorescence quantum yields of C_{60} and C_{70} in methylcyclohexane glass at 77 K were first reported to be excitation wavelength dependent.[11] However, results from subsequent experimental investigations apparently do not support the initial observation.[3,6,8] At room temperature in toluene and hexane, fluorescence quantum yields of C_{60} and C_{70} were determined systematically as a function of excitation wavelength. No dependence on excitation wavelength was observed and the fluorescence excitation spectra match the absorption spectra of C_{60} and C_{70}, also indicating the absence of any excitation wavelength dependence of fluorescence quantum yields.[6,8] According to results from several different laboratories, currently accepted values of C_{60} and C_{70} fluorescence quantum yields in room temperature toluene are $\sim 2 \times 10^{-4}$ and $\sim 5 \times 10^{-4}$, respectively, with the quantum yield ratio $\Phi_{F,C70}/\Phi_{F,C60}$ of ~ 2.5.[6,8,15,18] However, the fluorescence quantum yield determinations were based on spectral

responses in the wavelength range up to 850 nm due to limitations in the employed emission detectors. In fact, observed fluorescence intensities in the 800–850 nm wavelength range are also questionable because of the very large emission correction factors as a result of weak detector responses. The wavelength range is somewhat favourable to the spectrum of C_{70}, but less favourable to the spectrum of C_{60} because it extends into longer wavelengths. Thus, the fluorescence quantum yield of C_{60} has been under-estimated, and the ratio $\Phi_{F,C70}/\Phi_{F,C60}$ has been over-estimated. In order to determine the fluorescence quantum yields of C_{60} and C_{70} accurately, a near-infrared-sensitive emission spectrometer is required. It has been shown[6,8,9,15] that for both C_{60} and C_{70} there are significant discrepancies between the transition probabilities determined experimentally and those calculated from observed absorption and emission spectra in terms of the Strickler–Berg equation.[19] Such a fundamental issue in the photophysics of fullerenes can be addressed more quantitatively as accurate fluorescence quantum yields of the molecules become available. In addition, C_{60} and C_{70} are often used as references in fluorescence measurements of derivatized fullerenes and fullerene polymers.[20-22] An accurate determination of the fluorescence quantum yields of C_{60} and C_{70} under different solvent conditions is also important in this regard.

A quantitative examination of the fluorescence spectra and quantum yields of the fullerenes under different solvent conditions is also prompted by the observed extreme dependence of C_{60} solution colour on solvent environment.[23,24] Results from such an examination allow a quantitative evaluation of the role of solvent in the somewhat unusual photophysical behaviour of the fullerene molecules.

Experimental

Materials

[60]Fullerene ($>99.99\%$) and [70]fullerene ($>98\%$) were purchased from MER Co. and the purity was checked by HPLC and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopic methods. The samples were used without further purification. Hexane, toluene, o-xylene, dichloromethane, carbon disulfide and o-dichlorobenzene (all spectrophotometric grade) were obtained from Burdick & Jackson; 1,2,3,5-tetramethylbenzene (85% and the remaining fractions being other isomers), 1,2,4-trimethyl-

benzene (98%), and 1-methylnaphthalene (98%) were obtained from Aldrich; and chlorobenzene (spectrophotometric grade) was obtained from Mallinckrodt. The solvents were used as received because there was no interference of possible impurities in the wavelength range of interest according to absorption and emission spectroscopic measurements of the solvents. Rhodamine 101 (99%) was purchased from Fisher Scientific and used as a fluorescence standard.

Measurements

Absorption spectra were obtained using a computer-controlled Shimadzu UV2101-PC UV/VIS spectrophotometer. Emission spectra were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450 W xenon lamp, a Spex 340S dual-grating and dual-exit monochromator, and two detectors. The two gratings are blazed at 500 nm (1200 grooves per mm) and 1000 nm (600 grooves per mm). The room temperature detector consists of a Hamamatsu R928P photo-multiplier tube operated at 950 V, and the thermoelectronic-ally cooled detector consists of a near-infrared-sensitive Hamamatsu R5108 photomultiplier tube operated at 1500 V. In fluorescence measurements, a Schott 540 nm (GG-540) or 610 nm (RG-610) colour glass sharp-cut filter was placed before the emission monochromator to eliminate the excitation scattering. Minor distortion at the blue onset of the observed fluorescence spectra due to the filter was corrected by use of the transmittance profile of the filter. The slit of the excitation monochromator was 5 mm (19 nm resolution). For the emission monochromator, a wide slit of 5 mm (19 nm resolution) was used in fluorescence quantum yield measurements to reduce experimental uncertainties, and a narrow slit of 0.5 mm (2 nm resolution) was used in fluorescence spectral measurements to retain structures of the spectra.

Unless specified otherwise, fluorescence spectra were corrected for nonlinear instrumental response by use of pre-determined correction factors. The correction factors for the emission spectrometer were carefully determined using a calibrated radiation standard from Optronic Laboratories (OL 220C), which consists of a 200 W tungsten–halogen lamp (250–2500 nm) and a OL-65 precision DC constant current source. The configuration of the standard lamp and the emission spectrometer was made easy with a mounting kit provided by Spex. The emission correction factors thus obtained for the grating blazed at 1000 nm and the near-infrared-sensitive detector are shown in Fig. 1. Since the correction factors are relatively flat up to 1100 nm (Fig. 1), corrected emission spectra can be determined accurately in the corresponding wavelength range.

Temperature variations in fluorescence measurements were accomplished through fluid circulation. A Haake K20 circulating bath and a DC3 controller were used to keep a sample solution at a constant temperature. The actual temperature of the sample solution was monitored by use of an Omega DP116-KC1 digital thermometer and a temperature probe in contact with the solution in the cuvette through a small hole in the cap. The accuracy in the temperature reading is ±0.1 °C.

Results

Absorption and fluorescence spectra

Absorption spectra of C_{60} and C_{70} in 10 different solvents were measured at room temperature. The spectra in hexane, dichloromethane, toluene, chlorobenzene, o-dichlorobenzene and CS_2 are similar, except for minor spectral shifts from solvent to solvent. The spectra in hexane are somewhat better resolved (Figs. 2 and 3). However, the absorption spectra of C_{60} and C_{70} in toluene, o-xylene, 1,2,4-trimethylbenzene, 1,2,3,5-tetramethylbenzene and 1-methylnaphthalene are different in a rather characteristic fashion (Figs. 4 and 5). Except for 1-
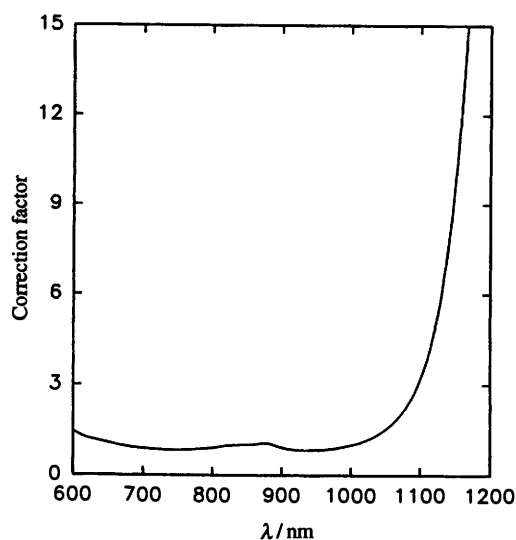

Fig. 1 Emission correction factors for Spex 340S monochromator with a grating blazed at 1000 nm and a thermoelectronically cooled detector consisting of a Hamamatsu R5108 photomultiplier tube
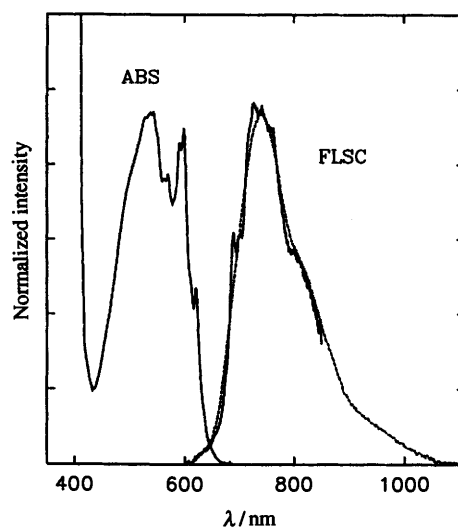

Fig. 2 Absorption and fluorescence spectra of C_{60} in room temperature hexane. The fluorescence spectra were obtained by using a regular detector and small slit (——) and a near-infrared-sensitive detector and large slit (– ·· – ·· –).
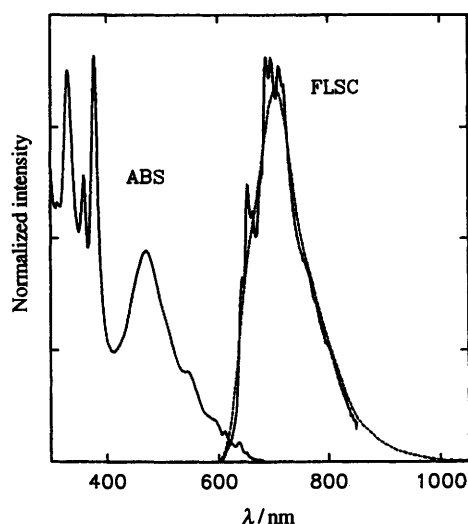

Fig. 3 Absorption and fluorescence spectra of C_{70} in room temperature hexane. The fluorescence spectra were obtained by using a regular detector and small slit (——) and a near-infrared-sensitive detector and large slit (– ·· – ·· –).
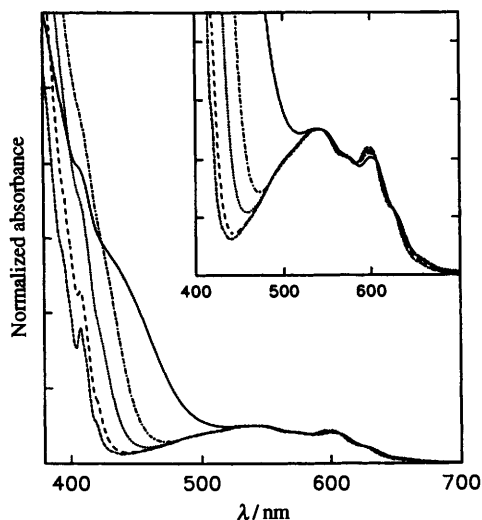
Fig. 4 Absorption spectra of C_{60} in toluene (- - - -), *o*-xylene (- - -), 1,2,4-trimethylbenzene (· · · ·), 1,2,3,5-tetramethylbenzene (- · - · -) and 1-methylnaphthalene (———) at room temperature

Fig. 5 Absorption spectra of C_{70} in toluene (- - - -), *o*-xylene (- - -), 1,2,4-trimethylbenzene (· · · ·), 1,2,3,5-tetramethylbenzene (- · - · -) and 1-methylnaphthalene (———) at room temperature
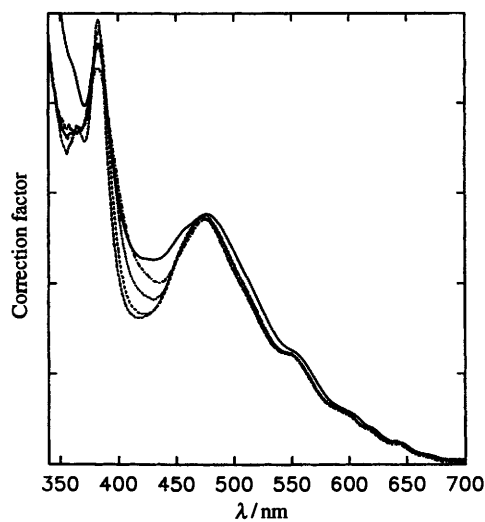

Fig. 6 Fluorescence spectra of C_{60} in room temperature 1,2,4-trimethylbenzene with excitation at 440 nm (- - - -) and 540 nm (———) (near-infrared-sensitive detector and large slit)

Fig. 7 Fluorescence spectra of C_{60} in toluene (- - - -), *o*-xylene (- - -), 1,2,4-trimethylbenzene (· · · ·), 1,2,3,5-tetramethylbenzene (- · - · -) and 1-methylnaphthalene (———) at room temperature (near-infrared-sensitive detector, large slit and λ_{EXC} = 540 nm)

methylnaphthalene, the solvents are methyl-substituted benzenes. For C_{60}, the first absorption band remains unchanged in all solvents, while the second absorption band red-shifts as the number of methyl substitution in the solvent increases (Fig. 4). There is a more dramatic change in the spectrum of C_{60} in 1-methylnaphthalene. The spectral 'valley' between the first and second absorption bands observed in other solvents is absent in 1-methylnaphthalene, so that the solution colour for C_{60} in 1-methylnaphthalene is very different. For C_{70}, the first absorption band is also basically unchanged in all solvents. While the peak at ~ 382 nm is not shifted, absorption in the spectral 'valley' (390–460 nm) increases with increasing number of methyl substitution in the solvent (Fig. 5).

Fluorescence spectra of C_{60} and C_{70} in the ten solvents were measured at different excitation wavelengths in the first and second absorption bands. Observed fluorescence spectra are excitation wavelength independent, even for those in the solvent series of methyl substituted benzenes. As shown in Fig. 6, fluorescence spectra of C_{60} in 1,2,3,5-tetramethylbenzene excited at 440 and 540 nm are essentially the same. Similar results were obtained in other solvents. Unlike absorption spectra, fluorescence spectra of C_{60} and C_{70} are hardly solvent dependent, except that the spectra in 1-methylnaphthalene are
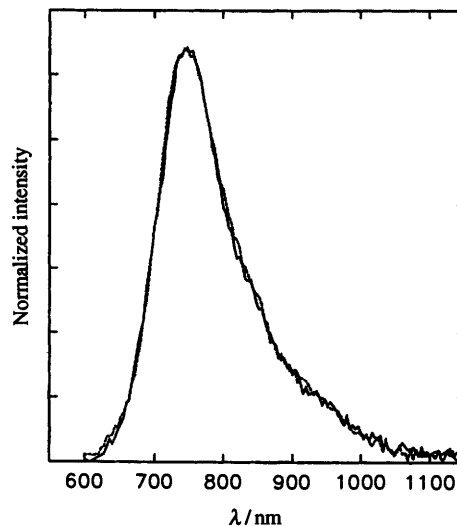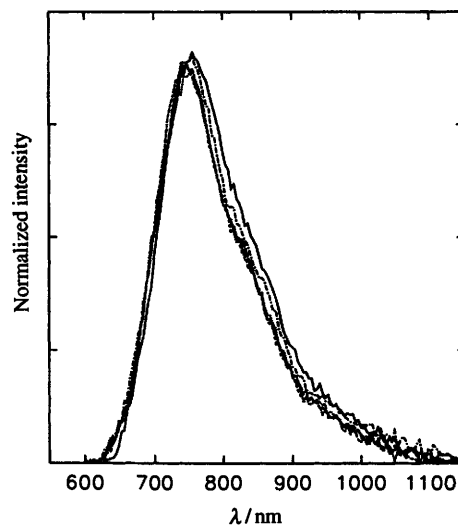
slightly red-shifted (Figs. 7 and 8). As shown in Figs. 2, 3 and 6–8, the fluorescence spectra of C_{60} and C_{70} extend well beyond 850 nm. In toluene, the integrated fluorescence intensities for the wavelength region > 850 nm account for 20 and 5% of the total integrated fluorescence intensities of C_{60} and C_{70}, respectively. Due to large emission slits (5 mm, 19 nm spectral resolution) the spectra obtained by using the near-infrared-sensitive detector appear to be very broad (Figs. 2 and 3). The use of large emission slits was necessary because the efficiency of Hamamatsu R5108 photomultiplier tube is significantly lower than that of the regular Hamamatsu R928P photomultiplier tube.

Fluorescence quantum yields

Fluorescence quantum yields of C_{60} and C_{70} were determined in the 10 different solvents at room temperature by using rhodamine 101 in ethanol as a fluorescence standard (Φ_F = 1.0).[25] In the wavelength region < 850 nm, the yields determined with the regular and near-infrared-sensitive detectors are essentially the same despite different spectral resolutions. For the wavelength region ≤ 850 nm only, the fluorescence yields of C_{60} and C_{70} in toluene are 2.6 × 10^{-4} and 5.4 × 10^{-4}, respectively,

Table 1 Observed fluorescence quantum yields of C_{60} and C_{70} and yield ratios ($\Phi_{F,C70}/\Phi_{F,C60}$) under different solvent conditions

Solvent	n	ε	$\Phi_{F,C60}(10^4)$	$\Phi_{F,C70}(10^4)$	$\Phi_{F,C70}/\Phi_{F,C60}$
Hexane	1.375	1.890	3.3	5.9	1.8
Dichloromethane	1.424	9.080	3.3	5.4	1.6
Chlorobenzene	1.524	5.710	2.8	5.3	1.9
o-Dichlorobenzene	1.552	9.930	3.0	4.8	1.6
Carbon disulfide	1.632	2.641	2.6	4.2	1.6
Toluene	1.496	2.379	3.2	5.7	1.8
o-Xylene	1.506	2.568	2.9	5.7	2.0
1,2,4-Trimethylbenzene	1.505		3.1	5.8	1.9
1,2,3,5-Tetramethylbenzene	1.513		3.2	5.7	1.8
1-Methylnaphthalene	1.618	2.920	3.7	6.2	1.7
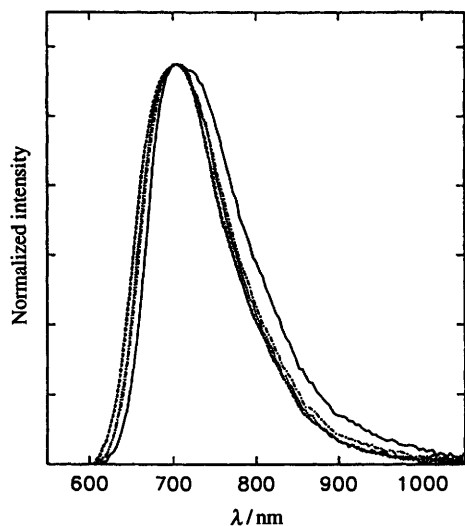
Fig. 8 Fluorescence spectra (19 nm spectral resolution) of C_{70} in toluene (- - - -), o-xylene (— — —), 1,2,4-trimethylbenzene (· · · ·), 1,2,3,5-tetramethylbenzene (– · – · –) and 1-methylnaphthalene (———) at room temperature (near-infrared-sensitive detector, large slit, and λ_{EXC} = 470 nm)
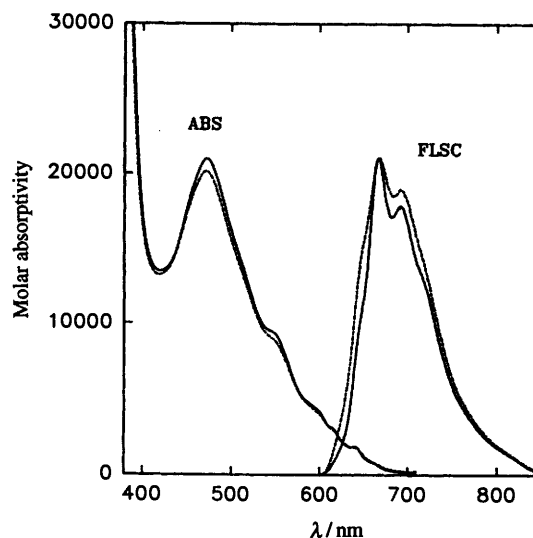
Fig. 9 Absorption and fluorescence (~ 5 nm resolution) spectra of C_{70} in toluene at 21 °C (———) and 96 °C (- - - -)

and the $\Phi_{F,C70}/\Phi_{F,C60}$ ratio is 2.1. With the use of the near-infrared-sensitive detector, the correct fluorescence yields of C_{60} and C_{70} over all emission wavelengths were determined. Shown in Table 1 are the results in the 10 different solvents, which have been corrected for effects of solvent refractive index differences according to eqn. (1)[26] where F_A presents the ratio between

$$\Phi_{F,SA}/\Phi_{F,SD} = (F_{A,SA}/F_{A,SD})(n_{SD}/n_{SA})^2 \qquad (1)$$

integrated fluorescence intensities and optical density at the excitation wavelength, and SD and SA denote the solvents for standard and sample, respectively. As shown in Table 1, the fluorescence quantum yields of both C_{60} and C_{70} are noticeably smaller in CS_2 and larger in 1-methylnaphthalene. The yield ratios for C_{60} and C_{70} in the two solvents (1-methylnaphthalene/CS_2) are 1.4 and 1.46, respectively. In the other eight solvents, variations in observed yields are within ~ 20%, somewhat larger than the estimated range of experimental uncertainties of ~ 10%.

While the yields are noticeably smaller in CS_2 and larger in 1-methylnaphthalene for both C_{60} and C_{70}, their ratios $\Phi_{F,C70}/\Phi_{F,C60}$ in the two solvents are similar to those in other solvents (Table 1). The ratios in all solvents differ within ~ 20%, with an average $\Phi_{F,C70}/\Phi_{F,C60}$ ratio of 1.8.

Temperature dependence

Absorption and fluorescence spectra of C_{70} in toluene were also measured as a function of temperature (20–100 °C). While absorption spectral profile and molar absorptivities are hardly temperature dependent, observed fluorescence spectra become somewhat broader at higher temperatures (Fig. 9). However,

the fluorescence quantum yields of C_{70} are essentially temperature independent.

Discussion

The absorption spectra of both C_{60} and C_{70} undergo characteristic changes in the solvent series of methyl-substituted benzenes, but remain essentially unchanged in other solvents. In the solvent series of benzenes substituted by monomethyl (toluene), dimethyl (o-xylene), trimethyl (1,2,4-trimethylbenzene) and tetramethyl (1,2,3,5-tetramethylbenzene), the C_{60} solutions exhibit dramatic colour changes.[23,24] The colour changes are due to significant shifts of the strong second absorption band, while the weak longer wavelength first absorption band remains the same. There are similar absorption spectral changes for C_{70} in the solvent series, but without dramatic solution colour changes because C_{70} has a much stronger first absorption band than C_{60}. The extremely different solvent dependencies of the long and short wavelength absorption bands observed in both C_{60} and C_{70} represent a rather unusual photophysical phenomenon. A simple explanation might be that the electronic transitions responsible for the two absorption bands have different transition probabilities (with the first absorption band being only weakly allowed), resulting in different solvatochromic shifts. In principle, solvatochromic effects on weakly allowed transitions are insignificant. A classical example can be found in the photophysics of long-chain polyenes.[27] Because the transitions responsible for the absorption and emission spectra of long-chain polyenes have different transition probabilities, solvatochromic shifts of the spectra are very different.[27,28] However, while the explanation seems reasonable for the fullerene molecules in the solvent series of methyl-substituted benzenes, it

becomes problematic when the results in other solvents are also considered. Despite very different dielectric properties in the solvents hexane, dichloromethane, CS_2, chlorobenzene and o-dichlorobenzene, the short wavelength absorption bands of C_{60} and C_{70} undergo only minor changes. The unusual solvatochromism in the solvent series of methyl-substituted benzenes is more likely a result of specific interactions.

The proposed specific interactions are unlikely to be associated with any ground state complexes.[23] The fluorescence spectra of C_{60} and C_{70} in a given solvent with excitation wavelengths in the first and second absorption bands are the same (Fig. 6), indicating that the emissions are from the same excited states. Despite different absorption spectra in the series of methyl-substituted benzenes (Figs. 4 and 5), the observed fluorescence spectra remain essentially unchanged (Figs. 7 and 8).

The fluorescence quantum yields of C_{60} and C_{70} in toluene reported here are larger than those in the literature.[6,8,15,18] The difference is particularly significant for C_{60} simply because the fluorescence of C_{60} extends well beyond 850 nm (Fig. 2). Consequently, the fluorescence quantum yield ratios $\Phi_{F,C70}/\Phi_{F,C60}$ become much smaller (1.8 in toluene) than the widely used literature values (2.5 in toluene). After all, the fluorescence of C_{60} is not so much weaker than that of C_{70}, as generally believed. It appears much weaker in the wavelength region < 850 nm because the fluorescence spectrum of C_{60} is much broader than that of C_{70}.

The fluorescence quantum yields of C_{60} and C_{70} are only weakly solvent dependent. The dependence appears to be random, hardly related to the dielectric properties of the solvents. The quantum yield ratios $\Phi_{F,C70}/\Phi_{F,C60}$ exhibit only small variations from solvent to solvent. For most applications, the average $\Phi_{F,C70}/\Phi_{F,C60}$ value of 1.8 (Table 1) can be used as a solvent independent constant.

For both C_{60} and C_{70} there are significant discrepancies between the electronic transition probabilities obtained experimentally and calculated from observed absorption and fluorescence spectra in terms of the Strickler–Berg equation.[6,8,9,15,19] The experimental fluorescence radiative rate constant $k_{F,e}$ can be obtained from observed fluorescence quantum yield Φ_F and lifetime τ_F,

$$k_{F,e} = \Phi_F/\tau_F \qquad (2)$$

Fluorescence lifetimes of C_{60} ($\sim$ 1.2 ns) and C_{70} ($\sim$ 650 ps) have been reported.[15,18] With the fluorescence quantum yield results shown in Table 1, the $k_{F,e}$ values are 2.7×10^5 s^{-1} for C_{60} and 8.8×10^5 s^{-1} for C_{70} in room temperature toluene. Theoretical fluorescence radiative rate constants $k_{F,c}$ can be calculated from the observed absorption and fluorescence spectra in terms of the Strickler–Berg equation.[19]

$$k_{F,c} = 2.880 \times 10^{-9} n^2 \langle v_F^{-3} \rangle_{AV}^{-1} (g_0/g_e) \int(\varepsilon/v)\mathrm{d}v \qquad (3)$$

$$\langle v_F^{-3} \rangle_{AV}^{-1} = [\int I_F(v)\mathrm{d}v]/[\int v^{-3} I_F(v)\mathrm{d}v] \qquad (4)$$

where g denotes state degeneracies and n represents refractive index of the solvent. By including the entire observed first absorption bands in the calculation of $\int(\varepsilon/v)\mathrm{d}v$ in eqn. (3), the $k_{F,c}$ values for C_{60} and C_{70} in toluene are $3.3 \times 10^6(g_0/g_e)$ s^{-1} and $8.1 \times 10^7(g_0/g_e)$ s^{-1}, respectively. g_0 is unity for both C_{60} and C_{70}. If $g_e = 3$ for C_{60} and $g_e = 1$ for C_{70} are assumed,[4,29-30] the $k_{F,c}$ values are significantly larger than the $k_{F,e}$ values, with $k_{F,c}/k_{F,e}$ ratios of 4 for C_{60} and 92 for C_{70}.

The difference between $k_{F,c}$ and $k_{F,e}$ might be due to an over-estimation of $k_{F,c}$,[9] namely that the observed first absorption bands of C_{60} and C_{70} are probably contributed by more than the lowest excited states of the fullerene molecules.[5,8,9,15] By assuming a mirror image relationship between the fluorescence and absorption associated with the lowest excited state,[6,8,12]
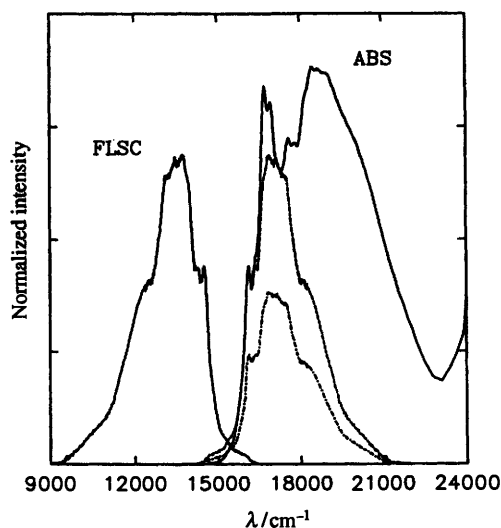

Fig. 10 An estimation of the absorption band due to the lowest excited states of C_{60} by assuming a mirror image relationship with the observed fluorescence spectrum and a correspondence between the absorption peak at 16 120 cm^{-1} and the fluorescence peak at 14 510 cm^{-1} (- - - -). A smaller absorption band (- $\cdot$ - $\cdot$ -) is required for $k_{F,c} = k_{F,e}$ [$g_e = 3$, eqn. (3)].

the term $\int(\varepsilon/v)\mathrm{d}v$ (eqn. 3) corresponding to the transition to the lowest excited singlet state can be calculated. However, the $k_{F,c}$ values thus calculated are still over-estimated.[6,8] With the improved fluorescence spectra and more accurate fluorescence quantum yield results reported here, the issue can be discussed in a more quantitative fashion.

As shown in Fig. 10, the portion of the first absorption band of C_{60} that is mirror image to the fluorescence spectrum can be determined by assuming a correspondence between the absorption peak at 16 120 cm^{-1} and the fluorescence peak at 14 510 cm^{-1}. A calculation based on eqns. (3) and (4) yields a $k_{F,c}$ value of $1.45 \times 10^6/g_e$ s^{-1} for C_{60} in toluene. The $k_{F,c}/k_{F,e}$ ratio becomes $5.4/g_e$, or 1.8 for $g_e = 3$. In order to have a unity $k_{F,c}/k_{F,e}$ ratio, the term $\int(\varepsilon/v)\mathrm{d}v$ (eqn. 3) should be even smaller.

The assumed g_e values for the lowest excited singlet states of C_{60} and C_{70}, which are based largely on theoretical calculations,[29,30] may also be questioned. The degeneracies in the excited states might be more than what have been predicted theoretically. There could even be pseudo-degeneracies such that the emissions are from a set of low-lying excited states of very close energies.[12] With the use of the entire observed first absorption bands in the calculation of $\int(\varepsilon/v)\mathrm{d}v$ [eqn. (3)], the required g_e values for $k_{F,c} = k_{F,e}$ are $\sim$ 12 for C_{60} and $\sim$ 94 for C_{70}.

It is quite possible that both the selection of g_e values and the over-estimation of the term $\int(\varepsilon/v)\mathrm{d}v$ [eqn. (3)] contribute to the observed discrepancies between $k_{F,e}$ and $k_{F,c}$. For C_{60}, other g_e values have been suggested on the basis of theoretical calculations.[4,29,30] If a g_e value of 5 for C_{60} is used, an agreement between $k_{F,e}$ and $k_{F,c}$ can be achieved by considering only the portion of the observed first absorption band that is the mirror image of the fluorescence spectrum in the Strickler–Berg equation calculation. A similar treatment can also be performed for C_{70}, although an estimation of the portion of the observed first absorption band corresponding to low-lying electronic transitions is somewhat more difficult because of a less clear mirror image relationship between the absorption and emission of C_{70}.

The fluorescence quantum yields of both C_{60} and C_{70} in a 77 K glass reported in the literature[11] are much smaller than those in room temperature solutions. Such substantial differences may not simply be attributable to experimental factors. However, at ambient temperatures (20–100 °C), the observed fluorescence quantum yields of C_{70} remain essentially un-

changed. The issue will be further addressed by a quantitative determination of fluorescence quantum yields of the fullerenes as a function of temperature from ambient to 77 K.

References

1 H. W. Kroto, A. W. Allaf and S. P. Balm, *Chem. Rev.*, 1991, **91**, 1213.
2 C. S. Foote, in *Topics in Current Chemistry: Electron Transfer I*, ed. J. Mattay, Springer-Verlag, Berlin, 1994, p. 347.
3 Y.-P. Sun, in *Fullerenes, Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, eds. R. S. Ruoff and K. M. Kadish. The Electrochemical Society Inc., 1995, p. 510.
4 (a) F. Negri, G. Orlandi and F. Zerbetto, *Chem. Phys. Lett.*, 1988, **144**, 31; (b) F. Negri, G. Orlandi and F. Zerbetto, *J. Chem. Phys.*, 1992, **97**, 6496.
5 J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez and R. B. Whetten, *J. Phys. Chem.*, 1991, **95**, 11.
6 Y.-P. Sun, P. Wang and N. B. Hamilton, *J. Am. Chem. Soc.*, 1993, **115**, 6378.
7 J. W. Arbogast and C. S. Foote, *J. Am. Chem. Soc.*, 1991, **113**, 8886.
8 Y.-P. Sun and C. E. Bunker, *J. Phys. Chem.*, 1993, **97**, 6770.
9 R. J. Sension, C. M. Phillips, A. Z. Szarka, W. J. Romanow, A. R. McGhie, J. P. McCauley, Jr., A. B. Smith and R. M. Hochstrasser, *J. Phys. Chem.*, 1991, **69**, 6075.
10 (a) M. R. Wasielewski, M. P. O'Neil, K. R. Lykke, M. J. Pellin and D. M. Gruen, *J. Am. Chem. Soc.*, 1991, **113**, 2774; (b) T. W. Ebbesen, K. Tanigaki and S. Kuroshima, *Chem. Phys. Lett.*, 1991, **181**, 501; (c) K. Tanigaki, T. W. Ebbesen and S. Kuroshima, *Chem. Phys. Lett.*, 1991, **185**, 189.
11 Y. Wang, *J. Phys. Chem.*, 1992, **96**, 764.
12 D. J. van den Heuvel, G. J. B. van den Berg, E. J. J. Groenen and J. Schmidt, *J. Phys. Chem.*, 1995, **99**, 11644.
13 R. M. Williams and J. W. Verhoeven, *Chem. Phys. Lett.*, 1992, **194**, 446.
14 S. P. Sibley, S. M. Argentine and A. H. Francis, *Chem. Phys. Lett.*, 1992, **188**, 187.
15 D. Kim, M. Lee, Y. D. Suh and S. K. Kim, *J. Am. Chem. Soc.*, 1992, **114**, 4429.
16 (a) J. Catalán and J. Elguero, *J. Am. Chem. Soc.*, 1993, **115**, 9249; (b) S.-K. Lin, L.-L. Shiu, K. M. Chien, T.-Y. Luh and T.-I. Lin, *J. Phys. Chem.*, 1995, **99**, 105.
17 Y.-P. Sun, B. Ma and C. E. Bunker, *J. Chem. Soc., Chem. Commun.*, 1994, 2099.
18 R. M. Williams, J. M. Zwier and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1995, **117**, 4093.
19 S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 1962, **37**, 814.
20 G. E. Lawson, A. Kitaygorodskiy, B. Ma, C. E. Bunker and Y.-P. Sun, *J. Chem. Soc., Chem. Commun.*, 1995, 2225.
21 (a) C. E. Bunker, G. E. Lawson and Y.-P. Sun, *Macromolecules*, 1995, **28**, 3744; (b) B. Ma, G. E. Lawson, C. E. Bunker, A. Kitaygorodskiy and Y.-P. Sun, *Chem. Phys. Lett.*, 1995, **247**, 51.
22 S. E. Webber, personal communication.
23 J. Catalán, J. L. Saiz, J. L. Laynez, N. Jagerovic and J. Elguero, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 105.
24 W. A. Scrivens and J. M. Tour, *J. Chem. Soc., Chem. Commun.*, 1993, 1207.
25 T. Karstens and K. Kobs, *J. Phys. Chem.*, 1980, **84**, 14.
26 C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968.
27 (a) B. S. Hudson, B. E. Kohler and K. Schulten, in *Excited States*, ed. E. C. Lim, Academic Press, New York, 1982, vol. 6, p. 1; (b) J. Saltiel and Y.-P. Sun, in *Photochromism, Molecules and Systems*, eds. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, p. 64; (c) B. E. Kohler, *Chem. Rev.*, 1993, **93**, 41.
28 (a) J. R. Andrews and B. S. Hudson, *J. Chem. Phys.*, 1978, **68**, 4587; (b) J. B. Birks, G. N. R. Tripathi and M. D. Lumb, *Chem. Phys.*, 1978, **33**, 185; (c) L. A. Sklar, B. S. Hudson, M. Petersen and J. Diamond, *Biochem.*, 1977, **16**, 813.
29 (a) R. C. Haddon, L. E. Brus and K. Raghavachari, *Chem. Phys. Lett.*, 1986, **125**, 459; (b) M. Kataoka and T. Nakajima, *Tetrahedron*, 1986, **42**, 6437.
30 (a) P. W. Fowler and J. Woolrich, *Chem. Phys. Lett.*, 1986, **127**, 78; (b) P. W. Fowler, P. Lazzeretti, M. Malagoli and R. Zanasi, *Chem. Phys. Lett.*, 1991, **179**, 174.