

Photoluminescence and fluorescence quenchings of C₆₀-pyrrolidine derivatives at room temperature

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Received 28 September 1995; revised 8 December 1995; accepted 17 April 1996

Abstract

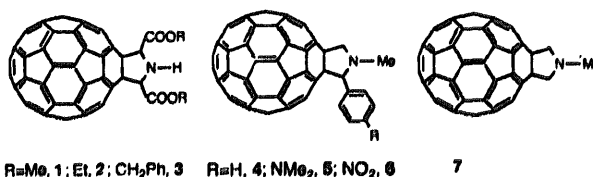
Weak room-temperature photoluminescence of seven different C₆₀-pyrrolidine derivatives; namely C₆₀C₆H₉NO₄ (1), C₆₀C₈H₁₃NO₄ (2), C₆₀C₁₈H₁₇NO₄ (3), C₆₀C₉H₁₁N (4), C₆₀C₁₁H₁₆N₂ (5), C₆₀C₉H₁₀NO₂ (6) and C₆₀C₃H₇N (7), were observed from their CHCl₃ or CS₂ solutions. The fluorescence intensity of the derivatives are three fold to four fold stronger than that of pure C₆₀. The singlet energies were estimated to be about 4–5 kcal/mol lower than that of their parent molecule C₆₀. Their fluorescence quenchings by concentration and by the aromatic electron donor *N,N*-dimethyl aniline (DMA) were investigated. Their fluorescence lifetimes were determined to be in the range 1.2–2.3 ns by the frequency domain method. The electron-donor-substituted groups can greatly decrease the fluorescence quenching ability of DMA.

Keywords: Fullerene; Pyrrolidine; Photoluminescence; Fluorescence; Quenching

1. Introduction

The discovery of an efficient isolation and purification method for fullerenes [1] greatly stimulated studies of their special chemical and physical properties [2–4]. Among these, the fluorescence properties of fullerenes and their derivatives are of great interest to chemists and spectroscopists [5–33]. In spite of extensive investigation, earlier studies have failed to detect their fluorescence at room temperature, presumably because of the very low fluorescence quantum yield. It is only recently that room-temperature fluorescence from solutions of C₆₀ and C₇₀ have been observed [16–18]. Contrary to the early results [17], recent studies indicate that the quantum yields of both C₆₀ and C₇₀ are excitation wavelength independent and thus obey Kasha's rule [22,23,28]. However, studies of the fluorescence properties of isomerically pure fullerene derivatives are still relatively rare. Only very recently have a few studies of the photophysical properties of C₆₀ derivatives been reported [30–33]. For example, Foote and coworkers [30] reported 1,9-(4-hydroxycyclohexano) buckminsterfullerene, Williams

et al. [33] reported a bridged C₆₀-aniline derivative and Liddell et al. [3] reported a porphyrin-C₆₀ dyad [31]. The intramolecular electron transfer quenching of the derivatives have been reported [31,33]. However, the substitution effect on the intermolecular fluorescence quenching by electron donors has not been investigated. To study the substitution effect to the fluorescence and quenching property, in this paper, seven C₆₀-pyrrolidines containing different substituents namely: C₆₀C₆H₉NO₄ (1), C₆₀C₈H₁₃NO₄ (2), C₆₀C₁₈H₁₇NO₄ (3), C₆₀C₉H₁₁N (4), C₆₀C₁₁H₁₆N₂ (5), C₆₀C₉H₁₀NO₂ (6) and C₆₀C₃H₇N (7), are employed (Scheme 1). Their room-temperature photoluminescence (PL) as well as fluorescence lifetimes were investigated. We also report the first observations of fluorescence quenching by concentration and by the electron donor: *N,N*-dimethyl aniline (DMA).



Scheme 1. Molecular structure of the seven C₆₀-pyrrolidine derivatives employed.

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2. Experimental details

2.1. Materials and synthesis

C_{60} (purity greater than 99%) was prepared by contact arc and purified through an adsorption method [34]. Sarcosine (purity greater than 99%) was bought from Fluka. Glycine ester hydrochlorides were prepared by the conventional method of esterification of glycine under a HCl atmosphere. Formaldehyde, 4-*N,N*-dimethylaminobenzaldehyde and 4-nitrobenzaldehyde were all A.R. grade from Beijing Chemical Factory (Beijing, People's Republic of China). The synthesis of the seven C_{60} -pyrrolidine derivatives were as follows.

Compounds 1–3 were prepared by the photochemical reaction between C_{60} and glycine esters [35,36]. A brief account of the preparation of 3 is as follows. To a solution of C_{60} (72 mg, 0.100 mmol) in toluene, a solution of glycine benzyl ester hydrochloride (2.00 mmol) and NaOH (2.00 mmol) in acetone/water was added. The mixture was irradiated by a high pressure luminescent bulb for 2 h. The color of the reaction mixture gradually turned from purple to reddish brown; then the solvent was removed on a Rotavapor. The residue was chromatographed on a silica gel column and finally recrystallized in CH_2Cl_2 petroleum ether to obtain 3 as irregular black crystals, (yield, about 40% based on C_{60} conversion).

Elemental anal. Found: C, 89.42, H, 1.77; N, 1.15. $C_{60}(C_{18}H_{17}NO_4) \cdot H_2O$ calc.: C, 89.23; H, 1.81; N, 1.33; 1H nucleus magnetic resonance (NMR) (400 MHz $CDCl_3$): δ 5.28 (d, 1H), 5.39 (d, 1H), 5.52 (1H) 7.20–7.26 (m, 2.5H), 7.27–7.30 (m, 2.5H) ppm. ^{13}C NMR (100.6 MHz $CDCl_3$): δ 168.62 (COO), 152.06(2), 149.42(2), 147.04(2), 146.32(2), 146.29(2), 146.26(2), 145.96(2), 145.91(2), 145.52(2), 145.48(2), 145.34(2), 145.28(2), 145.17(2), 144.96(2), 144.29(2), 144.17(2), 142.90(2), 142.62(4), 142.23(2), 142.15(2), 142.05(2), 141.96(2), 141.83(2), 141.55(2), 139.56(2), 136.63(2), 135.48(2), 134.53(2), 129.43 (Ph, 4), 128.94 (Ph, 2), 128.66 (Ph, 4), 77.12(sp^3 , 2), 73.14 (2CH), 68.12 (2 CH_2) ppm. DEPT spectroscopy ($CDCl_3$): 68.05 (CH_2), 73.14 (CH), 128.66 (Ph, CH), 128.94 (Ph, CH), 129.43 (Ph, CH). FD mass spectroscopy (MS): M/Z 1032 (33%, $M^+ + 1$), 721 (100%, $C_{60}^+ + H$). UV-visible (CH_2Cl_2): Δ 258, 312, 428 nm. Fourier transform IR (microscopy): 3295 ($\nu(N-H)$), 2973, 2955, 2928, 1737 ($\nu(C=O)$), 1473, 1457, 1438, 1429, 1383, 1371, 1329, 1294, 1263, 1248, 1233, 1217, 1196, 1150, 1123, 1095, 1072, 1029, 849, 821, 804, 795, 782, 760, 744, 734, 721, 674 cm^{-1} .

Compounds 4–7 were prepared by methods similar to those of Prato and coworkers [37]. A brief description of the synthesis of 6 is as follows [38]. To a solution of C_{60} (72 mg, 0.100 mmol) in toluene was added 4-nitrobenzaldehyde (30 mg, 0.200 mmol) and sarcosine (36 mg, 0.40 mmol). The mixture was refluxed for 1 h and its color turned from purple to reddish brown. The solvent was removed on a Rotavapor and the residue was chromatographed on a silica gel column.

Finally it was recrystallized in CS_2 -petroleum ether to obtain 6 as irregular black crystals, (yield about 90% based on C_{60} conversion).

Spectroscopic data for 6. 1H NMR (400 MHz CS_2-CDCl_3): δ 8.14 (b, 2H), 8.11 (b, 2H), 4.91 (s, 1H), 4.85 (d, 1H), 4.18 (d, 1H), 2.69 (s, 3H) ppm. ^{13}C NMR (100.6 MHz, CS_2-CDCl_3): δ 155.87, 153.67, 152.62, 152.10, 148.28 (Ph- NO_2), 147.66, 147.64, 146.68, 146.65, 146.58(2), 146.52, 146.49, 146.46, 146.32(2), 146.03, 146.00, 145.78, 145.74, 145.71(2), 145.68, 145.60, 145.57(2), 145.54, 145.06, 144.89, 144.76, 144.66, 144.36(2), 143.55, 143.45, 143.42, 143.13, 143.04, 143.01, 142.96, 142.56, 142.49(2), 142.40(2), 142.29(2), 142.22, 142.10, 142.07, 141.94, 140.68, 140.42, 139.99, 137.47, 136.67, 136.44, 135.92, 130.17 (Ph, 2), 128.00 (Ph), 124.14 (Ph, 2), 82.85 (CH), 76.96 (sp^3), 70.27 (CH_2), 69.22 (sp^3), 40.20 (CH_3) ppm. FD MS: m/z 898 (M^+ , 100%), 720 (C_{60}^+ , 64%).

2.2. Spectroscopic measurements

The absorption spectra of the derivatives in CH_2Cl_2 solutions were measured on a Shimadzu UV 3100 spectrophotometer. The photoluminescence (PL) spectra of the derivatives in $CHCl_3$ (1–3) or CS_2 (C_{60} and 4–7) solutions were measured at room temperature. They were excited by an unfocused Ar ion laser beam ($\lambda = 488.0$ nm) at an incident power density of about 1.5 $W\ cm^{-2}$. The PL of the sample was obtained with a HRD-1 mono chromometer system; then acquired from a 5101 lock-in amplifier which was connected to a S-1 photomultiplier detector cooled at -40 $^{\circ}C$ [39,40]. The PL excitation and emission spectra were recorded on a Hitachi 850 fluorescence spectrophotometer, using a 430 nm excitation cut-off filter. Excitation and emission bandwidths of 10 nm were employed and the spectra were corrected for non-linear instrumental response and blank solvents [41,42].

The fluorescence lifetime determination was performed on a SLM 48000 multi-frequency phase fluorometer, using the frequency-domain method with glycogen as the reference. They were measured in $CHCl_3$ (1–3) or CS_2 (4–7) solutions. A 640 nm long-pass filter was placed in the emission path to eliminate the interference from the solvent and stray light. The modulated frequency used ranges from 30 to 95 MHz. At each frequency both the phase shift and the relative modulation were measured six times, and averaged values were used to minimize the experimental error. A total of ten different frequencies was used, and the fluorescence lifetime was determined by using the least-square analysis method as that in Refs. [40,43].

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of the derivatives are similar and typical examples are shown in Fig. 1. Their spectra in the UV

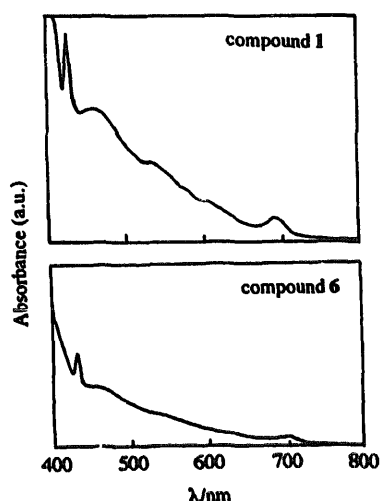


Fig. 1. Absorption spectra (visible region) of 1 and 4 in CH_2Cl_2 .

region are similar to those of C_{60} . Two strong bands at around 255 and 308 nm are observed. The spectra are distinctly different from that of C_{60} in the visible region. For example, in the 400–450 nm region, all the derivatives have a relatively sharp absorption peak at around 430 nm with a distinct shoulder around 410 nm (Table 1), while C_{60} has two small peaks. These bands are assigned to be the $\text{S}_0 \rightarrow \text{S}_n$ transitions [32].

Another noticeable difference between C_{60} and the derivatives is in the 450–800 nm region. In this region, the parent C_{60} has distinct fine structures: multiple pairs of peak-shoulders appear at 537–541, 560–569, 592–598 and 621 nm. However, these bands are obscured in the derivatives; also the derivatives exhibit several new bands in the 450–750 nm region. These bands are not well resolved, but several bands at around 460, 540, 640 and 710 nm can be distinguished. The band at around 460 nm in 1–3 is relatively stronger than that in 4–7, maybe owing to the presence of carbonyl groups. The onset absorptions red-shift significantly compared with C_{60} (about 635 nm for C_{60} , 720 nm for 1–3 and 735 nm for 4–7) with the first small evident band at around 690 nm (1–3) or 700–710 nm (4–7) as given in Table 1. The difference in the spectra of the derivatives may be due to the different electron-withdrawing properties of the substituents. From group symmetry consideration, among the various electronic states, only transitions from the $^1\text{A}_g$ group state to the $^1\text{T}_{1u}$ states in C_{60} are optically allowed. In the 450–800 nm region,

the broad absorption band corresponds to the forbidden states of the $\text{S}_0 \rightarrow \text{S}_1$ transition. The observed multiple vibrational structural features are the results of Herzberg-Teller coupling. The modification to C_{60} with the substituted pyrrolidine group reduces its symmetry from I_h to C_{2v} , C_2 or C_1 . Judging from the small absorption intensity in the 450–800 nm region from C_{60} and the derivatives, we may conclude that there is no conversion of the electronic forbidden to allowed states after chemical modification [32].

3.2. Room-temperature photoluminescence

The fluorescence spectra are almost the same under different excitation wavelengths (e.g. 430, 450, 550 and 580 nm). Both the peak position and the shape of the spectra are almost identical. This indicates that they may contain only one fluorescent chromophore, which is confirmed by the fluorescence lifetime determination.

The room-temperature PL spectra of 3 in CHCl_3 and C_{60} and of 6 and 7 in CS_2 excited by an Ar ion laser beam are shown in Fig. 2. The first emission peak of C_{60} is at 656 nm, followed by several weak multiple peaks. Two major bands at around 700 and 750 nm are observed, similar to that of C_{60} in methylcyclohexane solution [32]. The fluorescence spectrum of C_{60} is in good agreement with the earlier studies [25,32].

The emission spectra of the derivatives all exhibit two major bands in the near-IR region with positions that differ slightly from sample to sample. A weak broad shoulder at around 900 nm can also be observed. The spectra are not so well resolved compared with that reported by Williams et al. [33], owing to the higher concentration of the solution and wider fluorescence emission bandwidth employed. Some fluorescence data are summarized in Table 2. Contrary to that of C_{60} , the first band is the strongest of the three and the three bands are separated by about 1300 cm^{-1} . Because of the width of the bands, the uncertainty is greater than $\pm 100 \text{ cm}^{-1}$. This is assigned to be the totally symmetric pentagonal pinch mode which has been observed in the Raman spectrum as a strong peak at 1463 cm^{-1} in 1. Both the peak position and the relative intensity of the two bands are quite different from those of the C_{60} solution, but rather close to those of a C_{60} film deposited on a CaF_2 plate at 20 K [6]. Using the intersection of absorption and emission maxima, their singlet

Table 1
The absorption characteristics of the C_{60} -pyrrolidine derivatives in CH_2Cl_2

Compound	Absorption extrema (visible region) (nm)										Reference
1	410	428	460	533	627	688					This work
2	409	428	458	535	628	690					This work
3	410	427	459	535	629	690					This work
4	404	430	457	539	609	638	703				This work
5	404	432	459	541	612	638	707				This work
6	404	430	455	535	608	636	699				This work
7	402	428	470	537	611	635	670	690	704		[35]
C_{60}	404	422	428	537	541	560	569	592	598	621	[31]

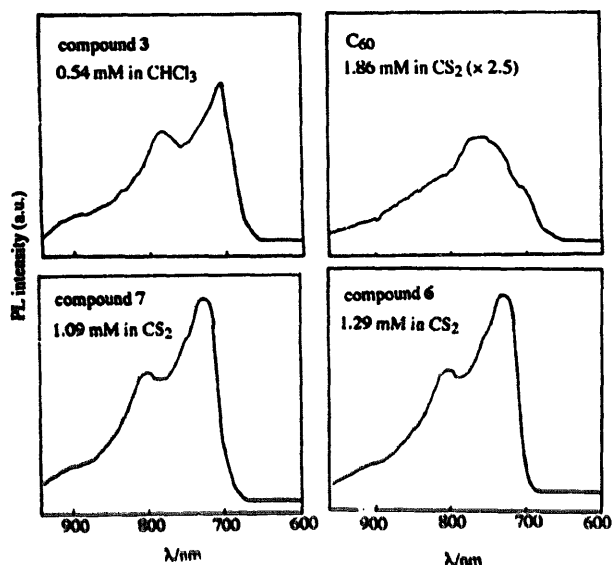


Fig. 2. The PL spectra of **3** in CHCl_3 and of C_{60} , **6** and **7** in CS_2 solution excited by an Arion laser beam ($\lambda = 488.0 \text{ nm}$).

energies can be estimated and are given in Table 2. We note that the singlet energies of **1–3** are about 1 kcal mol^{-1} higher than those of **4–7**. However, they are considerably lower than that of C_{60} and almost the same as that of 1,9-(4-hydroxycyclohexano) buckminsterfullerene ($40.2 \text{ kcal mol}^{-1}$) [30]. This similarity between the derivatives is not surprising considering that they are all dihydrofullerene derivatives at the 6,6 junction. It is also noteworthy that singlet energy of the strong electron acceptor substituted derivative (**6**) is considerably higher than that of the electron-donor-substituted derivative (**5**). The difference is attributed to the different electron donor abilities of the substituents.

It is very interesting that the derivatives exhibit a stronger fluorescence intensity than that of C_{60} . As shown in Fig. 2, the fluorescence intensity of the derivatives are almost four fold to five fold stronger than that of C_{60} under the same concentration. This indicates that the lowering of the sym-

metry of C_{60} by derivatization can substantially increase the fluorescence intensity (and thus the quantum yield) of the fullerene compound [32,33].

3.3. Fluorescence lifetime

By measuring the phase shift and the relative modulation of the samples at different frequency and using the methods in [4C,43], least-square analysis of the data indicate that all the derivatives contain only one fluorescence lifetime, which are given in Table 2. The deviation ($\pm 0.3 \text{ ns}$) is relatively large owing to the very low quantum yield (e.g. very weak fluorescence intensity) of the derivatives. The weaker fluorescence intensity of C_{60} makes it almost impossible to determine its fluorescence lifetime, and the typical literature value of 1.2 ns is listed. As given in Table 2, the lifetime of the derivative varies slightly from sample to sample; the lifetime of **1** is almost the same as that of C_{60} , but other derivatives exhibit a slightly longer lifetime, maybe owing to the different electron-acceptor effects of the substituents.

3.4. Fluorescence quenching by concentration

The relative PL intensities of the derivatives are quite different at different concentrations and typical examples of **1** and **4** are shown in Fig. 3(a). All the derivatives exhibit their strongest PL intensity at around the concentration 1–1.5 mM. In the low concentration region, the PL intensity increases with increasing concentration; however, it decreases with increasing concentration in the high concentration region. When the relative PL intensity per unit concentration of the derivative (equal to the PL intensity divided by its concentration) is plotted against the concentration, a decreased relative PL intensity with concentration is obtained (Fig. 3(b)). This indicates that the fluorescence intensity of the derivatives is effectively quenched by concentration. The fluorescence of the other derivatives exhibit similar performance.

Table 2
The photoluminescence parameters of C_{60} and the C_{60} -pyrrolidine derivatives

Compound	Emission bands (nm)										Singlet energy (kcal mol ⁻¹)	Lifetime (ns)	Reference
C_{60}	627	659	677	689	700	714	727	737	762	46.1	1.2	[30,31]	
C_{60}	656	675		686	700		760			–	–	This work	
1	712			780			880			40.9	1.2	This work	
2	712			780			882			40.8	1.5	This work	
3	712			780			880			40.8	1.6	This work	
4	728			804			905			40.0	1.9	This work	
5	730			807			910			39.8	2.3	This work	
5	706	716		741			786			40.5	1.28	[33] ^a	
6	723			797			900			40.2	1.7	This work	
7	728			802			902			40.0	1.7	This work	

^a The fluorescence lifetime of **5** was also studied by Williams et al. [33]; their results show that its fluorescence lifetime in methylcyclohexane is $1.28 \pm 0.04 \text{ ns}$. Our value is slightly longer ($2.3 \pm 0.3 \text{ ns}$), maybe owing to the larger deviation in our data and different experimental conditions. We also found that the wavelength of the emission bands is dependent on concentration. At lower concentrations, the wavelength of the emission bands is shifted to the blue. A concentration of 10^{-5} M was used in [33]; the concentration in this work is 10^{-3} M .

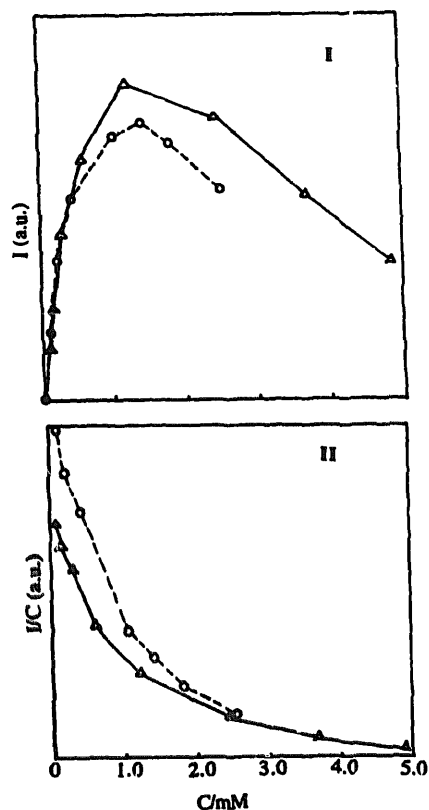


Fig. 3. Plot of the PL intensity of 1 in CHCl_3 (—) and 4 in CS_2 (---) against the concentration (a.u., arbitrary units): (a) PL intensity I vs. concentration C plot; (b) relative PL intensity per unit concentration, I/C vs. concentration plot.

The fluorescence quenching by concentration may be due to the intermolecular electronic transfer between the derivatives and the absorption of the solution to the excitation light. This is the first report on fluorescence quenching by concentration for fullerenes and their derivatives.

3.5. Fluorescence quenching by *N,N*-dimethyl aniline

Fullerenes are good electron acceptors; they could interact with electron donors through a charge-transfer interaction and form stable charge-transfer compounds. Their fluorescence quenching by electron donors, such as 1,2,4-trimethoxy benzene, *N,N*-dimethyl aniline, *N,N*-diethyl aniline and *N,N*-dimethyl-*p*-toluidine, have been reported [17,18,24]. However, no such study on fullerene derivatives has ever been reported. The fluorescence quenching patterns of the seven derivatives by DMA are different from each other, and they can be classified into three types. In the first (1–3), the PL is effectively quenched by DMA, and the pattern of spectrum shows hardly any change. In the second (4, 5, and 7), the PL cannot be quenched by DMA and the pattern of fluorescence also shows hardly any change. In the third (6), which is quite different from the first and second types, its PL could not be quenched in the low DMA concentration ($[\text{DMA}]$) region just like the second type; however, it can be quenched in the high $[\text{DMA}]$ region.

The different fluorescence quenching behaviors are due to the different electron withdrawing property of the substituents in the derivatives. In 1–3 or 6, the pyrrolidine ring is connected with strong electron-withdrawing groups (either carbonyl or 4-nitrophenyl) and so their PL could still be quenched by DMA, whereas the substituents in 4, 5 and 7 are either electron donating or very weak electron withdrawing. This is evident from their cyclic voltammetry data. Cyclic voltammetry of 1, 4 and C_{60} in CH_2Cl_2 shows the first reduction waves at -0.61 V, -0.65 V and -0.53 V, respectively and the corresponding oxidation waves at -0.53 V, -0.58 V and -0.46 V vs. Ag/AgCl. The first midpoint reduction potential of 1, 4 and C_{60} is thus estimated to be -0.57 V, -0.62 V and -0.50 V vs. Ag/AgCl. Derivatization of C_{60} reduces its electron reduction potential (electron-withdrawing ability), by 0.07 V in 1 and 0.12 V in 4; thus the fluorescence quenching by electron donor becomes more difficult. The higher the reduction potential, the more easily the quenching occurs.

The ratio of the fluorescence intensity I^0 without DMA to the fluorescence intensity I with DMA is plotted as a function of $[\text{DMA}]$ and typical examples of 3, 5 and 6 are shown in Fig. 4. According to the Stern-Volmer equation, a linear relationship between the quenching ratio I^0/I and quencher concentration $[\text{DMA}]$ is expected:

$$\frac{I^0}{I} = 1 + K_{\text{SV}}[\text{DMA}] \quad (1)$$

where K_{SV} is the Stern-Volmer constant and $[\text{DMA}]$ is the molar concentration of DMA. An estimate of the Stern-Vol-

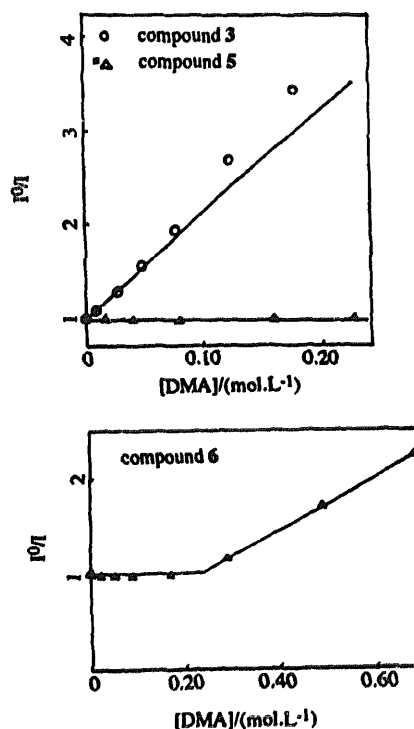


Fig. 4. Plot of the fluorescence quenching ratio I^0/I of 3 in CHCl_3 , and of 5 and 6 in CS_2 against the DMA concentration.

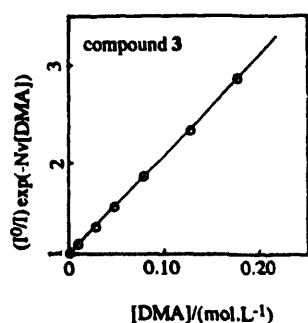


Fig. 5. Plot of the treated fluorescence quenching of 3 against the DMA concentration in-room temperature CHCl_3 based on a model in which both static and dynamic quenching are considered.

mer constant can be made by considering the data at low $[\text{DMA}]$ ($<0.1 \text{ M}$) [24], and K_{SV} values of 13.0 M^{-1} , 13.2 M^{-1} and 12.0 M^{-1} for 1, 2, and 3 respectively are obtained. The values of the three derivatives are almost the same because of their similar molecular structures, which differ only slightly in the alkyl ester group. The same estimate for 6 is also made by considering the data in the high $[\text{DMA}]$ region, and a K_{SV} value of 3.5 M^{-1} is obtained. Thus we can see that the K_{SV} values of the derivatives are much smaller than that of C_{60} in toluene (24 M^{-1}) solution [24], indicating that the electron-withdrawing ability of C_{60} is significantly reduced by derivatization.

As shown in Fig. 4, an upward deviation for 3 from the Stern-Volmer equation is observed, especially in the high $[\text{DMA}]$ region. The deviation is attributed to static fluorescence quenching, and the result can be treated by the following equation:

$$\frac{I_0}{I} = (1 + K_{\text{SV}}[\text{DMA}]) \exp(Nv[\text{DMA}]) \quad (2)$$

where N is Avogadro's constant and v is the static quenching volume; least-squares fits based on Eq. (2) yield K_{SV} and v values of 11.5 M^{-1} and 2000 \AA^3 for 1, 11.5 M^{-1} and 1800 \AA^3 for 2, and 10.0 M^{-1} and 1700 \AA^3 for 3, respectively (a typical example for 3 is shown in Fig. 5). The static quenching volumes are much smaller than that of C_{60} (5300 \AA^3) or C_{70} (5800 \AA^3), but their treated K_{SV} values are highly comparable with that of C_{60} (13 M^{-1}) or C_{70} (8.1 M^{-1}). Assuming a spherical static fluorescence quenching volume, we evaluated the static fluorescence quenching radii of 7.8 \AA , 7.5 \AA and 7.4 \AA for 1, 2 and 3 respectively. The static fluorescence quenching radii of the three derivatives are almost the same and the values are much smaller than those of pure fullerenes (10.8 \AA for C_{60}) and 11.1 \AA for C_{70}), indicating that the chemical derivatization of the C_{60} molecule greatly reduces its electron-withdrawing ability; thus the driving force for charge-transfer interaction between the derivative and the electron donor DMA molecules is greatly decreased which resulted in a much smaller fluorescence quenching radius.

The Stern-Volmer constant K_{SV} is expressed as [40]

$$K_{\text{SV}} = K_{\text{q}}\tau \quad (3)$$

where τ is the fluorescence lifetime of the molecules being quenched and K_{q} is the diffusion-controlled quenching rate constant. Using the fluorescence lifetime value described above (1.2 ns for 1, 1.5 ns for 2 and 1.6 ns for 3), we calculated the K_{q} values to be $0.96 \times 10^{10} \text{ M}^{-1} \text{ S}^{-1}$ for 1, $0.77 \times 10^{10} \text{ M}^{-1} \text{ S}^{-1}$ for 2 and $0.63 \times 10^{10} \text{ M}^{-1} \text{ S}^{-1}$ for 3. The K_{q} values are smaller than the reported values for C_{60} and C_{70} ($1.2 \times 10^{10} \text{ M}^{-1} \text{ S}^{-1}$); however, they are still typical for the diffusion-controlled fluorescence quenching rate constant [43].

4. Conclusion

In summary, we prepared several new C_{60} -pyrrolidines and studied their PL at room temperature. Derivatization of fullerene breaks its symmetry and changes some forbidden vibronic states to allowed symmetry with increasing probability. Increased fluorescence intensity (quantum yield) was observed by chemical modification. Singlet energy is decreased by about 4–5 kcal mol $^{-1}$ by derivatization. The fluorescence can be effectively quenched by the concentration of the derivatives. The fluorescence lifetimes of the C_{60} -pyrrolidine derivatives are slightly longer than the parent C_{60} molecules. The electron-withdrawing ability of the C_{60} skeleton is significantly reduced by derivatization. As a result the fluorescence quenching of the C_{60} derivatives by electron donors are greatly decreased or cannot be observed.

Acknowledgements

We thank Professor B.R. Zhang from Physics Department of Peking University for her help in measuring the fluorescence spectra. The financial support from Climbing Program (A National Fundamental Research Key Project of China) and the National Natural Science Foundation of China are greatly acknowledged.

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