Room-Temperature Photoluminescence of a C_{60} Derivative

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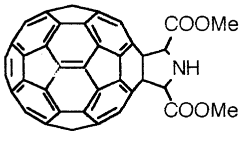
The first observations of weak room-temperature photoluminescence of a new C_{60} derivative: $C_{60}(NH(CHCOOMe)_2)$ (**1**) and its fluorescence quenching by concentration and N,N-dimethyl aniline in $CHCl_3$ solution are reported. Its singlet energy and fluorescence lifetime were estimated to be 40.9 kcal/mol and 1.2 ± 0.3 ns, respectively.

Recent studies show that C_{60} is weakly photoluminescent in the near infrared region and this has received much attention.[1-12] But the results are quite different. Typically, its fluorescence lifetime is around 1.2 ns with fluorescence quantum yield around 2×10^{-4}. However, studies on pure C_{60} derivatives are still rare and the effect of substituent on its photoluminescence remains to be well defined.[13] Here we report the first observations of room-temperature photoluminescence (PL) of a new C_{60} derivative (**1**), as well as its fluorescence lifetime and fluorescence quenching by concentration and N,N-dimethyl aniline (DMA).



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The compound **1** was prepared by the photochemical reaction between C_{60} and glycine methyl ester in toluene/methanol, separated by column chromatography on silica gel. Spectroscopic data indicate the molecular structure as depicted.[14]

Unlike C_{60}, which has its longest wavelength absorption at 620 nm, compound **1** in $CHCl_3$ has a weak absorption maximum at 692 nm (ε~400 $M^{-1}cm^{-1}$), typical for C_{60} monoadduct.[13] The PL was measured at room temperature in $CHCl_3$ solution excited by an unfocused Ar ion laser beam (λ=488.0 nm) and recorded by a S-1 photomultiplier. The PL of **1** exhibits two major bands at 708 and 784 nm with a broad weak shoulder around 880 nm (Figure 1a). The first band is the strongest of the three and the three bands are separated by about 1400 nm^{-1}. Because of the width of the bands, the uncertainty is greater than ±100 cm^{-1}. This progression is assigned to the totally symmetric pentagonal pinch mode which has been observed in the Raman spectra at 1463 cm^{-1}. Both the peak position and the relative intensity of the two bands are quite different from that of C_{60} in room temperature solution[6,11] and polycrystalline C_{60} solid at 5K,[12] but rather close to that of C_{60} film on CaF_2 at 20 K[1]. Using the intersection of the absorption and emission maxima,[13] the singlet energy is estimated to be 40.9 kcal mol^{-1}, about 5 kcal mol^{-1} lower than that of C_{60} and almost the same as the value of another C_{60} derivative 1,9-(4-hydroxycyclohexano)buckminsterfullerene[60] (40.2 kcal mol^{-1}).[13] This similarity between the two fullerene derivatives is not surprising considering that they are both dihydrofullerene derivatives at the 6,6-junction.

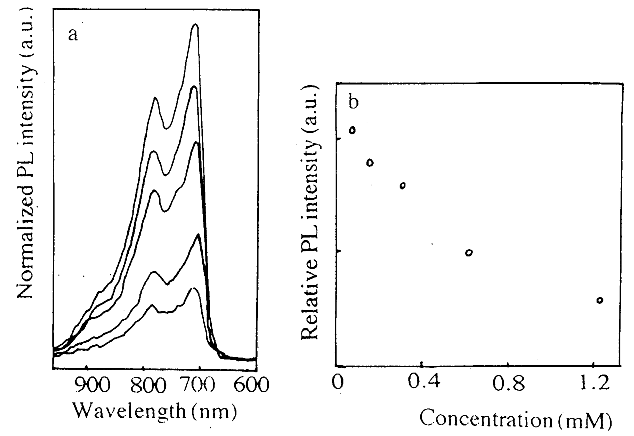

Figure 1. a) The PL spectra of **1** at different concentration (from top to bottom, 1.23, 0.61, 0.31, 0.16, 0.077 mM); b) Dependence of the relative PL intensity per molecule of **1** on concentration.

As shown in Figure 1a, the PL intensity increases slowly with the concentration in the high concentration region. However, If the relative PL intensity per molecule of **1** is plotted against the concentration, a decreased relative PL intensity with the concentration is observed (Figure 1b), indicating that the PL of **1** is quenched by the concentration.

The fluorescence lifetime was determined on a SLM 48000 Multi-Frequency Phase Fluorometer, using the frequency-domain method with glycogen as the reference.[15] At each frequency both the phase shift and the relative modulation value were measured 6 times and the averaged values were used to evaluate the fluorescence lifetime in order to minimize the experimental error. A total of 10 different frequencies ranging from 30 MHz to 95 MHz were used, and the final fluorescence lifetime was determined by least-square analysis of the 10 data which gave the minimum deviation between the experimental and theoretical values.

Because of the time lag between absorption and emission, the emission is delayed to the modulated excitation. The basic equations in frequency-domain method to determine the fluorescence lifetime are as follows[15]:

$$\tau_\phi = \tan\phi / \omega \qquad \tau_M = (1/\omega)([1/D^2]-1)^{0.5} \qquad (1)$$

where ϕ is the phase shift caused by the lifetime τ_ϕ of the sample, ω is the circular frequency of excitation, D is the ratio of the relative modulation of the sample and the glycogen reference. By measuring the phase shift and the relative modulation of the sample at different frequency and by using the method described above, least-square analysis of the data yields the lifetime to be 1.2 ± 0.3 ns. The lifetime is about the same as the previously reported value for C_{60}[6], indicating that the substituted glycine ester group does not affect the lifetime of C_{60} significantly. This phenominum is also observed by T.I. Lin et al.[16]

Fullerenes are good electron acceptors, they could interact with electron donors through charge-transfer interaction and their fluorescence could be quenched by electron donors. However,

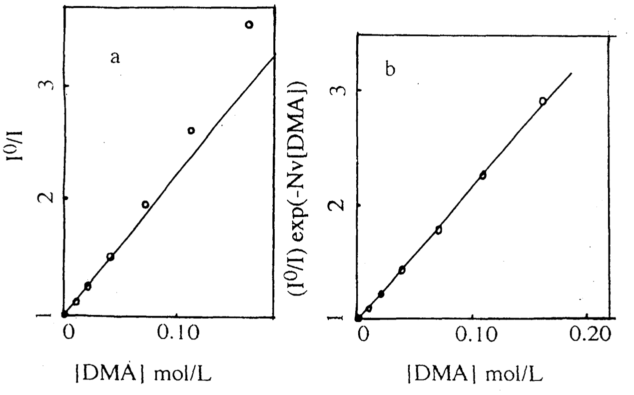

Figure 2. a) The fluorescence quenching ratio I^0/I of 1 at different DMA concentration; b) The treated fluorescence quenching ratio at different DMA concentration based on a model in which both static and dynamic quenching are considered.

no such reports for pure Fullerene derivatives have ever been investigated. In $CHCl_3$, the PL intensity of **1** is effectively quenched by DMA, and the pattern of spectra shows hardly any change. Ratios of the fluorescence intensity without (I^0) and with DMA (I) are plotted as a function of quencher concentration and is shown in Figure 2a. According to the Stern-Volmer equation, a linear relationship between the quenching ratio (I^0/I) and quencher concentration is expected.[11,15]

$$I^0/I=1+K_{sv}[DMA] \qquad (2)$$

where Ksv is the Stern-Volmer constant and [DMA] is the concentration of DMA. The Stern-Volmer constant can be estimated as 12.3 M^{-1} by considering the data at low DMA concentrations (<0.1M), which is much smaller than that of C_{60} in toluene (24 M^{-1}).[11]

As shown in Figure 2a, an upward deviation from the Stern-Volmer equation is observed, especially in the high DMA concentrations region. The deviation is attributed to static fluorescence quenching, and the results can be treated by the following equation.[15]

$$I^0/I=(1+K_{sv}[DMA])\exp(Nv[DMA]) \qquad (3)$$

where N is Avogardro's constant and v is the static quenching volume. Least-squares fits as given by Figure 2b of equation 4 yield Ksv and v of 11.5 M^{-1} and 2100 $Å^3$, respectively.The static quenching volume is much smaller than that of C_{60} (5300 $Å^3$). Assuming a spherical static fluorescence quenching volume, we evaluated the static fluorescence quenching radii to be 7.9 Å. The value is smaller than that of pure Fullerenes (10.8 Å for C_{60}, 11.1 Å for C_{70}),[11] which may be the result of the decreasing in the electron withdrawing property of C_{60} by functionalization.

The Stern-Volmer constant Ksv is expressed as,[15]

$$K_{sv}=K_q\tau \qquad (4)$$

where τ is the fluorescence lifetime of the molecules being quenched and Kq is the diffusion-controlled quenching rate constant. Using the fluorescence lifetime value described above (1.2 ns), we calculated the Kq value to be 0.96×10^{10} $M^{-1}S^{-1}$, which is slightly smaller than that of C_{60} and C_{70} (1.2×10^{10} M^{-1} S^{-1}), but still typical for the diffusion-controlled quenching rate constant.[11,15]

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14 Elemental analysis found: C, 89.15; H, 0.90; N, 1.63%. Calcd for $C_{60}(NH(CHCOOMe)_2)\cdot0.5H_2O$: C, 89.19; H, 1.11; N, 1.56%. ^1H-NMR ($CDCl_3$): 3.89 (3.54H), 5.55(1H) 6.06 (0.19H) (due to about 1: 6 inseparable cis-trans isomer). ^{13}C-NMR($CDCl_3$): 169.18 (COO), 152.18 (2C), 149.83 (2C), 147.17 (2C), 146.42(2C), 146.35(2C), 146.16(2C), 146.05 (4C), 145.54(2C), 145.47 (4C), 145.41 (2C), 145.30 (2C),145.04 (2C), 144.43 (2C), 144.29 (2C), 142.77(2C), 142.75(2C), 142.33 (6C), 142.18(2C), 142.08 (2C), 142.00 (2C), 141.81 (2C), 139.96 (2C), 139.86(2C), 136.79 (2C), 135.61(2C), 77.16 (2C), 73.88 (HC-N), 52.96 (OMe). FTIR (microscope): 3297 ($\nu_{N\text{-}H}$),1746 ($\nu_{C=O}$) cm^{-1}. FAB-MS: 817 (32%, M^+-2OMe), 720 (100%, $C_{60}{}^+$). UV-vis ($CHCl_3$) 258, 314, 429 nm.

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