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Strong Room-Temperature Photoluminescence from the Novel Adduct of C_{60} with Aliphatic Amines

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Abstract: Strong room-temperature photoluminescence from the adducts of C_{60} reacting with five different aliphatic amines, namely propylethylamine (PPA), n-butyl amine (BTA), n-heptylamine (HPA) and dodecylamine (DDA) and diethylamine (DEA), was firstly found from their toluene solution at relatively shorter wavelength around 519 nm.The fluorescence intensity has a good correlation with the length of n-alkyl group chain, the steric position and concentration of different amines and setting of solution as well as the UV-radiation. Their fluorescence quenching by concentration and by aromatic electron-donor N,N-dimethylaniline (DMA) were first investigated and determined.

Keywords: C_{60}, adduct, aliphatic amines, photoluminescence.

Fullerene C_{60} is a good electron-accepting molecule. It has been shown that it can form the charge-transfer complexes (CTC) with amines as the electron-donor[1-4]. Based on the weak CT interactions of C_{60} with various amines, the fluorescence emission spectra for both of C_{60} and its CTC (including the derivatives of C_{60}) frequently appear at relatively longer wavelengths more than 700 nm[2-4]. Whereas the fluorescence emission at relative shorter wavelengths are often neglected and have not been reported up to now. In this paper, we first observe a strong room-temperature fluorescence emission of C_{60} with alphatic amines, and there manifests a very good regulation of the emission intensity with the length of n-alkyl group chain, steric position and concentration of different amines. And contrary to the CTC of C_{60} reported elsewhere[2-6], this fluorescence emission appears at relatively shorter wavelength around 519 nm, which is much stronger than that from CTC. This is the first time that the strong fluorescence of C_{60}/amine adducts was found. Besides, we also report the first observations of fluorescence quenching by concentration and by aromatic electron-donor N,N-dimethylaniline (DMA).

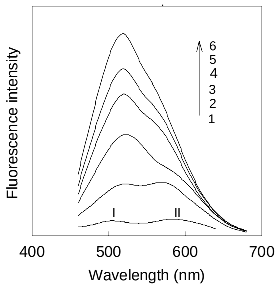
Experimental

C_{60} from Wuhan Yin-Han 3-D Carbon Cluster Hi-Tech. Co. Ltd (purity >99.9%).The working solution was prepared as 1.0×10^{-4} mol/L by diluting the stock solution with toluene to a final volume. All of the aliphatic amines were all analytical reagents.

Fluorescence spectra were recorded on a Hitichi F-4500 spectrofluorometer and the fluorescence measurements were made in the wavelength range of 420 nm~700 nm at regular intervals with fixed excitation and emission slits both at 10 nm.

Results and discussion

Figure 1. Fluorescence spectra of C_{60}/DDA change with time.



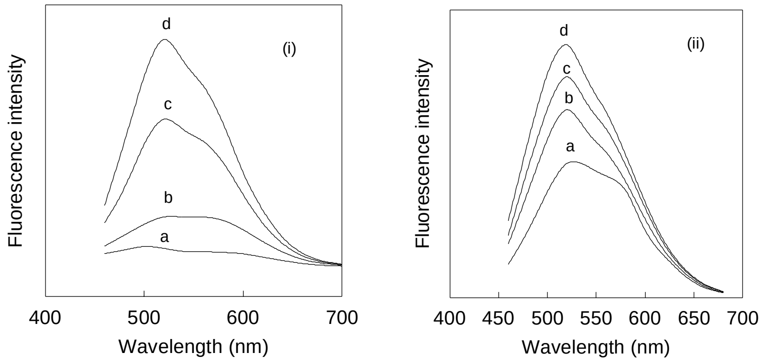
C_{60}: 1×10^{-4} mol/L; DDA: 0.2 mol/L; The solution has been standing for

14h (1), 40h (2), 69h (3), 114h (4), 159h (5) and 205h (6), respectively.

Figure 1 shows the situation of spectra of C_{60} with DDA as an example. It can be seen that two major emission bands appear at around 519 nm (I) and 585 nm (II), where the emission intensity at 585 nm is higher than that at 519 nm when the solution has been standing for 14 hours. At the initial, II is firstly formed and emits a weak fluorescence at relative longer wavelength. With progressive reaction between C_{60} and DDA, I also appears which emits a strong fluorescence at relative shorter wavelength. Nevertheless, it should be noted here that the fluorescence emission from I increases rapidly and quickly surpasses the emission intensity from II and reaches a maximum emission at last. This indicates that the chemical reaction between C_{60} and DDA has been near complete. At this time, the fluorescence emission from II is almost covered completely by I and the peak position is blue-shifted from 585 nm to 519 nm, meantime the color of solution changed from the purple of C_{60} itself to the transparent yellow-brown. Nevertheless, the fluorescence of C_{60} and its CTC is weak and usually appears in the relative long wavelength range[2-4]. Hence, it can be demonstrated by this that this strong fluorescence emission comes from the new electron-transfer (ET) adduct of C_{60}/amine not from CTC, and it may be the more stable thermal-dynamic product. Similar to C_{60}/DDA, the maximum fluorescence emissions are also blue-shifted from 577 nm to 521 nm for PPA, 580 nm to 521 nm for BTA and 581 nm to 521 nm for HPA at last.

Figure 2(i) shows the influence of steric position of different amines on the fluorescence emission efficiency of the ET products. For triethylamine (TEA), only very weak fluorescence emission can be observed due to its relatively larger steric hindrance effect. While for DEA, it exhibits a stronger fluorescence emission due to the relatively smaller steric hindrance effect. The fluorescence intensity is always the strongest for primary aliphatic amines, and the longer the length of n-alkyl group chain, the stronger the emission intensity (see **Figure 2(ii)**). Both the peak position and the shape of spectra under ultraviolet radiation are the same as that under the ambient conditions. But the color change of solution and the emission increase of product are speed up considerably, which indicates that the reaction between C_{60} and aliphatic amines is in fact a typical photocatalyzed process.

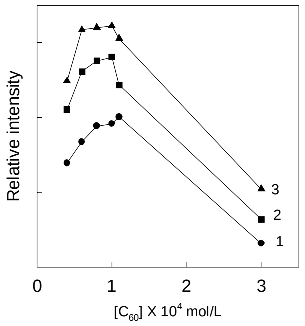
Figure 2 (i) Influence of steric position of amines on the fluorescence intensity of C_{60}-amines TEA (a) DEA (b) PPA (c) and BTA (d), respectively. The concentration of amines are all 0.5 mol/L; C_{60}:1×10^{-4} mol/L; The solution were all standing for six days. **(ii)** Influence of n-alkly group chain length on the fluorescence intensity of C_{60}-amines PPA (a) BTA (b) HPA (c) and DDA (d), respectively; The concentration of various amines were all 0.2mol/L and the solutions all has been standing for nine days.



When fixed amine concentration, changing the concentration of C_{60}, it was found that for all primary amines, the products exhibit their strongest photoluminescence intensity around 6×10^{-5} mol/L~1×10^{-4} mol/L. With continuous increasing concentration of C_{60}, the fluorescence is decreased (see **Figure 3**). This is also the first report on fluorescence quenching by concentration of its reaction adducts.

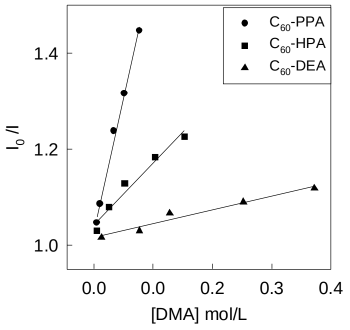
DMA, as a good electron-donor, has been found that it can quench the fluorescence both of C_{60} and its derivatives effectively[2]. However, no such study on fullerene adduct has ever been reported. The fluorescence quenching patterns by DMA are all similar. As DMA concentration increases, the fluorescence intensity is quenched accompanied by the red-shift of spectra, which may contribute to the emission from DMA/C_{60}/aliphatic amine exciplex. According to the Stern-Volmer equation, the K_{sv} value of 5.52 M^{-1} for PPA, 1.96 M^{-1} for HPA and 0.28 M^{-1} for DEA can be estimated, respectively (**Figure 4**). It can be seen that the K_{sv} values are all much smaller than that of C_{60} in toluene (24 M^{-1})[2]solution, indicating that the electron-withdrawing ability of C_{60} is significantly reduced after the chemical reaction of C_{60} with aliphatic amines to form the novel adduct.

Figure 3. Plot of fluorescence intensity of C_{60}-HPA adduct versus the concentration of C_{60} with fixed HPA concentration as 0.52 mol/L.



The setting time is for 1.5 days (1), 7.5 days (2) and 17.5 days (3). Other aliphatic amines have the similar Performance.

Figure 4. Stern-volmer plot of C_{60}-DEA, C_{60}-PPA and C_{60}-HPA adducts in the presence of DMA.



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