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Luminescence properties and kinetic analysis of singlet oxygen from fullerene solutions

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ABSTRACT

A systematic investigation on singlet oxygen ($O_2(a^1\Delta)$) photoluminescence (PL) from fullerene (C_{60}) solutions by using a pulsed Nd: YAG laser at 532 nm was reported. The results show that the $O_2(a^1\Delta)$ PL intensity first increases linearly, then declines fast, and eventually tends to level off with the increase of pump energy, while decreases monotonically with increasing irradiation time. The latter can evidently be attributed to the formation of photoinduced $O_2(a^1\Delta)$ quenchers, which was directly confirmed by the remarkable decrease of $O_2(a^1\Delta)$ lifetime with increasing irradiation time. Also, we further demonstrated that the $O_2(a^1\Delta)$ quencher should be $C_{60}O$ via electrospray ionization-mass spectrometry (ESI-MS) and a kinetic analysis on the formation rate of the $O_2(a^1\Delta)$ quenchers in irradiated C_{60} solutions. On this basis, the above pump-energy dependence of $O_2(a^1\Delta)$ PL was also rationalized kinetically. With the increase of pump energy, the initial linear increase is exactly attributable to the linear increase of $O_2(a^1\Delta)$ concentration, while the following drop should result from the fast formation of photoinduced $O_2(a^1\Delta)$ quenchers and the eventual smooth variation is evidently related to the inverse saturated absorption effect of C_{60}.

1. Introduction

The lowest electronic excited state of oxygen, known as $O_2(a^1\Delta)$, plays an important role in many natural photochemical and photobiological processes [1,2]. Studies on the physical and chemical properties of $O_2(a^1\Delta)$, as well as its generation methods, have been lasting for several decades [3–6]. On the other hand, due to its unique photophysical characteristics, fullerenes have attracted increasing attention in a wide variety of fields, including material chemistry, energy, biological, and biomedical domains [7–11]. In particular, high yield of C_{60} triplets on photoexcitation, its rapid energy transfer with oxygen and inertness to photooxidative destruction suggest it to be a potential $O_2(a^1\Delta)$ photosensitizer [12,13]. So far, there have been a lot of reports on the photosensitized production of $O_2(a^1\Delta)$ in fullerene solutions [14–18]. Recently, Danilov et al. found in photoexcited C_{60}–CCl_4 solutions that $O_2(a^1\Delta)$ PL intensity increases firstly and then decreases with the increase of pump energy [16,17]. It was further proposed that such dependence may be attributed to the following two factors: the inverse saturation absorption effect of C_{60} solutions and the formation of photoinduced $O_2(a^1\Delta)$ quenchers which was subsequently verified by the reduction of $O_2(a^1\Delta)$ lifetime in irradiated C_{60} solutions [15,16]. However, the chemical compositions of the photoinduced $O_2(a^1\Delta)$ quenchers and the related kinetic mechanism for the $O_2(a^1\Delta)$ PL behaviors from C_{60} solutions still remain unclear.

In this work, we have performed a systematic study on $O_2(a^1\Delta)$ PL from C_{60}–CCl_4 solutions by using a pulsed Nd: YAG laser at 532 nm in order to better understand their PL properties and related kinetic mechanism. The dependence of the $O_2(a^1\Delta)$ PL intensity (I_{PL}) on pump energy (E_P) and irradiation time (t_{ir}) were measured in detail, by and large consistent with the report from Ref. [16]. The variations of $O_2(a^1\Delta)$ lifetimes (τ_Δ) in irradiated C_{60} solutions with E_P and t_{ir} were studied thoroughly, directly confirming the formation of photoinduced $O_2(a^1\Delta)$ quenchers. More significantly, the components of the irradiated C_{60} solutions were further analyzed via ESI-MS, indicating that the $O_2(a^1\Delta)$ quenchers generated in the C_{60} photosensitization process should be $C_{60}O$. The kinetic mechanism for the formation of the photoinduced $O_2(a^1\Delta)$ quenchers, as well as the variation of I_{PL} with E_P, was also discussed in depth.

2. Experimental

2.1. Materials

Fullerene C_{60} powder with high purity (99.9%) was purchased from Sigma Aldrich. The CCl_4 solvent with a purity of $>99.5\%$ was also used as received without further purification.

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2.2. Singlet oxygen spectrum and lifetime measurement

The schematic of our experimental setup is shown in Fig. 1. In this experiment, C_{60} solutions, which were placed in a sealed quartz cuvette to avoid volatilizing, were excited by a pulsed Nd: YAG laser at 532 nm (Continuum, PRII 8000, repetition rate 10 Hz, pulse width 7 ns). The steady-state PL spectrum from the samples was recorded by a monochromator (Acton Research Co., Spectra-Pro-2500i) and a liquid-nitrogen cooled IR CCD (Acton Research Co., 7498-0001). An 800 nm long-pass filter was placed at the entrance of the spectrometer to cut off any stray and scattered light with wavelengths shorter than 800 nm. The $O_2(a^1\Delta)$ PL spectra from C_{60}–CCl_4 solutions are recorded over the range of 1245–1305 nm and the recording time is always 1 s in all spectral measurements.

The lifetime of $O_2(a^1\Delta)$ in C_{60}–CCl_4 solutions was measured by using a liquid-nitrogen cooled IR PMT (Hamamatsu, R5509-43) combined with a gated photon counter (GPC) (SRS Inc., SR400). The decay of PL signal at 1273 nm from the samples was recorded by IR PMT, which was sent in sequence to a GPC and a PC computer for further treatment and analysis. Then, the lifetime of $O_2(a^1\Delta)$ can be obtained via a monoexponential fit of the measured PL decay curve. It must be noted that, in order to avoid the influence of some $O_2(a^1\Delta)$ quenchers formed likely in a previous measurement on the next one, a new sample solution was always used for each change of E_p in the experiments of I_{PL} or τ_Δ vs E_P.

3. Results

3.1. Dependence of $O_2(a^1\Delta)$ PL intensity on pump energy and irradiation time

Fig. 2 shows a typical $O_2(a^1\Delta)$ PL spectrum from our C_{60}–CCl_4 solutions at room temperature with $E_P=10$ mJ/pulse. It is clear that the $O_2(a^1\Delta)$ PL spectrum exhibits symmetric single-peak characteristic with its peak position at 1273 nm and a spectral width of 16.4 nm, in good agreement with the previous observations by Black et al. [18] and Losev et al. [19].

Fig. 3 shows the dependence of $O_2(a^1\Delta)$ PL intensity (I_{PL}) from several C_{60}–CCl_4 solutions with different concentrations on pump energy (E_p). It is evident that, with the increase of E_p, I_{PL} first increases linearly, and arrives at its maximum when $E_P=30$ mJ/pulse, then begins to decrease fast from 40 to 110 mJ/pulse, and eventually tends to level off under higher E_p condition, which is similar to the previous report by Bagrov et al. [16,17]. In other words, there always exists an optimal pump energy for the photosensitization of C_{60} solutions. Also, it can still be seen from Fig. 3 that the higher the C_{60} concentration is, the faster I_{PL} decreases with the increase of E_p when E_p exceeds its optimal value. Similarly, the effect of irradiation time (t_{ir}) on I_{PL} from C_{60}–CCl_4 solutions under different pump energies was also shown in Fig. 4. It is clear that, for any fixed pump energy, I_{PL} always decreases monotonically with the increase of t_{ir}. Moreover, the higher E_P is, the faster I_{PL} decreases with t_{ir}. The related kinetic mechanism for these variations will be discussed in detail in Section 4.

3.2. Dependence of $O_2(a^1\Delta)$ lifetime on irradiation time and pump energy

It is noteworthy that the light sources used in our lifetime measurement and irradiation process are a same pulse laser and thus the irradiation process and the lifetime measurement always alternated in this experiment. In order to reduce the formation of some likely $O_2(a^1\Delta)$ quenchers during the lifetime measurement, a very low excitation energy of $E_P=0.02$ mJ/pulse was used in the process, while a relatively high laser energy was used during the irradiation process to generate faster detectable $O_2(a^1\Delta)$ quenchers.

Fig. 5 shows the variation of measured $O_2(a^1\Delta)$ lifetimes (τ_Δ) in C_{60}–CCl_4 solutions with t_{ir} respectively for two different pump energies of $E_P=10$ and 30 mJ/pulse. Obviously, for a fixed pump energy, τ_Δ decreases monotonically with the increase of t_{ir}, which directly manifests that some photoinduced $O_2(a^1\Delta)$ quenchers do form in the irradiated C_{60}–CCl_4 solutions. More interestingly, a positive correlation between I_{PL} and τ_Δ can be found from Fig. 5, indicating that the decrease of I_{PL} with t_{ir} completely derives from

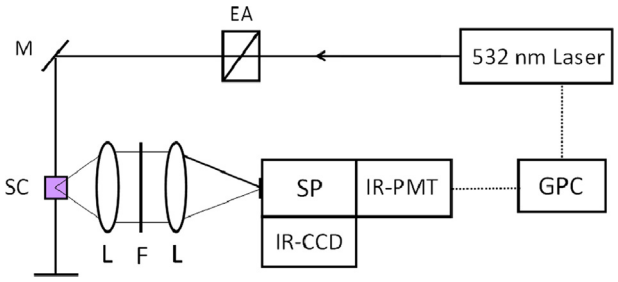

Fig. 1. Schematic of experimental setup. EA: energy attenuator, M: reflection mirror, SC: sample cell, L: lens, F: notch filter, SP: spectrometer, IR-PMT: IR photomultiplier, GPC: gated photon counter.

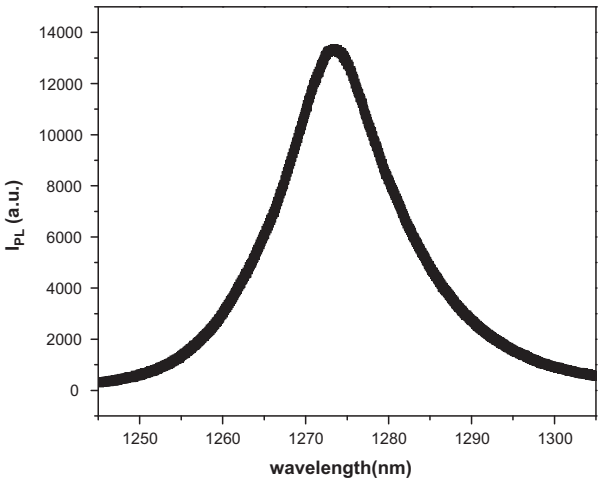

Fig. 2. $O_2(a^1\Delta)$ PL spectrum observed in C_{60}–CCl_4 solutions with $E_P=10$ mJ/pulse.

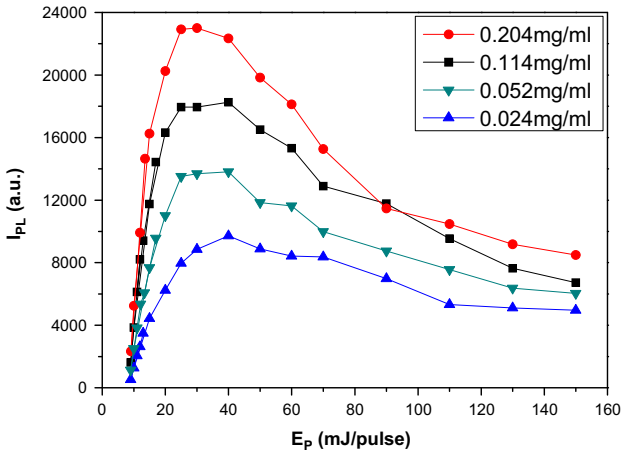

Fig. 3. Measured $O_2(a^1\Delta)$ PL intensity as functions of pump energy in C_{60}–CCl_4 solutions with different C_{60} concentrations.