

Transient Spectroscopic Properties of [60]Fullerene-Containing Cyclic Sulphoxide

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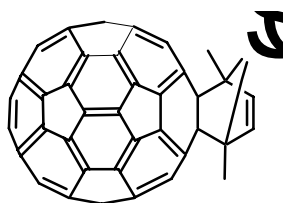
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Abstract: The properties of the triplet excited state of [60]fullerene-containing cyclic sulphoxide have been investigated by time-resolved absorption spectroscopy. Transient absorption bands of [60]fullerene-containing cyclic sulphoxide showed two decay-components, which were attributed to triplet excited states of different spin multiplicity. The properties of photoexcited states of [60]fullerene-containing cyclic sulphoxide are also reported.

Keywords: [60]Fullerene-containing cyclic sulphoxide, triplet excited state, transient spectroscopic property, time-resolved absorption spectroscopy.

Aiming at the development of new [60]fullerene-based organic photoconductivity¹, superconductivity², ferromagnetism³ and nonlinear optics⁴, a considerable number of derivatives of [60]fullerene have been explored⁵⁻⁸. Our interest in the synthesis and properties of derivatives of [60]fullerene has led to preparation of [60]fullerene-containing cyclic sulphoxide⁹ as shown in **Figure 1**.

Figure 1 The structure of C₆₀-C₆H₈SO



We expected the [60]fullerene with cyclic sulphoxide to exhibit better reduction potentials than the parent [60]fullerene. It would allow to address the attachment of the first electron either to [60]fullerene cage or to the cyclic sulphoxide moiety in the reduction process.

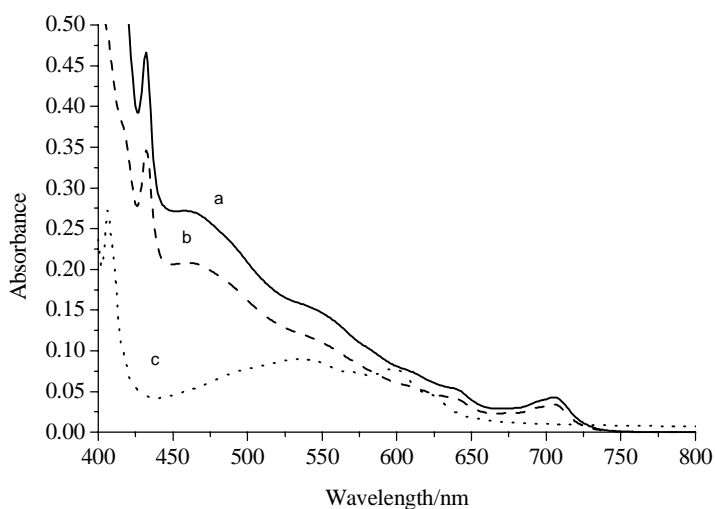
Photophysical and photochemical properties of [60]fullerene and its derivatives have attracted much attention recently¹⁰⁻¹⁶. In the present work we have observed the

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transient absorption spectra of [60]fullerene-containing cyclic sulphoxide for the first time by a nanosecond laser flash photolysis in the visible and near-infrared regions.

We will describe briefly the steady-state absorption spectra of [60]fullerene-containing cyclic sulphoxide in benzonitrile and toluene that were recorded between 400 nm and 800 nm as shown in **Figure 2**.

Figure 2 Steady-state absorption spectra in the UV/vis region $C_{60}-C_6H_8SO$ (0.1 mmol), a) in toluene; b) in benzonitrile; and c) C_{60} (0.1 mmol) in benzonitrile.

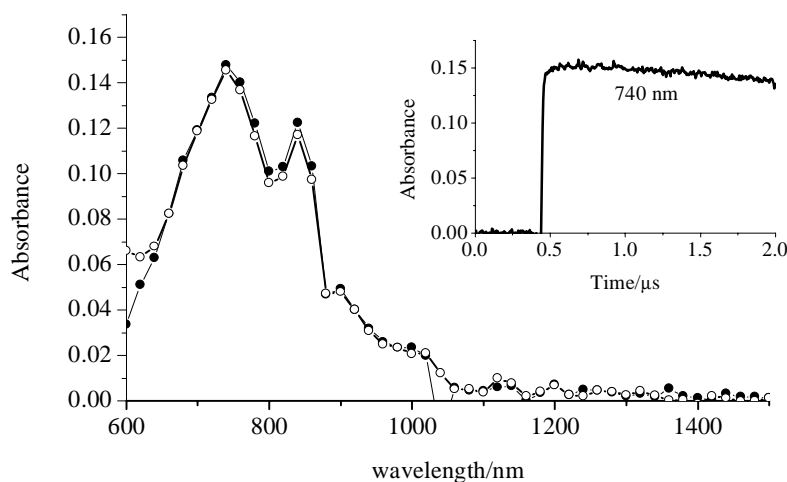


The absorption spectrum of [60]fullerene-containing cyclic sulphoxide in toluene and benzonitrile showed a different feature from the parent [60]fullerene that had absorption bands at 600 nm and 500 nm. However their absorption bands are similar in toluene and benzonitrile. Absorption peaks at 715 nm, 640 nm, 475 nm and 430 nm are characteristic of [60]fullerene-containing cyclic sulphoxide in which the mono-cycloadduct product is formed. Compared to [60]fullerene, the absorption peak at 715 nm is red-shifted. This finding will suggest that structure strained in the presence cyclic sulphoxide.

With the laser-light excitation of [60]fullerene-containing cyclic sulphoxide in toluene transient absorption bands appeared at 740 nm and 840 nm with broad band around 880 nm and 1000 nm which were attributed to excited state of different spin multiplicity as shown in **Figure 3**.

These absorption bands can be attributed to the triplet excited state of [60]fullerene-containing cyclic sulphoxide, because these absorption were efficiently quenched in the presence of oxygen, a triplet excited state energy acceptor. The quenching rate constant of [60]fullerene-containing cyclic sulphoxide by oxygen (K_{et}) was estimated to be $1.05 \times 10^7 \text{ mol/L S}^{-1}$.

Figure 3 Nanosecond time-resolved absorption spectra obtained by 532 nm laser photolysis of [60]fullerene-containing cyclic sulphoxide (0.1 mmol) in argon-saturated toluene. inset: time-profiles at 740 nm.



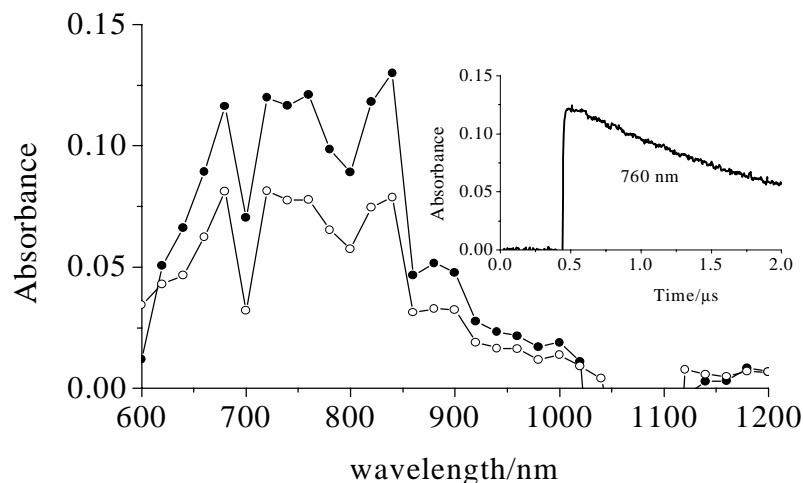
From the absorption –time profile at 740 nm and 840 nm, time profile as shown in the inset of **Figure 3**, the decay rate constant of [60]fullerene-containing cyclic sulphoxide was estimated to be $6.05 \times 10^4 \text{S}^{-1}$ and $7.63 \times 10^4 \text{S}^{-1}$, which corresponds to 16 μs and 13 μs of the triplet excited state lifetime. The lifetime of triplet excited state is quite shorter than those [60]fullerene(55 μs). Such short lifetime of triplet excited state of [60]fullerene-containing cyclic sulphoxide will result from vibrations of the bonds connecting cyclic sulphoxide which may efficiently quench the triplet excited state by the radiation process.

In the polar solvent, such as benzonitrile, the transient absorption bands appeared at 720-760 nm and 840 nm with broad peaks around 880 nm and 1000 nm as shown in **Figure 4**.

Time profile is shown in the inset of **Figure 4**. The decay rate constant of [60]fullerene-containing cyclic sulphoxide was estimated to be $4.7 \times 10^5 \text{S}^{-1}$ and $5.46 \times 10^5 \text{S}^{-1}$ which corresponds to 2.1 μs and 1.8 μs of lifetime of the triplet excited state respectively. The lifetime of triplet excited state of [60]fullerene-containing cyclic sulphoxide in the benzonitrile is much shorter than that in the toluene. This finding agrees with that deactivation of [60]fullerene-containing cyclic sulphoxide by intermolecular and/or intramolecular triplet-triplet(T-T) annihilation in the present experiments. The triplet excited state of [60]fullerene-containing cyclic sulphoxide was quenched efficiently. It may be due to the formation of the excited charge transfer complex under the present experiments.

In summary, we report the first observations of the transient spectra of [60]fullerene-containing cyclic sulphoxide on the nanosecond time scale. A further study on photoinduced electron transfer reaction of [60]fullerene-containing cyclic sulphoxide is under way.

Figure 4 Nanosecond time-resolved absorption spectra obtained by 532 nm laser photolysis of [60]fullerene-containing cyclic sulphoxide (0.1 mmol) in argon-saturated benzonitrile. inset: time-profiles at 740 nm.



Acknowledgments

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