Photophysical properties of various regioisomers of [60]fullerene-*o*-quinodimethane bisadducts

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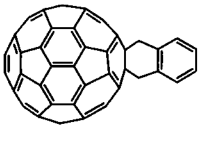
The absorption, fluorescence, and transient absorption spectra of three regioisomers of [60]fullerene bisadducts were remarkably different from one another and also different from those of typical monoadducts. These results indicate that the electronic structures of these bisadducts in both ground and excited states are significantly dependent on the addition pattern. The quantum yields of singlet oxygen production (Φ_Δ) for these bisadducts were also dependent on the addition pattern and less affected by the solvents or substituents, whereas the quantum yields of intersystem crossing (Φ_{isc}) were almost independent of the addition pattern.

Introduction

We have examined the electronic and photophysical properties of [60]fullerene-*o*-quinodimethane monoadducts such as **1** having various aromatic rings (benzene, naphthalene, phenanthrene and pyrene) in the vicinity of the [60]fullerene core.[1,2] These properties were found to be virtually independent of the attached aromatic rings, according to the measurements of the redox potentials, absorption spectra, fluorescence spectra, and transient absorption spectra. Thus, there is only a little through-bond or through-space electronic interaction between the [60]fullerene moiety and the aromatic rings as the part of addend.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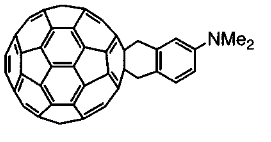

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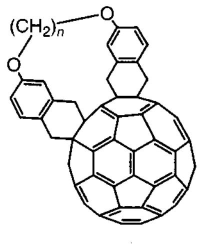

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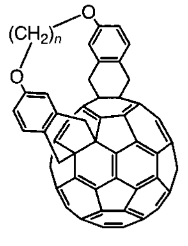
(n = 2, 3)



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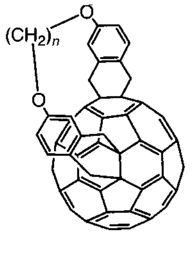
(n = 2, 3)



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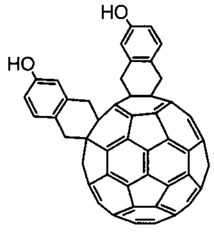
(n = 5)



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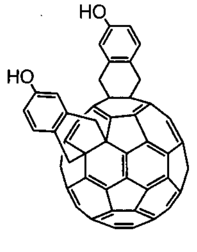
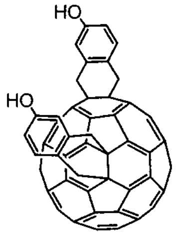


7: (A$_1$, D$_1$)



8: (A$_1$,H$_1$)

Furthermore, [60]fullerene adduct **2** possessing an *N*,*N*-dimethylaniline (DMA) moiety was synthesized, and its intramolecular electron transfer and exciplex formation were investigated in both cyclohexane and benzonitrile.[3] The electronic and photophysical properties of **2** in cyclohexane were found to be quite similar to those of **1**, although the fluorescence of **2** was significantly quenched in benzonitrile due to the intramolecular electron transfer from the DMA moiety to the S_1 state of the [60]fullerene moiety, where the rate constant was estimated as 1.5×10^{10} s^{-1}.

Recently, we have succeeded in the regio- and stereoselective synthesis of [60]fullerene bisadducts by the reactions of [60]fullerene with compounds in which two *o*-quinodimethane precursors are connected by an oligomethylene chain (n = 2–5).[4] By this method, only (A$_1$,C$_1$)- and (A$_1$,D$_1$)-isomers (**3** and **4**)[5] were selectively obtained when $n = 2$ and 3, while another (A$_1$,H$_1$)-isomer **5** was obtained when $n = 5$. The absorption spectra of **3**–**5** were found to be remarkably different from one another. The spectroscopic features were maintained in bisadducts **6**–**8** which were obtained by the cleavage of the tether of **3**–**5**, respectively. Therefore, the differences in the absorption spectra are expected to be ascribable to the difference in addition pattern, since it is unlikely that the alkoxy or hydroxy groups on the benzene rings alter the electronic structures of the [60]fullerene moiety.

Although the absorption spectra have been reported for a series of regioisomers of some [60]fullerene bisadducts,[6] other spectroscopic features have been hardly clarified. Thus, we were prompted to investigate the photophysical properties of bisadducts **3** ($n = 3$), **4** ($n = 3$), and **5** in detail; the fluorescence spectra and transient absorption spectra were measured and compared with those of typical monoadducts. Furthermore, their quantum yields of intersystem crossing (Φ_{isc}) were also determined on the basis of the quantum yields of singlet oxygen production by the triplet [60]fullerene derivatives (Φ_Δ). In this paper, the photophysical properties of a series of bisadducts are disclosed for the first time, by comparing among bisadducts and with typical monoadducts and [60]fullerene itself.

Results and discussion

Although the absorption spectra of **3**–**5** were reported previously,[4] their features are described here again. In (A$_1$,D$_1$)-bisadduct **4**, the $S_1 \leftarrow S_0$ band whose shape is similar to that in monoadduct **1** extends up to 740 nm, much red-shifted relative

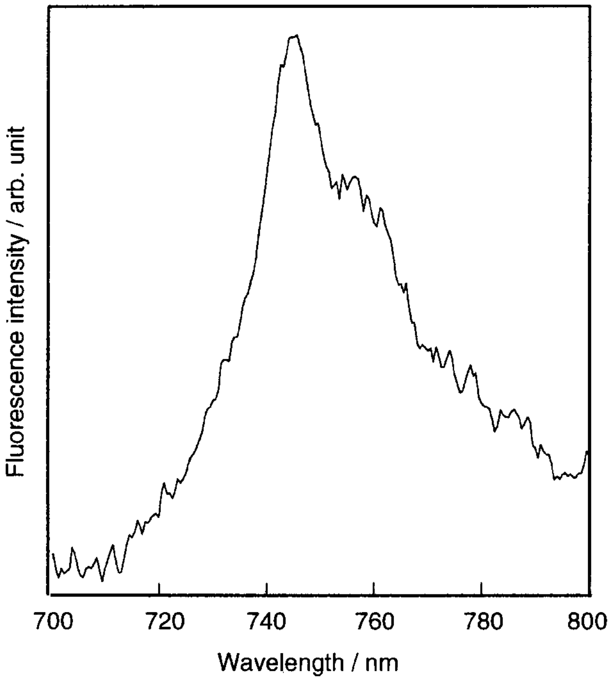


Fig. 1 Fluorescence spectrum of **4** upon 440 nm excitation in cyclohexane at room temperature.

to that in **1**, in spite of the loss of a double bond. On the other hand, the $S_1 \leftarrow S_0$ band in **3** and **5** is blue-shifted and ambiguous. The rather sharp band is also observed around 420 nm in **5**, as in the case of some (A_1,H_1)-bisadducts reported by other groups,[6,7] suggesting that this band is characteristic of this bisaddition pattern. Such a band is also observed in many [60]fullerene monoadducts at a similar position (*ca.* 430 nm).[2,8] Since the two addition sites are relatively remote from each other in (A_1,H_1)-bisadducts, the tendency in monoadducts seems to remain to some extent. These spectroscopic features were maintained in bisphenols **6**–**8** obtained from **3**–**5**, indicating that they are derived from the difference in addition sites rather than the substituents.

The fluorescence spectra of **3**–**5** were measured upon 440 nm excitation in cyclohexane at room temperature. The fluorescence behavior was remarkably different from one another, as in the case of the absorption spectra. Bisadduct **4** afforded a relatively well-defined emission with a maximum at 745 nm as shown in Fig. 1, whereas **3** and **5** only gave quite weak and poorly resolved emission. The fluorescence spectrum of **4**, consisting of some shoulders, exhibits the mirror image of the longest absorption band,[4] and the Stokes shift is extremely small (*ca.* 80 cm^{-1}). These observations resemble those in monoadduct **1**. The fluorescence intensity of **4** is also comparable to that of **1**, although the precise quantum yield has not been determined. The maximum position in the fluorescence of **4** is red-shifted (*ca.* 40 nm) relative to that of monoadduct **1**, corresponding to the shift in the $S_1 \leftarrow S_0$ band of their absorption spectra. The quite low fluorescence intensity of **3** and **5** is probably ascribed to the ambiguous $S_1 \leftarrow S_0$ absorption band. The tendency in the fluorescence spectra of **3**–**5** is also observed in **6**–**8** after the removal of the oligomethylene chain. Therefore, the differences in the fluorescence spectra among **3**–**5** or **6**–**8** are apparently brought about by the difference in the addition pattern, as in the case of the absorption spectra.

In order to examine mainly the T_1 state of bisadducts **3**–**5**, transient absorption spectra were measured by laser flash photolysis. The spectra were obtained at several delay times after laser pulsing at 355 nm in degassed cyclohexane at room temperature. Fig. 2 illustrates the spectra of these bisadducts, along with that of monoadduct **1** for the comparison.[2] The whole appearance of the spectra obtained for **3**–**5** is to some extent similar to the $T_n \leftarrow T_1$ absorption spectra of **1**, exhibiting broad bands around 700 and 350–450 nm. The transient absorption decays by first-order kinetics and completely disappears about 200 μs after laser pulsing for all adducts.[9] Furthermore, the transient is efficiently quenched by oxygen. Therefore, the observed absorption is also ascribed to the $T_n \leftarrow T_1$ transition of **3**–**5**.

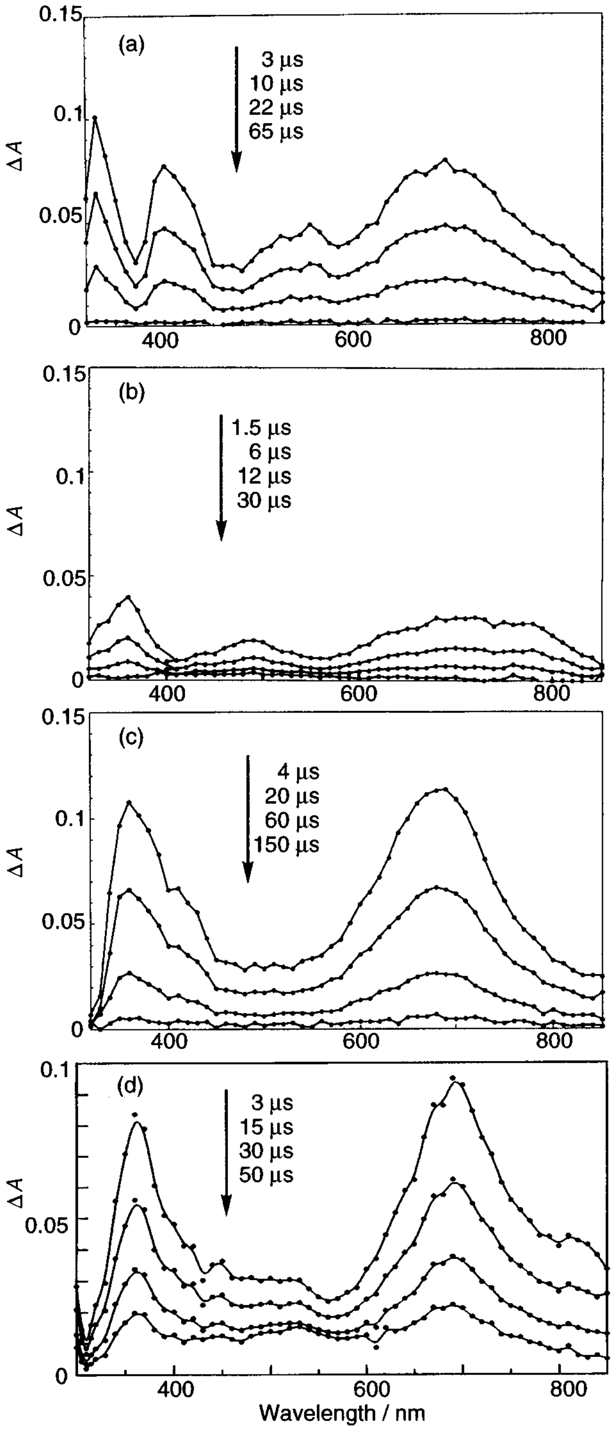


Fig. 2 Transient absorption spectra of (a) **3**, (b) **4**, (c) **5** and (d) **1** obtained by 355 nm laser flash photolysis in cyclohexane at room temperature.

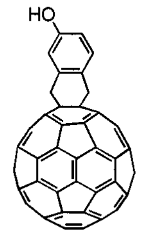
The behavior of the transient absorption is rather different among the three bisadducts. The spectra of **5** with maxima at 360 and 690 nm quite resemble those of monoadduct **1**. The lifetime (50 μs), however, is much longer than that for **1** (*ca.* 30 μs). The $T_n \leftarrow T_1$ absorption spectra of **3** have two maxima around 330 and 400 nm in addition to that around 700 nm, and the lifetime is rather short (16 μs). In bisadduct **4** showing three maxima around 360, 480 and 700 nm, the lifetime (6 μs) is much shorter than those of the other two bisadducts, in spite of similar experimental conditions. Furthermore, the initial absorbance of **4** seems to be rather small relative to **3** and **5**. Although the molar extinction coefficients of the $T_n \leftarrow T_1$ absorptions of **3**–**5** are unknown, this result may be associated with the quantum yield (Φ_{isc}) of the intersystem crossing from S_1 to T_1; the Φ_{isc} value of **4** may be smaller than that of the others.

Thus, we attempted to determine the Φ_{isc} values on the basis of the quantum yields (Φ_Δ) of singlet oxygen production. [60]Fullerene and its derivatives in the triplet state are quenched by $^3O_2$ to produce $^1O_2$ with Φ_Δ,[10–12] and the relationship between Φ_Δ and Φ_{isc} can be expressed by eqn. (1) where k_d is the decay

$$\Phi_\Delta = \Phi_{isc}k_q[^3O_2]/(k_d + k_q[^3O_2]) \qquad (1)$$

rate constant of each [60]fullerene derivative in the triplet state in the absence of any quenchers and k_q is the quenching rate constant of the triplet state by $^3O_2$. These rate constants for the bisadducts were obtained from the decay kinetics of the $T_n \leftarrow T_1$ absorption in both degassed and O_2-saturated benzene solution.

The Φ_Δ values were determined in benzene and benzonitrile[13] solution by monitoring the time-resolved phosphorescence corresponding to the O_2 ($^1\Delta_g$)→O_2 ($^3\Sigma_g$) transition at 1268 nm[14] upon laser excitation at 532 nm. Table 1 lists the Φ_Δ values for bisadducts **3**–**5**, **8** and monoadduct **9**. Apparently, all the bisadducts display lower $^1O_2$-producing ability than monoadduct **9** and [60]fullerene itself,[11] although some difference is observed among the regioisomers of bisadducts. It is noteworthy that Φ_Δ of **4** is much lower than those of **3** and **5** in both solvents. The Φ_Δ value of (A_1,H_1)-bisphenol **8** is comparable to that of (A_1,H_1)-bisadduct **5**. This result suggests that the $^1O_2$-generation ability apparently depends on the addition pattern on the [60]fullerene sphere rather than the substituents on the benzene rings, at least concerning the bisadducts treated here. The Φ_Δ value of each adduct in benzonitrile is comparable to that in benzene. The $^1O_2$-producing ability seems to be almost independent of the solvents.



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The k_d, k_q, and Φ_Δ values obtained for each derivative were converted into the Φ_{isc} value by using eqn. (1). The Φ_{isc} values are also summarized in Table 1. Apparently, the increase in the number of substituents causes the decrease in Φ_{isc}; 0.96 for [60]fullerene as a standard, 0.8 for monoadduct **9** and *ca.* 0.55 for bisadducts **3**–**5** and **8**. Noticeably, three regioisomers of bisadducts exhibit quite similar Φ_{isc} values, regardless of the positions of the two addends attached on the [60]fullerene hemisphere, though **4** gave a much smaller Φ_Δ value than **3** and **5**. The Φ_Δ is almost comparable to the Φ_{isc} for **3** and **5**, whereas the Φ_Δ is much smaller than the Φ_{isc} for **4** due to the relatively large k_d value. Since no significant difference was observed among the Φ_{isc} of **3**–**5**, the origin of the rather small initial absorbance in the $T_n \leftarrow T_1$ absorption spectra of **4** relative to **3** and **5** has not been clarified at the present stage. The molar extinction coefficients of the $T_n \leftarrow T_1$ absorption in **4** may be smaller than those in the other two bisadducts.

Table 1 Quantum yield of singlet oxygen generation (Φ_Δ)[a] and intersystem crossing (Φ_{isc}) by [60]fullerene derivatives

	Φ_Δ		Φ_{isc}	
[60]Fullerene derivatives	in benzene	in benzonitrile	in benzene	Addition sites
3	0.54	0.64	0.55	(A_1,C_1)
4	0.35	0.27	0.54	(A_1,D_1)
5	0.56	0.52	0.57	(A_1,H_1)
8	0.53	0.48	0.54	(A_1,H_1)
9	0.79	0.70	0.80	monoadduct

[a] Average of three runs with C_{60} (Φ_Δ = 0.96 ± 0.04) as standard (see ref. 10). The experimental error was within ±0.02.

Experimental

General

Absorption spectra were recorded on a JASCO Ubest-50 spectrophotometer. Fluorescence spectra were measured on a Hitachi-4010 spectrofluorimeter. These spectra were obtained in cyclohexane (spectroscopic grade) or benzonitrile (distilled over P_2O_5 under reduced pressure) with a quartz cell of 10 mm optical path at room temperature. The sample concentration is in the range of 10^{-5}–10^{-4} M.

Material

[60]Fullerene monoadduct **9** and bisadducts **3**–**8** were synthesized by the methods reported previously.[4]

Transient absorption spectra

Transient absorption spectra were measured by nanosecond time-resolved laser photolysis with a Nd^{3+} : YAG laser (Spectra-Physics GCR-130, the third harmonics, 355 nm, pulse width 6 ns). A 150-W xenon flash lamp (Ushio UXL 151D) was used as a probe light for the detection of the transients. The monitoring light passing through a monochrometer (Ritsu MC-20N) was detected by a photomultiplier tube (Hamamatsu R928) and recorded on a digitizing oscilloscope (Tektronix TDS 744). The time profiles were analyzed by a personal computer (NEC PC-9821 Ap). The sample solution was degassed by at least three freeze–pump–thaw cycles on a high vacuum line. The absorbance of the solutions was adjusted to *ca.* 0.7 at the excitation wavelength.

Determination of quantum yields of singlet oxygen production (Φ_Δ)

The Φ_Δ values were determined by the time-resolved single-photon counting of the phosphorescence corresponding to the O_2 ($^1\Delta_g$)→O_2 ($^3\Sigma_g$) transition at 1268 nm upon laser excitation at 532 nm, after O_2 was bubbled into the benzene or benzonitrile solution of [60]fullerene derivatives (3.0×10^{-5} M) for 10 min. The apparatus has been described in detail elsewhere.[15]

Acknowledgements

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References

1 T. Tago, T. Minowa, Y. Okada and J. Nishimura, *Tetrahedron Lett.*, 1993, **93**, 8461.
2 Y. Nakamura, T. Minowa, S. Tobita, H. Shizuka and J. Nishimura, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2351.

3 Y. Nakamura, T. Minowa, Y. Hayashida, S. Tobita, H. Shizuka and J. Nishimura, *J. Chem. Soc.*, *Faraday Trans.*, 1996, **92**, 377.

4 M. Taki, S. Sugita, Y. Nakamura, E. Kasashima, E. Yashima, Y. Okamoto and J. Nishimura, *J. Am. Chem. Soc.*, 1997, **119**, 926.

5 For the nomenclature of [60]fullerene bisadducts, see Y. Nakamura, M. Taki and J. Nishimura, *Chem. Lett.*, 1995, 703.

6 Q. Lu, D. I. Shuster and S. R. Wilson, *J. Org. Chem.*, 1996, **61**, 4764.

7 L. Isaacs, R. F. Haldimann and F. Diederich, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 2339.

8 C. S. Foote, *Top. Curr. Chem.*, 1994, **169**, 347.

9 All the [60]fullerene derivatives were stable enough under such irradiation conditions; the UV/Vis absorption spectra of these adducts after the irradiation showed no difference from those before the irradiation.

10 J. W. Arbogast and C. S. Foote, *J. Am. Chem. Soc.*, 1991, **113**, 8886.

11 J. W. Arbogast, A. P. Darmanuan, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz and R. L. Whetten, *J. Phys. Chem.*, 1991, **95**, 11.

12 J. L. Anderson, Y.-Z. An, Y. Rubin and C. S. Foote, *J. Am. Chem. Soc.*, 1994, **116**, 9763.

13 Since Φ_Δ for [60]fullerene is considered to be almost independent of solvents (see R. D. Scurlock, S. Nonell, S. E. Braslavsky and P. R. Ogilby, *J. Phys. Chem.*, 1995, **99**, 3521), we postulate that Φ_Δ of [60]fullerene in benzonitrile is 0.96.

14 T. Nagano, K. Arakane, A. Ryu, T. Masunaga, K. Shinmoto, S. Mashiko and M. Hirobe, *Chem. Pharm. Bull.*, 1994, **42**, 2291.

15 T. Nojima, K. Ishiguro and Y. Sawaki, *J. Org. Chem.*, 1997, **62**, 6911.

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