Synthesis and electronic properties of C_{60}–*o*-quinodimethane adducts

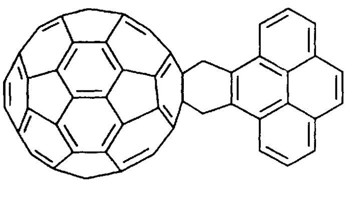
Yosuke Nakamura, Toshiyuki Minowa, Seiji Tobita, Haruo Shizuka and Jun Nishimura *
Department of Chemistry, Gunma University, Tenjin-cho, Kiryu, Gunma 376, Japan

Several C_{60}–*o*-quinodimethane adducts having various aromatic rings have been synthesized by the simple thermal reaction of C_{60} with dihydrocyclobutaarenes. According to MM2 calculations, the most stable conformation of the cyclohexene ring in these adducts is not the half-chair, but the half-boat. On the basis of variable temperature NMR results, its inversion rate was found to depend on the attached aromatic rings, mainly due to the steric effect. The absorption spectra in the visible region were substantially identical for all the adducts, exhibiting a weak and broad band around 700 nm with vibrational structures. The fluorescence spectra due to the C_{60} moiety of the adducts were also similar to each other and independent of the excitation wavelength. The fluorescence excitation spectra were in good agreement with the corresponding absorption spectra. No fluorescence could be observed from the attached aromatic rings even in the case of pyrene, because of the quenching by the intramolecular $S_{1(\text{pyrene})}$–$S_{0(\text{C60})}$ energy transfer. The similar transient absorption spectra of the C_{60} adducts were ascribed to the $T_n \leftarrow T_1$ absorption of the C_{60} moiety. These results show that little intramolecular electronic interaction between the C_{60} and aromatic moieties takes place in the adducts.

Introduction

The successful large scale synthesis and isolation of C_{60},[1] has attracted much scientific attention because of its various properties[2,3] and reactivities.[4] Some of the derivatives are of great interest in biochemistry.[5] The synthesis of new C_{60} derivatives is hoped to result in new functional materials.

In Diels–Alder reactions, C_{60} serves as a good dienophile to give adducts with dienes.[6] However, the adducts obtained are often subject to the reverse reactions to reproduce C_{60}, sometimes even at room temperature.[7] Among them, the adducts with *o*-quinodimethane or its derivatives have proved stable enough to be isolated, because their cleavage is endothermic due to the generation of unstable *o*-quinodimethane species.[7a,8] Recently, we have examined some dihydrocyclobutaarenes as a precursor of *o*-quinodimethane species and found that they underwent the thermally allowed conrotatory electrocyclic ring opening and gave stable adducts **1** and **2** with C_{60}.[9] In these adducts, the C_{60} moiety and the pyrene or phenanthrene ring are connected through a flexible and flipping cyclohexene ring.[9] Therefore, the attached aromatic ring can be located close to the C_{60} surface and some intramolecular interaction between the π-electron systems should arise. From such a viewpoint, **1** and **2** seem to be intriguing and attractive C_{60} derivatives.



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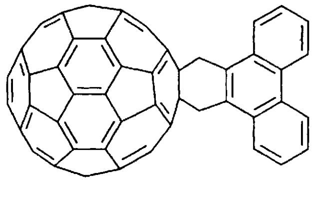

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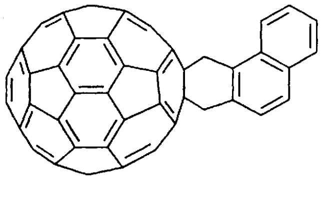

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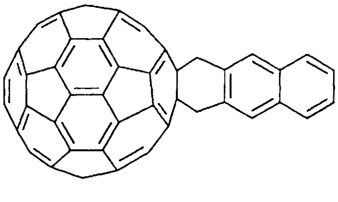

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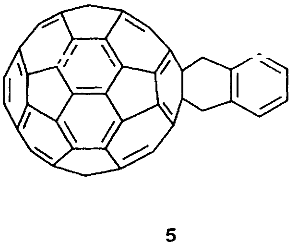

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In parallel with the various functionalization of C_{60}, the photochemical and photophysical properties of C_{60} and its derivatives have been investigated by many researchers,[10] though such studies towards derivatives are less intensive than those of C_{60} itself, probably due to the difficulty in their syntheses. The absorption spectrum of C_{60} has been established.[11] For its derivatives, also, some common features have been defined; the longest absorption band is remarkably red-shifted relative to that of the parent, and a sharp absorption is observed around 430 nm.[7a,12] On the other hand, it has been difficult to detect the fluorescence of C_{60} definitely, especially at room temperature, because of the low quantum yield ($\Phi_F \approx 10^{-4}$). After much effort, rather weak fluorescence with a maximum around 720 nm was finally observed.[13] Fluorescence spectra of C_{60} derivatives are, of course, extremely limited. The spectrum of the trimethylenemethane (TMM)–C_{60} adduct reported by Shiu *et al.*[14a] was probably the first example, although neither the excitation spectrum nor the relationship between the absorption and the fluorescence was given. Quite recently, during the preparation of this article, they reported the fluorescence of some analogous C_{60} derivatives, including the spectral mirror images of absorption and fluorescence.[14b] Foote and co-workers also reported on the emission of a dihydro-C_{60} derivative, whose excitation spectrum was in accordance with the absorption spectrum.[15] Furthermore, for the first time they presented the transient absorption spectra of the excited triplet species and the anion radical generated by electron transfer with *N,N*-dimethylaniline.[15] Generally speaking, however, their photochemical properties, especially in the excited states, have not been sufficiently disclosed. Of course, the influence of the additional intramolecular π-electron system on the photochemical behaviour of the C_{60} moiety is little known.

Therefore, we have investigated the photochemical and photophysical properties of the adducts **1** and **2** in detail, since the electronic state of the C_{60} moiety may be modified by the large π-electron system of the pyrene or phenanthrene ring in the vicinity of the C_{60} core. In addition to **1** and **2**, adducts **3** and **4** with a naphthalene ring and **5**[8] with a benzene ring were also synthesized for comparison, and the electronic properties of all the adducts were compared thoroughly in terms of the redox potentials, the absorption and fluorescence spectra and the transient absorption spectra.

Results and discussion

Synthesis and characterization

All the C_{60} adducts were synthesized by the simple Diels–Alder reaction of C_{60} and *o*-quinodimethane species which were generated *in situ*. For the preparation of **1–3**, the corresponding benzocyclobutene homologues, which bring about ring opening thermally to give *o*-quinodimethane homologues, were allowed to react with C_{60} in refluxed tetralin, instead of *m*-xylene as used in the previous report.[9] The isolated yields of below 10% obtained in refluxing *m*-xylene were increased up to 20–30% by using a solvent with a higher boiling point. In the synthesis of **4**, the 1,4-elimination of 2,3-bis(bromomethyl)naphthalene was employed in the same manner as in 1,2-bis(bromomethyl)-benzene.[8] Treatment of C_{60} with 2,3-bis(bromomethyl)naphthalene, KI and 18-crown-6 as a phase transfer catalyst in toluene at the reflux temperature afforded adduct **4** in 20% isolated yield. In all the reactions, not only the mono-adducts **1–4** but also di-adducts were obtained with the recovery of C_{60}. The mono-adducts **1–4** were isolated and purified by column-chromatography on silica gel. The di-adducts were found to be a mixture of some isomers, whose separation has been unsuccessful as yet, even by HPLC.

The structure of the adducts was determined mainly by ^1H and ^{13}C NMR experiments. The symmetry of the molecules is sensitively reflected by the number of the ^{13}C NMR signals. Adducts **1** and **2** are considered to be of C_{2v} symmetry, since less than 16 peaks for the sp^2 carbons of the C_{60} moiety in their ^{13}C NMR spectra were observed–the number expected for C_{60} adducts of C_{2v} symmetry. This symmetry results from the addition of the *o*-quinodimethane homologues at a [6,6]-junction (not [6,5]) of C_{60}, as reported for most C_{60} adducts[6–9,12] and the fast flipping motion of the cyclohexene ring connecting the C_{60} and the aromatic rings. The fast flipping was confirmed by the broad signal at 5.1–5.3 ppm corresponding to the four equivalent methylene protons in the ^1H NMR spectra. For adduct **4**, which was expected to have the same symmetry as **1** and **2**, at least 24 signals for C_{60} sp^2 carbons were observed at room temperature, indicating C_s symmetry instead of C_{2v}. This lower symmetry is apparently due to the slower flipping in **4** than that in **1** or **2**. In the ^1H NMR spectrum of **4**, in fact, the two doublet signals for the non-equivalent methylene protons at room temperature coalesced above 80 °C.

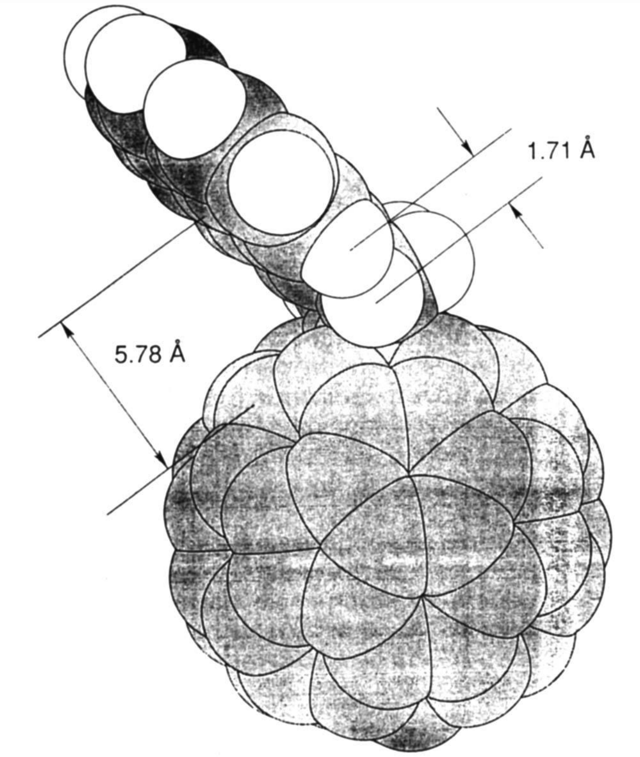

Fig. 1 Most stable conformation of **1** on the basis of MM2 calculations

Surprisingly, there were less than 16 C_{60} sp^2 carbon peaks in adduct **3**, in spite of the absence of a C_2 axis. This result strongly suggests the addition at a [6,6]-junction and the fast flipping of the cyclohexene ring as in **1** and **2**.

Variable temperature NMR measurements

As mentioned above, the inversion rate of the cyclohexene ring is clearly different among adducts **1–4**. Since the MM2 calculation suggests that the most stable conformation of the cyclohexene ring is the half-boat for all the adducts, as represented in Fig. 1, the inversion occurs between the two equivalent half-boat conformations. In order to estimate the difference in the inversion rate among the adducts, variable-temperature ^1H NMR measurements were carried out, and the coalescence temperature for the two doublet signals of the methylene protons was measured. On the basis of the coalescence temperature, the activation free energy of inversion at that temperature was calculated and is summarized in Table 1. The activation energies for **1**–**3** are comparable to each other, in spite of possessing different aromatic rings. The values are smaller than those of **4** and **5**, indicating the relative instability of the half-boat conformation in the ground state in **1**–**3**. Interestingly, the values for **3** and **4** with a naphthalene ring are quite different from each other. For the explanation for these results, therefore, it is most reasonable to consider a structural feature common to **1**–**3**, the presence of the aromatic peri-hydrogen(s) close to the methylene. The distance between the two hydrogen atoms was calculated to be *ca.* 1.7 Å, as depicted in Fig. 1. Such steric hindrance, apparently destabilizing the half-boat conformation, should be most critical for determining the inversion rate of the ring, since there is not significant difference in the activation energy among **1**–**3**. The slightly lower energy in **1** and **2** than that in **3** seems to result from the steric hindrance at two sites in the former. As for adducts **4** and **5** without such steric hindrance, the activation energy for **4** with a naphthalene ring is larger than that for **5** with a benzene ring, by 6 kJ mol^{-1}. This difference is tentatively considered to result, at least partly, from the electronic interaction between the π-electron systems of the C_{60} core and the overlying aromatic ring; the larger aromatic ring in **4** may stabilize the half-boat conformation, due to the electron-deficiency of the C_{60} core, even though the interaction could not be clearly detected by other spectroscopic methods mentioned below.

Absorption spectra

The absorption spectra of the adducts were measured in cyclohexane at room temperature. The spectra in the visible region, which are derived from the C_{60} moiety, have some common features, virtually independent of the attached aromatic rings. Fig. 2 illustrates the representative spectra of **1** and **4**. All the spectra exhibited a broad and weak absorption band around 700 nm with vibrational structures, as in the case of most C_{60}–cycloadducts reported so far.[7a,12] The position of the 0–0 transition is 703 nm for all these adducts, apparently shifted to the longer wavelength compared to that of C_{60} itself (*ca.* 620 nm).[11,13] The difference in the $S_1 \leftarrow S_0$ transition energies between them is *ca.* 1900 cm^{-1}. The sharp absorption at 433 nm, characteristic of most C_{60} adducts,[7a,12,16] was also observed in these adducts. The absorption in the region shorter than 350 nm reflects that of the attached aromatic rings to some extent, as well as the C_{60} moiety. Especially, the vibrational structures characteristic of pyrene can be observed clearly in adduct **1**, due to its large absorption coefficient, as shown in Fig. 2(*a*). Thus, the whole spectra are simply interpreted as the sum of the absorption of the C_{60} and the additional aromatic rings. The absence of the difference in the absorption bands of the C_{60} moiety is in good agreement with that in the redox potentials.† These results are ascribable to not only the lack of a strong through-bond electronic interaction between the C_{60} moiety and the attached aromatic rings due to the disconnection of both the π-conjugated systems at the cyclohexene ring, but also the lack of enough through-space interaction to modify the electronic state of the C_{60} moiety, in spite of the closeness (average *ca.* 5.8 Å, as shown in Fig. 1) of both the π-systems. The electronic interaction which brings about the difference in the activation energy of the ring inversion seems to be too small to perturb the electronic state of the C_{60} moiety. In the case of **1**, interestingly, two absorption bands absent in the other adducts were observed around 465 and 500 nm. The absorption bands of pyrene are not observed at such long wavelengths. Since pyrene has the largest π-electron system and the least ionization potential among these aromatic rings, these bands may suggest a kind of weak electronic interaction between the C_{60} and pyrene moieties, although the detail is obscure at the present stage.

Table 1 Coalescence temperature (T_c) of methylene protons and activation free energy ($\Delta G_c^{\ddagger}$) for inversion of the cyclohexene ring in adducts

Adducts	$T_c{}^a$/°C	$\Delta G_c^{\ddagger b}$/kJ mol^{-1}
1	20	55.0
2	21	55.2
3	29	57.1
4	80	69.3
5	50	63.5

[a] Measured in [$^2H_8$]toluene. [b] The activation free energy for the inversion at the coalescence temperature.

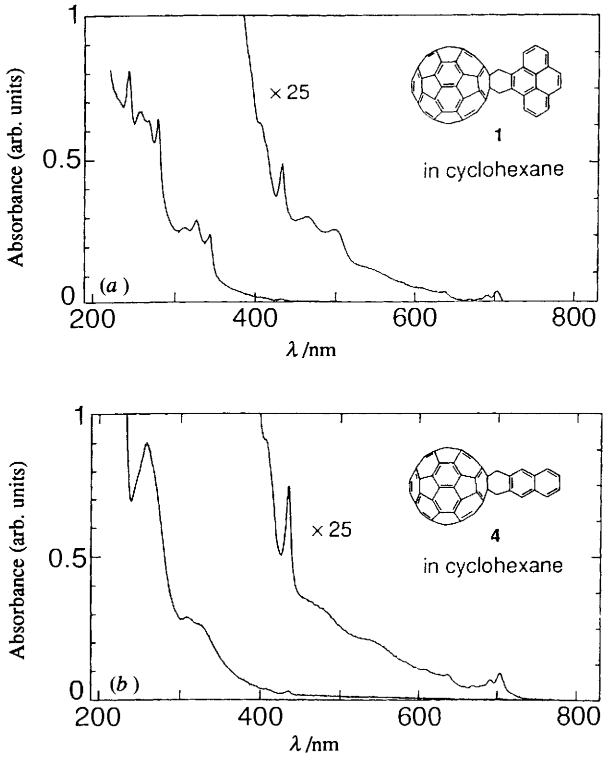

Fig. 2 Absorption spectra of (*a*) **1** and (*b*) **4** in cyclohexane at room temperature

Fluorescence spectra

The fluorescence spectra of adducts **1**–**5** were measured upon 433 nm excitation in cyclohexane at room temperature. At the excitation wavelength, only the C_{60} moiety of the adducts can be excited. For all the adducts, virtually identical fluorescence with a peak at 707 nm was observed, which resembles that of the reported TMM–C_{60} adduct.[14] Fig. 3 shows the typical fluorescence spectrum of **1**. All the spectra showed vibrational structures consisting of some shoulders, indicating the mirror image of the longest absorption band. Therefore, the peak at 707 nm can be reasonably assigned to the 0–0 component. The $S_1 \leftarrow S_0$ 0–0 transition energy in these adducts can be evaluated to be 14.2 × 10^3 cm^{-1} from the absorption and fluorescence spectra. The shape of the fluorescence spectra is also similar to that of C_{60} in the literature,[13] though the peak position is

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† The reduction potentials of adducts **1**–**5**, measured by cyclic voltammetry (CV) in benzonitrile at room temperature, were equal for all the adducts, −1.04, −1.45 and −2.01 V *vs.* the ferrocene/ferrocenium ion (Fc/Fc$^+$) redox couple. They are slightly negative-shifted compared to those of C_{60} itself (for C_{60}: −0.93, −1.35 and −1.83 V *vs.* Fc/Fc$^+$ under the same conditions), as observed in many C_{60} adducts in which one or two carbon atoms are bonded to the [6,6]-junction of the C_{60} moiety.[6,12a,c,22]

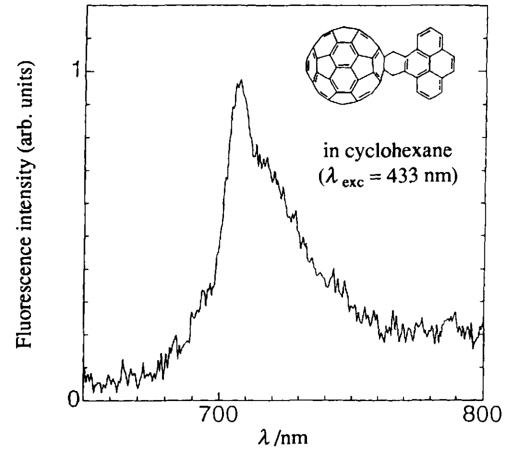

Fig. 3 Fluorescence spectrum of **1** upon 433 nm excitation in cyclohexane at room temperature

slightly blue-shifted. The Stokes shift, *i.e.* Franck–Condon instability energy, of the C_{60} adducts (~ 80 cm^{-1}) is extremely small compared to that (~ 1500 cm^{-1})[13b] of free C_{60}. The observed fluorescence intensity was weak, but intense enough to be detected at room temperature as shown in Fig. 3, while only weak and poorly resolved emission could be obtained for C_{60} itself with our fluorimeter under the same condition. Therefore, the fluorescence quantum yield (Φ_F) for the adducts was obviously enhanced relative to that of C_{60}, as has been pointed out in the case of some C_{60} derivatives reported.[14b,15] There are two possible reasons for the enhancement of C_{60} fluorescence by the substitution: (1) an increase in the fluorescence rate constant k_f compared to that of the symmetry-forbidden transition in C_{60}[17] and (2) a decrease in the rate constant of intersystem crossing from S_1 to T_1 since the completely spherical π-electron system in C_{60} is partially broken in the C_{60} adducts. The Φ_F values were almost the same in the adducts. These fluorescence spectra were independent of the excitation wavelength. Upon excitation at a wavelength shorter than 350 nm, no fluorescence due to the attached aromatic rings was observed. This is partly ascribed to much larger absorbance of the C_{60} moiety than that of the attached aromatic rings in most wavelength regions. Exceptionally, the pyrene part in **1** has almost the same absorption coefficient as the C_{60} part around 340 nm. However, even in the excitation of **1** at this wavelength, only the fluorescence such as described above was obtained without the emission from the pyrene part, though the fluorescence quantum yield of pyrene itself is known to be quite large ($\Phi_F \approx 0.6$–0.7).[18] This result suggests that the excited singlet state of the pyrene moiety ($S_{1(pyrene)}$) is efficiently quenched by the C_{60} moiety.

The fluorescence excitation spectra of **1** and **4** monitored at 707 nm are shown in Fig. 4. These spectra were in good agreement with the corresponding absorption spectra, including the sharp band at 433 nm in both compounds and also the additional bands at 465 and 500 nm in **1**. Therefore, the observed fluorescence undoubtedly results from the excited singlet state of the C_{60} moiety ($S_{1(C60)}$) of the adducts. More interestingly, the vibrational structures of pyrene could be also observed in adduct **1** [Fig. 4(*a*)], showing that the fluorescence originates not only directly from $S_{1(C60)}$ but also indirectly from $S_{1(C60)}$ *via* $S_{1(pyrene)}$. Since the energy level of $S_{1(pyrene)}$ is higher than that of $S_{1(C60)}$,‡ the energy transfer from $S_{1(pyrene)}$ to the ground state of the C_{60} moiety ($S_{0(C60)}$) obviously takes place rapidly. This is the reason why no emission from the pyrene moiety was observed. In addition, the electron transfer from $S_{1(pyrene)}$ to $S_{0(C60)}$ might compete with the energy transfer to some degree.

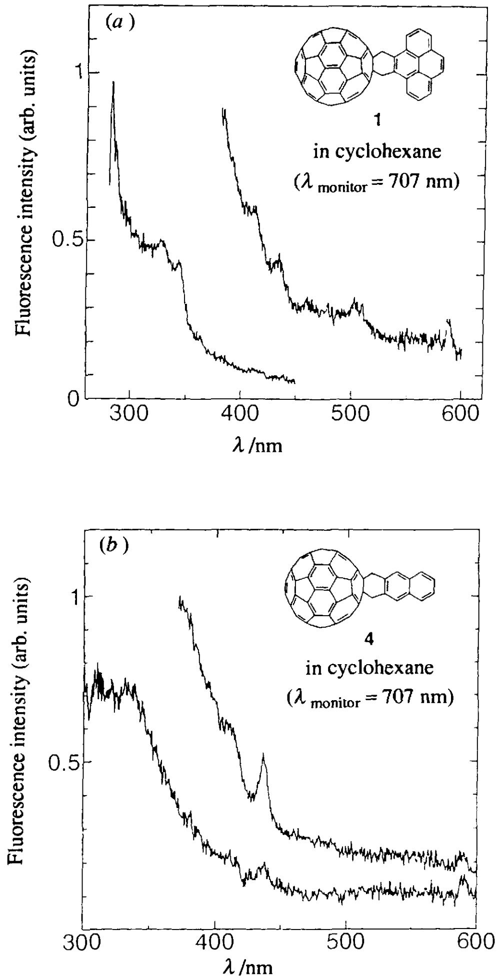

Fig. 4 Fluorescence excitation spectra of (*a*) **1** and (*b*) **4** monitored at 707 nm in cyclohexane at room temperature

Transient absorption spectra

In order to examine the photophysical and photochemical processes of adducts **1**–**5**, the transient absorption spectra were measured by laser flash photolysis. Particularly, it was interesting to examine the two possibilities of the intramolecular electron transfer from pyrene to the C_{60} part in adduct **1**. One was from $S_{1(pyrene)}$ to $S_{0(C60)}$, as described above, and the other was from $S_{0(pyrene)}$ to the triplet C_{60} moiety ($T_{1(C60)}$). The free energy changes in the intramolecular electron transfer processes for the $S_{1(pyrene)}$–$S_{0(C60)}$ and the $S_{0(pyrene)}$–$T_{1(C60)}$ systems were estimated to be −1.61 and 0.03 eV, respectively. The intermolecular electron transfer from donors such as amines to $T_{1(C60)}$ has been studied by many groups.[10,19] Foote and co-workers reported that the rate constant of intermolecular electron transfer quenching of $T_{1(C60)}$ by pyrene in benzonitrile is much smaller (k_q = 7.4 × 10^5 dm^3 mol^{-1} s^{-1}) than that by some aliphatic or aromatic amines (k_q = 10^8–10^9 dm^3 mol^{-1} s^{-1}).[19a] The quenching in adduct **1**, however, might occur more efficiently, since both pyrene and C_{60} are fixed within a molecule.

The transient absorption spectra were obtained at several delay times after laser pulsing at 308 or 355 nm in degassed

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‡ The energy levels of $S_{1(pyrene)}$ and $S_{1(C60)}$ are 322 and 170 kJ mol^{-1}, respectively, according to the S_0–S_1 absorption band of each moiety in **1**.

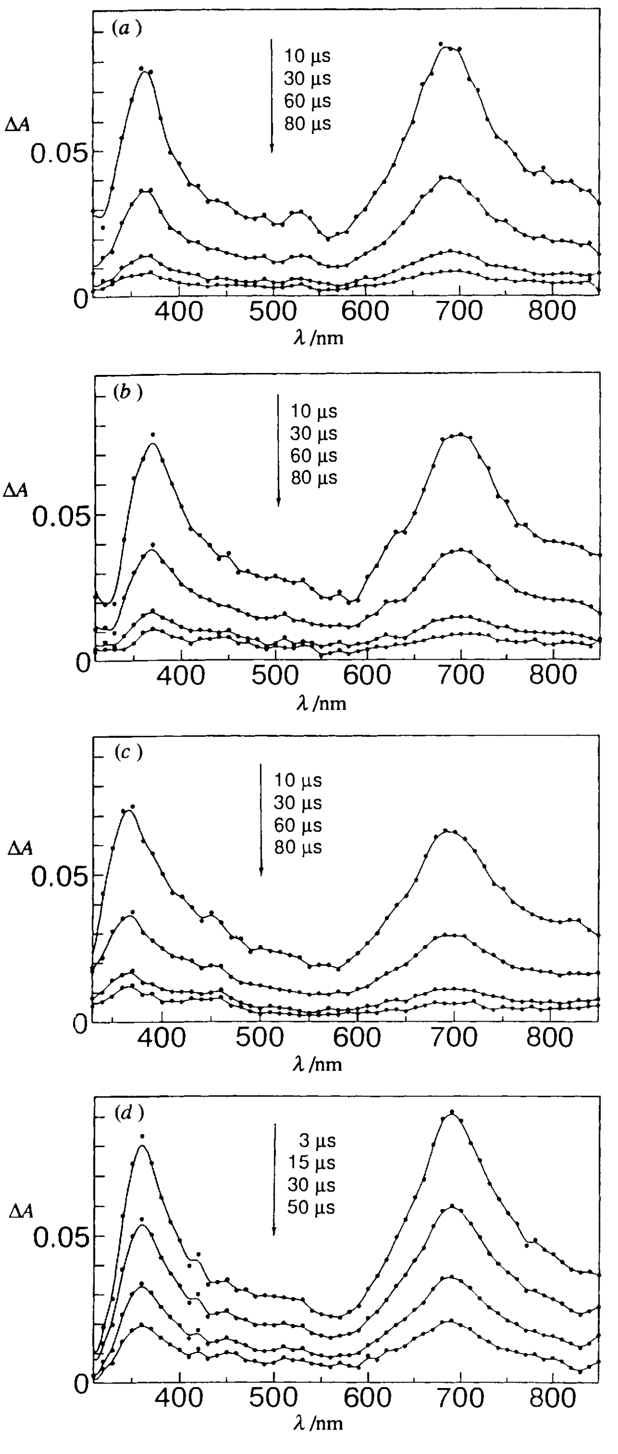

Fig. 5 Transient absorption spectra of **1** obtained by 355 nm laser photolysis in (*a*) cyclohexane and (*b*) benzonitrile, (*c*) **1** by 308 nm laser photolysis in benzonitrile and (*d*) **4** by 308 nm laser photolysis in cyclohexane at room temperature

cyclohexane (CH) or benzonitrile (BN). As in the cases of absorption and the fluorescence spectra, all the adducts showed almost identical transient absorption spectra, regardless of the solvents or the excitation wavelengths. Fig. 5 illustrates the spectra for **1** and **4**. These spectra with peaks at 370 and 700 nm are similar to that of the triplet–triplet (T–T) absorption of dihydro-C_{60} reported by Foote *et al.*,[15] and, also, that of C_{60} itself.[20] The transient absorption decays by first-order kinetics with a lifetime of about 30 μs. Therefore, it is concluded that the observed absorption is also due to the $T_n \leftarrow T_1$ transition of the C_{60} moiety in the adducts. All the adducts are considered to be photochemically stable under the experimental condition, since the transient species completely disappear about 150 μs after laser pulsing. The lifetime of the triplet species, apparently shorter than that of C_{60} measured under the similar condition, is approximately the same among the adducts, as summarized in Table 2. Upon 355 nm laser excitation of **1**, where only the C_{60} moiety is excited, the lifetimes in CH and BN are equal to each other, suggesting that $T_{1(C60)}$ is hardly quenched by the pyrene moiety. The quenching rate observed in the intermolecular reaction is not sufficiently increased even in the intramolecular case. On the other hand, the 308 nm excitation of **1** in BN may also enable the electron transfer from $S_{1(\text{pyrene})}$ to $S_{0(C60)}$. However, the obtained transient spectrum [Fig. 5(*c*)] was almost identical with that in the 355 nm laser photolysis [Fig. 5(*b*)]; the absorption due to the cation radical of the pyrene moiety could not be detected around 450 nm in Fig. 5(*c*). Therefore, the possibility of the electron transfer from $S_{1(\text{pyrene})}$ to $S_{0(C60)}$ and from $S_{0(\text{pyrene})}$ to $T_{1(C60)}$ is considered to be quite small.

Table 2 Lifetime in the triplet states of the C_{60}-adduct

Adduct	Solvent[a]	Excitation wavelength/nm	Lifetime/μs
1	CH	355	27 ± 1
1	BN	355	29 ± 1
2	CH	308	33 ± 1
4	CH	308	34 ± 1
5	CH	308	32 ± 1
5	BN	355	31 ± 1
C_{60}	CH	266	85 ± 1[b]

[a] CH and BN denote cyclohexane and benzonitrile, respectively. [b] According to ref. 10, the lifetime is in the range of 50–100 μs.

The observed agreement in the T–T absorption spectra and their lifetimes among the adducts indicates that, even in the triplet state, the electronic states of adducts **1**–**5** are almost independent of the attached aromatic rings.

Conclusions

In order to investigate the electronic properties of several stable C_{60}–*o*-quinodimethane adducts in both the ground and excited states, the redox potentials, the absorption spectra and fluorescence spectra, and the transient absorption spectra were measured. In each measurement, virtually identical results were obtained for all the adducts; the electronic properties of the C_{60} moiety in these adducts are independent of the attached aromatic rings. This result shows that there is only a little electronic interaction between the C_{60} moiety and aromatic rings, either through-space or through-bond.

On the other hand, in the activation energy of the ring inversion, a remarkable difference was found among the adducts. This difference is concluded to be mainly caused by the steric effect rather than the electronic interaction.

In variation of the aromatic rings attached to the C_{60} moiety, from benzene to pyrene, their electronic structures are almost the same as each other. It is, therefore, possible to prepare various C_{60} derivatives without altering the electronic state of the C_{60} core by this kind of cycloaddition, so that much wider modification can be allowed to design a structurally complex C_{60}-containing monomer or assembly unit in functional materials.

Experimental

General

^1H and ^{13}C NMR spectra were measured on a Varian Gemini-200 or a JEOL α-500 spectrometer. For measurements at room temperature, mixed solvent of $CDCl_3$ and CS_2 (1 : 1, v/v) was used, and $[^2H_8]$toluene in variable temperature measurements. The chemical shifts are given from Me_4Si as the internal standard. Absorption spectra were recorded on a JASCO Ubest-50 spectrophotometer. Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi-4010 spectrofluorimeter. These spectra were obtained in cyclohexane (spectroscopic grade) with a quartz cell of 10 mm optical path. The sample concentration is in the range of 10^{-5}–10^{-4} mol dm^{-3} The absorbance of the solutions was adjusted to *ca.* 0.4 at the excitation wavelength for fluorescence spectra. The excitation spectra were measured by monitoring the fluorescence at 707 nm at *ca.* 10^{-5} mol dm^{-3}. Spectra were corrected for instrumental response by use of a rhodamine B quantum counter.

Electrochemical measurements

Cyclic voltammetry (CV) was performed on a Hokuto HAB-151 potentiostat/galvanostat with a function generator. The working electrode was a platinum disk and the counter electrode a platinum wire. The reference electrode was an Ag/0.01 mol dm^{-3} $AgNO_3$ electrode filled with 0.1 mol dm^{-3} Bu_4NPF_6 in benzonitrile (BN). Measurements were run at room temperature on a 1 mmol dm^{-3} solution of the sample in BN containing 0.1 mol dm^{-3} Bu_4NPF_6 as the supporting electrolyte, after the solution was deaerated by bubbling argon gas. Voltammograms were recorded on a Graphtec WX-1100 X-Y recorder at a sweep rate of 200 mV s^{-1}. All the potentials were referenced to the Fc/Fc^+ redox couple observed at +0.07 V *vs.* $Ag/AgNO_3$.

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) or a XeCl excimer laser (Lambda Physik LEXTRA 50, 308 nm, pulse width 17 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 monochromator (Ritsu MC-20N) was detected by a photomultiplier tube (Hamamatsu R928) and recorded on a digitizing oscilloscope (Tektronix TDS 540). The time profiles were analysed by a personal computer (NEC PC-9821 Ap). The sample solution was degassed by at least three freeze-and-thaw cycles on a high vacuum line. The absorbance of the solutions was adjusted to *ca.* 0.7 at the excitation wavelength.

Preparation of adducts 1–3[9]

These adducts were synthesized by the reaction of C_{60} and the corresponding dihydrocyclobutaarenes, which were prepared by the methods reported previously.[21] For example, C_{60} (6.1 mg, 0.036 mmol) and 1,2-dihydrocyclobuta[*a*]naphthalene (5.6 mg, 0.036 mmol) dissolved in tetralin (1.8 cm^3) were maintained at the reflux temperature for 1 h, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, benzene–hexane) to afford the mono-adduct **3** (6.9 mg, 0.0079 mmol) and the di-adducts composed of some isomers, along with the recovery of C_{60}. The separation of the di-adducts was unsuccessful.

3. δ_H[500 MHz, $CDCl_3$–CS_2 (1 : 1), room temp.] 4.6–5.4 (4 H, br s), 7.57 (1 H, m), 7.63 (1 H, m), 7.80 (1 H, d, *J* 8.2 Hz), 8.03 (1 H, d, *J* 7.9 Hz), 8.03 (1 H, d, *J* 8.2 Hz) and 8.38 (1 H, d, *J* 7.9 Hz); δ_C[125 MHz, $CDCl_3$–CS_2 (1 : 1), room temp.] 39.75 (benzylic), 45.81 (benzylic), 66.15 (aliphatic quaternary carbon of C_{60}), 122.65, 125.61, 126.76, 127.88, 129.11, 131.20 (aromatic C–H), 133.37, 133.82, 135.91, 140.09, 141.53, 141.94, 142.06, 142.12, 142.47, 142.94, 144.57, 145.32, 145.63, 146.10, 146.36, 147.52 and 156.33; *m*/*z* (FAB) 874 (M^+).

Preparation of 4[8]

C_{60} (100 mg, 0.139 mmol), 1,2-bis(bromomethyl)naphthalene (43.6 mg, 0.139 mmol), 18-crown-6 (284 mg, 0.133 mmol) and KI (50.0 mg, 0.30 mmol) were refluxed in toluene under a nitrogen atmosphere for 6 h. The reaction mixture was allowed to cool to room temperature, washed with 5% aq. NaOH and then H_2O and then evaporated. The residue was stirred with MeOH (25 cm^3), THF (15 cm^3) and 10% aq. NaOH (40 cm^3) for 2 h at room temperature. The mixture was extracted with benzene three times and the extracts were washed with H_2O and dried ($MgSO_4$). After the solvent was evaporated, the residue was purified by column chromatography (SiO_2, benzene–hexane) to afford mono-adduct **4** (25.6 mg, 0.029 mmol) and the di-adducts composed of some isomers, along with the recovery of C_{60}: δ_H[500 MHz, $CDCl_3$–CS_2 (1 : 1), room temp.] 4.58 (2 H, d, *J* 13.7 Hz), 5.04 (2 H, d, *J* 13.7 Hz), 7.57 (2 H, m), 7.99 (2 H, m) and 8.11 (2 H, s); δ_C[125 MHz, $CDCl_3$–CS_2 (1 : 1), room temp.] 45.22 (benzylic), 65.62 (aliphatic quaternary carbon of C_{60}), 126.05, 126.46, 128.65 (aromatic C–H), 133.35, 135.22, 135.89, 136.13, 139.99, 140.25, 141.46, 141.66, 141.97, 142.02, 142.14, 142.50, 144.61, 145.01, 145.17, 145.34, 145.38, 145.50, 145.58, 146.10, 146.20, 146.35, 146.39, 147.58, 156.34 and 156.58; *m*/*z* (FAB) 874 (M^+).

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