

## Photophysical and Photochemical Properties of Decakis-Adduct of C<sub>120</sub> and Related Compounds

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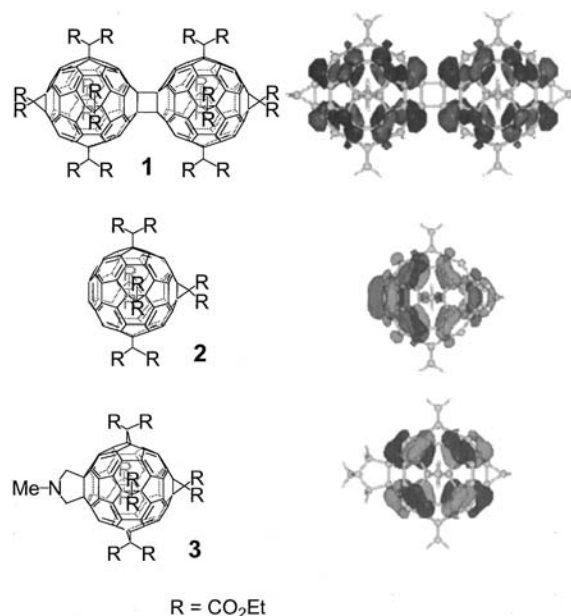
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Photophysical and photochemical properties of a decakis-adduct of C<sub>120</sub> and related compounds were investigated. Ground state absorption spectrum of the C<sub>120</sub> derivative showed structureless feature due to the interaction of fullerene-cages. The fluorescence quantum yields of the adducts showed ten times increase compared with pristine C<sub>60</sub>, while they were 1/6 of a hexapyrrolidine derivative of C<sub>60</sub>. Triplet absorption bands appeared at 670 nm. The quantum yields for the intersystem crossing of the adducts were as small as 0.12–0.19.

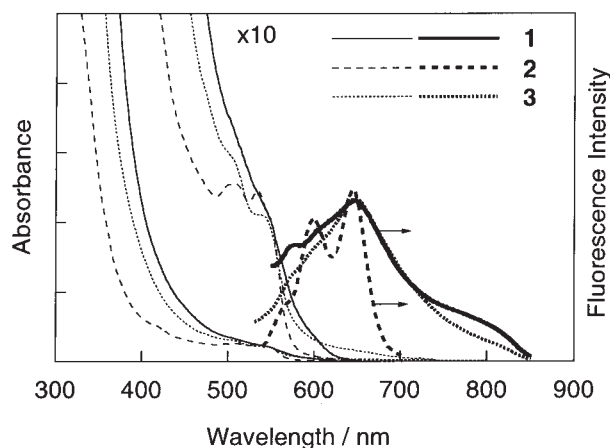
Recently, highly symmetrical adducts of fullerenes have been synthesized by some groups.<sup>1–7</sup> These fullerene adducts have been applied to a core block of a dendrimer molecule<sup>4</sup> or an organometallic ligand.<sup>5</sup> Furthermore, excellent fluorescence and phosphorescence properties of a hexapyrrolidine derivative of C<sub>60</sub> are interesting from the viewpoint of the application in the electroluminescence and magneto-optic media.<sup>6</sup> Fujiwara et al. reported that the highly symmetrical decakis-adduct of C<sub>120</sub> with D<sub>2h</sub> symmetry (**1**) can be obtained by the Bingel cyclopropanation reaction of C<sub>120</sub>, a dimer of C<sub>60</sub>, using 9,10-dimethylantracene as a template.<sup>7</sup> For the highly symmetrical adduct of fullerene-dimer, interesting properties such as high fluorescence yield can be expected. In the present paper, we report excited singlet and triplet properties of **1**, which are compared with pentakis-adduct of C<sub>60</sub> (**2**) and hexakis-adduct of C<sub>60</sub> (**3**) (Figure 1).

Compounds **1**, **2**, and **3** were synthesized as reported in the previous paper.<sup>7</sup> A toluene solution of **1** is yellow, which is similar to **3**. On the other hand, **2** in toluene is orange. It should be stressed that **1** and **3** have the similar electronic systems, while larger  $\pi$ -conjugation system is present in **2**, as indicated in HOMO patterns (Figure 1), which were estimated by PM3 calculations. Absorption spectrum of **1** is structureless compared with that of **3** (Figure 2): Shoulder bands of **3** at 538 nm and around 500 nm are obscure in absorption spectrum of **1**. Structureless feature of **1** can be attributed to the interaction of transition dipole moments of two fullerene-cages of **1**.

Upon excitation with 420 nm-light, which excited fullerene moiety, **1** showed a fluorescence band at 645 nm with shoulders around 800 and 590 nm (Figure 2). The observed fluorescence bands are close to those of **3**, which showed a peak at 647 nm with a shoulder around 600 nm. On the other hand, **2** showed fluorescence bands at 644 and 597 nm with a shoulder around 580 nm. These fluorescence bands of **1**, **2**, and **3** are located at shorter wavelength-side compared with those of pristine C<sub>60</sub>,<sup>8</sup> mono-adducts of C<sub>60</sub>,<sup>9</sup> and C<sub>120</sub>,<sup>10</sup> which showed fluorescence band around 730 nm. These findings are in agreement with the fact that the  $\pi$ -conjugation system of C<sub>120</sub> or C<sub>60</sub> is diminished in these highly symmetrical adducts. Fluorescence peak positions

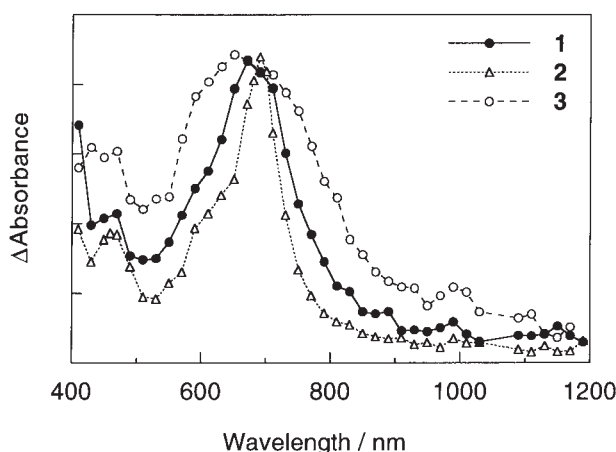


**Figure 1.** Molecular structures and HOMO patterns of highly symmetrical adducts of C<sub>120</sub> and C<sub>60</sub>.



**Figure 2.** Absorption (thin lines) and fluorescence (thick lines) spectra of **1**, **2**, and **3** in toluene. Excitation: 420 nm.

indicate that the HOMO-LUMO gaps of these adducts become large with increase of the number of the addends. Fluorescence quantum yields ( $\Phi_F$ ) were estimated to be  $3.4 \times 10^{-3}$ ,  $2.0 \times 10^{-3}$ , and  $3.7 \times 10^{-3}$  for **1**, **2**, and **3**, respectively, by using tetraphenylprophyrin as a standard ( $\Phi_F = 0.15$ ).<sup>11</sup> These values are 10 times larger than that of pristine C<sub>60</sub> ( $3.2 \times 10^{-4}$ ).<sup>12</sup> On the



**Figure 3.** Transient absorption spectra of **1**, **2**, and **3** in toluene at 100 ns after the 532 nm-laser irradiation.

other hand, compared with the previously reported hexapyrroline derivative of  $C_{60}$ , the  $\Phi_F$  values of **1** and **3** are smaller by factor of 1/6.<sup>6</sup> The smaller  $\Phi_F$  values of the present derivatives accord with the fact that the  $\Phi_F$  values of methanofullerenes are smaller than pyrrolidino-fullerenes.<sup>9,13</sup> The fluorescence lifetimes of **1**, **2**, and **3** were estimated to be 1.8, 2.3, and 1.8 ns, respectively. These values are longer than those of pristine  $C_{60}$  (1.3 ns),<sup>8</sup> mono-adducts of  $C_{60}$  (1.3 ns),<sup>9</sup> and  $C_{120}$  (1.6 ns).<sup>10</sup>

Upon 532 nm-laser excitation of **1** in toluene, a transient absorption band was observed at 670 nm as shown in Figure 3. The absorption band can be attributed to the triplet excited state of **1**, since the absorption band was quenched in the presence of molecular oxygen, a triplet energy quencher: The quenching rate constant was estimated to be  $3.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The transient peak position of **1** is located at shorter wavelength compared with **2** (690 nm),  $C_{120}$  (700 nm),<sup>14</sup> mono-adducts of  $C_{60}$  (680–700 nm)<sup>9</sup> and pristine  $C_{60}$  (750 nm).<sup>15</sup> The peak position of **1** is similar to that of **3** (660 nm), while **3** showed broad transient absorption spectrum. The transient absorption bands of **1** and **3** at shorter wavelength-side seem to result from diminished  $\pi$ -electron systems of these adducts. The lifetimes of the triplet excited states of **1**, **2**, and **3** were evaluated to be 31, 27, and 26  $\mu\text{s}$ , respectively, which are on the same order with other fullerene derivatives.<sup>9,14,15</sup>

It should be noted that the intensities of the transient absorption bands of **1**, **2**, and **3** were quite weak compared with that of pristine  $C_{60}$ . The extinction coefficients of the triplet absorption bands ( $\epsilon_T$ ) around 670 nm were evaluated to be  $8.3 \times 10^3$ ,  $1.1 \times 10^4$ , and  $6.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  for **1**, **2**, and **3**, respectively, which are similar values to those of  $C_{60}$  ( $1.6 \times 10^4$ ) and mono-adducts of  $C_{60}$  ( $0.6\text{--}1.4 \times 10^4$ ),<sup>9,15</sup> indicating that the  $\epsilon_T$  values of **1**, **2**, and **3** are sufficiently large to observe intense transient absorption bands. Thus the weak transient absorption bands of the present adducts can be attributed to the small quantum yields for the intersystem crossing processes ( $\Phi_{ISC}$ ). From the comparison of the emission intensities of the singlet oxygen generated by the energy transfer processes from the triplet excited adducts to molecular oxygen, the  $\Phi_{ISC}$  values were estimated to be 0.19, 0.12, and 0.17, for **1**, **2**, and **3**, respectively.<sup>16</sup> The estimated  $\Phi_{ISC}$  values were quite small compared with pristine  $C_{60}$  (0.98) and mono-adducts of  $C_{60}$  (0.8–

1.0).<sup>9,15</sup> These findings indicate that the singlet excited states of highly symmetrical adducts **1**, **2**, and **3** deactivate via the non-radiative deactivation processes, mainly.

After repeated laser irradiation of **1** in toluene, new absorption bands appeared at 534 and 495 nm in the ground state absorption spectrum. These absorption bands are essentially the same as those of **2**. The finding indicates that **1** generates **2** in the course of repeated laser irradiations by the dissociation of the [2 + 2] bonds connecting two fullerene-cages. Thus, the above laser flash photolysis experiments were conducted always with fresh sample. Since the  $\Phi_{ISC}$ ,  $\Phi_F$ , singlet and triplet lifetimes of **1** and **3** are almost identical, bond dissociation is considered to be a minor process of the singlet and/or triplet excited states of **1**.

In summary, highly symmetrical adducts of  $C_{120}$  showed interesting properties such as ground state interaction of fullerene cages and enhanced fluorescence yield. These adducts can be regarded as three-dimensional building blocks in the organic chemistry. Further interesting optical properties are expected for such organized compounds.

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