

## Unusual Photophysical Properties of Emerald Green [60]Fullerene

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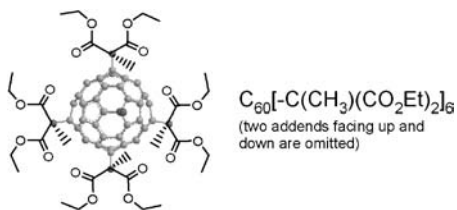
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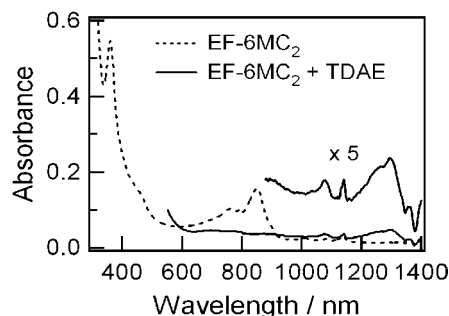
Near-IR absorptive emerald green [60]fullerene (EF-6MC<sub>2</sub>) is capable of highly light-harvesting molecule. Photoinduced intermolecular electron transfer between EF-6MC<sub>2</sub> and several electron donors in benzonitrile led to observation of the optical absorption of (EF-6MC<sub>2</sub>)<sup>-•</sup> at 1300 nm, the longest absorption wavelength among many [60]fullerenyl radical anions.

Fullerenyl chromophore materials exhibiting photovoltaic characteristics to facilitate the transfer of light energy into electrical current become current intense interest in materials research. In the presence of electron donors in either mixtures or covalent bonding environments, photoinduced intermolecular or intramolecular electron transfer occur efficiently from the donor moiety to the C<sub>60</sub> cage, especially, in the case of [60]-fullerene monoadducts.<sup>1</sup> Our emerald green fullerenes (EF<sub>n</sub>) represent a new class of hexafunctionalized C<sub>60</sub> derivatives exhibiting long-wavelength optical absorption and are named according to their intrinsic green color of the material. In general, as the number of covalently bound addends increases, electron affinity of the fullerene cage moiety decreases. This is not the case for highly near-IR absorptive EF<sub>n</sub> compounds<sup>2-5</sup> that may allow them to play an essential role in harvesting the light in long wavelength regions (>700 nm). Synthesis of one EF<sub>n</sub> analogous 8,13,18,40,45,50-hexa[2-(diethyl-2-methylmalonato)][60]fullerene, C<sub>60</sub>[-C(CH<sub>3</sub>)(CO<sub>2</sub>Et)<sub>2</sub>]<sub>6</sub>, (in short, EF-6MC<sub>2</sub>) was carried out by hexaanionic C<sub>60</sub> chemistry (Figure 1).<sup>5</sup> Here, we report unusual photophysical properties and electron-transfer behavior of EF-6MC<sub>2</sub> in comparison with that of pristine C<sub>60</sub>.

Compared with pristine C<sub>60</sub>, notable shifts of optical absorption peaks in the spectrum of EF-6MC<sub>2</sub> were observed in UV-vis and near-IR ranges (Figure 2) with four absorption maxima centered at 360, 460, 760, and 850 nm. Further red shift of these optical absorption peaks can be made by the addition of a strong reducing reagent tetrakis(dimethylamino)ethylene (TDAE) in *o*-dichlorobenzene. The addition induced several new broad absorption bands appearing in the 1000–1400 nm region with a peak maximum centered at 1300 nm, which was assigned to the absorption of EF<sub>n</sub> radical anion (EF-6MC<sub>2</sub>)<sup>-•</sup>. This wave-



**Figure 1.** The structure of one emerald green [60]fullerene (EF-6MC<sub>2</sub>).

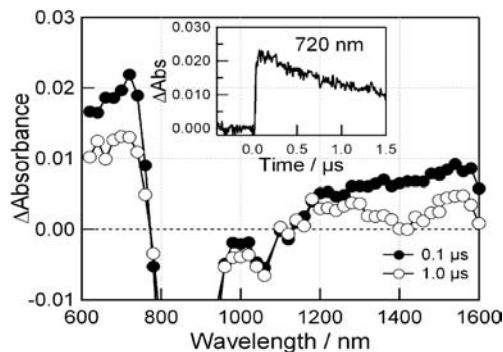


**Figure 2.** UV-vis and near-IR spectra of EF-6MC<sub>2</sub> in the absence and presence of TDAE in *o*-dichlorobenzene.

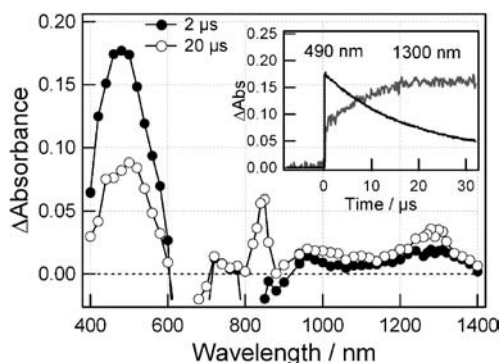
length is apparently much longer than that of pristine C<sub>60</sub> radical anion (C<sub>60</sub>)<sup>-•</sup> observed at 1080 nm.<sup>6</sup>

Steady-state emission spectrum of EF-6MC<sub>2</sub> in toluene upon photoexcitation at 360 nm showed broad weak fluorescence bands in the 700–900 nm region, which is longer than that of the pristine C<sub>60</sub> at 700 nm indicating a lower singlet excited state of EF-6MC<sub>2</sub> compared with that of pristine C<sub>60</sub>. The corresponding fluorescence time profile exhibited an exponential decay with a lifetime ( $\tau_f$ ) of 1.46 ns which is slightly longer than that of C<sub>60</sub> (1.2 ns).<sup>7</sup>

Nanosecond transient absorption studies of EF-6MC<sub>2</sub> were performed in Ar-saturated toluene and benzonitrile by applying 355-nm laser light. Transient absorption spectra of EF-6MC<sub>2</sub> (Figure 3) showed the absorption of its triplet state <sup>3</sup>(EF-6MC<sub>2</sub>)<sup>\*</sup> at 720 nm in close resemblance to the triplet state of pristine C<sub>60</sub>. Depletion of the peak intensity at 800–900 nm is attributed to the fluorescence of EF-6MC<sub>2</sub> in response to 355-nm excitation. It is notable that the broad bands were observed in the 1100–1600 nm region, which may be also corresponding to absorption of its triplet state. Such absorption bands in the longer wavelength



**Figure 3.** Transient absorption spectra obtained by 355-nm laser light of EF-6MC<sub>2</sub> (0.1 mM) in Ar-saturated benzonitrile. Inset: Time profile at 720 nm.



**Figure 4.** Transient absorption spectra obtained by 355-nm laser excitation of EF-6MC<sub>2</sub> (0.1 mM) and ZnPc (0.1 mM) in benzonitrile. Inset: Time profiles at 490 and 1300 nm ( $\times 10$ ).

of triplet state are also one of the characteristic of EF-6MC<sub>2</sub>.

From the time profile at 720 nm in inset of Figure 3, the lifetime of <sup>3</sup>(EF-6MC<sub>2</sub>)<sup>\*</sup> was evaluated to be 2.0 μs which is shorter than the reported values of pristine <sup>3</sup>C<sub>60</sub><sup>\*</sup> under various conditions (40–143 μs).<sup>7,8</sup> Decay rate of <sup>3</sup>(EF-6MC<sub>2</sub>)<sup>\*</sup> was found to be independent of molecular oxygen (O<sub>2</sub>) in solution, suggesting no energy transfer from <sup>3</sup>(EF-6MC<sub>2</sub>)<sup>\*</sup> to O<sub>2</sub>, implying no generation of singlet oxygen (<sup>1</sup>O<sub>2</sub><sup>\*</sup>). This revealed that the energy of <sup>3</sup>(EF-6MC<sub>2</sub>)<sup>\*</sup> is in comparable or lower than that of <sup>3</sup>O<sub>2</sub> (1.1 eV).<sup>9</sup> By the fact that <sup>3</sup>C<sub>60</sub><sup>\*</sup> can be fully quenched by O<sub>2</sub>, it is suggested that the energy of <sup>3</sup>(EF-6MC<sub>2</sub>)<sup>\*</sup> is appreciably lower than that of pristine <sup>3</sup>C<sub>60</sub><sup>\*</sup>.

In order to investigate electron transfer in a mixture system of EF-6MC<sub>2</sub> and zinc phthalocyanine (ZnPc), nanosecond transient absorption spectra (Figure 4) were recorded for photoexcitation of ZnPc in the presence of EF-6MC<sub>2</sub> upon 355-nm laser excitation in Ar-saturated benzonitrile. The spectrum at 2 μs after laser light exposure showed the characteristic peak of the triplet state of ZnPc (<sup>3</sup>ZnPc<sup>\*</sup>) at 490 nm with a decay rate constant equal to  $5.8 \times 10^5 \text{ s}^{-1}$ . Interestingly, in a long time scale (20 μs) after laser light exposure, the decay of <sup>3</sup>ZnPc<sup>\*</sup> was accompanied with the concomitant rise of two bands with peak maxima at 840 and 1300 nm. These two peaks can be assigned to the absorptions of ZnPc radical cation (ZnPc<sup>•+</sup>)<sup>10,11</sup> and (EF-6MC<sub>2</sub>)<sup>•-</sup>, respectively. The latter is in good agreement with the observed absorption band of (EF-6MC<sub>2</sub>)<sup>•-</sup> in Figure 2. These findings indicated clearly the occurrence of intermolecular electron transfer from <sup>3</sup>ZnPc<sup>\*</sup> to EF-6MC<sub>2</sub> in microsecond time scale. The second-order rate constant ( $k_q$ ) for <sup>3</sup>ZnPc<sup>\*</sup>-quenching was evaluated to be  $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which is almost the same with the electron-transfer rate constant when the electron-transfer quantum yield is high. The feasibility of the electron-transfer process from the <sup>3</sup>ZnPc<sup>\*</sup> to EF-6MC<sub>2</sub> is supported by the free-energy change ( $\Delta G_{\text{et}}$ ), which was evaluated to be  $-0.39 \text{ eV}$  in benzonitrile by the Rehm–Weller equation,<sup>12</sup> on employing the reported electrochemical data.<sup>5</sup> Contrarily, transient absorption spectra recorded in toluene exhibited only the absorption band of <sup>3</sup>ZnPc<sup>\*</sup> without the appearance of (EF-6MC<sub>2</sub>)<sup>•-</sup> suggesting no electron-transfer process in non-polar medium (see SI).<sup>13</sup>

For EF-6MC<sub>2</sub>/zinc naphthalocyanine (ZnNc) and EF-6MC<sub>2</sub>/zinc porphyrin (ZnP) mixtures, the electron-transfer processes were similarly observed in polar solvent (see SI).<sup>13</sup> Furthermore, by adding 4-(*N,N*-diethylamino)benzaldehyde

diphenylhydrazone (DBDH), which is one of the strong electron donors, electron-transfer process via <sup>3</sup>(EF-6MC<sub>2</sub>)<sup>\*</sup> was observed in benzonitrile (SI).<sup>13</sup> The higher  $k_q$  value of EF-6MC<sub>2</sub>/DBDH ( $1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) compared with EF-6MC<sub>2</sub>/ZnNc can be explained by more negative free-energy of the electron-transfer process for EF-6MC<sub>2</sub>/DBDH mixture system ( $-0.59 \text{ eV}$  in benzonitrile).

Backward electron-transfer process leading to the initial ground states was followed by a longer time-scale measurement until 200 μs after the laser-light pulse excitation. Accordingly, both species (EF-6MC<sub>2</sub>)<sup>•-</sup> and ZnPc<sup>•+</sup> showed slow decays after reaching maximal absorbance. The rate of back electron transfer was evaluated as  $3.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , on employing the molar extinction coefficient of ZnPc<sup>•+</sup> to be  $1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>10,11</sup>

In summary, near-IR absorptive emerald green [60]fullerene (EF-6MC<sub>2</sub>) showed unusual photophysical behavior as compared with the pristine C<sub>60</sub>. Photoinduced intermolecular electron transfer between EF-6MC<sub>2</sub> and excited triplet states of zinc porphyrins and zinc phthalocyanines as electron donors led to the observation of red-shifted absorption of the resulting emerald fullerene radical anion to 1300 nm. The electron transfer via <sup>3</sup>EF-6MC<sub>2</sub><sup>\*</sup> was observed by adding 4-(*N,N*-diethylamino)benzaldehyde in benzonitrile. These near-IR absorptive emerald green [60]fullerenes might be applicable to many nanoelectronic devices.

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- Nanosecond transient spectra of EF-6MC<sub>2</sub> with ZnP, ZnNc, and DBDH in benzonitrile are shown as Supporting Information, which is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journal/chem-lett/index.html>.