

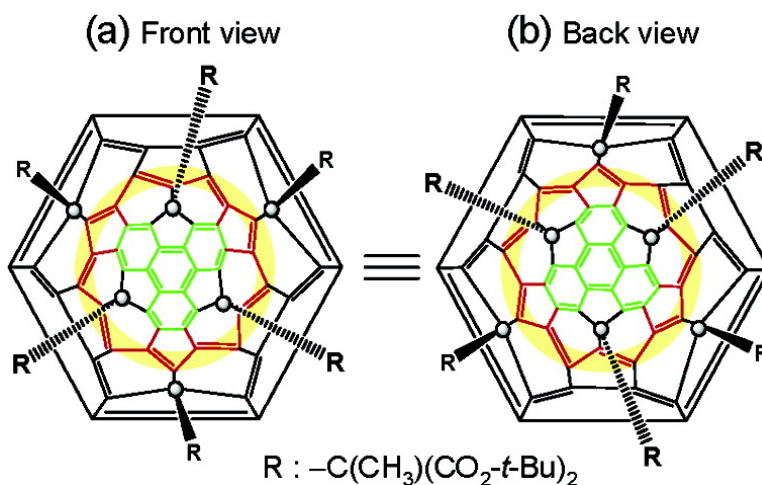
Communication

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Intense Near-Infrared Optical Absorbing Emerald Green [60]Fullerenes

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Synthesis of “emerald green fullerenes” (EF) was first reported by Taylor by S_N2' substitution reactions of anionic diethyl 2-bromomalonate in replacing three fluorine atoms of $C_{60}F_{18}$,^{1–3} located at the outer perimeter of the 18-fluorinated half-sphere. That resulted in the beltlike trannulene formation in $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ **1**.⁴ This conjugated trannulene ring is interconnected with a triphenylene moiety as the major chromophore structure in **1** that contributes to its optical absorption at λ_{max} 612 and 658 nm.

We *unexpectedly* found a new approach toward the synthesis of green-colored EF compounds in gram quantity by using hexaanionic C_{60} intermediate (C_{60}^{-6}), as a reagent in one-pot reaction, for attaching six addends on one C_{60} cage. We were also aware of the highly reactive and unstable nature of hexaanionic fullerene species in solution. Its low stability might be interpreted by ultrahigh negative charge density with repulsion among the six same charges in a close vicinity on the spherical surface of only 10 Å in diameter. Polyanionic C_{60} attracted numerous theoretical interests and calculations for prediction of their electronic characteristics.^{5,6} The hexaanionic C_{60} cage possesses delocalized π -electrons ring current as evidenced by strong endohedral shielding of the internally encapsulated 3He atom.⁷ The C_{60}^{-n} intermediates, including C_{60}^{-6} , were first prepared⁸ in 1991 and observed later by electrochemical signals upon accepting up to six electrons consecutively with confirmation of the redox reversibility in cyclic voltammetry measurements.⁹

The solution generation of polyanionic C_{60} and $^3He@C_{60}$ intermediates^{7,10} was reported by the treatment of C_{60} with excessive lithium metal or potassium with naphthalene.¹¹ The resulting polyanions were characterized by the corresponding single ^{13}C NMR peak at δ 156.7 for C_{60}^{-6} . C_{60}^{-n} intermediates were subsequently trapped by methyl iodide to afford polymethylated C_{60} derivatives.⁸ When C_{60}^{-n} intermediates were trapped by 1,4-butane-sultone as an electrophile with simultaneous quenching of excessive metal naphthalenide, hexa(sulfo-*n*-butyl)[60]fullerene regioisomers (FC₄S, a hexaadduct) were obtained as major products, indicating C_{60}^{-6} as the major component in the polyanionic mixture.¹² In further trapping experiments with diethyl 2-bromomalonate, we also found the formation of highly symmetrical pentakis(ethylmalonate) and known yellow hexakis(ethylmalonate) adducts of methano[60]-fullerene as major products from C_{60}^{-6} . The symmetrical structure of the former compound was confirmed by X-ray single-crystal structural analyses. That suggested possible even localization of fullerene anion α -bromoethylmalonate complex intermediate at the bimolecular reaction center. Additional investigation led to our discovery of a new series of emerald green [60]fullerenes EF-6MC_{*n*} in a chemical structure different from that of Taylor's fluorinated EF compounds.

Synthesis of EF-6MC₂ was made by the treatment of deoxygenated C_{60} solution in toluene–THF with sodium naphthalenide (10 equiv) for 2.0 h at ambient temperature. To the blackish suspension was added diethyl 2-bromo-2-methylmalonate (excess), and it was

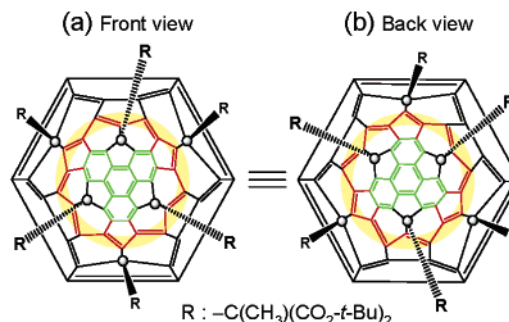


Figure 1. Schlegel diagram of EF-6MC₄ **3** showing bonding positions of six addends (a) in the front view and (b) in the back view, as determined by X-ray single-crystal structural analyses.

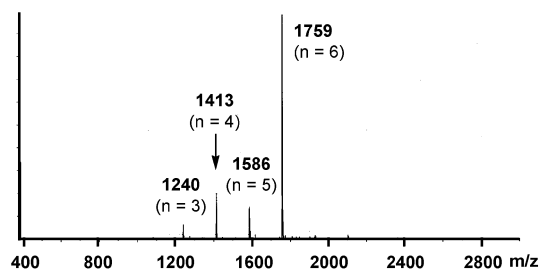


Figure 2. DCI[−] mass spectrum of $C_{60}[C(CH_3)(CO_2Et)_2]_n$ **2** ($n = 6$).

allowed to react for an additional 12 h at ambient temperature. After workup and separation of the solids by precipitation cycles, the products were purified via preparative thin-layer chromatography (PTLC, SiO₂, THF:toluene, 1:9) to afford $C_{60}[C(CH_3)(CO_2Et)_2]_6$ **2** (EF-6MC₂, $R_f = 0.3$) as dark green solids in roughly 30% yield and brown solids ($R_f = 0.3–0.4$, ~35% yield, assuming regioisomers of the hexaadduct). Similarly, $C_{60}[C(CH_3)(CO_2-t-Bu)_2]_6$ **3** (EF-6MC₄) was obtained in comparable yields by quenching C_{60}^{-6} with di-*tert*-butyl 2-bromo-2-methylmalonate.

Both EF compounds **2** and **3** gave bright green solution, such as in CHCl₃, THF, CS₂, and ClCH₂CH₂Cl. A green spot can be easily observed during elution on the TLC plate. Growth of EF-6MC₂ single crystals in an appreciable size was proven to be difficult. However, bulky hexaadduct EF-6MC₄ gave green crystals from ClCH₂CH₂Cl in reasonable quality that allowed subsequent structural determination by X-ray single-crystal structural analyses, showing a single covalent bond between each addend and the fullerene carbon with a bond length of 1.595 Å (Figure 1).¹³

Both FAB⁺ and desorption chemical ionization (DCI[−]) mass spectra of **2** showed the molecular ion peak (M^+) at m/z 1759 corresponding to the ion mass consisting of six addends on C_{60} (Figure 2). Subsequent fragmentation gave ion mass peaks at m/z 1586, 1413, and 1240, corresponding to the mass loss of one, two, and three addends, respectively. That confirmed the molecular weight of EF-6MC₂. Remarkably, ^{13}C NMR spectrum of **2** displayed only five aromatic carbon signals at δ 155.9, 152.2, 146.1, 142.7,

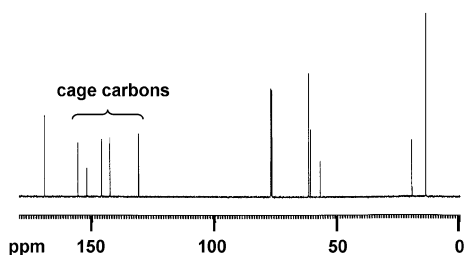


Figure 3. ^{13}C NMR spectrum of EF-6MC₂ **2** showing only five fullerenic carbon peaks in the region of 120–160 ppm.

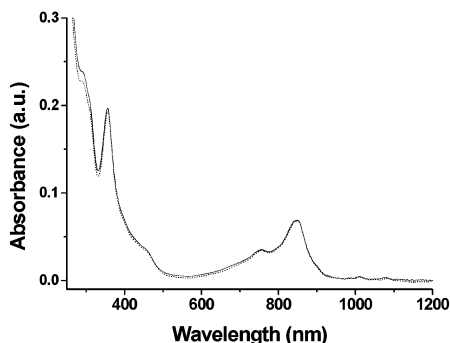


Figure 4. Steady-state UV–vis spectrum of **2** (—) and **3** (···) in chloroform (6.5×10^{-6} M).

and 131.0, corresponding to 54 fullerenic sp^2 carbons and a *single* fullerenic sp^3 carbon signal at δ 57.1 (Figure 3). Observation of a few fullerenic sp^2 and sp^3 carbon peaks revealed fascinating symmetrical arrangement of the addends on the cage surface that correlates to the highest possible molecular symmetry of this heptad.

Notable optical absorption spectra of this class of C_{60} derivatives were observed in the visible–near-IR range as shown in Figure 4. UV–vis spectra of all EF-6MC_{*n*} heptads in CHCl_3 showed a nearly identical profile with four optical absorption maxima at 360 ($\epsilon = 37\,755$), 460 ($\epsilon = 6377$), 760 ($\epsilon = 6632$), and 850 ($\epsilon = 12\,755$ L/mol·cm). Surprisingly, the latter two peaks were found to be located in the near-IR range that is, perhaps, responsible for the green color of the material. The coefficient value of the 850-nm band reaches nearly 33% of the 360-nm band, which is in the similar optical absorption range of pristine C_{60} . The long wavelength absorption peak extends beyond 940 nm. Because all alkyl addends are not photoactive in this region, to our knowledge, this is the longest strong optical absorption of the C_{60} cage among many [60]fullerene derivatives synthesized.

These results confirmed a facile chemical trapping method of C_{60}^{-6} for the preparation of C_{60} derivatives which consist of hexaaddends each attached on the cage carbon by a single covalent bond. Because each anion of C_{60}^{-6} is fully delocalized on the cage surface, a large number of regioisomers of the hexaadduct is expected. That is the case for the substitution reaction of C_{60}^{-6} with ethyl bromide under identical reaction conditions resulting in a mixture of the products unresolvable by chromatography. In the case of EF-6MC_{*n*} compounds, the fact that only few isolable products are obtained via PTLC may indicate a localized reaction transient state between the delocalizable anion and the incoming reactant at the bimolecular complex center during the stepwise reaction. Therefore, stereostructure and molecular size of the electrophile should play an important role in fixing the delocalized

anion at the vicinity of electrophile site for the reaction to occur. Influence of molecular size on the reaction mechanism was also observed in the case of $\text{C}_{60}\text{F}_{18}$, where trannulation occurs only if the incipient carbanion is of sufficient steric bulk.^{2,3}

By taking the electronic structure of Taylor's EF compound **1** as the reference,⁴ its [18]trans-annulene electron density system may be applied to **2** and **3** since the trannulene-containing structural face of **1** is in a close resemblance to either structural face of EF-6MC₄, as shown in Figure 1, parts a and b. Both structural faces show a shared trannulene moiety (marked by red) with all-trans double bonds in a continuous beltlike π -structure interconnected with two triphenylene moieties (marked by green) located at each side of the conjugation belt. Therefore, EF-6MC₄ heptad is, in fact, new unusual *double-triphenylene interlinked trannulene* chromophores. This may explain its capability to absorb strongly in the near-IR region. Electron delocalization along trannulene-triphenylene moieties should result in the stabilization and decrease of the LUMO energy of the molecule. In correlation to this trannulene structure, preliminary cyclic voltammetry measurements of **2** and **3** indicated similar affinity for electrons ($E^{\text{Red}} = -0.49$ V; $E_2^{\text{Red}}(5\text{e}^-) = -1.06$ V vs Ag/AgCl) close to those of pristine C_{60} even though they are hexasubstituted.

In conclusion, coupling of these near-IR optical properties with electron accepting characteristics of the C_{60} cage may allow the utility of EF-6MC_{*n*} as *n*-type photosensitizers in conjunction with broadband photovoltaic cells for harvesting light energy over 700–940 nm. We are further investigating the development of near-IR sensors and nonlinear optics.

Acknowledgment. We thank the National Science Council, Taiwan, for financial support and Yi-Hung Liu of Taiwan University Instrumentation Center for X-ray structural analyses.

Supporting Information Available: FAB⁺ mass spectrum,¹³C NMR spectrum, and crystallographic data of **3** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- X-ray structural analyses data of **3** in a single crystal: triclinic unit cell packing; *P1* symmetry space group; dimensions $a = 14.0900(10)$ Å, $b = 15.0660(2)$ Å, $c = 18.4050(2)$ Å, $\alpha = 70.2200(10)^\circ$, $\beta = 87.2200(10)^\circ$, $\gamma = 84.1400(10)^\circ$; cell formula units $Z = 2$; final residues of the refinement [$I > 2\sigma(I)$] $R_1 = 0.1136$.

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