Low Multielectron Reduction Potentials of Emerald Green [60]Fullerenes

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Unique double-triphenylene interconnected all-*trans* 18-trannulene electronic configuration of dodecaethylated emerald green fullerene (EF$_n$), $C_{60}[–C(CH_3)(CO_2Et)_2]_6$ or EF-6MC$_2$, allows the fullerene cage to retain similar affinity for electrons as C_{60} and high multielectron accepting capability with $E_1^{Red} = -0.36$ V, $E_2^{Red} = -0.88$ V, and $E_3^{Red} = -1.45$ V vs. Ag/AgCl.

Fullerenes and their derivatives with a low degree of functionalization exhibit high electronegativity and behave as electron acceptors.[1] As the number of covalently bound addends increases, the electron affinity of the fullerene cage decreases. A large loss of electron accepting capability is obvious on one hexaadduct example hexa(dialkylmalonato)[60]fullerene,[2] showing two irreversible reduction potential peaks at −1.69 and −2.35 V vs. Fc/Fc$^+$.[3] These values indicated much deviation from those of pristine C_{60} ($E_1^{Red} = -0.98$ V and $E_2^{Red} = -1.37$ V vs. Fc/Fc$^+$) by −0.7 and −0.98 V, respectively.[4]

Dodecaalkylated emerald green fullerenes EF-6MC$_n$ are a new class of C_{60} hexaadducts exhibiting strong near-infrared absorption at 760 ($\varepsilon = 6632$ L mol^{-1} cm^{-1}) and 850 ($\varepsilon = 12755$ L mol^{-1} cm^{-1}) nm and named according to their intrinsic green color.[5] Similar tris(α-bromomalonato)pentadecafluoro-[60]fullerene analogue of highly fluorinated EF compounds derived from $C_{60}F_{18}$ were also synthesized.[6] Formation of 18 π-trannulene electronic configuration on the fullerene cage was proposed for the origin of unique green dyes with absorption at λ_{max} 612 and 658 nm.[7] Our dodecaalkylated analogues of EF$_n$ derivatives were prepared by hexaanionic C_{60}, C_{60}^{6-},[8] substitution reaction in a one-pot reaction for attaching 6 dialkyl-α-methylmalonate addends on one C_{60} cage.[5] The resulting EF-6MC$_2$, $C_{60}[–C(CH_3)(CO_2Et)_2]_6$ (**1**), and dodeca(*t*-butylated) analogue $C_{60}[–C(CH_3)(CO_2\text{-}t\text{-}Bu)_2]_6$ (**2**) (EF-6MC$_{4t}$) represented two examples of EF$_n$ compounds. X-ray diffraction data analysis of the heptad EF-6MC$_{4t}$ in a single crystal form[5] allowed us to mark all sp^3 cage carbon positions each bound with one di(*t*-butyl)-α-methylmalonate, as shown in Figure 1. Structurally, a double-triphenylene interconnected all-*trans* 18-trannulene moiety of **1** and **2** was proposed to be responsible for their optical absorption in near-IR.

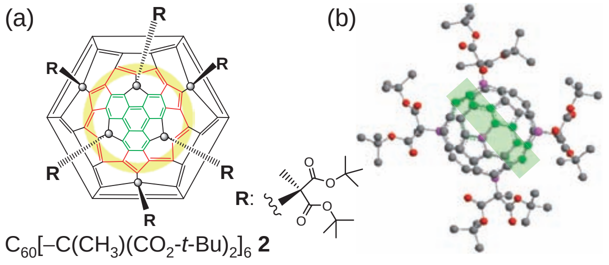

Figure 1. (a) Schlegel diagram of EF-6MC$_{4t}$ (**2**) and (b) the side-view showing *trans* 18-trannulene belt.[5]

Electron delocalization along the trannulene belt and triphenylene moieties of EF$_n$ compounds results in stabilization of the molecular LUMO energy that leads to lower electron reduction potentials. Accordingly, cyclic voltammetric (CV) measurements of EF-6MC$_2$ displayed a fully reversible one-electron reduction profile of E_1^{Red} at −0.35 V (or −0.93 V vs. Fc/Fc$^+$) and the corresponding re-oxidation potential E_1^{Ox} at −0.27 V vs. Ag/AgCl, as shown in Figure 2c. The experiment was carried out using tetra-*n*-butylammonium hexafluorophosphate (TBA$^+$-PF$_6^-$, 0.1 M) as the electrolyte in THF (1.0×10^{-3} M, freshly distilled from Na). Complete removal of trace oxygen and moisture from the solution was made by N_2-bubbling and freeze-pumping at 10^{-4} torr for 12 h. Upon extension of scanning voltage to −1.80 V, the second reduction potential E_2^{Red} recorded at −0.88 V vs. Ag/AgCl or −1.46 V vs. Fc/Fc$^+$ was found in a higher current intensity than E_1^{Red} (Figure 2b). Interestingly, it was accompanied with evident good reversibility of the third electron reduction wave at −1.45 V (or −2.03 V vs. Fc/Fc$^+$, E_3^{Red}) and the corresponding E_3^{Ox} at −1.40 V vs. Ag/AgCl, indicating good stability of (EF-6MC$_2$)$^{3-}$ species in THF. It also revealed no evidence of significant presence of O_2 to induce electron transfer from (EF-6MC$_2$)$^{3-}$ in this experiment.

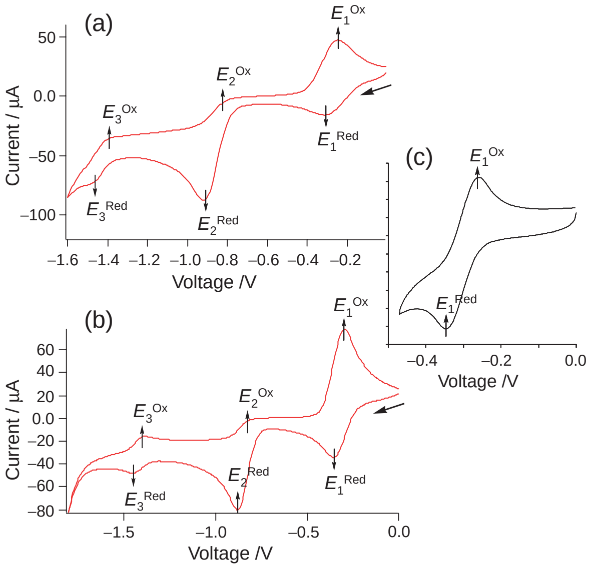

Figure 2. Cyclic voltammetry of EF-6MC$_2$ in THF (1.0×10^{-3} M) using TBA$^+$-PF$_6^-$ (0.1 M) as the electrolyte with platinum as working and counter electrodes and the silver wire as the reference electrode under (a) air-saturated and (b) and (c) N_2-saturated condition, with a scan rate of 100 mV/s.

Upon saturation of the sample **1** solution by ambient air, a slight shift of E_1^{Red} to -0.31 V was detected with a clear corresponding reversible re-oxidation potential E_1^{Ox} measured at -0.25 V (Figure 2a). The second and third reduction potentials remained in a similar potential value of -0.92 and -1.48 V, respectively, with weak or no clear corresponding re-oxidation potentials. The overall redox wave profiles showed good retention to those of Figure 2b.

The potential value may vary upon different experimental conditions applied. For the direct comparison of relative reduction potentials of EF-6MC$_2$ with other C$_{60}$ monoadducts, a model compound $C_{60}{>}(CO_2Et)_2$ (**3**) was prepared and its CV profile measured. Under identical experimental conditions in N$_2$-saturated THF, three reversible reduction waves were recorded at -0.54, -1.13, and -1.74 V vs. Ag/AgCl. Potential values of these reductive states are all higher than those of EF-6MC$_2$, indicating the latter having a relatively higher affinity for electrons than $C_{60}{>}(CO_2Et)_2$. Notably, the reduction potential values of EF-6MC$_2$ were found to be in a similar range to those for pristine C$_{60}$ in THF ($E_1^{\mathrm{Red}} = -0.31$ V, $E_2^{\mathrm{Red}} = -0.90$ V, and $E_3^{\mathrm{Red}} = -1.46$ V vs. Ag/AgCl),[9] revealing similar electron affinity as C$_{60}$ for EF-6MC$_2$ even though they are functionalized with six addends.

Attachment of organic addends on C$_{60}$ converts fullerenyl carbons at the conjunction into a sp^3 configuration with no direct conjugation with the rest of cage π electrons. That tends to interrupt the conjugation length, electronegativity, and electrochemical behavior of derivatized fullerenes as the number of addends increases to more than 6. It also makes electron reductions of the fullerene cage increasingly difficult and irreversible. In the case of EF-6MC$_n$ hexaadducts, the electrochemical behavior is in highly contrast to Bingel-type hexaadducts, such as hexa(diethylmalonato)methano[60]fullerene (**4**) which has the least electron affinity. Both the first and second reduction potential values of EF-6MC$_2$ are >0.7 V more positive than those of **4** (-1.69 V for E_1^{Red} and -2.35 V for E_2^{Red} vs. Fc/Fc$^+$, both irreversible).[3] It is also in a higher value than that of tris(diethylmalonato)[60]fullerene derivative, $C_{60}[{>}(CO_2Et)_2]_3$ known as C_3, ($E_1^{\mathrm{Red}} = -1.32$ V and $E_2^{\mathrm{Red}} = -1.53$ V vs. Fc/Fc$^+$ or $E_1^{\mathrm{Red}} = -0.74$ V and $E_2^{\mathrm{Red}} = -0.95$ V vs. Ag/AgCl) in CH$_2$Cl$_2$.[10]

Unlike redox processes of **3** showing nearly equal current peak intensity at each reduction wave under N$_2$, the redox cycle of **1** (Figure 2b) displayed unsymmetrical peaks of electron reduction waves with a higher current intensity for E_2^{Red} and E_1^{Ox}. Similar phenomena were observed in CV profiles of multifluorinated fullerene and its trannulene derivatives.[6b] One plausible explanation can be given by the involvement of disproportionation of (EF-6MC$_2$)$^{2-}$ with EF-6MC$_2$ to produce two molecules of (EF-6MC$_2$)$^{-\bullet}$ in both reductive and re-oxidative cycles. That resulted in a higher number of (EF-6MC$_2$)$^{-\bullet}$ intermediate available for the second electron reduction in the reductive cycle and the re-oxidation of (EF-6MC$_2$)$^{-\bullet}$ back to EF-6MC$_2$ in the E_1^{Ox} wave cycle. It was also correlated to a less amount of (EF-6MC$_2$)$^{2-}$ available for the third electron reduction at reductive potentials lower than -1.3 V, leading to a lower peak intensity of the E_3^{Red} wave and following E_3^{Ox} and E_2^{Ox} waves. On the basis of this interpretation, the overall redox wave profiles agreed well with good reversibility and relatively high stability of (EF-6MC$_2$)$^{n-}$ with $n \leq 3$.

Influence of the dissolved oxygen during the cyclic voltammetry process was evident in the case of the monoadduct $C_{60}{>}(CO_2Et)_2$. Irriversible redox waves were detected even after the second reduction of the CV experiment carried out in air-saturated THF. The second reduction potential value displayed a large shift to -1.51 V from -1.13 V for E_2^{Red}. Perhaps, electron transfer from a higher reduced state than $[C_{60}{>}(CO_2Et)_2]^{-\bullet}$ to molecular oxygen resulted in interference on subsequent redox processes and suppressed following reductive events. In contrast, the CV measurements of EF-6MC$_2$ performed in air-saturated THF illustrated a stable electrochemical behavior showing a similar redox profile shape in Figure 2a to that of Figure 2b. It clearly indicated better stability of [EF-6MC$_2$]$^{n-}$ than $[C_{60}{>}(CO_2Et)_2]^{n-}$ ($n > 1$) in the presence of O$_2$ in solution. We propose that six hindered diethyl-α-methylmalonate subunits of EF-6MC$_2$ symmetrically located surrounding the C$_{60}$ cage resembling "molecular encapsulation" may provide a tight steric barrier for the cage moiety and slow potential nucleophilic reactions or electron transfer by [EF-6MC$_2$]$^{n-}$. That significantly improves stability of polyanionic EF-6MC$_n$ intermediates.

In conclusion, unique double-triphenylene interconnected all-*trans* 18-trannulene electronic configuration of EF-6MC$_2$ allows the fullerene cage to retain similar affinity for electrons as C$_{60}$, while multiple addend groups provide high solubility, compatibility with other organics, and electrochemical stability. Unlike high reduction potential values of Bingel-type hexa(dialkylmalonato)[60]fullerene, EF-6MC$_n$ compounds consisting of six hindered dialkyl-α-methylmalonate addends attached on C$_{60}$ by a single covalent bond do not significantly alter the first to third reduction potential values from the parent pristine C$_{60}$. Electrochemical characteristics of EF-6MC$_2$ substantiated high multielectron-accepting capability of EF-6MC$_n$ that may allow their uses as electron acceptors in near-infrared active optoelectronic and broadband photovoltaic devices.

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