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Ligand effects on the electrochemical and spectroscopic behaviors of methano[60]fullerene derivatives

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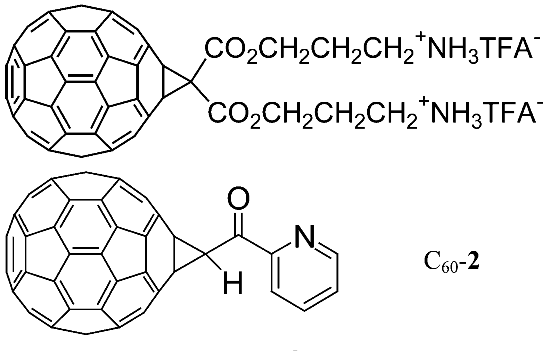
Effects of the ligand chemical structures on the electronic energy properties of two methano[60]fullerene derivatives were investigated voltammetrically and spectroscopically.

Buckminsterfullerene (C_{60}) exhibits efficient electron-accepting characteristics by undergoing up to six one-electron reduction reactions.[1,2] This unique property has been exploited in its very diverse applications, such as molecular electronics, photoenergy conversion (charge separation), biotherapeutics, *etc.*[3] However, the applications of pristine C_{60} are limited by its poor dispersity in a number of common media. Thus, chemical functionalization is typically employed to tailor the C_{60} solubility in a specific solvent, where the associated electron-transfer chemistry may change quite drastically. For instance, multiple fluorination of fullerenes ($C_{60}F_x$ and $C_{70}F_x$) led to significant *anodic* shifts of the fullerene redox reactions,[4] which was ascribed to the high electronegativity of fluorine and hence lowering of the fullerene electronic energy structures. Similar *anodic* shifts were also observed with fullеropyrrolidinium salts;[5] whereas saturation of a double bond of C_{60} in methanofullerenes typically results in a *cathodic* shift of about 30–350 mV of the first three waves.[2,6] Herein we report our recent investigation of the electrochemical and spectroscopic behaviours of two methanofullerene derivatives with similar methano mono-adduct linkage but different chemical nature of the organic tether (Scheme 1). Surprisingly, we observed an *anodic* shift of the C_{60} redox potentials in both of these derivatives, one of which even exhibits a shift of more than 600 mV.

The first fullerene derivative, bis(3-ammoniumpropoxycarbonyl)methano[60]fullerene ditrifluoroacetate (C_{60}-**1**) was synthesized and characterized by following a literature protocol.[7] The other, 2-pyridylcarbonylmethano[60]fullerene (C_{60}-**2**) was prepared as follows. A mixture of C_{60} (14.4 mg, 0.02 mmol), 2-acetylpyridine (4.8 μL, 0.04 mmol) and piperidine (4 μL, 0.04 mmol) was shaken by high-speed vibration milling for 30 min. The combined reaction mixture from three runs was separated on silica gel column with toluene as an eluent to afford a product in 26% yield (13.1 mg, 53% based on consumed C_{60}). The obtained sample was then subjected to thorough spectroscopic characterization.†

Figure 1 depicts the cyclic voltammograms of (A) pristine C_{60}, (B) C_{60}-**1**, and (C) C_{60}-**2**. One can see that for pristine C_{60} (panel A), three pairs of voltammetric peaks can be found at −0.55, −1.00, and −1.49 V (*vs.* Ag/AgCl),‡ with a peak splitting (ΔE_p) less than 90 mV at 100 mV s^{-1}, indicating quasi-reversible electron-transfer processes. These are attributed to the successive 1e⁻ reduction of C_{60} molecules, *i.e.*, $C_{60}^{0/-1}$, $C_{60}^{-1/-2}$ and $C_{60}^{-2/-3}$ couples, respectively, as observed previously.[1,2] For C_{60}-**2** (panel C), two voltammetric waves are observed at −0.53 and −0.95 V, which, with a small anodic shift (20–50 mV), correspond very well to the first two 1e⁻ reductions of C_{60} molecules as shown above. By contrast, C_{60}-**1** exhibits drastically different voltammetric behaviors. It can be seen from panel B that there are four pairs of well-defined voltammetric waves at +0.12, −0.26, −0.68, and −1.2 V, respectively. Most likely these also arise from the successive 1e⁻ reductions of the C_{60} moieties, but with an anodic shift of the redox potentials greater than 600 mV, as compared to those of pristine C_{60}. It should be noted that the ΔE_p for the first wave is *ca.* 140 mV, much larger than the others which are very close to those of pristine C_{60} and C_{60}-**2**, indicating somewhat sluggish electron-transfer dynamics.

As mentioned earlier, substantial anodic shifts (> 1.3 V) of the C_{60} redox reactions have been observed with fluorinated C_{60}.[4] The



C_{60}-**1**

C_{60}-**2**

Scheme 1

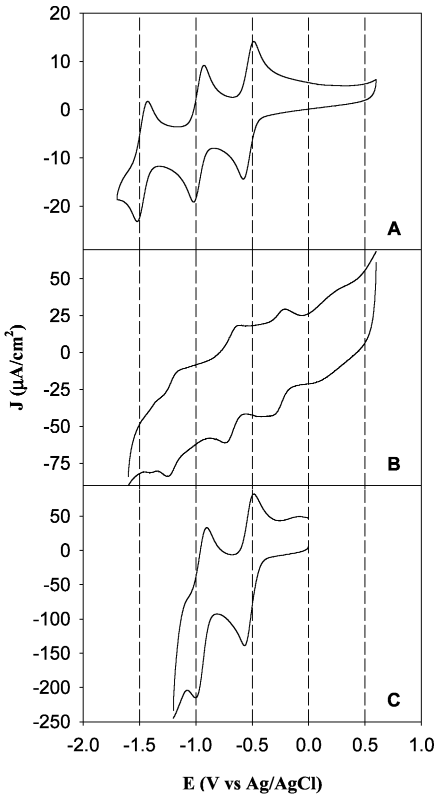


Fig. 1 Cyclic voltammograms of (A) C_{60}, (B) C_{60}-**1** and (C) C_{60}-**2** at a gold disk electrode (area 0.44 mm²). C_{60} and C_{60}-**2** solutions were both prepared in a mixed solvent of toluene and acetonitrile (v : v 2 : 1) with 0.1 M tetrabutylammonium perchlorate (TBAP). The concentration of C_{60} and C_{60}-**2** was 1.39 mM and 1.19 mM, respectively. C60-**1** was dissolved in dimethyl sulfoxide (DMSO) at a concentration of 0.85 mM, also with 0.1 M TBAP. Potential scan rate 100 mV s^{-1}.

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phenomenon was interpreted on the basis of the high electronegativity of fluorine, which led to the lowering of the energy levels of both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). It should be noted that in these fluorinated derivatives (*e.g.*, $C_{60}F_{46}$, $C_{60}F_{48}$, *etc.*), the fluorine was covalently attached to the C_{60} cage, and hence there was a strong electronic interaction with the cage π electrons. In fulleropyrrolidinium salts,[5] the electron-withdrawing nature of the positively charged ammonium moieties might also lead to similar electronic interactions and consequently anodic shifts of the C_{60} redox potentials. By contrast, for neutral fulleropyrrolidines, a very small cathodic shift was observed instead.[6]

In the present study, both ligands are tethered onto the C_{60} cage *via* a methano linkage (Scheme 1). As mentioned earlier, C_{60} derivatives with such functional moieties typically exhibit a cathodic shift of the redox potentials in comparison to those of pure C_{60}.[2,6] This is accounted for by the decrease of electron affinity because of the partial loss of conjugation of the C_{60} sphere. Surprisingly, both methanofullerene derivatives in the present study show *anodic* shifts of their redox potentials (Fig. 1). This might be partly attributed to the electron-withdrawing carbonyl moiety attached to the methano carbon in both molecules (Scheme 1). In particular, the vast difference observed between C_{60}-**1** and C_{60}-**2** strongly suggests that further functionalization of the methano moieties can have significant impacts on the electronic interactions with the cage π-electrons. One can see that the main structural disparity between C_{60}-**1** and C_{60}-**2** lies in two parts, the additional carbonyl (carboxylic) group (C_{60}-**1**) in place of a simple hydrogen (C_{60}-**2**), and the propoxy moiety (C_{60}-**1**) to replace the pyridyl group (C_{60}-**2**). Thus it is suspected the drastic anodic shift of redox potentials as observed above with C_{60}-**1** might also be interpreted on the basis of the strong electron-withdrawing nature[4,5] of the tethers in C_{60}-**1**. An additional contribution may arise from the proximal cationic quaternary ammonium groups at the end of the chains in C_{60}-**1** which help stabilize the anionic C_{60} unit.

Dramatic effects of the tether ligands can also be found in spectroscopic measurements. Figure 2 shows the UV-vis absorption and fluorescence spectra of these two C_{60} derivatives. One can see that in both cases, two very well-defined absorption peaks can be found at 260 nm and 330 nm, along with a small peak at 430 nm. These features correspond very well to those of other monoadducts and pristine C_{60}.[8,9] However, the associated fluorescence responses are quite different (Fig. 2). For C_{60}-**1**, the fluorescence profile peaks at 338 nm with a full width at half maximum (FWHM) of only 50 nm whereas for C_{60}-**2**, the maximum fluorescence intensity is found at a much lower energy, 430 nm, and the FWHM is much larger, 90 nm.§ Previously with Au nanoparticle-bound C_{60} through amination,[10] we observed a fluorescence emission peak at 433 nm.

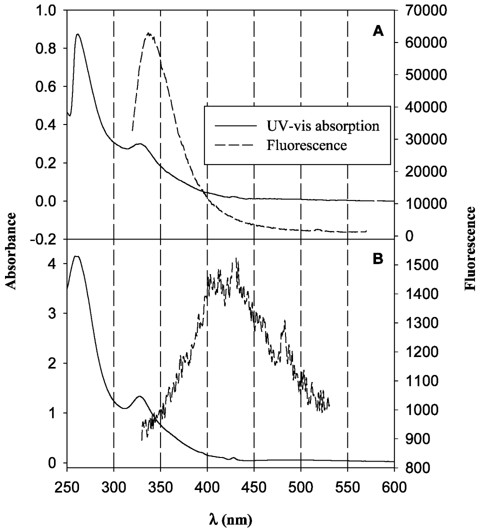

Fig. 2 UV-vis absorption and fluorescence spectra of (A) C_{60}-**1** and (B) C_{60}-**2**. C_{60}-**1** was dissolved in DMSO at a concentration of 16.9 μM, C_{60}-**2** in $CHCl_3$ at 59.5 μM. The excitation wavelength (λ_{ex}) for fluorescence is (A) 300 nm and (B) 310 nm respectively.

In addition, one can see from Fig. 2 that the fluorescence quantum efficiency of C_{60}-**1** should be substantially greater than that of C_{60}-**2**. In fact, the quantum yield[10] can be estimated to be 1.1×10^{-3} and 2.9×10^{-5} respectively for C_{60}-**1** and C_{60}-**2**. In comparison, the quantum yield[9] of pristine C_{60} in toluene is about 3.2×10^{-4} at room temperature whereas for triazolinofullerene,[11] it is 6.0×10^{-4}.

These studies strongly indicate that the electronic energy structure and electron-transfer dynamics of the C_{60} moieties can be sensitively manipulated by tethered organic ligands even though the functional group is not directly attached onto the C_{60} cage. Further work is desired to understand the molecular mechanism of these electronic interactions.

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Notes and references

† ^{1}H NMR (300 MHz, $CDCl_3 : CS_2 = 1 : 1$) δ 6.66 (s, 1H), 7.68 (ddd, J = 7.8, 4.2, 1.2 Hz, 1H), 8.04 (td, J = 7.8, 1.4 Hz, 1H), 8.34 (d, J = 7.8 Hz, 1H), 8.94 (d, J = 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3 : CS_2 = 1 : 1$) δ 40.72, 72.56, 122.10, 127.50, 136.02, 136.83, 140.16, 140.31, 140.56, 141.37, 141.52, 141.68, 141.97, 142.19, 142.37, 142.51, 142.70, 143.13, 143.38, 143.75, 143.92, 143.98, 144.04, 144.27, 144.39, 144.52, 144.61, 144.68, 145.05, 145.66, 148.29, 149.09, 152.16, 190.93; FT-IR (KBr) ν (cm^{-1}) 2927, 2850, 1694, 1580, 1429, 1334, 1217, 1186, 994, 779, 739, 691, 617, 575, 526, 493; UV-vis ($CHCl_3$) λ_{max} (nm) 259, 326, 427, 481.

‡ All potentials were calibrated against the formal potential of the ferrocene/ferrocenium couple, which was determined to be +0.54 V *vs.* Ag/AgCl.

§ An additional but much weaker fluorescence peak can be found at 700 nm, which has been observed previously in pristine C_{60}[11] and other monoadducts of C_{60} (*e.g.*, P. K. Sudeep, B. I. Ipe, K. G. Thomas, M. V. George, S. Barazzouk, S. Hotchandani and P. V. Kamat, *Nano Lett.*, 2002, **2**, 29).

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