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Synthesis and Structural, Electrochemical, and Stacking Properties of Conical Molecules Possessing Buckyferrocene on the Apex

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There has been a growing interest in functional liquid crystal materials.[1] For instance, incorporation of metal atoms into liquid crystalline materials (metallomesogens) provides new opportunities in materials science through tuning of anisotropic optical, electronic, and magnetic properties.[2,3] Mixed fullerene/ferrocene mesogens[4] have therefore attracted considerable attention for their donor/acceptor characteristics and potential redox switching activity.[5] Though the idea is simple, incorporation of a bulky fullerene and ferrocene units as integrated parts of the bulk liquid crystal supramolecular structure has been rather difficult in practice. We considered that the compact, C_5-symmetric buckyferrocene (fullerene and ferrocene sharing one of their pentagons in common, cf. **2**)[6] would serve as the core structure of such metallomesogens and that installation of extended side chains (cf. **5**) will allow the resulting conical, shuttlecock-like molecule to stack into a columnar supramolecular assembly (Figure 1).[7] Herein we report on the successful implementation of the design and describe the synthesis and electrochemical properties of buckyferrocene shuttlecocks and ordered supramolecular structures of the Fe(II) (**4**) and Fe(III) (**5**) compounds (Scheme 1).

Synthesis of the conical molecules started by converting I_h-symmetric C_{60} into C_s-symmetric $C_{60}(C_6H_4\text{-}OMe\text{-}4)_5H$ (**1**) by treatment of C_{60} with a (4-methoxyphenyl)copper reagent.[8] Complexation of **1** with $[FeCp(CO)_2]_2$ ($Cp = C_5H_5$) in benzonitrile at 175 °C afforded a buckyferrocene, $Fe[C_{60}(C_6H_4\text{-}OMe\text{-}4)_5]Cp$ (**2**),[9] which was deprotected with $BBr_3{\cdot}SMe_2$ in 1,2-dichlorobenzene at 165 °C to obtain the phenol derivative, $Fe[C_{60}(C_6H_4\text{-}OH\text{-}4)_5]Cp$ (**3**). Acylation of **3** with appropriate benzoic chloride derivatives possessing alkyl side chains afforded the desired conical molecules, $Fe[C_{60}\text{-}\{C_6H_4\text{-}(OCO\text{-}C_6H_3\text{-}(OR)_2\text{-}3,4)\text{-}4\}_5]Cp$ (**4a**, R = methyl; **4b**, R = dodecyl; **4c**, R = tetradecyl; **4d**, R = hexadecyl; **4e**, R = octadecyl) (Scheme 1). Their ^1H and ^{13}C NMR spectra were consisted with the expected η^5-coordinated, C_5-symmetric structure of **4a**−**e**. The elemental composition and the purity of the samples used for the subsequent studies were established by elemental analysis.

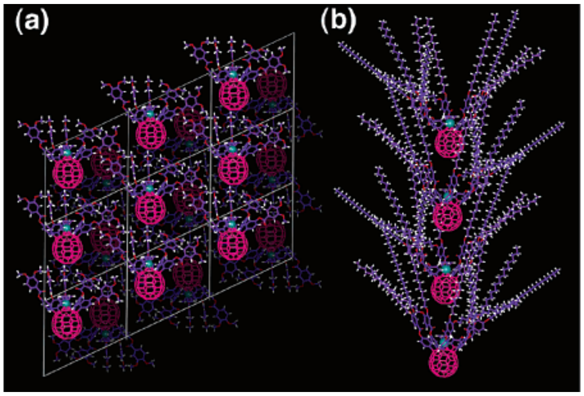
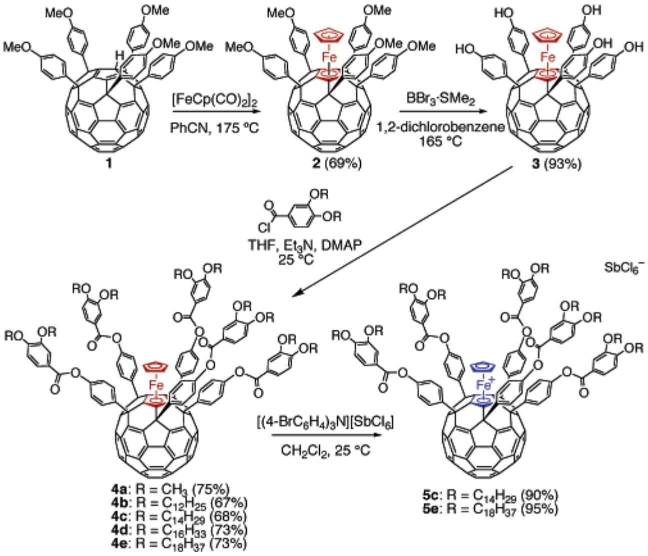


Figure 1. Columnar stacking of **4a** and **4e**. (a) Crystal structure of **4a**·(toluene)$_4$ from the *a*-axis. Toluene molecules in crystal packing are omitted for clarity. Views from the *b*- and *c*-axes are shown in Supporting Information. (b) A model of the stack of **4e** in liquid crystals (based on SAXD data described in the text).

Scheme 1



The compound lacking long side chains (**4a**, R = Me) gave crystals. Red prism crystals of **4a** suitable for X-ray crystallographic study were obtained by slow diffusion of methanol into a chloroform solution. The columnar structure of **4a** (view from the *a*-axis) is shown in Figure 1a. The bottom of the concave cavity formed by the five aryl groups in **4a** is filled by a ferrocene group (ca. 3.4 Å in height) and therefore is shallower than that of the corresponding compound lacking the ferrocene group (e.g., the protio compound **1** vs **2**).[7] The shallowness of the cavity made the intermolecular stacking structure much less ordered than in the protio compound. As a result, the molecular axis is tilted by 18.9° against the columnar axis (as opposed to 0° in the protio compound; see the crystal packing view along the *c*-axis in the Supporting Information). The intermolecular stacking distance within a column (17.8 Å) is much longer (by 6.7 Å) than in the corresponding protio case (11.1 Å),[7] hence leaving a space between the molecules within a column. Note that, in the protio case, the highly acidic cyclopentadienyl hydrogen[10] (cf. **1**) is in direct contact with the π-surface of the bottom of the next fullerene molecule in the stack, as if there is hydrogen bonding.

The molecules bearing longer side chains (**4d**,**e**) showed liquid crystalline behavior. The mesophases were identified by differential scanning calorimetry (DSC), polarizing optical microscopy, and small-angle X-ray diffraction analysis (SAXD). Compound **4e** showed clear mesomorphism over a wide temperature range. The

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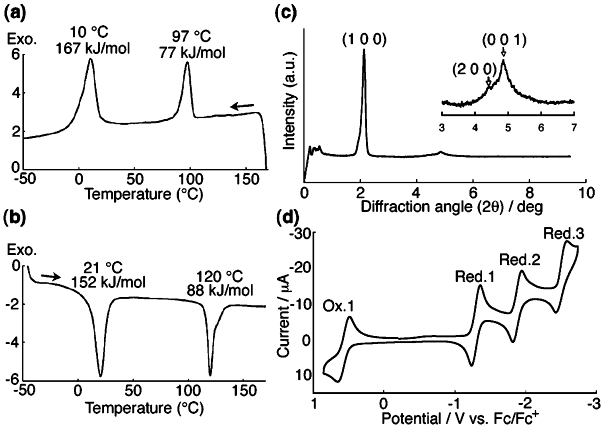

Figure 2. Characterization and electrochemical properties of **4e**. (a) DSC trace of **4e** recorded during the first cooling. (b) DSC trace of **4e** recorded during the second heating. (c) SAXD data for **4e** at 100 °C. (d) Cyclic voltammogram of **4e** at 25 °C in a THF solution containing *n*-Bu$_4$NClO$_4$ as a supporting electrolyte (scan rate 100 mV/s).

first cooling after heating to 170 °C (50 °C above the clearing point) showed two exothermic peaks at 97 and 10 °C (Figure 2a), and the second heating process showed two endothermic peaks at 21 and 120 °C (Figure 2b).

Noteworthy was a large transition enthalpy at the clearing temperature (77 and 88 kJ/mol), which was much larger than those of the corresponding pentaaryl-C_{60} protio compounds (5−21 kJ/mol),[7a] related silicon-tethered conical protio analogues (27−35 kJ/mol),[7b] and other nonconical fullerene/ferrocene hybrid mesogens (11.7 kJ/mol).[4a] We ascribe the observed supercoolability and the high transition enthalpies partially to the polarity of the buckyferrocene moiety.[6a]

Compound **4d** (see Supporting Information for details) also exhibited supercoolability and showed, during the second heating, a crystal-to-liquid crystal transition at −3 °C and a liquid crystal-to-isotropic liquid transition at 123 °C. The transition enthalpy at the clearing temperature was also very large (93 kJ/mol). As found in the protio series,[7] the isotropization temperature that is related to the fullerene/fullerene stacking did not change much as the side chains got longer, while the melting temperature that is related largely to the side chain/side chain interactions became lower (**4d**, −3 °C; **4e**, 20 °C). Compounds **4b**,**c**, having shorter side chains, did not show typical liquid crystalline behavior. Crystallization (at 85 °C for **4b**, 101 °C for **4c**) and melting (at 124 °C for **4b**, 120 °C for **4c**) peaks were observed during the heating.

SAXD analysis showed essentially the same characteristics observed previously for the protio analogues possessing the same side chains. On the basis of this parallelism as well as the crystal structure of **4a** and the DSC behavior of **4d**,**e**, we concluded that they form stacking structures in the liquid crystalline state. Thus, the SAXD data for **4e** at 100 °C (Figure 2c; **4d** in Supporting Information) showed reflections with *d*-spacing values of 41.3 (100), 20.0 (200), and 18.3 Å (001) and a broad halo typical of molten aliphatic moieties at 4.5 Å. Diffraction indexed to (110) was not observed. The (100) diffraction of 41.3 Å for **4e** corresponds to intercolumnar distance and is larger than the *d*-spacing values of 38.3 Å for **4d**. This suggests that column/column packing becomes more compact as the alkyl chains become shorter. The (001) diffraction of 18.3 Å for **4e** corresponds to the stacking period within a column and is almost the same as those of **4d** (18.2 Å) and **4a** (18.7 Å, crystal structure) but ca. 3.9 Å longer (perhaps by the height the ferrocene moiety) than those of the protio analogues (ca. 14.3 Å).[7]

The electrochemical behavior of compound **4e**, as studied within the window of THF, was essentially the same as that of Fe($C_{60}Ph_5$)Cp lacking the side chains (Figure 2d).[6] A reversible one-electron oxidation of the metal center was observed at 0.57 V (vs Fc/Fc$^+$). This potential is higher than that of Fe($C_{60}Ph_5$)Cp, which lacks the ester side chains (0.50 V). Upon reduction, **4e** showed three-step, one-electron reduction at −1.30, −1.88, and −2.35 V (vs Fc/Fc$^+$), which indicates that the compound is slightly easier to reduce than Fe($C_{60}Ph_5$)Cp, as one would expect.

We synthesized stable ferrocenium cations **5c** and **5e**. Compounds **4c** and **4e** were treated with an aminium salt [(4-BrC$_6$H$_4$)$_3$N][SbCl$_6$] in CH$_2$Cl$_2$ to obtain the corresponding ferrocenium derivatives **5c**,**e** (Scheme 1). The ferrocenium **5e** was paramagnetic character, showing *g*-values of 3.75 ($g_{\|}$) and 1.70 ($g_{\perp}$) at 4.4 K, and showed liquid crystalline behavior at the temperature range from 25 to 161 °C. Further characterization is underway.

In conclusion, we have synthesized a new class of metallomesogens that show reversible multielectron redox behavior, accepting and giving up total of at least four electrons. Given a vast variety of η^5-fullerene metal complexes available at this time,[11] we expect that a whole new generation of fullerene/metal complexes would be built into mesophases and utilized for a variety of applications.

Supporting Information Available: Procedures for synthesis of new compounds, crystallographic data of **2** and **4a**, optical textures and DSC data of **4b**−**e** and **5e**, and XRD data of **4d**,**e** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal structure of **2** is shown in Supporting Information.

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