J|A|C|S
COMMUNICATIONS

# Octupole-like Supramolecular Aggregates of Conical Iron Fullerene Complexes into a Three-Dimensional Liquid Crystalline Lattice

Chang-Zhi Li,† Yutaka Matsuo,*,†,‡ and Eiichi Nakamura*,†,‡

*Nakamura Functional Carbon Cluster Project, ERATO, Japan Science and Technology Agency (JST), Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, and Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Received August 16, 2010; E-mail: matsuo@chem.s.u-tokyo.ac.jp; nakamura@chem.s.u-tokyo.ac.jp

***Abstract:*** The installation of three structural features into a fullerene molecule, a conical shape, a polar iron-ferrocene complex, and long alkyl chains, allowed dipolar molecules **1** and **2** to undergo microphase separation and to form a three-dimensional lattice in a crystalline and a thermotropic liquid crystalline phase. The key feature is a tetrameric octupole-like aggregate, in which four dipoles are arranged supramolecularly to cancel the molecular polarity, forming a sphere. In addition to this lattice formation mechanism, the molecules incorporate noteworthy features, such as redox active $C_{60}$/ferrocene and luminescent cyclophenacene.

Despite their potential use in organic electronics and photonics,[1] thermotropic three-dimensional (3D) supramolecular arrays of mesogenic molecules are rare mesophases.[2] To construct a 3D liquid crystalline (LC) lattice that includes nanoscale aggregates that consist of several molecules (e.g., see Figure 1), effort has been expended toward designing a cone or crown-like molecules in which substituted aromatics serves as the apex of the molecular cone and allows the cone to aggregate as a spherical core through either hydrogen bonding or ionic interactions among the apexes.[3] A conical molecular shape is not sufficient to obtain a 3D fullerene liquid crystalline lattice, as, for example, seen in the shuttlecock-shaped pentaorgano[60]fullerenes that only form 1D columnar mesophases, 2D lamellar mesophases,[4] or bilayer membranes.[5,6] Herein, we report that conical iron fullerene complexes **1** ($n = C_{12}$) and **2** ($C_{18}$) bearing a dipolar ferrocene apex (bucky ferrocene) unit form a 3D tetragonal thermotropic liquid crystalline lattice (Figure 1). The key finding is that the dipole created by the added ferrocene moiety is canceled locally[7] as described in Figure 1, through the formation of a tetrameric supramolecular complex that has an octupolar character. Other features that probably contribute to the formation of the 3D lattice include the following: the conical shape of the molecule, the resulting spherical shape of the tetramer (see Figure 2c), the incompatibility (insolubility) of the fullerene and alkane, and the CH−$\pi$ interaction that endows additional stabilization of the apex−apex aggregation (Figure 2d), as has been found previously in a single crystal of a bucky ferrocene ($Fe(C_{60}Me_5)Cp$, where $Cp = C_5H_5$).[8]

The molecules were synthesized using a combination of the synthetic methods developed for bucky ferrocenes and bow-tie molecules,[6] and the 3D tetragonal crystals and liquid crystals were characterized using differential scanning calorimetry (DSC), polarized optical microscopy (POM), small-angle X-ray diffraction (SAXD), and single crystal X-ray analyses.

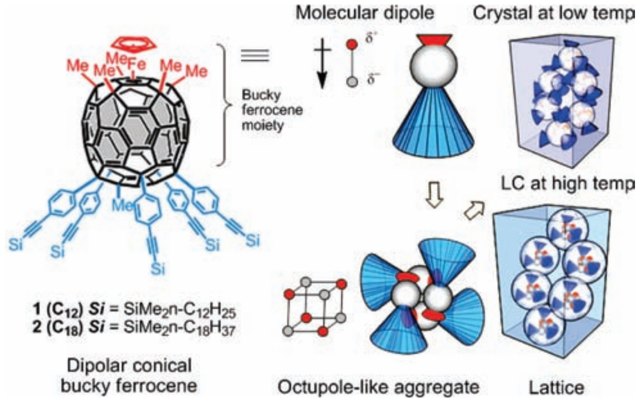

***Figure 1.*** A schematic illustration of dipolar conical molecules **1** and **2** and the formation of an octupole-like aggregate and a 3D lattice in the crystalline and LC lattices.

The 3D tetragonal crystalline lattice (Figure 2a) was first revealed using single crystal X-ray analysis for a yellow rectangular crystal of **1**, which was obtained through slow diffusion of methanol vapor into a 2-methyltetrahydrofuran solution of **1**. The diffraction at −153 °C exhibited a large tetragonal unit cell with a volume of 64.11 $nm^3$ (space group = $I4_1/a$, No. 88), in which six fullerene aggregates, each consisting of four molecules, are literally floating in amorphous (highly disordered) aliphatic chains (Figure 2a, 2b; see Supporting Information for larger pictures). We could identify a cubic octupole-like structure in the tetrameric aggregate that canceled the molecular dipole within the aggregate (Figures 1 and 2c). The aggregate is also stabilized by a series of C−H/$\pi$ and $\pi$−$\pi$ interactions. The fullerene's centroid-to-centroid distance is 0.98 nm, which is slightly shorter than that in a $C_{60}$ crystal (fcc, 1.00 nm).[9]

On heating to 55 °C, the crystal of **1** changed into a liquid crystal, and we observed an increase in the unit cell volume without an associated change in the overall molecular and supramolecular arrangement.[10] A DSC analysis of compound **1** showed a single mesophase over a wide temperature range ($T_{\text{cr-lc}}$ at 55 °C and $T_{\text{lc-iso}}$ at 230 °C, Figure 3a). The birefringence and fluidity of this phase were deduced from the POM study (Figure 3b). The 3D tetragonal lattice was determined using SAXD at 195 °C, which showed a sharp high-intensity (101) reflection and a number of low-intensity peaks at higher angles from the (103), (112), (004), (002), (202) reflections (Figure 3c and Table S2).[3c,11] Melting of the alkyl chains increased by 12%: the crystalline lattice volume was 64.11 $nm^3$ at −153 °C, and the liquid crystalline lattice volume was 71.99 $nm^3$ at 195 °C (Figure S7 and Table S4). Compound **2**, bearing $C_{18}$ aliphatic chains, was liquid crystalline over a wider temperature range than was compound **1**, from room temperature to 186 °C,

---

† Japan Science and Technology Agency.
‡ The University of Tokyo.

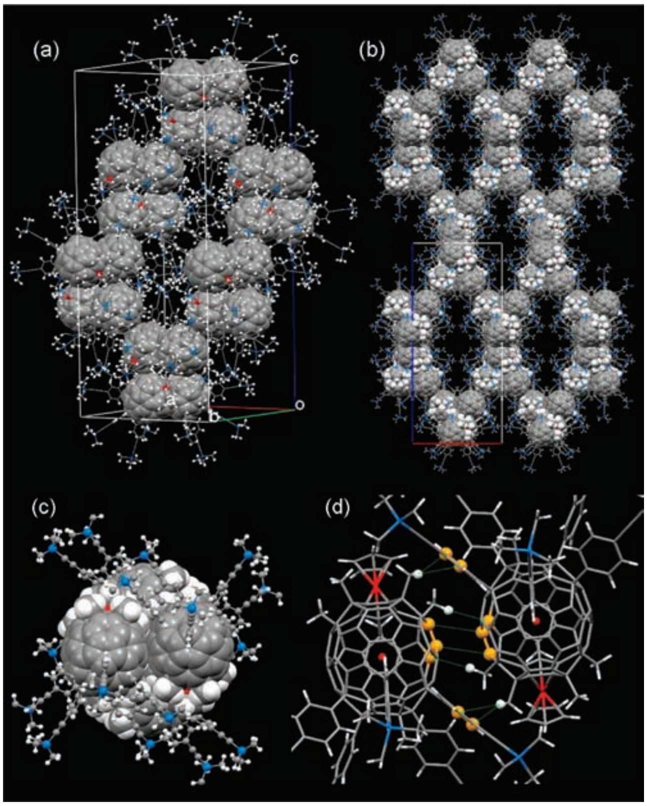

***Figure 2.*** Single-crystal X-ray structure of **1** ($C_{12}$) at −153 °C. Key to color codes: red = Fe (centroid of the fullerene is denoted by the red ball); gray = C; sky blue = Si; white = H; and yellow = reference carbon atoms to highlight the proximity of atoms. The $C_{12}$ chains were completely disordered and could not be identified, while the fullerene tetramers could be unambiguously identified. (a) The tetragonal crystal lattice in a unit cell (space-filling model for fullerene). (b) A slice viewed along the *b*-axis (space-filling model for bucky ferrocene). (c) The tetrameric aggregate viewed along the *c*-axis (space-filling model for bucky ferrocene). (d) A close-up view of two molecules along the *c*-axis. Neighboring carbon−carbon (3.39 Å) and carbon−proton (2.66−2.81 Å) distances are denoted by the green lines. The fullerene centroid-to-centroid distance is 9.82 Å.

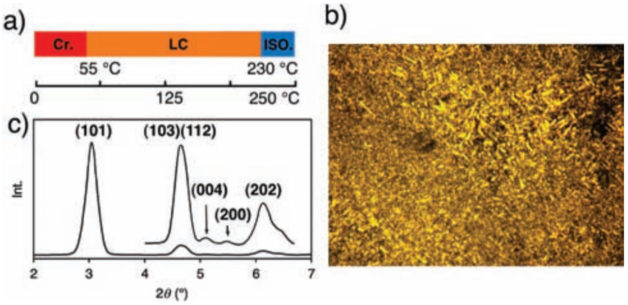

***Figure 3.*** Properties of compound **1**. (a) Thermal properties determined using DSC on the second heating process. (b) SAXD at 195 °C. (b) POM texture at 220 °C observed under a crossed polarizer.

and exhibited a 3D tetragonal thermotropic lattice with a larger volume of 74.62 $nm^3$ (at 170 °C).

A unique feature of mesogens **1** and **2** among the known 3D-lattice-forming mesogens[1−3,11,12] is their functional properties. Thus, compound **1** is redox active, undergoing reversible oxidation (0.17 V, $Fc/Fc^+$) and reduction (−2.16 V), as shown by cyclic voltammetry. The central cyclophenacene part (colored gray in Figure 1)[13] is of additional interest for its photo- and electroluminescence. Compound **1** shows an emission occurring at 480−700 nm on excitation at 366 nm with a quantum yield of $\Phi_{sol} = 0.01$ in cyclohexane and $\Phi_{film} = 0.01$ for a cast film (absolute measurement).[14]

In summary, we have achieved the microphase separation of supramolecular aggregates into a 3D crystalline or liquid crystalline lattice. The formation of a supramolecular octupole is the key element of the structural ordering, which will provide new insight for the design of nanoscale 3D lattice structures in crystals and in liquid crystals. The unique combination of redox activity and photophysical properties in the conical iron fullerene complexes is another feature of the present system that can be exploited in future material applications.

**Acknowledgment.** Financial support from MEXT, Japan (KAKENHI 22000008 and Global COE Program for Chemistry Innovation) is gratefully acknowledged.

**Supporting Information Available:** Synthesis, crystallography of deca **1a** ($C_{12}$) (CIF), DSC, optical textures, and XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) (a) Alam, M. A.; Motoyanagi, J.; Yamamoto, Y.; Fukushima, T.; Kim, J.; Kato, K.; Takata, M.; Saeki, A.; Seki, S.; Tagawa, S.; Aida, T. *J. Am. Chem. Soc.* **2009**, *131*, 17722. (b) Cao, W. Y.; Munoz, A.; Palffy-Muhoray, P.; Taheri, B. *Nat. Mater.* **2002**, *1*, 111. (c) Ichikawa, T.; Yoshio, M.; Hamasaki, A.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2007**, *129*, 10662.

(2) (a) Tschierske, C. *J. Mater. Chem.* **2001**, *11*, 2647. (b) Kato, T.; Mizoshita, N.; Kishimoto, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 38. (c) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Iman., M. R.; Percec, V. *Chem. Rev.* **2009**, *109*, 6275.

(3) (a) Rudick, J. G.; Percec, V. *Acc. Chem. Res.* **2008**, *41*, 1641. (b) Peterca, M.; Percec, V.; Imam, M. R.; Leowanawat, P.; Morimitsu, K.; Heiney, P. A. *J. Am. Chem. Soc.* **2008**, *130*, 14840. (c) Ungar, G.; Liu, Y. S.; Zeng, X. B.; Percec, V.; Cho, W. D. *Science* **2003**, *299*, 1208. (d) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539. (e) Percec, V.; Imam, M. R.; Peterca, M.; Wilson, D. A.; Heiney, P. A. *J. Am. Chem. Soc.* **2009**, *131*, 1294. (f) Percec, V.; Imam, M. R.; Peterca, M.; Wilson, D. A.; Graf, R.; Spiess, H. W.; Balagurusamy, V. S. K.; Heiney, P. A. *J. Am. Chem. Soc.* **2009**, *131*, 7662.

(4) (a) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702. (b) Matsuo, Y.; Muramatsu, A.; Hamasaki, R.; Mizoshita, N.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 432. (c) Matsuo, Y.; Muramatsu, A.; Kamikawa, Y.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, *128*, 9586. (d) Zhong, Y.-W.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2007**, *129*, 3052.

(5) Zhou, S.; Burger, C.; Chu, B.; Sawamura, M.; Nagahama, N.; Toganoh, M.; Hackler, U. E.; Isobe, H.; Nakamura, E. *Science* **2001**, *291*, 1944.

(6) Li, C.-Z.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2009**, *131*, 17058.

(7) (a) Nicoud, J. F.; Twieg, R. J. In *Non-Linear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press, Inc.: New York, 1987; Vol. 1, p 253. (b) Zyss, J.; Ledoux, I. *Chem. Rev.* **1994**, *94*, 77.

(8) Sawamura, M.; Kuninobu, Y.; Toganoh, M.; Matsuo, Y.; Yamanaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **2002**, *124*, 9354.

(9) Heiney, P. A.; Fischer, J. E.; McGhie, A. R.; McGhie, A. R.; Romanow, W. J.; Denenstein, A. M., Jr.; McCauley, J. P.; Smith, A.; B.; Cox, D. E. *Phys. Rev. Lett.* **1991**, *66*, 2911.

(10) Ziherl, P.; Kamien, R. *J. Phys. Chem. B* **2001**, *105*, 10147.

(11) Lee, M.; Cho, B.-K.; Jang, Y.-G.; Zin, W.-C. *J. Am. Chem. Soc.* **2000**, *122*, 7449.

(12) (a) Fuchs, P.; Tschierske, C.; Raith, K.; Das, M. K.; Diele, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 628. (b) Cheng, X.; Das, M. K.; Diele, S.; Tschierske, C. *Langmuir* **2002**, *18*, 6521.

(13) (a) Nakamura, E.; Tahara, K.; Matsuo, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2003**, *125*, 2834. (b) Matsuo, Y.; Tahara, K.; Sawamura, M.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 8725.

(14) The quantum yield was about 20 times lower than that of smectic decaaryl-LC, $MeAr_5C_{60}Ar_5Me$ ($\Phi_{sol} = 0.21$ and $\Phi_{film} = 0.18$),[6] which is because of fluorescence quenching from a charge separation interaction between the ferrocene donor and the cyclophenacene acceptor.

JA1073933