# Hierarchical supramolecular fullerene architectures with controlled dimensionality†

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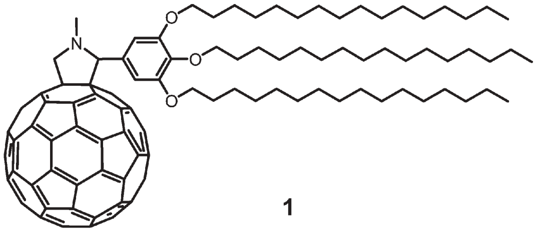
*Received (in Cambridge, UK) 1st September 2005, Accepted 14th October 2005*
*First published as an Advance Article on the web 8th November 2005*
**DOI: 10.1039/b512320h**

**Self-assembly of a fullerene derivative with long alkyl chains in different solvents results in the formation of hierarchically-ordered supramolecular assemblies with well-defined 1, 2 and 3D architectures such as vesicles, fibers, discs and cones, whose fundamental structural sub-unit consists of bilayers.**

The introduction of carbon nanoclusters, fullerenes,[1] carbon nanotubes,[2] and carbon nanohorns[3] into electronic devices, with the objective of constructing functional, molecular-based electronic systems, requires a detailed understanding of the interactions between individual nano-sized carbon building blocks, and is currently one of the most challenging research areas. The manipulation of weak intermolecular forces to construct new molecular architectures is a major theme of contemporary chemistry. An important challenge is to fabricate novel dimension-controllable nano/mesoscopic architectures which exploit the advantageous intrinsic properties of their carbon-based building blocks, *e.g.* high conductivity, rich electrochemistry and photoreactivity. An attractive example of graphitic nanotubes, formed by the self-assembly of an amphiphilic hexa-*peri*-hexabenzocoronene (HBC) derivative, has been reported recently.[4] Traditionally, the assembly of amphiphiles in water is driven by the hydrophobic effect, resulting in a variety of aggregate morphologies.[5] In the case of amphiphilic fullerene derivatives, vesicles,[6] 1-dimensional nanotubular structures[7] or other distinct assemblies[8] are formed in water or organic media. Recently, Miyazawa and co-workers established the liquid–liquid interfacial precipitation method for $C_{60}$ (or $C_{70}$) nanowhiskers and nanotubes.[9] All previous attempts to self-assemble supramolecular architectures based on hydrophobic long-chain alkylated fullerenes resulted exclusively in columnar structures[10] and multi-bilayer membranes.[11,12]

Our research is focused on the development of facile methods to fabricate carbon-based materials of defined dimensionality. This study investigates self-assembled objects of a fullerene derivative resulting from interactions of the curved π surface of fullerene moieties and the hydrophobic effect of the three long alkyl chains in solvents of different polarity. We report the first example of controlling the architecture and dimensionality of hierarchical fullerene nanostructures, "fullerene polymorphism", by varying the nature of the solvent system. The newly designed fullerene derivative, **1**, serves as a solvophilic hybrid material consisting of a π-conjugated $sp^2$-carbon fullerene moiety and three $sp^3$-$C_{16}$ alkyl chains. Based on our experience, we expected **1** to self-assemble into a bilayer arrangement composed of π-stacked $C_{60}$ residues and interdigitated long alkyl chains. Such bilayer motifs are likely to be precursors and structural sub-units of the supramolecular objects presented here. The incorporation of three alkyl chains provides a structural wealth similar to triglycerides.[13]



**1**

Fullerene **1** was synthesized using the Prato method[14] from the corresponding 3,4,5-trihexadecyloxybezaldehyde with *N*-methylglycine and $C_{60}$ in refluxing dry toluene, and unambiguously characterized by $^1H$ and $^{13}C$ NMR, FT-IR and UV-visible spectroscopy, as well as MALDI-TOF mass spectroscopy (ESI†).

Self-assembled supramolecular objects were prepared by evaporating a 1 mL chloroform solution of **1** ([**1**] = 4.0 mM) to dryness and adding 4 mL of solvent. Subsequently heating to 60 °C for 2 h resulted in light brown mixtures, which were aged at 20 °C for 24 h, prior to microscopic examination. Solvents of variable polarity used in these experiments included 1 : 1 2-propanol/toluene and $H_2O$/THF mixtures, 1-propanol, and 1,4-dioxane.

Fullerene **1** self-assembles in high yields in the 2-propanol/toluene system into spherical aggregates with an average diameter of 250 nm. The vesicle structure of these spheres was confirmed by SEM and TEM (Fig. 1a and 1b). The analysis revealed a wall thickness of 8–9 nm (HR-TEM in Fig. 1b inset), which is in agreement with a two-lamellae bilayer arrangement of **1**. The spheres are highly stable, and their size and shape did not change over a period of 4 months at 5 °C.

We explored different solvent conditions; for instance, 1-propanol directs the assembly to 1D structures. The resulting fibers and bundles of fibers have lengths of over 20 μm (Fig. 1c). In the TEM micrograph (Fig. 1d), the fibers appear as partially twisted 2D tapes. Such fibers are expected to reveal electroconductivity due to the redox activity of **1**.[4]

So far, no imaging studies of a 2D single isolated bilayer of a fullerene derivative have been reported. When 1,4-dioxane is used,

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† Electronic Supplementary Information (ESI) available: Procedures for synthesis, SEM, TEM, AFM and DSC data, Fig. S1–S4. See DOI: 10.1039/b512320h

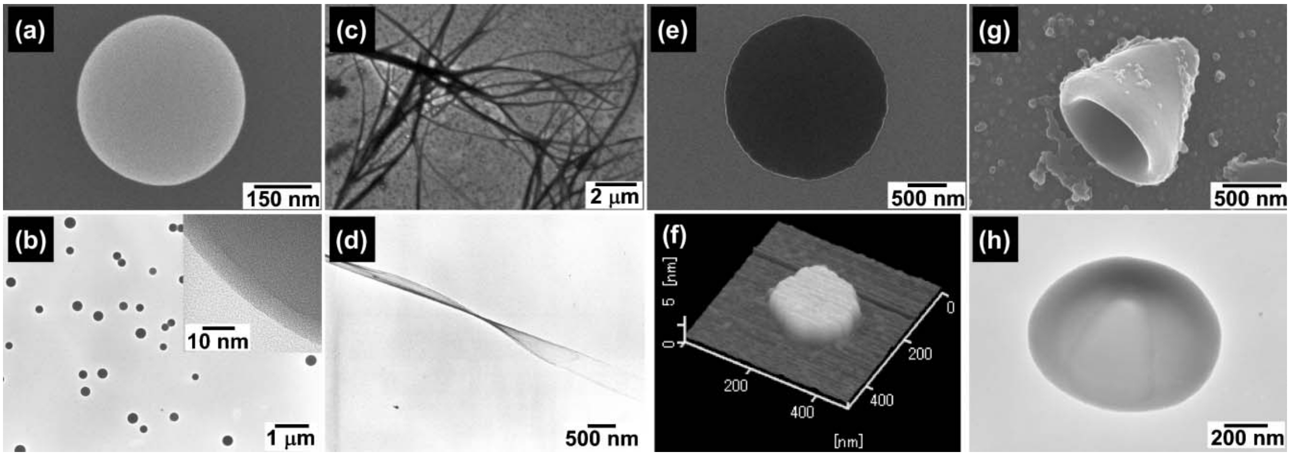

**Fig. 1** Images of hierarchical supramolecular objects of **1** formed in different solvents. SEM (a), TEM (b) and HR-TEM (inset, b) images of spherical vesicles formed from a 1 : 1 2-propanol/toluene mixture at 5 °C. SEM (c) and TEM (d) images of fibrous structures assembled from 1-propanol at 20 °C. SEM (e) and AFM (f) images of single bilayer nanodiscs formed from 1,4-dioxane at 20 °C. SEM (g) and TEM (h) images of conical objects assembled from a 1 : 1 THF/$H_2O$ mixture at 20 °C.

the brown colored supernatant contains self-assembled single bilayer discs (Fig. 1e, Fig. 1f and ESI†). The diameter of the discs are 0.2–1.5 μm. Interestingly, the layer thickness determined from AFM is about 4.4 nm, which corresponds to the thickness of an interdigitated bilayer of **1**.

Assuming an all-*trans* conformation for the alkyl chains, the Corey–Pauling–Koltun (CPK) space filling model suggests a thickness of approx. 4.3 nm (Fig. 2). The self-assembled single bilayer of **1** might be used in capacitor devices, where the conductive $C_{60}$ layers in the upper and lower parts are separated by an insulating alkyl chain layer.

When **1** is dispersed in a 1 : 1 $H_2O$/THF mixture, a turbid brown colored dispersion is obtained. SEM and TEM micrographs reveal cone-shaped objects of sub-micron size (Fig. 1g, Fig. 1h and ESI†), together with disc-like structures (SEM and TEM: ESI†). The cone apex has a hole with a diameter of *ca.* 60 nm (TEM: ESI†). The thickness of the shell of the conical objects is *ca.* ~150 nm, which corresponds to a multi-layer film. However, the detailed structure and formation mechanism for the conical objects has not been clarified. As far as we know, polymorphism in glycolipids is the only other instance showing the coexistence of disc- and cone-like structures.[15]

The X-ray diffraction (XRD) pattern of a cast film of **1** at 20.0 °C showed well-defined peaks with a *d* spacing of 4.28 nm (Fig. 3). This value is consistent with the CPK model shown in Fig. 2, where center-to-center separation of $C_{60}$ moieties is estimated to be 4.3 nm. Also, the *d* spacing is in agreement with the layer thickness of the single bilayer disc determined by AFM (Fig. 1f). In addition, a broad peak appeared at $2\theta \approx 9.5°$ ($d$ = 0.93 nm), which might correspond to the spacing of the $C_{60}$ moieties.

The IR spectra of cast films of **1** from $CHCl_3$, 1 : 1 mixtures of 2-propanol/toluene and $H_2O$/THF, 1-propanol, and 1,4-dioxane at 20.0 °C display $CH_2$ stretching vibrations at 2849 ($\nu_{sym}$) and 2918 $cm^{-1}$ ($\nu_{asym}$). These bands are blue-shifted to 2852 and 2922 $cm^{-1}$, respectively, on heating to 60.0 °C. Thus, the alkyl chains of **1** at low temperature tend to crystallize and adopt an all-*trans* conformation, while at elevated temperatures they are disordered, like in a liquid.[16] The spectral changes are reversible. In relation to these observations, differential scanning calorimetry (DSC) of **1** displays two endothermic peaks at 26.5 and 30.6 °C (ESI†). The enthalpy and entropy at 30.6 °C are calculated as $\Delta H$ = 41.6 kJ $mol^{-1}$ and $\Delta S$ = 136.9 J $mol^{-1}$ $K^{-1}$, respectively. The

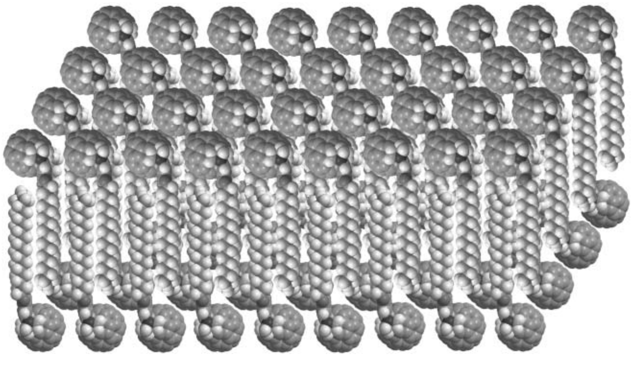

**Fig. 2** Schematic illustration of the proposed interdigitated bilayer of **1**.

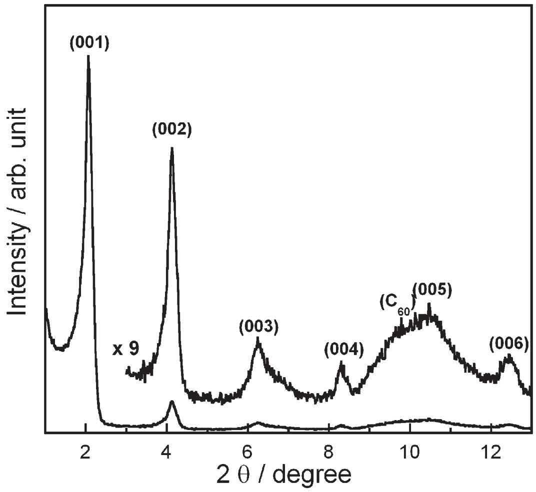

**Fig. 3** X-ray diffraction diagram of a cast film of **1**.

entropy value is in good agreement with the total entropy of phase transition for the alkyl chains ($\Delta S = 92.6$ J mol$^{-1}$ K$^{-1}$ is estimated for the three hexadecyl chains, since $\Delta S = 1.93$ J mol$^{-1}$ K$^{-1}$ per methylene unit)[17] and the $C_{60}$ part ($\Delta S = 30 \sim 40$ J mol$^{-1}$ K$^{-1}$).[11,18] The XRD, FT-IR and DSC data support the hypothesis that the supramolecular assemblies of **1** are based on a self-assembled bilayer structure.

In conclusion, we have succeeded in constructing 1, 2 and 3D supramolecular fullerene objects based on a simple fullerene derivative containing three long alkyl chains, which form a self-assembled bilayer structure as the fundamental structural sub-unit. The hierarchical supramolecular objects obtained include vesicles, fibers, discs and cones, providing hints of possible synthetic methodologies towards novel, dimension-controllable carbon materials. Detailed investigations of the supramolecular assembly mechanism of **1** and the application of these materials in fuel cells, field emission displays and functional parts of nano-sized electronic devices, such as conductive nanowires and nano-oriented capacitors, are under way in our laboratory.

This work was supported, in part, by a Grant-in-Aid for Scientific Research (no. 17750140) from the Ministry of Education, Science, Sports and Culture, Japan (T. N.), the Special Coordination Founds for Promoting Science and Technology from MEXT, Japan through an ICYS Fellowship (T. N. and W. S.), and the Iketani Science and Technology Foundation (T.N., grant 0171041-A). We are grateful to Dr. J. Jin and Mr. T. Sasaki of NIMS for assistance in the TEM measurements and to Dr. J. P. Hill of NIMS for helpful discussions.

## Notes and references

1 F. Diederich and M. Gómez-López, *Chem. Soc. Rev.*, 1999, **28**, 263; D. M. Guldi and N. Martín, *J. Mater. Chem.*, 2002, **12**, 1978; E. Nakamura and H. Isobe, *Acc. Chem. Res.*, 2003, **36**, 807; H. L. Anderson, R. Faust, Y. Rubin and F. Diederich, *Angew. Chem., Int. Ed.*, 1994, **33**, 1366; *Fullerenes: Chemistry, Physics, and Technology*, ed. K. M. Kadish and R. S. Rouff, Wiley & Sons, New York, 2000.

2 S. Iijima, *Nature*, 1991, **354**, 56; *The Science and Technology of Carbon Nanotubes*, ed. K. Tanaka, T. Yamabe and K. Fukui, Elsevier, Oxford, 1999; K. S. Chichak, A. Star, M. V. P. Altoé and J. F. Stoddart, *Small*, 2005, **1**, 452.

3 S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai and K. Takahashi, *Chem. Phys. Lett.*, 1999, **309**, 165; T. Yoshitake, Y. Shimakawa, S. Kuroshima, H. Kimura, T. Ichihashi, Y. Kudo, D. Kasuya, K. Takahashi, F. Kokai, M. Yudasaka and S. Iijima, *Physica B*, 2002, **323**, 124; H. Tanaka, H. Kanoh, M. Yudasaka, S. Iijima and K. Kaneko, *J. Am. Chem. Soc.*, 2005, **127**, 7511.

4 J. P. Hill, W. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii and T. Aida, *Science*, 2004, **304**, 1481.

5 T. Shimizu, M. Masuda and H. Minamikawa, *Chem. Rev.*, 2005, **105**, 1401; M. Dubois, B. Demé, T. Gulik-Krzywicki, J.-C. Dedieu, C. Vautrin, S. Désert, E. Perez and T. Zemb, *Nature*, 2001, **411**, 672.

6 M. Brettreich, S. Burghardt, C. Böttcher, T. Bayerl, S. Bayerl and A. Hirsch, *Angew. Chem., Int. Ed.*, 2000, **39**, 1845; M. Sano, K. Oishi, T. Ishii and S. Shinkai, *Langmuir*, 2000, **16**, 3773; S. Zhou, C. Burger, B. Chu, M. Sawamura, N. Nagahama, M. Toganoh, U. E. Hackler, H. Isobe and E. Nakamura, *Science*, 2001, **291**, 1944; J. Hao, H. Li, W. Liu and A. Hirsch, *Chem. Commun.*, 2004, 602; R. Charvet, D.-L. Jiang and T. Aida, *Chem. Commun.*, 2004, 2664.

7 A. M. Cassell, C. Lee Asplund and J. M. Tour, *Angew. Chem., Int. Ed.*, 1999, **38**, 2403; D. M. Guldi, A. Gouloumis, P. Vázquez, T. Torres, V. Georgakilas and M. Prato, *J. Am. Chem. Soc.*, 2005, **127**, 5811; N. Nakashima, T. Ishii, M. Shirakusa, T. Nakanishi, H. Murakami and T. Sagara, *Chem.–Eur. J.*, 2001, **7**, 1766.

8 Z. Shi, J. Jin, Y. Li, Z. Guo, S. Wang, L. Jiang and D. Zhu, *New J. Chem.*, 2001, **25**, 670; M. Braun, U. Hartnagel, E. Ravanelli, B. Schade, C. Böttcher, O. Vostrowsky and A. Hirsch, *Eur. J. Org. Chem.*, 2004, 1983; G. Angelini, C. Cusan, P. De Maria, A. Fontana, M. Maggini, M. Pierini, M. Prato, S. Schergna and C. Villani, *Eur. J. Org. Chem.*, 2005, 1884.

9 K. Miyazawa, Y. Kuwasaki, A. Obayashi and M. Kuwabara, *J. Mater. Res.*, 2002, **17**, 83; K. Miyazawa, J. Minato, T. Yoshii, M. Fujino and T. Suga, *J. Mater. Res.*, 2005, **20**, 688.

10 M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato and E. Nakamura, *Nature*, 2002, **419**, 702.

11 H. Murakami, Y. Watanabe and N. Nakashima, *J. Am. Chem. Soc.*, 1996, **118**, 4484; T. Nakanishi, M. Morita, H. Murakami, T. Sagara and N. Nakashima, *Chem.–Eur. J.*, 2002, **8**, 1641.

12 M. Chikamatsu, K. Kikuchi, H. Nishikawa, T. Kodama, I. Ikemoto, S. Kazaoui, K. Yase and N. Minami, *Synth. Met.*, 1999, **103**, 2403.

13 *Crystallization Processes in Fats and Lipid Systems*, ed. K. Sato and N. Garti, Marcel Dekker, New York, 2001; T. Unruh, K. Westesen, P. Bösecke, P. Lindner and M. H. J. Koch, *Langmuir*, 2002, **18**, 1796; O. O. Mykhaylyk and I. W. Hamley, *J. Phys. Chem. B*, 2004, **108**, 8069.

14 M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798.

15 S. Takeoka, K. Sou, C. Boettcher, J.-H. Fuhrhop and E. Tsuchida, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2151.

16 Y. Yamaguchi and N. Nakashima, *Anal. Sci.*, 1994, **10**, 863.

17 D. Chapman, *Biomembrane Structure and Function*, Verlag Chemie, Weinheim, 1984, pp. 1–42.

18 T. Matsuo, H. Suga, W. I. F. David, R. M. Ibberson, P. Bernier, A. Zahab, C. Fabre, A. Rassat and A. Dworkin, *Solid State Commun.*, 1992, **83**, 711.