J. Org. Chem. **1994,** *59,* 3503-3505 **3503**

The Synthesis and Characterization of a Self-Assembling Amphiphilic Fullerene

Craig J. Hawker,*[†] Paul M. Saville,[‡] and John W. White[‡]

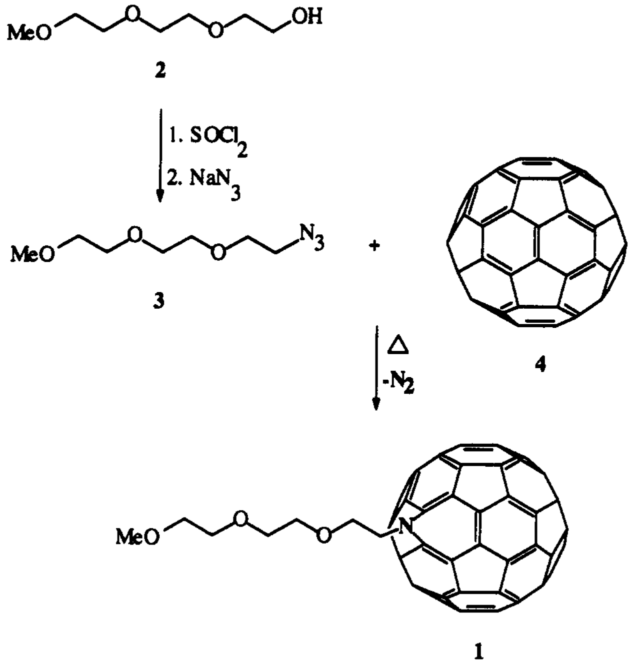
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California, 95120-6099, and Research School of Chemistry, Australian National University, GPO Box 4, Canberra, ACT, 2601, Australia

Received February 17, 1994

The study of fullerenes has witnessed explosive growth in the last few years with a large number of reports being devoted to the physics and chemistry of these unique molecules.[1] However, while fullerenes show great potential, the fabrication of devices based on C_{60} has received little attention. Specifically, thin films of fullerenes have been shown to exhibit a number of interesting properties such as superconductivity upon reduction,[2] charge transport,[3] and photochemical behavior.[4] However while the formation of monolayers of C_{60} has been reported by a number of workers[3,5,6] the monolayers are poorly behaved and transfer to solid substrates is problematic and unreliable. In an effort to overcome these difficulties and prepare stable well-defined fullerene monolayers, two approaches may be envisaged. Either a surface may be chemically modified with a reagent that allows covalent attachment of a fullerene,[7] or a fullerene can be chemically modified to give a derivative that allows for self-assembly. Herein, we report success with the latter approach by the rational synthesis of an amphiphilic derivative, **1**, in which a short hydrophilic linear chain is covalently attached to the hydrophobic C_{60} nucleus. In analogy with traditional surfactants, **1** would be expected to self-assemble at the air–water interface with the polar group associated with the water layer, thus giving an oriented monolayer.

The chemistry of buckminsterfullerene is a rapidly growing field[8] with C_{60} behaving as an electron-deficient alkene in most cases. In choosing a hydrophilic segment and functionalization reaction for the preparation of amphiphilic derivatives of C_{60} the following criteria were considered. The functionalization reaction had to be irreversible so that the monomolecular films obtained would be thermally stable and, due to the relative scarcity of C_{60}, it was desirable to obtain a fullerene derivative which did not require subsequent modification for amphiphilic character. A short poly(ethylene glycol) chain was chosen as the hydrophilic segment, and preliminary work has demonstrated the versatility of azide addition to the C_{60} nucleus, as well as the stability of the products obtained.[9] Therefore our first target was the monoazide **3**. This was prepared by reaction of the commercially available triethylene glycol monomethyl ether (**2**) with thionyl chloride followed by sodium azide. The desired monoazide **3** was obtained in good yield and constitutes the hydrophilic segment. Reaction of **3** with C_{60} (**4**) was found to proceed smoothly in refluxing chlorobenzene to give the amphiphilic monoadduct **1** as the main product in 62% yield after purification by flash chromatography eluting with dichloromethane (Scheme 1). Continued elution with 1:19 ether/dichloromethane gave minor amounts of the diaddition product **5**; however, no observable amounts of tri- or higher addition products could be detected.

Scheme 1



Interestingly the ^1H NMR of **1** was significantly different from that of the starting azide **3**. As can be seen in Figure 1 the covalent attachment of the fullerene nucleus to the triethylene glycol chain causes the resonances for the methylene protons to be inductively shifted downfield, the result of which is similar to that expected for a shift reagent. A similar observation has been noted by Prato and Wudl[9] for other substituents covalently attached to C_{60}. Structural information was also obtained from the ^{13}C NMR spectrum which exhibited seven resonances for the linear chain and 32 peaks for the fullerene nucleus in the aromatic region between 148 and 133 ppm. These results correlated with the monoaddition product **1** having the open azaannulene structure involving addition across a 6,5 junction. Mass spectral analysis also confirmed the covalent attachment of a single triethylene glycol chain. Significantly, the attachment of a single triethylene glycol chain to the fullerene nucleus was found to dramatically increase the solubility of **1** in solvents such as chloroform, THF, etc., unlike C_{60} which is essentially insoluble. The typical electrochemical properties ($E_{1/2}$ = −0.75, −1.15,

---

[†] Almaden Research Center.

[‡] Australian National University.

(1) Fischer, J. E.; Heiney, P. A.; Smith, A. B., III. *Acc. Chem. Res.* **1992**, *25*, 112 and additional articles in this issue.

(2) Hebard, A. F.; Rosseninsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T.; Ramirez, A. P. ; Kortan, A. R. *Nature* **1991**, *350*, 600.

(3) (a) Jehoulet, C.; Obeng, Y. S.; Kim, Y.; Zhou, F.; Bard, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 4237. (b) Bulhoes, L. O. S.; Obeng, Y. S.; Bard, A. J. *Chem. Mater.* **1993**, *5*, 110.

(4) Jehoulet, C.; Bard, A. J.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 5456.

(5) Obeng, Y. S.; Bard, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 6279.

(6) Maliszewskyj, N. C.; Heiney, P. A.; Jones, D. R.; Strongin, R. M.; Cichy, M. A.; Smith, A. B., III. *Langmuir* **1993**, *9*, 1439.

(7) (a) Chen, K.; Caldwell, W. B.; Mirkin, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 1193. (b) Chupa, J. A.; Xu, S.; Fischetti, R. F.; Strongin, R. M.; McCauley, J. P.; Smith, A. B.; Blaise, J. K.; Peticolas, L. J.; Bean, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 4383.

(8) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685.

(9) (a) Prato, M.; Li, Q. C.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148. (b) Hawker, C. J.; Wooley, K. L.; Frechet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1994**, in press.

0022-3263/94/1959-3503$04.50/0

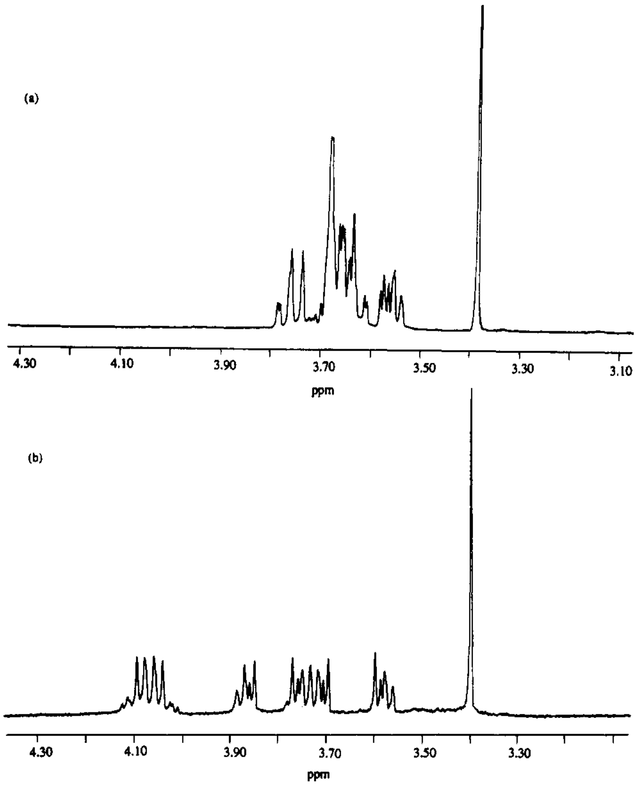


Figure 1. 300-MHz ^{1}H NMR spectra (region 3.10–4.30 ppm) of (a) monoazide **3**, and (b) amphiphilic fullerene derivative **1**.

and −1.55 V vs Ag/AgCl/3.8 M KCl) and UV-vis spectrum of an aza-substituted fulleroid nucleus were observed for **1**.

In studying the formation of monomolecular layers of C_{60} itself, unless extreme care is taken, multilayers are obtained with an average cross-sectional area of ca. 25 Å^2/molecule compared with the value for an ideal C_{60} monolayer of 93 Å^2/molecule.[10] The stability of these films can be improved by the use of matrix molecules,[11] for example a 1:1 mixture of C_{60} with icosanoic acid has been reported to give stable films, though multilayer formation and nonuniformity is again a serious problem. Recently, it has been shown[6] that under controlled conditions the monoepoxide, $C_{60}O$, forms monolayers which are more stable than C_{60} itself; in this case interaction of the oxygen with the water interface is believed to lead to stabilization. For the amphiphilic derivative, **1**, monomolecular films could be obtained by spreading toluene solutions of **1** at the air–water interface maintained at 20 °C. Interestingly, unlike the results obtained with $C_{60}O$, or C_{60} itself, the spreading solutions for **1** could be significantly more concentrated (ca. 10^{-3} M) and larger volumes could be used. Also no unphysically large molecular areas or pressure plateaus were observed due to the use of an aromatic solvent. Instead, a small increase in pressure is observed to begin at ca. 300 Å^2/molecule and continue to ca. 150 Å^2/molecule; this may point to either rafting of the molecules[12] or an intensive interaction of the hydrophilic segment of **1** with the water surface.[13] Further compression of the films leads to a steep pressure increase, which on extrapolation to zero pressure gives a limiting area of 103 ± 3 Å^2/molecule (Figure 2). This area is in close agreement with the theoretically expected value of 93 Å^2/molecule[10] and the experimentally[3,5,6] determined value of 96 Å^2/molecule for pure C_{60}. This slight increase in area may be due to the effect of the attached side chain or minor amounts of trapped solvent. Films were sufficiently stable that it was possible to hold these systems at constant pressure without any noticeable area loss.

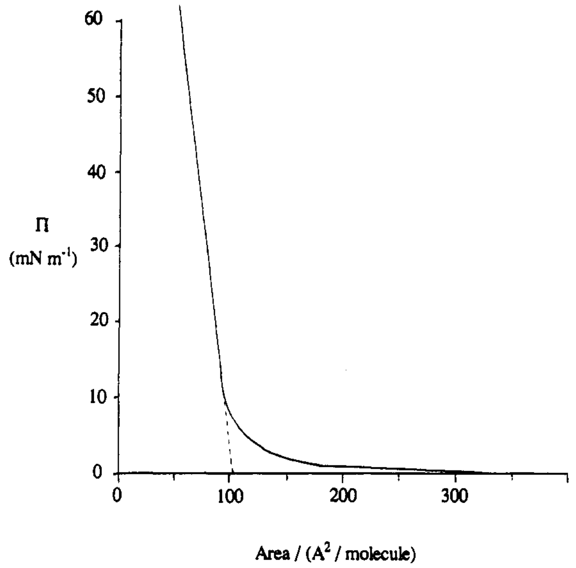


Figure 2. Surface pressure–area isotherms of fullerene derivative **1** on a pure aqueous phase at 21 °C.

In conclusion, we have shown that amphiphilic fullerene derivatives can be prepared by the reaction of C_{60} with suitably substituted azides and that these derivatives are capable of self-assembling at the air–water interface into stable monomolecular films. We believe that this concept of synthesizing fullerene derivatives with specific properties is of great promise since the desired properties of the fullerene nucleus is retained while other properties, such as film formation, is enhanced due to the added side chains. Future work will report the ability to form Langmuir–Blodgett films and their transference to solid substrates.

Experimental Section

1-Azido-3,6,9-trioxodecane (3). To a solution of triethylene glycol monomethyl ether (**2**) (16.4 g, 0.10 mol) in 100 mL of dry toluene was added dropwise a solution of thionyl chloride (18.0 g, 0.15 mol) in 20 mL of dry toluene. The reaction mixture was then heated at reflux under nitrogen for 2 h, after which the mixture was cooled and evaporated to dryness. Dry toluene (50 mL) was added, the mixture filtered, and the filtrate evaporated to dryness to remove residual traces of thionyl chloride. To the crude chloro derivative (18.0 g, 0.10 mol) dissolved in dry dimethyl sulfoxide (100 mL) was added sodium azide (13.0 g, 0.20 mol) and the mixture heated at 60 °C for 16 h. After it was cooled, the mixture was added to 500 mL of water and extracted with dichloromethane (5 × 50 mL), and the combined extracts were dried and evaporated to dryness. The crude azide was purified by distillation to afford 15.3 g (81%) of **3** as a clear oil: bp 120–123 °C/12mm; ^{1}H NMR ($CDCl_3$) δ 3.80–3.53 (complex m, 12 H), 3.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 71.80, 70.53, 70.47, 69.89, 58.88, 50.56, 40.90; IR (neat) 2920, 2095, 1280, 1105 cm^{-1}; FABMS

---

[10] Milliken, J.; Dominguez, D. D.; Nelson, H. H.; Barger, W. R. *Chem. Mater.* **1992**, *4*, 252.

[11] (a) Nakamura, T.; Tachibana, H.; Yumura, M.; Matsumoto, M.; Azumi, R.; Tanaka, M.; Kawabata, Y. *Langmuir* **1992**, *8*, 4. (b) Xiao, Y.; Yao, Z.; Jin, D.; Yan, F.; Xue, Q. *J. Phys. Chem.* **1993**, *97*, 7072.

[12] Kumaki, J. *Macromolecules* **1986**, *19*, 2258.

[13] Diederich, F.; Jonas, U.; Gramlich, V.; Herrmann, A.; Ringsdorf, H.; Thilgen, C. *Helv. Chem. Acta* **1993**, *76*, 2445.

(*m*-nitrobenzyl alcohol) *m/z* 190 (M + H)$^+$. Anal. Calcd for $C_7H_{15}N_3O_3$: C, 44.42; H, 7.99; N, 22.2. Found: C, 44.6; H, 8.05; N, 22.0.

1-Aza-3,6,9-trioxadecanefulleroid (1). In a 500-mL flask was placed buckminsterfullerene (C_{60}, 4) (500 mg, 0.69 mmol) and 300 mL of chlorobenzene. The mixture was heated at reflux under nitrogen until complete dissolution and the azide 3 (130 mg, 0.68 mmol) in chlorobenzene (10 mL) added dropwise. Heating was then continued for 24 h. The solution was evaporated to dryness and the crude residue purified by flash chromatography eluting with dichloromethane to afford 216 mg (62% based on unrecovered C_{60}) of the monoaddition product 1 as a purple solid: ^{1}H NMR ($CDCl_3$) δ 4.10 and 4.07 (m, 4 H), 3.86 and 3.58 (ABq, 4H), 3.77 and 3.73 (ABq, 4H), 3.39 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 147.79, 146.93, 145.02, 144.71, 144.68, 144.54, 144.43, 144.32, 144.28, 144.12, 143.81, 143.67, 143.50, 143.39, 143.36, 143.19, 143.08, 142.88, 142.77, 142.65, 142.62, 140.81, 140.71, 139.18, 138.46, 137.99, 137.76, 137.25, 137.21, 136.15, 135.74, 133.65, 71.91, 70.89, 70.70, 70.63, 70.34, 58.98, 51.68; IR (KBr) 2925, 1640, 1550, 1275, 1110 cm^{-1}; FABMS (*m*-nitrobenzyl alcohol) *m/z* 882 (M + H)$^+$, 720 (C_{60}^+). Anal. Calcd for $C_{67}H_{15}NO_3$: C, 91.25; H, 1.71; N, 1.59. Found: C, 91.03; H, 1.89; N, 1.36.

Continued elution with 1:19 methanol/dichloromethane gave the diaddition product 5 as a purple solid (35 mg, 15% based on unrecovered C_{60}): ^{1}H NMR ($CDCl_3$) δ 4.30 (t, 2 H), 4.08 (t, 2H), 3.77–3.50 (complex m, 20H), 3.39 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 163.44, 147.53, 146.76, 145.02, 144.78, 144.71, 144.47, 144.42, 144.39, 144.11, 144.01, 143.81, 143.61, 143.45, 143.37, 143.20, 143.05, 142.58, 141.92, 141.49, 141.30, 139.43, 139.22, 138.87, 137.19, 137.08, 137.03, 135.04, 134.47, 132.79, 130.59, 71.90, 71.83, 70.60, 70.50, 70.27, 69.91, 58.95, 50.58; FABMS (*m*-nitrobenzyl alcohol) *m/z* 1043 (M + H)$^+$, 720 (C_{60}^+). Anal. Calcd for $C_{74}H_{30}N_2O_6$: C, 85.21; H, 2.90; N, 2.69. Found: C, 85.56; H, 2.62; N, 2.33.