[8] a) J. S. Thompson, R. L. Harlow, J. F. Whitney, *J. Am. Chem. Soc.* **1983**, *105*, 3522–3527; b) J. S. Thompson, J. F. Whitney, *Inorg. Chem.* **1984**, *23*, 2813–2819; c) H. Masuda, N. Yamamoto, T. Taga, K. Machida, S. Kitagawa, M. Munakata, *J. Organomet. Chem.* **1987**, *322*, 121–129.
[9] a) L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, J. E. Young, Jr., *J. Chem. Phys.* **1963**, *42*, 2683–2686; b) D. M. P. Mingos in *Comprehensive Organometallic Chemistry, Vol. 3* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, New York, **1982**, pp. 1–88.
[10] C. Chuang, K. Lim, Q. Chen, J. Zubieta, J. W. Canary, *Inorg. Chem.* **1995**, *34*, 2562–2568.
[11] H. Masuda, K. Machida, M. Munakata, S. Kitagawa, H. Shimono, *J. Chem. Soc. Dalton Trans.* **1988**, 1907–1910.
[12] a) Y. Omote, N. Fukada, N. Sugiyama, *Nippon Kagaku Zasshi* **1969**, *90*, 1283–1285; b) M. G. Reinecke, J. F. Sebastian, H. W. Johnson, Jr., C. Pyun, *J. Org. Chem.* **1971**, *21*, 3091–3095; c) M. G. Reinecke, J. F. Sebastian, H. W. Johnson, Jr., C. Pyun, *J. Org. Chem.* **1972**, *22*, 3066–3068, and references therein.
[13] O. Yamauchi, M. Takani, K. Toyoda, H. Masuda, *Inorg. Chem.* **1990**, *29*, 1856–1860.
[14] M. Takani, H. Masuda, O. Yamauchi, *Inorg. Chim. Acta* **1995**, *235*, 367–374.
[15] R. Robson, *Inorg. Chim. Acta* **1982**, *57*, 71–77.

Self-Assembling Supramolecular Nanostructures from a C_{60} Derivative: Nanorods and Vesicles**

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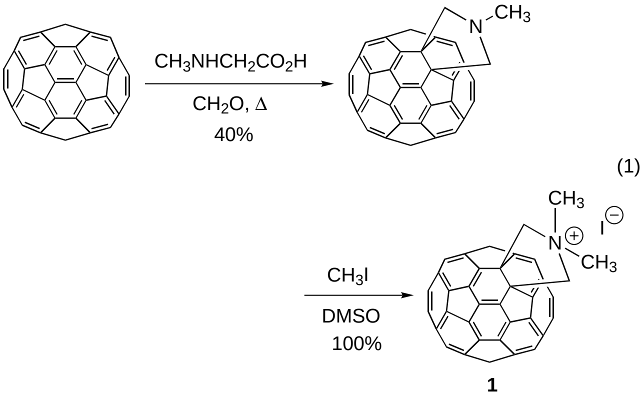
Extended fullerene structures such as those found in carbon nanotubes have attracted considerable interest from both structural and applications perspectives.[1] Similarly, nonextended C_{60} derivatives have shown promise for numerous applications.[1] In an effort to bridge the gap between self-assembling, extended structures and modified fullerene materials, we describe here the supramolecular assembly of a derivatized C_{60}. C_{60}-*N*,*N*-dimethylpyrrolidinium iodide (**1**),[2] prepared in two steps from C_{60} [Eq. (1)], can self-assemble into either nanorods or vesicles depending on how the solution is treated.



(1)

1

Nanorod structures were prepared from a two-phase mixture by diluting a solution of **1** in dimethylsulfoxide (DMSO) with one part water and then adding one part benzene (Scheme 1). Two layers were obtained, and the mixture was agitated by shaking until an emulsion formed. The emulsion dissipated after 15 min, and the two layers separated. The benzene layer contained a flocculent, hairlike material (75% yield), which was inspected by transmission electron microscopy (TEM). Rodlike structures were observed with diameters of 14–120 nm and lengths of over 70 μm (Figures 1a, b). The precise molecular orientation and spacing of **1** in the supramolecular structure is not known; however, that such extended fulleroid structures could self-assemble is striking, especially since a long hydrophobic tail is not appended onto the fullerene rings. To our knowledge, there is no similar process for the rapid supramolecular assembly of fullerenes or their derivatives in such high yields.

The scope of this process was investigated. Self-assembly of **1** into rodlike structures was not seen at concentrations less than 2.5 mM. The precise order of solvent addition was also critical: addition of benzene, then water, to a solution of **1** in DMSO followed by agitation failed to provide nanorods. To screen the effect of different solvents on nanorod formation, benzene was replaced by hexane, cyclohexane, diethyl ether, chloroform, and dichloromethane. The self-assembly experiments in chloroform and dichloromethane were inconclusive, resulting in thick milky white solutions. Using diethyl ether as solvent resulted in two clear layers absent of solid. No self-assembled structures were observed in these layers by TEM. Use of cyclohexane and hexane led to much shorter nanorods having lengths of 1–2 μm and diameters similar to those obtained with benzene.

We also explored changes to **1** that might affect assembly into nanorods. Changing the counterion in a surfactant can influence essential parameters necessary to form micellar structures.[3] In the case of **1**, exchanging the iodide for bromide, chloride, and nitrate did influence the formation of nanorods. Ion exchange of the iodide on **1** was performed by passing a solution of **1** in DMSO through an ion-exchange resin containing the desired anion. Anion exchange was detected by energy dispersive X-ray analysis (EDAX). In the case of nitrate, the absence of iodide by EDAX was proof of counterion exchange since the lighter elements cannot be detected with the system utilized. Under the same conditions employed with the iodide salt, nanorods formed from both the bromide and nitrate salts. However, no rods were detected when chloride was the counterion. We speculate that with the

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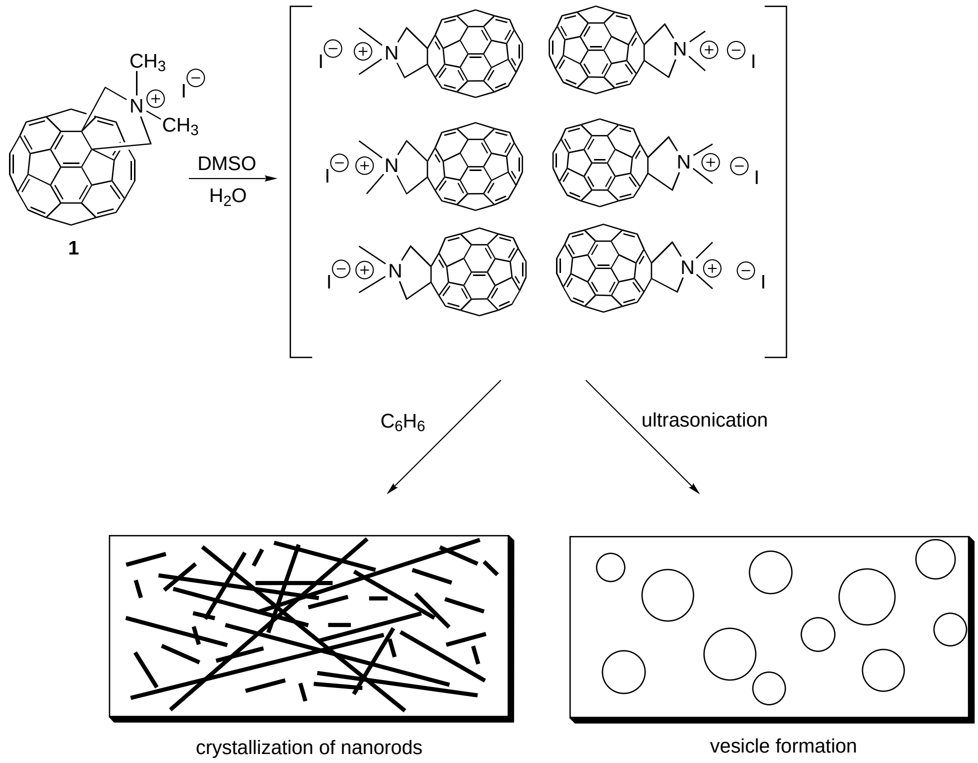

Scheme 1. Preparation of nanorods and vesicles of **1** by self-assembly. The structure shown in brackets was not observed or isolated. It merely suggests that ordering might ensue where the polar groups project outward toward the polar solvent (DMSO/H_2O), and then form a nanorod in the benzene layer.

chloride salt of **1** a tighter ion pair may inhibit the formation of rods. The TEM analysis data on the nanorods formed from the salts is shown in Table 1. While a broad range of sizes is attained with different counterions, the mean sizes are similar.

The extended fullerenes structures could be isolated and dried, but ultrasonication destroyed the assemblies. Although the full range of materials properties for these nanorods has not been investigated, their facile self-assembly and ease of manipulation is remarkable.

Table 1. Data derived from TEM of the nanorods obtained from **1** with different counterions.[a]

	NO_3^-	Br^-	I^-
mean diameter [nm]	44	39	53
no. of structures sampled	25	50	55
minimum diameter [nm]	14	9	14
maximum diameter [nm]	245	112	120

[a] All diameter measurements ±10%.

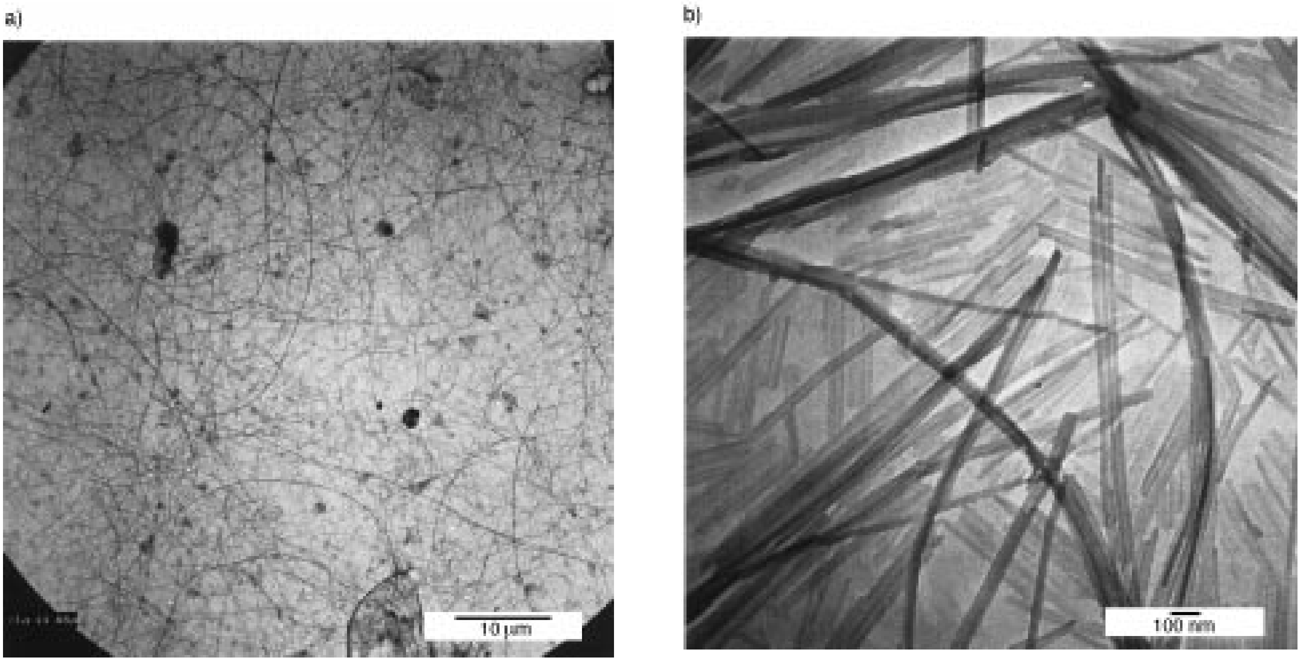

Figure 1. TEM micrographs of the nanorod formations of **1** a) at low magnification and b) at high magnification.

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Various methods have been described for preparing vesicles, including disruption of surfactant solutions by ultrasonication. Aqueous solutions of **1** were treated with ultrasonication, and ill-defined structures not containing rods were observed by TEM. No vesicles were easily seen; however, after passing the suspension through a 0.45-μm filter, the resulting clear suspension was imaged by TEM (Figure 2).

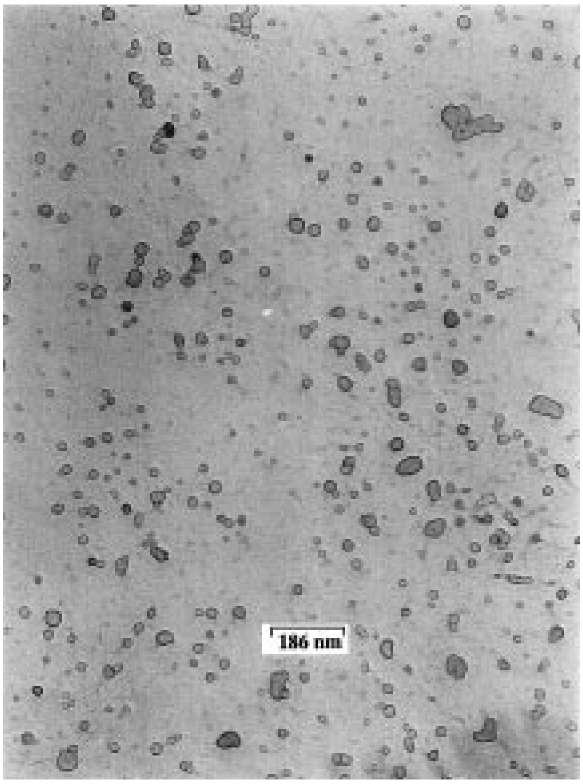

Figure 2. Vesicles of **1** observed by TEM analysis after filtration.

Vesicles had clearly formed that had diameters of 10–70 nm and wall thicknesses of 3–6 nm.[4] No rods were detected; the vast majority of the regions observed contained only these vesicle structures. Again this represents a rapid assembly of nanometer structures from a simple fullerene derivative.

These results demonstrate the facile access to various supramolecular fullerene nanostructures through simple modification of solution conditions. Further reactions such as photochemical cross-linking may provide covalently linked supramolecular structures that are more robust.[5] The breadth of fullerene and surfactant chemistry should permit routes to other derivatives and conditions capable of yielding supramolecular structures from these highly conjugated building blocks.

Experimental Section

TEM was performed on a Hitachi H-8000 electron microscope operating at an accelerating voltage between 100 and 200 keV. Copper grids (150 mesh) coated with a carbon film (Electron Microscopy Sciences) were prepared in the Electron Microscopy Center at the University of South Carolina or purchased from Ted Pella, Inc. Water (HPLC grade, triply distilled) and Dowex-1 ion-exchange resin were purchased from Sigma Aldrich. Polytetrafluoroethylene filters were used for the vesicle formation studies. EDAX was performed on a Hitachi S-2500Δ scanning electron microscope equipped with a Kevex detector. A Branson Model 5200 ultrasonic bath was used for vesicle formation.

Nanorod preparation: A soluion of **1** in DMSO (150 μL, 3.4 mM) was mixed with filtered, distilled water (150 μL). After 5 min benzene (300 μL) was added, and two layers formed. The mixture was agitated and an emulsion formed which separated into two layers after 15–30 min. The rods were contained in the top (benzene) layer in 75% yield. Nanorods were prepared for TEM analysis by placing a 2-μL drop of the suspension containing the nanotubes onto carbon-coated TEM grids. The grids were then wicked free of solvent by touching the grid with filter paper.

Vesicle preparation: A spatula tip of **1** (0.001 g, 0.0011 mmol) was placed in triply distilled water (3 mL) and sonicated for 12 h. Filtered (0.45-μm filter) and unfiltered materials were examined by TEM.

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[1] a) M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, **1996**; b) *Fullerenes, Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials* (Eds.: R. S. Ruoff, K. M. Kadish), Electrochemical Society, Pennington, NJ, **1995**; c) F. Arias, L. A. Godínez, S. R. Wilson, A. E. Kaifer, L. Echegoyen, *J. Am. Chem. Soc.* **1996**, *118*, 6086; d) U. Jonas, F. Cardullo, P. Belik, F. Diederich, A. Gügel, E. Harth, A. Herrmann, L. Isaacs, K. Müllen, H. Ringsdorf, C. Thilgen, P. Uhlmann, A. Vasella, C. A. A. Waldraff, M. Walter, *Chem. Eur. J.* **1995**, *1*, 243; e) S. Ravaine, F. Le Pecq, C. Mingotaud, P. Delhaes, J. C. Hummelen, F. Wudl, L. K. Patterson, *J. Phys. Chem.* **1995**, *99*, 9551; f) Y. Xiao, Z. Yao, D. Jin, *J. Phys. Chem.* **1994**, *98*, 5557; g) K. Chen, W. B. Caldwell, C. A. Mirkin, *J. Am. Chem. Soc.* **1993**, *115*, 1193; h) C. J. Hawker, P. M. Saville, J. W. White, *J. Org. Chem.* **1994**, *59*, 3503; i) A. M. Cassell, W. A. Scrivens, J. M. Tour, *Angew. Chem.* **1998**, *110*, 1670; *Angew. Chem. Int. Ed.* **1998**, *37*, 1528.

[2] a) R. Bullard-Dillard, K. E. Creek, W. A. Scrivens, J. M. Tour, *Biorg. Chem.* **1996**, *24*, 376; b) M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* **1993**, *115*, 9798.

[3] D. Myers, *Surfactant Science and Technology,* VCH, New York, **1988**.

[4] T. Kunitake, Y. Okahata, M. Shimomura, S. Yasunami, K. Takarabe, *J. Am. Chem. Soc.* **1981**, *103*, 5401.

[5] Y. P. Sun, B. Ma, C. E. Bunker, B. Liu, *J. Am. Chem. Soc.* **1995**, *117*, 12705.