

Supramolecular Gel-Assisted Formation of Fullerene Nanorods

Chun Zhang,* Jing Wang, Jing-Jing Wang, Min Li, Xiang-Liang Yang, and Hui-Bi Xu^[a]

Fullerene (C₆₀), a truncated icosahedron with 20 hexagons and 12 pentagons with a diameter of 7.1 Å, has attracted considerable attention because of its tremendous potential in material science as a promising building block with unique physical and chemical properties.^[1,2] During the past decade, construction of fullerene-based nanomaterials has been called for because they are of great importance in the development of optoelectronic and nanoelectronic devices. There is currently an intensive effort to develop methods for controlling the morphology of fullerene-based nanomaterials with low-dimensionality structures. So far, different methods have been developed to control the morphology of one-dimensional fullerene-based nanomaterials, including crystal/precipitation,^[3-6] template synthesis^[7-9] and amphiphilic assembly.^[10-12] Although different fullerene nanomaterials, such as nanowhiskers,^[13,14] nanowires,^[4,12] nanotubes,^[7,15,16] and nanorods^[17-19] have been prepared with these methods, developing a simple and efficient protocol for fabricating fullerene 1D nanomaterials from bottom-up strategies is still a challenge.

Recently, surfactant-assisted self-assembly (SAS) has been recognized as a promising protocol to fabricate organic nanostructures.^[20] In the SAS process, organic units are organized into different nanostructures with the assistance of surfactants. Similar to surfactants, low-molecular-weight organogelators (LMOGs) should possess the potential to fabricate organic nanostructures because of their strong self-assembly ability, and should hence be capable of forming supramolecular gels in certain organic solvents by noncovalent intermolecular interactions, such as H bonding and π - π stacking. Although organogelators have been successfully used to direct the growth of inorganic or hybrid one-dimensional nanomaterials following Shinkai's pioneering work,^[21,22] supramolecular gel-assisted self-assembly to fabricate fullerene nanostructure is unprecedented.

Herein, we report the synthesis of supramolecular gel based on bis(urea)-derived gelators (Figure 1) with toluene,

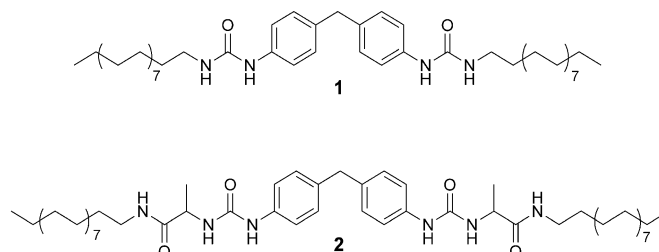


Figure 1. Chemical structures of gelators **1** and **2**.

which assisted fullerene self-assembling into nanorods with lengths of several micrometers. We have called this method supramolecular gel-assisted self-assembly (SGAS). Notably, the bis-urea derived gelator **1**^[23] was easily synthesized by a one-step reaction at room temperature in high yield from methylene diphenyl diisocyanate and octadecylamine. This easy method may be beneficial to fabricating fullerene nanorods in large scale for industrial application.

The bis-urea derived gelator **1** could form a thermoreversible physical gel in toluene (Figure 2). The thermal charac-

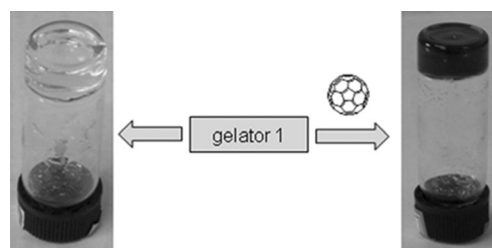


Figure 2. Photographs of gelator **1** gel in toluene (left), and gelator **1**-C₆₀ gel in toluene (right).

terization of the gel was carried out by the "vial-inverting method" to determine T_{gel} , that is, the temperature at which the sol-gel is transformed. As shown in Figure S1 in the Supporting Information, T_{gel} was found to increase from 49 to 66 °C by raising the concentration of gelator **1** from 2 to 5 wt %. Gelator **1** self-assembled into helical nanobelts with widths of approximately 50 nm, lengths of several micrometers and pitch of about 140 nm, as determined by SEM and TEM (Figure 3). The results inspired us to anticipate that co-assembly of fullerene with gelator **1** in toluene might fabricate ordered nanostructures of fullerene, which still remain a challenge because of the poor dispersibility of fullerene in common solvents.

[a] Dr. C. Zhang, J. Wang, J.-J. Wang, M. Li, Prof. X.-L. Yang, Prof. H.-B. Xu
College of Life Science and Technology
National Engineering Research Center for Nanomedicine
Huazhong University of Science and Technology
Wuhan, Hubei, 430074 (P.R. China)
Fax: (+86)27-87792234
E-mail: chunzhang@hust.edu.cn

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201202721>.

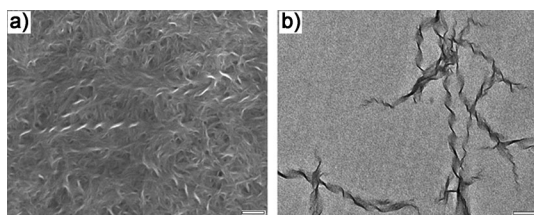


Figure 3. a) SEM, and b) TEM images of gelator **1** xerogel in toluene; scale bars: 500 nm.

As a typical protocol, gelator **1** was dissolved in a toluene solution of C_{60} (2 mg mL^{-1}) upon being heated at 110°C . Shortly after being cooled to room temperature a purple transparent gel was obtained (Figure 2). It should be noted that encapsulation of C_{60} molecules could reinforce the physical gel and increase the T_{gel} (Figure S2 in the Supporting Information). Casting the supramolecular gel onto a mica plate induced crystallization of fullerene and gelator **1**, which led to the formation of nanorods. As shown in Figure 4, SEM and TEM analysis displayed that these nano-

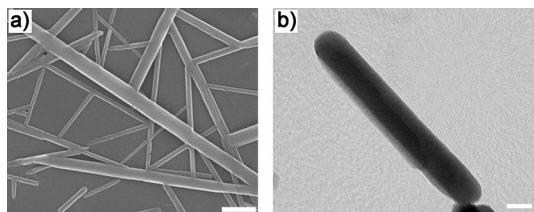


Figure 4. a) SEM (scale bar: $1 \mu\text{m}$), and b) TEM (scale bar: 100 nm) images of the xerogel prepared from gelator **1**/ C_{60} (1:1) in toluene.

rods have an average diameter of several hundred nanometers and length of several micrometers. This morphology is different from micropolyhedrons yielded by the ambient crystallization of fullerene from toluene solution (Figure S3 in the Supporting Information).

We considered that the ratio between fullerene and gelator **1** might have an important influence on the morphology of the product. We thus studied the effect of different ratios of fullerene/gelator **1** on the nanostructure of fullerene. When the molecular ratio of fullerene/gelator **1** was 1:2, a mixture of hybrid nanorods and gel helical nanobelts could be observed. When the ratio was increased to 2:1, the fullerene could not be dissolved completely because of its poor dispersibility of no more than 3 mg mL^{-1} in toluene.

The high-resolution transmission electron microscopy (HRTEM) image and selected area electron diffraction (SAED) pattern indicate that the nanorods are in a crystalline state (Figure 5). Moreover, the energy-dispersive X-ray spectroscopy (EDS) analysis of the nanorods indicated the presence of nitrogen and oxygen (Figure S4 in the Supporting Information). These results suggest that the fullerene nanorods might be enwrapped by gelator **1**.

On the basis of the above-mentioned information, we propose a possible mechanism for self-assembly (Scheme 1). In

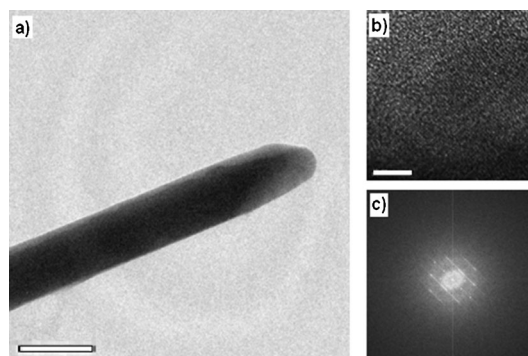
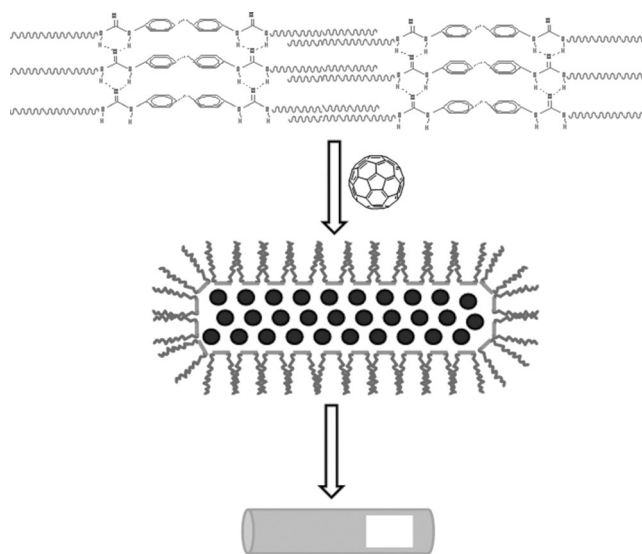


Figure 5. a), b) High-resolution TEM images of nanorods formed by gelator **1** and C_{60} (scale bars: 200 and 10 nm, respectively); and c) the corresponding SAED image.



Scheme 1. Proposed schematic illustration of the formation of nanorods by SGAS, directed by hydrogen bonding, π - π interactions and van der Waals forces.

the supramolecular gel, fullerenes were immobilized in the gel networks in single-molecule states. During the solvent evaporation, fullerenes were crystallized orderly in some domains with specific hydrophobic, hydrophilic, and other weak interactions provided by the strong hydrogen bonding and π - π interactions between gelators, and therefore formed into nanorods enwrapped by gelators.

To validate the generality of this supramolecular gel-assisted self-assembly method, we used another bis-urea gelator **2** synthesized in three steps (Scheme S2 in the Supporting Information) from diphenyl diisocyanate to co-assemble with fullerene. Gelator **2** is able to form supramolecular gel in toluene; the thermal characterization of the gel was carried out as shown in Figures S5 and S6 in the Supporting Information. Using the same protocol as mentioned above, we could obtain fullerene nanorods, which were characterized by SEM, TEM, HRTEM and SAED (Figures S7 and S8 in the Supporting Information).

In summary, we have developed a supramolecular gel-assisted self-assembly method to fabricate fullerene nanorods. This method might open a door to fabricate low-dimension nanomaterials based on small organic molecules. Further studies of the properties of the fullerene nanorods and their applications are in progress.

Experimental Section

Synthesis of gelator 1: The reaction was carried out under nitrogen atmosphere. Methylene diphenyl diisocyanate (120 mg, 0.472 mmol) and octadecylamine (260 mg, 0.963 mmol) was dissolved in CH₂Cl₂ (20 mL) and stirred at room temperature for 24 h, until the starting material could no longer be detected by thin layer chromatography (TLC). The white precipitate was filtered and washed with methanol; 290 mg (yield: 78%) of white powder with poor solubility in most solvents was obtained. MALDI-TOF-MS: *m/z* 812 [*M*+Na⁺]; IR (KBr): 3328.16, 2920.89, 2849.49, 1633.31, 1595.31, 1563.11 cm⁻¹; elemental analysis calcd (%) for C₅₁H₈₈N₄O₂: C 77.61, H 11.24, N 7.10; found: C 77.31, H 11.46, N 7.42.

Synthesis of gelator 2: Methylene diphenyl diisocyanate **3** (2 g, 8 mmol) and alanine methyl ester hydrochloride (2.42 g, 17.3 mmol) were suspended in CH₂Cl₂ (100 mL); dry Et₃N (3.5 mL) was added to this suspension. The mixture was stirred at room temperature, overnight. The white precipitate was filtered and rinsed with water to give 3.13 g (85.7% yield) of compound **4** as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.49 (2H, s), 7.26 (4H, *J* = 8.4 Hz, d), 7.04 (4H, *J* = 8.4 Hz, d), 6.49 (2H, *J* = 7.2 Hz, d), 4.23 (2H, *J* = 7.2 Hz, m), 3.76 (2H, s), 3.64 (6H, s), 1.29 ppm (6H, *J* = 7.2 Hz, d); ¹³C NMR (100 MHz, [D₆]DMSO): δ = 173.81, 154.52, 137.88, 134.43, 128.69, 117.75, 51.76, 47.93, 17.77 ppm; EI-MS: *m/z*: 456 [*M*⁺]; IR (KBr): 3307.43, 1734.98, 1631.58, 1566.96 cm⁻¹; elemental analysis calcd (%) for C₂₃H₂₈N₄O₆: C 60.52, H 6.18, N 12.27; found: C 60.40, H 6.22, N 12.01.

Compound **4** (1.74 g, 3.81 mmol) was dissolved in THF (90 mL), a solution of KOH (2.2 g, 39.2 mmol) in a mixture of water (9 mL) and methanol (45 mL) was added, then stirred and heated to reflux. The advancement of the reaction was monitored by TLC until no more ester was observed, after 2 h the reaction mixture was concentrated, neutralized with 1 N HCl aqueous solution and the precipitate was filtered and dried in vacuum for 12 h to obtain **5** (1.48 g, 91%) as a white powder, which was used directly without purification. Compound **5** (444 mg, 1.04 mmol), octadecylamine (643.8 mg, 2.39 mmol), EDC (467.8 mg, 2.44 mmol) and NHS (512.4 mg, 4.3 mmol) were dissolved in DMSO (120 mL) and stirred for 24 h at room temperature. The reaction mixture was poured into a large amount of water, then filtered, washed with CH₂Cl₂ to obtain 740 mg gelator **2** (76% yield) as a white solid. MALDI-TOF-MS: *m/z*: 952 [*M*+Na⁺]; IR (KBr): 3281.70, 2920.22, 2851.28, 1633.02, 1605.69, 1564.57 cm⁻¹; elemental analysis calcd (%) for C₅₇H₉₈N₆O₄: C 73.50, H 10.61, N 9.02; found: C 73.83, H 10.80, N 9.38.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20902031), the National Basic Research Program (2012CB932500 and 2011CB933103), the Fundamental Research Funds for the Central

Universities (HUST-2011TS148) and Wuhan ChenGuang Program (201150431118). We also thank the Analytical and Testing Center of Huazhong University of Science and Technology for related analysis.

Keywords: fullerenes • gels • nanorods • nanomaterials • self-assembly

- [1] A. Hirsch, M. Brettreich, in *Fullerenes*, Wiley-VCH, Weinheim, 2005.
- [2] S. S. Babu, H. Möhwald, T. Nakanishi, *Chem. Soc. Rev.* **2010**, *39*, 4021.
- [3] M. H. Nurmawati, P. K. Ajikumar, R. Renu, C. H. Sow, S. Valiya-veetil, *ACS Nano* **2008**, *2*, 1429.
- [4] J. Geng, W. Zhou, P. Skelton, W. Yue, I. A. Kinloch, A. H. Windle, B. F. G. Johnson, *J. Am. Chem. Soc.* **2008**, *130*, 2527.
- [5] H. S. Shin, S. M. Yoon, Q. Tang, B. Chon, T. Joo, H. C. Choi, *Angew. Chem.* **2008**, *120*, 705; *Angew. Chem. Int. Ed.* **2008**, *47*, 693.
- [6] S. Pekker, A. Jánossy, L. Mihaly, O. Chauvet, M. Carrard, L. Forró, *Science* **1994**, *265*, 1077.
- [7] H. Liu, Y. Li, L. Jiang, H. Luo, S. Xiao, H. Fang, H. Li, D. Zhu, D. Yu, J. Xu, B. Xiang, *J. Am. Chem. Soc.* **2002**, *124*, 13370.
- [8] R. Bai, M. Ouyang, Z.-Z. Li, L.-G. Yang, M.-M. Shi, G. Wu, M. Wang, H.-Z. Chen, *J. Mater. Chem.* **2008**, *18*, 4318.
- [9] S. I. Cha, K. i. Miyazawa, J.-D. Kim, *Chem. Mater.* **2008**, *20*, 1667.
- [10] S. Zhou, C. Burger, B. Chu, M. Sawamura, N. Nagahama, M. Toganoh, U. E. Hackler, H. Isobe, E. Nakamura, *Science* **2001**, *291*, 1944.
- [11] T. Kawauchi, J. Kumaki, E. Yashima, *J. Am. Chem. Soc.* **2006**, *128*, 10560.
- [12] R. Tsunashima, S.-I. Noro, T. Akutagawa, T. Nakamura, H. Kawakami, K. Toma, *Chem. Eur. J.* **2008**, *14*, 8169.
- [13] K. Miyazawa, Y. Kuwasaki, A. Obayashi, M. Kuwabara, *J. Mater. Res.* **2002**, *17*, 83.
- [14] M. Sathish, K. Miyazawa, T. Sasaki, *Chem. Mater.* **2007**, *19*, 2398.
- [15] K. Miyazawa, J. Minato, M. Fujino, T. Suga, *Diamond Relat. Mater.* **2006**, *15*, 1143.
- [16] C. Ringor, K. Miyazawa, T. Awane, *Synthesis of C-60 Fullerene Nanotubes by the Liquid-Liquid Interfacial Precipitation Method*, Materials Research Society Japan-Mrs-J, Tokyo, **2007**.
- [17] L. Wang, B. Liu, D. Liu, M. Yao, Y. Hou, S. Yu, T. Cui, D. Li, G. Zou, A. Iwasiewicz, B. Sundqvist, *Adv. Mater.* **2006**, *18*, 1883.
- [18] L. Wang, B. Liu, S. Yu, M. Yao, D. Liu, Y. Hou, T. Cui, G. Zou, B. Sundqvist, H. You, D. Zhang, D. Ma, *Chem. Mater.* **2006**, *18*, 4190.
- [19] T. Tsuchiya, R. Kumashiro, K. Tanigaki, Y. Matsunaga, M. O. Ishit-suka, T. Wakahara, Y. Maeda, Y. Takano, M. Aoyagi, T. Akasaka, M. T. H. Liu, T. Kato, K. Suenaga, J. S. Jeong, S. Iijima, F. Kimura, T. Kimura, S. Nagase, *J. Am. Chem. Soc.* **2008**, *130*, 450.
- [20] Y. S. Zhao, H. Fu, A. Peng, Y. Ma, Q. Liao, J. Yao, *Acc. Chem. Res.* **2010**, *43*, 409.
- [21] Y. Ono, K. Nakashima, M. Sano, Y. Kanekiyo, K. Inoue, J. Hojo, S. Shinkai, *Chem. Commun.* **1998**, 1477.
- [22] K. J. C. van Bommel, A. Friggeri, S. Shinkai, *Angew. Chem.* **2003**, *115*, 1010–1030; *Angew. Chem. Int. Ed.* **2003**, *42*, 980–999, and references therein.
- [23] K. Hanabusa, K. Shimura, K. Hirose, M. Kimura, H. Shirai, *Chem. Lett.* **1996**, 885.

Received: July 29, 2012

Revised: October 5, 2012

Published online: October 30, 2012