Fullerene-Centered Macromolecules as Unimolecular Micellar Structures

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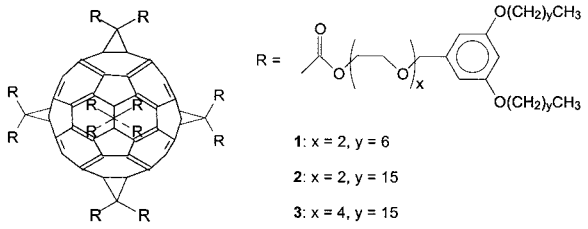
Dendritic macromolecules have attracted widespread attention for their unique structures and many potential applications.[1,2] Recently, the use of dendrimers as nanoscale reactors has also been discussed. For example, Fréchet and co-workers reported that high-generation dendrimers with benzylic ether as the repeating unit and terminated with tetradecyl behave as reverse micelles, in which E1 and S_N2 reactions may be accelerated.[3] Tomalia and co-workers used the PAMAM dendrimers as a template for the preparation and stabilization of copper-based nanocomposites.[4] On a closely related subject, Crooks and co-workers reported that metal nanoparticles such as platinum and palladium could be encapsulated in PAMAM dendrimers for homogeneous catalysis in hydrogenation reactions.[5]

Fullerene C_{60} as a spherical molecule is an ideal center block for highly symmetric dendritic structures. Fréchet, Wudl, and co-workers first prepared dendra that are attached to a methanofullerene cage.[6] Since then, there have been several reports on the synthesis of dendrimers with fullerene cages as end groups.[7] Recently, Hirsch and co-workers used C_{60} as the center block for the preparation of dendrimers that are symmetric in three dimensions, and they called these highly symmetric macromolecules globular dendrimers.[8] At the same time, we have been independently developing fullerene-centered dendritic macromolecular structures of different functionalities by using both convergent and divergent methods.[9] Here we report the synthesis of fullerene-centered core−shell macromolecules via hexakisadditions of malonic diester to a C_{60} cage (**1**−**3**). With the intramolecular phase separation due to block hydrophilic−hydrophobic moieties, these essentially unimolecular micellar structures allow the encapsulation of an aqueous or polar minor phase in a lipophilic solution, as demonstrated by ^{7}Li NMR and ^{2}H NMR spectroscopy, and also facilitate the preparation and stabilization of nanoscale metal particles.



The macromolecules **1**−**3** were synthesized via the Bingel−Hirsch-type hexakisaddition reactions.[10,11] For **3** as an example, the malonic diester for the hexakisaddition was prepared as follows. A solution of 11-[(3′,5′-dihexadecoxybenzyl)oxy]-3,6,9-trioxa-1-undecanol and pyridine in methylene chloride was stirred in an ice−water bath for 5 min, followed by dropwise addition of malonyl dichloride. The mixture was first kept at 0 °C for ∼1 h and then allowed to warm to the room temperature for stirring overnight. The dark blue-colored reaction mixture was washed with brine, and the aqueous layer was then extracted with chloroform until colorless. The organic portions were combined, dried with anhydrous $MgSO_4$, and concentrated on a rotary evaporator. The malonic diester was obtained via silica gel column chromatography separation (∼30% yield). In the hexakisaddition reaction, C_{60} was stirred with 10-fold of 9,10-dimethylanthracene in dry toluene for 2 h under nitrogen protection, followed by the addition of 10-fold of malonic diester, 10-fold of carbon tetrabromide, and 20-fold of 1,8-diazabicyclo[5.4.0]undec-7-ene.[10,11] The mixture was stirred for 5 days at room temperature under nitrogen protection, and the solution color turned from dark to red/orange. The hexakisadduct **3** was separated from the reaction mixture via silica gel column chromatography, with an estimated yield of 15% on the basis of consumed C_{60}, and positively identified by ^{1}H and ^{13}C NMR.[12] The other fullerene-centered core−shell macromolecules were synthesized, separated, and identified by using similar experimental procedures and conditions.[13]

Each highly symmetric dendrimerlike structure contains a functionalized C_{60} core, a layer of polar ethylene

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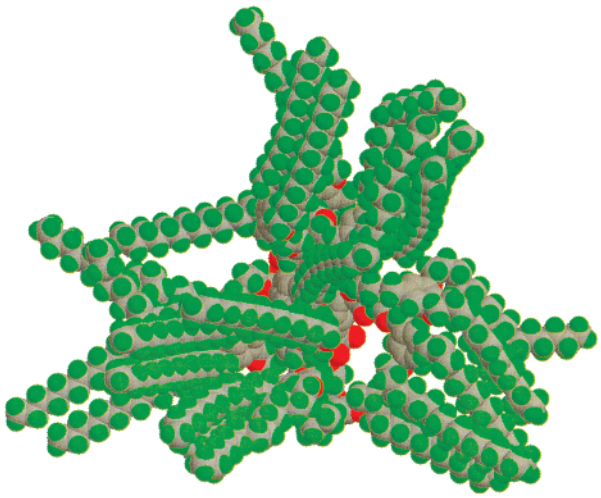

Figure 1. Structure of the dendritic macromolecule **3** optimized using the molecular mechanic method in the commercial software package PC Spantan Pro 1.0 (Wave function Inc.). Red: oxygen. Gray: carbon. Green: hydrogen.

glycol moiety, and an outer shell of lipophilic long chains (Figure 1); thus, they exhibit unimolecular micellar properties. The polar/hydrophilic cavities due to the ethylene glycol layer were probed in terms of ^{7}Li NMR spectroscopy. In a typical experiment, a solution of **2** in dodecane (3 mM) was sonicated with an aqueous LiCl solution (1 M) for 1 min for loading LiCl/water into the hydrophilic cavities of **2**. Then, the solution mixture was allowed to settle for 72 h or longer to ensure complete phase separation. A portion of the dodecane layer was carefully syringed and transferred to a 5 mm NMR tube, and the tube was immersed in D_2O in a 10 mm NMR tube, where D_2O was used as the lock. The ^{7}Li NMR spectrum of the solution has a signal at 0.4 ppm in reference to the external standard of an aqueous LiCl solution (Figure 2), and the signal may be attributed to the Li species in the hydrophilic cavities of **2**. No such signal was observed for the blank solution that was prepared via the same experimental procedures under the same conditions but without **2**. The ^{7}Li NMR signal intensity was apparently dependent on the concentration of the initial **2** solution in dodecane; a lower concentration (0.6 mM instead of 3 mM) resulted in a significantly lower signal-to-noise ratio in the ^{7}Li NMR spectrum obtained with the same number of scans.

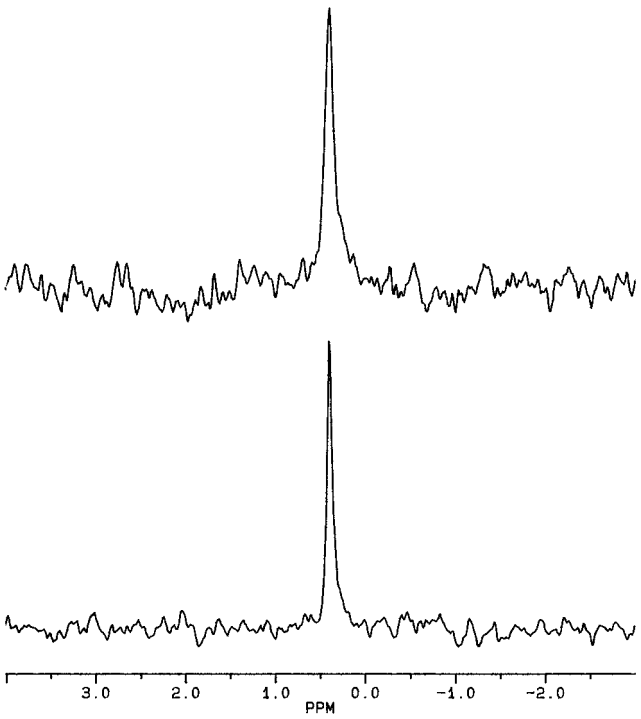

Figure 2. Comparison of the ^{7}Li NMR spectra of the core−shell macromolecules encapsulated with LiCl/H_2O in dodecane solutions. The top spectrum is for **2** with 17 000 scans, and the bottom spectrum is for **3** with 1020 scans but still a significantly better signal-to-noise ratio.

The intake of LiCl/water is also dependent on the size of the ethylene glycol layer in the macromolecular structures. When **3** instead of **2** was used under the same experimental conditions, the ^{7}Li NMR signal at 0.4 ppm became more intense, corresponding to a better signal-to-noise ratio with significantly fewer scans (Figure 2). For a rough estimate of the LiCl/water intake, LiCl/D_2O was loaded into the cavities of **3** via the same procedures as described above. The solution of **3** with encapsulated LiCl/D_2O in dodecane (1 mM) was used in the ^{2}H NMR analysis, where C_6D_6 was also added (33 mM) as the internal standard,. Scanning for 20 min resulted in a ^{2}H NMR spectrum consisting of three signals at 7.13 (C_6D_6), 4.69 (D_2O), and 1.2 (dodecane) ppm (Figure 3). According to the signal integrations, the average intake is ∼15 D_2O molecules/macromolecule **3**. Obviously, this is only the estimated intake under the specific loading conditions, which is probably lower than the maximum capacity of the micellar structure because our loading procedure is not optimized. In addition, the LiCl concentration in the cavities could be higher than that of the starting bulk aqueous solution (see below).

The polar/hydrophilic cavities in the micellar structures accommodate LiCl/methanol significantly better than LiCl/water, with a higher intake indicated by the corresponding much stronger ^{7}Li NMR signal. However, the chemical shift of the signal is close to zero (0.04 ppm), different from that of LiCl/water in the micellar structures. The results suggest that solvent molecules (methanol vs water) still play an important role in determining the chemical environment of Li species in the micellar cavities. Thus, it seems that Li cations are

(12) **3**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 72H, terminal CH_3, J = 6.9 Hz), 1.20−1.50 (m, 624H, C**H**$_2$), 1.75 (m, 48H, OC**H**$_2$CH$_2$), 3.5−3.8 (m, 168H), 3.91(m, 48H, OCH$_2$C$_{15}$H$_{31}$), 4.4−4.5 (m, 48H, COOCH$_2$ and benzyl CH$_2$), 6.35 (m, 12H, phenyl H), 6.46 (m, 24H, phenyl H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.23, 22.79, 26.18, 29.47, 29.54, 29.71, 29.74, 29.77, 29.81, 32.03, 45.17 (methano bridge), 65.87, 68.08, 68.62, 69.38, 70.68, 73.31, 100.51, 105.97, 140.57, 141.03 (sp^2 carbons on the cage), 145.87 (sp^2 carbons on the cage), 160.44, 163.61 (C=O) ppm.

(13) **1**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, 72H, terminal CH_3, J = 6.9 Hz), 1.30−1.50 (m, 192H, CH_2), 1.76 (m, 48H, OCH$_2$C**H**$_2$), 3.4−3.8 (m, 72H), 3.90 (m, 48H, OC**H**$_2$C$_6$H$_{13}$), 4.4−4.5 (m, 48H, COOCH$_2$ and benzyl CH$_2$), 6.34 (m, 12H, phenyl H), 6.47 (m, 24H, phenyl H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.18, 22.70, 26.11, 29.17, 29.38, 31.88, 45.22 (methano bridge), 65.87, 68.07, 68.65, 69.09, 69.53, 70.69, 73.31, 100.54, 105.95, 140.60, 141.11 (sp^2 carbons on the cage), 145.94 (sp^2 carbons on the cage), 160.44, 163.61 (C=O) ppm. **2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 72H, terminal CH_3, J = 6.9 Hz), 1.20−1.50 (m, 624H, CH_2), 1.75 (m, 48H, OCH$_2$C**H**$_2$), 3.5−3.8 (m, 72H), 3.90 (m, 48H, OC**H**$_2$C$_{15}$H$_{31}$), 4.4−4.5 (m, 48H, COOCH$_2$ and benzyl CH$_2$), 6.33 (m, 12H, phenyl H), 6.45 (m, 24H, phenyl H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.24, 22.80, 26.21, 29.42, 29.48, 29.59, 29.74, 29.78, 29.84, 31.69, 32.04, 45.18 (methano bridge), 65.89, 68.06, 68.66, 69.08, 69.50, 70.69, 73.31, 100.46, 105.92, 140.58, 141.11 (sp^2 carbons on the cage), 145.94 (sp^2 carbons on the cage), 160.43, 163.63 (C=O) ppm.

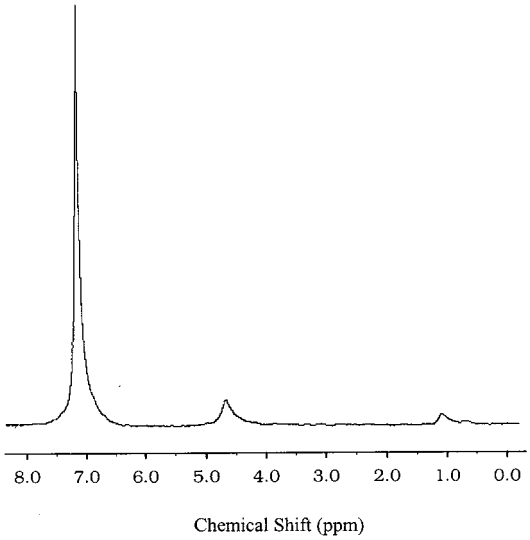

Figure 3. ^{2}H NMR spectrum of **3** encapsulated with LiCl/D_2O in a dodecane solution (C_6D_6 as the internal reference for signal intensity).

more likely encapsulated in the cavities rather than specifically bonded with the ethylene glycol moiety for crown ether type complexes, though this type of specific interaction may have helped the encapsulation.

We have experimented with the use of these unimolecular micellar structures as nanoreactors in the preparation of nanocrystalline silver particles. In a typical experiment, equal volumes of a **1** solution in hexane (1 mg/mL) and an aqueous solution of $AgNO_3$ (1 M) were mixed in a test tube and sonicated for 2 min. After phase separation, the upper hexane layer containing $AgNO_3$/**1** was pipetted into a flask. Similarly, equal volumes of the **1** solution in hexane and an aqueous solution of hydrazine (2.5 M) were mixed in another test tube and sonicated for 2 min, and the upper hexane layer containing hydrazine/**1** was pipetted into the same flask. The mixture in hexane was then stirred for 2 h under nitrogen protection to yield nanocrystalline silver particles via reduction. The nanoparticles thus prepared were likely stabilized by the core−shell macromolecules, showing no sign of precipitation. The particles were deposited on a collodion film supported by a copper grit for electron microscopy analysis. The transmission electron microscopy results of the sample are shown in Figure 4. The identification of the silver particles was confirmed by energy-dispersion X-ray analysis. Interestingly, however, while these particles appear to be uniform in size, each exhibits a small darker (higher

Figure 4. Transmission electron microscopy image of the silver nanoparticles obtained via chemical reduction using **1** as the template.

electron density) area, indicating that the individual silver particles have their own structures. Further investigations are required to explore the structural details of these nanoparticles and their relationships to the templating unimolecular micelles.

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