# A Salt-Free Zero-Charged Aqueous Onion-Phase Enhances the Solubility of Fullerene $C_{60}$ in Water

**Hongguang Li,[†] Xiangfeng Jia,[†] Yi Li,[†] Xingwang Shi,[†] and Jingcheng Hao*[,†,‡]**

*Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, P. R. China, and State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China*

An onion-phase (multilamellar vesicular phase or Lα-phase) was prepared from salt-free zero-charged cationic and anionic (catanionic) surfactant mixtures of tetradecyltrimethylammonium hydroxide (TTAOH)/lauric acid (LA)/$H_2O$. The $H^+$ and $OH^-$ counterions form water (TTAOH + LA → TTAL + $H_2O$), leaving the solution salt free. The onion-phase solution has novel properties including low conductivity, low osmotic pressure and unscreened electrostatic repulsions between cationic and anionic surfactants because of the absence of salt. The spherical multilamellar vesicles have an average 250 nm radius as measured by freeze-fracture transmission electron microscopy (FF-TEM) and the maximum interlayer distance, i.e., the thickness of the hydrophobic bilayer and the water layer, was calculated to be around 52 nm by small-angle X-ray scattering (SAXS). Extremely hydrophobic $C_{60}$ fullerene can be solubilized in this salt-free zero-charged aqueous onion-phase. As a typical result, 0.588 mg·mL$^{-1}$ (∼0.82 mmol·L$^{-1}$) $C_{60}$ has been successfully solubilized into a 50 mmol·L$^{-1}$ catanionic surfactant onion-phase aqueous solution. The weight ratio of fullerene to TTAL is calculated to be around 1:40. Solubilization of $C_{60}$ in the salt-free catanionic onion-phase solution was investigated by using different sample preparation routes, and a variety of techniques were used to characterize these vesicular systems with or without encapsulated $C_{60}$. The onion-phase solution changed color from slightly bluish to yellow or brown after $C_{60}$ was solubilized. $^1H$ and $^{13}C$ NMR measurements indicated that the $C_{60}$ molecules are located in the hydrophobic layers, i.e., in the central positions [ω-$CH_3$ and δ-$(CH_2)_x$] of the hydrophobic layers of the TTAL onion-phase. Salt-free zero-charged catanionic vesicular aqueous solutions are good candidates for enhancing the solubility of $C_{60}$ in aqueous solutions and may broaden the functionality of fullerenes to new potential applications in biology, medicine, and materials. Hopefully, our method can also be extended to solubilize functionalized carbon nanotubes in aqueous solutions.

## Introduction

Since the discovery[1] and production of $C_{60}$ in quantity,[2] $C_{60}$ fullerene has received much attention and shown great potential applications in physics, chemistry, life science, and materials science. Unfortunately, the extremely poor solubility of $C_{60}$ in water has greatly hindered its further study and practical (or potential) applications, especially in applications related to its biological activity.[3,4] To overcome this difficulty, two methods are usually adopted: (a) to synthesize water-soluble $C_{60}$ derivatives by chemically attaching some hydrophilic functional groups to the pristine $C_{60}$, which often leads to a disruption of the symmetry and pseudoaromaticity of $C_{60}$, or (b) to solubilize $C_{60}$ by suitable carriers which have hydrophobic cores or bilayers. For this purpose, macromolecules including γ-cyclodextrine,[5] calixerene,[6] and several aqueous micellar[7−12] or vesicular solutions[7,13] formed by surfactants have been used. However, to the best of our knowledge, the maximum solubility of $C_{60}$ achieved to date is about 0.4 mg·mL$^{-1}$ in aqueous solution. New candidates are needed to further improve the solubility of $C_{60}$ in water.

On the other hand, taking into consideration biological uses, vesicle solubilization of $C_{60}$ is of particular interest, because vesicles are expected to be good drug carriers and represent the simple model systems of biological membranes. Although good work has been done by Hungerbühler et al.[7] and Bensasson et al.[13] in using vesicular aqueous solutions as solubilization media of $C_{60}$, no systematic investigations have appeared on the solubilization of $C_{60}$ in catanionic surfactant solutions. Catanionic solutions have been well-known as easy to form thermodynamically stable vesicles in dilute solutions since the pioneering work of Kaler et al. in 1989.[14] However, as the concentrations of cationic and anionic surfactants increase, the excess salt formed by the counterions induces a high conductivity and ionic strength that screens electrostatic interactions between aggregates and further induces a high osmotic pressure that makes the colloidal solutions rather unstable, leading to the formation of precipitates when the stoichiometry between the cationic and anionic components is exactly 1.[15] In recent years, excess salt has been eliminated by the strategy of using $OH^-$ and $H^+$ as counterions of cationic and anionic surfactants, respectively, and by mixing them in equimolar ratios. The so-called salt-free catanionic surfactant systems thus obtained are fascinating. Pioneering studies of these systems have been done by Hoffmann et al.,[16] Zemb,[17] and our group.[18] Recent reports have demonstrated the production of novel self-assembled structures such as flat nanodiscs in the case of cationic surfactant excess,[17a,c] regular hollow icosahedra in anionic surfactant excess,[17b,c] and uni- and multilamellar vesicles with equimolar cationic/anionic surfactants.[18] Because they are salt-free, the unscreened electrostatic repulsion between aggregates induces a low osmotic pressure which highly stabilizes the colloidal

---

  * Address correspondence to this author. E-mail: jhao@sdu.edu.cn. Phone: +86-531-88366074. Fax: +86-531-88564464.

  † Shandong University.

  ‡ Lanzhou Institute.

Enhancement of the Solubility of Fullerene $C_{60}$ in Water

*J. Phys. Chem. B, Vol. 110, No. 1, 2006* **69**

solution. Thus, salt-free catanionic systems can be prepared at very high concentrations without any precipitation, making them good candidates to further improve the solubility of $C_{60}$ in aqueous solution.

On the basis of the recent report on the phase behavior and uni- and multilamellar vesicles (onion-phase) of catanionic surfactant systems of TTAOH mixing with different fatty acids[18b] including lauric acid (LA), here, the salt-free zero-charged catanionic surfactant onion-phase was chosen as the candidate to enhance the solubility of $C_{60}$ in aqueous solutions. It was found that the salt-free zero-charged catanionic surfactant onion-phase could greatly enhance the solubility of fullerene $C_{60}$ in water. Properties of solubilized $C_{60}$ in onion-phase aqueous solutions were investigated by using different sample preparation routes and a variety of techniques such as $^1H$ and $^{13}C$ NMR spectroscopy, indicating that $C_{60}$ molecules are present in the hydrophobic layers.

## Experimental Section

**Chemicals and Materials.** Tetradecyltrimethylammonium bromide (TTABr) was purchased from Merck and used without further purification. Lauric acid (LA, > 98%), toluene, and NaBr were all purchased from Shanghai Shiyi Chemicals Reagent Co. Ltd. and used without further purification. All the other reagents were analytical grade. $C_{60}$ was purchased from Sigma, 99% pure by HPLC, and was purified by crystallization from toluene before use. $D_2O$ and $C_6D_6$ were obtained from Cambridge Isotope Laboratories (CIL), Inc.

**Preparation of the Salt-free Zero-Charged Catanionic Surfactant Onion-Phase.** TTAOH stock solution was prepared from TTABr aqueous solution (140 mmol·L$^{-1}$) with use of a strong base anion exchanger (Ion exchanger III, Merck) at 40 °C. Bromide ions could not be detected by AgNO$_3$ in the TTAOH stock solution with excess HNO$_3$ (Ag$^+$ + Br$^-$ → AgBr, yellow precipitate), so the ion exchange with hydroxide was >99%. The total concentration of the stock TTAOH solution was determined by acid−base titration with 0.10 mol·L$^{-1}$ HCl to be 122.1 mmol·L$^{-1}$. To a known volume of TTAOH solution (100 mmol·L$^{-1}$) was added an equimolar solid LA to completely neutralize the free OH$^-$. Birefringent and bluish Tetradecyltrimethylammonium laurate (TTAL)
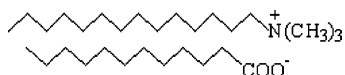


onion-phase (Lα-phase) solution was obtained after being kept at room temperature for two months to reach phase equilibrium. To obtain solid TTAL, the 100 mmol·L$^{-1}$ TTAL vesicular solution was dried in a N$_2$ stream below 40 °C.

**Freeze-Fracture Transmission Electron Microscopy (FF-TEM) Observations.** Birefringent Lα-phase solutions were characterized to determine their detailed structures by FF-TEM. Two typical samples are viscoelastically birefringent Lα-phase solutions with 50 and 100 mmol·L$^{-1}$ TTAL. A small amount of solution to be characterized was placed on a 0.1 mm thick copper disk then covered with a second copper disk. The copper sandwich with the sample was frozen by plunging this sandwich into liquid propane, which had been cooled by liquid nitrogen. Fracturing and replication were carried out at a temperature of −140 °C. Pt/C was deposited at an angle of 45°. The replicas were examined in a CEM 902 electron microscope (Zeiss, Germany) operated at 80 kV.

**Negative-Staining TEM Observations.** The structures of vesicular aqueous solutions containing $C_{60}$ were determined by

negative-staining TEM with uranyl acetate used as the negative stain dye. A drop of aqueous vesicular solution containing $C_{60}$ was placed on a TEM grid (copper grid, 3.02 mm, 200 mesh, coated with Formvar film) and stained with 2% uranyl acetate aqueous solution, which was absorbed off by a piece of filter paper 15 s later. After the solution was dried in air, TEM images were taken on a JEOL JEM 100-CXII instrument (Japan) at an accelerating voltage of 100 kV.

**Small-Angle X-ray Scattering (SAXS) Measurements.** Small-angle X-ray scattering experiments were operated at 298K by means of a Kratky compact small-angle system equipped with a position sensitive detector (OED 50M from Mbraun, Graz, Austria) containing 1024 channels of width 54 mm. The range of scattering angle was chosen from $h = 0.05$ to 6 nm$^{-1}$, with the magnitude of the scattering vector being $h = 2\pi \sin \theta/\lambda$, $\theta$ and $\lambda$ being respectively the scattering angle and incident X-ray wavelength of 0.1542 nm. The distance from sample to detector was 27.7 cm and the exposure time was 600 s for each sample.

**Rheological Measurements.** The rheological measurements were carried out on a HAAKE RS75 Rheometer or Bohlin CS 10 rheometer with a cone plate measuring system and oscillatory mode from 0.01 to 10 Hz.

**$^1H$ NMR and $^{13}C$ NMR Spectra.** The $^1H$ and $^{13}C$ NMR spectra were taken on a Bruker AVANCE-400 spectrometer at 25.0 ± 0.1 °C in 5-mm NMR sample tubes. To obtain the signal spectra, $D_2O$ and $C_6D_6$ were used to prepare the vesicular solutions with and without $C_{60}$. $^{13}C$ NMR spectra were measured for more than 21 500 scans.

**UV−Visible Spectroscopy.** UV−vis measurements were carried out on a computer-controlled spectrometer (UV−vis 4100, HITACHI HIGH-TECHNOLOGIES Co., Japan) at room temperature in a 1 cm path length quartz cell with water as a reference.

An ultrasonicator (Analytical Instrument Inc., Shanghai, KQ-250DB Maximum frequency, 40 kHz ± 10%) was used at 40% of maximum frequency to prepare homogeneous solutions. All samples were centrifuged (LXJ-II, Analytical Instrument Inc., Shanghai, maximum rotation speed, 4000 rpm) at 2500 rpm for 30 min before characterization and all the experiments were carried out at room temperature unless otherwise stated.

## Results and Discussion

**Properties and Structures of Salt-Free Zero-Charged Catanionic Onion-Phase Solutions without $C_{60}$ Incorporation.** The 100 mmol·L$^{-1}$ salt-free zero-charged TTAL catanionic surfactant onion-phase solutions are transparent, highly viscous, and birefringent. The sample exhibits yield stress, i.e., air bubbles can be trapped in these solutions. The rheological properties for a 100 mmol·L$^{-1}$ TTAL Lα-phase sample are shown in Figure 1. The storage modulus G′ describing the elastic properties of the sample and loss modulus G″ are almost frequency independent. G′ is almost a decade higher than G″. The complex viscosity, $|\eta^*|$, decreases throughout the whole frequency range from 0.01 to 10 Hz with a slope of −1.

When the concentration of the TTAL onion-phase aqueous solution was increased to 200 mmol·L$^{-1}$, the macroproperties of the onion-phase solution were very similar to those of the 100 mmol·L$^{-1}$ TTAL solution except for an increase in viscosity. When the vesicular solution was diluted to 50 mmol·L$^{-1}$, the onion-phase aqueous solution became less viscous and slightly bluish, but still birefringent. These onion-phase solutions could be kept for more than one year without
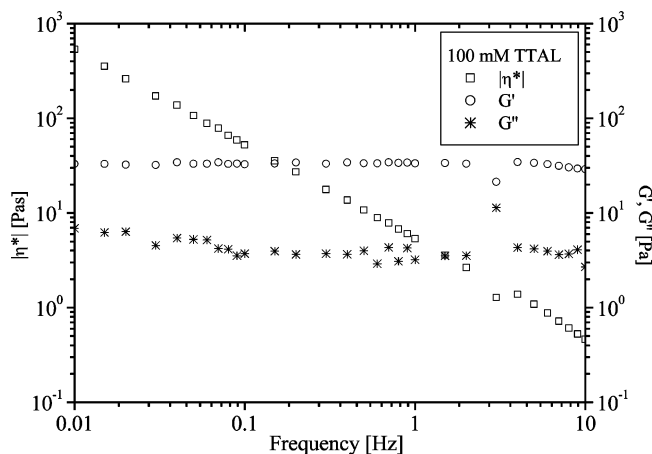
**Figure 1.** Rheogram of a 100 mmol·L$^{-1}$ salt-free zero-charged TTAL onion-phase solution: plots of storage modulus G′, loss modulus G″, and complex viscosity $|\eta^*|$ as a function of the angular frequency.
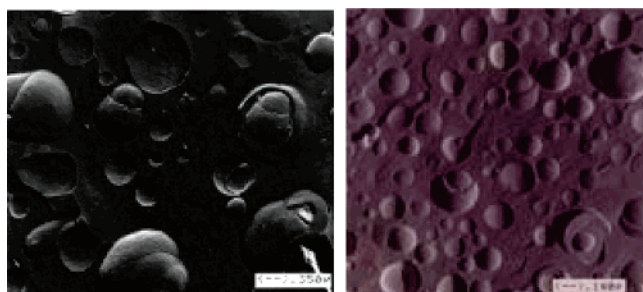


**Figure 2.** FF-TEM images of 50 (left) and 100 (right) mmol·L$^{-1}$ salt-free zero-charged TTAL onion-phase aqueous solutions. Glycerol (20 wt %) was added to the onion-phase aqueous solutions to avoid crystallization during the freezing process.

any changes at 25 °C, indicating that once formed, the onion-phase is stable.

The structural features of 50 and 100 mmol·L$^{-1}$ TTAL onion-phase aqueous solutions can be determined from FF-TEM images, as shown in Figure 2. From both images, one can see that uni- and multilamellar vesicles coexist. The unilamellar vesicles have a rather polydisperse distribution, with diameters ranging from about 30 to more than 300 nm and an average diameter of about 125 nm. The multilamellar onion-phase has an average diameter of about 500 nm based on the FF-TEM images.

SAXS measurements were carried out on salt-free zero-charged TTAL onion-phase solutions. A typical SAXS profile of a 100 mmol·L$^{-1}$ TTAL vesicular aqueous solution is shown in Figure 3, which clearly indicates the formation of lamellar aggregate structures. Four scattering peaks were observed at $q$ = 0.12, 0.24, 0.36, and 0.48 nm$^{-1}$. The relative peak positions, $q_1$:$q_2$:$q_3$:$q_4$, are strictly 1:2:3:4, which is typical for a Bragg scattering pattern for a one-dimensional lamellar structure, corresponding to the 001, 002, 003, and 004 planes of a layered structure. The interlayer distance $d = 2\pi/q_{max}$ was determined to be around 52 nm, meaning the thickness of the hydrophobic bilayer and the water layer.

To determine if the formation of the onion-phase was reversible, the 100 mmol·L$^{-1}$ TTAL onion-phase aqueous solution was dried in a N$_2$ stream below 40 °C. Solid TTAL (~12.0 g) was thus obtained and a 50 mmol·L$^{-1}$ vesicular solution was prepared by dissolving the solid TTAL in water. No insoluble fraction was found and the properties of so-
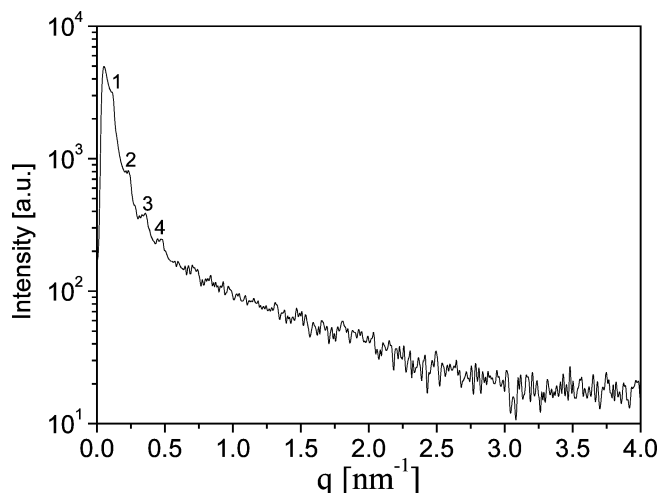


**Figure 3.** Small-angle X-ray scattering curve of a 100 mmol·L$^{-1}$ TTAL vesicular solution. The scattering peaks can be indexed as a lamellar structure.
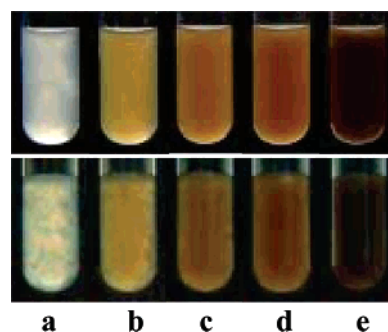


**Figure 4.** Representative photographs of a 50 mmol·L$^{-1}$ TTAL onion-phase aqueous solution without C$_{60}$ (a) and with increasing amounts of C$_{60}$ (b–e). The concentration of C$_{60}$ is (b) 0.10, (c) 0.20, (d) 0.30, and (e) 0.82 mmol·L$^{-1}$, respectively. The photographs were taken after centrifugation: top, without polarizers; bottom, with polarizers.

obtained onion-phase aqueous solutions, which were birefringent and bluish, were the same as those prepared by mixing TTAOH and LA.

**Solubilization of C$_{60}$ in Salt-Free Zero-Charged Catanionic Surfactant Onion-Phase Solutions.** Different routes were tested to solubilize C$_{60}$ into salt-free zero-charged catanionic surfactant aqueous vesicular solutions. Method 1: When solid C$_{60}$ was added to a 50 mmol·L$^{-1}$ TTAL vesicular solution and sonicated, the sample remained birefringent and slightly bluish with visible black C$_{60}$ clusters suspended in the solution, indicating that solid C$_{60}$ cannot be solubilized by the salt-free catanionic surfactant aqueous vesicular solution directly. Method 2: To a purple solution of C$_{60}$ (2.94 mg) in toluene (15 mL) was added 0.1163 g of solid TTAL and the mixed sample was sonicated for 5 min and further stirred overnight under a N$_2$ atmosphere. A homogeneous yellow toluene solution was obtained. After toluene was evaporated under a stream of N$_2$ at 40−50 °C, a TTAL-C$_{60}$ solid mixture was obtained, to which 5 mL of tridistilled water was added, then the sample was sonicated again for 5 min. A brown vesicular aqueous solution of about 50 mmol·L$^{-1}$ TTAL and ~0.82 mmol·L$^{-1}$ C$_{60}$ was obtained. No insoluble component was observed in the brown vesicular solution and the sample was kept at 25 °C for four weeks before characterization. By this preparation method, a series of vesicular solutions containing different amounts of C$_{60}$ were prepared (Figure 4). Birefringence of the solutions with low amounts of C$_{60}$ can still be observed, for example, sample "b" in Figure 4. However, at higher C$_{60}$ amounts, one cannot

Enhancement of the Solubility of Fullerene C$_{60}$ in Water

*J. Phys. Chem. B, Vol. 110, No. 1, 2006* **71**

observe the birefringence clearly due to the darkness of the brown solution. Method 3: A C$_{60}$ toluene solution (5 mL) (0.36 mg of C$_{60}$) was slowly injected into a 5 mL 50 mmol·L$^{-1}$ TTAL vesicular aqueous solution under vigorous stirring. A reddish emulsion was obtained, which was dried and redissolved in 5 mL of water following the procedures in Method 2.

According to the experimental results, both Methods 2 and 3 are successful in incorporate C$_{60}$ molecules into salt-free zero-charged TTAL onion-phase aqueous solutions. In our study we chose Method 2 as illustrated below: i.e.,

$$C_{60} \text{ solid} \xrightarrow{\text{toluene}} \text{purple } C_{60} \text{ toluene solution} \xrightarrow{\text{TTAL(s)}} \text{yellow}$$

$$\text{TTAL-}C_{60} \text{ toluene solution} \xrightarrow{\text{N}_2\text{-dried}} \text{TTAL-}C_{60} \text{ solid} \xrightarrow{\text{water}}$$

salt-free zero-charged TTAL onion-phase aqueous
solutions containing C$_{60}$
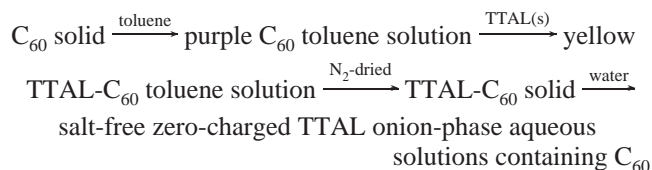
No visible changes were observed for all the samples containing C$_{60}$ during the period of phase equilibrium—at least 4 weeks at $T = 25.0 \pm 0.1$ °C. It could be concluded that the C$_{60}$ molecules were successfully solubilized into TTAL onion-phase aqueous solution by the following proofs: (a) after centrifugation of the samples in Figure 4 (b−e), the color of all the samples remained unchanged and no insoluble components were observed. (b) When each sample's vesicular structure was destroyed by diluting with water, yellow or brown precipitates were found at the bottom. The precipitates could be redissolved totally by evaporating water to increase the TTAL concentration, presumably thus re-forming the onion-phase. (c) Hoffmann et al. have reported that salt addition could induce the phase separation from densely packed vesicles (onion-phase) in the salt-free catanionic surfactant system CTAOH/HNC.[16a] A similar phenomenon has been observed in our experiments. When 0.025 g of NaBr was added to the sample "c" in Figure 4, a phase separation occurred with a dark-brown layer at the top and a clear phase at the bottom.

**Determination of the C$_{60}$ Solubilization Site in Onion-phase Aqueous Solutions by $^1$H and $^{13}$C NMR Spectroscopy.** The above observations indicate that the C$_{60}$ molecules were trapped inside the surfactant onion-phase bilayers and that there is a rather strong affinity between the C$_{60}$ molecules and the hydrophobic chains of the surfactants. The solubilization site of C$_{60}$ molecules in salt-free zero-charged TTAL onion-phase aqueous solutions was determined from analysis of $^1$H NMR and $^{13}$C NMR spectra (Figure 5). Figure 5a shows the $^1$H NMR spectra for the 20 mmol·L$^{-1}$ TTAL onion-phase aqueous solution (in D$_2$O) without and with 0.10 mmol·L$^{-1}$ C$_{60}$. The two samples are slightly viscoelastic L$\alpha$-phase. The $^1$H NMR spectra show brand broadening which could be due to incomplete motional narrowing in the viscoelastic L$\alpha$-phase. Comparing the $^1$H NMR spectra of salt-free zero-charged TTAL vesicular solutions with and without C$_{60}$, one can see that in the presence of C$_{60}$ the chemical shifts of $\alpha$-CH$_2$, $\delta$-(CH$_2$)$_x$ ($x$ = 9 for L$^-$ and 12 for TTA$^+$), and $\omega$-CH$_3$ groups of the TTAL molecules are shifted to higher field by 8 to 16 Hz, which should be induced by the solubilization of C$_{60}$. There is an interaction between the C$_{60}$ molecules and the TTAL hydrocarbon chains because C$_{60}$ are electron-rich and provide a strong screening effect on the $^1$H nuclei of TTAL. The magnitudes of the change in chemical shift for $\alpha$-CH$_2$, $\delta$-(CH$_2$)$_x$, and $\omega$-CH$_3$ groups can be calculated and have the following order: $\omega$-CH$_3$ (16 Hz) > $\delta$-(CH$_2$)$_x$ (12 Hz) > $\alpha$-CH$_2$ (8 Hz), indicating that the interaction between C$_{60}$ molecules and the $\omega$-CH$_3$ (16 Hz) group is the strongest, i.e., the solubilization site of C$_{60}$ molecules should be in the central site of hydrophobic layers formed by TTAL.

The $^{13}$C NMR spectrum of C$_{60}$ in C$_6$D$_6$ was obtained with $^1$H decoupling. In Figure 5b, an extremely sharp single resonance is observed at 142.5 ppm due to C$_{60}$. The $^{13}$C NMR spectrum of C$_{60}$ is well-known, and all 60 carbon atoms are chemically equivalent.[19] The peaks at 127 ppm are from the benzene solvent.

$^{13}$C NMR spectra of TTAL onion-phase aqueous solutions (in D$_2$O) with and without C$_{60}$ encapsulated are shown in Figure 5c, which clearly indicate that C$_{60}$ molecules exist in TTAL onion-phase aqueous solutions. $^{13}$C NMR spectra of TTAL molecules are absolutely identical in the TTAL onion-phase aqueous solutions with and without C$_{60}$ encapsulated. The C$_{60}$ resonance is clearly observed as an extremely sharp peak located at 142.5 ppm, just like C$_{60}$ in C$_6$D$_6$, indicating that the C$_{60}$ molecules were really solubilized but not degraded (oxidized) so are still present as C$_{60}$.

Two important conclusions can be drawn from the $^1$H and $^{13}$C spectra: (1) In the hydrophobic bilayers of the onion-phase, there are no nano-C$_{60}$ clusters which form in many cases when a solution of C$_{60}$ in an organic solvent is mixed with water and (2) the magnitude of the $^{13}$C chemical shift change for the $\omega$-CH$_3$ group is around 18 Hz. This is larger than for other groups, i.e., $\delta$-(CH$_2$)$_x$ ($x$ = 9 for L$^-$ and 12 for TTA$^+$), indicating that the C$_{60}$ molecules are located in the central site of hydrophobic bilayers of the onion-phase.

The salt-free zero-charged catanionic onion-phase aqueous solutions containing C$_{60}$ were quite stable, and showed no changes after storage at room temperature for more than three months. Two identical samples of 50 mmol·L$^{-1}$ TTAL onion-phase aqueous solution containing 0.30 mmol·L$^{-1}$ C$_{60}$ (the sample d in Figure 4) were placed in an oven and kept at 50 and 80 °C, respectively, for an hour, after which no obvious changes could be observed. The samples were also frozen at −4 °C and after the temperature recovered to room temperature, homogeneous solutions were again obtained without visible changes.

It is reasonable that the solubilizing capacity of the salt-free zero-charged onion-phase aqueous solutions for C$_{60}$ will increase with higher concentrations of vesicles. A sample with $c_{C_{60}}$ = 1.64 mmol·L$^{-1}$ in the 100 mmol·L$^{-1}$ TTAL onion-phase aqueous phase has been successfully prepared. Thus, salt-free zero-charged onion-phase aqueous solutions are perfect candidates to improve the solubility of C$_{60}$ in aqueous media and potentially also for solubilizing related compounds such as nanotubes.

**UV−Vis Measurements of Salt-Free Zero-Charged Onion-Phase Aqueous Solutions Containing C$_{60}$.** UV−vis spectroscopy was used to characterize aqueous and organic solutions containing C$_{60}$. The characteristic UV−vis absorption of C$_{60}$ in toluene is shown in Figure 6a. The absorption below 290 nm is shielded by the strong absorption of the aromatic chromophore in this region. Figure 6b shows the UV−vis absorption of the samples in Figure 4 (a−e), from which one can see that the strong absorption band of 50 mmol·L$^{-1}$ salt-free zero-charged TTAL onion-phase solution at lower wavelengths was enhanced and broadened after C$_{60}$ solubilization, extending to higher wavelengths with the increasing amount of C$_{60}$ solubilized. From Figure 6, one can also see that all the characteristic absorption peaks of C$_{60}$ at 329 nm and the 400−700 nm region are difficult to identify due to the complex fluid system.

During sample preparation, when solid TTAL was added to the purple solution of C$_{60}$ in toluene, the color of the solution changed from purple to yellow after sonication and stirring. To
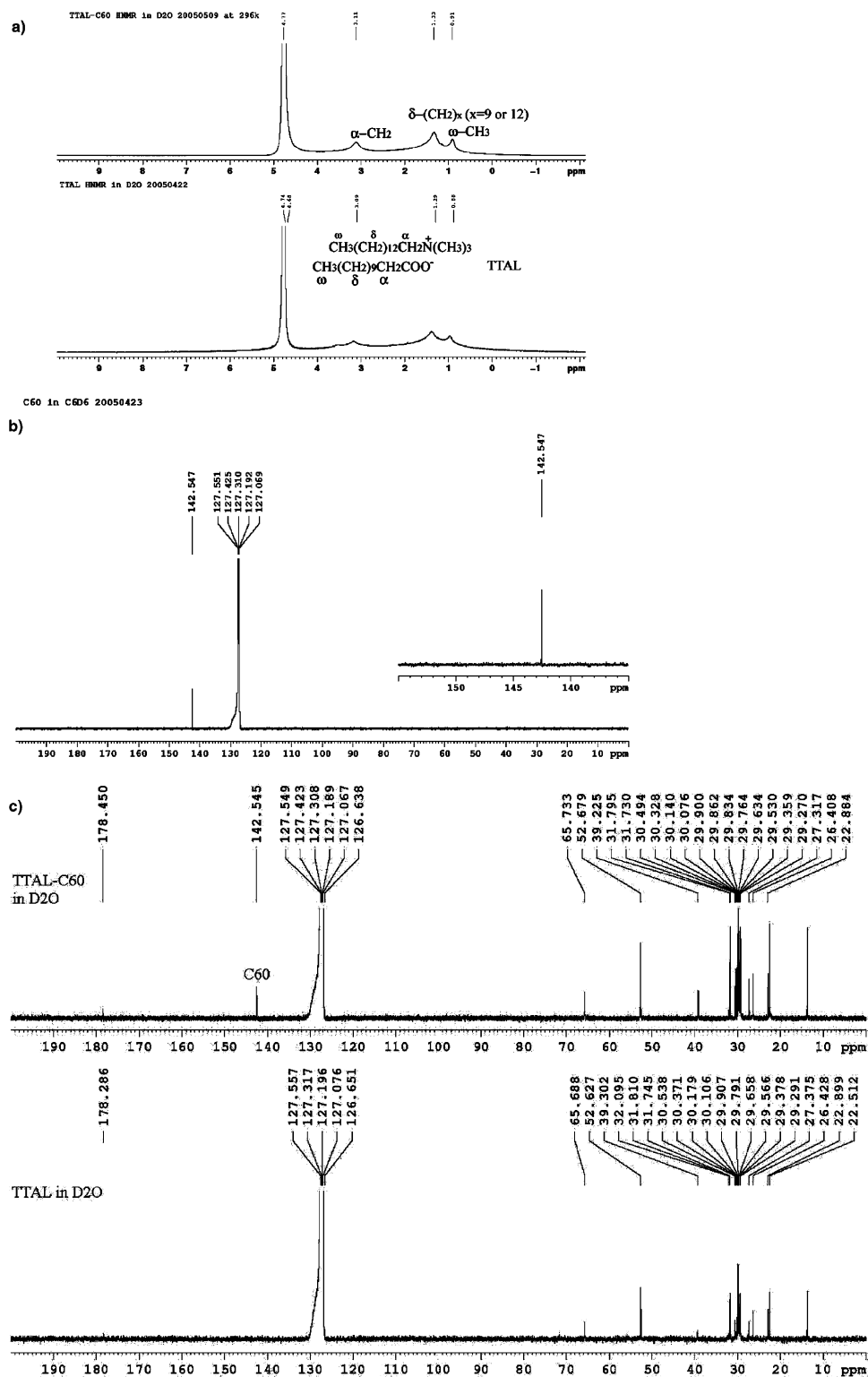
**Figure 5.** (a) $^1$H NMR spectra of TTAL onion-phase aqueous solution (in $D_2O$) with (above) and without (below) $C_{60}$ encapsulated; (b) $^{13}$C NMR spectrum of $C_{60}$ in $C_6D_6$, with $^1$H decoupling, 21 500 scans. The resonance at 142.5 ppm is assigned to $C_{60}$. (c) $^{13}$C NMR spectra of TTAL vesicular solutions with (above) and without (below) $C_{60}$. $C_6D_6$ was added into the sample for locking the field, but it did not affect the measurement of $^{13}$C NMR spectra or the discussion of the results.

obtain more information, we added excess solid TTAL to 0.10 mmol·L$^{-1}$ $C_{60}$ in toluene (4.5 mL). After sonication for 5 min, the sample was kept at 25 °C with frequent shaking before characterization. Some TTAL solid remained at the bottom and the color of the upper saturated solution was still purple 8 h later but changed slowly from purple to yellow within 2 days. UV−vis measurements were carried out on the solution before and after the color change (Figure 7). Comparing the UV−vis

spectra of $C_{60}$ alone and TTAL-$C_{60}$ in toluene, one can see that the purple solution of TTAL-$C_{60}$ in toluene has an identical UV−vis spectrum with $C_{60}$ in toluene, and the characteristic absorption of $C_{60}$ still appears. However, with time, the purple solution of TTAL-$C_{60}$ in toluene completely changed to yellow and the characteristic absorption of $C_{60}$ was lost from the spectrum. Since all samples were prepared under $N_2$ and below 50 °C, the influence of $O_2$ and chemical reactions induced by
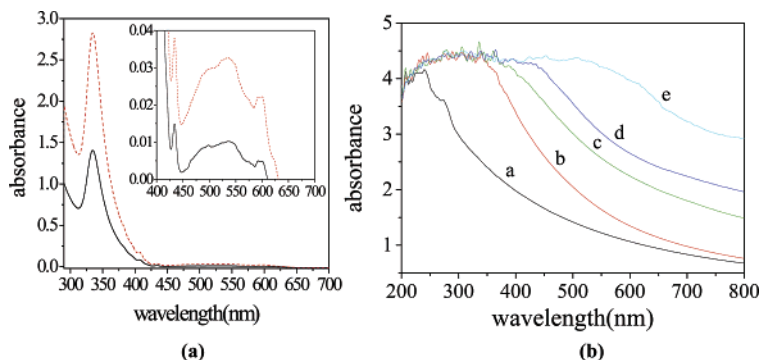
Enhancement of the Solubility of Fullerene $C_{60}$ in Water

*J. Phys. Chem. B, Vol. 110, No. 1, 2006* **73**



**Figure 6.** (a, left curves): UV−vis absorption of 25 $\mu$mol·L$^{-1}$ (solid line) and 50 $\mu$mol·L$^{-1}$ (dashed line) $C_{60}$ in toluene; the insert is the magnification between 400 and 700 nm. (b, right curves): 50 mmol·L$^{-1}$ salt-free zero-charged TTAL onion-phase solution with 0.10 to 0.82 mmol·L$^{-1}$ $C_{60}$ for the samples in Figure 4b−e and without $C_{60}$ for the sample in Figure 4a.
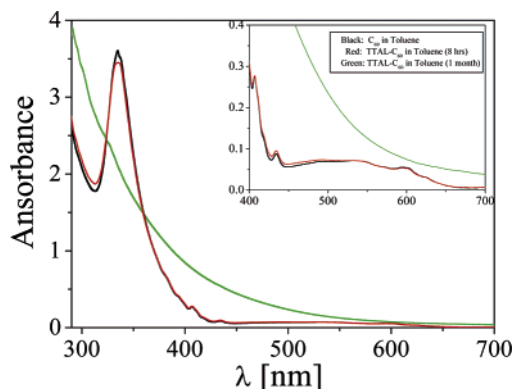


**Figure 7.** UV−vis spectra of $C_{60}$ in toluene and TTAL-$C_{60}$ in toluene 8 h (purple solution) and 1 month (yellow solution) after TTAL was added, $c_{C_{60}} = 0.10$ mmol·L$^{-1}$.

temperature can be excluded. The effects of sonication and stirring were also examined, but no direct influence on UV−vis absorption was found except for accelerating the process of color change by speeding up the dissolution of solid TTAL.

UV−vis measurements of $C_{60}$ mixed with the starting materials for TTAL, i.e., TTABr and LA, were also examined. (1) When 0.1680 g of TTABr was added to 5 mL of 0.10 mmol·L$^{-1}$ $C_{60}$ toluene solution, TTABr did not dissolve completely. After removing excess TTABr solid, we found that the solution of TTABr-$C_{60}$ in toluene was purple and became yellow over time. As shown in Figure 8a, the purple solution of TTABr-$C_{60}$ in toluene has an identical UV−vis spectrum with $C_{60}$ in toluene. However, after the purple solution of TTABr-$C_{60}$ in toluene turned yellow, the characteristic absorption of $C_{60}$ was found to be lost from the UV−vis spectrum, just as in the case of TTAL-$C_{60}$ in toluene. (2) When 0.10 g of LA was added to 4.5 mL of 0.10 mmol·L$^{-1}$ $C_{60}$ in toluene, the water-insoluble LA dissolved completely in a short time, and

no visible changes in the purple color of $C_{60}$ solution were observed. Keeping this mixture at 25.0 ± 0.1 °C for more than one month did not cause any visible change in color or UV−vis spectrum (Figure 8b). So it seems that the loss of the characteristic absorptions of $C_{60}$ was due to the existence of the cationic TTA$^+$ ions rather than the anionic L$^-$ ions.

**TEM Observations of Salt-Free Zero-Charged Catanionic Onion-Phase Aqueous Solutions Containing $C_{60}$.** After preparation of the samples with $C_{60}$ encapsulated in salt-free zero-charged TTAL onion-phase aqueous solutions, we used Negative-staining TEM to determine if the vesicle structures had been destroyed or not, or if the uni- and multilamellar vesicle-phase had converted to any other self-assembled structures. Figure 9
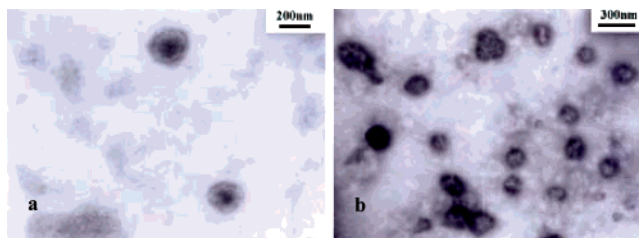


**Figure 9.** TEM micrographs of 50 and 100 mmol·L$^{-1}$ TTAL vesicular aqueous solutions containing 0.82 and 1.64 mmol·L$^{-1}$ $C_{60}$, respectively. Uranyl acetate was used as the negative-stained reagent.

shows the results for two typical samples of 50 and 100 mmol·L$^{-1}$ TTAL vesicular aqueous solutions containing 0.82 mmol·L$^{-1}$ and 1.64 mmol·L$^{-1}$ $C_{60}$, respectively. One can easily see that well-defined vesicles are present. The dimensions of the vesicles are between 100 and 300 nm, just as in the original vesicular structures in Figure 2. It is clear that the vesicles have not changed due to the solubilization of $C_{60}$ but some changes of the macroproperties of the vesicular solutions have been observed.
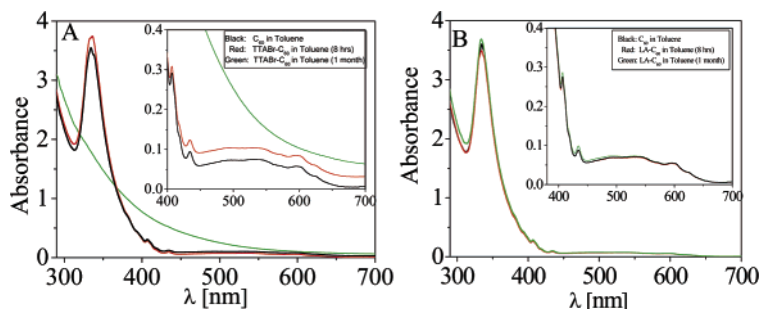


**Figure 8.** UV−vis spectra: (A) $C_{60}$ in toluene and TTABr-$C_{60}$ in toluene 8 h (purple solution) and 1 month (yellow solution) after addition of TTABr. (B) $C_{60}$ in toluene and LA-$C_{60}$ in toluene 8 h (purple solution) and 1 month (purple solution) after addition of LA. $c_{C_{60}} = 0.10$ mmol·L$^{-1}$ in both samples.
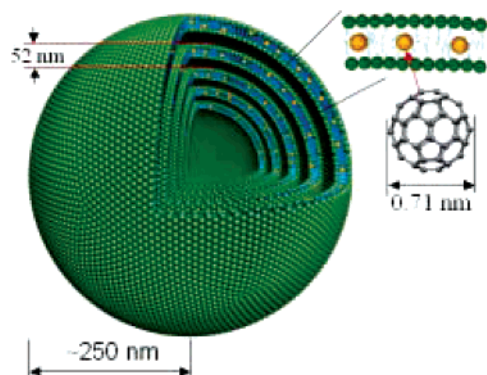
**Figure 10.** A sketch of $C_{60}$ molecules in a spherical multilamellar vesicle with 250 nm radius and the 52 nm thick hydrophobic bilayer and water layer. The model is based on analysis of experimental data from FF-TEM and SAXS measurements. The hydrophobic double-chain hydrocarbons are shown as blue rods, while the hydrophilic charged cationic−anionic groups are green balls. The extremely hydrophobic $C_{60}$ fullerenes (shown in orange) were located in the hydrophobic layers of vesicles. A sector in each layer has been cut out for enhanced visibility. According to the weight ratio of fullerene $C_{60}$ to TTAL surfactant (1:40), one could estimate approximately that the bilayers formed with 63 TTAL molecules contain 1 fullerene $C_{60}$ molecule. However, it is difficult to obtain the exact proportion of fullerene $C_{60}$ molecules to TTAL molecular bilayer. It is impossible to give an opinion of a fairly large quantity of quasi-insoluble fullerene $C_{60}$ in the surfactant matrix. So the quantity ratio of fullerene $C_{60}$ to TTAL molecules illustrated in the map may not be strictly consistent with the real case of the microstructure.

Before ending the sufficiently interesting study, the reversible experiment was carried out, the salt-free zero-charged TTAL vesicular aqueous solutions containing $C_{60}$ can be evaporated in $N_2$ atmosphere to obtain the mixed solids which are TTAL and $C_{60}$. When we dissolve the solid mixture in water, salt-free zero-charged TTAL vesicular aqueous solutions containing $C_{60}$ can be obtained again. Thus, the preparation of salt-free zero-charged TTAL onion-phase aqueous solutions containing $C_{60}$ is also reversible as for the case of TTAL vesicular solutions. A sketch map of $C_{60}$ molecules in a spherical multilamellar vesicle is given in Figure 10, which should assist in the comprehension of all the experimental observations and parameters.

## Conclusion

In conclusion, $C_{60}$ has been found to be solubilized by salt-free zero-charged cationic and anionic vesicular aqueous solutions and the solubilizing capacity of the catanionic surfactant onion-phase aqueous solution was found to be higher than those reported previously. The samples are very stable over a wide range of temperature, thus have great potential for biological and materials uses. We are continuing to investigate these systems with other insoluble substances in aqueous solutions, such as functionalized carbon nanotubes.

## References and Notes

(1) Kroto, H. W.; Heath, J.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(3) Friedman, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506.

(4) Tokuyama, H.; Yamago, S.; Nakamura, E.; Shiraki, T.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918.

(5) Andersson, Th.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604.

(6) Atwood, J. L.; Koutsantionis, G. A.; Raston, C. L. *Nature* **1994**, *368*, 229.

(7) Hungerbühler, H.; Guldi, D. M.; Asmus, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 3386.

(8) Beeby, A.; Eastoe, J.; Heenan, R. K. *J. Chem. Soc., Chem. Commun.* **1994**, 173.

(9) Yamakoshi, Y. N.; Yagami, T.; Fukuhara, K.; Sueyoshi, S.; Miyata, N. *J. Chem. Soc., Chem. Commun.* **1994**, 517.

(10) Eastoe, J.; Crooks, E. R.; Beeby, A.; Heenan, R. K. *Chem. Phys. Lett.* **1995**, *245*, 571.

(11) Moussa, F.; Trivin, F.; Ceolin, R.; Hadchouel, M.; Sizaret, P.-Y.; Greugny, V.; Fabre, C.; Rassat, A.; Szwarc, H. *Fullerene Sci. Technol.* **1996**, *4*, 21.

(12) Lai, D. T.; Neumann, M. A.; Matsumoto, M.; Sunamoto, J. *Chem. Lett.* **2000**, 64.

(13) Bensasson, R. V.; Bienvenue, E.; Dellinger, M.; Leach, S.; Seta, P. *J. Phys. Chem.* **1994**, *98*, 3492.

(14) Kaler, E. W.; Herrington, K. L.; Murthy, A. K.; Zasadzinski, J. A. N. *Science* **1989**, *245*, 1371.

(15) Horbaschek K.; Hoffmann, H.; Hao, J. *J. Phys. Chem. B* **2000**, *104*, 2781.

(16) (a) Hoffmann, H.; Kalus, J.; Schwander, B. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 99. (b) Horbaschek, K.; Hoffmann, H.; Thunig, C. *J. Colloid Inter. Sci.* **1998**, *206*, 439.

(17) (a) Zemb, Th.; Dubois, M.; Demè, B.; Gulik-Krzywicki, Th. *Science* **1999**, *283*, 816. (b) Dubois, M.; Demè, B.; Gulik-Krzywichi, Th.; Dedieu, J. C.; Vautrin, C.; Dèsert, S.; Perez, E.; Zemb, Th. *Nature* **2001**, *411*, 672. (c) Dubois, M.; Lizunov, V.; Meister, A.; Gulik-Krzywichi, Th.; Verbavatz, J. M.; Perez, E.; Zimmerberg, J.; Zemb, Th. *PNAS* **2004**, *101*, 15082.

(18) (a) Hao, J.; Hoffmann, H.; Horbaschek, K. *Langmuir* **2001**, *17*, 4151. (b) Hao, J.; Liu, W.; Xu, G.; Zheng, L. *Langmuir* **2003**, *19*, 10635. (c) Hao, J.; Hoffmann, H.; Horbaschek, K. *J. Phys. Chem. B* **2000**, *104*, 10144. (d) Hao, J.; Yuan, Z.; Liu, W.; Hoffmann, H. *J. Phys. Chem. B* **2004**, *108*, 19163. (e) Hao, J.; Li, H.; Liu, W.; Hirsch, A. *Chem. Commun.* **2004**, 602. (f) Song, A.; Dong, S.; Jia, X.; Hao, J.; Liu, W.; Liu, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 4018.

(19) (a) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983. (b) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *Chem. Commun.* **1990**, 1423.