Unexpected Discovery of a Novel Organic Gel System Comprised of [60]Fullerene-containing Amphiphiles

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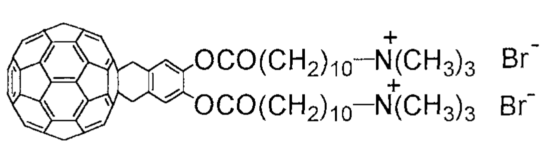
A [60]fullerene-containing amphiphile bearing two ammonium groups was synthesized. When the methanol solution was left at room temperature for a few days, it was totally transformed into an organic gel. The transformation process was fully characterized by transmission electron microscopy and X-ray diffraction. This is the first example for the [60]fullerene-containing organic gel.

The large availability of [60]fullerene has offered the increasing attention toward exploration of outstanding new physical and chemical properties of this fullerene. Its new properties are expected not only for monomeric [60]fullerene but also for various aggregated states. For example, Bard et al.[1] and Kajiyama et al.[2] were interested in the formation of the monolayer at the air-water interface whereas Jenekhe and Chen[3] reported the formation of a [60]fullerene-aggregated domain in solution by using a block copolymer. In general, however, to design the highly ordered aggregate from [60]fullerene has been considered to be difficult in solution. Recently, new molecular assemblies formed in an organic gel system have attracted considerable attention.[4-9] The gelators can be self assembled by the recrystallization-like operation and feature in most cases the fibrous structure.[4-9] Interestingly, some gelators with the chiral center result in a large strand with a helical structure.[4,7] It thus occurred to us that the gel system might be applicable to create new ordered [60]fullerene-based assemblies. We designed compound **1** with a [60]fullerene moiety and two ammonium groups, the primary research aim of which was to obtain a membrane-like assembly in solution. In fact, such aggregates were obtained after sonication in methanol.[10] However, we unexpectedly discovered that when this solution was left at room temperature for a few days, it was entirely gelated. To the best of our knowledge, this is the first example for the organic gel comprised of [60]fullerene-containing amphiphiles.



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Compound **1** was synthesized from a [60]fullerene derivative with dihydroxyl groups according to Scheme 1 and identified by ^{1}H NMR, ^{13}C NMR, IR, MASS spectra and elemental analysis.[11]

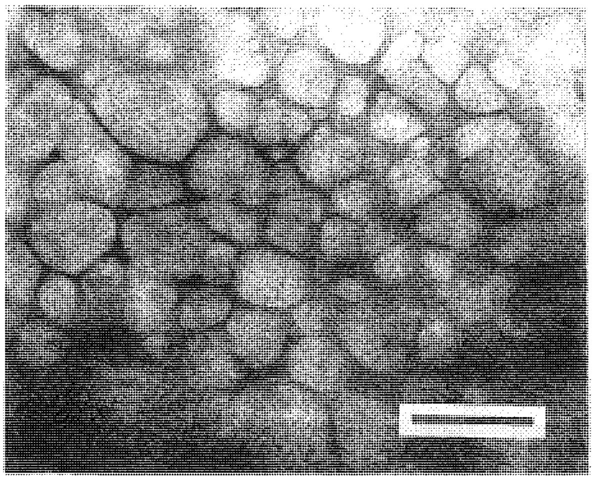
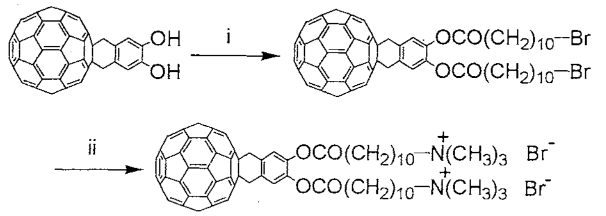


Figure 1. TEM image of the methanol solution. The sample was prepared by staining uranyl acetate solution (2%) after the amphiphile solution was picked up on a carbon grid. Bar represents 200 nm.



Scheme 1. Reagents and conditions: i, DCC, DMAP, 11-bromoundecane acid, dry CH_2Cl_2; ii, trimethylamine, dry toluene.

Under the sonication condition, compound **1** (10 mmol dm^{-3}) was insoluble in benzene, toluene, hexane, ethanol, and *tert*-butanol whereas it was soluble in DMSO, DMF, benzyl alcohol, and methanol. The transmission electron microscopy (TEM, Hitachi H7100) image of the methanol solution is shown in Figure 1. One can recognize globular aggregates with 90-135 nm diameter. The cast film of this solution on a glass plate was subjected to X-ray diffraction (XRD, Mac Science MXP18). The spectrum (Figure 2a) shows a broad peak with the maximum at a lattice period of 3.4 nm. The results indicate that the assemblies in Figure 1 possess a less-ordered structure.

When the methanol solutions of **1** (10-20 mmol dm^{-3}) were left at room temperature for a few days, the mixtures were totally gelated. Such a transformation was not observed for the methanol solutions containing **1** lower than 6.0 mmol dm^{-3}. Figure 3 shows the TEM image of the gel. As frequently seen for the organic gel systems,[3-8] a number of fibrous aggregates with 10-20 nm diameter are seen in the picture. The XRD pattern of the cast film (Figure 2b) shows sharp, periodical peaks up to the 13 order, indicating that the gel fibers consist of the well-ordered structure with a repeating unit of 2.24 nm. This period is less than the large-axis molecular size of **1**; we thus

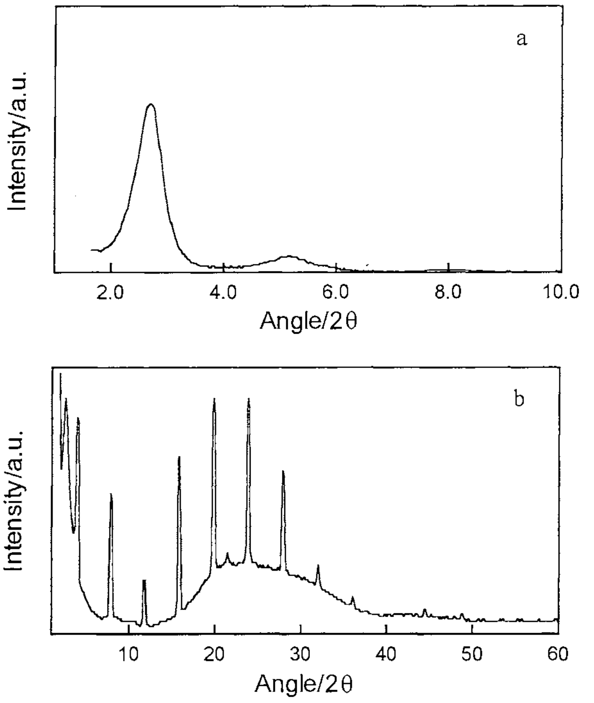


Figure 2. XRD spectra of the θ-2θ scan by the CuKα radiation.
(a): cast film from methanol solution (20 mmol dm^{-3})
(b): powder from methanol gel (20 mmol dm^{-3})

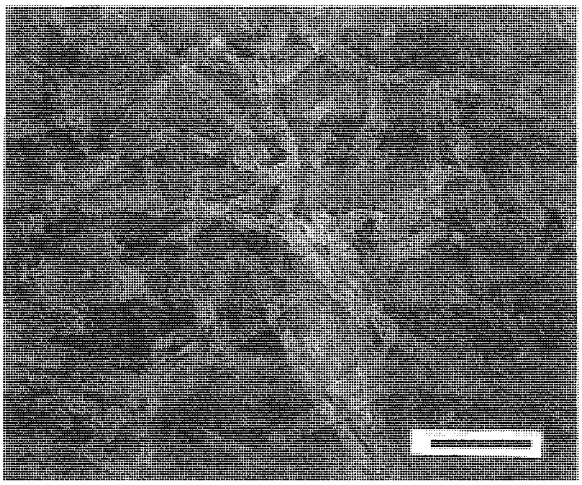


Figure 3. TEM image of the methanol gel. The sample was prepared by staining uranyl acetate solution (2%) after the dilute gel solution was picked up on a carbon grid. Bar represents 100 nm.

consider that this repeating unit reflects either the monolayer or the significantly tilted bilayer. As a summary of the foregoing results, one can now regard that a molecular orientation change in **1** from the less-ordered structure to the more-ordered structure induces a morphological change from globular aggregates to fibrous aggregates. This change is eventually linked to a macroscopic change from a solution state to a gel state.

In conclusion, this paper has shown that a [60]fullerene-appended amphiphile can act as a new organic gelator and is useful to create a new [60]fullerene aggregation state. Furthermore, the aggregation properties are profoundly influenced by the time-dependence. We now believe that new photochemical and catalytic reactions mediated by [60]fullerene, which are possible only in the ordered gel system, would be exploited.

Reference and Notes

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10 The full characterization of the membrane-like assemblies will be reported elsewhere.

11 **1**: Brown solid; IR (KBr, cm^{-1}): 2923, 2851, 1763 (ν_{CO}), 1100, 572; ^{1}H NMR (DMSO-d_6, 130 °C) 7.67 (s, 2 H, ArH), 4.77 (s, 4 H, CH_2), 3.36-3.30 (m, 4 H, CH_2N^+), 2.91 (s, 18H, $N^+(CH_3)_3$), 2.63 (t, J = 7.3 Hz, 4 H, $COCH_2$), 1.79-1.67 (m, 8 H, CH_2), 1.48-1.32 (m, 24 H, CH_2); ^{13}C NMR (DMSO-d_6, 130 °C) 169.89 (CO), 156.36, 146.60, 145.42, 145.16, 144.78, 144.37, 144.28, 143.68, 142.05, 141.53, 141.18, 141.01, 140.84, 140.53, 138.96, 135.85, 134.65 (C), 122.20 (CH), 121.61 (C), 65.52(CH_2N^+), 65.16 (fullerene sp^3C), 52.12 (N^+CH_3), 52.08 ($ArCH_2$), 32.85 ($COCH_2$), 28.1-27.5 (CH_2); MS (positive SIMS, NBA) *m/z* 1308 [$(M-2Br)^+$], 654 [$(M-2Br)^{2+}$]. Anal. Calcd for $C_{96}H_{64}Br_2N_2O_4$: C, 78.47; H, 4.39; N, 1.91%. Found: C, 78.28; H, 4.31; N, 1.89%.