Chirally-Ordered Fullerene Assemblies Found in Organic Gel Systems of Cholesterol-Appended [60]Fullerenes

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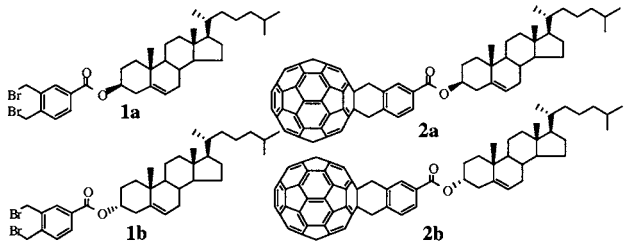
Cholesterol-appended [60]fullerene gelators **2a** and **2b** were prepared and their gelation properties were investigated. **2a** with a natural C-3 configuration can gelate dichloromethane whereas **2b** with an inverted C-3 configuration could not gelate any solvents. UV/Vis and CD spectroscopic studies indicated that the [60]-fullerene moiety in **2a** is enforced to chirally orient in the gel state.

It is well known that [60]fullerene and its homologues tend to randomly form three-dimensional aggregates. In spite of this disadvantage, ordered fullerene assemblies have been successfully formed in some specific fields, e.g., i) monolayers of fullerene and its derivatives with hydrophilic groups at the air-water interface,[1–3] ii) rods and vesicles of fullerenes with hydrophilic groups,[4] iii) encapsulated fullerenes in spherical aggregates of block copolymers,[5] and iv) self-assembled monolayers of thiol-containing fullerenes on gold.[1] To the best of our knowledge, however, chirally-ordered fullerene assemblies have never been reported. Recently, new supramolecular assemblies formed in organic gel systems have been of much concern.[6,7] In particular, cholesterol-based gelators, which can gelate various organic solvents leading to the formation of stable gels, result in chirally-ordered aggregates based on the helical packing of cholesterol moieties.[8–10] In order to create chirally-ordered [60]fullerene assemblies, we have designed two kinds of cholesterol-appended [60]fullerene gelators, **2a** with a natural C-3 (*S*)-configuration and **2b** with an inverted C-3 (*R*)-configuration.



In order to access **2a** and **2b**, cholesteryl 3,4-bis(bromomethyl)benzoates **1a** and **1b** were prepared by condensation reactions of 3,4-bis(bromomethyl)benzoic acid with cholesterol and with epicholesterol,[11] respectively, in the presence of DCC and DMAP in dichloromethane. The obtained **1a** and **1b** reacted with [60]fullerene in the presence of KI and 18-crown-6 in refluxing toluene to give the desired **2a**[12] and **2b**, respectively.[13]

The gelation test of **2** was carried out for 28 solvents using a test-tube-tilting method.[9] The mixture of **2** and the solvent (0.0243 mol dm^{-3}) was heated until the solid was dissolved. After the solution was cooled to room temperature, the solution state was checked visually. As a whole, **2a** and **2b** did not act as excellent gelators and tended to show the similar trends: insoluble in aliphatic hydrocarbons (*n*-hexane, *c*-hexane, methyl-*c*-hexane, etc.), in alcohols (methanol, ethanol, benzyl alcohol, etc.), and in polar solvents (acetone, acetonitrile, THF, DMF, DMSO, etc.); soluble in aromatic hydrocarbons (benzene, toluene, xylene, etc.); recrystallized from haloalkanes (chloroform, carbon tetrachloride, 1,1,2-trichloroethane, etc.). We found, however, that **2a** gelated dichloromethane at 25 °C whereas **2b** in dichloromethane afforded only a solution. The gelation of dichloromethane by **2a** occurred above the concentration of 0.0162 mol dm^{-3} leading to the transparent brown gel. On the other hand, below the concentration of 0.0121 mol dm^{-3} **2a** was freely soluble in dichloromethane. Between the concentrations of 0.0121 and 0.0162 mol dm^{-3} the viscous fluid of **2a** was formed.

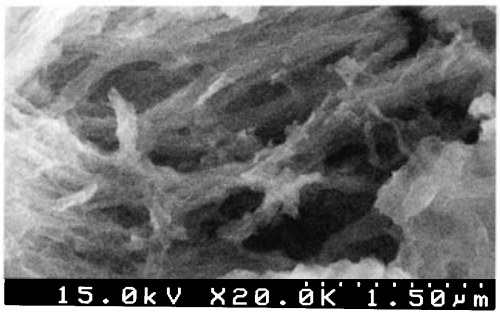


Figure 1. SEM picture of a xerogel obtained from **2a** in dichloromethane (0.0162 mol dm^{-3}) at -110 ˚C/0.1 torr.

The aggregate structure of **2a** can be observed by scanning electron microscopy (SEM, Hitachi S-4500). The SEM picture of the xerogel, which was obtained from **2a** in dichloromethane at –110 ˚C/0.1 Torr,[9] showed the fibrous structure with ca. 100 nm diameter (Figure 1).[14]

The aggregation of the [60]fullerene moiety of **2a** in the gel state was corroborated by means of UV/Vis and CD spectroscopy (Figure 2).[15] In the UV/Vis spectra, the sol samples of **2a** (0.0121 mol dm^{-3}) and **2b** (0.0162 mol dm^{-3}) in dichloromethane indicated a typical absorption pattern of [6,6]closed-[60]-fullerene monoadducts including a characteristic absorption maximum at 434 nm.[16] In the gel state (0.0162 mol dm^{-3}), in contrast, the UV/Vis spectrum of **2a** was considerably broadened, indicating the aggregation of the [60]fullerene moiety in **2a** (Figure 2-a).[2,17]

In the sol state, **2a** (0.0121 mol dm^{-3}) and **2b** (0.0162 mol dm^{-3}) in dichloromethane were CD (circular-dichroism)-silent (Figure 2-b). The results indicate that the chiral cholesterol moieties in **2a** and **2b** are too far from the achiral [60]fullerene chromophore to generate the induced CD.[18] In the gel state of **2a** (0.0162 mol dm^{-3}), one can find the two maxima around 370 and 440 nm in the CD spectrum (Figure 2-b). The comparison with the LD (linear dichroism) spectrum (Figure 2-c) suggests that the 370 nm band is mainly due to the component arising from LD. On the other hand, the 440 nm band with a plus CD sign was

reproducibly observable.[9] It should be emphasized that the Cotton effect observed around 440 nm, which coincided with a characteristic absorption maximum at 434 nm in the UV/Vis spectrum,[16] is due to the chiroptical contribution from the chirally-ordered [60]fullerene aggregate formed in the gel state.

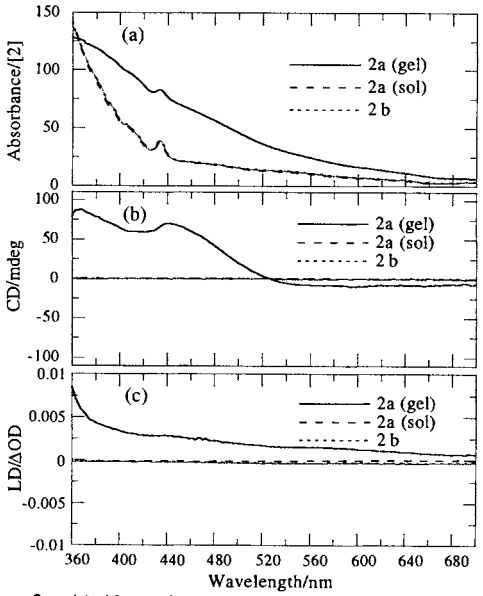


Figure 2. (a) Absorption spectra, (b) CD spectra and (c) LD spectra of **2a** and **2b** in dichloromethane in 0.01 cm width cell at 25 °C: the gel state of **2a** was observed at 0.0162 mol dm^{-3}, the sol state of **2a** was observed at 0.0121 mol dm^{-3}, and **2b** was observed at 0.0162 mol dm^{-3}.

As a summary of the foregoing results, it is concluded that **2a** can gelate dichloromethane leading to the formation of chirally-ordered [60]fullerene aggregates. In the gel state of **2a**, the cholesterol–cholesterol interaction and the fullerene–fullerene cohesive force cooperatively act to construct the chiral assembly: that is, the columnar one-dimensional packing of the cholesterol moieties constitutes the helical structure where the [60]fullerene moieties are chirally oriented outside the helical column.[9] The formed [60]fullerene aggregate with chiral mode results in the Cotton effect around 440 nm in the CD spectrum. Such a novel aggregate structure is possible only in **2a**, which has the extended structure arising from the (*S*)-configuration, whereas impossible in **2b**, which has the bent structure arising from the (*R*)-configuration, as reported in our previous studies of (*S*)- and (*R*)-cholesterol derivatives.[9]

An additional interesting result was obtained in the gelation test of **2a** in dichloromethane (0.0243 mol dm^{-3}) in the presence of ZnTPP (zinc tetraphenylporphyrin). By addition of > 0.5 equivalents of ZnTPP, the present **2a** gel was changed into a transparent solution, indicating that the gel structure of **2a** is not so stable and is easily collapsed by the fullerene-metalloporphyrin interaction[19] between **2a** and ZnTPP.

In conclusion, we have demonstrated that cholesterol-appended [60]fullerene acts as a gelator and is useful to create a chirally-ordered fullerene assembly. Further investigation of the gelation properties of the cholesterol-appended [60]-fullerenes is going on.

References and Notes

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13 **2a**: IR (KBr) ν_{max} 2944–2851 (ν_{CH}), 1717 (ν_{CO}), 1273, 1262, 1183, 527 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.70, 1.10 (s, each 3 H, Me), 0.86 (d, J = 6.6 Hz, 6 H, Me), 0.93 (d, J = 6.6 Hz, 3 H, Me), 0.96–2.16 (m, 26 H), 2.52–2.60 (m, 2 H), 4.44–4.60 (m, 2 H, CH_2), 4.79–5.01 (m, 3 H, CH_2 and OCH), 5.46 (d, J = 4.5 Hz, 1 H, C=CH), 7.75 (d, J = 8.1 Hz, 1 H, ArH), 8.25 (dd, J = 1.6, 8.1 Hz, 1 H, ArH), 8.35 (d, J = 1.6 Hz, 1 H, ArH); MS (negative SIMS, NBA) *m/z* 1237 (M^-). Anal. Calcd for $C_{96}H_{52}O_2$: C, 93.18; H, 4.24%. Found: C, 93.15; H, 4.34%. **2b**: IR (KBr) ν_{max} 2944–2851 (ν_{CH}), 1713 (ν_{CO}), 1271, 1262, 1183, 527 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.69, 1.09 (s, each 3 H, Me), 0.86 (d, J = 6.5 Hz, 6 H, Me), 0.90 (d, J = 6.5 Hz, 3 H, Me), 0.96–2.12 (m, 26 H), 2.40–2.51 (m, 1 H), 2.57–2.71 (m, 1 H), 4.42–4.60 (m, 2 H, CH_2), 4.77–4.95 (m, 2 H, CH_2), 5.28–5.46 (m, 2 H, OCH and C=CH), 7.75 (d, J = 7.7 Hz, 1 H, ArH), 8.20 (dd, J = 1.6, 7.7 Hz, 1 H, ArH), 8.30 (d, J = 1.6 Hz, 1 H, ArH); MS (negative SIMS, NBA) *m/z* 1237 (M^-). Anal. Calcd for for $C_{96}H_{52}O_2$: C, 93.18; H, 4.24%. Found: C, 92.71; H, 4.19%.
14 The almost fibrous structure of **2a** was decomposed during the freeze-drying treatment because of the unstability of the gel structure. The SEM picture of Figure 1 indicated the remaining fibrous structure in the xerogel. Therefore, further investigations such as UV/vis and CD spectroscopies of the xerogel have not yet been carried out.
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