JOURNAL OF
Materials
CHEMISTRY
Communication

Intermolecular porphyrin–fullerene interaction can reinforce the organogel structure of a porphyrin-appended cholesterol derivative†

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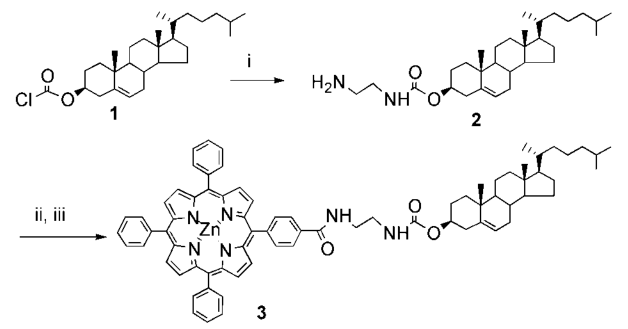
Received 7th June 2000, Accepted 7th August 2000
First published as an Advanced Article on the web 5th September 2000

The intermolecular Zn(II) porphyrin–fullerene interaction efficiently occurs in an organogel system: the gelation ability of Zn(II) porphyrin-appended cholesterol gelator 3 is enhanced by the formation of a 2 : 1 Zn(II) porphyrin/[60]fullerene sandwich complex.

Recently, porphyrin–fullerene systems have been of much concern as new architectural photosynthetic models.[1] The electronic interaction between porphyrin and fullerene chromophores in the ground state can be visualized by means of UV/Vis spectroscopy which shows the distinct bathochromic shift of the Soret absorption band of porphyrin chromophores.[2,3] However, the detection of the electronic interaction has been limited only to intramolecular systems of porphyrin-linked fullerenes,[2] whereas the intermolecular electronic interaction[4,5] between porphyrin and fullerene chromophores has never been reported except for one special case (inclusion of [60]fullerene in a cyclic Zn(II) porphyrin dimer).[3] Meanwhile, new organogel systems have attracted the attention of many chemists because they are useful as a new strategy to create supramolecular architectures in various organic solvents.[6] It is known that even porphyrins can be assembled as fibrous aggregates in an organogel system.[7] It thus occurred to us that the intermolecular porphyrin–fullerene interaction could be realized in an organogel system. In such two-component, low-molecular-weight gelator systems, the second component used as an additive can either reinforce or destabilize the gel structure composed of host–guest-type interactions.[8,9] This prompted us to test whether the intermolecular porphyrin–fullerene interaction can enhance the gelation ability of a porphyrin-appended gelator by the addition of [60]fullerene. Here, we demonstrate that this strategy really works to reinforce the gel structure composed of Zn(II) porphyrin-appended cholesterol gelator **3**.[10,11]

Compound **3** was prepared according to Scheme 1.‡ The gelation test of **3** was carried out for various solvents using a test-tube-tilting method.[10] The solution containing **3** (2.55×10^{-2} mol dm^{-3}) was heated until the solid was dissolved. Then, the gelation was checked visually at 5 °C and 20 °C. At 5 °C **3** can gelate aromatic hydrocarbons such as benzene, toluene and *p*-xylene; however, at 20 °C these transparent gels were changed into sols (for the UV/Vis and CD spectral data see electronic supplementary information (ESI)0†). Interestingly, the gelation ability of **3** for these solvents was efficiently improved by addition of [60]fullerene: in the presence of [60]fullerene (0.5 equivalent) the gel structure of **3** (2.55×10^{-2} mol dm^{-3}) was still maintained at 20 °C in benzene, toluene and *p*-xylene. The reinforcement of the gel structure is ascribed to the intermolecular porphyrin–fullerene interaction of the Zn(II) porphyrin moiety in **3** with [60]fullerene. The stoichiometric ratio can be estimated by the measurement of the sol–gel phase transition temperature (T_{gel}). When the concentration of **3** in toluene was kept constant (0.20 mol dm^{-3}: the solution was gelated at this concentration), T_{gel} increased with increasing [60]fullerene concentration from 29 °C to 78 °C up to $[C_{60}]/[\mathbf{3}] = 0.5$ and then maintained the constant value of 78 °C above $[C_{60}]/[\mathbf{3}] = 0.5$. The results indicate that the two porphyrin moieties in **3** interact with one [60]fullerene molecule to form the 2 : 1 Zn(II) porphyrin/fullerene sandwich complex.



Scheme 1 *Reagents and conditions*: i, Ethylenediamine, toluene, room temperature, 31%; ii, 5-(4-carboxyphenyl)-10,15,20-triphenyl-21*H*,23*H*-porphine,[12] DCC, DMAP, dichloromethane, room temperature, 5 h, 68%; iii, zinc acetate dihydrate, chloroform, 2 h, 96%.

Further evidence of the Zn(II) porphyrin–fullerene interaction can be obtained from UV/Vis and CD spectroscopy (Figs. 1 and 2).§ As described above, the high concentration solution of **3** (2.55×10^{-2} mol dm^{-3}) in toluene was gelated only in the presence of [60]fullerene at 20 °C. Under these conditions, the Soret absorption band in **3** in the presence of [60]fullerene (0.5 equivalent) was shifted bathochromically

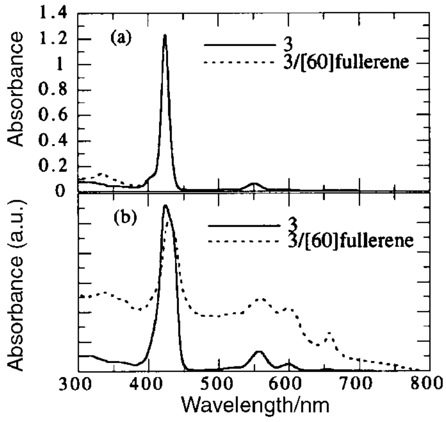


Fig. 1 UV/Vis spectra of **3** and **3**/[60]fullerene complex (1 : 2 molar ratio) in toluene at 20 °C: (a) at 2.55×10^{-4} mol dm^{-3} (for **3**) in a 0.01 cm width cell (sol phase) and (b) at 2.55×10^{-2} mol dm^{-3} (for **3**) with two quartz glass plates (sol phase for **3** and gel phase for **3**/[60]fullerene complex).

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†Electronic supplementary information (ESI) available: absorption and CD spectra of **3** (gel) in toluene. See http://www.rsc.org/suppdata/jm/b0/b004539j/

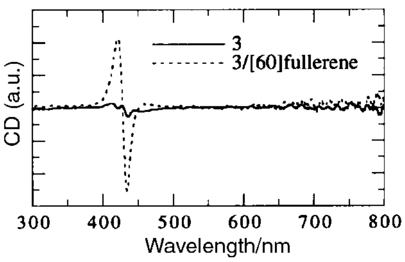

Fig. 2 CD spectra of **3** and **3**/[60]fullerene complex (1 : 2 molar ratio) in toluene at 2.55×10^{-2} mol dm^{-3} (for **3**) with two quartz glass plates at 20 °C (sol phase for **3** and gel phase for **3**/[60]fullerene complex).

from 425 to 430 nm.¶ This indicates that an intermolecular electronic interaction does exist between the Zn(II) porphyrin and the fullerene chromophores in the gel phase (Fig. 1b).[2,3] On the other hand, the low-toluene-concentration solution of **3** (2.55×10^{-4} mol dm^{-3}) was not gelated even in the presence of [60]fullerene and the Soret absorption band at 425 nm was scarcely shifted (Fig. 1a). This implies that the Zn(II) porphyrin–fullerene interaction is very weak in the sol phase.

The gel sample of the **3**/[60]fullerene complex (2 : 1 molar ratio) in toluene ([**3**] = 2[C_{60}] = 2.55×10^{-2} mol dm^{-3}) showed a negative excitation-coupling-type CD spectrum with $\lambda_{\theta=0}$ 430 nm which was in accord with the Soret absorption band at 430 nm: the first negative Cotton effect at 435 nm and the second positive Cotton effect at 422 nm (Fig. 2). This implies that the transition moments related to the Soret band of the Zn(II) porphyrin chromophores are oriented in an anticlockwise direction in the gel phase. On the other hand, the sol sample of **3** in the absence of [60]fullerene did not show an excitation-coupling pattern and the observed CD intensities were much weaker than those obtained from the gel sample of the **3**/[60]fullerene complex (Fig. 2).¶ The trend that ordered chromophores in the gel phase give stronger CD intensities than less-ordered ones in the sol phase has frequently been found in cholesterol-based gelators reported previously.[10,11]

The aggregate structures of **3** in the presence and the absence of [60]fullerene can be observed by scanning electron microscopy (SEM; Hitachi S-4500). The SEM picture of the xerogel, which was obtained from **3** in benzene at –5 °C/0.3 Torr, showed a fibrous structure with 100–300 nm diameter (Fig. 3a). A fibrous structure with 50–150 nm diameter was also found in the xerogel obtained from the **3**/[60]fullerene (2 : 1 molar ratio) system (Fig. 3b); however, these gel fibers were slightly twisted compared to those obtained in the absence of [60]fullerene. The results mean that the fibrous structure of **3** is twisted by the Zn (II) porphyrin–fullerene interaction. It is known that when cholesterol-based gelators pack into a one-dimensional helical column, the 3-*O*-substituents (Zn(II) porphyrin in the case of **3**) can interact with each other to stabilize the aggregate.[10] In the presence of [60]fullerene, one [60]fullerene molecule interacts with the two Zn(II) porphyrin moieties in the aggregate of **3** and the distance between the two porphyrin planes should be elongated to change the pitch length of the one dimensional helical column.

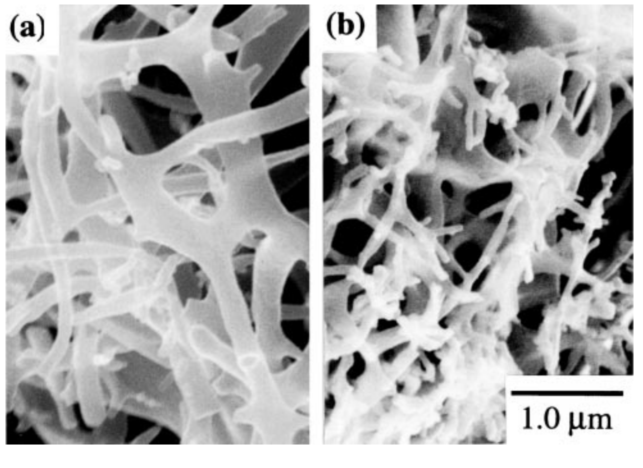

Fig. 3 SEM pictures of the xerogels obtained from (a) **3** and (b) **3**/[60]fullerene complex (1 : 2 molar ratio) in benzene at 2.55×10^{-2} mol dm^{-3} (for **3**) at –5 °C/0.3 Torr.

In conclusion, the present study has demonstrated that the intermolecular Zn(II) porphyrin–fullerene interaction really works to enhance the gelation ability of Zn(II) porphyrin-appended cholesterol. To the best of our knowledge, this is the first example of a significant intermolecular porphyrin–fullerene interaction realized by utilizing the supramolecular assembly system.

Notes and references

‡To a solution of **2** (100 mg, 0.09 mmol) in chloroform (9 mL) was added zinc acetate dihydrate (197 mg, 0.90 mmol) at room temperature under a nitrogen atmosphere. After the mixture was stirred at room temperature for 2 h, it was subjected to silica gel column chromatography eluting with chloroform to give **3** in 96% yield (101 mg, 0.086 mmol). *Selected data* for **3**: violet solid (chloroform/*n*-hexane); mp 223–225 °C; IR (KBr) ν_{max} 3395 (ν_{NH}), 1698 (ν_{CO}), 1653 (ν_{CO}), 1647 (ν_{CO}), 1638 (ν_{CO}) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.60, 0.91 (s, each 3 H, Me), 0.84 (d, J = 6.2 Hz, 6 H, Me), 0.68–1.93 (m, 29 H), 2.01–2.14 (m, 2 H), 2.81–2.94 (m, 2 H, NCH$_2$), 3.03–3.17 (m, 2 H, NCH$_2$), 3.75–3.96 (m, 1 H, OCH), 4.67–4.76 (m, 1 H, NHCOO), 5.23 (d, J = 4.1 Hz, 1 H, CH=C), 6.59–6.70 (m, 1 H, NHCO), 7.41–7.51 (m, 2 H, C$_6$H$_4$CO), 7.70–7.82 (m, 9 H, Ph-*m*,*p*-H), 8.11–8.17 (m, 2 H, C$_6$H$_4$CO), 8.19–8.27 (m, 6 H, Ph-*o*-H), 8.82, 8.93 (d, J = 4.7 Hz, each 2 H, pyrrole-H), 8.95 (s, 4 H, pyrrole-H). Anal. Calc. for $C_{75}H_{78}N_6O_3Zn \cdot 0.1CHCl_3$: C, 75.88; H, 6.62; N, 7.07. Found: C, 76.01; H, 6.64; N, 7.05%.

§Initially, the UV/Vis and CD spectra of **3** (2.55×10^{-2} mol dm^{-3}) in the presence and the absence of [60]fullerene were measured by using a 0.01 cm wide cell. However, the Soret band intensity was too strong to obtain reliable spectra. Therefore, the UV/Vis and CD spectra were measured by using two quartz glass plates which sandwiched the sample solutions to produce thin membranes.

¶Although the bathochromic shift of the Soret band (at 441 nm) was also found in the gel sample of **3** even in the absence of [60]fullerene (at 0.2 mol dm^{-3} in toluene), the excitation coupling CD pattern could not be observed. The large bathochromic shift could be ascribed to J-aggregate formation of the porphyrin chromophores, which would be constructed only in the less-ordered gel structure (judging from the CD pattern).

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