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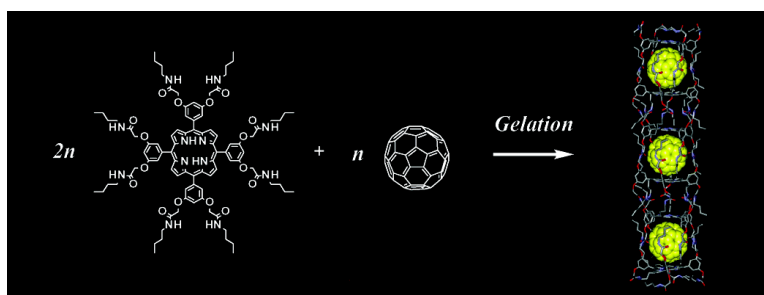
# [60]Fullerene-Motivated Organogel Formation in a Porphyrin Derivative Bearing Programmed Hydrogen-Bonding Sites

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# [60]Fullerene-Motivated Organogel Formation in a Porphyrin Derivative Bearing Programmed Hydrogen-Bonding Sites

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Molecular design of [60]fullerene ($C_{60}$) receptors has been of much concern because they enable us to immobilize or deposit $C_{60}$ in the desired positions without damaging its ample $\pi$-conjugate system by the introduction of substituents. Among the receptors developed thus far,[1–8] it is known that the large binding constants are obtained from a cyclic bisporphyrin system.[7] More recently, we found that a porphyrin-appended cholesterol-based gelator can solubilize a high concentration of $C_{60}$ into the organogel phase.[9] Surprisingly, this organogel system afforded a strict 1:2 $C_{60}$/porphyrin stoichiometry in sandwiched fashion in the superstructure.[9] This novel information stimulated us to design a new porphyrin-appended gelator, in which the hydrogen-bonding sites are programmed so that the resultant assembly can accept $C_{60}$, creating a cavity complementary to $C_{60}$ in its superstructure. A potential hint for this molecular design is obtained from calixarene-based molecular capsules demonstrated by Rebek's group: that is, two ligand (calixarene) moieties are connected by complementary hydrogen-bonding array, adjusting a distance between the two ligand moieties.[10] Previously, we synthesized amide-appended porphyrins **1** and **2** to design a new organogel system in which the $\pi$–$\pi$
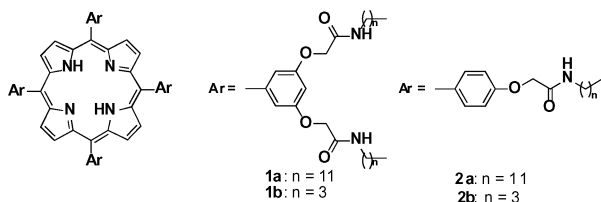


stacking interaction among the porphyrin moieties and the hydrogen-bonding interaction among the amide moieties can operate cooperatively.[11] UV–vis absorption spectral analysis and X-ray analysis of the single crystals show that porphyrins in **2** adopt the H aggregation mode, whereas those in **1** adopt the J aggregation mode.[11] We noticed on the basis of the computational modeling studies that when **1b** dimerizes into a capsular molecule by the hydrogen-bonding interaction, four amide groups in one porphyrin moiety and another four amide groups in another porphyrin moiety can form a circular hydrogen-bonding array according to the $\beta$-sheet motif and the inner space is exactly comparable with the size of $C_{60}$.[14] This strongly suggests that **1b** should assemble, in the presence of $C_{60}$, into the one-dimensional array, because four amide groups on the one side are used for the capsule formation and those on the another side are used for the "intercapsular" interaction (Scheme 1). If this is the case, a stoichiometry between $C_{60}$ and **1b** should become 1:2. With these objects in mind, we examined the influence of added $C_{60}$ on the aggregation properties of **1b** in the gel phase. Very interestingly, we have found that added $C_{60}$ induces a striking morphological change, forming a 1:2 $C_{60}$/**1b** complex. This process has thoroughly been investigated with various spectroscopic methods.

**Scheme 1.** Aggregation Mode of **1b**
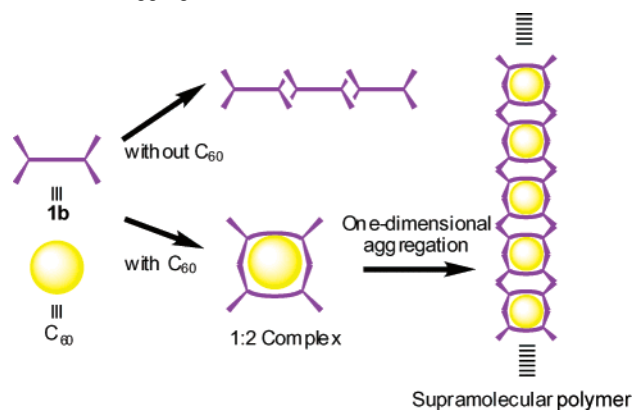


It is known that when **1b** (6.1 mM) was dissolved in refluxing solvent and then the solution was cooled to 25 °C, benzene and toluene gave the gel, whereas *p*-xylene and anisole gave the precipitate.[11] When $C_{60}$ (3.0 mM) was added, all four of the solvents noted above afforded the gel. In addition, the gel-to-sol phase-transition temperature ($T_{gel}$) for the benzene **1b** gel (79 °C) was enhanced up to 120 °C upon addition of $C_{60}$. These findings support the view that added $C_{60}$ efficiently improves the gel stability, probably by changing the morphology of the **1b** aggregate formed in the benzene gel.

To estimate the stoichiometry between $C_{60}$ and **1b**, we carried out the following experiment. The benzene gel containing **1b** (1.52 mM; constant) and $C_{60}$ (varied) was prepared. The superstructures formed in the gel phase were precipitated by a centrifuge. The concentration of $C_{60}$ bound to the superstructure was determined by elemental analysis of the precipitate, whereas that of $C_{60}$ solubilized in benzene was determined by UV–vis absorption spectroscopy. Both plots give a break-point at $C_{60}$/**1b** = 0.5, indicating that two porphyrin moieties sandwich one $C_{60}$.[14]

SEM images of the xerogels prepared from the benzene gels are shown in Figure 1, a–c. The assembly in the absence of $C_{60}$ features a sheetlike structure (Figure 1a).[11] Addition of 0.10 equiv $C_{60}$ partially changes the sheets to the fibers (Figure 1b). When the $C_{60}$ concentration is enhanced up to 0.50 equiv (a break-point molar ratio), one can recognize a fibrous network structure characteristic of the low-molecular-weight organogel system. Further increase in the $C_{60}$ concentration scarcely changes this morphology. TEM pictures taken without a staining reagent are also shown in Figure 1, d–f. In the absence of $C_{60}$, one can only recognize the low-contrast sheetlike structure (Figure 1d). Addition of $C_{60}$ changes the morphology into the fibrous structure, and the fibrils show the strong contrast due to the absorption of electron beam by $C_{60}$ (Figure 1, e and f). These SEM and TEM observations clearly support the view that added $C_{60}$ changes the two-dimensional aggregation mode into the one-dimensional one.
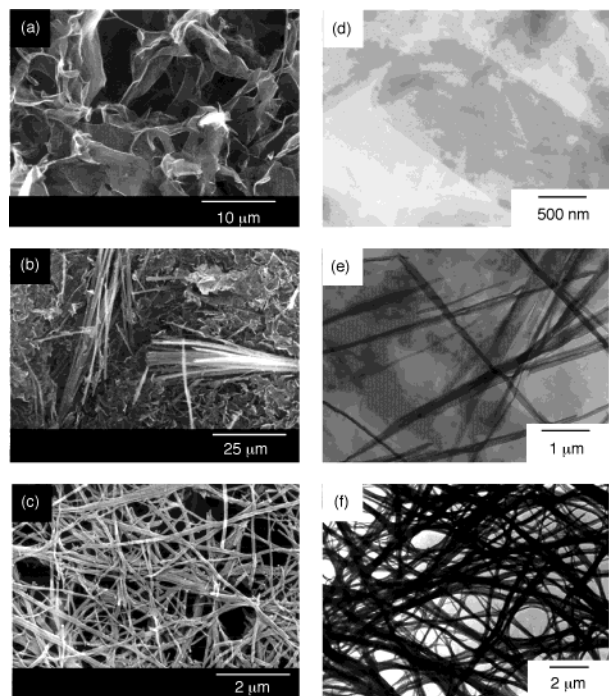
**Figure 1.** SEM (left column) and TEM (right column) pictures of the xerogels prepared from (a), (d); **1b** (1.52 mM) + benzene gel, (b), (e); **1b** (1.52 mM) with 0.10 equiv of $C_{60}$ + benzene gel, (c), (f); **1b** (1.52 mM) with 0.50 equiv of $C_{60}$ + benzene gel.
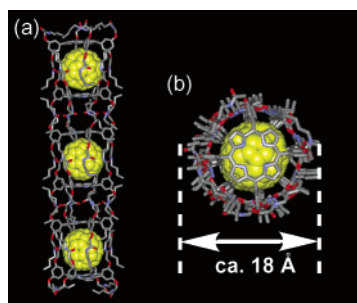


**Figure 2.** Energy-minimized structure of $(C_{60})_3 \cdot (1b)_6$ complex with Discover 3/Insight II 98.0; (a) side view, (b) top view.[12]

Here, we conducted the computational studies again, assuming the construction of a one-dimensional aggregate consisting of $C_{60}$ and **1b** in a 1:2 molar ratio. The energy-minimized structure for a $(C_{60})_3 \cdot (1b)_6$ complex is shown in Figure 2.[12] It is seen from Figure 2 that the porphyrin planes are warped so that they can contact $C_{60}$ as much as possible.[14] As a result, four amide groups in the $C_{60}$-including side form straight hydrogen-bonding bridges with those in another porphyrin, whereas four amide groups in the opposite side form bent hydrogen-bonding bridges with those in the next porphyrin. The one-dimensional aggregate of hexameric **1b** thus provides three cavities large enough to entrap $C_{60}$ and two cavities too small to accept it. This one-dimensional aggregation mode is further supported by the following several lines of spectroscopic evidence: (1) in the UV−vis absorption spectroscopy the $\lambda_{max}$ for the Soret band in the absence of $C_{60}$ shifted to longer wavelength due to the J-aggregate formation,[11] whereas that in the presence of $C_{60}$ (420 nm) was scarcely shifted from that in the dilute benzene solution, indicating that the aggregation mode is neither the H-aggregate nor the J-aggregate and the dipoles in each porphyrin ring are insulated from each other, (2) in the ATR IR spectroscopy

of the xerogel the hydrogen-bonded $\nu_{C=O}$ band (1664 cm$^{-1}$) shifted to low-frequency number region by 10 cm$^{-1}$, indicating that the hydrogen-bonding interaction is intensified by the addition of $C_{60}$, and (3) in the XRD diagrams, a $2\theta = 7.14°$ ($d = 1.24$ nm) peak, which was ascribed to the refraction from the (001) plane constructed by two-dimensional porphyrin layers,[11] disappeared and a $2\theta = 4.90°$ ($d = 1.80$ nm) peak newly appeared,[14] which is ascribable to the columnar diameter in the one-dimensional $(C_{60})_n \cdot (1b)_{2n}$ aggregate (Figure 2).

The foregoing findings consistently support the view that **1b** has a latent capability to create a one-dimensional multicapsular structure in the presence of $C_{60}$, although it is assembled into a two-dimensional sheetlike structure in the absence of $C_{60}$. These novel $C_{60}$-induced morphological changes are due to a strong porphyrin−$C_{60}$ interaction as well as skillfully programmed hydrogen-bonding sites. Although a variety of applications come to our mind, the most expeditious one would be photoinduced electron transfer from superstructural porphyrins constructing the multicapsular structure to $C_{60}$'s encapsulated in these cavities. The preliminary experiment showed that the strong fluorescence observed for the solution containing **1b** and $C_{60}$ is "completely" quenched in the one-dimensional $(C_{60})_n \cdot (1b)_{2n}$ aggregate.[14] The finding implies that the one-dimensional superstructure consisting of porphyrins and $C_{60}$'s would show very novel electron-transfer phenomena. Further investigations are continued in this laboratory.

**Supporting Information Available:** Pictures of fluorescence observed for the **1b** sol and gel in the presence of $C_{60}$, XRD patterns of **1b** xerogels with or without $C_{60}$, energy-minimized structure of $C_{60} \cdot (1b)_2$ complex, and C/N ratio in the precipitate and absorbance at 313.5 nm plotted against molar ratio of $C_{60}/1b$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

## References

(1) Anderson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604−606.
(2) Ikeda, A.; Yoshimura, M.; Udzu, H.; Fukuhara, C.; Shinkai, S. *J. Am. Chem. Soc.* **1999**, *121*, 4296−4297.
(3) Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 259−260.
(4) Komatsu, K.; Fujiwara, K.; Murata, Y.; Brann, T. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2963−2966.
(5) Kawase, T.; Tanaka, K.; Fujiwaka, N.; Darabi, H. R.; Oda, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1624−1628.
(6) (a) Sun, D.; Tham, F. S.; Reed, C. A.; Chaker, L.; Burgess, M.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2000**, *122*, 10704−10705. (b) Sun, D.; Tham, F. S.; Reed, C. A.; Chaker, L.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2002**, *124*, 6604−6612.
(7) Zheng, J.-H.; Tashiro, K.; Hirabayashi, Y.; Kinbara, K.; Saigo, K.; Aida, T.; Sakamoto, S.; Yamaguchi, K. *Angew. Chem., Int. Ed.* **2001**, *41*, 1858−1861.
(8) Kubo, Y.; Sugasaki, A.; Ikeda, M.; Sugiyasu, K.; Sonoda, K.; Ikeda, A.; Takeuchi, M.; Shinkai, S. *Org. Lett.* **2002**, *4*, 925−928.
(9) Ishi-i, T.; Iguchi, R.; Snip, E.; Ikeda, M.; Shinkai, S. *Langmuir* **2001**, *17*, 5825−5833.
(10) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *Angew. Chem., Int. Ed.* **2002**, *41*, 1488−1508 and references therein.
(11) Shirakawa, M.; Kawano, S.-i.; Fujita, N.; Sada, K.; Shinkai, S. *J. Org. Chem.* **2003**, *68*, 5037−5044.
(12) In the computational processes, the nitrogen−oxygen distance in the amide−amide hydrogen bonds was restrained to 0.28 nm which is generally obtained from crystal data of amide-containing compounds.
(13) Such a warping phenomenon of the porphyrin plane has been found in the structure of porphyrin−$C_{60}$ complexes as determined by X-ray crystallographic analysis and computational energy-minimization: see refs 6 and 7.
(14) See Supporting Information.

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