New Organic Gelalors Bearing a Porphyrin Group: A New Strategy to Create Ordered Porphyrin Assemblies

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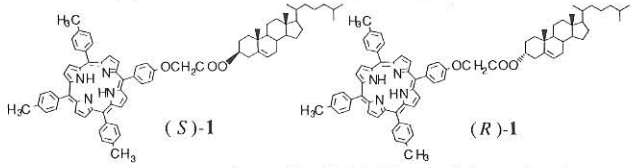
Cholesterol-based gelators **1** bearing a porphyrin moiety were synthesized. (*S*)-**1** with a natural C-3 configuration could gelatinize a few solvents whereas (*R*)-**1** with an inverted C-3 configuration could not gelatinize any solvent. The absorption and CD spectra for less cohesive (*R*)-**1** were changed only to a smaller extent at 10^{-5}~10^{-2} mol dm^{-3} whereas more cohesive (*S*)-**1** gave a new λ_{max} at 444 nm and its corresponding CD band only in the gel phase. The results indicate that "gelation" is a new strategy to create ordered porphyrin assemblies.

It is of current concern to construct large porphyrin arrays in relation to the design of artificial molecular systems aiming at mimicking the structure and function of photosynthetic centers. Thus, various interactions such as liquid crystals,[1] membrane-mimetic aggregates,[2,3] hydrogen-bonding interactions,[4] metal-ligand interactions,[5,6] *etc.* have been utilized to assemble porphyrins into the specific ordered structures. More recently, new molecular assemblies formed in an organic gel system have attracted considerable attention.[7-12] The gelators can be self-assembled by the recrystallization-like operation and feature in most cases the fibrous structure.[7-12] Interestingly, some gelators with the chiral center result in a large strand with a helical structure.[7,10] It thus occurred to us that the gel system might be applicable to create new ordered porphyrin-based assemblies. With these objects in mind we synthesized cholesterol-based gelators, (*S*)-**1** with a natural (*S*)-configuration at C-3 and (*R*)-**1** with an inverted (*R*)-configuration at C-3.



5-(4-Phenoxyacetic acid)-10,15,20-tritolylporphyrin was synthesized from 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin by the reaction with ethyl bromoacetate in the presence of Cs_2CO_3 followed by the ester cleavage with Et_4NOH in a THF-water(5:1 v/v) mixture. When this acid derivative was treated with cholesterol with DCC and 4-*N*,*N*-dimethylaminopyridine in dichloromethane, (*S*)-**1** with the natural C-3 configuration was afforded in 78% yield: mp 212-218 °C. When triphenylphosphine and diethyl azodicarboxylate were used as a condensation reagent, inversion of C-3 was induced[10] to afford (*R*)-**1** with the unnatural C-3 configuration in 33% yield: mp 181-187 °C. The products were identified by IR, ^{1}H and ^{13}C NMR, and Mass (positive SIMS) spectral evidence and elemental analyses.[13] In $CDCl_3$ the 3-CH proton and the 6-CH olefinic proton which characterize the configuration[10] appeared at 4.88 ppm and 5.43 ppm for (*S*)-**1** and at 5.26 ppm and 5.37 ppm for (*R*)-**1**.

The gelation test was carried out for 47 solvents with their 2.04 x 10^{-2} mol dm^{-3} solutions using a test-tube-tilting method. The solution was once heated at the reflux temperature or at 80 °C (for solvents with bp > 80 °C) and then cooled to 25 °C. Both (*S*)-**1** and (*R*)-**1** formed the precipitate from aliphatic solvents such as *n*-hexane, *n*-heptane, *n*-octane, *etc.* but were homogeneously solubilized in aromatic solvents such as benzene, toluene, *p*-xylene, nitrobenzene, *etc.* and in halogen solvents such as carbon tetrachloride, 1,2-dichloroethane, dichloromethane, chloroform, *etc.* Very interestingly, we found that (*S*)-**1** can gelatinize cyclohexane and methylcyclohexane at 25 °C and diphenyl ether at 4 °C whereas (*R*)-**1** is only soluble in these solvents.

We previously discussed the influence of the structural difference between (*S*)- and (*R*)-cholesterol derivatives on the aggregation properties.[10] When (*S*) cholesterol moieties constitute one-dimensional columnar stacking, the C-3-appended groups (the plane of which is immobilized perpendicular to the cholesterol plane) can enjoy the face-to-face-type interaction and stabilize the aggregate. In contrast, when (*R*) cholesterol moieties constitute one-dimensional columnar stacking, the C-3-appended groups (which have the L-shaped structure bent to the cholesterol plane) cannot take such a face-to-face orientation and the additional stabilization effect is not expected. This structural difference is reproduced in the present system: (*S*)-**1** is more cohesive, less soluble and can act as a gelator while (*R*)-**1** is less cohesive, more soluble and cannot act as a gelator.

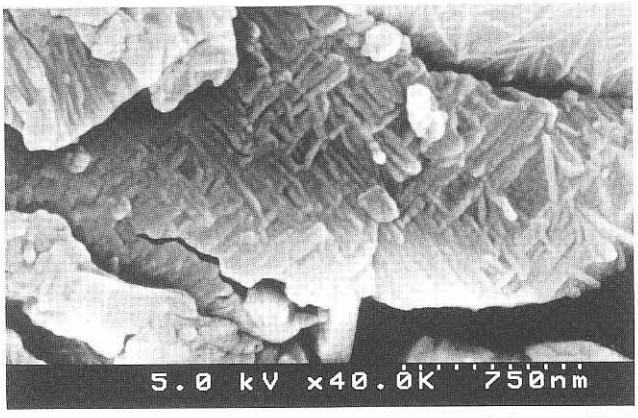


Figure 1. SEM picture of a xerogel prepared from a (*S*)-1 (2.04 x 10^{-2} mol dm^{-3}) plus cyclohexane system. For the preparation method see Reference 10.

To obtain a visual insight into the aggregation mode, we prepared a dry sample from a cyclohexane gel of (*S*)-**1**. The gel was first cooled in liquid nitrogen and then the solvent was removed under vacuum at 0 °C. The SEM picture (Figure 1) showed a flake structure consisting of fibers with 10 ~ 50 nm diameter. Judging from the fact that the gel is obtained only in

a few selected solvents and only at the high concentration (*vide post*), the present gel fiber would not be so stable. We presume that the less stable fibrils of (*S*)-**1** aggregate into the flake during the thawing-and-pumping treatment.[10]

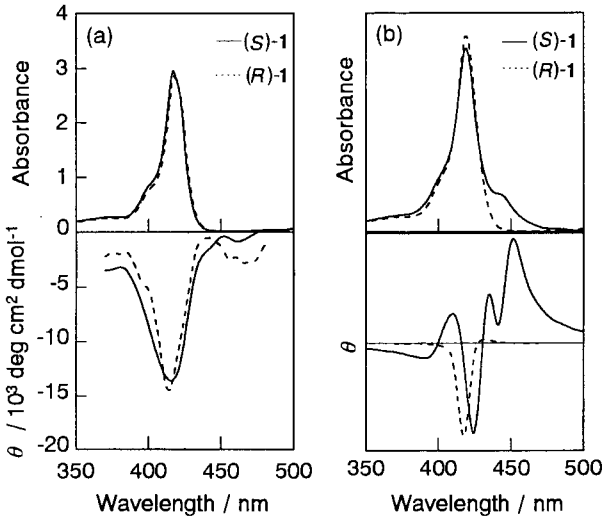


Figure 2. Absorption and CD spectra of (*S*)-**1** and (*R*)-**1** in cyclohexane (25 °C): (a) 1.00 x 10^{-5} mol dm^{-3}, cell width 1.0 cm; (b) 1.00 x 10^{-2} mol dm^{-3}.

Further gelation properties were studied with (*S*)-**1** in cyclohexane. The 2.04 x 10^{-2} mol dm^{-3} solution gave the sol-gel phase-transition temperature at 65 °C. At 25 °C, the solution was gelatinized above 9.0 x 10^{-3} mol dm^{-3}. As shown in Figure 2-(a), both (*S*)-**1** and (*R*)-**1** (1.00 x 10^{-5} mol dm^{-3}) showed a λ_{max} for the Soret band at 418 nm. A negative CD band appeared at this wavelength region. The results imply that in a homogeneous solution both the absorption and CD spectra are scarcely affected by the C-3 configuration. With increasing (*S*)-**1** or (*R*)-**1** concentration the Soret band gradually became broad, indicating that the aggregation of these compounds is induced even below the sol-gel phase-transition concentration. The half-height peak-width of the Soret band was not so different between (*S*)-**1** and (*R*)-**1** below 7.0 x 10^{-4} mol dm^{-3} but above this concentration the peak for (*S*)-**1** became broader than that for (*R*)-**1**, suggesting that (*S*)-**1** has the more cohesive nature than (*R*)-**1**.

At 1.00 x 10^{-2} mol dm^{-3}, on the other hand, the (*S*)-**1** solution was gelatinized whereas the (*R*)-**1** solution was not apparently gelatinized. We used a 0.005 cm width cell for the absorption and CD spectral measurements but the intensity of the Soret band was too strong to obtain the reliable spectra. We sandwiched the sample solution with two quartz glass plates and prepared a thin membrane. The spectra thus obtained are shown in Figure 2-(b) (since the thickness cannot be precisely defined, the ordinate is an arbitrary unit). Very interestingly, the absorption and CD spectra for less cohesive (*R*)-**1** are scarcely changed from those at 1.00 x 10^{-5} mol dm^{-3} whereas more cohesive and gelatinized (*S*)-**1** distinctly gives a new shoulder peak at 444 nm and a strong exciton-coupling-type CD band appears at this wavelength region in addition to that at Soret band region.[14] The red shift of the Soret band implies that the porphyrin rings in the gel phase are stacked according to the J-aggregation mode.[15]

In conclusion, this paper has shown that cholesterol-appended porphyrin can act as a new organic gelators and is useful to create a new porphyrin aggregation state. Furthermore, the aggregation properties are profoundly influenced by the C-3 configuration of the cholesterol moiety. We now believe that photochemical and catalytic reactions mediated by porphyrins and metalloporphyrins, which are possible only in the gel system, would be exploited.

References and Notes

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13 Identification of (*S*)-**1** and (*R*)-**1**
(*S*)-**1**: ^{1}H NMR ($CDCl_3$): δ 8.85 (s, 8H, ArH), 8.04-8.15 (m, 8H, ArH), 7.55 (d, 6H, ArH), 7.29 (d, 2H, ArH), 5.40-5.46 (m, 1H, 6CH), 4.88 (s, 2H, OCH_2COO), 4.83-4.93 (m, 1H, 3CH), 2.69 (s, 9H, $ArCH_3$), 0.86-2.50 (m, 40H, cholesterol CH), 0.67 (s, 3H, CH_3), -2.78 (s, 2H, NH); Anal. Calcd for $C_{76}H_{82}N_4O_3$: C, 83.02; H, 7.52; N, 5.10. Found: C, 82.94; H, 7.55; N, 5.01; MS (SIMS, NBA, positive) *m/z* 1099 $[(M+H)^+]$
(*R*)-**1**: ^{1}H NMR ($CDCl_3$): δ 8.85 (s, 8H, ArH), 8.05-8.15 (m, 8H, ArH), 7.55 (d, 6H, ArH), 7.29 (d, 2H, ArH), 5.35-5.40 (m, 1H, 6CH), 5.23-5.29 (m, 1H, 3CH), 4.88 (s, 2H, OCH_2COO), 2.69 (s, 9H, $ArCH_3$), 0.68-2.67 (m, 40H, cholesterol CH), 0.61 (s, 3H, CH_3), -2.77 (s, 2H, NH); Anal. Calcd for $C_{76}H_{82}N_4O_3$: C, 83.02; H, 7.52; N, 5.10. Found: C, 83.02; H, 7.55; N, 5.01; MS (SIMS, NBA, positive): *m/z* 1099 $[(M+H)^+]$

14 We confirmed that the contribution of the LD band is negligible to this CD band.[10]

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