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Complexes between hydrogen bonded bisporphyrin tweezers and cholesterol-appended fullerenes as organogelators and liquid crystals

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ABSTRACT

This paper reports the gelation and liquid crystal properties of a class of new complexes between zinc and copper bisporphyrin and C_{60} derivatives. The bisporphyrins are induced by intramolecular hydrogen bonding to adopt a preorganized 'U'-shaped conformation and therefore efficiently complex the C_{60} derivatives. As a result, the capacity of their mixtures to gelate alkanes is increased notably. The bisporphyrins themselves and their complexes with the C_{60} derivatives form the smectic liquid crystal phase. However, the glassy transition temperature of the complexes decreases considerably.

1. Introduction

The self-assembly of well-defined architectures may be induced by the selective association of molecular components through discrete noncovalent interactions. In this context, supramolecular organogelators and liquid crystals have received considerable interest due to their potential applications as biomedical, optical, and electronic materials.[1,2] It is well established that porphyrins and fullerenes form stacking complexes.[3] Such an interaction has been used to construct several classes of supramolecular organogels[4] and liquid crystals[5] from two discrete components that have a single porphyrin or fullerene unit. Although a number of porphyrin tweezers have been reported to display increased capacity to complex fullerene or its derivatives,[6] their possibility of forming supramolecular gels or liquid crystals has not been reported. We previously reported the self-assembly of a class of hydrogen bonding-driven foldamer-based porphyrin receptors that exhibit remarkably high binding affinity for C_{60} and its derivatives.[7] Considering that C_{60} can be readily modified with discrete functionalized units, such as the cholesterol unit, a typical moiety that facilitate the formation of organogels and liquid crystals,[8,9] we became interested in exploring the possibility of developing novel two-component functional entities. We herein describe that such kind of new complexes not only gelate hydrocarbons, but also form liquid crystals.

2. Results and discussion

Five new hydrogen bonding-driven preorganized bisporphyrin receptors H_4**1**, Zn_2**1**, Cu_2**1**, H_4**2**, and Zn_2**2** were designed and prepared, which bear four nonpolar aliphatic chains or four polar oligoglycol chains. The long side chains were expected to tune their solubility and assembling behavior in solvents of different polarity. Compounds **3**–**6**, which bear different side chains, were prepared as the guest molecules. Compounds **5** or **6** are introduced with one or two cholesterol units, which have been revealed efficient to induce the formation of organogels and liquid crystals.[8,9]

The synthetic route for H_4**1**, Zn_2**1**, and Cu_2**1** is shown in Scheme 1. Thus, porphyrin **10** was first prepared in 5% yield from the reaction of **7**, **8** and **9** in refluxing propanoic acid and then hydrolyzed to **11**. With this acid available, **13** was prepared from the palladium-catalyzed hydrogenation of **12**. This diamine was then coupled with **11** to give H_4**1** in 49% yield. Treatment of H_4**1** with zinc acetate and cupric acetate in methanol and dichloromethane gave rise to Zn_2**1** and Cu_2**1** in 80% and 91% yields, respectively. For the synthesis of H_4**2** and Zn_2**2** (Scheme 2), compound **16** was first prepared from the reaction of **14** and **15** in hot DMF. Its reaction with **8** and **9** in refluxing propanoic acid gave porphyrin **17** in 9% yield, which was

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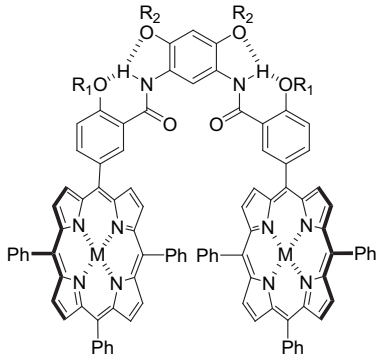
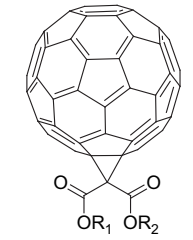
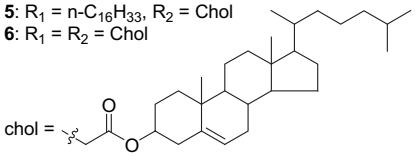
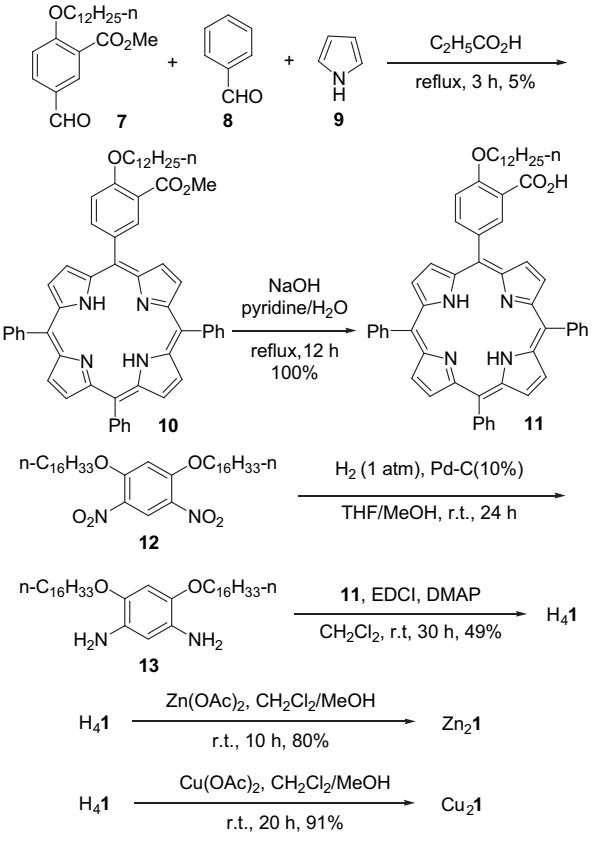


H_4**1**: R_1 = n-$C_{12}H_{25}$, R_2 = n-$C_{16}H_{33}$, M = 2H
Zn_2**1**: R_1 = n-$C_{12}H_{25}$, R_2 = n-$C_{16}H_{33}$, M = Zn
Cu_2**1**: R_1 = n-$C_{12}H_{25}$, R_2 = n-$C_{16}H_{33}$, M = Cu
H_4**2**: R_1 = $(CH_2CH_2O)_3Me$, R_2 = $(CH_2CH_2O)_4Me$, M = 2H
Zn_2**2**: R_1 = $(CH_2CH_2O)_3Me$, R_2 = $(CH_2CH_2O)_4Me$, M = Zn



3: R_1 = R_2 = n-$C_{16}H_{33}$
4: R_1 = R_2 = $(CH_2CH_2O)_4Me$
5: R_1 = n-$C_{16}H_{33}$, R_2 = Chol
6: R_1 = R_2 = Chol



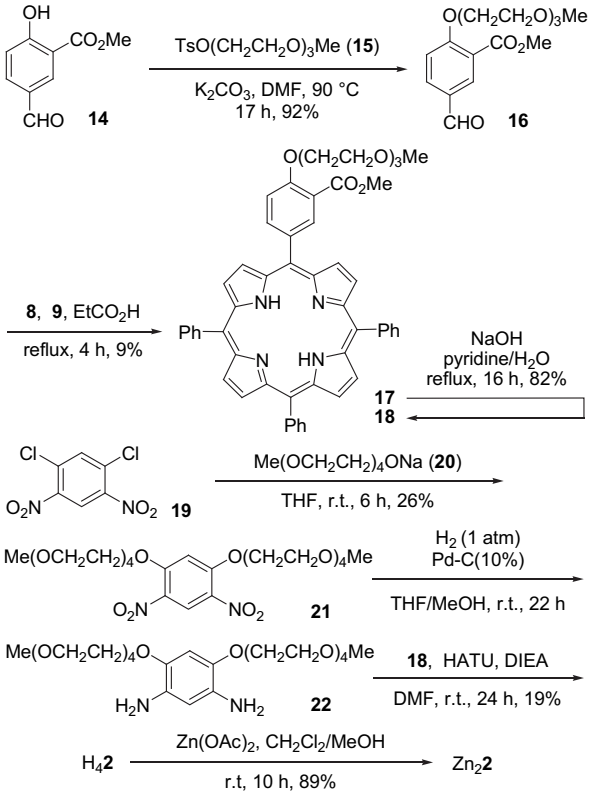


Scheme 1. Synthesis of compounds H_4**1**, Zn_2**1** and Cu_2**1**.

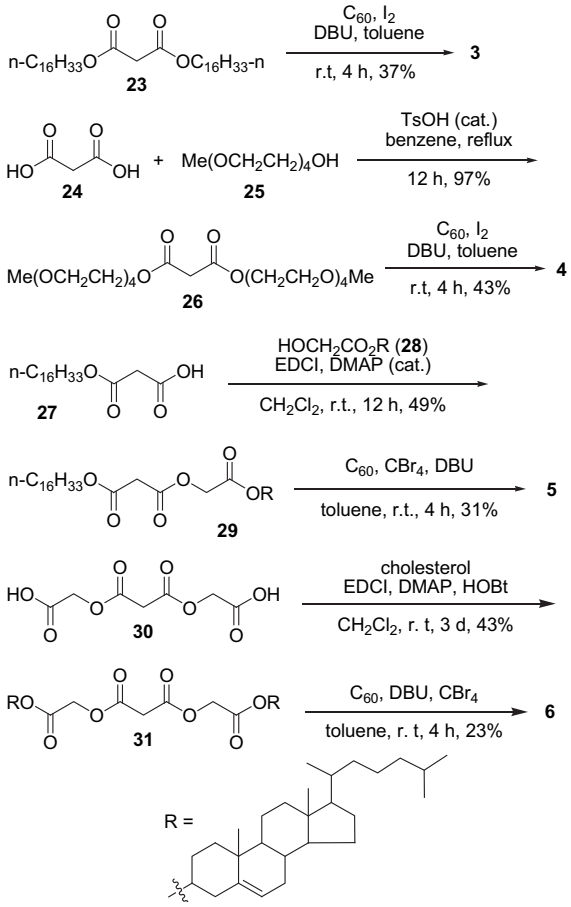
then hydrolyzed with sodium hydroxide to afford **18** in 82% yield. With **18** available, **21** was prepared from the reaction of **19** and **20** in 26% yield and further hydrogenated to give **22**. This diamine was then coupled with **18** in DMF to produce H_4**2** in 19% yield. Treatment of **19** with zinc acetate in methanol and dichloromethane generated Zn_2**2** in 89% yield. The synthesis of compounds **3**–**6** was straightforward and is shown in Scheme 3.

Previous investigation revealed that similar zinc porphyrin tweezers and C_{60} or its derivatives form 1:1 complexes.[7a] To evaluate the complexing stability of the new compounds, UV–vis titration experiments were carried out for complex Zn_2**1**·**3** in n-hexane, chloroform and 1,2-dimethoxyethane.[7a] The association constants were determined to be 1.3×10^4, 3.1×10^3 and 2.3×10^3 M^{-1}, respectively, which are comparable to those of the previously reported complexes,[7a] although it was reported that the complex may become less stable in polar solvent.[10] Because the complexes of Zn_2**1** and Cu_2**1** with **3**, **5**, and **6** exhibit a great capacity to gelate alkanes, especially decalin (Table 1, vide infra), the association constants of the corresponding 1:1 complexes Zn_2**1**·**3**, Zn_2**1**·**5**, Zn_2**1**·**6**, Cu_2**1**·**3**, Cu_2**1**·**5**, and Cu_2**1**·**6** in decalin were also determined. The values are 1.4×10^4, 1.3×10^4, 8.9×10^3, 1.3×10^4, 1.0×10^4, and 7.8×10^3 M^{-1}, respectively, indicating that both zinc and copper porphyrin strongly complex the C_{60} derivatives.

The gelation behaviors of the single and 1:1 samples in different solvents were evaluated. The samples did not gelate benzene, dichloromethane, chloroform or THF. However, porphyrins Zn_2**1** and Cu_2**1** themselves and most of their complexes with **3**, **5**, and **6** gelated alkanes, including decalin, *n*-decane, cyclohexane and *n*-hexane. Four complexes also partially gelate toluene. The results are



Scheme 2. Synthesis of compound Zn_2**2**.



Scheme 3. Synthesis of compounds **3**–**6**.

Table 1
The gelation results of compounds **1**–**6** and their 1:1 complexes for alkanes[a,b]

Sample	Decalin	*n*-decane	Cyclohexane	*n*-hexane	Toluene
H_4**1**	S	S	S	S	S
Zn_2**1**	*p*G	*p*G	*p*G	P	S
Cu_2**1**	*p*G	*p*G	*p*G	*p*G	S
Zn_2**2**	S	S	S	P	S
3	S	S	S	S	S
4	S	S	S	P	S
5	S	S	S	S	S
6	S	S	S	P	S
Zn_2**1**/**3**	*p*G	*p*G	*p*G	*p*G	S
Zn_2**1**/**4**	G	*p*G	*p*G	*p*G	S
Zn_2**1**/**5**	G (20)[c] G (28)	*p*G	G (30)	*p*G	*p*G
Zn_2**1**/**6**	G (20) G (25)	*p*G	*p*G	P	*p*G
Cu_2**1**/**3**	G (26)	*p*G	G (33)	*p*G	S
Cu_2**1**/**4**	*p*G	*p*G	*p*G	P	S
Cu_2**1**/**5**	G (18)	G (25)[c] G (40)	G (28)[d] G (30)	*p*G	*p*G
Cu_2**1**/**6**	G (20)[c] G (26)	G (27)[c] G (45)	G (30)[d] G (35)	P	*p*G
Zn_2**2**/**3**	S	P	S	P	S
Zn_2**2**/**4**	S	P	S	P	S
Zn_2**2**/**5**	S	P	S	P	S
Zn_2**2**/**6**	S	P	S	P	S

[a] G=gel; *p*G=partial gel; P=precipitate; S=solution; the tested concentration is 20 mM.
[b] The data in the parenthesis are the lowest concentration for forming a gel.
[c] At 0 °C.
[d] At 10 °C.

shown in Table 1. Generally, all the compounds and their 1:1 complexes had a low solubility in *n*-hexane. The gelation behavior in decalin, *n*-decane and cyclohexane has several tendencies. Compounds H_4**1**, H_4**2**, Zn_2**2**, **3**–**6** did not gelate any solvents, while Zn_2**1** and Cu_2**1** were able to partially gelate most of them. Adding 1 equiv of **3** to the systems of Zn_2**1** in decalin, *n*-decane or cyclohexane did not increase the gelation capacity. However, the mixture in *n*-hexane could partially gelate the solvent because their complexation caused the solubility of Zn_2**1** to increase considerably. Similar result was also displayed for the mixture of **3** and Cu_2**1** in *n*-hexane. Addition of **3** promoted the gelation of Cu_2**1** in decalin and cyclohexane. As a result, stable organogels could be formed. A comparison of the results of Zn_2**1** and Cu_2**1** with those of their mixtures with **5** and **6** also shows that the complexes were generally more efficient than Zn_2**1** and Cu_2**1** in gelation, while the complexes of Cu_2**1** were even more efficient than those of Zn_2**1**.[11] Control experiments revealed that simple Zn or Cu porphyrin, like that of **10**, or their mixtures with **3**, **5**, and **6** did not gelate any solvents. Therefore, the increase of the capacity of the above mixtures in gelating alkanes should be attributed to the formation of stable complexes as well as the appended cholesterol moiety. We may expect that the complexation would promote the parallel arrangement of the two porphyrin units of Zn_2**1** and Cu_2**1** and thus facilitate their ordered stacking. The long hexadecyl and cholesterol units in the C_{60} derivatives should also contribute significantly. The former should increase the van der Waals interaction between stacking complexes to promote the formation of an entangled structure, while the latter is well known to aggregate to induce the gel state. For all the cases, **4**, Zn_2**2**, their complex and those with others did not gelate the alkanes, which may be rationalized by considering that their polar oligoglycol chain would self-coil in alkanes and thus did not help the formation of an entangled structure.

SEM images indicated that all the organogels formed by the above complexes gave rise to fibrous structures. Figure 1 shows the representative results. In contrast, the samples that did not gelate the solvents did not form ordered structures (not shown). AFM images of the gel samples of the complexes also showed the formation of extended fibrils (Fig. 1), which were not observed for the single compounds, including Cu_2**1** and Zn_2**1**, even though they could partially gelate the solvents. The size of the fibers was generally smaller that exhibited on the SEM images because of the substantially lower concentration used.

To obtain insight into the stacking pattern of the porphyrin units in the gel state, UV–vis spectra in different states were recorded. The results for the system of Cu_2**1** and **5** are shown in Fig. 2. The Soret and Q bands of Cu_2**1** in the decalin solution occurred at 415 and 539 nm, which red-shifted to 417 and 544 nm in the partial gelation state and to 420 and 545 nm in the gel state in the presence of 1 equiv of **5**. Gelation also caused the generation of a shoulder peak at 390 nm.[12] These results supported that the porphyrin units of Cu_2**1** formed the J-aggregation in the gel state.[13] Similar red shifting (by 2 and 5 nm) was also observed for the Soret band of Zn_2**1** in the the partial gel state (10 mM) and the partial gel state (10 mM) in the presence of 1 equiv of **5** (not shown). In addition, it also generated a shoulder peak at 405 nm. These results indicate that the porphyrin units of Zn_2**1** might also undergo the J-aggregation in the gel state.

Previous study indicated that the complexation of similar preorganized bisporphyrin receptors for C_{60} derivatives that bear a chiral histidine unit caused the generation of the supramolecular chirality in the solution of chloroform or toluene.[7a] Circular dichroism (CD) investigation showed that this supramolecular chirality transfer also occurred in the gel of the complexes.[14] For example, the decalin gel of Cu_2**1** and **5** gave rise to a negative Cotton effect at 382 nm and a positive Cotton effect at 418 nm, which was close to the Soret band absorption of the porphyrin unit and might be attributed to the latter, while that of Cu_2**1** and **6** exhibited a positive Cotton effect at 418 nm. These signals were similar in shape to those observed for the same samples in solution, suggesting that the complexes adopted the identical binding patterns. The complexes of Zn_2**1** with **5** and **6** in decalin also exhibited the

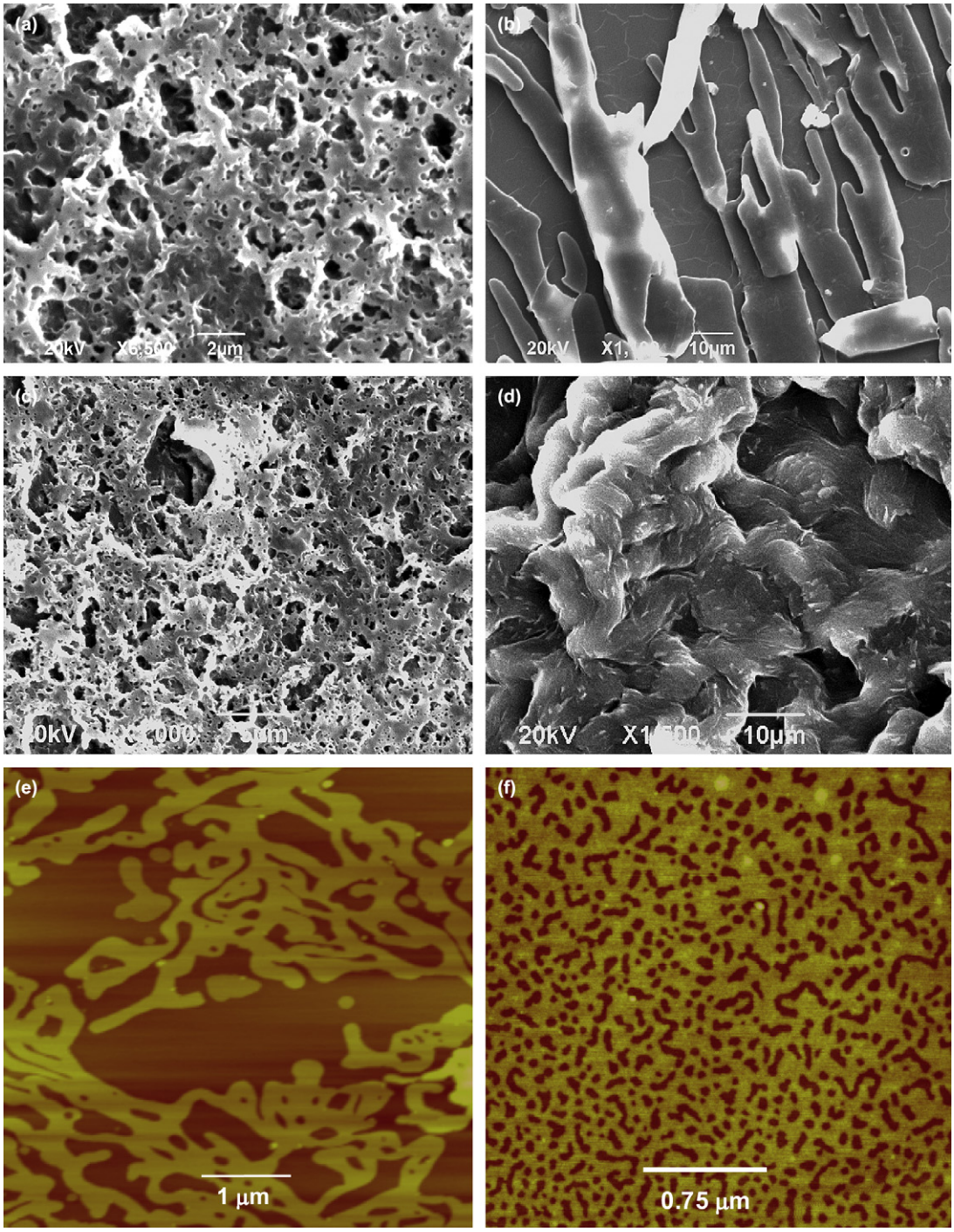


Figure 1. SEM images (20 mM) of a) Zn_2**1**/**5**, b) Cu_2**1**/**3**, c) Cu_2**1**/**5**, d) Cu_2**1**/**6**; AFM images (0.1 mM) of e) Zn_2**1**/**5** and f) Cu_2**1**/**5**. All the samples were obtained from the decalin gels or solutions after the solvent was evaporated.

similar CD property. The CD spectra of the complexes of Cu_2**1** with **3**, **5**, and **6** are provided in Fig. 3.

The liquid crystal behaviors of the complexes were then studied by the powder X-ray diffraction (PXRD). The experiments were conducted on both pristine and xerogel samples at 80 °C, at which all complexes formed liquid crystal phase, as revealed by the differential scanning calorimetry (DSC) experiments (Table 2, vide infra). Both samples exhibited similar results. The representative results of the pristine samples are shown in Fig. 4, while those of the xerogels are provided in ESI. The mixture of Zn_2**1** and **5** displayed three main Bragg diffractions at 2θ=4.1, 6.3, and 8.4°, which corresponded to the *d* spacings of 2.18, 1.38, and 1.05 nm, respectively (Fig. 3a). Based on the molecular model of the complex, the three peaks may be assigned to the 001, 010, and 002 plane diffractions, which also suggest that the complex shows a smectic phase.[15] The sample of Zn_2**1** and **6** displayed no 002 plane diffractions and the peaks for the 001 and 010 plane diffractions broadened (Fig. 3b), indicating a less ordered alignment. The sample of Cu_2**1** and **5** displayed all the three diffractions (Fig. 3c), suggesting that the complexes of the two metal porphyrins with **5** had a similar stacking pattern. The sample of Zn_2**1** and **5** also gave rise to a broad halo at ca. 4.4 nm, which can be assigned to the molten chains with the liquid-like order.[16] Similar peak of the samples of Zn_2**1** and **6** and Cu_2**1** and **5** was considerably weak, reflecting the low order of the molten chains.

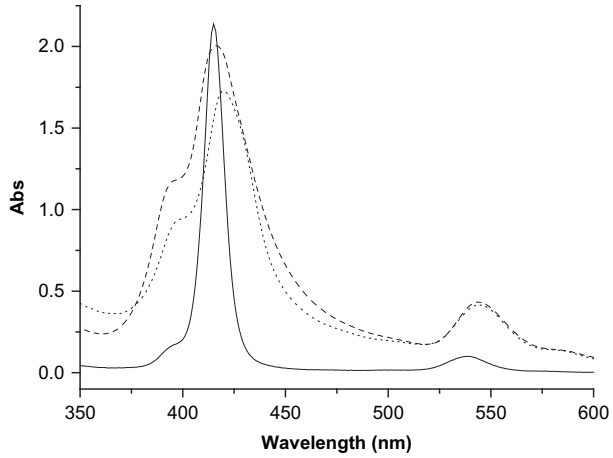


Figure 2. UV–vis spectra of Cu_2**1** in decalin (solid line: 2 μM, solution; dashed line: 20 mM, partial gelation) and Cu_2**1**/**5** (1:1, 20 mM) (dotted line: gel).

The liquid crystal behaviors of the single compounds and their 1:1 mixtures were further investigated by polarized light microscopy (PLM). The results are provided in Table 2 and the PLM results of H_4**1**, Cu_2**1** and its mixtures with **5** and **6** are presented in Fig. 5. It was found that C_{60} derivatives **3**, **5**, and **6** themselves did not form liquid crystal phase, even though several C_{60}-cholesterol blends were reported to display such a capacity,[17] while bisporphyrins H_4**1**, Zn_2**1**, and Cu_2**1** all exhibited an SmC liquid crystal phase with the glassy transition temperature at 45, 64, and 54 °C,[18] respectively. The temperature was reduced considerably in the presence of 1 equiv of **3**, **5**, or **6**, suggesting that complexation promoted the formation of the liquid crystal phase.[19] Notably, the decreases of the transition temperature caused by **3** were generally larger than those caused by **5** or **6**, which might be attributed to the rigidity of the cholesterol unit of **5** and **6**. The SmC phase of Cu_2**1** was a schlieren texture (Fig. 5b), in which the porphyrin units should be orientated on one side of the lamellar structure, while the long aliphatic chains were located on another side. When **3** was present, it should be embedded between the two porphyrin units, leaving its two long chains toward the breach of the tweezers.[20] The mixture of Cu_2**1** and **5** formed a dentritic texture (Fig. 5c), while the mixture of Cu_2**1** and **6** generated a blurred schlieren texture, possibly due to the decreased matching of the aliphatic chains of Cu_2**1** and the cholesterol moieties of **6**. The existence of cholesterol-free **3** did not change the SmC phase state, even though the mixture of

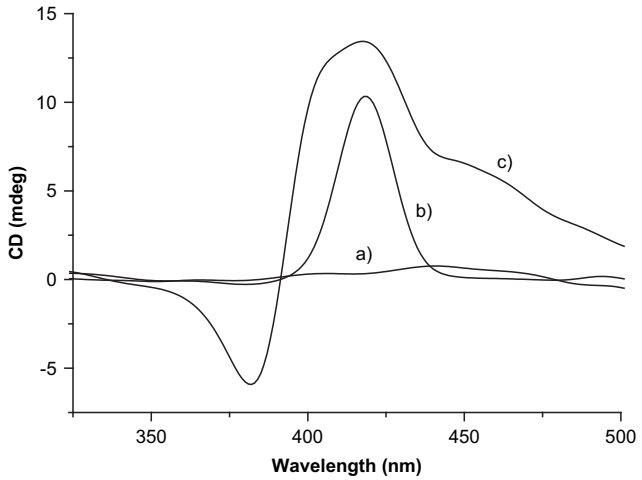


Figure 3. CD spectra of Cu_2**1** (20 mM) in the presence of **3** (20 mM) (dashed line), **5** (20 mM) (dotted line) and **6** (20 mM) (solid line). All were obtained by sandwiching the samples with two quartz plates.

Table 2
Thermo properties of porphyrins and fullerene derivatives

Sample	Phase-transition behaviors[a,b]						
H_4**1**	Gl	45	SmC	140	I		
Zn_2**1**	Gl	64	SmC	164	I		
Cu_2**1**	Gl	54	SmC	167	I		
3	No LC phase						
5	No LC phase						
6	No LC phase						
H_4**1**/**3**	Gl	40	Sm	124	I		
H_4**1**/**5**	Gl	43	Sm	130	I		
H_4**1**/**6**	Gl	43	Sm	130	I		
Zn_2**1**/**3**	Gl	46	SmC	131	I		
Zn_2**1**/**5**	Gl	51	SmC	140	I		
Zn_2**1**/**6**	Gl	50	SmC	160	I		
Cu_2**1**/**3**	Gl	36	SmC	74	Sx	150	I
Cu_2**1**/**5**	Gl	47	Sm	153	I		
Cu_2**1**/**6**	Gl	52	Sm	150	I		
10	Cr	182	I				
10/**3**	No LC phase						
10/**5**	No LC phase						
10/**6**	No LC phase						

[a] The data are transition temperatures (°C).
[b] Gl: glassy; S_C: smectic C; S_m: unidentified smectic phase; I: isotropic; Cr: crystalline. The phase structures were assigned by comparing the microscopic textures with reported ones.[18]

Cu_2**1** and **3** displayed another Sm phase state, which started at 74 °C. In contrast, the addition of **5** or **6** caused it to change to the Sm phase state. Again, this difference may be ascribed to the rigid

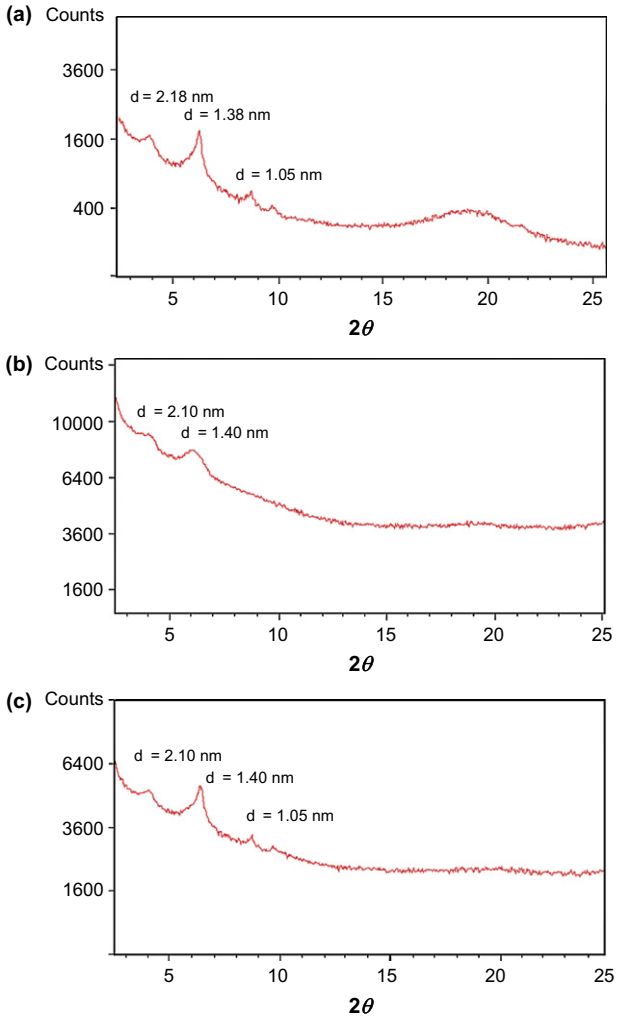


Figure 4. Powder XRD diagrams of the pristine samples, obtained from the solution of chloroform (35 mM), of (a) Zn_2**1**/**5** (1:1), (b) Zn_2**1**/**6** (1:1), and (c) Cu_2**1**/**5** (1:1) at 80 °C.

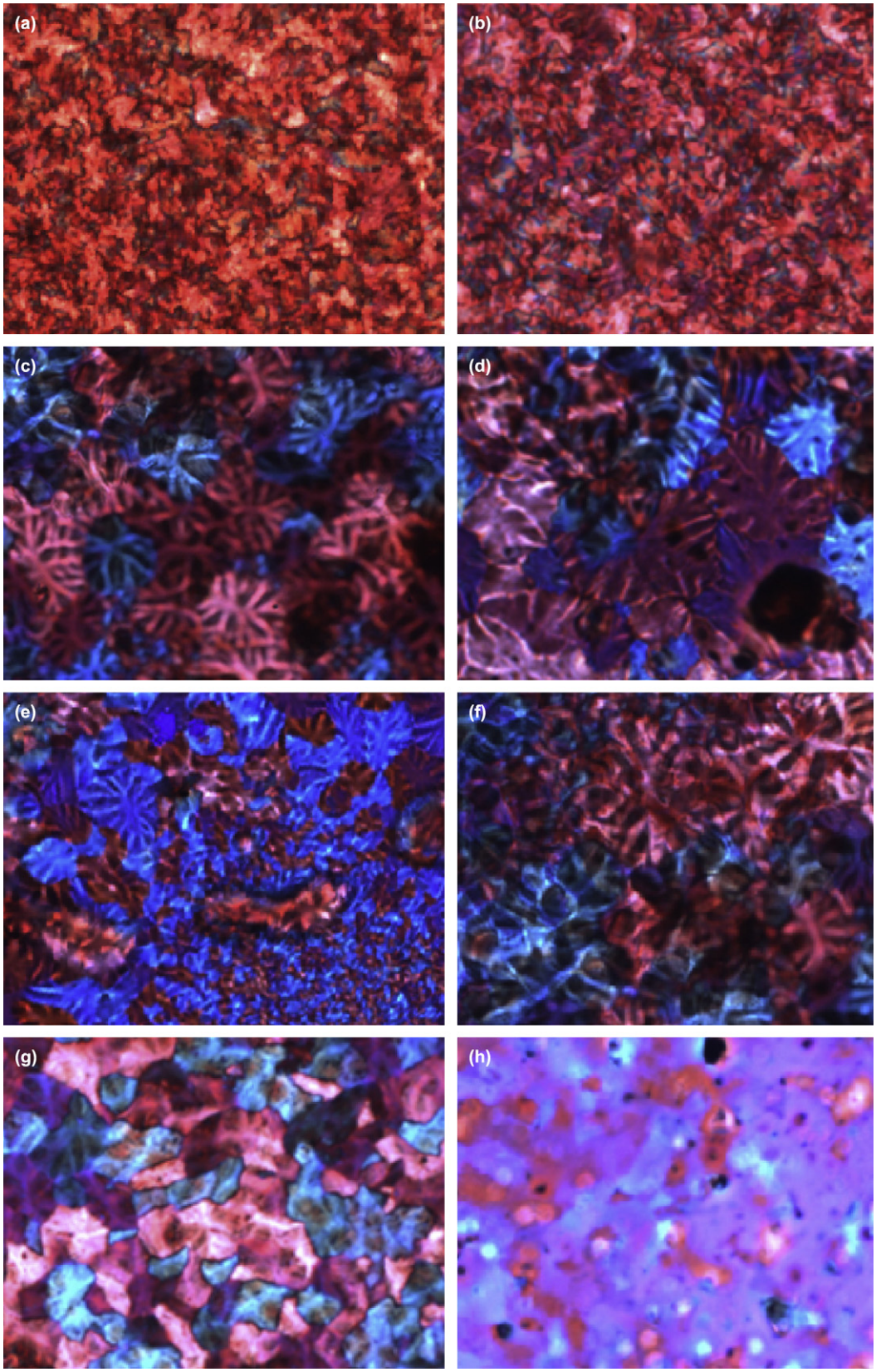


Figure 5. Polarizing light microscopy textures of (a) H_4**1** (80 °C), (b) Cu_2**1** (80 °C), (c) Cu_2**1**/**5** (1:1, 80 °C), (d) Cu_2**1**/**6** (1:1, 80 °C) (these samples were the dry assemblies prepared from the decalin solution and were sandwiched by two glass plates), (e) Cu_2**1** (120 °C), (f) Cu_2**1**/**5** (120 °C), (g) Cu_2**1** (150 °C), and (h) Cu_2**1**/**5** (150 °C) (these samples were prepared from their solution in chloroform). All images were obtained by slow cooling of the isotropic melts (ca. 1 °C/min).

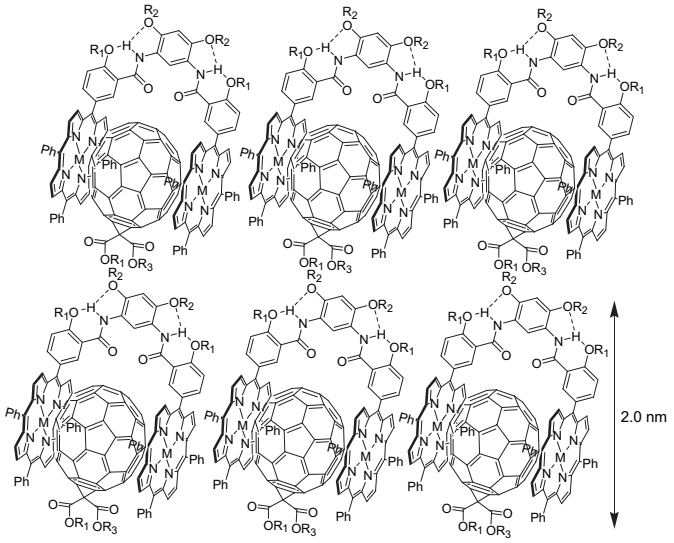


Figure 6. Tentative model for the formation of the SmC phase for the 1:1 complexes between the bisporphyrin tweezers and C_{60} derivatives.

cholesterol unit of **5** and **6**, which was powerful to induce the phase change. Figure 6 provides the tentative model for the formation of the SmC phase of the above liquid crystals.

To find more evidences for the formation of the liquid crystal mesophase, the pristine samples of Cu_2**1** and its 1:1 complex with **5** obtained in chloroform (35 mM) were also studied at different temperatures. Both samples did not gelate this solvent at any concentrations. At 25 °C, both samples exhibited order less structures, while at 120 and 150 °C (Fig. 5e–h), they gave rise to a mesophase that were similar to that observed for the xerogel samples. At the high temperature of 180 °C, the samples melted to form a film. These results further supported that within the two phase-transition temperatures, there existed a liquid crystal mesophase.

3. Conclusions

We have shown that complexes between hydrogen bonding-driven preorganized bisporphyrin receptors and C_{60} derivatives gelate alkanes and form smectic liquid crystals. Comparing to their metal-free analogs, the complexes of the zinc and copper porphyrins exhibit increased gelation capacity. For the liquid crystal behavior, the complexation causes the glassy transition temperature of the bisporphyrin to reduce considerably. The result shows that hydrogen bonding-driven preorganization of components is a new, efficient approach to tuning the structures and functions of supramolecular entities. In the future, we will design new dipodal components to study the possibility of tuning the functions of their supramolecular polymers by this approach. The bisporphyrin receptors may also be appended into polymeric systems. In this way, their capacity in gelating solvents and forming the phase of liquid crystals may also be amplified.

4. Experimental section

4.1. General methods

Unless otherwise indicated, all reactions were carried out under a nitrogen atmosphere. Starting materials were obtained from commercial suppliers and were used without further purification. The ^{1}H NMR spectra were recorded on 400 or 300 MHz spectrometers in the indicated solvents. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards (chloroform: δ 7.26 ppm; DMSO: δ 2.49 ppm). MALDI-TOF spectra were obtained on Voyager-DE STR or IonSpec 4.7 Tesla FTMS spectrometer. UV–vis spectra were recorded on a CARY 100 spectrometer. For the high concentration measurement, two quartz plates were used to sandwich a thin layer of the samples. Circular dichroism spectra were recorded on a J810 CD spectrometer. Elemental analysis was carried out at the SIOC analytical center. AFM pictures were obtained in the 'tapping' mode on a multimode SPM system equipped with a Nanoscope IV controller. SEM images were obtained with a JEOL model JSM-6390LV operating at 5 kV. PLM images were obtained on an Olympus BX51 polarizing microscope equipped with a Linkam LTS350 hot stage. The heating rate was 1 °C/min, and the samples were prepared by evaporating the decalin solution (20 mM). PXRD spectra were obtained on a X'Pert PRO X system using monochromated Cu $K\alpha$ (λ=0.1542 nm) radiation. DSC data were collected using a Q10P (TA) calorimeter during the second heating cycle (heating rate: 10 °C/min).

*4.1.1. Compound **10**.* To a stirred solution of **7**[7a] (6.96 g, 20.0 mmol) and **8** (6.36 g, 60.0 mmol) in propanoic acid (300 mL) was added **9** (5.5 mL, 80.0 mmol) dropwise. The solution was refluxed for 3 h, concentrated under reduced pressure and diluted with toluene (300 mL). The organic phase was washed with aqueous sodium bicarbonate solution (1 N, 100 mL), water (100 mL×2) and brine (100 mL) and dried over sodium sulfate. Upon removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography (CS_2/toluene 1:1) to give **10** as purple solid, which was further recrystallized from dichloromethane and methanol to afford pure product (0.91 g, 5%). ^{1}H NMR ($CDCl_3$): δ 8.87–8.83 (m, 8H), 8.63 (d, J=2.4 Hz, 1H), 8.20–8.23 (m, 7H), 7.71–7.80 (m, 9H), 7.24 (d, J=5.7 Hz, 1H), 4.28 (t, J=6.3 Hz, 2H), 3.91 (s, 3H), 2.02–1.98 (m, 2H), 1.63–1.60 (m, 2H), 1.26–1.53 (m, 16H), 0.90 (t, J=6.9 Hz, 3H), −2.78 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 167.0, 158.5, 142.2, 138.8, 136.8, 134.6, 133.9, 131.2, 127.7, 126.7, 120.2, 118.9, 118.6, 111.5, 69.4, 32.0, 29.8, 29.7, 29.5, 29.4, 26.1, 22.7, 14.1. MS (MALDI-TOF): m/z 858 $[M+H]^+$. Anal. Calcd for $C_{58}H_{56}N_4O_3$: C, 81.28; H, 6.59; N, 6.54. Found: C, 81.38; H, 6.48, N, 6.38.

*4.1.2. Compound **11**.* To a solution of **10** (0.43 g, 0.50 mmol) in pyridine (40 mL) was added a solution of sodium hydroxide (1.00 g, 25.0 mmol) in water (20 mL). The solution was stirred under reflux for 12 h, concentrated, diluted with water (10 mL), and neutralized with hydrochloric acid (3 N) to pH=3. The mixture was extracted with chloroform (80 mL×2). The organic phases were combined and washed with water (100 mL) and brine (100 mL) and dried over sodium sulfate. Upon removal of the solvent under reduced pressure, the crude product was obtained as a purple solid (0.42 mg, 100%). ^{1}H NMR ($CDCl_3$): δ 11.29 (br, 1H), 9.05 (s, 1H), 8.86–8.83 (m, 6H), 8.76 (d, J=3.9 Hz, 2H), 8.32 (d, J=8.7 Hz, 1H), 8.20 (br, 6H), 7.76 (br, 9H), 7.37 (d, J=8.7 Hz, 1H), 4.50 (2H), 2.10–2.07 (m, 2H), 1.65–1.61 (m, 2H), 1.26–1.45 (m, 16H), 0.92–0.89 (m, 3H), −2.80 (s, 2H). MS (MALDI-TOF): m/z 844.7 $[M+H]^+$. HRMS (MALDI-TOF): Calcd for $C_{57}H_{55}N_4O_3$: 843.4269. Found: 843.4248.

*4.1.3. Compound **13**.* A mixture of **12**[21] (1.30 g, 2.0 mmol) and Pd–C (10%, 0.50 g) in THF (50 mL) and methanol (50 mL) was stirred in a flask, connected with a hydrogen balloon, at rt for 24 h. The solid was filtrated and filtrate concentrated under vacuum to give **13** as crude product. The compound was instable and used for the next step without further purification.

*4.1.4. Compound H_4**1**.* To a stirred solution of **11** (0.42 g, 0.50 mmol), **13** (0.15 g, 0.25 mmol) and 4-(*N*,*N*-dimethylamino)-pyridine (10 mg) in CH_2Cl_2 (100 mL) was added EDCI (0.25 g, 1.30 mmol). The mixture was stirred at rt for 30 h, then washed with water (80 mL×3) and brine (80 mL) and dried over sodium sulfate. After removal of the solvent under vacuum, the resulting

residue was purified by column chromatography (petroleum ether/CH_2Cl_2 1:1) to give H_4**1** as purple solid (0.27 g, 49%). IR (KBr): ν 3444, 2923, 2852, 1659, 1537, 1469, 970, 800 cm^{-1}. UV–vis (decalin): 419, 514, 550, 591, 649 nm. ^1H NMR ($CDCl_3$): δ 10.21 (s, 2H), 9.48 (s, 1H), 9.17 (d, J=2.4 Hz, 2H), 8.75–8.85 (m, 16H), 8.16–8.21 (m, 14H), 7.59–7.76 (m, 18H), 7.35 (d, J=8.7 Hz, 2H), 6.68 (s, 1H), 4.46 (t, J=6.6 Hz, 4H), 4.16 (t, J=6.9 Hz, 4H), 2.12–2.09 (m, 4H), 1.97–1.92 (m, 4H), 1.14–1.60 (m, 88H), 0.88–0.78 (m, 12H), −2.80 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 162.9, 156.7, 146.1, 142.3, 142.2, 138.4, 135.2, 134.6, 127.6, 127.5, 126.6, 126.5, 121.7, 121.3, 120.1, 119.9, 119.2, 111.2, 70.1, 69.8, 32.0, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 26.0, 22.7, 22.6. 14.1, 14.0. MS (MALDI-TOF): m/z 2238 $[M+H]^+$. HRMS (MALDI-TOF): Calcd for $C_{152}H_{177}N_{10}O_6$: 2238.3928. Found: 2238.3847.

*4.1.5. Compound Zn_2**1**.* A mixture of H_4**1** (56 mg, 0.025 mmol) and zinc acetate dihydrate (38 mg, 0.17 mmol) in dichloromethane (15 mL) and methanol (5 mL) was stirred at rt for 20 h, concentrated under vacuum and then diluted with chloroform (50 mL). The solution was washed with water (40 mL×2) and brine (40 mL) and dried over sodium sulfate. After the solvent was removed with a rotavapor, the residue was purified by column chromatography (petroleum ether/CH_2Cl_2 1:1) to give Zn_2**1** as purple solid (47 mg, 80%). IR (KBr): 3386, 2923, 2852, 1658, 1535, 1486, 1467, 1003, 796 cm^{-1}. UV–vis (decalin): 428, 562, 602 nm. ^1H NMR ($CDCl_3$): δ 10.25 (s, 2H), 9.48 (s, 1H), 9.10 (2H), 8.83–8.94 (m, 16H), 8.10–8.21 (m, 14H), 7.60–7.73 (m, 18H), 7.28 (d, J=8.1 Hz, 2H), 6.67 (s, 1H), 4.46 (t, J=6.6 Hz, 4H), 4.16 (t, J=6.9 Hz, 4H), 2.12–2.09 (m, 4H), 1.98–1.94 (m, 4H), 1.14–1.60 (m, 88H), 0.78–0.88 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 163.0, 156.5, 150.4, 150.3, 150.2, 150.1, 150.0, 146.1, 143.0, 142.9, 135.9, 134.6, 134.5, 134.4, 134.3, 132.0, 131.8, 127.4, 127.3, 126.5, 126.3, 121.7, 121.1, 121.0, 120.9, 120.0, 111.0, 70.1, 69.8, 32.0, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 26.0, 22.7, 22.6, 14.1, 14.0. MS (MALDI-TOF): m/z 2367.2 $[M+H]^+$. Anal. Calcd for $C_{152}H_{172}Zn_2N_{10}O_6\cdot 3H_2O$: C, 75.44; H, 7.41; N, 5.79. Found: C, 75.40; H, 7.31; N, 5.58.

*4.1.6. Compound Cu_2**1**.* A mixture of H_4**1** (46 mg, 0.021 mmol) and copper acetate dihydrate (100 mg, 0.45 mmol) in dichloromethane (15 mL) and methanol (5 mL) was stirred at rt for 20 h. The solvent was removed under reduced pressure and the resulting residue was dissolved in chloroform (50 mL). The solution was then washed with water (40 mL×3) and brine (40 mL) and dried over sodium sulfate. The solvent was removed again and the resulting residue purified by column chromatography (petroleum ether/CH_2Cl_2 1:1) to give Cu_2**1** as red solid (40 mg, 91%). IR (KBr): 3389, 2924, 2853, 1658, 1537, 1490, 1468, 1004, 796 cm^{-1}. UV–vis (decalin): 415, 538 nm. MS (MALDI-TOF): m/z 2362.3, 2240.4. Anal. Calcd for $C_{152}H_{172}Cu_2N_{10}O_6$: C, 77.29; H, 7.34; N, 5.93. Found: C, 77.22; H, 6.67; N, 5.82.

*4.1.7. Compound **16**.* A suspension of **14**[22] (3.00 g, 16.7 mmol), **15**[23] (5.30 g, 16.7 mmol) and potassium carbonate (6.00 g, 43.5 mmol) in DMF (75 mL) were stirred at 90 °C for 17 h, cooled to rt and then filtrated. The filtrate was concentrated and diluted with dichloromethane (400 mL). The organic phase was washed with H_2O (200 mL×3) and brine (200 mL) and dried over sodium sulfate. After removal of the solvent, the resulting residue was subjected to flash chromatography (CH_2Cl_2) to give **16** as oil (5.01 g, 92%). ^1H NMR ($CDCl_3$): δ 9.82 (s, 1H), 8.26 (d, J=2.1 Hz, 1H), 7.95 (d, J=2.4 Hz, 1H), 7.06 (s, 1H), 4.25 (t, J=4.8 Hz, 2H), 3.88 (t, J=4.8 Hz, 2H), 3.84 (s, 3H), 3.72 (t, J=2.7 Hz, 2H), 3.58–3.63 (m, 4H), 3.49 (t, J=2.7 Hz, 2H), 3.30 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 190.0, 165.5, 134.4, 134.3, 129.2, 120.9, 113.5, 71.9, 71.1, 70.7, 70.5, 69.3, 69.2, 59.0, 52.2. MS (ESI): m/z 327.1 $[M+H]^+$. HRMS (MALDI-TOF): Calcd for $C_{16}H_{22}O_7Na$ [M+Na]: 349.1258. Found: 349.1248.

*4.1.8. Compound **17**.* To a stirred solution of **8** (6.36 g, 60.0 mmol) and **16** (4.51 g, 13.8 mmol) in propanoic acid (300 mL) was added **9** (5.36 g, 80.0 mmol) dropwise. The solution was stirred under reflux for 3 h, concentrated under vacuum and dissolved in dichloromethane (200 mL). The organic phase was washed with saturated sodium bicarbonate solution (100 mL), water (100 mL×3) and brine (100 mL) and dried over sodium sulfate. After removal of the solvent, the resulting residue was purified by column chromatography (CH_2Cl_2/EtOH 50:1–20:1) to give **17** as purple solid (1.01 g, 9%). ^1H NMR ($CDCl_3$): δ 8.80–8.85 (m, 8H), 8.63 (d, J=2.4 Hz, 1H), 8.20–8.22 (m, 7H), 7.71–7.80 (m, 9H), 7.32 (d, J=5.7 Hz, 1H), 4.47 (t, J=6.3 Hz, 2H), 4.08 (t, J=6.3 Hz, 2H), 3.90–3.93 (m, 5H), 3.70–3.78 (m, 4H), (t, J=1.8 Hz, 2H), 3.40 (s, 3H), −2.78 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 166.6, 158.1, 142.0, 138.6, 136.7, 134.4, 131.0128.9, 128.4, 127.9, 127.6, 126.6, 120.1, 119.0, 118.3, 111.9, 71.9, 71.8, 71.0, 70.7, 70.5, 69.6, 69.2, 58.9, 51.9. MS (MALDI-TOF): m/z 835.6 $[M+H]^+$. Anal. Calcd for $C_{53}H_{46}N_4O_6$: C, 76.24; H, 5.55; N, 6.71. Found: C, 76.68; H, 5.61; N, 6.35.

*4.1.9. Compound **18**.* To a stirred solution of **17** (0.42 g, 0.50 mmol) in pyridine (60 mL) was added a solution of sodium hydroxide (2.00 g, 50 mmol) in water (30 mL) slowly. The mixture was stirred under reflux for 16 h, concentrated under vacuum, diluted with water (30 mL) and acidified with hydrochloric acid to pH=5. The suspension was then extracted with dichloromethane (100 mL×3). The organic phases were combined and washed with water (200 mL×2) and brine (200 mL) and dried over sodium sulfate. After removal of the solvent, the resulting residue was purified by column chromatography (CH_2Cl_2/EtOH 20:1) to give **18** as purple solid (0.34 g, 82%). ^1H NMR ($CDCl_3$): δ 9.00 (d, J=1.8 Hz, 1H), 8.80–8.92 (m, 6H), 8.76 (d, J=4.8 Hz, 2H), 8.20–8.24 (m, 8H), 7.79–7.75 (m, 9H), 7.34 (d, J=5.7 Hz, 1H), 4.60–4.56 (m, 2H), 4.10–4.06 (m, 2H), 3.89–3.85 (m, 2H), 3.82–3.79 (m, 2H), 3.75–3.71 (m, 2H), 3.64–3.61 (m, 2H), 3.42 (s, 3H), −2.78 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 165.7, 157.2, 147.2, 142.1, 139.9, 138.5, 136.6, 134.6, 131.4, 129.0, 127.8, 126.7, 120.5, 120.4, 117.6, 117.1, 111.8, 72.0, 70.9, 70.7, 69.5, 68.8, 59.1. MS (MALDI-TOF): m/z 821.1 $[M+H]^+$. Anal. Calcd for $C_{52}H_{44}N_4O_6$: C, 76.08; H, 5.40; N, 6.82. Found: C, 75.46; H, 5.49; N, 6.34.

*4.1.10. Compound **21**.* A mixture of tetraethyleneglycol mono methyl ether (2.08 g, 10 mmol) and sodium hydride (1.00 g, 60%) in dry THF (25 mL) was stirred at room temperature for 12 h and then heated under reflux for 0.5 h to afford the solution of **20**. The suspension was cooled to room temperature, and then under stirring **19**[24] (1.00 g, 2.20 mmol) was added slowly. Stirring was continued for 6 h, the solvent was then removed under vacuum and diluted hydrochloric acid (0.01 N, 100 mL) added. The suspension was extracted with ethyl acetate (100 mL×3). The combined organic phase was washed with water (100 mL×2), brine (100 mL) and dried over sodium sulfate. After removal of the solvent with a rotavapor, the resulting residue was purified by column chromatography (AcOEt/MeOH 20:1) to give **21** as yellow oily liquid (0.81 g, 26%). ^1H NMR ($CDCl_3$): δ 8.69 (s, 1H), 6.86 (s, 1H), 4.34 (t, J=4.5 Hz, 4H), 3.93 (t, J=4.5 Hz, 4H), 3.73 (t, J=3.0 Hz, 4H), 3.59–3.65 (m, 16H), 3.52–3.48 (m, 4H), 3.34 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 157.8, 131.4, 125.4, 100.7, 72.6, 71.9, 71.1, 70.6, 70.5, 69.2, 61.7, 59.0. MS (ESI): m/z 603.2 $[M+Na]^+$. Anal. Calcd for $C_{24}H_{40}N_2O_{14}$: C, 49.65; H, 6.94; N, 4.83. Found: C, 49.50; H, 7.35; N, 4.43.

*4.1.11. Compound **22**.* A mixture of **21** (0.16 g, 0.28 mmol) and Pd–C (10%, 0.10 g) in THF (20 mL) and methanol (20 mL) was stirred in a flask, connected with a hydrogen balloon, at rt for 22 h. The solid was filtrated and filtrate concentrated under vacuum to give **21** as crude product. The compound was unstable and dissolved in DMF (10 mL) for the next reaction without further purification.

*4.1.12. Compound H_4**2**.* A solution of **18** (0.42 g, 0.51 mmol) and HATU (800 mg, 2.10 mmol) were in dry DMF (30 mL) was stirred for 1 h. Then, a solution of the above sample of **22** in DMF (10 mL) was

added dropwise. The mixture was stirred for another 24 h, concentrated under vacuum and diluted with dichloromethane (100 mL). The organic phase was washed with water (50 mL×3) and brine (50 mL) and dried over sodium sulfate. After removal of the solvent, the resulting residue was purified by column chromatography (CH_2Cl_2/methanol 20:1) to give H_4**2** as purple solid (0.10 g, 19%, two steps). ^{1}H NMR ($CDCl_3$): δ 10.27 (s, 2H), 9.32 (s, 1H), 9.10 (d, J=2.4 Hz, 2H), 8.75–8.85 (m, 16H), 8.16–8.21 (m, 14H), 7.59–7.76 (m, 18H), 7.35 (d, J=8.4 Hz, 2H), 6.81 (s, 1H), 4.68 (t, J=4.8 Hz, 4H), 4.34 (t, J=4.8 Hz, 4H), 4.13 (t, J=4.8 Hz, 4H), 3.92 (t, J=4.8 Hz, 4H), 3.78 (t, J=4.8 Hz, 4H), 3.35–3.65 (m, 36H), 3.32 (s, 6H), 3.26 (s, 6H), −2.83 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 163.0, 156.6, 146.4, 142.1, 138.0, 134.6, 130.8, 129.1, 127.6, 126.7, 122.6, 121.5, 120.1, 118.9, 111.9, 71.8, 70.9, 71.8, 70.9, 70.8, 70.7, 70.5, 70.4, 69.8, 69.6, 69.5, 59.1, 59.0. MS (MALDI-TOF): m/z 2127.1 $[M+H]^+$. HRMS (MALDI-TOF): Calcd for $C_{128}H_{129}N_{10}O_{20}$: 2125.9379. Found: 2125.9365.

4.1.13. Compound $Zn_2$2. A mixture of H_4**2** (30 mg, 0.014 mmol) and zinc acetate dihydrate (100 mg, 0.45 mmol) in dichloromethane (30 mL) and methanol (10 mL) was stirred at rt for 20 h, concentrated and diluted with chloroform (10 mL). The organic solution was washed with water (5 mL×3) and brine (5 mL) and dried over sodium sulfate. The solvent was removed again and the residue was purified by column chromatography (CH_2Cl_2/MeOH 20:1) to give Zn_2**2** as a purple solid (28 mg, 89%). ^{1}H NMR ($CDCl_3$): δ 9.94 (s, 2H), 9.13 (s, 1H), 8.80–8.95 (m, 18H), 8.16–8.22 (m, 14H), 7.65–7.76 (m, 18H), 7.35 (d, J=8.4 Hz, 2H), 6.66 (s, 1H), 4.52 (t, J=4.2 Hz, 4H), 4.15 (t, J=4.5 Hz, 4H), 3.98 (t, J=4.5 Hz, 4H), 3.71 (t, J=4.5 Hz, 4H), 3.62 (t, J=4.5 Hz, 4H), 3.33–3.43 (m, 12H), 3.13–3.17 (m, 6H), 3.04 (t, J=4.2 Hz, 4H), 2.91–2.97 (m, 6H), 2.79 (t, J=1.8 Hz, 4H), 2.70 (t, J=4.2 Hz, 4H), 2.65 (s, 6H), 2.54 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 163.3, 156.2, 150.1, 146.9, 143.1, 137.6, 137.5, 136.4, 134.5, 132.0, 131.8, 128.5, 127.3, 126.4, 122.1, 121.4, 120.9, 119.5, 118.4, 111.6, 100.5, 71.8, 71.1, 70.8, 70.4, 70.1, 69.9, 69.8, 69.6, 69.4, 69.3, 58.9, 58.3, 58.2. HRMS (MALDI-TOF): Calcd for $C_{128}H_{124}N_{10}O_{20}Zn$ $[M]^+$: 2248.7571. Found: 2248.7548.

4.1.14. Compound ***3****.* A solution of DBU (34 μL, 0.10 mmol), fullerene (72 mg, 0.10 mmol), iodine (66 mg, 0.20 mmol) and **23**[25] (55 mg, 0.10 mmol) in toluene (50 mL) was stirred at rt for 4 h and then concentrated under vacuum. The resulting residue was purified by column chromatography (first with CS_2 to remove unreacted fullerene and then with toluene) to afford **3** as a dark brown solid (47 mg, 37%). ^{1}H NMR ($CDCl_3$): δ 4.49 (t, J=6.3 Hz, 4H), 1.84 (t, J=7.2 Hz, 4H), 1.18–1.48 (m, 52H), 0.88 (t, J=6.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 163.7, 145.4, 145.3, 145.2, 144.9, 144.7, 144.6, 143.9, 143.1, 143.0, 142.2, 142.0, 141.0, 139.0, 71.8, 67.5, 31.9, 31.4, 30.2, 29.7, 29.6, 29.4, 29.3, 28.6, 26.0, 22.7, 14.1. MS (MALDI-TOF): m/z 1271 $[M+H]^+$. HRMS (MALDI-TOF): Calcd for $C_{95}H_{67}O_4$ $[M+H]^+$: 1271.5082. Found: 1271.5034.

4.1.15. Compound ***26****.* A solution of **24** (0.26 g, 2.5 mmol), **25** (1.04 g, 5.0 mmol) and *p*-toluenesulfonic acid (35 mg) in benzene (60 ml) was heated at reflux azeotropically for 6 h and then concentrated. The resulting residue was purified by column chromatography (CH_2Cl_2/EtOH 40:1) to give **26** as colorless liquid (1.17 g, 97%). ^{1}H NMR ($CDCl_3$): δ 4.30 (t, J=4.8 Hz, 4H), 3.71 (t, J=4.8 Hz, 4H), 3.63–3.66 (m, 20H), 3.55 (t, J=5.4 Hz, 4H), 3.45 (s, 2H), 3.38 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 166.4, 71.9, 70.6, 70.5, 68.8, 64.5, 59.0, 41.2. MS (ESI): m/z 485.2 $[M+H]^+$. HRMS (MALDI-TOF): Calcd for $C_{21}H_{40}O_{12}Na$ $[M+Na]^+$: 507.2417. Found: 507.2411.

4.1.16. Compound ***4****.* To a stirred solution of fullerene (144 mg, 0.20 mmol), iodine (50 mg, 0.20 mmol) and **26** (100 mg, 0.10 mmol) in toluene (80 mL) was added DBU (80 μL, 0.24 mmol). The solution was stirred for 20 h and then concentrated under vacuum. The resulting residue was purified by column chromatography (first toluene to remove unreacted fullerene, then toluene/EtOH 20:1) to afford **4** as a dark brown solid (103 mg, 43%). ^{1}H NMR ($CDCl_3$): δ 4.62 (4H), 3.85 (4H), 3.79–3.76 (m, 4H), 3.64–3.60 (m, 16H), 3.54–3.50 (m, 4H), 3.35 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 163.5, 146.5, 146.0, 145.3, 145.2, 144.9, 144.7, 144.6, 144.4, 144.0, 143.9, 143.5, 143.4, 143.0, 142.4, 142.2, 141.9, 141.7, 140.9, 139.1, 71.9, 71.4, 70.6, 70.5, 68.8, 66.2, 59.0. MS (MALDI-TOF): m/z 1225.6 $[M+Na]^+$. HRMS (MALDI-TOF): Calcd for $C_{81}H_{38}O_{12}Na$ $[M+Na]^+$: 1225.2255. Found: 1225.2245.

4.1.17. Compound ***29****.* To a stirred solution of **27**[26] (0.16 g, 0.50 mmol), **28** (0.11 g, 0.25 mmol) and DMAP (25 mg) in dichloromethane (30 mL) was added EDCI (0.25 g, 1.30 mmol). The mixture was stirred at rt for 12 h and then washed with water (20 mL×4), brine (20 mL) and dried over sodium sulfate. After removal of the solvent vacuum, the resulting residue was purified by column chromatography (petroleum ether/EtOAc 20:1) to give **29** as a colorless solid (92 mg, 49%). IR (KBr): ν 2920, 2851, 1749, 1468, 1203, 1140, 1062, 873 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.38 (d, J=3.6 Hz, 1H), 4.70–4.66 (m, 1H), 4.64 (s, 2H), 4.15 (t, J=6.9 Hz, 2H), 3.49 (s, 2H), 2.34 (d, J=7.8 Hz, 2H), 0.84–2.05 (m, 69H), 0.68 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 166.6, 166.1, 166.0, 139.2, 123.0, 75.5, 65.9, 61.6, 56.7, 56.2, 50.0, 42.3, 41.1, 39.5, 36.6, 36.2, 35.8, 31.9, 31.8, 29.7, 29.6, 29.5, 29.4, 29.2, 28.5, 25.8, 22.8, 22.7, 19.3, 18.7, 14.1. Anal. Calcd for $C_{48}H_{82}O_6$: C, 76.34; H, 10.94. Found: C, 76.24; H, 11.16.

4.1.18. Compound ***5****.* To a stirred solution of fullerene (0.14 g, 0.20 mmol), CBr_4 (66 mg, 0.20 mmol) and **29** (150 mg, 0.20 mmol) in toluene (150 mL) was added DBU (68 μL, 0.20 mmol). The solution was stirred at rt for 4 h and then concentrated. The resulting residue was purified by column chromatography (first CS_2 to remove unreacted C_{60}, then toluene) to afford **5** as a dark brown solid (92 mg, 31%). IR (KBr): ν 2920, 2850, 1747, 1464, 1262, 1197, 1096, 801, 526 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.39 (s, 1H), 4.95 (s, 2H), 4.77–5.73 (m, 1H), 4.54 (t, J=6.0 Hz, 2H), 2.38 (d, J=7.8 Hz, 2H), 0.84–2.05 (m, 69H), 0.68 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 165.8, 163.2, 163.1, 145.4, 145.3, 145.2, 145.1, 144.9, 144.7, 144.6, 143.9, 143.0, 142.9, 142.2, 141.9, 141.0, 139.4, 139.2, 138.8, 123.2, 77.3, 77.0, 76.8, 75.8, 71.4, 67.7, 62.8, 56.7, 56.2, 50.0, 42.3, 39.5, 36.2, 35.8, 31.9, 31.8, 29.8, 29.7, 29.4, 29.3, 28.2, 28.0, 23.8, 22.8, 22.7, 22.6, 19.4, 18.7, 14.1, 11.9. HRMS (MALDI-TOF): Calcd for $C_{108}H_{80}O_6Na$: 1495.5847. Found: 1495.5868 $[M+Na]^+$.

4.1.19. Compound ***31****.* To a stirred solution of **30**[27] (0.82 g, 3.70 mmol), cholesterol (3.00 g, 7.70 mmol), DMAP (0.30 g) and HOBt (0.10 g) in dichloromethane (100 mL) was added EDCI (3.50 g, 18.0 mmol). The mixture was stirred at rt for 72 h, then washed with water (100 mL×3) and brine (100 mL) and dried over sodium sulfate. After removal of the solvent under vacuum, the resulting residue was purified by column chromatography (CH_2Cl_2) to give **31** as a white solid (1.53 g, 43%). IR (KBr): ν 2938, 2868, 1782, 1755, 1468, 1224, 1140, 1070 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.39 (d, J=3.6 Hz, 2H), 4.72–4.69 (m, 2H), 4.65 (s, 4H), 3.62 (s, 2H), 2.39 (d, J=7.8 Hz, 4H), 0.84–2.05 (m, 76H), 0.68 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 166.5, 165.4, 139.2, 123.1, 75.6, 61.7, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 37.9, 36.9, 36.6, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 27.6, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.9. Anal. Calcd for $C_{61}H_{96}O_8$: C, 76.52; H, 10.11. Found: C, 76.21; H, 9.78.

4.1.20. Compound ***6****.* To a stirred solution of C_{60} (0.14 g, 0.20 mmol), CBr_4 (66 mg, 0.20 mmol) and **31** (0.19 g, 0.20 mmol) in toluene (150 mL) was added DBU (100 μL, 0.30 mmol). The solution was stirred at rt for 4 h and then concentrated under vacuum. The resulting residue was purified by column chromatography (first using CS_2 to remove unreacted C_{60}, then toluene) to afford **6** as a dark brown solid (77 mg, 23%). IR (KBr): ν 2961, 2866, 1747, 1465, 1262, 1197, 1096, 1025, 803, 527 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.39 (d, J=2.7 Hz, 2H), 4.97 (s, 4H), 4.78–4.75 (m, 2H), 2.37 (d, J=9.6 Hz, 4H), 0.85–2.03 (m, 76H), 0.67 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 165.9, 162.7,

145.2, 144.7, 143.9, 143.0, 142.2, 141.9, 141.0, 139.3, 123.2, 76.6, 75.8, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.0, 36.6, 36.2, 35.8, 31.9, 31.8, 29.7, 28.2, 28.0, 27.7, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 11.9. MS (MALDI-TOF): m/z 1698 $[M+Na]^+$.

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