ADVANCED MATERIALS

Supporting Information

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Helical Crystals with a Six-Fold Screw Axis

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Materials and methods

Di(ethylene glycol) and tri(ethylene glycol) (analytical degree) were purchased from Tianjin Chemical Reagent Factory I. Cholic acid (97%) and tetra(ethylene glycol) (99.5%) are ARCOS products. All the reagents were used as received. Other reagents and solvents are commercially available and of analytical grade.

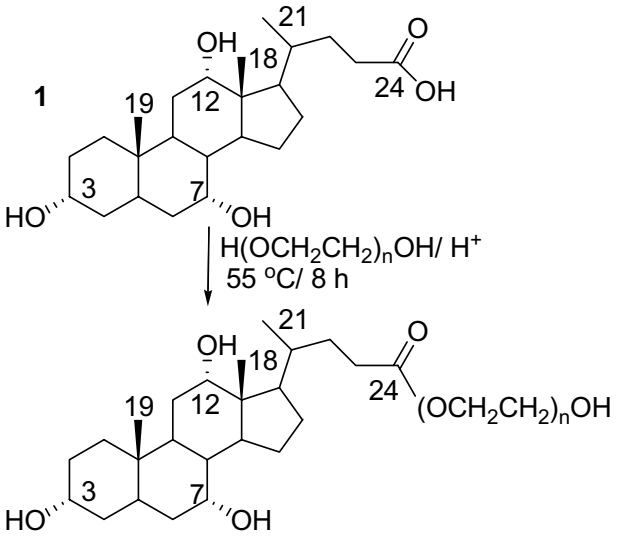
X-ray Diffraction

The helical self-assembed crystals in solution were placed directly on the glass plate and dried in air. The starting bulk crystalline sample (SI 1) was in the powder form. Both diffraction patterns were recorded on a Rigaku D/max powder diffractometer using graphite-monochromated Cu/K-αlpha1 radiation (40 kV, 30 mA). The spectra were measured at room temperature between 1^{o} and 41^{o} in the 2θ/θ scan mode with steps of 0.01^{o} in 2θ and 0.6-s measurement time per step (SI 2).

Small-Angle X-ray Scattering (SAXS)

The SAXS pattern was recorded on a NanoSTAR (20 kV, 8 mA, 3700 s). The SAXS data were collected for 3700 s.

Synthesis of (1'-hydroxy-3'-oxa)pentanyl 3α, 7α, 12α-trihydroxy-5β-cholanoate (**2**) (Scheme S1).



2: n=2 ($OCH_2CH_2OCH_2CH_2$)

3: n=3 ($OCH_2CH_2OCH_2CH_2OCH_2CH_2$)

4: n=4 ($OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2$)

Scheme S1. Synthesis of cholic acid esters.

Cholic acid (5.0 g) was dissolved in di(ethylene glycol) (50 mL). Concentrated hydrochloric acid was added dropwise to acidify the reactant to pH 3. The mixture was stirred at 55 °C for 8 h. Water was then added to the reactant to precipitate the product. The white precipitates were filtered and washed thoroughly with water. After drying in a vacuum oven at 60 °C for 24 h, product **2** was obtained in 91% yield. Mp 152-154 °C. FAB-MS (Instrument: VG ZAB-HS acquired on MASPE Ⅱ system) for **2** ($C_{28}H_{48}O_7$) calcd. 496.7; found 497.2. ^{1}H NMR (Varian Unity Plus-400, $CDCl_3$): δ=0.70 (s, H^{18}), 0.90 (s, H^{19}), 0.99-1.00 (d, H^{21}), 3.46 (m, H^3), 3.61-3.75 (m, EG), 3.86 (s, H^7), 3.99 (s, H^{12}), 4.25 (s, $H^{5'}$).

(1'-hydroxy-3', 6'-dioxa)octanyl 3α, 7α, 12α-trihydroxy-5β-cholanoate (**3**) and (1'-hydroxy-3', 6', 9'-trioxa)undecanyl 3α, 7α, 12α-trihydroxy-5β-cholanoate (**4**) were prepared under the same condition as **2**, but tri(ethylene glycol) and tetra(ethylene glycol) were used, respectively, instead of di(ethylene glycol). The separation of **3** and **4** was different from **2**: After the reaction, brine (50 mL) was added to the reactant. The mixture was extracted with ethyl acetate (3×100 mL). The organic layer gathered

was washed with brine (3×100 mL), then dried with anhydrous $MgSO_4$ and filtered. **3** was obtained by crystallization in ethyl acetate. **4** was separated by column chromatography on silica gel (100-200 meshes) with CH_2Cl_2-MeOH as eluent (20:1, v/v) (S1). The yields obtained were 34 and 72% for **3** and **4,** respectively. **3**: Mp 98-100°C. FAB-MS for **3** ($C_{30}H_{52}O_8$) calcd. 540.7; found 541.3. ^{1}H NMR ($CDCl_3$): δ=0.69 (s, H^{18}), 0.89 (s, H^{19}), 0.98-0.99 (d, H^{21}), 3.49 (m, H^3), 3.62-3.74 (m, EG), 3.86 (s, H^7), 3.99 (s, H^{12}), 4.24 (s, $H^{8'}$).

4: Mp 51-53 °C. FAB-MS for **4** ($C_{32}H_{56}O_9$) calcd. 584.7; found 585.3. ^{1}H NMR ($CDCl_3$): δ=0.68 (s, H^{18}), 0.89 (s, H^{19}), 0.98 (d, H^{21}), 3.44 (m, H^3), 3.61-3.73 (m, EG), 3.84 (s, H^7), 3.96 (s, H^{12}), 4.23 (s, $H^{11'}$).

Self-assembling potential

Figure S1. Photograph of hygrogels (1% w/v, 5% MeOH v/v) of **3** (left) and **4** (right).

Table S1. Organic solvent percentage[a] in hydrogels of **3** and **4**

Samples	In water (% v/v)					
	MeOH	EtOH	Acetone	THF	DMF	DMSO
3	5-25	5-20	15-20	5-15	5-20	5-45
4	5-20	5-15	15	10	5-20	5-45

[a] Gelation did not occur when CH_3CN and pyridine were used as organic solvents.

The cholic acid esters (**2**, **3**, and **4**) (10 mg) were dissolved respectively, in small

amounts of organic solvents (MeOH, EtOH, THF, DMF, DMSO, acetone, etc.) in a vial (16.5 mm diameter) with a screw cap, followed by the addition of water. The turbid solutions (1% w/v) were placed in a water bath at 55 ^{o}C for 4 h and were cooled down to room temperature within 12 h. The gelation was visually examined by vial inversion after 12 h at room temperature. **2** precipitated in aqueous solutions, while **3** and **4** formed hydrogels (Fig. S1and Table S1). Figure 1 shows two hydrogels (1% w/v, 5% MeOH v/v) of **3** (Left) and **4** (Right), respectively. Arrow shows the white insolubles in Fig. 1 (Left).

The gel-sol transition temperatures ($T_{gel\text{-}sol}$)

$T_{gel\text{-}sol}$ for the hydrogels of **4** was determined by vial inversion method. The vials were kept in a thermostatic water bath at the given temperature and the temperature was raised at 1 °C interval for 0.5 h, and then the vials were inversed to see whether the gels (1% w/v) still remained.

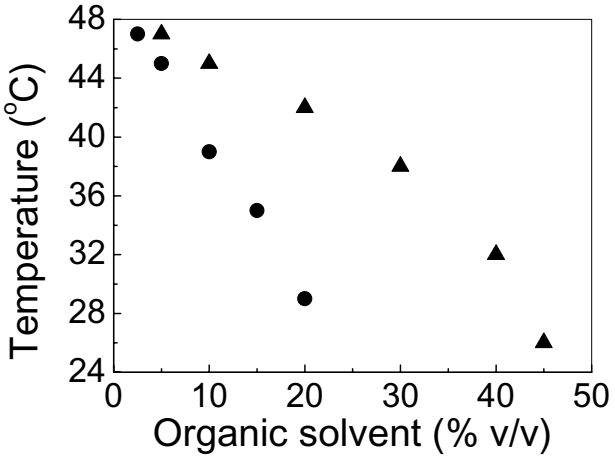


Figure S2. $T_{gel\text{-}sol}$ of **4** was plotted as a function of the percentage of organic solvent. MeOH/ H_2O (circle); DMSO/ H_2O (triangle).

$T_{gel\text{-}sol}$ values of **4** decrease with increasing percentage of the organic solvent, which increases the solubility of **4** (Fig. S2) (SI 3). $T_{gel\text{-}sol}$ decreases faster in MeOH/H_2O than in DMSO/H_2O at the same percentage.

LCSM and Polarizing microscope observations

A LCSM (Olympus FV1000S-IX81) was used to observe the morphology of the

self-assembled crystals in solution. Both handednesses coexist in the crystals (Fig. S3). The diameter seems uncontrollable. This should be attributed to the difference in the hierarchical self-assembling processes of the helical fibers with same handedness through hydrogen bonding interactions in aqueous medium.

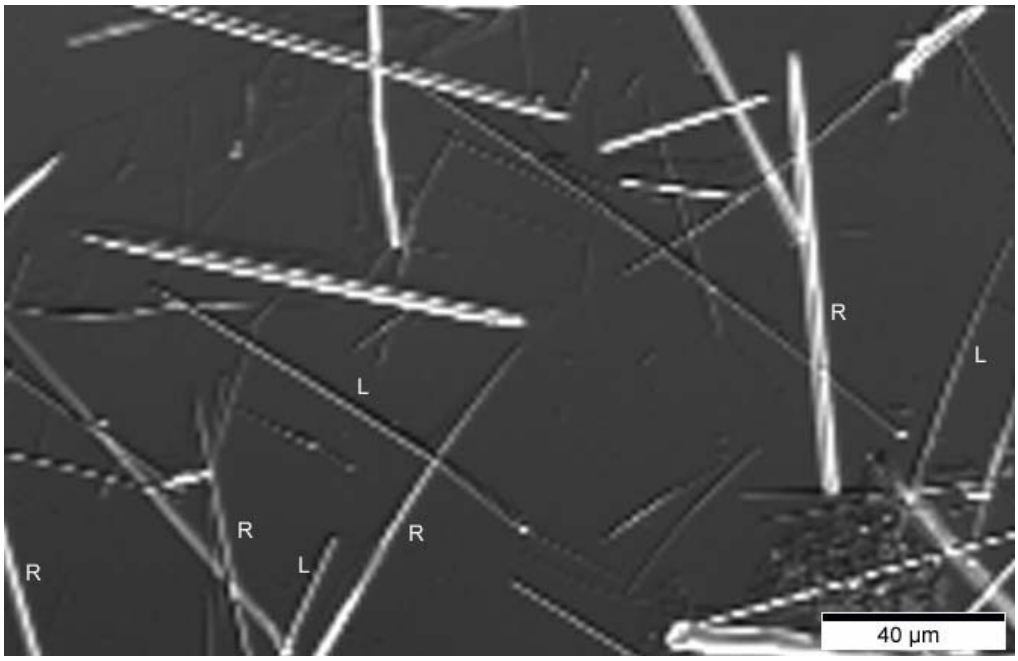


Figure S3. An overview LCSM image of the helical crystals (L: left-handed; R: right-handed).

A polarizing microscope (Olympus BX51 TRF) was used to investigate the polarizing behavior of the self-assembled crystals (SI 2). Figure S4 shows that periodic color strips appear on the self-assembled crystals which indicate the existence of periodic crystalline structures.

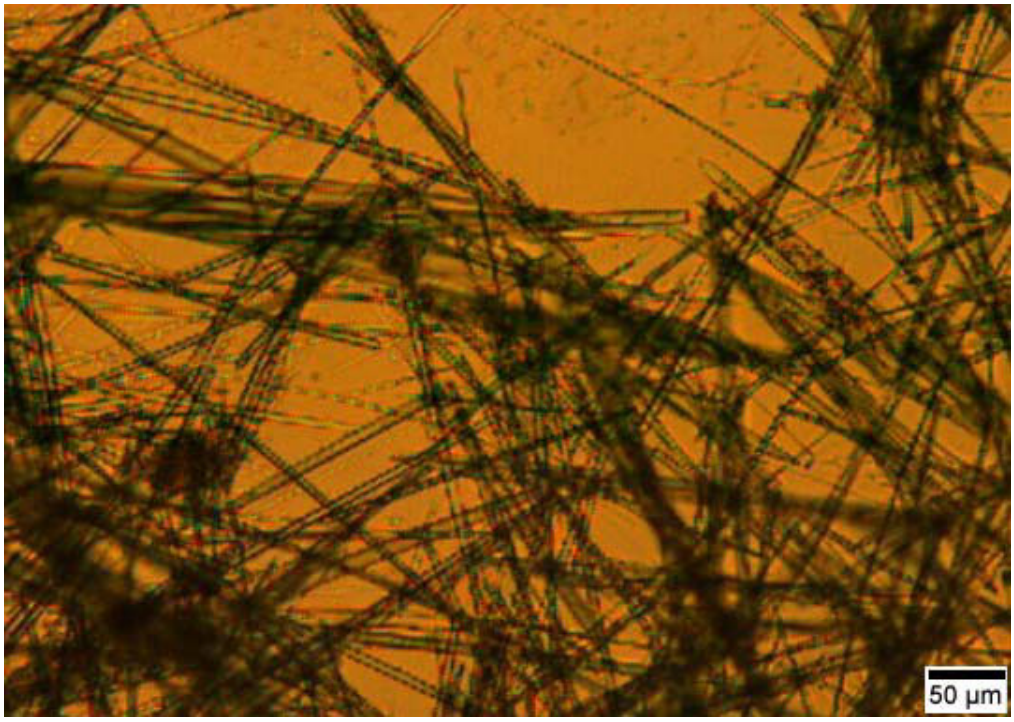


Figure S4. An overview polarizing micrograph of the self-assembled crystals (dehydrate).

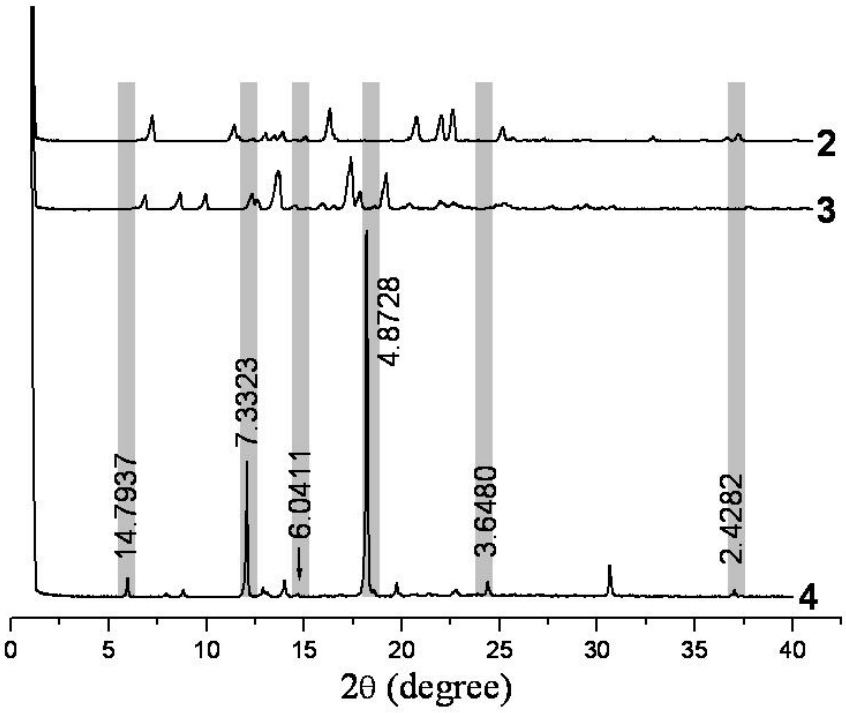


Figure S5. XRD patterns of crystalline powders of the cholic acid esters 2, 3 and

helical crystals of 4 (*d* value: Å). The crystalline powders of 2, 3 were obtained from EtOH/H_2O (1/4, v/v) and ethyl acetate, respectively.

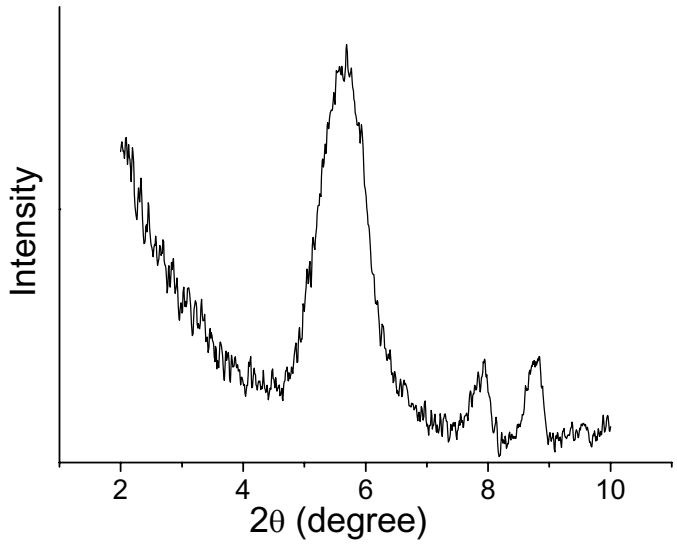
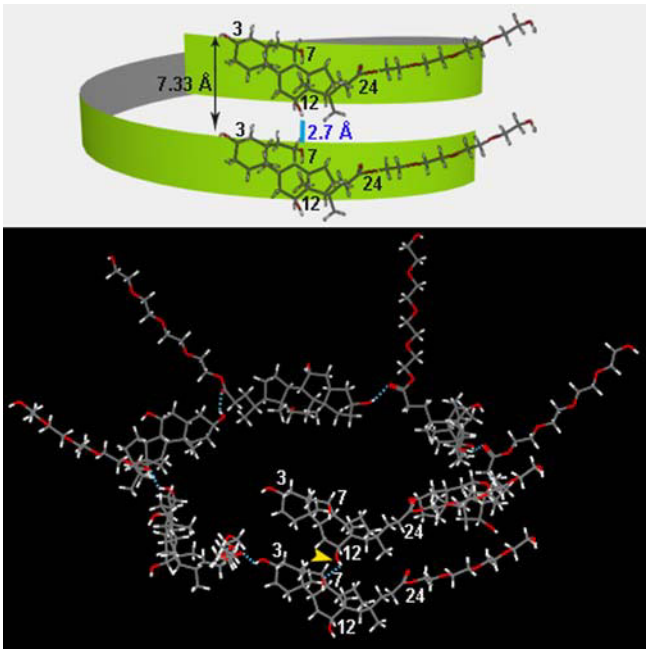


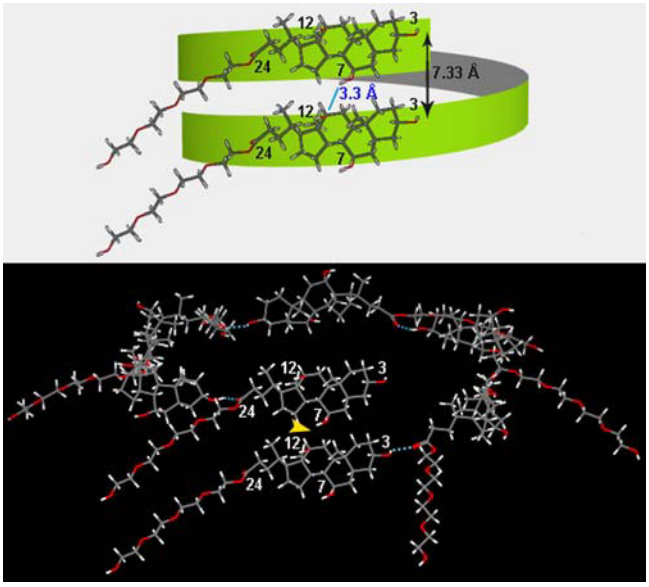
Figure S6. SAXS pattern of the helical crystals of the cholic acid ester 4.

Left-handed and right-handed helical self-assembled models



Scheme S2. Left-handed helical self-assembled model with a 6_1 axis (Pitch: 7.33 Å). The oxygen-oxygen distance of the 7-OH and 12-OH is ca. 2.7 Å, which is fit for

forming hydrogen bonding interaction (Arrow indicates).



Scheme S3. Right-handed helical self-assembling model with a 6_1 axis (Pitch: 7.33 Å): the oxygen-oxygen distance of the 7-OH and 12-OH is ca. 3.3 Å (Arrow indicate), which is out of the range of hydrogen bonding interaction.

Supporting note and references:

SI 1. The bulk crystals were obtained from the sticky oil of **4** within three months.

SI 2. Shimizu, T. & Masuda, M. *J. Am. Chem. Soc.* **119**, 2812 (1997).

SI 3. Sangeetha, N. M., Balasubramanian, R., Maitra, U., Ghosh, S., & Raju, A. R. *Langmuir* **18**, 7154 (2002).