Electronic Supplementary Information

Dissymmetrical-tails regulated helical nanoarchitectonics of amphiphilic ornithines: nanotubes, bundles and twists

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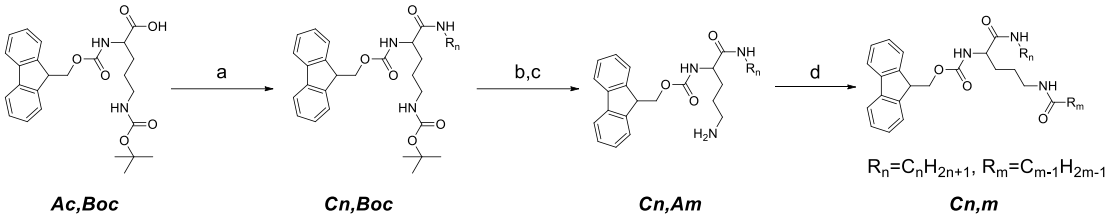
Contents:

1. Materials

All the chemical materials were used as received without further purification. The suppliers for the starting materials were listed as follows: N-Fmoc-N'-Boc-*L*-ornithine (***Ac,Boc***, TCI), EDC·HCl (Innochem), HOBt (J&K), $NaHCO_3$ (SCR), $C_{16}H_{33}NH_2$ (Alfa), $C_{18}H_{37}NH_2$ (Alfa), $C_{14}H_{29}COOH$ (Acros), $C_{16}H_{33}COOH$ (Alfa), $C_{18}H_{37}COOH$ (Acros) and $C_{20}H_{41}COOH$ (TCI). Trifluoroacetic acid, dichloromethane, ethanol, tetrahydrafuran and dimethylsulfoxide were purchased from Beijing Chemical Works. Deionized water (Milli-Q, 18.2 MΩ·cm) was used.

2. Synthetical procedures



Scheme S1. Synthetic routes of the dissymmetrical Fmoc-*L*-ornithine lipids ***Cn,m***. a) EDC·HCl, HOBt, $C_nH_{2n+1}NH_2$, CH_2Cl_2, r.t., 72 h; b) CH_2Cl_2, CF_3COOH, r.t., 10 h; c) $NaHCO_3$; d) EDC·HCl, HOBt, $C_{m-1}H_{2m-1}COOH$, CH_2Cl_2, r.t., 72 h.

Cn,m: ***Ac,Boc*** (1.497 g, 3.3 mmol), EDC·HCl (0.633 g, 3.3 mmol) and HOBt (0.447 g, 3.3 mmol) were dissolved in dichloromethane and stirred at room temperature for 15 min, after which $C_nH_{2n+1}NH_2$ (3.0 mmol) was added. The mixture was stirred at room temperature for 72 h and then concentrated under vacuum. The obtained solid was dissolved in THF, poured into a $NaHCO_3$ saturated aqueous solution and then filtered. The residue was recrystallized in ethanol three times to afford ***Cn,Boc*** as a white powder. ***Cn,Boc*** (1.5 mmol) was then dissolved in 30 mL dichloromethane, into which trifluoroacetic acid (5 mL) was added. The mixture was stirred for 10 h at room temperature and then the solvent was removed under vacuum. The solid was dissolved in ethanol and poured into saturated $NaHCO_3$ aqueous solution to precipitate the crude product, which was then filtrated and recrystallized in ethanol three times to yield ***Cn,Am*** a white powder. ***Cn,Am*** (1.0 mmol), EDC·HCl (0.211 g, 1.1 mmol) and HOBt (0.149 g, 1.1 mmol) were dissolved in dichloromethane and stirred at ambient temperature for 1 h, after which $C_{m-1}H_{2m-1}COOH$ (1.1 mmol) was added and stirred at room temperature for 72 h. The mixture was evaporated under vacuum to remove the solvent. The obtained solid was dissolved in THF, poured into $NaHCO_3$ saturated aqueous solution. The residue was filtered and recrystallized in ethanol three times to afford ***Cn,m*** as a white powder.

C18,20: 57 % overall yield. ^{1}H-NMR (500Hz, $CDCl_3$): δ 7.78 (d, 2H, J = 7.4 Hz), 7.62 (dd, 2H, J = 7.2, 3.4 Hz), 7.41 (t, 2H, J = 7.5 Hz), 7.34 (t, 2H, J = 7.4 Hz), 6.55-6.59 (m, 1H), 6.36-6.38 (m, 1H), 5.63-5.66 (m, 1H), 4.42-4.59 (m, 2H), 4.23-4.26 (m, 1H), 3.57-3.61 (m, 1H), 3.22-3.25 (m, 4H), 3.22-3.25 (m, 2H), 1.75-1.78 (m, 2H), 1.65-1.69 (m, 6H), 1.26-1.28 (m, 60H), 0.88 (t, 6H, J = 6.8 Hz). MALDI-TOF-MS: calcd for $C_{58}H_{97}N_3O_4$ $[M+K]^+$ 938.7116; found 938.9004.

C18,18: 55 % overall yield. ^{1}H-NMR (400Hz, $CDCl_3$): δ 7.76 (d, 2H, J = 7.5 Hz), 7.60 (dd, 2H, J = 7.3, 3.4 Hz), 7.40 (t, 2H, J = 7.4 Hz), 7.31 (t, 2H, J = 7.4 Hz), 6.59-6.66 (m, 1H), 5.67-5.75 (m, 2H), 4.37-4.39 (m, 2H), 4.20-4.23 (m, 1H), 3.61-3.64 (m, 1H), 3.20-3.23 (m, 4H), 2.15-2.23 (m, 2H), 1.74-1.76 (m, 2H), 1.60-1.64 (m, 6H), 1.26-1.28 (m, 56H), 0.88 (t, 6H, J = 6.8 Hz). MALDI-TOF-MS: calcd for $C_{56}H_{93}N_3O_4$ $[M+H]^+$ 872.7244; found 872.7252.

C18,16: 54 % overall yield. ^{1}H-NMR (400Hz, $CDCl_3$): δ 7.76 (d, 2H, J = 7.6 Hz), 7.61 (dd, 2H, J = 7.4, 3.3 Hz), 7.40 (t, 2H, J = 7.4 Hz), 7.31 (t, 2H, J = 7.0 Hz), 6.58-6.60 (m, 1H), 5.66-5.75 (m, 2H), 4.37-4.39 (m, 2H), 4.20-4.23 (m, 1H), 3.60-3.65 (m, 1H), 3.14-3.22 (m, 4H), 2.17-2.21 (m, 2H), 1.72-1.75 (m, 2H), 1.61-1.62 (m, 6H), 1.26-1.28 (m, 52H), 0.88 (t, 6H, J = 6.8 Hz). MALDI-TOF-MS: calcd for $C_{54}H_{89}N_3O_4$ $[M+H]^+$ 844.6931; found 844.6940.

C18,14: 51 % overall yield. ^{1}H-NMR (400Hz, $CDCl_3$): δ 7.76 (d, 2H, J = 7.7 Hz), 7.60 (dd, 2H, J = 7.4, 3.3 Hz), 7.40 (t, 2H, J = 7.4 Hz), 7.31 (t, 2H, J = 7.2 Hz), 6.58-6.60 (m, 1H), 5.69-5.72 (m, 2H), 4.37-4.40 (m, 2H), 4.22 (t, 1H, J = 7.0 Hz), 3.61-3.63 (m, 1H), 3.20-3.23 (m, 4H), 2.21-2.25 (m, 2H), 1.73-1.76 (m, 2H), 1.61-1.63 (m, 6H), 1.26-1.28 (m, 48H), 0.88 (t, 6H, J = 6.8 Hz). MALDI-TOF-MS: calcd for $C_{52}H_{85}N_3O_4$ $[M+H]^+$ 816.6618; found 816.6633.

C16,18: 50 % overall yield. ^{1}H-NMR (400Hz, $CDCl_3$): δ 7.76 (d, 2H, J = 7.6 Hz), 7.60 (dd, 2H, J = 7.2, 3.2 Hz), 7.40 (t, 2H, J = 7.3 Hz), 7.32 (t, 2H, J = 7.3 Hz), 6.58-6.60 (m, 1H), 5.62-5.69 (m, 2H), 4.37-4.39 (m, 2H), 4.20-4.23 (m, 2H), 3.09-3.26 (m, 4H), 2.17-2.19 (m, 2H), 1.61-1.77 (m, 8H), 1.26-1.28 (m, 52H), 0.88 (t, 6H, J = 6.8 Hz). MALDI-TOF-MS: calcd for $C_{54}H_{89}N_3O_4$ $[M+H]^+$ 844.6931; found 844.6944.

3. ^{1}H NMR spectra

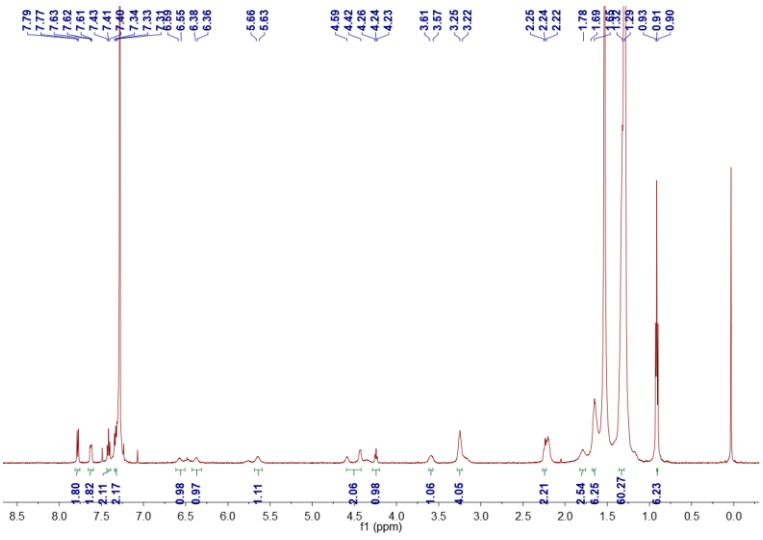


Fig. S1 ^{1}H NMR spectrum of lipid ***C18,20*** (500 MHz, $CDCl_3$).

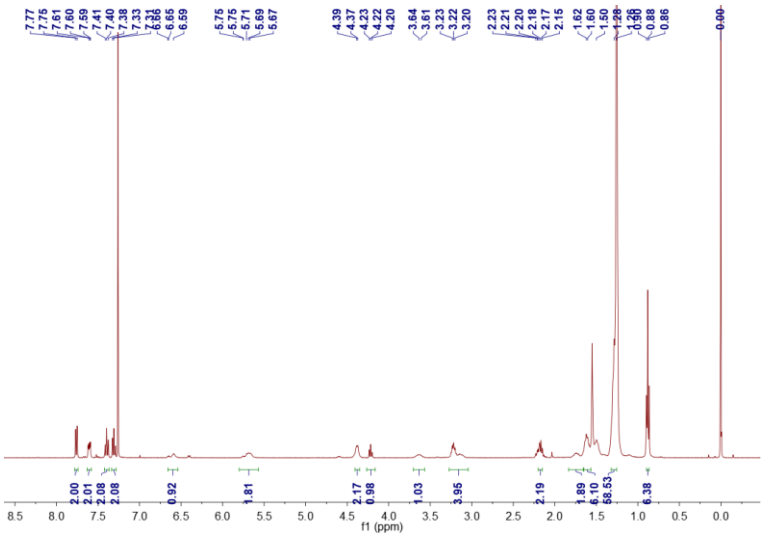


Fig. S2 ^{1}H NMR spectrum of lipid ***C18,18*** (400 MHz, $CDCl_3$).

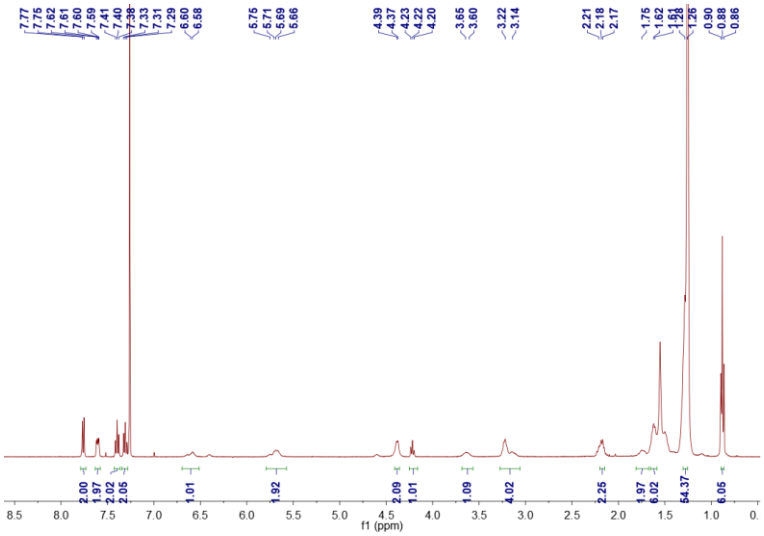


Fig. S3 ^{1}H NMR spectrum of lipid ***C18,16*** (400 MHz, $CDCl_3$).

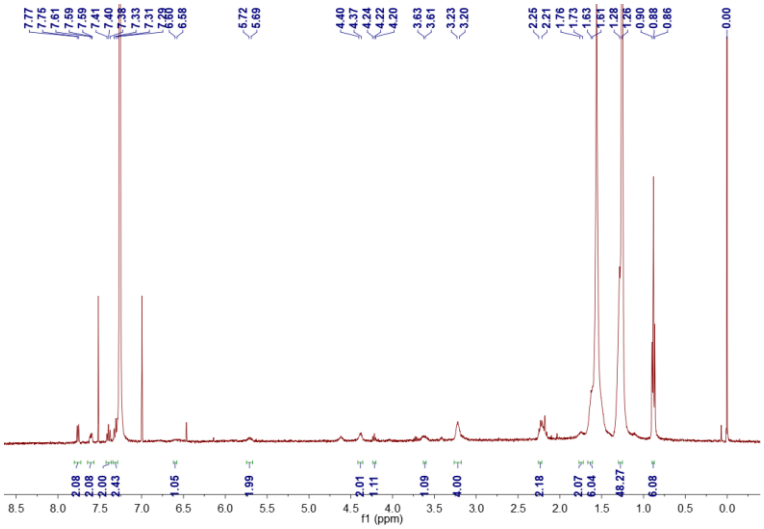


Fig. S4 ^{1}H NMR spectrum of lipid ***C18,14*** (400 MHz, $CDCl_3$).

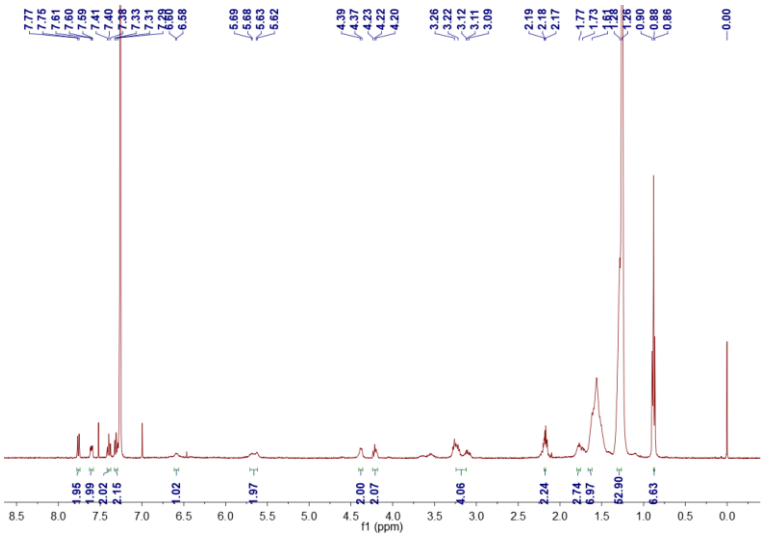


Fig. S5 ^{1}H NMR spectrum of lipid ***C16,18*** (400 MHz, $CDCl_3$).

4. Characterization

Preparation of supramolecular gels: ***Cn,m*** (0.01 mmol) was dispersed in 1 mL DMSO (HPLC grade) in a seal-capped vial. The suspension was heated to be a transparent solution and then stood to cool at room temperature until a white gel was formed, as confirmed by an inverse tube test.
The chemical structures of all the new compounds were confirmed by ^{1}H NMR spectra and MALDI-TOF MS mass spectra, recorded on a Bruker Avance 400 (400 MHz) spectrometer and a BIFLEIII matrix-assisted laser desorption/ionization time of fight mass spectrometry instrument, respectively.

UV-Vis, FL, CD and CPL spectra were performed on Hitachi U-3900, Hitachi F-4600, JASCO J-815 and JASCO CPL-200 spectrometers, respectively, using quartz cuvettes of 0.1 mm. Fluorescence lifetime measurements were recorded on an Edinburg FLS-980 fluorescence spectrometer with a calibrated integrating sphere using time-correlated single photon counting.

FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer. The samples for FT-IR measurements were firstly dried under vacuum and then processed into pellets with KBr.

XRD measurements were carried out on a Rigaku D/Max-2500 X-ray diffractometer with Cu Ka radiation (λ = 1.5406 Å) at a voltage of 40 kV and a current of 200 mA, with samples cast on glass substrates and dried under vacuum.

SEM was performed on a Hitachi S-4800 FE-SEM with an accelerating voltage of 10 kV. The sample was prepared by casting the supramolecular gels onto silica wafers, and was dried before coated with a thin layer of Pt.

TEM was performed on a JEM-1011 electron microscope at an accelerating voltage of 100 kV, by casting a small amount of DMSO-diluted gels on carbon-coated copper grids (300 mesh) and dried under vacuum.

5. Photographs of corresponding supramolecular gels

Fig. S6 Photographs of supramolecular gels self-assembled from lipids ***C18,18***, ***C18,16***, ***C18,20***, ***C16,18*** and ***C18,14*** in DMSO ($1*10^{-2}$ mol·L^{-1}, from left to right).

6. SEM and TEM images

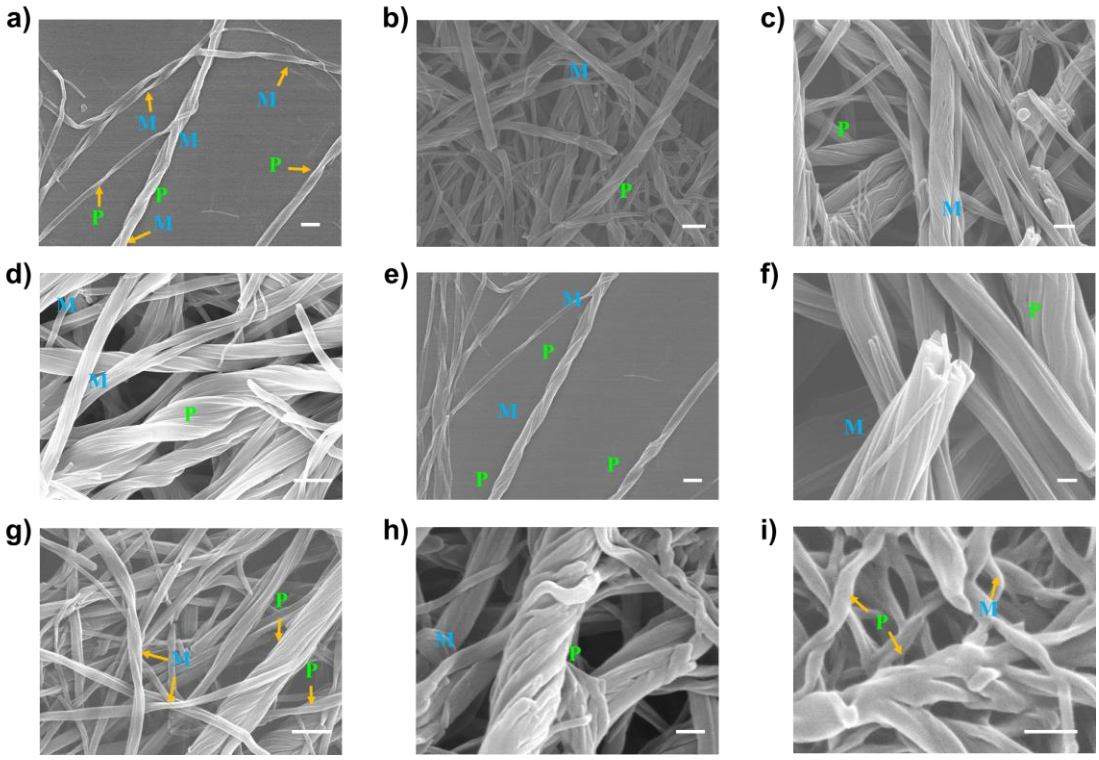


Fig. S7 SEM images displaying the coexistence of *P*- and *M*- handed nanostructures of self-assembled lipids ***Cn,m*** in DMSO ($1*10^{-2}$ mol·L^{-1}): a-f) ***C18,20***; g-h) ***C16,18***; i) ***C18,14***. Scale bar: 1 μm.

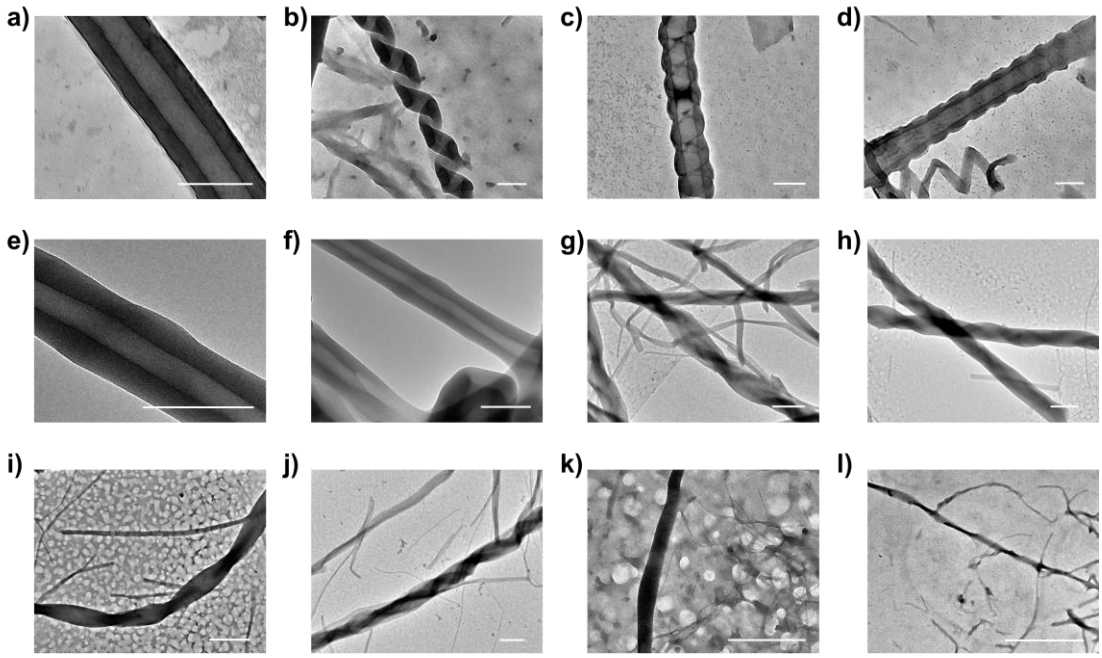


Fig. S8 TEM images of self-assembled lipids ***Cn,m*** in DMSO ($1*10^{-2}$ mol·L^{-1}): a-d) ***C18,18***; e-f) ***C18,16***; g-j) ***C18,20***; k) ***C16,18***; l) ***C18,14***. Scale bar: a-f) 200 nm; g-h) 1 µm.

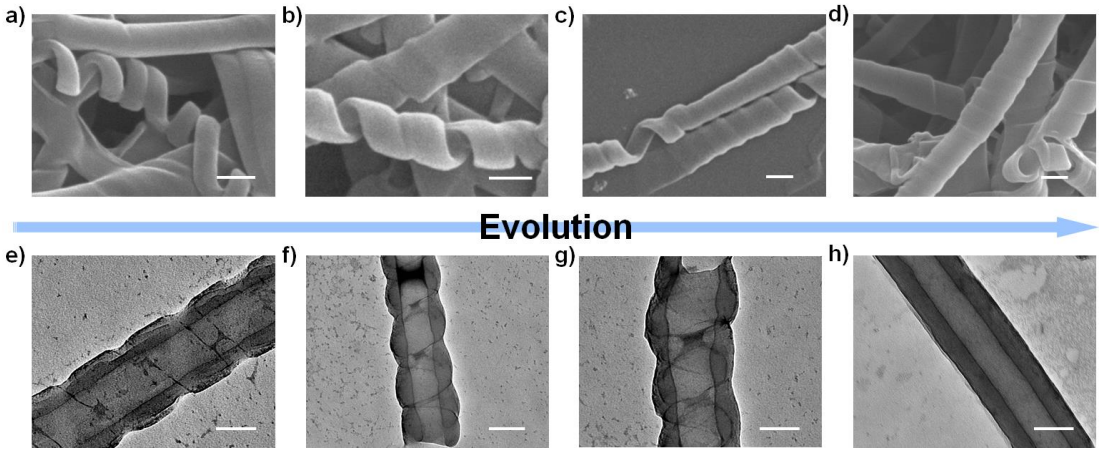


Fig. S9 SEM (a-d) and TEM (e-h) images of self-assembled lipids ***C18,18*** in DMSO ($1*10^{-2}$ mol·L^{-1}) displaying the evolution of nanotubes. Scale bar: a-d) 200 nm; e-h) 100 nm.

7. CD spectra

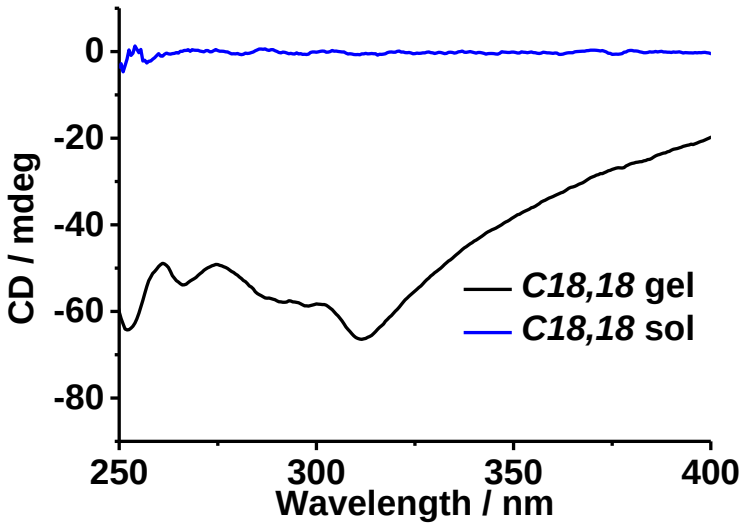


Fig. S10 CD spectra of lipid ***C18,18***: supramolecular gel prepared in DMSO ($1*10^{-2}$ mol·L^{-1}, black line) and solution in DMSO ($1*10^{-5}$ mol·L^{-1}, blue line).

8. CPL spectra

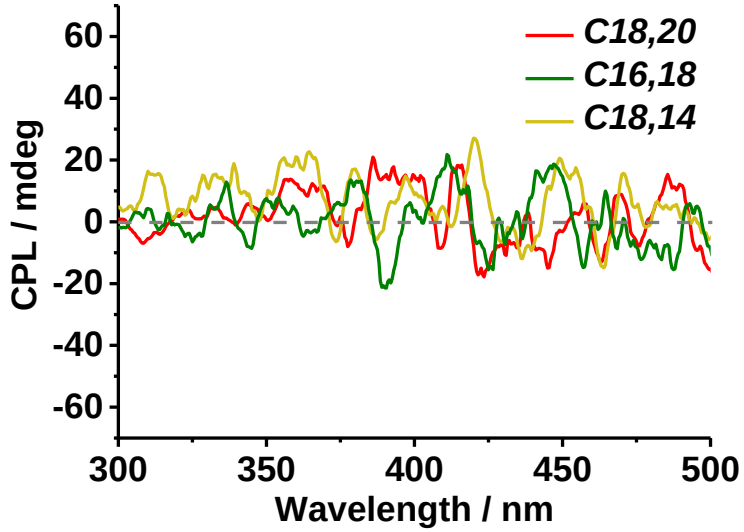


Fig. S11 CPL spectra of supramolecular gels prepared from lipids ***C18,20*** (red line), ***C16,18*** (green line) and ***C18,20*** (yellow line) in DMSO ($1*10^{-2}$ mol·L^{-1}).

9. FT-IR data

Lipids	ν_{NH}	Amide I			Amide II	δ_{CH2}	Amide III	δ_{CH2}
		α amine	acid	ω amine				
C18,18	3298	1690	1655	1643	1542	1468 1451	1259 1249	737 722
C18,16	3298	1690	1655	1643	1542	1468 1452	1259 1249	737 722
C18,20	3293	/	/	1638	1551	1468	1259	724
C16,18	3300	/	/	1638	1551	1469	1259	722
C18,14	3290	1686	1658	1639	1551 1542	1468 1451	1259	737 725

Table S1 FT-IR peaks of self-assembled lipids ***Cn,m*** ($1*10^{-2}$ mol·L^{-1}): ***C18,18***, ***C18,16***, ***C18,20***, ***C16,18*** and ***C18,14***.

10. XRD spectra

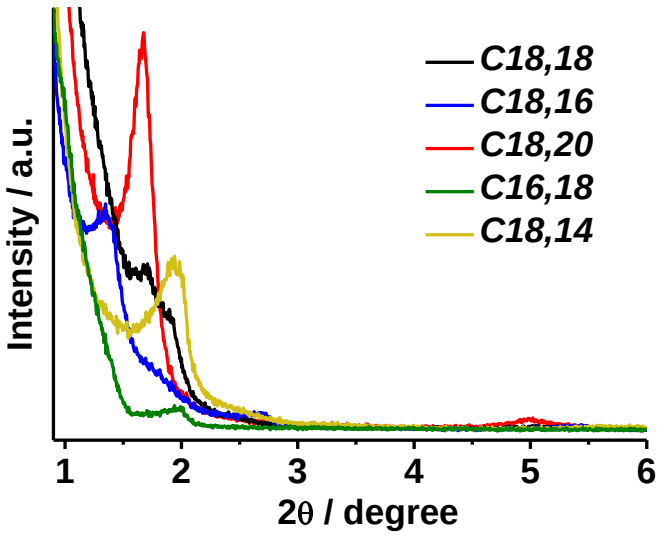


Fig. S12 X-ray diffraction spectra of supramolecular gels prepared from lipids ***Cn,m*** in DMSO ($1*10^{-2}$ mol·L^{-1}): ***C18,18*** (black line); ***C18,16*** (blue line); ***C18,20*** (red line); ***C16,18*** (green line) and ***C18,14*** (yellow line).