

Controlled packing of chiral assembly scaffolds to promote chiral J-aggregation of carbocyanine dyes

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Experimental details

Materials

Cy1 [5,5'-dimethyl-3,3'-bis(3-sulfopropyl)thiacyanine ammonium] was purchased from Merck KGaA (Darmstadt, Germany) and was used as received. Cy2 [3,3'-bis(3-sulfopropyl)-9-ethylthiacarbocyanine triethylammonium] was purchased from H.W. Sands Corp. (Florida, USA) and was used as received. Cy3 [5,5'-dichloro-3,3'-bis(4-sulfobutyl)-10-phenylthiacarbocyanine triethylammonium] was purchased from FEW Chemicals GmbH (Bitterfeld-Wolfen, Germany) and was used as received. Other chemicals were also purchased from commercial sources and were used without further purification. Millipore deionised water was used for all experiments.

Synthesis and structure confirmation of lysine- and ornithine-derived amphiphiles

N^{ω},N^{ϵ} -Dihexadecanoyl-L-lysine (16-Ly-OH) was synthesised using a previously reported method.¹⁸ N^{ω},N^{ϵ} -Didodecanoyl-L-lysine (12-Ly-OH), N^{ω},N^{ϵ} -ditetradecanoyl-L-lysine (14-Ly-OH), and N^{ω},N^{ϵ} -didodecanoyl-L-ornithine (12-Or-OH) were also synthesised using the same procedure with lauroyl chloride, myristoyl chloride, and L-ornithine as the starting materials. These compounds were reacted with 3-bromopropylamine in the presence of diethyl cyanophosphonate (DEPC) and N,N -diisopropylethylamine (DIPEA) in chloroform. The resulting product was reacted with excess pyridine or trimethylamine to afford the desired lysine- and ornithine-derived amphiphiles (Scheme S1).

Their chemical structures were confirmed *via* ^1H and ^{13}C NMR spectroscopy using a JNM-ECZ 400R Fourier transform NMR spectrometer (JEOL Ltd., Tokyo, Japan), attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) using an FT/IR-6300 FTIR spectrometer (JASCO Corp., Tokyo, Japan) equipped with an ATR Pro450-S (JASCO), and elemental analysis (EA) using a vario MICRO Cube elemental analyser (Elementar Japan K.K., Yokohama, Japan).

12-Ly [1-(3-(N^{ω},N^{ϵ} -didodecanoyl-L-lysynamido)propyl)pyridinium bromide]: white solid; 33% overall yield from 12-Ly-OH; m.p. 115–119 °C; ^1H NMR (400 MHz, CDCl_3 , 50 °C): δ = 0.88 (t, 6H, J = 6.6 Hz; $\text{CH}_3 \times 2$), 1.25 (s, 32H; $\text{CH}_3(\text{CH}_2)_8 \times 2$), 1.42–1.45 (m, 2H; CHCH_2CH_2), 1.51–1.64 (m, 6H; $\text{CH}(\text{CH}_2)_2\text{CH}_2$, $\text{CH}_3(\text{CH}_2)_8\text{CH}_2 \times 2$), 1.82–1.83 (m, 2H; CHCH_2), 2.19 (t, 2H, J = 7.8 Hz; CH_2CO), 2.33–2.37 (m, 2H; CH_2CO), 2.39–2.44 (m, 2H; $\text{CH}_2\text{CH}_2\text{N}$), 3.20–3.29 (m, 3H; $\text{NHCH}_2 \times 3/2$), 3.40–3.51 (m, 1H; $\text{NHCH}_2 \times 1/2$), 4.38 (q, 1H, J = 7.2 Hz; CH), 5.03 (t, 2H, J = 6.7 Hz; CH_2N), 6.29 (s, 1H; NHCH_2), 7.42 (d, 1H, J = 6.4 Hz; NHCH), 8.06 (t, 2H, J = 7.1 Hz; CHCHNCHCH), 8.21 (t, 1H, J = 4.8 Hz; NHCH_2), 8.44 (t, 1H, J = 7.8 Hz; NCHCHCH), 9.61 (d, 2H, J = 6.0 Hz; CHNCH) ppm (Fig. S1a); ^{13}C NMR (100 MHz, CDCl_3 , 50 °C): δ = 14.15 (CH_3), 22.78 (CH_3CH_2), 23.08 (CH_2), 26.01 (CH_2), 28.99 (CH_2), 29.45 (CH_2), 29.59 (CH_2), 29.76 (CH_2), 31.76 (CHCH_2), 32.03 (CH_2), 35.71 (CH_2CO), 36.74 (CH_2CO), 36.97 (NHCH_2), 38.84 (NHCH_2), 54.52 (CH_2N), 59.43 (CH), 128.41 (NCHCH), 144.98 (NCH), 145.84 (NCHCHCH), 173.85 (CO), 173.97 (CO), 174.55 (CO) ppm (Fig. S2a); IR (ATR): $\tilde{\nu}$ = 3311 ($\nu_{\text{N-H}}$), 2954 ($\nu_{\text{C-H}}$), 2916 ($\nu_{\text{C-H}}$), 2871 ($\nu_{\text{C-H}}$), 2848 ($\nu_{\text{C-H}}$), 1635 ($\nu_{\text{C=O}}$), 1554 ($\delta_{\text{N-H}}$), 1462 ($\delta_{\text{C-H}}$) cm^{-1} (Fig. S3a); EA: calcd for $\text{C}_{38}\text{H}_{69}\text{N}_4\text{O}_3\text{Br} \cdot 4.0\text{H}_2\text{O}$: C 58.37, H 9.93, N 7.17%; found: C 58.32, H 9.84, N 7.01%.

14-Ly [1-(3-(N^{ω},N^{ϵ} -ditetradecanoyl-L-lysynamido)propyl)pyridinium bromide]: white solid; 37% overall

yield from 14-Ly-OH; m.p. 121–126 °C; ¹H NMR (400 MHz, CDCl₃, 50 °C): δ = 0.88 (t, 6H, *J* = 6.9 Hz; CH₃ × 2), 1.25 (s, 40H; CH₃(CH₂)₁₀ × 2), 1.41–1.48 (m, 2H; CHCH₂CH₂), 1.52–1.66 (m, 6H; CH(CH₂)₂CH₂, CH₃(CH₂)₈CH₂ × 2), 1.83–1.92 (m, 2H; CHCH₂), 2.19 (t, 2H, *J* = 7.8 Hz; CH₂CO), 2.34–2.38 (m, 2H; CH₂CO), 2.40–2.47 (m, 2H; CH₂CH₂N), 3.16–3.33 (m, 3H; NHCH₂ × 3/2), 3.45–3.53 (m, 1H; NHCH₂ × 1/2), 4.43 (q, 1H, *J* = 6.9 Hz; CH), 5.08 (t, 2H, *J* = 7.8 Hz; CH₂N), 6.27 (s, 1H; NHCH₂), 7.43 (d, 1H, *J* = 7.8 Hz; NHCH), 8.04 (t, 2H, *J* = 7.1 Hz; CHCHNCHCH), 8.25 (t, 1H, *J* = 5.5 Hz; NHCH₂), 8.42 (t, 1H, *J* = 7.8 Hz; NCHCHCH), 9.67 (d, 2H, *J* = 5.5 Hz; CHNCH) ppm (Fig. S1b); ¹³C NMR (100 MHz, CDCl₃, 50 °C): δ = 14.06 (CH₃), 22.70 (CH₃CH₂), 22.91 (CH₂), 25.94 (CH₂), 28.78 (CH₂), 29.39 (CH₂), 29.50 (CH₂), 29.70 (CH₂), 29.74 (CH₂), 31.48 (CHCH₂), 31.96 (CH₂), 35.74 (CH₂CO), 36.69 (CH₂CO), 36.92 (NHCH₂), 38.74 (NHCH₂), 54.43 (CH₂N), 59.35 (CH), 128.29 (NCHCH), 144.80 (NCH), 145.79 (NCHCHCH), 173.89 (CO), 174.05 (CO), 174.56 (CO) ppm (Fig. S2b); IR (ATR): $\tilde{\nu}$ = 3307 ($\nu_{\text{N-H}}$), 2954 ($\nu_{\text{C-H}}$), 2916 ($\nu_{\text{C-H}}$), 2871 ($\nu_{\text{C-H}}$), 2848 ($\nu_{\text{C-H}}$), 1635 ($\nu_{\text{C=O}}$), 1554 ($\delta_{\text{N-H}}$), 1462 ($\delta_{\text{C-H}}$) cm⁻¹ (Fig. S3b); EA: calcd for C₄₂H₇₇N₄O₃Br·2.7H₂O: C 61.92, H 10.20, N 6.88%; found: C 61.99, H 9.89, N 6.75%.

16-Ly [1-(3-(*N*^α,*N*^ε-dihexadecanoyl-L-lysynamido)propyl)pyridinium bromide]: white solid; 50% overall yield from 16-Ly-OH; m.p. 123–128 °C; ¹H NMR (400 MHz, CDCl₃, 50 °C): δ = 0.88 (t, 6H, *J* = 6.9 Hz; CH₃ × 2), 1.26 (s, 48H; CH₃(CH₂)₁₂ × 2), 1.41–1.48 (m, 2H; CHCH₂CH₂), 1.54–1.65 (m, 6H; CH(CH₂)₂CH₂, CH₃(CH₂)₈CH₂ × 2), 1.79–1.92 (m, 2H; CHCH₂), 2.19 (t, 2H, *J* = 7.8 Hz; CH₂CO), 2.37 (t, 2H, *J* = 7.8 Hz; CH₂CO), 2.40–2.49 (m, 2H; CH₂CH₂N), 3.19–3.31 (m, 3H; NHCH₂ × 3/2), 3.47–3.55 (m, 1H; NHCH₂ × 1/2), 4.40–4.45 (m, 1H; CH), 5.03–5.10 (m, 2H; CH₂N), 6.09 (s, 1H; NHCH₂), 7.27–7.29 (m, 1H; NHCH), 8.04 (t, 2H, *J* = 7.1 Hz; CHCHNCHCH), 8.13 (s, 1H; NHCH₂), 8.42 (t, 1H, *J* = 7.8 Hz; NCHCHCH), 9.57 (d, 2H, *J* = 6.4 Hz; CHNCH) ppm (Fig. S1c); ¹³C NMR (100 MHz, CDCl₃, 50 °C): δ = 14.06 (CH₃), 22.70 (CH₃CH₂), 22.95 (CH₂), 25.93 (CH₂), 28.84 (CH₂), 29.39 (CH₂), 29.50 (CH₂), 29.75 (CH₂), 31.50 (CHCH₂), 31.97 (CH₂), 35.63 (CH₂CO), 36.69 (CH₂CO), 36.92 (NHCH₂), 38.73 (NHCH₂), 54.44 (CH₂N), 59.36 (CH), 128.28 (NCHCH), 144.80 (NCH), 145.78 (NCHCHCH), 173.76 (CO), 173.95 (CO), 174.49 (CO) ppm (Fig. S2c); IR (ATR): $\tilde{\nu}$ = 3307 ($\nu_{\text{N-H}}$), 2954 ($\nu_{\text{C-H}}$), 2916 ($\nu_{\text{C-H}}$), 2871 ($\nu_{\text{C-H}}$), 2848 ($\nu_{\text{C-H}}$), 1633 ($\nu_{\text{C=O}}$), 1556 ($\delta_{\text{N-H}}$), 1462 ($\delta_{\text{C-H}}$) cm⁻¹ (Fig. S3c); EA: calcd for C₄₆H₈₅N₄O₃Br·2.5H₂O: C 63.72, H 10.46, N 6.46%; found: C 63.72, H 10.07, N 6.38%.

12-Or [1-(3-(*N*^α,*N*^δ-didodecanoyl-L-ornithinamido)propyl)pyridinium bromide]: white solid; 43% overall yield from 12-Or-OH; m.p. 114–120 °C; ¹H NMR (400 MHz, CDCl₃, 50 °C): δ = 0.88 (t, 6H, *J* = 6.9 Hz; CH₃ × 2), 1.25 (s, 32H; CH₃(CH₂)₈ × 2), 1.55–1.70 (m, 6H; CHCH₂CH₂, CH₃(CH₂)₈CH₂ × 2), 1.78–1.85 (m, 1H; CHCH₂ × 1/2), 1.88–1.96 (m, 1H; CHCH₂ × 1/2), 2.20 (t, 2H, *J* = 7.8 Hz; CH₂CO), 2.33–2.35 (m, 2H; CH₂CO), 2.37–2.45 (m, 2H; CH₂CH₂N), 3.20–3.35 (m, 3H; NHCH₂ × 3/2), 3.44–3.52 (m, 1H; NHCH₂ × 1/2), 4.47–4.52 (m, 1H; CH), 5.05 (t, 2H, *J* = 7.5 Hz; CH₂N), 6.60 (t, 1H, *J* = 5.7 Hz; NHCH₂), 7.30 (d, 1H, *J* = 7.8 Hz; NHCH), 8.05 (t, 2H, *J* = 7.1 Hz; CHCHNCHCH), 8.32 (t, 1H, *J* = 5.5 Hz; NHCH₂), 8.42 (t, 1H, *J* = 7.8 Hz; NCHCHCH), 9.60 (d, 2H, *J* = 6.0 Hz; CHNCH) ppm (Fig. S1d); ¹³C NMR (100 MHz, CDCl₃, 50 °C): δ = 14.06 (CH₃), 22.70 (CH₃CH₂), 22.95 (CH₂), 25.93 (CH₂), 28.84 (CH₂), 29.39 (CH₂), 29.50 (CH₂), 29.75 (CH₂), 31.50 (CHCH₂), 31.97 (CH₂), 35.63 (CH₂CO), 36.69 (CH₂CO), 36.92 (NHCH₂), 38.73 (NHCH₂), 54.44 (CH₂N), 59.36 (CH), 128.28 (NCHCH), 144.80 (NCH), 145.78 (NCHCHCH), 173.76 (CO), 173.95 (CO),

174.49 (CO) ppm (Fig. S2d); IR (ATR): $\tilde{\nu} = 3307$ ($\nu_{\text{N-H}}$), 2954 ($\nu_{\text{C-H}}$), 2916 ($\nu_{\text{C-H}}$), 2871 ($\nu_{\text{C-H}}$), 2848 ($\nu_{\text{C-H}}$), 1633 ($\nu_{\text{C=O}}$), 1556 ($\delta_{\text{N-H}}$), 1462 ($\delta_{\text{C-H}}$) cm^{-1} (Fig. S3d); EA: calcd for $\text{C}_{37}\text{H}_{67}\text{N}_4\text{O}_3\text{Br}\cdot 2.0\text{H}_2\text{O}$: C 60.72, H 9.78, N 7.66%; found: C 60.66, H 9.58, N 7.52%.

12-Ly-Am [1-(3-(N^{α},N^{β} -didodecanoyl-L-lysineamido)propyl)- N,N,N -trimethylammonium bromide]: white solid; 26% overall yield from 12-Ly-OH; m.p. 125–127 °C; ^1H NMR (400 MHz, CD_3OD , 50 °C): $\delta = 0.90$ (t, 6H, $J = 6.9$ Hz; $\text{CH}_3 \times 2$), 1.30 (s, 32H; $\text{CH}_3(\text{CH}_2)_8 \times 2$), 1.38–1.45 (m, 2H; CHCH_2CH_2), 1.50–1.55 (m, 2H; $\text{CH}(\text{CH}_2)_2\text{CH}_2$), 1.57–1.65 (m, 4H; $\text{CH}_3(\text{CH}_2)_8\text{CH}_2 \times 2$), 1.66–1.82 (m, 2H; CHCH_2), 1.95–2.07 (m, 2H; $\text{CH}_2\text{CH}_2\text{N}$), 2.17 (t, 2H, $J = 7.5$ Hz; CH_2CO), 2.24–2.28 (m, 2H; CH_2CO), 3.14 (s, 9H; $\text{NCH}_3 \times 3$), 3.14 (t, 2H, $J = 7.1$ Hz; CH_2N), 3.22–3.27 (m, 1H; $\text{NHCH}_2 \times 1/2$), 3.35–3.42 (m, 3H; $\text{NHCH}_2 \times 3/2$), 4.10 (q, 1H, $J = 4.7$ Hz; CH) ppm (Fig. S1e); ^{13}C NMR (100 MHz, CD_3OD , 50 °C): $\delta = 14.33$ (CH_3), 23.63 (CH_3CH_2), 24.34 (CH_2), 26.36 (CH_2), 30.32 (CH_2), 30.37 (CH_2), 30.42 (CH_2), 30.56 (CH_2), 30.65 (CH_2), 32.21 (CHCH_2), 32.99 (CH_2), 36.85 (CH_2CO), 37.06 (CH_2CO), 37.26 (NHCH_2), 39.86 (NHCH_2), 53.82 (CH_3N), 55.58 (CH), 65.78 (NCH_2), 175.30 (CO), 176.29 (CO), 176.61 (CO) ppm (Fig. S2e); IR (ATR): $\tilde{\nu} = 3303$ ($\nu_{\text{N-H}}$), 2954 ($\nu_{\text{C-H}}$), 2916 ($\nu_{\text{C-H}}$), 2871 ($\nu_{\text{C-H}}$), 2850 ($\nu_{\text{C-H}}$), 1637 ($\nu_{\text{C=O}}$), 1552 ($\delta_{\text{N-H}}$), 1466 ($\delta_{\text{C-H}}$) cm^{-1} (Fig. S3e); EA: calcd for $\text{C}_{36}\text{H}_{73}\text{N}_4\text{O}_3\text{Br}\cdot 4.3\text{H}_2\text{O}$: C 56.35, H 10.72, N 7.30%; found: C 56.32, H 10.38, N 7.05%.

Characterisation of self-assembled amphiphiles

The formation of the self-assemblies of 12-Ly, 14-Ly, 16-Ly, 12-Or, and 12-Ly-Am amphiphiles in water was confirmed via scanning transmission electron microscopy (STEM) using a scanning electron microscope SU8600 (Hitachi High-Tech Corp., Tokyo, Japan). The dispersions of the amphiphiles were spotted on carbon-coated copper grids. The samples were then air-dried at 25 °C by blotting excess dispersion and post-stained with osmium tetroxide using an osmium plasma coater OPC60A (Filgen, Inc., Nagoya, Japan).

The gel-to-liquid crystalline phase transition temperature (T_m) and transition enthalpy (ΔH) values of the amphiphile assemblies in water were measured *via* differential scanning calorimetry (DSC) measurements using an EXSTAR DSC7020 calorimeter (Hitachi High-Tech). The dispersions (20 mM, 15 μL) were encapsulated in a silver capsule and scanned using a heating rate of 2.0 °C min^{-1} .

FTIR spectra of a 12-Ly dispersion were recorded using an FT/IR-6300 FTIR spectrometer by transmittance at 25 °C. 12-Ly (3.0 mM) was dispersed in heavy water (D_2O) instead of H_2O , and placed in a demountable liquid cell with CaF_2 windows.

Preparation of cyanine dye–amphiphile aqueous mixtures

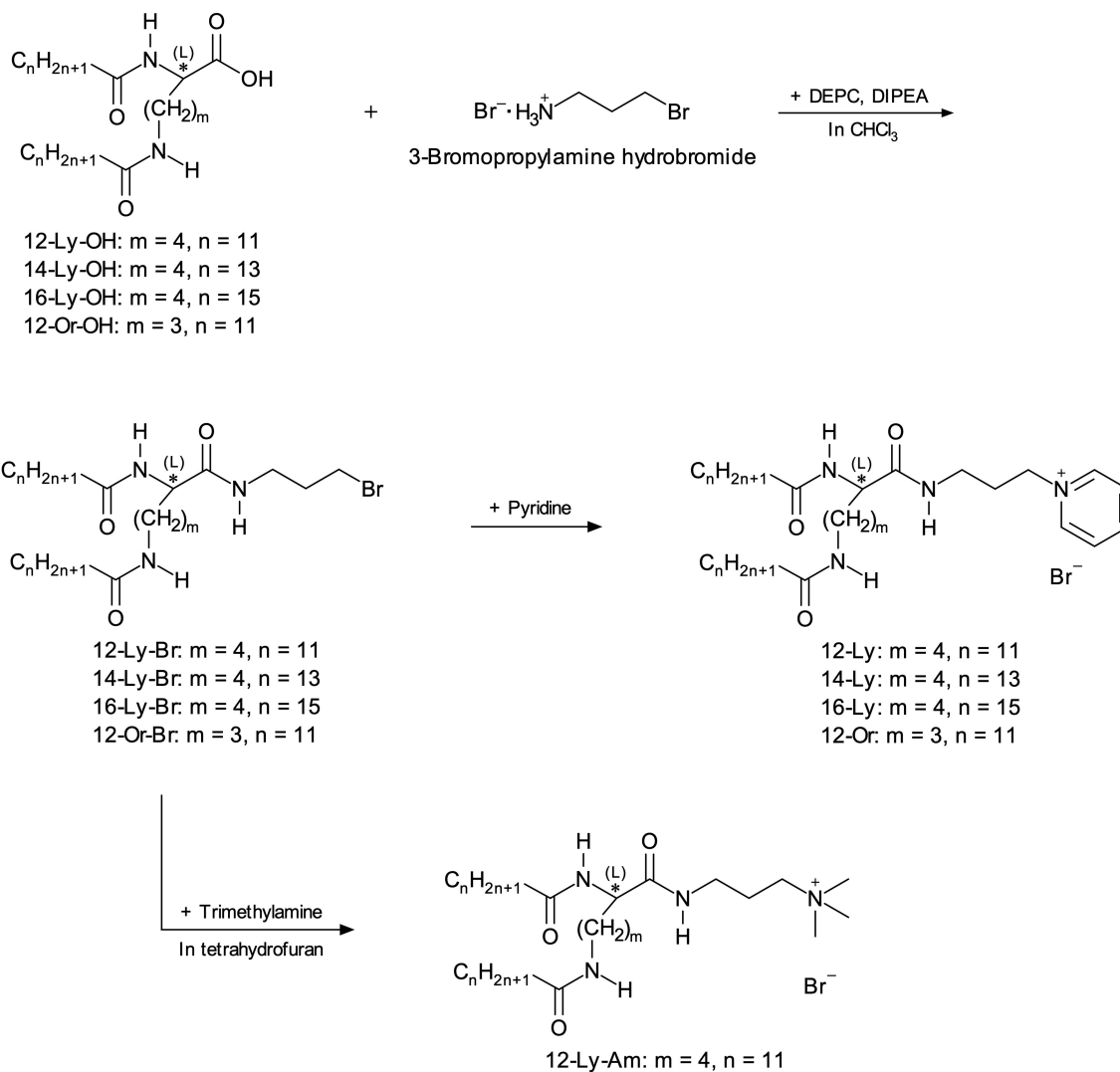
The amphiphiles were dissolved in water by heating over T_m s. Then, the cyanine dye aqueous solutions were added to the amphiphile dispersions and heated until the mixture turned homogeneous. The mixtures were cooled to 20 °C and their optical spectral measurements were obtained.

Optical spectral measurements

UV–visible absorption spectra were recorded using a V-560 UV/VIS spectrophotometer (JASCO) equipped with an ETC-505T temperature controller (JASCO). The circular dichroism (CD) and linear dichroism (LD)

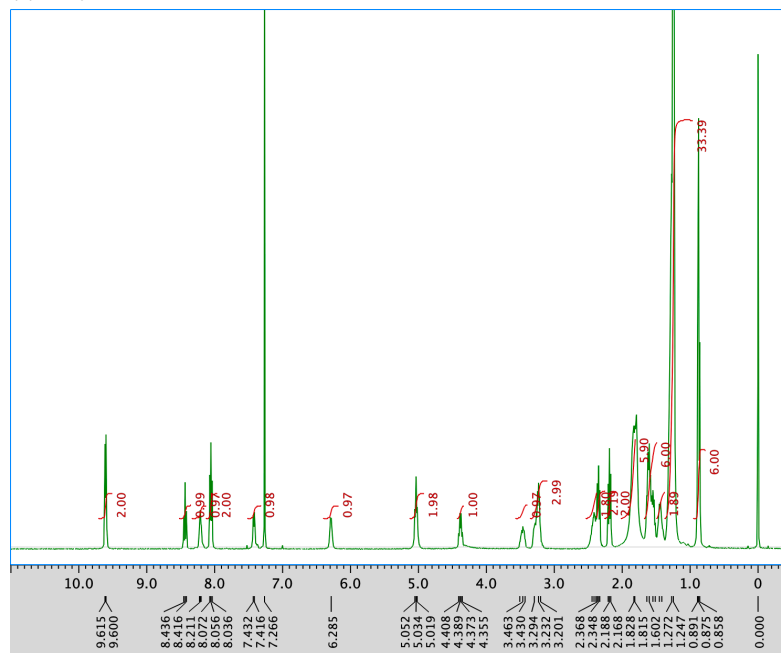
spectra were recorded using a J-820 spectropolarimeter (JASCO) equipped with an LD attachment (LD-403, JASCO) and a PTC-423L temperature controller (JASCO). The emission spectra were recorded using an FP-6600 spectrofluorometer (JASCO) equipped with an EHC-573T temperature controller (JASCO). The circularly polarised luminescence (CPL) spectra were recorded using a CPL-300 spectrofluoropolarimeter (JASCO) equipped with a PTC-423L temperature controller (JASCO). Prior to recording the spectra, the sample solutions were placed in a quartz cell (path length = 0.1 cm for UV–visible absorption, CD, and CPL spectra; 1 × 0.1 cm cell for emission spectra) and incubated at specific temperatures (20–90 °C).

Supplementary figures



Scheme S1 Synthesis of lysine- and ornithine-derived amphiphiles.

(a) 12-Ly



(b) 14-Ly

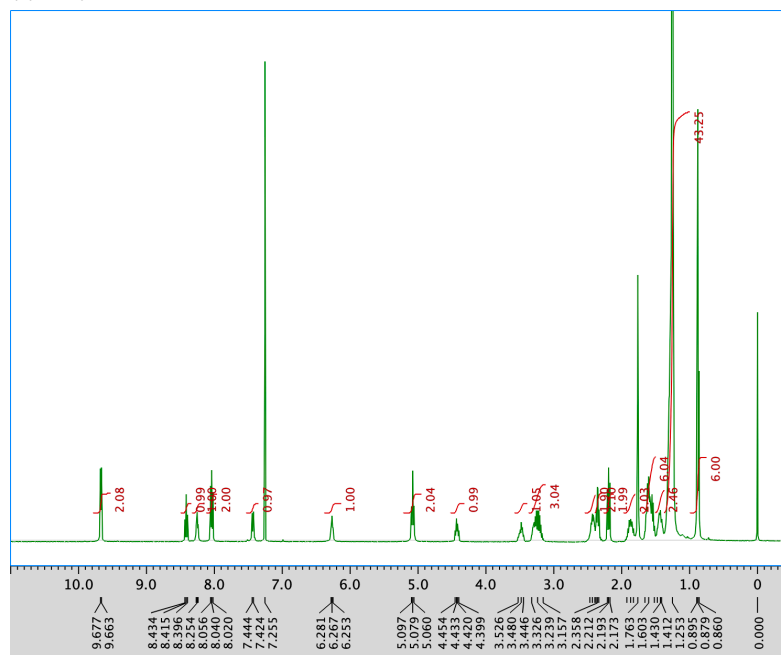
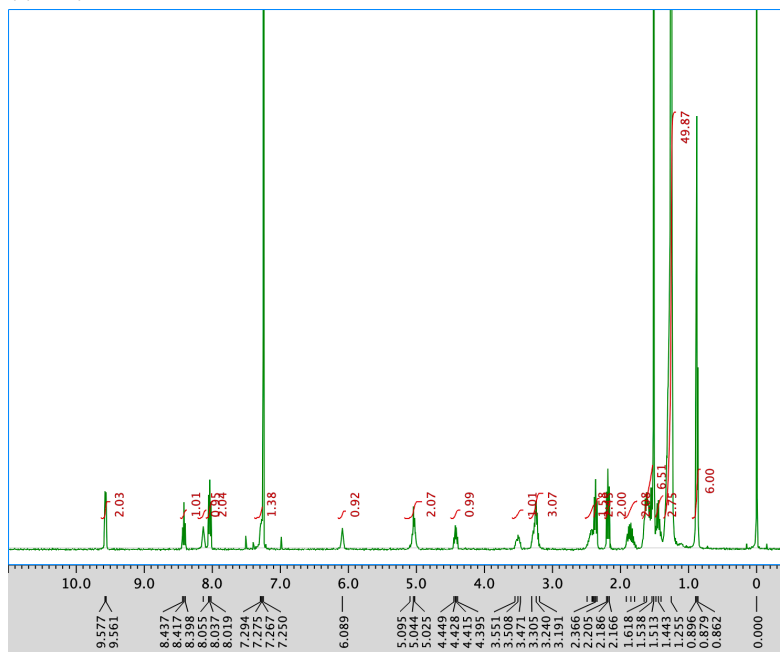


Fig. S1 ^1H NMR spectra of (a) 12-Ly, (b) 14-Ly, (c) 16-Ly, and (d) 12-Or in CDCl_3 and (e) 12-Ly-Am in CD_3OD ; 400 MHz, 50 °C.

(c) 16-Ly



(d) 12-Or

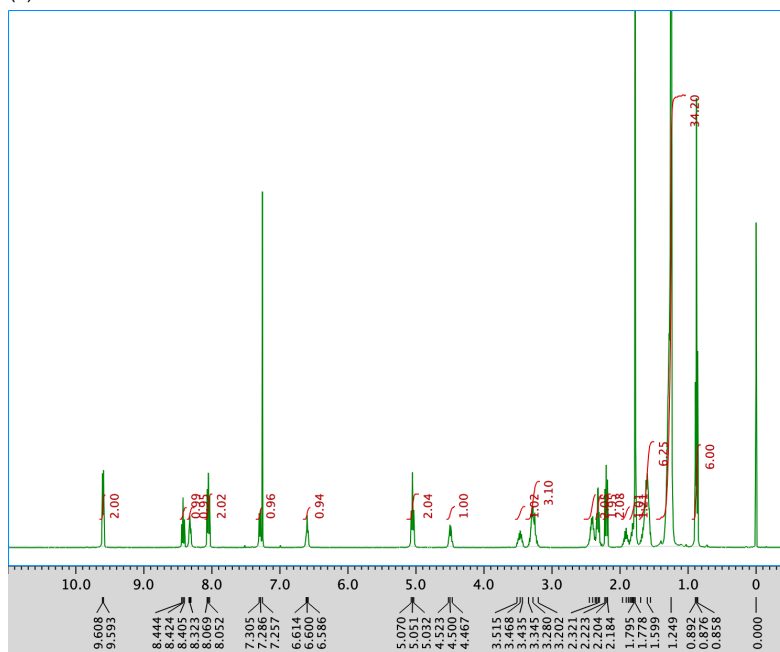


Fig. S1 (Continued) ¹H NMR spectra of (a) 12-Ly, (b) 14-Ly, (c) 16-Ly, and (d) 12-Or in CDCl₃ and (e) 12-Ly-Am in CD₃OD; 400 MHz, 50 °C.

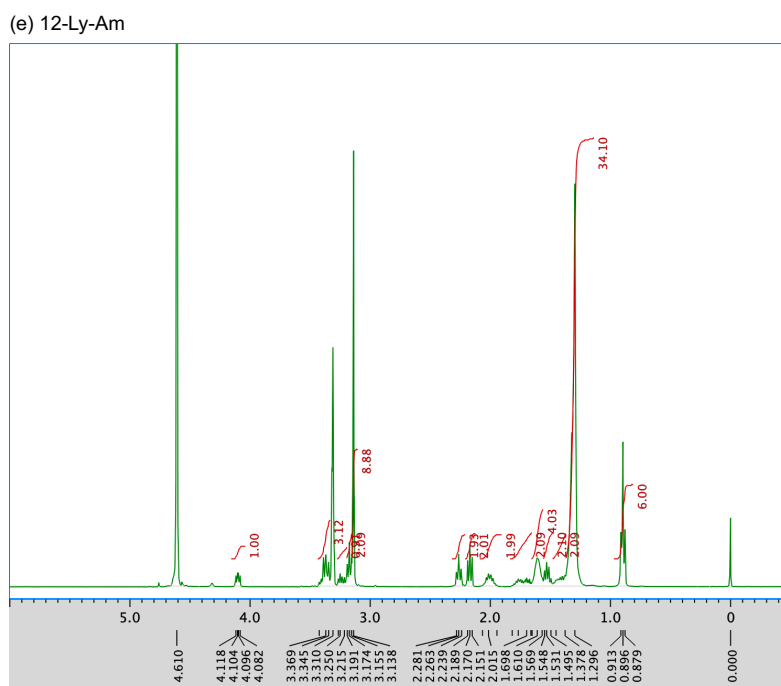


Fig. S1 (Continued) ^1H NMR spectra of (a) 12-Ly, (b) 14-Ly, (c) 16-Ly, and (d) 12-Or in CDCl_3 and (e) 12-Ly-Am in CD_3OD ; 400 MHz, 50 $^\circ\text{C}$.

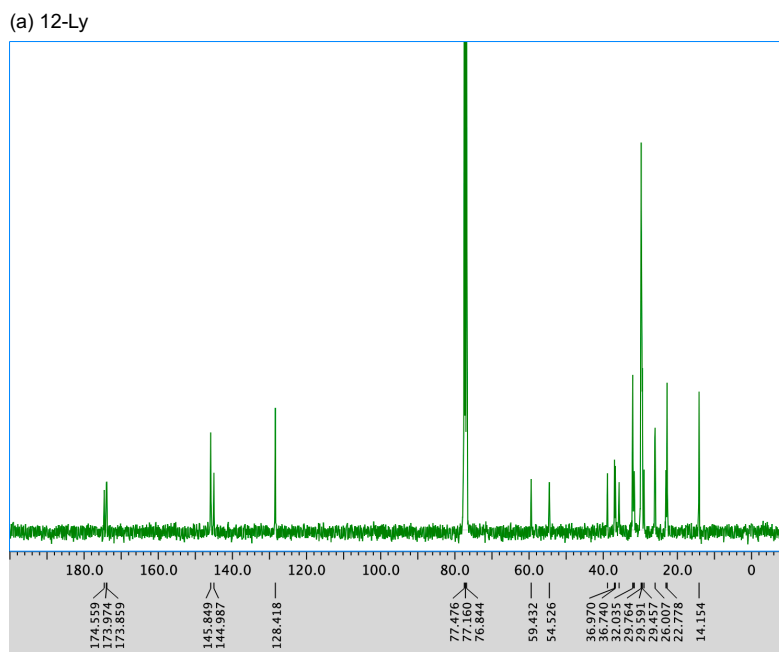
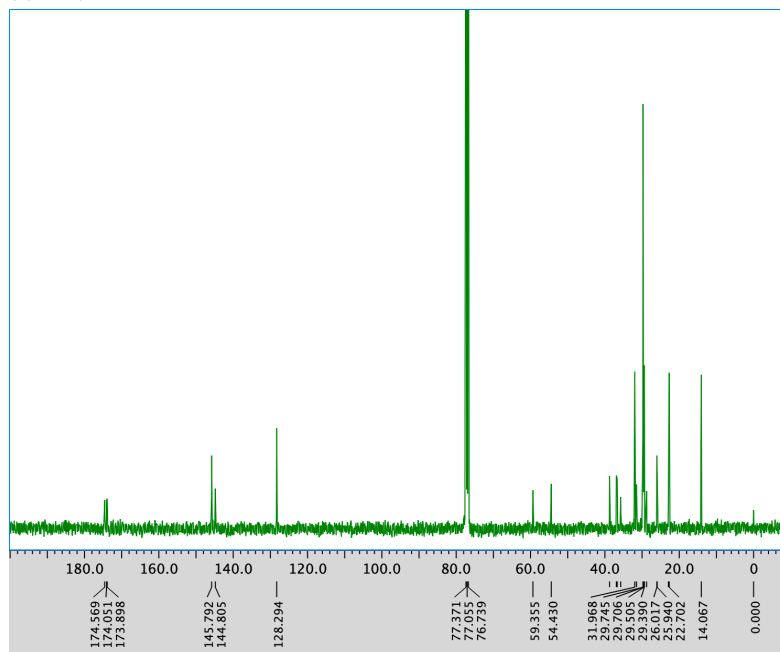


Fig. S2 ^{13}C NMR spectra of (a) 12-Ly, (b) 14-Ly, (c) 16-Ly, and (d) 12-Or in CDCl_3 and (e) 12-Ly-Am in CD_3OD ; 100 MHz, 50 $^\circ\text{C}$.

(b) 14-Ly



(c) 16-Ly

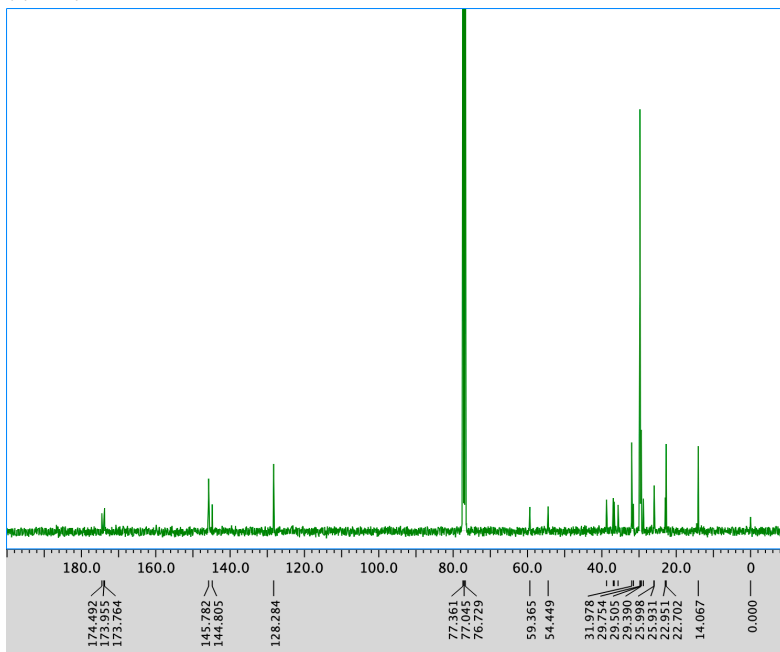
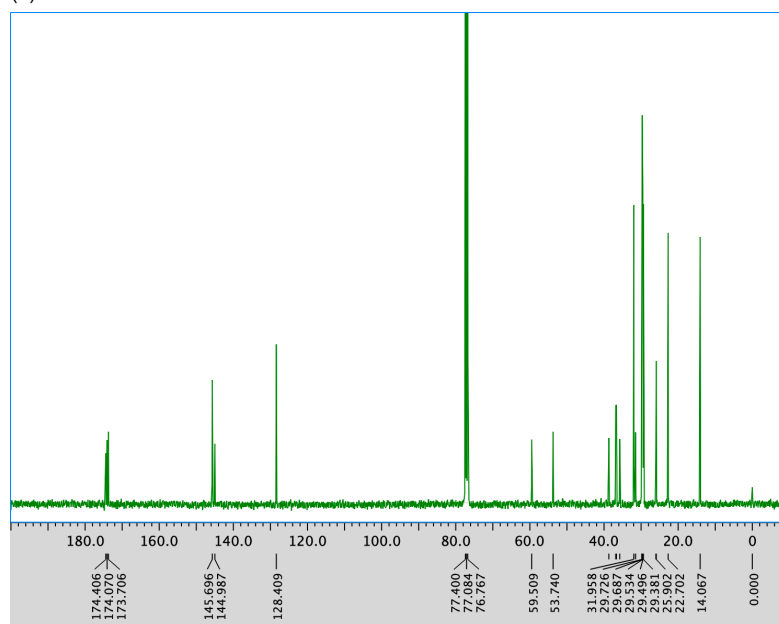


Fig. S2 (Continued) ¹³C NMR spectra of (a) 12-Ly, (b) 14-Ly, (c) 16-Ly, and (d) 12-Or in CDCl₃ and (e) 12-Ly-Am in CD₃OD; 100 MHz, 50 °C.

(d) 12-Or



(e) 12-Ly-Am

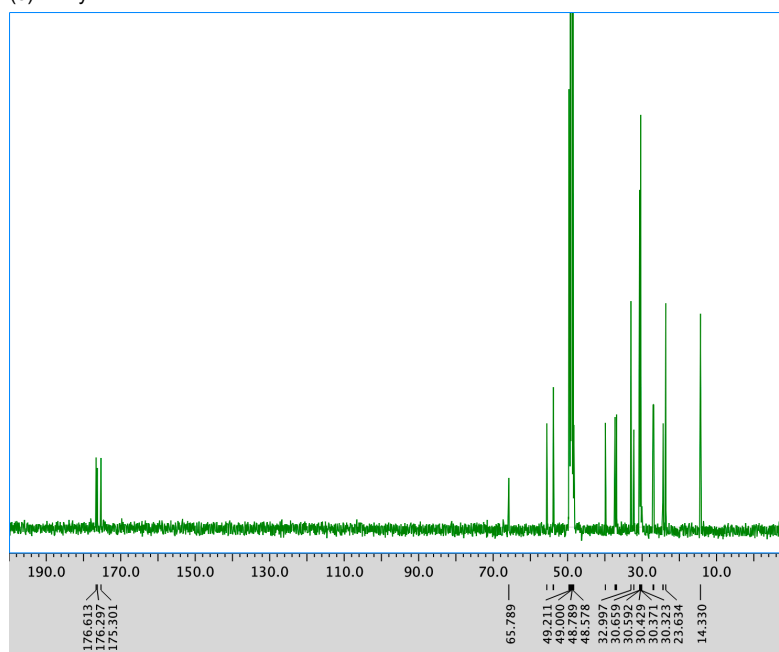


Fig. S2 (Continued) ¹³C NMR spectra of (a) 12-Ly, (b) 14-Ly, (c) 16-Ly, and (d) 12-Or in CDCl₃ and (e) 12-Ly-Am in CD₃OD; 100 MHz, 50 °C.

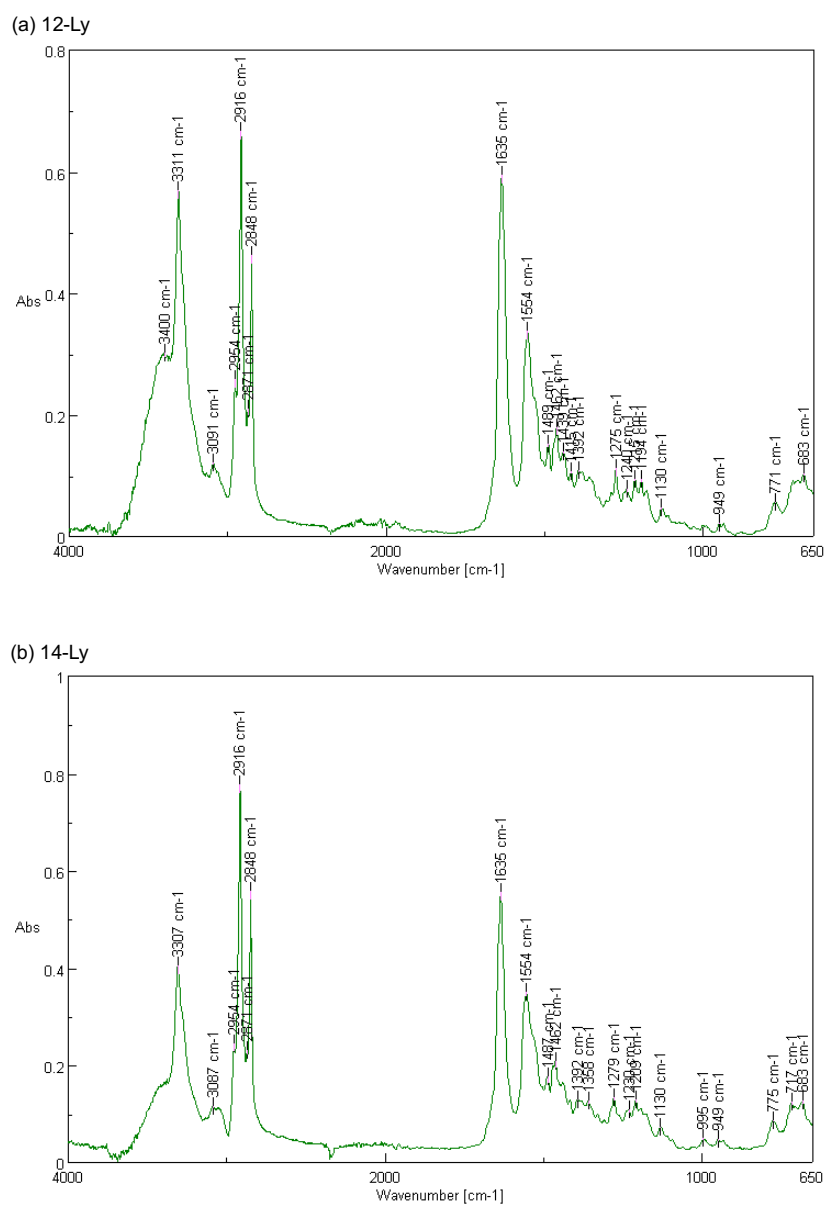


Fig. S3 ATR-FTIR spectra of (a) 12-Ly, (b) 14-Ly, (c) 16-Ly, (d) 12-Or, and (e) 12-Ly-Am.

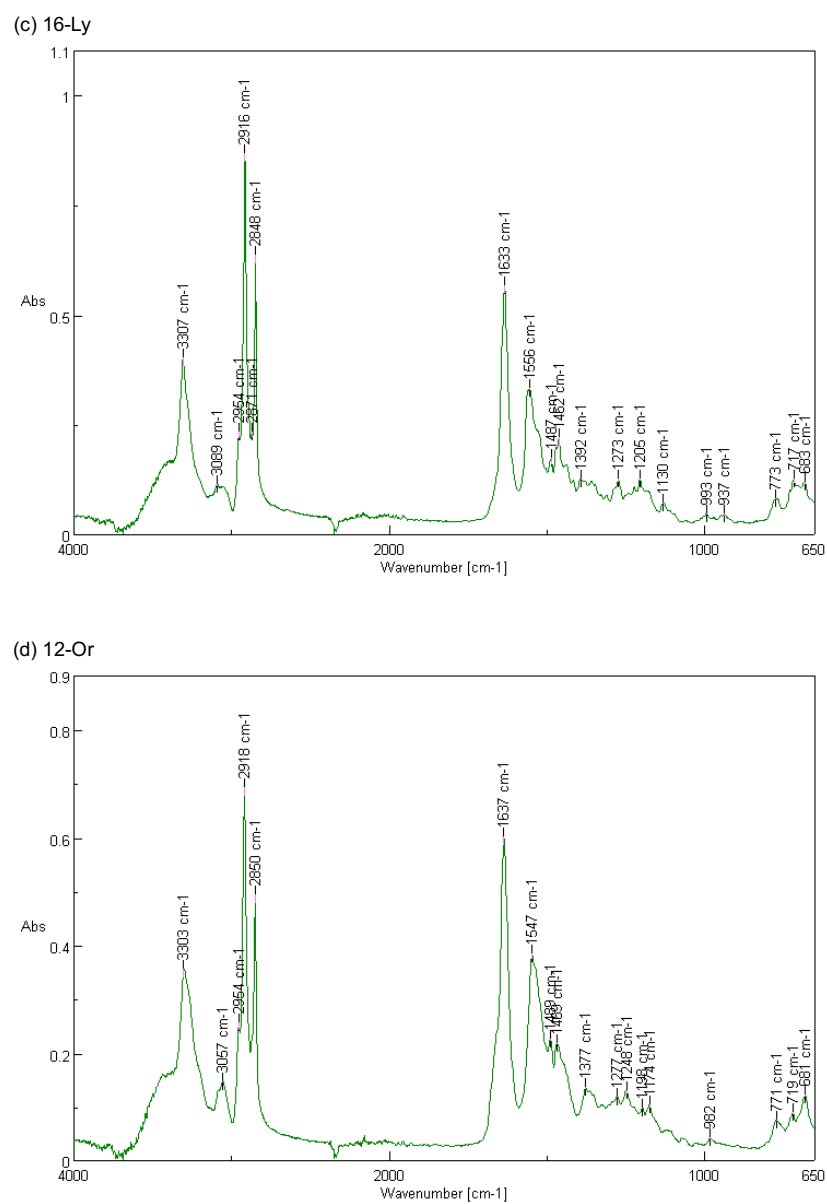


Fig. S3 (Continued) ATR-FTIR spectra of (a) 12-Ly, (b) 14-Ly, (c) 16-Ly, (d) 12-Or, and (e) 12-Ly-Am.

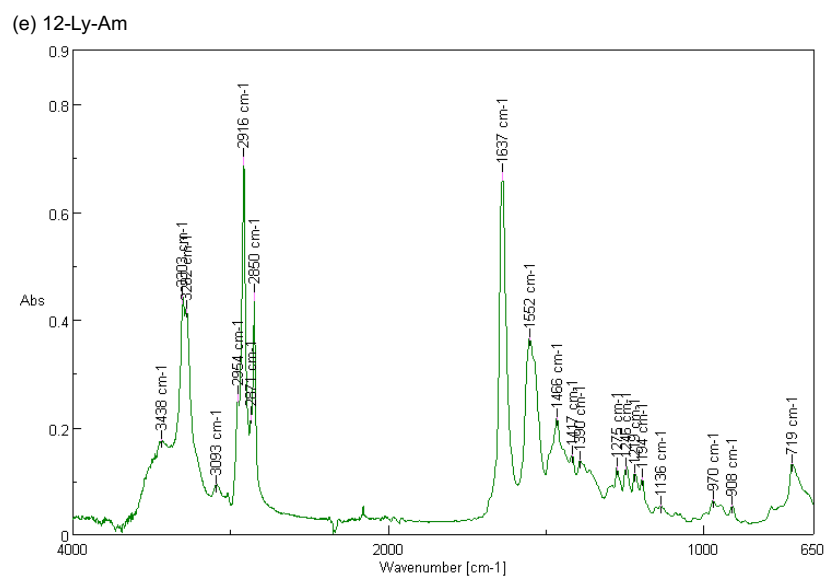


Fig. S3 (Continued) ATR-FTIR spectra of (a) 12-Ly, (b) 14-Ly, (c) 16-Ly, (d) 12-Or, and (e) 12-Ly-Am.

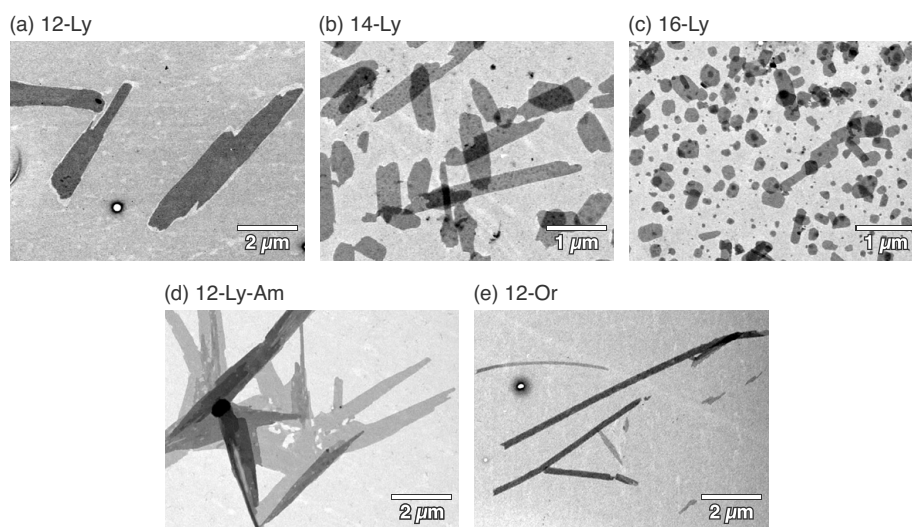


Fig. S4 STEM images of the cast films of (a) 12-Ly, (b) 14-Ly, (c) 16-Ly, (d) 12-Ly-Am, and (e) 12-Or assemblies prepared from their aqueous dispersions (0.6 mM) and post-stained with OsO₄.

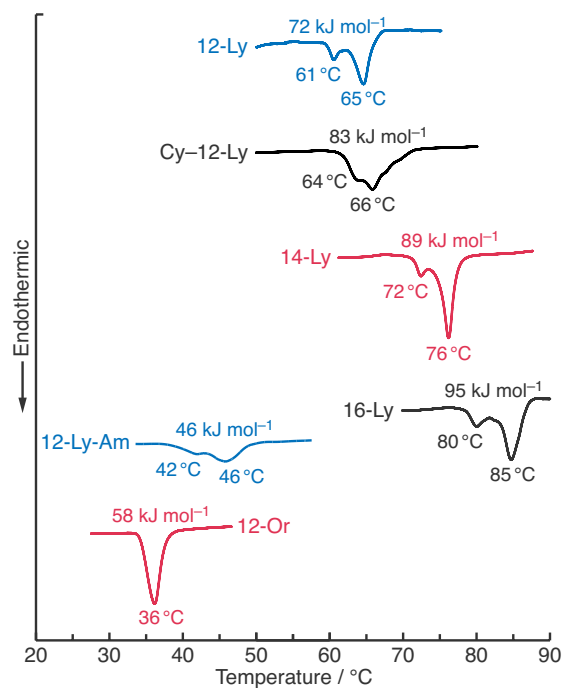


Fig. S5 DSC thermograms of 12-Ly, 14-Ly, 16-Ly, 12-Ly-Am, and 12-Or (20 mM) without or containing Cy2 (1 mM) in water during heating; heating rate: 2 °C min⁻¹.

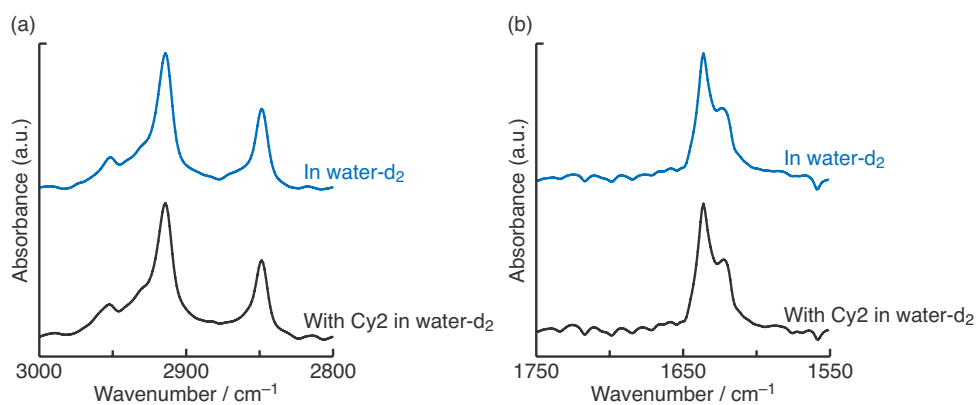


Fig. S6 FTIR spectra of 12-Ly (3.0 mM) without and containing Cy2 (0.15 mM) in water-d₂ at 25 °C.

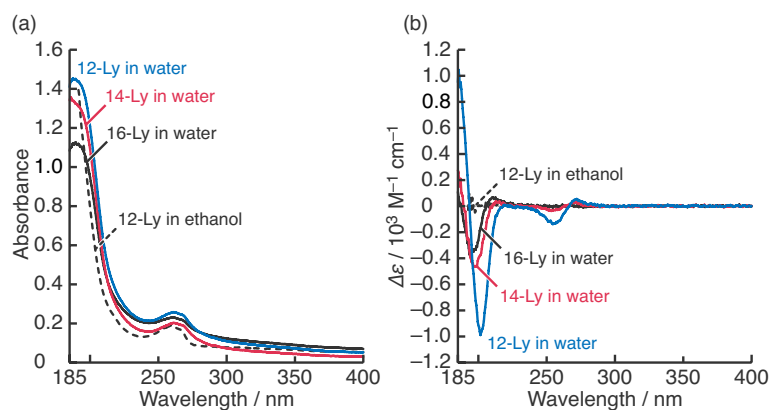


Fig. S7 (a) UV absorption and (b) CD spectra of 12-, 14-, and 16-Ly (0.6 mM) in water and ethanol at 20 °C; path length: 0.1 cm.

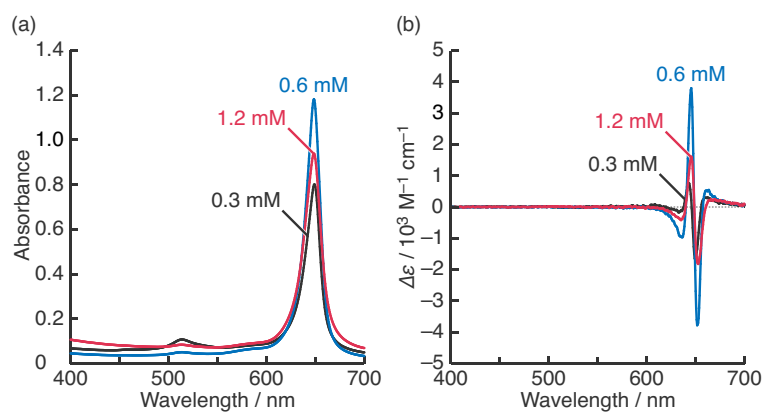


Fig. S8 (a) Visible absorption and (b) CD spectra of Cy2 (0.03 mM) in the presence of different concentrations of 12-Ly (0.3, 0.6, and 1.2 mM) in water at 20 °C; path length: 0.1 cm.

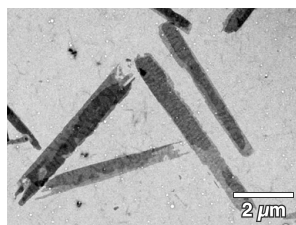


Fig. S9 STEM image of the cast film of 12-Ly assemblies (0.6 mM) containing Cy2 (0.03 mM) prepared from its aqueous mixture and post-stained with OsO₄.

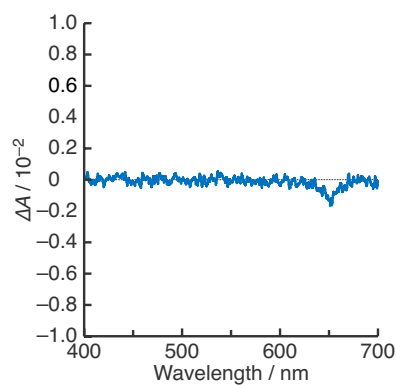


Fig. S10 LD spectrum of Cy2 (0.03 mM) in the presence of 12-Ly (0.6 mM) in water at 20 °C; path length: 0.1 cm.

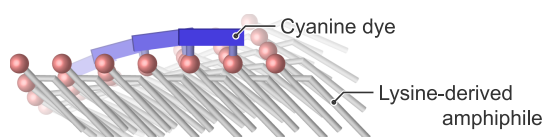


Fig. S11 Schematic of the proposed chiral J-aggregates of cyanine dye molecules on the lysine-derived amphiphile assembly. The double bilayer structure is omitted for clarity.

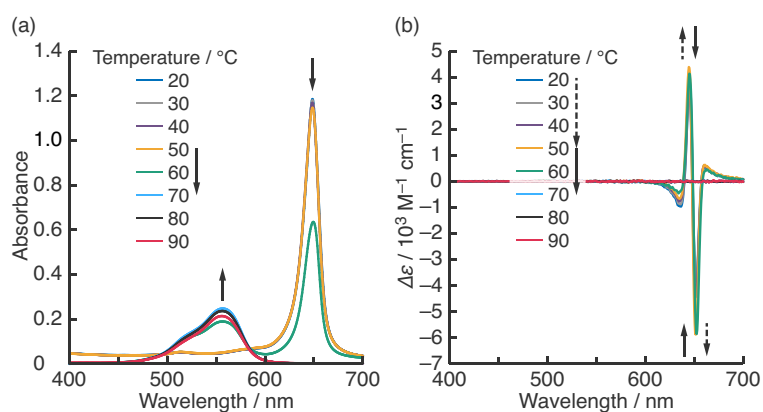


Fig. S12 (a) Visible absorption and (b) CD spectra of Cy2 (0.03 mM) in the presence of 12-Ly (0.6 mM) in water at different temperatures (20–90 °C); path length: 0.1 cm.

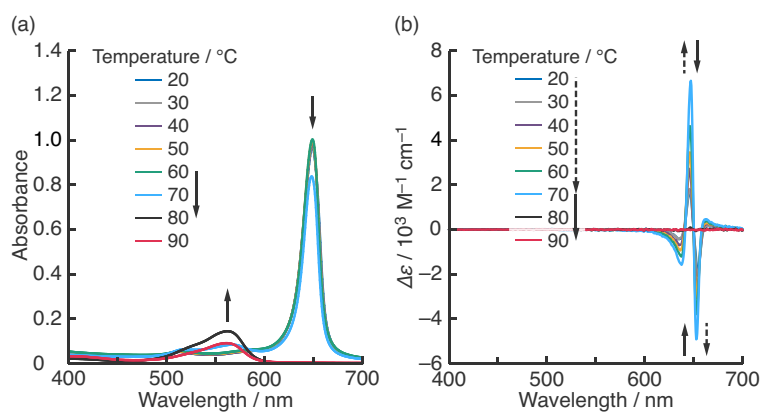


Fig. S13 (a) Visible absorption and (b) CD spectra of Cy2 (0.03 mM) in the presence of 14-Ly (0.6 mM) in water at different temperatures (20–90 °C); path length: 0.1 cm.

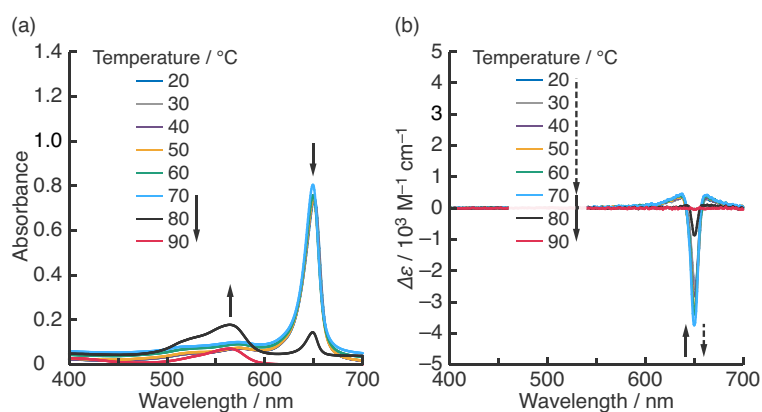


Fig. S14 (a) Visible absorption and (b) CD spectra of Cy2 (0.03 mM) in the presence of 16-Ly (0.6 mM) in water at different temperatures (20–90 °C); path length: 0.1 cm.

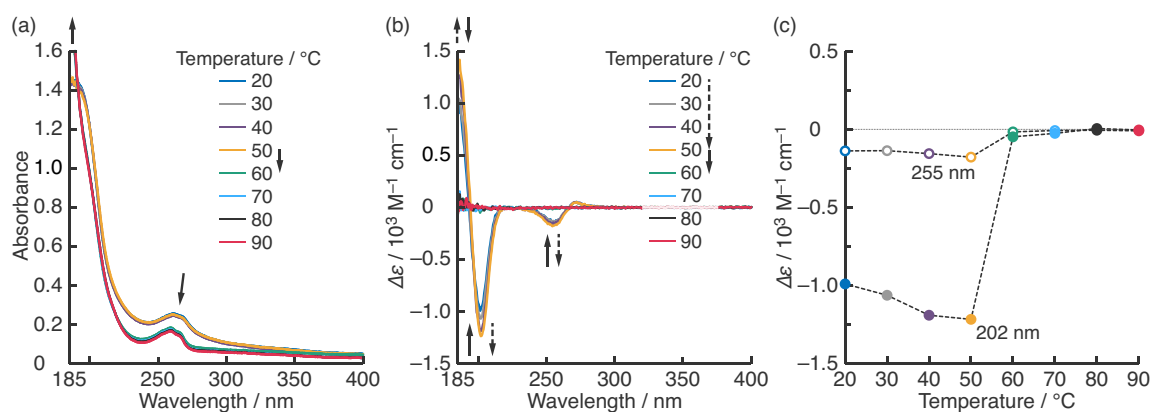


Fig. S15 (a) UV absorption and (b) CD spectra of 12-Ly (0.6 mM) in water at different temperatures; path length: 0.1 cm. (c) Variation in $\Delta\epsilon$ at 202 and 255 nm as a function of temperatures obtained from (b).

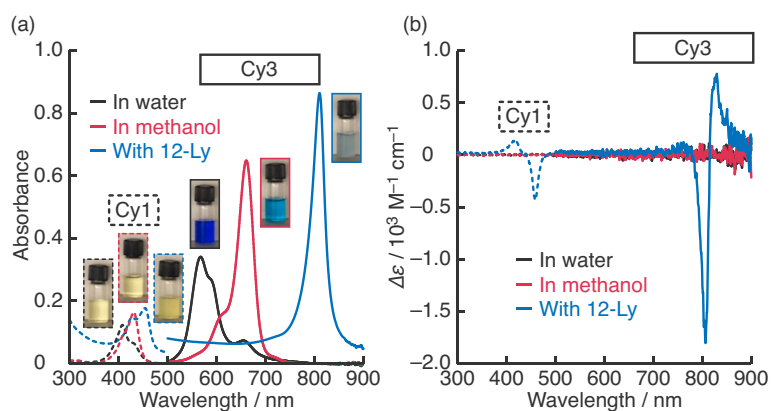


Fig. S16 (a) UV-visible absorption and (b) CD spectra of Cy1 and Cy3 (0.03 mM) in the presence and absence of 12-Ly (0.6 mM) in water and alone in methanol at 20 °C; path length: 0.1 cm. Dashed and solid lines denote the spectra of Cy1 and Cy3, respectively. Insets in (a) show images of the Cy1/Cy3–12-Ly aqueous mixture, Cy1/Cy3 aqueous solution, and Cy1/Cy3 methanol solution at 20 °C in daylight.

Author contributions

N. Ryu: Conceptualization (lead), Data curation, Formal analysis, Funding acquisition, Methodology, Project administration, Resources, Supervision, Visualization, and Writing – original draft (lead). **Y. Yamamoto:** Formal analysis, Investigation (lead), Validation, Visualization, and Writing – original draft. **Y. Okazaki:** Investigation and Writing – review & editing. **N. Hano:** Investigation. **Y. Iwamoto:** Investigation. **T. Shirosaki:** Investigation and Writing – review & editing. **S. Nagaoka:** Resources. **R. Oda:** Resources, Funding acquisition, and Writing – review & editing. **H. Ihara:** Conceptualization and Writing – review & editing. **M. Takafuji:** Data curation, Resources, Supervision, and Writing – review & editing.