

Supplementary Information

Co-assembling system that exhibits bright circularly polarized luminescence

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Experimental details

Materials

NK-77 (3,3'-diethyl-9-methylthiacarbocyanine iodide) was purchased from Nippon Kanko Shikiso Kenkyusho Co., Ltd. (Okayama, Japan) and was used as received. Sodium chloride and ethanol were purchased from Nacalai Tesque, Inc. (Kyoto, Japan) and were used as received. Other chemicals were also purchased commercially and were used without further purification. Millipore deionized water was used throughout this work.

Preparation and structure confirmation of amphiphile L-1 and D-1 (4-(N^α, N^ϵ -didodecanoyl-L- and D-lysine amido)butanoic acid)

N^α, N^ϵ -Didodecanoyl-L- and D-lysine (abbreviated as L-2 and D-2) and γ -aminobutyric acid benzyl ester *p*-toluenesulfonate were synthesized according to the procedure presented in a previous report.¹¹ These compounds were then coupled with diethyl cyanophosphonate (DEPC) in chloroform containing *N,N*-diisopropylethylamine (DIPEA), and were then catalytically reduced with hydrogen gas in the presence of palladium-activated carbon (Pd: 10%) in tetrahydrofuran (THF) (see Scheme S1).

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

L-1 (4-(N^α, N^ϵ -didodecanoyl-L-lysine amido)butanoic acid): white solid; 79% overall yield from L-2; m.p. 112–115°C; ^1H NMR (400 MHz, CDCl_3): δ =0.88 (t, 6H, J =6.6 Hz; $\text{CH}_3 \times 2$), 1.26 (s, 34H; $\text{CH}_3(\text{CH}_2)_8 \times 2$, CHCH_2CH_2), 1.43–1.54 (m, 1H; $\text{CH}(\text{CH}_2)_2\text{CH}_2$), 1.56–1.68 (m, 6H; $\text{CHCH}_2\text{CH}_2\text{CH}_2$, $\text{CH}_3(\text{CH}_2)_8\text{CH}_2 \times 2$), 1.78–1.90 (m, 2H; CHCH_2 , $\text{CH}_2\text{CH}_2\text{COOH}$), 1.90–2.01 (m, 1H; $\text{CH}_2\text{CH}_2\text{COOH}$), 2.14–2.27 (m, 4H; $\text{CH}_2\text{CONH} \times 2$), 2.34–2.41 (m, 1H; CH_2COOH), 2.45–2.52 (m, 1H; CH_2COOH), 3.17–3.25 (m, 1H; NHCH_2), 3.28–3.43 (m, 3H; $\text{NHCH}_2 \times 2$), 4.36 (q, 1H, J =7.0 Hz; CH), 5.76 (t, 1H, J =5.9 Hz; NHCH_2), 6.40 (d, 1H, J =7.3 Hz; NHCH), 6.74 (t, 1H, J =5.0 Hz; NHCH_2) ppm (Fig. S1a); ^{13}C NMR (100 MHz, CDCl_3): δ =14.13 ($\text{CH}_3 \times 2$), 22.15 (CH_2), 22.70 ($\text{CH}_3\text{CH}_2 \times 2$), 23.61 (CH_2), 25.67 (CH_2), 25.76 (CH_2), 29.09 (CH_2), 29.36 (CH_2), 29.53 (CH_2), 29.64 (CH_2), 31.93 (CH_2), 32.17 (CHCH_2), 36.64 (CH_2COOH), 36.88 (CH_2CONH), 38.76 (NHCH_2), 39.86 (NHCH_2), 52.83 (CH), 171.97 (CONH), 173.60 (CONH), 174.42 (CONH), 176.32 (COOH) ppm (Fig. S2a); IR (ATR): $\tilde{\nu}$ =3293 ($\nu_{\text{N-H}}$), 2953 ($\nu_{\text{C-H}}$), 2918 ($\nu_{\text{C-H}}$), 2850 ($\nu_{\text{C-H}}$), 1703 ($\nu_{\text{C=O}}$), 1633 ($\nu_{\text{C=O}}$), 1550 ($\delta_{\text{N-H}}$), 1467 ($\delta_{\text{C-H}}$), 945 ($\delta_{\text{O-H}}$), 719 ($\rho_{\text{C-H}}$) cm^{-1}

(Fig. S3a); EA: calcd for $C_{34}H_{65}N_3O_5$: C 68.53, H 10.99, N 7.05%; found: C 68.88, H 10.64, N 7.11%.

D-1 (4-(N^{α},N^{ϵ} -didodecanoyl-D-lysinaido)butanoic acid): white solid; 74% overall yield from **D-2**; m.p. 112–115°C; 1H NMR (400 MHz, $CDCl_3$): δ =0.88 (t, 6H, J =6.9 Hz; $CH_3 \times 2$), 1.25 (s, 34H; $CH_3(CH_2)_8 \times 2$, $CHCH_2CH_2$), 1.43–1.53 (m, 1H; $CH(CH_2)_2CH_2$), 1.55–1.68 (m, 6H; $CHCH_2CH_2CH_2$, $CH_3(CH_2)_8CH_2 \times 2$), 1.78–1.90 (m, 2H; $CHCH_2$, CH_2CH_2COOH), 1.91–2.00 (m, 1H; CH_2CH_2COOH), 2.14–2.27 (m, 4H; $CH_2CONH \times 2$), 2.34–2.41 (m, 1H; CH_2COOH), 2.44–2.51 (m, 1H; CH_2COOH), 3.17–3.26 (m, 1H; $NHCH_2$), 3.28–3.42 (m, 3H; $NHCH_2 \times 2$), 4.37 (q, 1H, J =7.2 Hz; CH), 5.81 (t, 1H, J =5.7 Hz; $NHCH_2$), 6.45 (d, 1H, J =7.8 Hz; $NHCH$), 6.81 (t, 1H, J =5.0 Hz; $NHCH_2$) ppm (Fig. S1b); ^{13}C NMR (100 MHz, $CDCl_3$): δ =14.12 ($CH_3 \times 2$), 22.25 (CH_2), 22.69 ($CH_3CH_2 \times 2$), 23.64 (CH_2), 25.66 (CH_2), 25.77 (CH_2), 29.08 (CH_2), 29.32 (CH_2), 29.35 (CH_2), 29.52 (CH_2), 29.63 (CH_2), 31.92 (CH_2), 32.06 ($CHCH_2$), 36.62 (CH_2COOH), 36.87 (CH_2CONH), 38.76 ($NHCH_2$), 39.70 ($NHCH_2$), 52.83 (CH), 171.98 ($CONH$), 173.64 ($CONH$), 174.39 ($CONH$), 176.30 ($COOH$) ppm (Fig. S2b); IR (ATR): $\tilde{\nu}$ =3292 (ν_{N-H}), 2953 (ν_{C-H}), 2918 (ν_{C-H}), 2850 (ν_{C-H}), 1702 ($\nu_{C=O}$), 1633 ($\nu_{C=O}$), 1551 (δ_{N-H}), 1467 (δ_{C-H}), 939 (δ_{O-H}), 720 (ρ_{C-H}) cm^{-1} (Fig. S3b); EA: calcd for $C_{34}H_{65}N_3O_5$: C 68.53, H 10.99, N 7.05%; found: C 68.83, H 10.62, N 7.14%.

Characterization of self-assembled amphiphile 1

Formation of the self-assembly of amphiphile **1** in water was confirmed via scanning transmission electron microscopy (STEM) and scanning electron microscopy (SEM) observations using an SU8000 scanning electron microscope (Hitachi High-Tech Corp., Tokyo, Japan). The dispersion of **1** was then spotted onto a carbon-coated copper grid. The sample was air-dried at room temperature by blotting excess dispersion, and the samples were then post-stained with osmium tetroxide using an osmium plasma coater (OPC60A, Filgen, Inc., Nagoya, Japan).

The gel-to-liquid crystalline phase transition temperature (T_c) and transition enthalpy (ΔH) values of the self-assembled amphiphile **1** in water were measured via differential scanning calorimetry (DSC) measurements using an EXSTAR DSC7020 calorimeter (Hitachi High-Tech). After encapsulation in a silver capsule, 5 mM dispersions (15 μ L) were scanned using a heating rate of 2.0°C min^{-1} .

Preparation of NK-77–amphiphile 1 aqueous mixtures

Amphiphile **1** was dissolved in basic water (containing NaCl) by heating. The resulting **1** dispersions were added to NK-77 and then heated to dissolve the NK-77. After cooling to 20°C, these solutions were then subjected to optical spectral measurements. The pH values of all samples were adjusted to the 10.0–10.5 range using NaOH.

Optical spectral measurements

The ultraviolet–visible (UV–vis) absorption, circular dichroism (CD) and linear dichroism (LD) spectra were measured 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 measured using an FP-6500 spectrofluorometer (JASCO) equipped with an ETC-273 temperature controller (JASCO). The circularly polarized luminescence (CPL) spectra were measured using a CPL-200 spectrofluoropolarimeter (JASCO) equipped with a PTC-423L temperature controller (JASCO). Sample solutions in a 0.1-cm-path-length quartz cell (for the UV–vis absorption, CD and CPL spectra) or a 1×0.1 cm quartz cell (for the emission spectra) were incubated in a sample holder for 5 min at specified temperatures before the measurements were performed.

Simulation of molecular structure

Simulations of the molecular structure of NK-77 were performed using a molecular modeling system (HyperChem, Hypercube Inc., Gainesville, FL, USA). The molecular structure was optimized using the molecular mechanics (MM+) and semi-empirical self-consistent-field molecular-orbital (PM3) methods.

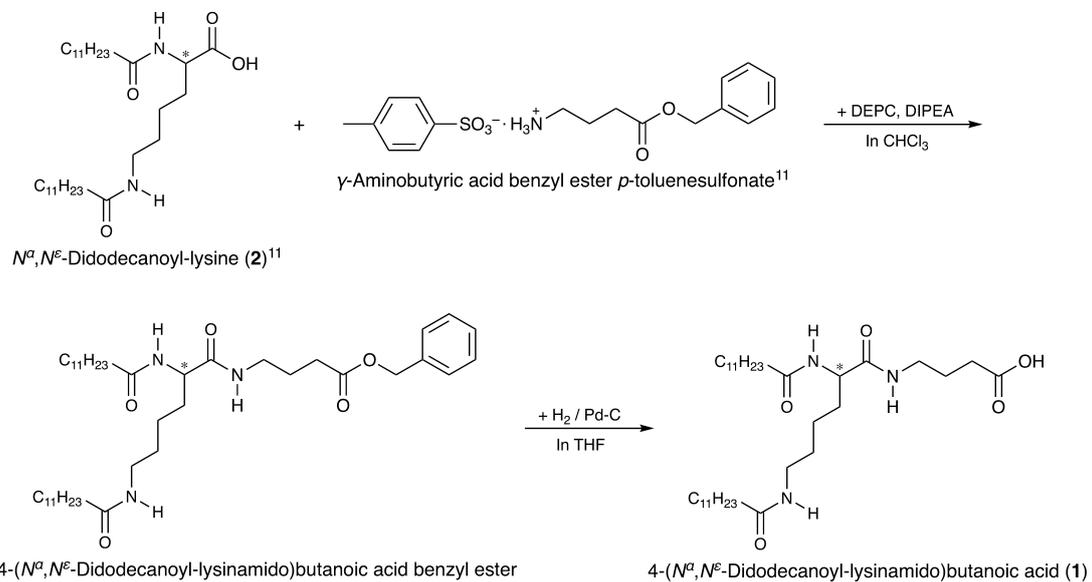
Emission quantum yield measurement

The emission quantum yield (ϕ) was measured using an absolute photoluminescence quantum yield measurement system (C9920-02, Hamamatsu Photonics K.K., Hamamatsu, Shizuoka, Japan) at ambient temperature (20°C).

Emission lifetime measurement

The time-resolved emission lifetime was measured using a fluorescence lifetime measurement system (Quantaaurus-Tau C11367-01, Hamamatsu Photonics K.K., Hamamatsu, Shizuoka, Japan) at ambient temperature (20 °C).

Supplementary figures



Scheme S1 Synthesis of amphiphile **1**.

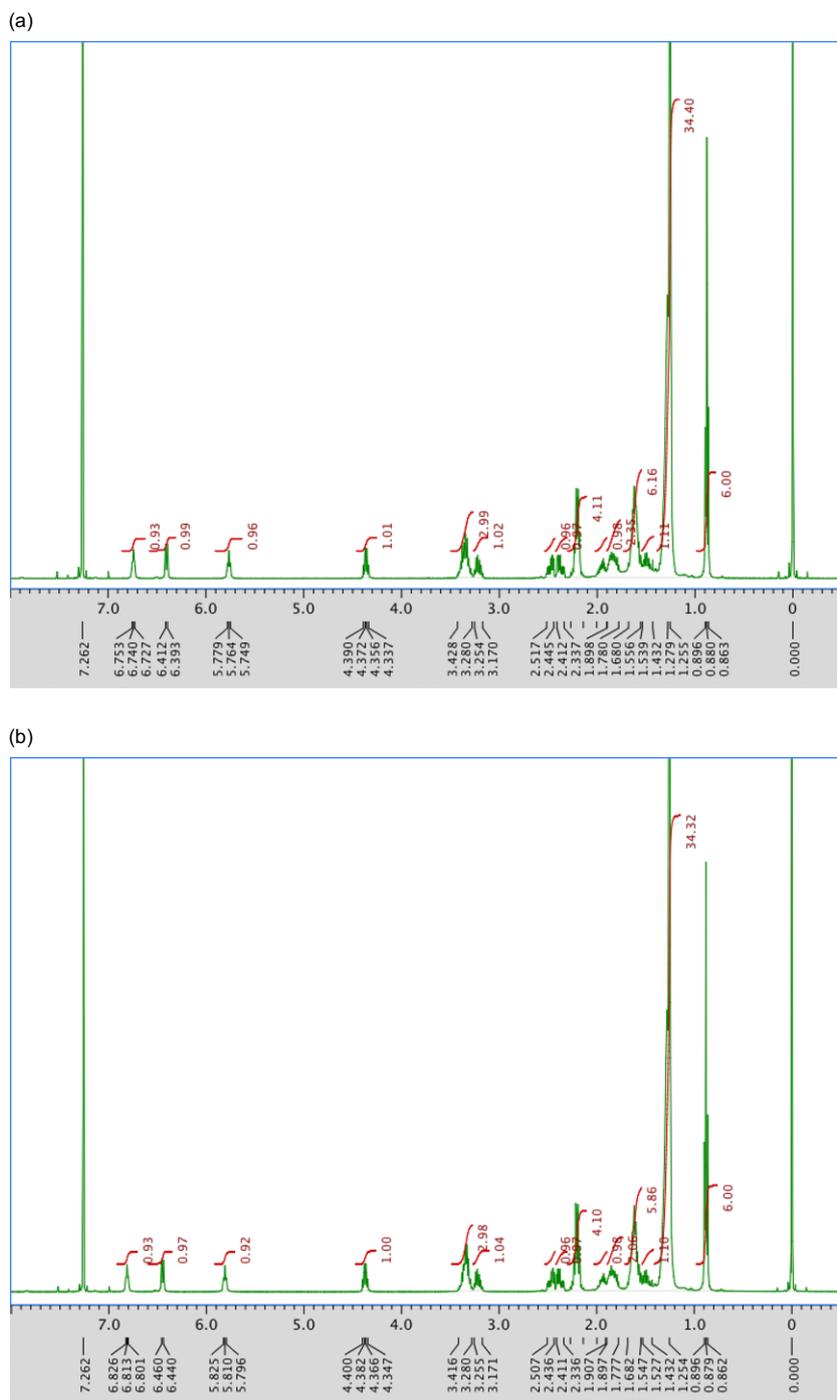


Fig. S1 ^1H NMR spectra of (a) L-1 and (b) D-1 in CDCl_3 ; 400 MHz, 50°C .

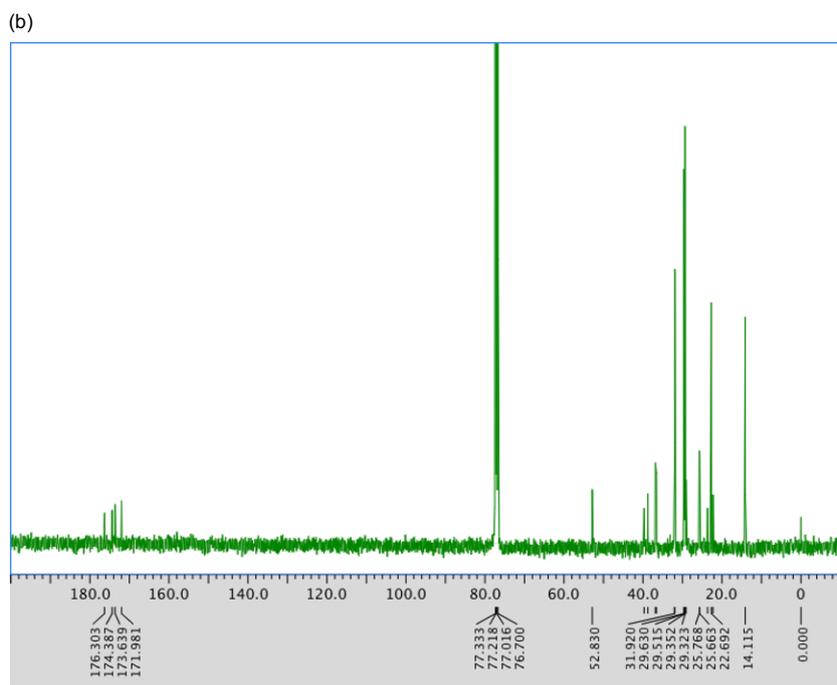
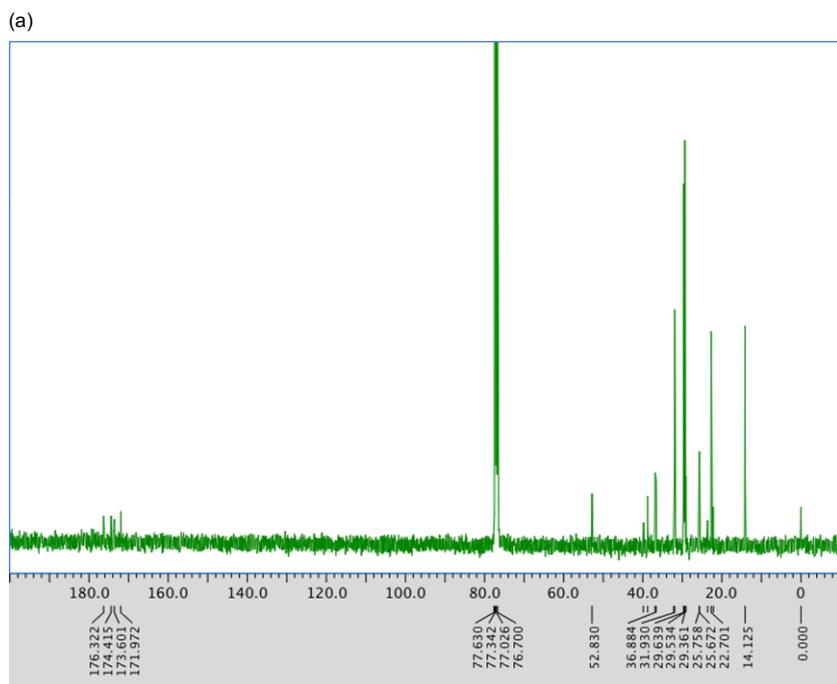


Fig. S2 ^{13}C NMR spectra of (a) L-1 and (b) D-1 in CDCl_3 ; 100 MHz, 50°C .

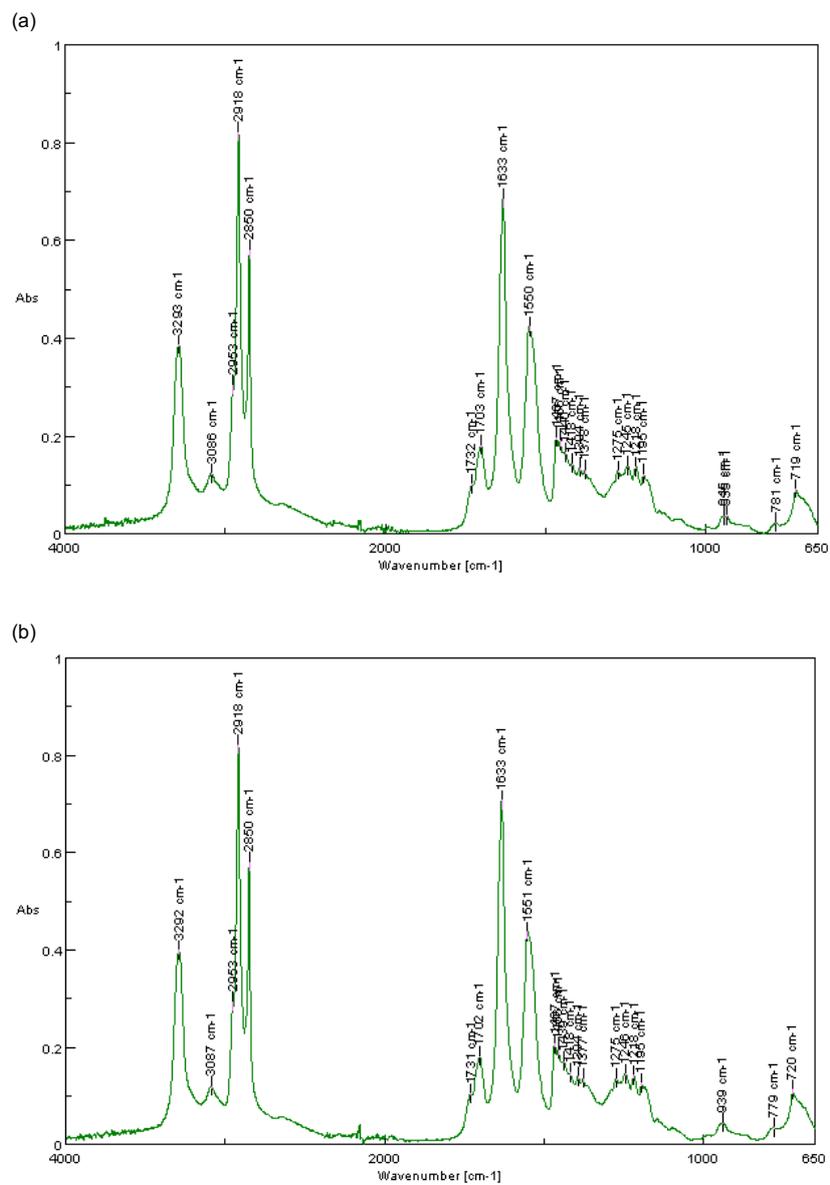


Fig. S3 FTIR spectra of (a) L-1 and (b) D-1 measured using the attenuated total reflectance method.

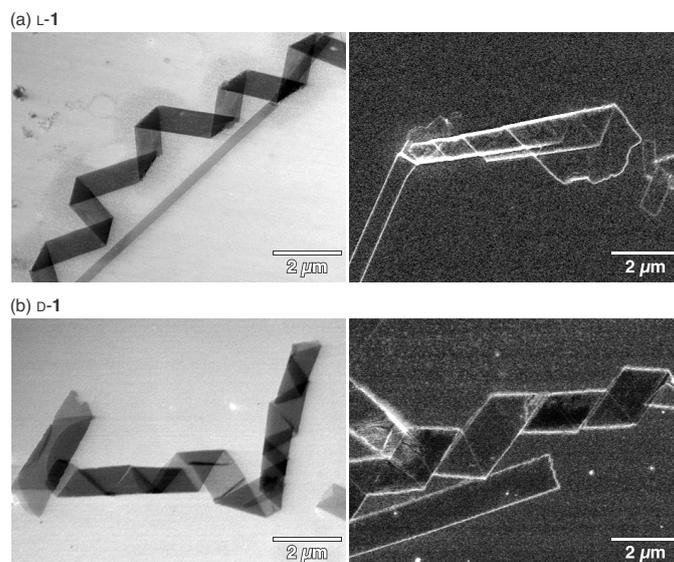


Fig. S4 STEM (left) and SEM (right) images of (a) L-1 and (b) D-1 assemblies in the cast film prepared from 0.2 mM aqueous dispersions without NaCl at pH 10 when post-stained with OsO₄. The images shown in (a) are taken from different areas of the same sample shown in Fig. 2b, inset (upper left).

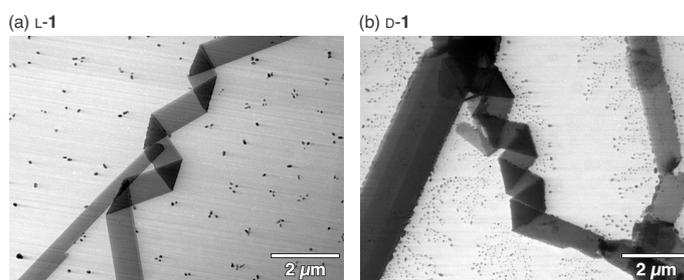


Fig. S5 STEM images of (a) L-1 and (b) D-1 assemblies in the cast film prepared from 0.2 mM aqueous dispersions containing NaCl (10 mM) at pH 10 when post-stained with OsO₄. The image shown in (a) are taken from different areas of the same sample shown in Fig. 2b, inset (lower right).

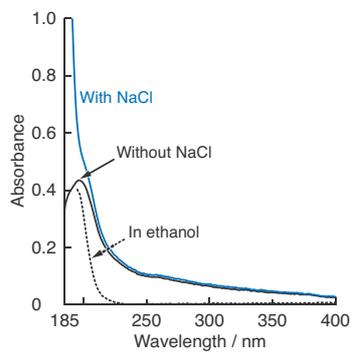


Fig. S6 UV absorption spectra of L-1 (0.2 mM) in water at pH 10 without and with NaCl (10 mM) and in ethanol at 20°C; path length: 0.1 cm.

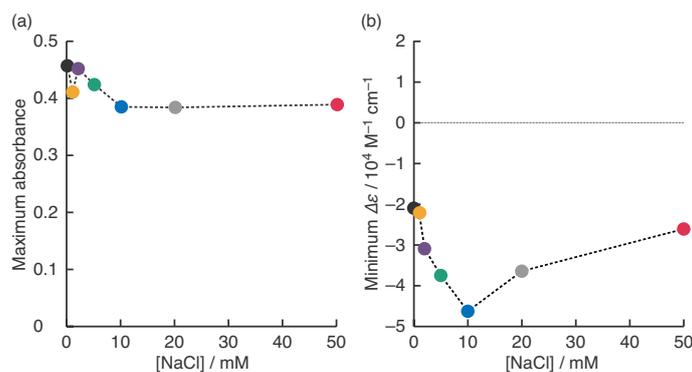


Fig. S7 Variations of (a) absorbance and (b) $\Delta\epsilon$ of NK-77 (0.01 mM) in the presence of L-1 (0.2 mM) in water at pH 10 containing various NaCl concentrations measured at 20°C; path length: 0.1 cm. These data were taken from Fig. 3.

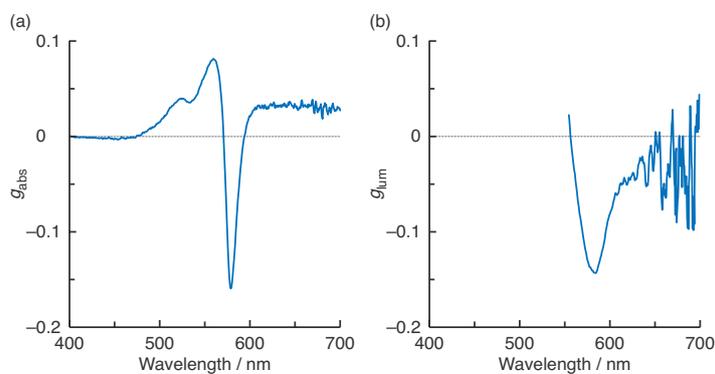


Fig. S8 (a) g_{abs} and (b) g_{lum} spectra of NK-77 (0.01 mM) in the presence of L-1 (0.2 mM) in water at pH 10 containing NaCl (10 mM) measured at 20°C.

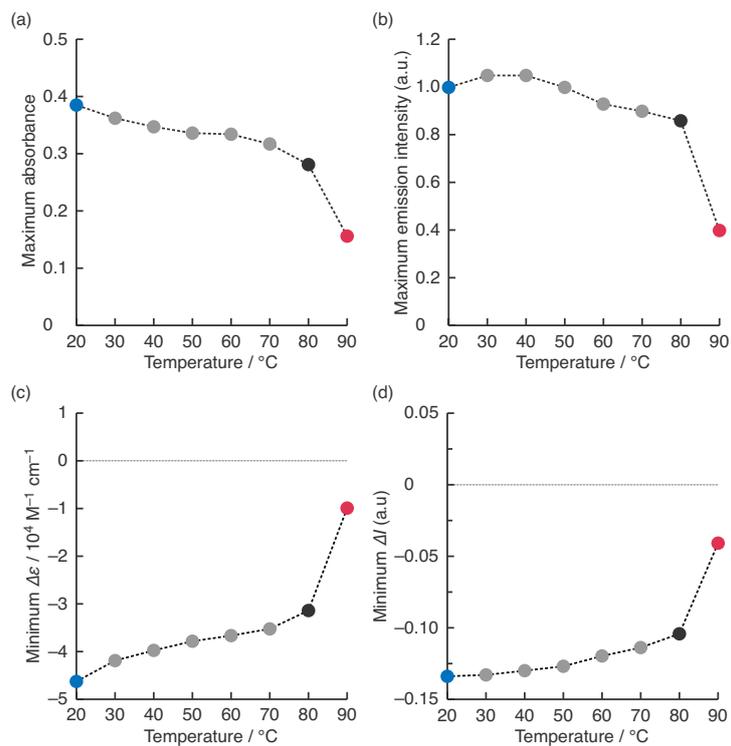


Fig. S9 Variations of (a) absorbance, (b) emission intensity, (c) $\Delta\varepsilon$ and (d) ΔI for NK-77 (0.01 mM) in the presence of L-1 (0.2 mM) in water at pH 10 containing NaCl (10 mM) as a function of temperature (20–90°C). These data were taken from Fig. 4a–d.

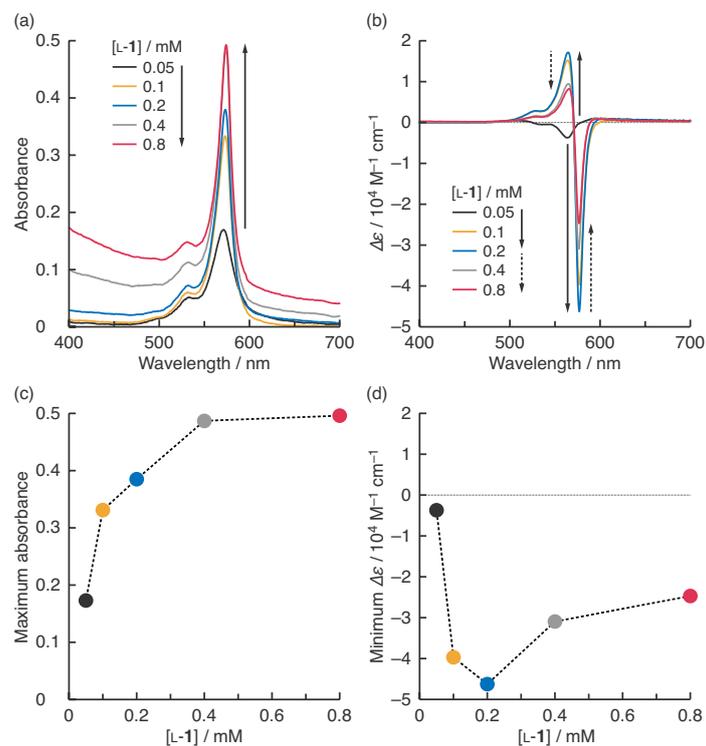


Fig. S10 (a) Visible absorption and (b) CD spectra, and variations of (c) absorbance and (d) $\Delta\epsilon$ of NK-77 (0.01 mM) in the presence of various concentrations of L-1 in water (pH 10) containing NaCl measured at 20°C; $[L-1] = 0.05, 0.1, 0.2, 0.4$ and 0.8 mM, $[L-1]:[NaCl] = 1:50$ mol/mol, and path length: 0.1 cm.

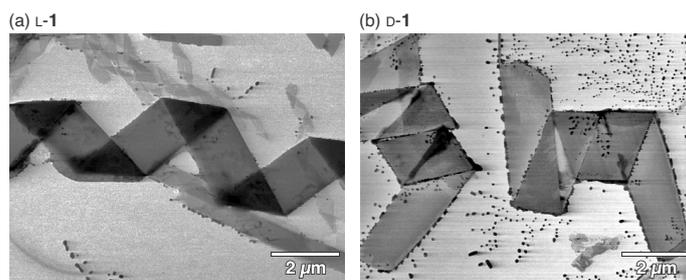


Fig. S11 STEM images of (a) L-1 and (b) D-1 assemblies with NK-77 in the cast film prepared from NK-77-1 aqueous dispersions (pH 10) containing NaCl when post-stained with OsO₄; $[NK-77] = 0.01$ mM, $[1] = 0.2$ mM, and $[NaCl] = 10$ mM.

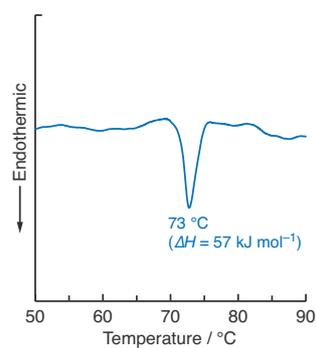


Fig. S12 DSC thermogram of the heating process for NK-77–L-1 co-assembly in basic water containing NaCl; [NK-77] = 0.25 mM, [L-1] = 5.0 mM, [NaCl] = 250 mM, and heating rate: 2°C min⁻¹.

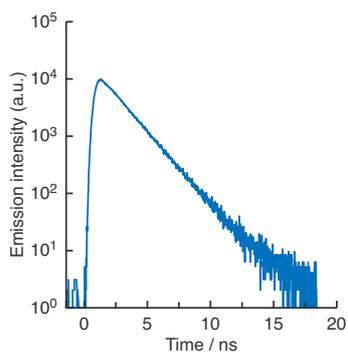


Fig. S13 Emission decay profile of NK-77 (0.01 mM) in the presence of L-1 (0.2 mM) in water at pH 10 containing NaCl (10 mM) measured at 20°C when monitored at 620 nm; excitation wavelength: 590 nm.

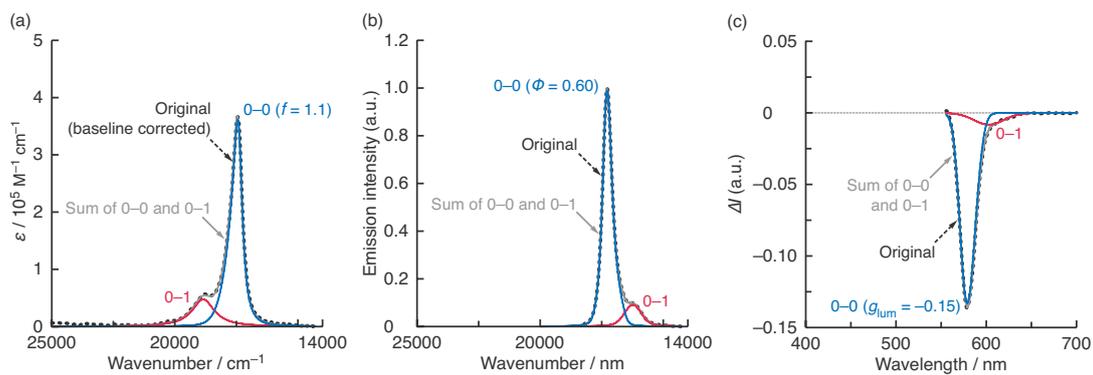


Fig. S14 (a) Visible absorption, (b) emission and (c) CPL spectra of NK-77 (0.01 mM) in the presence of L-1 (0.2 mM) in water at pH 10 containing NaCl (10 mM) measured at 20°C; path length: 0.1 cm (for (a)). Curve fittings were carried out using a Gaussian-Lorentzian function.

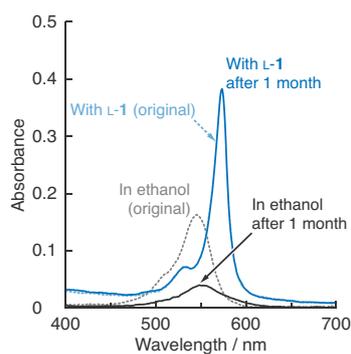


Fig. S15 Visible absorption spectra of NK-77 (0.01 mM) in the presence of L-1 (0.2 mM) in water at pH 10 containing NaCl (10 mM) and alone in ethanol measured at 20°C after 1 month from the measurements shown in Fig. 4a; path length: 0.1 cm.

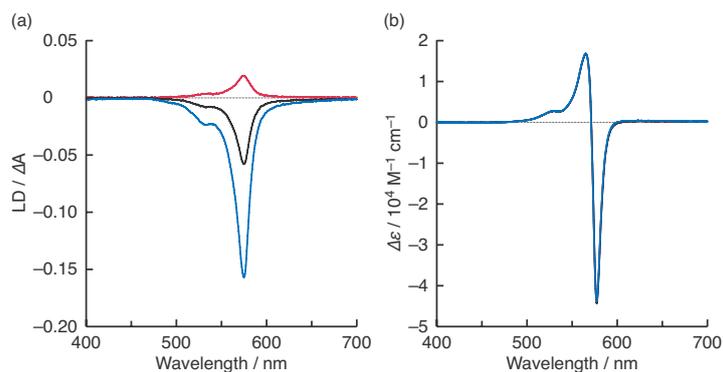


Fig. S16 (a) LD and (b) CD spectra of NK-77 (0.01 mM) in the presence of L-1 (0.2 mM) in water at pH 10 containing NaCl (10 mM) measured at 20°C. These spectra were obtained fortuitously by shaking the NK-77–L-1 dispersion.

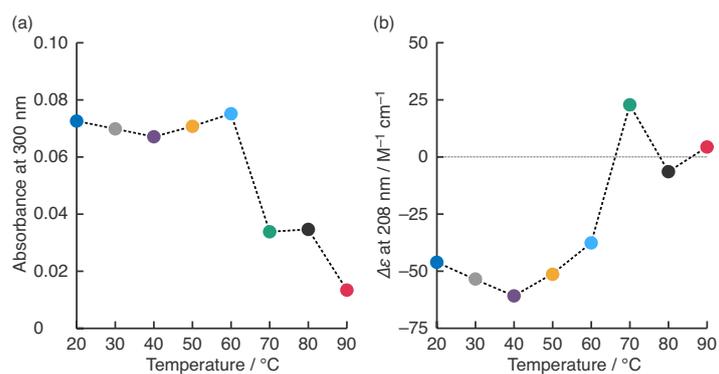


Fig. S17 Variations of (a) absorbance at 300 nm and (b) $\Delta\epsilon$ at 208 nm of L-1 (0.2 mM) in water at pH 10 containing NaCl (10 mM) measured at different temperatures (20–90°C); path length: 0.1 cm. These data were taken from Fig. 5a and b.