

Supplementary Information

**Fluorescence emission originated from H-aggregated cyanine dye  
with chiral gemini surfactant assemblies having narrow absorption  
band and remarkably large Stokes shift**

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## **Experimental details**

### **Materials and methods**

All gemini surfactants used in this study were previously synthesized.<sup>18</sup> 3,3'-Bis(sulfopropyl)-5,5'-dichloro-9-methylthiacarbocyanine triethylammonium (NK-2707) was purchased from Nippon Kanko Shikiso Kenkyusho Co., Ltd. (Okayama, Japan) and used as received. Other chemicals were also used without further purification. Millipore deionized water was used throughout this work.

### **Characterization of self-assembled gemini surfactants in water**

The formation of the self-assemblies of gemini surfactants in water was confirmed by transmission electron microscopy (TEM) observations with a JEOL JEM-1400Plus transmission electron microscope. Solutions of the gemini surfactants (0.4 mM) and their mixtures with NK-2707 were spotted onto carbon-coated copper grids. The samples were air-dried at room temperature by blotting excess solution using filter paper, after which the samples were post-stained with osmium tetroxide using a Filgen osmium plasma coater OPC60A.

Gel-to-liquid crystalline phase transition temperatures ( $T_c$ s) and transition enthalpies ( $\Delta H$ s) of self-assembled gemini surfactants in water was measured by differential scanning calorimetry (DSC) measurements with a SII EXSTAR DSC7020 calorimeter. Encapsulated in a silver capsule, 5 mM solutions (15  $\mu$ L) were scanned using a heating rate of 2.0  $^{\circ}$ C min<sup>-1</sup>.

### **Preparation of gemini surfactant–NK-2707 aqueous mixtures**

The gemini surfactants were dissolved in water by heating at 60  $^{\circ}$ C (above  $T_c$ ). After cooling to 20  $^{\circ}$ C for 3 h, the gemini surfactant solutions were added to NK-2707 aqueous solutions. These solutions were subjected to visible absorption, circular dichroism (CD), and fluorescence measurements after kept at 20  $^{\circ}$ C for 3 h from mixing. The pH of all samples was not adjusted in order to avoid ion exchange of tartrate counterions with other anions such as chloride. The pH was between 4.0 and 5.8. In this region of the pH, optical spectra of NK-2707 were not affected.

### **Visible absorption, CD and fluorescence spectral measurements**

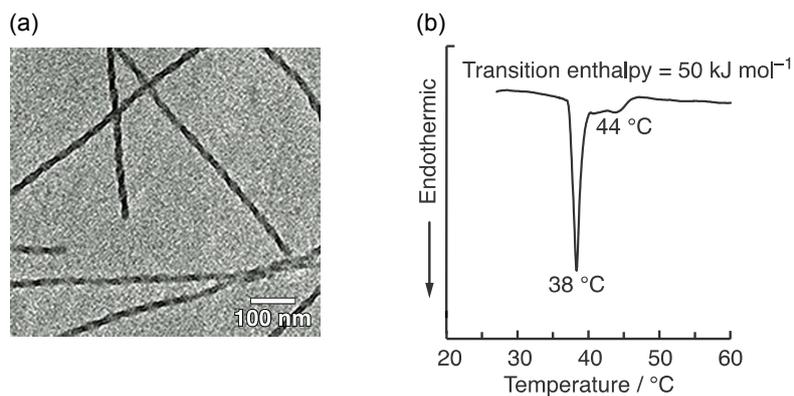
Samples in a 1.0 cm path length quartz cell were incubated in a sample holder for 10 min at 20  $^{\circ}$ C. Visible absorption spectra were measured with a JASCO Ubest V-560 UV/Vis spectrophotometer equipped with a JASCO ETC-505T temperature controller, CD spectra were measured with a JASCO J-820 spectropolarimeter equipped with a JASCO PTC-423L temperature controller, and fluorescence spectra were measured with a JASCO FP-6600 spectrofluorometer equipped with a JASCO EHC-573 temperature controller and a 390 nm cut-off filter (L-39, Toshiba Glass) in front of the excitation light.

### **Quantum yield and fluorescence lifetime measurements**

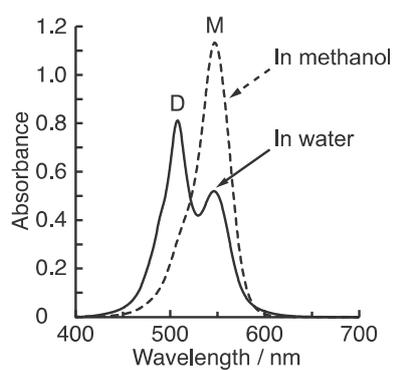
Fluorescence quantum yields of NK-2707 (0.01 mM) alone in methanol and in the presence of 16-2-16 L-tartrate (0.2 and 0.02 mM) in water were determined by the relative optical method using rhodamine B in ethanol as a reference (quantum yield: 0.54 [B. Valeur, in *Molecular Fluorescence: Principles and Applications*, ed. B. Valeur, Wiley-VCH, Weinheim, 2001, ch. 3, pp. 34–71.]). The fluorescence spectra of the solutions were measured by the front-face method.

Time-resolved fluorescence lifetime was measured with a fluorescence lifetime measurement system (Quantaaurus-Tau C11367-01, Hamamatsu Photonics K.K.) at room temperature. The detector was set to 582 nm for NK-2707 (0.05 mM) in methanol and 678 nm for NK-2707 (0.01 mM) in the presence of 16-2-16 L-tartrate (0.2 mM) in water. The both samples were excited at 470 nm.

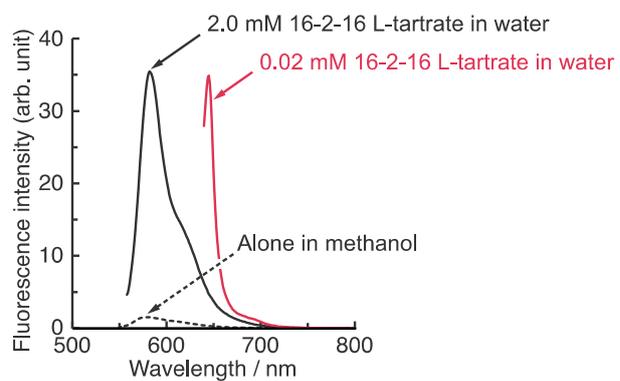
## Supplementary figures



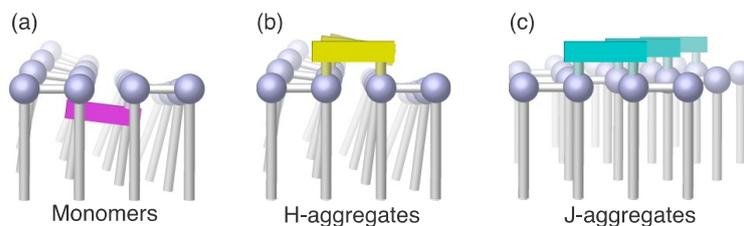
**Fig. S1** (a) TEM image of self-assembled 16-2-16 L-tartrate at 0.4 mM aged for 3 h at 20 °C in water post-stained with osmium tetroxide. (b) DSC thermogram of the heating process of 16-2-16 L-tartrate at 5.0 mM in water; heating rate: 2 °C min<sup>-1</sup>.



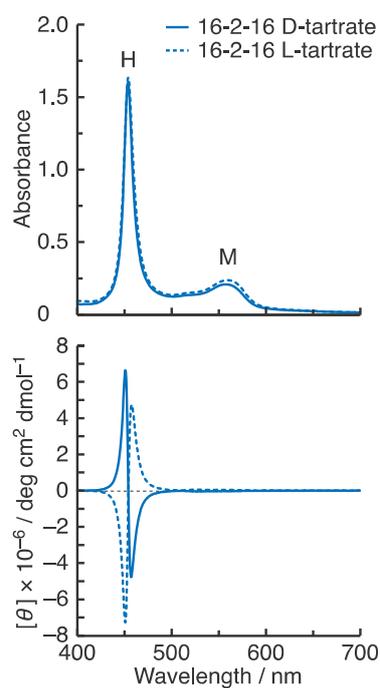
**Fig. S2** Visible absorption spectra of NK-2707 (0.01 mM) in water and methanol at 20 °C; path length: 1.0 cm. Monomer (M) and H-dimer (D) bands are labelled.



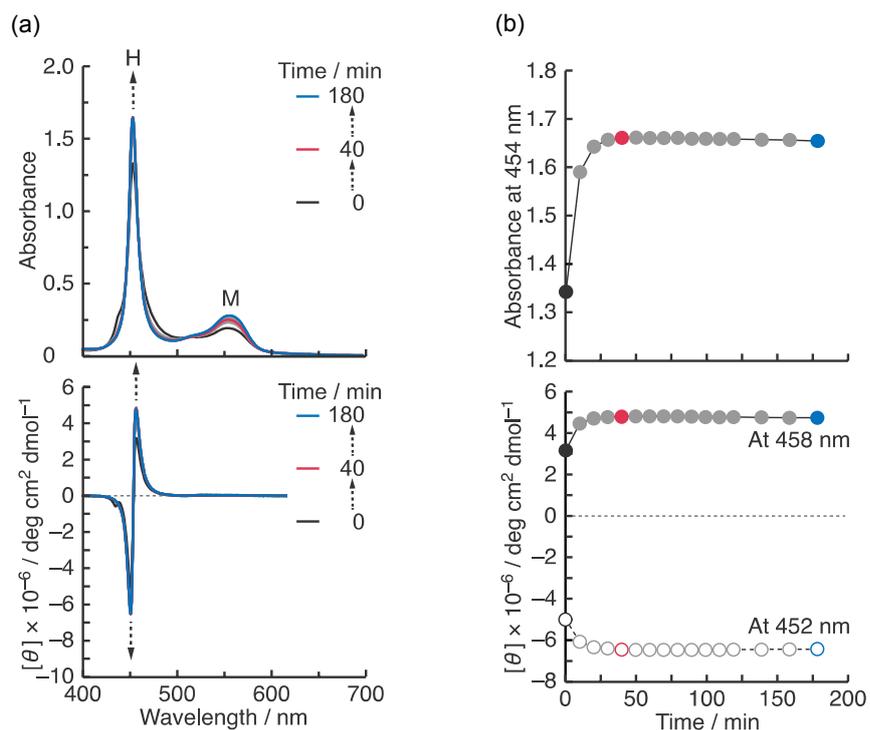
**Fig. S3** Fluorescence spectra of NK-2707 (0.01 mM) in the presence of 2.0 and 0.02 mM of 16-2-16 L-tartrate in water (excited at 554 nm for 2.0 mM and 638 nm for 0.02 mM) and alone in methanol (excited at 548 nm) at 20 °C; path length: 1.0 cm.



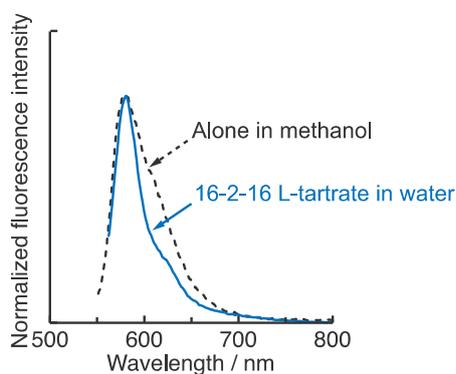
**Fig. S4** Schematic illustration of possible (a) monomer, (b) H- and (c) J-aggregate formation of NK-2707 induced by 16-2-16 L-tartrate assemblies. L-tartrate counterions and double bilayer structure are omitted for clarity.



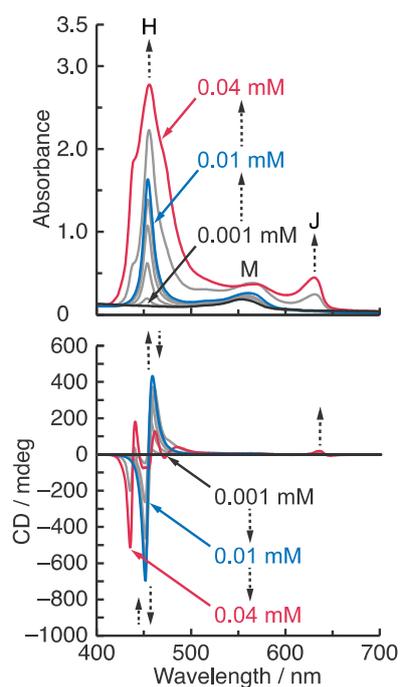
**Fig. S5** Visible absorption (top) and CD (bottom) spectra of NK-2707 (0.01 mM) in the presence of 16-2-16 D- and L-tartrate (0.2 mM) in water at 20 °C; path length: 1.0 cm. Monomer (M) and H-aggregate (H) bands are labelled.



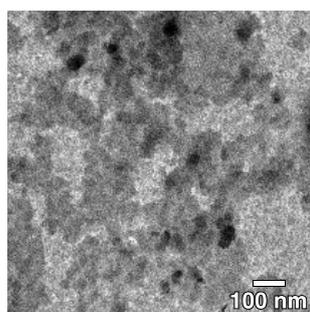
**Fig. S6** (a) Time dependence of visible absorption (top) and CD (bottom) spectra of NK-2707 (0.01 mM) in the presence of 16-2-16 L-tartrate (0.2 mM) in water at 20 °C; path length: 1.0 cm. Monomer (M) and H-aggregate (H) bands are labelled. (b) Time evolution of absorbance at 454 nm (top) and molar ellipticity at 452 and 458 nm (bottom) of NK-2707 (0.01 mM) in the presence of 16-2-16 L-tartrate (0.2 mM) in water at 20 °C; path length: 1.0 cm. These spectra were measured immediately after mixing.



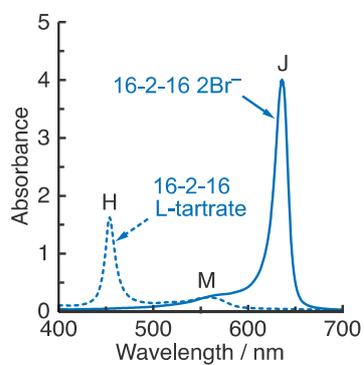
**Fig. S7** Normalized fluorescence spectra of NK-2707 (0.01 mM) in the presence of 0.2 mM of 16-2-16 L-tartrate in water (excited at 559 nm) and alone in methanol (excited at 548 nm) at 20 °C; path length: 1.0 cm.



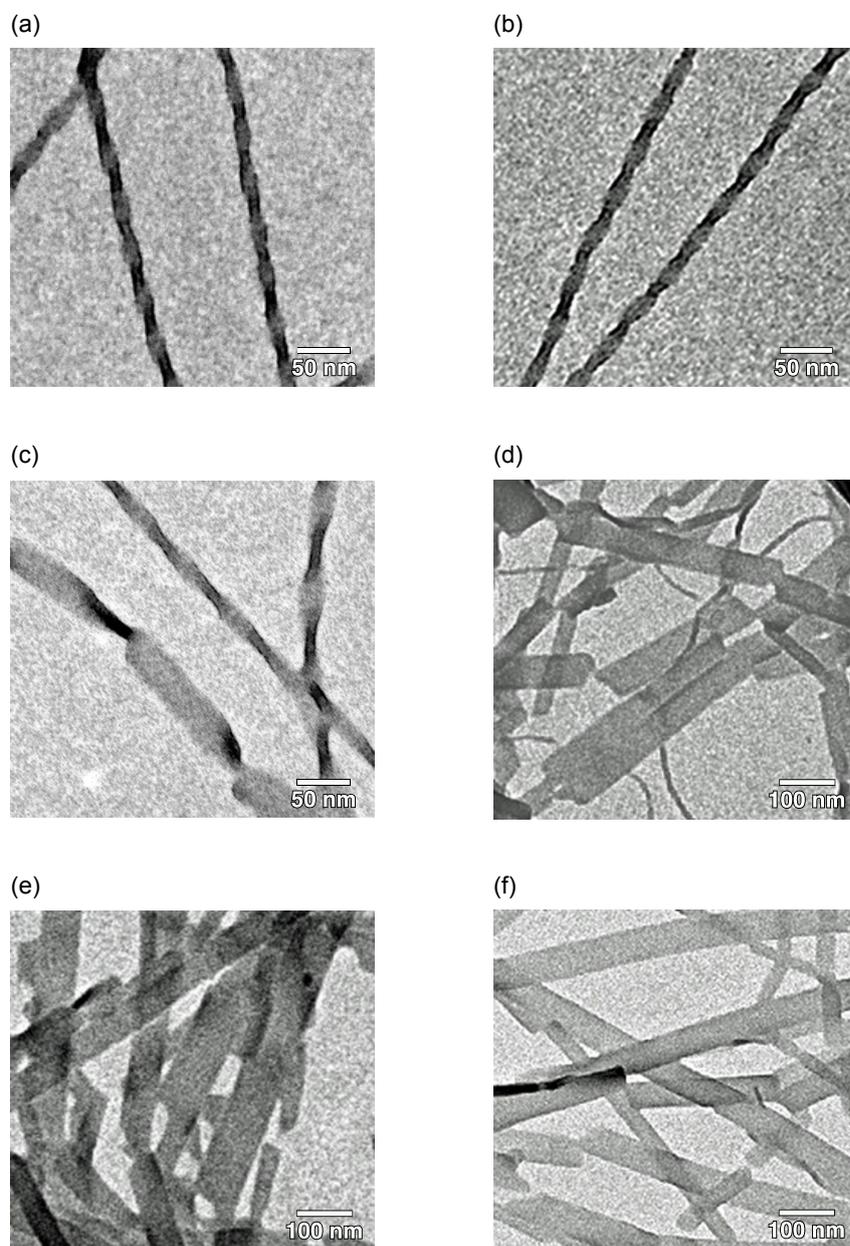
**Fig. S8** Visible absorption (top) and CD (bottom) spectra of various concentrations of NK-2707 in the presence of 16-2-16 L-tartrate (0.2 mM) in water at 20 °C; path length: 1.0 cm, [NK-2707] = 0.001, 0.002, 0.004, 0.006, 0.008, 0.01, 0.02 and 0.04 mM. Monomer (M) and H- (H) and J-aggregate (J) bands are labelled.



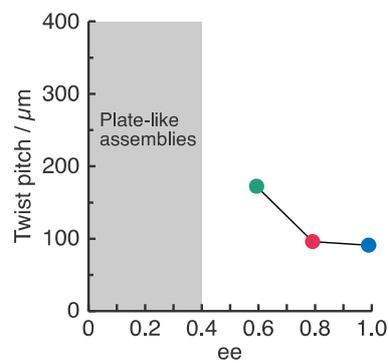
**Fig. S9** TEM image of self-assembled 16-2-16  $2\text{Br}^-$  at 0.4 mM aged for 3 h at 20 °C in water post-stained with osmium tetroxide.



**Fig. S10** Visible absorption spectra of NK-2707 (0.01 mM) in the presence of 0.02 mM of 16-2-16  $2\text{Br}^-$  and L-tartrate in water at 20 °C; path length: 1.0 cm. Monomer (M) and H- (H) and J-aggregate (J) bands are labelled.



**Fig. S11** TEM images of self-assembled 16-2-16 tartrate (0.4 mM) at different ee containing 0.02 mM NK-2707 in water post-stained with osmium tetroxide; ee: (a) 1.0, (b) 0.8, (c) 0.6, (d) 0.4, (e) 0.2 and (f) 0. These samples were prepared after 3 h mixing.



**Fig. S12** Variation of average twist pitch of ribbons prepared from mixture of 16-2-16 L- and DL-tartrate at 0.4 mM containing 0.02 mM NK-2707 as function of ee.