Electronic Supplemental Information (ESI)

Title

Qualitative / Chiral Sensing of Amino Acids by Naked-Eye Fluorescence Change Based on Morphological Transformation and Hierarchizing in Supramolecular Assemblies of Pyrene-Conjugated Glycolipids

Authors

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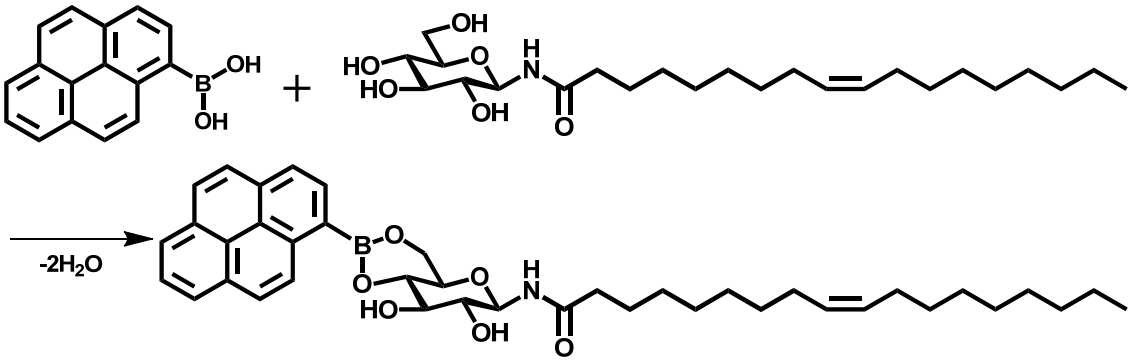

Scheme S1 Synthesis of fluorescent glycolipids **1** and **2**.

The glycolipid, N-(9-*cis*-octadecenoyl)-β-D-glucopyranosylamine, was synthesized as reported previously.* 1-pyreneboronic acid was purchased from Tokyo Chemical Co. and was used in the following reaction without purification. Quantitative dehydration reaction between the glycolipid (0.44 g, 1 mmol) and 1-pyreneboronic acid (0.25 g, 1 mmol) in toluene was performed under the reflux condition equipped with a Dean-Stark apparatus. After 3 h, the solvent was completely removed by evaporation. The obtained residue was washed with anhydrous THF for several times and was stored in vacuum desiccators. The fluorescent glycolipid **2** was synthesized by the boronate ester formation between N-(9-*cis*-octadecenoyl)-β-L-glucopyranosylamine and 1-pyreneboronic acid. The synthetic conditions and purification manners were similar to those of **1**.

*T. Shimizu et al., *Bull. Chem. Soc. Jpn.*, 2008, **81**, 1554.

1: 1H NMR (400 MHz, DMSO-d_6, 9.08 (d, J = 9.1 Hz, 1H: NH), 8.53 (d, J = 7.7 Hz, 1H: Pyrene), 8.44 (d, J = 7.7 Hz, 1H: Pyrene), 8.33–8.16 (m, 6H: Pyrene), 8.08 (t, J = 7.7 Hz, 1H, Pyrene), 5.59 (d, J = 5.5 Hz, 1H: Glucose-3OH), 5.33 (m, 2H: -CH=CH-), 5.18 (d, J = 5.9 Hz, 1H: Glucose-2OH), 5.01 (t, J = 9.1 Hz, 1H: Glucose-1), 4.03 (m, 1H: Glucose-6), 3.84-3.80 (m, 3H, Glucose-4, 5, 6), 3.60 (m, 1H: Glucose-3), 3.16 (m, 1H: Glucose-2), 2.18 (t, J = 7.3 Hz, 2H: -$COCH_2$-), 2.12 (m, 4H: -CH2-), 1.50 (m, 4H: -CH_2-), 1.24 (m, 18H: -CH_2-), 0.84 (t, J = 7.0 Hz, 3H: -CH_3). ESI-MS (m/z): 672.40 [M + OH]-. Anal. calcd for $C_{40}H_{54}BNO_6$: C 73.27, H 8.30, N 2.14. Found: C 72.97, H 8.34, N 2.13.

2: 1H NMR and ESI-MS data were similar to those of **1**. Anal. calcd for $C_{40}H_{54}BNO_6$: C 73.27, H 8.30, N 2.14. Found: C 72.91, H 8.40, N 2.12.

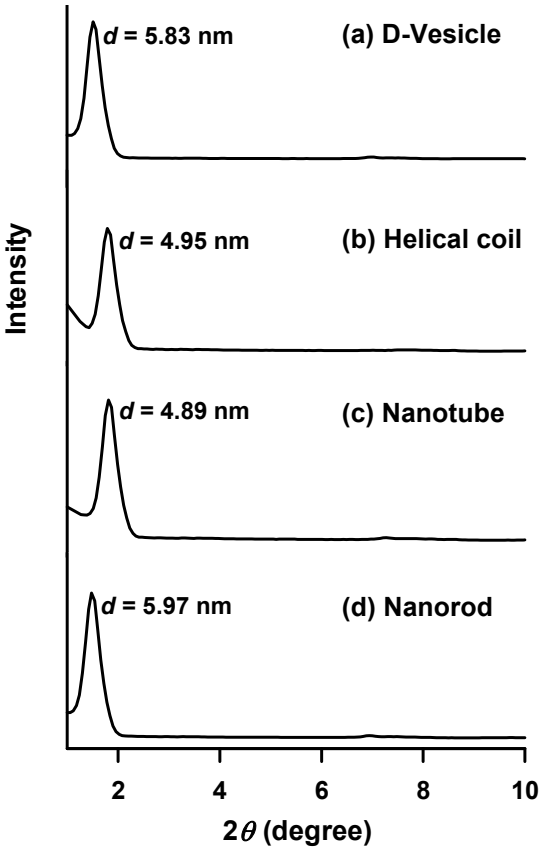

Fig. S1 XRD patterns of (a) the D-vesicle self-assembled from **1**, (b) the helical coil formed by the morphological transformation of the D-vesicle upon addition of L-tryptophan, (c) the nanotube formed by the morphological transformation of the D-vesicle upon addition of L-phenylalanine, (d) the nanorod formed by the morphological transformation of the D-vesicle upon addition of D-phenylalanine.

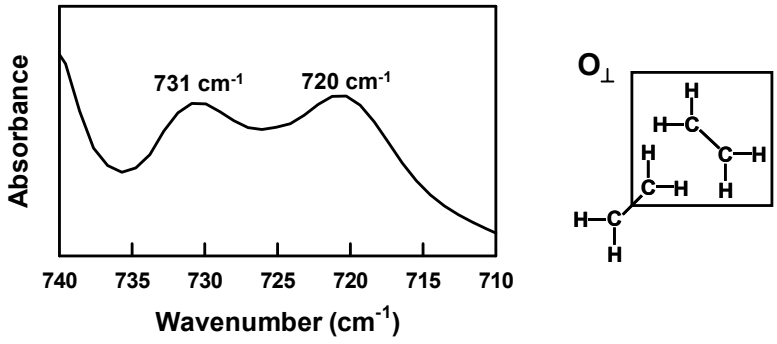

Fig. S2 The $\gamma(CH_2)$ rocking IR band of the D-vesicle and the subcell structure of the hydrocarbon chain.

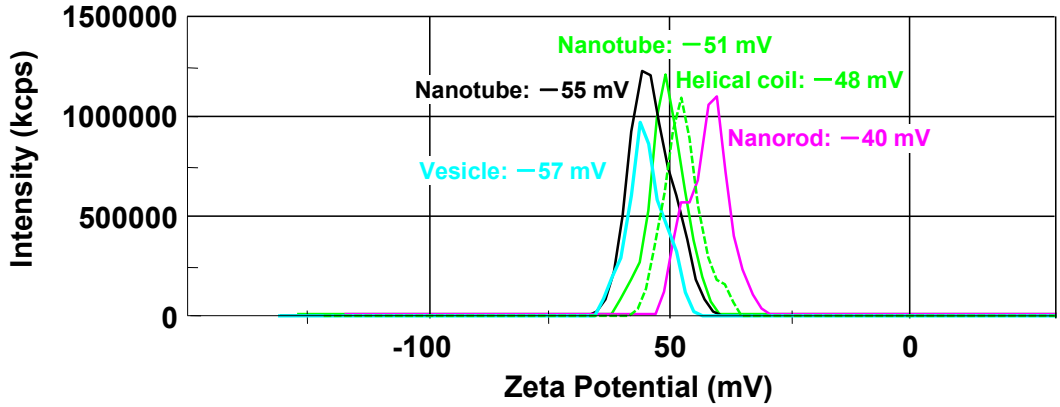

Fig. S3 The zeta potential distributions of the aqueous dispersions at pH 6.8 of D-vesicle (the blue line), the helical coil (the dotted green line) formed by the morphological transformation of the D-vesicle upon addition of L-tryptophan, the nanotube (the green line) formed by the morphological transformation of the D-vesicle upon addition of L-phenylalanine, the nanorod (the pink line) formed by the morphological transformation of the D-vesicle upon addition of D-phenylalanine and the nanotube (the black line) self-assembled from the glycolipid without 1-pyreneboronic acid. Each value was obtained from dynamic light scattering (DLS) measurements.

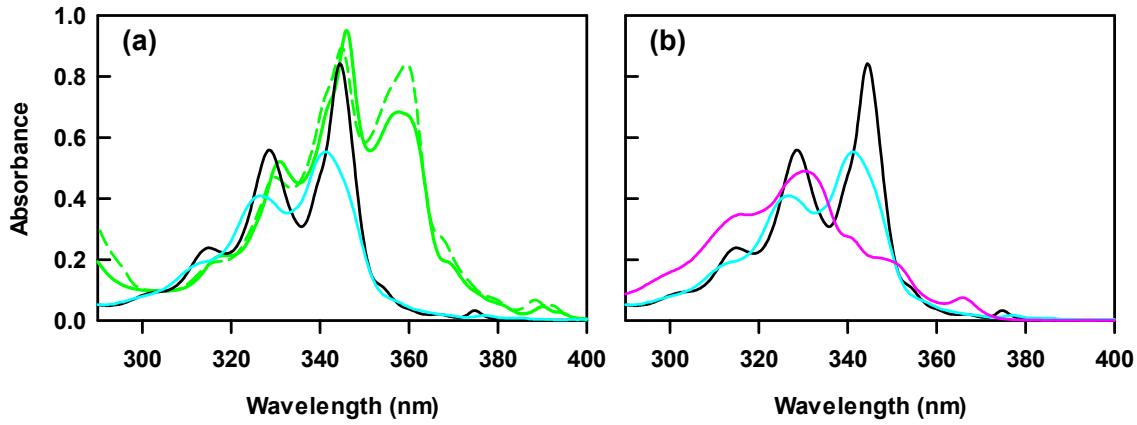

Fig. S4 (a) Absorption spectra of the aqueous dispersions of 1-pyreneboronic acid as the monomer state (the black line), the D-vesicle (the blue line) self-assembled from **1**, the helical coil (the dotted green line) formed by the morphological transformation of the D-vesicle upon addition of L-tryptophan and the nanotube (the green line) formed by the morphological transformation of the D-vesicle upon addition of L-phenylalanine. (b) Absorption spectra of the aqueous dispersions of 1-pyreneboronic acid as monomer state (the black line), the D-vesicle self-assembled from **1** (the blue line), the nanorod (the pink line) formed by the morphological transformation of the D-vesicle upon addition of D-phenylalanine.

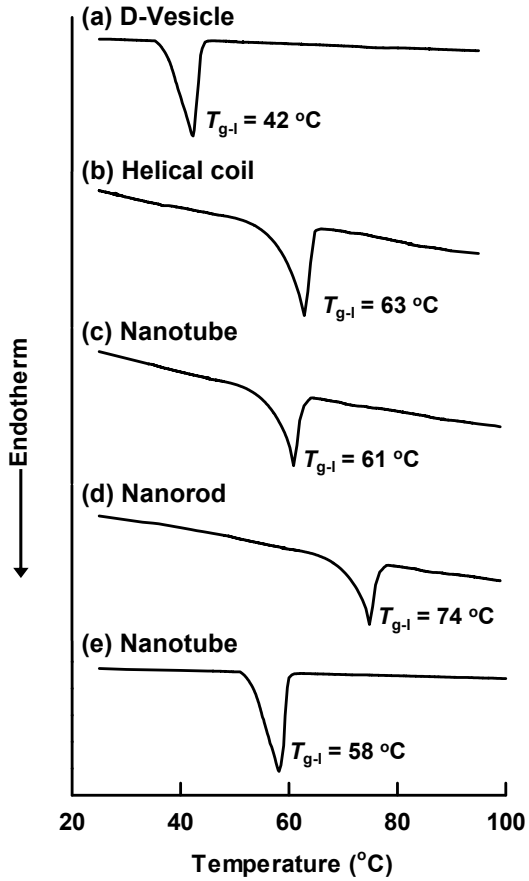

Fig. S5 DSC profiles of the fully hydrated self-assembled structures. Each nanostructure (1 mg) in the presence of water (20 mL) was placed in an aluminum pan to facilitate DSC measurements. (a) the D-vesicle self-assembled from **1**; (b) the helical coil formed by the morphological transformation of the D-vesicle upon addition of L-tryptophan; (c) the nanotube formed by the morphological transformation of the D-vesicle upon addition of L-phenylalanine; (d) the nanorod formed by the morphological transformation of the D-vesicle upon addition of D-phenylalanine; (e) the nanotube self-assembled from the glycolipid without 1-pyreneboronic acid.

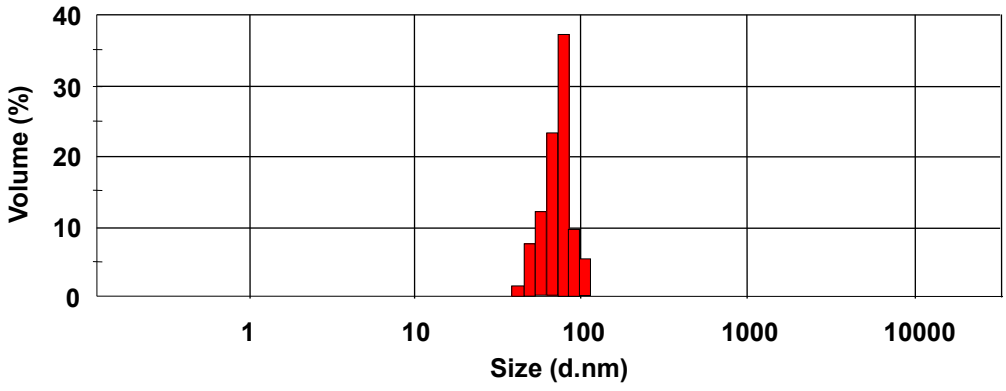

Fig. S6 The size distribution of the D-vesicle at 45 °C obtained from DLS measurements.

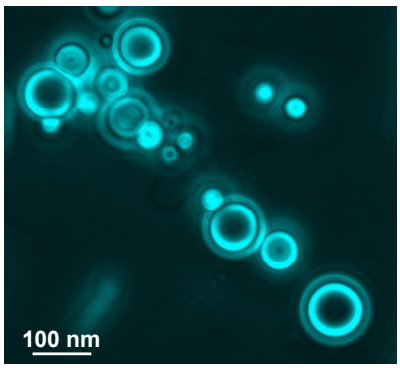

Fig. S7 Fluorescence microscopic image of the D-vesicle in water at 45 ^{o}C.

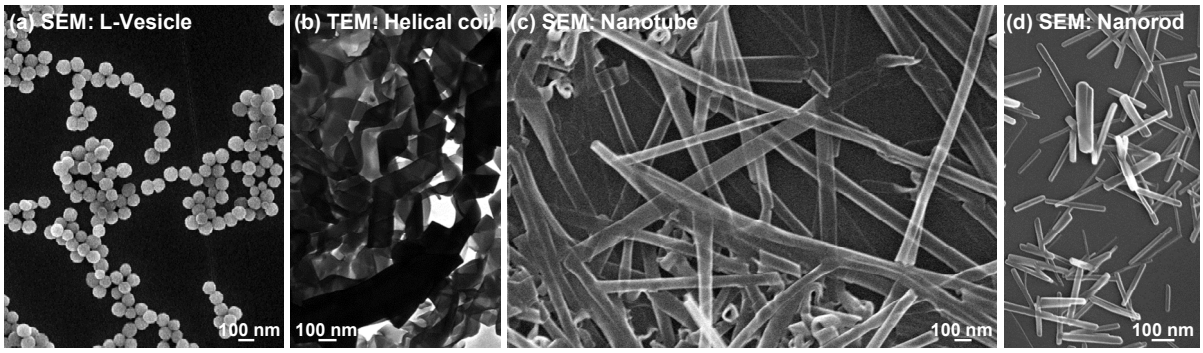

Fig. S8 SEM and TEM images of (a) the L-vesicles self-assembled from **2**, (b) the right-handed helical coils formed by the morphological transformation of the L-vesicle upon addition of D-tryptophan, (c) the nanotubes formed by the morphological transformation of the L-vesicle upon addition of D-phenylalanine, (d) the nanorods formed by the morphological transformation of the L-vesicle upon addition of L-phenylalanine.

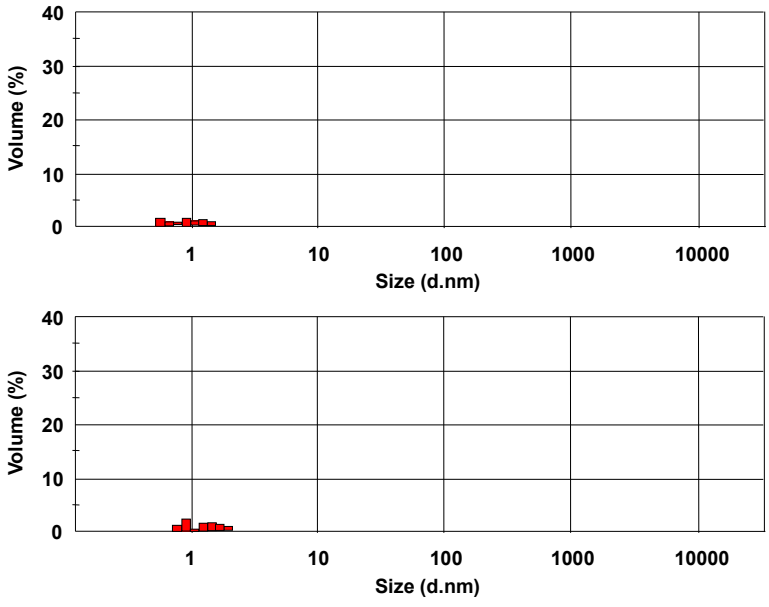

Fig. S9 DLS profiles of L-tryptophan (upper) and L-phenylalanine (lower).