

Supporting Information for
Self-Division of 2-D Sheets in Aromatic Macrocyclic Assembly

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1. General methods.

All reactions were performed either in oven-dried glassware under dry argon atmosphere. Toluene and tetrahydrofuran (THF) were dried by distillation from sodium benzophenone immediately prior to use. Dichloromethane (DCM) was dried by distillation from CaH_2 . Distilled water was polished by ion exchange and filtration. Other solvent and organic reagent were purchased from commercial vendors and used without further purification unless otherwise mentioned. The products were purified by flash column chromatography on silica gel (230–400 mesh). Thin-layer chromatography (TLC) was performed on precoated glass-backed plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm) or by treating the plates with iodine, anisaldehyde, KMnO_4 , phosphomolybdic acid, and vanillin followed by heating. ^1H and ^{13}C NMR spectra were obtained on 500 and 600 MHz FT-NMR spectrometers. All compounds are subjected to ^1H NMR analysis to confirm $\geq 98\%$ sample purity. Chemical shifts were reported in ppm relative to the tetramethylsilane peak (TMS, 0 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublets of doublets), dt (doublet of triplets), td (triplet of doublets), brs (broad singlet). Coupling constants are reported in Hz. MALDI TOF-MS spectroscopy (MALDI-TOF-MS) was performed on a Bruker autoflex TOF/TOF using α -cyano-4-hydroxy cinnamic acid (CHCA) as a matrix. UV/vis spectra were obtained from a Hitachi U-2900 Spectrophotometer. The fluorescence spectra were obtained from a Hitachi F-7000 Fluorescence Spectrophotometer. HPLC analysis was performed with Prominence LC-20AP (SHIMADAZU) equipped with YMC C4 reverse phase column (250 x 4.6 mm I.D., S-5 μm , 12nm and 250 x 20.0 mm ID, S 5 μm , 12 nm) for general separation (eluent condition: 85% CH_3CN in water, flow rate: 0.7 ml/min). Molecular dynamic simulations were performed using Macro Model and Desmond modules from Schrödinger Suites (Schrödinger K.K.).

TEM Experiments: To investigate the self-assembled structures in aqueous solution, a drop of each sample solution was placed on a carbon-coated copper grid (Carbon Type B (15-25 nm) on 200 mesh, with Formvar; Ted Pella, Inc.) and the solution was allowed to evaporate under ambient conditions. These samples were stained by depositing a drop of uranyl acetate aqueous solution (0.4–1.0 wt%) onto the surface of the sample-loaded grid. The dried specimen was observed by a JEOL-JEM HR2100 operated at 120 kV. The cryo-TEM experiments were performed with a thin film of aqueous solution of amphiphiles (3 μL) transferred to a lacy supported grid. The thin aqueous films were prepared under controlled temperature and humidity conditions (97–99%) within a custom-built environmental chamber in order to prevent evaporation of water from sample solution. The excess liquid was blotted with filter paper for 2–3 s, and the thin aqueous films were rapidly vitrified by plunging them into liquid ethane (cooled by liquid nitrogen) at its freezing point. The grid was transferred, on a Gatan 626 cryoholder, using a cryotransfer device and transferred to

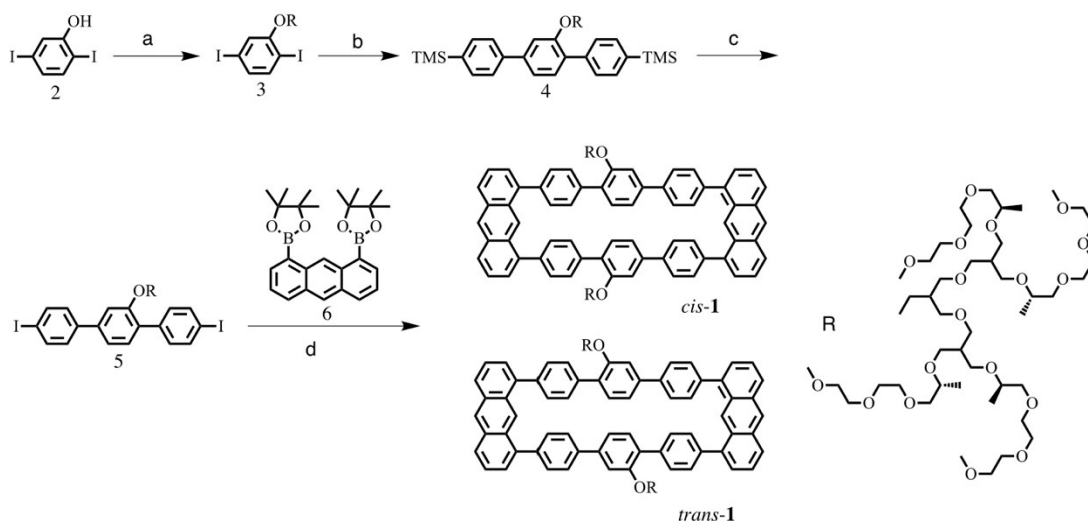
the JEOL-JEM HR2100 TEM. Direct imaging was carried out at a temperature of approximately $-175\text{ }^{\circ}\text{C}$ and with a 120 kV accelerating voltage, using the images acquired with a Dual vision 300 W and SC 1000 CCD camera (Gatan, Inc.; Warrendale, PA). The data were analyzed using Digital Micrograph software.

AFM Experiments: The sample films on mica surface were prepared from evaporation of sample solutions. The measurements were conducted on a Multi Mode 8 AFM with NanoScope V controller, NanoScope software and NanoScope Analysis software (Bruker AXS Corporation, Santa Barbara, CA, USA) in air at ambient temperature ($\approx 25\text{ }^{\circ}\text{C}$) in the scanasyt in air mode.

Molecular Simulation: The molecular dynamics simulations were calculated through Macro Model and Desmond module from Schrödinger Suites. The preliminary geometry of the molecules was optimized through the following parameters; force field: OPLS_2005, solvent: water, cutoff: Van der Waals (8.0) / electrostatic (20.0) / H-bond (4.0), minimization method: PRCG, maximum iterations: 2500, converge on: gradient, convergence threshold: 0.05, simulation temperature: 300.0 K.

Sampling Method: All sample solutions were prepared by evaporation of a CHCl_3 mixture of 1 ($64.5 \times 10^{-6}\text{ m}$), then water was added to the dry film and the solution was sonicated for 30 min in ice bath. The solution was then stored for 8 h.

2. Synthetic method.



Reagents and conditions: (a) ROTs, Cs_2CO_3 , CH_3CN , reflux, 12 h; (b) 4-(trimethylsilyl)phenylboronic acid, $\text{Pd}(\text{PPh}_3)_4$, 2M Na_2CO_3 (aq), THF, reflux, 12 h; (c) ICl, DCM, $0\text{ }^{\circ}\text{C}$, 2h; (d) $\text{Pd}(\text{PPh}_3)_4$, Cs_2CO_3 , toluene, $90\text{ }^{\circ}\text{C}$, 24 h.

Compound 4. Compound 3^{SI} (713mg, 0.575mmol), $\text{Pd}(\text{PPh}_3)_4$ (6.9 mg, 0.023 mmol) and 4-

(trimethylsilyl)phenylboronic acid (331.2mg, 1.725mmol) were refluxed in mixture of 2 M aqueous Na₂CO₃ (6 ml) and THF (6 ml) for 12 hours. After completion of the reaction as monitored by TLC, the reaction mixture was cooled down to room temperature. The resulting mixture was condensed under reduced pressure, and dissolved in ethyl acetate. The organic layer was washed with brine and dried over MgSO₄(s). The organic phase was filtered with Celite and the filtrate was condensed in a rotary evaporator. The crude product was purified by flash silica gel column chromatography (methanol: ethyl acetate= 1:20, v/v) to provide 68% yield. The pure product was characterized by ¹H-NMR spectroscopy (Figure S3).

¹H NMR (500 MHz, CD₂Cl₂) δ 7.80 (s, 1H), 7.74 (s, 1H), 7.62 – 7.41 (m, 8H), 7.31 – 7.26 (m, 1H), 4.17 (d, J = 5.4 Hz, 2H), 3.69 – 3.29 (m, 72H), 2.40 – 2.31 (m, 1H), 2.01 (dt, J = 11.5, 5.7 Hz, 2H), 1.09 (d, J = 6.2 Hz, 12H), 0.37 (s, 18H).

Compound 5. Compound 4 (420 mg, 0.252 mmol) was dissolved in anhydrous dichloromethane (DCM) (4.2 ml). ICl (1.0 M in DCM solution) (0.6 ml, 0.6 mmol) was added drop wise to the reactant solution at 0 °C ice bath. The mixture was stirred in 0 °C for 2 hours under atmosphere argon. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated Na₂S₂O₃ aqueous solution. The organic layer was washed with brine and dried over MgSO₄(s). The organic phase was filtered with Celite and the filtrate was condensed in a rotary evaporator. The crude product was purified by flash silica gel column chromatography (methanol: ethyl acetate= 1: 20, v/v) to provide 85% yield. The pure product was characterized by ¹H-NMR spectroscopy (Figure S3).

¹H NMR (500 MHz, CD₂Cl₂) δ 7.83 (dd, J = 21.1, 8.4 Hz, 4H), 7.50 – 7.36 (m, 6H), 7.28 (d, J = 8.3 Hz, 2H), 4.19 (d, J = 5.5 Hz, 2H), 3.67 – 3.32 (m, 72H), 2.38 (dt, J = 11.5, 5.9 Hz, 1H), 2.04 (dt, J = 11.7, 5.8 Hz, 2H), 1.11 (d, J = 6.2 Hz, 12H).

Compound *cis*-1 and *trans*-1. Compound 5 (152 mg, 0.11 mmol), compound 6^{S2} (46.55 mg, 0.11 mmol), and Cs₂CO₃ (177 mg, 0.542 mmol) were dissolved in anhydrous toluene (12 ml). The mixture was purged with argon for 5 min. Then Pd(PPh₃)₄ (1.3 mg, 0.0012 mmol) was added carefully under mild argon purge. The mixture was stirred at 90 °C for 24 hours under argon. After completion of the reaction as monitored by TLC, the reaction mixture was cooled down to room temperature and was diluted with ethyl acetate and washed with brine. The combined organic phase was dried over anhydrous MgSO₄ (s). The filtrate was condensed under reduced pressure and purified by silica gel flash column using ethyl acetate / methanol (20:1, v/v) as eluent. The purified products by column chromatography was further subjected to preparative HPLC (C4 column) to separate the regioisomers *cis*-1 and *trans*-1, using 85% CH₃CN in water as an eluent to provide 12% yield for *cis*-1 and 9% yield for *trans*-1 as light yellow waxy solids.

Compound *cis*-1. ¹H NMR (500 MHz, CD₂Cl₂) δ 8.84 (s, 1H), 8.76 (s, 1H), 8.64 (s, 2H), 8.14 (dd, J = 8.3, 4.8 Hz, 4H), 7.81 (d, J = 8.1 Hz, 2H), 7.79 – 7.56 (m, 17H), 7.52 (d, J = 8.8 Hz, 2H), 7.43 (dd, J = 5.1, 2H), 7.28 (d, J = 7.7 Hz, 2H), 7.20 (dd, J = 8.6, 2H), 7.08 (dd, J = 7.7, 2H), 7.01 (s, 1H), 4.24 (d, J = 4.0 Hz, 4H), 3.56 – 3.26 (m, 144H), 2.32 (m, 2H), 2.03 (m, 4H), 1.05 (d, J = 6.2, 24H). ¹³C NMR (151 MHz, CDCl₃) δ 156.55, 154.30, 143.73, 142.87, 141.06, 137.58, 135.17, 133.37, 129.84, 129.77,

129.47, 127.56, 127.07, 127.07, 119.93, 118.12, 75.00, 74.80, 74.80, 71.93, 70.72, 70.60, 70.52, 69.64, 69.37, 67.36, 59.01, 59.01, 40.80, 40.80, 40.62, 39.97, 39.97, 17.12, 17.12. MALDI-TOF mass: m/z calcd. for $C_{152}H_{216}O_{38}$ $[M+Na]^+$, 2674.35, $[M+K]^+$, 2690.46; found: $[M+Na]^+$, 2674.44, $[M+K]^+$, 2689.89.

Compound *trans*-1. 1H NMR (500 MHz, CD_2Cl_2) δ 8.80 (s, 2H), 8.64 (s, 2H), 8.14 (d, $J = 8.5$ Hz, 4H), 7.82 – 7.57 (m, 16H), 7.52 (d, $J = 8.5$ Hz, 2H), 7.43 (m, 4H), 7.26 (d, $J = 7.7$ Hz, 2H), 7.20 (dd, $J = 8.6$, 2H), 7.09 (d, $J = 9.1$ Hz, 2H), 7.01 (s, 2H), 4.23 (d, $J = 6.9$ Hz, 4H), 3.55 – 3.26 (m, 144H), 2.33 (m, 2H), 2.03 (m, 4H), 1.05 (d, $J = 6.2$ Hz, 24H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 143.54, 142.36, 138.79, 132.99, 131.76, 130.65, 129.42, 127.93, 126.99, 125.61, 119.84, 119.62, 74.90, 74.83, 74.81, 74.75, 74.67, 71.85, 70.64, 70.41, 70.32, 69.60, 69.35, 67.28, 67.21, 65.29, 58.54, 35.70, 31.90, 31.88, 29.75, 29.66, 29.48, 29.33, 29.28, 29.22, 29.12, 27.18, 27.15, 25.43, 22.69, 16.77, 13.83. MALDI-TOF mass: m/z calcd. for $C_{152}H_{216}O_{38}$ $[M+Na]^+$, 2674.35, $[M+K]^+$, 2690.46; found: $[M+Na]^+$, 2674.44, $[M+K]^+$, 2689.89.

3. Supplementary Figures.

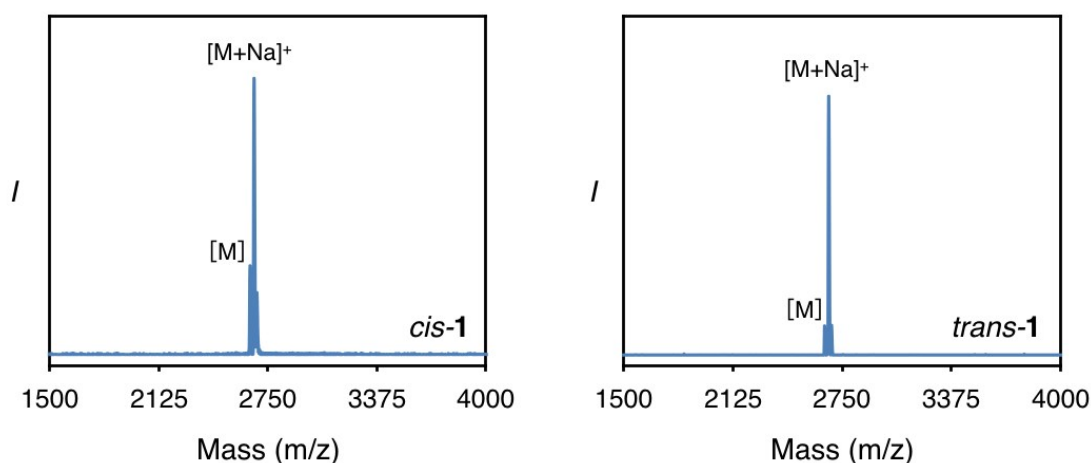


Figure S2. MALDI-TOF mass spectra of *cis*-1 and *trans*-1.

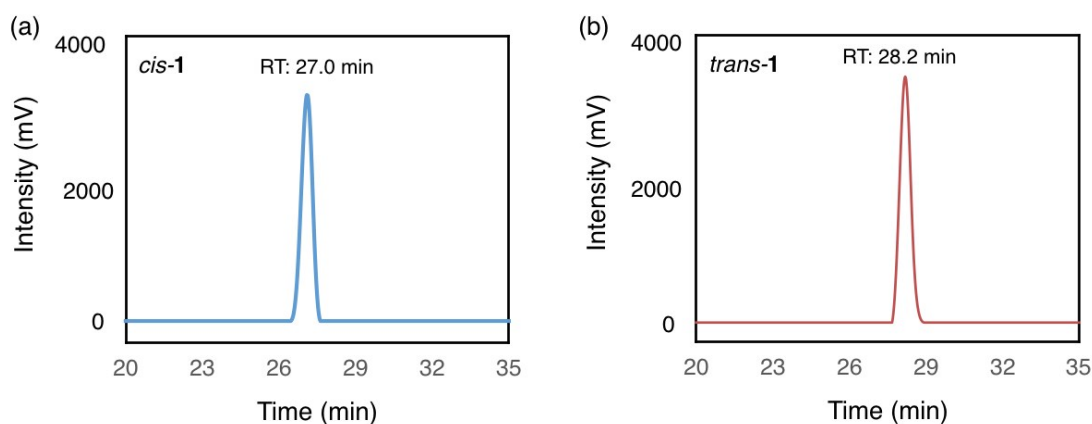


Figure S3. HPLC trace of (a) *cis*-1 and (b) *trans*-1 after separation. The respective regioisomers of *cis*-1 and *trans*-1 were able to be separated.

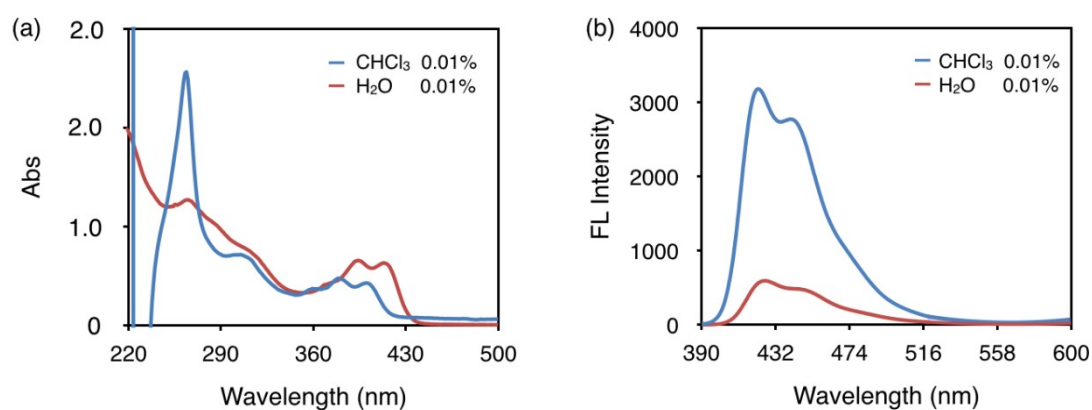


Figure S4. (a) Absorption and (b) emission spectra of *trans-1* in CHCl_3 (blue line) and aqueous solution (red line).

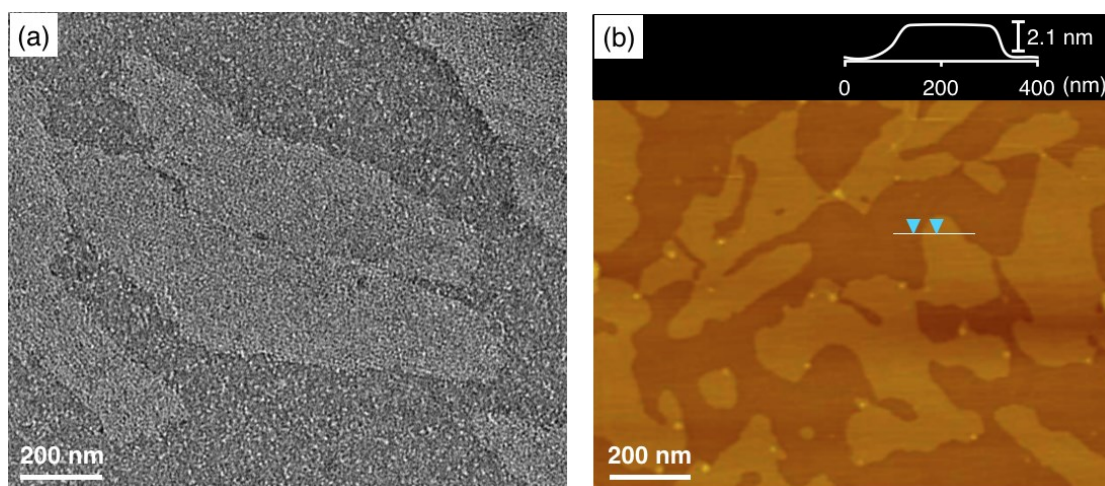


Figure S5. (a) Negatively stained TEM image and (b) AFM image of *trans-1* from 0.01 wt% aqueous solution.

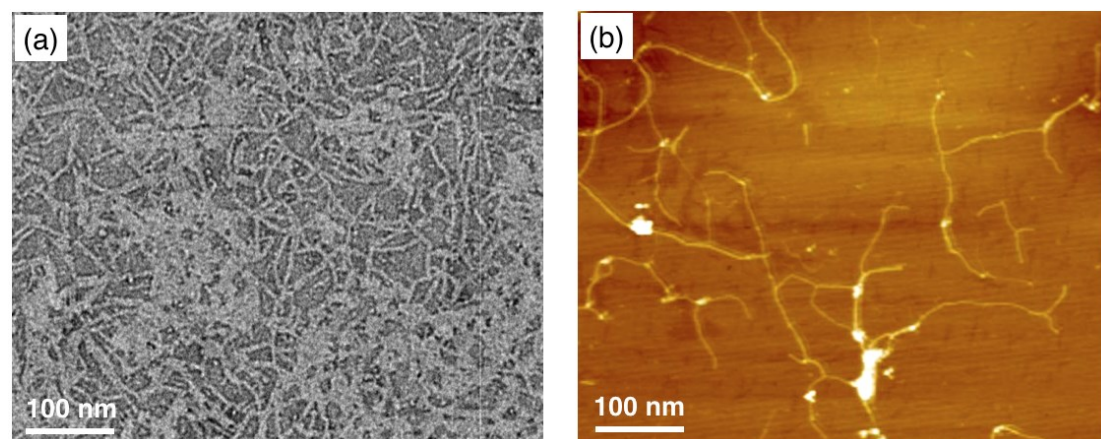


Figure S6. (a) Negative-stain TEM image and (b) AFM image of *trans-1* from 0.01 wt% aqueous solution at 40 °C.

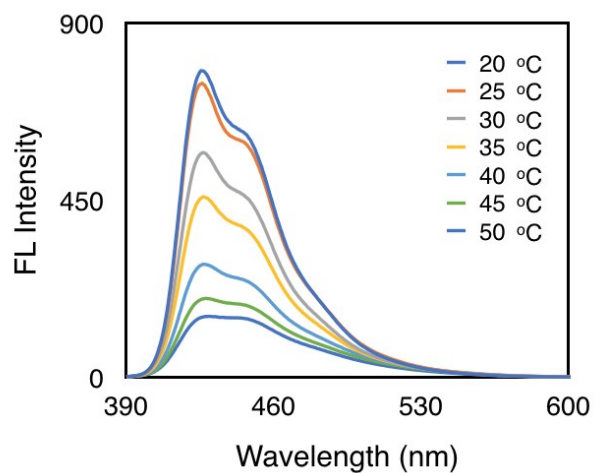


Figure S7. Temperature-dependent emission spectra of *trans-1* from 0.01 wt% aqueous solution.

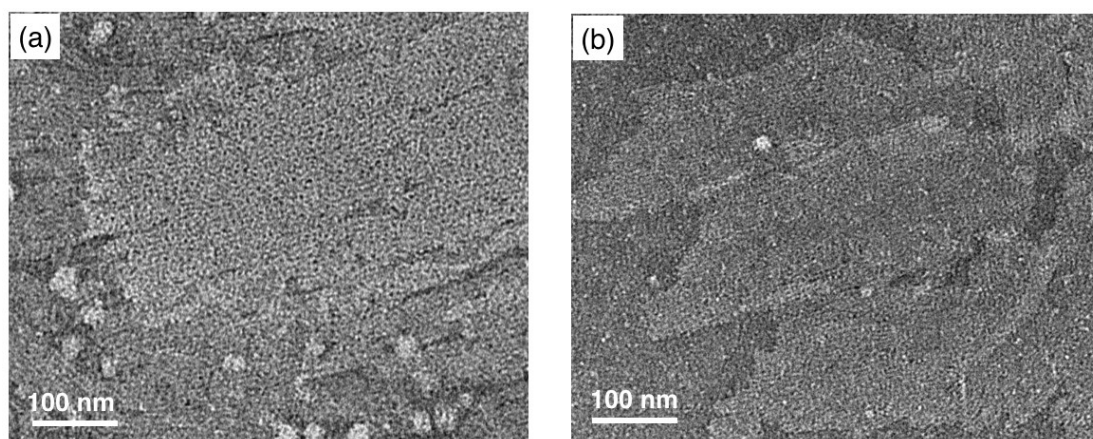


Figure S8. Negatively stained TEM images of *cis-1* (a) and *trans-1* (b) after heating treatment and then cooling to room temperature 24 h.

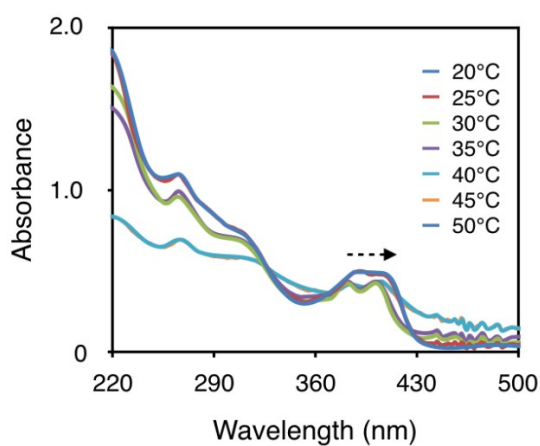


Figure S9. Temperature-dependent absorption spectra of *cis-1* from 0.01 wt% aqueous solution.

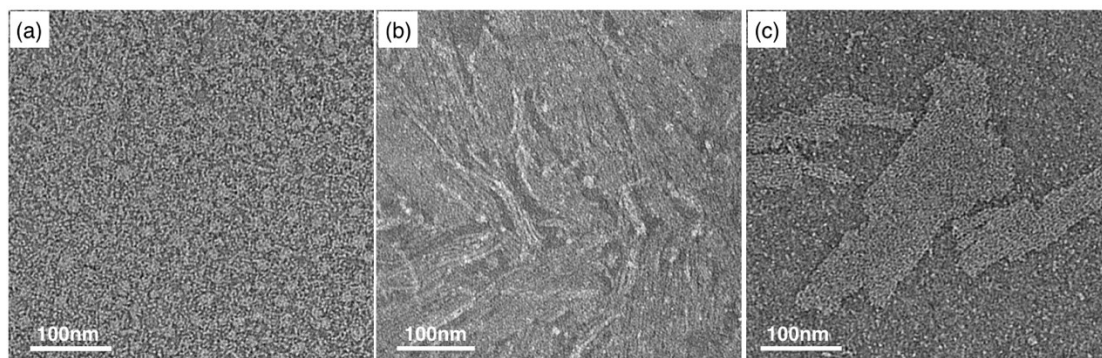


Figure S10. Time-dependent TEM images of *cis*-**1** from 0.01 wt% aqueous solution, (a) 0.5 h, (b) 1 h, (c) 5 h.

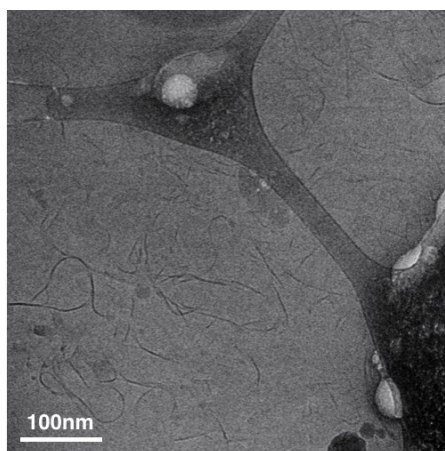


Figure S11. Cryo-TEM image of *trans*-**1** from 0.01 wt% aqueous solution.

4. References:

- S1) Y. Wang, Y. Kim, M. Lee, Static and Dynamic Nanosheets from Selective Assembly of Geometric Macrocycle Isomers, *Angew. Chem. Int. Ed.* **2016**, *55*, 13122–13126.
- S2) S. Saito, H. Yamaguchi, H. Muto, T. Makino, First Synthesis of Bidentate NHC-Pd Complexes with Anthracene and Xanthene Skeletons, *Tetrahedron Lett.* **2007**, *48*, 7498–7501.