Electronic Supplementary Information

A complementary guest induced morphology transition in a two-component multiple H-bonding self-assembly

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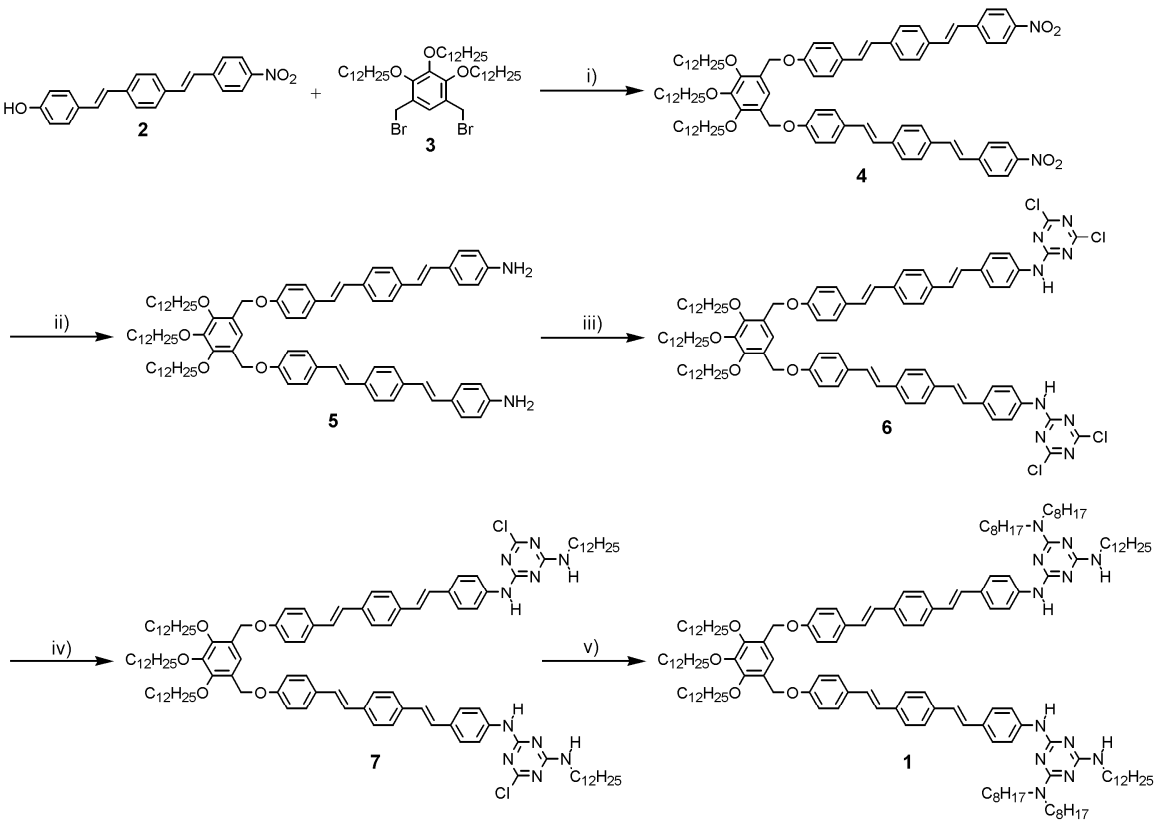
Materials and methods

Column chromatography was performed using 63–210 μm silica gel. All commercially available reagents and solvents were of reagent grade and used without further purification. ^{1}H NMR spectra were recorded by using a JEOL LA400 spectrometer and chemical shifts are reported in ppm with the signal of TMS as internal standard. Variable-temperature ^{1}H NMR spectra were recorded by using a JEOL LA500 spectrometer and chemical shifts are reported in ppm with the signal of residual solvents as internal standard. MALDI-TOF MS spectra were measured by using a Voyager DE Pro (Applied Biosystems). Elemental analyses were performed in Analytical Center of Chiba University. The solvents for the spectroscopic measurements and the gelation experiments were all spectral grade and used without further purification. UV/Vis and fluorescence spectra were recorded on a JASCO V660 spectrophotometer and a JASCO FP6600 spectrofluorometer, respectively. Circular dichroism spectra were recorded on a JASCO J840 spectropolarimeter. Molecular modeling calculations were performed on MacroModel version 9.0. Dynamic light scattering measurements were conducted on Beckmann Coulter N5 particle analyzer (25 mW He-Ne laser) with a scattering

angle of 90°. The hot sample solutions were filtered with Millipore membrane filter (pore size = 0.45 μm) before measurements to remove dust. AFM images of the nanostructures were acquired under ambient conditions using a Multimode Nanoscope IIIa (Veeco Instruments, Santa Barbara, CA) in tapping mode and a SPI4000/SPA400 (SII Nanotechnology Inc., Chiba, Japan) in a dynamic force (tapping) mode. Silicon cantilevers (OMCL-AC240TS-C2) with a spring constant of 2 N/m and frequency of 70 kHz (nominal value, Olympus, Japan) were used for the former instrument. For the latter, Silicon cantilevers (SI-DF20) with a spring constant of 15 N/m and frequency of 131 kHz (SII Nanotechnology Inc.) were used. AFM samples were prepared by spin-casting of methylcyclohexane solutions onto highly-oriented pyrolytic graphite (HOPG).

Synthesis

OPV dimer **1** was synthesized from OPV derivative **2**[1] and 1,3-bis(bromomethyl)-4,5,6-tridodecyloxybenzene (**3**)[2] according to Scheme S1.



Scheme S1 i) K_2CO_3, DMF, 65 °C; ii) Na_2S, dioxane, 100 °C; iii) 2,4,6-trichloro-1,3,5-triazine, diisopropylethylamine, THF, r.t.; iv) dodecylamine, diisopropylethylamine, THF, r.t.; v) dioctylamine, THF, 70 °C.

Compound **4**: Compound **2** (250 mg, 0.728 mmol) and potassium carbonate (3.02 g, 21.8 mmol) in dry DMF (20 mL) were heated at 65 °C under N_2. To this mixture, compound **3** (277 mg, 0.339 mmol) dissolved in DMF (20 mL) was added dropwise. The resulting mixture was stirred at 65 °C for 4.5 h. After cooling to r.t., the mixture was poured into ice-water. The resulting precipitates were collected by filtration and were washed by water. Purification by silica-gel column chromatography (eluent: chloroform) gave compound **4** as a yellow solid (370 mg, 81 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, J = 8.9 Hz, 4H), 7.62 (d, J = 8.8 Hz, 4H), 7.54–7.44 (m, 8H), 7.45 (d, J = 8.7 Hz, 4H), 7.29–7.23 (m, 3H), 7.13 (d, J = 16 Hz, 2H), 7.12 (d, J = 16 Hz, 2H), 7.00–6.95 (m, 6H), 5.06 (s, 4H), 4.10–3.98 (m, 6H), 1.82–1.68 (m, 6H), 1.52–1.36 (m, 6H), 1.34–1.20 (m, 48H), 0.88 (t, J = 6.8 Hz, 9H); MS (MALDI-TOF): 1364 $[M+Na]^+$.

Compound **5**: To a 1,4-dioxane (25 mL) solution of compound **4** (500 mg, 0.373 mmol), sodium sulfide (1.46 g, 18.7 mmol) dissolved in water (3 mL) was added to the solution. The mixture was stirred at 100 °C for 3 h. After cooling to r.t., 1,4-dioxane was removed by evaporation. The resulting solid was redissolved in chloroform, and washed with water for several times. Organic layer was subsequently dried over Na_2SO_4. After evaporation of the solvent, the residue was reprecipitated from chloroform/methanol mixture to give compound **5** as a brown solid (399 mg, 84 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.41 (m, 12H), 7.33 (d, J = 8.4 Hz, 4H), 7.27 (s, 1H), 7.08–6.88 (m, 12H), 6.67 (d, J = 8.2 Hz, 4H), 5.05 (s, 4H), 4.09–4.00 (m, 6H), 3.75 (br s, 4H), 1.82–1.68 (m, 6H), 1.52–1.36 (m, 6H), 1.34–1.20 (m, 48H), 0.87 (t, J = 6.3 Hz, 9H); MS

(MALDI-TOF): 1304 $[M+Na]^+$.

Compound **6**: To a THF solution (10 mL) of 2,4,6-trichloro-1,3,5-triazine (259 mg, 14.0 mmol) and diisopropylethylamine (100 μL), compound **5** (450 mg, 0.351 mmol) dissolved in dry THF (30 mL) was added at r.t. under N_2. After stirring for 11 h, the solvent was removed by evaporation. The residue was dissolved in chloroform and washed with water and then 2 % aq. HCl. Organic layer was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography over silica gel (eluent: chloroform) to give compound **6** as an orange solid (453 mg, 82 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 2H), 7.55 (s, 8H), 7.49 (s, 8H), 7.42 (d, J = 8.8 Hz, 4H), 7.25 (s, 1H), 7.07 (s, 4H), 7.07 (d, J = 16 Hz, 2H), 6.95 (d, J = 16 Hz, 2H), 6.93 (d, J = 8.9 Hz, 4H), 5.07 (s, 4H), 4.09–4.00 (m, 6H), 1.82–1.69 (m, 6H), 1.52–1.37 (m, 6H), 1.35–1.20 (m, 48H), 0.88 (t, J = 6.4 Hz, 9H).

Compound **7**: Compound **6** (280 mg, 0.177 mmol) and diisopropylethylamine (100 μL) were dissolved in 10 mL of dry THF. To this solution, dodecylamine (65.8 mg, 0.355 mmol) in dry THF (10 mL) was added at r.t. under N_2. After stirring for 2 h, the solvent was removed by evaporation. The residue was dissolved in chloroform and washed with water and then 2 % aq. HCl. Organic layer was dried over Na_2SO_4. After evaporation of the solvent, the residue was reprecipitated from chloroform/methanol mixture to give compound **7** as an orange solid (212 mg, 64 %).

^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2/DMSO-d_6, 100 °C): δ = 7.50 (d, J = 7.3 Hz, 4H), 7.42–7.34 (m, 16H), 7.19 (s, 1H), 7.04–6.86 (m, 12H), 5.42 (bs, 2H), 5.01 (s, 4H), 4.04–3.96 (m, 6H), 3.40–3.35 (m, 4H), 1.76–1.66 (m, 6H), 1.52–1.42 (m, 6H), 1.45–1.18 (m, 88H), 0.82 (t, J = 6.4 Hz, 15H).

Compound **1**: Compound **7** (100 mg, 0.0533 mmol) was dissolved in 10 mL of dry THF. To this solution, dioctylamine (257 mg, 1.06 mmol) in dry THF (10 mL) was added and stirred overnight at 70 °C. After cooling to r.t., water and chloroform was added and separated organic layer was washed with water and 2 % aq. HCl and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography over silica gel (eluent: 3 % methanol/chloroform), and subsequently reprecipitated from chloroform/methanol mixture to give compound **1** as an orange solid (103 mg, 85 %).

^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane, 100 °C) δ = 7.54 (d, J = 8.6 Hz, 4H), 7.45–7.36 (m, 16H), 7.22 (s, 1H), 7.03–6.88 (m, 12H), 5.03 (s, 4H), 3.51–3.31 (m, 12H), 1.79–1.68 (m, 6H), 1.64–1.52 (m, 12H), 1.32–1.21 (m, 130H), 0.88–0.82 (m, 27H); MS (MALDI-TOF): 2286 $[M+H]^+$; Anal. Calcd for $C_{150}H_{234}N_{12}O_5$: C 78.83, H 10.32, N 7.35; found C 78.36, H 10.45, N 7.09.

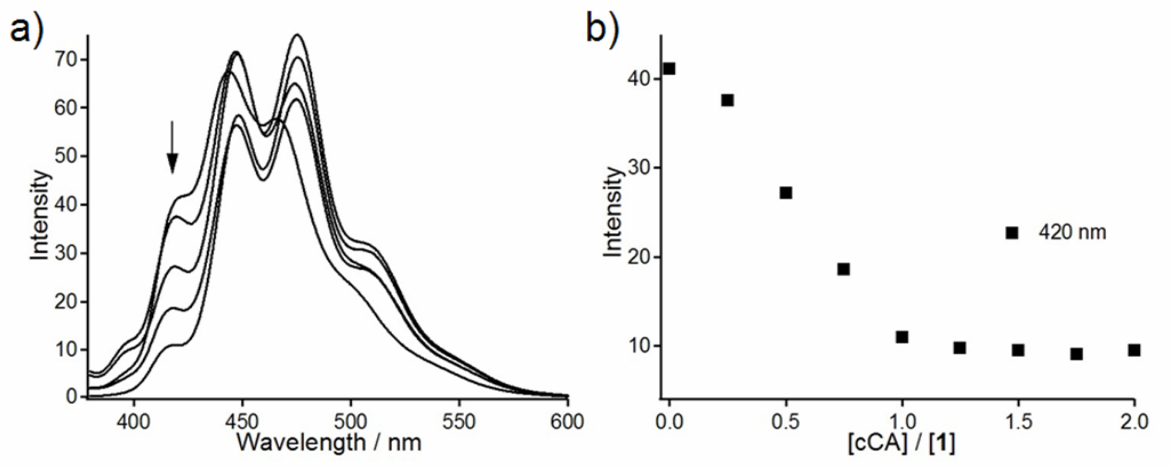


Fig. S1 a) Fluorescence spectral change of **1** (c = 1 × 10^{-5} M) upon addition of cCA (c = 0 to 1 × 10^{-5} M) in MCH at 25 °C. λ_{ex} = 367 nm. b) Plot of the fluorescence intensity at 420 nm versus [cCA]/[**1**].

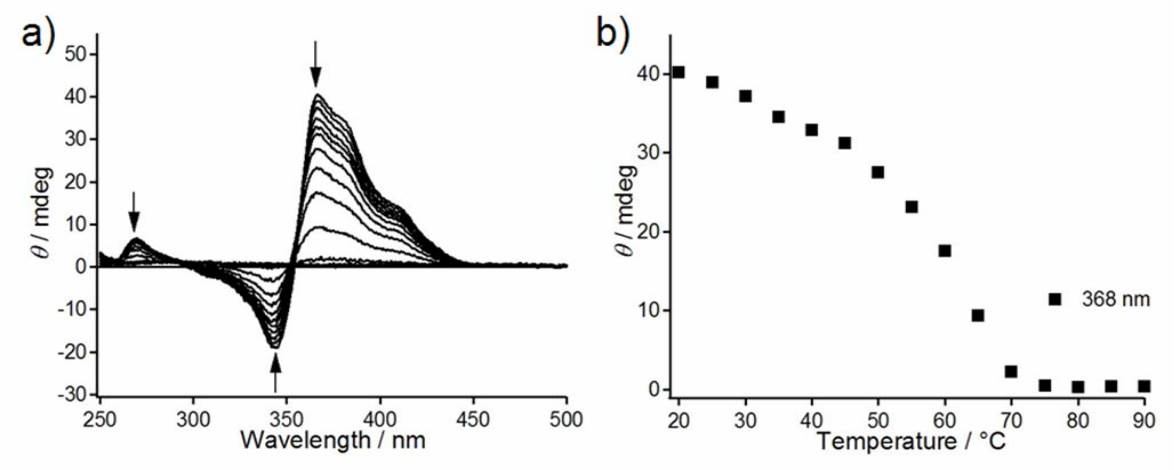


Fig. S2 a) Temperature-dependent CD spectra of **1**:cCA = 1:1 mixture in MCH (c = 1 × 10^{-5} M). Temperature range: 20–90 °C. b) Plot of CD intensities (at 368 nm) versus temperature.

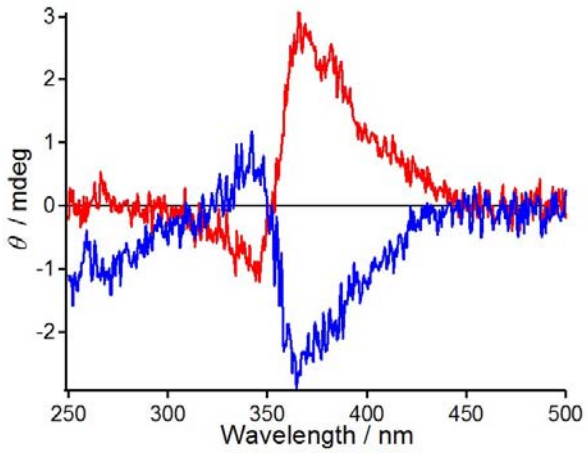


Fig. S3 CD spectra of **1**+(*R*)CA (red) and **1**+(*S*)CA (blue) in MCH (c = 1 × 10^{-5} M) at 25 °C.

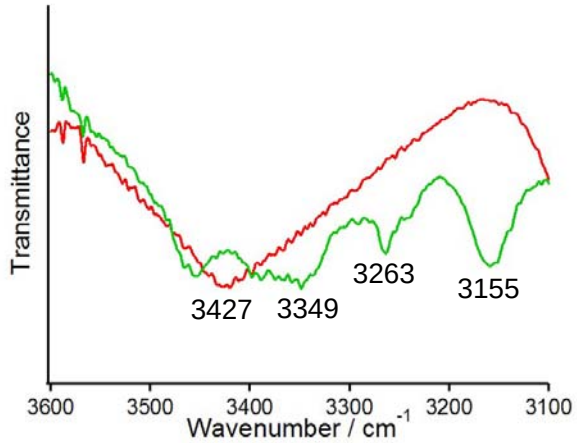


Fig. S4 FT-IR spectra of **1** in $CHCl_3$ (5×10^{-3} M, red line) and in MCH (1×10^{-3} M, green line).

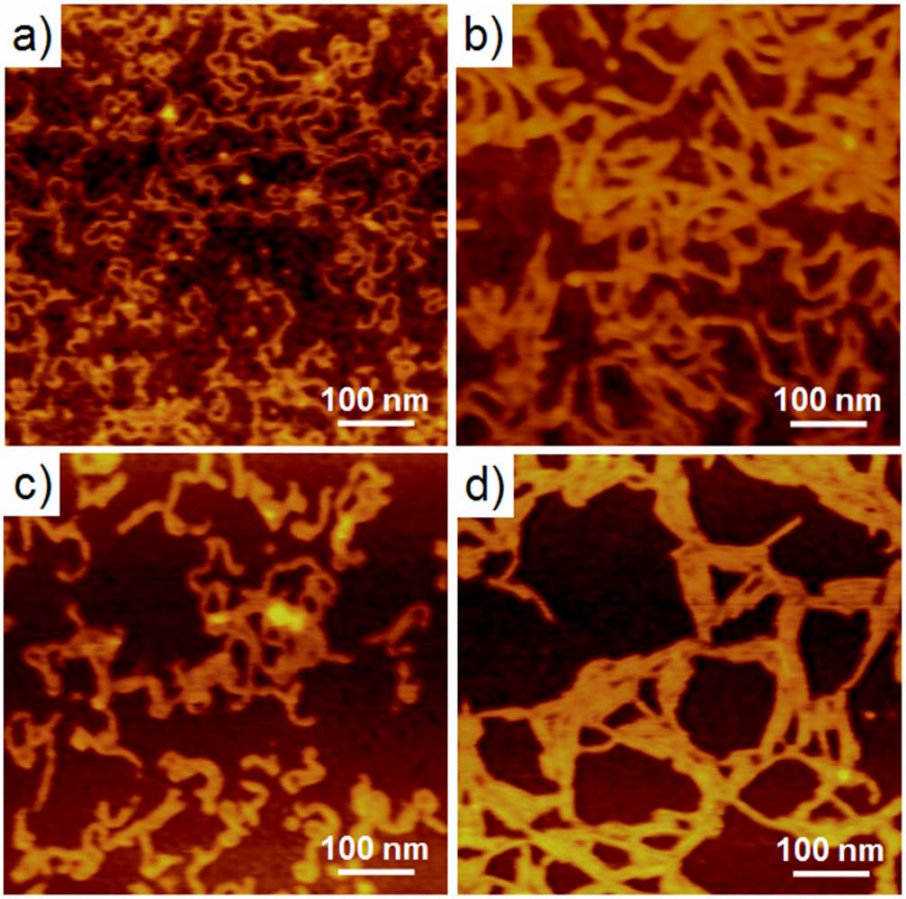


Fig. S5 AFM height images of nanostructures formed by **1** (a,c) and **1**+dCA (b,d). AFM samples were prepared by spin-coating of the corresponding solutions ($c = 1 \times 10^{-4}$ M) onto silicon (a,b) or mica (c,d) substrates.

References

S1 S. Yagai, S. Kubota, T. Iwashima, K. Kishikawa, T. Nakanishi, T. Karatsu and A. Kitamura, *Chem. Eur. J.*, 2008, **14**, 5246-5257.

S2 S. Yao, U. Beginn, T. Gress, M. Lysetska and F. Würthner, *J. Am. Chem. Soc.*, 2004, **126**, 8336-8348.