Electronic Supplementary Information

Self-sorting regioisomers through hierarchical organization of hydrogen-bonded rosettes

Keisuke Aratsu, Deepak D. Prabhu, Hidetaka Iwawaki, Xu Lin, Mitsuaki Yamauchi

Takashi Karatsu and Shiki Yagai*

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba

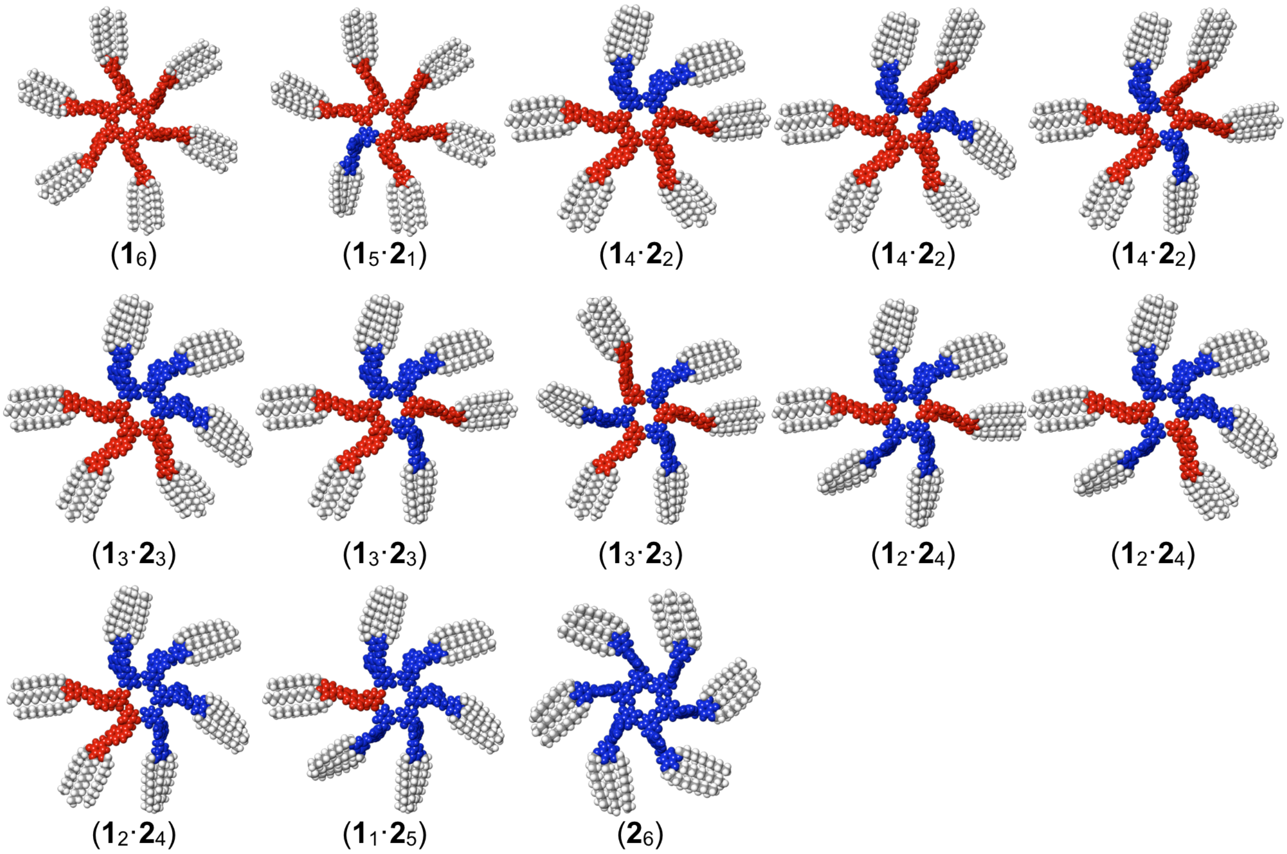
University, 1-33 Yayoi-cho, Inage-ku

Chiba 263-8522, Japan.

Materials and Methods

^{1}H NMR spectra were recorded on JEOL JNM- ECA500 NMR spectrometer and chemical shifts are reported in ppm (δ) with the signal of TMS as the internal standard. UV-vis spectra were recorded on a JASCO V660 spectrophotometer with Peltier device temperature-control unit. AFM images were acquired under ambient conditions using Multimode 8 Nanoscope V (Bruker Instruments) in Peak Force Tapping (Scanasyst) mode. Silicon cantilevers (SCANASYST-AIR) with a spring constant of 0.4 N/m and frequency of 70 kHz (nominal value, Bruker, Japan) were used. The samples were prepared by spin-coating the solutions onto freshly cleaved highly-oriented pyrolytic graphite (HOPG). Dynamic light scattering (DLS) measurements were performed on a Zetasizer Nano S (Malvern Instruments) using non-invasive back-scatter technology (NIBS) under 4.0 mW He-Ne laser (633 nm). The scattering angle was set at 173°.

Supporting Figures


$(\mathbf{1}_6)$ $(\mathbf{1}_5 \cdot \mathbf{2}_1)$ $(\mathbf{1}_4 \cdot \mathbf{2}_2)$ $(\mathbf{1}_4 \cdot \mathbf{2}_2)$ $(\mathbf{1}_4 \cdot \mathbf{2}_2)$

$(\mathbf{1}_3 \cdot \mathbf{2}_3)$ $(\mathbf{1}_3 \cdot \mathbf{2}_3)$ $(\mathbf{1}_3 \cdot \mathbf{2}_3)$ $(\mathbf{1}_2 \cdot \mathbf{2}_4)$ $(\mathbf{1}_2 \cdot \mathbf{2}_4)$

$(\mathbf{1}_2 \cdot \mathbf{2}_4)$ $(\mathbf{1}_1 \cdot \mathbf{2}_5)$ $(\mathbf{2}_6)$

Fig. S1 Possible rosette structures formed upon mixing **1** and **2**. Among these thirteen rosettes, only two are homomeric rosettes composed of either **1** or **2**. Thus, the proportion of homomeric rosettes are statistically calculated to be 0.15 (= 2/13).

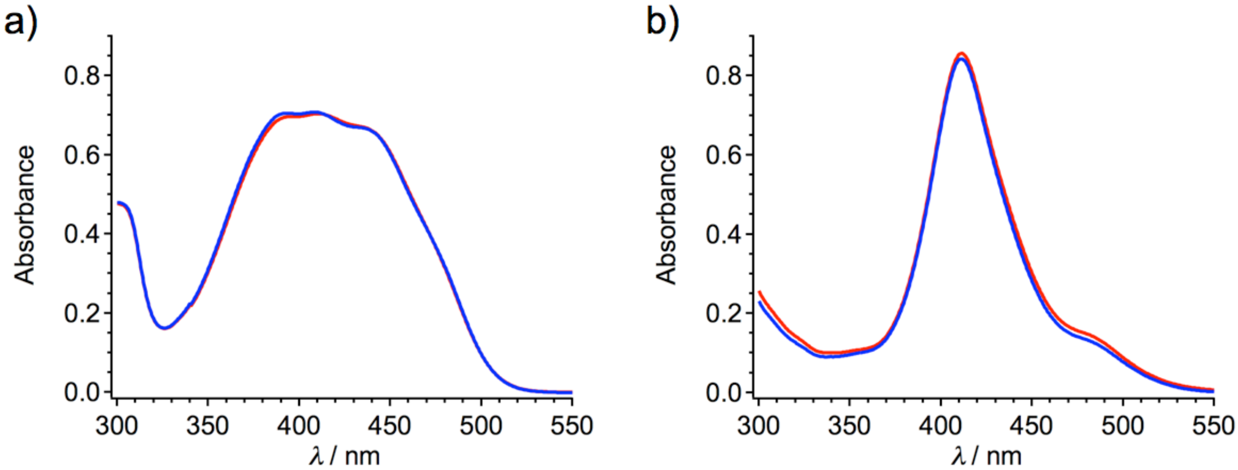


Fig. S2 UV-vis absorption spectra of a) **1** and b) **2** recorded after injecting 15 μL of a $CHCl_3$ solution of **1** (10 mM) and **2** (10 mM) into MCH (285 μL), respectively. The final concentrations: 0.5 mM; the final solvent ratio: $CHCl_3$:MCH = 5:95. The spectra were recorded after 2 min (red curves) and 120 min (blue curves), respectively.

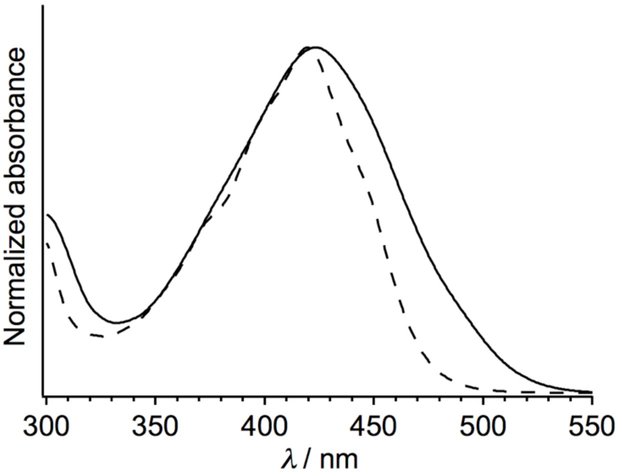


Fig. S3 Solid curve: UV-vis absorption spectrum recorded after injecting 5 μL of a $CHCl_3$ solution of the 1:1 mixture of **1** (100 mM) and **2** (100 mM) into the mixture of $CHCl_3$ (45 μL) and MCH (950 μL). The final concentrations: 0.5 + 0.5 mM; the final solvent ratio: $CHCl_3$:MCH = 5:95. The spectrum was recorded after 2 min from the injection. Dotted curve: The calculated spectrum obtained by summation of the spectra of the individual monomers **1** (0.5 mM) and **2** (0.5 mM) recorded at 90 °C in MCH.

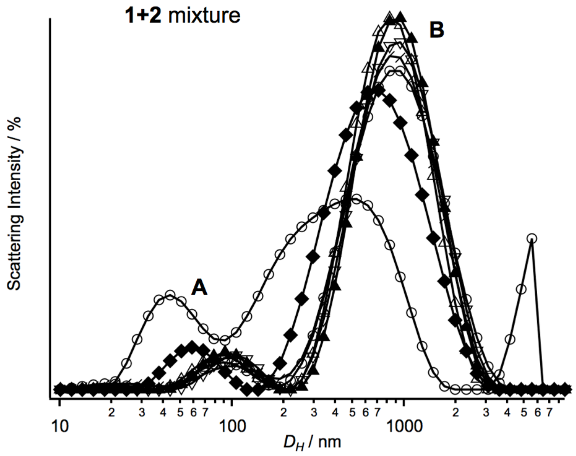


Fig. S4 DLS recorded after injecting 5 μL of a $CHCl_3$ solution of the 1:1 mixture of **1** (100 mM) and **2** (100 mM) into the mixture of $CHCl_3$ (45 μL) and MCH (950 μL). The final concentrations: 0.5 + 0.5 mM; the final solvent ratio: $CHCl_3$:MCH = 5:95. Time-dependent DLS profiles were recorded after 6 min (○), 30 min (◆), 60 min (△), 90 min (/), 120 min (+), 150 min (▽) and 180 min (▲) from the injection. Peaks attributed to nanorings and nanorods are marked with **A** and **B**, respectively.

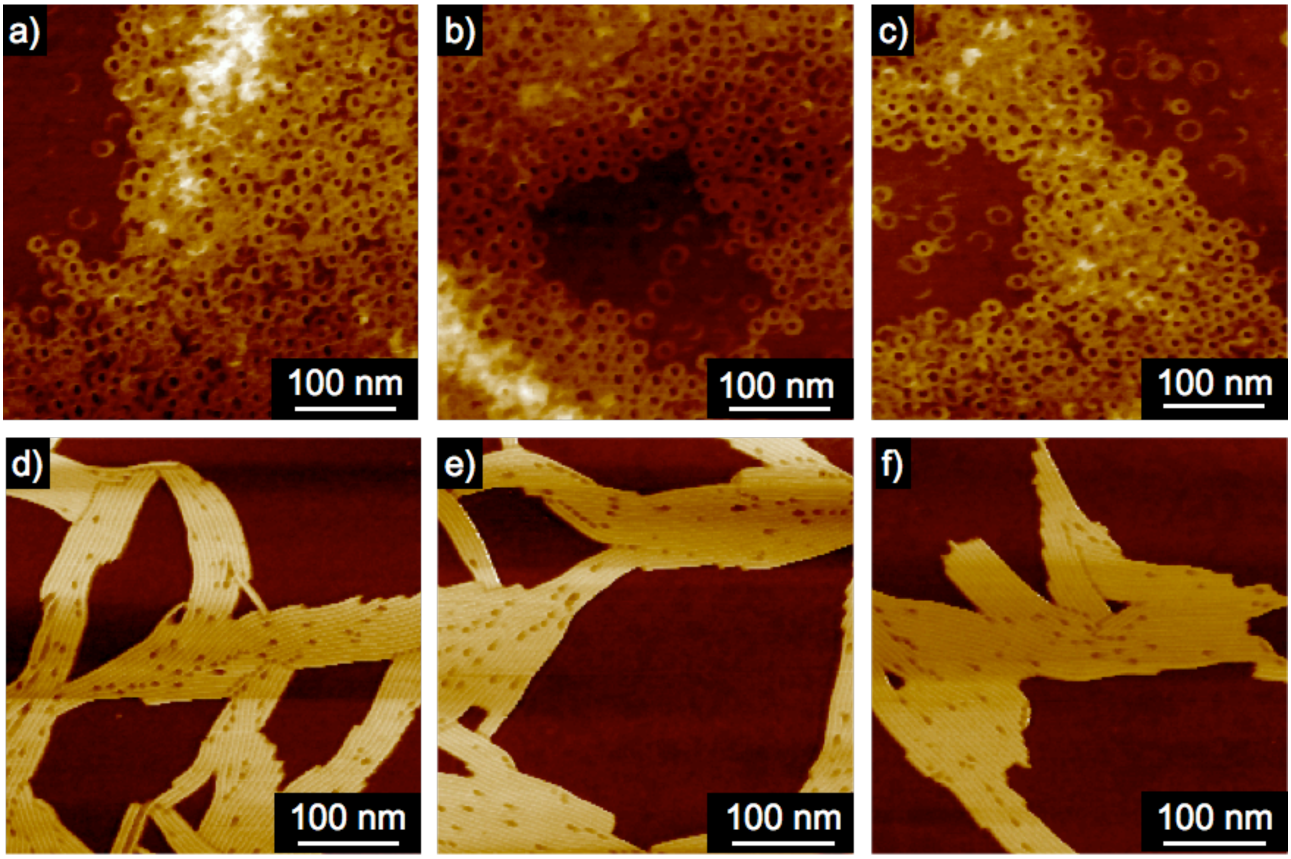


Fig. S5 AFM images of the nanostructures formed by injecting 15 μL of a $CHCl_3$ solution of **1** (10 mM) and **2** (10 mM) into the MCH (285 μL), respectively. The final concentrations: 0.5 mM; the final solvent ratio: $CHCl_3$:MCH = 5:95. The AFM samples of **1** (a–c) and **2** (d–f) were prepared by spin-coating the solution onto HOPG after equilibration time of 1 min (a, d), 30 min (b, e) and 60 min (c, f) from injection.

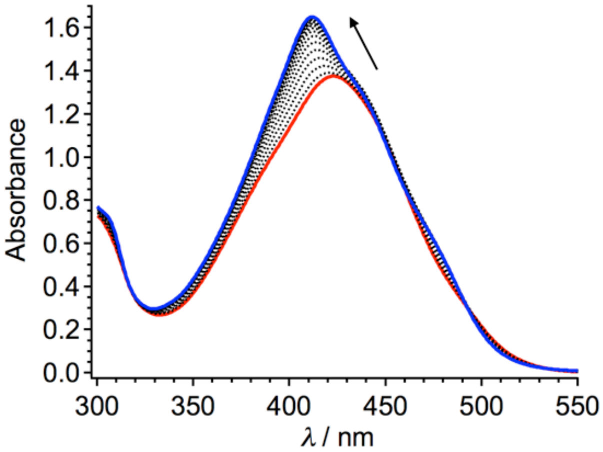


Fig. S6 Time-dependent UV-vis absorption spectra recorded after injecting 15 μL of a $CHCl_3$ solution of 1:1 mixture of **1** (10 mM) and **2** (10 mM) into MCH (285 μL). The final concentrations: 0.5 + 0.5 mM; the final solvent ratio: $CHCl_3$:MCH = 5:95. The spectra were recorded for 180 min at 2 min intervals from the injection. The spectra at equilibration time *t* = 2 and 180 min are shown by red and blue curves, respectively. Arrow indicates the absorption change with time.