

Multistep, site-selective noncovalent synthesis of two-dimensional block supramolecular polymers

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Table of Contents

1. Materials and Methods	2
2. Synthesis and Characterization.....	4
3. Supplementary Figures, Tables, and Movie	15
4. Supplementary References	37

1. Materials and Methods

Unless otherwise noted, reagents and solvents were purchased from commercial suppliers and used without further purification. Air- and/or water-sensitive reactions were conducted under argon atmosphere using dry solvents. Compounds **1_{Zn}**, **2_{Zn}**, and **2_H** were prepared according to reported procedures^{S1,S2}.

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-400 (400 MHz) spectrometer. All chemical shifts are reported in parts per million (ppm) from tetramethylsilane (0 ppm for ¹H), residual CHCl₃ (77 ppm for ¹³C), or hexafluorobenzene (−162 ppm for ¹⁹F) as an internal standard. Atmospheric pressure chemical ionization (APCI) mass spectra were obtained using a Thermo Fisher Scientific Exactive Plus spectrometer. Melting points were determined with a Yanako NP-500P micro melting point apparatus. Ultraviolet–visible absorption spectra were recorded using a quartz cuvette of 10 mm path length on a Jasco V-630 spectrophotometer equipped with a Jasco ETCS-761 cell holder for temperature control, or Jasco FS-110 spectrophotometer equipped with a Jasco ETCS-761 cell holder for temperature control. Spin-coating was performed using an Oshigane SC-300. Atomic force microscopy (AFM) was performed on a Bruker model MultiMode 8 atomic force microscope under ambient conditions in the scan assist mode. Silicon cantilevers (SCANASYST-AIR) with a spring constant of 0.4 N/m and a frequency of 70 kHz were used. AFM images were analyzed with Bruker Nanoanalysis and ImageJ.

Scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDS)

Drops of the solutions were dispersed on molybdenum grids covered with graphene films (AirMembrane Co.). The grids were dried at room temperature. An electron microscope (Themis Z; Thermo Fisher Scientific Inc.) equipped with a dual EDS detector (XFlash® 6-100; Bruker Co.) was operated at 30 kV for Annular dark field (ADF)–STEM observations and STEM–EDS analyses. The total solid angle of the EDS detector is 1.76 sr. The convergence semi-angle and collection semi-angle range were set as 49 mrad and 106–200 mrad. For STEM–EDS, the probe current, scan step, dwell time and total frames were set as 3.5–4.1 nA, 1.3–1.8 nm, 10 μs and 350–1250, respectively. A 9-pix average filter was applied to EDS net-intensity maps for each element, i.e., Ni, Cu, Zn (Figs. 2c,d, 2h–i, 2m–n, 4b,c, 4f–h, 4k–m, Supplementary Figs. 25h,i, 26h,i, 27h,i). Superimposing the single-elemental maps, we obtained multiple-elemental maps, i.e., Cu–Zn, Ni–Zn, Ni–Cu–Zn maps (Figs. 2e, 2j, 2o, 4d, 4i, 4n, Supplementary Figs. 25j, 26j, and 27j).

High-speed atomic force microscopy (AFM)

Recent technical advances in this field are the subject of two recent comprehensive reviews^{S3,S4}. AFM images were acquired using a laboratory-built high-speed AFM apparatus operating in the tapping mode. An optical beam deflection detector with a red laser ($\lambda = 670$ nm) was used to detect the cantilever deflection, and a 20× objective lens was employed to focus the laser onto the small cantilever. The cantilever (Olympus) developed for high-speed AFM has 6–7 μm in length, 2 μm in width, and 90 nm in thickness, with a spring constant of 0.2 N m^{−1}. Since the free vibration amplitude was approximately 2 nm and the set point amplitude was set at 80–90% of the free amplitude, the tapping force was estimated to be roughly less than < 50 pN. To gain a sharp probe, an amorphous carbon pillar was grown on the original probe by electron-beam deposition under observation by field-emission

scanning electron microscopy. The pillar length was several tens of nm, and the tip was sharpened to ~4 nm by plasma etching under argon gas.

High-speed AFM observations were performed in a dodecane/toluene mixed solvent at room temperature. On a HOPG substrate, a solution of SCTs containing of **1_{zn}** was spread (**[1_{zn}]** = 5 μM, 5 μL, dodecane/toluene=19:1), and excess amount of solvents was removed with Kimwipes. Before the substrate was completely dried, the HOPG substrate was immersed in a dodecane/toluene mixed solvent (~70 μL). During the observation, DMAP (10 μL, 60 mM, dodecane/toluene=19:1 followed by 2 μL, 630 mM, dodecane/toluene=19:1) was added to induce the depolymerization of SCTs. Compared to the solution experiments (Fig. 3a,b), excess amounts of DMAP were required (roughly 10 times) probably because of the stabilization of the SCTs by the HOPG substrate.

AFM analysis

AFM image of SCTs were analyzed by using the ImageJ software. For the histogram of the circumference and area distribution, 100 objects were measured to determine the number-average internal circumference (iC_n), number-average external circumference (eC_n), number-average area of the hole (hD_n), number-average area (A_n), weight-average area (A_w), and the value of A_w/A_n , based on the following equations ($O = ^iC, ^eC, ^hD$, or A of objects, N = number).

$$O_n = \frac{\sum_{i=1}^n N_i O_i}{\sum_{i=1}^n N_i}$$

$$A_w = \frac{\sum_{i=1}^n N_i A_i^2}{\sum_{i=1}^n N_i A_i}$$

2. Synthesis and Characterization

Synthesis of compound **1_{Cu}** and **1_{Ni}**

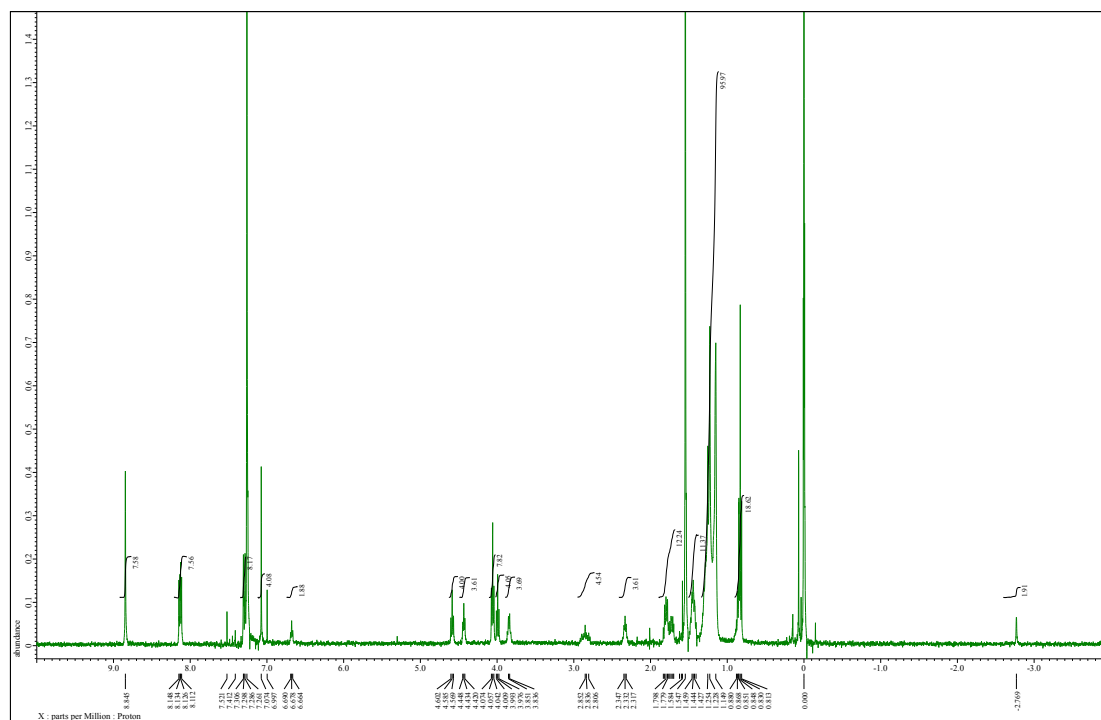


Supplementary Scheme S1. Synthesis of **1_{Cu}** and **1_{Ni}**.

Synthesis of **1_H**.

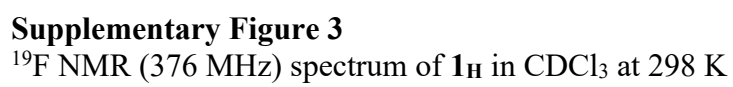
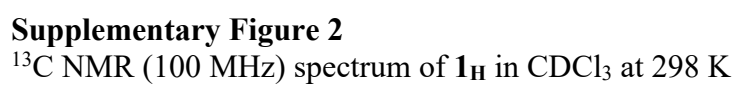
To a solution of compound **1_{Zn}** (27 mg, 0.01 mmol) in CH₂Cl₂ (4.6 mL), trifluoroacetic acid (46 μL, 0.6 μmol) was added under argon atmosphere. The solution was stirred at room temperature for 1 h in the dark. The reaction was quenched with triethylamine (83 μL) and diluted with CHCl₃. The mixture was washed with water, and dried over sodium sulfate anhydrous. The solvent was evaporated, and the solid residue was purified through column chromatography (silica gel, CHCl₃/acetone = 20:1 v/v) to yield compound **1_H** as a purple-red solid (22 mg, 86%).

¹H NMR (CDCl₃, 298 K) δ -2.77 (2H, br, inner-H), 0.80-0.87 (18H, m, CH₃-), 1.12-1.33 (96H, m, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-O-), 1.40-1.50 (12H, m, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-O-), 1.68-1.83 (12H, m, CH₃-(CH₂)₉-CH₂-CH₂-O-), 2.31-2.37 (4H, m, -NH-CH₂-CH₂-CH₂-O-), 2.78-2.92 (4H, m, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-), 3.81-3.87 (4H, m, -NH-CH₂-CH₂-CH₂-O-), 3.99 (4H, t, *J* = 6.8 Hz, CH₃-(CH₂)₉-CH₂-CH₂-O-), 4.06 (8H, t, *J* = 6.8 Hz, CH₃-(CH₂)₉-CH₂-CH₂-O-), 4.42 (4H, t, *J* = 5.6 Hz, -NH-CH₂-CH₂-CH₂-O-), 4.59 (4H, t, *J* = 6.8 Hz, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-), 6.66 (2H, t, *J* = 4.8 Hz, -NH-CH₂-CH₂-CH₂-O-), 7.07 (4H, s, Ar-*H*), 7.28-7.31 (8H, m, Ar-*H*) 8.12 (4H, d, *J* = 8.8 Hz, Ar-*H*), 8.14 (4H, d, *J* = 8.8 Hz, Ar-*H*), 8.85 (8H, s, β-pyrrole); ¹³C NMR (CDCl₃, 298 K) δ 14.1, 22.65, 22.68, 26.1, 29.24, 29.30, 29.38, 29.41, 29.59, 29.61, 29.67, 29.73, 30.3, 31.87, 31.92, 38.6, 60.3, 67.2, 69.5, 73.5, 105.8, 112.69, 112.75, 119.5, 119.6, 129.7, 135.0, 135.4, 135.6, 141.2, 153.2, 157.9, 158.4, 167.5; ¹⁹F NMR (CDCl₃, 298 K) δ -81.2 (3F, br. m, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-), -113.9 (2F, br. m, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-), -124.8 (2F, br. m, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-), -126.3 (2F, br. m, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-); HRMS (APCI, pos. mode, CH₂Cl₂): *m/z* calcd. for C₁₄₈H₂₀₃F₁₈N₆O₁₂ [M+H]⁺: 2599.5206 ; found: 2599.5200.



Supplementary Figure 1

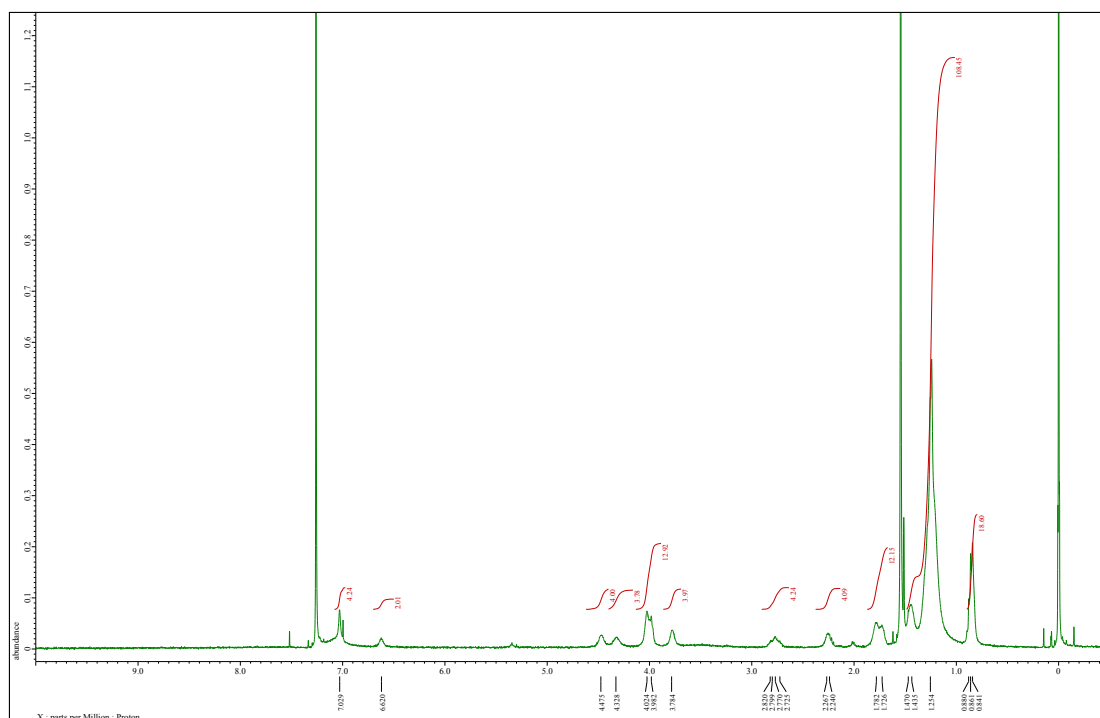
¹H NMR (400 MHz) spectrum of **1_H** in CDCl₃ at 298 K



Synthesis of **1_{Cu}**

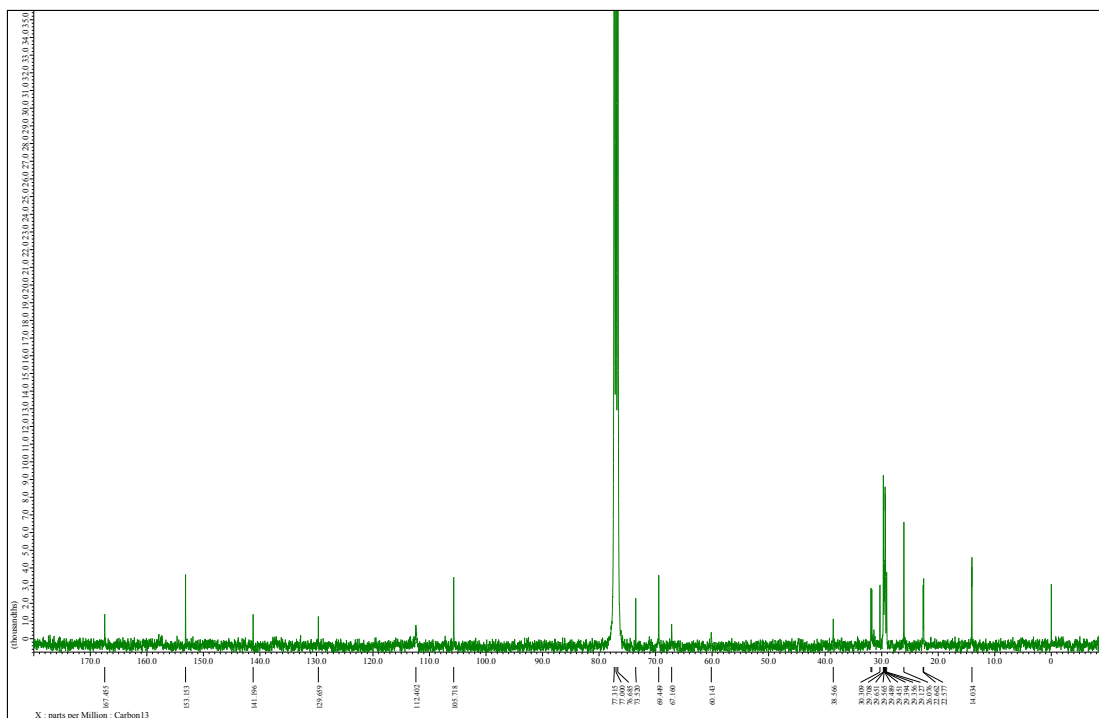
To a CHCl_3 solution (1.6 ml) of compound **1_H** (21 mg 8.0 μmol), $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20 mg, 99 μmol) in MeOH (1.6 ml) was added, and the mixture was refluxed with stirring for 2 h under an argon atmosphere. After cooling to room temperature, the solvents were evaporated, and the resultant residue was purified through column chromatography (silica gel, CHCl_3) and size exclusion chromatography (CHCl_3) to yield compound **1_{Cu}** as a pink solid (18 mg, 86%). *The paramagnetic nature of the copper ion hindered NMR characterization of tetrakis(4-alkoxyphenyl)porphyrinato copper (II) moiety in 1_{Cu}.*

m.p. = 172-178 °C; ^1H NMR (CDCl_3 , 298 K) δ 0.79-0.88 (18H, br, CH_3 -), 1.10-1.49 (108H, br, CH_3 -(CH_2)₉- CH_2 - CH_2 -O-), 1.67-1.84 (12H, br, CH_3 -(CH_2)₉- CH_2 - CH_2 -O-), 2.20-2.32 (4H, br, -NH- CH_2 - CH_2 - CH_2 -O-), 2.69-2.85 (4H, br, CF_3 -(CF_2)₂- CF_2 - CH_2 - CH_2 -O-), 3.74-3.82 (4H, br, -NH- CH_2 - CH_2 - CH_2 -O-), 3.94-4.08 (12H, br, CH_3 -(CH_2)₉- CH_2 - CH_2 -O-), 4.25-4.38 (4H, br, -NH- CH_2 - CH_2 - CH_2 -O-), 4.42-5.52 (4H, br, CF_3 -(CF_2)₂- CF_2 - CH_2 - CH_2 -O-), 6.59-6.66 (2H, br, -NH- CH_2 - CH_2 - CH_2 -O-), 6.98-7.08 (4H, br, Ar-H).; ^{13}C NMR (CDCl_3 , 298 K) δ 14.0, 22.6, 22.7, 26.1, 29.1, 29.36, 29.39, 29.45, 29.49, 29.6, 29.65, 29.71, 30.3, 31.7, 31.9, 38.6, 60.1, 67.2, 69.4, 73.5, 105.7, 112.4, 129.7, 141.2, 153.2, 167.5; ^{19}F NMR (CDCl_3 , 298 K) δ -81.2 (3F, br. m, CF_3 -(CF_2)₂- CF_2 - CH_2 - CH_2 -O-), -113.7 (2F, br. m, CF_3 -(CF_2)₂- CF_2 - CH_2 - CH_2 -O-), -124.7 (2F, br. m, CF_3 -(CF_2)₂- CF_2 - CH_2 - CH_2 -O-), -126.2 (2F, br. m, CF_3 -(CF_2)₂- CF_2 - CH_2 - CH_2 -O-).; HRMS (APCI, pos. mode, CH_2Cl_2): m/z calcd. for $\text{C}_{148}\text{H}_{201}\text{CuF}_{18}\text{N}_6\text{O}_{12}$ $[\text{M}+\text{H}]^+$: 2660.4333; found: 2660.4339.



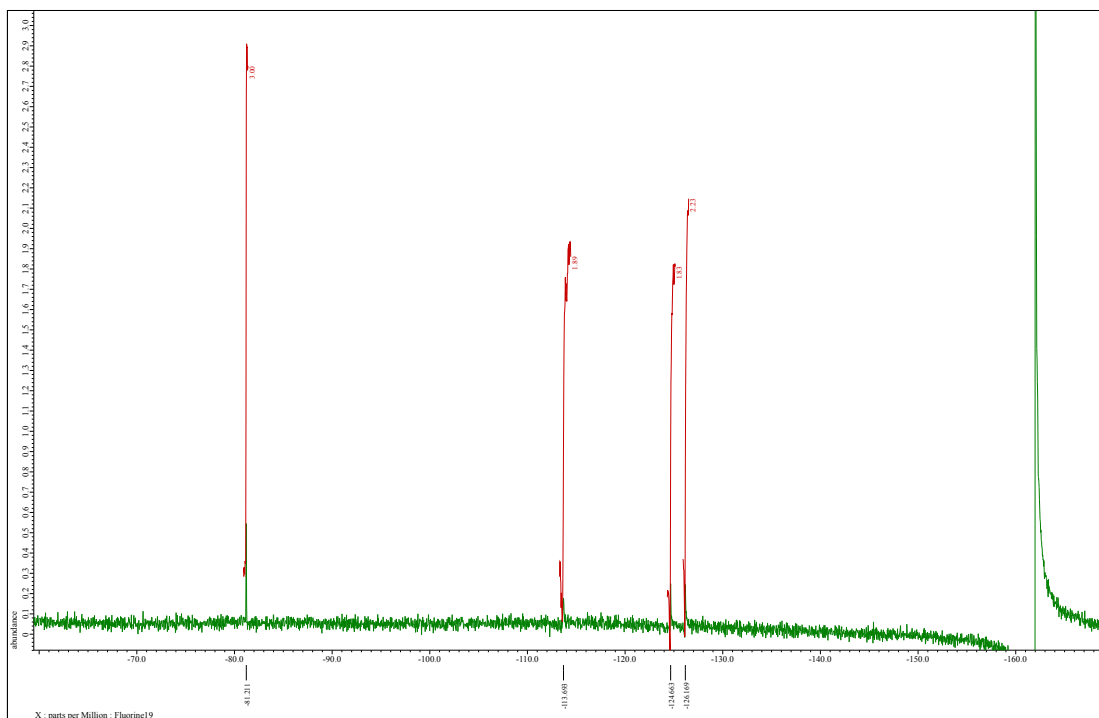
Supplementary Figure 4

^1H NMR (400 MHz) spectrum of **1_{Cu}** in CDCl_3 at 298 K



Supplementary Figure 5

¹³C NMR (100 MHz) spectrum of **1**_{Cu} in CDCl₃ at 298 K



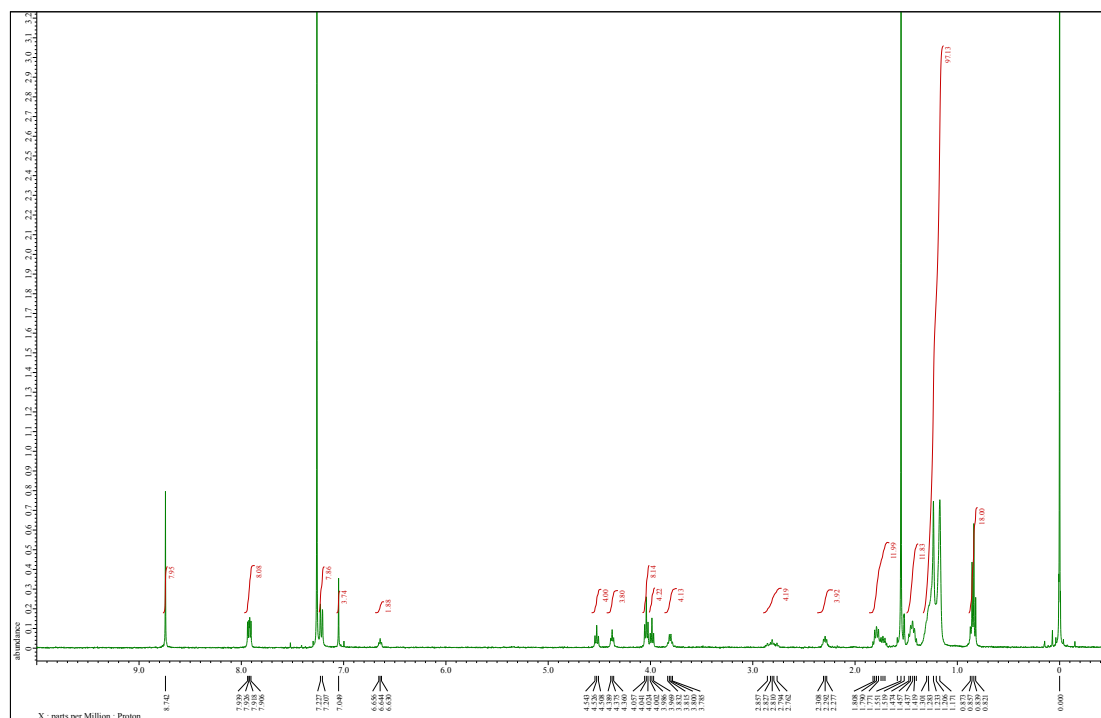
Supplementary Figure 6

¹⁹F NMR (376 MHz) spectrum of **1**_{Cu} in CDCl₃ at 298 K

Synthesis of 1_{Ni}

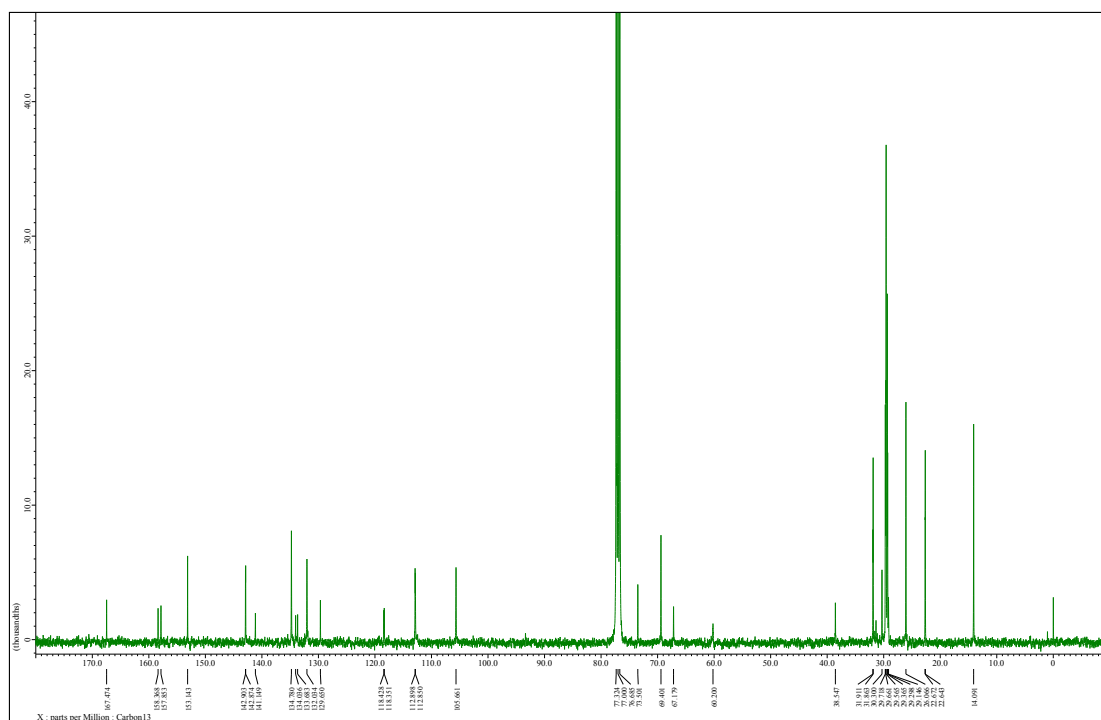
To a CHCl_3 solution (3.2 ml) of compound **1_H** (25 mg 9.6 μmol), $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (95 mg, 0.38 mmol) in MeOH (3.2 ml) was added, and the mixture was refluxed with stirring for 5 h under an argon atmosphere. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 . The mixture was washed with water, and dried over sodium sulfate anhydrous. The resultant residue was purified through column chromatography (silica gel, $\text{CHCl}_3/\text{acetone} = 20:1$ v/v) and size exclusion chromatography (CHCl_3) to yield compound **1_{Ni}** as a pink solid (13 mg, 52%).

m.p. = 188-191 °C; ¹H NMR (CDCl₃, 298 K) δ 0.81-0.88 (18H, m, CH₃-), 1.13-1.34 (96H, m, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-O-), 1.40-1.50 (12H, m, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-O-), 1.68-1.83 (12H, m, CH₃-(CH₂)₉-CH₂-CH₂-O-), 2.26-2.33 (4H, m, -NH-CH₂-CH₂-CH₂-O-), 2.74-2.88 (4H, m, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-), 3.78-3.83 (4H, m, -NH-CH₂-CH₂-CH₂-O-), 3.99 (4H, t, *J* = 6.4 Hz, CH₃-(CH₂)₉-CH₂-CH₂-O-), 4.04 (8H, t, *J* = 6.4 Hz, CH₃-(CH₂)₉-CH₂-CH₂-O-), 4.38 (4H, t, *J* = 5.6 Hz, -NH-CH₂-CH₂-CH₂-O-), 4.53 (4H, t, *J* = 6.8 Hz, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-), 6.64 (2H, t, *J* = 4.8 Hz, -NH-CH₂-CH₂-CH₂-O-), 7.05 (4H, s, Ar-*H*), 7.19-7.24 (8H, m, Ar-*H*), 7.92 (4H, d, *J* = 8.2 Hz, Ar-*H*), 7.93 (4H, d, *J* = 8.2 Hz, Ar-*H*), 8.74 (8H, s, β-pyrrole.); ¹³C NMR (CDCl₃, 298 K) δ 14.1, 22.64, 22.67, 26.1, 29.1, 29.3, 29.4, 29.57, 29.66, 29.72, 30.3, 31.86, 31.91, 38.5, 60.2, 67.2, 69.4, 73.5, 105.7, 112.85, 112.90, 118.35, 118.43, 129.7, 132.0, 133.7, 134.0, 134.8, 141.1, 142.87, 142.90, 153.1, 157.9, 158.4, 167.5; ¹⁹F NMR (CDCl₃, 298 K) δ -81.3 (3F, br. m, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-), -113.7 (2F, br. m, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-), -124.7 (2F, br. m, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-), -126.2 (2F, br. m, CF₃-(CF₂)₂-CF₂-CH₂-CH₂-O-); HRMS (APCI, pos. mode, CH₂Cl₂): *m/z* calcd. for C₁₄₈H₂₀₁F₁₈N₆NiO₁₂ [M+H]⁺: 2655.4397; found: 2655.4377.



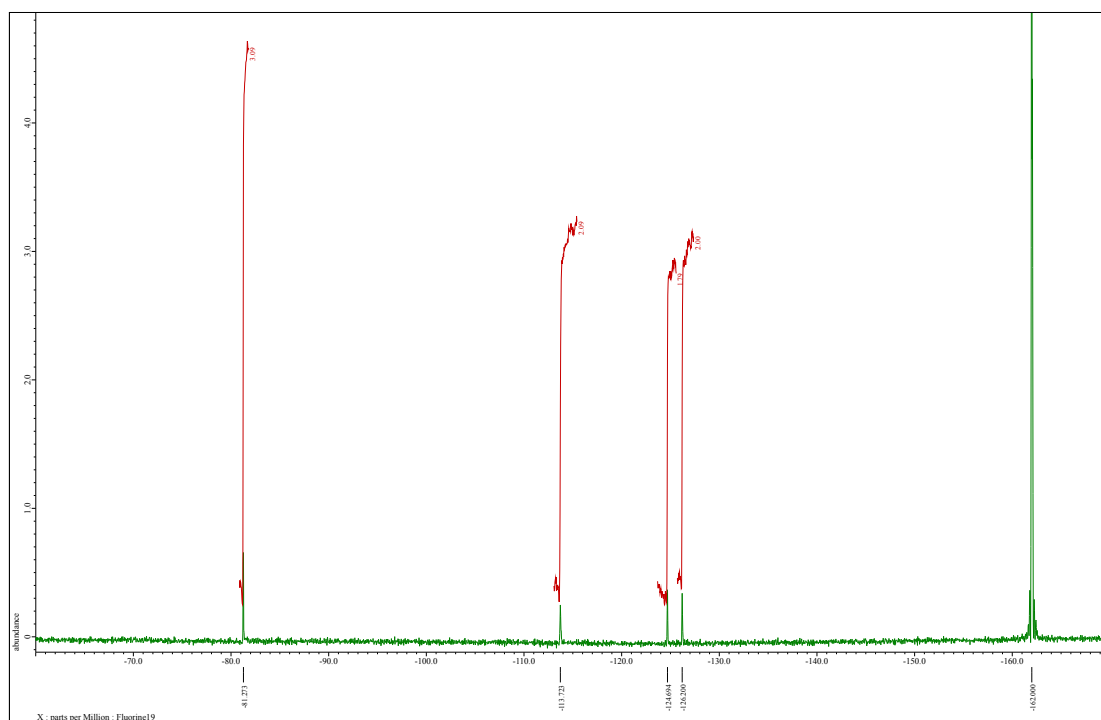
Supplementary Figure 7

¹H NMR (400 MHz) spectrum of **1_{Ni}** in CDCl₃ at 298 K



Supplementary Figure 8

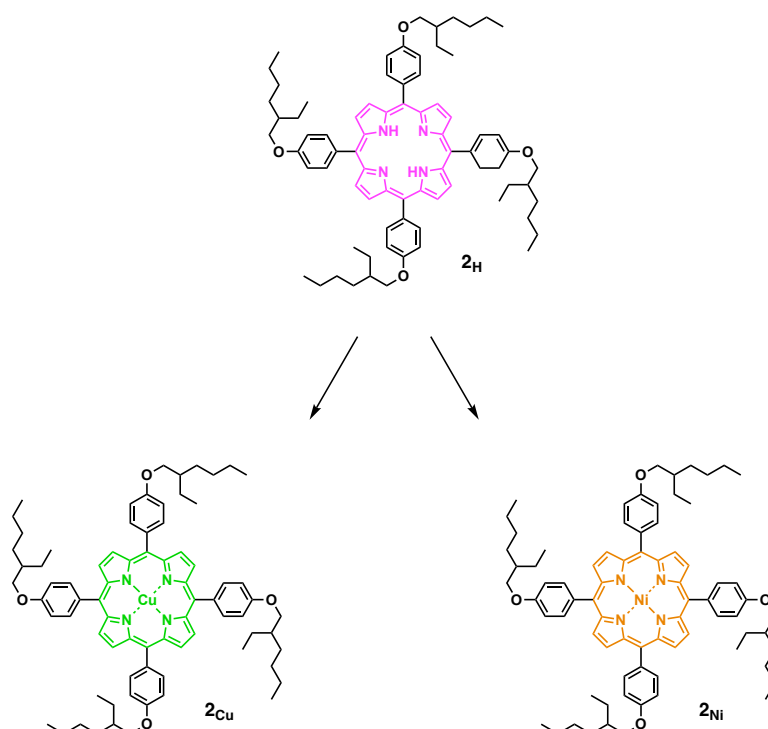
¹³C NMR (100 MHz) spectrum of **1**_{Ni} in CDCl₃ at 298 K



Supplementary Figure 9

¹⁹F NMR (376 MHz) spectrum of **1**_{Ni} in CDCl₃ at 298 K

Synthesis of compound **2_{Cu}** and **2_{Ni}**

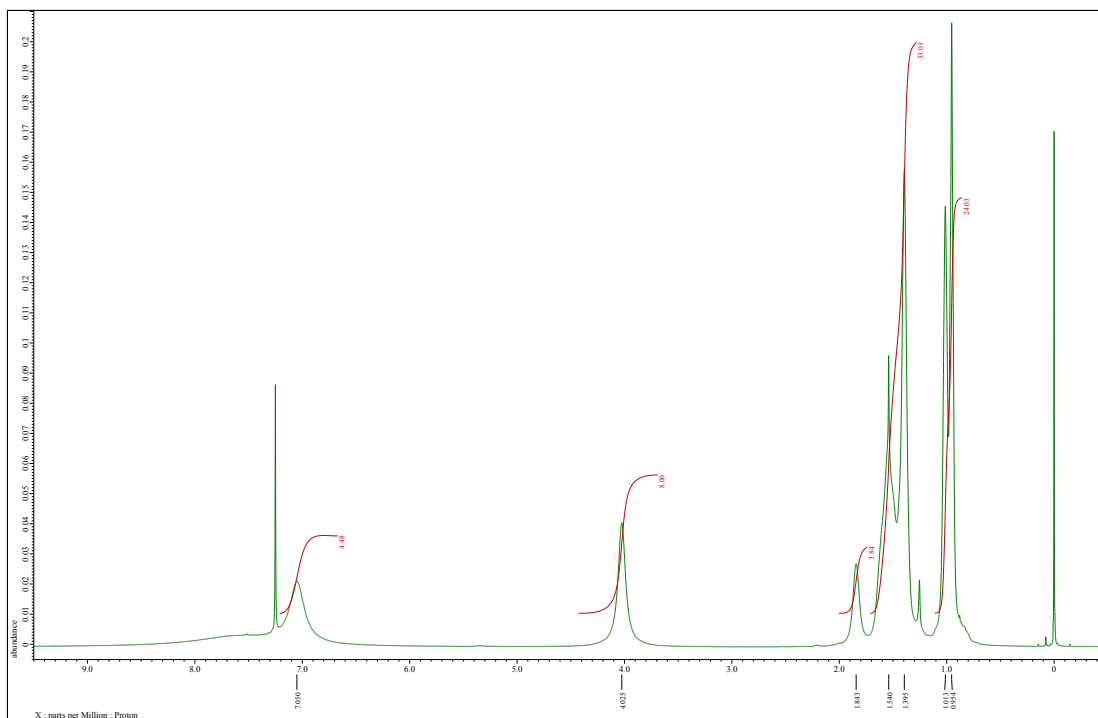


Supplementary Scheme S2. Synthesis of **2_{Cu}** and **2_{Ni}**.

Synthesis of **2_{Cu}**

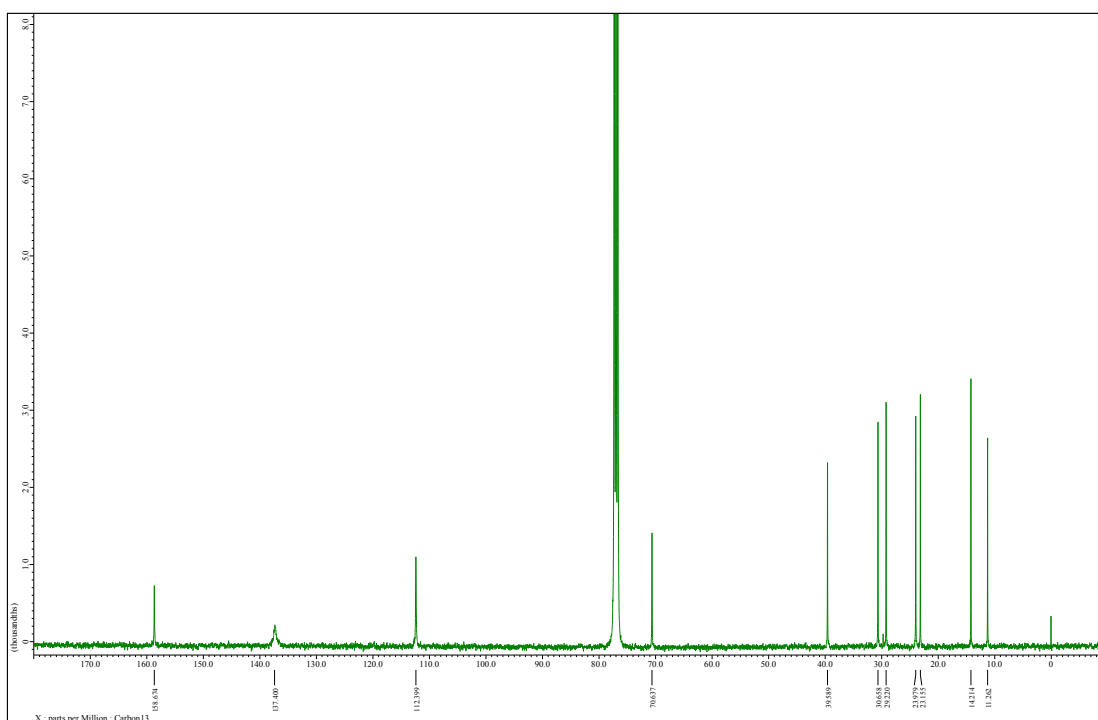
To a CHCl_3 solution (5.0 ml) of compound **2_H** (40 mg 35 μmol)^{S2}, $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (85 mg, 0.43 mmol) in MeOH (4.0 ml) was added, and the mixture was refluxed with stirring for 1 h under a nitrogen atmosphere. After cooling to room temperature, the solvents were diluted with CH_2Cl_2 , washed with brine, and then dried over anhydrous Na_2SO_4 . Insoluble materials were filtered off, and the filtrate was evaporated. The resultant residue was purified through column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:2$ v/v) to yield compound **2_{Cu}** as a pink solid (32 mg, 76%). *The paramagnetic nature of the copper ion hindered NMR characterization of tetrakis(4-alkoxyphenyl)porphyrinato copper (II) moiety in 2_{Cu}.*

m.p. = 179-181 °C; ^1H NMR (CDCl_3 , 298 K) δ 0.85-1.10 (24H, br, CH_3 -), 1.30-1.69 (32H, br), 1.74-1.92 (12H, br), 3.72-4.28 (8H, br, $-\text{O}-\text{CH}_2$), 6.80-7.25 (8H, br, Ar-H).; ^{13}C NMR (CDCl_3 , 298 K) δ 11.26, 14.21, 23.16, 23.98, 29.22, 30.66, 39.59, 70.64, 112.40, 137.40, 158.67; HRMS (APCI, pos. mode, CH_2Cl_2): m/z calcd. for $\text{C}_{76}\text{H}_{93}\text{CuN}_4\text{O}_4$ $[\text{M}+\text{H}]^+$: 1188.6487; found: 1188.6485.



Supplementary Figure 10

¹H NMR (400 MHz) spectrum of **2**_{Cu} in CDCl₃ at 298 K



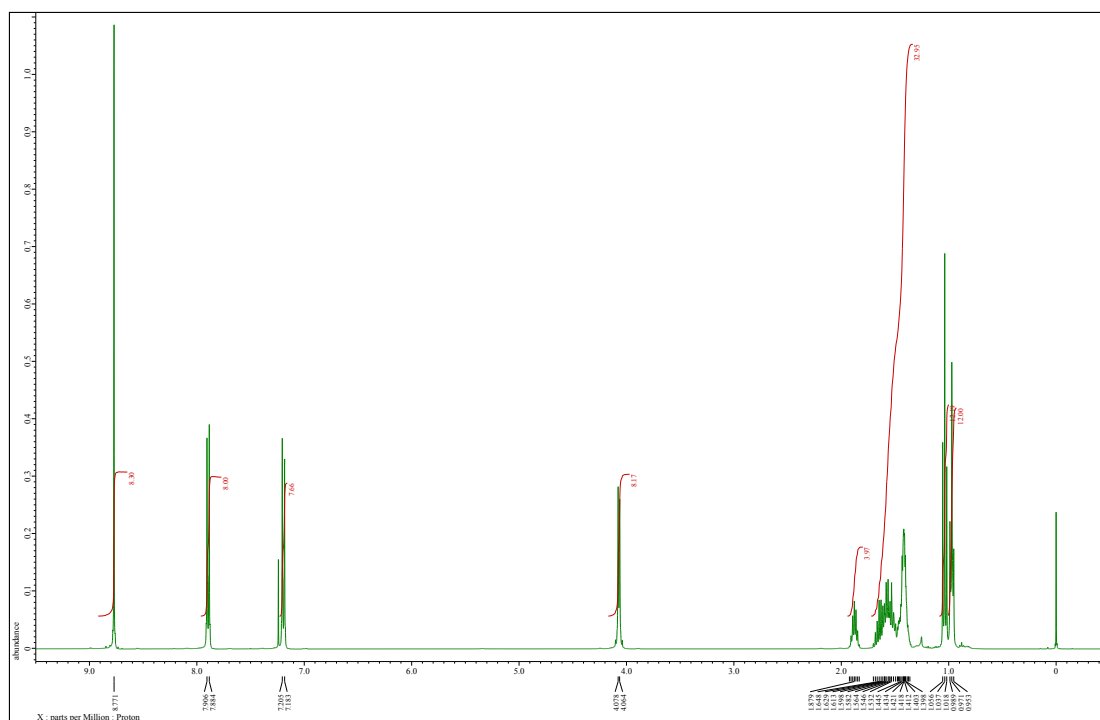
Supplementary Figure 11

¹³C NMR (100 MHz) spectrum of **2**_{Cu} in CDCl₃ at 298 K

Synthesis of 2_{Ni}

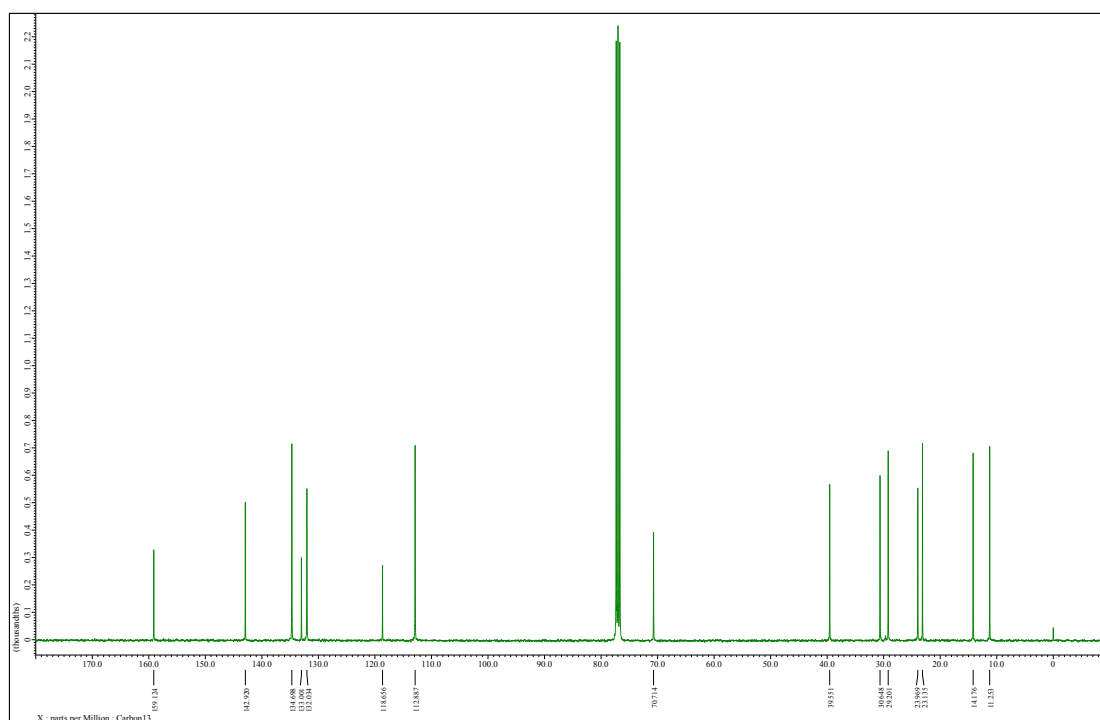
To a CHCl₃ solution (5.0 ml) of compound **2_H** (40 mg 35 μmol)^{S2}, Ni(OAc)₂·4H₂O (350 mg, 1.4 mmol) in MeOH (4.0 ml) was added, and the mixture was refluxed with stirring for 2 h under a nitrogen atmosphere. After cooling to room temperature, the solvents were diluted with CH₂Cl₂, washed with brine, and then dried over anhydrous Na₂SO₄. Insoluble materials were filtered off, and the filtrate was evaporated. The resultant residue was purified through column chromatography (silica gel, CH₂Cl₂/hexane = 1:2 v/v) to yield compound **2_{Ni}** as a purple solid (36 mg, 86%).

m.p. = 180-182 °C; ¹H NMR (CDCl₃, 298 K) δ 0.97 (12H, t, *J* = 7.2 Hz, CH₃-), 1.04 (12H, t, *J* = 7.6 Hz, CH₃-), 1.35-1.71 (32H, m), 1.83-1.92 (4H, m), 4.07 (8H, m, -O-CH₂), 7.19 (8H, d, *J* = 8.8 Hz Ar-*H*), 7.90 (8H, d, *J* = 8.8 Hz, Ar-*H*), 8.77 (8H, s, β-pyrrole).; ¹³C NMR (CDCl₃, 298 K) δ 11.25, 14.18, 23.14, 23.97, 29.20, 30.65, 39.55, 70.71, 112.89, 118.66, 132.03, 133.00, 134.70, 142.92, 159.12; HRMS (APCI, pos. mode, CH₂Cl₂): *m/z* calcd. for C₇₆H₉₃N₄NiO₄ [M+H]⁺: 1183.6545; found: 1183.6531.



Supplementary Figure 12

¹H NMR (400 MHz) spectrum of **2**_{Ni} in CDCl₃ at 298 K

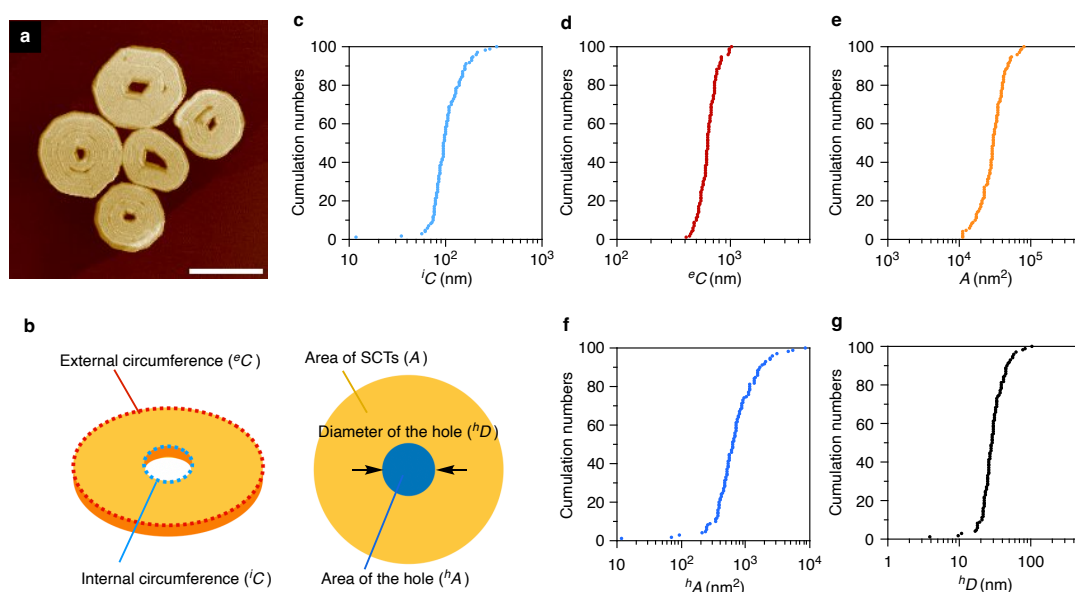


Supplementary Figure 13

¹³C NMR (100 MHz) spectrum of **2**_{Ni} in CDCl₃ at 298 K

3. Supplementary Figures, Tables, and Movie

AFM analysis of the supramolecular concentric toroids (SCTs) of 1_{Zn} prepared by the solvent-mixing protocol. This result has been reported previously.^{S1}



Supplementary Figure 14

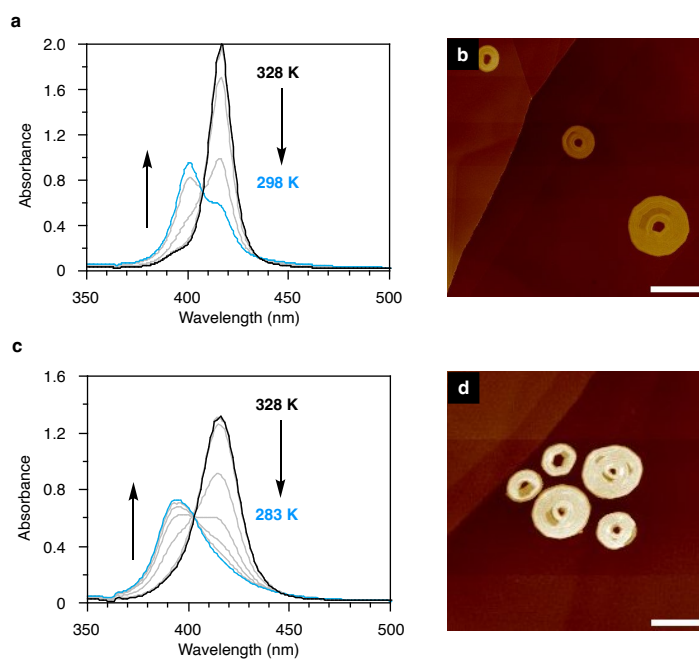
a, AFM image of SCTs of 1_{Zn} prepared through the solvent-mixing protocol established in our previous study^{S1}: HOPG substrate, scale bar = 200 nm. **b**, Schematic representation of structural parameters of SCTs discussed in this study. **c-g**, Cumulative histograms of the internal circumference (iC) (**c**), external circumference (eC) (**d**), area (A) (**e**), area of the hole (hA) (**f**), and diameter of the hole (hD) (**g**) of SCTs consisting of 1_{Zn} : $[1_{Zn}] = 5.0 \mu M$. Preparation is described in Methods in the main text.

Supplementary Table 1. AFM analysis of SCTs of 1_{Zn} obtained through the solvent-mixing protocol.

AFM data	iC_n (nm)	eC_n (nm)	A_n (nm ²)	A_w (nm ²)	A_w/A_n	hD_n^* (nm)
SFig. 14a	110	644	31900	37600	1.18	31

* Diameter of hole (hD) was calculated based on the area of hole (hA) of SCTs of 1_{Zn} (Supplementary Figure 14g).

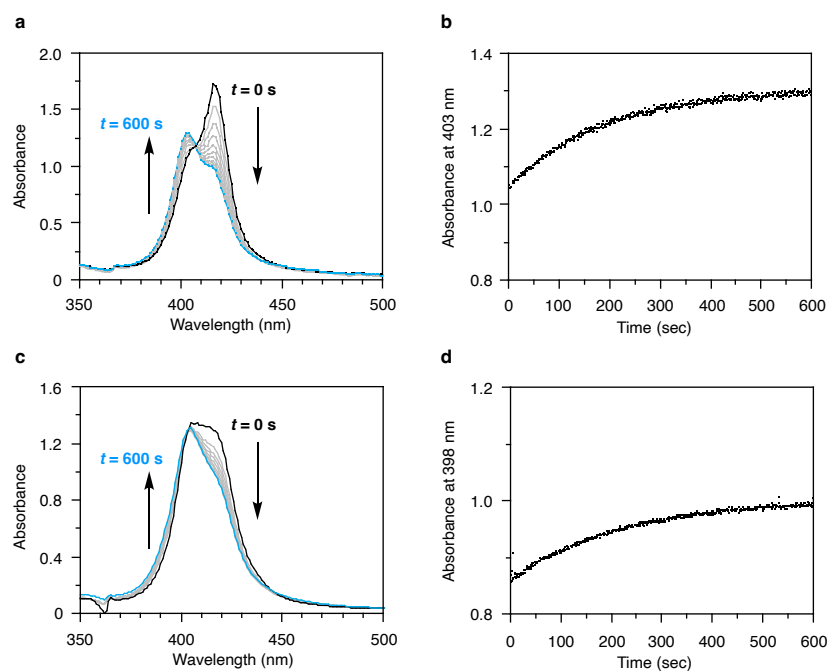
Formation of SCTs of **1_{Cu}** and **1_{Ni}**



Supplementary Figure 15

a,c, Temperature-dependent absorption spectral changes of a solution of **1_{Cu}** (**a**) and **1_{Ni}** (**c**) in dodecane: [**1_{Cu}** or **1_{Ni}**] = 5.0 μ M, -5 K/min. The spectral changes indicate the formation of H-aggregates upon cooling. **b,d**, AFM images of SCTs of **1_{Cu}** (**b**) and **1_{Ni}** (**d**) on HOPG substrate: scale bar = 200 nm.

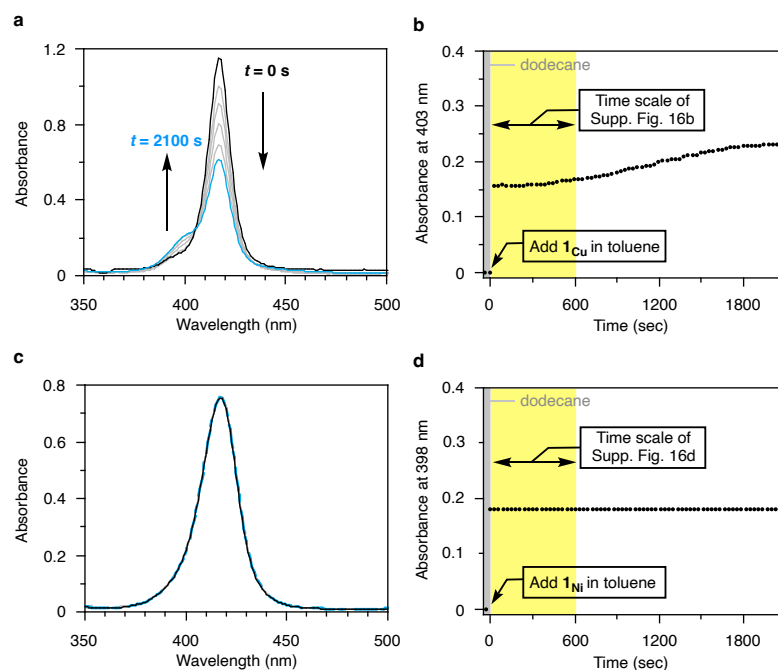
Seeded supramolecular polymerization using SCTs of 1_{Zn} as seeds



Supplementary Figure 16

a,c, Time-dependent absorption spectral changes after the addition of the toluene solution of 1_{Cu} (a) or 1_{Ni} (c) to the solution of SCTs of 1_{Zn} (used as seeds) in dodecane containing 5% toluene. **b,d,** Plots of the absorbance at 403 nm (b) and 398 nm (d) measured after the addition of the 1_{Cu} (b) and 1_{Ni} (d), respectively.

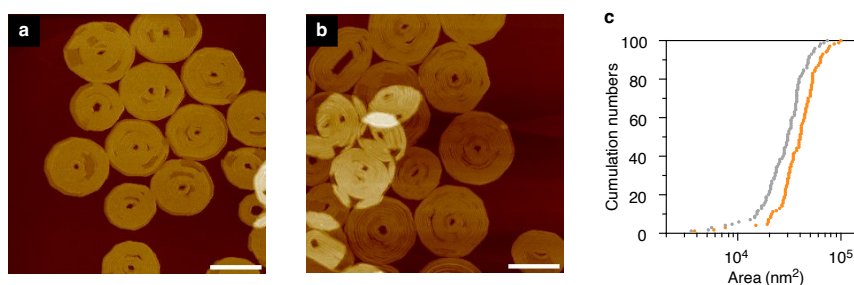
Kinetic studies of the self-assembly behavior of a **1_{Cu}** and **1_{Ni}**



Supplementary Figure 17

a,c, Time-dependent absorption spectral changes observed upon mixing a toluene solution of **1_{Cu}** (**a**) and **1_{Ni}** (**c**) with dodecane: $[1_{\text{Cu}}] = 2.5 \mu\text{M}$, $[1_{\text{Ni}}] = 2.5 \mu\text{M}$, toluene/dodecane = 1:19 (v/v), 298 K. **b,d**, Plots of the absorbances at 403 nm (**b**) and 398 nm (**d**) measured after the mixing a toluene solution of **1_{Cu}** and **1_{Ni}** with dodecane, respectively.

AFM analysis of the two-component SCTs prepared through the seeded supramolecular polymerization of 1_{Cu} using SCTs of 1_{Zn} as seeds



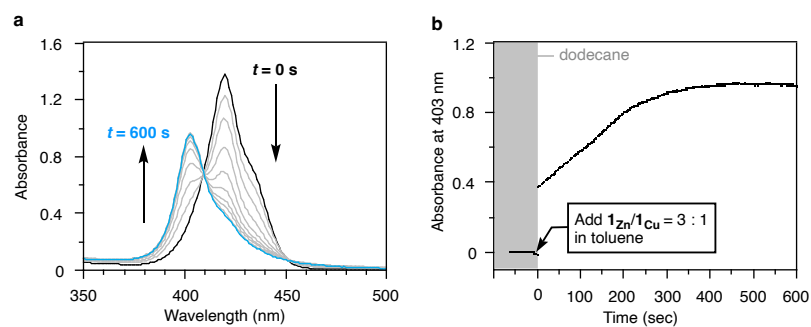
Supplementary Figure 18

a,b, AFM images of SCTs consisting of 1_{Zn} used as seeds (**a**) and two-component SCTs consisting of 1_{Zn} and 1_{Cu} obtained through the seeded supramolecular polymerization (**b**): scale bar = 200 nm. **c**, Cumulative histograms of area of the SCTs, showing that the area increased after the seeded supramolecular polymerization: seeds (grey) and two-component SCTs (orange).

Supplementary Table 2. AFM analysis of two-component SCTs obtained through the seeded supramolecular polymerization of 1_{Cu} using SCTs of 1_{Zn} as seeds.

AFM data	iC_n (nm)	eC_n (nm)	A_n (nm ²)	A_w (nm ²)	A_w/A_n
SFig. 18b	94	725	41600	48800	1.18

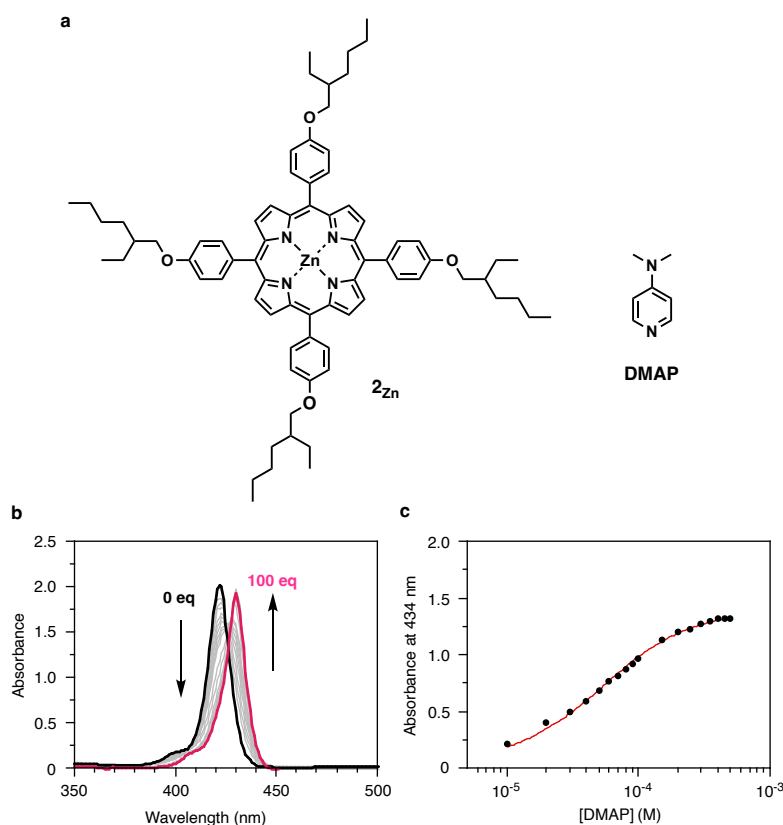
Self-assembling behavior of a mixture of 1_{Zn} and 1_{Cu} during one-shot supramolecular copolymerization



Supplementary Figure 19

a, Time-dependent absorption spectral changes observed upon mixing a toluene solution of 1_{Zn} and 1_{Cu} with dodecane: $[1_{Zn}] = 3.75\text{ }\mu\text{M}$, $[1_{Cu}] = 1.25\text{ }\mu\text{M}$, $1_{Zn}/1_{Cu} = 3/1$ (mol/mol), toluene/dodecane = 1:19 (v/v), 298 K. **b**, Plot of the absorbances at 403 nm as functions of time.

Titration of a soluble reference porphyrin 2_{Zn} with DMAP ^{S5}



Supplementary Figure 20

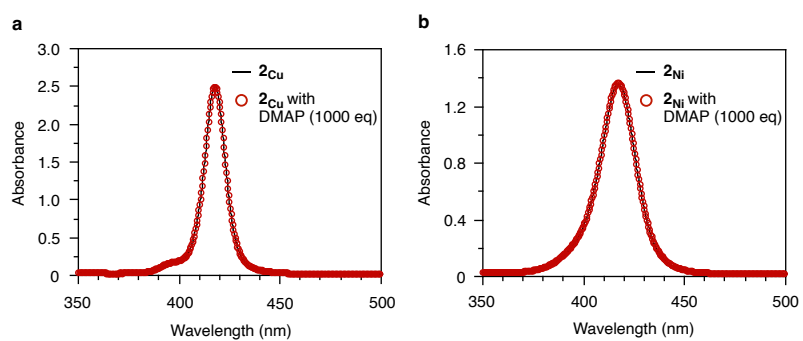
a, Chemical structure of reference 2_{Zn} and DMAP. **b**, Absorption spectral changes of 2_{Zn} upon addition of DMAP: $[2_{Zn}] = 5 \mu\text{M}$, toluene/dodecane mixtures (1:9, v/v). **c**, Corresponding titration curve probed for DMAP- 2_{Zn} complex at 434 nm with the fitting curve (red line, correlation coefficient of 0.998).

Titration experiment of 2_{Zn} with DMAP was performed in order to determine the binding constants of Zn(II) porphyrin for DMAP. The titration curve was fitted by using 1:1 binding isotherm equation S1: $K = 3.0 \times 10^4 \text{ M}^{-1}$ at 298 K. The Gibbs free energy of the DMAP- 2_{Zn} interaction was calculated from equation S2 in which R is the ideal gas constant: $\Delta G = -25.5 \text{ kJ/mol}$.

$$\frac{A - A_{\text{initial}}}{A_{\infty} - A_{\text{initial}}} = \frac{(K([\text{DMAP}] + [2_{Zn}]_0) + 1) - \sqrt{(K([\text{DMAP}] + [2_{Zn}]_0) + 1)^2 - 4K^2[2_{Zn}]_0[\text{DMAP}]}}{2K[2_{Zn}]_0} \quad (\text{S1})$$

$$\Delta G = -RT \ln K \quad (\text{S2})$$

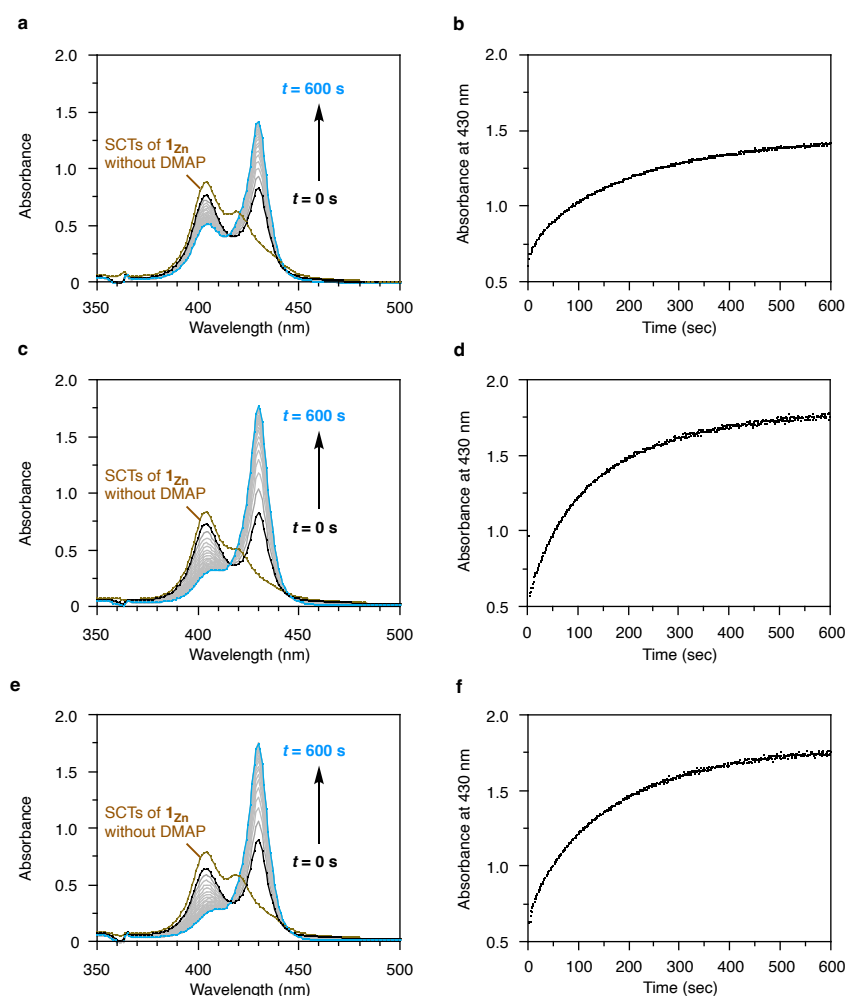
Absorption spectra of a soluble reference porphyrin 2_{Cu} and 2_{Ni} with DMAP



Supplementary Figure 21

a,b, Absorption spectra of 2_{Cu} (**a**) and 2_{Ni} (**b**) with and without DMAP : $[1_{\text{Cu}}] = 5 \mu\text{M}$, $[1_{\text{Ni}}] = 5 \mu\text{M}$, $[\text{DMAP}] = 5000 \mu\text{M}$, toluene/dodecane = 1:9 (v/v), 298 K.

DMAP-induced depolymerization process of SCTs of 1_{Zn}

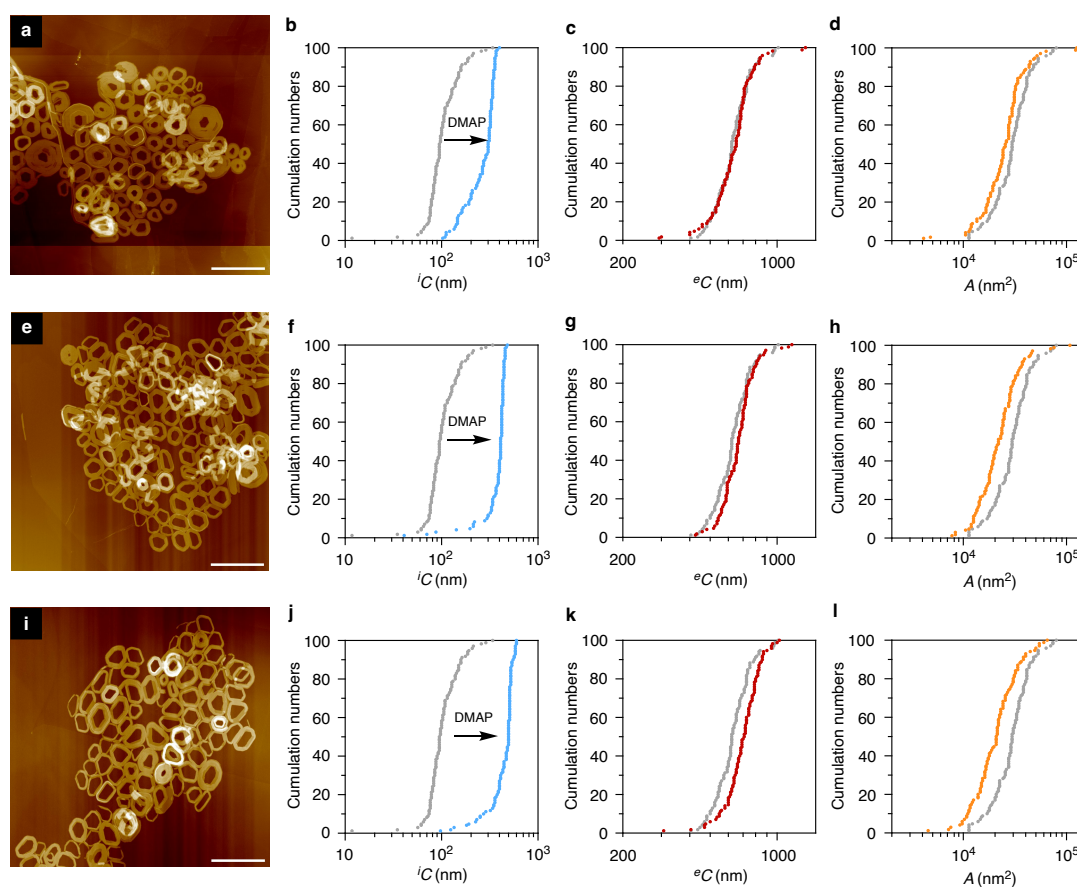


Supplementary Figure 22

Amounts of DMAP used in these experiments were 5.0 eq. (top row), 7.5 eq. (middle row), and 10.0 eq. (bottom row) with respect to 1_{Zn} .

a,c,e, Time-dependent absorption spectral changes of SCTs of 1_{Zn} upon addition of DMAP. **b,d,f**, Plots of the absorbances at 430 nm as functions of time monitored after the addition of DMAP: $[1_{Zn}] = 4.73 \mu\text{M}$, $[\text{DMAP}] = 23.7 \mu\text{M}$ (**a,b**), $35.5 \mu\text{M}$ (**c,d**), and $47.3 \mu\text{M}$ (**e,f**), toluene/dodecane = 1:9 (v/v), 298 K.

AFM analysis of the SCTs of 1_{Zn} after the DMAP treatment



Supplementary Figure 23

Amounts of DMAP used in these experiments were 5.0 eq. (top row), 7.5 eq. (middle row), and 10.0 eq. (bottom row) with respect to 1_{Zn} .

a,e,i, AFM images of SCTs of 1_{Zn} after the treatment with DMAP: HOPG substrate, scale bar = 600 nm. **b-d, f-h, j-l**, Corresponding structural parameters of SCTs of 1_{Zn} after the DMAP treatment: [1_{Zn}] = 4.73 μ M; [DMAP] = 23.7 μ M (**a-d**, top row), 35.5 μ M (**e-h**, middle row), and 47.3 μ M (**i-l**, bottom row). Cumulative histograms of the internal circumference (iC) (**b,f,j**: blue), external circumference (eC) (**c,g,k**: red), and area (A) (**d,h,l**: orange) of SCTs of 1_{Zn} . For comparison, the corresponding data of SCTs of 1_{Zn} before the DMAP treatment are shown together in grey.

Supplementary Table 3. AFM analysis of SCTs of 1_{Zn} obtained after the DMAP treatment.

AFM data	Added DMAP (μ M)	iC_n (nm)	eC_n (nm)	A_n (nm ²)	A_w (nm ²)	A_w/A_n
SFig. 23a	23.7 (5.0 eq.)	270	650	27900	38500	1.38
SFig. 23e	35.5 (7.5 eq.)	380	680	24500	32300	1.32
SFig. 23i	47.3 (10.0 eq.)	450	710	22900	28900	1.26

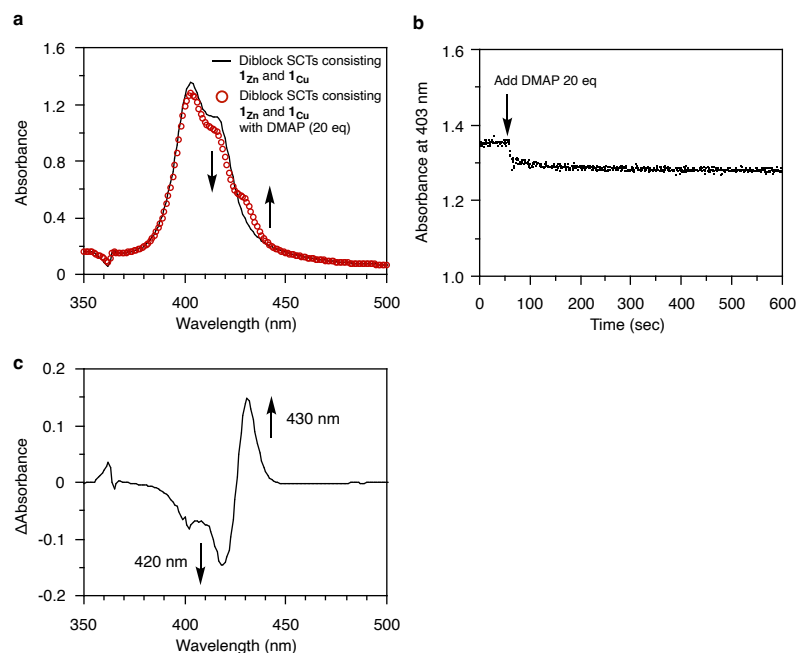
Real-time observation of depolymerization of SCTs induced by DMAP using high-speed AFM



Supplementary Movie 1 (see a separate file)

High-speed AFM observations were performed in a dodecane/toluene mixed solvent at room temperature. On a HOPG substrate, a solution of SCTs containing of **1_{Zn}** was spread ($[1_{\text{Zn}}] = 5 \mu\text{M}$, $5 \mu\text{L}$, dodecane/toluene=19:1), and excess amount of solvents was removed with Kimwipes. Before the substrate was completely dried, the HOPG substrate was immersed in a dodecane/toluene mixed solvent ($\sim 70 \mu\text{L}$). During the observation, DMAP ($10 \mu\text{L}$, 60 mM , dodecane/toluene=19:1 followed by $2 \mu\text{L}$, 630 mM , dodecane/toluene=19:1) was added to induce the depolymerization of SCTs.

Absorption spectral changes of diblock SCTs consisting 1_{Zn} and 1_{Cu} upon addition of DMAP^{S5}

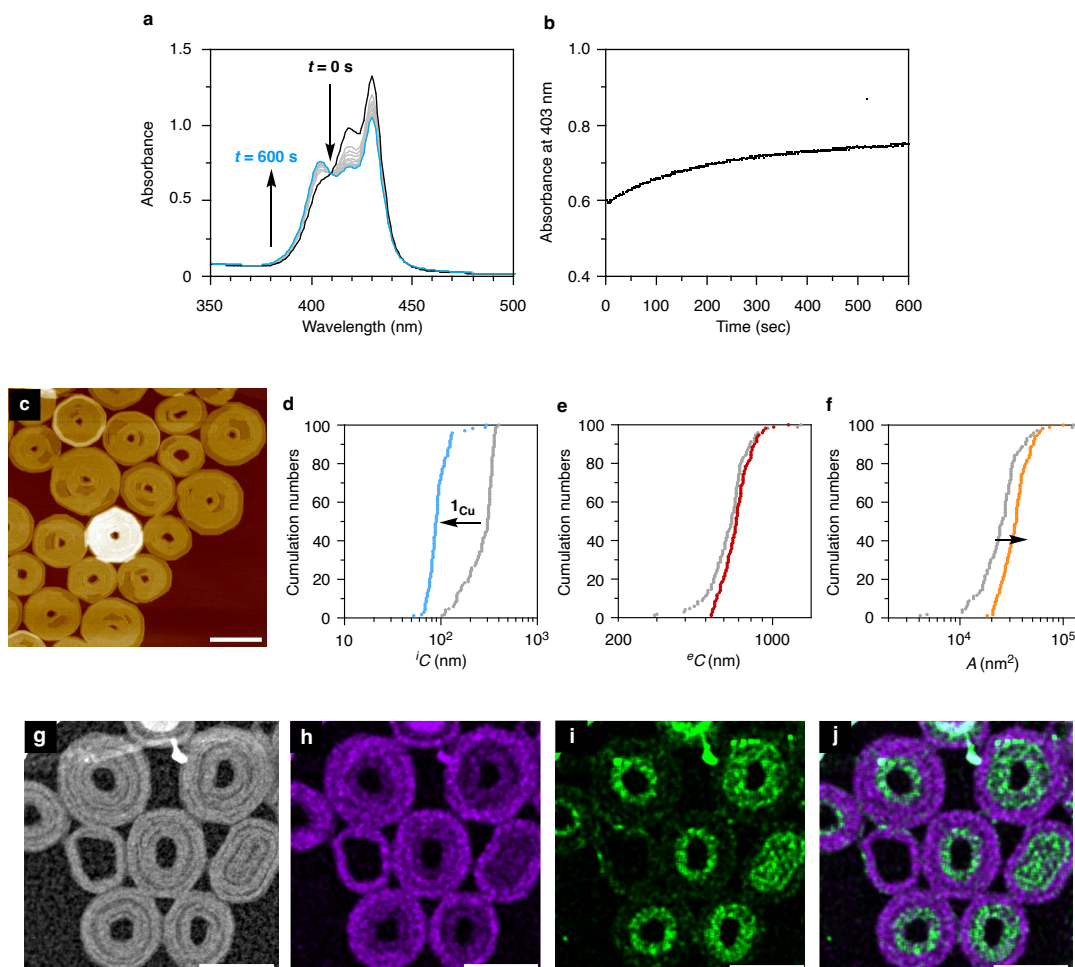


Supplementary Figure 24

a, Absorption spectra of diblock SCTs consisting of 1_{Zn} and 1_{Cu} in the absence and presence of DMAP. **b**, Plot of absorbances at 403 nm as functions of time monitored after the addition of DMAP : $[1_{Zn}] = 4.55 \mu\text{M}$, $[1_{Cu}] = 2.27 \mu\text{M}$, $[\text{DMAP}] = 90.9 \mu\text{M}$ (**a,b**), toluene/dodecane = 1:9 (v/v), 298 K. **c**, difference absorption spectrum of diblock SCTs consisting 1_{Zn} and 1_{Cu} in the absence and presence of DMAP.

As shown in Supplementary Figure 20, monomeric zinc porphyrin (2_{Zn}) has an absorption maximum at 420 nm, and its DMAP complex has an absorption maximum at 430 nm. When DMAP was added for SCTs consisting of 1_{Zn} and 1_{Cu} (see above), absorbance at 430 nm increased with a concomitant decrease in the absorbance at 420 nm (Supplementary Figures 24a,c). This result suggests that coexisting monomeric 1_{Zn} in the solution bind to DMAP. In other words, changes in absorbance observed in Supplementary Figure 24b was mainly due to the coexisting monomeric 1_{Zn} , rather than due to the depolymerization of the diblock SCTs. A similar trend was observed in our previous study^{S5}.

Characterization of the two-component SCTs consisting of 1_{Zn} and 1_{Cu} obtained using seeds of 1_{Zn} which were pretreated with DMAP (5.0 eq)

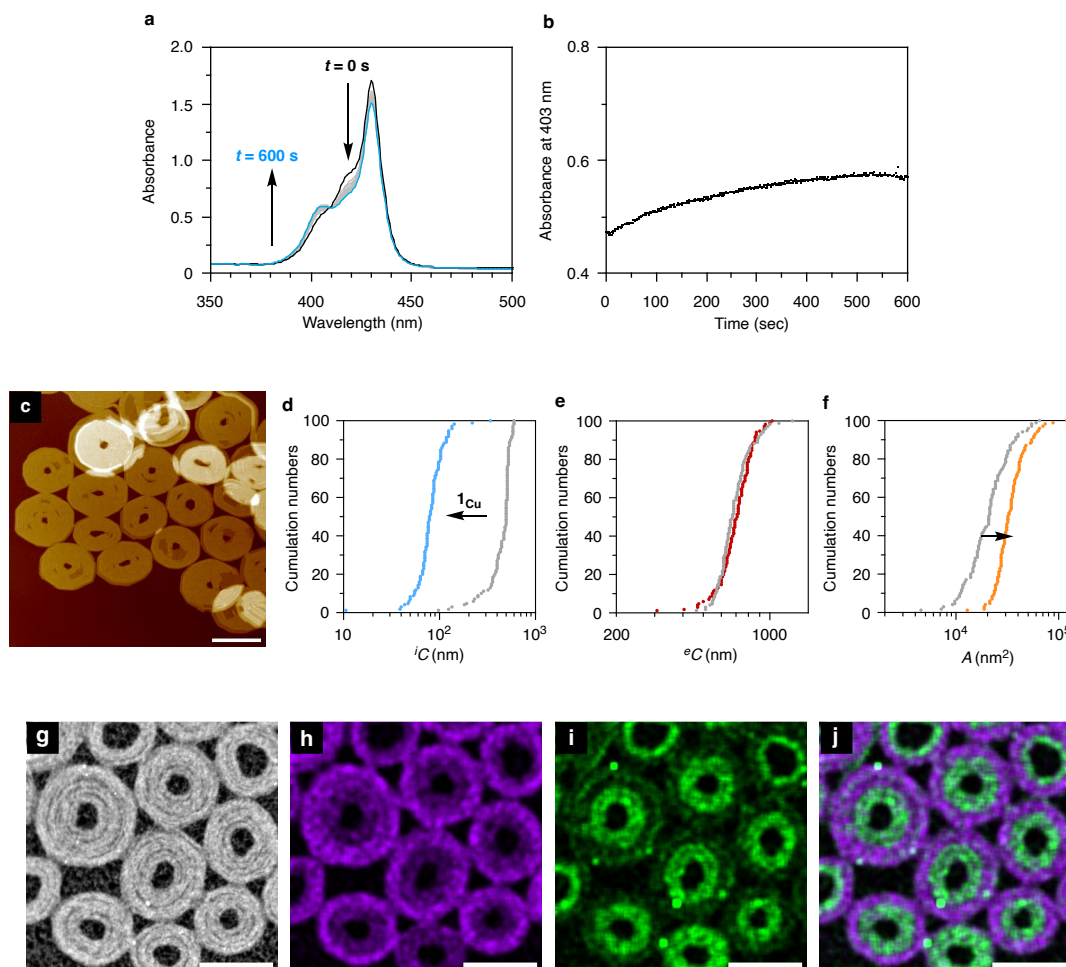


Supplementary Figure 25

Seeds used in these experiments were prepared as shown in Supplementary Figure 23 using 5.0 eq. of DMAP with respect to 1_{Zn} (i.e., Supplementary Fig. 23a).

a,b, Time-dependent absorption spectral changes (**a**) and plots of absorbance at 403 nm as a function of time (**b**), measured after the addition of a toluene solution of 1_{Cu} to the solution of SCTs of 1_{Zn} (i.e., seeds) which was treated with DMAP beforehand: $[1_{Zn}] = 4.4 \mu\text{M}$, $[\text{DMAP}] = 22 \mu\text{M}$, $[1_{Cu}] = 0.88 \mu\text{M}$; toluene/dodecane = 1:9 (v/v), 298 K. **c,** AFM images of two-component SCTs consisting of 1_{Zn} and 1_{Cu} obtained through seeded supramolecular polymerization using pretreated SCTs of 1_{Zn} as seeds; HOPG substrate, scale bar = 200 nm. (**d–f**) Cumulative histograms of the internal circumference (iC) (**d**, blue), external circumference (eC) (**e**, red), and area (A) (**f**, orange) of two-component SCTs consisting of 1_{Zn} and 1_{Cu} determined from the AFM images shown on the left. *For comparison, those of SCTs of 1_{Zn} used as seeds are shown together in grey.* **g–j,** ADF-STEM (**g**), and STEM-EDS (**h–j**) images of diblock SCTs consisting of 1_{Zn} and 1_{Cu} (scale bar = 200 nm). In elemental mapping, zinc and copper elements are shown in purple and green, respectively.

Characterization of the two-component SCTs consisting of 1_{Zn} and 1_{Cu} obtained using seeds of 1_{Zn} which were pretreated with DMAP (10.0 eq)

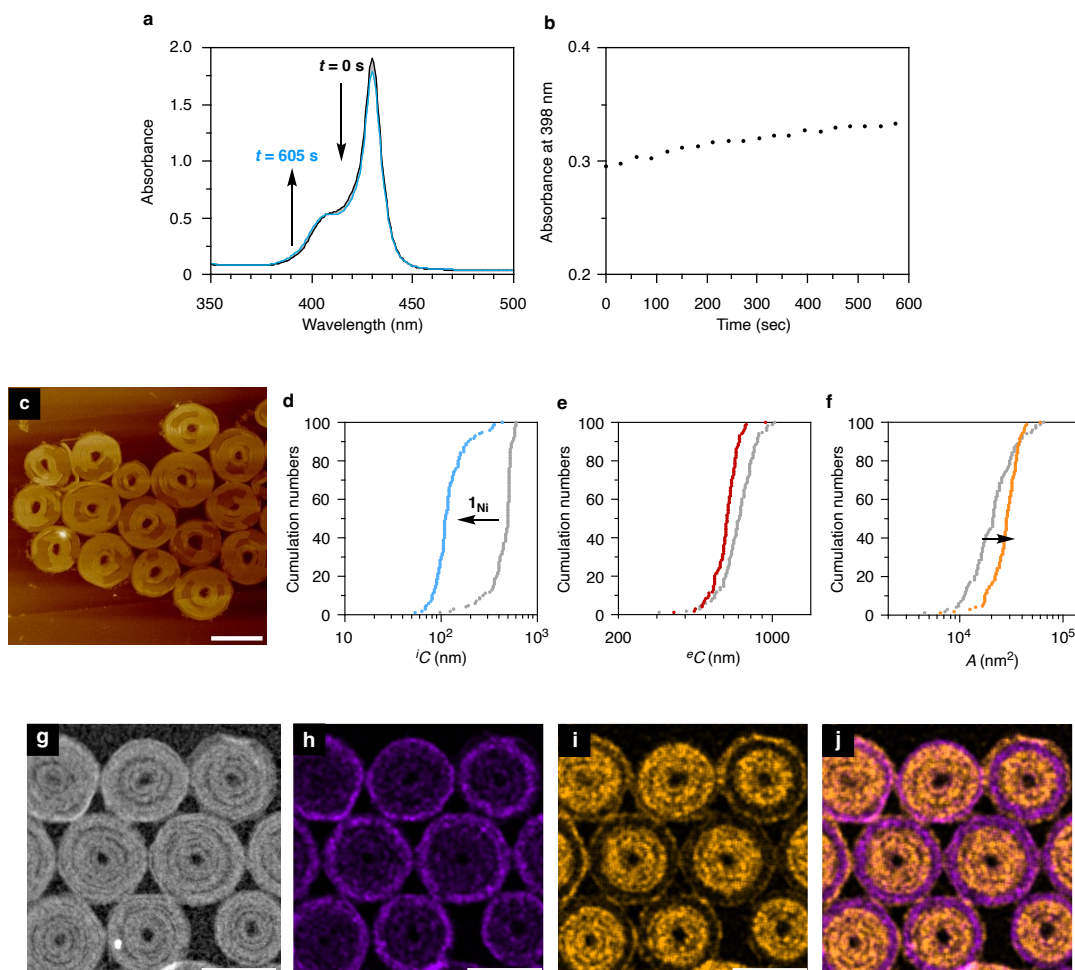


Supplementary Figure 26

Seeds used in these experiments were prepared as shown in Supplementary Figure 23 using 10.0 eq. of DMAP with respect to 1_{Zn} (i.e., Supplementary Fig. 23i).

a,b, Time-dependent absorption spectral changes (**a**) and plots of absorbance at 403 nm as a function of time (**b**), measured after the addition of a toluene solution of 1_{Cu} to the solution of SCTs of 1_{Zn} (i.e., seeds) which was treated with DMAP beforehand: $[1_{Zn}] = 4.4 \mu\text{M}$, $[\text{DMAP}] = 44 \mu\text{M}$, $[1_{Cu}] = 0.88 \mu\text{M}$; toluene/dodecane = 1:9 (v/v), 298 K. **c,** AFM images of two-component SCTs consisting of 1_{Zn} and 1_{Cu} obtained through seeded supramolecular polymerization using pretreated SCTs of 1_{Zn} as seeds; HOPG substrate, scale bar = 200 nm. **(d–f)** Cumulative histograms of the internal circumference (iC) (**d**, blue), external circumference (eC) (**e**, red), and area (A) (**f**, orange) of two-component SCTs consisting of 1_{Zn} and 1_{Cu} determined from the AFM images shown on the left. *For comparison, those of SCTs of 1_{Zn} used as seeds are shown together in grey.* **g–j,** ADF-STEM (**g**), and STEM-EDS (**h–j**) images of diblock SCTs consisting of 1_{Zn} and 1_{Cu} (scale bar = 200 nm). In elemental mapping, zinc and copper elements are shown in purple and green, respectively (Images of **g–j** are also shown in Fig. 4a–d).

Characterization of the two-component SCTs consisting of 1_{Zn} and 1_{Ni} obtained using seeds of 1_{Zn} which were pretreated with DMAP (10.0 eq)



Supplementary Figure 27

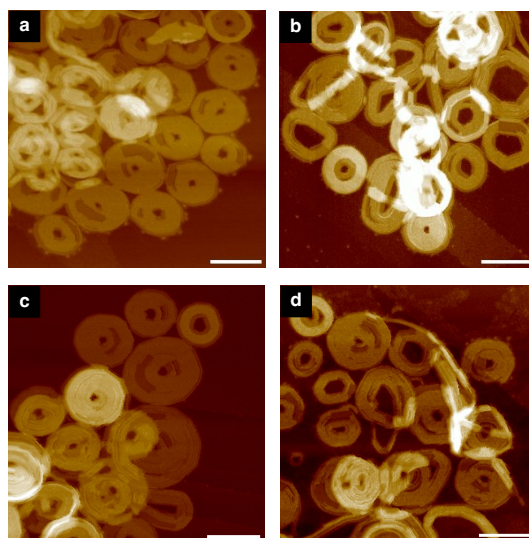
Seeds used in these experiments were prepared as shown in Supplementary Figure 23 using 10.0 eq. of DMAP with respect to 1_{Zn} (i.e., Supplementary Fig. 23i).

a,b, Time-dependent absorption spectral changes (**a**) and plots of absorbance at 403 nm as a function of time (**b**), measured after the addition of a toluene solution of 1_{Ni} to the solution of SCTs of 1_{Zn} (i.e., seeds) which was treated with DMAP beforehand: $[1_{Zn}] = 4.4 \mu M$, $[DMAP] = 44 \mu M$, $[1_{Ni}] = 0.88 \mu M$; toluene/dodecane = 1:9 (v/v), 298 K. *Note that absorption coefficient of H aggregate of 1_{Ni} is smaller than that of 1_{Cu} (Supplementary Fig. 26b).* **c,** AFM images of two-component SCTs consisting of 1_{Zn} and 1_{Ni} obtained through seeded supramolecular polymerization using pretreated SCTs of 1_{Zn} as seeds; HOPG substrate, scale bar = 200 nm. **(d–f)** Cumulative histograms of the internal circumference (iC) (**d**, blue), external circumference (eC) (**e**, red), and area (A) (**f**, orange) of two-component SCTs consisting of 1_{Zn} and 1_{Ni} determined from the AFM images shown on the left. *For comparison, those of SCTs of 1_{Zn} used as seeds are shown together in grey.* **g–j,** ADF-STEM (**g**), and STEM-EDS (**h–j**) images of diblock SCTs consisting of 1_{Zn} and 1_{Ni} (scale bar = 200 nm). In elemental mapping, zinc and nickel elements are shown in purple and orange, respectively.

Supplementary Table 4. AFM analysis of two-component SCTs consisting of 1_{Zn} and 1_{Cu} or 1_{Ni} obtained through seeded supramolecular polymerization using SCTs of 1_{Zn} which was treated with DMAP beforehand (see Supplementary Table 3).

AFM data	AFM of SCTs of 1_{Zn} used as seeds	iC_n (nm)	eC_n (nm)	A_n (nm ²)	A_w (nm ²)	A_w/A_n
SFig. 25c	SFig. 23a	97	695	35300	39700	1.12
SFig. 26c	SFig. 23i	85	700	36200	42500	1.17
SFig. 27c	SFig. 23i	131	621	28600	30900	1.08

AFM images of the di- and triblock SCTs prepared about 11 months ago

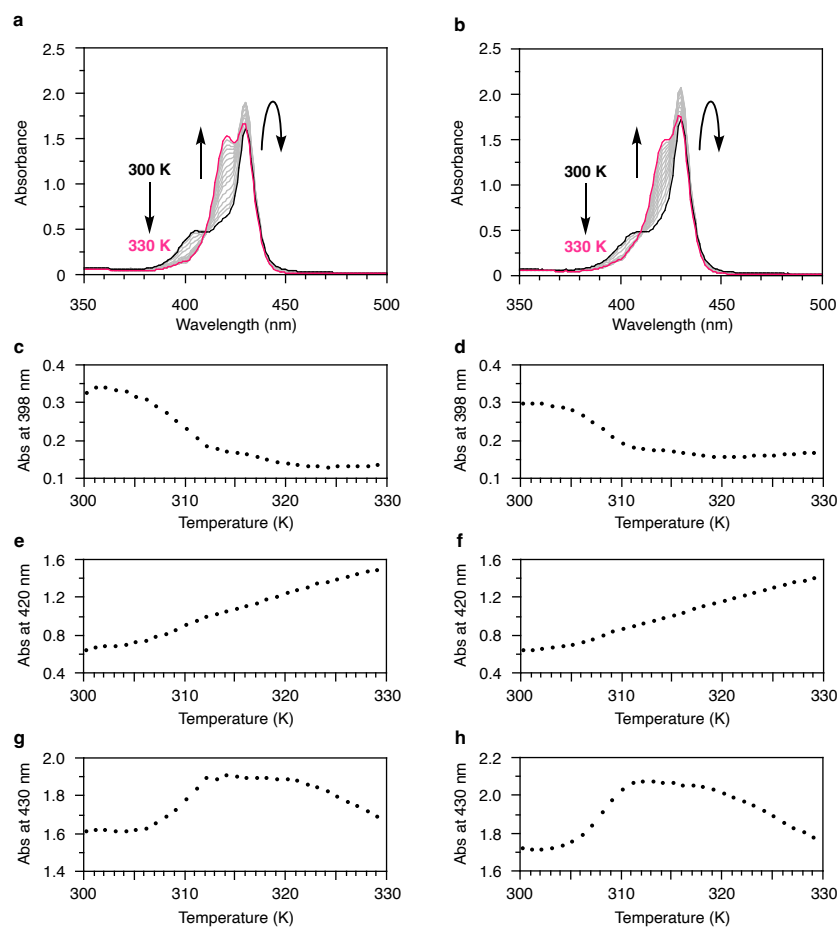


Supplementary Figure 28

a–d, AFM images of block SCTs obtained through seeded supramolecular polymerization using SCTs of 1_{Zn} pretreated with DMAP (5.0 eq.) (**a**) and DMAP (10.0 eq.) (**b–d**) (scale bar = 200 nm). AB type diblock (**a,b**), ABC type triblock (**c**) and ACB type (**d**) triblock SCTs were synthesized, where A, B, and C blocks consist of 1_{Zn} , 1_{Cu} , 1_{Ni} , respectively. Samples were prepared by spin-coating on HOPG substrate on January 17th, 2022 (**a,c**), January 4th, 2022 (**b**), and January 21st, 2022 (**d**) and then had been kept at ambient conditions. AFM images were obtained on December 10th, 2022 (**a,b**), December 4th, 2022 (**c,d**).

SCTs structures were observed, thus suggesting that block SCTs are stable under ambient conditions for several months.

Thermal stability of the diblock SCTs in solution



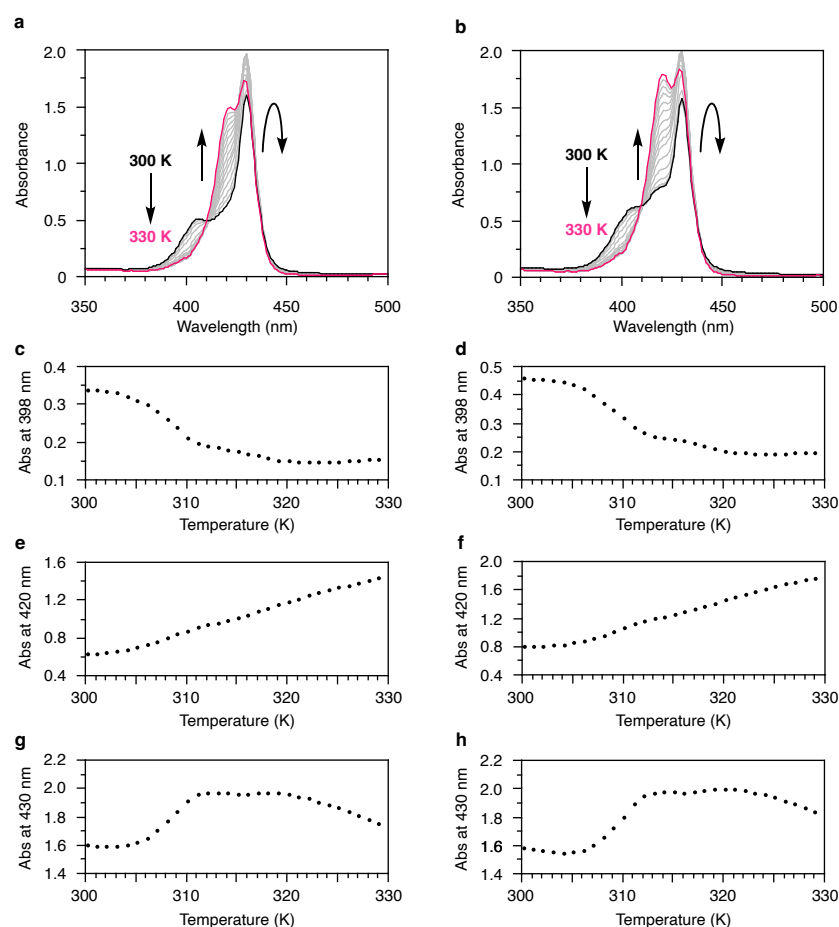
Supplementary Figure 29

Diblock SCTs used in these experiments were prepared as shown in Supplementary Figs. 26 and 27.

a,b, Temperature-dependent absorption spectral changes (upon heating) of solutions of diblock SCTs consisting of 1_{Zn} and 1_{Cu} (**a,c,e,g**) and those consisting of 1_{Zn} and 1_{Ni} (**b,d,f,h**).

The absorbance at 398 nm (H aggregates in SCTs) disappeared upon heating, with a concomitant increase in the absorbance at 420 nm (monomeric 1_{Zn} , 1_{Cu} , or 1_{Ni}) and 430 nm (DMAP- 1_{Zn} complex). Further heating of a solution decreased the peak at 430 nm with a concomitant increase in the absorbance at 420 nm (monomeric 1_{Zn}). Thus, SCTs are not thermally stable in solution.

Thermal stability of the triblock SCTs in solution



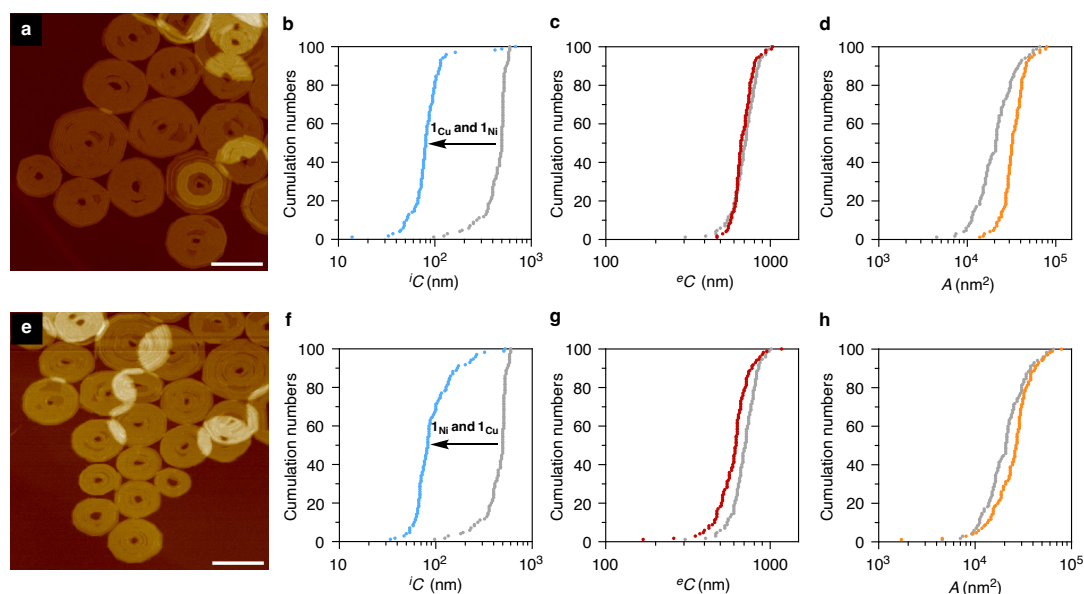
Supplementary Figure 30

Triblock SCTs used in these experiments were prepared as shown in Fig. 5b and Supplementary Fig. 33 (see also Methods).

a,b, Temperature-dependent absorption spectral changes (upon heating) of solutions of triblock SCTs: ABC type (**a,c,e,g**), and ACB type (**b,d,f,h**).

The absorbance at 398 nm (H aggregates in SCTs) disappeared upon heating, with a concomitant increase in the absorbance at 420 nm (monomeric 1_{Zn} , 1_{Cu} , or 1_{Ni}) and 430 nm (DMAP- 1_{Zn} complex). Further heating of a solution decreased the peak at 430 nm with a concomitant increase in the absorbance at 420 nm (monomeric 1_{Zn}). Thus, SCTs are not thermally stable in solution.

AFM analysis of the ABC type and ACB type three-component SCTs consisting of 1_{Zn} , 1_{Cu} and 1_{Ni} , obtained using seeds of 1_{Zn} which were pretreated with 10.0 eq. of DMAP



Supplementary Figure 31

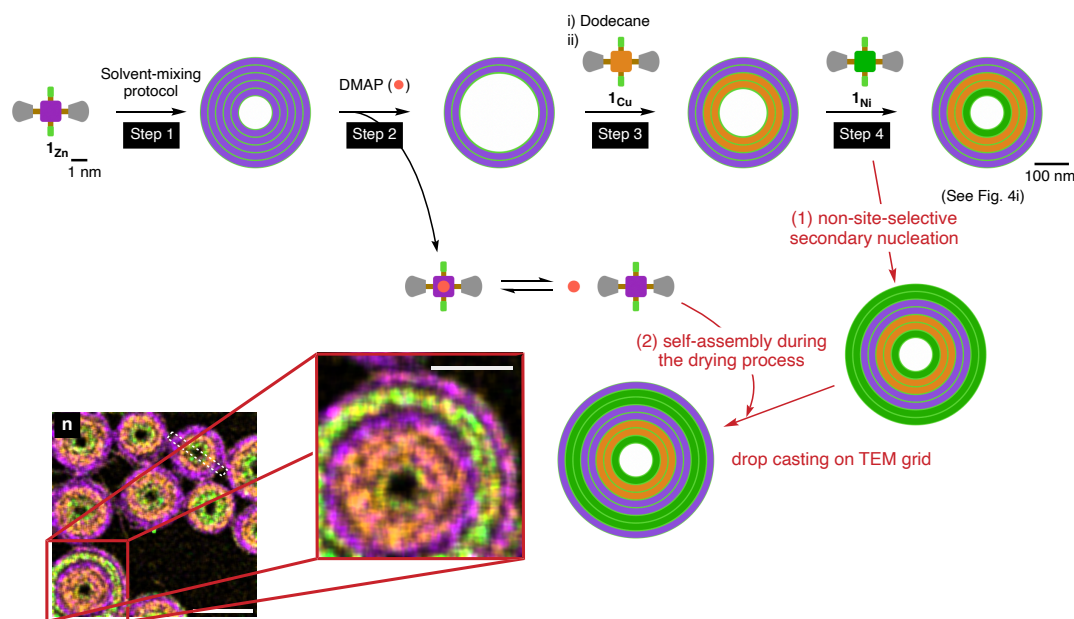
ABC type (i.e., Zn/Cu/Ni, top row) and ACB type (i.e., Zn/Ni/Cu, bottom row) triblock SCTs. Seeds used in these experiments were prepared as shown in Supplementary Figure 23 using 10.0 eq. of DMAP with respect to 1_{Zn} .

a,e, AFM images of three-component SCTs consisting of 1_{Zn} , 1_{Cu} and 1_{Ni} obtained through seeded supramolecular polymerization using SCTs of 1_{Zn} which was treated with DMAP beforehand: $[1_{Zn}] = 4.4 \mu\text{M}$, $[\text{DMAP}] = 44 \mu\text{M}$, $[1_{Cu}] = [1_{Ni}] = 0.44 \mu\text{M}$ (**a-d**); $[1_{Zn}] = 4.4 \mu\text{M}$, $[\text{DMAP}] = 44 \mu\text{M}$, $[1_{Cu}] = [1_{Ni}] = 0.44 \mu\text{M}$ (**e-h**), toluene/dodecane = 1:9 (v/v); HOPG substrate, scale bar = 200 nm. (**b-d, f-h**) Cumulative histograms of the internal circumference (iC) (**b,f**, blue), external circumference (eC) (**c,g**, red), and area (A) (**d,h**, orange) of triblock SCTs consisting of 1_{Zn} , 1_{Cu} and 1_{Ni} determined from the AFM images shown on the left. *For comparison, the corresponding data of SCTs of 1_{Zn} used as seeds are shown together in grey.*

Supplementary Table 5. AFM analysis of triblock SCTs consisting of 1_{Zn} , 1_{Cu} and 1_{Ni} obtained through seeded supramolecular polymerization using SCTs of 1_{Zn} which was treated with DMAP beforehand (see Supplementary Table 3).

AFM data	iC_n (nm)	eC_n (nm)	A_n (nm ²)	A_w (nm ²)	A_w/A_n
SFig. 31a	94	691	34500	38100	1.10
SFig. 31e	106	615	27300	32900	1.21

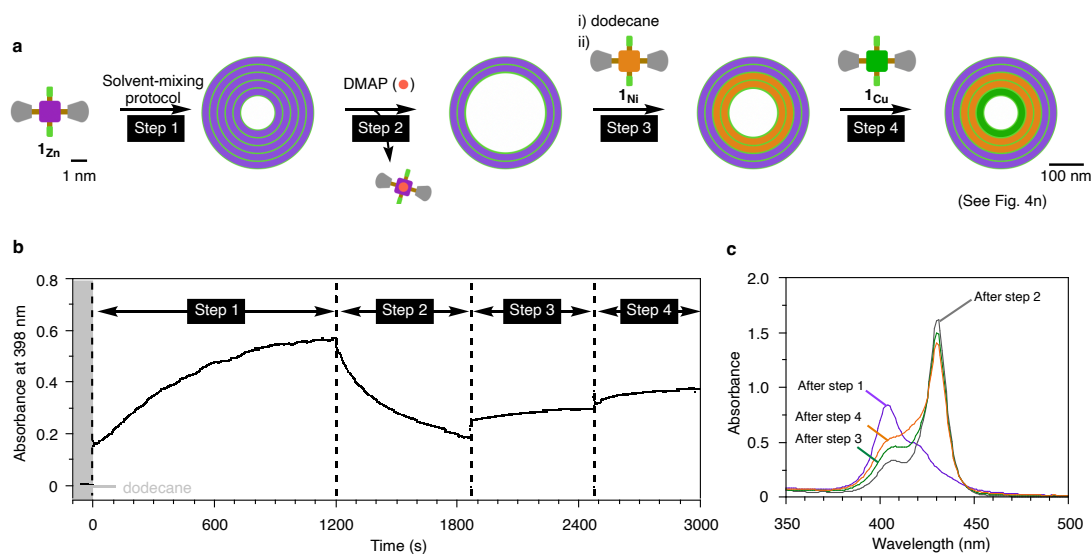
Plausible mechanism of the formation of “byproduct” having an incorrect sequence



Supplementary Figure 32 Plausible mechanism of the formation of 2D block supramolecular polymer with an incorrect sequence (see Figure 4n in the manuscript: scale bar = 200 nm, inset : scale bar = 100 nm).

We notice that the SCTs with incorrect sequence (i.e., by-product) is larger than those with the correct sequence, which suggests that it was formed from the SCTs with the correct sequence through digressing from the expected growth mechanism. At present the by-product is presumed to result (1) through non-selective secondary nucleation at the exterior surface and (2) during the drying process in the sample preparation as shown above.

Monitoring the multisteps noncovalent synthesis of ACB (Zn/Ni/Cu) type triblock SCTs



Supplementary Figure 33

a, Synthetic scheme toward the ACB type triblock SCTs. **b**, Changes in the absorbance at $\lambda = 398$ nm observed during the multistep noncovalent synthesis: $[1_{Zn}] = 4.4 \mu\text{M}$, $[\text{DMAP}] = 44 \mu\text{M}$, $[1_{Ni}] = 0.44 \mu\text{M}$, $[1_{Cu}] = 0.44 \mu\text{M}$, toluene/dodecane = 1:9 (v/v), 298 K. **c**, Absorption spectra obtained after each step of multistep noncovalent synthesis.

Supplementary References

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