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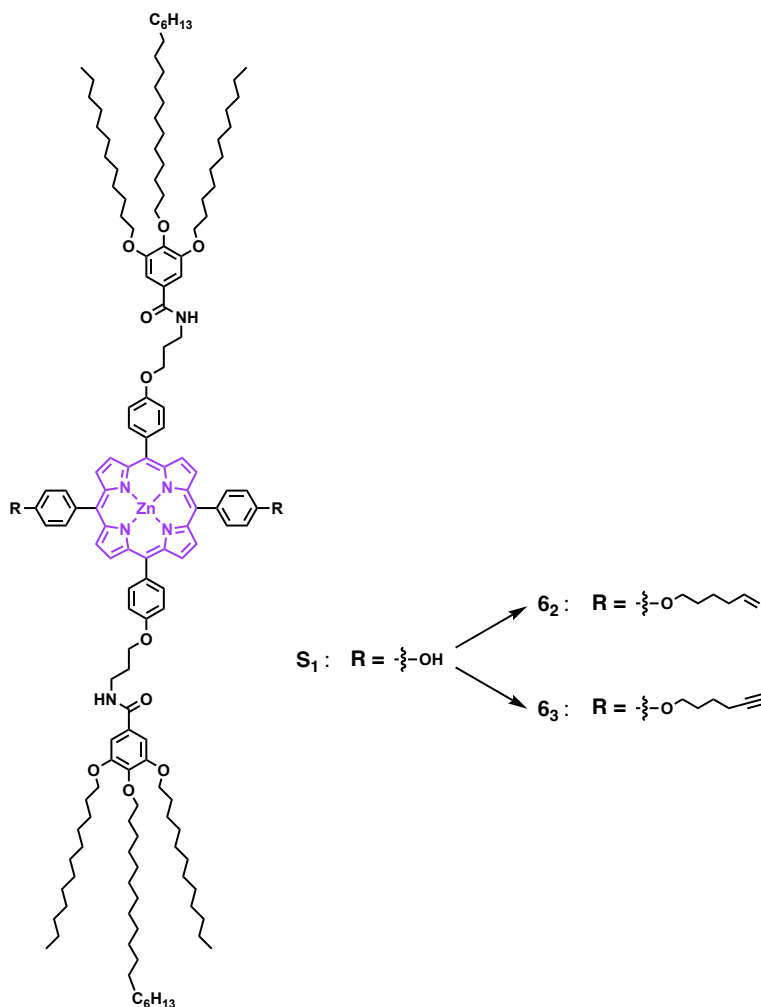
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Materials and Methods

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. Compound **S1** were prepared according to the reported procedures.^[1]

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-400 (400 MHz) and JEOL ECZ-600 (600 MHz) spectrometer. All chemical shifts are reported in parts per million (ppm) from tetramethylsilane (0 ppm for ^1H) or residual CHCl_3 (77 ppm for ^{13}C) as an internal standard. Melting points were determined with a Yanako NP-500P micro melting point apparatus. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained using a Shimadzu Maldi-8030. Ultraviolet–visible absorption spectra were recorded using a quartz cuvette of 1.0 cm or 1 mm path length on a Jasco V-730, V-670 and V-630 spectrophotometer equipped with a Jasco ETCS-761 cell holder for temperature control. Spin-coating was performed using a Oshigane SC-300. Atomic force microscopy (AFM) was performed on a Bruker Dimension Icon atomic force microscope under ambient conditions in the scan assist analysis. AFM images were analyzed with Bruker Nanoanalysis and ImageJ.

Syntheses and Characterizations



1. Synthesis of compound **6₂**

Synthesis of (6₂): A mixture of **S1** (21 mg, 0.00840 mmol), 6-bromo-1-hexene (55.0 μL , 0.416 mmol) and K_2CO_3 (39.0 mg, 0.282 mmol) in DMF (6 mL) and THF (5 mL) was refluxed at 70 °C for 12 h under argon atmosphere. Then, the crude was cooled to room temperature, diluted with CH_2Cl_2 , then the organic layer was washed with water, dried over Na_2SO_4 . The solvent was evaporated, and the obtained solid was purified by silica gel column chromatography ($\text{CHCl}_3/\text{acetone} = 15/1$) and further by recycling gel permeation chromatography (CHCl_3) to yield **6₂** as a purple solid (18.1 mg, 67.7%).

m.p. = 90-94 °C, $^1\text{H-NMR}$ (600 MHz, CDCl_3): d 0.80-0.89 (m, 18H, $\text{CH}_3\text{-(CH}_2\text{)}_{10}\text{-CH}_2\text{-O-}$, $\text{CH}_3\text{-(CH}_2\text{)}_{16}\text{-CH}_2\text{-O-}$), 1.09-1.33 (m, 120H, $\text{CH}_3\text{-(CH}_2\text{)}_8\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$, $\text{CH}_3\text{-(CH}_2\text{)}_{14}\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$), 1.41-1.47 (m, 12H, $\text{CH}_3\text{-(CH}_2\text{)}_8\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$, $\text{CH}_3\text{-(CH}_2\text{)}_{14}\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$), 1.70-1.82 (m, 16H, $\text{CH}_3\text{-(CH}_2\text{)}_8\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$, $\text{CH}_3\text{-(CH}_2\text{)}_{14}\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$, $\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$), 1.99-2.04 (m, 4H, $\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$), 2.24-2.35 (m, 8H, $\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$, $\text{-NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$), 3.81-3.86 (m, 4H, $\text{-NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$), 3.99 (t, $J = 6.5$ Hz, 4H, $\text{CH}_3\text{-(CH}_2\text{)}_{16}\text{-CH}_2\text{-O-}$), 4.02 (t, $J = 6.5$ Hz, 8H, $\text{CH}_3\text{-(CH}_2\text{)}_{10}\text{-CH}_2\text{-O-}$), 4.30

(t, $J = 6.3$ Hz, 4H, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 4.44 (t, $J = 5.4$ Hz, 4H, $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 5.04-5.07 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 5.11-5.16 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 5.90-5.98 (m, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 6.71 (t, $J = 5.5$ Hz, 2H, $-\text{NH}-$), 8.11 (d, $J = 8.4$ Hz, 4H, C_6H_4), 8.13 (d, $J = 8.0$ Hz, 4H, C_6H_4), 8.94 (d, $J = 4.6$ Hz, 4H, b-pyrrole), 8.98 (d, $J = 4.6$ Hz, 4H, b-pyrrole).; ^{13}C -NMR (101 MHz, CDCl_3): d 14.10, 14.12, 22.64, 22.69, 25.52, 26.09, 28.97, 29.16, 29.29, 29.36, 29.38, 29.57, 29.60, 29.66, 29.73, 30.33, 31.87, 31.92, 33.58, 38.59, 67.26, 68.04, 69.40, 73.50, 105.60, 112.49, 114.82, 120.44, 120.84, 128.79, 129.54, 130.92, 131.74, 131.97, 135.05, 135.37, 135.50, 135.76, 138.61, 141.14, 150.37, 150.52, 153.14, 158.22, 158.74, 167.43.; Maldi-TOF mass (Dithanol): calcd. for $\text{C}_{160}\text{H}_{234}\text{N}_6\text{O}_{12}\text{Zn}$: 2500.75; found: 2501.43.

2. Synthesis of compound 6₃

Synthesis of (6₃): A mixture of **S1** (25 mg, 0.0100 mmol), 6-bromo-1-hexyne (60.0 μL , 0.454 mmol) and K_2CO_3 (35.0 mg, 0.253 mmol) in DMF (2.4 mL) and THF (1.5 mL) was refluxed at 70 °C for 17 h under argon atmosphere. Then, the crude was cooled to room temperature, diluted with CH_2Cl_2 , then the organic layer was washed with water, dried over Na_2SO_4 . Solvent was evaporated, and the obtained solid was purified by silica gel column chromatography ($\text{CHCl}_3/\text{acetone} = 15/1$) and further by recycling gel permeation chromatography (CHCl_3) to yield **6₃** as a purple solid (21.3 mg, 79.7%).

m.p. = 90-92 °C, ^1H -NMR (400 MHz, CDCl_3): d 0.80-0.89 (m, 18H, $\text{CH}_3-(\text{CH}_2)_{10}-\text{CH}_2-\text{O}-$, $\text{CH}_3-(\text{CH}_2)_{16}-\text{CH}_2-\text{O}-$), 1.09-1.33 (m, 120H, $\text{CH}_3-(\text{CH}_2)_8-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$, $\text{CH}_3-(\text{CH}_2)_{14}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 1.40-1.48 (m, 12H, $\text{CH}_3-(\text{CH}_2)_8-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$, $\text{CH}_3-(\text{CH}_2)_{14}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 1.69-1.84 (m, 12H, $\text{CH}_3-(\text{CH}_2)_8-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$, $\text{CH}_3-(\text{CH}_2)_{14}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 1.88-1.96 (m, 4H, $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 2.04-2.06 (m, 2H, $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 2.09-2.17 (m, 4H, $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 2.30-2.37 (m, 4H, $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 2.40-2.45 (m, 4H, $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 3.82-3.87 (m, 4H, $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 3.99 (t, $J = 6.5$ Hz, 4H, $\text{CH}_3-(\text{CH}_2)_{16}-\text{CH}_2-\text{O}-$), 4.02 (t, $J = 6.5$ Hz, 8H, $\text{CH}_3-(\text{CH}_2)_{10}-\text{CH}_2-\text{O}-$), 4.30 (t, $J = 6.1$ Hz, 4H, $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 4.44 (t, $J = 5.4$ Hz, 4H, $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), 6.71 (t, $J = 5.5$ Hz, 2H, $-\text{NH}-$), 8.10 (d, $J = 8.1$ Hz, 4H, C_6H_4), 8.13 (d, $J = 8.0$ Hz, 4H, C_6H_4), 8.95 (d, $J = 4.7$ Hz, 4H, b-pyrrole), 8.98 (d, $J = 4.7$ Hz, 4H, b-pyrrole).; ^{13}C -NMR (101 MHz, CDCl_3): d 14.10, 14.14, 18.31, 22.64, 22.68, 25.25, 26.09, 28.53, 29.16, 29.29, 29.38, 29.39, 29.57, 29.60, 29.67, 29.73, 30.32, 31.86, 31.92, 38.54, 67.26, 67.55, 68.75, 69.40, 73.50, 84.17, 105.60, 112.53, 120.43, 120.82, 129.52, 131.76, 131.94, 135.18, 135.40, 135.49, 135.80, 141.14, 150.39, 150.51, 153.11, 158.20, 158.66, 167.44.; Maldi-TOF mass (Dithanol): calcd. for $\text{C}_{160}\text{H}_{238}\text{N}_6\text{O}_{12}\text{Zn}$: 2496.72; found: 2495.98.

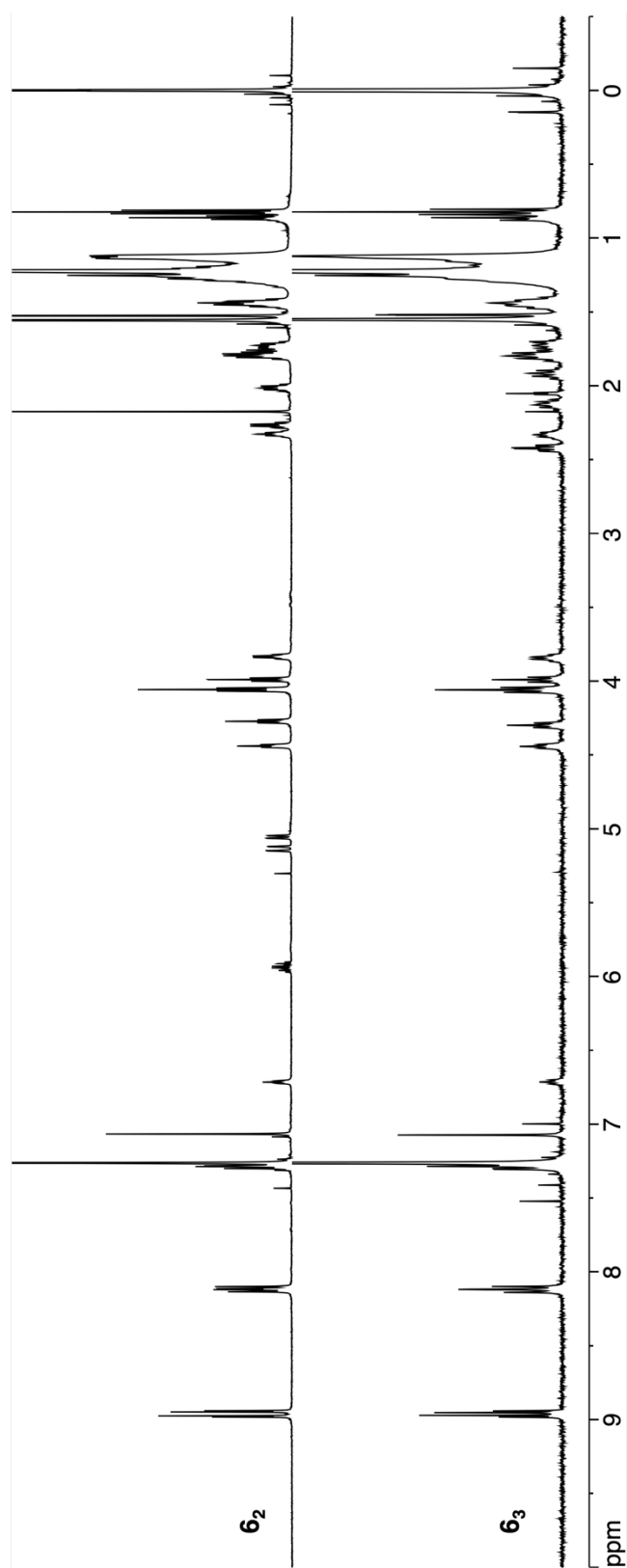


Figure S1. ^1H NMR spectra of **6₂** and **6₃** in CDCl_3 at 298 K.

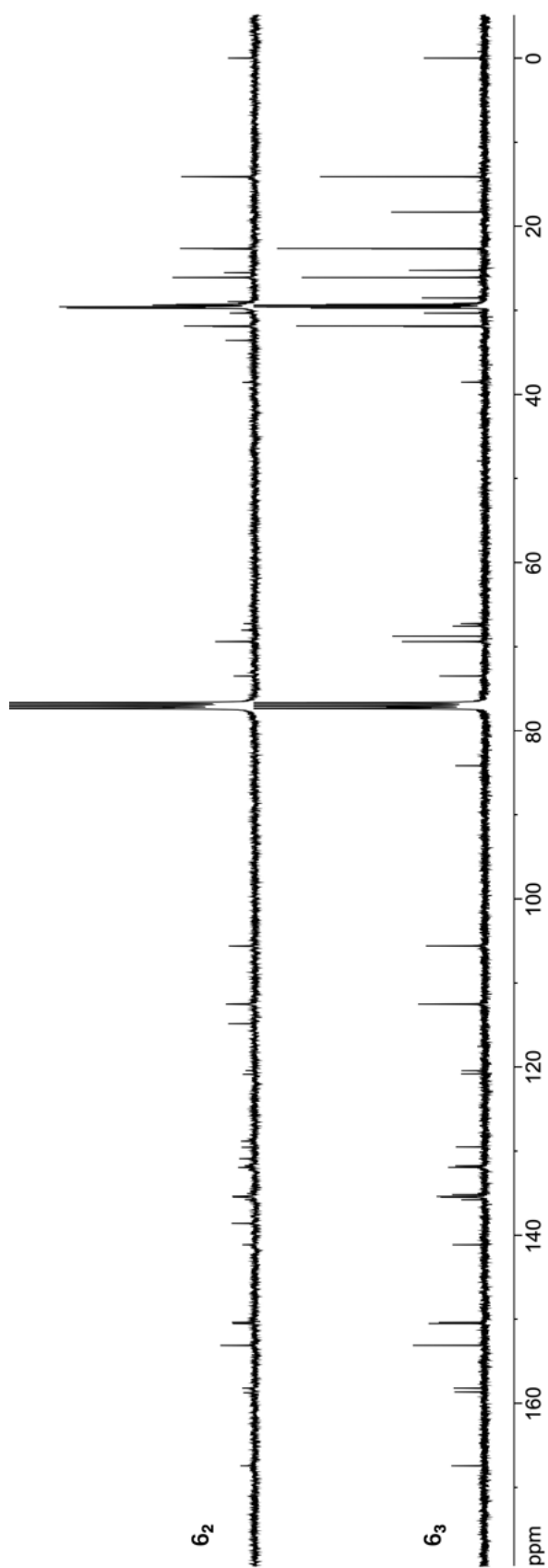


Figure S2. ^{13}C NMR spectra of **62** and **63** in CDCl_3 at 298 K.

Supplementary Figures

Seed-6₂, **Seed-6₃**, and **Seed-6N₃** were prepared according to the procedure described below.

Seed-6₂ and **Seed-6₃**: First, thermodynamically stable nanosheets consisting of each monomer were prepared under ambient condition, by spontaneous conversion from the corresponding metastable nanoparticles (**NP-6₂** and **NP-6₃**) in methyl cyclohexane (MCH) at room temperature. We then subjected the obtained nanosheets to sonication at 20 °C for 20 and 15 min, respectively, resulting in small fragments of nanosheets (referred to as **Small seed-6₂** and **Small seed-6₃**, respectively, in Figure S3). Upon mixing these seeds with **NP-6₂** and **NP-6₃**, we obtained **Seed-6₂** and **Seed-6₃** with controlled areas and narrow area distributions, which were used for subsequent supramolecular homopolymerization and heteropolymerization.

Seed-6N₃: We directly applied a sonication to a solution of **NP-6N₃** in MCH at 30°C for 4 hours, and obtained small fragments of nanosheets consisting of **6N₃**, which is referred to as **Small seed-6N₃** in Figure S3. Upon mixing **Small seed-6N₃** with **NP-6N₃**, we obtained **Seed-6N₃** with a controlled area and narrow area distribution, which were used for subsequent supramolecular homopolymerization and heteropolymerization.

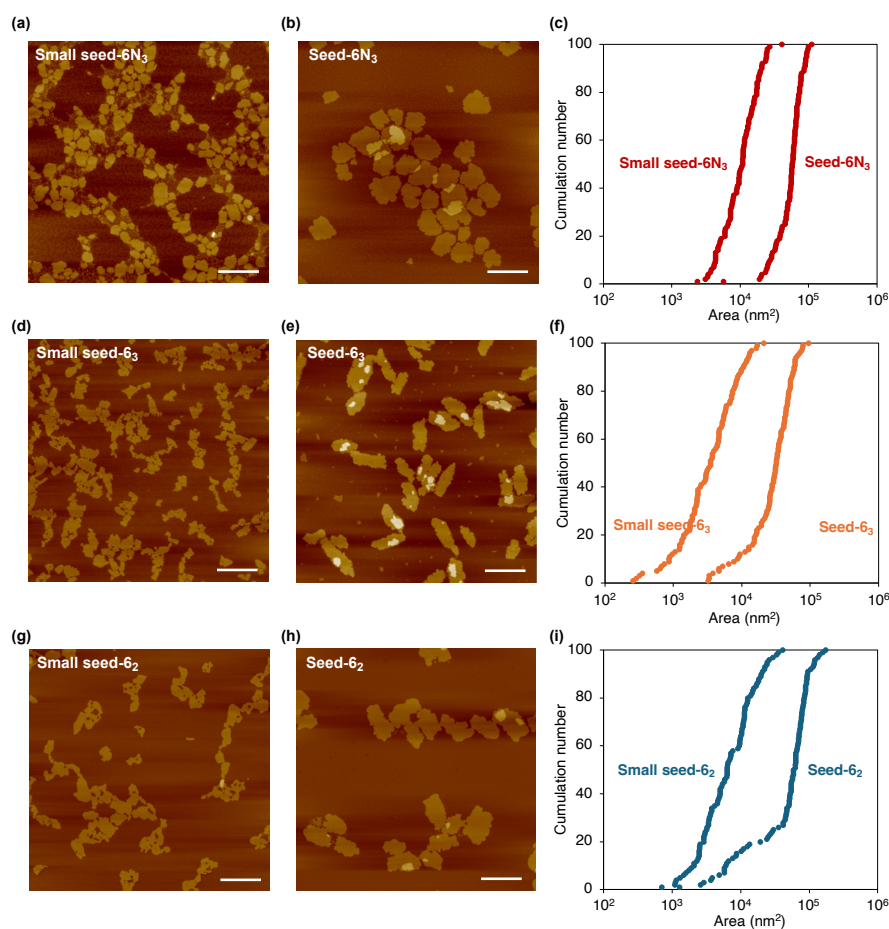


Figure S3. (a,b,d,e,g,h) AFM images of (a) **Small seed-6N₃**, (b) **Seed-6N₃**, (d) **Small seed-6₃**, (e) **Seed-6₃**, (g) **Small seed-6₂**, (h) **Seed-6₂**. (c,f,i) Histograms of area of **Small seed** and **Seed** consisting of (c) **6N₃**, (f) **6₃**, and (i) **6₂**.

Seeded homopolymerization: **Seed** and **Nanoparticle (NP)** were mixed in MCH: **[Small seed-6N₃] : [NP-6N₃] = 5 μM : 25 μM**, **[Small seed-6₃] : [NP-6₃] = 2.5 μM : 25 μM**, **[Small seed-6₂] : [NP-6₂] = 2.5 μM : 25 μM** with respect to the concentration of porphyrins.

Small seed-6N₃: $A_n=11700 \text{ nm}^2$, $A_w/A_n=1.32$; **Seed-6N₃**: $A_n= 57100 \text{ nm}^2$, $A_w/A_n=1.14$.

Small seed-6₃: $A_n=4750 \text{ nm}^2$, $A_w/A_n=1.73$; **Seed-6₃**: $A_n= 34000 \text{ nm}^2$, $A_w/A_n=1.31$.

Small seed-6₂: $A_n=9190 \text{ nm}^2$, $A_w/A_n=1.77$; **Seed-6₂**: $A_n= 58700 \text{ nm}^2$, $A_w/A_n=1.35$.

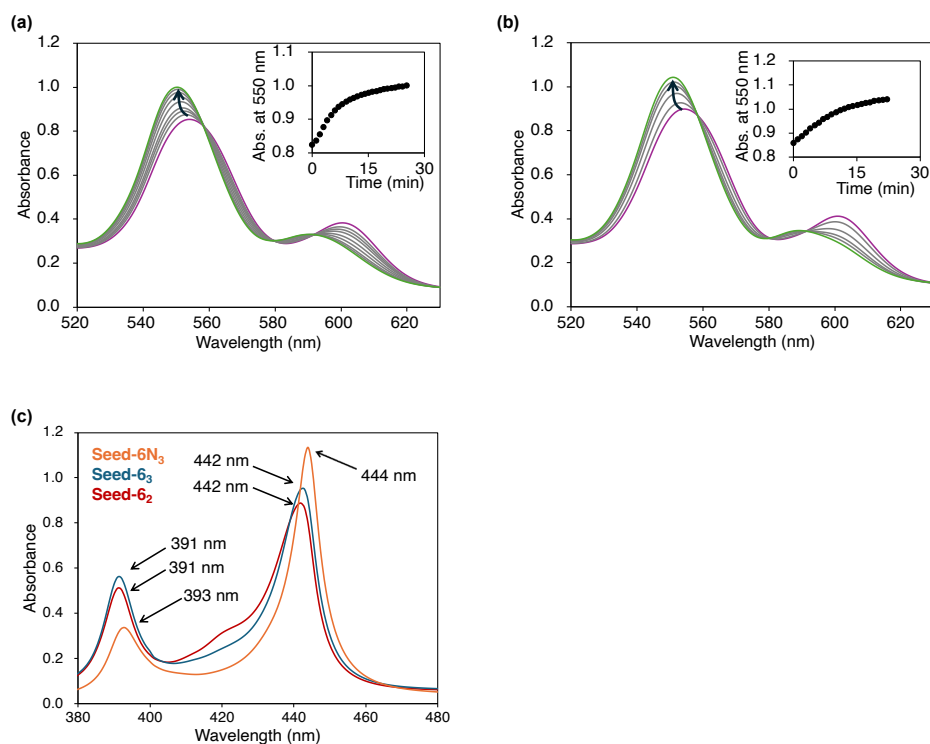


Figure S4. (a,b) Absorption spectral changes observed during seeded homopolymerization, **Seed** and **NP** were mixed in MCH solution: (a) [**Seed-6₃**] = [**NP-6₃**] = 25 μ M, (b) [**Seed-6₂**] = [**NP-6₂**] = 25 μ M, with respect to the concentration of porphyrin monomer. (Inset) Changes in the absorbance at 550 nm as a function of time. (c) Absorption spectra of **Seed-6N₃**, **Seed-6₃**, and **Seed-6₂**.

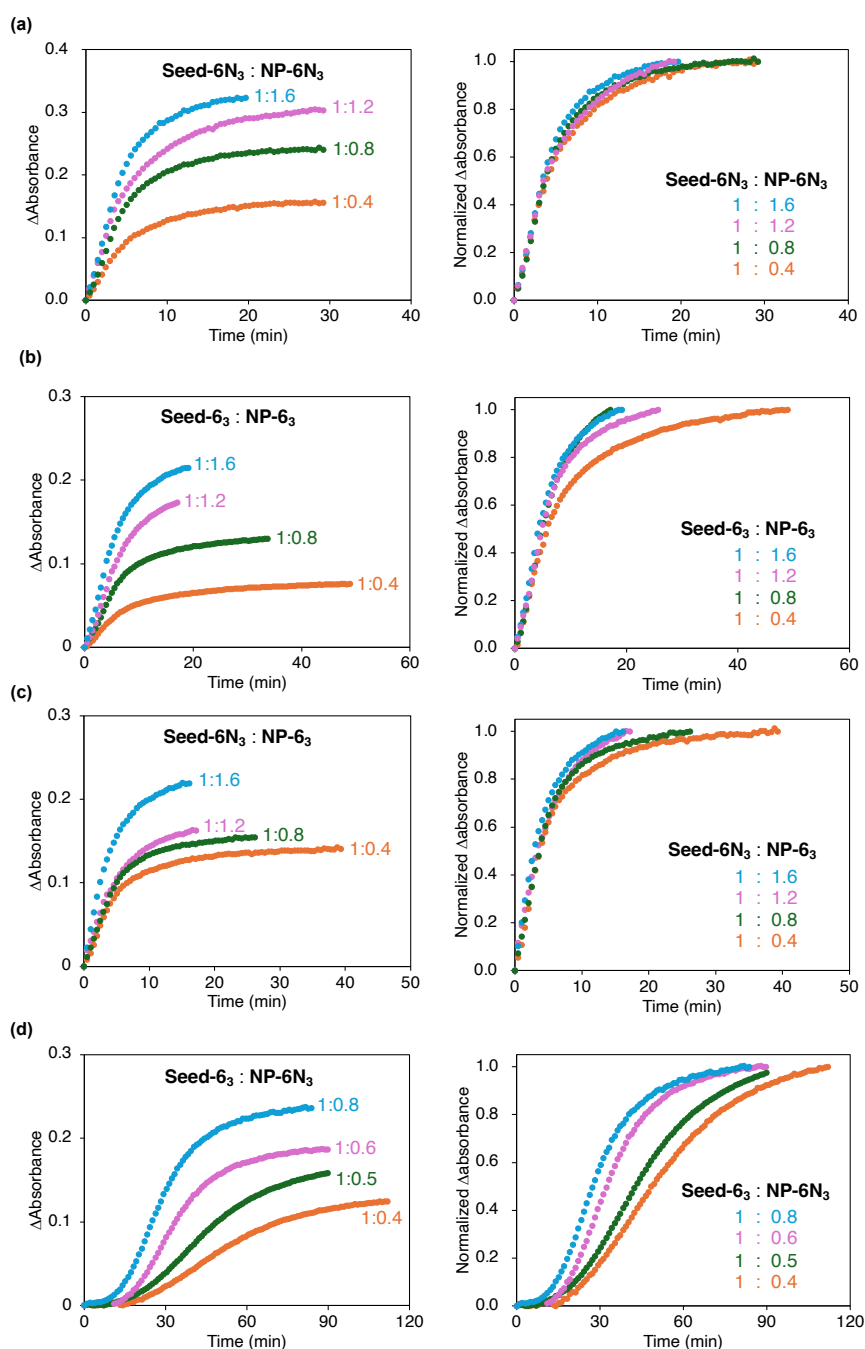


Figure S5. (a,b) Kinetics profiles of the homopolymerization and heteropolymerization depending on nanoparticles concentration: (a) **Seed-6N₃ + NP-6N₃**, (b) **Seed-6₃ + NP-6₃**, (c) **Seed-6N₃ + NP-6₃**, (d) **Seed-6₃ + NP-6N₃**. In all cases, [Seed] = 25 μM, with respect to porphyrin concentration, and changes in absorbance were observed at 550 nm. Changes in absorbance and normalized changes in absorbance are shown in left and right, respectively.

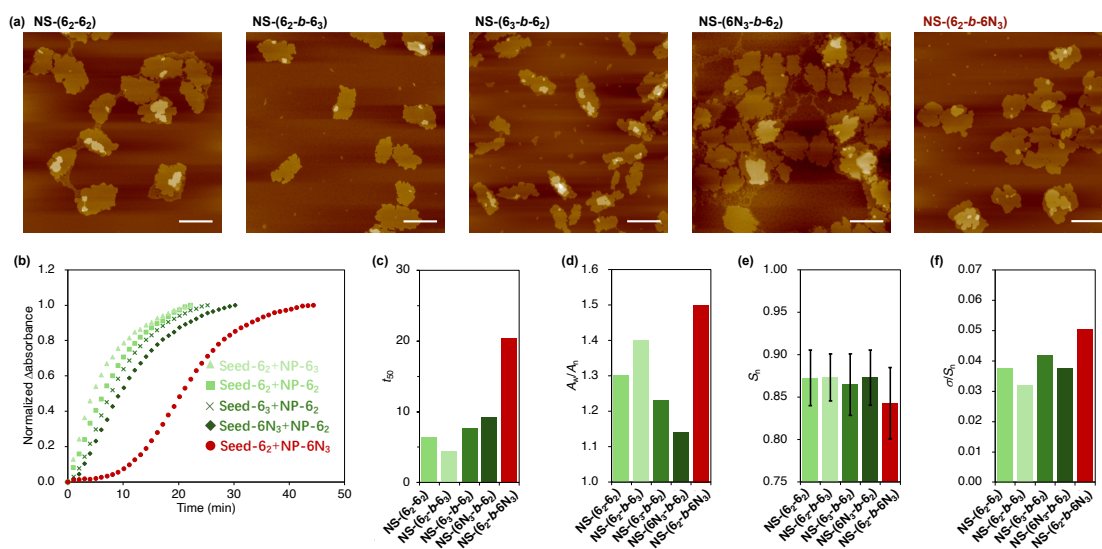


Figure S6. AFM images of (a) NS-(6₂-6₂), NS-(6₂-b-6₃), NS-(6₃-b-6₂), NS-(6N₃-b-6₂), and NS-(6₂-b-6N₃) (bar=500nm). (b) Changes in the absorbance observed during homo- and hetero-seeded polymerizations. (c) Values of t_{50} for the seeded growth process, determined from (b). (d) A_w/A_n values, (e) S_n , and (f) σ/S_n for the obtained nanosheets.

Supplementary References

- [1] a) T. Fukui, S. Kawai, S. Fujinuma, Y. Matsushita, T. Yasuda, T. Sakurai, S. Seki, M. Takeuchi, K. Sugiyasu, *Nat. Chem.* **2017**, 9, 493; b) Z. Jin, N. Sasaki, N. Kishida, M. Takeuchi, Y. Wakayama, K. Sugiyasu, *Chem. Eur. J.* **2023**, 29, e202302181.