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Living supramolecular polymerization based on reversible deactivation of a monomer by using a 'dummy' monomer

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Materials and Methods

Unless otherwise noted, reagents and solvents were purchased from commercial suppliers without further purification. Air- and/or water-sensitive reactions were conducted under argon atmosphere using dry solvents. Compound $3Me^1$, $3Ph^2$, $S1^3$, $S2^1$, and $S5^1$ were prepared according to reported procedures.

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) or residual CHCl₃ (77 ppm for ¹³C) as an internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained using a Shimadzu Axima-CFR plus station. Ultraviolet–visible absorption spectra were recorded using a quartz cuvette of 10 or 1 mm path length on a Jasco V-630 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. AFM images were analyzed by Bruker Nanoanalysis and ImageJ.

Synthesis and Characterization



Scheme S1. Synthesis of 2Me.

Synthesis of S3 Compound S2 in dry dichloromethane (15 mL) was added dropwise to a solution of compound S1 (472 mg, 1.58 mmol) and triethylamine (1.8 mL) in dry dichloromethane at 0 °C under argon atmosphere. The mixture was stirred for 5 h at room temperature, and then the reaction mixture was filtered to remove triethylammonium chloride. After evaporating the filtrate in vacuo to dryness, the residue was purified through column chromatography (SiO₂; CHCl₃) to yield compound S3 as white solid (515 mg, 62 %).

¹H NMR (CDCl₃, 298 K) δ 0.849-0.882 (9H, m), 1.25-1.29 (48H, m), 1.41-1.50 (6H, m), 1.65-1.82 (6H, m), 3.80-3.84 (2H, m), 3.95-4.00 (6H, m), 4.09-4.12 (2H, m), 6.40 (1H, -CON*H*-), 6.68 (2H, d, *J* = 8.8 Hz), 6.93 (2H, s), 7.55 (2H, d, *J* = 8.8 Hz).; ¹³C NMR (CDCl₃, 298 K) δ 14.12, 22.69, 26.01, 29.37, 29.39, 29.58, 29.64, 29.70, 30.30, 31.92, 39.48, 66.92, 69.39, 73.51, 82.29, 105.75, 116.84, 129.19, 138.36, 141.33, 153.12, 158.39, 167.65.; MALDI-TOF mass (dithranol): calcd. for C₅₁H₈₆NO₅I: 919.56; found: 920.69.

Synthesis of S4 A mixture of compound **S3** (1.11 g, 1.20 mmol), bis(pinacolate)diboron (340 mg, 1.34 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (45.3 mg, 0.062 mmol), and potassium acetate (345 mg, 3.52 mmol) in dry dimethyl sulfoxide was stirred at 80 °C for 24 h under argon atmosphere. After cooling to room temperature, saturated ammonium chloride aqueous solution was added to the reaction mixture. The mixture was extracted with ethylacetate and dried over Na₂SO₄. The filtrate was evaporated and obtained solid was purified through column chromatography (SiO₂; CHCl₃) to yield compound **S4** as white solid (633 mg, 57 %).

¹H NMR (CDCl₃, 298 K) δ 0.86-0.90 (9H, m, CH₃-), 1.26-1.33 (60H, m, (CH₃)₂-C-, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-CH₂-O-), 1.42-1.48 (6H, m, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-O-), 1.69-1.83 (6H, m, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-CH₂-O-), 3.85 (2H, dt, -NH-CH₂-CH₂-O-), 3.96-4.01 (6H, m, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-O-), 4.18 (2H, t, -NH-CH₂-CH₂-O-), 6.46 (1H, t, -NH-CH₂-CH₂-O-), 6.90 (4H, d, C₆H₄), 6.95 (2H, s, C₆H₂), 7.75 (2H, d, C₆H₄),; ¹³C NMR (CDCl₃, 298 K), δ 14.11, 22.68, 24.85, 26.07, 29.36, 29.39, 29.58, 29.63, 29.69, 29.72, 30.30, 31.92, 39.55, 66.66, 69.37, 73.50, 83.62, 105.75, 113.79, 129.31, 136.63, 141.27, 153.11, 161.02, 167.66.; MALDI-TOF mass (dithranol): calcd. for C₅₇H₉₈NO₇B: 919.74; found: 920.81.

Synthesis of 2Me To a solution of compound S4 (mg, mmol), compound S5 (mg, mmol), sodium carbonate (mg, mmol) in degassed DMF (mL), degassed EtOH (mL), and degassed water (mL), tetrakis(triphenylphosphine)palladium(0) (mg, mmol) was added. The reaction mixture was refluxed at 80 °C for 24 h under argon atmosphere. After cooling to room temperature, chloroform was added to the reaction mixture. The mixture was washed by water and obtained organic phase was dried over MgSO₄. The filtrate was evaporated and obtained solid was purified through column chromatography (SiO₂; CHCl₃) and SEC (bio-beads SX-1, DCM) to yield compound **2Me** as purple solid (103 mg, 52 %).

¹H NMR (CDCl₃, 298 K) δ 0.83-0.89 (18H, m, CH₃-), 1.22-1.33 (96H, m, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-O-), 1.43-1.47 (12H, m, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-O-), 1.71-1.85 (12H,

m, CH₃-(CH₂)₈-CH₂-CH₂-CH₂-O-), 3.81-3.84 (4H, m, -NH-CH₂-CH₂-O-), 3.98-4.03 (12H, m, CH₃-(CH₂)₈-CH₂-CH₂-C-), 4.09 (6H, s, CH₃-O-), 4.33 (4H, m, -NH-CH₂-CH₂-O-), 6.55 (2H, t, -NH-CH₂-CH₂-O-), 6.88 (4H, s, C₆H₂), 7.25-7.28 (8H, m, C₆H₄), 8.11 (4H, d, C₆H₄), 8.12 (4H, d, C₆H₄), 8.93 (4H, d, β-pyrrole), 8.96 (4H, d, β-pyrrole).; ¹³C NMR (CDCl₃, 298 K), δ 14.10, 22.66, 22.69, 26.10, 29.34, 29.39, 29.41, 29.63, 29.68, 29.76, 30.33, 31.89, 31.94, 39.62, 55.53, 67.05, 69.43, 73.51, 105.75, 112.02, 112.54, 120.37, 120.75, 129.09, 131.73, 131.92, 135.25, 135.38, 135.50, 135.91, 141.33, 150.36, 150.48, 153.07, 158.09, 159.19, 167.56.; MALDI-TOF mass (dithranol): calcd. for C₁₃₆H₁₉₄N₆O₁₂Zn: 2168.41; found: 2168.83.

Supplementary Figures



Figure S1. NMR spectrum of **2Me** in chloroform- d_1 at 298 K: (a) ¹H NMR and (b) ¹³C NMR.





Figure S2. Formation and transformation of the supramolecular assembly of 3Me. (a) Schematic representation of the self-assembling behavior of 3Me in MCH. The monomeric form of porphyrin derivative 3Me in a hot MCH self-assembles upon cooling to form nanoparticles consisting of J-aggregate (step 1). When stirred at 400 rpm, the nanoparticles convert into nanofibers composed of the H-aggregate of 3Me (step 2) in several hours. Both steps are reversible with heating leading back to the initial monomeric state (steps 3 and 4, respectively), which assembles again upon cooling (step 1): scale bar = 200 nm. (d) Absorption spectra of monomeric 3Me (black), nanoparticle (pink), and nanofiber (green) in MCH ([3Me] = 50 μ M).

Thermodynamic stability of J-aggregate of 2Me.



Figure S3. (a, b) Temperature-dependent absorption spectra of **2Me** observed during the cooling process: $[2Me] = 50 \ \mu\text{M}$ in MCH. (c) Degree of J-aggregation of **2Me** as a function of the total concentration of **2Me** obtained by fitting the apparent absorption coefficients at $\lambda = 436$ nm to the isodesmic model (Supplementary Equation 1) in which α_{Mono} is the degree of **2Me**_{Mono} (monomeric **2Me**), $\varepsilon_{\text{Mono}}$ and ε_{c} are the molar absorption coefficients of pure **2Me**_{Mono} and pure J-aggregate of **2Me**, respectively, and $\varepsilon(c)$ is the apparent absorption coefficient at the given concentration. The fitting to the isodesmic model yielded K_{I} at different temperatures. (d) Plot of the natural logarithm of K_{I} as a function of the reciprocal temperature (T^{-1}) (Supplementary Equation 2). Based on the above analysis, thermodynamic parameters for the formation of J-aggregate were obtained: $\Delta H_{\text{J-agg}} = -79 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{J-agg}} = -167 \text{ J K}^{-1} \text{ mol}^{-1}$.

$$\alpha_{J} = 1 - \alpha_{Mono} = 1 - \frac{\varepsilon(c) - \varepsilon_{J}}{\varepsilon_{Mono} - \varepsilon_{J}} = 1 - \frac{2K_{I}c_{T} + 1 - (4K_{I}c_{T} + 1)^{1/2}}{2K_{I}^{2}c_{T}^{2}}$$
(1)

$$\ln K_I = \frac{-\Delta_J H^{\circ}}{RT} + \frac{\Delta_J S^{\circ}}{R}$$
(2)

Quenching experiment for 2Me.



Figure S4. (a) Absorption spectra of 2Me in MCH observed after the quenching by using ice bath: $[2Me] = 50 \ \mu\text{M}$ in MCH. (b) Changes in the absorbance at 558 nm as a function of time. MCH solution of 2Me was heated at 100 °C to obtain monomeric state of 2Me. Hot solution of 2Me was quenched for 5 second by using ice bath (i). Quenched solution was quickly placed at 35 °C, and then, the monitoring by using absorption spectroscopy was started. (ii). After 5 min, the precipitation of H-aggregate of 2Me was observed (iii).

Formation process of coassemblies of 2Me/3Ph.



Figure S5. (a) Temperature-dependent changes in the absorption spectra of **2Me** in the presence of **3Me** in MCH. The temperature was changed from 373 to 283 K at a rate of – 1.0 K/min; $[2Me+3Ph] = 50 \ \mu\text{M}$, **2Me:3Ph** (molar ratio) = 5:5. (b) Plots of the changes in absorbance of **2Me** at 436 nm as a function of temperature, measured in the presence of **3Ph** with the [2Me] to the [2Me+3Ph] ratio of (i) 60, (ii) 50, (iii) 40, and (iv) 30. The temperature was changed from 373 to 283 K at a rate of –1.0 K/min; $[2Me+3Ph] = 50 \ \mu\text{M}$.

Energy landscape



Figure S6. Schematic representation of reversible deactivation of a monomer 2Me by using a dummy monomer 3Ph constructed as a consequence of the coupled equilibria.

Seed preparation of 2Me

 $2Me_{seed}$ was prepared by applying sonication to a MCH solution of 2Me (3 mL, 50 μ M) at 5 °C for 3 h. By applying continuous sonication for a long time at a low temperature, $2Me_{seed}$ with a short length and relatively narrow length distribution could be obtained.



Figure S7. (**a**, **b**) AFM height images $(2 \ \mu m \ x \ 2 \ \mu m)$ of **2Me**_{seed} spin-coated on a HOPG substrate: scale bar = 400 nm. (**c**) Cumulative histogram of the length distribution of 2Meseed obtained by tracing over 100 objects in the AFM images. The number-average length (L_n), weight-average length (L_w), and PDI (L_w/L_n) of **2Me**_{seed} were 134 nm, 156 nm, and 1.17, respectively.



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Figure S8. (a) Time course of the change in absorption at 558 nm while $2Me_{seed}/3Ph$ (molar ratio of $2Me_{seed}:3Ph = 50:50$, $[2Me_{seed}+3Ph] = 50 \mu$ M) was diluted with 2Me/3Ph, showing repeated polymerization on each addition of 2Me/3Ph but at increasingly slower rate. During the time ranges highlighted in gray, the sample compartment was opened to add 2Me/3Ph solution (molar ratio of 2Me:3Ph = 50:50, $[2Me+3Ph] = 50 \mu$ M). (b) Rate of absorption change as a function of the cycle number x; the rate decays exponentially with a base of 2^{-1} , proving that seeded supramolecular polymerization based on reversible deactivation of a monomer by using a dummy monomer is living supramolecular polymerization.

Living supramolecular polymerization based on deactivation of 2Me by using 3Ph



Figure S9. Optical microscope image of mixture of H-aggregate of **2Me** and J-aggregate of **3Ph**: scale bar = 20 μ m. Unlike the case of spontaneous supramolecular polymerization of **2Me**, there is no obvious precipitate in MCH solution.

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Figure S10. (**a**, **b**) AFM height images (2 μ m x 2 μ m) of **2Me** prepared through living supramolecular polymerization *via* deactivation of a monomer by using a dummy monomer ([**2Me**]/[**2Me**_{seed}] = 2): scale bar = 400 nm. (**b**) Cumulative histogram of the length distribution of **2Me** obtained by tracing over 100 objects in the AFM images. The number-average length (L_n), weight-average length (L_w), and PDI (L_w/L_n) of the obtained supramolecular polymers were 214 nm, 250 nm, and 1.17, respectively.



Figure S11. (**a**, **b**) AFM height images (2 μ m x 2 μ m) of **2Me** prepared through living supramolecular polymerization *via* deactivation of a monomer by using a dummy monomer ([**2Me**]/[**2Me**_{seed}] = 4): scale bar = 400 nm. (**b**) Cumulative histogram of the length distribution of **2Me** obtained by tracing over 100 objects in the AFM images. The number-average length (L_n), weight-average length (L_w), and PDI (L_w/L_n) of the obtained supramolecular polymers were 435 nm, 567 nm, and 1.36, respectively.

Supplementary References

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