Supporting Information

Real time self-assembly and reassembly of molecular nanowires of trigeminal porphyrins

Yongshu Xie, Jonathan P. Hill, Misaho Akada, Qingmin Ji, Richard Charvet and Katsuhiko Ariga

Contents

1. Materials and Methods

Solvents and reagents were obtained from Aldrich Chemical Co., Fischer Chemical Co., Wako Chemical Co., Tokyo Kasei Chemical Co. or Kanto Chemical Co. ^{1}H and ^{13}C NMR spectra were measured at 298 K from $CDCl_3$ solutions of the samples using a JEOL model AL300BX spectrometer with tetramethylsilane as internal standard. Electronic absorption spectra were measured from dichloromethane solutions of the samples using a Shimadzu model UV-3600 UV/Vis/NIR spectrophotometer. FTIR spectra were measured from samples cast on a barium fluoride disc using a Nicolet model 760X FTIR spectrometer. Matrix–assisted laser desorption/ionization time–of–flight mass spectrometry (MALDI–TOF–MS) was measured using a Shimadzu-Kratos model Axima CFR+ mass spectrometer with dithranol as matrix.

Electron Microscopy. Scanning electron microscopy images were obtained using a Hitachi model S3600 FE-SEM instrument (Operating voltage: 5 kV). Samples were cast on a passivated silicon substrate followed by coating with Pt (Hitachi E1030 Ion Sputterer). Scanning transmission electron microscopy was also conducted on a Hitachi S3600 FE-SEM instrument on samples cast on carbon-coated copper grids.

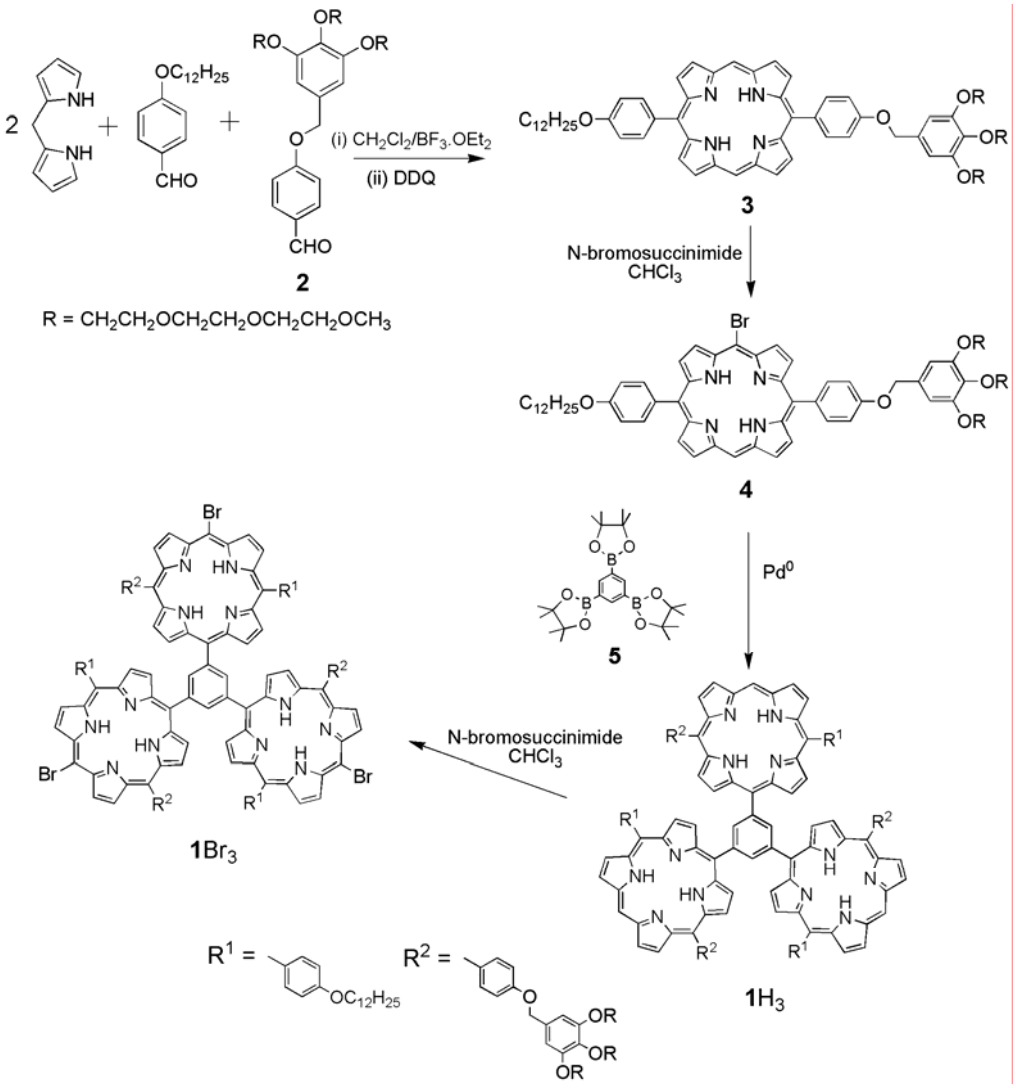
Atomic force microscopy (AFM) measurements. AFM measurements were carried out under ambient conditions. Samples were prepared by dropping a suspension of the preassembled molecules (100 μL; ~ 10^{-4} M) in dichloromethane/methanol onto a freshly cleaved mica surface at room temperature (27 °C) and relative humidity, R_H = 62 %. Relative humidity of the atmosphere was constantly monitored during AFM measurements. AFM images were obtained using a Seiko Instruments SPA400-SPI4000 equipped with a calibrated 20-μm xy-scan range and a 10 μm z-scan range PZT-scanner. All AFM images were taken in dynamic force mode at optimal force. Rectangular

shaped silicon cantilevers (Tip radius: ~10 nm; SI-DF20; Seiko Instruments Inc.), with spring constant of 11 N/m and resonance frequency of 122 kHz, were used for imaging in air. Supersharp tips (Tip radius: 2 – 3 nm; SI-DF20S; Seiko Instruments Inc.) were used for images shown in Fig. 2.

Nanowire erasure. For nanowire erasure, a rectangular shaped cantilever was used (SI-DF20). In dynamic force mode, an area for erasure was selected (either 50 or 100 nm) and the substrate rotated to present the nanowire perpendicular to the scanning direction of the probe tip then scan rate was increased to 4 Hz. Scanning force was increased until damage of the nanowire could be observed followed by scanning at that force until no structure could be observed, i.e. nanowire was erased. Residual nanowire fragments could be erased using the same procedure. Observation of the regrowth of the nanowires was made by returning to the initial conditions and using optimal imaging force.

Additional compounds. 3,4,5-[2-(2-(2-Methoxyethoxy)ethoxy)ethoxy]benzyl chloride(*S1*), 4-dodecyloxybenzaldehyde (*S2*), dipyrromethane (*S3*), 3,4,5-[2-(2-(2-methoxyethoxy)ethoxy) ethoxy]benzyl alcohol (*S4*) and compound **5** (*S5*) (see Scheme 1 below) were prepared as previously described. In the description of synthesis the 3,4,5-[2-(2-(2-methoxyethoxy) ethoxy)ethyl] (or methoxy-triethylene glycol groups are denoted using the abbreviation ‘TEG’.

2. Synthesis



Scheme S1. Synthesis of trigeminal porphyrin amphiphiles, **1**H_3 and **1**Br_3

4-{3,4,5-[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]benzyloxy}benzaldehyde, 2: A mixture of 3,4,5-[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]benzyl chloride (8.02 g, 13 mmol), 4-hydroxybenzaldehyde (1.34 g, 11 mmol), and K_2CO_3 (15.7 g, 114 mmol) in N,N-dimethylformamide (100 mL) was stirred at reflux for 40 hours, and cooled to room temperature. The mixture was filtered and the solid washed with N,N-dimethylformamide. The

combined filtrates were collected and the solvent was removed by rotary evaporation. To the residue was partitioned between dichloromethane (100 mL) and water (100 mL). The aqueous phase was then extracted with dichloromethane (2×50 mL). The organic phases were combined, dried over anhydrous Na_2SO_4 then solvents were removed under reduced pressure affording light yellow oil, which was used in the next reaction step without further purification.

5-(4-Dodecyloxyphenyl)-15-{4-[3,4,5-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzyloxy]phenyl} porphine, 3: Dry dinitrogen was bubbled into a solution of **2** (1.86 g, ~ 2 mmol), 4-dodecyloxybenzaldehyde (0.581 g, 2 mmol), dipyrromethane (0.585 g, 4 mmol) in a mixed solvent of dichloromethane (900 mL) and methanol (100 mL) for 10 min., then $BF_3.OEt_2$ (150 μL, 1.19 mmol) was added. The resulting solution was stirred at room temperature for 3 hours then DDQ (1.36 g, 6 mmol) was added. Stirring was maintained for 1 hour then triethylamine (0.2 mL) was added. Solvent was removed by rotary evaporation, and the residue was applied to a silica gel column, and eluted by gradient elution starting from 100% dichloromethane and ending at 97:3 dichloromethane:methanol. Three porphyrin bands were separated the 2nd which was the target porphyrin **3** (406 mg, 16%). UV/vis (CH_2Cl_2): λ_{max} ($\varepsilon/10^3$) = 410 (387), 504 (16.9), 540 (7.96), 578 (5.65), 633 (2.61). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 10.30 (2 H, s, *meso*-H), 9.39 (4 H, dd, *J* = 4.62 Hz, pyrrole-H), 9.11 (4 H, dd, *J* = 4.65 Hz, pyrrole-H), 8.19 (2 H, 8.55 Hz, o-phenyl), 8.17 (2 H, 8.79 Hz, o-phenyl), 7.41 (2 H, d, *J* = 8.76 Hz, *m*-phenyl), 7.34 (2 H, d, *J* = 8.79 Hz, *m*-phenyl), 6.90 (2 H, s, o-phenyl), 5.27 (2 H, s, benzyl-CH_2), 4.28 ~ 4.31 (6 H, m, OCH_2-TEG), 4.23 (2 H, t, *J* = 5.13 Hz, OCH_2-dodecyl), 3.93 (4 H, t, *J* = 5.01 Hz, TEG), 3.86 (2 H, t, *J* = 5.13 Hz, TEG), 3.76 ~ 3.81 (6 H, m, TEG), 3.66 ~ 3.73 (12 H, m, TEG), 3.54 ~ 3.58 (6 H, m, TEG), 3.39 (3 H, s, CH_3-TEG), 3.38 (6 H, s, CH_3-TEG), 2.01 (2 H, m, dodecyl-CH_2), 1.65 (2 H, m, dodecyl-CH_2), 1.32 (16 H, m, dodecyl-$(CH_2)_8$), 0.91 (3H, t, *J* = 6.84 Hz, dodecyl-CH_3), -3.07 (2H, s, inner NH) ppm. MALDI-TOF-MS (dithranol): Calcd. for $C_{72}H_{95}N_4O_{14}$ $[M + H]^+$: *m/z* = 1239.68; found: 1239.48.

5-(4-Dodecyloxyphenyl)-10-bromo-15-{4-[3,4,5-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy) benzyloxy]phenyl} porphine, 4: Compound **3** (406 mg, 0.328 mmol) was dissolved in $CHCl_3$ (150 mL). N-bromosuccinimde (58.3 mg, 0.328) was added in small portions over 20 min. After the

addition, the solution was stirred for 30 min. Solvent was removed under reduced pressure and the residue was applied to a silica gel column eluting with using 2% MeOH-$CHCl_3$. The two products of the reaction (mono- and dibrominated porphyrins) and the starting compound eluted successively from the column but they could not be fully separated. The amounts of compound **4** in the fractions collected were determined by NMR spectroscopy after removal of solvent, and the optimal fractions were combined. The mixture obtained contained 60-70 mol% of **4** (Yield: 328 mg) and it was used in the next step without further purification.

1,3,5-Tris{5-[10-(4-Dodecyloxyphenyl)-20-(4-(3,4,5-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzyloxy)phenyl)porphyrinyl]} benzene (1H_3).

Part A. The compounds **4** (328 mg, contains 0.17 mmol of **4**), **3** (9.1 mg, 0.02 mmol), K_2CO_3 (165 mg, 1.19 mmol), and $Pd(PPh_3)_4$ (7.6 mg, 6.6 μmol) were added to a mixed solvent of N,N-dimethylformamide (8 mL), toluene (8 mL) and water (0.4 mL) in a Schlenk tube and degassed. The mixture was stirred at 80°C under N_2 for 1 day. After cooling to room temperature, the reaction mixture was partitioned between CH_2Cl_2 (100 mL) and water (100 mL). After separation of the 2 phases, the organic phase was washed with water (3 × 100 mL), dried over Na_2SO_4 and evaporated. The residue dissolved in the minimum volume of CH_2Cl_2 and applied to a silica gel column and eluted using a gradient from 100% CH_2Cl_2 to 98:2 CH_2Cl_2:MeOH to remove starting materials, then finally with CH_2Cl_2-MeOH (96:4) to collect the crude product of **1**H_3 (34.5 mg), which was shown by MALDI-TOF-MS to contain small amounts of meso-brominated derivatives.

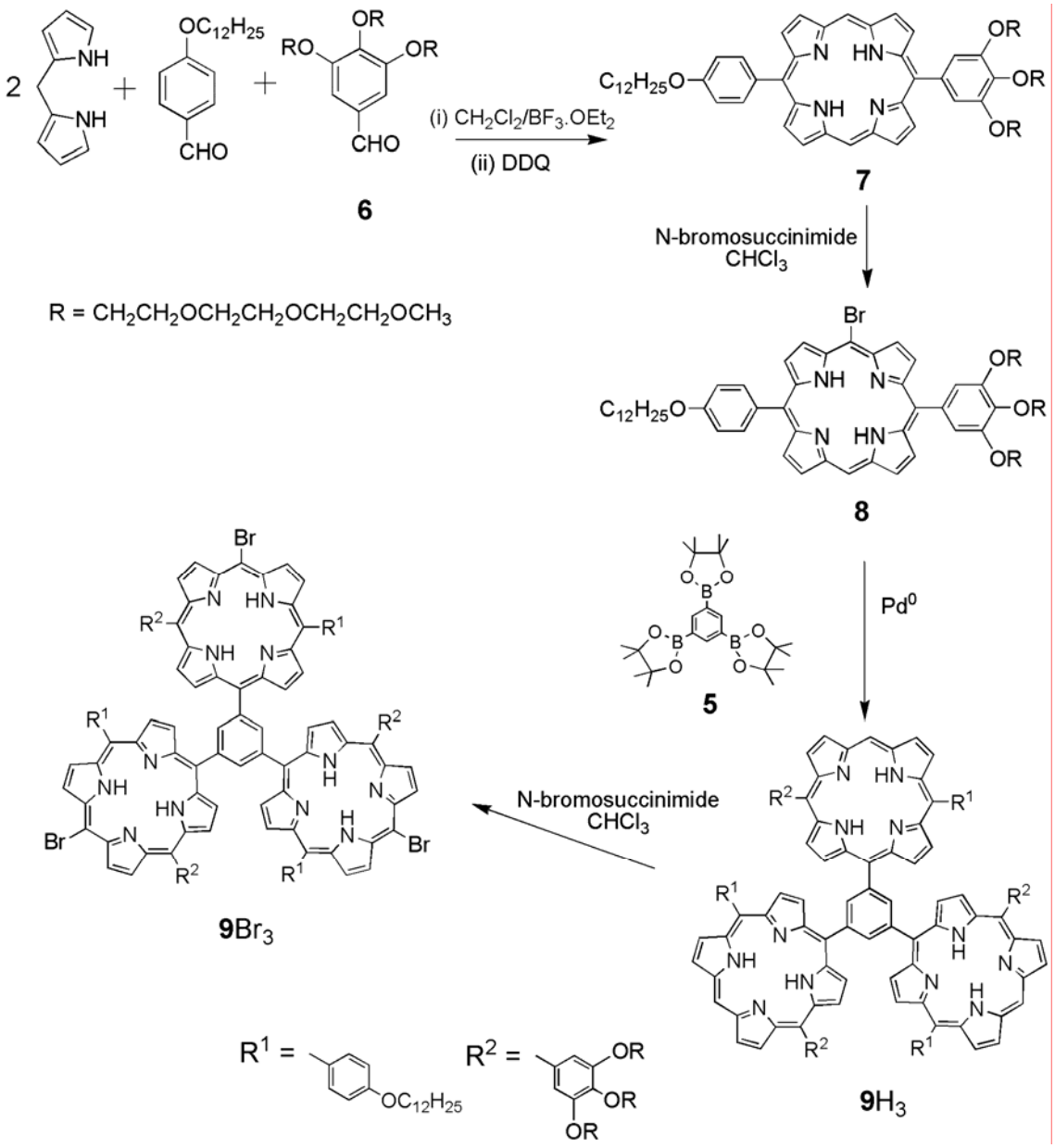
Part B. The crude product from Part A was debrominated according to a literature method (*S6*). It was dissolved in toluene (4 mL) in a Schlenk tube and $Pd(PPh_3)_4$ (3 mg, 2.6 μmol) was added. The solution was degassed, and formic acid (25 μL) and triethlamine (25 μL) were added. The mixture was heated at 100°C for 15 hours. After cooling to room temperature, the mixture was partitioned between CH_2Cl_2 (20 mL) and water (20 mL). After separation of the 2 phases, the organic phase was washed with water (3 × 20 mL), dried over Na_2SO_4 and solvents removed under reduced pressure. The resulting residue was loaded to a silica gel column and eluted with CH_2Cl_2-MeOH (97.5:2.5), affording **1**H_3 (15 mg, 20%). UV/vis (CH_2Cl_2): λ_{max} ($\varepsilon/10^4$) = 411 (66.5), 424 (72.7), 513 (5.84), 548

(2.68), 587 (1.85), 642 (1.19). FT-IR (BaF_2): ν = 3282.9 (w, N-H str), 3095.0 (w, Ar C-H str), 2922.4, 2869.7, 2853.5 (all s, C-H str), 1604.8 (m, C=C str), 1533.4 (w), 1514.3 (m), 1503.6 (m), 1467.1 (m, C-H def), 1456.2 (m), 1436.2 (m, C-H def), 1413.4 (w), 1376.0 (w), 1362.45 (w), 1351.0 (w), 1331.0 (m), 1285.1 (m), 1242.1 (s, C-O str), 1198.3 (w), 1175.4 (m), 1108.2 (br. s, C-O str, C-N str), 1049.4 (m), 1027.9 (m), 988.8 (m), 973.4 (m), 957 (s), 849 (s, Ar. C-H def), 794.9 (s, Ar. C-H def) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 10.17 (3 H, s, *meso*-H), 9.79 ~ 9.86 (6 H, m, pyrrole), 9.56 (3 H, s, central-C_6H_3), 9.28 ~ 9.31 (6 H, m, pyrrole), 9.18 ~ 9.24 (6 H, m, pyrrole), 8.99 ~ 9.04 (6 H, m, pyrrole), 8.13 (12 H, d, J = 6.78 Hz, o-Ph), 7.27 ~ 7.36 (12 H, m, m-Ph), 6.87 (s, 6 H, o-phenyl), 5.23 (6 H, s, benzyl-CH_2), 4.21 ~ 4.30 (24 H, m, OCH_2-TEG, OCH_2-dodecyl), 3.89 ~ 3.93 (12 H, m, TEG), 3.83 ~ 3.87 (6 H, m, TEG), 3.75 ~ 3.78 (18 H, m, TEG), 3.62 ~ 3.70 (36 H, m, TEG), 3.49 ~ 3.57 (18 H, m, TEG), 3.38 (9 H, s, CH_3-TEG), 3.33 (18 H, s, CH_3-TEG), 1.98~2.03 (6 H, m, dodecyl-CH_2), 1.28 ~ 1.51 (54 H, m, dodecyl-$(CH_2)_9$), 0.87~0.93 (9 H, m, dodecyl-CH_3), -2.87 (6 H, s, inner NH) ppm. MALDI-TOF-MS (dithranol): Calcd. for $C_{222}H_{282}N_{12}O_{42}$ $[M]^+$: *m/z* = 3788.03; found: 3788.52.

1,3,5-Tris{5-[10-(4-Dodecyloxyphenyl)-15-bromo-20-(4-(3,4,5-(2-(2-(2-methoxyethoxy)ethoxy) ethoxy)benzyloxy)phenyl)porphyrinyl]} benzene, (1Br_3): To a $CHCl_3$ (20 mL) solution of **1**H_3 (42 mg, 0.011 mmol) was added N-bromosuccinimde (7.5 mg, 0.042 mmol) in small portions. The mixture was stirred for 30 min then solvent was removed by rotary evaporation. The residue was purified by chromatography over silica gel and then dissolved in CH_2Cl_2 in a small vial and layered with hexane. The mixture was left for diffusion for 2 days. The precipitate was collected by filtration through a cotton plug. Yield: 29.5 mg (66%). UV/vis (CH_2Cl_2): λ_{max} ($\varepsilon/10^4$) = 421 (sh, 72.7), 429 (85.8), 521(5.21), 560 (4.29), 598 (1.66), 656 (2.05). FT-IR (BaF_2): ν = 3320.8 (w, N-H str), 3033.5 (w, Ar C-H str), 2955.5, 2922.0, 2851.6 (all s, C-H str), 1604.6 (m, C=C str), 1559.1 (w), 1540.0 (w), 1503.1 (m), 1465.1 (m, C-H def), 1436.9 (m), 1419.3 (w), 1399.1 (w), 1377.48 (w), 1334.3 (m), 1284.0 (m), 1244.7 (s, C-O str), 1199.2 (w), 1175.6 (m), 1108.6 (br. s, C-O str, C-N str), 1021, (w), 972.6 (w), 963.2 (w), 924.5 (w), 848.3 (w, Ar. C-H def), 798.1 (s, Ar. C-H def) cm^{-1}. ^1H NMR (300

MHz, $CDCl_3$, 25°C): δ = 9.63 (12 H, d, J = 4.65 Hz, pyrrole), 9.49 (3 H, s, central-C_6H_3), 9.04 ~ 9.09 (6 H, m, pyrrole), 8.87 ~ 8.93 (6 H, m, pyrrole), 8.05 ~ 8.08 (12 H, m, o-Ph), 7.25 ~ 7.33 (12 H, m, m-Ph), 6.86 (6 H, s, o-phenyl), 5.21 (6 H, s, benzyl-CH_2), 4.27 ~ 4.21 (24 H, m, OCH_2-TEG, OCH_2-dodecyl), 3.89 ~ 3.93 (12 H, m, TEG), 3.83 ~ 3.86 (6 H, m, TEG), 3.74 ~ 3.79 (18 H, m, TEG), 3.62~3.71 (36 H, m, TEG), 3.49 ~ 3.58 (18 H, m, TEG), 3.38 (9 H, s, CH_3-TEG), 3.33 (18 H, s, CH_3-TEG), 1.95 ~ 2.05 (6 H, m, dodecyl-CH_2), 1.26 ~ 1.52 (54 H, m, dodecyl-$(CH_2)_9$), 0.87 ~ 0.93 (9H, m, dodecyl-CH_3), -2.64 (6 H, s, inner NH) ppm. MALDI-TOF-MS (dithranol): Calcd. for $C_{222}H_{279}Br_3N_{12}O_{42}$ $[M]^+$: *m/z* = 4027.77; found: 4027.79.

Synthesis of more rigid (non-benzyloxy) Trigeminal Porphyrin Amphiphile



Scheme S2. Synthesis of less flexible trigeminal porphyrin amphiphiles.

3,4,5-Tris{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzaldehyde, 6. A solution of 3,4,5-tris{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}benzyl alcohol[5] (5.56 g, 0.00935 mol) in dry dichloromethane (40 mL) was added dropwise during 15 minutes to a suspension of pyridinium chlorochromate (5.04 g, 0.0234 mol) in dry dichloromethane (40 mL). The mixture turned from bright orange to dark brown. After the addition, the mixture was stirred for 4 hours, then it was

filtered through celite and the resulting cake was further washed with dichloromethane. The filtrate was concentrated and filtered through a filter paper then solvent was removed by rotary evaporation to yield a crude product (8.39 g). It was loaded to a silica gel column, and eluted with CH_2Cl_2-MeOH (98:2). A light yellow oil of **6** was obtained, which was used without further purification. Yield: 4.39 g (79%).

5-(4-Dodecyloxyphenyl)-15-{3,4,5-tris[2-(2-(2-methoxyethoxy)ethoxy)ethoxy]phenyl}porphine, 7: It was synthesized from the reaction of **6** (1.185 g, 2 mmol), 4-dodecyloxybenzaldehyde (0.581 g, 2 mmol) and dipyrromethane (0.585 g, 4 mmol) by a procedure similar to that for **1**H_3. Yield: 348 mg (15%). UV/vis (CH_2Cl_2): λ_{max} ($\varepsilon/10^4$) = 410 (383), 504 (17.3), 540 (7.35), 577 (5.71), 632 (2.24). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 10.23 (2 H, s, *meso*-H), 9.33 (4 H, dd, *J* = 4.86 Hz, pyrrole-H), 9.12 (2 H, d, *J* = 4.56 Hz, pyrrole-H), 9.08 (2 H, d, *J* = 4.59 Hz, pyrrole-H), 8.12 (2 H, d, *J* = 8.43 Hz, *o*-phenyl), 7.51 (2 H, s, *o*-phenyl), 7.29 (2 H, d, *J* = 8.61 Hz, *m*-phenyl), 4.52 (2 H, t, *J* = 5.15 Hz, OCH_2-TEG), 4.30 (4 H, t, *J* = 4.95 Hz, OCH_2-TEG), 4.21 (2 H, t, *J* = 6.50 Hz, OCH_2-dodecyl), 4.05 (2 H, t, *J* = 5.15 Hz, TEG), 3.87 ~ 3.92 (6 H, m, TEG), 3.77 ~ 3.80 (2 H, m, TEG), 3.70 ~ 3.75 (6 H, m, TEG), 3.57~3.62 (6 H, m, TEG), 3.47 ~ 3.51 (4 H, m, TEG), 3.41 (3 H, s, CH_3-TEG), 3.31 ~ 3.35 (4H, m, TEG), 3.19 (6H, s, CH_3-TEG), 1.96 (2H, m, dodecyl-CH_2), 1.61 (2H, m, dodecyl-CH_2), 1.31 (16 H, m, dodecyl-$(CH_2)_8$), 0.90 (3H, t, *J* = 6.78 Hz, dodecyl-CH_3), -3.09 (2H, s, inner NH) ppm.

5-(4-Dodecyloxyphenyl)-10-bromo-15-{3,4,5-tris[2-(2-(2-methoxyethoxy)ethoxy)ethoxy] phenyl} porphine, 8. This was synthesized and later employed according to the same procedures used for compound **4** (**Parts A** and **B** above). **7** (650 mg, 0.524 mmol) was reacted with NBS (93 mg, 0.473 mmol) in $CHCl_3$ (200 ml). Yield: 630 mg containing 60-70% of the required monobrominated porphyrin, **8**.

1,3,5-Tris(5-(10-(4-Dodecyloxyphenyl)-20-tris(3,4,5-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy) phenyl)porphyrinyl)) benzene (9H_3**)**. **9**H_3 was synthesized from the reaction of **8** (630 mg, contains

0.28 mmol of **8**), **5** (13.9 mg, 0.03 mmol), K_2CO_3 (252 mg, 1.82 mmol), and $Pd(PPh_3)_4$ (11.6 mg, 10 μmol) in a mixed solvent of DMF (12 mL), toluene (12 mL) and water (0.6 mL) followed by debromination according to the same procedure used for **1**H_3**.** Yield: 36 mg, 35%. UV/vis (CH_2Cl_2): λ_{max} ($\varepsilon/10^4$) = 411 (72.4), 424 (78.6), 512 (6.58), 547 (2.64), 586 (2.04), 641 (1.08). FT-IR (BaF_2): ν = 3308.0 (w, N-H str), 2922.3, 2852.3 (all s, C-H str), 1644.8 (m, C=C str), 1579.1 (m, C=C str), 1503.3 (w), 1466.2 (m, C-H def), 1418.4 (m), 1377.5 (w), 1340.3 (m), 1285.4 (m), 1243.6 (s, C-O str), 1200.1 (w), 1174.8 (w), 1111.5 (br. s, C-O str, C-N str), 998.1 (w), 966.0 (w), 957.2 (w), 941.5 (w), 921.6 (w), 846.7 (w, Ar. C-H def), 797.4 (s, Ar. C-H def) 763.6 (w), 742.9 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 10.17 (3 H, s, *meso*-H), 9.70 ~ 9.90 (6 H, m, pyrrole), 9.54 (3 H, s, central-C_6H_3), 9.16 ~ 9.31 (12 H, m, pyrrole), 9.02 ~ 9.06 (6 H, m, pyrrole), 8.09 ~ 8.19 (6H, s, o-Ph), 7.44 ~ 7.49 (6 H, m, *o*-phenyl), 7.29 ~ 7.36 (6 H, m, *m*-phenyl), 4.50 (6 H, m, OCH_2-TEG), 4.21 ~ 4.32 (18 H, m, OCH_2-TEG, OCH_2-dodecyl), 4.04 (6 H, m, TEG), 3.77 ~ 3.92 (24 H, m, TEG), 3.72 ~ 3.76 (6 H, m, TEG), 3.59 ~ 3.69 (18 H, m, TEG), 3.47 ~ 3.56 (12 H, m, TEG), 3.41 (9 H, s, CH_3-TEG), 3.32 ~ 3.38 (12 H, m, TEG), 3.14 ~ 3.25 (12 H, m, TEG), 3.02 ~ 3.08 (18 H, m, CH_3-TEG), 2.04 (6 H, m, dodecyl-CH_2), 1.26 ~ 1.58 (54 H, m, dodecyl-$(CH_2)_8$), 0.91 (9H, m, dodecyl-CH_3), -2.91 (6 H, s, inner NH) ppm. MALDI-TOF-MS (dithranol): Calcd. for $C_{201}H_{266}N_{12}O_{39}$ $[M + 2H]^+$: m/z = 3471.92; found: 3472.36.

References

S1. M. A. Oar, J. M. Serin, W. R. Dichtel, J. M. J. Fréchet, T. Y. Ohuchanskyy and P. N. Prasad, *Chem. Mater.* 2005, **17**, 2267.

S2. M. C. Lensen, J. A. A. W. Elemans, S. J. T. van Dingenen, J. W. Gerritsen, S. Speller, A. E. Rowan and R. J. M. Nolte, *Chem. Eur. J.* 2007, **13**, 7948.

S3. C.-H. Lee and J. S. Lindsey, *Tetrahedron* 1994, **50**, 11427.

S4. A. Hayek, F. Bolze, J.-F. Nicoud, P. L. Baldeck and Y. Mély, *Photochem. Photobiol. Sci.* 2006, **5**, 102.

S5. A. B. Morgan, J. L. Jurs and J. M. Tour, *J. Appl. Polym. Sci.* 2000, **76**, 1257.

S6. A. K. Sahoo, Y. Nakamura, N. Aratani, K. S. Kim, S. B. Noh, H. Shinokuba, D. Kim and A. Osuka, *Org. Lett.*. 2006, **8**, 4141.

3. Scanning electron microscopy of solution self-assemblies of $1Br_3$ and $1H_3$

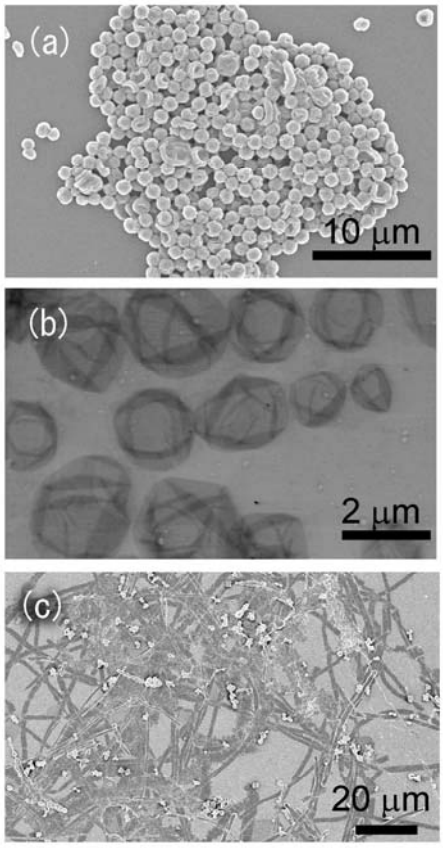


Fig. S1.

a, Hollow capsules of **1**Br_3 precipitated from dichloromethane/methanol.

b, Thin-walled vesicles (collapsed) of **1**Br_3 observed in CH_2Cl_2/methanol supernatant solution.

c, Thin-walled (collapsed) microtubules of **1**Br_3 self-assembled in CH_2Cl_2/hexane.

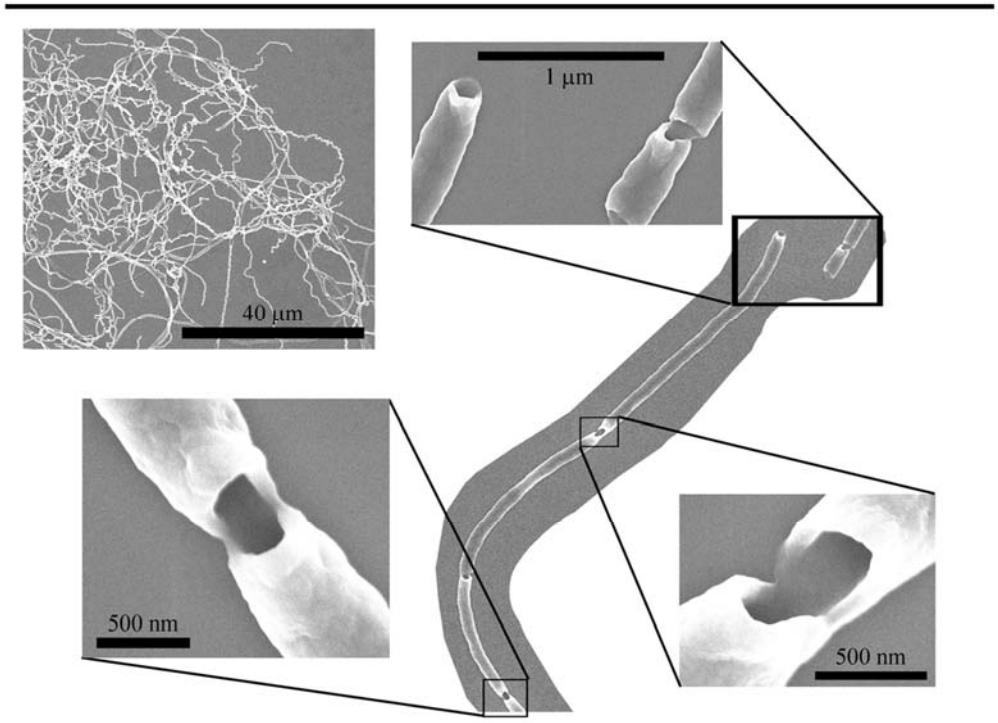


Figure S2. Thick-walled robust microtubules of **1**H_3 in CH_2Cl_2/methanol.

4. Scanning electron microscopy images of self-assembled nanowires on mica

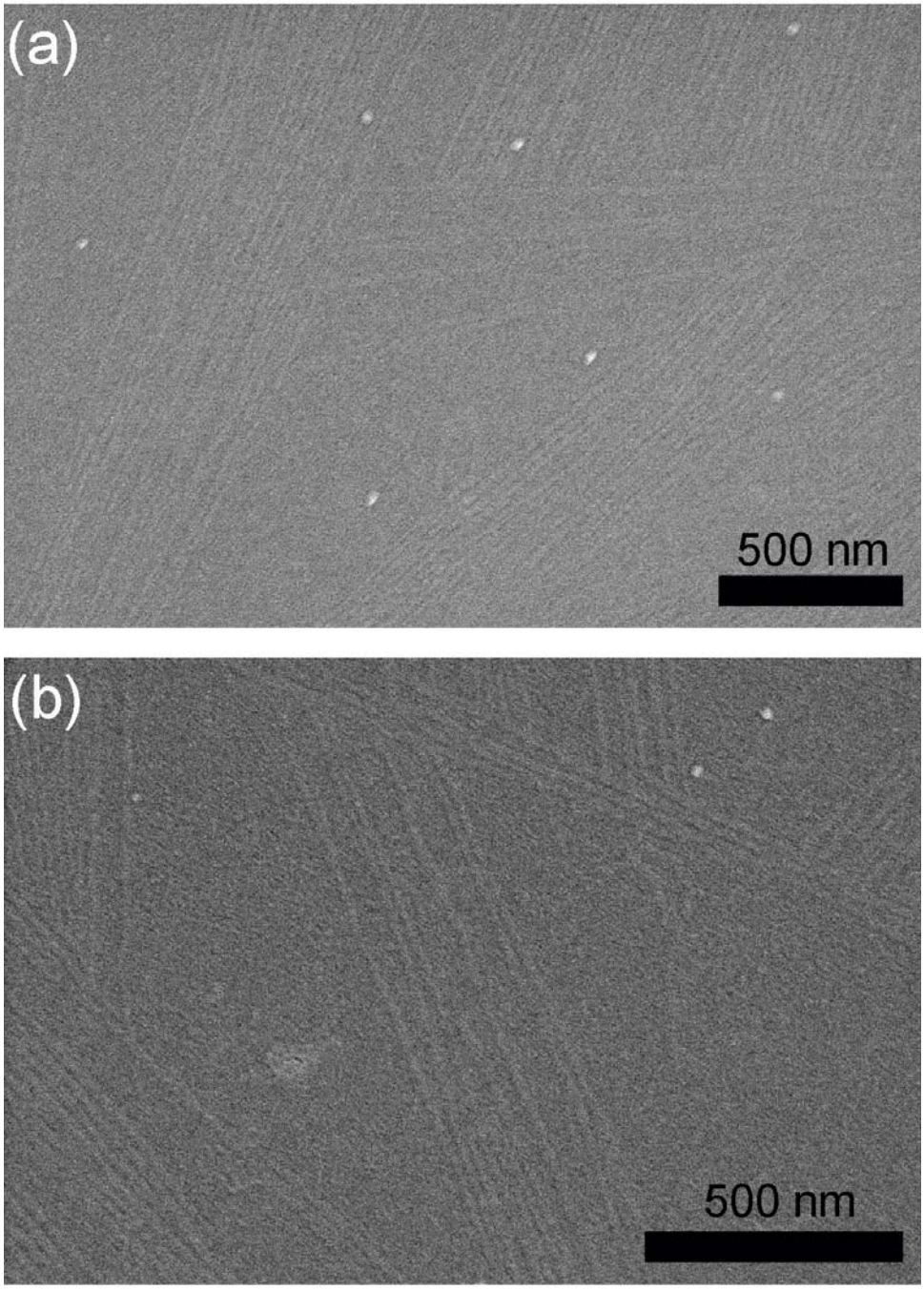


Figure S3. a, b, SEM images of the **1**Br_3 self-assembled nanowires on mica. A sputtered Pt coating of at least 10 nm was required to visualize the nanowires due to their small size.

5. Electronic absorption spectra

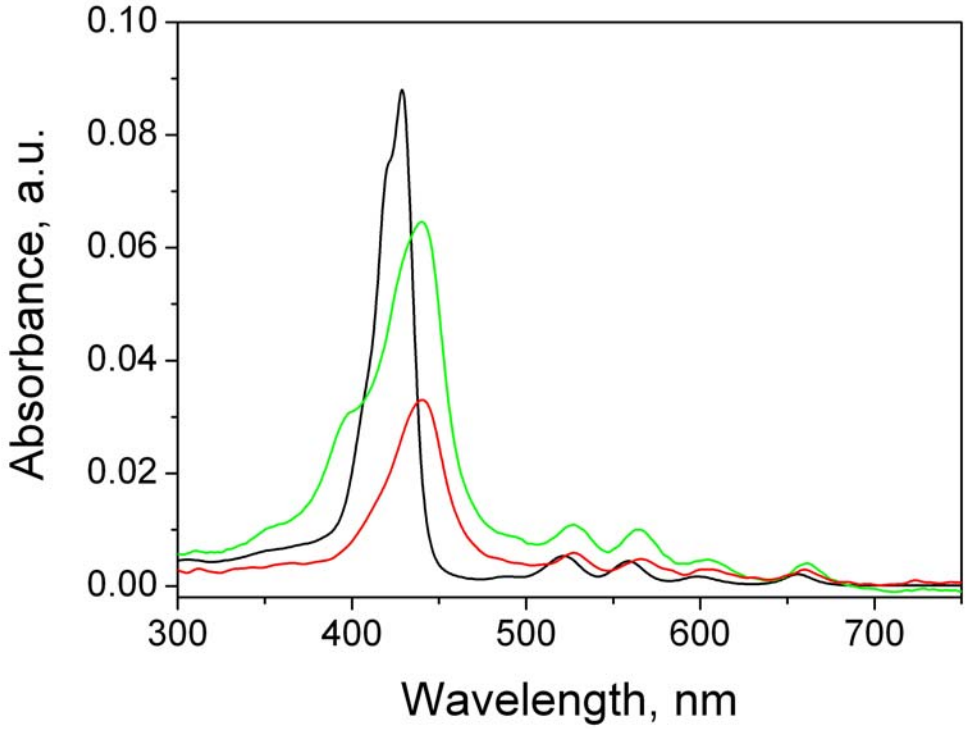


Fig. S4. Electronic absorption spectra **1**Br_3. **a**, Solution (~0.1 mg/mL in dichloromethane, 10 mm pathlength cell) black line. **b**, Suspension (~1 mg/mL in dichloromethane:methanol, 50:50 v/v, 1 mm pathlength cell) green line. **c**, Cast on a solid substrate (quartz) red line.