**Supplementary Information** for

# Repetitive Stepwise Rotaxane Formation toward Programmable Molecular Arraying

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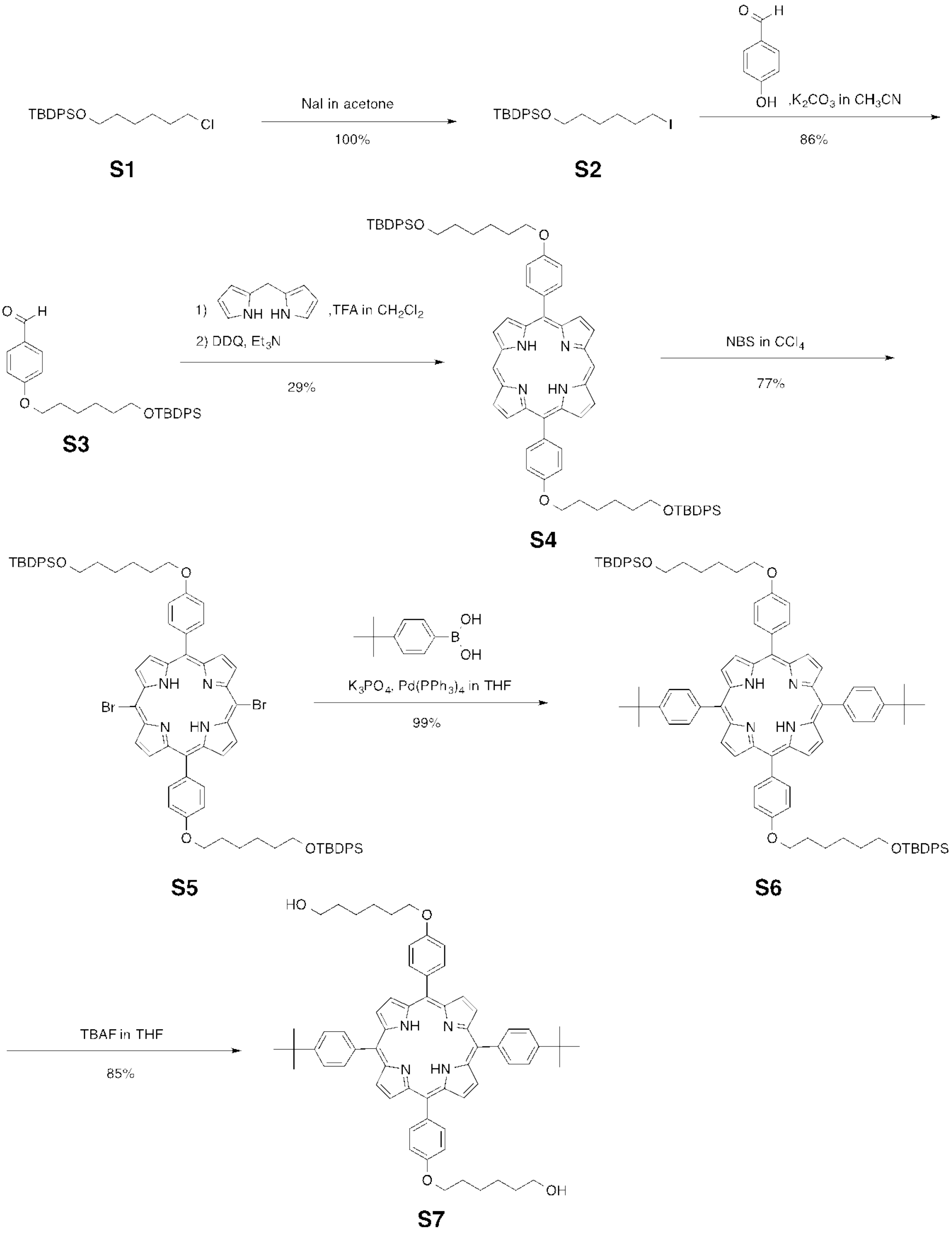
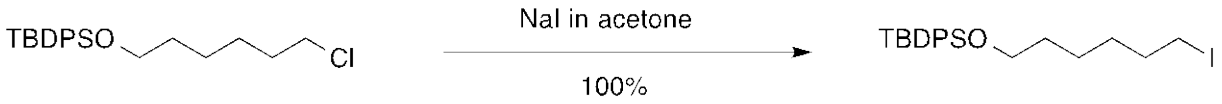
## General Methods.

Synthetic procedures were carried out under dry nitrogen atmosphere, unless otherwise specified. All reagents and solvents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. $^{1}H$, and $^{13}C$ spectra were recorded on a JEOL JNM-A600 (600 MHz for $^{1}H$; 150 MHz for $^{13}C$) spectrometer or a JEOL JNM-ECS400 (400 MHz for $^{1}H$; 100 MHz for $^{13}C$) spectrometer at a constant temperature of 298 K. Tetramethylsilane (TMS) was used as an internal reference for $^{1}H$ and $^{13}C$ NMR measurements in $CDCl_3$. Elemental analyses were performed on a Yanaco MT-6 analyzer. Silica gel column chromatographies and thin-layer (TLC) chromatography were performed using Merck silica gel 60 and Merck silica gel 60 (F254) TLC plates, respectively. GPC was performed using a JAI LC-9204 equipped with JAIGEL 1H-40/2H-40 columns. ESI mass spectrometry was performed with a Waters LCT-Premier XE Spectrometer controlled using Masslynx software. The absorption spectra were recorded with a Hitachi U-4100 spectrophotometer in $CH_2Cl_2$ solutions at 20 ± 0.1 °C in 1.0 cm quartz cells. Cyclic voltammetry measurements were performed.



*Scheme S1* Synthesis of a Porphyrin **S7** (a precursor of Porphyrin **1**).

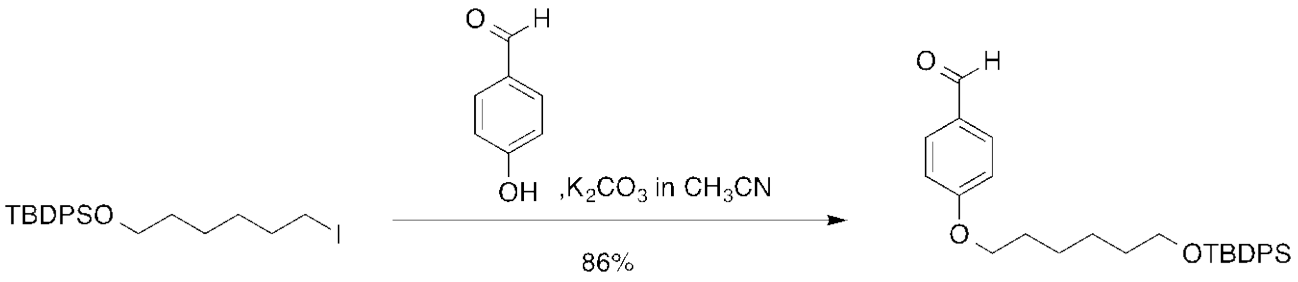
## Synthesis of 6-iodo-*tert*-butyldiphenylsioxyhexane **S2**



**S1** **S2**

To a solution of 6-chloro-*tert*-butyldiphenylsiloxyhexane **S1**[1] (54.0 g, 144 mmol) in acetone (500 mL) was added NaI (53.6 g, 358 mmol, 2.49 equiv). The reaction mixture was refluxed on an oil bath for 24.5 hrs. The solvent was evaporated off to obtain pale yellow oil (1.31 g). The crude product was dissolved in $CH_2Cl_2$ (500 mL) and the mixture was washed with 5% aqueous $Na_2S_2O_3$ (300 mL) and water (500 mL), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to afford the title compound **S2** as a colorless oil (67.1 g, 100 %). $^1$H NMR (600 MHz, $CDCl_3$) : $\delta$ = 7.66 (s, 4H), 7.38 (m, 6H including $CHCl_3$), 3.65 (t, $J$ = 6.4 Hz, 2H), 3.15 (t, $J$ = 7.2 Hz, 2H), 1.80 (t, $J$ = 7.2 Hz, 2H), 1.56 (t, $J$ = 6.4 Hz, 2H), 1.37 (s, 4H), 1.05 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) : $\delta$ = 135.6, 135.5, 129.5, 127.6, 63.7, 33.5, 32.3, 30.2, 26.9, 24.7, 7.1. IR (ATR/ZnSe) : 3078, 2951, 1715, 1571, 1442, 1326, 1261, 1245, 1197, 1146 cm$^{-1}$. ESI-TOF-MS (positive) : $m/z$ = 489 $[M+Na]^+$, 489 calcd $[M+Na]^+$.

## Synthesis of 4-((6-((*tert*-butyldiphenylsilyl)oxy)hexyl)oxy)benzaldehyde **S2**

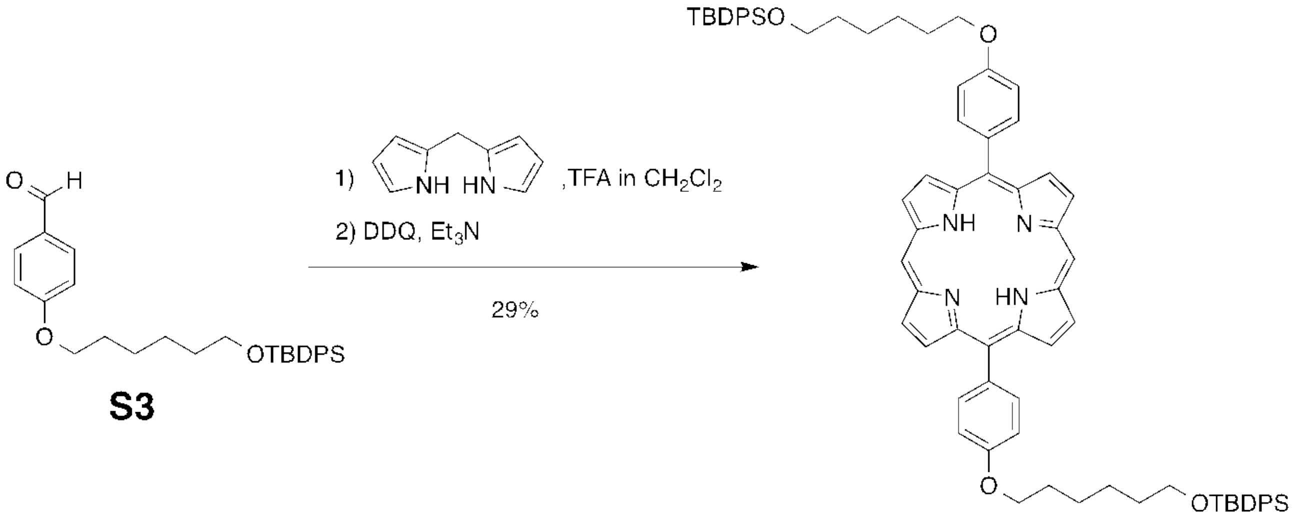


**S2** **S3**

*tert*-Butyl((6-iodohexyl)oxy)diphenylsilane **S2** (20.1 g, 43.0 mmol, 1.08 equiv), 4-hydroxybenz aldehyde (4.83 g, 40.0 mmol), and $K_2CO_3$ (7.26 g, 52.5 mmol, 1.31 equiv) were dissolved in $CH_3CN$ (65.0 mL). The mixture was stirred at a bath temperature of 125 ºC for 11.5 hrs. After AcOEt

(300 mL) and hexane (100 mL) were added, the resulting mixture was washed with 3M aqueous NaOH (70.0 mL), water (100 mL × 2), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to obtain pale yellow oil (19.0 g). The crude product was purified by silica gel column chromatography (12 cm $\phi \times$ 21 cm, hexane : $CH_2Cl_2$ = 6 : 5) to obtain the title compound **S3** as a pale yellow oil (17.1 g, 37.1 mmol, 86 %). $^1$H NMR (400 MHz, $CDCl_3$) : $\delta$ = 9.87 (s, 1H), 7.83 (d, $J$ = 8.8 Hz, 2H), 7.67 (d, $J$ = 6.5 Hz, 2H), 7.37 (m, 6H), 6.97 (d, $J$ = 8.8 Hz, 2H), 4.01 (t, $J$ = 6.4 Hz, 2H), 3.67 (t, $J$ = 6.1 Hz, 2H), 1.79 (dt, $J$ = 6.8 Hz, $J$ = 6.8 Hz, 2H), 1.60 (dt, $J$ = 6.6 Hz, $J$ = 6.6 Hz,2H), 1.44 (m, 4H), 1.05 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) : $\delta$ = 190.8, 164.2, 135.5, 134.1, 131.9, 129.7, 129.5, 127.6, 114.7, 68.3, 63.7, 32.4, 29.0, 26.8, 25.7, 25.5, 19.2.

Synthesis of 5,15-(4-((*t*-butyldiphenylsiloxyhexyl)oxy)phenyl)porphyrin **S4**

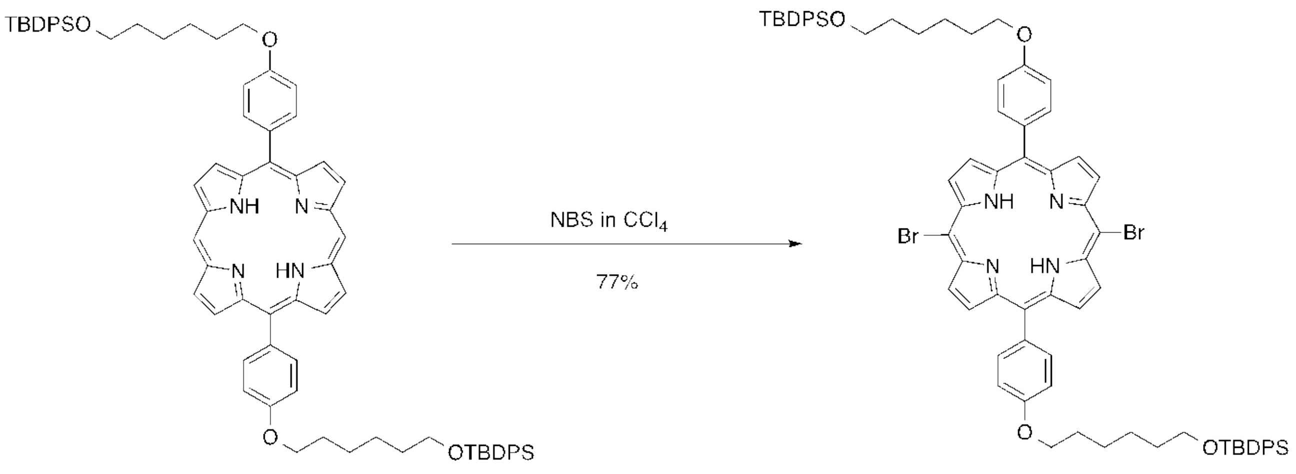


**S3**

**S4**

A solution of 4-((6-((*tert*-butyldiphenylsilyl)oxy)hexyl)oxy)benzaldehyde **S3** (10.0 g, 21.7 mmol) and diyprromethane[2] (3.24 g, 22.2 mmol, 1.02 equiv) in $CH_2Cl_2$ (2.05 L) was deoxygenated by $N_2$ bubbling for 20 min. Trifuluoroacetic acid (3.10 mL, 40.5 mmol, 1.87 equiv) was added to the solution. The reaction mixture was stirred for 30 min at room temperature. After DDQ (7.67 g, 33.8 mmol, 1.56 equiv) and $Et_3N$ (12.0 mL) were added, the volatile compounds were evaporated off. The crude product was purified by silica gel column chromatography (12 cm $\phi \times$ 21 cm, hexane : $CH_2Cl_2$ = 2 : 1) to obtain the title compound **S4** as a purple solid (3.66 g, 3.12 mmol, 29%). $^1$H NMR (270 MHz, $CDCl_3$) : $\delta$ = 10.28 (s, 2H), 9.37 (d, $J$ = 4.6 Hz, 4H), 9.10 (d, $J$ = 4.6 Hz, 4H), 8.16 (d, $J$ = 8.4 Hz, 4H), 7.72 (m, 8H), 7.42 (m, 12H), 7.31 (d, $J$ = 8.4 Hz, 4H), 4.25 (t, $J$ = 6.3 Hz, 4H), 3.77 (t, $J$ = 6.3 Hz, 4H), 2.04 (dd, $J$ = 6.8 Hz, 4H), 1.71 (dd, $J$ = 6.8 Hz, 4H), 1.6 (m, 8H), -3.07 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$ : $\delta$ = 159.1, 147.5, 145.1, 135.9, 135.6, 134.2, 133.6, 131.5, 131.0, 130.0, 127.6, 118.9, 113.1, 105.1, 68.3, 63.9, 32.6, 29.5, 26.9, 26.0, 25.7, 19.3. IR (ATR/ZnSe) : 2926, 2859, 1688, 1600, 1572, 1509, 1468, 1427, 1389, 1352, 1243, 1107, 1088, 955, 827, 795, 737, 699, 650, 616 cm$^{-1}$. ESI-TOF-MS (positive) : $m/z$ = 1172 $[M+H]^+$, 1172 calcd $[M+H]^+$.

Synthesis of 5,15-(4-((*t*-butyldiphenylsiloxyhexyl)oxy)phenyl)-10,20-dibromoporphyrin **S5**

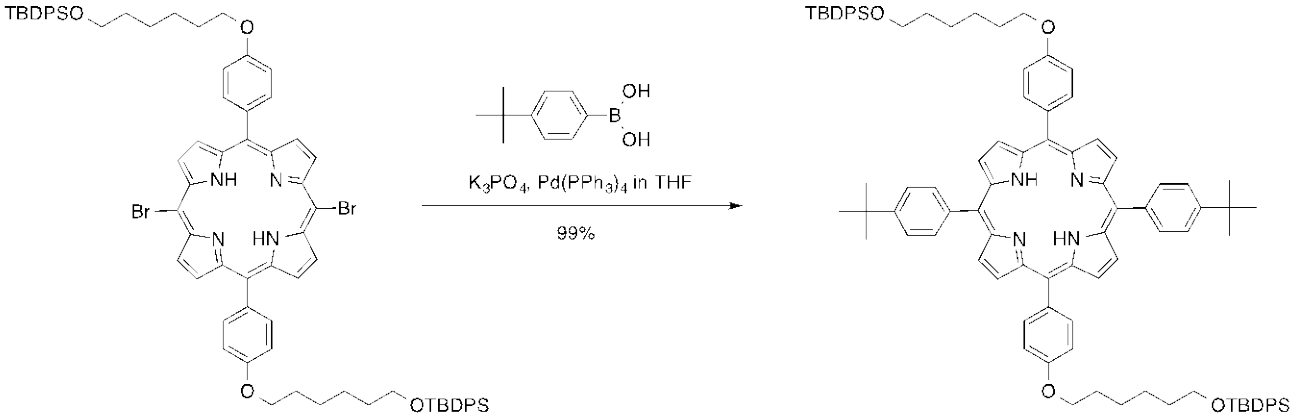


**S4** **S5**

NBS (22.5 mg, 126 µL, 2.73 equiv) was added to a solution containing **S4** (54.0 mg, 46.1 µmol), pyridine (62.0 µL) in $CCl_4$ (6.40 mL) on an ice bath. The resulting mixture was stirred for 14 hrs at room temperature. After the volatile compounds were evaporated off, the residue was dissolved in $CHCl_3$ (10.0 mL). The solution was washed with 5% aqueous $Na_2S_2O_3$ (10.0 mL), water (10.0 mL), and brine (10.0 mL), dried over anhydrous $Na_2SO_4$, and evaporated to obtain purple solid (54.3 mg, 89%). The crude product was purified by silica pad ($CHCl_3$) to obtain the title compound **S5** as a purple solid (47 mg, 35.4 µmol, 77%). $^1$H NMR (270 MHz, $CDCl_3$) : $\delta$ = 9.53 (d, $J$ = 4.6 Hz, 4H), 8.80 (d, $J$ = 4.6 Hz, 4H), 7.96 (d, $J$ = 6.8 Hz, 4H), 7.74 (t, $J$ = 1.9 Hz, 4H), 7.72 (t, $J$ = 1.9 Hz, 4H), 7.42 (m, 4H), 7.19 (d, $J$ = 8.5, 4H), 4.18 (t, $J$ = 6.3 Hz, 4H), 3.76 (t, $J$ = 6.3 Hz, 4H), 1.96 (dd, $J$ = 6.8 Hz, 4H), 1.70 (dd, $J$ = 6.8 Hz, 4H), 1.58 (m, 8H), 1.11 (s, 18H), -2.78 (s, 2H). $^{13}$C NMR (100

MHz, $CDCl_3$ : $\delta$= 159.1, 147.5, 145.1, 135.9, 135.6, 134.2, 133.6, 131.5, 131.0, 130.0, 127.6, 118.9, 113.1, 105.1, 68.3, 63.9, 32.6, 29.5, 26.9, 26.0, 25.7, 19.3. ESI-TOF-MS (positive) : *m*/*z* = 1329 $[M+H]^+$, 1329 calcd $[M+H]^+$.

Synthesis of 5,15-Bis(4-(6-*tert*-buthyldiphenylsiloxyhexyl-1-oxy)phenyl)-10,20-di(4-*tert*-buthyl phenyl)porphyrin **S6**



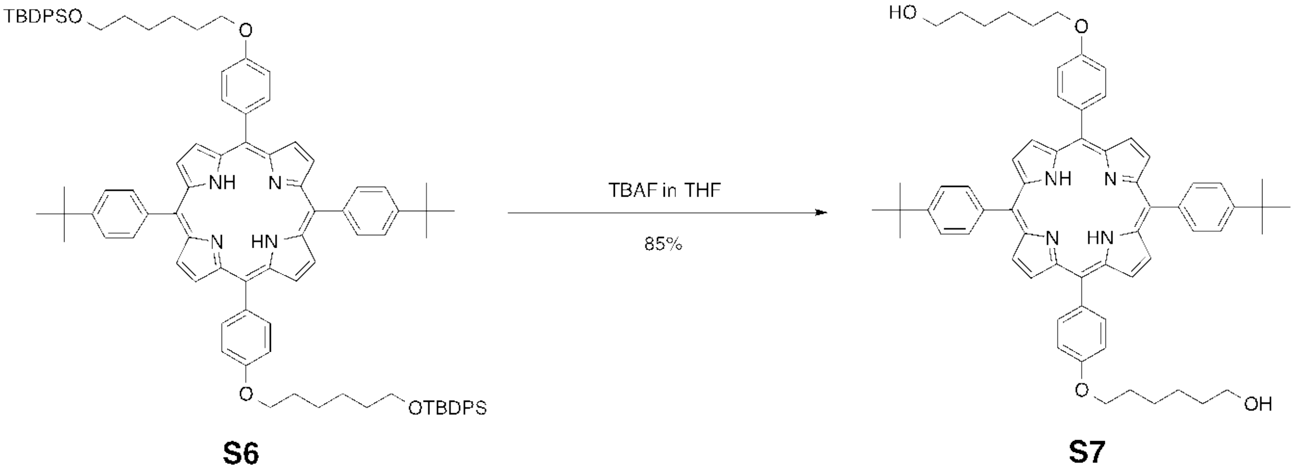
**S5**

**S6**

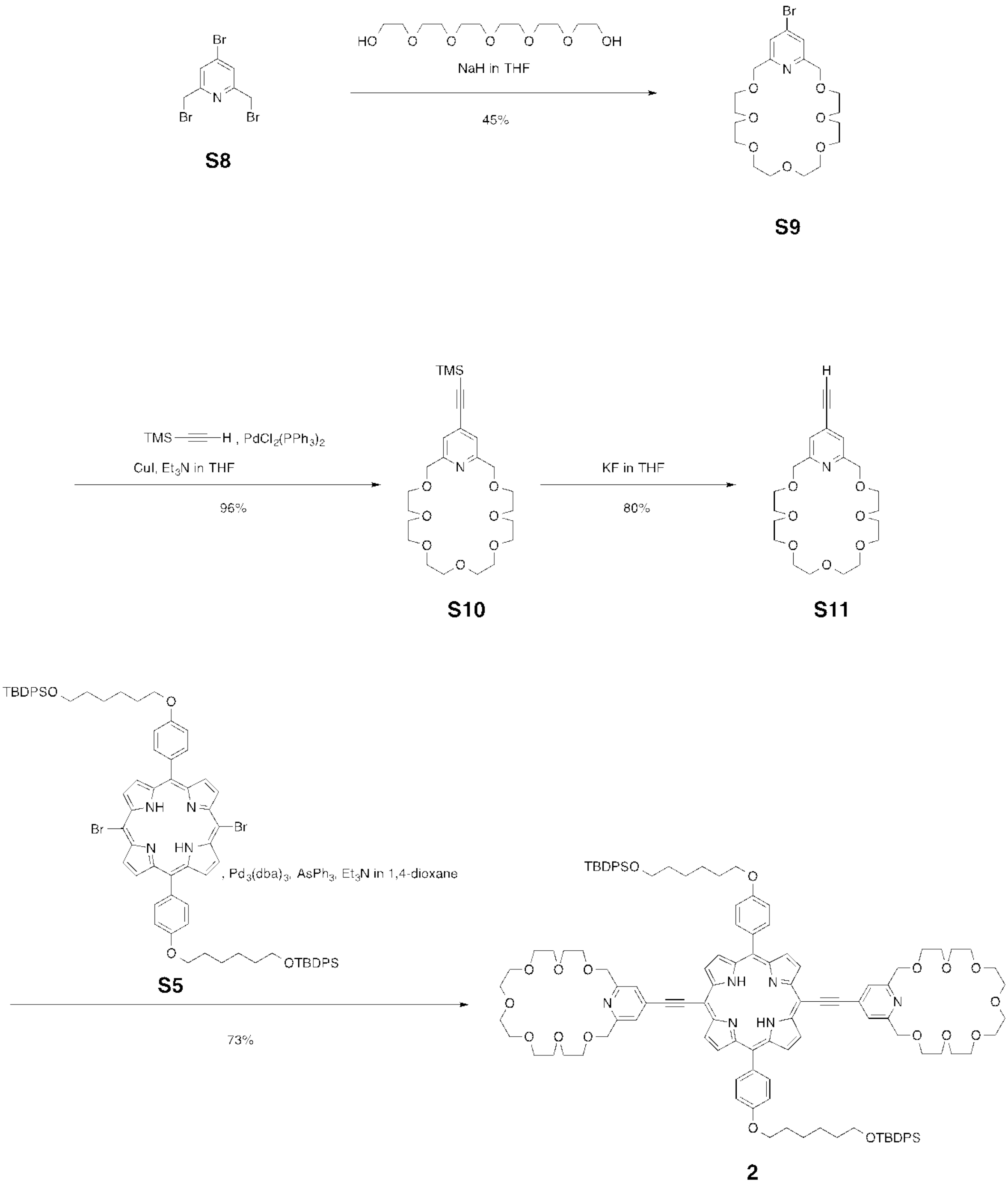
5,15-Bis(4-(6-*tert*-buthyldiphenylsiloxyhexyl-1-oxy)phenyl)-10,20-dibromoporphyrin **S5** (310 mg, 233 mmol), 4-*tert*-butylphenylboronic acid (859 mg, 4.83 mmol, 20.7 equiv), $Pd(PPh_3)_4$ (27.1 mg, 23.5 mmol, 0.10 equiv) and $K_3PO_4$ (993 mg, 4.68 mmol, 20.1 equiv) were suspended in dry THF (24.0 mL). The mixture was degassed with freeze-thaw method by 5 times. After the mixture was refluxed for 17 hrs, $CH_2Cl_2$ (50.0 mL) was added. The resulting mixture was washed with saturated aqueous $NaHCO_3$ (50.0 mL) and water (50.0 mL × 2), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to obtain dark purple solid (1.22 g). The crude product was purified by reprecipitation from $CH_2Cl_2$ (15.0 mL) and MeOH (150 mL) to give the title compound **S6** as a purple solid (332 mg, 231 mmol, 99%). $^1H$ NMR (400 MHz, $CDCl_3$) : $\delta$= 8.85 (s, 8H), 8.12 (dd, *J* = 8.1, 9.0 Hz, 8H), 7.75 (d, *J* = 9.0 Hz, 4H), 7.70 (d, *J* = 7.0 Hz, 8H), 7.40 (m, 12H), 7.25 (d, *J* = 8.1 Hz, 4H), 4.22 (t, *J* = 6.4 Hz, 4H), 3.74 (t, *J* = 6.4 Hz, 4H),1.96 (quin, *J* = 6.4 Hz, 4H), 1.67 (m, 4H), 1.60 (s, 18H), 1.50 (m, 11H including $H_2O$), 1.08 (s, 18H), -2.78 (s, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) : *d* =159.0, 150.6, 139.3, 135.7, 134.6, 134.5, 134.3, 131.1, 129.6, 127.7, 123.7, 120.2, 120.0, 112.8, 68.3, 64.0, 35.2, 32.6, 31.8, 30.0, 27.0, 26.1, 25.8, 19.4. ESI-TOF-MS (positive) : *m*/*z* = 1435 $[M+H]^+$, 1435 calcd $[M+H]^+$. Anal. Calcd. for $C_{198}H_{230}Cl_6O_{11}Si_4$ (2·**S6** + 3MeOH +

$3CH_2Cl_2$) : C, 73.78; H, 7.19; N, 3.48. Found. C, 73.76; H, 6.98; N, 3.08. (0.40% Error).

Synthesis of 5,15-Bis(4-(6-hydoxyhexyl-1-oxy)phenyl)-10,20-bis(4-*tert*-butylphenyl)porphyrin **S7**

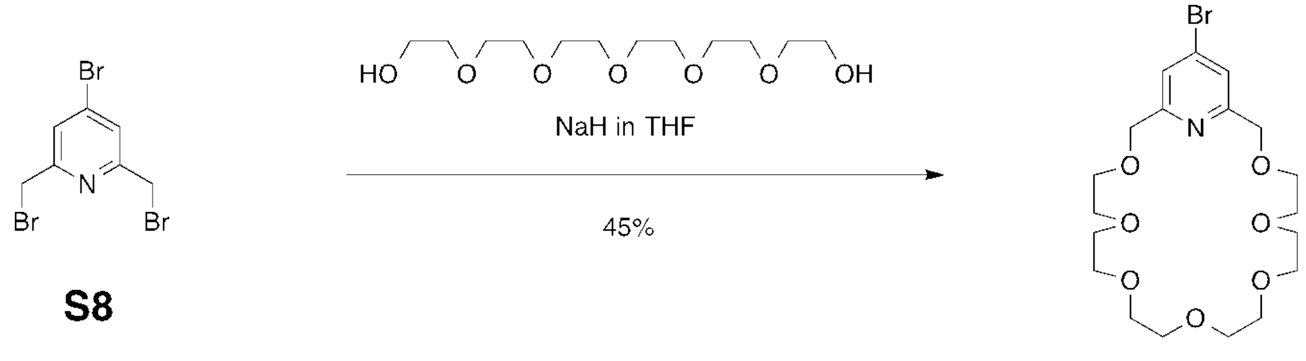


5,15-Bis(4-(6-*tert*-buthyldiphenylsiloxyhexyl-1-oxy)phenyl)-10,20-di(4-*tert*-buthylphenyl) porphyrin **S6** (300 mg, 209 μmol) was dissolved in dry THF (20.0 mL) and then TBAF (1 M in THF, 430 μ L, 430 μmol, 2.06 equiv) was added to the solution. The mixture was stirred at room temperature for 12 hrs and evaporated. The crude product was dissolved in $CHCl_3$ : MeOH =10: 1 (150 mL) and the solution was filtered through a silica pad. After MeOH (150 mL) was added to the filtrate, the purple precipitate was collected by suction filtration, washed with MeOH (50.0 mL) and hexane (50.0 mL) successively to obtain pure 5,15-bis(4-(6-hydoxyhexyl-1-oxy)phenyl)-10,20-bis(4-*tert*-butylphenyl)porphyrin **S7** as a purple solid (156 mg, 163 mmol, 78%). On the other hand, the crude solid obtained from the supernatants was purified by silica gel column chromatography twice (3.6 cm $\phi$ × 15cm, $CH_2Cl_2$ : MeOH = 10: 1 for 1st column, $CH_2Cl_2$ : MeOH = 20: 1 for 2nd column) to obtain purple solid (123 mg), which was purified by reprecipitation from $CHCl_3$ : MeOH (20: 1, 8.0 mL) and $Et_2O$ (32.0 mL) by three times to obtain **S7** as a purple solid (14.2 mg, 14.8 μmol, 7%). Totally, 170 mg (177 μmol, 85%) of the title compound **S7** was obtained. $^1$H NMR (400 MHz, $CDCl_3$) : $\delta$ = 8.85 (brs, 8H), 8.12 (dd, $J$ = 8.6, 10.1 Hz, 8H), 7.75 (d, $J$ = 8.6 Hz, 4H), 7.26 (d, $J$ = 10.1 Hz, 8H), 4.25 (t, $J$ = 7.5 Hz, 4H), 3.73 (t, $J$ = 6.4 Hz, 4H), 2.00 (quin, $J$ = 7.5 Hz, 4H), 1.68 (m, 8H), 1.50 (m, 5H including $H_2O$), -2.76 (s, 2H). ESI-TOF-MS (positive) : $m/z$ = 959 $[M+H]^+$, 959 calcd $[M+H]^+$.



*Scheme S2* Synthesis of a porphyrin monomer **2**.

Synthesis of 4-bromo-2,6-pyrido-24-crown-8 **S9**

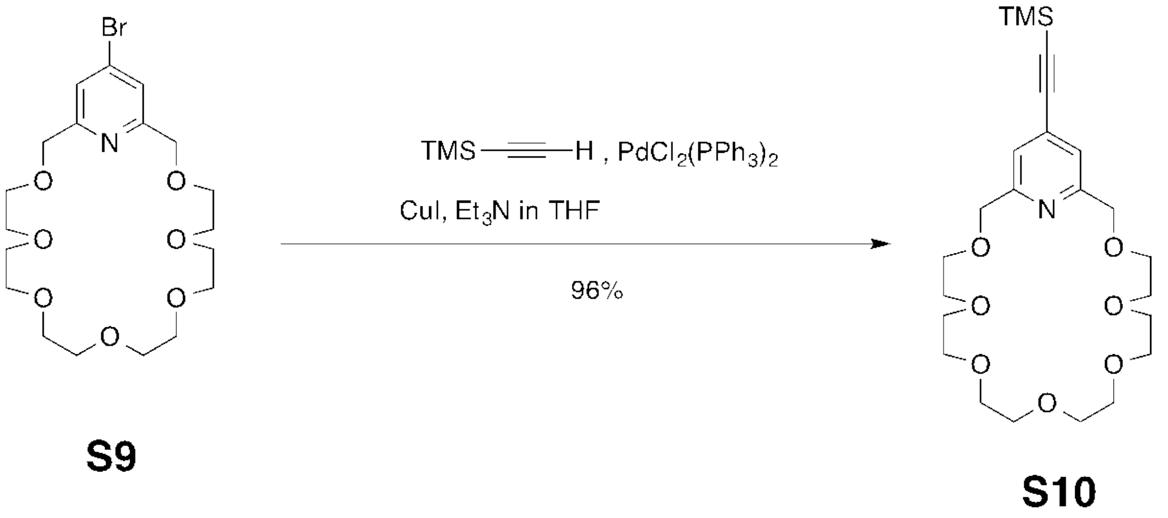


**S8**

**S9**

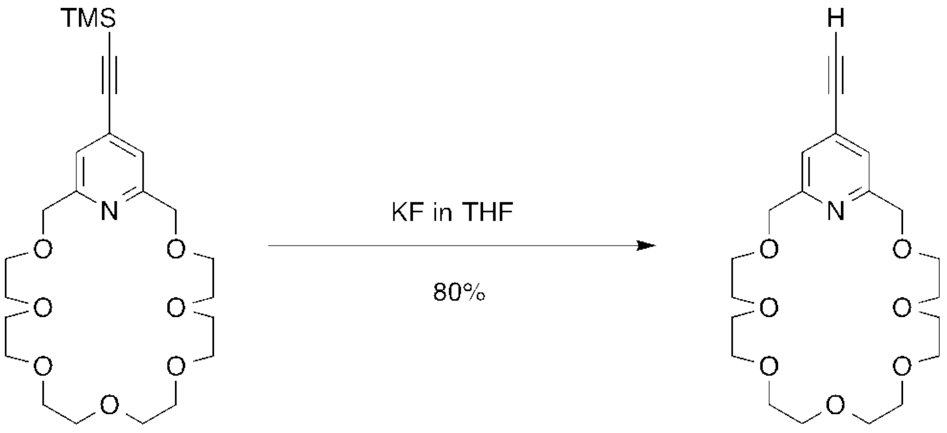
NaH (29.3 mg, 1.22 mmol, 8.3 equiv) was suspended in dry THF (5.00 mL). A THF (5.00 mL) solution containing **S8**[3] (50.6 mg, 148 μmol) and hexaethyleneglycol (37.0 μL, 147 μmol, 0.99 equiv) was added to the suspension of NaH over 3 hrs at 85 ºC. After the reaction was quenched by addition of water (5.00 mL), the reaction mixture was extracted with CHCl$_3$ (10.0 mL × 5). The combined organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and evaporated to obtain pale yellow oil (90.8 mg). The crude product was purified by alumina gel column chromatography (hexane : AcOEt = 2 :1 – 1 : 1) to afford the title compound **S9** as a pale yellow oil (31.0 mg, 66.8 μmol, 45%). $^{1}$H NMR (400 MHz, CDCl$_3$, TMS) : $\delta$= 7.57 (s, 2H), 4.69 (s, 4H), 3.76 (m, 4H), 3.70 (m, 4H), 3.61 (s, 8H), 3.58 (s, 8H). $^{13}$C NMR (100 MHz, CDCl$_3$, TMS) : $\delta$=159.7, 134.0, 123.5, 73.5, 71.0, 70.8, 70.8, 70.6, 70.6, 70.2. ESI-TOF-MS (positive) : *m*/*z* = 488 [M+Na]$^+$, 488 calcd [M+Na]$^+$.

Synthesis of 4-(trimethylsilylethynyl)-2,6-pyrido-24-crown-8 **S10**



4-Bromo-2,6-pyrido-24-crown-8 **S9** (429 mg, 924 μmol), $PdCl_2(PPh_3)_2$ (63.7 mg, 90.8 μmol, 0.10 equiv), and CuI (8.70 mg, 45.7 μmol, 0.0500 equiv) were dissolved in THF (4.00 mL) containing TEA (730 μL). The resulting mixture was degassed by freezing-thaw method by 5 times. After trimethylsilylacetylene (385 μL, 2.72 mmol, 2.90 equiv) was added, the mixture was heated for 2 days at 60 ºC. The volatile compounds were evaporated off to obtain black oil (732 mg). The crude product was purified by silica gel column chromatography (4.5 cm $\phi \times$ 20 cm, $CHCl_3$ : MeOH = 30 : 1) to give the title compound **S10** as a pale yellow oil (429 mg, 96%). $^1H$ NMR (400 MHz, $CDCl_3$) : $\delta$ = 7.39 (s, 2H), 4.68 (s, 4H), 3.75 (m, 4H), 3.69 (m, 4H), 3.61 (s, 8H), 3.58 (s, 8H), 0.25 (s, 9H). $^{13}C$ NMR (100 MHz, $CDCl_3$) : $\delta$ = 158.5, 132.5, 123.0, 102.9, 99.7, 77.0, 71.1, 71.1, 71.0, 70.9, 70.8, 70.4. IR (ATR/ZnSe) : 2863, 1598, 1551, 1452, 1351, 1295, 1250, 1104, 1039, 974, 942, 842, 760, 700, 649 $cm^{-1}$. ESI-TOF-MS (positive) : $m/z$ = 504 $[M+Na]^+$, 504 calcd $[M+Na]^+$.

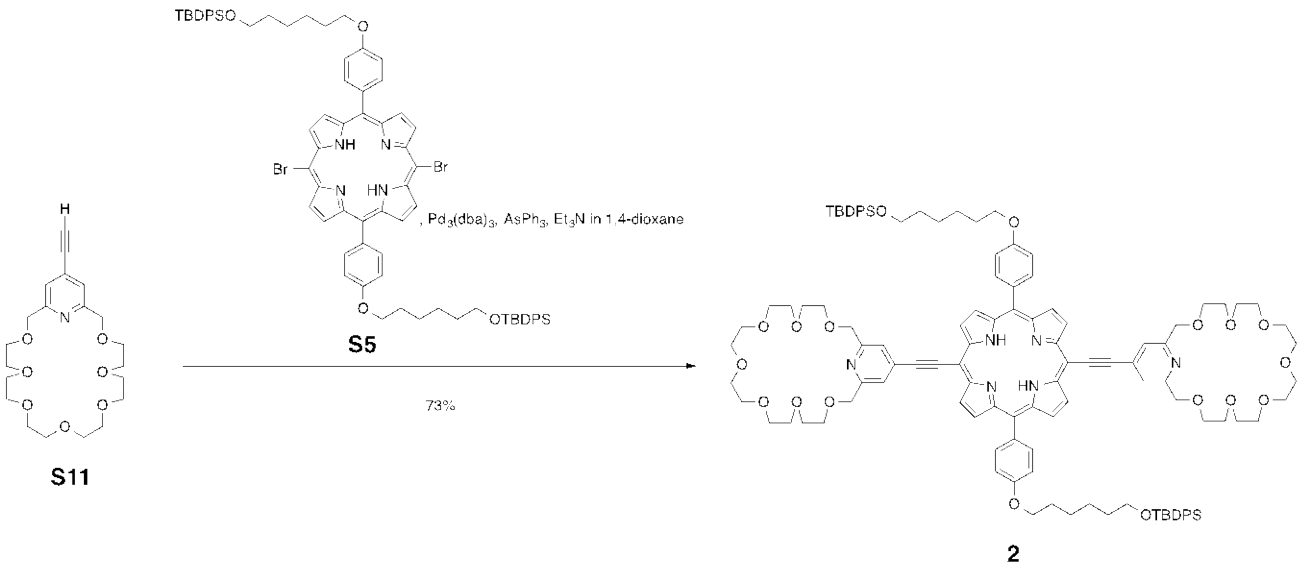
### Synthesis of 4-ethynyl-2,6-pyrido-24-crown-8 **S11**



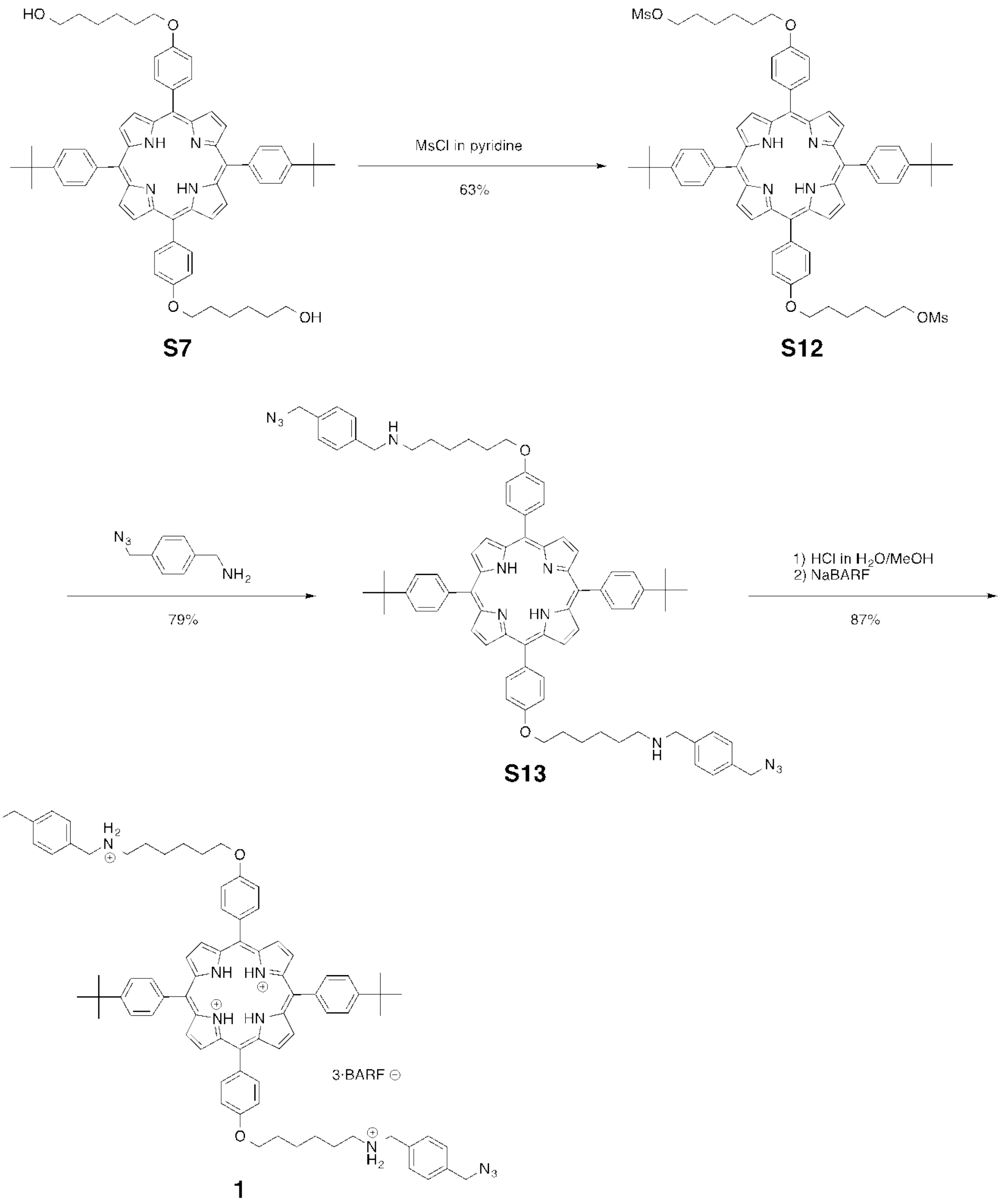
**S10** **S11**

4-(Trimethylsilylethynyl)-2,6-pyrido-24-crown-8 **S10** (27.7 mg, 57.5 µmol) and KF (10.2 mg, 176 µmol, 3.06 eq) were dissolved in dry THF (5.00 mL) and the solution was refluxed for 2 days. After the volatile compounds were evaporated off, the residue was dissolved in $CHCl_3$ (10.0 mL). The solution was washed with sat. aqueous $Na_2CO_3$ (10.0 mL), water (10.0 mL), and brine (10.0 mL), dried over anhydrous $Na_2SO_4$, and evaporated to obtain pale yellow oil (25.1 mg). The crude product was purified by silica gel column chromatography (1.8 cm $\phi \times$ 22 cm, $CHCl_3$ : MeOH = 20 : 1) to give the title compound **S11** as a pale orange oil (18.9 mg, 46.2 µmol, 80%). $^1$H NMR (400 MHz, $CDCl_3$) : $\delta$= 7.44 (s, 2H), 4.70 (s, 4H), 3.75 (m, 4H), 3.69 (m, 4H), 3.60 (s, 8H), 3.58 (s, 8H). ESI-TOF-MS (positive) : $m/z$ = 432 $[M+H]^+$, 432 calcd $[M+H]^+$. Anal. Calcd. for $C_{21}H_{31}NO_7$ (**S11**) : C, 61.60; H, 7.63; N, 3.42. Found. C, 61.49; H, 7.65; N, 3.09. (0.33% Error).

Synthesis of a porphyrin **2**.

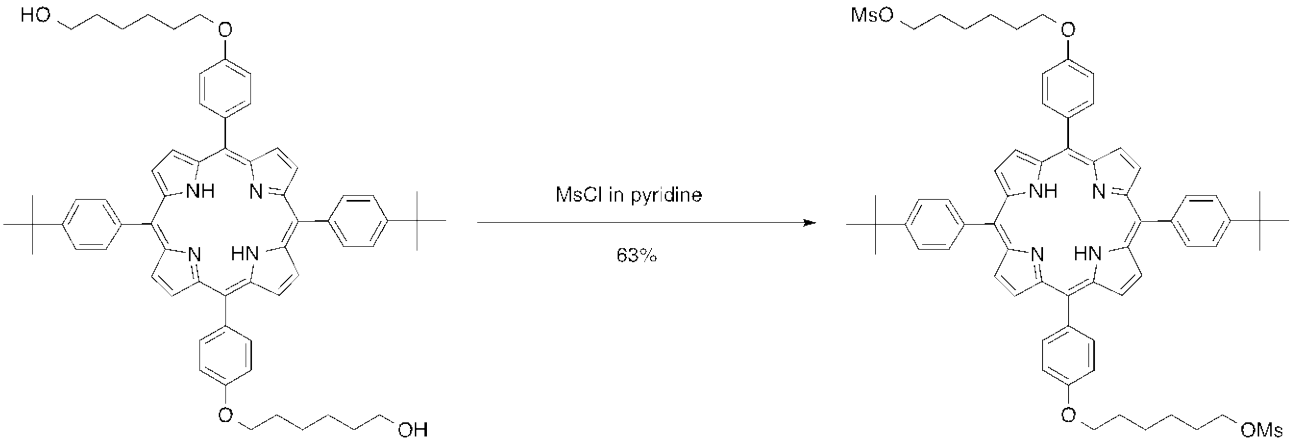


A dark violet solution containing $Pd_2(dba)_3$ (9.00 mg, 9.83 μmol, 0.23 equiv), $AsPh_3$ (30.6 mg, 100 μmol, 2.39 equiv), and $Et_3N$ (0.300 mL) in dry THF (1.30 mL) was stirred at room temperature. After stirring for 30 min, the color of the solution changed into blackish yellow. Then, 5,15-(4-((*t*-butyldiphenylsiloxyhexyl)oxy)phenyl)-10,20-dibromoporphyrin **S5** (55.7 mg, 41.9 μmol) and 4-ethynyl-2,6-pyrido-24-crown-8 **S11** (33.1 mg, 80.8 μmol, 1.93 equiv) were added to the solution. The mixture was degassed by freezing-thaw method by 4 times. After heating at 60 °C for 22 hrs, $CH_2Cl_2$ (30.0 mL) was added. The resulting mixture was washed with saturated aqueous $NaHCO_3$ (30.0 mL × 3), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to obtain green solid (132 mg). The crude product was purified by silica gel column chromatography (2.6 cm $\phi$ × 17 cm, $CHCl_3$ : MeOH = 25 : 1) to obtain the title compound **2** as a green solid (58.9 mg, 29.6 μmol, 73%). $^1$H NMR (400 MHz, $CDCl_3$) : $\delta$ = 9.68 (d, $J$ = 4.8 Hz, 4H), 8.91 (d, $J$ = 4.8 Hz, 4H), 8.10 (d, $J$ = 8.7 Hz, 4H), 7.95 (s, 4H), 7.72 (m, 8H), 7.43 (m, 12H), 7.32 (d, $J$ = 8.7 Hz, 4H), 4.88 (s, 8H), 4.27 (t, $J$ = 6.7 Hz, 4H), 3.90 (m, 8H), 3.81 (m, 8H), 3.76 (t, $J$ = 6.8 Hz, 4H), 3.68 (m, 8H), 3.67 (m, 8H), 3.60 (m, 8H), 3.59 (m, 8H), 2.00 (quin, $J$ = 6.7 Hz, 4H), 1.71 (quin, $J$ = 6.8 Hz, 4H), 1.63 (m, 8H), 1.09 (s, 18H), -2.00 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) : $\delta$ = 159.4, 158.8, 135.7, 134.3, 133.3, 133.0, 129.6, 127.7, 122.5, 122.3, 113.2, 99.9, 96.2, 95.2, 74.1, 71.1, 71.0, 70.9, 70.8, 70.7, 70.4, 68.4, 64.0, 32.7, 29.8, 29.6, 27.0, 26.1, 25.8, 19.4. ESI-TOF-MS (positive) : $m/z$ = 2007 $[M+Na]^+$, 2007 calcd $[M+Na]^+$. Anal. Calcd. for $C_{118}H_{142}N_6O_{19}$ $Si_2$ (**2**+$H_2O$) : C, 71.85; H, 7.26; N, 4.26. Found. C, 71.74; H, 7.13; N, 4.40. (0.14% Error).



***Scheme S3*** Synthesis of a porphyrin monomer **1**.

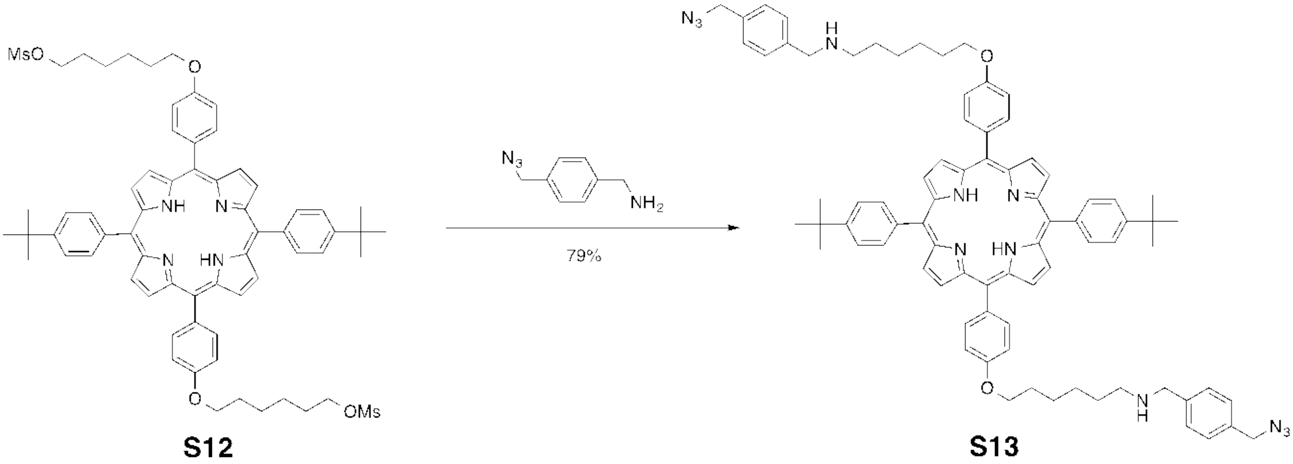
### Synthesis of 5,15-Bis(4-(6-methanesulfonylhexyl-1-oxy)phenyl)-10,20-bis(4-*tert*-butylphenyl)porphyrin **S12**



**S7** **S12**

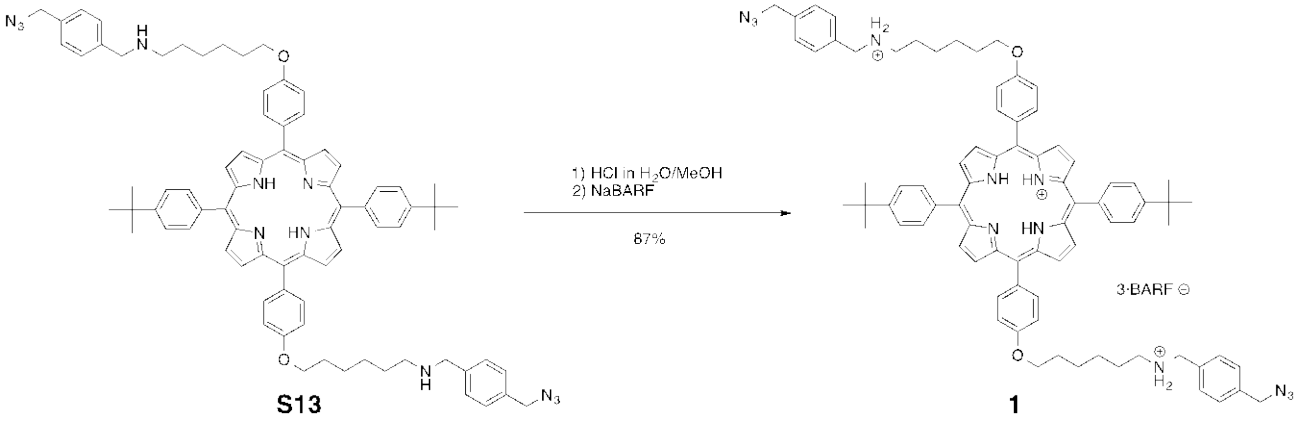
To the solution of 5,15-bis(4-(6-hydoxyhexyl-1-oxy)phenyl)-10,20-bis(4-*tert*-butylphenyl) porphyrin **S7** (153 mg, 160 μmol) in dry pyridine (1.50 mL) was added methansulfonyl chloride (MsCl) (35.0 μL, 452 μmol, 2.83 equiv) on an ice bath. The mixture was stirred on an ice bath for 3 hrs, and then at room temperature for 21 hrs. An additional amount of MsCl (120 μL, 1.52 mmol) and pyridine (1.50 mL) was added portionwise within 11 hrs. After $CH_2Cl_2$ (100 mL) was added, the mixture was washed with saturated aqueous $NaHCO_3$ (100 mL × 2), 5% aqueous $KHSO_4$ (100 mL × 2), water (100 mL), and saturated aqueous $Na_2CO_3$ (100 mL). The organic layer was dried over anhydrous $Na_2SO_4$, filtered, and evaporated to obtain crude solid (155.0 mg), which was purified by reprecipitation from $CH_2Cl_2$ (4.00 mL) and $Et_2O$ (40.0 mL) to give the title compound **S12** as a purple solid (86.7 mg, 77.7 μmol, 49%). On the other hand, the purple solid obtained from the supernatant was preabsorbed onto silica gel and then purified by silica gel column chromatography (3.2 cm $\phi$ × 15 cm, $CH_2Cl_2$) to give pure **S12** (24.6 mg, 22.1 μmol, 14%). Totally, 111.3 mg (99.8 μmol, 63%) of the title compound **S12** was obtained. $^1$H NMR (400 MHz, $CDCl_3$) : $\delta$ = 8.85 (brs, 8H), 8.12 (dd, $J$ = 8.1, 8.7 Hz, 8H), 7.75 (d, $J$ = 8.7 Hz, 4H), 7.26 (d, $J$ = 8.1 Hz, 4H), 4.30 (t, $J$ = 7.2 Hz, 4H), 4.24 (t, $J$ = 6.7 Hz, 4H), 1.99 (quin, $J$ = 7.2 Hz, 4H), 1.88 (quin, $J$ = 7.2 Hz, 4H), 1.68 (m, 8H), 1.60 (s, 18H), -2.76 (s, 2H). $^{13}$C NMR (149 MHz, $CDCl_3$) : $\delta$=158.9, 150.6, 139.3, 135.7, 134.7, 134.5, 131.1, 128.6, 128.3, 123.7, 120.2, 119.8, 112.8, 70.1, 68.0, 37.5, 35.0, 31.8, 29.4, 29.3, 25.9, 25.5. ESI-TOF-MS (positive) : $m/z$ = 1115 $[M+H]^+$, 1115 calcd $[M+H]^+$.

Synthesis of a porphyrin **S13**



5,15-Bis(4-(6-methansulfonylhexyl-1-oxy)phenyl)-10,20-bis(4-*tert*-butylphenyl)porphyrin **S12** (65.0 mg, 58.3 μmol) was dissolved in $\alpha$-Amino- $\alpha$'-azide-*p*-xylene (899 mg, 5.34 μmol, 91.6 equiv) at room temperature. The mixture was heated at 60 ºC for 11 hrs. After the mixture was dissolved in $CH_2Cl_2$ (30.0 mL), the solution was washed with 10% aqueous $KHSO_4$ (100 mL) and saturated aqueous $Na_2CO_3$ (100 mL), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to obtain purple solid (132 mg). The crude product was dissolved in $CH_2Cl_2$ and filtered through a silica pad. After the filtrate was evaporated, the residue was purified with GPC (JAIGEL, 1H-2H, $CHCl_3$ + 0.5% $Et_3N$) to obtain the title compound **S13** as a purple solid (57.5 mg, 46.1 μmol, 79%). $^1H$ NMR (400 MHz, $CDCl_3$) : $\delta$ = 8.85 (brs, 8H), 8.11 (dd, *J* = 7.6, 8.7 Hz, 8H), 7.74 (d, *J* = 7.6 Hz, 4H), 7.39 (d, *J* = 7.7 Hz, 12H), 7.29 (d, *J* = 8.7 Hz, 4H), 7.24 (d, *J* = 7.7 Hz, 4H), 4.31 (s, 4H), 4.23 (t, *J* = 6.9 Hz, 4H), 3.85 (s, 4H), 2.72 (t, *J* = 7.3 Hz, 4H), 1.97 (quin, *J* = 6.9 Hz, 4H), 1.67 (m, 8H), 1.63 (s, 18H), 1.54 (m, 4H), -2.76 (s, 2H). ESI-TOF-MS (positive) : *m*/*z* = 1247 $[M+H]^+$, 1247 calcd $[M+H]^+$.

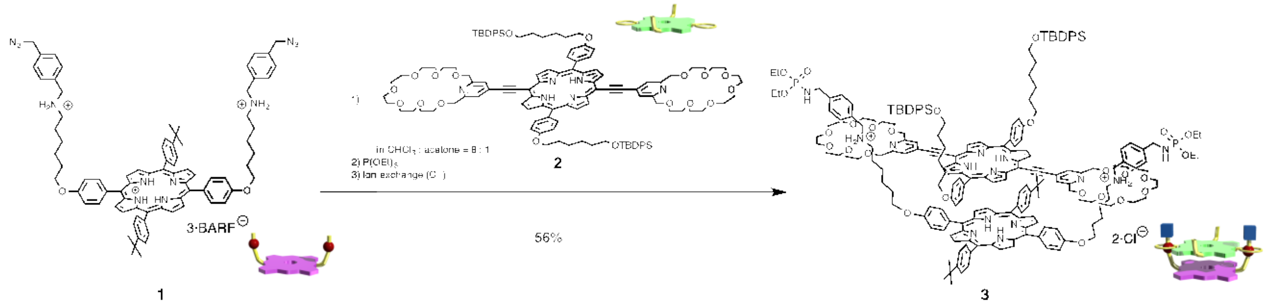
## Synthesis of **1**



A porphyrin **S13** (702 mg, 563 µmol) was dissolved in $CH_2Cl_2$ : MeOH = 1 : 1 (80 mL). After 1 M aqueous HCl (40 mL) was added to the solution, the volatile compounds were evaporated off. This procedure was repeated by three times to obtain the HCl salt of **S13** (770 mg).

To a solution of a HCl salt of **S13** (651 mg, 467 µmol) in MeOH (95.0 mL) was added a solution of NaBARF·$2H_2O$[4] (2.00 g, 2.17 mmol, 4.65 equiv) in MeOH (95.0 mL). After $H_2O$ (190 mL) was added dropwise, the green precipitate was collected by centrifugation (730 mg). The crude solid was purified by reprecipitation from MeOH (190 mL) and water (190 mL) to give the title compound **1** (1.97 g, 419 µmol, 87%) as a green solid. $^1$H NMR (400 MHz, $CDCl_3$) : $\delta$ = 9.04 (d, $J$ = 4.8 Hz, 4H), 9.00 (d, $J$ = 4.8 Hz, 4H), 8.20 (dd, $J$ = 6.4, 8.3 Hz, 8H), 7.87 (d, $J$ = 8.3 Hz, 4H), 7.66 (s, 24H), 7.46 (s, 12H), 7.31 (d, $J$ = 8.2 Hz, 4H), 7.26 (d, $J$ = 6.4 Hz, 20H including $CHCl_3$), 7.25 (d, $J$ = 8.0 Hz, 4H), 7.07 (d, $J$ = 8.0 Hz, 4H), 6.35 (br, 3H), 4.19 (s, 4H), 4.07 (t, $J$ = 6.0 Hz, 4H), 1.68 (br, 4H), 1.61 (s, 18H), 1.60 – 1.42 (m, 3H), 0.78 (br, 4H), 0.52 (br, 4H).

Synthesis of **3**.



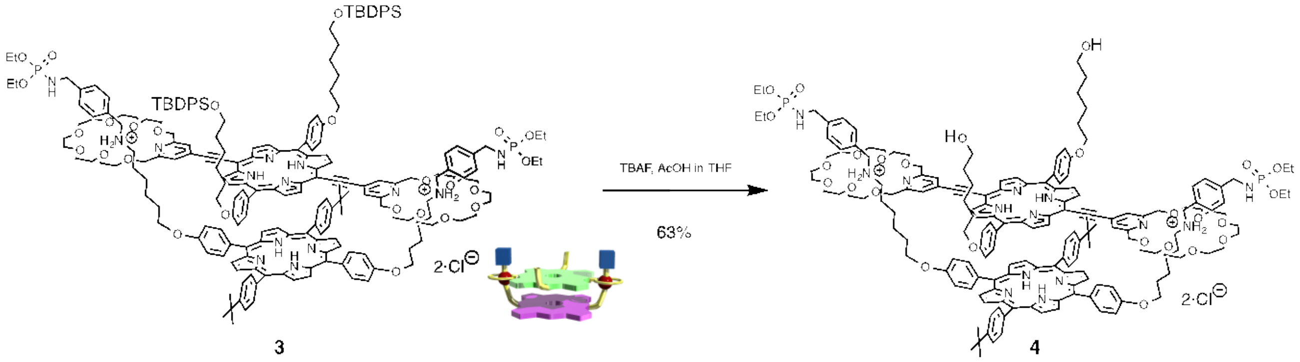
To a solution of **1** (378 mg, 99.8□□ mol) in acetone (7.0 mL) was added a solution of **2** (197 mg, 99.4□□ mol) in CHCl$_3$ (85 mL) and the resulting solution was stirred at ambient temperature for 11 hrs. After P(OEt)$_3$ (8.0 mL, 47 mmol) was added, the mixture was stirred for further 72 hrs, followed by addition of $H_2O$ (1.0 mL). The resulting mixture was stirred for 11 hrs, and then the volatile compounds were evaporated off. The residue was dissolved in CHCl$_3$ (20 mL). The solution was poured into hexane (80 mL) to give blackish-green stick precipitate, which was collected by centrifugation and dissolved in a 1:1 mixture of CHCl$_3$ and MeOH (v/v, 50 mL). After ion-exchange resin (IRA 400J CL (Cl$^-$ form), 50 mL) was added, the mixture was kept standing at ambient temperature for 30 min, and then the resin was removed by filtration. This ion exchange procedure was repeated by twice.

After the solvents were evaporated off, the crude product was purified by silica gel column chromatography twice (1st; 4 cm$\phi$ × 31 cm, CH$_2$Cl$_2$:MeOH = 10:1 – 8:1 – CHCl$_3$:MeOH:H$_2$O:brine = 20:80:5:1, 2nd; 3 cm$\phi$ × 29 cm, CH$_2$Cl$_2$:MeOH = 10:1 – 8:1 – CHCl$_3$:MeOH:H$_2$O:brine = 20:80:5:1 ) to give blackish-green solid (211 mg), which was further purified by reprecipitation from CHCl$_3$ / Et$_2$O to afford the pure rotaxane dimer **3** as a blackish-green solid (196 mg, 56 µmol, 56%)

$^1$H NMR (600 MHz, CDCl$_3$/TMS) : $\delta$= 8.52 (d, $J$ = 4.2 Hz, 4H), 8.30 (br, 4H), 8.20 (d, $J$ = 4.2 Hz, 4H), 7.90 (br, 4H), 7.81 (br, 4H), 7.74 (m, 8H), 7.67 (d, $J$ = 7.2 Hz, 4H), 7.53 (d, $J$ = 7.2 Hz, 4H), 7.50 (m, 4H), 7.43 (m, 28H), 7.09 (d, $J$ = 6.0 Hz, 2H) 6.97 (d, $J$ = 6.2 Hz, 2H), 6.77 (br, 4H), 6.61 (br, 4H), 4.72 (d, $J$ = 12.0 Hz, 4H), 4.64 (br, 4H), 4.44 (d, $J$ = 12.0 Hz, 4H), 4.20 (t, $J$ = 6.7 Hz, 4H), 4.15 (m, 4H), 4.09 (t, $J$ = 7.1 Hz, 4H), 4.01 (m, 12H), 3.85 (m, 8H), 3.80 (t, $J$ = 6.6 Hz, 4H), 3.76 (m, 4H), 3.70-3.48 (m, 40H), 3.24 (br, 4H), 2.03 (quin, $J$ = 7.2 Hz, 4H), 1.89 (quin, $J$ = 6.6 Hz, 4H), 1.76 (quin, $J$ = 7.1 Hz, 4H), 1.67 (m, 4H), 1.72-1.51 (m, 52H including $H_2O$), 1.22 (t, $J$ = 6.6 Hz, 12H), 1.12 (s, 18H), –3.16 (s, 2H), –3.74 (s, 2H). ESI-TOF-MS (positive): *m*/*z* 1727.9: Calcd for $C_{206}H_{250}N_{14}O_{26}P_2Si_2$ ([**3**-2Cl$^-$]$^{2+}$), Found 1727.8.

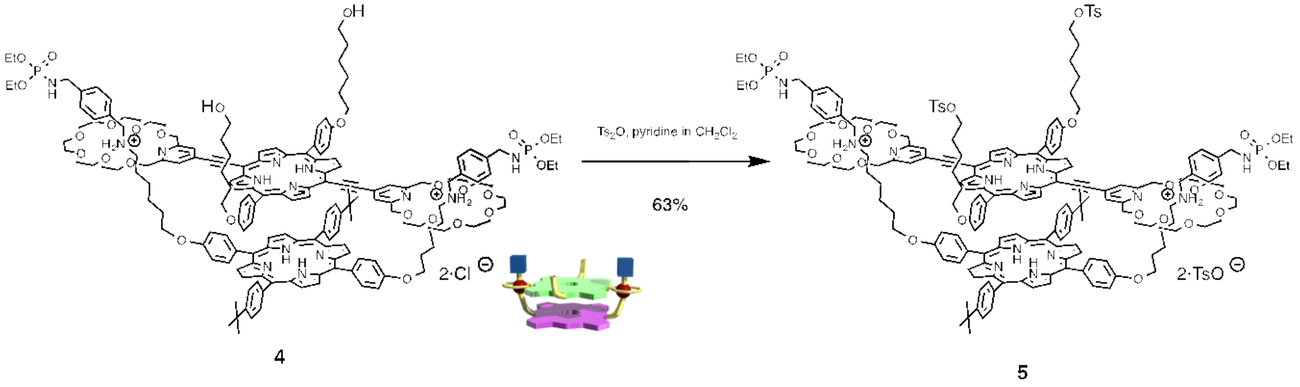
Elemental Analysis: Calcd. for $C_{231}H_{315}Cl_5N_{14}O_{34}P_2Si_2$(**3**+$CHCl_3$+6$Et_2O$+2$H_2O$); C: 67.22, H: 7.69, N: 4.75, Found; C: 67.81, H: 7.63, N: 4.33 (0.42% Error).

Synthesis of **4**.



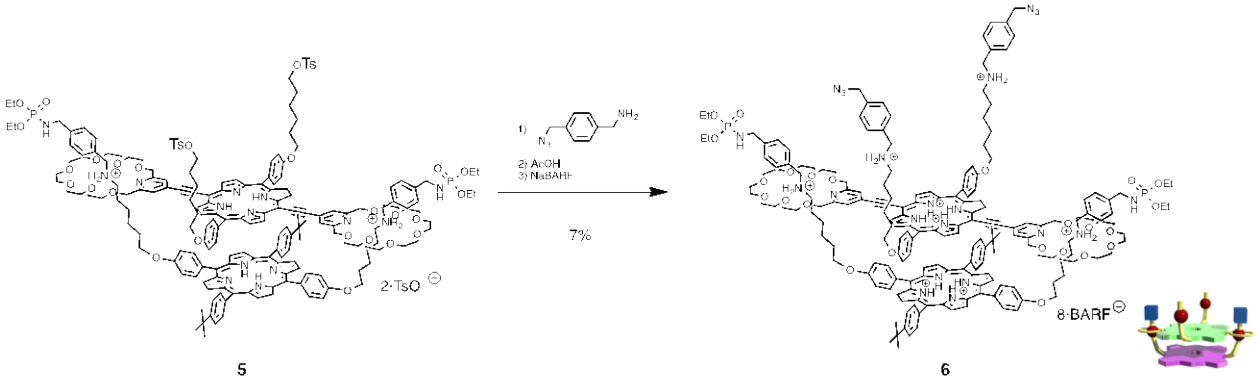
**3** (196 mg, 56 μmol) was dissolved in dry THF (4.0 mL). To the solution was added 1M TBAF in THF (2.0 mL, 2.0 mmol) and AcOH (500 μL, 8.7 mmol) successively, and the resulting mixture was stirred at ambient temperature for 18 hrs. After additional amounts of 1 M TBAF in THF (1.0 mL, 1.0 mmol) and AcOH (250 μL, 4.4 mmol) were added, the mixture was stirred for further 50 hrs. $CH_2Cl_2$ (100 mL) was added to the mixture. The resulting solution was washed with brine (50 mL × 3), dried over anhydrous $Na_2SO_4$, filtered, and evaporated to obtain green solid. The crude product was purified by silica gel column chromatography (3 cm$\phi$ × 24 cm, $CH_2Cl_2$:MeOH = 9:1 – 4:1 – $CHCl_3$:MeOH:$H_2O$:brine = 20:80:5:1) to obtain the title compound **4** as a green solid (143 mg, 47 mmol, 84%). $^1$H NMR (600 MHz, $CDCl_3$ / TMS) : $\delta$ = 8.48 (br, 4H), 8.30 (br, 4H), 8.20 (br, 4H), 7.87 (br, 4H), 7.76-7.65 (m, 12H), 7.54 (d, $J$ = 7.2 Hz, 4H), 7.53-7.48 (m, 6H), 7.45-7.36 (m, 16H), 7.07 (d, $J$ = 7.2 Hz, 2H) 6.99 (d, $J$ = 5.4 Hz, 4H), 6.74 (br, 4H), 6.57 (br, 4H), 4.64 (d, $J$ = 12.0 Hz, 4H), 4.60 (br, 4H), 4.36 (d, $J$ = 12.0 Hz, 4H), 4.20 (t, $J$ = 6.0 Hz, 4H), 4.17-4.12 (m, 4H), 4.08-3.98 (m, 12H), 3.84-3.69 (m, 16H), 3.69-3.45 (m, 48H), 3.38-3.46 (m, 8H), 3.20 (br, 4H), 2.03 (quin, $J$ = 6.9 Hz, 4H), 1.86 (quin, $J$ = 6.3 Hz, 4H), 1.83-1.40 (m, 95H including $H_2O$), 1.21 (t, $J$ = 6.6 Hz, 12H), -3.18 (s, 2H), -3.74 (s, 2H). ESI-TOF-MS (positive): $m/z$ 1489.3: Calcd for $C_{174}H_{214}N_{14}O_{26}P_2$ ([**4**–2Cl$^-$]$^{2+}$), Found 1489.2.

Synthesis of **5**.



**4** (143 mg, 47 μmol) was dissolved in dry $CH_2Cl_2$ (4.0 mL). To the solution was added pyridine (75 μL, 932 μmol) and $Ts_2O$ (155 mg, 475 μmol), successively. The resulting solution was stirred at ambient temperature for 24 hrs, followed by addition of AcOEt (40 mL) to obtain green precipitate (163 mg). The precipitate was collected by centrifugation. After the precipitate was dissolved in $CH_2Cl_2$ (4 mL), toluene (40 mL) was added to give green precipitate (148 mg), which was dissolved in $CHCl_3$ (100 mL). The solution was washed with $H_2O$ (100 mL × 3), dried over $Na_2SO_4$, filtered, and evaporated to afford green residue (130 mg). Finally, the residue was purified by reprecipitation from $CHCl_3$ (5.0 mL) / $Et_2O$ (30 mL) to give the title compound **5** as a green solid (128 mg, 38 μmol, 75%). $^1$H NMR (600 MHz, $CDCl_3$ / TMS) : $\delta$ = 8.55 (br, 4H), 8.29 (br, 4H), 8.19 (d, $J$ = 4.2 Hz, 4H), 7.96-7.83 (m, 16H), 7.65 (d, $J$ = 7.8 Hz, 4H), 7.53-7.38 (m, 24H), 7.12-7.05 (m, 2H), 7.07 (d, $J$ = 8.4 Hz, 4H), 6.93 (br, 2H), 6.81 (br, 4H), 6.64 (br, 4H), 4.73 (d, $J$ = 12.3 Hz, 4H), 4.63 (m, 4H), 4.43 (d, $J$ = 12.3 Hz, 4H), 4.20-4.13 (m, 12H), 4.08 (t, $J$ = 6.0 Hz, 4H), 4.01-3.93 (m, 12H), 3.86 (dd, $J$ = 9.6, 5.4 Hz, 4H), 3.79-3.49 (m, 52H), 3.23 (br, 4H), 2.46 (s, 6H), 2.24 (s, 6H), 1.99 (quin, $J$ = 6.9 Hz, 4H), 1.88 (quin, $J$ = 6.3 Hz, 4H), 1.83 (quin, $J$ = 7.5 Hz, 4H), 1.73-1.50 (m, 79H including $H_2O$), 1.18 (t, $J$ = 7.2 Hz, 12H), -3.18 (s, 2H), -3.75 (s, 2H). ESI-TOF-MS (positive): *m*/*z* 1096.2: Calcd for $C_{188}H_{227}N_{14}O_{30}P_2S_2$ ([**5**–2TsO$^-$+H$^+$]$^{3+}$), Found 1096.1.

Synthesis of **6**.



**5** **6**

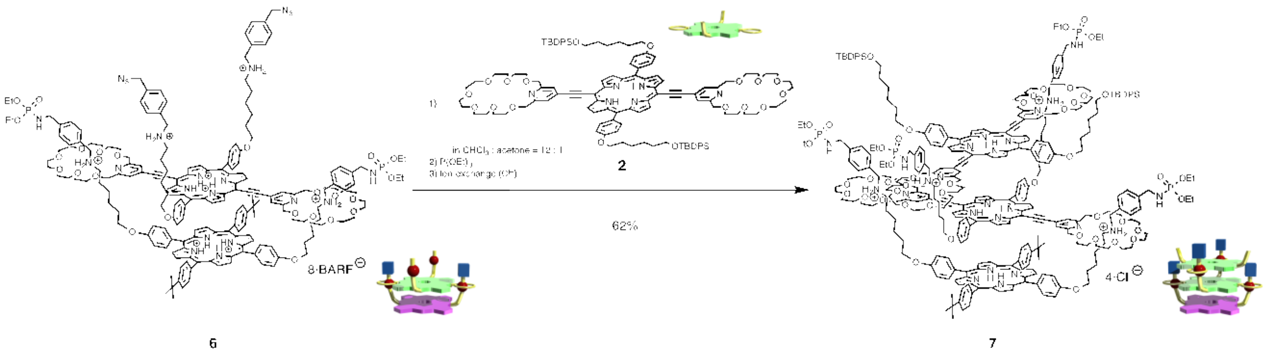
**5** (119 mg, 35 μmol) was dissolved in *α*-amino- *α*'-azide-*p*-xylene (1.05 g, 6.45 mmol) at room temperature. The resulting homogeneous solution was stirred at 40 °C for 24 hrs under nitrogen atmosphere. After $CH_2Cl_2$ (150 mL) was added, the solution was washed with $H_2O$ containing 2% AcOH (100 mL × 4), brine containing 2% AcOH, dried over $Na_2SO_4$, filtered, and evaporated to afford yellowish green residue (167 mg). The crude product was purified by silica gel column chromatography (3 cm*ϕ* × 22 cm, $CHCl_3$ : MeOH = 6:1 + 0.5% AcOH – 3:1 + 0.5% AcOH – 1:1 + 0.5% AcOH – $CHCl_3$:MeOH:$H_2O$:brine = 20:80:5:1+ 0.5% AcOH) to obtain a fraction containing the desired compound. The solid obtained from the fraction (24 mg) was subjected to PTLC ($CHCl_3$ : MeOH = 6:1 + 0.5% AcOH) to give green solid. After the solid was dissolved in $CHCl_3$ (50 mL), the solution was washed with $H_2O$ containing 2% AcOH (100 mL × 3), brine containing 2% AcOH, dried over $Na_2SO_4$, filtered, and evaporated to afford green solid (21 mg, 5.6 μmol, 16%).

$^1$H NMR (600 MHz, $CDCl_3$ / TMS) : *δ* = 8.48 (br, 4H), 8.31 (br, 4H), 8.22 (d, *J* = 3.6 Hz, 4H), 7.93-7.67 (m, 8H), 7.62 (d, *J* = 6.6 Hz, 4H), 7.57 (d, *J* = 7.8 Hz, 4H), 7.51 (d, *J* = 7.8 Hz, 4H), 7.41 (d, *J* = 8.4 Hz, 4H), 7.38 (d, *J* = 7.2 Hz, 4H), 7.31 (d, *J* = 7.8 Hz, 4H), 7.30-7.16 (m, 21H including $CHCl_3$), 7.15-6.96 (br, 8H), 6.72 (br, 4H), 6.55 (br, 8H), 4.66 (d, *J* = 11.4 Hz, 4H), 4.62 (br, 4H), 4.38 (d, *J* = 11.4 Hz, 4H), 4.22 (t, *J* = 6.3 Hz, 4H), 4.14-3.94 (m, 16H), 3.90-3.34 (m, 48H), 3.20 (br, 4H), 3.79-3.49 (m, 52H), 2.84 (t, *J* = 7.5 Hz, 4H), 2.83 (br, 20H), 2.10-1.96 (m, 8H), 1.87 (quin, *J* = 6.3 Hz, 4H), 1.80 (quin, *J* = 6.6 Hz, 4H), 174-1.50 (m, 36H including $H_2O$), 1.34-1.24 (m, 8H), 1.20 (t, *J* = 6.9 Hz, 12H), -3.16 (s, 2H), -3.72 (s, 2H). ESI-TOF-MS (positive): *m*/*z* 817.4: Calcd for $C_{190}H_{232}N_{22}O_{24}P_2$ ([**6**–4BARF$^-$]$^{4+}$), Found 817.4.

The obtained salt of the rotaxane dimer (21 mg, 5.6 μmol) and NaBARF·$2H_2O$ (46 mg, 50 μmol) were dissolved in MeOH containing 0.5 % AcOH (5.0 mL). After $H_2O$ (5.0 mL) was added, the resulting green precipitate was collected by centrifugation. The residue was redissolved in MeOH containing 0.5 % AcOH (5.0 mL). To the solution was added $H_2O$ (5.0 mL) to give the title compound as a green precipitate (24 mg, 2.4 μmol, 42% from **6**).

$^1$H NMR (600 MHz, $CDCl_3$ / TMS) : $\delta$ = 8.83 (br, 8H), 8.21 (br, 4H), 8.07 (br, 4H), 7.88 (br, 4H), 7.80 (br, 8H), 7.73-7.64 (m, 8H), 7.63-7.34 (m, 110H), 7.30 (dd, *J* = 8.4, 2.4 Hz, 4H), 7.06-6.88 (m, 8H), 4.68-4.62 (m, 4H), 4.90-4.69 (m, 212 H including $H_2O$), 4.56 (d, *J* = 11.4 Hz, 4H), 4.46-4.37 (m, 8H), 4.20 (t, *J* = 6.6 Hz, 4H), 3.94 (d, *J* = 11.4 Hz, 4H), 3.92 (br, 4H), 3.83-3.50 (m, 80H), 3.44 (br, 4H), 3.29-3.12 (m, 204H including $CH_3OH$), 2.15 (quin, *J* = 7.8 Hz, 4H), 2.04-1.50 (m, 70H including $CH_3COOH$), 1.34-1.20 (m, 46H), 0.98 (t, *J* = 7.2 Hz, 12H). ESI-TOF-MS (positive): *m*/*z* 1089.6: Calcd for $C_{190}H_{231}N_{22}O_{24}P_2$ ([**6**–8BARF$^-$–5H$^+$]$^{3+}$), Found 1089.5.

Synthesis of **7**.



To a solution of **6** (24 mg, 2.4□µmol) in acetone (0.25 mL) was added a solution of **2** (7.1 mg, 3.6□□ mol) in $CHCl_3$ (85 mL) and the resulting solution was stirred at ambient temperature for 6.5 hrs. After $P(OEt)_3$ (0.20 mL, 1.2 mmol) was added, the mixture was stirred for further 67 hrs, followed by addition of $H_2O$ (0.5 mL). The resulting mixture was stirred for 22 hrs, and then added dropwise to hexane to give green precipitate (32 mg). After the precipitate was dissolved in a 1:1 mixture of $CHCl_3$ and MeOH (v/v, 50 mL), ion-exchange resin (IRA 400J CL ($Cl^-$ form), 50 mL) was added to the mixture. The resulting mixture was kept standing at ambient temperature for 30 min, and then the resin was removed by filtration. This ion exchange procedure was repeated by three times.

After the solvents were evaporated off, the crude product was PTLC twice (1st; $CHCl_3$:MeOH = 6:1 – 4:1 – 1:1 , 2nd; 3 cm$\phi$ × 29 cm, $CHCl_3$:MeOH = 4:1) to give green solid (10.6 mg), which was further purified by reprecipitation from $CHCl_3$ / $Et_2O$ to afford the title compound **7** as a blackish-green solid (8.2 mg, 1.5 µmol, 62%)

$^1$H NMR (600 MHz, $CDCl_3$/TMS) : $\delta$ = 8.79 (br, 4H), 8.18 (br, 4H), 8.14 (br, 4H), 7.83 (br, 4H), 7.76 (br, 2H), 7.73-7.57 (m, 24H), 7.54-7.46 (m, 12H), 7.42-7.30 (m, 20H), 7.28-7.18 (m, 45H including $CHCl_3$), 7.06 (d, $J$ = 7.2 Hz, 2H), 7.02 (s, 2H), 6.96 (d, $J$ = 7.2 Hz, 2H) 6.88 (d, $J$ = 7.2 Hz, 2H), 6.74 (br, 4H), 6.70 (br, 2H), 6.36 (br, 4H), 6.14 (br, 4H), 4.86 (d, $J$ = 12.0 Hz, 4H), 4.75 (br, 4H), 4.70 (d, $J$ = 11.4 Hz, 4H), 4.66 (br, 4H), 4.52-4.46 (m, 8H), 4.27 (t, $J$ = 6.3 Hz, 2H), 4.22 (m, 4H), 4.16 (m, 4H), 4.12-3.93 (m, 24H), 3.92-3.36 (m, 110H), 3.20 (m, 4H), 1.99 (quin, $J$ = 5.7 Hz, 4H), 1.81 (br, 4H), 1.76-1.35 (m, 92H including $H_2O$), 1.28 (t, $J$ = 6.9 Hz, 12H), 1.21 (t, $J$ = 7.2 Hz, 12H), 1.04 (s, 18H), –3.16 (s, 2H), –3.74 (s, 2H).

ESI-TOF-MS (positive): $m/z$ 1368.9: Calcd for $C_{316}H_{394}N_{24}O_{48}P_4Si_2$ ([**7**–4$Cl^-$]$^{4+}$), Found 1368.9.

Elemental Analysis: Calcd. for $C_{341}H_{447}Cl_{31}N_{24}O_{54}P_4Si_2$(**7**+$9CHCl_3$+$4Et_2O$+$2H_2O$); C: 58.30, H: 6.41, N: 4.32, Found; C: 58.50, H: 6.37, N: 4.32 (0.46% Error).

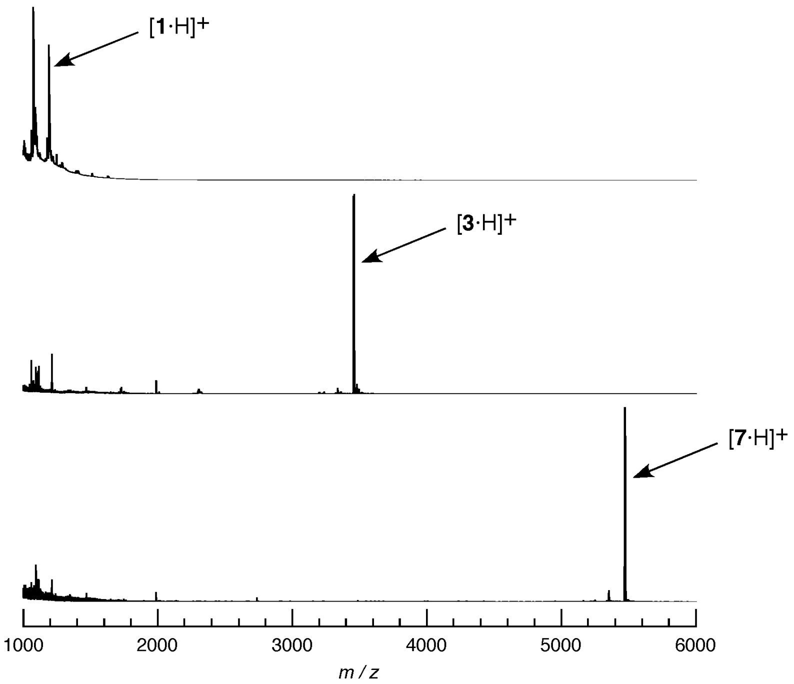


**Fig. S1** MALDI-TOF mass spectra of (a) a monomer **1**, (b) a dimer **3**, (c) a trimer **7**.

The repetitive elongation of the supramolecular array was clearly demonstrated by MALDI-TOF MS spectroscopic study. Fig. S1 summarizes the MALDI-TOF MS spectra of the terminal unit **1**, the dimer **3**, and the trimer **7**. Differential between the signals in Figure S1a (m/z = 1248) and S1b (m/z = 3456) corresponds to the mass change during the two-fold rotaxane formation reaction of **1** and **2**. Likewise, differential between the signals in Figure S1b (m/z = 3456) and S1c (m/z = 5476) is identical to the mass change by the introduction of the two threads and the second two-fold rotaxane formation with another **2**.

## $^1$H-NMR, COSY and ROESY spectra of **3**.

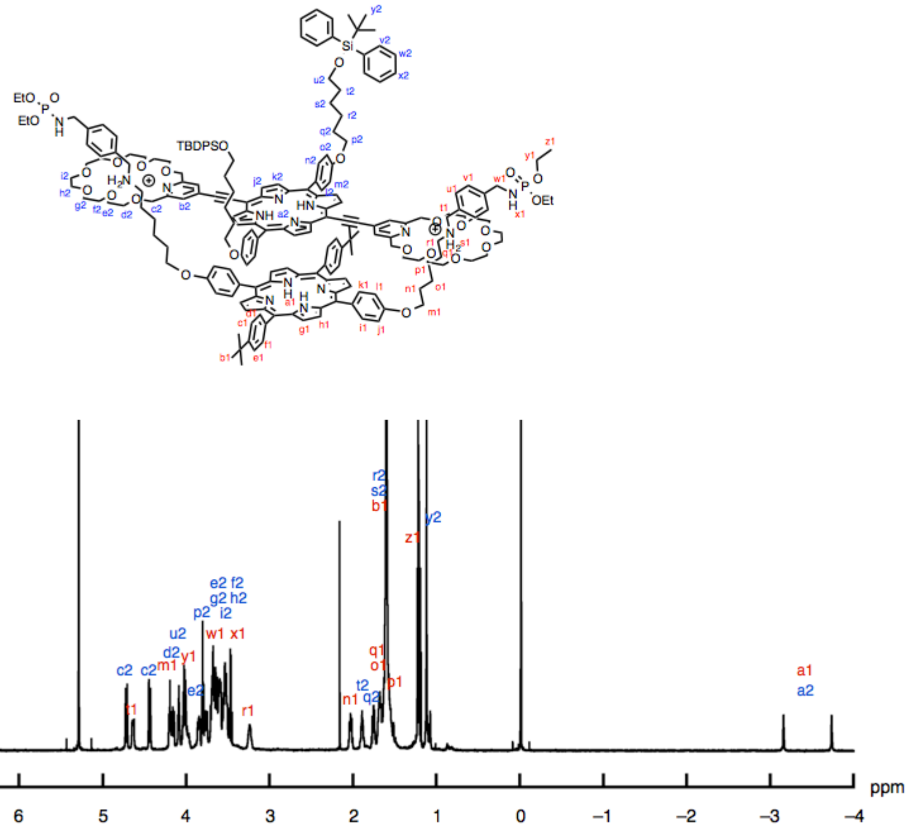


***Fig. S2.*** $^1$H-NMR spectrum of **3** in $CDCl_3$ at 298 K.

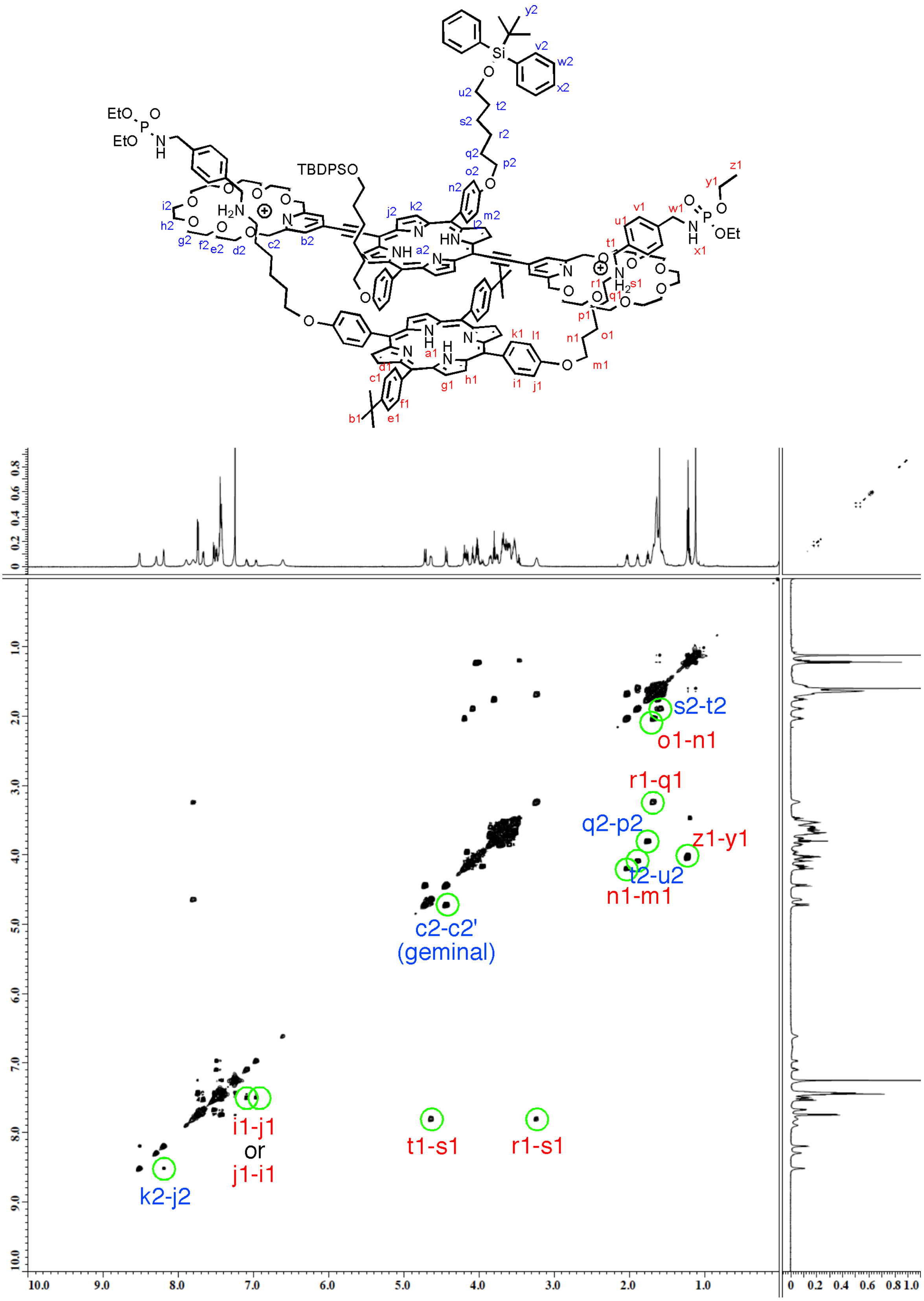


*Fig. S3.* COSY spectrum of **3** in $CDCl_3$ at 298 K.

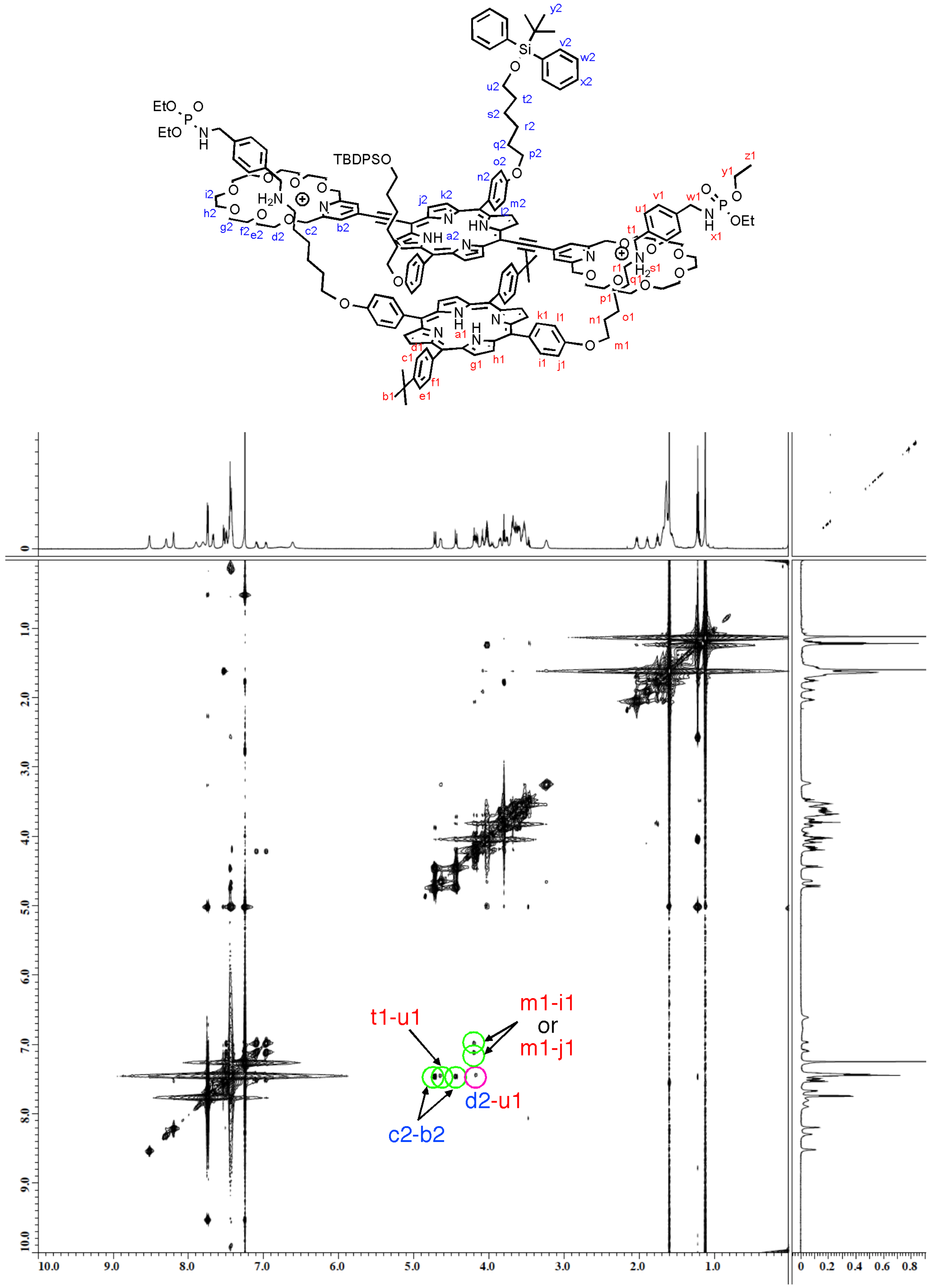


*Fig. S4.* ROESY spectrum of **3** in $CDCl_3$ at 298 K.

## $^1$H-NMR, COSY and ROESY spectra of **7**.

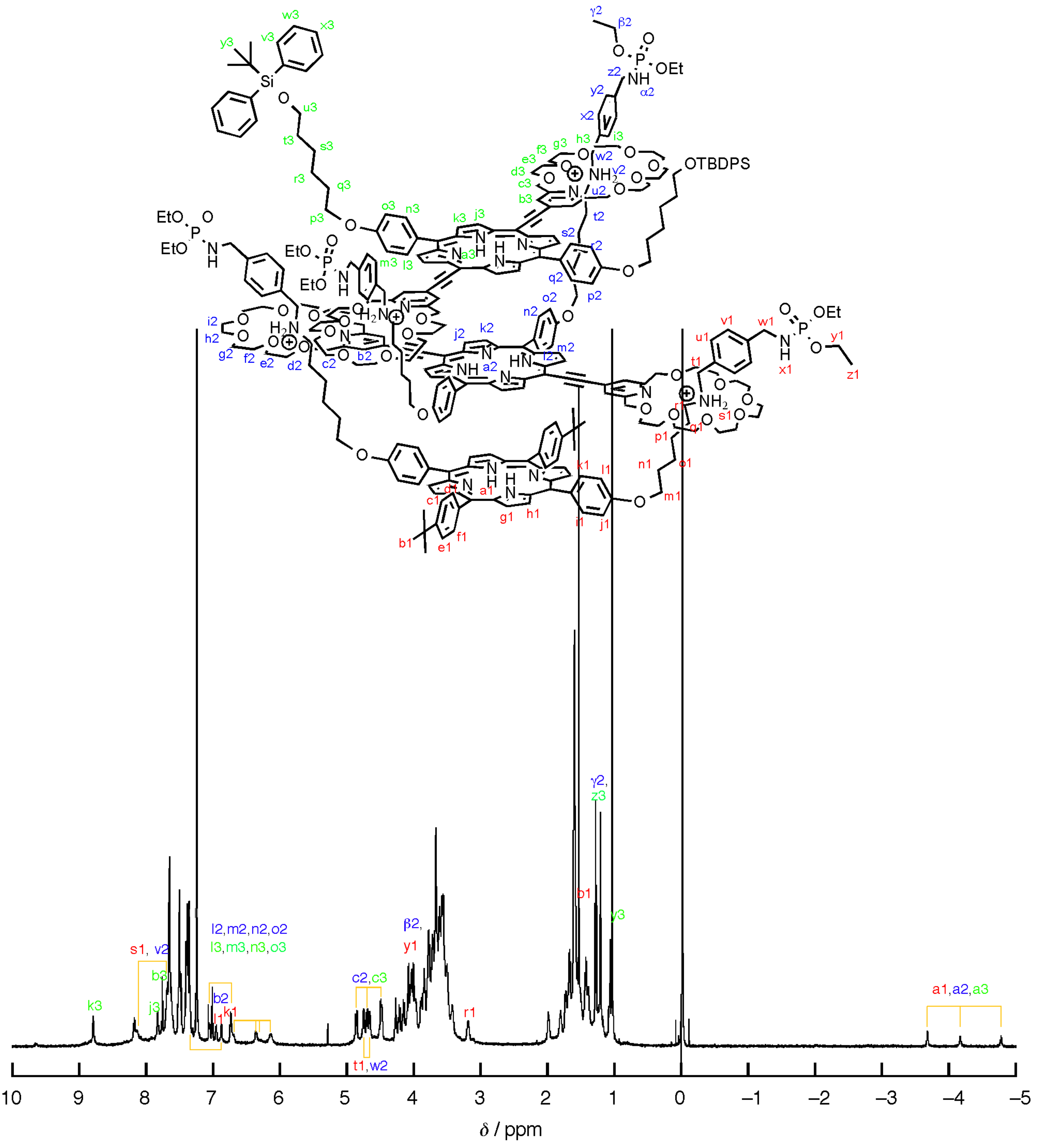


***Fig. S5.*** $^1$H-NMR spectrum of **7** in $CDCl_3$ at 298 K.

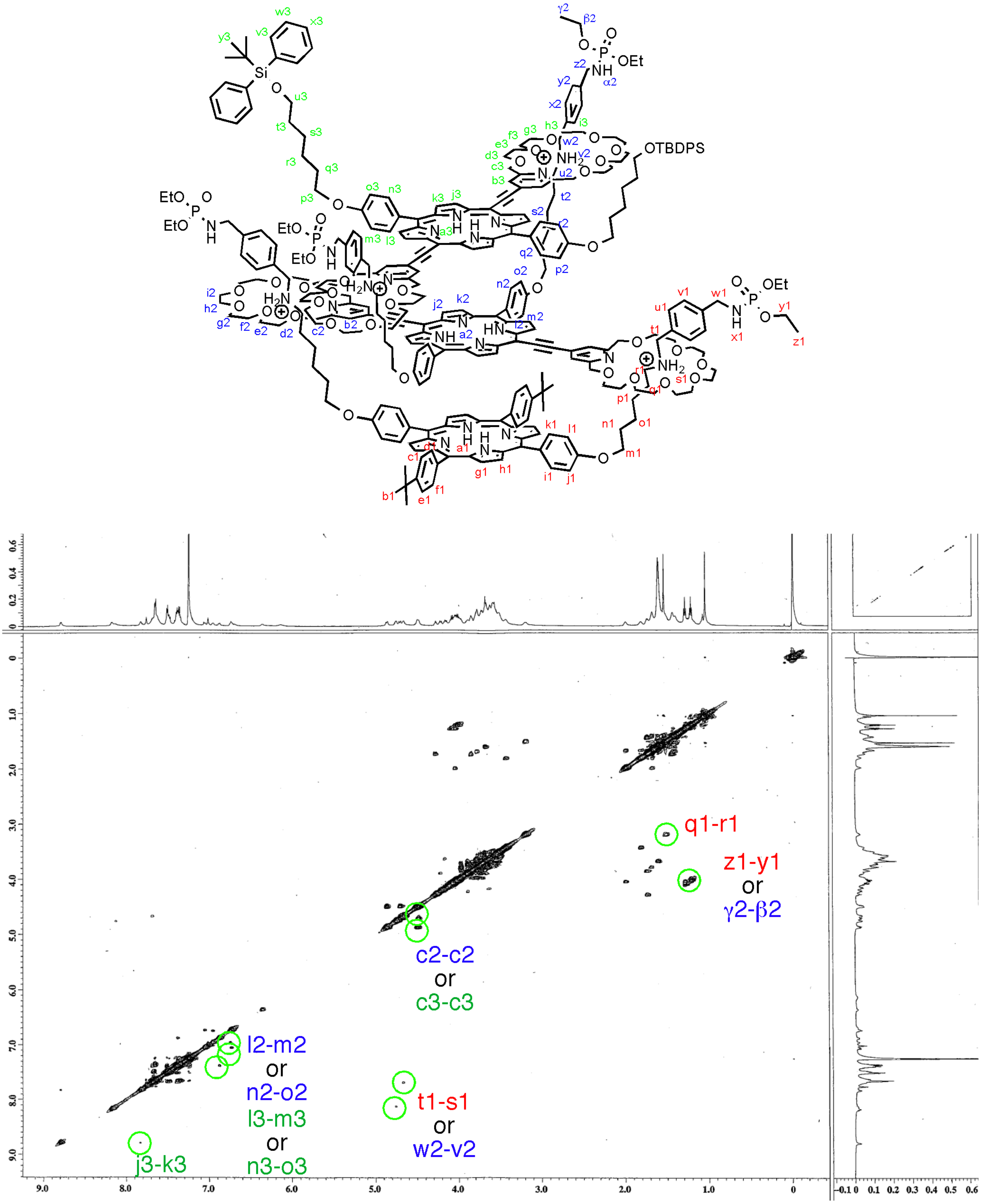


*Fig. S6.* COSY spectrum of **7** in $CDCl_3$ at 298 K.

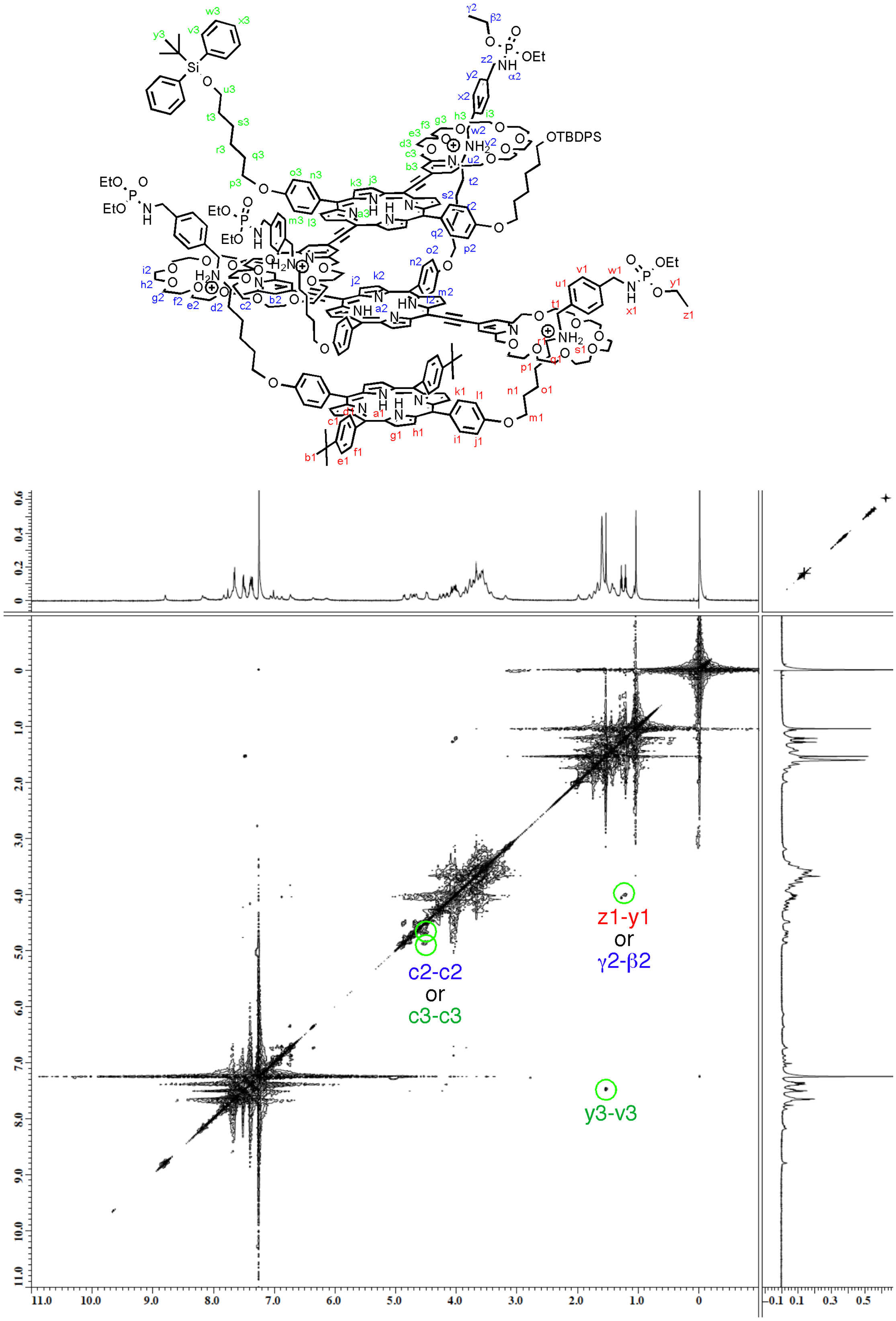


*Fig. S7.* ROESY spectrum of **7** in $CDCl_3$ at 298 K.

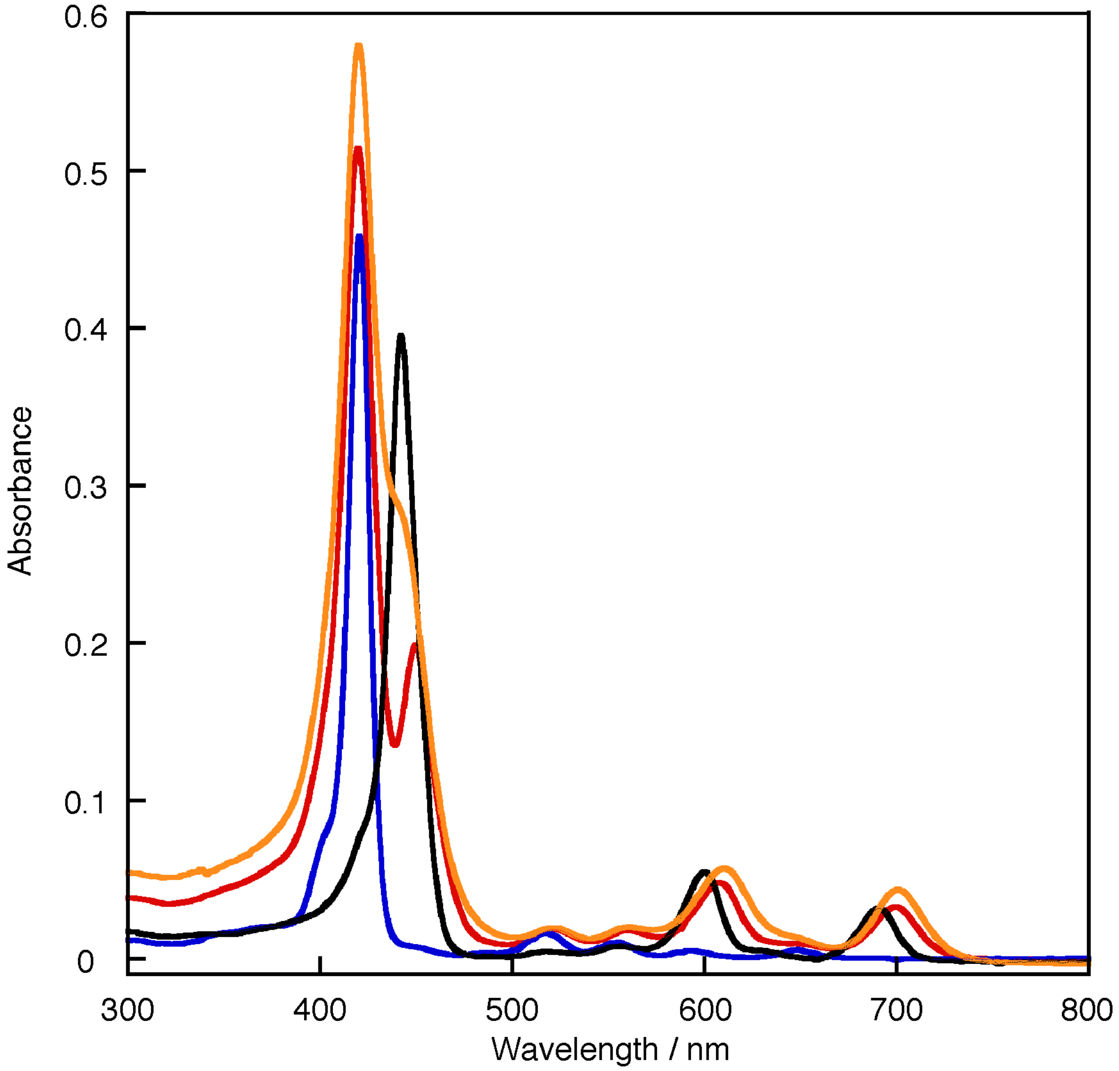


***Fig. S8.*** UV-vis absorption spectra of **S7** (a precursor of **1**: the detailed structure is shown in the Supporting Information) (blue), **2** (black), a stacked porphyrin dimer **3** (red), and a stacked trimer **7** (orange) in $CH_2Cl_2$ at 20 °C.

**References.**

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