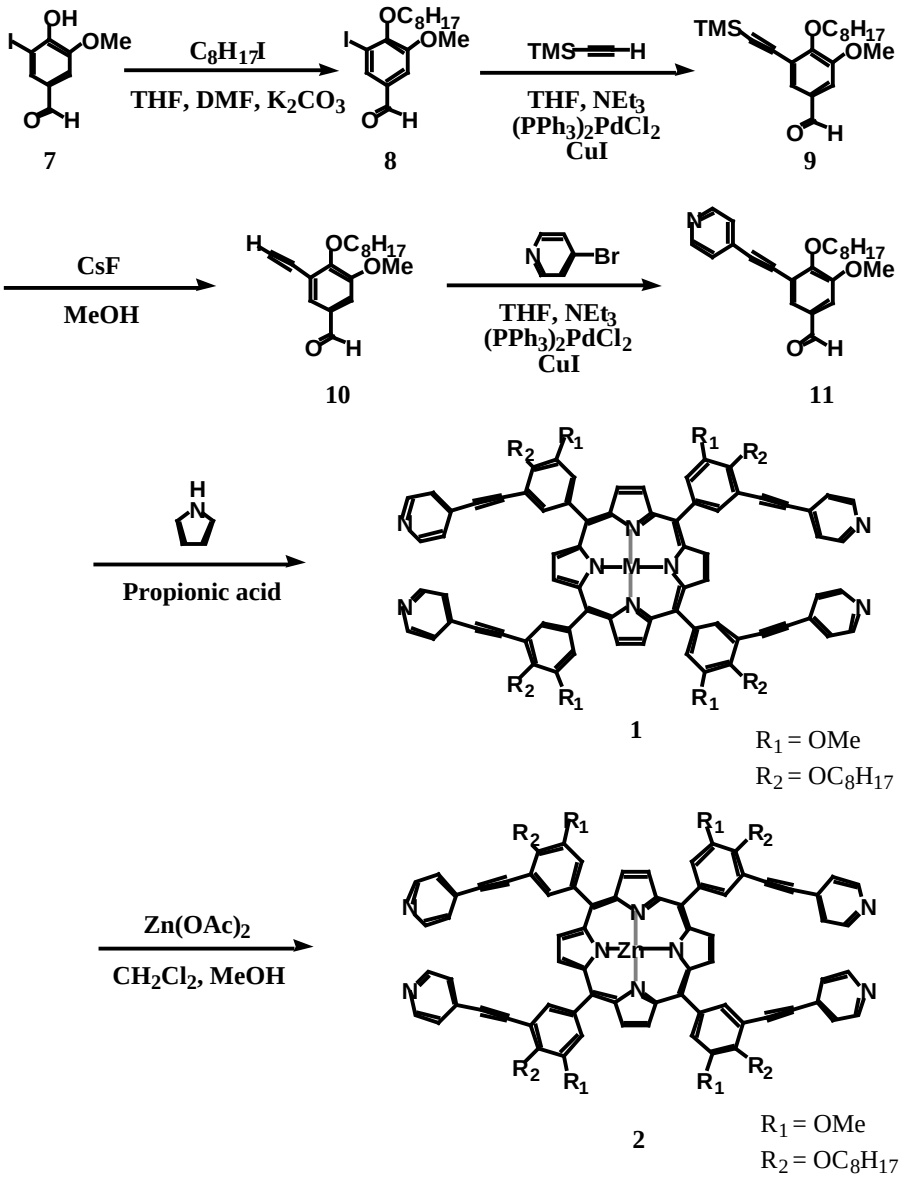
Supporting Information

Scheme



Melting points were determined on a Micro Melting Point Apparatus (Yanaco MP-500D) and uncorrected. ^{1}H NMR spectra were measured on a Bruker DRX 600 spectrometer or a Bruker AC250P spectrometer. The samples of the self-assembled structures **5** and **6** for NMR measurements were prepared by mixing the solutions of the corresponding pyrdylporphyrin **1** or **2** and Pd(II)

complexes at required ratios. Compounds **3**[10b] was prepared according to literature procedures.

5-Iodo-3-methoxy-4-octhoxybenzaldehyde (8). A mixture of 5-iodovanillin (2.00 g, 7.19 mmol), 1-iodooctane (8.63 g, 35.9 mmol), and K_2CO_3 (5.04 g, 36.5 mmol) in THF 40mL and DMF 10 mL was stirred at reflux temperature for 24 h. After cooling, the filtrate was concentrated in vacuo. After isolation by column chromatography (silica gel, chloroform/hexane = 1:1 v/v), 2.03 g of colorless oil (R_f = 0.40, chloroform/hexane = 1:1 v/v, silica plate) was obtained: yield, 72%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.82 (s, 1H, CHO), 7.85 (d, J = 1.9 Hz, 1H, ArH), 7.40 (d, J = 1.9 Hz, 1H, ArH), 4.09 (t, J = 6.6 Hz, 2H, OCH_2), 3.90 (s, 3H, OMe), 1.92-1.76 (m, 2H, OCH_2CH_2), 1.58-1.29 (m, 10H, $(CH_2)_5$), 0.89 (t, J = 6.8 Hz, 3H, CH_2CH_3).

3-Methoxy-4-octhoxy-5-trimethylsilylethynylbenzaldehyde (9). A mixture of **8** (1.50 g, 3.85 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.53 g, 0.75 mmol), and copper(I) iodide (0.14 g, 0.75 mmol) in THF 40 mL and triethylamine 10 mL was stirred at room temperature under nitrogen. After the addition of trimethylsilylacetyrene (0.58 mL, 4.00 mmol) in the mixture, the mixture was stirred at room temperature for 1 h and at 90 °C for 5 h. After cooling, the reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was dissolved in chloroform and the solution was washed twice with water and dried over $MgSO_4$. After evaporation to dryness, the residue was purified by column chromatography (silica gel, chloroform). 1.30 g of pale yellow oil (R_f = 0.83, chloroform, silica plate)was obtained: yield, 94%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.65 (s, 1H, CHO), 7.35 (d, J = 1.9 Hz, 1H, ArH), 7.20 (d, J = 1.9 Hz, 1H, ArH), 4.04 (t, J = 6.6 Hz, 2H, OCH_2), 3.71 (s, 3H, OMe), 1.67-1.55 (m, 2H, OCH_2CH_2), 1.38-1.03 (m, 10H, $(CH_2)_5$), 0.70 (t, J = 6.8 Hz, 3H, CH_2CH_3), 0.08 (s, 9H, $Si(CH_3)_3$).

3-Methoxy-4-octhoxy-5-ethynylbenzaldehyde (10). A mixture of **9** (1.00 g, 2.77 mmol) and CsF (0.60 g, 3.95 mmol) in MeOH 20 mL was stirred at room temperature for 24 h. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, chloroform). 0.72 g of pale

yellow oil (R_f = 0.80, chloroform, silica plate) was obtained: yield, 90%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.85 (s, 1H, CHO), 7.57 (d, J = 1.6 Hz, 1H, ArH), 7.42 (d, J = 1.6 Hz, 1H, ArH), 4.25 (t, J = 6.5 Hz, 2H, OCH_2), 3.91 (s, 3H, OMe), 3.30 (s, 1H, CCH), 1.85-1.72 (m, 2H, OCH_2CH_2), 1.58-1.24 (m, 10H, $(CH_2)_5$), 0.86 (t, J = 6.0 Hz, 3H, CH_2CH_3).

3-Methoxy-4-octhoxy-5-(4-pyridin-ylethnyl)benzaldehyde (11). A mixture of 4-bromopyridine hydrochloride (0.47 g, 2.43 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.17 g, 0.24 mmol), and copper(I) iodide (0.05 g, 0.24 mmol) in THF 10 mL and triethylamine 30 mL was stirred at room temperature. After the addition of **10** (0.77 g, 2.43 mmol) in the mixture, the mixture was stirred at room temperature for 1 h and at 90 °C for 12 h. After cooling, the reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was dissolved in chloroform and the solution was washed twice with water and dried over $MgSO_4$. After evaporation to dryness, the residue was purified by column chromatography (silica gel, ethyl acetate). 0.55 g of pale yellow oil (R_f = 0.60, ethyl acetate, silica plate)was obtained: yield, 62%; ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.85 (s, 1H, CHO), 8.63 (d, J = 5.8 Hz, 2H, α-PyH), 7.61 (s, 1H, ArH), 7.45 (s, 1H, ArH), 7.39 (d, J = 5.8 Hz, 2H, β-PyH), 4.26 (t, J = 6.6 Hz, 2H, OCH_2), 3.93 (s, 3H, OMe), 1.83-1.73 (m, 2H, OCH_2CH_2), 1.50-1.25 (m, 10H, $(CH_2)_5$), 0.85 (t, J = 6.8 Hz, 3H, CH_2CH_3).

Tetrakis(3-(4-pyridine-ylethynyl)-4-octhyloxy-5-methoxy)phenylporphyrin (1). A mixture of **11** (1.00 g, 2.74 mmol) and pyrrol (0.18 g, 2.68 mmol) in propionic acid 100 mL was stirred at reflux temperature for 3 h. The solvent was evaporated, and the residue was dissolved in chloroform. The solution was washed with aqueous Na_2CO_3 and water and dried over anhydrous Na_2SO_4. After evaporation to dryness, the residue was purified by column chromatography (alumina gel, chloroform/hexane = 1:1 v/v) and gelpermition chromatography. 0.25 g of purple solid (R_f = 0.50, chloroform, alumina plate) was obtained: yield, 22%; mp 102-105 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (s, 8H, β-H), 8.60 (d, J = 5.8 Hz, 8H, α-PyH), 7.97

(d, J = 5.5 Hz, 4H, ArH), 7.82 (d, J = 5.5 Hz, 4H, ArH), 7.39 (d, J = 5.8 Hz, 8H, β-PyH), 4.48 (t, 8H, J = 6.6 Hz, OCH_2), 3.98 (s, 12H, OMe), 2.03-2.01 (m, 8H, OCH_2CH_2), 1.80-1.25 (m, 40H, $(CH_2)_5$), 0.91 (t, J = 6.8 Hz, 12H, CH_2CH_3), -2.81 (s, 2H, NH); MALDI-TOF MS: *m/z* 1651.9 ($M+H^+$). Anal. Calcd for $C_{108}H_{114}N_8O_8 \cdot 3H_2O$: C, 76.03; H, 7.09; N, 6.57. Found: C, 75.96; H, 7.10; N, 6.30.

Zn(II) tetrakis(3-(4-pyridine-ylethynyl)-4-octhyloxy-5-methoxy)phenylporphyrin (2). A mixture of **1** (30 mg, 0.018 mmol) and zinc acetate (15 mg, 0.083 mmol) in methanol (3 mL) and dichloromethane (3 mL) was stirred at room temperature for 20 min. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, chloroform/methanol = 9:1 v/v). 31 mg of purple solid (R_f = 0.50, chloroform/methanol = 9:1 v/v, silica plate) was obtained: yield, 99%; mp 115-118 °C; MALDI-TOF MS: *m/z* 1713.8 ($M+H^+$). Anal. Calcd for $C_{108}H_{112}N_8O_8Zn \cdot 3H_2O$: C, 73.31; H, 6.72; N, 6.33. Found: C, 73.52; H, 6.82; N, 6.17.

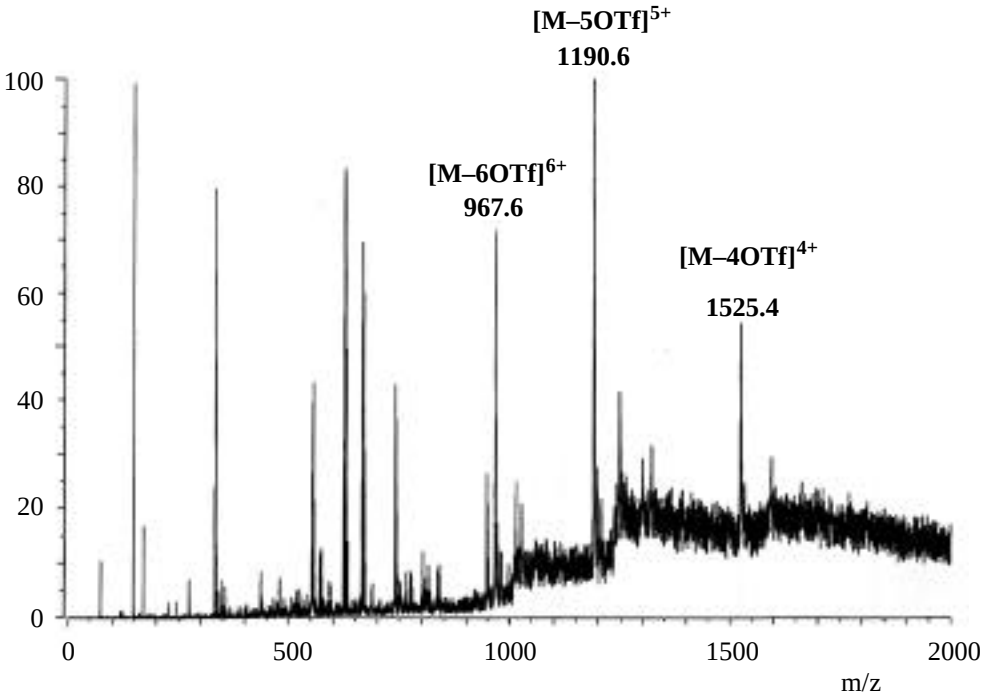


Figure S1. Coldspray ionization MS spectrum of **6** (1:2 mixture of **2** and **3**) (needle voltage: 2.7 kV; needle current: 300-700 nA; orifice voltage: 84 V; ringlens voltage: 300 V; ion source temperature: 298 K; flow rate: 17 μL/min; solvent: CH_2Cl_2:DMF = 75:1 v/v).

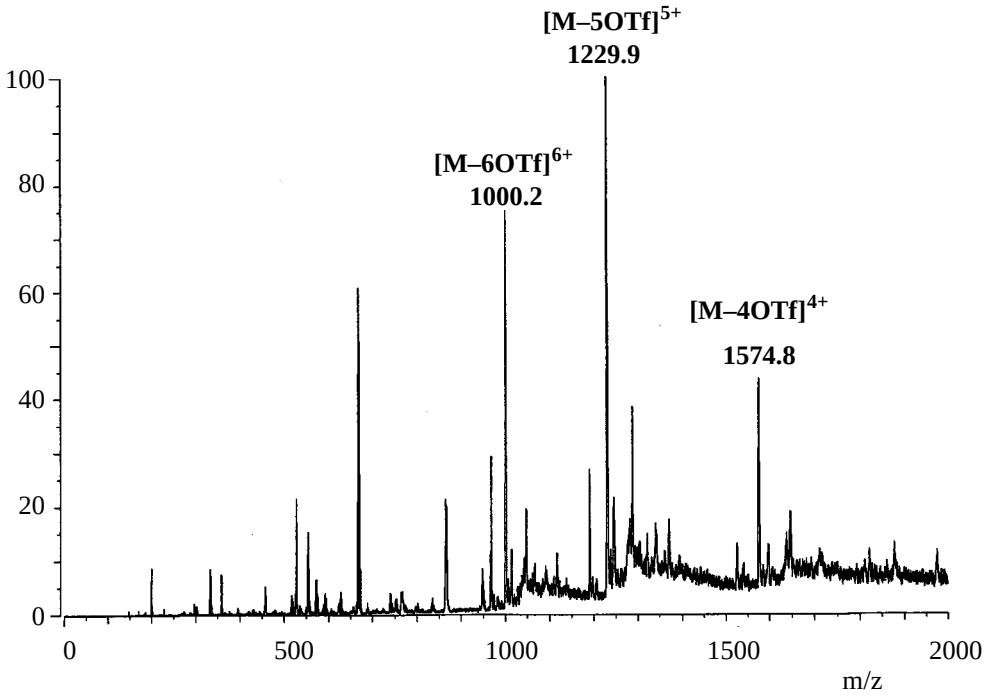


Figure S2. Coldspray ionization MS spectrum of **6·4** complex (1:1 mixture of **6** and **4**) (needle voltage: 2.3 kV; needle current: 300-700 nA; orifice voltage: 90 V; ringlens voltage: 257 V; ion source temperature: 298 K; flow rate: 17 μL/min; solvent: CH_2Cl_2:DMF = 75:1 v/v).

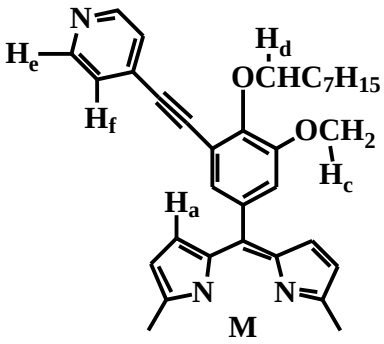
Table Characterization of **1**, **5**, **6**, **4**, and **6·4** complex by ^{1}H-NMR spectra

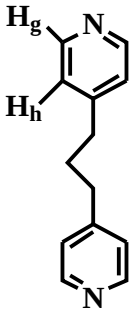
	1	**5**	**6**	**4**	**6·4**[(i)]
H_a	8.96	8.80 (−0.16)	8.92	−	8.82 (−0.10)
H_b	−2.81	−3.12 (−0.31)	−	−	−
H_c	3.98	3.93 (−0.05)	3.93	−	3.81 (−0.12)
H_d	4.48	4.37 (−0.11)	4.38	−	4.33 (−0.05)
H_e	8.60	8.97 (+0.37)	8.95	−	8.95 (0)
H_f	7.39	7.14 (−0.25)	7.12	−	7.17 (+0.05)
H_g	−	−		8.82	2.22 (−6.60)
H_h	−	−		7.67	4.57 (−3.10)

The numbers indicate the chemical shifts ($\Delta\delta_H$): 600 MHz, $CDCl_3$, 27 °C, [**1**] = 2.2 mM, [**5**] = 1.1 mM, [**2**] = 1.5 mM, [**6**] = 0.8 mM, [**4**] = 0.8 mM.

The spectrum of **2** is broadened in $CDCl_3$, so it could not be characterized.

[(i)]The complex was formed by **6** and **4** in 1:1 ratio.





M = 2H$_b$, Zn