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A [2]Catenane and Pretzelane Based on Sn–Porphyrin and Crown Ether

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A [2]catenane and a pretzelane that consist of one aromatic dialkylammonium spacer, one dibenzo-24-crown-8 (DB24C8) unit, and one Sn–porphyrin dihydroxide component were synthesized. In the [2]catenane, dibenzo-24-crown-8 and the Sn–porphyrin dihydroxide are two independent components, whereas in the pretzelane, dibenzo-24-crown-8 and the Sn–porphyrin dihydroxide are linked covalently. The interlocked molecules were obtained by the axial ligation of Sn–porphyrin dihydroxide with the resorcinol moieties of both termini in the aromatic dialkylammonium spacer.

Introduction

Mechanically interlocked molecules, such as catenanes,[1] rotaxanes,[2] knots,[1a,3] and Borromean links,[4] based on molecular recognition and self-assembly have attracted interest because of their fascinating topological features and potential as components of molecular-scale devices.[5] Therefore, it remains necessary to devise new synthetic strategies for the construction of such systems. Catenanes comprise two or more interlocked macrocyclic components, in which the macrocycles are not linked covalently to each other. Pretzelanes[6] are bridged [2]catenanes that are connected by covalent bonds, which have also been studied extensively in recent years. The first pretzelane was synthesized by Vögtle et al.[7] from sulfonamide-based macrocycles and catenanes. Stoddart et al.[6,8] developed some donor–acceptor pretzelanes, which were composed of an electron-deficient tetracationic cyclophane tethered to and mechanically interlocked with an electron-rich macrocyclic polyether. To the best of our knowledge, these are the only two reported examples of pretzelanes to date.

Porphyrin chromophores are among the most widely used building blocks in the preparation of synthetic devices that are able to undergo photoinduced energy- and electron-transfer processes.[9] Because of their remarkable spectroscopic and electrochemical properties as well as easy substitution and metallation, such chromophores are versatile components for constructing rotaxanes and catenanes. For example, a series of [2]rotaxanes and [2]catenanes that incorporate porphyrin, fullerene, and other functional moieties have been described.[10,11] Most of these molecular architectures have been constructed through the *meso* and β-pyrrol functionalizations of porphyrin. Examples that incorporate porphyrin into mechanically interlocked molecules by axial ligation are extremely limited.[12]

In this study, we report the syntheses of the porphyrin-based macrocycle **1**, [2]catenane **2**, and pretzelane **3** (Scheme 1). In **1**–**3**, the main macrocycle was obtained by the axial ligation of Sn–porphyrin dihydroxide with two resorcinol moieties of the termini of the aromatic dialkylammonium spacer. When we replaced Sn–porphyrin dihydroxide with an Sn–porphyrin dihydroxide–crown ether conjugate, **3** was obtained in one step by using a template-directed protocol.

Results and Discussion

We designed Sn–porphyrin dihydroxide **6** and Sn–porphyrin dihydroxide–crown ether conjugate **9** as the lock. Sn–porphyrin phenolates[13] are the stable products of the equilibrium-based condensation reaction of substituted phenols with Sn–porphyrin dihydroxide in an organic medium. Because of the inherent simplicity of their axial ligation and flexibility of the choice of phenol ligand, we used Sn–porphyrin phenolates to extend and complement the construction of molecular architectures. The synthetic routes to **6** and **9** are shown in Scheme 2. The synthesis of **6** was carried out according to a described procedure.[14] The starting material for the synthesis of **9** was the free porphyrin–crown ether conjugate **7**, which was obtained after tedious purification of the product of the condensation reaction of 4-formyldibenzo-24-crown-8 (1 equiv.) and benzalaldehyde (3 equiv.) with pyrrole (4 equiv.) in propionic acid. Heating of a mixture of **7** and $SnCl_2 \cdot 2H_2O$ in pyridine afforded the dichlorido complex **8** in 81% yield. This was converted to the dihydroxide species **9** in 85% yield by treatment with K_2CO_3 in THF/H_2O with heating.

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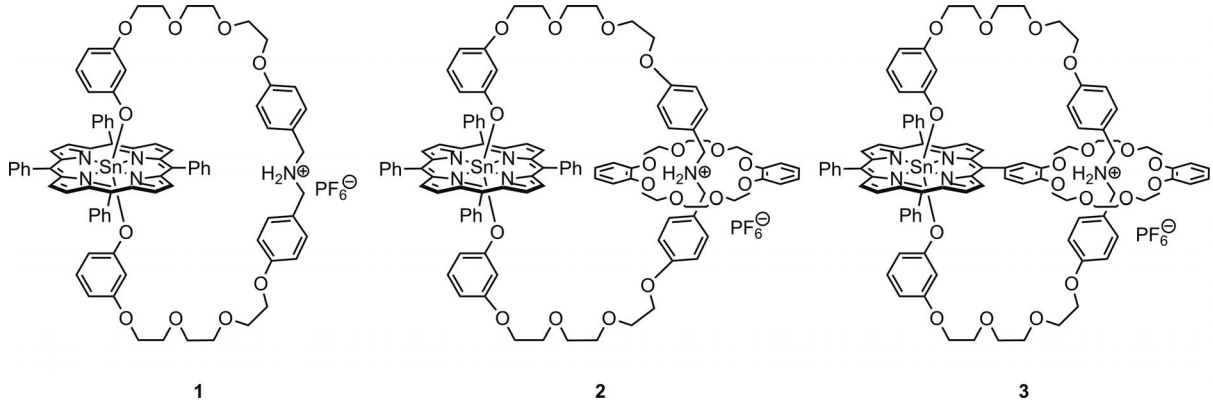
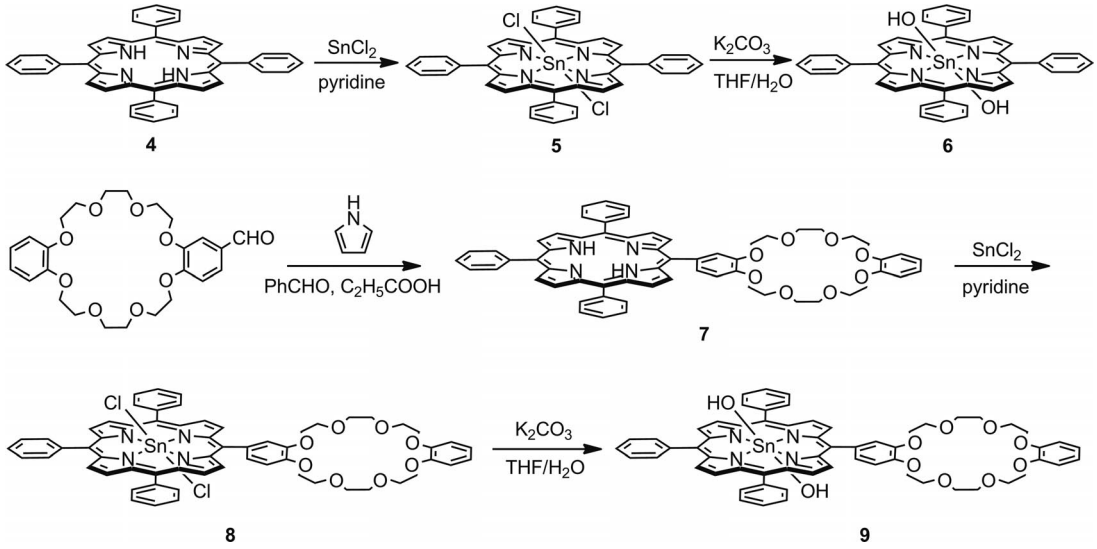


Scheme 1. Structures of **1**, **2**, and **3**.

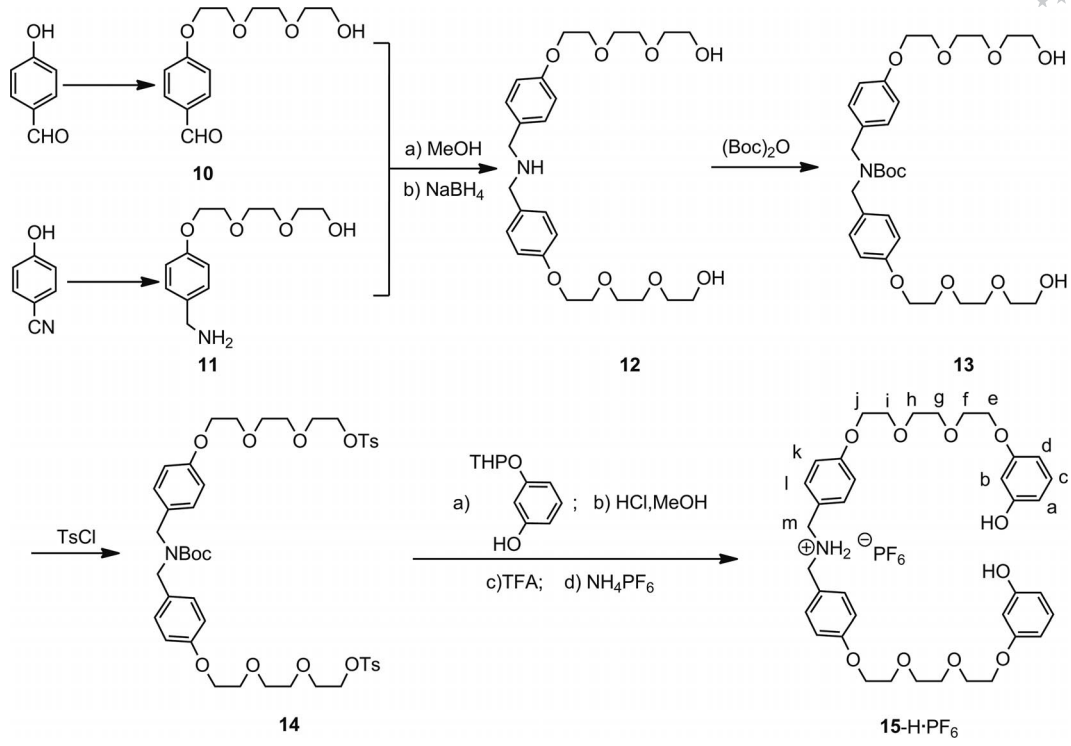


Scheme 2. Synthesis of **6** and **9**.

We designed an axis molecule that bears one resorcin moiety at each terminus and a dialkylammonium binding station in the middle. To choose two triethylene glycol connectors between the dialkylammonium and resorcinol units is basic for CPK models, in which its space can allow another dibenzo-24-crown-8 (DB24C8) to encircle the dialkylammonium moiety. The synthetic route to **15**-H·PF_6 is shown in Scheme 3. The synthesis of **15**-H·PF_6 started from **10**, which was prepared from the condensation of 4-hydroxybenzaldehyde with 8-tosyloxy-3,6-dioxaoctanol. Compound **11** was obtained from the reaction of 4-hydroxybenzonitrile with 8-tosyloxy-3,6-dioxaoctanol followed by reduction with $LiAlH_4$. Condensation of **10** with **11** followed by reduction gave bis(benzyl)amine **12**; $(Boc)_2O$-protected **12** reacted with TsCl to give bis(tosylate) **14** in 80% yield. Compound **14** reacted with a monoprotected resorcinol derivative[15] in the presence of K_2CO_3 followed by deprotection with ethanol/aqueous HCl at room temperature and removal of the Boc group with trifluoroacetic acid (TFA) to give free **15** in 85% yield. Acidification with HCl followed by anion exchange with NH_4PF_6 afforded the dialkylammonium salt **15**-H·PF_6.

To prepare macrocycle **1**, the reaction of **6** with 1 equiv. of **15**-H·PF_6 was carried out in $CHCl_3/CH_3CN$ (10:1) at room temperature (Figure 1). Although polymerization between **6** and **15**-H·PF_6 could occur in the ring-closing process, **1** was successfully produced and isolated by column chromatography. Encouraged by the fact that DB24C8 is able to complex dialkylammonium ions to form rotaxanes and pseudorotaxanes,[16] we examined the ring-closing reaction of **1** in the presence of DB24C8 and obtained **2**. Because of the lower temperature of the reaction and the low solvent polarity, the formation of a pseudorotaxane between DB24C8 and the dialkylammonium moiety was expected to be more preferable from the viewpoint of enthalpy.

Macrocycle **1** and [2]catenane **2** were characterized by ^1H NMR spectroscopy and HR mass spectrometry (ESI). The latter provides convincing evidence for the formation of **1** and **2**. Figure 2 shows the HR mass spectra of **1** and **2**, which show molecular ion peaks at m/z = 1408.448 and 1856.649 corresponding to $[\mathbf{1}\text{-}PF_6]^+$ and $[\mathbf{2}\text{-}PF_6]^+$, respectively, and their isotopic patterns are in excellent agreement with the theoretical distributions. In the ^1H NMR spectrum



Scheme 3. Synthesis of **15**-H·PF_6.

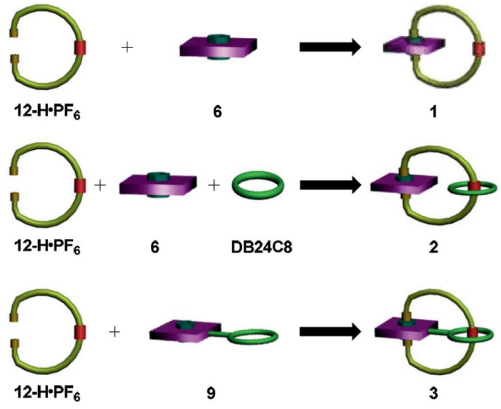


Figure 1. Synthesis of **1**, **2**, and **3**.

of **1** (Figure 3c), the most diagnostic signals to judge the formation of the macrocyclic complex are the resorcinol resonances, which are shifted significantly to higher field [$\Delta\delta$ = –5.0 (H_a), –4.75 (H_b), –1.67 (H_c), –0.87 (H_d) ppm]. The significant upfield shifts of these resonances are a result of the large shielding effect of the porphyrin ring current and confirm that the resorcinol moieties are linked to the Sn–porphyrin moiety by Sn–phenoxide coordination.[11,17] The disappearance of the axial hydroxy proton resonance at δ = 7.4 ppm is associated with these chemical shift changes as these protons are exchanged for resorcinol ligands. The same resorcinol chemical shift changes were found in the ^{1}H NMR spectrum of **2**. In addition, a large downfield shift (by 0.45 ppm) of the signal for the benzylic methylene protons (H_m) adjacent to the dialkylammonium center and significant changes in the chemical shifts of the protons of DB24C8 were observed, which suggests that a DB24C8 moiety encircled the dialkylammonium binding station of the macrocycle and confirms the formation of **2**. Moreover, the upfield shift of the H_l and H_k signals of the axis molecule, which may be due to a π–π stacking interaction between the phenyl groups in the salt and the catechol rings in the crown subunits,[14b] is also in keeping with the assembly structure. The coordination of DB24C8 restricts the rotation of the macrocycle around the O–Sn–O axis so that signals corresponding to the protons of the dialkylammonium and porphyrin moieties are split.

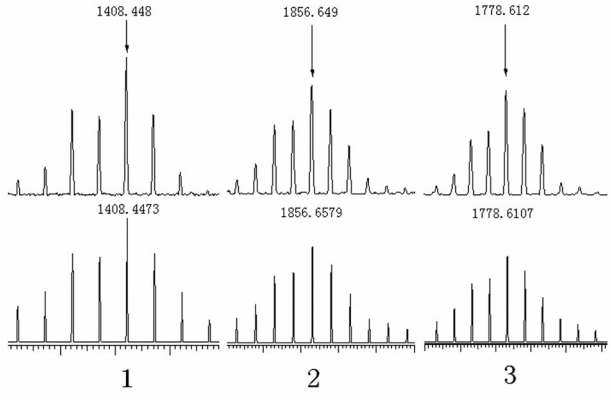


Figure 2. Calculated (bottom) and experimental (top) HR mass spectra (ESI) of **1**, **2**, and **3**.

With the successful preparation of **2** in hand, we prepared **3**. Because **9** comprises a macrocycle and a stopper in one molecule, we were able to synthesize **3** according to

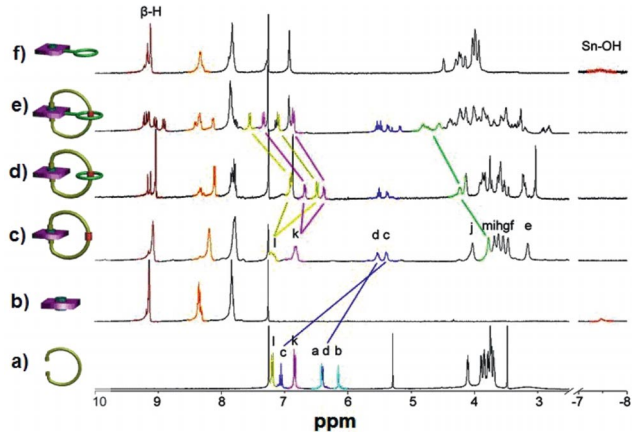


Figure 3. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 300 K) of (a) **15**, (b) **6**, (c) **1**, (d) **2**, (e) **3**, and (f) **9**.

a template-directed protocol. Compound **9** reacted with **15**-H·PF_6 in $CHCl_3$/CH_3CN at room temperature to afford **3** (Figure 1). Pretzelane **3** was characterized in a manner similar to those for **1** and **2**. In the HR mass spectrum of **3**, the molecular ion peak at *m*/*z* = 1778.612, which corresponds to [**3**-PF_6]$^+$, was observed, and its isotopic pattern is in excellent agreement with the theoretical distribution (Figure 2). In the ^{1}H NMR spectrum of **3**, the same chemical shift changes for the resorcinol moieties as seen in **2** and the large downfield shift (δ = 0.8 ppm) of the signal of H_m demonstrate the formation of **3**. Compared to those in the ^{1}H NMR spectrum of **2**, the signals for H_l, H_k, and H_m in **3** are subject to considerable downfield shifts. This is explained by the fact that the porphyrin moiety and DB24C8 are connected by a C–C bond in **3**, which causes the dialkylammonium moiety to be closer to the edge of the Sn–porphyrin unit. The dialkylammonium unit is therefore located in the deshielding region of the porphyrin ring current, which causes these downfield shifts.

Photophysical data of the porphyrin derivatives **1**–**9** were measured in $CHCl_3$ solution and are collected in Table S1 (Supporting Information). These data provide further evidence for the formation of the desired molecular architectures. UV/Vis spectroscopy is a powerful tool for monitoring the metallation of porphyrins. The UV/Vis spectra of **4** and **7** showed characteristic absorption bands for free porphyrin with Soret bands at 418 and 420 nm, respectively. Generally, both the position and number of bands changes upon metallation. The bathochromic shifts of the Soret bands, the disappearance of four Q-bands in the free-base porphyrin, and the appearance of two new Q-bands in the metalloporphyrins **1**, **2**, **3**, **5**, **6**, **8**, and **9** confirm the formation of the metallated products.[18] Metallation of the porphyrin derivatives also causes a blueshift of the emission bands and a decrease of the fluorescence intensity. Compared with free porphyrins **4** and **7**, Sn–porphyrin derivatives showed lower quantum yields and lifetimes owing to the heavy-atom effect of the metal.

Conclusions

We have demonstrated that the synthesis of a new [2]catenane and pretzelane can be achieved from Sn–porphyrin and DB24C8. The new synthetic strategies for **2** and **3** offer the potential for the design and synthesis of even more intricate systems that incorporate interlocked components.

Experimental Section

Instrumentation: NMR spectra were recorded with a Varian 400 spectrometer. Positive-ion matrix-assisted laser desorption ionization mass spectrometry was performed with an IonSpec QFT-MALDI MS. UV/Vis spectra were recorded with a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. Steady-state fluorescence spectra were recorded with a VARIAN CARY Eclipse equipped with a VARIAN CARY single-cell Peltier accessory to keep the temperature at 25 °C. The fluorescence quantum yields were recorded with an Edinburgh Analytical Instruments FLS920 spectrometer.

Synthesis of 5-[4-(Dibenzo-24-crown-8)]-10,15,20-triphenylporphyrin (7): A mixture of 4-formyldibenzo-24-crown-8 (4.0 g, 8.4 mmol) and propionic acid (600 mL) was heated at 110 °C with stirring. Benzaldehyde (2.7 mL, 25.2 mmol) and pyrrole (2.4 mL, 38 mmol) were successively and slowly added to this solution. The resulting mixture was heated under reflux for 1.5 h, allowed to cool to room temperature, and the solvents were evaporated to dryness. The residue was neutralized with aqueous ammonia, filtered through a glass frit, and washed several times with water. The crude material was extracted with $CHCl_3$ and purified by column chromatography on dry silica gel. The desired product was isolated on elution with $CHCl_3$/CH_3OH (100:1). Evaporation of the solvent afforded **7** as purple powder (0.5 g; 6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.78 (s, 2 H), 3.90–3.92 (m, 4 H), 3.97–3.98 (m, 6 H), 4.00–4.01 (m, 4 H), 4.12 (t, 2 H), 4.19 (t, 2 H), 4.23 (t, 2 H), 4.29 (t, 2 H), 6.90–6.95 (m, 4 H), 7.22 (d, *J* = 8.0 Hz, 1 H), 7.70–7.81 (m, 11 H), 8.21 (d, *J* = 6.8 Hz, 6 H), 8.84–8.95 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0, 148.7, 146.9, 142.2, 135.2, 134.6, 128.0, 127.8, 126.7, 121.5, 120.5, 120.2, 120.1, 119.9, 114.0, 111.7, 71.6, 71.5, 71.4, 70.1, 70.1, 70.0, 70.0, 69.7, 69.6, 69.5, 69.4 ppm. ESI-MS: *m*/*z* = 985.68 [M + H]$^+$. HRMS (ESI): calcd. for $C_{62}H_{56}N_4O_8$ [M]$^+$ 984.410; found 984.413.

Synthesis of Dichlorido{5-[4-(dibenzo-24-crown-8)]-10,15,20-triphenylporphyrinato}tin(IV) (8): Compound **7** (300 mg, 0.3 mmol) was heated under reflux with stirring with finely ground $SnCl_2$·$2H_2O$ (344 mg, 1.5 mmol) in pyridine (50 mL) overnight. Complete Sn insertion was confirmed by UV-spectroscopic examination of a drop of the reaction mixture diluted with dichloromethane or chloroform. The crude product was precipitated by the addition of water and collected by vacuum filtration through Celite. Methanol was washed through the Celite plug to remove excess water, followed by chloroform to extract the porphyrin. The chloroform filtrate was washed with aqueous hydrochloric acid (6 M, 2× 10 mL) and water (2× 10 mL) and dried (anhydrous sodium sulfate). The solvent was evaporated, and the residue was purified by chromatography on silica gel ($CHCl_3$/methanol, 20:1) to afford **8** (350 mg) as a purple solid in 100% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90–3.94 (m, 4 H), 3.94–3.99 (m, 6 H), 4.00–4.03 (m, 4 H), 4.14 (t, 2 H), 4.20 (t, 2 H), 4.23 (t, 2 H), 4.27 (t, 2 H), 4.48

(t, 2 H), 6.90–6.93 (m, 4 H), 7.28–7.29 (m, 1 H), 7.79–7.86 (m, 11 H), 8.31 (d, J = 6.4 Hz, 6 H), 9.16–9.26 (m, 8 H) ppm. HRMS (ESI): calcd. for $C_{62}H_{54}Cl_2N_4O_8Sn$ $[M]^+$ 1173.242; found 1173.246.

Synthesis of Dihydroxido{5-[4-(dibenzo-24-crown-8)]-10,15,20-triphenylporphyrinato}tin(IV) (9): Potassium carbonate (1.7 g, 12 mmol) and **8** (350 mg, 0.3 mmol) were dissolved in a mixture of tetrahydrofuran (THF, 160 mL) and water (40 mL) and heated under reflux for 3 h. The organic solvent was removed, and the aqueous layer was extracted with dichloromethane (60 mL). The organic layer was washed with water (2× 40 mL), dried with anhydrous sodium sulfate, filtered, and the solvent was removed to give the crude product, which was purified by chromatography on silica gel to give **9** (315 mg, 90%) as a metallic-purple crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = –7.50 to –7.38 (br., 2 H), 3.90–3.95 (m, 4 H), 3.98–4.00 (m, 6 H), 4.02–4.04 (m, 4 H), 4.15 (t, 2 H), 4.22 (t, 2 H), 4.24 (t, 2 H), 4.29 (t, 2 H), 4.45 (t, 2 H), 6.90–6.95 (m, 4 H), 7.29–7.30 (m, 1 H), 7.82–7.88 (m, 11 H), 8.30–8.50 (m, 6 H), 9.11–9.23 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 149.0, 147.1, 147.0, 146.7, 146.7, 141.3, 135.2, 134.2, 132.9, 132.7, 132.6, 128.5, 128.3, 127.1, 121.5, 121.3, 121.2, 121.2, 120.9, 114.1, 111.8, 71.7, 71.6, 71.5, 71.4, 70.1, 70.1, 70.0, 69.7, 69.6, 69.5 ppm. ESI-MS: m/z = 1137.49 $[M + H]^+$. HRMS (ESI): calcd. for $C_{62}H_{56}N_4O_{10}Sn$ $[M]^+$ 1136.312; found 1136.317.

Synthesis of *p*-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}benzaldehyde (10): A mixture of 4-hydroxybenzaldehyde (5.5 g, 45 mmol), 8-tosyloxy-3,6-dioxaoctanol (15 g, 49.3 mmol), and K_2CO_3 (13.8 g, 100 mmol) in dry acetonitrile (300 mL) was heated to reflux under N_2 overnight. The reaction mixture was cooled to room temperature, filtered, and washed with dichloromethane. The filtrate was concentrated, and the crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:1) to afford **10** (5.15 g, 45%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.61 (t, 2 H), 3.70–3.74 (m, 6 H), 3.89 (t, 2 H), 4.21 (t, 2 H), 7.02 (d, J = 8.8 Hz, 2 H), 7.82 (d, J = 8.8 Hz, 2 H), 9.87 (s, 1 H) ppm.

Synthesis of *p*-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}benzylamine (11): A mixture of 4-hydroxybenzonitrile (5.3 g, 45 mmol), 8-tosyloxy-3,6-dioxaoctanol (15 g, 49.3 mmol), and K_2CO_3 (13.8 g, 100 mmol) in dry acetonitrile (300 mL) was heated to reflux under N_2 overnight. The reaction mixture was cooled to room temperature, filtered, and washed with dichloromethane. The filtrate was concentrated, and the crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether, 2:1) to afford *p*-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}benzonitrile (4.5 g, 39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.61 (t, 2 H), 3.68–3.74 (m, 6 H), 3.88 (t, 2 H), 4.17 (t, 2 H), 6.98 (d, J = 8.8 Hz, 2 H), 7.58 (d, J = 8.8 Hz, 2 H) ppm. To a solution of *p*-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}benzonitrile (4.5 g, 17.9 mmol) in THF (260 mL) was added $LiAlH_4$ (1.8 g, 47.4 mmol). After stirring at room temperature for 3 h, the reaction mixture was quenched with water and extracted with dichloromethane. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated, and the residue was purified by chromatography on silica gel (CH_2Cl_2/methanol, 2:1) to afford **11** (4.05 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.60 (t, 2 H), 3.68–3.73 (m, 8 H), 3.78 (s, 2 H, NH_2), 3.85 (t, 2 H), 4.12 (t, 2 H), 6.89 (d, J = 8.4 Hz, 2 H), 7.20 (d, J = 8.4 Hz, 2 H) ppm.

Synthesis of Bis(*p*-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}benzyl)amine (12): Triethylamine (2.5 mmol, 0.35 mL), $MgSO_4$ (8.3 mmol, 1 g), and **10** (6.0 mmol, 1.56 g) were added to a solution of **11** (5.0 mmol, 1.3 g) in methanol (15 mL). The reaction mixture was stirred at room temperature for 10 h and cooled to –5 °C. $NaBH_4$ (35 mmol, 1.33 g) was added in small portions over 30 min. The reaction mixture was stirred at –5 °C for 2 h and at 0 °C for 1 h. The reaction was quenched by addition of water (100 mL). The product was extracted with CH_2Cl_2 (3× 100 mL), and the combined CH_2Cl_2 extracts were washed with water (4× 100 mL) and dried with Na_2SO_4. The solvent was evaporated, and the residue was purified by chromatography on silica gel (CH_2Cl_2/methanol, 10:1) to afford **12** (1.6 g, 57%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.61 (t, 4 H), 3.68–3.73 (m, 16 H), 3.86 (t, 4 H), 4.12 (t, 4 H), 6.87 (d, J = 8.8 Hz, 4 H), 7.23 (d, J = 8.8 Hz, 4 H) ppm. ESI-MS: m/z = 494.23 $[M + H]^+$.

Synthesis of *N*-Boc-bis(*p*-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}benzyl)amine (13): Di-*tert*-butyl hydrogen carbonate (3.3 mmol, 0.7 g) dissolved in chloroform (15 mL) was added dropwise to a solution of **12** (3.3 mmol, 1.6 g) in chloroform (25 mL) with stirring and cooling in an ice bath over 3 h. The reaction mixture was stirred at room temperature for 12 h and was washed with water (3× 50 mL). The organic phase was dried with Na_2SO_4. The solvent was evaporated, and the residue was purified by chromatography on silica gel (CH_2Cl_2/methanol, 10:1) to afford **13** (1.8 g, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 9 H), 3.62 (t, 4 H), 3.70–3.74 (m, 12 H), 3.87 (t, 4 H), 4.13 (t, 4 H), 4.22 (s, 2 H), 4.31 (s, 2 H), 6.86 (d, J = 8.8 Hz, 4 H), 7.10 (d, J = 8.8 Hz, 4 H) ppm. ESI-MS: m/z = 616.41 $[M + Na]^+$.

Synthesis of *N*-Boc-bis(*p*-{2-[2-(2-tosyloxyethoxy)ethoxy]ethoxy}benzyl)amine (14): To a mixture of **13** (1.8 g, 3 mmol) and sodium hydroxide (0.48 g, 12 mmol) in THF/H_2O (10/10 mL) in an ice bath was added tosyl chloride (1.23 g, 6.5 mmol) in THF (20 mL) dropwise over 3 h. The mixture was stirred overnight before THF was evaporated under reduced pressure. The residue was extracted with ethyl acetate and dried with anhydrous magnesium sulfate. After the solvent had been removed in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether, 2:1) to afford **14** (2.7 g, 95%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 9 H), 2.43 (s, 6 H), 3.61 (t, 4 H), 3.66 (t, 4 H), 3.70 (t, 4 H), 3.82 (t, 4 H), 4.10 (t, 4 H), 4.16 (t, 4 H), 4.22 (s, 2 H), 4.31 (s, 2 H), 6.85 (d, J = 8.4 Hz, 4 H), 7.11 (dd, 4 H), 7.32 (d, J = 8.0 Hz, 4 H), 7.79 (d, J = 8.4 Hz, 4 H) ppm. ESI-MS: m/z = 924.50 $[M + Na]^+$.

Synthesis of Bis[*p*-(2-{2-[2-(3-phenyl)ethoxy]ethoxy}ethoxy)benzyl]-amine (15): A suspension of cesium carbonate (4.0 g, 12 mmol) in dry acetonitrile (50 mL) was stirred vigorously for 10 min and then heated to 100 °C under N_2. To this mixture was added dropwise a solution of mono-THP-protected resorcinol (1.4 g, 7.2 mmol) and **14** (2.7 g, 3.0 mmol) in dry acetonitrile (50 mL). The reaction mixture was stirred at 100 °C for 1 d. After cooling to ambient temperature, the mixture was filtered and washed with CH_2Cl_2 (60 mL). The filtrate was concentrated under reduced pressure to give a residue, which was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:1) to afford **15** (2.2 g, 78%) as a colorless oil. This oil (1.0 g, 1 mmol) was dissolved in methanol (15 mL) under N_2 and stirred vigorously at room temperature. To this was added dropwise a solution of HCl (1 M, 3 mL). The mixture was stirred at room temperature overnight. Methanol was evaporated under reduced pressure, and the residue was extracted with ethyl acetate and dried with anhydrous magnesium sulfate. The filtrate was concentrated under reduced pressure to give an intermediate as a colorless oil. TFA (4.4 mL) was added dropwise to a solution of the intermediate in chloroform (5 mL) with stirring. The reaction mixture was stirred at room temperature for 12 h and was then washed with NaOH (1 M, 3× 50 mL) until the organic phase had become colorless. The organic phase was dried

($MgSO_4$), and the solvent was evaporated. The residue was subjected to column chromatography on silica gel ($CHCl_3$/methanol, 10:1) to obtain **15**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 1 H, NH), 3.69 (t, 4 H, H_g), 3.73–3.75 (m, 8 H, H_h + H_f), 3.78 (t, 4 H, H_i), 3.84 (t, 4 H, H_m), 3.89 (t, 4 H, H_e), 4.10 (t, 4 H, H_j), 5.29 (s, 2 H, OH), 6.15 (t, 2 H, H_b), 6.41 (d, 4 H, H_a + H_d), 6.84 (d, J = 8.8 Hz, 4 H, H_k), 7.06 (t, 2 H, H_c), 7.20 (d, J = 8.8 Hz, 4 H, H_l) ppm. ESI-MS: m/z = 678.29 $[M + H]^+$. After a protonation and ion-exchange process, **15**-H·PF_6 was afforded as white precipitate (0.71 g, total yield 82%). ^{1}H NMR (400 MHz, CD_3CN): δ = 3.66–3.70 (m, 8 H, H_g + H_h), 3.76–3.80 (m, 8 H, H_f + H_i), 4.04–4.10 (m, 4 H, H_m), 4.12–4.20 (m, 8 H, H_e + H_j), 6.37–6.45 (m, 6 H, H_a + H_b + H_d), 6.98 (d, J = 8.8 Hz, 4 H, H_k), 7.10 (t, 2 H, H_c), 7.39 (d, J = 8.4 Hz, 4 H, H_l) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 160.36, 160.07, 158.35, 132.09, 130.35, 122.68, 115.05, 108.04, 106.15, 101.96, 101.92, 70.59, 70.55, 69.54, 69.42, 67.79, 67.45 ppm. ESI-MS: m/z = 678.4 [**15**-H]$^+$. HRMS (ESI): calcd. for $C_{38}H_{48}NO_{10}$ [**15**-H]$^+$ 678.328; found 678.327.

Synthesis of 1: A solution of **6** (57 mg, 0.07 mmol) in dry $CHCl_3$ (50 mL) was stirred vigorously at room temperature under N_2. To this was added dropwise a solution of **15**-H·PF_6 (50 mg, 0.07 mmol) in dry acetonitrile (5 mL). The reaction mixture was stirred at room temperature overnight. After the solvent had been removed in vacuo, the crude product was purified by column chromatography on basic alumina ($CHCl_3$) to afford **1** (30 mg, 30%) as a purple solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30–1.50 (m, 4 H, H_a + H_b), 3.16 (s, 4 H, H_e), 3.45 (s, 4 H, H_f), 3.56 (s, 4 H, H_g), 3.62 (s, 4 H, H_h), 3.68 (s, 4 H, H_i), 3.77 (s, 4 H, H_m), 4.03 (s, 4 H, H_j), 5.39 (d, J = 6.0 Hz, 2 H, H_c), 5.53 (d, J = 7.2 Hz, 2 H, H_d), 6.80–6.90 (m, 4 H, H_k), 7.10–7.25 (m, 2 H, H_l), 7.70–7.90 (m, 12 H, Ph-H), 8.10–8.30 (m, 8 H, Ph-H), 9.05–9.20 (m, 8 H, β-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 155.9, 147.5, 147.1, 141.2, 141.0, 135.2, 135.1, 135.0, 132.8, 132.7, 132.1, 128.7, 128.6, 128.5, 127.2, 127.2, 127.0, 126.5, 126.5, 122.0, 115.1, 115.0, 114.8, 110.6, 110.6, 110.6, 104.1, 103.6, 71.1, 71.0, 70.87, 69.97, 69.94, 69.78, 69.74, 67.9, 67.8, 67.7, 67.6, 66.5, 66.5 ppm. HRMS (ESI): calcd. for $C_{82}H_{74}N_5O_{10}Sn$ [**1**-PF_6]$^+$ 1408.4473; found 1408.448.

Synthesis of 2: A solution of **6** (50 mg, 0.065 mmol) and dibenzo-24-crown-8 (88 mg, 0.20 mmol) in dry $CHCl_3$ (50 mL) was stirred vigorously at room temperature under N_2. To this was added dropwise a solution of **15**-H·PF_6 (54 mg, 0.065 mmol) in dry acetonitrile (5 mL). The reaction mixture was stirred at room temperature overnight. After the solvent had been removed in vacuo, the crude product was purified by column chromatography on basic alumina ($CHCl_3$) to afford **2** (25 mg, 21%) as a purple solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20–1.40 (m, 4 H, H_a + H_b), 3.00–3.10 (m, 4 H, –OCH_2CH_2O–), 3.15–3.30 (m, 8 H, –OCH_2CH_2O–), 3.45–3.65 (m, 14 H, –OCH_2CH_2O–), 3.70–3.80 (m, 6 H, –OCH_2-CH_2O–), 3.80–4.00 (m, 12 H, –OCH_2CH_2O–), 4.10–4.20 (m, 4 H, H_j), 4.20–4.30 (m, 4 H, H_m), 5.35–5.55 (m, 4 H, H_d + H_c), 6.35–6.41 (m, 2 H, H_k), 6.47–6.50 (m, 2 H, H_l), 6.66–6.70 (m, 2 H, H_k), 6.87–7.10 (m, 10 H, H_l + Ph-H), 7.78–7.90 (m, 12 H, Ph-H), 8.09–8.20 (m, 4 H, Ph-H), 8.30–8.40 (m, 4 H, Ph-H), 9.04–9.16 (m, 8 H, β-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 159.5, 157.3, 156.1, 156.0, 149.3, 147.7, 147.5, 147.4, 147.3, 147.1, 141.1, 141.1, 141.0, 141.0, 135.3, 135.2, 135.1, 133.1, 133.0, 132.9, 132.8, 132.8, 132.7, 130.9, 130.7, 128.7, 128.6, 128.6, 127.3, 127.2, 126.5, 124.0, 122.0, 121.9, 121.8, 121.8, 115.1, 115.0, 114.8, 114.6, 113.0, 112.7, 110.6, 110.5, 104.0, 103.6, 71.1, 70.9, 70.8, 70.5, 70.3, 70.0, 69.8, 69.7, 69.6, 69.3, 69.2, 68.4, 68.4, 68.1, 67.7, 67.6, 66.7, 66.5 ppm. HRMS (ESI): calcd. for $C_{106}H_{106}N_5O_{18}Sn$ [**2**-PF_6]$^+$ 1856.6579; found 1856.649.

Synthesis of 3: A solution of **9** (60 mg, 0.05 mmol) in dry $CHCl_3$ (50 mL) was stirred vigorously at room temperature under N_2. To this was added dropwise a solution of **15**-H·PF_6 (45 mg, 0.05 mmol) in dry acetonitrile (5 mL). The reaction mixture was stirred at room temperature overnight. After the solvent had been removed in vacuo, the crude product was purified by column chromatography on basic alumina ($CHCl_3$) to afford **3** (25 mg, 25%) as a purple solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20–1.43 (m, 4 H, H_a + H_b), 2.80–4.83 (m, 48 H, –OCH_2CH_2O–), 4.50–4.90 (m, 2 H, H_m), 5.19–5.60 (m, 4 H, H_d + H_c), 6.85–7.00 (m, 6 H, H_k + Ph-H), 7.10 (d, J = 8.4 Hz, 2 H, H_l), 7.14 (d, J = 8.4 Hz, 1 H, Ph-H), 7.33 (d, J = 8.4 Hz, 2 H, H_k), 7.55 (d, J = 8.4 Hz, 2 H, H_l), 7.75–7.90 (m, 11 H, Ph-H), 8.12–8.14 (m, 2 H, Ph-H), 8.34–8.45 (m, 4 H, Ph-H), 8.90–9.22 (m, 8 H, β-H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 161.2, 160.1, 159.1, 158.4, 158.4, 148.3, 148.1, 148.0, 147.2, 147.8, 147.6, 141.5, 141.4, 141.3, 135.8, 135.7, 135.6, 135.5, 133.8, 133.7, 133.0, 132.7, 132.2, 132.1, 131.9, 131.0, 129.8, 129.7, 128.3, 128.2, 128.2, 127.5, 123.0, 122.7, 122.1, 116.5, 115.9, 111.0, 108.8, 107.0, 103.8, 102.7, 72.1, 71.8, 71.6, 71.4, 71.4, 71.3, 71.2, 71.0, 70.6, 70.3, 70.3, 70.1, 68.9, 68.7, 68.3, 67.6, 67.4 ppm. HRMS (ESI): calcd. for $C_{100}H_{100}N_5O_{18}Sn$ [**3**-PF_6]$^+$ 1778.6107; found 1778.612.

Supporting Information (see footnote on the first page of this article): Experimental procedures and characterization for all compounds, absorption spectra and emission spectra of porphyrin derivatives.

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