

Functionally Layered Dendrimers: A New Building Block and its Application to the Synthesis of Multichromophoric Light Harvesting Systems

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Supporting Information

Experimental

General Methods: ¹H and ¹³C NMR spectra were recorded on a Bruker AMX 300 (¹H: 300 MHz, ¹³C: 75 MHz), Bruker AM-400 (¹H: 400 MHz, ¹³C: 100 MHz) or a Bruker DRX 500 (¹H: 500 MHz, ¹³C: 125 MHz) spectrometer with TMS as internal standard. SEC measurements were performed on a Waters 150CV plus SEC system equipped with a differential refractive index detector and a M486 UV detector (254 nm detection wavelength) using THF as the mobile phase at 45 °C and a flow rate of 1 mL/min. The samples were separated through four 5 µm PL Gel columns (Polymer Laboratories) with porosities of 100 Å, 500 Å, 1000 Å and mixed C. The columns were calibrated with 18 narrow polydispersity polystyrene samples. MALDI-TOF mass spectra were measured on a Perseptive Biosystems Voyager-DE spectrometer in delayed extraction mode and an acceleration voltage of 20 keV. Samples were prepared using a 1:20 ratio of analyte (5 mg/mL in THF) to matrix solution (a saturated solution of α-cyano-4-hydroxycinnamic acid in THF). Absorption spectra were recorded in THF on a Cary 50 UV-Visible Spectrophotometer. Fluorescence spectra were measured of nitrogen saturated solutions (1cm cells, OD_{max} < 0.1) using an ISA/SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, double excitation and double emission monochromators, and a digital photon-counting photomultiplier. Correction for variations in lamp intensity over time and

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wavelength was achieved with a solid-state silicon photodiode as the reference. The spectra were further corrected for variations in photomultiplier response over wavelength and for the path difference between the sample and the reference by multiplication with emission correction curves generated on the instrument. Polystyrene bound carbodiimide (PS-carbodiimide) was purchased from Argonaut Technologies and contained a loading of 1.28 mmol/g of carbodiimide functionality.

Preparation of G2-(Acetonide)₃₂[Cou]₁₆[Naph]₈TPP 1: Porphyrin **12** (0.0050 g, 0.00095 mmol), Coumarin monomer **9** (0.011 g, 0.027 mmol), DMAP (0.0035 g, 0.028 mmol), and DPTS (0.0083 g, 0.028 mmol) were dissolved in 200 μ L of pyridine. PS-carbodiimide (0.024 g, 0.027 mmol) was added and the solution was stirred overnight. The reaction progress was monitored by MALDI-TOF spectrometry, and if the reaction did not achieve completion after overnight stirring, the mixture was filtered through a fritted funnel, the solvent evaporated, and the residue resubjected to the reaction conditions. When the reaction was complete, the crude product was purified by filtration, evaporation of the solvent, and chromatography by preparative TLC using 2:1 CH₂Cl₂:THF mobile phase, giving 0.0049 g of pure **2** (43% yield). **2**: ¹H NMR (500 MHz, THF, 25 °C, TMS): δ 8.93 (s, 16H, Cou NH), 8.83 (s, 8H, beta H), 8.63 (s, 16H, Cou vinyl), 7.81-7.11 (broad m, 124H, cou, naph, and TPP aromatic peaks), 6.87 (m, 12H, naph vinyl and TPP Ar-H), 4.50 (broad m, 96H, -CH₂CONH-, all CH₂O₂C-), 4.48 (d, ²J(H,H) = 12 Hz, 32H, CH₂OC(CH₃)₂), 3.86 (d, ²J(H,H) = 12 Hz, 32H, CH₂OC(CH₃)₂), 2.60 (m, 96H, all α -hydrogens), 1.46 (s, 48H, CH₃), 1.36 (s, 48H, CH₃). SEC (polystyrene standards): M_n = 10350, M_w = 10655, PDI = 1.02. MALDI-MS: Calcd for C₅₅₈H₅₅₈F₂₄N₂₈O₂₁₆ *m/z* 11928.74. Found *m/z* 11930.88. UV/Vis (ϵ), CHCl₃: 294.9 (232000), 337.9 (165000), 423.0 (251000), 518.0 (14000), 551.0 (4970), 589 (4850), 645.0 (2250).

Preparation of Naphthopyranone-OH 2: 2,7-Naphthalenediol (13.30 g, 83.0 mmol) and ethyl trifluoroacetoacetate (22.93 g, 124.5 mmol) were added to a 500 mL round bottom flask cooled to 0 °C. Chilled concentrated sulfuric acid (83 mL) was added, and the resulting red solution was stirred for 4 h. The reaction mixture was poured into 500 mL of ice water, and the green precipitate was collected by filtration. Recrystallization of

the crude product from 600 mL of ethanol afforded 16.29 g of **2** as a green solid (70.0% yield). **2**: ^1H NMR (500 MHz, DMSO, 25 °C, TMS): δ 10.35 (s, 1H, -OH), 8.17 (d, $^2J(\text{H,H}) = 9$ Hz, 1H, Ar-H), 7.95 (d, $^2J(\text{H,H}) = 8$ Hz, 1H, Ar-H), 7.67 (s, 1H, Ar-H), 7.37 (d, 1H, $^2J(\text{H,H}) = 9$ Hz, Ar-H), 7.19 (dd, $^2J(\text{H,H}) = 8$ Hz, $^2J(\text{H,H}) = 3$ Hz, 1H, Ar-H), 7.13 (s, 1H, vinyl-H); ^{13}C NMR (125 MHz, DMSO): δ 158.3, 157.8, 156.0, 139.8 (q, $^3J(\text{C,F}) = 32$ Hz), 135.37, 131.4, 129.1, 125.2, 122.6 (q, $^2J(\text{C,F}) = 275$ Hz), 116.9 (q, $^4J(\text{C,F}) = 8$ Hz), 114.0, 107.7 (q, $^4J(\text{C,F}) = 8$ Hz). Anal. Calcd for $\text{C}_{14}\text{H}_7\text{O}_3\text{F}_3$: C, 60.01; H, 2.52; F, 20.34. Found: C, 59.84; H, 2.37; F, 20.09.

Preparation of Naphthopyranone-CO₂tBu 3: Naphthopyranone **2** (6.00 g, 21.4 mmol) was dissolved in 15 mL of DMF at 60 °C. Upon addition of K_2CO_3 (5.92 g, 42.8 mmol), the reaction mixture turned red. *t*-Butyl bromoacetate (4.11 mL, 27.8 mmol) was added, and the mixture returned to a greenish yellow color while stirring overnight. The solution was cooled to rt, and the product precipitated from solution. The green solids were collected by filtration and were washed with 100 mL of water. The crude product was recrystallized from 100 mL of ethanol to give 5.897 g of pure **3** as small green needles (69.9% yield). **3**: ^1H NMR (500 MHz, CDCl_3 , 25 °C, TMS): δ 8.00 (d, $^2J(\text{H,H}) = 9$ Hz, 1H, Ar-H), 7.84 (d, $^2J(\text{H,H}) = 8$ Hz, 1H, Ar-H), 7.72 (d, $^2J(\text{H,H}) = 2$ Hz, 1H, Ar-H), 7.37 (d, $^2J(\text{H,H}) = 9$ Hz, 1H, Ar-H), 7.15 (dd, $^2J(\text{H,H}) = 9$ Hz, 2 Hz, 1H, Ar-H), 7.01 (s, 1H, vinyl-H) 4.68 (s, 2H, OCH_2 -), 1.51 (s, 9H, CH_3). ^{13}C NMR (125 MHz, DMSO): δ 167.4, 158.8, 158.0, 156.3, 141.2 (q, $^3J(\text{C,F}) = 32$ Hz), 135.1, 131.1, 129.1, 126.8, 126.6 (q, $^2J(\text{C,F}) = 276$ Hz), 118.1, 116.6 (q, $^4J(\text{C,F}) = 8$ Hz), 115.3, 108.6, 106.2 (q, $^4J(\text{C,F}) = 8$ Hz), 82.8, 65.3, 28.0. Anal. Calcd for $\text{C}_{20}\text{H}_{17}\text{O}_5\text{F}_3$: C, 60.92; H, 4.35; F, 14.45. Found: C, 61.05; H, 4.46; F, 14.61.

Preparation of Naphthopyranone-CO₂H 4: Naphthopyranone **3** (5.00 g, 12.6 mmol) was dissolved in 26 mL. Trifluoroacetic acid (2.5 mL) was added, and the solution was stirred under nitrogen. After 3 hours, the product acid began to precipitate from solution. The cloudy solution was stirred under nitrogen for two days. The precipitate was isolated by filtration and was recrystallized from 100 mL of ethanol to give 4.21 g of **4** as extremely fluffy yellow crystals (98.2% yield). **4**: ^1H NMR (500 MHz, DMSO, 25 °C, TMS): δ 13.21 (broad s, 1H, CO_2H), 8.23 (d, $^2J(\text{H,H}) = 9$ Hz, 1H, Ar-H), 8.05 (d, $^2J(\text{H,H}) = 9$ Hz, 1H, Ar-H), 7.58 (d, $^2J(\text{H,H}) = 2$ Hz, 1H, Ar-H), 7.47 (d, $^2J(\text{H,H}) = 9$ Hz, 1H, Ar-

H), 7.36 (dd, $^2J(\text{H,H}) = 9 \text{ Hz}$, 2 Hz, 1H, Ar-H), 7.17 (s, 1H, vinyl-H), 4.82 (s, 2H, CH_2). ^{13}C NMR (125 MHz, DMSO): δ 169.7, 158.2, 157.6, 156.0, 139.2 (q, $^3J(\text{C,F}) = 31 \text{ Hz}$), 135.4, 131.4, 128.4, 126.3, 124.0 (q, $^2J(\text{C,F}) = 275 \text{ Hz}$), 117.7 (q, $^4J(\text{C,F}) = 9 \text{ Hz}$), 117.0, 115.3, 107.9, 106.2 (q, $^4J(\text{C,F}) = 9 \text{ Hz}$). Anal. Calcd for $\text{C}_{16}\text{H}_9\text{O}_5\text{F}_3$: C, 56.82; H, 2.68; F, 16.85. Found: C, 57.02; H, 2.83; F, 16.66.

Preparation of (Acetonide)[Naph]-OH 6: 1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (1.56 g, 8.13 mmol) was added to a solution of 5-amino-5-hydroxymethyl-2,2-dimethyl-1,3-dioxane **5**³ (2.14 g, 1.33 mmol), 1-hydroxybenzotriazole hydrate (1.24 g, 8.13 mmol), and naphthopyranone **8** (2.50 g, 7.39 mmol) in 20 mL of DMF at 0 °C. The mixture was allowed to warm to room temperature while stirring overnight. The reaction mixture was poured in 250 mL ethyl acetate and was washed with 3 x 150 mL of 0.3 M NaHSO_4 , 3 x 150 mL of 0.3 M Na_2CO_3 , and 1 x 150 mL of brine. The organic layer was dried over MgSO_4 , filtered, and the solvent evaporated. Chromatography (silica gel) eluting with 7:93 methanol/dichloromethane afforded 2.10 g of **6** (48.6% yield). **6:** ^1H NMR (500 MHz, CDCl_3 , 25 °C, TMS): δ 8.01 (d, $^2J(\text{H,H}) = 9 \text{ Hz}$, 1H, Ar-H), 7.88 (d, $^2J(\text{H,H}) = 9 \text{ Hz}$, 1H, Ar-H), 7.86 (d, $^2J(\text{H,H}) = 2 \text{ Hz}$, 1H, Ar-H), 7.60 (s, 1H, NH), 7.40 (d, $^2J(\text{H,H}) = 9 \text{ Hz}$, 1H, Ar-H), 7.31 (dd, $^2J(\text{H,H}) = 9 \text{ Hz}$, 2H, 1H, Ar-H), 7.02 (s, 1H, vinyl-H), 4.85 (br s, 1 H, -OH), 4.69 (s, 2H, CH_2CONH), 3.88 (s, 4H, CH_2O), 3.76 (s, 2H, CH_2OH), 1.45 (s, 3H, CH_3), 1.32 (s, 3H, CH_3). ^{13}C NMR (125 MHz, CDCl_3): δ 168.4, 159.1, 156.8, 156.5, 140.4 (q, $^3J(\text{C,F}) = 31 \text{ Hz}$), 135.1, 131.4, 129.2, 127.2, 125.4 (q, $^2J(\text{C,F}) = 267 \text{ Hz}$), 117.2, 116.9 (q, $^4J(\text{C,F}) = 9 \text{ Hz}$), 116.0, 109.4, 108.3 (q, $^4J(\text{C,F}) = 9 \text{ Hz}$), 99.0, 67.3, 64.6, 63.7, 55.4, 28.1, 18.7. Calcd for $\text{C}_{23}\text{H}_{22}\text{F}_3\text{NO}_7$ $m/z = 482.143540$. Found $m/z = 482.142662$.

Preparation of (Acetonide)[Naph]-CO₂H 7: DMAP (0.051 g, 0.42 mmol) was added to a solution of succinic anhydride (0.106 g, 1.06 mmol) and (Acetonide)[Naph]-OH **6** (0.500 g, 1.04 mmol) in 4 mL acetonitrile. The mixture was refluxed overnight, then cooled back to rt. The solvent was evaporated, and the resulting solid was loaded onto silica gel in the presence of 0.2 mL triethylamine. The dry silica gel was loaded onto a column and was flushed with 300 mL of a 3:1 mixture of CH_2Cl_2 :THF. The product was eluted using a 3:1 CH_2Cl_2 :THF mixture containing 0.2% acetic acid. The solvent was evaporated from the combined column fractions, and the product was redissolved in 300

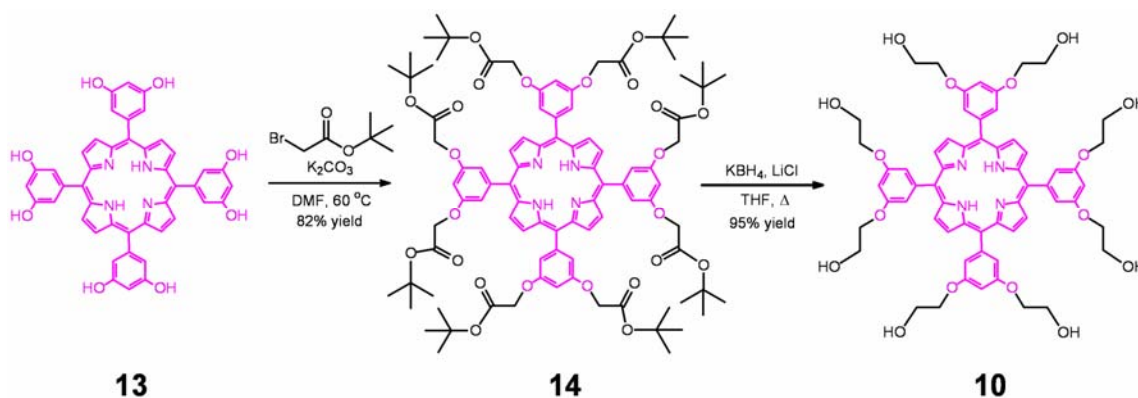
mL ethyl acetate. The ethyl acetate was washed with 3 x 300 mL 0.1 M NaHSO₄, 1 x 150 mL brine, was dried over MgSO₄, and the solvent evaporated to give 0.320 g of **7** as a yellow solid (52.9% yield). **7**: ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 7.98 (d, ²J(H,H) = 9 Hz, 1H, Ar-H), 7.85 (d, ²J(H,H) = 9 Hz, 1H, Ar-H), 7.76 (d, ²J(H,H) = 2 Hz, 1H, Ar-H), 7.36 (d, ²J(H,H) = 9 Hz, 1H, Ar-H), 7.34 (dd, ²J(H,H) = 9 Hz, 2 Hz, 1H, Ar-H), 7.13 (s, 1H, Ar-H), 6.99 (s, 1H, vinyl-H), 4.58 (s, 2H, -CH₂CONH-), 4.56 (s, 2H, -CH₂O₂CCH₂-), 4.36 (d, ²J(H,H) = 12 Hz, 2H, CH₂OC(CH₃)₂), 3.78 (d, ²J(H,H) = 12 Hz, 2H, CH₂OC(CH₃)₂), 2.60 (m, 4H, -O₂CCH₂CH₂CO₂-), 1.41 (s, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 176.4, 172.6, 168.1, 158.7, 157.0, 156.4, 141.1 (q, ³J(C,F) = 31 Hz), 135.1, 131.3, 129.1, 127.1, 125.9 (q, ²J(C,F) = 267 Hz), 117.6, 116.9 (q, ⁴J(C,F) = 9 Hz), 115.9, 108.7, 107.1 (q, ⁴J(C,F) = 9 Hz), 104.9, 99.8, 67.2, 63.6, 62.6, 61.8, 60.4, 53.4, 49.9, 29.2, 28.7, 27.2. Calcd for C₂₇H₂₆F₃NO₁₀ *m/z* = 582.157020 Found *m/z* = 582.158706. UV/Vis (ε), CHCl₃: 287.0 (4970), 359.0 (8620).

Preparation of (Acetonide)[Cou]-OH **8:** 1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide (13.1 g, 68.2 mmol) was added to a solution of **5**³ (10.0 g, 62.0 mmol) and coumarin-3-carboxylic acid (11.8 g, 62.0 mmol) in 300 mL of CH₂Cl₂ at 0 °C. The mixture was allowed to warm to room temperature while stirring overnight. The reaction mixture was washed with 1M NaHSO₄ and brine, dried over MgSO₄, and the solvent evaporated. Chromatography (silica gel, 3% methanol in CH₂Cl₂) afforded 12.50 g of **8** as a white solid (60.5%). **8**: ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 9.82 (broad s, 1 H, NH), 8.91 (s, 1H, HC=C), 7.70 (m, 2H, aryl), 7.42 (m, 2H, aryl), 5.10 (t, ³J(H,H) = 7 Hz, 1 H, OH), 3.98 (d, ²J(H,H) = 11 Hz, CHHO), 3.94 (d, ²J(H,H) = 11 Hz, CHHO), 3.81 (d, ³J(H,H) = 7 Hz, 2 H, CH₂OH), 1.52 (s, 3H, CH₃), 1.49 (s, 3H, CH₃); ¹³C NMR (125 MHz, CDCl₃): δ 162.3, 161.3, 154.6, 148.7, 134.4, 129.9, 125.4, 118.5, 118.4, 116.7, 99.0, 64.4, 55.9, 27.4, 19.7. Anal. Calcd for C₁₇H₁₉O₆N: C, 61.25; H, 5.75; N, 4.20. Found: C, 61.07; H, 5.67; N, 3.99.

Preparation of (Acetonide)[Cou]-CO₂H **9:** DMAP (0.18 g, 1.5 mmol) was added to a solution of **9** (5.00 g, 15.0 mmol) and succinic anhydride (1.58 g, 15.8 mmol) in 125 mL of acetonitrile and was refluxed for 18 h. The mixture was cooled, and the solvent evaporated. Chromatography (silica gel, 5% methanol in CH₂Cl₂) afforded 3.18 g of **9** as a white solid (49% yield). **9**: ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 9.00 (broad s,

1 H, NH), 8.87 (s, 1 H, HC=C), 7.69 (m, 2H, aryl), 7.41 (m, 2H, aryl), 4.65 (s, 2 H, CH₂O₂C), 4.29 (d, ²*J*(H,H) = 12 Hz, 2 H, CHHO), 3.96 (d, ²*J*(H,H) = 12 Hz, 2 H, CHHO), 2.66 (m, 4 H, CH₂CH₂CO₂H), 1.52 (s, 3 H, CH₃), 1.44 (s, 3 H, CH₃); ¹³C NMR (125 MHz, CDCl₃): δ 175.6, 171.6, 161.7, 161.5, 148.5, 134.3, 129.9, 125.4, 118.6, 118.5, 116.7, 98.9, 63.4, 62.7, 53.2, 28.9, 28.6, 24.2, 22.8. HRMS (FAB): Calcd for C₂₁H₂₃NO₉ *m/z* = 434.1451. Found *m/z* = 434.1461. UV/Vis (ε), CHCl₃: 290.0 (15600), 326.0 (8930).

Scheme 1. Synthesis of Porphyrin 10.



Preparation of tetrakis(3,5-bis(2'-hydroxy-1'-ethoxy)phenyl)porphyrin 10:

Porphyrin **14** (0.300 g, 0.181 mmol) was dissolved in 10.0 mL THF and heated to reflux. KBH₄ (0.156 g, 2.90 mmol) and LiCl (0.123 g, 2.90 mmol) were added and the mixture was stirred for 7 hours. The reaction was monitored by MALDI-TOF MS. When complete, the reaction mixture was poured into 20 mL THF, which was washed with 3 x 10 mL of a 4:1 mixture of brine and 1M NaHSO₄, 15 mL of a 4:1 mixture of brine and 1M Na₂CO₃, and 15 mL of brine. Drying over MgSO₄ followed by evaporation of the solvent gave 0.189 g of **10** (95.4% yield). **10**: ¹H NMR (400 MHz, *d*₃-MeOD, 25 °C, TMS): δ 9.0 (broad s, 8H, β H), 7.42 (d, ⁴*J*(H,H) = 2 Hz, 8H, *o*-aryl H), 6.99 (t, ⁴*J*(H,H) = 2 Hz, 4H, *p*-aryl H), 4.18 (m, 16H, TPP-OCH₂-), 3.89 (m, 16H, TPP-OCH₂CH₂-). HRMS (FAB): Calcd for C₆₀H₆₂N₄O₁₆ *m/z* = 1094.4161. Found *m/z* = 1094.4174.

Preparation of G1-(Acetonide)₈[Naph]₈TPP 11: PS-carbodiimide (0.086 g, 0.097 mmol) was added to a solution containing porphyrin **10** (0.035 g, 0.032 mmol),

naphthopyranone monomer **7** (0.225 g, 0.386 mmol), DMAP (0.012 g, 0.097 mmol), and DPTS (0.019 g, 0.064 mmol) in 1.6 mL pyridine. The reaction progress was monitored by MALDI-TOF spectrometry, and when complete, the mixture was filtered through a fritted funnel and the solvent was evaporated under high vacuum. Chromotography (silica gel) of the crude reaction mixture using 2:1 CH₂Cl₂:THF afforded pure **11** (0.150 g, 83.3% yield) in the early fractions as an amorphous purple solid. **11**: ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 8.82 (s, 8H, beta-H), 7.62 (m, 8H, Naph Ar-H), 7.61 (m, 8H, NH), 7.58 (s, 8H, Naph Ar-H), 7.32 (d, ²J(H,H) = 2 Hz, 8H, Naph Ar-H), 7.23 (dd, ²J(H,H) = 9 Hz, 3 Hz, 8H, Naph Ar-H), 7.03 (s, 8H, TPP Ar-H), 6.96 (d, ²J(H,H) = 9 Hz, 8H, Naph Ar-H), 6.86 (m, 12H, Naph vinyl and TPP Ar-H), 4.55 (s, 16H, -CH₂CONH-), 4.47 (s, 16H, -CH₂O₂CCH₂-), 4.42 (m, 16H, TPP-OCH₂-), 4.34 (d, ²J(H,H) = 12 Hz, 16H, CH₂OC(CH₃)₂), 4.20 (m, 16H, TPP-OCH₂CH₂O-), 3.76 (d, ²J(H,H) = 12 Hz, ²J(H,H) = 12 Hz, CH₂OC(CH₃)₂), 2.65 (m, 32H, -O₂CCH₂CH₂CO₂-), 1.38 (s, 24H, CH₃), 1.36 (s, 24H, CH₃). MALDI-MS: Calcd for C₂₇₆H₂₅₄F₂₄N₁₂O₈₈ *m/z* 5602.96. Found *m/z* 5604.02. UV/Vis (ε), CHCl₃: 286.9 (41200), 364.0 (75900), 423.0 (255000), 516.0 (11400), 551.0 (2400), 591.0 (2470), 649.9 (1180).

Preparation of G1-(OH)₁₆[Naph]₈TPP **12:** Porphyrin **11** (0.080 g, 0.014 mmol) was added to a 10 mL round bottom flask. 1.2 mL of acetonitrile was added, and the mixture was heated to 60 °C. 0.34 mL of a borate buffer (pH 7, 20 mM) was added dropwise, after which the porphyrin remained undissolved. THF (0.1 mL) and cerium ammonium nitrate (0.0040 g, 0.0073 mmol) were added and the solution was stirred for five hours. The reaction progress was monitored by MALDI-TOF spectrometry, and when complete, the reaction mixture was poured in 20 mL THF. The THF was washed with 2 x 10 mL saturated NaHCO₃, 10 mL brine, was dried over MgSO₄, filtered and the solvent evaporated to give **12** (0.049 g, 59.6% yield) as an amorphous purple solid. **12**: ¹H NMR (500 MHz, THF, 25 °C, TMS): δ 8.86 (s, 8H, beta-H), 7.71 (m, 24H, Naph Ar-H, NH), 7.38 (d, ²J(H,H) = 2 Hz, 8H, Naph Ar-H), 7.22 (dd, ²J(H,H) = 9 Hz, 2 Hz, 8H, Naph Ar-H), 7.05 (d, ²J(H,H) = 9 Hz, 8H, Naph Ar-H), 6.99 (s, 8H, TPP Ar-H), 6.95 (m, 12 H, TPP Ar-H and Naph vinyl-H), 4.52 (s, 16H, -CH₂CONH-), 4.44 (m, 16H, TPP-OCH₂-), 4.33 (d, ²J(H,H) = 12 Hz, 32H, CH₂OC(CH₃)₂, TPP-OCH₂CH₂O-), 3.72 (m, 16H,

CH₂OH), 3.64 (m, 16H, CH₂OH), 2.55 (m, 32H, -O₂CCH₂CH₂CO₂-). MALDI-MS: Calcd for C₂₅₂H₂₂₂F₂₄N₁₂O₈₈ *m/z* 5282.45. Found *m/z* 5274.93.

Preparation of 5,10,15,20-Tetrakis(3',5'-dihydroxyphenyl)porphyrin 13.³ 5,10,15,20-Tetrakis(3',5'-dimethoxyphenyl)porphyrin¹ (1.50 g, 1.75 mmol) was dissolved in 250 mL of dry CH₂Cl₂ and the solution was cooled to 0 °C. Boron tribromide (17.0 mL of a 0.91 M solution in CH₂Cl₂, 15.4 mmol) was added over a period of 0.5 h. It was stirred at rt for additional 24 h. Excess reagent was quenched with methanol, 5 mL of triethylamine and 200 mL of water were added, and the mixture was stirred for 18 h. Evaporation of the organic solvent followed by addition of water and filtration afforded the desired product as purple crystals (1.30 g, 100%). Characterization was in agreement with the literature.³

Preparation of Tetrakis{di-*t*-butyl 2,2'-[(3,5-phenylene)bis(oxy)]diacetate}porphyrin 14: Porphyrin **13** (0.200 g, 0.269 mmol) and *t*-butyl bromoacetate (0.48 mL, 3.23 mmol) were added to 0.5 mL of DMF. Potassium carbonate (0.595 g, 4.31 mmol) was added and the mixture was heated to 60 °C and stirred for six hours. The course of the reaction was monitored by MALDI-TOF mass spectrometry. After the reaction was complete, the reaction mixture was poured into 30 mL of ethyl acetate. The ethyl acetate mixture was filtered through celite and washed with 3 x 25 mL 1M NaHSO₄, brine, dried over MgSO₄, and the solvent evaporated. Chromatography (silica gel) eluting with 15:85 ethyl acetate/hexanes gradually increasing to 50:50 ethyl acetate/hexanes afforded 0.366 g of **14** (82.2%). **14**: ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS): δ 8.88 (s, 8H, β H), 7.38 (d, 8H, *o*-aryl H, ⁴*J*(H,H) = 2 Hz), 6.96 (t, 4H, *p*-aryl H, (H,H) = 2 Hz), 4.67 (s, 16H, -OCH₂CO₂-), 1.43 (s, 72H, CH₃), -2.93 (s, 2H, NH). HRMS (FAB): Calcd for C₉₂H₁₁₀N₄O₂₄ *m/z* = 1654.7510. Found *m/z* = 1654.7513.

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