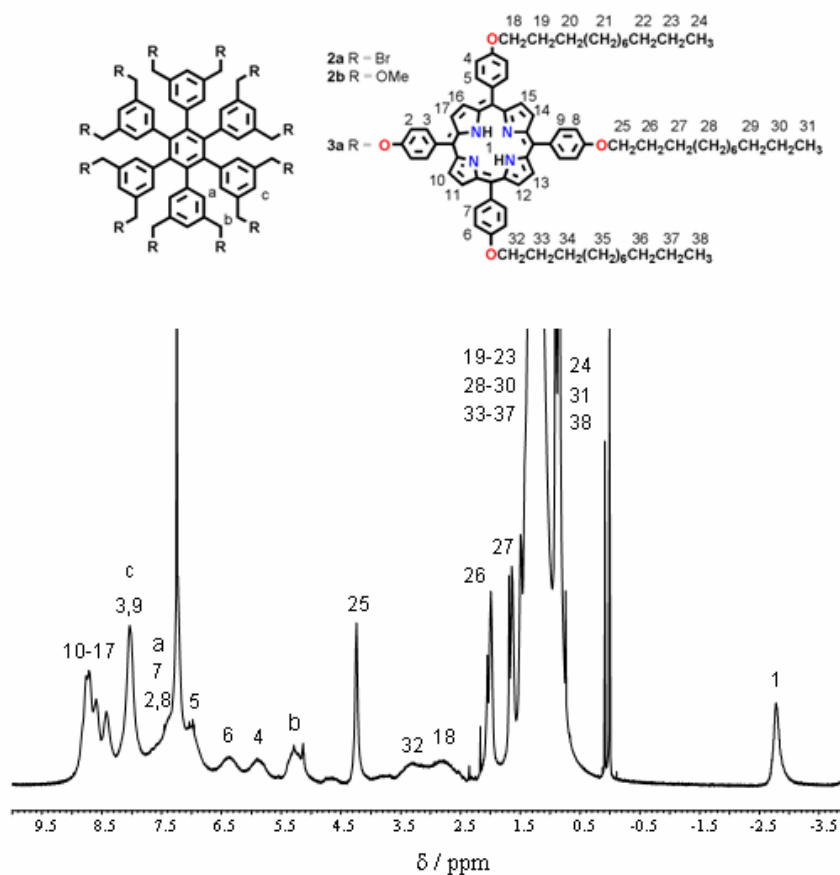


Supporting information

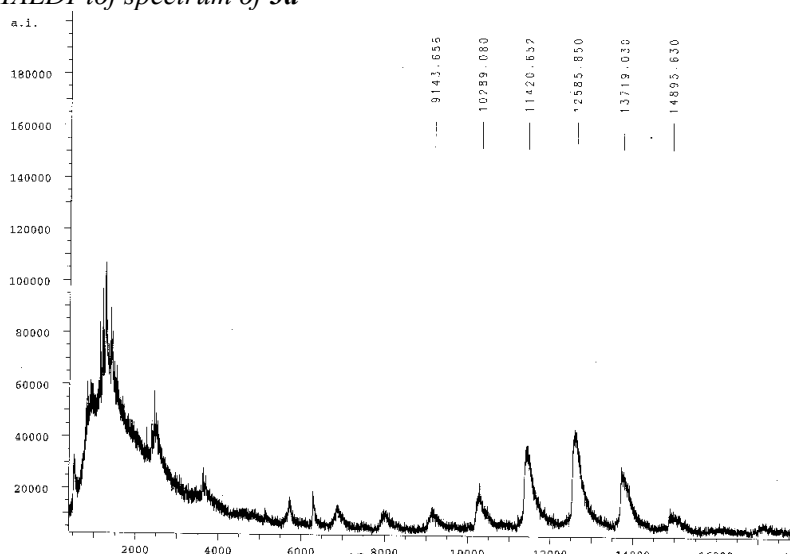
Synthesis of **3a**

To a solution of **1** (180 mg, 152 μmol) in 10 mL of distilled DMF, **2** (10.7 mg, 6.53 μmol) was added. During 1.5 hrs nitrogen was led through the solution. The solution was heated to 90 $^{\circ}\text{C}$ and potassium carbonate (133 mg, 961 μmol) was added. The reaction mixture was heated to 130 $^{\circ}\text{C}$ and stirred for 3 days after which the reaction was stopped and the DMF was evaporated. The product was purified by chromatography using a silica column (size 0.035 mm – 0.070 mm, pore size 6 nm, eluent 5% methanol in chloroform) and subsequently by size exclusion column chromatography (eluent dichloromethane). The first fraction was the product. Yield: 0.053 g (3.59 μmol , 55%) of **3a** as a purple solid. Mp 127 $^{\circ}\text{C}$. MALDI-TOF MS: calculated for $\text{C}_{1014}\text{H}_{1254}\text{N}_{48}\text{O}_{48}$ 14883; found $m/z = 14896$ g/mol. Elemental analysis: calculated C: 81.83, H: 8.49, N: 4.52; found C: 81.73, H: 8.46, N: 4.65. ^1H -NMR (CDCl_3 , 500,13 MHz) δ (ppm): 8.75 (bs, 24H, *H17*, *H10*); 8.7 (bs, 24H, *H14*, *H13*); 8.6 (bs, 24H, *H16*, *H15*); 8.4 (bs, 24H, *H12*, *H11*); 8.03 (bs, 6H, *Hc*); 8.0 (bd, 48H, *H9*, *H3*); 7.59 (bs, 12H, *Ha*); 7.4 (bs, 24H, *H7*); 7.2 (bd, 48H, *H8*, *H2*); 7.0 (b, 24H, *H5*); 6.4 (b, 24H, *H6*); 5.9 (b, 24H, *H4*); 5.3 (b, 24H, *Hb*); 4.22 (bt, 24H, *H25*); 3.2 (bt, 24H, *H32*); 2.7 (bt, 24H, *H18*); 1.99 (bq, 24H, *H26*); 1.63 (bm, 24H, *H27*); 1.5-1.0 (b, 192H, *H30*, *H29*, *H28*); 1.5-1.0 (b, 240H, *H37*-*H33*); 1.5-1.0 (b, 240H, *H23*-*H19*); 0.9-0.8 (bt, 36H, *H24*); 0.87 (bt, 36H, *H31*); 0.87 (bt, 36H, *H38*); -2.78 (bs, 24H, *H1*). ^{13}C -NMR (CDCl_3 , 75,47 MHz) δ (ppm): 136 (*C9*, *C3*); 135 (*C7*); 134 (*C5*); 129.0 (*Cc*); 128.2 (*Ca*); 113 (*C2*); 112.6 (*C8*); 111 (*C6*); 110 (*C4*); 70.6 (*Cb*); 68.3 (*C25*); 67.9 (*C32*); 67.4 (*C18*); 32.0 (*C36*, *C29*, *C22*); 29.8 (*C26*); 29.7 (*C35*, *C28*, *C21*); 26.8 (*C27*); 26.5 (*C33*, *C20*, *C19*); 26 (*C34*); 23.0 (*C37*, *C30*, *C23*); 14.1 (*C38*, *C31*, *C24*). UV-vis (CHCl_3) λ/nm , $\log(\epsilon/M^{-1}\text{cm}^{-1})$ 423 (6.6), 520 (5.3), 558 (5.2), 595 (4.8), 653 (4.9). Fluorescence emission 655 nm (excitation at 423 nm).

^1H -NMR spectrum of **3a** and proton designations



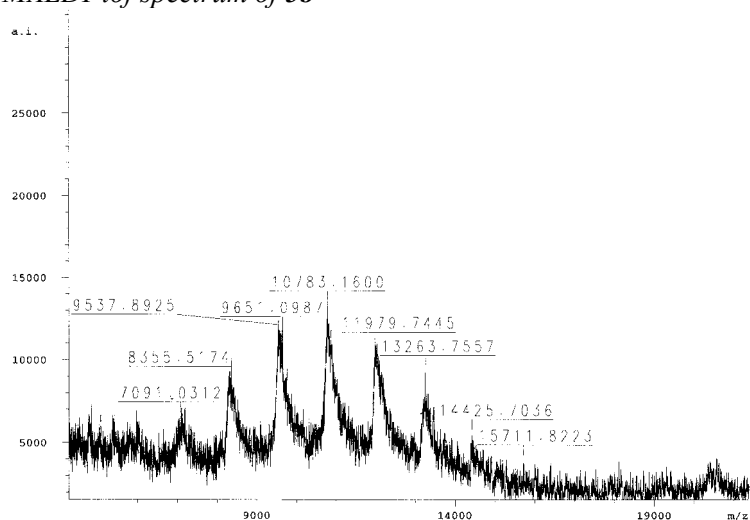
MALDI-tof spectrum of **3a**

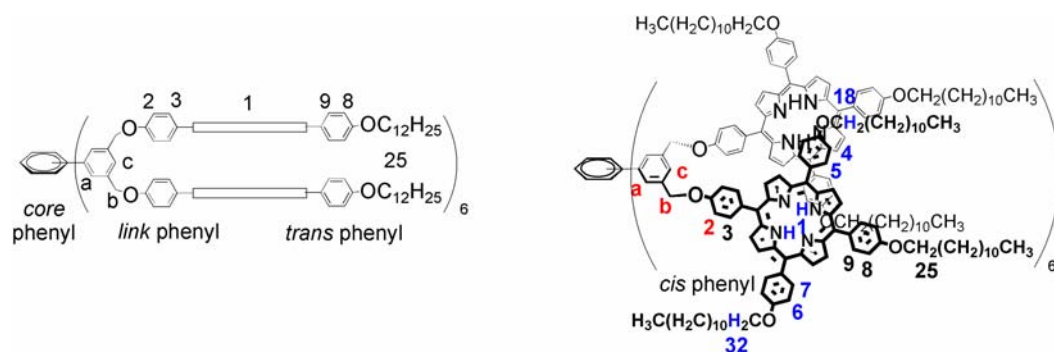


Synthesis of **3b**

To a solution of **3a** (0.012 g, 0.81 μ mol) in chloroform (10 mL) and methanol (5 mL) zinc(II) acetate dihydrate (0.017 g, 75.6 μ mol) was added. The solution was refluxed for 16 hrs. After cooling, the solution was washed with water (3x). The solvent was evaporated and the product was purified on a silica column (size 0.035 mm – 0.070 mm, pore size 6 nm, eluent: 1% methanol, 1% triethylamine in chloroform). Yield: 0.011 g (0.70 μ mol, 86%) of **3b** as a purple solid. Mp 129 °C. MALDI-TOF MS: calculated for $C_{1014}H_{1230}N_{48}O_{48}Zn_{12}$ 15644; found $m/z = 15712$ g/mol. Elemental analysis: calculated C: 77.85, H: 7.92, N: 4.30; found C: 77.68, H: 8.22, N: 4.16. 1H -NMR ($CDCl_3$, 300,13 MHz) δ (ppm): 8.7 (bs, 48H, *H17*, *H10*, *H14*, *H13*); 8.6 (bs, 24H, *H16*, *H15*); 8.4 (bs, 24H, *H12*, *H11*); 7.99 (bs, 6H, *Hc*); 7.97 (bd, 48H, *H9*, *H3*); 7.62 (bs, 12H, *Ha*); 7.51 (bs, 24H, *H7*); 7.23 (bd, 24H, *H2*); 7.22 (bd, 24H, *H8*); 7.16 (b, 24H, *H5*); 6.5 (b, 24H, *H6*); 6.1 (b, 24H, *H4*); 5.3 (b, 24H, *Hb*); 4.24 (bt, 24H, *H25*); 3.4 (bt, 24H, *H32*); 3.0 (bt, 24H, *H18*); 1.98 (bq, 24H, *H26*); 1.67 (bm, 24H, *H27*); 1.5-1.0 (b, 192H, *H30*, *H29*, *H28*); 1.5-1.0 (b, 240H, *H37-H33*); 1.5-1.0 (b, 240H, *H23-H19*); 0.87 (bt, 108H, *H38*, *H31*, *H24*). ^{13}C -NMR ($CDCl_3$, 75,47 MHz) δ (ppm): 135 (*C9*, *C3*, *C7*, *C5*); 132 (*Cc*); 120 (*Ca*); 113 (*C2*); 112.5 (*C8*); 112 (*C6*, *C4*); 68.3 (*Cb*); 68.0-67.4 (*C25*, *C32*, *C18*); 31.9 (*C36*, *C29*, *C22*); 29.6 (*C26*); 29.4 (*C35*, *C28*, *C21*); 26.3 (*C27*); 26.0 (*C33*, *C20*, *C19*, *C34*); 22.7 (*C37*, *C30*, *C23*); 14.1 (*C38*, *C31*, *C24*). UV-vis ($CHCl_3$) λ /nm, log ($\epsilon/M^{-1}cm^{-1}$) 424 (6.7) 522 (5.6) 580 (5.1). Fluorescence emission 610 nm (excitation at 424 nm).

MALDI-tof spectrum of **3b**

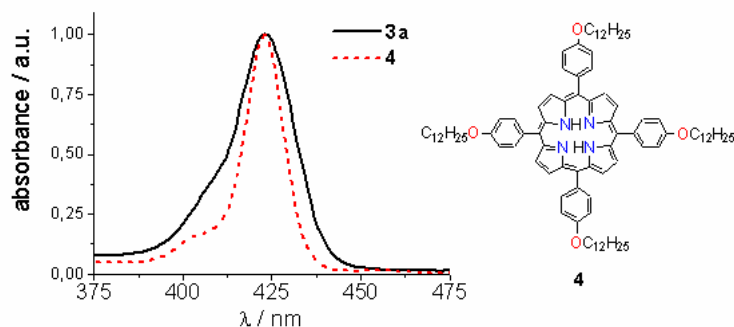




¹H-NMR shifts (ppm) of **1**, **2b**, **3a** and **3b** and the $\Delta\delta$ values

	1	2b (OMe)	3a	3b	$\Delta\delta$ (3a-1)	$\Delta\delta$ (3a-2b)
NH H1	-2.65	-	-2.78	-	-0.13	-
Core Ha	-	6.83 (6.70)	7.59	7.62	-	+0.76 (+0.89)
Core Hc	-	6.90 (6.61)	8.03	7.99	-	+1.13 (+1.43)
Benzyl Hb	-	4.17 (3.99)	5.3	5.3	-	+1.13 (+1.31)
link phenyl H2	6.86	-	7.2	7.23	+0.34	-
link phenyl H3	7.91	-	8.0	7.97	+0.09	-
Cis phenyl H4/H6	7.14	-	5.9/ 6.4	6.1 / 6.5	-1.24/ -0.74	-
Cis phenyl H5/H7	8.01	-	7.0 / 7.4	7.16 / 7.51	-1.01/ -0.61	-
trans phenyl H8	7.17	-	7.2	7.22	+0.03	-
trans phenyl H9	8.04	-	8.0	7.97	-0.04	-
OCH₂ cis H18/H32	4.11	-	2.7 / 3.2	3.0 / 3.4	-1.43 / -0.91	-
OCH₂ trans H25	4.13	-	4.22	4.24	+0.11	-

UV/Vis-spectrum of **3a** and reference porphyrin **4**



Experimental procedure for UV/Vis- and ¹H-NMR titrations of **3b** with DABCO

For the UV/Vis-titration a stock solution A of **3b** in chloroform (0.14 μ M) was prepared. This stock solution was used to make a solution B of DABCO in 40-fold excess (5.4 μ M) with respect to **3b**. Aliquots of 10, 25 and 50 μ L of solution B were added to 1.40 mL of solution A in a quartz cuvette and the UV/Vis-absorption spectrum was recorded after each addition on a Varian Cary 50 spectrophotometer.

For the ¹H-NMR titration 5.4 mg (0.35 μ mol) of **3b** was dissolved in 500 μ L of CDCl₃ (0.69 mM). To this solution, aliquots of 10 μ L of a DABCO solution in CDCl₃ (3.9 mg in 1 mL) were added, each corresponding to 1 equiv. of DABCO with respect to **3b**. ¹H-NMR spectra were recorded after each addition on a Bruker AMX 500 MHz instrument.

STM procedure

STM measurements were carried out in the constant current mode using a home-built low-current STM. For each experiment the HOPG surface was freshly cleaved and the STM tips were mechanically cut from a Pt:Ir (80:20) wire. A drop of a nearly saturated solution of molecules or complexes in 1-phenyloctane was brought to the surface. Typically, an STM image (1024 lines \times 1024 points) was recorded over a period of 10 minutes. All STM experiments were carried out at least in

duplicate, and the raw data were processed only by the application of a background flattening. Before and after the experiments the piezo was calibrated *in situ* by lowering the bias voltage to 100 mV and raising the tunnelling current to 50 pA, which allowed imaging of the HOPG surface underneath the molecules.