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Supporting Information

Molecular brakes based on Zn(II) porphyrin dimer

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Experimental section

General procedures. Solvents were dried using standard techniques: CH_2Cl_2 and $CHCl_3$ were distilled over CaH_2. All air and water sensitive experiments were carried out under argon atmosphere using standard vacuum line techniques. All chemicals were obtained commercially and used without further purification, except pyrrole, which was purified over an alumina column before use.

^1H, ^{13}C NMR spectra were acquired on either a Bruker AV 300 (300MHz) or a Bruker AV 400 (400 MHz) spectrometer, with a deuterated solvent as the lock and residual solvent as the internal reference. Absorption spectra were recorded using either a Lambda 650S spectrophotometer (PerkinElmer) or an Evolution 210 spectrophotometer (Thermo Scientific). A MicroTOF-Q LC (Bruker Daltonics, Bremen) spectrometer equipped with an electrospray source was used for the high-resolution electrospray mass spectrometry measurements (HR ESI-MS). BioRad Bio Beads S-X3 gel was used for the gel-permeation chromatography (GPC).

X-ray diffraction data for **D-DMAP** and **D-H** were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N2 device, using a molybdenum microfocus sealed tube generator with mirror-monochromated Mo-Kα radiation (λ = 0.71073 Å), operated at 50 kV/600 mA. The diffraction data were corrected for absorption. Structures were solved using SHELXS-97[1] and refined by full matrix least-squares on F2 using SHELXL-2014[2]. The hydrogen atoms were introduced at calculated positions and not refined (riding model).

X-ray diffraction data for **D-DMSO** were collected at 100(2) K on a Bruker KAPPA APEX II automatic four-circle diffractometer with area detector using a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The unit cell parameters were refined over the whole dataset.[3] The diffraction data were corrected for absorption using SADABS program.[4] The structure was solved using SHELXS97[1] and refined by full matrix least-squares on F2 using SHELXL-2014[2] in the anisotropic approximation for all nonhydrogen atoms. Olex2 was used as GUI for refinement.[5] The hydrogen atoms were placed in the geometrically calculated positions with the isotropic temperature factors equal to 1.2- (CH group) or 1.5-fold (CH_3 group) equivalent isotropic temperature factor of the C atom to which they are bound and not refined.

Synthesis. 5-(2-(trimethylsilyl)ethynyl)-10,15,20-triphenylporphyrin and 5-ethynyl-10,15,20-triphenylporphyrin were synthesized following described procedures.[6–8] Dimer **D** was obtained using Pd-catalyzed Cu-free coupling reaction.[9] The handles **H1** and **H2** was synthesized following described technique.[10]

5-(2-(trimethylsilyl)ethynyl)-10,15,20-triphenylporphyrin (1). Trifluoroboron etherate (0.14 ml, 1.23 mmol, 0.18 eq.) was added to a mixture of pyrrole (1.18 ml, 17 mmol, 2.5 eq.), benzaldehyde (1.04 ml, 10.2 mmol, 1.5 eq.) and (trimethylsilyl)propiolaldehyde (1 ml, 6.8 mmol, 1 eq.) in chloroform (1.5 L). The reaction mass was stirred at room temperature for 6 h in the dark. DDQ (1.93 g, 8.5 mmol, 1.25 eq.) was added and the resulting mixture was further stirred for 1 h. The solvent was evaporated to dryness under reduced pressure. The desired porphyrin was separated from the crude residue by column chromatography (silica gel, eluting with dichloromethane-cyclohexane mixture 3:7). The 5th green fraction was collected. After recrystallization from DCM and cyclohexane, the product **1** was isolated in 5% yield (0.1 g, 0.159 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ -2.39 (s, 2H, NH), 0.63 (s, 9H, $CH_{3\ TMS}$), 7.78 (m, 9H, $CH_{Ph\ meta/para}$), 8.21 (m, 6H, $CH_{Ph\ ortho}$), 8.78 (s, 4H, $CH_{\beta\text{-pyrrolic}}$), 8.90 (d, ^{3}J = 4.7 Hz, 2H, $CH_{\beta\text{-pyrrolic}}$), 9.68 (d, ^{3}J = 4.8 Hz, 2H, $CH_{\beta\text{-pyrrolic}}$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, ppm: 0.8 ($CH_3$), 99.4 (C), 102.3 (C), 107.5 (C), 121.4 (C), 122.4 (C), 127.0 (CH), 127.1 (CH), 128.2 (CH), 134.7 (CH), 134.8 (CH), 142.1 (C), 142.3 (C).

5-ethynyl-10,15,20-triphenylporphyrin (2). A solution of TBAF (0.2 ml, 0.2 mmol, 1.3 eq., 1M in THF) was slowly added to a solution of 5-(2-(trimethylsilyl)ethynyl)-10,15,20-triphenylporphyrin (100 mg, 0.16 mmol, 1 eq.) in a mixture of dry THF and DCM (4:1). A spatula of $CaCl_2$ was added to quench the reaction after 1 h of stirring. The reaction mixture was washed with water (3 x 200 ml), the organic layer was dried over anhydrous Na_2SO_4 and concentrated. The solvent was evaporated. The obtained crude product was recrystallized from chloroform-methanol mixture, affording 90 mg (0.159 mmol, quantitative yield) of pure compound **2**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ -2.44 (s, 2H, NH), 4.19 (s, 1H, $CH_{Ethynyl}$), 7.79 (m, 9H, $CH_{Ph\ meta/para}$), 8.20 (m, 6H, $CH_{Ph\ ortho}$), 8.79 (s, 4H, $CH_{\beta\text{-pyrrolic}}$), 8.92 (d, ^{3}J = 4.3 Hz, 2H, $CH_{\beta\text{-pyrrolic}}$), 9.70 (d, ^{3}J = 4.5 Hz, 2H, $CH_{\beta\text{-pyrrolic}}$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 84.0 (CH), 121.0 (C), 126.7 (CH), 126.8 (CH), 127.9 (CH), 134.4 (CH), 134.5 (CH), 141.7 (C), 142.0 (C).

Dimer D. 5-ethynyl-10,15,20-triphenylporphyrin (90 mg, 0.16 mmol, 1 eq.) was dissolved in a chloroform-methanol mixture (150/30 ml). Zinc acetate dihydrate (0.5 g, 2.28 mmol, 14 eq.) was added. The mixture was stirred during 4 h before solvents were evaporated under reduced pressure. The solid was dissolved in $CHCl_3$, washed with water, the organic fraction was concentrated and passed through a pad of silica and evaporated. The violet solid was dissolved in 50 ml of toluene. Trimethylamine (10 ml) and bis(triphenylphosphine)palladium(II) dichloride (56 mg, 0,08 mmol, 0.5 eq) were added and the mixture was stirred during 24 h at 50 °C. The solvent was removed under reduced pressure and the crude solid was purified by column chromatography (alumina, cyclohexane-toluene 1:1) affording 65 mg (0.052 mmol, yield 65%) of the pure product as a green solid. ^{1}H NMR (THF-d_8, 400 MHz): δ 7.85 (m, 18H, $CH_{Ph\ meta/para}$), 8.27 (m, 12H, $CH_{Ph\ ortho}$), 8.83 (s, 8H, $CH_{\beta\text{-pyrrolic}}$), 9.06 (d, ^3J = 4.6 Hz, 4H, $CH_{\beta\text{-pyrrolic}}$), 10.01 (d, ^3J = 4.7 Hz, 4H, $CH_{\beta\text{-pyrrolic}}$). ^{13}C NMR ($CDCl_3$+DMSO-$d_6$, 100 MHz): δ 102.9 (C), 121.7 (C), 126.0 (CH), 126.1 (CH), 127.1 (CH), 131.2 (CH) 131.7 (CH), 132.7 (CH), 133.7 (CH), 133.8 (CH), 142.0 (C), 148.8 (C), 149.0 (C), 149.9 (C), 152.4 (C). UV-Vis (THF) λ max (nm) (logε, mol^{-1} L cm^{-1}): 451 (5.58), 483 (5.36), 569 (4.43), 637 (4.80), 690 (4.83). HR-ESI MS: *m/z* obsd 1250.2315, calcd 1250.2403 [M]; M = $C_{80}H_{46}N_8Zn_2$.

Handle H1. 1 g of 2,2′-Thiodiethanol (8.2mmol) was dissolved in 80 ml of dry THF at room temperature. To this solution was added 5.83 g of the commercially available hydrochloride salt of nicotinoyl chloride (4eq.). After stirring for 30 min, 5 ml of triethylamine was added, and the mixture was stirred for three days. After evaporation to dryness, the residue was poured into 60 ml of an aqueous solution of Na_2CO_3 (1.2 M). The mixture was extracted with CH_2Cl_2 (3 × 50 ml). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed. The residue was then purified by column chromatography [SiO_2, CH_2Cl_2/CH_3OH 98/2] affording the pure product (2.18g, 6.56 mmol, 80%, 91° C). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.00 (t, ^3J = 6.8 Hz, 4H, CH_2), 4.55 (t, ^3J = 6.8 Hz, 4H, CH_2), 7.39 (dd, ^3J = 7.9 Hz, ^3J = 4.8 Hz, 2H, CH_{Py}), 8.29 (ddd, ^3J = 7.9 Hz, ^4J = 1.9 Hz, ^4J = 1.9 Hz, 2H, CH_{Py}), 8.78 (dd, ^3J = 4.9 Hz, ^4J = 1.5 Hz, 2H, CH_{Py}), 9.23 (d, ^4J = 1.8 Hz, 2H, CH_{Py}). ^{13}C NMR ($CDCl_3$, 150 MHz) δ, ppm: 31.0 (CH_2), 64.2 (CH_2), 123.5 (CH), 126.0 (C), 137.2 (CH), 151.1 (CH), 153.8 (CH), 165.2 (C). Found: C, 57.5; H, 5.0; N, 8.4; S, 9.9%. Calc. for $C_{16}H_{16}N_2O_4S$: C, 57.8; H, 4.9; N, 8.4; S, 9.7%.. Mp : 91°C

Handle H2. Nicotinoyl chloride hydrochloride (3.04 g, 17 mmol, 2 eq.) was added into dry dichloromethane (30 ml) under argon. The obtained suspension was stirred 10 min and triethyleneglycol (1.14 ml, 8.5 mmol, 1 eq.) dissolved in 30 ml of dichloromethane was added. The obtained mixture was kept in the ice bath, then, triethylamine (4 ml, 29 mmol, 3.4 eq.) was added dropwise during 45 min. The resulting mixture was stirred overnight at room temperature. The reaction mass was washed with a saturated solution of $NaHCO_3$ (50 ml) and water (3 times × 150 ml) and isolated. Evaporation of solvents and following drying afforded 2.11 g (5.86 mmol) pale yellow solid in 69% yield. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.70 (s, 4H, CH_2), 3.83 (m, 4H, CH_2), 4.48 (m, 4H, CH_2), 7.38 (dd, ^3J = 8.0 Hz, ^3J = 3.9 Hz, 2H, CH_{Py}), 8.30 (ddd, ^3J = 8.0 Hz, ^4J = 2.0 Hz, ^4J = 2.0 Hz, 2H, CH_{Py}), 8.74 (dd, ^3J = 5.0 Hz, ^4J = 1.8 Hz, 2H, CH_{Py}), 9.21 (d, ^4J = 2.0 Hz, 2H, CH_{Py}).

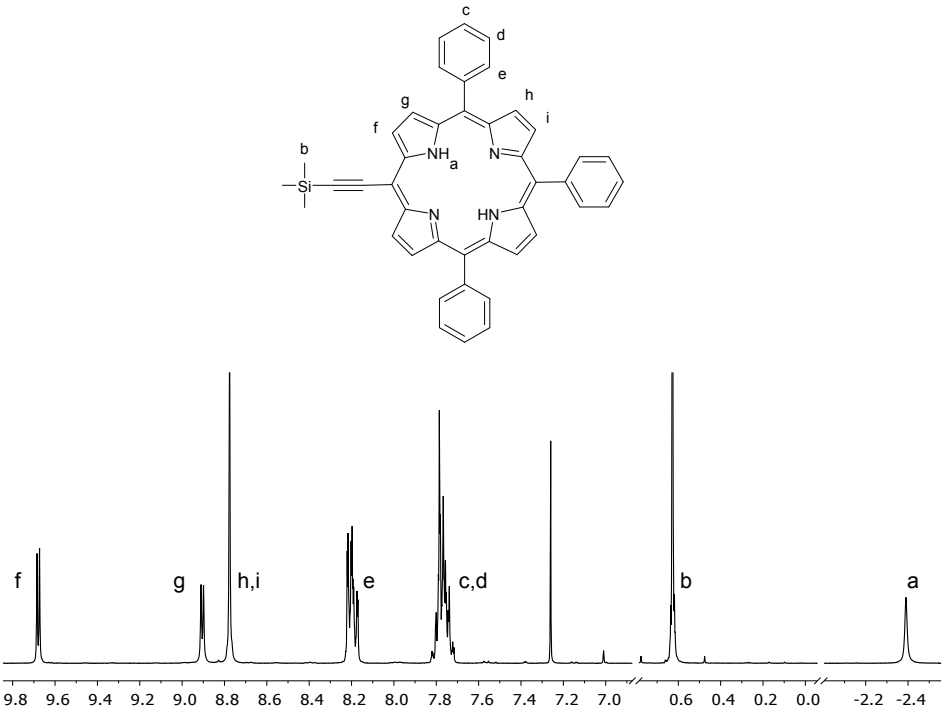

Figure S1 ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) spectrum of 5-(2-(trimethylsilyl)ethynyl)-10,15,20-triphenylporphyrin.

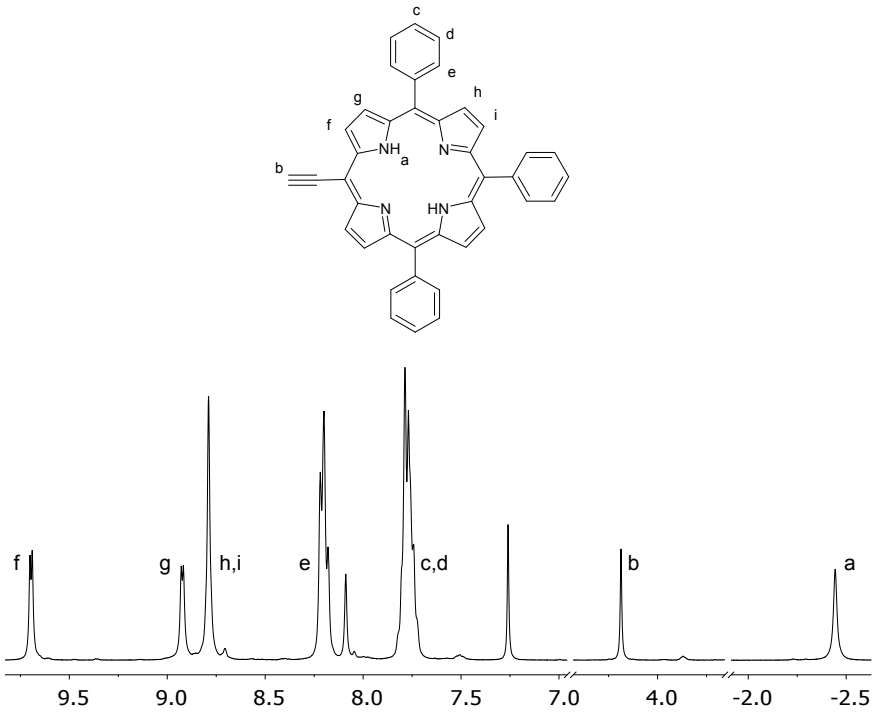

Figure S2 ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) spectrum of 5-ethynyl-10,15,20-triphenylporphyrin.

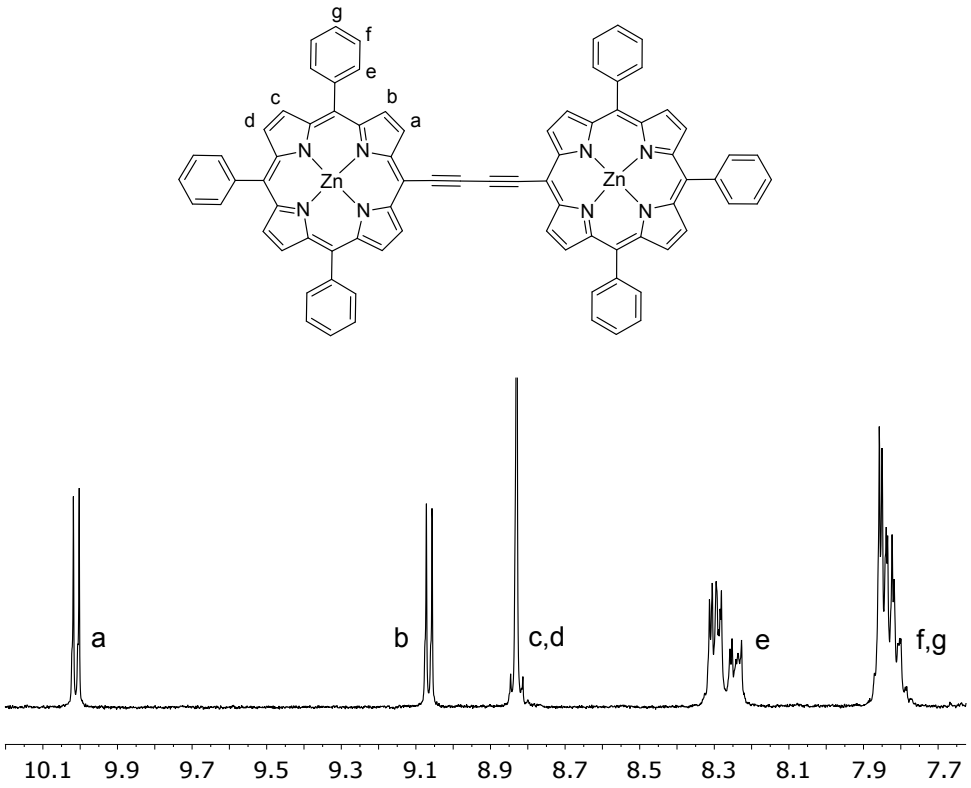

Figure S3 ^{1}H NMR (THF-d_8, 400 MHz, 25 °C) spectrum of dimer **D**.

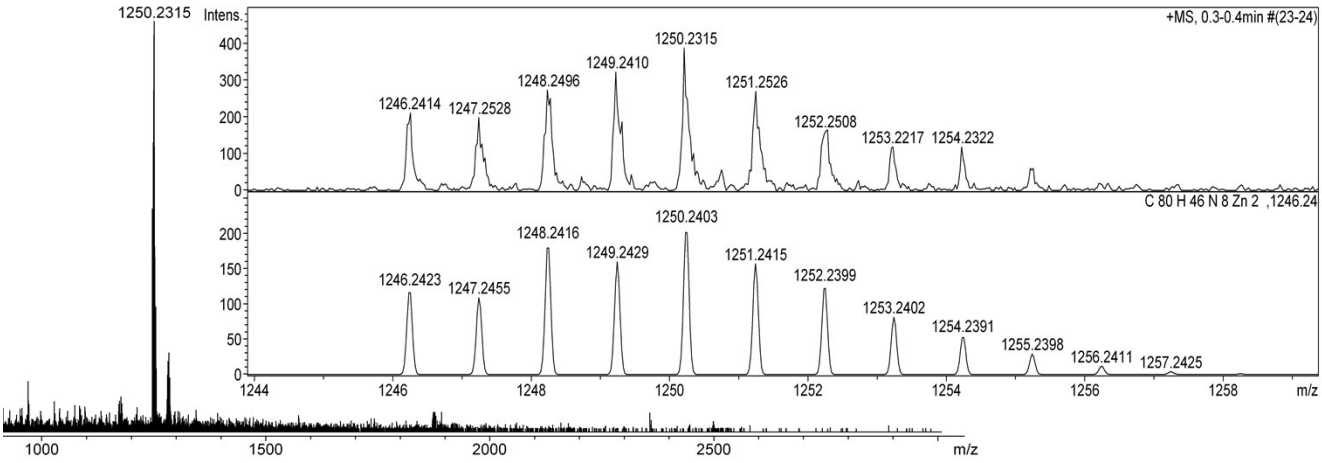

Figure S4 HR-ESI TOF spectrum of the dimer **D**.

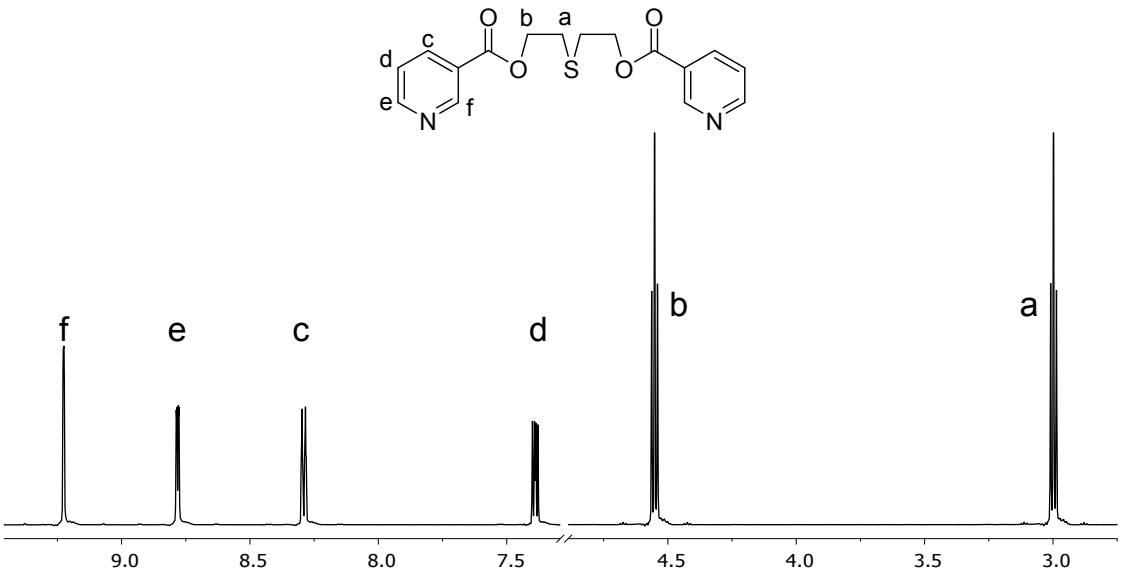

Figure S5 ^{1}H NMR ($CDCl_3$, 600 MHz, 25 °C) spectrum of handle **H1.**

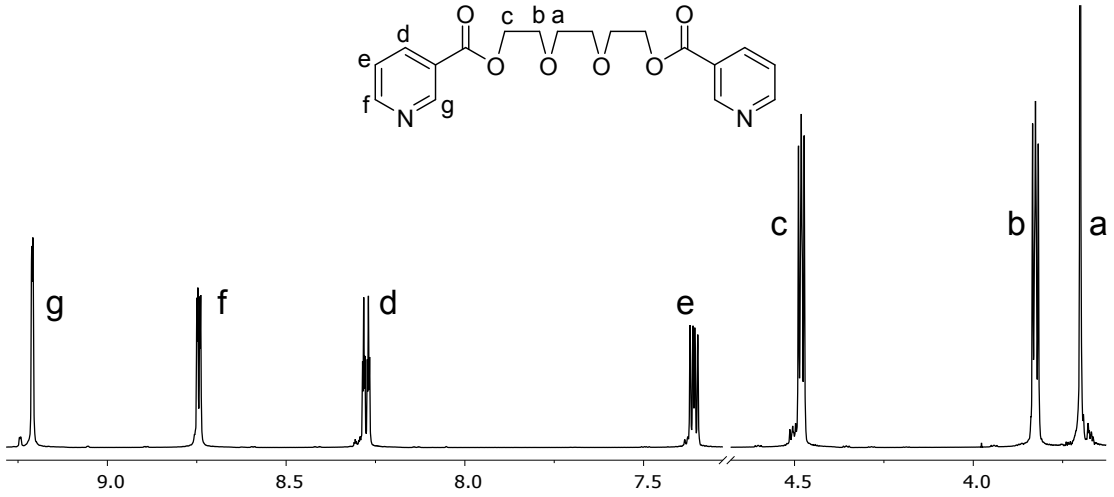

Figure S6 ^{1}H NMR ($CDCl_3$, 600 MHz, 25 °C) spectrum of handle **H2.**

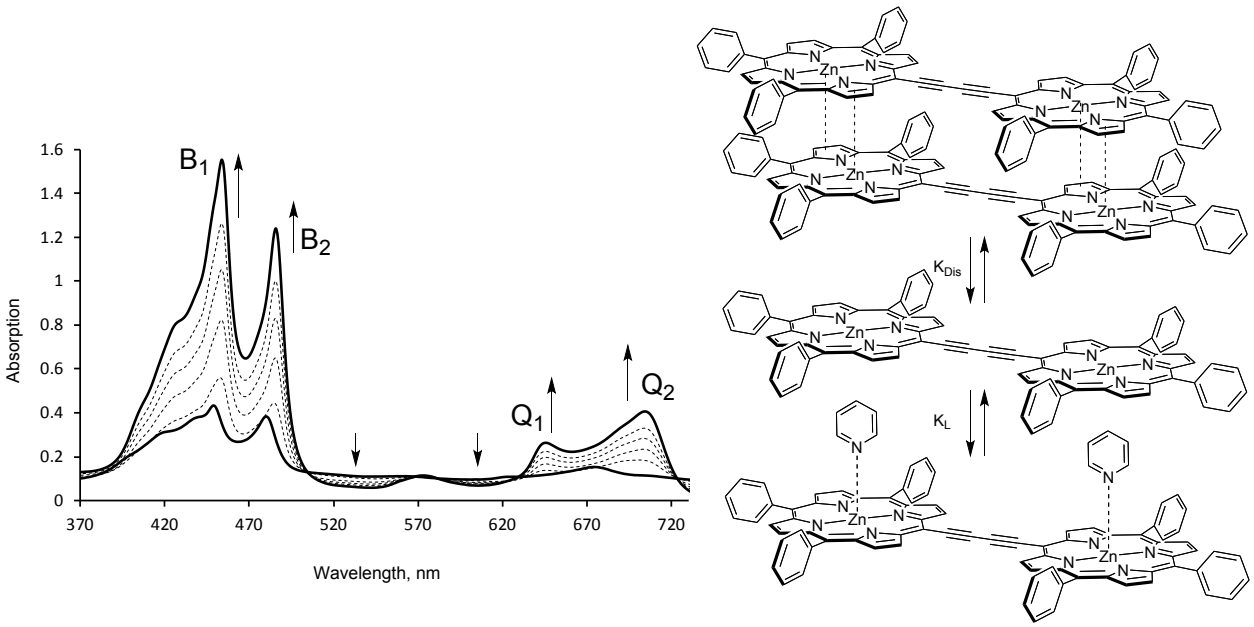

Figure S7 Titration of a CH_2Cl_2 solution of **D** (c = $4.7 \cdot 10^{-6}$ M) with pyridine (0-220 equiv).

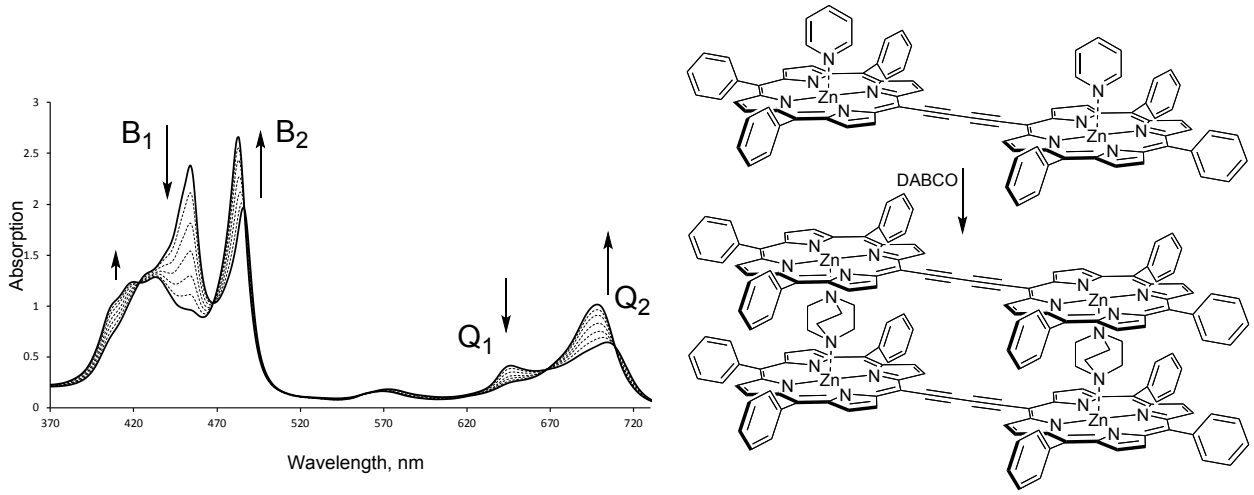

Figure S8 Titration of a CH_2Cl_2 solution of **D** (c = $8 \cdot 10^{-6}$ M) with DABCO (40 equiv of pyridine; 0-15 equiv of DABCO).

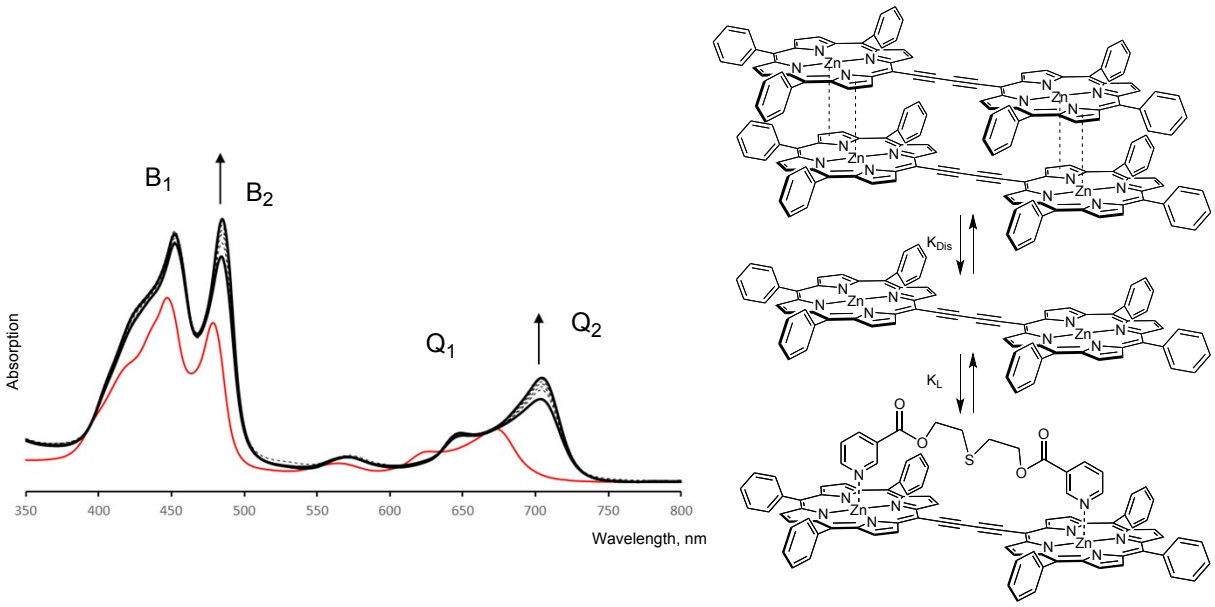

Figure S9 Red curve – spectrum of **D** in DCM (c = 4.7 x 10^{-6}); black curves – following titration of this solution with **H1** (1-40 equiv).

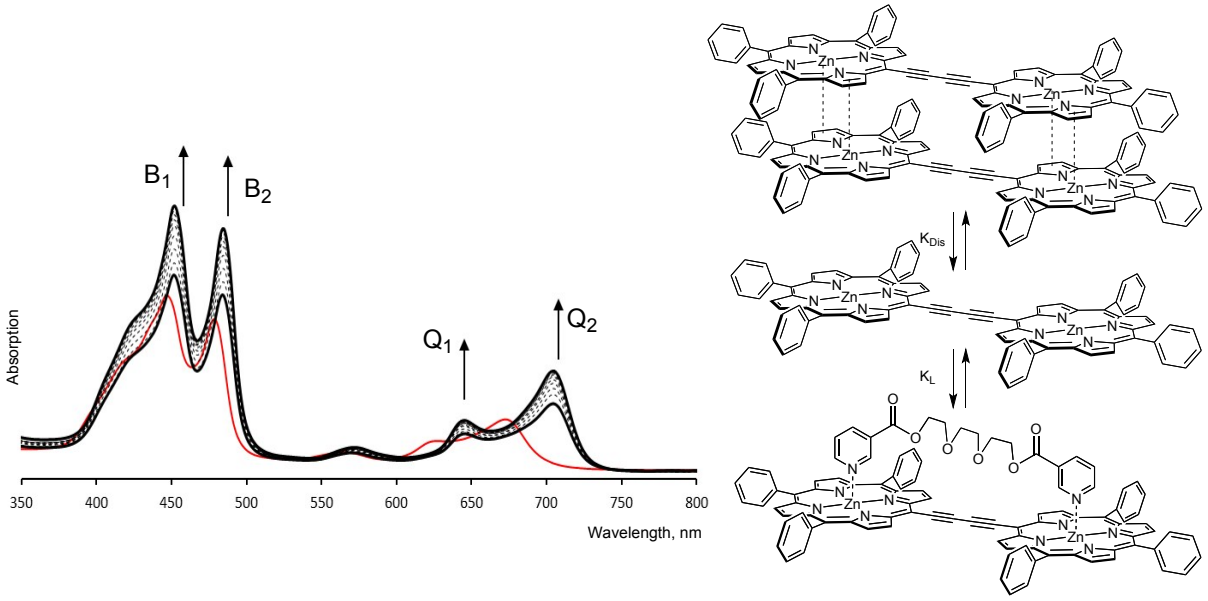

Figure S10 Red curve – spectrum of **D** in DCM (c = 4.7 x 10^{-6}); black curves – following titration of this solution with **H2** (1-40 equiv).

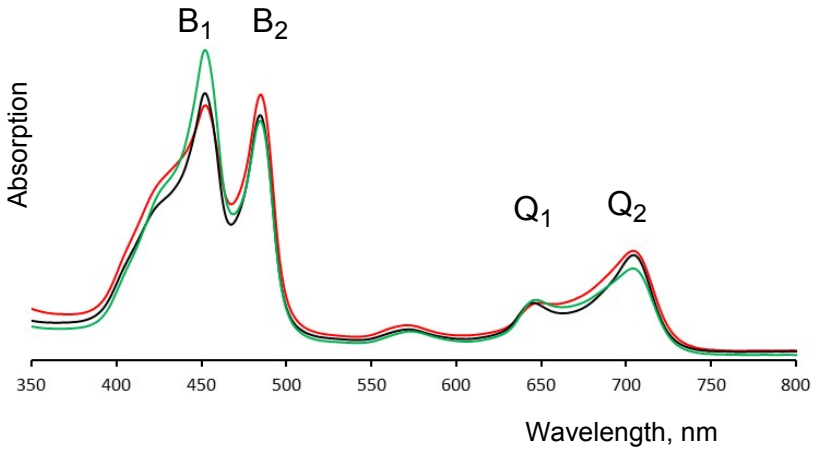

Figure S11 Comparison of UV-Vis spectra in CH_2Cl_2 of **D-Py** (torsion-free, green); **D-H1** (red), **D-H2** (black).

Crystallographic data.

Table S1 Crystallographic data for complex **D-DMAP** ($(C_{94}H_{66}N_{12}Zn_2)\cdot 1.7(CHCl_3)$), and **D-DMSO** ($(C_{84}H_{58}N_8O_2S_2Zn_2)\cdot CCl_4$).

	D-DMAP	**D-DMSO**
Formula	$C_{95.70}H_{67.70}Cl_{5.10}N_{12}Zn_2$	$C_{85}H_{58}Cl_4N_8O_2S_2Zn_2$
FW	1697.30	1560.05
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
a, Å	12.5752(10)	27.288(2)
b, Å	16.1287(8)	12.4967(9)
c, Å	23.4657(19)	21.3304(15)
α, °	106.0120(10)	90
β, °	92.051(2)	91.548(4)
γ, °	111.422(2)	90
V, Å^3	4208.8(5)	7271.1(9)
Z	2	4
T, K	173(2)	100(2)
μ, mm^{-1}	0.787	0.920
Refls. coll.	31007	40471
Ind. refls. (R_{int})	18140 (0.0684)	8324 (0.1268)
R_1 (I>2σ(I))[a]	0.0854	0.0702
wR_2 (I>2σ(I))[a]	0.2322	0.1423
R_1 (all data)[a]	0.1770	0.1671
wR_2 (all data)[a]	0.2875	0.1783
GOF	1.029	1.010

Table S2 Selected X-ray data for **D-DMAP** and **D-Py** complexes. Both DMAP and pyridine behave as axial ligands.[11]

Bond	**Length (Å)**		**Bond**	**Angle (degree)**	
	Dimer (DMAP)	**Dimer (pyridine)**[11]		**Dimer (DMAP)**	**Dimer (pyridine)**[11]
Zn-$N_{Pyr.}$	2.115(5), 2.135(5)	2.144(4), 2.163(4)	N_{Pyr}-Zn-N_{Porph}	95.0(2), 94.2(2)	96.68, 96.41
Zn-$N_{Porph.}$	2.067(5) – 2.115(5)	2.052 – 2.080	N-Zn-N_{trans} N-Zn-N_{cis}	158.28(19) – 163.3(2); 87.7(2) – 89.0(2)	159.82 – 161.22; 88.11 – 88.74

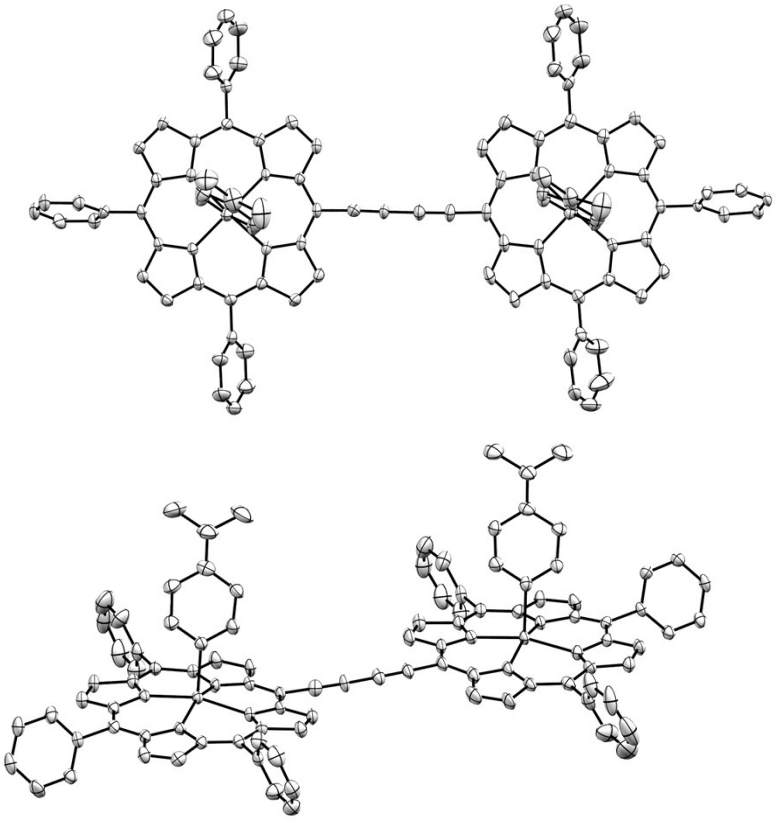

Figure S12 X-ray structure of **D-DMAP** with thermal ellipsoids drawn at the 30% probability level.

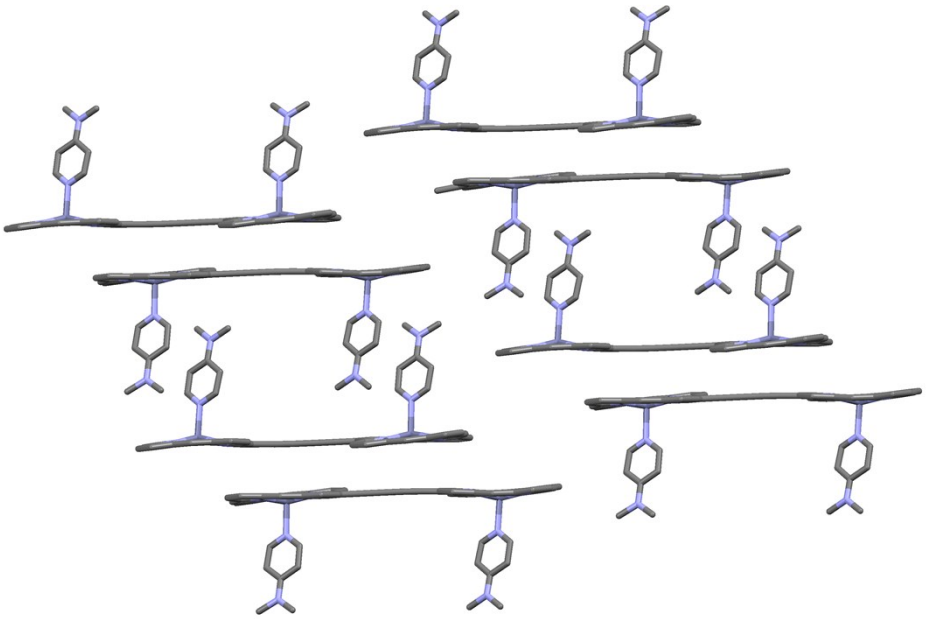

Figure S13 Crystal packing in the single crystal of **D-DMAP** (solvent molecules and *meso*-phenyl substituents are omitted for clarity).

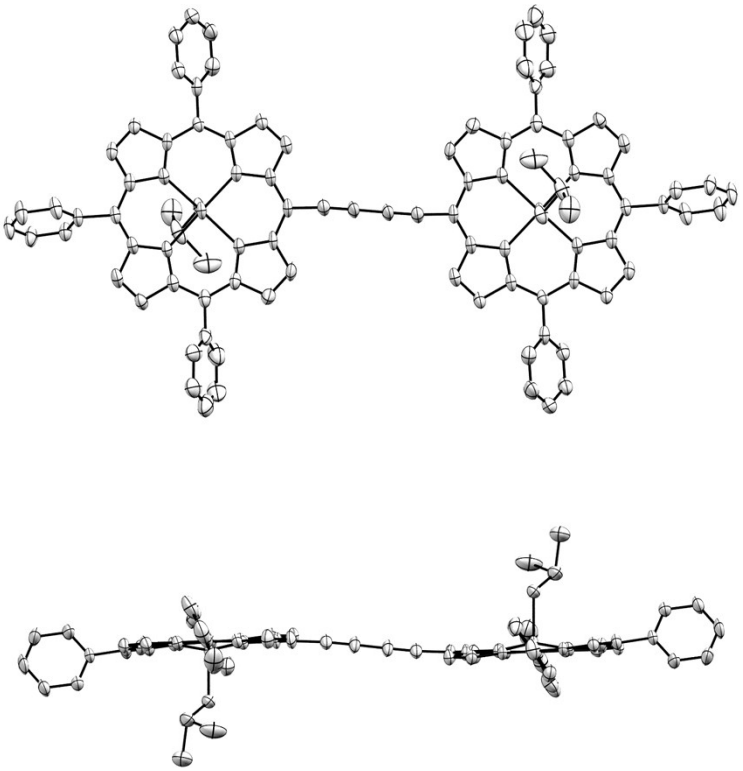

Figure S14 X-ray structure of **D-DMSO** with thermal ellipsoids drawn at the 30% probability level.

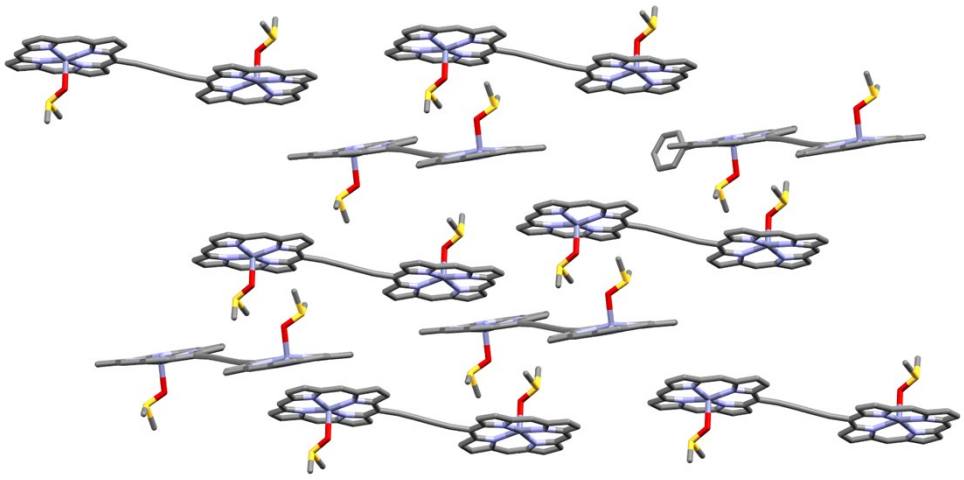

Figure S15 Crystal packing in the single crystal of **D-DMSO** (solvent molecules and *meso*-phenyl substituents are omitted for clarity).

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