# Tren-Capped Hexaphyrin Zinc Complexes : Interplaying Molecular Recognition, Möbius Aromaticity and Chirality

**Hervé Ruffin, Gildas Nyame Mendendy Boussambe, Thierry Roisnel, Vincent Dorcet, Bernard Boitrel* and Stéphane Le Gac***

Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, Université de Rennes 1, 263 avenue du Général Leclerc, 35042 Rennes cedex, France. bernard.boitrel@univ-rennes1.fr; stephane.legac@univ-rennes1.fr

# SUPPORTING INFORMATION

## Table of content

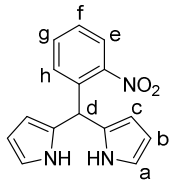
**III. UV-vis-NIR absorption spectra**

## I. Experimental part

### General

All chemicals were commercial products used as received. All reactions were conducted under inert atmosphere. Pyrrole was filtered through a plug of basic alumina before use. Anhydrous $CH_2Cl_2$ and THF were obtained, respectively, by distillation over $CaH_2$ and Na/benzophenone according to standard procedures. $^1H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded at 298 K (unless otherwise stated), at 500 MHz, 125 MHz and 376 MHz, respectively. Residual traces of solvent were used as internal standard. Chemical shifts are expressed in parts per million (ppm; s = singlet [$s_b$ = broad singlet, and so on], d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, and br = broad signal) and coupling constants are given in Hz. The NMR experiments were conducted in 5 mm standard NMR tubes.

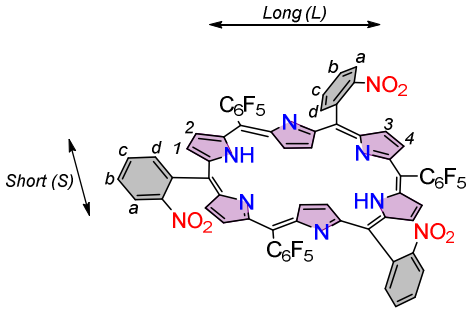
### Synthesis of 5-(2-nitrophenyl)dipyrromethane[1]




Under inert atmosphere, 2-nitrobenzaldehyde (25.0 g, 164 mmol) was solubilized in 275 mL of pyrrole (4.11 mol) and the mixture was degassed by argon bubbling during 15 min. TFA (1.3 mL, 16 mmol) was then added and the reaction was stirred at RT for 45 min. Upon addition of *ca.* 2 mL of $Et_3N$, pyrrole was removed under vacuum. The crude mixture was extracted with hexane from a $CH_2Cl_2$ solution and purified by silica gel column chromatography (eluent: $CH_2Cl_2$) to afford 5-(2-nitrophenyl)dipyrromethane as a reddish oil (35.4 g, 80%).

$^1H$ NMR ($CDCl_3$, 298 K) $\delta$ 5.89 (s, 2H, c), 5.82 (d, J = 5.9 Hz, 2H, b), 6.21 (s, 1H, d), 6.73 (m, 2H, a), 7.28 (dd, J1 = 7.8 Hz, J2 = 1.3 Hz, 1H, h), 7.38 (td, J1 = 7.8 Hz, J2 = 1.3 Hz, 1H, g), 7.51 (td, J1 = 7.8 Hz, J2 = 1.3 Hz, 1H, f), 7.87 (dd, J1 = 7.8 Hz, J2 = 1.3 Hz, 1H, e), 8.16 (s, 2H, NH).

## Synthesis of 1

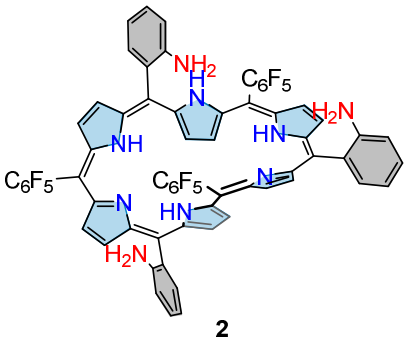



**1**
(mixture of atropisomers)

Under inert atmosphere, at 0°C, MSA (440 µL, 6.8 mmol) was added to a solution of 5-(2-nitrophenyl)dipyrromethane (30.0 g, 112 mmol) and pentafluorobenzaldehyde (22.0 g, 112 mmol) in $CH_2Cl_2$ (3.6 L). After 1h30, DDQ (76.3 g, 336 mmol) was added and the reaction was stirred at RT for an additional 2h. $Et_3N$ (2 mL, 14 mmol) was added to stop the reaction and the solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography (eluent: $CH_2Cl_2$) to provide hexaphyrin **1** as a purple solid (6.4 g, 16 %).

$^1$H NMR ($CDCl_3$, 330 K, average spectrum) $\delta$ -2.36 (m, 4H, $\beta\pi_{in}$), -1.83 (m, 2H, NH), 7.95-8.20 (m, 8H, Ar), 8.39 (m, 1H, $Ar_{d(S)}$), 8.60 (m, 3H, $Ar_{a(S+L)}$), 8.86 (d, *J* = 4.7 Hz, 2H, $\beta\pi_1$), 8.99 (d, *J* = 4.7 Hz, 2H, $\beta\pi_4$), 9.26 (d, *J* = 4.7 Hz, 2H, $\beta\pi_2$), 9.33 (d, *J* = 4.8 Hz, 2H, $\beta\pi_3$). $^{19}$F NMR ($CDCl_3$, 298 K, complex spectrum corresponding to a mixture of atropisomers, see Figure S5) $\delta$ -164.35 (m, $F_{meta}$), -164.01 (m, $F_{meta}$), -162.99 (m, $F_{meta}$), -162.50 (m, $F_{meta}$), -161.26 (m, $F_{meta}$), -160.92 (m, $F_{meta}$), -160.54 (m, $F_{meta}$), -154.87 (m, $F_{para}$), -150.70 (t, J = 20.9 Hz, $F_{para}$), -138.52 (d, J = 24.2 Hz, $F_{ortho}$), -138.29 (d, J = 23.4 Hz, $F_{ortho}$), -137.62 (d, *J* = 24.4 Hz, $F_{ortho}$), -137.28 (d, *J* = 24.4 Hz, $F_{ortho}$), -137.01 (d, *J* = 24.7 Hz, $F_{ortho}$), -136.80 (m, $F_{ortho}$), -136.64 (d, *J* = 24.4 Hz, $F_{ortho}$), -136.21 (m, $F_{ortho}$), -136.07 (d, *J* = 26.4 Hz, $F_{ortho}$), -135.76 (d, *J* = 24.1 Hz, $F_{ortho}$), -135.58 (d, *J* = 24.0 Hz, $F_{ortho}$). UV-visible ($CHCl_3$, $\lambda_{max}$ nm/ε L·mol$^{-1}$·cm$^{-1}$): 566 (141149), 600 (51758), 714 (18735), 744 (8639), 901 (7728), 1024 (11970). HRMS (ESI-TOF, positive ion mode): *m/z* calcd for $C_{66}H_{27}N_9O_6F_{15}$: 1326.1844 [M+H$^+$]; found 1326.1854.

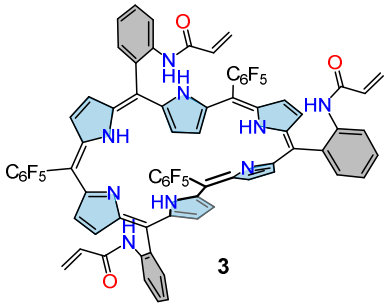
## Synthesis of 2




**2**
(not isolated)

In a sealed reactor, Pd(0)/C (30 wt. % loading, 12.5 mg) was added to hexaphyrin **1** (250 mg, 190 µmol) in AcOEt (20 mL). The reaction was stirred under a pressure of $H_2$ (80 bar) for 24 h at 30 °C, then filtered through a plug of celite. AcOEt was removed under reduced pressure affording **2** as the major compound. The crude mixture was used in the next steps without purification.

## Synthesis of 3

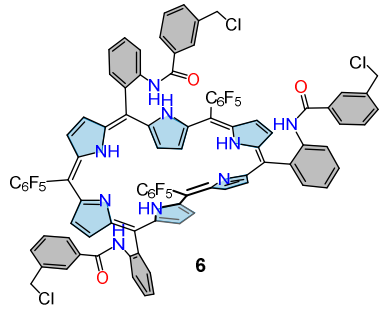


**3**

Under inert atmosphere, the crude hexaphyrin **2**, obtained from 250 mg of **1**, was solubilized in anhydrous THF (10 mL) and, at -50°C, DIPEA (164 µL, 940 µmol) and acryloyl chloride (55 µL, 670 µmol) were added. After 30 min of stirring, the excess of acyl chloride was quenched by addition of of MeOH (1 mL). THF was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: $CH_2Cl_2$/AcOEt 97:3) to afford hexaphyrin **3** as a blue solid (109 mg, 41 % overall yield from **1**).

$^1$H NMR ($CDCl_3$, 298 K): broad spectrum due to fast equilibrium between Möbius conformers (see text and Figure S6a). UV-visible ($CHCl_3$, $\lambda_{max}$ nm): 393, 446, 604, 774, 866, 913, 1022. HRMS (ESI-TOF, positive ion mode): *m/z* calcd for $C_{75}H_{41}N_9O_3F_{15}$: 1400.3093 [M+H$^+$]; found 1400.3086.

## Synthesis of 6

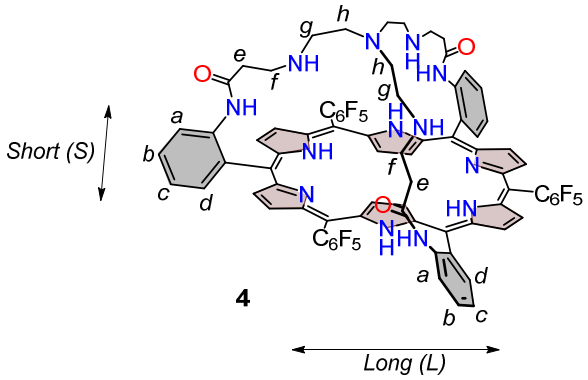


**6**

Under inert atmosphere, the crude hexaphyrin **2**, obtained from 250 mg of **1**, was solubilized in anhydrous THF (10 mL) and, at 0°C, $Et_3N$ (128 µL, 912 µmol) and 3-(chloromethyl)benzoyl chloride (97 µL, 682 µmol) were successively added. After 30 min of stirring, the excess of acyl chloride was quenched by addition of butylamine (75 µL, 760 µmol). THF was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: $CH_2Cl_2$) to afford hexaphyrin **6** as a blue solid (150 mg, 46 % overall yield from **1**).

$^{1}$H NMR ($CDCl_3$, 298 K): broad spectrum due to fast equilibrium between Möbius conformers (see text and Figure S6b). UV-visible ($CHCl_3$, $\lambda_{max}$ nm/ε L·mol$^{-1}$·cm$^{-1}$): 398 (30237), 454 (29580), 604 (174408), 633 (88085), 774 (13620), 865 (8400), 913 (7527), 1036 (3807). HRMS (ESI-TOF, positive ion mode): *m/z* calcd for $C_{90}H_{50}N_9O_3F_{15}{}^{35}Cl_3$: 1694.2857 [M+H$^+$]; found 1694.2852.

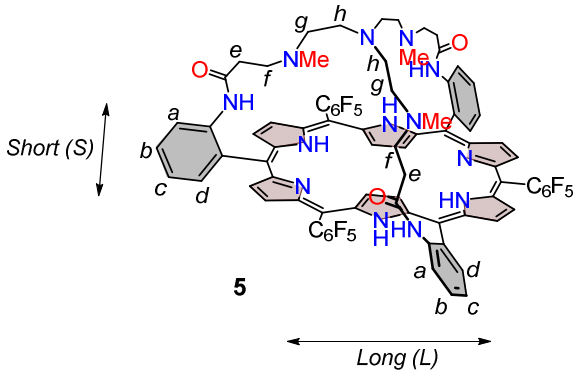
## Synthesis of 4




Under inert atmosphere, a solution of hexaphyrin **3** (51 mg, 36 µmol) and tris(2-aminoethyl)amine (5.4 µL, 36 µmol) in MeOH/$CHCl_3$ (9:1, 50 mL) was stirred overnight at 45°C. The solvents were then removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: $CH_2Cl_2$/MeOH 90:10, with 5 % v:v of $Et_3N$), then washed twice with water to afford hexaphyrin **4** as a reddish solid (23 mg, 41 %).

$^{1}$H NMR ($CDCl_3$, 298 K) $\delta$ 2.40 ($s_b$, 2H, $NH_{out}$) 2.73 (m, 2H, $CH_{2e(S)}$), 2.91 (m, 2H, $CH_{2e(L)}$), 3.16 (d, J = 4.6 Hz, 2H, $\beta\pi_{out}$), 3.36 (m, 6H, $\beta\pi_{out}$), 3.49 (m, 2H, $CH_{2e(L)}$), 3.68 (m, 2H, $CH_{2f(S)}$), 3.95 (m, 2H, $CH_{2f(L)}$), 4.17 (m, 2H, $CH_{2f(L)}$), 5.29 (m, 2H, $CH_{2g(L)}$), 5.53 (m, 2H, $CH_{2g(S)}$), 5.89 (m, 2H, $CH_{2g(L)}$), 6.07 (d, J = 7.8 Hz, 2H, $Ar_{d(L)}$), 6.09 (d, J = 8.4 Hz, 1H, $Ar_{d(S)}$), 6.16 (m, 2H, $CH_{2h(S)}$), 6.57 (t, J = 7.4 Hz, 1H, $Ar_{c(S)}$), 6.61 (t, J = 7.4 Hz, 2H, $Ar_{c(L)}$), 6.76 (t, J = 7.6 Hz, 2H, $Ar_{b(L)}$), 6.86 (m, 2H, $CH_{2h(L)}$), 6.87 (t, J = 7.6 Hz, 1H, $Ar_{b(S)}$), 6.98 (m, 2H, $CH_{2h(L)}$), 7.08 (d, J = 7.7 Hz, 2H, $Ar_{a(L)}$), 7.77 (d, J = 8.0 Hz, 1H, $Ar_{a(S)}$), 8.36 (s, 2H, $CONH_{(L)}$), 11.19 (s, 1H, $CONH_{(S)}$), 19.93 ($s_b$, 2H, $\beta\pi_{in}$), 20.52 ($s_b$, 2H, $\beta\pi_{in}$), 26.79 ($s_b$, 2H, $NH_{in}$). $^{19}$F NMR ($CDCl_3$, 298 K) $\delta$ -160.72 (dt, J1 = 21.8 Hz, J2 = 8.1 Hz, 1F, $F_{m(S)}$), -160.58 (m, 3F, $F_{m(S+L)}$), -159.44 (dt, J1 = 22.7 Hz, J2 = 8.1 Hz, 2F, $F_{m(L)}$), -154.73 (t, J = 21.0 Hz, 1F, $F_{p(S)}$), -153.03 (t, J = 21.1 Hz, 2F, $F_{p(L)}$), -139.82 (d, J = 23.6 Hz, 2F, $F_{o(L)}$), -139.55 (dd, J1 = 24.8, J2 = 8.3 Hz, 1F, $F_{o(S)}$), -139.34 (dd, J1 = 24.6, J2 = 8.5 Hz, 1F, $F_{o(S)}$), -138.55 (d, J = 21.6 Hz, 2F, $F_{o(L)}$). Partial $^{13}$C from 2D HSQC ($CDCl_3$, 298 K) $\delta$ 35.3 (1C, $C_{e(S)}$), 36.6 (2C, $C_{e(L)}$), 45.4 (2C, $C_{f(L)}$), 46.3 (1C, $C_{f(S)}$), 47.2 (2C, $C_{g(L)}$), 48.6 (1C, $C_{g(S)}$), 54.7 (2C, $C_{h(L)}$), 57.3 (1C, $C_{h(S)}$), 122.3 (1C, $C_{a(S)}$), 123.5 (2C, $C_{\beta\pi in}$), 123.9 (1C, $C_{c(S)}$), 124.9 (2C, $C_{\beta\pi in}$), 125.2 (2C, $C_{a(L)}$), 125.8 (2C, $C_{c(L)}$), 126.1 (2C, $C_{\beta\pi out}$), 128.4 (1C, $C_{b(S)}$), 128.5 (2C, $C_{\beta\pi out}$), 128.9 (2C, $C_{d(L)}$), 129.0 (2C, $C_{b(L)}$), 129.1 (1C, $C_{d(S)}$), 130.5 (2C, $C_{\beta\pi out}$), 132.4 (2C, $C_{\beta\pi out}$). UV-visible ($CHCl_3$, $\lambda_{max}$ nm/ε L·mol$^{-1}$·cm$^{-1}$): 426 (39220), 488 (105568), 526 (61807), 577 (66258), 608 (47290). HRMS (ESI-TOF, positive ion mode): *m/z* calcd for $C_{81}H_{59}N_{13}O_3F_{15}$: 1546.4618 [M+H$^+$]; found 1546.4616.

## Synthesis of 5

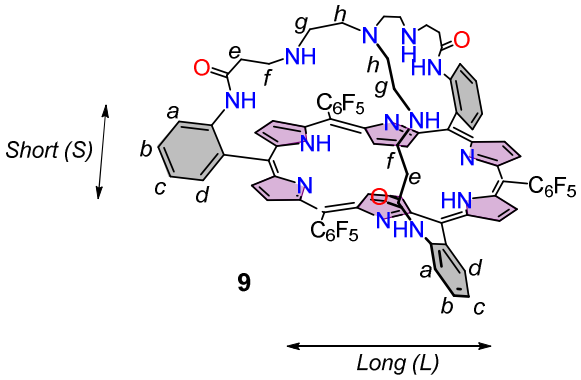



Under inert atmosphere, a solution of hexaphyrin **3** (60 mg, 42 µmol) and tris[2-(methylamino)ethyl]amine (9 µL, 43 µmol) in MeOH/$CHCl_3$ (9:1, 60 mL) was stirred overnight at 45°C. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: $CH_2Cl_2$/MeOH 90:10, with 1 % v:v of $Et_3N$), then washed twice with water to afford hexaphyrin **5** as a reddish solid (46 mg, 67 %).

$^1$H NMR ($CDCl_3$, 298 K) $\delta$ 3.08 (m, 4H, $CH_{2e(L)}$), 3.15 (d, J = 5.1 Hz, 2H, $\beta\pi_{out}$), 3.21 (m, 4H, $\beta\pi_{out}$), 3.27 (m, 2H, $CH_{2e(S)}$), 3.39 (d, J = 5.3 Hz, 2H, $\beta\pi_{out}$), 3.73 (s, 3H, $CH_{3(S)}$), 3.81 (m, 4H, $CH_{2f(L)}$), 4.16 (m, 2H, $CH_{2f(S)}$), 4.97 (s, 6H, $CH_{3(L)}$), 5.82 (m, 6H, $CH_{2h(S+L)+g(L)}$), 5.95 (m, 3H, $Ar_{d(S)}$ + $CH_{2h(L)}$), 6.20 (d, J = 7.7 Hz, 2H, $Ar_{d(L)}$), 6.53 (t, J = 6.8 Hz, 2H, $Ar_{c(L)}$), 6.57 (t, J = 7.8 Hz, 1H, $Ar_{c(S)}$), 6.75 (t, J = 7.2, 2H, $Ar_{b(L)}$), 6.86 (t, J = 7.6 Hz, 1H, $Ar_{b(S)}$), 7.01 (m, 2H, $CH_{2g(L)}$), 7.52 (d, J = 8.1 Hz, 2H, $Ar_{a(L)}$), 7.94 (d, J = 8.1 Hz, 1H, $Ar_{a(S)}$), 8.49 ($m_b$, 2H, $CH_{2g(S)}$), 8.97 (s, 2H, $CONH_{(L)}$), 11.07 (s, 1H, $CONH_{(S)}$), 20.37 ($s_b$, 2H, $\beta\pi_{in}$), 20.53 ($s_b$, 2H, $\beta\pi_{in}$), 27.07 ($s_b$, 2H, $NH_{in}$). $^{19}$F NMR ($CDCl_3$, 298 K) $\delta$ -160.74 (dt, J1 = 20.5 Hz, J2 = 9.9 Hz, 1F, $F_{m(S)}$), -160.34 (dt, J1 = 20.9 Hz, J2= 8.3 Hz, 1F, $F_{m(S)}$), -159.74 (m, 2F, $F_{m(L)}$), -158.28 (m, 2F, $F_{m(L)}$), -154.58 (t, J = 21.2 Hz, 1F, $F_{p(S)}$), -152.25 (t, J = 20.9 Hz, 2F, $F_{p(L)}$), -140.15 (dd, J1 = 24.3 Hz, J2 = 8.3 Hz, 1F, $F_{o(S)}$), -139.52 (dd, J1 = 24.4, J2 = 8.5 Hz, 1F, $F_{o(S)}$), -139.14 (d, J = 23.9 Hz, 2F, $F_{o(L)}$), -138.16 (d, J = 23.6 Hz, 2F, $F_{o(L)}$). Partial $^{13}$C from 2D HSQC ($CDCl_3$, 298 K) $\delta$ 34.5 (1C, $C_{e(S)}$), 34.9 (2C, $C_{e(L)}$), 41.2 (1C, $NMe_{(S)}$), 43.5 (2C, $NMe_{(L)}$), 51.7 (1C, $C_{h(S)}$), 53.0 (1C, $C_{f(S)}$), 54.0 (2C, $C_{h(L)}$), 54.1 (2C, $C_{f(L)}$), 57.7 (2C, $C_{g(L)}$), 59.9 (1C, $C_{g(S)}$), 121.6 (2C, $C_{a(L)}$), 122.4 (1C, $C_{a(S)}$), 124.4 (2C, $C_{c(L)}$), 124.6 (4C, $C_{\beta\pi in}$), 124.7 (1C, $C_{c(S)}$), 126.0 (2C, $C_{\beta\pi out}$), 128.6 (1C, $C_{b(S)}$), 128.7 (2C, $C_{\beta\pi out}$), 129.0 (2C, $C_{d(L)}$), 129.3 (2C, $C_{b(L)}$), 129.6 (1C, $C_{d(S)}$), 130.4 (2C, $C_{\beta\pi out}$), 132.9 (2C, $C_{\beta\pi out}$). UV-visible ($CHCl_3$, $\lambda_{max}$ nm/ε L·mol$^{-1}$·cm$^{-1}$): 484 (114279), 528 (56238), 578 (63088). HRMS (ESI-TOF, positive ion mode): *m/z* calcd for $C_{84}H_{65}N_{13}O_3F_{15}$: 1588.5088 [M+H$^+$]; found 1588.5087.

## Synthesis of 9

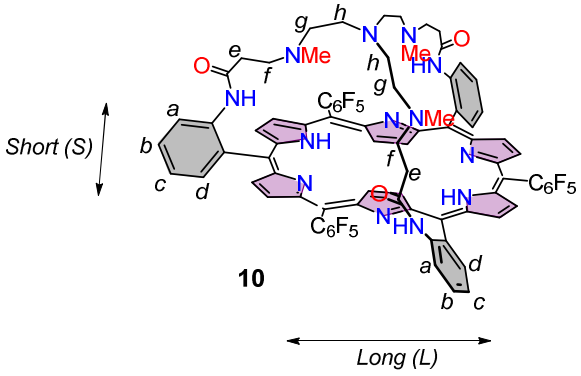
*Note:* compound **9** could not be isolated with high purity due to tedious purification, and was thus formed by addition of DDQ to an NMR tube solution of **4** for spectroscopic characterization.




In a NMR tube, hexaphyrin **4** (3 mg, 1.9 µmol) was dissolved in 500 µL of 9:1 $CDCl_3/CD_3OD$. At 25 °C DDQ (0.5 mg, 2.2 µmol) was added to this solution. After 30 min, $Et_3N$ (16 µL) was added. $^1H$ NMR spectrum showed quasi-quantitative formation of **9**. Note: an excess of both $CD_3OD$ and $Et_3N$ was needed to obtain a well resolved NMR spectrum.

$^1H$ NMR (9:1 $CDCl_3/CD_3OD$, 298 K) $\delta$ -3.10 (4H, $d_b$, $\beta\pi_{in}$), -2.02 (m, 2H, $CH_{2g/h}$) -1.51 (m, 2H, $CH_{2g/h}$), -1.37 (m, 2H, $CH_{2g/h}$), -1.20 (m, 2H, $CH_{2g/h}$), -1.08 (m, 2H, $CH_{2g/h}$), -1.02 (m, 2H, $CH_{2g/h}$), 0.11 (m, 2H, $CH_{2e/f}$), 0.91 (m, 2H, $CH_{2e/f}$), 1.05 (m, 2H, $CH_{2e/f}$), 1.35 (m, 2H, $CH_{2e/f}$), 1.54 (m, 2H, $CH_{2e/f}$), 1.71 (m, 2H, $CH_{2e/f}$), 7.65 (t, J = 6.7 Hz, 1H, $Ar_{c(S)}$), 7.75 (m, 2H, $Ar_{c(L)}$), 7.93 (m, 4H, $Ar_{b(L+S)}$), 8.22 (d, J = 8.4 Hz, 2H, $Ar_{a(L)}$), 8.30 (m, 1H, $Ar_{d(S)}$), 8.41 (m, 2H, $Ar_{d(L)}$), 8.72 (d, J = 8.8 Hz, 1H, $Ar_{a(S)}$), 9.09 (m, 2H, $\beta\pi_{out}$), 9.23 (m, 2H, $\beta\pi_{out}$), 9.47 (m, 2H, $\beta\pi_{out}$), 9.51 (m, 2H, $\beta\pi_{out}$). Partial $^{13}C$ from 2D HSQC (9:1 $CDCl_3/CD_3OD$, 298 K) $\delta$ 121.8 (2C, $C_{\beta\pi in}$), 122.5 (1C, $C_{a(S)}$), 122.8 (2C, $C_{\beta\pi in}$), 123.7 (1C, $C_{c(S)}$), 124.6 (2C, $C_{c(L)}$), 124.9 (2C, $C_{a(L)}$), 129.9 (2C, $C_{b(L)}$), 130.5 (1C, $C_{b(S)}$), 131.7 (2C, $C_{\beta\pi out}$), 134.1 (2C, $C_{\beta\pi out}$), 134.4 (2C, $C_{\beta\pi out}$), 135.0 (1C, $C_{d(S)}$), 135.4 (2C, $C_{d(L)}$), 136.4 (2C, $C_{\beta\pi out}$).

## Synthesis of 10

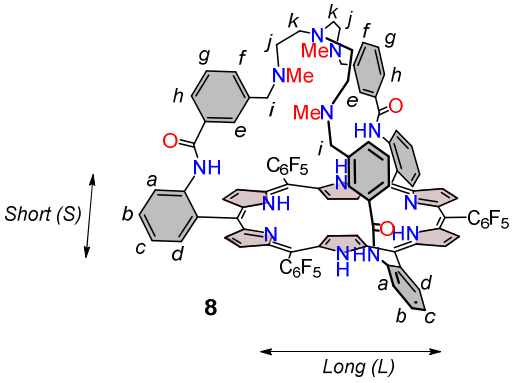



DDQ (4.8 mg, 21.1 µmol) was added to a solution of hexaphyrin **5** (17 mg, 10.7 µmol) in $CHCl_3$ (2 mL). After stirring for 10 min at room temperature, $Et_3N$ (100 µL) was added. $CHCl_3$ was removed under

reduced pressure and the crude product was purified by silica gel column chromatography (eluent: $CH_2Cl_2$/MeOH 90:10, with 1 % v/v of $Et_3N$) to afford hexaphyrin **10** as a purple solid (14 mg, 82 %).

$^1$H NMR ($CDCl_3$, 298 K) $\delta$ -3.18 (d, J = 3.8 Hz, 2H, $\beta\pi_{in}$), -3.05 (d, J = 3.8 Hz, 2H, $\beta\pi_{in}$), -2.85 (m, 2H, $CH_{2g/h(S)}$), -2.46 (m, 2H, $CH_{2g/h(L)}$), -1.25 (m, 4H, $CH_{2g/h(L)}$), -1.01 (m, 2H, $CH_{2g/h(L)}$), -0.77 (m, 2H, $CH_{2g/h(S)}$), -0.47 (s, 6H, $CH_{3(L)}$), 0.49 (s, 3H, $CH_{3(S)}$), 0.74 (m, 2H, $CH_{2e/f(S)}$), 1.15 (m, 2H, $CH_{2e/f(L)}$), 1.19 (m, 2H, $CH_{2e/f(S)}$), 1.39 (m, 2H, $CH_{2e/f(L)}$), 1.69 (m, 2H, $CH_{2e/f(L)}$), 1.79 (m, 2H, $CH_{2e/f(L)}$), 7.69 (t, J = 7.7 Hz, 1H, $Ar_{c(S)}$), 7.72 (t, J = 7.5 Hz, 2H, $Ar_{c(L)}$), 7.97 (t, J = 7.8 Hz, 1H, $Ar_{b(S)}$), 8.00 (t, J = 8.0 Hz, 2H, $Ar_{b(L)}$), 8.16 (d, J = 7.3 Hz, 2H, $Ar_{d(L)}$), 8.38 (d, J = 8.4 Hz, 1H, $Ar_{d(S)}$), 8.50 (d, J = 8.4 Hz, 2H, $Ar_{a(L)}$), 8.78 (d, J = 8.8 Hz, 1H, $Ar_{a(S)}$), 9.10 (d, J = 4.7 Hz, 2H, $\beta\pi_{out}$), 9.30 (d, J = 4.7 Hz, 2H, $\beta\pi_{out}$), 9.37 (s, 2H, $NHCO_{(L)}$), 9.53 (d, J = 4.7 Hz, 2H, $\beta\pi_{out}$), 9.61 (d, J = 4.8 Hz, 2H, $\beta\pi_{out}$), 9.82 (s, 1H, $NHCO_{(S)}$). $^{19}$F NMR ($CDCl_3$, 298 K) $\delta$ -163.20 (td, J1 = 23.1 Hz, J2 = 7.8 Hz, 2F, $F_{m(L)}$), -162.32 (td, J1 = 22.0 Hz, J2 = 7.2 Hz, 2F, $F_{m(L)}$), -160.77 (m, 2F, $F_{m(S)}$), -153.14 (t, J = 20.8 Hz, 2F, $F_{p(L)}$), -150.24 (t, J = 20.7 Hz, 1F, $F_{p(S)}$), -139.21 (d, J = 23.5 Hz, 2F, $F_{o(L)}$), -137.51 (d, J = 23.3 Hz, 2F, $F_{o(L)}$), -136.76 (dd, J1 = 24.9 Hz, J2 = 8.1 Hz, 1F, $F_{o(S)}$), -136.46 (dd, J1 = 27.1 Hz, J2 = 8.4 Hz, 1F, $F_{o(S)}$). Partial $^{13}$C from 2D HSQC ($CDCl_3$, 298 K) $\delta$ 32.8 (1C, $C_{e/f(S)}$), 33.0 (2C, $C_{e/f(L)}$), 37.0 (1C, $NMe_{(S)}$), 37.6 (2C, $NMe_{(L)}$), 43.0 (1C, $C_{g/h(S)}$), 46.7 (2C, $C_{g/h(L)}$), 49.2 (1C, $C_{e/f(S)}$), 50.9 (1C, $C_{g/h(S)}$), 51.0 (2C, $C_{e/f(L)}$), 51.6 (2C, $C_{g/h(L)}$), 122.4 (2C, $C_{\beta\pi in}$), 122.5 (2C, $C_{\beta\pi in}$), 122.9 (1C, $C_{a(S)}$), 123.4 (1C, $C_{c(S)}$), 124.2 (2C, $C_{a(L)}$), 124.6 (2C, $C_{c(L)}$), 129.9 (2C, $C_{b(L)}$), 131.0 (1C, $C_{b(S)}$), 131.6 (2C, $C_{\beta\pi out}$), 134.0 (2C, $C_{\beta\pi out}$), 134.3 (2C, $C_{\beta\pi out}$), 135.3 (1C, $C_{d(S)}$), 135.9 (2C, $C_{d(L)}$), 137.3 (2C, $C_{\beta\pi out}$). UV-visible ($CHCl_3$, $\lambda_{max}$ nm/$\varepsilon$ $L{\cdot}mol^{-1}{\cdot}cm^{-1}$): 488 (49153), 570 (160870), 581 (175624), 607 (68791), 718 (16335), 779 (3917), 904 (6035), 1028 (13156). HRMS (ESI-TOF, positive ion mode): *m/z* calcd for $C_{84}H_{63}N_{13}O_3F_{15}$: 1586.4931 [M+H$^+$]; found 1586.4931.

## Synthesis of 8



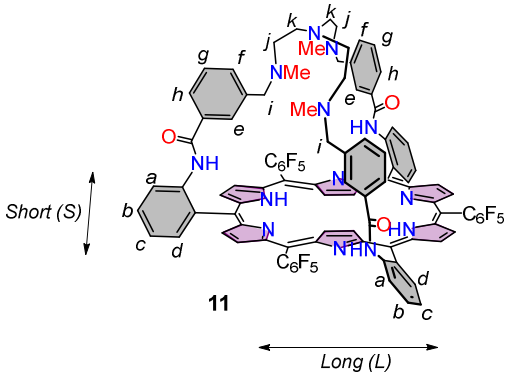

Under inert atmosphere, sodium iodide (51 mg, 340 µmol) and DIPEA (57 µL, 340 µmol) were successively added to a solution of **6** (57 mg, 34 µmol) in anhydrous THF (60 mL) and the mixture was refluxed for 4 hours. Tris[2-(methylamino)ethyl]amine (7 µL, 34 µmol) was then added and the reaction was stirred at 50 °C overnight. THF was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: $CH_2Cl_2$/MeOH 90:10, with 2 % v/v of $Et_3N$) affording, after washing with water, hexaphyrin **8** as a reddish solid (33 mg, 55 %).

$^1$H NMR ($CDCl_3$, 298 K) $\delta$ 2.80 ($s_b$, 2H, $NH_{out}$), 3.03 (s, 3H, $CH_{3(S)}$), 3.45 (m, 2H, $\beta\pi_{out}$), 3.47 (s, 6H, $CH_{3(L)}$), 3.55 ($d_b$, J = 4.6 Hz, 2H, $\beta\pi_{out}$), 3.59 (d, J = 4.7 Hz, 2H, $\beta\pi_{out}$), 3.68 (d, J = 4.9 Hz, 2H, $\beta\pi_{out}$), 3.75-3.85

(m, 10H, $CH_{2j/k}$), 4.01 (m, 2H, $CH_{2j/k}$), 4.43 (s, 2H, $CH_{2i(S)}$), 4.73 (d, J = 13.6 Hz, 2H, $CH_{2i(L)}$), 4.78 (d, J = 13.6 Hz, 2H, $CH_{2i(L)}$), 6.38 (d, J = 7.2 Hz, 3H, $Ar_{d(S+L)}$), 6.70 (t, J = 7.2 Hz, 2H, $Ar_{c(L)}$), 6.71 (t, J = 7.2 Hz, 1H, $Ar_{c(S)}$), 6.87 (t, J = 7.1 Hz, 2H, $Ar_{b(L)}$), 6.97 (t, J = 7.4 Hz, 1H, $Ar_{b(S)}$), 7.16 (s, 2H, $NHCO_{(L)}$), 7.47 (d, J = 7.9 Hz, 2H, $Ar_{a(L)}$), 7.77 (t, J = 7.5 Hz, 1H, $Ar_{g(S)}$), 7.84 (d, J = 7.7 Hz, 1H, $Ar_{h(S)}$), 7.91 (s, 1H, $NHCO_{(S)}$), 8.03 (d, J = 7.7 Hz, 1H, $Ar_{a(S)}$), 8.04 (d, J = 7.8 Hz, 1H, $Ar_{f(S)}$), 8.14 (d, J = 7.4 Hz, 2H, $Ar_{h(L)}$), 8.21 (t, J = 7.5 Hz, 2H, $Ar_{g(L)}$), 8.30 (s, 1H, $Ar_{e(S)}$), 8.37 (d, J = 7.5 Hz, 2H, $Ar_{f(L)}$), 8.45 (s, 2H, $Ar_{e(L)}$), 19.01 ($s_b$, 2H, $\beta\pi_{in}$), 19.14 ($s_b$, 2H, $\beta\pi_{in}$), 25.73 (m, 2H, $NH_{in}$). $^{19}F$ NMR ($CDCl_3$, 298 K) $\delta$ -160.62 (m, 4F, $F_m$), -158.79 ($t_b$, J = 22.3 Hz, 2F, $F_m$), -154.50 (t, J = 21.7 Hz, 1F, $F_{p(S)}$), -152.79 (t, J = 22.1 Hz, 2F, $F_{p(L)}$), -139.77 (dd, J1 = 24.6 Hz, J2 = 8.4 Hz, 1F, $F_{o(S)}$), -139.06 (dd, J1 = 24.4, J2 = 8.6 Hz, 1F, $F_{o(S)}$), -138.52 (d, J = 21.9 Hz, 2F, $F_{o(L)}$), -137.32 (d, J = 23.8 Hz, 2F, $F_{o(L)}$). Partial $^{13}C$ from 2D HSQC ($CDCl_3$, 298 K) $\delta$ 44.2 (1C, $NMe_{(S)}$), 45.1 (2C, $NMe_{(L)}$), 55.3-56.8 (6C, $C_{j/k}$), 64.0 (3C, $C_i$), 121.3 (1C, $C_{a(S)}$), 123.2 (2C, $C_{a(L)}$), 123.9 (2C, $C_{\beta\pi in}$), 124.2 (2C, $C_{\beta\pi in}$), 125.5 (3C, $C_{c(S+L)}$), 126.6 (2C, $C_{\beta\pi out}$), 126.7 (2C, $C_{h(L)}$), 126.9 (1C, $C_{h(S)}$), 128.3 (1C, $C_{e(S)}$), 128.6 (2C, $C_{\beta\pi out}$), 129.3 (3C, $C_{b(S)+e(L)}$), 129.7 (5C, $C_{b(L)+d(S+L)}$), 130.1 (3C, $C_{g(S+L)}$), 131.2 (2C, $C_{\beta\pi out}$), 132.3 (2C, $C_{\beta\pi out}$), 133.6 (1C, $C_{f(S)}$), 134.2 (2C, $C_{f(L)}$). UV-visible ($CHCl_3$, $\lambda_{max}$ nm/ε $L{\cdot}mol^{-1}{\cdot}cm^{-1}$): 410 (23768), 439 (44683), 488 (93368), 579 (76945), 606 (57401). HRMS (ESI-TOF, positive ion mode): *m/z* calcd for $C_{99}H_{71}N_{13}O_3F_{15}$: 1774.5563 [$M+H^+$]; found 1774.5541.

## Synthesis of 11

*Note:* compound **11** could not be isolated with high purity due to tedious purification, and was thus formed by addition of DDQ to an NMR tube solution of **8** for spectroscopic characterization.




In a NMR tube, hexaphyrin **8** (10 mg, 5.6 µmol) was dissolved in 500 µL of $CDCl_3$. At 25 °C, DDQ (1.5 mg, 6.6 µmol) was added to this solution. After 30 min, $Et_3N$ (16 µL) was added. $^1H$ NMR spectrum showed quasi-quantitative formation of **11**. Note: a large excess of $Et_3N$ was needed to obtain a well resolved NMR spectrum.

$^1H$ NMR ($CDCl_3$, 298 K) $\delta$ -2.99 ($d_b$, J = 4.1 Hz, 2H, $\beta\pi_{in}$), -2.96 ($d_b$, J = 4.1 Hz, 2H, $\beta\pi_{in}$), 0.07 (m, 2H, $CH_{2j/k(L)}$), 0.17 (m, 2H, $CH_{2j/k(L)}$), 0.21 (s, 6H, $CH_{3(L)}$), 0.41 (m, 4H, $CH_{2j/k(L)}$), 0.63 (m, 2H, $CH_{2j/k(S)}$), 0.87 (m, 2H, $CH_{2j/k(S)}$), 1.20 (s, 3H, $CH_{3(S)}$), 1.51 (d, J = 12.0 Hz, 2H, $CH_{i(L)}$), 1.83 (m, 2H, $CH_{i(L)}$), 2.55 (s, 2H, $CH_{i(S)}$), 5.94 (s, 2H, $Ar_{e(L)}$), 6.52 (m, 5H, $Ar_{g(L)+f(L)+e(S)}$), 6.66 (t, J = 7.5 Hz, 1H, $Ar_{g(S)}$), 6.81 (d, J = 7.5 Hz, 1H, $Ar_{f(S)}$), 7.05 (m, 3H, $Ar_{h(S+L)}$), 7.66 (t, J = 8.5 Hz, 2H, $Ar_{c(L)}$), 7.69 (s, 1H, $NHCO_{(S)}$), 7.77 (t, J = 7.6 Hz, 1H, $Ar_{c(S)}$), 7.90 (d, J = 7.4 Hz, 2H, $Ar_{d(L)}$), 8.01 (t, J = 8.5 Hz, 2H, $Ar_{b(L)}$), 8.04 (t, J = 7.6 Hz, 1H, $Ar_{b(S)}$), 8.35 (d, J = 7.3

Hz, 1H, $Ar_{d(S)}$), 8.61 (d, J = 8.4 Hz, 2H, $Ar_{a(L)}$), 8.73 (d, J = 7.7 Hz, 1H, $Ar_{a(S)}$), 9.08 (d, J = 4.2 Hz, 2H, $\beta\pi_{out}$), 9.23 (s, 2H, $NHCO_{(L)}$), 9.37 (d, J = 4.2 Hz, 2H, $\beta\pi_{out}$), 9.54 (d, J = 4.2 Hz, 2H, $\beta\pi_{out}$), 9.58 (d, J = 4.2 Hz, 2H, $\beta\pi_{out}$). Partial $^{13}C$ from 2D HSQC ($CDCl_3$, 298 K) $\delta$ 41.6 (2C, $NMe_{(L)}$), 42.8 (1C, $NMe_{(S)}$), 51.2 (2C, $C_{j/k(L)}$), 51.7 (1C, $C_{j/k(S)}$), 53.0 (3C, $C_{j/k(L+S)}$), 61.3 (2C, $C_{i(L)}$), 62.1 (1C, $C_{i(S)}$), 121.8 (2C, $C_{\beta\pi in}$), 123.1 (2C, $C_{\beta\pi in}$), 123.4 (1C, $C_{a(S)}$), 124.5 (2C, $C_{a(L)}$), 124.7 (1C, $C_{c(S)}$), 124.9 (2C, $C_{c(L)}$), 125.9 (2C, $C_{e(L)}$), 126.2 (3C, $C_{h(S+L)}$), 126.7 (1C, $C_{e(S)}$), 128.4 (2C, $C_{f/g(L)}$), 128.8 (1C, $C_{g(S)}$), 130.3 (2C, $C_{b(L)}$), 131.2 (1C, $C_{b(S)}$), 131.5 (2C, $C_{f/g(L)}$), 131.8 (2C, $C_{\beta\pi out}$), 132.4 (1C, $C_{f(S)}$), 134.1 (2C, $C_{\beta\pi out}$), 134.6 (2C, $C_{\beta\pi out}$), 136.4 (1C, $C_{d(S)}$), 136.9 (2C, $C_{d(L)}$), 137.4 (2C, $C_{\beta\pi out}$). HRMS (ESI-TOF, positive ion mode): *m/z* calcd for $C_{99}H_{69}N_{13}O_3F_{15}$: 1772.5406 [$M+H^+$]; found 1772.5393.

## Metallation of 8 with Zn(II)

- General procedures, pathway A and B:

***Pathway A.*** The three following solutions were prepared:

- **S1**: 12.3 mg of $Zn(OTf)_2$ in 9:1 $CDCl_3/CD_3OD$ (500 µL).
- **S2**: 10.5 mg of $Bu_4NOAc$ in 9:1 $CDCl_3/CD_3OD$ (500 µL).
- **S3**: 3.4 µL of butylamine in 9:1 $CDCl_3/CD_3OD$ (500 µL).

In a NMR tube, hexaphyrin **8** (4.8 mg, 2.7 µmol) was dissolved in 9:1 $CDCl_3/CD_3OD$ (500 µL). To this solution, 40 µL of S1 (1 equiv.), 40 µL of S2 (1 equiv.) and 40 µL of S3 (1 equiv.) were successively added at room temperature. A $^1H$ NMR spectrum recorded at 298 K showed quasi-quantitative formation of **$8Zn^{OAc}_{NH2Bu}.H^+,OTf^-$**.

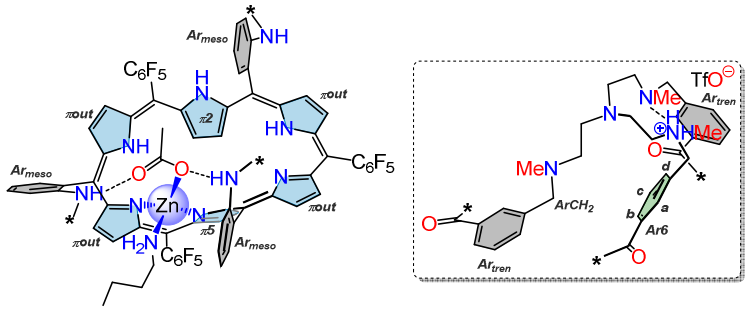
***Pathway B.*** The following solution was prepared:

- **S4**: 7.4 mg of $Zn(OAc)_2$ in 9:1 $CDCl_3/CD_3OD$ (500 µL).

In a NMR tube, hexaphyrin **8** (4.8 mg, 2.7 µmol) was dissolved in 9:1 $CDCl_3/CD_3OD$ (500 µL). To this solution, 1 µL (3 equiv.) of butylamine, 3.5 µL (7 equiv.) of DIPEA and 140 µL (3.5 equiv.) of S4 were added at room temperature. A $^1H$ NMR spectrum recorded at 298 K showed quasi-quantitative formation of **$8Zn^{OAc}_{NH2Bu}$.**

- NMR description of **$8Zn^{OAc}_{NH2Bu}[.H^+,OTf^-]$**, pathway A *vs.* B (partial descriptions because of a strong overlapping and/or highly broaden signals [*e.g.* $CH_2$ tren protons])

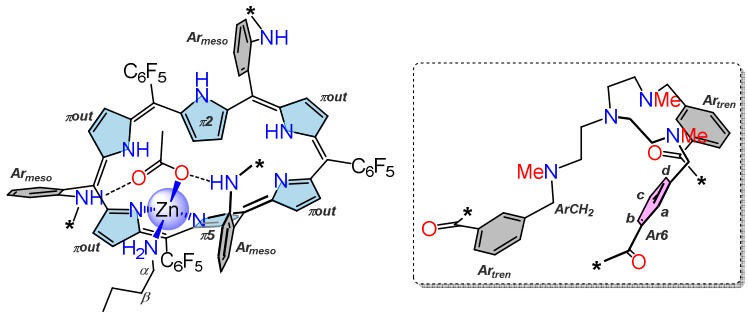
***Pathway A:***



$^{8}Zn^{OAc}_{NH_2Bu}.H^{+},OTf^{-}$

$^{1}$H NMR (9:1 $CDCl_3/CD_3OD$, 298 K) $\delta$ -3.50 (d, J = 4.3 Hz, 1H, βπ2), -2.21 (s, 3H, $CH_{3OAc}$), -1.72 (d, J = 4.4 Hz, 1H, βπ2), 1.28 (m, 1H, Ar6b), 1.96 (m, 1H, $ArCH_2$), 2.30 (d, J = 11.4 Hz, 1H, $ArCH_2$), 2.44 (d, J = 12.6 Hz, 1H, $ArCH_2$), 2.69 (d, J = 12.6 Hz, 1H, $ArCH_2$), 3.07 (m, 1H, Ar6c), 3.41 (m, 1H, Ar6d), 3.57 (d, J = 12.8 Hz, 1H, $ArCH_2$), 4.27 (m, 1H, $ArCH_2$), 4.37 (d, J = 3.9 Hz, 1H, βπ5), 4.59 (d, J = 4.6 Hz, 1H, βπ5), 6.52 (s, 1H, Ar6a), 6.54 (d, J = 7.8 Hz, 1H, $Ar_{meso}$), 6.64 (s, 1H, $Ar_{tren}$), 6.85 (d, J = 7.8 Hz, 1H, $Ar_{tren}$), 6.97 (t, J = 7.9 Hz, 1H, $Ar_{meso}$), 7.01 (t, J = 7.5 Hz, 1H, $Ar_{tren}$), 7.09 (d, J = 4.7 Hz, 1H, $\beta\pi_{out}$), 7.12 (d, J = 7.4 Hz, 1H, $Ar_{meso}$), 7.19 (d, J = 5.1 Hz, 1H, $\beta\pi_{out}$), 7.24 (t, J = 8.2 Hz, 1H, $Ar_{meso}$), 7.37 (t, J = 7.7 Hz, 1H, $Ar_{meso}$), 7.43 (m, 2H, $Ar_{tren}$+ $\beta\pi_{out}$), 7.60 (m, 3H, $Ar_{meso}$+2$Ar_{tren}$), 7.69 (t, J = 7.9 Hz, 1H, $Ar_{meso}$), 7.72 (t, J = 7.9 Hz, 1H, $Ar_{meso}$), 7.78 (d, J = 7.9 Hz, 1H, $Ar_{meso}$), 7.88 (d, J = 4.8 Hz, 1H, $\beta\pi_{out}$), 7.99 (d, J = 4.3 Hz, 1H, $\beta\pi_{out}$), 8.06 (s, 1H, $Ar_{tren}$), 8.13 (m, 2H, $Ar_{tren}$+$\beta\pi_{out}$), 8.23 (d, J = 8.5 Hz, 1H, $Ar_{meso}$), 8.29 (m, 2H, $Ar_{meso}$+ $\beta\pi_{out}$), 8.43 (d, J = 4.3 Hz, 1H, $\beta\pi_{out}$), 8.56 (d, J = 8.6 Hz, 1H, $Ar_{meso}$). $^{19}$F NMR (9:1 $CDCl_3/CD_3OD$, 298 K) $\delta$ -162.70 (dt, J1 = 22.9 Hz, J2 = 8.1 Hz, 1F, $F_m$), -162.29 (m, 3F, $F_o$), -160.78 (m, 2F, $F_o$), -154.23 (t, J = 20.9 Hz, 1F, $F_p$), -154.19 (t, J = 20.9 Hz, 1F, $F_p$), -152.33 (m, 1F, $F_p$), -140.19 (dd, J1 = 22.4 Hz, J2 = 6.8 Hz, 1F, $F_o$), -139.22 (d, J = 24.4 Hz, 1F, $F_o$), -138.20 (m, 2F, $F_o$), -137.61 (dd, J1 = 24.7 Hz, J2 = 8.3 Hz, 1F, $F_o$), -137.27 (m, 1F, $F_o$).

***Pathway B:***



$^{8}Zn^{OAc}_{NH_2Bu}$

$^{1}$H NMR (9:1 $CDCl_3/CD_3OD$, 298 K) $\delta$ -3.77 ($d_b$, 1H, βπ2), -2.12 ($d_b$, 1H, βπ2), -2.04 (s, 3H, $CH_{3OAc}$), 0.89 (m, 1H, $CH_{2\_\beta BuNH2}$), 1.10 (m, 1H, $CH_{2\_\beta BuNH2}$), 1.26 (s, 3H, NMe), 1.43 (m, 1H, $CH_{2\_\alpha BuNH2}$), 1.54 (m, 1H, Ar6b), 1.58 (m, 1H, $CH_{2\_\alpha BuNH2}$), 1.60 (s, 3H, NMe), 1.91 (s, 3H, NMe), 2.05 (d, J = 11.4 Hz, 1H, $ArCH_2$), 2.23 (d, J = 11.4 Hz, 1H, $ArCH_2$), 2.51 (m, 1H, $ArCH_2$), 2.66 (m, 1H, $ArCH_2$), 2.83 (d, J = 14.3 Hz, 1H,

$ArCH_2$), 3.26 (m, 1H, $ArCH_2$), 3.68 (m, 1H, Ar6c), 4.20 ($d_b$, 1H, βπ5), 4.52 ($d_b$, 1H, βπ5), 5.19 (m, 1H, Ar6d), 6.72 (s, 1H, $HAr_{tren}$), 6.78 (s, 1H, Ar6a), 6.84 ($d_b$, J = 6.9 Hz, 1H, $HAr_{tren}$), 6.88 ($d_b$, J = 7.7 Hz, 1H, $HAr_{meso}$), 6.94 (t, J = 7.6 Hz, 1H, $HAr_{meso}$), 6.97 (t, J = 7.7 Hz, 1H, $HAr_{tren}$), 7.09-7.22 ($m_b$, $HAr_{meso}$ + $HAr_{tren}$ + $\beta\pi_{out}$), 7.34-7.55 ($m_b$, $HAr_{meso}$ + $HAr_{tren}$ + $\beta\pi_{out}$), 7.59 (d, J = 7.6 Hz, 1H, $HAr_{meso}$), 7.69 (m, 2H, $HAr_{meso}$ + $\beta\pi_{out}$), 7.78 (m, 2H, $HAr_{meso}$), 8.02 (d, J = 4.8 Hz, 1H, $\beta\pi_{out}$), 8.19 (m, 4H, $HAr_{meso}$ + $\beta\pi_{out}$), 8.26 (d, J = 7.6 Hz, 1H, $HAr_{meso}$), 8.51 (m, 1H, $\beta\pi_{out}$), 8.53 (d, J = 7.6 Hz, 1H, $HAr_{meso}$). $^{19}F$ NMR (9:1 $CDCl_3/CD_3OD$, 298 K) $\delta$ -162.75 (m, 2F, $F_m$), -162.45 (m, 2F, $F_m$), -162.16 (m, 1F, $F_m$), -160.76 (m, 1F, $F_m$), -154.18 (t, J = 20.9 Hz, 1F, $F_p$), -153.44 (m, 2F, $F_p$), -140.25 (m, 1F, $F_o$), -139.24 (m, 1F, $F_o$), -138.72 (m, 1F, $F_o$), -138.27 (dd, J1 = 23.9 Hz, J2 = 8.0 Hz, 1F, $F_o$), -137.42 (dd, J1 = 24.4 Hz, J2 = 8.3 Hz, 1F, $F_o$), -135.58 (m, 1F, $F_o$). UV-visible (9:1 $CHCl_3/CH_3OH$, $\lambda_{max}$ nm): 396, 566, 607, 636, 807, 880, 901, 990.

## Crystallographic data for 1 [CCDC 1560725]

($C_{45.33}H_{18.67}Cl_4F_{10}N_6O_4$); *M* = 1043.13. D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), *T* = 150(2) K; Triclinic *P* -1 (I.T.#2), *a* = 14.7140(6), *b* = 15.8048(7), *c* = 17.2717(7) Å, *α* = 78.0620(10), *β* = 69.3740(10), *γ* = 64.0160(10) °, *V* = 3372.5(2) Å$^3$. *Z* = 3, *d* = 1.541 g.cm$^{-3}$, *μ* = 0.356 mm$^{-1}$. The structure was solved by direct methods using the *SIR97* program,[2] and then refined with full-matrix least-square methods based on $F^2$ (*SHELXL-97*).[3] The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,[4] implemented as the *SQUEEZE* option in *PLATON*.[5] A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on $F^2$ with 15413 unique intensities and 869 parameters converged at $\omega R(F^2)$ = 0.3138 ($R(F)$ = 0.1160) for 11260 observed reflections with $I > 2\sigma(I)$.

## Crystallographic data for 5 [CCDC 1560726]

($C_{84}H_{64}F_{15}N_{13}O_3$); *M* = 1588.48. D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), *T* = 150(2) K; monoclinic *P* $2_1/c$ (I.T.#14), *a* = 18.035(2), *b* = 31.918(4), *c* = 16.6641(18) Å, *β* = 112.641(4) °, *V* = 8853.2(17) Å$^3$. *Z* = 4, *d* = 1.192 g.cm$^{-3}$, *μ* = 0.096 mm$^{-1}$. The structure was solved by dual-space algorithm using the *SHELXT* program,[6] and then refined with full-matrix least-square methods based on $F^2$ (*SHELXL-2014*).[7] The contribution of the disordered solvents to the structure factors was calculated by the *PLATON* SQUEEZE procedure[8] and then taken into account in the final *SHELXL-2014<:I>* least-square refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on $F^2$ with 20275 unique intensities and 1051 parameters converged at $\omega R(F^2)$ = 0.2874 (R(F) = 0.1062) for 13083 observed reflections with $I > 2\sigma(I)$.

## Crystallographic data for $8Zn^{OAc}_{NH2Bu}.H^+,OTf^-$ [CCDC 1560727]

($C_{105}H_{84}F_{15}N_{14}O_5Zn$, $CF_3O_3S$, 2($CHCl_3$)); *M* = 2360.03. D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), *T* = 150 K; monoclinic *P* $2_1/n$ (I.T.#14), *a* = 14.8223(7), *b* = 30.7285(17), *c* = 27.9264(15) Å, *β* = 97.487(2) °, *V* = 12611.1(11) Å$^3$. *Z* = 4, *d* = 1.243 g.cm$^{-3}$, *μ* = 0.419 mm$^{-1}$. The structure was solved by dual-space algorithm using the *SHELXT* program,[6] and then refined with full-matrix least-square methods based on $F^2$ (*SHELXL-2014*).[7] The contribution of the disordered solvents to the structure factors was calculated by the *PLATON* SQUEEZE procedure[8] and then taken into account in the final *SHELXL-2014* least-square refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except nitrogen $N_{151}$ linked hydrogen atom that was introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. A final refinement on $F^2$ with 28823 unique intensities and 1363 parameters converged at $\omega R(F^2)$ = 0.2972 ($R(F)$ = 0.1208) for 16927 observed reflections with $I > 2\sigma(I)$.

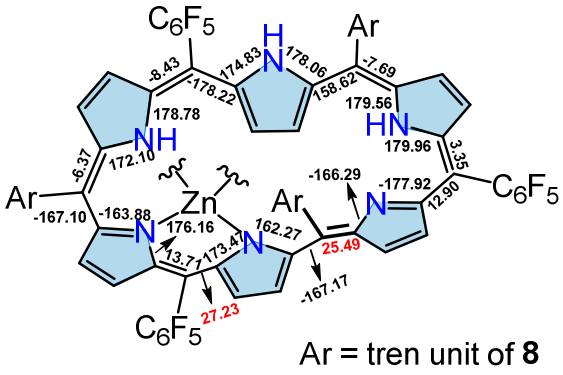



**Figure S1.** Dihedral angles (°) of **8Zn$^{OAc}_{NH2Bu}$.H$^{+}$,OTf$^{-}$** along the SMC.

## II. NMR spectral data

### Selected NMR spectra of 1

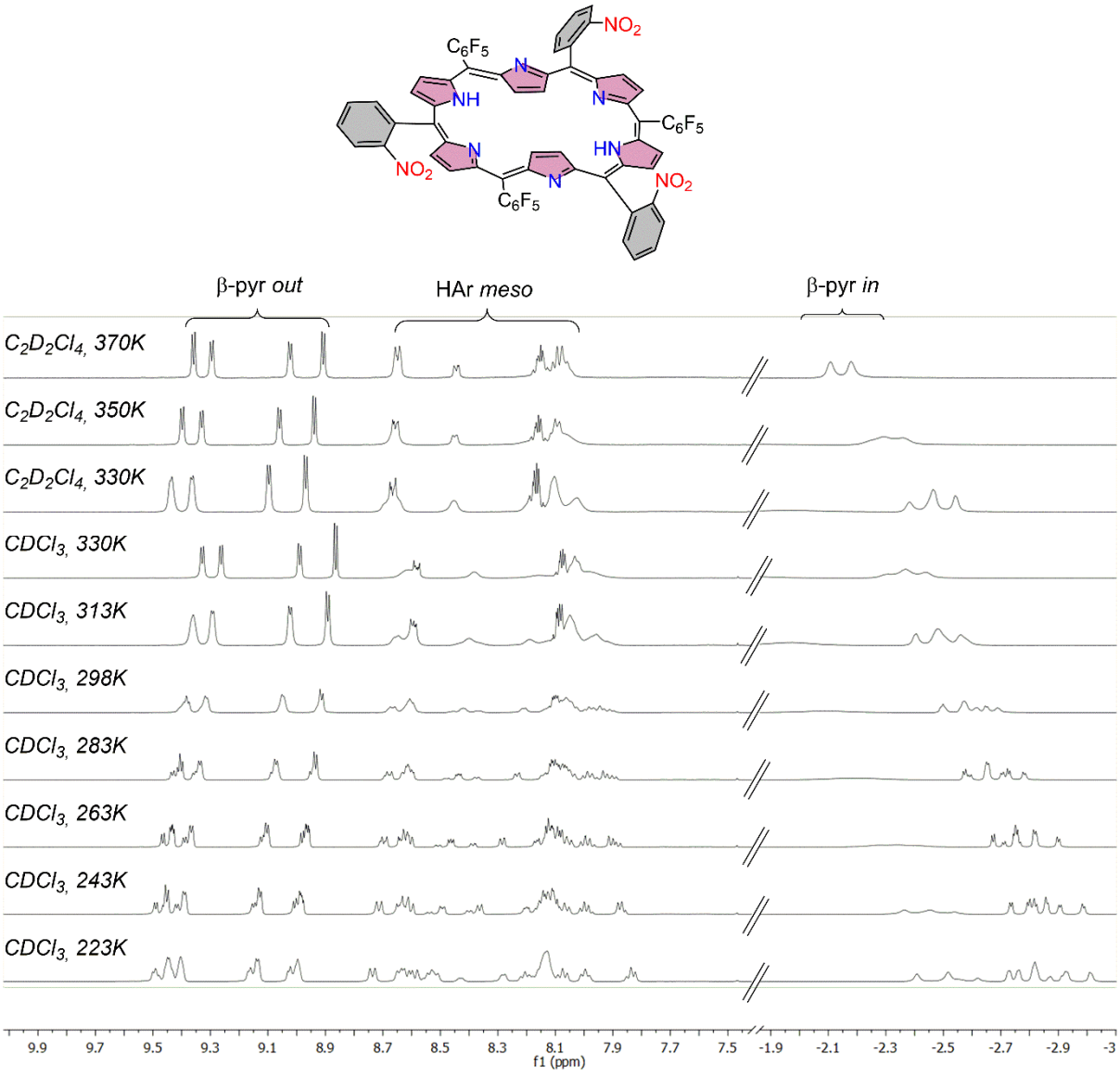



**Figure S2.** VT $^{1}$H NMR spectra of **1.**

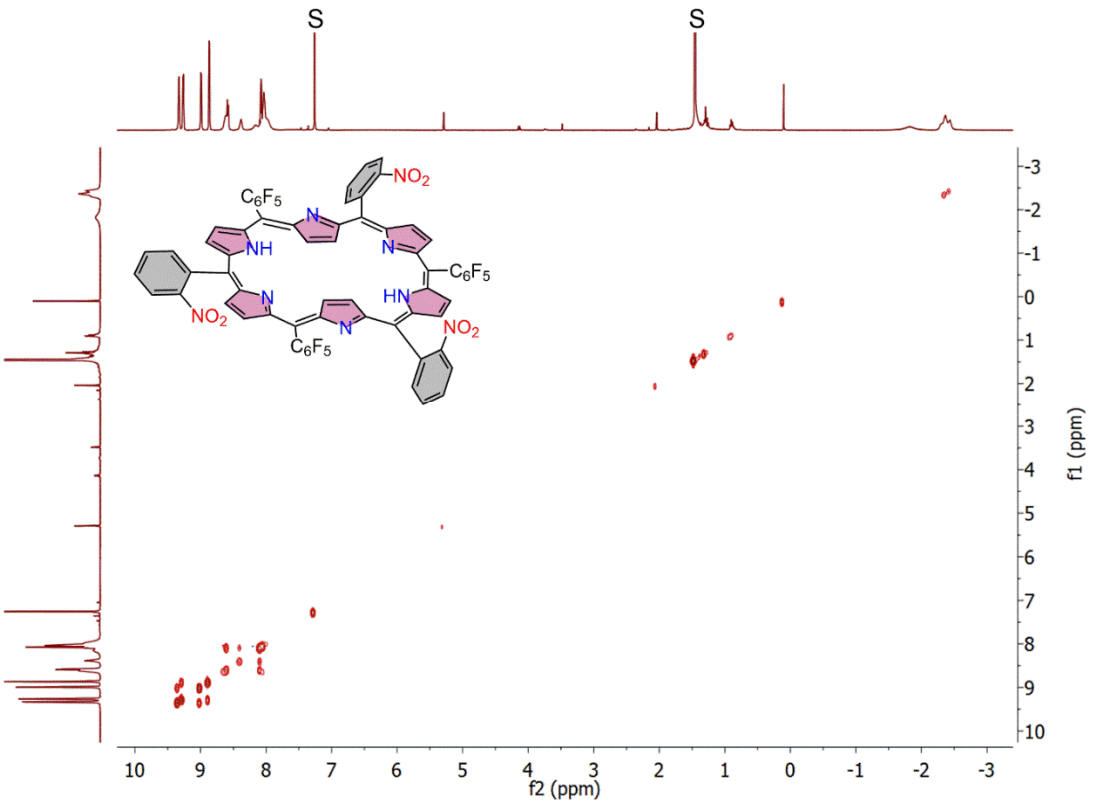



**Figure S3.** 2D COSY NMR spectrum ($CDCl_3$, 330 K) of **1**. S = solvent, G = grease.

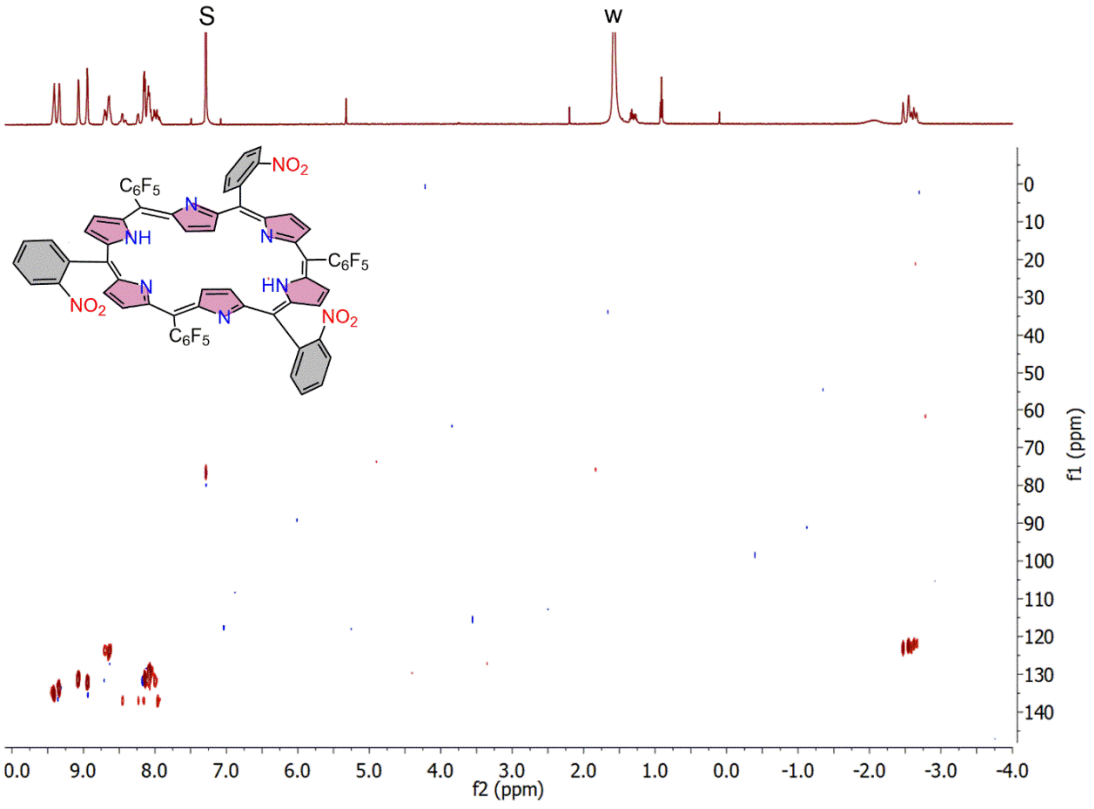



**Figure S4.** 2D HSQC NMR spectrum ($CDCl_3$, 298 K) of **1**. S = solvent, W = water.

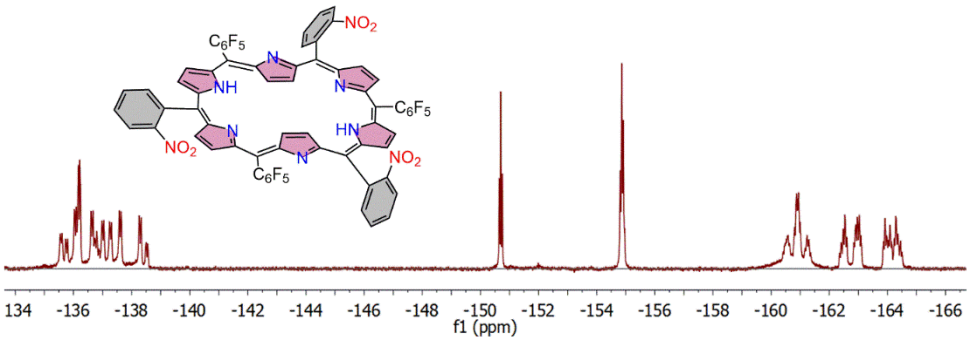



**Figure S5.** $^{19}$F NMR spectra ($CDCl_3$, 298 K) of **1**.

## Selected NMR spectra of 3 and 6

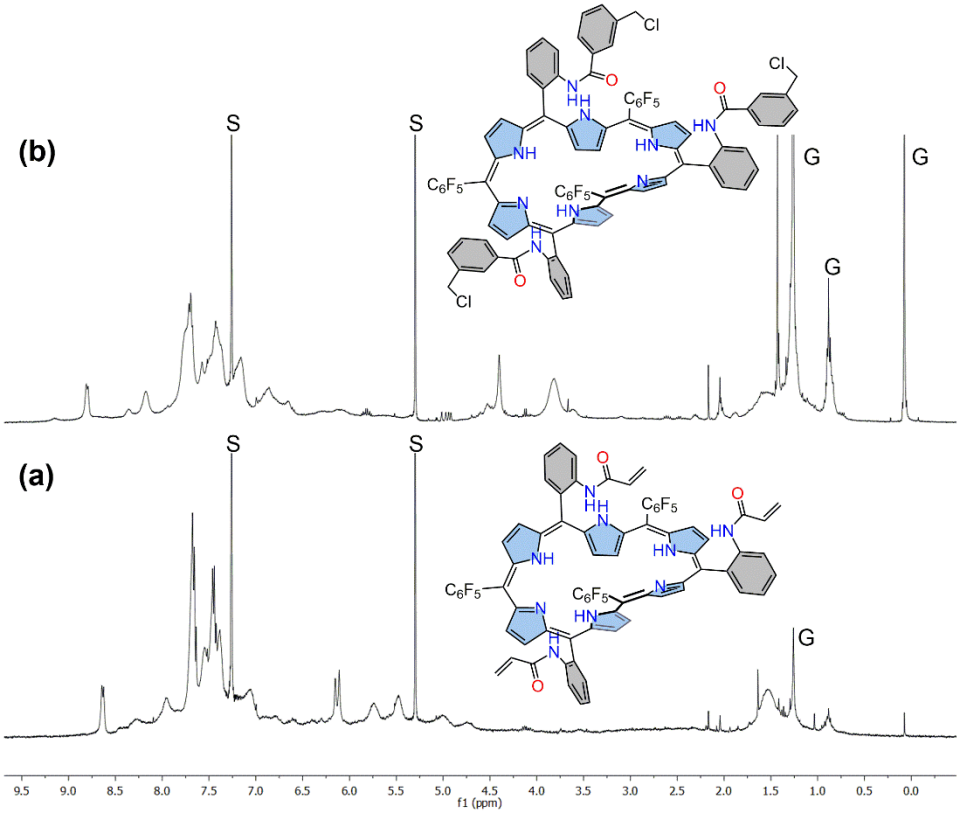



**Figure S6.** $^{1}$H NMR spectra ($CDCl_3$, 298 K) of **3** (a) and **6** (b). S = solvent, G = grease.

*Note:* the $^{1}$H NMR spectra of **3** and **6** are ill defined at 298 K, likely due to both the fast interconversion between several Möbius conformations and *meso*-aryl atropisomers.

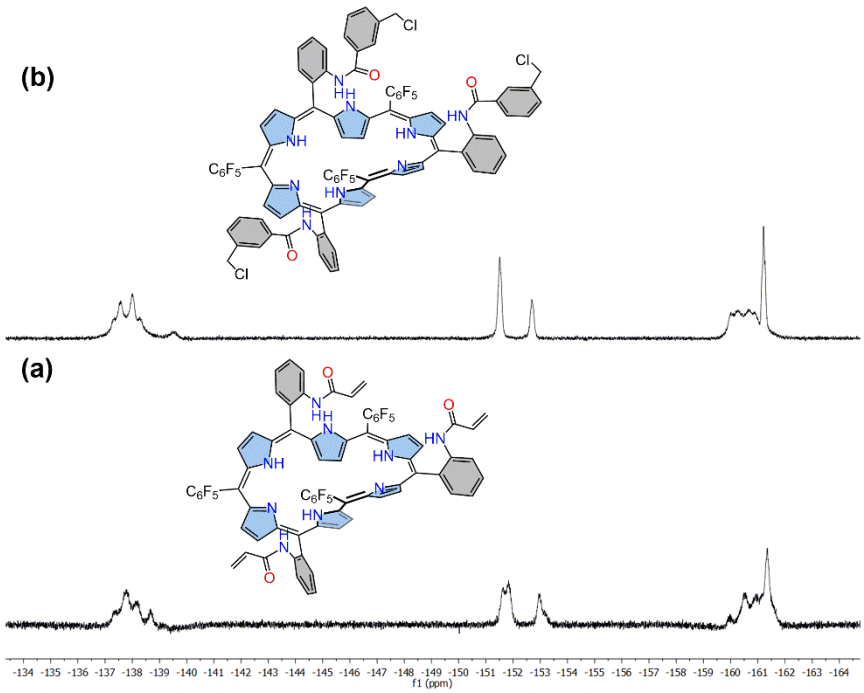



**Figure S7.** $^{19}F$ NMR spectra ($CDCl_3$, 298 K) of **3** (a) and **6** (b).

## Selected NMR spectra of 4

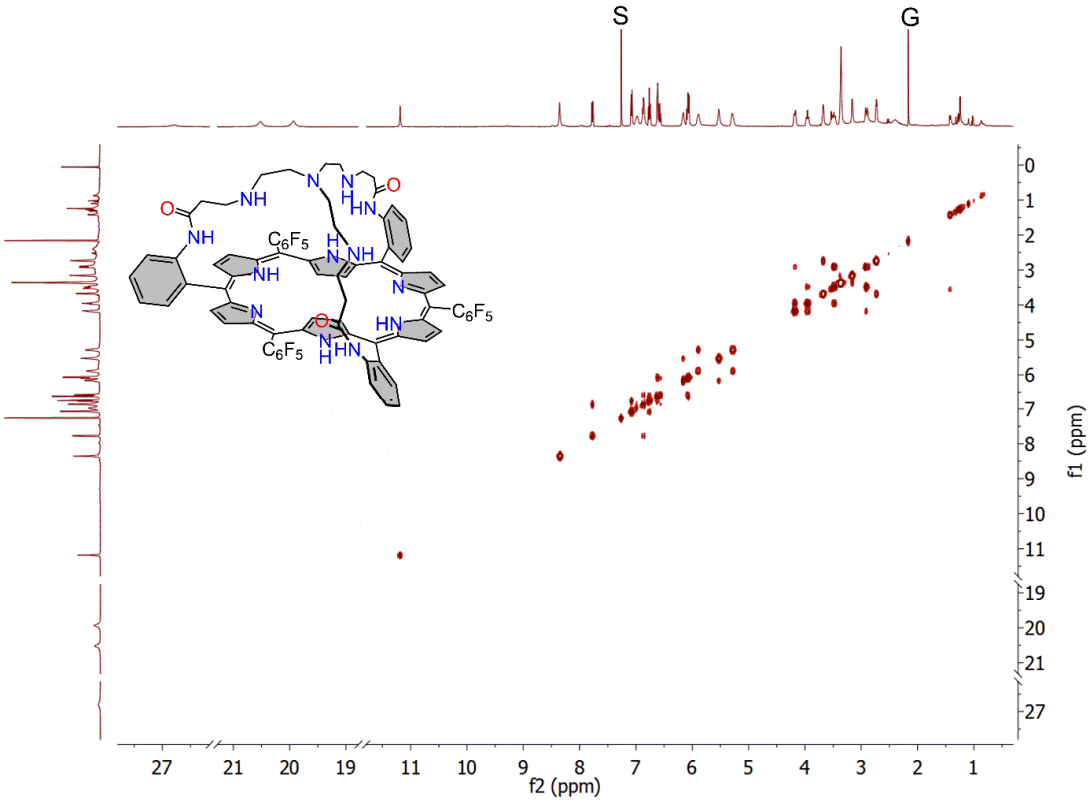



**Figure S8.** 2D COSY NMR spectrum ($CDCl_3$, 298 K) of **4**. S = solvent, G = grease.

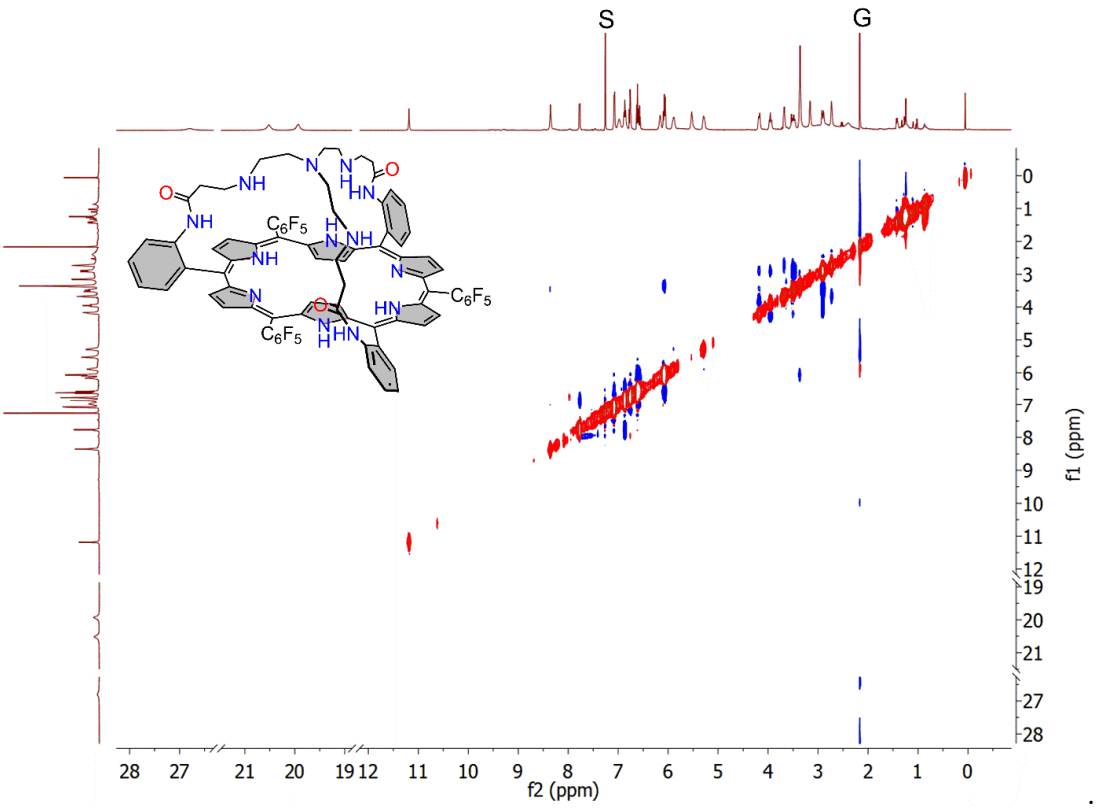



**Figure S9.** 2D ROESY NMR spectrum ($CDCl_3$, 298 K) of **4**. S = solvent, G = grease.

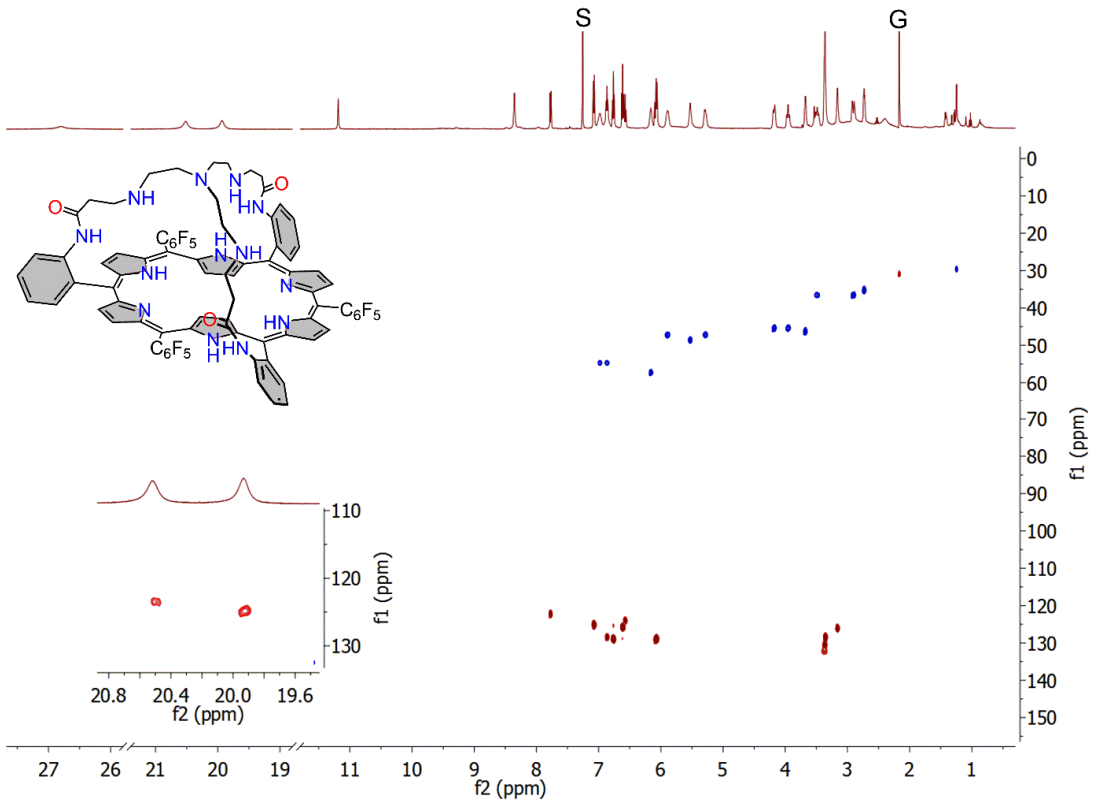



**Figure S10.** 2D HSQC NMR spectrum ($CDCl_3$, 298 K) of **4**. S = solvent, G = grease.

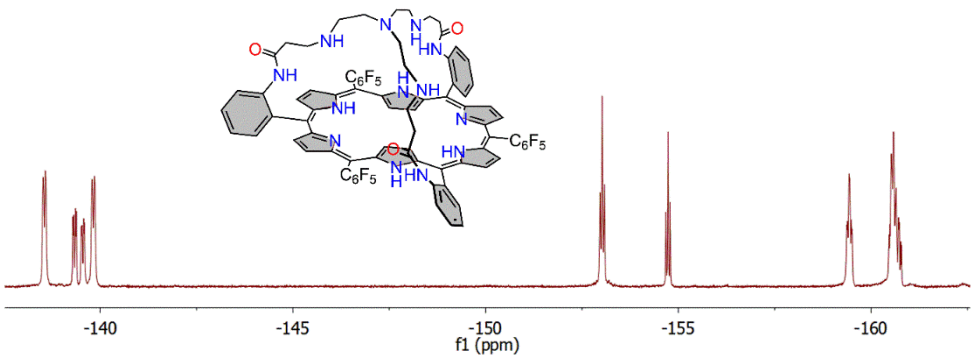



**Figure S11.** $^{19}F$ NMR spectrum ($CDCl_3$, 298 K) of **4**.

## Selected NMR spectra of 5

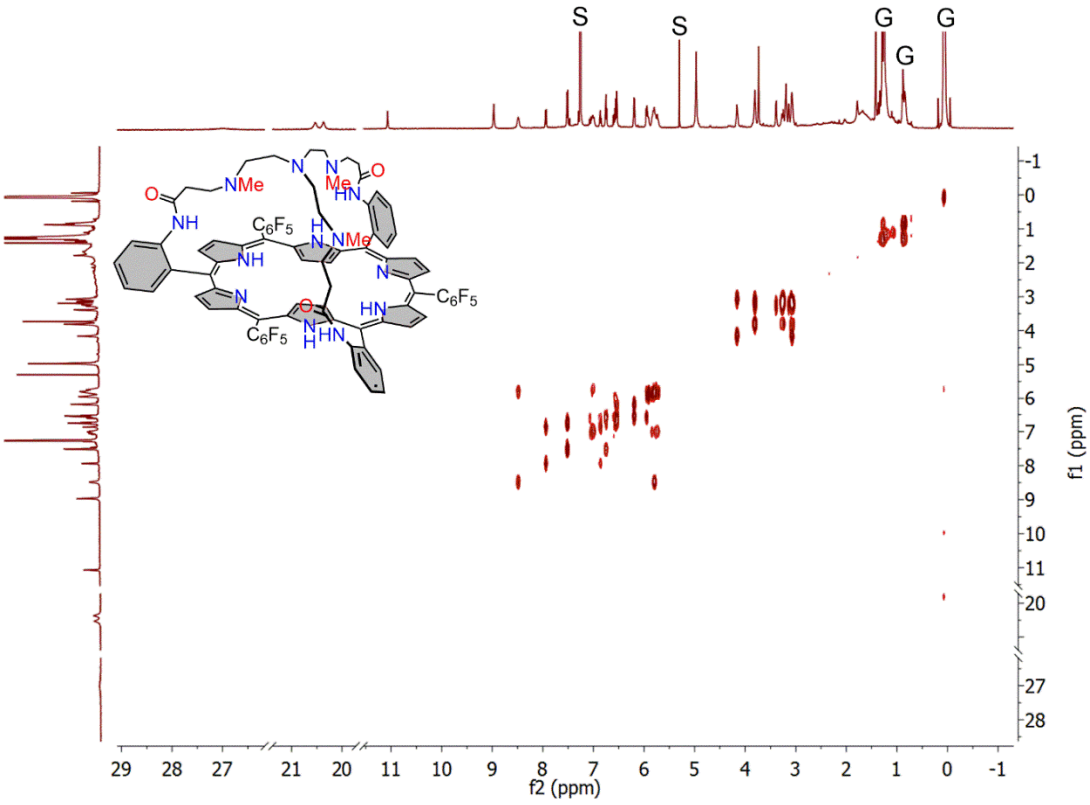



**Figure S12.** 2D COSY NMR spectrum ($CDCl_3$, 298 K) of **5**. S = solvent, G = grease.

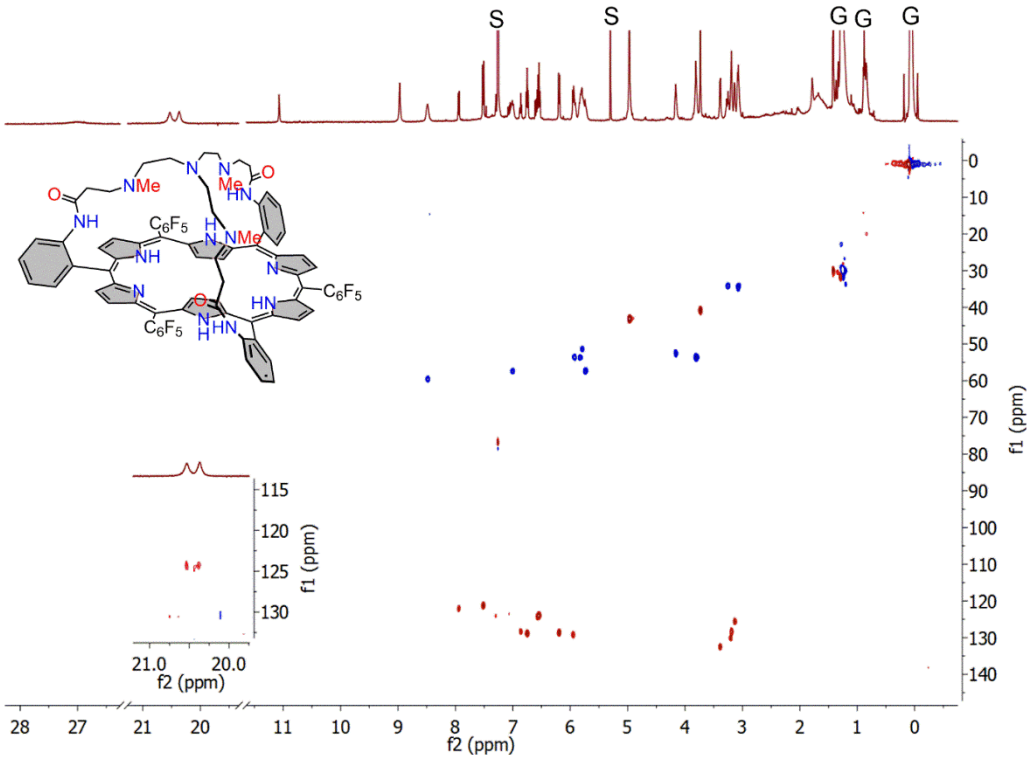



**Figure S13.** 2D HSQC NMR spectrum ($CDCl_3$, 298 K) of **5**. S = solvent, G = grease.

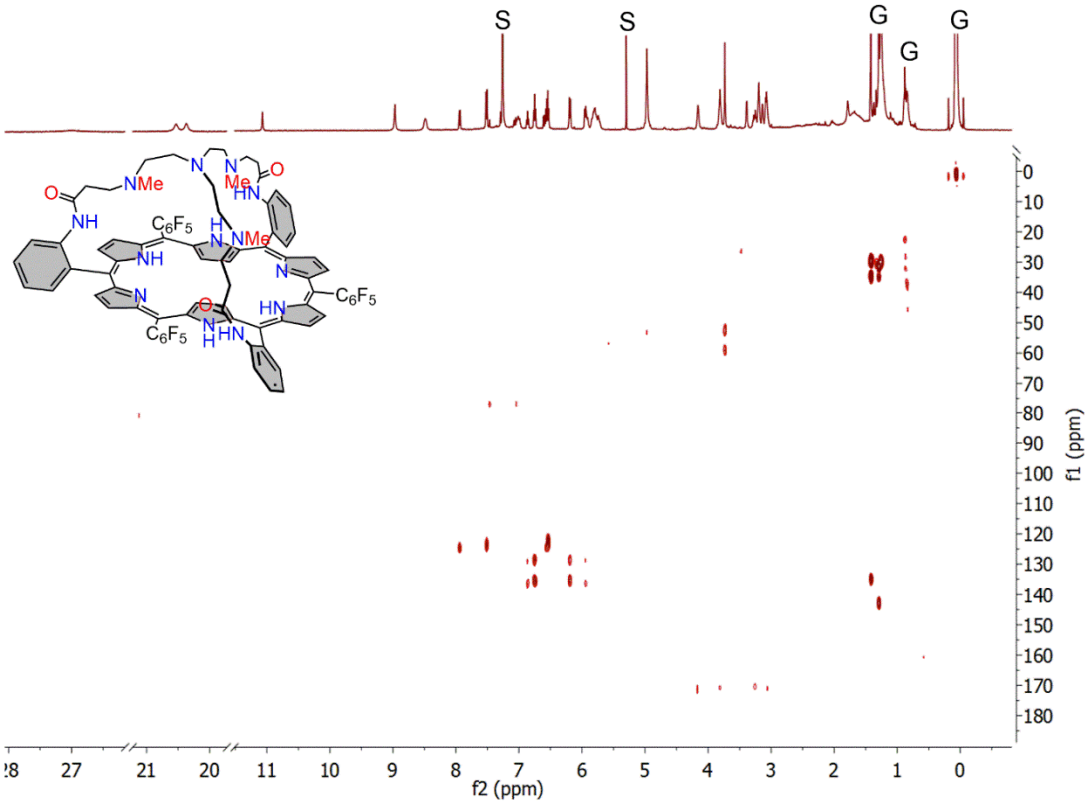



**Figure S14.** 2D HMBC NMR spectrum ($CDCl_3$, 298 K) of **5**. S = solvent, G = grease.

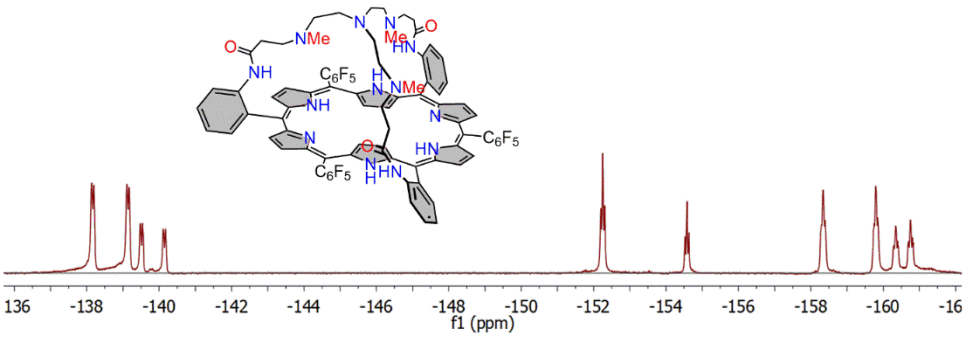



**Figure S15.** $^{19}F$ NMR spectrum ($CDCl_3$, 298 K) of **5**.

## Selected NMR spectra of 9

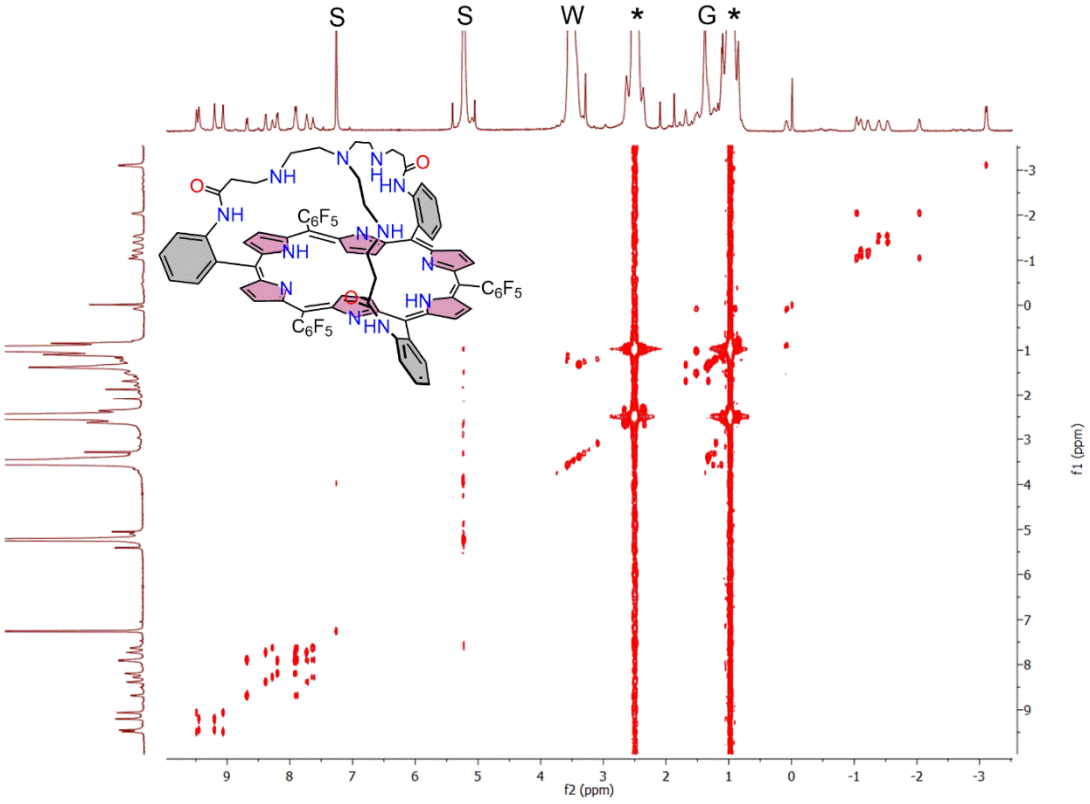



**Figure S16.** 2D COSY NMR spectrum (9:1 $CDCl_3/CD_3OD$, 298 K) of **9**. S = solvent, G = grease, W = water, * = $Et_3N$.

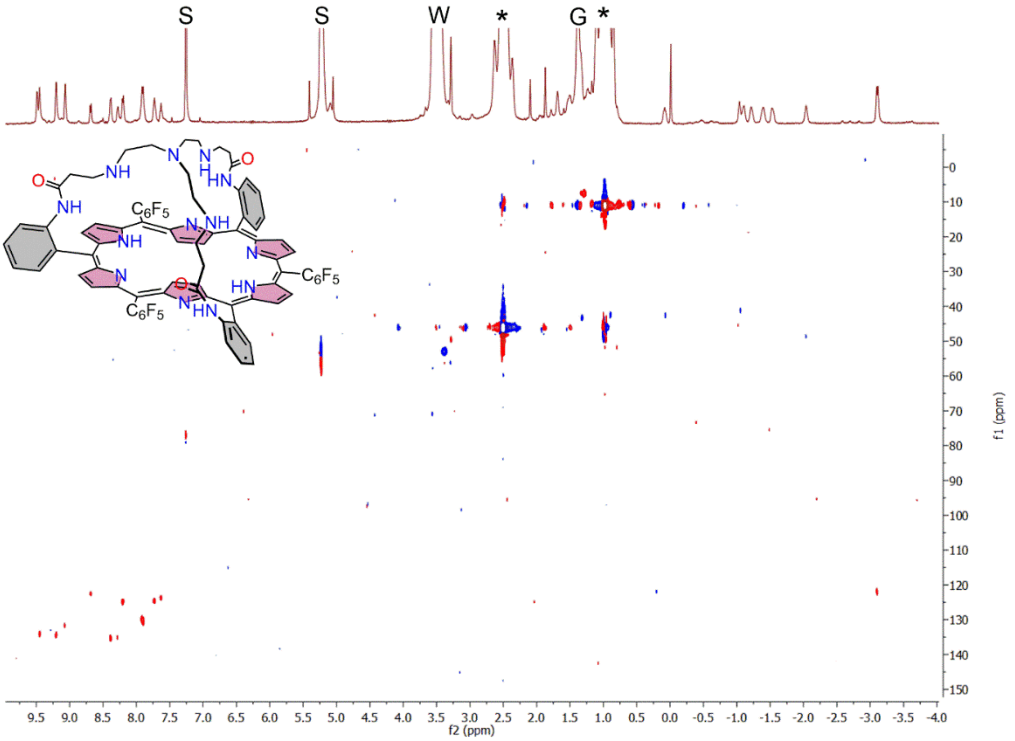



**Figure S17.** 2D HSQC NMR spectrum (9:1 $CDCl_3/CD_3OD$, 298 K) of **9**. S = solvent, G = grease, W = water, * = $Et_3N$.

## Selected NMR spectra of 10

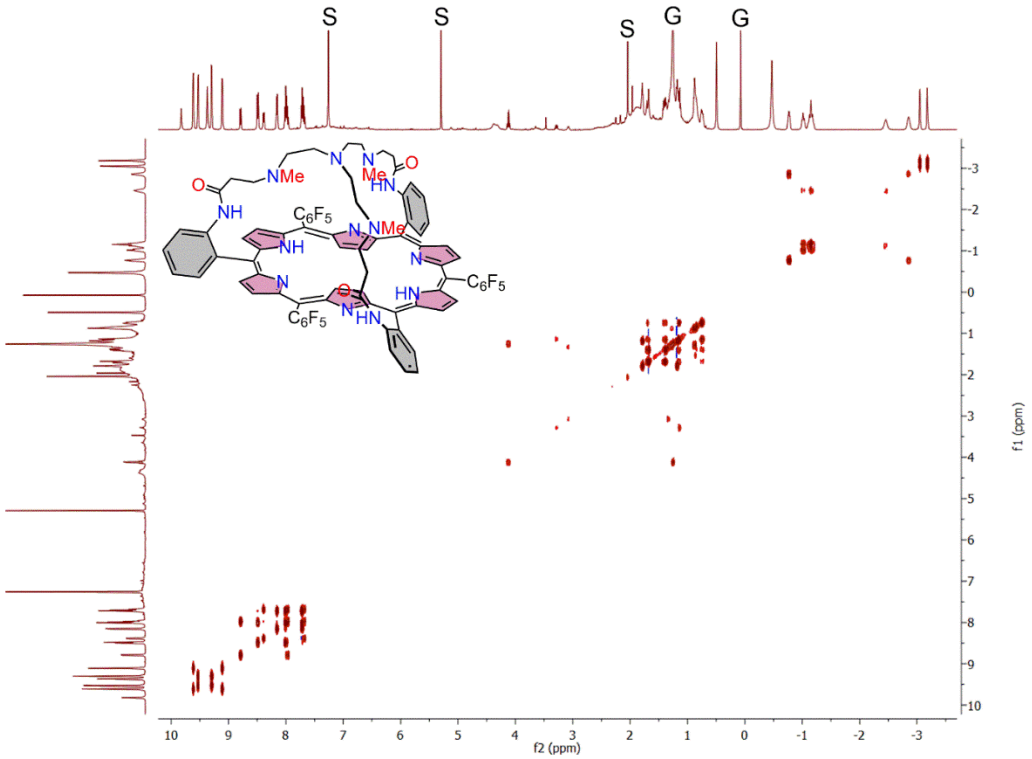



**Figure S18.** 2D COSY NMR spectrum ($CDCl_3$, 298 K) of **10**. S = solvent, G = grease.

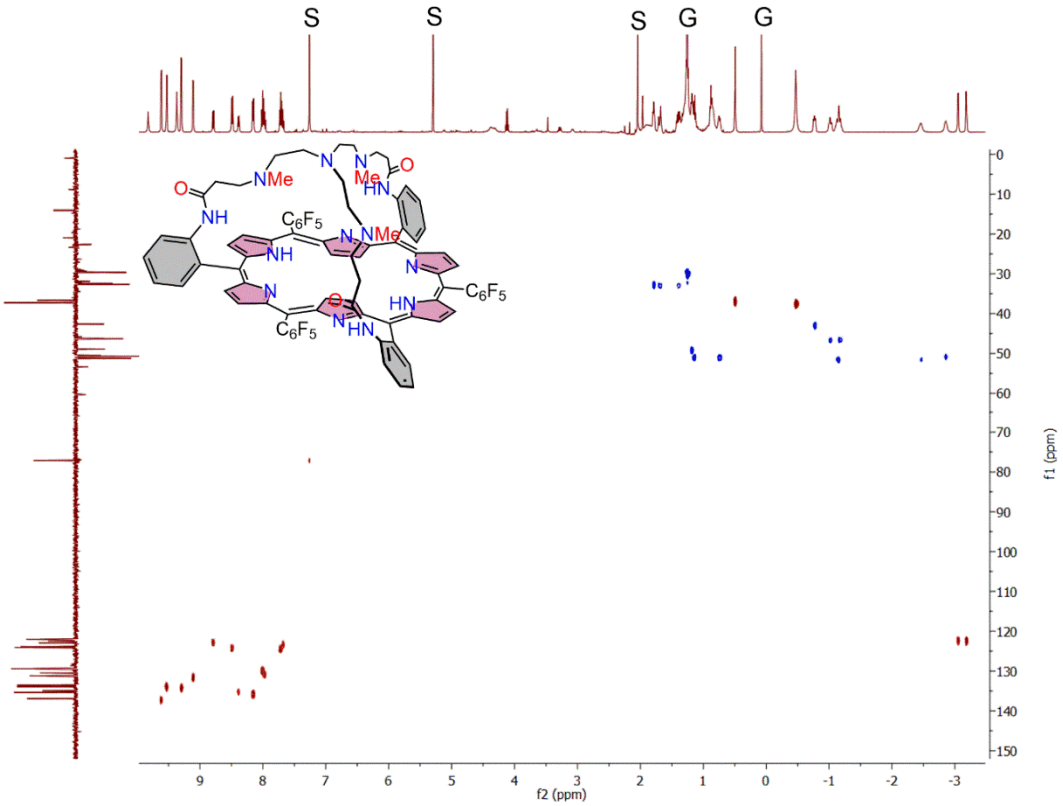



**Figure S19.** 2D HSQC NMR spectrum ($CDCl_3$, 298 K) of **10**. S = solvent, G = grease.

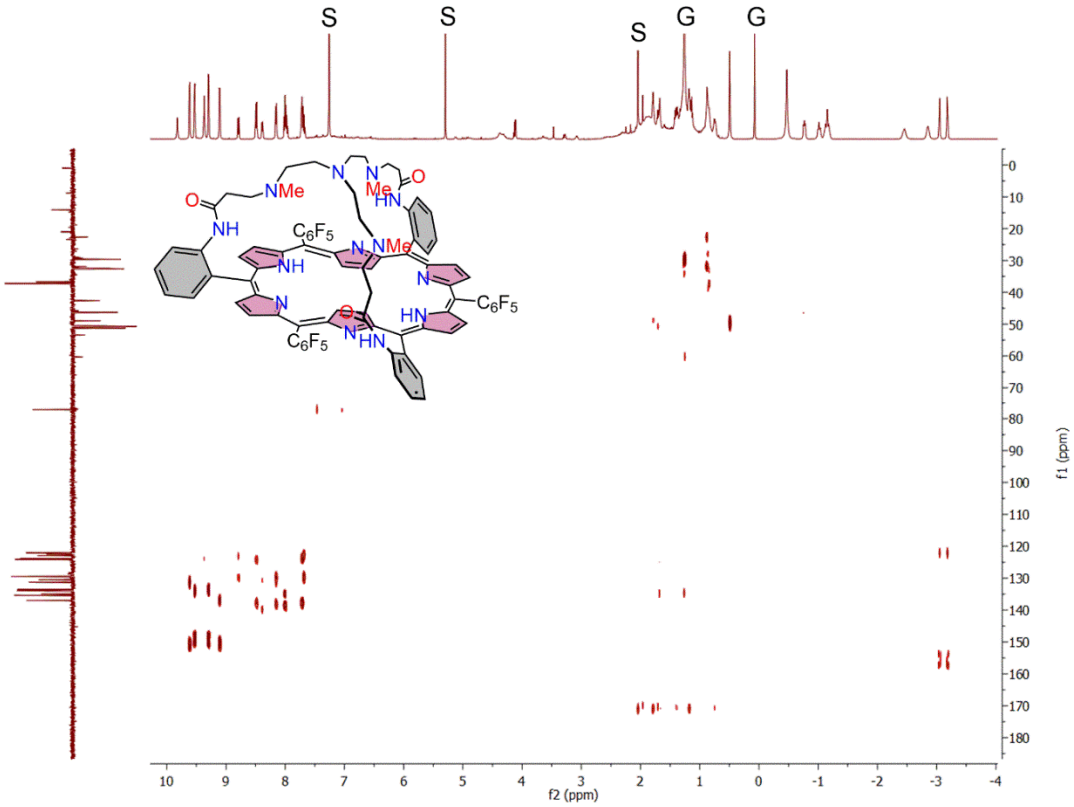



**Figure S20.** 2D HMBC NMR spectrum ($CDCl_3$, 298 K) of **10**. S = solvent, G = grease.

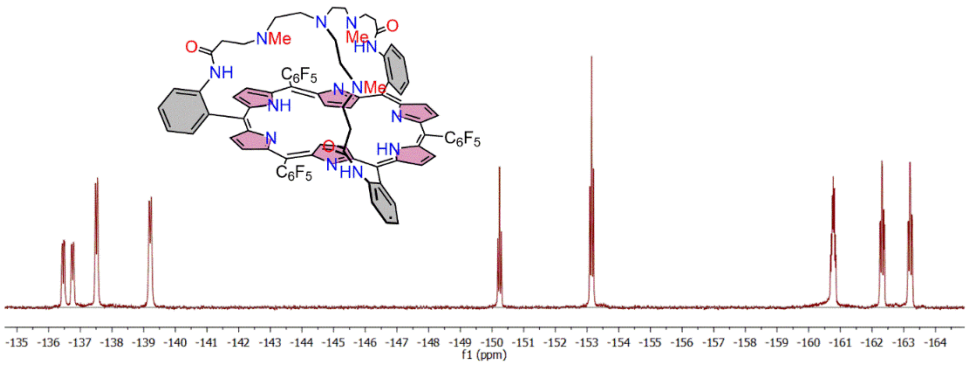



**Figure S21.** $^{19}F$ NMR spectrum ($CDCl_3$, 298 K) of **10**.

## Selected NMR spectra of 8

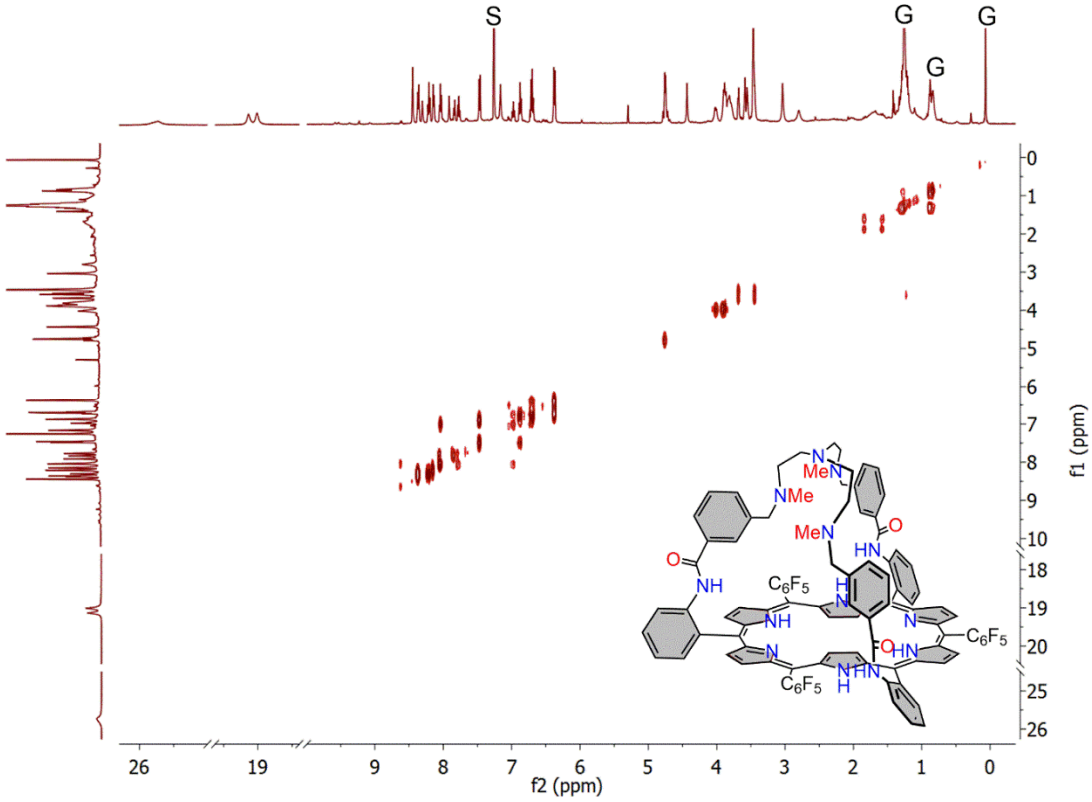



**Figure S22.** 2D COSY NMR spectrum ($CDCl_3$, 298 K) of **8**. S = solvent, G = grease.

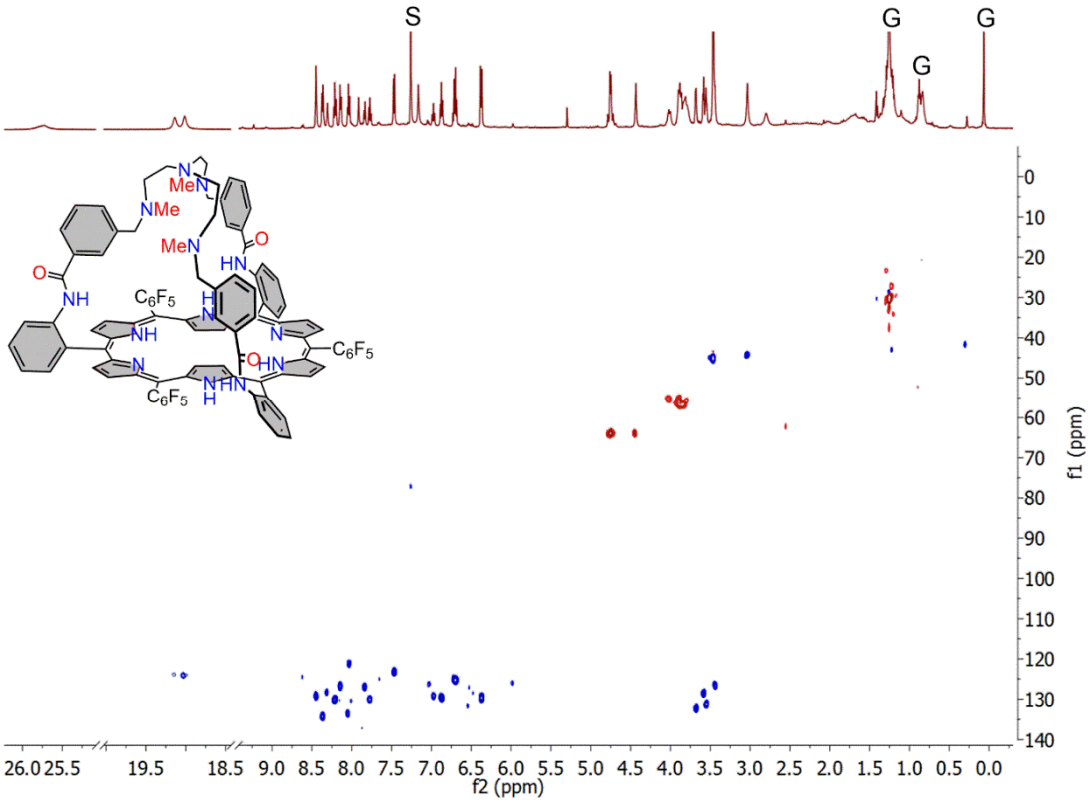



**Figure S23.** 2D HSQC NMR spectrum ($CDCl_3$, 298 K) of **8**. S = solvent, G = grease.

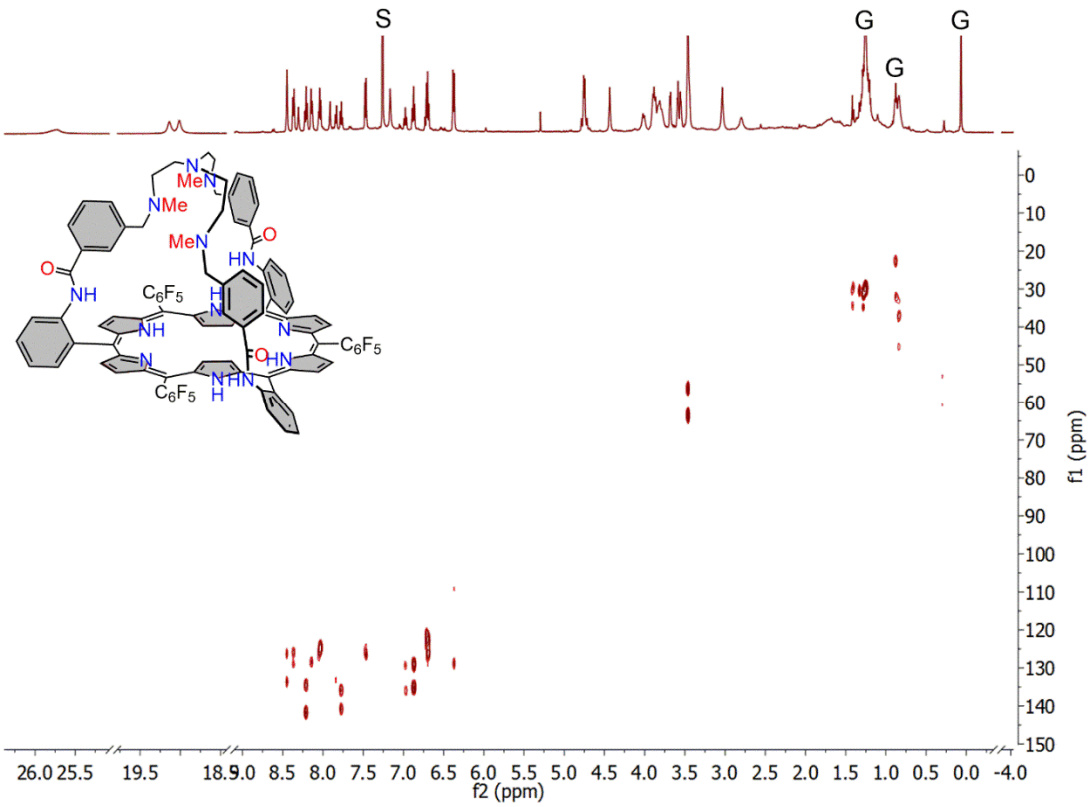



**Figure S24.** 2D HMBC NMR spectrum ($CDCl_3$, 298 K) of **8**. S = solvent, G = grease.

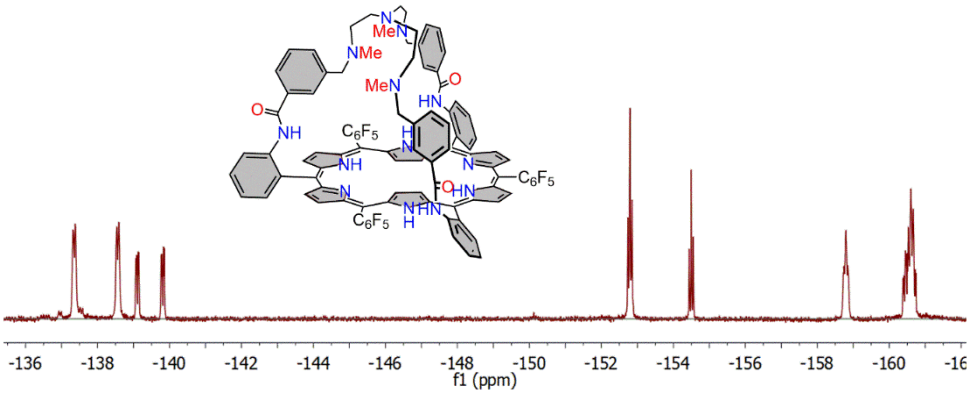



**Figure S25.** $^{19}F$ NMR spectrum ($CDCl_3$, 298 K) of **8**.

## Selected NMR spectra of 11

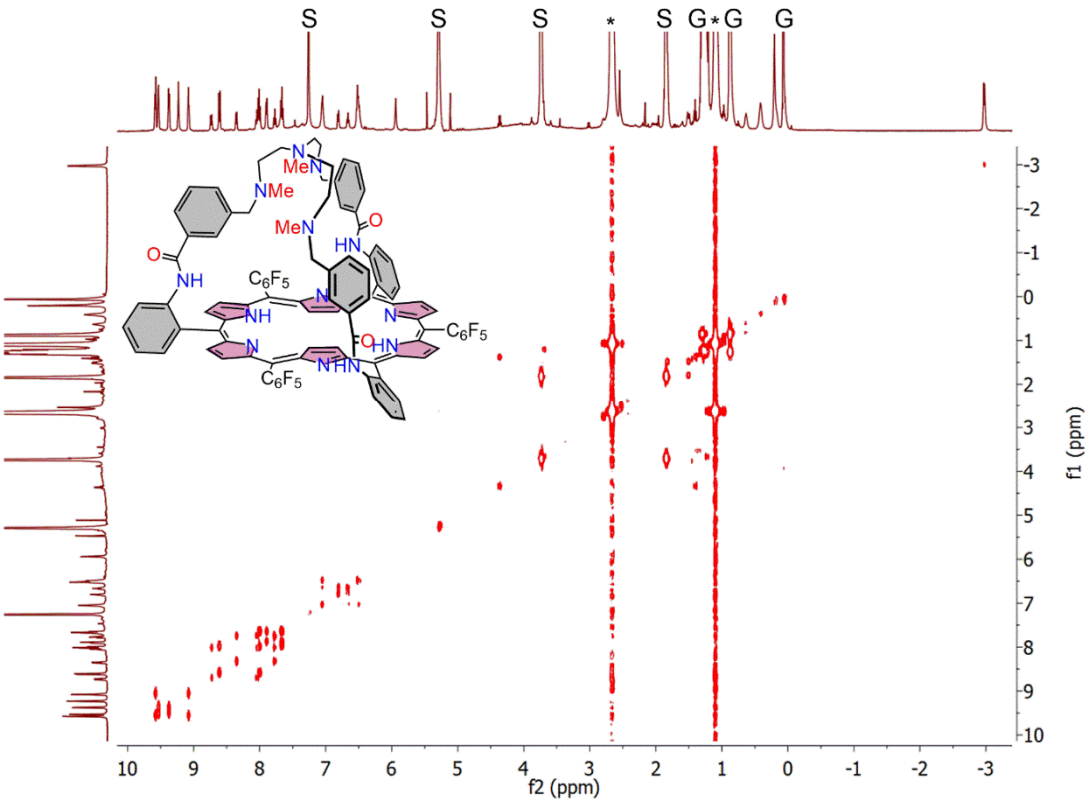



**Figure S26.** 2D COSY NMR spectrum ($CDCl_3$, 298 K) of **11**. S = solvent, G = grease, * = $Et_3N$.

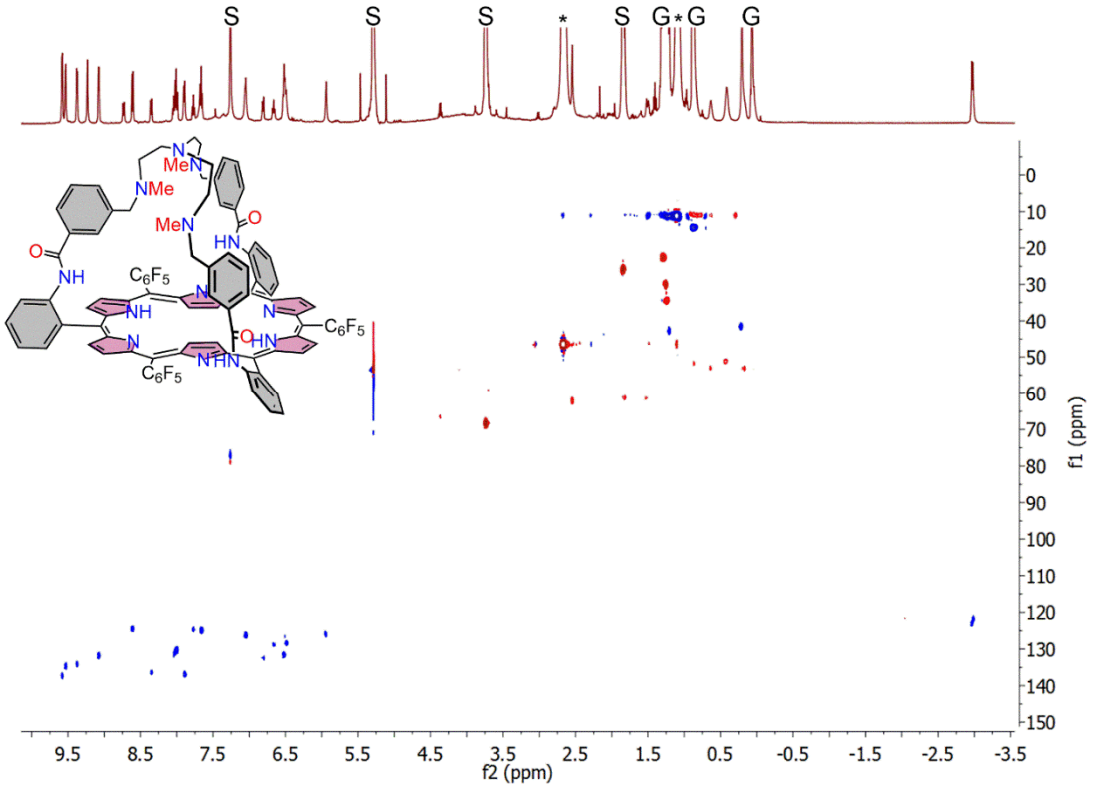



**Figure S27.** 2D HSQC NMR spectrum ($CDCl_3$, 298 K) of **11**. S = solvent, G = grease, * = $Et_3N$.

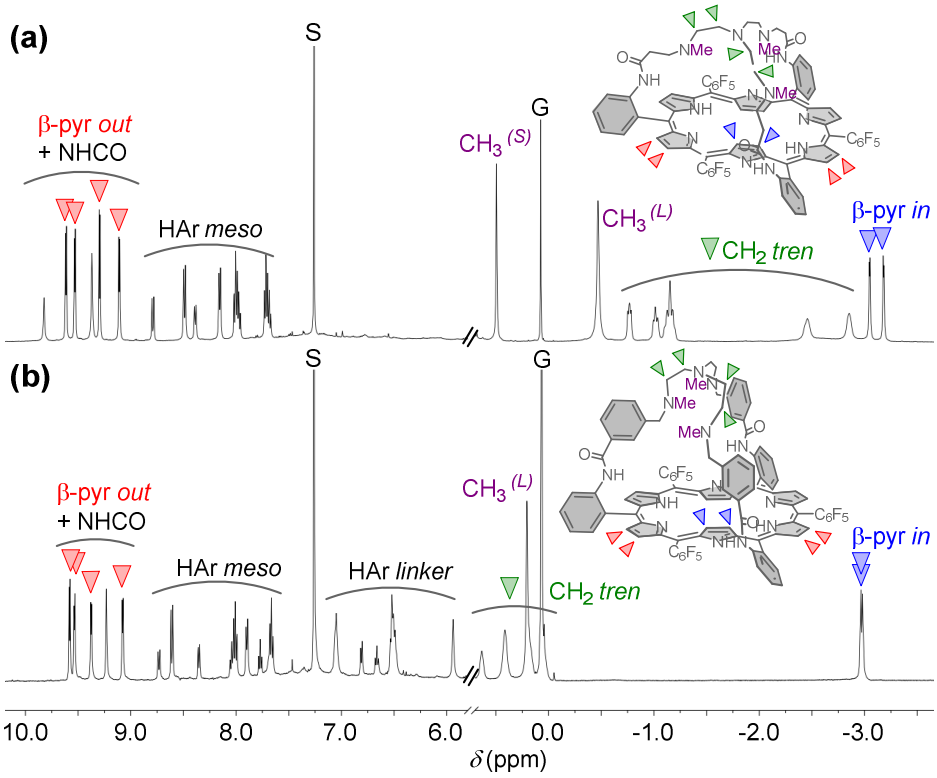



**Figure S28.** Comparison of the $^{1}$H NMR spectra (selected parts) of **10** (a) and **11** (b) ($CDCl_3$, 298 K, 500 MHz). S = solvent; G = grease; "L"/"S" italicized stand for "long"/"short".

***Additional comment.*** Shielding effects are opposite to those observed for the parent 28$\pi$ compounds: (i) the inner β-pyrrolic protons (-2.9 to -3.2 ppm for **10** and **11**) are located in the highfield region, (ii) the outer β-pyrrolic protons are deshielded (9.0 to 9.6 ppm for **10** and **11**), (iii) the tren $CH_2$ and NMe protons are markedly upfield shifted ($\delta_{CH2}$ down to –2.85 and 0.05 ppm for **10** and **11**; $\delta_{NMe(L)}$ = –0.47 and 0.21 ppm for **10** and **11**). Similarly to the parent 28$\pi$ compounds, the tren cap of **10** lies much closer to the hexaphyrin than that of **11**. An extended conformation of the former, stabilized by intramolecular H-bonds, is also expected.

## Selected NMR spectra of $8Zn^{OAc}_{NH2Bu}.H^{+},OTf^{-}$ and $8Zn^{OAc}_{NH2Bu}$

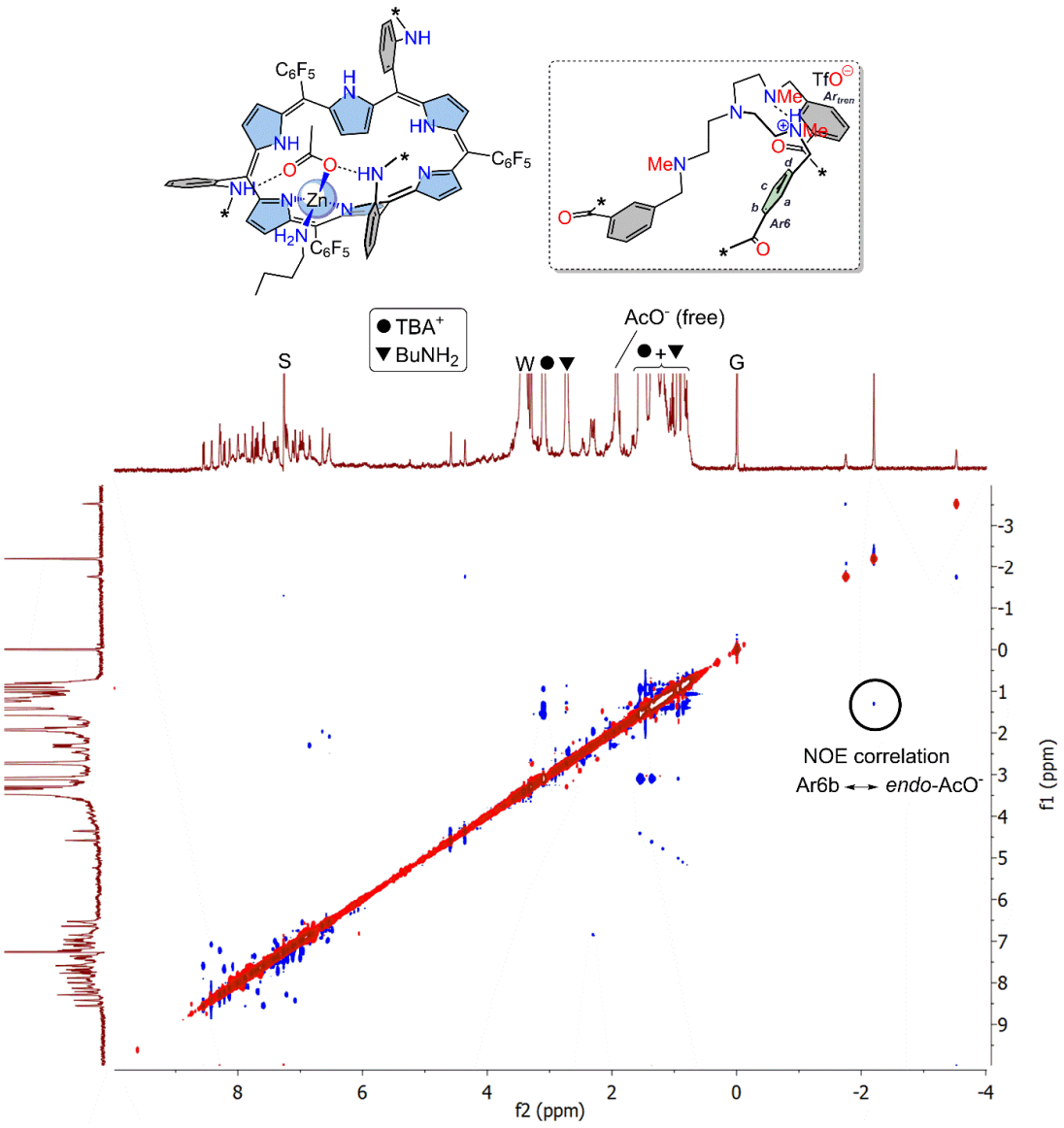



**Figure S29.** 2D ROESY NMR spectrum (9:1 $CDCl_3/CD_3OD$, 298 K) of **$8Zn^{OAc}_{NH2Bu}.H^{+},OTf^{-}$**. S = solvent, G = grease, W = water.

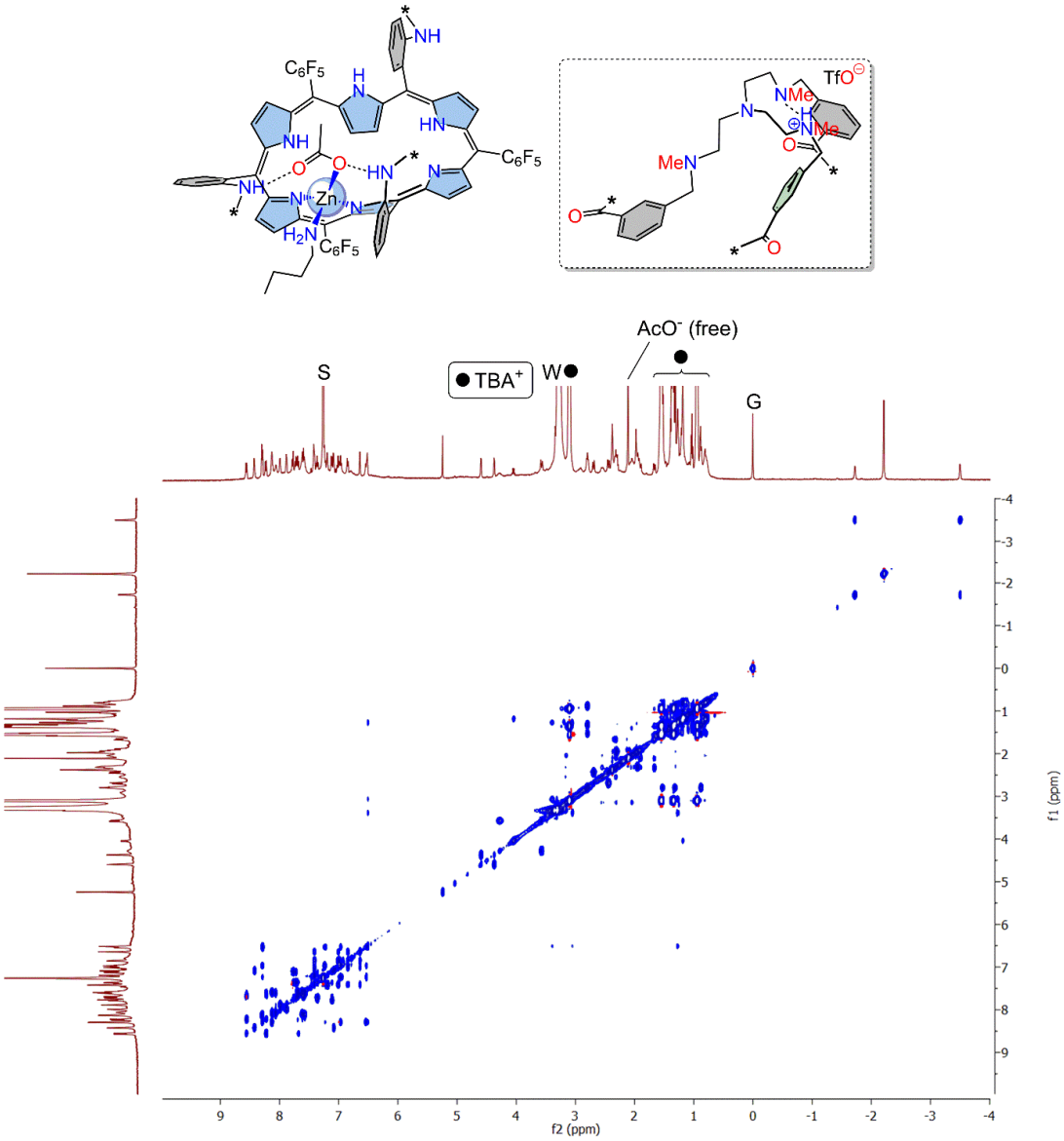



**Figure S30.** 2D TOCSY NMR spectrum (9:1 $CDCl_3/CD_3OD$, 298 K) of **8Zn$^{OAc}_{NH2Bu}$.H$^+$,OTf$^-$**. S = solvent, G = grease, W = water.

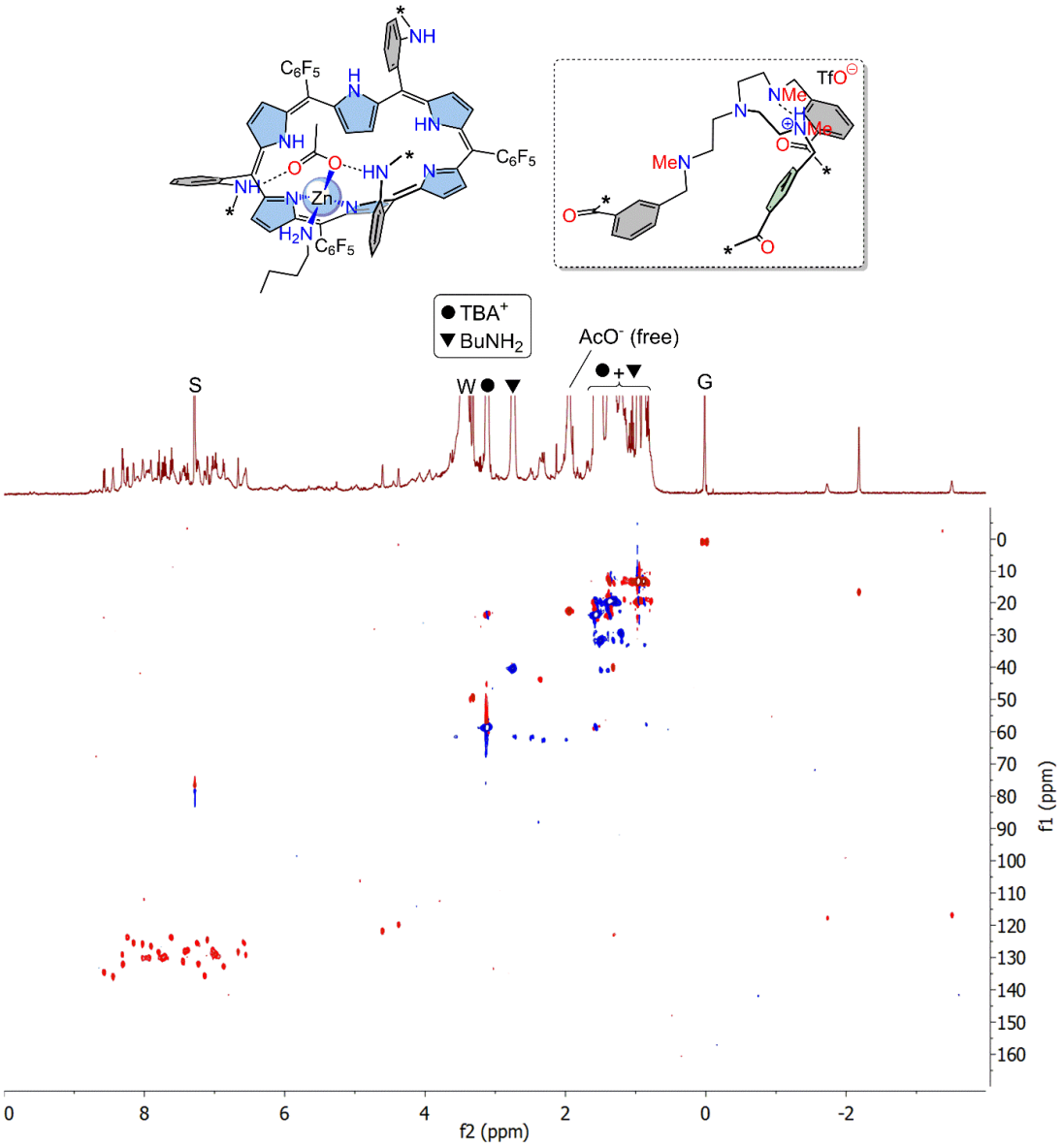



**Figure S31.** 2D HSQC NMR spectrum (9:1 $CDCl_3/CD_3OD$, 298 K) of **8Zn$^{OAc}_{NH2Bu}$.H$^+$,OTf$^-$**. S = solvent, G = grease, W = water.

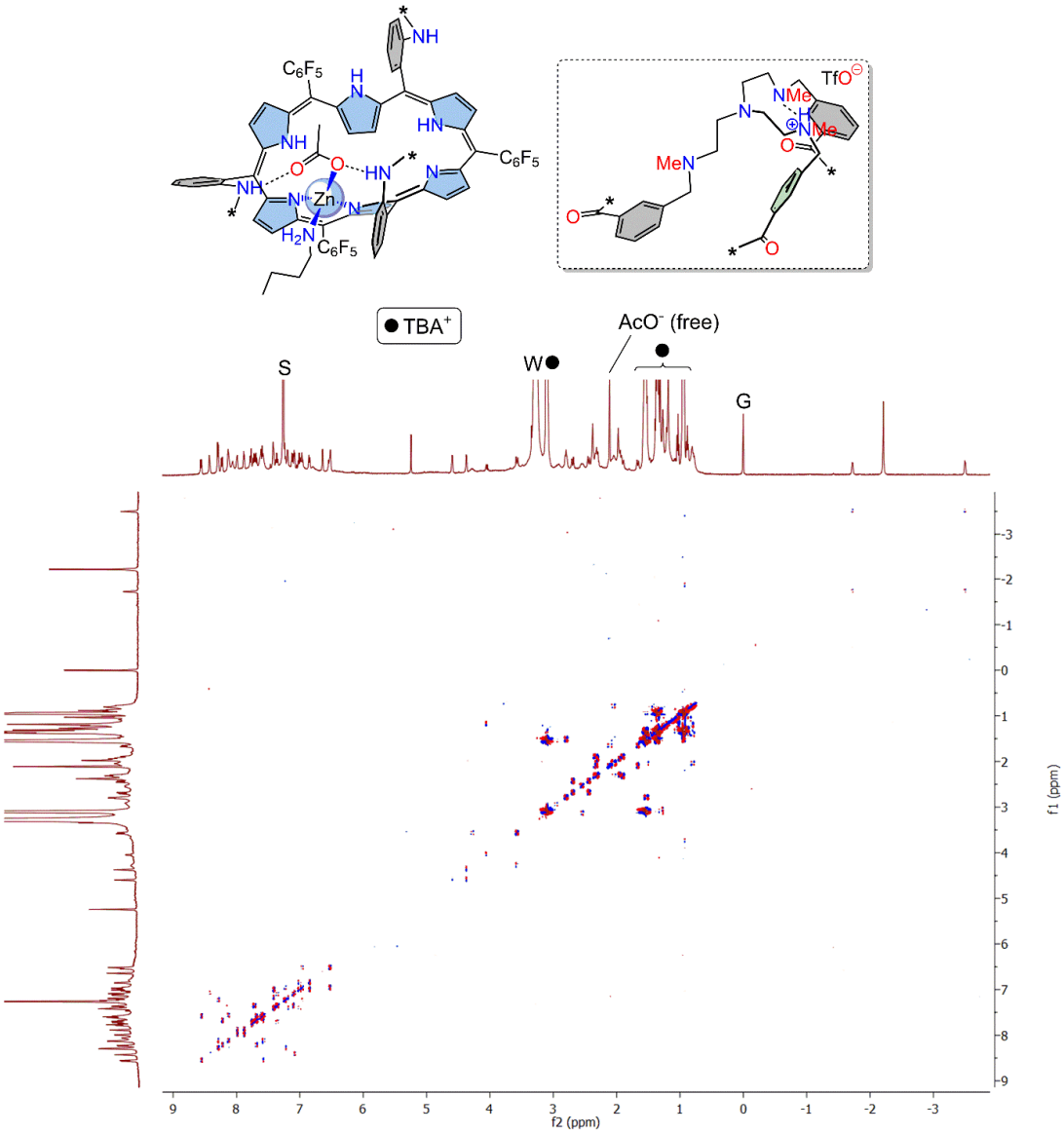



**Figure S32.** 2D COSY NMR spectrum (9:1 $CDCl_3/CD_3OD$, 298 K) of **8Zn$^{OAc}_{NH2Bu}$.H$^+$,OTf$^-$**. S = solvent, G = grease, W = water.

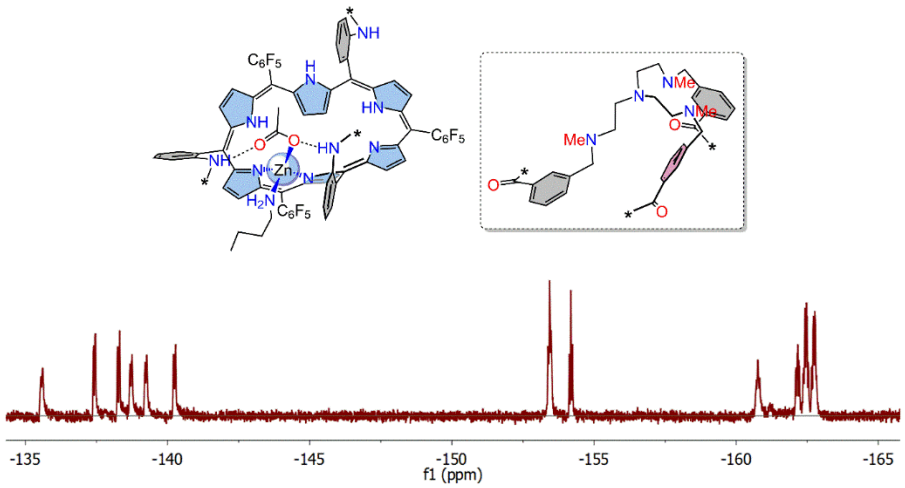



**Figure S33.** $^{19}$F NMR spectra (9:1 $CDCl_3/CD_3OD$, 298 K) of **8Zn$^{OAc}_{NH2Bu}$**.

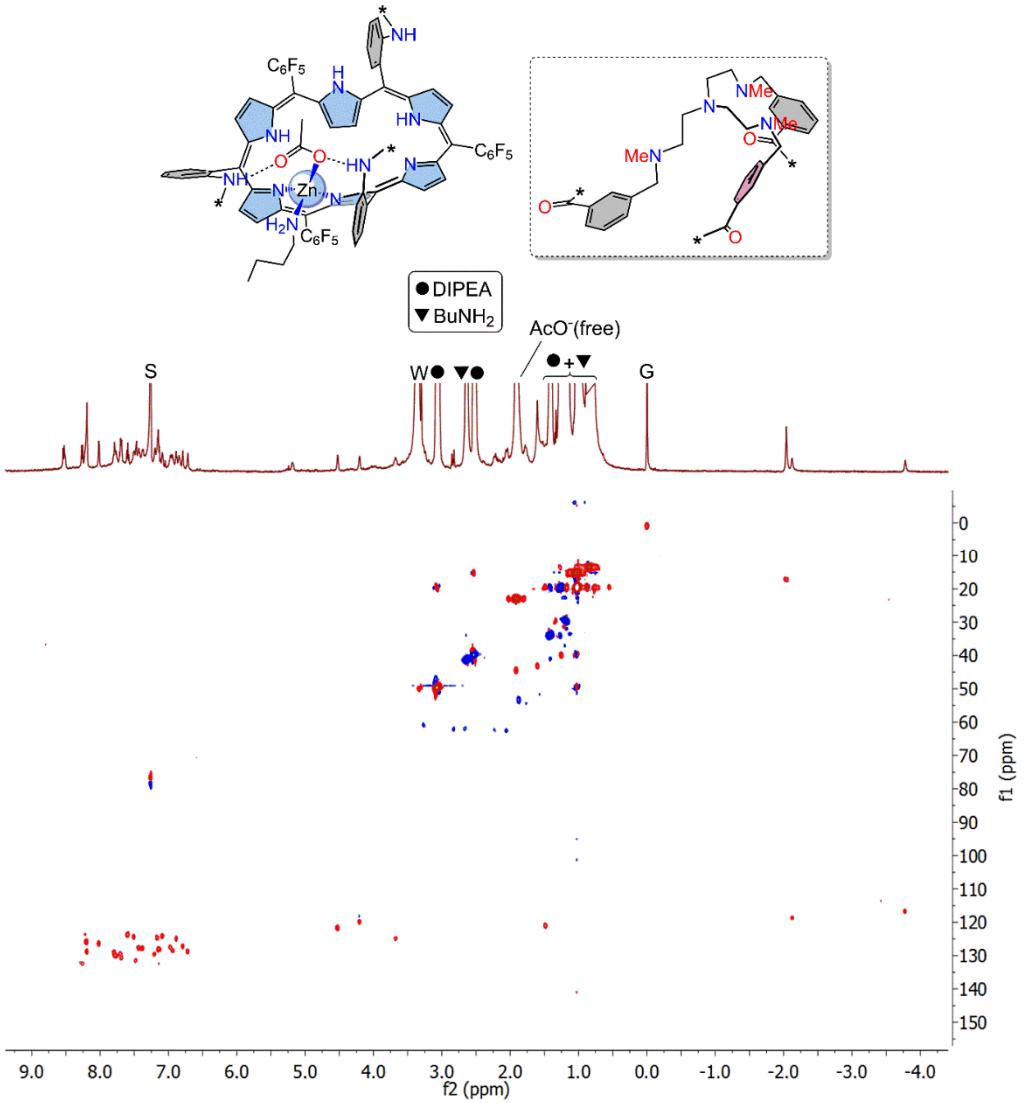



**Figure S34.** 2D HSQC NMR spectrum (9:1 $CDCl_3/CD_3OD$, 298 K) of **8Zn$^{OAc}_{NH2Bu}$**. S = solvent, G = grease, W = water.

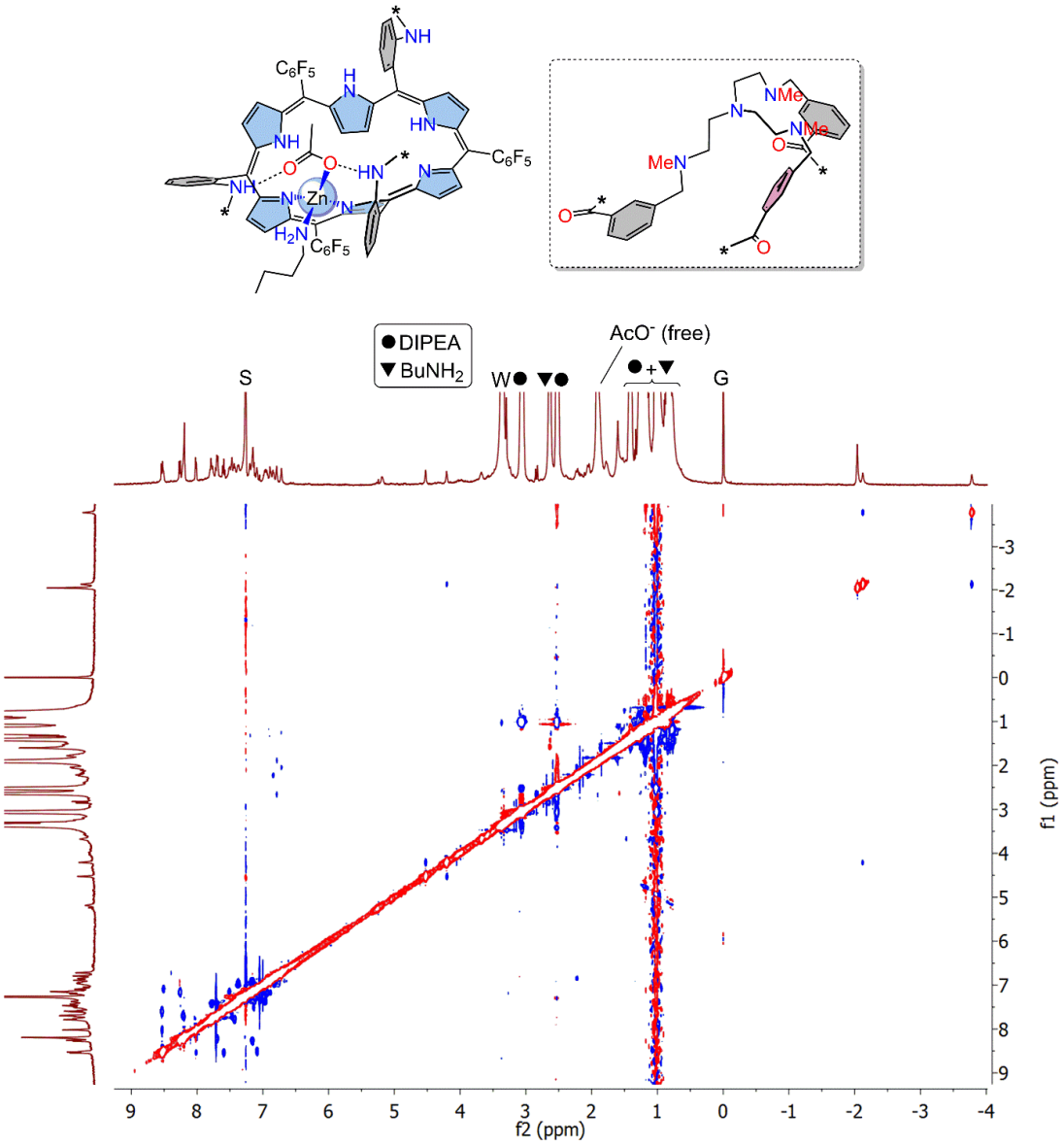



**Figure S35.** 2D ROESY NMR spectrum (9:1 $CDCl_3/CD_3OD$, 298 K) of **8Zn**$^{OAc}_{NH2Bu}$. S = solvent, G = grease, W = water.

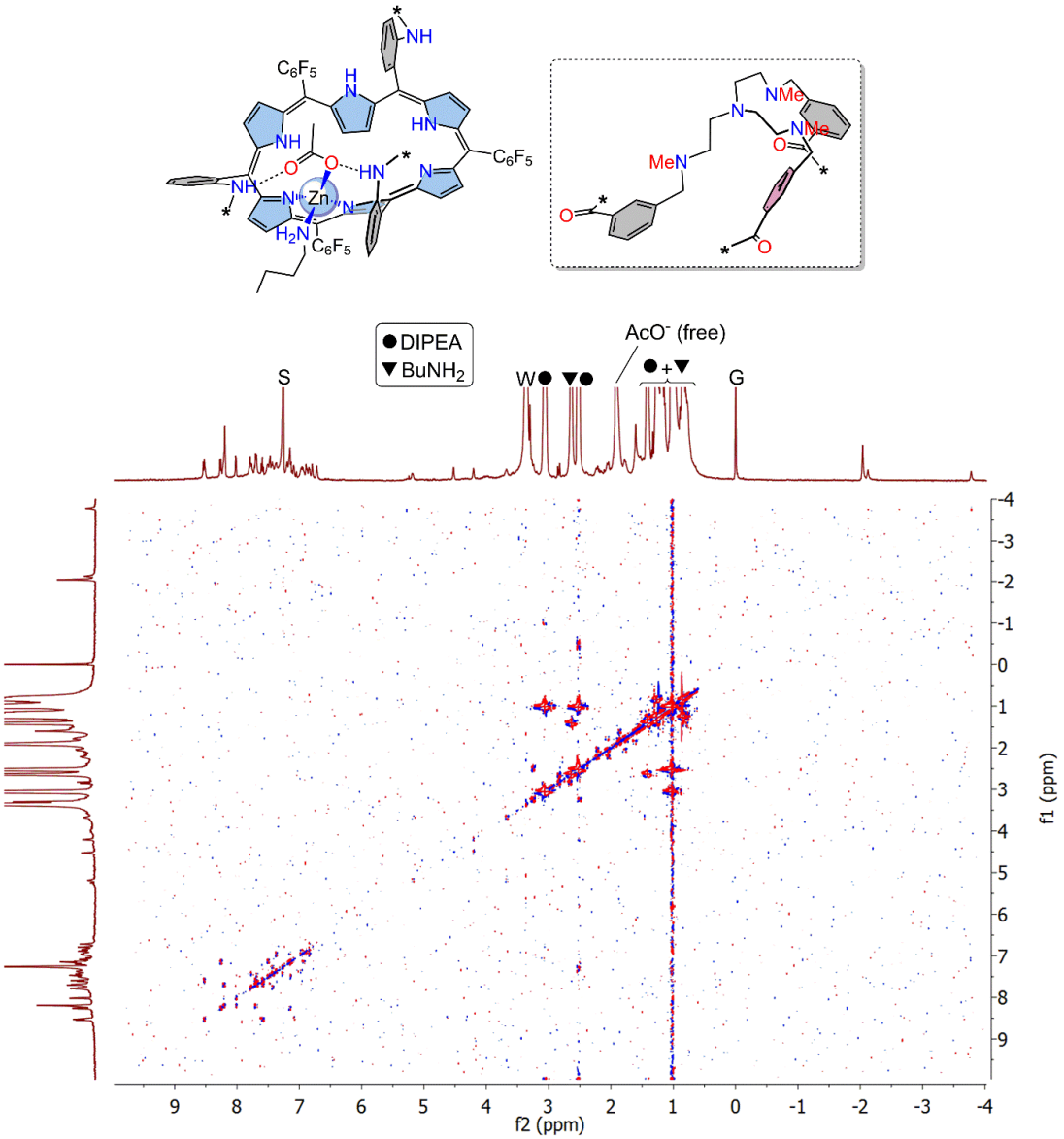



**Figure S36.** 2D COSY NMR spectrum (9:1 $CDCl_3/CD_3OD$, 298 K) of **8Zn$^{OAc}_{NH2Bu}$**. S = solvent, G = grease, W = water.

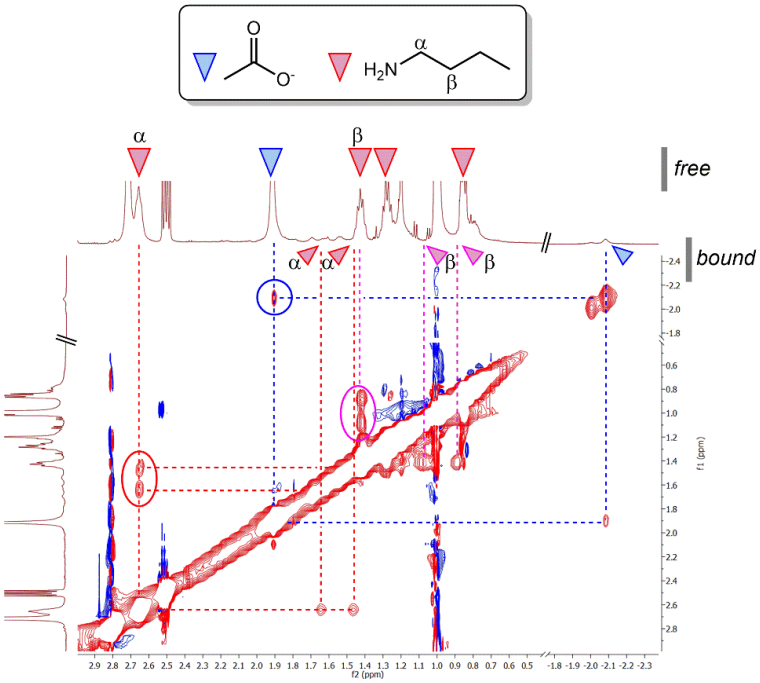



**Figure S37.** 2D ROESY NMR spectrum (9:1 $CDCl_3/CD_3OD$, 330 K) of **8Zn$^{OAc}_{NH2Bu}$**: expanded view on the exchange correlations of the butylamino and acetato ligands.

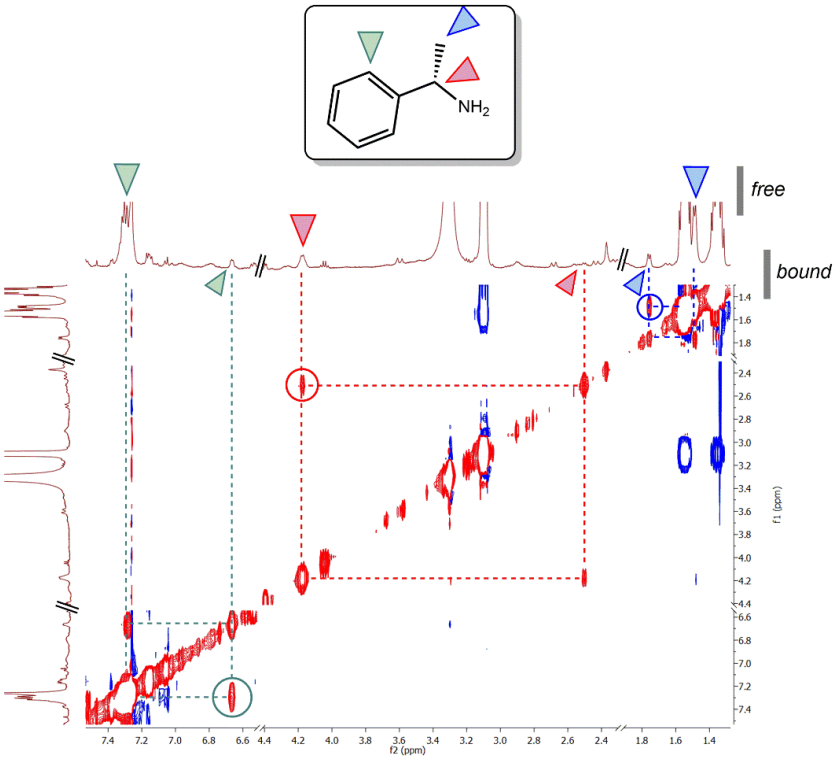



**Figure S38.** 2D ROESY NMR spectrum (9:1 $CDCl_3/CD_3OD$, 298 K) of **8Zn$^{OAc}_{RNH2}$.H$^+$,OTf$^-$** ($RNH_2$ = *(S)*-MBA): expanded view on the exchange correlations of the MBA ligand.

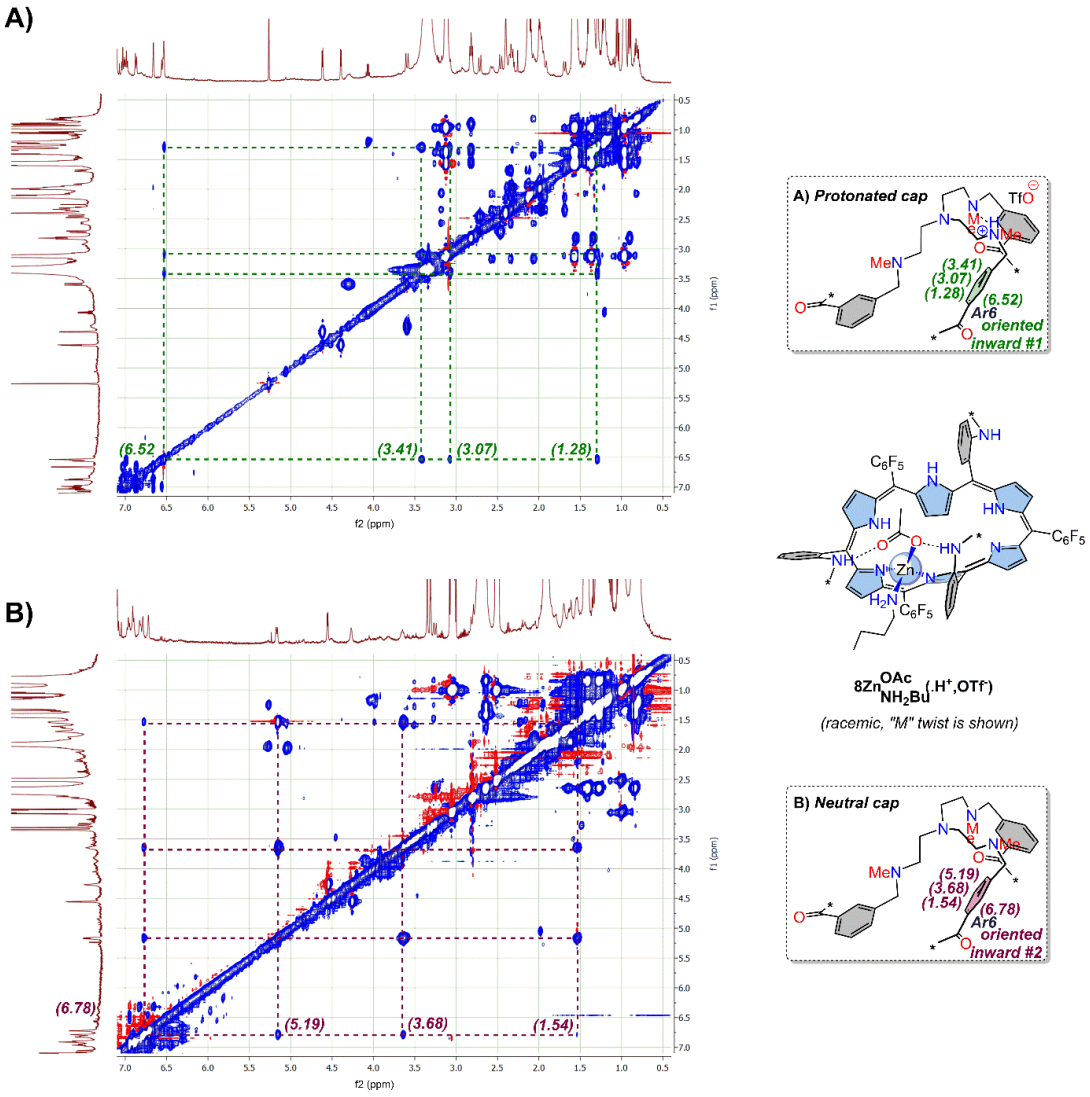



**Figure S39.** 2D TOCSY NMR spectrum (9:1 $CDCl_3/CD_3OD$) of (a) **8Zn$^{OAc}_{NH2Bu}$.H$^+$,OTf$^-$** (298 K) and (b) **8Zn$^{OAc}_{NH2Bu}$** (330 K): expanded view on the Ar6 moiety.

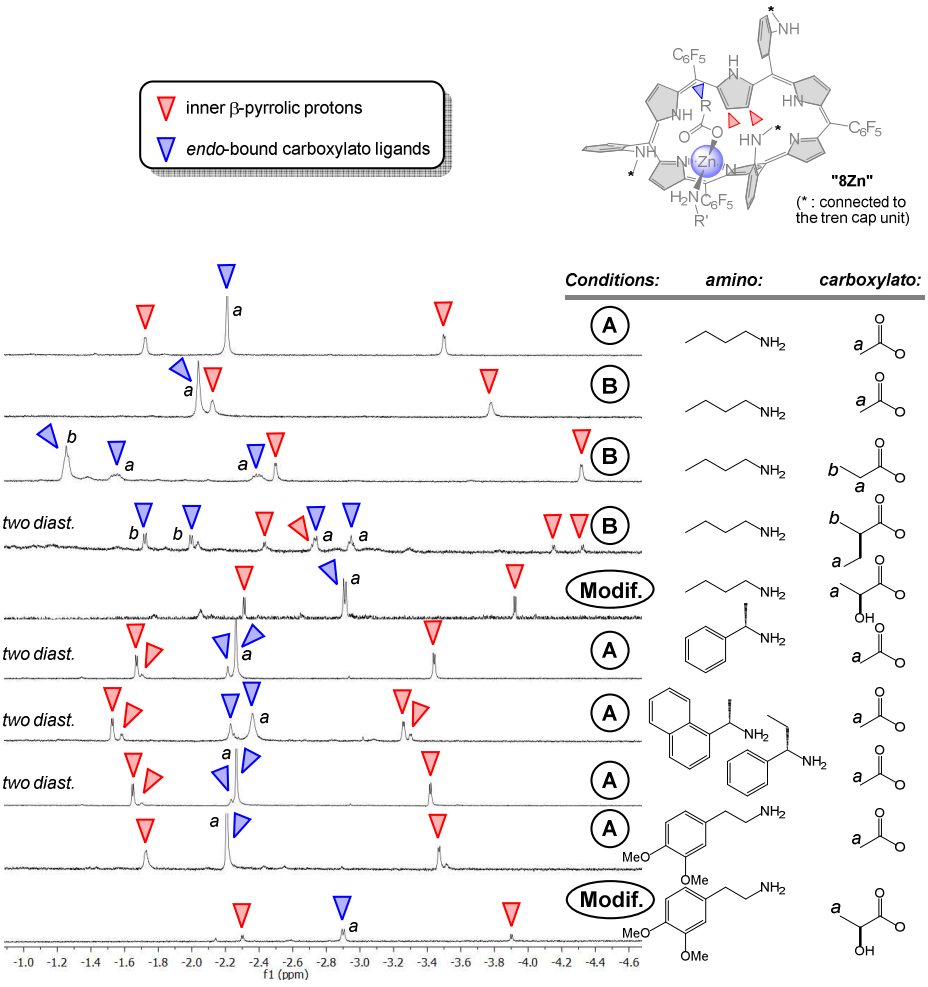



**Figure S40.** $^{1}$H NMR spectra (9:1 $CDCl_3/CD_3OD$) of "**8Zn**", with different combinations of carboxylato and amino ligands: expanded view on the highfield regions (conditions: Pathway A, Pathway B, or modified conditions [excess of all reactants, see text]).

## III. UV-vis-NIR absorption spectra

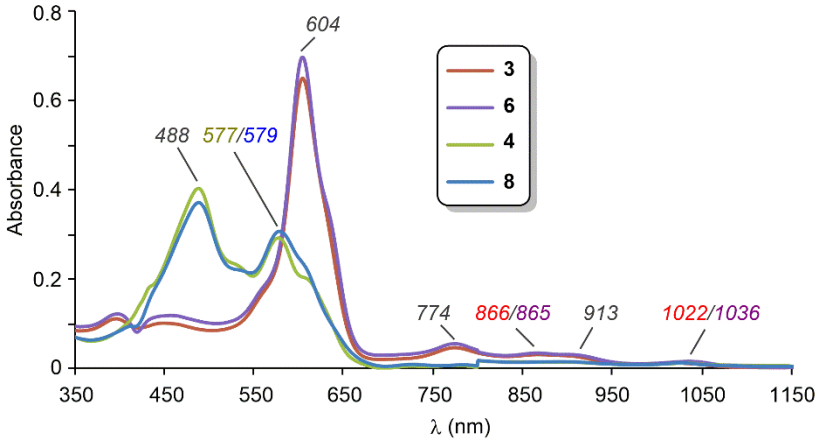



**Figure S41.** UV-vis-NIR absorption spectra of compounds **3**, **4**, **6** and **8** ($CH_2Cl_2$).

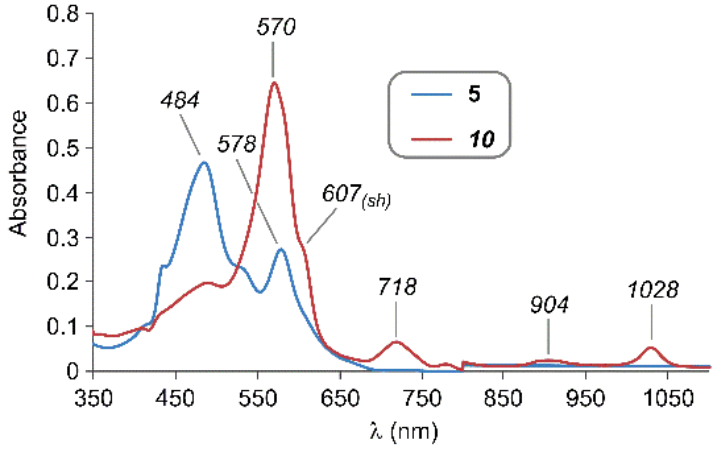



**Figure S42.** UV-vis-NIR absorption spectra of compounds **5** and **10** ($CH_2Cl_2$).

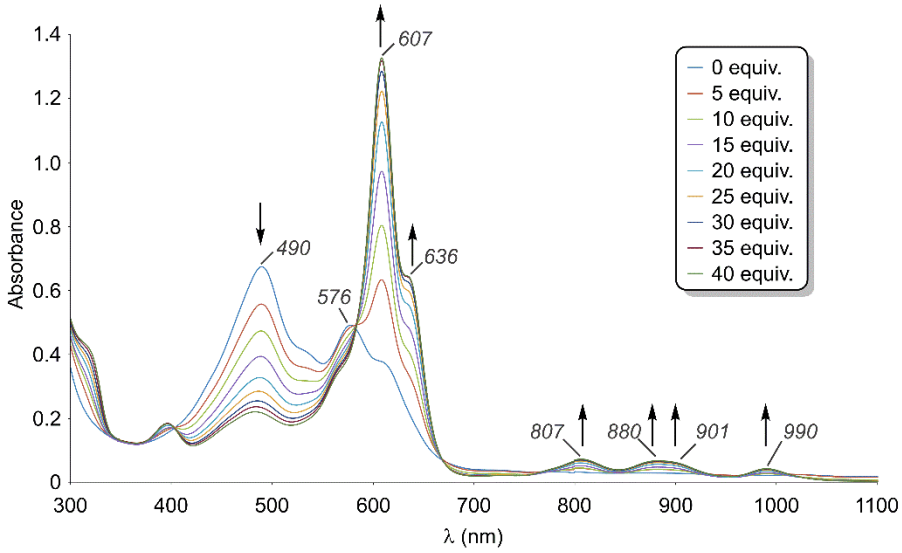



**Figure S43.** UV-vis-NIR absorption spectra for the titration of **8** by a 1:1 mixture of $Zn(OAc)_2$ and $BuNH_2$ (9:1 $CHCl_3/CH_3OH$, DIPEA). Note: the same final absorption spectrum was obtained with a mixture of $Zn(OTf)_2$ and TBAOAc instead of $Zn(OAc)_2$.

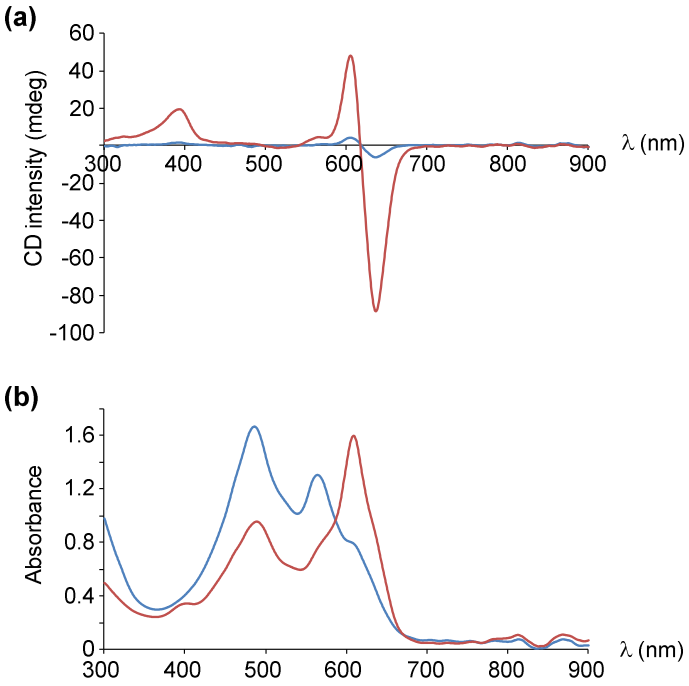



**Figure S44.** Circular dichroism (a) and UV-vis (b) absorption spectra, recorded at 20 °C in 9:1 $CHCl_3$/MeOH, of: (i) a solution of **8**, $Zn(OTf)_2$ and *(R)*-MBA heated 15 min at 50 °C (blue curves); (ii) a solution of **8**, $Zn(OTf)_2$, *(R)*-MBA and TBAOAc heated 15 min at 50 °C (red curves). Conditions: [**8**] = 50 µM, 20 equiv. of $Zn(OTf)_2$, 40 equiv. of *(R)*-MBA, 40 equiv. of TBAOAc. Note: the blue CD spectrum shows a weak "Möbius-type" hexaphyrin signature, likely due to undesired contamination with acetate ions, as attested by the absorption band at 609 nm in the corresponding UV spectra (formation of ***P-(R)*-8Zn$^{OAc}_{MBA}$[.H$^+$,OTf$^-$]**).

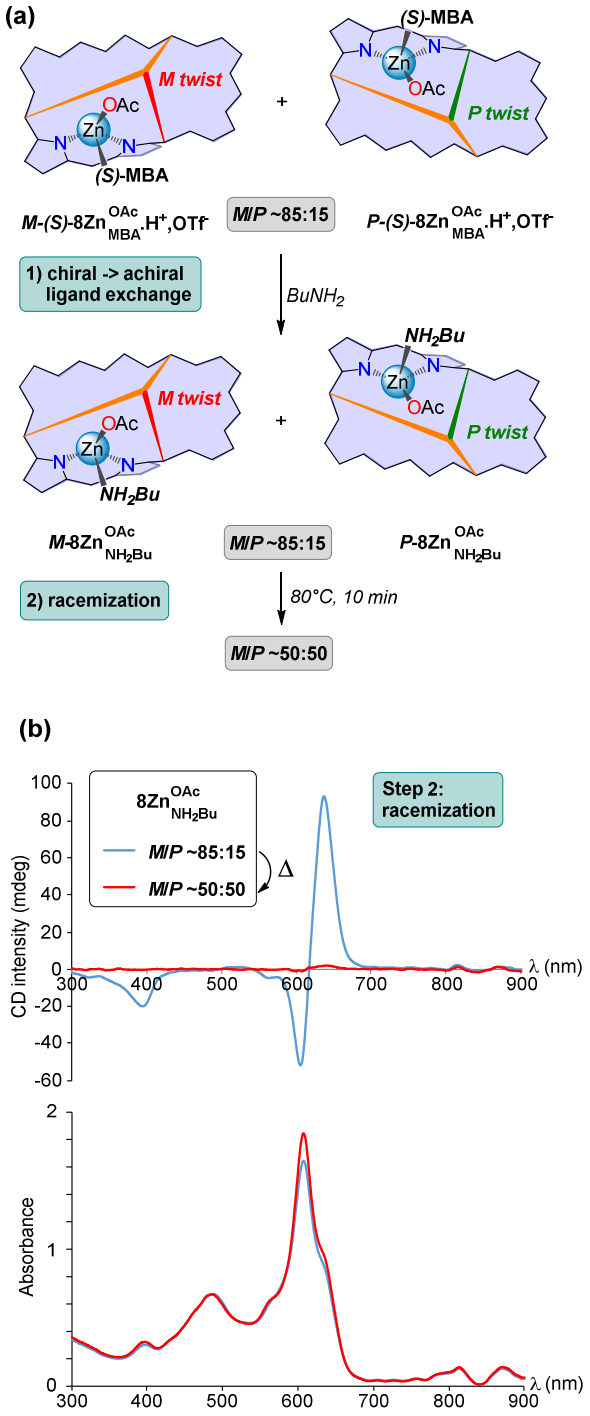



**Figure S45.** Racemization study for the *M* <-> *P* twist interconversion in "**8Zn**". Conditions: pathway A, NMR tube solution analyzed by CD and UV-vis spectroscopies ($CHCl_3$/$CH_3OH$ 9:1).

*Procedure:* to the 85:15 mixture of ***[M/P]*-(*S*)-8Zn$^{OAc}_{MBA}$.H$^+$,OTf$^-$** was added an excess of an achiral ligand such as butylamine (4 equiv.). The MBA <-> $BuNH_2$ exchange proceeds instantaneously and quantitatively (deduced from $^1$H NMR), leading to the two neutral enantiomers ***[M/P]*-8Zn$^{OAc}_{BuNH2}$**. At room temperature, no change in the CD spectrum was observed, indicating amino ligand exchange without loss of chiral induction. In a second step, decreasing of the intensity of the CD signal with the time was monitored. After 10 min at 80 °C, no CD signal was anymore detected, while the UV-vis spectrum was not affected.

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