Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Aromaticity Control via Modifications of a Macrocyclic Frame: 5,6-Dimethoxyphenanthriporphyrin and 5,6-Dioxophenanthriporphyrin

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Supporting Information

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Materials

Chemicals and solvents like methanol were of at least pure grade and used without further purification unless otherwise specified. Dichloromethane was distilled over CaH_2.

Instrumentation

NMR spectroscopy

NMR spectra were measured on Bruker Avance III 500 MHz and Bruker Avance III 600 MHz spectrometers. ^{1}H and ^{13}C shifts were referenced to the residual resonances of deuterated solvents ($CDCl_3$ – 7.24 ppm, 77.2 ppm, CD_2Cl_2 – 5.32 ppm, 54.0, C_6D_6 – 7.16 ppm , 128.4 ppm).

Electronic spectroscopy

UV-Vis absorption spectra were recorded in $CHCl_3$ solutions on Varian Carry-50 Bio and Varian Carry-60 Agilent spectrophotometers.

Mass Spectrometry

Mass spectra (High Resolution and Accurate Mass) were recorded on a Bruker micrOTOF-Q spectrometer using the electrospray technique.

X-ray crystallography

The X-ray diffraction data for **2**, **2**-H^+ and **2**-BF_2-H^{2+} were collected on Xcalibur PX diffractometer with an Onyx detector (Cu-Kα radiation, λ= 1.54175 Å). Single crystals suitable for the SXRD experiment were obtained by slow solvent evaporation: dichloromethane/*n*-octane for **2**; benzene saturated $HBF_4{\cdot}Et_2O$ for **2**-H^+ (in fridge) and dichloromethane-d_2 saturated $BF_3{\cdot}Et_2O$ for **2**-BF_2-H^{2+} (in fridge). The data were collected at 100 K using an Oxford Cryosystem device. Data reduction and analysis were carried out with the CrysAlis 'RED' program.[52] Space groups were determined using the XPREP program.[53] Structures were solved by direct methods using the SHELXS program and refined using all F^2 data, as implemented by the SHELXL

program.[54] H atoms bonded to carbon atoms were placed at their calculated position. H atoms bonded to nitrogen atoms were found on Δρ maps. According to low quality of diffraction data and presence of disorder in the structure, squeeze procedure[55] (for disordered solvent molecules), as well as, SIMU and ISOR constrains for disordered anions were applied during refinement of **2**-BF_2-H^{2+}.

DFT calculations

Geometry optimizations were carried out within unconstrained C_1 symmetry in vacuo, with starting coordinates derived from X-ray or preoptimized models using Gaussian software.[56] Calculations were performed at the B3LYP/6-31G(d,p) level of theory.[57;58] Harmonic frequencies were calculated using analytical second derivatives as a verification of local minimum achievement with no negative frequencies observed. NMR shifts were calculated for optimized structures using the GIAO method and B3LYP/6-31G(d,p) set with TMS shieldings as a reference. Relative energies were calculated including zero-point correction.

Synthesis

5,6-Dioxophenanthriporphyrin (**2**).

5,6-Dimethoxyphenanthriporphyrin **1** (20 mg, 0.032 mmol) was placed in an ice bath. After 15 minutes 85% sulfuric acid*** (10 ml) was slowly added. The solution was heated at 40 °C for 28 hours and then cooled in an ice bath and neutralized with saturated solution of $NaHCO_3$ (for 1.5 h). The reaction mixture was extracted with $CHCl_3$. The organic layer was washed with $NaHCO_3$, twice with H_2O, filtered by cotton and then chromatographed on a short (3 cm) basic Al_2O_3 column (III° grade). At the beginning, a green fraction of phenanthriporphyrin was eluted with CH_2Cl_2. Next, a green-blue band of the desired product was eluted with 1% of MeOH/CH_2Cl_2. Product was washed with MeOH. Yield: 13.4 mg (70 %).

*** The higher concentration of sulfuric acid causes decomposition and/or sulfonation of the compound **1**.

^{1}H NMR (600 MHz, CD_2Cl_2, 300 K): δ 8.56 (d, 2H, ^{3}J = 8.3 Hz, 3,8-H), 7.75 (dd, 2H, ^{3}J = 8.3 Hz, ^{4}J = 1.6 Hz, 2,9-H), 7.68 – 7.60 (m, Ph), 7.57 – 7.52 (m, Ph), 7.33 (d, 2H, ^{3}J = 5.1 Hz, 13,19-H), 7.11 (d, 2H, ^{3}J = 5.1 Hz, 14,18-H), 6.32 (s, 2H, 22,25-H). NH not detectable. **HRMS** (ESI): *m/z*: 603.2068 $[M+H]^+$, calcd for $C_{43}H_{27}N_2O_2^+$: 603.2067. **UV-Vis** ($CHCl_3$, 298 K): λ_{max} (log ε): 293 (4.8), 384 (4.8), 509 (4.1), 658 (4.6).

^{13}C NMR collected for **2**-H^+ to increase the solubility (Figure S3).

Monocationic form of 5,6-dioxophenanthriporphyrin (**2**-H^+).

2 was dissolved in $CDCl_3$ in NMR tubes. Solution was titrated with TFA to give green-bluish **2**-H^+.

*** Solubility of neutral form **2** is very low, addition of small portion of any acid increases solubility. Addition of gaseous hydrochloride to the solution of **2** in $CDCl_3$ generates monocationic form with little changed of spectrum in comparison to addition of TFA (influence of the anion – Figure S6).

^{1}H NMR (600 MHz, $CDCl_3$, 215 K, with TFA): δ 9.18 (b, 2H, 26,27-NH), 8.56 (d, 2H, ^{3}J = 8.3 Hz, 3,8-H), 7.79 (d (dd), 2H, ^{3}J = 8.3 Hz, 2,9-H), 7.73 – 7.49 (m, 15H, *o*,*m*,*p*-Ph), 7.38 (d, 2H, ^{3}J = 5.0 Hz, 13,19-H), 7.14 (d, 2H, ^{3}J = 5.0 Hz, 14,18-H), 6.08 (b, 2H, 22,25-H). **^{13}C NMR** (151 MHz, $CDCl_3$, 215 K): δ 179.3, 159.4, 159.2, 159.0, 158.8, 155.7, 146.4, 143.3, 138.3, 138.2, 136.7, 135.2, 132.6, 131.1, 130.3, 130.2, 129.2, 128.9, 128.7, 126.9, 117.2, 115.3, 113.4, 111.8, 111.5. **^{13}C NMR** (151 MHz, CD_2Cl_2, 300 K): δ 179.8, 157.1, 147.3, 143.8, 139.1, 138.7, 137.7, 135.6 (13,19), 133.5, 132.8 (2,9), 132.7, 131.3 (14,18), 130.4 (3,8), 130.4, 130.0, 129.2, 129.1, 129.0, 127.7 (22,25), 112.2.

Tricationic form of 5,6-Dioxophenanthriporphyrin (**2**-H_3^{3+}).

5,6-Dioxophenanthriporphyrin **2** was dissolved in CD_2Cl_2 in ^1H NMR tube. The solution was titrated with $HBF_4{\cdot}Et_2O$ in low temperature (195 K) to give **2**-H_3^{3+} (the color of the solution changed from green-bluish to reddish). An addition of a nitrogen base (i.e. TEA; 2,4,6-collidine) reversed the reaction.

^{1}H NMR (600 MHz, CD_2Cl_2, 195 K): δ 10.14 (d, 2H, ^3J = 8.5 Hz, 3,8-H), 9.85 (d, 2H, ^3J = 8.5 Hz, 2,9-H), 8.62 (d, 2H, ^3J = 7.1 Hz, 16-*o*-Ph), 8.52 (d, 4H, ^3J = 7.0 Hz 11,21-*o*-Ph), 8.39 (d, 2H, ^3J = 4.1 Hz, 14,18-H), 8.27 (d, 2H, ^3J = 4.1 Hz, 13,19-H), 8.20 – 8.03 (m, 9H, *m*,*p*-Ph {8.16 (2H, 11,21-*p*-Ph), 8.13 (2H, 16-*m*-Ph), 8.09 (5H, 11,21-*m*-Ph, 16-*p*-Ph}), 2.54 (b, 2H, 26,27-NH), -1.04 (b, 2H, 22,25-H). **^{13}C NMR** (151 MHz, CD_2Cl_2, 195 K): δ 167.3 (5,6), 156.4 (12,20/15,17), 155.6 (12,20/15,17), 155.3, 141.5, 141.2 (16-*o*-Ph), 139.2, 139.0, 138.9 (11,21-*o*-Ph), 137.4, 136.7 (2,9), 135.6 (13,19), 134.1, 133.5, 133.0 (14,18), 132.2 (22,25), 129.8 (3,8), 129.7, 129.2, 129.1, 119.3 (11,21).

Isophenanthriporphyrin (**1**-H_2^{2+}).

5,6-Dimethoxyphenanthriporphyrin **1** was dissolved in CD_2Cl_2 in ^1H NMR tube. The solution was titrated with $HBF_4{\cdot}Et_2O$ at low temperature (250 K) to give **1**-H_2^{2+} (the color of the solution changed from greenish to reddish). An addition of a nitrogen base (i. e. TEA; 2,4,6-collidine) reverses the reaction.

^{1}H NMR (600 MHz, CD_2Cl_2, 250 K): δ 10.00 (b, 2H, 26,27-NH), 8.76 (d, 2H, ^3J = 8.6 Hz, 3,8-H), 8.09 (dd, 2H, ^3J = 8.6 Hz, ^4J = 1.5 Hz, 2,9-H), 7.96 (t (tt), 2H, ^3J = 7.4 Hz, 11,21-*p*-Ph), 7.89 (b, 2H, 11,21-*o*-Ph), 7.85 (dd, 2H, ^3J = 4.7 Hz, ^4J = 1.6 Hz, 13,19-H), 7.80 (t, 4H, 11,21-*m*-Ph), 7.72 (d, 2H, ^3J = 7.4 Hz, 16-*o*-Ph), 7.63 (dd, 2H, ^3J = 4.7 Hz, ^4J = 1.6 Hz, 14,18-H), 7.59 (t, 2H, 16-*m*-Ph), 7.55 (m (t), 1H, 16-*p*-Ph), 7.23 (s, 2H, 22,25-H), 5.50 (s, 1H, 16-

H), 4.31 (s, 6H, 5,6-OCH_3). **^{13}C NMR** (151 MHz, CD_2Cl_2, 250 K): δ 169.7 (4,7), 150.1 (15,17), 148.9 (5,6), 143.2 (12,20), 143.1 (13,19), 137.0 (11,21-*o*-Ph), 136.4 (11,21-*i*-Ph), 136.3 (11,21-*p*-Ph), 136.0 (22,25), 134.9 (11,21), 134.3 (1,10), 132.8 (16-*i*-Ph), 131.5 (2,9), 130.0 (11,21-*m*-Ph), 129.7 (16-*p*-Ph), 129.7 (16-*m*-Ph), 128.8 (16-*o*-Ph), 127.8 (23,24), 124.4 (3,8), 123.9 (14,18), 62.1 (OCH_3), 45.1 (16).

NMR spectra

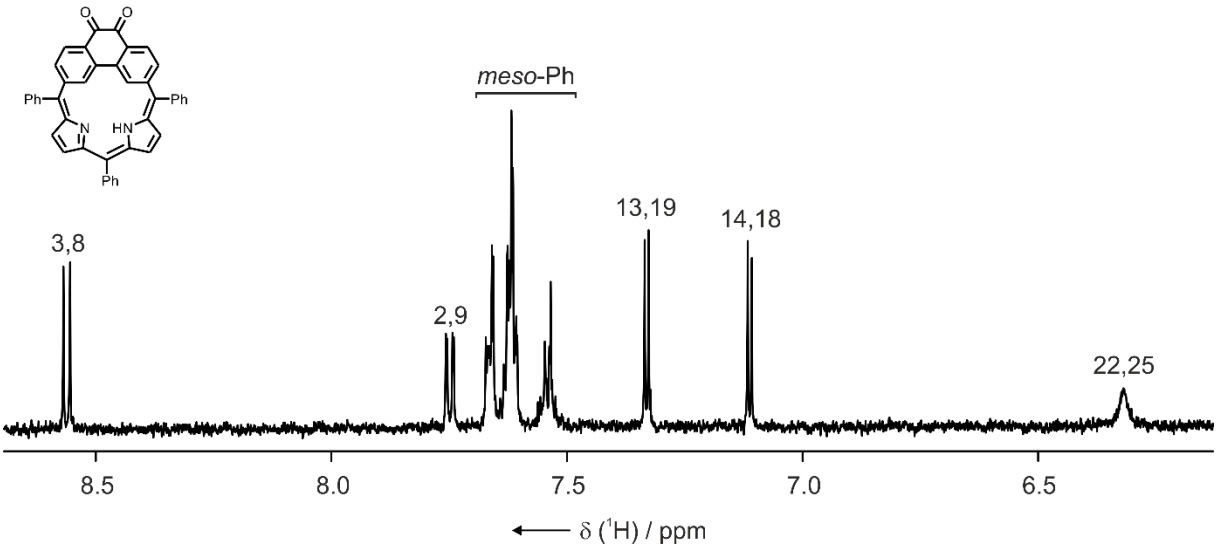


Figure S1. ^{1}H NMR spectrum of **2** (600 MHz, CD_2Cl_2, 300 K).

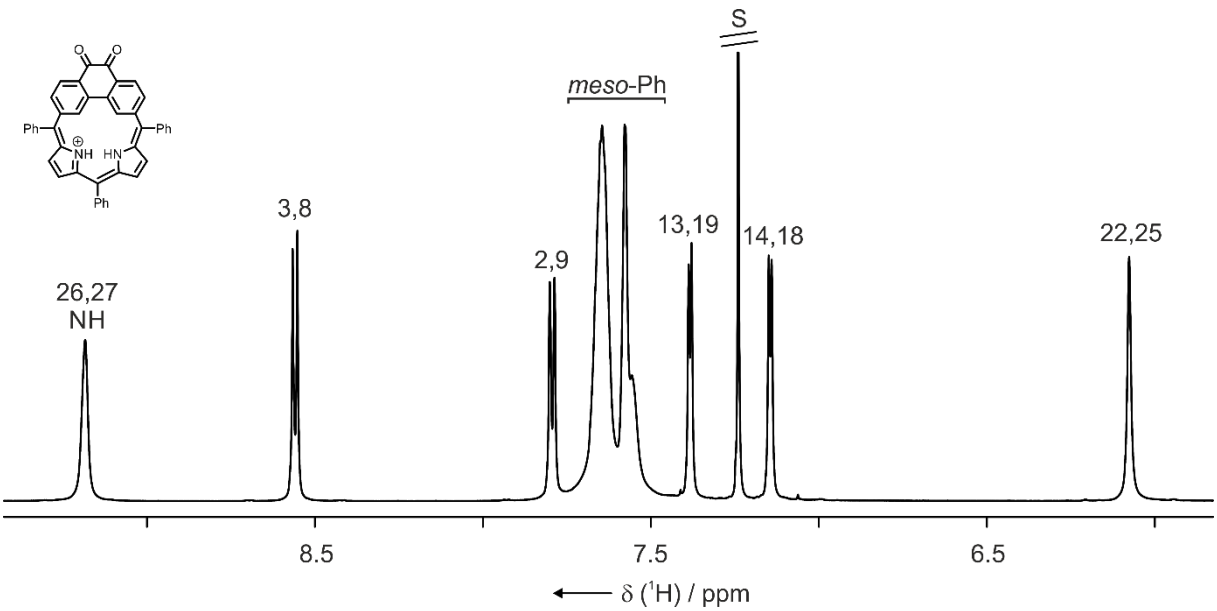


Figure S2. ^{1}H NMR spectrum of **2**-H^{+} (600 MHz, $CDCl_3$, 215 K).

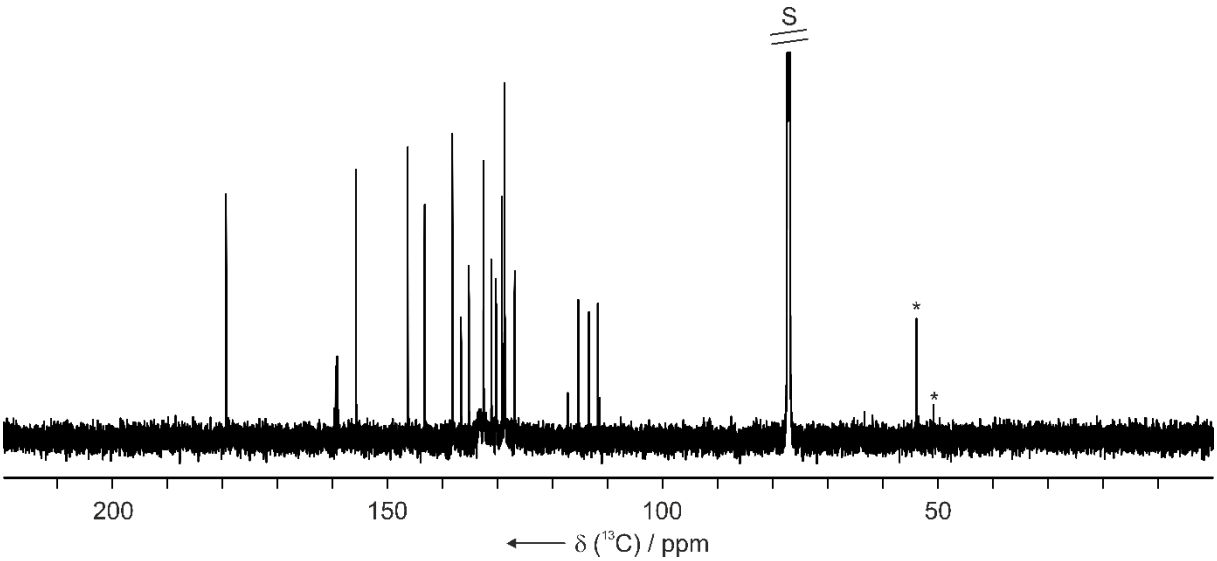


Figure S3. ^{13}C NMR spectrum of **2**-H^{+} (151 MHz, $CDCl_3$, 215 K).

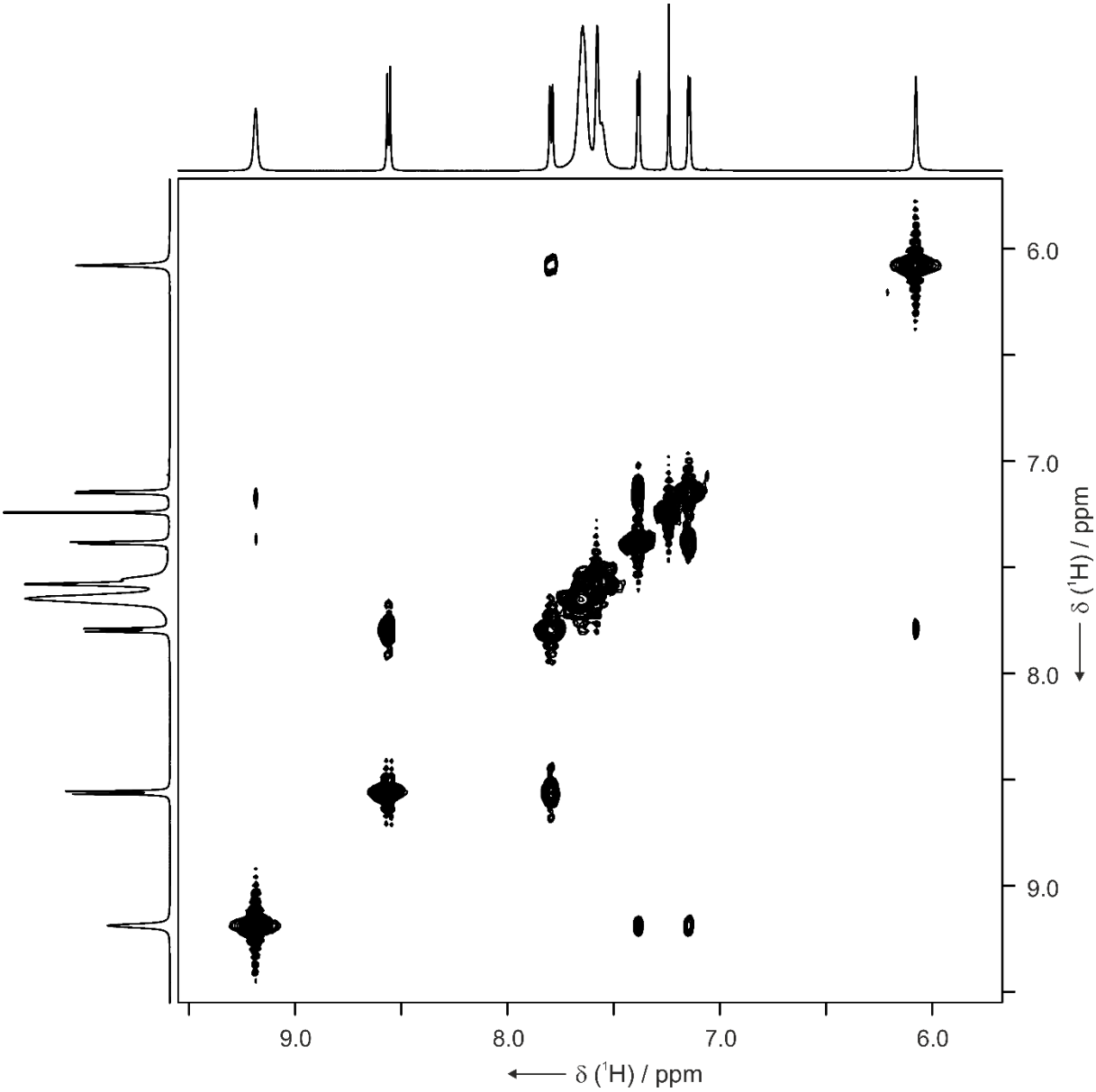


Figure S4. Part of the ^{1}H-^{1}H COSY spectrum of **2**-H^{+} (600 MHz, $CDCl_3$, 215 K).

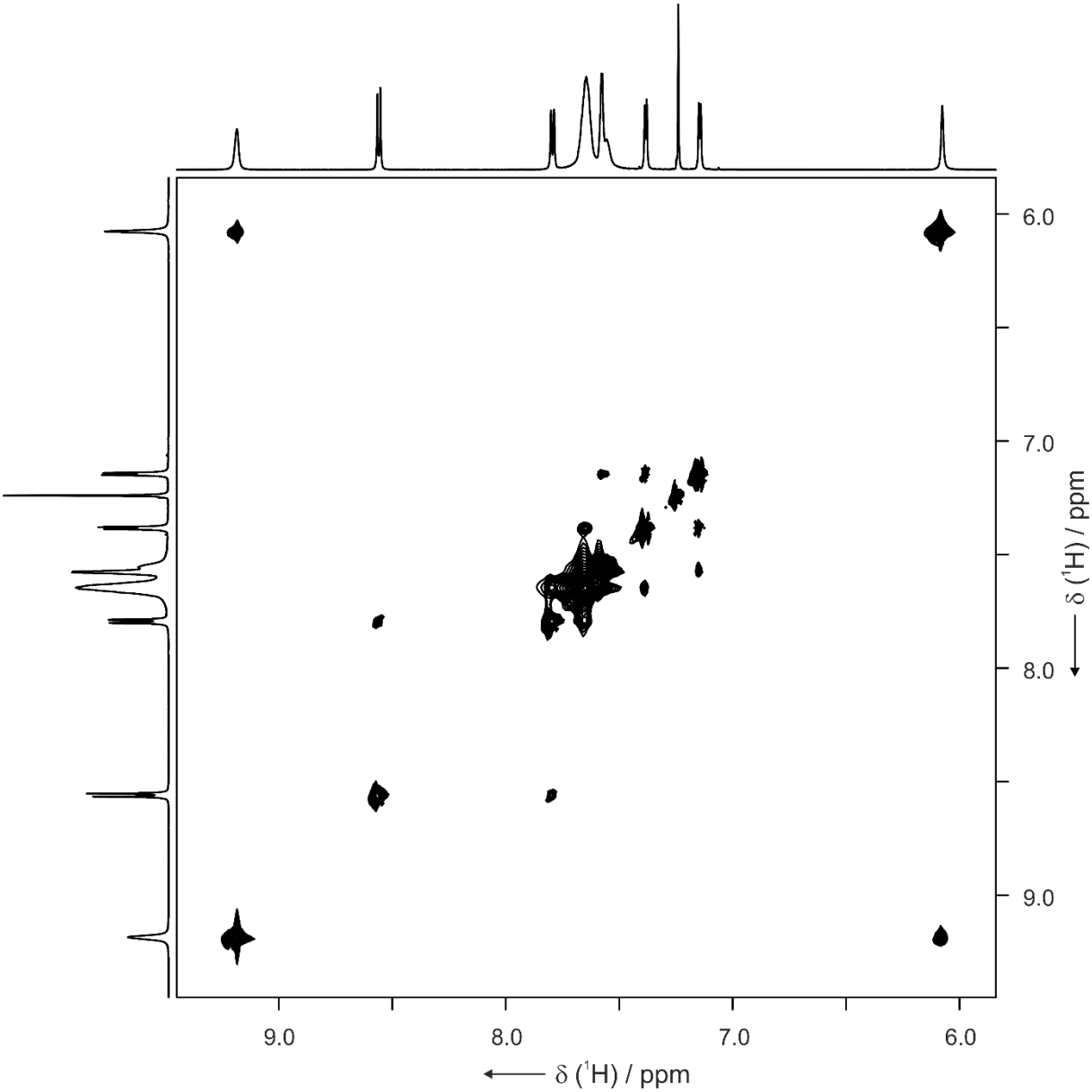


Figure S5. Part of the ^{1}H-^{1}H NOESY spectrum of **2**-H^{+} (600 MHz, $CDCl_3$, 215 K).

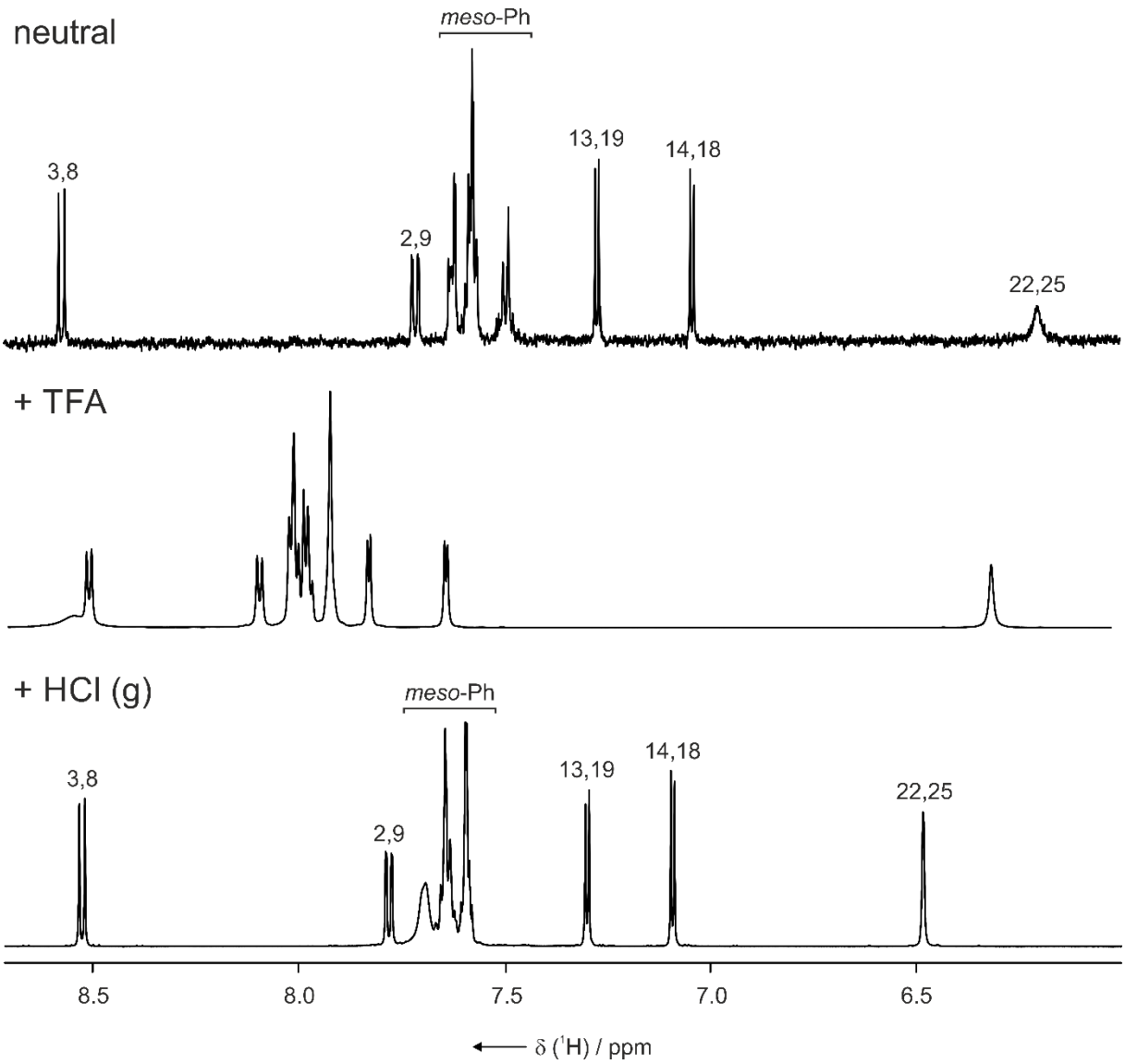


Figure S6. Influence of anion: the spectrum of **2**-H^+ - at this temperature NH signal was not observed (600 MHz, CD_2Cl_2, 300 K).

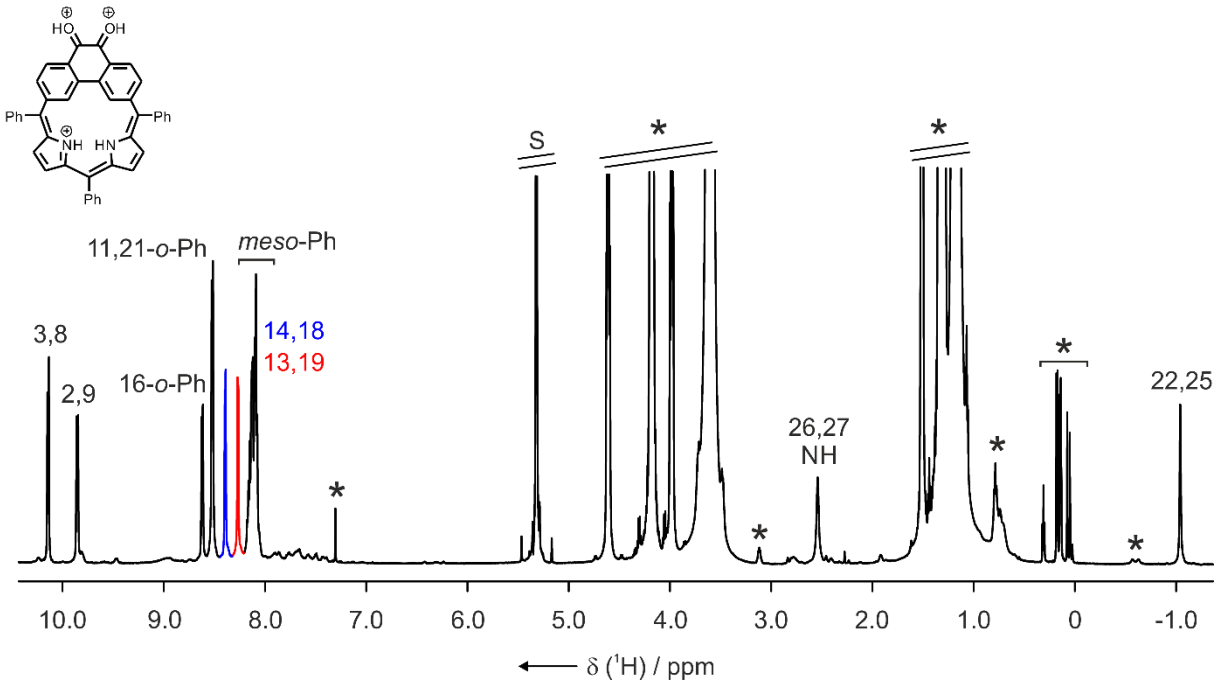


Figure S7. ^{1}H NMR spectrum of **2**-H_3^{3+} (600 MHz, CD_2Cl_2, 195 K).

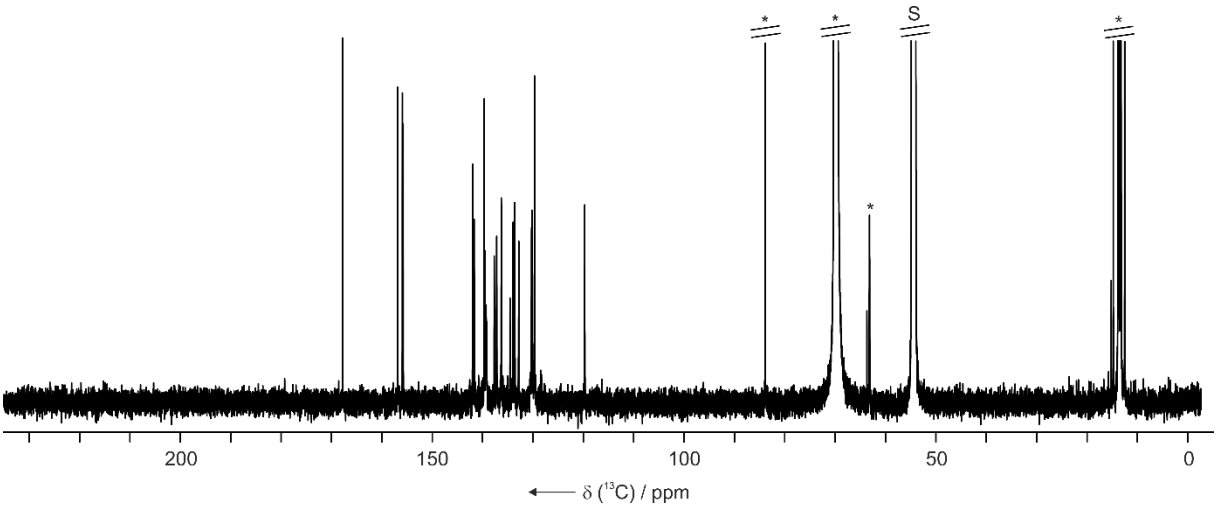


Figure S 8. ^{13}C NMR spectrum of **2**-H_3^{3+} (151 MHz, CD_2Cl_2, 195 K).

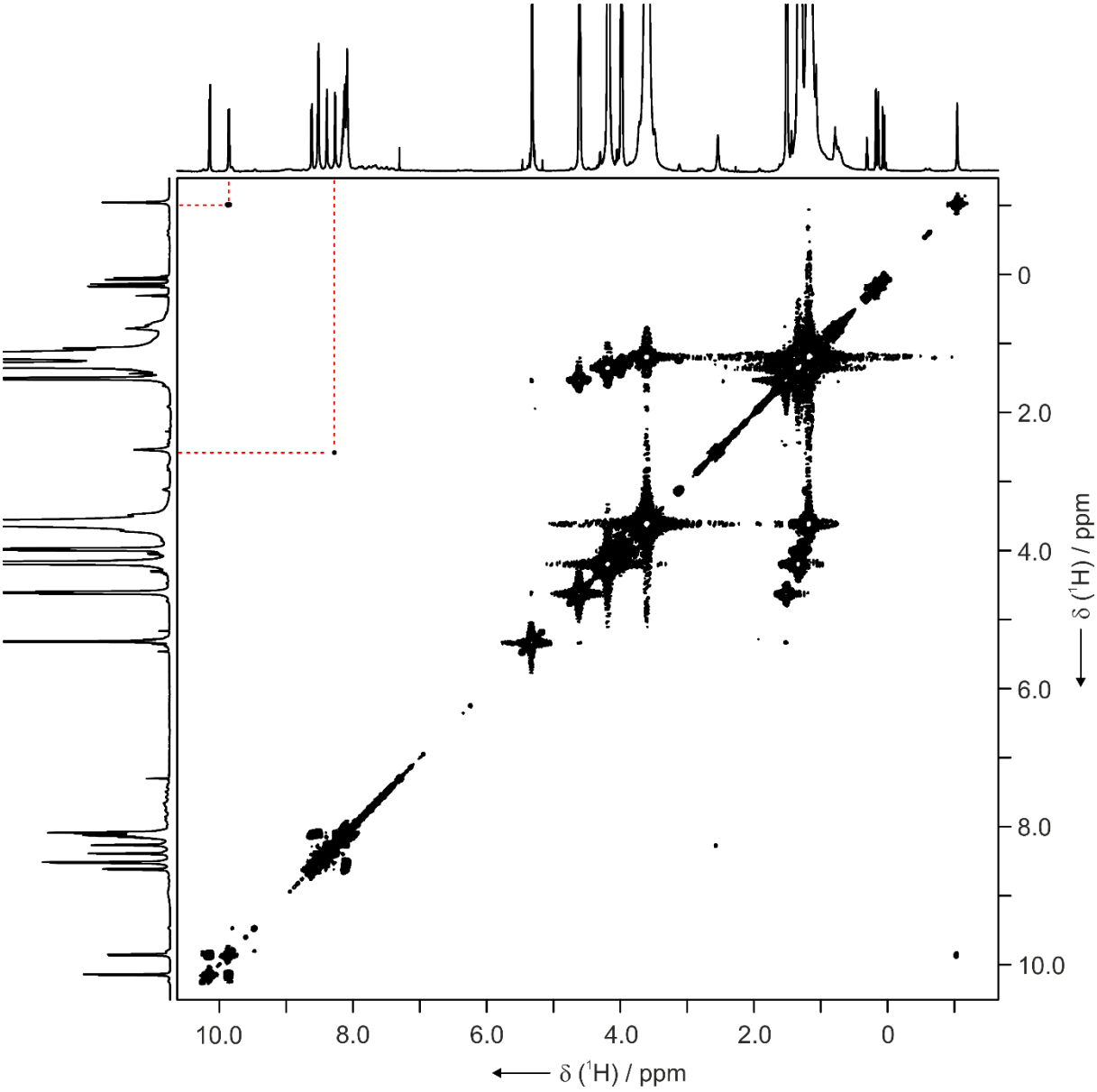


Figure S9. Part of the ^{1}H-^{1}H COSY spectrum of **2**-H_3^{3+} (600 MHz, CD_2Cl_2, 195 K).

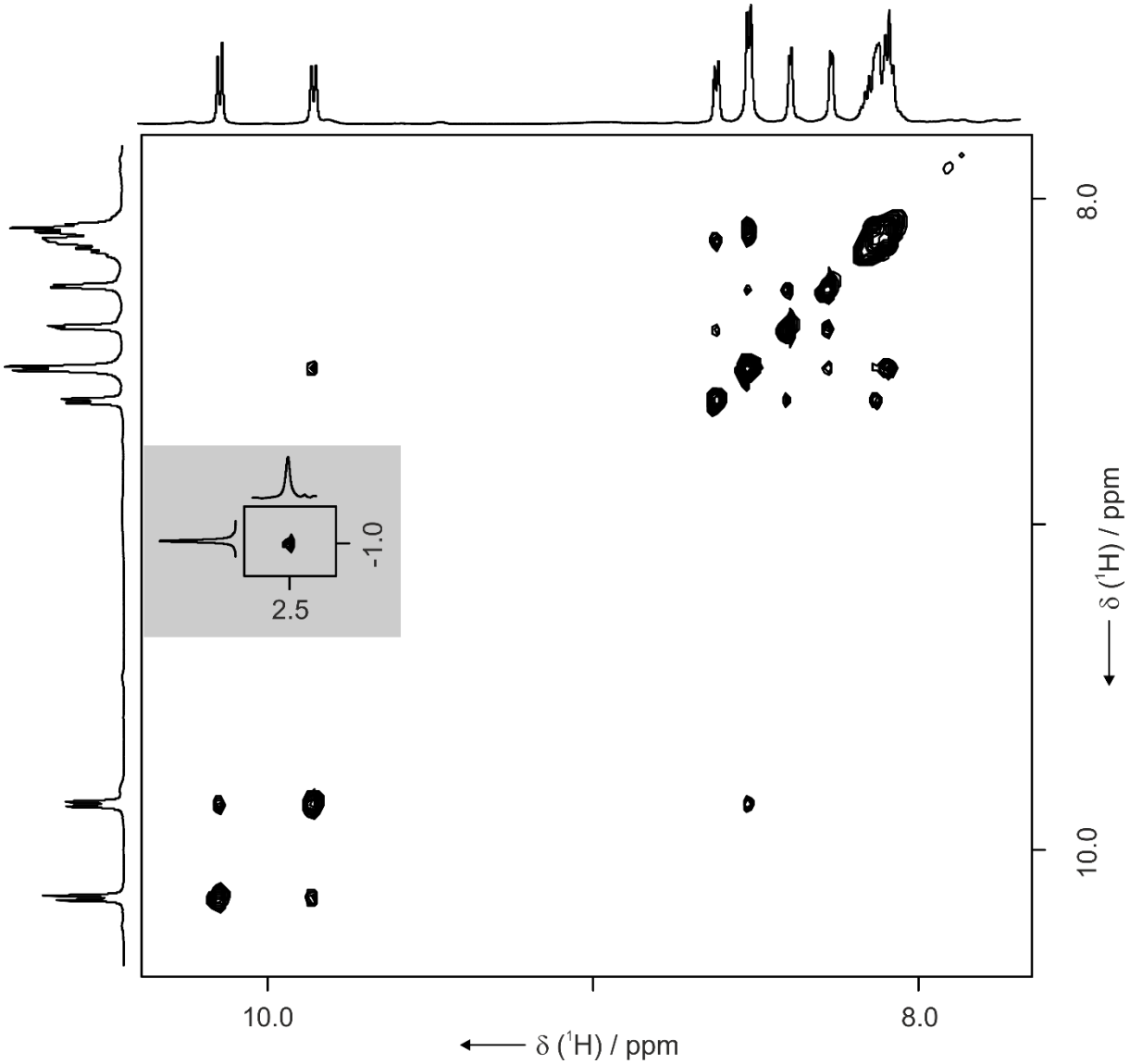


Figure S10. Part of the ^{1}H-^{1}H NOESY spectrum of **2**-H_3^{3+} (600 MHz, CD_2Cl_2, 195 K).

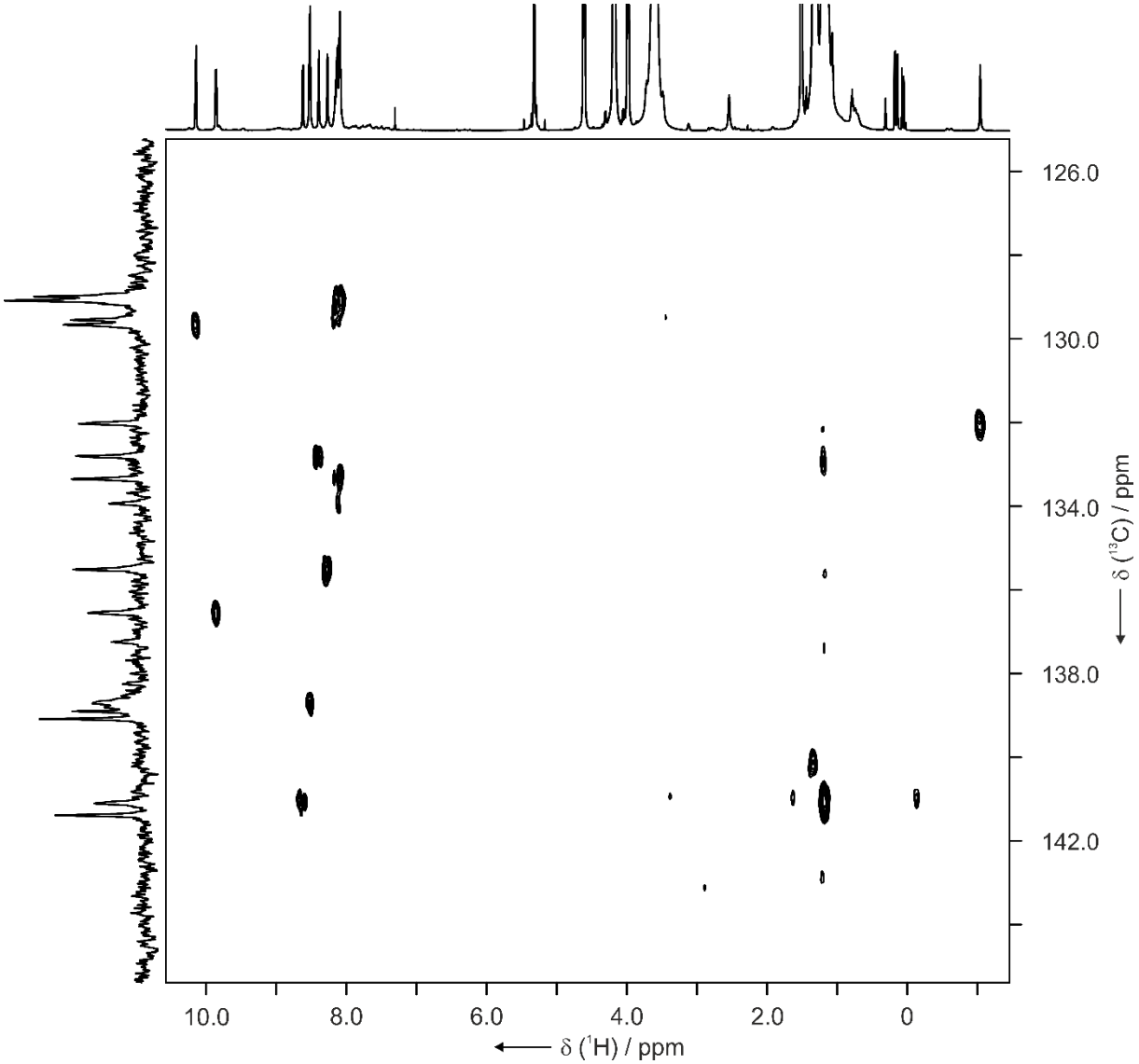


Figure S11. Part of the ^{1}H-^{13}C HMQC spectrum of **2**-H_3^{3+} (600 MHz, CD_2Cl_2, 195 K).

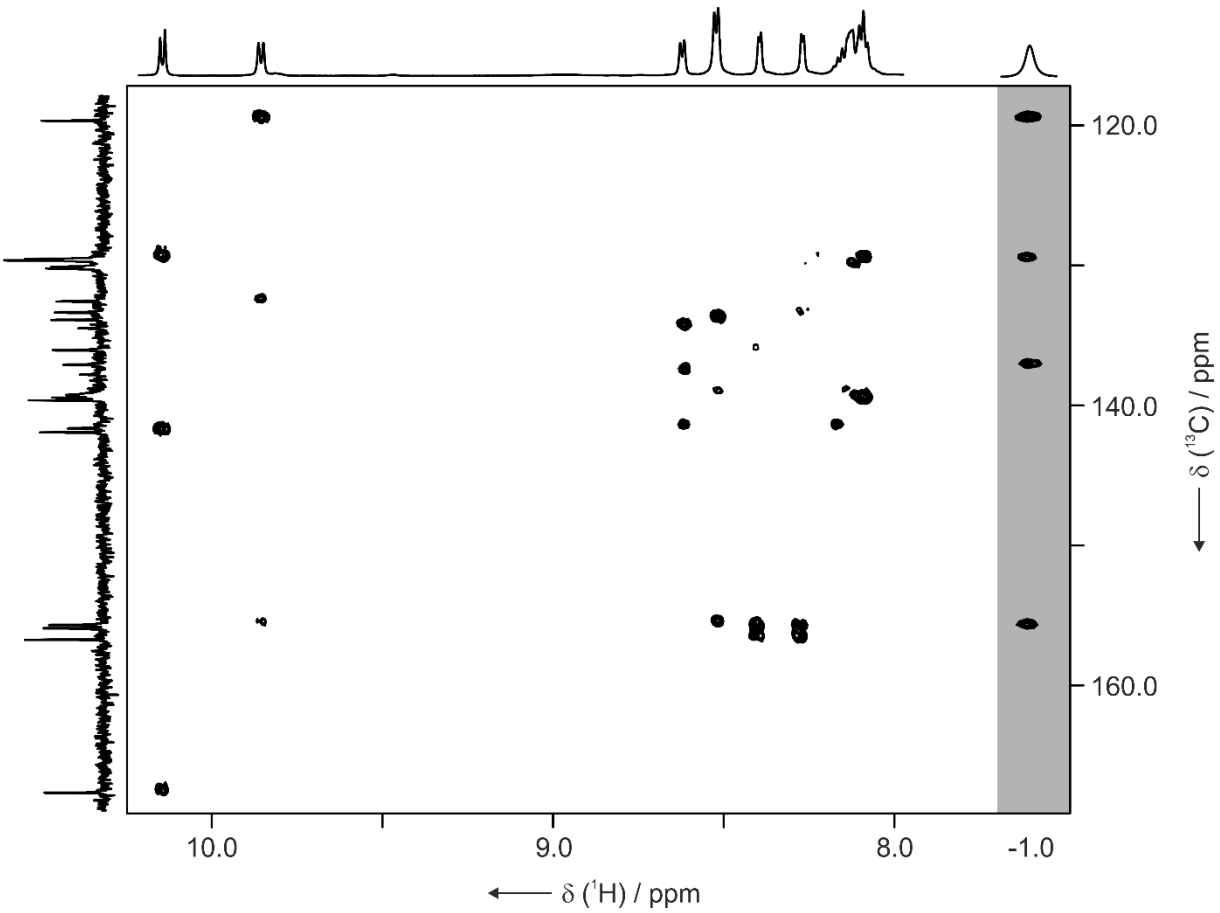


Figure S12. Part of the ^{1}H-^{13}C HMBC spectrum of **2**-H_3^{3+} (600 MHz, CD_2Cl_2, 195 K).

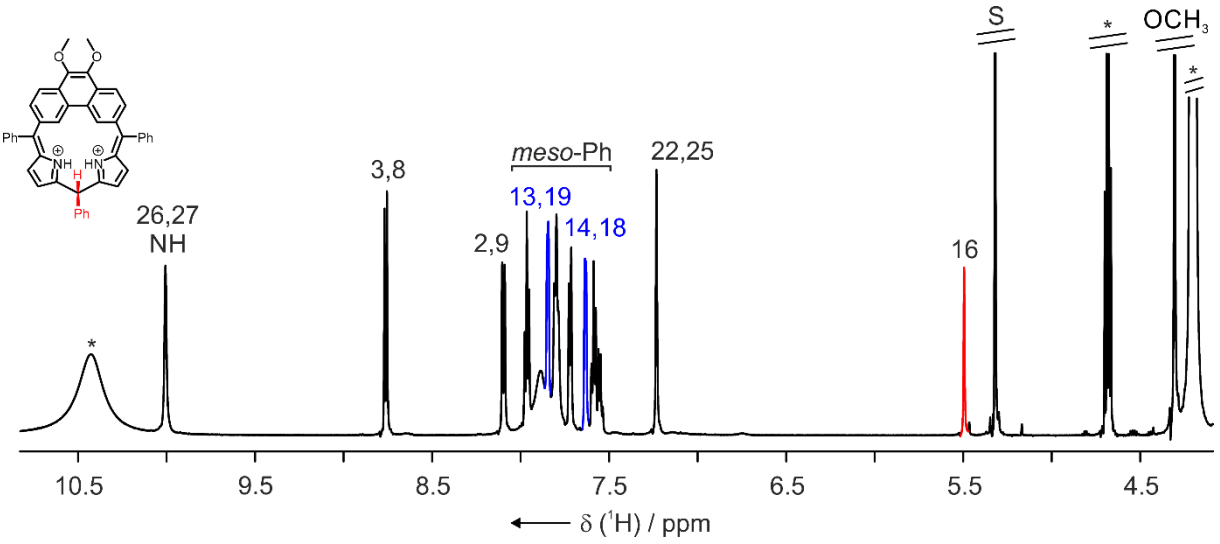


Figure S13. ^{1}H NMR spectrum of **1**-H_2^{2+} (600 MHz, CD_2Cl_2, 250 K).

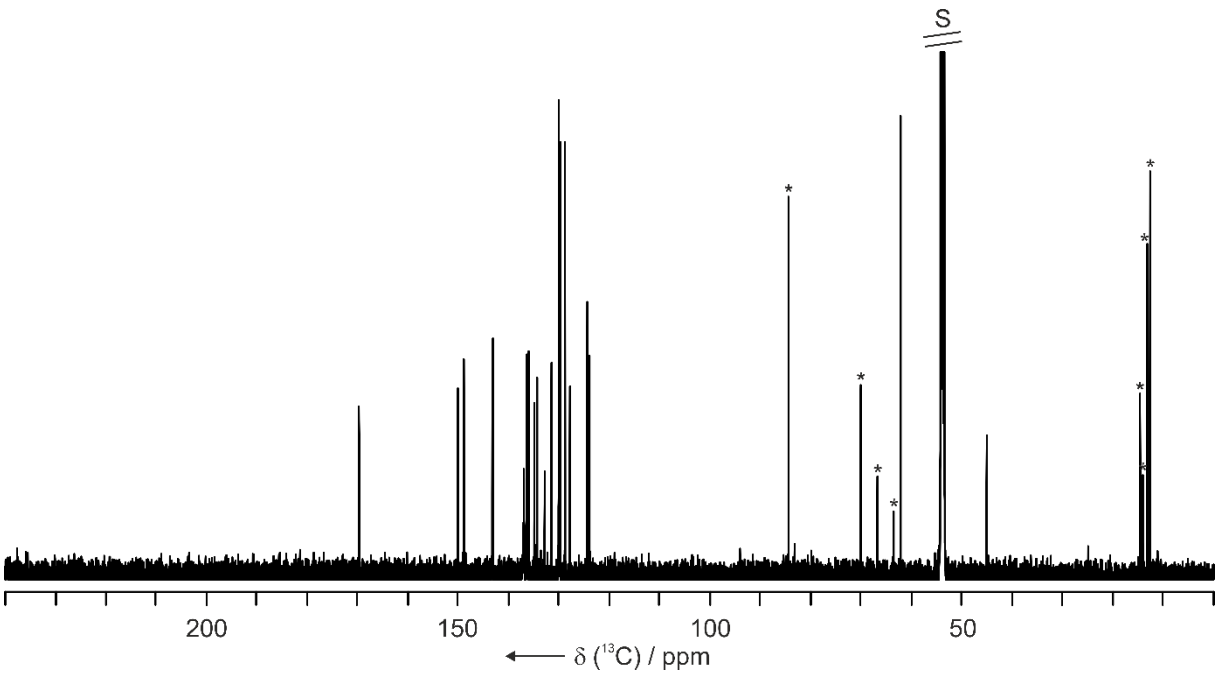


Figure S14. ^{13}C NMR spectrum of **1**-H_2^{2+} (151 MHz, CD_2Cl_2, 250 K).

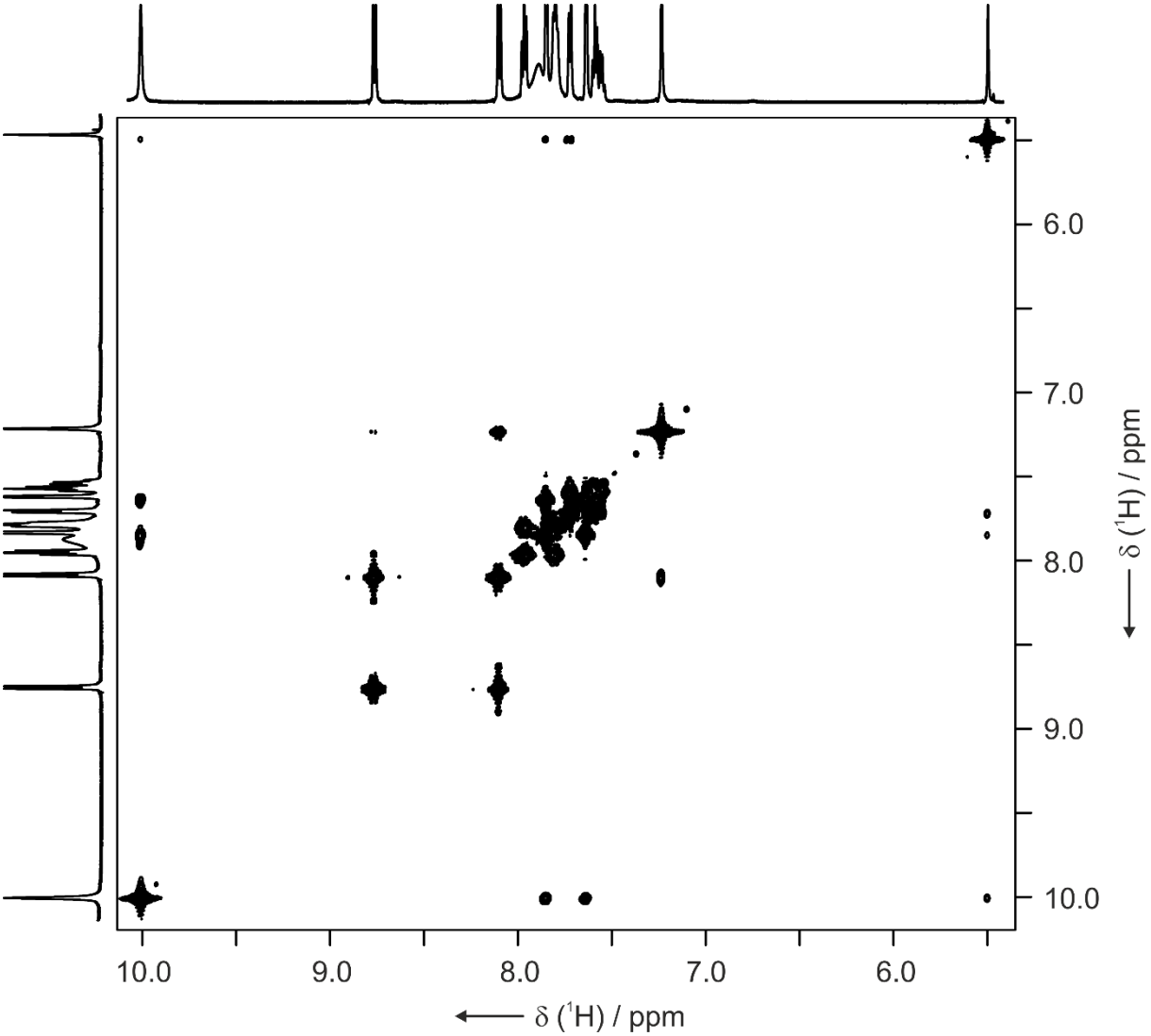


Figure S15. Part of the ^{1}H-^{1}H COSY spectrum of **1**-H_2^{2+} (600 MHz, CD_2Cl_2, 250 K).

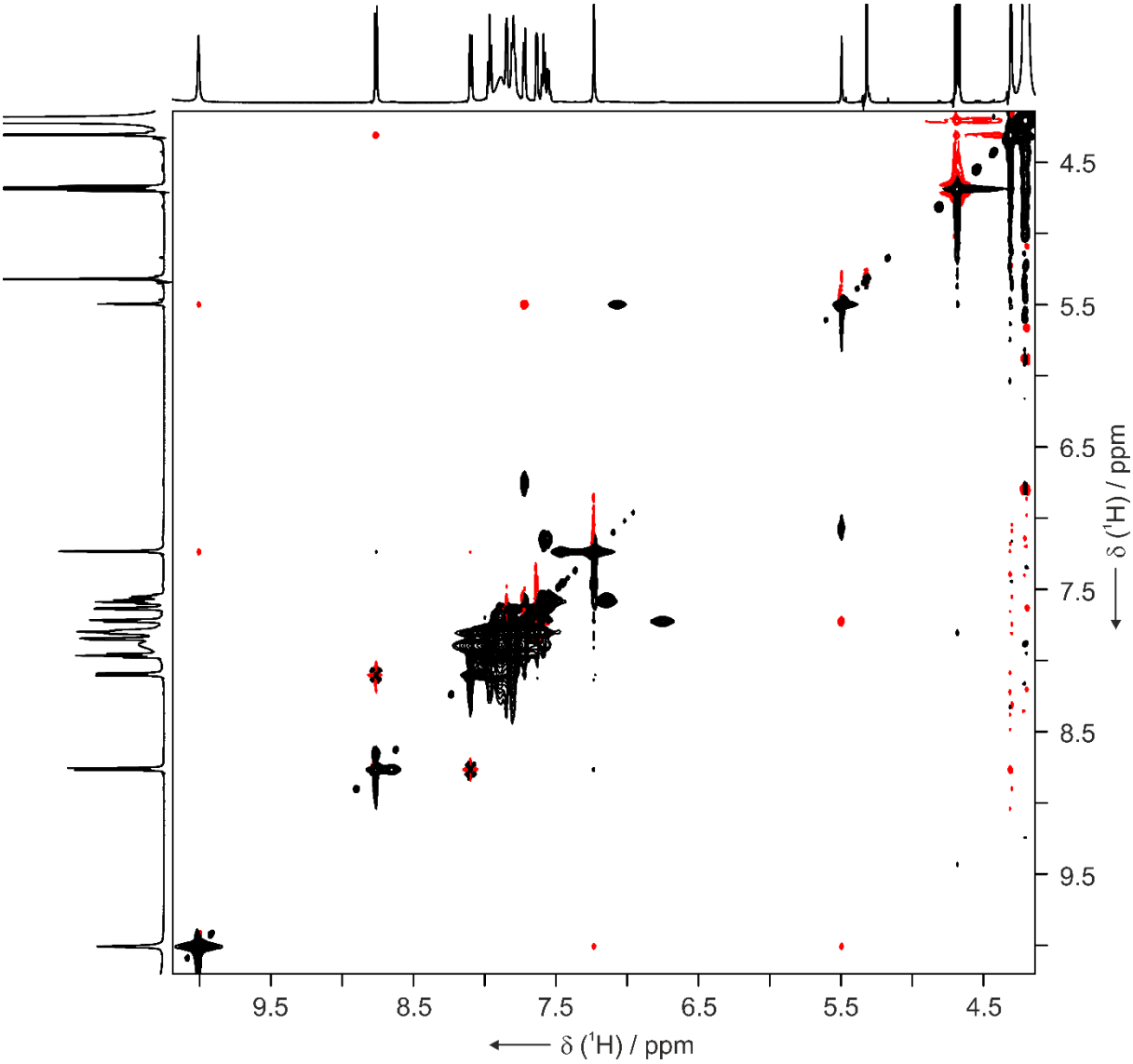


Figure S16. Part of the ^{1}H-^{1}H NOESY spectrum of **1**-H_2^{2+} (600 MHz, CD_2Cl_2, 250 K).

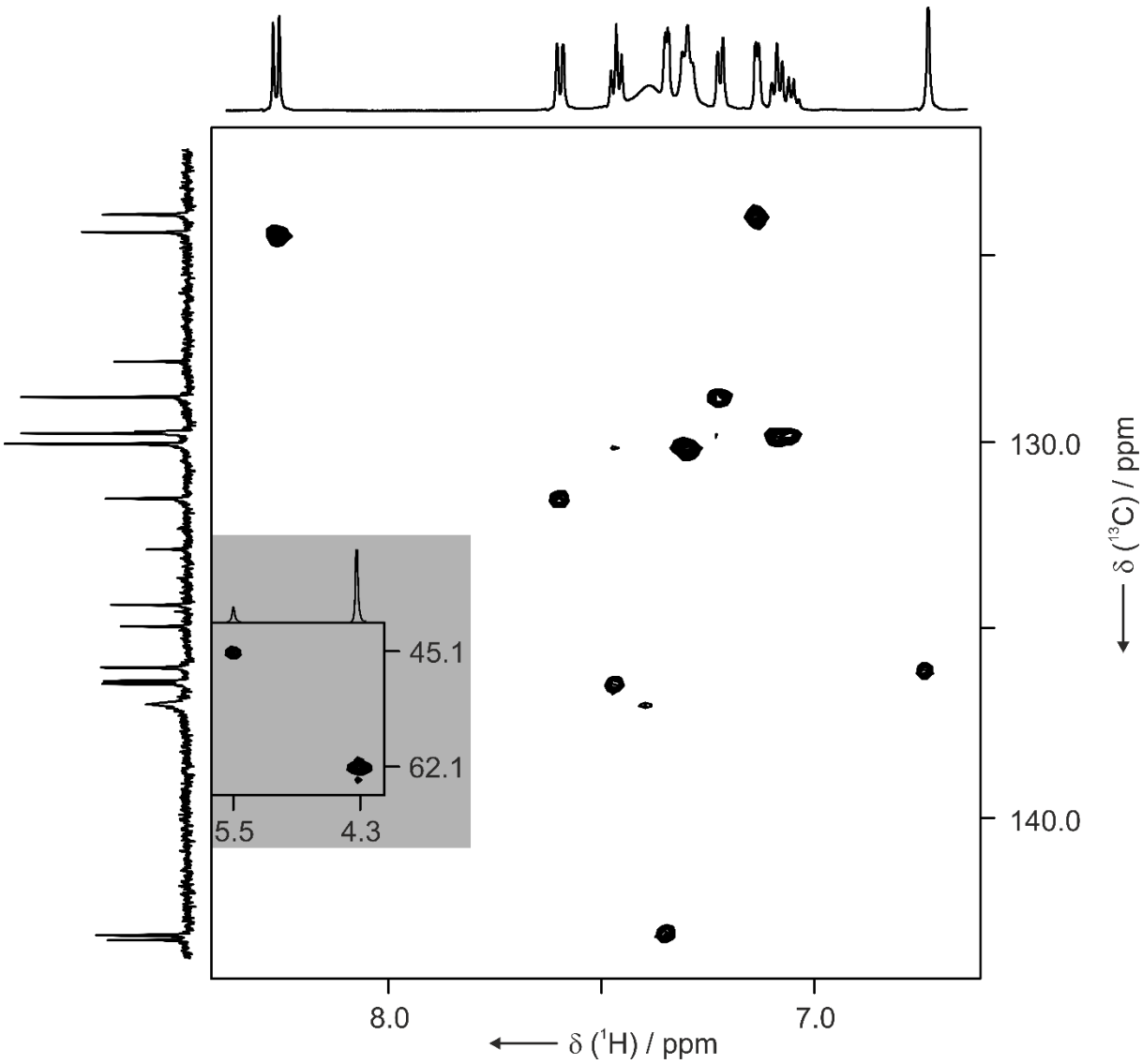


Figure S17. Part of the ^{1}H-^{13}C HSQC spectrum of **1**-H_2^{2+} (600 MHz, CD_2Cl_2, 250 K).

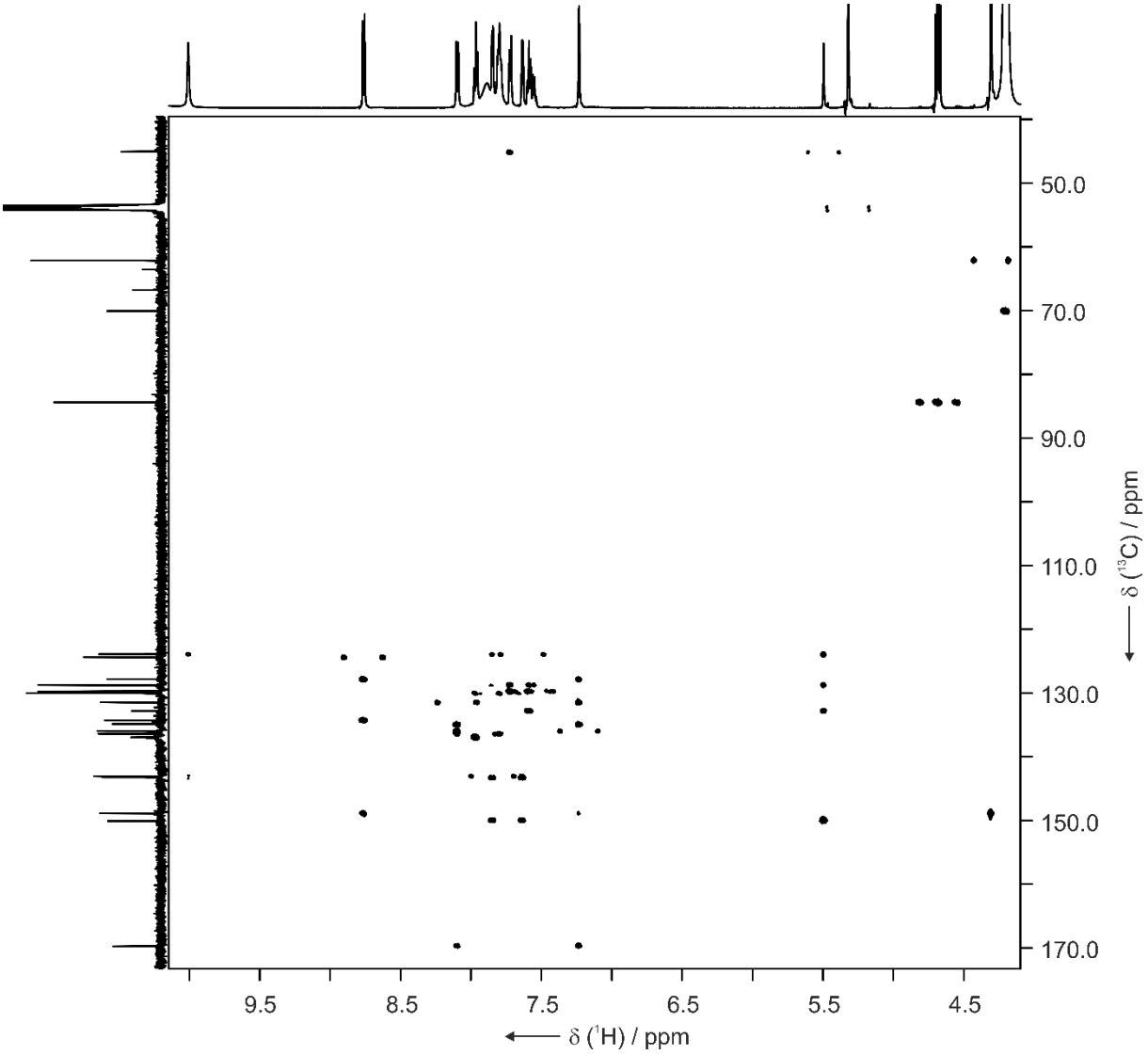


Figure S18. Part of the ^{1}H-^{13}C HMBC spectrum of **1**-H_2^{2+} (600 MHz, CD_2Cl_2, 250 K).

Tables

Table S1. Comparison of chemical shifts for: **2**-H^+ ($CDCl_3$, 215 K); [a] **2**-H_3^{3+} (CD_2Cl_2, 195 K); [b] **2**-H_3^{3+} (C_6D_6, 280 K) and **5**-S-H_2^{2+} ($CDCl_3$, 220 K).

Position	**2**-H^+	[a] **2**-H_3^{3+}	[b] **2**-H_3^{3+}	(**5**-S-H_2^{2+})[2]
2,9	7.79	9.85	8.95	7.38
3,8	8.56	10.14	9.15	8.28
13,19	7.38	8.27	8.68	7.76
14,18	7.14	8.39	8.32	6.81
22,25 or 27,30[2]	6.08	−1.04	−0.77	8.14
NH	9.18	2.54	-	13.32

Table S2. ^{1}H NMR chemical shifts (ppm) of the porphyrin skeleton for (**1**, **1**-H^+, **1**-H_2^{2+}, **2**, **2**-H^+ and **2**-H_3^{3+}) using the GIAO method (Calc. - calculated, Exp. - experimental).

Position	**1**		**1**-H^+		**1**-H_2^{2+}		**2**		**2**-H^+		**2**-H_3^{3+}	
	Calc.	Exp.	Calc.	[a] Exp.	Calc.	[b] Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	[c] Exp.
2,9	5.42	5.94	5.62	5.83	8.42	8.09	7.81	7.75	8.02	7.79	9.70	9.85
3,8	6.54	6.94	7.15	6.89	9.36	8.76	8.77	8.56	8.99	8.56	9.88	10.14
5,6-OCH_3	3.53	3.71	3.70	3.66	4.57	4.31	-	-	-	-	-	-
13,19	5.09	5.59	5.49	5.60	7.86	7.85	7.37	7.33	7.66	7.38	9.07	8.27
14,18	4.70	5.24	4.74	5.09	7.60	7.63	7.11	7.11	7.27	7.14	8.76	8.39
16	-	-	-	-	6.22	5.50	-	-	-	-	-	-
22,25	20.18	16.70	18.44	17.42	6.88	7.23	6.09	6.32	6.13	6.08	3.07	−1.04
26,27(NH)	20.28	16.70	16.78	20.57	7.00	10.00	6.03	Not observed	4.25	9.18	2.06	2.54

Standard measurement in $CDCl_3$ or CD_2Cl_2 at 300 K [(**a**) $CDCl_3$, 215 K, (**b**) CD_2Cl_2, 250 K, (**c**) CD_2Cl_2, 195 K].

Table S3. Comparison of selected bonds length of **1**-H^+, **1**-H_2^{2+}, **2**-H^+, **2**-H_3^{3+}, **2**-BF_2-H^{2+} and **3**-H^+ determined by DFT.

Bonds	**1**-H^+	**1**-H_2^{2+}	**2**-H^+	**2**-H_3^{3+}	**2**-BF_2-H^{2+}	* **3**-H
C(5)–O	1.368	1.355	1.215	1.382	1.274	-
C(6)–O	1.369	1.356	1.215	1.350	1.274	-
C(4)–C(5)	1.445	1.439	1.488	1.432	1.423	-
C(5)–C(6)	1.375	1.391	1.544	1.372	1.475	-
C(6)–C(7)	1.445	1.438	1.488	1.441	1.423	-
C(23)–C(24)	1.454	1.457	1.484	1.456	1.469	1.491
$\mathbf{C_\alpha}$–$\mathbf{C_{meso}}$						
C(1)–C(21)	1.477	1.463	1.472	1.474	1.451	1.473
C(20)–C(21)	1.385	1.414	1.388	1.386	1.423	1.387
C(10)–C(11)	1.477	1.462	1.472	1.479	1.451	1.475
C(11)–C(12)	1.385	1.414	1.388	1.384	1.423	1.386
C(15)–C(16)	1.412	1.525	1.411	1.411	1.424	1.412
C(16)–C(17)	1.413	1.525	1.412	1.414	1.424	1.410

* Values of corresponding bonds of **1** are shown for **3**-H (despite changed numbering scheme in **3**-H).

Table S4. Experimental and theoretical bond lengths of 2-H^+ and **2**-BF_2-H^{2+}.

Bonds	**2**-H^+		**2**-BF_2-H^{2+}	
	X-Ray	**DFT**	**X-Ray**	**DFT**
C(5)–O	1.208(3)	1.215	1.326(6)	1.274
C(6)–O	1.211(3)	1.215	1.318(7)	1.274
C(4)–C(5)	1.470(3)	1.488	1.428(8)	1.423
C(5)–C(6)	1.543(3)	1.544	1.438(8)	1.475
C(6)–C(7)	1.471(3)	1.488	1.388(8)	1.423
C(23)–C(24)	1.478(3)	1.484	1.453(8)	1.469

Table S5. Crystal data and structure refinement for **2**.

Identification code	**2**
Empirical formula	$C_{43}H_{26}N_2O_2$
Formula weight	602.66
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	triclinic
Space group	$P\bar{1}$ (2)
Unit cell dimensions	a = 9.516(3) α = 91.24(4)°
	b = 11.551(6) β = 106.05(4)°
	c = 13.616(7) γ = 99.94(3)°
Volume	1412.9(12)
Z	2
Density (calculated)	1.417 Mg/m^3
Absorption coefficient	0.685 mm^{-1}
F(000)	628
Crystal size	0.109 x 0.034 x 0.027 mm^3
Theta range for data collection	3.387 to 74.468
Index ranges	$-6 \leq h \leq 11$, $-14 \leq k \leq 14$, $-17 \leq l \leq 16$
Reflections collected	4981
Independent reflections	1131 [R(int) = 0.2960]
Completeness to theta = 67.684°	91.6%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4981 / 0 / 424
Goodness-of-fit on F^2	0.895
Final R indices [$I > 2\sigma(I)$]	R1 = 0.1221, wR2 = 0.2214
R indices (all data)	R1 = 0.3027, wR2 = 0.3452
Largest diff. peak and hole	0.374 and –0.333 $e \cdot Å^{-3}$

Table S6. Crystal data and structure refinement for **2**-H^+.

Identification code	**2**-H^+
Empirical formula	$C_{43}H_{27}N_2O_2$, 3(C_6H_6),BF_4
Formula weight	924.80
Temperature	100(2) K
Wavelength	1.54175 Å
Crystal system	monoclinic
Space group	$P2_1/n$ (14)
Unit cell dimensions	a = 14.154(3) α = 90°
	b = 17.553(3) β = 106.78(3)°
	c = 19.832(3) γ = 90°
Volume	4717.4(16)
Z	4
Density (calculated)	1.302 Mg/m^3
Absorption coefficient	0.721 mm^{-1}
F(000)	1928
Crystal size	0.538 x 0.422 x 0.100 mm^3
Theta range for data collection	3.416 to 68.103
Index ranges	$-17 \leq h \leq 16$, $-20 \leq k \leq 21$, $-21 \leq l \leq 23$
Reflections collected	8435
Independent reflections	6112 [R(int) = 0.0460]
Completeness to theta = 67.676°	98.2%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8435 / 0 / 639
Goodness-of-fit on F^2	0.947
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0564, wR2 = 0.1492
R indices (all data)	R1 = 0.0708, wR2 = 0.1600
Largest diff. peak and hole	0.420 and –0.261 $e \cdot Å^{-3}$

Table S7. Crystal data and structure refinement for **2**-BF_2-H^{2+}.

Identification code	**2**-BF_2-H^{2+}
Empirical formula	2($C_{43}H_{27}BF_2N_2O_2$), 3(B_2F_6O) +solvent
Formula weight	1759.81
Temperature	100(2) K
Wavelength	1.54175 Å
Crystal system	triclinic
Space group	$P\bar{1}$ (2)
Unit cell dimensions	a = 8.090(2) α = 82.58(2)°
	b = 12.074(3) β = 89.11(2)°
	c = 24.254(3) γ = 70.85(3)°
Volume	2218.3(9)
Z	1
Density (calculated)	1.317 Mg/m^3
Absorption coefficient	0.113 mm^{-1}
F(000)	892
Crystal size	0.654 x 0.041 x 0.035 mm^3
Theta range for data collection	1.838 to 80.508
Index ranges	$-5 \leq h \leq 9$, $-15 \leq k \leq 15$, $-30 \leq l \leq 29$
Reflections collected	9238
Independent reflections	2150 [R(int) = 0.1544]
Completeness to theta = 67.676°	99.6%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9238 / 120 / 632
Goodness-of-fit on F^2	0.664
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0810, wR2 = 0.1883
R indices (all data)	R1 = 0.2001, wR2 = 0.2196
Largest diff. peak and hole	0.391 and –0.369 $e \cdot Å^{-3}$

Table S8. DFT calculated Cartesian coordinates for **1**-H^+.

C	-1.87123100	-4.47017500	0.47990400
C	-0.53803200	-4.79963700	0.54156300
C	0.47460300	-3.82335900	0.21079100
C	-2.27849100	-3.12099500	0.16052000
C	-1.31350100	-2.17599800	-0.27543300
C	0.09427800	-2.53855300	-0.26063200
C	-1.73955200	-0.86504600	-0.56338000
C	1.10449800	-1.59779300	-0.53498100
O	-2.86264400	-5.35550000	0.80631400
O	-0.10135200	-6.04297400	0.90966100
C	-2.99743700	-6.49238800	-0.07018900
C	-0.41280200	-6.45343100	2.25633100
C	-3.62039000	-2.70384500	0.32527200
C	-3.98111000	-1.38433300	0.15106000
C	-3.03088900	-0.41667300	-0.28106600
C	1.84802700	-4.10187700	0.40847900
C	2.44843300	-1.83250000	-0.24227500
C	2.80708500	-3.12920400	0.22027200
C	-3.39482000	1.01473800	-0.31405300
C	3.46046400	-0.76142000	-0.33741100
C	-2.48629000	2.03679800	-0.09563800
N	-1.11623000	1.90213000	0.20455400
C	-0.49799800	3.12238600	0.32077400
C	-1.53934800	4.10733200	0.12731200
C	-2.70610300	3.46276600	-0.15332100
C	3.15738700	0.57852600	-0.16016900
N	1.90734300	1.11561900	0.22738000
C	1.94655000	2.49332800	0.25309900
C	3.99425200	1.72628700	-0.40046100
C	3.28665100	2.86130000	-0.13348100
C	0.88087200	3.40254300	0.43885000
C	1.27384500	4.84663000	0.59202500
C	1.24092600	5.72938200	-0.49866300
C	1.70182900	5.32501100	1.83863300
C	1.62055800	7.06309100	-0.34215800
C	2.04065000	7.53016600	0.90480900
C	2.08164000	6.65898200	1.99420700
C	4.86617900	-1.14468900	-0.60100600
C	5.92478300	-0.64719800	0.18313200
C	5.16618300	-2.03575200	-1.65081100
C	7.24174900	-1.01411300	-0.08709700
C	7.52559800	-1.87917300	-1.14503000
C	6.48397100	-2.38826500	-1.92558400
C	-4.82130900	1.36453800	-0.52501400
C	-5.51588300	2.20529000	0.36429500
C	-6.85516700	2.52187000	0.14168500
C	-7.52139600	2.00864700	-0.97205300
C	-6.84636200	1.16371200	-1.85708000
C	-5.51314900	0.83372100	-1.63088700
H	-3.83050300	-7.07467200	0.32450300
H	-3.22951700	-6.16233900	-1.08828000
H	-2.08697200	-7.09662000	-0.07765200
H	0.02678600	-7.44438100	2.37299300
H	0.03941800	-5.76414200	2.97761200
H	-1.49188300	-6.49869100	2.41944700
H	-4.35025600	-3.43381900	0.65432700
H	-4.99578100	-1.07406100	0.37007700
H	2.12858700	-5.08927900	0.75493200
H	3.84371700	-3.34696100	0.44891300
H	-1.37203800	5.17259000	0.14940400

H	-3.64827300	3.91907000	-0.41497100
H	4.99728500	1.66953100	-0.79514100
H	3.61705600	3.88084600	-0.25796800
H	0.92252900	5.36633900	-1.47186300
H	1.73202200	4.64959600	2.68874300
H	1.59208700	7.73491600	-1.19456300
H	2.33608500	8.56768000	1.02579800
H	2.40755200	7.01646900	2.96610000
H	5.70607100	-0.00005900	1.02636400
H	4.36143300	-2.43030300	-2.26289200
H	8.04471400	-0.63271000	0.53583000
H	8.55185500	-2.16330900	-1.35537500
H	6.69987500	-3.06082000	-2.74973200
H	-5.01084900	2.58189500	1.24805900
H	-7.38021100	3.16122400	0.84446000
H	-8.56366500	2.25730700	-1.14530300
H	-7.36015200	0.76128600	-2.72445000
H	-4.99246200	0.17834200	-2.32207800
H	-1.04268900	-0.18111100	-1.02734100
H	0.83712900	-0.65275000	-0.98599100
H	1.25564400	0.55630500	0.75512700
H	-0.70892400	1.01242200	0.42873400

Table S9. DFT calculated Cartesian coordinates for **1**-H_2^{2+}-A1.

C	0.72481900	4.16920300	0.75187700
C	-0.66544200	4.15182600	0.81451200
C	-1.40637400	3.01611900	0.33309800
C	1.45225900	3.00634800	0.32084500
C	0.74484400	1.88148500	-0.19211700
C	-0.71193000	1.89651400	-0.20819400
C	1.47748400	0.76338700	-0.59792500
C	-1.45742900	0.79659400	-0.64131800
O	1.45992200	5.23393700	1.15974300
O	-1.39299000	5.19548300	1.28147600
C	1.27927300	6.47653500	0.43243200
C	-1.15836200	5.62896000	2.64528600
C	2.86902200	2.95033300	0.40546800
C	3.56410500	1.81707200	0.04314400
C	2.87202700	0.67517700	-0.45624800
C	-2.82340300	2.97391500	0.41689200
C	-2.85290800	0.72399200	-0.50574200
C	-3.53260400	1.86160900	0.01808900
C	3.54692300	-0.57426300	-0.80742200
C	-3.54155100	-0.51210800	-0.88059300
C	2.86024800	-1.80042300	-0.63723600
N	1.76017600	-1.95741900	0.21675500
C	1.20864800	-3.18350800	0.06967400
C	1.93826800	-3.86171800	-0.92642400
C	2.96757400	-3.02486900	-1.34659400
C	-2.87559600	-1.74832400	-0.70413500
N	-1.79537900	-1.92320600	0.17192700
C	-1.26419100	-3.15965000	0.03936200
C	-2.98967900	-2.97184300	-1.41434000
C	-1.98495400	-3.82629700	-0.97129700
C	-0.04144300	-3.63865700	0.81111000
C	-0.05664000	-3.31352000	2.30764600
C	-0.04937700	-2.00299700	2.81756200
C	-0.07811200	-4.37883800	3.21643800
C	-0.06267600	-1.77012500	4.19405800
C	-0.08384000	-2.84282400	5.08527200
C	-0.09166400	-4.14756000	4.59225500
C	-4.87802600	-0.48611500	-1.44916200

C	-5.79793100	-1.53519100	-1.19619000
C	-5.28483100	0.58973800	-2.27832600
C	-7.06842100	-1.50716300	-1.75491900
C	-7.44515100	-0.44552600	-2.58501700
C	-6.55038200	0.59907800	-2.84703100
C	4.89393100	-0.57565200	-1.35313100
C	5.79317100	-1.63355200	-1.06598800
C	7.07421600	-1.63344400	-1.60118300
C	7.48167900	-0.59207500	-2.44211700
C	6.60699400	0.46020400	-2.73884200
C	5.33129900	0.47914600	-2.19333000
H	1.93079100	7.19757700	0.92412400
H	1.58906200	6.34406600	-0.60817700
H	0.24179200	6.81309100	0.47289800
H	-1.82644800	6.47540600	2.79769100
H	-1.41725500	4.82256100	3.33789800
H	-0.12119900	5.93066500	2.79684900
H	3.39309500	3.81061100	0.80397000
H	4.63919800	1.77786300	0.17653900
H	-3.33858700	3.83244100	0.83021000
H	-4.60916900	1.83426500	0.14268200
H	1.71626000	-4.85159200	-1.29928900
H	3.67977900	-3.21988500	-2.13492400
H	-3.68871400	-3.15564500	-2.21703800
H	-1.77336100	-4.82088100	-1.33763500
H	-0.03281400	-1.13337900	2.16091900
H	-0.08414100	-5.40084000	2.84814400
H	-0.05601000	-0.75122600	4.56785700
H	-0.09395500	-2.66246800	6.15501700
H	-0.10810600	-4.98926900	5.27685600
H	-5.52427000	-2.33461100	-0.51660500
H	-4.58448900	1.38545400	-2.50691300
H	-7.77335000	-2.30189600	-1.53505800
H	-8.43828800	-0.42823900	-3.02259100
H	-6.84338800	1.41428200	-3.50002700
H	5.49476100	-2.41772400	-0.37907200
H	7.76299100	-2.43456800	-1.35489800
H	8.48272700	-0.59669700	-2.86158900
H	6.92355000	1.25918700	-3.40085200
H	4.64676700	1.28035500	-2.44898400
H	0.96485300	-0.06455500	-1.06458100
H	-0.95416800	-0.02900800	-1.12275600
H	-0.05101100	-4.72762800	0.71769900
H	-1.60176500	-1.30091400	0.94358400
H	1.56262000	-1.33375600	0.98633100

Table S10. DFT calculated Cartesian coordinates for **1**-H_2^{2+}-A2.

C	-0.98939100	-4.54248100	0.98396000
C	0.39907700	-4.60238800	1.05242600
C	1.20358300	-3.51468800	0.56215500
C	-1.64763100	-3.34350000	0.54056800
C	-0.87731000	-2.26860900	0.01106100
C	0.57594300	-2.36656100	-0.00100300
C	-1.54367000	-1.11231500	-0.40263800
C	1.38336100	-1.31338400	-0.43994200
O	-1.78575400	-5.55792200	1.40106200
O	1.06572800	-5.67775400	1.53719400
C	-1.67013800	-6.81992300	0.69399600
C	0.80115500	-6.07848800	2.90600900
C	-3.05728100	-3.20143700	0.63388700
C	-3.68351100	-2.02874800	0.27241700
C	-2.92720600	-0.93535100	-0.24239500
C	2.61931100	-3.54676900	0.66238900
C	2.77759500	-1.31005900	-0.27962900

C	3.38993100	-2.47576900	0.26535200
C	-3.53175400	0.35469000	-0.57096400
C	3.54023400	-0.11231800	-0.63220200
C	-2.77920300	1.54191900	-0.41641400
N	-1.62728500	1.64805000	0.37723100
C	-1.05813700	2.87213800	0.24780000
C	-1.83511900	3.60160800	-0.67356600
C	-2.89741600	2.79661000	-1.06889600
C	2.94864000	1.16204100	-0.47551300
N	1.83397800	1.41683200	0.33775800
C	1.42980300	2.70571100	0.21989100
C	3.21858400	2.39160400	-1.13104900
C	2.27915900	3.32849200	-0.71624500
C	0.22285200	3.21587500	1.00062600
C	0.32585100	4.68095300	1.41905400
C	0.38527700	5.73166700	0.49072100
C	0.36191300	4.98295500	2.78576500
C	0.47859800	7.05342100	0.92577400
C	0.51378700	7.34344000	2.29083200
C	0.45526500	6.30533100	3.22032000
C	4.89663200	-0.21789300	-1.14679300
C	5.87828900	0.75404700	-0.82885500
C	5.25902800	-1.30118000	-1.98618100
C	7.16590000	0.64600800	-1.33702300
C	7.49895500	-0.41920200	-2.18086600
C	6.54277900	-1.38880300	-2.50586000
C	-4.89789500	0.43381500	-1.06633100
C	-5.74058900	1.51778000	-0.71459000
C	-7.03875800	1.58724500	-1.20264100
C	-7.51883900	0.59173900	-2.06039100
C	-6.70052300	-0.48583300	-2.41979900
C	-5.40897400	-0.57555500	-1.91997400
H	-2.36436600	-7.49549700	1.19172900
H	-1.96510400	-6.68628700	-0.35073300
H	-0.65348900	-7.21332300	0.74733300
H	1.42163900	-6.95760000	3.07375800
H	1.09975300	-5.27735000	3.58855600
H	-0.25157100	-6.32139700	3.05575000
H	-3.62981600	-4.02524000	1.04261000
H	-4.75204300	-1.92073000	0.41872500
H	3.08362600	-4.42669700	1.09065300
H	4.46419400	-2.50135400	0.40775500
H	-1.63744300	4.60912300	-1.00278500
H	-3.65113400	3.03941400	-1.80330600
H	3.98432600	2.53498800	-1.87904800
H	2.21005400	4.35416500	-1.04148900
H	0.35975200	5.53377100	-0.57638000
H	0.31693100	4.18262900	3.52024200
H	0.52375100	7.85643900	0.19715700
H	0.58637300	8.37266000	2.62657400
H	0.48199200	6.52150200	4.28333700
H	5.63595400	1.55422300	-0.13834800
H	4.51364100	-2.03930900	-2.26122300
H	7.91684100	1.38082000	-1.06678200
H	8.50548100	-0.49850000	-2.57920500
H	6.80267400	-2.20756300	-3.16836800
H	-5.38620000	2.26633500	-0.01464700
H	-7.68413600	2.40736300	-0.90634600
H	-8.53267700	0.65125800	-2.44331800
H	-7.07325800	-1.24986600	-3.09372600
H	-4.76906100	-1.39743200	-2.22181300
H	-0.98672200	-0.32410200	-0.88814100
H	0.93105900	-0.47114200	-0.94377100
H	1.50144700	0.76455200	1.03322300
H	-1.37227300	0.95896700	1.06993400
H	0.19422500	2.62939900	1.92966500

Table S11. DFT calculated Cartesian coordinates for **1**-H_2^{2+}-A3.

C	1.22657200	-4.59381500	-0.75442500
C	-0.16731200	-4.78304200	-0.66726200
C	-1.02193100	-3.71466000	-0.17685000
C	1.80407000	-3.33897300	-0.43673800
C	0.99642800	-2.29675000	0.12576100
C	-0.43956600	-2.49846900	0.24705000
C	1.59868200	-1.10297600	0.48259800
C	-1.28185100	-1.45764700	0.64615600
O	2.03679500	-5.59624400	-1.21182000
O	-0.83162200	-5.87638800	-1.01242300
C	2.69401200	-6.37937800	-0.19024200
C	-0.29929900	-6.97187400	-1.79884600
C	3.18611200	-3.06374700	-0.68218300
C	3.73955700	-1.84385300	-0.39468000
C	2.95169900	-0.79921100	0.20269000
C	-2.42911600	-3.83591500	-0.14384100
C	-2.66546100	-1.54039900	0.61380600
C	-3.23704900	-2.77206000	0.23602900
C	3.46800100	0.51339800	0.45193600
C	-3.47182800	-0.27642400	1.01448300
C	2.61032600	1.66908700	0.55796200
N	1.31874900	1.77398100	0.05731900
C	0.82868000	3.05176300	0.25718500
C	1.81616300	3.76370400	0.96859000
C	2.89969600	2.91432500	1.16530600
C	-2.95717300	0.93260400	0.24153400
N	-1.78737700	1.56001900	0.55244600
C	-1.58227300	2.67232900	-0.27710700
C	-3.51371700	1.61771700	-0.86113200
C	-2.69293300	2.69350400	-1.16402000
C	-0.45386300	3.51545400	-0.22740100
C	-0.56666800	4.89550000	-0.68326500
C	-1.77157700	5.61864100	-0.49349300
C	0.52024600	5.54290200	-1.32216400
C	-1.88136300	6.93147000	-0.93128100
C	-0.80184900	7.54898200	-1.57225000
C	0.39627200	6.85134900	-1.76744400
C	-4.98904200	-0.39776500	0.92745500
C	-5.64447100	-0.74222400	-0.26593000
C	-5.75734700	-0.14318400	2.06961700
C	-7.03627600	-0.82477500	-0.31065000
C	-7.79200700	-0.56617600	0.83487600
C	-7.14973100	-0.22732500	2.02550800
C	4.90805500	0.73226500	0.59655600
C	5.54991400	1.84648800	0.00481300
C	6.91891500	2.03220500	0.15179200
C	7.67199300	1.12998300	0.91052500
C	7.05284300	0.02902400	1.51214200
C	5.68958000	-0.17923500	1.34766100
H	3.32273500	-7.09455900	-0.72018100
H	3.31371200	-5.74588700	0.45228600
H	1.96129700	-6.91209600	0.42523700
H	-1.18186800	-7.53235400	-2.10359500
H	0.24114500	-6.59805100	-2.66714100
H	0.34825500	-7.60277500	-1.18968100
H	3.78138400	-3.82830300	-1.16740500
H	4.76753900	-1.64361600	-0.67110800
H	-2.88212000	-4.77370700	-0.44113600
H	-4.31266500	-2.89717900	0.23438800
H	1.70528000	4.77333300	1.33636000

H	3.79728100	3.13210500	1.72408000
H	-4.42845000	1.34148200	-1.36120800
H	-2.81360700	3.39209100	-1.97924900
H	-2.59207200	5.15944200	0.04636300
H	1.43863100	4.99665600	-1.50575800
H	-2.79975500	7.48279700	-0.75975200
H	-0.89124600	8.57522500	-1.91405400
H	1.22638400	7.33015900	-2.27586200
H	-5.07132100	-0.96266500	-1.16260700
H	-5.26755100	0.12004100	3.00379600
H	-7.52960000	-1.09543200	-1.23882200
H	-8.87448900	-0.63289500	0.79901400
H	-7.72935100	-0.02997600	2.92146100
H	4.97721400	2.53189400	-0.61031700
H	7.40407600	2.87465900	-0.32980000
H	8.73938100	1.28408000	1.03216800
H	7.63505000	-0.66049300	2.11432000
H	5.20811800	-1.01801900	1.83876000
H	1.02759100	-0.37366800	1.03626500
H	-0.82481900	-0.53060000	0.94806800
H	-3.23209600	-0.08924100	2.07052400
H	0.92205500	1.12428600	-0.60813900
H	-1.29178600	1.42941400	1.42335700

Table S12. DFT calculated Cartesian coordinates for **1**-H_2^{2+}-A4.

C	4.81250300	-0.16167100	-0.94581400
C	4.64908700	-1.55915300	-1.04014200
C	3.38213200	-2.17434500	-0.68254300
C	3.72810600	0.66844600	-0.56421500
C	2.49735900	0.08133800	-0.12618700
C	2.32980600	-1.36012400	-0.20713500
C	1.47879000	0.90761500	0.31674700
C	1.08609300	-1.94698400	0.04018200
O	6.00255300	0.42204700	-1.28190300
O	5.56119500	-2.42684500	-1.45525800
C	6.88190900	0.72406300	-0.17539800
C	6.77959700	-2.09068800	-2.16577900
C	3.81136100	2.09560200	-0.61628200
C	2.75531600	2.89209300	-0.25671600
C	1.52857300	2.31759500	0.22755700
C	3.14564100	-3.56030600	-0.84626100
C	0.83092400	-3.29396800	-0.15901000
C	1.89606800	-4.10917800	-0.59574400
C	0.37495500	3.10426600	0.55202500
C	-0.59067900	-3.83079100	0.04612500
C	-0.95786600	2.55226100	0.53835200
N	-1.35966900	1.41059900	-0.14287000
C	-2.72380400	1.22792400	-0.01434200
C	-3.19654000	2.25095700	0.83399000
C	-2.11521200	3.05209300	1.18372600
C	-1.58680500	-2.90569800	-0.62370700
N	-1.96160100	-1.70643200	-0.09988200
C	-2.91804000	-1.09168200	-0.91974300
C	-2.26905800	-3.06619900	-1.84755300
C	-3.11000900	-1.97505300	-2.01795300
C	-3.46575600	0.19039800	-0.69901400
C	-4.80055500	0.49513300	-1.19499100
C	-5.79558300	-0.51487200	-1.23938400
C	-5.13562000	1.79785600	-1.64286800
C	-7.06755100	-0.23027100	-1.71676600
C	-7.37533300	1.05893400	-2.16491800
C	-6.40677700	2.06959900	-2.12786600

C	-0.99456100	-4.10046200	1.50530800
C	-0.41327400	-3.43678700	2.59227200
C	-2.01870500	-5.02967500	1.74359600
C	-0.85073400	-3.69874000	3.89417600
C	-1.86999400	-4.62220500	4.12180900
C	-2.45221900	-5.29024200	3.04171700
C	0.51197700	4.51944700	0.89894700
C	-0.39366300	5.49160800	0.41060500
C	-0.24242800	6.83037400	0.74984400
C	0.79510300	7.22574000	1.60068600
C	1.69347200	6.27739000	2.10178200
C	1.56582100	4.94099700	1.74605700
H	7.75237900	1.21435100	-0.61070800
H	6.39671100	1.39631700	0.53935200
H	7.18948100	-0.19182900	0.34034600
H	7.11585400	-3.04045200	-2.57911600
H	6.57906300	-1.37237600	-2.95929300
H	7.52983900	-1.69936800	-1.47846200
H	4.71664200	2.54158000	-1.01130700
H	2.82539900	3.96508100	-0.38776900
H	3.95199700	-4.19174000	-1.19858900
H	1.73910600	-5.17186200	-0.75382700
H	-4.21476800	2.34299700	1.18289300
H	-2.12547100	3.88799600	1.86677900
H	-2.13549100	-3.89599900	-2.52706200
H	-3.73777000	-1.76334900	-2.87158400
H	-5.57442200	-1.50075800	-0.84619600
H	-4.37969800	2.57496200	-1.64975500
H	-7.82726000	-1.00459900	-1.72491400
H	-8.37082600	1.27834000	-2.53757900
H	-6.64655000	3.06418400	-2.48860700
H	0.40988800	-2.74630600	2.43919200
H	-2.47154500	-5.56060100	0.90992800
H	-0.38047700	-3.19064300	4.73032500
H	-2.20146300	-4.83042000	5.13389600
H	-3.23652600	-6.02107300	3.21107500
H	-1.18052900	5.19605800	-0.27466500
H	-0.92635300	7.56988300	0.34684100
H	0.90405900	8.27091000	1.87199400
H	2.48753400	6.58296000	2.77491800
H	2.24694400	4.20474000	2.15900100
H	0.61679600	0.46594200	0.79298800
H	0.27420100	-1.30677600	0.33875700
H	-0.66171600	-4.77999700	-0.49397500
H	-1.82541500	-1.47327800	0.87659000
H	-0.80368500	0.95852900	-0.85596300

Table S13. DFT calculated Cartesian coordinates for **1**-H_2^{2+}-A5.

C	-3.47312900	-3.44982000	0.37300400
C	-2.38236200	-4.30088900	0.11846400
C	-1.09500200	-3.73335100	-0.25344200
C	-3.30684400	-2.04420900	0.29749200
C	-2.06179600	-1.49861400	-0.16057300
C	-0.96290600	-2.36596000	-0.39318300
C	-1.94081200	-0.11391000	-0.32838500
C	0.37736800	-1.75444500	-0.67106300
O	-4.68369000	-3.95580400	0.76448200
O	-2.36905000	-5.62744700	0.20553100
C	-5.67280000	-4.07669700	-0.28047500
C	-3.40141200	-6.43007300	0.82974700
C	-4.32343600	-1.12381900	0.70622500
C	-4.14045200	0.23223300	0.62276000
C	-2.93267700	0.79120800	0.06400900

C	0.07352400	-4.56306100	-0.44049200
C	1.58351200	-2.63856600	-0.52556500
C	1.33997000	-4.04675800	-0.56867000
C	-2.72571600	2.21484300	-0.08572800
C	2.85485600	-2.08664500	-0.31054500
C	-1.42793100	2.79751400	-0.23811900
N	-0.20217300	2.22776700	0.11639400
C	0.83476900	3.07655400	-0.21128800
C	0.26048800	4.20159800	-0.84554500
C	-1.11533700	4.03246800	-0.86218400
C	3.09310100	-0.69286100	-0.07267400
N	2.24410900	0.37906500	-0.30785400
C	2.82626900	1.57650500	0.13148000
C	4.24212900	-0.14798000	0.59061700
C	4.08242000	1.20793100	0.71560400
C	2.24231000	2.84511400	0.04805500
C	3.09729900	4.03367800	0.20468000
C	4.36733600	4.09323900	-0.41183300
C	2.66443200	5.13657500	0.97422400
C	5.17541200	5.21446800	-0.25640000
C	4.73935400	6.29048200	0.52160800
C	3.48412600	6.24721900	1.13727000
C	4.06062900	-2.96618000	-0.18792100
C	4.19520800	-3.86945400	0.87929800
C	5.08792000	-2.87602300	-1.14150500
C	5.33229600	-4.67050600	0.98407000
C	6.34346300	-4.58204400	0.02497100
C	6.21929800	-3.68480700	-1.03746900
C	-3.87062200	3.12514300	-0.12422900
C	-3.83551100	4.36939500	0.55088100
C	-4.92959900	5.22489500	0.51096700
C	-6.06787400	4.87331400	-0.22170800
C	-6.11573600	3.65319300	-0.90560700
C	-5.03814400	2.77935800	-0.84800700
H	-6.57644500	-4.44635500	0.20383300
H	-5.87384400	-3.10714200	-0.74746500
H	-5.34648200	-4.78606300	-1.04871900
H	-2.94717000	-7.41444400	0.93327800
H	-3.67085900	-6.02416000	1.80375500
H	-4.28053900	-6.49422600	0.18792000
H	-5.23320900	-1.52213800	1.14022500
H	-4.90202900	0.89711900	1.01182500
H	-0.06077800	-5.63831100	-0.42620600
H	2.18172100	-4.72563800	-0.63080900
H	0.82121200	5.01566600	-1.27955300
H	-1.83917400	4.68121100	-1.33181200
H	5.05415500	-0.74575300	0.97548800
H	4.73581700	1.89234100	1.23592500
H	4.69335100	3.27792600	-1.04898100
H	1.70261800	5.10000700	1.47492200
H	6.13961300	5.25641700	-0.75211100
H	5.37273700	7.16322500	0.64341900
H	3.15017500	7.07836100	1.74953000
H	3.41795800	-3.93207700	1.63534100
H	4.99273300	-2.18444000	-1.97377000
H	5.43013900	-5.35960000	1.81680500
H	7.22577400	-5.20851200	0.10677700
H	7.00158900	-3.61520700	-1.78640400
H	-2.96785800	4.63133500	1.14649900
H	-4.90174900	6.16252400	1.05599400
H	-6.91719300	5.54796400	-0.25901100
H	-6.99264600	3.39063900	-1.48792600
H	-5.06834500	1.84819600	-1.40331600
H	-1.06757400	0.26953300	-0.83237500
H	0.37669300	-1.33086200	-1.69173500
H	0.48802000	-0.91020200	0.01124200

H	-0.11288000	1.46901700	0.77815700
H	1.55849000	0.38029300	-1.04752500

Table S14. DFT calculated Cartesian coordinates for **2**-H^+.

C	0.90158000	-5.23054400	-0.70471900
C	-0.64166500	-5.26522700	-0.72425300
C	-1.36123400	-4.00166000	-0.40747700
C	1.55569600	-3.94029200	-0.35821800
C	0.80816000	-2.83591600	0.10424300
C	-0.67529600	-2.86335400	0.06938700
C	1.49996200	-1.66582000	0.43586600
C	-1.42314300	-1.71602300	0.35052900
O	1.53255100	-6.22918400	-0.99043400
O	-1.22078800	-6.29211600	-1.01904900
C	2.94462000	-3.82757800	-0.51792200
C	3.59336200	-2.62463400	-0.29452400
C	2.87248600	-1.49782600	0.16964600
C	-2.74683500	-3.94853500	-0.61943500
C	-2.79778300	-1.61996200	0.06468800
C	-3.45638500	-2.77632800	-0.41614800
C	3.53995300	-0.18801300	0.25357600
C	-3.52728900	-0.34930700	0.20756000
C	2.88266300	1.02431500	0.09390100
N	1.52057700	1.22627800	-0.18219600
C	1.21034000	2.56295300	-0.26087900
C	2.45748300	3.26552000	-0.06888300
C	3.43974900	2.35380900	0.17724100
C	-2.91660600	0.89390700	0.11110500
N	-1.57973600	1.15432300	-0.26415800
C	-1.30917600	2.50899200	-0.20050700
C	-3.47124800	2.17966600	0.44261100
C	-2.52452900	3.14186000	0.23835500
C	-0.06504300	3.16138000	-0.34645600
C	-0.12141700	4.66087400	-0.42774800
C	0.19661900	5.46294100	0.67950800
C	-0.52316900	5.27799500	-1.62147100
C	0.12327700	6.85335300	0.58926200
C	-0.27050300	7.45834100	-0.60597200
C	-0.59447500	6.66875200	-1.71016200
C	-4.98890200	-0.39923600	0.44143700
C	-5.88102300	0.36832300	-0.33233000
C	-5.51406200	-1.23171200	1.45040300
C	-7.25291900	0.31466600	-0.09448000
C	-7.75680000	-0.49901100	0.92164800
C	-6.88351800	-1.27059700	1.69348800
C	5.01344600	-0.17273300	0.43917700
C	5.86354000	0.49969400	-0.45816300
C	7.24371200	0.49864300	-0.26209700
C	7.79585200	-0.16742500	0.83313300
C	6.96309800	-0.84638600	1.72659900
C	5.58555500	-0.86046800	1.52673300
H	3.48723700	-4.69841400	-0.87026900
H	4.65170000	-2.53557500	-0.50605300
H	-3.23796100	-4.84317700	-0.98734000
H	-4.51299100	-2.73621700	-0.65145400
H	2.55141000	4.33992700	-0.07174100
H	4.46887100	2.56367300	0.42387700
H	-4.45805100	2.32211800	0.85607100
H	-2.61196400	4.19741300	0.44471100
H	0.49191000	4.99507800	1.61439400
H	-0.77228500	4.66617500	-2.48362700
H	0.36840200	7.46256400	1.45371300
H	-0.32679200	8.54009900	-0.67508900

H	-0.90133000	7.13375100	-2.64180300
H	-5.49656800	0.97867200	-1.14320700
H	-4.84051100	-1.82812000	2.05755900
H	-7.92863700	0.90007100	-0.70988700
H	-8.82550200	-0.53902800	1.10679800
H	-7.27102200	-1.90268000	2.48608800
H	5.44137500	0.99388200	-1.32749600
H	7.88757100	1.00962700	-0.97094600
H	8.87044900	-0.16594100	0.98554700
H	7.38784400	-1.36617800	2.57947600
H	4.94297700	-1.38810500	2.22477800
H	0.97077900	-0.86442200	0.93175800
H	-0.94355500	-0.86349300	0.80803000
H	-1.09553400	0.52156900	-0.88347300
H	0.89338600	0.46856500	-0.37959000

Table S15. DFT calculated Cartesian coordinates for **2**-H_3^{3+}.

C	0.78931500	-5.09475500	-0.70711500
C	-0.58273000	-5.12156200	-0.70138600
C	-1.34781900	-3.95372500	-0.38267000
C	1.50363900	-3.89270900	-0.35961500
C	0.77957300	-2.77586700	0.13277400
C	-0.67585100	-2.79978100	0.11381200
C	1.49999400	-1.61205900	0.46819900
C	-1.43824600	-1.65620300	0.40528000
O	1.51563400	-6.17048600	-1.07815000
O	-1.17251000	-6.28807000	-1.14881700
C	2.90168900	-3.79079000	-0.53782600
C	3.55682700	-2.59804900	-0.31340800
C	2.85706200	-1.46147500	0.17973400
C	-2.74552900	-3.88721200	-0.60521700
C	-2.80036200	-1.55941400	0.11114200
C	-3.44926900	-2.72161600	-0.39199300
C	3.54571800	-0.15521400	0.26593400
C	-3.53176500	-0.28622000	0.23951800
C	2.90159900	1.05656900	0.08945100
N	1.53762700	1.25771600	-0.20079800
C	1.22446400	2.59209600	-0.27846300
C	2.47115000	3.29781600	-0.07269300
C	3.45266300	2.38925200	0.18115000
C	-2.92258400	0.95299200	0.11727500
N	-1.57955200	1.19991600	-0.25528000
C	-1.29810100	2.54992500	-0.21681700
C	-3.46844000	2.25013800	0.41852100
C	-2.51378500	3.20092400	0.20046500
C	-0.04851200	3.19251100	-0.37527800
C	-0.09509400	4.69273400	-0.47114700
C	0.16901900	5.50220600	0.64469500
C	-0.43001600	5.30407300	-1.68791100
C	0.10764500	6.89249700	0.54167800
C	-0.22168800	7.49091000	-0.67610300
C	-0.49139900	6.69459800	-1.78994900
C	-4.99187300	-0.33614100	0.48224100
C	-5.89191600	0.42402200	-0.28910500
C	-5.50829700	-1.16547800	1.49785900
C	-7.26202700	0.36934500	-0.04019000
C	-7.75685300	-0.43952500	0.98400600
C	-6.87581100	-1.20584500	1.75215100
C	5.01411100	-0.15936200	0.47998100
C	5.88999000	0.52395100	-0.38380600
C	7.26570200	0.50598900	-0.15886700
C	7.78909700	-0.19030100	0.93149300
C	6.93128900	-0.88277800	1.79024500
C	5.55828200	-0.87891600	1.56140600

H	3.44431300	-4.65252100	-0.90866700
H	4.61361100	-2.51753400	-0.53752100
H	-3.25549300	-4.74885000	-1.02303500
H	-4.50262900	-2.67901800	-0.64268500
H	2.56108000	4.37259300	-0.07047500
H	4.47777300	2.60261800	0.44168700
H	-4.45739100	2.40996100	0.82052900
H	-2.59677300	4.26187500	0.37836600
H	0.41627500	5.03901700	1.59579100
H	-0.63719100	4.68667800	-2.55721900
H	0.31235400	7.50680100	1.41315200
H	-0.26943800	8.57246600	-0.75547600
H	-0.74794200	7.15424000	-2.73942000
H	-5.51448000	1.03056600	-1.10598300
H	-4.82757000	-1.75763900	2.10114100
H	-7.94344400	0.95076500	-0.65325000
H	-8.82402200	-0.47992900	1.17814400
H	-7.25597700	-1.83454700	2.55116300
H	5.49068000	1.04024700	-1.25095500
H	7.92873100	1.02728600	-0.84222100
H	8.86027300	-0.20238500	1.10636400
H	7.33331300	-1.42718000	2.63891100
H	4.89602500	-1.41757500	2.23202000
H	0.98446300	-0.80800500	0.97528000
H	-0.95648800	-0.80761500	0.86951000
H	-1.08518200	0.54033100	-0.83646000
H	0.92164900	0.49535200	-0.41674700
H	-1.87329300	-6.56087600	-0.53986700
H	0.89010400	-6.87740000	-1.31050800

Table S16. DFT calculated Cartesian coordinates for **2**-BF_2-H^{2+}.

F	7.60734100	-0.35293000	1.10067100
F	7.60735200	0.35287100	-1.10064600
O	5.89124200	-1.14092300	-0.36460100
O	5.89124900	1.14087600	0.36461300
N	-1.80218700	1.53764800	0.21139900
C	3.49306500	-1.43387300	-0.37925500
C	-1.48109700	-2.85812000	0.11008600
N	-1.80220100	-1.53763500	-0.21141000
C	-5.24059500	0.00002300	0.00000500
C	-3.60613600	-2.41503900	0.81474000
H	-4.56461600	-2.47644500	1.30810500
C	1.02149700	2.82742000	0.25369400
C	1.11523300	-1.44388800	0.02796900
C	-5.96208200	1.00864100	0.67951100
H	-5.42707700	1.76736800	1.24100100
C	-2.63134800	-3.38660600	0.77285600
H	-2.67071700	-4.36195500	1.23389500
C	4.70342800	0.70318800	0.22169500
C	-3.76986400	0.00001400	-0.00000200
C	3.42653300	2.81452100	0.69310400
H	4.34034100	3.33726200	0.95586500
C	-1.24167300	5.72284100	0.72908000
H	-1.93853900	5.19488600	1.37187200
C	-0.23789000	3.52550200	0.07346000
C	-0.35461500	-7.79950300	0.12854500
H	-0.38508600	-8.88308300	0.17953100
C	-1.48107400	2.85813100	-0.11009600
C	3.42651400	-2.81455000	-0.69310200
H	4.34031900	-3.33729900	-0.95585900
C	3.49307300	1.43384300	0.37925500
C	2.21997700	-3.48655100	-0.66739300
H	2.18863100	-4.53184700	-0.94681900

C	-2.63132400	3.38662800	-0.77286000
H	-2.67068800	4.36197800	-1.23389500
C	-0.26799900	-4.99448600	-0.00730100
C	-3.10036400	-1.24432700	0.17934400
C	4.70342400	-0.70322800	-0.22169100
C	-1.27304300	-7.11191300	-0.66976300
H	-2.00758200	-7.66009400	-1.25029800
C	-3.10035200	1.24435100	-0.17935100
C	-8.05017700	0.00004000	0.00001800
H	-9.13537500	0.00004600	0.00002400
C	2.28828500	0.72662700	0.10667500
C	1.11524400	1.44387800	-0.02798200
C	-1.24170300	-5.72283000	-0.72912000
H	-1.93854200	-5.19486700	-1.37193400
C	-0.23791700	-3.52550200	-0.07346900
C	-7.35199000	-1.00139200	-0.68247700
H	-7.89395200	-1.76826500	-1.22586500
C	0.66020200	-5.70667300	0.78775200
H	1.38990700	-5.16561000	1.38104600
C	-5.96210100	-1.00858600	-0.67949500
H	-5.42711000	-1.76731900	-1.24099100
C	2.28828000	-0.72664700	-0.10668400
C	-3.60611800	2.41506700	-0.81474400
H	-4.56460100	2.47648100	-1.30810400
B	6.93999100	-0.00002700	0.00001000
C	0.60519600	-7.09297700	0.86228300
H	1.30530300	-7.62620700	1.49682500
C	2.22000100	3.48653100	0.66739100
H	2.18866200	4.53182800	0.94681700
C	0.66028200	5.70666200	-0.78772900
H	1.39000300	5.16558900	-1.38099600
C	-7.35197100	1.00146300	0.68250700
H	-7.89391900	1.76834300	1.22590000
C	0.60529500	7.09296600	-0.86226200
H	1.30543100	7.62618800	-1.49677900
C	-1.27299500	7.11192400	0.66972200
H	-2.00754600	7.66011400	1.25023200
C	-0.26795400	4.99448500	0.00729200
C	1.02147600	-2.82743100	-0.25370000
C	-0.35453200	7.79950400	-0.12855600
H	-0.38498900	8.88308400	-0.17954300
H	0.25789900	0.93929600	-0.44022300
H	0.25789100	-0.93929600	0.44020300
H	-1.32802400	-1.01978600	-0.93810600
H	-1.32800400	1.01978800	0.93808400

Table S17. DFT calculated Cartesian coordinates for **3**-H^+.

C	-1.43349800	-4.56401700	-0.54061000
C	1.52158100	-4.38429100	-0.91215400
C	0.79527000	-3.38293600	-0.24620700
C	-0.69458700	-3.42150000	-0.18822300
C	1.50499100	-2.25956800	0.20759200
C	-1.40955400	-2.24697000	0.07651200
C	2.89065300	-4.24462500	-1.13802900
C	3.55671000	-3.08384600	-0.76502700
C	2.86127600	-2.04833300	-0.10322100
C	-2.81921600	-4.49603000	-0.68663800
C	-2.79944200	-2.13543100	-0.11179400
C	-3.49959600	-3.29695000	-0.50722400
C	3.54415700	-0.76160800	0.12918100
C	-3.50736800	-0.85353900	0.04829700
C	2.90052200	0.46424100	0.07781500
N	1.54266400	0.69537100	-0.20341400

C	1.24337100	2.03584800	-0.19258000
C	2.49091000	2.71281900	0.07613600
C	3.46262300	1.77887700	0.27477900
C	-2.89534600	0.38968800	-0.01019200
N	-1.54963400	0.66517400	-0.34683200
C	-1.27569800	2.01344800	-0.20256500
C	-3.45383400	1.66226800	0.36672300
C	-2.50012600	2.62964900	0.23461100
C	-0.02249400	2.65665400	-0.27355400
C	-0.05709900	4.15940300	-0.25662100
C	0.21648900	4.88102700	0.91583500
C	-0.39275900	4.86203500	-1.42297900
C	0.16440800	6.27540300	0.91706700
C	-0.16466700	6.96542500	-0.25131100
C	-0.44424200	6.25658600	-1.42046800
C	-4.97269600	-0.88522100	0.28676300
C	-5.85564200	-0.13406800	-0.51109700
C	-5.50614700	-1.67451900	1.32432000
C	-7.22871500	-0.16399200	-0.27217500
C	-7.74179200	-0.93685800	0.77042000
C	-6.87643800	-1.69012500	1.56849800
C	5.01377600	-0.78996900	0.33627900
C	5.89113300	-0.02594300	-0.45545300
C	7.26719400	-0.07382300	-0.23729500
C	7.78931800	-0.88019100	0.77517200
C	6.93003100	-1.65295600	1.56068300
C	5.55664000	-1.61959000	1.33647800
H	3.43109300	-5.03196100	-1.65365100
H	4.60297300	-2.95529200	-1.01450800
H	-3.37026700	-5.38659800	-0.97132400
H	-4.56662700	-3.25075500	-0.68670200
H	2.59109400	3.78403200	0.15111100
H	4.48818300	1.96331300	0.55439200
H	-4.44994700	1.78906200	0.76250600
H	-2.59016200	3.67386300	0.49130900
H	0.46218600	4.34658900	1.82915400
H	-0.60750800	4.31294800	-2.33518600
H	0.37548400	6.82133000	1.83143900
H	-0.20506400	8.05016100	-0.24936800
H	-0.70093300	6.78766200	-2.33182700
H	-5.46245200	0.44999400	-1.33715700
H	-4.83821500	-2.25690000	1.95104600
H	-7.89734700	0.41031600	-0.90568600
H	-8.81077600	-0.95779900	0.95746300
H	-7.27034600	-2.28924800	2.38341500
H	5.49316700	0.57810100	-1.26458200
H	7.93150800	0.51098800	-0.86577400
H	8.86075100	-0.91473300	0.94536000
H	7.33107700	-2.28318300	2.34818400
H	4.89296800	-2.22142500	1.94940300
H	1.00655500	-1.53738500	0.84208500
H	-0.88077700	-1.38449600	0.44939500
H	-1.06163900	0.07547300	-1.00433600
H	1.01944600	-5.26588600	-1.29282300
H	-0.93668100	-5.51232100	-0.71048000
H	0.91047200	-0.04849500	-0.43759900

Correlations of theoretical and experimental ^{1}H NMR chemical shifts

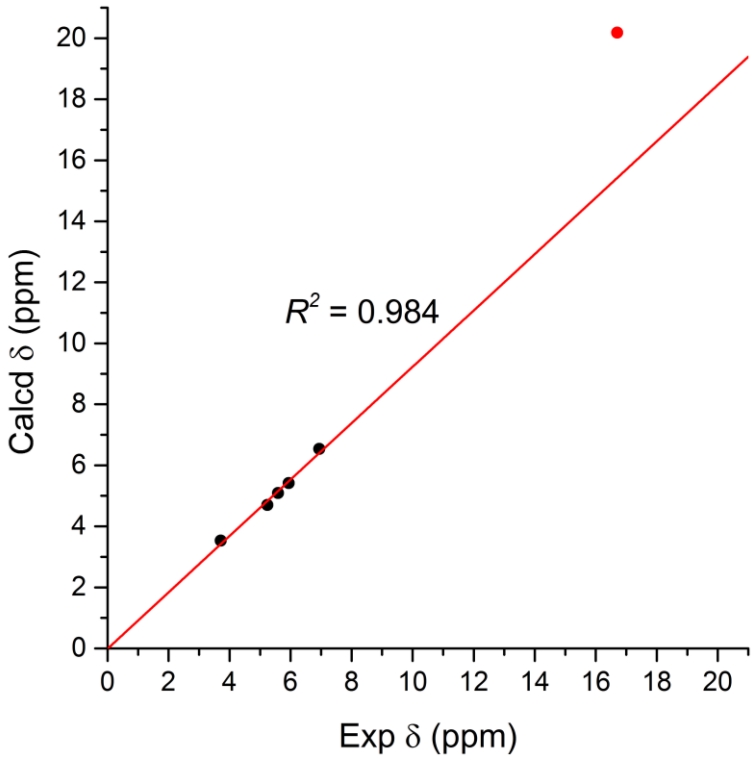


Figure S19. Comparison of theoretical and experimental ^{1}H NMR shifts for **1** (only CH hydrogen of the carbaporphyrin frame considered).

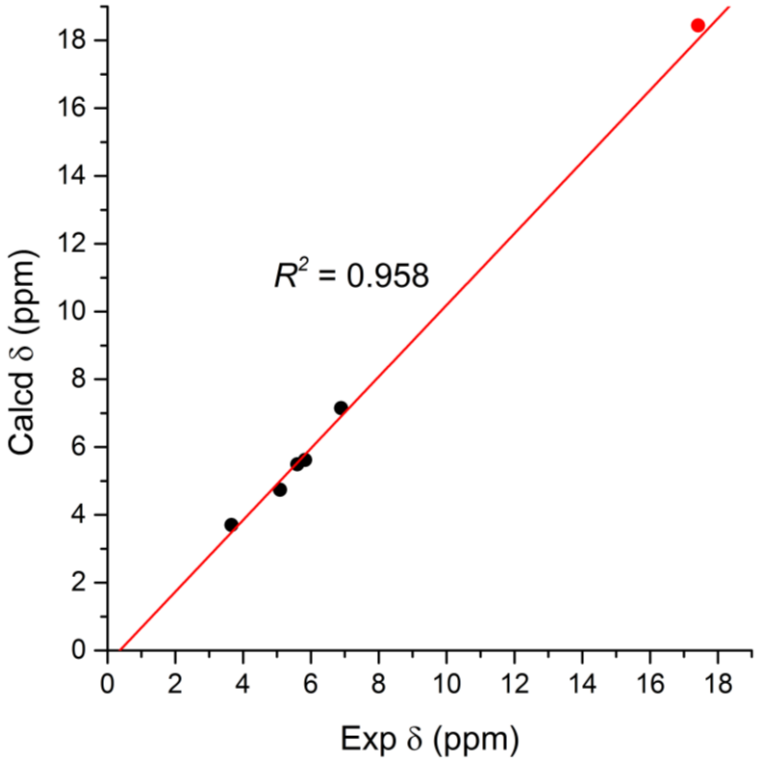


Figure S20. Comparison of theoretical and experimental ^{1}H NMR shifts for **1**-H$^+$ (only CH hydrogen of then carbaporphyrin frame considered).

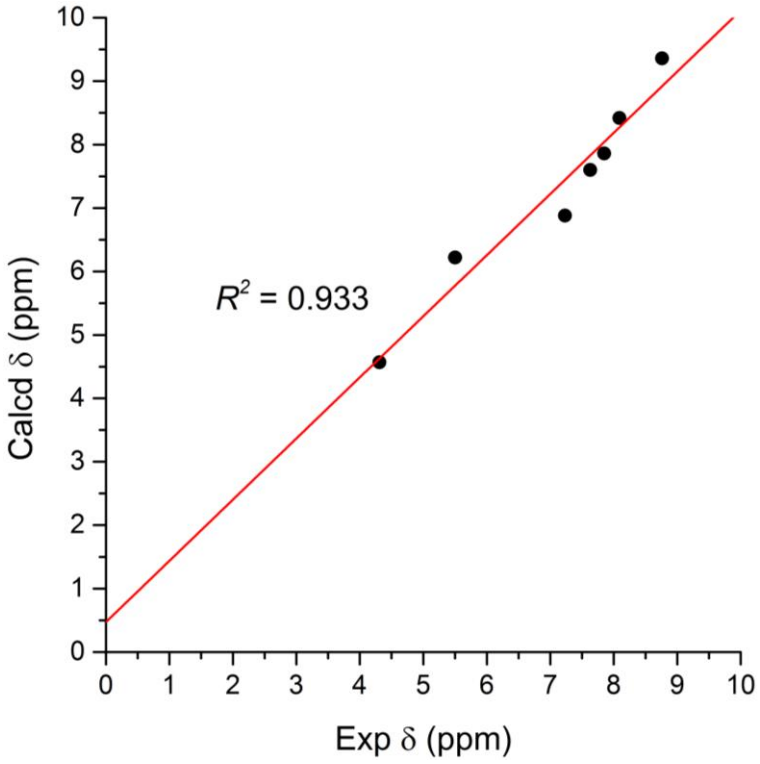


Figure S21. Comparison of theoretical and experimental ^{1}H NMR shifts for **1**-H_2^{2+} (only CH hydrogen of the carbaporphyrin frame considered).

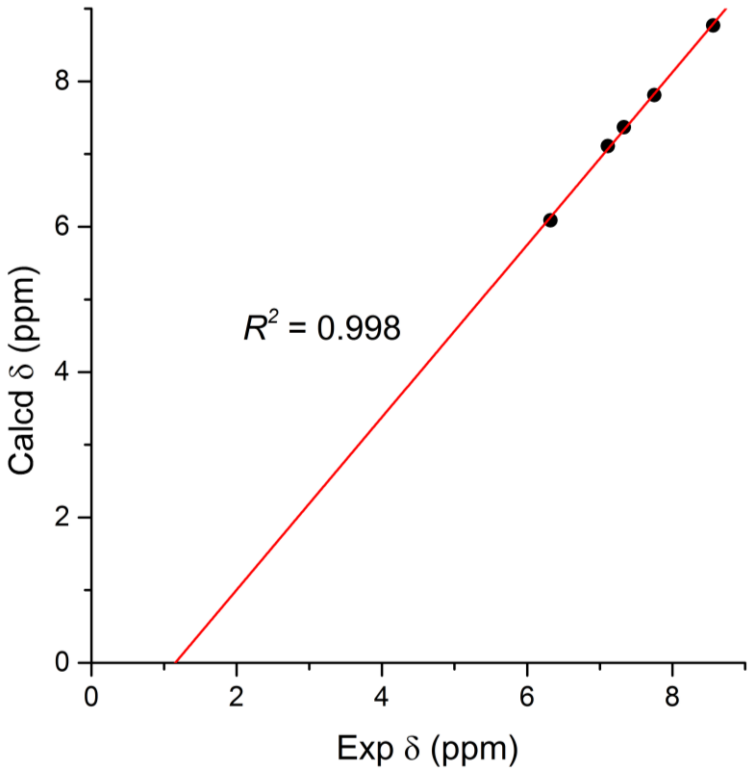


Figure S22. Comparison of theoretical and experimental ^{1}H NMR shifts for **2** (only CH hydrogen of the carbaporphyrin frame considered).

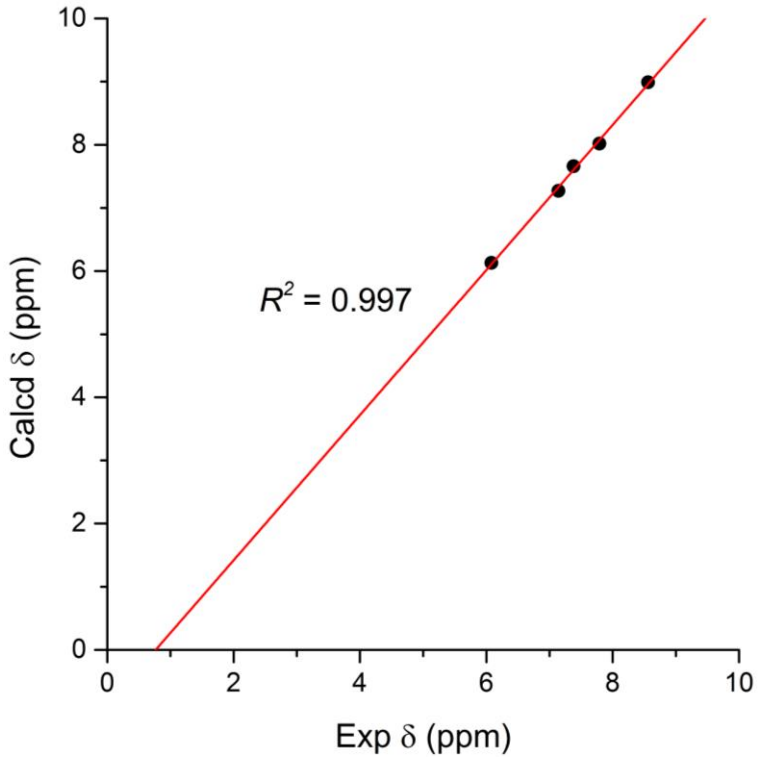
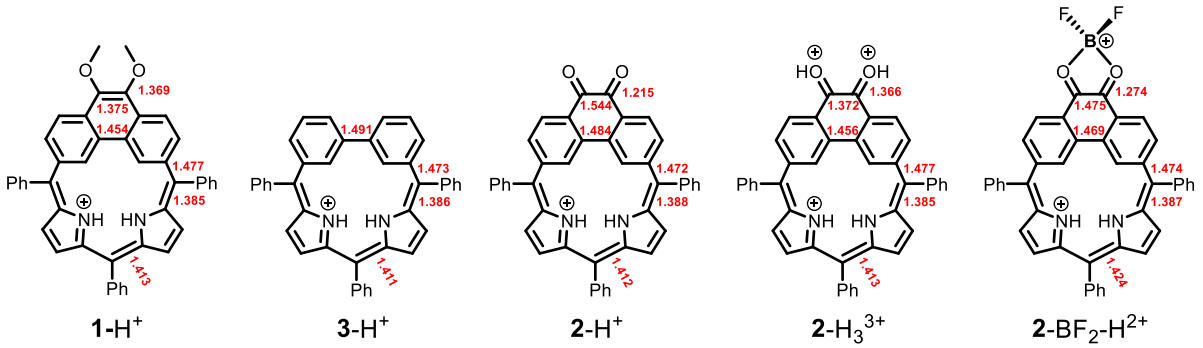


Figure S23. Comparison of theoretical and experimental ^{1}H NMR shifts for **2**-H$^+$ (only CH hydrogen of the carbaporphyrin frame considered).

Schemes – bond lengths



Scheme S1. The representative calculated bond lengths determined for protonated biphenylcorrole and related porphyrinoids - optimized at the B3LYP/6-31G(d,p) level.

Mass spectra

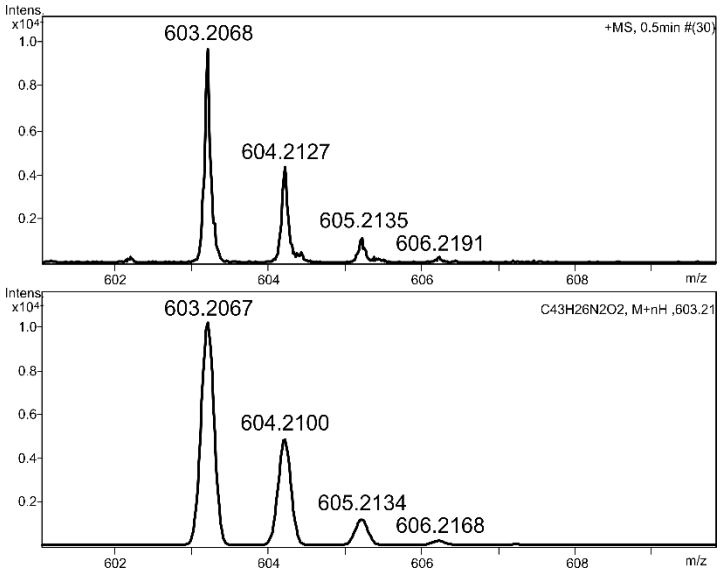


Figure S24. HRMS (ESI) of **2**: *m/z*: 603.2068 $[M+H]^+$, calcd for $C_{43}H_{27}N_2O_2^+$: 603.2067.

UV-Vis spectra

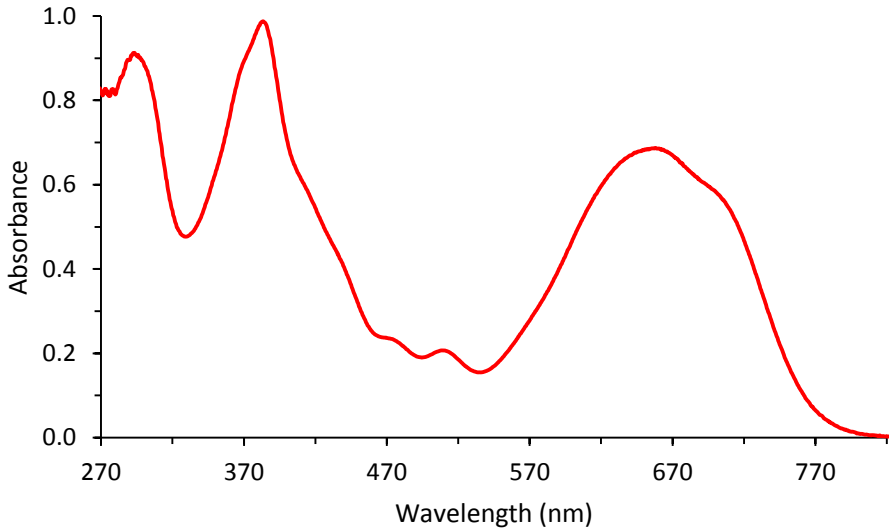


Figure S25. Electronic absorption spectram of **2** in $CHCl_3$ (298 K).

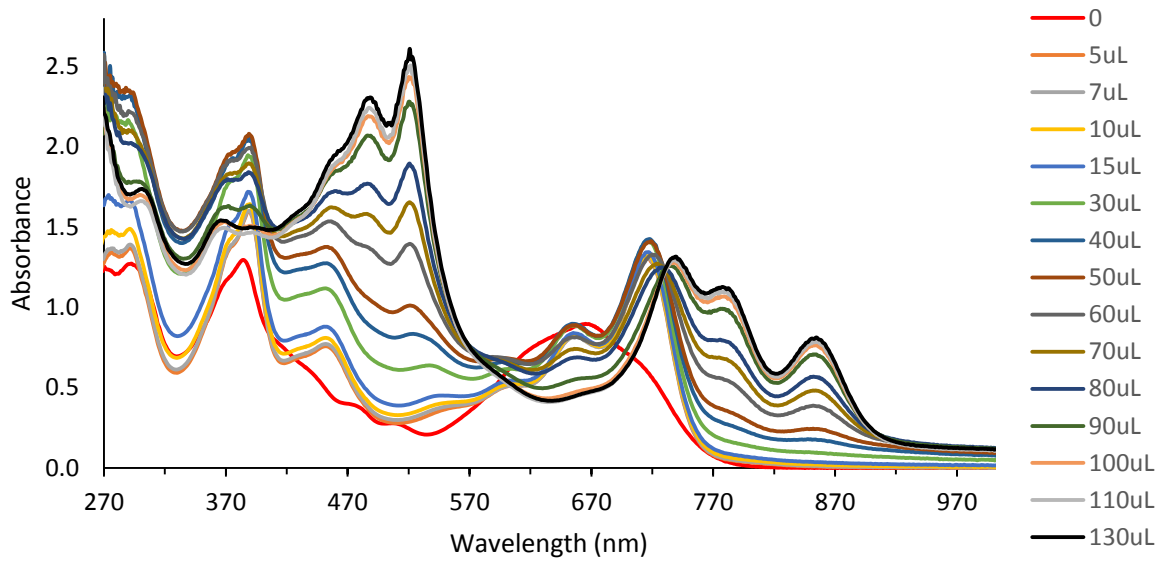


Figure S26. Electronic absorption spectra recorded during titration of **2** with diluted solution of $HBF_4 \cdot Et_2O$ (in chloroform – v/v 1:20, 298 K).

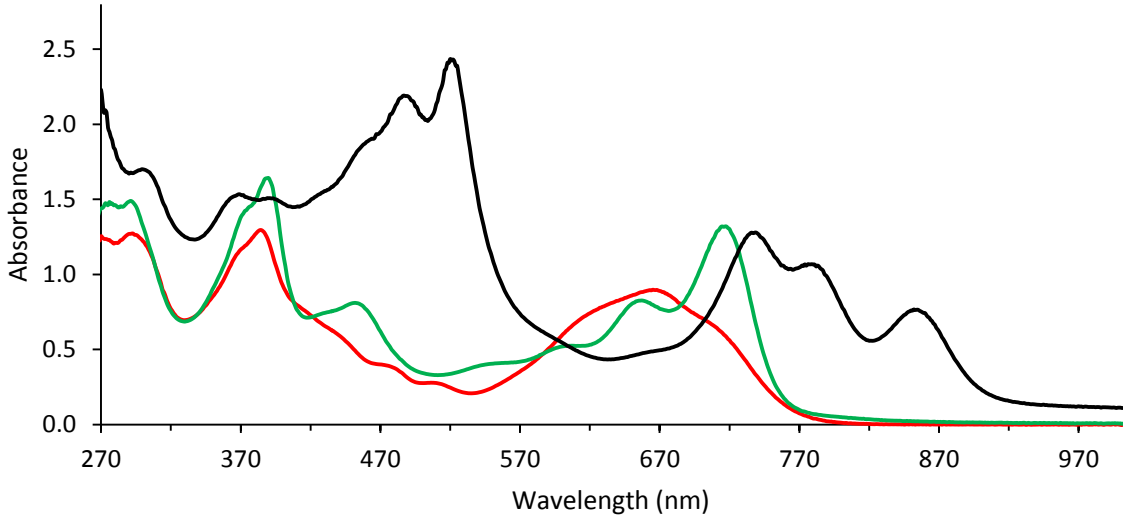


Figure S27. Protonation of **2** by diluted solution of $HBF_4 \cdot Et_2O$ (in chloroform – v/v 1:20, 298 K): red – **2**, green – **2**-H^+, black – **2**-H_3^{3+}.

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