

Supporting Information

Redox- and Protonation-Driven Baird and Clar Aromatic Duality in Asymmetric Multicyclic Octaphyrins

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General Experimental Section

Materials and Methods

All chemicals used for synthesis were of reagent grade unless otherwise specified. Boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$), trifluoroacetic acid (TFA), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were obtained from Sigma-Aldrich and were used as such. Solvents such as petroleum ether (60-80°C), ethyl acetate, and dichloromethane purchased from Merck, Korea, and were used without further purification. Column chromatography was performed on aluminum oxide active basic (70-200 mesh, pH value 8.5-10).

^1H (1D and 2D) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on Bruker 400 and 300 MHz FT-NMR spectrometers in CDCl_3 and CD_2Cl_2 using tetramethylsilane as the internal reference. The $^{13}\text{C}\{^1\text{H}\}$ NMR frequencies are 100.6 and 75.4 MHz for the 400 and 300 MHz instruments, respectively. Structural assignments were made using additional information from ^1H - ^1H COSY and ^1H - ^1H NOESY experiments as needed.

High-resolution mass spectroscopy (HR-MS) spectra were recorded with a ThermoFisher Exploris_240 mass spectrometer using positive mode ESI methods in acetonitrile or methanol. MALDI-TOF/TOF measured with Bruker Autoflex Max Mass Spectrometer using dithranol (1,8,9-trihydroxyanthracene) and trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrixes. UV-visible absorption spectra were recorded on a double-beam UV-Vis/NIR spectrophotometer (V-770, JASCO). Stock solutions of the compounds (10^{-5} M) were prepared using HPLC-grade chloroform. EPR spectra were

recorded on a Bruker EMX Plus with X-band CW EPR model equipped with a cryostat controller.

All electrochemical measurements were conducted using a CH Instruments (Austin, TX) model 760E potentiostat and carried out at room temperature in a three-electrode system with platinum wire as the counter electrode and an Ag/AgCl (1 M KCl) reference electrode. The reported potentials were calibrated to RHE, using the following equation: $E(\text{RHE}) = E(\text{Ag/AgCl}) + (0.222 + 0.059 \text{ pH}) \text{ V}$. The concentrations of the samples were maintained at 0.1 M containing tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte (0.1 M) in dichloromethane at 25 °C under an argon atmosphere at a scan rate of 100 mV/s.

Spectro-electrochemical measurements were performed in UV-Vis/NIR spectrophotometer (V-770, JASCO) by incorporation of CH Instrument Electrochemical Analyzer in 1 M tetrabutylammonium hexafluorophosphate (supporting electrolyte) solution prepared in freshly distilled dichloromethane. The assembly consisted of a thin layer quartz glass cell (optical path length of 1 mm), and a three electrode setup (Pt gauze, Pt wire, and silver nitrate as the reference electrode). A UV-vis spectrum was recorded every 1 min, while adjusting the potential corresponding to the second oxidation waves.

Single crystals of **5** were mounted on a MiTeGen MicroLoops after it was coated with Parabar oil. The data were collected at 298 K using monochromated Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$) and a Hybrid Pixel Array Detector in a Rigaku XtaLab Synergy-i diffractometer and processed using CrysAlisPro 1.171.42.77a (Rigaku Oxford Diffraction, 2022). The crystal structures were solved by the direct method with SHELX-XT,¹ and refined by full matrix least-squares calculations with the SHELX-XL² in the Olex2³ program package. Deposition CCDC 2432301 (for compound **5**) contains the supplementary crystallographic data for this paper.

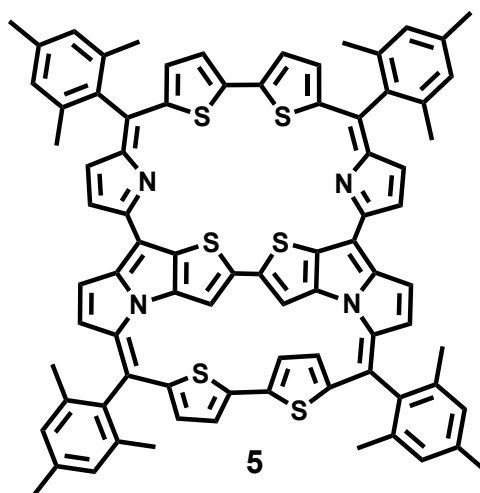
Femtosecond transient absorption (TA) experiments were conducted using a custom-built TA spectrometer, powered by a Ti: Sapphire regenerative amplifier system (800 nm, 350 μ J, 10 kHz, 35 fs, Spitfire Pro, Spectra-Physics). A pump pulse was generated using a commercial optical parametric amplifier (TOPAS, Spectra-Physics). For the probe pulse, a fraction of the fundamental pulse was focused onto an 8 mm sapphire crystal, creating a white-light continuum (WLC). The time delay between the pump and probe beams was adjusted using a linear motor stage (ILS300LM-S, Newport) situated in the probe generation beamline. The dispersed WLC probe spectra were captured by a high-speed spectrometer (Ultrafast Systems), enabling us to acquire TA spectra at a rate of 2 kHz. To mitigate polarization-dependent signals, the pump polarization was set to the magic angle (54.7°) relative to the horizontally polarized probe pulse, using a Glan-laser calcite polarizer (GL10-A, Thorlabs) and an achromatic half-wave plate (AQWP05M-600, Thorlabs). The diameter of the pump pulse (at a $1/e^2$ height) was adjusted to 1 mm at the sample stage by manipulating the position of a plano-convex lens. For accuracy and to account for long-term laser fluctuations, each data set was compiled from five individual scans. The absence of sample degradation throughout the experiment was confirmed by comparing the decay kinetics across each scan, as well as by recording the UV-vis-NIR spectrum of each sample before and after the TA measurements.

Computational Methods

All the calculations were performed using of the Gaussian G16 program package.⁴ The DFT method, hybrid functional B3LYP with basis set 6-311G(d,p)⁵ was used to optimize the geometries of the compounds **5**, **5•2H⁺**, **6**, **6'** and **6•2H⁺** in their ground (S_0 and T_1) states. The minimum energy surfaces of the optimized geometries of compounds were verified by vibrational analyses, and no imaginary frequencies were found. The vertical excitation energies

and oscillator strengths were obtained for the 50 lowest $S_0 \rightarrow S_n$ transitions at the optimized S_0 -state equilibrium geometries using the TD-DFT method that was carried out at the same level of theory.⁶

General procedure for synthesis of octaphyrins (5-6)



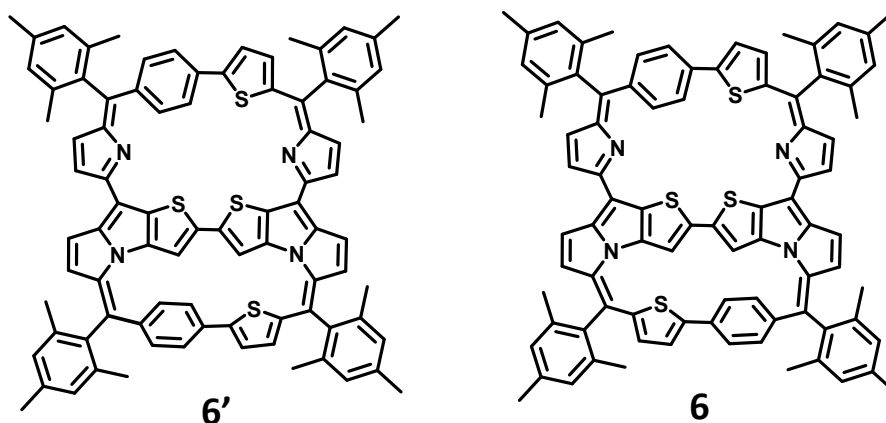
Synthesis of 5: A sample of appropriate bithiophene tripyrrane **7** (300 mg, 0.53 mmol) and 2,2-bithiophene carboxaldehyde **9** (50mg, 0.22 mmol) in dry dichloromethane was stirred for 15 min under N_2 atmosphere. A catalytic amount of *p*-toluenesulfonic acid (15 mg, 0.08 mmol) was added to the above mixture and the reaction mixture was stirred for overnight under N_2 atmosphere. The oxidant, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 350 mg, 1.5 mmol), was added with stirring continued in the open air for an additional 2 h. The volatiles were removed on rotary evaporator under vacuum. The resulted crude product was purified by basic alumina column chromatography using petroleum ether/ CH_2Cl_2 as the eluent. A brown band that eluted with petroleum ether/dichloromethane (60:40) was collected and the volatiles removed under vacuum to afford the desired octaphyrin as a dark brown solid in 11% yield.

1H NMR (300 MHz, CD_2Cl_2 , 253K) δ 7.36 (d, $J = 3.7$ Hz, 2H, β -th), 7.19 (d, $J = 4.4$ Hz, 2H, β -py), 7.10 (d, $J = 3.8$ Hz, 2H, β -th), 6.94 (d, $J = 3.6$ Hz, 8H, *mes*-CH), 6.82 (d, $J = 4.7$, 2H, β -th), 6.77 (d, $J = 5.9$ Hz, 2H, β -py), 6.59 (d, $J = 4.4$ Hz, 2H, β -py), 6.50 (d, $J = 4.7$ Hz, 2H,

β -th), 5.89 (d, $J = 5.8$ Hz, 2H, β -py), 5.42 (s, 2H, β -th), 2.36 (s, 6H), 2.32 (d, $J = 3.1$ Hz, 12H), 2.28 (s, 6H), 2.12 (s, 6H), 2.04 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2 , 253K) δ 162.1, 152.8, 141.9, 140.6, 139.6, 138.4, 138.0, 137.6, 136.8, 136.1, 135.7, 134.8, 128.7, 127.9, 126.6, 126.2, 122.8, 109.3, 100.0, 31.5, 29.6, 22.6, 20.8, 20.7, 20.4, 19.7, 19.6, 13.8. UV-vis (in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$, $\log \epsilon$) = 340 (4.49), 483 (4.74), 553 (4.60). MALDI-TOF mass ($\text{C}_{82}\text{H}_{62}\text{N}_4\text{S}_6$): 1295.566 (M+H) $^+$.

[5] $^{2+}$: The dicationic species was synthesized via the addition of excess NOSbF_6 to a solution of **5** in dichloromethane at -20 °C. Subsequently, the solution was stirred for 5 minutes at the same temperature. A subtle color change from brown to purple indicated the formation of dicationic species **[5] $^{2+}$** . It was washed with pentane and obtained in quantitative yield (80%).

^1H NMR (300 MHz, CDCl_3 , 298K) δ 10.74 (s, 2H, β -CH), 9.84 (dd, $J = 11.4$, 4.8 Hz, 6H, β -CH), 9.09 (dd, $J = 11.8$, 4.8 Hz, 4H, β -CH), 7.48 (d, $J = 9.8$ Hz, 4H, *mes*-CH), 7.35 (d, $J = 10.0$ Hz, 6H, *mes*-CH, β -CH), 2.78 (s, 6H), 2.68 (s, 6H), 2.18 (s, 6H), 2.09 (s, 6H), 1.99 (s, 6H), 1.86 (s, 6H). UV-vis (in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$, $\log \epsilon$) = 546 (4.91), 711 (4.89), 1054 (4.23). HR-MS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $(\text{C}_{82}\text{H}_{62}\text{N}_4\text{S}_6)^{2+}$ 647.6649; Found 647.6648.



Synthesis of 6/6': A sample of the appropriate benzothiophene tripyrrane **8** (300 mg, 0.54 mmol) and 2,2-bithiophene carboxaldehyde **9** (50 mg, 0.22 mmol) in dry dichloromethane was

stirred for 15 min under N₂ atmosphere. A catalytic amount of *p*-toluenesulfonic acid (15 mg, 0.08 mmol) was added to the above mixture and the reaction mixture was stirred for overnight under an N₂ atmosphere. The oxidant, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 360 mg, 1.6 mmol), was added and stirring was continued in open air for additional 2 h. The volatiles were removed on rotary evaporator under vacuum. The resulting crude product was purified by basic alumina column chromatography using petroleum ether/CH₂Cl₂ as the eluent. The first brown band (*syn*) and second brown band (*anti*) that eluted with petroleum ether/dichloromethane (70:30) and (60:40) were collected, respectively, and the volatiles were removed to afford the desired octaphyrin **6/6'** as dark brown solids in 9-10% yields.

6': ¹H NMR (400 MHz, CDCl₃, 298K) δ 7.94 (d, *J* = 8.0 Hz, 4H), 7.72 (d, *J* = 8.0 Hz, 4H), 7.31 (s, 2H), 6.95 (d, *J* = 12.9 Hz, 8H), 6.73 (dd, *J* = 7.1, 4.2 Hz, 4H), 6.55 (t, *J* = 5.3 Hz, 4H), 6.51 (d, *J* = 3.8 Hz, 2H), 5.80 (d, *J* = 5.7 Hz, 2H), 2.36 (d, *J* = 12.6 Hz, 12H), 2.20 (s, 12H), 2.15 (s, 12H).

UV-vis (in CH₂Cl₂, λ_{max}/nm, log ε) = 375 (4.45), 481 (4.75), 540 (4.58). MALDI-TOF mass (C₈₆H₆₆N₄S₄): 1283.594 (M+H)⁺.

6: ¹H NMR (400 MHz, CDCl₃, 298K) δ 8.19 (s, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 3.8 Hz, 1H), 7.21 (d, *J* = 3.9 Hz, 1H), 7.14 (d, *J* = 4.0 Hz, 1H), 6.98 (d, *J* = 6.5 Hz, 12H), 6.94 (d, *J* = 5.9 Hz, 2H), 6.87 (d, *J* = 4.7 Hz, 2H), 6.69 (dd, *J* = 9.5, 4.3 Hz, 2H), 6.14 (d, *J* = 5.6 Hz, 1H), 6.10 (d, *J* = 5.8 Hz, 1H), 5.05 (s, 1H), 4.39 (s, 1H), 2.40 – 2.35 (m, 18H), 2.25 (s, 6H), 2.16 (d, *J* = 3.3 Hz, 12H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 145.1, 141.3, 139.9, 138.5, 138.3, 138.0, 137.6, 137.3, 137.2, 135.5, 130.9, 128.8, 128.2, 127.9, 126.4, 123.2, 122.8, 110.7, 29.7, 21.20, 21.17, 20.9, 20.6, 20.1. UV-vis (in CH₂Cl₂, λ_{max}/nm, log ε) = 350 (4.39), 465 (4.76), 527 (4.50). MALDI-TOF mass (C₈₆H₆₆N₄S₄): 1283.423 (M+H)⁺.

[6]²⁺: The dicationic species was synthesized via the addition of excess of NOSbF_6 to a solution of **6** in dichloromethane at $-20\text{ }^\circ\text{C}$. Subsequently, the solution was stirred for 5 minutes at the same temperature. A subtle color change from brown to purple indicated the formation of dicationic species **[6]²⁺**. It was further washed with pentane and obtained in quantitative yield (80%).

$^1\text{H NMR}$ (300 MHz, CDCl_3 , 338K) δ 13.03 (s, 2H), 12.20 (d, $J = 13.4\text{ Hz}$, 4H), 12.05 (d, $J = 5.0\text{ Hz}$, 2H), 11.45 (d, $J = 4.8\text{ Hz}$, 2H), 11.37 (d, $J = 4.9\text{ Hz}$, 2H), 9.59 (d, $J = 10.7\text{ Hz}$, 4H), 9.46 (d, $J = 12.0\text{ Hz}$, 4H), 8.21 (s, 1H), 7.87 (s, 1H), 4.78 (s, 6H), 4.68 (s, 6H), 4.41 (s, 6H), 4.31 (s, 6H), 4.23 (s, 6H), 4.09 (s, 6H). UV-vis (in CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$, $\log \epsilon$) = 524 (4.71), 680 (4.56), 1097 (4.17). HR-MS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $(\text{C}_{86}\text{H}_{66}\text{N}_4\text{S}_4)^{2+}$ 642.2085; Found 642.2152.

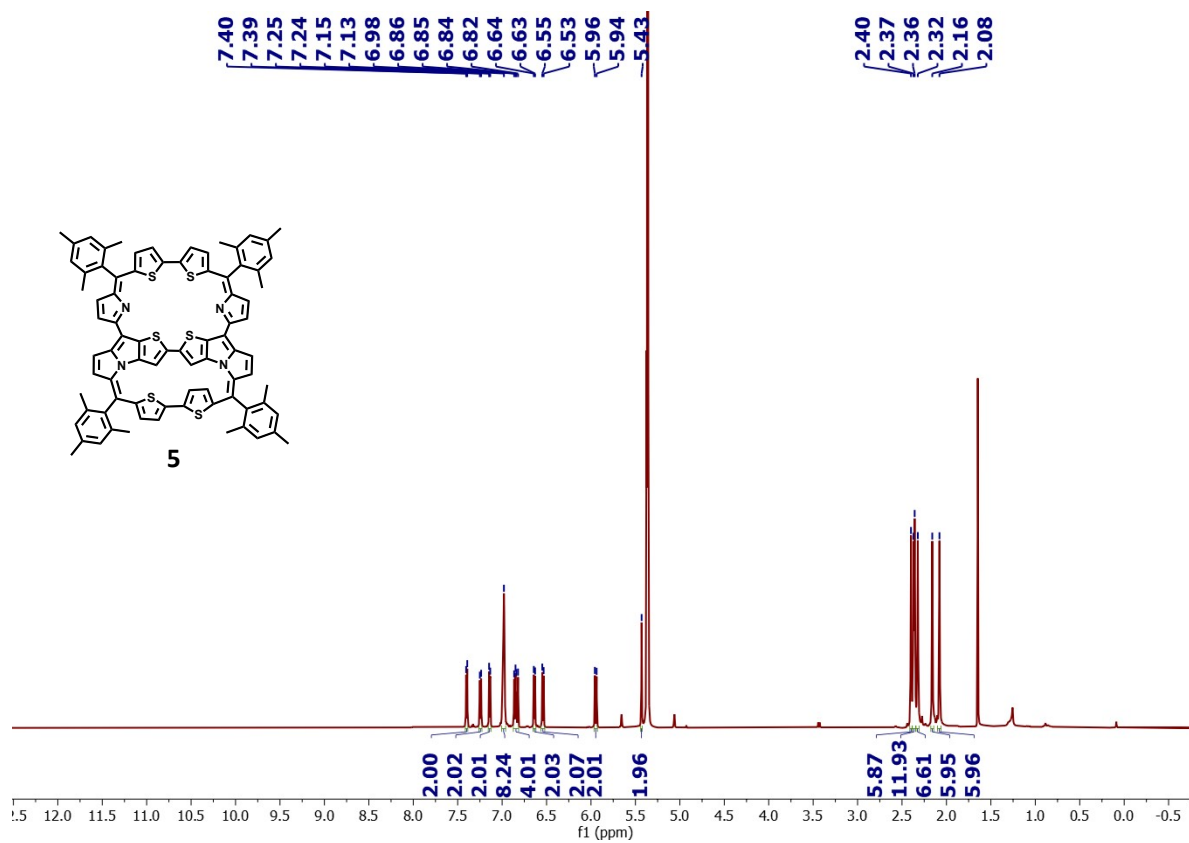


Figure S1. ¹H NMR Spectra of compound **5** in CD₂Cl₂ recorded on a 300 MHz FT-NMR spectrometer at -20 °C.

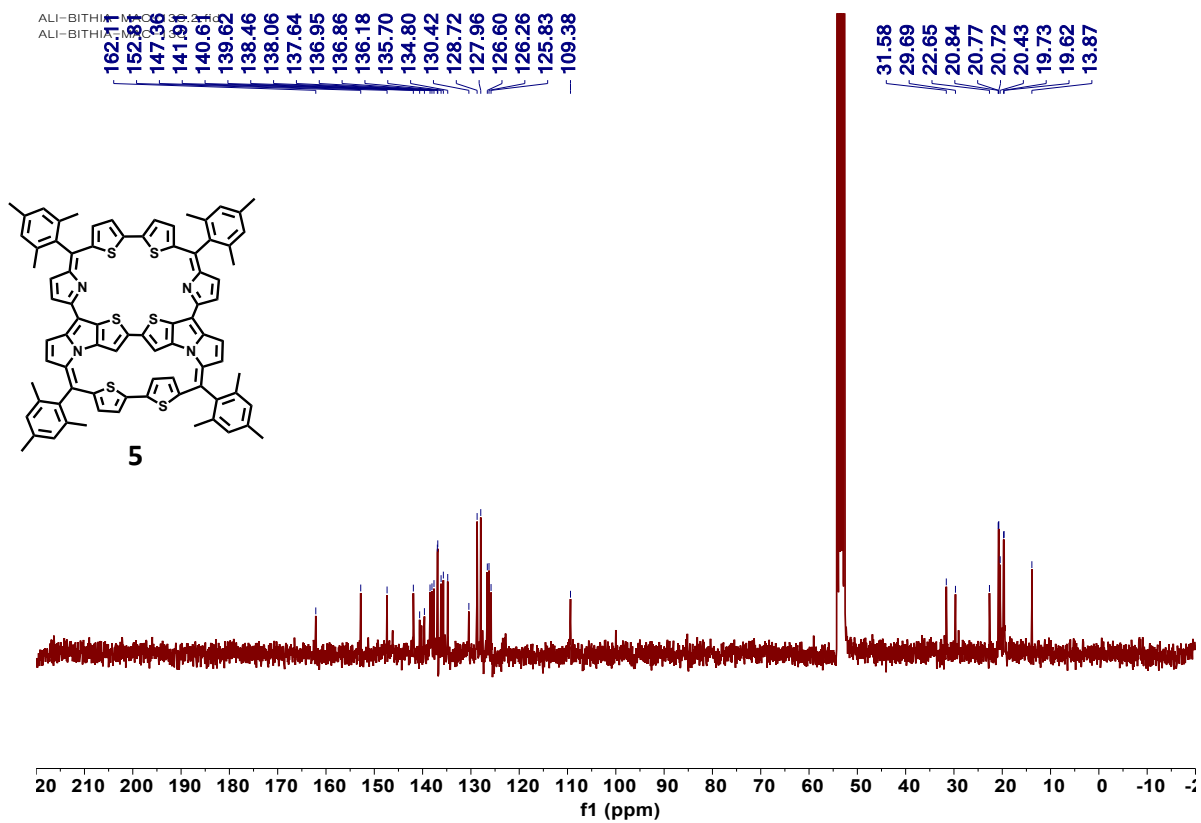
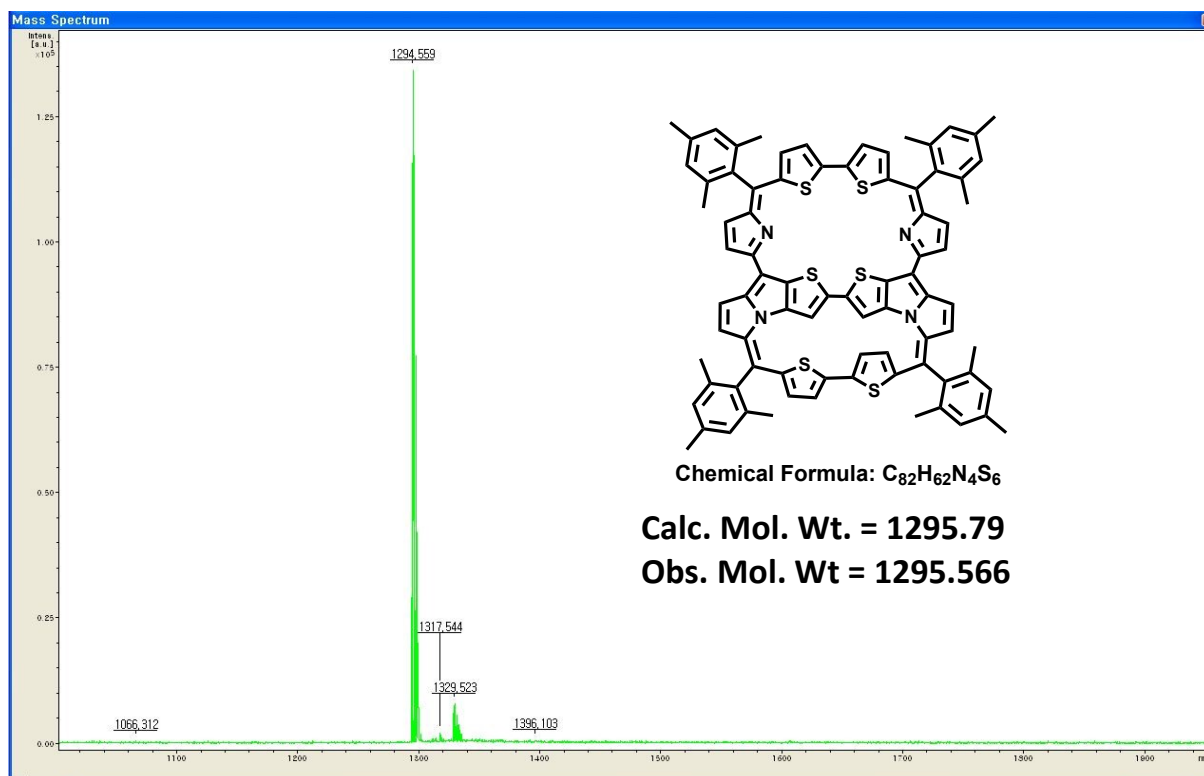


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the macrocycle **5** recorded in CD_2Cl_2 on a 400 MHz FT-NMR spectrometer at 25 °C.



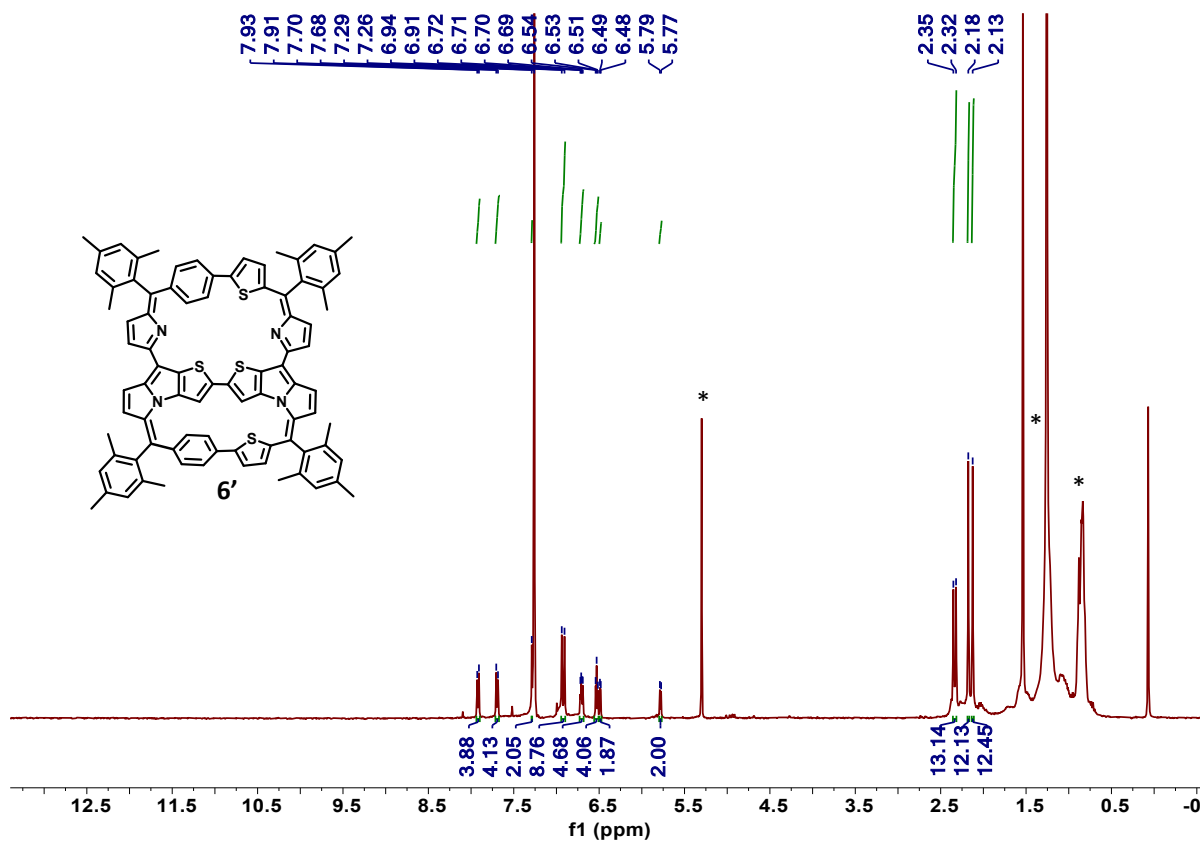


Figure S4. ^1H NMR spectra of compound **6'** recorded in CDCl_3 on a 400 MHz FT-NMR spectrometer at 25 °C.

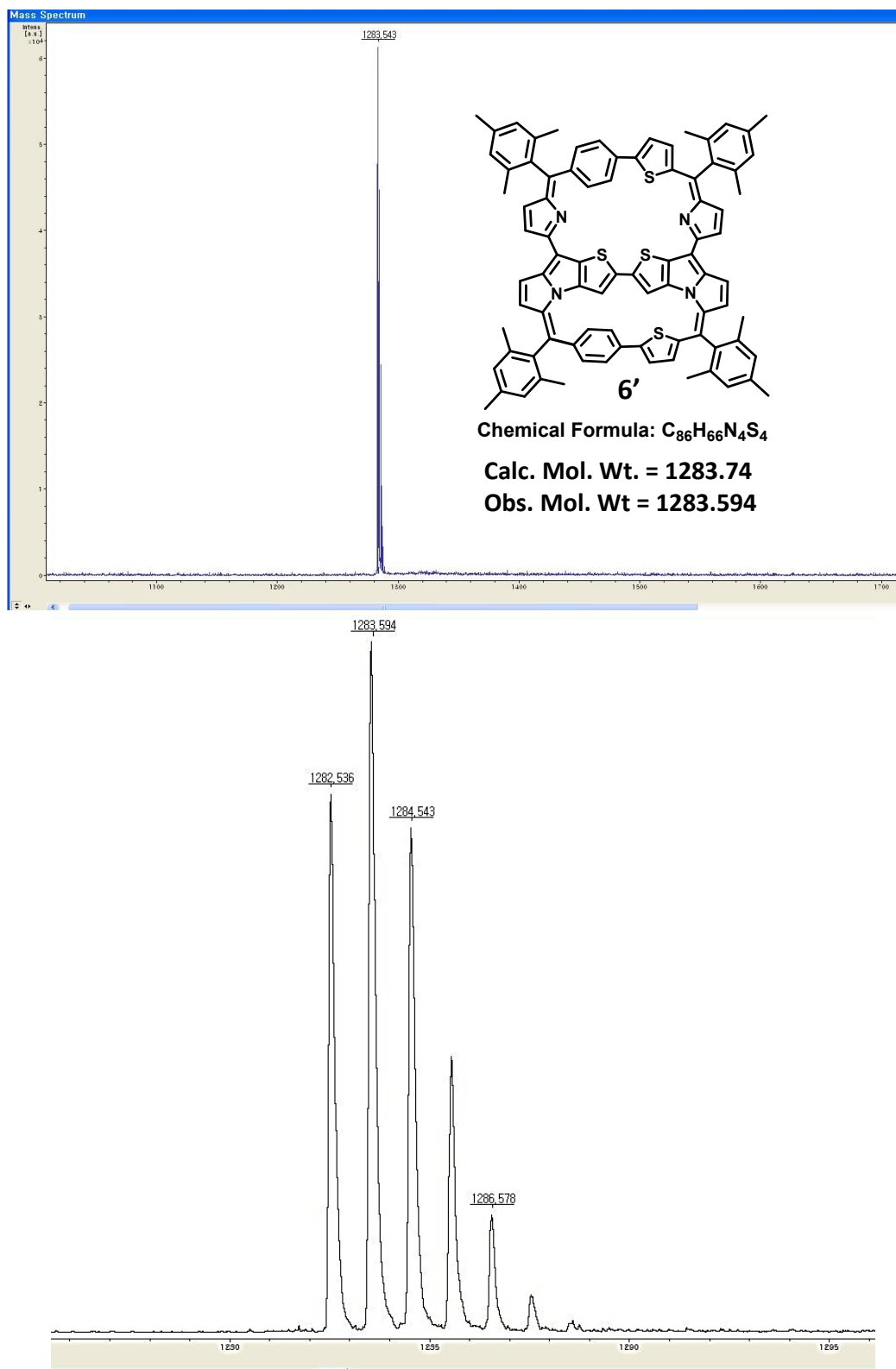


Figure S5. MALDI spectrum of compound **6'**.

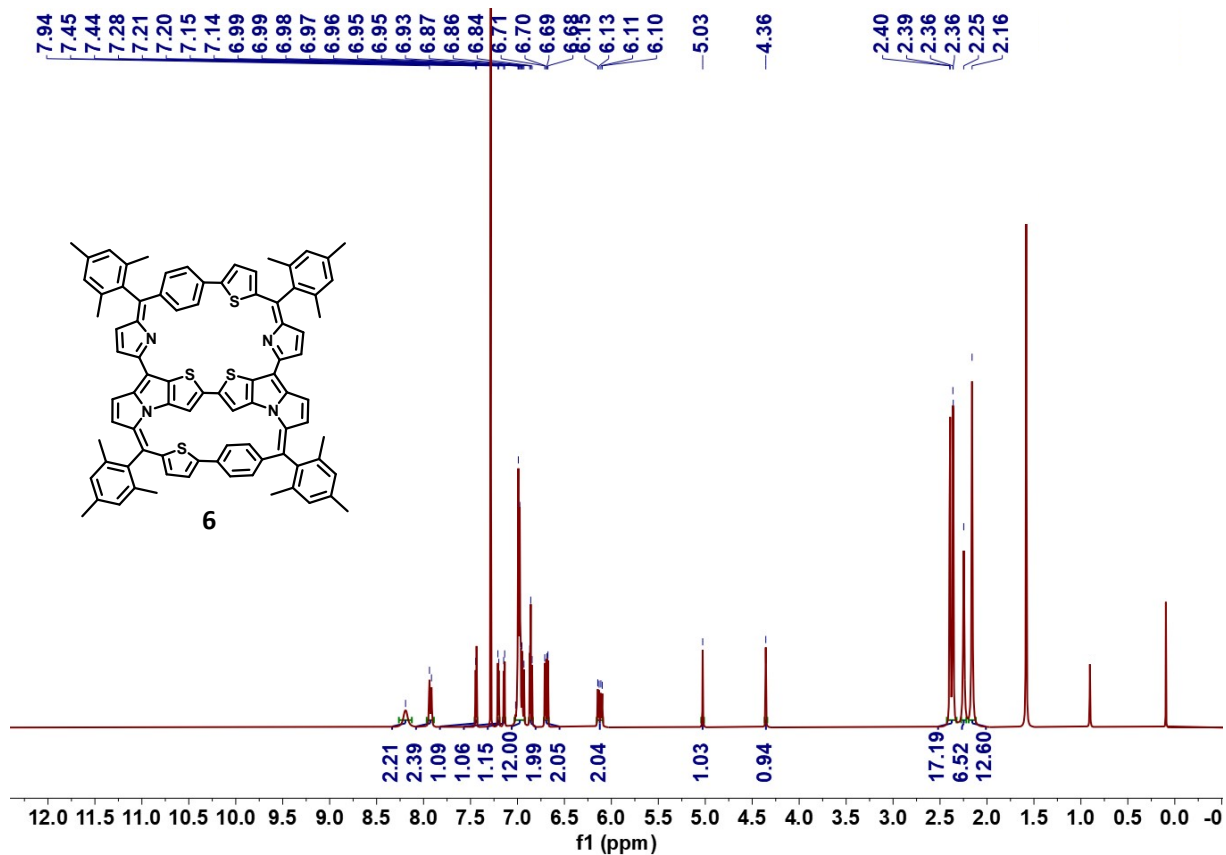


Figure S6. ¹H NMR spectra of compound **6** recorded in CDCl₃ on a 400 MHz FT-NMR spectrometer at 25 °C

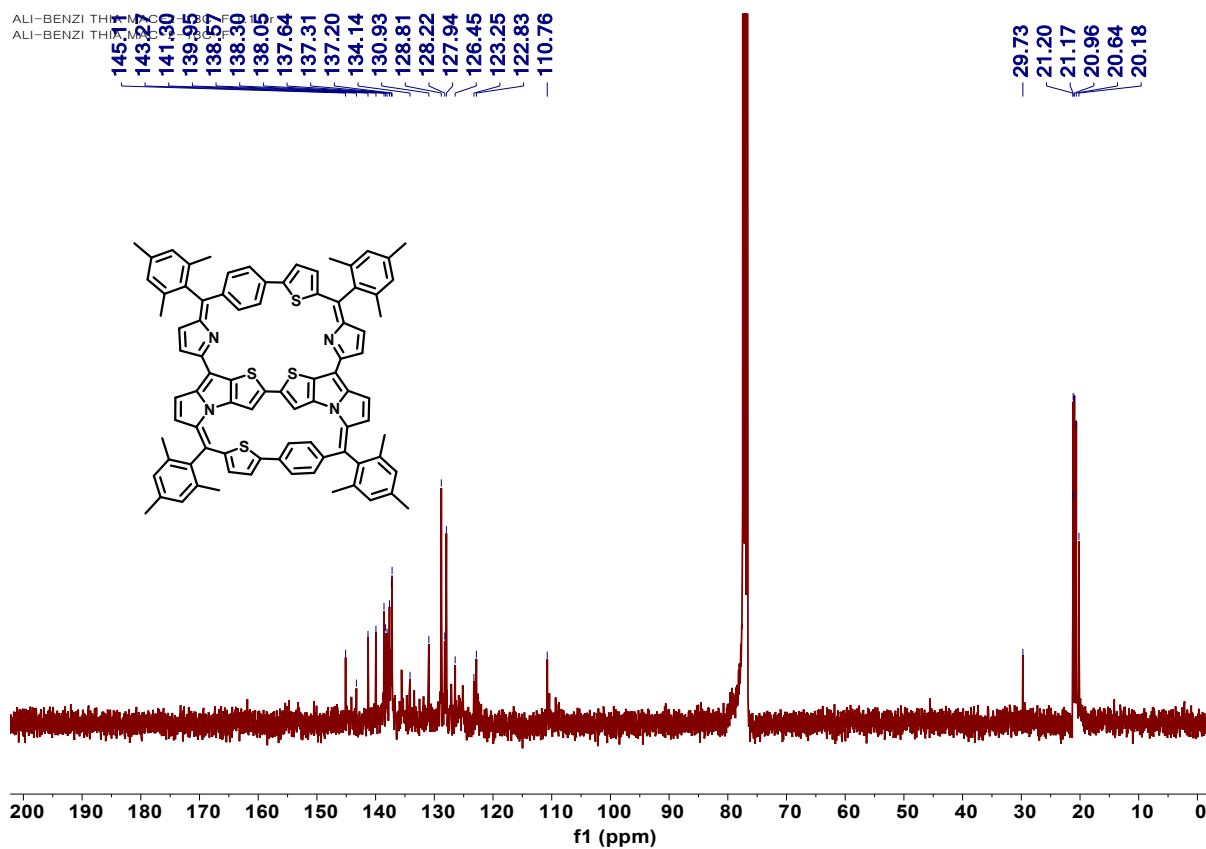


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the macrocycle **6** recorded in CD_2Cl_2 on a 400 MHz FT-NMR spectrometer at 25 °C.

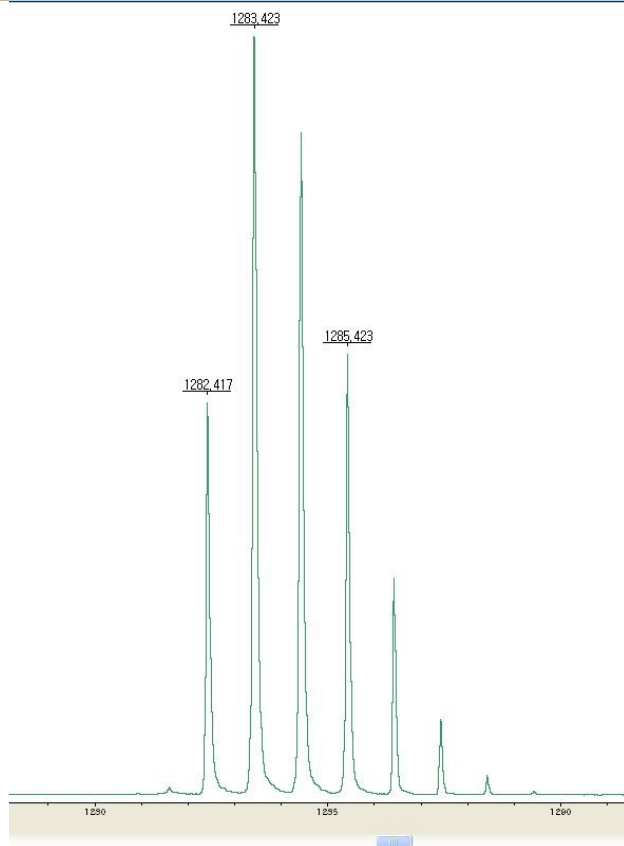
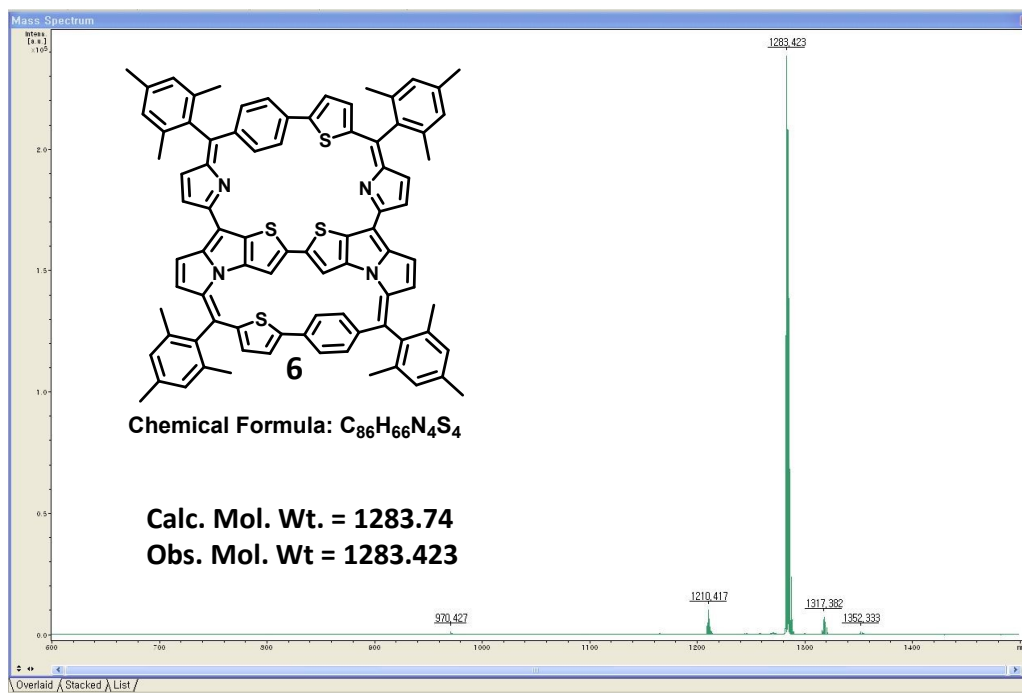


Figure S8. HRMS spectrum of compound **6**.

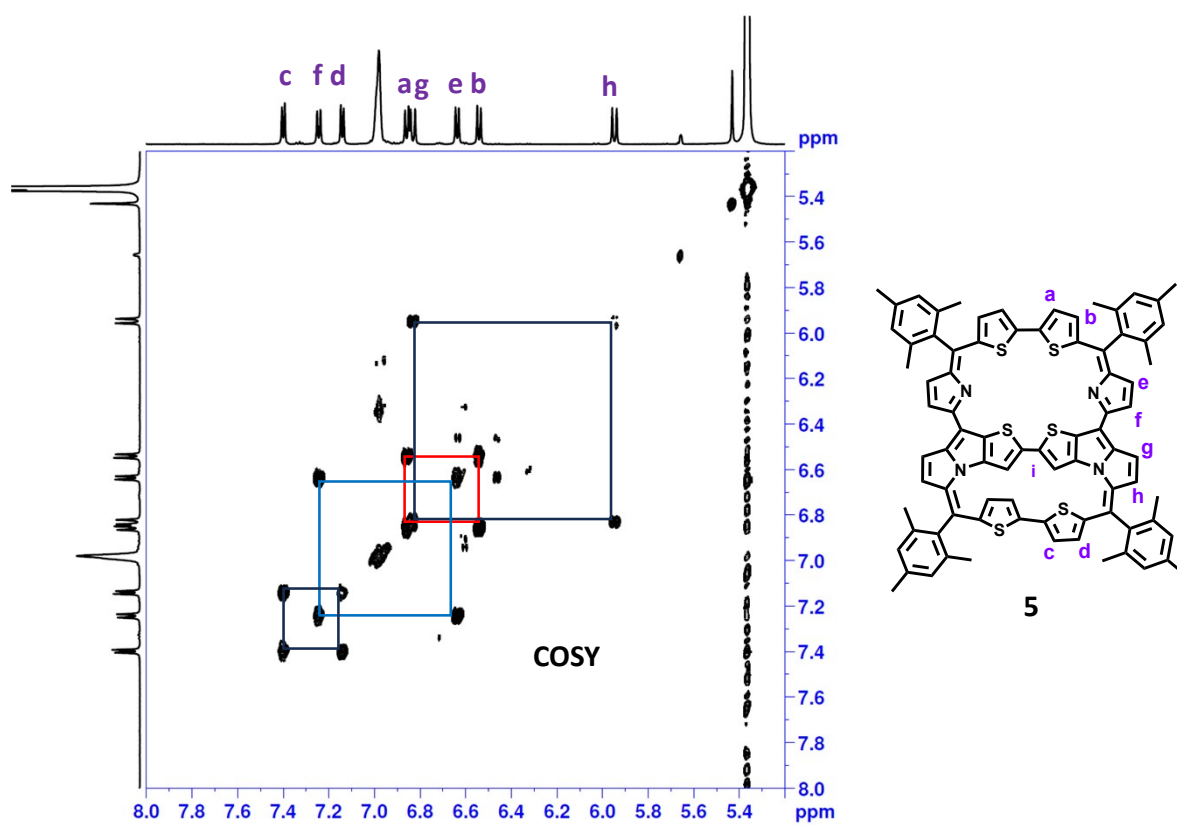


Figure S9. ^1H - ^1H COSY spectrum of compound **5** recorded in CD_2Cl_2 at -20°C .

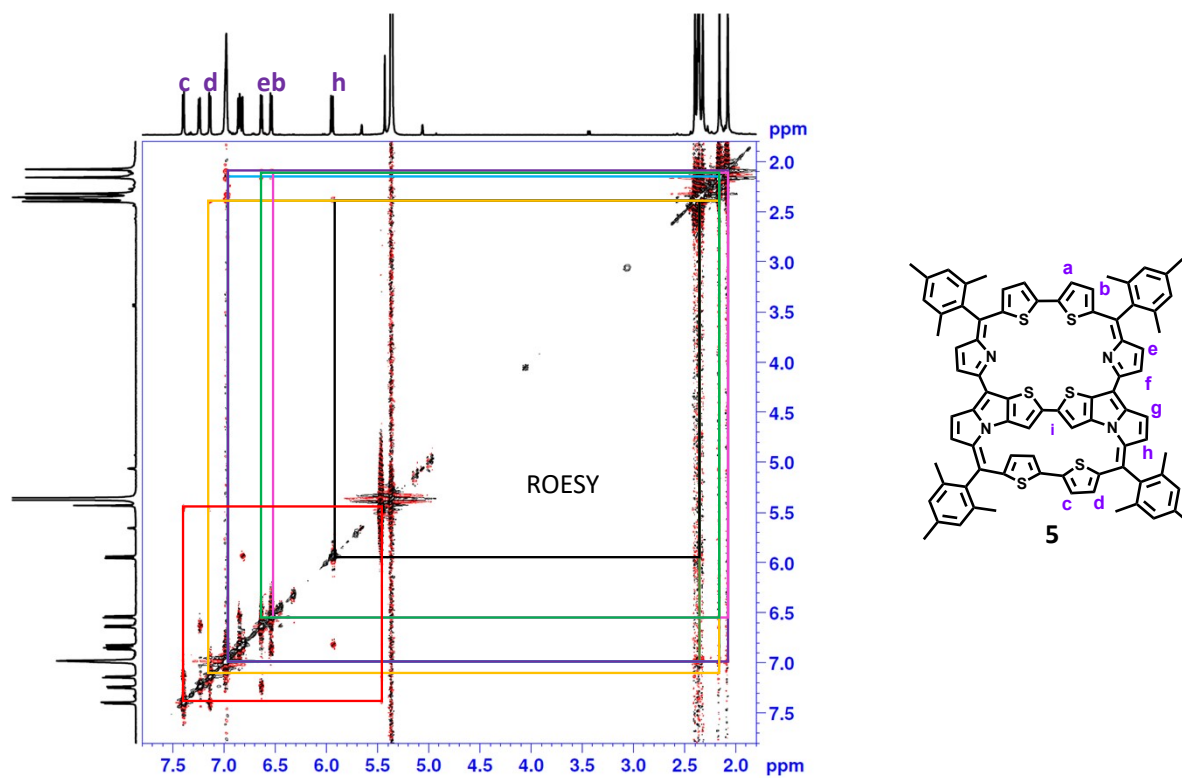


Figure S10. ^1H - ^1H ROESY spectrum of compound **5** recorded in CD_2Cl_2 at $-20\text{ }^\circ\text{C}$.

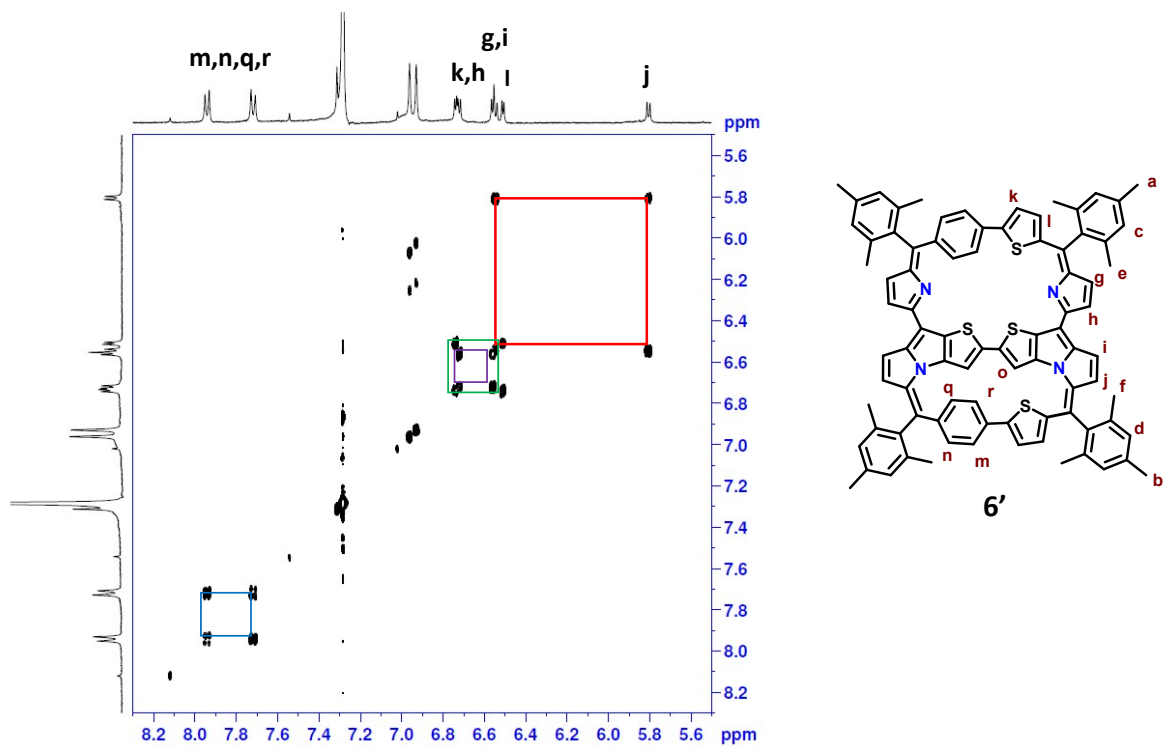


Figure S11. ^1H - ^1H COSY spectrum of compound **6'** recorded in CDCl_3 at 25°C .

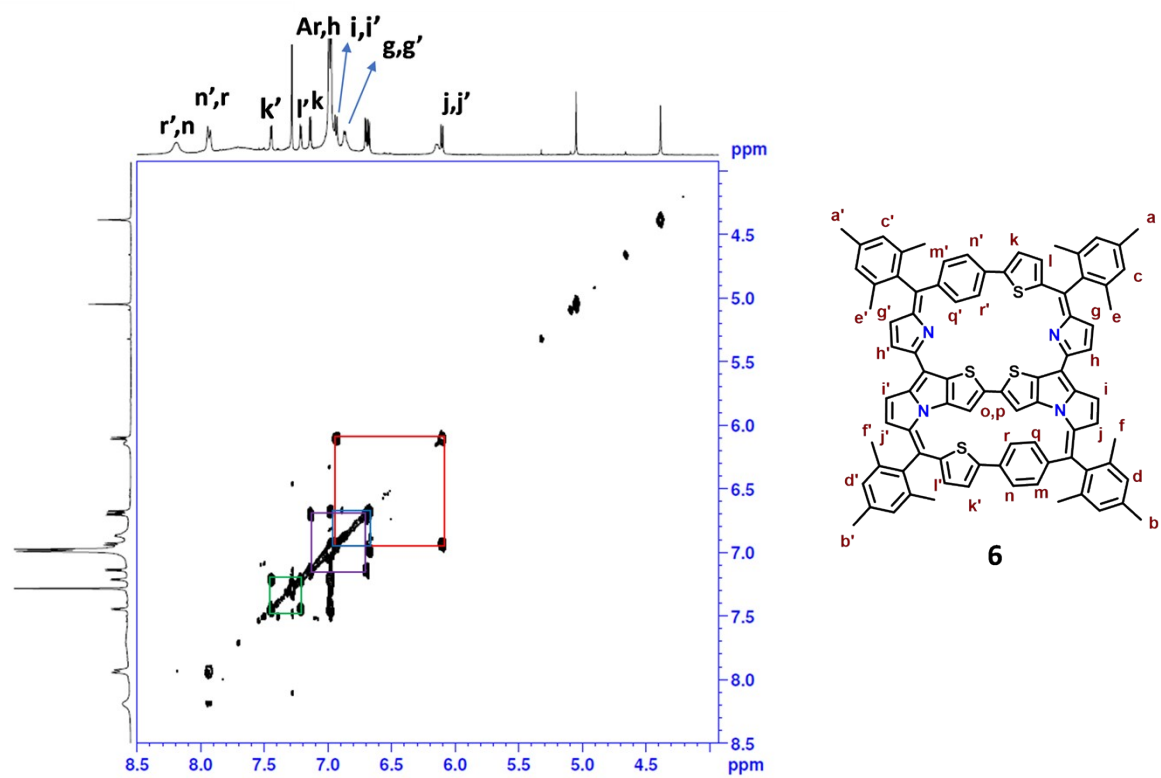


Figure S12. ^1H - ^1H COSY spectrum of compound **6** recorded in CDCl_3 at 25°C .

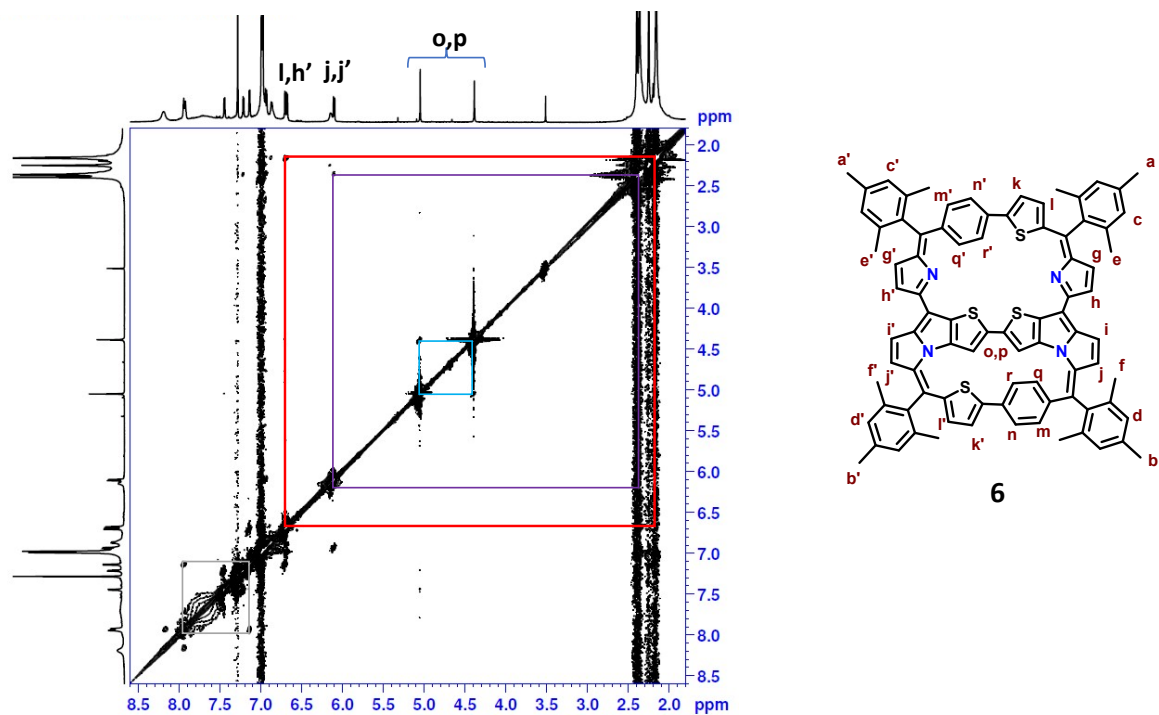


Figure S13. ^1H - ^1H ROESY spectrum of compound **6** recorded in CDCl_3 at 25°C .

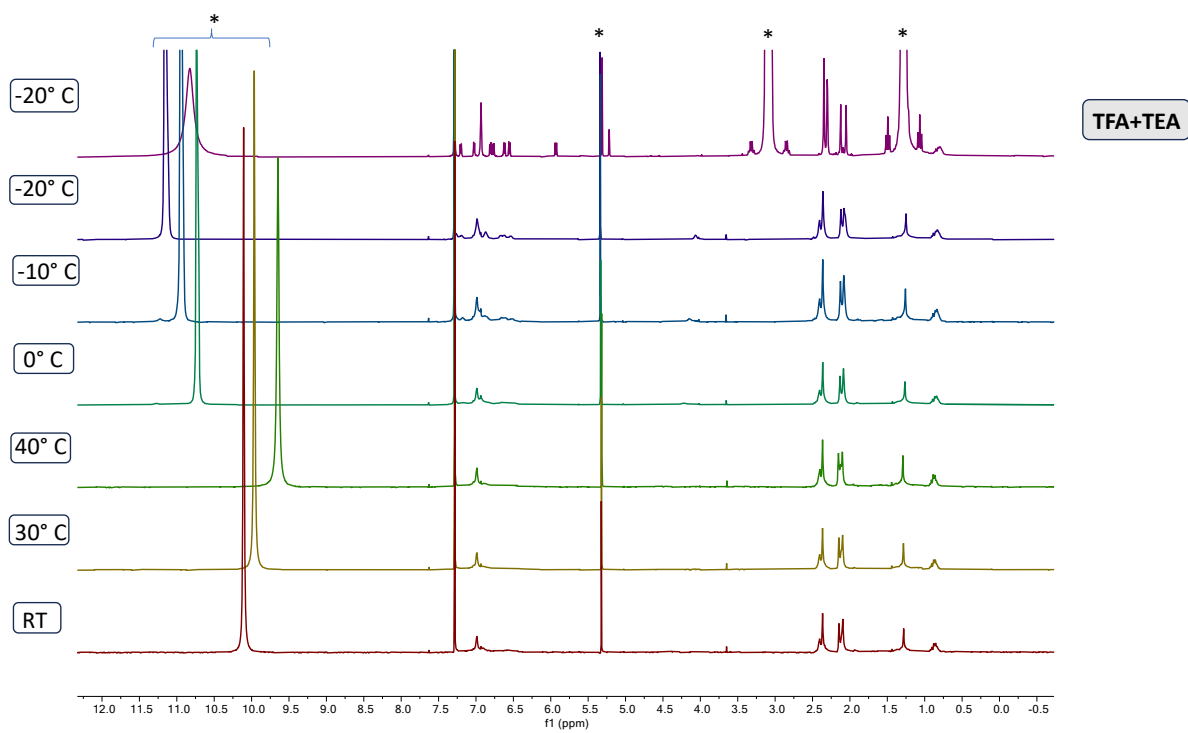


Figure S14. ^1H NMR of **5** recorded in the presence of TFA in CDCl_3 at different temperatures.

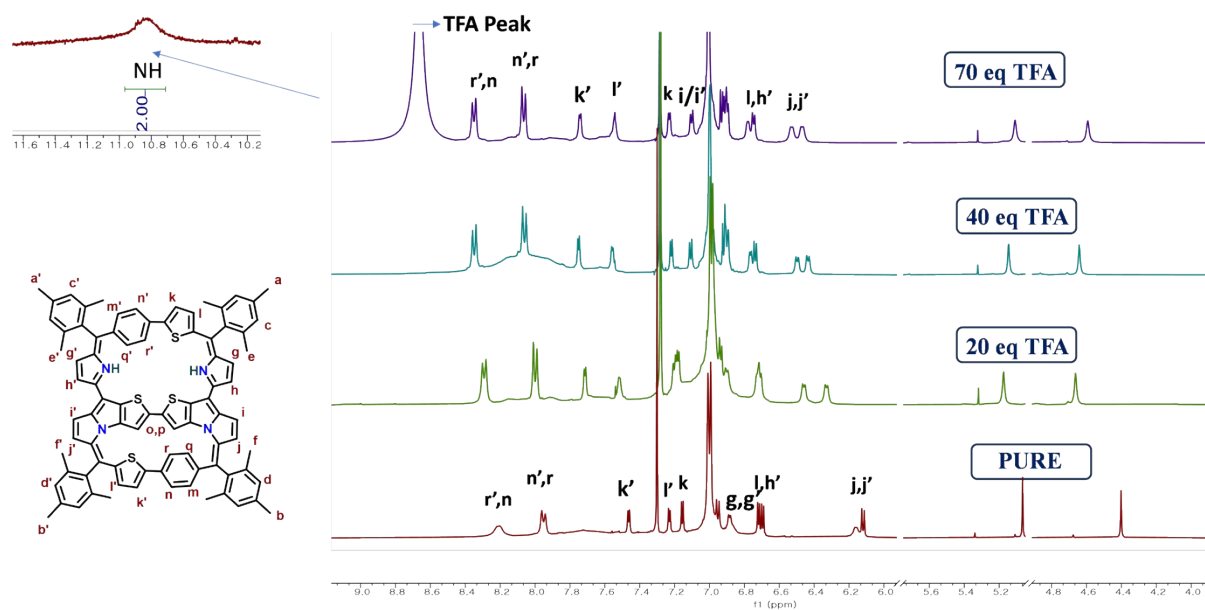


Figure S15. ^1H NMR titration experiment of macrocycle **6** with a dilute solution of TFA in CDCl_3 at 25°C .

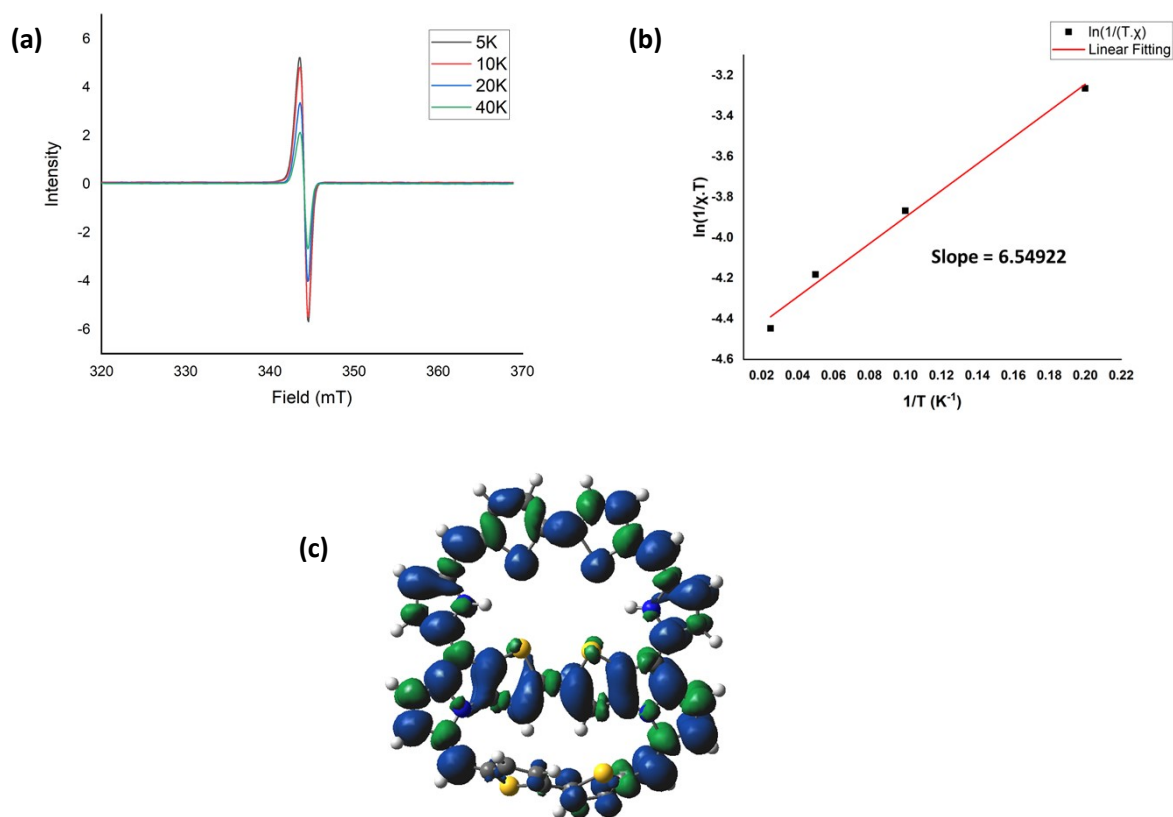


Figure S16. (a) EPR spectrum of the protonated form $5 \cdot 2H^+$ performed in toluene at different temperatures from 5 K to 40 K. (b) Temperature-dependent fit to the Bleaney-Bowers equation with a ΔE_{S-T} of 0.013 kcal mol⁻¹. (c) Mulliken electron spin density plot of $5 \cdot 2H^+$ in the T_1 state calculated using UCAM-B3LYP /6-311G(d, p) level of theory.

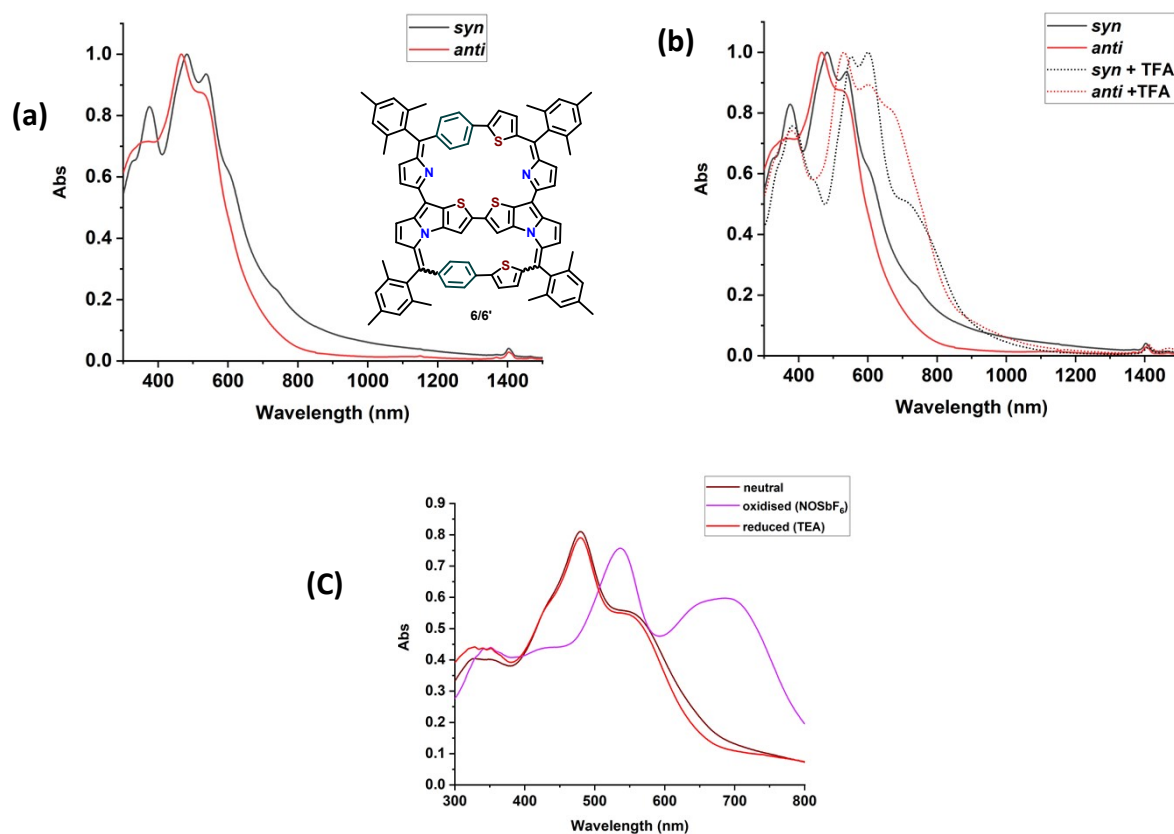


Figure S17. (a) Comparison of UV-Vis-NIR spectrum of *syn* (6') and *anti* (6) octaphyrin in CH_2Cl_2 . (b) Comparison of UV-Vis-NIR spectrum of neutral *syn* (6') and *anti* (6) octaphyrin with the protonated form (6'•2H⁺ and 6•2H⁺) with TFA in CH_2Cl_2 . (c) Comparison of UV-Vis-NIR spectra of neutral **5** (brown line), oxidized from [5]²⁺ (pink line) and reduced form with triethylamine (TEA) (red line).

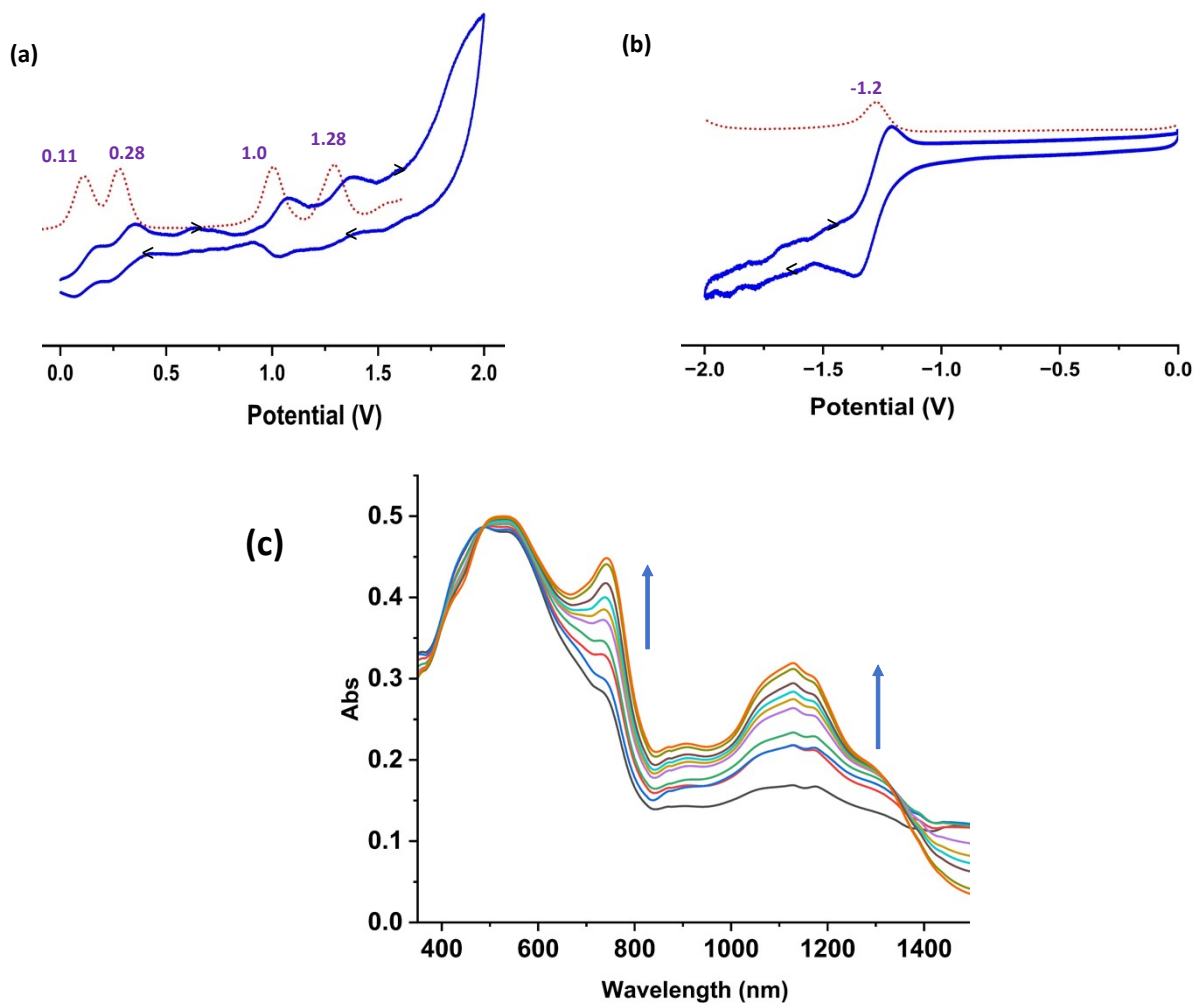


Figure S18. Cyclic voltammograms and differential pulse voltammograms upon (a) oxidation and (b) reduction of macrocycle **5** recorded in CH_2Cl_2 with TBAPF_6 (0.1 M) as the supporting electrolyte and Ag/AgNO_3 as the reference electrode at a scan rate of 100 mV/s at 25 °C. (c) Oxidative spectroelectrochemical titrations carried out at the second oxidation potential of 0.45 V (the data were recorded at an interval of 60 s).

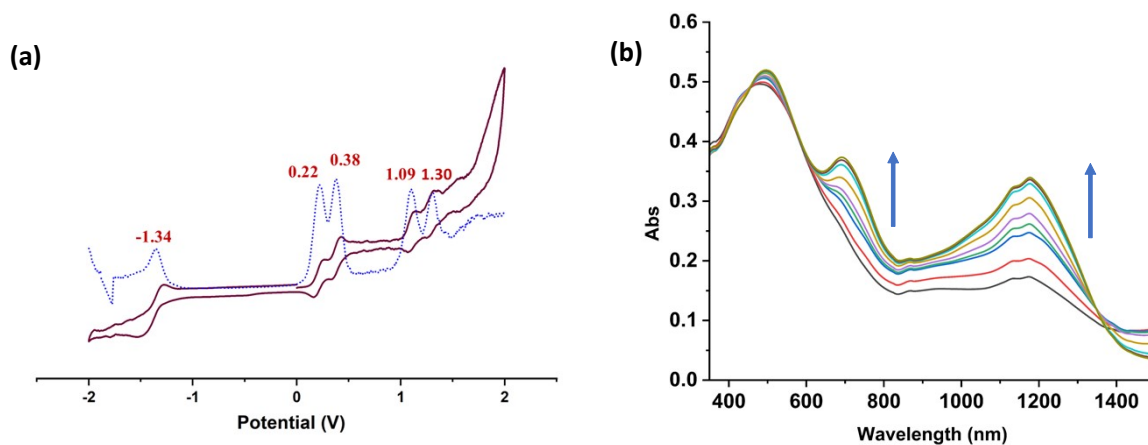


Figure S19. (a) Cyclic voltammograms and differential pulse voltammograms of the macrocycle **6** recorded in CH_2Cl_2 with TBAPF_6 (0.1 M) as the supporting electrolyte and Ag/AgNO_3 as the reference electrode at a scan rate of 100 mV/s at 25 $^\circ\text{C}$. (b) Oxidative spectroelectrochemical titrations carried out at the second oxidation potential of 0.51 V (the data were recorded at an interval of 60 s).

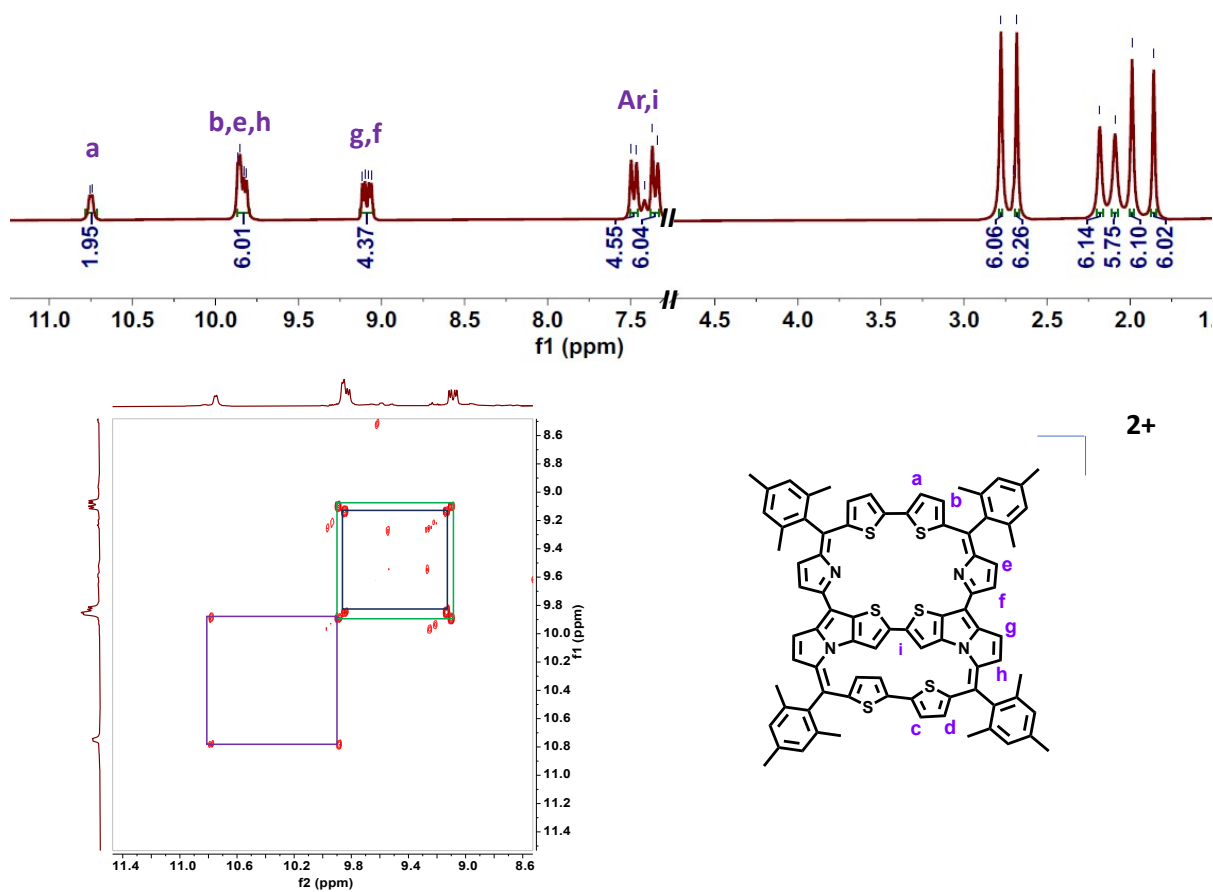


Figure S20. ^1H NMR (expanded) and COSY spectra of compound $[5]^{2+}$ in CDCl_3 on 300 MHz FT-NMR spectrometer at 25°C (solvent impurities were hidden for clarity).

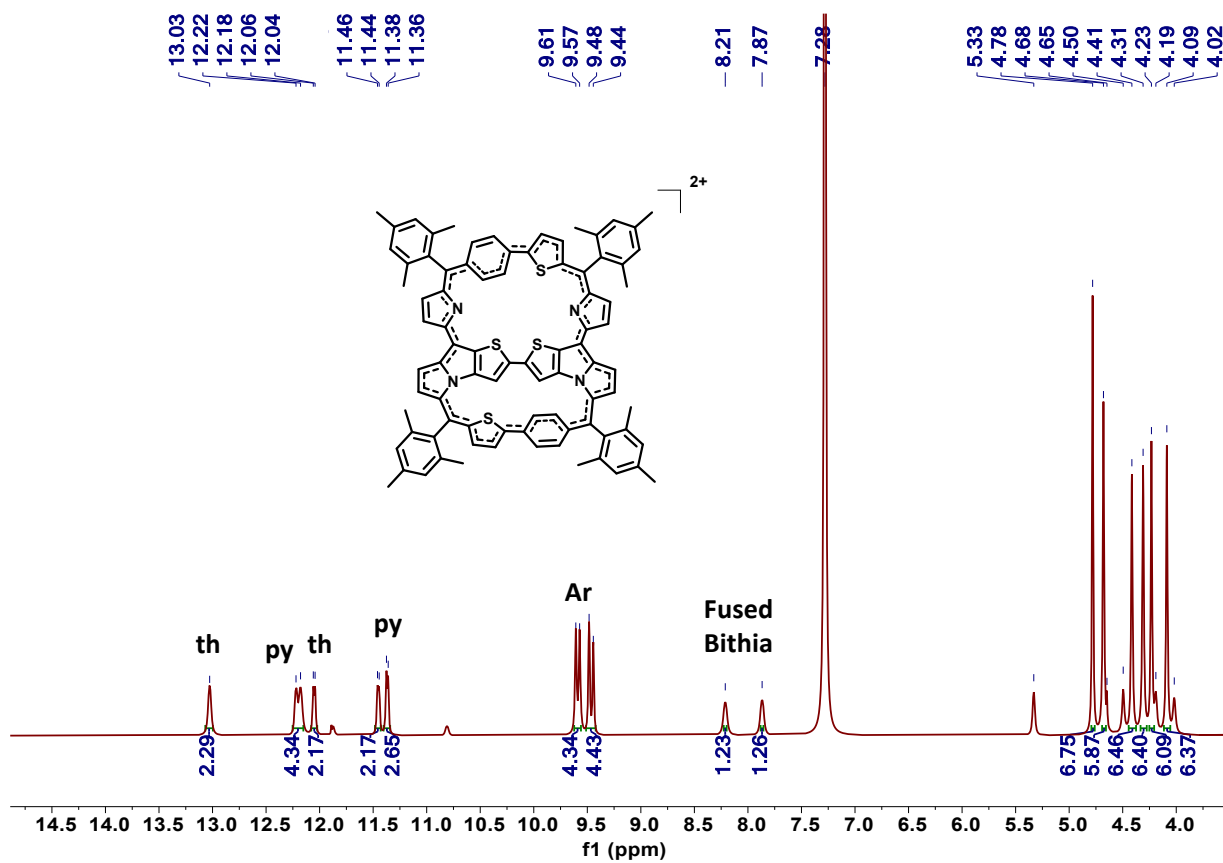


Figure S22. ^1H NMR spectrum of compound $[\mathbf{6}]^{2+}$ in CDCl_3 on 300 MHz FT-NMR spectrometer at 40°C .

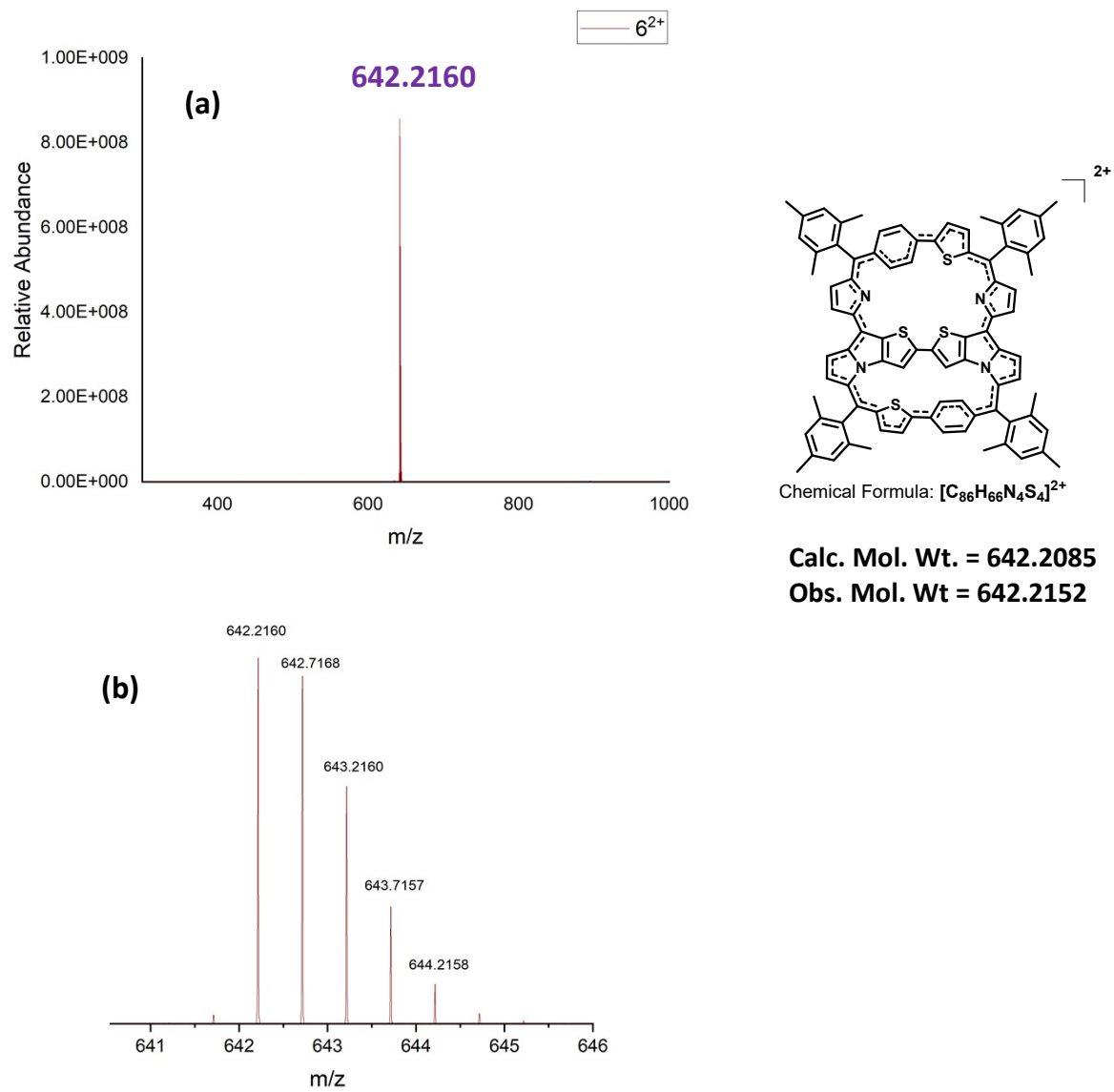


Figure S23. HRMS spectrum of oxidized octaphyrin $[6]^{2+}$ plotted in Origin.

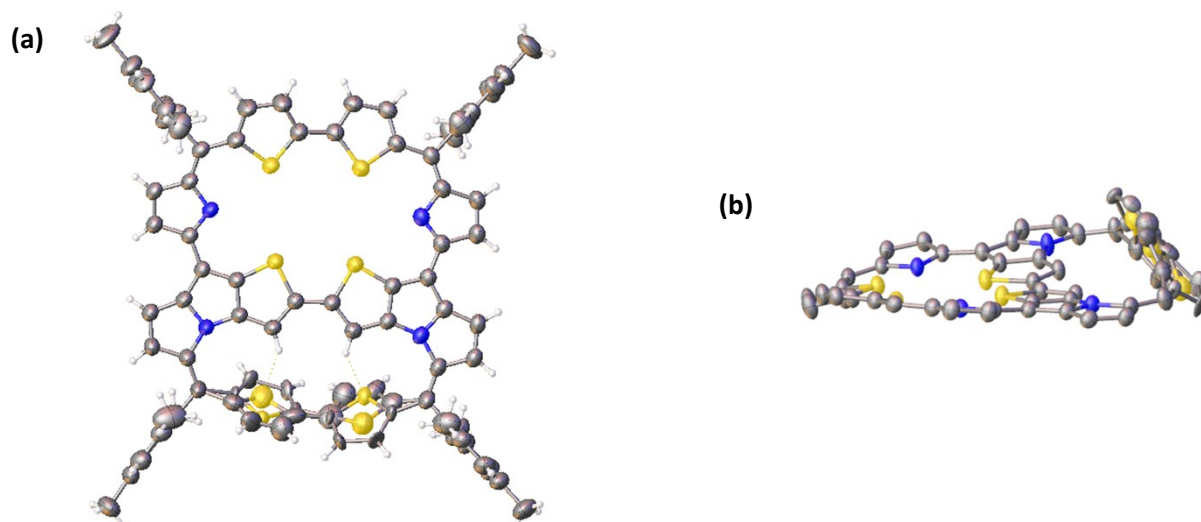


Figure S24: (a) X-ray crystal structure of macrocycle **5**. (b) Side view of macrocycle **5** (ellipsoids set at the 50% probability level). [(b) *Meso*-aryls and hydrogen atoms are omitted for clarity.]

Table S1. Crystal data for macrocycle **5**.

CCDC No	2432301
Empirical formula	C ₈₂ H ₆₂ N ₄ S ₆
Formula weight	1295.71
Temperature/K	298
Crystal system	monoclinic
Space group	I2/a
a/Å	16.8793(2)
b/Å	16.1714(2)
c/Å	56.9401(9)
α/°	90
β/°	92.6640(10)
γ/°	90
Volume/Å ³	15525.7(4)
Z	8
ρ _{calc} /g/cm ³	1.109
μ/mm ⁻¹	1.954
F(000)	5424.0
Crystal size/mm ³	0.18 × 0.08 × 0.03
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	5.682 to 136.494
Index ranges	-20 ≤ h ≤ 17, -17 ≤ k ≤ 19, -68 ≤ l ≤ 66
Reflections collected	45317
Independent reflections	13988 [R _{int} = 0.0479, R _{sigma} = 0.0433]
Data/restraints/parameters	13988/130/931
Goodness-of-fit on F ²	1.033
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0581, wR ₂ = 0.1734
Final R indexes [all data]	R ₁ = 0.0696, wR ₂ = 0.1821
Largest diff. peak/hole / e Å ⁻³	0.44/-0.46

Table S2. Bond length of crystal 5.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
S1	C1	1.739(3)		C43	C44	1.373(3)
S1	C4	1.728(3)		C44	C45	1.410(4)
S2	C5	1.731(3)		C45	C46	1.390(4)
S2	C8	1.741(3)		C47	C48	1.398(4)
S5	C39	1.703(3)		C47	C52	1.406(4)
S5	C42	1.750(2)		C48	C49	1.379(4)
S6	C43	1.752(3)		C48	C53	1.509(5)
S6	C46	1.700(3)		C49	C50	1.381(5)
N1	C34	1.320(3)		C50	C51	1.372(5)
N1	C37	1.392(3)		C50	C54	1.524(5)
N2	C10	1.400(3)		C51	C52	1.393(4)
N2	C13	1.316(3)		C52	C55	1.495(5)
N3	C29	1.418(3)		C56	C57	1.407(5)
N3	C32	1.395(3)		C56	C61	1.390(5)
N3	C40	1.404(3)		C57	C58	1.388(5)
N4	C15	1.389(3)		C57	C62	1.487(6)
N4	C18	1.430(3)		C58	C59	1.366(6)
N4	C45	1.411(3)		C59	C60	1.379(6)
C1	C2	1.376(4)		C59	C63	1.505(5)
C1	C38	1.444(4)		C60	C61	1.391(5)
C2	C3	1.385(5)		C61	C64	1.510(5)
C3	C4	1.373(4)		C65	C66	1.391(4)
C4	C5	1.451(4)		C65	C70	1.393(5)
C5	C6	1.380(4)		C66	C67	1.385(4)
C6	C7	1.376(4)		C66	C71	1.495(5)
C7	C8	1.376(4)		C67	C68	1.388(5)
C8	C9	1.445(4)		C68	C69	1.369(5)
C9	C10	1.359(4)		C68	C72	1.513(5)
C9	C47	1.501(4)		C69	C70	1.379(5)
C10	C11	1.454(4)		C70	C73	1.518(5)
C11	C12	1.336(4)		C74	C75	1.389(4)
C12	C13	1.457(4)		C74	C79	1.394(4)
C13	C14	1.434(4)		C75	C76	1.395(4)
C14	C15	1.397(4)		C75	C80	1.505(5)
C14	C46	1.427(4)		C76	C77	1.374(5)
C15	C16	1.433(4)		C77	C78	1.353(5)
C16	C17	1.335(4)		C77	C81	1.521(4)
C17	C18	1.459(4)		C78	C79	1.392(4)
C18	C19	1.355(4)		C79	C82	1.500(5)
C19	C56	1.504(4)		S3A	C24A	1.713(7)
C19	C20A	1.489(6)		S3A	C27A	1.742(5)
C19	C20B	1.536(9)		S4A	C20A	1.761(6)

C28	C29	1.341(4)		S4A	C23A	1.663(11)
C28	C65	1.495(4)		C20A	C21A	1.367(8)
C28	C27A	1.531(5)		C21A	C22A	1.483(7)
C28	C27B	1.516(8)		C22A	C23A	1.412(15)
C29	C30	1.458(4)		C23A	C24A	1.460(10)
C30	C31	1.346(4)		C24A	C25A	1.326(10)
C31	C32	1.418(4)		C25A	C26A	1.472(6)
C32	C33	1.398(4)		C26A	C27A	1.387(8)
C33	C34	1.427(3)		S3B	C24B	1.704(11)
C33	C39	1.420(3)		S3B	C27B	1.715(9)
C34	C35	1.447(4)		S4B	C20B	1.663(9)
C35	C36	1.336(4)		S4B	C23B	1.673(17)
C36	C37	1.448(4)		C20B	C21B	1.335(13)
C37	C38	1.356(4)		C21B	C22B	1.240(13)
C38	C74	1.511(3)		C22B	C23B	1.49(2)
C39	C40	1.387(3)		C23B	C24B	1.451(19)
C40	C41	1.404(4)		C24B	C25B	1.371(14)
C41	C42	1.370(4)		C25B	C26B	1.239(12)
C42	C43	1.448(4)		C26B	C27B	1.314(12)

Table S3. Bond Angles for the macrocycle **5**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C4	S1	C1	92.08(13)		C46	C45	N4	106.0(2)
C5	S2	C8	92.04(13)		C46	C45	C44	112.9(2)
C39	S5	C42	90.78(12)		C14	C46	S6	136.6(2)
C46	S6	C43	90.81(12)		C45	C46	S6	112.37(19)
C34	N1	C37	105.4(2)		C45	C46	C14	111.0(2)
C13	N2	C10	105.8(2)		C48	C47	C9	121.2(3)
C32	N3	C29	109.4(2)		C48	C47	C52	120.1(3)
C32	N3	C40	108.3(2)		C52	C47	C9	118.6(3)
C40	N3	C29	142.2(2)		C47	C48	C53	121.0(3)
C15	N4	C18	109.3(2)		C49	C48	C47	119.0(3)
C15	N4	C45	108.1(2)		C49	C48	C53	120.0(3)
C45	N4	C18	142.5(2)		C48	C49	C50	122.2(3)
C2	C1	S1	109.5(2)		C49	C50	C54	120.5(4)
C2	C1	C38	124.7(2)		C51	C50	C49	118.1(3)
C38	C1	S1	125.6(2)		C51	C50	C54	121.4(4)
C1	C2	C3	114.5(3)		C50	C51	C52	122.5(3)
C4	C3	C2	113.1(3)		C47	C52	C55	121.4(3)
C3	C4	S1	110.7(2)		C51	C52	C47	118.1(3)
C3	C4	C5	123.3(3)		C51	C52	C55	120.5(3)
C5	C4	S1	125.9(2)		C57	C56	C19	119.2(3)
C4	C5	S2	126.4(2)		C61	C56	C19	119.9(3)
C6	C5	S2	110.5(2)		C61	C56	C57	120.8(3)
C6	C5	C4	123.2(3)		C56	C57	C62	122.1(3)
C7	C6	C5	113.2(3)		C58	C57	C56	117.9(4)
C8	C7	C6	114.9(3)		C58	C57	C62	120.0(3)
C7	C8	S2	109.3(2)		C59	C58	C57	122.8(4)
C7	C8	C9	123.8(2)		C58	C59	C60	117.8(3)
C9	C8	S2	126.8(2)		C58	C59	C63	121.1(4)
C8	C9	C47	114.4(2)		C60	C59	C63	121.1(4)
C10	C9	C8	127.2(2)		C59	C60	C61	122.7(4)
C10	C9	C47	118.5(2)		C56	C61	C60	117.9(3)
N2	C10	C11	108.9(2)		C56	C61	C64	122.0(3)
C9	C10	N2	125.1(2)		C60	C61	C64	120.1(4)
C9	C10	C11	125.9(2)		C66	C65	C28	119.9(3)
C12	C11	C10	107.2(2)		C66	C65	C70	119.7(3)
C11	C12	C13	106.0(2)		C70	C65	C28	120.4(3)
N2	C13	C12	112.2(2)		C65	C66	C71	121.2(3)
N2	C13	C14	120.6(2)		C67	C66	C65	119.1(3)
C14	C13	C12	127.1(2)		C67	C66	C71	119.7(3)
C15	C14	C13	130.3(2)		C66	C67	C68	121.7(3)

C15	C14	C46	104.1(2)		C67	C68	C72	120.1(4)
C46	C14	C13	125.3(2)		C69	C68	C67	117.8(3)
N4	C15	C14	110.7(2)		C69	C68	C72	122.1(4)
N4	C15	C16	107.6(2)		C68	C69	C70	122.3(3)
C14	C15	C16	141.7(3)		C65	C70	C73	122.0(3)
C17	C16	C15	108.6(2)		C69	C70	C65	119.3(3)
C16	C17	C18	110.4(2)		C69	C70	C73	118.8(4)
N4	C18	C17	104.1(2)		C75	C74	C38	120.1(2)
C19	C18	N4	131.4(2)		C75	C74	C79	119.9(2)
C19	C18	C17	124.4(2)		C79	C74	C38	119.9(3)
C18	C19	C56	118.1(3)		C74	C75	C76	118.9(3)
C18	C19	C20A	130.3(3)		C74	C75	C80	122.2(3)
C18	C19	C20B	114.7(4)		C76	C75	C80	118.9(3)
C56	C19	C20B	125.1(4)		C77	C76	C75	121.6(4)
C20A	C19	C56	110.3(3)		C76	C77	C81	119.6(4)
C29	C28	C65	120.4(2)		C78	C77	C76	118.4(3)
C29	C28	C27A	117.7(3)		C78	C77	C81	122.0(4)
C29	C28	C27B	124.8(3)		C77	C78	C79	122.7(3)
C65	C28	C27A	120.0(3)		C74	C79	C82	121.3(3)
C65	C28	C27B	109.5(3)		C78	C79	C74	118.4(3)
N3	C29	C30	104.5(2)		C78	C79	C82	120.3(3)
C28	C29	N3	129.6(2)		C24A	S3A	C27A	91.8(3)
C28	C29	C30	125.8(3)		C23A	S4A	C20A	93.9(5)
C31	C30	C29	109.7(2)		C19	C20A	S4A	115.5(4)
C30	C31	C32	108.8(2)		C21A	C20A	C19	132.1(5)
N3	C32	C31	107.5(2)		C21A	C20A	S4A	111.6(4)
N3	C32	C33	110.0(2)		C20A	C21A	C22A	108.9(5)
C33	C32	C31	142.4(2)		C23A	C22A	C21A	114.1(5)
C32	C33	C34	128.8(2)		C22A	C23A	S4A	109.9(5)
C32	C33	C39	104.5(2)		C22A	C23A	C24A	126.5(9)
C39	C33	C34	126.7(2)		C24A	C23A	S4A	123.5(9)
N1	C34	C33	121.0(2)		C23A	C24A	S3A	119.1(8)
N1	C34	C35	112.0(2)		C25A	C24A	S3A	112.5(4)
C33	C34	C35	127.0(2)		C25A	C24A	C23A	127.0(8)
C36	C35	C34	106.5(2)		C24A	C25A	C26A	114.3(5)
C35	C36	C37	106.5(2)		C27A	C26A	C25A	109.4(4)
N1	C37	C36	109.6(2)		C28	C27A	S3A	115.9(4)
C38	C37	N1	124.4(2)		C26A	C27A	C28	131.9(4)
C38	C37	C36	126.0(2)		C26A	C27A	S3A	112.0(3)
C1	C38	C74	114.8(2)		C24B	S3B	C27B	92.9(5)
C37	C38	C1	125.3(2)		C20B	S4B	C23B	95.9(8)
C37	C38	C74	119.8(2)		C19	C20B	S4B	114.6(6)
C33	C39	S5	137.2(2)		C21B	C20B	C19	141.4(9)

C40	C39	S5	111.69(19)		C21B	C20B	S4B	103.6(8)
C40	C39	C33	111.1(2)		C22B	C21B	C20B	127.0(13)
C39	C40	N3	106.2(2)		C21B	C22B	C23B	105.9(13)
C39	C40	C41	113.9(2)		C22B	C23B	S4B	107.5(12)
C41	C40	N3	139.9(2)		C24B	C23B	S4B	127.7(12)
C42	C41	C40	111.1(2)		C24B	C23B	C22B	118.9(14)
C41	C42	S5	112.52(19)		C23B	C24B	S3B	129.4(11)
C41	C42	C43	128.2(2)		C25B	C24B	S3B	109.5(9)
C43	C42	S5	119.00(19)		C25B	C24B	C23B	120.7(11)
C42	C43	S6	118.42(18)		C26B	C25B	C24B	107.8(12)
C44	C43	S6	112.17(19)		C25B	C26B	C27B	127.6(13)
C44	C43	C42	129.2(2)		C28	C27B	S3B	111.4(6)
C43	C44	C45	111.6(2)		C26B	C27B	C28	146.0(9)
C44	C45	N4	141.0(2)		C26B	C27B	S3B	101.5(8)

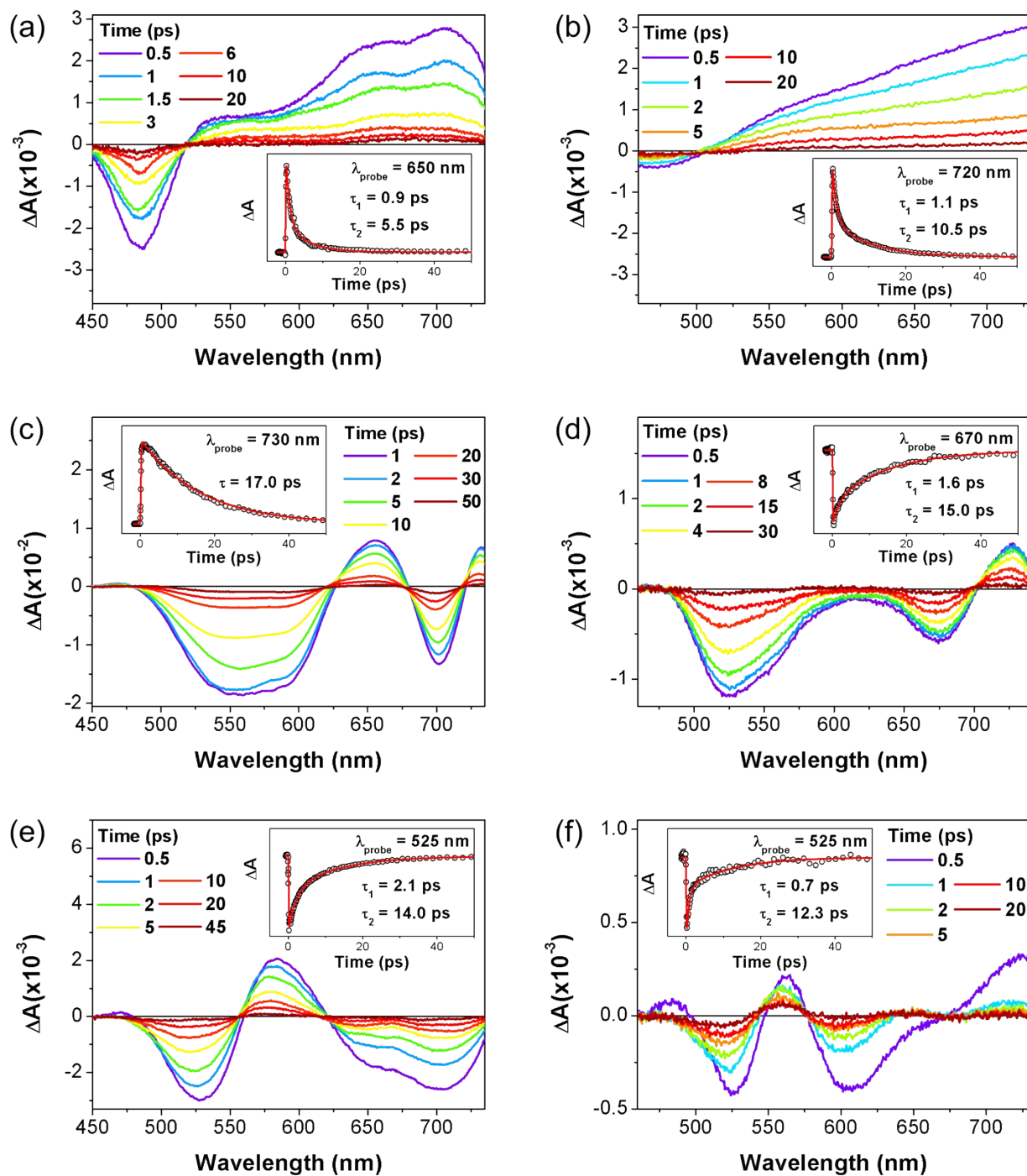


Figure S25. Femtosecond transient absorption spectra (left) and decay profiles (right) of (a) **5**, (b) **6**, (c) **5** with NOSbF_6 , (d) **6** with NOSbF_6 , (e) **5** with CF_3COOH , and (f) **6** with CF_3COOH in CH_2Cl_2 .

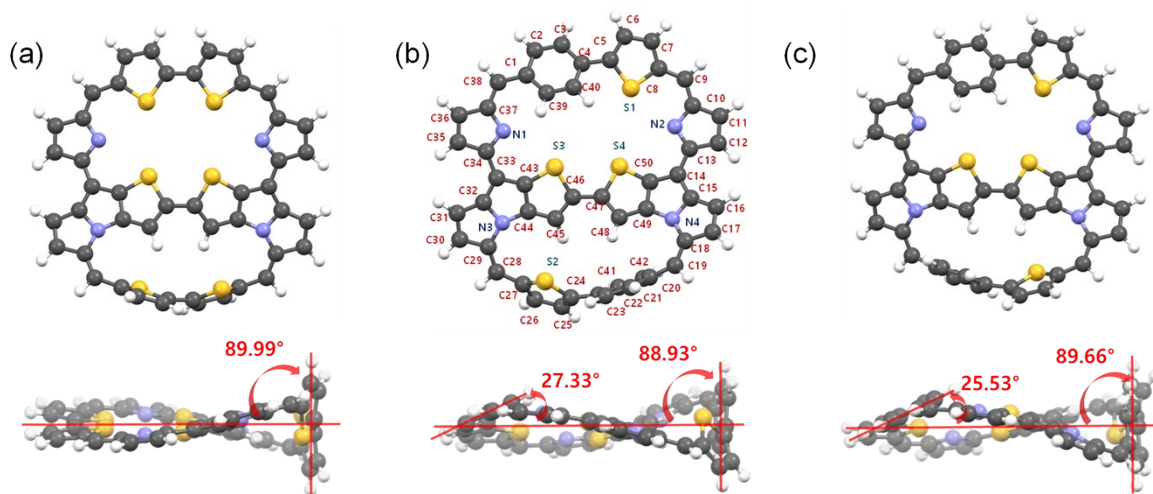


Figure S26. Optimized structures of (a) **5**, (b) **6**, and (c) **6'** calculated with B3LYP/6-311G(d,p).

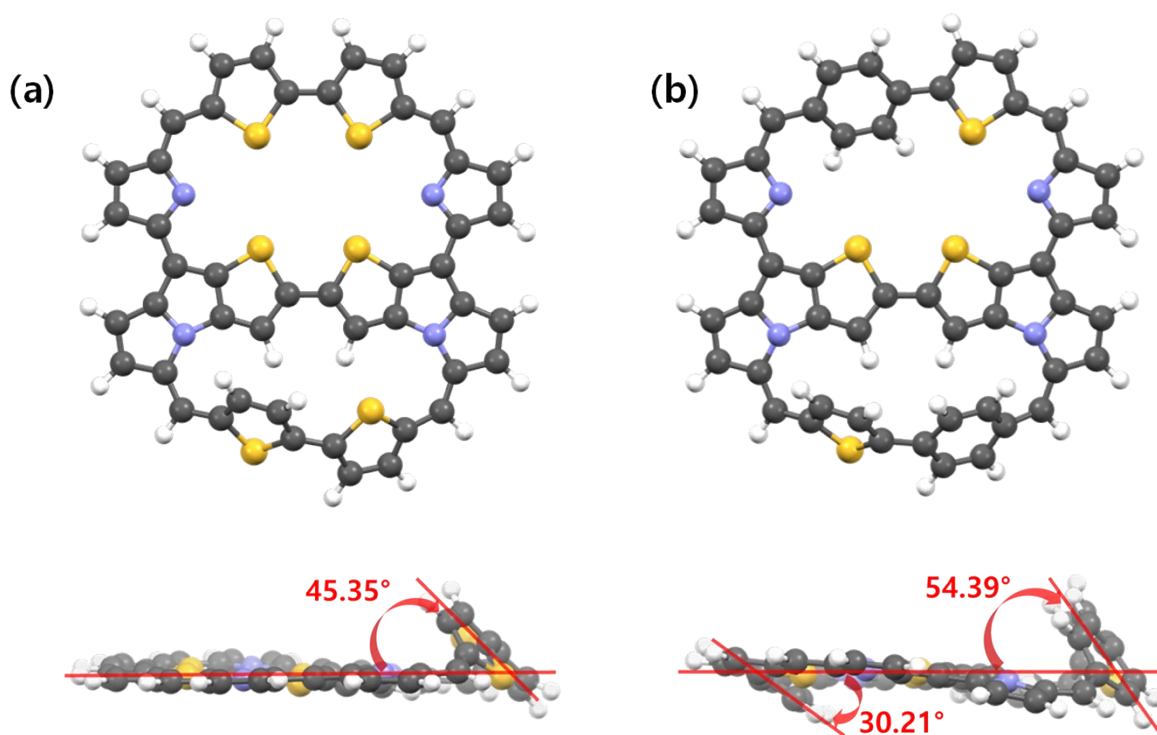


Figure S27. Optimized structures of (a) $[5]^{2+}$ and (b) $[6]^{2+}$ calculated with B3LYP/6-311G(d,p).

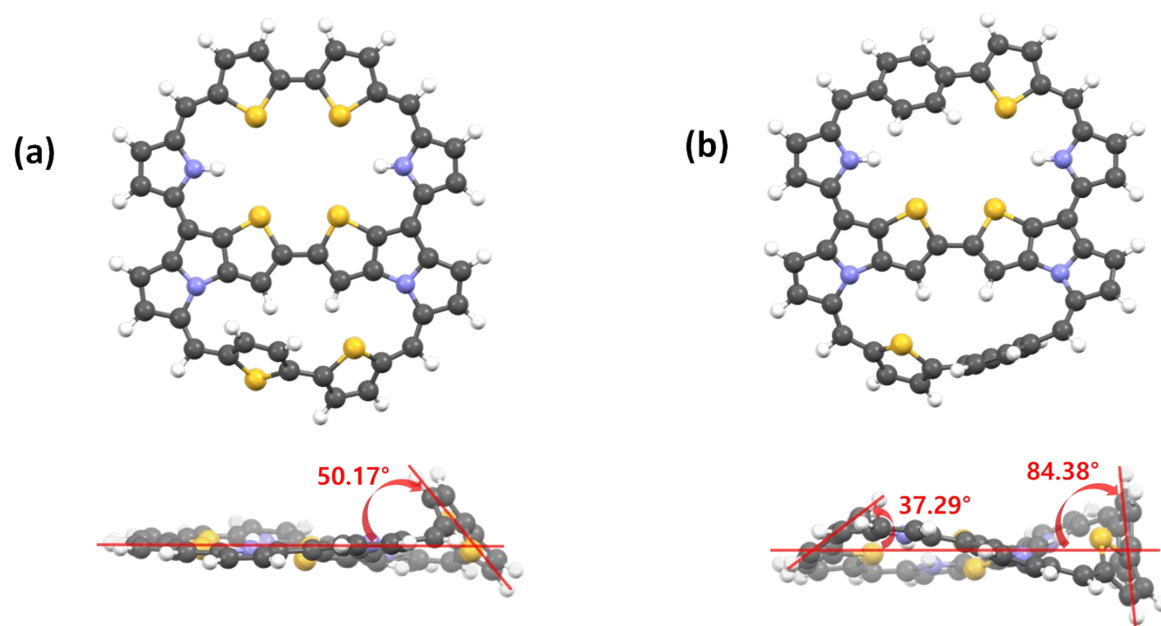
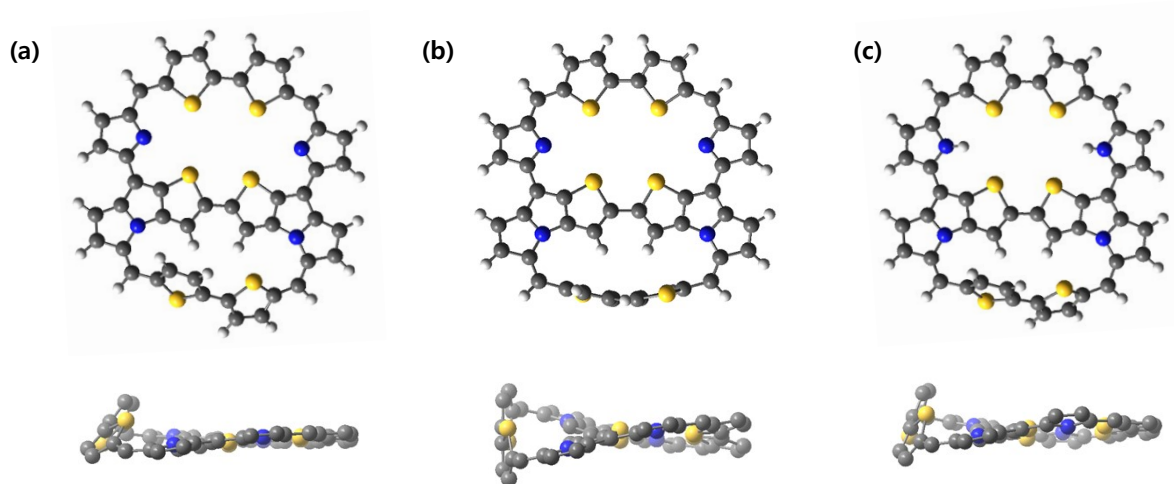
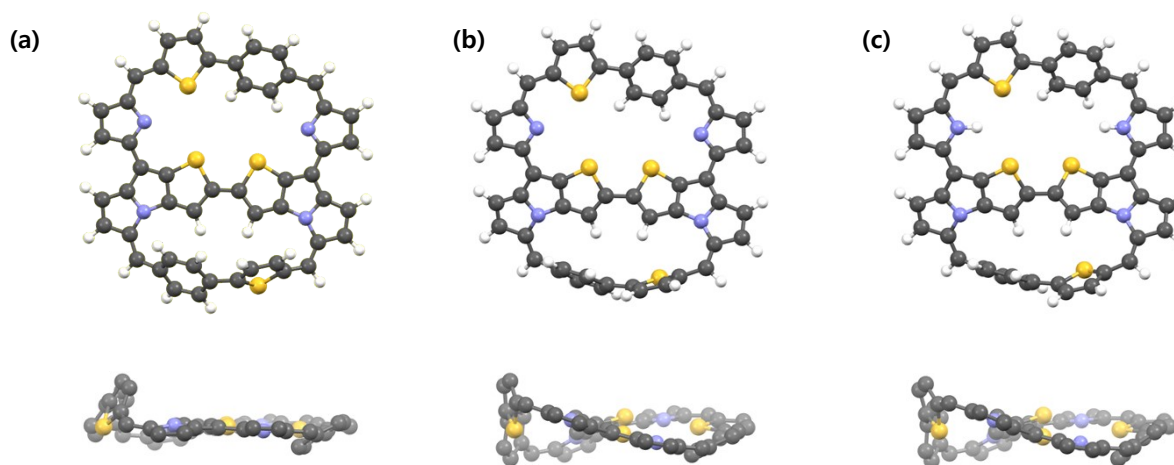


Figure S28. Optimized structures of (a) $5\bullet 2H^+$ and (b) $6\bullet 2H^+$ calculated with B3LYP/6-311G(d,p).



Figures S29. Optimized structures of (a) 5^{2+} , (b) 5 and (c) $5 \cdot 2H^+$ calculated with CAM-B3LYP/6-311G(d,p)



Figures S30. Optimized structures of (a) 6^{2+} , (b) 6 and (c) $6 \cdot 2H^+$ calculated using CAM-B3LYP/6-311G(d,p)

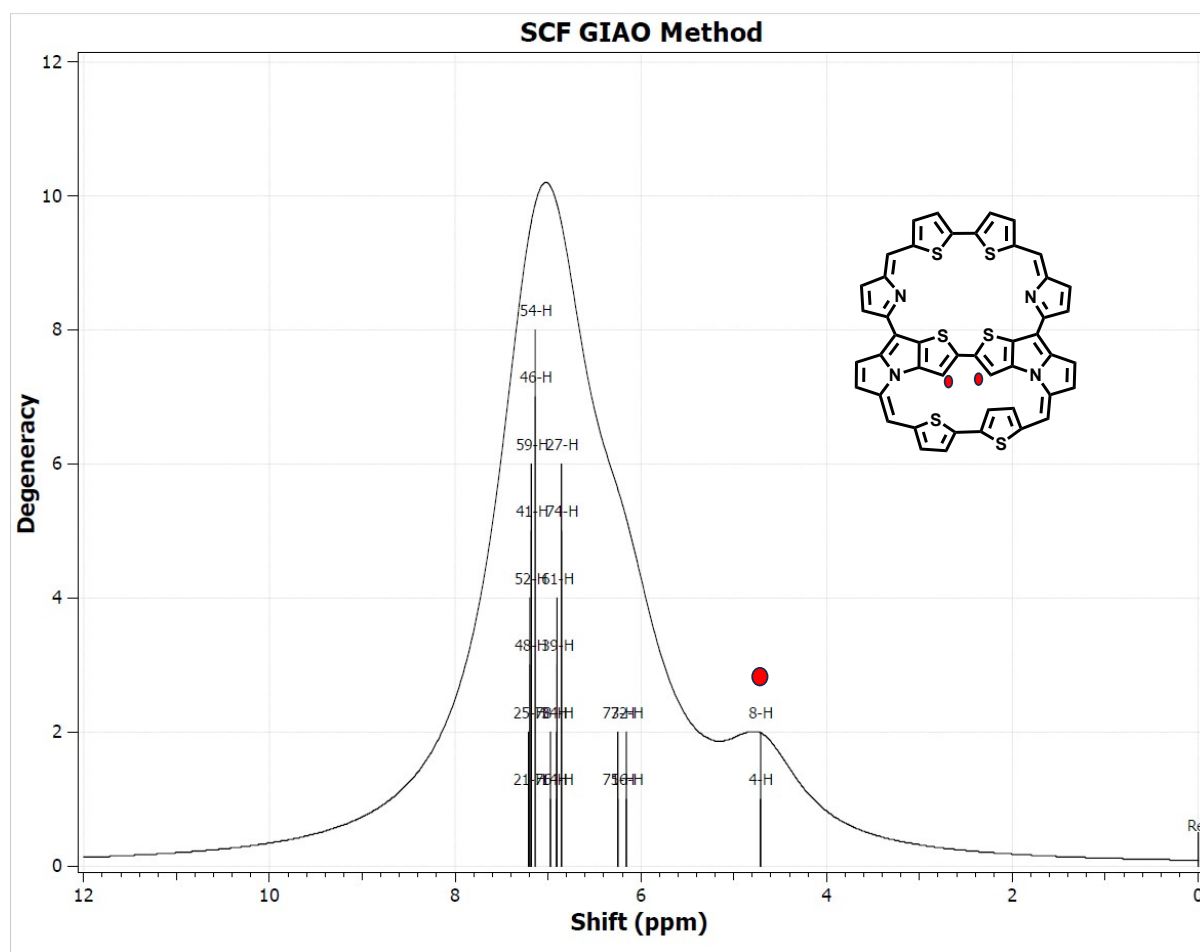


Figure S31. Calculated ^1H NMR chemical shifts for compound **5** obtained using the GIAO method at CAM-B3LYP levels

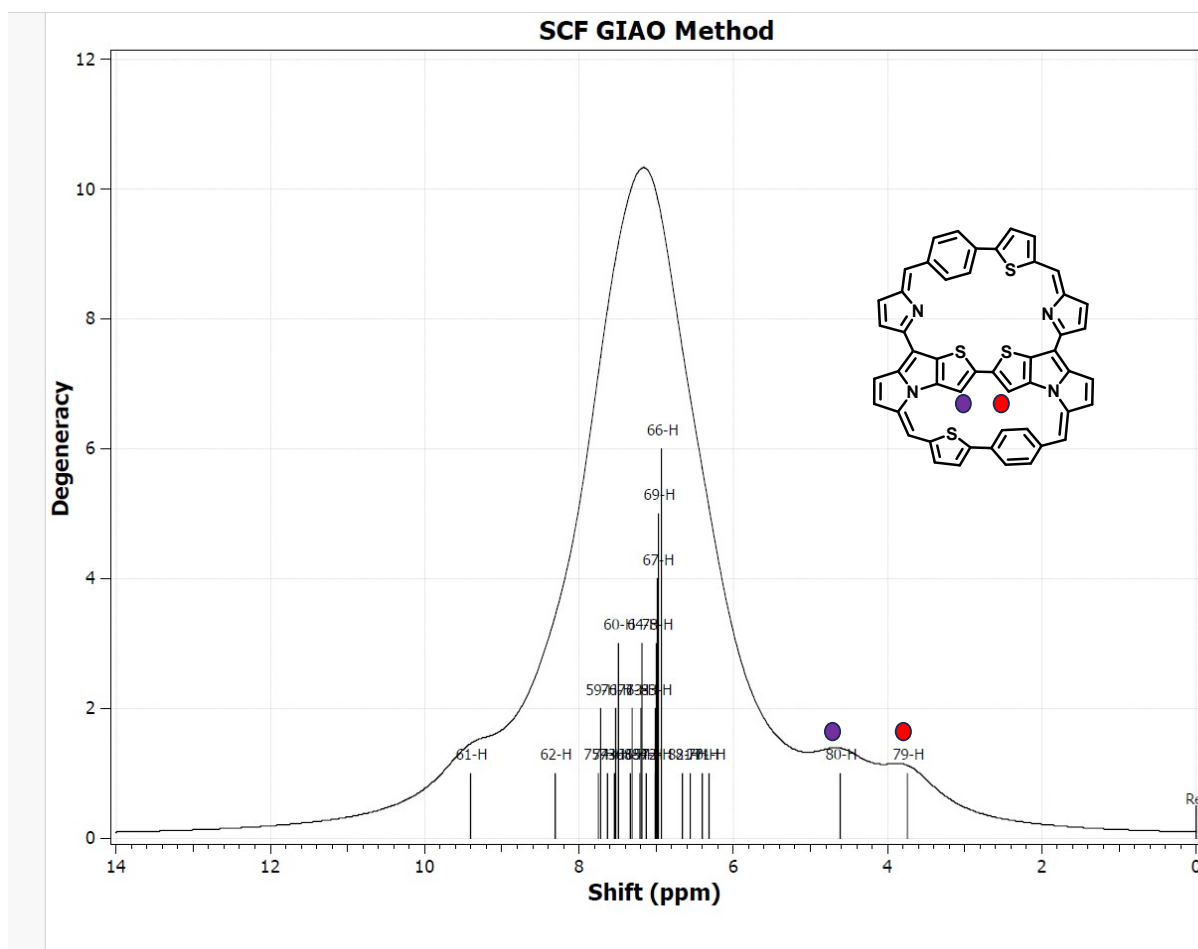


Figure S32. Calculated ^1H NMR chemical shifts for compound **6** obtained using the GIAO method at CAM-B3LYP levels

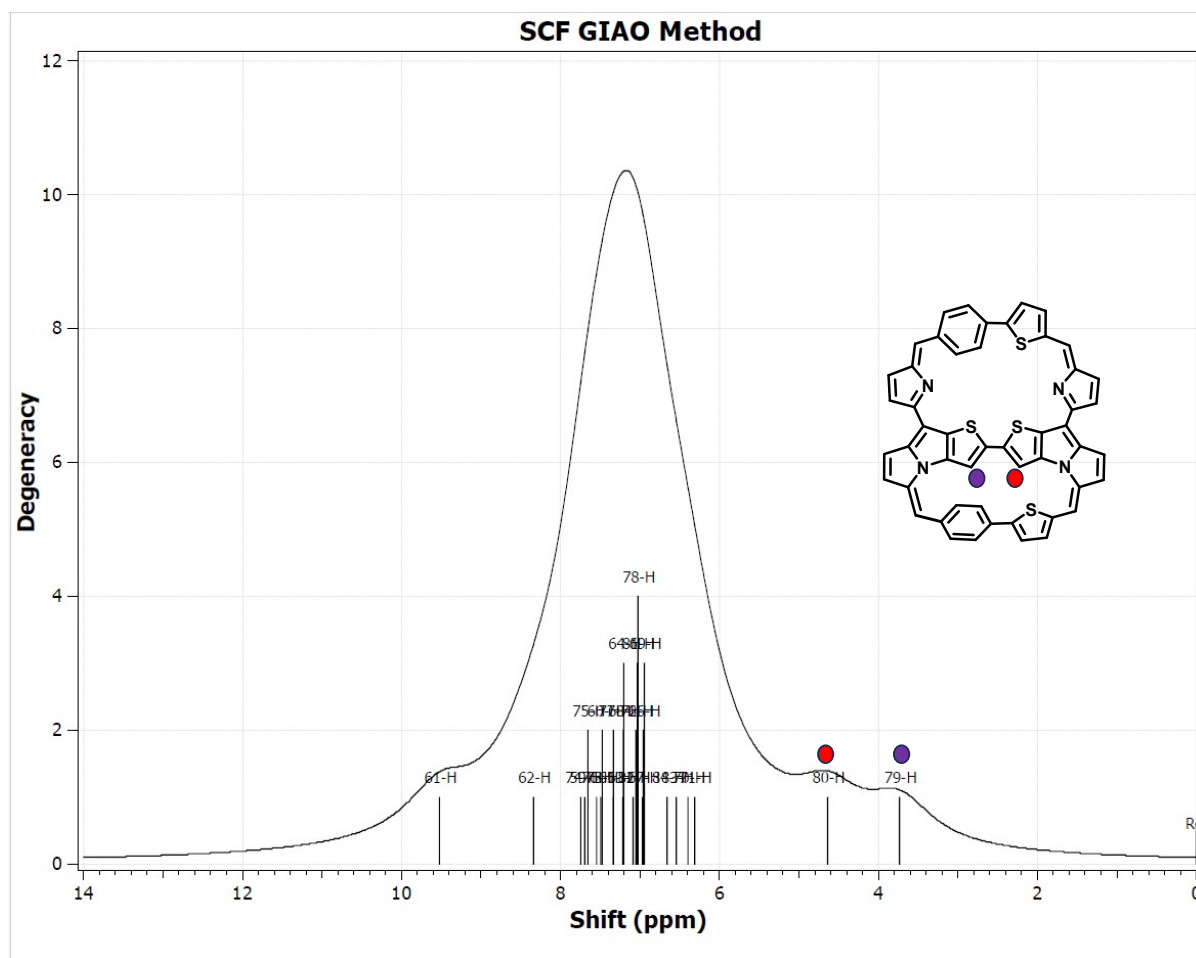


Figure S33. Calculated ¹H NMR chemical shifts for compound **6'** obtained using the GIAO method at CAM-B3LYP levels

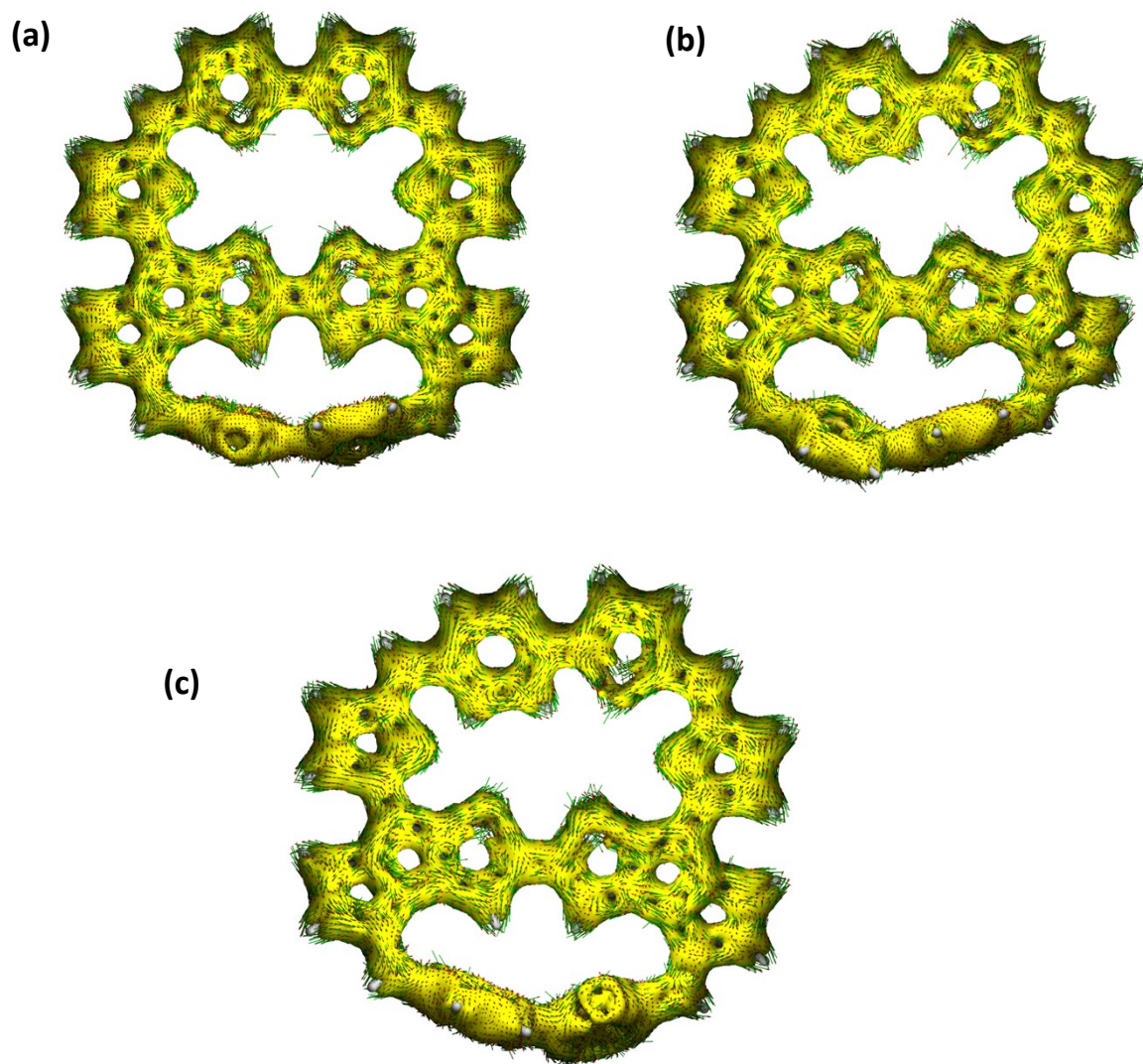


Figure S34. ACID plots for (a) **5**, (b) **6**, and (c) **6'** in S_0 state at isovalue of 0.04 calculated with B3LYP/6-311G(d,p) level of Theory. For clarity, mesityl substituents are omitted in the ACID calculations.

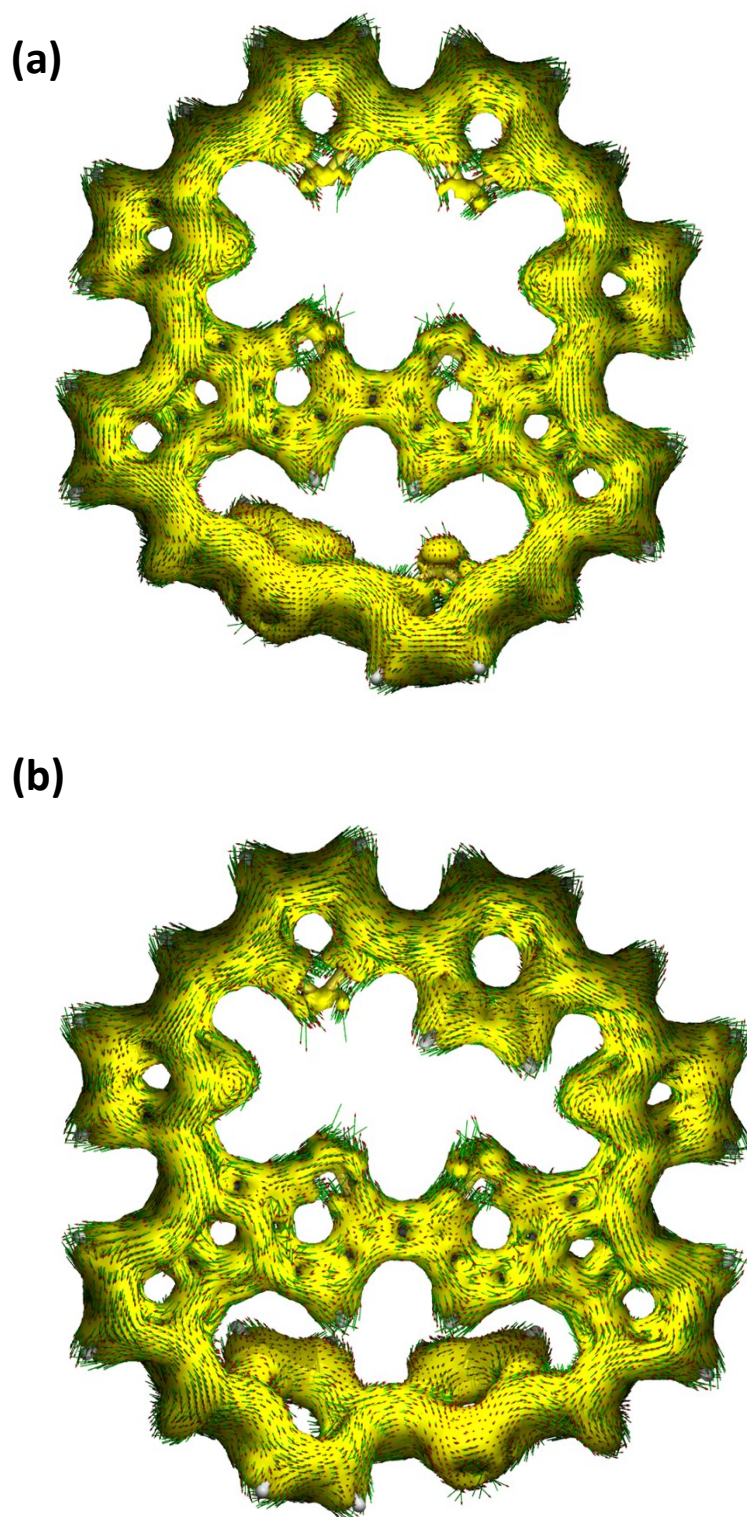


Figure S35. ACID plots for (a) $[5]^{2+}$ and $[6]^{2+}$ in S_0 state at isovalue of 0.04 calculated with B3LYP/6-311G(d,p) level of Theory.

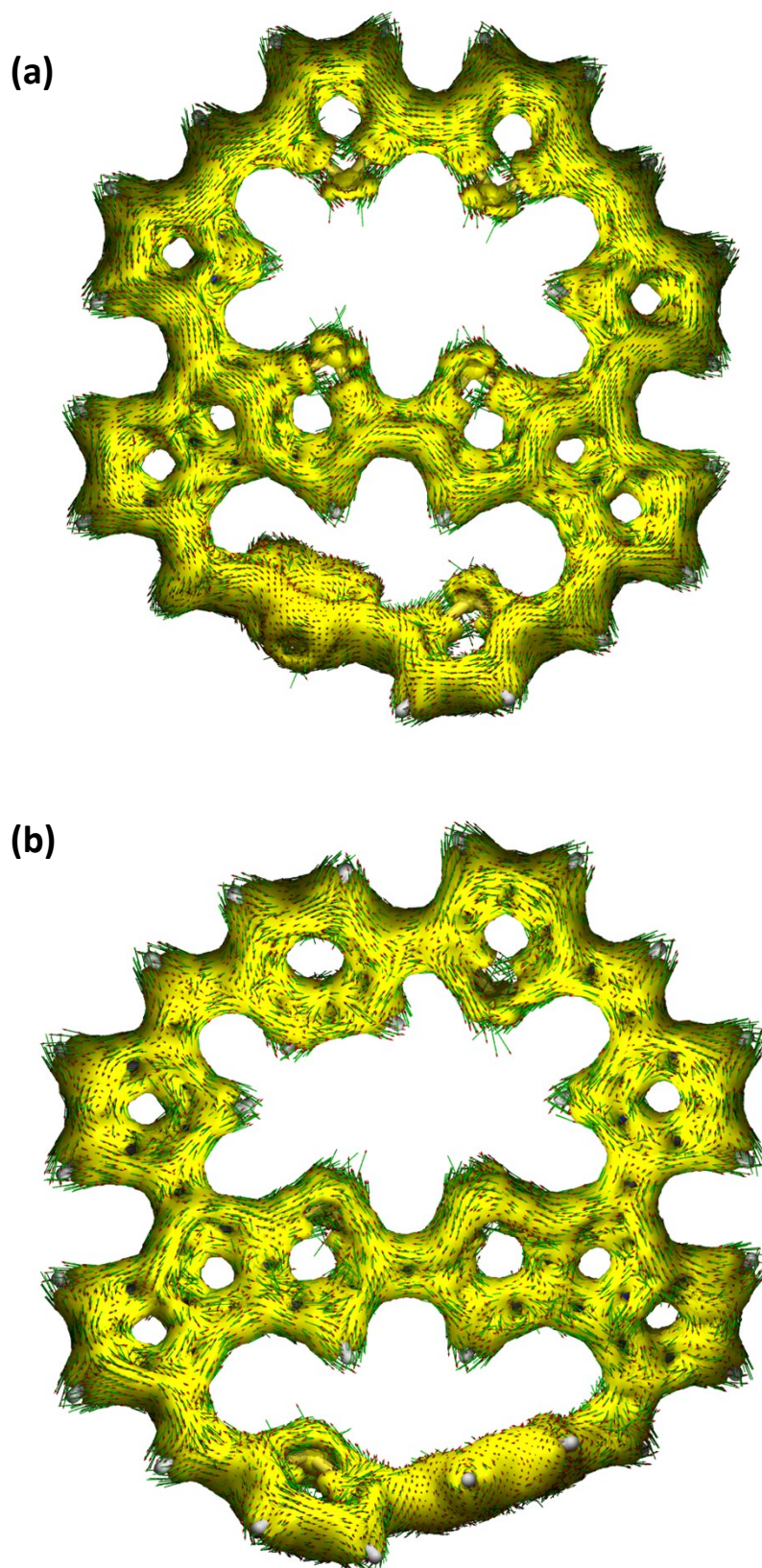


Figure S36. ACID plots for (a) $5 \cdot 2H^+$ in T_1 state and (b) $6 \cdot 2H^+$ in S_0 state at isovalue of 0.04 calculated with B3LYP/6-311G(d,p) level of Theory.

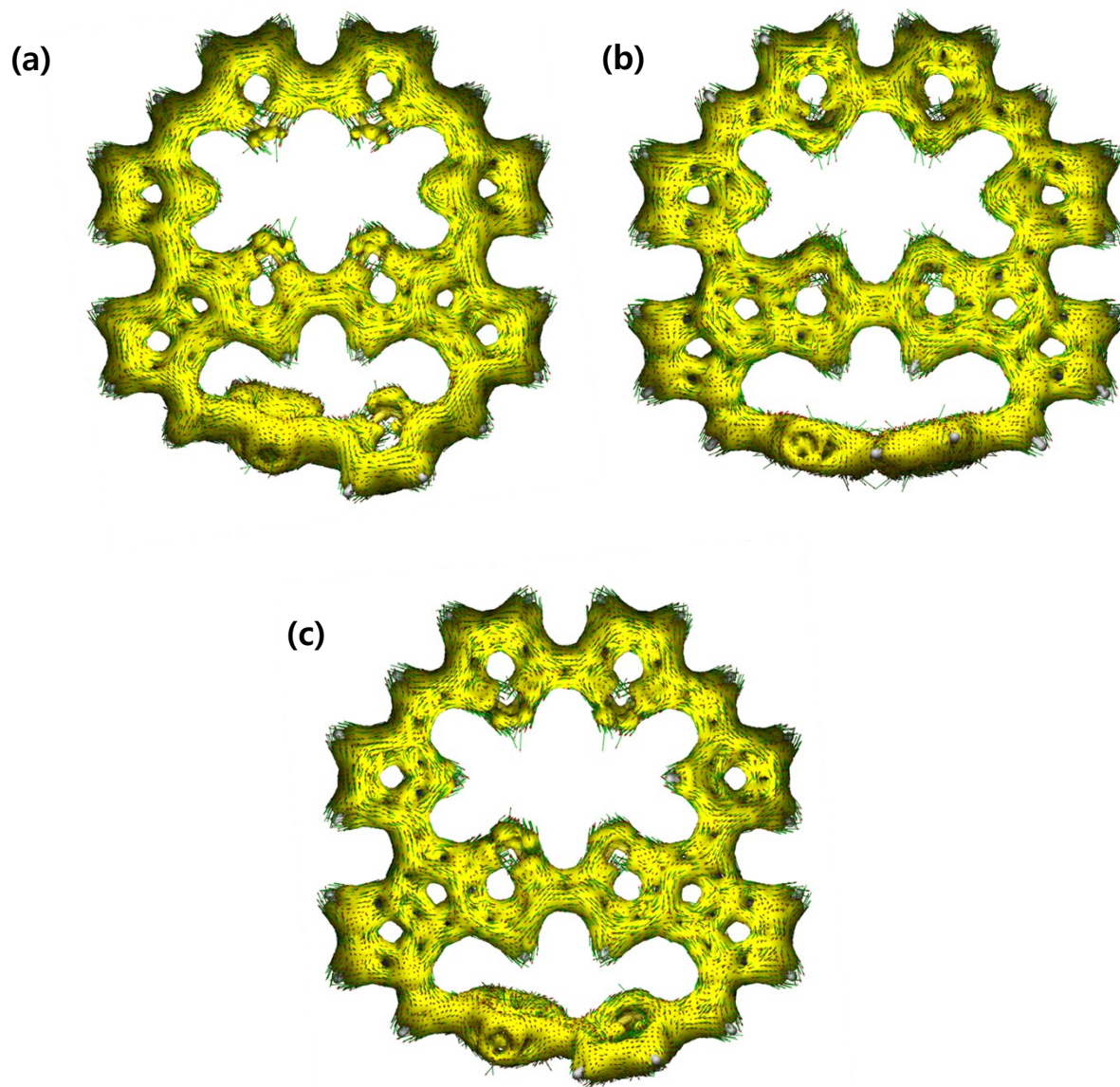


Figure S37. ACID plots for (a) 5^{2+} , (b) 5 in S_0 state and (c) $5 \cdot 2H^+$ in T_1 state at isovalue of 0.04 calculated with CAM-B3LYP/6-311G(d,p) level of Theory.

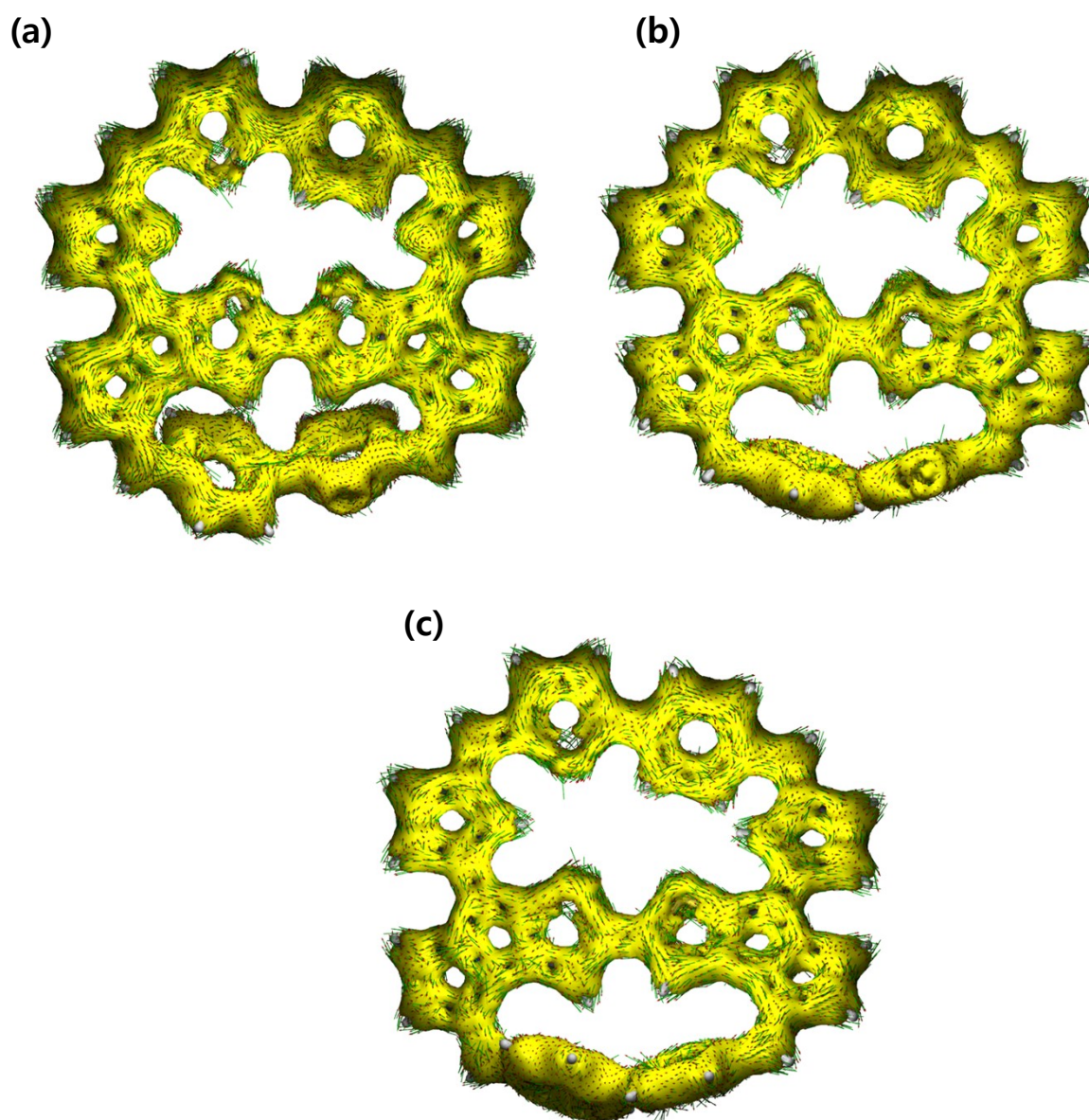


Figure S38. ACID plots for (a) 6^{2+} , (b) **6** in S_0 state and (c) $6 \cdot 2H^+$ at isovalue of 0.04 calculated with CAM-B3LYP/6-311G(d,p) level of Theory.

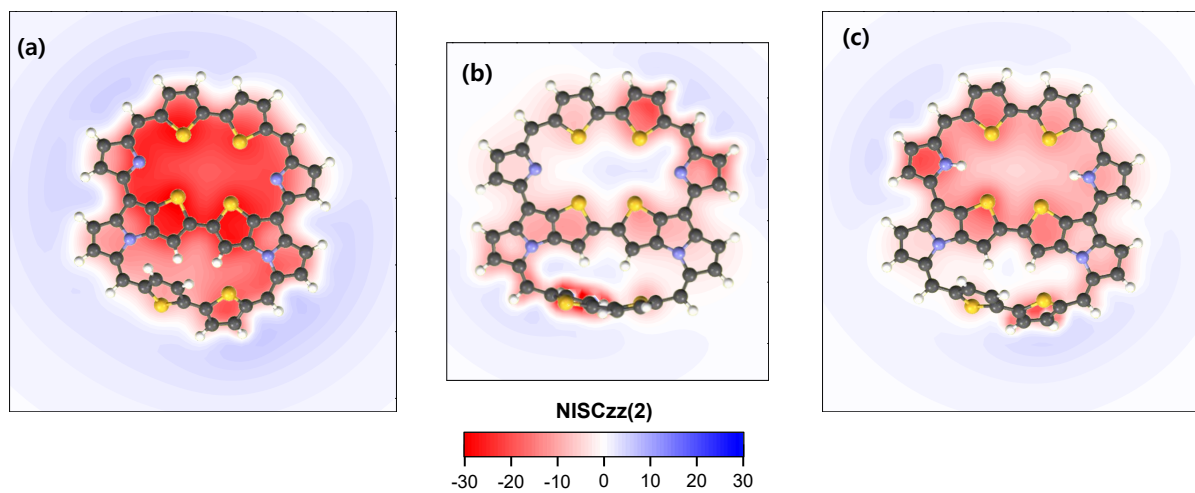


Figure S39. NICS_{zz}(2) scans of octaphyrins (a) 5^{2+} (S_0), (b) **5** (S_0) and (c) $5 \cdot 2H^+$ (T_1) calculated with CAM-B3LYP/6-311G(d,p) level of Theory.

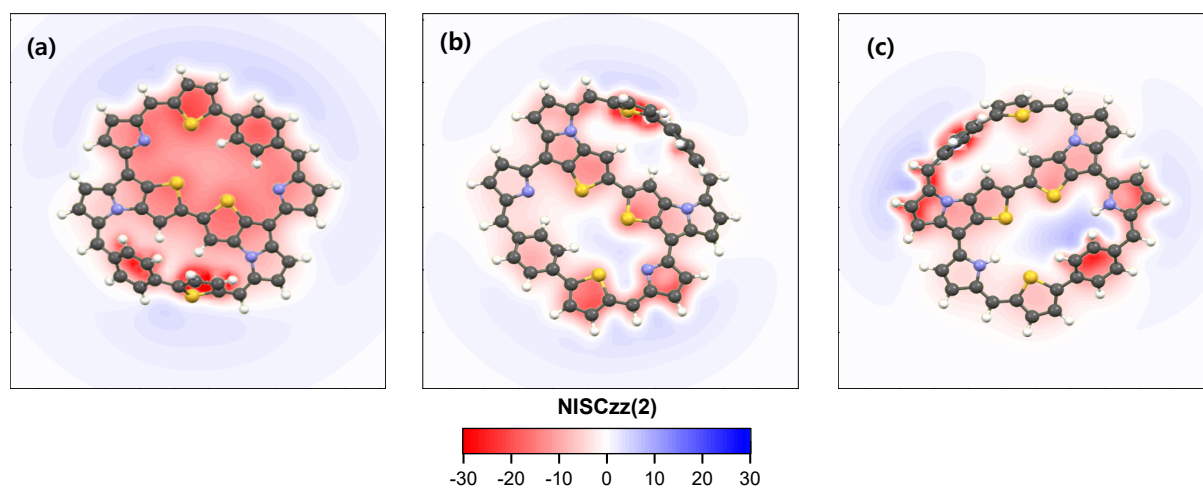


Figure S40. NICS_{zz}(2) scans of octaphyrins (a) 6^{2+} (S_0), (b) **6** (S_0) and (c) $6 \cdot 2H^+$ (S_0) calculated with CAM-B3LYP/6-311G(d,p) level of Theory.

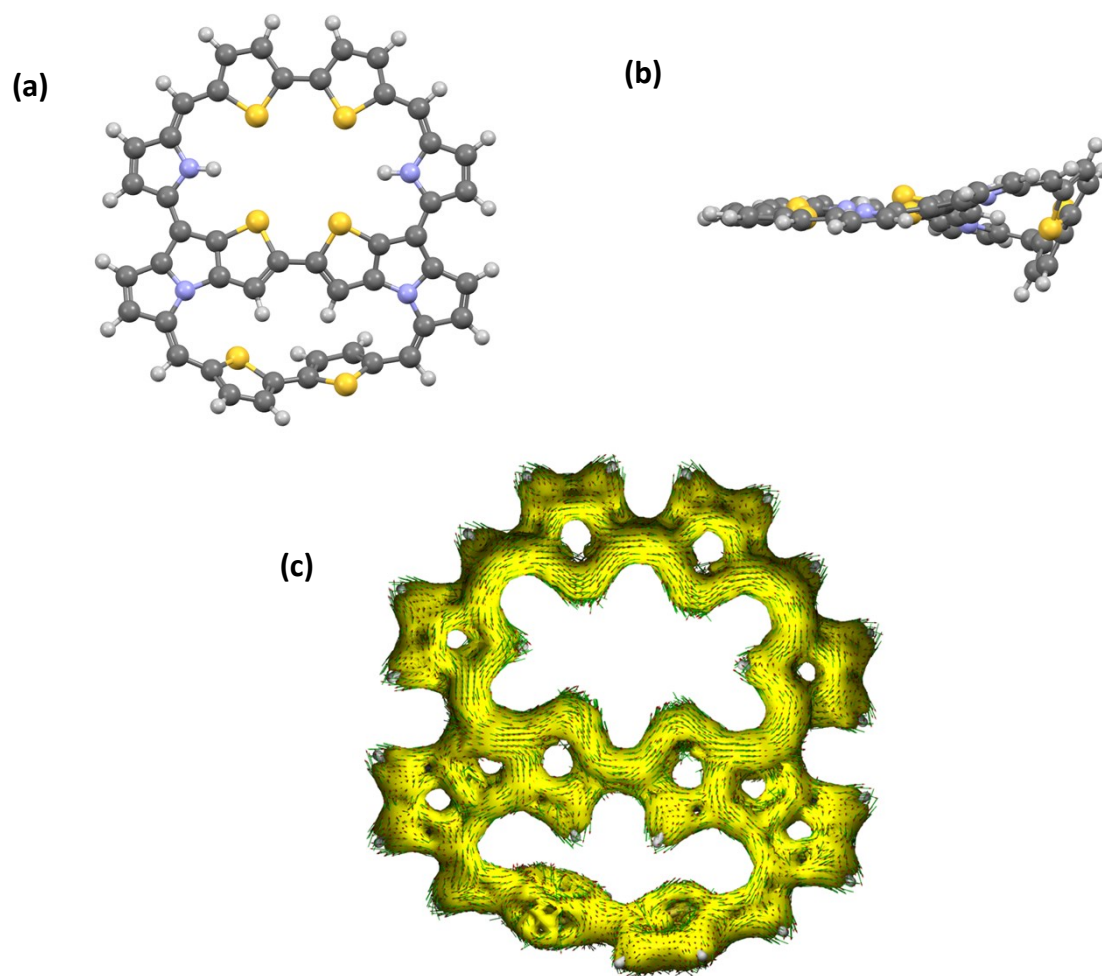


Figure S41. Optimized structure of singlet state (S_0) of $5\bullet 2H^+$ (a) front view, (b) side view and (c) AICD plot calculated with CAM-B3LYP/6-311G(d,p)

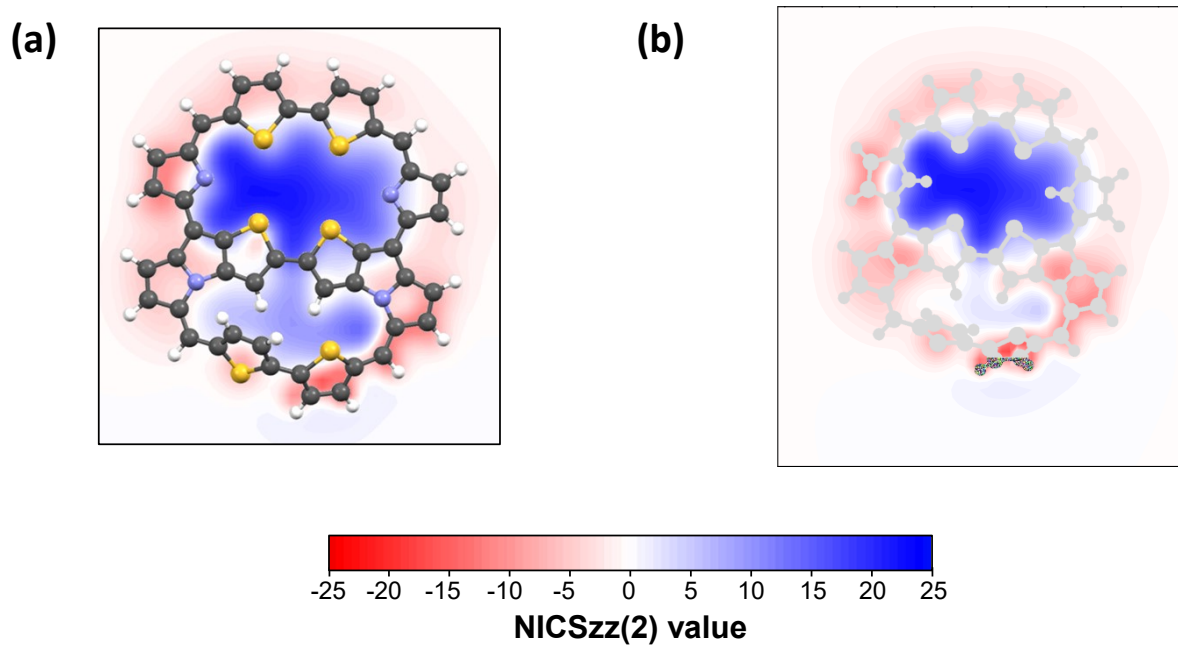
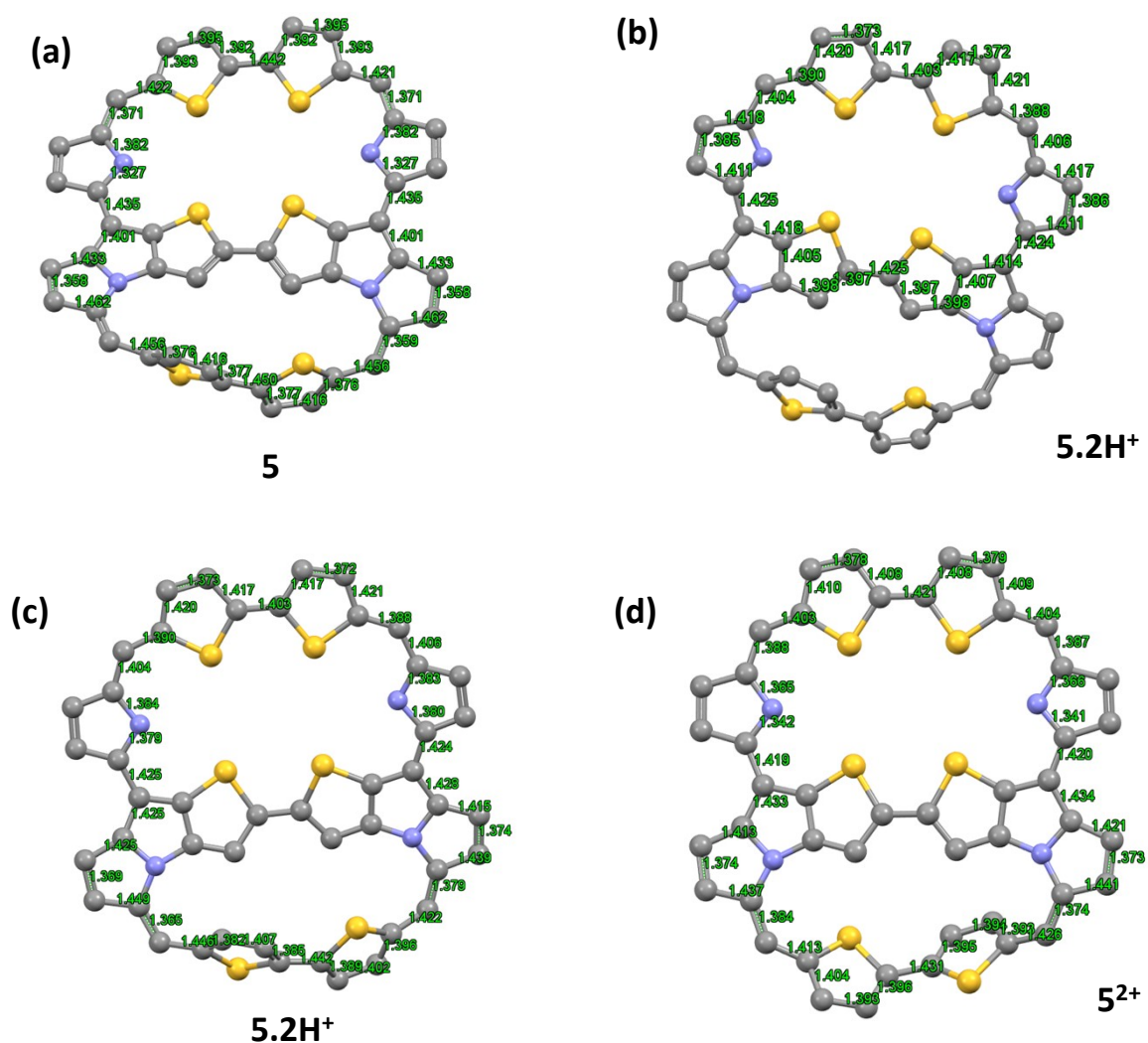
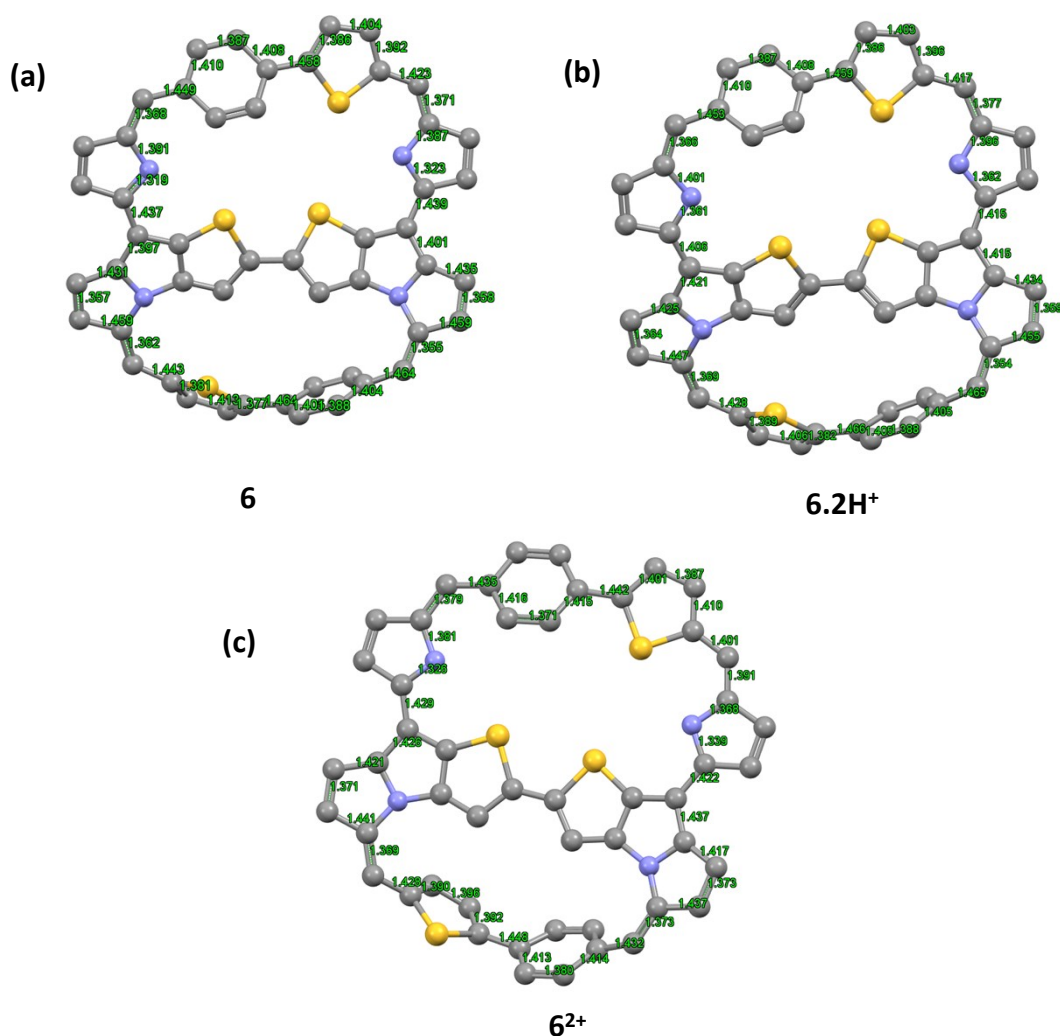


Figure S42. NICS_{zz} Scan for 5•2H⁺ in S₀ state with (a) B3LYP/6-311G(d,p) and (b) CAM-B3LYP/6-311G(d,p) level of Theory.



Compound	R _{avg}	EN	GEO	HOMA	BLA
5	1.404	0.066	0.289	0.64	0.065
5.2H ⁺ (upper ring)	1.399	0.031	0.146	0.82	0.026
5.2H ⁺ (full ring)	1.401	0.043	0.149	0.81	0.042
5 ²⁺	1.401	0.044	0.159	0.80	0.041

Figure S43. HOMA values of (a) [36] π -electron conjugation pathway for **5**. (b) [28] π - and (c) [36] π -electron conjugation pathways for **5•2H⁺**. (d) [34] π -electron conjugation pathways for **[5]²⁺**.



Compound	R_{avg}	EN	GEO	HOMA	BLA
6	1.401	0.044	0.320	0.63	0.064
6.2H⁺	1.401	0.044	0.325	0.63	0.056
6²⁺	1.400	0.037	0.272	0.69	0.052

Figure S44. HOMA values for [36] π -electron conjugation pathways for (a) **6**, (b) **6•2H⁺** and (c) **[6]²⁺**. The α and R_{opt} (Å) values were taken as 257.7 Å⁻² and 1.397, 1.334 respectively for C-C and C-N. *Meso*-substituents and protons are omitted for clarity.

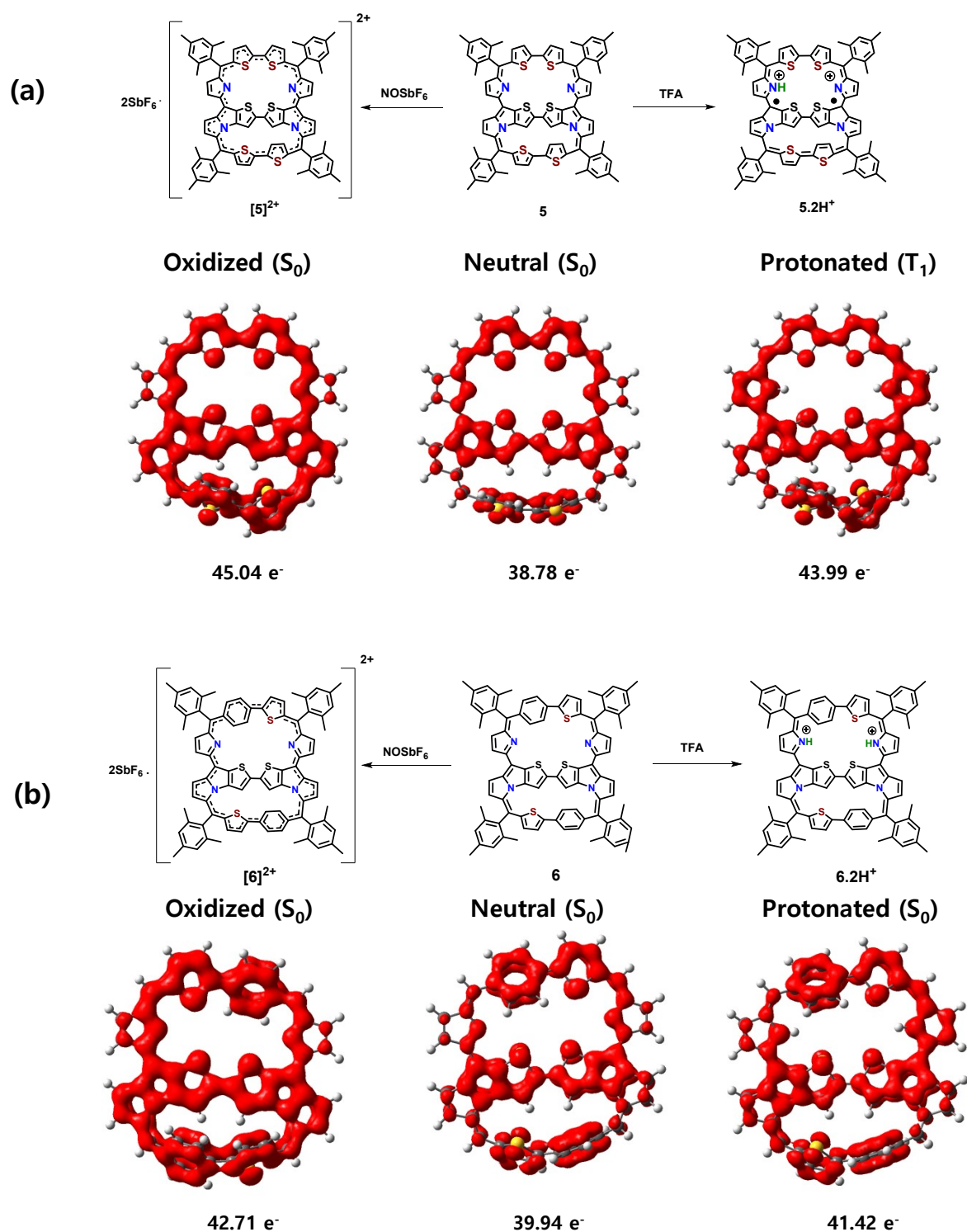


Figure S45. Electron density of delocalized bonds (EDDB) analysis of (a) **5** in neutral, two-electron oxidized, and diprotonated states, where **5•2H⁺** was calculated in the T₁ state, and (b) **6** in its neutral, two-electron oxidized, and diprotonated states. The values indicate quantitative delocalized electron density.

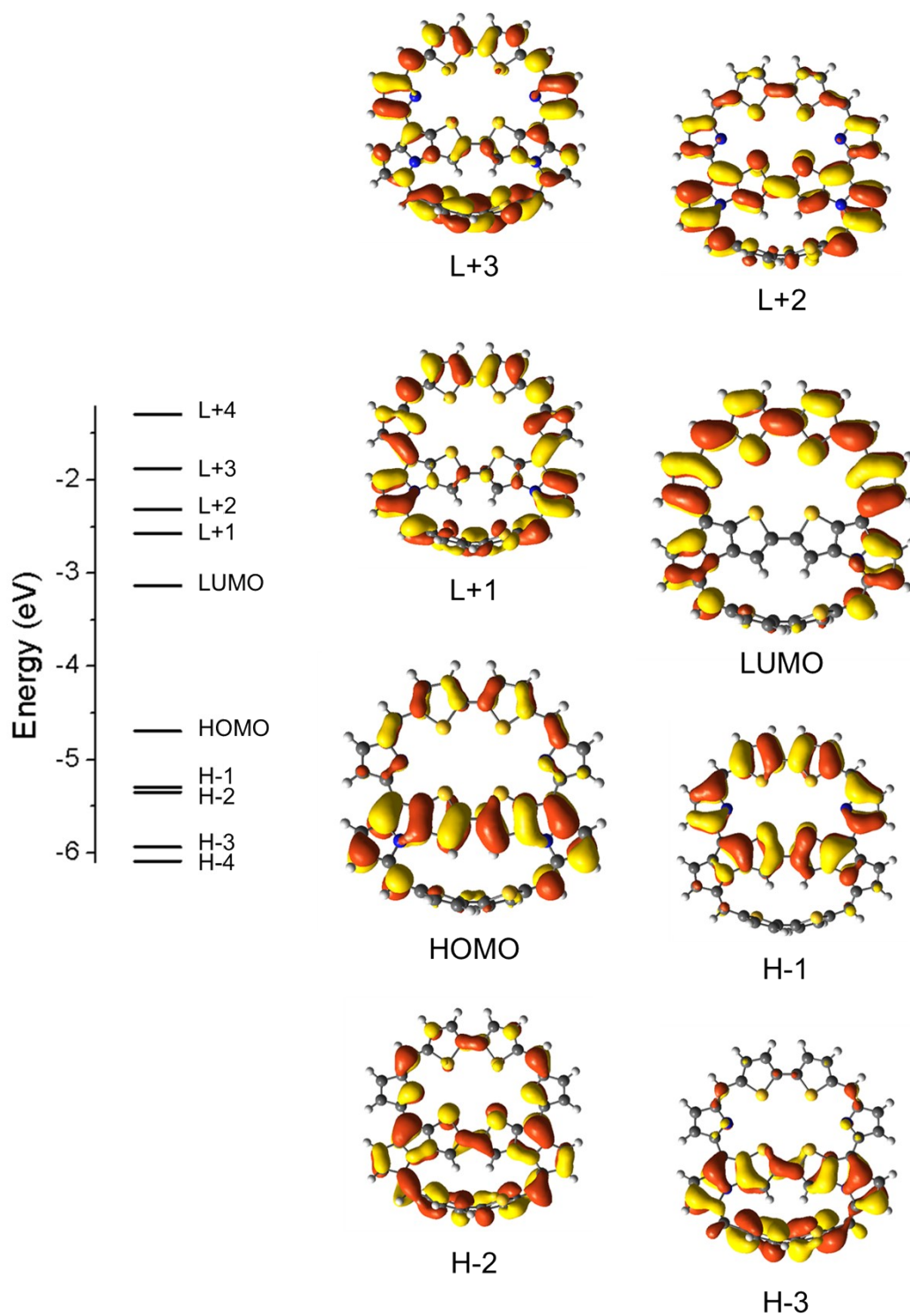


Figure S46. Frontier MO diagram of **5** in its neutral S_0 state.

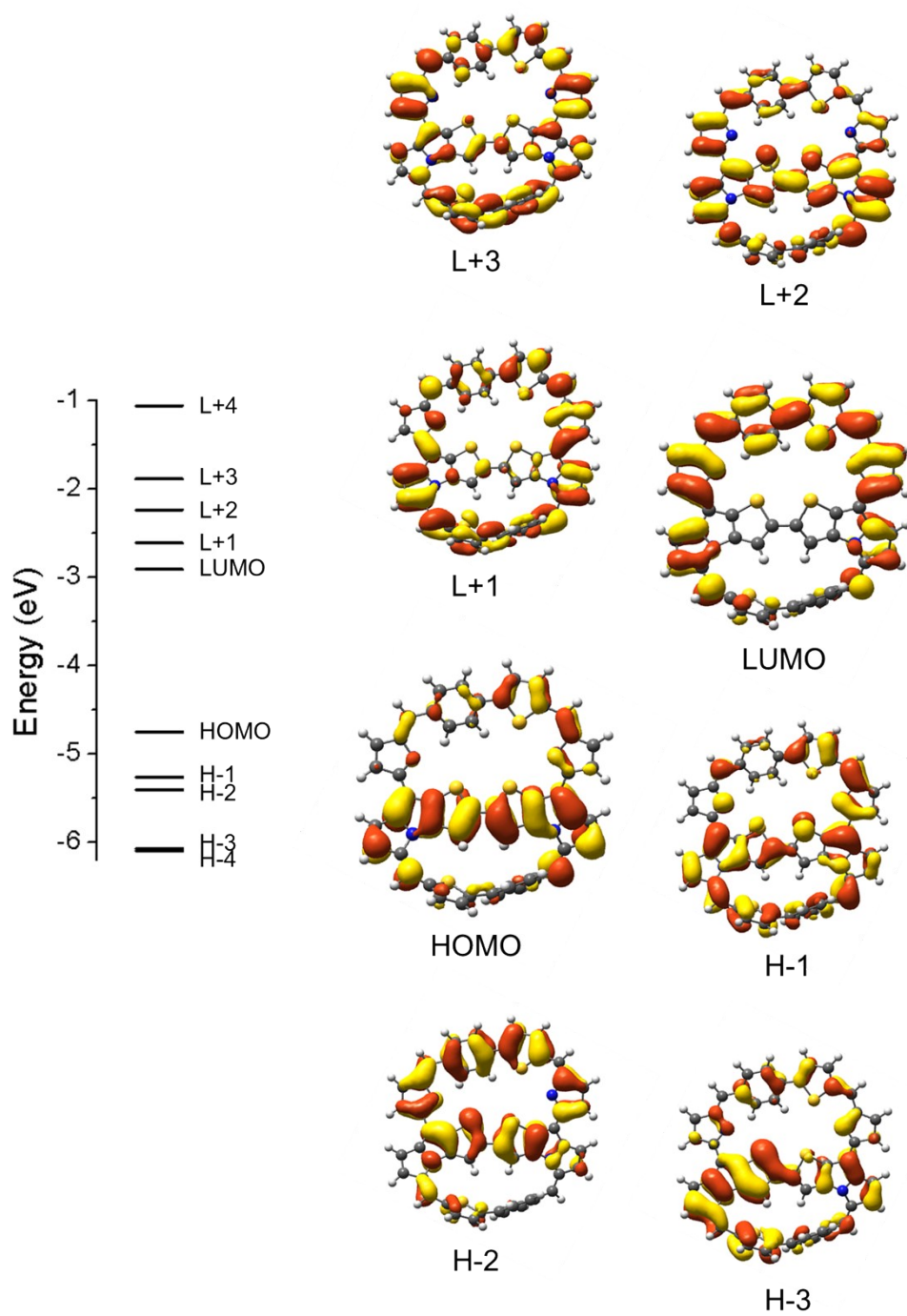


Figure S47. Frontier MO diagram of **6** in its neutral S_0 state.

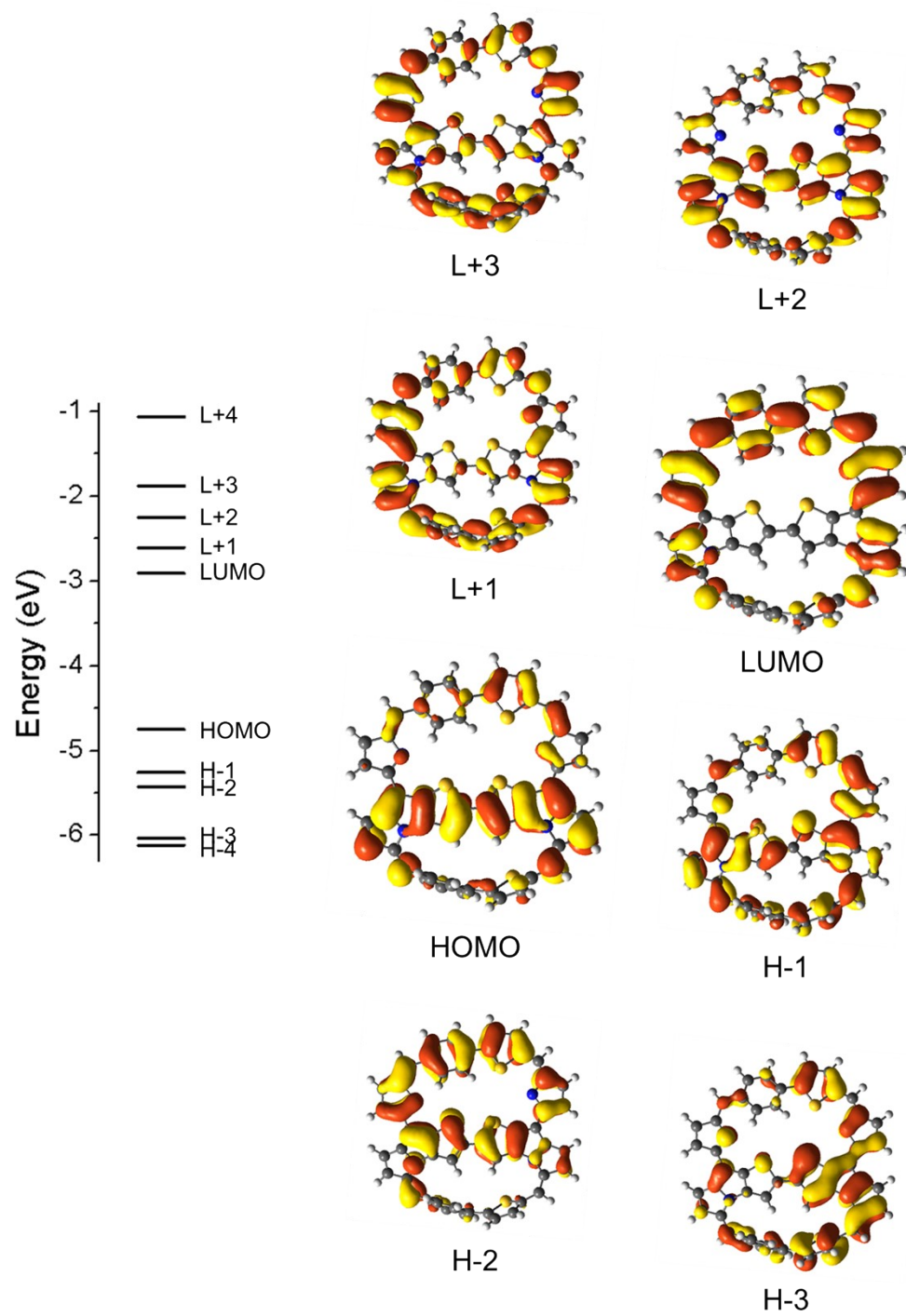


Figure S48. Frontier MO diagram of neutral **6'** in its neutral S_0 state.

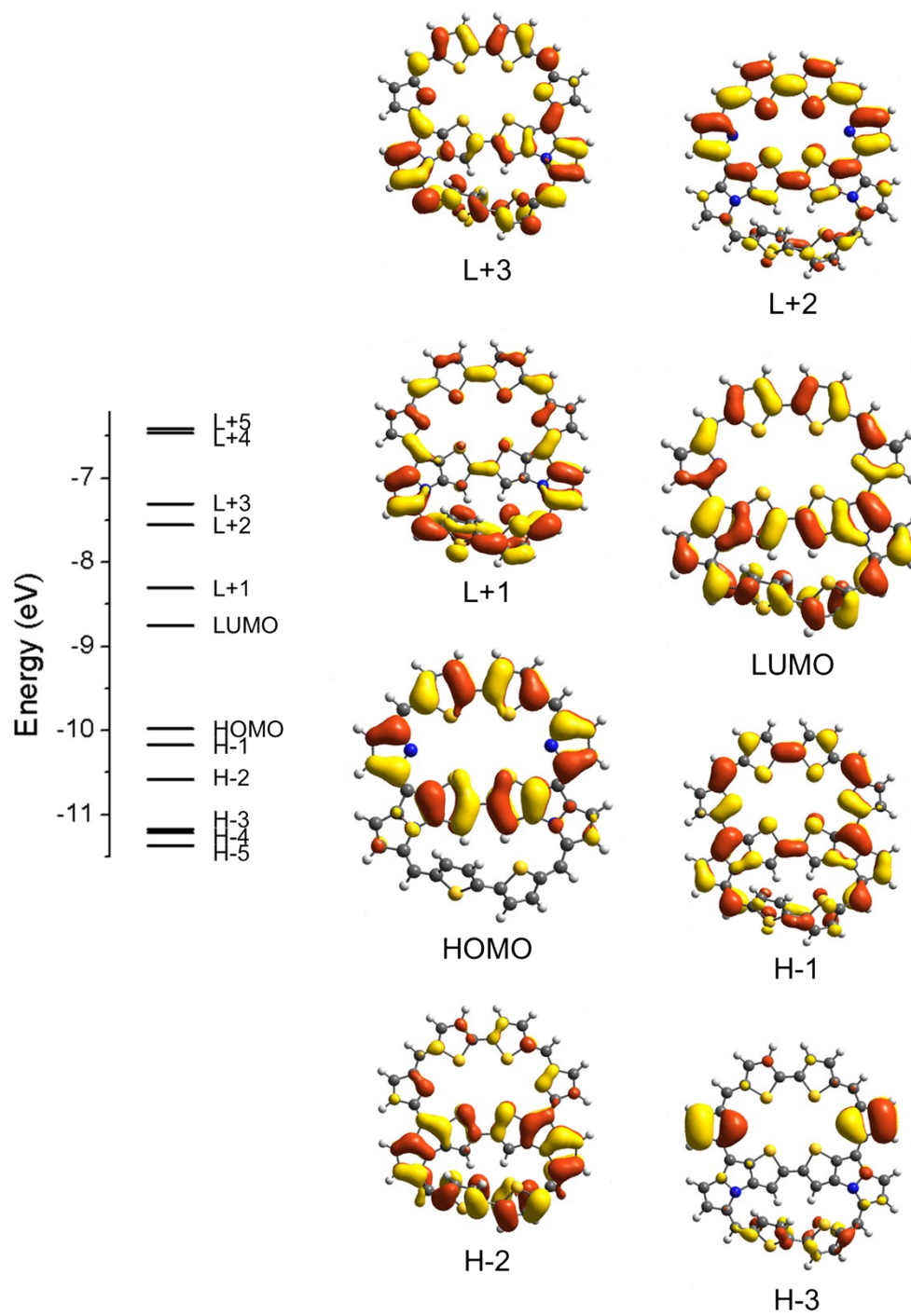


Figure S49. Frontier MO diagram of $[5]^{2+}$ in its S_0 state.

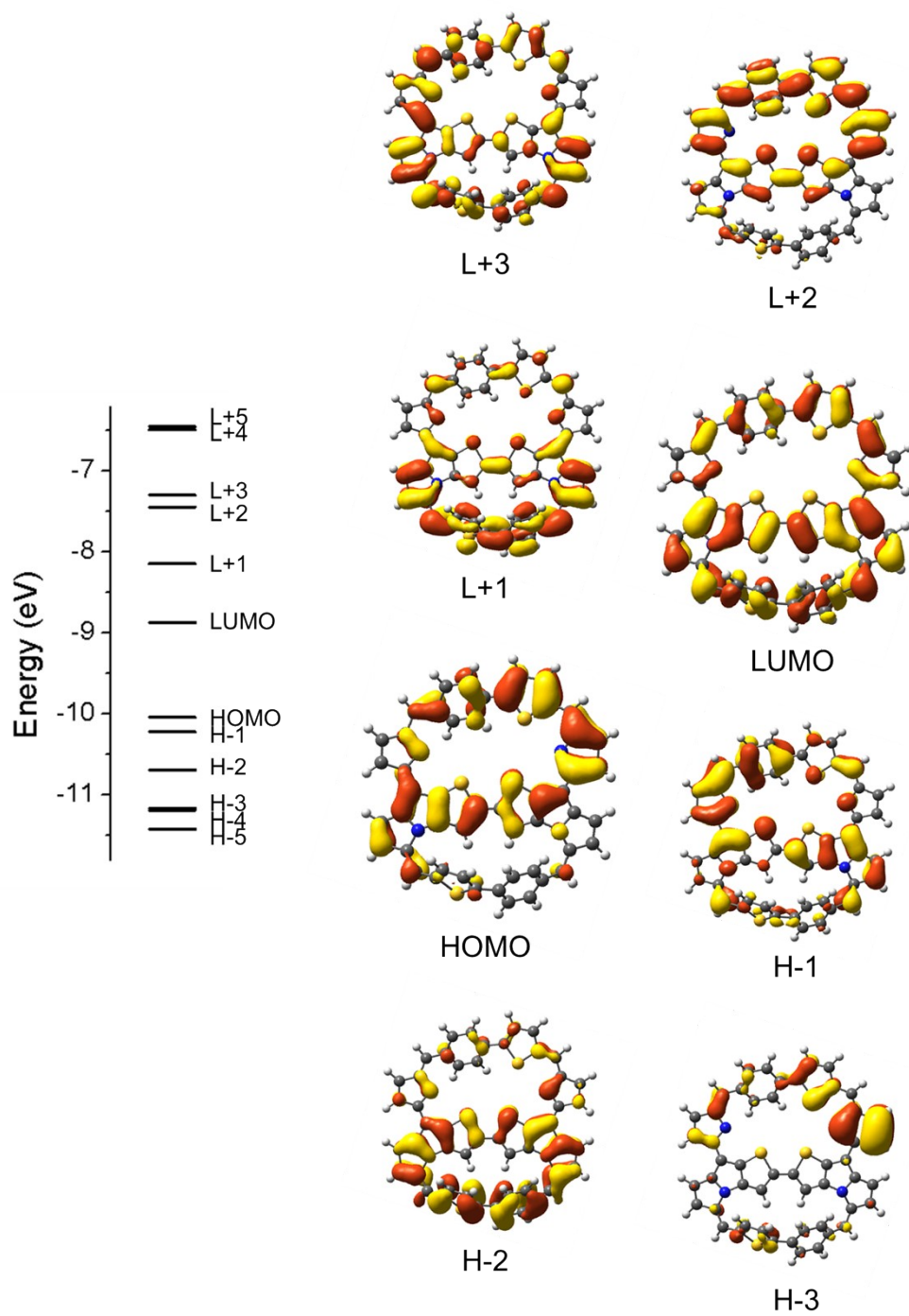


Figure S50. Frontier MO diagram of $[6]^{2+}$ in its S_0 state.

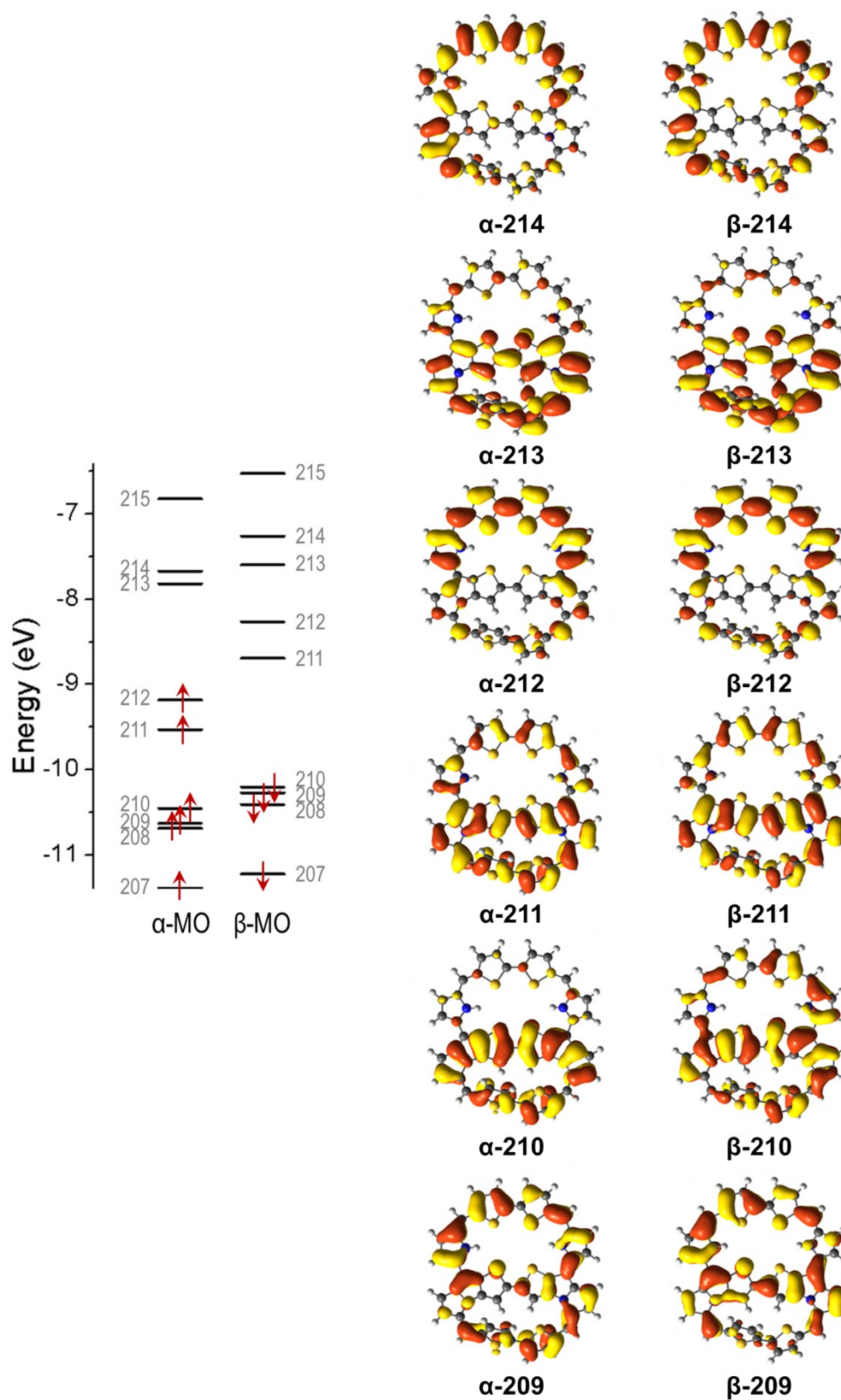


Figure S51. Frontier MO diagram of $5\cdot 2H^+$ in its T_1 state.

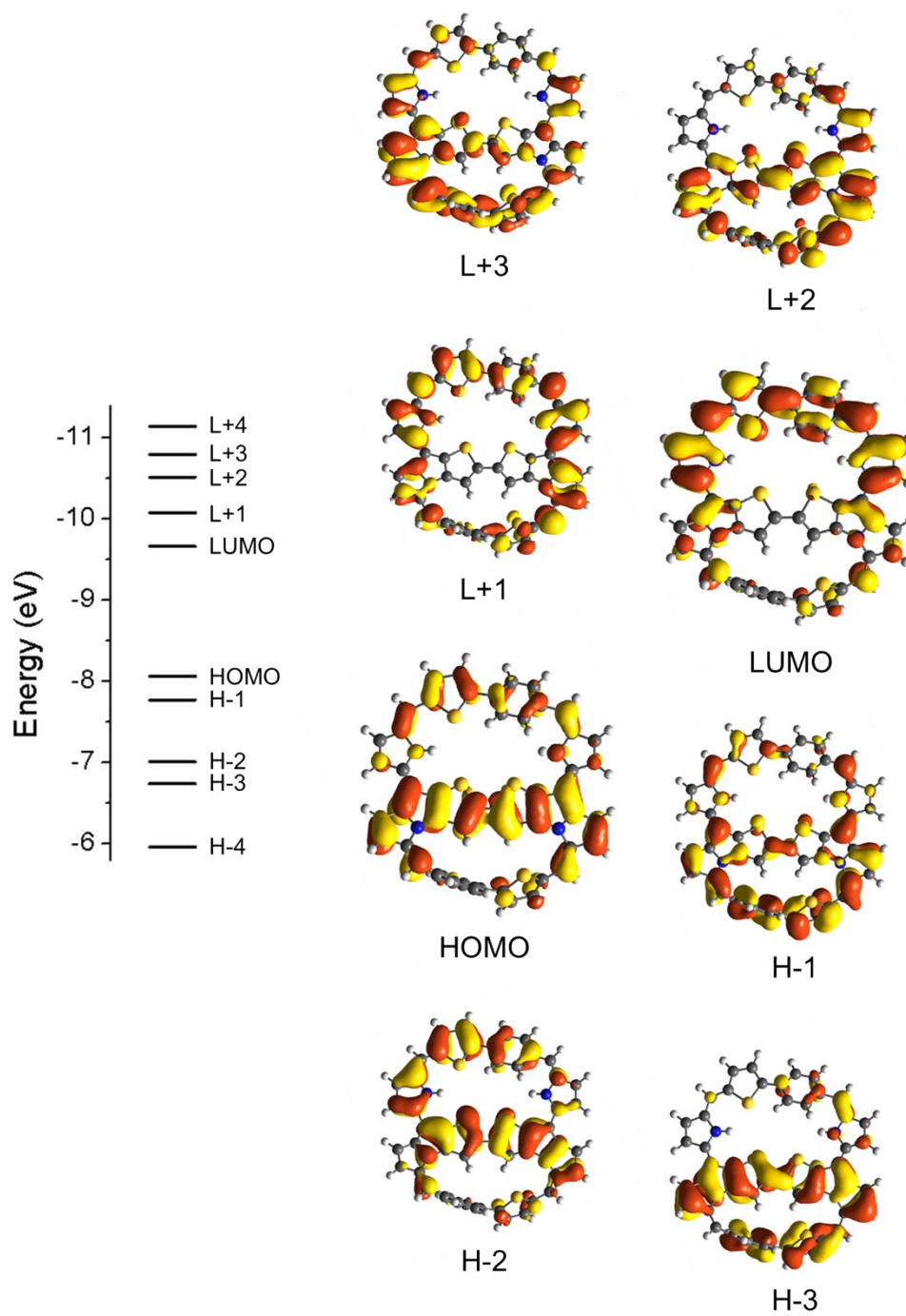


Figure S52. Frontier MO diagram of $6\bullet 2H^+$ in its S_0 state.

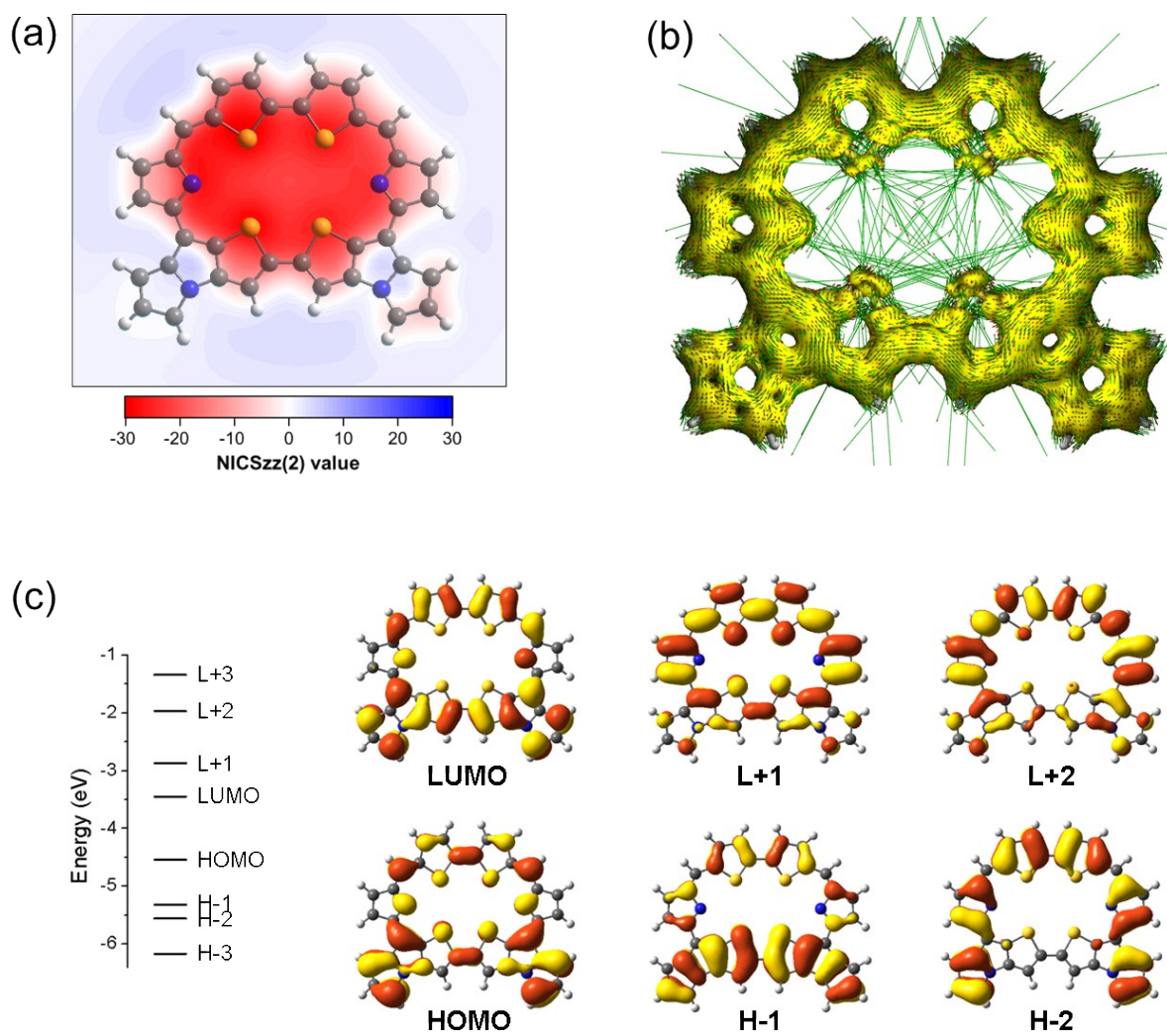


Figure S53. (a) $\text{NICS}_{zz}(2)$ map, (b) ACID plot, and (c) MO diagram of the isolated upper sub-macrocycle present in **5**.

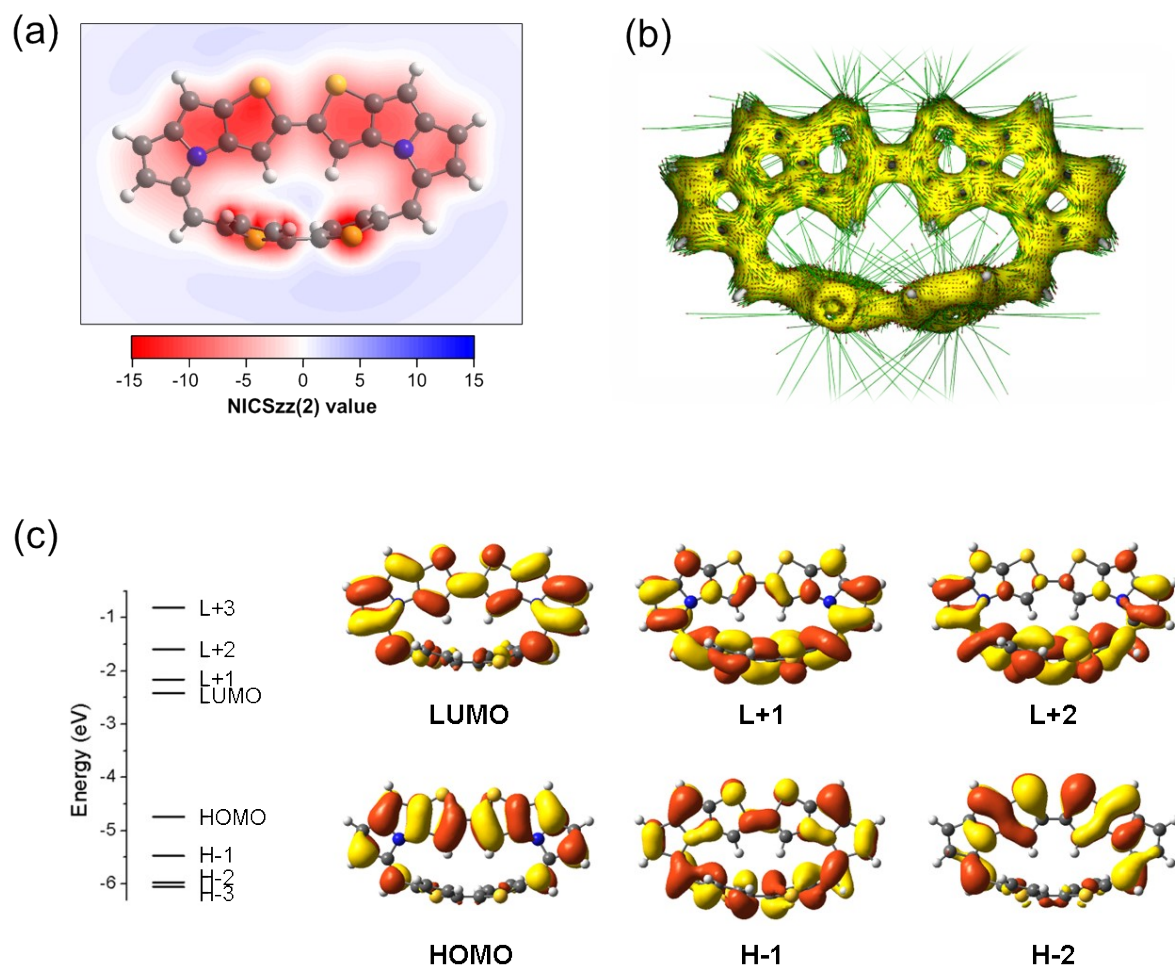


Figure S54. (a) $\text{NICS}_{zz}(2)$ map, (b) ACID plot, and (c) MO diagram of the isolated bottom sub-macrocycle present in **5**.

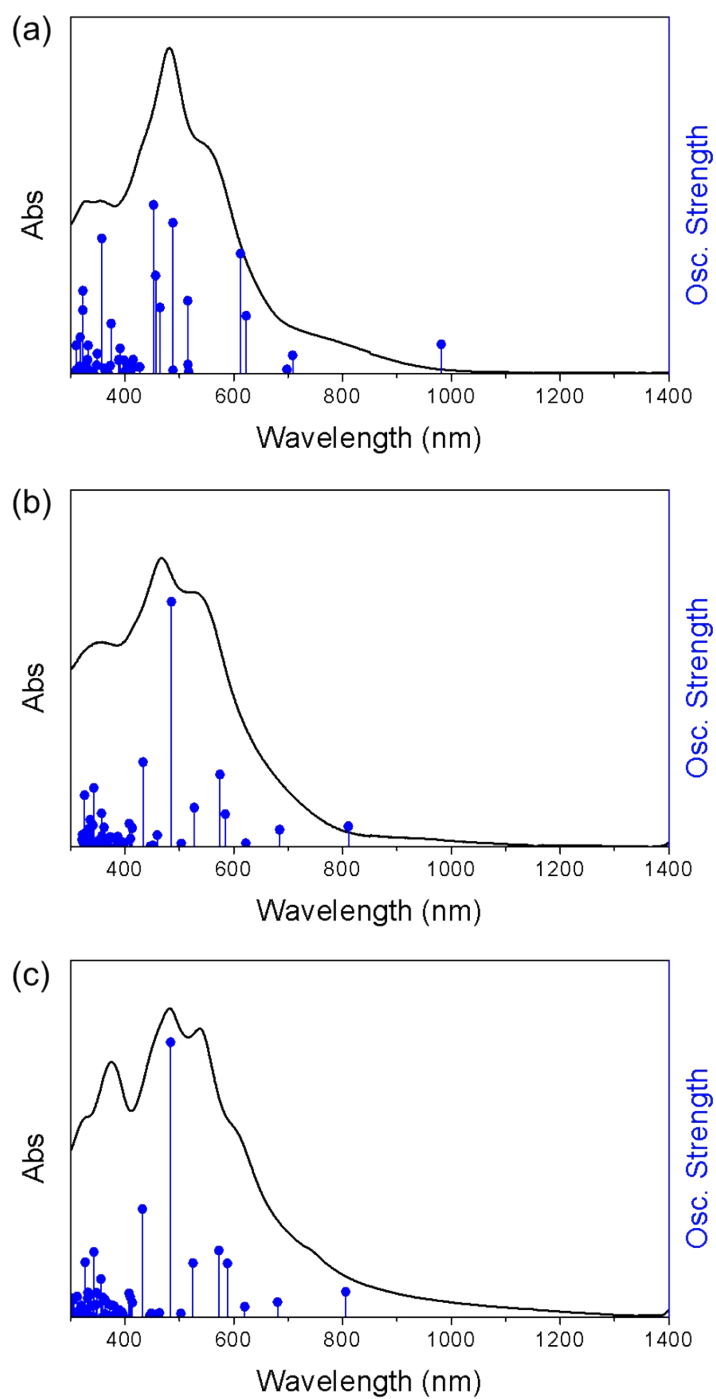


Figure S55: UV-Vis-NIR absorption spectra of (a) **5**, (b) **6**, and (c) **6'** with their simulated electronic transitions.

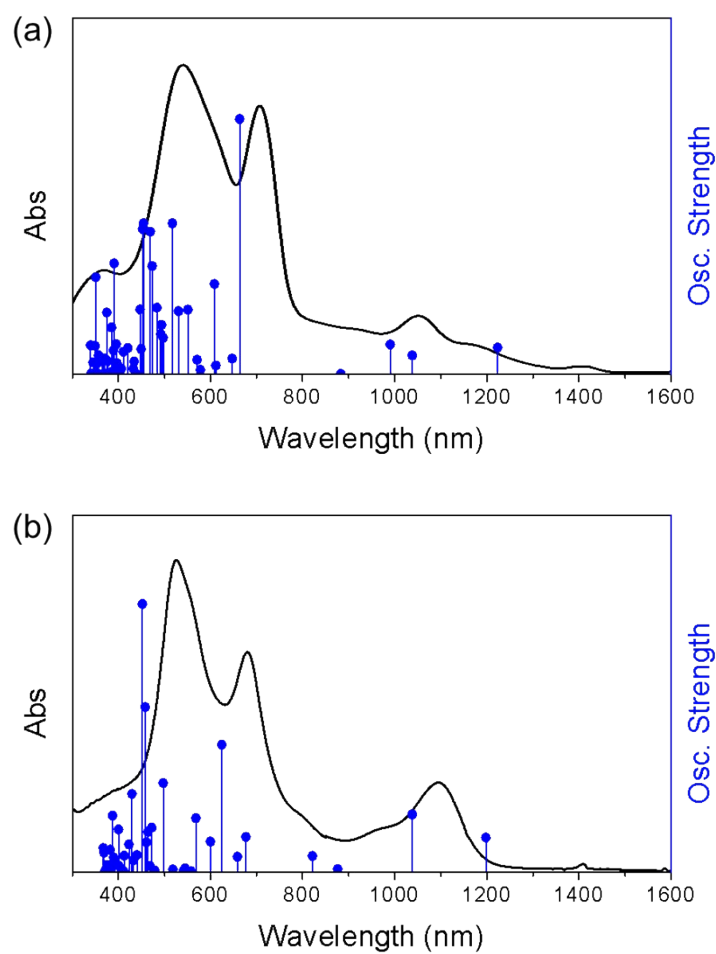


Figure S56. UV-Vis-NIR absorption spectra of (a) $[5]^{2+}$ and (b) $[6]^{2+}$ with their simulated electronic transitions.

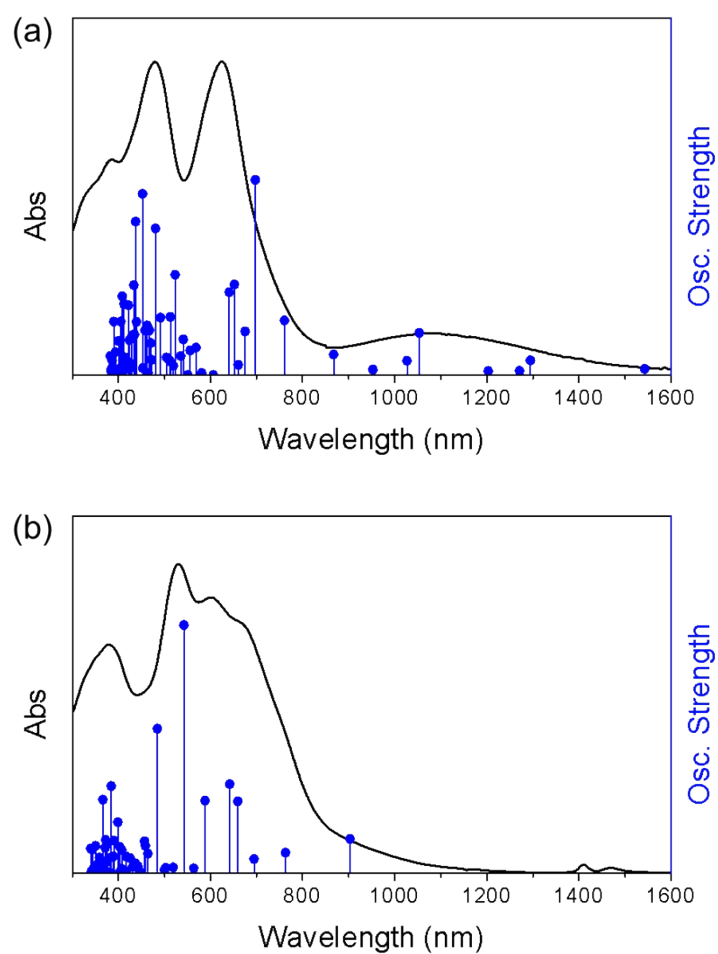


Figure S57. UV-Vis-NIR absorption spectra of (a) $5\bullet 2H^+$ in the T_1 state and (b) $6\bullet 2H^+$ in the S_0 state with their simulated electronic transitions.

Table S4: Coordinates for S₀ optimized geometry of the normal conformer of *meso* free compound **5** at B3LYP/6-311G** level of theory # Sum of imaginary frequencies=0 # Total Energy (hartree) = -4374.733733

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.219098000	-3.098809000	0.086822000	C	3.179853000	-6.340721000	0.773128000
C	-1.564851000	-2.911778000	-0.222703000	H	3.849474000	-7.168483000	0.958887000
C	-1.941182000	-1.555338000	-0.318645000	C	3.567142000	-4.937136000	0.670299000
H	-2.898117000	-1.177790000	-0.632141000	C	4.850779000	-4.461146000	0.750295000
C	-0.878815000	-0.720136000	-0.019276000	C	5.347825000	-3.139683000	0.584492000
C	-0.878886000	0.720133000	0.019593000	C	6.696740000	-2.804109000	0.680167000
C	-1.941331000	1.555259000	0.318877000	H	7.453123000	-3.540713000	0.920101000
H	-2.898255000	1.177667000	0.632367000	C	6.969356000	-1.456368000	0.445611000
C	-1.565052000	2.911727000	0.223047000	H	7.960605000	-1.028790000	0.501311000
C	-0.219289000	3.098848000	-0.086375000	C	5.835325000	-0.704023000	0.153567000
C	0.100706000	4.485575000	-0.139430000	C	5.835265000	0.704428000	-0.153700000
C	-1.109093000	5.136596000	0.136564000	C	6.969224000	1.456866000	-0.445778000
C	-1.666892000	6.431527000	0.395256000	H	7.960506000	1.029369000	-0.501510000
H	-1.133250000	7.365709000	0.315354000	C	6.696489000	2.804583000	-0.680336000
C	-2.963987000	6.267361000	0.763834000	H	7.452802000	3.541245000	-0.920312000
H	-3.674792000	7.038845000	1.017712000	C	5.347548000	3.140042000	-0.584632000
C	-3.311125000	4.847063000	0.742640000	C	4.850392000	4.461464000	-0.750452000
C	-4.532467000	4.356010000	1.080945000	C	3.566738000	4.937384000	-0.670343000
C	-5.019866000	2.985272000	1.027350000	C	3.179370000	6.340947000	-0.773155000
C	-5.814683000	0.887517000	1.693480000	H	3.848942000	7.168746000	-0.958928000
H	-6.133290000	0.128752000	2.396724000	C	1.838503000	6.379584000	-0.577898000
C	-5.655909000	0.635397000	0.349187000	H	1.194760000	7.246463000	-0.586861000
C	-5.655982000	-0.636020000	-0.348784000	C	1.422731000	4.991676000	-0.373749000
C	-5.815314000	-0.888074000	-1.693028000	N	-2.123801000	-4.193419000	-0.341768000
H	-6.134401000	-0.129313000	-2.396059000	N	-2.124122000	4.193324000	0.341903000
C	-5.476274000	-2.210425000	-2.068515000	N	2.451846000	4.155506000	-0.436418000
H	-5.507457000	-2.571439000	-3.088335000	N	2.452198000	-4.155313000	0.436454000
C	-5.019759000	-2.985709000	-1.027420000	S	4.401126000	-1.713645000	0.186044000
C	-4.531955000	-4.356245000	-1.081489000	S	4.400991000	1.713947000	-0.186063000
C	-3.310574000	-4.847185000	-0.743092000	S	0.605319000	1.607884000	-0.336216000
C	-2.963189000	-6.267410000	-0.764848000	S	-5.115106000	-2.088273000	0.476943000
H	-3.673818000	-7.038896000	-1.019210000	S	-5.115665000	2.087677000	-0.476887000
C	-1.666180000	-6.431529000	-0.395930000	S	0.605417000	-1.607787000	0.336620000
H	-1.132405000	-7.365653000	-0.316228000	C	-5.475728000	2.209980000	2.068706000
C	-1.108656000	-5.136618000	-0.136569000	H	-5.506549000	2.571077000	3.088508000
C	0.101051000	-4.485512000	0.139610000	H	-5.221341000	-5.097719000	-1.475951000
C	1.423123000	-4.991538000	0.373834000	H	5.624360000	-5.197908000	0.949669000
C	1.838971000	-6.379419000	0.577975000	H	-5.222197000	5.097512000	1.474756000
H	1.195255000	-7.246318000	0.587039000	H	5.623909000	5.198265000	-0.949928000

Table S5: Coordinates for S_0 optimized geometry of the *anti* conformer of *meso* free compound **6** at B3LYP/6-311G** level of theory; # sum of imaginary frequencies=0 # Total Energy (hartree) = -3733.196131

Atom	X	Y	Z	Atom	X	Y	Z
C	-5.332358000	4.206154000	0.110637000	C	3.847652000	-4.294380000	-1.859075000
C	-4.476368000	5.276203000	-0.102204000	C	5.648154000	-1.888362000	0.424367000
C	-3.193745000	5.088407000	-0.657551000	C	6.239237000	-1.686236000	1.651421000
C	-2.862578000	3.795491000	-1.111007000	C	6.532215000	-0.331334000	1.924055000
C	-3.724900000	2.737704000	-0.922138000	C	6.124449000	0.534206000	0.928704000
C	-4.956189000	2.900528000	-0.257359000	S	5.506170000	-0.369635000	-0.435433000
C	-5.760426000	1.731209000	0.075658000	C	6.184558000	1.975462000	0.947598000
S	-4.972585000	0.176883000	0.209269000	C	0.005309000	-3.230476000	-0.148479000
C	-6.478986000	-0.614178000	0.614764000	C	0.993607000	-2.220624000	-0.192502000
C	-7.515369000	0.315060000	0.650673000	C	0.477582000	-0.986776000	0.171492000
C	-7.113800000	1.627791000	0.354057000	S	-1.244844000	-1.083580000	0.583152000
C	-2.242717000	6.181422000	-0.685601000	S	0.243035000	1.758044000	-0.244947000
C	-5.592159000	-2.947517000	0.784768000	C	1.151937000	0.297005000	0.170786000
C	-6.595480000	-2.014213000	0.839421000	C	2.490618000	0.569460000	0.409977000
C	-0.879467000	6.067233000	-0.665392000	C	2.791063000	1.939527000	0.212299000
C	-5.746294000	-4.391858000	0.899479000	H	-6.277347000	4.372227000	0.614572000
C	-4.517016000	-4.921574000	0.683899000	H	-4.772750000	6.267118000	0.226369000
C	-3.619357000	-3.784502000	0.458232000	H	-1.908686000	3.634565000	-1.587590000
N	-4.265416000	-2.632283000	0.533890000	H	-3.436658000	1.757645000	-1.282435000
N	-0.199515000	4.857276000	-0.575643000	H	-8.536397000	0.030853000	0.873701000
C	1.080003000	5.150610000	-0.450923000	H	-7.793902000	2.468420000	0.314269000
C	1.308754000	6.600949000	-0.490176000	H	-6.668873000	-4.915127000	1.107014000
C	0.085158000	7.167132000	-0.618189000	H	-4.235938000	-5.963791000	0.706035000
C	-2.206642000	-3.848794000	0.193555000	H	2.260115000	7.105569000	-0.411965000
C	2.023134000	4.089006000	-0.228887000	H	-0.155900000	8.219408000	-0.671380000
C	1.674767000	2.709774000	-0.114090000	H	-2.570052000	-6.820752000	-0.782147000
C	3.398023000	4.124122000	0.014374000	H	-0.238518000	-7.627661000	-1.766687000
C	-1.261697000	-2.776443000	0.226804000	H	6.556789000	4.721654000	0.789468000
C	-1.462148000	-4.956164000	-0.233076000	H	4.411021000	6.115549000	0.068874000
C	-1.641316000	-6.272421000	-0.776503000	H	2.506107000	-5.154633000	1.134857000
C	-0.455903000	-6.678693000	-1.300100000	H	4.179670000	-3.535064000	1.913687000
C	0.561760000	-5.658981000	-1.067925000	H	5.414936000	-2.861379000	-2.145279000
N	-0.121452000	-4.605405000	-0.405744000	H	3.751042000	-4.500986000	-2.919333000
N	3.884876000	2.832119000	0.261748000	H	6.419425000	-2.491445000	2.351827000
C	5.255019000	2.914567000	0.616774000	H	6.963906000	0.017429000	2.853440000
C	5.569704000	4.339089000	0.578790000	H	2.009901000	-2.346890000	-0.527915000
C	4.475413000	5.047283000	0.201962000	H	3.178496000	-0.188749000	0.739909000
C	1.871197000	-5.768046000	-1.399789000	H	7.115079000	2.396585000	1.318181000
C	2.965359000	-4.904001000	-0.952978000	H	2.122094000	-6.607588000	-2.041841000
C	3.150056000	-4.660839000	0.416761000	H	-7.599871000	-2.370987000	1.049357000
C	4.106038000	-3.760952000	0.856826000	H	-2.651279000	7.187220000	-0.633715000

C	4.899102000	-3.049729000	-0.058960000					
C	4.785001000	-3.368055000	-1.422512000					

Table S6: Coordinates for S_0 optimized geometry of the *syn* conformer of *meso* free compound **6'** at B3LYP/6-311G** level of theory; # sum of imaginary frequencies = 0 # Total Energy (hartree) = -3733.196043

Atom	X	Y	Z	Atom	X	Y	Z
C	6.479505000	2.168131000	0.034217000	C	-5.540006000	0.972401000	0.889819000
C	6.057213000	3.475843000	0.218413000	C	-5.282199000	2.256648000	0.441173000
C	4.782834000	3.765346000	0.748236000	C	-5.733500000	-1.447474000	0.468052000
C	4.010677000	2.683219000	1.217327000	C	-6.070691000	-1.946513000	1.706235000
C	4.442751000	1.384412000	1.056248000	C	-5.526236000	-3.222827000	1.971534000
C	5.656781000	1.088302000	0.406284000	C	-4.720499000	-3.702641000	0.958378000
C	5.989193000	-0.291587000	0.074342000	S	-4.768025000	-2.614523000	-0.411024000
S	4.696238000	-1.454453000	-0.103250000	C	-3.945278000	-4.919319000	0.962839000
C	5.822148000	-2.724560000	-0.525637000	C	-1.912176000	2.866037000	-0.162470000
C	7.124640000	-2.232148000	-0.525781000	C	-2.133731000	1.469234000	-0.220701000
C	7.218642000	-0.871070000	-0.194609000	C	-0.995393000	0.759104000	0.132725000
C	4.275487000	5.122593000	0.713767000	S	0.355026000	1.830016000	0.541298000
C	2.960322000	5.492824000	0.644278000	S	0.788090000	-1.347780000	-0.288074000
C	5.431939000	-4.059176000	-0.823370000	C	-0.797854000	-0.677393000	0.130598000
C	4.163187000	-4.579757000	-0.824039000	C	-1.729745000	-1.671700000	0.379387000
C	2.450650000	6.854884000	0.473995000	C	-1.182888000	-2.963028000	0.194553000
C	1.113015000	6.745218000	0.293431000	H	7.426892000	1.978737000	-0.456734000
C	0.814138000	5.308409000	0.356419000	H	6.689597000	4.290753000	-0.118791000
N	1.899160000	4.595767000	0.587339000	H	3.055472000	2.880608000	1.677061000
N	3.024312000	-3.844528000	-0.532790000	H	3.820506000	0.576186000	1.421376000
C	2.013828000	-4.699564000	-0.568012000	H	7.977327000	-2.859619000	-0.754192000
C	2.464067000	-6.051800000	-0.911767000	H	8.154779000	-0.332435000	-0.129642000
C	3.806753000	-5.969615000	-1.075969000	H	3.046869000	7.756384000	0.482334000
C	-0.436521000	4.633843000	0.142728000	H	0.404630000	7.543213000	0.127350000
C	0.663491000	-4.289460000	-0.289130000	H	1.840683000	-6.923976000	-1.035308000
C	0.175609000	-2.956009000	-0.132313000	H	4.494365000	-6.761113000	-1.338143000
C	-0.452307000	-5.098569000	-0.049068000	H	-1.840488000	7.288063000	-0.829270000
C	-0.615969000	3.218378000	0.212868000	H	-4.230401000	6.620104000	-1.775490000
C	-1.674799000	5.123060000	-0.288010000	H	-2.689572000	-7.387824000	0.784826000
C	-2.287391000	6.306306000	-0.820924000	H	-0.145688000	-7.311917000	0.024813000
C	-3.502810000	5.964596000	-1.321243000	H	-5.744356000	1.770954000	-2.885541000
C	-3.755775000	4.547454000	-1.079318000	H	-6.151163000	-0.524230000	-2.097047000
N	-2.583160000	4.070840000	-0.438814000	H	-5.450442000	0.748386000	1.945808000
N	-1.581751000	-4.315283000	0.222238000	H	-5.024830000	3.032574000	1.152423000
C	-2.653770000	-5.161980000	0.604013000	H	-6.662399000	-1.387158000	2.419268000
C	-2.101943000	-6.511348000	0.557682000	H	-5.656220000	-3.751622000	2.907062000
C	-0.807067000	-6.470608000	0.154698000	H	-3.036458000	0.987013000	-0.558661000
C	-4.900641000	3.891039000	-1.387275000	H	-2.729371000	-1.448579000	0.707016000
C	-5.295812000	2.557628000	-0.929358000	H	6.246133000	-4.736512000	-1.065528000
C	-5.685182000	1.549588000	-1.825508000	H	5.012539000	5.917170000	0.632509000
C	-5.912828000	0.254244000	-1.380751000	H	-4.460480000	-5.795646000	1.346527000

C	-5.797431000	-0.068122000	-0.018239000	H	-5.597696000	4.435908000	-2.017539000
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Table S7: Coordinates for S_0 optimized geometry of the normal conformer of *meso* free compound [5]²⁺ at B3LYP/6-311G** level of theory; # sum of imaginary frequencies=0 # Total Energy (hartree) = -4374.240155

Atom	X	Y	Z	Atom	X	Y	Z
C	0.499843000	3.018790000	-0.169515000	C	-2.541322000	6.606306000	0.291815000
C	1.854838000	2.684608000	-0.339371000	H	-3.130858000	7.505517000	0.393415000
C	2.072854000	1.329607000	-0.548753000	C	-3.064450000	5.241680000	0.238781000
H	3.015653000	0.862485000	-0.768575000	C	-4.412576000	4.916427000	0.299679000
C	0.873782000	0.596538000	-0.443013000	C	-5.040576000	3.663098000	0.251661000
C	0.732159000	-0.817079000	-0.424132000	C	-6.439687000	3.498995000	0.306588000
C	1.765047000	-1.772437000	-0.344591000	H	-7.109233000	4.344770000	0.392904000
H	2.808032000	-1.508976000	-0.384746000	C	-6.857031000	2.186851000	0.240166000
C	1.248938000	-3.049533000	-0.172796000	H	-7.895215000	1.890079000	0.271829000
C	-0.154732000	-3.110198000	-0.174650000	C	-5.795904000	1.266989000	0.134274000
C	-0.604274000	-4.445092000	-0.119972000	C	-5.946804000	-0.143516000	0.058516000
C	0.600387000	-5.220707000	-0.071088000	C	-7.179868000	-0.822788000	0.037375000
C	1.069357000	-6.557104000	-0.189668000	H	-8.133923000	-0.317122000	0.069514000
H	0.455535000	-7.442112000	-0.232289000	C	-7.048767000	-2.193898000	-0.030887000
C	2.439402000	-6.509375000	-0.260917000	H	-7.883256000	-2.882443000	-0.054996000
H	3.112478000	-7.349933000	-0.339695000	C	-5.713983000	-2.644412000	-0.064211000
C	2.880656000	-5.145470000	-0.116701000	C	-5.361283000	-4.002532000	-0.111005000
C	4.180889000	-4.712093000	-0.017158000	C	-4.106403000	-4.592620000	-0.130295000
C	4.581849000	-3.446591000	0.503175000	C	-3.868113000	-6.035637000	-0.129995000
C	4.587647000	-1.510187000	1.802550000	H	-4.629327000	-6.801800000	-0.130491000
H	4.294139000	-0.854860000	2.612287000	C	-2.524113000	-6.195959000	-0.120579000
C	5.501602000	-1.133233000	0.818235000	H	-1.974446000	-7.124233000	-0.112633000
C	5.894241000	0.196770000	0.466765000	C	-1.966178000	-4.845925000	-0.125009000
C	6.854071000	0.632421000	-0.449227000	N	2.578255000	3.902982000	-0.258933000
H	7.605660000	-0.022760000	-0.869809000	N	1.699190000	-4.380960000	-0.025193000
C	6.719484000	1.974947000	-0.794560000	N	-2.923905000	-3.907904000	-0.131468000
H	7.352078000	2.479809000	-1.513181000	N	-2.048112000	4.339104000	0.110868000
C	5.610493000	2.599581000	-0.203209000	S	-4.251789000	2.100468000	0.114528000
C	5.121724000	3.882305000	-0.537121000	S	-4.611197000	-1.279701000	-0.012377000
C	3.862978000	4.452771000	-0.468871000	S	-0.869405000	-1.555840000	-0.342578000
C	3.659524000	5.873443000	-0.538319000	S	4.869308000	1.530384000	0.961694000
H	4.462242000	6.580941000	-0.682857000	S	5.808618000	-2.467334000	-0.278848000
C	2.336317000	6.167548000	-0.312681000	S	-0.524092000	1.639030000	-0.182413000
H	1.892741000	7.148879000	-0.274479000	C	4.064893000	-2.788691000	1.616858000
C	1.655582000	4.938549000	-0.160957000	H	3.336253000	-3.245478000	2.272602000
C	0.326488000	4.410466000	-0.065390000	H	5.871253000	4.554622000	-0.946280000
C	-0.922531000	5.068916000	0.074618000	H	-5.097805000	5.753736000	0.393832000
C	-1.195936000	6.498816000	0.189216000	H	-6.207541000	-4.683036000	-0.121952000
H	-0.472225000	7.298692000	0.195519000	H	4.943601000	-5.399513000	-0.370695000

Table S8: Coordinates for S_0 optimized geometry of the *anti* conformer of *meso* free compound $[6]^{2+}$ at B3LYP/6-311G** level of theory; # sum of imaginary frequencies=0 # Total Energy (hartree) = -3732.692803

Atom	X	Y	Z	Atom	X	Y	Z
C	-5.996991000	3.300357000	0.414386000	C	5.117862000	-4.176880000	-0.729359000
C	-5.325673000	4.507048000	0.374461000	C	5.640265000	-0.891458000	0.962032000
C	-4.023585000	4.599916000	-0.175229000	C	5.188024000	-0.042075000	1.968442000
C	-3.497875000	3.458963000	-0.829398000	C	5.212681000	1.307923000	1.613246000
C	-4.171619000	2.265751000	-0.802697000	C	5.729716000	1.534268000	0.343278000
C	-5.405504000	2.133823000	-0.122382000	S	6.255412000	0.037998000	-0.390150000
C	-5.982069000	0.823971000	0.054732000	C	5.792269000	2.785833000	-0.342232000
S	-4.941425000	-0.574067000	-0.036129000	C	0.605727000	-3.169575000	-0.231877000
C	-6.280733000	-1.650165000	0.289170000	C	1.395668000	-2.029562000	-0.282754000
C	-7.470814000	-0.913940000	0.460206000	C	0.621906000	-0.853277000	-0.136376000
C	-7.302645000	0.458273000	0.346483000	S	-1.100861000	-1.227625000	0.048599000
C	-3.261567000	5.806238000	-0.025859000	S	-0.102434000	1.824969000	-0.041245000
C	-4.999489000	-3.799428000	0.265946000	C	1.071849000	0.497812000	-0.119263000
C	-6.161741000	-3.043214000	0.377129000	C	2.403284000	0.979339000	-0.140765000
C	-1.886027000	5.904499000	-0.055876000	C	2.443384000	2.368164000	-0.091434000
C	-4.934294000	-5.255035000	0.312186000	H	-6.955413000	3.241219000	0.914800000
C	-3.628704000	-5.577795000	0.150798000	H	-5.773540000	5.381814000	0.832055000
C	-2.917498000	-4.306909000	0.022212000	H	-2.554416000	3.537032000	-1.345060000
N	-3.752548000	-3.262546000	0.095153000	H	-3.754350000	1.412720000	-1.323375000
N	-1.039049000	4.816446000	-0.137094000	H	-8.419929000	-1.395652000	0.657446000
C	0.193102000	5.306270000	-0.103905000	H	-8.109711000	1.172281000	0.435442000
C	0.200754000	6.766878000	-0.003493000	H	-5.771844000	-5.922964000	0.448944000
C	-1.101546000	7.136095000	0.045254000	H	-3.198795000	-6.566600000	0.152621000
C	-1.514442000	-4.117739000	-0.114470000	H	1.065557000	7.410057000	0.053422000
C	1.285712000	4.384752000	-0.104869000	H	-1.503575000	8.135140000	0.128311000
C	1.173119000	2.981502000	-0.055764000	H	-1.241483000	-7.184201000	-0.807432000
C	2.689695000	4.621359000	-0.187971000	H	1.329193000	-7.689589000	-1.278368000
C	-0.776300000	-2.917736000	-0.084353000	H	5.757829000	5.578732000	-0.945880000
C	-0.518509000	-5.132267000	-0.323003000	H	3.360297000	6.699471000	-0.644264000
C	-0.422244000	-6.491670000	-0.709759000	H	2.723195000	-4.305923000	1.690279000
C	0.900369000	-6.746441000	-0.973781000	H	3.947966000	-2.350646000	2.475595000
C	1.684371000	-5.575709000	-0.690494000	H	6.651636000	-2.703360000	-0.867276000
N	0.748316000	-4.579787000	-0.311984000	H	5.466409000	-4.717699000	-1.601662000
N	3.385742000	3.427367000	-0.103299000	H	4.812496000	-0.395923000	2.918346000
C	4.748911000	3.670083000	-0.400975000	H	4.879516000	2.111561000	2.255788000
C	4.834189000	5.077140000	-0.698253000	H	2.463334000	-2.009722000	-0.425034000
C	3.604288000	5.656304000	-0.523803000	H	3.259312000	0.325803000	-0.188197000
C	3.056377000	-5.539230000	-0.704185000	H	6.709612000	3.075328000	-0.845873000
C	3.910513000	-4.560416000	-0.101225000	H	3.527972000	-6.353083000	-1.248096000
C	3.564078000	-3.935480000	1.117392000	H	-7.085621000	-3.585679000	0.553919000
C	4.265943000	-2.842995000	1.566143000	H	-3.812602000	6.716458000	0.192461000

C	5.303572000	-2.287503000	0.780042000					
C	5.785351000	-3.043951000	-0.311997000					

Table S9: Coordinates for T₁ optimized geometry of the normal conformer of *meso* free compound **5•2H⁺** at UB3LYP/6-311G** level of theory; # sum of imaginary frequencies=0 # Total Energy (hartree) = -4375.507608

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.560928000	-3.005648000	-0.179961000	H	3.141688000	-7.387289000	0.834140000
C	-1.916477000	-2.714748000	-0.417220000	C	3.146272000	-5.224606000	0.349464000
C	-2.172190000	-1.360333000	-0.651798000	C	4.509771000	-4.884063000	0.391634000
H	-3.117439000	-0.934317000	-0.938929000	C	5.154210000	-3.657736000	0.307466000
C	-1.023946000	-0.580592000	-0.492097000	C	6.564499000	-3.486831000	0.330263000
C	-0.898097000	0.839021000	-0.480255000	H	7.233989000	-4.333944000	0.405444000
C	-1.893718000	1.799056000	-0.284204000	C	6.986034000	-2.183875000	0.244849000
H	-2.936371000	1.541752000	-0.208479000	H	8.027653000	-1.895353000	0.248517000
C	-1.351107000	3.079843000	-0.142172000	C	5.936319000	-1.236173000	0.151546000
C	0.048221000	3.130874000	-0.258565000	C	6.075833000	0.157064000	0.065235000
C	0.515307000	4.466655000	-0.170315000	C	7.291509000	0.884272000	0.063208000
C	-0.670542000	5.236609000	0.004245000	H	8.255659000	0.400403000	0.130597000
C	-1.142370000	6.581422000	0.019708000	C	7.135702000	2.245276000	-0.027588000
H	-0.527783000	7.467235000	-0.003235000	H	7.959337000	2.947393000	-0.037159000
C	-2.510064000	6.542624000	0.056150000	C	5.787731000	2.684498000	-0.102338000
H	-3.180352000	7.388388000	0.088999000	C	5.398358000	4.015449000	-0.193219000
C	-2.960313000	5.167876000	0.135081000	C	4.129366000	4.613503000	-0.241606000
C	-4.246576000	4.741541000	0.295638000	C	3.840769000	5.992096000	-0.409124000
C	-4.639451000	3.411838000	0.705351000	H	4.584879000	6.762130000	-0.543594000
C	-4.717347000	1.404770000	1.896018000	C	2.465417000	6.157664000	-0.400039000
H	-4.475238000	0.716861000	2.695973000	H	1.930351000	7.083421000	-0.536352000
C	-5.527357000	1.061414000	0.826115000	C	1.875663000	4.887068000	-0.228151000
C	-5.903270000	-0.259089000	0.384845000	N	-2.602113000	-3.936764000	-0.344949000
C	-6.809272000	-0.646078000	-0.593890000	N	-1.773706000	4.394007000	0.079921000
H	-7.530338000	0.032762000	-1.030565000	N	2.905328000	3.973629000	-0.151146000
C	-6.667429000	-1.983605000	-0.989700000	N	2.086875000	-4.370173000	0.103339000
H	-7.265180000	-2.448187000	-1.763431000	S	4.383126000	-2.067804000	0.190246000
C	-5.609487000	-2.645213000	-0.363890000	S	4.719417000	1.273994000	-0.072283000
C	-5.129426000	-3.945349000	-0.684348000	S	0.710451000	1.565691000	-0.575721000
C	-3.875318000	-4.511972000	-0.592096000	S	-4.914849000	-1.621542000	0.875408000
C	-3.638138000	-5.930021000	-0.645822000	S	-5.744644000	2.437628000	-0.243816000
H	-4.421187000	-6.655097000	-0.809774000	S	0.390365000	-1.565578000	-0.100676000
C	-2.317315000	-6.197246000	-0.375132000	C	-4.210323000	2.715519000	1.819810000
H	-1.859746000	-7.171932000	-0.319963000	H	-3.554419000	3.152570000	2.561006000

C	-1.660474000	-4.956398000	-0.196705000	H	2.191685000	-3.442605000	-0.279067000
C	-0.354314000	-4.398402000	-0.052074000	H	2.788869000	3.020989000	0.159581000
C	0.891346000	-5.057136000	0.150860000	H	-5.879061000	-4.620328000	-1.089076000
C	1.201456000	-6.397338000	0.465485000	H	5.172456000	-5.733439000	0.524435000
H	0.483283000	-7.185956000	0.621090000	H	-5.021357000	5.481180000	0.114604000
C	2.578355000	-6.502212000	0.581285000	H	6.220733000	4.722524000	-0.237147000

Table S10: Coordinates for S_0 optimized geometry of the *anti* conformer of *meso* free compound **6•2H⁺** at B3LYP/6-311G** level of theory; # sum of imaginary frequencies=0 # Total Energy (hartree) = -3733.964838

Atom	X	Y	Z	Atom	X	Y	Z
C	5.705866000	3.720561000	-0.332996000	C	-4.249671000	-3.846831000	1.908358000
C	4.972775000	4.879224000	-0.124543000	C	-5.844010000	-1.262101000	-0.336429000
C	3.770224000	4.855064000	0.610865000	C	-6.564180000	-1.032084000	-1.492998000
C	3.412603000	3.646486000	1.245202000	C	-6.718120000	0.333126000	-1.792373000
C	4.153893000	2.498132000	1.054302000	C	-6.056855000	1.171433000	-0.903160000
C	5.284428000	2.494326000	0.214547000	S	-5.393960000	0.243945000	0.422397000
C	5.949849000	1.236417000	-0.105245000	C	-5.894850000	2.581896000	-1.055299000
S	5.008866000	-0.231145000	-0.095448000	C	-0.399117000	-3.296395000	0.098216000
C	6.382553000	-1.212631000	-0.565562000	C	-1.268711000	-2.181157000	0.159373000
C	7.505250000	-0.396744000	-0.711861000	C	-0.631046000	-1.015258000	-0.217643000
C	7.259718000	0.962724000	-0.466798000	S	1.049936000	-1.309776000	-0.693031000
C	2.918192000	6.029982000	0.675888000	S	-0.093434000	1.651462000	0.354860000
C	5.248463000	-3.471033000	-0.704224000	C	-1.141030000	0.341124000	-0.213066000
C	6.327380000	-2.616083000	-0.754157000	C	-2.407888000	0.799554000	-0.512031000
C	1.552935000	6.012098000	0.692022000	C	-2.545806000	2.186096000	-0.255622000
C	5.261468000	-4.902094000	-0.809846000	H	6.584210000	3.756968000	-0.965755000
C	3.985572000	-5.368855000	-0.641186000	H	5.299104000	5.804127000	-0.586042000
C	3.124621000	-4.241581000	-0.446824000	H	2.575836000	3.624504000	1.932218000
N	3.910010000	-3.130304000	-0.501556000	H	3.867057000	1.593659000	1.577113000
N	0.758088000	4.867148000	0.551426000	H	8.475301000	-0.791808000	-0.985066000
C	-0.562948000	5.190267000	0.492069000	H	8.024999000	1.725173000	-0.518928000
C	-0.647023000	6.617995000	0.672997000	H	6.148748000	-5.489032000	-0.993400000
C	0.619478000	7.109789000	0.780855000	H	3.661027000	-6.395423000	-0.687883000
C	1.725902000	-4.161770000	-0.246665000	H	-1.563771000	7.181956000	0.725283000
C	-1.555330000	4.221753000	0.262649000	H	0.906240000	8.139328000	0.933793000
C	-1.366886000	2.801875000	0.143857000	H	1.733481000	-7.183179000	0.700475000
C	-2.929675000	4.416936000	-0.042584000	H	-0.670555000	-7.708365000	1.689670000
C	0.900042000	-2.987333000	-0.291756000	H	-5.933030000	5.366979000	-1.016045000
C	0.851756000	-5.186072000	0.188720000	H	-3.694448000	6.514990000	-0.172163000
C	0.881565000	-6.522519000	0.709103000	H	-3.228038000	-4.938285000	-1.145210000
C	-0.344894000	-6.787020000	1.230695000	H	-4.730399000	-3.132197000	-1.863080000
C	-1.229084000	-5.650108000	1.021045000	H	-5.585492000	-2.207656000	2.250624000
N	-0.422730000	-4.677110000	0.361101000	H	-4.133056000	-4.059657000	2.964785000
N	-3.532191000	3.197474000	-0.310411000	H	-6.954574000	-1.831067000	-2.108939000

C	-4.868124000	3.430997000	-0.739446000	H	-7.234866000	0.704860000	-2.667811000
C	-5.013250000	4.870409000	-0.745863000	H	-2.285984000	-2.194895000	0.514613000
C	-3.867446000	5.458953000	-0.298740000	H	-3.161381000	0.154639000	-0.927350000
C	-2.535367000	-5.589302000	1.371061000	H	-6.730296000	3.083576000	-1.537278000
C	-3.515449000	-4.580284000	0.961989000	H	-2.883193000	-6.398079000	2.008269000
C	-3.741001000	-4.339858000	-0.401798000	H	7.280791000	-3.090554000	-0.963656000
C	-4.601410000	-3.331610000	-0.806319000	H	3.390114000	7.006253000	0.640320000
C	-5.225394000	-2.502195000	0.141031000	H	1.133838000	3.977839000	0.256777000
C	-5.069041000	-2.801150000	1.504927000	H	3.568022000	-2.197793000	-0.328144000

Table S11: Coordinates for T₁ optimized geometry of the *anti* conformer of *meso* free compound **6•2H⁺** at UB3LYP/6-311G** level of theory; # sum of imaginary frequencies=0 # Total Energy (hartree) = -3733.938396

Atom	X	Y	Z	Atom	X	Y	Z
C	5.889676000	3.751602000	-0.086300000	C	-4.231382000	-3.888307000	1.861859000
C	5.147834000	4.899410000	0.053472000	C	-5.952905000	-1.284142000	-0.260818000
C	3.811865000	4.867005000	0.556716000	C	-6.733634000	-1.028589000	-1.369708000
C	3.360328000	3.619606000	1.088638000	C	-6.881702000	0.344026000	-1.643607000
C	4.106480000	2.483652000	0.966370000	C	-6.158906000	1.160969000	-0.782172000
C	5.363986000	2.484984000	0.298163000	S	-5.446003000	0.206320000	0.496429000
C	6.011855000	1.253404000	0.001243000	C	-5.974105000	2.566783000	-0.929990000
S	5.125475000	-0.254126000	0.173020000	C	-0.409177000	-3.279776000	0.078651000
C	6.464728000	-1.212772000	-0.444654000	C	-1.285724000	-2.191572000	0.060639000
C	7.561423000	-0.355309000	-0.709704000	C	-0.621314000	-0.992773000	-0.231328000
C	7.306140000	0.983335000	-0.484015000	S	1.103383000	-1.260068000	-0.557943000
C	2.984028000	6.010922000	0.511807000	S	-0.046286000	1.682932000	0.171381000
C	5.302199000	-3.452624000	-0.588972000	C	-1.131529000	0.337828000	-0.227508000
C	6.404209000	-2.584104000	-0.669295000	C	-2.442596000	0.781497000	-0.437313000
C	1.581066000	6.013548000	0.534093000	C	-2.573399000	2.160400000	-0.256518000
C	5.293897000	-4.859101000	-0.763219000	H	6.869546000	3.811318000	-0.543236000
C	3.994589000	-5.314190000	-0.604475000	H	5.556846000	5.842945000	-0.289397000
C	3.172158000	-4.197045000	-0.343777000	H	2.441273000	3.584692000	1.658169000
N	3.985828000	-3.093674000	-0.341538000	H	3.740504000	1.567568000	1.414761000
N	0.797974000	4.882333000	0.343442000	H	8.505684000	-0.735801000	-1.077223000
C	-0.535467000	5.204182000	0.352027000	H	8.038260000	1.761842000	-0.649030000
C	-0.618559000	6.591484000	0.608329000	H	6.165411000	-5.454239000	-0.988099000
C	0.672384000	7.089736000	0.701085000	H	3.654449000	-6.331631000	-0.708166000
C	1.757987000	-4.097196000	-0.149705000	H	-1.529506000	7.152734000	0.737971000
C	-1.534088000	4.207927000	0.131471000	H	0.957702000	8.109370000	0.909238000
C	-1.351865000	2.812963000	0.031622000	H	1.763783000	-7.121419000	0.730889000
C	-2.929632000	4.391566000	-0.098529000	H	-0.692652000	-7.732697000	1.540655000

C	0.934157000	-2.949227000	-0.212444000	H	-5.968907000	5.335401000	-0.937777000
C	0.866769000	-5.139666000	0.223088000	H	-3.667110000	6.485109000	-0.264040000
C	0.895166000	-6.483873000	0.697056000	H	-3.390383000	-4.959935000	-1.252848000
C	-0.361467000	-6.792522000	1.125750000	H	-4.917876000	-3.134848000	-1.869813000
C	-1.254481000	-5.666114000	0.910818000	H	-5.553506000	-2.258551000	2.293332000
N	-0.431535000	-4.657099000	0.327006000	H	-4.054683000	-4.109905000	2.907983000
N	-3.560551000	3.161338000	-0.287454000	H	-7.166699000	-1.812951000	-1.975912000
C	-4.916397000	3.400526000	-0.658628000	H	-7.437533000	0.734779000	-2.486199000
C	-5.043619000	4.834323000	-0.696114000	H	-2.335154000	-2.227780000	0.305538000
C	-3.861491000	5.427481000	-0.334602000	H	-3.224337000	0.107548000	-0.737452000
C	-2.571731000	-5.647941000	1.219774000	H	-6.815520000	3.087221000	-1.380000000
C	-3.559914000	-4.618187000	0.869497000	H	-2.925442000	-6.510869000	1.777856000
C	-3.858118000	-4.365815000	-0.476680000	H	7.332967000	-3.053826000	-0.976051000
C	-4.733535000	-3.347266000	-0.823778000	H	3.456495000	6.979968000	0.389940000
C	-5.308323000	-2.531625000	0.165057000	H	1.170848000	4.028793000	-0.043094000
C	-5.076968000	-2.842605000	1.514363000	H	3.671558000	-2.155903000	-0.148804000

Table S12: Coordinates for T₁ optimized geometry of the normal conformer of *meso* free compound **5•2H⁺** at UCAM-B3LYP/6-311G** level of theory in dichloromethane using the PCM solvation model; # sum of imaginary frequencies=0 # Sum of electronic and zero-point Energies= -4375.147849

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.570898000	-3.003911000	-0.224639000	H	3.107360000	-7.377904000	0.883666000
C	-1.927860000	-2.706632000	-0.450989000	C	3.122935000	-5.236871000	0.317381000
C	-2.183277000	-1.351342000	-0.675541000	C	4.487033000	-4.900237000	0.362980000
H	-3.127259000	-0.916006000	-0.953849000	C	5.133469000	-3.673192000	0.296004000
C	-1.029519000	-0.577667000	-0.519823000	C	6.544078000	-3.509836000	0.315296000
C	-0.894636000	0.838987000	-0.503999000	H	7.204948000	-4.365799000	0.368117000
C	-1.887286000	1.804163000	-0.319975000	C	6.974652000	-2.207478000	0.251976000
H	-2.931289000	1.545673000	-0.277412000	H	8.017376000	-1.921165000	0.250676000
C	-1.338971000	3.078214000	-0.158036000	C	5.930163000	-1.252761000	0.182555000
C	0.063275000	3.123223000	-0.255870000	C	6.074871000	0.141167000	0.106879000
C	0.531708000	4.457261000	-0.174455000	C	7.291277000	0.866400000	0.117936000
C	-0.653159000	5.231214000	-0.014283000	H	8.251849000	0.376795000	0.198752000
C	-1.116284000	6.578199000	-0.005185000	C	7.136914000	2.228135000	0.022658000
H	-0.487671000	7.454684000	-0.032677000	H	7.958450000	2.933337000	0.019585000
C	-2.485265000	6.544315000	0.031246000	C	5.791373000	2.670344000	-0.067671000
H	-3.157404000	7.389268000	0.060982000	C	5.410008000	4.002181000	-0.178070000
C	-2.940257000	5.171720000	0.117309000	C	4.142926000	4.602988000	-0.244941000
C	-4.227213000	4.753807000	0.299396000	C	3.855582000	5.973328000	-0.472803000
C	-4.617644000	3.431553000	0.726406000	H	4.603773000	6.731973000	-0.646380000
C	-4.646810000	1.408427000	1.893980000	C	2.478543000	6.140723000	-0.470314000
H	-4.352978000	0.707306000	2.665115000	H	1.933070000	7.054134000	-0.648900000

C	-5.507693000	1.077466000	0.861256000	C	1.891983000	4.877902000	-0.240845000
C	-5.893600000	-0.238817000	0.418310000	N	-2.616660000	-3.925331000	-0.366756000
C	-6.799630000	-0.614559000	-0.563975000	N	-1.757932000	4.393668000	0.058004000
H	-7.509649000	0.073818000	-1.004686000	N	2.918889000	3.967365000	-0.127946000
C	-6.666254000	-1.951086000	-0.970067000	N	2.069750000	-4.381990000	0.043548000
H	-7.261424000	-2.407414000	-1.750881000	S	4.369665000	-2.074393000	0.222564000
C	-5.615519000	-2.624328000	-0.349080000	S	4.718819000	1.259331000	-0.045078000
C	-5.146550000	-3.928991000	-0.673675000	S	0.722594000	1.554460000	-0.566582000
C	-3.894025000	-4.496748000	-0.593980000	S	-4.911743000	-1.613006000	0.897545000
C	-3.664337000	-5.918227000	-0.633399000	S	-5.781697000	2.473228000	-0.174218000
H	-4.457266000	-6.636501000	-0.780847000	S	0.386986000	-1.568175000	-0.144749000
C	-2.342792000	-6.188834000	-0.370292000	C	-4.138542000	2.718127000	1.808374000
H	-1.879274000	-7.160141000	-0.296845000	H	-3.430360000	3.136702000	2.511399000
C	-1.680158000	-4.947190000	-0.215952000	H	2.179859000	-3.504457000	-0.444953000
C	-0.371068000	-4.395463000	-0.088081000	H	2.802136000	3.055525000	0.290330000
C	0.871451000	-5.059251000	0.119190000	H	-5.903450000	-4.604428000	-1.063923000
C	1.168265000	-6.390161000	0.480296000	H	5.150363000	-5.749533000	0.495006000
H	0.433907000	-7.159305000	0.661966000	H	-5.000131000	5.495172000	0.118226000
C	2.546273000	-6.501876000	0.594842000	H	6.237529000	4.702833000	-0.232083000

Table S13: Coordinates for S_0 optimized geometry of the normal conformer of *meso* free compound **5•2H⁺** at CAM-B3LYP/6-311G** level of theory in dichloromethane using the PCM solvation model; # sum of imaginary frequencies=0 # Sum of electronic and zero-point Energies= -4375.157778

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.626360000	-3.003278000	-0.128541000	C	3.046994000	-5.260900000	0.421505000
C	-1.949290000	-2.715347000	-0.435437000	C	4.386158000	-4.950900000	0.462170000
C	-2.196963000	-1.345992000	-0.695588000	C	5.075724000	-3.715622000	0.348499000
H	-3.119555000	-0.921224000	-1.053084000	C	6.466487000	-3.595893000	0.325054000
C	-1.072862000	-0.579003000	-0.469463000	H	7.113420000	-4.462318000	0.378381000
C	-0.927295000	0.856356000	-0.455117000	C	6.929506000	-2.283588000	0.216161000
C	-1.871644000	1.817987000	-0.162732000	H	7.978176000	-2.022431000	0.176738000
H	-2.898366000	1.568054000	0.040488000	C	5.913375000	-1.332924000	0.158150000
C	-1.295476000	3.107658000	-0.103646000	C	6.077169000	0.092036000	0.060329000
C	0.075724000	3.131435000	-0.327181000	C	7.280055000	0.794693000	0.099667000
C	0.572160000	4.474963000	-0.255256000	H	8.237116000	0.307455000	0.224163000
C	-0.576988000	5.257450000	-0.003145000	C	7.128637000	2.175458000	-0.026093000
C	-1.016441000	6.620836000	0.116442000	H	7.952688000	2.877545000	-0.009842000
H	-0.372854000	7.485832000	0.071281000	C	5.805045000	2.600813000	-0.161509000
C	-2.365448000	6.604679000	0.276743000	C	5.417814000	3.957718000	-0.281590000
H	-3.021389000	7.453571000	0.400411000	C	4.179745000	4.557402000	-0.339523000
C	-2.844453000	5.223282000	0.325265000	C	3.905347000	5.957366000	-0.494326000
C	-4.116816000	4.838968000	0.575820000	H	4.668763000	6.711089000	-0.618055000
C	-4.568091000	3.478132000	0.870655000	C	2.547161000	6.143711000	-0.485939000
C	-4.856605000	1.431818000	1.961877000	H	2.009311000	7.071281000	-0.602445000

H	-4.726843000	0.714342000	2.762791000	C	1.932613000	4.863004000	-0.328807000
C	-5.490959000	1.131850000	0.777348000	N	-2.643840000	-3.936546000	-0.384324000
C	-5.844619000	-0.171088000	0.243313000	N	-1.681298000	4.433430000	0.126675000
C	-6.644655000	-0.497639000	-0.835517000	N	2.933653000	3.938687000	-0.263815000
H	-7.282313000	0.219528000	-1.336967000	N	1.980213000	-4.395181000	0.185203000
C	-6.518151000	-1.841536000	-1.246346000	S	4.347772000	-2.114433000	0.257635000
H	-7.045312000	-2.265022000	-2.091948000	S	4.736413000	1.199000000	-0.156522000
C	-5.580906000	-2.559620000	-0.521449000	S	0.678134000	1.555240000	-0.707202000
C	-5.148109000	-3.904968000	-0.779538000	S	-4.962331000	-1.580870000	0.795407000
C	-3.921162000	-4.492826000	-0.651744000	S	-5.507395000	2.542877000	-0.276535000
C	-3.707146000	-5.929332000	-0.656306000	S	0.314421000	-1.562455000	0.021009000
H	-4.504614000	-6.638103000	-0.824395000	C	-4.332135000	2.748932000	2.009755000
C	-2.411354000	-6.208729000	-0.332923000	H	-3.779200000	3.145613000	2.851269000
H	-1.961047000	-7.182464000	-0.218194000	H	2.077658000	-3.494336000	-0.261954000
C	-1.733663000	-4.961082000	-0.168847000	H	2.790457000	2.993679000	0.062573000
C	-0.437349000	-4.416458000	0.019488000	H	-5.919357000	-4.576883000	-1.147703000
C	0.792539000	-5.071648000	0.231564000	H	5.040666000	-5.803688000	0.613210000
C	1.094618000	-6.435213000	0.546365000	H	-4.852693000	5.638686000	0.598703000
H	0.354878000	-7.207197000	0.689563000	H	6.253411000	4.649892000	-0.327042000
C	2.453950000	-6.549642000	0.655096000				
H	3.018365000	-7.435295000	0.906983000				

Table S14: Coordinates for S_0 optimized geometry of the normal conformer of *meso* free compound **5** at CAM-B3LYP/6-311G** level of theory # Sum of imaginary frequencies=0 # Total Energy (hartree) = -4373.675018

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.244128000	-3.081270000	0.028337000	C	3.123927000	-6.317640000	0.853596000
C	-1.577191000	-2.907738000	-0.299889000	H	3.780511000	-7.142283000	1.088871000
C	-1.967343000	-1.547076000	-0.367774000	C	3.525770000	-4.920274000	0.738354000
H	-2.918644000	-1.162458000	-0.689086000	C	4.782143000	-4.437604000	0.873071000
C	-0.924027000	-0.724174000	-0.031382000	C	5.259880000	-3.099575000	0.697155000
C	-0.923969000	0.724253000	0.031390000	C	6.572188000	-2.731431000	0.900193000
C	-1.967216000	1.547241000	0.367787000	H	7.320799000	-3.433410000	1.242801000
H	-2.918550000	1.162707000	0.689109000	C	6.828185000	-1.380993000	0.630854000
C	-1.576950000	2.907870000	0.299891000	H	7.790984000	-0.909395000	0.763603000
C	-0.243878000	3.081294000	-0.028349000	C	5.713731000	-0.698567000	0.199678000
C	0.086647000	4.465573000	-0.068122000	C	5.713790000	0.698137000	-0.199623000
C	-1.092508000	5.116791000	0.238682000	C	6.828299000	1.380466000	-0.630814000
C	-1.647922000	6.428975000	0.459623000	H	7.791053000	0.908781000	-0.763581000
H	-1.101864000	7.354745000	0.371994000	C	6.572411000	2.730919000	-0.900181000
C	-2.941584000	6.284668000	0.793881000	H	7.321071000	3.432822000	-1.242837000
H	-3.652986000	7.063291000	1.021056000	C	5.260131000	3.099171000	-0.697157000
C	-3.298771000	4.859853000	0.800273000	C	4.782488000	4.437223000	-0.873155000
C	-4.517617000	4.378389000	1.083897000	C	3.526153000	4.919993000	-0.738442000
C	-4.912480000	2.969890000	1.063329000	C	3.124411000	6.317382000	-0.853747000

C	-5.391627000	0.796645000	1.727094000	H	3.781053000	7.141966000	-1.089069000
H	-5.504759000	-0.019079000	2.428217000	C	1.802395000	6.352333000	-0.600405000
C	-5.433459000	0.624555000	0.371996000	H	1.149636000	7.211693000	-0.599374000
C	-5.433547000	-0.624150000	-0.371973000	C	1.404940000	4.966211000	-0.349233000
C	-5.391738000	-0.796243000	-1.727071000	N	-2.109017000	-4.190486000	-0.457370000
H	-5.504761000	0.019496000	-2.428193000	N	-2.108670000	4.190660000	0.457370000
C	-5.103369000	-2.128877000	-2.117186000	N	2.418325000	4.141986000	-0.433492000
H	-4.985136000	-2.445462000	-3.143949000	N	2.417998000	-4.142174000	0.433437000
C	-4.912779000	-2.969526000	-1.063302000	S	4.322318000	-1.736480000	0.149851000
C	-4.517992000	-4.378046000	-1.083875000	S	4.322492000	1.736198000	-0.149681000
C	-3.299173000	-4.859590000	-0.800267000	S	0.554491000	1.595422000	-0.328438000
C	-2.942089000	-6.284431000	-0.793894000	S	-5.165334000	-2.138063000	0.442049000
H	-3.653552000	-7.063000000	-1.021062000	S	-5.164990000	2.138422000	-0.442026000
C	-1.648432000	-6.428836000	-0.459662000	S	0.554362000	-1.595465000	0.328438000
H	-1.102440000	-7.354648000	-0.372054000	C	-5.103130000	2.129252000	2.117210000
C	-1.092920000	-5.116697000	-0.238707000	H	-4.984895000	2.445831000	3.143976000
C	0.086290000	-4.465574000	0.068083000	H	-5.269807000	-5.111314000	-1.355279000
C	1.404549000	-4.966320000	0.349161000	H	5.556001000	-5.153087000	1.134092000
C	1.801900000	-6.352479000	0.600298000	H	-5.269386000	5.111703000	1.355302000
H	1.149073000	-7.211787000	0.599257000	H	5.556395000	5.152633000	-1.134231000

Table S15: Coordinates for S_0 optimized geometry of the normal conformer of *meso* free compound $[5]^{2+}$ at CAM-B3LYP/6-311G** level of theory # Sum of imaginary frequencies=0 # Total Energy (hartree) = -4373.147993

Atom	X	Y	Z	Atom	X	Y	Z
C	-0.556184000	-2.984257000	-0.153776000	C	2.391053000	-6.609373000	0.368007000
C	-1.908819000	-2.627599000	-0.340346000	H	2.958467000	-7.519594000	0.489770000
C	-2.102911000	-1.284256000	-0.542941000	C	2.943189000	-5.265631000	0.305542000
H	-3.029423000	-0.793056000	-0.776835000	C	4.289462000	-4.963115000	0.377919000
C	-0.886174000	-0.569657000	-0.409922000	C	4.926711000	-3.722431000	0.311934000
C	-0.729625000	0.825264000	-0.386001000	C	6.319163000	-3.578948000	0.381878000
C	-1.753373000	1.793171000	-0.290293000	H	6.975477000	-4.430450000	0.500718000
H	-2.800539000	1.542031000	-0.315296000	C	6.752458000	-2.276776000	0.286969000
C	-1.220361000	3.052880000	-0.125629000	H	7.791463000	-1.988520000	0.329629000
C	0.188405000	3.087304000	-0.150547000	C	5.706101000	-1.359697000	0.141885000
C	0.656037000	4.403852000	-0.112864000	C	5.883123000	0.051735000	0.026064000
C	-0.516990000	5.191320000	-0.047276000	C	7.119697000	0.686981000	-0.045044000
C	-0.945998000	6.554254000	-0.118959000	H	8.061659000	0.160006000	-0.032242000
H	-0.298748000	7.414433000	-0.160767000	C	7.018231000	2.063217000	-0.141885000
C	-2.299643000	6.553102000	-0.143559000	H	7.866286000	2.731030000	-0.205732000
H	-2.950516000	7.413227000	-0.187227000	C	5.706809000	2.530409000	-0.147580000
C	-2.790430000	5.191989000	-0.014322000	C	5.385115000	3.907205000	-0.213356000
C	-4.072861000	4.815385000	0.146423000	C	4.161324000	4.509215000	-0.211659000
C	-4.473582000	3.498577000	0.590796000	C	3.935825000	5.949560000	-0.236783000
C	-4.547006000	1.545763000	1.836976000	H	4.705658000	6.705317000	-0.275456000

H	-4.303745000	0.877222000	2.651790000	C	2.601286000	6.123399000	-0.194481000
C	-5.364720000	1.190780000	0.789186000	H	2.059198000	7.055497000	-0.194216000
C	-5.783733000	-0.130530000	0.395255000	C	2.032683000	4.781129000	-0.153960000
C	-6.720961000	-0.489457000	-0.557282000	N	-2.645818000	-3.839241000	-0.275557000
H	-7.412833000	0.214397000	-0.998542000	N	-1.629801000	4.389976000	0.009518000
C	-6.647835000	-1.836578000	-0.910563000	N	2.957824000	3.842128000	-0.164910000
H	-7.273662000	-2.302061000	-1.660219000	N	1.953693000	-4.345849000	0.153289000
C	-5.613599000	-2.512925000	-0.273967000	S	4.167406000	-2.161986000	0.123792000
C	-5.165090000	-3.806470000	-0.615136000	S	4.584443000	1.208294000	-0.033827000
C	-3.922778000	-4.381521000	-0.533903000	S	0.878476000	1.535778000	-0.320009000
C	-3.722432000	-5.794835000	-0.615981000	S	-4.862333000	-1.499623000	0.916014000
H	-4.521636000	-6.497706000	-0.798310000	S	-5.565701000	2.513598000	-0.321371000
C	-2.410640000	-6.094629000	-0.357763000	S	0.486322000	-1.625667000	-0.146879000
H	-1.963656000	-7.073740000	-0.326341000	C	-4.038843000	2.850673000	1.720491000
C	-1.744081000	-4.871979000	-0.174537000	H	-3.371844000	3.310170000	2.436106000
C	-0.405291000	-4.358178000	-0.050212000	H	-5.921855000	-4.458767000	-1.041477000
C	0.819947000	-5.045861000	0.110229000	H	4.960983000	-5.807681000	0.496630000
C	1.053683000	-6.472552000	0.244409000	H	6.246971000	4.564858000	-0.259844000
H	0.310876000	-7.253831000	0.252505000	H	-4.835734000	5.562378000	-0.045137000

Table S16: Coordinates for S_0 optimized geometry of the normal conformer of *meso* free compound **6** at CAM-B3LYP/6-311G** level of theory # Sum of imaginary frequencies=0 # Total Energy (hartree) = -3732.060860

Atom	X	Y	Z	Atom	X	Y	Z
C	4.672423000	4.726852000	-0.168844000	C	-4.259284000	-3.804392000	1.316526000
C	3.719985000	5.695032000	0.093946000	C	-3.279874000	-4.631341000	1.838635000
C	2.508764000	5.366429000	0.712643000	C	-5.120587000	-2.439033000	-0.602837000
C	2.332590000	4.051364000	1.158777000	C	-5.459827000	-2.233454000	-1.910358000
C	3.292112000	3.094923000	0.920273000	C	-5.957874000	-0.933712000	-2.164923000
C	4.460610000	3.399831000	0.213687000	C	-5.979543000	-0.141421000	-1.054892000
C	5.398493000	2.335915000	-0.143763000	S	-5.477986000	-1.029175000	0.347057000
S	4.812300000	0.715118000	-0.302811000	C	-6.347928000	1.263620000	-0.970514000
C	6.396215000	0.126811000	-0.703384000	C	0.354288000	-3.199597000	0.249742000
C	7.306438000	1.162025000	-0.722245000	C	-0.746314000	-2.304564000	0.298744000
C	6.743849000	2.412766000	-0.407293000	C	-0.389334000	-1.054288000	-0.139925000
C	1.449815000	6.361245000	0.807401000	S	1.304146000	-0.963770000	-0.613601000
C	5.833602000	-2.291611000	-0.853408000	S	-0.483032000	1.686730000	0.279908000
C	6.699538000	-1.253404000	-0.927175000	C	-1.213431000	0.149662000	-0.159106000
C	0.125328000	6.097540000	0.778618000	C	-2.553606000	0.262193000	-0.437417000
C	6.151344000	-3.710195000	-0.940405000	C	-3.010682000	1.595874000	-0.246805000
C	5.005440000	-4.369163000	-0.681485000	H	5.568541000	4.991430000	-0.716535000
C	3.986976000	-3.338495000	-0.457390000	H	3.889106000	6.713170000	-0.239235000
N	4.479500000	-2.135180000	-0.576505000	H	1.421916000	3.782744000	1.669419000

N	-0.406334000	4.817107000	0.625693000	H	3.124219000	2.086026000	1.275853000
C	-1.695288000	4.957280000	0.510794000	H	8.355010000	1.006203000	-0.940038000
C	-2.104560000	6.363904000	0.615763000	H	7.309877000	3.331691000	-0.345334000
C	-0.969607000	7.067500000	0.780281000	H	7.124390000	-4.124636000	-1.159160000
C	2.599799000	-3.565304000	-0.144369000	H	4.843306000	-5.435917000	-0.667511000
C	-2.506366000	3.798787000	0.244068000	H	-3.112569000	6.744234000	0.555770000
C	-1.998932000	2.471615000	0.110078000	H	-0.859527000	8.136715000	0.886140000
C	-3.852967000	3.686180000	-0.021486000	H	3.367743000	-6.415036000	0.928386000
C	1.531850000	-2.616946000	-0.194000000	H	1.185344000	-7.470018000	1.994386000
C	2.020697000	-4.716540000	0.355525000	H	-7.076496000	3.939130000	-0.702652000
C	2.376916000	-5.990060000	0.932933000	H	-5.097159000	5.549770000	0.010685000
C	1.274249000	-6.518913000	1.492354000	H	-1.655751000	-5.407790000	-1.020134000
C	0.126165000	-5.644146000	1.244733000	H	-3.373037000	-3.932699000	-1.946635000
N	0.661396000	-4.527559000	0.560734000	H	-4.982148000	-3.347178000	1.982142000
N	-4.185961000	2.364350000	-0.310631000	H	-3.238245000	-4.808417000	2.906908000
C	-5.559952000	2.293264000	-0.627115000	H	-5.316342000	-2.979745000	-2.678966000
C	-6.046748000	3.673474000	-0.520526000	H	-6.240484000	-0.573027000	-3.144225000
C	-5.043170000	4.486031000	-0.155435000	H	-1.727945000	-2.523839000	0.685610000
C	-1.152324000	-5.922450000	1.533589000	H	-3.137792000	-0.570362000	-0.789511000
C	-2.300168000	-5.176844000	1.010786000	H	-7.368173000	1.524448000	-1.230932000
C	-2.398153000	-4.969445000	-0.364939000	H	-1.334934000	-6.792989000	2.154224000
C	-3.376197000	-4.150384000	-0.886896000	H	7.740713000	-1.474853000	-1.139557000
C	-4.292721000	-3.512264000	-0.048849000	H	1.751087000	7.404556000	0.822373000

Table S17: Coordinates for S_0 optimized geometry of the normal conformer of *meso* free compound **6•2H⁺** at CAM-B3LYP/6-311G** level of theory # Sum of imaginary frequencies=0 # Total Energy (hartree) = -3732.823129

Atom	X	Y	Z	Atom	X	Y	Z
C	5.143807000	4.202164000	-0.421522000	C	-3.780310000	-4.150572000	1.915183000
C	4.326260000	5.289424000	-0.170269000	C	-5.454770000	-1.769356000	-0.475742000
C	3.200842000	5.160646000	0.650219000	C	-5.993258000	-1.622138000	-1.725617000
C	2.986619000	3.939540000	1.301763000	C	-6.324664000	-0.286451000	-2.034578000
C	3.813388000	2.862042000	1.066200000	C	-5.992820000	0.589943000	-1.034663000
C	4.879324000	2.962903000	0.166952000	S	-5.405892000	-0.252155000	0.362182000
C	5.669690000	1.777749000	-0.169879000	C	-6.080083000	2.028354000	-1.101716000
S	4.890886000	0.236743000	-0.202083000	C	-0.082628000	-3.313142000	0.176191000
C	6.360285000	-0.582857000	-0.643310000	C	-1.056153000	-2.282029000	0.243905000
C	7.387650000	0.332858000	-0.760725000	C	-0.550695000	-1.090427000	-0.200963000
C	6.996190000	1.658703000	-0.502513000	S	1.119736000	-1.230934000	-0.734097000
C	2.251709000	6.261738000	0.782556000	S	-0.284687000	1.601231000	0.386522000
C	5.500476000	-2.944031000	-0.757616000	C	-1.192868000	0.216171000	-0.206180000
C	6.469780000	-1.991745000	-0.818062000	C	-2.477815000	0.546313000	-0.538809000
C	0.912975000	6.105830000	0.792208000	C	-2.747103000	1.918477000	-0.282509000

C	5.658739000	-4.370250000	-0.819627000	H	5.971499000	4.305123000	-1.111808000
C	4.448920000	-4.955646000	-0.620953000	H	4.532188000	6.235639000	-0.656014000
C	3.480052000	-3.913568000	-0.451758000	H	2.190234000	3.847117000	2.029683000
N	4.133607000	-2.740778000	-0.552090000	H	3.639394000	1.936365000	1.600419000
N	0.243855000	4.888072000	0.599680000	H	8.398164000	0.042703000	-1.015546000
C	-1.087900000	5.067980000	0.559731000	H	7.673407000	2.500573000	-0.525399000
C	-1.332446000	6.471283000	0.796472000	H	6.601268000	-4.866487000	-0.994378000
C	-0.137350000	7.090038000	0.924883000	H	4.225698000	-6.009435000	-0.625851000
C	2.090717000	-3.973946000	-0.225047000	H	-2.307888000	6.922127000	0.868159000
C	-1.973099000	4.014149000	0.300579000	H	0.037350000	8.137614000	1.117750000
C	-1.644330000	2.624758000	0.148624000	H	2.454673000	-6.936652000	0.803393000
C	-3.339518000	4.085919000	-0.023562000	H	0.155715000	-7.679699000	1.882183000
C	1.150900000	-2.890295000	-0.277366000	H	-6.415424000	4.794678000	-0.959439000
C	1.350737000	-5.053437000	0.278699000	H	-4.298630000	6.112202000	-0.074441000
C	1.537902000	-6.370888000	0.828006000	H	-2.530117000	-5.249229000	-1.034868000
C	0.371889000	-6.743464000	1.390505000	H	-4.079160000	-3.549646000	-1.882466000
C	-0.635242000	-5.711438000	1.176769000	H	-5.243670000	-2.608442000	2.137334000
N	0.050716000	-4.673813000	0.485014000	H	-3.699086000	-4.321654000	2.981771000
N	-3.813119000	2.838521000	-0.340250000	H	-6.130604000	-2.448374000	-2.408556000
C	-5.167835000	2.956231000	-0.757231000	H	-6.740435000	0.031454000	-2.980910000
C	-5.452017000	4.381388000	-0.702331000	H	-2.051048000	-2.372511000	0.647382000
C	-4.376965000	5.051067000	-0.241013000	H	-3.155459000	-0.166845000	-0.974410000
C	-1.932178000	-5.784157000	1.501918000	H	-7.003506000	2.432443000	-1.505777000
C	-2.967756000	-4.860894000	1.031621000	H	-2.227662000	-6.619917000	2.128218000
C	-3.127931000	-4.671753000	-0.340698000	H	7.473301000	-2.356964000	-1.007981000
C	-4.011400000	-3.724923000	-0.816845000	H	2.634458000	7.275689000	0.817065000
C	-4.745214000	-2.930792000	0.067523000	H	0.713408000	4.048398000	0.294569000
C	-4.647508000	-3.182793000	1.438243000	H	3.693868000	-1.846497000	-0.402815000

Table S18: Coordinates for S_0 optimized geometry of the normal conformer of *meso* free compound **6**²⁺ at CAM-B3LYP/6-311G** level of theory # Sum of imaginary frequencies=0
Total Energy (hartree) = -3731.529695

Atom	X	Y	Z	Atom	X	Y	Z
C	-5.764474000	3.464584000	0.498086000	C	5.547294000	-3.179678000	-0.352146000
C	-5.064651000	4.653078000	0.435779000	C	4.878711000	-4.307488000	-0.773092000
C	-3.817021000	4.717405000	-0.199909000	C	5.466247000	-1.057871000	0.953838000
C	-3.357135000	3.585467000	-0.889982000	C	5.118698000	-0.232339000	1.994812000
C	-4.062198000	2.410464000	-0.844532000	C	5.259576000	1.133010000	1.688321000
C	-5.249559000	2.311508000	-0.104763000	C	5.740476000	1.347304000	0.423042000
C	-5.880519000	1.015404000	0.069673000	S	6.070618000	-0.138477000	-0.391592000
S	-4.895759000	-0.399043000	0.025551000	C	5.899612000	2.633134000	-0.215858000
C	-6.273303000	-1.420703000	0.308794000	C	0.526405000	-3.175829000	-0.243320000
C	-7.431595000	-0.653280000	0.438286000	C	1.343677000	-2.083827000	-0.288340000

C	-7.210744000	0.713787000	0.314343000	C	0.598716000	-0.866741000	-0.125091000
C	-3.015856000	5.916623000	-0.094481000	S	-1.131284000	-1.181438000	0.062391000
C	-5.092086000	-3.611863000	0.293803000	S	-0.037637000	1.810620000	-0.040368000
C	-6.213623000	-2.817981000	0.396534000	C	1.088054000	0.438985000	-0.105338000
C	-1.659733000	5.955382000	-0.113656000	C	2.451119000	0.873740000	-0.122771000
C	-5.068905000	-5.057651000	0.345199000	C	2.539946000	2.240940000	-0.082441000
C	-3.776146000	-5.419658000	0.181165000	H	-6.688086000	3.415436000	1.060366000
C	-3.037797000	-4.177577000	0.041734000	H	-5.456254000	5.530576000	0.936521000
N	-3.825982000	-3.117378000	0.115085000	H	-2.439644000	3.643822000	-1.452872000
N	-0.853061000	4.821688000	-0.167011000	H	-3.698556000	1.553549000	-1.397476000
C	0.378032000	5.254789000	-0.139725000	H	-8.402177000	-1.100132000	0.608253000
C	0.460280000	6.709702000	-0.067670000	H	-7.988741000	1.461631000	0.365178000
C	-0.816334000	7.141907000	-0.037111000	H	-5.924943000	-5.699259000	0.489068000
C	-1.627337000	-4.023453000	-0.112011000	H	-3.376476000	-6.420347000	0.190600000
C	1.438971000	4.282360000	-0.126547000	H	1.355803000	7.308840000	-0.017288000
C	1.277574000	2.902999000	-0.059456000	H	-1.170337000	8.160055000	0.022148000
C	2.836078000	4.468661000	-0.211787000	H	-1.528594000	-7.065613000	-0.847166000
C	-0.859793000	-2.874042000	-0.081002000	H	1.006064000	-7.713325000	-1.341753000
C	-0.674846000	-5.073541000	-0.352813000	H	5.926880000	5.398192000	-0.864590000
C	-0.666059000	-6.429635000	-0.747185000	H	3.539734000	6.544317000	-0.636686000
C	0.630780000	-6.752983000	-1.020250000	H	2.511766000	-4.457214000	1.656709000
C	1.480601000	-5.631904000	-0.734452000	H	3.725060000	-2.485405000	2.429616000
N	0.602695000	-4.588684000	-0.344997000	H	6.408167000	-2.833705000	-0.910965000
N	3.500520000	3.272351000	-0.114448000	H	5.213889000	-4.838264000	-1.656033000
C	4.880082000	3.497452000	-0.350350000	H	4.741477000	-0.591337000	2.941382000
C	4.988095000	4.913111000	-0.642663000	H	5.018331000	1.939253000	2.366654000
C	3.775240000	5.500538000	-0.511614000	H	2.411207000	-2.092524000	-0.434382000
C	2.834873000	-5.677051000	-0.721244000	H	3.281137000	0.185788000	-0.157340000
C	3.701328000	-4.699887000	-0.123449000	H	6.875643000	2.944847000	-0.572173000
C	3.354887000	-4.086892000	1.087702000	H	3.282647000	-6.531353000	-1.220101000
C	4.047933000	-2.987387000	1.527722000	H	-7.161177000	-3.321669000	0.560321000
C	5.078367000	-2.445165000	0.745694000	H	-3.538645000	6.853955000	0.069019000

Table S19: Coordinates for S_0 optimized geometry of the normal conformer of *meso* free compound **6'** at CAM-B3LYP/6-311G** level of theory # Sum of imaginary frequencies=0 # Total Energy (hartree) = -3732.060905

Atom	X	Y	Z	Atom	X	Y	Z
C	6.087316000	2.776996000	0.063922000	C	-5.336966000	1.816628000	0.392287000
C	5.552129000	4.033508000	0.281627000	C	-5.297121000	-1.898750000	0.648930000
C	4.280949000	4.188177000	0.845391000	C	-5.339500000	-2.279511000	1.960540000
C	3.617362000	3.041365000	1.297827000	C	-4.710928000	-3.523142000	2.206362000
C	4.162355000	1.792626000	1.103436000	C	-4.171245000	-4.081701000	1.085220000
C	5.382140000	1.630376000	0.437891000	S	-4.524582000	-3.121067000	-0.314111000

C	5.860666000	0.293480000	0.087181000	C	-3.389399000	-5.304768000	0.986330000
S	4.712929000	-0.979225000	-0.157381000	C	-2.193942000	2.627663000	-0.265644000
C	5.971156000	-2.105137000	-0.562373000	C	-2.271030000	1.209891000	-0.318932000
C	7.205011000	-1.492472000	-0.508800000	C	-1.099399000	0.633561000	0.106724000
C	7.144603000	-0.136107000	-0.141689000	S	0.110762000	1.824147000	0.566616000
C	3.654781000	5.503109000	0.849360000	S	0.869633000	-1.278524000	-0.329308000
C	2.329285000	5.738369000	0.738363000	C	-0.756522000	-0.784283000	0.123613000
C	5.741608000	-3.476187000	-0.896755000	C	-1.569474000	-1.851019000	0.412764000
C	4.553209000	-4.124553000	-0.915496000	C	-0.890055000	-3.084608000	0.224088000
C	1.676126000	7.038185000	0.576991000	H	7.035359000	2.680477000	-0.450650000
C	0.377934000	6.785604000	0.330423000	H	6.097021000	4.909680000	-0.052456000
C	0.240738000	5.323294000	0.351530000	H	2.652754000	3.139559000	1.768901000
N	1.371437000	4.733007000	0.612270000	H	3.619429000	0.923365000	1.453631000
N	3.340645000	-3.520350000	-0.599144000	H	8.123822000	-2.023561000	-0.720740000
C	2.439088000	-4.465029000	-0.637186000	H	8.011827000	0.499104000	-0.027788000
C	3.019112000	-5.757507000	-1.014014000	H	2.168195000	7.998022000	0.633385000
C	4.335713000	-5.537318000	-1.190522000	H	-0.411289000	7.498970000	0.148428000
C	-0.925189000	4.525726000	0.082732000	H	2.483439000	-6.684363000	-1.144323000
C	1.057908000	-4.205810000	-0.319174000	H	5.098362000	-6.247166000	-1.474929000
C	0.438378000	-2.930938000	-0.143249000	H	-2.507860000	7.022896000	-0.994097000
C	0.058458000	-5.117345000	-0.051531000	H	-4.782926000	6.129844000	-2.011245000
C	-0.967284000	3.100841000	0.168196000	H	-1.924306000	-7.655938000	0.690456000
C	-2.162467000	4.883616000	-0.416337000	H	0.584565000	-7.296622000	-0.073908000
C	-2.865836000	6.005810000	-0.988417000	H	-5.843294000	1.069577000	-2.866856000
C	-4.014771000	5.552402000	-1.520327000	H	-5.925103000	-1.197873000	-1.927863000
C	-4.149675000	4.117954000	-1.256619000	H	-5.200787000	0.406809000	1.979629000
N	-2.954255000	3.756334000	-0.593784000	H	-5.147586000	2.663843000	1.039577000
N	-1.130134000	-4.466330000	0.267586000	H	-5.772068000	-1.664907000	2.737348000
C	-2.107214000	-5.425736000	0.611438000	H	-4.609822000	-3.968974000	3.186150000
C	-1.426645000	-6.719567000	0.491337000	H	-3.096773000	0.631452000	-0.699971000
C	-0.158091000	-6.534406000	0.095191000	H	-2.576215000	-1.723225000	0.770724000
C	-5.228436000	3.367454000	-1.518120000	H	6.630487000	-4.048619000	-1.143018000
C	-5.447929000	2.021083000	-0.982820000	H	4.316499000	6.364142000	0.836821000
C	-5.721801000	0.925550000	-1.799715000	H	-3.883089000	-6.230774000	1.261154000
C	-5.763097000	-0.352341000	-1.269519000	H	-6.003535000	3.820124000	-2.126970000
C	-5.544268000	-0.566759000	0.093161000				
C	-5.382878000	0.545096000	0.922228000				

References

1. G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3–8.
2. G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3–8.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339–341.

4. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

5. (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 1372–1377; (b) W. J. Hehre, *Acc. Chem. Res.* 1976, **9**, 399–406.

6. J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* 2005, **105**, 2999–3093.