Supporting Information

For

Reversible Redox Switching between Local and Global aromaticity for Expanded Isophlorinoids

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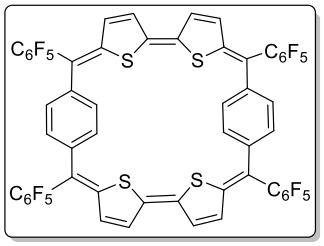
Materials and Methods

All reagents were purchased from commercial sources and used as received without further purification, unless otherwise noted. Reagent grade solvents were distilled prior to use. Column chromatography was performed on silica (silica gel, 120–230 mesh), basic alumina and size exclusion using Bio-Beads S-X1 (BIO-RAD). ^{1}H NMR spectra were recorded on Bruker 400MHz spectrometers and were calibrated to the residual solvent signals. J values are given in Hz. The following abbreviations were used to assign multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, br s = broad singlet. High-resolution mass spectra (HRMS) obtained using WATERS G2 Synapt mass Spectrometer and matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) on Bruker spectrometer. UV/vis spectra were recorded on Perkin-Elmer λ-35 UV/Vis spectrometer and all spectroscopy measurements were conducted with spectroscopic grade solvents. Conventional quartz cells with path length 1 cm were used. Single-crystal diffraction analysis data were collected at 100K with a BRUKER KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite monochromatic Mo K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by least-squares against F2 utilizing the software packages SHELXL-97,[1a,b] and WINGX.[1c] In case of disordered solvent molecules, the contributions to the scattering arising from the disordered solvents in the crystal were removed by use of the utility SQUEEZE in the PLATON software package.[2] All non-hydrogen atoms were refined anisotropically. All the CIF files of crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under CCDC numbers **2110014** for **4** and **1588228** for **6** These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data.request/cif.

Computations

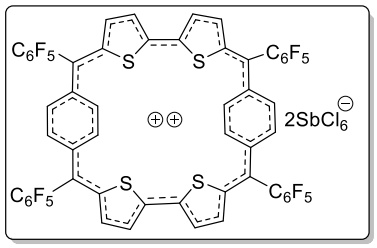
DFT calculations were performed using the Gaussian 09[3] program package with Becke's three-parameter hybrid exchange functional (B3LYP) and 6-31G (d, p) as a basis set for all the atoms employed in the calculations. The structures were geometry optimized followed by frequency calculations on the optimized structure. The nucleus independent chemical shift (NICS) calculations were carried out on optimized structures employing gauge independent atomic orbital (GIAO) method. Time-dependent (TD)-DFT calcualtions were performed using (B3LYP/631G(d)). ACID[4,5] calculations were performed using the method developed by Prof. Herges and only π-electrons are considered.

Synthesis of macrocycle 4.



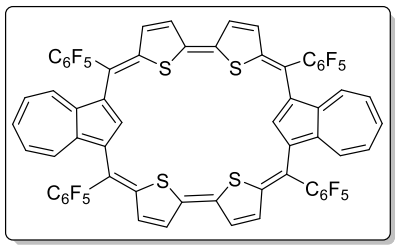
To a stirred dry dichloromethane solution of benzotrithiophene **3** (538 mg, 0.893 mmol, 1.00 eq.) was added anhydrous $FeCl_3$ (500 mg, 3.08 mmol, 3.4 eq.). The resulting mixture was stirred for 1 h under dark and quenched by adding few drops of triethylamine. The crude mixture was passed through a short pad of basic alumina column and concentrated under reduced pressure. The residue was purified by basic alumina column chromatography (Hexane/CH_2Cl_2) to give desired macrocycle **4** as an orange solid in 6 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 6.71 (d, J = 5.6 Hz, 4H), 6.12 (d, J = 5.6 Hz, 4H), 7.78 (s, 8H) ppm. **HRMS** (ESI-TOF): **HRMS (ESI-TOF)**: *m/z* calcd for ($C_{56}H_{16}F_{20}S_4$) 1195.9815; found 1195.9795. **UV/Vis** (CH_2Cl_2): λ_{max} (ε, $Lmol^{-1}cm^{-1}$) = 484 nm **Single crystal X-ray data**: $C_{56}H_{16}F_{20}S_4$ (+ solvent), M_r = 11196.93, triclinic space group *P -1*, *a* = 6.0812 (13), *b* =12.799(3), *c* = 19.883(4) Å, α = 76.448 (6), β = 82.742(5), γ = 78.168(5), *V* = 1467.5 (6) Å^3, *Z* = 1, *T* = 100(2) K, ρ_{calcd} = 1.354 g·cm^{-3}, μ = 0.260 mm^{-1}, $F_{(000)}$ = 987, *GooF*(F^2) = 0.886, R_1 = 0.045, wR^2 = 0.1296 for I>2σ(I), R_1 = 0.0650, wR^2 = 0.1412 for all data, 7377 independent reflections with a completeness of 98.6% and 361 parameters, 0 restraints. **CCDC**: 2110014

Synthesis of macrocycle $[4]^{2+}$.



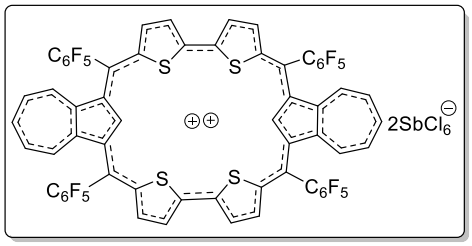
To a solution of **4** (2.5 mg, 2.1 µmol, 1.00 eq.) in dry dichloromethane at -20 °C was slowly added Meerwein's salt $[Et_3O]^+[SbCl_6]^-$ (2.5 mg, 23.05 µmol, 2.7 eq.). The resulting solution was stirred for 10 minutes under an inert atmosphere and allow it to cool down to room temperature for 1 h. Evaporation of the solvent and washed with hexane several times resulted in purple solid in a quantitative yield. **^{1}H NMR** (400 MHz, Acetonitrile-d_3, -238K): δ = 12.73 (br s, 4H), 11.89 (br s, 4H), 9.98 (br s, 4H), -1.43 (br s, 4H) ppm. **HRMS** (ESI-TOF): *m/z* calcd for $(C_{56}H_{16}F_{20}S_4)^{+2}$ 597.9907, found 597.9895. **UV/Vis** (CH_2Cl_2): λ_{max} (ε, $Lmol^{-1}cm^{-1}$) 581 nm with a broad low energy absorption band in near infrared region at 986 nm.

Synthesis of macrocycle 6.



An equimolar concentration of **5** (109.0 mg, 0.195 mmol, 1.00 eq.) and azulene (25.0 mg, 0.195 mmol, 1.00 eq.) were dissolved in dry dichloromethane (200 mL) and stirred for 10 minutes under an inert atmosphere. Catalytic amount of borontrifluoride etherate (BF_3OEt_2) (24.07 µL, 0.195 mmol, 1.00 eq.) was slowly added in dark. The resulting solution was stirred for 1 h and few drops of triethylamine was used to quench the reaction. DDQ (133 mg, 0.585 mmol) was added and the solution stirred for further two hours in an open atmosphere. The reaction mixture was passed through short pad of basic alumina column, concentrated under reduced pressure. The residue was purified by using basic alumina column chromatography (CH_2Cl_2/petrolium ether.....) to give desired macrocycle **6** as a brown solid in 4.0% yield. **^{1}H NMR**: (400 MHz, $CDCl_3$, 25 °C): δ = 9.45 (s, 1H), 7.82 (d, J = 9.7Hz, 2H), 7.60 (t, J = 9.8Hz, 1H), 7.50 (d, J = 5.9Hz, 2H), 7.11 (t, J = 10Hz, 2H), 6.82 (d, J = 5.9Hz, 2H) ppm. **HRMS** (ESI-TOF): *m/z* calcd for ($C_{64}H_{20}F_{20}S_4$) 1296.0128, found 1296.0140. **UV/Vis**: (CH_2Cl_2): λ_{max} (ε, L $mol^{-1}cm^{-1}$) 498 nm. **Single crystal X-ray data:** $C_{64}H_{20}F_{20}S_4$, Mr = 1553.82, triclinic space group P-*1*, *a* = 12.034 (4), *b* = 16.046 (5), *c* = 17.758 (5) Å, *α* = 72.188 (7)°, *β* = 80.299 (7)°, *γ* = 70.456 (7)°, V = 3068.2(17) Å^3, *Z* = 2, T = 100K, ρ_{calcd} = 1.704 g·cm^{-3}, μ = 0.524 mm^{-1}, $F_{(000)}$ = 2312, *GooF*(F^2) = 1.328, R_1 = 0.0894, wR^2 = 0.2280 for I>2σ(I), R_1 = 0.1589, *w*R^2 = 0.2564 for all data, 15433 independent reflections with a completeness of 97.3% and 882 parameters, 0 restraints. **CCDC**: 1588228

Synthesis of macrocycle $[6]^{2+}$.



The dication **$[6]^{2+}$** was obtained, by the addition of $[Et_3O]^+[SbCl_6]^-$ (7.42 mg, 17.0 µmol, 2.2 eq.) to a solution of the free base macrocycle, **6** (10.0 mg, 7.71 µmol, 1.00 eq.) in dichloromethane at -20°C and reaction mixture was stirred for 10 minutes. Cooling of the solution in dry ice acetone bath and layering it with diethyl ether gave golden colored crystals after two hours which are submitted directly to ^{1}HNMR. **^{1}H NMR:** (400 MHz, Acetonitrile-d_3, 25 °C): δ = -1.79 (s, 1H), 8.39 (broad, 4H), 8.77 (d, J = 11 Hz, 2H), 9.64 (broad, 1H), 10.23 (broad, 2H) ppm. **HRMS** (ESI-TOF): m/z calcd for $(C_{64}H_{20}F_{20}S_4)^{+2}$ 648.0064, found 648.0060. **UV/Vis** (CH_3CN): λ_{max} (ε, L mol^{-1}cm^{-1}) 638 nm with a broad low energy absorption band in near infrared region at 1374 nm.

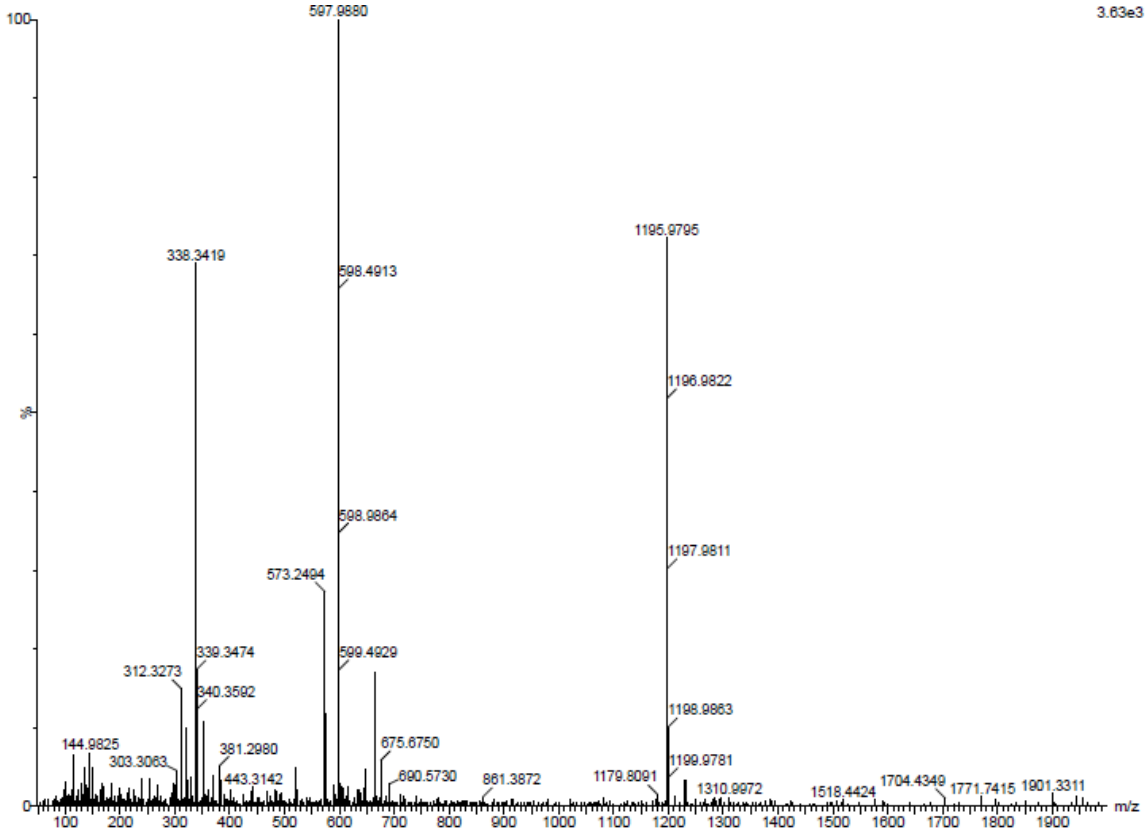


Figure S1. HRMS (ESI-TOF) spectrum of macrocycle **4**.

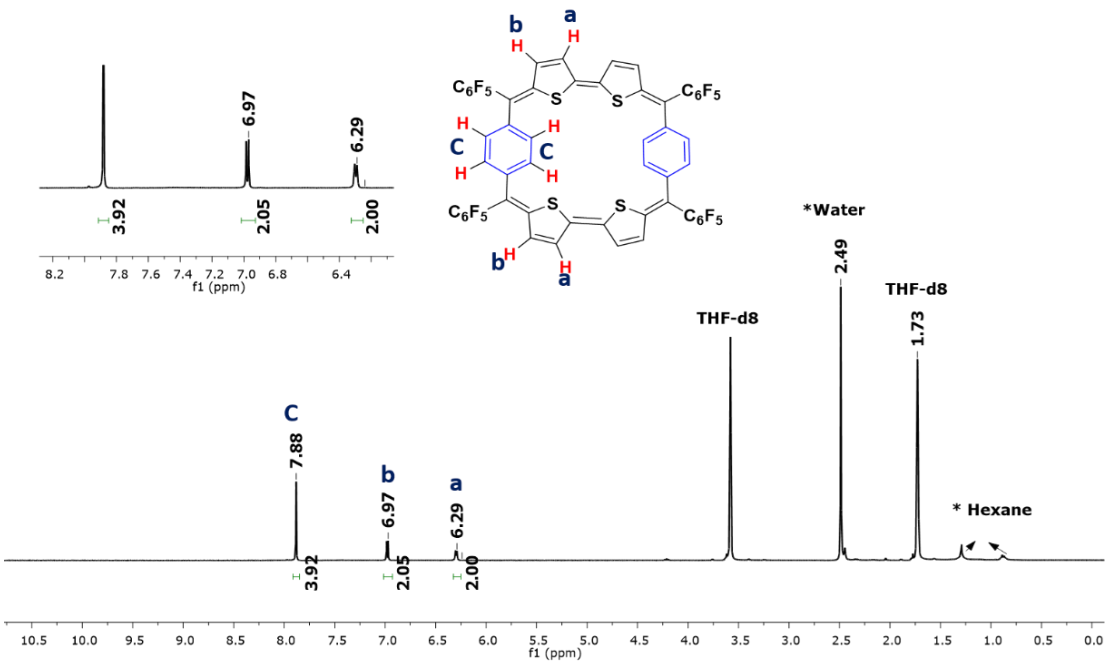


Figure S2. ^{1}H NMR of macrocycle **4** (400 MHz, Tetrahydrofuran-d_8 at 25 °C).

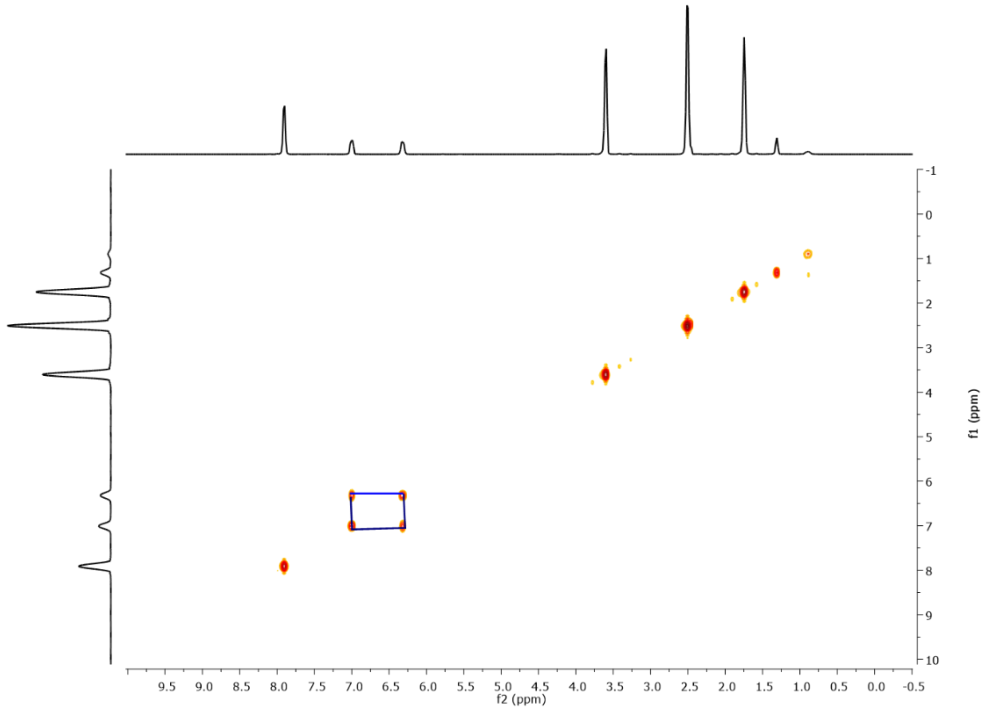


Figure S3. ^{1}H–^{1}H COSY spectrum of macrocycle **4** (400 MHz, Tetrahydrofuran-d_8 at 25 °C).

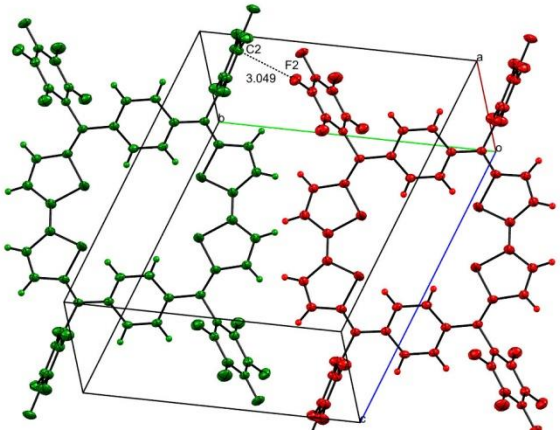


Figure S4. Molecular structure of **4** in the solid state with unit cell packing. Thermal ellipsoids are shown at 50% probability.

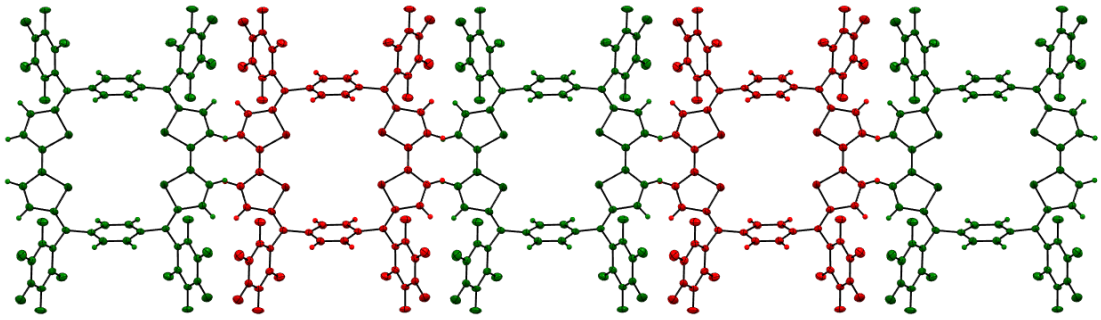


Figure S5. Molecular structure of **4** in the solid state with 2D packing (ball and sticks).

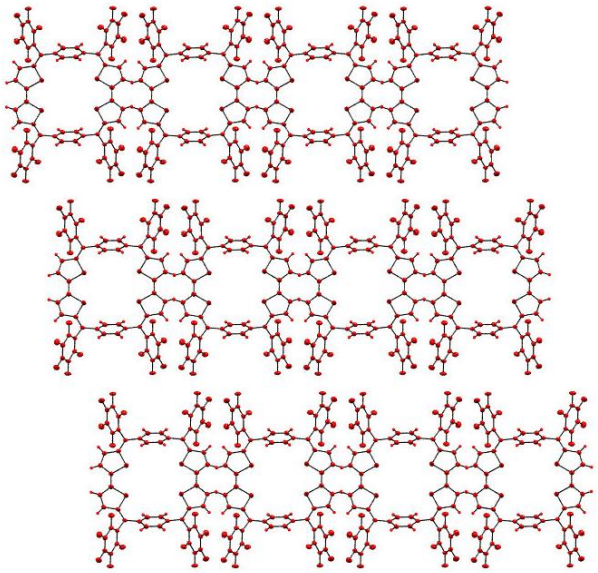


Figure S6. Molecular structure of **4** in the solid state with 3D packing (ball and sticks).

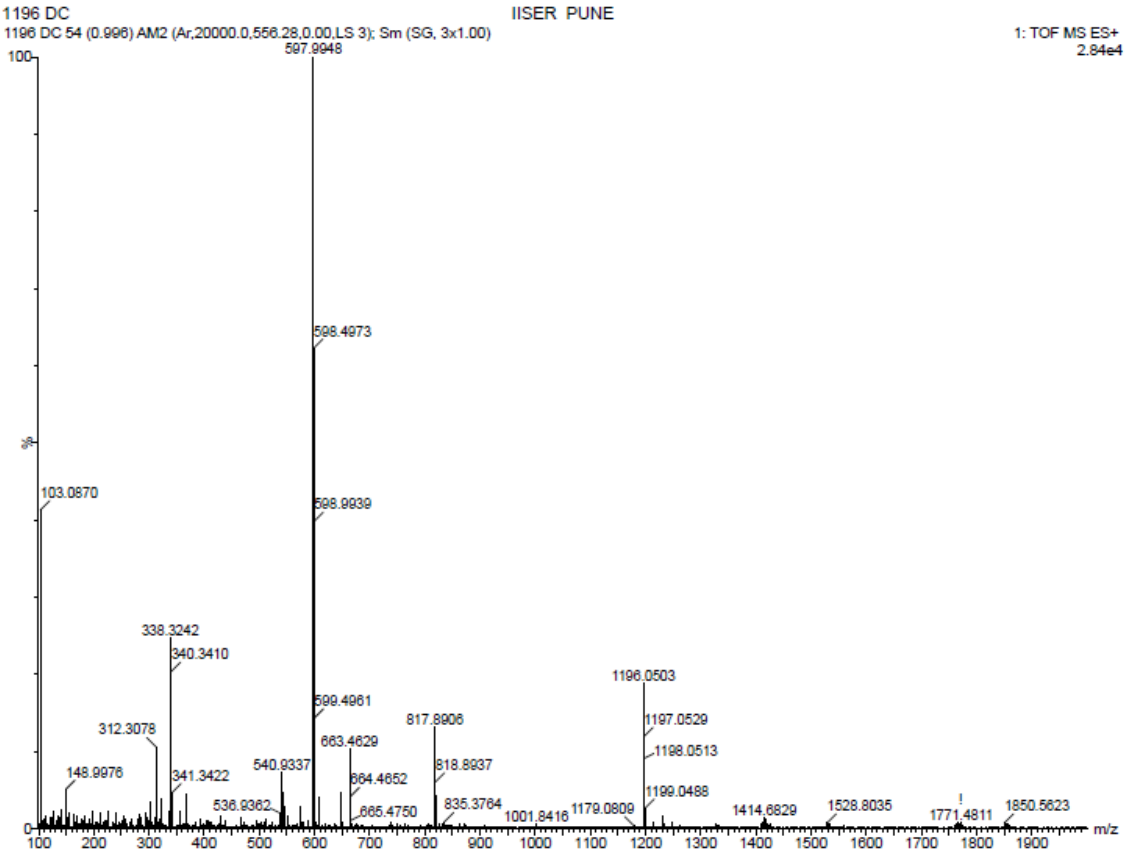


Figure S7. HRMS (ESI-TOF) spectrum of macrocycle **[4]**$^{2+}$

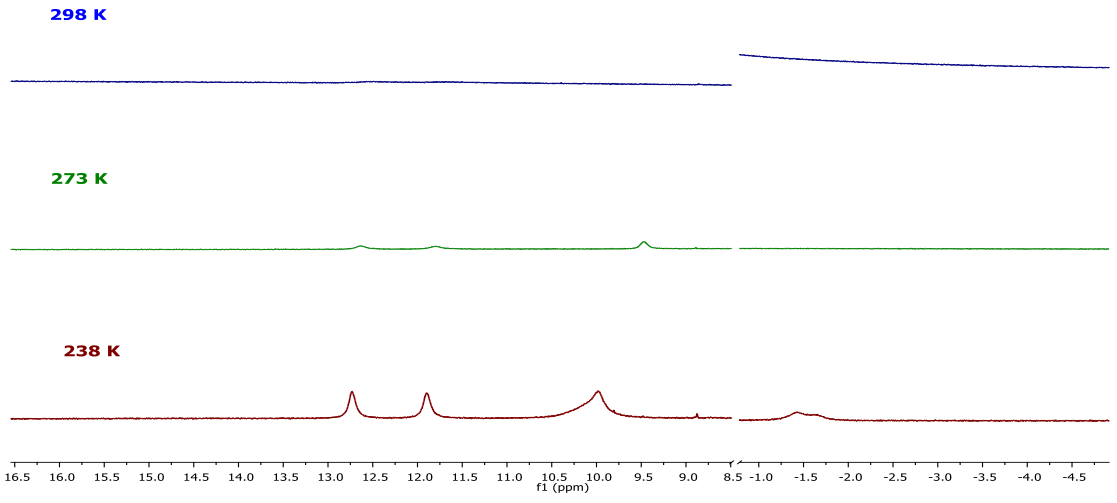


Figure S8. Variable temperature (VT) ^{1}H NMR spectrum of **[4]**$^{2+}$ (400 MHz, acetonitrile-d_3)

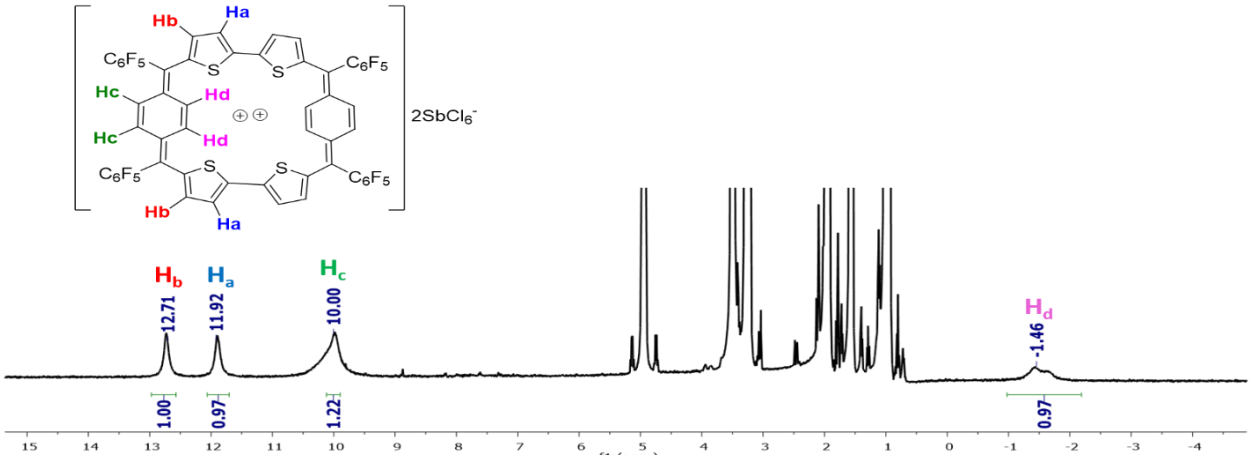


Figure S9. ^{1}H NMR spectrum of **[4]$^{2+}$** (400 MHz, acetonitrile-d_3)

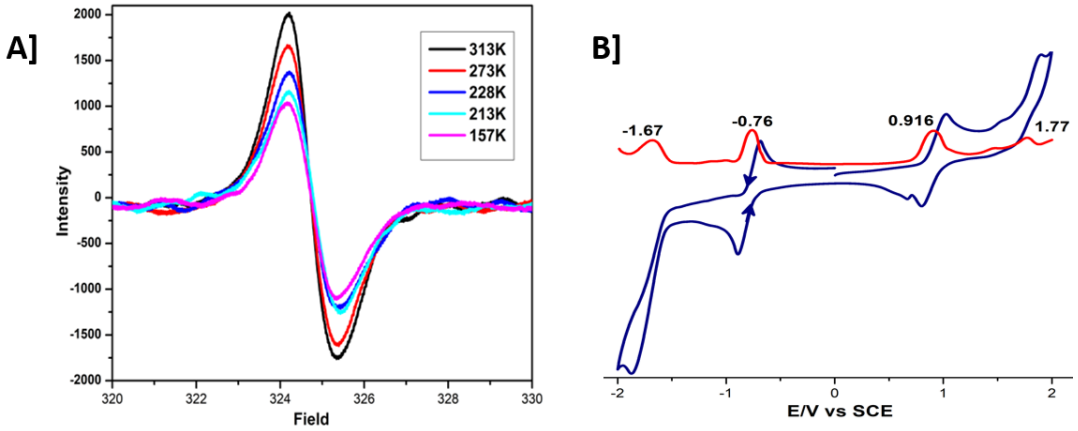


Figure S10. A] Variable temperature (VT) EPR spectrum of **[4]$^{2+}$** in solid state. B] Cyclic (Blue) and Differential pulse (red) voltammograms of **5** in dichloromethane containing 0.1M tetrabutylammonium perchlorate as the supporting electrolyte recorded at 50 mVs^{-1}

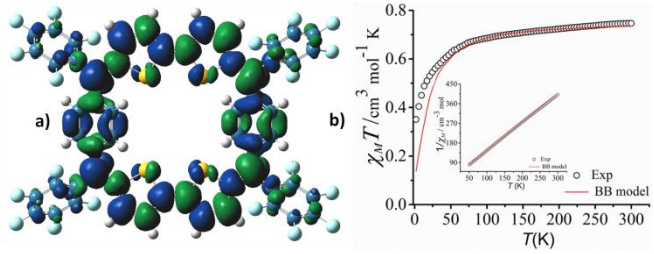


Figure S11. calculated spin density distribution map (iso-value = 0.02) for **4 b**) Measured (dot) and fitted (red plot) ($\chi_M \cdot T$ - T) curve in the SQUID measurement. Inset the plot of 1/χ_M vs T and the solid lines are the best fitting using BB model.

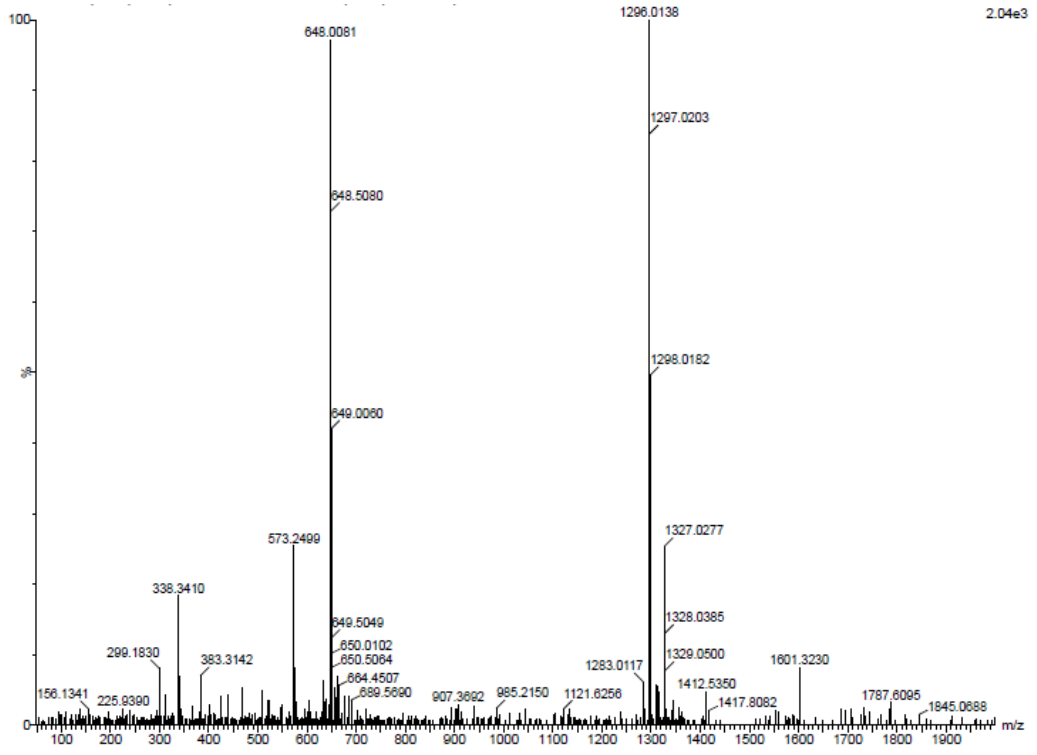


Figure S12. HRMS (ESI TOF) spectrum of macrocycle **6**

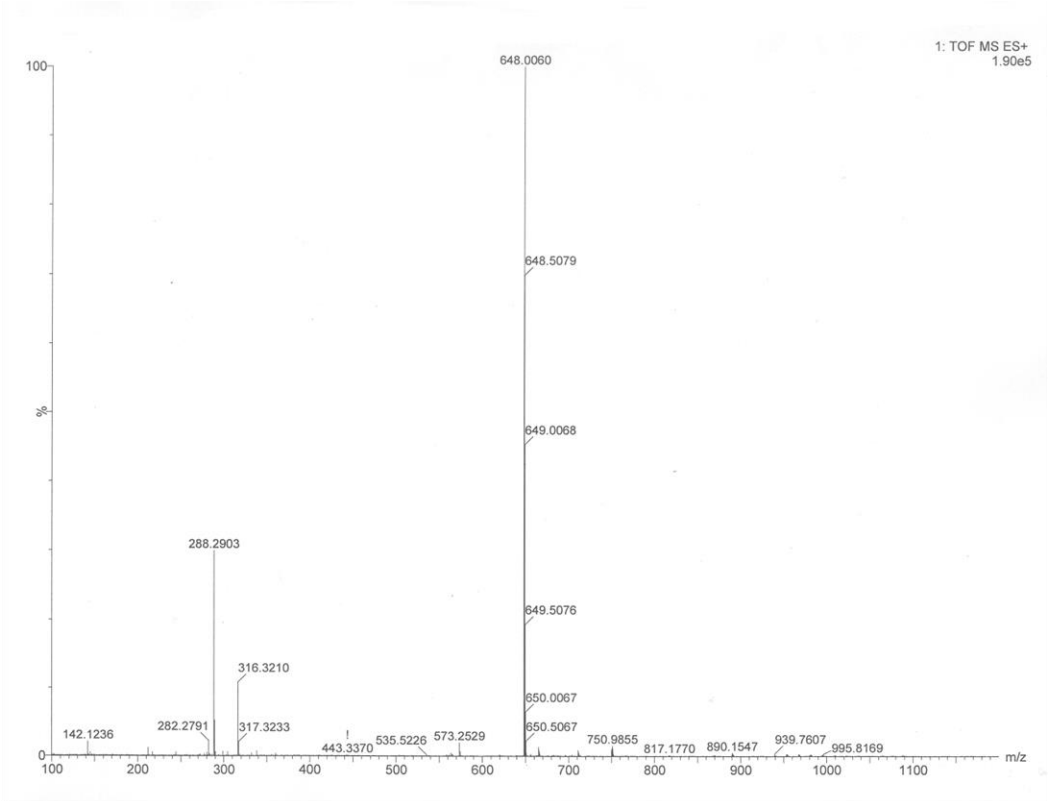


Figure S13. HRMS (ESI TOF) spectrum of macrocycle **[6]$^{2+}$**.

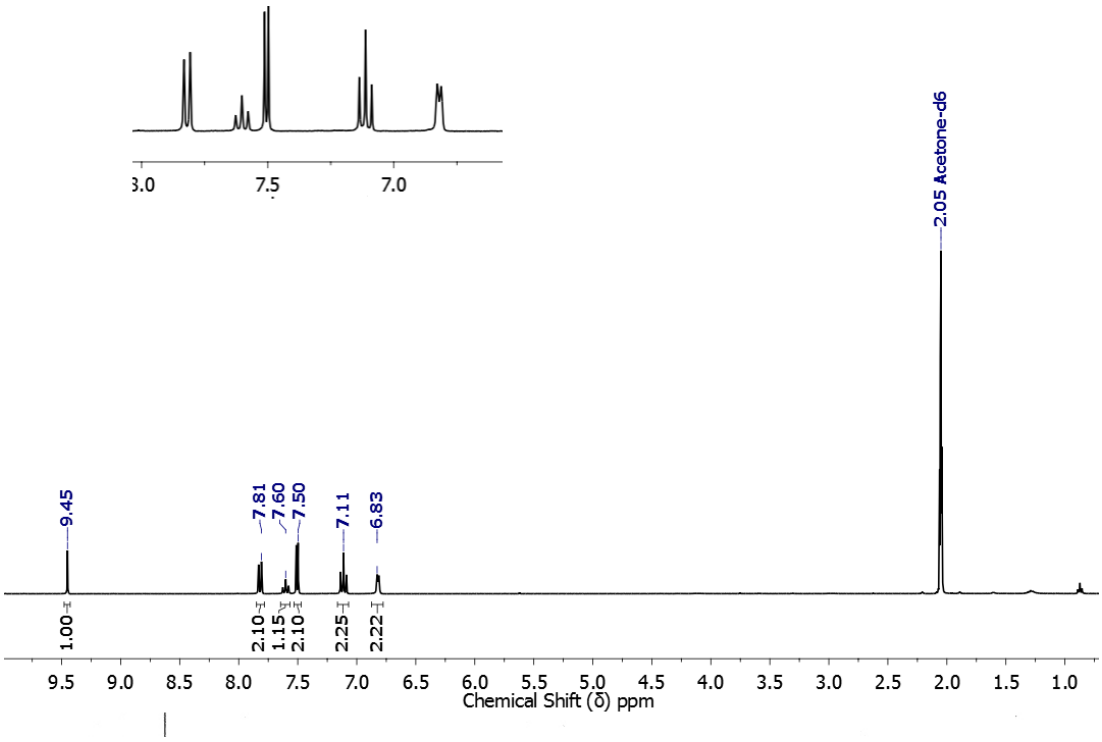


Figure S14. ^{1}H NMR spectrum of **6** (400 MHz, Acetone-d_6, 25 °C).

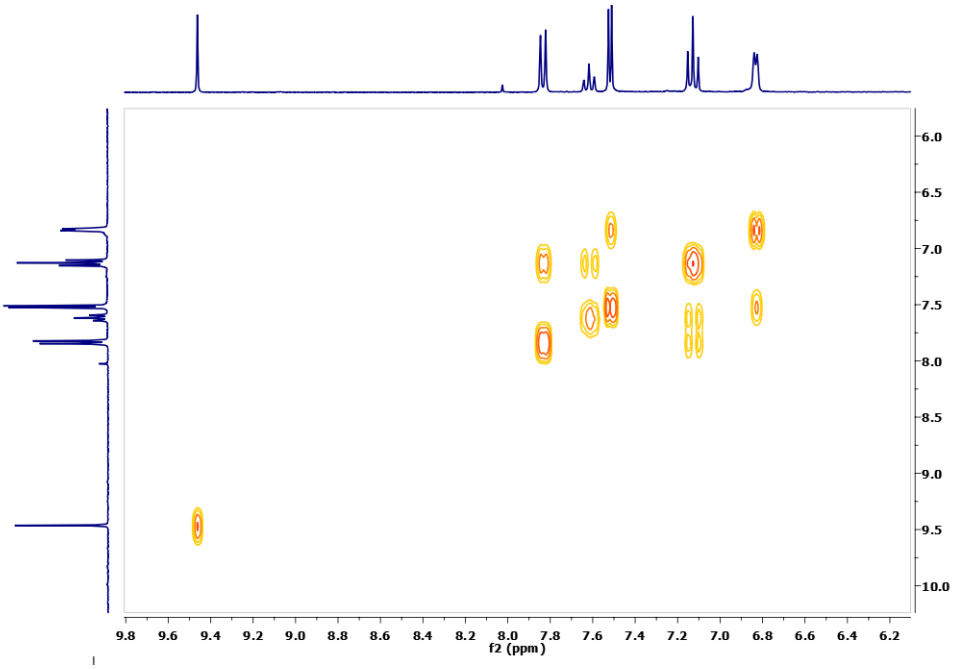


Figure S15. Partial ^{1}H–^{1}H COSY spectrum of **6** (400 MHz, Acetone-d_6, 25 °C).

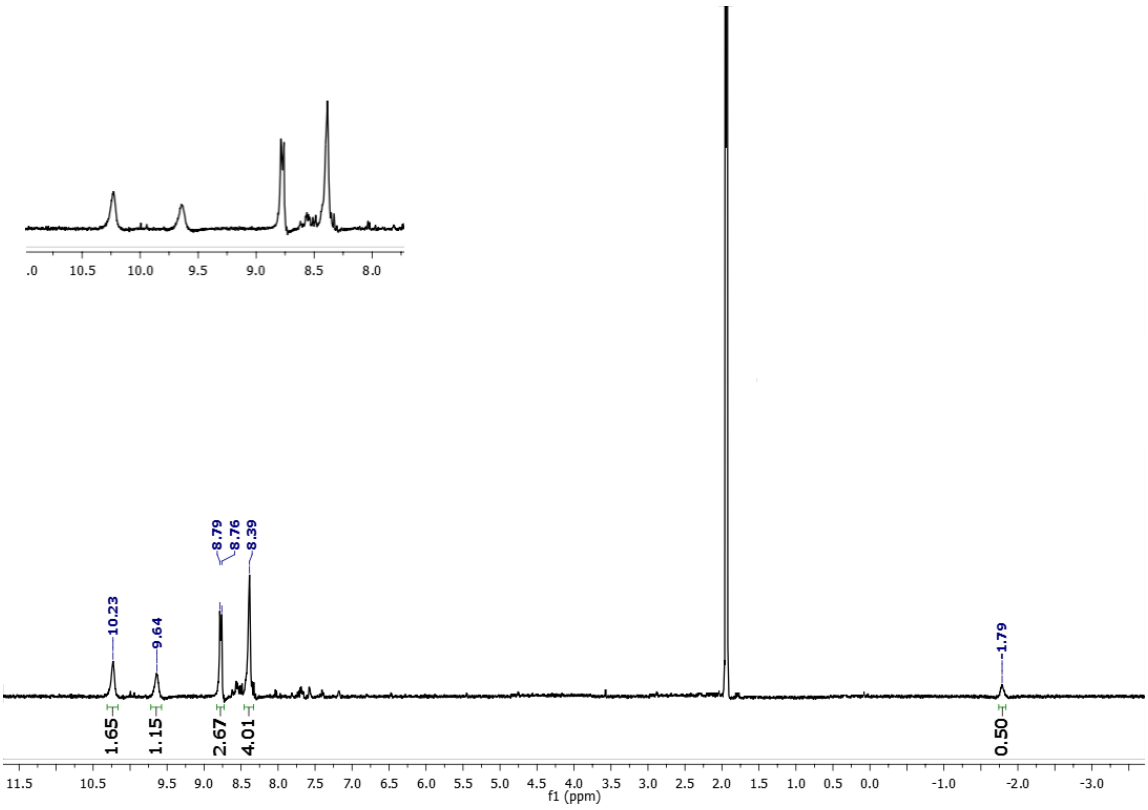


Figure S16. ^{1}H NMR spectrum of **[6]$^{2+}$** (400 MHz, Acetone-d_6, 25 °C).

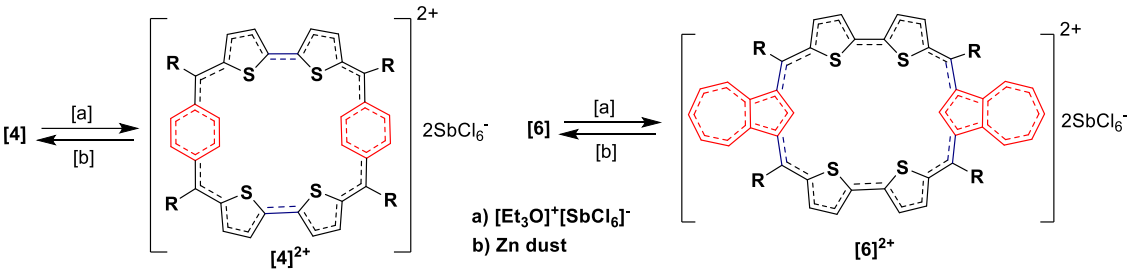


Figure S17. Schematic π-electron delocalization pathways for **[4]$^{2+}$** and **[6]$^{2+}$** after two-electron oxidation of **4** and **6**.

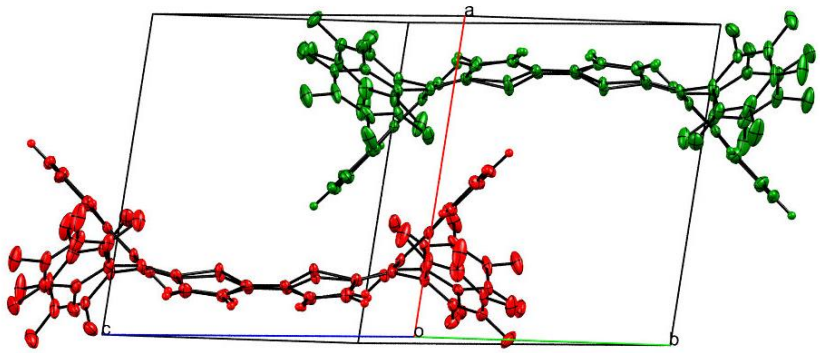


Figure S18. Molecular structure of **6** in solid state with unit cell packing (ball and sticks)

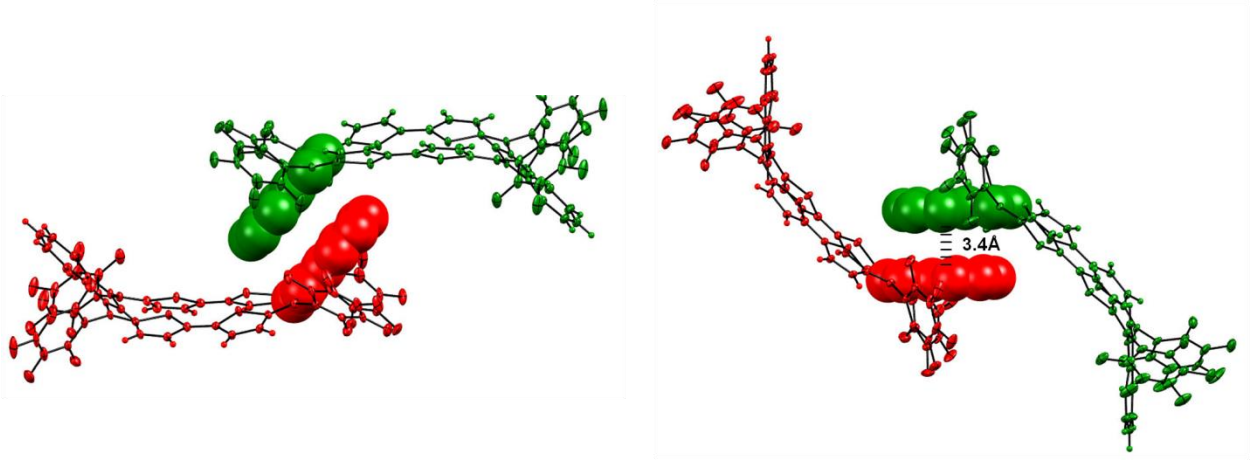


Figure S19. Solid state packing of **6** with π-π interactions between two azulene units.

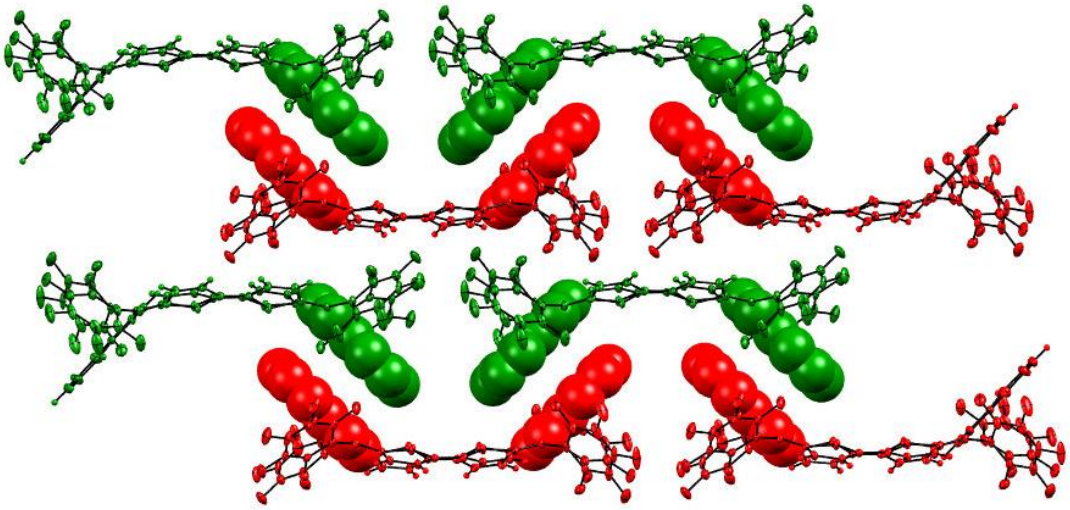


Figure S20. Solid state network of **6** formed by intermolecular interactions between the molecules

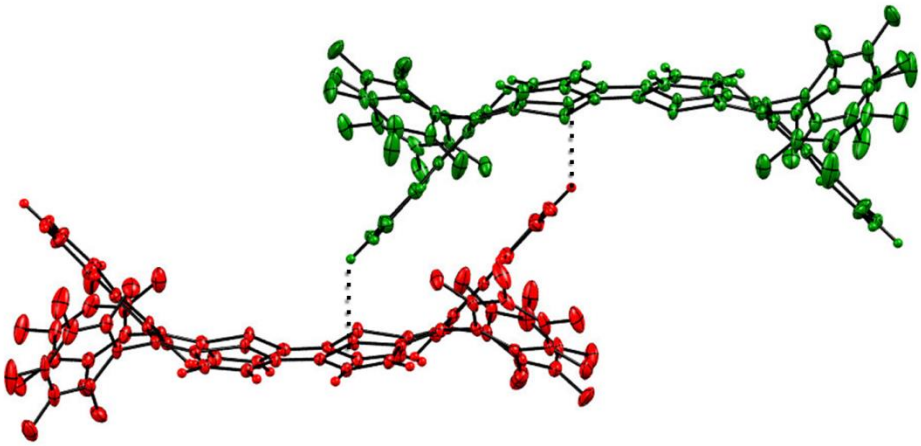


Figure S21. Solid state packing of **6** with C-H···π intermolecular interactions. Thermal ellipsoids are shown at 50% probability

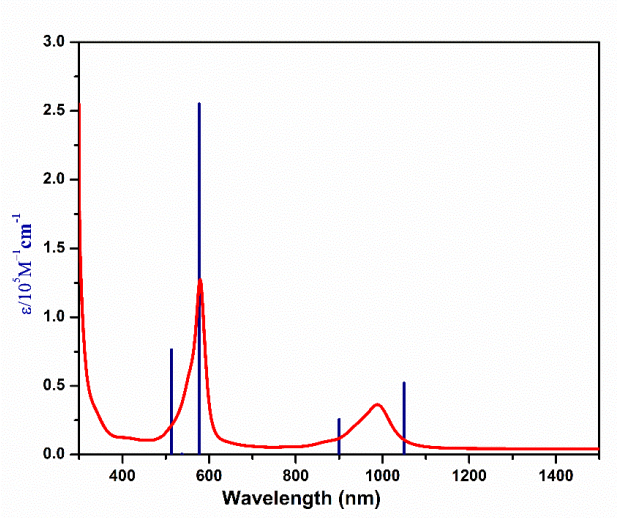


Figure S22. Experimental absorption spectrum of **[4]**$^{2+}$ (red line) with theoretical vertical excitation energies (blue bar) using TD-DFT calculations at the UB3LYP/6-31G(d,p) level of theory.

Energy (eV)	Calcd. λ [nm]	Osc. Strength (*f*)	Major Contribution
5994.354	1668.236	0.0000	HOMO(A)->L+1(A) (51%), HOMO(B)->L+1(B) (51%)
9519.021	1050.528	0.5199	HOMO(A)->LUMO(A) (49%), HOMO(B)->LUMO(B) (49%)
11106.33	900.3873	0.2566	H-1(A)->LUMO(A) (12%), HOMO(A)->L+1(A) (38%), H-1(B)->LUMO(B) (12%), HOMO(B)->L+1(B) (38%)
17330.55	577.0156	2.5503	H-1(A)->LUMO(A) (38%), HOMO(A)->L+1(A) (13%), H-1(B)->LUMO(B) (38%), HOMO(B)->L+1(B) (13%)
18564.59	538.6598	0.0019	H-3(A)->LUMO(A) (49%), H-3(B)->LUMO(B) (49%)
18590.4	537.912	0.0034	H-5(A)->LUMO(A) (49%), H-5(B)->LUMO(B) (49%)
19483.26	513.261	0.7629	H-1(A)->L+1(A) (45%), H-1(B)->L+1(B) (45%)

Table S23. Selected TD-DFT calculated energies, oscillator strengths and compositions of the major electronic transitions of **[4]**$^{2+}$ at UB3LYP/6-31G (d, p) level of theory. The α and β-orbitals are distinguished as **A** and **B** in the parenthesis, respectively.

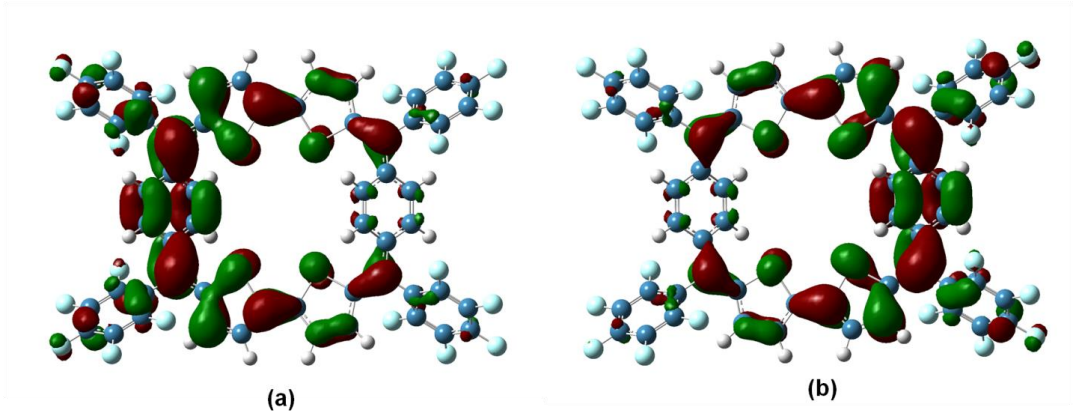


Figure S24. Selected, a) SOMO-α and b) SOMO-β for **[4]**$^{2+}$ calculated at UCAM-B3LYP/6-31G (d, p) level of theory.

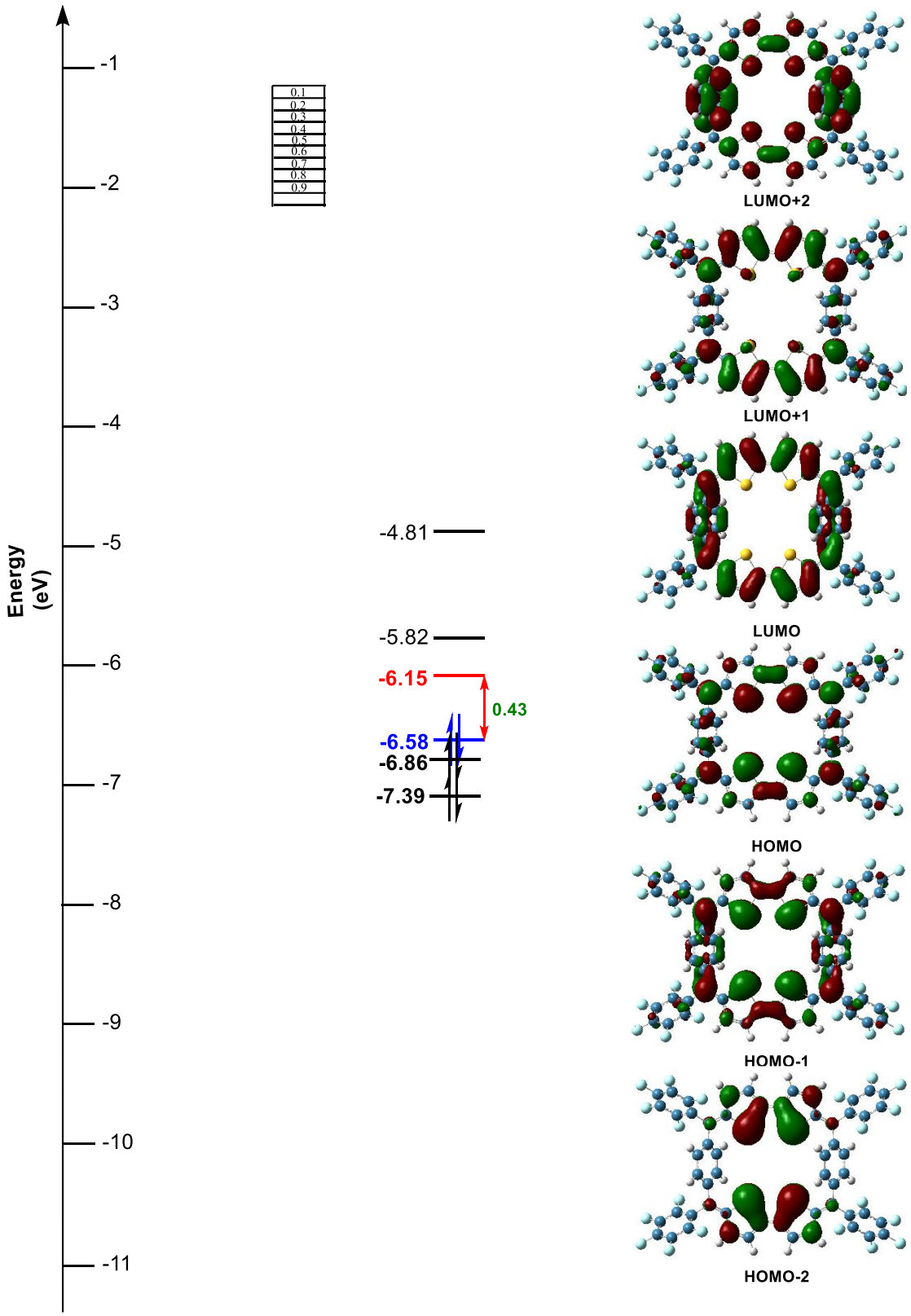


Figure S25. Selected frontier MOs of **4** calculated at B3LYP/6-31G (d, p) level of theory

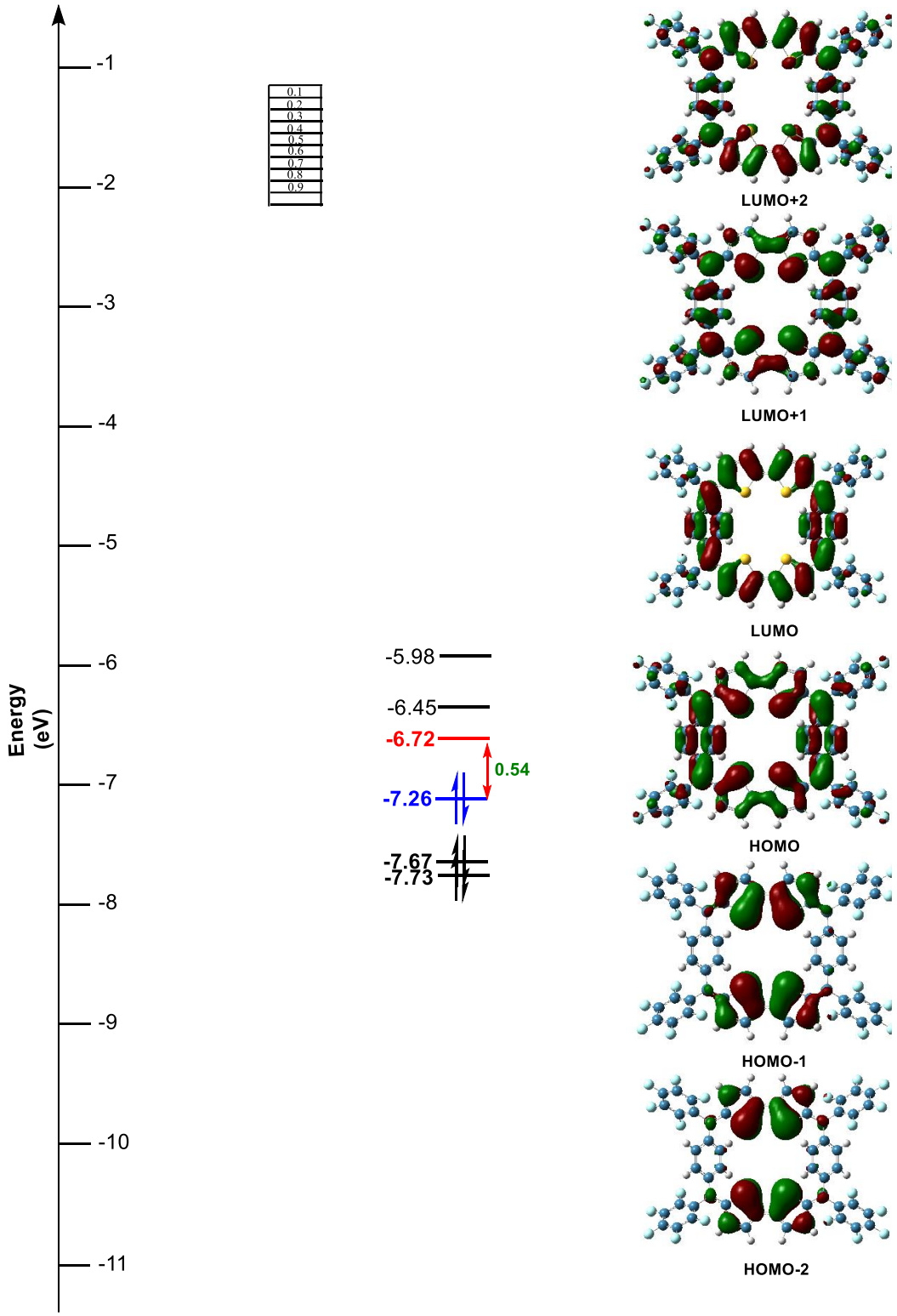


Figure S26. Selected frontier MOs of **[4]**$^{2+}$ calculated at B3LYP/6-31G (d, p) level of theory.

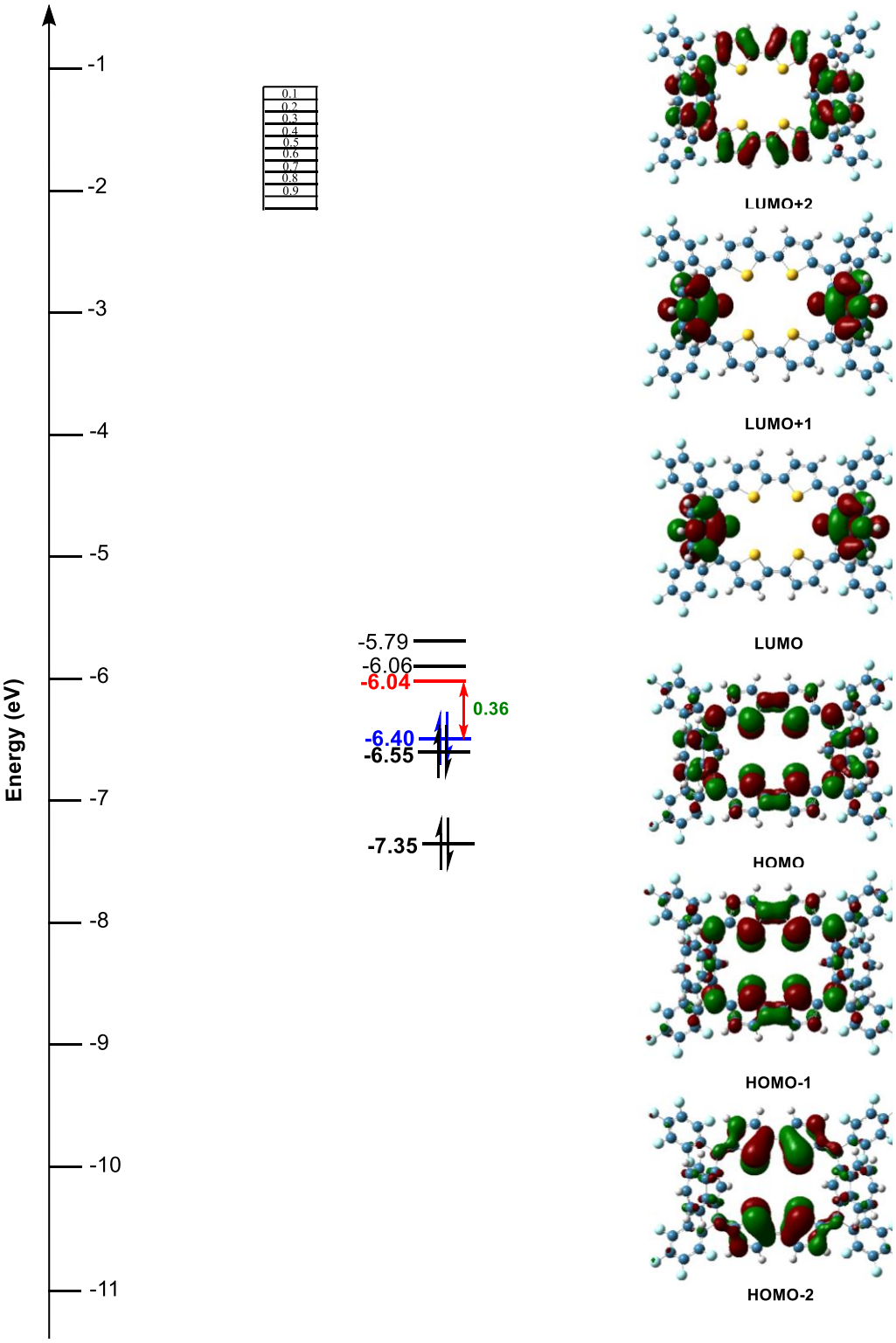


Figure S27. Selected frontier MOs of **6** calculated at B3LYP/6-31G (d, p) level of theory.

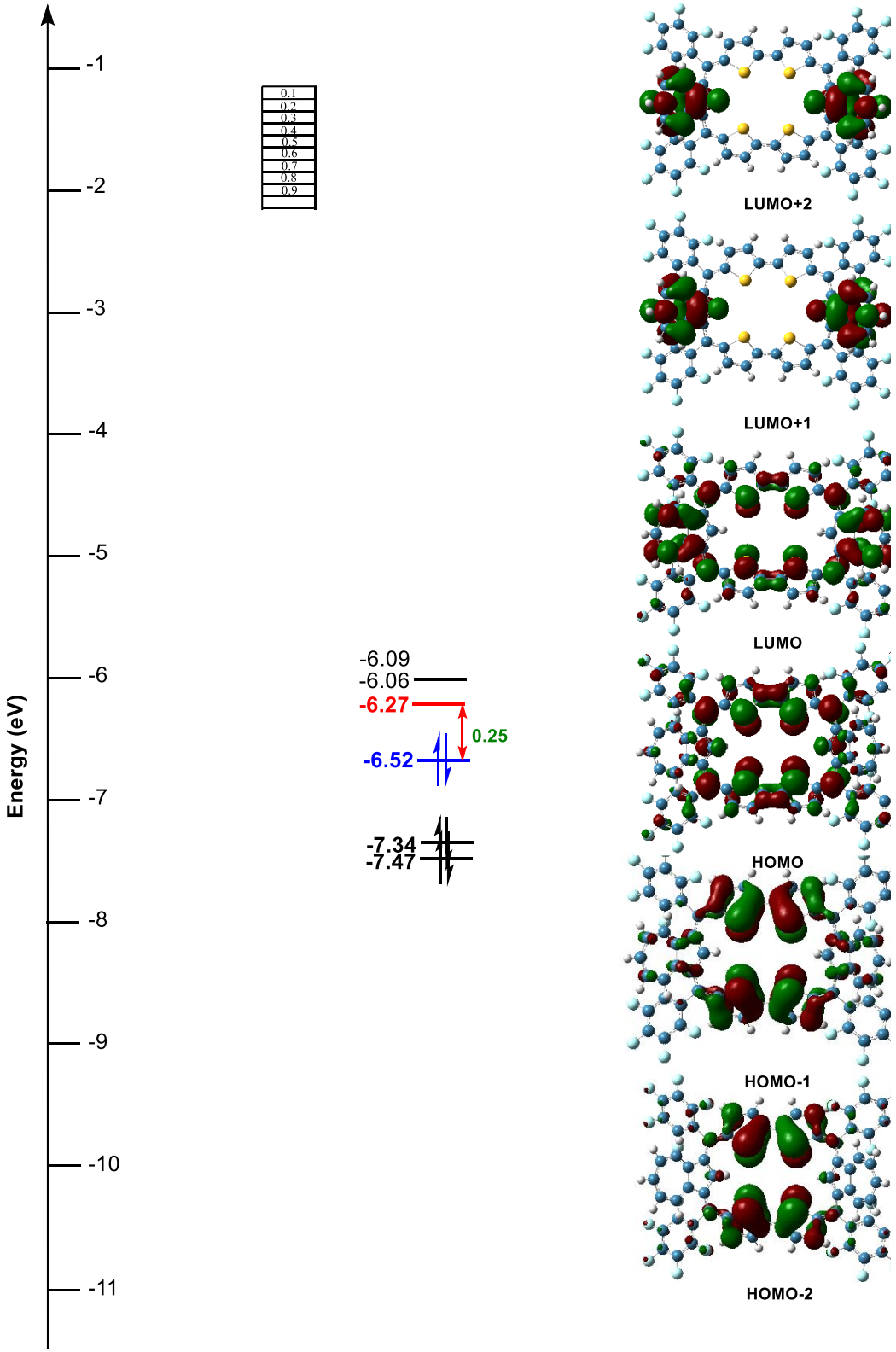


Figure S28. Selected frontier MOs of **[6]**$^{2+}$ calculated at the B3LYP/6-31G (d, p) level of theory.

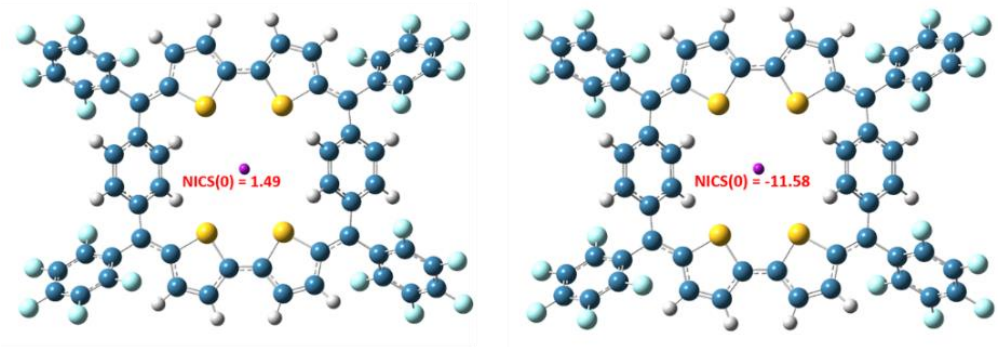
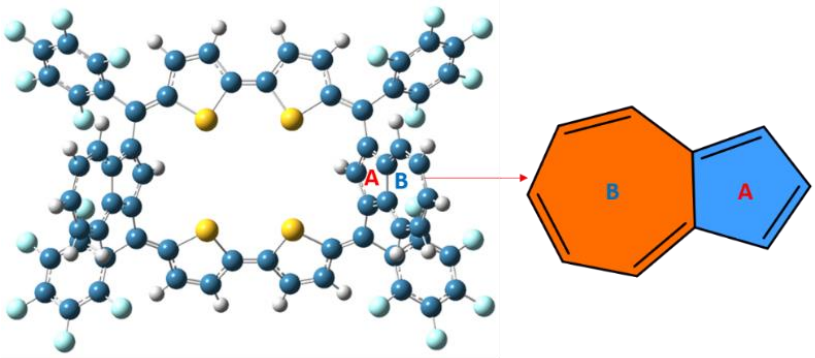


Figure S29. Calculated NICS (0) values of **4** (left) and **[4]**$^{2+}$ (right) at B3LYP/6-31G (d, p) level of theory.



Macrocycles	NICS at the center of macrocycle (ppm)	NICS at A (ppm)	NICS at B (ppm)
6	1.29	-18.11	-6.25
[6]$^{2+}$	-9.10	-9.82	-1.56

Figure S30. Calculated NICS (0) values of **6** and **[6]**$^{2+}$ at B3LYP/6-31G (d, p) level of theory.

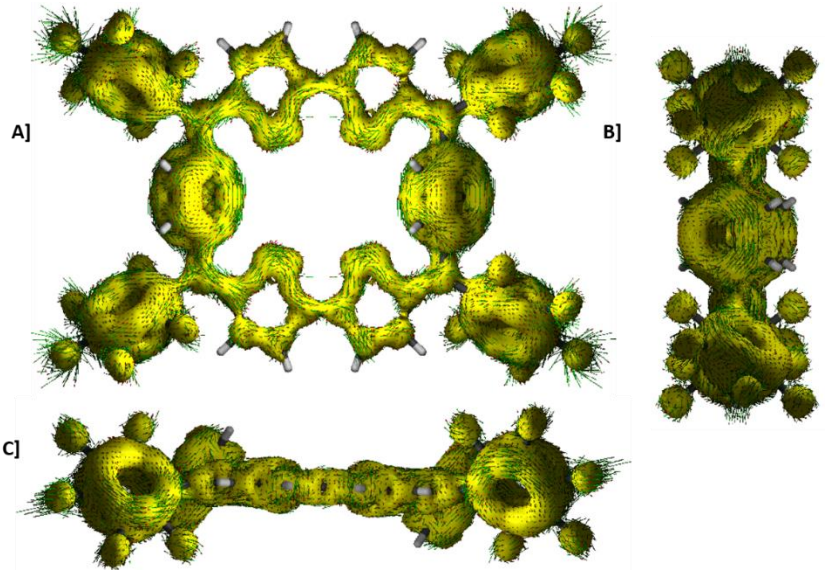


Figure 31. Calculated ACID plots for **4** are shown (top and side views), with a magnetic field along the z axis; showing weak paratropic ring current flow calculated at B3LYP/6-31G(d,p) level of theory with isovalue 0.05.

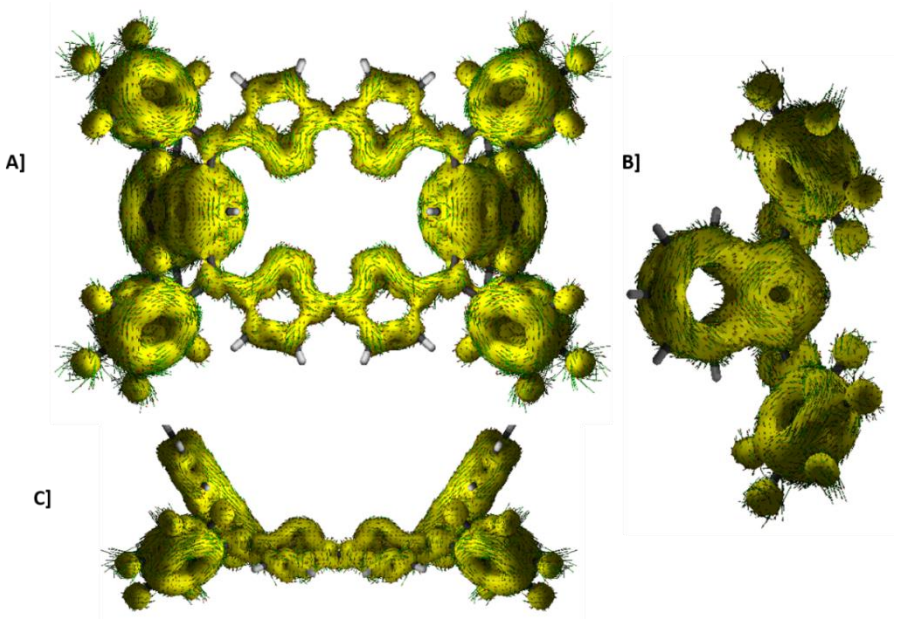


Figure 32. Calculated ACID plots for **6** are shown (top and side views), with a magnetic field along the z axis; showing weak paratropic ring current flow calculated at B3LYP/6-31G(d,p) level of theory with isovalue 0.05.

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Table S33. Cartesian coordinates for **4** at B3LYP/6-31G(d,p) level of theory.

Symbol	X	Y	Z
C	8.170755	5.054926	0.221467
C	7.162652	5.253819	1.159043
C	5.957119	4.568364	1.035724
C	5.702838	3.675492	-0.01787
C	6.746571	3.504157	-0.94408
C	7.960572	4.172715	-0.83521
C	4.441725	2.90316	-0.144
C	3.225889	3.533344	-0.13998
C	2.917797	4.946059	-0.12894

H	3.703405	5.688724	-0.16948
C	1.592558	5.26719	-0.06835
H	1.232247	6.288791	-0.0475
C	0.683564	4.153985	-0.02991
C	-0.68352	4.153991	0.029405
C	-1.5925	5.2672	0.067944
H	-1.23218	6.2888	0.047107
C	-2.91774	4.94608	0.128597
H	-3.70333	5.688758	0.169224
C	-3.22585	3.533369	0.139624
C	-4.44169	2.903196	0.143802
C	-5.70282	3.675498	0.017844
C	-5.95733	4.56829	-1.03577
C	-7.1629	5.253704	-1.15892
C	-8.17084	5.054845	-0.22115
C	-7.96044	4.172706	0.83554
C	-6.7464	3.504199	0.944239
C	-4.55219	1.420057	0.224227
C	-3.88111	0.696304	1.229323
H	-3.36278	1.229294	2.017607
C	-3.88112	-0.69622	1.229365
H	-3.36279	-1.22917	2.01768
C	-4.55223	-1.42003	0.224325
C	-5.29882	-0.69779	-0.7278
H	-5.84158	-1.23107	-1.50175
C	-5.29881	0.697763	-0.72784
H	-5.84158	1.230999	-1.50181
F	-5.00233	4.775954	-2.01074
F	-7.3677	6.113938	-2.21207
F	-9.36333	5.724613	-0.33517
F	-8.94714	3.982521	1.77314
F	-6.56689	2.661806	2.019785
F	5.001901	4.776105	2.010464
F	7.36723	6.114145	2.212158
F	9.363201	5.724749	0.335648
F	8.947439	3.982517	-1.77263
F	6.567272	2.661706	-2.0196
S	-1.63774	2.587824	0.091168
S	1.637765	2.587811	-0.09174
C	-8.17076	-5.05493	-0.22147
C	-7.16265	-5.25382	-1.15904
C	-5.95712	-4.56837	-1.03572
C	-5.70284	-3.67549	0.017872
C	-6.74657	-3.50415	0.944074

C	-7.96057	-4.17271	0.835207
C	-4.44172	-2.90316	0.143995
C	-3.22589	-3.53334	0.139977
C	-2.9178	-4.94606	0.128933
H	-3.70341	-5.68872	0.169479
C	-1.59256	-5.26719	0.068345
H	-1.23225	-6.28879	0.047491
C	-0.68356	-4.15399	0.029903
C	0.683517	-4.15399	-0.02941
C	1.5925	-5.2672	-0.06795
H	1.232185	-6.2888	-0.04711
C	2.91774	-4.94608	-0.1286
H	3.70333	-5.68876	-0.16923
C	3.225848	-3.53337	-0.13963
C	4.441693	-2.9032	-0.1438
C	5.702823	-3.6755	-0.01784
C	5.957332	-4.56829	1.035776
C	7.162903	-5.2537	1.158923
C	8.170836	-5.05485	0.221157
C	7.960436	-4.17271	-0.83554
C	6.746395	-3.5042	-0.94424
C	4.552195	-1.42006	-0.22423
C	3.881106	-0.69631	-1.22932
H	3.362778	-1.22929	-2.01761
C	3.881115	0.696222	-1.22937
H	3.362789	1.229167	-2.01768
C	4.552229	1.420033	-0.22433
C	5.298824	0.697789	0.72779
H	5.841588	1.231066	1.501739
C	5.298818	-0.69776	0.727829
H	5.841594	-1.231	1.5018
F	5.002327	-4.77595	2.01075
F	7.367696	-6.11393	2.212077
F	9.363328	-5.72461	0.335177
F	8.947137	-3.98253	-1.77314
F	6.56689	-2.66181	-2.01979
F	-5.0019	-4.77611	-2.01046
F	-7.36723	-6.11415	-2.21215
F	-9.3632	-5.72475	-0.33564
F	-8.94744	-3.98251	1.772627
F	-6.56727	-2.6617	2.019601
S	1.637737	-2.58782	-0.09117
S	-1.63777	-2.58781	0.091737

Table S34. Cartesian coordinates for **[4]$^{2+}$** at B3LYP/6-31G(d,p) level of theory.

Symbol	X	Y	Z
C	-8.020224	-5.092356	0.333796
C	-6.944682	-5.277041	1.205922
C	-5.769018	-4.562352	1.007619
C	-5.622368	-3.645265	-0.051802
C	-6.734112	-3.476056	-0.901636
C	-7.914204	-4.188766	-0.726049
C	-4.387726	-2.865447	-0.267735
C	-3.148725	-3.527502	-0.265799
C	-2.898818	-4.925605	-0.333445
H	-3.693502	-5.643334	-0.491292
C	-1.569277	-5.274779	-0.223069
H	-1.211028	-6.295373	-0.281986
C	-0.70351	-4.167015	-0.056083
C	0.703447	-4.16702	0.056182
C	1.569207	-5.274793	0.223154
H	1.210951	-6.295385	0.28206
C	2.898752	-4.92563	0.333518
H	3.693435	-5.643367	0.491341
C	3.148669	-3.527528	0.265881
C	4.387677	-2.865488	0.267783
C	5.622299	-3.645327	0.051819
C	5.768857	-4.5625	-1.00754
C	6.9445	-5.277215	-1.205878
C	8.020111	-5.092469	-0.33385
C	7.91418	-4.188796	0.725934
C	6.734106	-3.476063	0.901557
C	4.48726	-1.425919	0.41543
C	3.585658	-0.68842	1.229013
H	2.924969	-1.213414	1.908642
C	3.585672	0.688409	1.229003
H	2.924994	1.213425	1.908626
C	4.487288	1.425879	0.41541
C	5.486469	0.689604	-0.276304
H	6.213592	1.21945	-0.881447
C	5.486456	-0.689674	-0.276294
H	6.213569	-1.219543	-0.881427
F	4.773281	-4.741919	-1.884398
F	7.053024	-6.122473	-2.22606
F	9.140153	-5.772237	-0.513733
F	8.934575	-4.018208	1.559641
F	6.657731	-2.628536	1.932028

F	-4.773522	-4.741698	1.884582
F	-7.053295	-6.122214	2.226166
F	-9.140285	-5.7721	0.513646
F	-8.934533	-4.018234	-1.559847
F	-6.657652	-2.628612	-1.932169
S	1.614326	-2.675554	0.033819
S	-1.61438	-2.675544	-0.033697
C	8.020224	5.092362	-0.333806
C	6.944679	5.277045	-1.205929
C	5.769016	4.562355	-1.00762
C	5.622371	3.645268	0.051802
C	6.734119	3.476061	0.901633
C	7.91421	4.188772	0.72604
C	4.387729	2.865449	0.26774
C	3.148727	3.527505	0.265805
C	2.89882	4.925609	0.333446
H	3.693505	5.643339	0.491292
C	1.569278	5.274783	0.223069
H	1.211029	6.295378	0.281984
C	0.70351	4.167018	0.056086
C	-0.703448	4.167023	-0.056179
C	-1.569209	5.274795	-0.223151
H	-1.210953	6.295388	-0.28206
C	-2.898754	4.925631	-0.333514
H	-3.693438	5.643367	-0.491337
C	-3.14867	3.527529	-0.265874
C	-4.387677	2.865487	-0.267776
C	-5.622301	3.645324	-0.051815
C	-5.768864	4.562498	1.007541
C	-6.94451	5.27721	1.205875
C	-8.020117	5.09246	0.333843
C	-7.914181	4.188785	-0.725939
C	-6.734105	3.476055	-0.901557
C	-4.487256	1.425917	-0.415421
C	-3.585644	0.68842	-1.228994
H	-2.924947	1.213415	-1.908614
C	-3.585658	-0.688409	-1.228985
H	-2.924971	-1.213424	-1.9086
C	-4.487282	-1.425879	-0.415403
C	-5.48647	-0.689606	0.276302
H	-6.213598	-1.219452	0.881437
C	-5.486457	0.689672	0.276293
H	-6.213577	1.219541	0.881418
F	-4.773292	4.74192	1.884402

F	-7.05304	6.122469	2.226056
F	-9.140162	5.772225	0.513722
F	-8.934573	4.018193	-1.559648
F	-6.657725	2.628526	-1.932025
F	4.773517	4.7417	-1.884581
F	7.053287	6.122218	-2.226173
F	9.140284	5.772107	-0.513661
F	8.934543	4.018242	1.559834
F	6.657664	2.628618	1.932167
S	-1.614326	2.675555	-0.033815
S	1.614381	2.675547	0.0337

Table S35. Cartesian coordinates for **6** at B3LYP/6-31G(d,p) level of theory.

Symbol	X	Y	Z
S	1.670784	2.214518	0.026659
S	1.670685	-2.21439	0.026428
S	-1.67072	2.214469	0.026591
S	-1.67073	-2.21445	0.026489
F	-6.46035	1.793952	-1.90874
F	-5.03015	5.019278	1.264462
F	6.460342	1.793878	-1.9089
F	5.030544	-5.01876	1.265206
F	-6.46002	-1.79402	-1.90921
F	6.459738	-1.79445	-1.90943
F	5.030296	5.019341	1.264242
F	-9.11596	-5.56876	-1.00427
F	-8.7041	3.222768	-2.3363
F	-9.11602	5.568843	-1.00373
F	-7.25712	6.460505	0.78978
F	-5.03045	-5.01905	1.264556
F	8.704082	3.222648	-2.33659
F	8.703437	-3.22337	-2.33721
F	-8.70377	-3.22283	-2.337
F	9.115788	-5.569	-1.00399
F	7.257465	-6.46012	0.790369
F	9.116077	5.568782	-1.00413
F	-7.25741	-6.46029	0.789651
F	7.257248	6.460528	0.789413
C	5.363559	0.743821	1.524657
C	4.615846	-1.15995	0.387989
C	-2.87662	4.364143	-0.90921

H	-3.65352	5.048105	-1.22631
C	-4.42603	-2.54252	-0.07785
C	5.363542	-0.74369	1.524725
C	-1.5478	4.627103	-1.01771
H	-1.15301	5.55286	-1.41932
C	-4.16046	0.000006	-0.2682
H	-3.59657	0.000013	-1.19272
C	1.547835	4.627079	-1.01781
H	1.153032	5.552805	-1.41948
C	4.426092	2.542561	-0.07787
C	3.191998	3.074404	-0.34206
C	-5.64723	3.360891	-0.32085
C	4.61589	1.160006	0.38791
C	-5.3635	-0.74377	1.524675
C	1.547836	-4.62724	-1.01741
H	1.153051	-5.55308	-1.41883
C	-6.63233	2.93116	-1.22321
C	-3.19194	3.07439	-0.34201
C	-5.64726	-3.36083	-0.321
C	-5.36352	0.743749	1.524676
C	-0.6876	-3.57148	-0.55823
C	-4.61584	1.159986	0.387952
C	0.687611	3.571427	-0.55827
C	0.687578	-3.57147	-0.55823
C	-2.87666	-4.36424	-0.90908
H	-3.65357	-5.04824	-1.22605
C	2.876662	4.364121	-0.90934
H	3.65354	5.048057	-1.22653
C	4.160496	-4E-06	-0.26818
H	3.596608	-2.8E-05	-1.19271
C	-4.42603	2.542548	-0.07777
C	4.425989	-2.54251	-0.07767
C	-5.91092	1.586877	2.4879
H	-5.73654	2.648508	2.332228
C	-1.54783	-4.62723	-1.01751
H	-1.15303	-5.55302	-1.41904
C	-4.61583	-1.15997	0.387914
C	2.876656	-4.36425	-0.90891
H	3.653585	-5.04828	-1.22576
C	3.191932	-3.07438	-0.34193
C	5.647288	3.360879	-0.32103
C	-3.19197	-3.0744	-0.34205
C	-7.79563	3.65878	-1.45635
C	-0.68756	3.571416	-0.55828

C	6.632355	2.93111	-1.22341
C	-6.63218	-2.93116	-1.22359
C	-5.91079	-1.58695	2.487887
H	-5.73629	-2.64856	2.332206
C	-6.63712	1.262676	3.637824
H	-6.97863	2.10783	4.229851
C	-5.89795	4.570147	0.34094
C	6.964079	0.000119	4.137497
H	7.539223	0.00015	5.061254
C	5.647203	-3.3609	-0.32078
C	-6.96399	-0.0001	4.137504
H	-7.53911	-0.00012	5.061278
C	5.898109	-4.56993	0.3413
C	5.910763	-1.58682	2.488018
H	5.736207	-2.64844	2.332464
C	-8.00475	-4.86087	-0.78416
C	7.795242	-3.6591	-1.45684
C	-7.79546	-3.65876	-1.45685
C	-7.0522	5.317616	0.123112
C	6.631987	-2.93144	-1.2236
C	-6.63697	-1.26283	3.637863
H	-6.97834	-2.10803	4.229906
C	6.636976	-1.26263	3.63797
H	6.978295	-2.1078	4.230082
C	5.898051	4.570163	0.340699
C	7.795653	3.658711	-1.45663
C	8.004847	4.860906	-0.78407
C	6.637252	1.262877	3.637723
H	6.978816	2.108063	4.22967
C	5.911014	1.587007	2.487811
H	5.736651	2.64863	2.332062
C	-8.00478	4.860949	-0.78374
C	8.004606	-4.86105	-0.7839
C	-5.8981	-4.57001	0.340846
C	7.052322	-5.31744	0.123406
C	7.052294	5.317614	0.122793
C	-7.05234	-5.31747	0.122917

Table S36. Cartesian coordinates for **[6]$^{2+}$** at B3LYP/6-31G(d,p) level of theory.

Symbol	X	Y	Z
S	-1.67676	-2.11031	-0.05809
S	-1.67676	2.110311	-0.05811

S	1.676764	-2.11031	-0.05804
S	1.676759	2.110311	-0.05808
F	6.850791	-1.8856	-1.47456
F	4.499102	-5.14272	1.061619
F	-6.85075	-1.88558	-1.47474
F	-4.49908	5.142717	1.061418
F	6.850799	1.885574	-1.47463
F	-6.85077	1.8856	-1.47477
F	-4.49913	-5.14273	1.06146
F	8.78222	6.079159	-0.62089
F	8.912388	-3.59387	-1.73214
F	8.782283	-6.07912	-0.62067
F	6.56506	-6.84037	0.769256
F	4.499059	5.14274	1.061442
F	-8.91234	-3.59385	-1.7324
F	-8.91233	3.593905	-1.73243
F	8.912365	3.593872	-1.73228
F	-8.78221	6.079171	-0.62099
F	-6.565	6.840405	0.768977
F	-8.78227	-6.07911	-0.62096
F	6.564988	6.84042	0.769016
F	-6.56509	-6.84038	0.769019
C	-5.73323	-0.72607	1.311139
C	-4.71779	1.160629	0.361842
C	2.880643	-4.12166	-1.20967
H	3.653164	-4.77103	-1.60004
C	4.456507	2.501242	-0.08202
C	-5.73323	0.726065	1.311137
C	1.536644	-4.34786	-1.39306
H	1.144658	-5.2056	-1.9248
C	4.102415	-8E-06	-0.14049
H	3.363555	-2.1E-05	-0.92965
C	-1.5366	-4.34785	-1.39312
H	-1.1446	-5.20559	-1.92485
C	-4.4565	-2.50126	-0.08206
C	-3.18641	-2.93795	-0.48728
C	5.589156	-3.45348	-0.20971
C	-4.71778	-1.16064	0.361853
C	5.733207	0.726083	1.311248
C	-1.53662	4.347764	-1.39328
H	-1.14462	5.205469	-1.92507
C	6.756521	-3.09412	-0.90789
C	3.186422	-2.93795	-0.48718
C	5.58914	3.453473	-0.20983

C	5.733204	-0.72605	1.311269
C	0.703304	3.356713	-0.82007
C	4.717773	-1.16063	0.361969
C	-0.70328	-3.35677	-0.81997
C	-0.70329	3.356714	-0.82008
C	2.880639	4.12157	-1.20985
H	3.653159	4.770914	-1.60027
C	-2.88061	-4.12165	-1.20976
H	-3.65312	-4.77102	-1.60016
C	-4.10241	-9E-06	-0.14058
H	-3.36354	-1.3E-05	-0.92973
C	4.456508	-2.50126	-0.08194
C	-4.45651	2.50124	-0.08209
C	6.463423	-1.57248	2.148269
H	6.252426	-2.63101	2.045524
C	1.536635	4.34776	-1.39326
H	1.144649	5.205463	-1.92506
C	4.717776	1.160635	0.361931
C	-2.88062	4.121574	-1.20989
H	-3.65314	4.77092	-1.60031
C	-3.18641	2.937911	-0.48734
C	-5.58915	-3.45348	-0.20988
C	3.186415	2.93791	-0.48729
C	7.830083	-3.96668	-1.0542
C	0.703307	-3.35677	-0.81995
C	-6.7565	-3.09411	-0.90809
C	6.75651	3.094111	-0.908
C	6.463425	1.572535	2.148228
H	6.252433	2.631055	2.045457
C	7.433098	-1.25631	3.102755
H	7.888535	-2.10651	3.603177
C	5.559889	-4.74536	0.346525
C	-7.88006	-4E-06	3.516316
H	-8.6514	-4E-06	4.281939
C	-5.58914	3.453474	-0.20991
C	7.879991	0.000042	3.516477
H	8.651324	0.000051	4.282114
C	-5.55986	4.745367	0.346307
C	-6.46346	1.572506	2.148117
H	-6.25247	2.631027	2.045366
C	7.763602	5.241804	-0.49089
C	-7.83004	3.966698	-1.05446
C	7.830055	3.96668	-1.05434
C	6.624001	-5.6321	0.214892

C	-6.75649	3.094126	-0.90811
C	7.4331	1.25638	3.102722
H	7.888538	2.106597	3.603123
C	-7.43316	1.256339	3.10259
H	-7.8886	2.106549	3.602996
C	-5.5599	-4.74537	0.346342
C	-7.83006	-3.96666	-1.05443
C	-7.76364	-5.24177	-0.49095
C	-7.43316	-1.25635	3.102583
H	-7.88861	-2.10656	3.602984
C	-6.46347	-1.57251	2.148112
H	-6.25247	-2.63103	2.045356
C	7.76365	-5.24178	-0.4907
C	-7.76359	5.241813	-0.49098
C	5.559851	4.745376	0.346361
C	-6.62395	5.632119	0.214633
C	-6.62401	-5.6321	0.21467
C	6.623948	5.632125	0.214695