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Electronic Supporting Information

Revisiting the intense NIR active bronzaphyrin, a 26-π aromatic expanded porphyrin: Synthesis and structural analysis

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Contents

1. Instrumentation and reagents:

NMR spectra were recorded on a Bruker Avance-400 and 500 MHz FT NMR spectrometers using tetramethylsilane (TMS, $\delta = 0$) as an internal standard at room temperature. Mass spectral determinations were carried out by Shimadzu-LCMS-2010 and Bruker Maxis Spectrometer by ESI techniques. UV-visible spectra were recorded on Perkin Elmer Lambda-35 spectrometer. Spectroscopic grade solvents were used for all absorbance measurement. Melting points were determined on MR-Vis+ visual melting point range apparatus from LABINDIA instruments private limited. IR spectra were recorded on a JASCO-FT-IR model 5300 and NICOLET 5700 FT-IR spectrometer.

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were done using Zahner Zennium Electrochemical Workstation and electrodes were purchased from CH Instruments Inc. All measurements were done in dichloromethane under flow of nitrogen and 0.1M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) used as a supporting electrolyte. Platinum disc as working electrode, platinum wire as counter electrode and Ag/AgCl in (1M) KCl as reference electrode were used. Ferrocenium/Ferrocene, Fc^+/Fc couple was used as external reference for calibration. The redox potentials were referenced vs. sat. calomel electrode, SCE (0.48V vs SCE for Fc^+/Fc couple). All cyclic voltammetric data were recorded at 100 mV/s scan rate.

Crystallographic data for **8** was collected on Oxford Gemini A Ultra diffractometer with dual source. Cu-Kα ($\lambda = 1.54184$ Å) radiation was used to collect the X-ray reflections of the crystals. Data reduction was performed using CrysAlisPro 171.33.55 software.[S1] Structures were solved by using Olex2-1.0 with anisotropic displacement parameters for non-H atoms and final refinement was done by SHELXL-2014/7.[S2] Crystallographic data for **8**.$(TFA)_2$ were collected on BRUKER SMART-APEX CCD diffractometer. Mo α ($\lambda = 0.71073$ Å) radiation was used to collect X-ray reflections on the single crystal. Data reduction was performed using Bruker SAINT software.[S3] Intensities for absorption were corrected using SADABS [S4] and refined using SHELXL-2014/7 with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on O and N were experimentally located in difference electron density maps. A check of the final CIF file using PLATON [S5] did not show any missed symmetry.

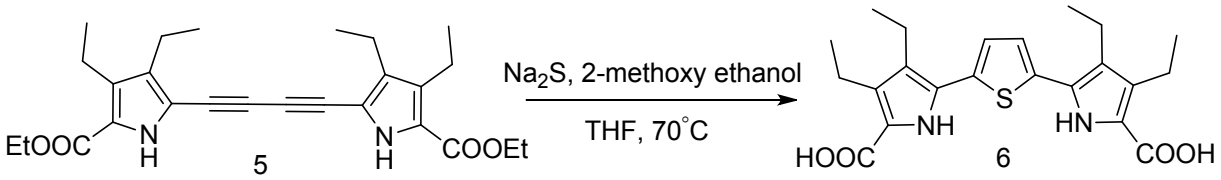
Crystallographic data (including the structure factor) for structures **8** and **8.$(TFA)_2$** in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1500785 and CCDC 1869467. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Commercially available solvents were distilled before use. Reagents were purchased from Sigma Aldrich and used as received without further purification unless otherwise stated. Solvents for the reactions were dried according to literature methods.

2. Experimental details:

Synthetic details of compounds are described below.

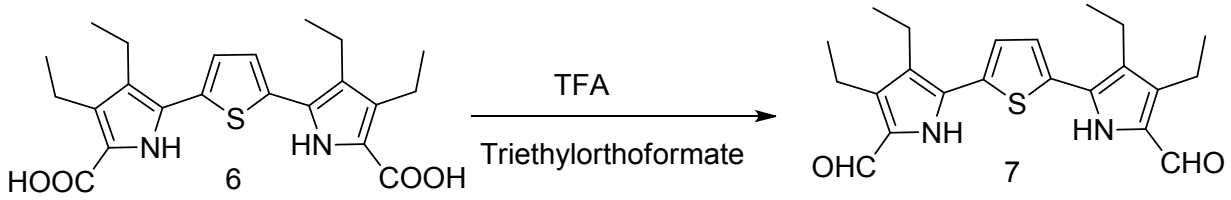
Synthesis of thiophene substituted terpyrrole diacid 6:



Butadiyne bridged bipyrrole **5** (436 mg, 1 mmol) and Na_2S (1.2 g, 5 mmol) were dissolved in THF/2-methoxyethanol and heated at 70°C for 4 h. The solution thus obtained, poured in excess water and treated with HCl solution, yielding the desired product as precipitate (370 mg, 90%).

Melting point: 195-197°C; FTIR data: 3442, 2962, 1655, 1458 cm^{-1}; ^1H NMR (500 MHz, MeOH-d_4): δ in ppm 7.27 (s, 2H, *β*-CH thiophene), 2.80 (q, 4H, J = 7.5 Hz, CH_2 alkyl), 2.69 (q, 4H, J = 7.5 Hz, CH_2 alkyl), 1.18 (m, 12H, CH_3 alkyl); ^{13}C NMR not recorded due to lack of solubility; HRMS m/z calcd. for $(M+H)^+$ $C_{22}H_{27}N_2O_4S$:415.1692, found 415.1689.

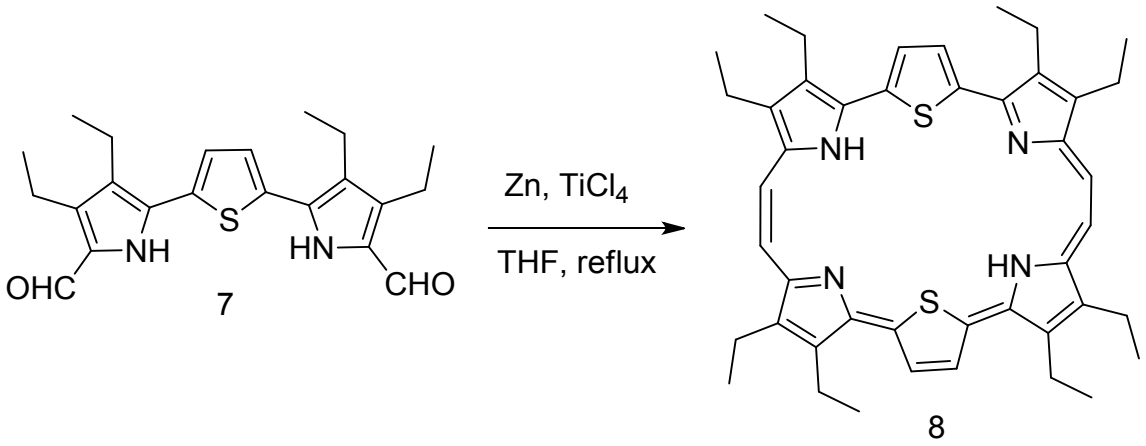
Synthesis of thiophene substituted terpyrrole dialdehyde 7:



The diacid derivative **6 (**100 mg, 0.24 mmol) was dissolved in TFA (1 mL) under nitrogen atmosphere while maintaining the reaction flask at 0°C and stirred for further 15 min. Then triethyl orthoformate (500 µL, 3 mmol) was added and stirred for 3h at rt. The reaction mixture was quenched using 1N NaOH solution and extracted with dichloromethane. After complete evaporation of the solvent, the crude product was purified by column chromatography in 20% EtOAc + 80% Hexane to obtain the dialdehyde **7** in 38% yield.

Melting point: 248-250°C; FTIR data: 3292, 2957, 1644, 1412 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ in ppm 9.63 (s, 2H, -CHO), 9.34 (s, 2H, NH), 7.28 (s, 2H, *β*-CH thiophene), 2.74 (m, 8H, CH_2 alkyl), 1.29 (t, 6H, J=7.6Hz, CH_3 alkyl), 1.22 (t, 6H, J=7.6Hz, CH_3 alkyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ in ppm 176.94, 138.85, 133.45, 130.07, 128.55, 125.60, 125.54, 17.70, 17.59, 17.00, 15.50; HRMS m/z calcd. for $(M+H)^+$ $C_{22}H_{27}N_2O_2S$:383.1793, found 383.1793.

Synthesis of dithiabronzaphyrin 8:



To a three-neck round bottom flask fitted with a dropping funnel and a reflux condenser, activated zinc dust (654 mg, 10 mmol) was added followed by THF (50 mL). Keeping the flask in an ice bath, $TiCl_4$ (550 μL, 5 mmol) was added and subsequently, the reaction mixture was refluxed for 4h. Then thiophene substituted terpyrrole dialdehyde **7** (96 mg, 0.25 mmol) along with pyridine (1 mL) in THF (50 mL) was added slowly and the reflux continued for another 18 h. The reaction mixture was quenched using 10% K_2CO_3 solution, filtered and the aqueous layer was extracted with chloroform/ethyl acetate. After complete evaporation of solvent, the solid thus obtained was dissolved again in chloroform/dichloromethane, stirred for 1h to open air and was purified by column chromatography using 50% hexane in dichloromethane to obtain the desired pure macrocycle **8** (20 mg, 24%).

Melting point: >300˚C; FTIR data: 2957, 2926, 1459, 1423 cm^{-1}; UV-Vis ($CHCl_3$): λ in nm (ε) 467 (4.48), 548 (4.07), 867 (4.35), 904 (4.38); ($CHCl_3$/TFA): λ in nm (ε) 501 (4.73), 574 (4.26), 888 (4.62); Fluorescence ($CHCl_3$, λ_{ex} = 450nm with slit widths of 14nm) λ_{max}: 959 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ in ppm 8.85 (s, 4H, meso CH), 6.50 (s, 2H, NH), 3.92 (q, 8H, *J*=7.6 Hz, CH_2 alkyl), 3.67 (q, 8H, *J*=7.6 Hz, CH_2 alkyl), 1.87 (t, 12H, *J*=7.6 Hz, CH_3 alkyl), 1.72 (t, 12H, *J*=7.6 Hz, CH_3 alkyl); ^{13}C NMR not recorded due to lack of solubility; HRMS m/z calcd. for $(M+H)^+$ $C_{44}H_{51}N_4S_2$:699.3555, found 699.3555.

3. ^{1}H NMR, ^{13}C NMR and HRMS spectra of compounds:

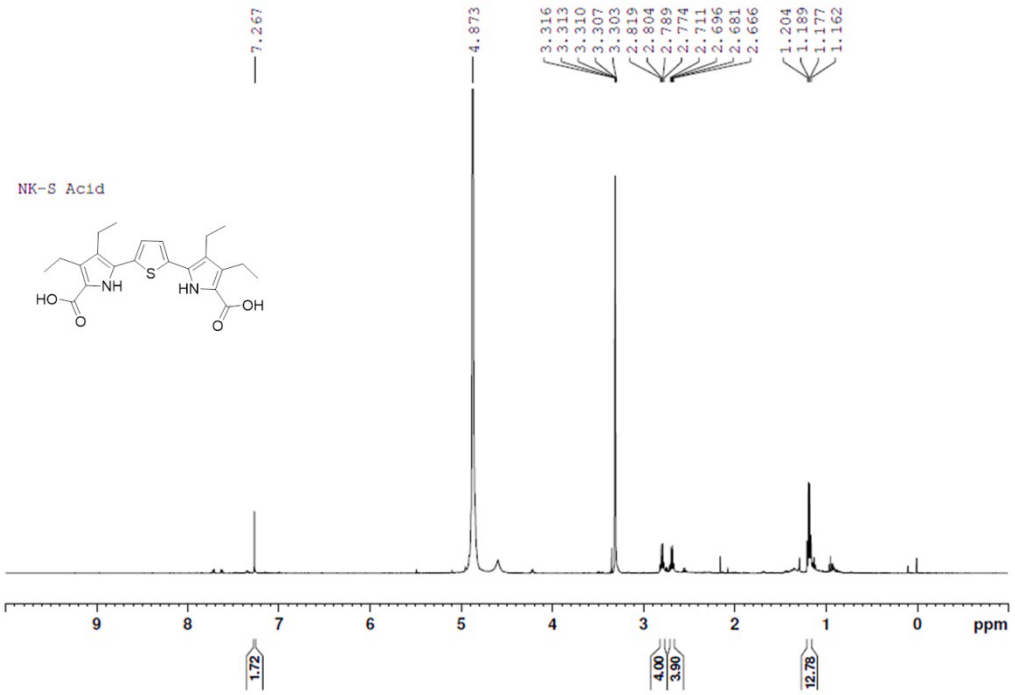


Figure S1: ^{1}H NMR spectrum of **6** in Methanol-d_4.

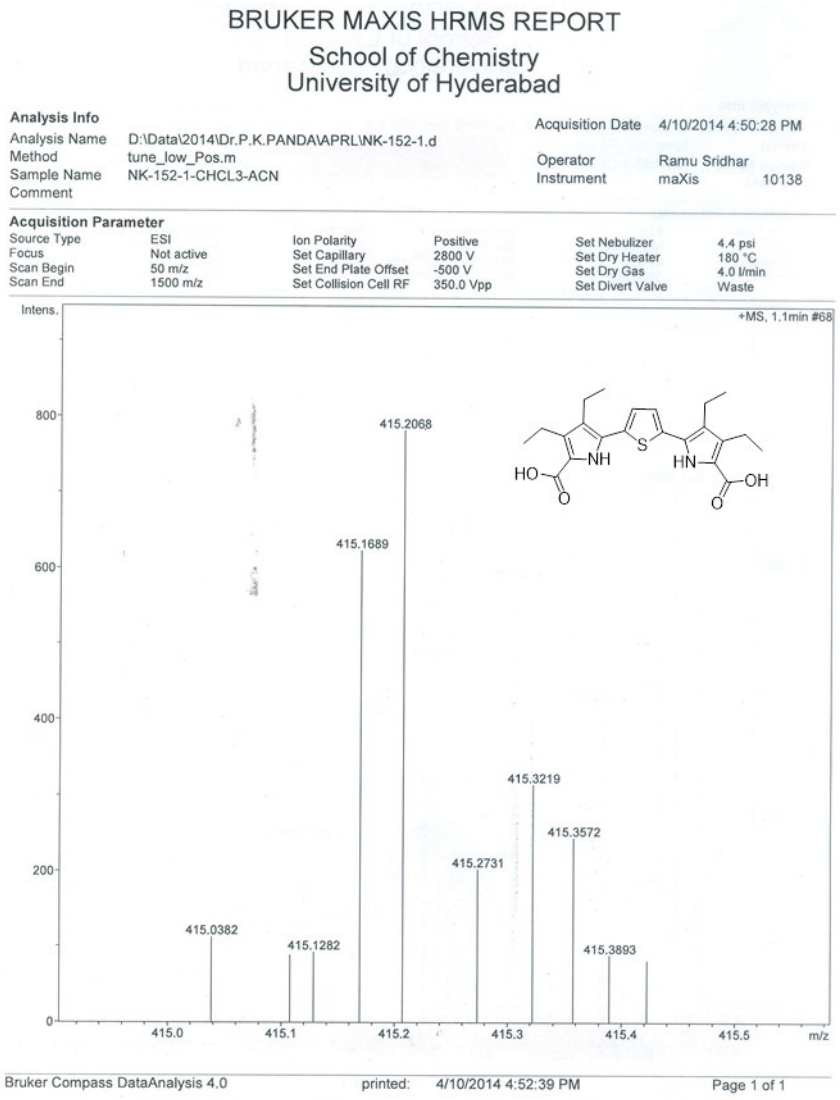


Figure S2: HRMS spectrum of **6** $(M+H)^+$: Calculated for $C_{22}H_{27}N_2O_4S$: 415.1692; found: 415.1689.

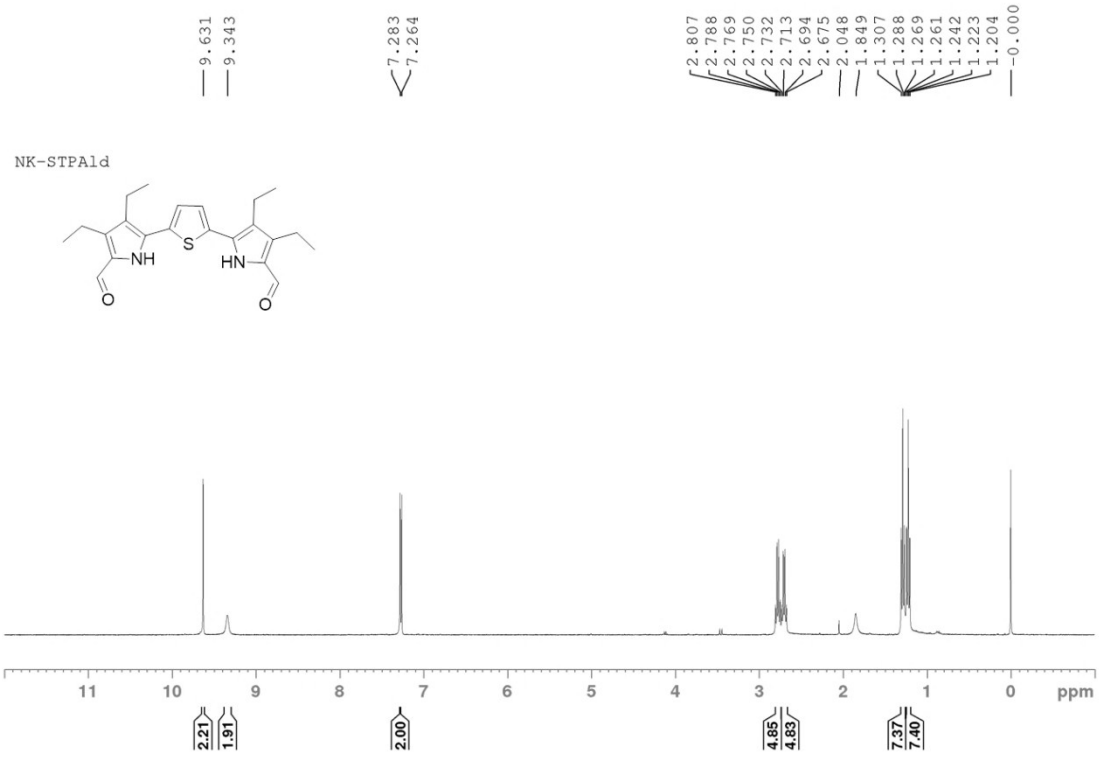


Figure S3: ^{1}H NMR spectrum of **7** in $CDCl_3$.

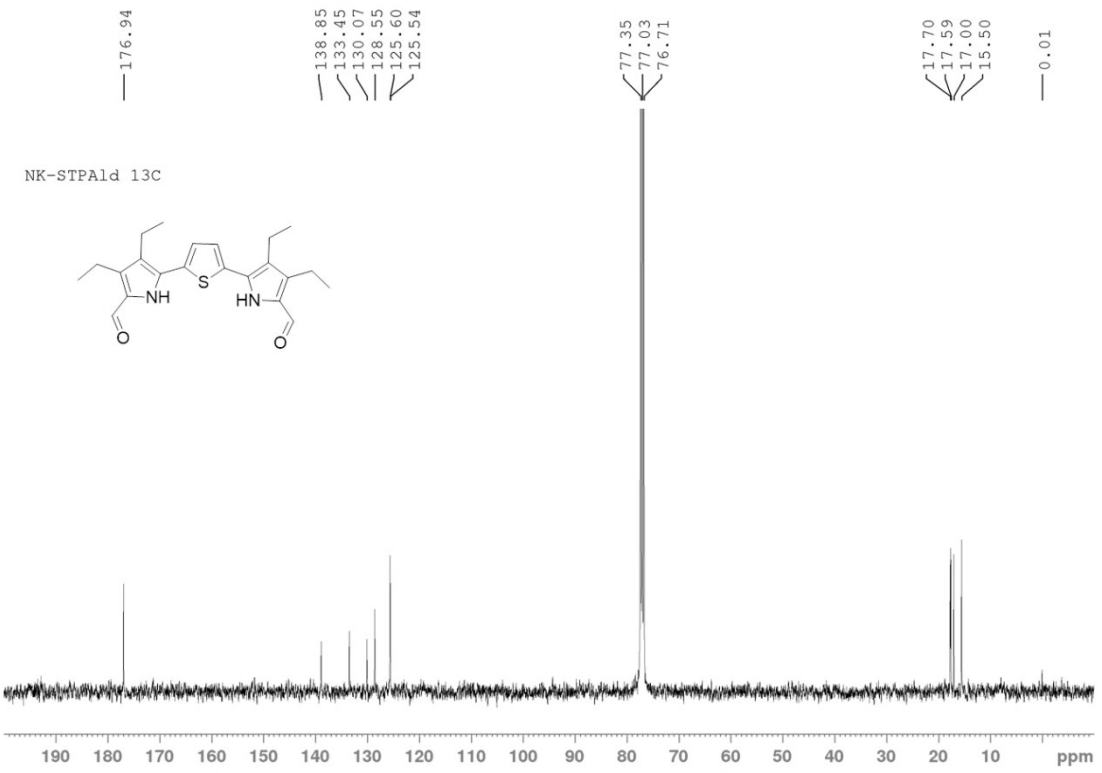


Figure S4. ^{13}C NMR spectrum of **7** in $CDCl_3$.

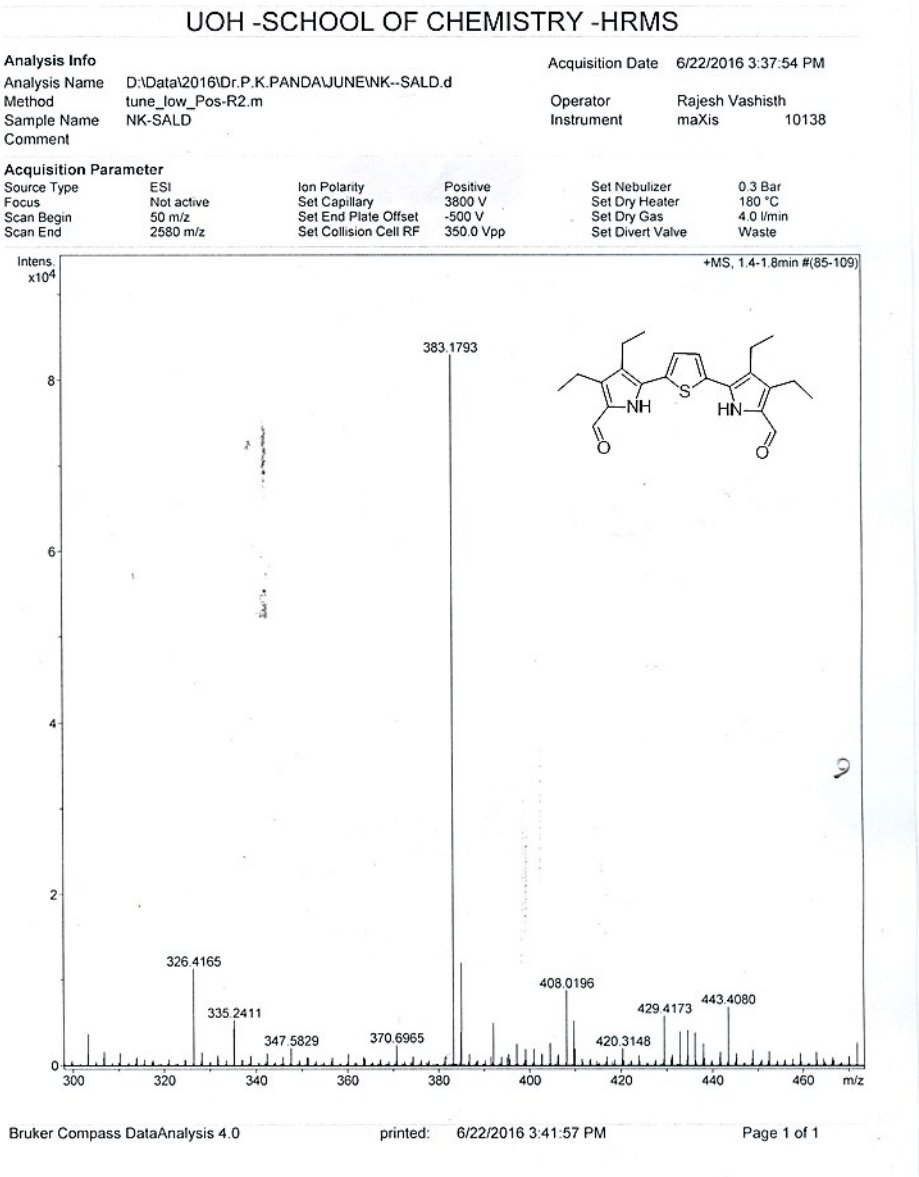


Figure S5: HRMS spectrum of **7** $(M+H)^+$; Calculated for $C_{22}H_{27}N_2O_2S$: 383.1793; found: 383.1793.

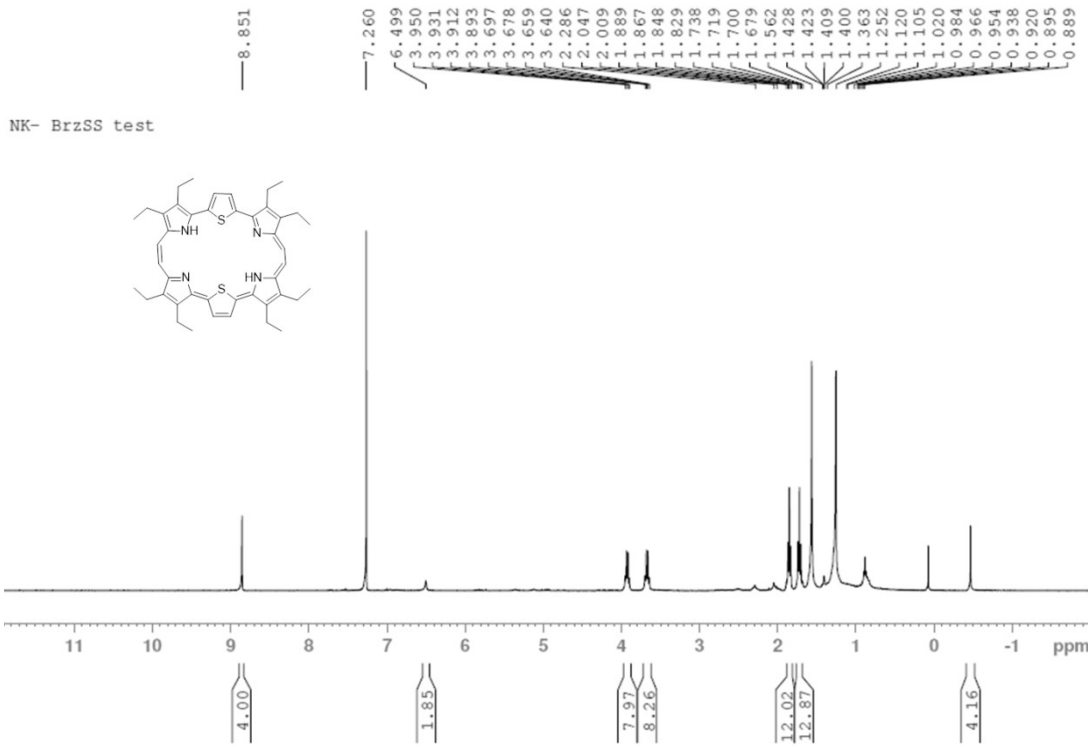


Figure S6: ^{1}H NMR spectrum of **8** in $CDCl_3$.

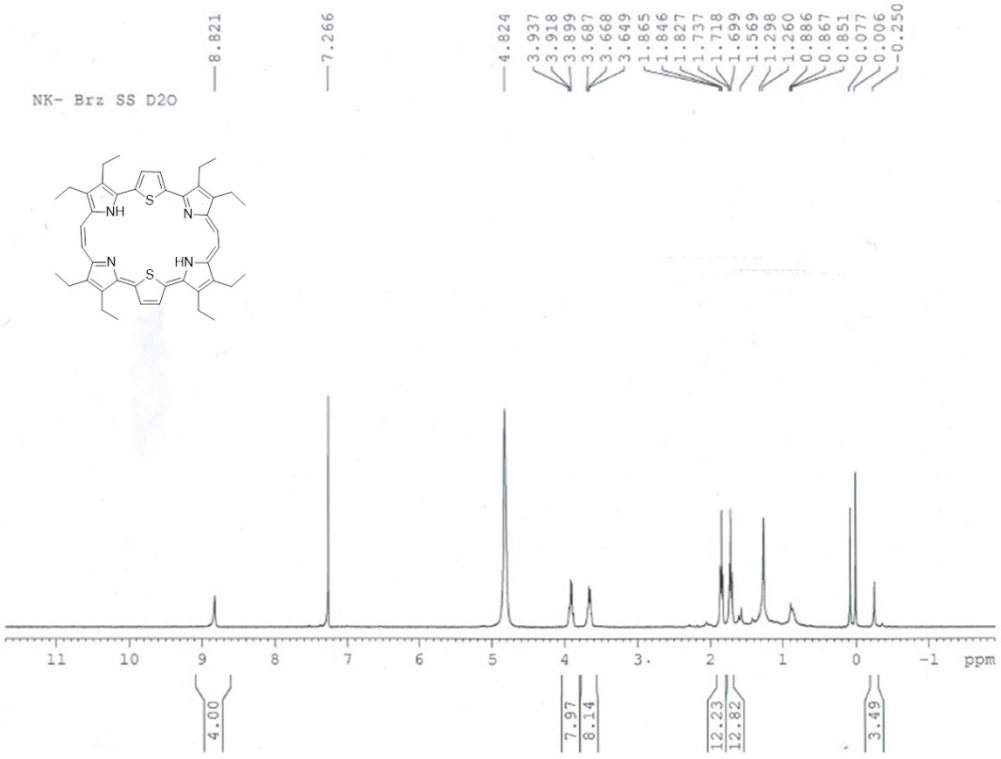


Figure S7: ^{1}H NMR spectrum of 8 in $CDCl_3$ + D_2O.

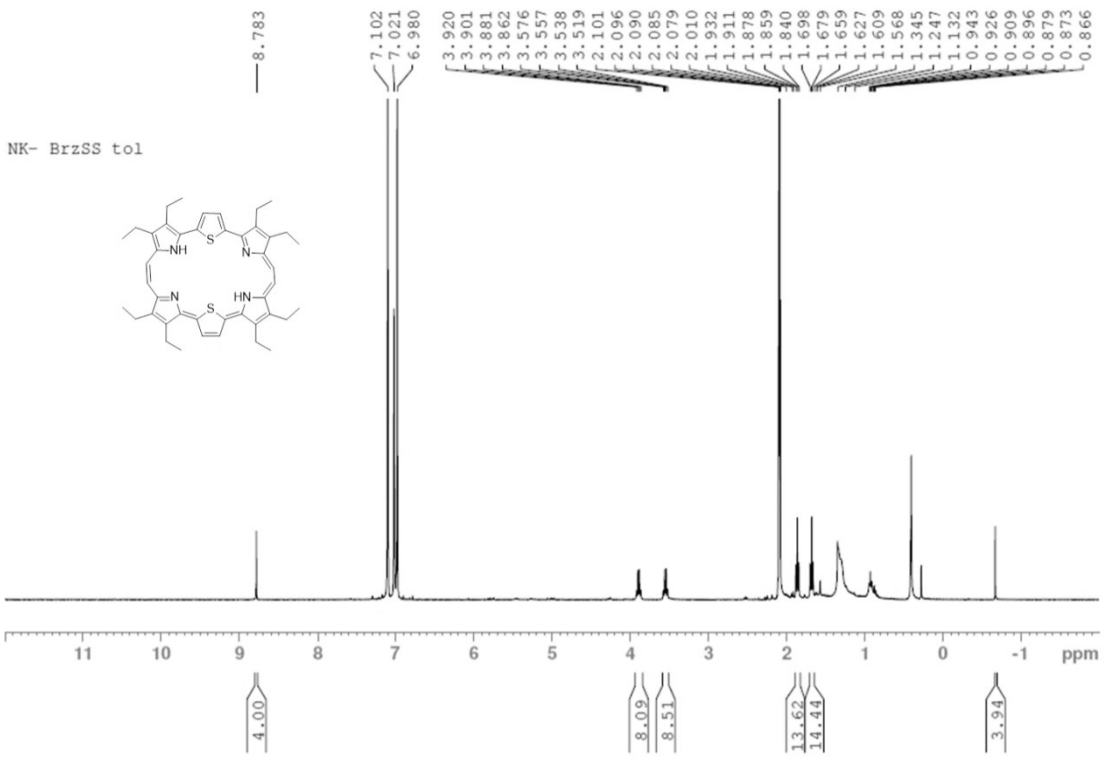


Figure S8: ^{1}H NMR spectrum of 8 at RT in toluene-d_8.

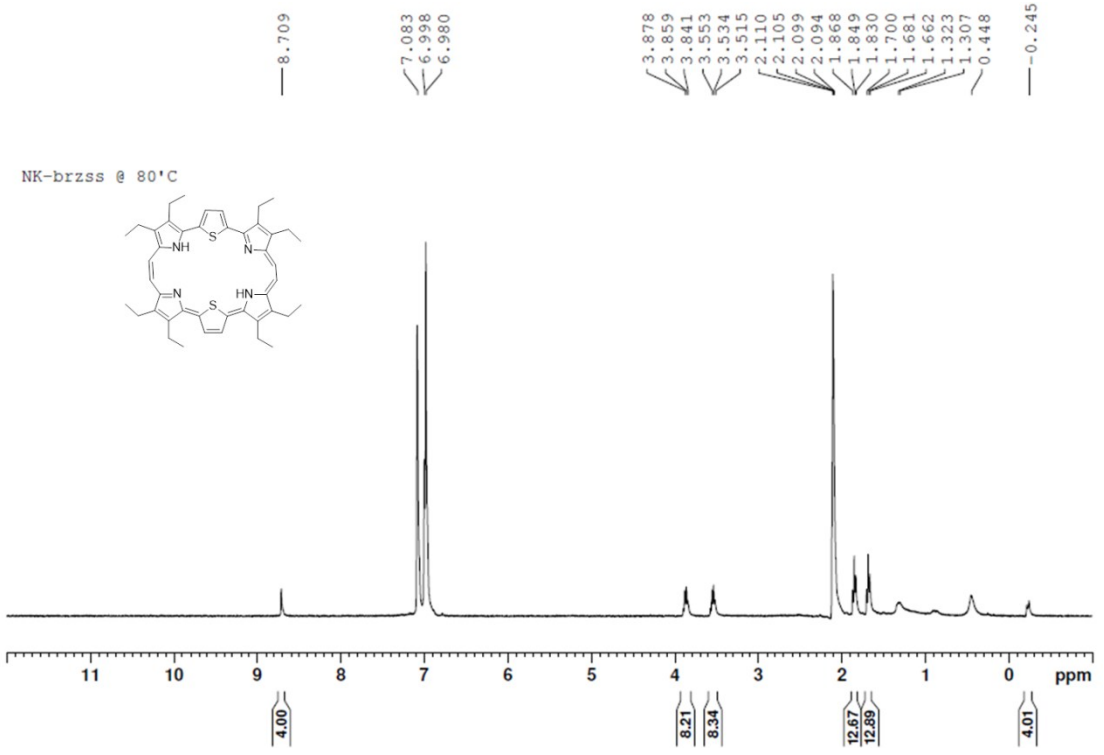


Figure S9: ^{1}H NMR spectrum of 8 at 80°C in toluene-d_8.

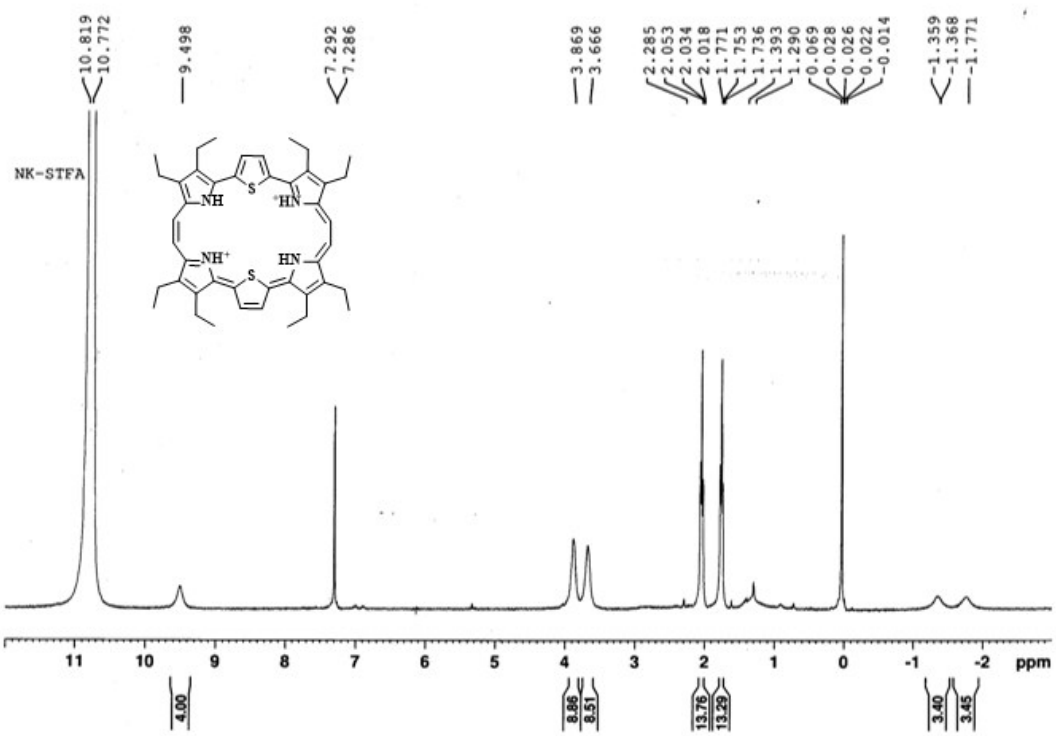


Figure S10: ^{1}H NMR spectrum of **8** in $CDCl_3$ + TFA.

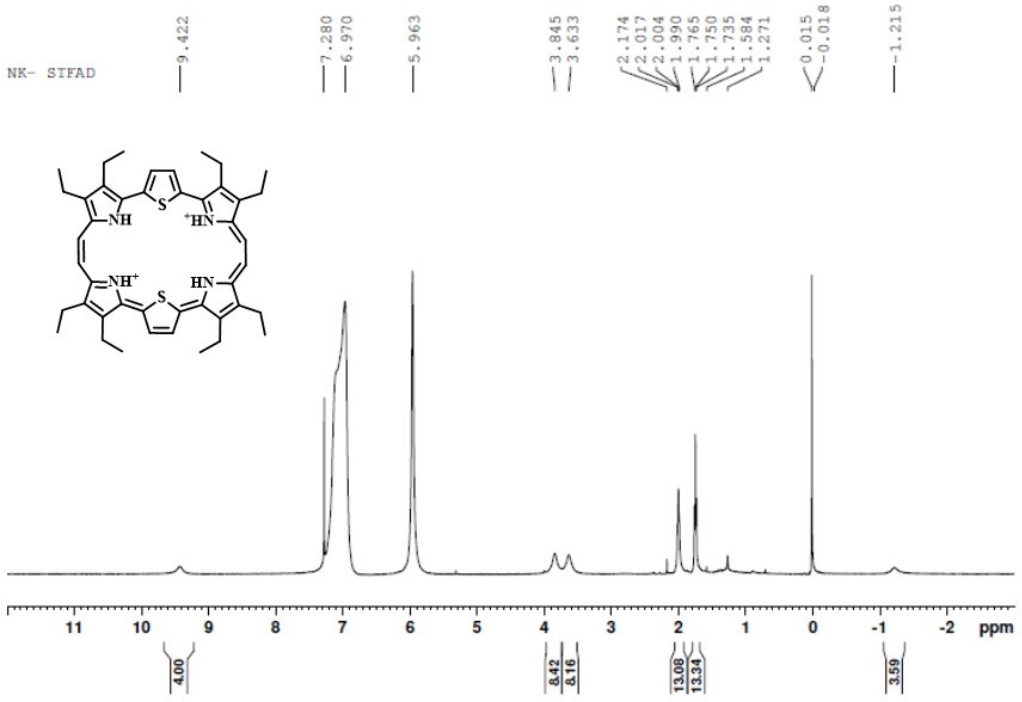


Figure S11: ^{1}H NMR spectrum of **8** in $CDCl_3$ + TFA + D_2O.

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Analysis Info

Analysis Name	D:\Data\2012\Dr.P.K.Panda\OCT\NK-BRZSS.d	Acquisition Date	10/3/2012 12:35:36 PM
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Sample Name	NK-BRZSS	Instrument	maXis 10138
Comment			

Acquisition Parameter

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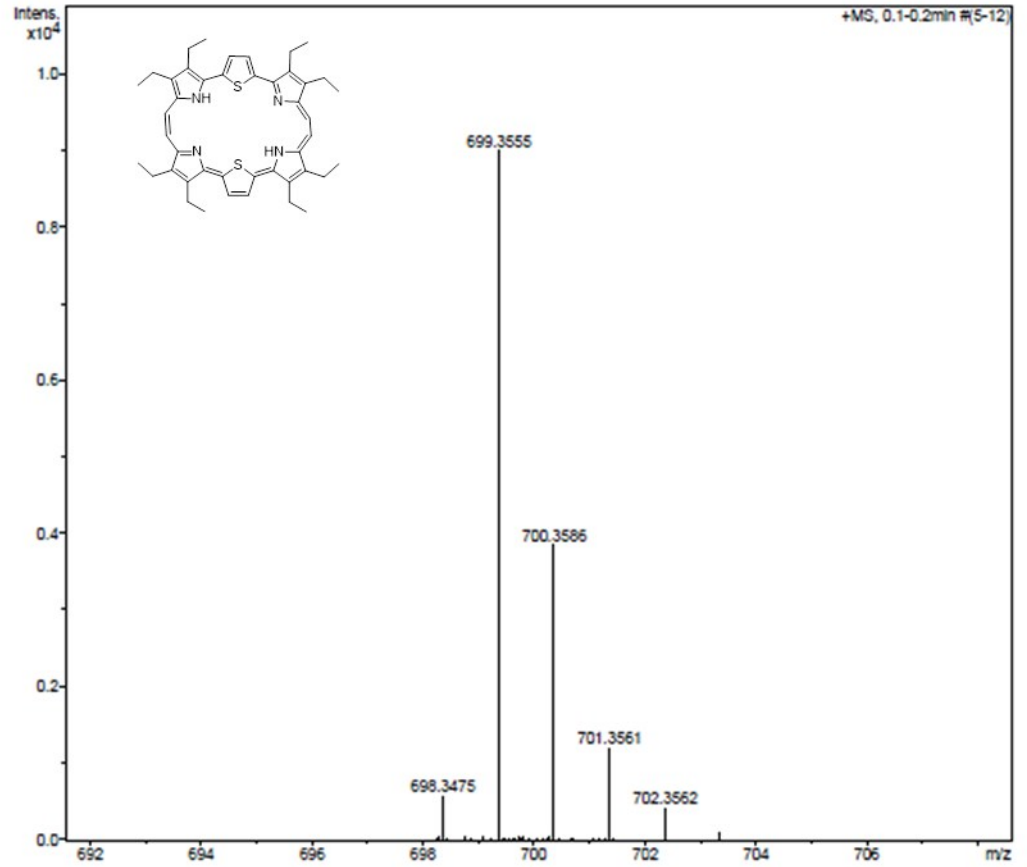
Scan End	2580 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 10/3/2012 12:42:36 PM Page 1 of 1

Figure S12: HRMS spectrum of **8** $(M+H)^+$; Calculated for $C_{44}H_{51}N_4S_2$: 699.3555; found: 699.3555.

4. Computational Studies:

Quantum mechanical calculations were performed using Gaussian 09 program provided by CMSD facility of University of Hyderabad.[S6] All calculations were carried out by density functional theory (DFT) with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) was used. The cc-pVDZ and 6-31G basis sets were used for all the calculations and the molecular orbitals were visualized using Gauss view 5. The NICS values were obtained with gauge independent atomic orbital (GIAO) method and HOMA (Harmonic Oscillator Model of Aromaticity) was calculated by using R_{opt} (C-C) = 1.388 Å and R_{opt} (C-N) = 1.334 Å.

Optimization results of normal and inverted conformers and their coordinates for the two bronzaphyrins 8 and 4a:

Table S1: Comparative stabilities of the two different conformers of **8** after structure optimization

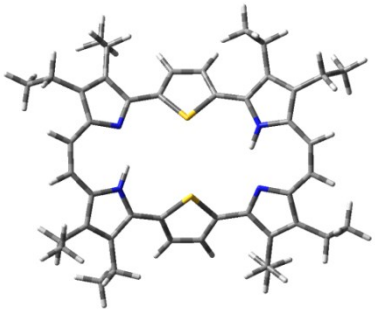
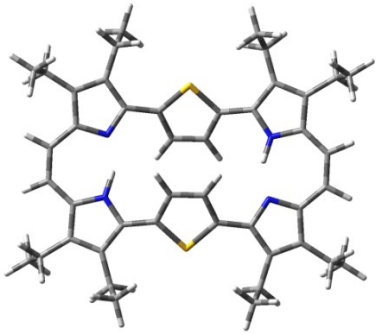
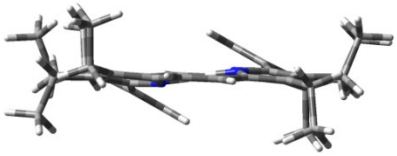
Conformer	Top view	Side view	Total Energy difference (in eV)
Normal			**0.14**
Inverted			**0**

Table S2: Coordinates of the optimized structure of normal isomer of **8**

Atom Label	Symbol	X	Y	Z	Atom Label	Symbol	X	Y	Z
1	C	1.356197	2.762181	0.514457	51	H	1.300718	4.526094	1.818073
2	C	0.743953	3.815149	1.215675	52	H	-1.26264	4.569608	1.631579
3	C	-0.64383	3.84066	1.114261	53	H	-2.81063	0.488568	-0.22663
4	C	-1.18384	2.802045	0.339086	54	H	-1.23657	-4.47201	1.946468
5	S	0.115593	1.760395	-0.24581	55	H	1.320506	-4.5297	1.685238
6	C	2.740405	2.527579	0.277097	56	H	2.817412	-0.49958	-0.29184
7	C	-2.5481	2.651589	-0.04227	57	H	6.409315	1.081259	-1.31083
8	N	3.207044	1.356196	-0.2325	58	H	-6.42599	-1.09745	-1.13118
9	C	4.528067	1.568491	-0.51044	59	H	6.325005	-1.17587	-1.60772
10	C	4.921256	2.933294	-0.16958	60	H	-6.34621	1.154036	-1.47035
11	C	3.803485	3.536833	0.362199	61	H	5.667983	-4.81066	-1.68841
12	C	-3.49668	3.7044	-0.28903	62	H	6.374209	-3.26587	-2.12653
13	C	-4.65032	3.107406	-0.79294	63	H	7.856879	-4.48181	-0.52
14	C	-4.43476	1.691004	-0.8068	64	H	7.249431	-2.98795	0.244397
15	N	-3.14738	1.461606	-0.37908	65	H	6.538806	-4.55641	0.679846
16	C	-1.32581	-2.74824	0.592132	66	H	4.276208	-5.69703	-0.23181
17	C	-0.69549	-3.78064	1.307861	67	H	2.89958	-5.44909	0.814184
18	C	0.688747	-3.81155	1.167959	68	H	2.278847	-6.89185	-1.12753
19	C	1.208215	-2.79891	0.347493	69	H	1.370555	-5.36152	-1.22933
20	S	-0.10585	-1.77265	-0.23194	70	H	2.788953	-5.62048	-2.27001
21	C	-2.7159	-2.51848	0.384795	71	H	-2.71992	-5.38426	0.728972
22	C	2.56258	-2.65988	-0.07686	72	H	-4.45845	-5.54373	0.56283
23	N	-3.19504	-1.35796	-0.13711	73	H	-3.73323	-6.10346	2.891993
24	C	-4.52291	-1.57447	-0.37654	74	H	-4.81954	-4.68992	2.892795
25	C	-4.90721	-2.93165	0.001768	75	H	-3.07723	-4.45891	3.107825
26	C	-3.77603	-3.52495	0.5174	76	H	-6.7309	-3.22395	-1.08923
27	C	3.509583	-3.71443	-0.32369	77	H	-6.19997	-4.62638	-0.17441
28	C	4.6525	-3.12077	-0.85668	78	H	-8.23294	-3.61322	0.865957
29	C	4.434173	-1.70504	-0.88413	79	H	-6.85319	-3.48509	1.98911
30	N	3.153695	-1.47341	-0.43831	80	H	-7.38326	-2.05845	1.074659
31	C	5.448703	0.6376	-1.03822	81	H	6.716312	3.204967	-1.31248
32	C	-5.45682	-0.6513	-0.89518	82	H	6.209366	4.623822	-0.40962
33	C	5.404231	-0.73952	-1.21438	83	H	8.268293	3.628424	0.595709
34	C	-5.41507	0.722319	-1.09685	84	H	6.918123	3.521761	1.756438
35	C	5.916955	-3.81493	-1.28716	85	H	7.424207	2.078264	0.854831
36	C	6.950781	-3.96948	-0.15707	86	H	2.756927	5.403412	0.561987
37	C	3.294419	-5.20069	-0.18284	87	H	4.491557	5.553894	0.354997
38	C	2.378509	-5.8024	-1.26355	88	H	3.8205	6.158519	2.689034
39	C	-3.6751	-4.93258	1.040514	89	H	4.901736	4.741029	2.691207

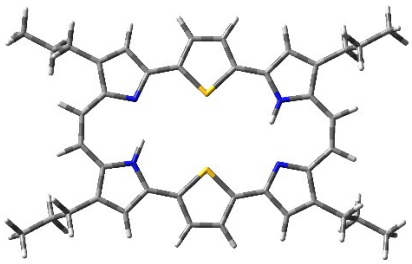
40	C	-3.83197	-5.05401	2.568014	90	H	3.163835	4.520688	2.949349
41	C	-6.28232	-3.52803	-0.12763	91	H	-2.22289	5.43151	-0.24418
42	C	-7.24354	-3.1497	1.014824	92	H	-3.81697	5.716546	-0.9232
43	C	6.292666	3.526479	-0.34522	93	H	-3.60424	6.815378	1.313615
44	C	7.28304	3.168316	0.778683	94	H	-4.86653	5.557044	1.361537
45	C	3.717215	4.954279	0.861013	95	H	-3.28221	5.240065	2.085412
46	C	3.908358	5.102988	2.382148	96	H	-5.96745	4.793952	-0.79353
47	C	-3.28796	5.185834	-0.11467	97	H	-6.78626	3.249561	-0.95372
48	C	-3.78563	5.73079	1.236429	98	H	-6.85719	4.506229	-3.11481
49	C	-5.89164	3.807631	-1.27742	99	H	-5.89596	3.01794	-3.32359
50	C	-5.93375	3.989631	-2.80567	100	H	-5.07531	4.584113	-3.15823

Table S3: Coordinates of the optimized structure of inverted isomer of **8**

Atom Label	Symbol	X	Y	Z	Atom Label	Symbol	X	Y	Z
1	C	-4.66343	1.719688	-0.10102	51	H	-1.2897	0.408667	-1.61547
2	C	-4.74255	3.174233	0.012838	52	H	1.321214	0.356135	-1.62151
3	C	-3.44596	3.646788	-0.10111	53	H	3.154255	0.256522	-0.15183
4	C	-2.61754	2.471416	-0.32163	54	H	-6.82063	3.55409	-0.35667
5	N	-3.37054	1.341501	-0.29996	55	H	-5.84976	5.001564	-0.13382
6	C	-1.22026	2.319988	-0.58176	56	H	-7.34879	4.627315	1.837612
7	C	-0.66034	1.185557	-1.18745	57	H	-5.64107	4.500073	2.340336
8	C	0.729091	1.16099	-1.18886	58	H	-6.61078	3.027989	2.122291
9	C	1.326346	2.280522	-0.58958	59	H	-3.73899	5.698605	0.422975
10	S	0.073422	3.413127	-0.06546	60	H	-2.06333	5.181241	0.49674
11	C	2.725498	2.400978	-0.34158	61	H	-2.41856	6.706734	-1.44971
12	C	3.619737	3.513297	-0.19611	62	H	-1.97433	5.085679	-2.04199
13	C	4.912914	2.985173	-0.08916	63	H	-3.67026	5.616893	-2.10744
14	C	4.799239	1.551307	-0.13639	64	H	4.022297	5.555318	-0.6903
15	N	3.474602	1.256093	-0.29566	65	H	2.330866	5.091229	-0.849
16	C	-5.99482	3.975697	0.242244	66	H	2.637466	6.609099	1.106621
17	C	-6.42516	4.03674	1.719641	67	H	2.117076	5.005589	1.683825
18	C	-2.98851	5.081122	-0.09689	68	H	3.820656	5.489509	1.831852
19	C	-2.74846	5.656152	-1.50471	69	H	6.976763	3.277932	-0.58002
20	C	3.222774	4.964633	-0.21256	70	H	6.068551	4.766807	-0.34488
21	C	2.933171	5.549885	1.181727	71	H	7.66692	4.396243	1.543
22	C	6.202095	3.746804	0.051006	72	H	5.991991	4.337004	2.153267
23	C	6.720595	3.832594	1.498618	73	H	6.90027	2.829459	1.917188
24	C	-4.79645	-1.54855	0.007641	74	H	-3.15193	-0.25617	0.042599
25	C	-4.90804	-2.98252	-0.05109	75	H	-1.31532	-0.35054	1.497307
26	C	-3.61727	-3.51033	0.062984	76	H	1.294486	-0.4025	1.482768
27	C	-2.72432	-2.40001	0.231424	77	H	-6.08767	-4.7503	0.213548

28	N	-3.47415	-1.25452	0.188884	78	H	-6.99805	-3.25167	0.33438
29	C	-1.3244	-2.27981	0.473941	79	H	-7.56365	-4.45001	-1.78681
30	C	-0.72482	-1.15763	1.06657	80	H	-6.76625	-2.90019	-2.16962
31	C	0.66428	-1.18169	1.060422	81	H	-5.8523	-4.41871	-2.29075
32	C	1.222826	-2.31877	0.457675	82	H	-4.00766	-5.55591	-0.41302
33	S	-0.07232	-3.41587	-0.04749	83	H	-2.30606	-5.12782	-0.46559
34	C	2.618837	-2.47067	0.19358	84	H	-2.77741	-6.58027	1.511879
35	C	3.445698	-3.64499	-0.0371	85	H	-2.25622	-4.96919	2.067586
36	C	4.741978	-3.17234	-0.15549	86	H	-3.97924	-5.40882	2.11886
37	C	4.664133	-1.71839	-0.03428	87	H	3.736221	-5.69366	-0.57447
38	N	3.373256	-1.34095	0.174752	88	H	2.060191	-5.17616	-0.63659
39	C	-6.19095	-3.74744	-0.23128	89	H	2.426976	-6.71331	1.299229
40	C	-6.61912	-3.8877	-1.7037	90	H	1.983766	-5.09625	1.902915
41	C	-3.23521	-4.96626	0.106227	91	H	3.68069	-5.62573	1.956855
42	C	-3.05136	-5.51284	1.533385	92	H	5.849612	-5.00042	-0.02204
43	C	2.988367	-5.07934	-0.04713	93	H	6.822428	-3.554	0.198684
44	C	2.755919	-5.66266	1.358554	94	H	7.335237	-4.62107	-2.00238
45	C	5.992439	-3.97344	-0.39594	95	H	6.596522	-3.02039	-2.27726
46	C	6.412844	-4.03021	-1.87639	96	H	5.624283	-4.49107	-2.49326
47	C	5.824507	0.574567	-0.07405	97	H	6.83393	0.991942	-0.03584
48	C	5.762214	-0.81951	-0.0969	98	H	6.737973	-1.31048	-0.15125
49	C	-5.76111	0.821073	-0.0467	99	H	-6.73791	1.311104	-0.00347
50	C	-5.82131	-0.57355	-0.07	100	H	-6.82933	-0.99261	-0.12406

Table S4: Comparative stabilities of normal and inverted conformers of **4a** after structure optimization

Conformer	**Top view**	**Side view**	**Total Energy difference (in eV)**
Normal			**0**

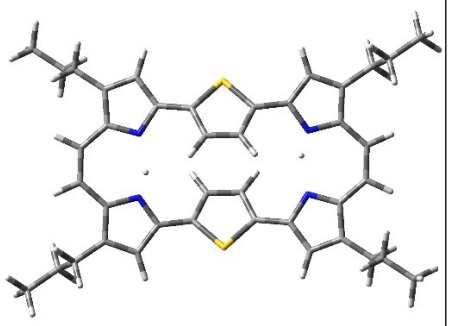
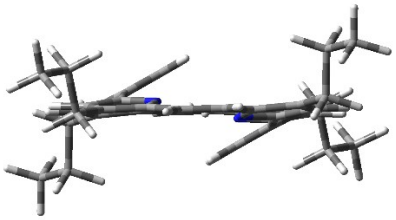
Inverted			**0.42**

Table S5: Coordinates of the optimized structure of normal isomer of **4a**

Atom Label	Symbol	X	Y	Z	Atom Label	Symbol	X	Y	Z
1	C	-1.24259	2.935193	-0.09702	45	H	-6.60216	1.26313	0.464867
2	C	-0.65175	4.202233	-0.27435	46	H	6.637746	-1.22559	-0.04757
3	C	0.733117	4.185656	-0.29766	47	H	-6.65402	-0.99549	0.729914
4	C	1.295646	2.902205	-0.14345	48	H	6.702024	1.046986	-0.0693
5	S	0.013384	1.708656	0.034943	49	H	-6.08112	-4.63269	1.35577
6	C	-2.63375	2.67715	-0.0152	50	H	-6.87793	-3.07143	1.536808
7	C	2.687085	2.638714	-0.12539	51	H	-7.12268	-2.9141	-0.97503
8	N	-3.22449	1.466606	0.170776	52	H	-6.32461	-4.47693	-1.14343
9	C	-4.57177	1.720135	0.216994	53	H	6.935499	-3.31915	0.532888
10	C	-4.84656	3.150987	0.044613	54	H	6.101148	-4.84964	0.277614
11	C	4.937199	3.032039	-0.12795	55	H	6.028882	-4.41492	-2.19387
12	C	4.694721	1.615724	-0.06512	56	H	6.849758	-2.87333	-1.95926
13	N	3.327468	1.423714	-0.05801	57	H	-6.85868	3.410348	0.765268
14	C	1.260903	-2.92403	0.169649	58	H	-6.06014	4.891682	0.244067
15	C	0.664241	-4.19962	0.22157	59	H	-6.2201	4.151875	-2.15004
16	C	-0.71701	-4.17762	0.32425	60	H	-7.00877	2.658013	-1.64821
17	C	-1.27094	-2.88157	0.354487	61	H	6.170197	4.714082	-0.56026
18	S	0.014883	-1.68299	0.251297	62	H	6.99125	3.166048	-0.74769
19	C	2.65176	-2.6658	0.081992	63	H	6.976452	2.866208	1.76462
20	C	-2.65687	-2.60946	0.461192	64	H	6.165966	4.422152	1.936565
21	N	3.249246	-1.44483	0.047015	65	C	8.234814	4.570881	1.294609
22	C	4.596246	-1.69805	-0.00974	66	H	8.157084	5.584086	0.864332
23	C	4.862852	-3.14067	-0.0195	67	H	8.641734	4.671339	2.313443
24	C	-4.8961	-2.98594	0.709312	68	H	8.973706	4.013992	0.693223
25	C	-4.65586	-1.57428	0.575643	69	C	-8.24334	4.42646	-1.41072
26	N	-3.29475	-1.39159	0.433904	70	H	-8.14362	5.500929	-1.1797
27	C	-5.61548	0.795742	0.42315	71	H	-8.71931	4.341151	-2.40085
28	C	5.648825	-0.76118	-0.03574	72	H	-8.9366	3.99404	-0.66878
29	C	-5.65264	-0.58488	0.582585	73	C	-8.317	-4.59066	-0.28827

30	C	5.693331	0.628386	-0.05007	74	H	-8.82564	-4.74273	-1.25363
31	C	-6.23144	-3.65801	0.860968	75	H	-8.19048	-5.58074	0.182152
32	C	-6.97207	-3.88553	-0.47251	76	H	-8.99334	-4.00388	0.356732
33	C	6.198083	-3.82368	-0.11686	77	C	8.11521	-4.6034	-1.62211
34	C	6.760983	-3.89535	-1.55116	78	H	8.04681	-5.63934	-1.24801
35	C	-6.1886	3.825282	-0.00887	79	H	8.492881	-4.64662	-2.65634
36	C	-6.88563	3.722155	-1.38098	80	H	8.873181	-4.08319	-1.01146
37	C	6.276386	3.71323	-0.10844	81	C	3.700833	3.643692	-0.17072
38	C	6.878236	3.864468	1.303582	82	H	3.517194	4.713579	-0.22026
39	H	-1.24057	5.110866	-0.38317	83	C	3.634572	-3.73383	0.039113
40	H	1.339421	5.079603	-0.43212	84	C	-3.62214	3.737357	-0.10023
41	H	2.936899	0.46173	-0.02299	85	C	-3.66537	-3.60588	0.632635
42	H	1.246443	-5.11817	0.18324	86	H	-3.48077	-4.6742	0.706381
43	H	-1.32771	-5.07761	0.369324	87	H	-3.42176	4.796886	-0.24397
44	H	-2.90665	-0.43463	0.320923	88	H	3.429034	-4.80193	0.056364

Table S6: Coordinates of the optimized structure of inverted isomer of **4a**

Atom Label	Symbol	X	Y	Z	Atom Label	Symbol	X	Y	Z
1	S	0.104145	3.382268	0.047595	45	C	1.13009	-2.29107	-0.69141
2	N	-3.31728	1.34439	0.622456	46	C	-3.63271	-3.45792	0.183501
3	N	3.501338	1.217217	-0.08225	47	C	-1.39346	-2.24068	-0.44445
4	C	4.904406	2.952087	-0.44735	48	C	-4.79834	-1.51447	0.400647
5	C	-3.36719	3.634239	0.443797	49	C	2.542518	-2.45817	-0.57224
6	C	4.61723	-1.74566	-0.55506	50	C	0.52376	-1.14916	-1.23271
7	C	5.800377	0.534044	-0.61577	51	C	-2.76052	-2.35889	-0.05962
8	H	6.798743	0.946785	-0.78145	52	C	5.916401	-4.05125	-0.35888
9	C	-4.67889	3.205334	0.456727	53	H	5.680145	-5.07498	-0.696
10	C	0.858791	1.119169	1.095002	54	H	6.688857	-3.6727	-1.05261
11	C	-1.1301	2.291053	0.691302	55	C	-5.72785	0.860616	0.609949
12	C	3.63273	3.45795	-0.18348	56	H	-6.69676	1.3626	0.686056
13	C	1.39347	2.240722	0.444476	57	C	6.5152	-4.12059	1.061252
14	C	4.798359	1.514489	-0.40052	58	H	5.746634	-4.50897	1.75235
15	C	-2.54252	2.458137	0.572109	59	H	6.746184	-3.09803	1.407853
16	C	-0.52376	1.149177	1.232664	60	C	-6.15977	-3.74573	0.672829
17	C	2.760535	2.358936	0.059682	61	H	-5.89133	-4.72607	1.102171
18	C	-5.9164	4.051238	0.358846	62	H	-6.79149	-3.24483	1.427213
19	H	-5.68012	5.074978	0.695915	63	C	-6.99104	-3.97173	-0.60675
20	H	-6.68882	3.672715	1.052631	64	H	-6.35993	-4.48032	-1.35652
21	C	5.727851	-0.86062	-0.60986	65	H	-7.25387	-2.99287	-1.04514
22	H	6.696755	-1.3626	-0.68594	66	H	-1.49	-0.31203	-1.46335
23	C	-6.51529	4.120527	-1.06126	67	H	1.112675	-0.37404	-1.7178
24	H	-5.74676	4.508885	-1.75241	68	H	-3.16053	-0.22124	0.22609

25	H	-6.74629	3.097953	-1.40781	69	H	3.355099	4.508416	-0.11837
26	C	6.159802	3.745728	-0.6728	70	H	-3.01629	4.664759	0.402431
27	H	5.891358	4.726046	-1.10218	71	H	-3.35508	-4.50838	0.118322
28	H	6.791514	3.244787	-1.42716	72	H	3.016296	-4.66479	-0.40263
29	C	6.991072	3.971784	0.60677	73	C	-8.26025	-4.78669	-0.35221
30	H	6.359964	4.480411	1.356517	74	H	-8.83332	-4.93751	-1.28102
31	H	7.253897	2.99294	1.045206	75	H	-8.02193	-5.78258	0.058769
32	H	1.490014	0.312108	1.463447	76	H	-8.92356	-4.28227	0.37119
33	H	-1.11268	0.374059	1.717763	77	C	7.770856	-4.99145	1.132214
34	H	3.160573	0.221242	-0.22576	78	H	8.175919	-5.03062	2.156155
35	S	-0.10415	-3.38228	-0.04769	79	H	7.558574	-6.0274	0.816874
36	N	3.317278	-1.34442	-0.62257	80	H	8.56656	-4.60382	0.472979
37	N	-3.50131	-1.21718	0.082447	81	C	8.260287	4.786719	0.352197
38	C	-4.90438	-2.95207	0.447415	82	H	8.021971	5.7826	-0.05883
39	C	3.367192	-3.63427	-0.44396	83	H	8.833353	4.937577	1.280993
40	C	-4.61723	1.745639	0.55504	84	H	8.923594	4.282265	-0.37118
41	C	-5.80037	-0.53405	0.615911	85	C	-7.77095	4.991387	-1.13217
42	H	-6.79873	-0.94679	0.78159	86	H	-7.55865	6.027343	-0.81688
43	C	4.678886	-3.20535	-0.45681	87	H	-8.17607	5.030516	-2.15609
44	C	-0.85879	-1.11912	-1.09496	88	H	-8.56661	4.603779	-0.47288

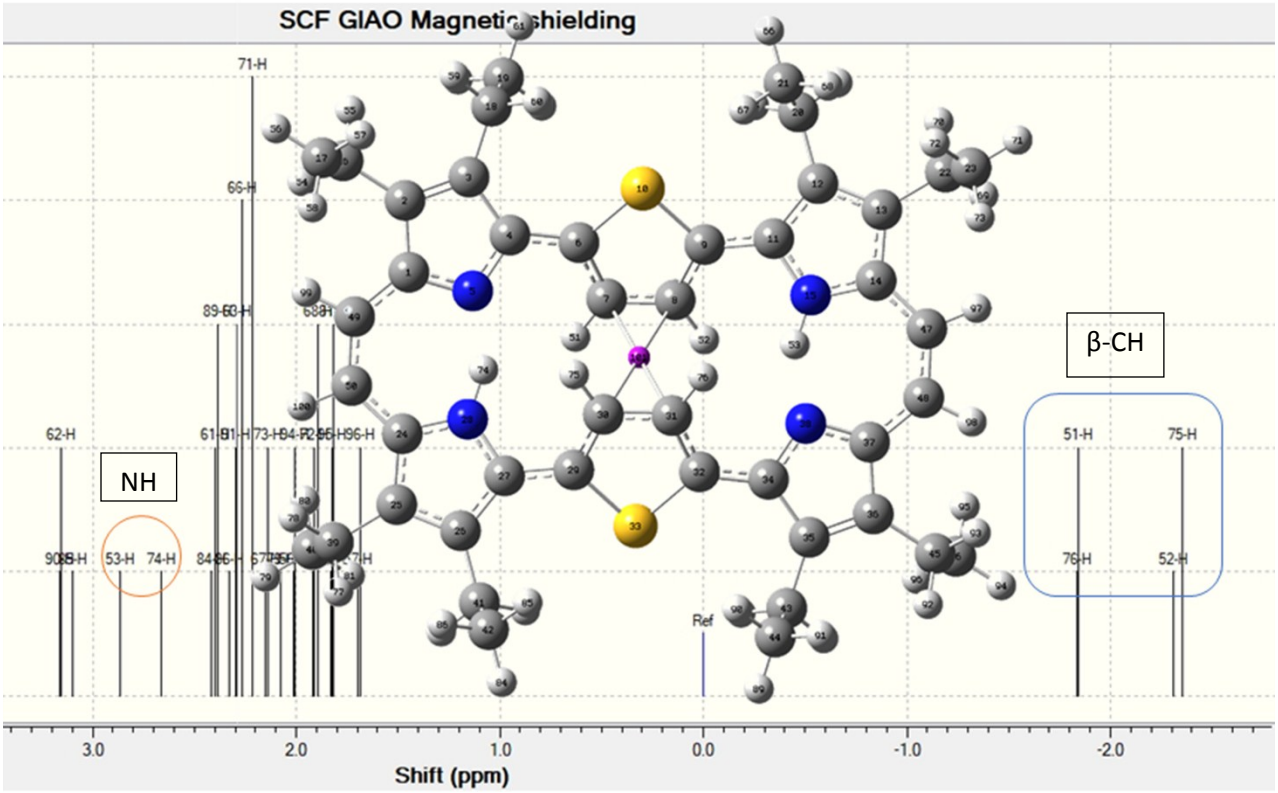


Figure S13: Theoretical ^{1}H NMR spectrum of **8** indicating NH and β-CH of thiophene.

MOs and energy levels of bronzaphyrins 8 and $8.H_2^{2+}$:

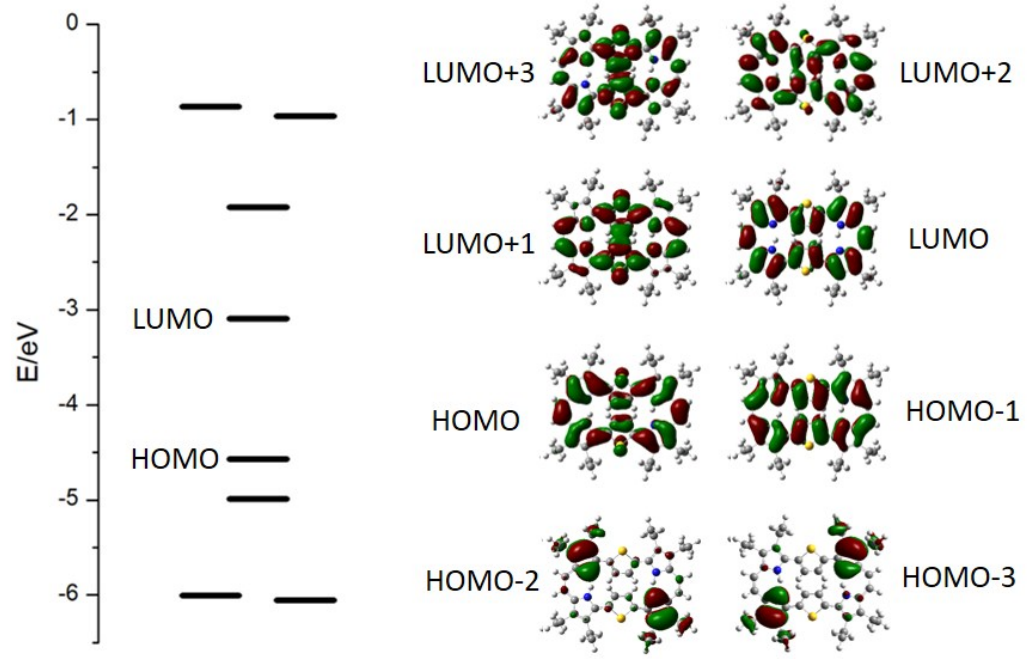


Figure S14: Delocalized electron densities of **s**elected MOs of **8** with energy level diagram.

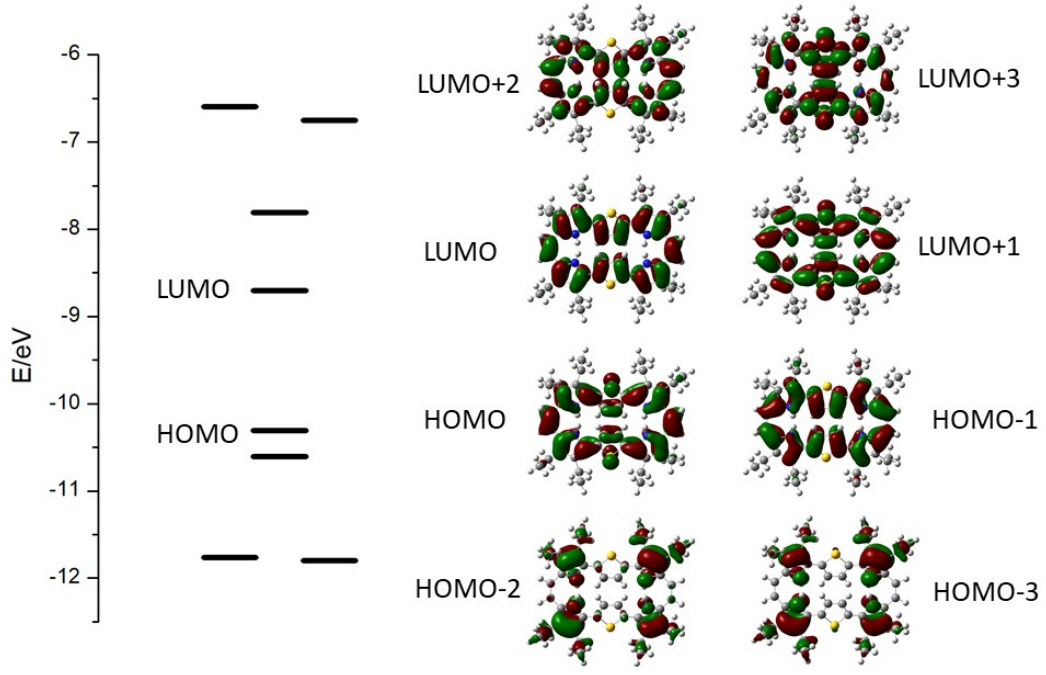


Figure S15: Delocalized electron densities of **s**elected MOs of $\mathbf{8.H_2^{2+}}$ with energy level diagram.

NICS and HOMA calculation results:

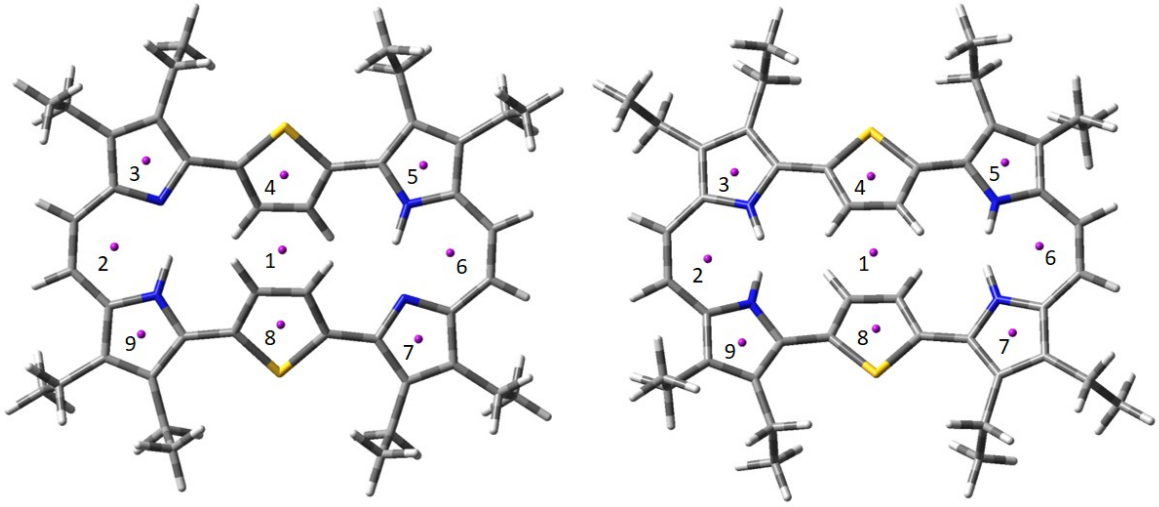


Figure S16: Selected positions for calculating NICS values of compounds **8** and **8.H_2^{2+}.** 1-9 represent the ghost **Bq** atoms

Table S7: NICS values of selected positions of compounds **8** and **8.H_2^{2+}.**

Bq atom no.	**8**	**8.H_2^{2+}**
1	-18.5	-18.3
2	-16.2	-18.8
3	-2.4	-11.9
4	-8.7	-9.3
5	-11.1	-12.9
6	-16.1	-18.8
7	-2.4	-11.9
8	-8.3	-9.3
9	-10.7	-12.9

Table S8: Summary of **HOMA*** index values (* = calculated by considering the conjugation path of 26π e). **ΔR_x** = Bond length alteration from the crystal structure.

Molecule	**π-e**	**ΔR_x (Å)**	**HOMA**
8	26	0.106	0.75
8.H_2^{2+}	26	0.075	0.75

Table S9: Selected transitions, oscillator strength, symmetry calculated (H = HOMO, L = LUMO) from DFT analysis for bronzaphyrin 8

S. No.	Wavelength (nm)	Oscillator strength	Symmetry	Major contributors
1	810.401	0.4128	Singlet-A	H-1->L+1 (11%), H->L (85%)
2	761.100	0.1204	Singlet-A	H-1->L (73%), H->L+1 (20%)
3	483.780	0.425	Singlet-A	H-3->L (37%), H-1->L (18%), H->L+1 (44%)
4	423.4403	0.2607	Singlet-A	H-5->L (63%), H-1->L+1 (25%)
5	414.687	1.1666	Singlet-A	H-6->L (11%), H-5->L (18%), H-1->L+1 (60%)

Table S10: Selected transitions, oscillator strength, symmetry calculated (H = HOMO, L = LUMO) from DFT analysis for bronzaphyrin 8.H_2^{2+}

S. No.	Wavelength (nm)	Oscillator strength	Symmetry	Major contributors
1	802.845	0.2895	Singlet-A	H-1->L+1 (20%), H->L (82%)
2	771.857	0.0569	Singlet-A	H-1->L (71%), H->L+1 (29%)
3	496.868	0.6741	Singlet-A	H-1->L (33%), H->L+1 (72%)
4	439.673	1.701	Singlet-A	H-1->L+1 (79%), H->L (23%)
5	383.019	0.082	Singlet-A	H-8->L (98%)
6	352.015	0.071	Singlet-A	H-3->L+1 (98%)

5. Crystallographic parameters for 8 and 8. H_2^{2+}

Crystal data and structure refinement for 8

Identification code	BrzSS	
Empirical formula	C44 H50 N4 S2	
Formula weight	699.00	
Temperature	298(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 8.7071(7) Å	α= 98.972(5)°.
	b = 9.6083(5) Å	β= 106.931(7)°.
	c = 12.2192(8) Å	γ = 103.162(6)°.
Volume	924.76(12) $Å^3$	
Z	1	
Density (calculated)	1.255 Mg/m^3	
Absorption coefficient	1.581 mm^{-1}	
F(000)	374	
Crystal size	0.18 x 0.16 x 0.14 mm^3	
Theta range for data collection	3.894 to 70.066°.	
Index ranges	$-10 \leq h \leq 9$, $-8 \leq k \leq 11$, $-14 \leq l \leq 14$	
Reflections collected	5814	
Independent reflections	3487 [R(int) = 0.0325]	
Completeness to theta = 67.684°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.83196	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3487 / 0 / 230	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.1242	
R indices (all data)	R1 = 0.0616, wR2 = 0.1370	
Largest diff. peak and hole	0.419 and -0.307 $e.Å^{-3}$	

Crystal data and structure refinement for 8. H_2^{2+}

Identification code	BrzSStfa	
Empirical formula	C52 H54 F12 N4 O8 S2	
Formula weight	1155.11	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.4875(4) Å	α = 90°.
	b = 12.9069(4) Å	β = 98.0780(10)°.
	c = 16.8517(6) Å	γ = 90°.
Volume	2689.12(15) $Å^3$	
Z	2	
Density (calculated)	1.427 Mg/m^3	
Absorption coefficient	0.197 mm^{-1}	
F(000)	1196	
Crystal size	0.16 x 0.14 x 0.10 mm^3	
Theta range for data collection	2.281 to 27.558°.	
Index ranges	$-16 \le h \le 16$, $-16 \le k \le 16$, $-21 \le l \le 21$	
Reflections collected	69513	
Independent reflections	6206 [R(int) = 0.0526]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6669	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6206 / 0 / 368	
Goodness-of-fit on F^2	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0605, wR2 = 0.1541	
R indices (all data)	R1 = 0.0751, wR2 = 0.1648	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.892 and -1.039 $e.Å^{-3}$	

6. ORTEP Diagrams:

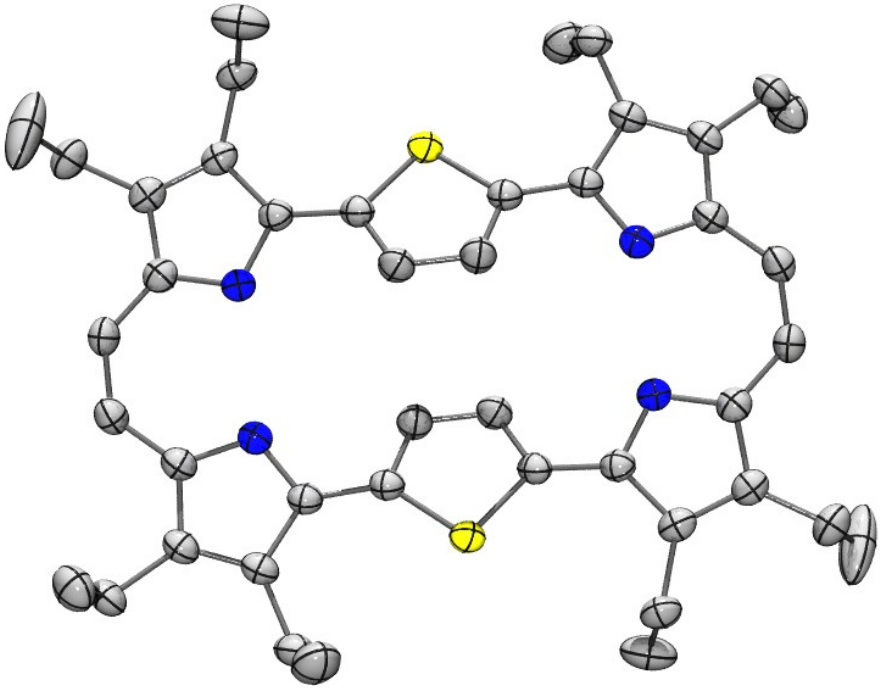


Figure S17: ORTEP-POVRAY diagram of **8** (top view). All hydrogens are excluded for clarity and thermal ellipsoids are scaled up to 50% probability level. Color code: grey = Carbon, blue = Nitrogen and yellow = Sulphur.

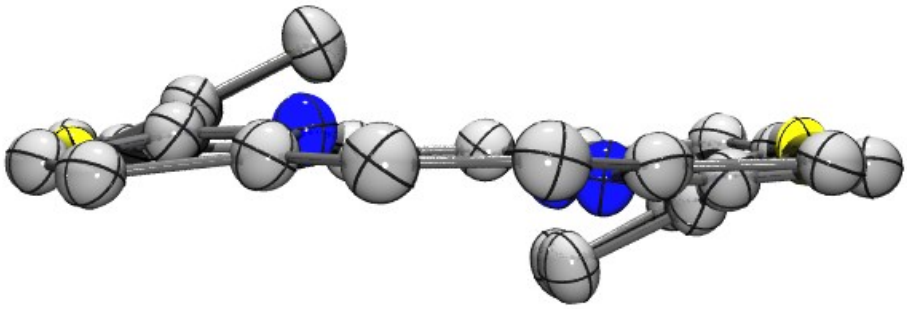


Figure S18: ORTEP-POVRAY diagram of **8** (side view). All hydrogens and ethyl groups are excluded for clarity and thermal ellipsoids are scaled up to 50% probability level. Color code: grey = Carbon, blue = Nitrogen and yellow = Sulphur.

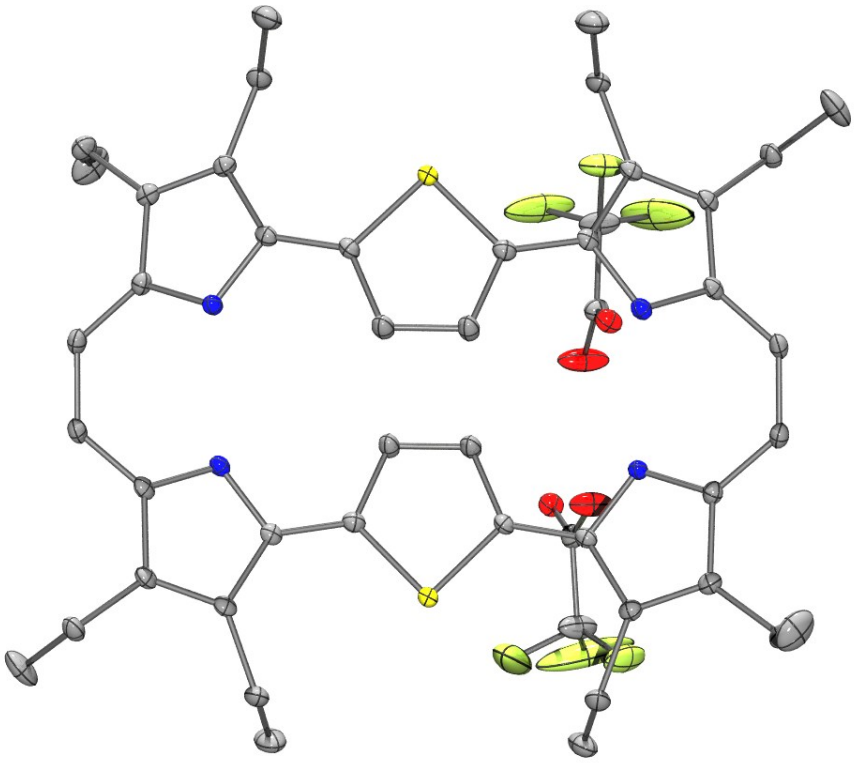


Figure S19: ORTEP-POVRAY diagram of **8.H$_2^{2+}$** (top view). All hydrogens are excluded for clarity and thermal ellipsoids are scaled up to 50% probability level. Color code: grey = Carbon, blue = Nitrogen, yellowish green = Fluorine and yellow = Sulphur.

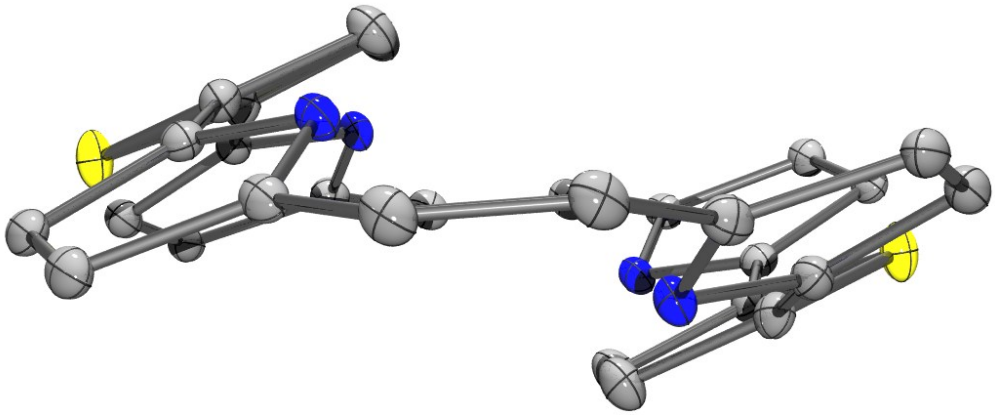


Figure S20: ORTEP-POVRAY diagram of **8.H$_2^{2+}$** (side view). All hydrogens, TFA and ethyl groups are excluded for clarity and thermal ellipsoids are scaled upto 50% probability level. Color code: grey = Carbon, blue = Nitrogen and yellow = Sulphur.

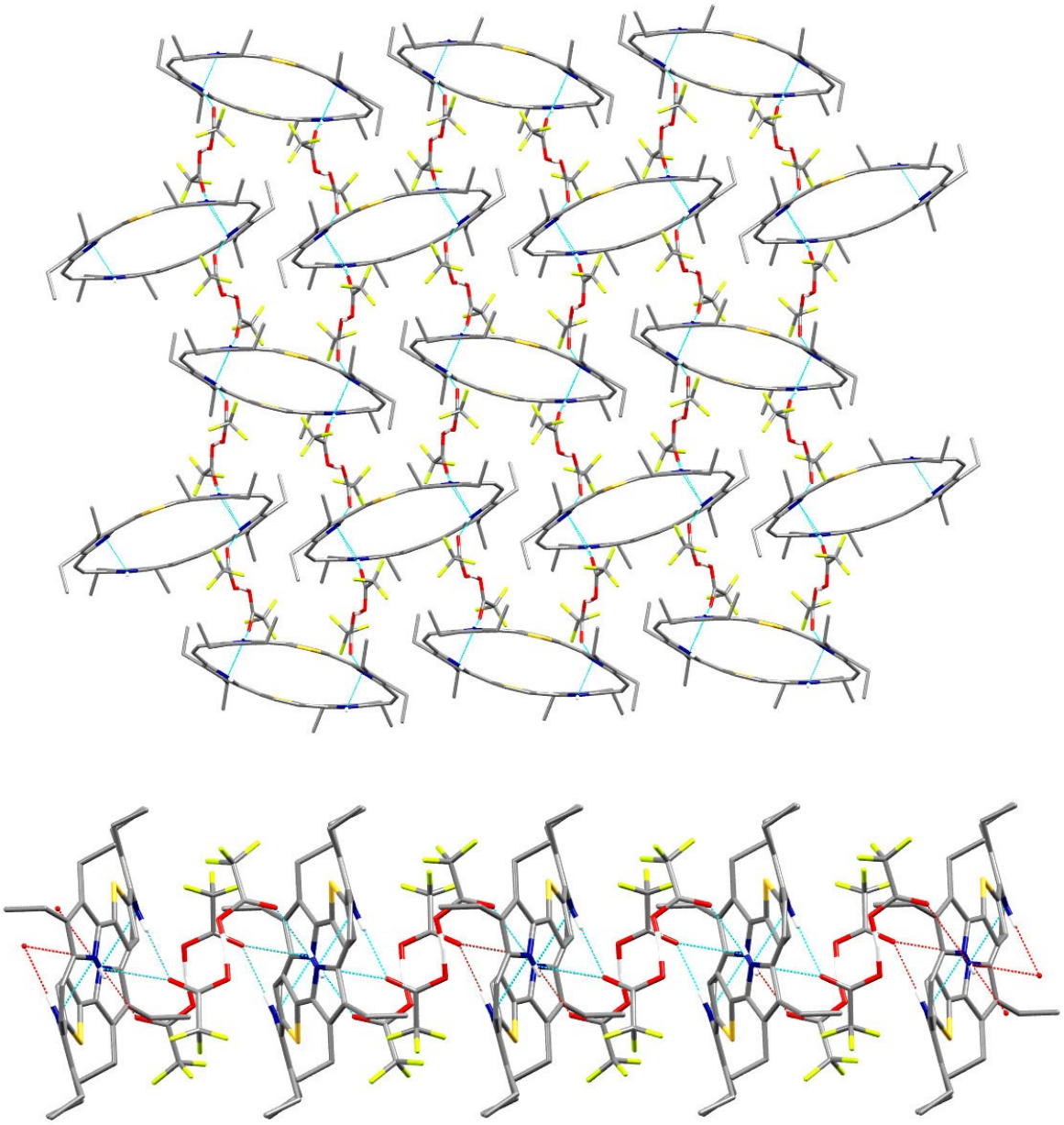


Figure S21: Packing diagrams of **8.H$_2^{2+}$** showing anion bridging viewed along the crystallographic axis a (top) and b (bottom).

7. Absorption and emission studies:

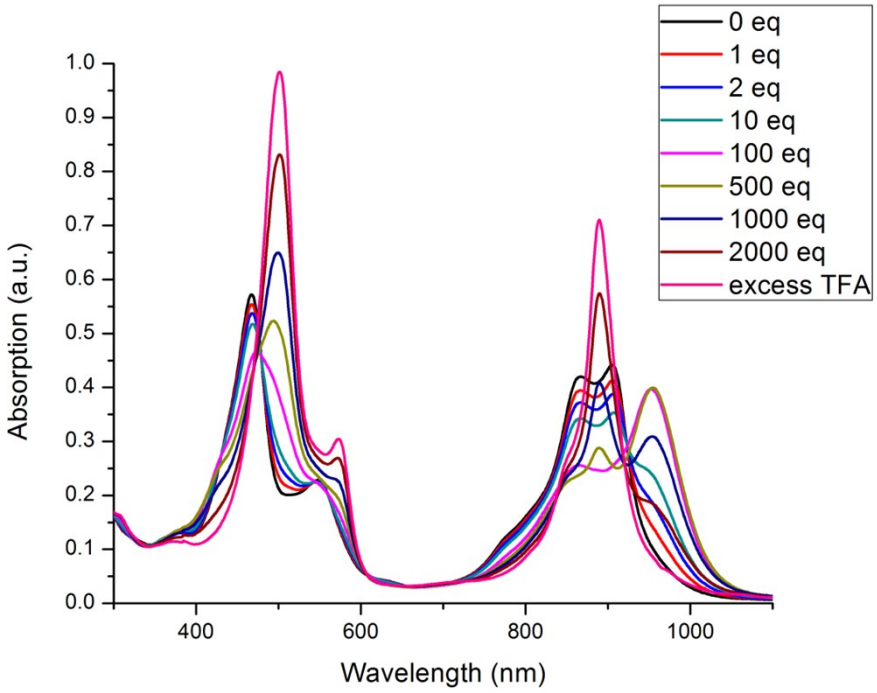


Figure S22: Acidometric titration spectra of **8** in chloroform with TFA.

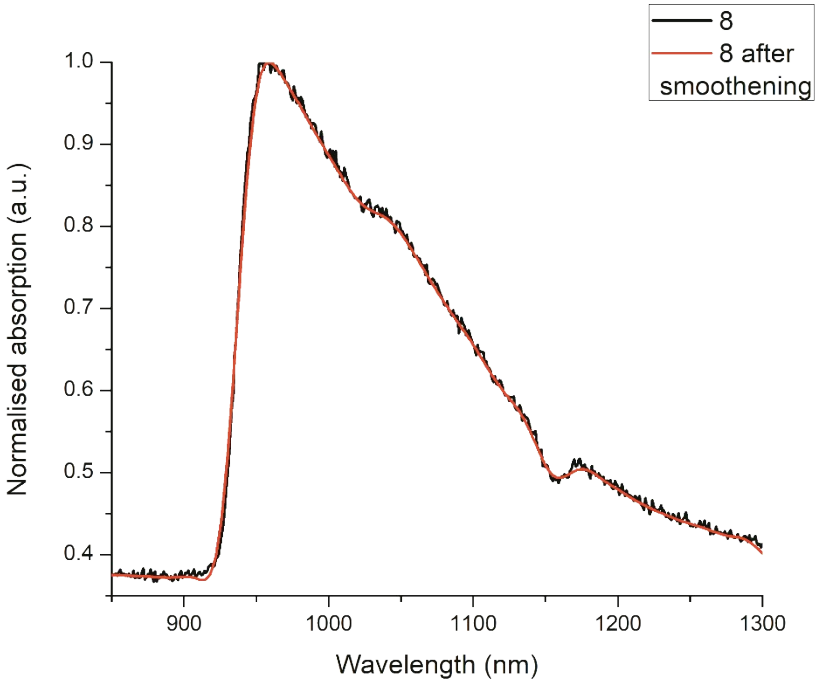


Figure S23: Emission spectrum of bronzaphyrin **8** with peak maxima at 959nm (λ_{ex} = 450nm with slit widths of 14nm).

8. Electrochemical studies:

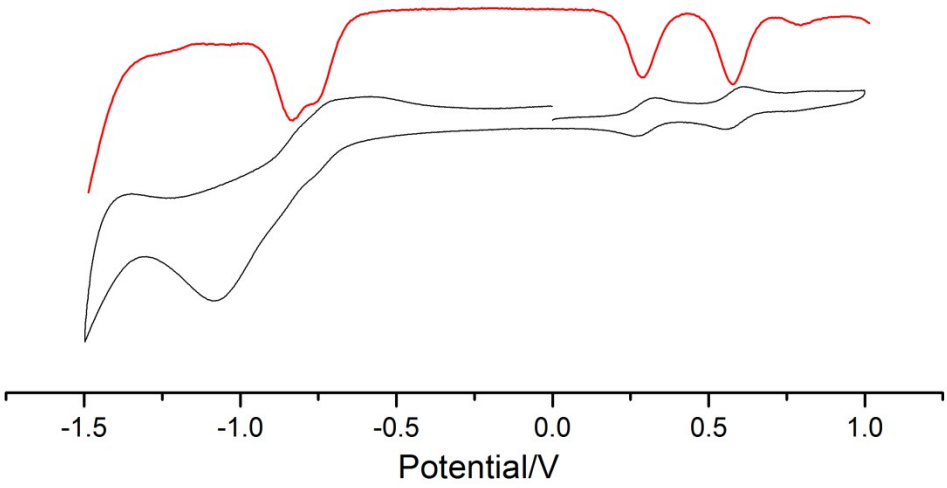


Figure S24: CV (below) and DPV (above) of bronzaphyrin **8** in dichloromethane measured at 298K.

9. References

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