Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Monothia [22]pentaphyrin(2.0.1.1.0): A core modified isomer of Sapphyrin

Sipra Sucharita Sahoo, Sameeta Sahoo and Pradeepta K. Panda*

School of Chemistry, University of Hyderabad, Hyderabad, India, 500046

Email: pkpsc@uohyd.ernet.in ; pradeepta.panda@uohyd.ac.in

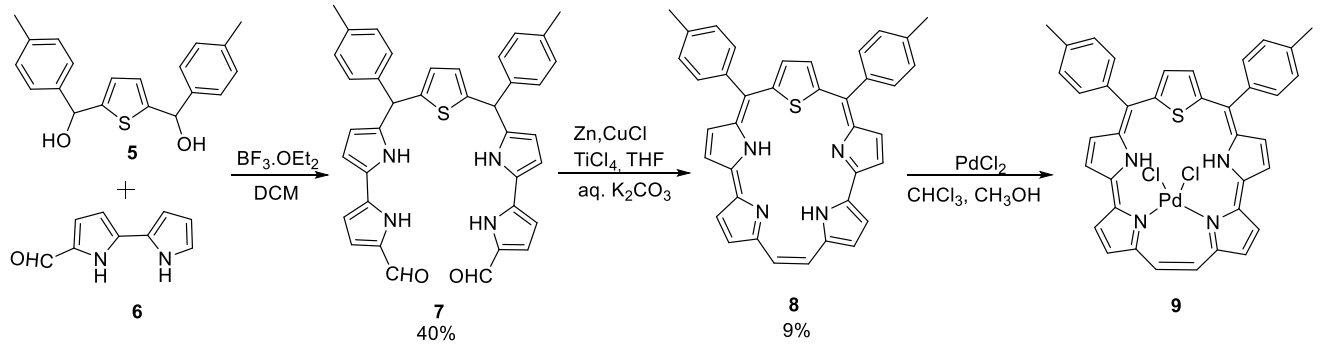
Table of Contents

Instrumentation and reagents:

NMR spectra were recorded on a Bruker Ascend-500 and Bruker Avance-500 MHz FT NMR spectrometer using tetramethylsilane (TMS, δ = 0) as an internal standard at room temperature. Mass spectral determinations were carried out by Bruker Maxis HRMS by ESI techniques. UV Visible-NIR spectra were recorded on a Perkin Elmer Lambda 35 UV-Visible spectrometer. Fluorescence spectra was recorded on a JASCO FP-8500 spectrofluorometer. Spectroscopic grade solvents were used for all absorbance measurement. Commercially available solvents were distilled before use. Reagents were used as received.

All crystallographic data were collected in Rigaku XtaLAB Synergy, single source X-ray diffractometer. Mo-Kα (λ = 0.71073 Å) radiation was used to collect the X-ray reflections of the crystal. Data reduction was performed using CrysAlisPro 1.171.40.35a.[S1]Intensities for absorption were corrected using CrysAlisPro 1.171.40.35a.[S1] and refined using SHELXL2014/7.[S2a,S2b] with anisotropic displacement parameters for non-H atoms. Crystallographic data (including the structure factor) for all structures in this paper have been deposited in the Cambridge Crystal Crystallographic Data Centre as supplementary publication number CCDC 2125056-2125057.

Experimental Procedures



Compound **5** and **6** has been synthesized following reported literature. [S3]

Synthesis of 5',5'''-(thiophene-2,5-diylbis(p-tolylmethylene))bis((1H,1'H-[2,2'-bipyrrole]-5-carbaldehyde) 7:

2,5-Bis(4-tolylhydroxymethyl)thiophene (**5**) (200 mg, 0.62 mmol) and [2,2'-bipyrrole]-5-carboxaldehyde (**6**) (247 mg, 1.54 mmol) were taken in an oven dried 500 mL two necked RB and dissolved in CH_2Cl_2 (300 mL). The solution was bubbled with N_2 for 20 min and then $BF_3.OEt_2$ (60 µL) was added to it. The mixture was stirred at room temperature in dark under N_2 atmosphere for 6 h. Then the reaction mixture was washed with water and organic layer was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The resulting solid was purified by column chromatography with 20% ethyl acetate:hexane mixture to obtain **7** as bright yellow coloured solid. Yield: 40%; Decomposed >180 °C before melting. ^{1}H NMR (500 MHz, DMSO-D_6) δ in ppm: 11.89 (s, 2H), 11.06 (s, 2H), 9.31 (s, 2H), 7.18 (d, J = 8.28 Hz, 4H), 7.14(d, J = 8.13 Hz, 4H), 6.99 (dd, *J* = 2.27 Hz, 2H), 6.62 (s, 2H), 6.60 (t, *J* = 2.84 Hz, 2H), 6.51(dd, *J* = 2.24 Hz, 2H), 5.82 (t, *J* = 2.66 Hz, 2H), 5.58 (s, 2H), 2.51 (s, 6H); ^{13}C NMR (125 MHz, DMSO-D_6) δ in ppm: 177.7,146.4, 140.4, 136.4, 136.2, 134.7, 132.3, 129.5, 128.5, 125.4, 123.7, 109.0, 108.2, 106.9, 45.3, 21.1; HRMS(ESI+): m/z calculated for $C_{38}H_{32}N_4SO_2$ ($M+H^+$): 609.2323; found: 609.2325; IR (ν in cm^{-1}): 3259, 3212, 1599, 1544, 1509.

Synthesis of sapphycene 8:

A low-valent titanium reagent was prepared in situ by adding $TiCl_4$ (0.36 mL,3.28 mmol) to a solution of activated Zn (426 mg, 6.56 mmol), CuCl (64.98 mg, 0.656 mmol) and THF in a three-necked RB at 0 °C and then heating to reflux for 3 h. To this slurry, THF solution of compound **7** (100mg, 0.164 mmol**)** was added dropwise for 1 h under reflux condition. After completion of addition, the reaction mixture was kept for refluxing for additional 2 h and then slowly brought to room temperature. Then it was cooled to 0 °C and hydrolysed with aqueous K_2CO_3 solution. It was kept for open air oxidation overnight and then the rection mixture was filtered using celite. The filtrate was washed with water and the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silicagel column chromatography with 80:20 of hexane-ethyl acetate mixture as eluent to obtain **8** as blue colour solid. Yield: 9%. M.P: >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ in ppm: 10.38 (s, 2H), 10.36 (d, *J* = 4.17 Hz, 2H), 10.19 (d, *J* = 4.61Hz, 2H), 9.99 (s, 2H), 9.68 (d, *J* = 4.17 Hz, 2H), 9.43 (d, *J* = 4.59 Hz, 2H), 8.37 (d, *J* = 7.74 Hz, 4H), 7.76 (d, *J* = 7.53 Hz, 4H), 2.81 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ in ppm: 144.6, 143.4, 141.0, 138.8, 138.1, 134.3,134.3, 132.5, 132.4, 129.3, 128.4, 128.4, 127.8, 126.7, 126.2, 112.9, 21.6; UV-vis-NIR data in $CHCl_3$ (λ_{max} nm, log ε): 447 (5.50), 467 (5.24), 542 (3.98), 579 (4.27), 622 (4.79), 699 (3.86), 773 (4.61); HRMS (ESI+): m/z calculated for $C_{38}H_{28}N_4S$ ($M+H^+$): 573.2113; found:573.2100; IR (ν in cm^{-1}): 2920, 2581, 1597, 1510.

Synthesis of palladium(II)-sapphycene 9:

Thiasapphycene **8** (2 mg) was taken in a two-necked RB in N_2 atmosphere and dissolved in 5 mL chloroform and methanol (1 mL) was added to it and then $PdCl_2$ (25 mg) was added to the above solution and kept for stirring at rt. Reaction was monitored using TLC and absorption spectroscopy. After 10-15 min all the starting material was consumed and it was concentrated under reduced pressure. Then the crude product was purified by silicagel column chromatography to yield **9** as brown colour solid. Yield: quantitative. ^{1}H NMR (500 MHz, CD_2Cl_2) δ in ppm: 10.58 (s, 2H), 10.21 (s, 2H),10.06 (d, *J* = 4.46 Hz, 2H), 9.81 (d, 2H, *J* = 4.47 Hz), 9.66 (d, *J* = 4.44 Hz, 2H), 9.27 (d, *J* = 4.57 Hz, 2H), 8.71 (bs, 4H), 7.94 (d, *J* = 7.66 Hz, 4H), 2.84 (s, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ in ppm: 149.7, 142.2, 140.2, 138.3, 138.0, 137.1, 136.3, 134.8, 132.4, 129.7, 129.6, 129.4, 126.7, 124.2, 115.5, 21.4; UV-vis-NIR data in $CHCl_3$ (λ_{max} nm, log ε): 491 (5.13), 623 (4.12), 667 (3.96), 804 (4.27); HRMS (ESI+): m/z calculated for $C_{38}H_{28}ClN_4PdS$ ($M-Cl^-$): 713.0757, found: 713.0754; IR (ν in cm^{-1}): 2959, 2918, 2851,1588.

Results and Discussion

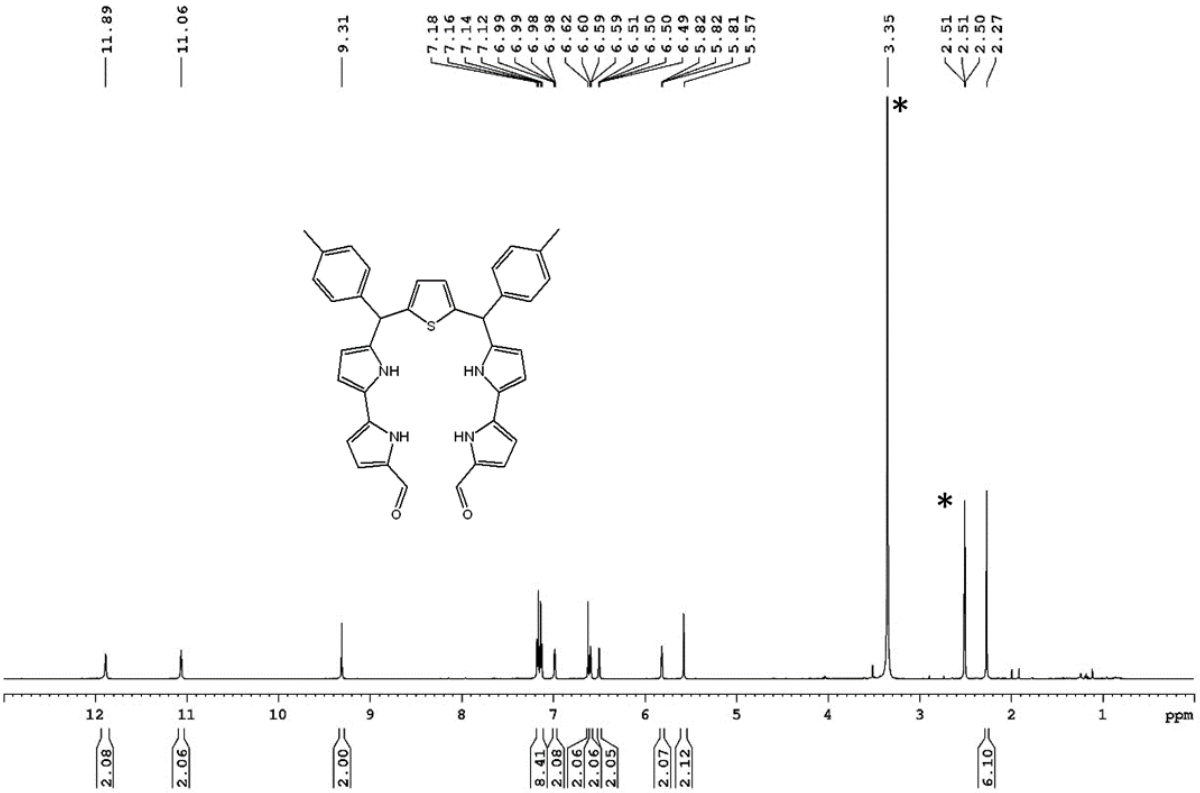


Figure S1: ^{1}H NMR spectrum of **7** in DMSO-d_6 (*water and residual protons of solvent).

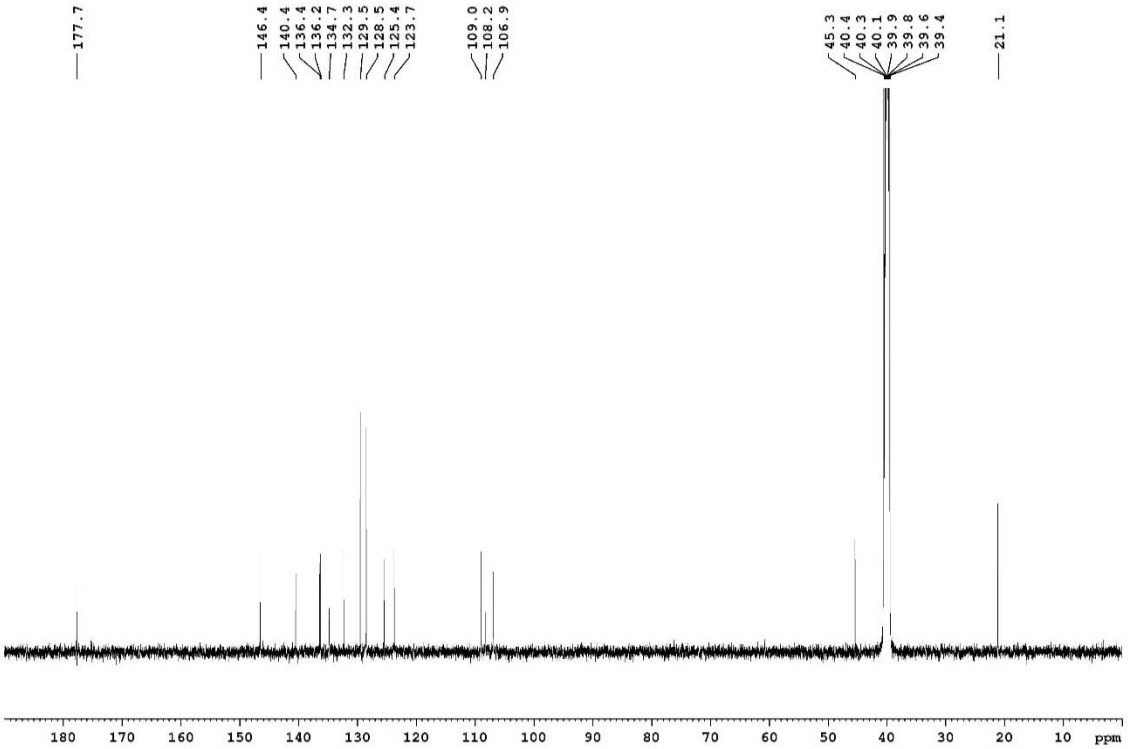


Figure S2: ^{13}C NMR spectrum of **7** in DMSO-D_6.

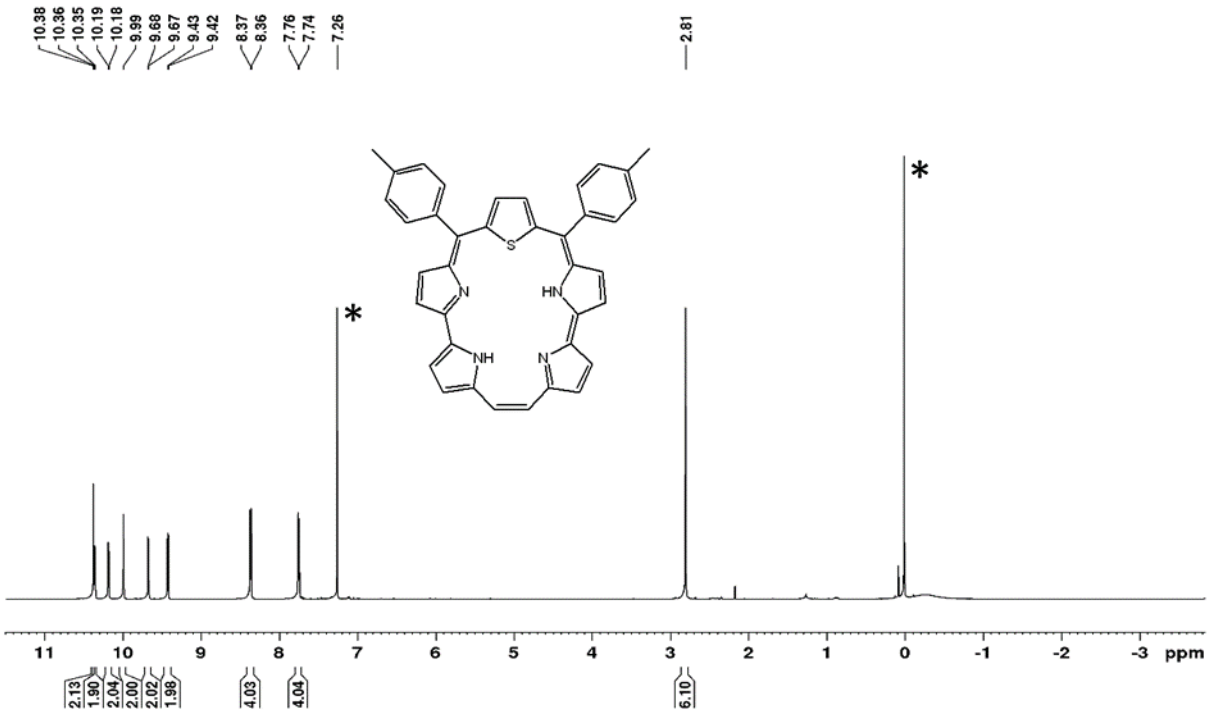


Figure S3: ^{1}H NMR spectrum of compound **8** in $CDCl_3$ (* water and residual protons of solvent).

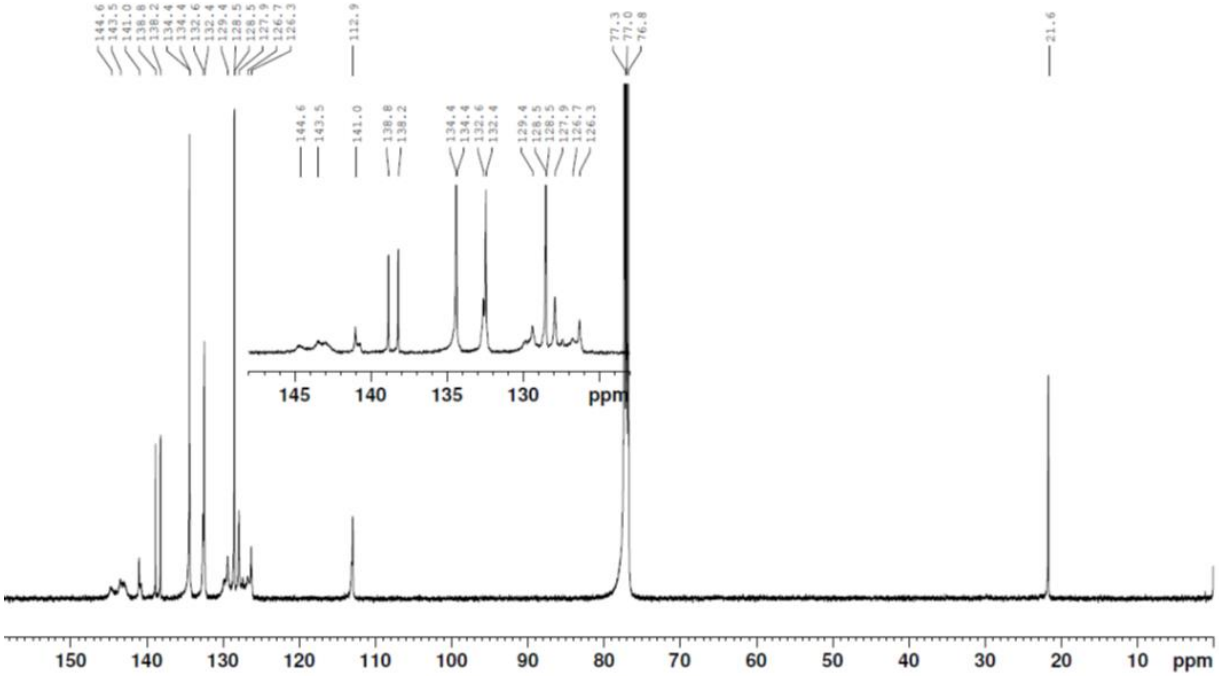


Figure S4: ^{13}C NMR spectrum of **8** in $CDCl_3$.

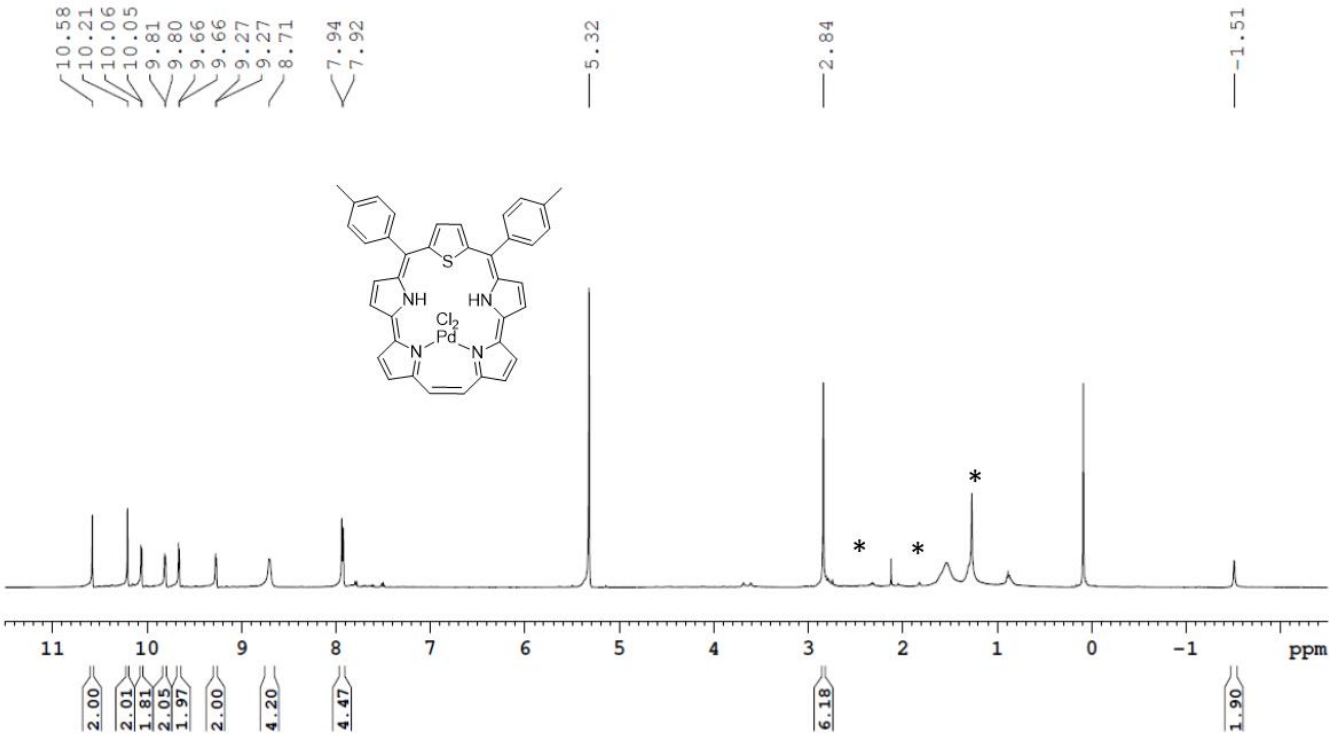


Figure S5: ^{1}H NMR spectrum of **9** in CD_2Cl_2 (* water and residual protons of solvent and impurities due to less solubility of sample).

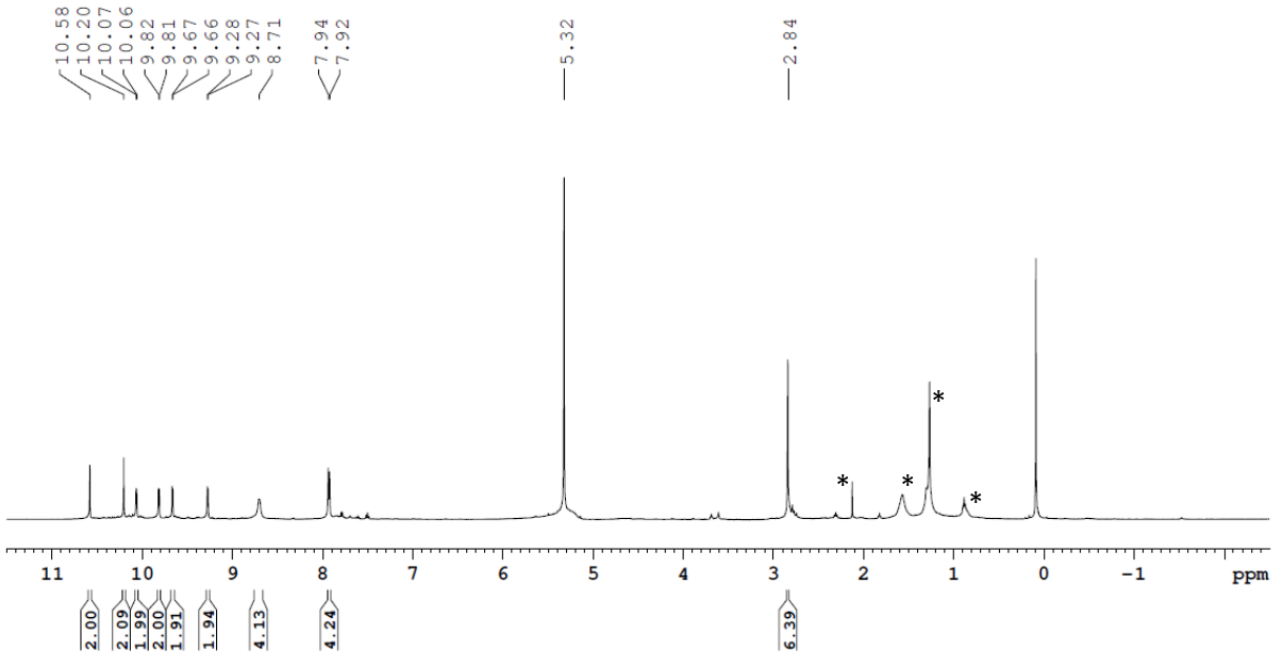


Figure S6: D_2O exchange ^{1}H NMR spectrum of **9** in CD_2Cl_2 (* water and residual protons of solvent and impurities due to less solubility of sample).

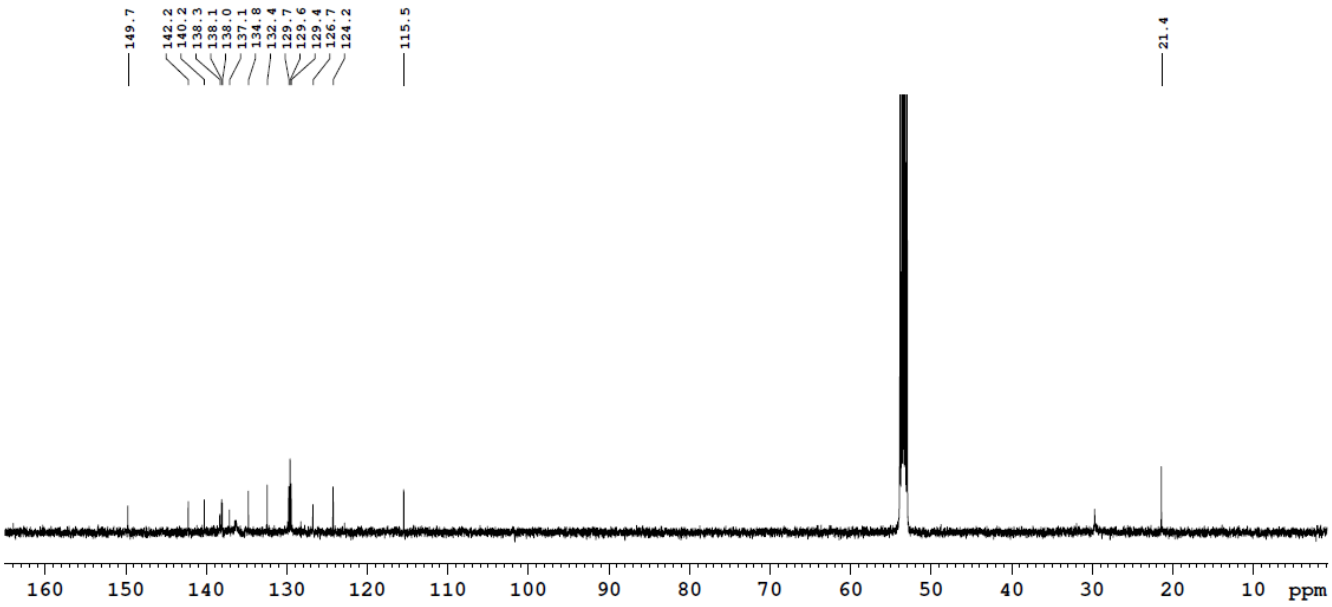


Figure S7: ^{13}C NMR spectrum of **9** in CD_2Cl_2.

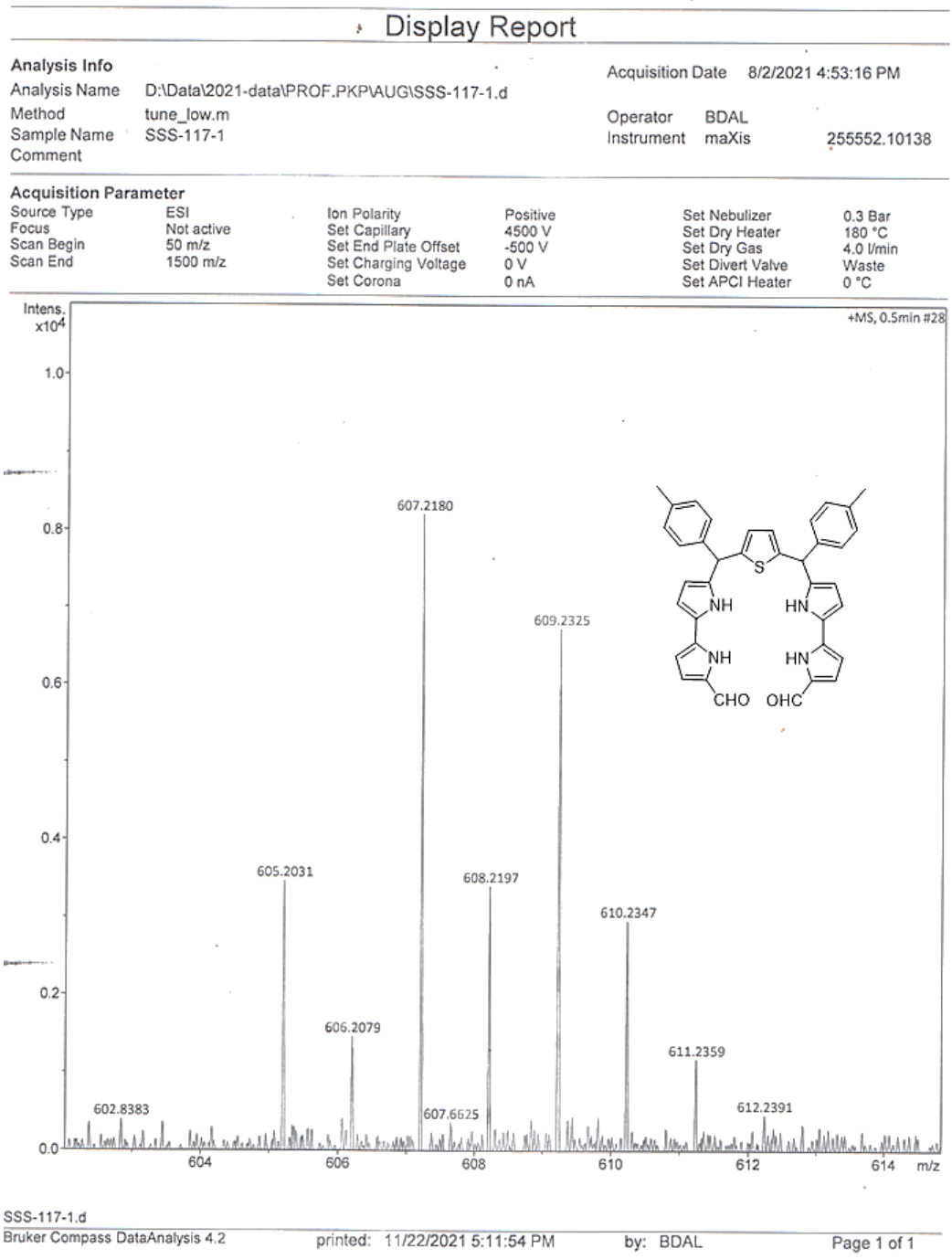


Figure S8: HRMS data of **7**: m/z calculated for $C_{38}H_{32}N_4SO_2$ ($M+H^+$): 609.2323; found: 609.2325.

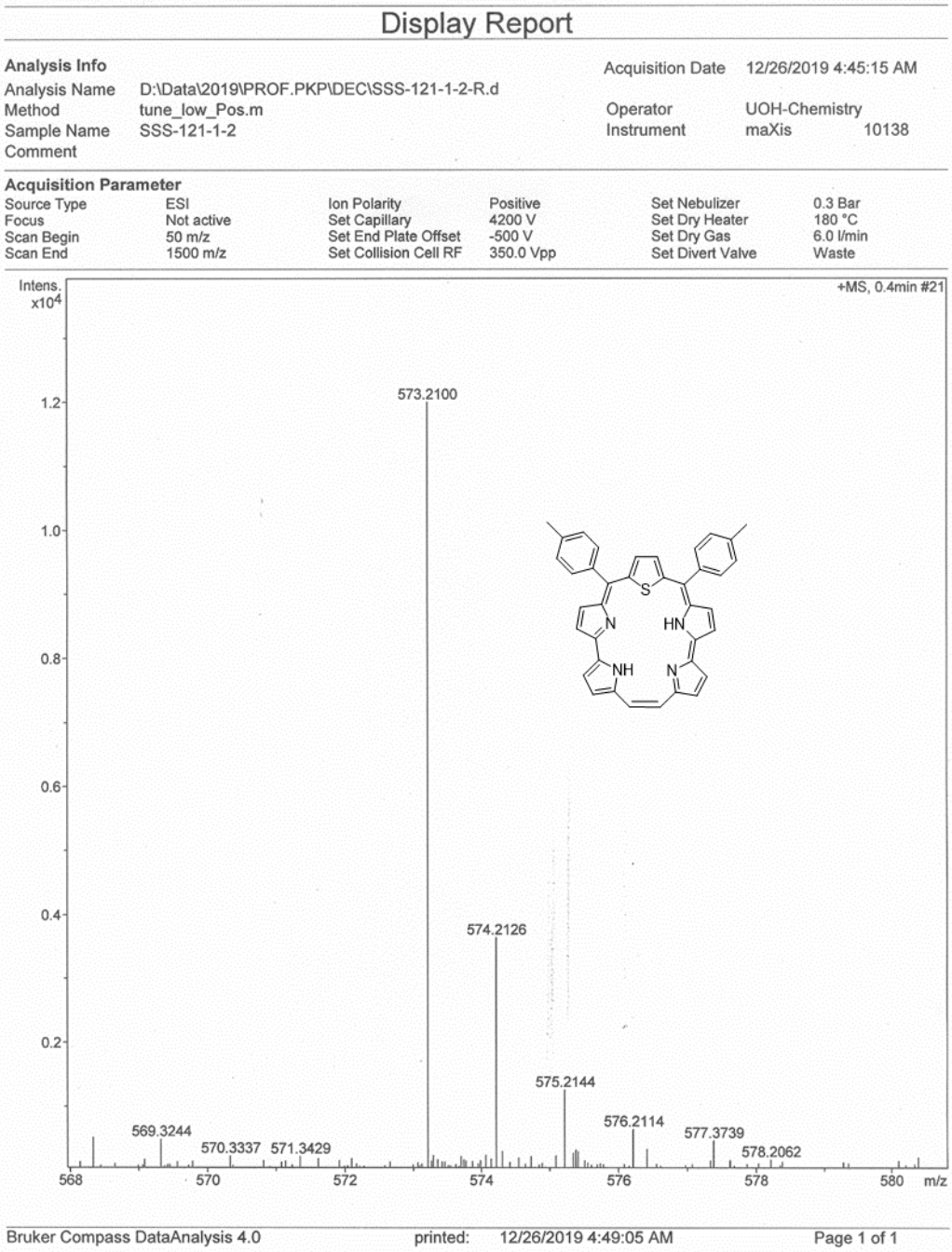


Figure S9: HRMS data of **8**. Calculated m/z $C_{38}H_{28}N_4S$ ($M+H^+$): 573.2113; found:573.2100.

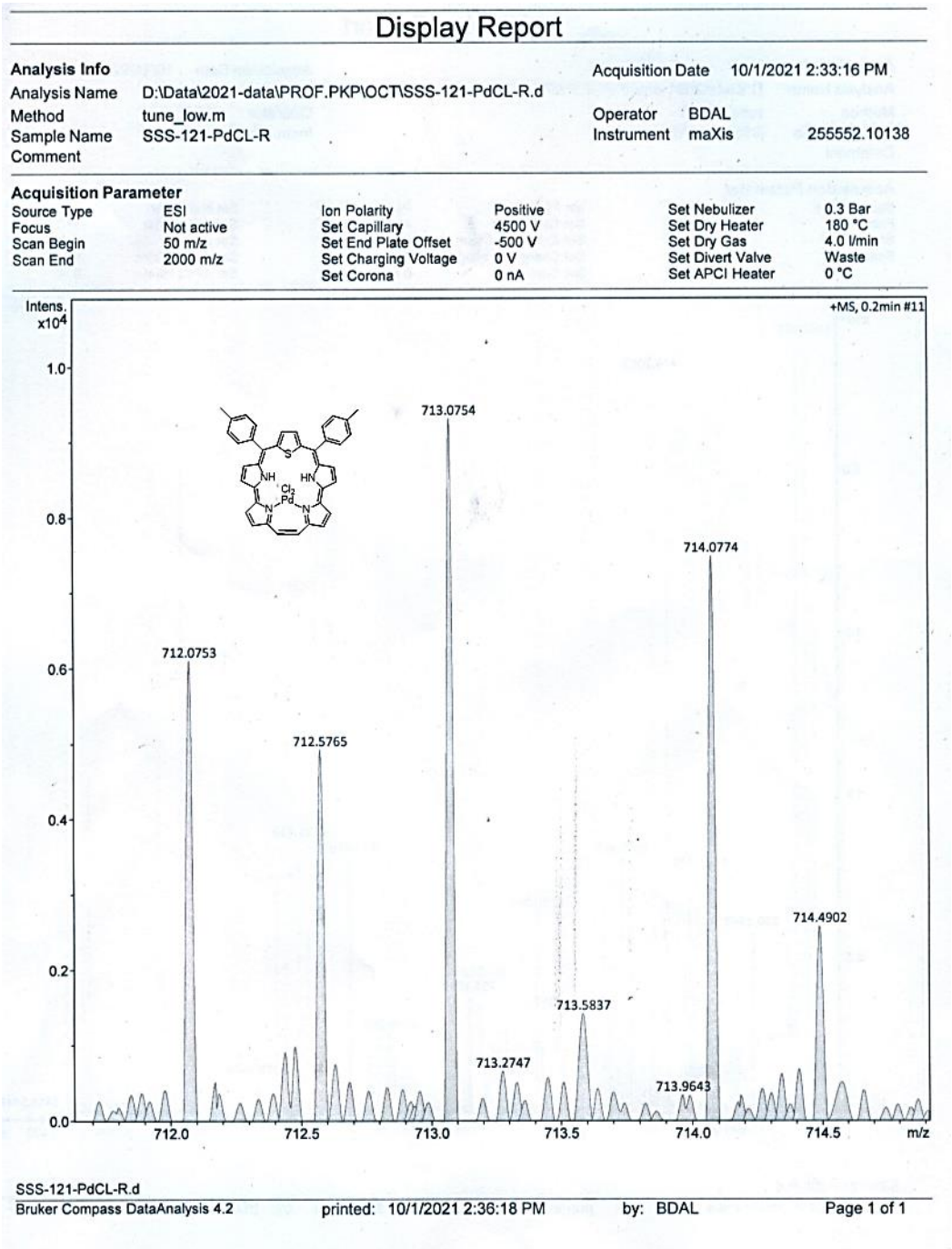


Figure S10: HRMS data of **9**: m/z calculated for $C_{38}H_{28}ClN_4PdS$ ($M\text{-}Cl^-$): 713.0757; found: 713.0754.

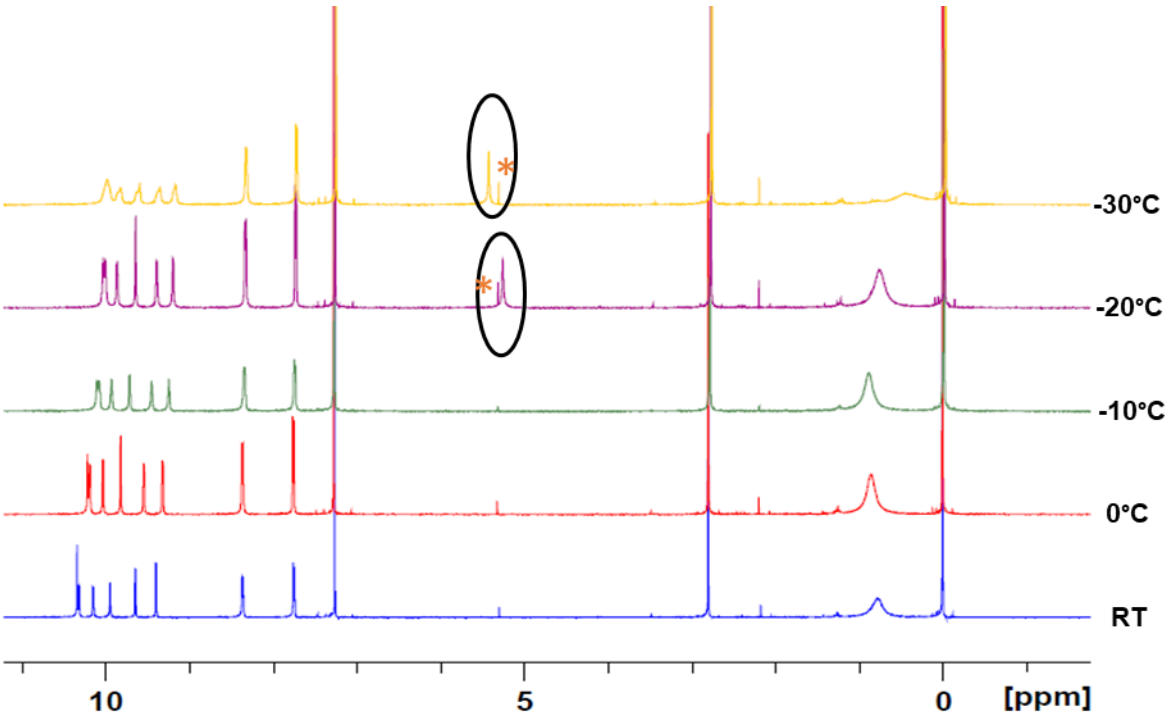


Figure S11: Variable temperature ^{1}H NMR spectra of **8** in $CDCl_3$ (*DCM impurity).

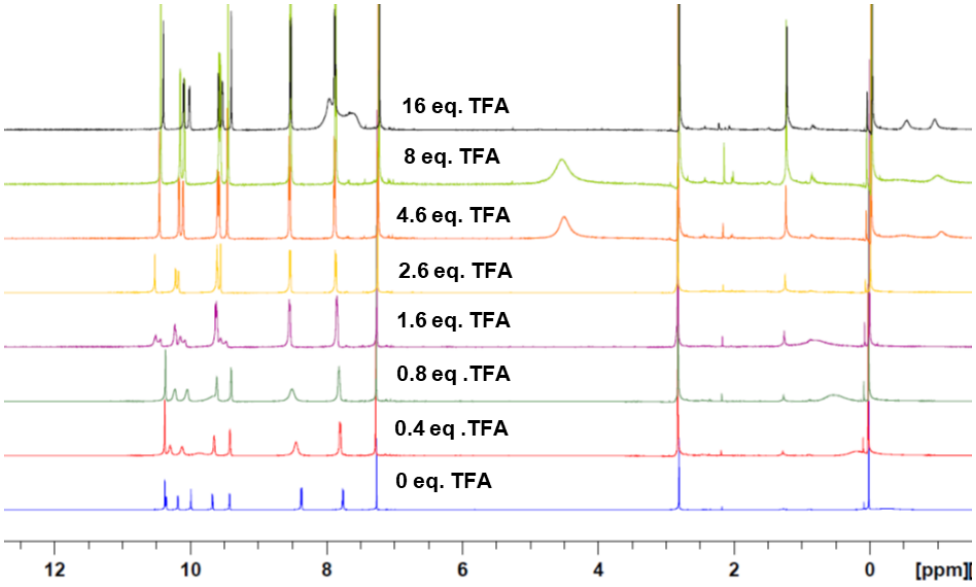


Figure S12: ^{1}H NMR spectra of compound **8** in $CDCl_3$ titrated with TFA.

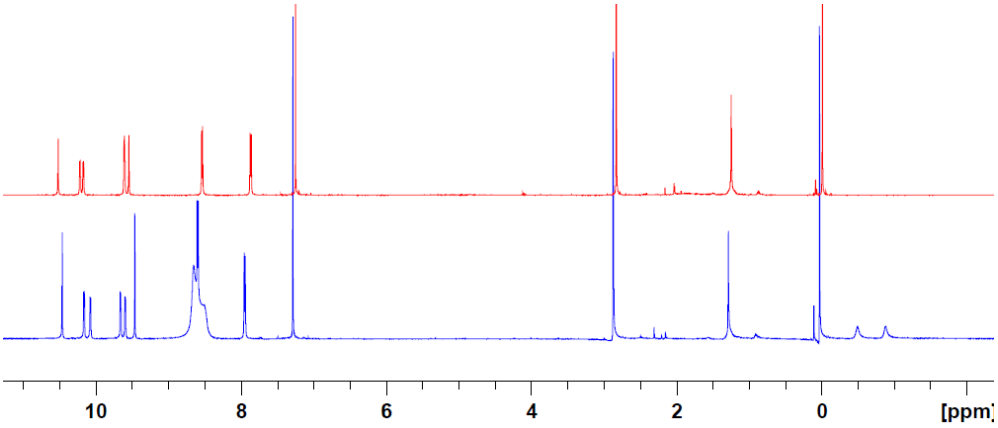


Figure S13: ^{1}H NMR spectra of **8.2TFA** (blue) and **8.2TFA** with D_2O (red) in $CDCl_3$.

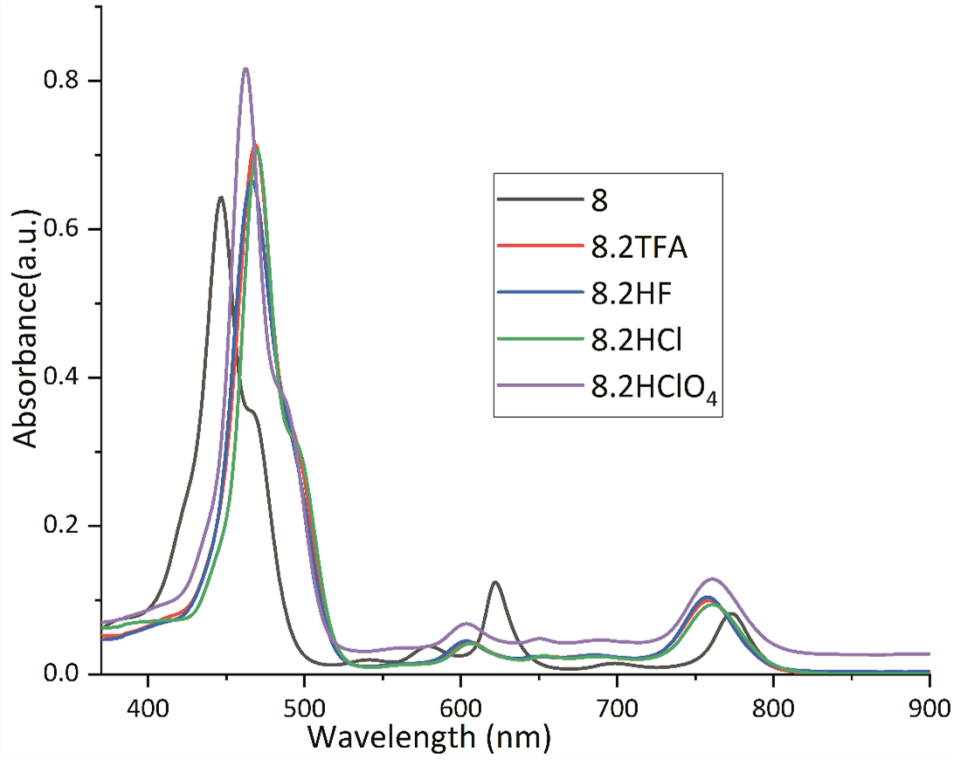


Figure S14: UV-vis-NIR absorption spectra of **8** (2 µM in $CHCl_3$) protonated with acids (methanolic solution).

.

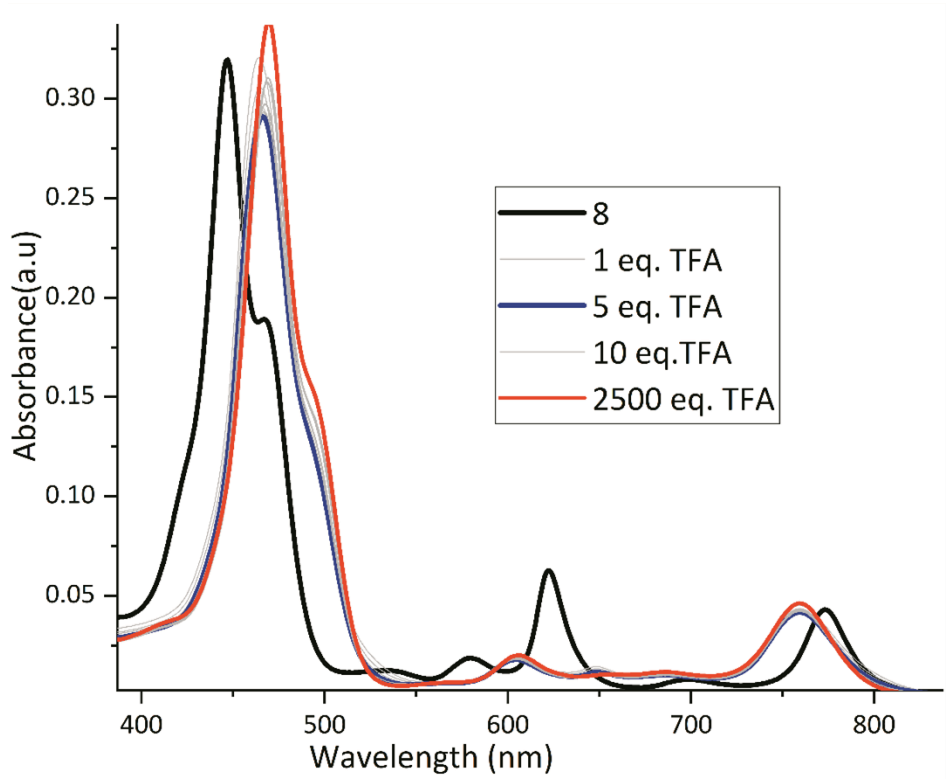


Figure S15: UV-vis-NIR spectra of compound **8** (1 µM in $CHCl_3$) titration against TFA (in $CHCl_3$).

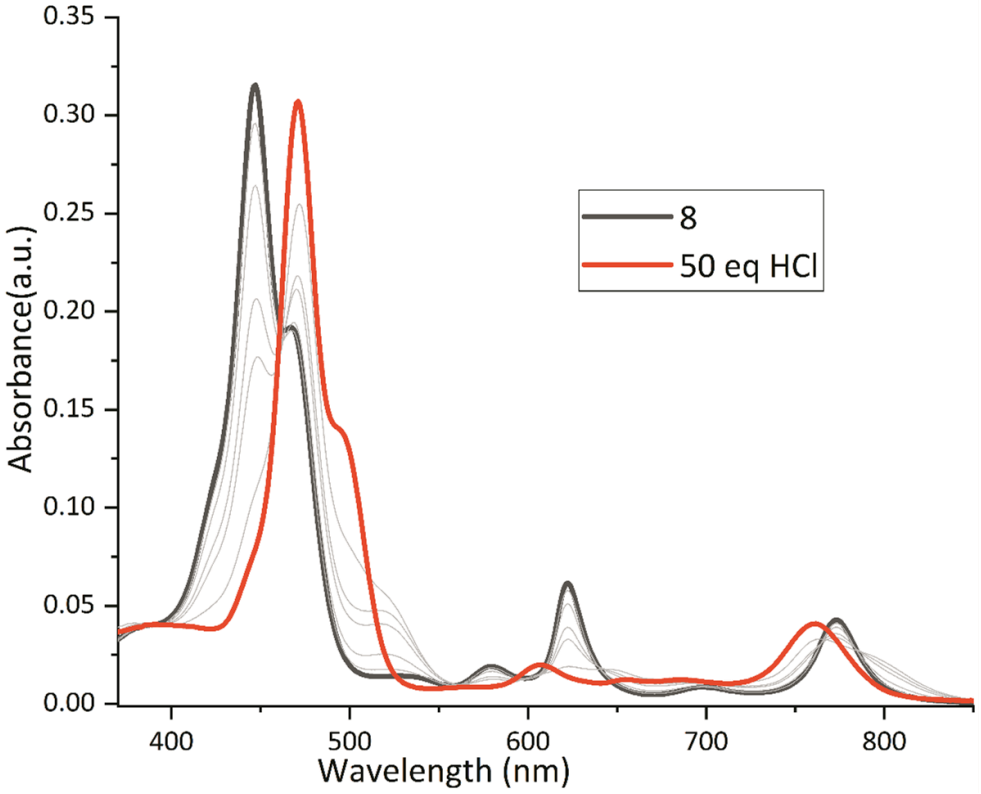


Figure S16: UV-vis-NIR spectra of compound **8** (1 µM in $CHCl_3$) titration against HCl (in methanol).

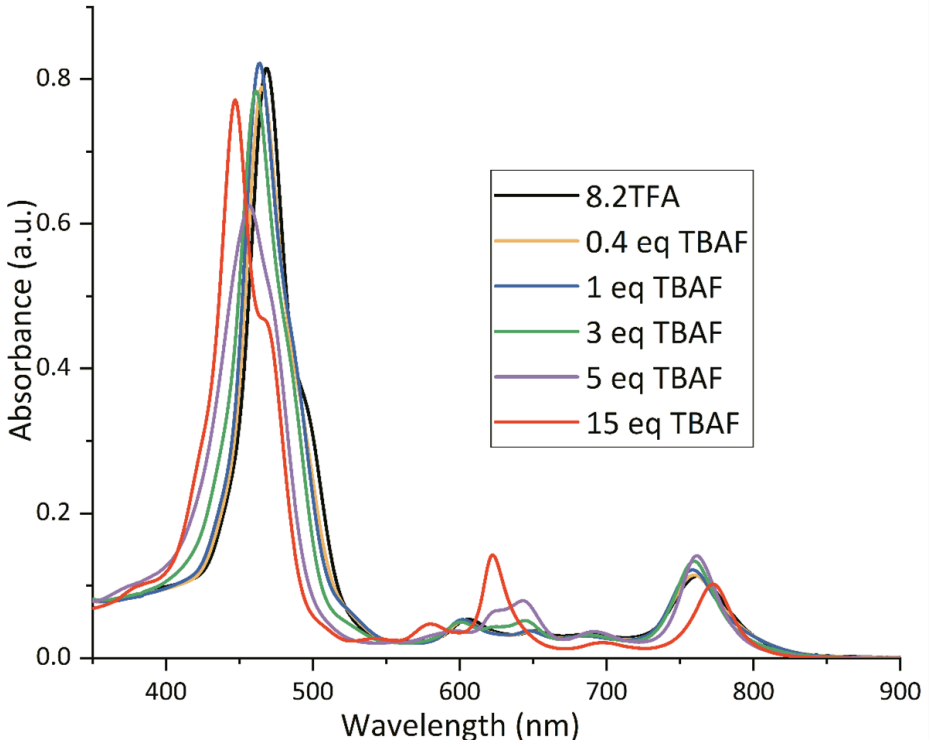


Figure S17: Fluoride binding with **8.TFA** (10 µM) using TBAF.$3H_2O$ in $CHCl_3$.

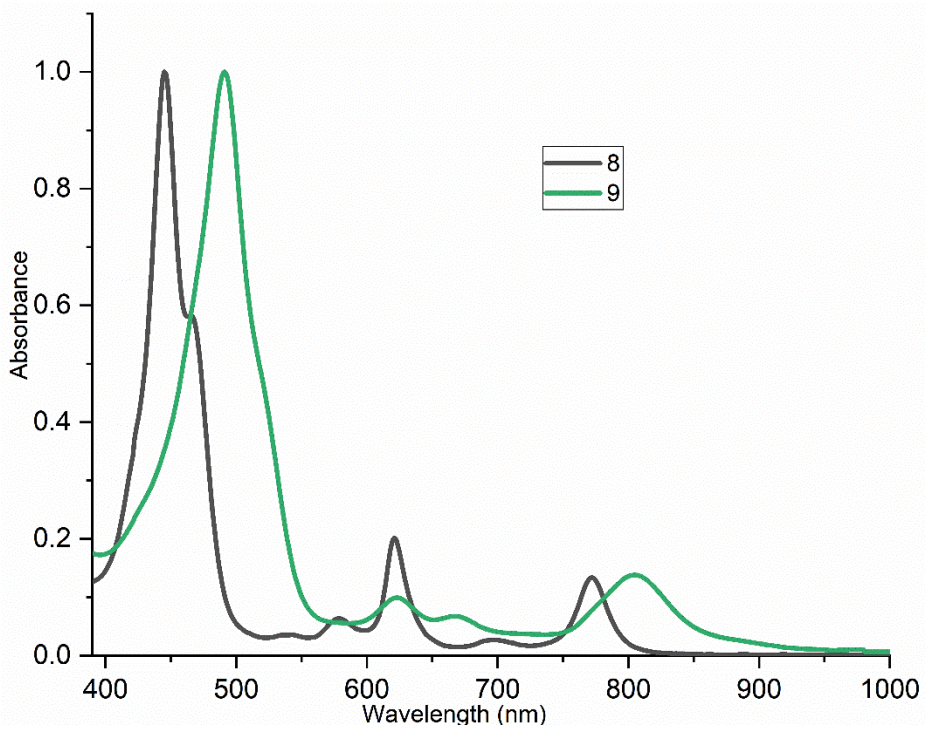


Figure S18: UV-vis-NIR spectra of **8** and **9**in $CHCl_3$.

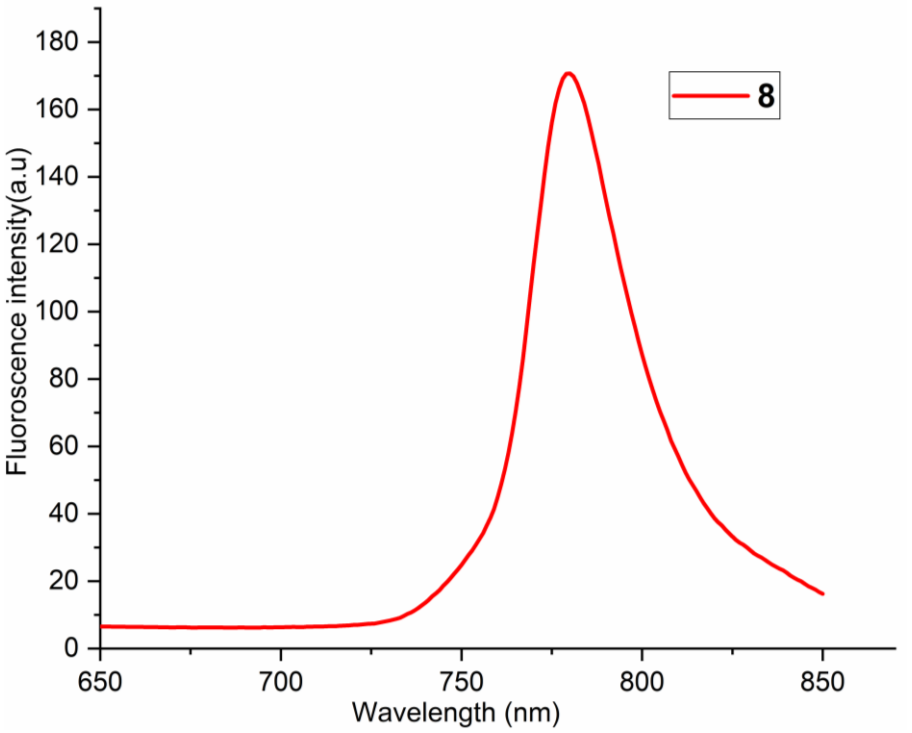


Figure S19: Emission spectrum of **8** in chloroform (λ_{ex}: 428 nm).

Computational studies

All quantum mechanical calculations are performed by Gaussian 09 programme[S4] provided by CMSD facility at University of Hyderabad. Ground state optimisation has been performed by density functional theory (DFT) using Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) employing 6-31G(D,P) basis set for C, H, N, S and LANL2DZ for Pd atom. The NICS values were obtained with gauge independent atomic orbital (GIAO) method based on the optimized geometries.[S5] HOMA (Harmonic Oscillator Model of Aromaticity) indices were calculated by using Ropt (C-C) = 1.388 Å and Ropt = 1.334 Å.[S6-S8] The molecular orbitals were visualized using Gauss view 5.

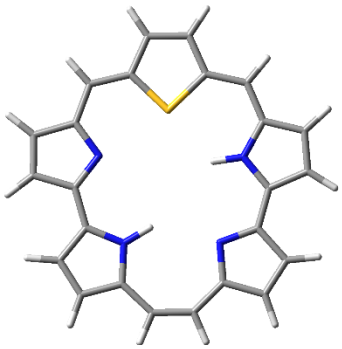
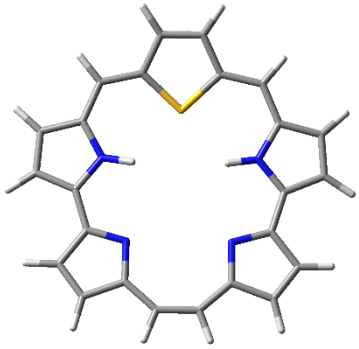
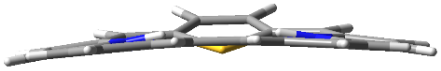
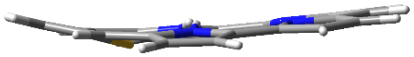
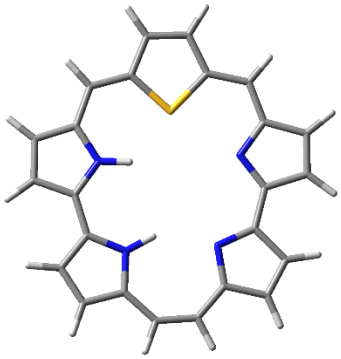
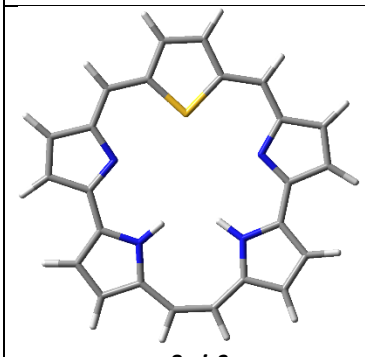
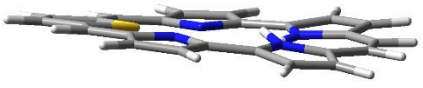
Front view	Side views	Optimized energy difference in gas phase (kcal/mol)	HOMO-LUMO gap (kcal/mol)	Optimized energy difference in $CHCl_3$(kcal/mol)
 **8-*trans***	 	0	48.66	0
 **8-*cis1***	 	12.9	48.20	10.37
 **8-*cis2***	 	6.68	48.20	5.07
 **8-*cis3***	 	4.15	50.73	3.22

Table S1: Optimised properties of different tautomers of **8** (tolyl groups are removed for clarity).

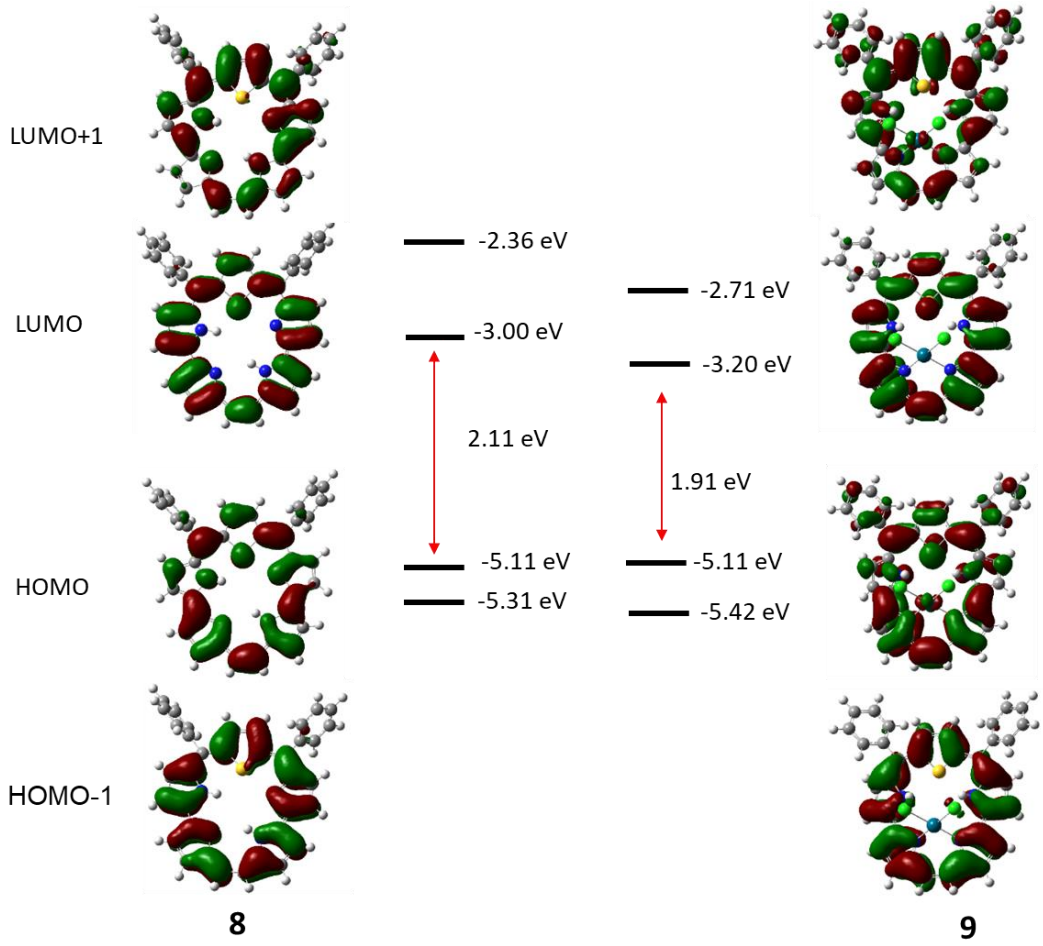
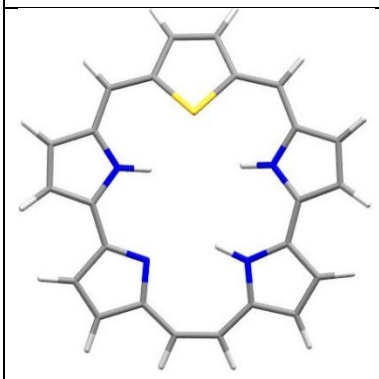
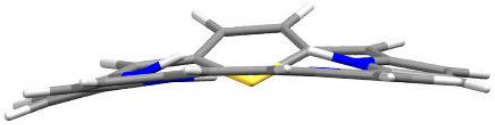
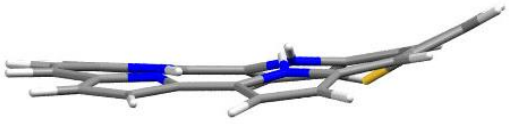


Figure S20: Frontier orbital diagram of **8** and **9**.

Front View	Side Views	Relative energies(kcal/mol)
 **8.H**	 	0
		4.76

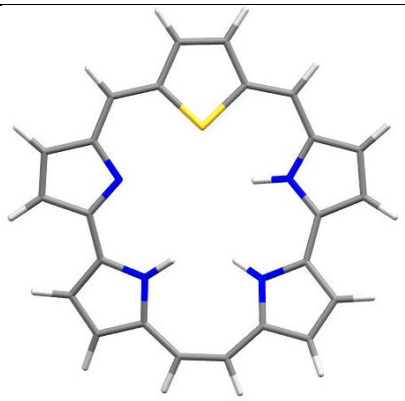
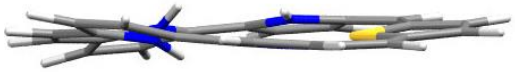
 **8-Ha**		

Table S2: Relative energies of optimized geometries of different modes of mono-protonation of **8** in chloroform (tolyl groups are removed for clarity).

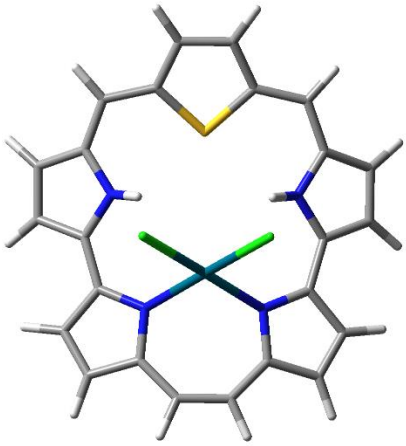
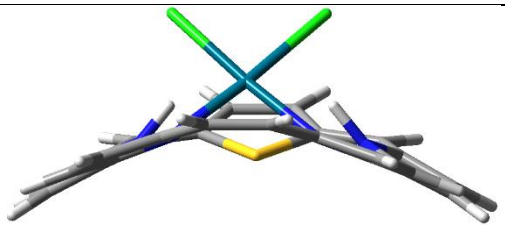
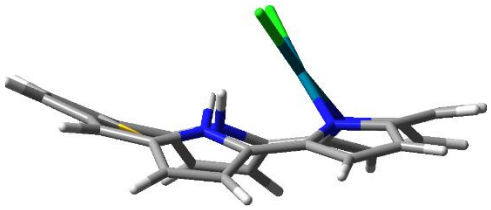
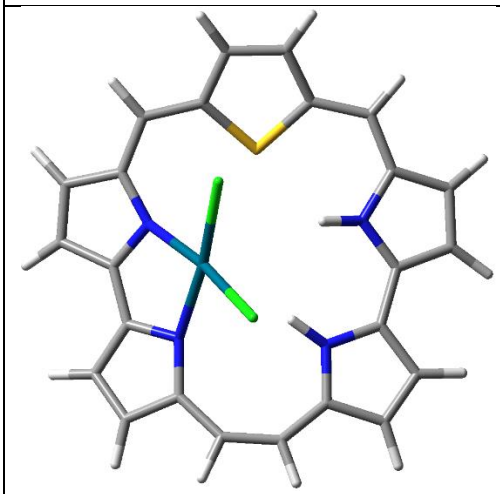
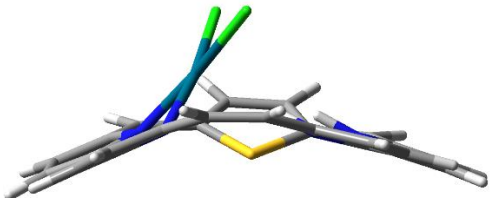
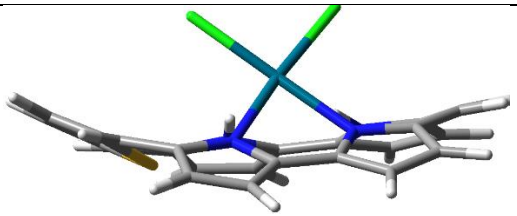
Front View	Side Views	Relative energies (kcal/mol)
 **9**	 	0
 **9′**	 	9.68

Table S3: Relative energies of conformations having different mode of binding of Pd to **8** (tolyl groups are removed for clarity).

Table S4: Coordinates of optimized geometry of **1**:

Label	Symbol	X	Y	Z	Label	Symbol	X	Y	Z
1	C	1.13788	3.423046	0.000396	24	C	4.671015	1.920132	0.000252
2	C	0.682926	4.785286	0.00042	25	C	3.210254	1.878127	0.000322
3	C	-0.68286	4.785294	0.000054	26	N	2.753893	0.595952	0.000047
4	C	-1.13782	3.423058	-0.00016	27	C	2.486453	3.084017	0.000561
5	N	0.000022	2.632457	0.000069	28	C	-3.93064	-1.57914	0.000252
6	C	-3.88673	-0.18532	-7.8E-05	29	C	3.930612	-1.57919	-0.0005
7	C	-5.09211	0.63036	-0.00035	30	H	1.347371	5.638613	0.000667
8	C	-4.67098	1.9202	-0.00061	31	H	-1.34729	5.638629	-4.3E-05
9	C	-3.21022	1.878171	-0.00045	32	H	0.000018	1.623225	-4.9E-05
10	N	-2.75389	0.595987	-0.00017	33	H	-6.10569	0.24956	-0.00036
11	C	-2.4864	3.084049	-0.00047	34	H	-5.26758	2.823903	-0.00087
12	C	-0.70578	-3.18045	0.000269	35	H	-3.12346	3.964648	-0.00067
13	C	-1.55291	-4.32334	0.000602	36	H	-1.20868	-5.34731	0.000781
14	C	-2.86299	-3.88535	0.000693	37	H	-3.75812	-4.4919	0.000945
15	C	-2.84943	-2.46377	0.000418	38	H	-1.28612	-1.08701	-7.5E-05
16	N	-1.5245	-2.07581	0.000193	39	H	1.208601	-5.34733	-0.00033
17	C	0.705726	-3.18046	0.000007	40	H	3.758054	-4.49195	-0.00086
18	C	1.552842	-4.32337	-0.00029	41	H	1.286101	-1.08703	0.000164
19	C	2.862925	-3.88539	-0.00057	42	H	6.105692	0.249469	-0.0003
20	C	2.84939	-2.46381	-0.00044	43	H	5.267626	2.823826	0.000441
21	N	1.524465	-2.07583	-0.00012	44	H	3.123522	3.964607	0.000825
22	C	3.886727	-0.18537	-0.00023	45	H	-4.9149	-2.03775	0.000372
23	C	5.09212	0.630286	-0.00012	46	H	4.914866	-2.03782	-0.00074

Table S5: Coordinates of optimized geometry of **2**:

Label	Symbol	X	Y	Z	Label	Symbol	X	Y	Z
1	C	-1.129715	2.888314	0.000583	24	C	-2.413416	2.312226	0.000387
2	C	-0.692927	4.243636	0.000344	25	N	-2.595623	0.962673	0.000021
3	C	0.692776	4.243665	-0.000023	26	C	4.199282	-1.756075	0.000194
4	C	1.129634	2.888357	0.000014	27	C	-4.199181	-1.756131	-0.000386
5	N	-0.000014	2.117153	0.000489	28	C	4.63919	-0.443263	-0.000108
6	C	3.947799	0.783671	-0.000283	29	C	-4.639201	-0.443354	-0.00059
7	C	4.637645	2.062075	-0.000628	30	H	-1.344023	5.106147	0.000509
8	C	3.670342	3.025883	-0.000557	31	H	1.343841	5.106199	-0.000318
9	C	2.413374	2.31235	-0.00022	32	H	-0.000016	1.111	0.000127
10	N	2.595597	0.962745	-0.000128	33	H	5.712229	2.194139	-0.000831
11	C	0.71388	-2.85653	0.000159	34	H	3.795722	4.100451	-0.000695
12	C	1.446223	-4.08365	0.000341	35	H	1.011245	-5.069663	0.000277
13	C	2.787641	-3.793923	0.000457	36	H	3.611179	-4.494427	0.000583
14	C	2.935816	-2.382249	0.000292	37	H	1.547796	-0.82154	0.000062
15	N	1.657392	-1.841635	0.000088	38	H	-1.011151	-5.069674	0.000247
16	C	-0.713807	-2.856549	0.000087	39	H	-3.61114	-4.494453	-0.00059
17	C	-1.446169	-4.083679	-0.00002	40	H	-1.547714	-0.82157	-0.000085
18	C	-2.787573	-3.793979	-0.000345	41	H	-5.712265	2.19409	-0.000099
19	C	-2.935743	-2.382286	-0.000253	42	H	-3.795746	4.100383	0.000794
20	N	-1.657317	-1.841659	0.000031	43	H	4.998017	-2.494102	0.000328

21	C	-3.947866	0.783603	-0.000214		44	H	5.721257	-0.333586	-0.000204
22	C	-4.637681	2.06201	-0.000033		45	H	-5.721264	-0.33378	-0.000877
23	C	-3.670373	3.025816	0.00045		46	H	-4.997899	-2.494185	-0.000615

Table S6: Coordinates of optimized geometry of **3**:

Label	Symbol	X	Y	Z		Label	Symbol	X	Y	Z
1	C	-4.403494	1.310985	0.000007		24	N	2.741451	1.443464	-7E-06
2	C	-4.126718	-0.057968	-0.000005		25	C	2.577124	2.804757	0.000016
3	N	-2.835334	-0.557149	-0.000038		26	C	3.880668	3.36567	0.000039
4	C	-2.925621	-1.892387	-0.000009		27	C	4.80243	2.320942	0.000028
5	C	-4.313905	-2.317508	0.000037		28	C	0.149711	2.698223	-8.2E-05
6	C	-5.062321	-1.169318	0.000041		29	C	1.296287	3.441997	0.000009
7	C	-1.731082	-2.681655	-0.000008		30	H	-5.44041	1.63243	0.000054
8	N	-0.498405	-2.073796	-0.000025		31	H	-4.6717	-3.33868	0.000065
9	C	0.51412	-2.996352	-0.000006		32	H	-6.14203	-1.08711	0.00007
10	C	-0.104548	-4.266216	0.000023		33	H	-0.35794	-1.07616	-3.8E-05
11	C	-1.490535	-4.071158	0.000022		34	H	0.414276	-5.2143	0.000041
12	C	1.894056	-2.61395	-0.000003		35	H	-2.2525	-4.83784	0.000038
13	N	2.293745	-1.330427	-0.000004		36	H	5.17698	-3.05912	0.000001
14	C	3.68066	-1.364237	-0.000002		37	H	2.971388	-4.60745	0
15	C	4.141614	-2.742039	0		38	H	5.576038	-0.40764	0.00001
16	C	3.024336	-3.526876	-0.000001		39	H	-4.28085	4.357883	0.000119
17	C	4.502789	-0.240986	0.000003		40	H	-1.72775	5.190419	0.000091
18	C	-3.395316	2.305973	-0.000022		41	H	-1.86137	0.929505	-0.00011
19	C	4.073936	1.103037	0.000004		42	H	2.045767	0.699008	0.00001
20	C	-3.397995	3.732657	0.000057		43	H	4.095602	4.425563	0.000053
21	C	-2.072139	4.165676	0.000045		44	H	5.880931	2.401435	0.000035
22	C	-1.23907	3.009732	-0.000049		45	H	0.294179	1.620176	-0.00019
23	N	-2.079913	1.936469	-0.000099		46	H	1.278639	4.527973	0.000092

Table S7: Coordinates of optimized geometry of **4**:

Label	Symbol	X	Y	Z		Label	Symbol	X	Y	Z
1	C	0.806784	-3.043877	-0.000336		24	C	4.343076	-2.438044	-0.001126
2	C	0.438406	-4.422792	-0.000388		25	C	3.764328	-1.10777	-0.000454
3	C	-0.93378	-4.496766	0.000361		26	N	2.400978	-1.16597	-0.000208
4	C	-1.464015	-3.168065	0.000684		27	C	4.601099	0.034215	0.000091
5	N	-0.362973	-2.321055	0.000228		28	C	4.361786	1.393027	0.000845
6	C	-3.973022	0.584305	-0.00016		29	H	1.135472	-5.247431	-0.000876
7	C	-5.207749	-0.124883	0.000192		30	H	-1.544628	-5.38927	0.000537
8	C	-4.916456	-1.472869	0.000791		31	H	-6.184438	0.339055	-0.000006
9	C	-3.495296	-1.629068	0.000808		32	H	-5.615587	-2.298073	0.001172
10	C	-2.818903	-2.853594	0.001084		33	H	-0.550422	5.267089	-0.001425
11	C	-0.365681	2.997764	-0.000343		34	H	-3.182153	4.754968	-0.002046
12	C	-1.030959	4.299836	-0.001096		35	H	1.585757	5.078609	0.001175
13	C	-2.364393	4.045551	-0.001447		36	H	4.118871	4.201165	0.002114
14	C	-2.502987	2.601145	-0.000891		37	H	3.339351	-4.395899	-0.001709
15	N	-1.263465	1.987029	-0.000246		38	H	5.402792	-2.659586	-0.001441
16	C	1.054606	2.914724	0.000269		39	H	5.657752	-0.224618	-0.000025
17	C	1.914095	4.050984	0.000964		40	H	5.258462	2.008314	0.001336

18	C	3.216676	3.605163	0.001492	41	H	1.598733	0.812111	-0.000017
19	C	3.192919	2.184643	0.000955	42	H	-0.363322	-1.312572	0.000796
20	N	1.86813	1.799412	0.000331	43	N	-2.966318	-0.355242	0.000217
21	C	-3.740742	1.963268	-0.000789	44	H	-2.001075	-0.035155	0.000209
22	C	2.104649	-2.499129	-0.00064	45	H	-4.621708	2.597732	-0.001197
23	C	3.299561	-3.315304	-0.001258	46	H	-3.472332	-3.720455	0.001499

Table S8: Coordinates of optimized geometry of **8-*trans***:

Label	Symbol	X	Y	Z	Label	Symbol	X	Y	Z
1	C	2.782798	2.63726	-0.00108	34	H	-3.63534	2.422627	-0.00903
2	C	2.642509	4.057078	0.054295	35	H	0.316997	-5.83795	-0.08665
3	C	1.298931	4.352392	0.057504	36	H	-2.22752	-5.00789	-0.09414
4	C	0.559426	3.125389	0.000142	37	H	2.570975	-5.83642	-0.00859
5	N	1.515938	2.118437	-0.03542	38	H	5.163934	-5.12801	-0.01837
6	C	-2.29509	-0.67861	0.002646	39	H	2.847753	-1.59205	0.009348
7	C	-3.35348	0.262024	0.004982	40	H	5.507776	3.533421	0.016589
8	C	-2.94928	1.585233	0.000715	41	H	7.24436	1.469424	0.00262
9	C	-1.54286	1.754203	0.011326	42	H	7.092724	-0.93136	-0.01809
10	S	-0.75764	0.173061	0.022565	43	H	6.438059	-3.06549	-0.01868
11	C	-0.83972	2.977899	0.009913	44	C	-4.28469	-3.34899	1.101117
12	C	0.775972	-3.6071	0.00723	45	C	-5.56418	-3.91027	1.079207
13	C	-0.04116	-4.81877	-0.04465	46	C	-6.35421	-3.81468	-0.06955
14	C	-1.33513	-4.40016	-0.04625	47	C	-5.85708	-3.15387	-1.19658
15	C	-1.28977	-2.94421	0.010752	48	C	-4.57933	-2.58975	-1.17323
16	N	0.00906	-2.503	0.041494	49	C	-3.7763	-2.682	-0.02487
17	C	2.195255	-3.64437	0.004906	50	H	-3.67412	-3.42128	1.996436
18	C	2.973705	-4.8349	-0.0065	51	H	-5.94271	-4.42018	1.960584
19	C	4.302438	-4.47455	-0.01087	52	H	-7.34821	-4.25217	-0.08702
20	C	4.377479	-3.05303	-0.005	53	H	-6.46144	-3.0798	-2.09625
21	N	3.079724	-2.58342	0.006965	54	H	-4.19256	-2.084	-2.05331
22	C	-2.40228	-2.08547	-0.00058	55	C	-1.65048	4.241635	0.026141
23	C	3.9675	1.87303	-0.00572	56	C	-2.29817	4.659577	1.199214
24	C	5.285916	2.475081	0.006421	57	C	-3.05178	5.836007	1.21552
25	C	6.162281	1.433414	-0.00152	58	C	-3.17215	6.608982	0.057118
26	C	5.361429	0.218654	-0.01427	59	C	-2.53359	6.199776	-1.11672
27	N	4.029038	0.508716	-0.01859	60	C	-1.77762	5.024528	-1.13172
28	C	6.009964	-1.03933	-0.01586	61	H	-2.20234	4.062041	2.101312
29	C	5.607904	-2.3626	-0.01348	62	H	-3.54191	6.148446	2.133205
30	H	3.461156	4.760134	0.097561	63	H	-3.75906	7.522821	0.069181
31	H	0.847556	5.331882	0.106369	64	H	-2.62417	6.792924	-2.02226
32	H	1.348971	1.123893	-0.08921	65	H	-1.28531	4.706392	-2.04629
33	H	-4.39056	-0.0486	0.008193					

Table S9: Coordinates of optimized geometry of **8-*cis-1***:

Label	Symbol	X	Y	Z	Label	Symbol	X	Y	Z
1	C	-1.90274	-3.43756	-0.14224	33	H	-1.91848	5.643807	-0.41792
2	C	-1.34708	-4.73332	-0.30249	34	H	0.752894	5.397357	-0.41604

3	C	0.029917	-4.6067	-0.29767
4	C	0.3586	-3.22696	-0.13159
5	N	-0.85213	-2.55948	-0.05754
6	C	1.954552	1.289536	-0.04307
7	C	3.212144	0.689493	0.243786
8	C	3.212504	-0.68781	0.243837
9	C	1.955236	-1.28852	-0.04301
10	S	0.787366	0.00018	-0.38306
11	C	1.655121	-2.65773	-0.05532
12	C	-1.90452	3.436663	-0.14204
13	C	-1.34952	4.732685	-0.30229
14	C	0.027556	4.60671	-0.29764
15	C	0.356896	3.227131	-0.13171
16	N	-0.8535	2.559053	-0.05749
17	C	-3.25595	3.026383	-0.05838
18	C	-4.39668	3.933867	-0.06003
19	C	-5.48431	3.131059	0.07055
20	C	-4.98486	1.750941	0.132241
21	N	-3.6229	1.73269	0.056139
22	C	1.653725	2.658559	-0.05547
23	C	-3.25437	-3.02799	-0.05877
24	C	-4.39465	-3.93606	-0.06094
25	C	-5.48271	-3.13384	0.069573
26	C	-4.98396	-1.75347	0.131779
27	N	-3.62201	-1.73452	0.056099
28	C	-5.91156	-0.70153	0.235173
29	C	-5.9119	0.698483	0.235412
30	H	0.755615	-5.39703	-0.41602
31	H	4.08323	1.286661	0.480905
32	H	4.083921	-1.28452	0.480889

35	H	-4.36411	5.012324	-0.14011
36	H	-6.52689	3.421095	0.113632
37	H	-4.36155	-5.01448	-0.14136
38	H	-6.52516	-3.42439	0.112277
39	H	-6.92503	-1.09392	0.30833
40	H	-6.92556	1.090346	0.308788
41	C	2.946482	4.457185	1.156222
42	C	4.020299	5.346123	1.244967
43	C	4.965953	5.41089	0.217719
44	C	4.832315	4.579589	-0.89808
45	C	3.761604	3.686861	-0.98384
46	C	2.80343	3.615394	0.040813
47	H	2.2158	4.406319	1.95808
48	H	4.118626	5.985286	2.117763
49	H	5.799675	6.103637	0.28591
50	H	5.559023	4.627307	-1.70406
51	H	3.656483	3.045804	-1.85431
52	C	2.805303	-3.61396	0.041047
53	C	2.948742	-4.45554	1.156593
54	C	4.022977	-5.34395	1.245484
55	C	4.968684	-5.40841	0.218258
56	C	4.83466	-4.57734	-0.89766
57	C	3.763521	-3.68514	-0.98358
58	H	2.218046	-4.4049	1.958448
59	H	4.121608	-5.98295	2.118368
60	H	5.802733	-6.10075	0.286528
61	H	5.561404	-4.62483	-1.70362
62	H	3.658074	-3.04427	-1.85415
63	H	-1.01111	1.577446	0.129126
64	H	-1.01017	-1.578	0.129426
65	H	-1.9156	-5.64471	-0.41819

Table S10: Coordinates of optimized geometry of **8-*cis*-2**:

Label	Symbol	X	Y	Z
1	C	-0.97388	-3.45446	-0.05094
2	C	-0.24173	-4.73058	0.000627
3	C	1.07851	-4.41903	0.021242
4	C	1.143842	-2.9612	-0.02911
5	N	-0.10689	-2.41815	-0.0723
6	C	1.668064	1.687299	-0.02712
7	C	3.067243	1.448491	0.031749
8	C	3.404448	0.109799	0.032717
9	C	2.297768	-0.78014	-0.00469
10	S	0.806506	0.144162	-0.0884
11	C	2.321641	-2.18573	0.000663
12	C	-2.62213	2.693501	0.001915
13	C	-2.44434	4.098256	-0.12145
14	C	-1.08876	4.359197	-0.137

34	H	-3.24118	4.821377	-0.21117
35	H	-0.61613	5.323861	-0.24247
36	H	-5.27356	3.711141	0.08095
37	H	-7.16482	1.799109	0.126668
38	H	-3.41545	-0.14385	0.008282
39	H	-2.77172	-5.64719	-0.0991
40	H	-5.35191	-4.91028	-0.05881
41	H	-6.56721	-2.84996	0.028189
42	H	-7.20808	-0.68665	0.097988
43	C	1.919607	5.013059	1.079225
44	C	2.714125	6.162171	1.06673
45	C	3.463044	6.486178	-0.068
46	C	3.414511	5.653121	-1.18924
47	C	2.623336	4.501853	-1.17494

15	C	-0.38501	3.125916	-0.02089
16	N	-1.36739	2.141111	0.057901
17	C	-3.85575	2.000583	0.038312
18	C	-5.12264	2.641835	0.070134
19	C	-6.09259	1.66354	0.097198
20	C	-5.4447	0.399537	0.077425
21	N	-4.08407	0.635858	0.048555
22	C	1.016833	2.931958	-0.02723
23	C	-2.39371	-3.40583	-0.05079
24	C	-3.16864	-4.64357	-0.06984
25	C	-4.4743	-4.27637	-0.05153
26	C	-4.48571	-2.82266	-0.01661
27	N	-3.21952	-2.31321	-0.02174
28	C	-5.73202	-2.15289	0.02764
29	C	-6.13052	-0.83052	0.070724
30	H	-0.67237	-5.72048	0.035166
31	H	1.920293	-5.09466	0.076691
32	H	3.793108	2.250587	0.077612
33	H	4.42381	-0.2535	0.065632
48	C	1.864712	4.168529	-0.04126
49	H	1.342769	4.761239	1.964451
50	H	2.749516	6.80132	1.944354
51	H	4.079751	7.380156	-0.07825
52	H	3.990191	5.899227	-2.07692
53	H	2.583179	3.858594	-2.04922
54	C	3.649914	-2.87444	0.052484
55	C	4.442546	-2.82374	1.210814
56	C	5.677403	-3.4752	1.259293
57	C	6.141259	-4.18543	0.148355
58	C	5.361476	-4.24115	-1.01008
59	C	4.125533	-3.59124	-1.05747
60	H	4.080012	-2.2818	2.079626
61	H	6.273443	-3.43151	2.166479
62	H	7.101159	-4.69231	0.185769
63	H	5.714397	-4.78922	-1.8791
64	H	3.523415	-3.63298	-1.96044
65	H	-1.18798	1.15797	0.210808

Table S11: Coordinates of optimized geometry of **8-*cis3:***

Label	Symbol	X	Y	Z
1	C	1.797309	-3.40845	-0.0417
2	C	1.28586	-4.77294	-0.1068
3	C	-0.06858	-4.66166	-0.04325
4	C	-0.35901	-3.23238	0.051544
5	N	0.812874	-2.50774	0.060127
6	C	-1.90108	1.263915	-0.03262
7	C	-3.1905	0.692872	-0.02405
8	C	-3.19058	-0.69247	0.024544
9	C	-1.90124	-1.26369	0.032851
10	S	-0.67142	0.000036	0.000159
11	C	-1.63417	-2.66223	0.054739
12	C	1.797733	3.408248	0.041565
13	C	1.286444	4.772809	0.106545
14	C	-0.06801	4.661672	0.043071
15	C	-0.35861	3.232416	-0.05156
16	N	0.81319	2.507641	-0.06014
17	C	3.176868	3.062653	0.104181
18	C	4.289495	3.901206	0.312255
19	C	5.423967	3.100116	0.316891
20	C	5.031219	1.75436	0.113083
21	N	3.654	1.771802	-0.00477
22	C	-1.63384	2.662422	-0.05465
23	C	3.176484	-3.06301	-0.10434
24	C	4.289001	-3.90169	-0.31249
25	C	5.423575	-3.10075	-0.31709
26	C	5.030999	-1.75495	-0.11321
34	H	1.87435	5.67696	0.191728
35	H	-0.79917	5.456824	0.076235
36	H	4.244591	4.970843	0.456514
37	H	6.448017	3.415853	0.461896
38	H	3.045714	1.011929	-0.2707
39	H	4.243963	-4.97132	-0.45681
40	H	6.447581	-3.41661	-0.46214
41	H	6.977573	-1.09301	-0.10824
42	H	6.97771	1.092179	0.10811
43	C	-3.15776	4.295987	-1.22213
44	C	-4.2497	5.168359	-1.22897
45	C	-5.01179	5.348982	-0.07183
46	C	-4.67713	4.650224	1.091883
47	C	-3.58891	3.774407	1.096881
48	C	-2.81434	3.589122	-0.05939
49	H	-2.56678	4.156516	-2.12272
50	H	-4.50298	5.705657	-2.13852
51	H	-5.85905	6.028615	-0.07619
52	H	-5.26093	4.787957	1.997619
53	H	-3.32833	3.236749	2.004088
54	C	-2.81478	-3.58879	0.059465
55	C	-3.58963	-3.77367	-1.09669
56	C	-4.67794	-4.64937	-1.09171
57	C	-5.01243	-5.34841	0.07188
58	C	-4.25007	-5.1682	1.228902
59	C	-3.15803	-4.29595	1.222081

27	N	3.653781	-1.77223	0.004679
28	C	5.970164	-0.6868	-0.05479
29	C	5.97025	0.686086	0.054673
30	H	1.873659	-5.67715	-0.19211
31	H	-0.79983	-5.45672	-0.07647
32	H	-4.09116	1.292316	-0.05049
33	H	-4.09132	-1.2918	0.051109

60	H	-3.32918	-3.23579	-2.00381
61	H	-5.26194	-4.78678	-1.99736
62	H	-5.85977	-6.02795	0.076228
63	H	-4.50322	-5.70573	2.138361
64	H	-2.56685	-4.1568	2.122585
65	H	3.045598	-1.01229	0.270668

Table S12: Coordinates of optimized geometry of **8-H**:

Label	Symbol	X	Y	Z
1	C	2.023189	3.134978	-0.24962
2	C	1.582682	4.468373	-0.52217
3	C	0.209588	4.48213	-0.4769
4	C	-0.24855	3.15724	-0.18093
5	N	0.896043	2.376824	-0.07324
6	C	-2.10895	-1.18485	-0.01585
7	C	-3.28108	-0.54331	0.445041
8	C	-3.2101	0.840881	0.459057
9	C	-1.97861	1.368288	0.008206
10	S	-0.94678	0.0421	-0.51996
11	C	-1.58267	2.725124	-0.03844
12	C	1.708488	-3.30629	-0.18216
13	C	1.165538	-4.59163	-0.47816
14	C	-0.20706	-4.48431	-0.48397
15	C	-0.55799	-3.13098	-0.19426
16	N	0.647202	-2.45006	-0.04467
17	C	3.078777	-2.99256	-0.04111
18	C	4.108671	-3.9724	0.039329
19	C	5.300296	-3.31653	0.238539
20	C	5.037019	-1.9167	0.261957
21	N	3.67643	-1.7528	0.100298
22	C	-1.84827	-2.57313	-0.07366
23	C	3.354951	2.678255	-0.15169
24	C	4.4775	3.599127	-0.20449
25	C	5.585281	2.838627	-0.00531
26	C	5.124405	1.4647	0.138464
27	N	3.761767	1.387803	0.048086
28	C	6.07949	0.439341	0.330232
29	C	6.045796	-0.94364	0.390783
30	H	2.229408	5.304426	-0.74228
31	H	-0.43859	5.324743	-0.66432
32	H	0.928685	1.42138	0.252659
33	H	-4.13599	-1.10148	0.804663

Label	Symbol	X	Y	Z
34	H	-4.00397	1.476609	0.829209
35	H	1.744072	-5.47854	-0.6891
36	H	-0.91652	-5.26728	-0.70469
37	H	3.952992	-5.03932	-0.01849
38	H	6.281899	-3.75388	0.353778
39	H	3.258839	-0.82244	0.029533
40	H	4.421531	4.668118	-0.35331
41	H	6.61889	3.156888	0.034891
42	H	7.08604	0.83913	0.424576
43	H	7.020759	-1.4025	0.532833
44	C	-3.04038	-4.51321	1.006543
45	C	-4.131	-5.38023	1.094869
46	C	-5.19819	-5.26087	0.19942
47	C	-5.17287	-4.26509	-0.78243
48	C	-4.08906	-3.39001	-0.86601
49	C	-3.0061	-3.50653	0.024617
50	H	-2.22078	-4.60217	1.712837
51	H	-4.14802	-6.14524	1.865193
52	H	-6.04399	-5.93833	0.266649
53	H	-5.99493	-4.17117	-1.48545
54	H	-4.06891	-2.62497	-1.6362
55	C	-2.64349	3.766241	0.090801
56	C	-2.57138	4.743303	1.099814
57	C	-3.567	5.714978	1.218724
58	C	-4.64443	5.729705	0.327923
59	C	-4.72496	4.763606	-0.68021
60	C	-3.73601	3.785435	-0.79522
61	H	-1.74324	4.730074	1.801821
62	H	-3.50199	6.457068	2.008686
63	H	-5.41629	6.487921	0.418592
64	H	-5.55527	4.773069	-1.37985
65	H	-3.79767	3.0444	-1.58651
66	H	0.720112	-1.51096	0.319693

Table S13: Coordinates of optimized geometry of **8-Ha**:

Label	Symbol	X	Y	Z
1	C	-2.38636	3.033951	-0.02841
2	C	-2.05354	4.408123	-0.21189
3	C	-0.68486	4.526709	-0.1315

Label	Symbol	X	Y	Z
34	H	3.905346	1.911199	0.215678
35	H	-0.98989	-5.82348	0.219221
36	H	1.623902	-5.25006	0.047041

4	C	-0.12487	3.229022	0.092654	37	H	-3.31448	-5.48477	0.673394
5	N	-1.20943	2.361843	0.171423	38	H	-5.76083	-4.37403	0.714559
6	C	2.15185	-0.96031	-0.03628	39	H	-2.93974	-1.43628	-0.41248
7	C	3.327919	-0.18054	0.045147	40	H	-4.94947	4.145605	-0.75183
8	C	3.109502	1.184392	0.121529	41	H	-6.90539	2.30729	-0.8056
9	C	1.745226	1.552321	0.070258	42	H	-7.13883	-0.08056	-0.1962
10	S	0.749959	0.096338	-0.06603	43	H	-6.7393	-2.22613	0.19305
11	C	1.237234	2.873871	0.100689	44	C	3.806707	-3.77328	-1.26773
12	C	-1.22561	-3.56501	0.045311	45	C	5.010391	-4.48321	-1.28829
13	C	-0.53107	-4.85008	0.114947	46	C	5.798365	-4.56303	-0.13651
14	C	0.792149	-4.56095	0.022663	47	C	5.378555	-3.92781	1.036345
15	C	0.887426	-3.10515	-0.08559	48	C	4.178634	-3.21227	1.056972
16	N	-0.36642	-2.53897	-0.08762	49	C	3.380295	-3.13016	-0.09503
17	C	-2.63501	-3.43567	0.148153	50	H	3.197222	-3.712	-2.16461
18	C	-3.56566	-4.45516	0.46621	51	H	5.329662	-4.97304	-2.20339
19	C	-4.82333	-3.8841	0.491204	52	H	6.732008	-5.11726	-0.15199
20	C	-4.69981	-2.50024	0.187719	53	H	5.982455	-3.99024	1.936736
21	N	-3.349	-2.26137	0.001934	54	H	3.853932	-2.72588	1.972318
22	C	2.084422	-2.37579	-0.08227	55	C	2.22078	4.003078	0.104937
23	C	-3.66822	2.44744	-0.11683	56	C	3.062247	4.224796	-0.99818
24	C	-4.8647	3.098825	-0.4992	57	C	3.967742	5.287918	-0.99353
25	C	-5.87121	2.151553	-0.53271	58	C	4.051731	6.13532	0.115758
26	C	-5.31995	0.892926	-0.17794	59	C	3.221594	5.918366	1.219327
27	N	-3.97087	1.1027	0.052255	60	C	2.307356	4.862059	1.212944
28	C	-6.07928	-0.29883	-0.09181	61	H	2.995724	3.573776	-1.86481
29	C	-5.82618	-1.64395	0.100872	62	H	4.604944	5.454384	-1.85682
30	H	-2.76282	5.200456	-0.39961	63	H	4.75895	6.959177	0.119341
31	H	-0.10585	5.428657	-0.25822	64	H	3.283842	6.569731	2.085822
32	H	-1.13626	1.380004	0.39356	65	H	1.66628	4.694691	2.073442
33	H	4.311709	-0.63054	0.05814	66	H	-3.39527	0.457675	0.574147

Table S14: Coordinates of optimized geometry of **9**:

Label	Symbol	X	Y	Z	Label	Symbol	X	Y	Z
1	Pd	-2.367	-0.00041	0.831746	35	N	-3.15148	-1.5327	-0.38442
2	Cl	-1.57421	-1.6476	2.322792	36	N	-0.18762	-2.40876	-0.36861
3	S	1.471644	0.000194	-0.53787	37	H	-0.3326	-1.7632	0.41242
4	N	-3.1522	1.531341	-0.38457	38	C	3.37185	-3.6428	-0.09563
5	N	-0.18871	2.408498	-0.36929	39	C	-4.50997	-1.66265	-0.47146
6	H	-0.33328	1.762639	0.411567	40	C	-1.25379	-3.11024	-0.86376
7	C	3.370237	3.64413	-0.09613	41	C	2.274587	-2.64675	-0.20365
8	C	-4.51076	1.660736	-0.47139	42	C	3.711807	-0.69167	0.574361
9	C	-1.25523	3.109712	-0.86402	43	H	4.506712	-1.29173	0.999008
10	C	2.273408	2.647594	-0.20431	44	C	-2.61416	-2.72903	-0.79722
11	C	3.711506	0.693341	0.574157	45	C	-4.84648	-2.986	-0.93116
12	H	4.506143	1.293892	0.99862	46	H	-5.85344	-3.34625	-1.0938
13	C	-2.61544	2.727958	-0.79729	47	C	0.989418	-3.11604	-0.55578
14	C	-4.84789	2.984001	-0.93087	48	C	5.623295	-4.38855	-0.64463
15	H	-5.85502	3.343849	-1.09332	49	H	6.565486	-4.22013	-1.15828

16	C	0.988031	3.116312	-0.5564		50	C	4.209061	-5.76998	0.742356
17	C	5.62156	4.39079	-0.64435		51	H	4.052705	-6.67083	1.328607
18	H	6.563922	4.222905	-1.15777		52	C	4.606473	-3.44047	-0.74033
19	C	4.206507	5.77132	0.742692		53	H	4.754377	-2.54546	-1.33641
20	H	4.049799	6.671694	1.329418		54	C	-3.67113	-3.63399	-1.16999
21	C	4.605073	3.442384	-0.74061		55	H	-3.53452	-4.63836	-1.54413
22	H	4.753398	2.547712	-1.33701		56	C	-5.51546	-0.69173	-0.25921
23	C	-3.67284	3.632523	-1.16978		57	H	-6.50812	-1.13388	-0.21028
24	H	-3.53671	4.637001	-1.54382		58	C	-0.72751	-4.30462	-1.44713
25	C	-5.51579	0.689348	-0.25915		59	H	-1.30448	-5.04111	-1.98657
26	H	-6.50866	1.131001	-0.21013		60	C	0.634455	-4.31564	-1.24525
27	C	-0.72952	4.304452	-1.44714		61	H	1.341158	-5.05185	-1.59869
28	H	-1.30688	5.040897	-1.9862		62	C	2.557262	-1.2739	0.000455
29	C	0.632477	4.315943	-1.2455		63	C	5.42889	-5.55604	0.09742
30	H	1.338818	5.052568	-1.59878		64	C	3.189092	-4.82449	0.646641
31	C	2.556716	1.274903	0.000052		65	H	2.249176	-4.98428	1.165338
32	C	5.426588	5.557942	0.098059		66	Cl	-1.57506	1.647428	2.322519
33	C	3.186881	4.82552	0.646434		67	H	6.220293	6.295401	0.173447
34	H	2.246823	4.984751	1.164966		68	H	6.222825	-6.2933	0.172342

Table S15: Coordinates of optimized geometry of **9'**:

Label	Symbol	X	Y	Z		Label	Symbol	X	Y	Z
1	Pd	-1.77204	0.533115	0.855049		35	N	0.454775	-2.67124	-0.351
2	Cl	0.034982	0.769378	2.324775		36	H	0.118788	-1.81701	0.082928
3	S	1.332443	0.184743	-0.85831		37	C	4.242678	-2.67057	-0.16246
4	N	-3.46846	0.555515	-0.44723		38	C	-3.87629	-3.19614	-0.2655
5	N	-1.13172	2.039114	-0.54258		39	C	-0.32207	-3.77401	-0.59849
6	C	1.952547	4.200092	-0.1622		40	C	2.881288	-2.09021	-0.31727
7	C	-4.76925	0.128438	-0.45731		41	C	3.653341	0.232034	0.311011
8	C	-2.27244	2.542409	-1.09536		42	H	4.582088	-0.09119	0.76335
9	C	1.204905	2.927131	-0.357		43	C	-1.73167	-3.82543	-0.54553
10	C	3.206707	1.53921	0.317168		44	C	-3.85276	-4.59975	-0.49812
11	H	3.746008	2.359361	0.772239		45	H	-4.73236	-5.22686	-0.53914
12	C	-3.46375	1.798114	-1.04307		46	C	1.803441	-2.9841	-0.48776
13	C	-5.59555	1.153503	-1.05672		47	C	6.589287	-2.74631	-0.80432
14	H	-6.66343	1.064008	-1.20827		48	H	7.402301	-2.37883	-1.42372
15	C	-0.17056	3.020121	-0.65836		49	C	5.766241	-4.23822	0.907706
16	C	3.815984	5.674153	-0.68681		50	H	5.940208	-5.02215	1.63897
17	H	4.719723	5.874983	-1.25507		51	C	5.314547	-2.20043	-0.94335
18	C	2.166747	6.358068	0.940898		52	H	5.135256	-1.41646	-1.67242
19	H	1.793064	7.083737	1.657377		53	C	-2.54096	-4.98329	-0.68568
20	C	3.133572	4.473539	-0.87561		54	H	-2.17281	-5.97777	-0.89184
21	H	3.501767	3.746435	-1.59301		55	C	-5.05419	-2.44268	-0.05744
22	C	-4.77712	2.176115	-1.45316		56	H	-5.91016	-3.09645	0.093738
23	H	-5.04819	3.092487	-1.95872		57	C	0.561004	-4.83819	-0.93216
24	C	-5.39389	-1.10707	-0.12271		58	H	0.25119	-5.83234	-1.2191
25	H	-6.46878	-0.96273	-0.03059		59	C	1.850751	-4.36032	-0.85948
26	C	-2.05624	3.870024	-1.60196		60	H	2.758092	-4.89886	-1.08724

27	H	-2.78542	4.48083	-2.11591	61	C	2.740838	-0.68281	-0.26344
28	C	-0.76257	4.18109	-1.30191	62	C	6.819535	-3.76668	0.121434
29	H	-0.22368	5.081237	-1.55937	63	C	4.488999	-3.69721	0.767467
30	C	1.923997	1.71515	-0.24998	64	H	3.677232	-4.05077	1.395074
31	C	3.335487	6.619396	0.222922	65	Cl	-2.74493	-0.97455	2.351427
32	C	1.478297	5.160691	0.749268	66	H	3.870089	7.553096	0.371795
33	H	0.58123	4.947054	1.321636	67	H	7.81392	-4.18937	0.231232
34	N	-2.57758	-2.76123	-0.32492	68	H	-2.30683	-1.84401	0.023095

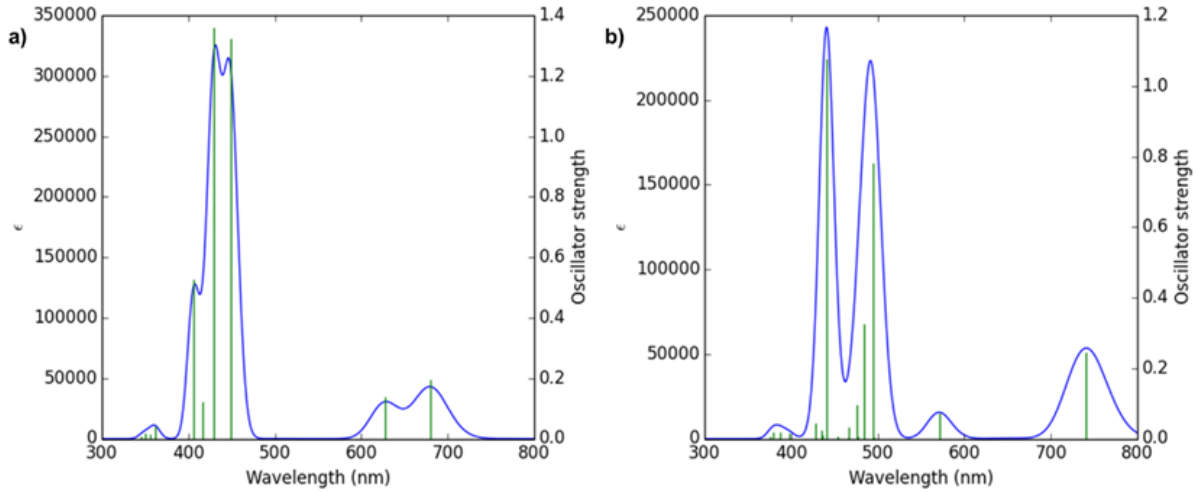


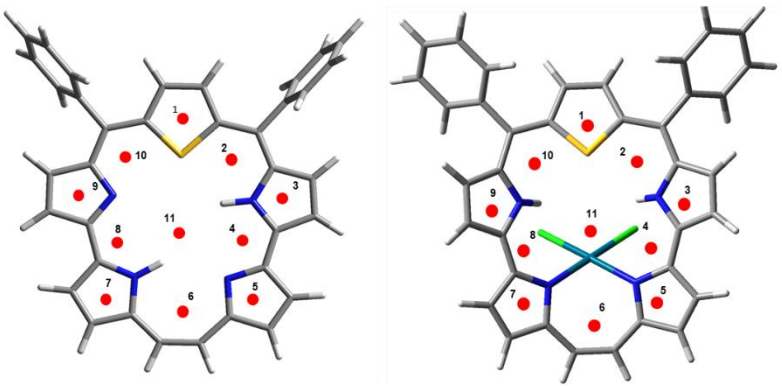
Figure S21: Calculated absorption spectra of a) sapphycene **8** and b) its Pd(II)-complex **9** in chloroform.

Table S16: Calculated electronic transition of **8** in chloroform.

Sl. No	Wavelength(nm)	Oscillator strength	Electronic transition
1	406	0.528	H-3 → LUMO (81%), H-1 → L+1 (11%)
2	429	1.360	H-1 → L+1 (68%), HOMO → LUMO (15%)
3	448	1.324	HOMO → L+1 (67%), H-1 → LUMO (26%)
4	627	0.1379	H-1 → LUMO (57%), HOMO → L+1 (21%)
5	679	0.196	HOMO → LUMO (63%), H-1 → LUMO (15%), H-1 → L+1 (15%)

Table S17: Calculated electronic transition of **9** in chloroform.

Sl. No	Wavelength(nm)	Oscillator strength	Electronic transition
1	441	1.078	H-1 → L+1 (44%), H-1 → L+2 (37%)
2	484	0.326	H-1 → L+1 (32%), H-1 → L+2 (57%)
3	494	0.782	H-1 → LUMO (26%), HOMO → L+1 (40%), HOMO → L+2 (20%)
4	740	0.246	HOMO → LUMO (82%)



Positions	NICS(0) for **8**	NICS(0) for **9**
1	-20.4	-19.2
2	-22.7	-22.2
3	-13.5	-13.9
4	-29.6	-29.1
5	-2.9	-7.2
6	-21.5	-20.5
7	-14.7	-7.2
8	-29.7	-29.1
9	-0.8	-13.9
10	-21.9	-22.2
11	-13.6	-10.1

Compounds	NICS(0)	$NICS_{zz}(1)$	HOMA
8	-13.6	-12.7	0.738
9	-10.1	-11.9	0.669

Figure S22. NICS(0), $NICS_{zz}(1)$ and HOMA indices of **8** and **9** calculated from optimized geometries.

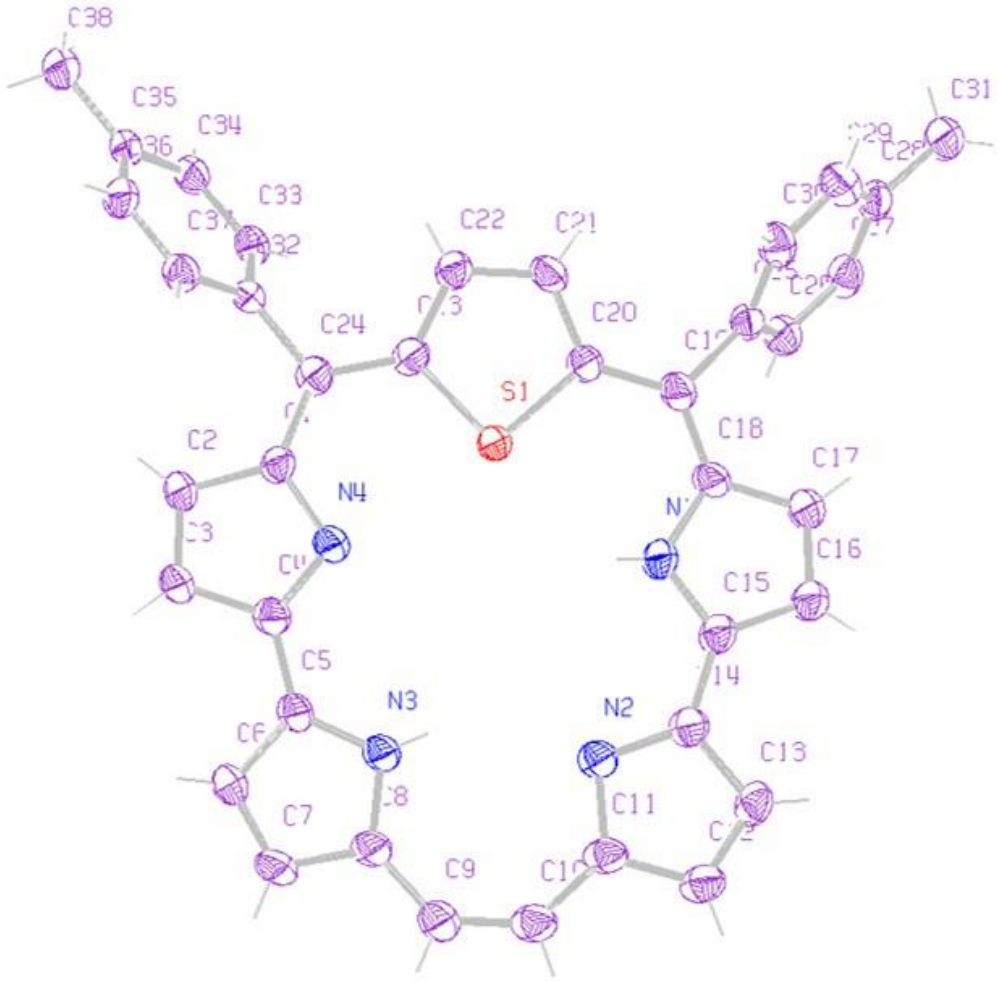


Figure S23: ORTEP diagram (with 40% thermal ellipsoid) of **8.**

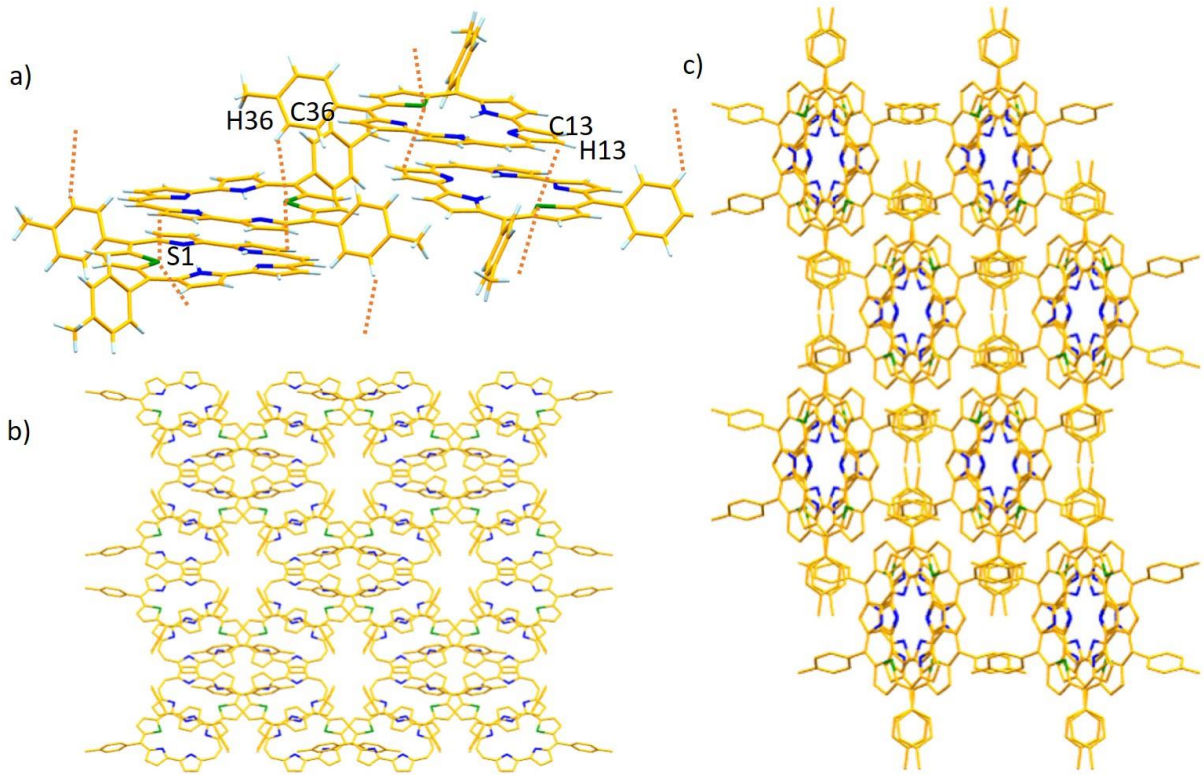


Figure S24: packing diagram of **8:** a) showing alignment of π-stacked planes, b) along *a*-axis, c) along *c*-axis (hydrogens are removed for clarity)**.**

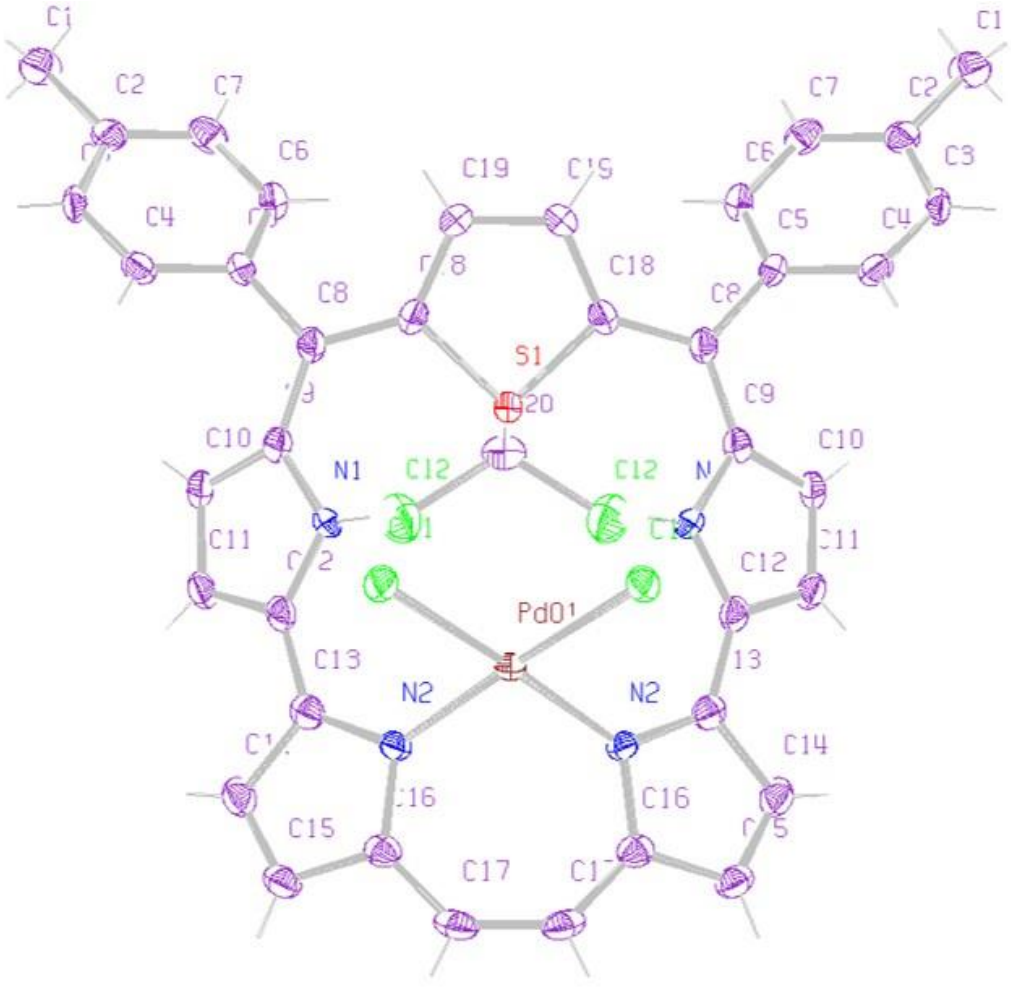


Figure S25: ORTEP diagram (with 40% thermal ellipsoid) of **9.**

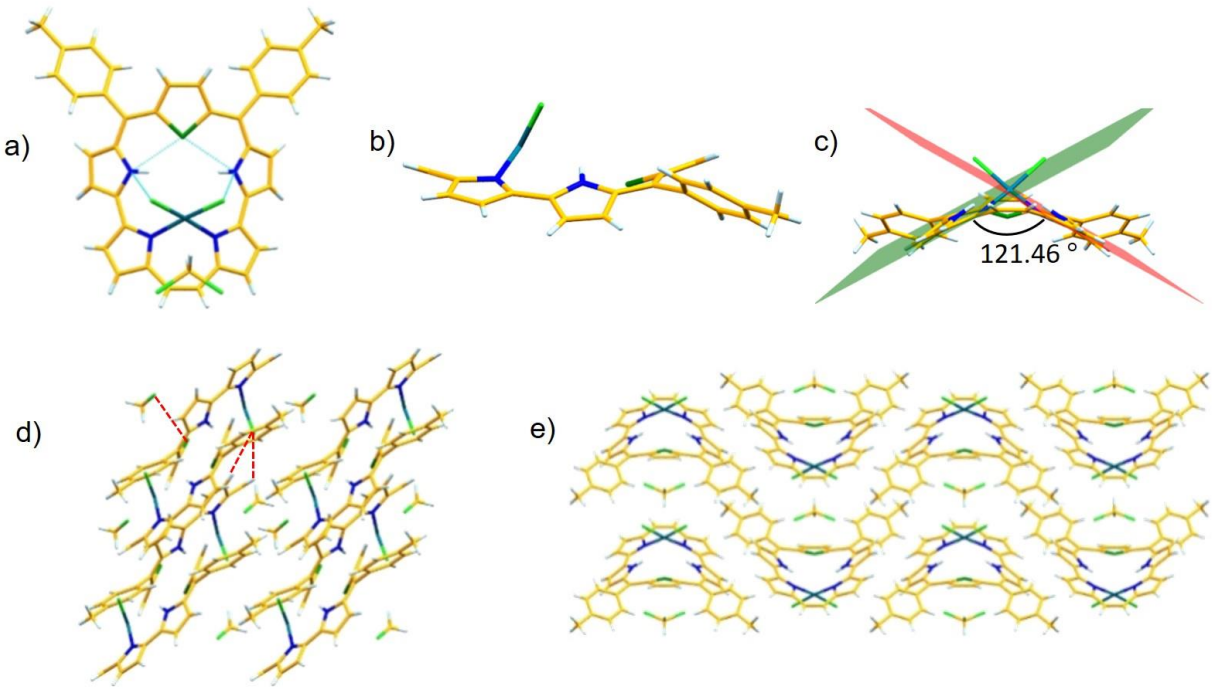


Figure S26: crystal structure of 9: a) front view b) side view c) side view showing dihedral planes of bipyrroles and d) packing diagram along *b*-axis e) packing diagram along *a*-axis.

Table S18: Crystal data and structure refinement parameters for sapphycene **8:**

Empirical formula	$C_{38}H_{28}N_4S$
Formula weight	572.2
Temperature	109(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, I 2/a
Unit cell dimensions	alpha = 90 deg. a = 12.4940(3) Å beta = 91.562(2) deg. b = 22.0708(8) Å gamma = 90 deg. c = 20.4806(8) Å
Volume	5645.5(3) $Å^{-3}$
Z, Calculated density	8, 1.348 Mg/m^3
Absorption coefficient	0.151 mm^{-1}
F(000)	3150
Crystal size	0.14 x 0.12 x 0.08 mm
Theta range for data collection	1.874 to 25.999 deg.
Limiting indices	$-15 \le h \le 15, -27 \le k \le 27, -24 \le l \le 25$
Reflections collected / unique	24633 / 5472 [R(int) = 0.1331]
Completeness to theta = 25.242	98.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5472 / 12 / 398
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0723, wR2 = 0.1720
R indices (all data)	R1 = 0.1337, wR2 = 0.2162
Extinction coefficient	n/a
Largest diff. peak and hole	0.663 and -0.802 $e.Å^{-3}$

Table S19: Crystal data and structure refinement data for Pd(II)sapphycene **9**:

Empirical formula	$C_{39}H_{30}Cl_4N_4PdS$
Formula weight	834.93
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/m
Unit cell dimensions	alpha = 90 deg. a = 7.9019(2) Å

	beta = 102.071(3) deg. b = 22.3765(6) Å gamma = 90 deg. c = 9.7921(4) Å
Volume	1693.13(9) $Å^3$
Z, Calculated density	2, 1.638 mg/m^3
Absorption coefficient	0.963 mm^{-1}
F(000)	844
Crystal size	0.200 x 0.150 x 0.100 mm
Theta range for data collection	2.313 to 25.026 deg.
Limiting indices	$-9 \leq h \leq 9$, $-26 \leq k \leq 26$, $-11 \leq l \leq 11$
Reflections collected / unique	10880 / 3009 [R(int) = 0.0686]
Completeness to theta = 25.026	97.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3009 / 0 / 227
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.1044
R indices (all data)	R1 = 0.0548, wR2 = 0.1124
Extinction coefficient	n/a
Largest diff. peak and hole	1.0158 and -1.000 e. $Å^{-3}$

References:

[1] CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.
[2] a) SHELXL -Version 2014/7; Program for the Solution and Refine-ment of Crystal Structures, University of Göttingen, Germany, 1993-2014; b) Sheldrick, G. M. A short history of SHELX. *Acta Cryst.* 2008, A64, 112.
[3] a) J. Ostapko, K. Nawara, M. Kijak, J. Buczyńska, B. Leśniewska, M. Pietrzak, G. Orzanowska, J. Waluk, *Chem. Eur. J*. **2016**, *22*, 17311; b) Eun-K. Sim, S.-D. Jeong, D.-W. Yoon, S.-J. Hong, Y. Kang, C.-H. Lee, *Org. Lett.*, 2006, **8**, 3355.
[4] Gaussian 09, (Revision C.01), M. J. Frisch et al. Gaussian, Inc., Wallingford CT, 2010.
[5] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.,* 1996,**118**, 6317.
[6] T. M. Krygowski, M. Cryański, *Tetrahedron,* 1996, **52**, 1713.
[7] T. M. Krygowski, M. Cryański, *Tetrahedron,* 1996, **52**, 10255.
[8] T. M. Krygowski, M. Cryański, *Chem. Rev.,* 2001, **101**, 1385.