

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

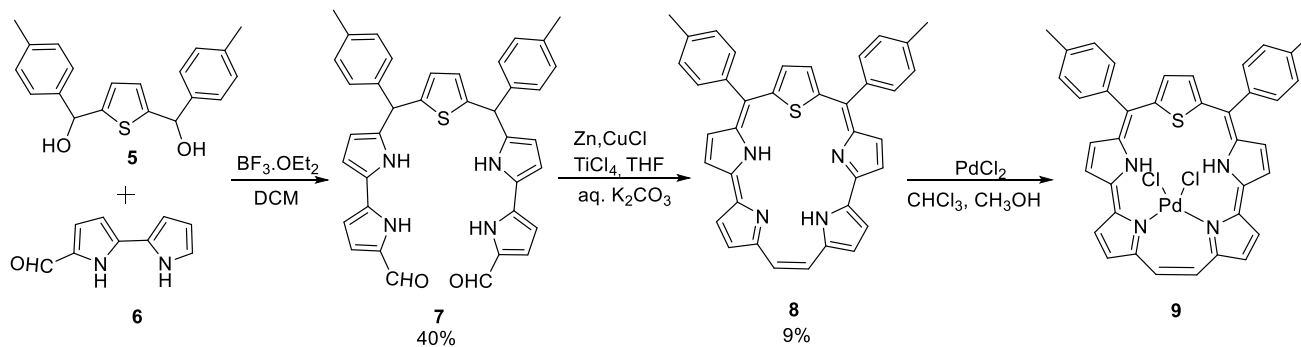
1	Instrumentation and reagents	2
2	Experimental procedures	3
3	¹ H NMR and ¹³ C NMR spectra	4-7
4	HRMS data	8-10
5	Comparative NMR spectra	11
6	UV-vis absorption spectral analysis	12-14
7	Emission spectrum	14
8	Computational studies	14-27
	8.1. Optimized energies of tautomers	16
	8.2. Frontier molecular orbital diagrams	17
	8.3. Energies of mode of protonation of 8	17-18
	8.4. Energies of Pd mode of binding	18
	8.5. Coordinates of optimized geometries of 1,2,3,4, 8 , its tautomers, 8-H and 9	19-27
	8.6. Absorption spectra	28
	8.7. NICS and HOMA calculations	28
9	Crystal structure and packing diagrams of 8 and 9	27-28
10	Crystallographic parameters	28-29
11	References	29

Instrumentation and reagents:

NMR spectra were recorded on a Bruker Ascend-500 and Bruker Avance-500 MHz FT NMR spectrometer using tetramethylsilane (TMS, $\delta = 0$) 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 were 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-K α ($\lambda = 0.71073 \text{ \AA}$) 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.⁵³

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 CH₂Cl₂ (300 mL). The solution was bubbled with N₂ for 20 min and then BF₃·OEt₂ (60 μL) was added to it. The mixture was stirred at room temperature in dark under N₂ atmosphere for 6 h. Then the reaction mixture was washed with water and organic layer was dried over anhydrous Na₂SO₄ 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. ¹H NMR (500 MHz, DMSO-D₆) 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); ¹³C NMR (125 MHz, DMSO-D₆) 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 C₃₈H₃₂N₄SO₂ (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 TiCl₄ (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** (100 mg, 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 K₂CO₃ solution. It was kept for open air oxidation overnight and then the reaction mixture was filtered using celite. The filtrate was washed with water and the organic layer was dried over anhydrous Na₂SO₄ 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. ¹H NMR (500 MHz, CDCl₃) δ in ppm: 10.38 (s, 2H), 10.36 (d, J = 4.17 Hz, 2H), 10.19 (d, J = 4.61 Hz, 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); ¹³C NMR (125 MHz, CDCl₃) 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 CHCl₃ (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 C₃₈H₂₈N₄S (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 N₂ atmosphere and dissolved in 5 mL chloroform and methanol (1 mL) was added to it and then PdCl₂ (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. ¹H NMR (500 MHz, CD₂Cl₂) 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); ¹³C NMR (125 MHz, CD₂Cl₂) 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 CHCl₃ (λ_{max} nm, log ε): 491 (5.13), 623 (4.12), 667 (3.96), 804 (4.27); HRMS (ESI+): m/z calculated for C₃₈H₂₈ClN₄PdS (M-Cl⁻): 713.0757; found: 713.0754; IR (ν in cm⁻¹): 2959, 2918, 2851, 1588.

Results and Discussion

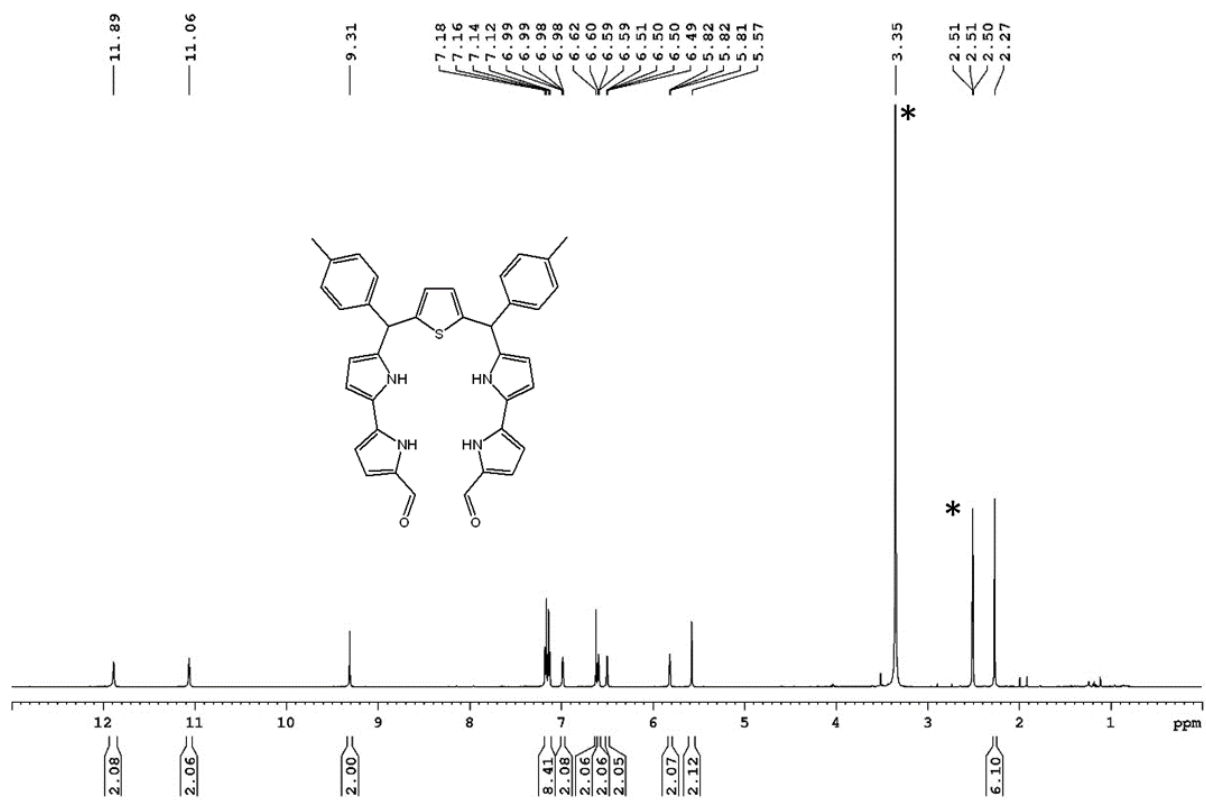


Figure S1: ¹H NMR spectrum of 7 in DMSO-*d*₆ (*water and residual protons of solvent).

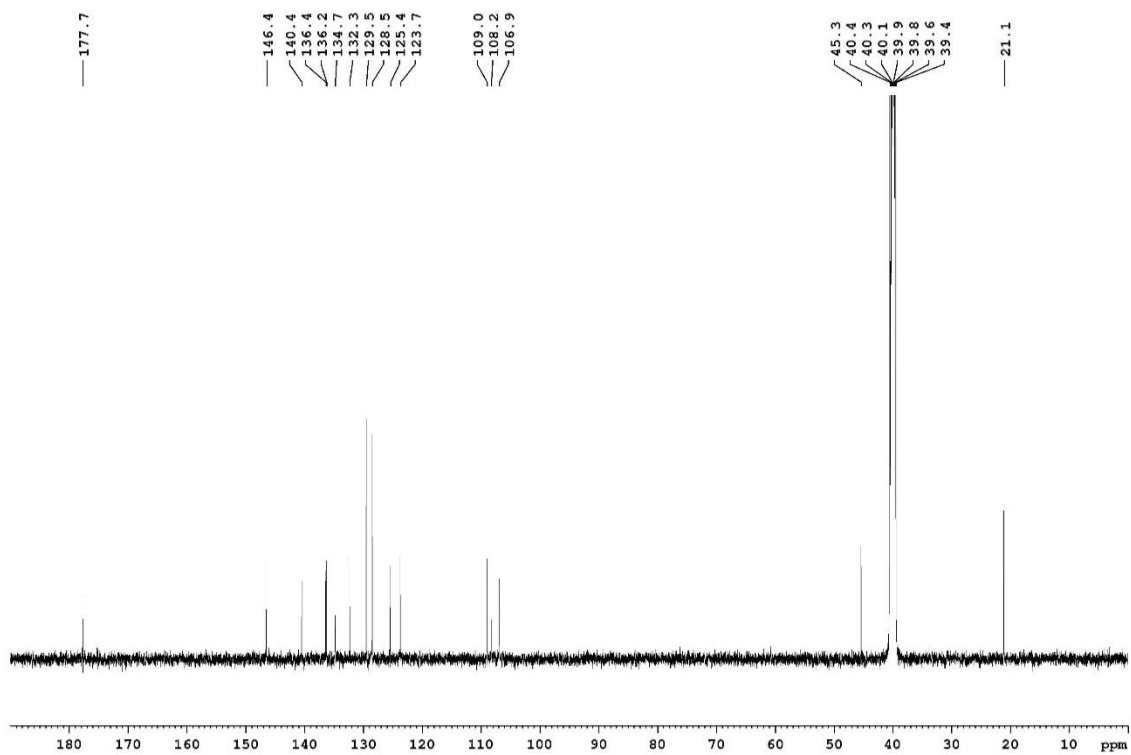


Figure S2: ¹³C NMR spectrum of 7 in DMSO-*D*₆.

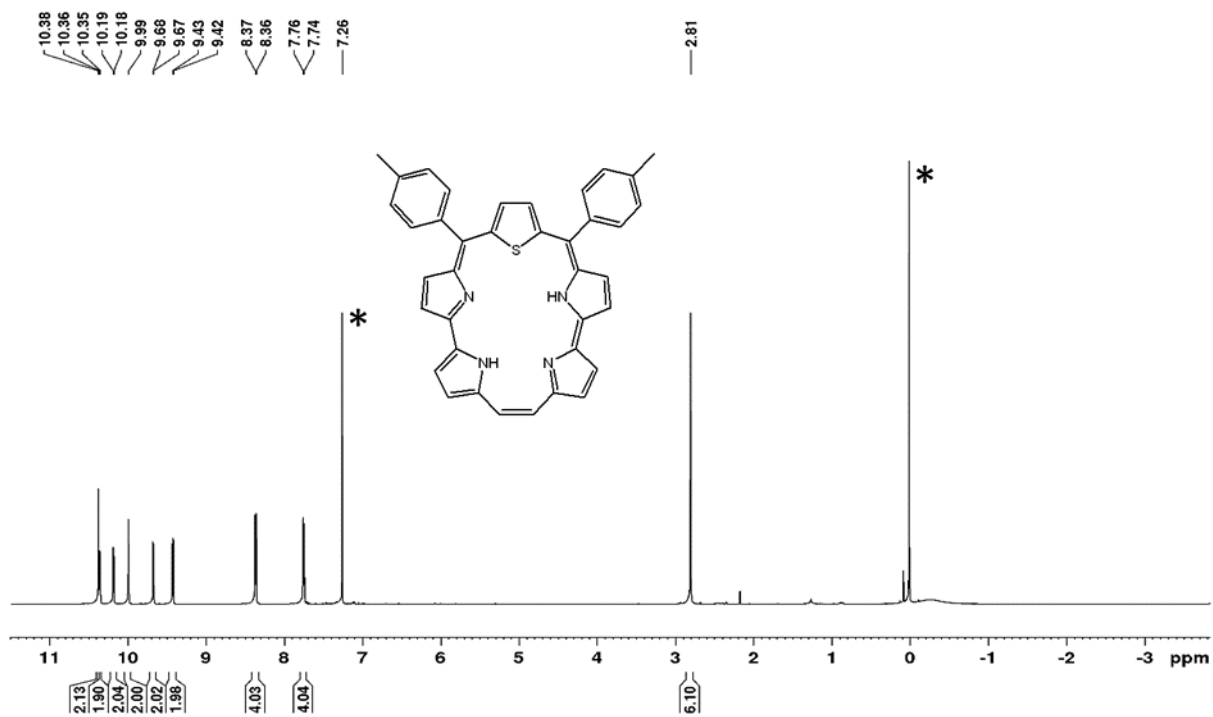


Figure S3: ¹H NMR spectrum of compound 8 in CDCl₃ (* water and residual protons of solvent).

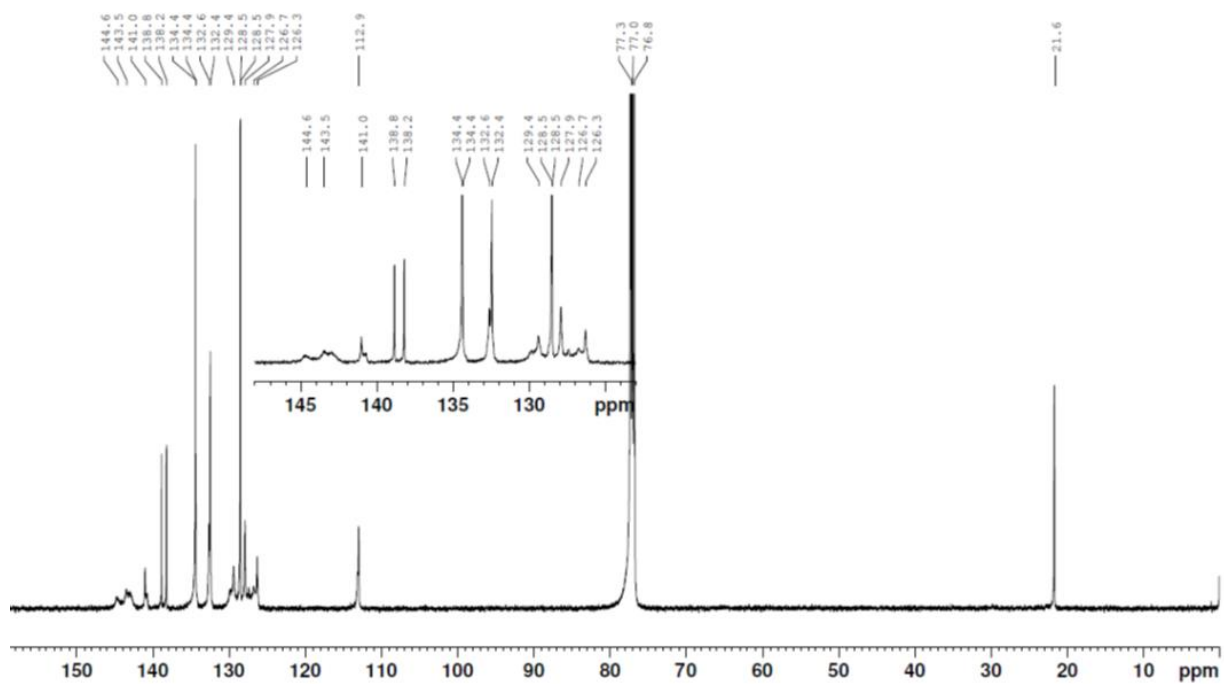


Figure S4: ¹³C NMR spectrum of 8 in CDCl₃.

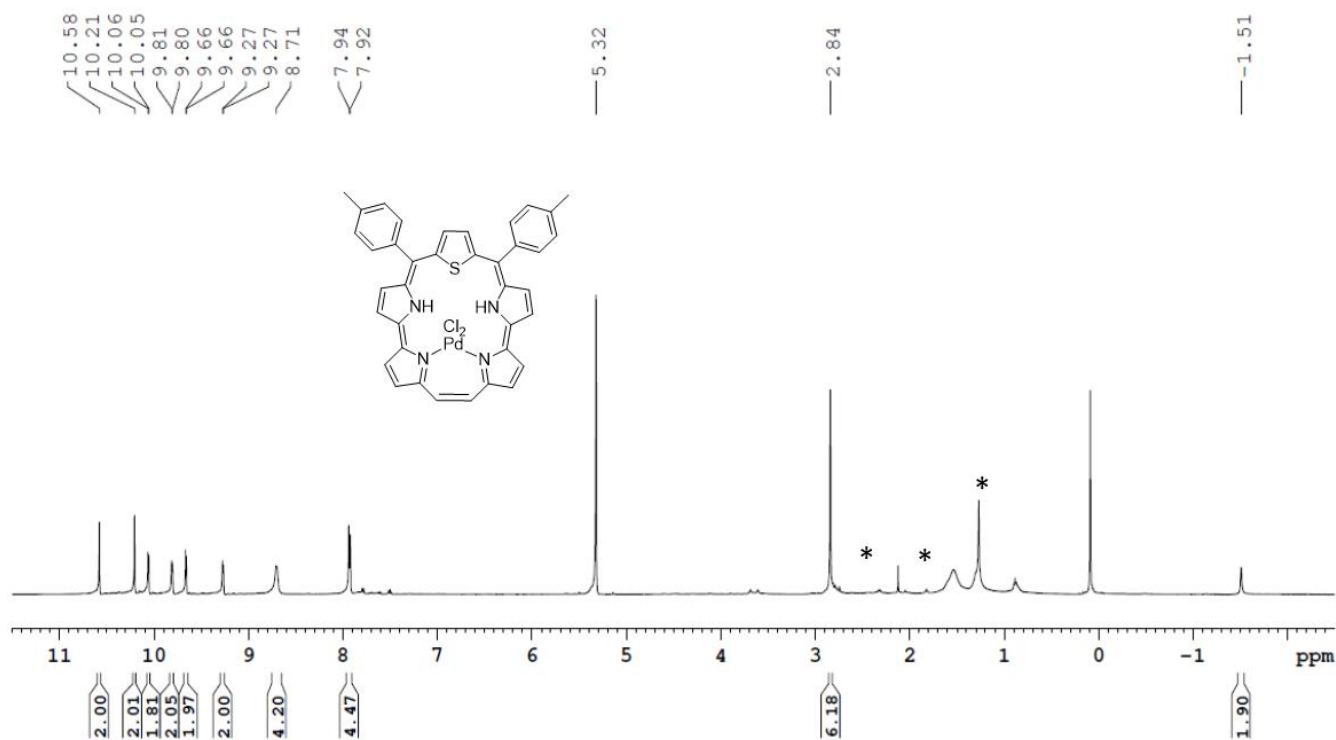


Figure S5: ¹H NMR spectrum of 9 in CD₂Cl₂ (* water and residual protons of solvent and impurities due to less solubility of sample).

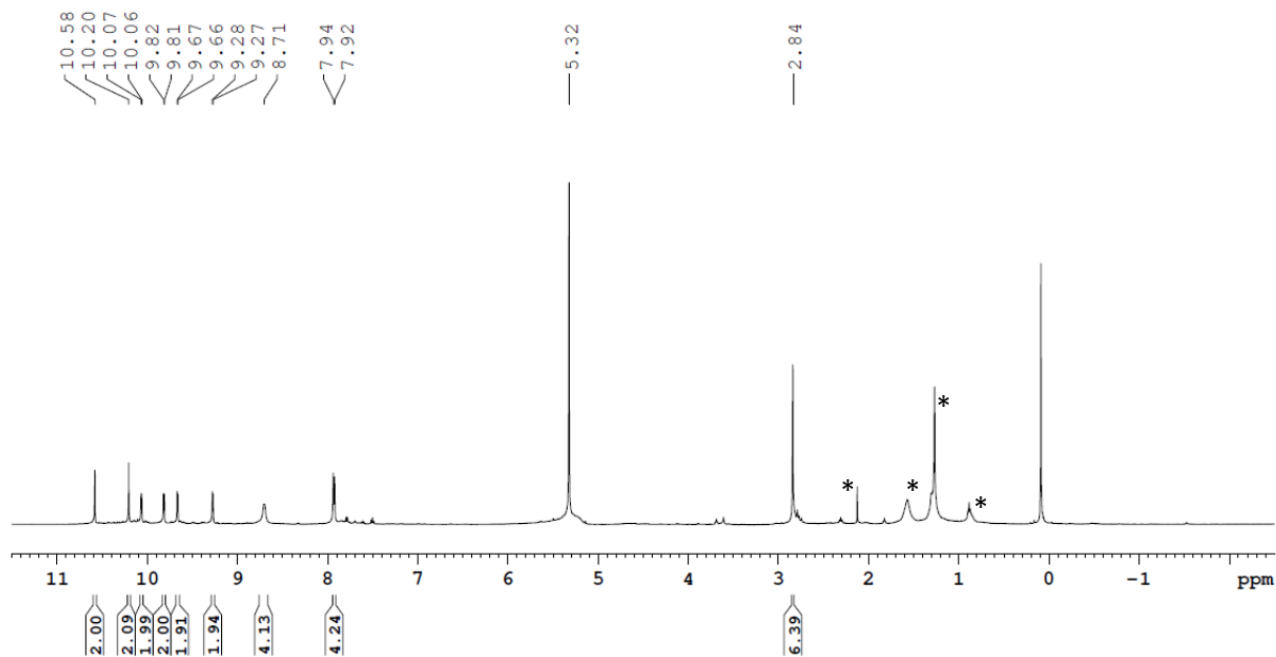


Figure S6: D₂O exchange ¹H NMR spectrum of 9 in CD₂Cl₂ (* water and residual protons of solvent and impurities due to less solubility of sample).

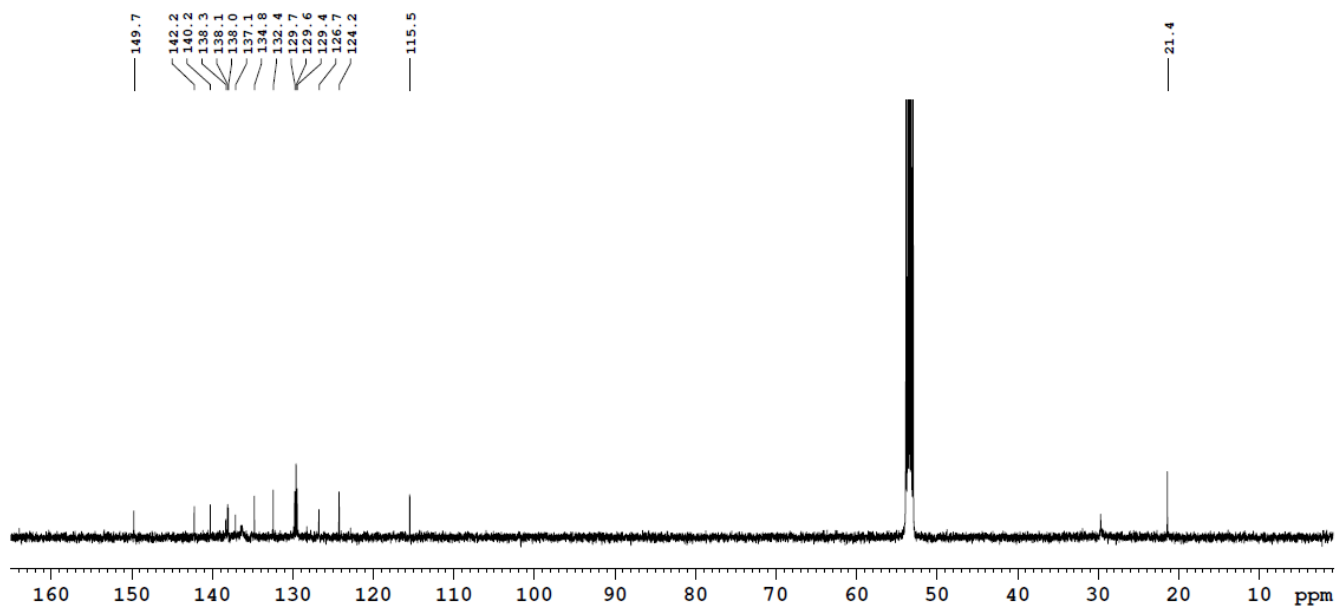


Figure S7: ^{13}C NMR spectrum of 9 in CD_2Cl_2 .

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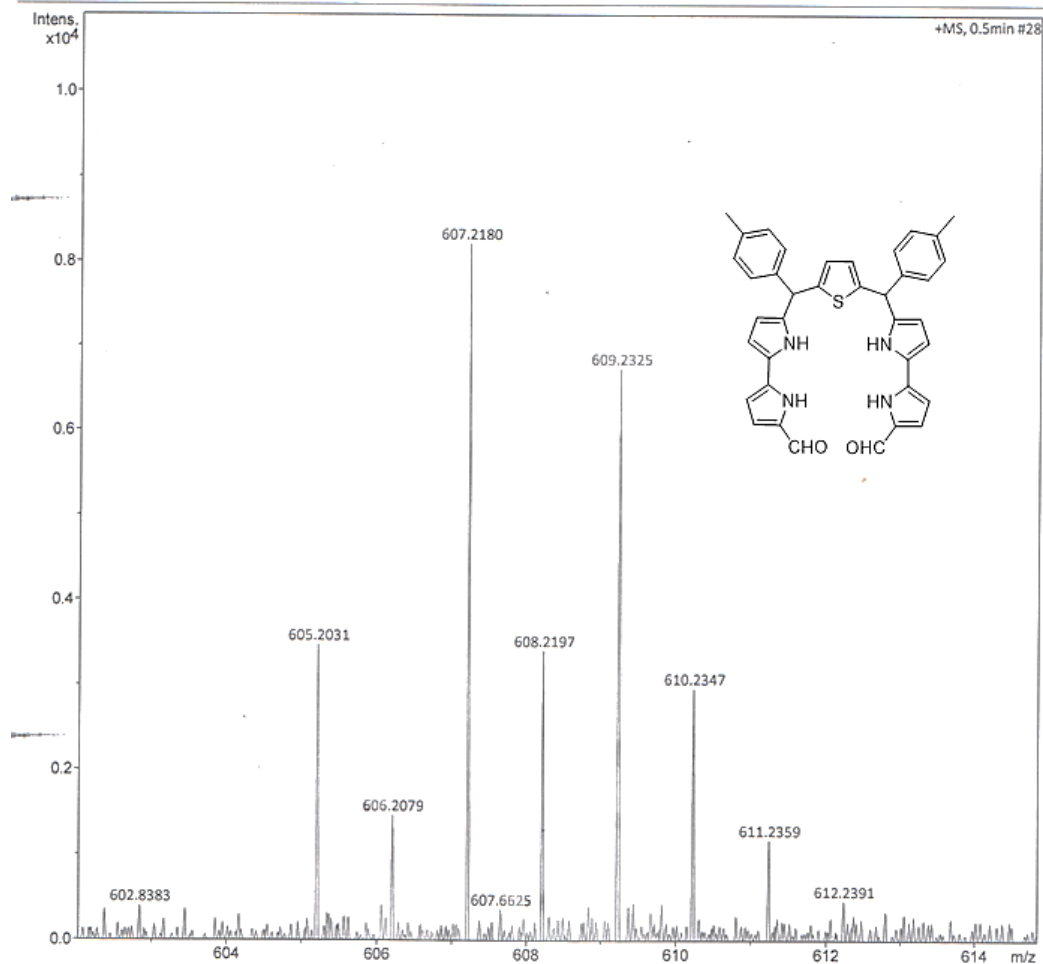
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Instrument maXis 255552.10138

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		Set Corona	0 nA	Set APCI Heater	0 °C



SSS-117-1.d

Bruker Compass DataAnalysis 4.2

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Page 1 of 1

Figure S8: HRMS data of **7**: m/z calculated for C₃₈H₃₂N₄SO₂ (M+H⁺): 609.2323; found: 609.2325.

Display Report

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Instrument maXis 10138

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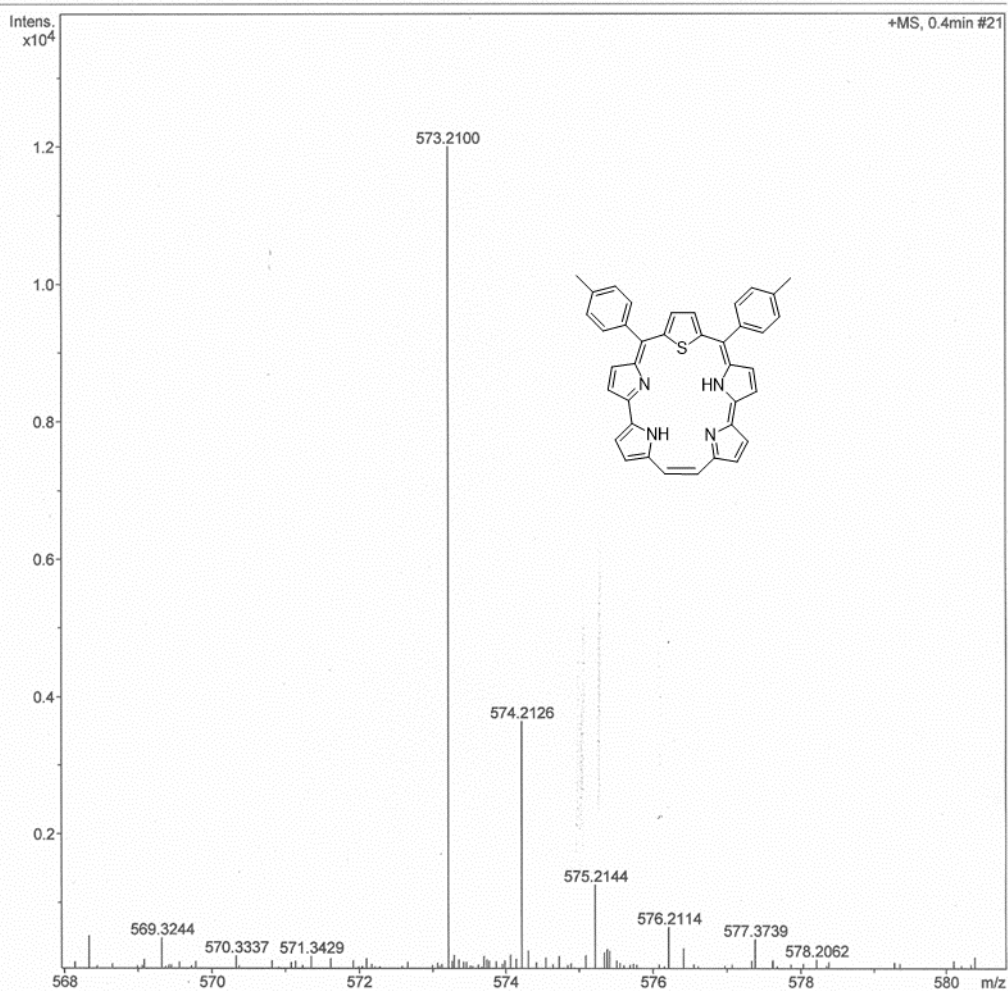


Figure S9: HRMS data of **8**. Calculated m/z $C_{38}H_{28}N_4S$ ($M+H^+$): 573.2113; found:573.2100.

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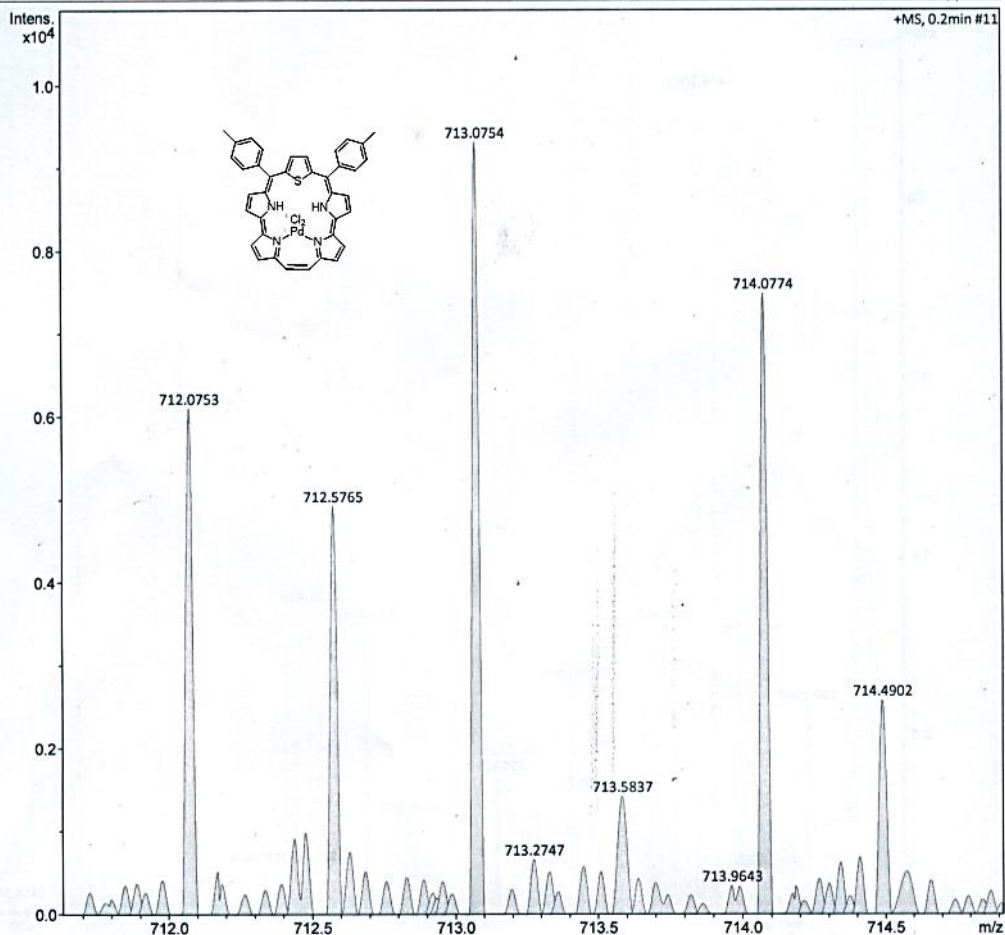
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Instrument maXis 255552.10138

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SSS-121-PdCL-R.d

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Page 1 of 1

Figure S10: HRMS data of **9**: m/z calculated for C₃₈H₂₈ClN₄PdS (M-Cl): 713.0757; found: 713.0754.

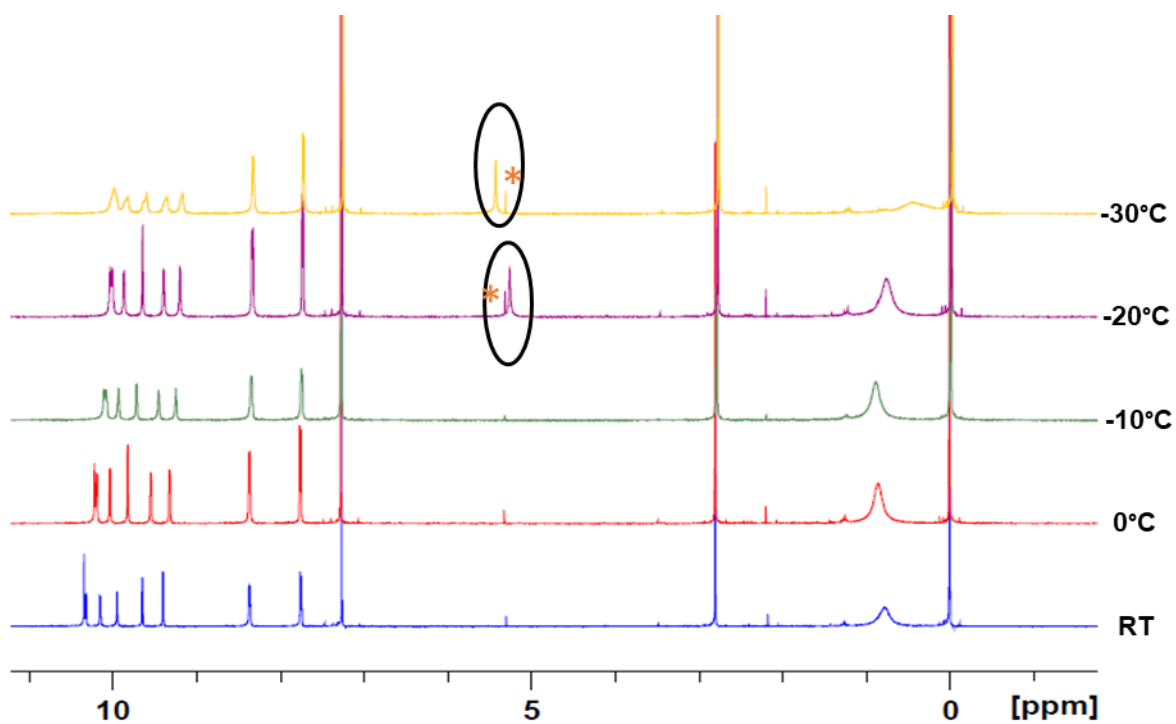


Figure S11: Variable temperature ^1H NMR spectra of **8** in CDCl_3 (*DCM impurity).

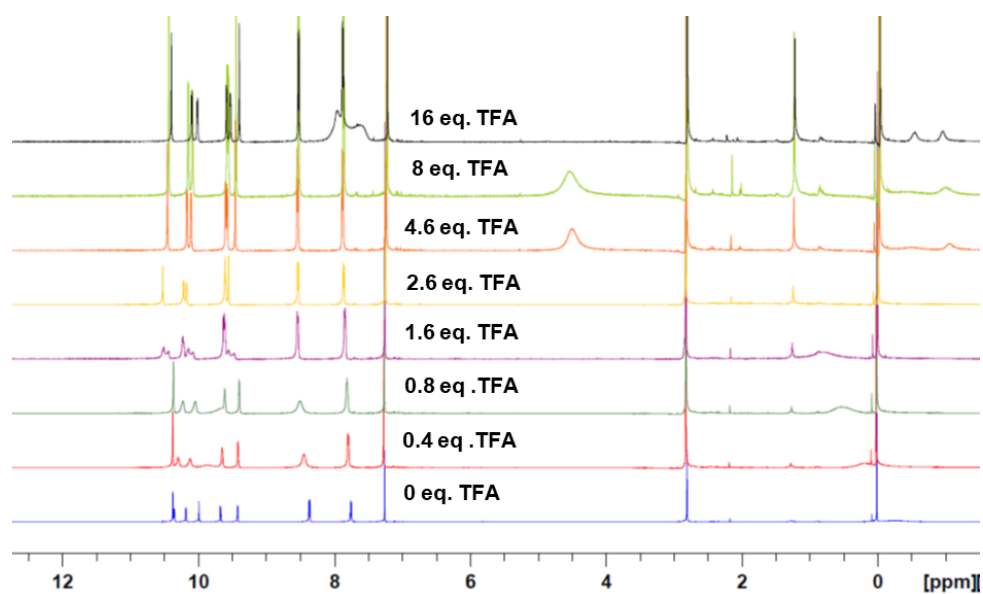


Figure S12: ^1H NMR spectra of compound **8** in CDCl_3 titrated with TFA.

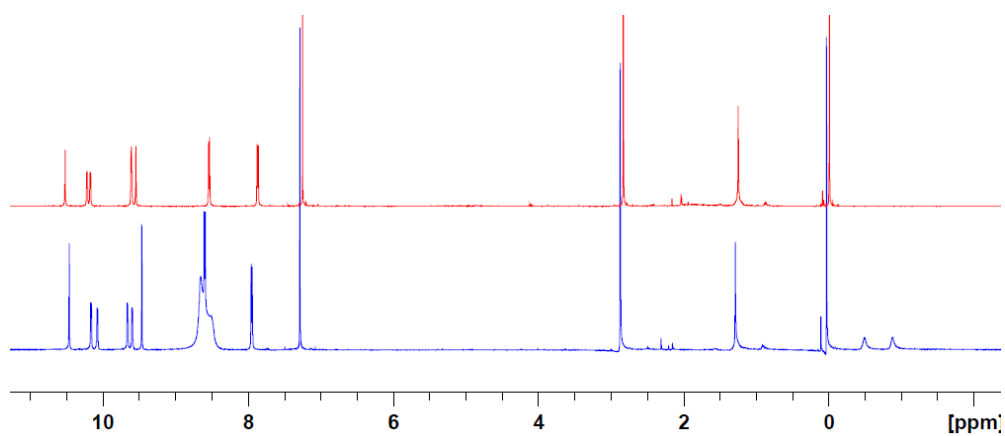


Figure S13: ^1H NMR spectra of **8.2TFA** (blue) and **8.2TFA** with D_2O (red) in CDCl_3 .

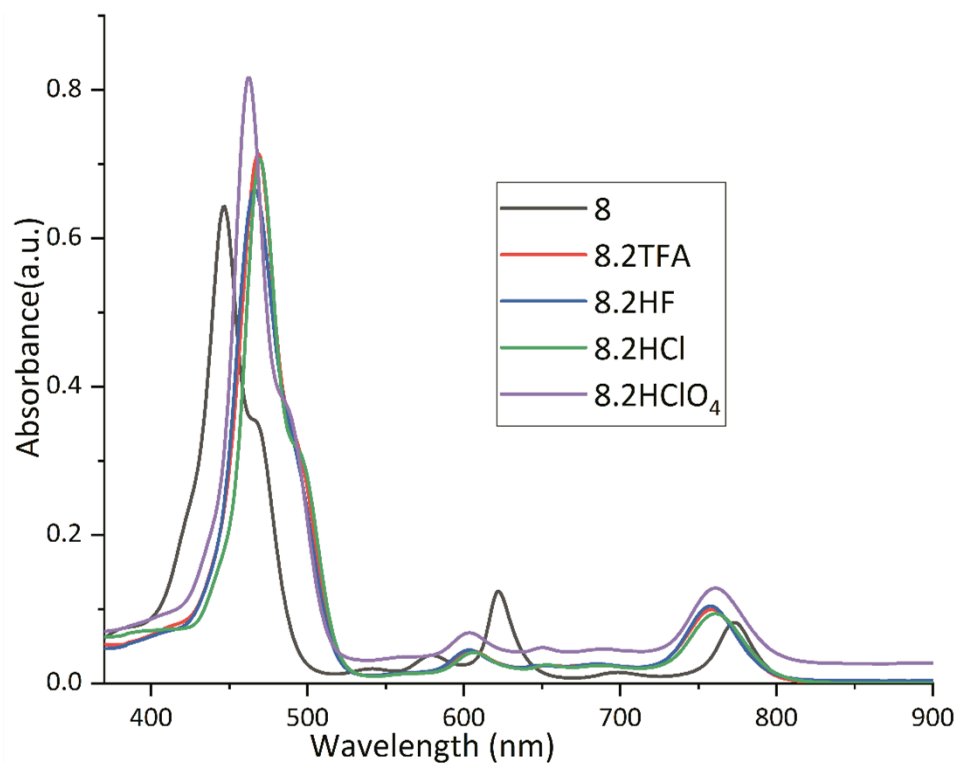


Figure S14: UV-vis-NIR absorption spectra of **8** ($2 \mu\text{M}$ in CHCl_3) protonated with acids (methanolic solution).

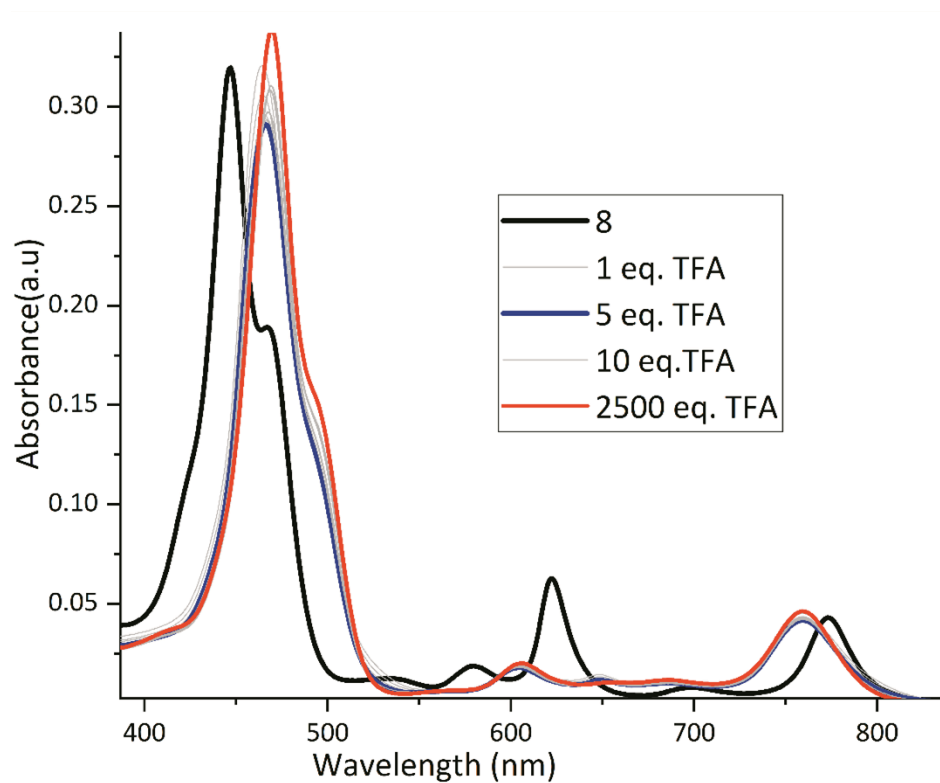


Figure S15: UV-vis-NIR spectra of compound **8** ($1 \mu\text{M}$ in CHCl_3) titration against TFA (in CHCl_3).

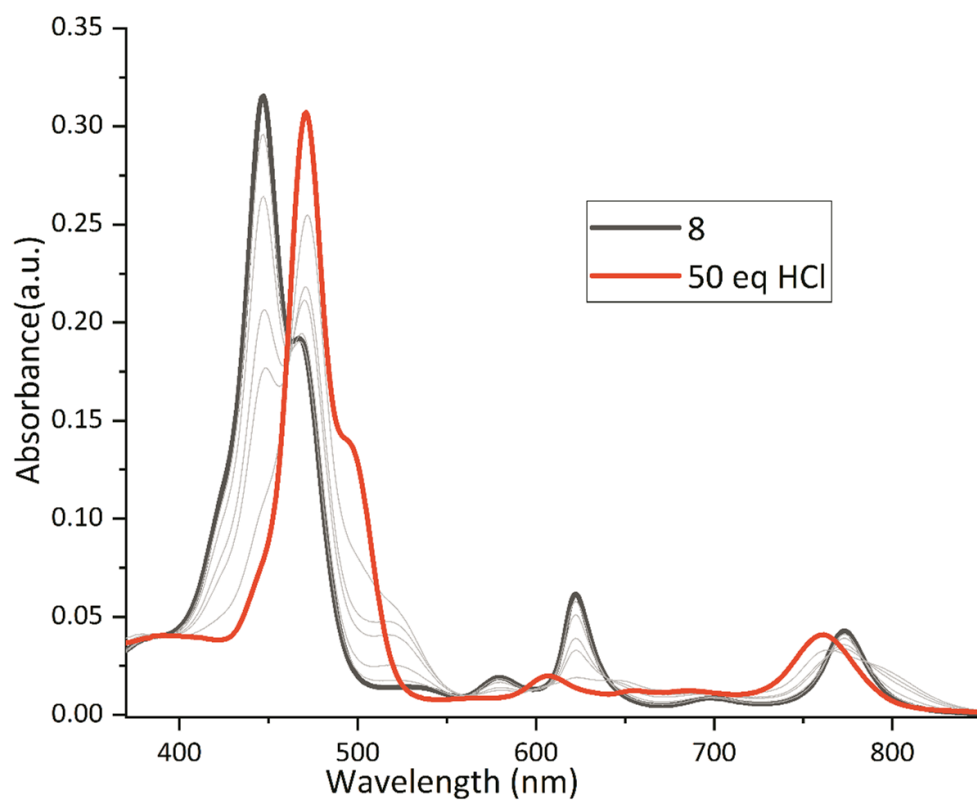


Figure S16: UV-vis-NIR spectra of compound **8** ($1 \mu\text{M}$ in CHCl_3) titration against HCl (in methanol).

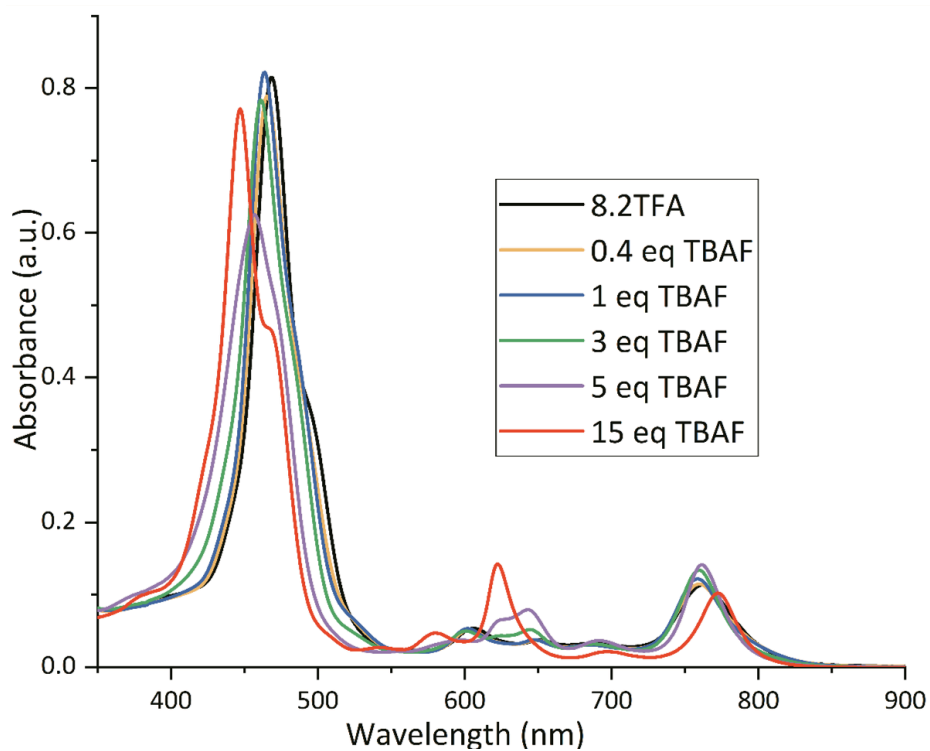


Figure S17: Fluoride binding with **8.TFA** ($10 \mu\text{M}$) using $\text{TBAF} \cdot 3\text{H}_2\text{O}$ in CHCl_3 .

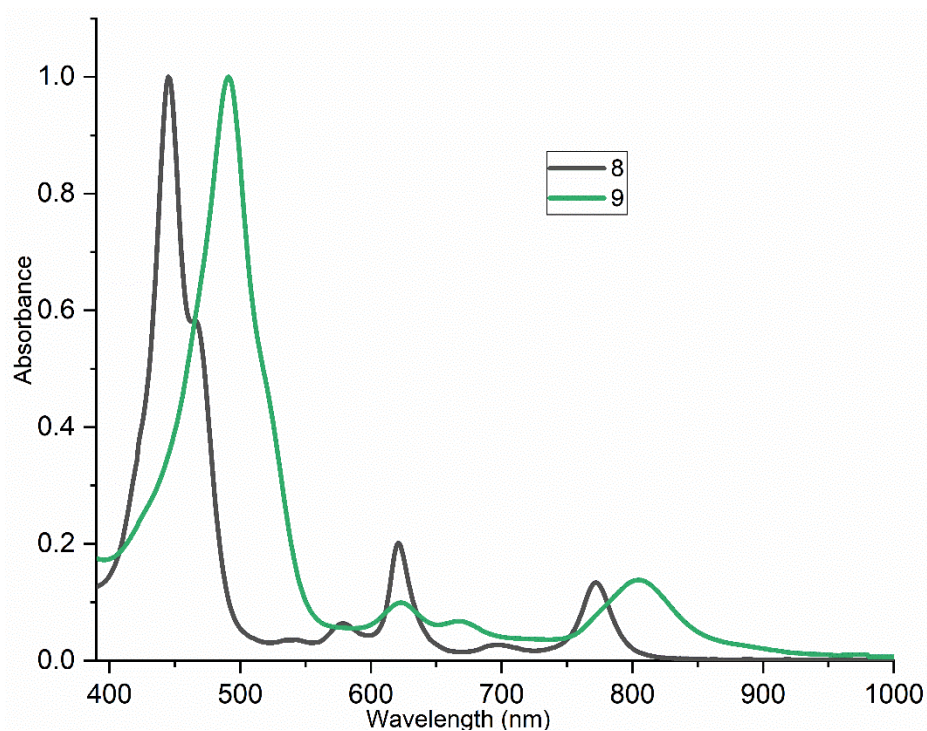


Figure S18: UV-vis-NIR spectra of **8** and **9** in CHCl_3 .

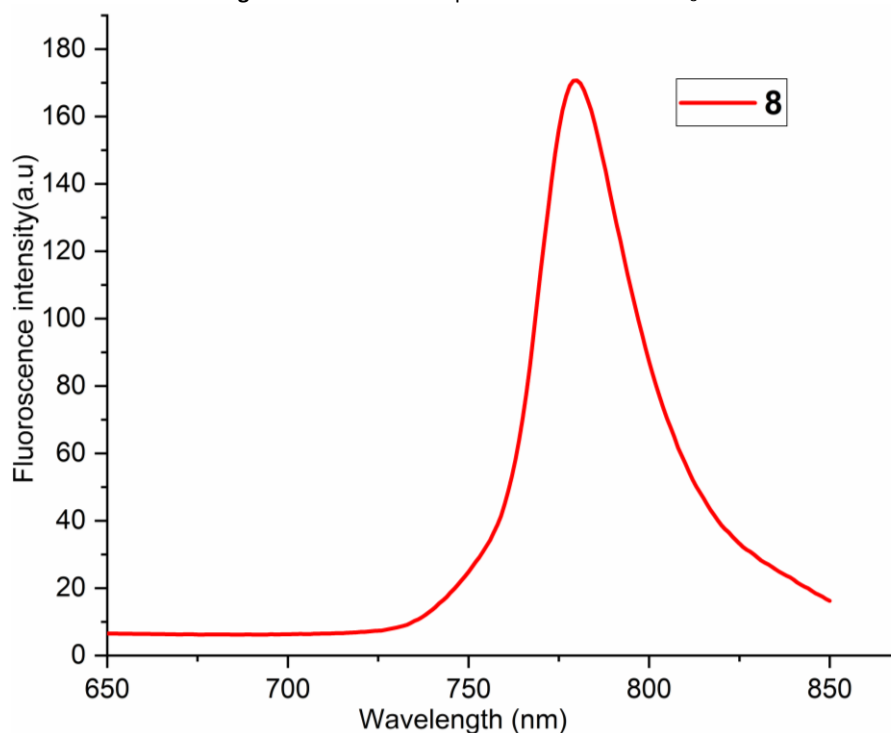


Figure S19: Emission spectrum of **8** in chloroform (λ_{ex} : 428 nm).

Computational studies

All quantum mechanical calculations are performed by Gaussian 09 programme⁵⁴ 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.⁵⁵ HOMA (Harmonic Oscillator Model of Aromaticity) indices were calculated by using $\text{Ropt}(\text{C-C}) = 1.388 \text{ \AA}$ and $\text{Ropt} = 1.334 \text{ \AA}$.⁵⁶⁻⁵⁸ The molecular orbitals were visualized using Gauss view 5.

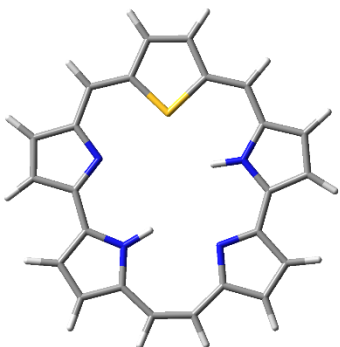
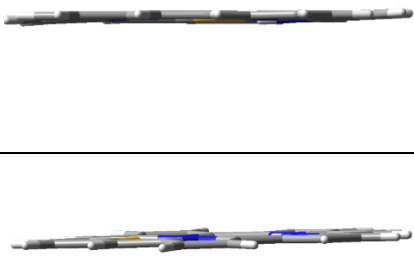
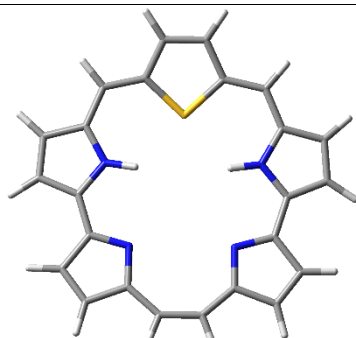
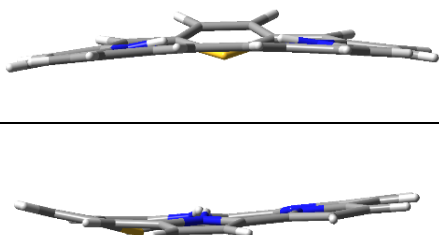
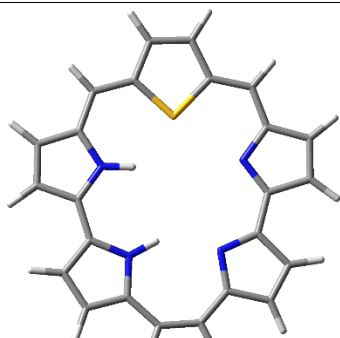
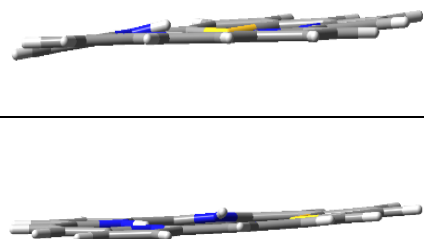
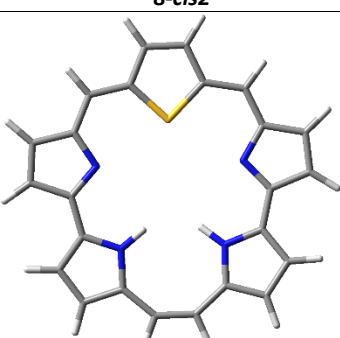
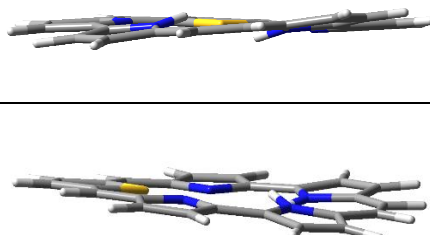
Front view	Side views	Optimized energy difference in gas phase (kcal/mol)	HOMO-LUMO gap (kcal/mol)	Optimized energy difference in CHCl ₃ (kcal/mol)
 <p>8-trans</p>		0	48.66	0
 <p>8-cis1</p>		12.9	48.20	10.37
 <p>8-cis2</p>		6.68	48.20	5.07
 <p>8-cis3</p>		4.15	50.73	3.22

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

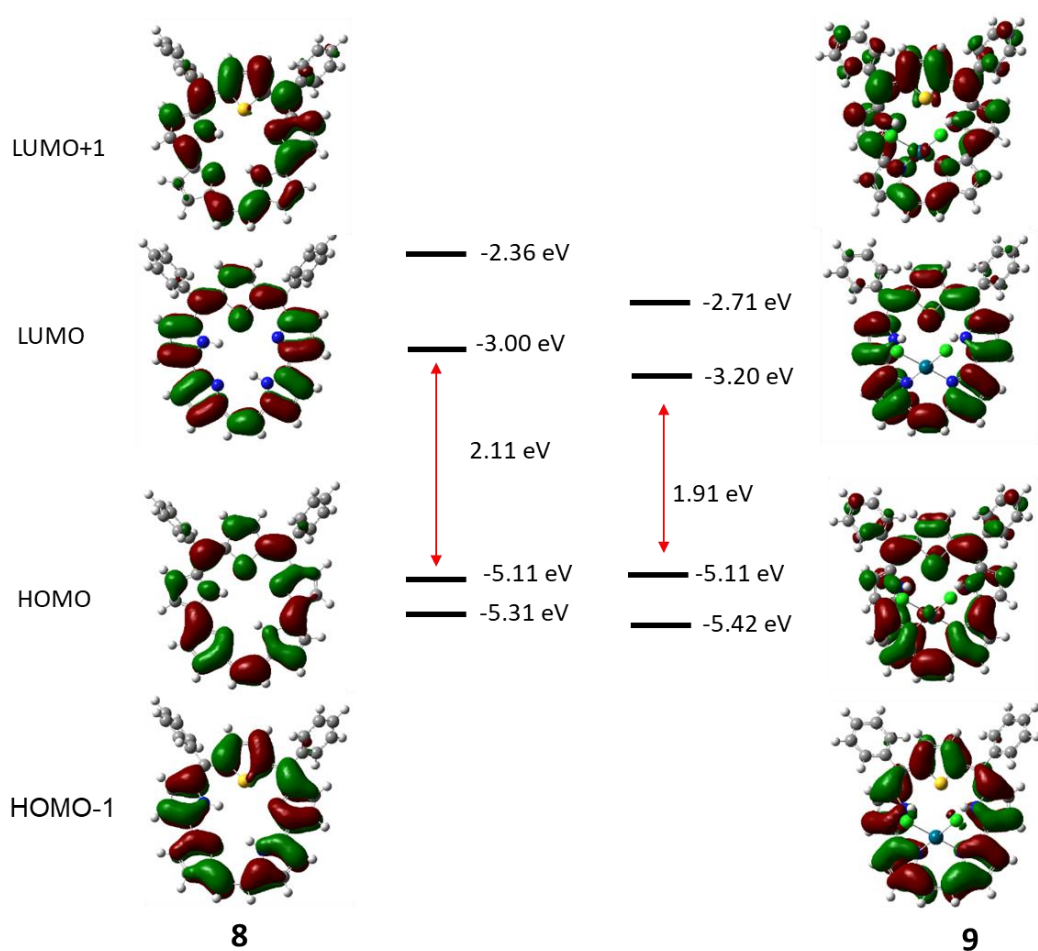


Figure S20: Frontier orbital diagram of 8 and 9.

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

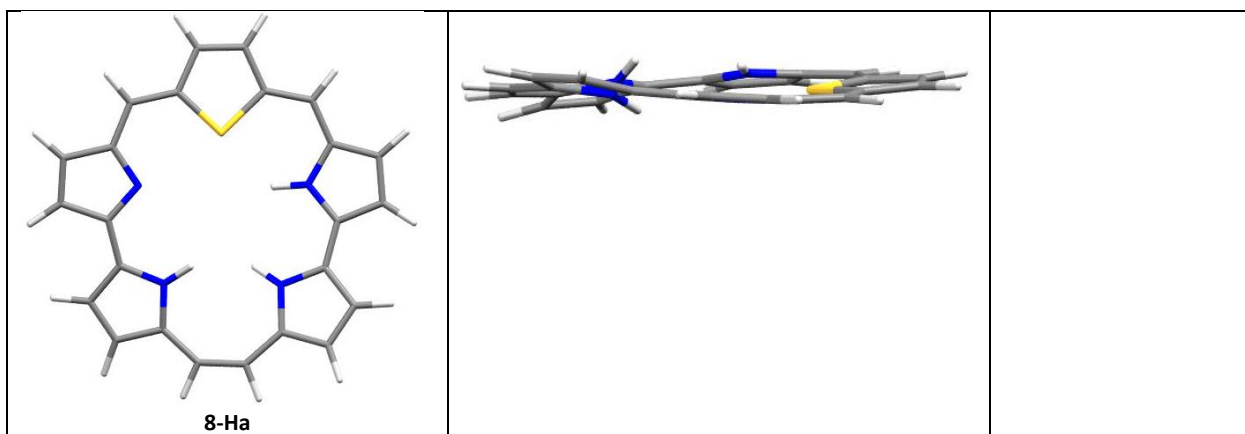


Table S2: Relative energies of optimized geometries of different modes of mono-protonation of **8** in chloroform (tolyl groups are removed for clarity).

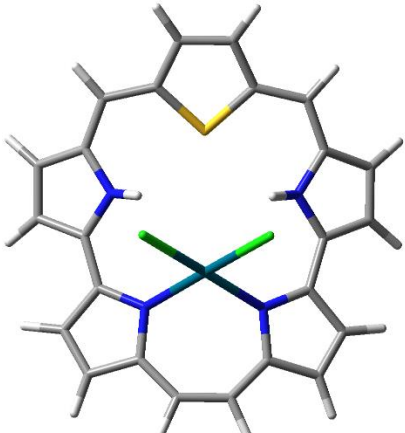
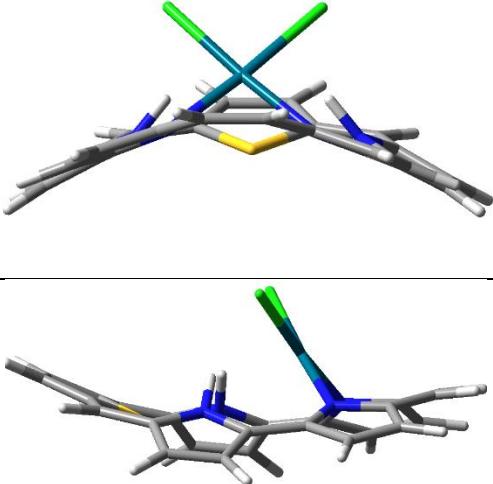
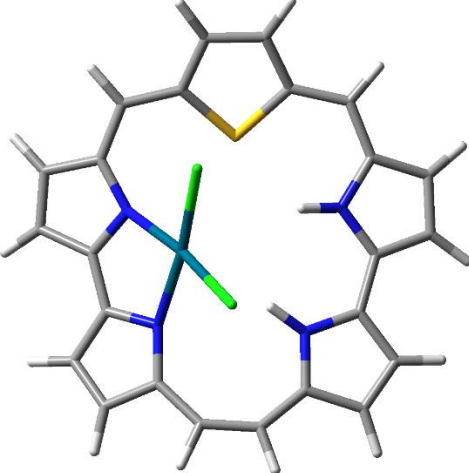
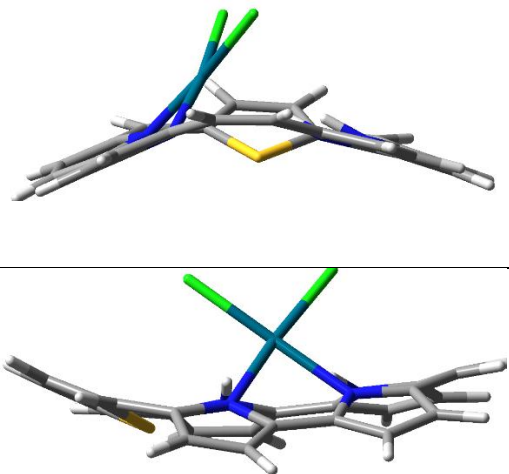
Front View	Side Views	Relative energies (kcal/mol)
 <p style="text-align: center;">9</p>		0
 <p style="text-align: center;">9'</p>		9.68

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	35	H	-4.36411	5.012324	-0.14011
4	C	0.3586	-3.22696	-0.13159	36	H	-6.52689	3.421095	0.113632
5	N	-0.85213	-2.55948	-0.05754	37	H	-4.36155	-5.01448	-0.14136
6	C	1.954552	1.289536	-0.04307	38	H	-6.52516	-3.42439	0.112277
7	C	3.212144	0.689493	0.243786	39	H	-6.92503	-1.09392	0.30833
8	C	3.212504	-0.68781	0.243837	40	H	-6.92556	1.090346	0.308788
9	C	1.955236	-1.28852	-0.04301	41	C	2.946482	4.457185	1.156222
10	S	0.787366	0.00018	-0.38306	42	C	4.020299	5.346123	1.244967
11	C	1.655121	-2.65773	-0.05532	43	C	4.965953	5.41089	0.217719
12	C	-1.90452	3.436663	-0.14204	44	C	4.832315	4.579589	-0.89808
13	C	-1.34952	4.732685	-0.30229	45	C	3.761604	3.686861	-0.98384
14	C	0.027556	4.60671	-0.29764	46	C	2.80343	3.615394	0.040813
15	C	0.356896	3.227131	-0.13171	47	H	2.2158	4.406319	1.95808
16	N	-0.8535	2.559053	-0.05749	48	H	4.118626	5.985286	2.117763
17	C	-3.25595	3.026383	-0.05838	49	H	5.799675	6.103637	0.28591
18	C	-4.39668	3.933867	-0.06003	50	H	5.559023	4.627307	-1.70406
19	C	-5.48431	3.131059	0.07055	51	H	3.656483	3.045804	-1.85431
20	C	-4.98486	1.750941	0.132241	52	C	2.805303	-3.61396	0.041047
21	N	-3.6229	1.73269	0.056139	53	C	2.948742	-4.45554	1.156593
22	C	1.653725	2.658559	-0.05547	54	C	4.022977	-5.34395	1.245484
23	C	-3.25437	-3.02799	-0.05877	55	C	4.968684	-5.40841	0.218258
24	C	-4.39465	-3.93606	-0.06094	56	C	4.83466	-4.57734	-0.89766
25	C	-5.48271	-3.13384	0.069573	57	C	3.763521	-3.68514	-0.98358
26	C	-4.98396	-1.75347	0.131779	58	H	2.218046	-4.4049	1.958448
27	N	-3.62201	-1.73452	0.056099	59	H	4.121608	-5.98295	2.118368
28	C	-5.91156	-0.70153	0.235173	60	H	5.802733	-6.10075	0.286528
29	C	-5.9119	0.698483	0.235412	61	H	5.561404	-4.62483	-1.70362
30	H	0.755615	-5.39703	-0.41602	62	H	3.658074	-3.04427	-1.85415
31	H	4.08323	1.286661	0.480905	63	H	-1.01111	1.577446	0.129126
32	H	4.083921	-1.28452	0.480889	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	Label	Symbol	X	Y	Z
1	C	-0.97388	-3.45446	-0.05094	34	H	-3.24118	4.821377	-0.21117
2	C	-0.24173	-4.73058	0.000627	35	H	-0.61613	5.323861	-0.24247
3	C	1.07851	-4.41903	0.021242	36	H	-5.27356	3.711141	0.08095
4	C	1.143842	-2.9612	-0.02911	37	H	-7.16482	1.799109	0.126668
5	N	-0.10689	-2.41815	-0.0723	38	H	-3.41545	-0.14385	0.008282
6	C	1.668064	1.687299	-0.02712	39	H	-2.77172	-5.64719	-0.0991
7	C	3.067243	1.448491	0.031749	40	H	-5.35191	-4.91028	-0.05881
8	C	3.404448	0.109799	0.032717	41	H	-6.56721	-2.84996	0.028189
9	C	2.297768	-0.78014	-0.00469	42	H	-7.20808	-0.68665	0.097988
10	S	0.806506	0.144162	-0.0884	43	C	1.919607	5.013059	1.079225
11	C	2.321641	-2.18573	0.000663	44	C	2.714125	6.162171	1.06673
12	C	-2.62213	2.693501	0.001915	45	C	3.463044	6.486178	-0.068
13	C	-2.44434	4.098256	-0.12145	46	C	3.414511	5.653121	-1.18924
14	C	-1.08876	4.359197	-0.137	47	C	2.623336	4.501853	-1.17494

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

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

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

27	N	3.653781	-1.77223	0.004679	60	H	-3.32918	-3.23579	-2.00381
28	C	5.970164	-0.6868	-0.05479	61	H	-5.26194	-4.78678	-1.99736
29	C	5.97025	0.686086	0.054673	62	H	-5.85977	-6.02795	0.076228
30	H	1.873659	-5.67715	-0.19211	63	H	-4.50322	-5.70573	2.138361
31	H	-0.79983	-5.45672	-0.07647	64	H	-2.56685	-4.1568	2.122585
32	H	-4.09116	1.292316	-0.05049	65	H	3.045598	-1.01229	0.270668
33	H	-4.09132	-1.2918	0.051109					

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

Label	Symbol	X	Y	Z	Label	Symbol	X	Y	Z
1	C	2.023189	3.134978	-0.24962	34	H	-4.00397	1.476609	0.829209
2	C	1.582682	4.468373	-0.52217	35	H	1.744072	-5.47854	-0.6891
3	C	0.209588	4.48213	-0.4769	36	H	-0.91652	-5.26728	-0.70469
4	C	-0.24855	3.15724	-0.18093	37	H	3.952992	-5.03932	-0.01849
5	N	0.896043	2.376824	-0.07324	38	H	6.281899	-3.75388	0.353778
6	C	-2.10895	-1.18485	-0.01585	39	H	3.258839	-0.82244	0.029533
7	C	-3.28108	-0.54331	0.445041	40	H	4.421531	4.668118	-0.35331
8	C	-3.2101	0.840881	0.459057	41	H	6.61889	3.156888	0.034891
9	C	-1.97861	1.368288	0.008206	42	H	7.08604	0.83913	0.424576
10	S	-0.94678	0.0421	-0.51996	43	H	7.020759	-1.4025	0.532833
11	C	-1.58267	2.725124	-0.03844	44	C	-3.04038	-4.51321	1.006543
12	C	1.708488	-3.30629	-0.18216	45	C	-4.131	-5.38023	1.094869
13	C	1.165538	-4.59163	-0.47816	46	C	-5.19819	-5.26087	0.19942
14	C	-0.20706	-4.48431	-0.48397	47	C	-5.17287	-4.26509	-0.78243
15	C	-0.55799	-3.13098	-0.19426	48	C	-4.08906	-3.39001	-0.86601
16	N	0.647202	-2.45006	-0.04467	49	C	-3.0061	-3.50653	0.024617
17	C	3.078777	-2.99256	-0.04111	50	H	-2.22078	-4.60217	1.712837
18	C	4.108671	-3.9724	0.039329	51	H	-4.14802	-6.14524	1.865193
19	C	5.300296	-3.31653	0.238539	52	H	-6.04399	-5.93833	0.266649
20	C	5.037019	-1.9167	0.261957	53	H	-5.99493	-4.17117	-1.48545
21	N	3.67643	-1.7528	0.100298	54	H	-4.06891	-2.62497	-1.6362
22	C	-1.84827	-2.57313	-0.07366	55	C	-2.64349	3.766241	0.090801
23	C	3.354951	2.678255	-0.15169	56	C	-2.57138	4.743303	1.099814
24	C	4.4775	3.599127	-0.20449	57	C	-3.567	5.714978	1.218724
25	C	5.585281	2.838627	-0.00531	58	C	-4.64443	5.729705	0.327923
26	C	5.124405	1.4647	0.138464	59	C	-4.72496	4.763606	-0.68021
27	N	3.761767	1.387803	0.048086	60	C	-3.73601	3.785435	-0.79522
28	C	6.07949	0.439341	0.330232	61	H	-1.74324	4.730074	1.801821
29	C	6.045796	-0.94364	0.390783	62	H	-3.50199	6.457068	2.008686
30	H	2.229408	5.304426	-0.74228	63	H	-5.41629	6.487921	0.418592
31	H	-0.43859	5.324743	-0.66432	64	H	-5.55527	4.773069	-1.37985
32	H	0.928685	1.42138	0.252659	65	H	-3.79767	3.0444	-1.58651
33	H	-4.13599	-1.10148	0.804663	66	H	0.720112	-1.51096	0.319693

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

Label	Symbol	X	Y	Z	Label	Symbol	X	Y	Z
1	C	-2.38636	3.033951	-0.02841	34	H	3.905346	1.911199	0.215678
2	C	-2.05354	4.408123	-0.21189	35	H	-0.98989	-5.82348	0.219221
3	C	-0.68486	4.526709	-0.1315	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

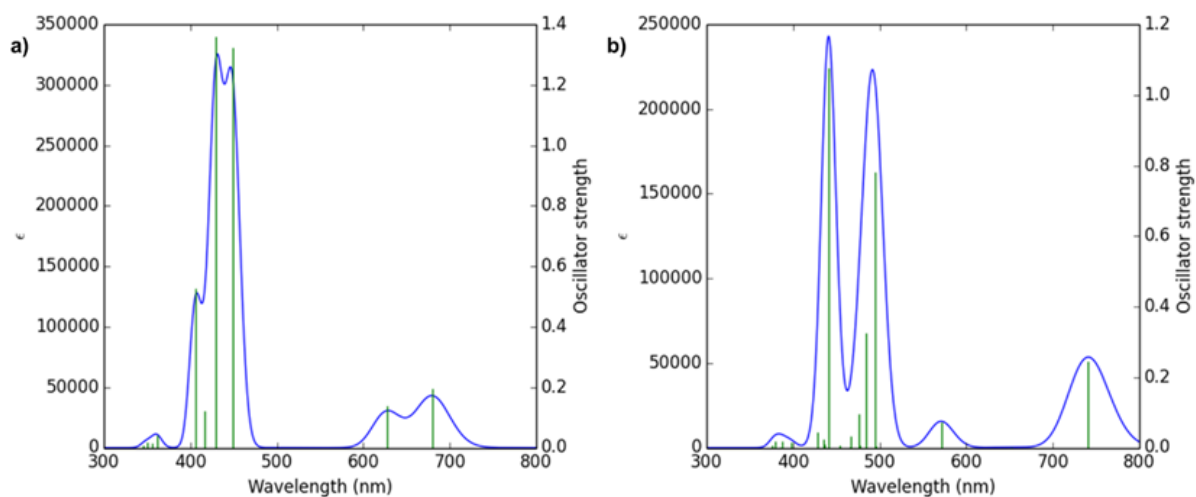


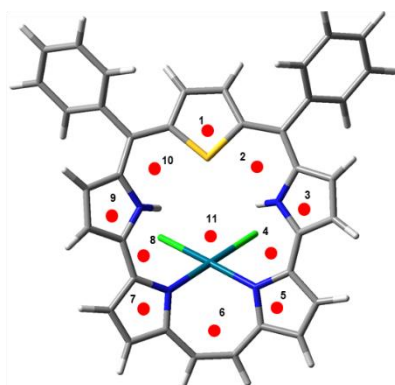
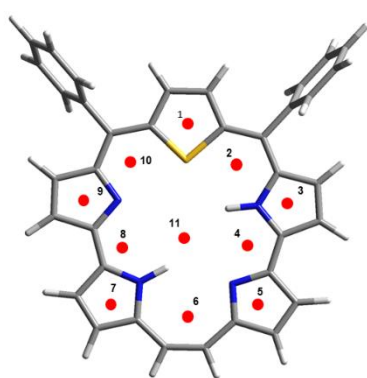
Figure S21: Calculated absorption spectra of a) sapphycene **8** and b) its Pd(II)-complex **9** in chloroform.

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.

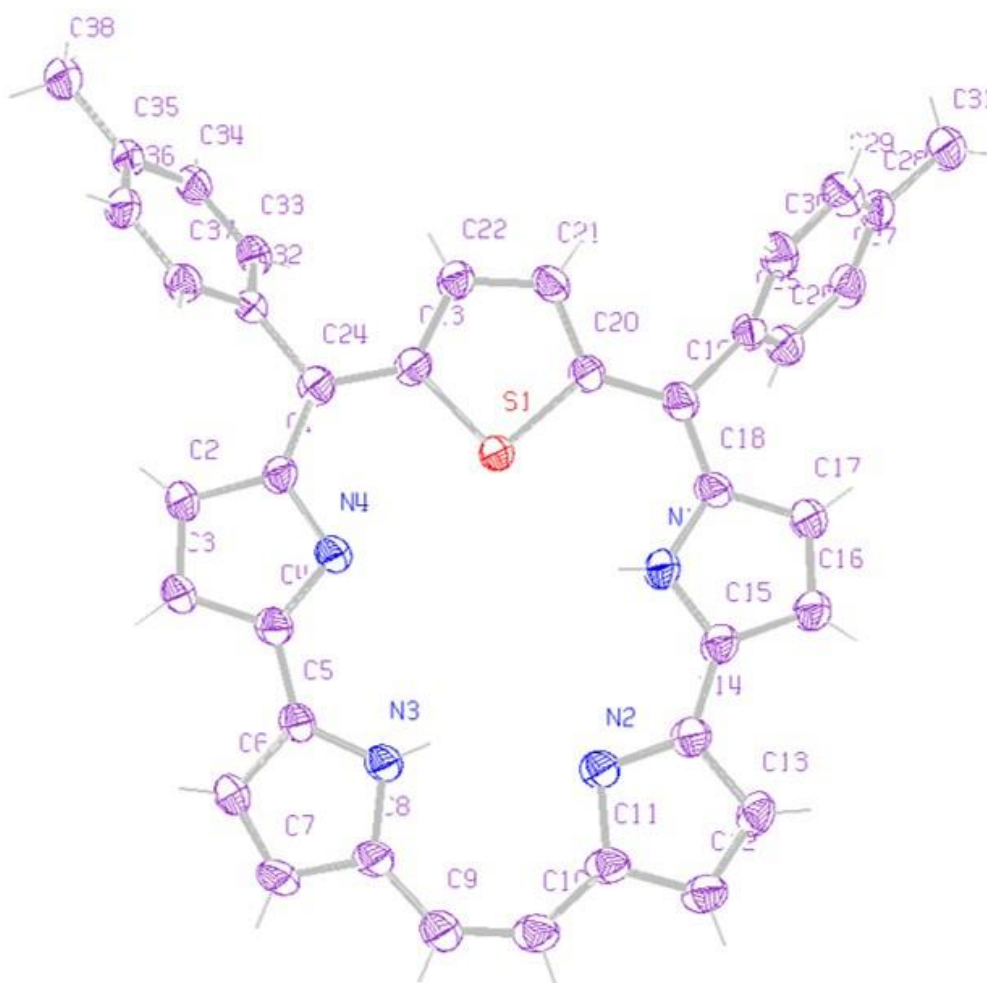


Figure S23: ORTEP diagram (with 40% thermal ellipsoid) of **8**.

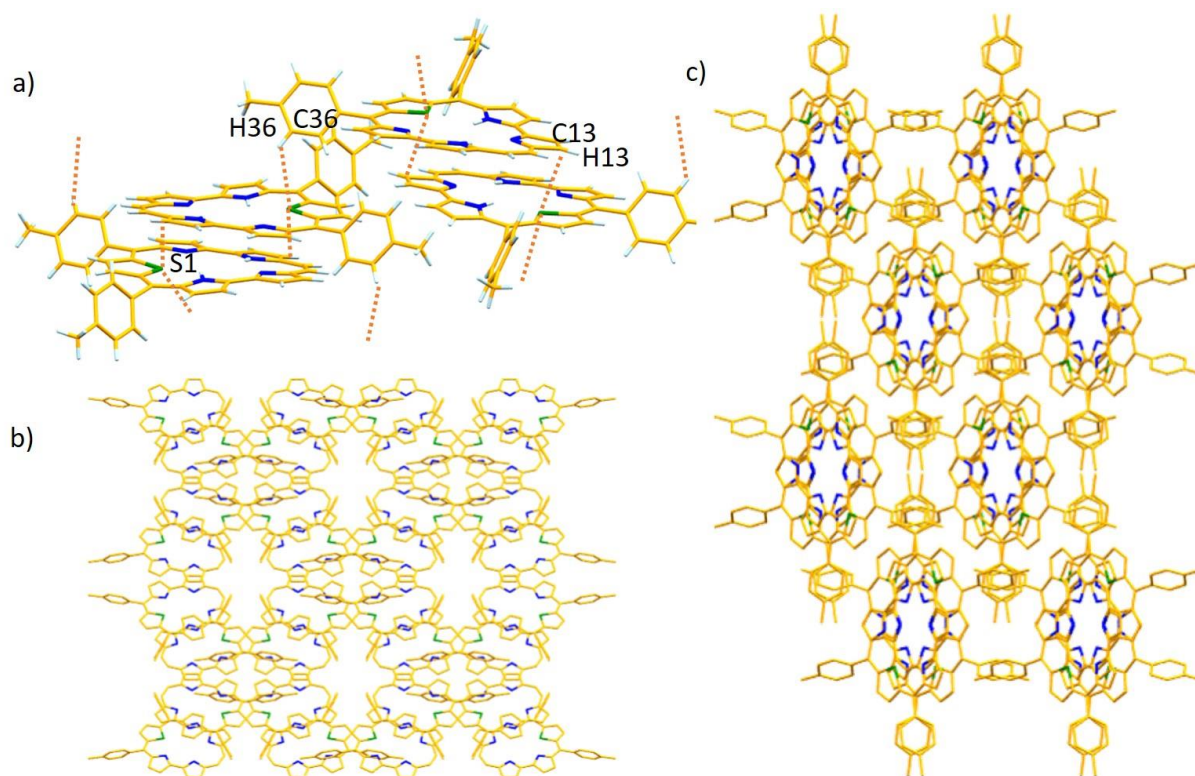


Figure S24: packing diagram of **8**: a) showing alignment of π -stacked planes, b) along a -axis, c) along c -axis (hydrogens are removed for clarity).

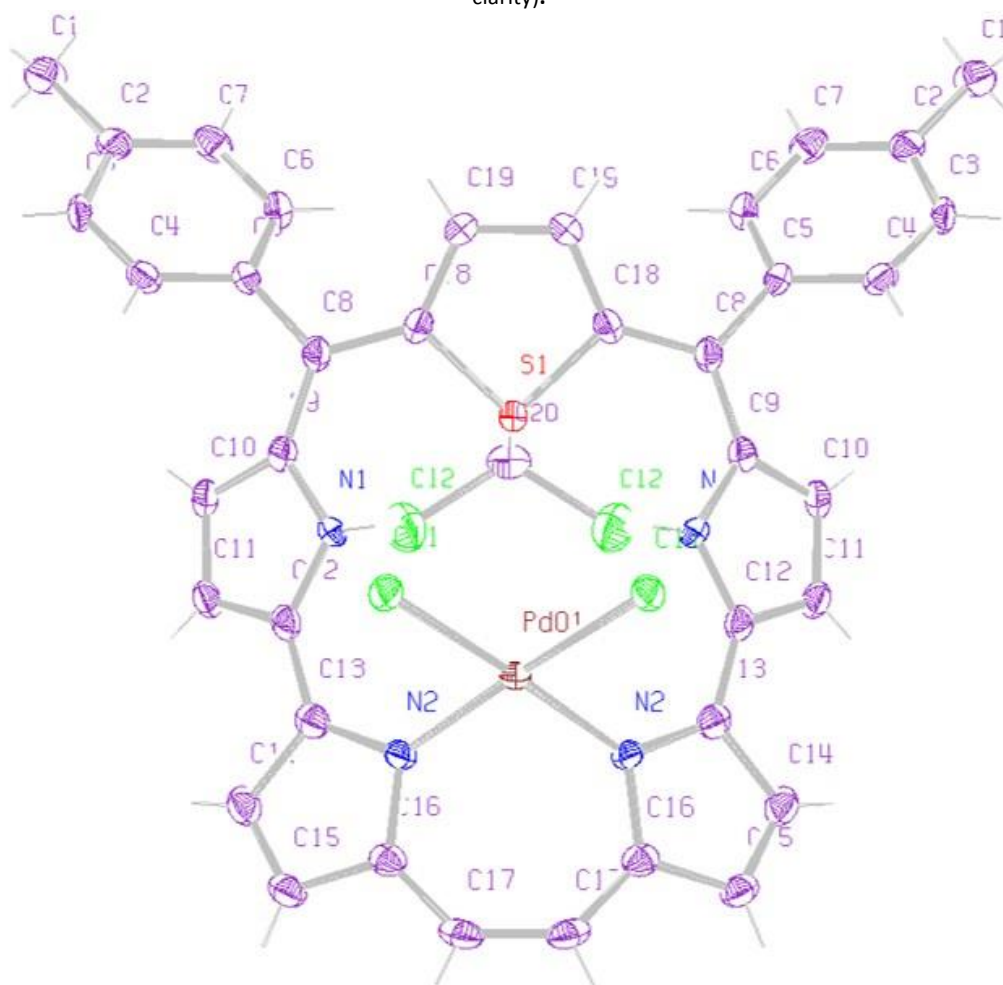


Figure S25: ORTEP diagram (with 40% thermal ellipsoid) of **9**.

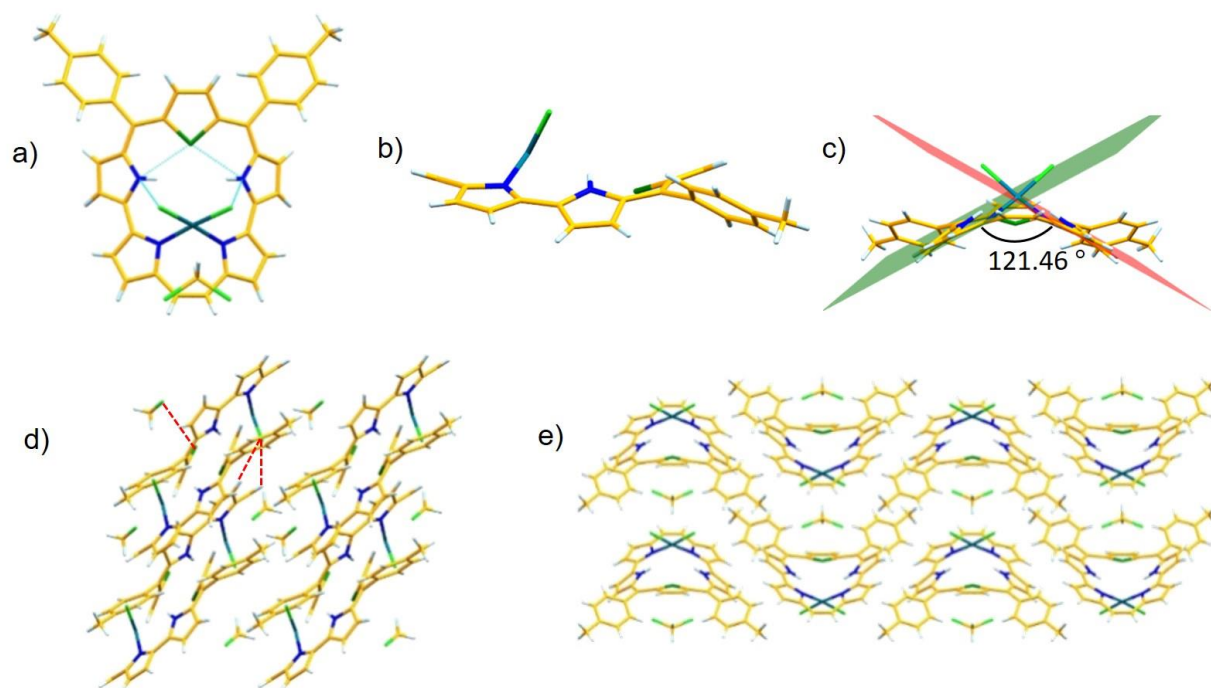


Figure S26: crystal structure of 9: a) front view b) side view c) side view showing dihedral planes of bipyrroles and d) packing diagram along *b*-axis e) packing diagram along *a*-axis.

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

Empirical formula	C ₃₈ H ₂₈ N ₄ S
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 ≤ h ≤ 15, -27 ≤ k ≤ 27, -24 ≤ l ≤ 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 > 2σ(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 ₄ N ₄ PdS
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 ≤ h ≤ 9, -26 ≤ k ≤ 26, -11 ≤ l ≤ 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 > 2σ(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

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