Electronic Supplementary Information (ESI)

$PtCl_2$ Mediated Peripheral Transformation of Carbatriphyrin(3.1.1) into *meso*-Fused *β-β′* Dimer and Its Monomer Analogue

M. Murugavel, B. Adinarayana, Mainak Das, S. Peruncheralathan, Narasinga Rao Palepu and A. Srinivasan*[a]

[a] School of Chemical Sciences, National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar-752050, Odisha, India.
E-mail: srini@niser.ac.in.

Table of Contents:

1. General Information : 2
2. Syntheses and spectral characterizations : 3 - 4
3. Mass spectral analyses : 5 - 6
4. NMR spectral analyses : 7 - 12
5. IR spectral analysis : 13
6. Single crystal X-ray structural analyses of **6** and **7** : 14 - 18
7. Electronic absorption spectral analyses : 19 - 26
8. The proposed mechanism for the formation of **6** and **7** : 27 - 28
9. Reaction of **8** with other group-10 salts and **8a** with $PtCl_2$: 29

1. General Information:

The reagents and materials for the syntheses were used as obtained from Sigma Aldrich chemical suppliers. All solvents were purified and dried by standard methods prior to use. The NMR solvents were used as received and the spectra were recorded in Bruker 400 and 700 MHz spectrometers with TMS as an internal standard. The ESI and HR-ESI-MS mass spectra were recorded in Bruker, micro-TOF-QII mass spectrometer. The Electronic absorption spectra were recorded in JASCO V-750 UV-Visible spectrophotometer. The IR spectral data were collected in Thermo SCIENTIFIC Nicolet iS5 Spectrometer. The X-ray quality crystals of **6** and **7** were grown by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **6** and **7**. Single-crystal X-ray diffraction data of **6** and **7** were collected in a Rigaku Oxford Diffraction single crystal X-ray diffractometer with CrysAlis^{Pro} and CuKα (λ = 1.54184). The crystal structures of **6** and **7** have been deposited in the Cambridge Crystallographic Data Centre with reference numbers CCDC **1954598** and CCDC **1954599** respectively.

2. Syntheses and spectral characterizations

Synthesis of 8: The compound **8** was synthesized as per the reported procedure[S1] and its spectral data as follows.

Spectral Data for 8: ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 12.28 (s, 1H), 8.11 (s, 1H), 7.33 (d, *J* = 7.6, 1H), 7.21 (t, *J* = 7.6, 1H), 7.12 (dd, *J* = 5.8, 3.5, 2H), 7.00 (m, 2H), 6.96 (s, 2H), 6.91 (s, 1H), 6.83 (d, *J* = 7.8, 1H), 6.58 (d, *J* = 5.1, 1H), 6.41 (d, *J* = 5.0, 1H), 6.02 (d, *J* = 4.9, 1H), 2.39 (s, 3H), 2.28 (s, 3H), 2.26 (d, *J* = 1.9, 6H), 2.14 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.85, 139.85, 137.63, 136.92, 136.70, 134.76, 132.95, 131.40, 129.84, 128.25, 127.73, 127.67, 127.63, 127.42, 126.24, 125.97, 125.65, 125.57, 124.96, 124.23, 21.14, 20.15, 20.11, 20.08, 19.99, 19.71; ESI-MS: m/z calculated for $C_{47}H_{35}F_5N_2$ = 722.2720; found = 723.2779 (M+1); UV-Vis (CH_2Cl_2): λ_{max} (nm) (ε x 10^4 [$M^{-1}cm^{-1}$]) = 365 (3.14), 605 (1.71).

Synthesis of 6 and 7: Compound **8** (10 mg, 0.01 mmol) was dissolved in 10 mL of dry chlorobenzene. $PtCl_2$ (18 mg, 0.07 mmol) was added and the reaction mixture was refluxed at 130 °C under aerial condition for 48 h. The crude reaction mixture was subjected to neutral alumina column chromatography and eluted with (1:4) CH_2Cl_2/*n*-hexane. The separated pink (**6**) and brown (**7**) fractions were further purified by washing with ice-cold *n*-pentane which afforded analytically pure **6** and **7** in 8% and 17% yields respectively.

Spectral Data for 6: ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.77 (d, *J* = 7.3, 2H), 7.68 (s, 2H), 7.61 (d, *J* = 7.3, 2H), 7.52 (t, *J* = 7.3, 2H), 7.45 (s, 2H), 7.24 (s, 4H), 7.20 (t, *J* = 7.3, 2H), 7.12 (t, *J* = 7.3, 2H), 7.06 (s, 2H), 6.96 (s, 2H), 6.93 (d, *J* = 7.3, 2H), 6.88 (s, 2H), 6.69 (s, 2H), 6.45 (s, 2H), 5.96 (d, *J* = 5.4, 2H), 5.83 (d, *J* = 5.4, 2H), 2.75 (s, 6H), 2.39 (s, 6H), 2.35 (s, 6H), 2.27 (s, 6H), 2.10 (s, 6H); ^{13}C NMR (176 MHz, CD_2Cl_2) δ = 144.60, 144.36, 141.48, 140.10, 139.60, 139.38, 137.64, 136.10, 135.04, 134.83, 132.49, 132.19, 131.77, 129.37, 129.25, 129.21, 129.12, 129.08, 127.80, 127.42, 126.97, 126.66, 105.82, 88.09, 25.48, 22.44, 21.51, 21.17, 20.36; ^{19}F NMR (377 MHz, CD_2Cl_2) δ = -134.02 (d, *J* = 22.4), -138.76 (s), -157.12 (t, *J* = 20.8), -164.70 (s), -165.06 (d, *J* = 21.4); ESI-MS: m/z calculated for $C_{94}H_{64}F_{10}N_4$ = 1438.4971; found = 1437.4927 (M-1); UV-Vis (CH_2Cl_2): λ_{max} (nm) (ε x 10^4 [$M^{-1}cm^{-1}$]): **6** = 355 (1.20), 505 (1.11).

Spectral Data for 7: ^{1}H NMR (700 MHz, CD_2Cl_2) δ = 10.91 (s, 1H), 8.39 (s, 1H), 7.65 (d, *J* = 7.5, 1H), 7.54 (s, 1H), 7.38 (s, 1H), 7.29 (m, 2H), 7.27 (m, 1H), 7.20 (d, *J* = 7.6, 1H), 7.16 (t, *J* = 7.0, 2H), 6.96 (d, *J* = 7.7, 2H), 6.87 (s, 1H), 6.11 (d, *J* = 5.1, 1H), 5.78 (d, *J* = 4.3, 1H), 2.60 (s, 2H), 2.43 (s, 2H), 2.39 (s, 2H), 2.27 (s, 2H), 2.09 (s, 2H); ^{13}C NMR (176 MHz, CD_2Cl_2) δ = 162.32, 159.04, 151.50, 145.66, 142.64, 141.82, 141.09, 139.51, 139.35, 138.97, 137.45,

136.52, 136.45, 135.72, 135.32, 134.76, 134.63, 134.06, 133.67, 133.53, 132.08, 129.20, 129.13, 128.49, 127.63, 127.23, 127.02, 126.65, 125.92, 125.85, 125.45, 124.65, 25.33, 22.01, 20.90, 20.77, 20.03; ^{19}F NMR (377 MHz, CD_2Cl_2) δ = -135.07 (s), -138.47 (d, *J* = 24.0), -156.96 (d, *J* = 21.3), -161.33 (s), -165.02 (d, *J* = 22.1); ESI-MS: m/z calculated for $C_{47}H_{31}F_5N_2O$ = 734.2357; found = 735.2429 (M+1); UV-Vis (CH_2Cl_2): λ_{max} (nm) (ε x 10^4 [$M^{-1}cm^{-1}$]): **7** = 355 (1.10), 500 (0.47), 695 (0.29).

3. Mass spectral analyses:

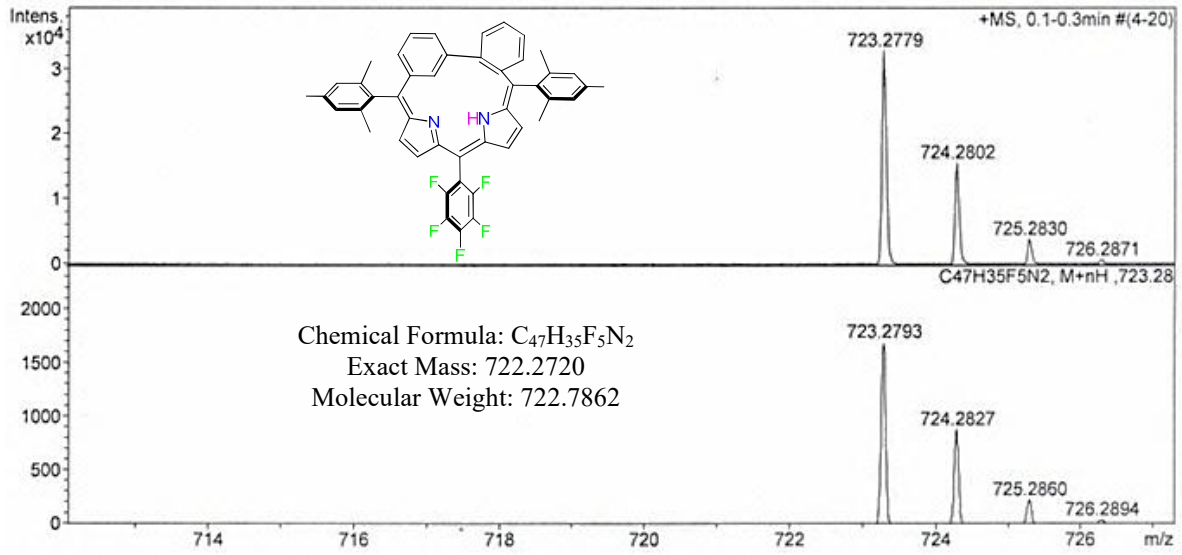


Fig. S1 HR-ESI-MS spectrum of **8**.

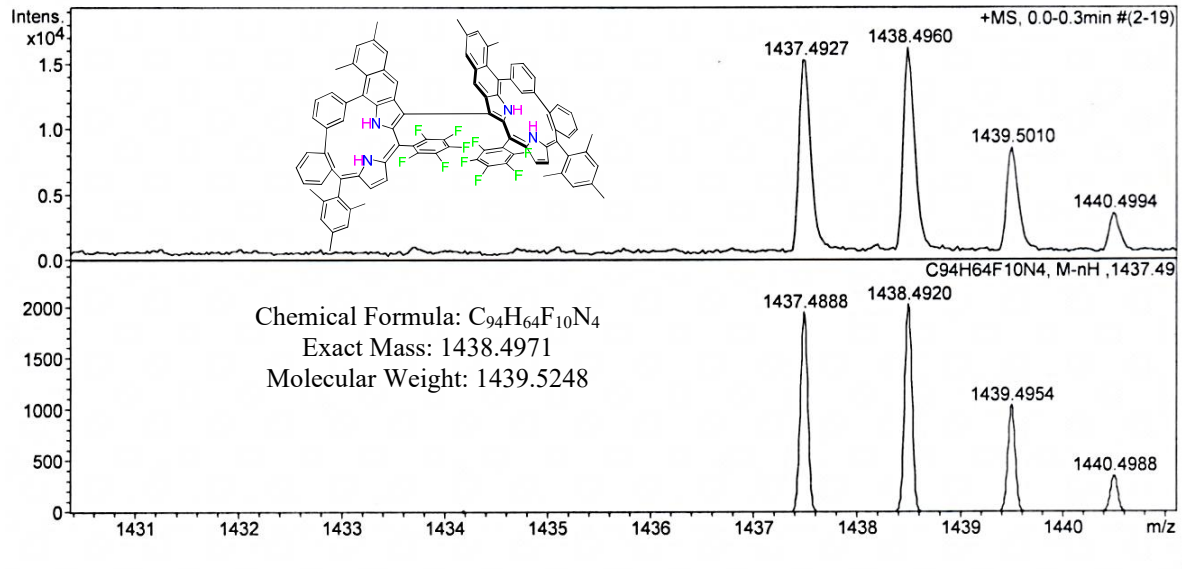


Fig. S2 HR-ESI-MS spectrum of **6**.

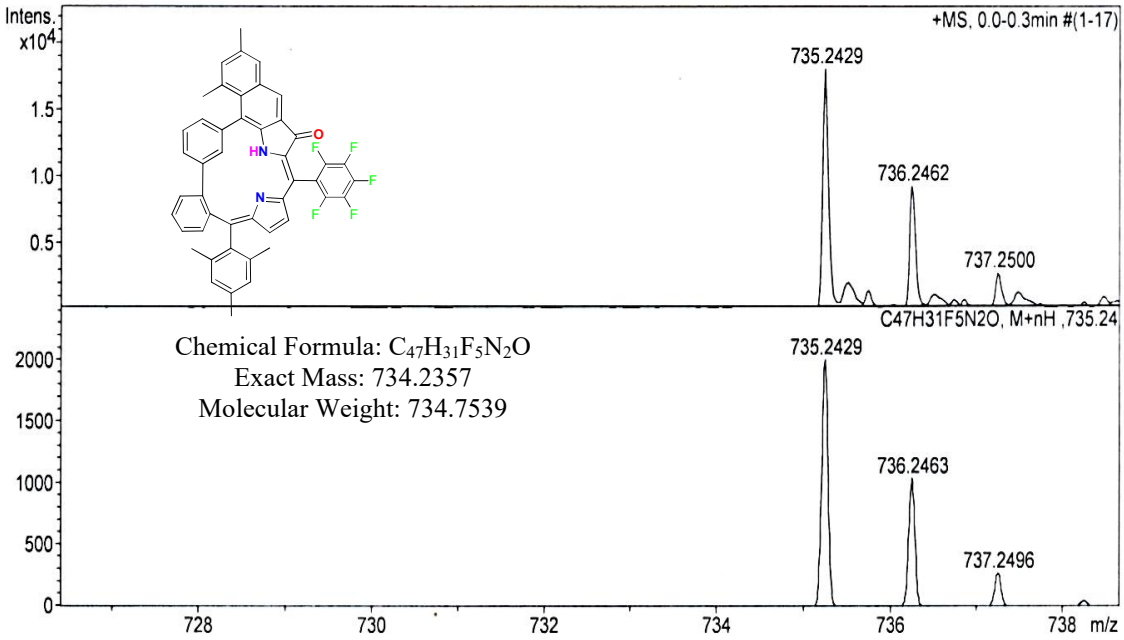


Fig. S3 HR-ESI-MS spectrum of **7**.

.

4. NMR spectral analyses:

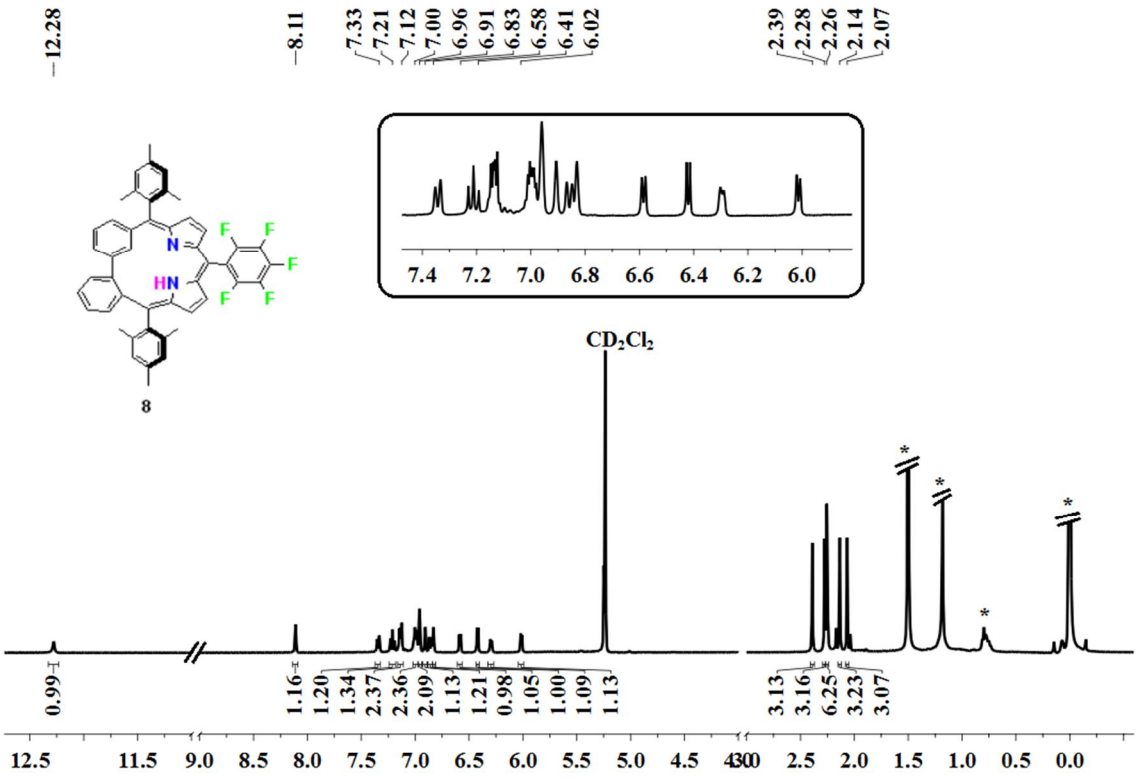


Fig. S4 ^{1}H-NMR spectrum of **8** in CD_2Cl_2 (*Residual solvents and impurity grease).

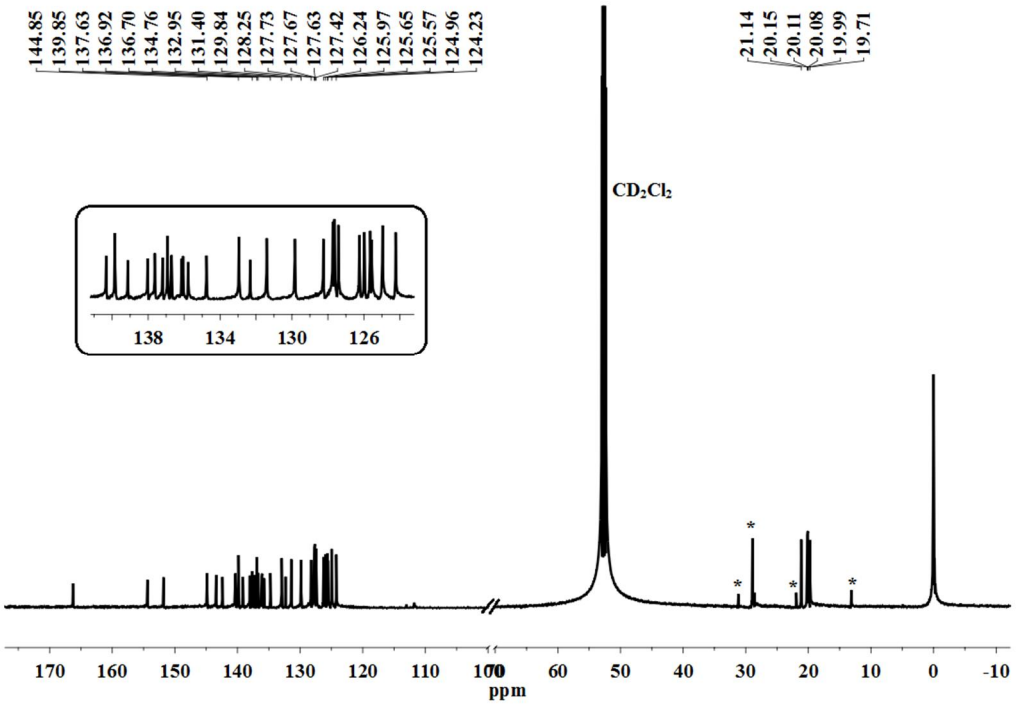


Fig. S5 ^{13}C-NMR spectrum of **8** in CD_2Cl_2 (*Residual solvents and impurity grease).

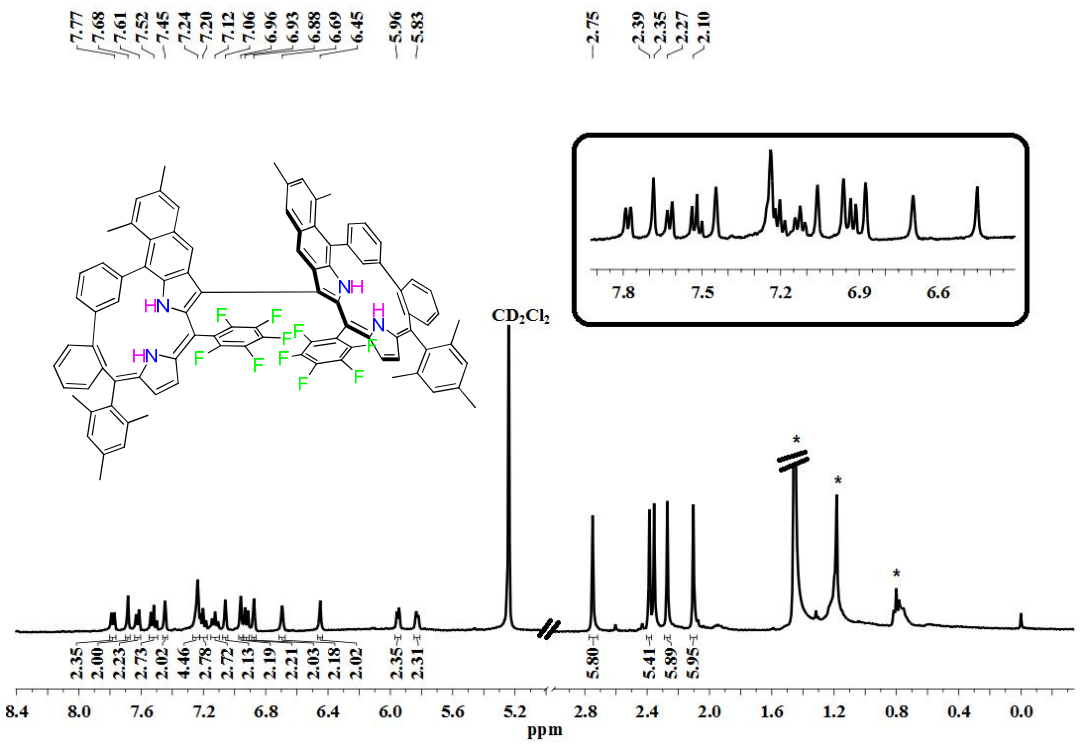


Fig. S6 ^{1}H-NMR spectrum of **6** in CD_2Cl_2 (*Residual solvents and impurity grease).

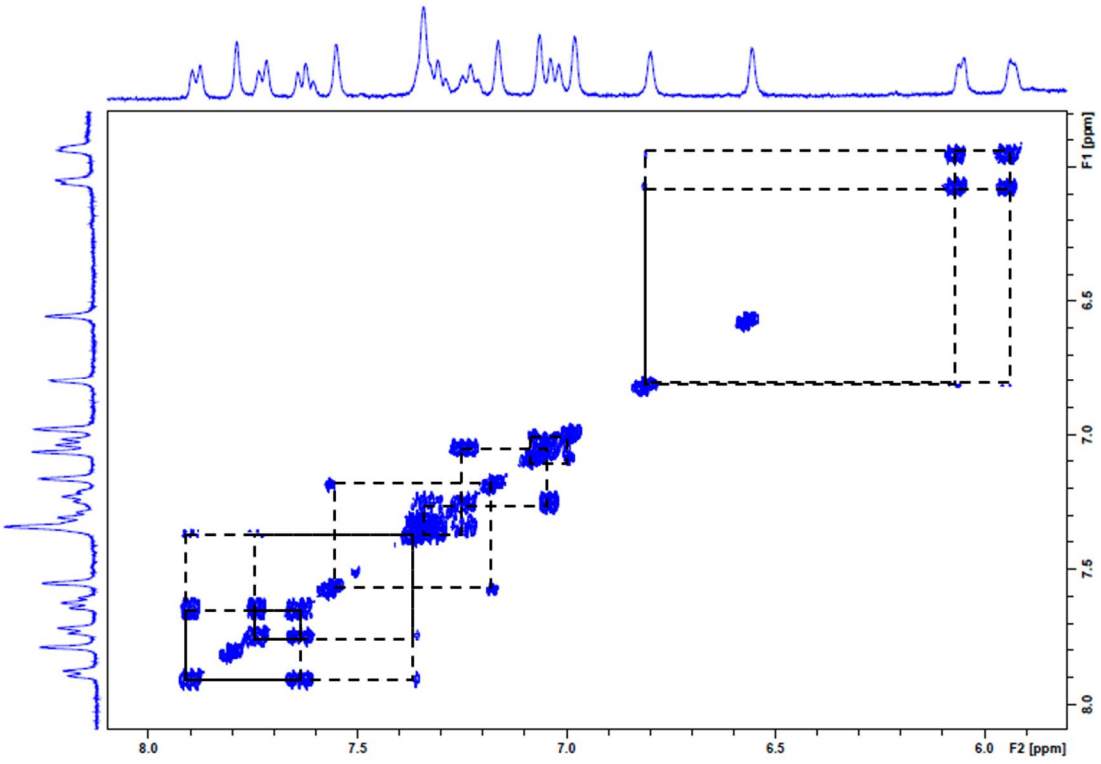


Fig. S7 Aromatic region of ^{1}H-^{1}H COSY spectrum of **6** in CD_2Cl_2.

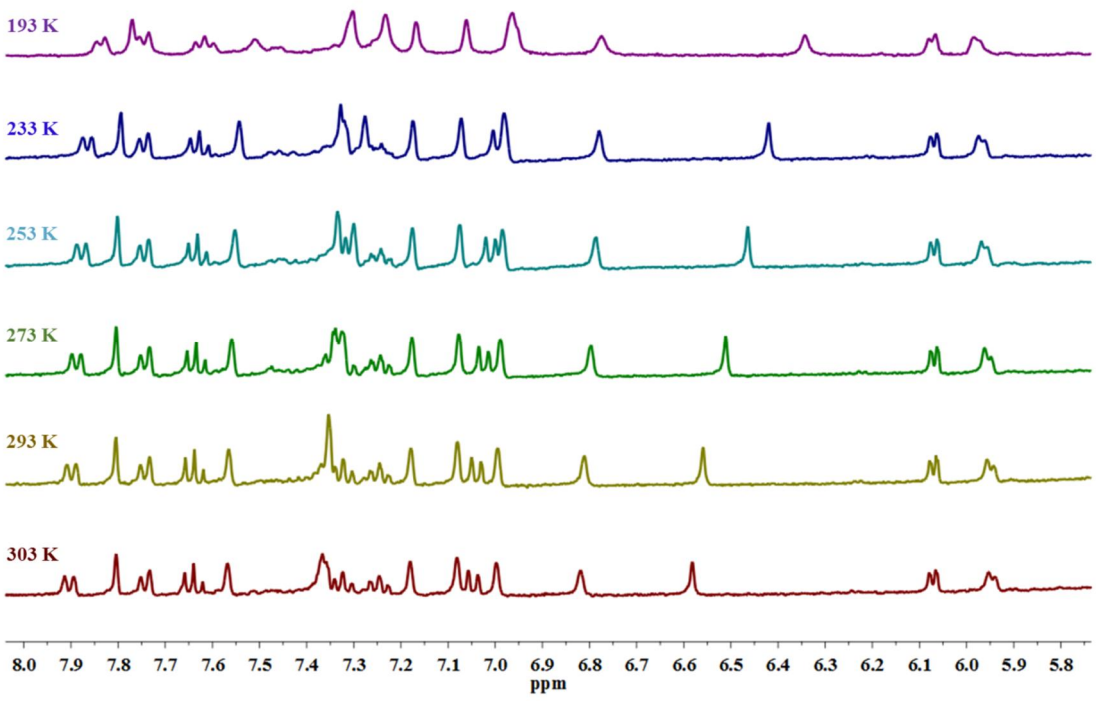


Fig. S8 Variable temperature ^{1}H-NMR spectra of **6** in CD_2Cl_2.

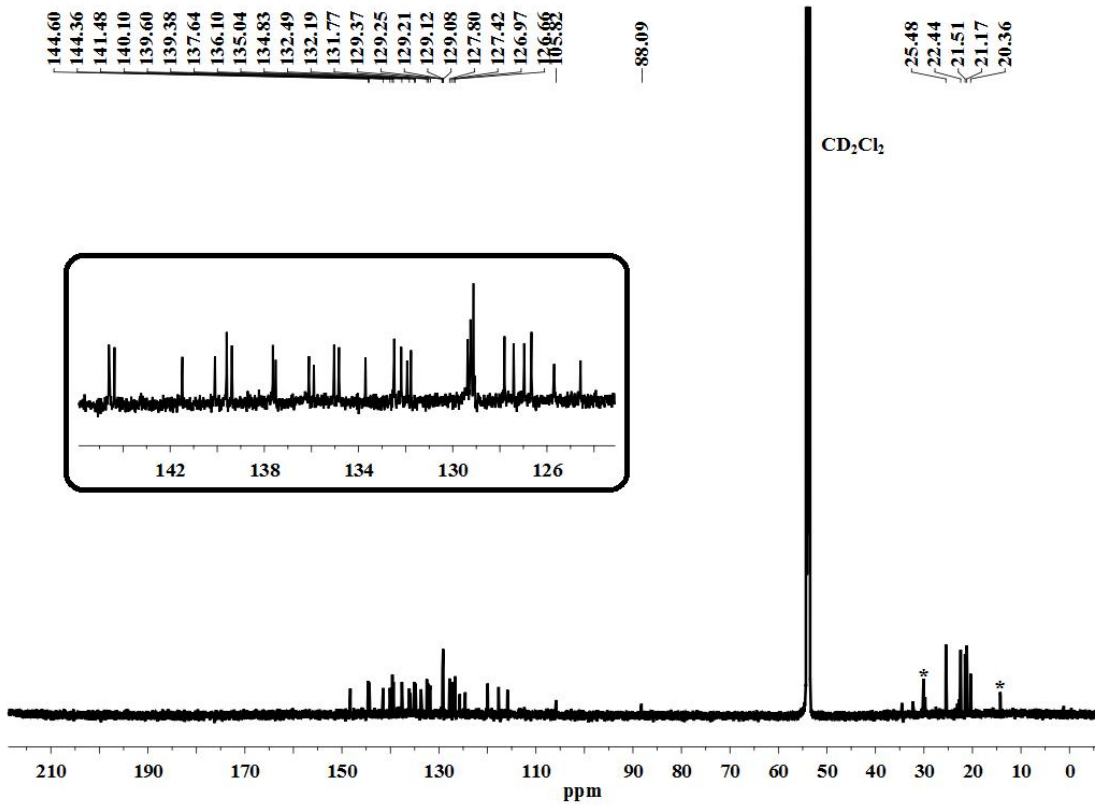


Fig. S9 ^{13}C-NMR spectrum of **6** in CD_2Cl_2 (*Residual solvents and impurity grease).

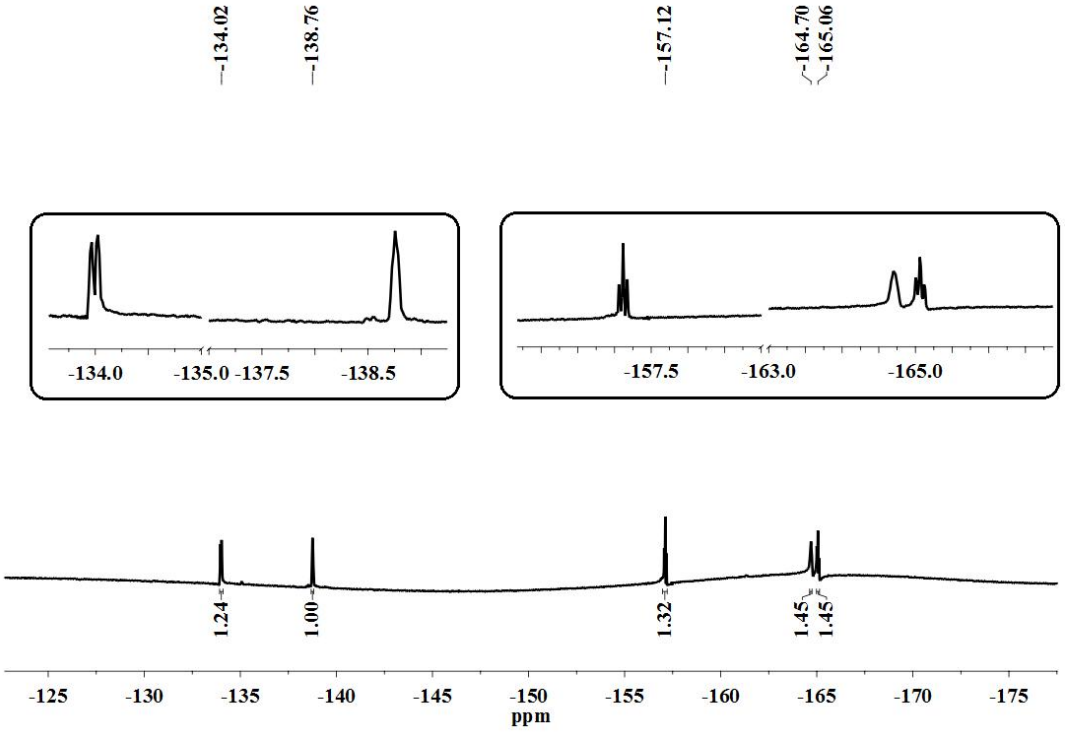


Fig. S10 ^{19}F-NMR spectrum of **6** in CD_2Cl_2.

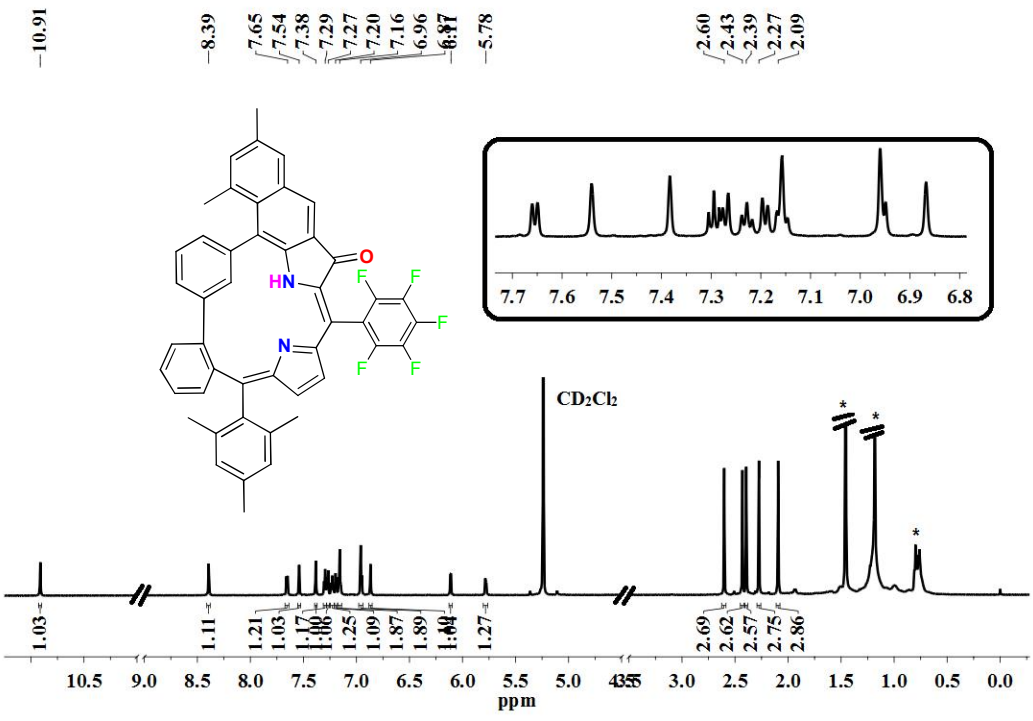


Fig. S11 ^{1}H-NMR spectrum of **7** in CD_2Cl_2 (*Residual solvents and impurity grease).

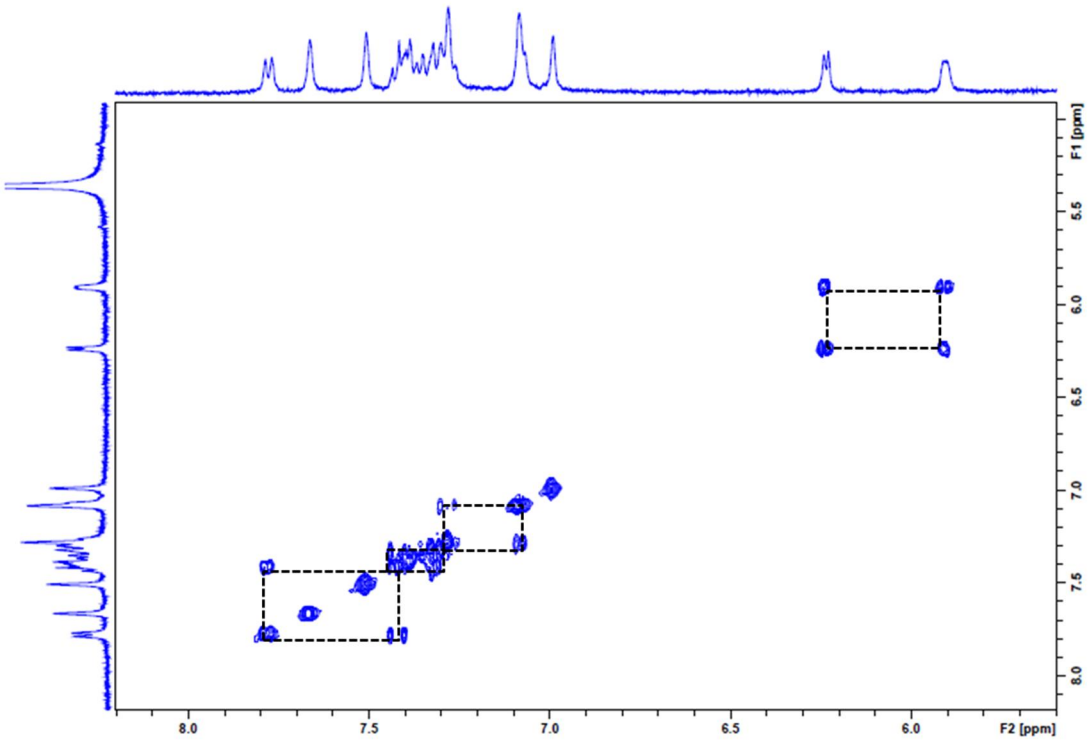


Fig. S12 Aromatic region of ^{1}H-^{1}H COSY spectrum of **7** in CD_2Cl_2.

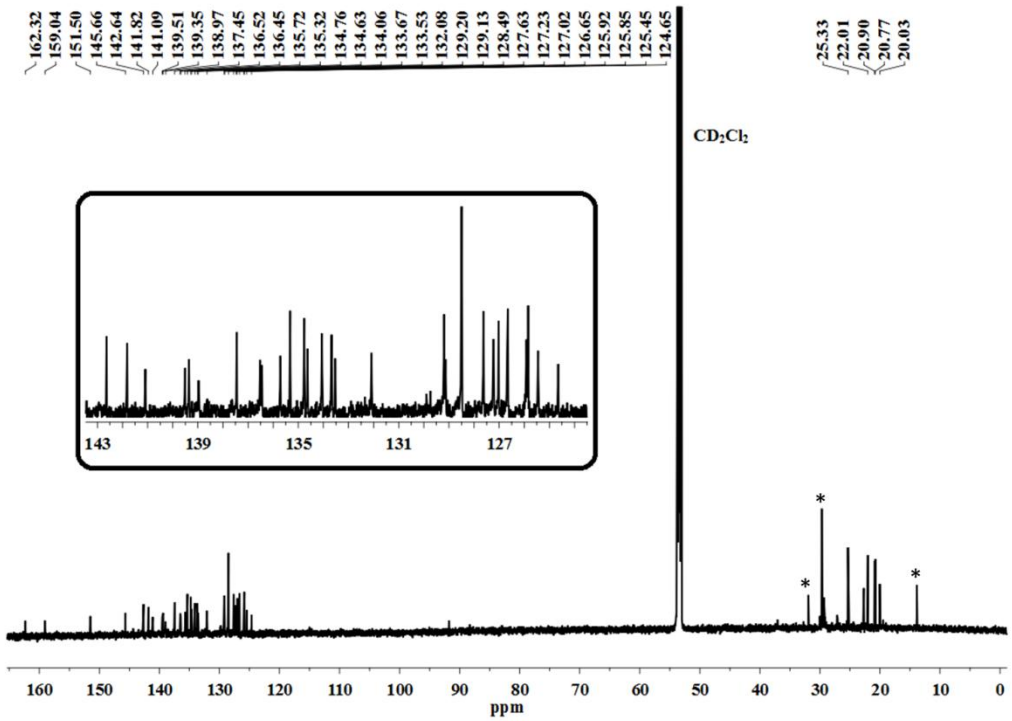


Fig. S13 ^{13}C-NMR spectrum of **7** in CD_2Cl_2 (*Residual solvents and impurity grease).

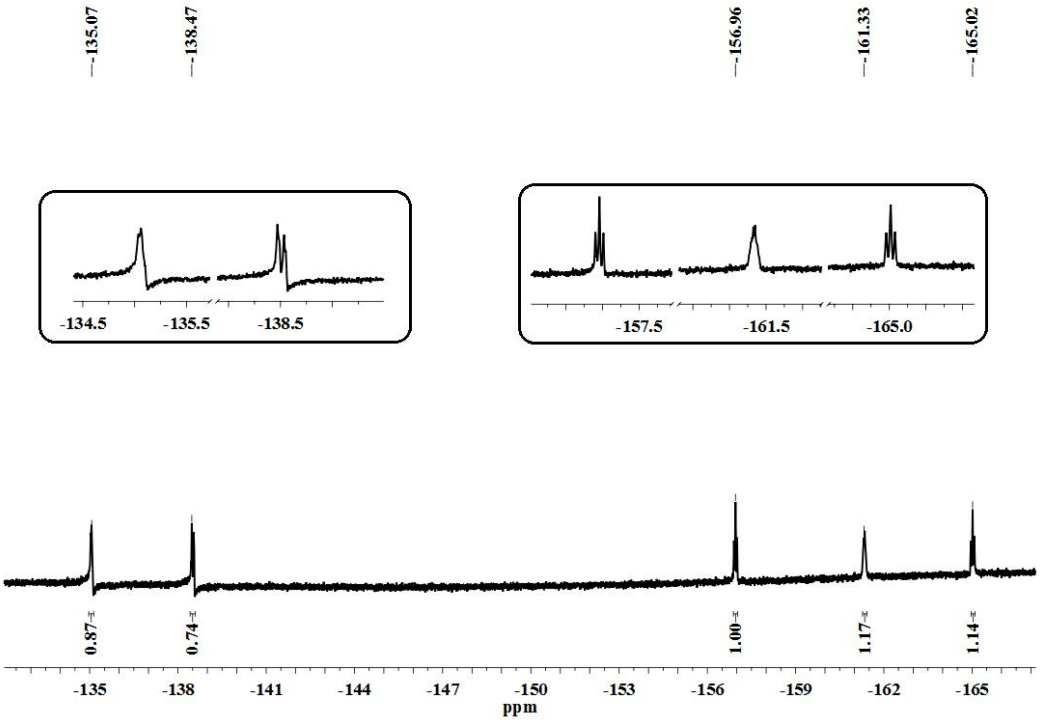


Fig. S14 ^{19}F-NMR spectrum of **7** in CD_2Cl_2.

5. IR spectral analysis

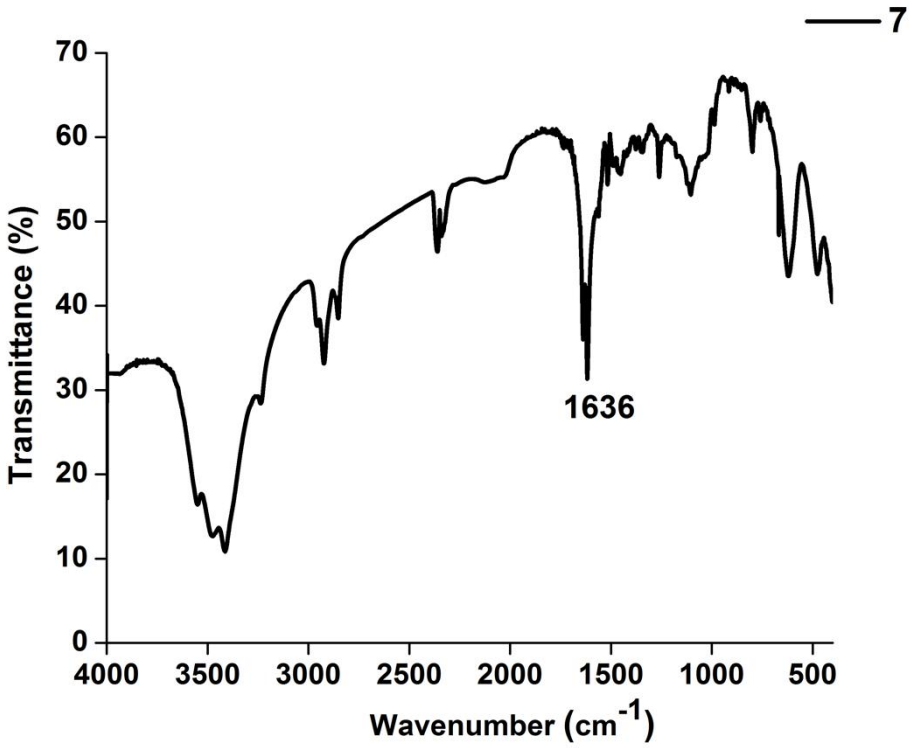


Fig. S15 FT-IR spectrum of **7**.

6. Single crystal X-ray structural analyses of 6 and 7

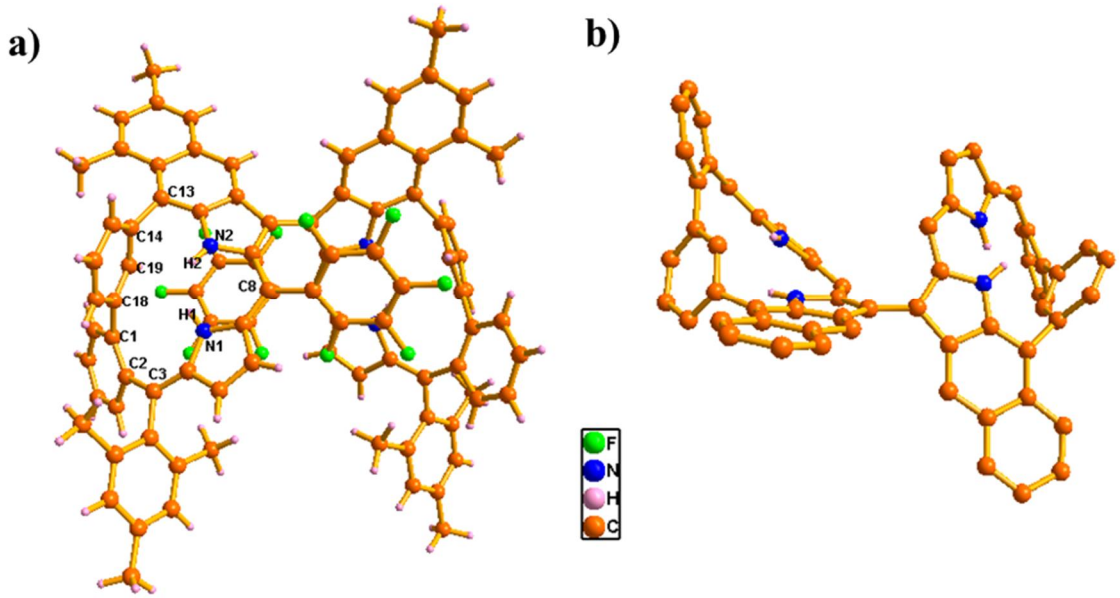


Fig. S16 Single crystal X-ray structure of **6**. a) Top view and b) side view. The *meso* aryl groups and peripheral hydrogen atoms are omitted for clarity in the side view.

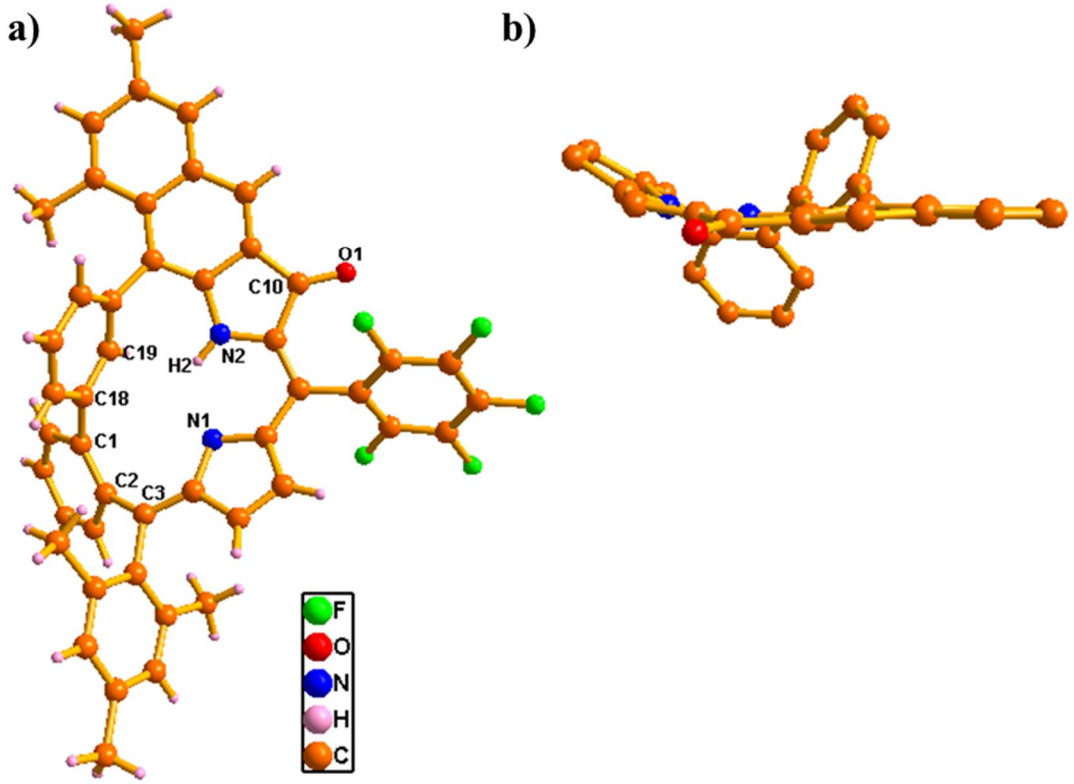


Fig. S17 Single crystal X-ray structure of **7**. a) Top view and b) side view. The *meso* aryl groups and peripheral hydrogen atoms are omitted for clarity in the side view.

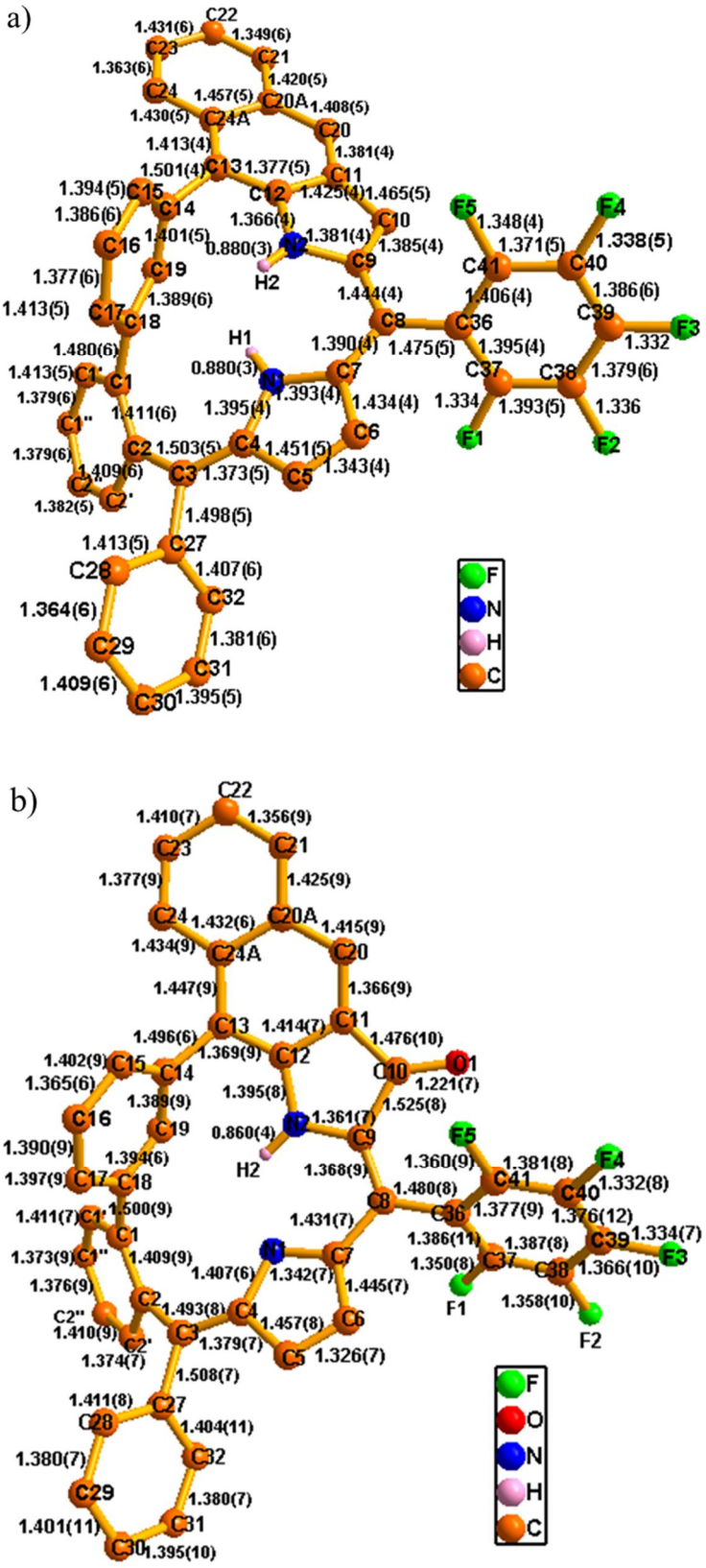


Fig. S18 Bond lengths in **6** (a) and **7** (b) in Å.

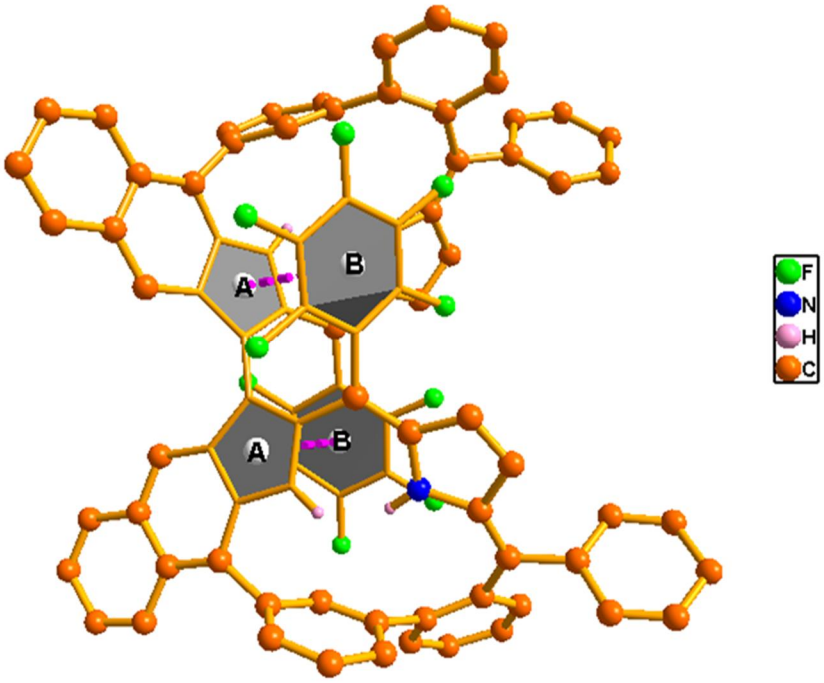


Fig. S19 Single crystal X-ray analysis of **6** with π-π interaction between *meso*-fused pyrrolic [Py(π)] unit **A** and *meso*-pentafluorophenyl group [C_6F_5(π)] **B**. The bond distance between [Py(π)] and [C_6F_5(π)] is 3.677Å.

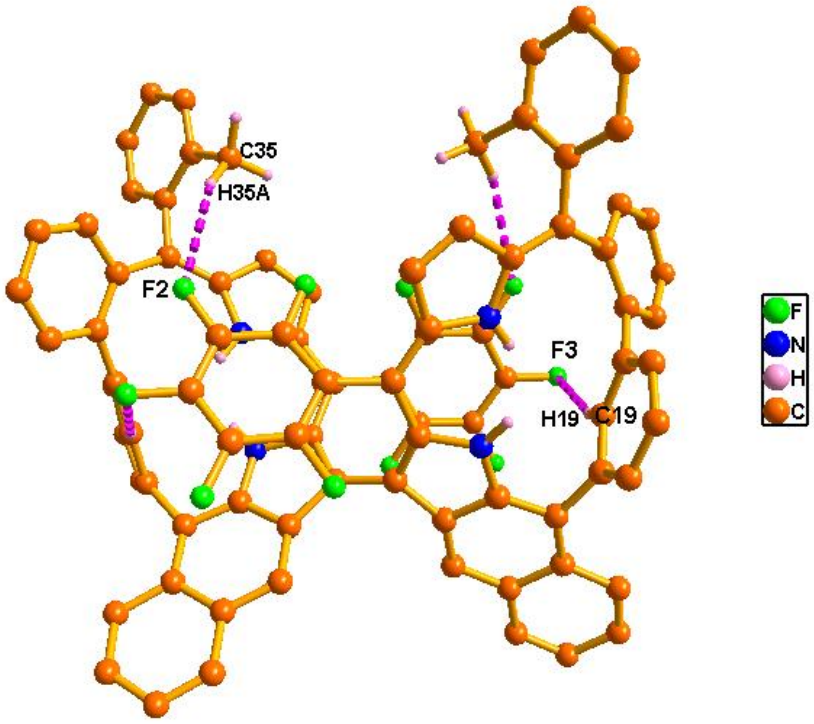


Fig. S20 Single crystal X-ray analysis of **6** with intramolecular hydrogen bonding interactions. The bond distances and angles are: C35-F2: 3.789(4)Å & C35-H35A…F2: 162.00(2)° and C19-F3: 3.536(3)Å & C19-H19…F3: 161.76(2)° respectively.

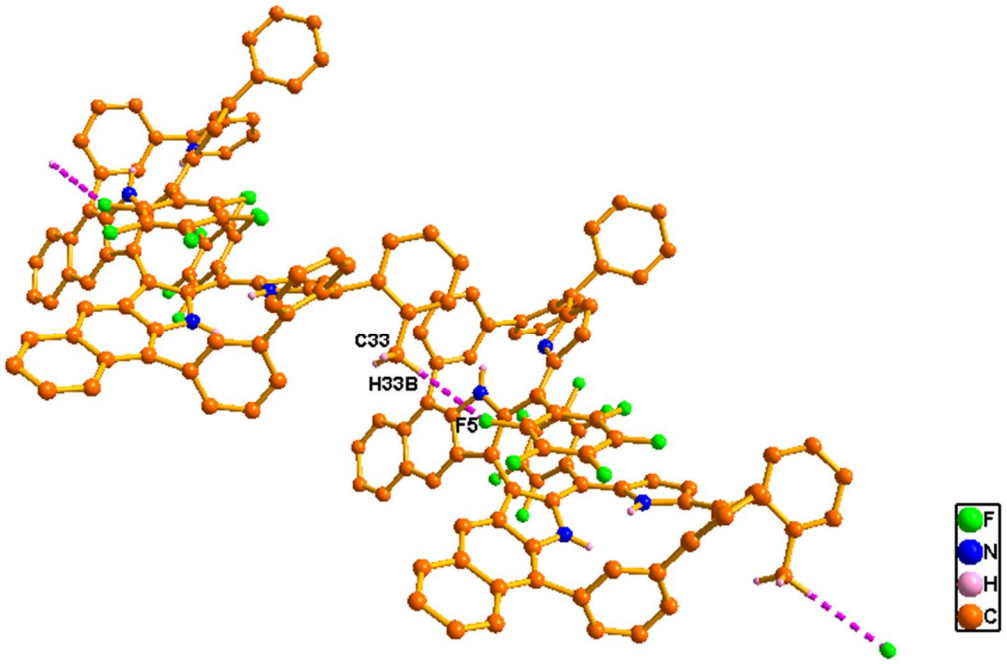


Fig. S21 Single crystal X-ray analysis of **6** with 1-D array. The bond distance and angle is: C33-F5: 3.736(4) Å and C33-H33B…F5: 150.65(2)°.

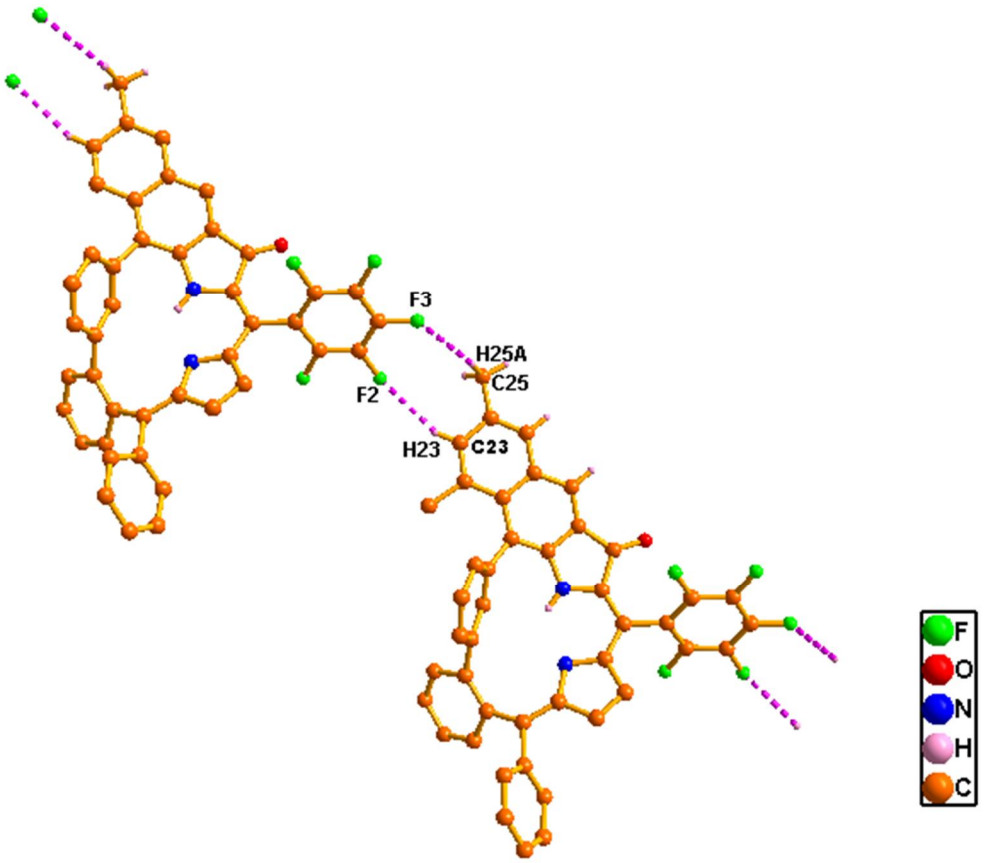


Fig. S22 Single crystal X-ray analysis of **7** with 1-D array. The bond distances and angles are: a) C23-F2: 3.562(7) Å & C23-H23...F2: 155.25(5)° and b) C25-F3: 3.683(9) Å & C25-H25A...F3: 163.23(6)°.

Table S1: Crystal data for **6** and **7**.

Crystal parameters	**6**	**7**
Formula	$C_{94}H_{64}F_{10}N_4$	$C_{47}H_{31}F_5N_2O$
M/g mol^{-1}	1439.49	755.48
T/K	100 K	113 K
Crystal dimensions/mm^3	0.38 × 0.26 × 0.22	0.93 × 0.35 × 0.27
Crystal system	monoclinic	triclinic
Space group	$C12/c1$	$P\bar{1}$
a/Å	24.2592(6)	10.4374(7)
b/Å	14.9349(6)	13.2672(8)
c/Å	21.0144(5)	16.3284(12)
α/°	90	71.893(4)
β/°	90.863(2)	73.259(7)
γ/°	90	69.076(6)
V/Å^3	7612.8(4)	1967.1(3)
Z	4	28
ρcalcd/mg m^{-3}	1.256	1.496
μ/mm^{-1}	0.744	1.834
F(000)	2984.0	885.0
Reflns. collected	27832	28432
Indep.reflns.[R(int)]	6937 [R(int) = 0.0885]	7189 [R(int) = 0.1887]
Max/min transmission	0.791, 0.855	0.725, 1.000
Data/restraints/parameters	6937/0/492	7189/0/501
GOF on F^2	1.055	1.026
Final R indices[$I > 2\sigma(I)$]	R_1 = 0.0900, wR_2 = 0.2422	R_1 = 0.1015, wR_2 = 0.2768
R indices (all data)	R_1 = 0.0998, wR_2 = 0.2506	R_1 = 0.1592, wR_2 = 0.3138

The crystals have been deposited in the Cambridge Crystallographic Data Centre and the **CCDC** numbers for each are **CCDC 1954598** (**6**) and **CCDC 1954599** (**7**). respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7. Electronic absorption spectral analyses

Table S2*:* Electronic absorption spectral data of **6-8**.

Compound	λ_{max} (nm) (ε x 10^4 [$M^{-1}cm^{-1}$])
6	355 (1.20), 505 (1.11)
7	355 (1.10), 500 (0.47), 695 (0.29)
8	365 (3.14), 605 (1.71)

DFT calculations were carried out using the Gaussian 16 program.[S2] All structures were fully optimized without any symmetry restriction. All calculations were performed with a restricted B3LYP (Becke's three-parameter hybrid exchange and Lee-Yang-Parr correlation functionals)[S3] level, employing the basis sets 6-31G(d, p)[S4] for carbon, hydrogen, nitrogen, oxygen and fluorine atoms. The integral equation formalism for the polarizable continuum model (IEF-PCM) used to treat solvent effect.[S5]

The experimental data (Table S2) are corroborated with computational calculations. The electronic absorption spectral pattern of **6** and **7** are similar to that of simulated spectra obtained by TD-DFT method (Fig. S25-S26). The calculated oscillator strength at λ_{max} with percentage of orbital contributions are listed (Table S3).

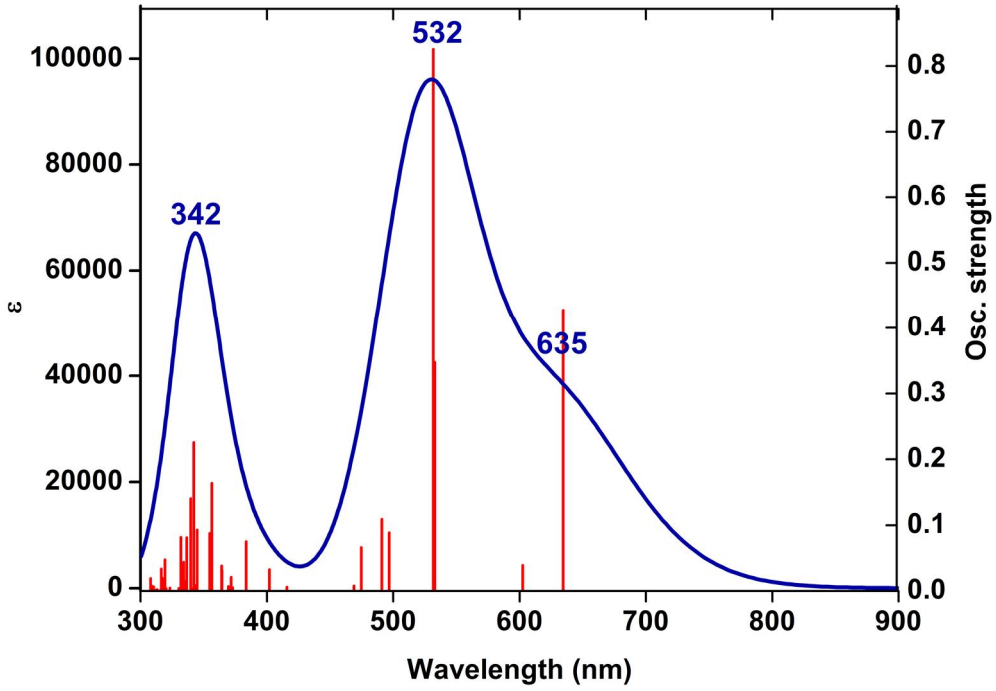


Fig. S23 Simulated electronic absorption spectrum of **6**.

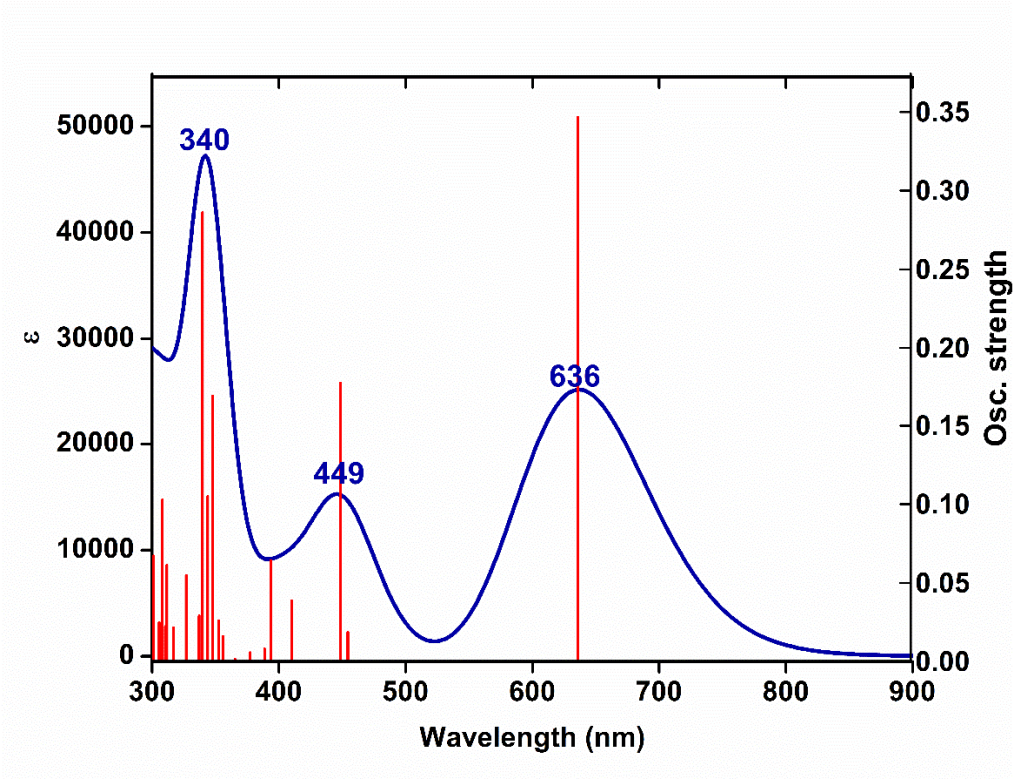


Fig. S24 Simulated electronic absorption spectrum of **7**.

Table S3*:* λ_{max} (nm), oscillator strength **f**, and compositions of the major electronic transitions in **6** and **7** at TD-DFT/IEF-PCM/6-31G(d,p) level.

Compd.	λ_{max} (nm)	Osc. strength, **f**	Major contributions
6	342	0.2256	H-5->L+1 (13%), H-3->L+2 (24%), HOMO->L+8 (29%), HOMO->L+11 (19%)
	532	0.8258	H-1->LUMO (69%), HOMO->L+1 (28%)
	635	0.4274	HOMO->LUMO (98%)
7	340	0.2857	H-9->LUMO (17%), H-8->LUMO (12%), H-1->L+1 (32%), HOMO->L+2 (16%)
	449		
	636	0.1778	H-1->LUMO (89%)
		0.3467	HOMO->LUMO (98%)

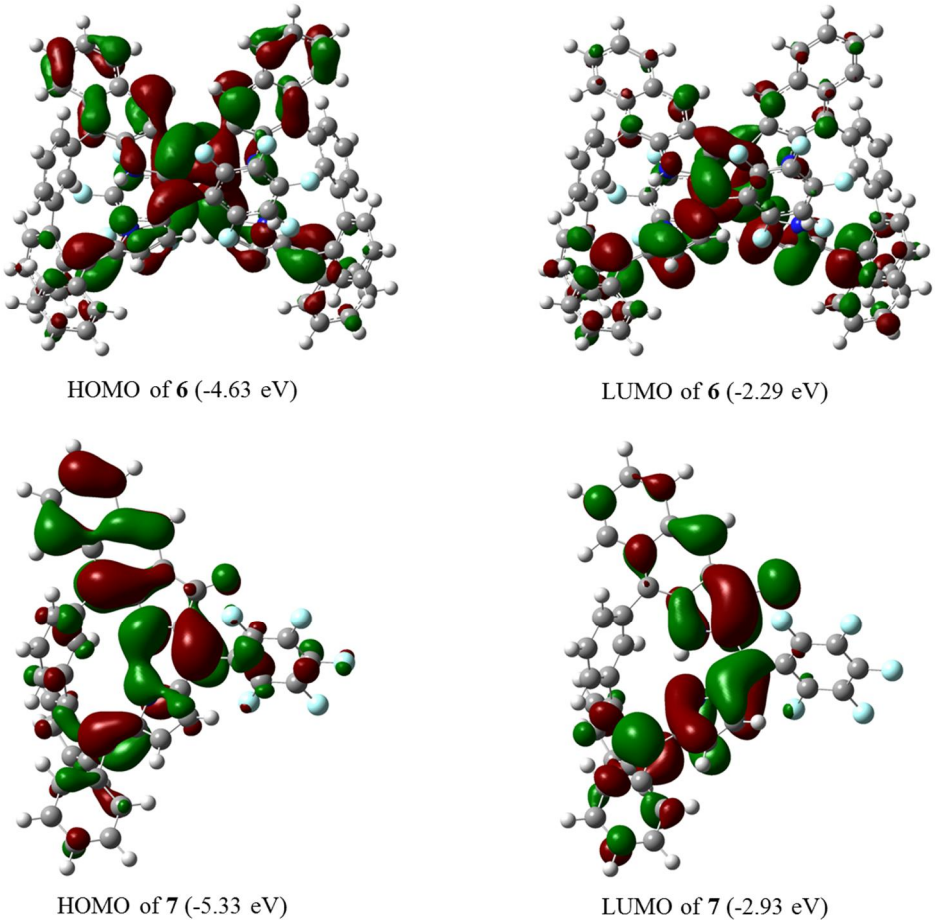


Fig. S25 HOMO and LUMO distributions for **6** and **7**

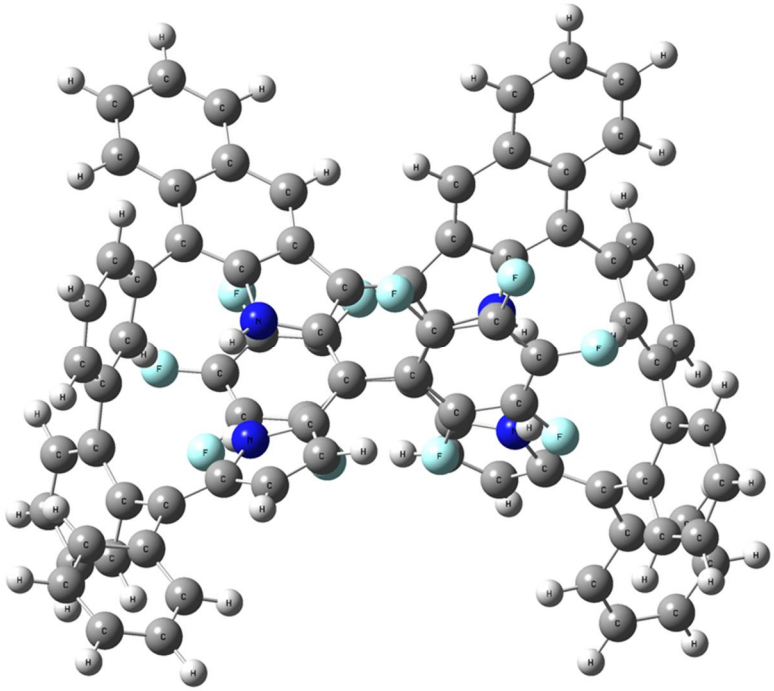


Fig. S26 Optimized structure of **6** calculated at the B3LYP/ 6-31G (d, p) level.

Table S4. Standard orientation of **6**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	-0.914389	1.909336	1.116416
2	9	0	0.872700	-1.654618	3.684304
3	9	0	-3.281012	1.600826	2.340898
4	9	0	-3.590499	-0.279917	4.291810
5	9	0	-1.482852	-1.887311	4.985870
6	7	0	2.871283	-1.205830	0.333985
7	1	0	3.656358	-0.764490	0.785360
8	7	0	3.435552	1.396848	1.066169
9	1	0	3.419283	1.349137	0.056846
10	6	0	2.301139	1.119659	1.843597
11	6	0	-1.006231	0.985193	2.084699
12	6	0	0.073795	0.144345	2.365146
13	6	0	1.321619	0.184570	1.555773
14	6	0	1.553711	-0.907085	0.628494
15	6	0	1.623817	-2.832037	-0.608468
16	6	0	4.331345	2.233111	1.748064
17	6	0	2.955486	-2.363389	-0.389535
18	6	0	3.726050	2.427159	3.059511
19	1	0	4.206666	2.942406	3.876739
20	6	0	-2.232153	0.846659	2.724345
21	6	0	2.506013	1.830638	3.087785
22	1	0	1.831110	1.775032	3.930300
23	6	0	0.733060	-1.869587	0.023120
24	6	0	-0.122457	-0.818117	3.362979
25	6	0	-1.333562	-0.957684	4.036865
26	6	0	5.505341	2.749996	1.255302
27	6	0	3.966424	-4.187060	-1.547473
28	6	0	-2.400519	-0.127853	3.701752
29	6	0	5.359337	-2.225272	-0.446155
30	6	0	5.975873	2.610900	-0.166263
31	6	0	1.477272	-4.006469	-1.337281
32	1	0	0.493788	-4.415422	-1.550738
33	6	0	2.628226	-4.694503	-1.798110
34	6	0	6.312793	0.038630	-0.300334
35	6	0	5.475542	-0.903810	-0.911604
36	1	0	4.834503	-0.579634	-1.725108
37	6	0	6.332942	1.425800	-0.860544
38	6	0	4.119835	-2.971604	-0.831131
39	6	0	6.303260	3.694746	2.084970
40	6	0	5.078814	-4.919228	-2.052034
41	6	0	6.216988	-2.637382	0.583863
42	1	0	6.146797	-3.649882	0.970130
43	6	0	7.703457	3.553742	2.147936
44	6	0	7.104210	-1.725058	1.163549
45	1	0	7.755743	-2.051174	1.969242
46	6	0	8.481632	4.415830	2.915271
47	1	0	9.557995	4.275187	2.955638
48	6	0	7.129074	-0.389200	0.757839
49	1	0	7.793297	0.314462	1.249738
50	6	0	6.728229	1.525410	-2.209022
51	1	0	7.003460	0.612556	-2.728226
52	6	0	2.500755	-5.911780	-2.531092
53	1	0	1.500465	-6.293820	-2.718781

54	6	0	7.884589	5.458099	3.628870
55	6	0	6.795618	2.741308	-2.877608
56	1	0	7.111277	2.774317	-3.916035
57	6	0	6.502993	5.633749	3.554347
58	1	0	6.029023	6.457230	4.081073
59	6	0	3.599574	-6.593407	-2.992916
60	6	0	6.067981	3.835014	-0.866023
61	1	0	5.805513	4.746364	-0.338495
62	6	0	4.904013	-6.088776	-2.751862
63	1	0	5.767597	-6.630222	-3.127358
64	6	0	6.462352	3.910827	-2.195170
65	1	0	6.506290	4.875113	-2.692725
66	6	0	5.722757	4.768197	2.787138
67	9	0	0.914805	1.908379	-1.117098
68	9	0	-0.873600	-1.655219	-3.684549
69	9	0	3.281227	1.599077	-2.341736
70	9	0	3.589948	-0.281887	-4.292613
71	9	0	1.481789	-1.888718	-4.986320
72	7	0	-2.871239	-1.205939	-0.333672
73	1	0	-3.656340	-0.764774	-0.785169
74	7	0	-3.435606	1.396576	-1.066574
75	1	0	-3.419311	1.349153	-0.057241
76	6	0	-2.301305	1.119090	-1.844028
77	6	0	1.006287	0.984098	-2.085293
78	6	0	-0.074019	0.143553	-2.365571
79	6	0	-1.321713	0.184119	-1.556005
80	6	0	-1.553698	-0.907264	-0.628392
81	6	0	-1.623673	-2.831922	0.609035
82	6	0	-4.331559	2.232470	-1.748737
83	6	0	-2.955374	-2.363359	0.390094
84	6	0	-3.726466	2.425925	-3.060351
85	1	0	-4.207227	2.940706	-3.877788
86	6	0	2.232120	0.845153	-2.725020
87	6	0	-2.506382	1.829478	-3.088509
88	1	0	-1.831588	1.773544	-3.931092
89	6	0	-0.732978	-1.869612	-0.022817
90	6	0	0.121852	-0.819007	-3.363376
91	6	0	1.332863	-0.958999	-4.037345
92	6	0	-5.505512	2.749462	-1.255942
93	6	0	-3.966158	-4.186741	1.548634
94	6	0	2.400092	-0.129458	-3.702393
95	6	0	-5.359222	-2.225264	0.446949
96	6	0	-5.975379	2.610864	0.165916
97	6	0	-1.477034	-4.006130	1.338195
98	1	0	-0.493516	-4.414959	1.551741
99	6	0	-2.627927	-4.694065	1.799321
100	6	0	-6.312467	0.038740	0.300852
101	6	0	-5.475368	-0.903751	0.912270
102	1	0	-4.834286	-0.579560	1.725717
103	6	0	-6.332155	1.426013	0.860759
104	6	0	-4.119661	-2.971487	0.831968
105	6	0	-6.303878	3.693697	-2.085669
106	6	0	-5.078489	-4.918806	2.053468
107	6	0	-6.216877	-2.637403	-0.583050
108	1	0	-6.146764	-3.649936	-0.969246
109	6	0	-7.704142	3.552757	-2.147545
110	6	0	-7.103985	-1.725044	-1.162855
111	1	0	-7.755519	-2.051171	-1.968542
112	6	0	-8.482805	4.414319	-2.914974

113	1	0	-9.559205	4.273710	-2.954465
114	6	0	-7.128717	-0.389128	-0.757329
115	1	0	-7.792811	0.314528	-1.249410
116	6	0	-6.726532	1.526075	2.209472
117	1	0	-7.001540	0.613421	2.729148
118	6	0	-2.500359	-5.911121	2.532653
119	1	0	-1.500044	-6.293071	2.720386
120	6	0	-7.886208	5.456020	-3.629771
121	6	0	-6.793353	2.742191	2.877716
122	1	0	-7.108297	2.775547	3.916348
123	6	0	-6.504553	5.631665	-3.556302
124	1	0	-6.030908	6.454758	-4.083927
125	6	0	-3.599125	-6.592653	2.994746
126	6	0	-6.066959	3.835215	0.865311
127	1	0	-5.804760	4.746370	0.337305
128	6	0	-4.903599	-6.088146	2.753624
129	1	0	-5.767139	-6.629520	3.129323
130	6	0	-6.460470	3.911478	2.194692
131	1	0	-6.504031	4.875920	2.691975
132	6	0	-5.723828	4.766650	-2.788996
133	1	0	-3.473528	-7.517714	3.549634
134	1	0	-6.076534	-4.528469	1.876584
135	1	0	-8.180273	2.755390	-1.585408
136	1	0	-8.494046	6.131088	-4.224691
137	1	0	-4.655797	4.939793	-2.707073
138	1	0	3.474049	-7.518635	-3.547541
139	1	0	6.076833	-4.528797	-1.875208
140	1	0	8.179920	2.755907	1.586740
141	1	0	8.492053	6.133578	4.223707
142	1	0	4.654763	4.941222	2.704439

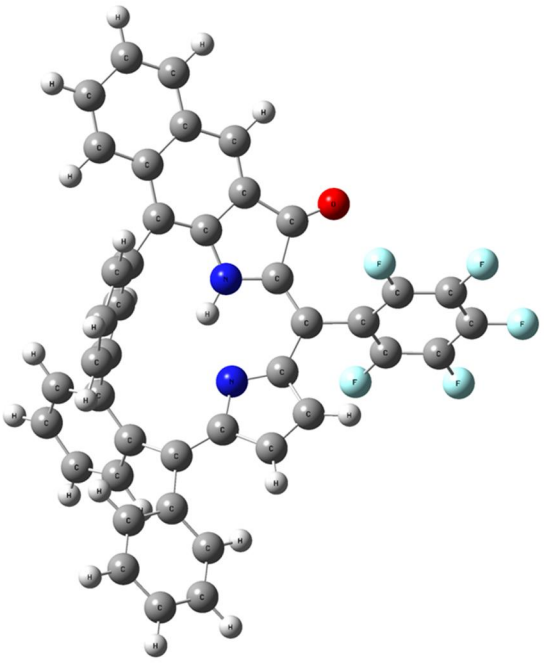


Fig. S27 Optimized structure of **7** calculated at the B3LYP/ 6-31G (d, p) level.

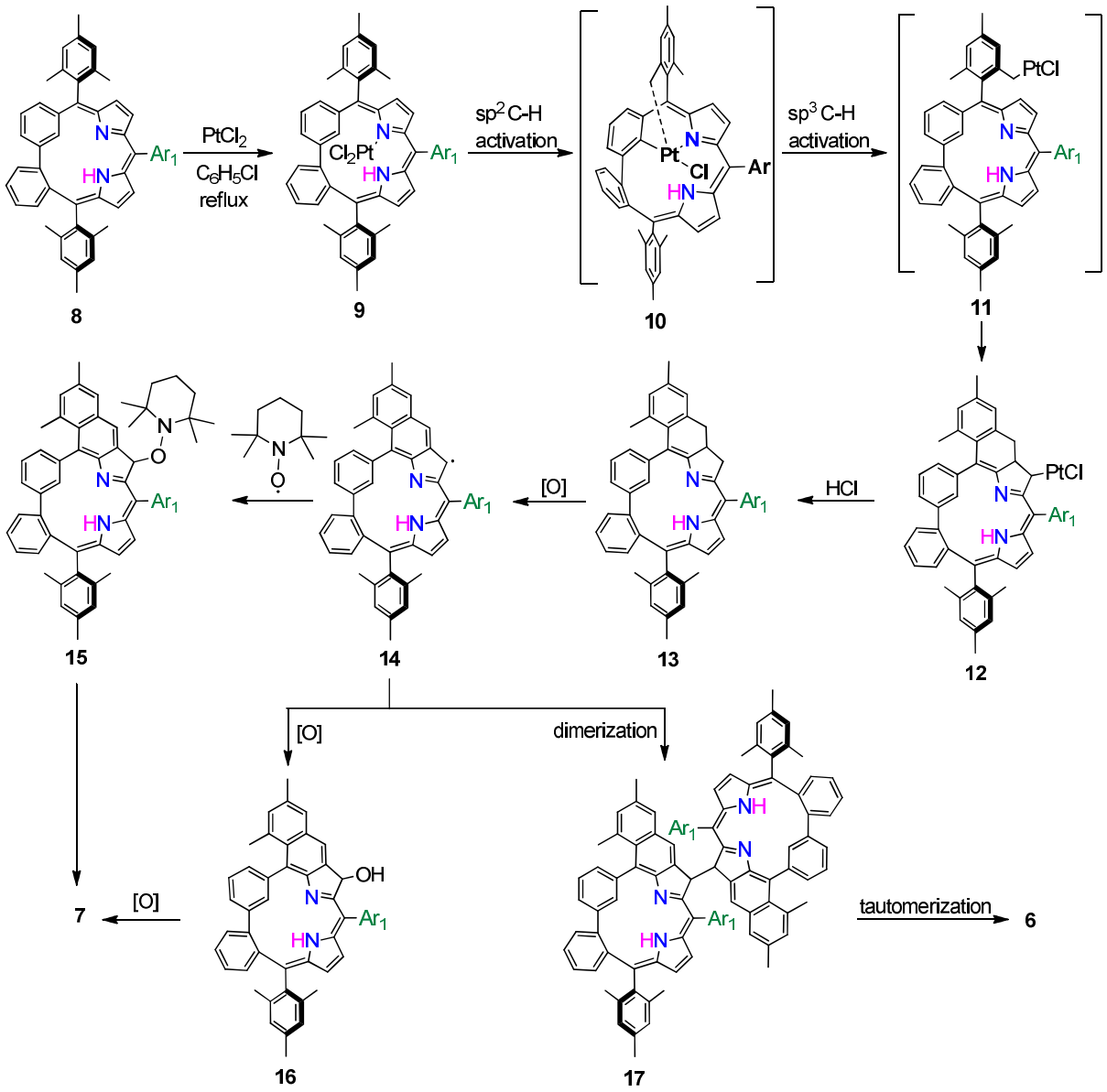
Table S5. Standard orientation of **7**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	-1.511266	-3.495209	1.850851
2	9	0	-3.370762	-5.450087	1.752437
3	9	0	-5.445440	-5.278232	-0.017087
4	9	0	-5.625776	-3.139698	-1.701793
5	9	0	-3.760013	-1.201198	-1.639327
6	8	0	-4.268266	0.346348	0.694183
7	7	0	0.909607	-0.879586	0.279170
8	7	0	-0.875557	1.082563	0.347877
9	1	0	0.107469	0.805189	0.295331
10	6	0	3.521490	1.245949	1.057907
11	6	0	4.751225	1.367648	3.173416
12	1	0	5.116542	1.961073	4.006139
13	6	0	4.015962	1.969407	2.158462
14	1	0	3.819701	3.036595	2.197383
15	6	0	3.777111	-0.144222	0.987899
16	6	0	5.020118	0.002090	3.099495
17	1	0	5.593940	-0.493456	3.876674
18	6	0	4.549681	-0.727973	2.015355
19	1	0	4.762309	-1.790549	1.961942
20	6	0	3.332047	-1.124439	-0.060211
21	6	0	2.026487	-1.475544	-0.318903
22	6	0	1.570611	-2.589904	-1.162529
23	1	0	2.191675	-3.199486	-1.800950
24	6	0	0.234390	-2.700623	-0.973280
25	1	0	-0.441971	-3.413184	-1.425341
26	6	0	-0.150010	-1.593653	-0.093752
27	6	0	-1.531908	-1.214941	0.192018
28	6	0	-1.834914	0.114753	0.379156
29	6	0	-3.170075	0.844282	0.527242
30	6	0	-2.810361	2.284640	0.409392
31	6	0	-1.400066	2.358847	0.260966
32	6	0	-0.714192	3.521588	-0.040549
33	6	0	0.720887	3.346132	-0.400590
34	6	0	1.204639	3.616081	-1.691270
35	1	0	0.590092	4.173308	-2.391738
36	6	0	2.436179	3.101035	-2.097715
37	1	0	2.795994	3.303923	-3.102306
38	6	0	3.188359	2.286980	-1.247525
39	1	0	4.126548	1.864071	-1.593095
40	6	0	2.744699	2.037411	0.057793
41	6	0	1.540986	2.617693	0.473629
42	1	0	1.194247	2.423473	1.483899
43	6	0	-3.569966	3.424882	0.329420
44	1	0	-4.650571	3.382045	0.433433
45	6	0	-2.924516	4.670519	0.082161
46	6	0	-3.674702	5.873000	0.004624
47	1	0	-4.749550	5.820976	0.156783
48	6	0	-3.065911	7.080714	-0.255400
49	6	0	-1.666717	7.132475	-0.446302
50	1	0	-1.186839	8.087105	-0.641891
51	6	0	-0.902555	5.986081	-0.379642

52	6	0	-1.493943	4.722481	-0.119852
53	6	0	4.452176	-1.882932	-0.686417
54	6	0	5.522506	-1.180052	-1.270937
55	6	0	6.582316	-1.855432	-1.869247
56	1	0	7.387289	-1.291309	-2.330959
57	6	0	6.616331	-3.252041	-1.867985
58	6	0	5.583777	-3.964307	-1.258295
59	1	0	5.614176	-5.049467	-1.226535
60	6	0	4.512938	-3.288690	-0.672762
61	6	0	-2.580634	-2.261383	0.129503
62	6	0	-2.514615	-3.382344	0.967342
63	6	0	-3.465553	-4.397696	0.929514
64	6	0	-4.524787	-4.310738	0.030390
65	6	0	-4.618410	-3.214495	-0.823466
66	6	0	-3.650403	-2.216547	-0.773697
67	1	0	-3.654877	7.990858	-0.310128
68	1	0	0.172896	6.039945	-0.513863
69	1	0	3.731395	-3.849508	-0.171836
70	1	0	7.448557	-3.778848	-2.325062
71	1	0	5.514014	-0.094964	-1.258527

8. The proposed mechanism for the formation of 6 and 7

Mechanistically, the formation of **6** and **7** are not known at this stage, however, the preliminary investigations revealed that these products are achieved via simultaneous C-H activations, fusion and radical formation.[S6] To support, two of the intermediates are elucidated by mass spectral analyses and shown in Fig. S28-S29.



Scheme S1. The plausible mechanism for the formation of **6** and **7**.

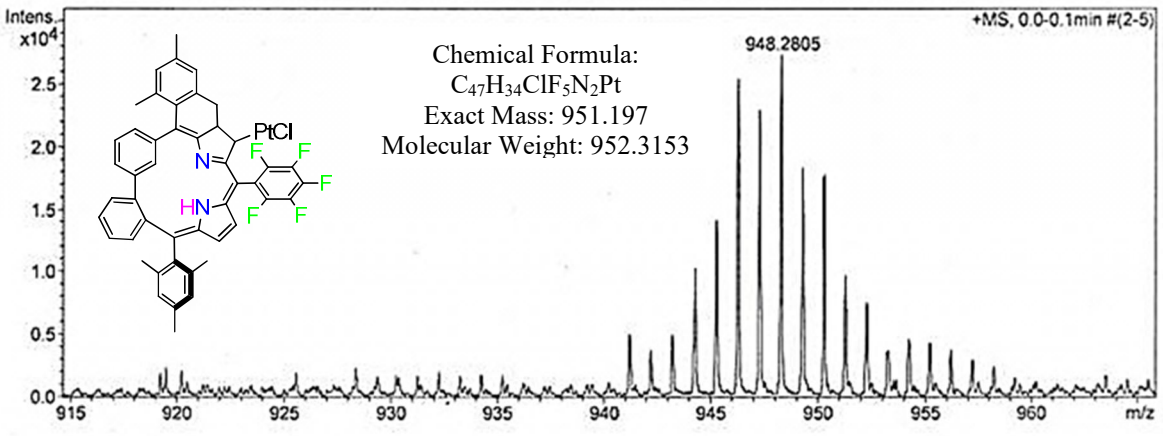


Fig. S28. ESI-MS spectrum of **12** observed as (M-3) from the reaction crude.

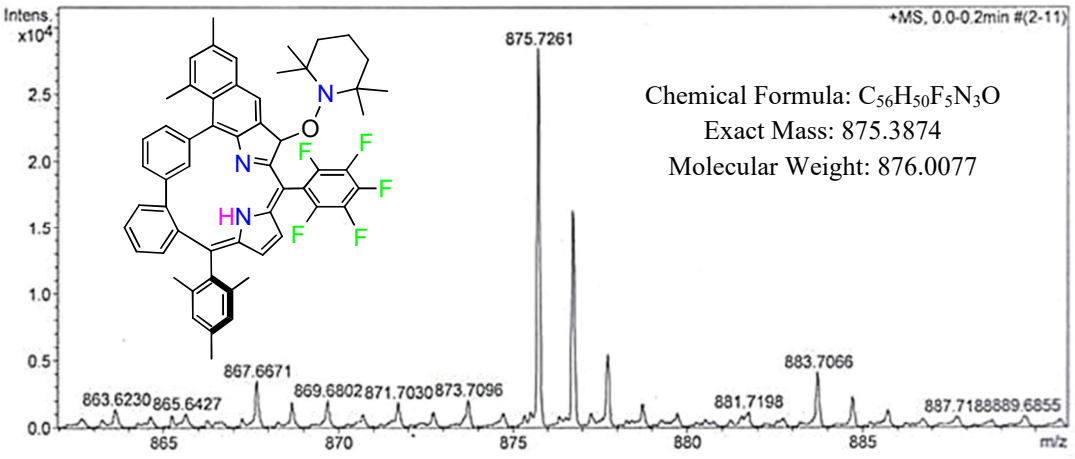
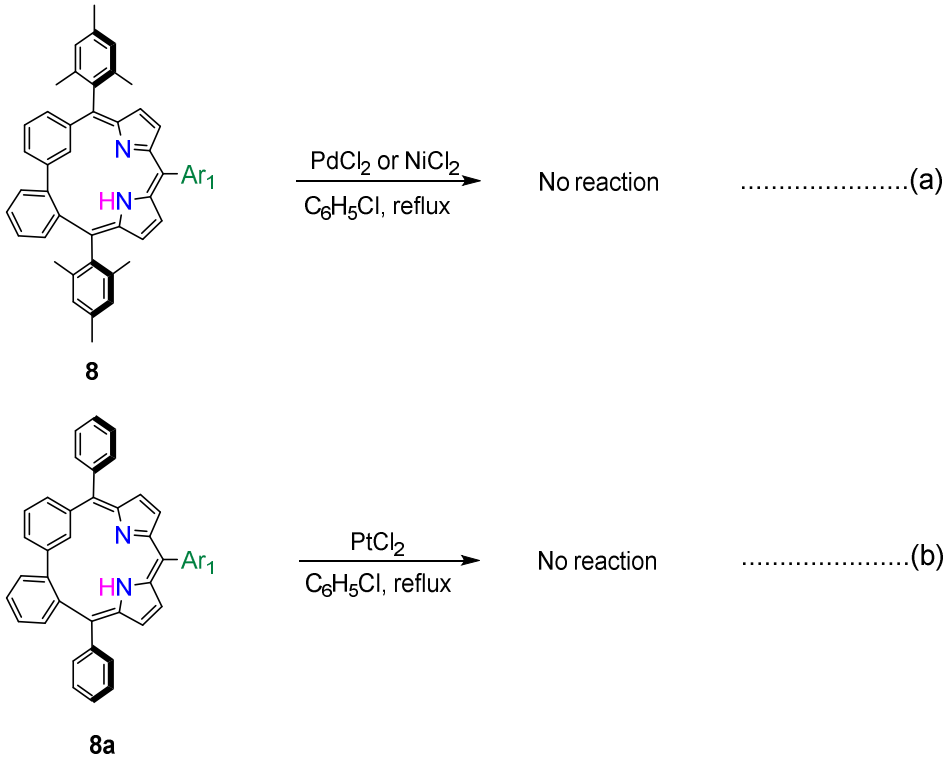


Fig. S29. ESI-MS spectrum of **15** from the reaction crude.

8. Reaction of 8 with group-10 metal salts & 8a with $PtCl_2$:



Scheme S2. Reaction of **8** with a) $PdCl_2$ or $NiCl_2$ and b) Reaction of **8a** with $PtCl_2$ under similar experimental conditions.

References:

[S1] B. Adinarayana, A. P. Thomas, P. Yadav, V. Mukundam, A. Srinivasan, *Chem. Eur. J.*, 2017, **23**, 2993-2997.

[S2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.

[S3] (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648−5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.* 1988, **37**, 785−789.

[S4] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* 1972, **56**, 2257-2261.

[S5] B. Mennucci, E. Cancès, J. Tomasi, *J. Phys. Chem. B* 1997, **101**, 10506-10517.

[S6] S. H. Crosby, G. J. Clarkson, J. P. Rourke, *J. Am. Chem. Soc.* 2009, **131**, 14142-14143.