Electronic Supporting Information

Unveiling Protonated Form of 2,6-Di-*m*-phenylpyridine Embedded Isosmaragdyrin analogue and Its Organo-Pd(II) complex

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1. Mass Spectral Analyses:

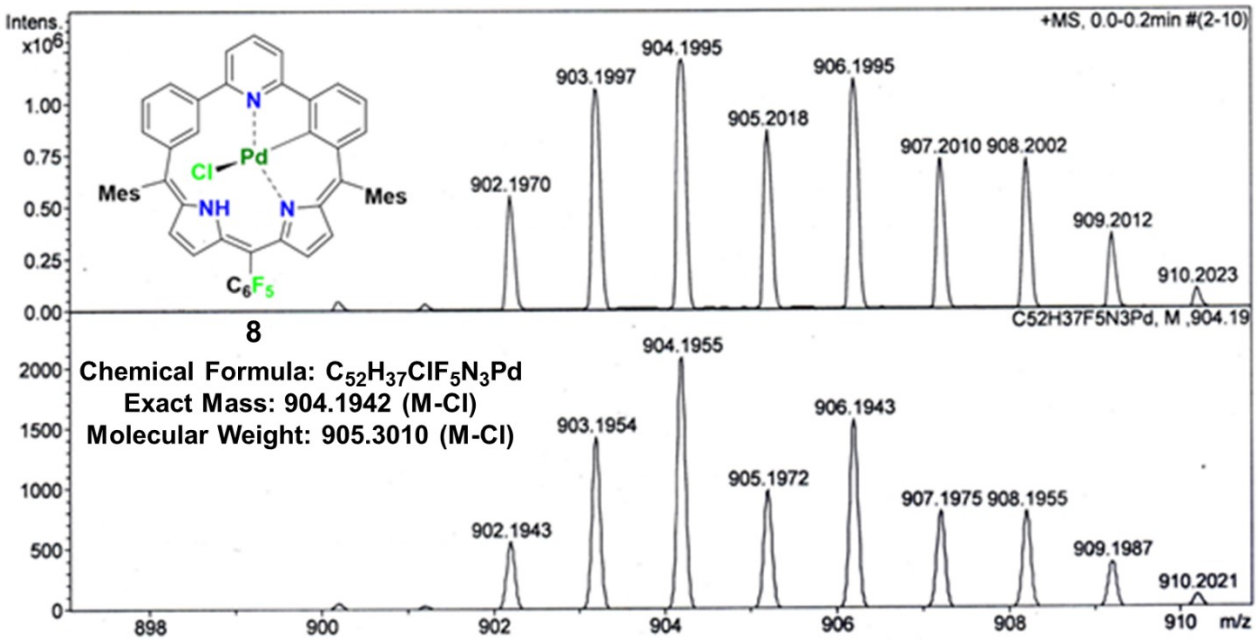

Fig. S1 HR-ESI MS spectrum of **8**.

2. NMR Spectral analysis:

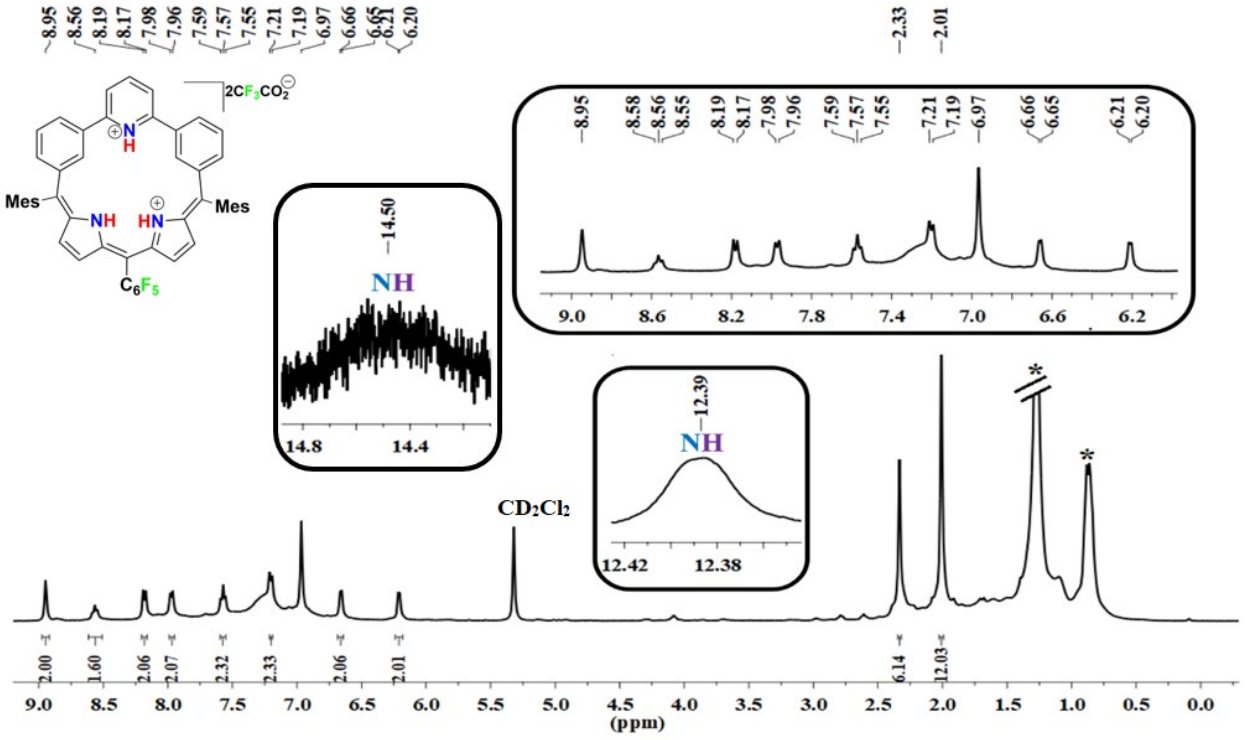

Fig. S2 ^{1}H NMR spectrum of $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$ with 38 eq. of TFA in CD_2Cl_2 at 298 K. (*Residual solvents and impurity grease).

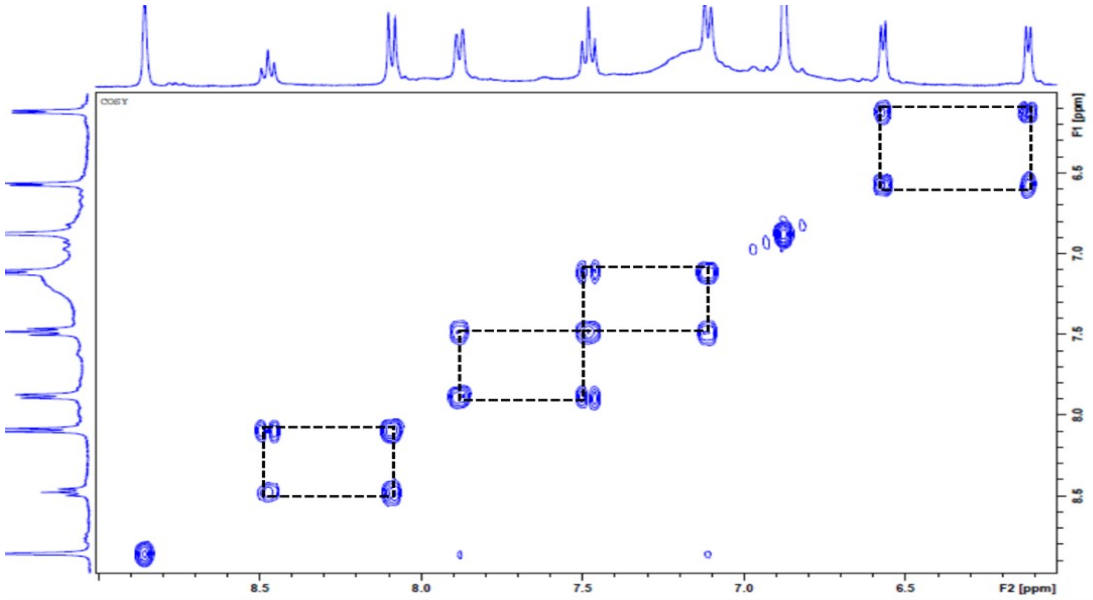

Fig. S3 ^{1}H-^{1}H COSY spectrum of $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$ with 38 eq. of TFA in CD_2Cl_2 at 298 K.

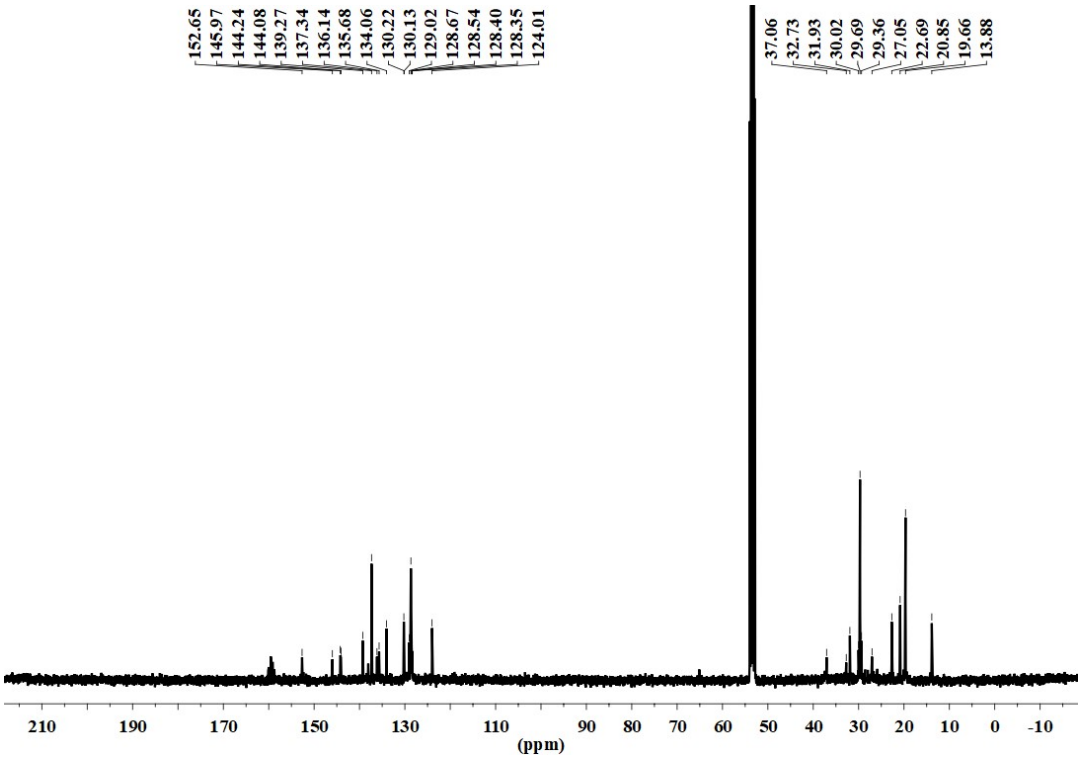

Fig. S4 ^{13}C NMR spectrum of $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$ with 38 eq. of TFA in CD_2Cl_2 at 298 K.

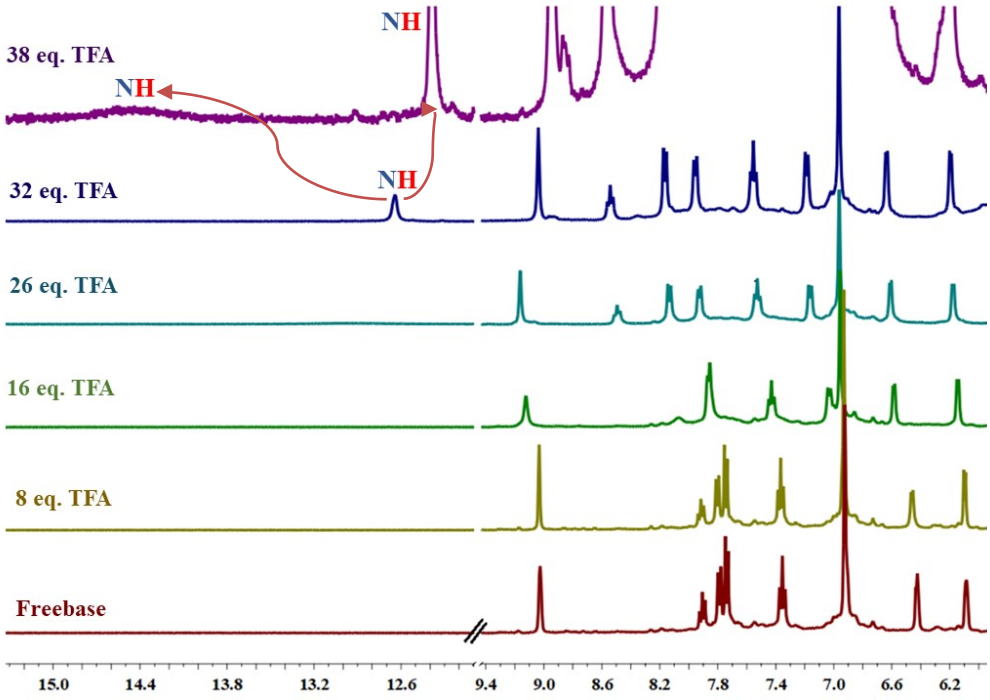

Fig. S5 ^{1}H-NMR spectra of $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$ with increasing concentration of TFA in CD_2Cl_2 at 298 K.

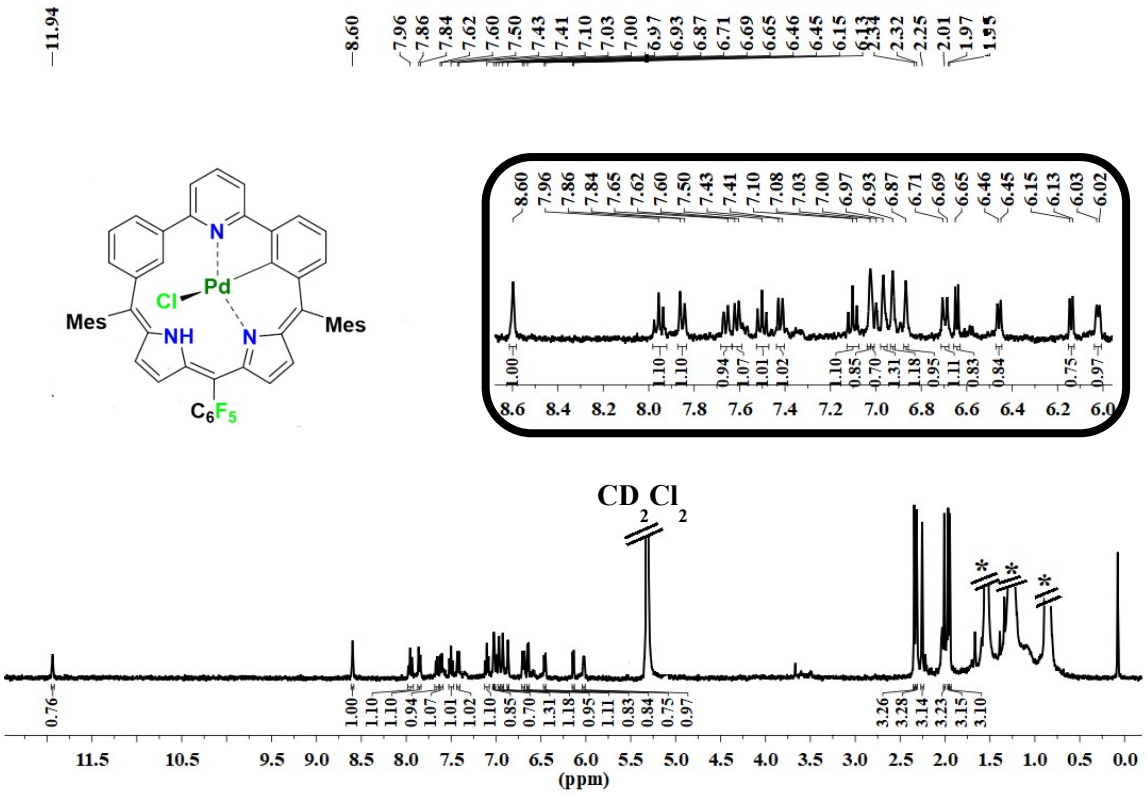

Fig. S6 ^{1}H-NMR spectrum of **8** in CD_2Cl_2 at 298 K. (*Residual solvents and impurity grease).

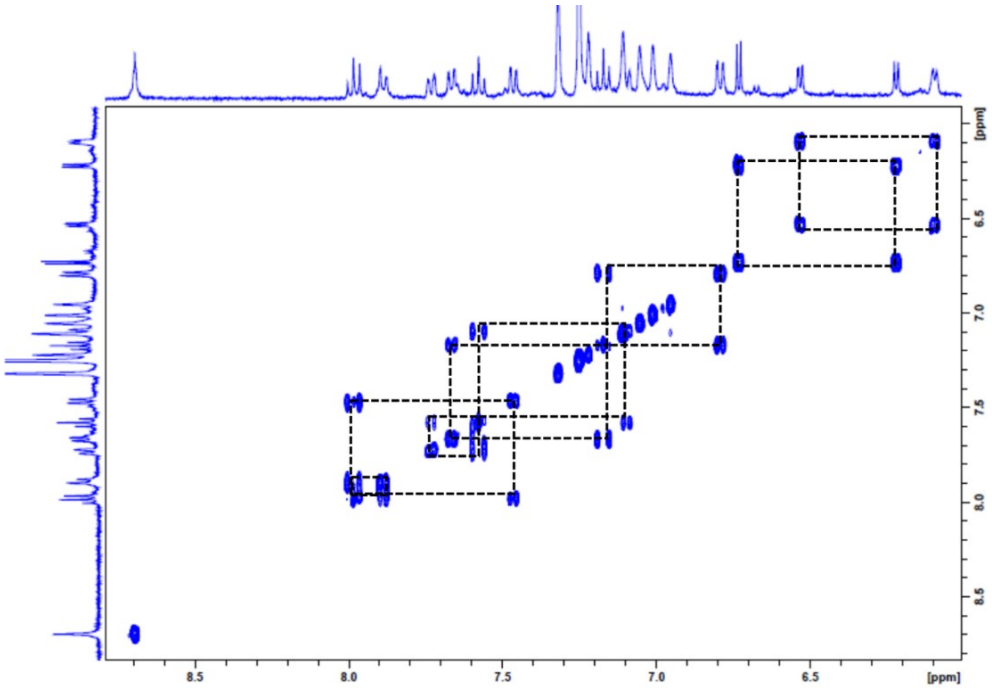

Fig. S7 ^{1}H-^{1}H COSY spectrum of **8** in CD_2Cl_2 at 298 K.

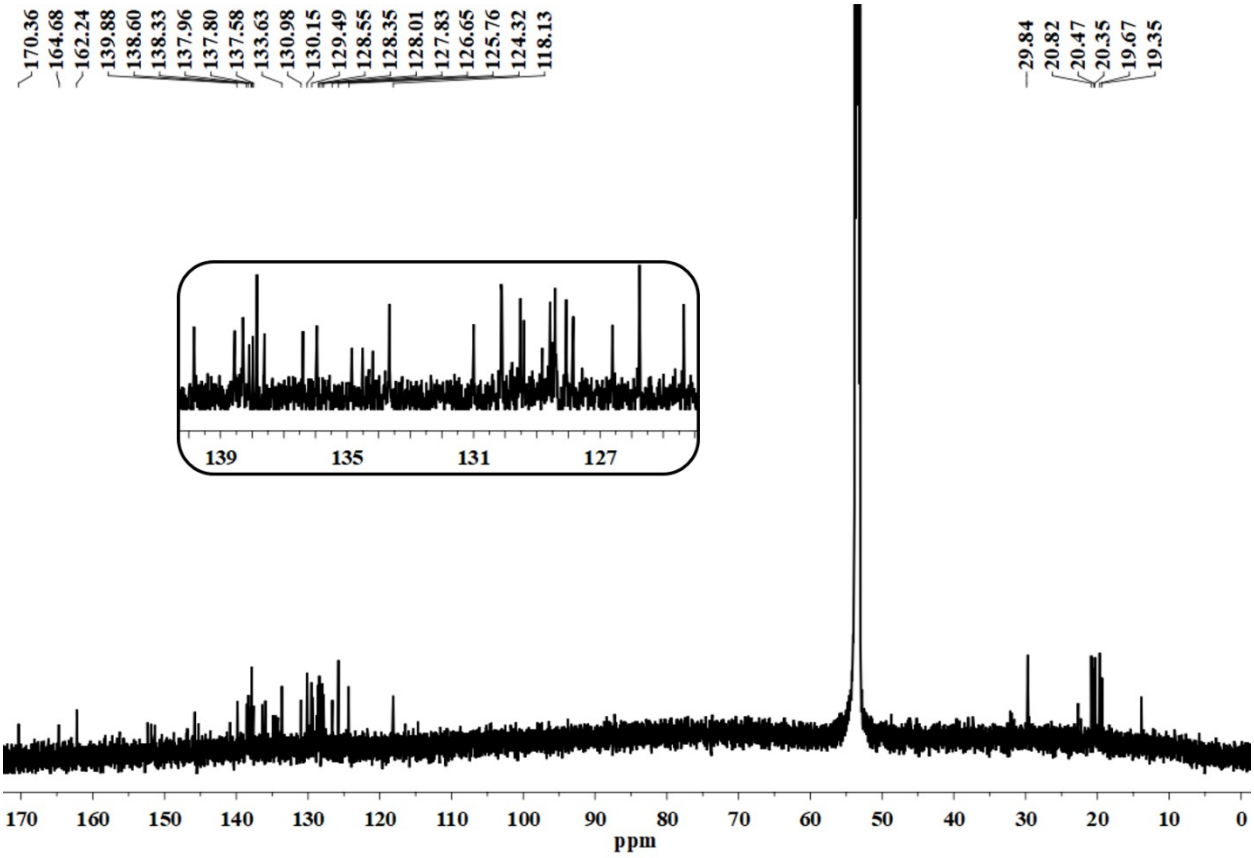

Fig. S8 ^{13}C-NMR spectrum of **8** in CD_2Cl_2 at 298 K.

3. Single crystal X-ray structural analyses of $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$ and 8:

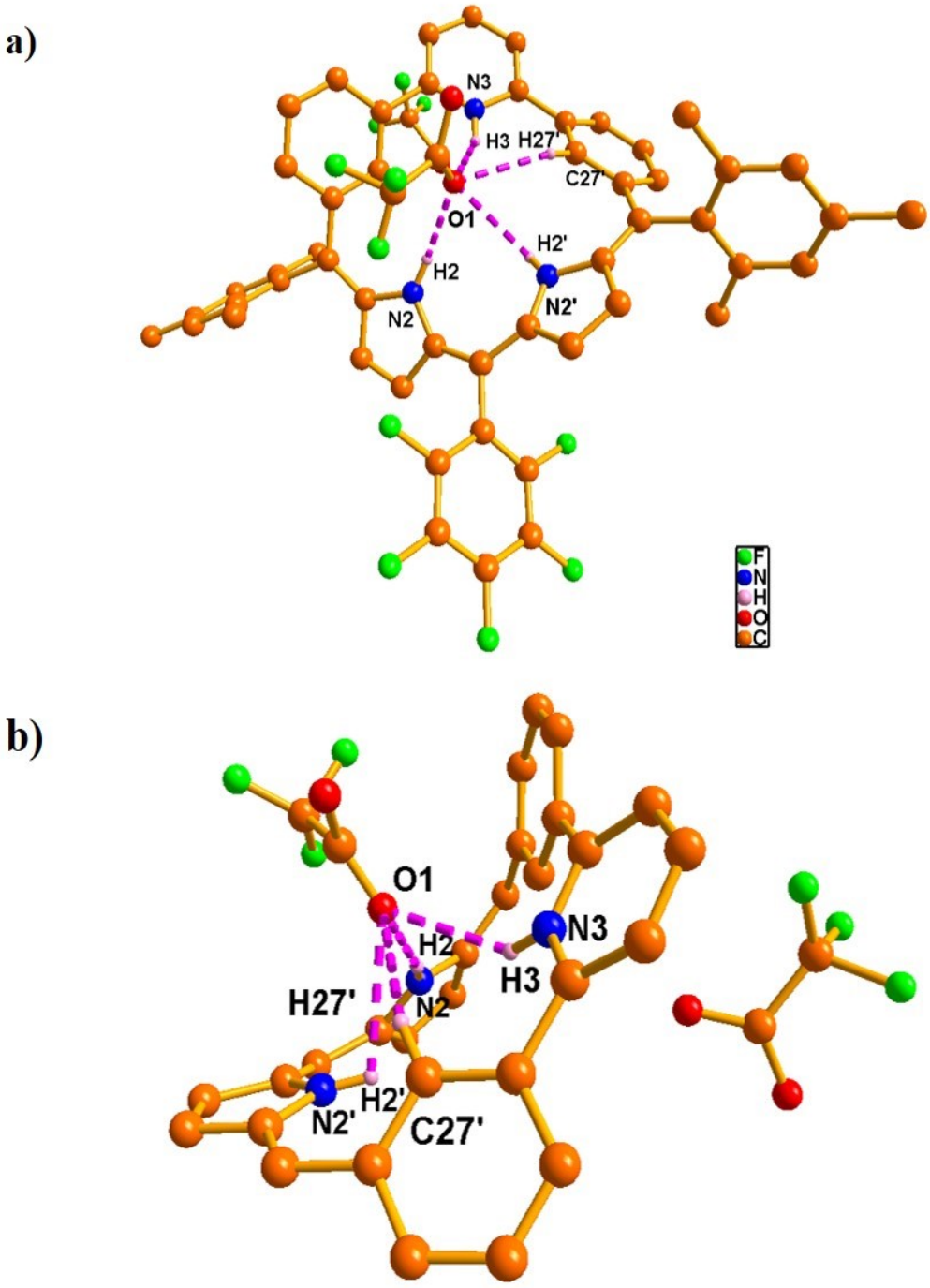

Fig. S9 Single crystal X-ray structure of $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$. a) Top view and b) side view. Peripheral H-atoms in a) & b) and *meso*-aryl groups in b) are omitted for clarity.

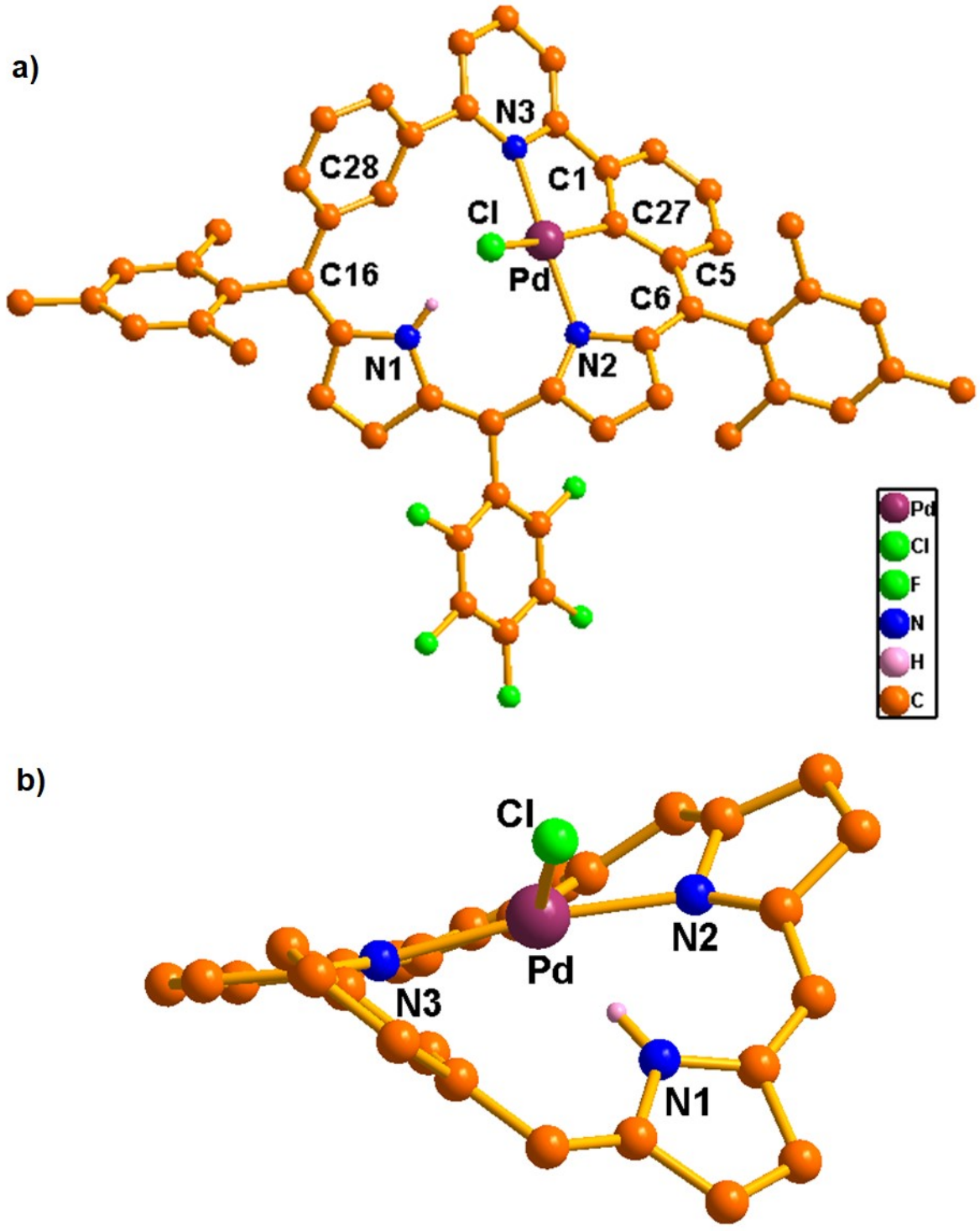

Fig. S10 Single crystal X-ray structure of **8**. a) Top view and b) side view. Peripheral H-atoms in a) & b) and *meso*-aryl groups in b) are omitted for clarity.

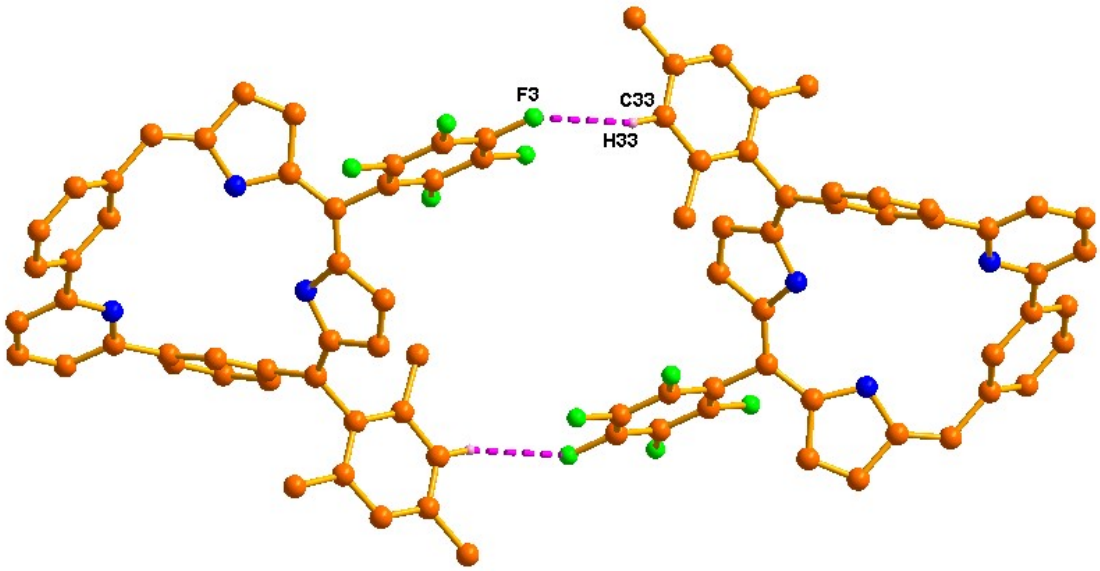

Fig. S11 Self-assembled dimer in $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$. The bond distance and angle are: C33-H33…F3: 2.753(2) Å & 167.02(3)°. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

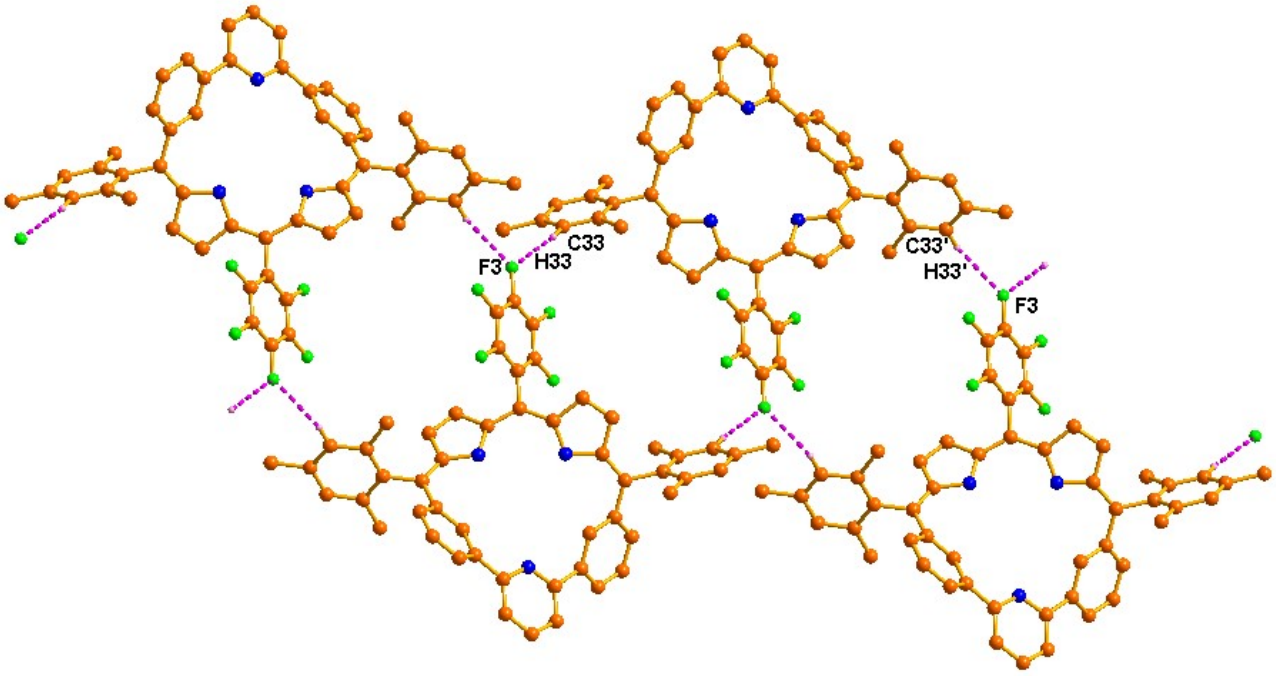

Fig. S12 Single crystal X-ray analysis of $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$ in 2-D array. The bond distances and angles are C33-H33…F3: 2.753(2) Å and 167.02(3)° ; C33'-H33'…F3: 2.753(2) Å and 167.02(3)° respectively. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

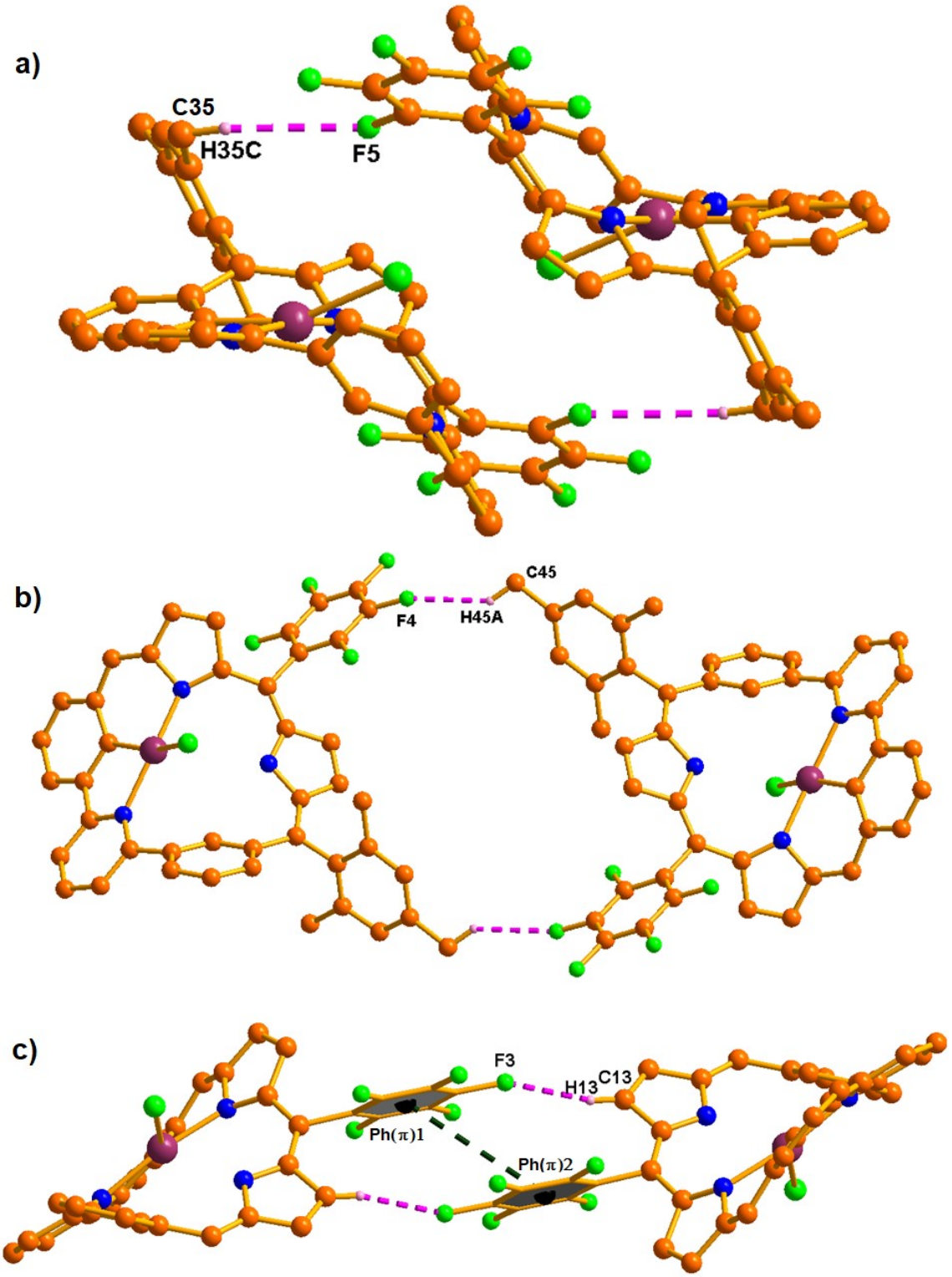

Fig. S13. Single crystal X-ray analysis of **8**. a), b) and c) are Self-assembled dimers. The bond distances and angles are: a) C35-H35C…F5: 2.859(2) Å & 154.74(4)°; b) C45-H45…F4: 2.559(3) Å & 144.02(4)° ; c) C13-H13…F3: 2.566(4) Å and 159.7(4)°; Ph(π)1-Ph(π)2: 4.47(1) Å respectively. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

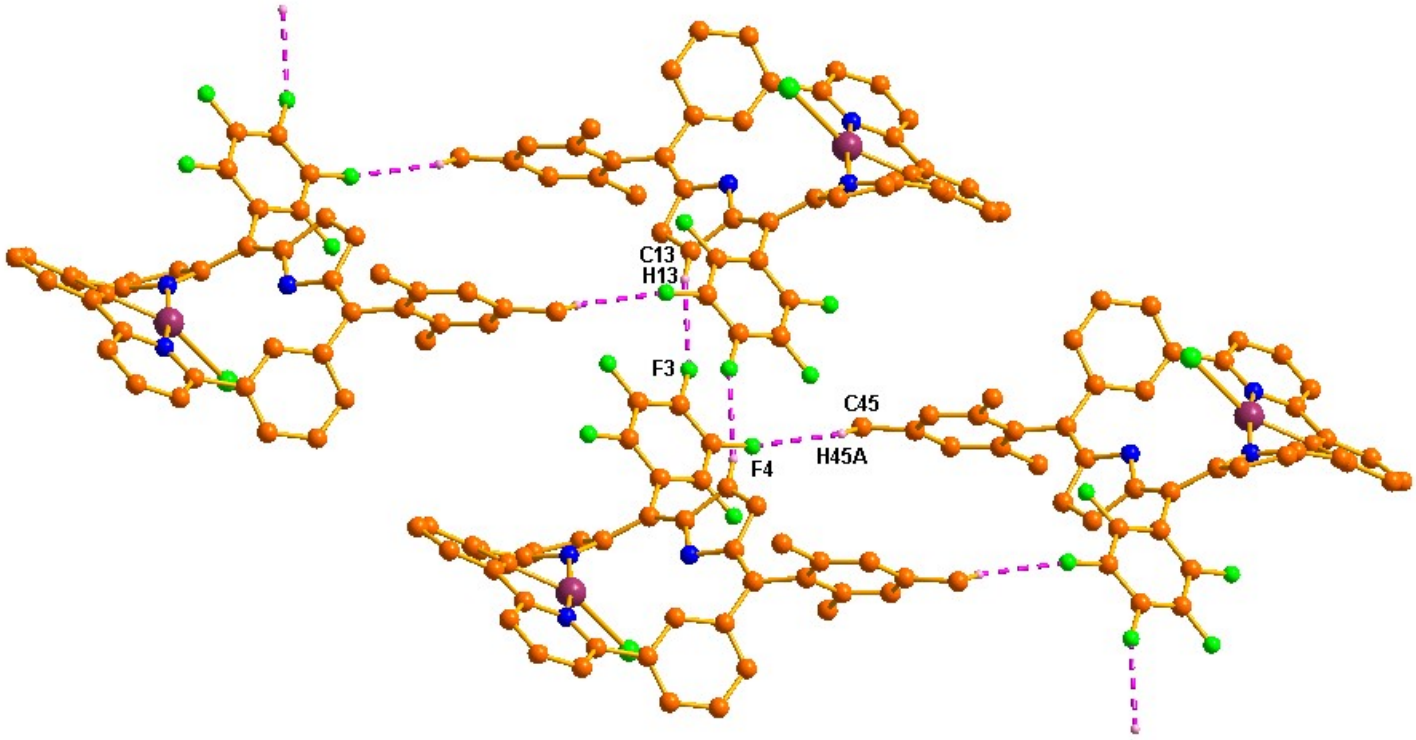

Fig. S14 Single crystal X-ray analysis of **8** in 2-D array. The bond distances and angles are C13-H13…F3: 2.567(4) Å and 159.69(4)°; C45-H45A…F4: 2.559(3) Å and 144.02(4)° respectively. The hydrogen atoms and the *meso*-aryl groups are omitted for clarity.

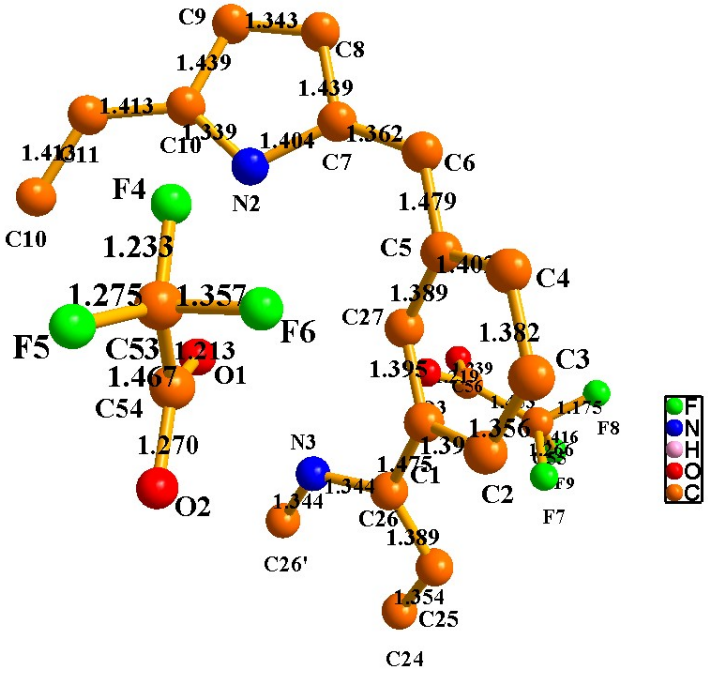

Fig. S15 Bond Lengths in $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$ (Å).

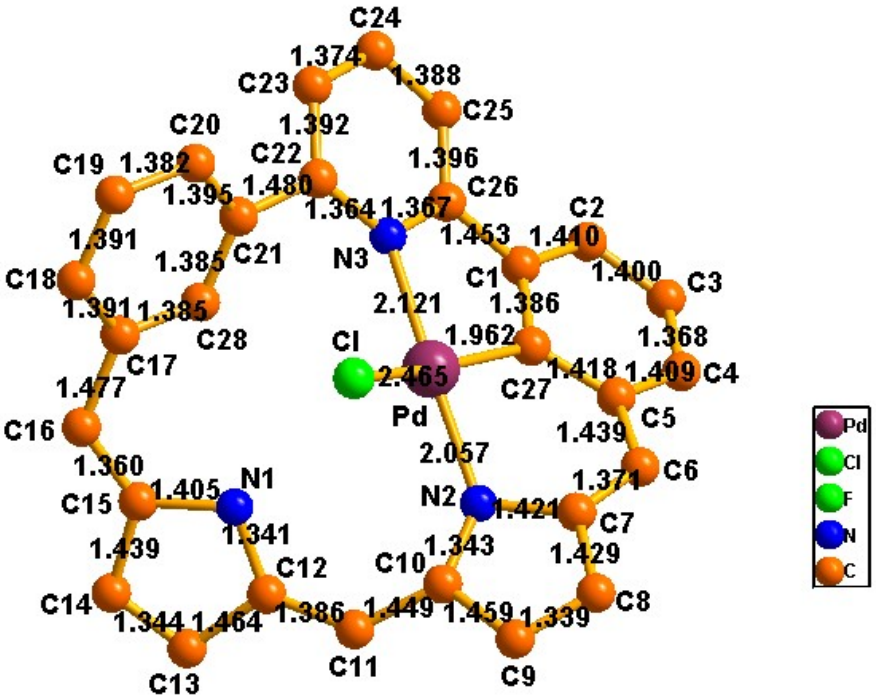

Fig. S16 Bond Lengths in **8** (Å).

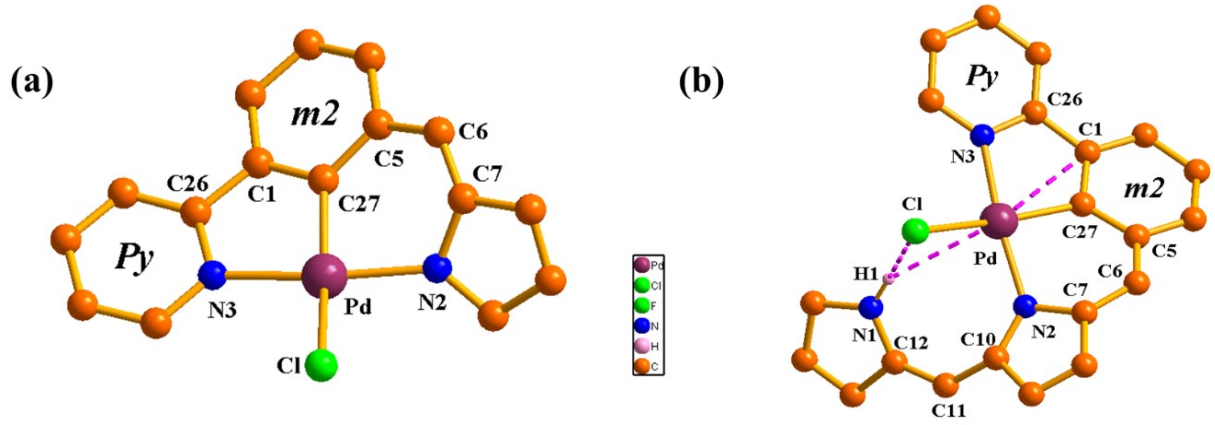

Fig. S17 (a) Organo-Pd(II) pincer type complex and (b) intramolecular hydrogen bonding and metal–arene interactions in **8**.

Table S1: Crystal data for H_2**5**$^{2+}$**.**$2CF_3CO_2^-$ and **8**

Crystal parameters	H_2**5**$^{2+}$**.**$2CF_3CO_2^-$	**8**
Formula	$C_{60}H_{40}F_{17}N_3O_8$	$C_{52}H_{37}ClF_5N_3Pd$
M/g mol^{-1}	1253.95	940.70
T/K	293(2)	112.6(5)
Crystal dimensions/mm^3	0.2 × 0.1 ×0.1	0.362 × 0.28 × 0.22
Crystal system	monoclinic	triclinic
Space group	*C*2/c	*P*-1
a/Å	17.3774(4)	12.7701(2)
b/Å	19.4464(3)	13.7846(2)
c/Å	20.1641(4)	14.2357(2)
α/°	90	92.4420(10)
β/°	97.8318(19)	111.581(2)
γ/°	90	102.638(2)
V/Å^3	6750.4(2)	2252.78(7)
Z	4	2
ρcalcd/mg m^{-3}	1.443	1.494
μ/mm^{-1}	2.860	4.938
F(000)	2552	1033
Reflns. collected	45950	31042
Indep.reflns.[*R*(int)]	5733 [0.0796]	8219 [0.1376]
Max/min transmission	0.751, 0.745	1.000, 0.325
Data/restraints/parameters	5733/210/531	8219/0/565
GOF on F^2	1.050	1.130
Final R indices[I > 2σ(I)]	R1 = 0.0732, wR2 = 0.2160	R1 = 0.0945, wR2 = 0.2425
R indices (all data)	R1 = 0.0784, wR2 = 0.2201	R1 = 0.0966, wR2 = 0.2454
Largest diff peak and hole [e Å^{-3}]	0.23 and -0.232	4.20 and -2.01

The crystals have been deposited in the Cambridge Crystallographic Data Centre with reference no. **CCDC 1957038** (H_2**5**$^{2+}$**.**$2CF_3CO_2^-$) and **CCDC 2238652** (**8**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4. Electronic absorption spectral analysis

Table S2. Electronic absorption spectral data for $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$ and **8** (concentration ≈ 10^{-6} M)

Compd.	λ_{max}/nm (ε[$M^{-1}cm^{-1}$]x10^4)
$H_2\mathbf{5}^{2+}.2CF_3CO_2^-$	344 (4.56), 615 (3.39), 659 (4.37)
8	312 (2.41), 378 (2.54), 460 (0.50), 620 (1.80), 673 (2.58)

5. Theoretical Calculations:

Computational calculations were performed with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP)[1, 2] and the 6-31G(d) basis set for all atoms except the palladium metal, and the CEP-31G (Stevens/Basch/Krauss ECP) for palladium metal.

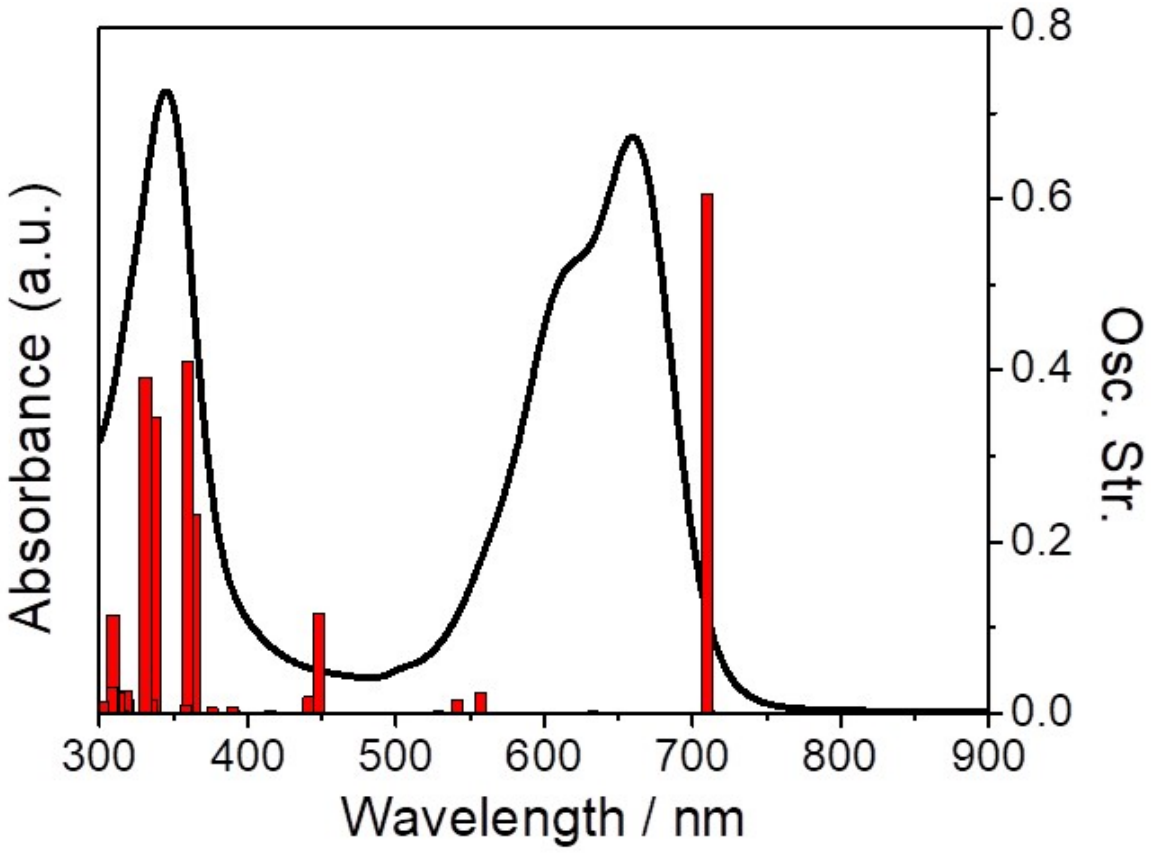

Fig. S18 Absorption spectrum of $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$ along with the calculated vertical transitions (red) obtained by TD-DFT (B3LYP/6-31g(d)) method.

Table S3. Selected TD-DFT calculated energies, oscillator strengths and compositions of the major electronic transitions of $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$. The terms H and L refer to HOMO and LUMO, respectively.

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major Transitions
14079	710	0.6065	H → L (93%)
22338	448	0.1155	H → L+3 (87%)
27468	364	0.2307	H-7 → L+1 (95%)
30219	331	0.3916	H-8 → L+1 (91%)

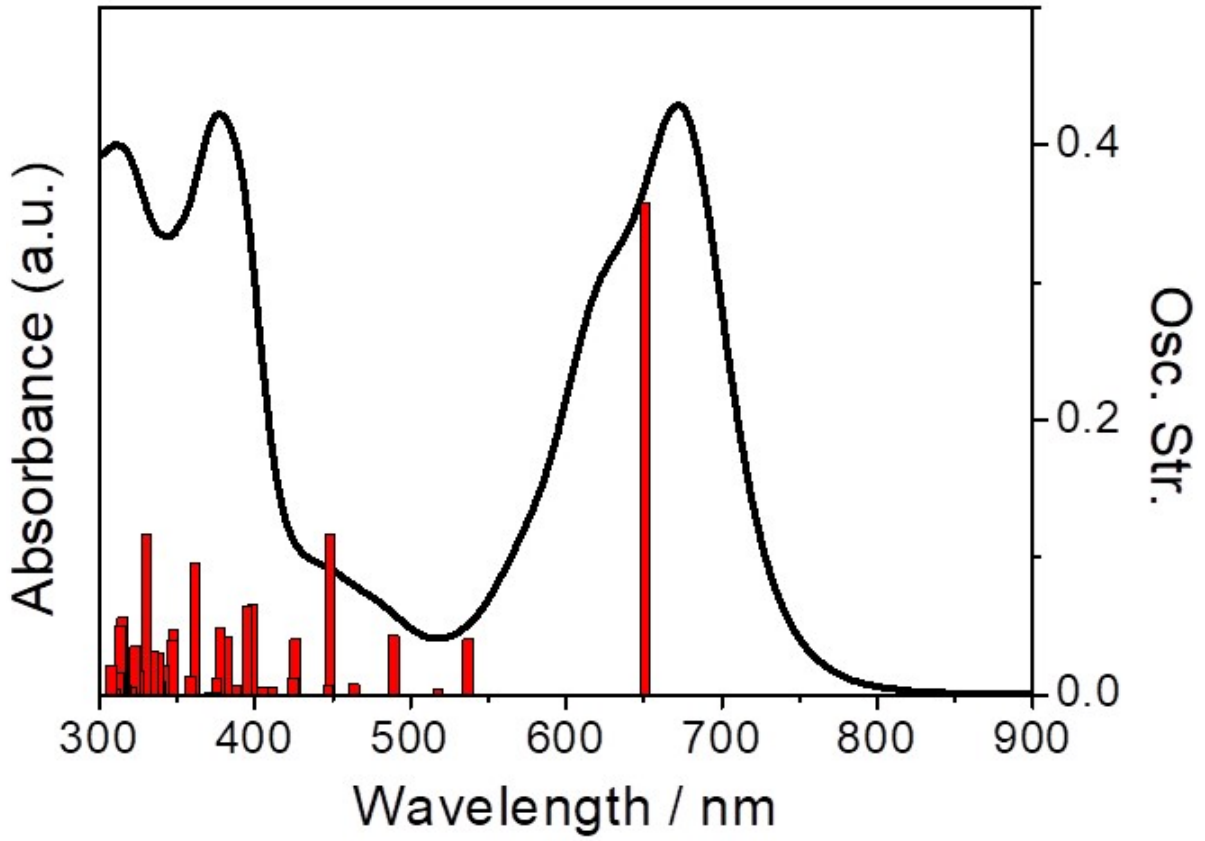

Fig. S19 Absorption spectrum of **8** along with the calculated vertical transitions (red) obtained by TD-DFT (B3LYP/6-31g(d)) method.

Table S4. Selected TD-DFT calculated energies, oscillator strengths and compositions of the major electronic transitions of **8**. The terms H and L refer to HOMO and LUMO, respectively.

Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major Transitions
15362	651	0.3574	H → L (95%)
22308	448	0.1162	H-4 → L (23%), H → L+2 (58%)
25086	399	0.0653	H-5 → L (28%), H-4 → L (21%)

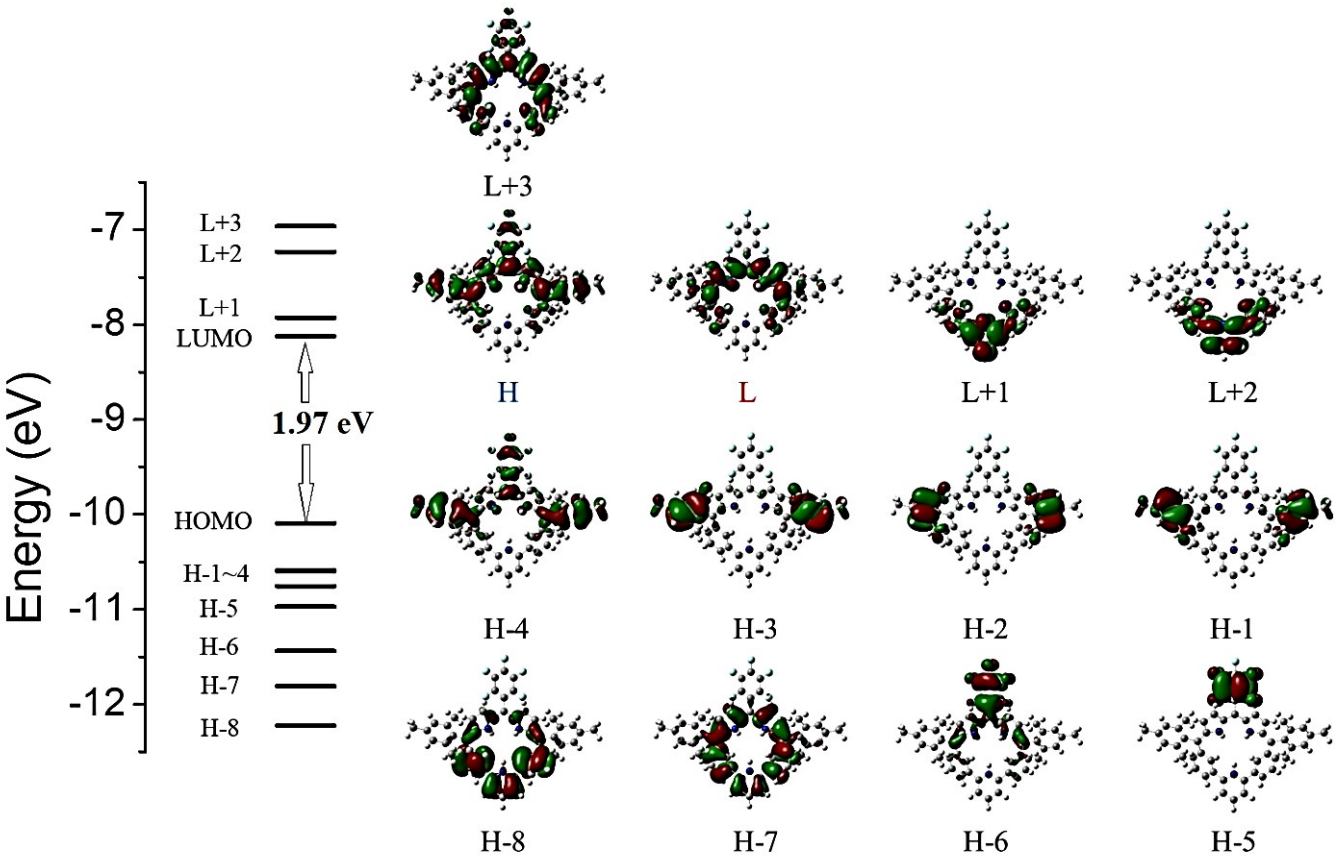

Fig. S20 Molecular orbital energy diagrams of $H_2\mathbf{5}^{2+}.2CF_3CO_2^-$ obtained from DFT calculation (B3LYP/6-31g(d)) method.

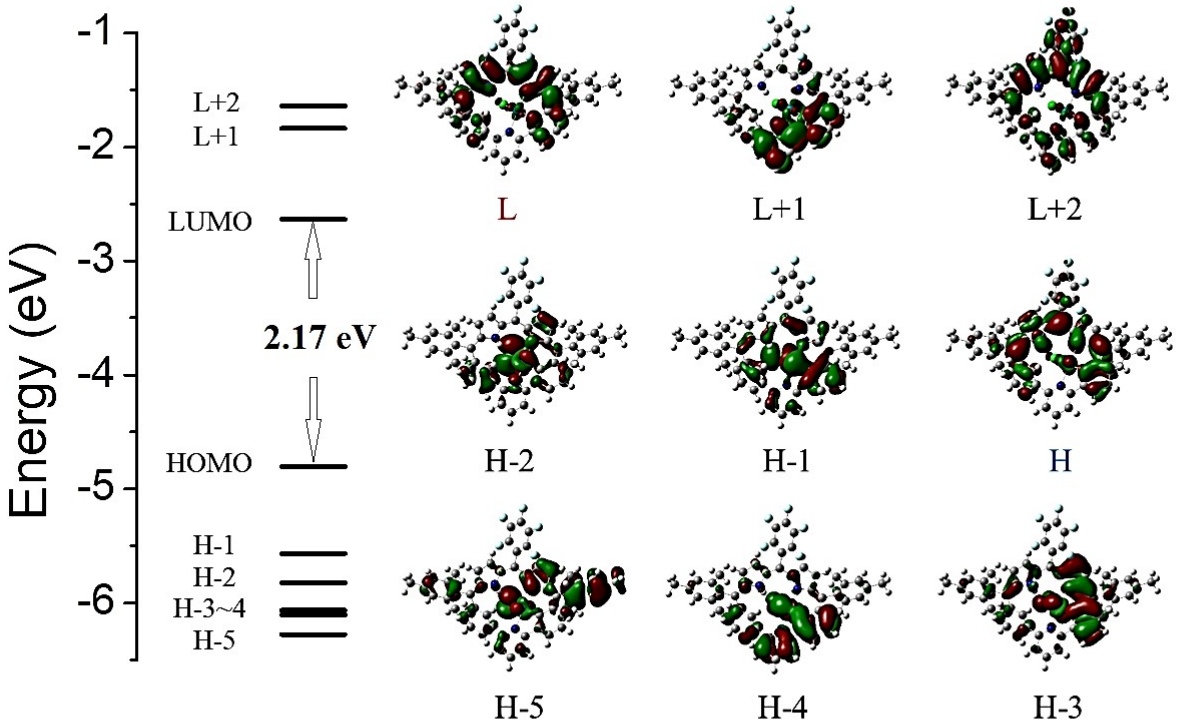

Fig. S21 Molecular orbital energy diagrams of **8** obtained from DFT calculation (B3LYP/6-31g(d)) method.

Optimized structure of molecules at B3LYP/6-31G(d) level. All the X, Y, Z coordinates are given in Å.

Atoms and their X, Y, Z Coordinates of $H_2$5^{2+}.2$CF_3CO_2^-$:

Structure $H_2$5^{2+}.2$CF_3CO_2^-$

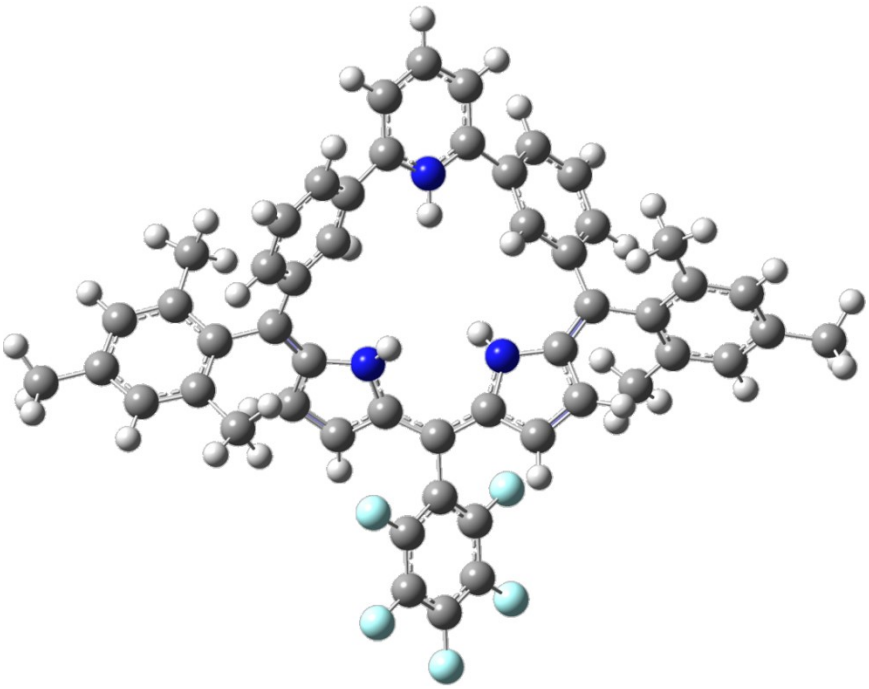

Fig. S22 Optimized structure of $H_2$5^{2+}.2$CF_3CO_2^-$ at B3LYP/6-31G(d) level.

All the X, Y, Z coordinates are given in Å.

F	1.95103	3.75936	1.35244
N	1.6549	0.3043	-0.05728
H	1.30212	-0.15069	0.77557
N	0.00009	-4.26267	-0.00003
H	0.00007	-3.24751	-0.00001
F	-0.00017	7.81646	-0.00006
F	1.948	6.45589	1.33633
C	-0.00005	2.1769	0.0000
C	-0.00008	3.66464	-0.00002

C	3.56895	-2.00276	0.69728
C	1.1881	1.54942	-0.43293
C	3.01781	0.18057	-0.43272
C	3.93061	-0.75919	-0.01438
C	2.4753	-2.79558	0.31387
H	1.90386	-2.49322	-0.56087
C	5.37908	-0.47044	-0.21747
C	1.11101	-4.88032	0.49175
C	3.29982	1.33574	-1.24642
H	4.22989	1.47958	-1.77799
C	0.98536	4.40203	0.67671
C	2.21939	-4.02685	0.9434
C	2.21229	2.15519	-1.24123
H	2.09529	3.0939	-1.76339
C	6.14572	-1.28524	-1.09099
C	4.39547	-2.46652	1.74248
H	5.25571	-1.87436	2.03578
C	5.99501	0.59745	0.48521
C	0.99863	5.79302	0.68069
C	3.04895	-4.45652	1.99367
H	2.84323	-5.38939	2.50892
C	1.10901	-6.27404	0.49498
H	1.98159	-6.80895	0.84895
C	7.49765	-0.99585	-1.26611
H	8.07816	-1.605	-1.95502
C	-0.00014	6.49142	-0.00004
C	7.36069	0.82577	0.28868
H	7.83933	1.62858	0.84402

C	0.00014	-6.96216	-0.00008
H	0.00017	-8.04792	-0.0001
C	5.52665	-2.42624	-1.86872
H	5.27823	-3.27599	-1.22072
H	6.21936	-2.79199	-2.631
H	4.60426	-2.12284	-2.37793
C	8.1298	0.05472	-0.58716
C	4.12598	-3.6685	2.3917
H	4.76271	-3.99763	3.20664
C	5.25323	1.46139	1.48745
H	4.64418	2.23711	1.00813
H	5.96364	1.97174	2.14307
H	4.58083	0.87522	2.12392
C	9.59206	0.34755	-0.80906
H	10.17986	-0.57432	-0.86987
H	10.00552	0.96607	-0.00757
H	9.74115	0.88726	-1.75317
F	-1.95119	3.75925	-1.35246
N	-1.65492	0.30424	0.05732
H	-1.30213	-0.15076	-0.77552
F	-1.94828	6.45577	-1.33641
C	-3.56888	-2.00289	-0.69725
C	-1.18817	1.54938	0.43294
C	-3.01782	0.18046	0.43277
C	-3.93058	-0.75935	0.01444
C	-2.47519	-2.79567	-0.31387
H	-1.90376	-2.49331	0.56087
C	-5.37906	-0.47063	0.21751

C	-1.11081	-4.88034	-0.49182
C	-3.29988	1.33564	1.24643
H	-4.22996	1.47946	1.77799
C	-0.98555	4.40198	-0.67675
C	-2.21923	-4.02691	-0.94345
C	-2.21239	2.15513	1.24122
H	-2.09542	3.09386	1.76335
C	-6.14569	-1.28538	1.0911
C	-4.39538	-2.46664	-1.74247
H	-5.25564	-1.87451	-2.03575
C	-5.995	0.59722	-0.48521
C	-0.99887	5.79297	-0.68076
C	-3.04877	-4.45657	-1.99373
H	-2.84301	-5.38942	-2.50901
C	-1.10875	-6.27407	-0.49511
H	-1.98131	-6.809	-0.8491
C	-7.49761	-0.99598	1.26623
H	-8.07812	-1.60509	1.95518
C	-7.36069	0.82555	-0.28867
H	-7.83933	1.62833	-0.84405
C	-5.52658	-2.42628	1.86895
H	-5.27763	-3.27588	1.22097
H	-6.21948	-2.79231	2.63092
H	-4.60449	-2.12263	2.37857
C	-8.12978	0.05455	0.58722
C	-4.12584	-3.66859	-2.39173
H	-4.76255	-3.99772	-3.20668
C	-5.25324	1.46111	-1.48749

H	-4.64421	2.23688	-1.00821
H	-5.96364	1.97141	-2.14315
H	-4.58081	0.87493	-2.12392
C	-9.59204	0.34737	0.80912
H	-10.17991	-0.5745	0.86935
H	-10.00537	0.96635	0.00793
H	-9.7412	0.88654	1.75352

Atoms and their X, Y, Z Coordinates of 8:

Structure 8

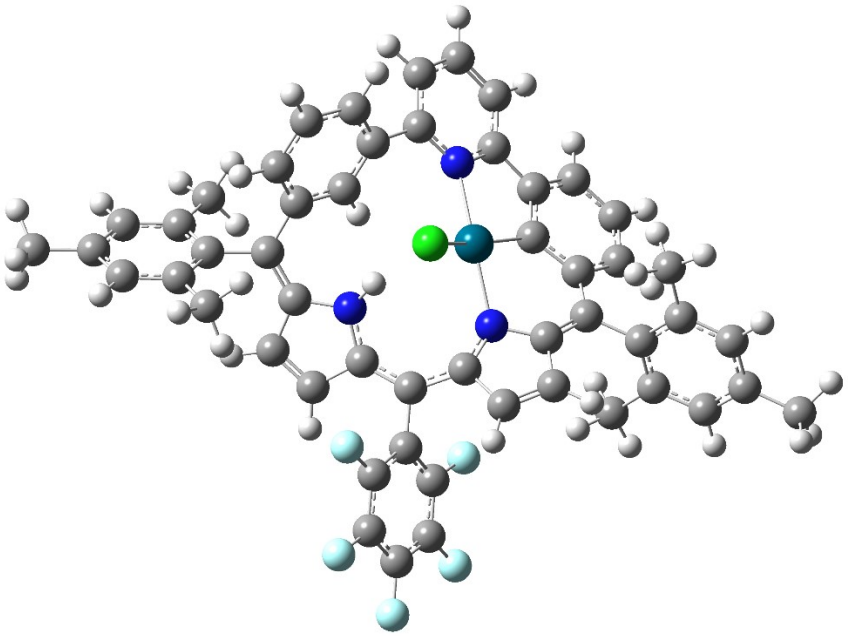

Fig. S23 Optimized structure of **8** at B3LYP/6-31G(d) level.

All the X, Y, Z coordinates are given in Å.

Pd	0.69409	-1.73103	-0.27902
Cl	-0.61373	-1.13581	-2.30505
F	1.88191	3.23224	1.72567
F	-1.40626	4.22489	-1.55359
F	0.9048	7.69686	0.61814

F	-0.96159	6.85557	-1.18782
F	2.32186	5.86793	2.06628
N	1.58156	0.17243	-0.30618
N	-1.94681	0.57406	-0.07735
H	-1.58888	-0.05058	-0.81668
N	-0.10869	-3.69943	0.24848
C	2.21769	-2.43317	0.77515
C	0.2188	3.62176	0.07181
C	-1.5341	-5.63773	0.19729
H	-2.48433	-6.06753	-0.09641
C	-2.28802	2.55862	0.95139
H	-2.06817	3.51472	1.40329
C	-3.29896	0.63019	0.2955
C	-2.7712	-2.30505	-0.12805
H	-2.1885	-1.90464	0.69464
C	-1.27961	-4.29187	-0.1031
C	2.22265	2.18686	-1.20412
H	2.12606	3.19609	-1.57741
C	1.16771	4.09698	0.98978
C	-0.02443	2.15487	-0.11683
C	0.78804	-4.40935	0.99917
C	2.02872	-3.71076	1.34476
C	3.87395	-0.70124	-0.01243
C	1.14272	1.43211	-0.56726
C	3.32709	1.40866	-1.21867
H	4.31407	1.65267	-1.58408
C	-4.6897	-2.18655	-1.59103
H	-5.5854	-1.67453	-1.92919

C	-3.90649	-1.61047	-0.57384
C	-4.30592	-3.38856	-2.18106
H	-4.89801	-3.8064	-2.99039
C	-0.4861	4.59365	-0.65217
C	-1.31256	1.74374	0.23415
C	-2.39019	-3.51648	-0.70317
C	2.96421	0.17017	-0.56233
C	4.52247	-2.49902	1.56022
H	5.50964	-2.05152	1.60271
C	-0.60417	-6.37648	0.91562
H	-0.7925	-7.41757	1.16211
C	3.5151	-1.86684	0.79379
C	5.33158	-0.39646	-0.215
C	0.55546	-5.74812	1.34068
H	1.29075	-6.29422	1.91743
C	4.27591	-3.68055	2.24879
H	5.05708	-4.1336	2.85211
C	-3.16255	-4.05509	-1.74372
H	-2.85989	-4.98456	-2.2172
C	0.68562	6.39069	0.44199
C	-5.70265	0.02535	0.23352
C	3.04344	-4.31	2.1103
H	2.88448	-5.27038	2.59076
C	1.40954	5.45472	1.17763
C	-0.26801	5.95863	-0.47596
C	-8.44287	0.60247	0.63802
C	-6.42546	-0.63117	1.25882
C	-3.46936	1.89436	0.98233

H	-4.39024	2.20439	1.4565
C	-6.35917	0.96345	-0.59561
C	-4.2608	-0.305	0.01157
C	5.98638	0.52576	0.63043
C	8.07043	0.16867	-0.60097
C	-5.7551	-1.63569	2.16919
H	-5.44169	-2.5322	1.62154
H	-6.4337	-1.94998	2.96818
H	-4.85381	-1.21873	2.63383
C	5.36623	-2.03465	-2.16432
H	4.95294	-2.88233	-1.60498
H	6.07097	-2.4294	-2.90262
H	4.52954	-1.57747	-2.70539
C	6.04573	-1.0424	-1.24697
C	-7.71757	1.22839	-0.37704
H	-8.22118	1.94217	-1.02605
C	7.40114	-0.74433	-1.42158
H	7.94751	-1.24097	-2.22124
C	-7.77528	-0.32632	1.44451
H	-8.3211	-0.8277	2.24176
C	-5.64564	1.67495	-1.72686
H	-5.00595	2.48701	-1.36045
H	-6.36978	2.11455	-2.42
H	-4.99845	0.99838	-2.29447
C	-9.89989	0.92641	0.87357
H	-10.34649	1.41851	0.0035
H	-10.02397	1.6006	1.73165
H	-10.48244	0.02315	1.0882

C	9.52852	0.49479	-0.82879
H	10.07599	-0.36833	-1.22295
H	10.01798	0.81292	0.09795
H	9.64488	1.31102	-1.5546
C	7.3456	0.7869	0.42183
H	7.84955	1.49346	1.0786
C	5.25229	1.2198	1.75819
H	4.46651	1.88902	1.38829
H	5.94442	1.81615	2.36082
H	4.76147	0.49946	2.42345

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