Supporting Information

Synthesis, Crystal Structure, Solution and Spectroscopic Properties, and Hydrogen-Evolving Activity of [K(18-Crown-6)][Pt(II)(2-phenylpyridinato)Cl_2]

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Table S1. Cartesian coordinates of a fully optimized structure of $[Pt(ppy)Cl_2]^-$ in water. The structure was optimized using the B3LYP level of DFT and the LanL2DZ basis set using the PCM method (water) in Gaussian 03.

Atom	X	Y	Z
Pt1	-0.818631	-0.091014	-0.000284
Cl2	-2.804487	1.582869	0.004778
Cl3	-2.458425	-1.923135	-0.003948
C4	0.795402	-1.275555	0.000059
N5	0.624662	1.349478	0.000053
C6	0.832280	-2.689760	0.000770
C7	2.042805	-0.572910	0.000493
C8	0.371501	2.689289	-0.000738
C9	1.930768	0.888513	-0.000127
C10	3.274478	-1.267621	0.001478
C11	2.063693	-3.379357	0.001953
C12	2.999333	1.807348	-0.001111
C13	1.404091	3.634050	-0.001873
H14	-0.673485	2.975558	-0.000517
H15	-0.095833	-3.253966	0.000535
C16	3.286802	-2.672371	0.002310
C17	2.740739	3.186026	-0.002065
H18	1.158640	4.693945	-0.002593
H19	4.023907	1.442696	-0.001336
H20	4.219582	-0.724151	0.001875
H21	2.068541	-4.470184	0.002597
H22	3.564075	3.899217	-0.003035
H23	4.233348	-3.211757	0.003285

E(RB+HF-LYP) = -628.039926164 Hartree

Table S2. Cartesian coordinates of a fully optimized structure of Pt(ppy)Cl(OH_2) (**2)** in water. The structure was optimized using the B3LYP level of DFT and the LanL2DZ basis set using the PCM method (water) in Gaussian 03.

Atom	X	Y	Z
Pt1	-0.831680	-0.389162	-0.000306
C2	0.059142	1.392014	-0.002499
C3	1.636428	3.768457	0.005492
C4	1.490277	1.333791	0.003027
C5	-0.555920	2.664212	-0.004478
C6	0.225926	3.839964	-0.000662
C7	2.268659	2.513123	0.007220
N8	1.094565	-1.017302	-0.003096
C9	3.797256	-1.719732	-0.002762
C10	1.455450	-2.330719	-0.010295
C11	2.053756	-0.021032	0.001763
C12	3.418840	-0.368144	0.002559
C13	2.800614	-2.717554	-0.009987
Cl14	-3.158210	0.376042	-0.005433
H15	0.644594	-3.050427	-0.017885
H16	3.054112	-3.775470	-0.015584
H17	4.851733	-1.993152	-0.002079
H18	4.175508	0.413113	0.006783
H19	3.357723	2.460611	0.011645
H20	2.231962	4.680701	0.008771
H21	-0.266933	4.812906	-0.002163
H22	-1.639858	2.742234	-0.008439
O23	-1.640871	-2.481271	0.011733
H24	-2.043691	-2.773956	0.867580
H25	-2.242085	-2.709614	-0.740861

E(RB+HF-LYP) = -689.341595451 Hartree

Table S3. Cartesian coordinates of a fully optimized structure of Pt(ppy)Cl(OH_2) (**3**) in water. The structure was optimized using the B3LYP level of DFT and the LanL2DZ basis set using the PCM method (water) in Gaussian 03.

Atom	X	Y	Z
Pt1	-0.776888	-0.481419	-0.000025
N2	0.017682	1.372418	-0.000258
C3	1.152909	-0.985358	-0.000232
Cl4	-3.272917	0.182515	-0.000878
O5	-1.458745	-2.487013	0.001044
C6	1.402615	1.437013	-0.000646
C7	-0.726502	2.514251	0.000613
C8	1.686914	-2.291723	0.000907
C9	2.054141	0.123268	-0.000668
H10	-1.936730	-2.782403	0.816904
H11	-1.935303	-2.784362	-0.815004
C12	-0.127671	3.779130	0.001009
C13	2.042480	2.691289	-0.000013
C14	3.452751	-0.077765	-0.001171
C15	3.085202	-2.489179	0.000601
H16	1.019890	-3.150645	0.002441
H17	-1.802506	2.383672	0.000685
C18	1.279185	3.868761	0.000725
C19	3.968360	-1.385992	-0.000561
H20	3.486074	-3.503487	0.001557
H21	4.138629	0.769929	-0.001728
H22	3.129074	2.741456	-0.000095
H23	-0.755215	4.667684	0.001623
H24	5.045742	-1.547662	-0.000554
H25	1.771050	4.840731	0.001149

E(RB+HF-LYP) = -689.338549926 Hartree

Table S4. Cartesian coordinates of a fully optimized structure of $Pt_2(ppy)_2(\mu\text{-}Cl)_2$ (**4**) in water. The structure was optimized using the B3LYP level of DFT and the LanL2DZ basis set using the PCM method (water) in Gaussian 03.

Atom	X	Y	Z	Atom	X	Y	Z
C1	3.477479	-1.309177	0.010551	Pt23	-1.951936	0.024886	-0.019448
C2	5.847110	-2.878750	0.033221	Cl24	-0.101600	1.683736	-0.030753
C3	4.766544	-0.693219	0.020108	C25	-3.474514	1.309334	0.003869
C4	3.397637	-2.717509	0.011438	C26	-5.840141	2.884507	0.039664
C5	4.576626	-3.494979	0.023250	C27	-3.391295	2.717476	0.007586
C6	5.942211	-1.476492	0.031418	C28	-4.764831	0.696269	0.021592
H7	2.431596	-3.215521	0.003291	C29	-5.938522	1.482515	0.038564
H8	4.501394	-4.582888	0.024163	C30	-4.568270	3.497719	0.024750
H9	6.924844	-1.004246	0.039723	H31	-2.424085	3.213267	-0.003701
H10	6.750492	-3.487450	0.042661	H32	-6.922204	1.012527	0.050706
N11	3.472124	1.308161	0.009428	H33	-4.490324	4.585461	0.026503
C12	5.683686	3.018281	0.025477	H34	-6.741994	3.495392	0.053088
C13	3.290981	2.658685	0.008576	N35	-3.474764	-1.307641	-0.002136
C14	4.747784	0.771666	0.018803	C36	-5.689186	-3.013704	0.042382
C15	5.865946	1.627239	0.027525	C37	-4.749280	-0.768641	0.020643
C16	4.375120	3.543036	0.016060	C38	-3.296119	-2.658494	-0.002346
H17	2.268174	3.017803	0.000050	C39	-4.381639	-3.540911	0.019866
H18	6.868240	1.204881	0.035123	C40	-5.868836	-1.622311	0.042318
H19	4.190475	4.615029	0.013342	H41	-2.274141	-3.019612	-0.017673
H20	6.545599	3.684360	0.031118	H42	-4.198959	-4.613253	0.020287
Pt21	1.951600	-0.026935	-0.008844	H43	-6.870136	-1.197923	0.061233
Cl22	0.100826	-1.687773	-0.039650	H44	-6.552117	-3.678219	0.060775

E(RB+HF-LYP) = -1225.79278314 Hartree

Table S5. Cartesian coordinates of a fully optimized structure of $[Pt(ppy)Cl(OH)]^-$ (**5**) in water. The structure was optimized using the B3LYP level of DFT and the LanL2DZ basis set using the PCM method (water) in Gaussian 03.

Atom	X	Y	Z
Pt1	-0.831882	-0.452360	-0.000229
C2	-0.015298	1.389547	0.000741
C3	1.505099	3.826203	-0.001187
C4	1.423312	1.387110	0.000316
C5	-0.654153	2.657224	0.000189
C6	0.090518	3.855066	-0.000776
C7	2.170369	2.588713	-0.000570
N8	1.113691	-0.980937	-0.000945
C9	3.835696	-1.589343	0.001734
C10	1.516328	-2.282095	-0.001165
C11	2.034305	0.052514	0.000243
C12	3.412343	-0.251675	0.001675
C13	2.873398	-2.622644	0.000182
Cl14	-3.201807	0.211736	0.001952
H15	0.710830	-3.010676	-0.002187
H16	3.165236	-3.670725	0.000138
H17	4.899052	-1.826377	0.003167
H18	4.142730	0.554276	0.002950
H19	3.260857	2.567023	-0.001096
H20	2.074072	4.755428	-0.002010
H21	-0.429404	4.814461	-0.001316
H22	-1.741447	2.707088	0.000357
O23	-1.414064	-2.480728	-0.001758
H24	-2.399232	-2.557289	-0.002912

E(RB+HF-LYP) = -688.863379892 Hartree

Table S6. Cartesian coordinates of a fully optimized structure of $[Pt(ppy)Cl(OH)]^-$ (**6**) in water. The structure was optimized using the B3LYP level of DFT and the LanL2DZ basis set using the PCM method (water) in Gaussian 03.

Atom	X	Y	Z
Pt1	0.777260	-0.537513	-0.001233
N2	0.033605	1.371361	0.000568
C3	-1.163995	-0.964511	0.001387
Cl4	3.301727	0.074937	0.006040
O5	1.316880	-2.499515	-0.006603
C6	-1.350298	1.470829	0.000466
C7	0.793778	2.504232	0.000332
C8	-1.741674	-2.254698	0.001562
C9	-2.034587	0.171714	0.001856
H10	2.305032	-2.551479	-0.005034
C11	0.222120	3.782071	-0.001226
C12	-1.967332	2.737996	-0.001357
C13	-3.439852	0.008478	0.002389
C14	-3.143160	-2.413092	0.002068
H15	-1.086986	-3.123373	0.001004
H16	1.867742	2.354344	0.001234
C17	-1.183462	3.901961	-0.002289
C18	-3.994479	-1.283186	0.002427
H19	-3.574932	-3.414969	0.001692
H20	-4.101244	0.875550	0.002472
H21	-3.052828	2.809179	-0.002057
H22	0.867526	4.658014	-0.001240
H23	-5.076404	-1.412663	0.002680
H24	-1.656140	4.883290	-0.004132

E(RB+HF-LYP) = -688.872273756 Hartree

Table S7. Cartesian coordinates of a fully optimized structure of $[Pt(ppy)(OH_2)_2]^+$ (**7**) in water. The structure was optimized using the B3LYP level of DFT and the LanL2DZ basis set using the PCM method (water) in Gaussian 03.

Atom	X	Y	Z
Pt1	-0.978996	-0.309122	-0.000369
C2	0.824859	-1.140893	-0.001335
C3	3.527576	-2.020505	-0.001238
C4	1.904004	-0.203444	0.000661
C5	1.123969	-2.519095	-0.004130
C6	2.467985	-2.954411	-0.003813
C7	3.246122	-0.642417	0.000795
N8	0.115670	1.375107	-0.000375
C9	1.770324	3.621687	0.001865
C10	-0.432879	2.621385	-0.000681
C11	1.489568	1.204340	0.001159
C12	2.329234	2.333756	0.002466
C13	0.368110	3.769065	0.000148
O14	-2.046262	-2.123514	0.002265
H15	-2.417740	-2.477673	0.847736
H16	-2.584231	-2.384936	-0.785377
H17	-1.516028	2.669753	-0.000985
H18	-0.101520	4.750222	-0.000221
H19	2.416871	4.498444	0.002818
H20	3.409224	2.203611	0.003848
H21	4.067850	0.074306	0.002300
H22	4.560761	-2.365971	-0.001137
H23	2.687767	-4.022573	-0.005850
H24	0.320435	-3.252275	-0.007602
O25	-2.951518	0.743775	-0.000898
H26	-3.505816	0.720303	-0.819971
H27	-3.516572	0.693678	0.809524

E(RB+HF-LYP) = -750.635073323 Hartree

Table S8. Cartesian coordinates of a fully optimized structure of Pt(ppy)(OH)(OH_2) (**8**) in water. The structure was optimized using the B3LYP level of DFT and the LanL2DZ basis set using the PCM method (water) in Gaussian 03.

Atom	X	Y	Z
Pt1	-1.020577	-0.279673	-0.001622
C2	0.783226	-1.171432	-0.006029
C3	3.502126	-2.072733	-0.002042
C4	1.883498	-0.248750	0.005818
C5	1.095204	-2.553480	-0.021226
C6	2.434063	-2.999675	-0.017841
C7	3.225221	-0.694597	0.008115
N8	0.119654	1.362386	-0.000570
C9	1.806520	3.581641	0.006748
C10	-0.412818	2.616184	-0.006744
C11	1.490583	1.165585	0.007764
C12	2.346241	2.286293	0.012926
C13	0.405190	3.750974	-0.004525
O14	-2.167410	-2.053087	-0.014244
H15	-2.077677	-2.689403	0.737629
H16	-3.100968	-2.005928	-0.339813
H17	-1.498021	2.655409	-0.011198
H18	-0.047728	4.740020	-0.010131
H19	2.466352	4.448521	0.010382
H20	3.424269	2.141344	0.020379
H21	4.051076	0.017775	0.016923
H22	4.533368	-2.424273	0.000171
H23	2.647560	-4.069528	-0.028954
H24	0.294436	-3.293035	-0.041176
O25	-2.791198	0.862404	-0.015092
H26	-3.610692	0.322315	0.113201

E(RB+HF-LYP) = -750.160800211 Hartree

Table S9. Cartesian coordinates of a fully optimized structure of Pt(ppy)(OH)(OH_2) (**9**) in water. The structure was optimized using the B3LYP level of DFT and the LanL2DZ basis set using the PCM method (water) in Gaussian 03.

Atom	X	Y	Z
Pt1	-0.950486	-0.461982	-0.000089
N2	-0.074117	1.379625	-0.001419
C3	1.307703	3.816392	0.001444
C4	1.311547	1.380867	0.000327
C5	-0.759907	2.557266	-0.002755
C6	-0.103029	3.793489	-0.001600
C7	2.013068	2.602538	0.002329
C8	0.944943	-1.035417	0.000278
C9	3.742339	-1.563870	-0.000817
C10	1.423320	-2.364632	-0.001004
C11	1.897809	0.033509	0.000932
C12	3.286374	-0.233902	0.000385
C13	2.809620	-2.626780	-0.001440
O14	-3.047405	0.314464	-0.001294
H15	-3.603753	0.182110	-0.807785
H16	-3.588492	0.220150	0.820806
H17	0.706892	-3.183319	-0.001260
H18	3.165518	-3.657913	-0.002511
H19	4.811518	-1.773869	-0.001289
H20	4.010430	0.581484	0.000588
H21	3.100968	2.600836	0.004570
H22	1.845405	4.763669	0.003097
H23	-0.686680	4.711653	-0.002766
H24	-1.842042	2.479985	-0.005270
O25	-1.681730	-2.359485	0.004320
H26	-2.672654	-2.344135	-0.003999

E(RB+HF-LYP) = -750.171657739 Hartree

Table S10. Electronic transitions of $[Pt(ppy)Cl_2]^-$ in water based on the TD-DFT (B3LYP/LanL2DZ, PCM, water) calculations (The corresponding MO diagrams are shown in Figures S5 and S6).

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Major contributions	|CI coef| (> 0.3)
3	28673	348.76	0.0598	55 → 58 (HOMO-2 → LUMO)	0.53138
				56 → 60 (HOMO-1 → LUMO+2)	0.38247
7	30765	325.04	0.0576	57 → 59 (HOMO → LUMO+1)	0.63949
13	35291	283.36	0.3369	53 → 58 (HOMO-4 → LUMO)	0.41296
				55 → 59 (HOMO-2 → LUMO+1)	0.49087
18	40011	249.93	0.1619	56 → 61 (HOMO-1 → LUMO+3)	0.37714
				57 → 61 (HOMO → LUMO+3)	0.38828
19	40019	249.88	0.0834	56 → 61 (HOMO-1 → LUMO+3)	0.55271
22	41603	240.37	0.1042	55 → 61 (HOMO-2 → LUMO+3)	0.58435
23	41902	238.65	0.0704	52 → 60 (HOMO-5 → LUMO+2)	0.62880
35	46733	213.98	0.0711	57 → 63 (HOMO → LUMO+4)	0.60918
37	47407	210.94	0.3829	50 → 60 (HOMO-7 → LUMO+2)	0.47566
44	49159	203.42	0.0735	48 → 60 (HOMO-9 → LUMO+2)	0.35099
				56 → 63 (HOMO-1 → LUMO+4)	0.48884
45	49643	201.44	0.0511	55 → 63 (HOMO-2 → LUMO+4)	-0.40005
				56 → 64 (HOMO-1 → LUMO+5)	0.47170

[a]Oscillator strength.

Table S11. Electronic transitions of **2** in water based on the TD-DFT (B3LYP/LanL2DZ, PCM, water) calculations (The corresponding MO diagrams are shown in Figures S7 and S8).

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Major contributions	|CI coef| (> 0.3)
3	29569	338.19	0.0867	56 → 59 (HOMO-2 → LUMO)	0.61703
10	33718	296.58	0.111	55 → 59 (HOMO-3 → LUMO)	0.44383
				56 → 60 (HOMO-2 → LUMO+1)	0.42174
12	35718	279.97	0.3425	55 → 59 (HOMO-3 → LUMO)	-0.37240
				56 → 60 (HOMO-2 → LUMO+1)	0.50237
15	40261	248.38	0.1252	53 → 59 (HOMO-5 → LUMO)	0.44973
				58 → 62 (HOMO → LUMO+3)	-0.40805
19	42615	234.66	0.2911	56 → 62 (HOMO-2 → LUMO+3)	0.47912
				58 → 62 (HOMO → LUMO+3)	0.36399
32	47601	210.08	0.0987	53 → 60 (HOMO-5 → LUMO+1)	0.52970
36	49111	203.62	0.0618	54 → 63 (HOMO-4 → LUMO+4)	0.60886
38	49436	202.28	0.1093	57 → 65 (HOMO-1 → LUMO+6)	0.66467
39	49593	201.64	0.0581	56 → 65 (HOMO-2 → LUMO+6)	0.31708

[a]Oscillator strength.

Table S12. Electronic transitions of **3** in water based on the TD-DFT (B3LYP/LanL2DZ, PCM, water) calculations (The corresponding MO diagrams are shown in Figures S9 and S10).

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Major contributions	|CI coef| (> 0.3)
6	32285	309.74	0.0751	56 → 59 (HOMO-2 → LUMO)	0.56223
9	33887	295.10	0.1967	54 → 59 (HOMO-4 → LUMO)	0.55252
14	38168	262.00	0.3410	56 → 60 (HOMO-2 → LUMO+1)	0.56750
18	40962	244.13	0.3015	58 → 62 (HOMO → LUMO+3)	0.53804
33	47179	211.96	0.0605	58 → 65 (HOMO → LUMO+6)	0.56468
35	47941	208.59	0.3613	51 → 61 (HOMO-7 → LUMO+2)	-0.30245
				52 → 61 (HOMO-6 → LUMO+2)	0.43066
39	49576	201.71	0.1029	57 → 65 (HOMO-2 → LUMO+6)	0.66200

[a]Oscillator strength.

Table S13. Electronic transitions of $Pt_2(ppy)_2(\mu\text{-}Cl)_2$ (**4**) in water based on the TD-DFT (B3LYP/LanL2DZ, PCM, water) calculations (The corresponding MO diagrams and the simulated absorption spectra are shown in Figures S11, S12 and S26).

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Transition	|CI coef| (> 0.3)
9	28811	347.09	0.0775	105 → 107 (HOMO-1 → LUMO)	0.53911
				106 → 108 (HOMO → LUMO+1)	-0.41947
15	30802	324.65	0.1381	102 → 107 (HOMO-4 → LUMO)	0.56866
17	31821	314.26	0.0893	105 → 111 (HOMO-1 → LUMO+4)	0.35343
				106 → 110 (HOMO → LUMO+3)	0.49004
24	33780	296.03	0.2521	99 → 107 (HOMO-7 → LUMO)	-0.32755
				100 → 108 (HOMO-6 → LUMO+1)	0.33926
				105 → 111 (HOMO-1 → LUMO+4)	0.32673
32	34740	287.85	0.1433	105 → 111 (HOMO-1 → LUMO+4)	-0.41014
				106 → 110 (HOMO → LUMO+3)	0.44699
43	37081	269.68	0.4676	102 → 111 (HOMO-4 → LUMO+4)	0.51652
49	39712	251.81	0.0671	99 → 111 (HOMO-7 → LUMO+4)	-0.40162
				100 → 110 (HOMO-6 → LUMO+3)	0.49487
51	40130	249.19	0.2124	95 → 107 (HOMO-11 → LUMO)	-0.33924
				96 → 108 (HOMO-10 → LUMO+1)	0.36712
				106 → 113 (HOMO → LUMO+6)	0.34099
59	41651	240.09	0.2875	96 → 108 (HOMO-10 → LUMO+1)	-0.33800
				106 → 113 (HOMO → LUMO+6)	0.47092
62	42626	234.60	0.2960	105 → 114 (HOMO-1 → LUMO+7)	0.59094
70	43725	228.70	0.1381	95 → 107 (HOMO-11→ LUMO)	-0.32910
				96 → 108 (HOMO-10 → LUMO+1)	-0.30837
				97 → 109 (HOMO-9 → LUMO+2)	0.31743
				98 → 112 (HOMO-8 → LUMO+5)	0.38540
74	44258	225.95	0.1048	102 → 114 (HOMO-4 → LUMO+7)	0.45871
79	45177	221.35	0.0546	106 → 115 (HOMO → LUMO+8)	0.36692
93	47414	210.91	0.2120	96 → 110 (HOMO-10 → LUMO+3)	0.42472
109	49232	203.12	0.1456	95 → 111 (HOMO-11 → LUMO+4)	0.36086
111	49574	201.72	0.1434	99 → 114 (HOMO-7 → LUMO+7)	0.31642
				100 → 113 (HOMO-6 → LUMO+6)	0.43581
115	49816	200.74	0.0587	89 → 107 (HOMO-17 → LUMO)	0.35165
				99 → 114 (HOMO-7 → LUMO+7)	0.36196

[a]Oscillator strength.

Table S14. Electronic transitions of **5** in water based on the TD-DFT (B3LYP/LanL2DZ, PCM, water) calculations (The corresponding MO diagrams are shown in Figures S13 and S14).

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Major contributions	|CI coef| (> 0.3)
5	28730	348.07	0.0945	56 → 59 (HOMO-2 → LUMO)	0.64316
11	33872	295.23	0.0521	52 → 59 (HOMO-6 → LUMO)	0.51296
				56 → 60 (HOMO-2 → LUMO+1)	0.36080
13	35283	283.42	0.1970	52 → 59 (HOMO-6 → LUMO)	-0.37768
				56 → 60 (HOMO-2 → LUMO+1)	0.41706
15	36660	272.78	0.2162	58 → 62 (HOMO → LUMO+3)	0.55798
18	37919	263.72	0.2097	55 → 60 (HOMO-3 → LUMO+1)	0.57519
24	41873	238.82	0.0734	58 → 65 (HOMO → LUMO+6)	0.55351
28	43869	227.95	0.3145	53 → 61 (HOMO-5 → LUMO+2)	0.46910
				54 → 61 (HOMO-7 → LUMO+2)	-0.35047
41	48305	207.02	0.1101	57 → 65 (HOMO-1 → LUMO+6)	0.67294
42	48403	206.60	0.0628	50 → 60 (HOMO-8 → LUMO+1)	0.42044
46	49960	200.16	0.1025	49 → 60 (HOMO-9 → LUMO+1)	0.47133
				52 → 62 (HOMO-6 → LUMO+3)	0.33210

[a]Oscillator strength.

Table S15. Electronic transitions of **6** in water based on the TD-DFT (B3LYP/LanL2DZ, PCM, water) calculations (The corresponding MO diagrams are shown in Figures S15 and S16).

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Major contributions	|CI coef| (> 0.3)
3	25816	387.36	0.0665	57 → 59 (HOMO-1 → LUMO)	0.57528
4	28618	349.43	0.1161	58 → 60 (HOMO → LUMO+1)	0.61452
9	34363	291.01	0.2523	54 → 59 (HOMO-4 → LUMO)	0.60065
20	40368	247.72	0.4548	57 → 61 (HOMO-1 → LUMO+2)	0.53371
30	44342	225.52	0.0546	57 → 63 (HOMO-1 → LUMO+4)	0.59227
39	47522	210.43	0.1044	56 → 65 (HOMO-2 → LUMO+6)	0.67877
41	48914	204.44	0.0904	49 → 60 (HOMO-9 → LUMO+1)	0.52684
44	49210	203.21	0.1237	50 → 60 (HOMO-8 → LUMO+1)	0.37904
				54 → 61 (HOMO-4 → LUMO+2)	-0.31722

[a]Oscillator strength

Table S16. Electronic transitions of **7** in water based on the TD-DFT (B3LYP/LanL2DZ, PCM, water) calculations (The corresponding MO diagrams are shown in Figures S17 and S18).

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Major contributions	|CI coef| (> 0.3)
6	33008	302.96	0.0813	57 → 60 (HOMO-2 → LUMO)	0.51823
				58 → 62 (HOMO-1 → LUMO+2)	-0.32227
8	34579	289.19	0.2366	56 → 60 (HOMO-3 → LUMO)	0.46859
12	38679	258.54	0.2629	57 → 61 (HOMO-2 → LUMO+1)	0.56063
14	40876	244.64	0.1735	54 → 60 (HOMO-5 → LUMO)	0.46582
				59 → 63 (HOMO → LUMO+3)	0.37466
19	42203	236.95	0.1535	54 → 60 (HOMO-5 → LUMO)	-0.33536
				58 → 64 (HOMO-1 → LUMO+4)	0.52274
20	42883	233.19	0.0686	58 → 64 (HOMO-1 → LUMO+4)	-0.40035
				59 → 63 (HOMO → LUMO+3)	0.39853
27	48119	207.82	0.0951	54 → 61 (HOMO-5 → LUMO+1)	0.58887

[a]Oscillator strength

Table S17. Electronic transitions of **8** in water based on the TD-DFT (B3LYP/LanL2DZ, PCM, water) calculations (The corresponding MO diagrams are shown in Figures S19 and S20).

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Major contributions	|CI coef| (> 0.3)
5	30314	329.88	0.0607	57 → 60 (HOMO-2 → LUMO)	0.62458
7	32816	304.73	0.0878	55 → 60 (HOMO-4 → LUMO)	0.45099
				56 → 60 (HOMO-3 → LUMO)	0.36868
				57 → 61 (HOMO-2 → LUMO+1)	-0.30553
14	37067	269.78	0.3029	57 → 61 (HOMO-2 → LUMO+1)	0.50562
15	37392	267.44	0.2029	56 → 61 (HOMO-3 → LUMO+1)	0.41534
				59 → 63 (HOMO → LUMO+3)	0.45756
16	37488	266.75	0.1106	55 → 61 (HOMO-2 → LUMO+1)	0.42503
				56 → 61 (HOMO-3 → LUMO+1)	-0.35455
				59 → 63 (HOMO → LUMO+3)	0.32649
18	38671	258.59	0.0602	55 → 61 (HOMO-4 → LUMO+1)	0.46282
				56 → 61 (HOMO-3 → LUMO+1)	0.35735
26	43491	229.93	0.0867	57 → 63 (HOMO-2 → LUMO+3)	0.40500
29	44279	225.84	0.0613	57 → 63 (HOMO-2 → LUMO+3)	0.33044
34	46812	213.62	0.1261	55 → 63 (HOMO-4 → LUMO+3)	0.35015
				56 → 63 (HOMO-3 → LUMO+3)	0.32522
39	49036	203.93	0.0635	49 → 60 (HOMO-10 → LUMO)	0.31328
				52 → 61 (HOMO-7 → LUMO+1)	-0.34936
				58 → 66 (HOMO-1 → LUMO+6)	0.40083
40	49147	203.47	0.0621	58 → 66 (HOMO-1 → LUMO+6)	0.44374
41	49717	201.14	0.0755	55 → 64 (HOMO-4 → LUMO+4)	0.47138
42	49828	200.69	0.0614	57 → 65 (HOMO-2 → LUMO+5)	0.47189

[a]Oscillator strength

Table S18. Electronic transitions of **9** in water based on the TD-DFT (B3LYP/LanL2DZ, PCM, water) calculations (The corresponding MO diagrams are shown in Figures S21 and S22).

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Major contributions	|CI coef| (> 0.3)
3	26721	374.24	0.0571	58 → 60 (HOMO-1 → LUMO)	0.58018
				59 → 61 (HOMO → LUMO+1)	-0.30106
4	29339	340.84	0.1110	59 → 61 (HOMO → LUMO+1)	0.60925
9	34666	288.47	0.3099	56 → 60 (HOMO-3 → LUMO)	0.60956
11	36232	276.00	0.0507	57 → 63 (HOMO-2 → LUMO+3)	0.48839
				57 → 64 (HOMO-2 → LUMO+4)	-0.39301
18	40634	246.10	0.2241	54 → 60 (HOMO-5 → LUMO)	0.40873
				58 → 62 (HOMO-1 → LUMO+2)	-0.38786
20	41679	239.93	0.1652	54 → 60 (HOMO-5 → LUMO)	0.37467
				58 → 62 (HOMO-1 → LUMO+2)	0.37779
				59 → 65 (HOMO → LUMO+5)	0.36634
23	42492	235.34	0.0616	59 → 65 (HOMO → LUMO+5)	0.52591
36	47578	210.18	0.0862	51 → 60 (HOMO-8 → LUMO)	0.30649
				52 → 61 (HOMO-7 → LUMO+1)	-0.37901
				54 → 61 (HOMO-5 → LUMO+1)	0.37825
37	47884	208.84	0.1043	57 → 66 (HOMO-2 → LUMO+6)	0.68233
38	48759	205.09	0.0797	52 → 61 (HOMO-7 → LUMO+1)	0.41921

[a]Oscillator strength

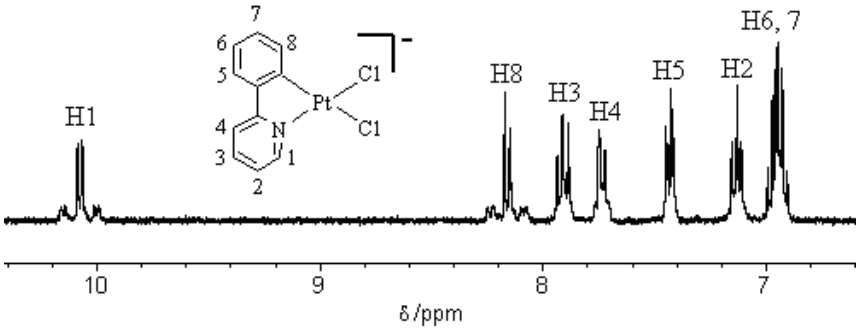

Fig. S1 ^{1}H NMR spectrum of **1** in $(CD_3)_2CO$, where only the aromatic proton region is shown.

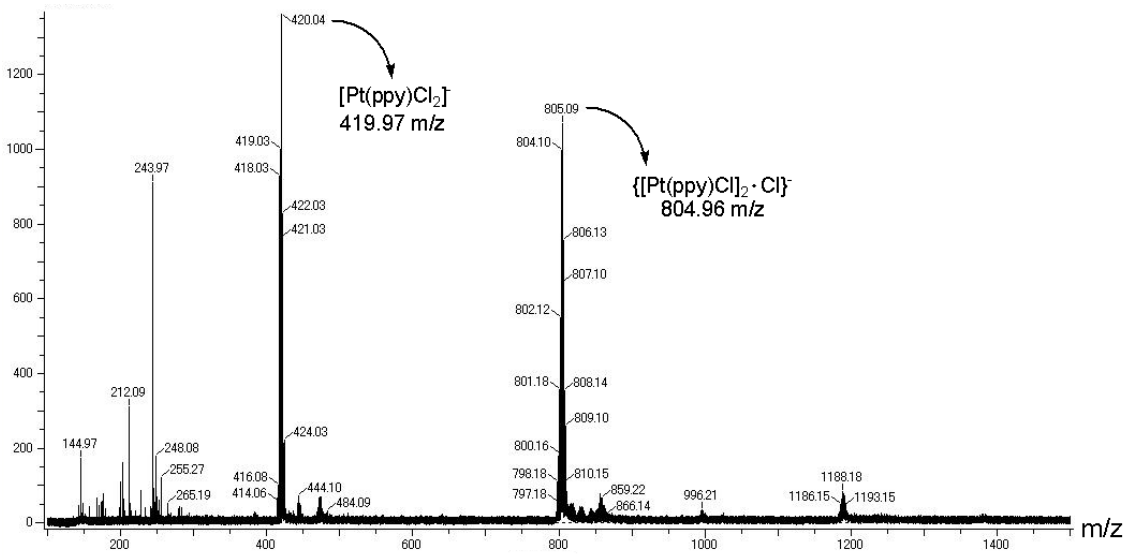

Fig. S2 ESI-TOF mass spectrum of **4** in methanol.

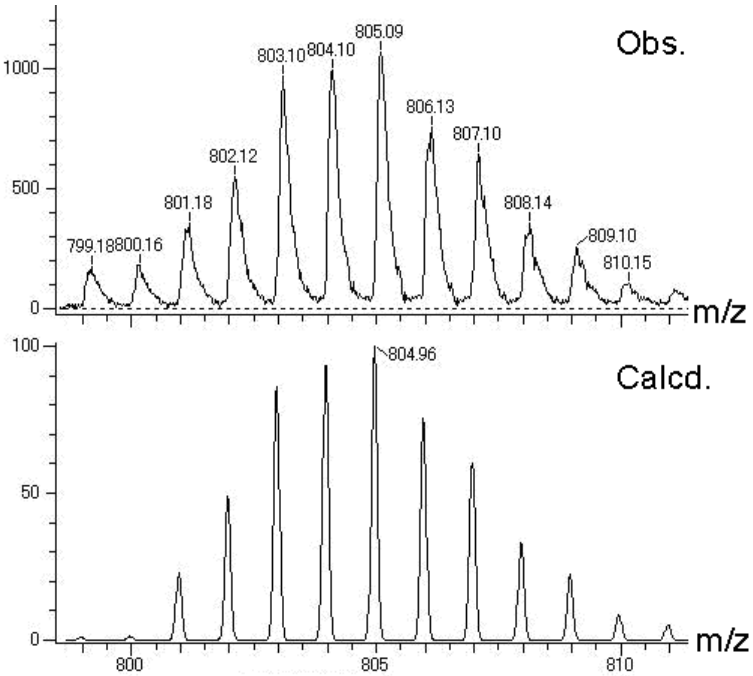

Fig. S3 The observed (top) and calculated (bottom) negative-ion ESI-TOF mass spectra obtained for a solution of **4** in methanol, in which monovalent anion $\{[Pt(ppy)Cl]_2 \cdot Cl\}^-$ is detected.

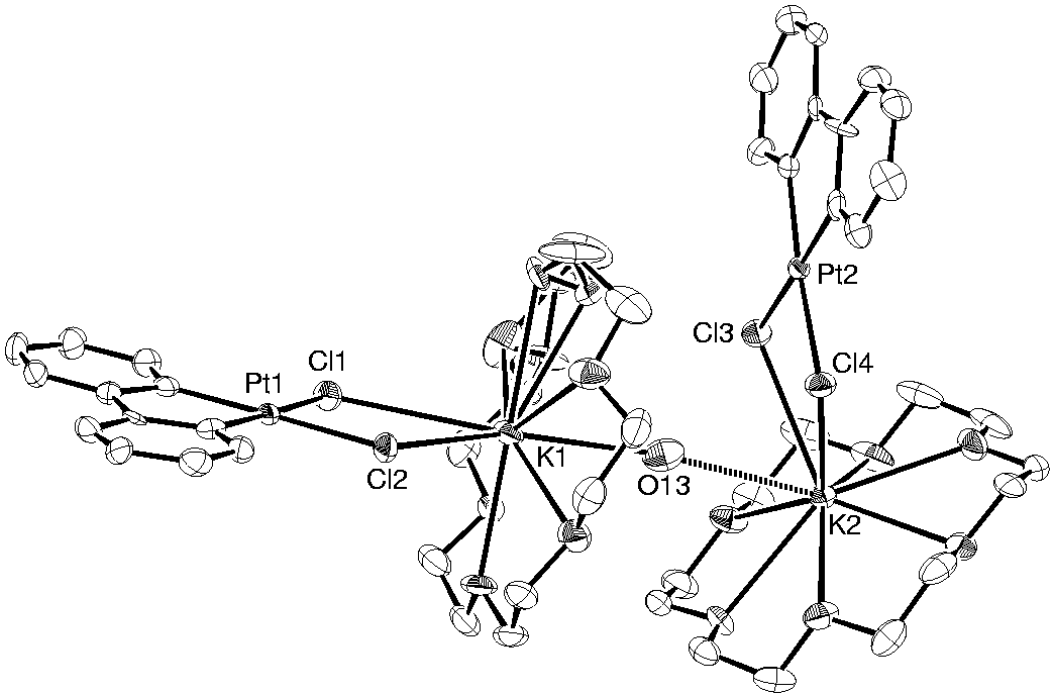

Fig. S4 The manner how the two independent molecules in the crystal of **1** are associated with each other, where the O(water) atom is weakly associated to the K ion in the adjacent molecule at a distance of O(13)•••K(2) = 3.30(1) Å.

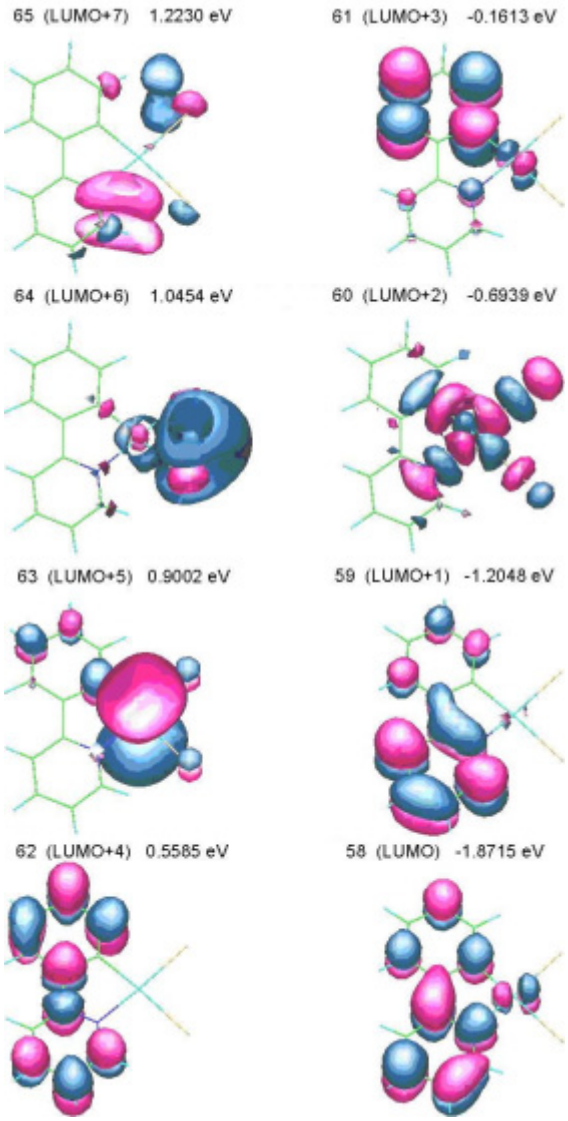

Fig. S5 Contour plots of the B3LYP/LANL2DZ derived LUMO through LUMO+7 molecular orbitals of $[Pt(ppy)Cl_2]^-$, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

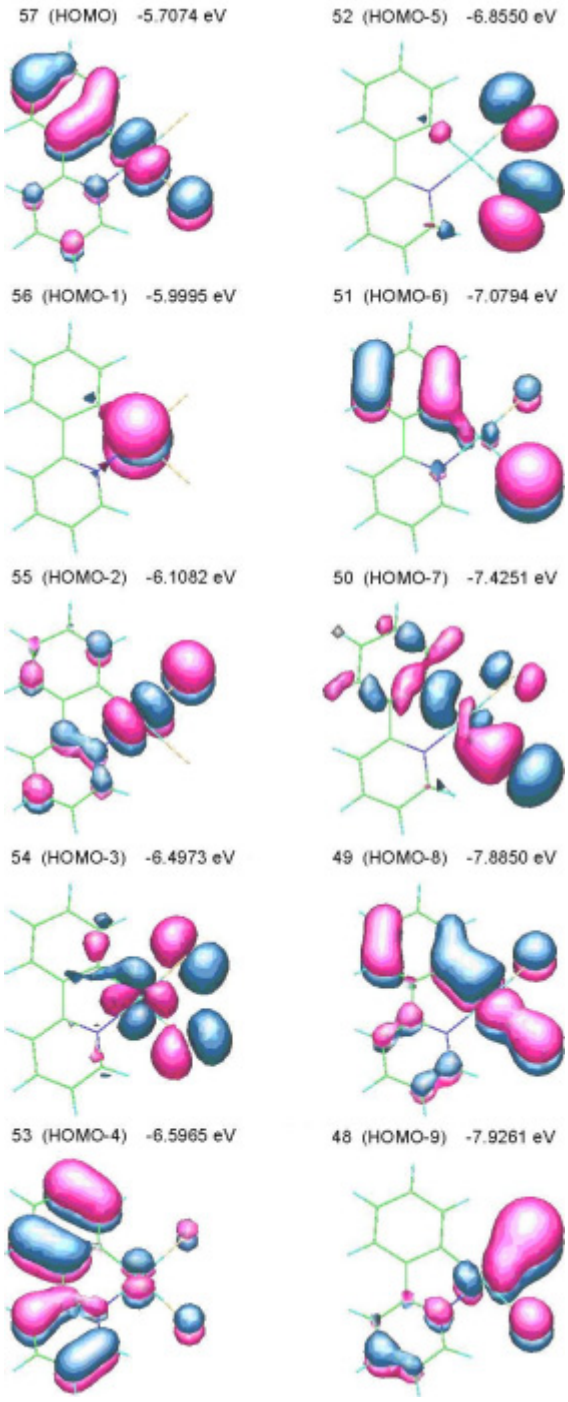

Fig. S6 Contour plots of the B3LYP/LANL2DZ derived HOMO-9 through HOMO molecular orbitals of $[Pt(ppy)Cl_2]^-$, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

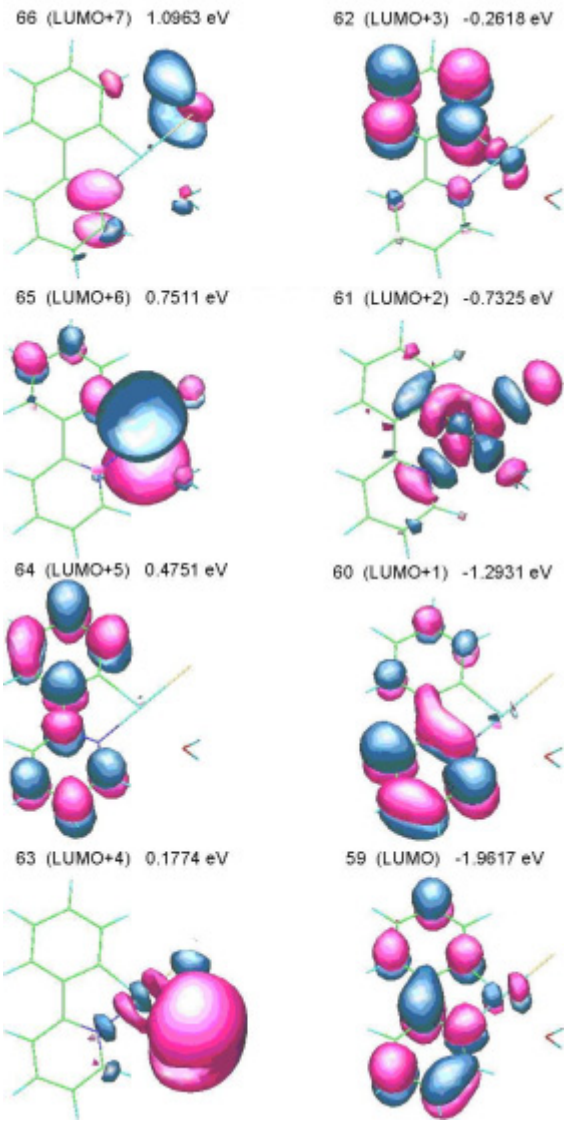

Fig. S7 Contour plots of the B3LYP/LANL2DZ derived LUMO through LUMO+7 molecular orbitals of **2**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

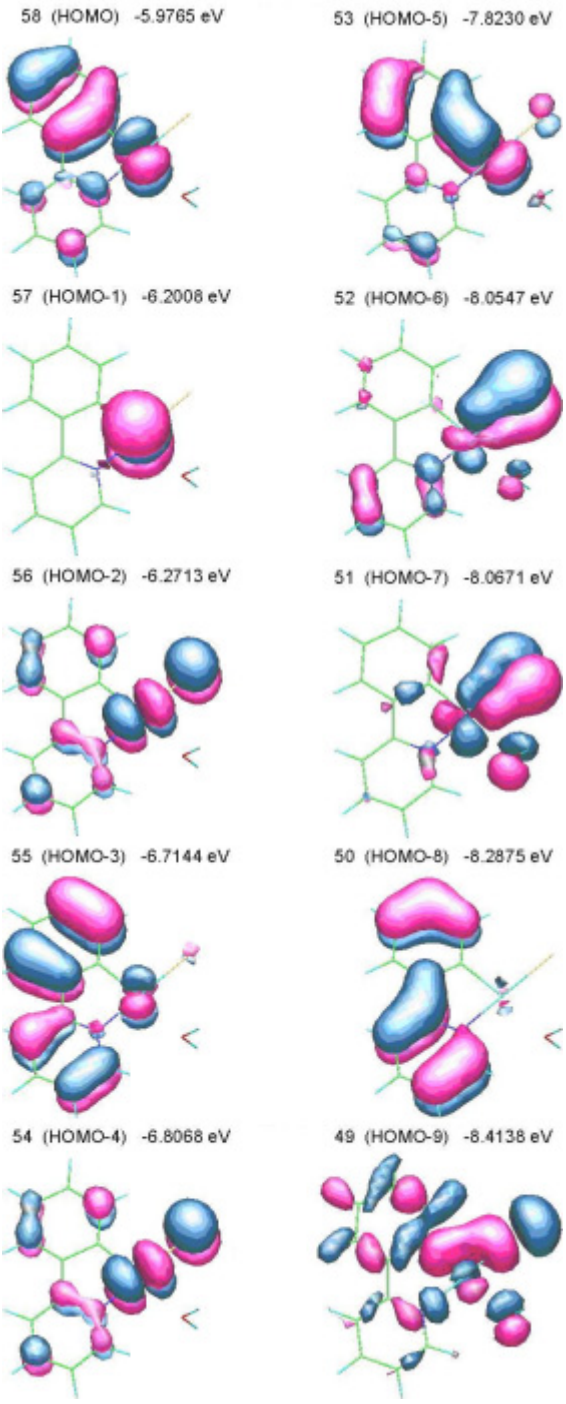

Fig. S8 Contour plots of the B3LYP/LANL2DZ derived HOMO-9 through HOMO molecular orbitals of **2**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

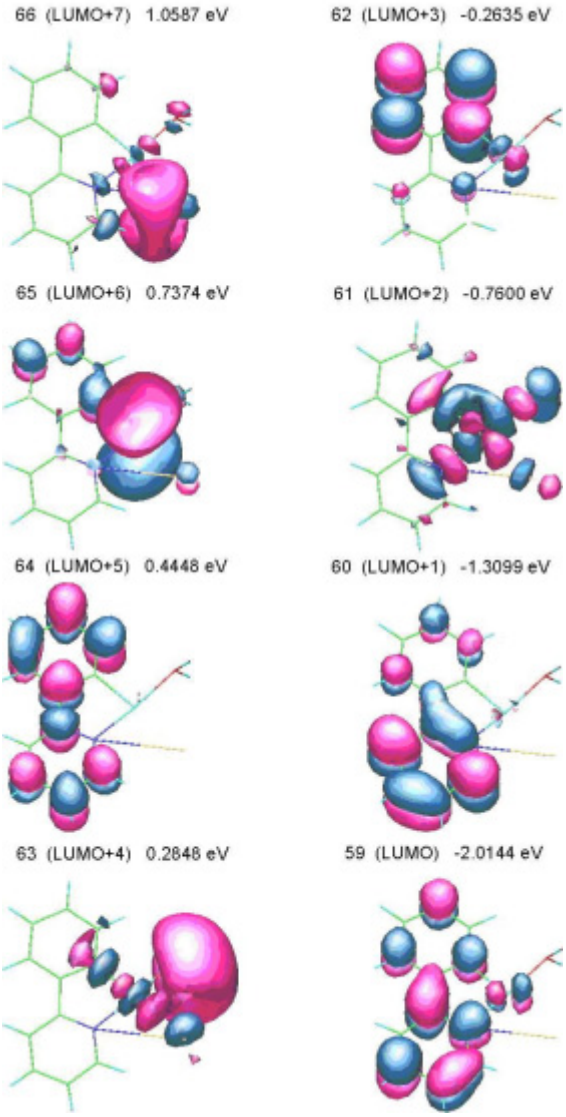

Fig. S9 Contour plots of the B3LYP/LANL2DZ derived LUMO through LUMO+7 molecular orbitals of **3**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

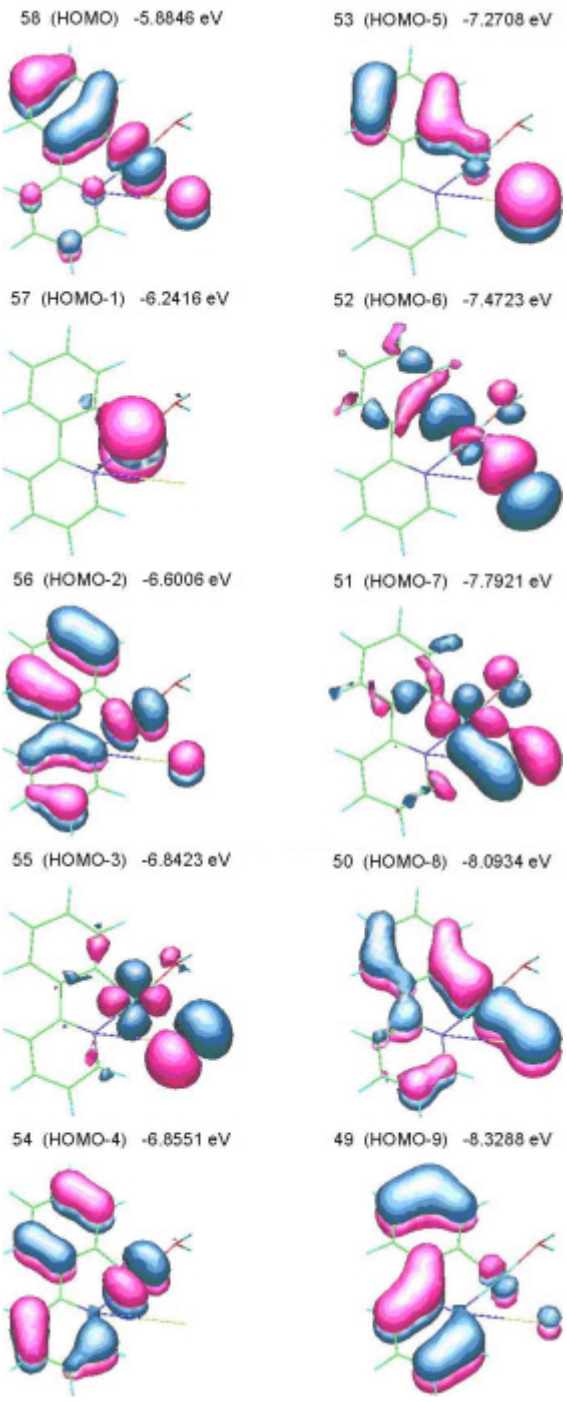

Fig. S10 Contour plots of the B3LYP/LANL2DZ derived HOMO-9 through HOMO molecular orbitals of **3**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

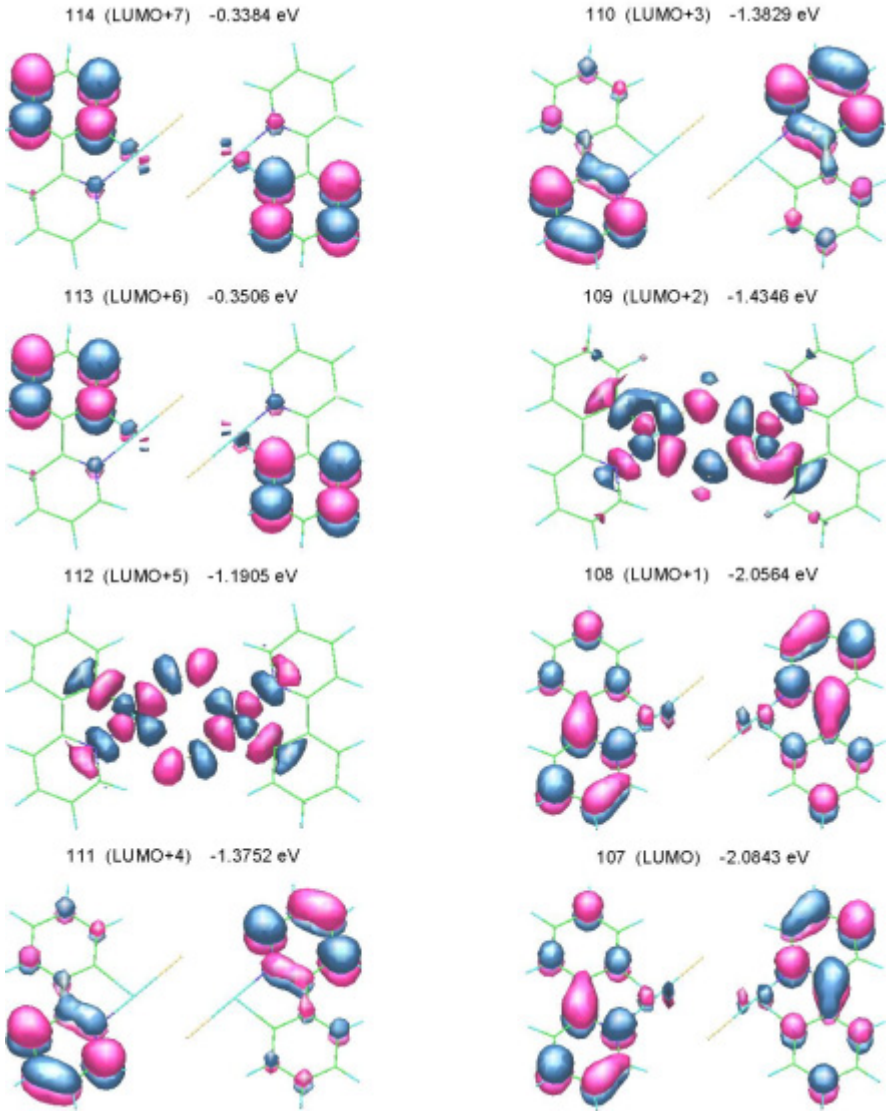

Fig. S11 Contour plots of the B3LYP/LANL2DZ derived LUMO through LUMO+7 molecular orbitals of **4**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

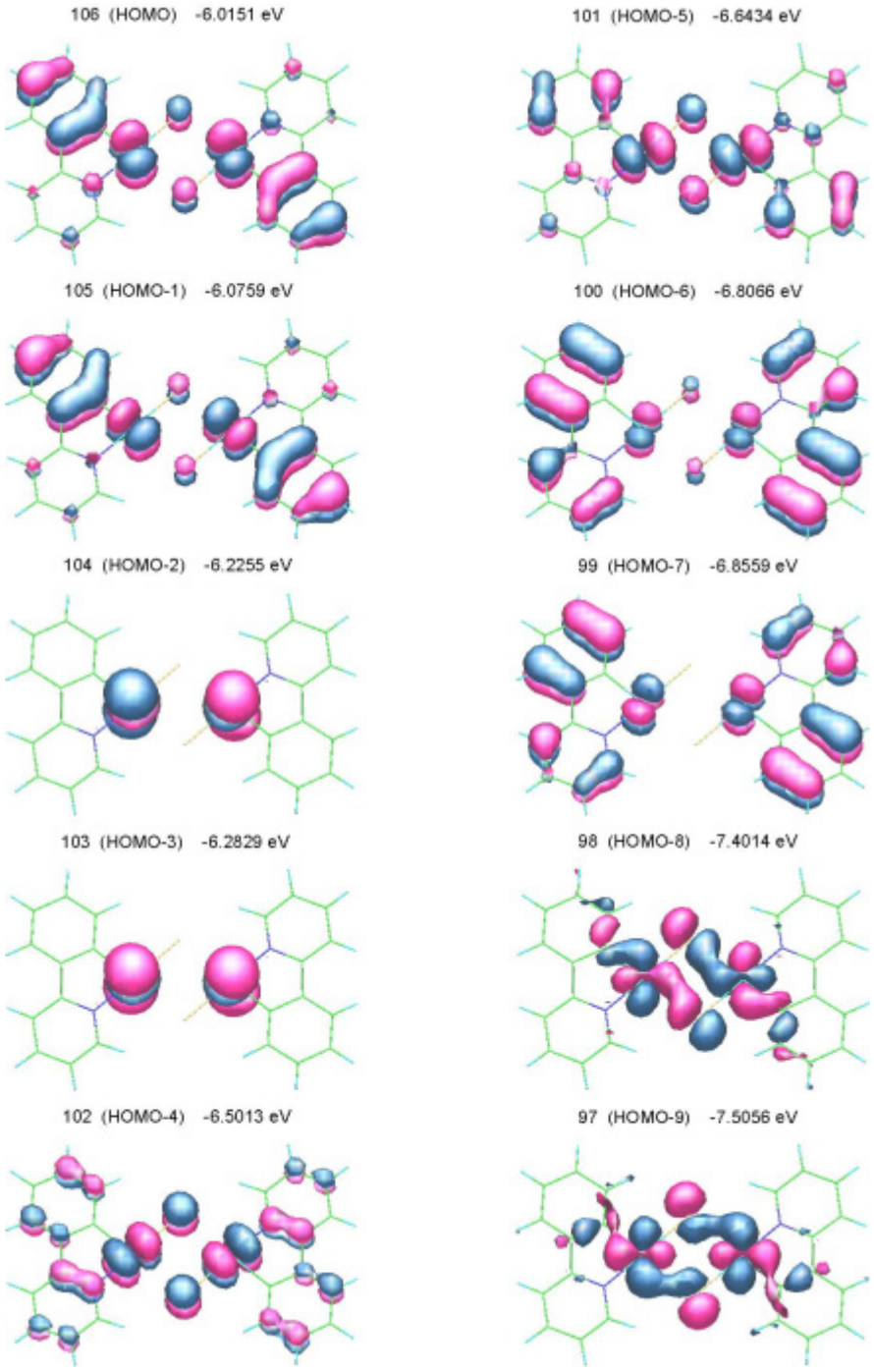

Fig. S12 Contour plots of the B3LYP/LANL2DZ derived HOMO-9 through HOMO molecular orbitals of **4**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

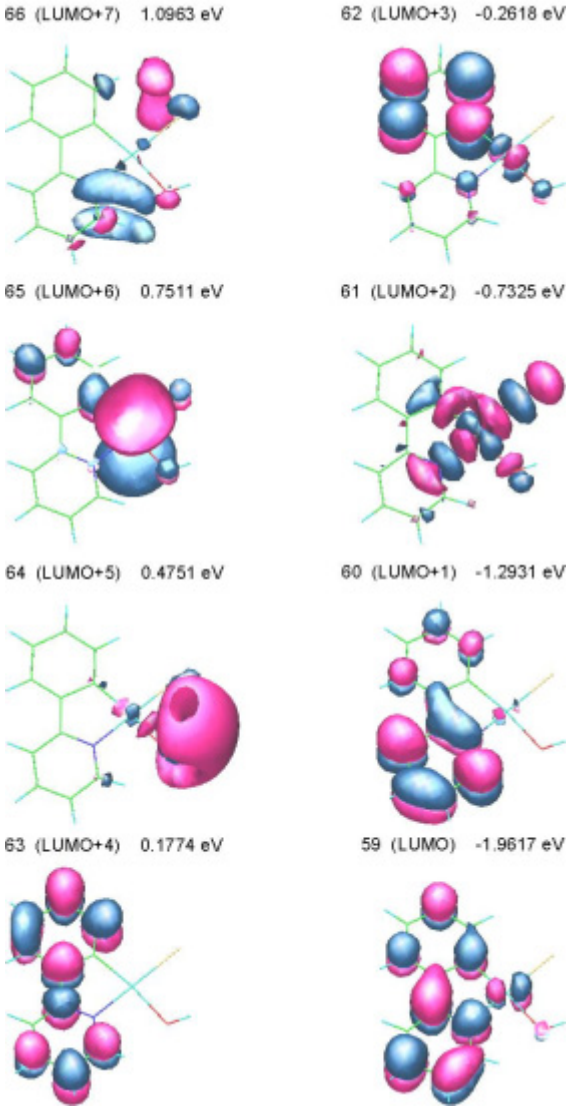

Fig. S13 Contour plots of the B3LYP/LANL2DZ derived LUMO through LUMO+7 molecular orbitals of **5**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

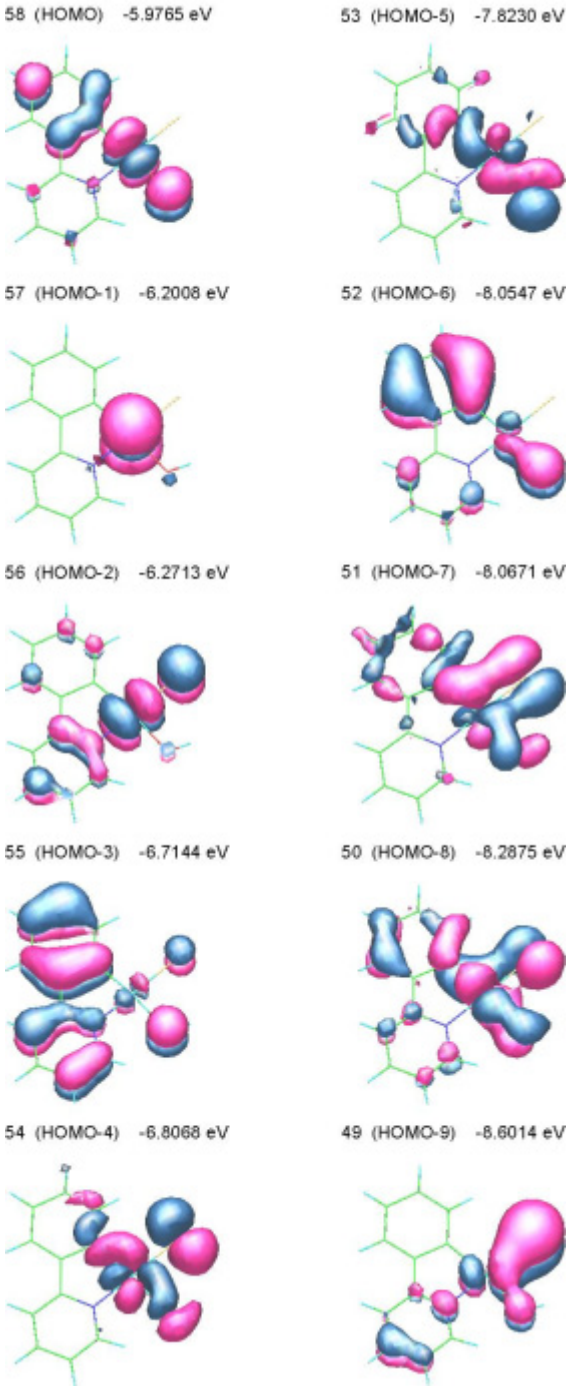

Fig. S14 Contour plots of the B3LYP/LANL2DZ derived HOMO-9 through HOMO molecular orbitals of **5**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

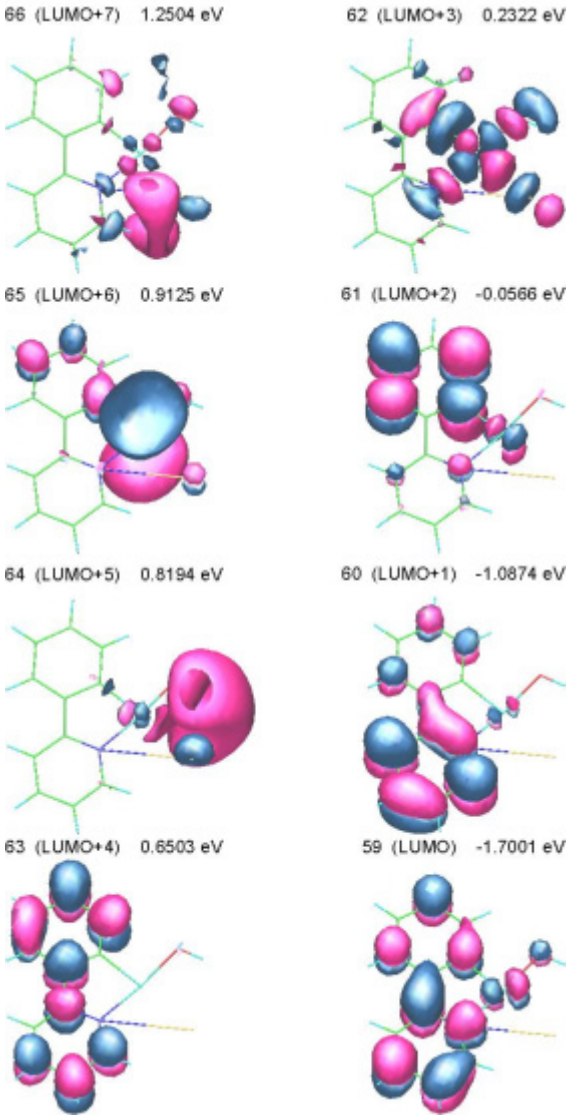

Fig. S15 Contour plots of the B3LYP/LANL2DZ derived LUMO through LUMO+7 molecular orbitals of **6**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

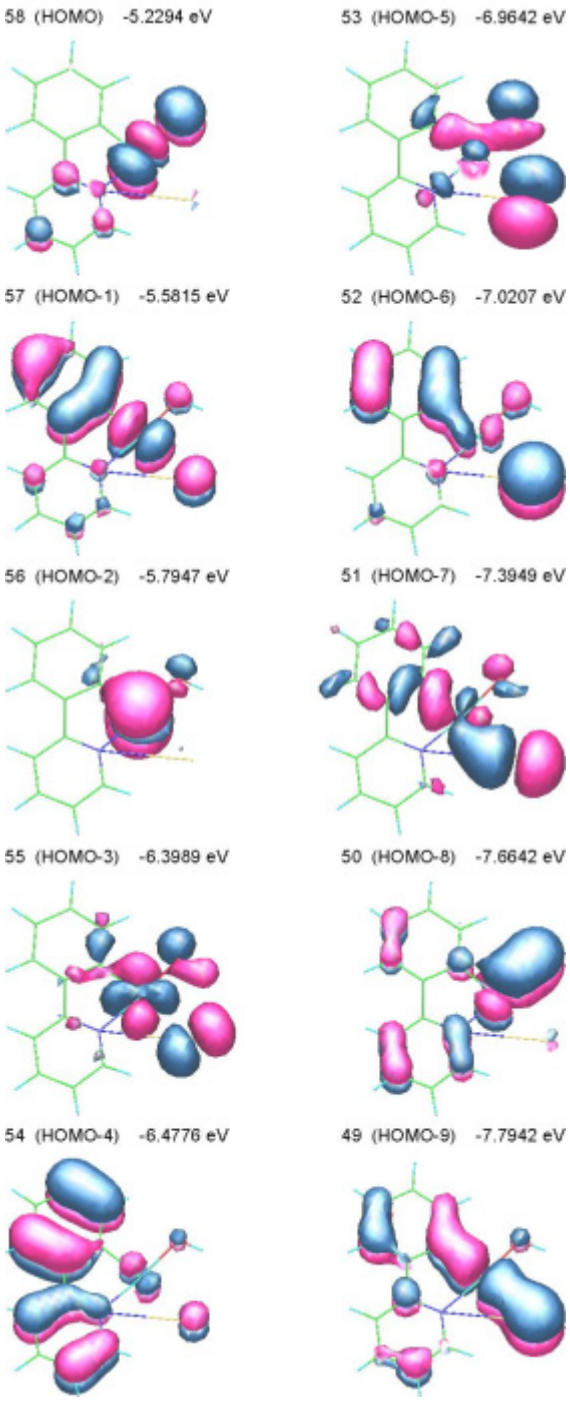

Fig. S16 Contour plots of the B3LYP/LANL2DZ derived HOMO-9 through HOMO molecular orbitals of **6**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

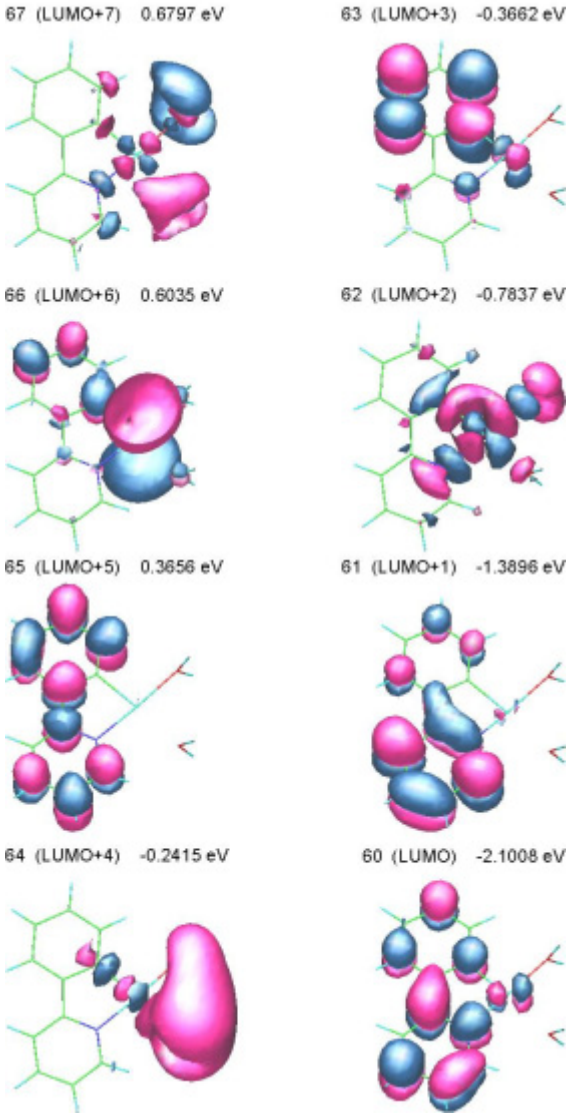

Fig. S17 Contour plots of the B3LYP/LANL2DZ derived LUMO through LUMO+7 molecular orbitals of **7**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

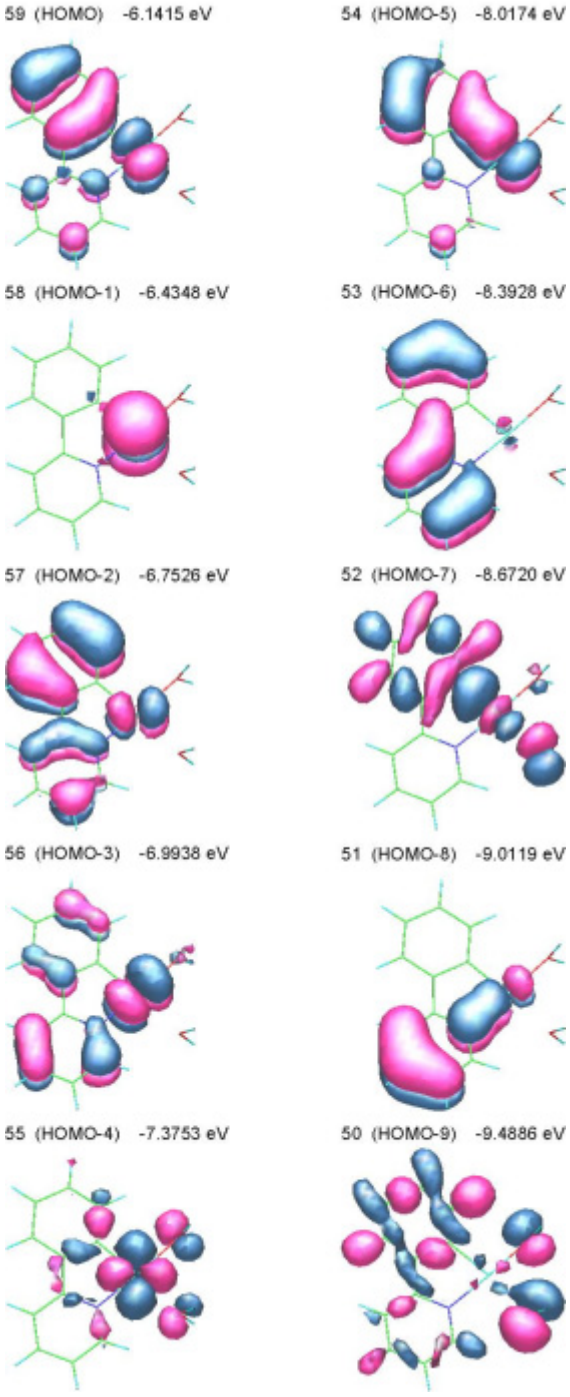

Fig. S18 Contour plots of the B3LYP/LANL2DZ derived HOMO-9 through HOMO molecular orbitals of **7**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

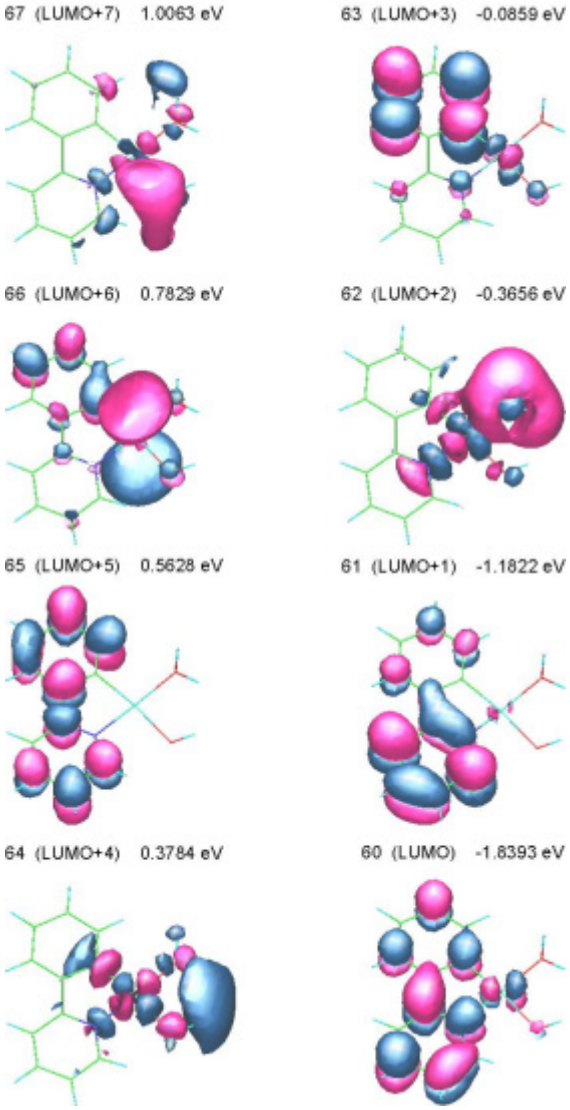

Fig. S19 Contour plots of the B3LYP/LANL2DZ derived LUMO through LUMO+7 molecular orbitals of **8**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

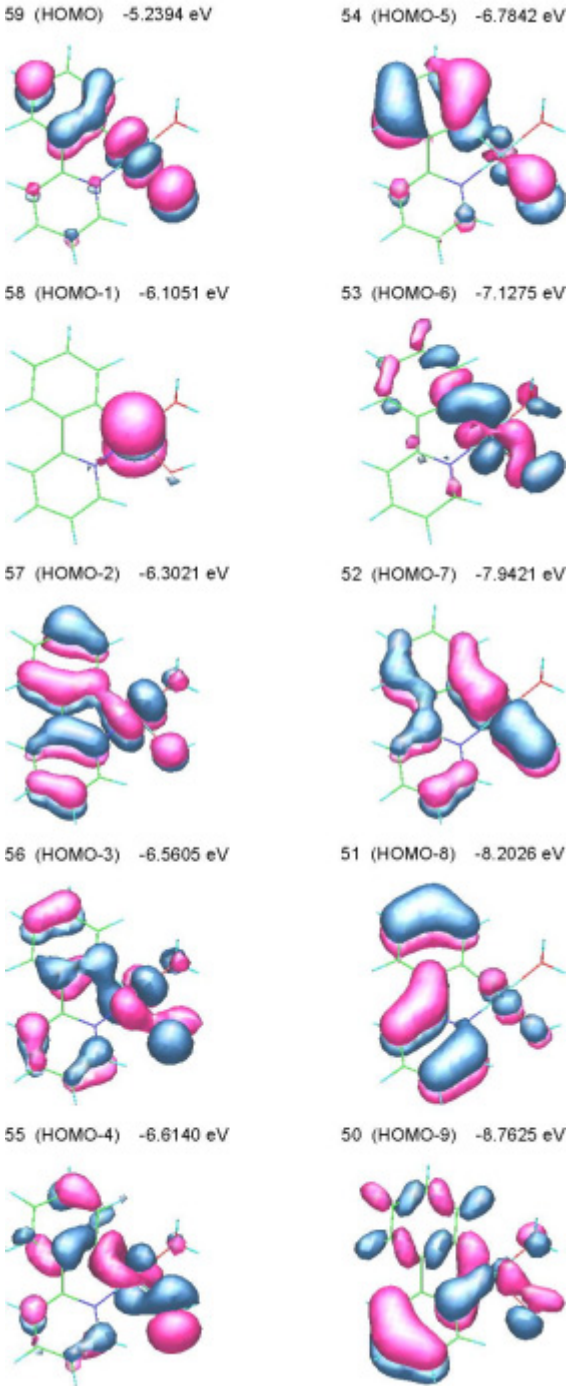

Fig. S20 Contour plots of the B3LYP/LANL2DZ derived HOMO-9 through HOMO molecular orbitals of **8**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

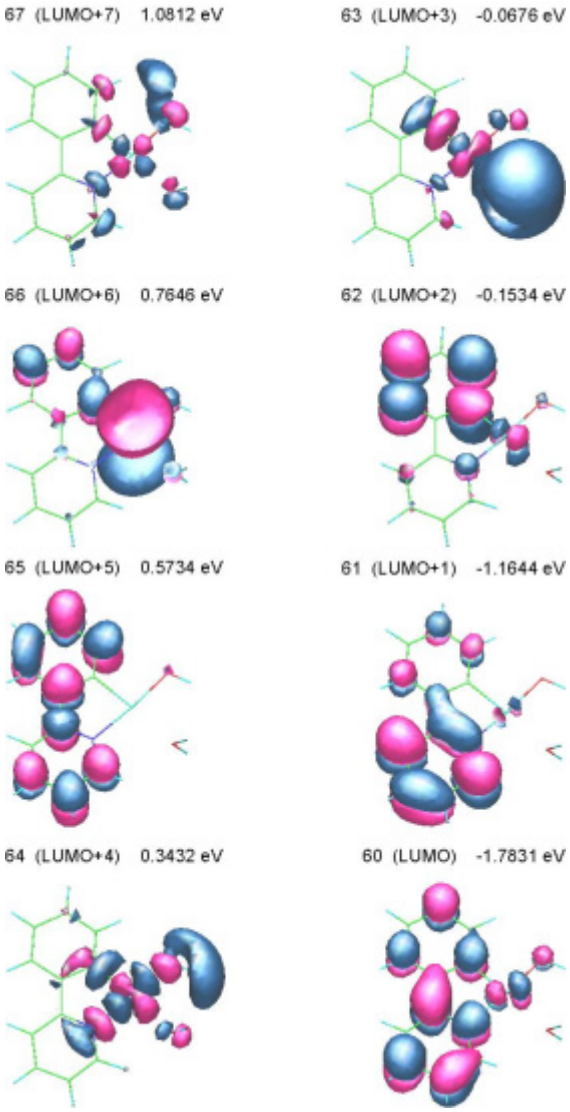

Fig. S21 Contour plots of the B3LYP/LANL2DZ derived LUMO through LUMO+7 molecular orbitals of **9**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

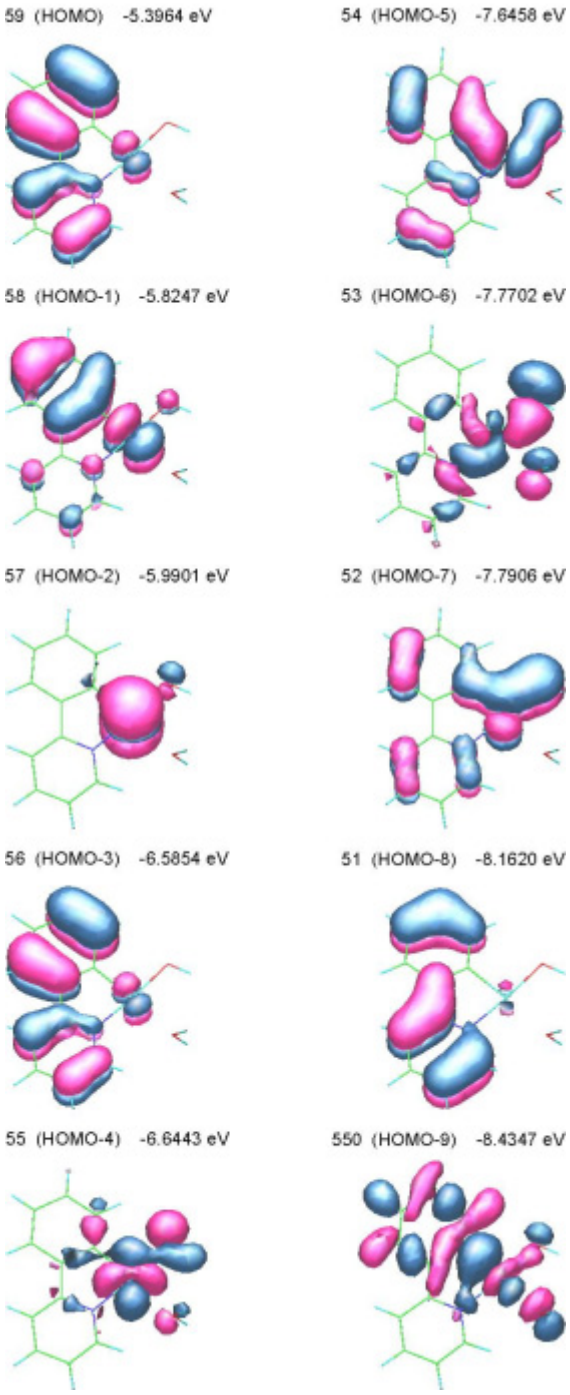

Fig. S22 Contour plots of the B3LYP/LANL2DZ derived HOMO-9 through HOMO molecular orbitals of **9**, where the structure in aqueous media was computed using the polarizable continuum model (PCM) in Gaussian 03.

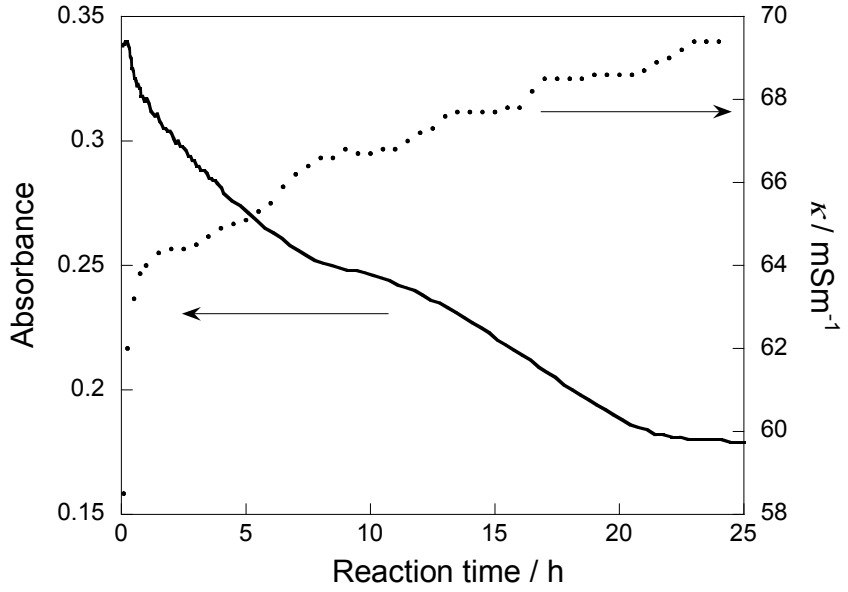

Fig. S23 Solidline: The time course of the change in absorbance at 40 kcm^{-1} after dissolution of **1** into water (1.8×10^{-5} M) at 25 °C in air. Dotted line: The time course in the change of electrical conductivity (κ) after dissolution of **1** into water (2.9×10^{-5} M) at 25 °C in air. The pH values were measured at the start and the end of the hydrolysis reaction (start (2 min): 5.40, end (24 h): 6.07).

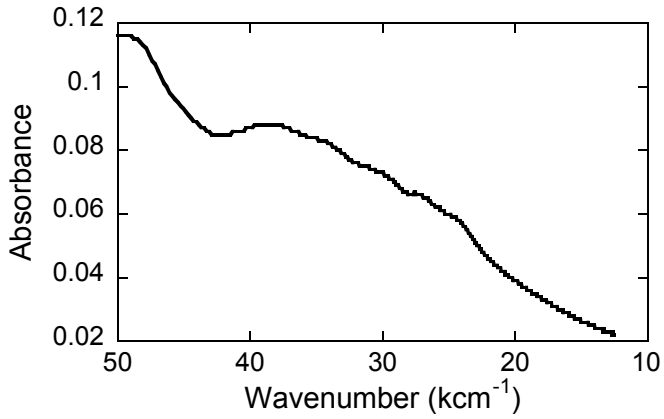

Fig. S24 The solid-state UV-visible absorption spectrum of $Pt_2(ppy)_2(\mu\text{-}Cl)_2$ (**4**) observed by the Nujol-Mull method using a liquid paraffin matrix.

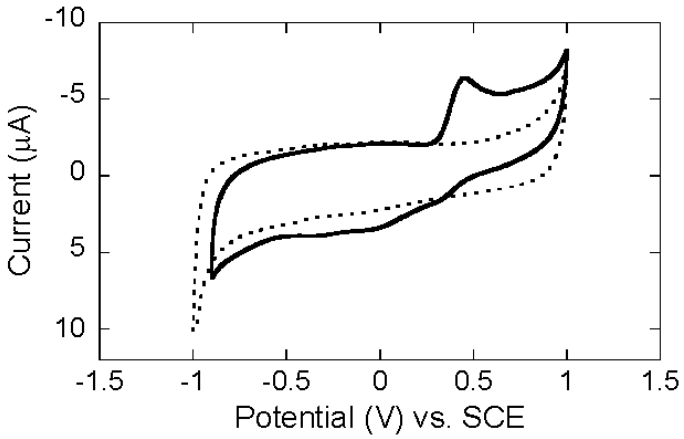

Fig. S25 The cyclic voltammogram of [K(18-crown-6)][Pt(ppy)Cl_2]·0.5H_2O (**1**) in aqueous 1.0 M KCl solution, at 20 °C, recorded at a scan rate of 100 mV/s. The dashed line corresponds to a blank scan in the absence of **1**.

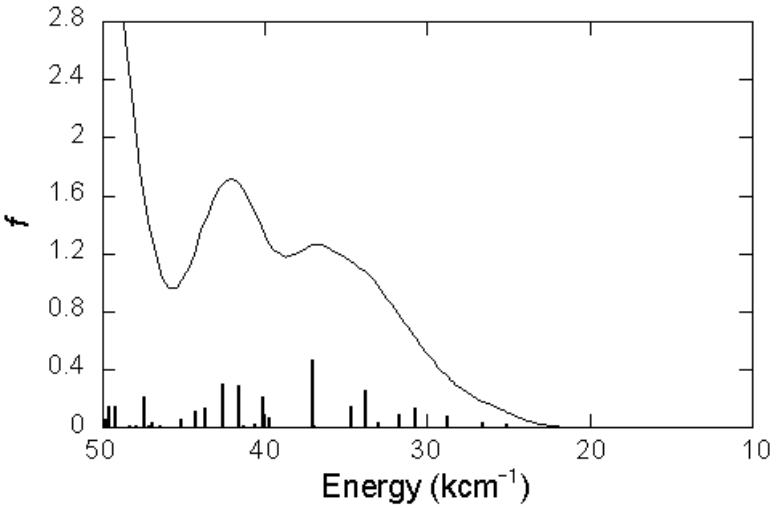

Fig. S26 The absorption spectrum of $Pt_2(ppy)_2(\mu\text{-}Cl)_2$ (**4**) in water computed based on the TD-DFT calculations (B3LYP/LanL2DZ) using the PCM method in Gaussian 03. The simulated spectrum roughly coincides with that observed in the solid state (see Fig. S24).