Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Aqueous Emissive Cyclometalated Iridium Photoreductant: Synthesis, Computational and Photocatalytic Reduction of 4-nitrophenol

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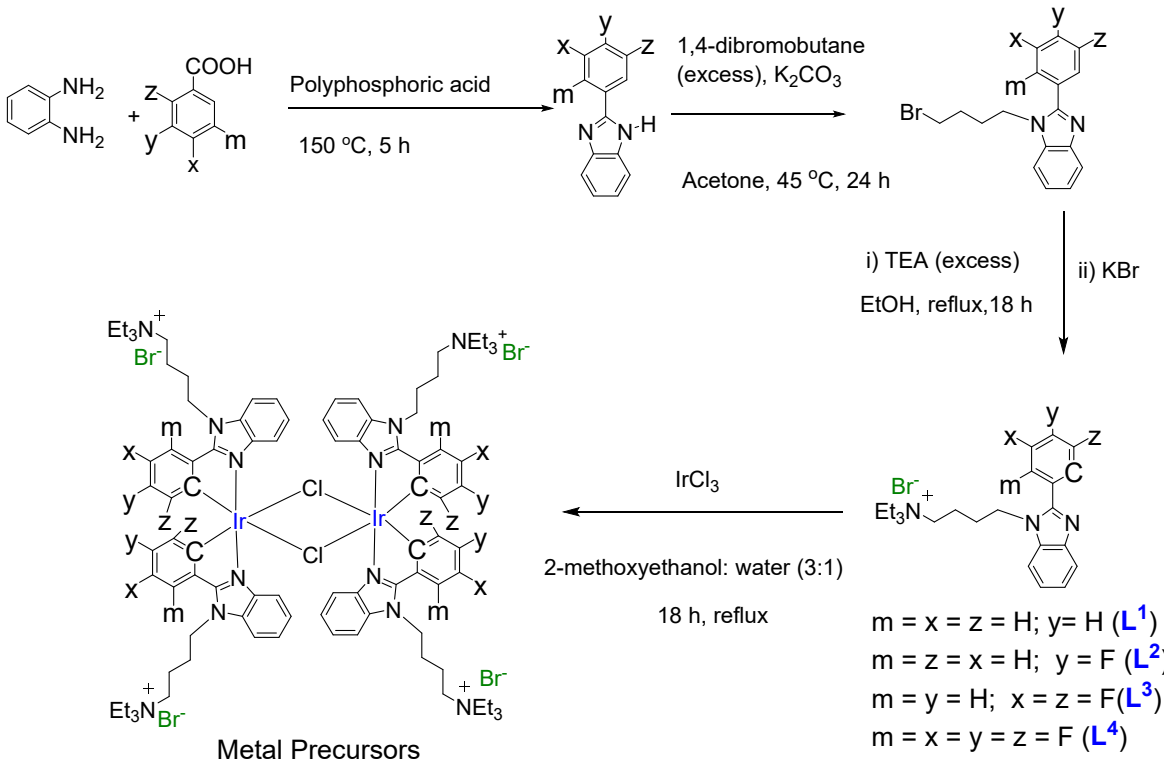
Scheme S1. Synthetic Scheme for the preparation of ligands **L[1]** – **L[4]** and their dimeric precursors.



Scheme S2. Synthetic scheme for the preparation of complexes

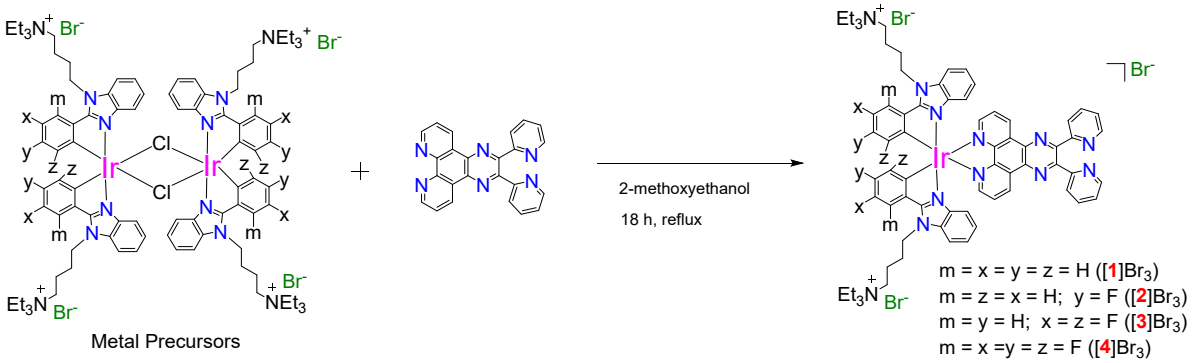


Figure S1. ^{1}H NMR spectra of the ligands **L^{1}** – **L^{4}** in $(CD_3)_2SO$.

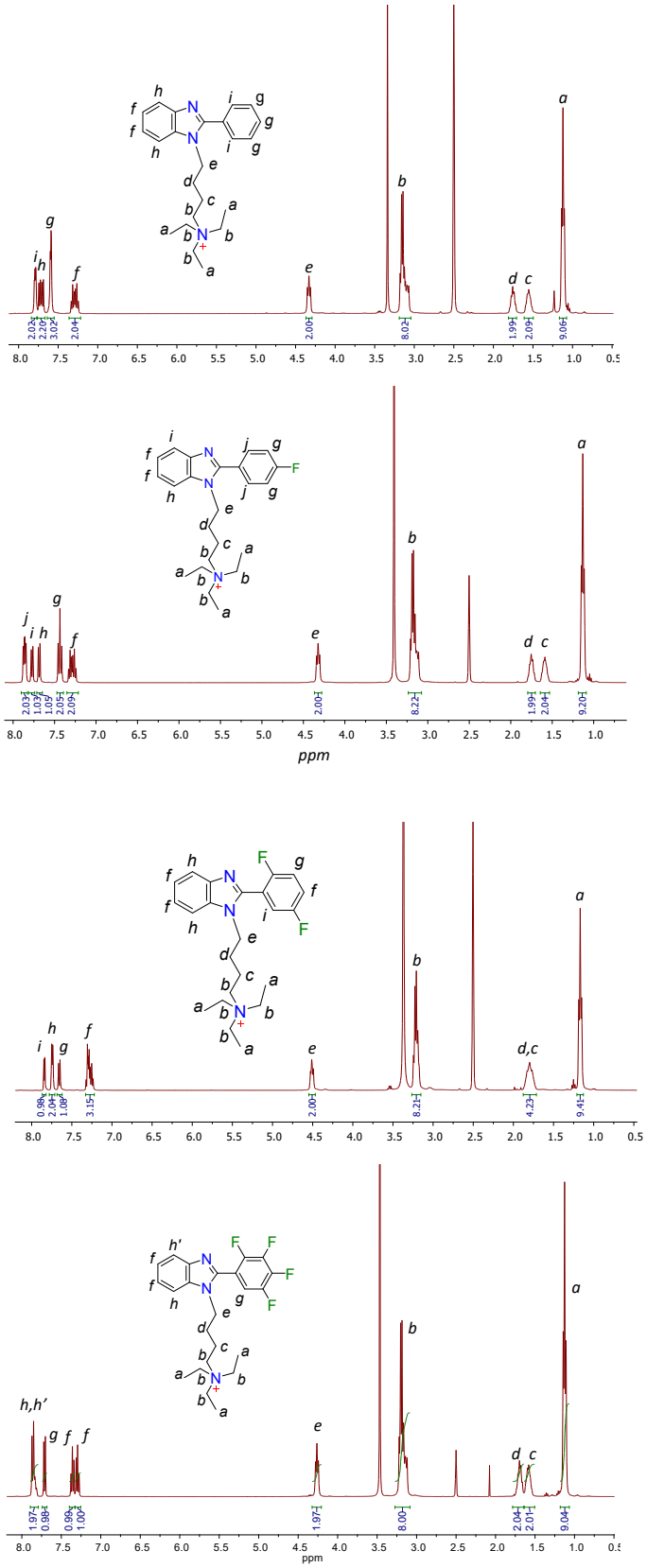


Figure S2. Experimental (blue) and simulated (red) high-resolution mass spectra (HRMS) of the complexes $[\mathbf{1}]^{3+}$ - $[\mathbf{4}]^{3+}$.

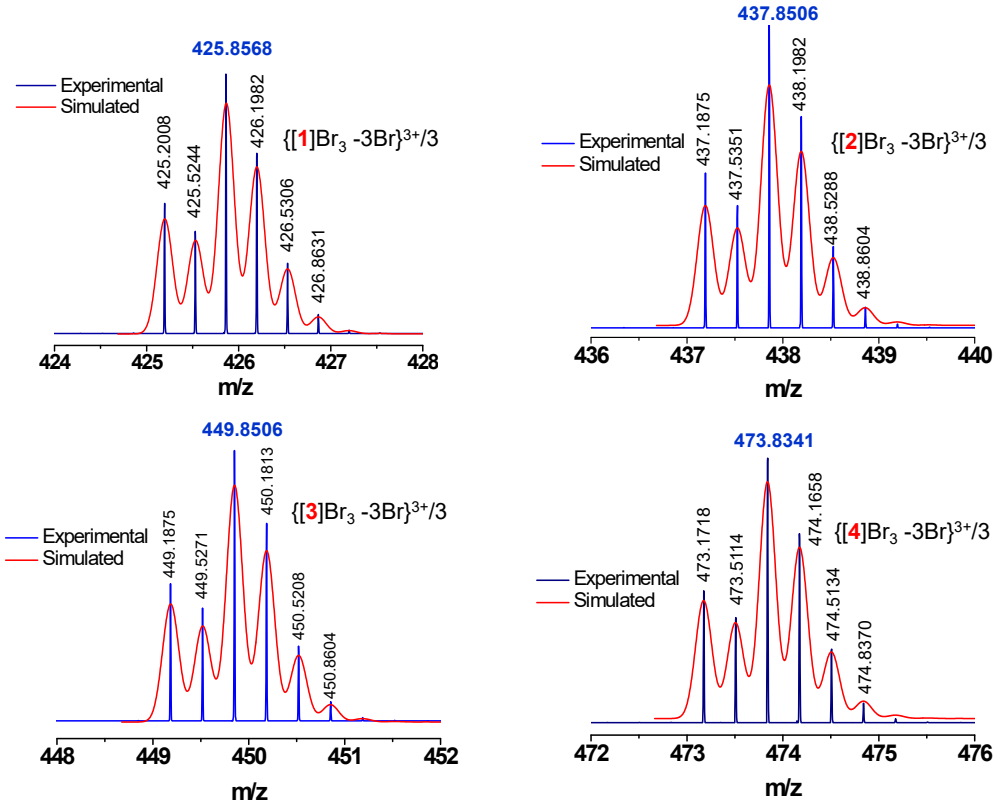


Figure S3. ^{1}H NMR spectra of the complexes [**1**]$^{3+}$ – [**4**]$^{3+}$ in $(CD_3)_2SO$.

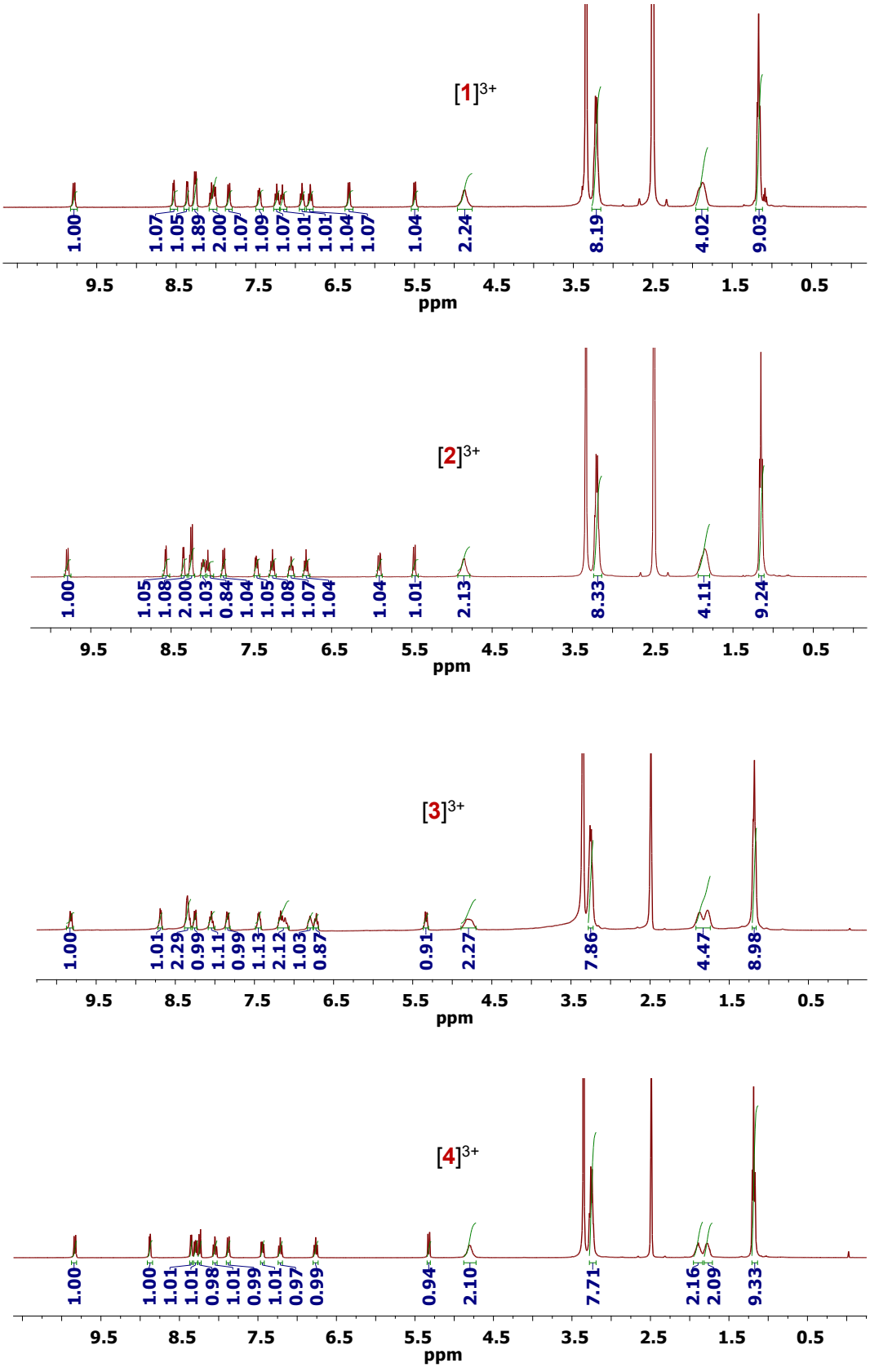


Figure S4. $^{13}C\{^{1}H\}$ NMR spectra of the complexes [**1**]$^{3+}$ – [**4**]$^{3+}$ in $(CD_3)_2SO$.

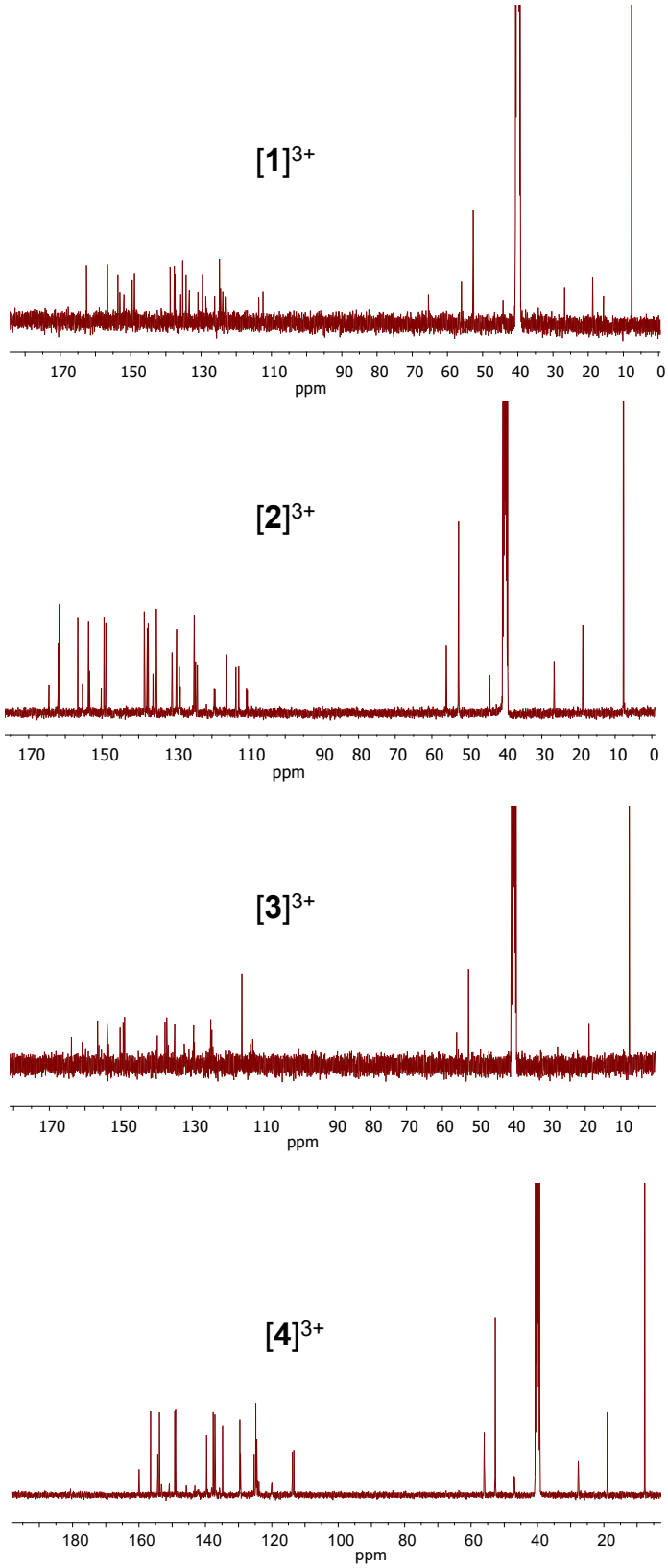


Figure S5. ^{19}F NMR spectra of the complexes $[\mathbf{2}]^{3+}$ – $[\mathbf{4}]^{3+}$ in $(CD_3)_2SO$.

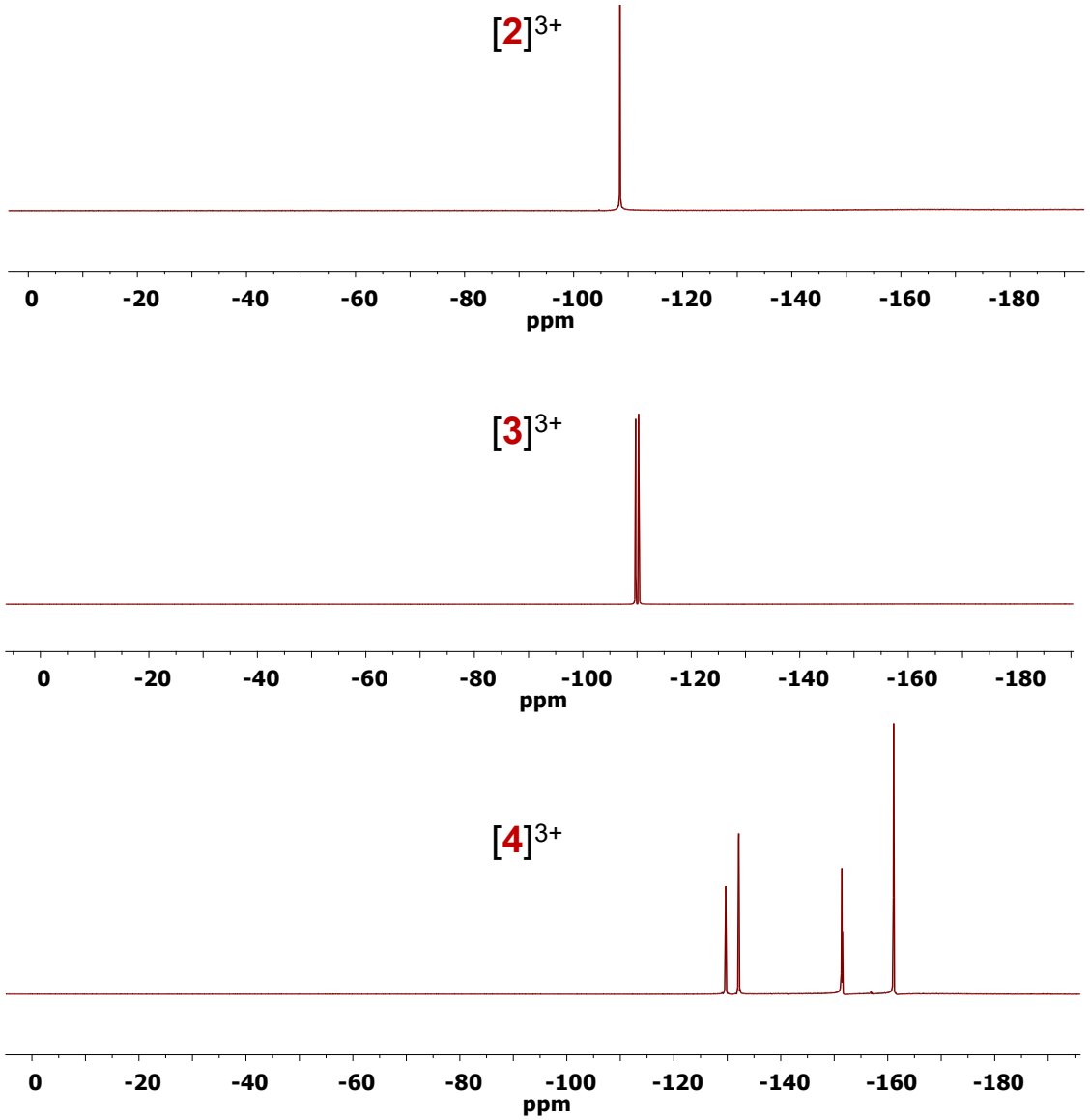


Figure S6. ^{1}H-^{1}H COSY spectra of complex [**1**]$^{3+}$ in $(CD_3)_2SO$.

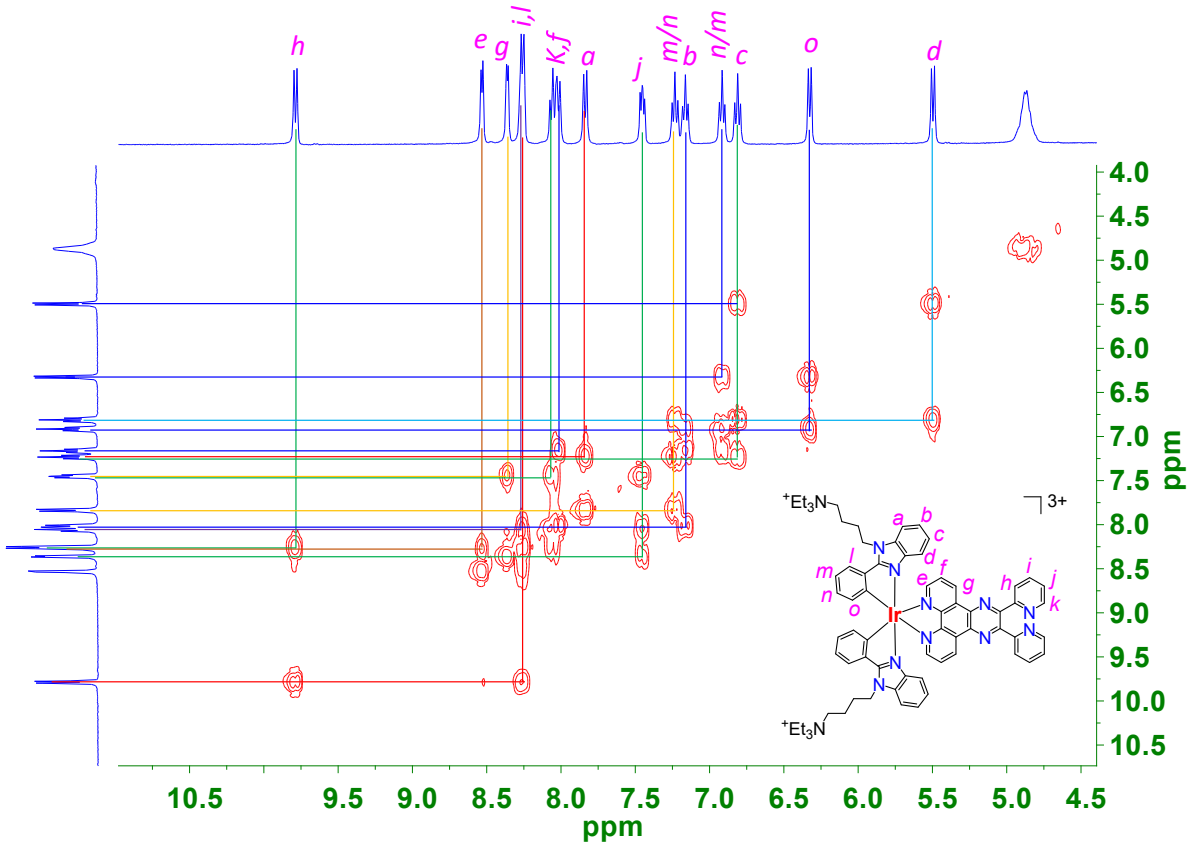


Table S1. B3LYP optimised coordinates of complex [**1**]$^{3+}$ in gas phase.

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	77	0.000659	-0.94071	0.015312
2	7	1.828125	-1.11524	1.003288
3	7	-1.82755	-1.10234	-0.9735
4	7	-0.81786	0.81527	1.089588
5	7	0.833562	0.805861	-1.06329
6	7	3.77727	-2.16377	1.297713
7	7	-3.78338	-2.13819	-1.26866
8	7	0.959614	5.643955	-1.02795
9	7	-0.9147	5.653808	1.034107
10	7	-1.47619	8.901599	-0.06542
11	7	1.535613	8.895399	0.055392
12	6	0.906636	-2.38217	-1.09251
13	6	-0.91919	-2.36989	1.127732
14	6	0.404593	-2.99231	-2.2524
15	1	-0.58521	-2.72861	-2.61162
16	6	1.150924	-3.92645	-2.97437
17	1	0.730475	-4.37754	-3.86945
18	6	2.43899	-4.27831	-2.56116
19	1	3.021469	-4.99661	-3.13016
20	6	2.973671	-3.69475	-1.41781
21	1	3.984038	-3.95847	-1.12581
22	6	2.218273	-2.76707	-0.67716
23	6	2.647329	-2.06059	0.518385
24	6	2.43029	-0.56405	2.125472
25	6	2.017042	0.438787	3.010224
26	1	1.067616	0.940819	2.877483
27	6	2.862144	0.76094	4.067598
28	1	2.566604	1.535373	4.768479
29	6	4.092663	0.103207	4.252335
30	1	4.724934	0.380453	5.089844
31	6	4.514465	-0.89828	3.380952
32	1	5.46485	-1.40066	3.531871
33	6	3.665101	-1.21755	2.31994
34	6	4.849167	-3.15398	1.241342
35	6	-0.42404	-2.97944	2.290811
36	1	0.56847	-2.72449	2.64892
37	6	-1.18104	-3.90135	3.017477
38	1	-0.7659	-4.35228	3.915122
39	6	-2.47318	-4.24057	2.606243
40	1	-3.06431	-4.94831	3.179486
41	6	-3.00104	-3.65748	1.459495
42	1	-4.01495	-3.91005	1.169804
43	6	-2.2346	-2.7431	0.713649
44	6	-2.65524	-2.03904	-0.48613
45	6	-1.99872	0.442265	-2.98927
46	1	-1.04633	0.93843	-2.85587
47	6	-4.86148	-3.12182	-1.21388
48	6	-1.65272	0.789859	2.132051
49	1	-1.92014	-0.1941	2.501707
50	6	-2.14624	1.958539	2.72892
51	1	-2.81881	1.882428	3.576792
52	6	-1.7605	3.190687	2.228902
53	1	-2.11704	4.122138	2.654632
54	6	-0.8801	3.240603	1.131906
55	6	-0.43554	2.019756	0.581012
56	6	0.459075	2.014698	-0.55929
57	6	1.668557	0.771054	-2.10537
58	1	1.929415	-0.21605	-2.47134
59	6	2.169917	1.934187	-2.70648
60	1	2.842305	1.850526	-3.55379
61	6	1.791815	3.170714	-2.21143
62	1	2.154349	4.098206	-2.64073
63	6	0.911437	3.230544	-1.11493
64	6	0.466952	4.48977	-0.53637
65	6	-0.42833	4.494695	0.547858
66	6	-0.4942	6.794226	0.502101
67	6	0.545091	6.789112	-0.50141
68	6	1.264857	8.019113	-0.92482
69	6	1.683674	8.19118	-2.2487
70	1	1.445432	7.444432	-2.99807
71	6	2.393537	9.346394	-2.57161
72	1	2.719565	9.525792	-3.59202
73	6	2.67478	10.26605	-1.56232
74	1	3.225308	11.17846	-1.76855
75	6	2.230943	9.988449	-0.26544
76	1	2.444001	10.6761	0.550398
77	6	-1.2078	8.02988	0.919502
78	6	-1.62391	8.211385	2.242957
79	1	-1.3878	7.467965	2.996305
80	6	-2.3283	9.371504	2.560198
81	1	-2.65205	9.558218	3.580024
82	6	-2.60709	10.2865	1.545979
83	1	-3.1534	11.20244	1.747714
84	6	-2.16637	9.999472	0.250097
85	1	-2.37765	10.6833	-0.56941
86	6	-2.42206	-0.55271	-2.10047
87	6	-2.83772	0.764428	-4.05155

88	1	-2.53424	1.53292	-4.75557	128	1	-11.3787	-5.87065	1.786838
89	6	-4.07199	0.114166	-4.23725	129	1	-10.2116	-7.18002	1.651976
90	6	-3.66082	-1.19843	-2.29558	130	1	9.491728	-4.65693	1.730084
91	6	-4.50387	-0.87936	-3.36164	131	1	10.33522	-3.13238	1.449862
92	1	-5.45692	-1.37644	-3.51333	132	6	11.58932	-4.8893	1.277295
93	1	-4.46489	-4.04944	-0.79597	133	1	10.18697	-3.47656	-2.24899
94	1	-5.1402	-3.34102	-2.25015	134	1	11.4962	-4.25575	-1.36315
95	6	-6.09662	-2.63839	-0.43166	135	6	11.25983	-2.14865	-0.92551
96	1	4.441978	-4.08413	0.839276	136	1	10.50058	-1.36266	-0.89509
97	1	5.139628	-3.36283	2.276403	137	1	11.96699	-1.877	-1.71605
98	6	6.076919	-2.68722	0.437763	138	1	11.81563	-2.14523	0.015516
99	1	5.785539	-2.51281	-0.60557	139	1	11.54577	-5.94667	1.004385
100	6	7.22123	-3.71974	0.507034	140	1	11.85271	-4.84629	2.339203
101	1	6.415815	-1.72311	0.836714	141	1	12.40319	-4.41163	0.726268
102	1	-5.82173	-2.46755	0.616642	142	1	8.724616	-5.96993	0.042562
103	6	-7.25389	-3.65464	-0.5223	143	1	10.28903	-6.07823	-0.75868
104	1	-6.41492	-1.66969	-0.83676	144	6	8.649315	-5.67977	-2.10443
105	1	-6.91694	-4.61835	-0.12351	145	1	7.67668	-5.18161	-2.14327
106	1	-7.50414	-3.81306	-1.57759	146	1	8.472958	-6.74777	-2.26849
107	6	-8.47127	-3.13914	0.253806	147	1	9.262329	-5.32811	-2.93796
108	1	6.862283	-4.68036	0.119672	148	1	-9.42828	-4.98027	-1.62027
109	1	7.491404	-3.8777	1.557389	149	6	-10.4034	-3.10616	-2.10284
110	6	8.427935	-3.22463	-0.29842	150	1	-11.1068	-4.88271	-1.09923
111	1	-8.2128	-3.01012	1.306131	151	6	-10.6479	-2.99661	2.447043
112	7	-9.72694	-4.01444	0.237437	152	1	-11.7573	-3.85685	0.798853
113	1	-8.7798	-2.1649	-0.13179	153	1	-10.9774	-2.32227	0.421416
114	1	8.152468	-3.08748	-1.34645	154	1	-9.49423	-2.52274	-2.27218
115	7	9.674233	-4.11394	-0.30231	155	1	-11.1928	-2.43884	-1.74787
116	1	8.756527	-2.25689	0.08479	156	1	-10.7268	-3.48959	-3.07604
117	6	9.339727	-5.54182	-0.75159	157	1	-10.5588	-3.91019	3.040483
118	6	10.25339	-4.16982	1.11935	158	1	-11.5375	-2.46785	2.804663
119	6	10.69493	-3.51869	-1.28463	159	1	-9.79056	-2.35074	2.654311
120	1	-4.69912	0.390964	-5.07877					
121	6	-9.41866	-5.34415	0.940231					
122	6	-10.1823	-4.3131	-1.19751					
123	6	-10.8559	-3.26299	0.960159					
124	1	-8.65284	-5.82863	0.332334					
125	6	-10.5984	-6.28926	1.146275					
126	1	-8.96724	-5.07868	1.898366					
127	1	-11.0492	-6.62695	0.209711					

Table S2. B3LYP optimised coordinates of complex [**2**]$^{3+}$ in gas phase.

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	77	0.082774	-0.766205	-0.02147
2	7	-1.729921	-1.140914	-0.985663
3	7	1.928809	-0.743623	0.950567
4	7	0.67637	1.060962	-1.110512
5	7	-0.911998	0.868909	1.080021
6	7	-3.539089	-2.418365	-1.27101
7	7	3.957945	-1.626202	1.256279
8	7	-1.591935	5.660823	1.049712
9	7	0.213781	5.878817	-1.061837
10	7	0.42546	9.172659	0.025686
11	7	-2.565538	8.818962	-0.025452
12	6	-0.637032	-2.303901	1.088973
13	6	1.136426	-2.089557	-1.153672
14	6	-0.045688	-2.854243	2.232917
15	1	0.908603	-2.499407	2.605855
16	6	-0.682276	-3.872582	2.935541
17	6	-1.923747	-4.382219	2.561693
18	1	-2.386255	-5.165573	3.151528
19	6	-2.533008	-3.850405	1.431733
20	1	-3.511769	-4.227035	1.157615
21	6	-1.902376	-2.837644	0.685862
22	6	-2.424515	-2.181512	-0.499138
23	6	-2.404904	-0.66083	-2.100143
24	6	-2.128981	0.391084	-2.982186
25	1	-1.250842	1.011005	-2.856076
26	6	-3.01756	0.610067	-4.03067
27	1	-2.827389	1.419652	-4.728333
28	6	-4.157115	-0.195548	-4.210671
29	1	-4.825559	0.004021	-5.042122
30	6	-4.442757	-1.245645	-3.341145
31	1	-5.323191	-1.863532	-3.488031
32	6	-3.551311	-1.460426	-2.288746
33	6	-4.489691	-3.525425	-1.211585
34	6	0.707657	-2.729131	-2.328161
35	1	-0.300755	-2.561247	-2.692414
36	6	1.544373	-3.569708	-3.066336
37	1	1.205596	-4.055454	-3.976091
38	6	2.847907	-3.776582	-2.62691
39	6	3.333729	-3.174505	-1.47846
40	1	4.367456	-3.354145	-1.212452
41	6	2.476128	-2.343946	-0.735098
42	6	2.830534	-1.611988	0.469115
43	6	1.97564	0.816627	2.962825
44	1	0.992316	1.245892	2.821884
45	6	5.096939	-2.541311	1.216383
46	6	1.485366	1.12973	-2.171449
47	1	1.859986	0.183404	-2.545709
48	6	1.824347	2.345524	-2.781833
49	1	2.48268	2.34468	-3.644124
50	6	1.308418	3.526217	-2.275278
51	1	1.5438	4.491124	-2.710594
52	6	0.45446	3.477553	-1.157416
53	6	0.168409	2.215583	-0.594574
54	6	-0.690631	2.111661	0.56757
55	6	-1.708134	0.742039	2.145307
56	1	-1.846466	-0.267139	2.517283
57	6	-2.320357	1.842106	2.761956
58	1	-2.954455	1.684381	3.627981
59	6	-2.09966	3.112373	2.257308
60	1	-2.553307	3.99352	2.697507
61	6	-1.263079	3.269472	1.136334
62	6	-0.982541	4.569351	0.545707
63	6	-0.123586	4.673261	-0.562567
64	6	-0.320077	6.965247	-0.518862
65	6	-1.32651	6.843984	0.51127
66	6	-2.173105	7.984409	0.950042
67	6	-2.577854	8.113623	2.283117
68	1	-2.238258	7.402824	3.028361
69	6	-3.407274	9.181978	2.620254
70	1	-3.727477	9.328129	3.647778
71	6	-3.815503	10.058406	1.615946
72	1	-4.461518	10.903088	1.833372
73	6	-3.373837	9.826762	0.309321
74	1	-3.683848	10.481197	-0.502749
75	6	0.237767	8.272971	-0.952792
76	6	0.601857	8.496924	-2.285045
77	1	0.436463	7.72926	-3.032884
78	6	1.162018	9.729083	-2.61789
79	1	1.440509	9.948573	-3.644515
80	6	1.356194	10.672803	-1.610314
81	1	1.789953	11.644487	-1.824244
82	6	0.978988	10.341166	-0.304973
83	1	1.128438	11.046942	0.50949
84	6	2.475028	-0.148119	2.079411

85	6	2.782763	1.200173	4.028887	130	6	-11.012303	-5.916532	-1.427469
86	1	2.420793	1.946697	4.728837	131	1	-9.885734	-4.334571	2.126781
87	6	4.059635	0.640496	4.224348	132	1	-11.080678	-5.245421	1.205032
88	6	3.757923	-0.699168	2.282064	133	6	-11.026489	-3.130951	0.741974
89	6	4.568795	-0.31899	3.353136	134	1	-10.342916	-2.277918	0.724699
90	1	5.554544	-0.745391	3.511035	135	1	-11.785112	-2.915368	1.501406
91	1	4.765328	-3.488949	0.78701	136	1	-11.543871	-3.193516	-0.218686
92	1	5.369026	-2.749781	2.256593	137	1	-10.879314	-6.963034	-1.142266
93	6	6.314593	-1.980592	0.458961	138	1	-11.239006	-5.906417	-2.498656
94	1	-3.984497	-4.397305	-0.791414	139	1	-11.887675	-5.514389	-0.911668
95	1	-4.740688	-3.780452	-2.24681	140	1	-8.109499	-6.707761	-0.069648
96	6	-5.773094	-3.187719	-0.430303	141	1	-9.684683	-6.952482	0.679483
97	1	-5.520377	-2.983537	0.617813	142	6	-8.140411	-6.38286	2.073715
98	6	-6.808596	-4.328483	-0.519257	143	1	-7.218551	-5.79817	2.138301
99	1	-6.19948	-2.262729	-0.837737	144	1	-7.874755	-7.427843	2.263674
100	1	6.042768	-1.797991	-0.588114	145	1	-8.812984	-6.075733	2.878446
101	6	7.515733	-2.945739	0.538233	146	1	9.718344	-4.220745	1.615886
102	1	6.583154	-1.007814	0.8894	147	6	10.628404	-2.335445	2.177316
103	1	7.227993	-3.911075	0.106659	148	1	11.399175	-4.051953	1.120685
104	1	7.758759	-3.12363	1.592065	149	6	10.918504	-2.045802	-2.358789
105	6	8.719577	-2.354808	-0.204433	150	1	12.039449	-2.918972	-0.72496
106	1	-6.372936	-5.245353	-0.105378	151	1	11.190859	-1.432645	-0.305409
107	1	-7.026313	-4.524169	-1.575342	152	1	9.700775	-1.783384	2.351808
108	6	-8.08422	-3.940908	0.237853	153	1	11.404134	-1.634777	1.858468
109	1	8.467786	-2.200083	-1.254945	154	1	10.9473	-2.743706	3.141861
110	7	10.008571	-3.180356	-0.202168	155	1	10.872045	-2.940339	-2.985273
111	1	8.984426	-1.383324	0.218512	156	1	11.791766	-1.471198	-2.684467
112	1	-7.860056	-3.766739	1.292698	157	1	10.039669	-1.426054	-2.555603
113	7	-9.240428	-4.944944	0.210971	158	9	3.673787	-4.570234	-3.338704
114	1	-8.48932	-3.013484	-0.170833	159	9	-0.082805	-4.376431	4.026442
115	6	-8.790194	-6.328682	0.695273					
116	6	-9.756696	-5.073081	-1.229956					
117	6	-10.350123	-4.43674	1.145167					
118	1	4.658931	0.963107	5.06977					
119	6	9.763327	-4.493113	-0.959514					
120	6	10.455791	-3.515591	1.227014					
121	6	11.116445	-2.357287	-0.879236					
122	1	9.012695	-5.032581	-0.3797					
123	6	10.98229	-5.381177	-1.188894					
124	1	9.310512	-4.208916	-1.911476					
125	1	11.442076	-5.731922	-0.261557					
126	1	11.747719	-4.910649	-1.81082					
127	1	10.634315	-6.269453	-1.72625					
128	1	-8.929971	-5.494678	-1.803653					
129	1	-9.921617	-4.052002	-1.579743					

Table S3. B3LYP optimised coordinates of complex [**3**]$^{3+}$ in gas phase.

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	77	0.051352	-0.807593	-0.001899
2	7	-1.848522	-0.967829	-0.839679
3	7	1.957699	-0.822216	0.834559
4	7	0.741347	0.959164	-1.110714
5	7	-0.78612	0.886189	1.12206
6	7	-3.787878	-2.043836	-1.084793
7	7	3.970357	-1.753835	1.081441
8	7	-1.141829	5.712757	1.079129
9	7	0.627094	5.796949	-1.07323
10	7	1.090053	9.070654	-0.004124
11	7	-1.919665	8.923647	-0.000336
12	6	-0.770711	-2.291668	1.13526
13	6	0.987991	-2.211023	-1.152357
14	6	-0.199015	-2.971885	2.212529
15	6	-0.88145	-3.874381	3.021132
16	1	-0.36187	-4.352243	3.845083
17	6	-2.22704	-4.130876	2.76985
18	1	-2.809724	-4.800293	3.392242
19	6	-2.826231	-3.495817	1.697014
20	6	-2.134193	-2.622873	0.844267
21	6	-2.643513	-1.918691	-0.330183
22	6	-2.482884	-0.425075	-1.945823
23	6	-2.109145	0.57905	-2.84762
24	1	-1.16633	1.098534	-2.748837
25	6	-2.983881	0.880514	-3.885516
26	1	-2.717442	1.655491	-4.597397
27	6	-4.20666	0.199968	-4.0388
28	1	-4.862248	0.459936	-4.863833
29	6	-4.588339	-0.802235	-3.152225
30	1	-5.530055	-1.326225	-3.279155
31	6	-3.709404	-1.0971	-2.107033
32	6	-4.821615	-3.082417	-1.084924
33	6	0.474379	-2.924361	-2.237604
34	6	1.227452	-3.765276	-3.050074
35	1	0.749101	-4.274527	-3.88018
36	6	2.587557	-3.921042	-2.794514
37	1	3.222047	-4.539103	-3.419362
38	6	3.131878	-3.251573	-1.713424
39	6	2.371531	-2.440835	-0.857678
40	6	2.822436	-1.708778	0.323194
41	6	2.09855	0.7332	2.847034
42	1	1.121809	1.18487	2.743623
43	6	5.067392	-2.725514	1.088914
44	6	1.525224	0.963646	-2.192205
45	1	1.818549	-0.008406	-2.572238
46	6	1.937077	2.149653	-2.816247
47	1	2.570527	2.097633	-3.695361
48	6	1.521948	3.366743	-2.302996
49	1	1.8154	4.310167	-2.750025
50	6	0.696265	3.384818	-1.16306
51	6	0.335201	2.149077	-0.586571
52	6	-0.496789	2.109381	0.597405
53	6	-1.561713	0.815606	2.207177
54	1	-1.758657	-0.180169	2.587987
55	6	-2.082909	1.956837	2.832846
56	1	-2.704052	1.844752	3.715136
57	6	-1.790169	3.207936	2.316929
58	1	-2.172219	4.118753	2.764688
59	6	-0.973956	3.305128	1.17423
60	6	-0.619704	4.57996	0.568624
61	6	0.21828	4.619818	-0.559995
62	6	0.181947	6.919799	-0.524487
63	6	-0.808724	6.872388	0.527221
64	6	-1.567227	8.070013	0.973975
65	6	-1.937672	8.234219	2.313123
66	1	-1.633514	7.506437	3.057278
67	6	-2.686275	9.358557	2.65738
68	1	-2.977029	9.532209	3.68935
69	6	-3.052119	10.254867	1.654297
70	1	-3.635122	11.142851	1.877187
71	6	-2.651264	9.986077	0.341565
72	1	-2.930787	10.655355	-0.469447
73	6	0.820369	8.184039	-0.975324
74	6	1.172468	8.378568	-2.315368
75	1	0.938622	7.622726	-3.05696
76	6	1.810784	9.567668	-2.663891
77	1	2.083285	9.764701	-3.696648
78	6	2.090676	10.497831	-1.663901
79	1	2.587035	11.436206	-1.890066
80	6	1.71733	10.196662	-0.35003
81	1	1.931946	10.892239	0.458595
82	6	2.547398	-0.238947	1.944665
83	6	2.94484	1.093467	3.889809
84	1	2.620837	1.845583	4.602341

85	6	4.21245	0.501651	4.046718	130	1	-11.585482	-4.357671	1.091507
86	6	3.819043	-0.820632	2.108077	131	6	-11.468875	-2.353341	0.280277
87	6	4.669603	-0.4669	3.158341	132	1	-10.773153	-1.517855	0.166491
88	1	5.64673	-0.920927	3.287291	133	1	-12.274968	-2.008906	0.936307
89	1	4.7357	-3.630218	0.586224	134	1	-11.919795	-2.577299	-0.689757
90	1	5.245657	-2.981894	2.13882	135	1	-11.241596	-6.445153	-0.904822
91	6	6.359175	-2.19071	0.447931	136	1	-11.485937	-5.643125	-2.44906
92	1	-4.428108	-3.966935	-0.591038	137	1	-12.24254	-4.977171	-1.007529
93	1	-4.995669	-3.344328	-2.134079	138	1	-8.555962	-6.022182	0.290684
94	6	-6.135373	-2.628154	-0.427322	139	1	-10.179119	-6.129716	0.966051
95	1	-5.929809	-2.337162	0.607506	140	6	-8.716018	-5.338232	2.340752
96	6	-7.192748	-3.750133	-0.459321	141	1	-7.779255	-4.774302	2.363389
97	1	-6.513219	-1.739055	-0.947162	142	1	-8.499569	-6.339128	2.728229
98	1	6.146511	-1.901675	-0.585852	143	1	-9.425871	-4.877969	3.032757
99	6	7.473861	-3.255813	0.478426	144	1	9.463283	-4.904908	1.411623
100	1	6.683279	-1.287369	0.979396	145	6	10.530586	-3.255868	2.3292
101	1	7.13969	-4.125583	-0.097806	146	1	11.181719	-4.848965	1.030213
102	1	7.628601	-3.588488	1.511402	147	6	11.129469	-2.240383	-2.065027
103	6	8.76816	-2.676178	-0.102331	148	1	12.053478	-3.469702	-0.540435
104	1	-6.812267	-4.608205	0.105908	149	1	11.304533	-1.997629	0.073665
105	1	-7.336624	-4.079405	-1.494868	150	1	9.659793	-2.633251	2.552772
106	6	-8.509552	-3.241556	0.13757	151	1	11.397894	-2.610126	2.17095
107	1	8.593115	-2.329068	-1.122217	152	1	10.738604	-3.852408	3.223422
108	7	9.975056	-3.61613	-0.184116	153	1	11.073099	-3.013198	-2.835784
109	1	9.094874	-1.816784	0.487385	154	1	12.060405	-1.688713	-2.231887
110	1	-8.352373	-2.903523	1.164361	155	1	10.31012	-1.531235	-2.209645
111	7	-9.675726	-4.232764	0.193775	156	9	-0.837923	-2.8063	-2.563308
112	1	-8.872173	-2.388813	-0.439016	157	9	4.477069	-3.386485	-1.523505
113	6	-9.278079	-5.515854	0.934222	158	9	1.101857	-2.755136	2.533721
114	6	-10.088522	-4.601441	-1.237884	159	9	-4.15893	-3.730445	1.513738
115	6	-10.841158	-3.572604	0.94641					
116	1	4.844131	0.805555	4.875394					
117	6	9.659228	-4.747519	-1.171955					
118	6	10.294079	-4.234124	1.183497					
119	6	11.194065	-2.805834	-0.650456					
120	1	8.822546	-5.295362	-0.7361					
121	6	10.80381	-5.70352	-1.490774					
122	1	9.301755	-4.258463	-2.080233					
123	1	11.156827	-6.259658	-0.618768					
124	1	11.655173	-5.212036	-1.9682					
125	1	10.418258	-6.440648	-2.202709					
126	1	-9.227883	-5.113554	-1.670882					
127	1	-10.215468	-3.65461	-1.766455					
128	6	-11.337879	-5.465026	-1.378917					
129	1	-10.445051	-3.305674	1.927005					

Table S4. B3LYP optimised coordinates of complex [**4**]$^{3+}$ in gas phase.

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	77	0.055301	-0.48792	0.051371
2	7	1.925417	-0.48987	0.971519
3	7	-1.80877	-0.67321	-0.86373
4	7	-0.82736	1.206189	1.120335
5	7	0.782615	1.257528	-1.05257
6	7	3.909058	-1.44467	1.341568
7	7	-3.71326	-1.78973	-1.19814
8	7	0.677136	6.095802	-1.06133
9	7	-1.17284	6.032802	1.023179
10	7	-1.89944	9.236421	-0.11187
11	7	1.10701	9.375471	0.004761
12	6	1.042723	-1.91206	-1.03838
13	6	-0.80438	-1.97091	1.170846
14	6	0.570659	-2.61909	-2.14012
15	6	1.360966	-3.49607	-2.88599
16	6	2.693928	-3.67977	-2.53849
17	6	3.201807	-3.00275	-1.4384
18	6	2.402707	-2.16052	-0.65448
19	6	2.800181	-1.40392	0.529743
20	6	2.474459	0.119799	2.089545
21	6	2.002258	1.12733	2.940254
22	1	1.039693	1.59199	2.778768
23	6	2.807594	1.506667	4.00793
24	1	2.465466	2.286112	4.681472
25	6	4.057397	0.900714	4.239972
26	1	4.656866	1.221947	5.085741
27	6	4.537595	-0.10232	3.404298
28	1	5.501271	-0.56562	3.589196
29	6	3.727517	-0.47624	2.32956
30	6	4.974746	-2.44771	1.428213
31	6	-0.26896	-2.61431	2.282137
32	6	-0.97941	-3.54037	3.048707
33	6	-2.29413	-3.84233	2.71333
34	6	-2.86278	-3.23033	1.604502
35	6	-2.14002	-2.33967	0.800613
36	6	-2.60525	-1.64432	-0.39595
37	6	-2.02161	0.88649	-2.86793
38	1	-1.09662	1.427165	-2.72483
39	6	-4.70702	-2.86684	-1.25764
40	6	-1.6424	1.146059	2.176856
41	1	-1.85289	0.154574	2.560939
42	6	-2.18627	2.293164	2.771567
43	1	-2.83986	2.189297	3.631079
44	6	-1.87371	3.539345	2.255435
45	1	-2.27186	4.454329	2.68012
46	6	-1.01453	3.626078	1.143566
47	6	-0.51752	2.424981	0.595646
48	6	0.358451	2.453238	-0.55526
49	6	1.605153	1.250899	-2.10489
50	1	1.910389	0.275298	-2.46542
51	6	2.04153	2.430469	-2.72423
52	1	2.706385	2.369516	-3.57921
53	6	1.610699	3.652922	-2.23724
54	1	1.922939	4.591673	-2.68141
55	6	0.742937	3.68311	-1.12909
56	6	0.245475	4.923931	-0.55487
57	6	-0.63464	4.894992	0.541476
58	6	-0.81603	7.187337	0.475476
59	6	0.21547	7.224096	-0.53796
60	6	0.875974	8.482804	-0.97092
61	6	1.285294	8.666309	-2.29615
62	1	1.080594	7.906005	-3.04179
63	6	1.941661	9.851067	-2.62559
64	1	2.258297	10.04002	-3.64718
65	6	2.182068	10.78734	-1.62109
66	1	2.69071	11.72254	-1.83258
67	6	1.752455	10.49683	-0.32194
68	1	1.935159	11.19742	0.49013
69	6	-1.58849	8.389783	0.882524
70	6	-2.01199	8.564649	2.204446
71	1	-1.7394	7.842221	2.965853
72	6	-2.77139	9.692979	2.509832
73	1	-3.10285	9.875239	3.527917
74	6	-3.09502	10.58186	1.48588
75	1	-3.68477	11.47248	1.67834
76	6	-2.64234	10.30243	0.192202
77	1	-2.8879	10.96589	-0.63438
78	6	-2.40962	-0.13432	-1.99116
79	6	-2.85924	1.177431	-3.93865
80	1	-2.58191	1.965044	-4.63218
81	6	-4.05863	0.470458	-4.14868
82	6	-3.61299	-0.8322	-2.20886
83	6	-4.45421	-0.54791	-3.28735
84	1	-5.37803	-1.09115	-3.45676
85	1	-4.29534	-3.74518	-0.76644
86	1	-4.82688	-3.11629	-2.31718
87	6	-6.06531	-2.48498	-0.64509
88	1	4.616054	-3.36785	0.972132

89	1	5.120944	-2.65357	2.493455	127	6	11.60457	-2.10958	-0.32917
90	6	6.297325	-2.00141	0.78202	128	1	11.0186	-1.22531	-0.06475
91	1	6.090868	-1.64244	-0.23086	129	1	12.37979	-1.77912	-1.0283
92	6	7.300817	-3.17027	0.724216	130	1	12.11602	-2.47896	0.563332
93	1	6.720466	-1.16006	1.344355	131	1	11.02849	-6.27513	0.47325
94	1	-5.91039	-2.15772	0.387585	132	1	11.5145	-5.66831	2.049291
95	6	-7.03953	-3.68053	-0.67553	133	1	12.19991	-4.94093	0.602136
96	1	-6.4887	-1.63549	-1.19541	134	1	8.379359	-5.50464	-0.38927
97	1	-6.60607	-4.49446	-0.0841	135	1	9.880159	-5.61422	-1.30345
98	1	-7.13678	-4.04178	-1.70608	136	6	8.301501	-4.56901	-2.34128
99	6	-8.4035	-3.26322	-0.1146	137	1	7.388944	-3.99591	-2.15401
100	1	6.831658	-3.99842	0.182282	138	1	8.000208	-5.49952	-2.83343
101	1	7.509678	-3.52244	1.740666	139	1	8.927396	-4.02424	-3.0529
102	6	8.589932	-2.7244	0.027444	140	1	-8.78337	-5.57296	-1.61089
103	1	-8.28626	-2.89015	0.904339	141	6	-10.0406	-4.08636	-2.56378
104	7	-9.48221	-4.34785	-0.03919	142	1	-10.5002	-5.73804	-1.25373
105	1	-8.82962	-2.45639	-0.7151	143	6	-10.8239	-3.09729	1.803995
106	1	8.359197	-2.28424	-0.94508	144	1	-11.5635	-4.47138	0.303062
107	7	9.635061	-3.80759	-0.24233	145	1	-11.0141	-2.92576	-0.34072
108	1	9.093818	-1.96249	0.624638	146	1	-9.25444	-3.35759	-2.77973
109	6	9.040967	-4.95941	-1.06537	147	1	-10.9872	-3.55791	-2.42715
110	6	10.13642	-4.36522	1.096855	148	1	-10.1531	-4.71313	-3.45438
111	6	10.79052	-3.18418	-1.04188	149	1	-10.6536	-3.83655	2.590862
112	1	-4.6851	0.723497	-4.99805	150	1	-11.827	-2.68748	1.961143
113	6	-9.03987	-5.42091	0.966068	151	1	-10.12	-2.27064	1.93176
114	6	-9.69812	-5.01441	-1.40336	152	9	0.990036	-2.36835	2.703863
115	6	-10.8017	-3.69588	0.401872	153	9	-4.16571	-3.52634	1.37159
116	1	-8.13794	-5.86676	0.544036	154	9	-0.70125	-2.48831	-2.57317
117	6	-10.0593	-6.50894	1.288746	155	9	4.525636	-3.18775	-1.19597
118	1	-8.7543	-4.88216	1.871705	156	9	3.484434	-4.48218	-3.25746
119	1	-10.3378	-7.11214	0.420928	157	9	0.853916	-4.1402	-3.93448
120	1	-10.9664	-6.12348	1.760736	158	9	-0.41472	-4.11941	4.10555
121	1	-9.58718	-7.18665	2.00756	159	9	-3.00897	-4.69491	3.451812
122	1	9.268307	-4.82787	1.569211					
123	1	10.41954	-3.49675	1.694848					
124	6	11.28487	-5.36562	1.022422					
125	1	10.33786	-2.77814	-1.94779					
126	1	11.43146	-4.01709	-1.33598					

Figure S7. B3LYP optimised geometry of the complexes [**1**]$^{3+}$ – [**3**]$^{3+}$ and their SCF energies in gas phase.

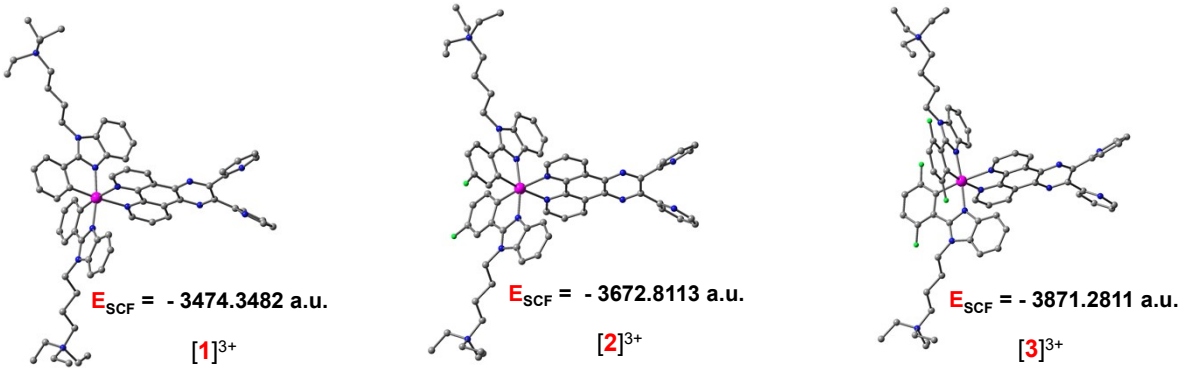


Figure S8. DFT optimised frontier orbitals of complex [**1**]$^{3+}$ in gas phase.

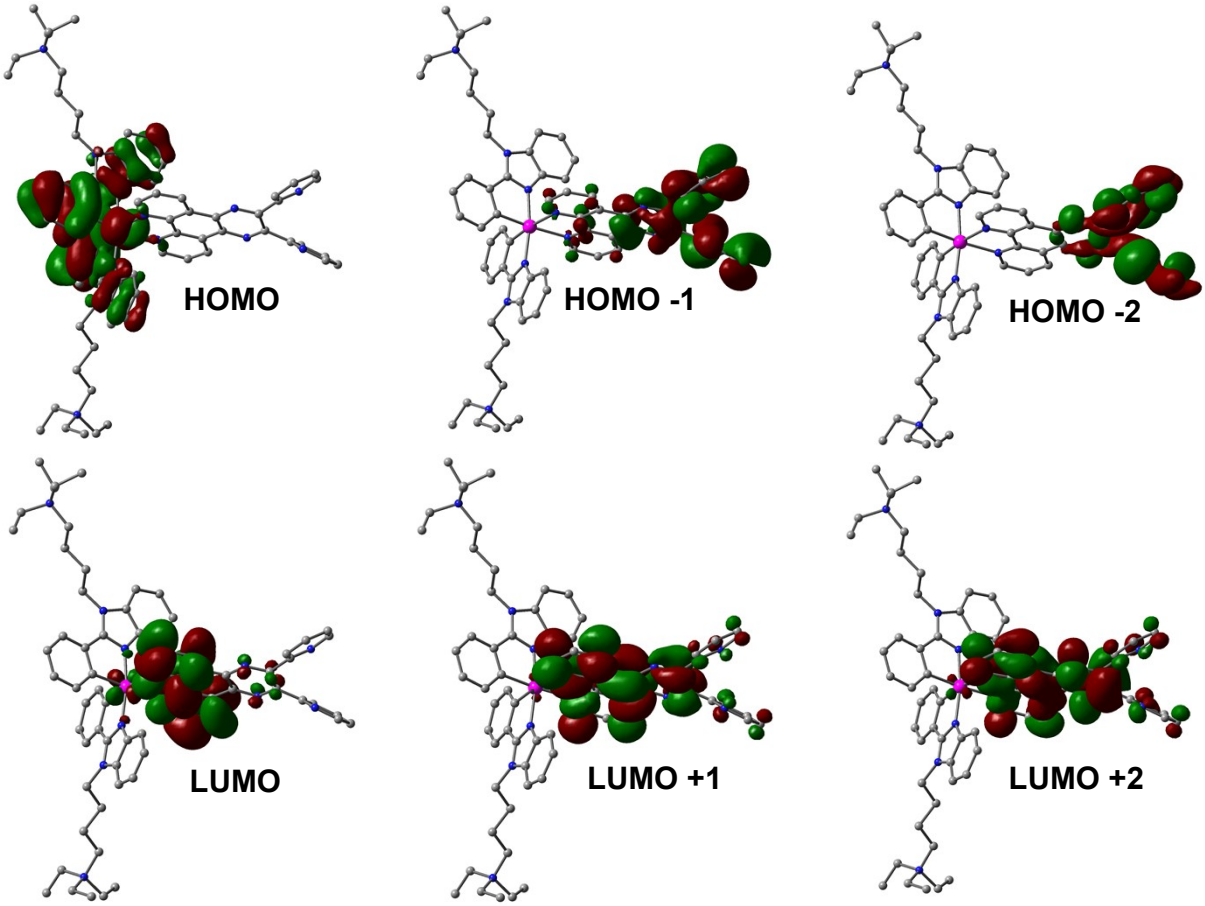


Figure S9. DFT optimised frontier orbitals of complex [**2**]$^{3+}$ in gas phase.

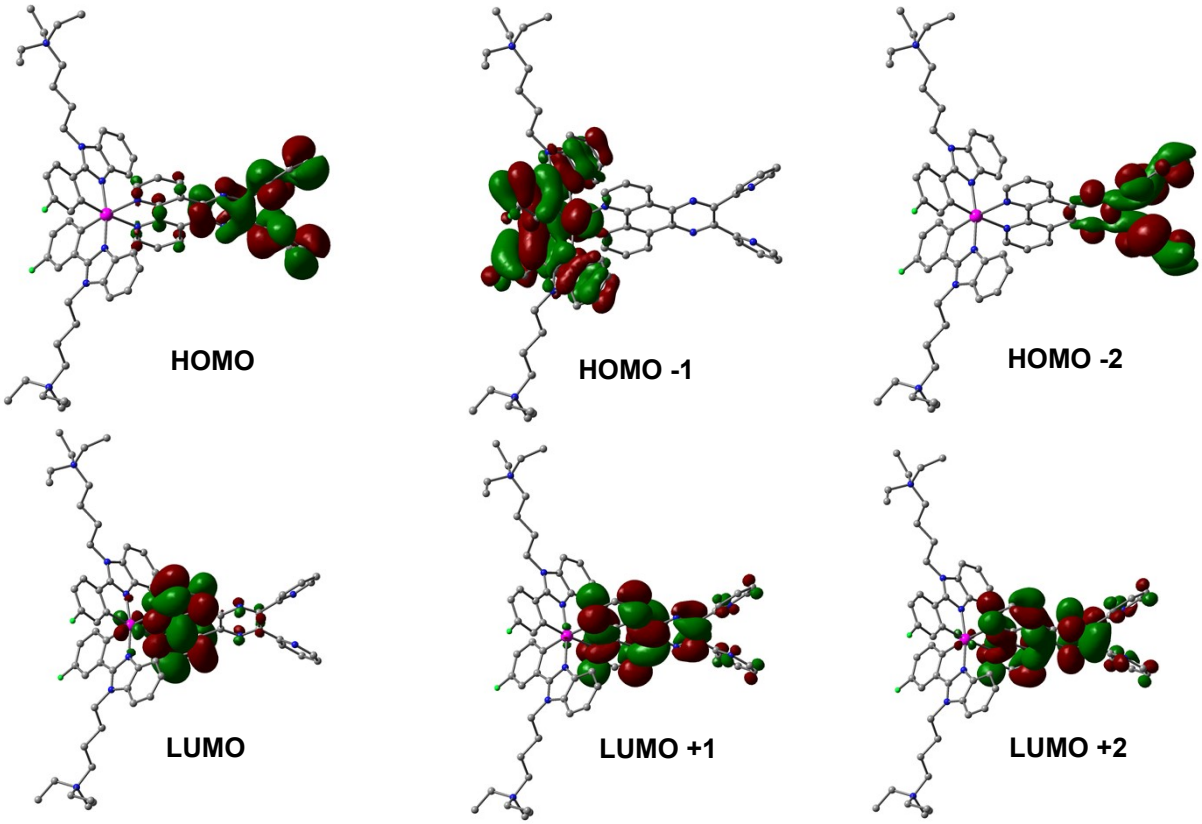


Figure S10. DFT optimised frontier orbitals of the complex [**3**]$^{3+}$ in gas phase.

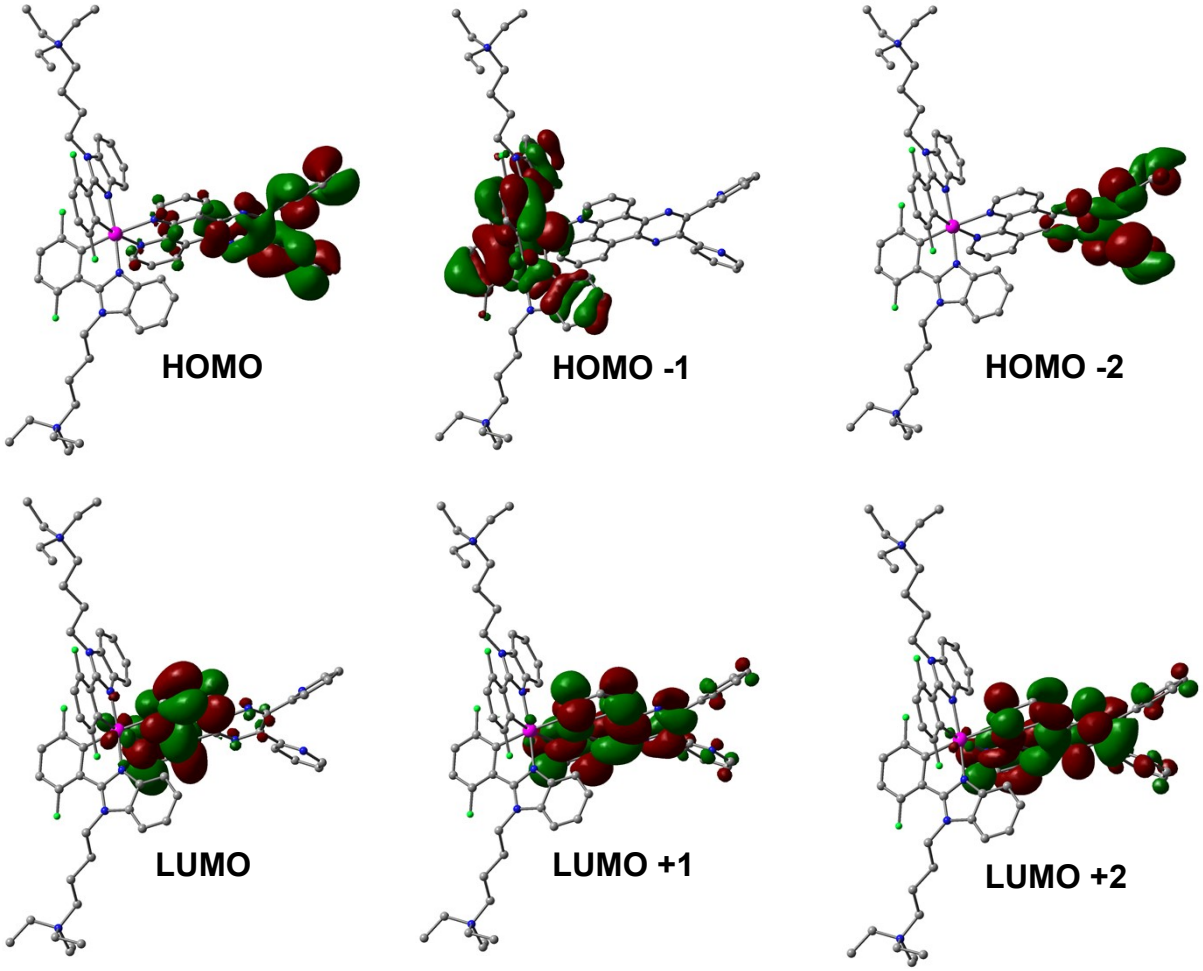


Figure S11. DFT optimised frontier orbitals of the complex [**4**]$^{3+}$ in gas phase.

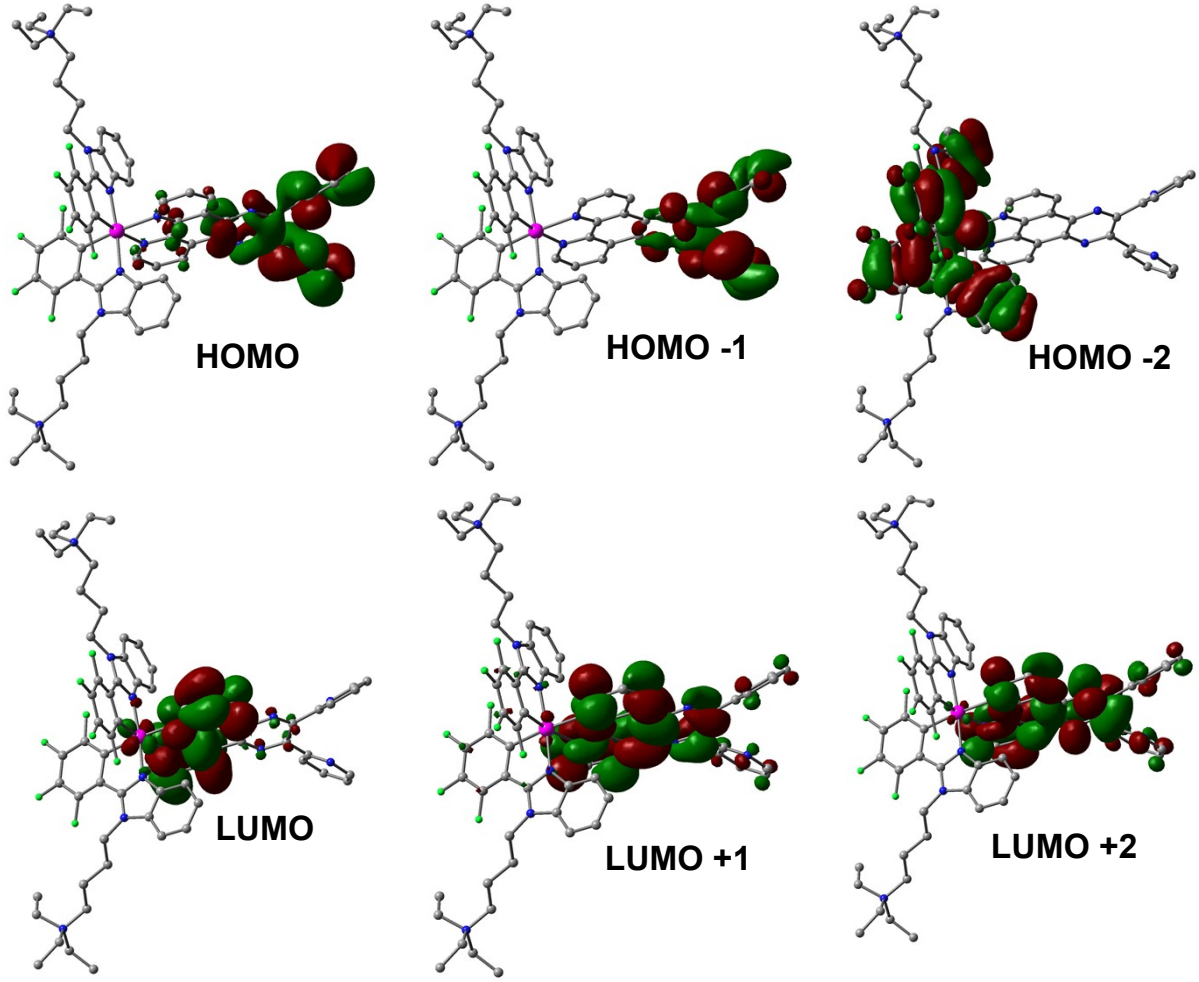
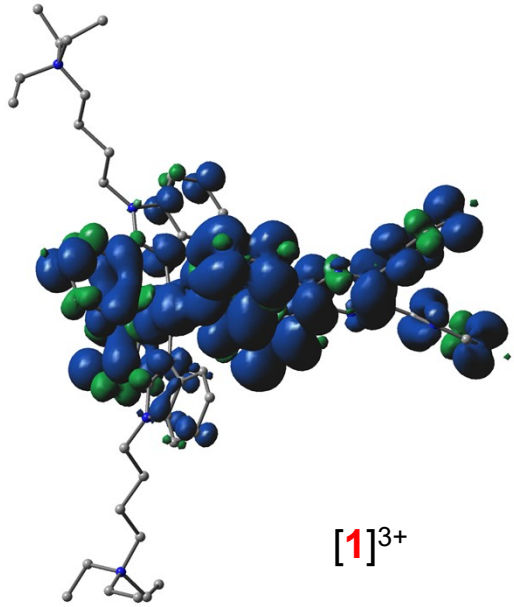
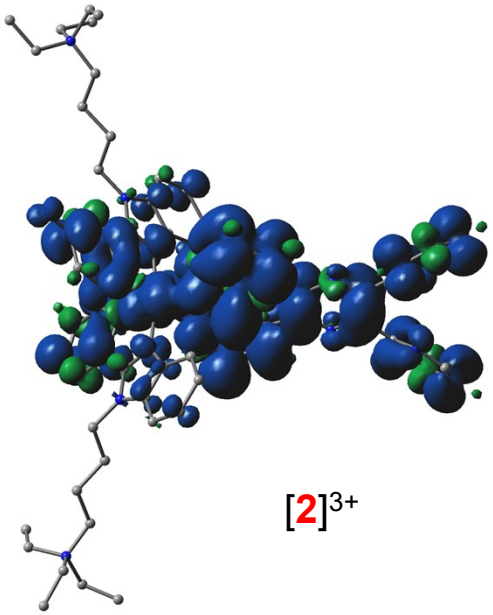


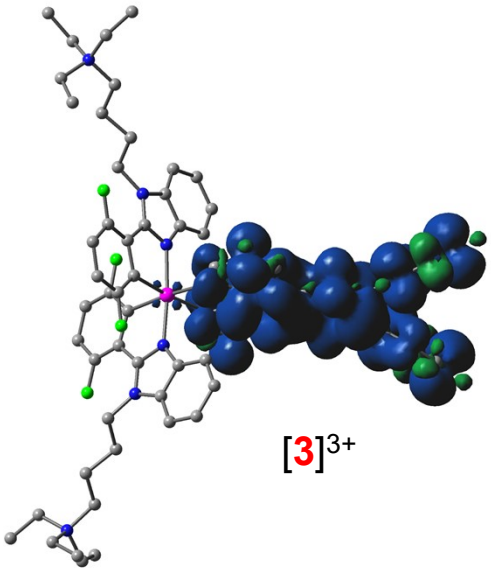
Figure S12. Spin density plot (T1 state) for complexes $[\mathbf{1}]^{3+}$ - $[\mathbf{4}]^{3+}$.



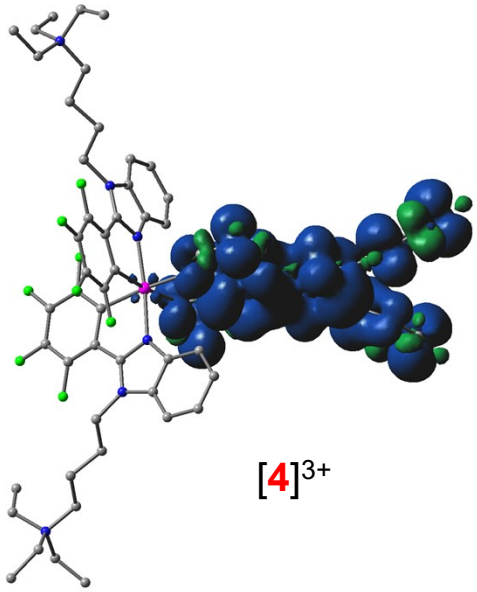
$[\mathbf{1}]^{3+}$



$[\mathbf{2}]^{3+}$



$[\mathbf{3}]^{3+}$



$[\mathbf{4}]^{3+}$

Table S5. Molecular orbital composition of the complexes $[\mathbf{1}]^{3+}$

MOs	eV	imd2	phpy	imd1	Ir
L+10	-4.65	40	8	43	8
L+9	-4.79	53	3	39	5
L+8	-4.83	44	5	41	10
L+7	-4.84	37	7	49	6
zL+6	-5.07	5	89	5	2
L+5	-5.3	0	99	0	0
L+4	-6.22	48	2	47	3
L+3	-6.37	48	1	49	2
L+2	-6.57	0	99	0	1
L+1	-6.74	1	98	1	0
LUMO	**-7.02**	**0**	**97**	**0**	**3**
HOMO	**-10.28**	**32**	**1**	**32**	**35**
H-1	-10.32	0	100	0	0
H-2	-10.58	0	100	0	0
H-3	-10.61	40	2	39	19
H-4	-10.78	0	99	0	0
H-5	-10.8	29	3	30	38
H-6	-10.94	0	100	0	0
H-7	-11.06	37	5	33	25
H-8	-11.14	40	1	43	16
H-9	-11.31	1	98	1	0
H-10	-11.38	49	2	49	1

Table S6. Molecular orbital composition of the complexes [**2**]$^{3+}$

MO	eV	Phpy	imd1	imd2	Ir
L+10	-4.76	7	14	67	12
L+9	-4.89	2	73	18	6
L+8	-4.95	7	17	69	7
L+7	-5.02	15	69	8	7
L+6	-5.15	78	12	8	2
L+5	-5.37	99	0	0	0
L+4	-6.32	2	79	16	2
L+3	-6.52	1	17	80	2
L+2	-6.63	99	0	0	1
L+1	-6.81	98	1	1	0
LUMO	**-7.1**	**97**	**0**	**0**	**3**
HOMO	**-10.36**	**100**	**0**	**0**	**0**
H-1	-10.39	1	27	40	32
H-2	-10.62	100	0	0	0
H-3	-10.68	2	55	28	15
H-4	-10.82	99	1	0	0
H-5	-10.94	5	16	41	37
H-6	-10.98	97	0	1	1
H-7	-11.16	5	53	15	27
H-8	-11.27	2	21	61	16
H-9	-11.35	98	1	1	0
H-10	-11.53	4	44	50	3

Table S7. Molecular orbital composition of the complexes [**3**]$^{3+}$

	eV	imd2	imd1	phpy	Ir
L+10	-4.72	14	15	69	2
L+9	-4.74	45	47	4	4
L+8	-5	46	35	4	15
L+7	-5.03	35	47	5	14
L+6	-5.2	2	2	95	2
L+5	-5.43	0	0	99	0
L+4	-6.46	49	43	4	3
L+3	-6.52	45	51	1	3
L+2	-6.7	0	0	99	1
L+1	-6.89	1	2	96	0
LUMO	**-7.19**	**0**	**0**	**97**	**2**
HOMO	**-10.39**	**0**	**0**	**100**	**0**
H-1	-10.62	32	31	2	35
H-2	-10.65	0	0	99	0
H-3	-10.82	48	35	2	15
H-4	-10.85	34	47	1	18
H-5	-10.86	0	0	99	0
H-6	-11.02	0	0	100	0
H-7	-11.17	58	25	1	16
H-8	-11.18	25	58	2	14
H-9	-11.28	49	49	2	1
H-10	-11.38	0	0	99	0

Table S8. Molecular orbital composition of the complexes [**4**]$^{3+}$

MOs	eV	Ir	phpy	imd1	imd2
L+10	-4.97	5	3	41	51
L+9	-5.02	2	4	51	43
L+8	-5.23	28	4	34	35
L+7	-5.32	25	11	29	35
L+6	-5.35	3	90	3	3
L+5	-5.56	0	99	0	0
L+4	-6.7	3	5	51	41
L+3	-6.77	2	1	43	54
L+2	-6.83	1	99	0	0
L+1	-7.05	0	96	2	2
LUMO	**-7.37**	**2**	**97**	**0**	**0**
HOMO	**-10.48**	**0**	**100**	**0**	**0**
H-1	-10.73	0	100	0	0
H-2	-10.86	28	1	36	35
H-3	-10.94	0	100	0	0
H-4	-11.02	10	1	43	46
H-5	-11.1	1	98	1	1
H-6	-11.13	22	4	39	35
H-7	-11.37	13	2	9	75
H-8	-11.39	14	1	76	9
H-9	-11.46	0	99	0	0
H-10	-11.64	2	2	46	50

Table S9. TDDFT calculated vertical transition of complex [**1**]$^{3+}$

Wavelength (nm)				
Observed	Computed	Osc. Strength	Major contribution	Character
400	433.59	0.0668	H-1 → LUMO (97%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
400	411.98	0.0314	H-3 → LUMO (95%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$;
400	394.53	0.0494	H-2 → LUMO (30%), H-1 → L+1 (67%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$; $phpy_{\pi} \rightarrow phpy_{\pi^*}$
400	391.75	0.0778	H-1 → L+2 (78%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
400	385.79	0.1078	HOMO → L+3 (94%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$
358	379.50	0.0568	H-2 → L+1 (80%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
358	371.97	0.061	H-4->LUMO (84%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
358	352.95	0.0225	H-7 → LUMO (36%), H-5 → L+1 (53%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$
358	345.29	0.0322	H-3 → L+2 (89%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$
319	333.86	0.3266	H-6 → L+1 (68%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
319	332.858	0.0272	H-5 → L+2 (20%), H-5 → L+3 (32%), H-3 → L+4 (36%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$;
319	326.19	0.0272	H-5 → L+3 (24%), H-1 → L+4 (61%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $phpy_{d\pi} \rightarrow imd_{\pi^*}$

Table S10. TDDFT calculated vertical transition of complex [**2**]$^{3+}$

Wavelength (nm)				Character
Observed	Computed	Osc. Strength	Major contributions	
396	439.9255	0.0577	HOMO → LUMO (98%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
396	412.2911	0.0292	H-3 → LUMO (93%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$
396	399.1250	0.0489	H-2 → LUMO (24%), HOMO → L+1 (73%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$; $phpy_{\pi} \rightarrow phpy_{\pi^*}$
396	394.8164	0.0801	HOMO → L+2 (74%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
396	386.5928	0.1085	H-1 → L+3 (95%)	$phpy_{d\pi} \rightarrow imd_{\pi^*}$
396	382.7499	0.0571	H-2 → L+1 (79%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
358	376.1542	0.062	H-4 → LUMO (86%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
358	355.3167	0.0224	H-7 → LUMO (74%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$
358	350.8821	0.0256	H-4 → L+2 (75%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
358	344.9659	0.0187	H-3 → L+3 (71%), HOMO → L+3 (20%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$; $phpy_{\pi} \rightarrow phpy_{\pi^*}$
322	336.2009	0.3227	H-6 → L+1 (65%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
322	328.3479	0.0623	H-5 → L+3 (49%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$

Table S11. TDDFT calculated vertical transition of complex [**3**]$^{3+}$

Wavelength (nm)				Character
Observed	computed	Osc. Strength	Major contributions	
394	447.8065	0.0462	HOMO → LUMO (98%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
394	407.2265	0.0275	H-4 → LUMO (29%), H-3 → LUMO (65%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$;
394	404.6614	0.0471	HOMO → L+1 (80%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
394	398.1381	0.0631	HOMO → L+2 (71%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
394	386.8461	0.0594	H-2 → L+1 (77%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
394	381.6659	0.0659	H-5 → LUMO (89%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
356	379.8535	0.0222	H-2 → L+2 (81%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
356	367.9929	0.0774	H-1 → L+3 (90%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$
356	353.3723	0.0233	H-5 → L+2 (78%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$
356	339.4966	0.3281	H-6 → L+1 (60%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$

Table S12. TDDFT calculated vertical transition of complex [**4**]$^{3+}$

Wavelength (nm)				Character
Observed	Computed	Osc. Strength	Major contributions	
396	463.3678538	0.0387	HOMO → LUMO (99%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
396	414.7709643	0.0467	HOMO → L+1 (90%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
396	405.6117272	0.0698	HOMO → L+2 (62%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
396	394.6879847	0.0362	H-1 → L+1 (72%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
396	392.3647477	0.0912	H-3 → LUMO (78%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
396	386.0244618	0.0231	H-1 → L+2 (84%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$
363	364.1962713	0.0946	H-2 → L+3 (91%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$
363	361.5728686	0.0141	H-7 → LUMO (85%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$

Table S13. Calculated triplet states for complex [**1**]$^{3+}$

Triplet states	Computed Wavelength (nm)	Major contributions	Transition	Nature
T_1	486.728	HOMO → LUMO (70%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT
T_2	474.999	H-1 → L+1 (47%), HOMO → LUMO (27%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}LC; ^{3}MLLCT
T_3	466.211	H-1 → LUMO (62%), H-1 → L+2 (25%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$; $phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC; ^{3}LC
T_4	452.315	H-3 → L+4 (25%), HOMO → L+3 (57%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$	^{3}MLLCT; ^{3}MLLCT
T_5	448.276	H-3 → L+3 (33%), HOMO → L+4 (30%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$	^{3}MLLCT; ^{3}MLLCT
T_6	446.548	H-1 → L+2 (38%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC
T_7	425.492	H-3 → LUMO (61%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT
T_8	420.456	H-2 → LUMO (20%), H-2 → L+2 (44%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$; $phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC; ^{3}LC
T_9	415.524	HOMO → L+1 (90%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT
T_{10}	415.121	H-5 → LUMO (64%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT

Table S14. Calculated triplet states for complex [**2**]$^{3+}$

Triplet states	Computed Wavelength (nm)	Major contributions	Transition	Nature
T_1	486.7278805	HOMO → LUMO (70%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC
T_2	474.9988239	H-1 → L+1 (47%), HOMO → LUMO (27%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$; $phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT; ^{3}LC
T_3	466.2111492	H-1 → LUMO (62%), H-1 → L+2 (25%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT; ^{3}MLLCT
T_4	452.3154683	H-3 → L+4 (25%), HOMO → L+3 (57%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $phpy_{\pi} \rightarrow imd_{\pi^*}$	^{3}MLLCT; ^{3}LC
T_5	448.2760612	H-3 → L+3 (33%), HOMO- → L+4 (30%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $phpy_{\pi} \rightarrow imd_{\pi^*}$	^{3}LC; ^{3}LC
T_6	446.5485072	H-1 → L+2 (38%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT
T_7	425.4922716	H-3 → LUMO (61%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT
T_8	420.4564332	H-2 → LUMO (20%), H-2 → L+2 (44%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$; $phpy_{\pi} \rightarrow imd_{\pi^*}$	^{3}LC; ^{3}LC
T_9	415.5244755	HOMO → L+1 (90%)	$phpy_{\pi} \rightarrow phpy_{\pi}$	^{3}LC
T_{10}	415.1210132	H-5 → LUMO (64%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT

Table S15. Calculated triplet states for complex [**3**]$^{3+}$

Triplet states	Computed Wavelength (nm)	Major contributions	Transitions	Nature
T_1	483.8785193	HOMO → L+1 (61%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC
T_2	476.9907014	HOMO → LUMO (72%)	$phpy_{\pi} \rightarrow phpy_{\pi}$	^{3}LC
T_3	454.6541731	H-1 → LUMO (89%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT
T_4	450.1314007	HOMO → L+2 (63%)	$phpy_{\pi} \rightarrow phpy_{\pi}$	^{3}LC
T_5	446.8059858	H-4 → L+3 (20%), H-3 → L+4 (34%), H-1 → L+3 (29%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$	^{3}MLLCT; ^{3}MLLCT; ^{3}MLLCT
T_6	446.4681059	H-3 → L+3 (38%), H-1 → L+4 (24%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$	^{3}MLLCT; ^{3}MLLCT
T_7	425.3463001	H-2 → LUMO (33%), H-2 → L+2 (40%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$; $phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC; ^{3}LC
T_8	420.0433412	H-3 → LUMO (80%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT
T_9	415.1766166	H-4 → LUMO (69%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT
T_{10}	402.689899	H-2 → L+1 (64%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC

Table S16. Calculated triplet states for complex [**4**]$^{3+}$

Triplet states	Computed Wavelength (nm)	Major contributions	Transition	Nature
T_1	490.4438	HOMO → LUMO (79%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC
T_2	489.3598	HOMO → L+1 (65%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC
T_3	456.7983	HOMO → L+2 (73%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC
T_4	452.299	H-4 → L+4 (26%), H-2 → L+3 (34%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$	^{3}MLLCT; ^{3}MLLCT
T_5	451.0813	H-4 → L+3 (31%), H-2 → L+4 (28%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$	^{3}MLLCT; ^{3}MLLCT
T_6	442.3268	H-2 → LUMO (89%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT
T_7	433.0569	H-1 → LUMO (52%), H-1 → L+2 (30%)	$imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$; $imd_{\pi}/Ir_{d\pi} \rightarrow imd_{\pi^*}$	^{3}MLLCT; ^{3}MLLCT
T_8	414.7877	H-4 → LUMO (69%)	$imd_{\pi}/Ir_{d\pi} \rightarrow phpy_{\pi^*}$	^{3}MLLCT
T_9	411.9761	H-1 → LUMO (38%), H-1 → L+2 (23%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$; $phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC; ^{3}LC
T_{10}	410.4893	H-1 → L+1 (62%)	$phpy_{\pi} \rightarrow phpy_{\pi^*}$	^{3}LC

Figure S13. ^{1}H NMR spectra of photocatalytic reduction of 4-nitrophenol to 4-aminophenol at different time interval. The reaction mixture consists of 4-nitrophenol (10 mM), [**4**]$^{3+}$ (0.1 mM) and NEt_3 (1.0 M) in tris buffer (pH-9.1) solution.

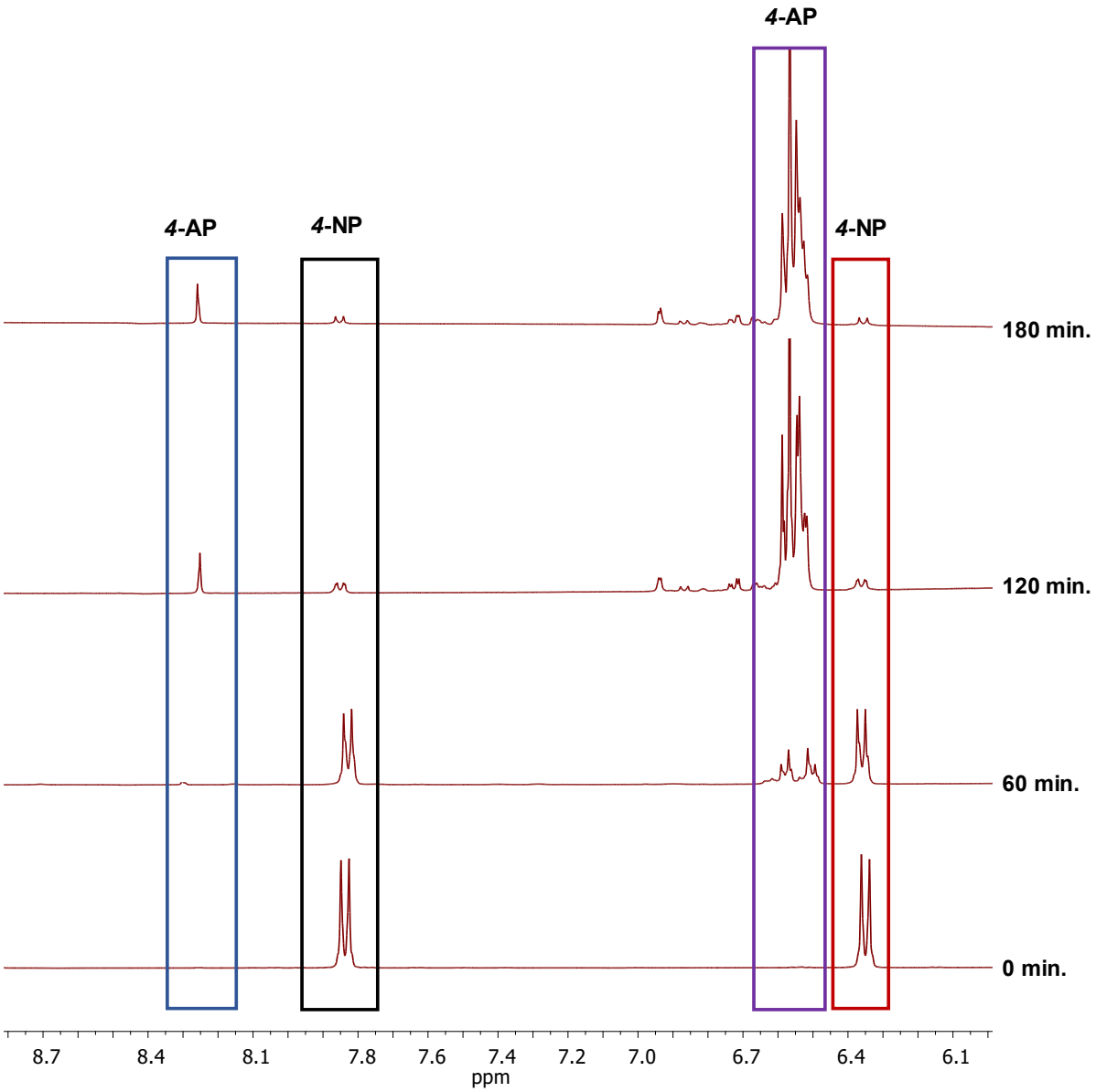
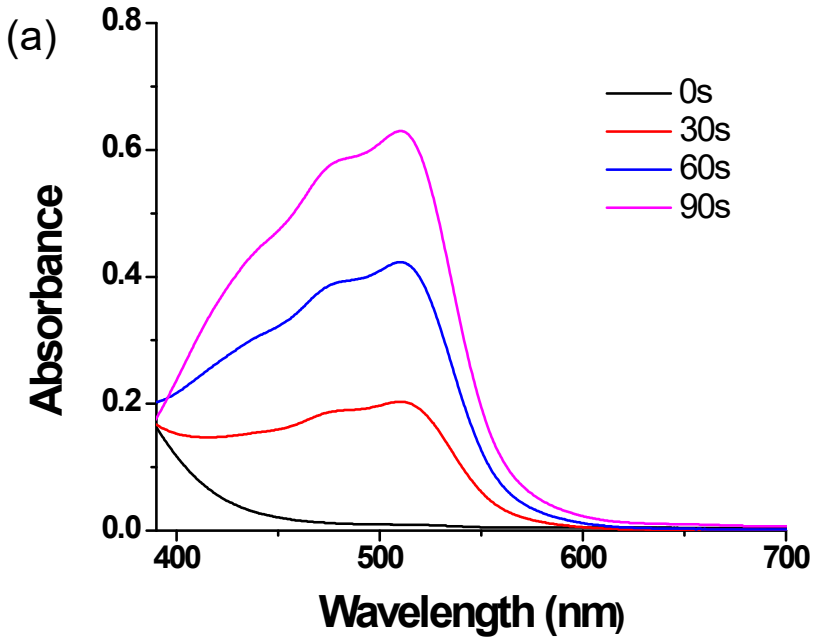


Figure S14. Plot for the (a) Absorption spectra of $[Fe(Phen)_3]^{2+}$ and (b) absorbance of $[Fe(Phen)_3]^{2+}$ (at 510 nm) at different time interval



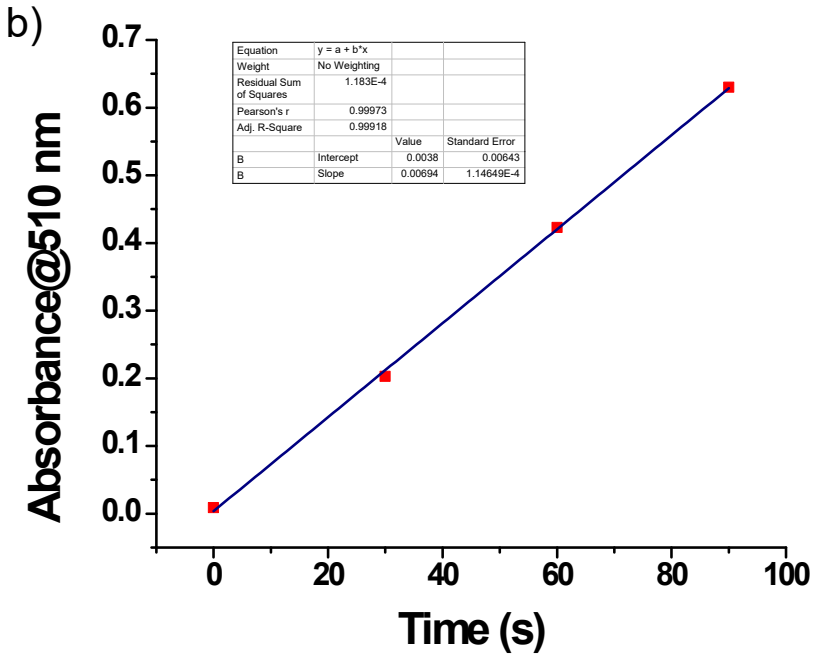
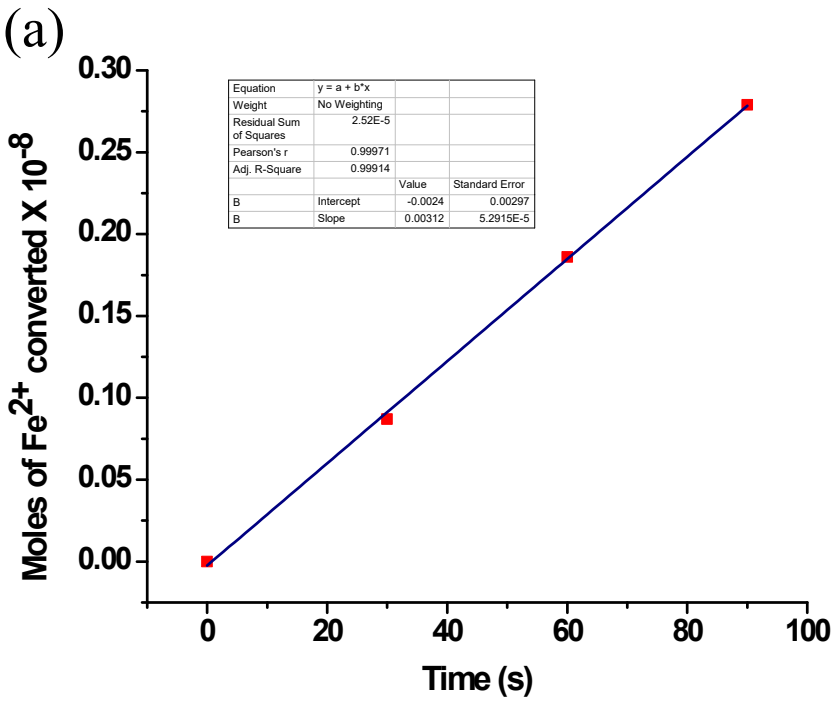


Figure S15. Plot for the (a) number of moles of Fe^{2+} formed with respect to time (b) number of moles of 4-nitrophenol reduced with respect to the moles of photons absorbed by the complex [**4**]$^{3+}$.



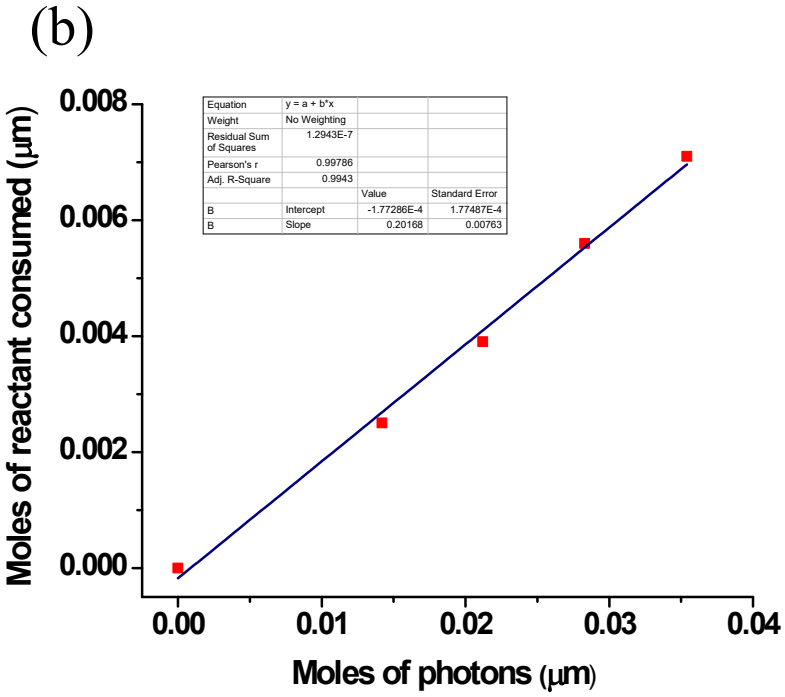
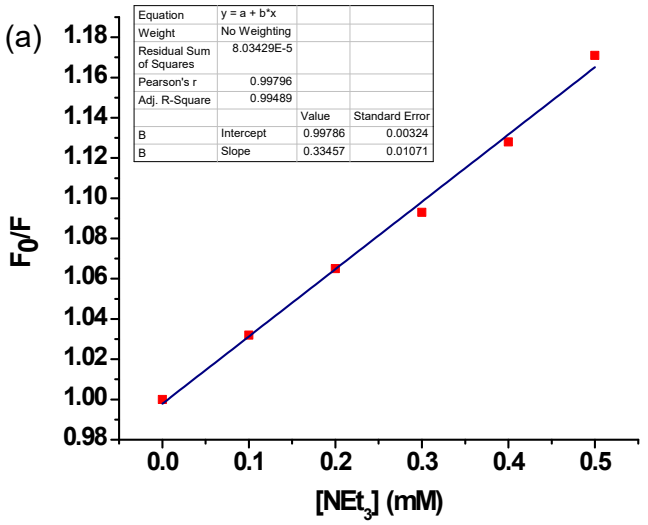
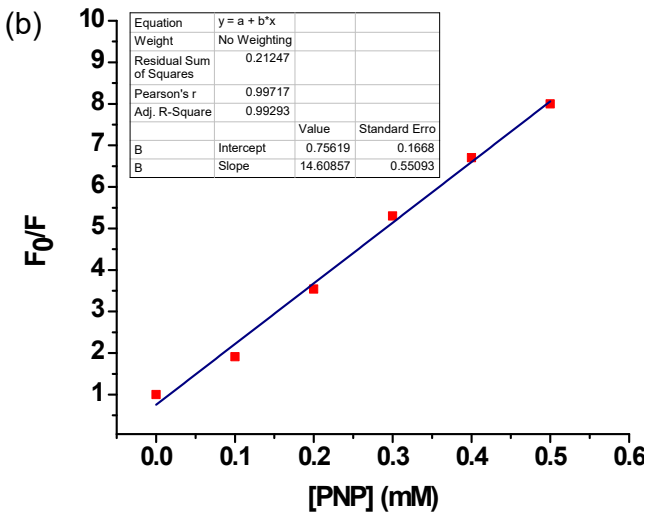


Figure S16. Stern-Volmer plot for fluorescence quenching of [**4**]$^{3+}$ in the presence of (a) NEt_3 and (b) 4-nitrophenol and (c) dioxygen in pH-9.1 buffer solution.





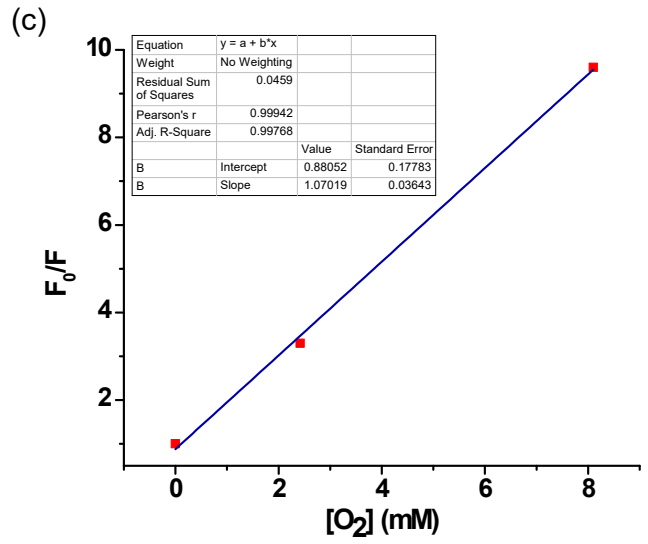
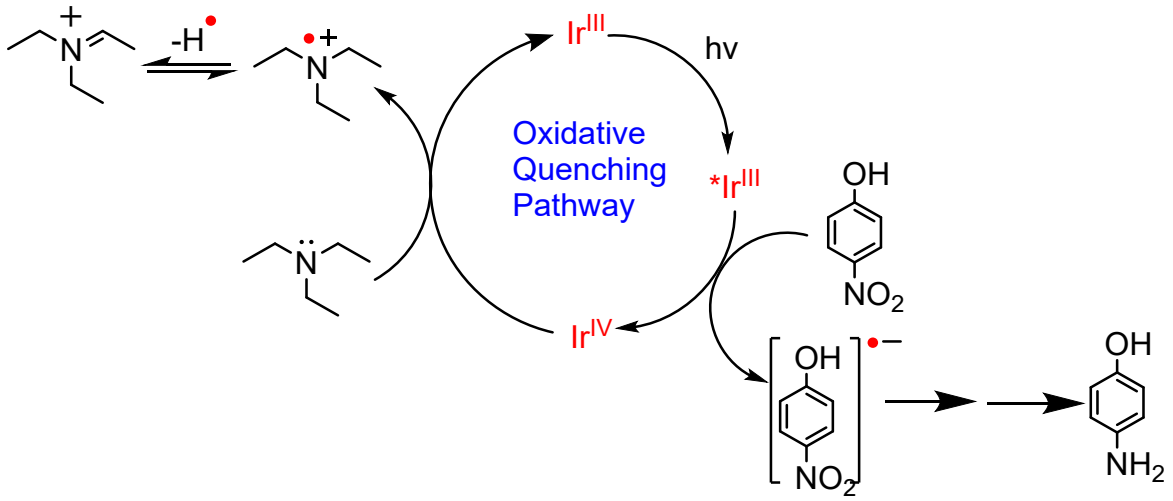


Figure S17. Plausible mechanism for the reduction of 4-nitrophenol by [**4**]$^{3+}$.[1]



Reference

1. A.R. Tripathy, A. Kumar, R. Rahmathulla, A. K. Jha and V. R. Yatham, *Org. Lett.* 2022, **24**, 5186–5191