Electronic Supplementary Information (ESI) for

Tuning of intramolecular charge transfer properties and charge distributions in ferrocene-appended catechol derivatives by chemical substitution

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Contents

1. Characterization of new compounds

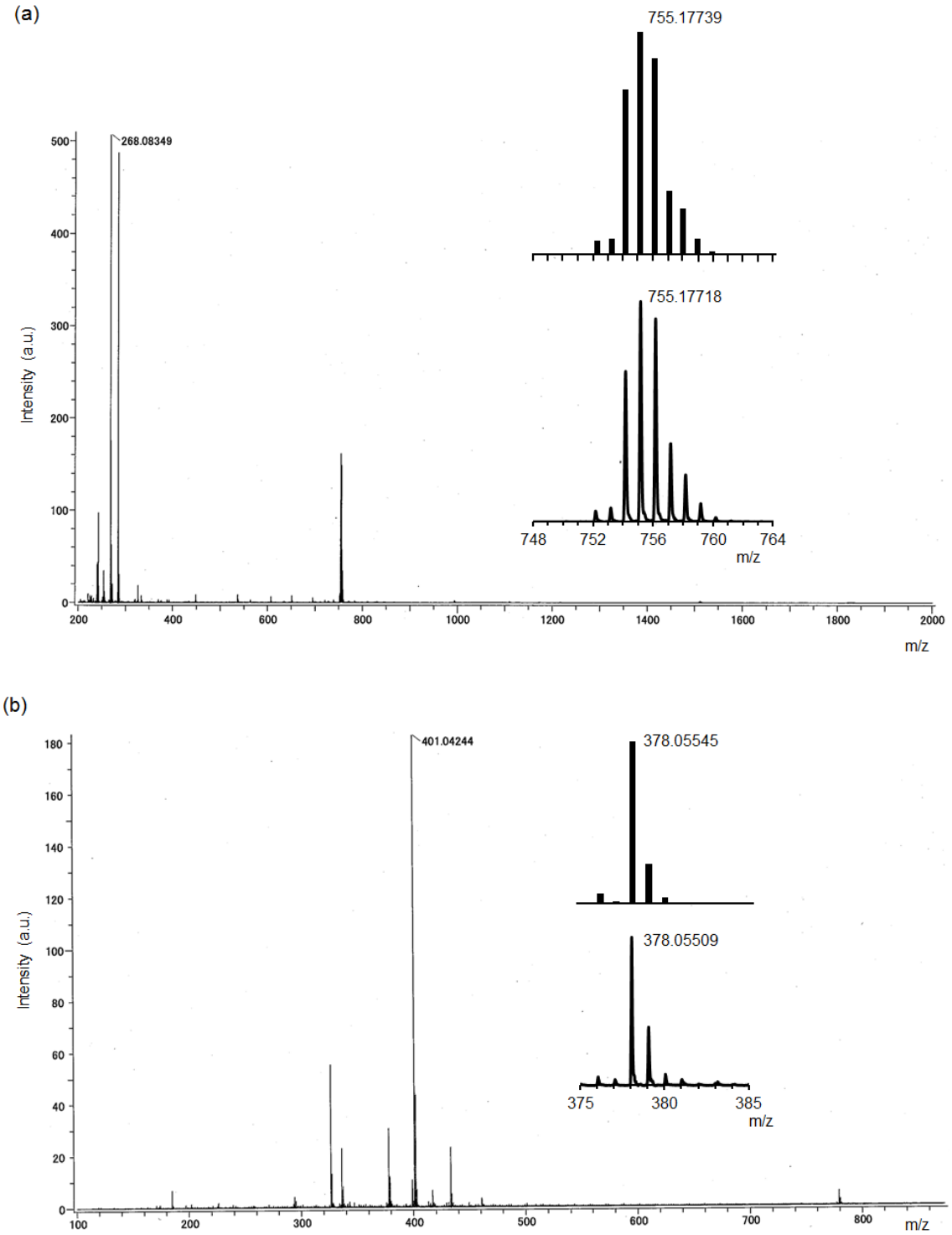

Figure S1. HR-ESI-MS of (a) **3** and (b) **5**. Inset: experimental (bottom) and theoretical (top) isotopic distributions for $[M]^+$.

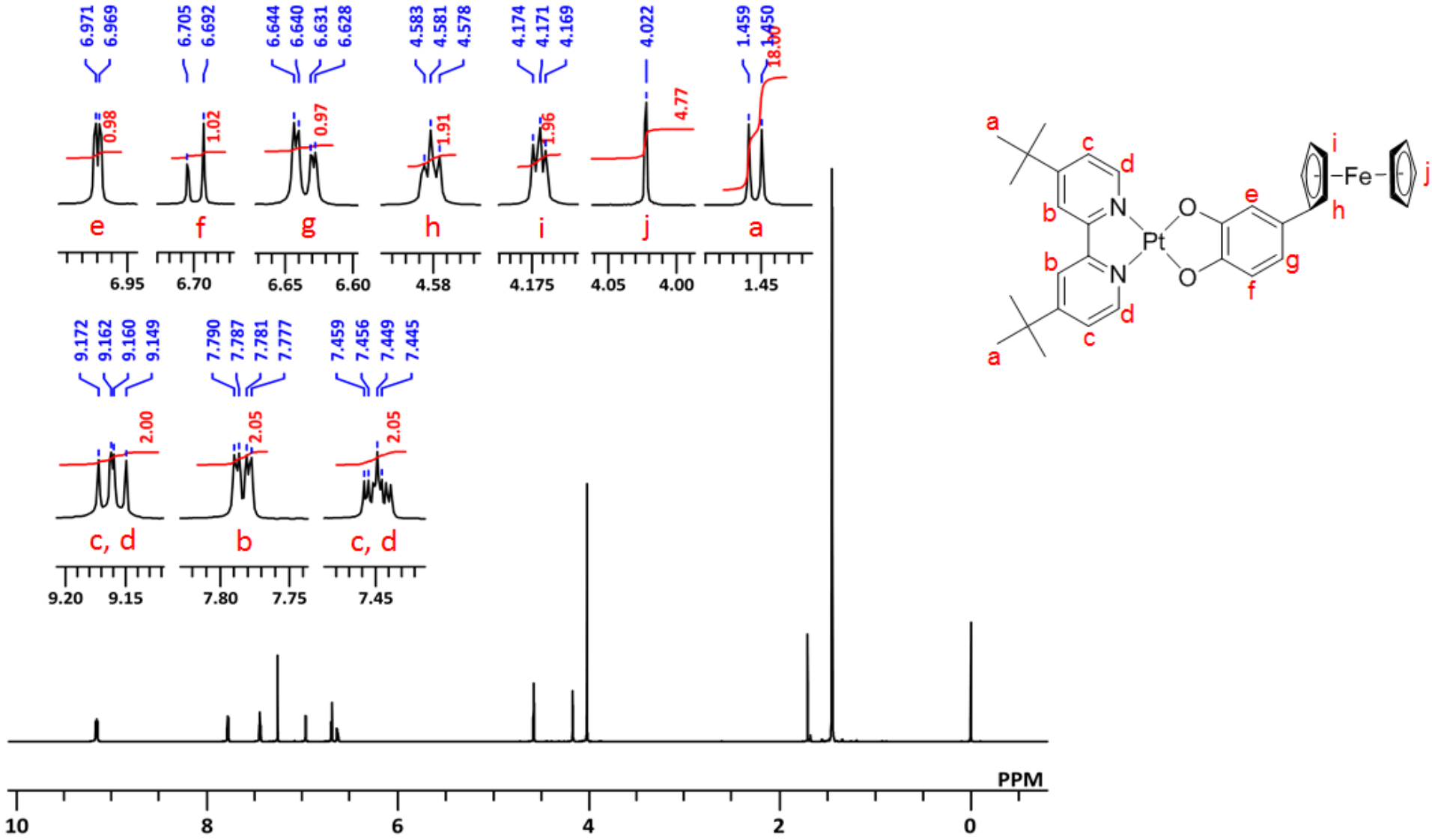

Figure S2. ^{1}H-NMR spectrum of **3** in $CDCl_3$ (600 MHz).

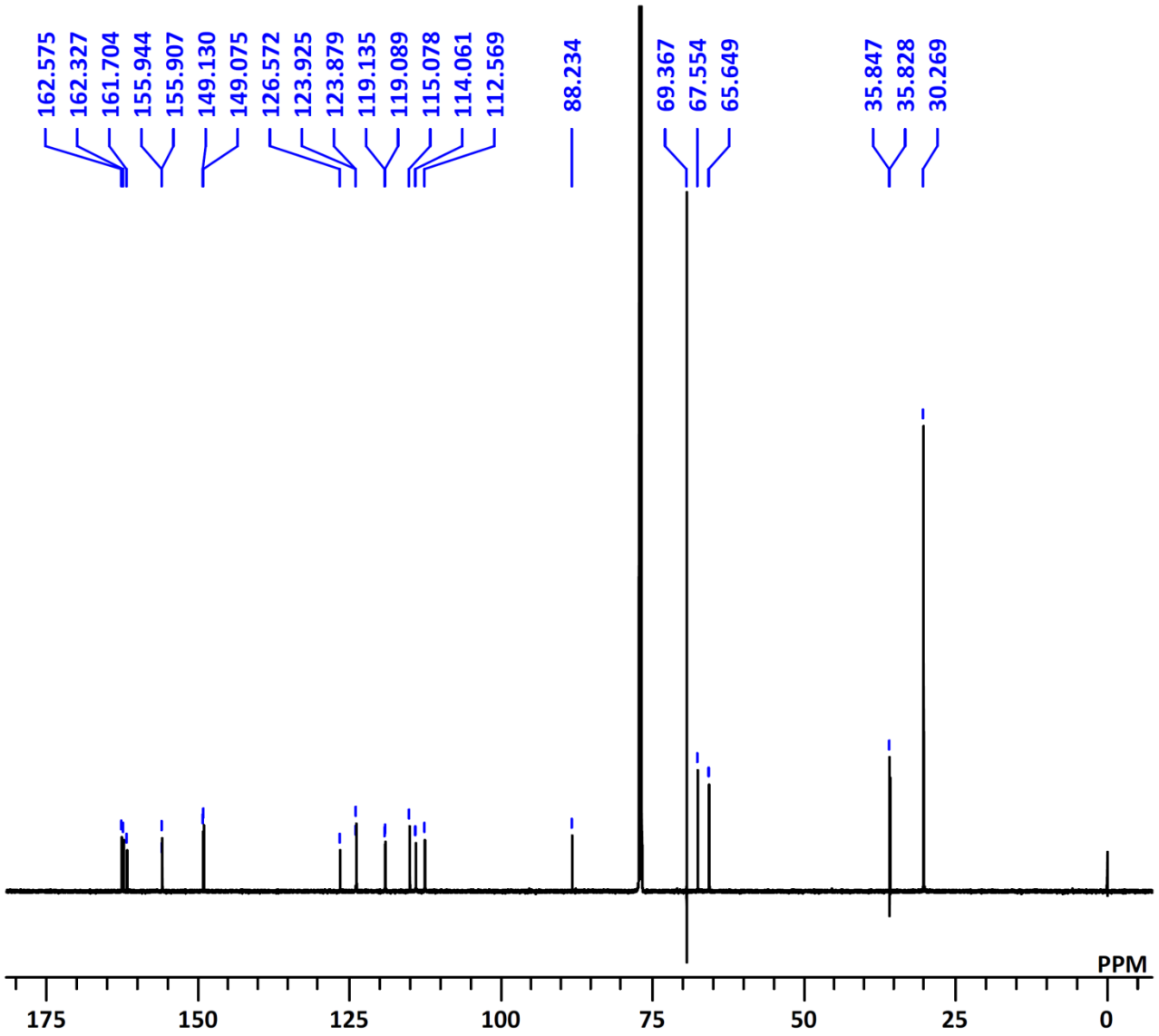

Figure S3. ^{13}C-NMR spectrum of **3** in $CDCl_3$ (150 MHz).

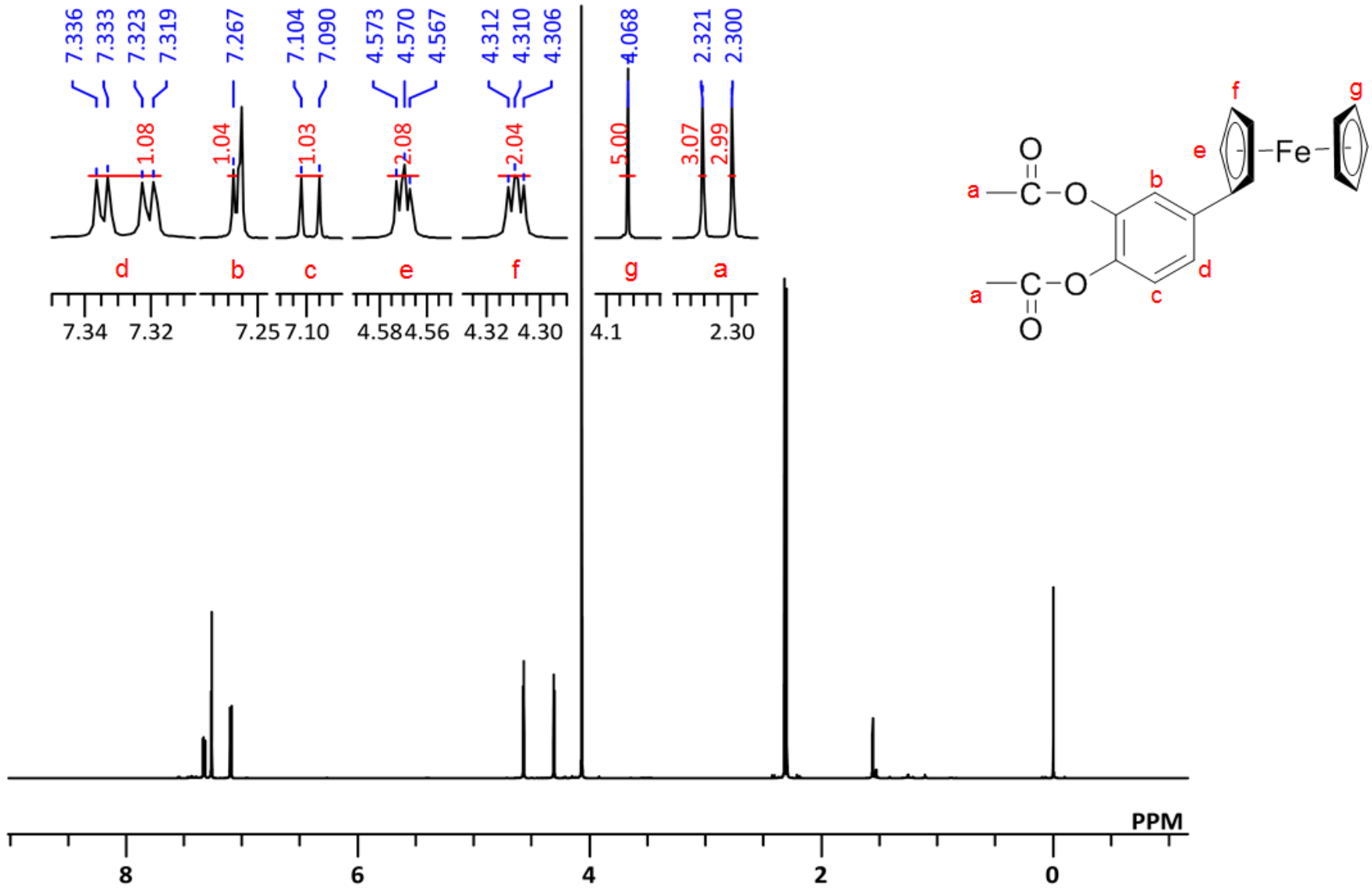

Figure S4. ^{1}H-NMR spectrum of **5** in $CDCl_3$ (600 MHz).

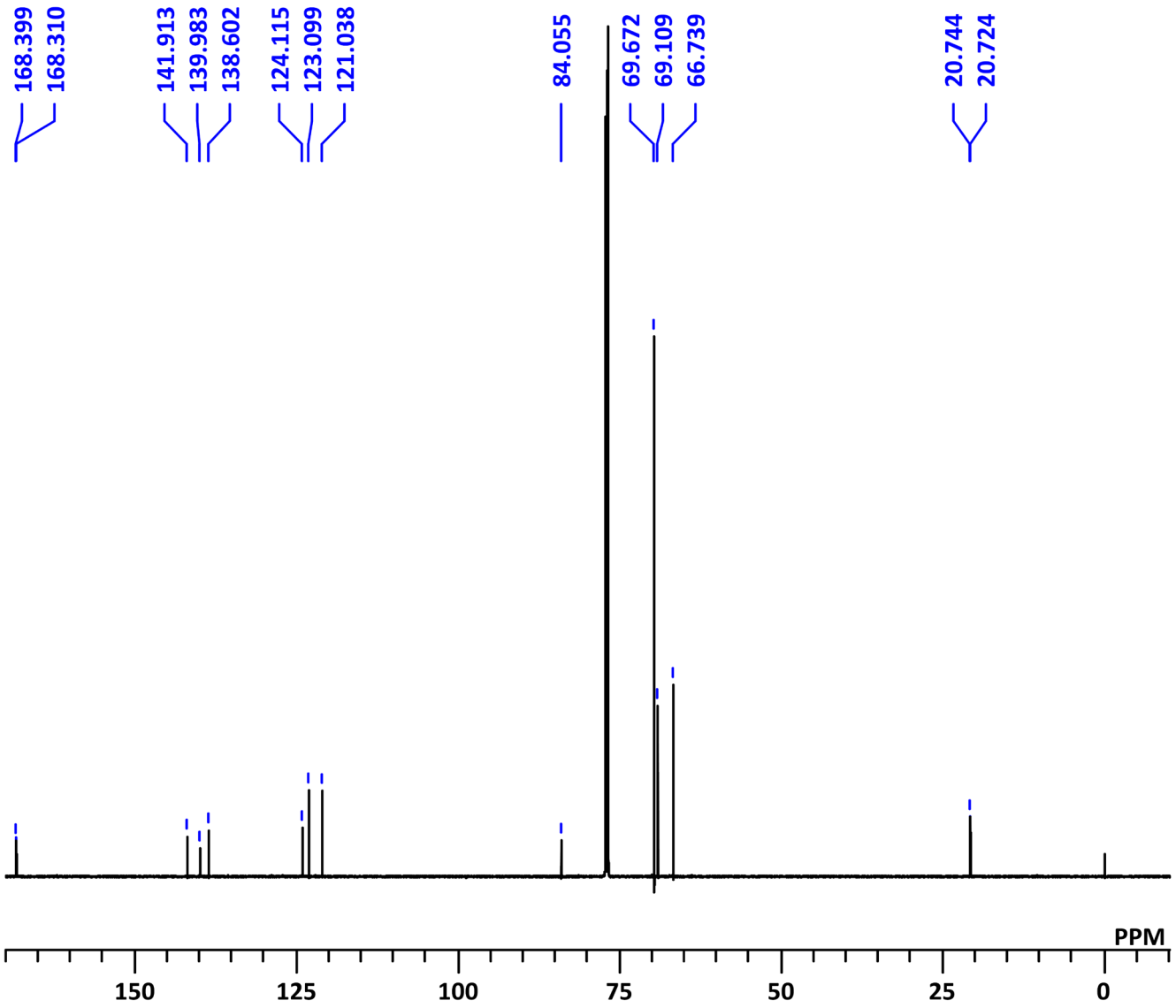

Figure S5. ^{13}C-NMR spectrum of **5** in $CDCl_3$ (150 MHz).

2. Differential NOE experiments

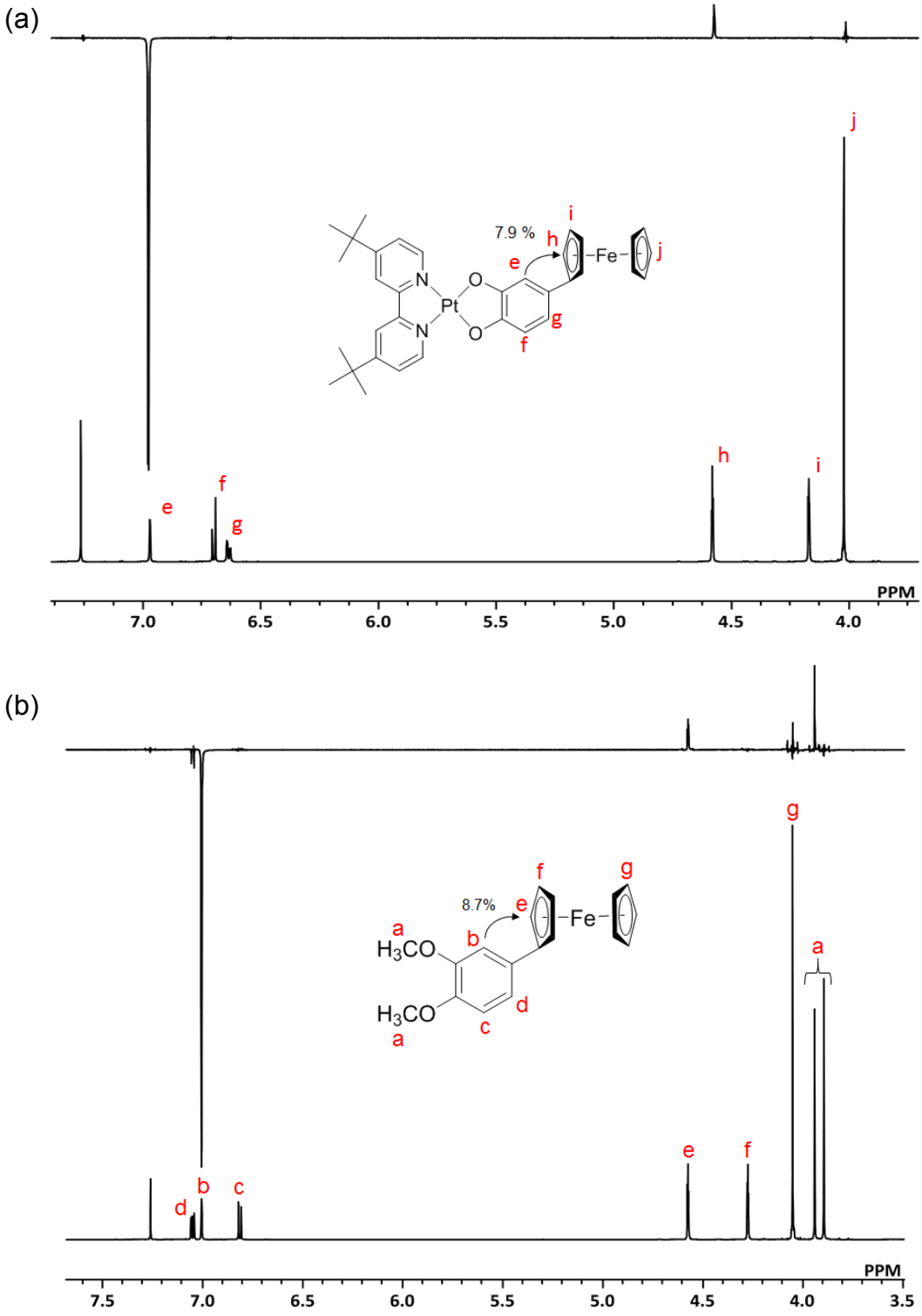

Figure S6. Partial ^{1}H-NMR (bottom) and differential NOE (top) spectra of (a) **3** and (b) **1** in $CDCl_3$. A nuclear overhauser effects between protons is indicated as an arrow.

3. Electrochemical data

Table S1. Electrochemical data for Fc derivatives.[a]

compound	$E_{1/2}{}^1$	$E_{1/2}{}^2$
1	568[b]	1668[c]
2	486[b]	653[b]
3	321	845
4	588	1938[c]
5	649	1922[c]
Pt(^{t}Bu$_2$bpy)(C)	534	1570

[a]Potentials in mV vs. Fc*$^+$/Fc*. In CH_2Cl_2 (1.0 mM) containing 0.1M ^{n}Bu$_4$NPF$_6$. [b]Previous work.[1] [c] $E_{ox}{}^2$ values were adopted because irreversible waves were observed.

References

1. Tahara, K.; Akita, T.; Katao, S.; Kikuchi, J. *Dalton Trans.* **2014**, *43*, 1368-1379.

4. Chemical oxidation

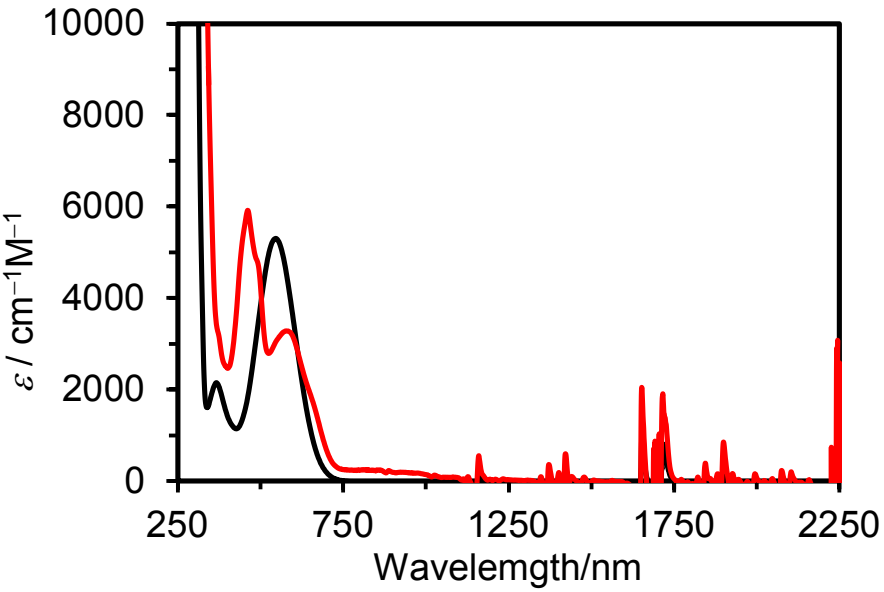

Figure S7. UV-vis-NIR spectra of Pt(^{t}Bu$_2$bpy)(C) in the absence (black line) and presence of 1.0 equiv. of magic blue (black line) in CH_2Cl_2.

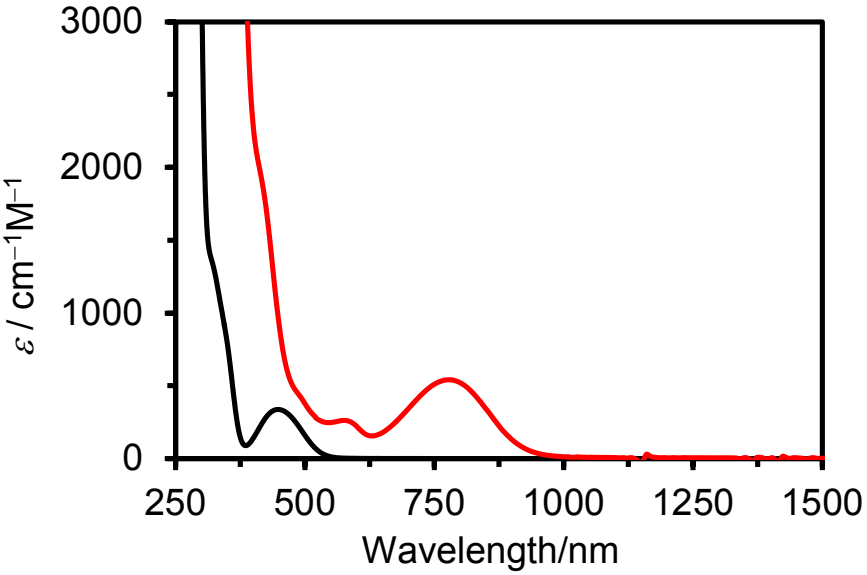

Figure S8. UV-vis-NIR spectra of **4** in the absence (black line) and presence of 0.8 equiv. of magic blue (black line) in CH_2Cl_2.

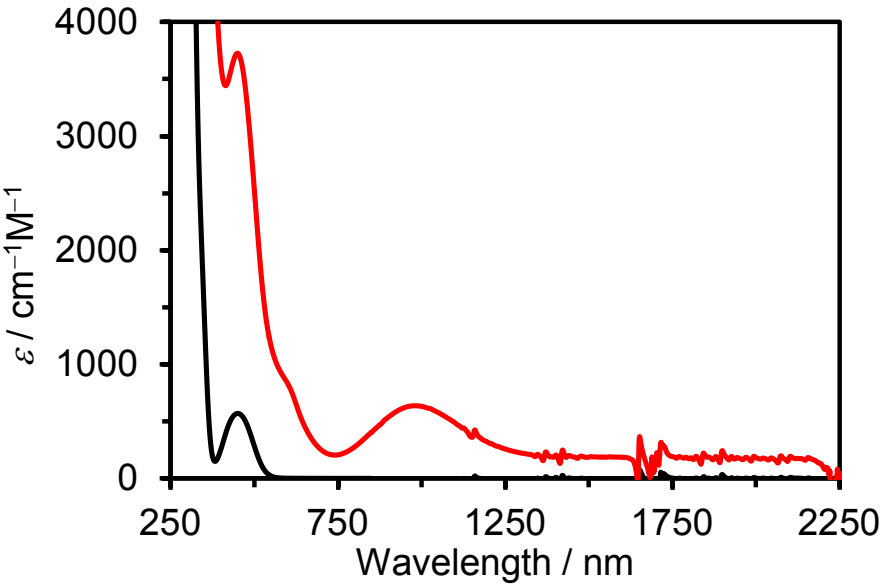

Figure S9. UV-vis-NIR spectra of **2** in the absence (black line) and presence of 1.0 equiv. of magic blue (black line) in CH_2Cl_2.

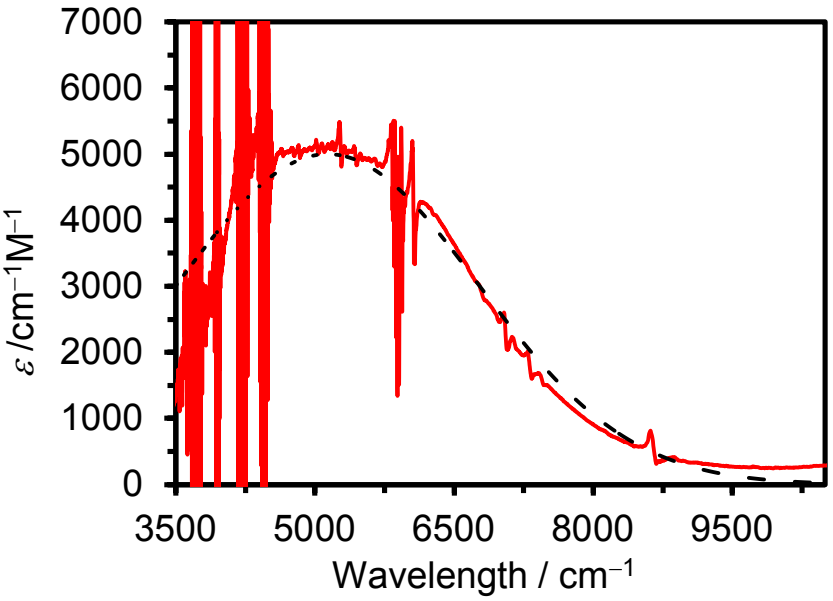

Figure S10. NIR spectra of $\mathbf{3}^+$ (red line) with Gaussian deconvolution (black broken line).

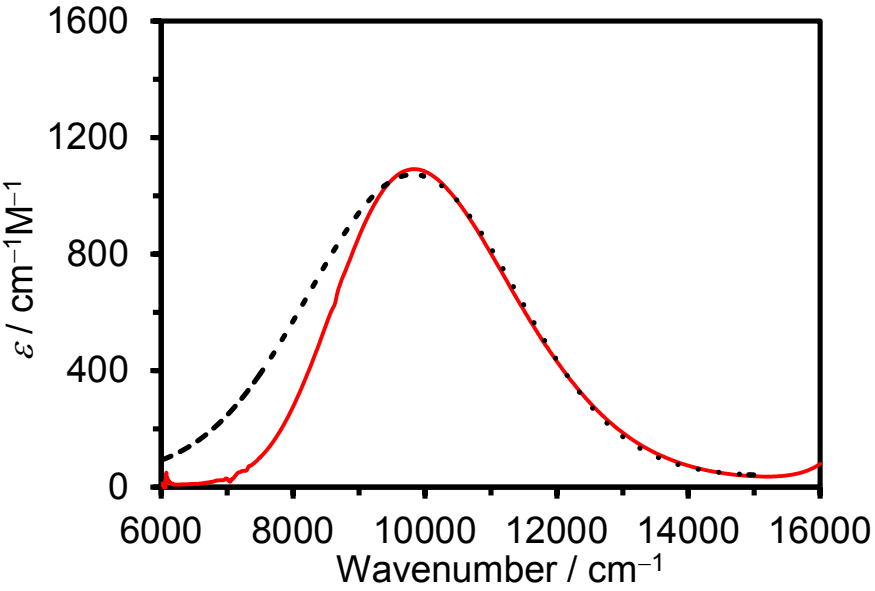

Figure S11. NIR spectra of $\mathbf{1}^{+}$ (red line) with Gaussian deconvolution (black broken line).

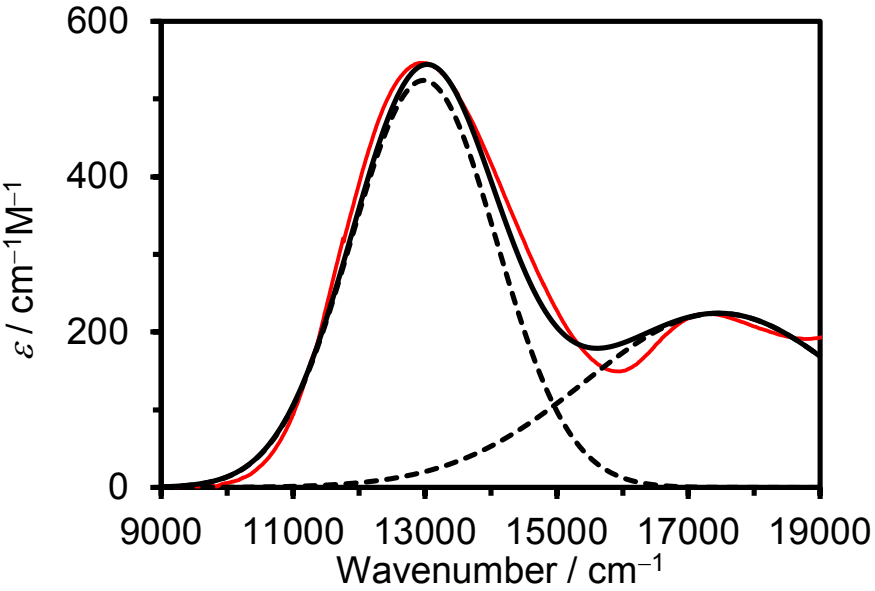

Figure S12. NIR spectra of $\mathbf{5}^{+}$ (red line) with Gaussian deconvolution (black broken line) and the sum (black line).

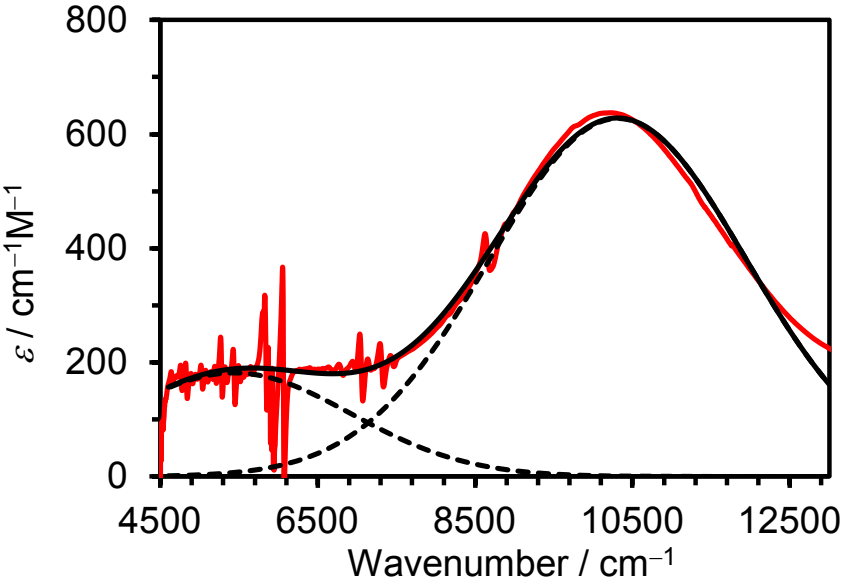

Figure S13. NIR spectra of $\mathbf{2}^{+}$ (red line) with Gaussian deconvolution (black broken line).

Table S2. Parameters of IVCT and ICT bands and electronic coupling of $\mathbf{2}^{+}$.

	IVCT	ICT
$\Delta\upsilon_{1/2}$ (cm^{-1})	3510	3840
υ_{max} (cm^{-1})	5430	10310
ε_{max} (cm^{-1})	180	630
r_{DA} (Å)	6.808[a]	5.847[b]
H_{AB} (cm^{-1})	180	560
α[c]	0.033	0.054
ΔG^0 (cm^{-1})	0	9630
λ (cm^{-1})	5430	680

[a] The distance between Fe atoms. [b] Average of distances between Fe and the center of C-C-C-O of the catecholate moiety. [c] Delocalization parameter $\alpha = H_{AB}/\upsilon_{max}$.

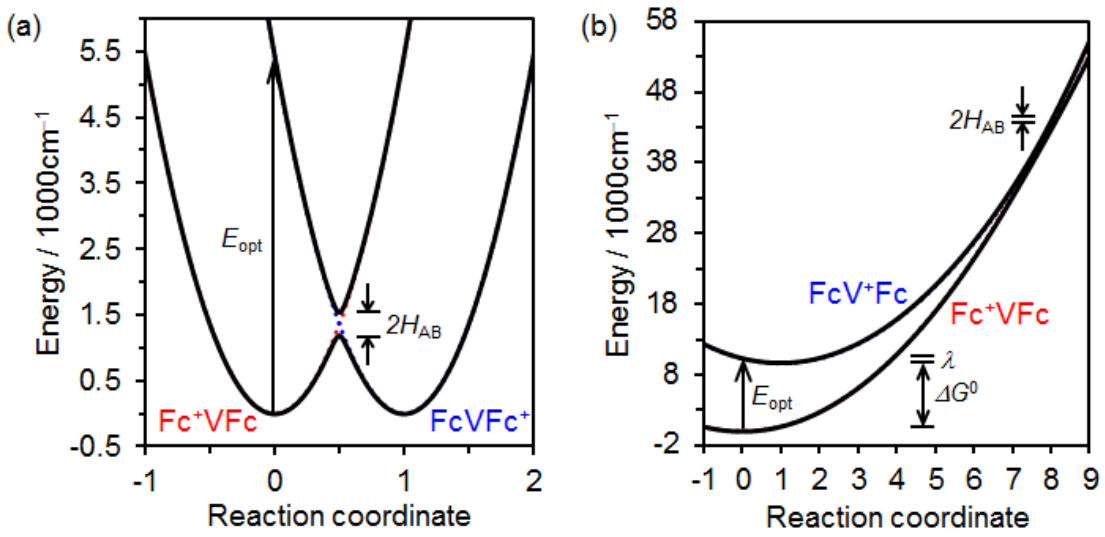

Figure S14. Diabatic (dashed line) and adiabatic (solid line) potential energy surfaces of (a) the $Fc^{+}VFc$ and $FcVFc^{+}$ states and (b) the $Fc^{+}VFc$ and $FcV^{+}Fc$ states for $\mathbf{2}^{+}$ as a function the ET reaction coordinate.

4. DFT calculations

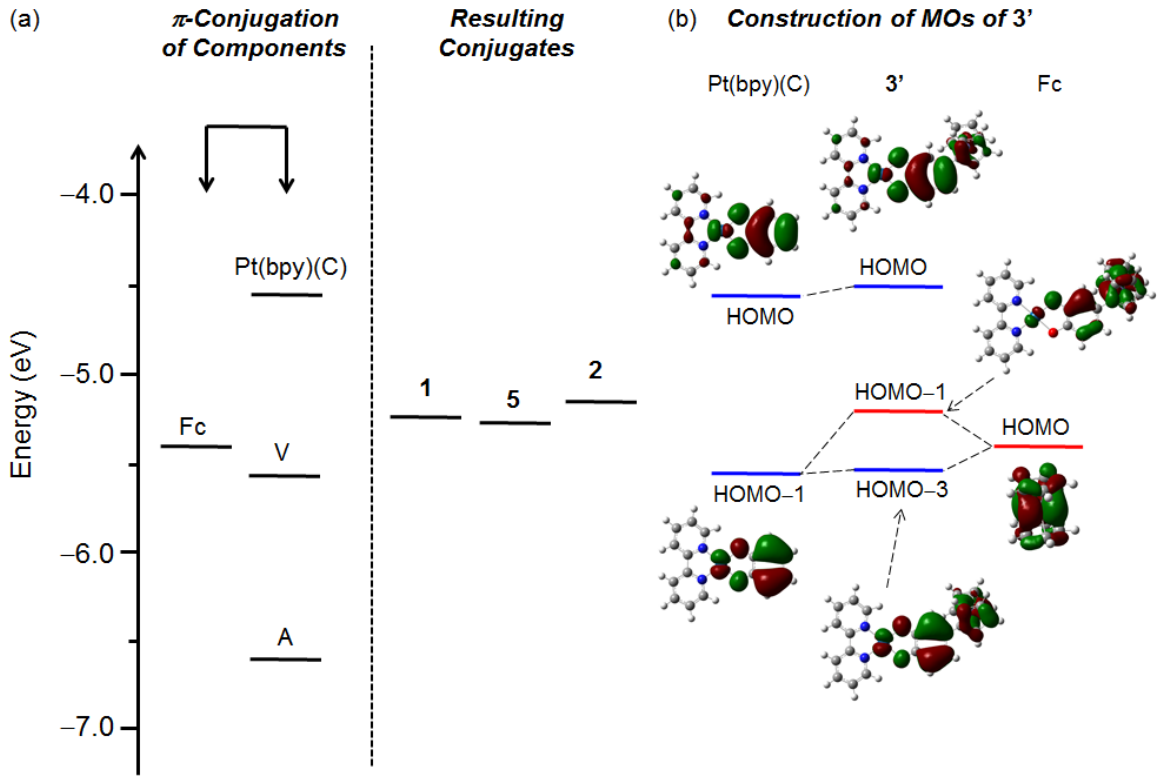

Figure S15. (a) Calculated HOMO levels with IEFPCM (CH_2Cl_2). (b) Selected molecular orbitals (MOs) for **3** calculated using a DFT method with IEFPCM (CH_2Cl_2).

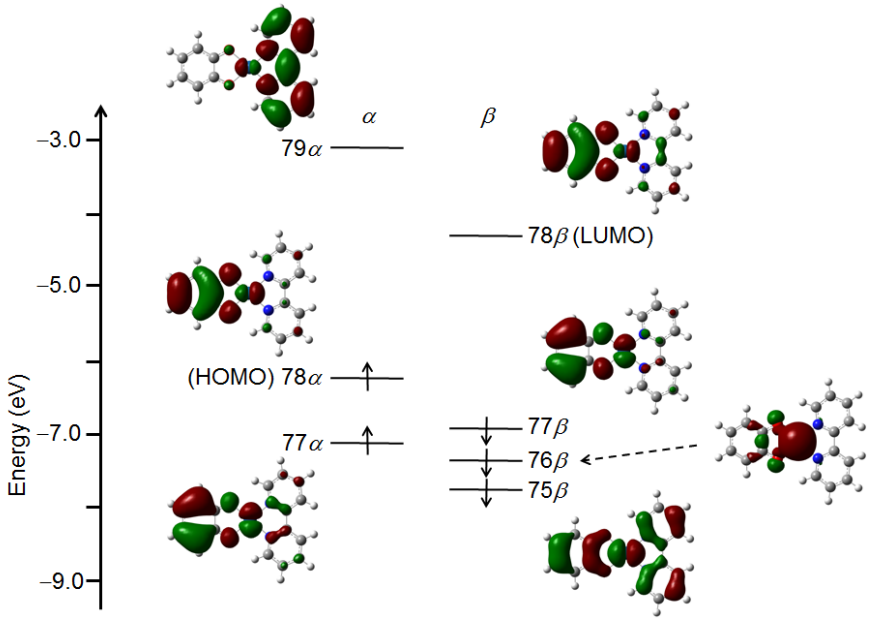

Figure S16. Selected molecular orbitals for $[Pt(bpy)(C)]^{\bullet+}$ calculated using a DFT method with IEFPCM (CH_2Cl_2).

Table S3. Coordinates of optimized gas-phase geometries of **3** and $\mathbf{3}^{+}$ calculated using a DFT method (B3LYP or UB3LYP/ Lanl2DZ (Fe and Pt atoms) and 6-31G(d) (all other atoms) levels of theory) with IEFPCM (CH_2Cl_2).

3

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	7	4.155601	-1.02445	0.265403
2	7	3.558831	1.474992	-0.09122
3	8	0.59662	0.768977	-0.45732
4	8	1.193167	-1.81415	-0.08741
5	6	-0.40135	-0.12773	-0.54575
6	6	-0.07416	-1.50489	-0.34194
7	6	-1.08433	-2.47976	-0.42227
8	6	-2.39134	-2.10651	-0.7033
9	1	-3.15215	-2.87686	-0.77338
10	6	-1.7115	0.231506	-0.82839
11	6	4.329922	-2.34884	0.428902
12	1	3.432132	-2.95133	0.354407
13	6	5.584316	-2.8924	0.676387
14	1	5.686859	-3.96398	0.803151
15	6	6.686908	-2.04007	0.755947
16	1	7.678564	-2.43555	0.948217
17	6	6.503008	-0.67013	0.585099
18	1	7.347483	0.00608	0.642962
19	6	5.221523	-0.17581	0.338876
20	6	4.882965	1.240373	0.137907
21	6	5.791851	2.298709	0.16627
22	1	6.842773	2.110371	0.349049
23	6	5.336549	3.598296	-0.04241
24	1	6.034799	4.428278	-0.02231
25	6	3.977886	3.81718	-0.27651
26	1	3.585474	4.813682	-0.44351
27	6	3.114453	2.728997	-0.29398
28	1	2.04902	2.823342	-0.46894
29	1	-0.82	-3.52219	-0.26995
30	1	-1.93043	1.282782	-0.98672
31	6	-2.73293	-0.74966	-0.9123
32	6	-4.09347	-0.37662	-1.23852
33	6	-5.25288	-1.23562	-1.26325
34	6	-4.5974	0.953034	-1.47832
35	6	-6.39571	-0.47738	-1.65336
36	1	-5.25786	-2.2973	-1.06009
37	6	-5.98815	0.884735	-1.78542
38	1	-4.01061	1.861001	-1.47051
39	1	-7.39625	-0.86477	-1.79143
40	1	-6.62155	1.72268	-2.04425
41	1	-4.0796	0.072697	2.562878
42	6	-5.0912	0.302724	2.254432
43	6	-6.14343	-0.63813	2.078312
44	6	-5.56847	1.581379	1.854479
45	6	-7.28984	0.065039	1.588994
46	1	-6.08203	-1.70216	2.264037

47	6	-6.93296	1.441411	1.452409
48	1	-4.99107	2.496183	1.834562
49	1	-8.25067	-0.37246	1.353272
50	1	-7.5729	2.234463	1.089409
51	26	-5.73338	0.248339	0.171107
52	78	2.361218	-0.15427	-0.09455

3^{+}

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	7	4.155601	-1.02445	0.265403
2	7	3.558831	1.474992	-0.09122
3	8	0.59662	0.768977	-0.45732
4	8	1.193167	-1.81415	-0.08741
5	6	-0.40135	-0.12773	-0.54575
6	6	-0.07416	-1.50489	-0.34194
7	6	-1.08433	-2.47976	-0.42227
8	6	-2.39134	-2.10651	-0.7033
9	1	-3.15215	-2.87686	-0.77338
10	6	-1.7115	0.231506	-0.82839
11	6	4.329922	-2.34884	0.428902
12	1	3.432132	-2.95133	0.354407
13	6	5.584316	-2.8924	0.676387
14	1	5.686859	-3.96398	0.803151
15	6	6.686908	-2.04007	0.755947
16	1	7.678564	-2.43555	0.948217
17	6	6.503008	-0.67013	0.585099
18	1	7.347483	0.00608	0.642962
19	6	5.221523	-0.17581	0.338876
20	6	4.882965	1.240373	0.137907
21	6	5.791851	2.298709	0.16627
22	1	6.842773	2.110371	0.349049
23	6	5.336549	3.598296	-0.04241
24	1	6.034799	4.428278	-0.02231
25	6	3.977886	3.81718	-0.27651
26	1	3.585474	4.813682	-0.44351
27	6	3.114453	2.728997	-0.29398
28	1	2.04902	2.823342	-0.46894
29	1	-0.82	-3.52219	-0.26995
30	1	-1.93043	1.282782	-0.98672
31	6	-2.73293	-0.74966	-0.9123
32	6	-4.09347	-0.37662	-1.23852
33	6	-5.25288	-1.23562	-1.26325
34	6	-4.5974	0.953034	-1.47832
35	6	-6.39571	-0.47738	-1.65336
36	1	-5.25786	-2.2973	-1.06009
37	6	-5.98815	0.884735	-1.78542
38	1	-4.01061	1.861001	-1.47051
39	1	-7.39625	-0.86477	-1.79143
40	1	-6.62155	1.72268	-2.04425
41	1	-4.0796	0.072697	2.562878
42	6	-5.0912	0.302724	2.254432
43	6	-6.14343	-0.63813	2.078312

44	6	-5.56847	1.581379	1.854479
45	6	-7.28984	0.065039	1.588994
46	1	-6.08203	-1.70216	2.264037
47	6	-6.93296	1.441411	1.452409
48	1	-4.99107	2.496183	1.834562
49	1	-8.25067	-0.37246	1.353272
50	1	-7.5729	2.234463	1.089409
51	26	-5.73338	0.248339	0.171107
52	78	2.361218	-0.15427	-0.09455

Table S4. Coordinates of optimized gas-phase geometries of Pt(bpy)(C) and $[Pt(bpy)(C)]^{\bullet+}$ calculated using a DFT method (B3LYP or UB3LYP/ Lanl2DZ (Pt atom) and 6-31G(d) (all other atoms) levels of theory) with IEFPCM (CH_2Cl_2).

Pt(bpy)(C)

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	7	1.392852	-1.29844	0.00013
2	7	1.3928	1.298451	-0.00014
3	8	-1.66794	1.33968	-0.00024
4	8	-1.66796	-1.33974	0.000325
5	6	-2.86641	0.708875	-9.3E-05
6	6	-2.86642	-0.70891	0.000138
7	6	-4.07962	-1.40422	0.000119
8	6	-5.29103	-0.69872	0.000026
9	1	-6.23063	-1.2458	0.000031
10	6	-4.0796	1.404209	-0.00015
11	6	1.255941	-2.63842	0.000152
12	1	0.234047	-3.00022	0.000311
13	6	2.357948	-3.48281	-0.00001
14	1	2.209274	-4.5566	0.000004
15	6	3.638913	-2.92446	-0.00024
16	1	4.518785	-3.55912	-0.00041
17	6	3.777344	-1.5396	-0.00024
18	1	4.762514	-1.08872	-0.00044
19	6	2.636109	-0.73446	-8E-06
20	6	2.636079	0.734522	0.000012
21	6	3.777278	1.539717	0.000236
22	1	4.762468	1.088877	0.000454
23	6	3.638782	2.924565	0.000197
24	1	4.518623	3.559268	0.00036
25	6	2.357791	3.482856	-7.7E-05
26	1	2.20907	4.556641	-0.00015
27	6	1.255823	2.638425	-0.00023
28	1	0.23391	3.000169	-0.00046
29	1	-4.06207	-2.49178	0.000205
30	1	-4.06202	2.491768	-0.00026
31	6	-5.29102	0.698726	-9.8E-05
32	78	-0.1644	-0.00002	0.000019
33	1	-6.23061	1.245824	-0.00016

$[Pt(bpy)(C)]^{\bullet+}$

Center Number	Atomic Number	Coordinates (Å)		
		X		
1	7	1.394696	1	7
2	7	1.394702	2	7
3	8	-1.70886	3	8
4	8	-1.70885	4	8
5	6	-2.86767	5	6
6	6	-2.86767	6	6
7	6	-4.09736	7	6
8	6	-5.27359	8	6
9	1	-6.22393	9	1
10	6	-4.09737	10	6
11	6	1.24718	11	6
12	1	0.22672	12	1
13	6	2.348863	13	6
14	1	2.196432	14	1
15	6	3.627861	15	6
16	1	4.506133	16	1
17	6	3.77319	17	6
18	1	4.759825	18	1
19	6	2.636763	19	6
20	6	2.636766	20	6
21	6	3.773198	21	6
22	1	4.759831	22	1
23	6	3.627878	23	6
24	1	4.506153	24	1
25	6	2.348883	25	6
26	1	2.196458	26	1
27	6	1.247195	27	6
28	1	0.226737	28	1
29	1	-4.08236	29	1
30	1	-4.08236	30	1
31	6	-5.27359	31	6
32	78	-0.14991	32	78
33	1	-6.22393	33	1

Table S5. Coordinates of optimized gas-phase geometries of **5** and $\mathbf{5}^{+}$ calculated using a DFT method (B3LYP or UB3LYP/ Lanl2DZ (Fe atom) and 6-31G(d) (all other atoms) levels of theory) with IEFPCM (CH_2Cl_2).

5

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	26	3.080847	-0.01848	0.029842
2	6	-2.00426	0.052409	0.335059
3	6	-0.66403	-0.09119	0.662092
4	6	0.089419	-1.1571	0.140501
5	6	1.51312	-1.32021	0.489139
6	6	2.512933	-1.99359	-0.29218
7	6	3.747474	-1.95337	0.419749
8	6	3.527977	-1.25247	1.644247
9	6	2.158731	-0.8578	1.687479

10	6	2.31112	1.609766	-1.01263
11	6	3.273968	0.925184	-1.81538
12	6	4.522803	0.946264	-1.12114
13	6	4.331541	1.643405	0.110778
14	6	2.964299	2.053182	0.177927
15	6	-2.62996	-0.86056	-0.51706
16	6	-1.90228	-1.92471	-1.0369
17	6	-0.55408	-2.0709	-0.71048
18	1	-0.20548	0.647126	1.311316
19	1	2.364539	-2.42193	-1.27464
20	1	4.69292	-2.34901	0.072457
21	1	4.274576	-1.03406	2.396609
22	1	1.68413	-0.30547	2.48779
23	1	1.260961	1.733556	-1.24397
24	1	3.083697	0.448361	-2.76812
25	1	5.444182	0.487013	-1.45492
26	1	5.08191	1.802003	0.874481
27	1	2.498019	2.579905	1.000403
28	1	-2.39768	-2.63214	-1.69419
29	1	-0.00218	-2.91625	-1.10857
30	8	-2.74986	1.091944	0.889664
31	6	-2.81136	2.273111	0.189204
32	8	-2.23859	2.450226	-0.85946
33	8	-3.95495	-0.66815	-0.90109
34	6	-4.94016	-1.03484	-0.01438
35	8	-4.70906	-1.53275	1.060953
36	6	-6.29591	-0.72865	-0.59244
37	1	-7.07071	-1.04202	0.107587
38	1	-6.38446	0.344707	-0.78935
39	1	-6.4228	-1.24861	-1.54731
40	6	-3.67225	3.266208	0.922992
41	1	-3.71045	4.200909	0.363217
42	1	-4.68299	2.864736	1.048063
43	1	-3.26532	3.446601	1.923116

5^{+}

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	26	-2.9736	-0.05309	0.005197
2	6	2.030288	0.014249	-0.28436
3	6	0.713372	-0.14204	-0.69256
4	6	-0.02664	-1.26174	-0.28119
5	6	-1.44842	-1.38572	-0.64348
6	6	-2.45656	-2.08498	0.108466
7	6	-3.71198	-1.93153	-0.55274
8	6	-3.50203	-1.12295	-1.71179
9	6	-2.11692	-0.78001	-1.76441
10	6	-2.10906	1.635309	0.913137
11	6	-2.78693	0.84618	1.891962
12	6	-4.16849	0.768865	1.523301
13	6	-4.34526	1.511814	0.31556
14	6	-3.07207	2.041178	-0.06458
15	6	2.646069	-0.96646	0.502745

16	6	1.931883	-2.09863	0.883622
17	6	0.598236	-2.24113	0.506867
18	1	0.25847	0.635595	-1.29355
19	1	-2.30166	-2.59566	1.049318
20	1	-4.66271	-2.31142	-0.20401
21	1	-4.26324	-0.79044	-2.40429
22	1	-1.65707	-0.14902	-2.51278
23	1	-1.04498	1.835963	0.876194
24	1	-2.32773	0.350523	2.736702
25	1	-4.93405	0.207296	2.04164
26	1	-5.26713	1.610143	-0.24147
27	1	-2.86452	2.611819	-0.95997
28	1	2.425617	-2.85308	1.486617
29	1	0.051463	-3.12619	0.814507
30	8	2.785577	1.116486	-0.65413
31	6	2.339299	2.378797	-0.32768
32	8	1.304966	2.588499	0.261075
33	8	3.934051	-0.78377	0.978374
34	6	4.981659	-0.89025	0.084957
35	8	4.825256	-1.18916	-1.07271
36	6	6.280705	-0.58983	0.779822
37	1	7.108946	-0.74364	0.088011
38	1	6.279636	0.447296	1.131686
39	1	6.398107	-1.23422	1.656448
40	6	3.322693	3.409349	-0.80736
41	1	2.943864	4.406946	-0.58504
42	1	4.288345	3.259857	-0.31358
43	1	3.484435	3.299121	-1.88422

Table S6. Coordinates of optimized gas-phase geometries of $\mathbf{1}^+$ and $\mathbf{2}^+$ calculated using a DFT method (UB3LYP/ Lanl2DZ (Fe atom) and 6-31G(d) (all other atoms) levels of theory) with IEFPCM (CH_2Cl_2).

$\mathbf{1}^+$

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	26	-2.36827	-0.0471	0.001554
2	8	3.681281	1.824475	0.099851
3	8	4.782448	-0.47415	0.534316
4	6	3.141263	3.120769	-0.14049
5	6	2.881779	0.746805	-0.10823
6	6	1.559001	0.80198	-0.52503
7	6	0.804237	-0.37841	-0.71995
8	6	-0.58249	-0.30733	-1.1859
9	6	-1.50253	-1.40777	-1.33445
10	6	-2.73935	-0.91888	-1.85283
11	6	-2.6254	0.497903	-1.99112
12	6	-1.31747	0.874519	-1.56032
13	6	-1.85168	0.138273	2.032284
14	6	-2.69524	-0.999	1.843105
15	6	-3.9437	-0.54462	1.30803
16	6	-3.86925	0.873667	1.160617
17	6	-2.57403	1.294537	1.60174

18	6	5.457374	-1.70693	0.78673
19	6	3.493064	-0.51767	0.131009
20	6	2.748674	-1.68186	-0.06469
21	6	1.419467	-1.61332	-0.48573
22	1	2.291437	3.327901	0.521616
23	1	2.827381	3.234348	-1.1853
24	1	3.948068	3.822192	0.074822
25	1	1.10259	1.767	-0.70336
26	1	-1.30716	-2.43975	-1.0783
27	1	-3.62116	-1.51195	-2.05394
28	1	-3.40325	1.173157	-2.32061
29	1	-0.95466	1.891822	-1.51629
30	1	-0.82706	0.120365	2.377963
31	1	-2.42324	-2.02929	2.029545
32	1	-4.77766	-1.17106	1.021767
33	1	-4.6359	1.511236	0.741814
34	1	-2.1937	2.306902	1.575063
35	1	5.505827	-2.32438	-0.1176
36	1	4.968044	-2.26894	1.590522
37	1	6.466222	-1.43169	1.095396
38	1	3.199764	-2.65223	0.10376
39	1	0.877247	-2.5398	-0.63928

2^{+}

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	26	-3.39123	-1.12998	0.029473
2	26	3.416356	-1.07282	-0.00496
3	8	1.109192	4.328563	-0.53621
4	8	-1.21424	4.195285	0.607398
5	6	2.371519	4.465539	-1.18205
6	6	0.615551	3.077634	-0.35113
7	6	1.256724	1.899946	-0.69983
8	6	0.675334	0.63041	-0.46341
9	6	1.467862	-0.56468	-0.79319
10	6	1.473056	-1.83366	-0.10946
11	6	2.391321	-2.71183	-0.76216
12	6	3.006866	-1.98641	-1.82885
13	6	2.457884	-0.66863	-1.83387
14	6	4.055372	0.34659	1.412345
15	6	3.965559	-0.94493	2.015091
16	6	4.863222	-1.82191	1.323984
17	6	5.504927	-1.07158	0.291441
18	6	4.999966	0.265843	0.342297
19	6	-2.48689	4.196711	1.252856
20	6	-0.66271	3.006567	0.269902
21	6	-1.25357	1.763312	0.464012
22	6	-0.62124	0.561115	0.090113
23	6	-1.34771	-0.716	0.288958
24	6	-1.54414	-1.76601	-0.67209
25	6	-2.22458	-2.84456	-0.03185
26	6	-2.46951	-2.46911	1.324064
27	6	-1.9391	-1.15968	1.521748

28	6	-4.36391	0.489804	-0.84751
29	6	-4.60888	-0.69613	-1.60328
30	6	-5.25461	-1.63949	-0.74686
31	6	-5.40853	-1.0364	0.538351
32	6	-4.85712	0.280065	0.477199
33	1	3.173764	4.002827	-0.5936
34	1	2.551283	5.538559	-1.257
35	1	2.354342	4.026069	-2.18677
36	1	2.247816	1.94846	-1.13341
37	1	0.899823	-2.07295	0.773789
38	1	2.620769	-3.726	-0.46459
39	1	3.777554	-2.35489	-2.49213
40	1	2.747197	0.123301	-2.51128
41	1	3.466162	1.213998	1.677228
42	1	3.302845	-1.22364	2.823288
43	1	4.995293	-2.87732	1.519716
44	1	6.209295	-1.45791	-0.43262
45	1	5.261415	1.067089	-0.33592
46	1	-2.45358	3.639447	2.196363
47	1	-3.26292	3.774354	0.603653
48	1	-2.71307	5.244113	1.454903
49	1	-2.24825	1.700496	0.885774
50	1	-1.24617	-1.72959	-1.71175
51	1	-2.54115	-3.76501	-0.50455
52	1	-2.99716	-3.05798	2.06286
53	1	-1.97022	-0.58862	2.44081
54	1	-3.85704	1.375563	-1.20677
55	1	-4.32561	-0.86247	-2.63442
56	1	-5.54243	-2.64799	-1.01392
57	1	-5.83506	-1.50706	1.414585
58	1	-4.80403	0.983982	1.297721

Table S7. Selected vertical excitation energies for $\mathbf{3}^{+}$ and $[Pt(bpy)(C)]^{\bullet+}$ predicted by TD-DFT with IEFPCM (CH_2Cl_2).

$\mathbf{3}^{+}$

#	*f*	eV	nm	transition[a]	coefficients
2	0.0109	0.8881	1396.09	$119\beta \rightarrow 120\beta$	0.82151
4	0.2493	1.5614	794.06	$120\alpha \rightarrow 121\alpha$	0.76312
				$119\beta \rightarrow 120\beta$	0.52422
14	0.1967	2.5703	482.36	$119\beta \rightarrow 122\beta$	0.62573
				$119\alpha \rightarrow 121\alpha$	0.60675
				$118\beta \rightarrow 120\beta$	0.20117

$[Pt(bpy)(C)]^{\bullet+}$

#	*f*	eV	nm	transition[a]	coefficients
4	0.0323	2.5135	493.27	$78\alpha \rightarrow 79\alpha$	0.98325

5	0.2255	2.5893	478.84	$75\beta \rightarrow 78\beta$	0.98693

[a] Main contributions (> 0.2) are shown.

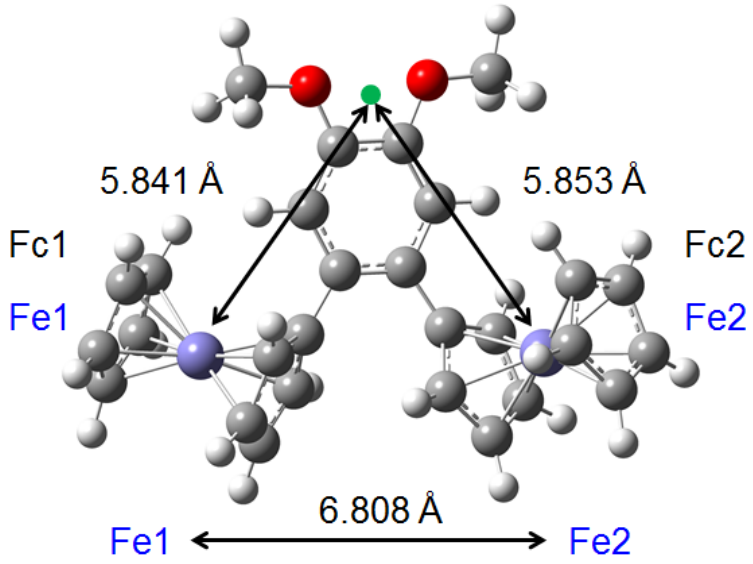

Figure S17. Optimized structures of $\mathbf{2}^{+}$ calculated using a DFT method (B3LYP/Lanl2DZ (Fe atom) and 6-31G(d) (all other atoms) levels of theory) with IEFPCM (CH_2Cl_2). The green dot indicates the center of C-C-C-O of the catecholate moiety.

Table S8. DFT-calculated NPA charges of fragments with IEFPCM (CH_2Cl_2).[a]

Compound	Fc1	Fc2	$C_6H_2O_2$	CH_3
2	–0.019	–0.019	–0.620	0.659
$\mathbf{2}^{+}$	0.0066	0.8643	–0.5510	0.6798
	(–0.003)	(1.019)	(–0.016)	–0.0001)

[a]NPA spin densities are also shown in parentheses.

Table S9. DFT-calculated frontier molecular orbital compositions of $\mathbf{2}^{+}$ (%) with IEFPCM (CH_2Cl_2).

MO	*E* /eV	Fc1	Fc2	$C_6H_2O_2$	CH_3
121β (LUMO)	–4.18	0	99	1	0
120β (HOMO)	–5.71	85.2	1.3	13.0	0.4

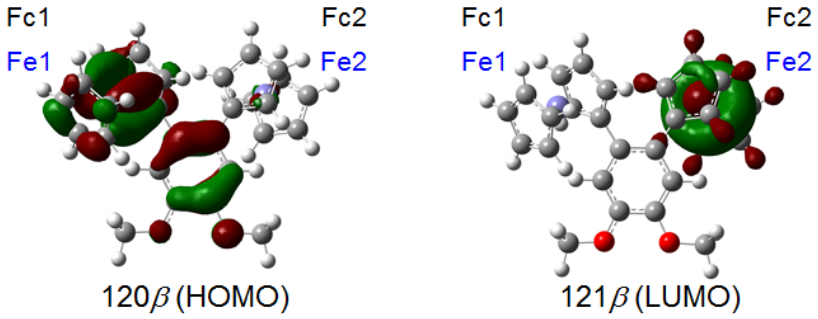

Figure S18. Frontier orbitals of $\mathbf{2}^{+}$ with IEFPCM (CH_2Cl_2).

6. X-ray crystallographic data

Table S10. Summary of crystallographic data and refinement parameters for [FcV](I_3), [FcVFc](I_3), and [FcVFc](I_3)$_2$.

	[FcV](I_3)	[FcVFc](I_3)	[FcVFc](I_3)$_2$
empirical formula	$C_{18}H_{18}FeI_3O_2$	$C_{28}H_{26}Fe_2I_3O_2$	$C_{28}H_{26}Fe_2I_6O_2$
formula weight	702.90	886.92	1267.63
crystal dimensions (mm)	0.100 × 0.070 × 0.020	0.070 × 0.040 × 0.010	0.110 × 0.080 × 0.030
crystal system	triclinic	monoclinic	monoclinic
crystal colour, habit	brown, block	brown, block	brown, block
space group	P-1 (#2)	$P2_1/n$ (#14)	C2/c (#15)
temperature (°C)	–150.0	–150.0	–150.0
a (Å)	9.8756(2)	10.3656(2)	12.4059(3)
b (Å)	10.3246(2)	27.5580(5)	14.7753(3)
c (Å)	10.3781(2)	10.6174(2)	18.8792(4)
α (deg)	84.8912(7)	90	90
β (deg)	79.7892(7)	112.2398(7)	102.6439(7)
γ (deg)	88.3020(7)	90	90
V (Å^3)	1037.16(4)	2807.29(9)	3376.6(1)
Z	2	4	4
ρ_{calcd} (g cm^{-3})	2.251	2.098	2.493
F(000)	654.00	1684.00	2320.00
μ (MoK$_\alpha$) (cm^{-1})	52.005	43.566	63.702
$2\phi_{max}$ (deg)	55.0	55.0	54.9
GOF	1.128	1.094	1.160
R1[a]	0.0436	0.0173	0.0349
wR2[b]	0.1116	0.0389	0.1165
$\Delta\rho_{max}/\Delta\rho_{min}$ (e/Å^3)	4.49/–0.92	0.75/–0.44	4.99/–1.13
CCDC No.	987994	987989	987990

[a] $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$.

7. Chemical oxidation followed by ^{1}H-NMR

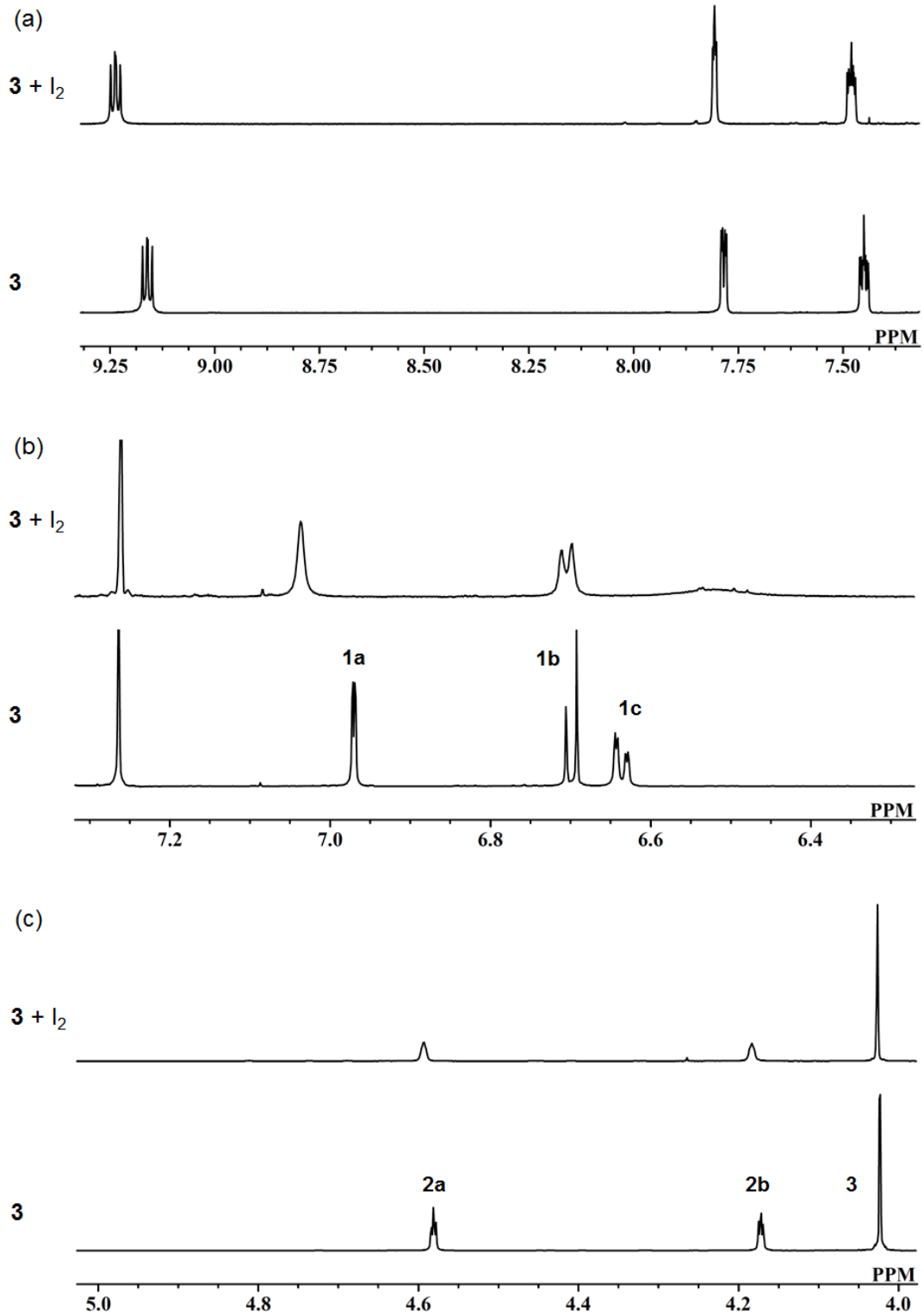

Figure S18. Partial ^{1}H-NMR spectra of **1** (5.0 mM) in the absence (bottom) and presence of 0.020 equiv. of I_2 (top) corresponding to (a) bpy, (b) $C_6H_3O_2$, and (c) Fc moieties.