Electronic Supplementary Information (ESI) for

A Pd(II) catecholato complex bearing 5,5'-divinyl-2,2'-bipyridine: synthesis, characterization, and electrochemical disproportionation in solutions and electropolymerized films

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1. Characterization of new compounds

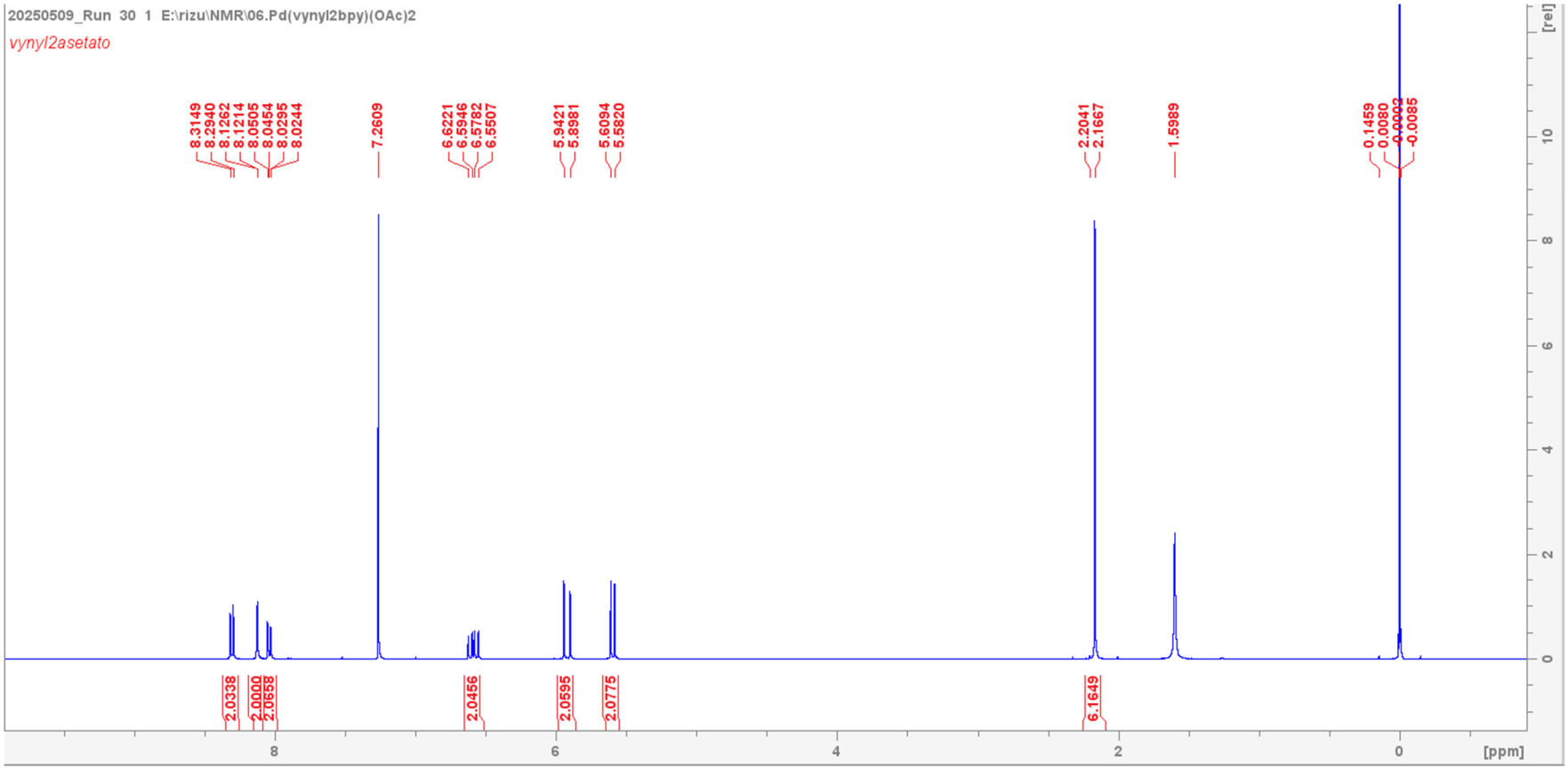

Figure S1 ^{1}H NMR spectrum of $Pd(OAc)_2$(VinylBpy) in $CDCl_3$ (400 MHz).

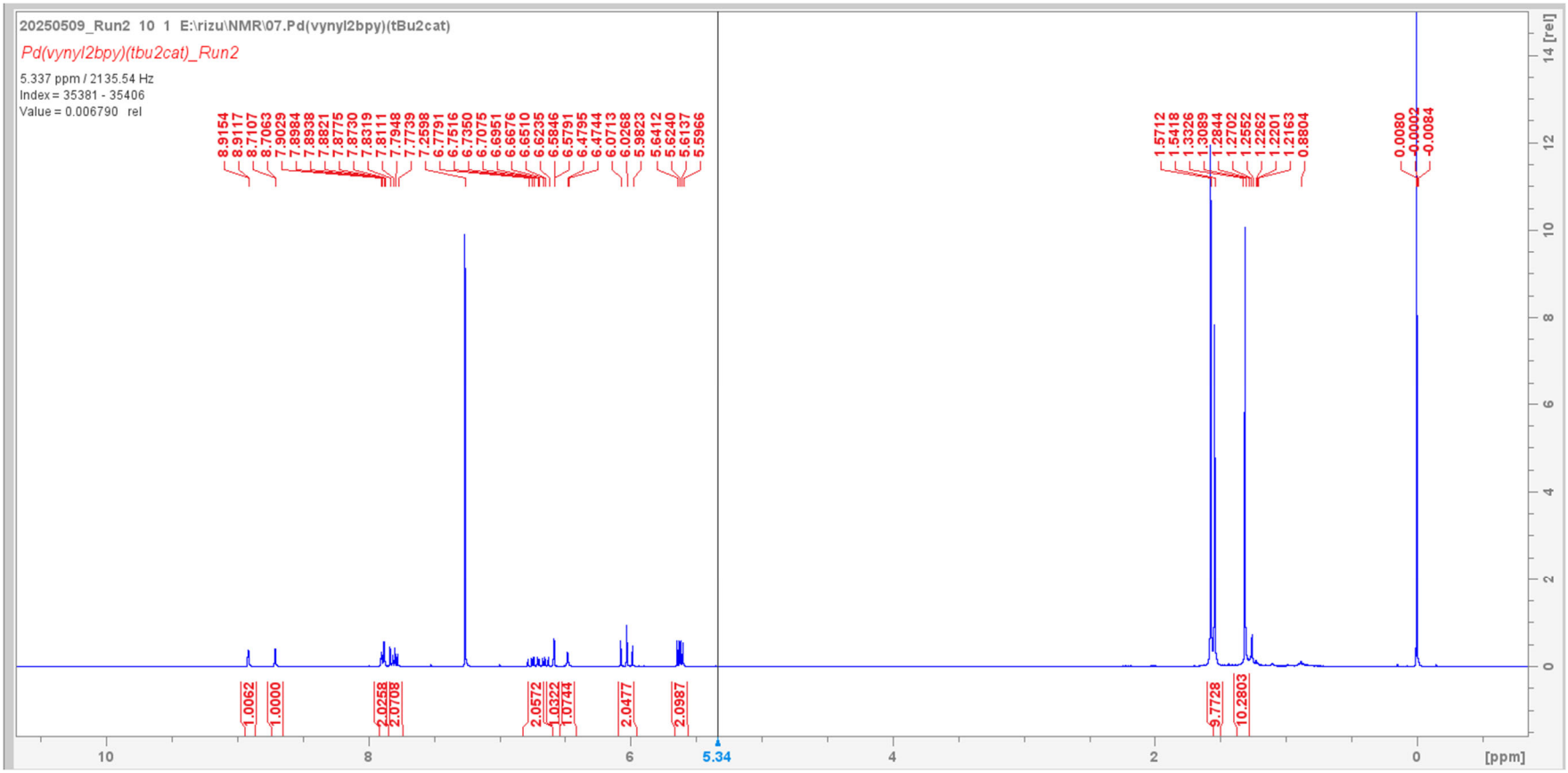

Figure S2 ^{1}H NMR spectrum of **2** in $CDCl_3$ (400 MHz).

2. DFT calculation

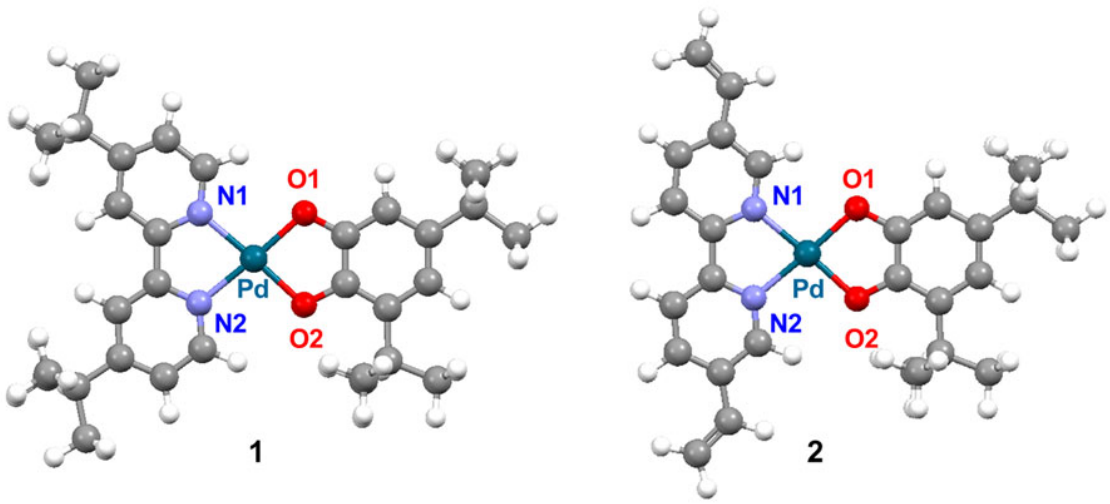

Figure S3 DFT-optimized structures of **1** and **2** calculated using a DFT method (B3LYP/Lanl2DZ (Pd atoms) and 6-31G(d) (all other atoms) levels of theory) with IEFPCM (CH_2Cl_2).

Table S1 Coordinates of optimized geometries of Pd complexes calculated using a DFT method (B3LYP/Lanl2DZ (Pd atoms) and 6-31G(d) (all other atoms) levels of theory) with IEFPCM (CH_2Cl_2).

1 with IEFPCM(CH_2Cl_2)

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	7	-1.43764	-1.448806	0.000022
2	7	-1.403294	1.173707	-0.000007
3	8	1.661566	1.1566	-0.000011
4	8	1.618059	-1.517377	0.000037
5	6	2.861307	0.513587	-0.000006
6	6	2.827832	-0.902611	0.000018
7	6	4.011434	-1.641006	0.000021
8	6	5.261038	-0.997282	-0.000001
9	6	4.099961	1.190244	-0.000023
10	6	-1.343212	-2.783896	0.000041
11	1	-0.333362	-3.180551	0.000053
12	6	-2.466391	-3.604827	0.000046
13	1	-2.318577	-4.676985	0.000062
14	6	-3.749638	-3.04142	0.000024
15	6	-3.81956	-1.638923	0.000014
16	1	-4.785446	-1.149086	0.000016
17	6	-2.664458	-0.860999	0.000011
18	6	-2.644942	0.617567	-0.000003
19	6	-3.779636	1.424701	-0.000012
20	1	-4.757371	0.959222	-0.00001
21	6	-3.674292	2.824918	-0.00002

22	6	-2.377148	3.355469	-0.000022
23	1	-2.20241	4.423569	-0.000028
24	6	-1.275336	2.505939	-0.000016
25	1	-0.256068	2.877266	-0.000018
26	1	3.931439	-2.725678	0.000038
27	6	5.2712	0.403768	-0.000021
28	1	6.223921	0.91495	-0.000037
29	6	-4.939975	3.692788	-0.000023
30	6	-5.772814	3.370931	-1.264805
31	6	-5.772813	3.370937	1.264762
32	6	-4.611241	5.19765	-0.000027
33	1	-5.205018	3.588597	-2.176267
34	1	-6.078821	2.320046	-1.29888
35	1	-6.681685	3.983068	-1.275189
36	1	-5.205018	3.588613	2.176222
37	1	-6.681686	3.983072	1.275141
38	1	-6.078815	2.320052	1.298845
39	1	-5.543806	5.771572	-0.00003
40	1	-4.042339	5.492469	0.888974
41	1	-4.042335	5.492464	-0.889027
42	6	-5.036571	-3.87769	0.000039
43	6	-5.861432	-3.535331	1.264674
44	6	-5.861273	-3.535657	-1.264788
45	6	-4.744783	-5.390095	0.000249
46	1	-5.29993	-3.768406	2.176223
47	1	-6.140341	-2.476939	1.29942
48	1	-6.785709	-4.123955	1.273915
49	1	-5.299634	-3.768919	-2.176206
50	1	-6.785521	-4.124326	-1.274022
51	1	-6.140231	-2.477288	-1.299821
52	1	-5.691171	-5.94089	0.000189
53	1	-4.183128	-5.698807	-0.888621
54	1	-4.18336	-5.698608	0.889334
55	6	6.551197	-1.841191	-0.000003
56	6	6.587121	-2.739823	1.259687
57	6	6.587119	-2.739821	-1.259695
58	6	7.825594	-0.97498	-0.000003
59	1	6.579559	-2.131813	2.172228
60	1	5.724513	-3.41342	1.300023
61	1	7.495008	-3.35706	1.269806
62	1	6.579546	-2.131808	-2.172234
63	1	7.495012	-3.357049	-1.269822
64	1	5.724518	-3.413425	-1.300027
65	1	8.712273	-1.620091	-0.000011
66	1	7.881217	-0.3335	-0.887052
67	1	7.881225	-0.333511	0.887052
68	6	4.158254	2.731377	-0.000043
69	6	3.455142	3.279007	-1.266188
70	6	3.455163	3.279036	1.266102
71	6	5.601499	3.273417	-0.00006
72	1	3.983827	2.953299	-2.170745
73	1	2.424247	2.922345	-1.324266
74	1	3.448565	4.377323	-1.258225
75	1	3.983863	2.953348	2.170658

76	1	3.448586	4.377352	1.258114
77	1	2.424269	2.922376	1.324206
78	1	5.576963	4.369927	-0.000071
79	1	6.160848	2.955061	0.887397
80	1	6.160833	2.955042	-0.887521
81	46	0.164805	-0.159603	0.000007

2 with IEFPCM(CH_2Cl_2)

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	7	-2.399516	1.501645	-0.000047
2	7	-2.41522	-1.127132	-0.000016
3	8	0.649513	-1.161063	0.000064
4	8	0.651883	1.510844	-0.000094
5	6	1.860593	-0.5398	0.000067
6	6	1.85148	0.876497	-0.000068
7	6	3.046935	1.595465	-0.000169
8	6	4.284747	0.930227	-0.000088
9	6	3.087342	-1.238038	0.000205
10	6	-2.262981	2.832008	0.000026
11	1	-1.238356	3.191619	-0.000035
12	6	-3.356711	3.709466	0.000178
13	6	-4.635912	3.121372	0.000319
14	6	-4.773571	1.741098	0.000244
15	1	-5.762085	1.297368	0.000402
16	6	-3.633057	0.929281	0.000017
17	6	-3.641837	-0.5394	-0.000123
18	6	-4.79276	-1.336484	-0.000392
19	1	-5.775541	-0.880043	-0.000587
20	6	-4.673061	-2.718385	-0.000465
21	6	-3.401482	-3.322683	-0.000283
22	6	-2.296667	-2.459135	-0.000086
23	1	-1.277293	-2.832709	0.000013
24	1	2.98525	2.681225	-0.000297
25	6	4.271004	-0.471235	0.000111
26	1	5.215033	-0.998224	0.00019
27	6	5.589179	1.751905	-0.000225
28	6	5.640003	2.649513	-1.260119
29	6	5.640082	2.64985	1.259423
30	6	6.848491	0.86385	-0.000139
31	1	5.62192	2.041687	-2.172621
32	1	4.788962	3.337671	-1.300203
33	1	6.558248	3.251136	-1.270382
34	1	5.622008	2.042269	2.172089
35	1	6.558353	3.251435	1.269488
36	1	4.789078	3.338062	1.29936
37	1	7.746049	1.493683	-0.000219
38	1	6.893183	0.221667	0.887014
39	1	6.89317	0.221474	-0.887152
40	6	3.11971	-2.779807	0.000436
41	6	2.407543	-3.31521	1.266729
42	6	2.407663	-3.315629	-1.265742
43	6	4.553791	-3.345745	0.00059

44	1	2.940466	-2.996649	2.171307
45	1	1.382067	-2.943145	1.324151
46	1	2.384261	-4.413241	1.259788
47	1	2.94071	-2.997422	-2.170372
48	1	2.384335	-4.413657	-1.258403
49	1	1.382212	-2.943536	-1.323429
50	1	4.510609	-4.441623	0.000807
51	1	5.118349	-3.037122	-0.886989
52	1	5.1183	-3.036766	0.888076
53	46	-0.822932	0.179786	-0.000022
54	1	-5.570814	-3.327223	-0.000678
55	1	-5.525711	3.741779	0.000504
56	6	-3.166612	-4.771388	-0.000316
57	1	-2.118174	-5.064433	-0.000218
58	6	-4.102658	-5.730176	-0.000445
59	1	-5.168501	-5.519312	-0.000537
60	1	-3.820225	-6.778144	-0.000456
61	6	-3.103166	5.154995	0.000211
62	1	-2.050957	5.434216	0.000244
63	6	-4.02676	6.125785	0.000184
64	1	-3.73075	7.17	0.000209
65	1	-5.095259	5.928783	0.000131

Table S2 Selected vertical excitation energies predicted by TD-DFT.

Optimized structure of **1** with IEFPCM(CH_2Cl_2)

#	*f*	eV	nm	transition[a]	coefficients	assignment
1	0.0963	1.6165	767.00	142→143	0.70608	LL'CT
3	0.0089	2.4220	511.91	142→144	0.70564	LL'CT
21	0.2988	4.3451	285.35	136→143	0.64046	π-π* of Bpy
22	0.2349	4.6656	265.74	142→149	0.64132	π-π* of Cat

[a] Main contribution is shown. Total number of states in the calculation: 30.

Optimized structure of **2** with IEFPCM(CH_2Cl_2)

#	*f*	eV	nm	transition[a]	coefficients	assignment
1	0.0908	1.2722	974.57	124→125	0.70662	LL'CT
4	0.0115	2.4088	514.72	124→127	0.70575	LL'CT
11	0.4906	3.3770	367.15	121→125	0.54085	π-π* of Bpy
13	0.3207	3.6190	342.59	119→125	0.61500	LLCT, MLCT

[a] Main contribution is shown. Total number of states in the calculation: 30.

Optimized structure of **2** with IEFPCM(EtOH)

#	*f*	eV	nm	transition[a]	coefficients	assignment
1	0.0823	1.3698	905.13	124→125	0.70637	LL'CT
10	0.5586	3.3749	367.38	121→125	0.5586	π-π* of Bpy
13	0.2293	3.6798	336.93	119→125	0.63292	LLCT, MLCT
25	0.2233	4.4167	280.72	121→127	0.63981	π-π* of Bpy

[a] Main contribution is shown. Total number of states in the calculation: 30.

Optimized structure of **2** with IEFPCM(toluene)

#	*f*	eV	nm	transition[a]	coefficients	assignment
1	0.1254	1.0193	1216.33	124⟶125	0.70891	LL'CT
12	0.2076	3.3272	372.64	122⟶128	0.49190	π-π* of Cat, LMCT
15	0.6801	3.5096	353.27	119⟶125	0.58250	LLCT, MLCT
26	0.2103	4.3610	284.30	121⟶126	0.63882	π-π* of Bpy

[a] Main contribution is shown. Total number of states in the calculation: 30.

Table S3 DFT-calculated frontier molecular orbital compositions (%) of **1** and **2**.

Compound	MO	*E* /eV	Pd	Bpy ligand	^{t}Bu$_2$Cat
2 with IEFPCM (EtOH)	125 (LUMO)	−2.71	2	96	2
	124 (HOMO)	−4.49	5	3	92
2 with IEFPCM (toluene)	125 (LUMO)	−2.80	3	93	4
	124 (HOMO)	−4.15	4	5	90

3. Disproportionation in homogeneous solutions

Chemical oxidation of **2** was performed with AgTFSI (Silver Bis(trifluoromethanesulfonyl)imide, one equivalent vs. **2**) in a homogeneous CH_2Cl_2 solution to generate **2**$^{\bullet+}$. After the filtration, the dark blue solid of the target SQ complex **2**$^{\bullet+}$TFSI^{-} was reprecipitated by addition of *n*-hexane to the reaction solution. **2**$^{\bullet+}$TFSI^{-} was dissolved in DMF with ^{n}Bu$_4$NCl (two equivalents vs. **2**$^{\bullet+}$). After 2 h, the disproportionation products were detected by ^{1}H NMR (Fig. S7). The yields of **1** and ^{t}BuQ were determined to be 22% and 31%, respectively.

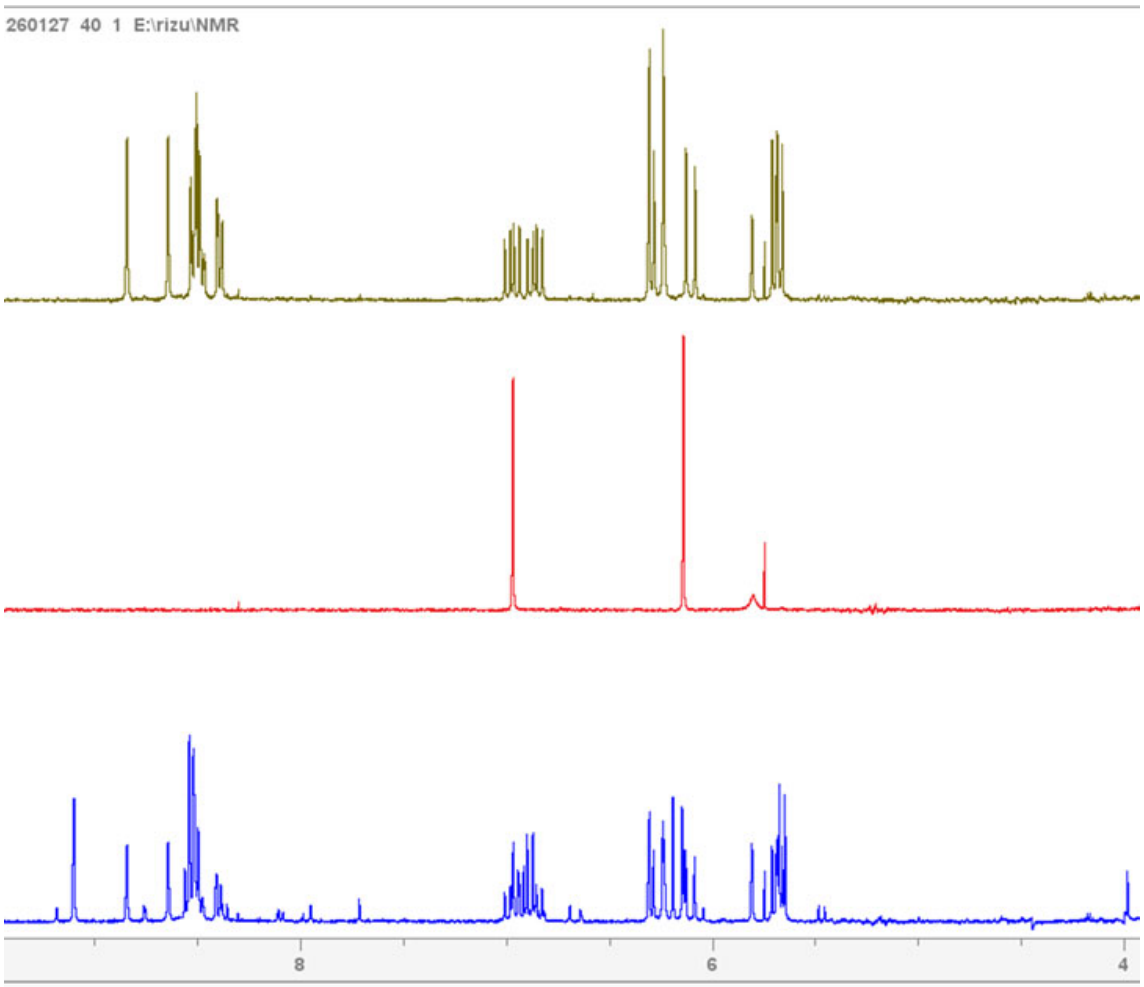

Figure S4 ^{1}H NMR spectra of the standard samples of (top) **2**, (middle) ^{t}BuQ, and (bottom) the reaction mixture of **2**$^{\bullet+}$TFSI^{-} treated with DMF and ^{n}Bu$_4$NCl for 2 h in DMSO-d_6 (400 MHz).

4. Electrochemical behavior

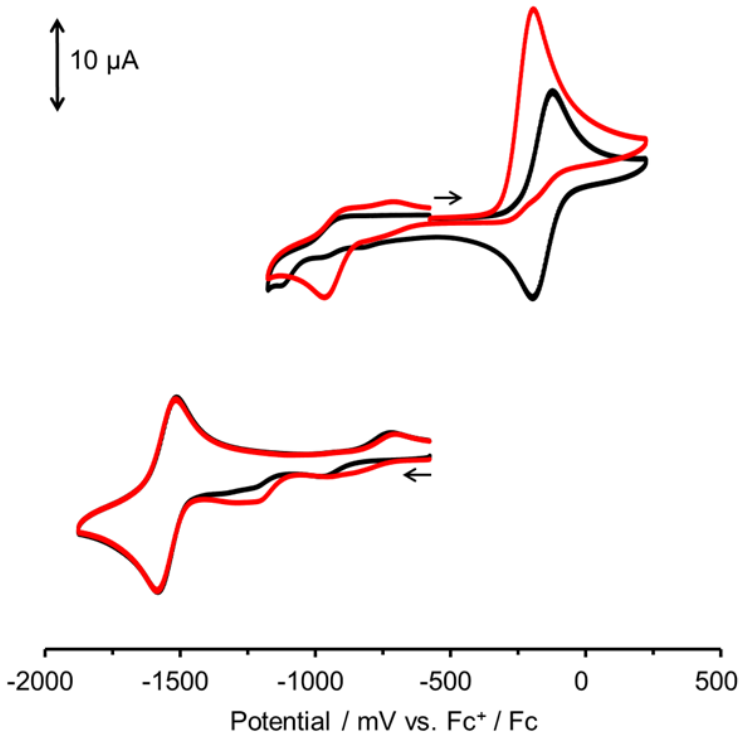

Figure S5 (a) Cyclic voltammograms of **2** (1.0 mM) in the absence (black line) and presence of DTAC (1.0 mM) (red line) in DMF/^{n}Bu$_4$NPF$_6$. Scan rate: 100 mV / s.

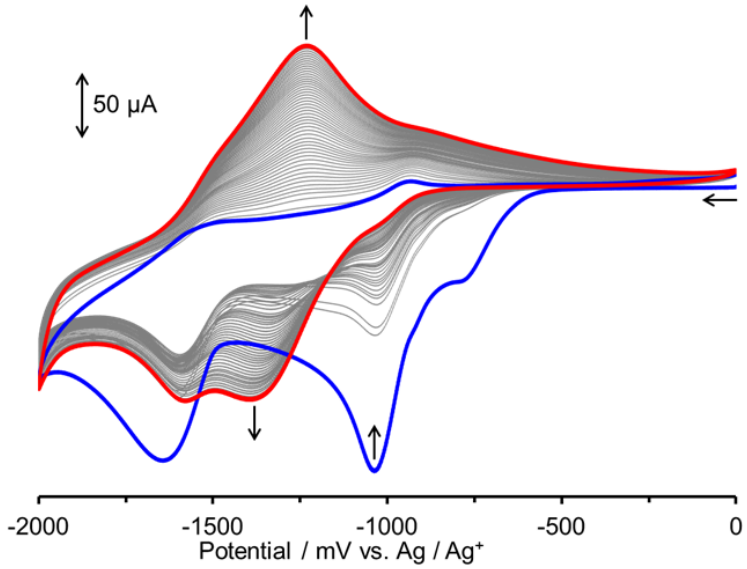

Figure S6 Cyclic voltammograms upon reductive electropolymerization of **2** (1.0 mM) on an ITO electrode pretreated with Si(vinyl)(OMe)$_3$ by 50 repeated cyclic scans in DMF/^{n}Bu$_4$NPF$_6$. Scan rate: 100 mV / s. 1st and 50th cycles are shown in blue and red, respectively.

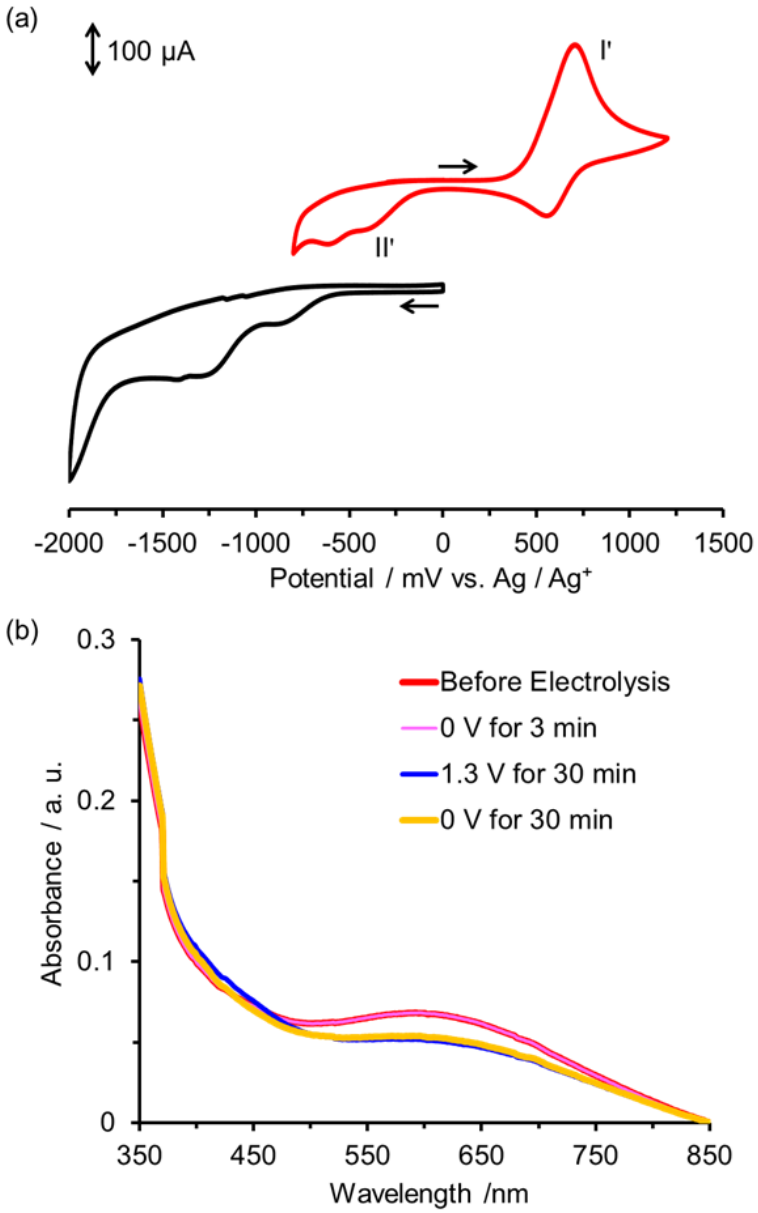

Figure S7 (a) Cyclic voltammograms of polymer **2** on an ITO electrode in DMF/^{n}Bu$_4$NPF$_6$ in the absence of DTAC. Scan rate: 100 mV / s. The first and second scan were shown in red and black, respectively. (b) UV-vis spectral change of polymer **2** on an ITO electrode in DMF/^{n}Bu$_4$NPF$_6$ in the absence of DTAC recorded during controlled potential electrolysis.