Electronic Supplementary Information (ESI) for

New π-extended catecholato complexes of Pt(II) and Pd(II) containing a benzothienobenzothiophene (BTBT) moiety: synthesis, electrochemical behavior and charge transfer properties

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Contents

1. Characterization of new compounds

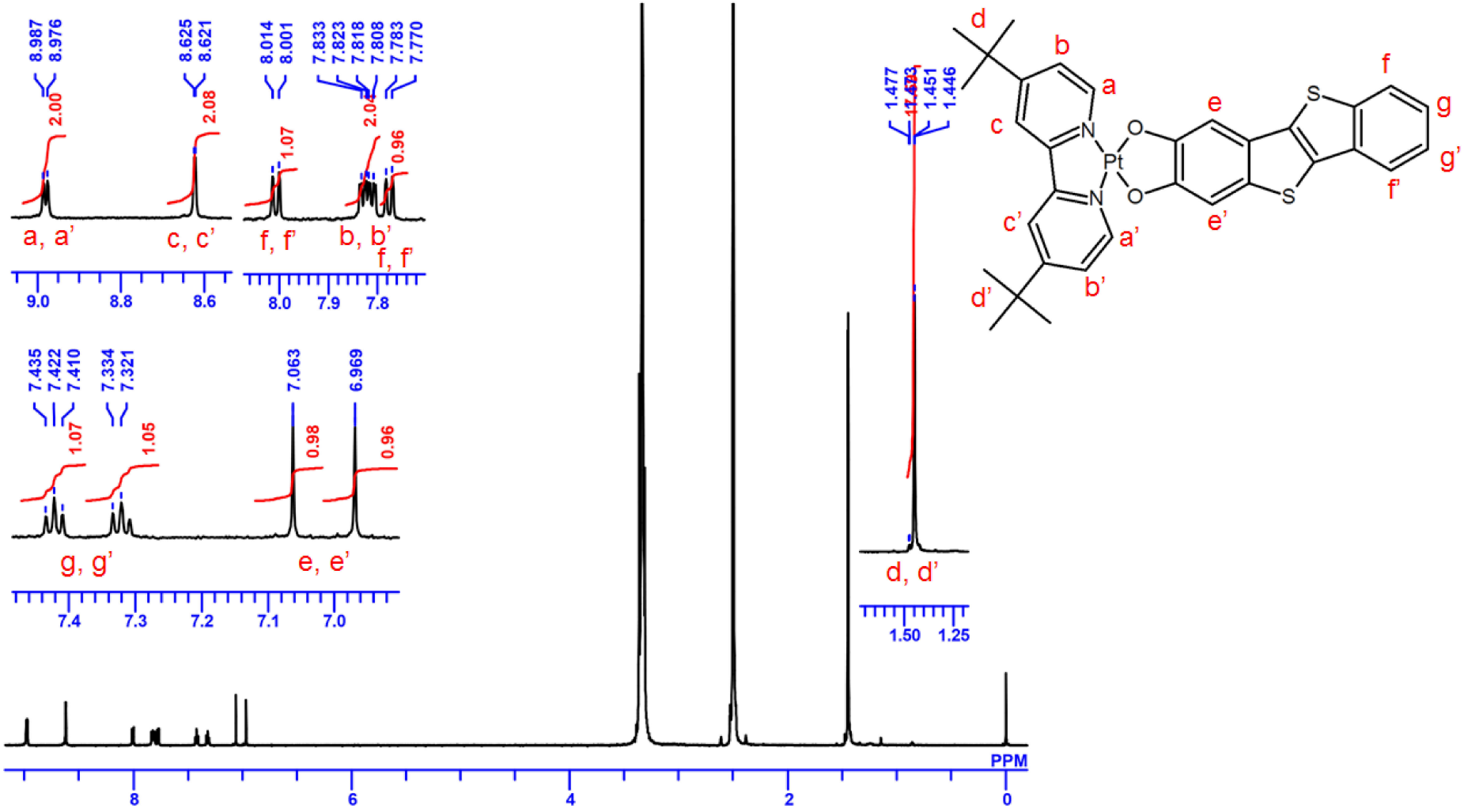

Figure S1 ^{1}H-NMR spectrum of **3Pt** in DMSO-d_6 (600 MHz).

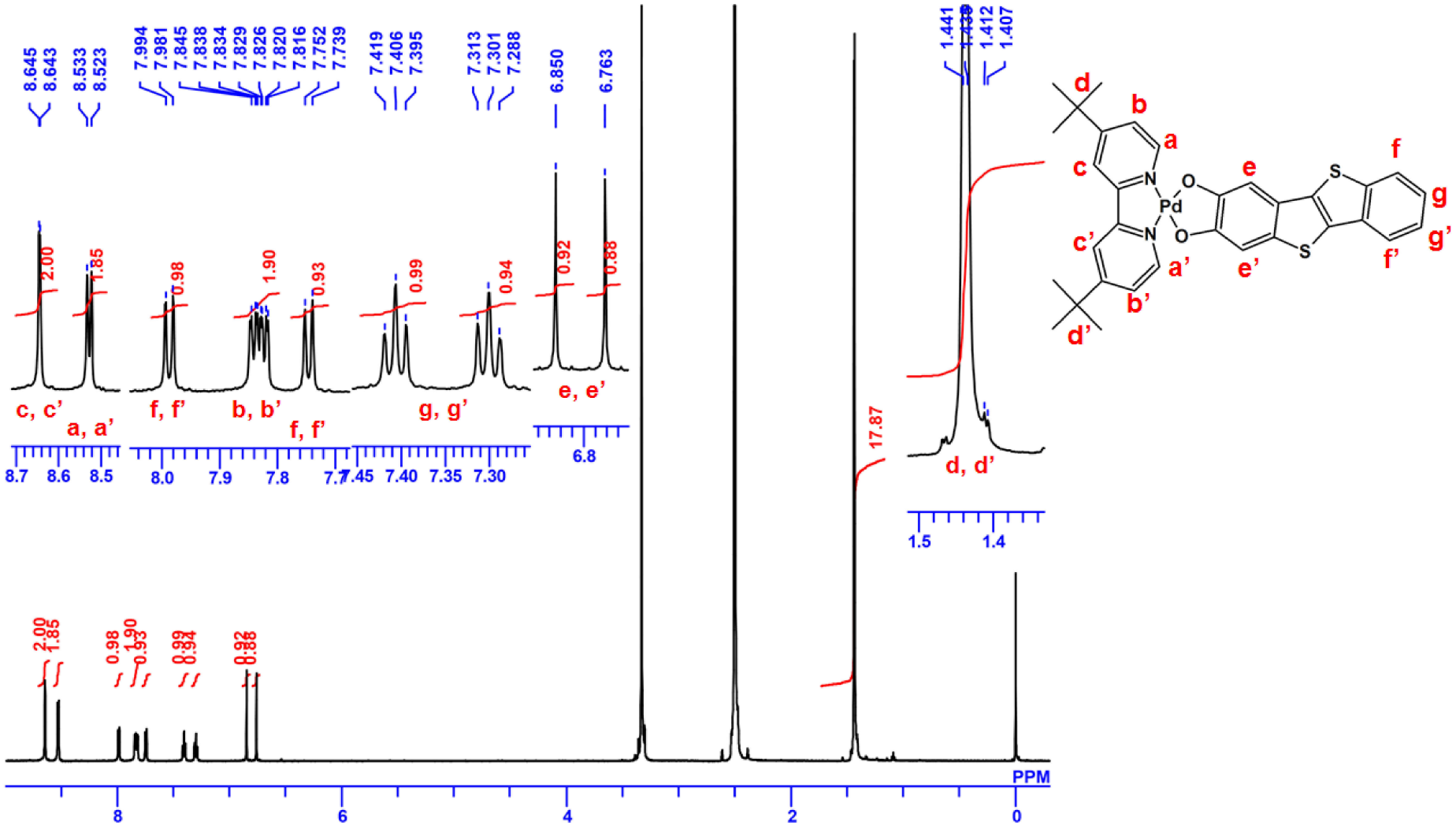

Figure S2 ^{1}H-NMR spectrum of **3Pd** in DMSO-d_6 (600 MHz).

2. DFT calculation

Table S1 Coordinates of optimized geometries of catecholato complexes calculated using a DFT method (B3LYP or UB3LYP/ Lanl2DZ (Fe and Pt atoms) and 6-31G(d) (all other atoms) levels of theory) with or without IEFPCM (CH_2Cl_2).

3Pt′ in gas phase

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	16	4.281716	-2.191467	-0.000102
2	16	5.183867	1.94188	0.000032
3	6	2.736783	-1.316517	0.000207
4	6	1.467769	-1.897539	0.000248
5	6	0.356839	-1.052841	0.000309
6	6	0.5169	0.366219	0.000387
7	6	1.784137	0.936461	0.000247
8	6	2.912407	0.095475	0.000201
9	6	4.310009	0.416918	0.00015
10	6	5.15896	-0.668542	0.000122
11	6	6.553885	-0.336708	-0.000094
12	6	7.694046	-1.159904	-0.000298
13	6	8.958616	-0.583202	-0.00066
14	6	9.113297	0.813278	-0.000796
15	6	7.999222	1.650788	-0.000638
16	6	6.727877	1.075379	-0.000337
17	1	1.322487	-2.97336	0.00001
18	1	1.885272	2.017827	0.000176
19	1	7.580627	-2.240701	-0.000265
20	1	9.838762	-1.220428	-0.000854
21	1	10.109427	1.246904	-0.001004
22	1	8.118557	2.730691	-0.000661
23	8	-0.902375	-1.530333	0.000249
24	78	-2.236653	-0.04427	0.000636
25	7	-3.922896	-1.153284	-0.000126
26	7	-3.629209	1.414072	-0.000096
27	8	-0.610447	1.109465	0.000518
28	6	-3.933411	-2.502272	-0.000223
29	6	-5.099513	-0.454402	-0.000563
30	6	-4.933202	0.999309	-0.000484
31	6	-3.333545	2.730317	-0.000074
32	1	-2.953154	-2.967237	0.000175
33	6	-5.119483	-3.219527	-0.000768
34	6	-6.322284	-1.134919	-0.001107
35	6	-5.97014	1.939001	-0.000812
36	6	-4.326612	3.69727	-0.000421
37	1	-2.273317	2.960795	0.000263
38	1	-5.089452	-4.303585	-0.000812
39	6	-6.335639	-2.524158	-0.001217
40	1	-7.25279	-0.578323	-0.001468
41	1	-7.002468	1.607406	-0.001097
42	6	-5.668586	3.29525	-0.000788
43	1	-4.0519	4.746375	-0.000367

44	1	-7.27909	-3.060812	-0.001656
45	1	-6.466067	4.03153	-0.001055

3Pt′ with IEFPCM (CH_2Cl_2)

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	16	-4.298633	-2.191982	-0.000190
2	16	-5.199925	1.942041	-0.000163
3	6	-2.751535	-1.315217	-0.000009
4	6	-1.478946	-1.895376	0.000139
5	6	-0.363796	-1.054545	0.000213
6	6	-0.524039	0.368012	0.000158
7	6	-1.794280	0.933394	0.000059
8	6	-2.927725	0.093084	-0.000044
9	6	-4.325901	0.415190	-0.000163
10	6	-5.177793	-0.668737	-0.000235
11	6	-6.573683	-0.336308	-0.000355
12	6	-7.714916	-1.159262	-0.000491
13	6	-8.979412	-0.580116	-0.000651
14	6	-9.133001	0.817017	-0.000683
15	6	-8.017713	1.654507	-0.000565
16	6	-6.747394	1.075940	-0.000402
17	1	-1.337124	-2.972223	0.000159
18	1	-1.898564	2.015163	0.000030
19	1	-7.604292	-2.240302	-0.000487
20	1	-9.860044	-1.216368	-0.000759
21	1	-10.128452	1.251614	-0.000797
22	1	-8.136227	2.734262	-0.000576
23	8	0.890553	-1.541108	0.000313
24	78	2.245439	-0.043479	0.000373
25	7	3.937973	-1.158512	0.000105
26	7	3.646144	1.419317	0.000082
27	8	0.597860	1.118473	0.000184
28	6	3.950442	-2.504858	0.000087
29	6	5.110168	-0.459746	-0.000074
30	6	4.944951	1.000343	-0.000069
31	6	3.356872	2.734361	0.000090
32	1	2.975652	-2.978800	0.000235
33	6	5.139834	-3.221705	-0.000114
34	6	6.333613	-1.132289	-0.000271
35	6	5.986990	1.929614	-0.000232
36	6	4.355880	3.698956	-0.000051
37	1	2.300734	2.978225	0.000233
38	1	5.111174	-4.305322	-0.000132
39	6	6.350010	-2.524406	-0.000292
40	1	7.262632	-0.575116	-0.000423
41	1	7.017141	1.594243	-0.000366
42	6	5.691382	3.290140	-0.000215
43	1	4.085550	4.748722	-0.000030
44	1	7.295075	-3.057074	-0.000457
45	1	6.493248	4.020864	-0.000332

3Pt′$^{+}$ with IEFPCM (CH_2Cl_2)

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	16	-4.294771	-2.194364	-0.000264
2	16	-5.190568	1.956496	-0.000283
3	6	-2.751057	-1.323785	-0.000285
4	6	-1.505928	-1.909763	-0.000274
5	6	-0.375783	-1.058160	-0.000272
6	6	-0.534194	0.396728	-0.000321
7	6	-1.812297	0.963985	-0.000349
8	6	-2.924963	0.119903	-0.000314
9	6	-4.313587	0.436347	-0.000278
10	6	-5.159110	-0.659856	-0.000213
11	6	-6.549910	-0.335884	-0.000083
12	6	-7.683468	-1.173117	0.000043
13	6	-8.947496	-0.601823	0.000196
14	6	-9.105090	0.797571	0.000225
15	6	-8.000694	1.647178	0.000097
16	6	-6.726194	1.077551	-0.000061
17	1	-1.360624	-2.984654	-0.000244
18	1	-1.917932	2.043812	-0.000365
19	1	-7.563295	-2.252572	0.000034
20	1	-9.826227	-1.239301	0.000301
21	1	-10.103533	1.224364	0.000343
22	1	-8.130116	2.724893	0.000109
23	8	0.838914	-1.530067	-0.000211
24	78	2.251258	-0.043476	-0.000090
25	7	3.934039	-1.161759	0.000160
26	7	3.642886	1.415205	0.000219
27	8	0.565998	1.113453	-0.000307
28	6	3.938017	-2.506246	0.000106
29	6	5.105963	-0.464258	0.000361
30	6	4.940964	0.996988	0.000419
31	6	3.344296	2.726272	0.000239
32	1	2.964997	-2.982885	-0.000043
33	6	5.127151	-3.226721	0.000240
34	6	6.325422	-1.138302	0.000494
35	6	5.978424	1.927259	0.000668
36	6	4.342216	3.694323	0.000477
37	1	2.288780	2.970926	0.000055
38	1	5.095103	-4.309923	0.000193
39	6	6.336345	-2.532382	0.000431
40	1	7.256256	-0.584686	0.000646
41	1	7.009692	1.596205	0.000835
42	6	5.676214	3.288320	0.000696
43	1	4.068694	4.742923	0.000485
44	1	7.280100	-3.066927	0.000533
45	1	6.476151	4.020890	0.000884

3Pd′ in gas phase

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	16	0	-4.00738	-2.19468

2	16	0	-4.90637	1.939069
3	6	0	-2.46173	-1.32019
4	6	0	-1.19215	-1.90115
5	6	0	-0.07825	-1.05883
6	6	0	-0.23774	0.361537
7	6	0	-1.50603	0.930373
8	6	0	-2.63645	0.09076
9	6	0	-4.03349	0.413115
10	6	0	-4.88414	-0.67143
11	6	0	-6.27846	-0.33817
12	6	0	-7.4197	-1.16001
13	6	0	-8.68381	-0.58209
14	6	0	-8.83736	0.814432
15	6	0	-7.72215	1.650705
16	6	0	-6.45142	1.074214
17	1	0	-1.04748	-2.97731
18	1	0	-1.60656	2.012068
19	1	0	-7.30738	-2.241
20	1	0	-9.56455	-1.21866
21	1	0	-9.8331	1.249098
22	1	0	-7.84034	2.730834
23	8	0	1.17837	-1.54448
24	7	0	4.195553	-1.17648
25	7	0	3.896131	1.422813
26	8	0	0.887216	1.110698
27	6	0	4.211636	-2.51879
28	6	0	5.358103	-0.46642
29	6	0	5.189607	0.996234
30	6	0	3.604821	2.733247
31	1	0	3.233079	-2.98941
32	6	0	5.404199	-3.2325
33	6	0	6.588047	-1.13409
34	6	0	6.234764	1.926939
35	6	0	4.603275	3.700011
36	1	0	2.544394	2.967188
37	1	0	5.384303	-4.31682
38	6	0	6.610791	-2.52527
39	1	0	7.515804	-0.57314
40	1	0	7.266063	1.59248
41	6	0	5.939377	3.286677
42	1	0	4.336515	4.7512
43	1	0	7.559542	-3.05304
44	1	0	6.742688	4.016985
45	46	0	2.481306	-0.05501

3Pd′ with IEFPCM (CH_2Cl_2)

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	16	-4.29477	-2.19436	-0.00026
2	16	-5.19057	1.956496	-0.00028
3	6	-2.75106	-1.32379	-0.00029
4	6	-1.50593	-1.90976	-0.00027
5	6	-0.37578	-1.05816	-0.00027

6	6	-0.53419	0.396728	-0.00032
7	6	-1.8123	0.963985	-0.00035
8	6	-2.92496	0.119903	-0.00031
9	6	-4.31359	0.436347	-0.00028
10	6	-5.15911	-0.65986	-0.00021
11	6	-6.54991	-0.33588	-8.3E-05
12	6	-7.68347	-1.17312	0.000043
13	6	-8.9475	-0.60182	0.000196
14	6	-9.10509	0.797571	0.000225
15	6	-8.00069	1.647178	0.000097
16	6	-6.72619	1.077551	-6.1E-05
17	1	-1.36062	-2.98465	-0.00024
18	1	-1.91793	2.043812	-0.00037
19	1	-7.5633	-2.25257	0.000034
20	1	-9.82623	-1.2393	0.000301
21	1	-10.1035	1.224364	0.000343
22	1	-8.13012	2.724893	0.000109
23	8	0.838914	-1.53007	-0.00021
24	78	2.251258	-0.04348	-0.00009
25	7	3.934039	-1.16176	0.00016
26	7	3.642886	1.415205	0.000219
27	8	0.565998	1.113453	-0.00031
28	6	3.938017	-2.50625	0.000106
29	6	5.105963	-0.46426	0.000361
30	6	4.940964	0.996988	0.000419
31	6	3.344296	2.726272	0.000239
32	1	2.964997	-2.98289	-4.3E-05
33	6	5.127151	-3.22672	0.00024
34	6	6.325422	-1.1383	0.000494
35	6	5.978424	1.927259	0.000668
36	6	4.342216	3.694323	0.000477
37	1	2.28878	2.970926	0.000055
38	1	5.095103	-4.30992	0.000193
39	6	6.336345	-2.53238	0.000431
40	1	7.256256	-0.58469	0.000646
41	1	7.009692	1.596205	0.000835
42	6	5.676214	3.28832	0.000696
43	1	4.068694	4.742923	0.000485
44	1	7.2801	-3.06693	0.000533
45	1	6.476151	4.02089	0.000884

3Pd′$^{+}$ with IEFPCM (CH_2Cl_2)

Center Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	16	-4.022592	-2.195346	-0.00031
2	16	-4.920312	1.939207	-0.000114
3	6	-2.474553	-1.319296	-0.000195
4	6	-1.201408	-1.89943	-0.000157
5	6	-0.083409	-1.060525	-0.000031
6	6	-0.243299	0.363481	0.000047
7	6	-1.514883	0.927557	0.000001
8	6	-2.650013	0.08829	-0.000117
9	6	-4.047681	0.411269	-0.000171

10	6	-4.901238	-0.671655	-0.000284
11	6	-6.296608	-0.337617	-0.000332
12	6	-7.439086	-1.15897	-0.000432
13	6	-8.702962	-0.578287	-0.000445
14	6	-8.855043	0.818966	-0.000359
15	6	-7.738517	1.654982	-0.000257
16	6	-6.468955	1.074959	-0.000243
17	1	-1.060148	-2.976513	-0.000208
18	1	-1.618855	2.009545	0.000062
19	1	-7.32986	-2.24017	-0.000496
20	1	-9.58431	-1.21359	-0.000521
21	1	-9.849953	1.254819	-0.00037
22	1	-7.855642	2.734918	-0.00019
23	8	1.168461	-1.552208	0.000033
24	7	4.207257	-1.180637	0.000254
25	7	3.912168	1.427723	0.000159
26	8	0.876065	1.117508	0.000164
27	6	4.225265	-2.521483	0.000312
28	6	5.367621	-0.471275	0.000131
29	6	5.201732	0.995745	0.000081
30	6	3.6293	2.73853	0.000114
31	1	3.252473	-3.001193	0.000419
32	6	5.419938	-3.234933	0.000242
33	6	6.597124	-1.133407	0.000055
34	6	6.252028	1.916223	-0.000042
35	6	4.634186	3.701043	-0.000006
36	1	2.573686	2.987945	0.000178
37	1	5.40018	-4.318771	0.000291
38	6	6.622082	-2.526899	0.000109
39	1	7.523765	-0.572467	-0.000049
40	1	7.280794	1.576827	-0.000108
41	6	5.964292	3.279988	-0.000084
42	1	4.372539	4.753032	-0.000038
43	1	7.571827	-3.051584	0.000049
44	1	6.772451	4.004042	-0.000182
45	46	2.492823	-0.053134	0.000345

Table S2 Selected vertical excitation energies predicted by TD-DFT with IEFPCM (CH_2Cl_2).[a]

Complex	#	energy (eV)	wavelength (nm)	oscillator strength	transition	coefficients
2Pt′	1	1.6669	743.81	0.1407	78 → 79	0.70634
	17	4.3001	288.33	0.2265	72 → 79	0.58795
	22	4.7496	261.04	0.1741	75 → 81	0.50810
	25	4.8390	256.22	0.3494	74 → 81	0.58686
3Pt′	1	1.6812	737.49	0.1962	119 → 120	0.70525
	10	3.3511	369.98	0.4887	118 → 122	0.46373
	11	3.4242	362.08	0.2258	119 → 123	0.50235
	14	3.7934	326.84	0.2225	118 → 123	0.67942
	25	4.2960	288.60	0.1585	110 → 120	0.41930
2Pd′	1	1.5730	788.22	0.0840	78 → 79	0.70617
	20	4.3277	286.49	0.3213	72 → 79	0.64983
	23	4.8039	258.09	0.1986	78 → 85	0.64283
3Pd′	1	1.6172	766.68	0.1164	119 → 120	0.70476
	12	3.3697	367.94	0.6130	119 → 124	0.55599
	16	3.7961	326.6	0.2261	118 → 124	0.67553
	27	4.3205	286.97	0.2590	113 → 120	0.40737
2Pt′$^+$	4	2.5135	493.27	0.0323	$78\alpha \rightarrow 79\alpha$	0.98325
	5	2.5893	478.84	0.2255	$75\beta \rightarrow 78\beta$	0.98693
	27	4.076	304.18	0.0274	$75\beta \rightarrow 79\beta$	0.62845
	28	4.0989	302.48	0.0323	$75\alpha \rightarrow 79\alpha$	0.65412
3Pt′$^+$	3	1.9953	621.38	0.4155	$116\beta \rightarrow 119\beta$	0.90142
	9	2.7319	453.84	0.1071	$113\beta \rightarrow 119\beta$	0.87151
	12	2.9294	423.24	0.0853	$118\beta \rightarrow 124\beta$	0.45985
	22	3.3671	368.23	0.2389	$119\alpha \rightarrow 123\alpha$	0.49931
2Pd′$^+$	1	1.5419	804.08	0.0043	$77\beta \rightarrow 78\beta$	0.98342
	6	2.5797	480.62	0.0235	$78\alpha \rightarrow 79\alpha$	0.98679
	11	3.0753	403.16	0.1673	$74\beta \rightarrow 78\beta$	0.97454
3Pd′$^+$	5	2.1119	587.07	0.3300	$116\beta \rightarrow 119\beta$	0.89678
	16	2.9368	422.17	0.1746	$118\beta \rightarrow 124\beta$	0.47550
	24	3.3749	367.37	0.3015	$119\alpha \rightarrow 124\alpha$	0.56988

[a] Main contributions are shown. Total number of states in the calculation: 50 for **2Pd′** and **2Pd′**$^+$ and 30 for other complexes.

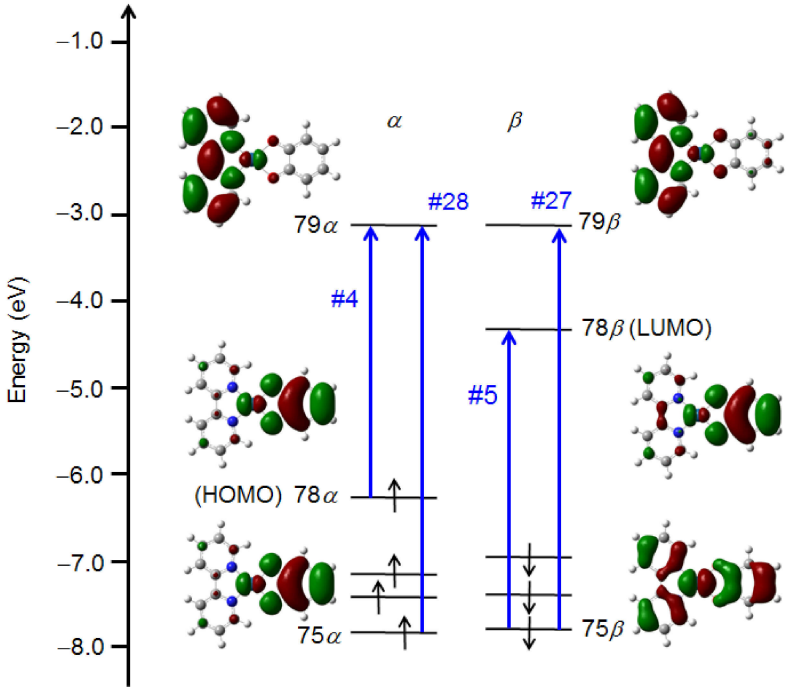

Figure S3 DFT-calculated selected molecular orbitals for **2Pt'**$^{+}$ and TD-DFT-predicted selected vertical excitation with IEFPCM (CH_2Cl_2).

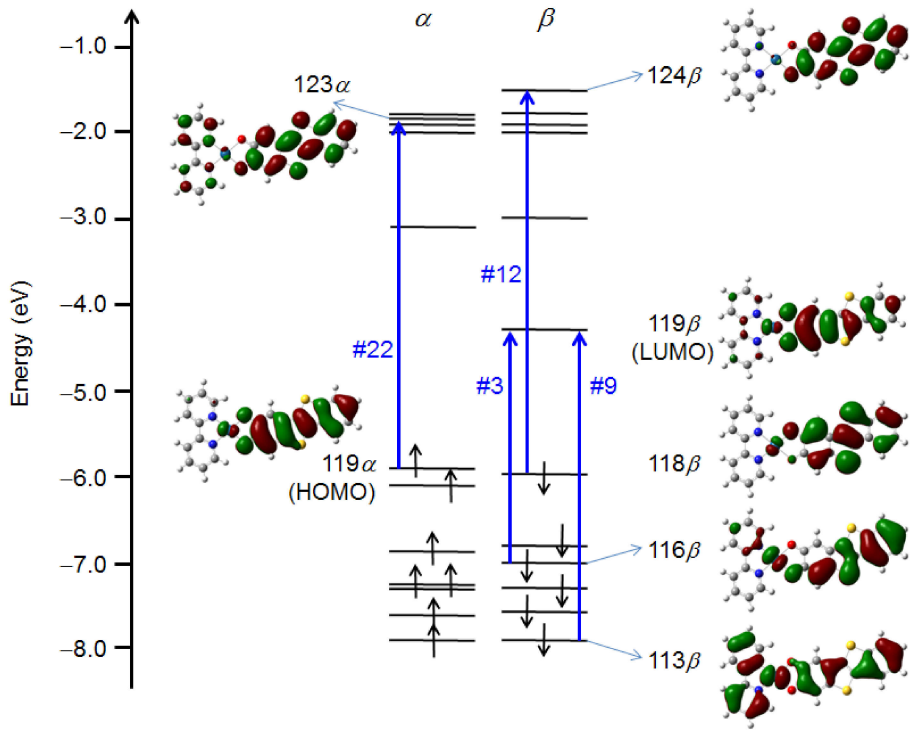

Figure S4 DFT-calculated selected molecular orbitals for **3Pt'**$^{+}$ and TD-DFT-predicted selected vertical excitation with IEFPCM (CH_2Cl_2).

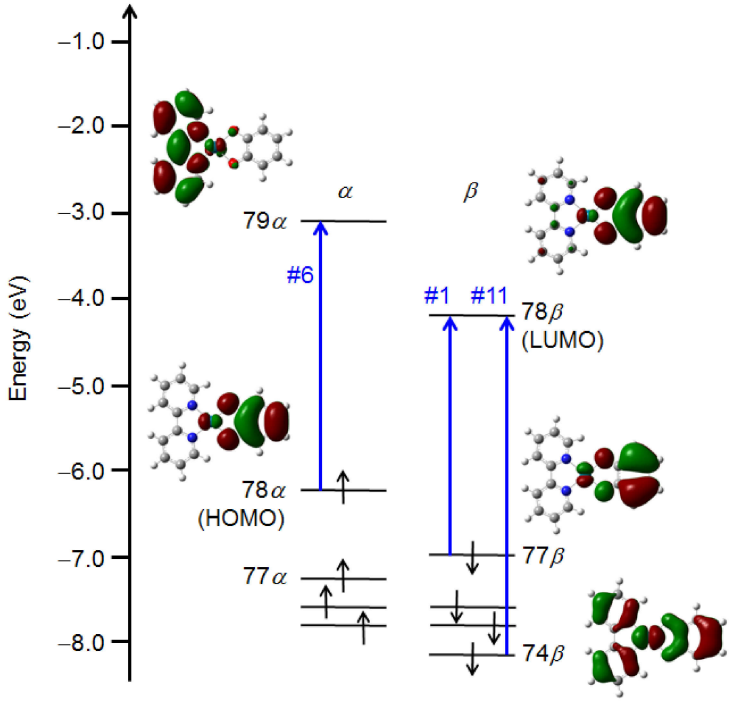

Figure S5 DFT-calculated selected molecular orbitals for **2Pd′**$^{+}$and TD-DFT-predicted selected vertical excitation with IEFPCM (CH_2Cl_2).

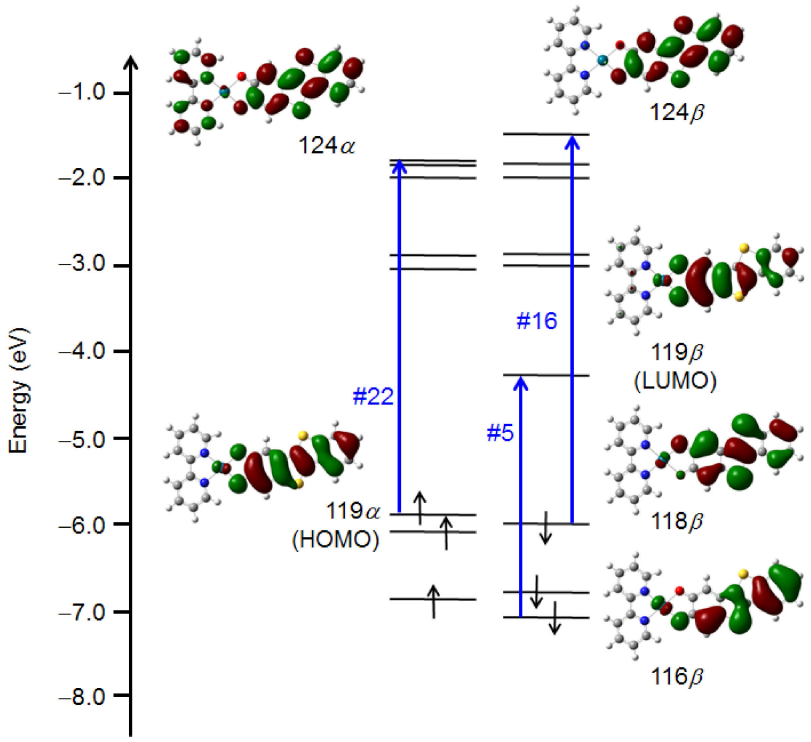

Figure S6 DFT-calculated selected molecular orbitals for **3Pd′**$^{+}$and TD-DFT-predicted selected vertical excitation with IEFPCM (CH_2Cl_2).

4. X-ray crystallographic data

Table S3 Summary of crystallographic data and refinement parameters.

	3Pd
empirical formula	$C_{33}H_{31.5}N_{2.5}O_2PdS_2$
formula weight	665.63
crystal dimensions (mm)	0.05 × 0.03 × 0.02
crystal system	monoclinic
crystal color, habit	purple, block
space group	$P2_1/n$ (#14)
temperature (K)	100
a (Å)	12.413(3)
b (Å)	17.240(5)
c (Å)	14.457(4)
β (deg)	109.918(8)
V (Å^3)	2908.7(14)
μ (mm^{-1})	0.4
Z	4
ρ_{calcd} (g cm^{-3})	1.52
F(000)	1364
wavelength (Å)	0.3009
θ_{max} (°)	11.3
meas. refl.	43288
indep. refl.	6670
obsvd. [$I > 2\sigma(I)$] refl.	5270
R_{int}	0.070
R_1, wR_2, GOF	0.034, 0.076, 1.00
$\Delta\rho_{max}/\Delta\rho_{min}$ (e/Å^3)	0.69/−0.78
CCDC No.	1885430

$R_1 = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o|$ ($F_o > 4\sigma(F_o)$). $wR_2 = [\ \Sigma\ (w(F_o^2 - F_c^2)^2)/\ \Sigma\ w(F_o^2)^2\ ]^{1/2}$.

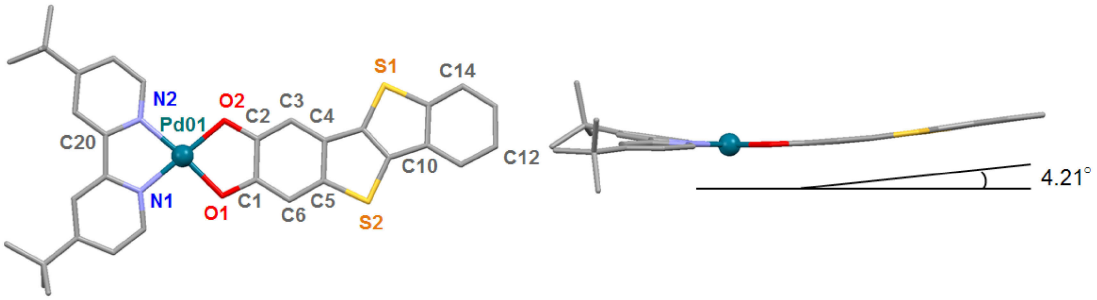

Figure S7 Crystal structures of **3Pd**. Hydrogen atoms, cocrystalized CH_3CN molecule, and the minor one of the two disordered O_2BTBT fragments are omitted for clarity.

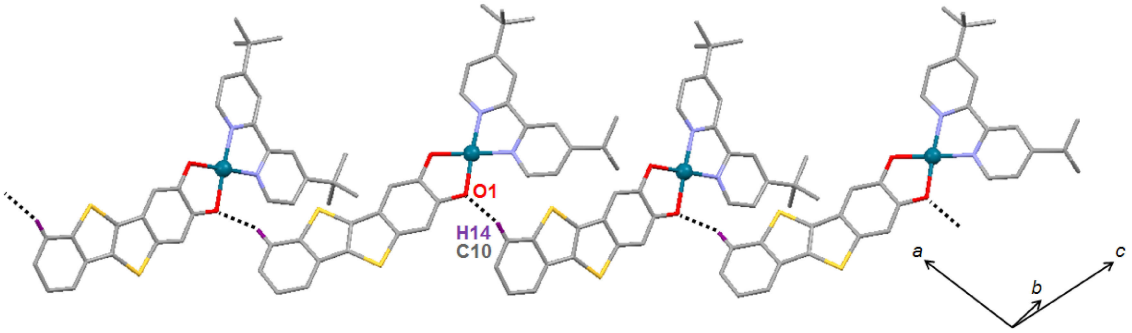

Figure S8 Expanded structure of **3Pd**. Hydrogen atoms, cocrystalized CH_3CN molecules, and the minor one of the two disordered O_2BTBT fragments are omitted for clarity except H14 (purple). Short contacts are indicated as dotted lines.

Table S4 Selected bond lengths and angles in crystal and DFT-optimized structures.

		crystal structure			optimized structure	
		1	Pd(bpy)(^{t}Bu$_2$Cat)	**3Pd**	**3Pd′** with IEFPCM	**3Pd′** in gas phase
bond lengths (Å)	Pd1-N1	−	2.001(5)	1.990(2)	2.052	2.049
	Pd1-N2	−	1.999(5)	2.002(2)	2.051	2.046
	Pd1-O1	−	1.973(4)	2.020(3)	2.000	1.979
	Pd1-O2	−	1.959(4)	1.963(3)	1.996	1.975
	C1-O1	1.380(3)	1.351(6)	1.347(5)	1.345	1.347
	C2-O2	1.384(3)	1.371(6)	1.351(5)	1.350	1.352
	C1-C2	1.386(3)	1.423(7)	1.440(5)	1.433	1.429
	C2-C3	1.371(4)	1.404(7)	1.382(5)	1.391	1.390
	C3-C4	1.402(3)	1.392(7)	1.397(6)	1.412	1.408
	C4-C5	1.377(3)	1.403(7)	1.434(5)	1.418	1.422
	C5-C6	1.401(4)	1.390(7)	1.400(4)	1.399	1.396
	C1-C6	1.416(3)	1.411(7)	1.392(5)	1.398	1.396
	C4-C7	1.436(3)	−	1.422(6)	1.435	1.434
	C7-C8	1.369(3)	−	1.386(5)	1.379	1.378
	C8-C10	1.434(3)	−	1.431(5)	1.435	1.434
	C7-S1	1.737(2)	−	1.747(4)	1.760	1.758
	C9-S1	1.751(3)	−	1.752(4)	1.774	1.771
	C5-S2	1.746(3)	−	1.769(3)	1.779	1.776
	C8-S2	1.739(2)	−	1.745(3)	1.759	1.758
angles (°)	N1-Pd1-N2	−	80.3(2)	80.23(9)	79.54	79.44
	O1-Pd1-O2	−	84.5(2)	84.78(13)	84.45	85.00
	C5-S2-C8	90.57(10)	−	90.38(16)	90.47	90.42
	C7-S1-C9	90.70(11)	−	91.28(19)	90.57	90.53
dihedral angles between planes (°)	N1-Pd1-N2 vs. O1-Pd1-N2	−	1.17	1.95	0.01	0.01
	C1-C2-C3-C6 vs. BTT moiety	2.62	−	4.21	0.00	0.00
	two pyridine rings	−	2.45	7.55	0.00	0.00
temperature (K)		293	100	100	−	−
CCDC number		1529674	187891	1885430	−	−
		Ref. 19	Ref. 4a	this work	this work	this work

5. Solvatochromic behavior

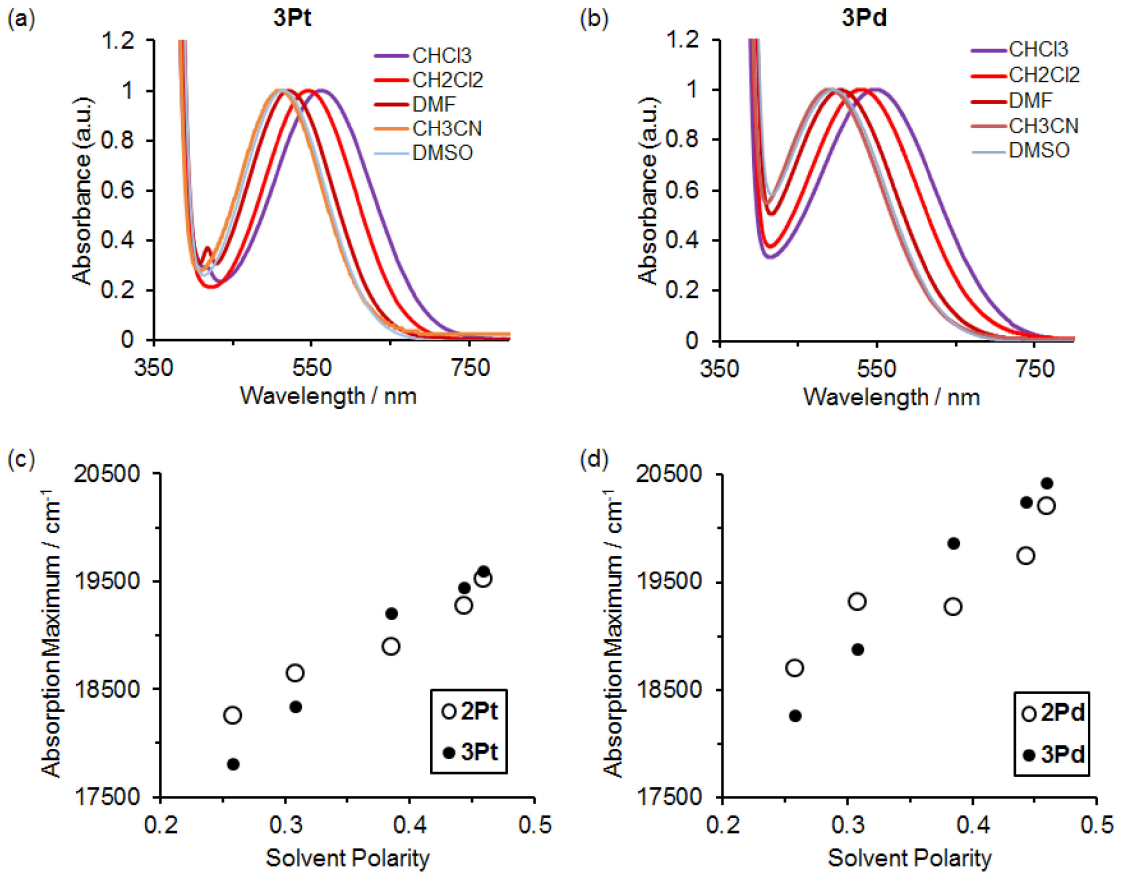

Figure S9 Normalized absorption spectra of (a) **3Pt** and (b) **3Pd** in several solvents. (b) Absorption maximum against the solvent polarity parameter for (c) Pt and (d) Pd complex series.

6. Electrochemical data

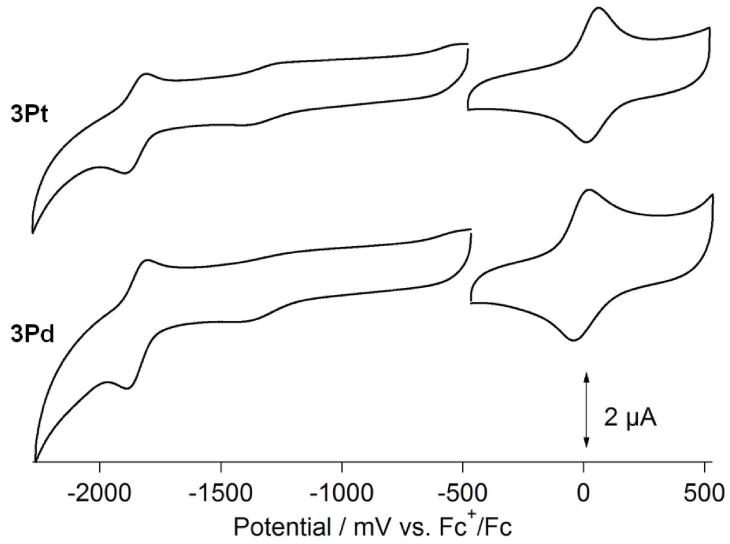

Figure S10 Cyclic voltammograms of **3Pt** and **3Pd** (0.050 mM) in CH_2Cl_2 containing $^{n}Bu_4NPF_6$ (0.1 M). Scan rate: 100 mV s^{-1}.