Electronic Supplementary Information for New Journal of Chemistry

SUPPLEMENTARY INFORMATION

For

Synthesis and structures of platinum diphenylacetylene and dithiolate complexes bearing diphosphinidenecyclobutene ligands (DPCB-Y)

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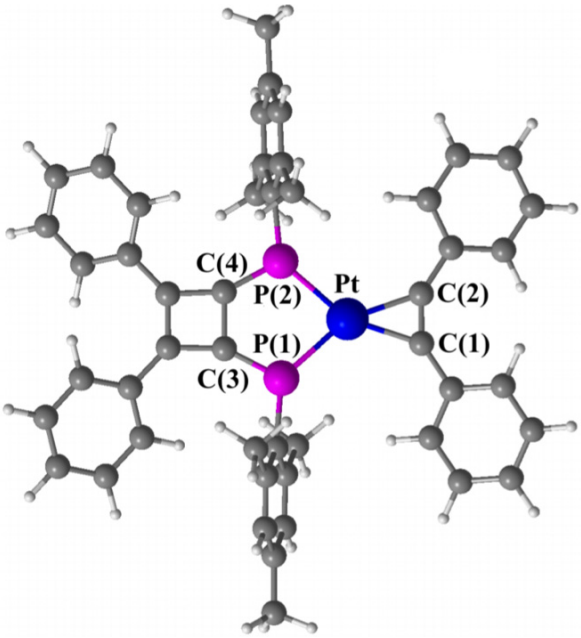

Fig. S1 Optimized structure of a model compound of **2b** (**2b'**). The 2,4,6-tri-*tert*-butylphenyl groups (Mes*) in **2b** are replaced with mesityl groups (Mes) in **2b'**. Selected bond distances (Å) and angles (deg) are as follows: Pt–P(1) = Pt–P(2) = 2.340, Pt–C(1) = Pt–C(2) = 2.054, P(1)–C(3) = 1.689, P(2)–C(4) = 1.687, C(1)–C(2) = 1.306; P(1)–Pt–P(2) = 82.30, C(1)–Pt–C(2) = 37.06, Pt–P(1)–C(3) = 110.95, Pt–P(2)-C(4) = 110.83, Pt–C(1)–C(2) = 71.46, Pt–C(2)–C(1) = 71.47.

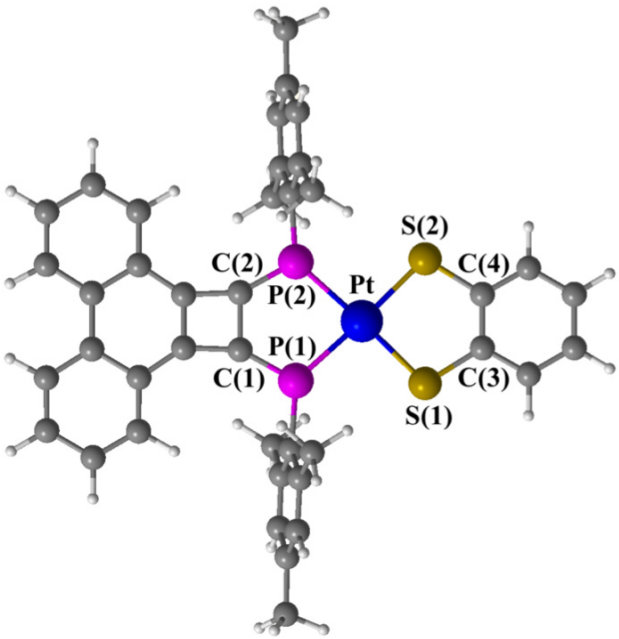

Fig. S2 Optimized structure of a model compound of **6a** (**6a'**). The 2,4,6-tri-*tert*-butylphenyl groups (Mes*) in **6a** are replaced with mesityl groups (Mes) in **6a'**. Selected bond distances (Å) and angles (deg) are as follows: Pt–P(1) = 2.341, Pt–P(2) = 2.342, Pt–S(1) = 2.338, Pt–S(2) = 2.339, P(1)–C(1) = 1.680, P(2)–C(2) = 1.679, C(1)–C(2) = 1.506; P(1)–Pt–P(2) = 83.89, S(1)–Pt–S(2) = 89.02, Pt–P(1)–C(1) = 109.14, Pt–P(2)–C(2) = 109.14, Pt–S(1)–C(3) = 103.78, Pt–S(2)–C(4) = 103.72.

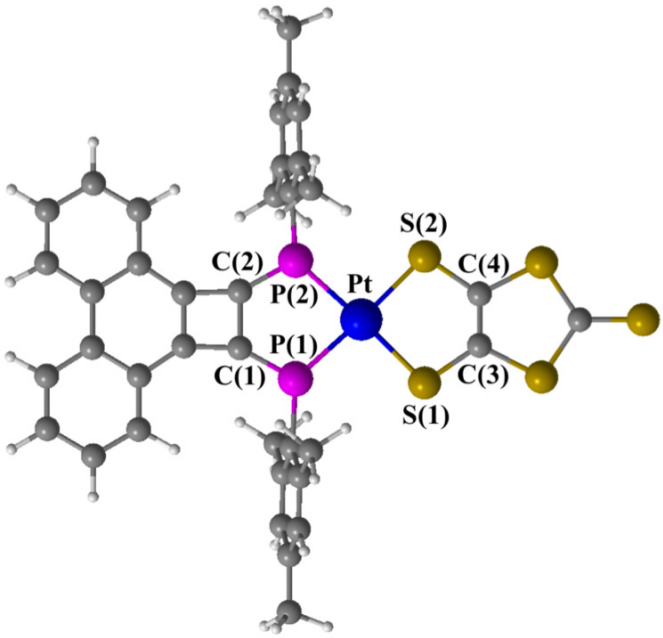

Fig. S3 Optimized structure of a model compound of **6b** (**6b'**). The 2,4,6-tri-*tert*-butylphenyl groups (Mes*) in **6b** are replaced with mesityl groups (Mes) in **6b'**. Selected bond distances (Å) and angles (deg) are as follows: Pt–P(1) = 2.334, Pt–P(2) = 2.334, Pt–S(1) = 2.357, Pt–S(2) = 2.357, P(1)–C(1) = 1.679, P(2)–C(2) = 1.680, C(1)–C(2) = 1.497; P(1)–Pt–P(2) = 83.98, S(1)–Pt–S(2) = 90.03, Pt–P(1)–C(1) = 109.09, Pt–P(2)–C(2) = 109.08, Pt–S(1)–C(3) = 100.64, Pt–S2–C4 = 100.64.

Table S1 Cartesian coordinates for optimized structure of [Pt(tolan-H)(DPCB-H')] (**2b'**)

Pt	0.190849	0.002207	5.102563
P	1.912381	-1.53574	4.720698
C	2.088617	-3.35819	4.752047
C	2.178095	-6.18724	4.826167
C	2.151796	-5.43838	6.010267
C	2.148241	-5.49962	3.60454
C	2.10389	-4.03606	5.999669
C	2.101393	-4.10025	3.541714
C	2.252142	-7.69761	4.862462
H	3.287535	-8.04776	4.750447
H	1.874323	-8.09406	5.810447
H	1.669881	-8.14653	4.050324
H	2.164097	-5.95456	6.966696
H	2.15558	-6.06487	2.676183
C	2.075024	-3.28306	7.313953
H	2.958725	-2.6443	7.433768
H	1.199692	-2.62584	7.386279
H	2.046434	-3.97816	8.158356
C	2.071939	-3.41902	2.190054
H	2.993589	-2.85398	2.006564
H	1.965404	-4.15512	1.387714
H	1.239088	-2.70982	2.111037
P	1.914761	1.543562	4.746096
C	2.04403	3.365006	4.602482
C	2.082168	6.19003	4.41961
C	2.533642	5.537223	5.5752

C	1.609486	5.407905	3.356752
C	2.519194	4.140252	5.691805
C	1.575136	4.007079	3.425607
C	2.076046	7.700224	4.334903
H	1.145716	8.116002	4.745524
H	2.904191	8.137012	4.903331
H	2.155887	8.043655	3.29815
H	2.904156	6.127848	6.408999
H	1.256952	5.896273	2.45197
C	3.019881	3.495832	6.966864
H	2.278434	2.806875	7.389768
H	3.933951	2.915916	6.791755
H	3.244195	4.254541	7.722567
C	1.054333	3.215913	2.243431
H	0.23126	2.550534	2.531855
H	0.689738	3.88534	1.45866
H	1.834449	2.579459	1.807845
C	3.371456	-0.74203	4.425494
C	4.816812	-0.6942	4.085681
C	7.598474	-3.82009	3.181729
C	7.763908	-2.54901	2.614524
C	6.519983	-4.05788	4.042037
C	6.866645	-1.52288	2.910919
C	5.61556	-3.03597	4.33787
C	5.777128	-1.74573	3.785396
H	8.298993	-4.61607	2.950181
H	8.589077	-2.36069	1.934831
H	6.379844	-5.04026	4.481396
H	6.992459	-0.54879	2.452167
H	4.782132	-3.22995	5.002534
C	3.367669	0.755175	4.399788
C	4.81215	0.711323	4.092256
C	7.720733	3.830113	3.71588
C	6.376603	4.073627	3.409291
C	8.112191	2.555979	4.149905
C	5.430218	3.054078	3.529903
C	7.172285	1.53208	4.267267
C	5.812188	1.760818	3.951656
H	8.454657	4.624402	3.624431
H	6.062565	5.058562	3.079212
H	9.149755	2.363719	4.40438
H	4.391825	3.252469	3.293572
H	7.481153	0.555862	4.622707
C	-1.709	0.655177	5.531449
C	-1.72084	-0.64943	5.477034
C	-3.93309	4.222471	6.32657
C	-4.43277	2.975514	6.725048
C	-2.69532	4.293477	5.674605
C	-3.70907	1.810573	6.465293
C	-1.96476	3.131232	5.420684
C	-2.46077	1.866259	5.80077
H	-4.49902	5.126991	6.526793
H	-5.38633	2.911833	7.240782

H	-2.2963	5.255692	5.368201
H	-4.09314	0.849884	6.790132
H	-1.00141	3.187322	4.926979
C	-4.07591	-4.21791	5.626409
C	-2.67844	-4.29157	5.687373
C	-4.69677	-2.9673	5.507816
C	-1.90876	-3.12816	5.632862
C	-3.93056	-1.80153	5.461104
C	-2.51822	-1.86008	5.528972
H	-4.67397	-5.12308	5.665473
H	-2.18735	-5.25627	5.771957
H	-5.77917	-2.90147	5.449392
H	-0.82694	-3.18483	5.666333
H	-4.41584	-0.83785	5.353054

Table S2 Cartesian coordinates for optimized structure of [Pt(bdt)(DPCB-phen')] (**6a'**)

Pt	0.043068	-0.000199	4.878141
P	1.779175	-1.564756	4.734523
C	1.897476	-3.378125	4.679366
C	2.010557	-6.199482	4.602104
C	1.738901	-5.524667	5.799979
C	2.218753	-5.440670	3.441611
C	1.669016	-4.126347	5.864720
C	2.158629	-4.040257	3.449658
C	2.042202	-7.710241	4.554241
H	2.731149	-8.073364	3.784349
H	2.349174	-8.135319	5.515436
H	1.048784	-8.116451	4.320208
H	1.572360	-6.097986	6.707660
H	2.421197	-5.949284	2.502992
C	1.353717	-3.456170	7.184939
H	2.145606	-2.760376	7.488020
H	0.421330	-2.881242	7.127662
H	1.241089	-4.200978	7.978002
C	2.366658	-3.282873	2.154614
H	3.302147	-2.710907	2.160510
H	2.405085	-3.974270	1.308017
H	1.554022	-2.570258	1.970284
P	1.778907	1.564604	4.734337
C	1.896866	3.377993	4.679098
C	2.009356	6.199365	4.601691
C	2.217406	5.440534	3.441141
C	1.738145	5.524560	5.799628
C	2.157579	4.040144	3.449268
C	1.668553	4.126195	5.864450
C	2.040793	7.710122	4.553601
H	2.340268	8.135592	5.516954
H	2.735485	8.073273	3.788858
H	1.049076	8.115892	4.311731
H	2.419522	5.949149	2.502446
H	1.571709	6.097889	6.707317
C	2.365411	3.282696	2.154231
H	3.300678	2.710377	2.160171
H	1.552509	2.570386	1.969867
H	2.404126	3.974080	1.307637
C	1.353686	3.456039	7.184782
H	2.145774	2.760409	7.487722

H	1.241099	4.200870	7.977827
H	0.421394	2.880933	7.127750
C	3.242563	-0.753276	4.592475
C	4.722772	-0.698895	4.458933
C	8.317026	-2.877976	4.151961
C	8.328520	-1.489645	4.146897
C	7.103180	-3.588617	4.260191
C	7.133782	-0.735646	4.248565
C	5.909757	-2.895171	4.361887
C	5.900075	-1.478165	4.357154
H	9.253326	-3.420808	4.072525
H	9.282839	-0.984591	4.063297
H	7.107549	-4.673442	4.264749
H	4.966959	-3.425432	4.449133
C	3.242433	0.753368	4.592397
C	4.722657	0.699218	4.458837
C	8.316494	2.878915	4.151498
C	7.102517	3.589348	4.259624
C	8.328248	1.490585	4.146653
C	5.909224	2.895699	4.361437
C	7.133652	0.736381	4.248447
C	5.899807	1.478690	4.356928
H	9.252693	3.421909	4.071972
H	7.106689	4.674174	4.264009
H	9.282662	0.985697	4.063125
H	4.966325	3.425794	4.448596
S	-1.619910	1.638954	5.006683
S	-1.619687	-1.639577	5.006821
C	-3.123976	0.704514	5.145438
C	-3.123880	-0.705331	5.145504
C	-4.347914	1.397453	5.253648
C	-4.347723	-1.398427	5.253783
C	-5.550426	0.701857	5.361099
C	-5.550330	-0.702985	5.361167
H	-4.341645	2.483144	5.251670
H	-4.341305	-2.484117	5.251907
H	-6.484478	1.248690	5.444225
H	-6.484307	-1.249937	5.444346

Table S3 Cartesian coordinates for optimized structure of [Pt(dmit)(DPCB-phen')] (**6b'**)

Pt	0.015899	0.000351	4.92795
P	1.746104	-1.56167	4.813034
C	1.839507	-3.37363	4.751768
C	1.909955	-6.19485	4.662005
C	1.673061	-5.52108	5.868106
C	2.107526	-5.43461	3.500372
C	1.62491	-4.12248	5.93983
C	2.068104	-4.03381	3.514125
C	1.916156	-7.70535	4.607732
H	2.577431	-8.07636	3.81781
H	2.241776	-8.13948	5.558571
H	0.909938	-8.09346	4.399538
H	1.516211	-6.09576	6.77648
H	2.284661	-5.94261	2.556497
C	1.347955	-3.45365	7.269335
H	2.154269	-2.76782	7.556585

H	0.420444	-2.86909	7.237851
H	1.245677	-4.19995	8.062129
C	2.264645	-3.27405	2.218887
H	3.205473	-2.71068	2.213728
H	2.285475	-3.96277	1.369712
H	1.45564	-2.55416	2.047092
P	1.747773	1.561776	4.813502
C	1.838799	3.374286	4.752007
C	1.90647	6.195679	4.661959
C	1.67066	5.521749	5.868253
C	2.104397	5.435542	3.500414
C	1.623967	4.123154	5.940117
C	2.066308	4.034613	3.514308
C	1.910955	7.706198	4.607899
H	2.557997	8.077709	3.806594
H	2.253037	8.140342	5.553012
H	0.900967	8.093823	4.417842
H	1.513499	6.096341	6.776646
H	2.280661	5.943631	2.556437
C	1.34814	3.454248	7.269797
H	2.155675	2.769989	7.557349
H	0.421753	2.867922	7.238341
H	1.244363	4.20063	8.062329
C	2.262736	3.275119	2.218899
H	3.202582	2.710135	2.214168
H	2.285228	3.964156	1.370023
H	1.452721	2.556539	2.046365
C	3.208275	-0.74812	4.678483
C	4.686713	-0.6952	4.552539
C	8.276337	-2.88138	4.258556
C	8.290296	-1.49264	4.25517
C	7.061394	-3.5906	4.359463
C	7.096098	-0.7382	4.35176
C	5.868107	-2.89554	4.456479
C	5.862195	-1.47927	4.45412
H	9.212157	-3.42542	4.183142
H	9.245803	-0.98916	4.176685
H	7.064579	-4.67533	4.36205
H	4.923995	-3.42464	4.537683
C	3.211947	0.74856	4.678571
C	4.683781	0.697894	4.552845
C	8.278659	2.876835	4.257495
C	8.290521	1.488039	4.254664
C	7.065069	3.588341	4.358117
C	7.095779	0.734468	4.351615
C	5.871001	2.894921	4.455468
C	5.862824	1.4782	4.453787
H	9.215442	3.419183	4.181776
H	9.245331	0.98331	4.176277
H	7.069865	4.673035	4.360178
H	4.927697	3.425341	4.536294
S	-1.64657	1.668368	5.021465
C	-5.73957	0.004469	5.286232

S	-4.72873	-1.50631	5.221926
S	-4.7265	1.513736	5.221795
C	-3.09236	-0.67573	5.120627
C	-3.09137	0.680733	5.120559
S	-7.41937	0.005714	5.393617
S	-1.64901	-1.66543	5.021668

Table S4 Computed low-energy absorption for **2b'**

state no.	calculated energy/eV	*f*	constitution*
1	1.75	0.0260	189-190 (45%)
2	2.17	0.1519	188-190 (11%), 189-191(36%)
3	2.79	0.0294	187-190 (10%), 188-190(32%), 188-191 (32%)
4	2.83	0.2915	185-190 (1%), 187-191 (12%), 188-190 (23%), 188-191 (3%), 189-191 (4%)
5	2.88	0.0183	186-190 (23%), 187-190 (19%), 188-191 (6%)
6	2.89	0.0154	185-190 (43%), 186-190 (4%)
7	3.00	0.0039	185-191 (40%), 186-191 (7%)
8	3.09	0.0475	185-191 (4%), 186-191 (24%), 187-191 (16%), 188-190 (2%)
9	3.17	0.1789	185-190 (4%), 186-190 (19%), 187-190 (15%), 188-191 (3%)
10	3.31	0.1566	189-192 (44%)

*189 strands for HOMO, 190 stands for LUMO

Table S5 Computed low-energy absorption for **6a'**

state no.	calculated energy/eV	*f*	constitution*
1	1.77	0.0024	177-179 (47%)
2	1.85	0.2284	174-179 (10%), 176-179 (6.0%), 177-178 (37%)
3	2.04	0.0002	176-178 (45%)
4	2.27	0.0001	177-180 (47%)
5	2.29	0.1304	175-178 (1.5%), 176-179 (4.2%), 177-178 (3.5%)
6	2.62	0.0004	176-180 (46%)
7	2.88	0.0143	174-179 (17%), 175-178 (31%)
8	2.96	0.0000	177-181 (48%)
9	2.99	0.0003	174-178 (27%), 175-179 (25%)
10	3.06	0.0019	173-178 (48%)

*177 strands for HOMO, 178 stands for LUMO

Table S6 Computed low-energy absorption for **6b'**

state no.	calculated energy/eV	*f*	constitution*
1	1.71	0.0026	190-192 (47%)
2	1.73	0.2684	188-192 (13%), 190-191 (41%)
3	1.95	0.0000	190-193 (47%)
4	2.47	0.0012	188-191 (44%)
5	2.61	0.0012	185-192 (2.1%), 187-191 (27%), 188-192 (19%)
6	2.64	0.0001	189-191 (48%)
7	2.87	0.0867	188-193 (15%), 189-192 (16%), 189-193 (1.4%), 190-195 (26%)
8	2.87	0.0318	188-192 (1.3%), 188-193 (5.7%), 189-192 (26%), 189-193 (11%), 190-195 (13%)
9	2.89	0.0412	187-192 (43%)
10	2.89	0.0009	188-193 (38%), 189-192 (7.7%)

*190 strands for HOMO, 191 stands for LUMO