Can Excited State Electronic Coherence be Tuned via Molecular Structural Modification? A First-Principles Quantum Electronic Dynamics Study of Pyrazolate-Bridged Pt(II) Dimers

David B. Lingerfelt,[†] Patrick J. Lestrange,[†] Joseph J. Radler,[†] Samantha E. Brown-Xu,[‡] Pyosang Kim,[¶,‡] Felix N. Castellano,[§] Lin X. Chen,[¶,‡] and Xiaosong Li[*,†]

[†]*Department of Chemistry, University of Washington, Seattle, WA, 98195*

[‡]*Department of Chemistry, Northwestern University, Evanston, IL 60208, USA*

[¶]*Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA*

[§]*Department of Chemistry, North Carolina State University, Raleigh, NC, 27695-8204*

E-mail: xsli@uw.edu

Presented below are the coordinates (in Å) extracted from X-ray crystallography results for each of the studied complexes.

$[(\mathbf{ppy})\mathbf{Pt}(\mu\text{-}\mathbf{pz})]_2$

C	1.944683	2.842746	0.489229
C	2.407732	3.802153	1.374152
C	3.323527	3.453798	2.345023
C	3.762670	2.137134	2.419803
C	3.263968	1.190183	1.522441
C	3.561607	-0.244030	1.551228
C	4.490536	-0.820641	2.411362
C	4.713116	-2.189565	2.378428
C	3.995081	-2.967579	1.506644
C	3.049228	-2.392036	0.648365
C	2.824314	-1.023044	0.637968
C	-2.105026	-2.701271	1.015382
C	-2.735154	-3.493403	1.962075
C	-3.712808	-2.929935	2.758058
C	-4.009607	-1.598914	2.617179
C	-3.341375	-0.815907	1.674329
C	-3.503059	0.624504	1.477675
C	-4.349988	1.420988	2.240910
C	-4.374499	2.787533	2.042431
C	-3.573848	3.347022	1.060411
C	-2.758984	2.551584	0.269941
C	-2.695775	1.170462	0.442750
C	1.310927	-2.581935	-2.232117
C	0.279908	-3.358224	-2.690077
C	-0.870761	-2.742102	-2.240493
C	0.827844	2.190019	-2.778591
C	-0.317647	2.626324	-3.413420
C	-1.338183	1.927463	-2.805996
H	2.553262	-2.951356	0.061549
H	-1.429162	-3.086187	0.467960
H	-2.498108	-4.408328	2.062611
H	-4.175987	-3.460379	3.396458
H	-4.675190	-1.204529	3.167363
H	-4.911085	1.025491	2.899242
H	-4.935188	3.338576	2.574568
H	1.320265	3.091000	-0.181869
H	-3.584257	4.288518	0.926966

H	-2.230553	2.957988	-0.406277
H	2.233981	-2.754884	-2.382528
H	0.344561	-4.151907	-3.207105
H	-1.756997	-3.048394	-2.394940
H	1.708097	2.488556	-2.974693
H	-0.386662	3.268453	-4.111354
H	-2.257146	2.005453	-3.031809
H	2.095175	4.698756	1.312686
H	3.651116	4.106261	2.955499
H	4.396516	1.880250	3.078148
H	4.972646	-0.277741	3.022415
H	5.357786	-2.583651	2.954138
H	4.140984	-3.904666	1.484775
N	2.365491	1.551374	0.564390
N	-2.421127	-1.399941	0.845748
N	0.826211	-1.538034	-1.543106
N	-0.537012	-1.639290	-1.549070
N	0.509752	1.267481	-1.833212
N	-0.853047	1.121736	-1.857686
Pt	1.632878	0.044968	-0.562084
Pt	-1.627448	-0.174974	-0.542709

$[(\mathbf{ppy})\mathbf{Pt}(\mu\text{-}\mathbf{Me_2pz})]_2$

C	-2.237116	-2.680887	0.886887
C	-2.887386	-3.558047	1.781735
C	-3.740300	-3.049760	2.660411
C	-3.987073	-1.666990	2.720334
C	-3.329438	-0.860428	1.811531
C	-3.421020	0.584619	1.730251
C	-4.284309	1.326478	2.576392
C	-4.253032	2.715840	2.473411
C	-3.411244	3.372350	1.613099
C	-2.575399	2.629384	0.765670
C	-2.594102	1.226943	0.787461
C	2.246274	2.725701	0.846776
C	2.751958	3.624775	1.774655
C	3.463435	3.096731	2.856724
C	3.680722	1.781186	2.986837
C	3.137852	0.908795	1.983596
C	3.245783	-0.561195	1.972461
C	3.904229	-1.270246	2.992192
C	3.931351	-2.638318	2.891599
C	3.342593	-3.326535	1.805579
C	2.671463	-2.567333	0.823545
C	2.615154	-1.209295	0.874504
C	-1.244341	2.223804	-2.429390
C	-0.192215	2.862182	-3.044526
C	0.966423	2.332304	-2.454237
C	-0.868398	-2.429744	-2.375437
C	0.278723	-2.908378	-2.965847
C	1.340208	-2.233431	-2.428251
C	-2.710026	2.333557	-2.681578
C	2.423244	2.587589	-2.819255
C	2.822891	-2.327376	-2.679167
C	-2.290561	-2.798209	-2.662479
H	-2.002120	3.071201	0.183620
H	1.766141	3.056153	0.121896
H	2.623516	4.541110	1.680133
H	3.794017	3.675464	3.505090
H	4.167237	1.443028	3.703477
H	4.305958	-0.829637	3.706147
H	4.352187	-3.130431	3.560806
H	-1.645243	-3.038471	0.265111
H	3.396041	-4.253092	1.739672
H	2.253160	-3.009778	0.119586

H	-0.237222	3.509126	-3.711610
H	0.324757	-3.571936	-3.616974
H	-3.181381	1.734797	-2.095903
H	-2.997025	3.235256	-2.514087
H	-2.897388	2.102238	-3.593194
H	-2.721117	-4.472815	1.755296
H	2.992893	2.100555	-2.221096
H	2.581500	2.297318	-3.721157
H	2.610105	3.526878	-2.747818
H	3.279523	-1.662918	-2.155094
H	3.135716	-3.200338	-2.430932
H	3.000617	-2.176382	-3.609716
H	-2.873814	-2.295278	-2.091555
H	-2.492810	-2.599918	-3.579617
H	-2.416353	-3.736391	-2.503415
H	-4.184130	-3.617534	3.247894
H	-4.572112	-1.308175	3.349166
H	-4.849144	0.902289	3.180780
H	-4.826329	3.216361	3.008182
H	-3.393178	4.302413	1.593249
N	-2.430419	-1.381423	0.896224
N	2.422102	1.401127	0.950307
N	-0.752849	1.346666	-1.506059
N	0.618209	1.421682	-1.568903
N	-0.520629	-1.498383	-1.514386
N	0.859060	-1.383470	-1.526785
Pt	-1.571282	-0.056065	-0.349703
Pt	1.655380	0.047977	-0.351498

$[(\mathbf{ppy})\mathbf{Pt}(\mu\text{-}^{t}\mathbf{Bu}_2\mathbf{pz})]_2$

C	2.202903	0.257467	-2.031529
C	2.083588	1.465700	-2.669298
C	2.632999	1.679496	-3.925554
C	3.282786	0.646892	-4.571294
C	3.383913	-0.580474	-3.955665
C	2.844218	-0.760724	-2.674724
C	2.877378	-2.024414	-1.926425
C	2.094346	-3.139365	0.020559
C	2.672421	-4.315181	-0.421456
C	3.378820	-4.336232	-1.615259
C	3.471937	-3.184539	-2.370202
C	-1.046080	-1.103932	2.876709
C	0.067859	-1.354991	3.654342
C	1.179072	-1.083859	2.861455
C	2.607121	-0.919389	3.365720
C	3.677308	-1.296847	2.339715
C	2.740891	0.555808	3.744893
C	2.800770	-1.766891	4.629146
C	-2.473139	-1.071336	3.405716
C	-3.558598	-1.072582	2.333358
C	-2.593477	0.218688	4.236696
C	-2.703089	-2.273953	4.320426
C	1.186792	2.992760	0.364158
C	0.088597	3.815140	0.518366
C	-1.036830	3.022809	0.455847
C	-2.442055	3.520720	0.725291
C	-3.521900	2.449200	0.730813
C	-2.811255	4.602085	-0.297709
C	-2.438080	4.179871	2.116941
C	2.637582	3.449945	0.510014
C	2.927322	4.532770	-0.539780
C	2.770543	4.064033	1.915940
C	3.682478	2.343151	0.358056
C	-3.042302	-1.902619	-1.751836
C	-3.709385	-3.064412	-2.135966
C	-3.542241	-4.228891	-1.402892
C	-2.688667	-4.229060	-0.316091
C	-2.055706	-3.052187	0.044285
C	-3.105482	-0.637738	-2.461053
C	-2.333285	0.383960	-1.890403
C	-2.288189	1.608025	-2.538079
C	-3.028012	1.833906	-3.694994

C	-3.796715	0.805514	-4.236939
C	-3.824801	-0.414163	-3.635668
H	1.624167	2.157465	-2.251643
H	2.562183	2.513395	-4.332212
H	3.652631	0.779493	-5.413105
H	3.806511	-1.287132	-4.385619
H	1.625757	-3.139430	0.821960
H	2.586411	-5.091870	0.083711
H	3.788340	-5.120123	-1.905213
H	3.934243	-3.190422	-3.174942
H	0.075088	-1.648002	4.536915
H	0.105781	4.735845	0.641072
H	-4.265125	-3.058953	-2.882484
H	-3.998796	-5.002562	-1.639445
H	-2.541064	-5.008882	0.169600
H	-1.483139	-3.053410	0.777654
H	-1.755995	2.288645	-2.195450
H	-3.009770	2.669011	-4.103953
H	-4.291432	0.953245	-5.011185
H	-4.324007	-1.103155	-4.009276
H	3.598441	-2.228025	2.124427
H	4.545735	-1.125486	2.707389
H	3.557722	-0.772345	1.544578
H	2.573575	1.102566	2.973260
H	3.628185	0.725011	4.068939
H	2.103318	0.770018	4.430756
H	2.233428	-1.434017	5.326676
H	3.717120	-1.717152	4.910375
H	2.574057	-2.680250	4.441962
H	-3.376595	-0.380187	1.693529
H	-4.412130	-0.916950	2.741690
H	-3.566469	-1.923790	1.888191
H	-2.457453	0.980122	3.669700
H	-1.929868	0.214108	4.932633
H	-3.467974	0.264916	4.630188
H	-3.590650	-2.236084	4.682414
H	-2.063321	-2.258556	5.037612
H	-2.598996	-3.085039	3.816852
H	-3.562963	2.032745	-0.134875
H	-4.370464	2.850871	0.933240
H	-3.312917	1.788770	1.395345
H	-2.194973	5.334566	-0.225400
H	-3.702516	4.914584	-0.125335
H	-2.768128	4.233456	-1.181477
H	-2.177798	3.531961	2.775258

H	-3.319143	4.504947	2.320792
H	-1.817428	4.911828	2.123870
H	3.804455	4.893569	-0.394729
H	2.275534	5.233250	-0.465673
H	2.881869	4.145724	-1.419640
H	2.500436	3.419061	2.572671
H	2.208118	4.840807	1.981598
H	3.683409	4.316637	2.070884
H	3.505233	1.646375	0.993741
H	4.556986	2.705570	0.516240
H	3.641623	1.982160	-0.532245
N	2.196167	-1.959514	-0.702994
N	0.741222	-0.720649	1.632680
N	-0.638768	-0.728759	1.650360
N	0.739791	1.735171	0.183683
N	-0.638833	1.748075	0.228740
N	-2.246770	-1.886614	-0.645735
Pt	-1.471576	-0.101640	-0.155551
Pt	1.502666	-0.167306	-0.200510

$[(\mathbf{ppy})\mathbf{Pt}(\mu\text{-}\mathbf{Ph_2pz})]_2$

C	-2.193901	1.643108	-1.376019
C	-2.194100	1.496555	-2.753054
C	-2.725365	2.462320	-3.587605
C	-3.275400	3.614640	-3.047357
C	-3.282011	3.796188	-1.686416
C	-2.722659	2.809415	-0.859534
C	-2.645440	2.911987	0.602409
C	-3.061988	4.012370	1.361227
C	-2.932819	3.986899	2.738813
C	-2.401997	2.862044	3.348409
C	-1.992385	1.793660	2.584498
C	2.022812	1.718266	-1.499589
C	2.036256	1.450723	-2.847415
C	2.430884	2.418285	-3.754330
C	2.778236	3.680391	-3.327818
C	2.784700	3.960934	-1.971768
C	2.401147	2.964367	-1.071715
C	2.396428	3.120953	0.385264
C	2.707766	4.300170	1.072412
C	2.604986	4.342741	2.445305
C	2.215798	3.210092	3.137334
C	1.904393	2.042877	2.456181
C	1.242916	-1.648043	2.348060
C	2.686430	-1.889225	2.568764
C	3.090919	-2.873940	3.469871
C	4.418838	-3.081080	3.742236
C	5.384285	-2.324514	3.111986
C	5.025018	-1.365816	2.191409
C	3.668850	-1.147662	1.940716
C	0.160312	-2.241580	2.993898
C	-1.003038	-1.701593	2.417270
C	-2.396273	-2.035224	2.685408
C	-2.692247	-3.034792	3.622471
C	-4.006700	-3.460465	3.821547
C	-5.030241	-2.911567	3.088512
C	-4.760746	-1.898977	2.193142
C	-3.466450	-1.459295	2.007829
C	1.150082	-2.106781	-2.024111
C	0.050636	-2.790775	-2.524506
C	-1.078341	-2.086387	-2.086738
C	-2.486901	-2.443213	-2.312800

C	-2.795474	-3.465527	-3.237996
C	-4.104694	-3.873349	-3.406891
C	-5.133897	-3.290868	-2.689909
C	-4.833912	-2.279567	-1.800810
C	-3.535803	-1.855739	-1.622048
C	2.586133	-2.433121	-2.199485
C	3.603850	-1.562189	-1.894118
C	4.937755	-1.907540	-2.144662
C	5.242701	-3.130813	-2.679699
C	4.238635	-4.021735	-2.954899
C	2.908983	-3.673393	-2.726308
H	-2.322642	2.829401	4.274396
H	-1.639354	1.042763	3.006887
H	1.776599	0.611649	-3.153082
H	2.463270	2.212915	-4.660935
H	3.007448	4.339101	-3.943490
H	3.039347	4.801009	-1.665159
H	2.982327	5.054930	0.602233
H	2.795867	5.127889	2.904212
H	2.162126	3.231475	4.065770
H	1.630753	1.292120	2.933370
H	2.448920	-3.398649	3.892731
H	4.669686	-3.734881	4.355424
H	6.283038	-2.462603	3.310386
H	5.672276	-0.870117	1.745619
H	3.420922	-0.487859	1.334560
H	-1.826935	0.727337	-3.125547
H	0.200374	-2.873315	3.674658
H	-2.003974	-3.416722	4.118569
H	-4.190077	-4.119178	4.451747
H	-5.900587	-3.222361	3.195640
H	-5.452178	-1.510041	1.711005
H	-3.305512	-0.760562	1.416358
H	0.062468	-3.561986	-3.044093
H	-2.714790	2.337948	-4.509494
H	-2.115811	-3.861853	-3.733056
H	-4.294877	-4.551556	-4.011843
H	-6.011685	-3.575749	-2.804891
H	-5.518458	-1.878244	-1.315808
H	-3.359501	-1.162533	-1.027262
H	3.404639	-0.736000	-1.515716
H	5.618650	-1.305589	-1.948066
H	-3.638886	4.264485	-3.605834
H	6.126738	-3.357049	-2.855458
H	4.444417	-4.862910	-3.296216

H	2.233144	-4.278347	-2.927846
H	-3.654142	4.562406	-1.316978
H	-3.426042	4.757270	0.940714
H	-3.200561	4.716154	3.248475
N	-2.093536	1.803125	1.205240
N	1.993273	1.977305	1.074137
N	0.709257	-1.022419	-1.328570
N	-0.659479	-1.017174	-1.359307
N	0.764630	-0.772323	1.427148
N	-0.604921	-0.825050	1.466429
Pt	-1.454627	0.370512	-0.023919
Pt	1.452148	0.442946	-0.073539

Table S1: S_1-S_2 energy gap (eV) from LR-TDDFT using various exchange-correlation functionals, mixes of exact (Hartree-Fock) exchange and semi-local DFT exchange, and range separation cutoffs for the range-separated hybrids.

	B3LYP	PBE0	B3PW91	LC-ωPBE
1	0.078	0.0847	0.0800	0.0891
2	0.1337	0.1432	0.1399	0.103
3	0.2047	0.2139	0.2029	0.2847
4	0.2583	0.2703	0.2556	0.3828