

Supporting Information

for

***Cis* and *Trans*-bis(Tetrathiafulvalene-Acetylide) Platinum(II) Complexes : Syntheses, Crystal Structures, and Influence of the Ancillary Ligands on their Electronic Properties**

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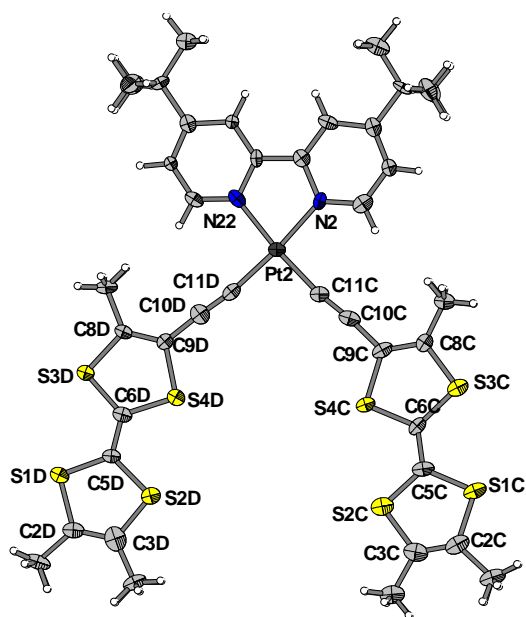


Fig. S1 ORTEP drawing of the second crystallographically independent molecule of complex **2** with the main numbering scheme. Thermal ellipsoids drawn at the 50 % probability level.

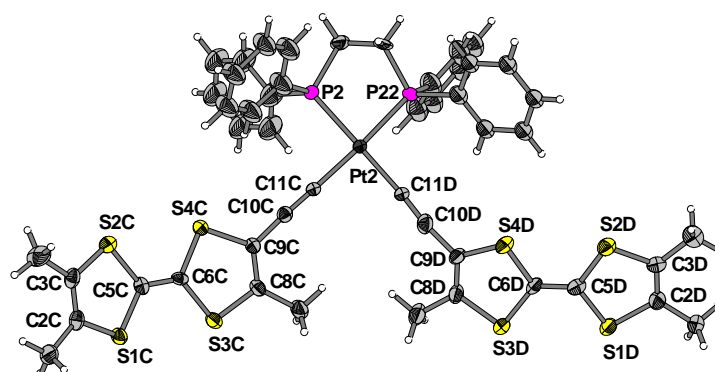


Fig. S2 ORTEP drawing of the second crystallographically independent molecule of complex **3** with the main numbering scheme. Thermal ellipsoids drawn at the 50 % probability level.

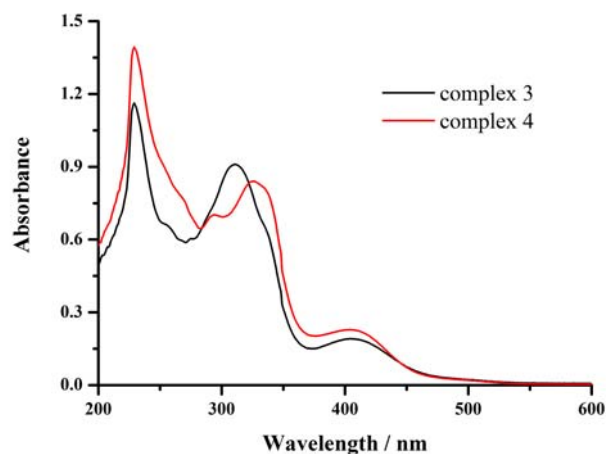


Fig. S3 UV-vis absorption spectra of complexes **3** and **4** in dichloromethane at room temperature, ($c \sim 10^{-5} \text{ mol.L}^{-1}$).

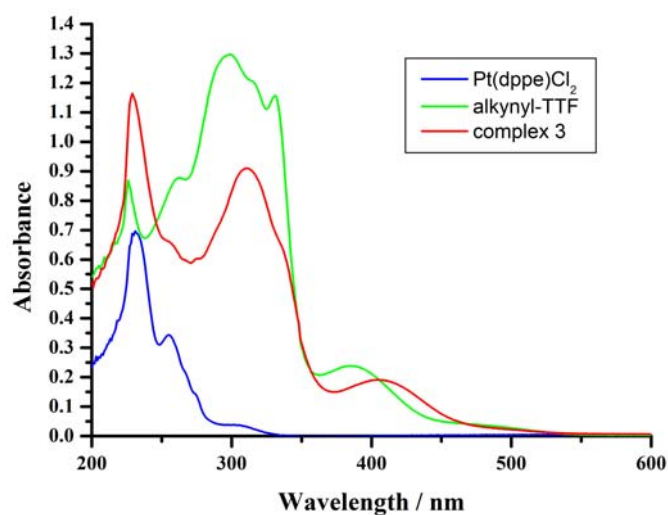


Fig. S4 UV-visible absorption spectra of complex **3**, the alkynyl-TTF precursor and the Pt(dppe)Cl₂ precursor in dichloromethane at room temperature, ($c \sim 10^{-5} \text{ mol.L}^{-1}$).

Computational Details

DFT calculations (spin unrestricted for all open shell systems) were performed on gas phase molecules using the Gaussian 03, Revision D.02 program package, the B3LYP functional and the LanL2DZ basis set. The latter employs the Dunning/Huzinaga valence double zeta D95V[1] basis set for first row atoms and the Los Alamos Effective Core Potential plus DZ on atoms from Na-Bi.[2–4]

- 1 T. H. Dunning Jr and P. J. Hay, Modern Theoretical Chemistry, Plenum, New York, 1976.
- 2 P. J. Hay and W. R. Wadt, J. Chem. Phys., 1985, 82, 270.
- 3 W. R. Wadt and P. J. Hay, J. Chem. Phys., 1985, 82, 284.
- 4 P. J. Hay and W. R. Wadt, J. Chem. Phys., 1985, 82, 299.

Full parameters for common bases sets are available at <https://bse.pnl.gov/bse/portal>
Parameters for the LanL2DZ basis set are reproduced next.

LanL2DZ basis set

When publishing results obtained from use of the Basis Set Exchange (BSE) software and the EMSL Basis Set Library, please cite:

The Role of Databases in Support of Computational Chemistry Calculations

Feller, D., J. Comp. Chem., 17(13), 1571-1586, 1996.

Basis Set Exchange: A Community Database for Computational Sciences

Schuchardt, K.L., Didier, B.T., Elsethagen, T., Sun, L., Gurumoorthi, V., Chase, J., Li, J., and Windus, T.L.
J. Chem. Inf. Model., 47(3), 1045-1052, 2007, doi:10.1021/ci600510j.

```
! LANL2DZ ECP EMSL Basis Set Exchange Library 4/26/11 8:55 AM
! Elements References
! -----
! H - Ne: T. H. Dunning Jr. and P. J. Hay, in Methods of Electronic Structure
! Theory, Vol. 2, H. F. Schaefer III, ed., PLENUM PRESS (1977)
! Na - Hg: P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 270 (1985).
! P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 284 (1985).
! P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 299 (1985).
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    19.2384000 0.0328280
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    0.4962000 1.0600910
S 1 1.00
    0.1533000 1.0000000
P 4 1.00
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P 1 1.00
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Ru 0
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P	3	1.00	
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		0.4413000	0.3668144
P	2	1.00	
		0.5725000	-0.0880864
		0.0830000	1.0283970
P	1	1.00	
		0.0250000	1.0000000
D	3	1.00	
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		1.3770000	0.5105223
		0.4828000	0.5730028
D	1	1.00	
		0.1501000	1.0000000

! Elements

References

! -----	-----
! Na - Hg:	P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 270 (1985).
!	P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 284 (1985).
!	P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 299 (1985).
!	

P	0		
P-ECP	2	10	
d	potential		
5			
1	462.1211423	-10.0000000	
2	93.6863701	-79.4864658	
2	21.2349094	-28.3668251	
2	6.3388415	-9.8577589	
2	2.0620684	-1.0163783	
s-d	potential		
5			
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1	58.9576810	12.9104154	
2	36.0571255	150.0250298	
2	11.2464453	71.7083146	
2	2.6757561	23.0397012	
p-d	potential		
6			
0	75.1617880	5.0000000	
1	57.4544041	6.3446507	
2	47.9481748	198.5585104	
2	18.4588360	111.1470820	
2	5.9414190	40.3944144	
2	1.8487507	6.4483233	
S	0		
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d	potential		
5			
1	532.6685222	-10.0000000	
2	108.1342248	-85.3593846	
2	24.5697664	-30.4513290	
2	7.3702438	-10.3745886	
2	2.3712569	-0.9899295	
s-d	potential		
5			
0	106.3176781	3.0000000	
1	100.8245833	10.6284036	
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2	3.1778402	28.7609065	
p-d	potential		
6			
0	101.9709185	5.0000000	
1	93.2808973	6.0969842	
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2	24.6347440	147.1448413	
2	7.8120535	53.6569778	
2	2.3112730	8.9249559	
RU	0		
RU-ECP	3	28	
f	potential		
5			
0	554.3796303	-0.0515270	
1	155.1066871	-20.1816536	

2	48.4976263	-105.9966915
2	14.7701594	-42.2166788
2	5.2077363	-3.7675024
s-f potential		
5		
0	66.7118060	2.9578344
1	77.3503632	25.3748707
2	18.3571445	536.1262372
2	11.8404727	-651.2057221
2	8.1179479	381.3816943
p-f potential		
5		
0	54.9937915	4.9651557
1	13.9399212	23.8861501
2	15.2118246	464.4631344
2	10.5460691	-714.4451788
2	7.5539486	377.5503594
d-f potential		
4		
0	60.3444595	3.0352988
1	45.2100305	23.2901723
2	19.1190074	146.0926620
2	4.2712090	28.9129770

Input Files.

Cartesian Coordinates of Optimized Geometry,

And Selection of Distances and Angles in the Optimized Geometry

Geometry Optimization of Complex 2 : input file.

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#B3LYP/LanL2DZ opt
```

```
cisPt bipyTbu TTF)2 neutre singulet
```

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0 1
Pt 0 -1.165500 -0.061000 -2.131000
N 0 -2.640500 -0.097000 -3.571000
C 0 -3.971500 -0.145000 -3.327000
C 0 -4.903500 -0.112000 -4.329000
C 0 -4.482500 -0.050000 -5.687000
C 0 -3.120500 -0.044000 -5.890000
C 0 -2.229500 -0.057000 -4.853000
C 0 -5.523500 -0.024000 -6.799000
C 0 -4.846500 0.046000 -8.204000
C 0 -6.423500 1.189000 -6.618000
N 0 -0.063500 0.027000 -3.862000
C 0 -6.368500 -1.279000 -6.730000
C 0 1.285500 0.104000 -3.928000
C 0 1.962500 0.104000 -5.147000
C 0 1.271500 0.023000 -6.328000
C 0 -0.114500 -0.020000 -6.257000
C 0 -0.762500 -0.012000 -5.029000
C 0 1.995500 0.003000 -7.665000
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C 0 2.823500 1.290000 -7.800000
C 0 1.076500 -0.091000 -8.849000
C 0 -2.404500 -0.142000 -0.625000
C 0 -3.217500 -0.177000 0.233000
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C 0 -5.512500 -0.166000 1.191000
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S 0 -6.468500 -0.085000 2.655000
S 0 -3.540500 -0.137000 2.952000
C 0 -5.110500 -0.123000 3.772000
C 0 -5.236500 -0.085000 5.088000
S 0 -6.764500 -0.085000 5.929000
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C 0 -4.771500 -0.059000 7.635000
C 0 -3.930500 -0.067000 8.887000
C 0 0.391500 -0.018000 -0.945000
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H 0	-5.882500	2.006000	-6.653000
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H 0	-7.030500	-1.266000	-7.451000
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H 0	-5.792500	-2.066000	-6.828000
H 0	1.785500	0.162000	-3.123000
H 0	2.911500	0.158000	-5.158000
H 0	-0.625500	-0.057000	-7.056000
H 0	3.557500	-1.163000	-6.919000
H 0	3.441500	-1.242000	-8.513000
H 0	2.404500	-2.042000	-7.592000
H 0	3.439500	1.363000	-7.041000
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H 0	0.538500	-0.908000	-8.779000
H 0	1.606500	-0.119000	-9.673000
H 0	0.484500	0.689000	-8.866000
H 0	-6.475500	0.747000	-0.373000
H 0	-7.132500	-0.655000	0.034000
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H 0	-4.513500	-0.108000	9.673000
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H 0	3.571500	0.254000	-1.883000
H 0	3.351500	-0.966000	8.152000
H 0	3.423500	0.632000	8.247000
H 0	4.690500	-0.252000	8.665000
H 0	6.963500	0.625000	7.707000
H 0	7.738500	-0.179000	6.558000
H 0	6.896500	-0.974000	7.665000

Cartesians Coordinates for the Optimized Geometry of Complex **2** (-1858.598128 Hartrees)

Pt	0.00020	1.06621	-0.00279
N	-1.31734	2.68722	-0.07442
C	-2.67150	2.59227	-0.15755
C	-3.49003	3.72100	-0.21252
C	-2.92840	5.02173	-0.18490
C	-1.52462	5.09592	-0.09920
C	-0.73651	3.93102	-0.04464
C	-3.83709	6.26406	-0.25037
C	-3.03376	7.58694	-0.20121
C	-4.82048	6.23872	0.95804
N	1.31941	2.68575	0.07164
C	-4.64925	6.22817	-1.57970
C	2.67348	2.58928	0.15442
C	3.49314	3.71707	0.21172
C	2.93279	5.01841	0.18705
C	1.52908	5.09419	0.10160
C	0.73982	3.93020	0.04453
C	3.84272	6.25970	0.25527
C	4.82594	6.23616	-0.95333
C	4.65503	6.21991	1.58439
C	3.04069	7.58348	0.20927
C	-1.37974	-0.31577	-0.06357

C	-2.30142	-1.14371	-0.09861
C	-3.36490	-2.07429	-0.13297
C	-3.28832	-3.39333	-0.45936
C	-2.03519	-4.13199	-0.84797
S	-4.82771	-4.38631	-0.42262
S	-5.04505	-1.41321	0.32867
C	-5.93834	-2.98414	0.00780
C	-7.27827	-3.11029	0.09243
S	-8.16837	-4.69296	-0.20634
S	-8.39639	-1.71723	0.53265
C	-9.85855	-3.97493	-0.03483
C	-10.97273	-4.96427	-0.27359
C	-9.95956	-2.66721	0.28987
C	-11.21278	-1.85313	0.49831
C	1.37877	-0.31721	0.05675
C	2.29974	-1.14595	0.09184
C	3.36260	-2.07724	0.12624
C	3.28568	-3.39558	0.45531
C	2.03271	-4.13273	0.84727
S	5.04240	-1.41839	-0.34006
S	4.82437	-4.38971	0.41750
C	5.93556	-2.98818	-0.01343
C	7.27571	-3.11408	-0.09488
S	8.39437	-1.72181	-0.53612
S	8.16572	-4.69580	0.20904
C	9.95735	-2.66856	-0.27945
C	11.21075	-1.85308	-0.48116
C	9.85605	-3.97558	0.04797
C	10.97001	-4.96256	0.29727
H	-3.07280	1.58628	-0.18025
H	-4.56229	3.57129	-0.27716
H	-1.03574	6.06068	-0.07587
H	-3.72587	8.43580	-0.25521
H	-2.33881	7.67604	-1.04681
H	-2.46472	7.68632	0.73273
H	-5.48373	7.11219	0.91690
H	-4.27639	6.26647	1.91074
H	-5.45030	5.34141	0.95533
H	-5.31604	7.09828	-1.63230
H	-5.26905	5.32717	-1.65596
H	-3.98262	6.25410	-2.45110
H	3.07378	1.58284	0.17498
H	4.56525	3.56616	0.27589
H	1.04116	6.05948	0.08045
H	5.45474	5.33813	-0.95283
H	5.49019	7.10877	-0.91019
H	4.28176	6.26680	-1.90589
H	5.27421	5.31829	1.65830
H	3.98854	6.24412	2.45594
H	5.32244	7.08942	1.63908
H	2.47160	7.68555	-0.72434
H	3.73364	8.43154	0.26508
H	2.34596	7.67132	1.05518
H	-2.12344	-4.56591	-1.85343
H	-1.82365	-4.95200	-0.14718
H	-1.18595	-3.44223	-0.84279
H	-10.89601	-5.81533	0.41661
H	-10.93281	-5.36240	-1.29638
H	-11.95386	-4.50226	-0.12943
H	-11.26863	-1.02480	-0.22090
H	-11.23584	-1.41899	1.50715
H	-12.11054	-2.46626	0.37608
H	2.12197	-4.56419	1.85370
H	1.81998	-4.95440	0.14878
H	1.18374	-3.44263	0.84137
H	11.26173	-1.02458	0.23822
H	11.23883	-1.41907	-1.48993
H	12.10854	-2.46518	-0.35399

H	10.89789	-5.81690	-0.38937
H	10.92507	-5.35599	1.32166
H	11.95139	-4.50014	0.15615

Selection of distances (Å) for the Optimized Geometry of Complex **2**

Pt-N : 2.090

Pt-C≡C-C : 1.954, 1.239, 1.414

TTF Central C-C distance : 1.349

Selection of angles (°) for the Optimized Geometry of Complex **2**

Pt-C≡C : 176.9

C≡C-C : 179.2

Geometry Optimization of Complex **2**⁺ : input file.

```
#B3LYP/LanL2DZ opt
```

```
cisPt bipyTbu TTF)2 cation doublet
```

```
1 2
Pt 0 -1.165500 -0.061000 -2.131000
N 0 -2.640500 -0.097000 -3.571000
C 0 -3.971500 -0.145000 -3.327000
C 0 -4.903500 -0.112000 -4.329000
C 0 -4.482500 -0.050000 -5.687000
C 0 -3.120500 -0.044000 -5.890000
C 0 -2.229500 -0.057000 -4.853000
C 0 -5.523500 -0.024000 -6.799000
C 0 -4.846500 0.046000 -8.204000
C 0 -6.423500 1.189000 -6.618000
N 0 -0.063500 0.027000 -3.862000
C 0 -6.368500 -1.279000 -6.730000
C 0 1.285500 0.104000 -3.928000
C 0 1.962500 0.104000 -5.147000
C 0 1.271500 0.023000 -6.328000
C 0 -0.114500 -0.020000 -6.257000
C 0 -0.762500 -0.012000 -5.029000
C 0 1.995500 0.003000 -7.665000
C 0 2.935500 -1.223000 -7.673000
C 0 2.823500 1.290000 -7.800000
C 0 1.076500 -0.091000 -8.849000
C 0 -2.404500 -0.142000 -0.625000
C 0 -3.217500 -0.177000 0.233000
C 0 -4.193500 -0.187000 1.312000
C 0 -5.512500 -0.166000 1.191000
C 0 -6.289500 -0.175000 -0.097000
S 0 -6.468500 -0.085000 2.655000
S 0 -3.540500 -0.137000 2.952000
C 0 -5.110500 -0.123000 3.772000
C 0 -5.236500 -0.085000 5.088000
S 0 -6.764500 -0.085000 5.929000
S 0 -3.833500 -0.080000 6.153000
C 0 -6.065500 -0.087000 7.567000
C 0 -7.072500 -0.078000 8.671000
C 0 -4.771500 -0.059000 7.635000
C 0 -3.930500 -0.067000 8.887000
C 0 0.391500 -0.018000 -0.945000
C 0 1.389500 -0.020000 -0.310000
C 0 2.555500 -0.020000 0.506000
C 0 3.841500 0.014000 0.124000
C 0 4.320500 0.036000 -1.287000
S 0 2.265500 -0.041000 2.266000
S 0 5.068500 -0.003000 1.378000
```

C 0	3.959500	-0.016000	2.748000
C 0	4.369500	-0.022000	4.006000
S 0	3.217500	-0.080000	5.357000
S 0	6.029500	0.032000	4.503000
C 0	4.436500	-0.121000	6.646000
C 0	3.932500	-0.181000	8.049000
C 0	5.709500	-0.087000	6.241000
C 0	6.933500	-0.160000	7.120000
H 0	-4.269500	-0.200000	-2.427000
H 0	-5.827500	-0.132000	-4.119000
H 0	-2.789500	-0.031000	-6.778000
H 0	-5.537500	0.057000	-8.901000
H 0	-4.270500	-0.736000	-8.330000
H 0	-4.307500	0.863000	-8.265000
H 0	-7.090500	1.210000	-7.334000
H 0	-5.882500	2.006000	-6.653000
H 0	-6.875500	1.133000	-5.751000
H 0	-7.030500	-1.266000	-7.451000
H 0	-6.826500	-1.315000	-5.865000
H 0	-5.792500	-2.066000	-6.828000
H 0	1.785500	0.162000	-3.123000
H 0	2.911500	0.158000	-5.158000
H 0	-0.625500	-0.057000	-7.056000
H 0	3.557500	-1.163000	-6.919000
H 0	3.441500	-1.242000	-8.513000
H 0	2.404500	-2.042000	-7.592000
H 0	3.439500	1.363000	-7.041000
H 0	2.222500	2.066000	-7.809000
H 0	3.334500	1.264000	-8.634000
H 0	0.538500	-0.908000	-8.779000
H 0	1.606500	-0.119000	-9.673000
H 0	0.484500	0.689000	-8.866000
H 0	-6.475500	0.747000	-0.373000
H 0	-7.132500	-0.655000	0.034000
H 0	-5.764500	-0.623000	-0.791000
H 0	-7.518500	-0.949000	8.715000
H 0	-7.738500	0.621000	8.502000
H 0	-6.623500	0.102000	9.521000
H 0	-3.390500	0.749000	8.924000
H 0	-3.339500	-0.850000	8.878000
H 0	-4.513500	-0.108000	9.673000
H 0	4.679500	-0.846000	-1.525000
H 0	5.023500	0.711000	-1.384000
H 0	3.571500	0.254000	-1.883000
H 0	3.351500	-0.966000	8.152000
H 0	3.423500	0.632000	8.247000
H 0	4.690500	-0.252000	8.665000
H 0	6.963500	0.625000	7.707000
H 0	7.738500	-0.179000	6.558000
H 0	6.896500	-0.974000	7.665000

Cartesians Coordinates for the Optimized Geometry of Complex 2^+ (-1858.4071051 Hartrees)

Pt	-0.00001	1.45536	-0.00012
N	-1.30348	3.07714	-0.22945
C	-2.63751	2.98466	-0.47420
C	-3.44165	4.11455	-0.63180
C	-2.88507	5.41398	-0.54155
C	-1.50056	5.48441	-0.28571
C	-0.72832	4.31960	-0.13309
C	-3.77306	6.65848	-0.72399
C	-2.97577	7.97839	-0.58293
C	-4.89799	6.64190	0.35450
N	1.30346	3.07713	0.22936
C	-4.41378	6.61577	-2.14429
C	2.63748	2.98462	0.47409
C	3.44162	4.11450	0.63178
C	2.88504	5.41394	0.54163

C	1.50053	5.48439	0.28581
C	0.72829	4.31959	0.13309
C	3.77304	6.65842	0.72417
C	4.89801	6.64190	-0.35428
C	4.41372	6.61562	2.14449
C	2.97578	7.97836	0.58316
C	-1.34606	0.06150	-0.23239
C	-2.20625	-0.81970	-0.38349
C	-3.16429	-1.83625	-0.55424
C	-3.00741	-2.98740	-1.28217
C	-1.77066	-3.38174	-2.04412
S	-4.40623	-4.14584	-1.35361
S	-4.79832	-1.59957	0.28576
C	-5.52554	-3.15758	-0.30997
C	-6.79171	-3.56106	-0.00140
S	-7.51178	-5.12611	-0.59112
S	-7.91535	-2.58227	1.04345
C	-9.13835	-4.90074	0.23888
C	-10.11240	-6.02946	0.01071
C	-9.31798	-3.77138	0.96470
C	-10.53975	-3.34283	1.73809
C	1.34603	0.06149	0.23220
C	2.20621	-0.81972	0.38331
C	3.16427	-1.83623	0.55414
C	3.00746	-2.98726	1.28228
C	1.77079	-3.38148	2.04442
S	4.79823	-1.59968	-0.28604
S	4.40629	-4.14568	1.35379
C	5.52554	-3.15756	0.30994
C	6.79171	-3.56103	0.00140
S	7.91527	-2.58238	-1.04367
S	7.51187	-5.12594	0.59136
C	9.31797	-3.77139	-0.96472
C	10.53971	-3.34289	-1.73819
C	9.13842	-4.90062	-0.23869
C	10.11254	-6.02925	-0.01032
H	-3.03879	1.98116	-0.54330
H	-4.49844	3.96921	-0.82674
H	-1.01810	6.44901	-0.20638
H	-3.65336	8.82862	-0.72199
H	-2.18533	8.06490	-1.34034
H	-2.52356	8.08120	0.41251
H	-5.54662	7.51685	0.22489
H	-4.47747	6.67682	1.36754
H	-5.52750	5.74727	0.27926
H	-5.06217	7.48934	-2.28390
H	-5.02702	5.71892	-2.29177
H	-3.64484	6.63355	-2.92704
H	3.03877	1.98112	0.54311
H	4.49841	3.96916	0.82670
H	1.01807	6.44900	0.20657
H	5.52752	5.74726	-0.27908
H	5.54664	7.51684	-0.22459
H	4.47752	6.67688	-1.36734
H	5.02694	5.71876	2.29193
H	3.64475	6.63337	2.92721
H	5.06212	7.48918	2.28417
H	2.52358	8.08122	-0.41228
H	3.65339	8.82857	0.72226
H	2.18534	8.06485	1.34057
H	-1.97828	-3.47964	-3.11811
H	-1.37485	-4.34358	-1.69164
H	-0.99793	-2.61967	-1.91039
H	-9.70771	-6.98053	0.38017
H	-10.33121	-6.15165	-1.05796
H	-11.05827	-5.84524	0.52686
H	-10.93765	-2.39448	1.35420
H	-10.30446	-3.20161	2.80087

H	-11.33341	-4.09133	1.66822
H	1.97845	-3.47887	3.11845
H	1.37514	-4.34354	1.69237
H	0.99793	-2.61960	1.91038
H	10.93744	-2.39436	-1.35460
H	10.30443	-3.20206	-2.80103
H	11.33348	-4.09125	-1.66805
H	9.70782	-6.98044	-0.37943
H	10.33152	-6.15109	1.05836
H	11.05832	-5.84515	-0.52668

Selection of distances (Å) for the Optimized Geometry of Complex **2**⁺

Pt-N : 2.093

Pt-C≡C-C : 1.952, 1.241, 1.407

TTF Central C-C distance : 1.364

Selection of angles (°) for the Optimized Geometry of Complex **2**⁺

Pt-C≡C : 179.7

C≡C-C : 179.0

Geometry Optimization of Complex **3** : input file.

#B3LYP/LanL2DZ opt

cisPt dppe TTF)2 neutre singulet

	0	1	
Pt 0	0.704500	-0.143000	0.384500
P 0	1.751500	1.007000	2.070500
P 0	2.306500	0.742000	-0.979500
C 0	3.330500	-0.423000	-1.923500
C 0	3.138500	-1.769000	-1.847500
C 0	3.979500	-2.613000	-2.551500
C 0	5.041500	-2.179000	-3.221500
C 0	5.220500	-0.833000	-3.294500
C 0	4.395500	0.066000	-2.683500
C 0	1.713500	1.929000	-2.201500
C 0	0.998500	1.523000	-3.281500
C 0	0.500500	2.410000	-4.228500
C 0	0.719500	3.702000	-4.119500
C 0	1.473500	4.150000	-3.049500
C 0	1.982500	3.280000	-2.101500
C 0	0.822500	1.895000	3.343500
C 0	0.930500	3.258000	3.569500
C 0	0.209500	3.896000	4.582500
C 0	-0.629500	3.166000	5.365500
C 0	-0.763500	1.796000	5.157500
C 0	-0.048500	1.184000	4.129500
C 0	2.920500	0.037000	3.063500
C 0	3.666500	0.625000	4.067500
C 0	4.605500	-0.093000	4.757500
C 0	4.793500	-1.404000	4.523500
C 0	4.042500	-1.999000	3.565500
C 0	3.118500	-1.302000	2.815500
C 0	2.815500	2.249000	1.252500
C 0	3.554500	1.594000	0.071500
S 0	-2.984500	-3.808000	-4.569500
S 0	-0.840500	-1.798000	-4.836500
S 0	-3.580500	-3.599000	-7.753500
S 0	-1.591500	-1.460000	-7.997500
C 0	-0.128500	-1.105000	-1.151500
C 0	-0.649500	-1.629000	-2.106500
C 0	-1.335500	-2.243000	-3.192500
C 0	-2.304500	-3.161000	-3.106500

C 0	-2.819500	-3.725000	-1.796500
C 0	-2.121500	-2.696000	-5.634500
C 0	-2.412500	-2.594000	-6.936500
C 0	-3.611500	-2.665000	-9.234500
C 0	-4.615500	-3.071000	-10.262500
C 0	-2.707500	-1.677000	-9.330500
C 0	-2.551500	-0.707000	-10.487500
S 0	-3.141500	-0.872000	4.412500
S 0	-4.121500	-3.640000	4.465500
S 0	-3.814500	-0.494000	7.524500
S 0	-4.722500	-3.282000	7.742500
C 0	-0.715500	-0.925000	1.566500
C 0	-1.583500	-1.425000	2.209500
C 0	-2.546500	-1.961000	3.135500
C 0	-3.046500	-3.187000	3.149500
C 0	-2.836500	-4.291000	2.066500
C 0	-3.802500	-2.167000	5.396500
C 0	-4.079500	-2.020000	6.693500
C 0	-4.150500	-1.101000	9.140500
C 0	-3.953500	-0.096000	10.240500
C 0	-4.554500	-2.364000	9.239500
C 0	-4.980500	-3.120000	10.492500
H 0	2.435500	-2.125000	-1.315500
H 0	3.789500	-3.545000	-2.554500
H 0	5.647500	-2.781000	-3.634500
H 0	5.958500	-0.501000	-3.792500
H 0	4.542500	0.999000	-2.775500
H 0	0.833500	0.594000	-3.396500
H 0	-0.005500	2.080000	-4.962500
H 0	0.368500	4.311000	-4.757500
H 0	1.644500	5.081000	-2.963500
H 0	2.514500	3.609000	-1.385500
H 0	1.510500	3.773000	3.020500
H 0	0.306500	4.830000	4.724500
H 0	-1.125500	3.593000	6.055500
H 0	-1.337500	1.282000	5.712500
H 0	-0.165500	0.255000	3.971500
H 0	3.527500	1.540000	4.278500
H 0	5.134500	0.343000	5.414500
H 0	5.436500	-1.900000	5.018500
H 0	4.156500	-2.931000	3.403500
H 0	2.622500	-1.741000	2.135500
H 0	2.260500	3.000000	0.926500
H 0	3.471500	2.607000	1.900500
H 0	4.220500	0.945000	0.404500
H 0	4.028500	2.287000	-0.457500
H 0	-2.489500	-3.177000	-1.055500
H 0	-2.499500	-4.644000	-1.689500
H 0	-3.798500	-3.718000	-1.798500
H 0	-5.514500	-2.843000	-9.949500
H 0	-4.558500	-4.038000	-10.411500
H 0	-4.431500	-2.601000	-11.101500
H 0	-2.984500	-1.077000	-11.283500
H 0	-1.598500	-0.567000	-10.669500
H 0	-2.966500	0.148000	-10.256500
H 0	-3.703500	-4.535000	1.676500
H 0	-2.429500	-5.081000	2.475500
H 0	-2.246500	-3.950000	1.359500
H 0	-4.316500	-0.451000	11.075500
H 0	-4.419500	0.736000	10.008500
H 0	-2.996500	0.087000	10.349500
H 0	-4.595500	-2.689000	11.283500
H 0	-4.662500	-4.047000	10.438500
H 0	-5.958500	-3.116000	10.560500

Cartesians Coordinates for the Optimized Geometry of Complex **3** (-2066.8664987 Hartrees)

Pt	0.01092	-1.48158	0.08916
P	1.61205	-3.32611	0.04410
P	-1.66788	-3.22032	-0.15903
C	-3.13578	-3.25883	1.00353
C	-3.11817	-2.43621	2.14854
C	-4.19194	-2.47675	3.05763
C	-5.28500	-3.33200	2.82449
C	-5.30810	-4.14454	1.67375
C	-4.23758	-4.10686	0.76227
C	-2.37022	-3.38393	-1.89062
C	-2.69270	-2.19415	-2.58108
C	-3.24169	-2.25690	-3.87435
C	-3.46269	-3.50259	-4.49311
C	-3.13576	-4.68950	-3.81072
C	-2.59504	-4.63112	-2.51216
C	3.11616	-3.31930	-1.07196
C	3.40453	-4.38248	-1.95436
C	4.55579	-4.33650	-2.76361
C	5.42636	-3.23285	-2.69274
C	5.14004	-2.17095	-1.81278
C	3.98900	-2.21113	-1.00683
C	2.27784	-3.78297	1.74019
C	3.22290	-4.82005	1.89762
C	3.68669	-5.16185	3.18030
C	3.21426	-4.46523	4.31110
C	2.28287	-3.42211	4.15368
C	1.81546	-3.07818	2.87051
C	0.62181	-4.87120	-0.47634
C	-0.76553	-4.85931	0.19205
S	-4.28435	4.40673	0.00066
S	-4.92962	1.40930	0.25973
S	-7.56419	5.10473	-0.19629
S	-8.22193	2.11274	0.05580
C	-1.35348	-0.05194	0.11750
C	-2.19128	0.86060	0.11047
C	-3.14228	1.90738	0.09746
C	-2.87484	3.23743	-0.01449
C	-1.50676	3.85333	-0.14388
C	-5.58973	3.11123	0.06414
C	-6.90550	3.39585	-0.01622
C	-9.32053	4.58729	-0.42267
C	-10.26620	5.72916	-0.70369
C	-9.60995	3.27211	-0.31157
C	-10.95524	2.60057	-0.43808
S	4.64993	1.76639	-0.63613
S	4.64060	4.00317	1.46990
S	7.80412	2.58647	-1.49065
S	7.78881	4.82989	0.60838
C	1.41013	-0.09463	0.29472
C	2.24862	0.80825	0.42619
C	3.22944	1.81714	0.57274
C	3.23694	2.82256	1.48839
C	2.17849	3.07390	2.52956
C	5.59314	3.11940	0.16764
C	6.85392	3.45321	-0.17524
C	9.39706	3.45436	-1.14696
C	10.55819	2.96056	-1.97437
C	9.38963	4.44101	-0.22436
C	10.54115	5.30809	0.22195
H	-2.28815	-1.75445	2.31174
H	-4.18062	-1.83054	3.93141
H	-6.11766	-3.35486	3.52340
H	-6.15797	-4.79509	1.48217
H	-4.27816	-4.71798	-0.13612
H	-2.51341	-1.22843	-2.11566

H	-3.48970	-1.33586	-4.39516
H	-3.88164	-3.54767	-5.49550
H	-3.30129	-5.65480	-4.28326
H	-2.35046	-5.56163	-2.00559
H	2.74770	-5.24470	-2.02758
H	4.76864	-5.15780	-3.44381
H	6.31452	-3.19794	-3.31912
H	5.79853	-1.30845	-1.75542
H	3.76711	-1.37864	-0.34624
H	3.61424	-5.34457	1.02833
H	4.41756	-5.95848	3.29665
H	3.57791	-4.72684	5.30195
H	1.92771	-2.87165	5.02119
H	1.11319	-2.25797	2.74264
H	0.52248	-4.84746	-1.56825
H	1.17647	-5.77427	-0.19558
H	-0.67524	-4.92470	1.28291
H	-1.36823	-5.71389	-0.13492
H	-0.74380	3.06991	-0.11137
H	-1.31268	4.56498	0.67096
H	-1.40351	4.39781	-1.09253
H	-10.00544	6.23364	-1.64376
H	-10.22464	6.47943	0.09760
H	-11.30007	5.38027	-0.78346
H	-11.74979	3.33121	-0.61616
H	-11.20522	2.04703	0.47732
H	-10.96097	1.88432	-1.27069
H	1.76394	4.08749	2.43774
H	2.58448	2.97083	3.54533
H	1.36325	2.35453	2.40658
H	11.46317	3.54286	-1.77725
H	10.33589	3.03692	-3.04741
H	10.77912	1.90732	-1.75512
H	11.45305	5.07796	-0.33688
H	10.75241	5.16321	1.28982
H	10.31245	6.37176	0.07068

Selection of distances (Å) for the Optimized Geometry of Complex **3**

Pt-P : 2.430 or 2.443

Pt-C≡C-C : 1.976, 1.239, 1.414 or 1.981, 1.239, 1.415

TTF Central C-C distance : 1.349

Selection of angles (°) for the Optimized Geometry of Complex **3**

Pt-C≡C : 178.4 or 176.6

C≡C-C : 179.6 or 178.7

Geometry Optimization of Complex **3**⁺ : input file.

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#B3LYP/LanL2DZ opt
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cisPt dppe TTF)2 cation doublet
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1 2
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Pt	0.01092	-1.48158	0.08916
P	1.61205	-3.32611	0.04410
P	-1.66788	-3.22032	-0.15903
C	-3.13578	-3.25883	1.00353
C	-3.11817	-2.43621	2.14854
C	-4.19194	-2.47675	3.05763
C	-5.28500	-3.33200	2.82449
C	-5.30810	-4.14454	1.67375
C	-4.23758	-4.10686	0.76227
C	-2.37022	-3.38393	-1.89062

C	-2.69270	-2.19415	-2.58108
C	-3.24169	-2.25690	-3.87435
C	-3.46269	-3.50259	-4.49311
C	-3.13576	-4.68950	-3.81072
C	-2.59504	-4.63112	-2.51216
C	3.11616	-3.31930	-1.07196
C	3.40453	-4.38248	-1.95436
C	4.55579	-4.33650	-2.76361
C	5.42636	-3.23285	-2.69274
C	5.14004	-2.17095	-1.81278
C	3.98900	-2.21113	-1.00683
C	2.27784	-3.78297	1.74019
C	3.22290	-4.82005	1.89762
C	3.68669	-5.16185	3.18030
C	3.21426	-4.46523	4.31110
C	2.28287	-3.42211	4.15368
C	1.81546	-3.07818	2.87051
C	0.62181	-4.87120	-0.47634
C	-0.76553	-4.85931	0.19205
S	-4.28435	4.40673	0.00066
S	-4.92962	1.40930	0.25973
S	-7.56419	5.10473	-0.19629
S	-8.22193	2.11274	0.05580
C	-1.35348	-0.05194	0.11750
C	-2.19128	0.86060	0.11047
C	-3.14228	1.90738	0.09746
C	-2.87484	3.23743	-0.01449
C	-1.50676	3.85333	-0.14388
C	-5.58973	3.11123	0.06414
C	-6.90550	3.39585	-0.01622
C	-9.32053	4.58729	-0.42267
C	-10.26620	5.72916	-0.70369
C	-9.60995	3.27211	-0.31157
C	-10.95524	2.60057	-0.43808
S	4.64993	1.76639	-0.63613
S	4.64060	4.00317	1.46990
S	7.80412	2.58647	-1.49065
S	7.78881	4.82989	0.60838
C	1.41013	-0.09463	0.29472
C	2.24862	0.80825	0.42619
C	3.22944	1.81714	0.57274
C	3.23694	2.82256	1.48839
C	2.17849	3.07390	2.52956
C	5.59314	3.11940	0.16764
C	6.85392	3.45321	-0.17524
C	9.39706	3.45436	-1.14696
C	10.55819	2.96056	-1.97437
C	9.38963	4.44101	-0.22436
C	10.54115	5.30809	0.22195
H	-2.28815	-1.75445	2.31174
H	-4.18062	-1.83054	3.93141
H	-6.11766	-3.35486	3.52340
H	-6.15797	-4.79509	1.48217
H	-4.27816	-4.71798	-0.13612
H	-2.51341	-1.22843	-2.11566
H	-3.48970	-1.33586	-4.39516
H	-3.88164	-3.54767	-5.49550
H	-3.30129	-5.65480	-4.28326
H	-2.35046	-5.56163	-2.00559
H	2.74770	-5.24470	-2.02758
H	4.76864	-5.15780	-3.44381
H	6.31452	-3.19794	-3.31912
H	5.79853	-1.30845	-1.75542
H	3.76711	-1.37864	-0.34624
H	3.61424	-5.34457	1.02833
H	4.41756	-5.95848	3.29665
H	3.57791	-4.72684	5.30195
H	1.92771	-2.87165	5.02119

H	1.11319	-2.25797	2.74264
H	0.52248	-4.84746	-1.56825
H	1.17647	-5.77427	-0.19558
H	-0.67524	-4.92470	1.28291
H	-1.36823	-5.71389	-0.13492
H	-0.74380	3.06991	-0.11137
H	-1.31268	4.56498	0.67096
H	-1.40351	4.39781	-1.09253
H	-10.00544	6.23364	-1.64376
H	-10.22464	6.47943	0.09760
H	-11.30007	5.38027	-0.78346
H	-11.74979	3.33121	-0.61616
H	-11.20522	2.04703	0.47732
H	-10.96097	1.88432	-1.27069
H	1.76394	4.08749	2.43774
H	2.58448	2.97083	3.54533
H	1.36325	2.35453	2.40658
H	11.46317	3.54286	-1.77725
H	10.33589	3.03692	-3.04741
H	10.77912	1.90732	-1.75512
H	11.45305	5.07796	-0.33688
H	10.75241	5.16321	1.28982
H	10.31245	6.37176	0.07068

Cartesians Coordinates for the Optimized Geometry of Complex 3^+ (-2066.6758857 Hartrees)

Pt	0.00005	-1.47216	-0.00038
P	-1.63272	-3.26420	-0.22255
P	1.63259	-3.26432	0.22237
C	3.13306	-3.22721	-0.89622
C	2.95435	-2.75104	-2.21378
C	4.03673	-2.73950	-3.11085
C	5.30475	-3.18996	-2.69374
C	5.48709	-3.64629	-1.37491
C	4.40423	-3.66670	-0.47508
C	2.22711	-3.55877	1.97190
C	2.19185	-2.48384	2.88659
C	2.63553	-2.66823	4.20937
C	3.11038	-3.92507	4.62946
C	3.14465	-5.00040	3.72025
C	2.70854	-4.81804	2.39529
C	-3.13281	-3.22668	0.89653
C	-2.95340	-2.75099	2.21417
C	-4.03547	-2.73913	3.11162
C	-5.30387	-3.18879	2.69479
C	-5.48690	-3.64463	1.37590
C	-4.40435	-3.66536	0.47569
C	-2.22784	-3.55887	-1.97184
C	-2.70994	-4.81805	-2.39473
C	-3.14645	-5.00062	-3.71952
C	-3.11193	-3.92558	-4.62907
C	-2.63641	-2.66883	-4.20948
C	-2.19233	-2.48423	-2.88686
C	-0.71862	-4.86152	0.27583
C	0.71839	-4.86157	-0.27602
S	4.48180	4.17193	1.04472
S	4.93234	1.39907	-0.15507
S	7.68669	4.94399	0.49174
S	8.14889	2.17844	-0.71003
C	1.39005	-0.07940	0.18729
C	2.24796	0.80827	0.31392
C	3.22843	1.80863	0.44468
C	3.04742	3.05891	0.97733
C	1.75396	3.59809	1.52721
C	5.65785	3.00964	0.27944
C	6.96519	3.32982	0.05548
C	9.37909	4.55622	-0.11689
C	10.37170	5.67903	0.05259

C	9.58439	3.32835	-0.65052
C	10.86044	2.75893	-1.21825
S	-4.93174	1.39941	0.15563
S	-4.48242	4.17120	-1.04709
S	-8.14790	2.17900	0.71247
S	-7.68691	4.94351	-0.49216
C	-1.38987	-0.07935	-0.18836
C	-2.24776	0.80830	-0.31518
C	-3.22838	1.80852	-0.44600
C	-3.04791	3.05833	-0.97994
C	-1.75495	3.59711	-1.53140
C	-5.65774	3.00952	-0.27976
C	-6.96492	3.32980	-0.05503
C	-9.58357	3.32871	0.65302
C	-10.85913	2.75966	1.22224
C	-9.37881	4.55612	0.11813
C	-10.37166	5.67866	-0.05161
H	1.98485	-2.37392	-2.53249
H	3.89396	-2.37168	-4.12353
H	6.14242	-3.17659	-3.38643
H	6.46651	-3.98291	-1.04486
H	4.56274	-4.00667	0.54412
H	1.82344	-1.51309	2.56690
H	2.60694	-1.83513	4.90666
H	3.44900	-4.06679	5.65259
H	3.51051	-5.97310	4.03855
H	2.74699	-5.66089	1.70923
H	-1.98360	-2.37447	2.53268
H	-3.89216	-2.37169	4.12436
H	-6.14130	-3.17518	3.38778
H	-6.46661	-3.98063	1.04607
H	-4.56338	-4.00496	-0.54355
H	-2.74861	-5.66067	-1.70839
H	-3.51283	-5.97325	-4.03743
H	-3.45085	-4.06747	-5.65207
H	-2.60762	-1.83595	-4.90703
H	-1.82343	-1.51355	-2.56755
H	-0.72260	-4.89338	1.37173
H	-1.27296	-5.73632	-0.08082
H	0.72237	-4.89339	-1.37192
H	1.27266	-5.73643	0.08060
H	0.96235	2.85467	1.39727
H	1.45590	4.52121	1.01229
H	1.84068	3.82744	2.59789
H	10.48221	5.95160	1.11011
H	10.04976	6.57593	-0.49215
H	11.35757	5.39441	-0.32431
H	11.67766	3.48236	-1.15564
H	10.73486	2.48495	-2.27379
H	11.16763	1.85743	-0.67246
H	-1.45629	4.52045	-1.01721
H	-1.84272	3.82597	-2.60210
H	-0.96328	2.85369	-1.40189
H	-11.67646	3.48295	1.15962
H	-10.73270	2.48661	2.27791
H	-11.16665	1.85766	0.67746
H	-11.35719	5.39433	0.32643
H	-10.48311	5.95019	-1.10930
H	-10.04934	6.57613	0.49197

Selection of distances (Å) for the Optimized Geometry of Complex **3⁺**

Pt-P : 2.434

Pt-C≡C-C : 1.977, 1.241, 1.407

TTF Central C-C distance : 1.364

Selection of angles (°) for the Optimized Geometry of Complex **3⁺**

Pt-C≡C : 179.0

C≡C-C : 179.3

Geometry Optimization of Complex 4 : input file.

#B3LYP/LanL2DZ opt

Pt PPh3)2 TTF)2 neutre singulet

```
0 1
Pt 0 0.000000 0.000000 0.000000
P 0 0.600000 -2.220000 0.148000
S 0 -2.497000 -1.024000 4.992000
S 0 -4.509000 1.086000 5.514000
S 0 -3.530000 -2.653000 7.614000
S 0 -5.428000 -0.489000 8.231000
C 0 -0.261000 -3.309000 1.348000
C 0 -0.147000 -3.015000 2.704000
C 0 -0.775000 -3.833000 3.638000
C 0 -1.519000 -4.924000 3.241000
C 0 -1.634000 -5.223000 1.893000
C 0 -0.999000 -4.405000 0.950000
C 0 0.326000 -3.062000 -1.447000
C 0 -0.875000 -2.773000 -2.104000
C 0 -1.193000 -3.424000 -3.288000
C 0 -0.318000 -4.350000 -3.828000
C 0 0.884000 -4.621000 -3.203000
C 0 1.207000 -3.984000 -2.009000
C 0 2.357000 -2.402000 0.618000
C 0 2.910000 -3.653000 0.901000
C 0 4.245000 -3.750000 1.298000
C 0 5.017000 -2.621000 1.424000
C 0 4.472000 -1.371000 1.165000
C 0 3.145000 -1.266000 0.766000
C 0 -1.185000 -0.032000 1.609000
C 0 -1.931000 0.064000 2.570000
C 0 -2.761000 0.169000 3.721000
C 0 -3.695000 1.111000 3.955000
C 0 -4.097000 2.202000 3.011000
C 0 -3.791000 -0.439000 6.041000
C 0 -4.197000 -1.101000 7.128000
C 0 -5.571000 -1.978000 9.167000
C 0 -6.641000 -1.954000 10.235000
C 0 -4.721000 -2.954000 8.887000
C 0 -4.617000 -4.321000 9.536000
P 0 -0.600000 2.220000 -0.148000
S 0 2.497000 1.024000 -4.992000
S 0 4.509000 -1.086000 -5.514000
S 0 3.530000 2.653000 -7.614000
S 0 5.428000 0.489000 -8.231000
C 0 0.261000 3.309000 -1.348000
C 0 0.147000 3.015000 -2.704000
C 0 0.775000 3.833000 -3.638000
C 0 1.519000 4.924000 -3.241000
C 0 1.634000 5.223000 -1.893000
C 0 0.999000 4.405000 -0.950000
C 0 -0.326000 3.062000 1.447000
C 0 0.875000 2.773000 2.104000
C 0 1.193000 3.424000 3.288000
C 0 0.318000 4.350000 3.828000
C 0 -0.884000 4.621000 3.203000
C 0 -1.207000 3.984000 2.009000
C 0 -2.357000 2.402000 -0.618000
C 0 -2.910000 3.653000 -0.901000
C 0 -4.245000 3.750000 -1.298000
C 0 -5.017000 2.621000 -1.424000
```

C 0	-4.472000	1.371000	-1.165000
C 0	-3.145000	1.266000	-0.766000
C 0	1.185000	0.032000	-1.609000
C 0	1.931000	-0.064000	-2.570000
C 0	2.761000	-0.169000	-3.721000
C 0	3.695000	-1.111000	-3.955000
C 0	4.097000	-2.202000	-3.011000
C 0	3.791000	0.439000	-6.041000
C 0	4.197000	1.101000	-7.128000
C 0	5.571000	1.978000	-9.167000
C 0	6.641000	1.954000	-10.235000
C 0	4.721000	2.954000	-8.887000
C 0	4.617000	4.321000	-9.536000
H 0	0.356000	-2.261000	2.989000
H 0	-0.691000	-3.638000	4.564000
H 0	-1.952000	-5.467000	3.889000
H 0	-2.138000	-5.977000	1.611000
H 0	-1.077000	-4.608000	0.025000
H 0	-1.474000	-2.132000	-1.738000
H 0	-2.013000	-3.233000	-3.729000
H 0	-0.545000	-4.800000	-4.634000
H 0	1.490000	-5.242000	-3.589000
H 0	2.029000	-4.179000	-1.576000
H 0	2.379000	-4.436000	0.823000
H 0	4.622000	-4.602000	1.483000
H 0	5.926000	-2.695000	1.688000
H 0	5.005000	-0.590000	1.261000
H 0	2.773000	-0.410000	0.590000
H 0	-3.561000	2.141000	2.194000
H 0	-3.949000	3.073000	3.436000
H 0	-5.046000	2.106000	2.787000
H 0	-6.724000	-2.845000	10.633000
H 0	-7.497000	-1.695000	9.834000
H 0	-6.396000	-1.307000	10.929000
H 0	-5.261000	-4.382000	10.274000
H 0	-3.710000	-4.449000	9.884000
H 0	-4.814000	-5.014000	8.872000
H 0	-0.356000	2.261000	-2.989000
H 0	0.691000	3.638000	-4.564000
H 0	1.952000	5.467000	-3.889000
H 0	2.138000	5.977000	-1.611000
H 0	1.077000	4.608000	-0.025000
H 0	1.474000	2.132000	1.738000
H 0	2.013000	3.233000	3.729000
H 0	0.545000	4.800000	4.634000
H 0	-1.490000	5.242000	3.589000
H 0	-2.029000	4.179000	1.576000
H 0	-2.379000	4.436000	-0.823000
H 0	-4.622000	4.602000	-1.483000
H 0	-5.926000	2.695000	-1.688000
H 0	-5.005000	0.590000	-1.261000
H 0	-2.773000	0.410000	-0.590000
H 0	3.561000	-2.141000	-2.194000
H 0	3.949000	-3.073000	-3.436000
H 0	5.046000	-2.106000	-2.787000
H 0	6.724000	2.845000	-10.633000
H 0	7.497000	1.695000	-9.834000
H 0	6.396000	1.307000	-10.929000
H 0	5.261000	4.382000	-10.274000
H 0	3.710000	4.449000	-9.884000
H 0	4.814000	5.014000	-8.872000

Cartesians Coordinates for the Optimized Geometry of Complex **4** (-2451.4764955 Hartrees)

Pt	0.00000	0.00000	0.00000
P	0.33848	-2.39836	0.08242

S	-2.30944	-0.77278	5.10353
S	-5.24568	0.13076	5.17255
S	-2.61942	-2.00718	8.22221
S	-5.55353	-1.09361	8.29240
C	-1.00178	-3.45076	0.87250
C	-1.23131	-3.35207	2.26194
C	-2.24821	-4.10911	2.86729
C	-3.05060	-4.96654	2.08914
C	-2.82945	-5.06143	0.70281
C	-1.80906	-4.30549	0.09404
C	0.57352	-3.18681	-1.60520
C	-0.14616	-2.66904	-2.70193
C	-0.02694	-3.26490	-3.97009
C	0.81824	-4.37640	-4.15226
C	1.54467	-4.88818	-3.06059
C	1.42205	-4.29675	-1.78899
C	1.88818	-2.80798	1.06218
C	2.04590	-4.05600	1.70310
C	3.22699	-4.34243	2.41246
C	4.25842	-3.38656	2.48483
C	4.10149	-2.14053	1.84812
C	2.92101	-1.84942	1.13994
C	-1.36231	-0.07598	1.47734
C	-2.18528	-0.07915	2.40687
C	-3.05423	-0.11624	3.52257
C	-4.35207	0.28510	3.57760
C	-5.14515	0.86984	2.43913
C	-3.87005	-0.69899	6.06671
C	-3.99633	-1.18916	7.31687
C	-4.93490	-2.11304	9.70076
C	-5.96898	-2.37989	10.76687
C	-3.64511	-2.51452	9.67048
C	-2.89897	-3.33246	10.69573
P	-0.33848	2.39836	-0.08242
S	2.30944	0.77278	-5.10353
S	5.24568	-0.13076	-5.17255
S	2.61942	2.00718	-8.22221
S	5.55353	1.09361	-8.29240
C	1.00178	3.45076	-0.87250
C	1.23131	3.35207	-2.26194
C	2.24821	4.10911	-2.86729
C	3.05060	4.96654	-2.08914
C	2.82945	5.06143	-0.70281
C	1.80906	4.30549	-0.09404
C	-0.57352	3.18681	1.60520
C	0.14616	2.66904	2.70193
C	0.02694	3.26490	3.97009
C	-0.81824	4.37640	4.15226
C	-1.54467	4.88818	3.06059
C	-1.42205	4.29675	1.78899
C	-1.88818	2.80798	-1.06218
C	-2.04590	4.05600	-1.70310
C	-3.22699	4.34243	-2.41246
C	-4.25842	3.38656	-2.48483
C	-4.10149	2.14053	-1.84812
C	-2.92101	1.84942	-1.13994
C	1.36231	0.07598	-1.47734
C	2.18528	0.07915	-2.40687
C	3.05423	0.11624	-3.52257
C	4.35207	-0.28510	-3.57760
C	5.14515	-0.86984	-2.43913
C	3.87005	0.69899	-6.06671
C	3.99633	1.18916	-7.31687
C	4.93490	2.11304	-9.70076
C	5.96898	2.37989	-10.76687
C	3.64511	2.51452	-9.67048
C	2.89897	3.33246	-10.69573
H	-0.63282	-2.68249	2.87193

H	-2.42137	-4.00990	3.93523
H	-3.84160	-5.54726	2.55790
H	-3.44536	-5.71894	0.09383
H	-1.64725	-4.39311	-0.97606
H	-0.77296	-1.79084	-2.57332
H	-0.57511	-2.85120	-4.81240
H	0.92044	-4.82840	-5.13596
H	2.20858	-5.73852	-3.19635
H	1.99928	-4.69285	-0.95860
H	1.24981	-4.79474	1.66843
H	3.33748	-5.30434	2.90718
H	5.16932	-3.60786	3.03613
H	4.89013	-1.39433	1.90636
H	2.79876	-0.88452	0.65605
H	-4.49889	0.99077	1.56499
H	-5.55430	1.85484	2.70368
H	-5.98790	0.22054	2.16326
H	-5.54677	-2.95406	11.59687
H	-6.81655	-2.94733	10.35969
H	-6.36470	-1.43953	11.17415
H	-3.53245	-3.56649	11.55641
H	-2.01763	-2.78989	11.06393
H	-2.54876	-4.28030	10.26533
H	0.63282	2.68249	-2.87193
H	2.42137	4.00990	-3.93523
H	3.84160	5.54726	-2.55790
H	3.44536	5.71894	-0.09383
H	1.64725	4.39311	0.97606
H	0.77296	1.79084	2.57332
H	0.57511	2.85120	4.81240
H	-0.92044	4.82840	5.13596
H	-2.20858	5.73852	3.19635
H	-1.99928	4.69285	0.95860
H	-1.24981	4.79474	-1.66843
H	-3.33748	5.30434	-2.90718
H	-5.16932	3.60786	-3.03613
H	-4.89013	1.39433	-1.90636
H	-2.79876	0.88452	-0.65605
H	4.49889	-0.99077	-1.56499
H	5.55430	-1.85484	-2.70368
H	5.98790	-0.22054	-2.16326
H	5.54677	2.95406	-11.59687
H	6.81655	2.94733	-10.35969
H	6.36470	1.43953	-11.17415
H	3.53245	3.56649	-11.55641
H	2.01763	2.78989	-11.06393
H	2.54876	4.28030	-10.26533

Selection of distances (Å) for the Optimized Geometry of Complex **4**

Pt-P : 2.424

Pt-C≡C-C : 2.011, 1.242, 1.415

TTF Central C-C distance : 1.349

Selection of angles (°) for the Optimized Geometry of Complex **4**

Pt-C≡C : 177.7

C≡C-C : 176.1

Geometry Optimization of Complex **4**⁺ : input file.

#B3LYP/LanL2DZ opt

Pt PPh3)2 TTF)2 cation doublet

	1	2	
Pt	0.00000	0.00000	0.00000
P	0.33848	-2.39836	0.08242
S	-2.30944	-0.77278	5.10353
S	-5.24568	0.13076	5.17255
S	-2.61942	-2.00718	8.22221
S	-5.55353	-1.09361	8.29240
C	-1.00178	-3.45076	0.87250
C	-1.23131	-3.35207	2.26194
C	-2.24821	-4.10911	2.86729
C	-3.05060	-4.96654	2.08914
C	-2.82945	-5.06143	0.70281
C	-1.80906	-4.30549	0.09404
C	0.57352	-3.18681	-1.60520
C	-0.14616	-2.66904	-2.70193
C	-0.02694	-3.26490	-3.97009
C	0.81824	-4.37640	-4.15226
C	1.54467	-4.88818	-3.06059
C	1.42205	-4.29675	-1.78899
C	1.88818	-2.80798	1.06218
C	2.04590	-4.05600	1.70310
C	3.22699	-4.34243	2.41246
C	4.25842	-3.38656	2.48483
C	4.10149	-2.14053	1.84812
C	2.92101	-1.84942	1.13994
C	-1.36231	-0.07598	1.47734
C	-2.18528	-0.07915	2.40687
C	-3.05423	-0.11624	3.52257
C	-4.35207	0.28510	3.57760
C	-5.14515	0.86984	2.43913
C	-3.87005	-0.69899	6.06671
C	-3.99633	-1.18916	7.31687
C	-4.93490	-2.11304	9.70076
C	-5.96898	-2.37989	10.76687
C	-3.64511	-2.51452	9.67048
C	-2.89897	-3.33246	10.69573
P	-0.33848	2.39836	-0.08242
S	2.30944	0.77278	-5.10353
S	5.24568	-0.13076	-5.17255
S	2.61942	2.00718	-8.22221
S	5.55353	1.09361	-8.29240
C	1.00178	3.45076	-0.87250
C	1.23131	3.35207	-2.26194
C	2.24821	4.10911	-2.86729
C	3.05060	4.96654	-2.08914
C	2.82945	5.06143	-0.70281
C	1.80906	4.30549	-0.09404
C	-0.57352	3.18681	1.60520
C	0.14616	2.66904	2.70193
C	0.02694	3.26490	3.97009
C	-0.81824	4.37640	4.15226
C	-1.54467	4.88818	3.06059
C	-1.42205	4.29675	1.78899
C	-1.88818	2.80798	-1.06218
C	-2.04590	4.05600	-1.70310
C	-3.22699	4.34243	-2.41246
C	-4.25842	3.38656	-2.48483
C	-4.10149	2.14053	-1.84812
C	-2.92101	1.84942	-1.13994
C	1.36231	0.07598	-1.47734
C	2.18528	0.07915	-2.40687
C	3.05423	0.11624	-3.52257
C	4.35207	-0.28510	-3.57760
C	5.14515	-0.86984	-2.43913
C	3.87005	0.69899	-6.06671
C	3.99633	1.18916	-7.31687
C	4.93490	2.11304	-9.70076
C	5.96898	2.37989	-10.76687

C	3.64511	2.51452	-9.67048
C	2.89897	3.33246	-10.69573
H	-0.63282	-2.68249	2.87193
H	-2.42137	-4.00990	3.93523
H	-3.84160	-5.54726	2.55790
H	-3.44536	-5.71894	0.09383
H	-1.64725	-4.39311	-0.97606
H	-0.77296	-1.79084	-2.57332
H	-0.57511	-2.85120	-4.81240
H	0.92044	-4.82840	-5.13596
H	2.20858	-5.73852	-3.19635
H	1.99928	-4.69285	-0.95860
H	1.24981	-4.79474	1.66843
H	3.33748	-5.30434	2.90718
H	5.16932	-3.60786	3.03613
H	4.89013	-1.39433	1.90636
H	2.79876	-0.88452	0.65605
H	-4.49889	0.99077	1.56499
H	-5.55430	1.85484	2.70368
H	-5.98790	0.22054	2.16326
H	-5.54677	-2.95406	11.59687
H	-6.81655	-2.94733	10.35969
H	-6.36470	-1.43953	11.17415
H	-3.53245	-3.56649	11.55641
H	-2.01763	-2.78989	11.06393
H	-2.54876	-4.28030	10.26533
H	0.63282	2.68249	-2.87193
H	2.42137	4.00990	-3.93523
H	3.84160	5.54726	-2.55790
H	3.44536	5.71894	-0.09383
H	1.64725	4.39311	0.97606
H	0.77296	1.79084	2.57332
H	0.57511	2.85120	4.81240
H	-0.92044	4.82840	5.13596
H	-2.20858	5.73852	3.19635
H	-1.99928	4.69285	0.95860
H	-1.24981	4.79474	-1.66843
H	-3.33748	5.30434	-2.90718
H	-5.16932	3.60786	-3.03613
H	-4.89013	1.39433	-1.90636
H	-2.79876	0.88452	-0.65605
H	4.49889	-0.99077	-1.56499
H	5.55430	-1.85484	-2.70368
H	5.98790	-0.22054	-2.16326
H	5.54677	2.95406	-11.59687
H	6.81655	2.94733	-10.35969
H	6.36470	1.43953	-11.17415
H	3.53245	3.56649	-11.55641
H	2.01763	2.78989	-11.06393
H	2.54876	4.28030	-10.26533

Cartesians Coordinates for the Optimized Geometry of Complex 4^+ (-2451.2846444 Hartrees)

Pt	0.00000	0.00000	0.00000
P	0.40055	-2.40197	0.01610
S	-2.39609	-1.05183	5.04600
S	-5.27338	-0.03219	5.08211
S	-2.75751	-2.15396	8.19379
S	-5.62890	-1.11870	8.22924
C	-0.92323	-3.48598	0.78873
C	-1.06799	-3.51308	2.19275
C	-2.06849	-4.30246	2.78449
C	-2.94092	-5.06117	1.97964
C	-2.80474	-5.02746	0.57978
C	-1.79923	-4.24254	-0.01622
C	0.61550	-3.12347	-1.70297
C	-0.16136	-2.59999	-2.75798
C	-0.06846	-3.15525	-4.04669

C	0.80764	-4.23052	-4.29127
C	1.59143	-4.74621	-3.24182
C	1.49500	-4.19684	-1.94914
C	1.96168	-2.80623	0.97361
C	2.18345	-4.09930	1.49741
C	3.37215	-4.38452	2.19351
C	4.34643	-3.38309	2.37121
C	4.12503	-2.09278	1.85338
C	2.93713	-1.80328	1.15660
C	-1.34092	-0.15524	1.47406
C	-2.16645	-0.20392	2.40348
C	-3.04887	-0.27139	3.49481
C	-4.34087	0.18726	3.53954
C	-5.07143	0.86493	2.41167
C	-3.93777	-0.86825	5.99697
C	-4.08710	-1.31125	7.27706
C	-5.01159	-1.96244	9.74461
C	-6.02125	-2.04495	10.86205
C	-3.73834	-2.42250	9.72935
C	-2.99090	-3.14051	10.82505
P	-0.40055	2.40197	-0.01610
S	2.39609	1.05183	-5.04600
S	5.27338	0.03219	-5.08211
S	2.75751	2.15396	-8.19379
S	5.62890	1.11870	-8.22924
C	0.92323	3.48598	-0.78873
C	1.06799	3.51308	-2.19275
C	2.06849	4.30246	-2.78449
C	2.94092	5.06117	-1.97964
C	2.80474	5.02746	-0.57978
C	1.79923	4.24254	0.01622
C	-0.61550	3.12347	1.70297
C	0.16136	2.59999	2.75798
C	0.06846	3.15525	4.04669
C	-0.80764	4.23052	4.29127
C	-1.59143	4.74621	3.24182
C	-1.49500	4.19684	1.94914
C	-1.96168	2.80623	-0.97361
C	-2.18345	4.09930	-1.49741
C	-3.37215	4.38452	-2.19351
C	-4.34643	3.38309	-2.37121
C	-4.12503	2.09278	-1.85338
C	-2.93713	1.80328	-1.15660
C	1.34092	0.15524	-1.47406
C	2.16645	0.20392	-2.40348
C	3.04887	0.27139	-3.49481
C	4.34087	-0.18726	-3.53954
C	5.07143	-0.86493	-2.41167
C	3.93777	0.86825	-5.99697
C	4.08710	1.31125	-7.27706
C	5.01159	1.96244	-9.74461
C	6.02125	2.04495	-10.86205
C	3.73834	2.42250	-9.72935
C	2.99090	3.14051	-10.82505
H	-0.40674	-2.92592	2.82411
H	-2.17007	-4.31614	3.86612
H	-3.71533	-5.67079	2.43850
H	-3.47186	-5.61182	-0.04877
H	-1.69910	-4.23848	-1.09732
H	-0.82045	-1.75400	-2.58079
H	-0.66831	-2.74458	-4.85457
H	0.88349	-4.65651	-5.28857
H	2.27435	-5.57183	-3.42529
H	2.11197	-4.60064	-1.15204
H	1.43139	-4.87541	1.38378
H	3.53394	-5.38115	2.59600
H	5.26267	-3.60463	2.91272
H	4.86852	-1.31269	1.99663

H	2.76506	-0.80403	0.76680
H	-4.40341	0.97526	1.55367
H	-5.42063	1.86327	2.70697
H	-5.94811	0.28269	2.09718
H	-5.60387	-2.55474	11.73438
H	-6.91562	-2.59721	10.54587
H	-6.34111	-1.04391	11.17912
H	-3.62017	-3.27609	11.70870
H	-2.10008	-2.57644	11.13060
H	-2.66068	-4.13317	10.49253
H	0.40674	2.92592	-2.82411
H	2.17007	4.31614	-3.86612
H	3.71533	5.67079	-2.43850
H	3.47186	5.61182	0.04877
H	1.69910	4.23848	1.09732
H	0.82045	1.75400	2.58079
H	0.66831	2.74458	4.85457
H	-0.88349	4.65651	5.28857
H	-2.27435	5.57183	3.42529
H	-2.11197	4.60064	1.15204
H	-1.43139	4.87541	-1.38378
H	-3.53394	5.38115	-2.59600
H	-5.26267	3.60463	-2.91272
H	-4.86852	1.31269	-1.99663
H	-2.76506	0.80403	-0.76680
H	4.40341	-0.97526	-1.55367
H	5.42063	-1.86327	-2.70697
H	5.94811	-0.28269	-2.09718
H	5.60387	2.55474	-11.73438
H	6.91562	2.59721	-10.54587
H	6.34111	1.04391	-11.17912
H	3.62017	3.27609	-11.70870
H	2.10008	2.57644	-11.13060
H	2.66068	4.13317	-10.49253

Selection of distances (Å) for the Optimized Geometry of Complex 4⁺

Pt-P : 2.435

Pt-C≡C-C : 1.999, 1.244, 1.405

TTF Central C-C distance : 1.363

Selection of angles (°) for the Optimized Geometry of Complex 4⁺

Pt-C≡C : 177.7

C≡C-C : 177.3