

Supporting information

C-H activation of 2,4,6-triphenylphosphinine: Synthesis and characterization of the first homoleptic phosphinine-Ir(III) complexes *fac*-[Ir(C[^]P)₃]

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I. Synthesis

All experiments were performed under an inert argon atmosphere, using standard Schlenk techniques or in a MBraun dry box. All glassware was dried prior to use to remove traces of water. The ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer and chemical shifts are reported relative to residual proton resonance of the deuterated solvents. The mass characterization has been performed by positive mode reflection MALDI-TOF using a Voyager-DE PRO instrument. Elemental analysis were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr (Germany).

fac-[tris-(2-phenylene-κC²-4,6-diphenylphosphinine-κP)iridium(III)] **2**:

In a hydrothermal autoclave (acid digestion bomb) [Ir(acac)₃] (50.8 mg, 0.10 mmol, 1.0 equiv) and 2,4,6-triphenylphosphinine (100.6 mg, 0.31 mmol, 3.0 equiv) were added and heated at 220°C for 63 hours, to obtain [Ir(C[^]P)₃] **2** as a yellow-brown solid (96.8 mg, 80.6%). This solid was dissolved in dichloromethane and purified by filtration over Celite and silica gel. After removal of the solvent, orange crystals were formed by slowly diffusing Et₂O out of a mixture of [Ir(C[^]P)₃] in toluene/Et₂O (91.0 mg, 75.7%). ¹H NMR (400.16 MHz, CD₂Cl₂, 25°C): 6.45 (6H, d, ³J_{(H,H)}} = 8.0 Hz, H_{arom}), 6.83-6.88 (12H, m, H_{arom}), 7.08 (3H, dd, ³J_{(H,H)}} = 7.4 Hz, ³J_{(H,H)}} = 7.4 Hz, H_{arom}), 7.20 (3H, ddd, ³J_{(H,H)}} = 8.0 Hz, J_{(H,H)}} = 4.0 Hz, J_{(H,H)}}

= 4.0 Hz, H_{arom}), 7.41-7.46 (3H, m, H_{arom}), 7.51-7.59 (9H, m, H_{arom}), 7.66-7.70 (6H, m, H_{arom}), 8.05 (3H, br d, $^3J_{\text{(H,P)}} = 8.0$ Hz, H_{β}), 8.45-8.54 (3H, m, H_{β}) ppm. ^{13}C NMR (100.63 MHz, CD_2Cl_2 , 25°C): 121.6 (dd, $J_{\text{(C,P)}} = 14.4$ Hz, $J_{\text{(C,P)}} = 8.1$ Hz), 123.6, 126.9, 127.6 (br s), 127.6, 128.0 (dd, $J_{\text{(C,P)}} = 6.8$ Hz, $J_{\text{(C,P)}} = 3.9$ Hz), 128.4 (dd, $J_{\text{(C,P)}} = 5.4$ Hz, $J_{\text{(C,P)}} = 3.4$ Hz), 129.0, 129.4 (br s), 134.9-135.1 (m), 136.2 (br), 139.3 (dd, $J_{\text{(C,P)}} = 8.2$ Hz, $J_{\text{(C,P)}} = 4.2$ Hz), 139.9 (dd, $J_{\text{(C,P)}} = 17.1$ Hz, $J_{\text{(C,P)}} = 9.0$ Hz), 142.4 (br s), 143.9 (dd, $J_{\text{(C,P)}} = 21.1$ Hz, $J_{\text{(C,P)}} = 11.1$ Hz), 152.6-153.0 (m), 153.7-154.1 (m), 156.1-156.4 (m), 165.2-165.8 (m) ppm. ^{31}P NMR (162.00 MHz, CD_2Cl_2 , 25°C): $\delta = +167.6$ ppm. MALDI-TOF (m/z): 1160.21 g/mol [M⁺]. Elemental analysis calcd (%) for $\text{C}_{69}\text{H}_{48}\text{IrP}_3$ (1162.26 g/mol): C 71.30, H 4.16; found: C 70.77, H 4.22.

II. Characterizations

a) *X-ray crystal structure determination of 2*: $\text{C}_{69}\text{H}_{48}\text{IrP}_3$ + disordered solvent, Fw = 1162.18^[*], pale brown needle, 0.21 x 0.10 x 0.08 mm³, monoclinic, P2₁ (no. 4), a = 13.7200(12), b = 13.5181(12), c = 51.965(5) Å, $\beta = 92.2338(19)^\circ$, V = 9630.4(15) Å³, Z = 6, $D_x = 1.202$ g/cm³^[*], $\mu = 2.19$ mm⁻¹^[*]. 140000 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073$ Å) up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.56$ Å⁻¹ at a temperature of 150(2) K. Intensity data were integrated with the Saint software.^[1] Absorption correction and scaling was performed based on multiple measured reflections with SADABS^[2] (0.66-0.74 correction range). 27578 Reflections were unique ($R_{\text{int}} = 0.071$), of which 24091 were observed [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using the program SHELXS-97^[3] and refined with SHELXL-97^[3] against F^2 of all reflections. Non hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. The crystal structure contains solvent accessible voids (2514 Å³ / unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of PLATON^[4] resulting in 772 electrons / unit cell). Two of the phenyl substituents were refined with a disorder model for different orientations. 2065 Parameters were refined with 277 restraints (concerning the disordered phenyl groups). R1/wR2 [$I > 2\sigma(I)$]: 0.0401 / 0.0762. R1/wR2 [all refl.]: 0.0503 / 0.0785. S = 1.023. Flack parameter x = 0.022(3).^[5] Residual electron density between -1.15 and 0.99 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.^[4]

CCDC 833934 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[*] derived values do not contain the contribution of the disordered solvent.

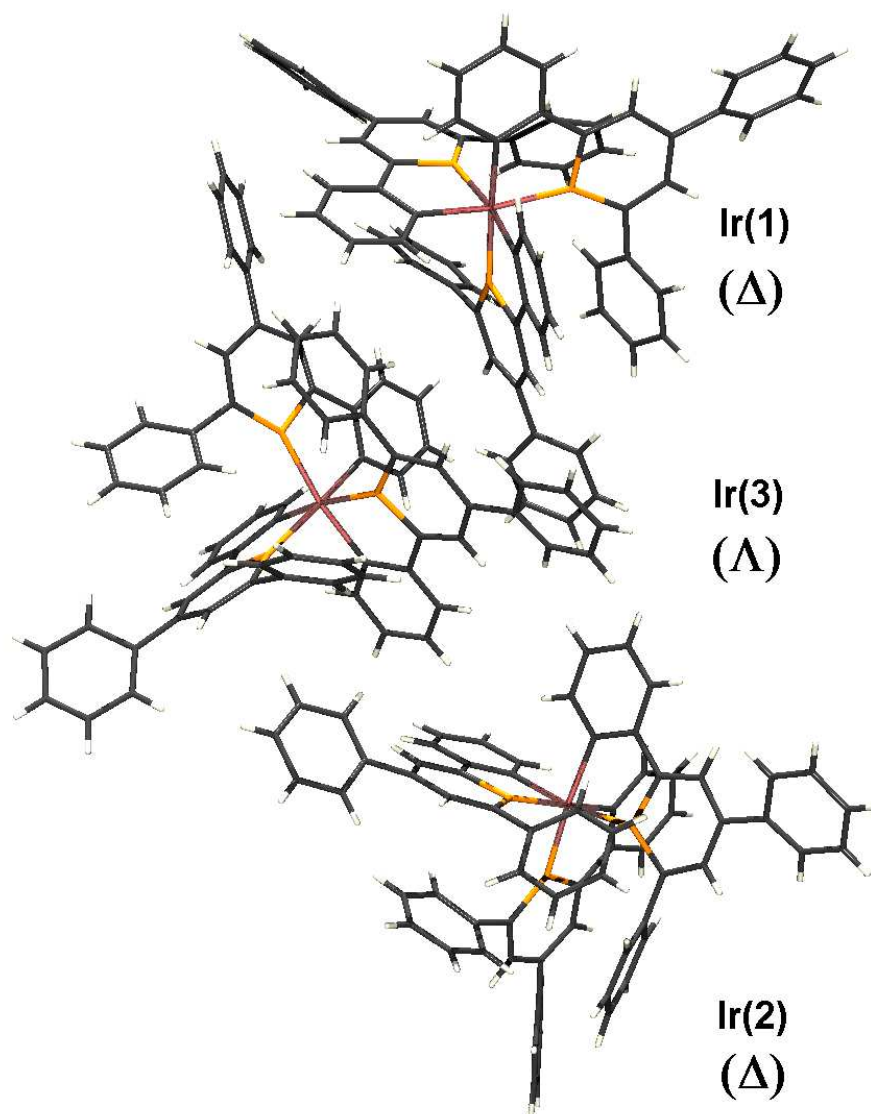


Figure S1: Molecular structures of **2** in the crystal.

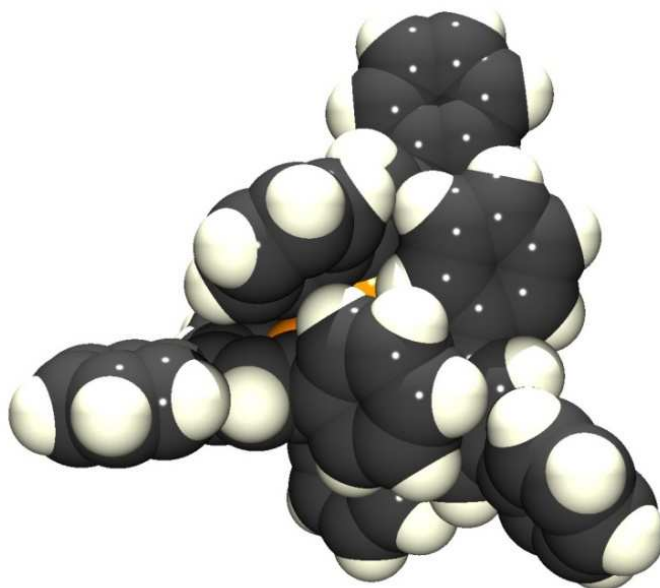


Figure S2: Space-filling model of **2** in the crystal.

b) Determination of optical data: UV-Visible spectra were recorded at room temperature on a UVIKON 942 spectrophotometer. The UV-Vis-NIR emission and excitation spectra measurements were recorded on a FL 920 Edinburgh Instrument equipped with a Hamamatsu R5509-73 photomultiplier for the NIR domain (300-1700 nm) and corrected for the response of the photomultiplier.

c) Cyclic voltammetry measurements: The electrochemical studies were carried out under argon using an Eco Chemie Autolab PGSTAT 30 potentiostat for cyclic voltammetry with the three-electrode configuration: the working electrode was a platinum disk, the reference electrode a saturated calomel electrode and the counter-electrode a platinum wire. All potential were internally referenced to the ferrocene/ferrocenium couple. For the measurements concentrations of 10^{-3} M of the electroactive species were used in freshly distilled and degassed dichloromethane (*Lichrosolv*, Merck) and 0.2 M tetrabutylammonium hexafluorophosphate (TBAHFP, Fluka) which was twice recrystallized from ethanol and dried under vacuum prior to use.

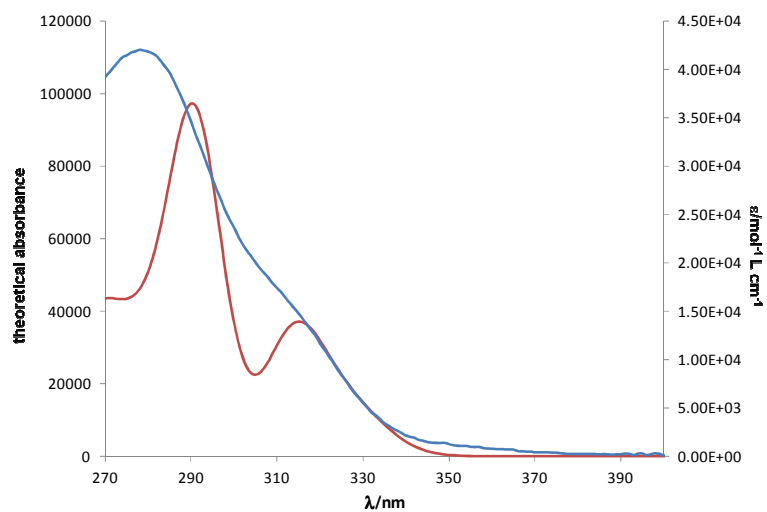


Figure S3. Absorption spectra of **1** (continuous blue line) in CH_2Cl_2 and TD-DFT simulated spectrum of **1** (continuous red line).

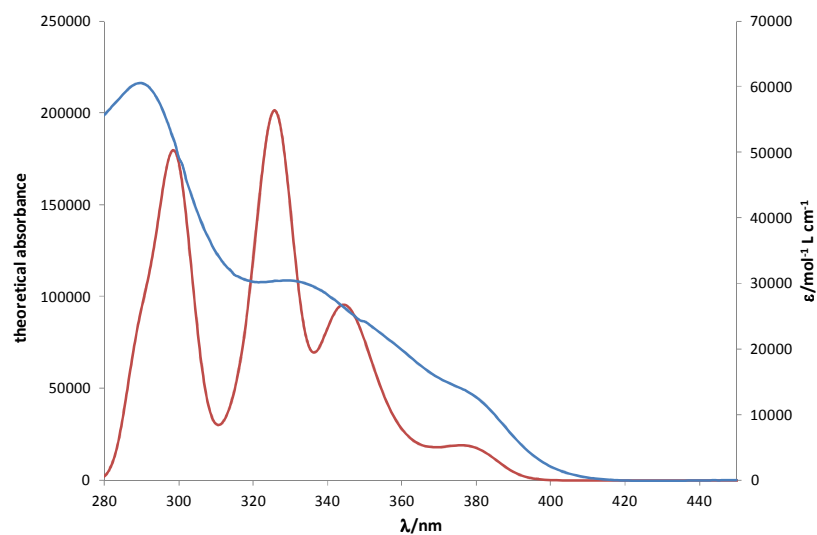


Figure S4. Absorption spectra of **2** (continuous blue line) in CH_2Cl_2 and TD-DFT simulated spectrum of **2** (continuous red line).

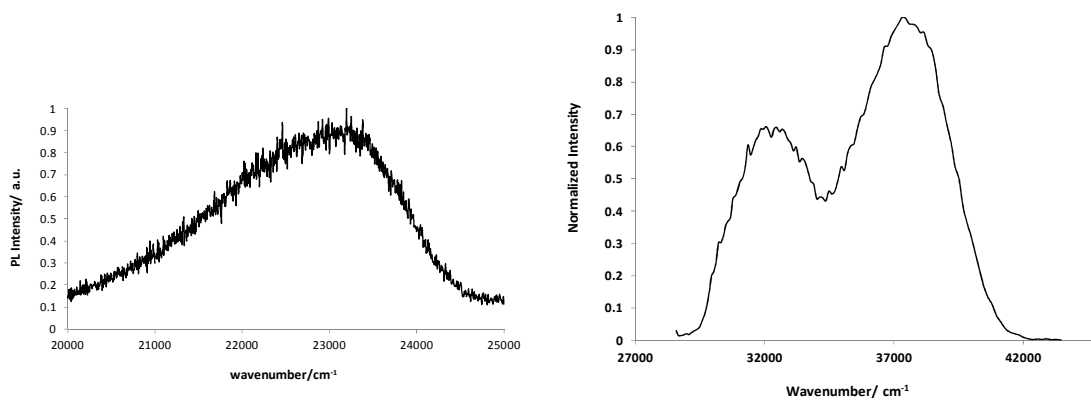


Figure S5. Emission ($\lambda_{\text{ex}} = 315$ nm, left) and excitation (right) spectra and of the ligand **1** recorded in CH_2Cl_2 at 298 K.

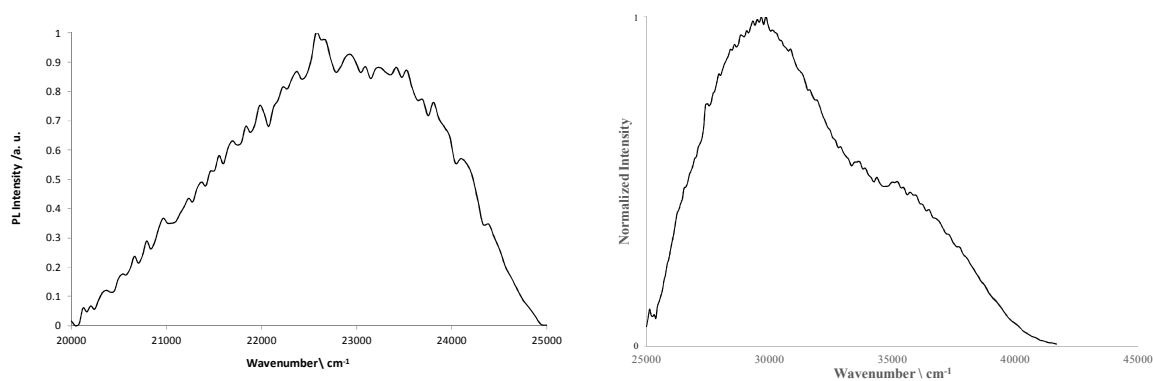


Figure S6. Emission ($\lambda_{\text{ex}} = 390$ nm, left) and excitation (right) spectra of complex **2** recorded in CH_2Cl_2 at 298 K.

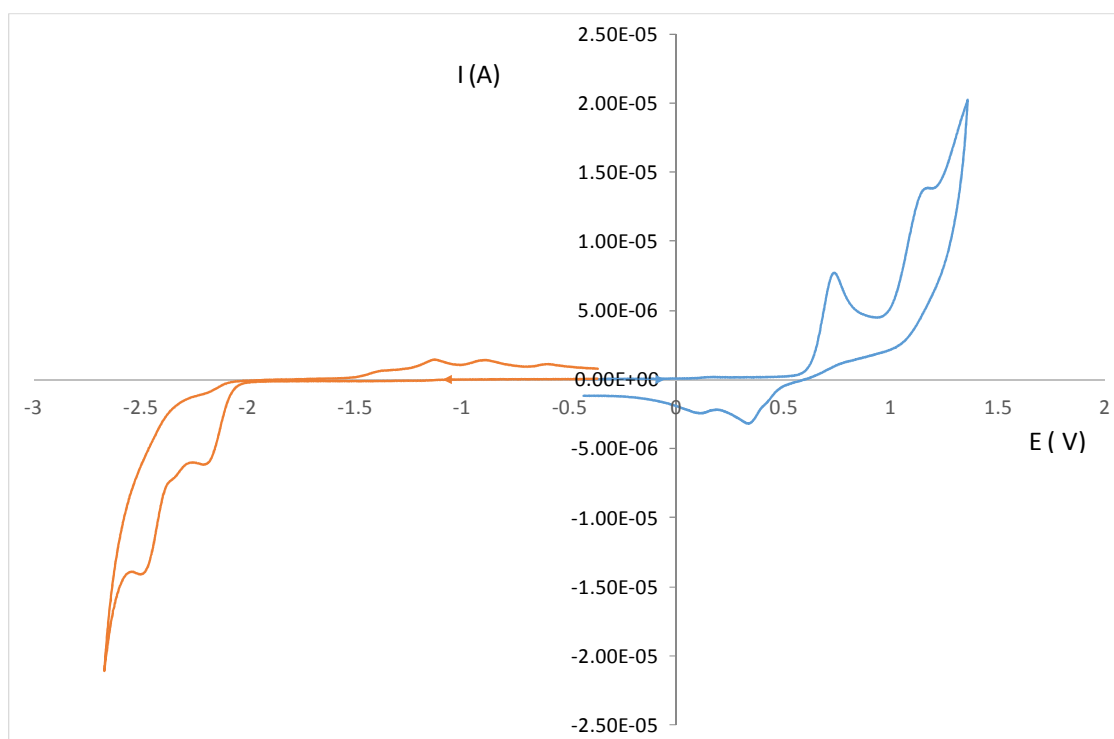


Figure S7. Cyclic voltammogram of complex **2** ($c = 1 \times 10^{-3}$ M) in CH_2Cl_2 .

III. Theoretical Calculations

DFT and TDDFT calculations were performed using the PBE1PBE functional^[6] and the double zeta LANL2DZ basis set augmented with polarization functions on all atoms (except hydrogen ones) and a diffuse *d* AO on iridium atom. The gaussian09 package^[7] has been used. The solvent effect (CH_2Cl_2) has been taken into account using the PCM model.^[8]

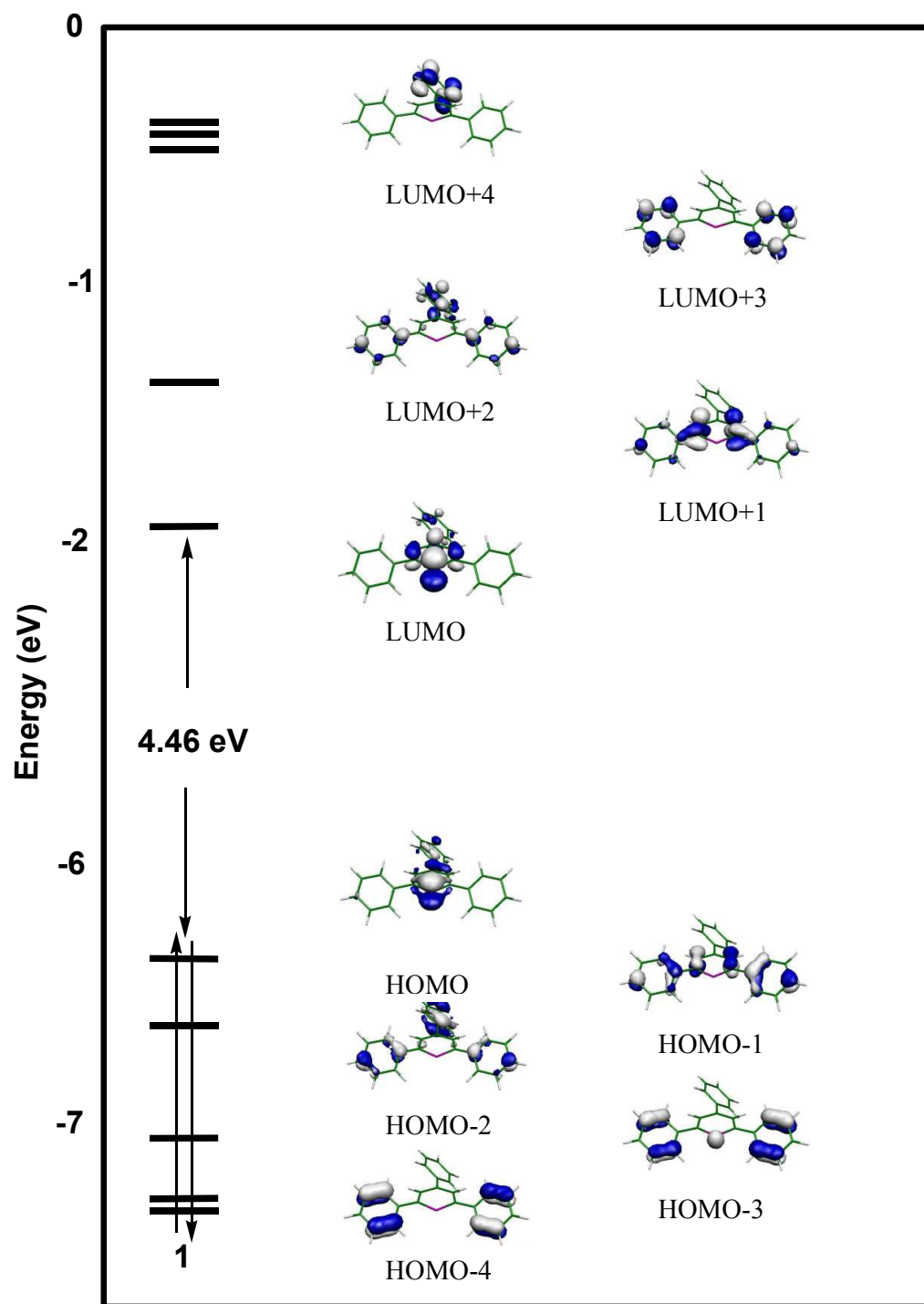


Figure S6. Frontier MOs diagram of ligand 1

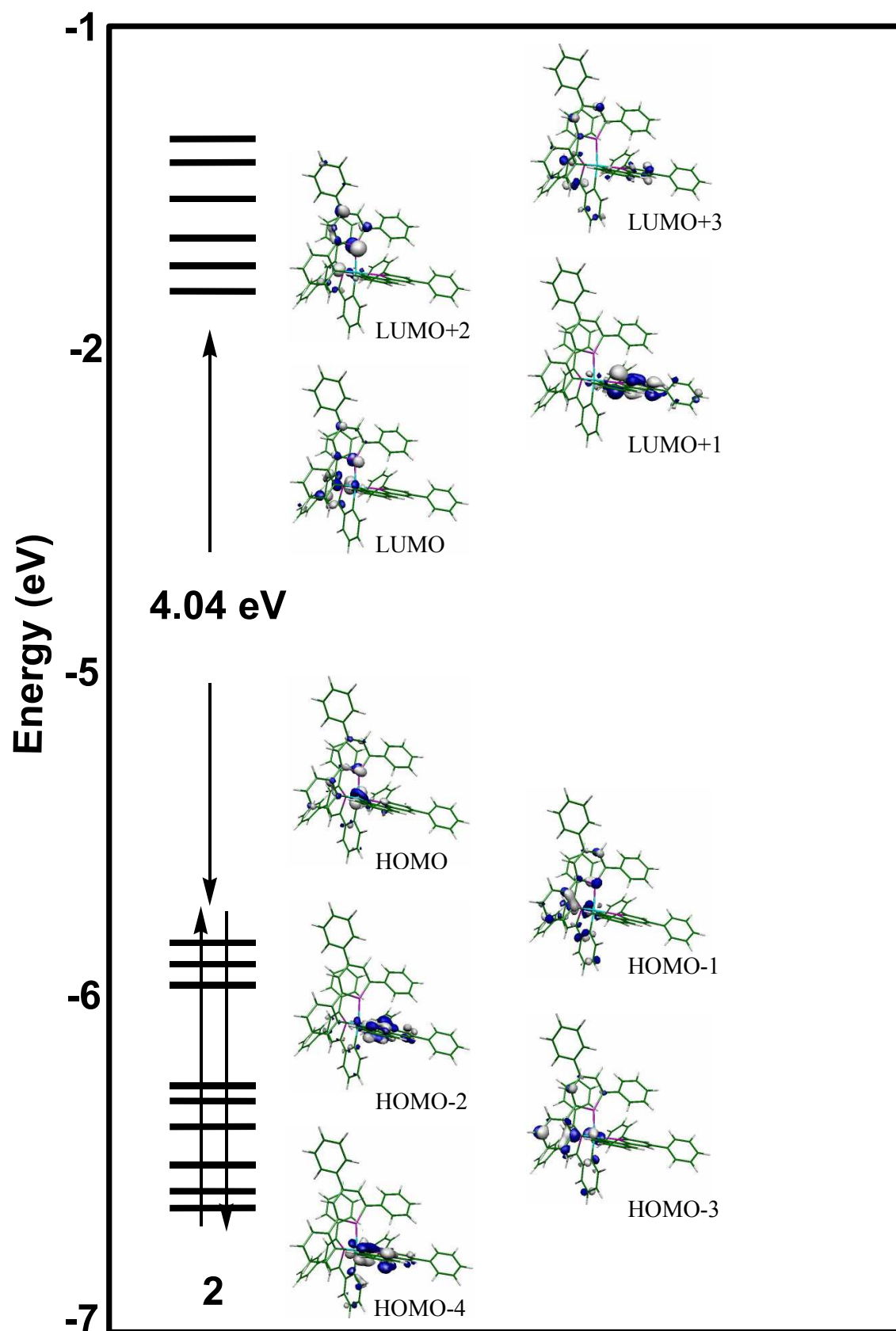


Figure S7. Frontier MOs diagram of complex 2

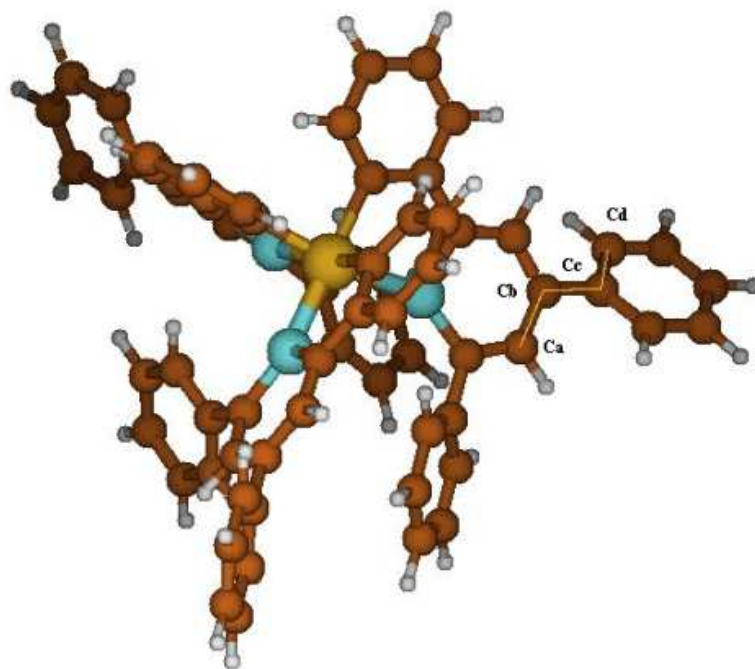


Figure S8: Optimized structure of complex **2**.

Table S1. Optimized and X-ray geometrical parameters (Distances in Å and angles in deg) of complex **2**.

Bond length (Å)	Optimized	X-ray
Ir-P	2.31-2.32	2.259(2)-2.2798(16)
Ir-C	2.10-2.11	2.129(7)-2.158(7)
Angle (°)		
P-Ir-P	99-102	98.35(7)-102.55(7)
P-Ir-C	80-89	78.54(19)-91.21(16)
P _{al} -Ir-C _{al}	170-171	168.53(17)-171.46(19)
C-Ir-C	91-92	89.5(2)-93.8(3)
Dihedral angle (°)		
C _a -C _b -C _c -C _d	140	124.20-172.82

Optimized geometries in xyz coordinates (in angstroms)

Compound 1

E = -892.235180187 a. u. (PBE1PBE/LANL2DZ+pol.)

Atom	X	Y	Z (Angstrom)
C	-0.991099	4.966309	0.521310
C	-0.986767	3.568909	0.573730
C	-0.009006	2.823850	-0.112810
C	0.963053	3.520052	-0.856400
C	0.956711	4.917332	-0.913070
C	-0.019711	5.647930	-0.223460
C	-0.004663	1.340270	-0.051950
C	-1.228372	0.647348	-0.051640
C	-1.362390	-0.744522	-0.012870
P	0.006362	-1.857250	0.071330
C	-2.722059	-1.342564	-0.008670
C	-2.999347	-2.517515	-0.733840
C	-4.277516	-3.085537	-0.717380
C	-5.304747	-2.490558	0.026090
C	-5.040779	-1.322188	0.753720
C	-3.763290	-0.754376	0.736920
C	1.223258	0.656542	-0.013370
C	1.368230	-0.734008	0.024220
C	2.732111	-1.320165	0.083550
C	3.045793	-2.493305	-0.629630
C	4.327064	-3.050813	-0.565220
C	5.320993	-2.447091	0.215590
C	5.020261	-1.280782	0.932140
C	3.739770	-0.723154	0.867190
H	6.322424	-2.882349	0.266410
H	4.551495	-3.956692	-1.134530
H	5.784970	-0.806610	1.553150
H	3.512338	0.171166	1.453420
H	2.136857	1.259684	-0.017620
H	-2.211256	-2.978513	-1.336440
H	1.716634	2.964563	-1.420940
H	-4.473285	-3.992647	-1.295250
H	-3.564671	0.141394	1.331190
H	1.713680	5.437413	-1.506040
H	-6.303816	-2.933970	0.039060
H	-2.144403	1.240897	-0.136350
H	-5.832280	-0.854639	1.345490
H	-1.736856	3.052997	1.178960
H	-0.023892	6.740190	-0.266430
H	-1.752600	5.525577	1.071240
H	2.284264	-2.961506	-1.260230

Compound 2 (C₁)

E = -2779.71424600 a. u. (PBE1PBE/LANL2DZ+pol.)

Atom	X	Y	Z (Angstrom)
C	-3.717589	1.182472	4.107415
C	-3.076807	-0.047108	4.305694
C	-3.256397	2.022977	3.096684
C	-4.377440	7.331325	-0.506539
C	-3.618832	8.486536	-0.736807
C	-2.001227	-0.419272	3.491269
C	2.091901	1.834487	4.595839
C	-2.167190	1.655975	2.278643
C	-3.743707	6.105667	-0.278043
C	-2.220284	8.402063	-0.737464
C	-2.201062	3.835369	0.936442
C	1.155259	1.300740	3.703134
C	-1.504962	0.400819	2.458275
C	-2.339272	6.008458	-0.277505
C	3.463203	1.680278	4.354181
C	-1.668661	2.582376	1.247521
C	-1.587444	7.175451	-0.511316
C	-1.671899	4.703630	-0.035479
C	1.524684	0.588289	2.544627
C	3.870087	0.994726	3.211485
C	-4.286221	1.748089	-3.080514
C	1.184273	-3.656097	3.753665
C	1.119612	-2.404584	3.130650
C	-0.519927	4.384095	-0.775541
C	-4.162213	0.640493	-2.236415
C	0.164715	-2.091023	2.142423
C	0.283903	-4.667982	3.396322
C	2.930713	0.451929	2.310276
C	-3.163067	2.254531	-3.748503
C	0.234797	3.205522	-0.684386
C	-0.742207	-3.139860	1.789084
C	-0.668791	-4.401673	2.415334
C	-2.910778	0.026167	-2.040656
C	-1.756205	-2.880077	0.753738
C	-2.797857	-1.177482	-1.182956
C	-5.399954	-5.191067	0.079164
C	-2.789645	-3.736768	0.369554
C	-3.718711	-2.224396	-1.337773
C	-6.393300	-6.129809	-0.217254
C	-3.738728	-3.437542	-0.625554
C	-1.915021	1.649265	-3.557322
C	-1.786467	0.548268	-2.704363
C	-4.793338	-4.435066	-0.941988
C	3.382551	-0.260669	1.102684
C	1.439300	3.043349	-1.532597
C	2.639589	2.550336	-0.991291

C	-6.799014	-6.334868	-1.542533
C	-5.209868	-4.649317	-2.269601
C	-6.201390	-5.589745	-2.567391
C	4.704067	-0.474135	0.705256
C	1.413609	3.417617	-2.890023
C	3.783867	2.427466	-1.786621
C	2.739398	-1.561722	-1.272110
C	2.556979	3.293835	-3.684693
C	5.080409	-1.108765	-0.493798
C	3.747529	2.796382	-3.136854
C	0.831272	-3.034554	-1.980770
C	1.869345	-2.148711	-2.318907
C	0.018609	-3.590634	-2.974988
C	4.134323	-1.608314	-1.408577
C	7.453656	-1.565066	0.208619
C	6.524889	-1.261412	-0.804736
C	2.079982	-1.833003	-3.674338
C	0.231808	-3.268688	-4.320974
C	1.266814	-2.388647	-4.667019
C	8.813955	-1.705841	-0.084211
C	6.999630	-1.101245	-2.120435
C	9.274685	-1.543030	-1.397280
C	8.359965	-1.239517	-2.414136
H	-4.560305	1.484218	4.734635
H	-3.412577	-0.722912	5.097792
H	-3.749921	2.986089	2.947165
H	1.745731	2.373760	5.482546
H	-5.469467	7.382162	-0.512649
H	-4.113534	9.445106	-0.913672
H	-3.072242	4.186916	1.496226
H	0.098503	1.440618	3.929991
H	-4.348758	5.207777	-0.124730
H	-1.528295	-1.381510	3.684457
H	4.204284	2.092751	5.043586
H	-1.616997	9.298162	-0.905442
H	-0.495192	7.131177	-0.488895
H	-5.263704	2.218638	-3.215747
H	-5.040244	0.257440	-1.709016
H	1.944220	-3.839087	4.519070
H	1.834227	-1.644601	3.444878
H	0.326833	-5.651210	3.871728
H	4.939391	0.881058	3.016957
H	-3.261176	3.116128	-4.414108
H	-0.163908	5.128560	-1.494812
H	-5.112828	-5.024655	1.121012
H	-1.365846	-5.192621	2.127828
H	-6.858753	-6.697578	0.592765
H	2.686394	2.298991	0.071321
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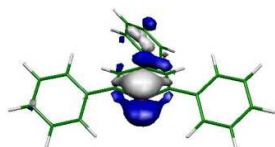
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H	7.106586	-1.721091	1.233676
H	-0.780215	-4.282387	-2.694081
H	2.517176	3.585061	-4.737724
H	4.642730	2.703468	-3.757378
H	2.872393	-1.130672	-3.947750
H	9.516017	-1.953182	0.716455
H	-0.403988	-3.701863	-5.097539
H	4.514190	-2.127883	-2.294383
H	1.437413	-2.128085	-5.714955
H	6.301617	-0.841574	-2.921005
H	10.337885	-1.652427	-1.626351
H	8.707954	-1.101465	-3.441274
Ir	0.093786	-0.199984	1.218580
P	-0.279183	1.952317	0.413314
P	-1.533782	-1.328560	0.002763
P	2.047374	-0.782872	0.120350

Computed electronic spectrum (wavelength, wave number, transition energy, oscillator strength, Singlet excited state (S), transitions between MOs, weight of the transition)

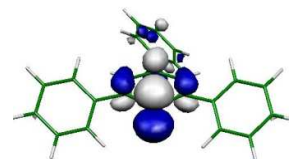
(nm ,1000 cm⁻¹, eV) (f) (Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)

Ligand 1

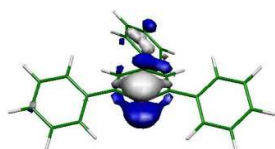
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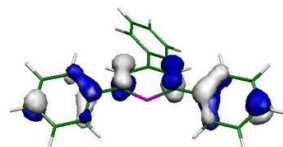
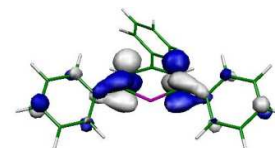
H → L



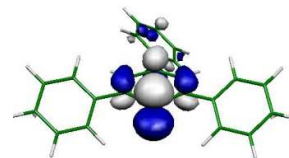
291.0 34.4 4.26 0.7101 S H-0->L+1(+76%) H-1->L+0(+19%)



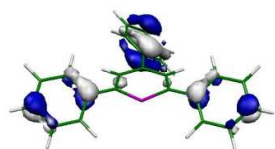
H → L+1



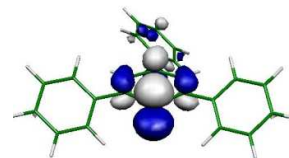
H-1 → L



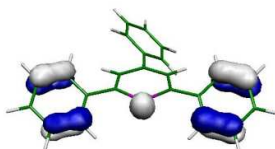
281.2 35.6 4.41 0.1732 S H-2->L+0(+73%)



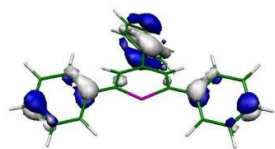
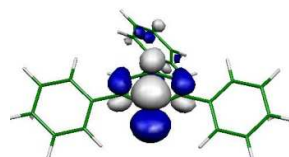
H-2 → L



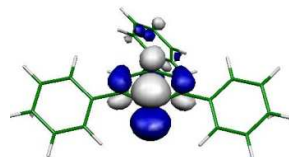
274.4 36.4 4.52 0.1549 S H-3->L+0(+63%) H-2->L+0(20%)



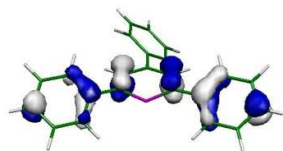
H-3 → L



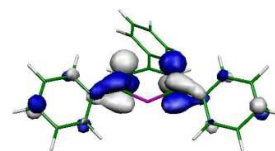
H-2 → L



266.8 37.5 4.65 0.2416 S H-1->L+1(+90%)

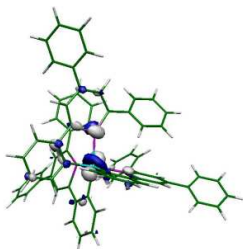


H-1 → L+1

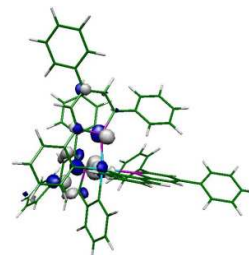


Complex 2 (significant MLCT character indicated)

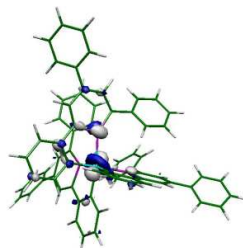
380.7 26.3 3.26 0.0611 S H-0->L+0(+92%)



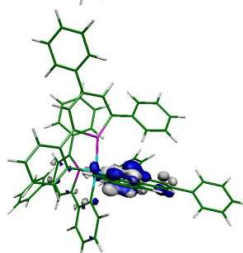
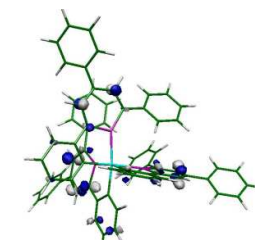
H → L+0
MLCT



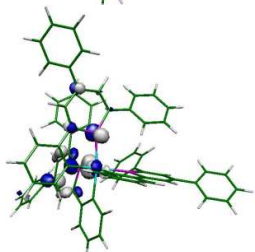
349.8 28.6 3.54 0.0987 S H-0->L+3(+50%) H-2->L+0(+21%)



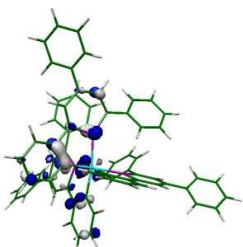
H → L+3
MLCT
ILCT



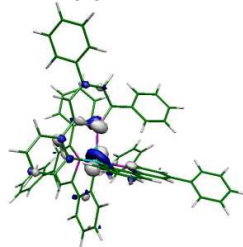
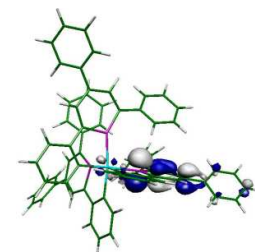
H-2 → L+0



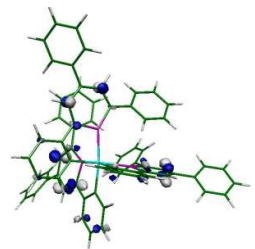
347.4 28.8 3.57 0.0988 S H-1->L+1(+31%) H-0->L+3(+16%)



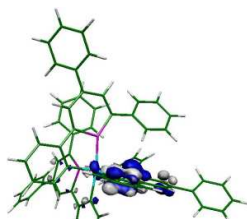
H-1 → L+1



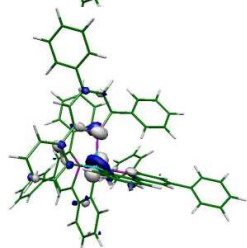
H → L+3
MLCT



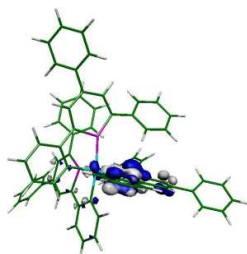
339.3 29.5 3.65 0.1513 S H-2->L+2(+32%) H-0->L+4(+20%) H-2->L+3 (16%)



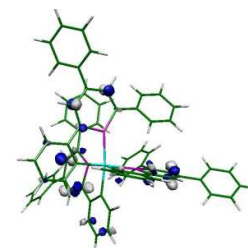
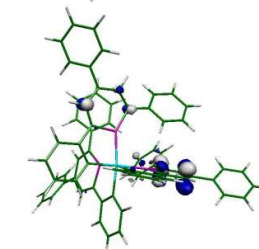
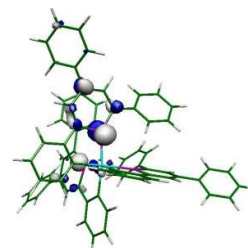
H-2 → L+2



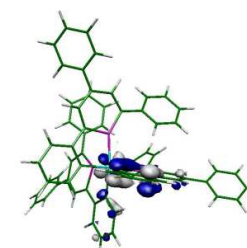
H → L+4
MLCT



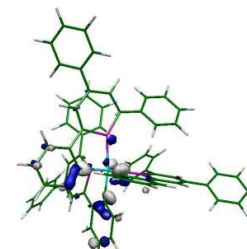
H-2 → L+3



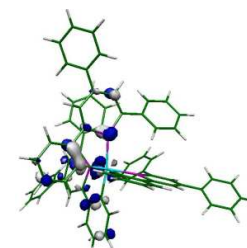
327.6 30.5 3.79 0.2860 S H-4->L+0(+48%) H-5->L+0(14%) H-1->L+3(11%)



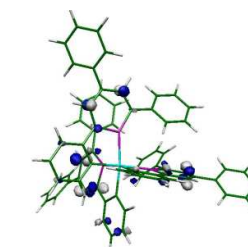
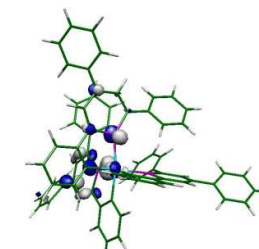
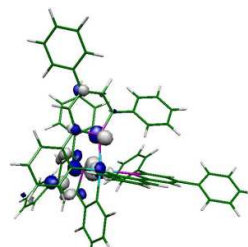
H-4 → L
MLCT



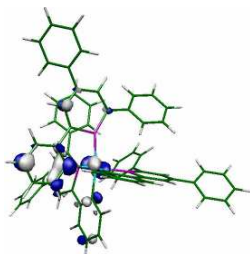
H-5 → L



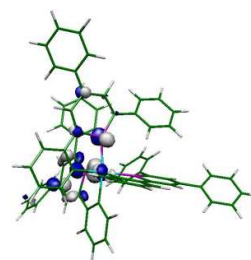
H-1 → L+3



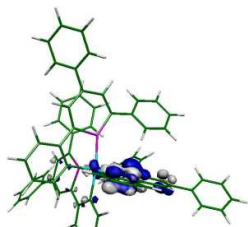
326.9 30.6 3.79 0.3545 S H-3->L+0(+50%)



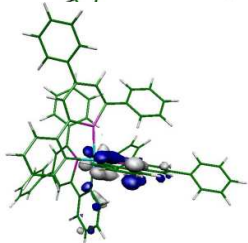
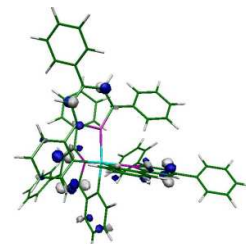
H-3 → L
MLCT



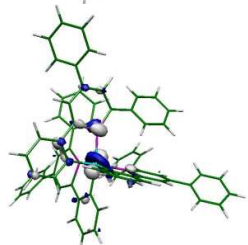
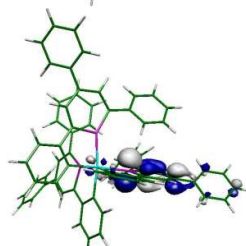
324.3 30.8 3.82 0.1262 S H-2->L+3(+31%) H-4->L+1(16%) H-0->L+4(14%)



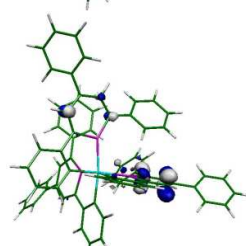
H-2 → L+3



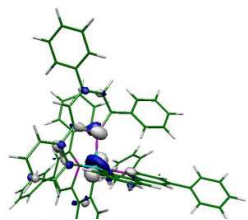
H-4 → L+1
MLCT



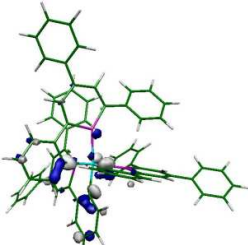
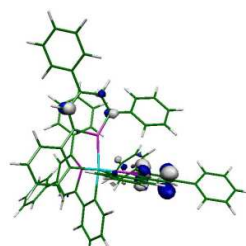
H → L+4
MLCT



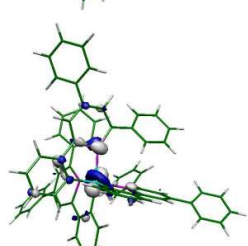
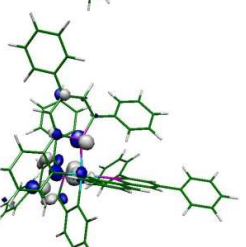
323.3 30.9 3.84 0.1122 S H-0->L+4(+16%) H-5->L+0(14%) H-0->L+5(13%)



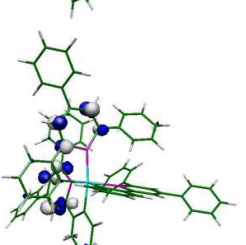
H → L+4
MLCT



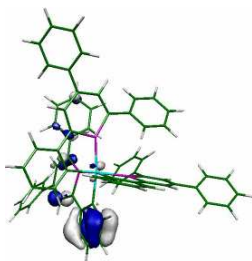
H-5 → L



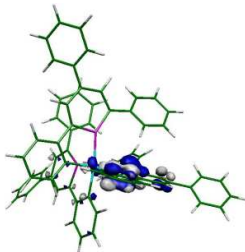
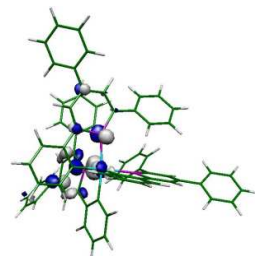
H → L+5
MLCT



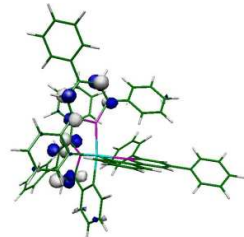
301.3 33.2 4.11 0.1296 S H-7->L+0(+53%) H-2->L+5(+11%)



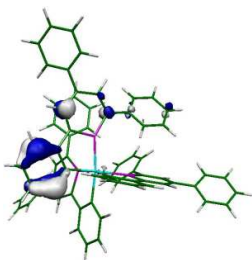
H-7 → L



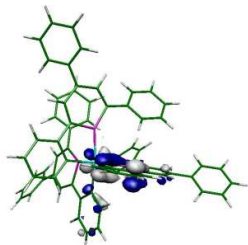
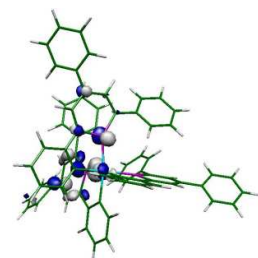
H-2 → L+5



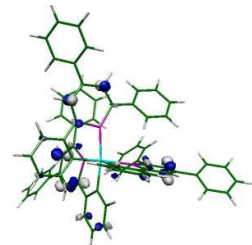
300.4 33.3 4.13 0.2518 S H-6->L+0(+38%) H-4->L+3(+14%)



H-6 → L



H-4 → L+3
MLCT



References:

- [1] Bruker (2001). SAINT-Plus. Bruker AXS Inc., Madison, Wisconsin, USA.
- [2] G. M. Sheldrick, SADABS: Area-Detector Absorption Correction, v2.10, Universität Göttingen, 1999, Germany.
- [3] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
- [4] A.L. Spek, *Acta Cryst.* **2009**, *D65*, 148-155.
- [5] H. D. Flack, *Acta Cryst.* **1983**, *A39*, 876-881.
- [6] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158.
- [7] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [8] (a) S. Miertus, E. Scrocco and J. Tomasi, *J. Chem. Phys.* **1981**, *55*, 117-129; (b) V. Barone, M. Cossi and J. Tomasi, *J. Chem. Phys.*, **1997**, *107*, 3210–3221. (c) M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys.*, **2002**, *117*, 43–54.