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A Multifunctional Organometallic Switch with Carbon-Rich Ruthenium and Diarylethene Units

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Electronic Supplementary Information

I - Synthetic procedures.

General Comments. The reactions were achieved under an inert atmosphere, using the Schlenk techniques. Solvents were freshly distilled under argon using standard procedures. The diethynyl-substituted dithienylethene[1] and the ruthenium precursor[2] were prepared as previously reported. All the reactions and handling of the compound are carried out in the dark.

Synthesis of [Cl-(dppe)$_2$Ru-C≡C-($C_{15}S_2F_6H_6$)-C≡C-Ru(dppe)$_2$-Cl] (1o):

In a Schlenk tube, [Cl(dppe)$_2$Ru][OTf] (172 mg, 0.16 mol) and the diethynyl-substituted dithienylethene (33.08 mg, 0.08 mmol) were pumped for 30 min. Then, well degassed dichloromethane (20 mL) was transferred onto the solids. The mixture was stirred in the dark for four days before addition of triethylamine (0.2 mL, 3.2 mmol). After 30 min, the reacting solution was evaporated. The dichloromethane solution was washed with degassed water (4 × 10 mL), dried (Na_2SO_4), and the residue obtained after evaporation was washed with pentane (2 × 10 mL). An amount of 100 mg of **1o** as a light green solid was recovered after drying under vacuum (55% yield). ^{31}P NMR (81 MHz, $CDCl_3$, 297 K): δ 50.3 (s, PPh_2). ^{1}H NMR (200 MHz, $CDCl_3$, 297 K): δ 7.55-6.97 (m, 80 H, Ph), 6.17 (s, 2 H, ArH), 2.69 (m, 16 H, CH_2), 1.78 (s, 6 H, $ArCH_3$). ^{13}C NMR (75.5 MHz, C_6D_6, 297 K): δ 136.67-127.23 (Ph dppe), 135.36, 130.13 124.77, 124.64 (DTE), 103.92 (Ru-C≡$\underline{C}$), 30.97 (m, $|^1J_{PC} + {}^3J_{PC}|$ = 23 Hz), 14.77 ($ArCH_3$). ^{19}F NMR (188.3 MHz, CD_2Cl_2, 297 K): δ -110.144 (t, J = 6 Hz, 4 F), -132.287 (m, 2 F). IR (KBr): ν = 2055 cm^{-1} (C≡C). HR-MS FAB$^+$ (m/z): 2261.2958 ([M -. F]$^+$, calcd: 2261.2865).

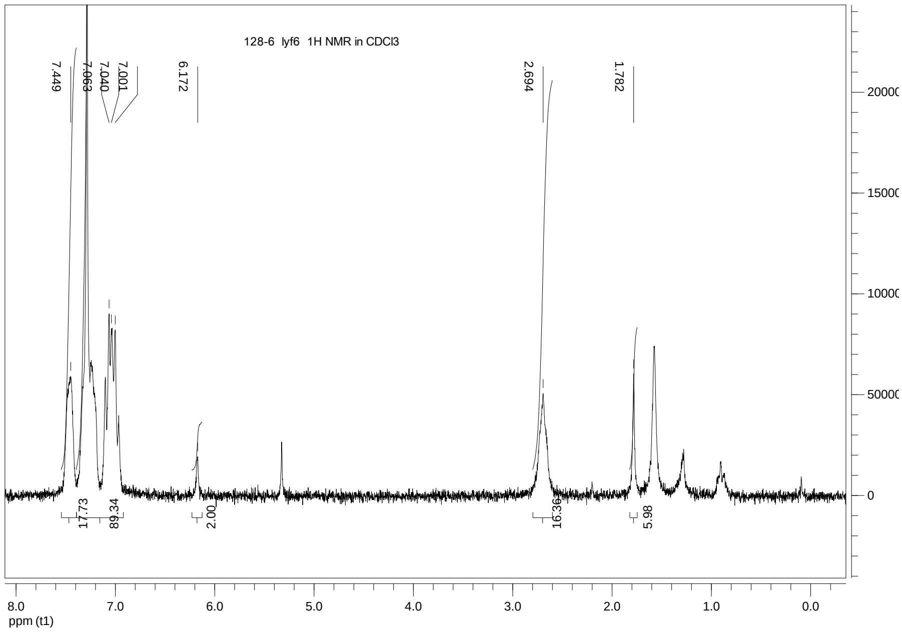


Figure S1. ^{1}H NMR spectrum of **1o** in $CDCl_3$

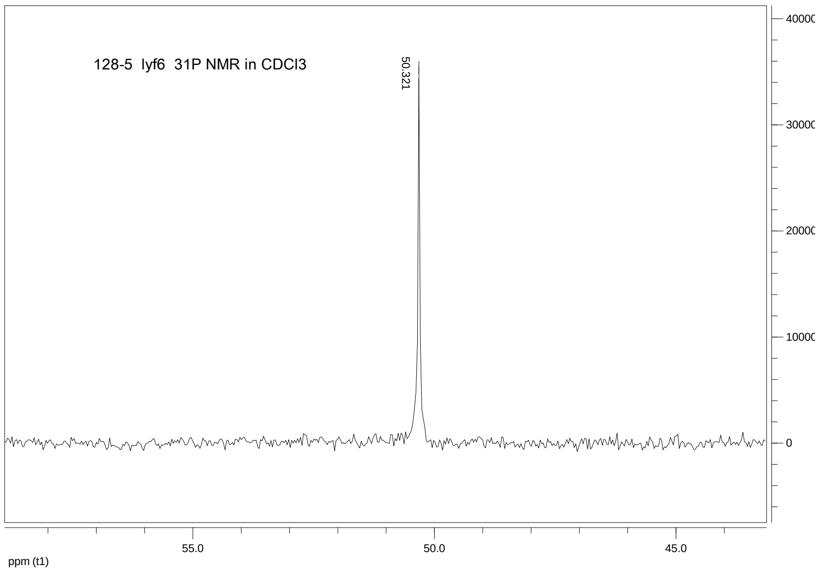


Figure S2. ^{31}P NMR spectrum of **1o** in $CDCl_3$

II – Isomerization studies

General Comments. UV-vis irradiation were performed with a LS series Light Source of ABET technologies, Inc (150 W xenon lamp), with single wavelength light filters of "350FS 10-25", "450FS 20-25", "650FS 10-25" and "750FS 40-25". UV-vis-NIR spectra were recorded with a Cary 5000 apparatus.

^{31}P and ^{1}H NMR studies

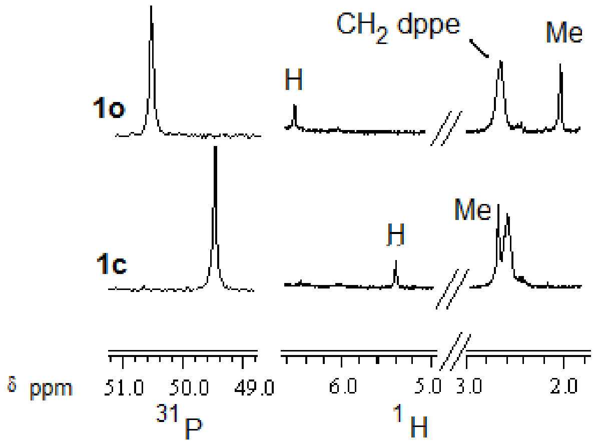


Figure S3. ^{31}P and selected ^{1}H NMR signals in C_6D_6 of **1o** and of **1c** after excitation at 350 nm. Initial spectra were recovered after bleaching at 750 nm**.**

Data for 1C: ^{31}P NMR (81 MHz, C_6D_6, 297 K): δ 49.5 (s, PPh_2). ^{1}H NMR (200 MHz, C_6D_6, 297 K): δ 7.84-6.95 (m, 80 H, Ph), 5.43 (s, 2 H, ArH), 2.61 (s, 6 H, $ArCH_3$), 2.52 (m, 16 H, PCH_2CH_2P). IR (KBr): $\nu = 2009$ cm^{-1} (C≡C).

IV – Electrochemistry

General Comments. Electrochemical studies were carried out under argon using an instrument consisted of a Tacussel GSTP4 programmer and a home-built potentiostat equipped with a positive feedback compensation device (CH_2Cl_2, 0.2 M Bu_4NPF_6).[3] The voltammograms were recorded with a 310 Nicolet oscilloscope. The working electrode was a Pt disk, the counter electrode was a Pt wire and SCE electrode was used a reference electrode. After each series of experiments, ferrocene and decamethylferrocene were added to the electrolyte and the corresponding couples served as internal probes.[4]

Macroelectrolyses under argon atmosphere were performed at controlled potential with a three electrode configuration in a two-compartment cell. A Pt plate (3 cm^2) was used as a working electrode, a Pt disk (1 mm of diameter) was used as a secondary working electrode, a SCE electrode with an extension (CH_2Cl_2, 0.2 M Bu_4NPF_6) served as a reference electrode and a Pt grid was the counter electrode. Experiments were performed with a EGG PAR-173 potentiostat and a EGG PAR-175 universal programmer equipped with a EGG PAR-179 digital coulometer. For each macroscale electrolysis, a dilute CH_2Cl_2 solution (ca. 10^{-3} M) of the compounds was prepared with Bu_4NPF_6 (0.2 M) as the supporting electrolyte. The applied oxidation potentials were calibrated upon performing cyclic voltammetry before electrolysis. By recording CVs, the secondary Pt electrode was used to control the consumption of the starting materials throughout the bulk electrolysis. Electrolyses were stopped after the current was dropped to less than 10 % of its initial value. All the reactions and handling of the compound were carried out in the dark.

UV-vis-NIR spectroelectrochemistry (SEC) experiments were performed in CH_2Cl_2 at 20 °C, under argon, with a home-made Optically Transparent Thin-Layer Electrosynthetic (OTTLE) cell, path length = 1 mm, using a Varian CARY 5000 spectrometer and an EG&G PAR model 362 potentiostat. A Pt mesh was used as the working electrode, a Pt wire as the counter electrode, and an Ag wire as a pseudo-reference electrode. The electrodes were arranged in the cell such that the Pt mesh was in the optical path of the quartz cuvette. The anhydrous freeze-pump-thaw degassed sample-electrolyte solution (0.2 M Bu_4NPF_6) was cannula-transferred under argon into the cell previously thoroughly deoxygenated. The oxidation potentials were calibrated upon performing cyclic voltammetry before electrolysis. Nice isosbestic points observed along the whole experiment show the clean conversion processes.

Cyclic voltametry

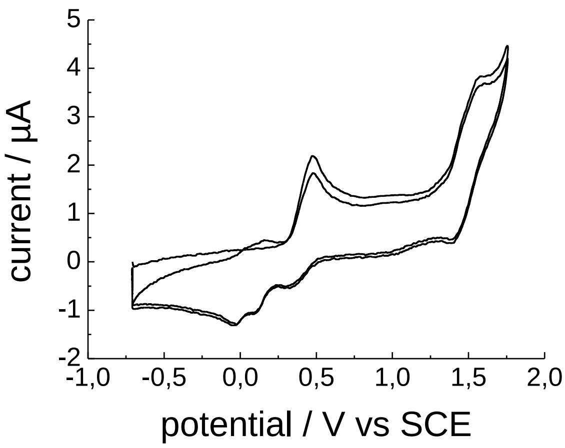


Figure S4. Cyclic voltammetry of **1o** (CH_2Cl_2 0.2 M Bu_4NPF_6) at 0.1 V.s^{-1}.

Study of the mechanism: Numerical simulations.

Numerical simulations of the voltammograms were performed with the DigiElch simulation software (Elchsoft), [5] using the defaults numerical options with the assumption of a planar diffusion and a Butler-Volmer law for the electron transfer. The charge-transfer coefficient, α, was taken as 0.5.

Two distinct mechanisms were tested.

Mechanism 1(closing in the $1o^{2+}$ state)

$1o = 1o^{+} + e^{-}$	$E_1° = 0.405$ V	$k^1_s = 0.2$ cm.s^{-1}	
$1o^{+} = 1o^{2+} + e^{-}$	$E^{2}° = 0.490$ V	$k^2_s = 0.2$ cm.s^{-1}	
$1o^{2+} = 1c^{2+}$	$K = 10^8$	$k_f = 15$ s^{-1}	$k_b = 1.5\ 10^{-7}$ s^{-1}
$1c^{2+} + e^{-} = 1c^{+}$	$E_3° = 0.130$ V	$k^3_s = 0.2$ cm.s^{-1}	
$1c^{+} + e^{-} = 1c$	$E_{3'}° = 0.009$ V	$k^{3'}_s = 0.2$ cm.s^{-1}	

$1o^{2+} + 1c = 1o^{+} + 1c^{+}$	$K = 1.35\ 10^8$	$k_f = 10^8$ s^{-1}	$k_b = 0.74$ s^{-1}
$1o^{2+} + 1c^{+} = 1o^{+} + 1c^{2+}$	$K = 1.21\ 10^6$	$k_f = 10^8$ s^{-1}	$k_b = 83$ s^{-1}
$1o^{+} + 1c = 1o + 1c^{+}$	$K = 4.9\ 10^6$	$k_f = 10^8$ s^{-1}	$k_b = 20$ s^{-1}
$1o^{+} + 1c^{+} = 1o + 1c^{2+}$	$K = 4.4\ 10^5$	$k_f = 10^8$ s^{-1}	$k_b = 2250$ s^{-1}
$1o^{+} + 1o^{+} = 1o + 1o^{2+}$	$K = 0.037$	$k_f = 10^8$ s^{-1}	$k_b = 2.7\ 10^9$ s^{-1}

Mechanism 2 (closing in the $1o^{+}$ state)

$1o = 1o^{+} + e^{-}$	$E_1° = 0.405$ V	$k^1_s = 0.2$ cm.s^{-1}	
$1o^{+} = 1o^{2+} + e^{-}$	$E^{2}° = 0.490$ V	$k^2_s = 0.2$ cm.s^{-1}	
$1o^{+} = 1c^{+}$	$K = 10^8$	$k_f = 1.5$ s^{-1}	$k_b = 1.5\ 10^{-8}$ s^{-1}
$1c^{2+} + e^{-} = 1c^{+}$	$E_3° = 0.130$ V	$k^3_s = 0.2$ cm.s^{-1}	
$1c^{+} + e^{-} = 1c$	$E_{3'}° = 0.009$ V	$k^{3'}_s = 0.2$ cm.s^{-1}	

$1o^{2+} + 1c = 1o^{+} + 1c^{+}$	$K = 1.35\ 10^8$	$k_f = 10^8$ s^{-1}	$k_b = 0.74$ s^{-1}
$1o^{2+} + 1c^{+} = 1o^{+} + 1c^{2+}$	$K = 1.21\ 10^6$	$k_f = 10^8$ s^{-1}	$k_b = 83$ s^{-1}
$1o^{+} + 1c = 1o + 1c^{+}$	$K = 4.9\ 10^6$	$k_f = 10^8$ s^{-1}	$k_b = 20$ s^{-1}
$1o^{+} + 1c^{+} = 1o + 1c^{2+}$	$K = 4.4\ 10^5$	$k_f = 10^8$ s^{-1}	$k_b = 2250$ s^{-1}
$1o^{+} + 1o^{+} = 1o + 1o^{2+}$	$K = 0.037$	$k_f = 10^8$ s^{-1}	$k_b = 2.7\ 10^9$ s^{-1}

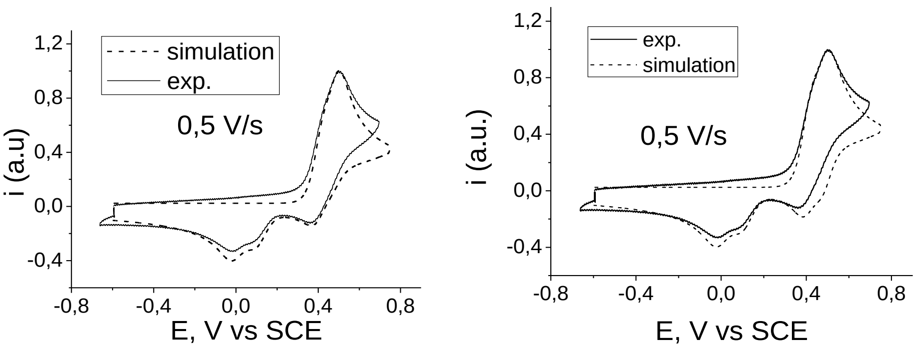
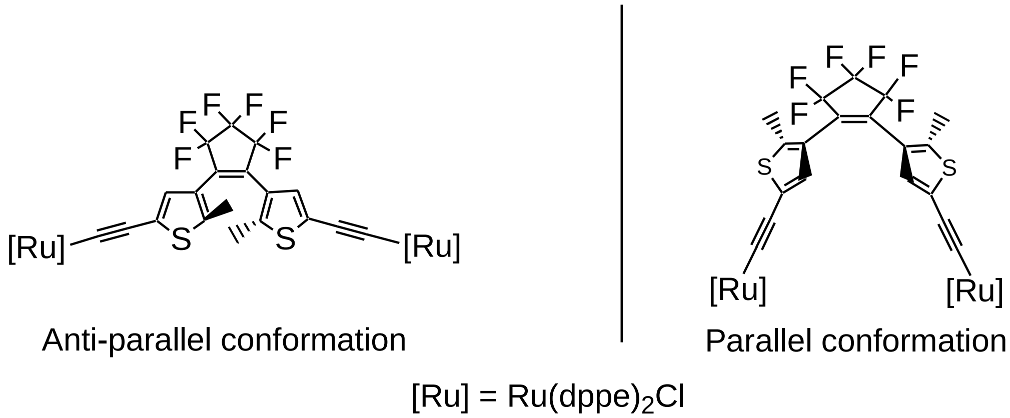


Figure S5. Cyclic voltammetry of **1o** in CH_2Cl_2 0.2 M Bu_4NPF_6 on a Pt disk electrode at 0.5 V.s^{-1}. Solid line : experimental data. Dotted line: simulation. On the left, simulation according to *mechanism 1*. On the right, simulation according to *mechanism 2*

III – Theoretical calculations

General Comments. Density functional theory (DFT) calculations were performed with the Amsterdam Density Functional package (ADF 2007.01)[6] on slightly simplified models of $\mathbf{1o}^{n+}$ and $\mathbf{1c}^{n+}$ (phenyl groups were replaced by hydrogen atoms), n = 0, 1, 2. The singlet and triplet states were considered for dications, $\mathbf{1c}^{2+}$ in its high spin state was not fully converged and is not reported. The geometries were fully optimized without constraints (*C_1* symmetry). The bonding energies and cartesian coordinates of each structure is given in Table S1. Because of the size of the molecules and thus of computational limits, frequency analysis were not performed, but the geometry optimization convergence criteria were more drastic than default ones (energy change < 0.0005 Hartree, atomic position displacement < 0.005 Å). Conformational studies were performed on **1c** in order to evaluate the influence of the spatial orientation of the $[ClRu(dpe)_2]$ groups toward the organic DTE bridge on the electronic excitation energies. Three orientations were chosen: $\mathbf{1c_1}$ where the dpe (1,2-diphosphinoethane) ligands of each metallic fragments span below and above the DTE plane; $\mathbf{1c_2}$ where the dpe ligands of one metallic fragments span below and above the DTE plane, the other is rotated by ~ 90°; $\mathbf{1c_3}$ which shows intermediate positions of the metallic moieties toward the organic plane (see schemes included in Table S1). The orientation of $\mathbf{1c_1}^{2+}$ and $\mathbf{1c_1}^{+}$ is arbitrarily chosen as the one of $\mathbf{1c_1}$.
Electron correlation was treated within the local density approximation (LDA) in the Vosko-Wilk-Nusair parametrization.[7] The non-local corrections of Becke and Perdew were added to the exchange and correlation energies, respectively.[8] The analytical gradient method implemented by Verluis and Ziegler was used.[9] The standard ADF TZP basis set was used, i.e., triple-ξ STO basis set for the valence core augmented with a 3d polarisation function for C, P. Orbitals up to 1s, 2p, and 4p were kept frozen for C, P, and Ru, respectively. The excitation energies and oscillator strengths were calculated following the procedure described by van Gisbergen and co-wokers.[10] In that case, the functional used was PBE.[11]



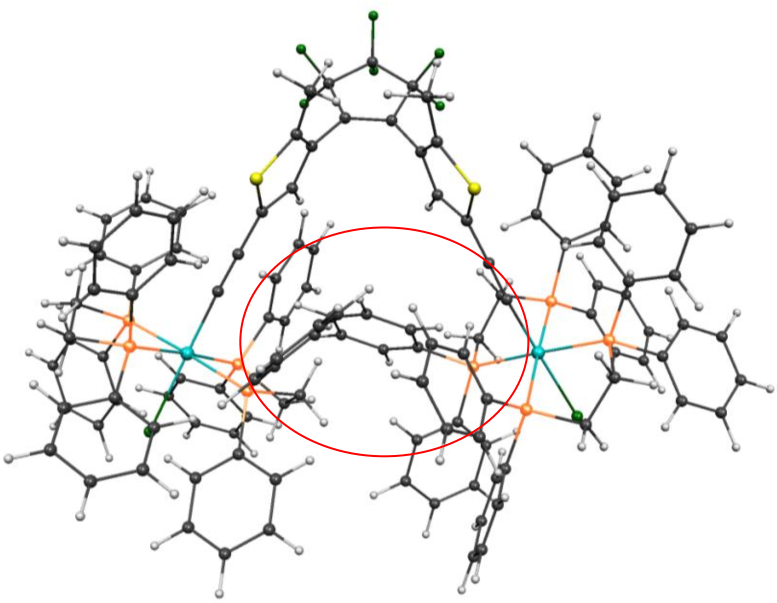


Figure S6. Top: Anti parallel and parallel conformations of **1o**. Bottom: Unstable structural arrangement of **1o** in its parallel conformation (main distances and angles taken from the optimized **1o** anti-parallel geometry). Inter-group C-H and H-H distances are too short (much less than the sum of the van der Waals radii) in this conformation whatever the orientation of the metallic moieties is chosen.

Table S1. Optimized Cartesian coordinates of **1o**$^{n+}$ and **1c**$^{n+}$, n = 0, 1, 2 and their total bonding energies.

1o				**1o^{+}**			
E = -471.819 eV				E = -466.234 eV			
C	.133568	-.089908	.033189	C	.130106	-.105162	.023572
C	.176753	-.239897	1.532466	C	.187435	-.278677	1.521961
C	1.688466	-.080109	1.937019	C	1.704355	-.104612	1.913614
C	2.424502	.215991	.577006	C	2.419659	.245063	.553009
C	1.350783	.204317	-.481783	C	1.334371	.219780	-.496046
F	-.586639	.725838	2.155512	F	-.584508	.668609	2.154698
F	-.312312	-1.452617	1.962314	F	-.281968	-1.503722	1.926935
F	2.161825	-1.219412	2.515893	F	2.200269	-1.254935	2.440399
F	1.858038	.941720	2.822766	F	1.866922	.891640	2.822166
F	3.392263	-.736060	.334970	F	3.407805	-.668995	.276369
F	3.081077	1.424539	.642356	F	3.027910	1.474598	.629648
C	1.671065	.474641	-1.902271	C	1.640029	.490052	-1.919543
C	2.128326	-.537789	-2.797031	C	2.067087	-.524671	-2.808092
C	2.322925	-.100039	-4.097250	C	2.278215	-.085798	-4.116322
S	1.952034	1.628578	-4.183123	S	1.942979	1.653970	-4.204577
C	1.529141	1.718973	-2.495440	C	1.524393	1.743081	-2.520433
H	2.300145	-1.570951	-2.503058	H	2.228066	-1.560218	-2.516968
C	1.058634	3.011643	-1.896669	C	1.100629	3.044819	-1.911194
H	1.063734	2.953277	-.800675	H	1.061706	2.965126	-.818020
H	.033904	3.253615	-2.217977	H	.105055	3.346098	-2.269616
H	1.707080	3.850647	-2.186238	H	1.801532	3.852342	-2.163019
H	.026556	-5.033364	-8.300322	H	.022998	-5.038773	-8.319751
C	2.722111	-.821000	-5.234401	C	2.685040	-.817349	-5.223721
C	3.062722	-1.470442	-6.231146	C	3.039410	-1.476396	-6.222743
Ru	3.691933	-2.591956	-7.801625	Ru	3.669785	-2.574517	-7.754934
P	2.193287	-4.340520	-7.299996	P	2.178674	-4.364370	-7.299332
C	.875238	-4.417885	-8.630097	C	.872572	-4.419739	-8.639577
C	.435125	-2.994401	-9.005337	C	.429249	-2.993438	-9.002270
P	1.943220	-1.892204	-9.223001	P	1.925207	-1.881178	-9.216307
H	2.601512	-5.705860	-7.248221	H	2.623958	-5.715691	-7.274859
H	1.410298	-4.317717	-6.104831	H	1.394800	-4.375143	-6.106284
H	1.358207	-4.914280	-9.486148	H	1.354980	-4.909403	-9.499252
H	-.159187	-2.543757	-8.195052	H	-.165982	-2.550474	-8.188264
H	-.176021	-2.986547	-9.918653	H	-.184837	-2.982100	-9.913196
H	1.330350	-.602573	-9.191009	H	1.316219	-.590767	-9.192438
H	2.168292	-1.977883	-10.629024	H	2.189759	-1.974774	-10.612587

P	5.463101	-3.341907	-6.450874	P	5.480976	-3.367946	-6.446253
C	6.831643	-2.058383	-6.421625	C	6.852018	-2.090926	-6.436013
C	6.943357	-1.393717	-7.802521	C	6.949109	-1.415484	-7.813169
P	5.232720	-.924413	-8.414246	P	5.242136	-.920245	-8.407556
H	5.095863	.405171	-7.911106	H	5.122340	.416220	-7.923064
H	5.513837	-.599270	-9.774758	H	5.484839	-.632886	-9.780885
H	7.600920	-.513501	-7.780061	H	7.612338	-.540100	-7.788441
H	7.340474	-2.103365	-8.545397	H	7.336980	-2.118670	-8.566259
H	7.781559	-2.514823	-6.110336	H	7.804073	-2.555553	-6.144848
H	6.537275	-1.322241	-5.657133	H	6.579228	-1.359899	-5.658687
H	6.170403	-4.523153	-6.829261	H	6.145326	-4.544712	-6.895312
H	5.321249	-3.617629	-5.058260	H	5.372547	-3.680843	-5.060789
Cl	4.507041	-4.054651	-9.742632	Cl	4.491455	-4.000369	-9.674259
C	-1.143072	-.198597	-.709972	C	-1.147520	-.205742	-.718310
C	-1.664568	-1.387160	-1.198330	C	-1.693009	-1.393986	-1.207145
S	-3.148637	-1.079976	-2.055293	S	-3.163258	-1.079976	-2.073347
C	-3.078704	.659762	-1.755303	C	-3.065840	.663847	-1.783276
C	-1.940744	.939694	-1.014863	C	-1.916228	.935091	-1.036405
C	-1.112486	-2.780934	-1.095612	C	-1.165001	-2.791970	-1.082110
H	-1.115063	-3.141070	-.056358	H	-1.211103	-3.141700	-.040752
H	-.076222	-2.821450	-1.462670	H	-.114543	-2.841864	-1.402783
H	-1.702820	-3.485630	-1.694296	H	-1.739324	-3.492585	-1.699272
H	-1.688481	1.951777	-.706979	H	-1.658527	1.945287	-.727103
C	-4.042767	1.562969	-2.233453	C	-4.008177	1.570790	-2.250793
C	-4.810016	2.454277	-2.619203	C	-4.789035	2.470662	-2.623916
Ru	-6.012334	4.029388	-3.058512	Ru	-5.982449	4.002066	-3.059568
P	-5.587239	4.719802	-.855427	P	-5.598092	4.772979	-.853600
C	-6.658672	3.741956	.332802	C	-6.672568	3.807719	.337127
C	-8.045572	3.527961	-.292980	C	-8.051744	3.562537	-.295591
P	-7.851589	2.944426	-2.067627	P	-7.853738	2.935908	-2.051760
H	-5.860791	6.065521	-.459948	H	-5.914042	6.127110	-.539841
H	-4.304125	4.582622	-.248422	H	-4.321536	4.690880	-.225766
H	-6.722060	4.250962	1.304755	H	-6.754427	4.335647	1.297143
H	-6.143012	2.779767	.479491	H	-6.147552	2.855852	.514695
H	-8.598608	4.479029	-.348835	H	-8.618711	4.503287	-.372134
H	-8.648203	2.813193	.284456	H	-8.646870	2.852854	.295111
H	-9.184741	3.097120	-2.550945	H	-9.167872	3.103421	-2.572333
H	-7.851503	1.525742	-1.905010	H	-7.862648	1.521099	-1.873945
P	-4.226285	5.210688	-4.040071	P	-4.223927	5.253228	-4.048850
C	-4.138651	4.867671	-5.886293	C	-4.125895	4.894157	-5.888648
C	-5.549746	4.598436	-6.431839	C	-5.527325	4.589020	-6.440880
P	-6.445556	3.407331	-5.295106	P	-6.410296	3.380648	-5.315413
H	-2.857692	5.037552	-3.670657	H	-2.854079	5.135657	-3.667759
H	-4.269731	6.636452	-4.009867	H	-4.340628	6.671791	-4.012112

H	-3.654705	5.706313	-6.405996	H	-3.658403	5.737825	-6.414624
H	-6.154739	5.518499	-6.416067	H	-6.151549	5.495744	-6.442898
H	-5.522747	4.211344	-7.460064	H	-5.481701	4.195917	-7.465856
H	-3.497570	3.979847	-6.004618	H	-3.464003	4.020290	-5.996113
H	-7.758303	3.439983	-5.850689	H	-7.727597	3.398022	-5.854394
H	-6.038222	2.140969	-5.820289	H	-5.984782	2.118926	-5.830680
Cl	-7.507274	6.043769	-3.589707	Cl	-7.492333	5.962545	-3.562486

1o^{2+} singlet state				**1o**$^{2+}$ triplet state			
E = -458.096 eV				E = -458.229 eV			
C	0.143599	-0.131935	-0.004968	C	0.129281	-0.100369	0.006684
C	0.199179	-0.305583	1.497386	C	0.166437	-0.267415	1.509729
C	1.726831	-0.215185	1.873574	C	1.686974	-0.141950	1.912875
C	2.423004	0.267326	0.542970	C	2.414497	0.243130	0.565665
C	1.342893	0.218112	-0.516123	C	1.340024	0.212737	-0.498931
F	-0.505910	0.696954	2.117866	F	-0.575405	0.714887	2.119071
F	-0.342898	-1.493174	1.908799	F	-0.351787	-1.469941	1.910408
F	2.190865	-1.442203	2.223783	F	2.150126	-1.327734	2.380200
F	1.941973	0.647712	2.892341	F	1.869089	0.808972	2.858811
F	3.480047	-0.539202	0.219623	F	3.419051	-0.644255	0.280758
F	2.916096	1.540777	0.692954	F	2.987427	1.485954	0.662191
C	1.656962	0.489440	-1.937741	C	1.671597	0.478812	-1.919546
C	1.988395	-0.537335	-2.837533	C	2.071131	-0.532397	-2.809255
C	2.277128	-0.089935	-4.138957	C	2.327222	-0.079832	-4.114773
S	2.111472	1.682394	-4.194205	S	2.073448	1.679241	-4.182467
C	1.671853	1.767865	-2.521448	C	1.625846	1.752104	-2.512022
H	2.051543	-1.589712	-2.568202	H	2.188573	-1.578307	-2.533880
C	1.366605	3.088079	-1.885431	C	1.234196	3.054543	-1.888057
H	1.249194	2.981617	-0.800823	H	1.199004	2.969874	-0.795637
H	0.441541	3.518982	-2.297427	H	0.242811	3.375115	-2.244086
H	2.171331	3.813943	-2.067696	H	1.945822	3.851056	-2.143503
H	0.123396	-5.127232	-8.396783	H	0.068951	-5.088947	-8.383706
C	2.663047	-0.826678	-5.234697	C	2.711384	-0.809829	-5.215946
C	3.046395	-1.500894	-6.226204	C	3.060465	-1.490662	-6.215497
Ru	3.695109	-2.568322	-7.730653	Ru	3.669263	-2.567700	-7.725812
P	2.240899	-4.423073	-7.329336	P	2.183529	-4.396898	-7.304512
C	0.961265	-4.480843	-8.692111	C	0.917135	-4.456077	-8.679481
C	0.482056	-3.060896	-9.035543	C	0.456408	-3.036559	-9.047890
P	1.939198	-1.897289	-9.224509	P	1.924800	-1.884845	-9.229758
H	2.752692	-5.749283	-7.331757	H	2.666926	-5.733248	-7.273553
H	1.448838	-4.488310	-6.144542	H	1.377574	-4.420418	-6.127716
H	1.464781	-4.944225	-9.553953	H	1.424393	-4.937121	-9.529370
H	-0.134539	-2.647481	-8.221673	H	-0.169372	-2.607564	-8.249244
H	-0.124335	-3.053520	-9.951666	H	-0.136403	-3.036233	-9.973011

H	1.304361	-0.622362	-9.183210	H	1.299375	-0.604971	-9.197690
H	2.244633	-1.965832	-10.611265	H	2.242473	-1.960189	-10.613117
P	5.545964	-3.418473	-6.461983	P	5.535900	-3.400095	-6.471822
C	6.961255	-2.198212	-6.535390	C	6.934714	-2.161660	-6.552237
C	7.004901	-1.511597	-7.910226	C	6.976298	-1.491676	-7.935799
P	5.298207	-0.923832	-8.401640	P	5.263637	-0.931916	-8.439111
H	5.242527	0.395073	-7.863735	H	5.194462	0.399128	-7.934770
H	5.464554	-0.605791	-9.777164	H	5.421371	-0.648906	-9.823158
H	7.708060	-0.667550	-7.914743	H	7.668525	-0.638964	-7.948133
H	7.316148	-2.219832	-8.693139	H	7.300151	-2.205619	-8.708286
H	7.908360	-2.707639	-6.310279	H	7.887424	-2.654866	-6.315897
H	6.775574	-1.465671	-5.733945	H	6.733999	-1.421787	-5.761475
H	6.113407	-4.630053	-6.943036	H	6.117248	-4.603806	-6.956082
H	5.470337	-3.717559	-5.071971	H	5.472565	-3.699230	-5.081291
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C	-1.136843	-0.210008	-0.742352	C	-1.145611	-0.189936	-0.744437
C	-1.777989	-1.397297	-1.140232	C	-1.707633	-1.386283	-1.227409
S	-3.249990	-1.057729	-1.981822	S	-3.174356	-1.081961	-2.088957
C	-3.037314	0.699456	-1.806529	C	-3.071924	0.667191	-1.802013
C	-1.834329	0.947113	-1.118492	C	-1.913198	0.941998	-1.053232
C	-1.341885	-2.809442	-0.912042	C	-1.192344	-2.781351	-1.066097
H	-1.566915	-3.122289	0.118884	H	-1.284186	-3.109986	-0.020028
H	-0.256774	-2.910437	-1.051283	H	-0.126406	-2.834911	-1.330967
H	-1.847668	-3.504838	-1.591655	H	-1.740884	-3.492146	-1.694170
H	-1.514664	1.957427	-0.874755	H	-1.658505	1.954071	-0.747121
C	-3.951335	1.621539	-2.257916	C	-3.997030	1.570926	-2.273394
C	-4.732969	2.543621	-2.608953	C	-4.770847	2.502556	-2.616371
Ru	-5.964415	4.001148	-3.033392	Ru	-5.969040	3.989745	-3.036458
P	-5.712468	4.915682	-0.835810	P	-5.655221	4.848339	-0.834053
C	-6.879488	4.038778	0.334412	C	-6.775261	3.931363	0.348998
C	-8.195407	3.695846	-0.382986	C	-8.129000	3.643020	-0.323585
P	-7.848069	2.905728	-2.042237	P	-7.869748	2.927928	-2.033985
H	-6.055292	6.288048	-0.687939	H	-5.995448	6.214671	-0.629149
H	-4.486096	4.896324	-0.112166	H	-4.402264	4.810397	-0.158008
H	-7.056546	4.657853	1.224453	H	-6.901520	4.506446	1.276206
H	-6.357619	3.124895	0.659306	H	-6.253224	2.994839	0.600828
H	-8.774514	4.606663	-0.598008	H	-8.701312	4.572235	-0.465722
H	-8.821660	3.029403	0.225454	H	-8.738129	2.957103	0.280076
H	-9.112289	2.955845	-2.688331	H	-9.151008	3.061787	-2.633241
H	-7.788499	1.515537	-1.736323	H	-7.856057	1.522489	-1.801243
P	-4.304969	5.369167	-4.090298	P	-4.273598	5.327991	-4.085527
C	-4.238010	4.978755	-5.922534	C	-4.217329	4.955095	-5.921241
C	-5.630157	4.582198	-6.440582	C	-5.616532	4.591883	-6.440896
P	-6.420544	3.337806	-5.290346	P	-6.435145	3.352549	-5.302034

H	-2.922608	5.367058	-3.741958	H	-2.892364	5.281901	-3.734997
H	-4.546850	6.770204	-4.060780	H	-4.478466	6.734021	-4.036060
H	-3.834325	5.838376	-6.474716	H	-3.796280	5.812844	-6.464259
H	-6.306611	5.450124	-6.450948	H	-6.275191	5.473861	-6.443569
H	-5.578883	4.175433	-7.459755	H	-5.573678	4.193263	-7.464138
H	-3.526667	4.144883	-6.032010	H	-3.521871	4.108717	-6.039994
H	-7.758045	3.280121	-5.766875	H	-7.769613	3.324105	-5.791169
H	-5.942636	2.091232	-5.791180	H	-5.977765	2.102637	-5.814430
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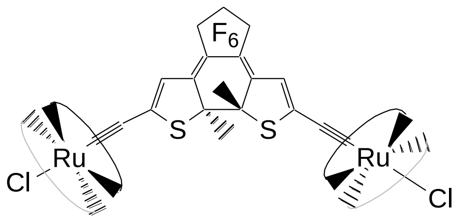				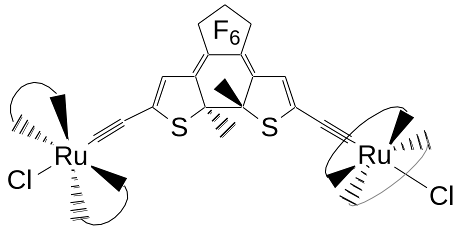			
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P	0.058693	0.114047	2.282589	P	0.056873	0.105340	2.302307
C	1.818088	0.119337	2.937091	C	1.816935	0.131887	2.953093
C	2.716115	-0.725180	2.019744	C	2.720100	-0.710307	2.038879
P	2.382205	-0.285091	0.227890	P	2.377269	-0.277266	0.247942
H	-0.515166	1.180066	3.037716	H	-0.527650	1.169331	3.051141
H	-0.519916	-0.982474	2.987847	H	-0.509453	-0.995036	3.011683
H	2.140139	1.172460	2.937601	H	2.128475	1.188185	2.944275
H	1.840438	-0.242949	3.974293	H	1.845471	-0.222533	3.992768
H	3.780665	-0.593064	2.257977	H	3.784108	-0.569215	2.274227
H	2.468865	-1.794474	2.110448	H	2.480746	-1.781060	2.133871
H	3.112112	-1.310233	-0.442378	H	3.104805	-1.301656	-0.426095
H	3.292727	0.793089	0.010409	H	3.282570	0.803579	0.021781
Cl	-0.212789	-2.525041	0.092443	Cl	-0.198907	-2.529348	0.094368
P	-2.277839	0.111636	-0.343936	P	-2.284077	0.109509	-0.334178
H	-3.159487	-0.639592	0.486708	H	-3.174168	-0.643376	0.485812
H	-2.977310	1.356707	-0.313996	H	-2.977727	1.357387	-0.300183
C	-2.722744	-0.553717	-2.037831	C	-2.724354	-0.543324	-2.034394
H	-2.664077	-1.649277	-1.944005	H	-2.670015	-1.639697	-1.948714
H	-3.753368	-0.279878	-2.303202	H	-3.753206	-0.264119	-2.301014
C	-1.711626	-0.041587	-3.075851	C	-1.709506	-0.028130	-3.066599
H	-1.817759	-0.563532	-4.036975	H	-1.811445	-0.548032	-4.029222
H	-1.851889	1.035594	-3.257347	H	-1.850007	1.048981	-3.247845
H	0.759365	0.595573	-3.328934	H	0.762392	0.607250	-3.309599
P	0.039044	-0.235302	-2.419335	P	0.037665	-0.223358	-2.403086
H	0.416042	-1.505258	-2.947338	H	0.416464	-1.493231	-2.929561

C	0.262941	2.017821	-0.187025	C	0.240022	2.015111	-0.139920
C	0.377354	3.254640	-0.192778	C	0.342209	3.253173	-0.166793
C	0.430715	4.643347	-0.069425	C	0.337340	4.643950	-0.264061
S	1.638117	5.619833	-0.962836	S	1.321164	5.656980	0.838576
C	-0.408724	5.429162	0.708615	C	-0.382293	5.405901	-1.174804
H	-1.233242	4.989236	1.265562	H	-0.982792	4.936438	-1.950862
C	-0.144539	6.809893	0.684407	C	-0.247636	6.799101	-1.042207
C	-0.879423	7.856813	1.208131	C	-0.697475	7.811540	-1.868908
C	1.205217	7.157951	0.027338	C	0.442785	7.218640	0.270302
C	1.042940	8.448593	-0.815395	C	1.376451	8.424417	-0.006443
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C	-0.510142	9.225282	0.976953	C	-0.364606	9.187163	-1.623210
C	-2.103335	7.765281	2.042305	C	-1.543045	7.673167	-3.080088
C	-2.402423	9.244949	2.515732	C	-1.910517	9.150878	-3.509358
C	-1.316395	10.151042	1.808958	C	-1.135997	10.095735	-2.505746
F	-3.209851	7.268617	1.357194	F	-0.901609	7.032617	-4.138419
F	-1.973962	6.934119	3.144871	F	-2.702072	6.937897	-2.879610
C	2.266261	7.294658	1.144141	C	-0.654117	7.529111	1.315268
H	3.260988	7.469221	0.716115	H	-0.208141	7.759023	2.290619
H	2.015740	8.137420	1.805680	H	-1.254565	8.392272	0.991221
H	2.284923	6.371147	1.737524	H	-1.312571	6.656292	1.415351
F	-3.661653	9.631193	2.159762	F	-1.532826	9.398649	-4.796918
F	-2.312065	9.342750	3.873859	F	-3.257848	9.353457	-3.431169
F	-1.939611	11.159484	1.087218	F	-0.351319	10.995364	-3.213701
F	-0.573937	10.824302	2.776943	F	-2.050995	10.894536	-1.822767
S	2.650748	9.161875	-1.485742	S	2.106076	9.229125	1.531530
C	2.182633	10.817564	-0.990592	C	1.734109	10.867815	0.911931
C	1.058046	10.824009	-0.176174	C	0.913560	10.831761	-0.207122
H	0.684885	11.749671	0.256273	H	0.549059	11.749085	-0.663965
C	2.899808	11.949408	-1.381514	C	2.218195	12.029754	1.515471
C	0.086183	8.270571	-2.017102	C	2.557122	8.074638	-0.941530
H	-0.030888	9.233985	-2.530328	H	3.137657	8.984235	-1.143860
H	0.481831	7.530715	-2.723697	H	3.210950	7.324471	-0.480033
H	-0.900864	7.930561	-1.669474	H	2.181143	7.673287	-1.894538
C	3.370258	13.066395	-1.655073	C	2.570881	13.165747	1.873747
Ru	3.989349	14.943008	-2.045064	Ru	3.097056	15.063403	2.294348
P	4.038916	14.584876	-4.376636	P	5.396002	14.549437	2.382675
P	1.749271	15.539938	-2.467959	P	3.538926	15.385101	0.003196
P	3.950228	15.534845	0.238120	P	0.858191	15.804233	2.193885
P	6.258928	14.485809	-1.587659	P	2.622449	14.875089	4.599033
C	2.527729	15.385342	-5.147840	C	6.207414	15.123757	0.791449
C	1.302678	15.153748	-4.249130	C	5.283747	14.824497	-0.399895
C	6.736344	15.353503	0.003616	C	1.100872	15.898941	4.983449
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H	1.380417	16.914445	-2.361280
H	0.642918	14.969343	-1.772110
H	3.752934	16.914175	0.540988
H	3.059751	14.976191	1.203492
H	6.707584	13.151315	-1.345463
H	7.314108	14.902688	-2.450868
H	3.987439	13.268578	-4.928879
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H	5.760770	15.851881	1.905908
H	5.568777	14.154296	1.409690
H	7.696343	14.973908	0.380224
H	6.860392	16.412447	-0.271993
H	0.999786	14.094963	-4.265076
H	0.442398	15.758439	-4.568227
H	2.364542	15.003026	-6.165012
H	2.764621	16.458922	-5.213455
Cl	4.760633	17.332715	-2.553566

H	3.527240	16.714950	-0.514930
H	2.793007	14.748154	-1.031805
H	0.648552	17.171958	1.850262
H	-0.148441	15.220460	1.367622
H	2.288519	13.614259	5.181783
H	3.520943	15.334774	5.605874
H	5.854139	13.199843	2.475773
H	6.258376	15.131846	3.356499
H	-0.767906	16.428144	3.961394
H	-0.396181	14.688568	3.948229
H	0.705394	15.649386	5.977800
H	1.452395	16.942426	4.995610
H	5.220859	13.740520	-0.584199
H	5.638327	15.306272	-1.321698
H	7.193954	14.655718	0.668842
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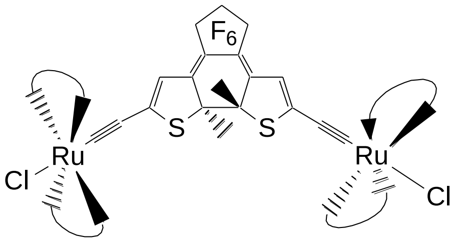
Cl	3.760166	17.480775	2.821737

1c$_3$



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C	4.125874	-0.250059	-2.207376
P	2.408714	0.205090	-2.804237
H	3.122721	0.902286	1.366713
H	3.228289	-1.211573	0.911592
H	4.456523	1.444005	-0.868045
H	5.271642	-0.049942	-0.345308
H	4.886376	0.082761	-2.927350
H	4.141405	-1.350524	-2.167461
H	2.293151	-0.619588	-3.961525
H	2.639515	1.452009	-3.460299
Cl	1.031694	-2.493533	-1.208791
P	-0.606864	-0.292604	0.784451
H	-0.350242	-1.248324	1.810320
H	-1.024854	0.792734	1.613066
C	-2.235329	-0.923420	0.105294

1c$_1^+$

E = -466.628 eV

Ru	.060883	.064871	-.072100
P	.046676	.125363	2.301254
C	1.805231	.115687	2.951266
C	2.703756	-.725176	2.030203
P	2.386976	-.276360	.239713
H	-.530751	1.183310	3.063108
H	-.546521	-.983415	2.969372
H	2.131602	1.167562	2.963117
H	1.826437	-.254796	3.985357
H	3.767113	-.594958	2.273902
H	2.458014	-1.794861	2.115936
H	3.088599	-1.308141	-.445411
H	3.306880	.792506	.022272
Cl	-.212811	-2.441715	.099576
P	-2.298181	.109329	-.339314
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H	-3.016560	1.342439	-.307696
C	-2.727689	-.570445	-2.028800
H	-2.664941	-1.664936	-1.929857
H	-3.759423	-.304431	-2.296695
C	-1.721495	-.057638	-3.071622
H	-1.828401	-.585790	-4.029161
H	-1.869037	1.017215	-3.261507
H	.752825	.582630	-3.345320

H	-2.068838	-1.991215	-0.105565	P	.031381	-.235434	-2.427210
H	-3.028758	-0.835774	0.860546	H	.419615	-1.516704	-2.910950
C	-2.589672	-0.164122	-1.182741	C	.255382	2.026247	-.192348
H	-3.423366	-0.640005	-1.717495	C	.371502	3.273401	-.214167
H	-2.881823	0.873262	-0.956286	C	.433555	4.642798	-.119118
H	-1.504806	0.953204	-3.218993	S	1.672086	5.606811	-.957055
P	-1.081283	-0.051335	-2.297623	C	-.434615	5.461348	.642269
H	-1.245936	-1.191502	-3.137986	H	-1.290911	5.033423	1.159249
C	0.797219	2.055152	-0.814197	C	-.124110	6.807945	.649775
C	0.740060	3.287599	-0.667798	C	-.858376	7.876650	1.197081
C	0.540295	4.658443	-0.509845	C	1.228407	7.147870	.007947
S	1.805442	5.706518	0.205294	C	1.060789	8.436344	-.846743
C	-0.595598	5.373990	-0.863963	C	.527603	9.551861	.059997
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C	-1.453343	7.746326	-0.919616	C	-2.392099	9.261126	2.508102
C	0.600926	7.141024	0.361626	C	-1.303504	10.158392	1.789721
C	1.164941	8.514399	-0.083180	F	-3.165155	7.265402	1.356179
C	0.019433	9.541859	-0.103393	F	-1.918838	6.959324	3.144509
C	-1.196263	9.125335	-0.610364	C	2.291723	7.301174	1.121126
C	-2.740893	7.589853	-1.639824	H	3.283282	7.467686	.682784
C	-3.422707	9.016868	-1.599628	H	2.047043	8.153808	1.771447
C	-2.380640	9.972201	-0.891701	H	2.320442	6.389132	1.731145
F	-2.593368	7.187352	-2.965483	F	-3.643695	9.635631	2.134805
F	-3.589483	6.644997	-1.081849	F	-2.297441	9.372190	3.859157
C	0.082649	7.142295	1.818572	F	-1.909181	11.150390	1.049407
H	0.899869	7.342993	2.522067	F	-.535657	10.814416	2.735806
H	-0.689253	7.915804	1.946743	S	2.651060	9.141616	-1.545259
H	-0.356407	6.161748	2.044494	C	2.242416	10.785045	-1.004435
F	-3.710235	9.461390	-2.857090	C	1.116904	10.783584	-.145522
F	-4.595437	8.970211	-0.903219	H	.780960	11.702875	.328803
F	-2.112867	11.065121	-1.703980	C	2.939883	11.907860	-1.383962
F	-2.958442	10.522383	0.250884	C	.092706	8.242171	-2.037465
S	2.428533	9.268209	1.091663	H	-.043308	9.196324	-2.562480
C	1.637587	10.872001	0.993710	H	.493787	7.502484	-2.741114
C	0.402945	10.810345	0.362259	H	-.887209	7.891771	-1.681214
H	-0.227799	11.692311	0.277903	C	3.384164	13.049691	-1.647896
C	2.217412	12.030288	1.513826	Ru	3.968237	14.897804	-2.031262
C	1.812395	8.477466	-1.486720	P	4.024560	14.600387	-4.384357
H	2.132138	9.490936	-1.762427	P	1.714631	15.509909	-2.439504
H	2.682110	7.809025	-1.496840	P	3.928952	15.533400	.257365
H	1.085961	8.118747	-2.231185	P	6.259544	14.483778	-1.558747
C	2.570792	13.166328	1.871852	C	2.502929	15.406851	-5.123080
Ru	3.097876	15.063313	2.294183	C	1.279582	15.150499	-4.227436

P	5.396243	14.547961	2.382268
P	3.540336	15.386240	0.003274
P	0.858775	15.803689	2.194249
P	2.622673	14.874816	4.599173
C	6.208563	15.122667	0.791776
C	5.284692	14.824360	-0.399701
C	1.100557	15.897785	4.983907
C	0.046571	15.693404	3.884544
H	3.529957	16.716505	-0.513942
H	2.793502	14.750251	-1.031552
H	0.647739	17.171184	1.850685
H	-0.148543	15.220163	1.368279
H	2.289877	13.613828	5.181892
H	3.520907	15.334804	5.606082
H	5.853829	13.198042	2.474823
H	6.258972	15.129107	3.356553
H	-0.768548	16.426197	3.961839
H	-0.396160	14.687093	3.948616
H	0.705186	15.647503	5.978161
H	1.451486	16.941479	4.996778
H	5.220726	13.740392	-0.583945
H	5.639411	15.306297	-1.321363
H	7.194911	14.654061	0.669434
H	6.351713	16.208285	0.910405
Cl	3.761686	17.480102	2.823144

C	6.718431	15.385079	.014670
C	5.598844	15.228635	1.055649
H	1.359532	16.882829	-2.299641
H	.614818	14.925117	-1.747081
H	3.698047	16.913487	.517960
H	3.045125	14.972535	1.226314
H	6.714673	13.156444	-1.300442
H	7.295390	14.899338	-2.442180
H	3.993226	13.298484	-4.967964
H	5.067790	15.169674	-5.166175
H	5.739201	15.908965	1.906637
H	5.569003	14.200168	1.448268
H	7.681323	15.020633	.397869
H	6.835047	16.439811	-.278022
H	.983067	14.090287	-4.262989
H	.415597	15.752962	-4.539829
H	2.336755	15.043391	-6.146432
H	2.731573	16.482770	-5.172076
Cl	4.712411	17.263091	-2.519100

$1c_1^{2+}$ singlet state

E = -458.942 eV

Ru	.057300	.125769	-.085311
P	.041122	.113401	2.310079
C	1.800421	.049045	2.953037
C	2.683523	-.785526	2.012816
P	2.393970	-.288124	.230850
H	-.526408	1.151102	3.105128
H	-.579666	-1.016454	2.908932
H	2.147767	1.093277	2.997745
H	1.809483	-.350814	3.975833
H	3.748527	-.679593	2.261328
H	2.421414	-1.852757	2.072179
H	3.042759	-1.329323	-.487258
H	3.345310	.754572	.031044
Cl	-.209104	-2.363772	.087185
P	-2.322527	.121843	-.343876
H	-3.130936	-.639040	.542727

H	-3.062315	1.341344	-.337198	
C	-2.739774	-.614080	-2.013713	
H	-2.663423	-1.704135	-1.884279	
H	-3.776521	-.369968	-2.281610	
C	-1.750370	-.115697	-3.078356	
H	-1.857300	-.674806	-4.018214	
H	-1.917067	.949789	-3.302989	
H	.719239	.557345	-3.400855	
P	.013549	-.245612	-2.459897	
H	.428604	-1.537616	-2.881402	
C	.257419	2.044600	-.208968	
C	.392339	3.302220	-.248281	
C	.481832	4.651029	-.135550	
S	1.766785	5.620374	-.880860	
C	-.421858	5.490902	.610608	
H	-1.314472	5.069944	1.068820	
C	-.078112	6.807577	.664419	
C	-.837905	7.888705	1.222630	
C	1.269272	7.164325	.037072	
C	1.051465	8.425644	-.864346	
C	.519821	9.542254	.032005	
C	-.529216	9.197361	.945976	
C	-2.031863	7.766070	2.130134	
C	-2.411828	9.255867	2.518213	
C	-1.388533	10.162617	1.716003	
F	-3.085457	7.154652	1.491879	
F	-1.760343	7.025421	3.249135	
C	2.322646	7.401409	1.144001	
H	3.306790	7.588773	.697229	
H	2.047879	8.269771	1.760574	
H	2.391975	6.519948	1.793934	
F	-3.684454	9.538836	2.156823	
F	-2.276061	9.446341	3.851286	
F	-2.049990	11.036735	.894796	
F	-.638398	10.922547	2.583196	
S	2.608815	9.139537	-1.605524	
C	2.255332	10.769649	-1.009090	
C	1.123450	10.752806	-.117758	
H	.819076	11.659210	.400612	
C	2.948768	11.884686	-1.351303	
C	.066155	8.163996	-2.026531	
H	-.112332	9.091178	-2.585937	
H	.476929	7.412319	-2.711661	
H	-.896652	7.796870	-1.642184	

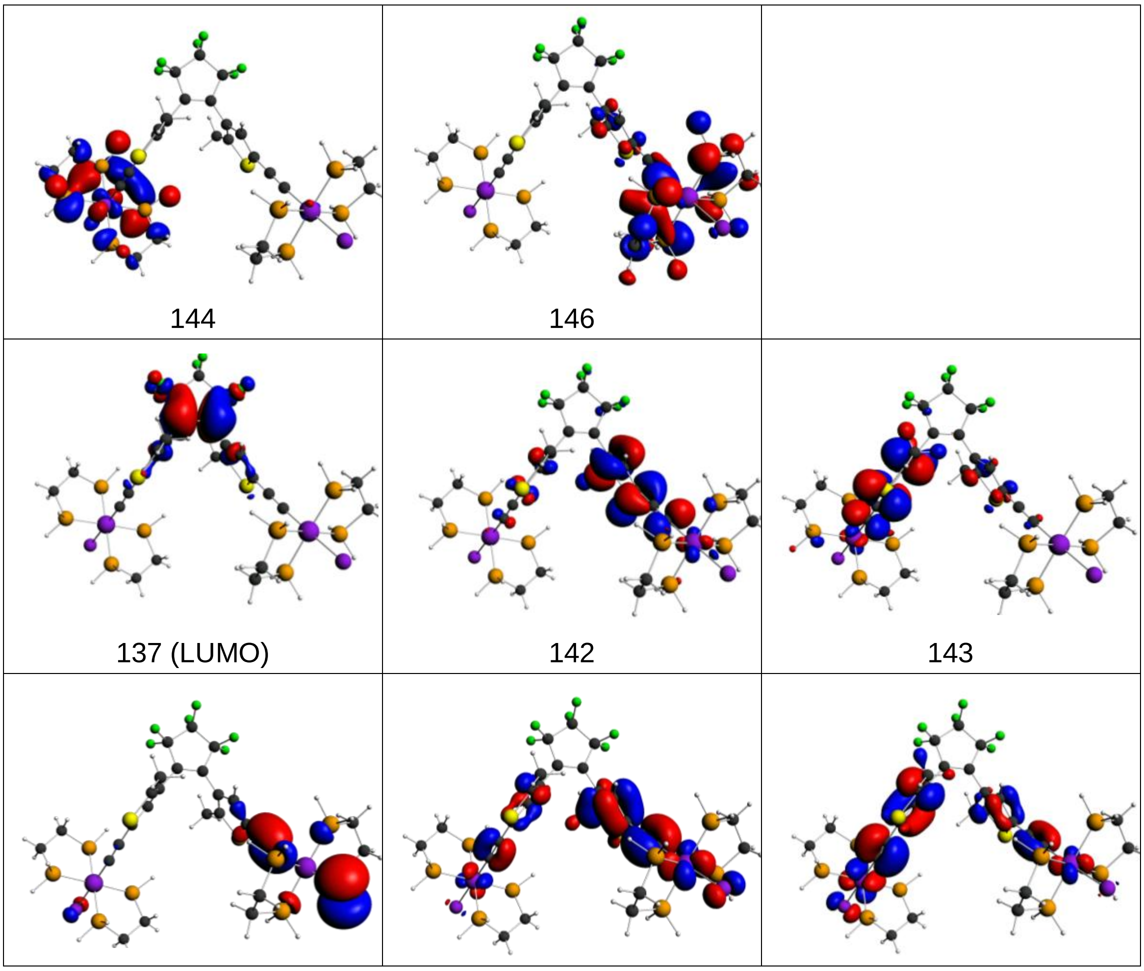
C	3.376765	13.047258	-1.612707	
Ru	3.953130	14.849860	-2.004104	
P	4.017288	14.565037	-4.380836	
P	1.711857	15.566971	-2.449953	
P	3.940271	15.560935	.283129	
P	6.279473	14.471648	-1.548178	
C	2.534846	15.434060	-5.123542	
C	1.292509	15.228341	-4.241862	
C	6.731837	15.400492	.009069	
C	5.618315	15.261746	1.059795	
H	1.460395	16.958643	-2.301533	
H	.574974	15.045585	-1.767780	
H	3.722857	16.952502	.474511	
H	3.057191	15.044172	1.275314	
H	6.745063	13.150709	-1.283104	
H	7.281271	14.890509	-2.465045	
H	3.950789	13.266500	-4.966149	
H	5.099402	15.104077	-5.127235	
H	5.769778	15.954860	1.898498	
H	5.589504	14.240446	1.471128	
H	7.694780	15.039222	.395276	
H	6.854072	16.450310	-.297439	
H	.947233	14.183029	-4.284133	
H	.459701	15.869369	-4.562130	
H	2.363966	15.074995	-6.147561	
H	2.806676	16.499312	-5.174481	
Cl	4.700445	17.185270	-2.535736	

Table S2. Calculated main electronic excitations in **1o** and **1c**, 3 different rotamers were considered for the latter (**1c$_1$**, **1c$_2$**, **1c$_3$** for rotamers 1, 2 and 3 respectively). The orbitals mainly involved in the excitations are plotted (for **1c**, the orbitals are given in the **1c$_2$** geometry).

Cpnd	Energy (nm)	Oscillator strength[a]	Composition (%)[b]	λ_{max}[c] calc.	assignment
1o	387	0.07	129→137 50 135→142 22 135→146 6		
	389	0.13	129→137 46 135→142 16 135→146 7 135→145 6 135→143 5		
	358	0.09	135→146 36 135→142 10 136→150 10 135→150 6 136→146 6	370	$[Cl(dppe)_2Ru\text{-}C_2]$ → π* DTE/(Ru-P)*

[a] Only the transition with calculated oscillator strengths > 0.05 are reported. [b] Only the contribution > 5 % are given. [c] Maximum of absorption in nm in a simulated spectra obtained from all the excitations of the TDDFT results.

Molecular orbitals of **1o**:

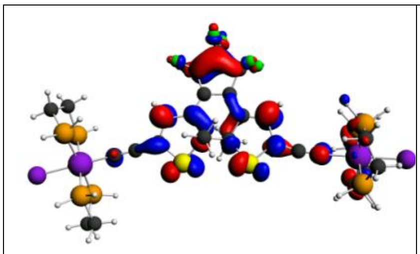
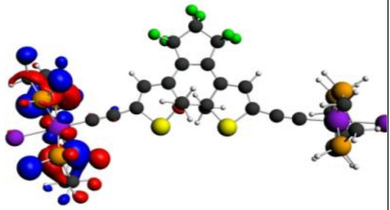
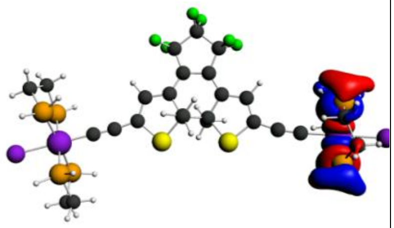
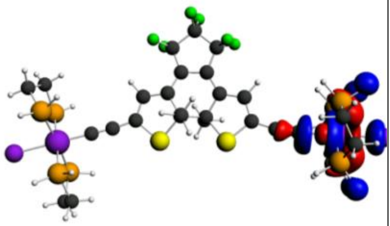
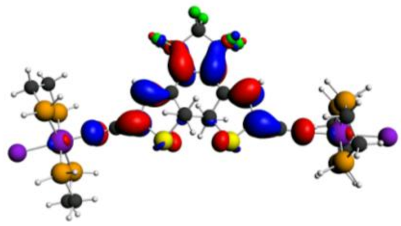
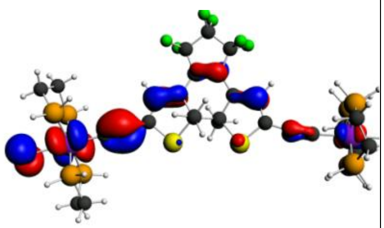
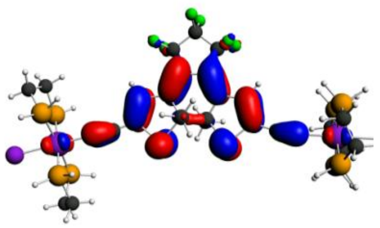
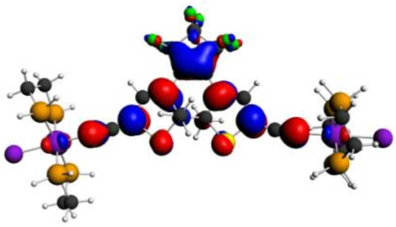
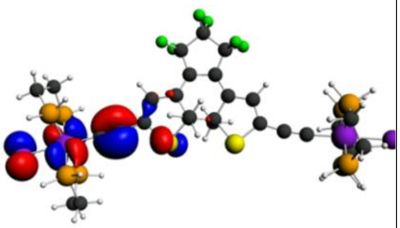
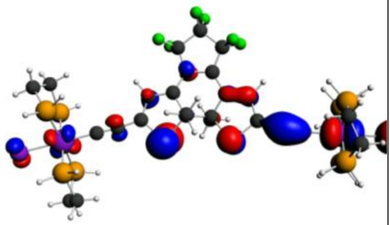
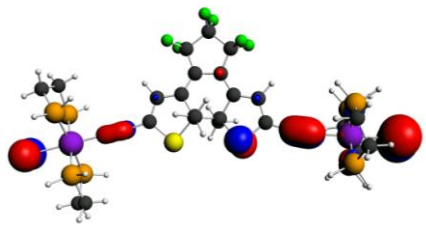


129	135	136 (HOMO)

Cpnd	Energy (nm)	Oscillator strength[a]	Composition (%)[b]		λ_{max}[c] calc.	assignment
1c$_1$	766	0.62	136→137	97	766	π C_2-DTE→π* C_2-DTE
	500	0.26	132→137	95	500	d/π [Cl-Ru-C_2]/S→π* C_2-DTE
	395	0.06	130→137 136→153 136→154 136→152	33 27 7 5		
	383	0.14	136→154 136→152 130→137	53 28 6		
	367	0.19	127→137 136→142 133→137 136→146 136→146	36 19 11 7 5	373	d/π [Cl-Ru-C_2]/S/DTE→π* C_2-DTE/(Ru-P)*
	328	0.06	131→142 124→137	52 37		
1c$_2$	697(2)	0.77	136→137 136→139	86 10	687	π C_2-DTE→π* C_2-DTE/(Ru-P)*
	690(3)	0.08	136→139 136→137	90 10		
	499(9)	0.26	132→137 133→137 136→142	75 8 7	499	d/π [Cl-Ru-C_2]/S/DTE→π* C_2-DTE
	384(40)	0.08	136→152 134→141 136→154	25 24 21		
	368(45)	0.17	128→137 136→142 136→155 134→137	35 18 8 20	379	d/π [Cl-Ru-C_2]-DTE→π* C_2-DTE/(Ru-P)*
1c$_3$	706	0.70	136→137 136→139	86 10	706	π C_2-DTE→π* C_2-DTE/(Ru-P)*
	532	0.14	132→137 133→137 136→142	75 8 7	529	d/π [Cl-Ru-C_2]/S/DTE→π* C_2-DTE
	387	0.07	136→152 134→141 136→154	25 24 21	390	
	363(56)	0.06	136→152 134→141 136→154	25 24 21		d/π [Cl-Ru-C_2]-DTE→π* C_2-DTE/(Ru-P)*

[a] Only the transition with calculated oscillator strengths > 0.05 are reported. [b] Only the contribution > 5 % are given. [c] Maximum of absorption in nm in a simulated spectra obtained from all excitations of the TDDFT results.

Molecular orbitals of **1c$_2$**:

 152	 155	
 139	 141	 142
 134	 136 (HOMO)	 137 (LUMO)
 133	 132	 128

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