Journal Name

ARTICLE

π-stacking attraction *vs* electrostatic repulsion: competing supramolecular interactions in a tpphz-bridged Ru(II)/Au(III) complex

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Electronic Supplementary Information

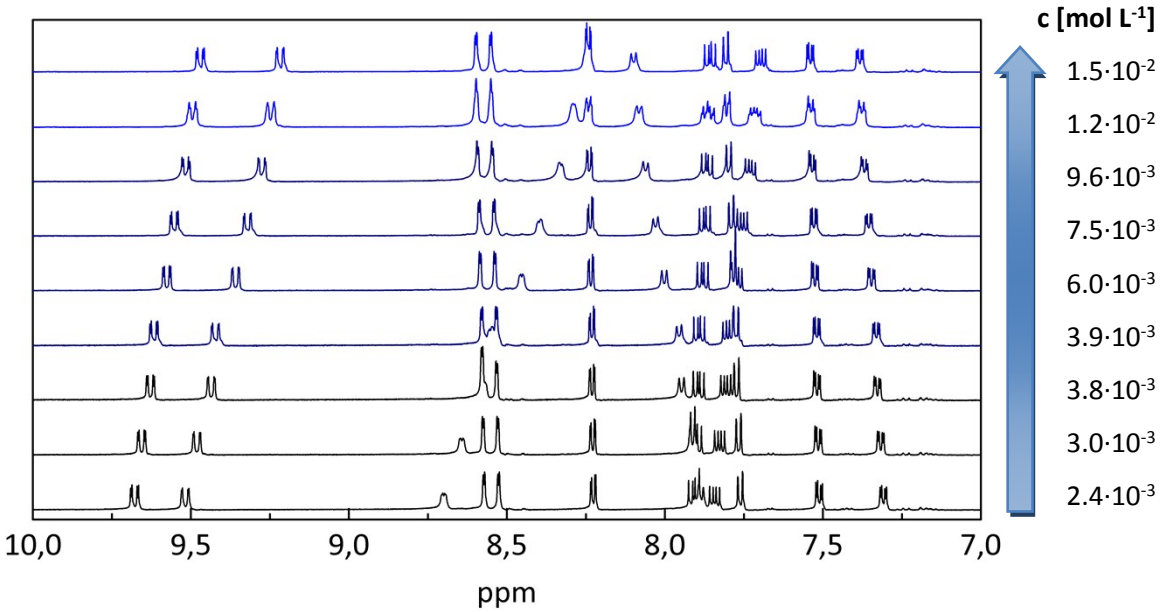


Figure S1: ^{1}H-NMR spectra of **[Ru]** in acetonitrile-d_3 at different concentrations as indicated on the right hand side.

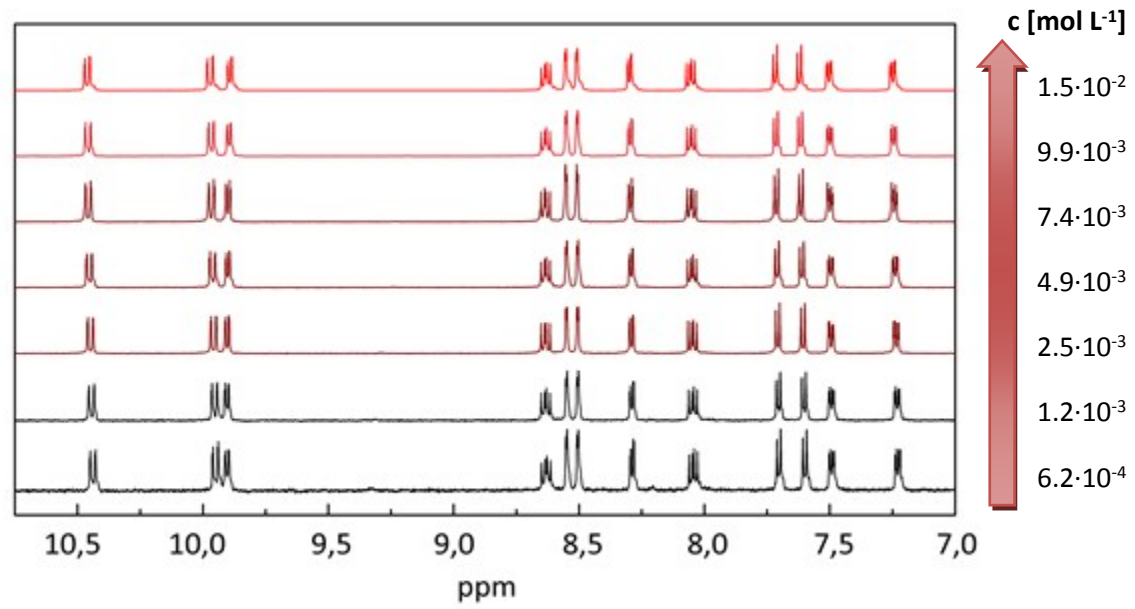


Figure S2: ^{1}H-NMR spectra of [RuAu] in acetonitrile-d_3 at different concentrations.

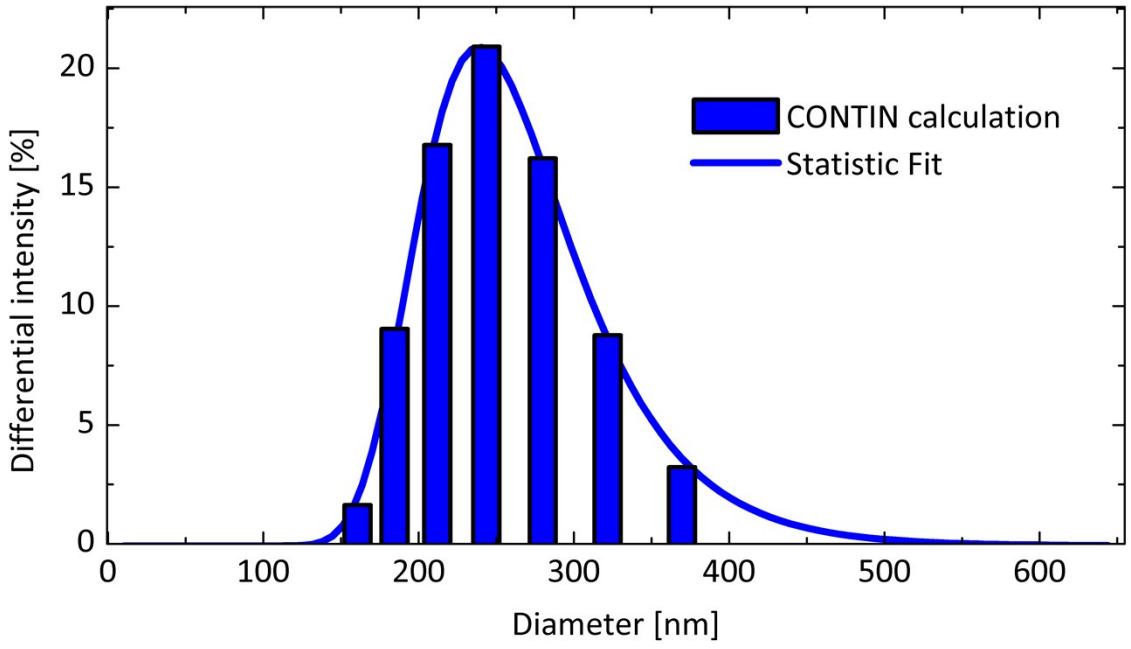


Figure S3: CONTIN calculation and mathematic fit of the DLS results obtained from a catalysis mixture of [RuAu] after 27 hours of illumination.

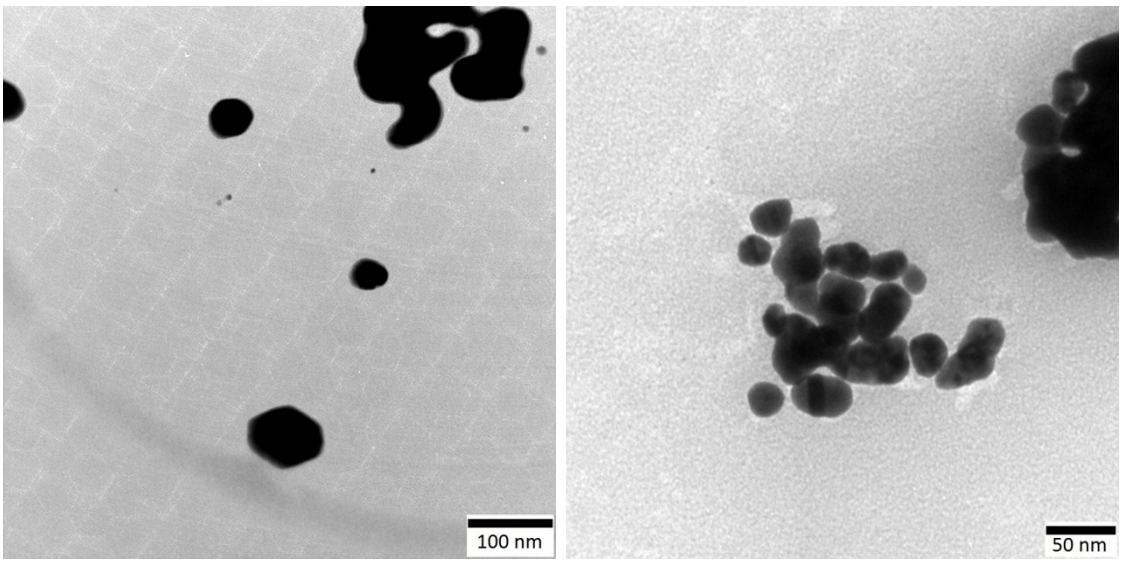


Figure S4: TEM images obtained from a catalysis solution of [RuAu] after 27 hours of illumination.

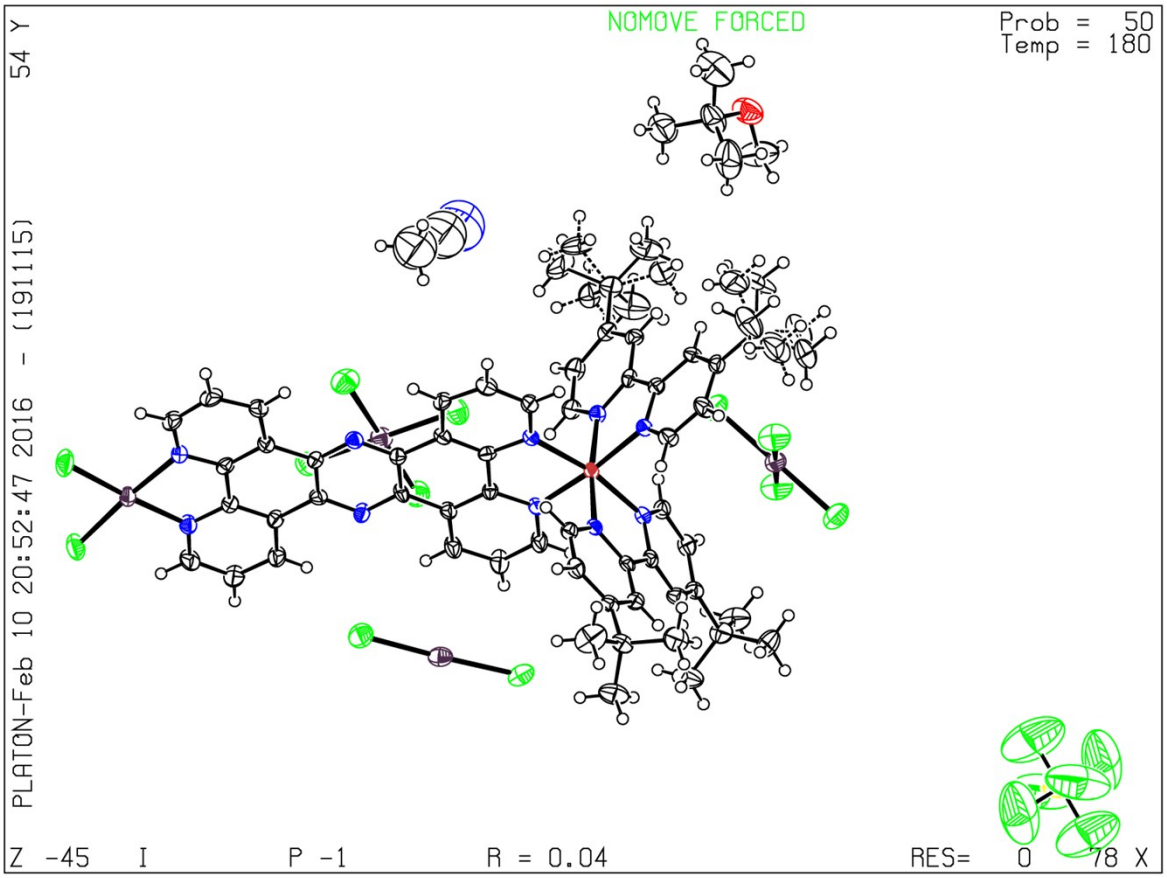


Figure S5: ORTEP depiction of the solid-state structure of **[RuAu] (A)**, ellipsoids at 50% probability.

Table 1. Crystal data and structure refinement for **[RuAu] (A)**

Empirical formula	C67 H75 Au3.5 Cl10 F3 N11 O P0.5 Ru	
Formula weight	2267.81	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 11.7043(3) Å	α= 78.063(2)°.
	b = 15.0514(4) Å	β= 79.898(2)°.
	c = 24.0777(4) Å	γ = 67.501(2)°.
Volume	3812.28(17) $Å^3$	
Z	2	
Density (calculated)	1.976 Mg/m^3	
Absorption coefficient	7.323 mm^{-1}	
F(000)	2174	
Crystal size	0.1525 x 0.0947 x 0.0753 mm^3	
Theta range for data collection	3.424 to 26.372°.	
Index ranges	-14<=h<=12, -18<=k<=18, -30<=l<=28	
Reflections collected	43402	
Independent reflections	15558 [R(int) = 0.0362]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15558 / 51 / 929	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0785	
R indices (all data)	R1 = 0.0542, wR2 = 0.0855	
Largest diff. peak and hole	1.959 and -1.309 e·$Å^{-3}$	

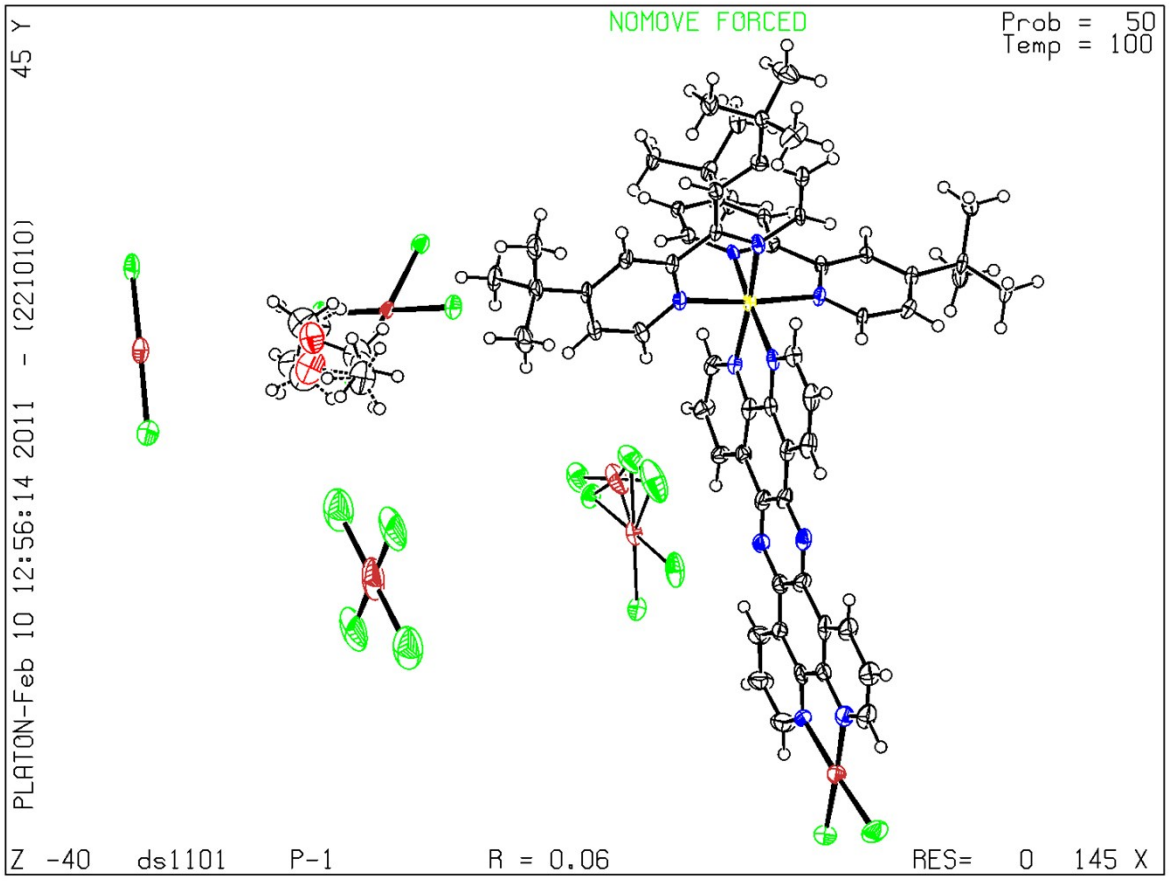
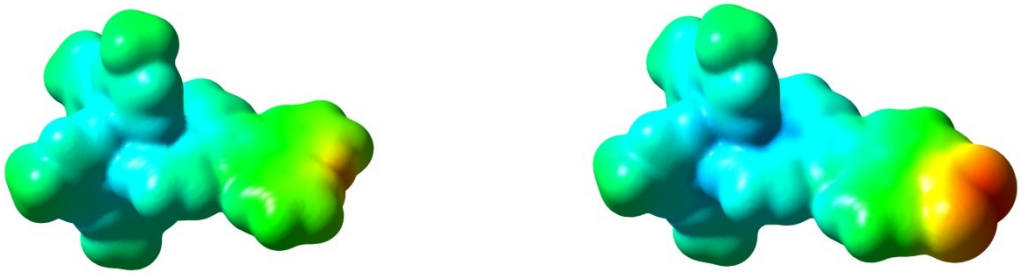


Figure S6: ORTEP depiction of the solid-state structure of **[RuAu] (B)**, ellipsoids at 50% probability.

Table 2. Crystal data and structure refinement for **[RuAu] (B)**

Empirical formula	C64 H70 Au4 Cl11 N10 O Ru	
Formula weight	2274.20	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 11.2792(14) Å	α= 78.519(2)°.
	b = 15.2758(19) Å	β= 78.669(2)°.
	c = 23.259(3) Å	γ = 68.620(2)°.
Volume	3623.2 (8) $Å^3$	
Z	2	
Density (calculated)	2.085 Mg/m^3	
Absorption coefficient	8.727 mm^{-1}	
F(000)	2158	
Crystal size	0.14 x 0.12 x 0.09 mm^3	
Theta range for data collection	2.36 to 27.19°.	
Index ranges	-14<=h<=12, -19<=k<=19, -29<=l<=29	
Reflections collected	56329	
Independent reflections	15930 [R(int) = 0.0541]	
Completeness to theta = 25.242°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15930 / 114 / 921	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1399	
R indices (all data)	R1 = 0.0786, wR2 = 0.1544	
Largest diff. peak and hole	5.958 and -7.342 e·$Å^{-3}$	



Ru **RuPt**

Figure S7: ESP maps of **[Ru]** and **[RuPt]**.

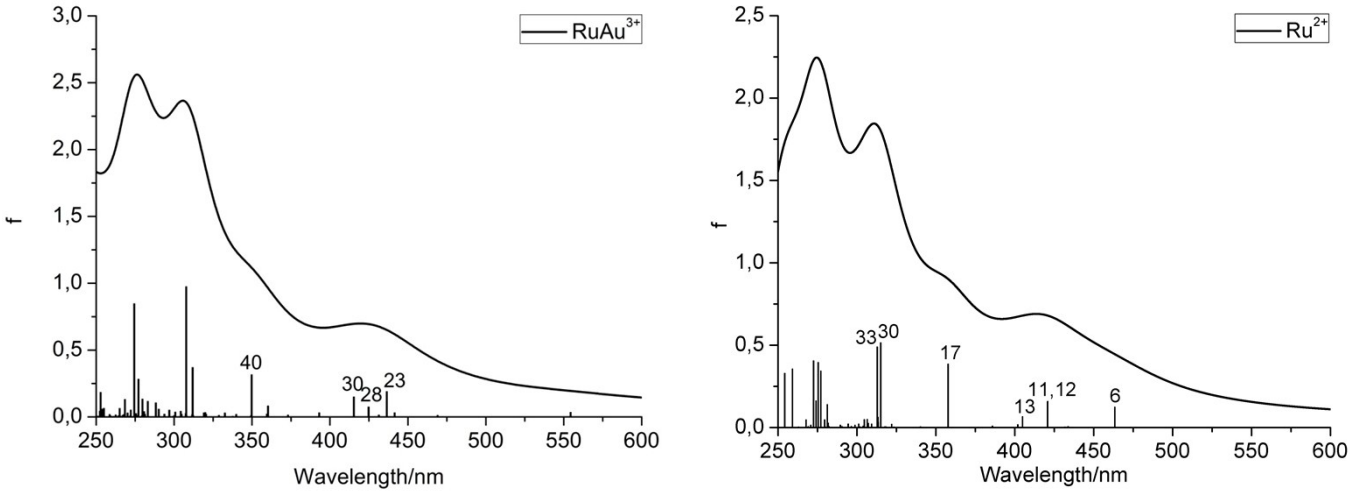


Figure S8: Calculated absorption spectra of **[RuAu]** and **[Ru]**.

Table S3: Calculated excited states properties of **[RuAu]**.

State number	Transition	Weight (%)	E^e (eV)	λ (nm)	f	$\langle S^2 \rangle$
S5	228 ->232 228 ->233	78 19	2.24	554	0.035	0.000
S17	228 ->234 229 ->235	88 5	2.64	469	0.012	0.000
S22	217 ->231	97	2.81	441	0.032	0.000
S23	228 ->235 228 ->236	78 14	2.84	436	0.190	0.000
S25	229 ->236 228 ->237 229 ->235	47 44 5	2.87	431	0.015	0.000
S28	228 ->236 229 ->237 228 ->235	53 36 5	2.92	424	0.075	0.000
S30	228 ->237 229 ->236	51 45	2.99	415	0.150	0.000
S31	229 ->237 230 ->238 228 ->236	44 21 20	3.15	393	0.033	0.000
S34	229 ->238 227 ->232	78 7	3.44	360	0.083	0.000
S36	227 ->232 229 ->238 227 ->233	77 8 7	3.45	359	0.023	0.000
S40	224 ->232 225 ->234	81 6	3.54	349	0.316	0.000

Table S4: Calculated excited states properties of **[Ru]**.

State number	Transition	Weight (%)	E^e (eV)	λ (nm)	f	$\langle S^2 \rangle$
S_6	$d_{Ru}(203) \rightarrow \pi^*_{tpphz}(205)$ (MLCT) $d_{Ru}(203) \rightarrow \pi^*_{tpphz}(206)$ (MLCT)	82 11	2.68	463	0.126	0.0
S_{11}	$d_{Ru}(203) \rightarrow \pi^*_{tpphz}(206)$ (MLCT) $d_{Ru}(202) \rightarrow \pi^*_{tbbpy}(209)$ (MLCT) $d_{Ru}(202) \rightarrow \pi^*_{tpphz}(207)$ (MLCT) $d_{Ru}(203) \rightarrow \pi^*_{tpphz}(205)$ (MLCT) $d_{Ru}(203) \rightarrow \pi^*_{tbbpy}(208)$ (MLCT) $d_{Ru}(204) \rightarrow \pi^*_{tpphz}(207)$ (MLCT)	34 25 18 7 7 6	2.95	421	0.161	0.0
S_{12}	$d_{Ru}(202) \rightarrow \pi^*_{tbbpy}(208)$ (MLCT) $d_{Ru}(203) \rightarrow \pi^*_{tbbpy}(209)$ (MLCT) $d_{Ru}(202) \rightarrow \pi^*_{tpphz}(206)$ (MLCT) $d_{Ru}(203) \rightarrow \pi^*_{tpphz}(207)$ (MLCT)	47 40 6 5	2.95	421	0.158	0.0
S_{13}	$d_{Ru}(202) \rightarrow \pi^*_{tpphz}(207)$ (MLCT) $d_{Ru}(202) \rightarrow \pi^*_{tbbpy}(209)$ (MLCT)	67 29	3.06	405	0.067	0.0
S_{17}	$\pi_{tpphz}(200) \rightarrow \pi^*_{tpphz}(205)$ (IL) $\pi_{tpphz}(201) \rightarrow \pi^*_{tpphz}(207)$ (IL)	86 10	3.47	358	0.386	0.0
S_{30}	$d_{Ru}(204) \rightarrow \pi^*_{tbbpy}(214)$ (MLCT) $\pi_{tpphz}(201) \rightarrow \pi^*_{tpphz}(207)$ (IL)	45 32	3.94	315	0.516	0.0
S_{33}	$\pi_{tpphz}(201) \rightarrow \pi^*_{tpphz}(207)$ (IL) $d_{Ru}(204) \rightarrow \pi^*_{tbbpy}(214)$ (MLCT) $d_{Ru}(202) \rightarrow \pi^*_{tbbpy}(213)$ (MLCT) $\pi_{tpphz}(200) \rightarrow \pi^*_{tpphz}(205)$ (IL) $d_{Ru}(202) \rightarrow \pi^*_{tbbpy}(214)$ (MLCT)	43 19 7 6 5	3.96	313	0.490	0.0

Table S5: Orbitals of **[RuAu]**.

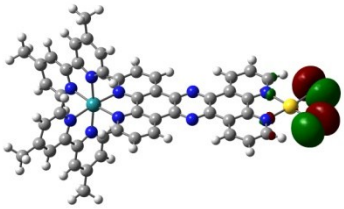
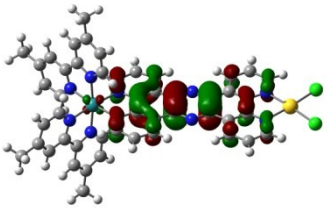
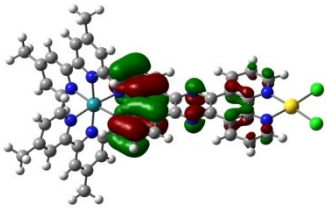
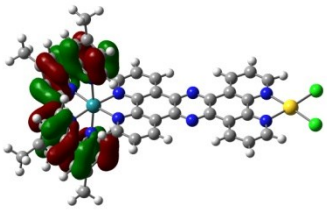
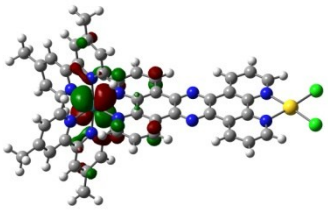
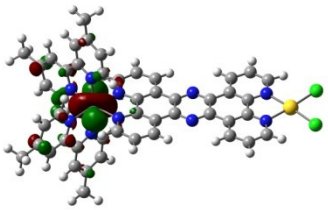
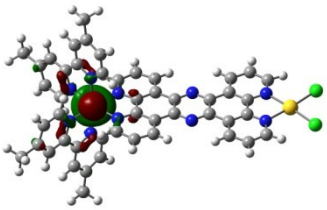
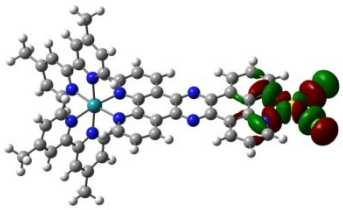
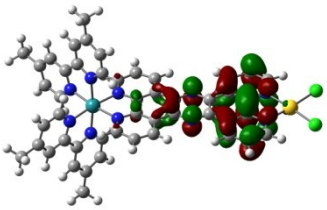
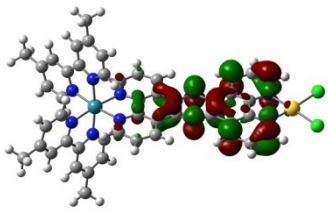
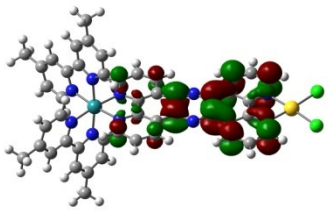
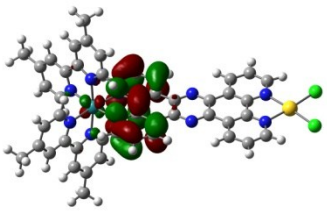
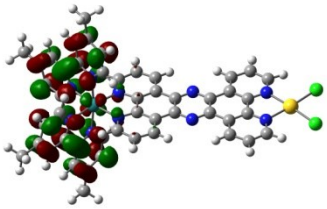
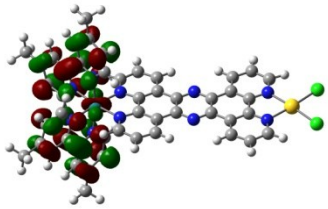
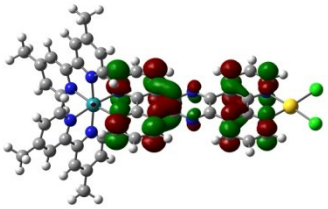
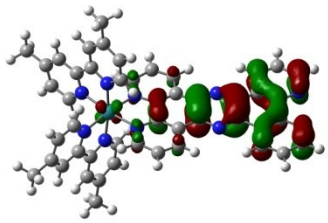
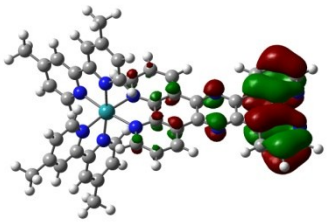
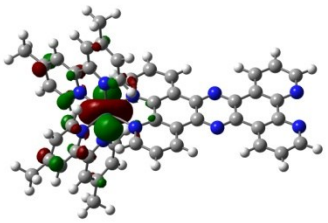
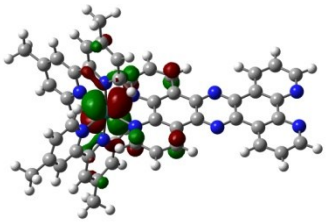
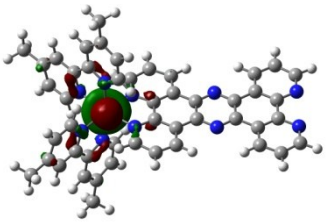
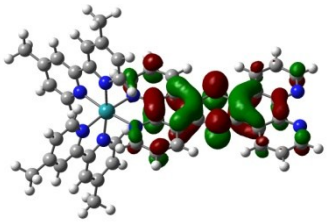
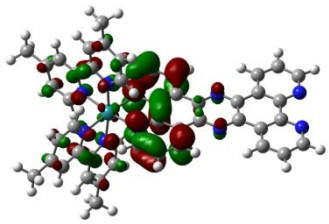
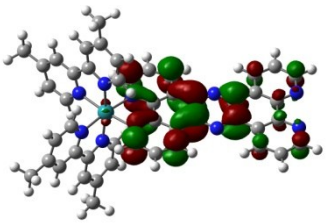
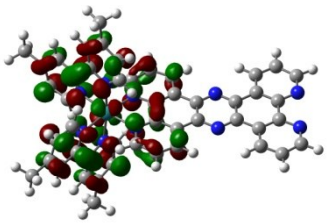
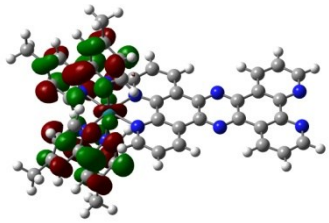
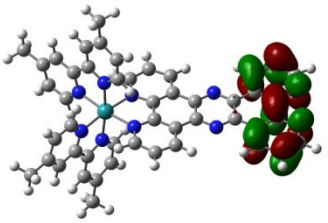
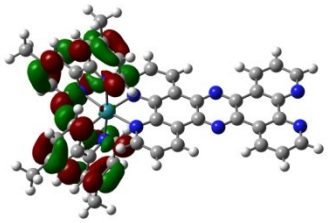
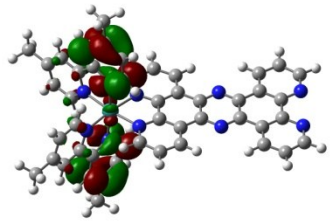
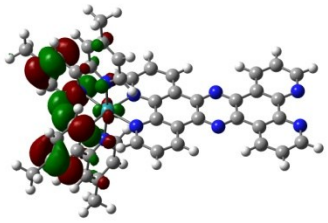
 217	 224	 225
 227	 228	 229
 230 (HOMO)	 231 (LUMO)	 232
 233	 234	 235
 236	 237	 238

Table S6: Orbitals of **[Ru]**.

 200	 201	 202
 203	 204 (HOMO)	 205 (LUMO)
 206	 207	 208
 209	 210	 211
 213	 214	