

Two-Photon Absorption Cooperative Effects within Multi-dipolar Ruthenium Complexes: The Decisive Influence of Charge Transfers

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Synthesis and main characterizations.

Most manipulations were performed using Schlenk techniques under an Ar atmosphere. All solvents were dried and purified by standard procedures. The bipyridyl ligands L^T , L^C , L^F were synthesized following previously reported procedures.^{46,58} NMR spectra were recorded on Bruker DPX-200, AV 300 or AV 500 MHz spectrometers. 1H and ^{13}C chemical shifts are given versus SiMe₄ and were determined by reference to residual 1H and ^{13}C solvent signals. UV-vis absorption spectra were recorded using a UVIKON 9413 or Biotek Instruments XS spectrophotometer using quartz cuvettes of 1 cm path length. Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 or Tau-3 spectrofluorimeter. The two-photon absorption (TPA) measurements were performed with femtosecond mode-locked laser pulse using a Ti: Sapphire laser (Coherent, Chameleon Ultra II: pulse duration: ~140 fs; repetition rate: 80 MHz; wavelength range: 680-1040 nm). Electrospray ionization mass spectrometric (ESI-MS) measurements have been made on a Bruker Daltonics Amazon SL ion trap and Agilent Q-TOF MS mass spectrometer. Elemental analyses were performed at the Centre de Mesures Physiques de l'Ouest (CRMPO) in Rennes.

$[RuL^T(bpy)_2]^{2+}$, $2(PF_6^-)$: Yield: 73 mg, 36 %. 1H NMR (400 MHz, CD₂Cl₂) δ 8.54 (s, 2H), 8.46 (d, J = 6 Hz, 4H), 8.10 (t, J = 7.1 Hz, 4H), 7.86 (d, J = 5.6 Hz, 2H), 7.75 (d, J = 5.6 Hz, 2H), 7.59 – 7.48 (m, 14H), 7.34 (t, J = 5.6 Hz, 8H), 7.17 – 7.12 (m, 14H), 7.27 (d, J = 5.6 Hz, 4H). ^{13}C NMR (101 MHz, CD₂Cl₂) δ 156.66, 156.49, 151.43, 149.28, 147.54, 146.91, 137.79, 129.48, 128.86, 128.63, 125.26, 123.94, 123.75, 121.92, 121.15. MALDI-TOF-MS: calc. for $[C_{70}H_{54}N_8F_6PRu]^+$ m/z = 1253.3157, found m/z = 1257.729 Anal. Calcd. For $[C_{70}H_{54}N_8F_{12}P_2Ru]$: C, 60.13; H, 3.89; N, 8.01. Found: C, 59.77; H, 3.86; N, 7.90.

$[RuL^C(bpy)_2]^{2+}$, $2(PF_6^-)$: Yield: 144.7 mg, 30 %. 1H NMR (400 MHz, acetone-d₆) δ 9.11 (s, 2H), 8.88 (d, J = 8 Hz, 4H), 8.53 (s, 2H), 8.26 – 8.23 (m, 8H), 8.13 (d, J = 8 Hz, 2H), 8.05 (d, J = 16 Hz, 2H), 7.95 (d, J = 8 Hz, 2H), 7.90 (dd, J = 4 Hz, 8 Hz, 2H), 7.75 – 7.60 (m, 12H), 7.51 (d, J = 16 Hz, 2H), 7.30 (t, J = 8 Hz, 2H), 4.53 (t, J = 8 Hz, 4H), 1.95 (m, 4H), 1.45 – 1.23 (m, 20H), 0.88 (t, J = 8 Hz, 6H). ^{13}C NMR (101 MHz, acetone-d₆) δ 157.42, 157.34, 157.30, 151.81, 151.81, 151.61, 151.19, 147.70, 141.43, 141.11, 137.97, 137.92, 127.91, 127.84, 126.92, 126.31, 125.41, 124.39, 123.87, 123.31, 122.65, 120.99, 120.56, 120.31, 120.21, 119.52, 109.71, 109.59, 109.43, 42.78, 31.59, 29.7, 29.5, 29.1, 26.90, 22.34, 13.41. MALDI-TOF-MS: calc. for $[C_{74}H_{74}N_8F_6PRu]^+$ m/z = 1321.4722, found m/z = 1322.404. Anal. Calcd. For $[C_{74}H_{74}N_8F_{12}P_2Ru, 0.5CH_2Cl_2]$: C, 59.28; H, 5.01; N, 7.43. Found: C, 59.32; H, 5.52; N, 7.07.

$[RuL^F(bpy)_2]^{2+}$, $2(PF_6^-)$: Yield: 20 mg, 12 %. 1H NMR (400 MHz, CD₂Cl₂) δ 8.54 (d, J = 2.0 Hz, 2H), 8.46 (d, J = 8.2 Hz, 6H), 8.08 (t, J = 7.9 Hz, 6H), 7.85 (dd, J = 5.8, 1.3 Hz, 2H), 7.75 (d, J = 5.6 Hz, 2H), 7.69 (d, J = 4.3 Hz, 2H), 7.66 – 7.59 (m, 6H), 7.54 – 7.47 (m, 10H), 7.27 (t, J = 7.7 Hz, 10H), 7.10 (d, 6H), 7.03 (m, J = 6.7, 6.1 Hz, 6H), 2.02 – 1.81 (m, 8H), 1.25 – 1.03 (m, 40H), 0.83 (t, J = 6.9 Hz, 12H), 0.68 (s, 8H). ^{13}C NMR (101 MHz, CD₂Cl₂) δ 156.8, 156.8, 156.7, 152.8, 151.5, 151.2, 151.2, 150.7, 148.0, 147.8, 147.8, 147.4, 143.2, 137.9, 137.9, 137.8, 135.1, 133.4, 129.1, 128.0, 127.9, 127.3, 124.1, 124.1, 124.0, 123.1, 122.7, 122.1, 121.7, 120.7, 120.7, 119.4, 118.8, 55.1, 40.1, 31.7, 29.9, 29.3, 29.2, 23.9, 22.6, 13.8. MALDI-TOF-MS: calc. for $[C_{116}H_{126}N_8F_6PRu]^+$ m/z = 1877.8791, found m/z = 1879.2596. Anal. Calcd. For $[C_{116}H_{126}N_8F_{12}P_2Ru], CH_2Cl_2$: C, 66.64; H, 6.12; N, 5.32. Found: C, 66.62; H, 5.97; N, 5.21.

General synthetic procedure for the Ru(L)₂(bpy)(PF₆)₂ complexes: Ru(bpy)Cl₂(DMSO)₂ (35 mg, 0.072 mmol) and the bipyridine L (2 eq., 0.144 mmol) were heated at 90°C for two days in degassed dimethylformamide (3 mL) under argon. The products were treated and purified as indicated above to give the expected products as red powders.

[Ru(L^T)₂(bpy)]²⁺, 2(PF₆⁻): Yield: 45 mg, 68 %. ¹H NMR (300 MHz, CD₂Cl₂) δ 8.42 (s, 4H), 8.36 (d, *J* = 8.8 Hz, 2H), 7.90 (t, *J* = 6.8 Hz, 2H), 7.80 (d, *J* = 6.8 Hz, 2H), 7.57 (d, *J* = 6.8 Hz, 2H), 7.50 – 7.41 (m, 20H), 7.35 – 7.26 (m, 20H), 7.28 – 7.23 (m, 24H), 6.95 (d, *J* = 6.8 Hz, 8H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 156.78, 149.00, 146.70, 135.62, 129.39, 129.32, 129.32, 128.64, 128.32, 128.32, 125.30, 124.97, 124.97, 123.85, 123.85, 123.53, 121.38, 121.38, 121.28, 119.98. MALDI-TOF-MS: calc. for ([C₁₁₀H₈₄N₁₀F₆PRu]⁺) *m/z* = 1791.5166, found *m/z* = 1793.365. Anal. Calcd. For [C₁₁₀H₈₄N₁₀F₁₂P₂Ru], 1.5 CH₂Cl₂: C, 64.75; H, 4.26; N, 6.81. Found: C, 64.36; H, 4.67; N, 6.83.

[Ru(L^C)₂(bpy)]²⁺, 2(PF₆⁻): Yield: 96 mg, 74 %. ¹H NMR (400 MHz, acetone-d₆) δ 9.13 (s, 4H), 8.90 (d, *J* = 8 Hz, 2H), 8.55 (d, *J* = 8 Hz, 4H), 8.29-8.20 (m, 8H), 8.11 (d, *J* = 8 Hz, 2H), 8.08 (d, *J* = 8 Hz, 2H), 8.04 (d, *J* = 8 Hz, 2H), 7.97 (d, *J* = 4 Hz, 2H), 7.92 (t, *J* = 8 Hz, 4H), 7.79-7.74 (m, 4H), 7.72-7.62 (m, 10H), 7.56-7.48 (m, 8H), 7.30-7.25 (m, 4H), 4.53 (m, 8H), 1.94 (m, 8H), 1.42-1.24 (m, 40H), 0.87 (t, *J* = 8 Hz, 12H). ¹³C NMR (101 MHz, acetone-d₆) δ 151.22, 141.44, 141.12, 126.94, 126.32, 125.40, 123.32, 122.63, 121.06, 120.51, 120.29, 119.53, 109.72, 42.78, 31.59, 31.57, 26.91, 22.35, 22.33, 13.42, 13.40. MALDI-TOF-MS: calc. for ([C₁₁₈H₁₂₄N₁₀F₆PRu]⁺) *m/z* = 1927.8696, found *m/z* = 1929.8841. Anal. Calcd. For [C₁₁₈H₁₂₄N₁₀F₁₂P₂Ru]: C, 68.36; H, 6.03; N, 6.76. Found: C, 67.44; H, 5.86; N, 6.94.

[Ru(L^F)₂(bpy)]²⁺, 2(PF₆⁻): Yield: 33 mg, 29 %. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.62 (s, 4H), 8.51 (d, *J* = 9 Hz, 2H), 8.14 (t, *J* = 9 Hz, 2H), 7.93 (d, *J* = 6.8 Hz, 2H), 7.77 (d, *J* = 6.8 Hz, 2H), 7.67 – 7.52 (m, 30H), 7.38 – 7.27 (m, 20H), 7.17 (m, 20H), 7.10 – 7.02 (m, 10H), 2.02 – 1.81 (m, 16H), 1.25 – 1.03 (m, 80H), 0.83 (t, *J* = 6.9 Hz, 24H), 0.68 (s, 16H). ¹³C NMR (101 MHz, CD₂Cl₂) δ 157.09, 152.86, 151.51, 150.73, 147.98, 147.88, 143.20, 137.59, 135.24, 133.54, 129.20, 127.30, 124.06, 123.20, 122.77, 120.78, 119.46, 118.93, 40.18, 31.80, 29.97, 29.32, 29.22, 23.92, 22.61, 18.35. MALDI-TOF-MS: calc. for ([C₂₀₂H₂₂₈N₁₀F₆PRu]⁺) *m/z* = 3042.6906, found *m/z* = 3044.0561. Anal. Calcd. For [C₂₀₂H₂₂₈N₁₀F₁₂P₂Ru], 1.5 CH₂Cl₂: C, 73.73; H, 7.03; N, 4.23. Found: C, 73.18; H, 7.22; N, 4.12.

General synthetic procedure for the Ru(L)₃(PF₆)₂ complexes: RuCl₂(DMSO)₄ (20.5 mg, 0.042 mmol) and the bipyridine L (0.131 mmol) were heated at 90°C for one day and 130°C for two days in 3 mL degassed dimethylformamide, under argon. The products were treated and purified as indicated above to give the expected products as red powders.

[Ru(L^T)₃]²⁺, 2(PF₆⁻): Yield: 55 mg, 54 %. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.55 (s, 6H), 7.66 (d, *J* = 5.8 Hz, 6H), 7.56 (d, *J* = 16.0 Hz, 6H), 7.53 (d, *J* = 7.6 Hz, 12H), 7.46 (d, *J* = 5.8 Hz, 6H), 7.33 (t, *J* = 7.1 Hz, 24H), 7.15 (m, 24H), 7.14 (m, 12H), 7.13 (d, *J* = 16.0 Hz, 6H), 7.04 (d, *J* = 7.6 Hz, 12H). ¹³C NMR (101 MHz, CD₂Cl₂) δ 156.99, 150.29, 149.49, 147.20, 146.92, 136.43, 129.45, 128.70, 128.46, 125.38, 124.00, 123.46, 121.73, 121.69, 120.95. MALDI-TOF-MS: calc. for ([C₁₅₀H₁₁₄N₁₂F₆PRu]⁺) *m/z* = 2329.7975, found *m/z* = 2329.2915. Anal. Calcd. For [C₁₅₀H₁₁₄N₁₂F₁₂P₂Ru], CH₂Cl₂: C, 70.83; H, 4.57; N, 6.56. Found: C, 70.23; H, 4.47; N, 6.74.

[Ru(L^C)₃]²⁺, 2(PF₆⁻): Yield: 68 mg, 60 %. ¹H NMR (400 MHz, acetone-d₆) δ 9.20 (s, 6H), 8.51 (s, 6H), 8.20 (d, *J* = 6 Hz, 5H), 8.17 (d, *J* = 9 Hz, 5H), 8.10 (d, *J* = 15 Hz, 6H), 7.91 (d, *J* = 9 Hz, 5H), 7.84 (d, *J* = 6 Hz, 7H), 7.73 (d, *J* = 6 Hz, 6H), 7.69 (d, *J* = 9 Hz, 6H), 7.55 (d, *J* = 6 Hz, 7H), 7.53 (d, *J* = 15 Hz, 6H), 7.31 (t, *J* = 6 Hz, 7H), 4.53 (t, *J* = 6 Hz, 12H), 1.93 (q, *J* = 7.1 Hz, 12H), 1.48 – 1.22 (m, 60H), 0.90 (d, *J* = 7.0 Hz, 18H). ¹³C NMR (101 MHz, acetone-d₆) δ 147.41, 141.42, 141.10, 127.13, 126.97, 125.37, 123.31, 122.63, 120.28, 119.52, 109.73, 109.61, 42.79, 31.68, 31.58, 26.90, 22.40, 22.34, 13.41, 13.25. MALDI-TOF-MS: calc. for ([C₁₆₂H₁₇₄N₁₂F₆PRu]⁺) *m/z* = 2534.2670, found *m/z* = 2538.8442. Anal. Calcd. For [C₁₆₂H₁₇₄N₁₂F₁₂P₂Ru].2C₇H₁₆.3.5CH₂Cl₂: C, 67.88; H, 6.76; N, 5.30. Found: C, 68.77; H, 6.68; N, 5.28.

[Ru(L^F)₃]²⁺, 2(PF₆⁻): Yield: 41 mg, 38 %. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.65 (s, 6H), 7.81 – 7.60 (m, 48H), 7.40 – 7.28 (m, 36H), 7.17 – 7.03 (m, 36H), 2.02 – 1.80 (m, 24H), 1.25 – 1.03 (m, 120H), 0.83 (t, *J* = 8 Hz, 36H), 0.68 (s, 24H). ¹³C NMR (101 MHz, CD₂Cl₂) δ 157.08, 152.89, 151.56, 147.99, 147.88, 147.16, 143.21, 137.60, 135.23, 133.52, 129.20, 127.30, 124.07, 123.93, 123.20, 122.78, 121.77, 120.79, 119.46, 118.93, 40.17, 31.80, 29.97, 29.68, 29.31, 29.21, 23.91, 22.61, 13.85. MALDI-TOF-MS: calc. for ([C₂₈₈H₃₃₀N₁₂F₆PRu]⁺) *m/z* = 4206.4983, found *m/z* = 4206.2824. Anal. Calcd. For [C₂₈₈H₃₃₀N₁₂F₁₂P₂Ru], 1.5 CH₂Cl₂: C, 77.63; H, 7.50; N, 3.76. Found: C, 77.20; H, 7.80; N, 3.46.

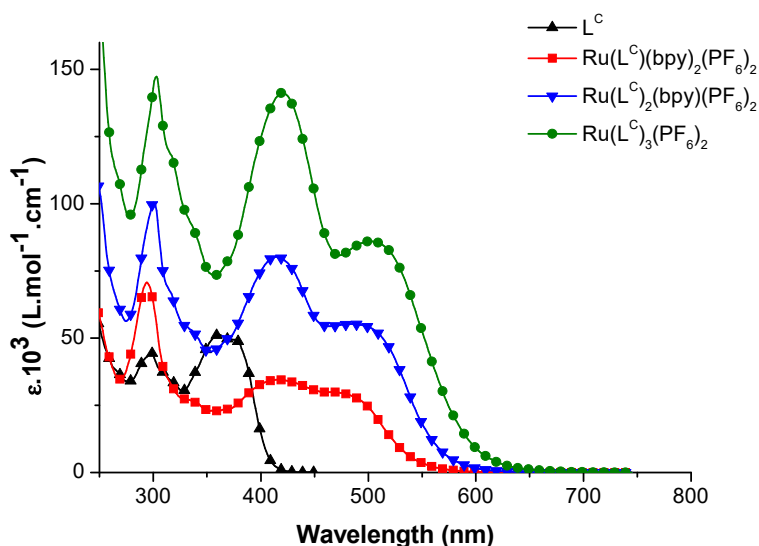


Figure S1. UV-vis absorption spectra of L^C and [Ru(L^C)_{3-n}(bpy)_n]²⁺ (*n* = 0-2) complexes; THF; *c* = 1.0 × 10⁻⁵ mol.L⁻¹, 25 °C.

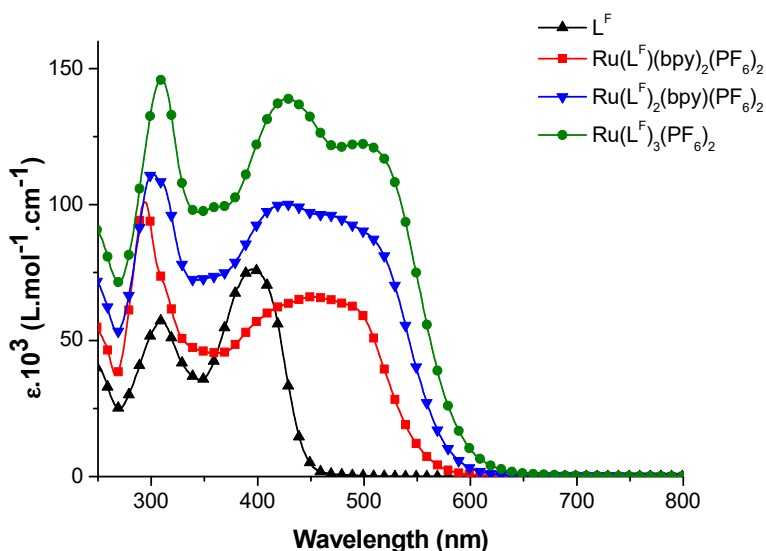


Figure S2. UV-vis absorption spectra of L^F and [Ru(L^F)_{3-n}(bpy)_n]²⁺ (*n* = 0-2) complexes; THF; *c* = 1.0 × 10⁻⁵ mol.L⁻¹, 25 °C.

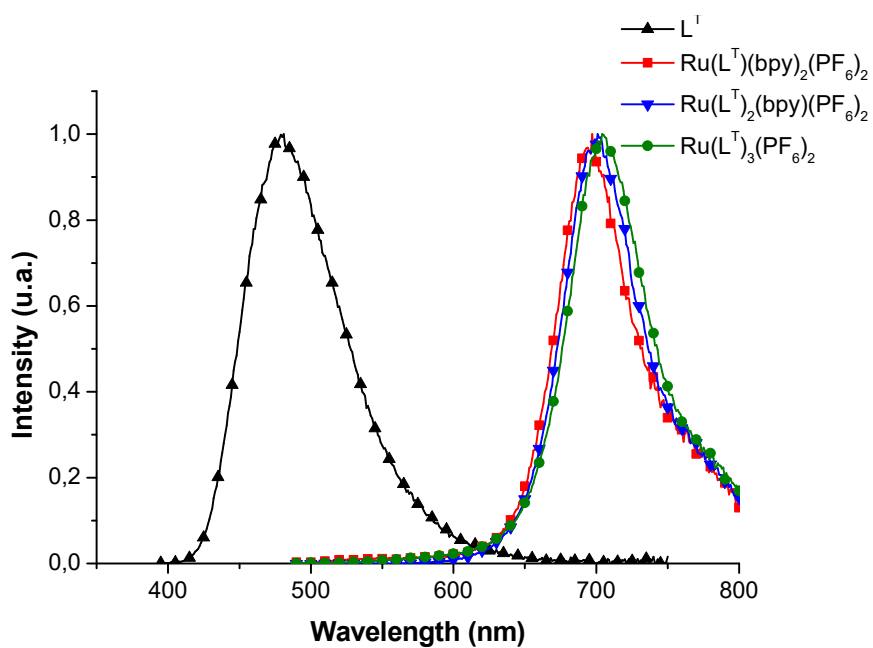


Figure S3. Emission spectra of L^T and $[Ru(L^T)_{3-n}(bpy)_n]^{2+}$ ($n = 0-2$) complexes; degassed THF ; $c = 1.0 \times 10^{-5} \text{ mol.L}^{-1}$, 25 °C.

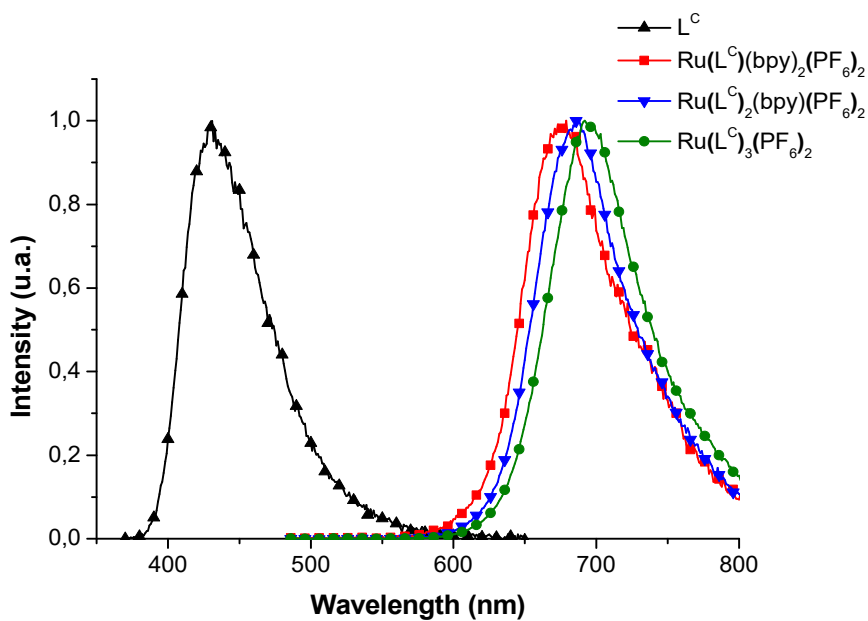


Figure S4. Emission spectra of L^C and $[Ru(L^C)_{3-n}(bpy)_n]^{2+}$ ($n = 0-2$) complexes; degassed THF ; $c = 1.0 \times 10^{-5} \text{ mol.L}^{-1}$, 25 °C.

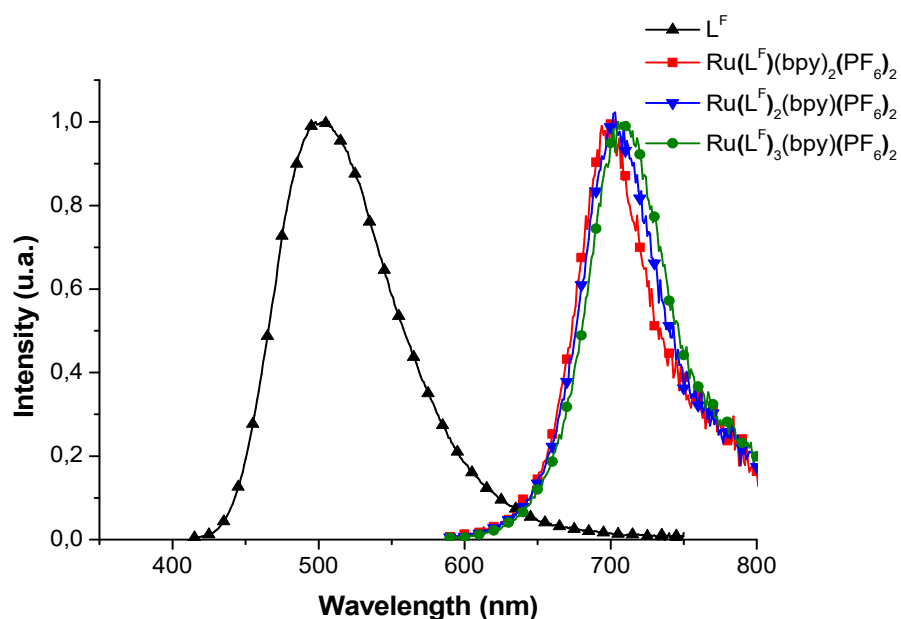
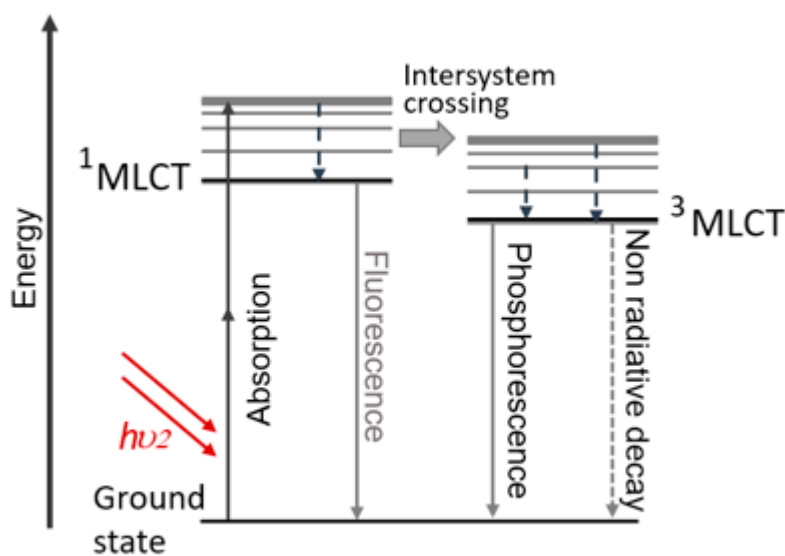


Figure S5. Emission spectra of L^F and $[Ru(L^F)_{3-n}(bpy)_n]^{2+}$ ($n = 0-2$) complexes; degassed THF ; $c = 1.0 \times 10^{-5} \text{ mol.L}^{-1}$, 25 °C.



Scheme S1. Simplified Jablonski diagram for two-photon excitations in $[Ru(bpy)_3]^{2+}$ -like complexes. Two-photon excitation occurs between the ground state and the vibrational levels of the first electronic excited state. After excitation process, the fluorophore relaxes to the lowest energy level of the first excited electronic states 1MLCT via vibrational processes, followed by intersystem crossing to the lowest triplet state of the complexes from where emission occurs. The subsequent emission processes for both one- and two-photon excitations are thus the same.

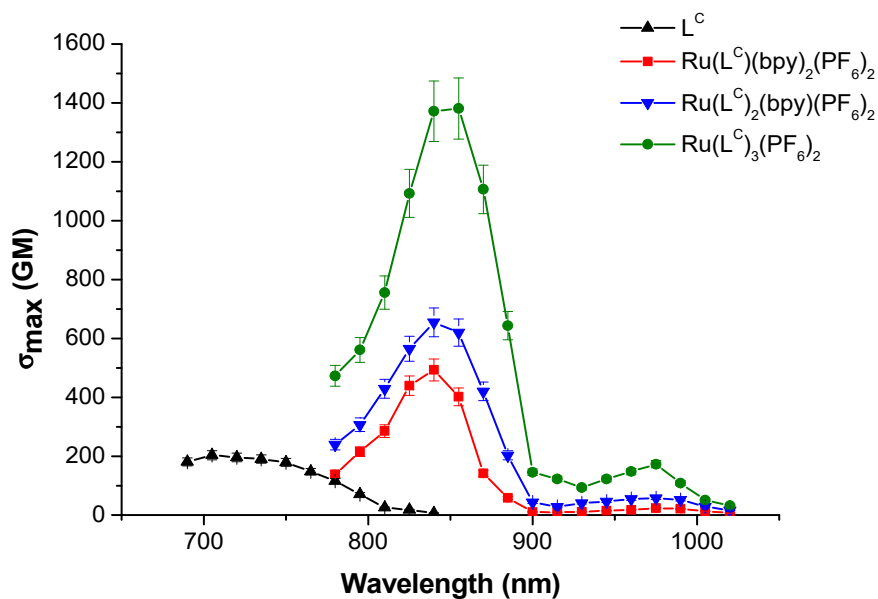


Figure S6. TPA spectra of L^C and $[Ru(L^C)_{3-n}(bpy)_n]^{2+}$ ($n = 0-2$) complexes; THF; $c = 1.0 \times 10^{-5} \text{ mol.L}^{-1}$, 25°C .

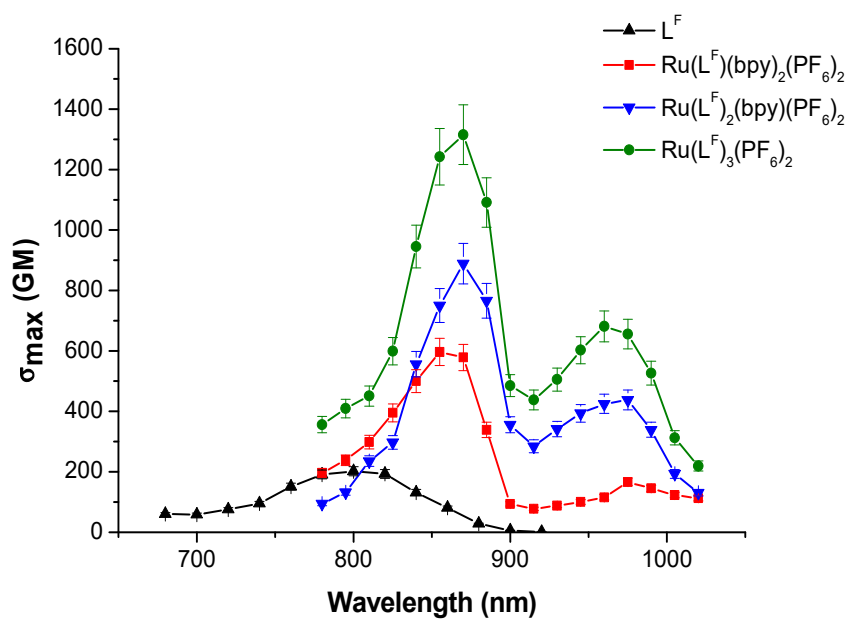
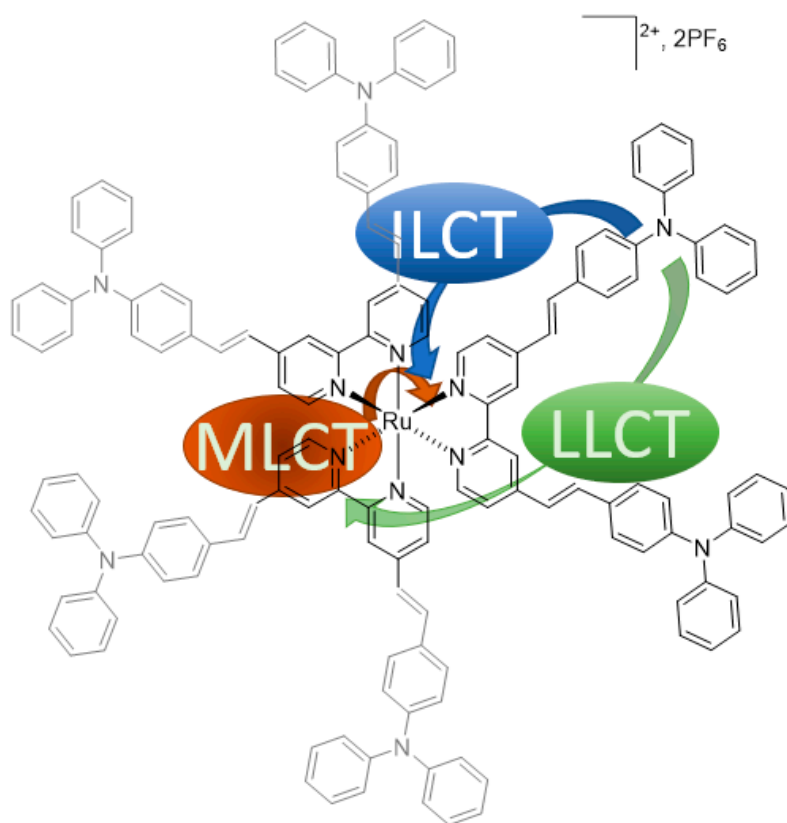


Figure S7. TPA spectra of L^F and $[Ru(L^F)_{3-n}(bpy)_n]^{2+}$ ($n = 0-2$) complexes; THF; $c = 1.0 \times 10^{-5} \text{ mol.L}^{-1}$, 25°C .



Scheme S2. Main charge transfers upon excitation within $\text{Ru}(\text{L}^{\text{T}})_3$ as a model of complexes containing extended π -system ligands

Examples of calculation of the effective number of electrons involved in two-photon transitions.

Ligand L^T :

$$\delta'_{\max} = \frac{\delta_{\max}}{N_{\text{eff}}^2} \quad N_{\text{eff}} = \sqrt{\sum_i N_i^2}$$

N= number of π -electron in the conjugated part of the molecule

A= 2, number of donor -acceptor parts

B= 14, number of π -electrons in a donor- acceptor part

$$N_{\text{eff}} = \sqrt{A * B^2 + C^2 * D} = 23.1$$

C= 6, number of π -electrons in a phenyl moiety

D= 4, number of phenyl units per molecule

[Ru(L^T)(bpy)₂]²⁺ :

N= number of π -electrons in the conjugated part of the molecule

$$N_{\text{eff}} = \sqrt{A * B^2 + C^2 * D + E^2 * F + G^2} = 28.7$$

A= 2, number of donor acceptor parts

B= 14, number of π -electrons in a donor- acceptor part

C= 6, number of π -electrons in a phenyl moiety

D= 4, number of phenyl units in the molecule

E= 6, number of π -electrons in a pyridine moiety

F= 4, number of pyridine units in the molecule

G= 12, number of electrons in [Ru(L^T) (bpy)₂]²⁺ bonds

Kuzyk, M. G. Fundamental Limits on Two-Photon Absorption Cross Sections. *J. Chem. Phys.* **2003**, 119 (16), 8327–8334.
<https://doi.org/10.1063/1.1611474>.

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<https://doi.org/10.1063/1.2104407>.

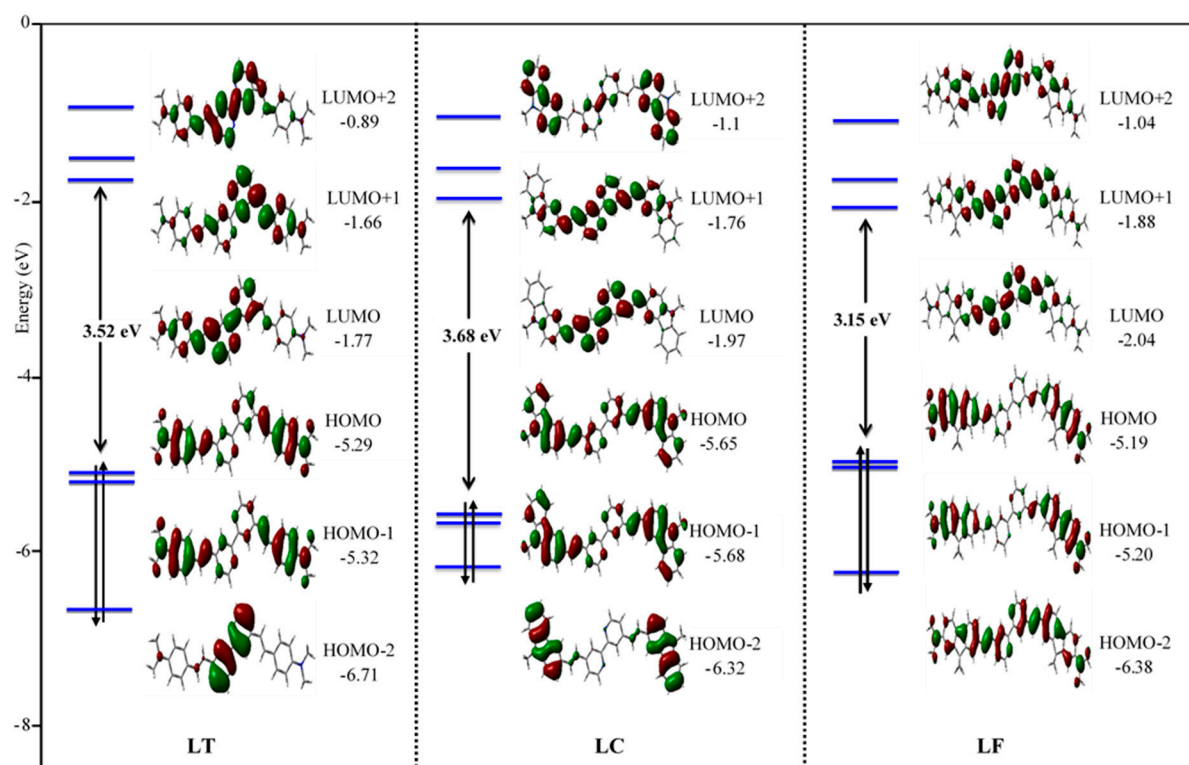


Figure S8. Energy diagram of the frontier MOs of the ligands.

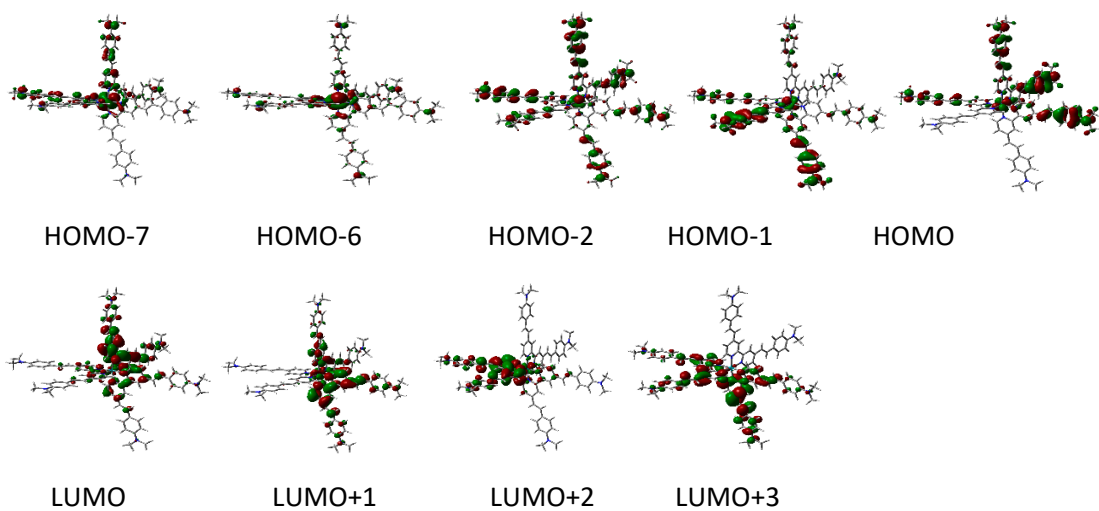


Figure S9 : main MOs of $[\text{Ru}(\text{L}^{\text{T}})_3]^{2+}$

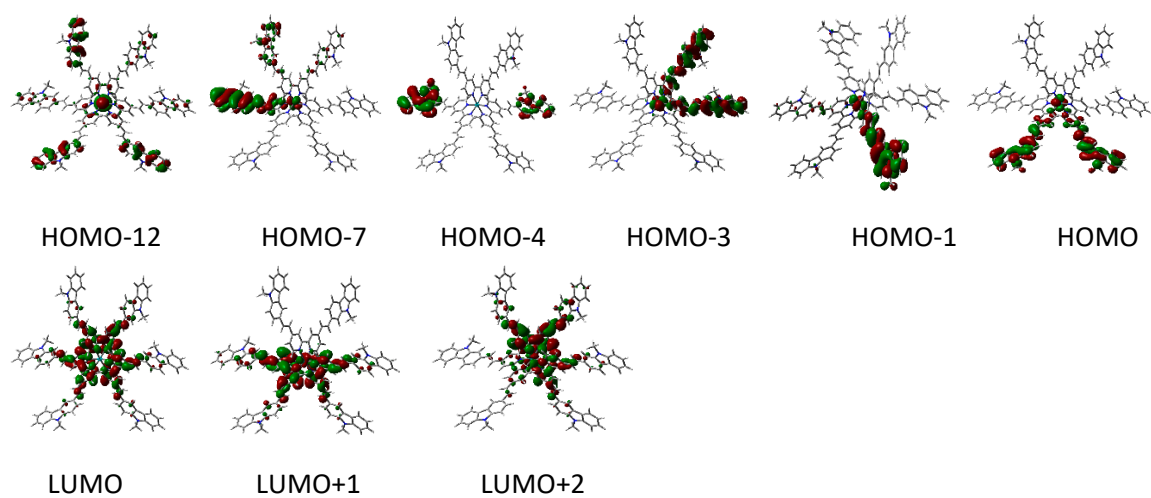


Figure S10 : main MOs of $[\text{Ru}(\text{L}^{\text{C}})_3]^{2+}$

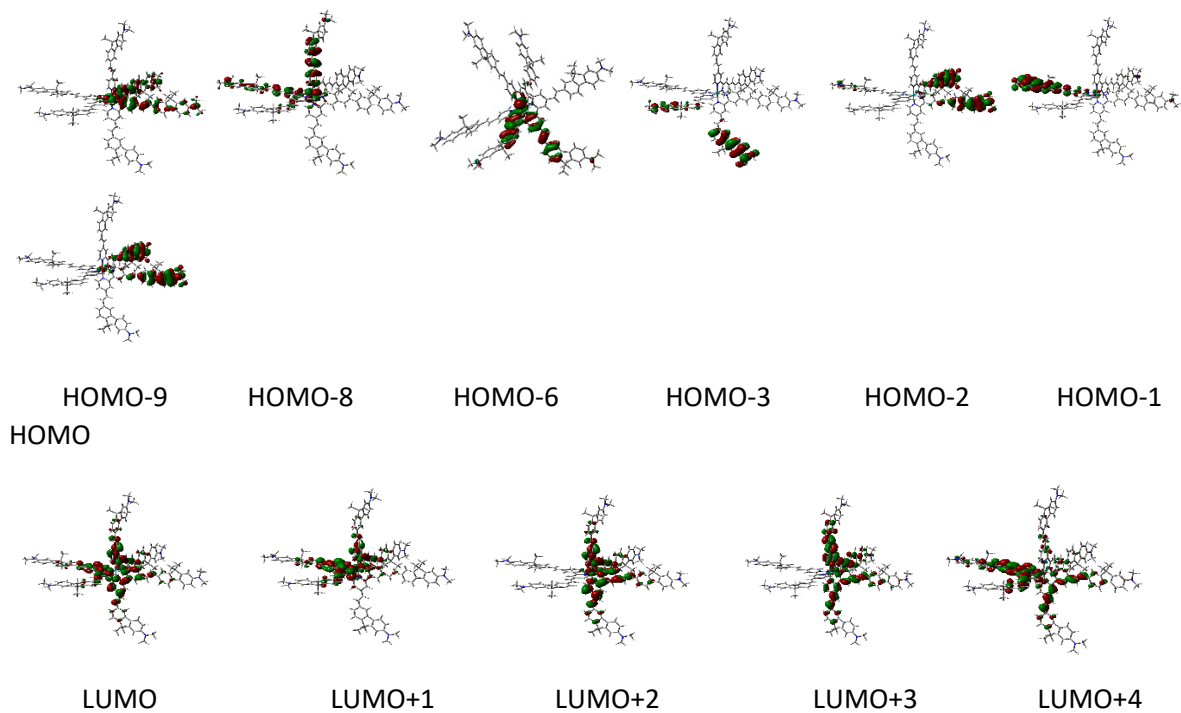


Figure S11 : main MOs of $[\text{Ru}(\text{L}^{\text{F}})_3]^{2+}$

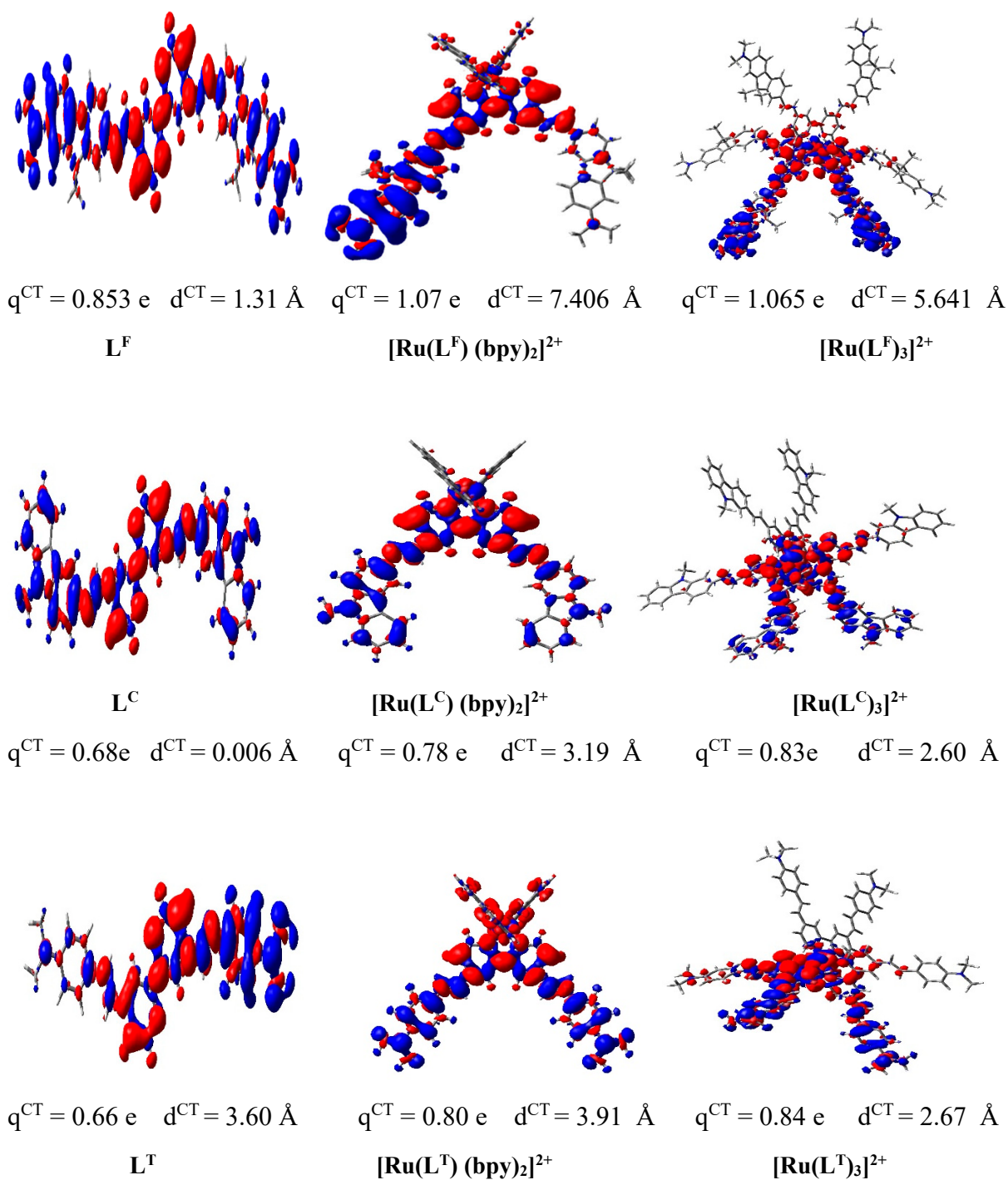


Figure S12: Density differences plots ($D\rho(r) = \rho^{S1}(r) - \rho^{S0}(r)$) of L and related $[RuL_{3-n}(bpy)_n]^{2+}$ complexes ($n = 0-2$), between $S1$ – $S0$ states (red=increase, blue=decrease of electron density; isovalue 0.03 au).

Table S1. Main structural characteristics of $[\text{RuL}_{3-n}(\text{bpy})_n]^{2+}$ complexes ($n = 0-2$).

		$[\text{Ru}(\text{L}^{\text{C}})(\text{bpy})_2]^{2+}$	$[\text{Ru}(\text{L}^{\text{C}})_3]^{2+}$	$[\text{Ru}(\text{L}^{\text{F}})(\text{bpy})_2]^{2+}$	$[\text{Ru}(\text{L}^{\text{F}})_3]^{2+}$	$[\text{Ru}(\text{L}^{\text{T}})(\text{bpy})_2]^{2+}$	$[\text{Ru}(\text{L}^{\text{T}})_3]^{2+}$
Bond lengths (Å)	Ru-N1	2.060	2.058	2.060	2.058	2.060	2.057
	Ru-N2	2.060	2.057	2.060	2.058	2.060	2.057
	Ru-N3	2.058	2.057	2.058	2.056	2.058	2.056
	Ru-N4	2.060	2.057	2.059	2.057	2.059	2.058
	Ru-N5	2.059	2.057	2.060	2.057	2.059	2.057
	Ru-N6	2.058	2.056	2.058	2.056	2.058	2.057
Bond angles (°)	N1-Ru-N2	78.58	78.58	78.57	78.59	78.53	78.62
	N2-Ru-N3	88.37	88.07	88.18	88.30	88.16	88.76
	N3-Ru-N4	78.90	78.62	78.88	78.61	78.88	78.68
	N4-Ru-N5	87.96	88.18	88.05	88.37	88.02	88.03
	N5-Ru-N6	78.88	78.63	78.87	78.63	78.88	78.59
	N6-Ru-N1	88.26	88.09	87.72	88.39	88.32	88.37

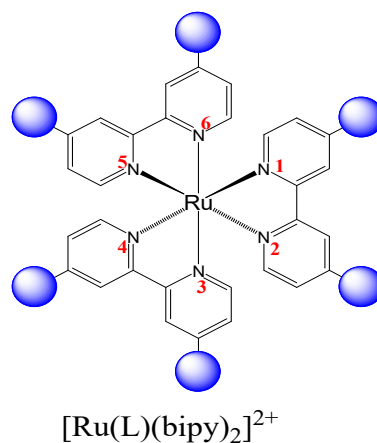
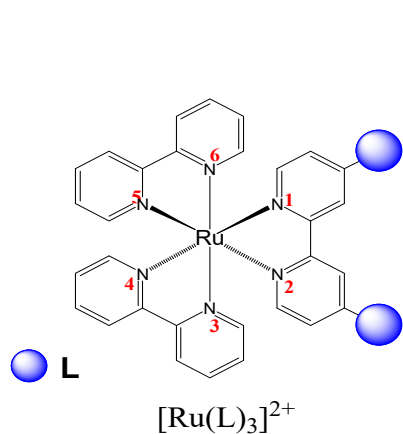


Table S2: Energies of the frontier MOs of bipyridines $L = L^T, L^C, L^F$

	HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
L^T	-6.99	-6.92	-6.71	-5.32	-5.29	-1.77	-1.66	-0.89	-0.21
L^C	-6.77	-6.32	-6.32	-5.68	-5.65	-1.97	-1.76	1.1	-1.06
L^F	-6.81	-6.40	-6.38	-5.20	-5.19	-2.04	-1.88	-1.04	-0.52

Table S3 : Energies and percentage contributions of the frontier MOs of $[RuL^{T_{3-n}}(bpy)_n]^{2+}$ complexes ($n = 0 ; 2$).

$[Ru(L^T)(bpy)_2]^{2+}$										
	HOMO-7	HOMO-6	HOMO-4	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
Energy (eV)	-7.80	-7.80	-6.98	-6.81	-5.83	-5.82	-3.10	-2.98	-2.95	-2.39
Ru (%)	1	0	66	66	9	18	7	20	11	0
L^T (%)	81	76	3	22	69	64	8	1	73	78
$(bpy)_2$ (%)	0	0	27	8	6	3	77	74	6	1
$[Ru(L^T)_3]^{2+}$										
Energy (eV)	-6.62	-6.48	-5.78	-5.68	-5.67	-5.67	-2.92	-2.78	-2.72	-2.36
Ru (%)	54	65	0	10	11	11	1	6	5	1
L^T_1 (%)	20	13	52	28	43	11	12	4	93	48
L^T_2 (%)	28	11	15	34	8	46	68	24	3	1
L^T_3 (%)	5	11	27	23	35	26	21	67	7	63

Table S4 : Energies and percentage contributions of the frontier MOs of $[\text{RuL}^{\text{C}}_{3-\text{n}}(\text{bpy})_{\text{n}}]^{2+}$ complexes (n = 0 - 2).

$[\text{Ru}(\text{L}^{\text{C}})(\text{bpy})_2]^{2+}$														
	HOMO-12	HOMO-7	HOMO-6	HOMO-5	HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+9
Energy (eV)	-8.43	-7.48	-7.04	-7.02	-6.90	-6.72	-6.71	-6.14	-6.13	-3.19	-3.04	-2.99	-2.53	-1.50
Ru (%)	1	8	69	48	64	7	7	4	5	2	4	6	1	0
L^{C} (%)	93	88	10	41	24	79	92	93	92	78	18	0	98	93
$(\text{bipy})_2$ (%)	2	2	20	8	10	1	1	1	1	20	78	94	0	0
$[\text{Ru}(\text{L}^{\text{C}})_3]^{2+}$														
Energy (eV)	-6.79	-6.32	-6.29	6.29	-6.29	-6.23	-6.14	-6.07	-6.04	-3.20	-3.07	-3.07	-2.54	-1.47
Ru(%)	36	8	0	0	0	21	1	10	12	1	6	6	1	0
L^{C}_1 (%)	21	65	0	17	78	2	46	6	44	32	55	8	1	32
L^{C}_2 (%)	20	16	75	1	1	28	3	80	1	34	2	56	48	37
L^{C}_3 (%)	19	1	2	79	17	41	48	2	42	32	37	27	46	27

Table S5 : Energies and percentage contributions of the frontier MOs of $[\text{RuL}^{\text{F}}_{3-\text{n}}(\text{bpy})_{\text{n}}]^{2+}$ complexes (n = 0 ; 2).

$[\text{Ru}(\text{L}^{\text{F}})(\text{bpy})_2]^{2+}$													
	HOMO-8	HOMO-7	HOMO-6	HOMO-5	HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
Energy (eV)	-7.39	-7.27	-7.28	-7.15	-6.99	-6.72	-6.71	-5.53	-5.52	-3.20	-3.04	-2.98	-2.59
Ru (%)	3	49	36	43	66	32	43	1	1	2	4	6	1
LF (%)	94	22	51	43	16	60	49	92	92	83	13	0	98
(bipy) ₂ (%)	1	28	7	10	18	5	6	0	0	15	83	94	0
$[\text{Ru}(\text{L}^{\text{F}})_3]^{2+}$													
Energy (eV)	-6.48	-6.46	-6.38	-5.56	-5.55	-5.55	-5.51	-5.49	-5.48	-3.16	-3.04	-3.03	-2.51
Ru (%)	43	42	44	0	0	0	0	0	0	0	6	6	0
L^{F}_1 (%)	2	18	25	3	77	14	5	87	0	33	61	2	1
L^{F}_2 (%)	26	2	4	88	1	0	47	3	44	32	25	34	55
L^{F}_3 (%)	26	21	26	1	13	79	42	2	48	33	7	55	38

Table S6. PBE0-GD3BJ and CAM-B3LYP-GD3BJ simulated UV-visible spectra of L^T and related $[RuL^T_{3-n}(bpy)_n]^{2+}$ complexes ($n = 0 ; 2$).

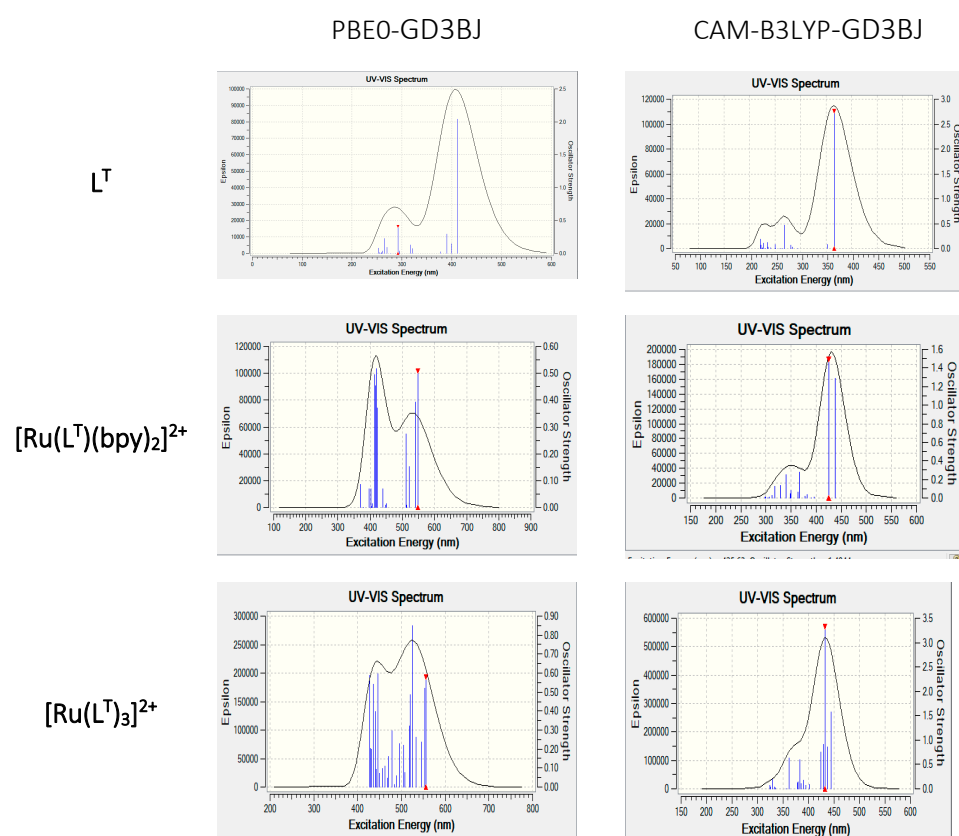


Table S7. PBE0-GD3BJ/Lanl2DZP and CAM-B3LYP-GD3BJ/Lanl2DZP Simulated UV-visible spectra of L^C and related $[RuL^C_{3-n}(bpy)_n]^{2+}$ complexes ($n = 0 ; 2$).

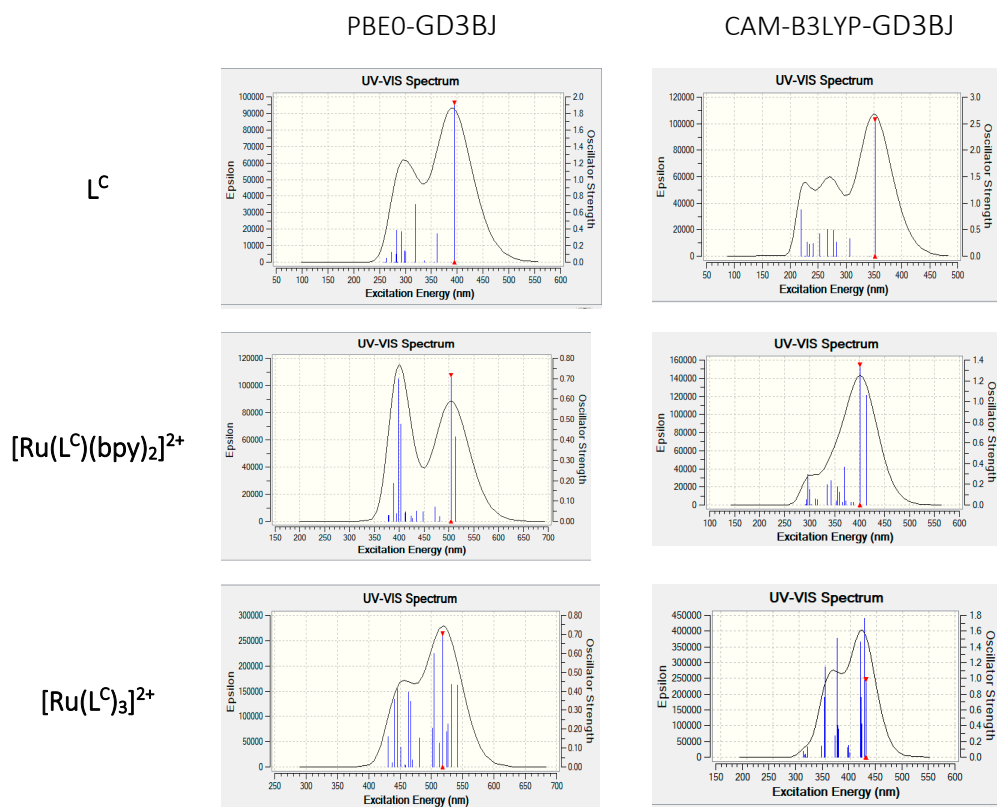


Table S8. PBE0-GD3BJ/Lanl2DZP and CAM-B3LYP-GD3BJ/Lanl2DZP Simulated UV-visible spectra of L^F and related $[RuL^F_{3-n}(bpy)_n]^{2+}$ complexes ($n = 0 ; 2$).

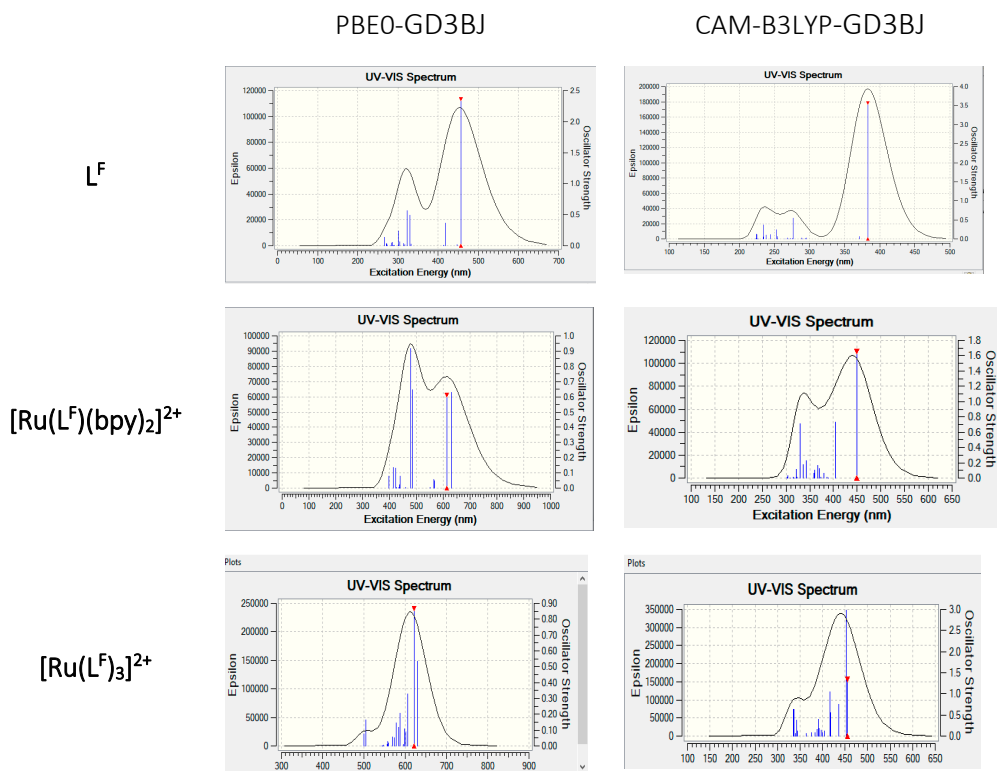


Table S9. PBE0-GD3BJ and CAM-B3LYP-GD3BJ calculated maximum absorption wavelengths (λ , nm) and oscillator strengths (f) in THF for L^T and related $[RuL^T_{3-n}(bpy)_n]^{2+}$ complexes ($n = 0 ; 2$).

		$\lambda_{max}(nm)$	$\lambda_{calc} (f)$	Main transitions (weight)
$1GL^T$	PBE0-GD3BJ	411	411 (2.04)	H-1->L (56%); H->L (21%); H->L+1(20%)
		285	293 (0.41)	H-2->L (73%); H-4->L (9%)
	CAM-B3LYP-GD3BJ	365	365 (2.77)	H-1->L (41%); H->L+1(39%)
		268	268 (0.47)	H-2->L (62%); H-1->L (12%)
$[Ru(L^T)(bpy)_2]^{2+}$	PBE0-GD3BJ	530	548 (0.51)	H->L (88%)
			541 (0.40)	H-1->L (94%)
			511 (0.30)	H-1->L+1(89%)
	CAM-B3LYP-GD3BJ	415	420 (0.52)	H-1->L+3(37%); H-4->L (34%)
		430	437 (1.30)	H->L (61%); H-1->L+3(19%)
			426 (1.50)	H-1->L (64%); H->L+3(14%)
$[Ru(L^T)_3]^{2+}$	PBE0-GD3BJ	350	367(0.30)	H-2->L (48%); H-4->L+1(29%)
		525	557 (0.60)	H->L(66%); H-2->L(18%)
			553 (0.52)	H-2->L(59%); H->L(21%)
			525(0.85)	H-1->L+1 (66%)
	CAM-B3LYP-GD3BJ	447	447(3.30)	H-1-> L+3 (60%); H-2-> L+3 (17%)
		434	444(1.60)	H->L(47%); H-7->L(10%)
			433 (3.32)	H->L+1(13%); H-1->L+2(11%)
		370	383 (0.60)	H-6->L(22%); H-3->L+1(10%)

λ_{calc} are the TD-DFT computed wavelengths ; λ_{max} are the maximum of the simulated bands

Table S10. PBE0-GD3BJ and CAM-B3LYP-GD3BJ calculated maximum absorption wavelengths (λ , nm) and oscillator strengths (f) in THF for L^C and related $[RuL^C_{3-n}(bpy)_n]^{2+}$ complexes ($n = 0 ; 2$).

		$\lambda_{max}(nm)$	λ_{calc} (f)	Main transitions (weight)
L^C	PBE0-GD3BJ	390	395 (1.93)	H-1->L (74%); H->L+1(23%)
		297	319 (0.70)	H-3->L (+40%); H-1->L+2(21%); H->L+3(18%)
	CAM-B3LYP-GD3BJ	350	352 (2.58)	H-1->L (43%); H->L+1(41%)
		270	278 (0.49)	H-4 -> L (19%); H-3->L+2 (17%); H-2->L+1(15%)
$[Ru(L^C)(bpy)_2]^{2+}$	PBE0-GD3BJ	500	513 (0.42)	H->L (50%); H-1->L (36%)
			504 (0.72)	H-1->L (52%); H->L(39%)
		400	403 (0.48)	H->L+3 (45%); H-1->L+3(29%)
	CAM-B3LYP-GD3BJ		399(0.70)	H-1->L+3(42%); H->L+3(24%); H-6->L+2(11%)
		400	414 (1.05)	H-1->L (48%); H->L+3(15%); H-4->L(15%)
		300	401 (1.35)	H-1->L(48%); H-5->L(14%)
$[Ru(L^C)_3]^{2+}$	PBE0-GD3BJ		296(0.30)	H->L+9(41%); H-3->L(14%) ; H-3->L+9(13%)
		518	541 (0.43)	H->L (72%)
			532 (0.44)	H-1 -> L (57%)
			518(0.70)	H-3->L (67%); H-1->L+2(10%)
	CAM-B3LYP-GD3BJ		504 (0.60)	H-1->L+1 (30%); H-3->L+2(23%); H->L+1 (16%)
		455	467(0.34)	H-7->L (40%); H-2->L+1(26%)
			463 (0.40)	H-2->L+1 (48%); H-7->L (19%)
		420	429 (0.99)	H->L (28%); H->L+2(14%)
	CAM-B3LYP-GD3BJ		427(1.76)	H-1->L (24%); H-1->L+2(14%)
		360	373 (1.50)	H-12->L (18%); H-4->L+2(5%)

Table S11. PBE0-GD3BJ and CAM-B3LYP-GD3BJ calculated maximum absorption wavelengths (λ , nm) and oscillator strengths (f) in THF for L^F and related $[RuL^F_{3-n}(bpy)_n]^{2+}$ complexes ($n = 0 ; 2$).

		$\lambda_{max}(nm)$	$\lambda_{calc} (f)$	Main transitions (weight)
L^F	PBE0-GD3BJ	455	458 (2.36)	H-1->L (71%); H->L+1(25%)
		323	330 (0.49)	H-1->L+2 (81%)
			323 (0.56)	H-3->L (52%); H-2->L+1 (13%); H-2->L (11%)
	CAM-B3LYP-GD3BJ	383	383 (3.57)	H-1->L (39%); H->L+1(39%)
		276	276 (0.54)	H-4->L (49%); H-1>L (25%)
$[Ru(L^F)(bpy)_2]^{2+}$	PBE0-GD3BJ	615	631 (0.63)	H->L (94%)
			615 (0.61)	H-1->L (96%)
	CAM-B3LYP-GD3BJ	479	479(0.91)	H->L+3(91%)
		430	450 (1.66)	H->L (56%); H->L+3(18%); H-3->L (14%)
			404 (0.73)	H-1->L (42%); H-2->L (27%); H-1->L+3(11%)
$[Ru(L^F)_3]^{2+}$	PBE0-GD3BJ	335	330 (0.71)	H-2->L+3(21%); H-1->L (14%); H-5->L (11%); H-6->L (11%)
		605	630 (0.54)	H->L (84%)
			622(0.87)	H-1->L (79%)
	CAM-B3LYP-GD3BJ	504	504 (0.17)	H-6->L (80%)
		435	455 (1.34)	H->L (26%); H-2-> L+2 (14%); H-8->L (12%);
				H->L+1(11%)
			453 (2.97)	H-1->L (19%); H-1->L+1(18%)
$[Ru(L^F)_3]^{2+}$	CAM-B3LYP-GD3BJ	340	335 (0.64)	H-3->L (15%); H->L(8%); H-9->L+1(+6%);
				H-6->L+4(+6%); H->L+3(5%)

Table S12 : Computed dipole moments (Debye) for the ground S0 and vertical S1 states

	$[\text{Ru}(\text{L}^{\text{T}})_3]^{2+}$	$[\text{Ru}(\text{L}^{\text{C}})_3]^{2+}$	$[\text{Ru}(\text{L}^{\text{F}})_3]^{2+}$
μ_{S0}	0.30	0.03	1.81
μ_{S1}	8.60	4.30	13.19
$\Delta\mu$	8.30	4.27	11.38