Switching of excited states in cyclometalated platinum complexes incorporating pyridyl-acetylide ligands (Pt–C≡C-py): a combined experimental and theoretical study.

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Experimental part

Synthesis: General Procedure. All manipulations were performed using Schlenk techniques under an Ar atmosphere. All solvents were dried and purified by standard procedures. NMR spectra were recorded on Bruker DPX-200, AV 300 or AV 500 MHz spectrometers. ^{1}H and ^{13}C chemical shifts are given versus $SiMe_4$ and were determined by reference to residual ^{1}H and ^{13}C solvent signals. Assignments of carbon atoms were based on HMBC, HMQC and COSY experiments. Elemental analyses and High resolution mass spectra (HRMS) were performed on a MS/MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. 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, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube. The spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Luminescence quantum yields were determined using the method of continuous dilution, using $[Ru(bpy)_3]Cl_2$ as the standard (Φ = 0.028 in air-equilibrated aqueous solution) and correcting for the refractive index. Compounds **1** and **3** were synthesized following the reported procedures. [1-2]

Synthesis of 2. $[Pt(^tBu_2\text{-}C\text{^}N\text{^}N)Cl]$[1] (200 mg, 0.35 mmol) was added to a solution of ethynylpyridine[3] (200 mg, 0.23 mmol) and MeONa (145.8 mg, 2.7 mmol) in 20 mL anhydrous methanol. The solution was degassed using freeze-pump-thaw technique and the solution was stirred at 40°C overnight. Solvents were removed under vacuum and the crude product was dissolved in CH_2Cl_2, washed with brine and dried with $MgSO_4$. Column chromatography (SiO_2, CH_2Cl_2/Ethylacetate , 7/3) yielded **2** as a yellow solid. Yield: 108 mg, 53%. ^{1}H NMR – 300 MHz ($CDCl_3$): δ 9.02 (dd, 1H, $^3J_{H\text{-}H}$ = 5.7 Hz, $^3J_{Pt\text{-}H}$ = 18 Hz, H^{6py}); 8.46 (d, 2H, ^3J = 6.1 Hz, H^{meta}); 7.86 (ddd, 1H, $^3J_{H\text{-}H}$ = 7.4 Hz, $^3J_{Pt\text{-}H}$ = 64 Hz, $^4J_{H\text{-}H}$ = 1.1 Hz, H^{phe6}); 7.84 (d, 1H, $^4J_{H\text{-}H}$ = 1.0 Hz, H^{3py}); 7.57 (s, 1H, H^{5py*}); 7.56 (s, 1H, H^{3py*}); 7.52 (dd, 1H, $^3J_{H\text{-}H}$ = 5.7 Hz, $^4J_{H\text{-}H}$ = 1.8 Hz, H^{5py}); 7.38 (m, 3H, H^{ortho}, H^{phe3}); 7.16 (ddd, 1H, $^3J_{H\text{-}H}$ = 7.3 Hz, $^3J_{H\text{-}H}$ = 6.0 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz, H^{phe5}); 7.06 (ddd, 1H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^3J_{H\text{-}H}$ = 6.2 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz, H^{phe4}); 1.46 (s, 9H, ^{t}Bupy*); 1.43 (s, 9H, ^{t}Bupy). ^{13}C [^{1}H] NMR – 75 MHz ($CDCl_3$): δ 165.1 (C^{6py*}); 163.8 (C^{4py*}); 163. 7 (C^{4py}); 158.1 (C^{2py}); 154.4 (C^{2py*}); 151.5 (C^{py6}); 149.2 (C^{meta}); 147.1 (C^{2phe}); 141.9 (C^{1phe}); 138.4 (C^{6phe}); 136.9 (C^{ipso});131.3 (C^{5phe}); 126.3 (C^{ortho}); 124.6 (C^{5py}); 124.2 (C^{3phe}); 123.7 (C^{4phe}); 119.2 (C^{3py}); 119.1 (C^{β}); 115.6 (C^{5py*}); 114.6 (C^{3py*}); 104.1 (C^{α}); 36.0 (C^{tBupy*}); 35.7 (C^{tBupy}); 30.5 (CH_3); 30.4 (CH_3). Elemental Analysis Calcd. (%) for $C_{31}H_{31}N_3Pt$: C, 58.09, H, 4.88, N, 6.56; Found: C, 58.18, H, 5.01, N, 6.43.

Synthesis of 4. In a Schlenk tube, methyl iodide (0.025 mL, 0.40 mmol) was added to a solution of **2** (50 mg, 0.08 mmol) in anhydrous CH_2Cl_2 (10 mL). The solution was stirred at room temperature, for 48h. Brine (10 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The organic layer was dried over $MgSO_4$ and solvents were removed under vacuum. **4** was obtained as a pale yellow solid after flash chromatography (basic Al_2O_3, CH_2Cl_2), (32 mg, 50% yield). ^1H NMR – 500 MHz ($CDCl_3$): δ 9.14 (dd, 1H, $^3J_{H\text{-}H}$ = 5.8 Hz, $^3J_{Pt\text{-}H}$ = 18 Hz, H^{6py}); 8.96 (d, 2H, ^3J = 6.7 Hz, H^{meta}); 8.13 (d, 1H, $^4J_{H\text{-}H}$ = 1.7 Hz, H^{3py}); 7.93-7.87 (m, 3H, H^{phe6}, H^{5py*}, H^{3py*}); 7.85 (dd, 1H, $^3J_{H\text{-}H}$ = 5.7 Hz, $^4J_{H\text{-}H}$ = 1.2 Hz, H^{5py}); 7.71 (d, 2H, ^3J = 6.7 Hz, H^{ortho}) , 7.35 (ddd, 1H, $^3J_{H\text{-}H}$ = 7.3 Hz, $^3J_{H\text{-}H}$ = 6.0 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, H^{phe3}); 7.36 (ddd, 1H, $^3J_{H\text{-}H}$ = 7.3 Hz, $^3J_{H\text{-}H}$ = 6.0 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, H^{phe5}); 7.21 (ddd, 1H, $^3J_{H\text{-}H}$ = 7.5 Hz, $^3J_{H\text{-}H}$ = 6.2 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, H^{phe4}); 4.46 (s, 3H, N-CH_3); 1.59 (s, 9H, ^{t}Bupy*); 1.56 (s, 9H, ^{t}Bupy). ^{13}C [^1H] NMR – 125.77 MHz ($CDCl_3$): δ 166.3 (C^{6py*}); 165.8 (C^{4py*}); 162.2 (C^{4py}); 156.7 (C^{2py}); 152.0 (C^{2py*}); 151.5 (C^{py6}); 144.2 (C^{meta}); 143.7 (C^{2phe}); 138.5 (C^{1phe}); 135.3 (C^{6phe}); 133.6 (C^{ipso});131.3 (C^{5phe}); 130.8 (C^{ortho}); 126.6 (C^{5py}); 125.7 (C^{3phe}); 121.7 (C^{4phe}); 118.5 (C^{3py}); 117.6 (C^{5py*}); 114.0 (C^{3py*}); 98.9 (C^{α}); 48.54 (N-CH_3); 36.9 (C^{tBupy*}); 36.6 (C^{tBupy}); 31.5 (CH_3); 31.1 (CH_3). Elemental Analysis Calcd. (%) for $C_{32}H_{34}IN_3Pt$: C, 49.09, H, 4.38, N, 5.37; Found: C, 48.75, H, 4.01, N, 5,23.

Computational details: The ground state geometries of all compounds have been fully optimized using the standard B3LYP functional [4-6] and the LANL2DZ basis set [7] augmented with polarization functions on all atoms except hydrogen ones, with the gaussian09 program. [8] All the studies took into account the solvent (CH_2Cl_2 or CH_3CN) using the PCM model. [9-10] The vibration modes of vibration have been computed for all complexes at the same level of theory. All vibration frequencies have been found real, confirming that the optimized geometries are minima on the potential energy surface. The computations of the electronic absorption spectra were carried out using TD-DFT at the same level of theory with the same

Gaussian09 package, using the previously optimized ground state geometries. With the aim of estimating the phosphorescence wavelengths, the optimization of the geometry of all complexes considered in their triplet state have been carried out, the obtained optimized geometry being then used in a TD-DFT calculation in order to get the transition energies between the relaxed triplet state and the singlet ground state.

Drawings of molecular structures and orbitals were done using the Molekel program[11-12] whilst theoretical absorption spectra were plotted using SWizard [13] the half-bandwidths for the gaussian model being taken equal to 4000 cm^{-1}. Percentage compositions of molecular orbitals were analyzed using the *AOMix* program.[14]

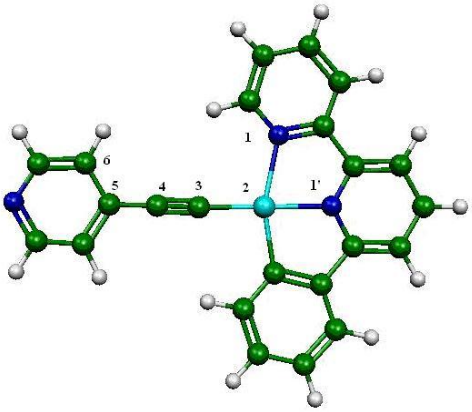


Figure SI1: atom numbering and definition of the 1-2/5-6 dihedral angle φ (for complex **2**)

Table S1: experimental and theoretical spectroscopic data (neutral complexes)

complex	λ_{exp} (nm)	λ_{max} (nm)^{a}	λ_{calc} (nm)	Oscillator strength	Main transitions (weight)
1	455 434	483	483	0.1719	H-0->L+0(+98%)

	366	349	366	0.1380	H-1->L+1(+90%)
	335		345	0.1654	H-4->L+0(+92%)
	281	288	293	0.2690	H-4->L+1(+70%) H-0->L+3(+14%)
			288	0.3563	H-0->L+3(+55%) H-6->L+0(+17%)
			277	0.1508	H-4->L+1(11%)
					H-7->L+0(+31%) H-1->L+3(27%)
					H-8->L+0(+22%)
2	430	445	445	0.1933	H-0->L+0(+97%)
	360	354	364	0.2224	H-1->L+1(+74%) H-0->L+1(19%)
	330		346	0.1969	H-4->L+0(+92%)
	280	292	312	0.1224	H-1->L+2(+87%)
			299	0.2233	H-0->L+3(+72%)
			292	0.1579	H-4->L+1(+79%)
			285	0.2697	H-7->L+0(+78%)
			276	0.1043	H-8->L+0(+51%) H-9->L+0(28%)
3	410	438	439	0.2620	H-0->L+0(+79%) H-1->L+0(+19%)
	350	350	364	0.3133	H-1->L+1(+75%) H-0->L+1(+18%)
			346	0.1987	H-4->L+0(+90%)
	322	328	326	0.2254	H-0->L+2(+54%) H-0->L+3(19%)
		290	294	0.1508	H-4->L+1(+84%)
			283	0.1876	H-11->L+0(+78%)

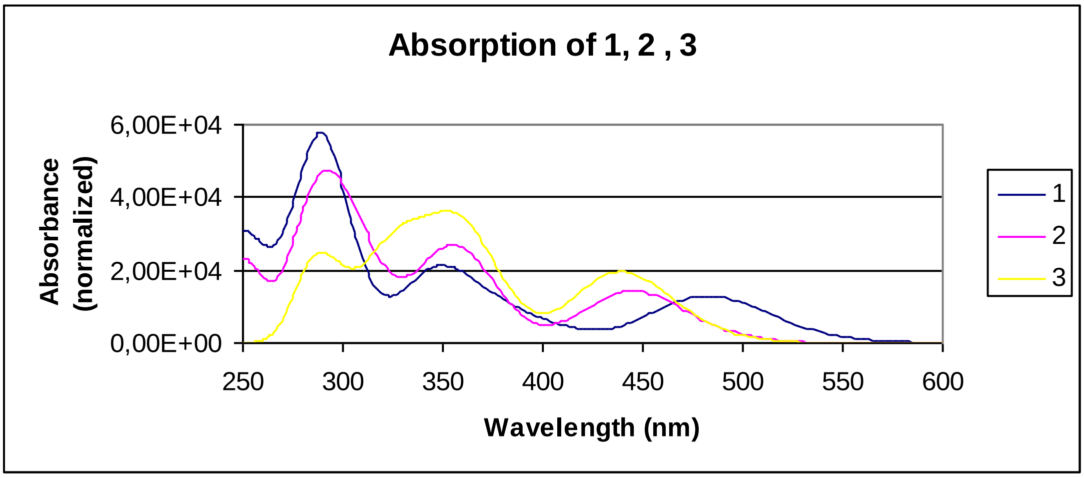


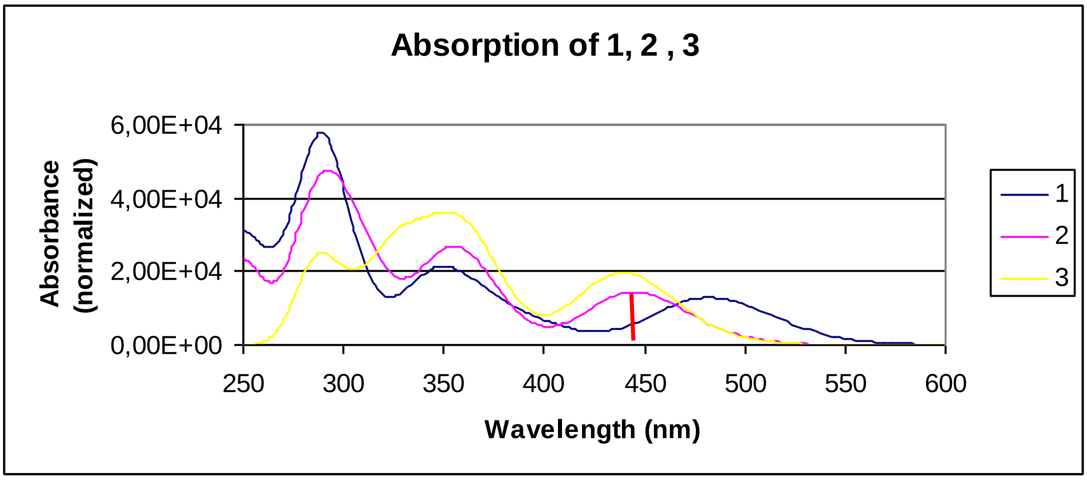
Figure S1: theoretical absorption spectra of **1**, **2** and **3**

Table S2: experimental and theoretical spectroscopic data (cationic species)

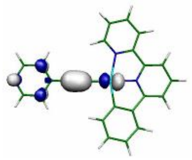
complex	λ_{exp} (nm)	λ_{max} (nm)[a]	λ_{calc} (nm)	Oscillator strength	Main transitions (weight)
2-H+		415	418	0.4194	H-1->L+0(+94%)
		355	357	0.3313	H-0->L+2(+53%) H-1->L+1(28%)
			349	0.1231	H-1->L+1(+55%) H-0->L+2(+19%)
		290	289	0.2192	H-5->L+0(+72%)
			287	0.1386	H-4->L+2(+42%) H-1->L+3(+22%)
			281	0.0314	H-6->L+0(+71%) H-4->L+2(+10%)
			262	0.1143	H-5->L+1(+52%) H-8->L+0(+42%)
3-H+		422	424	0.5153	H-1->L+0(+61%) H-2->L+0(+22%)
			415	0.1123	H-3->L+0(+69%) H-1->L+0(+11%) H-0->L+1(+11%)
		366	364	0.2990	H-1->L+1(+39%) H-3->L+1(+22%) H-0->L+3(17%)
		294	297	0.1506	H-9->L+0(+81%)

		272	269	0.1577	H-9->L+1(+62%) H-6->L+2(23%)
4		420	420	0.4995	H-1->L+0(+94%)
		357	359	0.3679	H-0->L+2(+43%) H-1->L+1(+41%)
		288	291	0.2245	H-5->L+0(+85%)
			288	0.1413	H-4->L+2(+44%) H-6->L+0(15%) H-1->L+3(14%) H-1->L+4(14%)
		261	264	0.1253	H-5->L+1(+54%) H-8->L+0(40%)

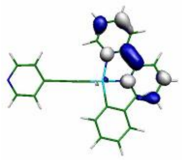
Assignments of the absorption band of higher wavelength



Complex 2 :



λ_{max}= 445 nm; f= 0.1933
H ➔ L (98%)



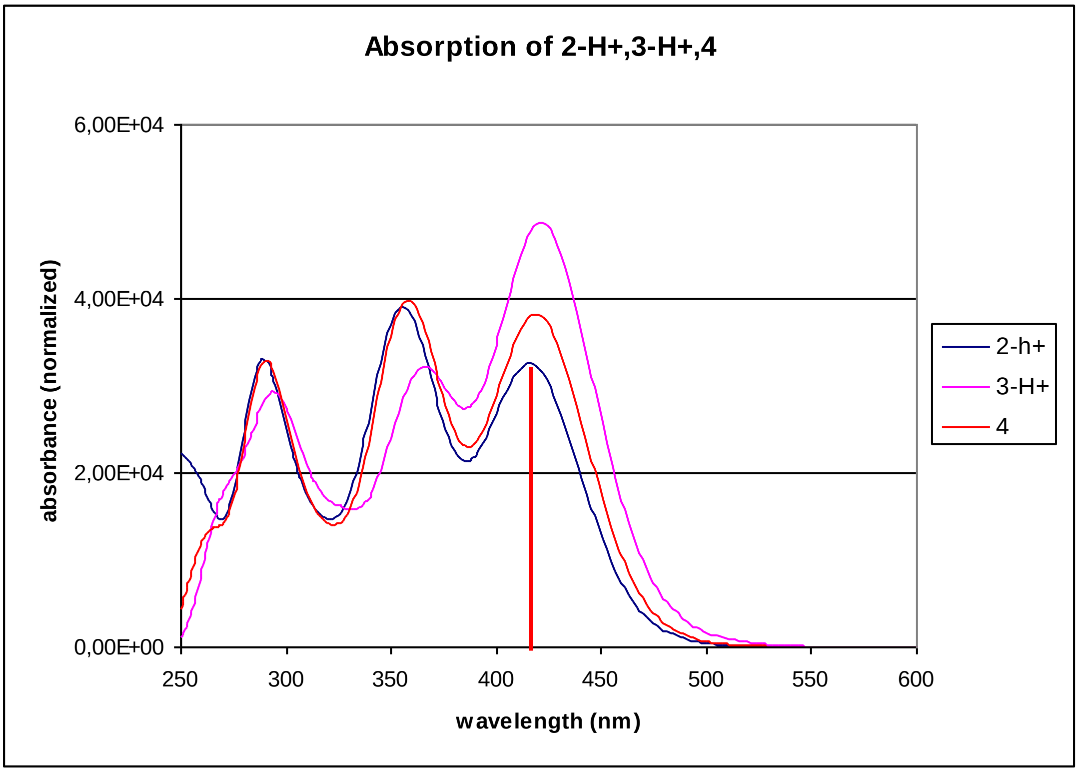
HOMO COMPOSITION

M ➔ Pt 23%
L’ ➔ C≡C 45%
Pyridine ➔ 24%

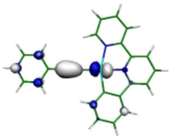
LUMO COMPOSITION

L➔ Bipyridine 82%

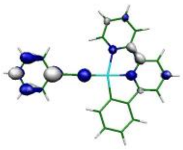
Nature of the excitation: MLCT +L’LCT



<u>Complex 2-H+</u> :



λ_{max}= 418 nm; f= 0.4194
H-1 ➔ L (94%)



HOMO-1

LUMO

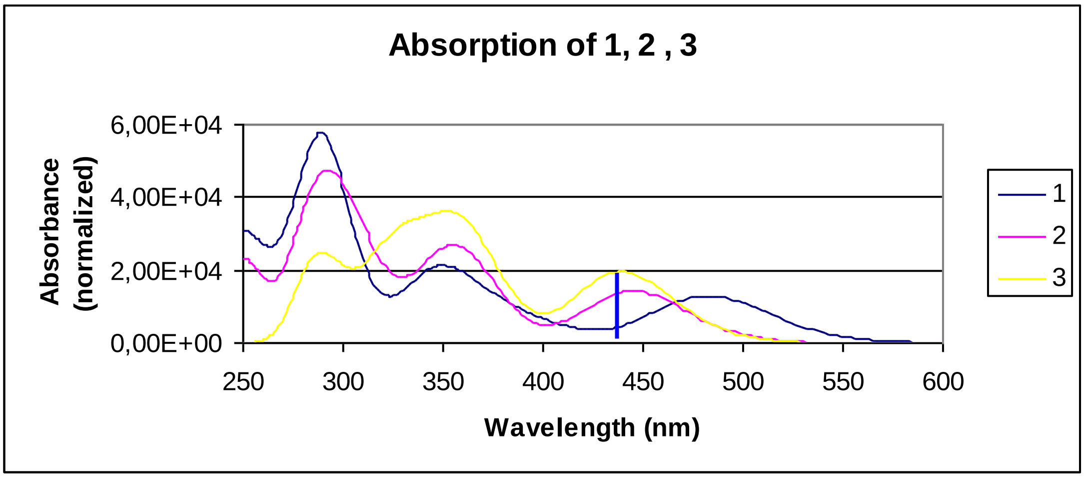
HOMO-1 COMPOSITION

M ➔ Pt 28%
L’ ➔ C≡C 33%
Pyridinium ➔16%

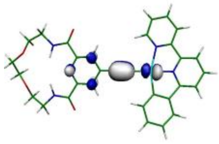
LUMO COMPOSITION

L➔ 39%
M➔ 5%
L’➔ 55%

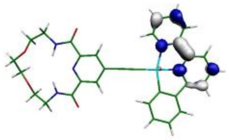
Nature of the excitation: ML’CT +L’LCT + MLCT + L’L’CT



Complex 3:



λ_{max}= 438 nm; f= 0.2620



First transition H ➔ L (79%)

HOMO

LUMO

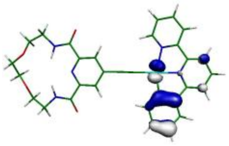
HOMO COMPOSITION

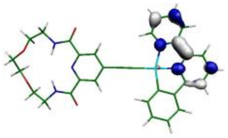
L' ➔ 66%
M ➔ 23%

LUMO COMPOSITION

M ➔ 5%
L ➔ 89%

Nature of the excitation: MLCT + L'LCT





Second transition H-1 ➔ L (19%)

HOMO-1

LUMO

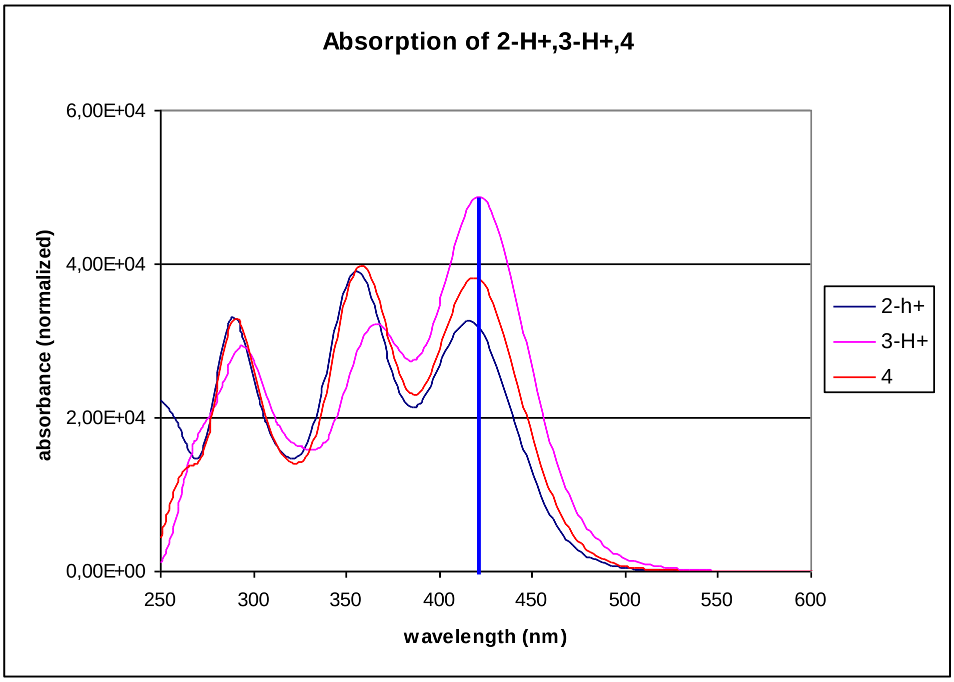
HOMO-1 COMPOSITION

L ➔ 74%
M ➔ 26%

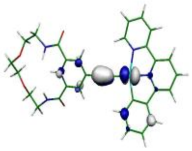
LUMO COMPOSITION

M ➔ 5%
L ➔ 89%

Nature of the excitation: MLCT + LLCT

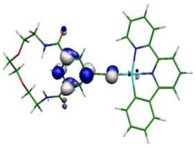


Complex 3-H+ :



λ_{max}= 422 nm; λ_{calc}=424 nm f= 0.5130

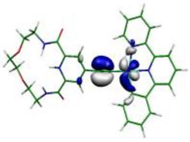
First transition: H-1 ➔ L (61%)



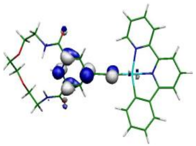
HOMO -1 **LUMO**

HOMO -1 COMPOSITION	LUMO COMPOSITION
L’ ➔ 41 %	L’ ➔ 83%
M ➔ 30%	M ➔ 4%
L ➔ 24%	L ➔ 8%

Nature of the excitation: M’LCT + L’L’CT



Second transition: H-2 ➔ L (22%)



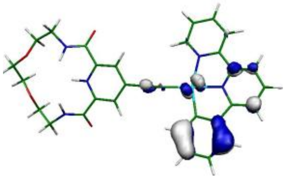
HOMO -2 **LUMO**

HOMO -2 COMPOSITION	LUMO COMPOSITION
L’ ➔ 51 %	L’ ➔ 83%
M ➔ 33%	M ➔ 4%
L ➔ 12%	L ➔ 8%

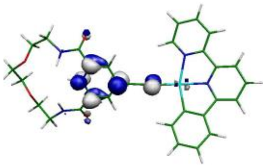
Nature of the excitation: ML’CT + L’L’CT

λ_{calc}=415 nm f= 0.1123 (minority)

H-3 ➔ L (69%)



HOMO -3



LUMO

HOMO -3 COMPOSITION

L’ ➔ 12 %
M ➔ 11%
L ➔ 75 %

LUMO COMPOSITION

L’ ➔ 83%
M ➔ 4%
L ➔ 8%

Nature of the excitation: LL’CT

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