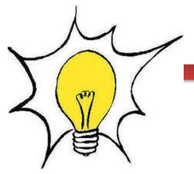
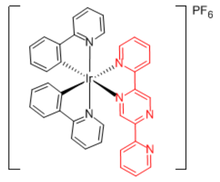
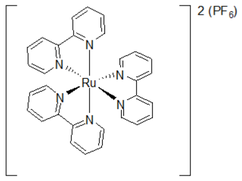
Synthesis, Design and Characterization of Luminescent Mono- and Dinuclear Iridium Complexes

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INTRODUCTION

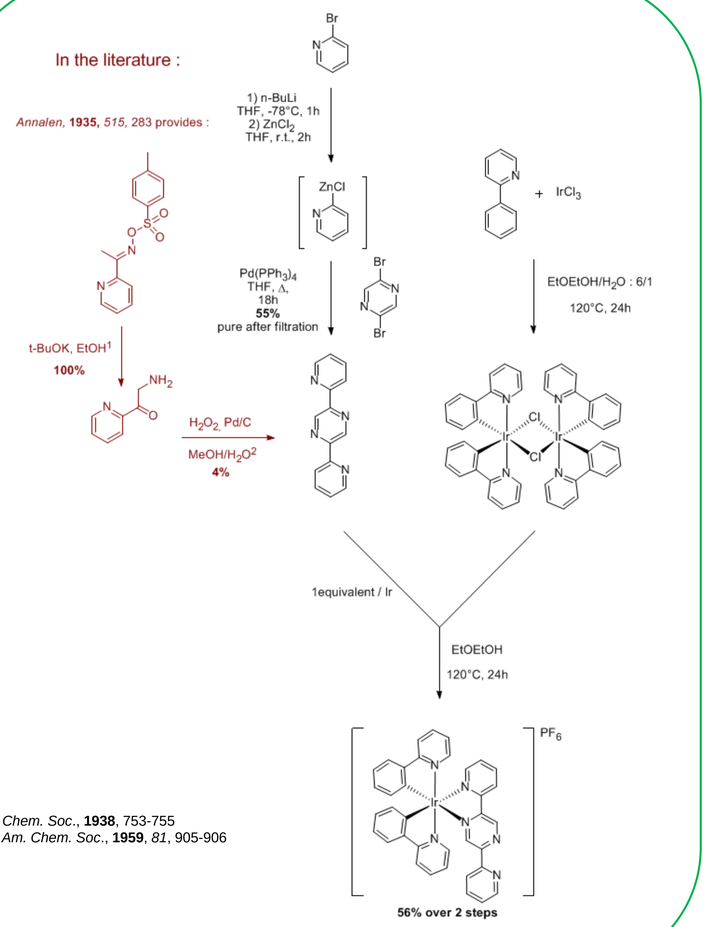
Many mononuclear Iridium (III) complexes have been studied over the last decade thanks to their great photophysical and physicochemical properties : high photoluminescence quantum yields, lifetimes ranging from hundreds of nanoseconds to microseconds, emission from blue to red and their enhanced thermal and chemical stabilities. Such properties make these Iridium complexes very useful within visual display applications such as light-emitting electrochemical cells (LEECs) or Organic Light-Emitting Diodes (OLEDs).

Dinuclear Iridium complexes are a far less explored category of luminescent materials. Dinuclear complexes wherein the two metals are electronically coupled are of particular interest as in these cases, new charge transfer states can be accessed, leading to potentially improved properties. Within this context, this poster presents our work on dinuclear assemblies incorporating the 2,5-di-(2-pyridyl)pyrazine ligand (dpp) and compare them with mononuclear model systems. DFT/TDDFT calculations along with electrochemical and photophysical studies are highlighted.

SYNTHESIS

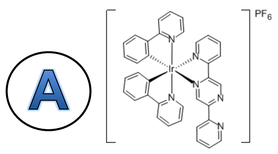
In the literature :

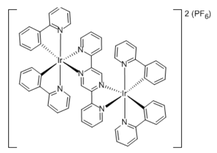
Annalen, **1935**, *515*, 283 provides :

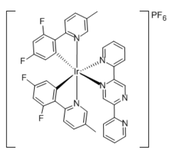


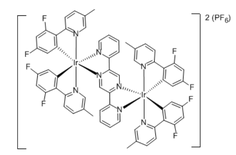
1 *J. Chem. Soc.*, **1938**, 753-755
2 *J. Am. Chem. Soc.*, **1959**, *81*, 905-906

CALCULATIONS

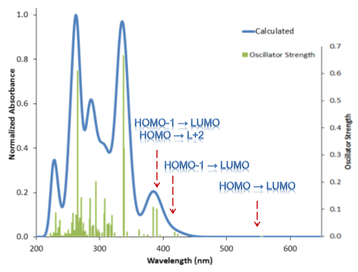


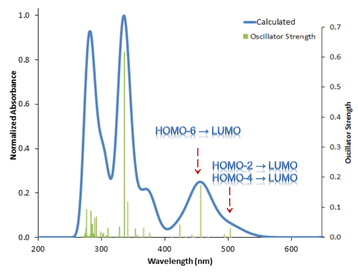


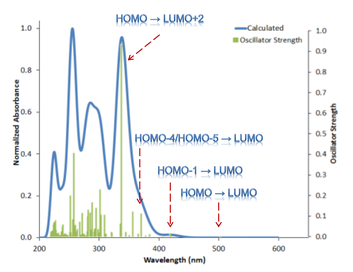


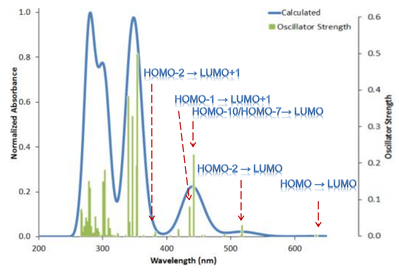


•Computed Absorption Spectra :









•Low Energy Absorption Transitions :

State	Nature of transition (Contribution in %)	Primary Character	Energy		Oscillator strength
			(eV)	(nm)	(f)
S_1	HOMO->LUMO (98%)	MLCT/LLCT	2.23	555	0.0002
S_3	H-1->LUMO (70%)	LLCT	2.98	416	0.0169
S_4	H-3->LUMO (77%)	MLCT/LLCT	3.20	388	0.1012
S_6	HOMO->L+2 (96%)	LC	3.25	382	0.1073

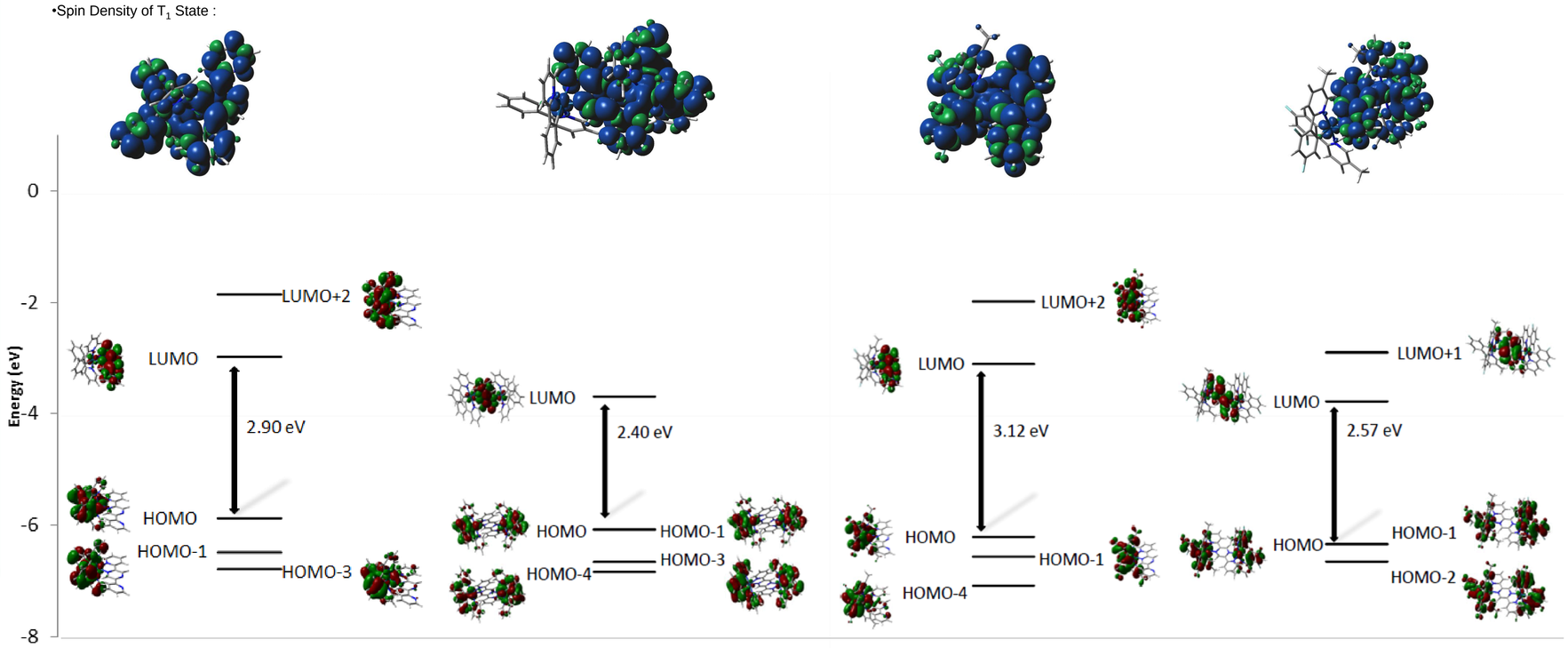
State	Nature of transition (Contribution in %)	Primary Character	Energy		Oscillator strength
			(eV)	(nm)	(f)
S_2	H-1->LUMO (98%)	MLCT/LLCT	1.78	698.1	0.0013
S_3	H-2->LUMO (95%)	MLCT/LLCT	2.46	504	0.0292
S_4	H-4->LUMO (71%)	MLCT/LLCT	2.51	494.5	0.0102
S_9	H-6->LUMO (80%)	MLCT/LLCT	2.72	456.5	0.1735

State	Nature of transition (Contribution in %)	Primary Character	Energy		Oscillator strength
			(eV)	(nm)	(f)
S_1	HOMO->LUMO (98%)	MLCT/LLCT	2.46	503	0.0002
S_2	H-1->LUMO (98%)	LLCT	2.96	419	0.0148
S_6	H-5->LUMO (28%), H-4->LUMO (60%)	MLCT/LLCT	3.35	370	0.1116
S_8	HOMO->L+2 (96%)	LC	3.48	356	0.1211

State	Nature of Transition (Contribution in %)	Primary Character	Energy		Oscillator strength
			(eV)	(nm)	(f)
S_1	HOMO->LUMO (98%)	MLCT/LLCT	1.95	635	0.0001
S_3	H-2->LUMO (98%)	MLCT/LLCT	2.39	518	0.0288
S_9	H-10->LUMO (25%), H-7->LUMO (45%), H-6->LUMO (12%), H-1->L+1 (13%)	MLCT/LLCT	2.81	442	0.2222
S_{11}	H-1->L+1 (84%)	MLCT/LLCT	2.84	436	0.0800
S_{13}	H-10->LUMO (66%), H-7->LUMO (31%)	MLCT/LLCT	2.97	418	0.0175

Predicted Phosphorescence : 596nm | **Predicted Phosphorescence : 769nm** | **Predicted Phosphorescence : 533nm** | **Predicted Phosphorescence : 680nm**

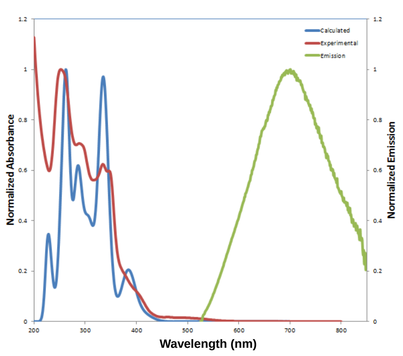
•Spin Density of T_1 State :



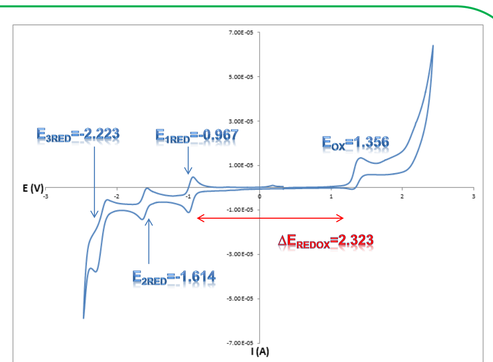
PHOTOPHYSICAL DATA of A

Absorbance 298 K (nm)[a]	Emission (λ_{max})	Φ	Lifetime (τ)
[Molar Absorptivities ($M^{-1}cm^{-1}$)]	298 K (nm)[a]	(%)[a,b]	298 K (ns)[a]
252 [6372]; 290 [4428]; 334 [4110]; 375 [1300]; 460 [128]	690	4.0	537 (54%)
			44 (46%)

[a] Measured in ACN. [b] Measured at 298 K using $[Ru(bpy)_3]$ $(PF6)_2$ = 9.5% in ACN



Emission and Absorption Spectra



Cyclic Voltammetry

CONCLUSION AND FUTURE WORK

The computations indicate that the dinuclear complexes are significantly red-shifted in their absorption and emission compared to their mononuclear counterparts. The synthesis and the characterization of the mononuclear complexe $[(ppy)_2\ Ir(dpp)]$ (PF_6) have been achieved successfully.

We will now focus on the synthesis of the other complexes to complete the study.

Finally, we plan to design a non-symmetrical dinuclear complex bearing two different cyclometallating ligands to see the effect on the nature of the charge transfer between metal centers, and how that impacts the photophysical properties.

ACKNOWLEDGEMENTS AND FUNDING

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