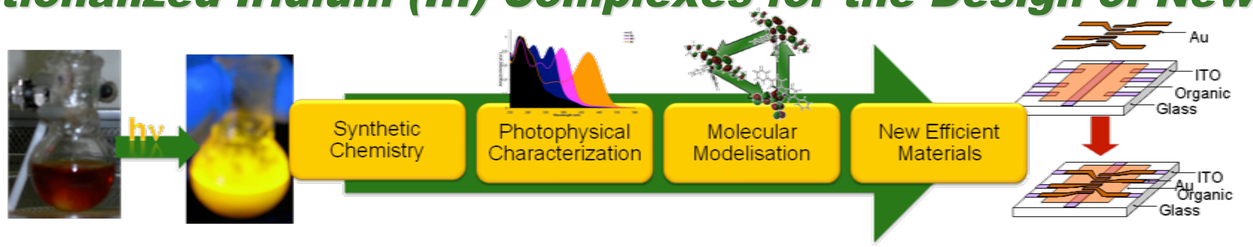
Synthesis of Functionalized Iridium (III) Complexes for the Design of New Efficient Materials.



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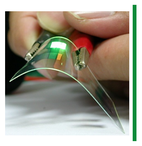
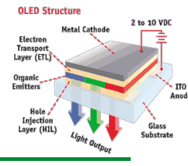
Introduction

Producing light or capturing solar energy in more efficient ways than the traditional light bulb or solar cell is the next goal in becoming eco-energetically friendly. In the Zysman-Colman laboratory, one of our objectives is to better understand the relationship between the structure of the chromophore and the properties of OLEDs. The mastery of this relationship will enable us to obtain new and efficient organic materials for commercial applications. Our lab is interested in the study of the photophysical properties of highly luminescent iridium complexes.

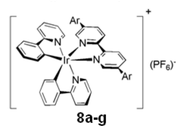


Facts about OLEDs :

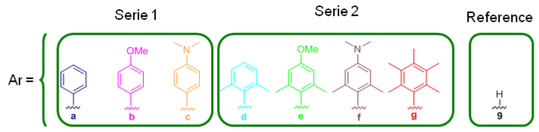
- Very simple assembly
  - Lower cost of fabrication compare to LCD
  - Many types of applications possible
- Energitically friendly
  - Low working voltage
- Pixel directly emmits lights
  - Greater effiency, vision angle, contrast
- Greater range of color



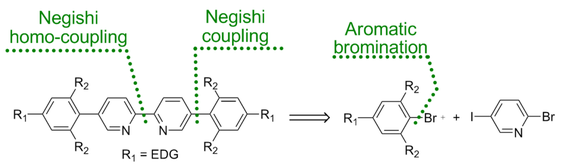
Target Complexes



8a-g



Retro synthetic approach



Synthesis of ligands

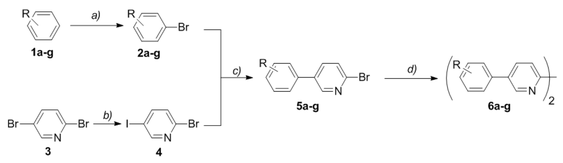


Table 1. Synthesis of ligand **6a-g**.

Yield (%)	a	b (OMe)	c (NMe_2)	d	e (OMe)	f (NMe_2)	g
2a-g	-	98	97	-	99	84	99
5a-g	72	86	67	68	55	49	54
6a-g	43	52	70	34	67	73	39
Total	29	44	45	23	30	30	20

a) NBS, ACN, r.t.; b) *n*-BuLi, I_2, Et_2O, -78C to r.t.; c) *n*-BuLi, $ZnCl_2$, THF, -78°C, $Pd(PPh_3)_4$, reflux; d) *n*-BuLi, $ZnCl_2$, THF, -78°C, $Pd(PPh_3)_4$, reflux.

Synthesis of Complexes

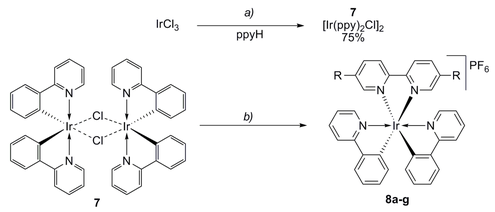


Table 2. Synthesis of complexes **8a-g**.

Yield (%)	a	b (OMe)	c (NMe_2)	d	e (OMe)	f (NMe_2)	g
8	69	89	80	70	81	99	95

a) ethylene glycol, 110°C; b) i) **6a-g**, ethylene glycol, 150°C, ii) NH_4PF_6.

X-ray Structural Analysis

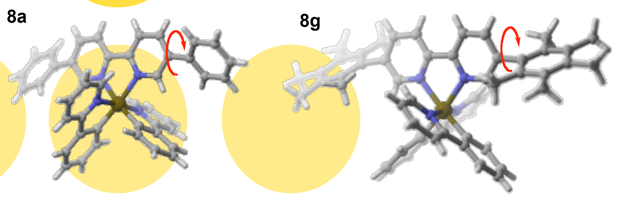
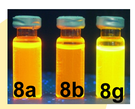


Table 3: Crystallographic data

Complex	Bond lenght (nm) Ir-N (bpy*)	Ir-N (ppy)	Ir-C(ppy)	Dihedral angle (°) Aryl-bipyridyl
8a	2.13	2.05	1.99	35
8g	2.15	2.01	2.04	64



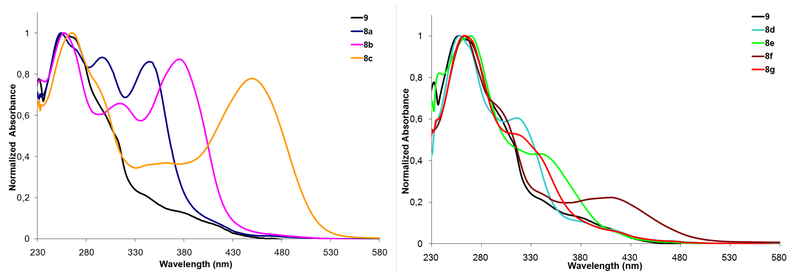
Photophysical Data

Table 4: Photophysical charaterisation[a]

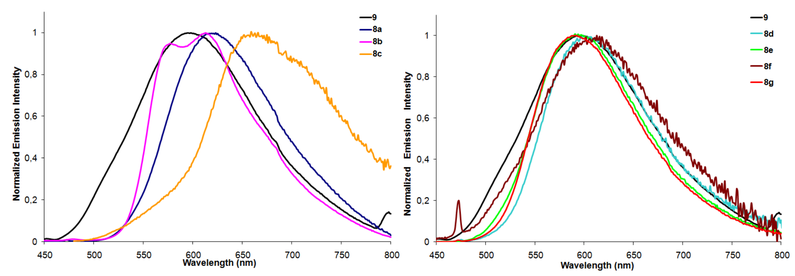
	Absorption 298 K (nm)	Absorptivities[b] ($x10^4$ $M^{-1}cm^{-1}$)	Emission (nm) 77 K [b]	298 K [b]	Stokes shifts (nm) 77 K	298 K	Quantum Yield (%) [c]	Lifetime[d] 77 K (µs)	298 K (ns)	k_r ($x10^5s^{-1}$)	k_{nr} ($x10^5s^{-1}$)
9	256, 270, 300, 344, 380, 415	2.4	532	595	117	180	6.2	(5.00)[e]	(269)[f]	-	-
8a	254, 266, 297, 344, 415, 465	11.9	531	623	121	208	16.7	3.84	575	2.90	14.5
8b	254, 315, 375	3.4	551	613	151	193	21.2	7.26	934	2.27	8.40
8c	266, 295, 361, 450	6.0	619	659	169	209	0.7	10.0	12.4	5.84	801
8d	258, 316, 379, 410, 471	3.9	516	599	99	182	22.0	3.97	668	3.29	11.7
8e	264, 270, 338, 415	4.0	506	596	91	166	16.0	3.69	932	1.72	9.00
8f	266, 304, 418, 442	3.6	563	613	113	198	2.0	3.76	508	0.39	19.3
8g	263, 309, 410, 474	5.4	513	592	98	177	20.8	3.87	947	2.20	8.40

[a] Mesured in 2-MeTHF. [B] $\lambda_{(max)}$. [c] In ACN ± 5%, using $Ru(bpy)_3(PF_6)_2$ as standard (Φ=6.2%). [d] ± 5%. [e] From K. S. Schanze *et al.*, *Chem. Commun.*, **2002**, 2504 in EtOH/MeOH glass. [f] From S. Bernhard *et al.*, *J. Am. Chem. Soc.*, **2004**, *126*, 14129.

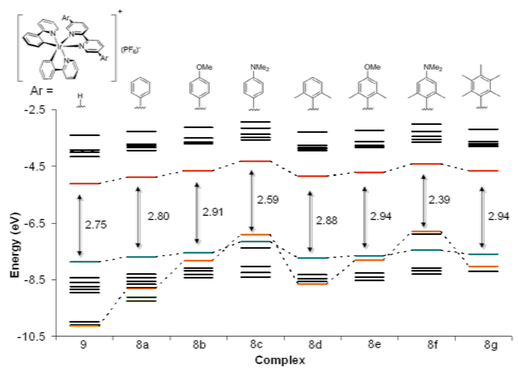
Absorption Spectra (298 K) in 2-MeTHF



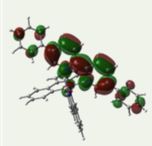
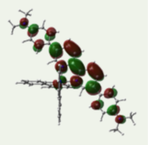
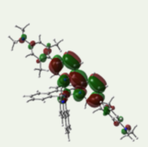
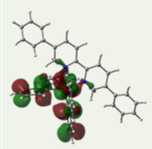
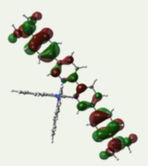
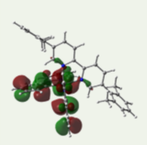
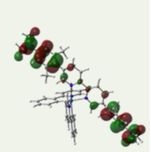
Emission Spectra (298 K) in 2-MeTHF



Computational Results



Electronic density mostly localised on π–π*(bpy and/or ppy) and d (Ir) (**black**). Most energetic bonding π(bpy) (**organge**), π(ppy) (**green**) and lowest energetic π(bpy) (**red**) orbitals.

Complexes	8a	8c	8d	8f
T1 (HSOMO)				
S0 (HOMO)				

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UNIVERSITÉ DE SHERBROOKE
Département de Chimie
Faculté des Sciences

RÉSEAU QUÉBÉCOIS DE CALCUL DE HAUTE PERFORMANCE

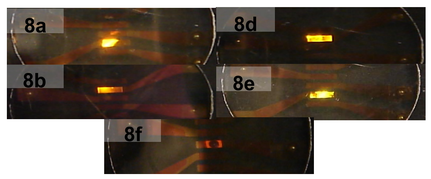
Cornell University

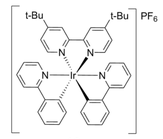
OLED Characterisation

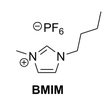
Table 6: OLEDs architecture optimisation

Luminophore	Comments	TOT[2] (min)	η_{max}(%)	$\Phi_{sol.}$ (%)	$Radiance_{max}$ (nW)	$t_{1/2}$ (min)	λ_{max} (nm)	λ_{max}sol. (nm)
10	litt.[1]	940	1.75	23.5	-	988	573	581
8a	8V	26.9	0.65	16.7	85 000	0.03	609	623
	4V	5431.3[3]	0.30		4 020	4679	-	
	4V, doped 0.188% BMIM	5.8	0.40		85 900	4.98	-	
	4V, doped 0.5% BMIM	22.5	0.51		88 600	4.78	-	
8b	8V (other conditions failed)	11.2	0.25	21.2	30 000	0.02	608	613
8c	device failed	-	-	0.7	-	-	-	659
8d	8V	13.6	0.06	22.0	21 000	0.72	615	599
	8V, doped 0.188% BMIM	5.3	0.11		35 600	0.67	-	
	bias of 4 V	298.4	0.1		-	153	-	
8e	8V	8.8	0.22	16.0	57 000	0.03	576	596
	4V	1153.2[3]	0.57		230	-	-	
	4V, doped 0.188% BMIM	5.5[3]	0.14		14 300	18.7	-	
	4V, doped 0.5% BMIM	33.8[3]	< 0.01		49.9	-	-	
8f	8V	2.2	0.02	2.0	500	1	630	613
8g	device failed	-	-	20.8	-	-	-	592

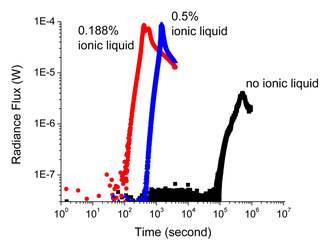
[1] Chem. Mater. (**2008**), *20*, 388. [2] Turn on time. Defined as the time necessary to obtain maximum radiance. [3] Defined as the time necessary to obtain half of maximum radiance.

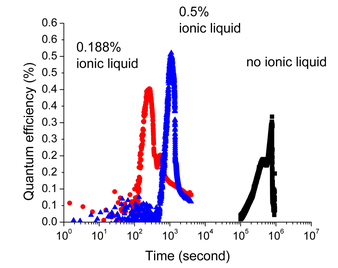


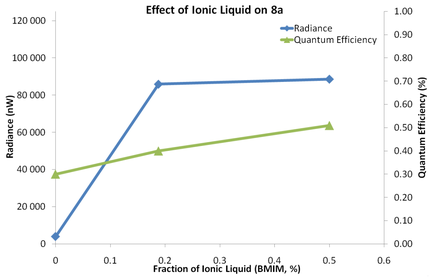


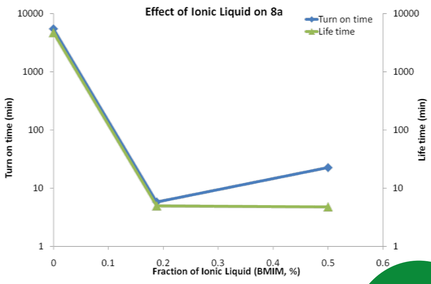


Ionic Liquid Effects on **8a** OLEDs









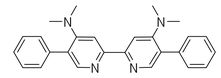
Conclusion

An efficient and rapid synthesis of functionalised 5,5'-diaryl-bypiridine was undertaken via an iterative Negishi coupling sequence. Complexes **8a-g** were obtain in a good overall yields, and their photophysical properties were determined.

The photophysical data that were obtained indicate that introduction of small electronic effect on the bypiridine ligands of $[Ir(ppy)_2bpy^*]PF_6$ complexes influences the absorbance, emission, lifetime and quantum yield properties in a reasonably predictable manner. Conjugative electron-donating groups (Series 1) showed a moderate tuning effect (68 nm) while a smaller effect (21 nm) was induced by inductive electron-withdrawing groups (Series 2).

Future Work

Taking into account the results and the tuning effect that we obtained in our first investigation, we design a second generation of bpy ligands bearing a 5,5' aryl groups but with introduction of EDG in the 4,4' positions. This design is believed to enhance the electron donating effect to obtain a blue shift compare to the first generation emitters and at the same time maintain an elevated steric hindrance around the metal center to conserve high quantum yields.



2nd generation bpy

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