Impact of the Use of Sterically Congested C^N Ligands on the Photoluminescent Properties of Iridium(III) Complexes

Claus Hierlinger,[1,2] Eli Zysman-Colman*,[1] Véronique Guerchais*[2]

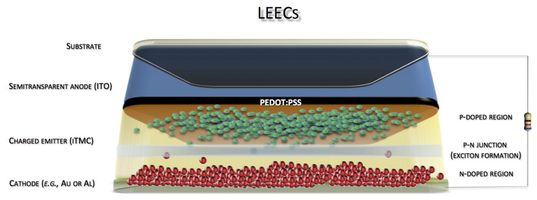
[1] *Organic Semiconductor Centre, EaStCHEM School of Chemistry North Haugh, University of St Andrews, St Andrews, Fife, UK KY16 9ST*

[2] *UMR 6226 CNRS - University of Rennes I, Institut des Sciences Chimiques de Rennes, Campus Beaulieu, Rennes. France*

ch254@st-andrews.ac.uk, claus.hierlinger@univ-rennes1.fr, http://www.zysman-colman.com

Introduction

A promising artificial lighting technology is the light emitting electrochemical cell (LEEC), with an emissive layer based on luminescent cationic iridium complexes. This device possesses a simpler architecture compared to organic light emitting diodes (OLEDs), which can lower significantly the production costs. Excited state self-quenching during the operation can limit the lifetime of the device. *A strategy to circumvent this issue is to control the inter-nuclear distance by decorating the complexes with bulky, hydrophobic substituents.*



Objectives

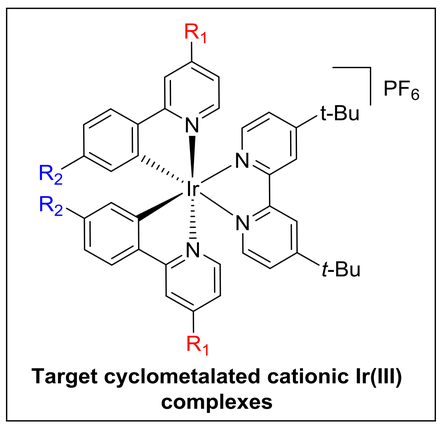
Design and synthesise a family of cationic Ir(III) complexes by modulating the size of substituents R_1 and R_2 on the C^N ligands.

These groups will:

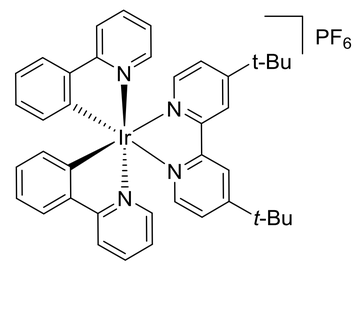
- hinder disadvantageous attack by small molecules
- increase inter-nuclear distances
- impede excited state self-quenching

→Leading to enhanced performance of the LEECs

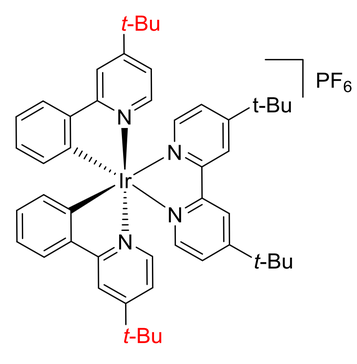
Family of sterically congested cationic Ir(III) complexes



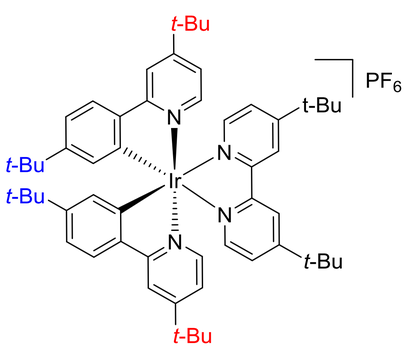
Target cyclometalated cationic Ir(III) complexes



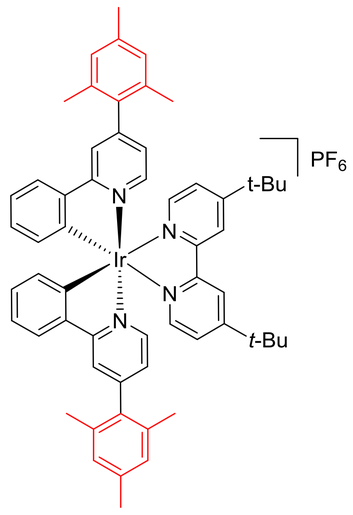
Ir-1a



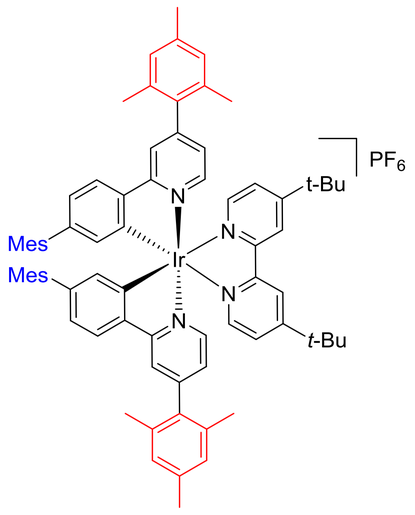
Ir-2a



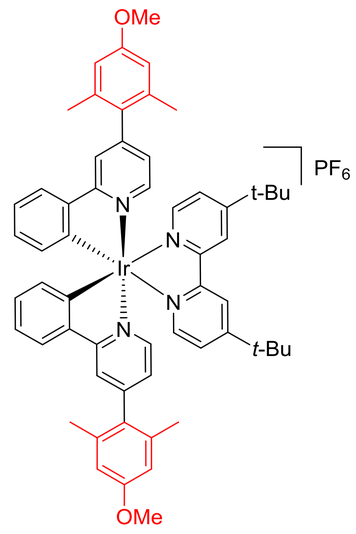
Ir-2b



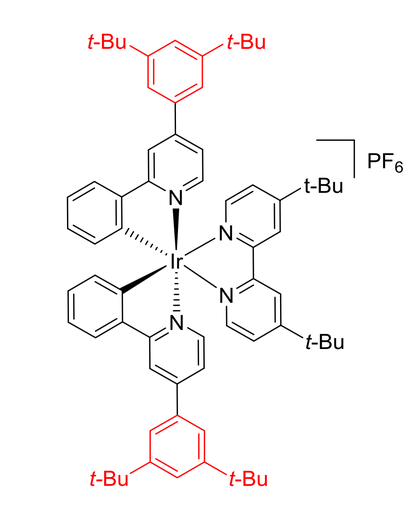
Ir-3a



Ir-3c

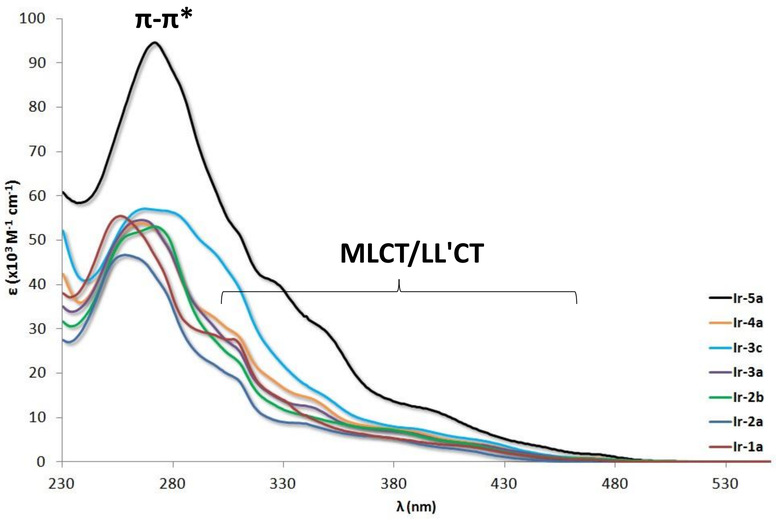


Ir-4a



Ir-5a

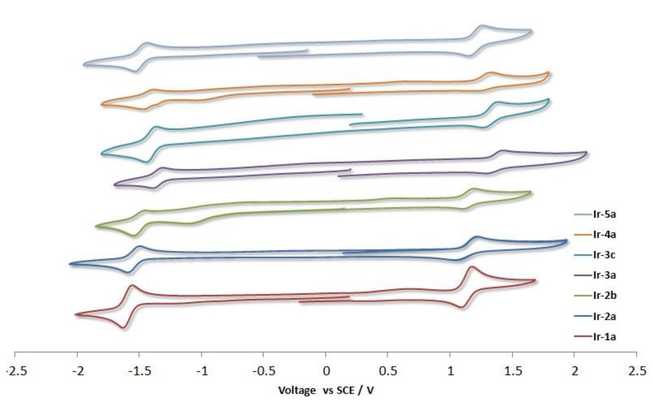
UV-vis Absorption spectra



Recorded in aerated MeCN at 298 K

- intense high-energy π-π* transition
- low-energy MLCT/LL'CT transition bands, insensitive to the nature of the C^N ligand

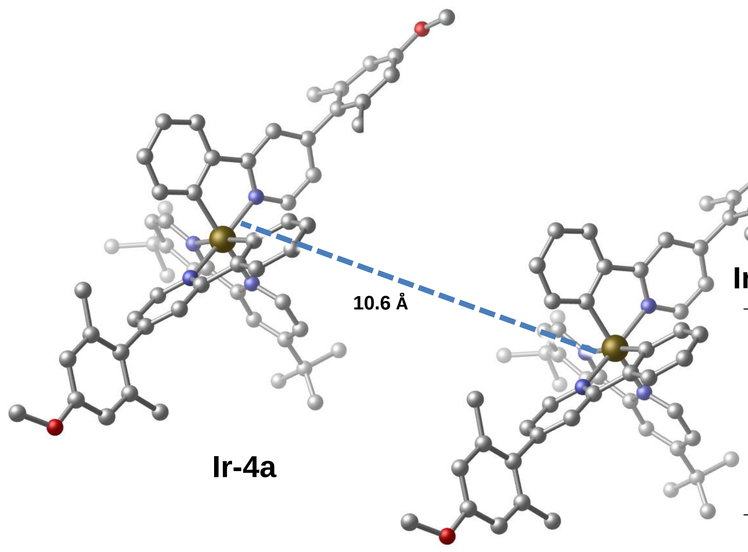
Electrochemistry



Recorded in deaerated ACN with 0.1M $(n\text{-}Bu_4N)PF_6$ at 298 K

- quasi-reversible oxidation → Ir(III) to Ir(IV)
- quasi-reversible reduction → π* orbitals of the N^N ligand

X-ray Structures



Ir-4a

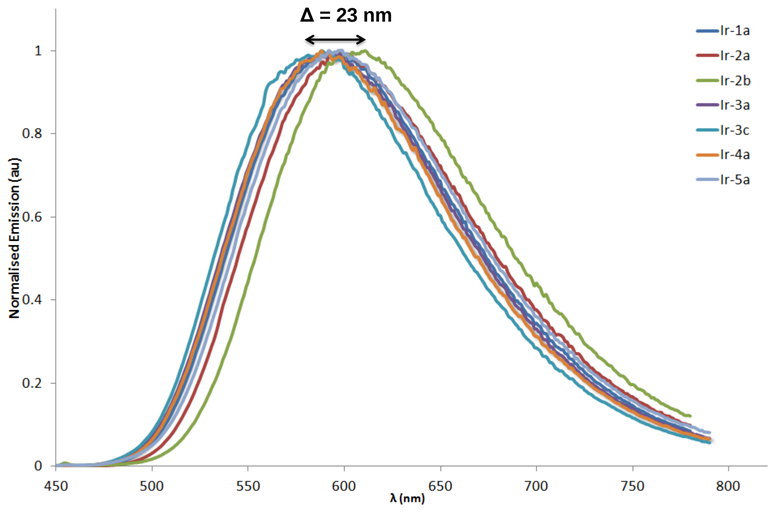
Ir···Ir distances (Å)

Ir-2a	7.2
Ir-3a	10.5
Ir-4a	10.6
Ir-2b	10.7

- longer inter-nuclear distance by increasing the size of the C^N ligand

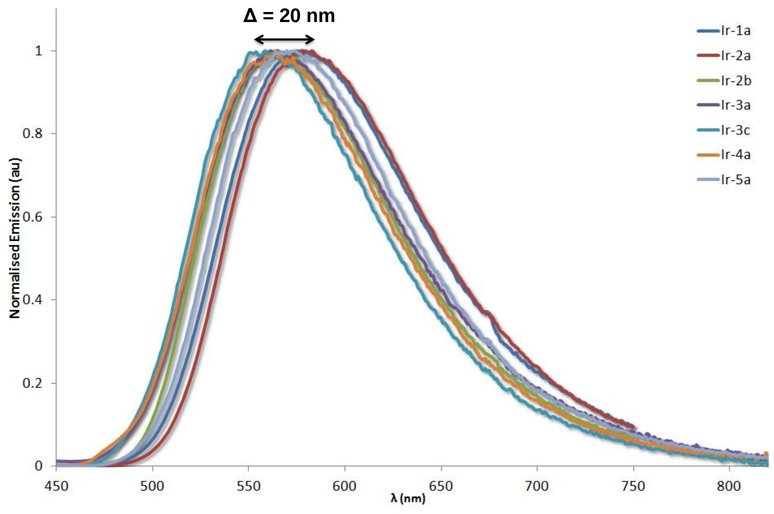
Luminescence Properties

a) deaerated MeCN solution



Normalised emission spectra, recorded in deaerated MeCN at 298 K, with λ_{exc} = 400 nm

b) Neat film



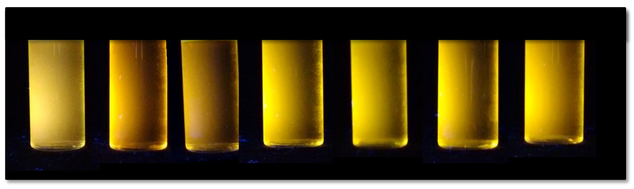
Normalised emission spectra of neat film obtained from dropcast neat film, with λ_{exc} = 400 nm

c) Photophysical Data

	deaerated MeCN solution			Neat film		
	λ_{em} [nm][a]	τ [ns][a]	Φ_{PL} [%][a,b]	λ_{em} [nm][c]	τ [ns][c] with contributions	Φ_{PL} [%][d]
Ir-1a	592	581	21	578	180 (57.7 %)	23
Ir-2a	597	497	17	579	200 (53.1 %)	**40**
Ir-2b	611	250	8	565	225 (68.9 %)	27
Ir-3a	592	**643**	19	565	171 (46.1 %)	15
Ir-3c	588	575	**22**	559	156 (38.3 %)	14
Ir-4a	588	623	19	564	179 (50.1 %)	16
Ir-5a	598	501	17	570	183 (51.9 %)	**40**

[a] recorded at 298 K in deaerated MeCN, with λ_{exc} = 400 nm, [b] 10^{-5} M Tris(2,2'-bipyridine)ruthenium(II) chloride hexahydrate in H_2O was used as reference [c] values refer to dropcast thin films at 298 K, with λ_{exc} = 400 nm, only long life component is displayed [d] values refer to dropcast thin films at 298 K using an integration sphere in deaerated environment

- yellow phosphorescence in solution state and neat films
- blue-shift of 30 nm going from solution to solid-state
- luminescence lifetime: 500 ns in solution
- luminescence quantum yield : in solution ~20% ; in solid up to 40%



Ir-1a Ir-2a Ir-2b Ir-3a Ir-3c Ir-4a Ir-5a

Conclusion

- **Straightforward synthesis of new family of sterically congested cationic Ir(III) complexes**
- **Increased inter-nuclear distance → reduction of concentration quenching**
- **Yellow phosphorescence**
- **Good quantum yields in solid-state**

→Promising candidates for LEECs

→Preparation of devices in progress, in collaboration with Dr. Henk Bolink, Valencia/Spain

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