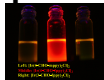


Facile and Efficient Chloro-Bridged Iridium (III) Dimers as OLED Materials: Opening Up New Possibilities

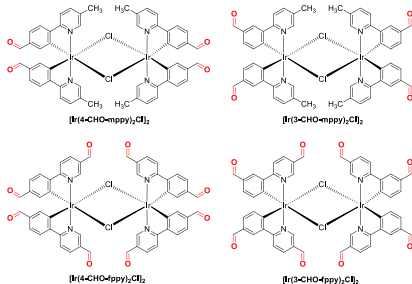


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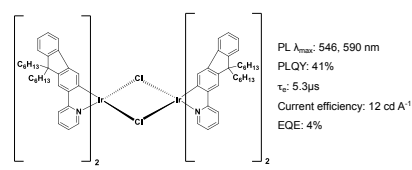
INTRODUCTION

Iridium chloro-bridged dimers have been long regarded as poor materials for OLED due to their weak emission. Yet, we discovered that we could turn on emission when the dimers were suitably substituted. In this study, a series of four iridium chloro-bridged dimers using formylated ligands have been synthesized and their optoelectronic properties characterized. The OLED device fabricated with $[\text{Ir}(\text{3-CHO-fppy})_2\text{Cl}]_2$ showed a decent external quantum efficiency (EQE) of 2.6%. This study suggests iridium chloro-bridged dimers can be a potential emitter class for OLED application.

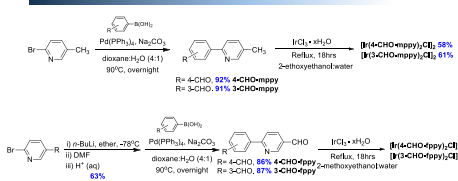


PRIOR ART

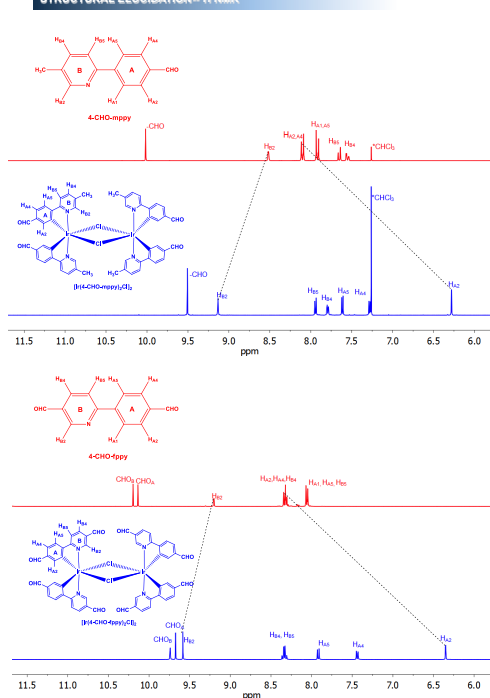
A. M. Hamed, A. S. Batsanov, M. A. Fox, M. R. Bryce, K. Abdullah, H. A. Al-Attar, A. P. Monkman, *J. Mater. Chem.*, 2012, 22, 13529-13540



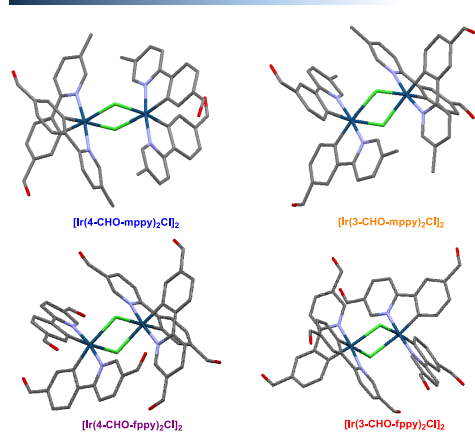
SYNTHESIS



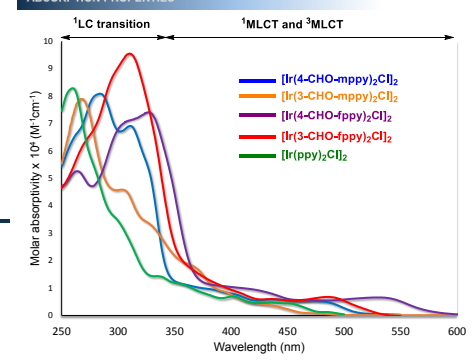
STRUCTURAL ELUCIDATION—¹H NMR



STRUCTURAL ELUCIDATION—CRYSTAL STRUCTURES



ABSORPTION PROPERTIES

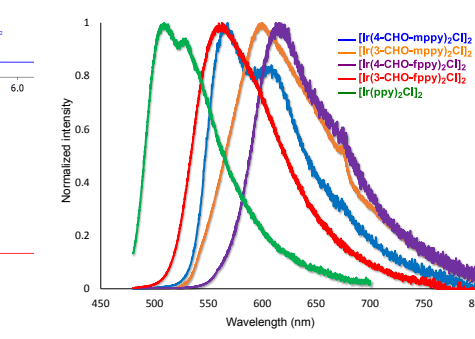


• Formyl group on pyridine ring causes a bathochromic shift in the absorption spectra.
• Formyl group placed at the 4-position of the phenyl ring results in a red-shifted absorption spectrum compared with the 3-formyl analogues.

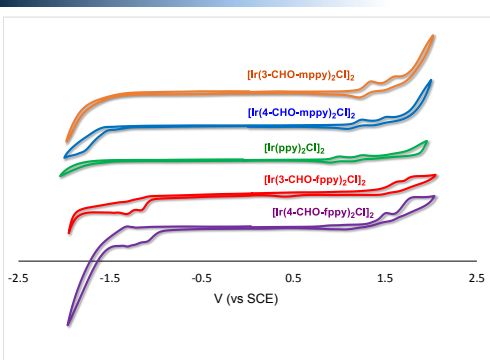
PHOTOPHYSICAL PROPERTIES*

Dimer Complex	λ_{em} (nm)	Φ^a (%)	τ_2 (ns)	k_r ($\times 10^6 \text{ s}^{-1}$)	k_{nr} ($\times 10^6 \text{ s}^{-1}$)
$[\text{Ir}(\text{ppy})_2\text{Cl}]_2$	520	0.5	125	0.40	79.60
$[\text{Ir}(\text{4-CHO-mppy})_2\text{Cl}]_2$	563, 600	2.5	206	1.21	47.33
$[\text{Ir}(\text{3-CHO-mppy})_2\text{Cl}]_2$	600	emission too weak			
$[\text{Ir}(\text{4-CHO-fppy})_2\text{Cl}]_2$	611, 670(sh)	15.7	1980	0.79	4.26
$[\text{Ir}(\text{3-CHO-fppy})_2\text{Cl}]_2$	556	0.9	601	0.15	16.49

* Photophysical measurements were performed in degassed DCM at room temperature.
* Ru(bpy)₃(PF₆)₃ ($\Phi_{\text{int}} = 9.5\%$) was used as standard for quantum yield measurements.



ELECTROCHEMICAL PROPERTIES

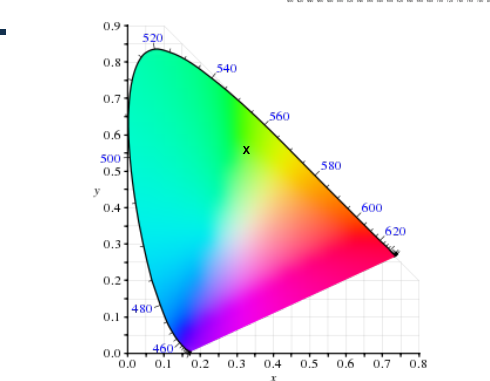
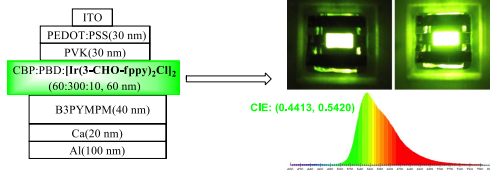


Conditions: complex concentration in 10^{-4} M with $0.1 \text{ M } n\text{-Bu}_4\text{NPF}_6$ in N_2 -saturated DCM at room temperature. Scan rate: 50 mV s^{-1} .

Complex	$E_{\text{ox}, \text{pc}_1}^a$ (V)	$E_{\text{ox}, \text{pc}_2}^a$ (V)	$E_{\text{red}, \text{pc}_1}^a$ (V)	$E_{\text{red}, \text{pc}_2}^a$ (V)	ΔE_{redox} (V)
$[\text{Ir}(\text{ppy})_2\text{Cl}]_2$	1.00	1.26			
$[\text{Ir}(\text{4-CHO-mppy})_2\text{Cl}]_2$	1.25	1.51			
$[\text{Ir}(\text{3-CHO-mppy})_2\text{Cl}]_2$	1.35	1.61			
$[\text{Ir}(\text{4-CHO-fppy})_2\text{Cl}]_2$	1.46	1.67	-1.10	-1.30	2.56
$[\text{Ir}(\text{3-CHO-fppy})_2\text{Cl}]_2$	1.58	1.72	-1.16	-1.31	2.74

* Potentials reported versus SCE.

OLED FABRICATION



Complex	Volt. at 1 cd/m ² (V)	Max. luminance (cd/m ²)	Max. Current Eff. (cd/A)	Max. EQE (%)	Emission/peaks (nm)
$[\text{Ir}(\text{3-CHO-fppy})_2\text{Cl}]_2$	7.7	>6000	9.086	2.593	551
$[\text{Ir}(\text{3-CHO-mppy})_2\text{Cl}]_2$	5.7	630	0.508	0.211	557
$[\text{Ir}(\text{4-CHO-fppy})_2\text{Cl}]_2$	8.1	178	0.441	0.366	612
$[\text{Ir}(\text{4-CHO-mppy})_2\text{Cl}]_2$	6.5	982	1.286	0.637	447, 562

CONCLUSIONS

In this work, the synthesis and characterization of a series of four novel chloro-bridged iridium dimers with formylated ligands were studied. The absorption, electrochemical and photophysical properties were found to be significantly affected by the number of formyl groups and their regiochemistry. More importantly, preliminary OLEDs fabricated using $[\text{Ir}(\text{3-CHO-fppy})_2\text{Cl}]_2$ as the dopant gave a decent EQE of 2.6%. This result challenges the widely accepted notion that iridium dimers cannot be a good OLED materials and encourages further study of chloro-bridged iridium dimers as emitters in solid-state lighting.

ACKNOWLEDGEMENTS AND FUNDING

