Palladium(0) – An Underexplored Route to Efficient Phosphorescence

Adam F. Henwood[a], Mathieu Lesieur[a], Ashu K. Bansal[b], Vincent Lemeur[c], David Beljonne[c], David G. Thompson[d], Duncan Graham[d], Alexandra M. Z. Slawin[a], Ifor D. W. Samuel[b], Catherine S. J. Cazin[a] and Eli Zysman-Colman[a]*

[a]*Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, UK, KY16 9ST, eli.zysman-colman@st-andrews.ac.uk, http://www.zysman-colman.com*

[b]*SUPA School of Physics and Astronomy, University of St. Andrews*

[c]*Chimie des Matériaux Nouveauz & Centre d'Innovation et de Recherche en Matériaux Polymères, Université de Mons*

[d]*WestCHEM Department of Pure and Applied Chemistry and Centre for Molecular Nanometrology, University of Strathclyde*

Introduction

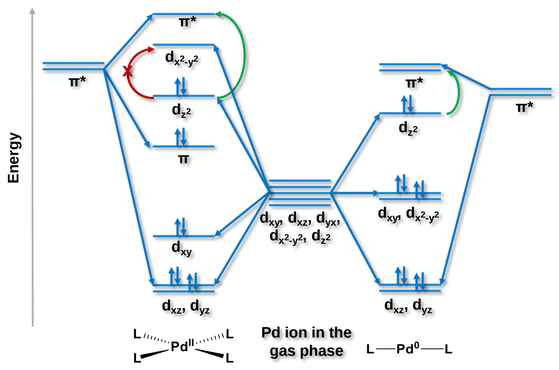
Phosphorescent iridium(III) complexes are unparalleled in their performance as phosphors for OLEDs.[1] However, the scarcity of iridium necessitates exploring alternative, potentially more abundant materials that may serve as suitable candidates to replace iridium as the premier class of emitter for these applications.

The most common alternatives to iridium(III) are platinum(II) and copper(I) complexes, but they too have drawbacks in terms of scarcity (platinum) or stability (copper).[2] Thus in this work, we assess the viability of employing the underexplored family of palladium(0) complexes as phosphors for OLED applications. Palladium is more abundant than both iridium and platinum, and the family of complexes reported herein demonstrates exceptionally bright luminescence and good colour tunability from blue-green to orange. The first OLEDs using Pd(0) based emitters have been fabricated from these materials and their properties have been investigated.

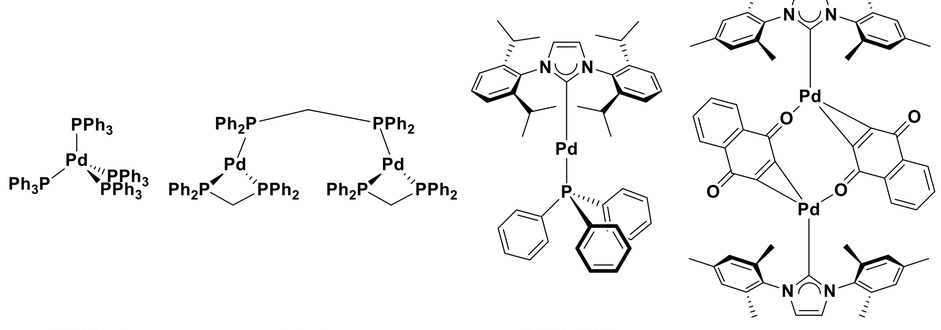
[1] K.-H. Kim, S. Lee, C.-K. Moon, S.-Y. Kim, Y.-S. Park, J.-H. Lee, J. W. Lee, J. Huh, Y. You and J.-J. Kim, *Nat. Commun.*, 2014, **5**, 4769

[2] N. Armaroli, G. Accorsi, F. Cardinali and A. Listorti, *Top. Curr. Chem.*, 2007, **280**, 69.

Background and Context



- Luminescent Pd(II) complexes are more heavily explored, but these are usually poorly luminescent due to low lying **metal centred** (**MC**) states.
- Pd(0) complexes only have accessible **metal-to-ligand charge transfer** (**MLCT**) states, and thus in principle should be highly emissive.
- However, until now reports on luminescent Pd(0) complexes have been sparse.[3-6]



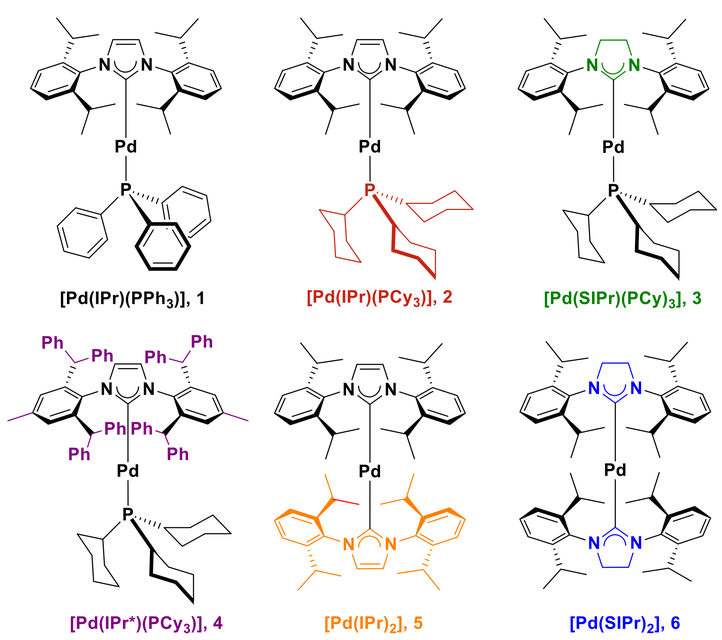
$Pd(PPh_3)_4$
λ_{max} = 646 nm
τ_e = 3.61 µs
Φ_{PL} = 1%
J. Am. Chem. Soc., 1985, **107**, 6718

$Pd_2(dppm)_3$
λ_{max} = 710 nm
τ_e = 5.93 µs
J. Am. Chem. Soc., 1988, **110**, 2145

$Pd(IPr)(PPh_3)$
λ_{max} = 515 nm.
Inorg. Chem. Commun., 2013, **35**, 110

$[Pd(IMes)(quinone)]_2$
λ_{max} (77 K) = 564 nm
J. Organomet. Chem., 2005, **690**, 6051

Target Complexes



$[Pd(IPr)(PPh_3)]$, 1

$[Pd(IPr)(PCy_3)]$, 2

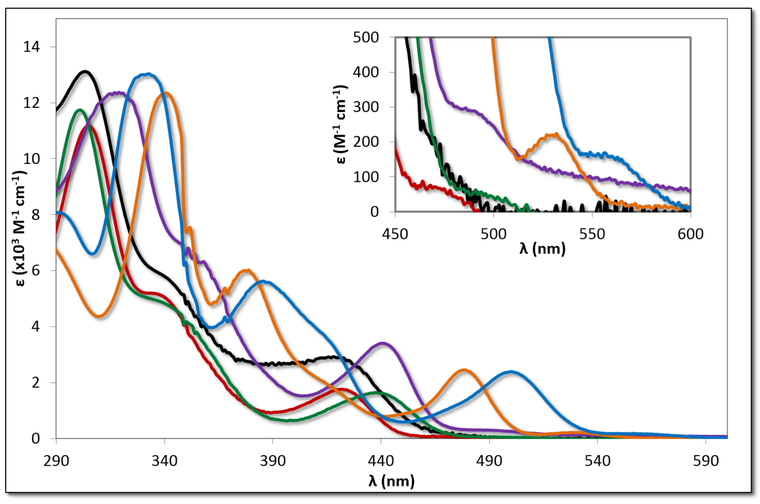
$[Pd(SIPr)(PCy_3)]$, 3

$[Pd(IPr^*)(PCy_3)]$, 4

$[Pd(IPr)_2]$, 5

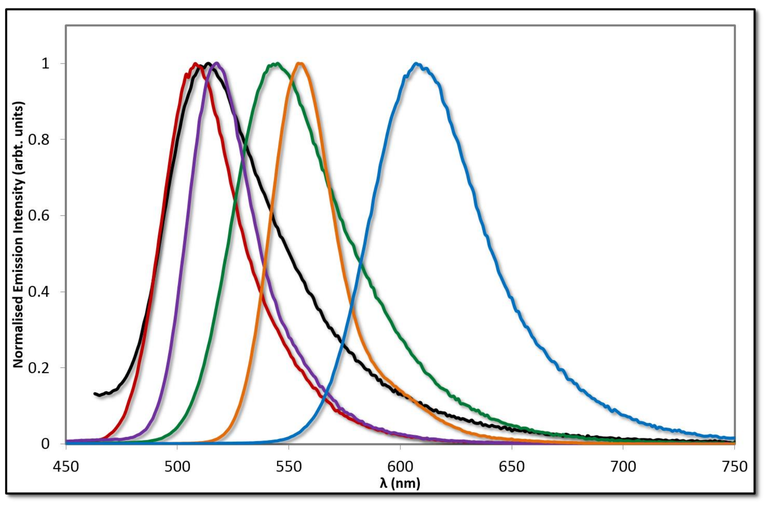
$[Pd(SIPr)_2]$, 6

UV-Vis Absorption Spectroscopy



UV-Vis absorption spectra in degassed toluene solution of complexes **1 – 6**

Solution State Emission Spectroscopy



Emission spectra in toluene solution of complexes **1 – 6**.

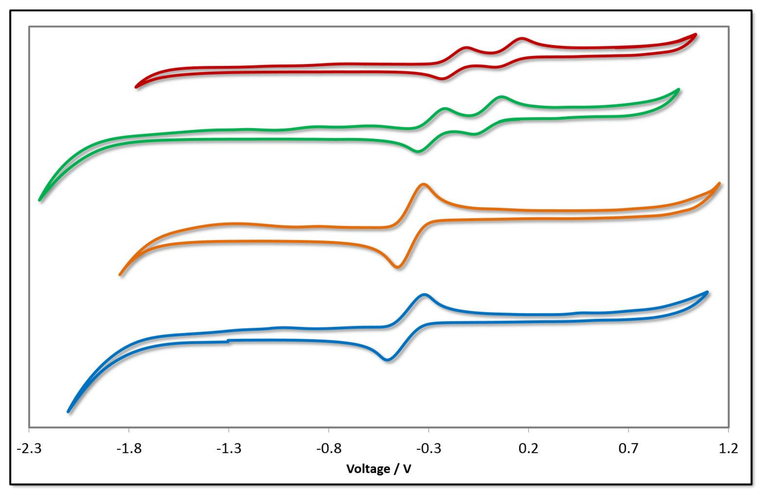
Complex	λ_{em} / nm	Φ_{PL} / %	τ_e / µs
1	512	1	0.014
2	508	16	1.56
3	543	69	5.46
4	515	14	0.36 (15 %), 1.59 (85%)
5	555	70	2.93
6	608	70	5.62

Electrochemistry

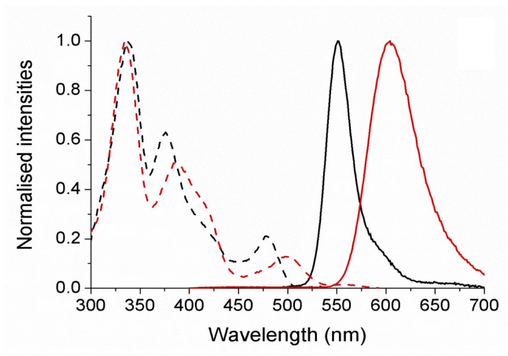
Complex	$E_{1/2}$ (V) [ΔE_p (mV)]	$E_{1/2}$ (V) [ΔE_p (mV)]	E_{HOMO} (eV)	E_{LUMO} (eV)
2	-0.17 [114]	0.10 [119]	-4.07	-1.39
3	-0.29 [119]	0.00 [115]	-3.95	-1.38
5	-0.39 [149]	-	-3.85	-1.46
6	-0.45 [236]	-	-3.79	-1.53

Cyclic voltammetry of complexes **2**, **3**, **5** and **6** in THF solution *vs* SCE using Fc/Fc$^+$ as an internal standard (0.56 V in THF).[7]

[7] N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877



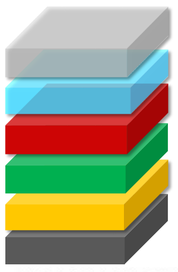
Solid State Photophysics



Solid state UV-vis absorption spectra of complexes **5** (black dashed line) and **6** (red dashed line). Solid state emission spectra of **5** (black solid line) and **6** (red solid line)

Complex	λ_{em} / nm	Φ_{PL} / %	τ_e / µs
5	550	10	0.27 (40 %), 0. 65 (60 %)
6	604	20	0.70 (23 %), 2.28 (77 %)

OLEDs



Anode: ITO

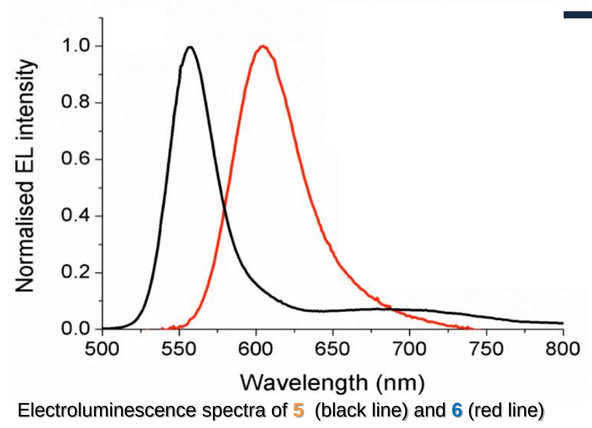
PEDOT:PSS 40 nm hole injection layer

Hole transport layer: PVK

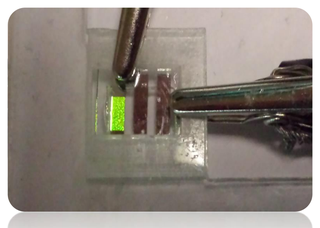
Emitter: **5** or **6**

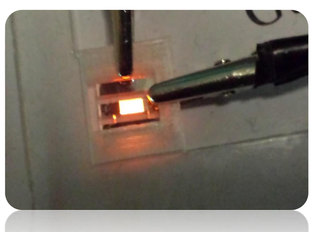
Electron transport layer: TPBI

Cathode: Ca/Al



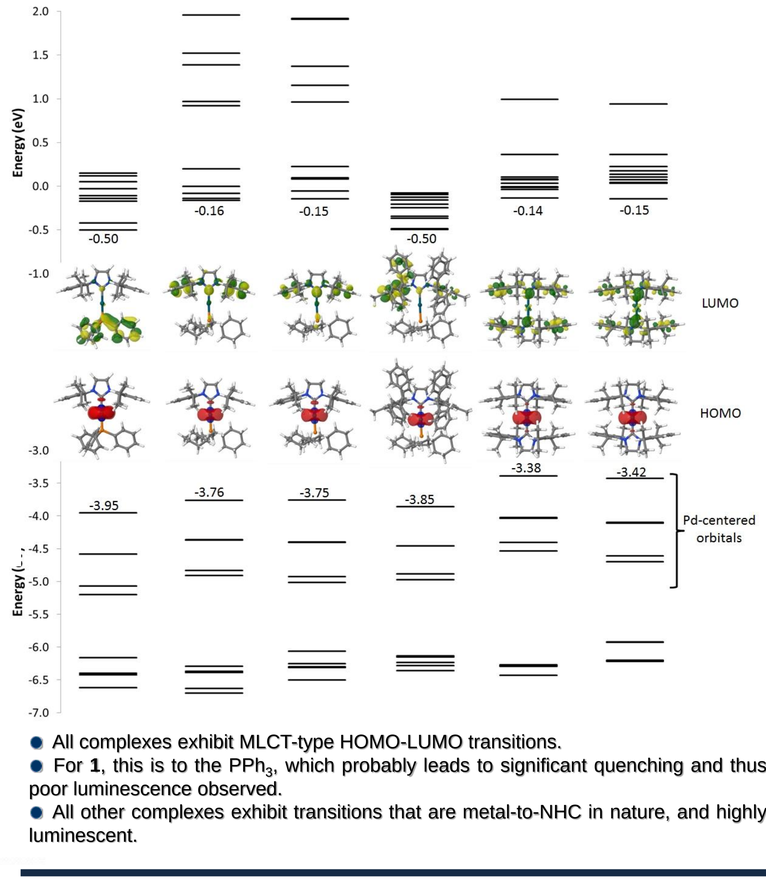
Electroluminescence spectra of **5** (black line) and **6** (red line)





Complex	Turn on voltage (V)	Current density (mA cm^{-2})	Luminance (cd m^{-2})	EQE (%)	Power efficiency (lm W^{-1})
5	8.2	35.2	342	0.28	0.20
6	6.2	54.5	766	0.70	0.28

Computations



- All complexes exhibit MLCT-type HOMO-LUMO transitions.
- For **1**, this is to the PPh_3, which probably leads to significant quenching and thus poor luminescence observed.
- All other complexes exhibit transitions that are metal-to-NHC in nature, and highly luminescent.

Conclusions

Six di-coordinated neutral Pd(0) complexes bearing a combination of NHC and/or PR_3 ligands have had their full solution state photophysics characterised. Complex **1**, with a metal-to-phosphine ^{3}MLCT excited state, is poorly luminescent. By contrast, the other complexes are characterised by a metal-to-NHC ^{3}MLCT excited state that leads to intense luminescence observed in solution, with complexes **3**, **5** and **6** demonstrating record Φ_{PL} values for any palladium complex reported to date. Bright luminescence coupled with a large range of accessible emission wavelengths are important criteria in considering new materials for device applications, and these materials successfully achieve both of these, with scope for further structural improvements that suggests even brighter emission at the extremities of the visible spectrum is readily achievable. As a proof of concept, the first OLEDs adopting Pd(0) emitters were successfully fabricated using complexes **5** and **6**, with initial studies achieving EQEs of 0.28 and 0.70 %, respectively. Further optimisation in charge balance behaviour should lead to improved device performances.[8]

[8] A. F. Henwood, M. Lesieur, A. K. Bansal, V. Lemaur, D. Beljonne, D. G. Thompson, D. Graham, A. M. Z. Slawin, I. D. W. Samuel*, C. S. J. Cazin* and E. Zysman-Colman*, *Chem. Sci.*, 2015, **6**, 3248

ACKNOWLEDGEMENTS AND FUNDING