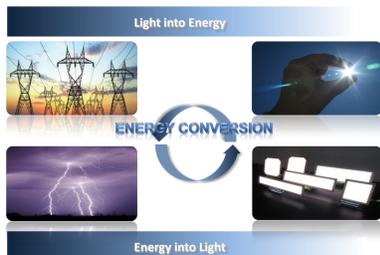


Overview

The Zysman-Colman Group

- Work in the Zysman-Colman group revolves around the theme of energy conversion: light into energy and energy into light.
- We are interested in harnessing light through photophysically active materials and converting that energy to useful work, either in the form of electrical (solar cells) or chemical potential (photoredox catalysis, solar fuels).
- Alternatively, our interest in efficient lighting technologies such as Organic Light Emitting Diodes (OLEDs) and Light Emitting Electrochemical Cells (LEECs) has led us to design efficient emissive molecules that generate light upon the application of an external potential. We are also interested in using the same systems in the context of electrochemiluminescence, which is targeted for bioimaging.
- Some examples of work we have done is shown.



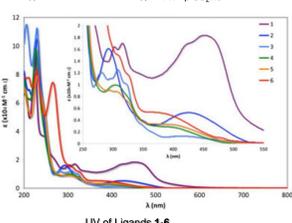
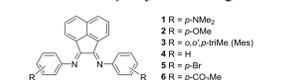
Light Harvesting for Energy

Introduction:

- Solar cells require highly absorptive materials capable of absorbing over a broad spectral range, to instigate efficient light-to-electricity energy transfer.
- We have explored various ligand scaffolds to do this, which are notable for their strong charge-transfer character between donor-acceptor that lead to favourable absorption properties.

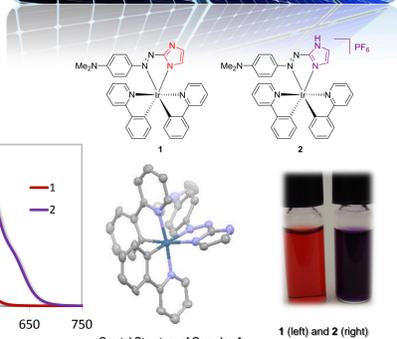
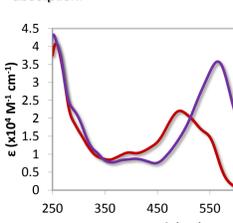
1-Aryl-BIAN Ligands:

- UV: highly absorptive small molecule organics.
- NMe₂ confers a red-shift in absorption and an increase in absorptivity at low energies.



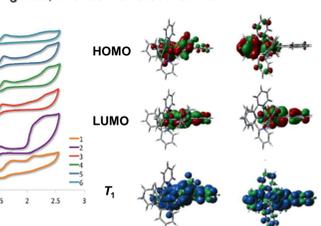
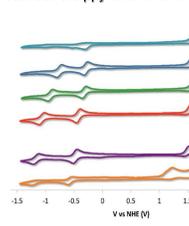
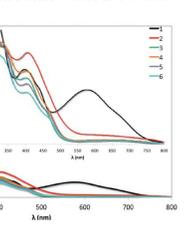
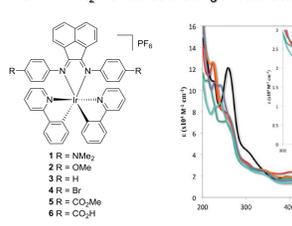
Azo-Imidazole Iridium Complexes:

- Complexes: strong donors (-NMe₂) and acceptor (imidazole) facilitate charge transfer and deep red absorption.
- UV: less accepting deprotonated imidazole in 1 results in reduced charge transfer and blue-shifting absorption.



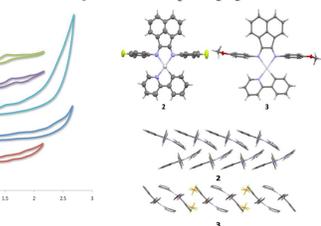
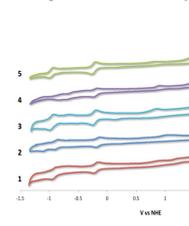
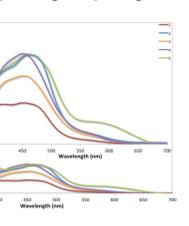
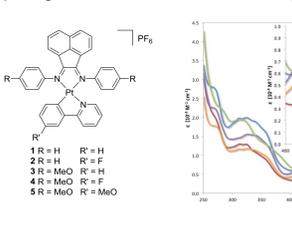
2-Aryl-BIAN Iridium Complexes:

- Exploration of Aryl-BIAN ligands 1-6 as ancillary ligands in [Ir(C^N)₂(N^N)](PF₆)₂ complexes.
- UV: As with the free ligand, greatest absorptivity and red-shifting of absorption is conferred by -NMe₂ functionality.
- CV: -NMe₂ introduces an additional oxidation wave at 1.22 V, leading to the narrowest HOMO-LUMO gap. Reduction waves are largely reversible and centered on the π* orbitals of the Ar-BIAN ligands, undergoing significant shifts as a function of ligand decoration.
- DFT: -NMe₂ introduces a change in the excited state. While 2 is mixed CT between the ppy and Ar-BIAN ligands, 1 is ILCT on the Ar-BIAN.



3-Platinum Complexes:

- Exploration of complexes of the form [Pt(C^N)₂(N^N)](PF₆)₂, where the electronics on one or both of the C^N and N^N ligands was varied.
- UV: A combination of -OMe groups on both the C^N and N^N ligands leads to the greatest and most red-shifted absorption profile.
- CV: oxidation is irreversible due to instability of Pt(II)/Pt(III) redox couple, but reversible in the reduction regime for most waves. The determined excited state oxidation potentials demonstrate that these molecules can be compatible as dyes for dye sensitised solar cells (DSSCs).
- X-Ray: 2 and 3 show typical square planar structures, with aryl-imino groups orthogonal to the metal plane to minimise steric interactions. Long range packing of 2 shows offset π-stacks, which adopt herringbone packing between the layers. 3 forms dimeric pairs, linked by CH-π and PF₆⁻ bridging interactions.



Conclusions:

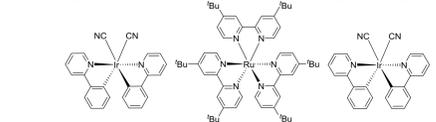
- Aryl-BIANs and Azo-imidazole ligands demonstrate panchromatic absorption and high molar extinction coefficients both as organic compounds and as ligands on complexes.
- They show exciting promise as candidates for solar cells, and work is in progress to incorporate suitably functionalised analogues into devices.

References:
*K. Hasan and E. Zysman-Colman, *J. Phys. Org. Chem.*, 2013, 26, 274.
*K. Hasan and E. Zysman-Colman, *Eur. J. Inorg. Chem.*, 2013, 4421.
*C. O'Brien, D. B. Cordes, A. M. Z. Slawin and E. Zysman-Colman, *Organometallics*, 2014, submitted.

Supramolecular Assembly of Emitters

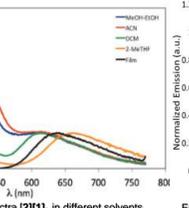
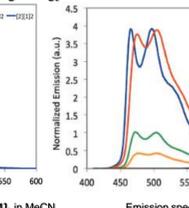
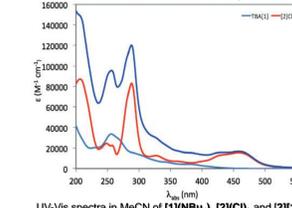
Introduction:

- We are interested in using supramolecular chemistry as a tool to control inter luminophore spacing leading to improved emitter performance in solid-state lighting.
- Here we show white light can be generated by mediating energy transfer between a blue and red emitter.
- White light is crucial for industrial applications of light emitting devices.



Soft Salts:

- Energy transfer modulated between a "soft-salt" of an anionic blue-green emitting iridium complex, [Ir(ppy)₂(CN)₂]⁻, [1], and a red emitting ruthenium complex, [Ru(dibutylpy)₃]²⁺, [2], in the context of generating white light. [2][1]₂ is compared with the monometallic counterparts (NBu₄)[1] and [2](PF₆)₂
- UV: structural features of both (NBu₄)[1] and [2](Cl)₂ are present. The low energy broad band at 450 nm is characteristic of ¹MLCT transitions seen in Ru complexes, while higher energy intense bands are ascribed as typical ¹LC transitions arising from both complexes.
- Emission: colour tuning from blue to yellow, through white, can be achieved. At elevated concentrations or in polar media, intimate ion pairs are formed that result in a shorter Ir-Ru distance, facilitating energy transfer.



Conclusions:

- White light generation in this fashion is normally only possible through careful control of ion ratios.
- We have shown that control of supramolecular ion pair formation through varying solvent or concentration allows for fine colour tuning of emission that is not possible with individual constituent ions.
- This work is of particular interest to the field of burgeoning field of white-light emitting materials.

References:
*M. Sandroni and E. Zysman-Colman, *Dalton Trans.*, 2014, 43, 3676

Towards Bright Deep Blue Emitting Iridium Complexes

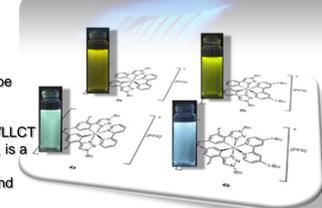
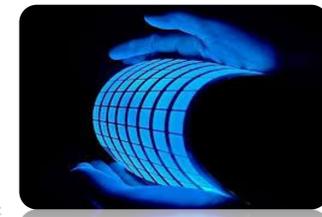
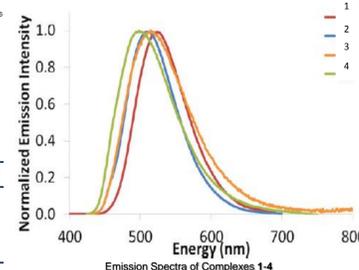
Non-Traditional Ligands:

- White lighting devices are normally fabricated from constituent emissive layers of red, green and blue. Thus for efficient lighting, each of these colours must perform well in the device.
- However, a serious challenge in this area is the design of stable, bright blue emitting complexes.
- Iridium complexes of the form [Ir(C^N)₂(N^N)]⁺, where C^N and N^N denote cyclometalating and diimine derivatives, respectively, are the most widely explored luminescent materials for these applications and are the main focus of this group.
- Through a combination of computational methods, organic/inorganic synthesis and spectroscopy, we have designed new and diverse ligand scaffolds that might lead to the development of new efficient deep blue emitters to solve this problem.

1,2,3-Triazole Cyclometalating Ligands:

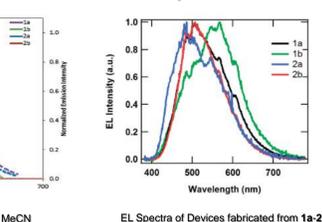
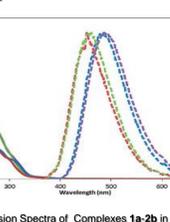
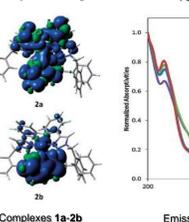
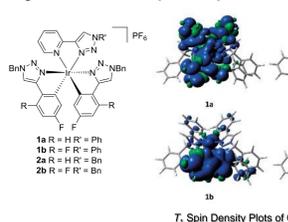
- Typical cyclometalating C^N ligands are derivatives of 2-phenylpyridine-type ligands (1 and 2).
- By changing the C^N pyridyl ring for a more electron rich 1,2,3-triazole, the HOMO-LUMO gap can be increased, leading to C^N triazole analogues with blue-shifted emission.
- Emission: 3 and 4 are blue-shifted by 480 and 549 cm⁻¹, respectively, compared with their pyridyl analogues 1 and 2. Broad, unstructured emission profiles across the series are characteristic of MLCT/LLCT transitions from the metal and C^N ligands to the N^N ancillary ligand. The bluest of these, 4 (498 nm), is a very bright sky blue upon irradiation.
- DFT: Assignment of charge transfer excited state corroborated by electron density plots of HOMO and LUMO. Increased HOMO-LUMO gap with use of triazoles supports experimental evidence.
- Excited state kinetics: reasonably short emission lifetimes in the 1 μs regime, with high Φ_{PL} values ranging from 61-80%.

Complexes	λ _{em} (nm)	τ _e (μs)	Φ _{PL} (%)
1	527	1.07	61
2	512	1.19	78
3	514	1.11	73
4	498	1.20	80



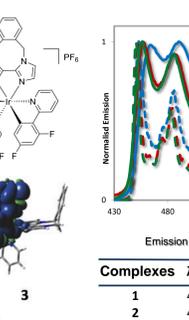
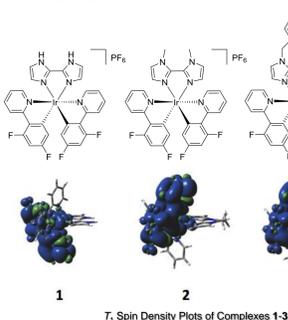
2,1,2-Triazole Ancillary Ligands:

- To further blue-shift emission, we substituted the bipyridine N^N ancillary for a more electron rich pyridyl/triazole.
- DFT: T₁ spin density plots show complexes 1b and 2b, which are the most blue, have the most ligand centred ³LC character. However, significant metal contribution explains the CT character of the emission spectra.
- UV: strong absorption in the near UV is typical of ¹π-π* transitions seen for other aryltriazole complexes.
- Emission spectra: 1b and 2b, with an additional fluorine, are the bluest of these complexes in solution. However, contrary to the norm, the EL spectrum of the device demonstrates a blue-shift in the solid with enhanced emission, with 2a still one of the bluest devices reported to date (487 nm). That said, the brightness of these complexes is poor, with complex decay kinetics and Φ_{PL} values of <1% in solution that inhibit the overall device performance.

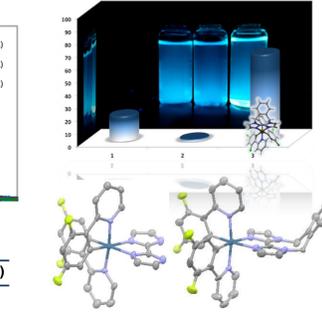


3,2'-Biimidazole Ancillary Ligands:

- To overcome the issue of brightness, we explored forcing a co-planar conformation of a biimidazole ancillary ligand through a tethering strategy with the goal of enhanced luminescence in the complex.
- DFT: T₁ density plots show inhibition of distortion of 3 compared with 2; 2 twists to alleviate steric strain while 3 is not distorted in the excited state.
- Emission: all three complexes are deep blue emitters, with alkylation leading to minimal changes in emission energy.
- Excited state kinetics: short lifetime (90 ns) and poor Φ_{PL} (2%) of 2 suggests twisting of the ancillary effectively deactivates the excited state. The enhanced rigidity of 3 by contrast leads to a long lifetime (3.84 μs) and gratifyingly, exceptionally bright emission (Φ_{PL} = 68%) for a deep blue emitter in MeOH solution.

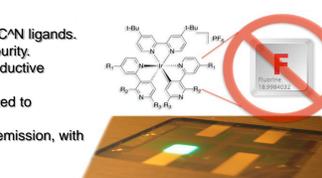
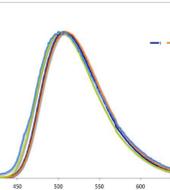
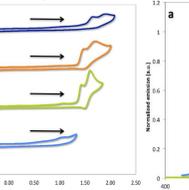
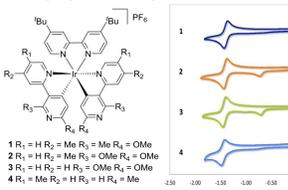


Complexes	λ _{em} (nm)	τ _e (μs)	Φ _{PL} (%)
1	464, 490	1.34	20
2	457, 486	0.09	2
3	457, 487	3.84	68



4,2'-Bipyridyl Cyclometalating Ligands:

- As shown, blue-shifting emission is typically achieved through fluorination of the phenyl rings of the C^N ligands. However, these materials are prone to defluorination in the device, which reduces stability and colour purity.
- By combining cyclometalated pyridyl rings and MeO substituents, the HOMO can be stabilised by inductive withdrawing effects to a similar magnitude as the commonly used dFppy ligands.
- CV: reversible reduction wave attributed to LUMO of N^N, while irreversible oxidation for 1-3 attributed to degradation of the -OMe substituents.
- Emission: blue-green unstructured emission profiles are indicative of MLCT-type transitions. Bright emission, with Φ_{PL} values ranging from 41-66%.
- Bright green-emitting LEEC devices have been synthesized.



Complexes	λ _{em} (nm)	τ _e (μs)	Φ _{PL} (%)
1	515	1.34	41
2	517	1.30	53
3	510	1.36	66
4	514	1.83 (86%); 6.30 (14%)	45

Conclusions:

- Many families of green-blue to blue emitting iridium complexes have been synthesised and explored.
- Simultaneously overcoming the challenges of bright emission, high colour purity and stable devices is a great challenge.
- We have gone some way to solving these problems, reporting some of the brightest blue emitting complexes in solution, devices that are among the bluest reported to date, and stable, blue-green fluorine-free alternatives.
- However, challenges still remain and thus we are still devising new ligand scaffolds to improve on work that is an exciting, topical area of research.

References:
*S. Ladouceur, D. Fortin and E. Zysman-Colman, *Inorg. Chem.*, 2011, 50, 11514.
*J. M. Fernández-Hernández, S. Ladouceur, Y. Shen, A. Jordache, X. Wang, L. Donato, S. Gallagher-Duval, M. de Arda Villa, J. D. Slinker, L. De Cola, E. Zysman-Colman, *J. Mater. Chem. C*, 2013, 1, 7440.
*A. F. Henwood, S. Evariste, A. M. Z. Slawin and E. Zysman-Colman, *Faraday Discuss.*, 2014, ASAP, DOI: 10.1039/C4FD00107A
*S. Evariste, M. Sandroni, T. W. Rees, C. Roldán-Carmona, L. Gil-Escrig, H. J. Bolink, E. Baranoff and E. Zysman-Colman, *J. Mater. Chem. C*, 2014, 2, 5793.

The Zysman-Colman Group

- The Zysman-Colman group is composed of a dynamic and international team of researchers working under the large umbrella theme of optoelectronic materials for energy conversion.
- Work is highly interdisciplinary and highly applied. We combine expertise in DFT computations, organic and inorganic synthesis, and optoelectronic characterisation to elucidate structure-property relationships and develop new materials with improved properties.
- We regularly collaborate to achieve tangible goals in topical areas such as efficient lighting, solar cells, green catalysis and bioimaging.

Thank you to Adam Henwood for creating this poster.