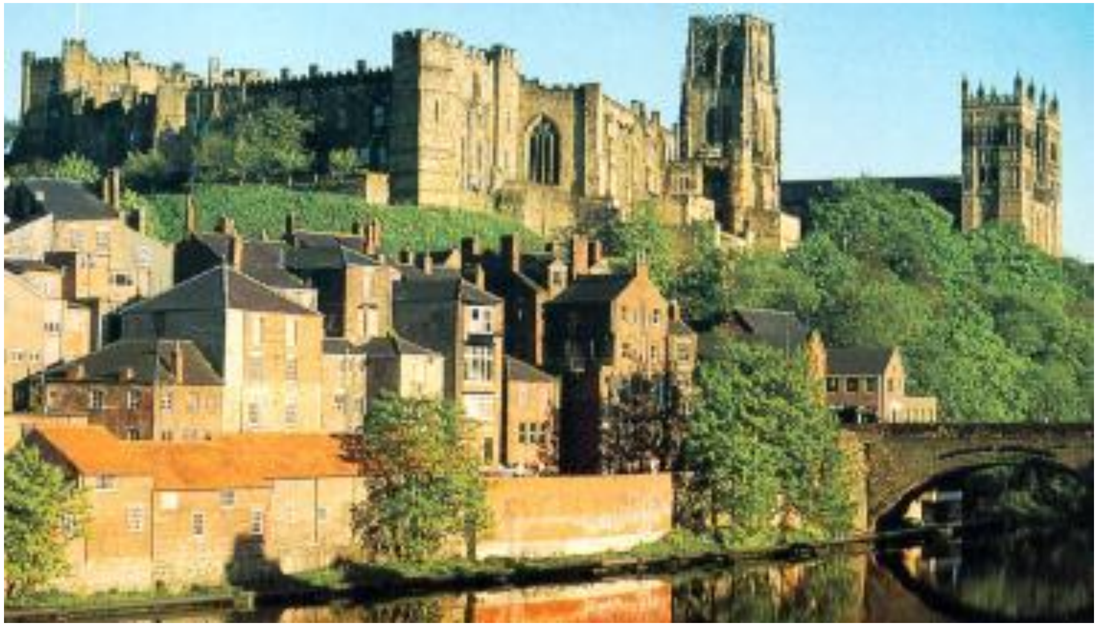
New Functionalised Organic Materials for Organic Light-Emitting Devices (OLEDs) and Lighting Technologies

Martin R. Bryce

Department of Chemistry, and Centre for Molecular and Nanoscale Electronics, Durham University, UK
m.r.bryce@durham.ac.uk



SCI, London, April 09, 2014

Durham University

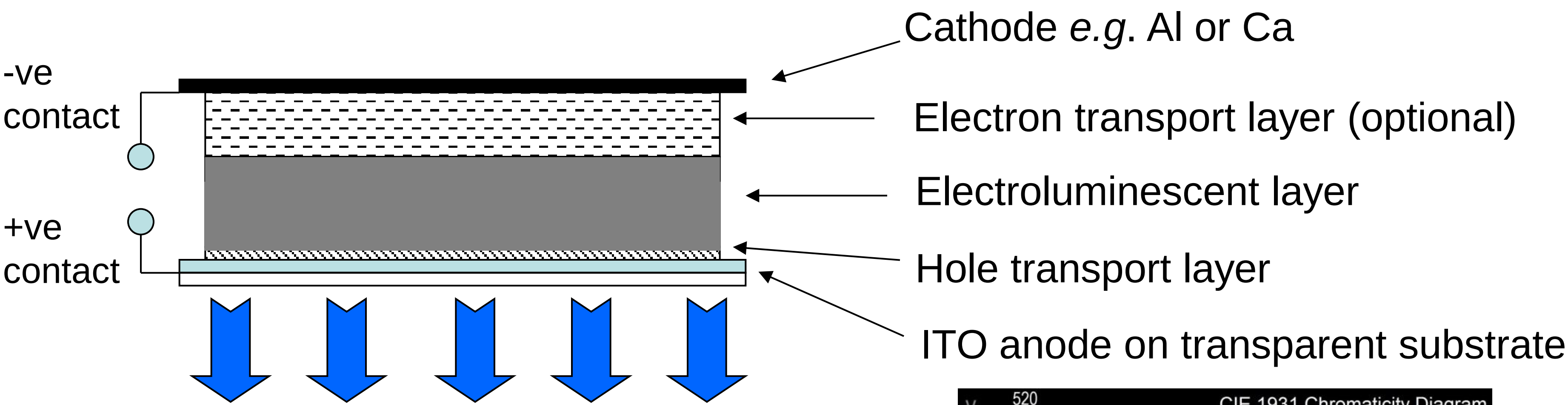
Outline

- Brief introduction to OLED technology
- New fluorescent copolymers with intramolecular charge transfer
- White-light emission and SSL
- New iridium complexes and PhOLEDs

Organic Light Emitting Device (OLED) Structure

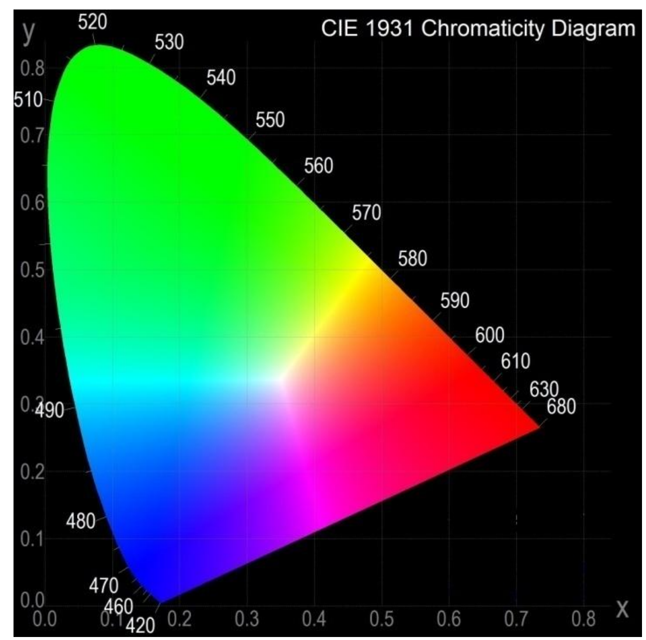
Durham University

Organic layers (*ca.* 30-100 nm thick) are assembled by vacuum deposition or spin-coating from solution



Light emitted from singlet excited states generated in the EL layer

- Wavelength (colour) of emitted light depends on the bandgap of the emissive layer
- Colours are defined by CIE coordinates of the Chromaticity Diagram



Why OLEDs ?

Durham University

Advantages and prospects of the technology

- Large area displays, including flexible displays
- Thin, lightweight panels
- High efficiency
- Bright screens with wide viewing angles
- Low voltage operation and fast switching times
- Durable and operational over a wide temperature range
- Low cost production

OLED Products in 2013

Durham University

2013, Samsung flexible phone ‘Youm’

2013, Audi ‘The swarm’

2013, Panasonic Ultra HD 56 inch OLED TV

2013, LG 55 inch curved OLED TV

2013, Toshiba OLED wrist watch

Major Challenges of OLED Technology

Durham University

For chemists, physicists and device engineers

- Synthesis of new emitters and charge-transport materials
- Fundamental understanding of charge-transport processes in thin films, especially at interfaces
- Simplify device architectures: new deposition techniques
- Choice of electrodes, encapsulation

For applications – flat panel displays, lighting, *etc*.

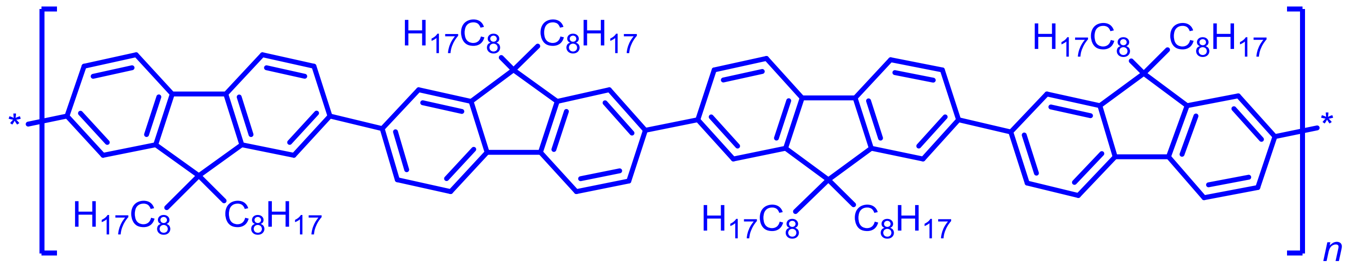
- High efficiency / brightness
- Colour purity and stability - red, green, blue, white
- Long operating lifetimes

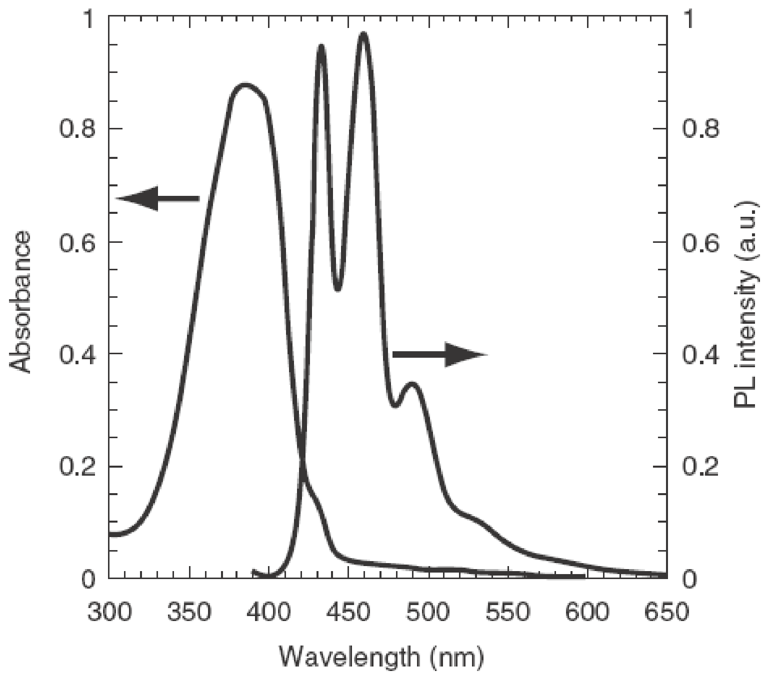
- **High-tier niche markets for lighting**

  – entrance lobbies, desk lights, architectural lighting, art galleries, museums, car dashboards, etc.

Reviews of white OLEDs: B. W. D'Andrade, S. R. Forrest, *Adv. Mater.* **2004**, *16*, 1585;
K. T. Kamtekar, M. R. Bryce, A. P. Monkman, *Adv. Mater*. **2010**, *22*, 572.

Polyfluorene: An Efficient Blue Emitting Polymer





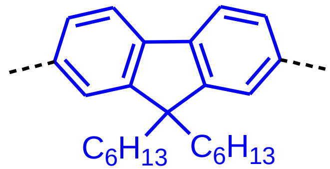
Linearly conjugated
POLY- / OLIGO-FLUORENES:

- wide band gap (~ 3 eV)
- good charge carrier mobility
- highly fluorescent in solution (PLQY 60-80%) and thin films (30-40%)
- high thermal and electrochemical stability
- functionality can be introduced at C9
- copolymers can be readily obtained

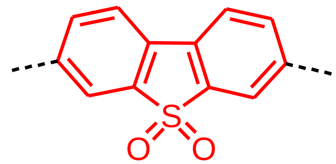
X. Gong, P. K. Iyer, D. Moses, G. C. Bazan, A. J. Heeger, S. S. Xiao, *Adv. Funct. Mater.* **2003**, *13*, 325.

- Brief introduction to OLED technology
- New fluorescent copolymers with intramolecular charge transfer
- White-light emission and SSL
- New iridium complexes and PhOLEDs

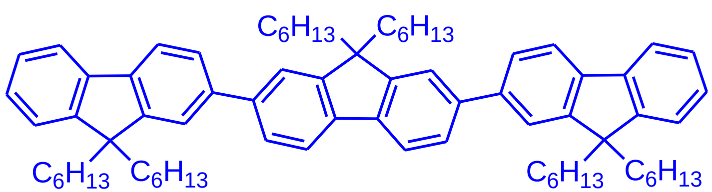
Dibenzothiophene-*S,S*-dioxide: A Highly Fluorescent Electron-Deficient Unit



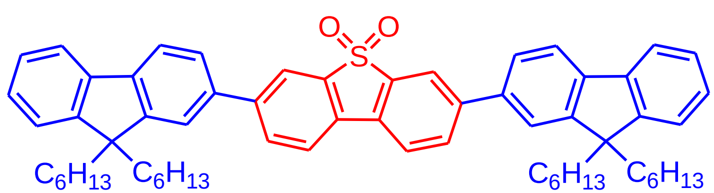
F



S Highly fluorescent



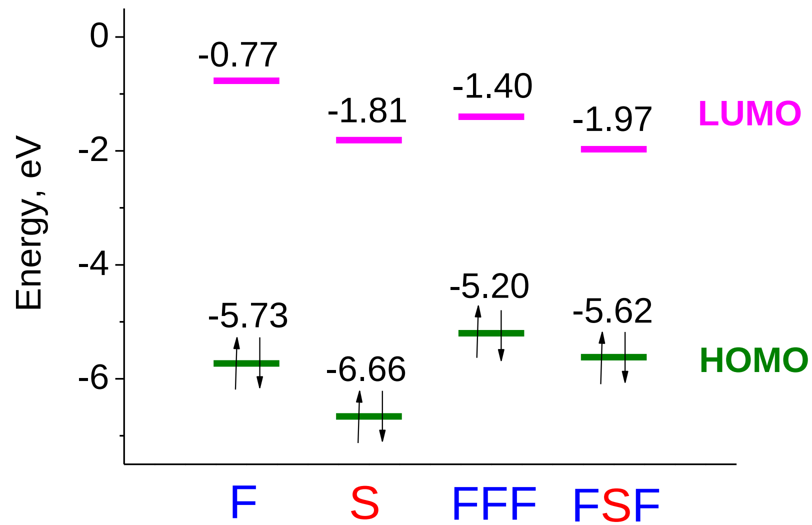
FFF

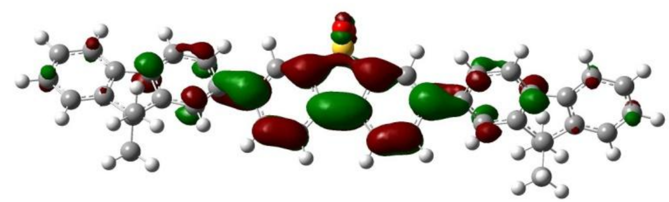


FSF

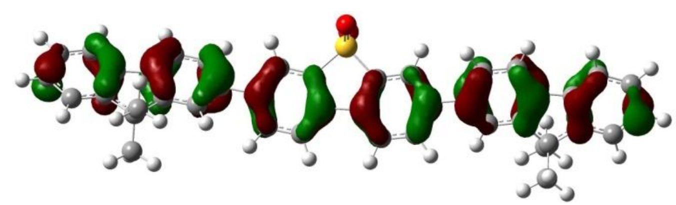
reduced HOMO-LUMO gap

DFT Calculations
B3LYP/6-31(d)





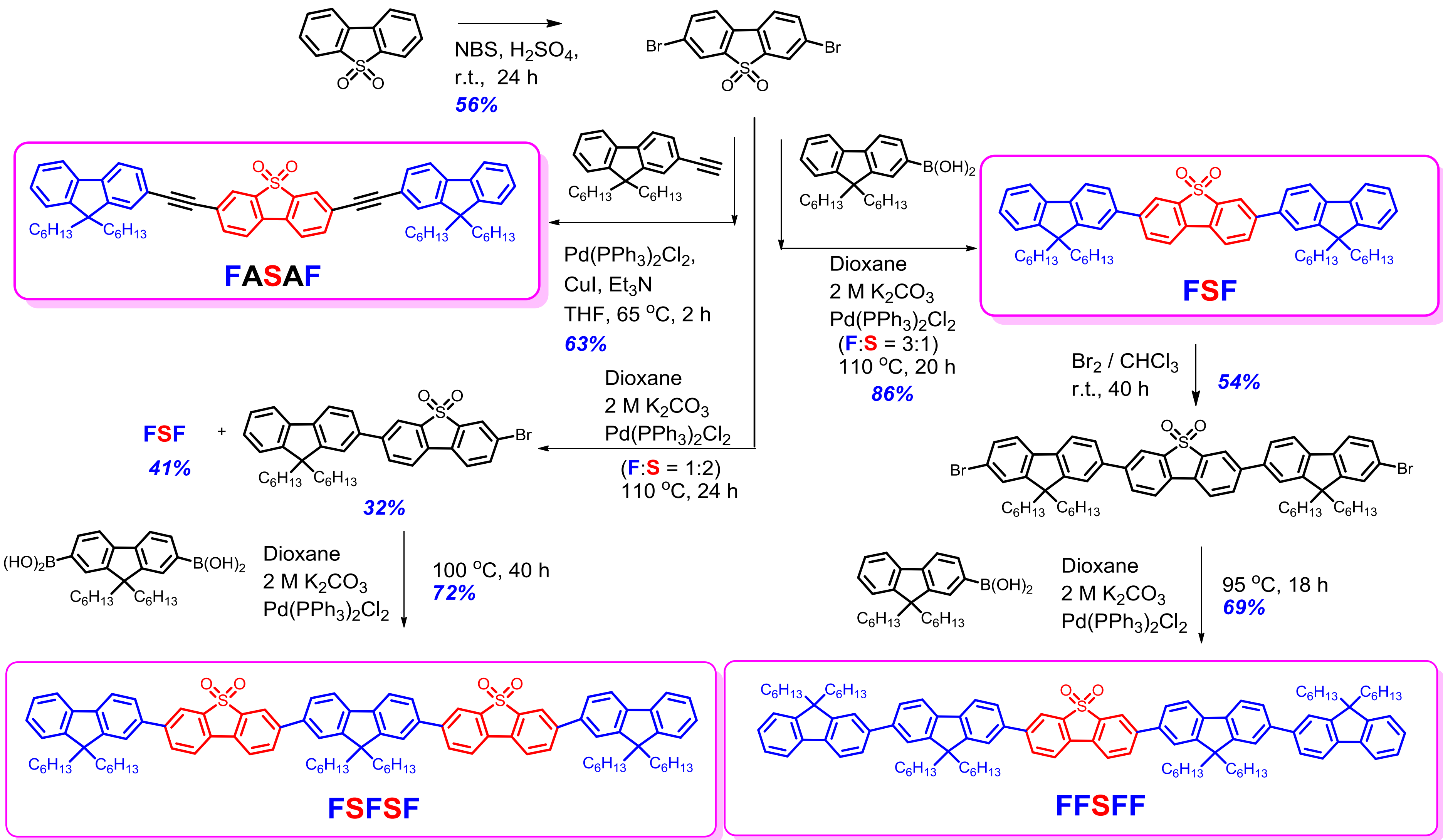
LUMO



HOMO

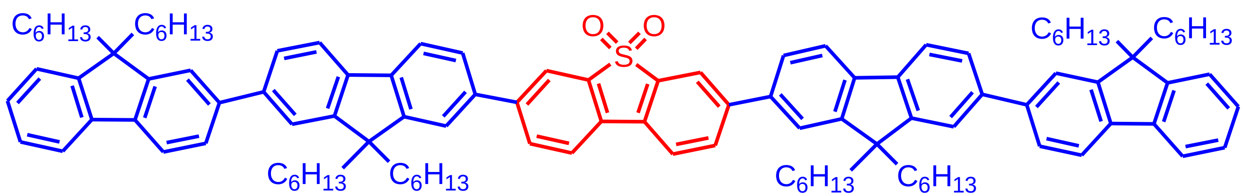
I. I. Perepichka, I. F. Perepichka, M. R. Bryce, L.-O. Pålsson, *Chem. Commun.* **2005**, 3397.

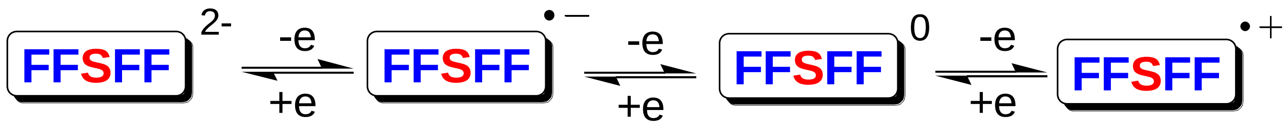
Fluorene–Dibenzothiophene-*S,S*-dioxide Co-oligomers



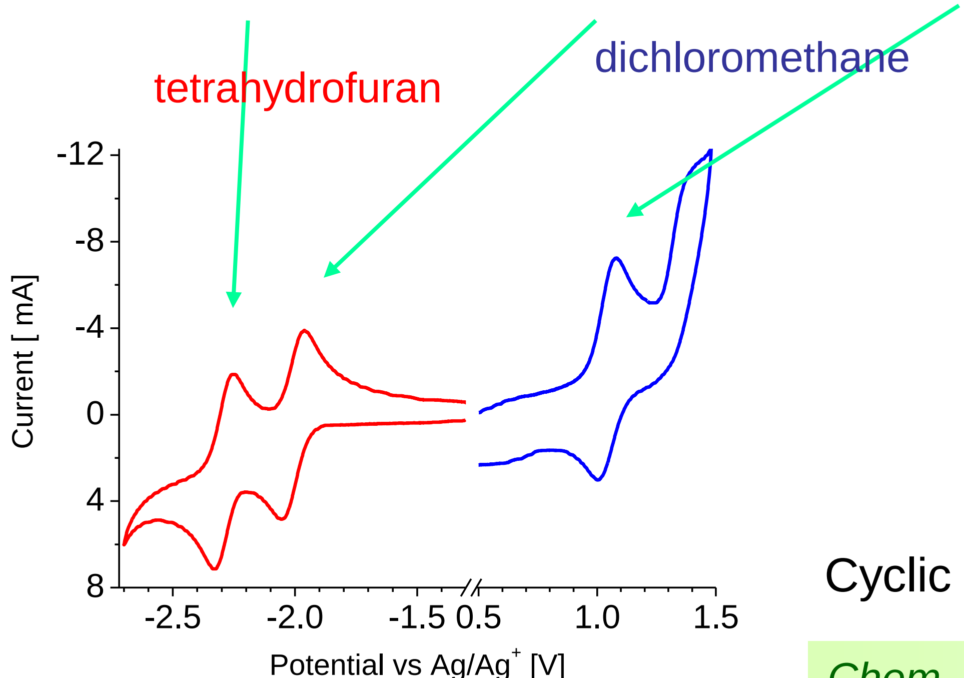
Chem. Commun. **2005**, 3397.

Reversible Electrochemical Oxidation and Reduction





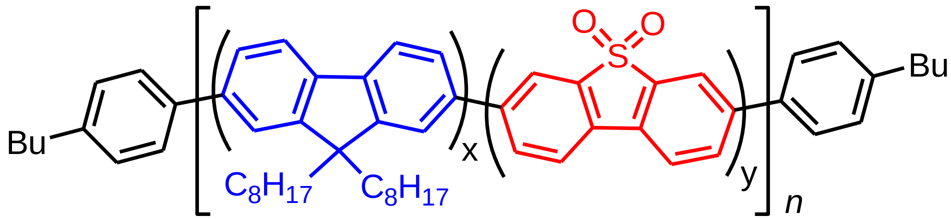
$E_{1/2}$ = -2.29V -2.01 V +1.04 V



Cyclic voltammetry

Chem. Commun. **2005**, 3397.

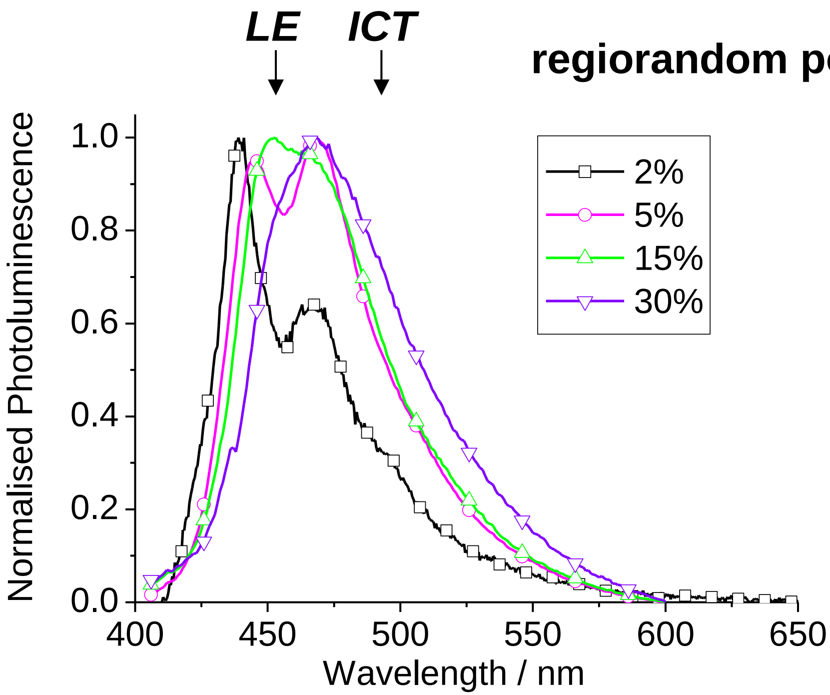
Solid-State Emission of FS Copolymers (Thin Films on Quartz)



regiorandom poly(FS)

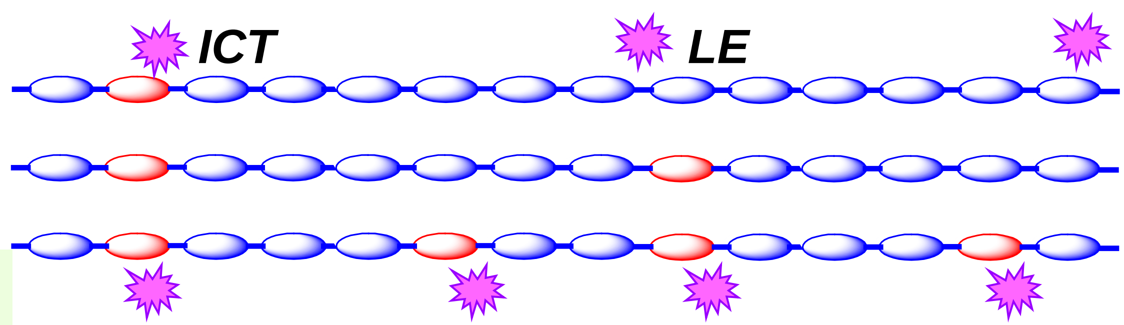
pFS-2%, x:y = 98:2
pFS-5%, x:y = 95:5
pFS-15%, x:y = 85:15
pFS-30%, x:y = 70:30

MW ca. 100,000



- **pFS-2%** predominantly ***LE*** emission
- **pFS-5…15%** dual ***LE*** and ***ICT*** emission
- **pFS-30%** predominantly ***ICT*** emission (broadened and red-shifted)

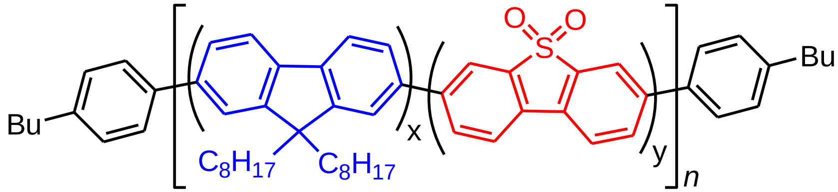
LE = local excited state
ICT = intramolecular charge transfer state



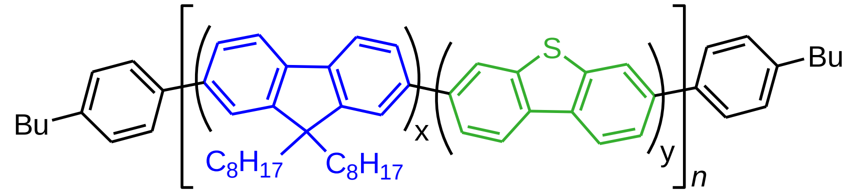
J. Phys. Chem. B **2006**, *110*, 19329.
J. Phys. Chem. B **2008**, *112*, 6557.

Temperature Dependence of Solid-State Emission

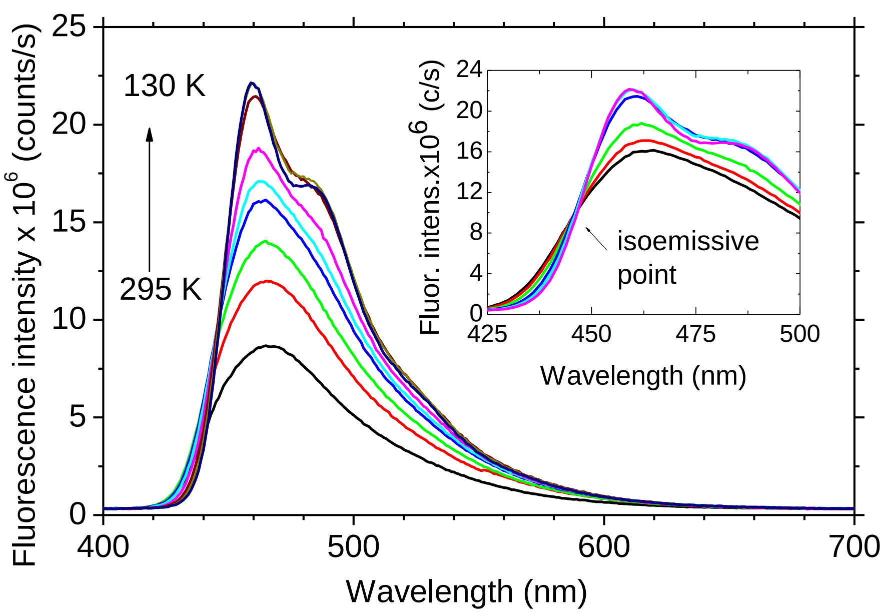
Durham University

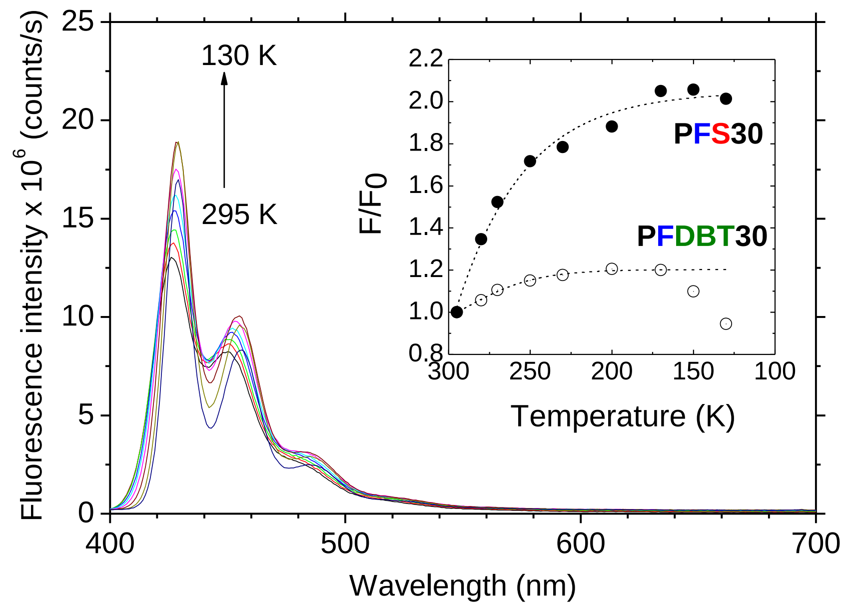


pFS-30 x:y = 70:30



pFDBT-30 x:y = 70:30





- ➢ >100% increased fluorescence intensity at low T
- ➢ Increased intensity of local excited state at low T

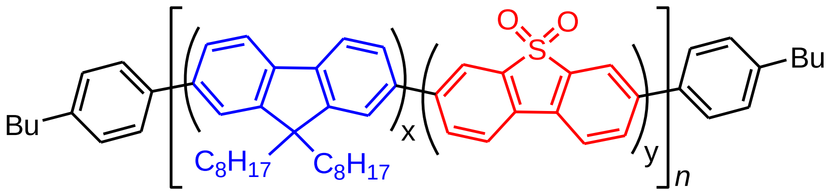
Conclusion: At low T torsions and dipole-dipole interactions which stabilise the ICT state are frozen out

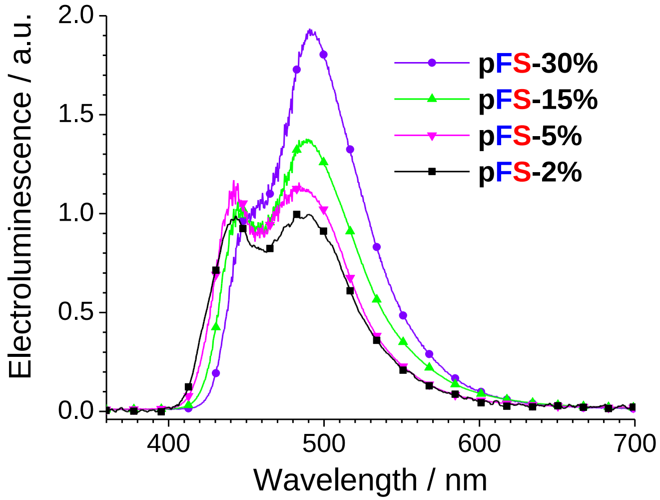
J. Phys. Chem. B **2008**, *112*, 6557.

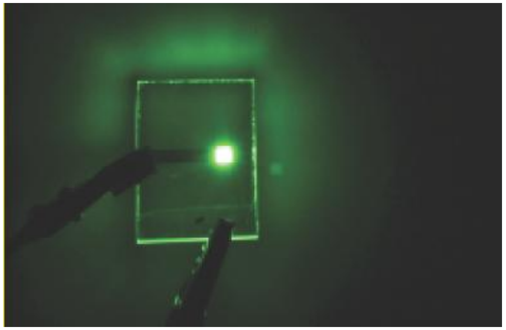
- ➢ No ICT state emission when S replaced by DBT
- ➢ Increased vibrational resolution
- ➢ 20% increased fluorescence intensity at low T

***Conclusion*: ICT emission and broadening are due to F-S interactions (not aggregation)**

Single-Polymer OLEDs with Colour-Tuneable Emission



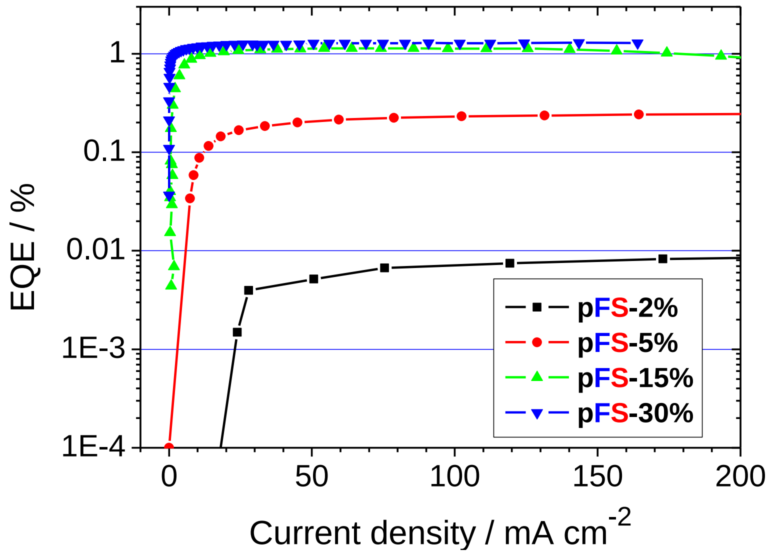




pFS-30%

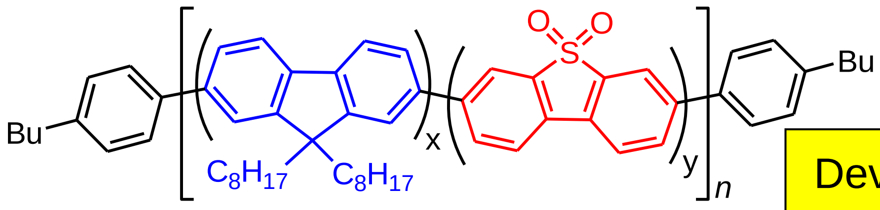
Devices: ITO / PEDOT:PSS/ **FS copolymer** / Ca/Al

*Increasing the content of **S** units in **FS** copolymer drastically improves the performance of the OLED*



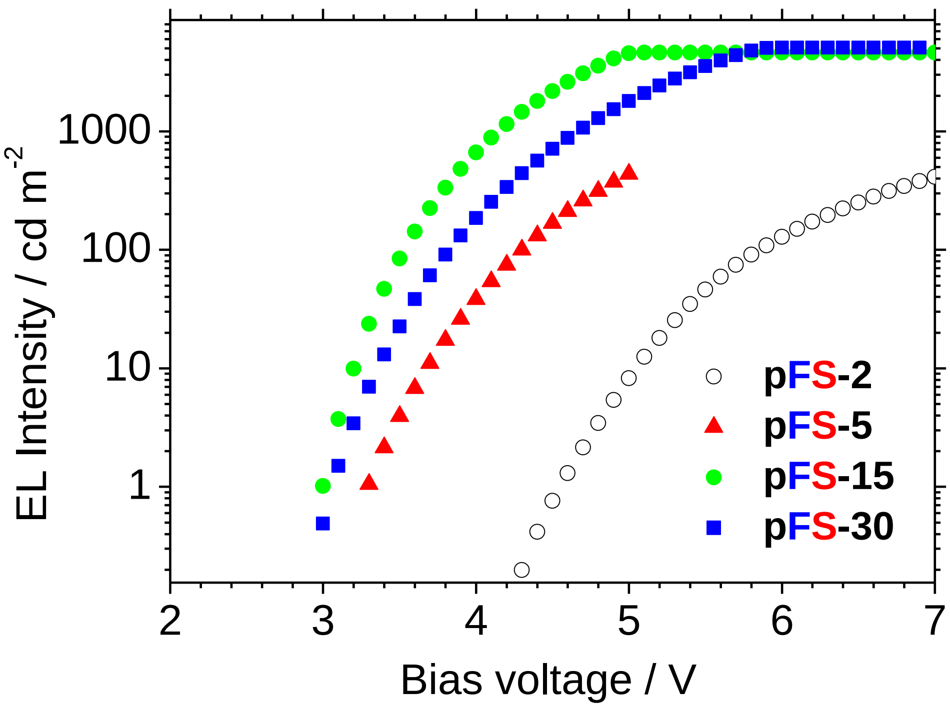
- Dual LE and ICT electroluminescence
- “Greenish-white” light
- External EL quantum efficiency 1.3%
- Increased colour stability compared to PFO
- Devices were not optimised

Adv. Funct. Mater. **2009**, *19*, 586.



OLED Characteristics

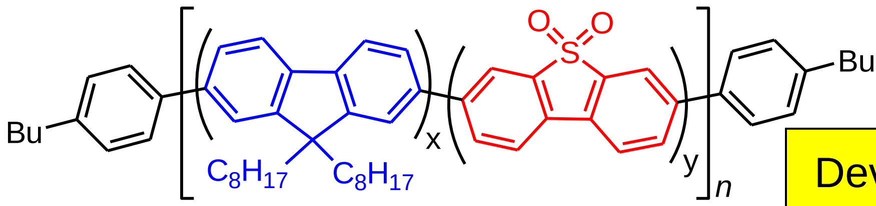
Devices: ITO / PEDOT:PSS / **FS copolymer** / Ca/Al



Light output – Voltage data:

- Decrease in turn-on voltage for copolymers with ≥5% S content.
- Light emission is observable at >3 V.
- Maximum brightness: pFS-30 ca. 4000 cd/m^2 at 6 V.

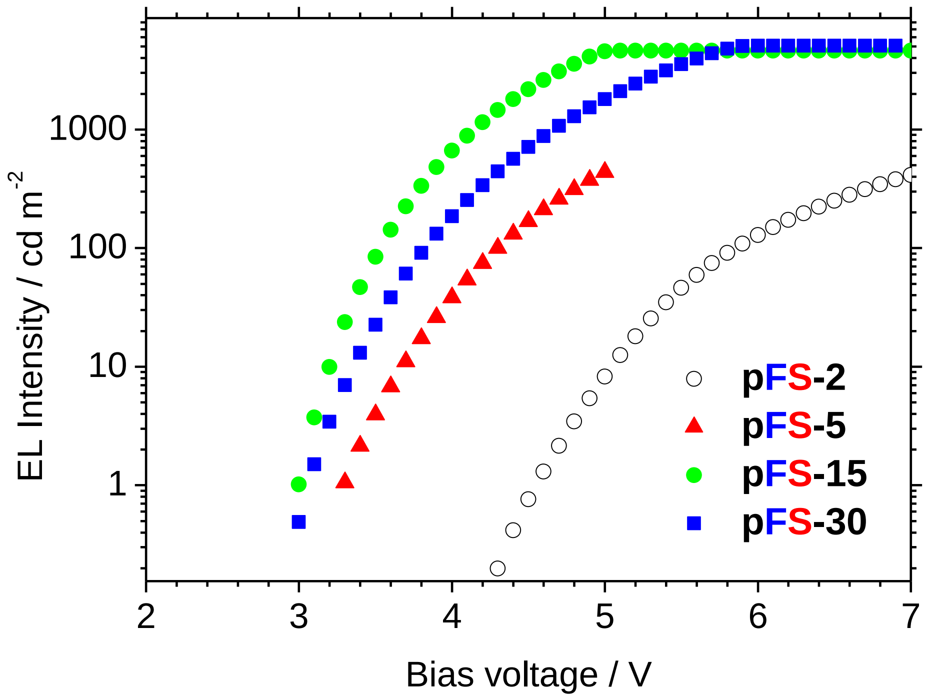
Adv. Funct. Mater. **2009**, *19*, 586.



OLED Characteristics

Durham University

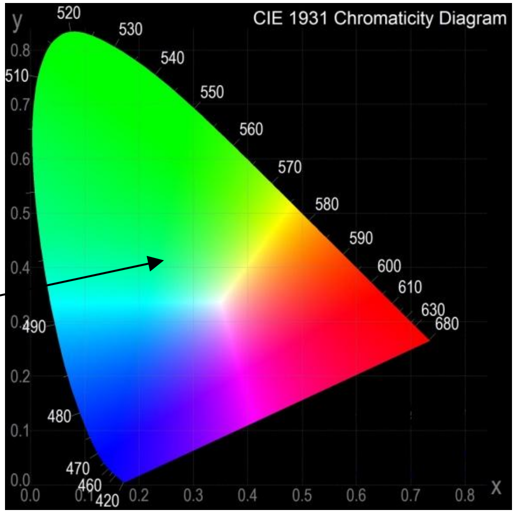
Devices: ITO / PEDOT:PSS / **FS copolymer** / Ca/Al



Light output – Voltage data:

- Decrease in turn-on voltage for copolymers with ≥5% S content.
- Light emission is observable at >3 V.
- Maximum brightness: pFS-30 ca. 4000 cd/m^2 at 6 V.

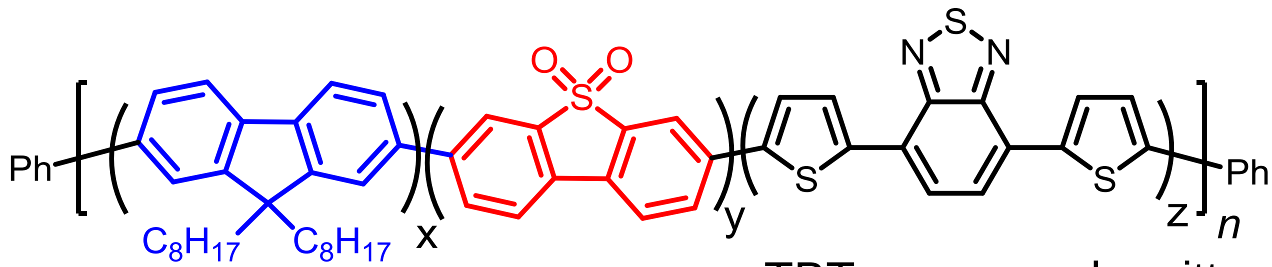
x 0.24
y 0.41



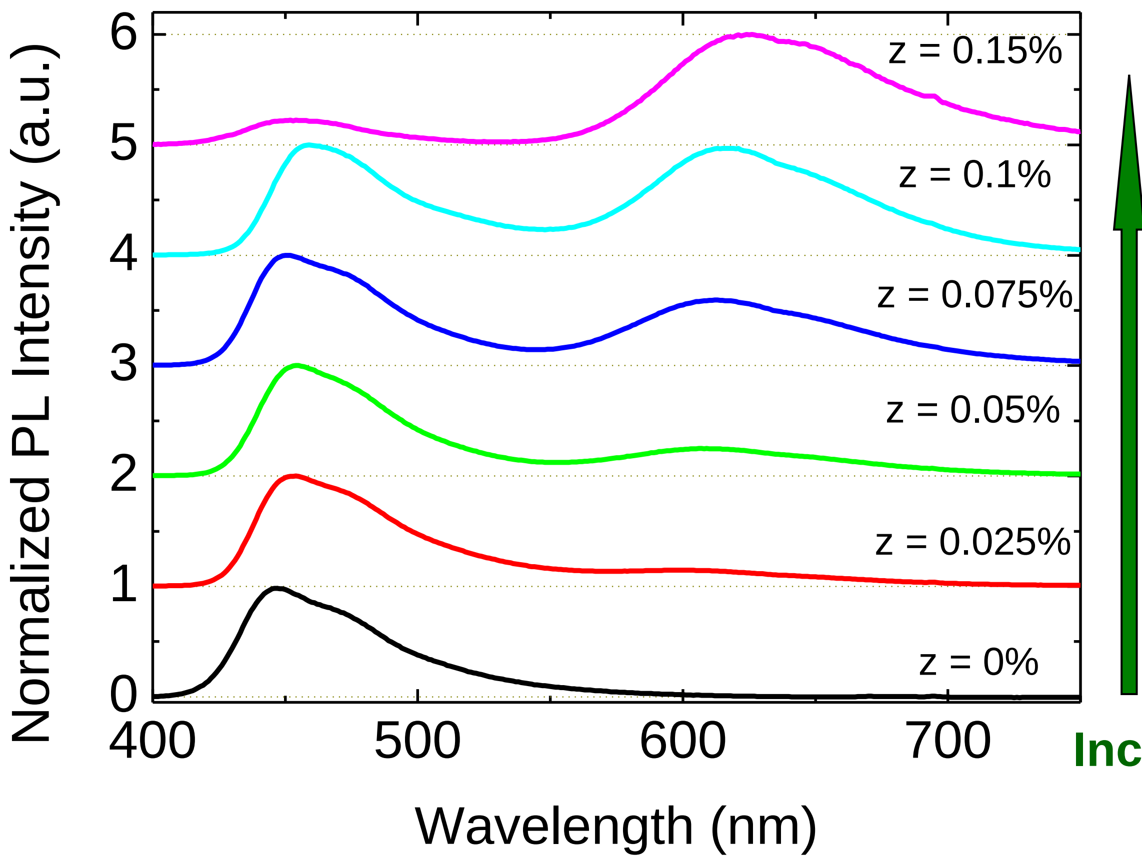
Adv. Funct. Mater. **2009**, *19*, 586.

- Brief introduction to OLED technology
- New fluorescent copolymers with intramolecular charge transfer
- White-light emission and SSL
- New iridium complexes and PhOLEDs

Colour Tuning: Covalent Incorporation of TBT into Random Copolymer



TBT orange-red emitter



Increasing TBT content

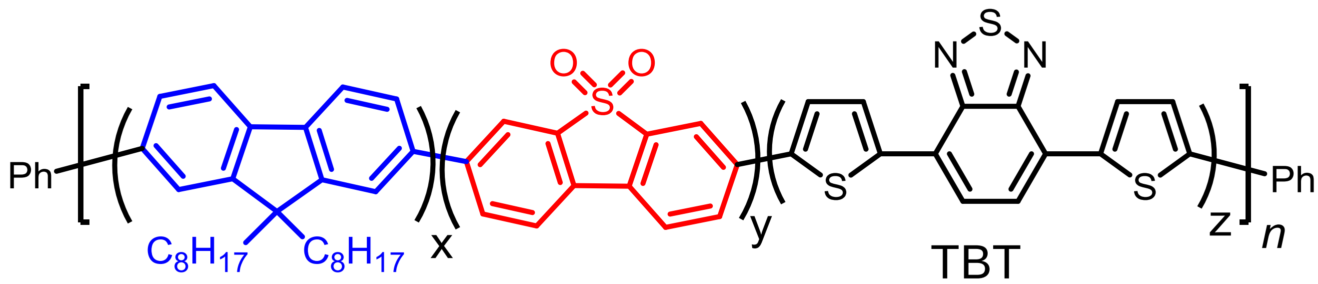
$x = 1\text{-}y\text{-}z$; $y = 0.30$;
$z = 0.00025 – 0.0015$

PL spectra of copolymer films. λ_{ex} 375 nm

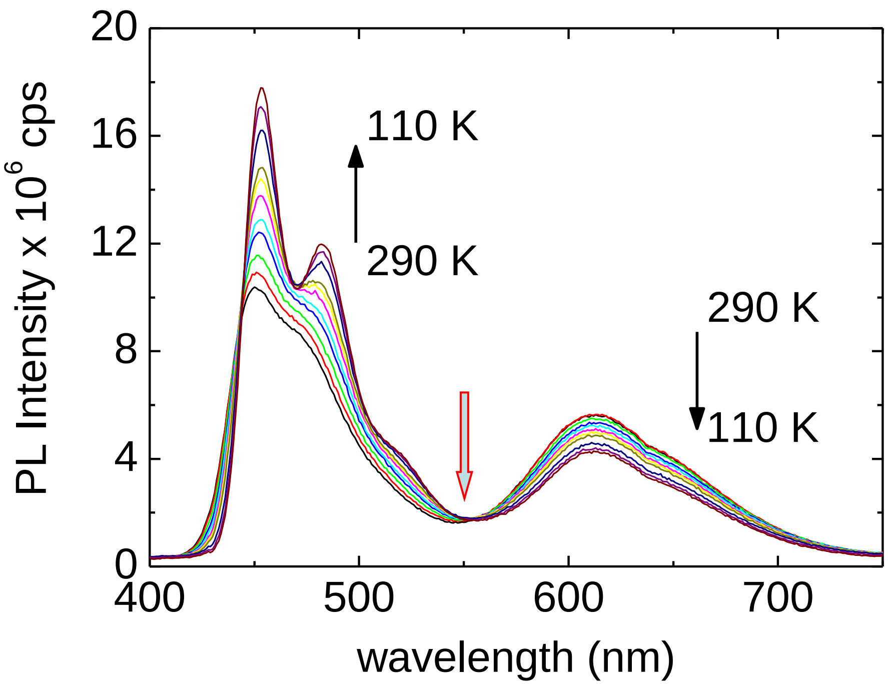
Note the increase in TBT emission (612 nm) at the expense of pFS-30 emission (450 nm).

ChemPhysChem. **2009**, *10*, 2096.

Probing Energy Transfer in pFS-30 – TBT Random Copolymer



pFS-30 +
z = 0.075%



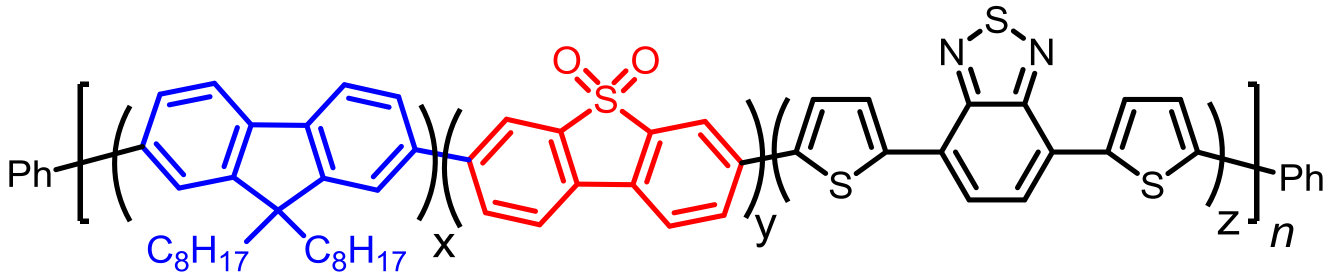
Note the isoemissive point at ca. 550 nm, between the pFS-30 and TBT emission bands.

- Thermally-assisted energy transfer (exciton diffusion) occurs between pFS-30 regions and TBT moieties.
- As the temperature decreases the fraction of excitons that do not find a TBT trap site during their lifetime increases.

PL spectra of copolymer films as a function of temperature. λ_{ex} 375 nm

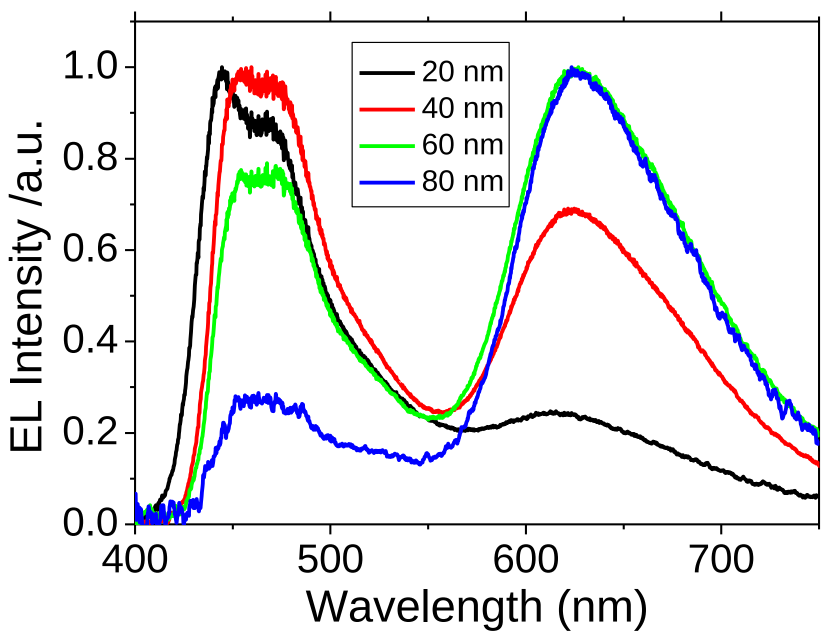
ChemPhysChem. **2009**, *10*, 2096.

Colour Tuning: Electroluminescence as a Function of Film Thickness



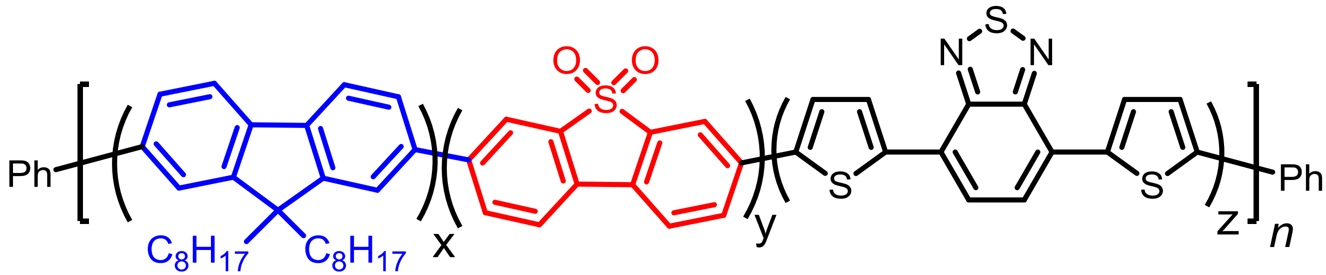
pFS-30 +
z = 0.1%

EL Devices: ITO / PEDOT:PSS / **copolymer** / Ba/Al



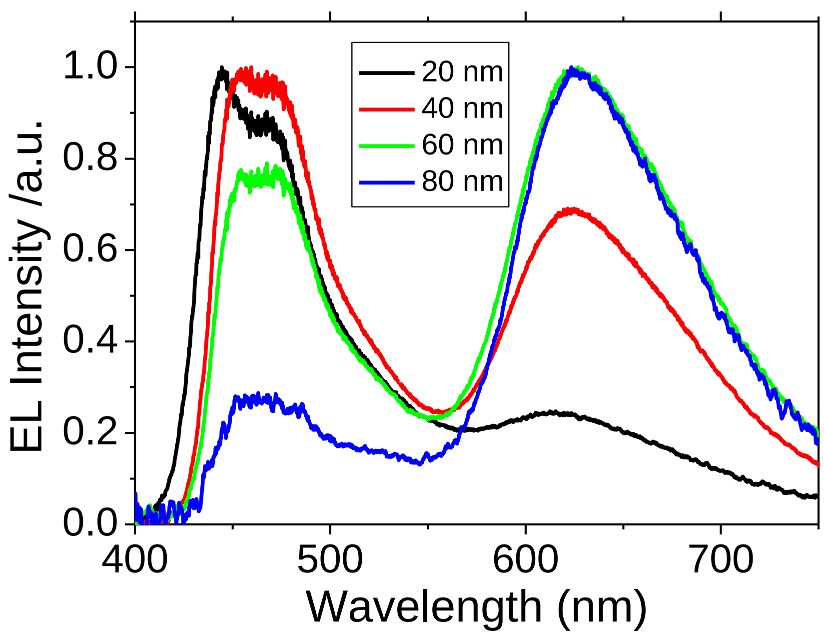
- Thicker film: more re-absorption and more orange/red emission.
- White light emitted by 40-60 nm thick films

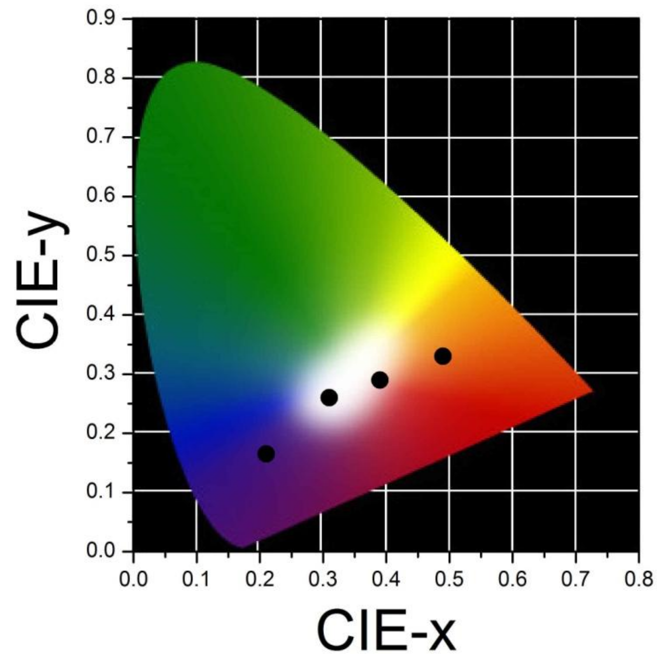
Colour Tuning: Electroluminescence as a Function of Film Thickness



pFS-30 +
z = 0.1%

EL Devices: ITO / PEDOT:PSS / **copolymer** / Ba/Al



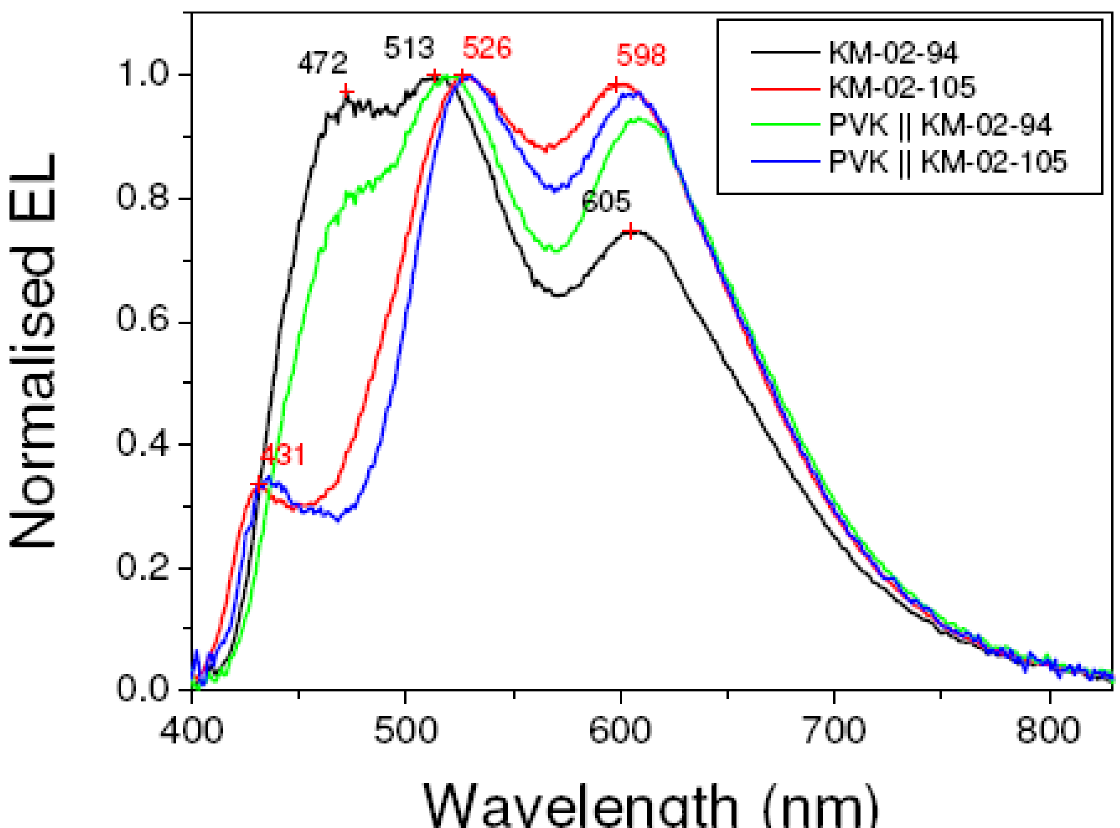


- Thicker film: more re-absorption and more orange/red emission.
- White light emitted by 40-60 nm thick films

White Electroluminescence from a Single Copolymer

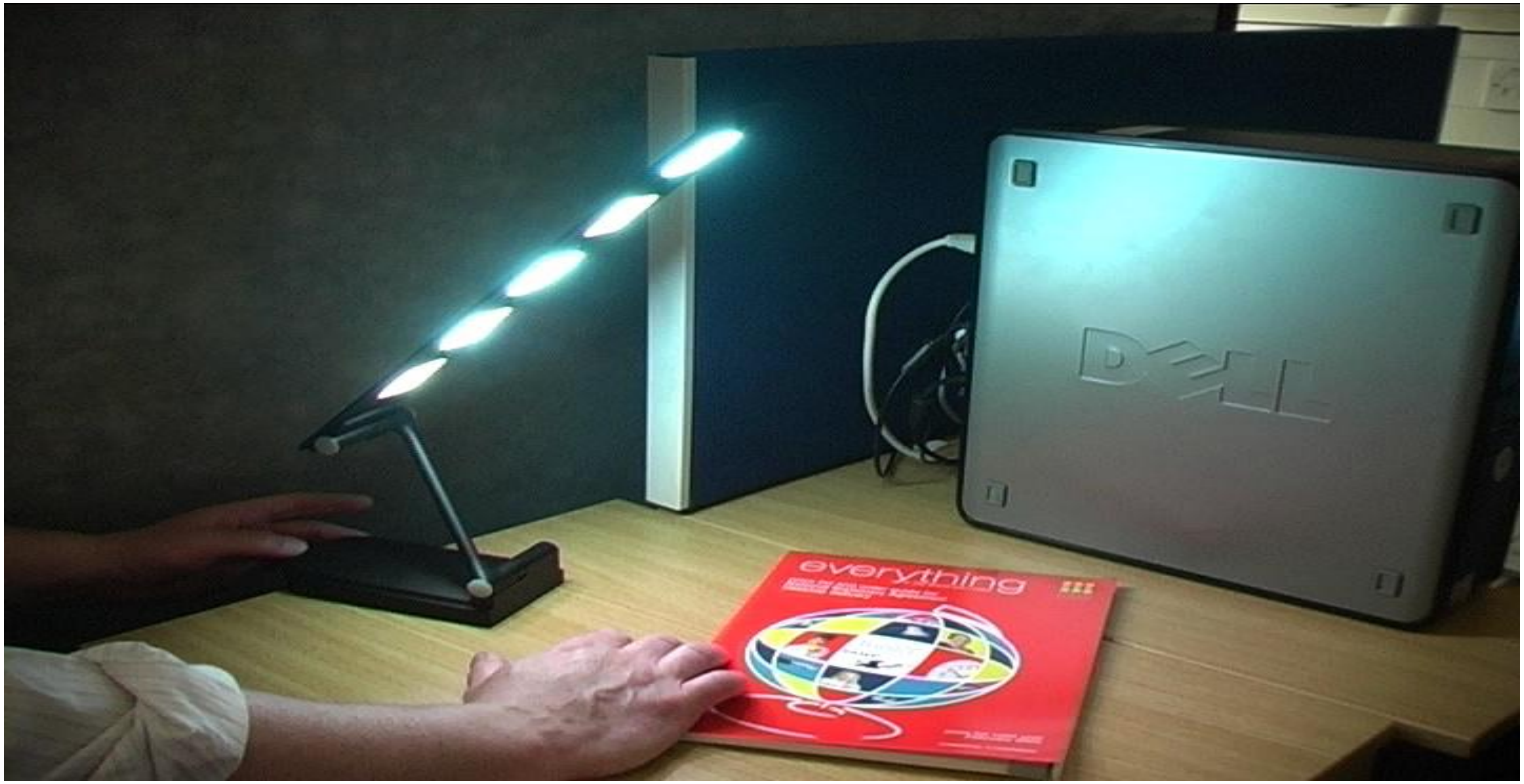
Chemical modification to the copolymer affords pure white electroluminescence

EL Devices: ITO / PEDOT:PSS / **copolymer** / Ba/Al



Photograph of a white polymer LED

OLED Products for Lighting

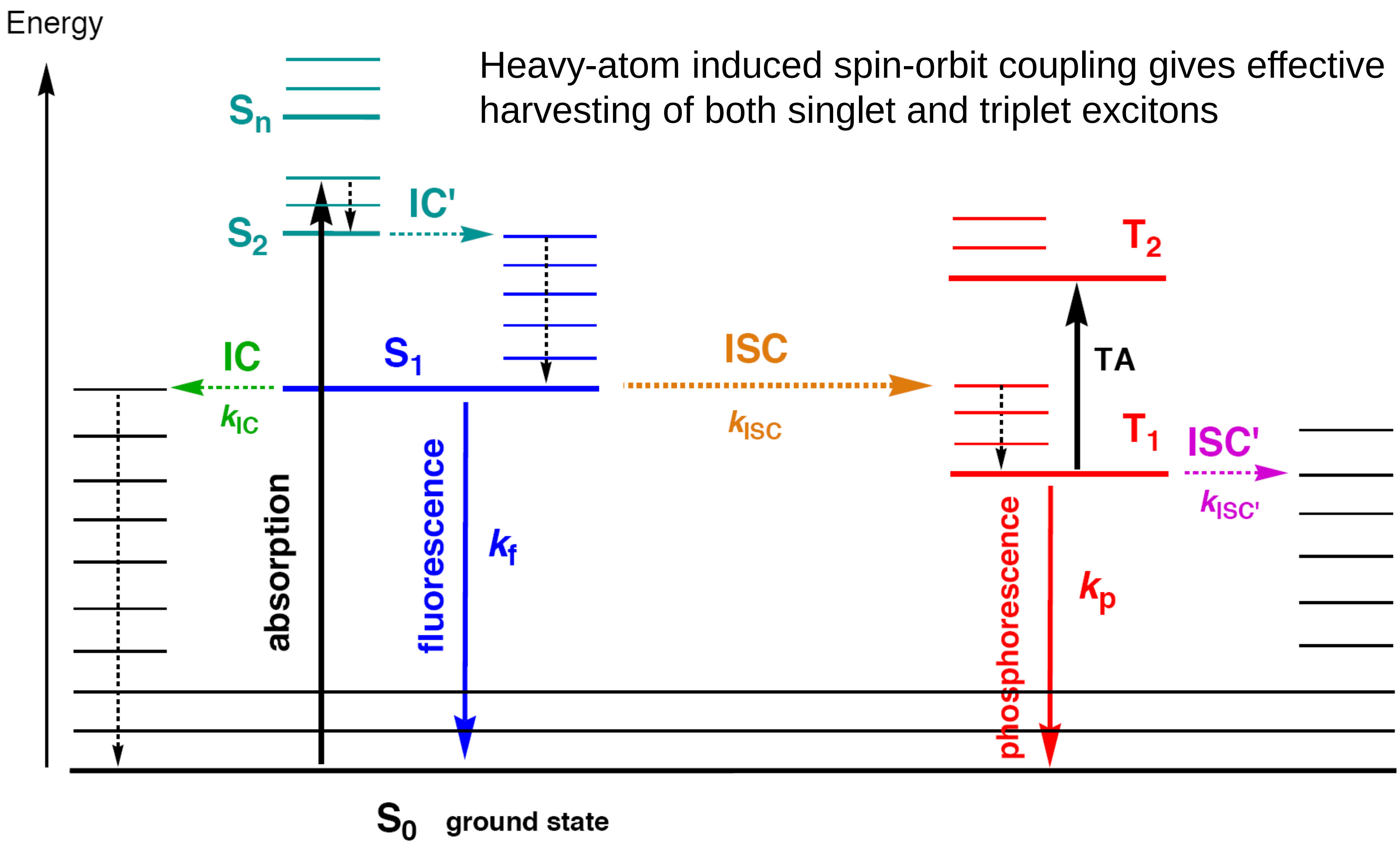


2010, A demonstrator lamp from the TSB-funded TOPLESS Project
“Thin Organic Polymer Light-Emitting Semiconductor Surfaces”

Thorn Lighting – Durham University – Cambridge Display Technology

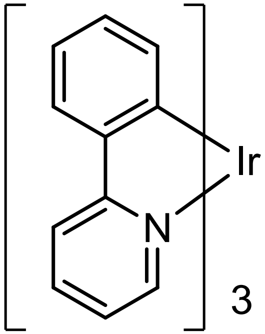
- Brief introduction to OLED technology
- New fluorescent copolymers with intramolecular charge transfer
- White-light emission and SSL
- New iridium complexes and PhOLEDs

Light-emitting Metal Complexes: Electrophosphorescent Devices



IC and IC' = internal conversion   ISC and ISC' = intersystem crossing   = vibrational relaxation

Electrophosphorescent Iridium Complexes

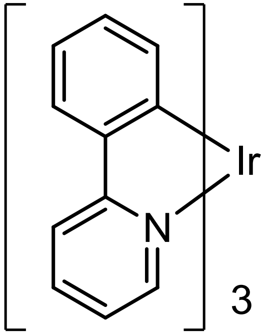


fac-Ir(ppy)$_3$

Prototype green emitter

M. E. Thompson, S. R. Forrest, et al., *Appl. Phys. Lett*. **1999**, *75*, 4

Electrophosphorescent Iridium Complexes

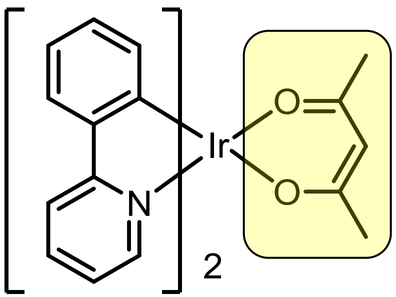


fac-$Ir(ppy)_3$

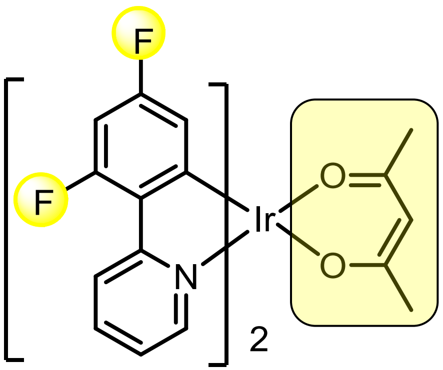
Prototype green emitter

M. E. Thompson, S. R. Forrest, et al., *Appl. Phys. Lett*. **1999**, *75*, 4

Ancillary ligands and substituents tune the colour

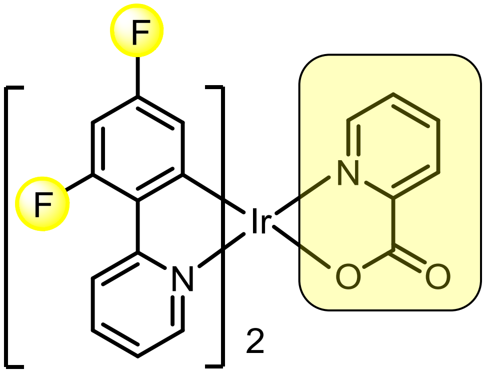


$(ppy)_2Ir(acac)$



$(F_2\text{-}ppy)_2Ir(acac)$

Electron-withdrawing substituents on phenyl ring lower the HOMO energy, leading to blue-shifted emission

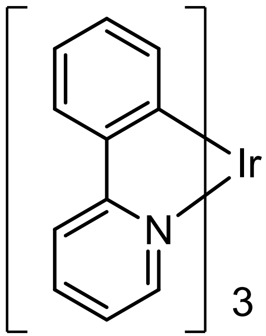


$(F_2\text{-}ppy)_2Ir(pic)$

S. Lamansky, et al.,
J. Am. Chem. Soc. **2001**, *123*, 4304

Electrophosphorescent Iridium Complexes

Durham University

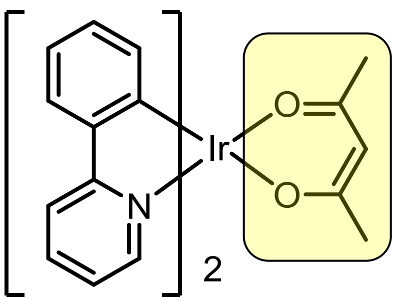


fac-Ir(ppy)$_3$

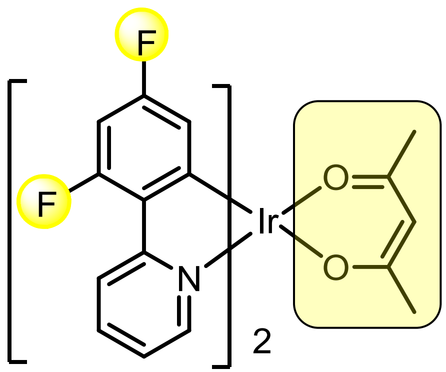
Prototype green emitter

M. E. Thompson, S. R. Forrest, et al., *Appl. Phys. Lett*. **1999**, *75*, 4

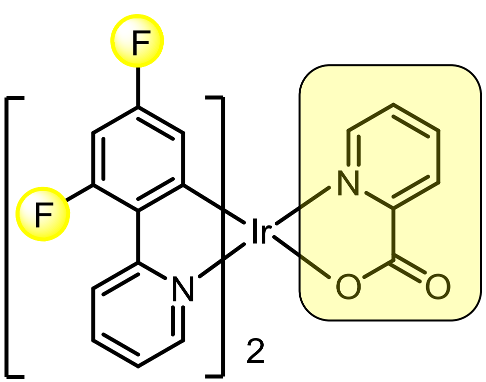
Ancillary ligands and substituents tune the colour



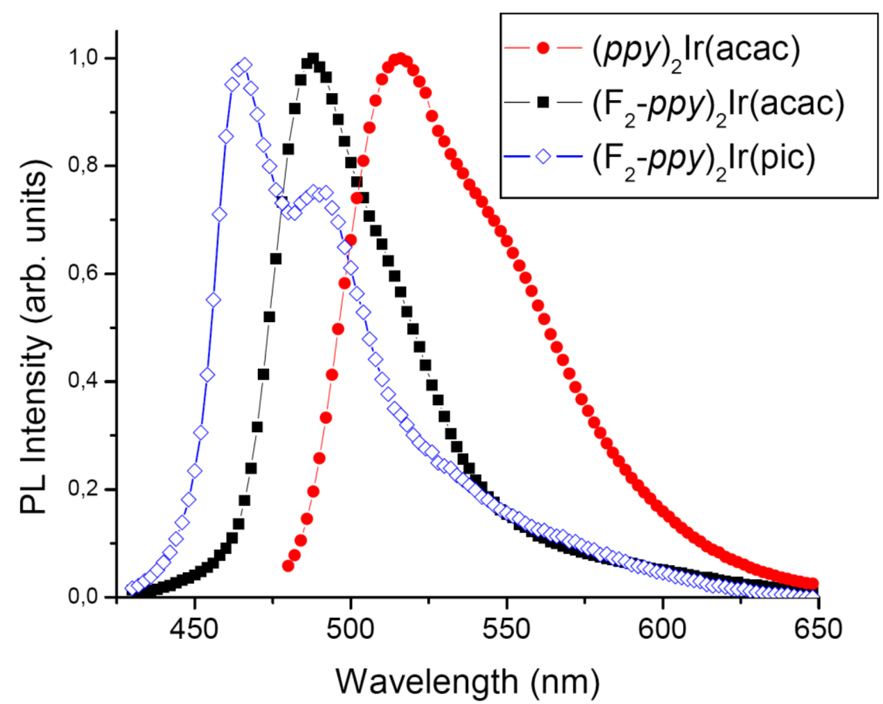
(ppy)$_2$Ir(acac)



(F$_2$-ppy)$_2$Ir(acac)



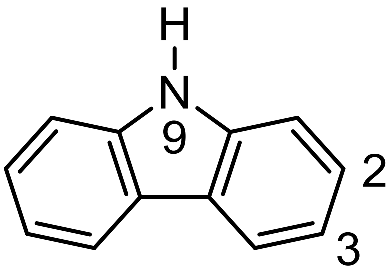
(F$_2$-ppy)$_2$Ir(pic)



Ir(III) Complexes of Carbazole-Based Ligands

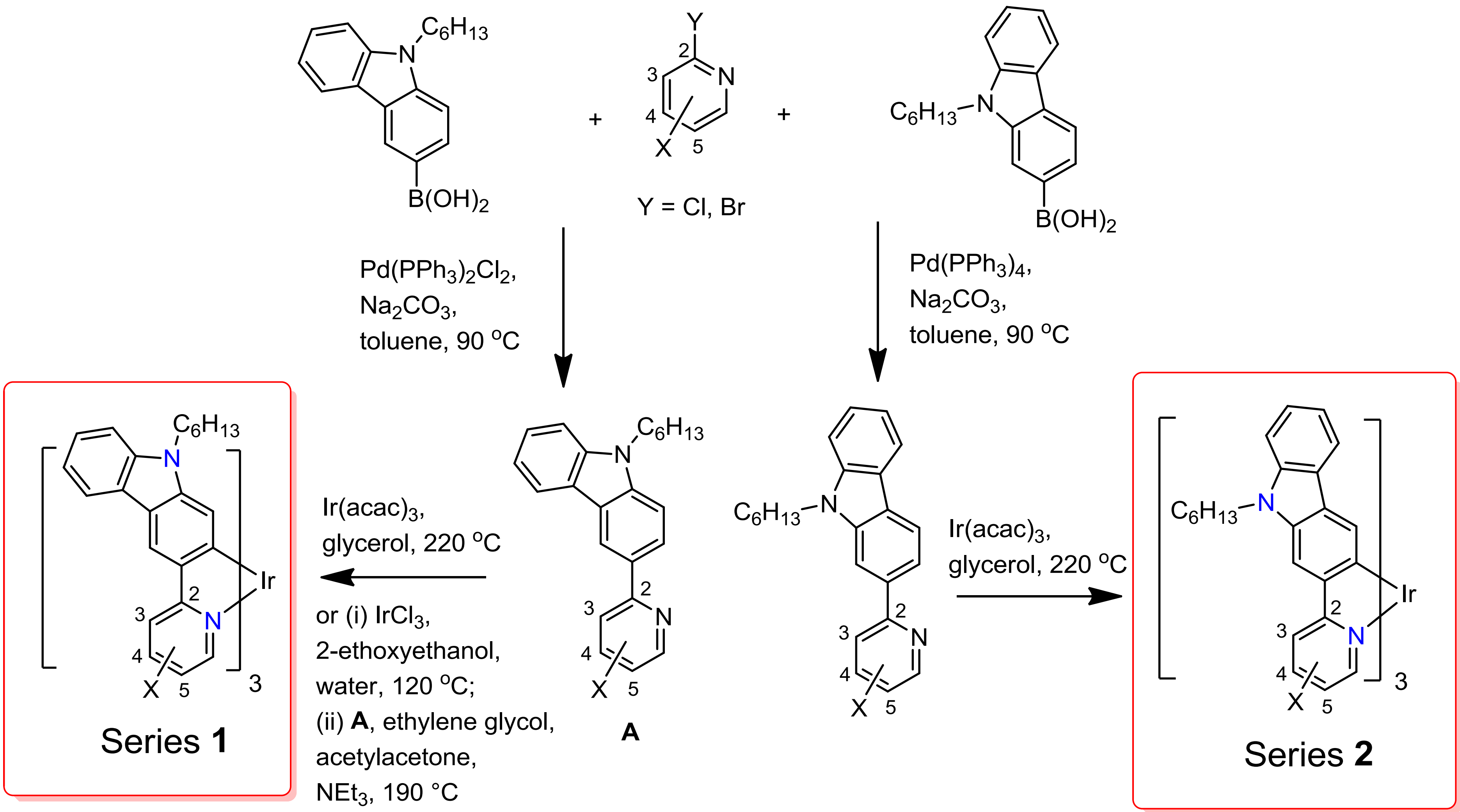
Durham University

Why carbazole?



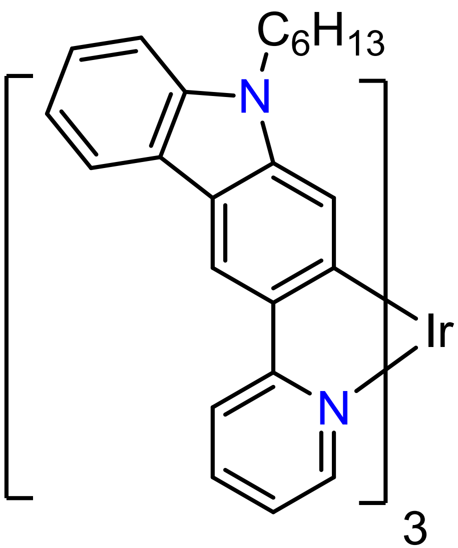
- Very stable electron-rich molecule
- Widely used as a hole-transporting unit
- Can be functionalised at positions 2, 3 and 9
- There were no reports of cyclometallation of carbazole derivatives, so fundamentally new chemistry would be explored

Ir(III) Complexes of Carbazole-Based Ligands

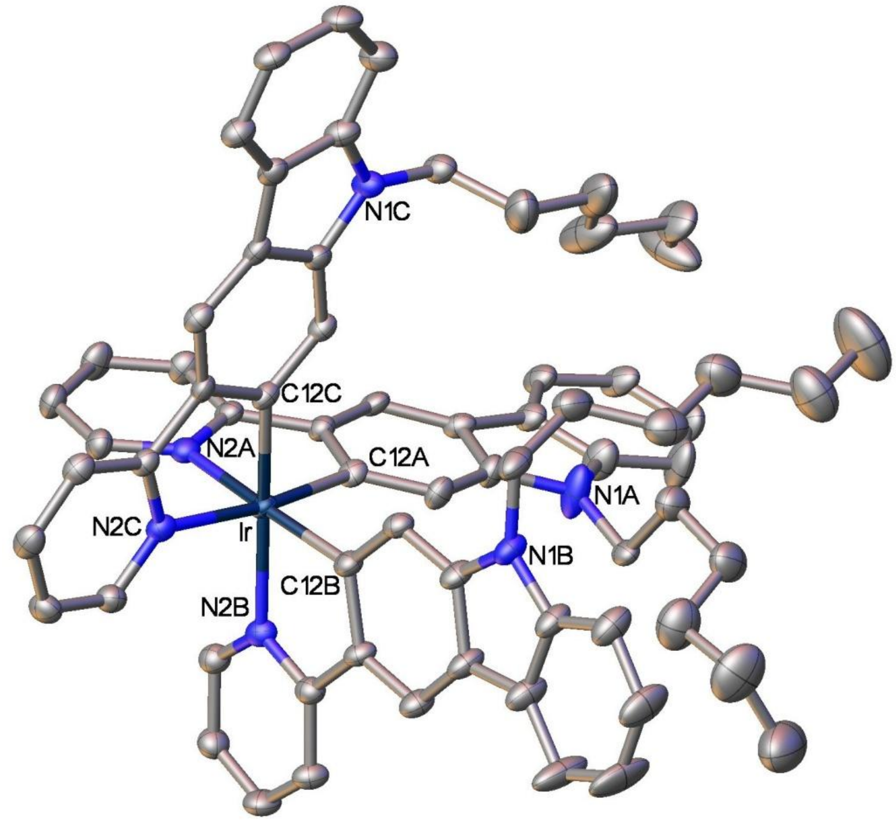


Chem. Eur. J. **2007**, *13*, 1423; *J. Mater. Chem.* **2012**, *22*, 6419

Ir(III) Complexes of Carbazole-Based Ligands



Fac-isomer

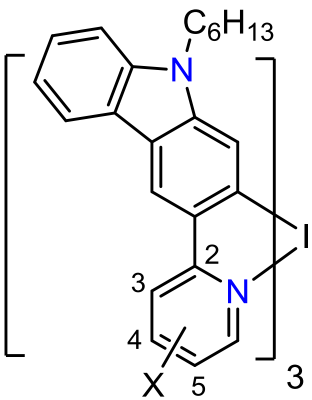


X-Ray molecular structure

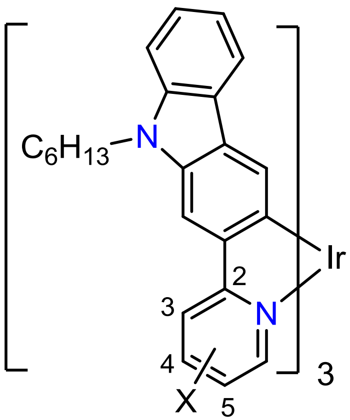
Chem. Eur. J. **2007**, *13*, 1423

Ir(III) Complexes of Carbazole-Based Ligands

Photoluminescence spectra in degassed toluene at 300 K. Substituent effects lead to colour tuning between λ_{max} 494 and 637 nm (blue-green to orange-red).

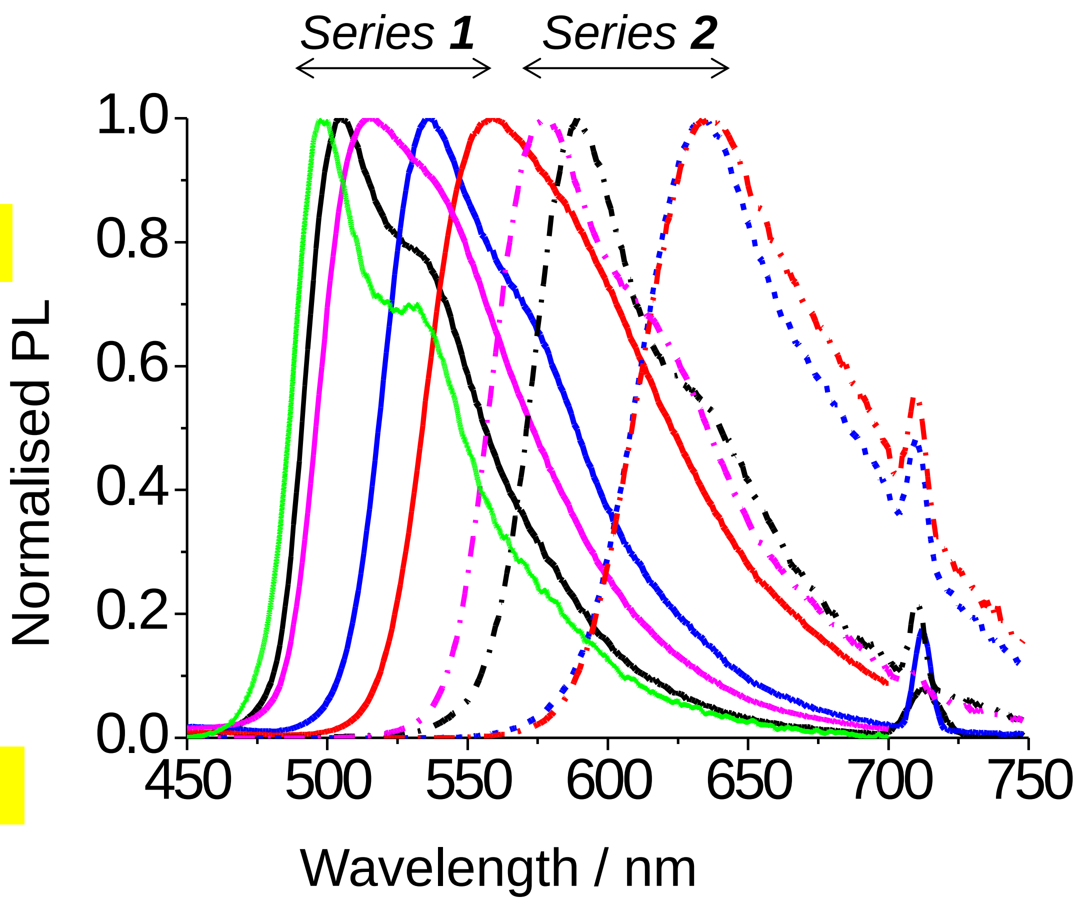


Series **1** Φ PL 0.35-0.63



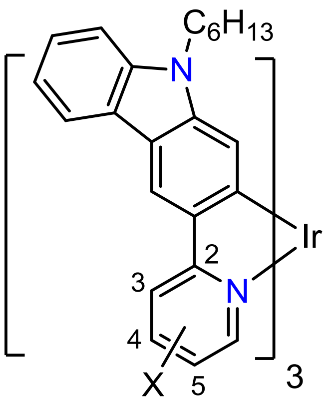
Series **2** Φ PL 0.10-0.15

X = **a** H, **b** 4-CF_3, **c** 4-OMe
d 5-CF_3, **e** 5-OMe

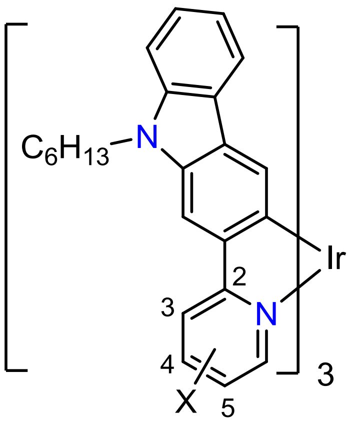


Adv. Funct. Mater. **2011**, *22*, 6419; *J. Mater. Chem.* **2012**, *22*, 6419

Ir(III) Complexes of Carbazole-Based Ligands



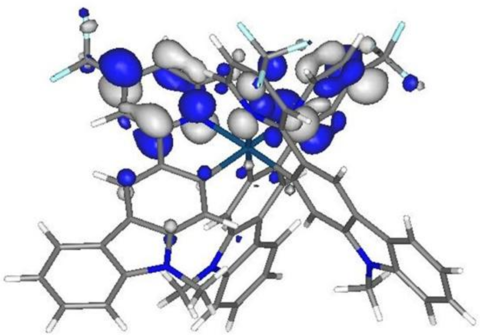
Series **1**

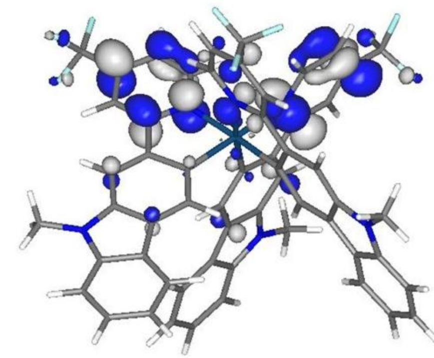


Series **2**

X = **a** H, **b** 4-CF_3, **c** 4-OMe
d 5-CF_3, **e** 5-OMe

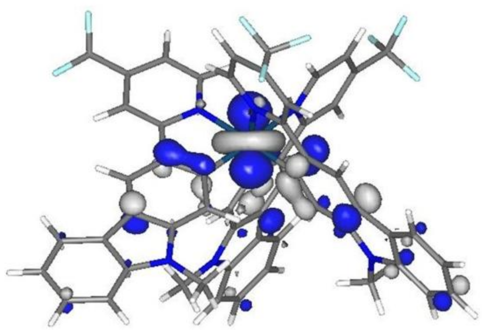
DFT/TD-DFT computations correctly predict the phosphorescence emission maxima

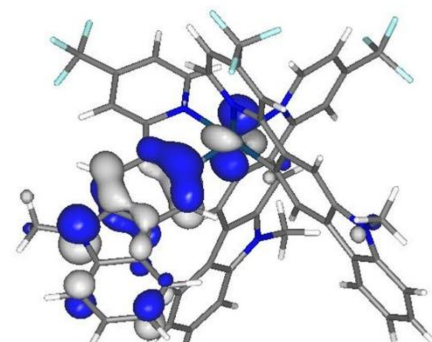




1b'	LUMO	2b'
86	% pyridyl	64
2	% metal	1
12	% carbazolyl	35

1b' ***H-L Gap 3.26 eV*** ***H-L Gap 2.95 eV*** **2b'**





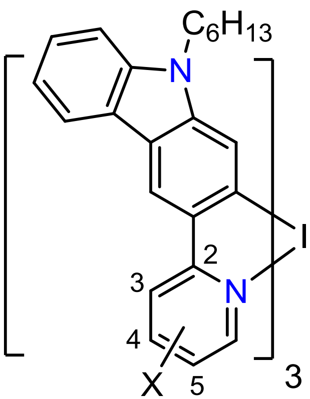
1b'	HOMO	2b'
8	% pyridyl	4
36	% metal	28
56	% carbazolyl	68

The lower PLQYs for series **2** could be due to the increased carbazole contribution to the excited state resulting in decreased radiative decay.

Adv. Funct. Mater. **2011**, *22,* 6419; *J. Mater. Chem.* **2012**, *22,* 6419

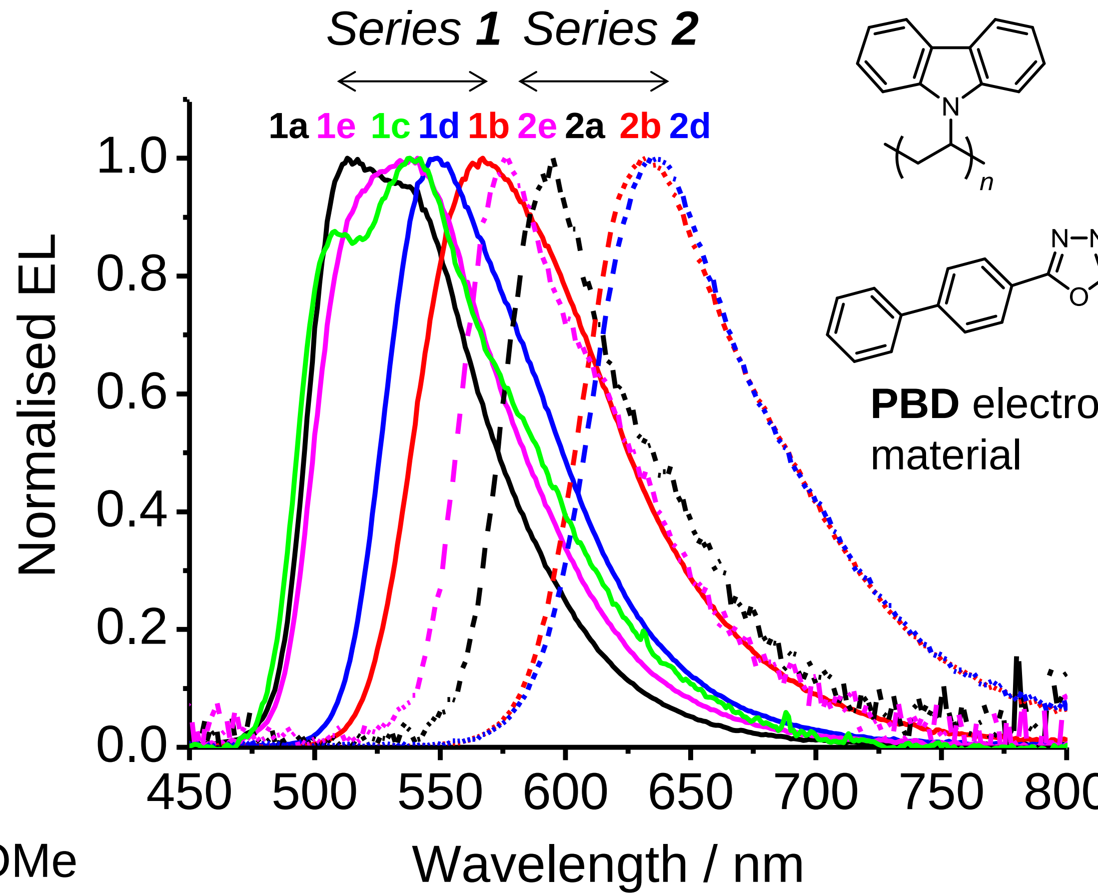
Ir(III) Complexes of Carbazole-Based Ligands

Devices: ITO / PEDOT:PSS/ **PVK:PBD:Ir complex** / Ba/Al



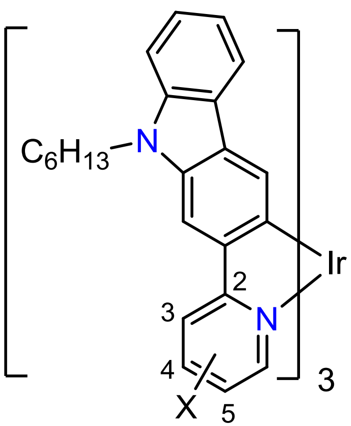
Series **1**

Electroluminescence spectra. Similar colour tuning between λ_{max} 506 (complex **1a**) and 638 nm (complex **2d**)



PVK host matrix

PBD electron-transport material



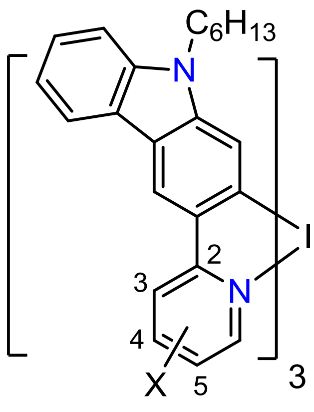
Series **2**

X = **a** H, **b** 4-CF_3, **c** 4-OMe **d** 5-CF_3, **e** 5-OMe

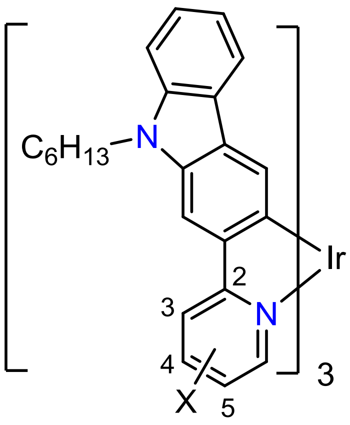
Adv. Funct. Mater. **2011***, 22,* 6419; *J. Mater. Chem.* **2012***, 22,* 6419

Ir(III) Complexes of Carbazole-Based Ligands

Devices: ITO / PEDOT:PSS/ **PVK:PBD:Ir complex** / Ba/Al

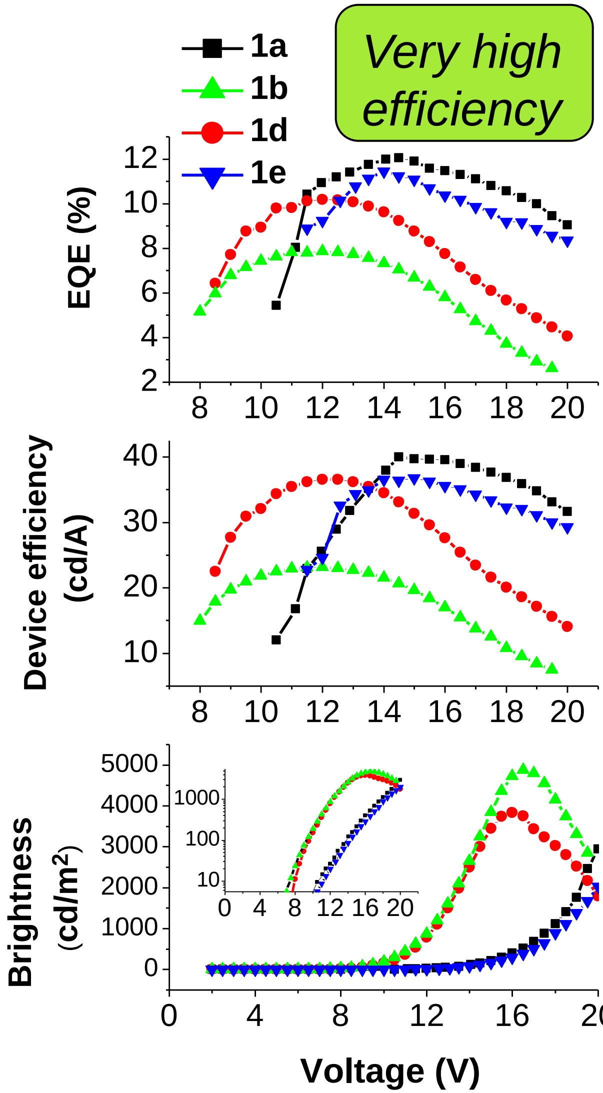


Series **1**



Series **2**

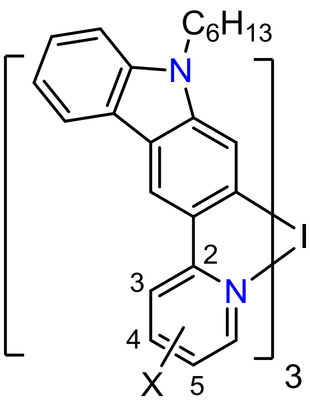
X = **a** H, **b** 4-CF_3, **c** 4-OMe
d 5-CF_3, **e** 5-OMe



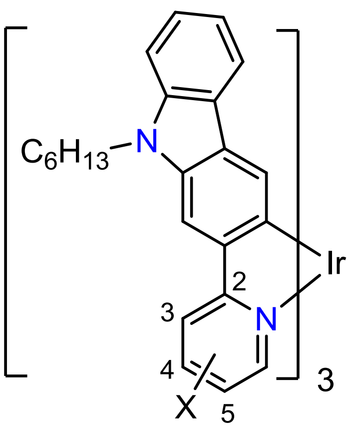
Adv. Funct. Mater. **2011**, 22, 6419; *J. Mater. Chem.* **2012**, *22*, 6419

Ir(III) Complexes of Carbazole-Based Ligands

Devices: ITO / PEDOT:PSS/ **PVK:PBD:Ir complex** / Ba/Al

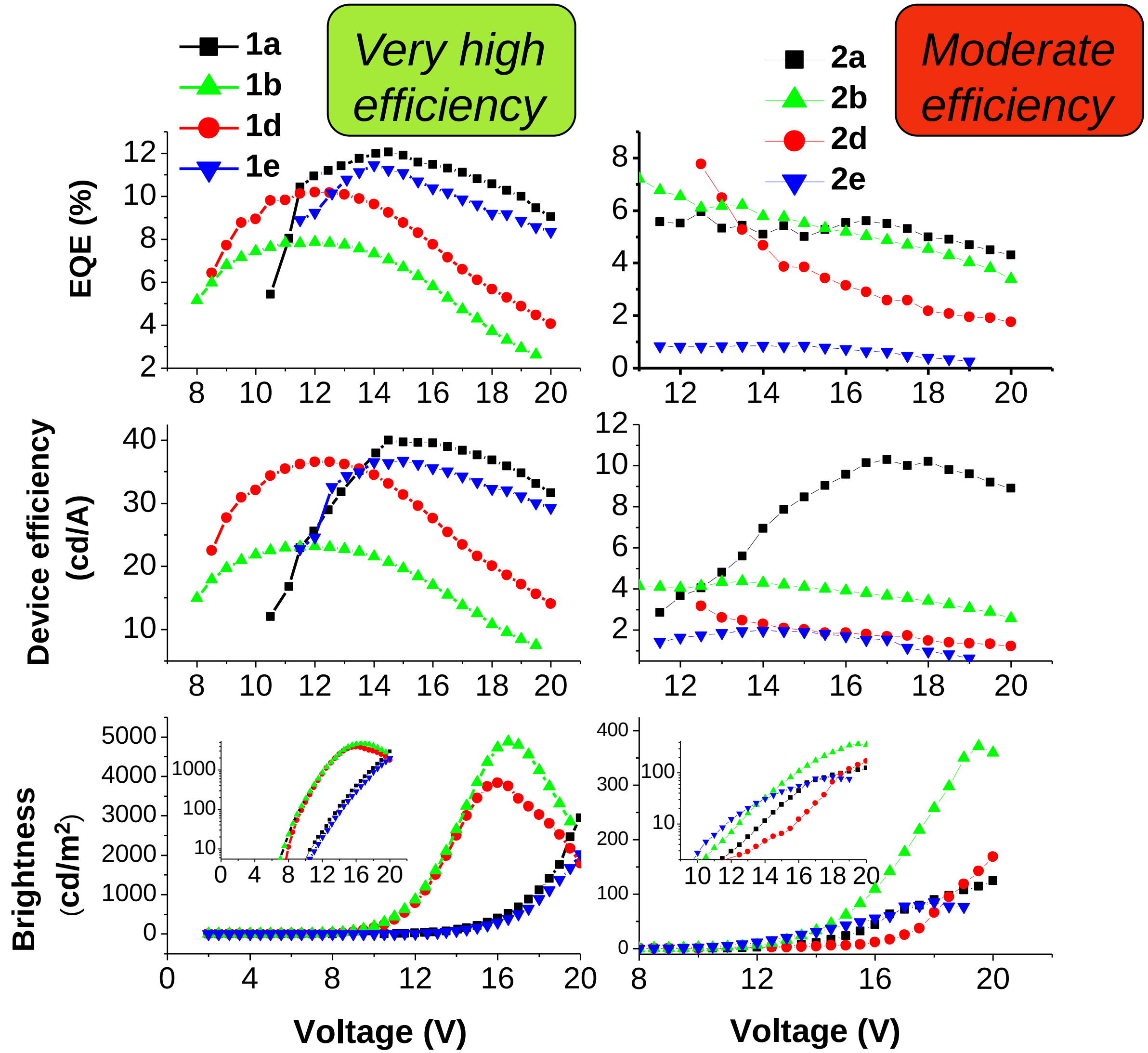


Series **1**



Series **2**

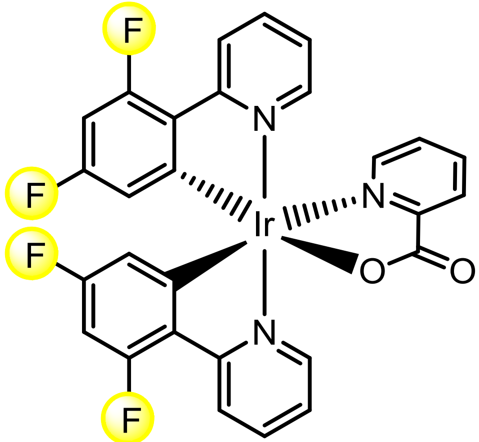
X = **a** H, **b** 4-CF_3, **c** 4-OMe
d 5-CF_3, **e** 5-OMe



Adv. Funct. Mater. **2011**, 22, 6419; *J. Mater. Chem.* **2012**, *22*, 6419

Improved blue electroluminescence is a major challenge

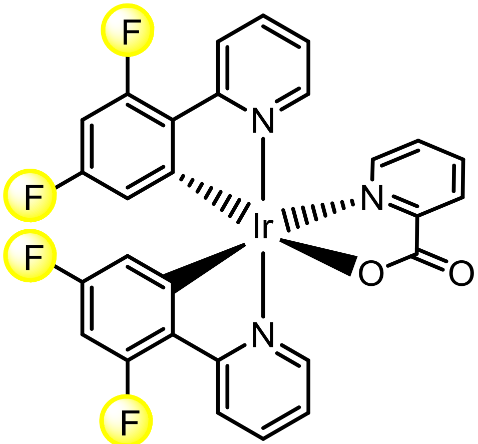
We have modified the benchmark blue emitter FIrpic



FIrpic

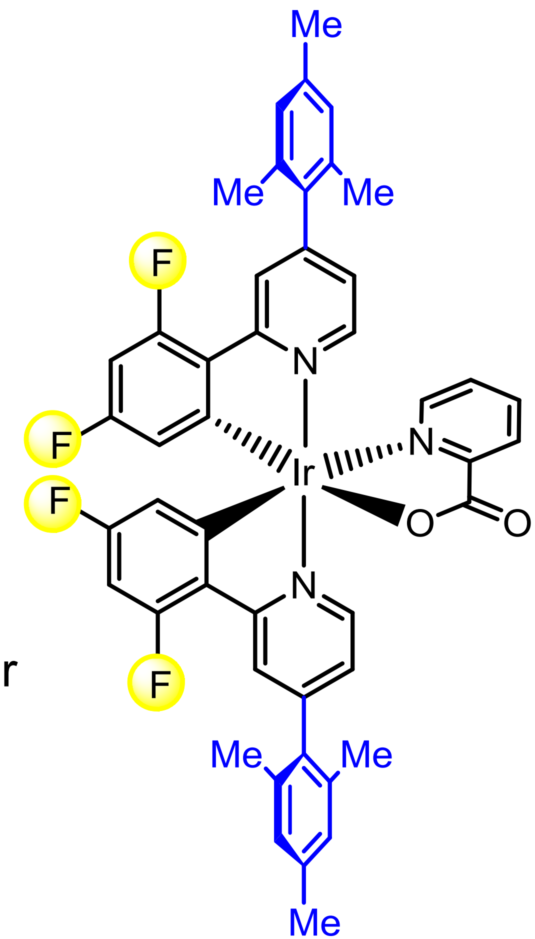
Solution-processable Analogs of FIrpic

Durham University



FIrpic

- Common "sky-blue" emitter for PhOLEDs
- Low solubility in organic solvents
- Devices usually fabricated by thermal evaporation which may degrade FIrpic



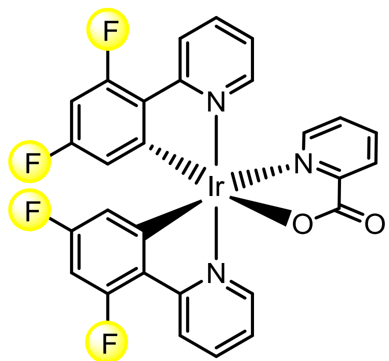
FIrpic-Mes$_2$

Key Design Features

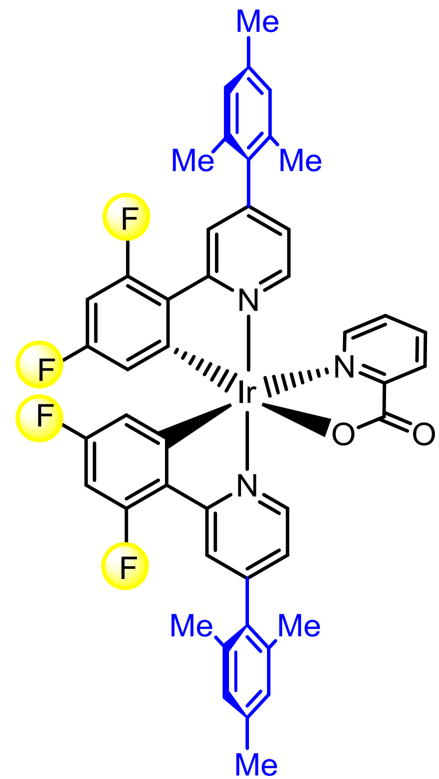
- Mesityl groups for enhanced solubility to facilitate solution processing of PhOLEDs under mild conditions

- *Ortho*-Me groups will prevent biaryl conjugation and so blue emission should be retained

Solution-processable Analogs of FIrpic



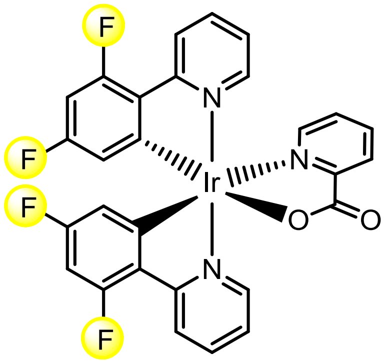
FIrpic



FIrpic-Mes_2

	PhMe	film	PhMe	film
$\lambda_{PL\ max}$ (nm) at 20 ^{o}C	469	470	473	474
PLQY (PhMe) (± 5%)	0.54		0.92	

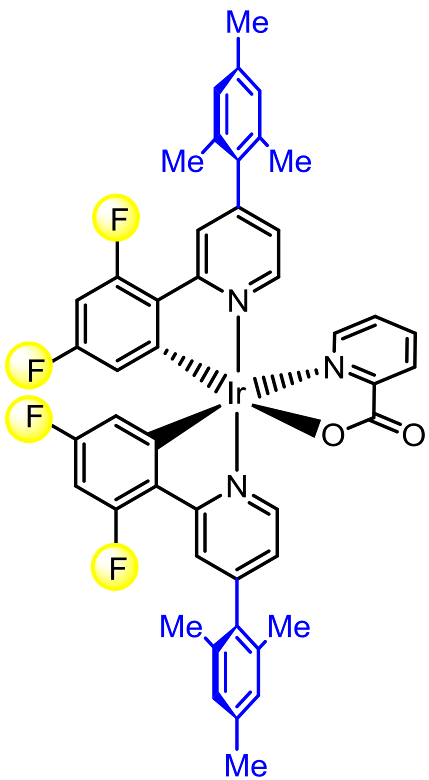
Solution-processable Analogs of FIrpic



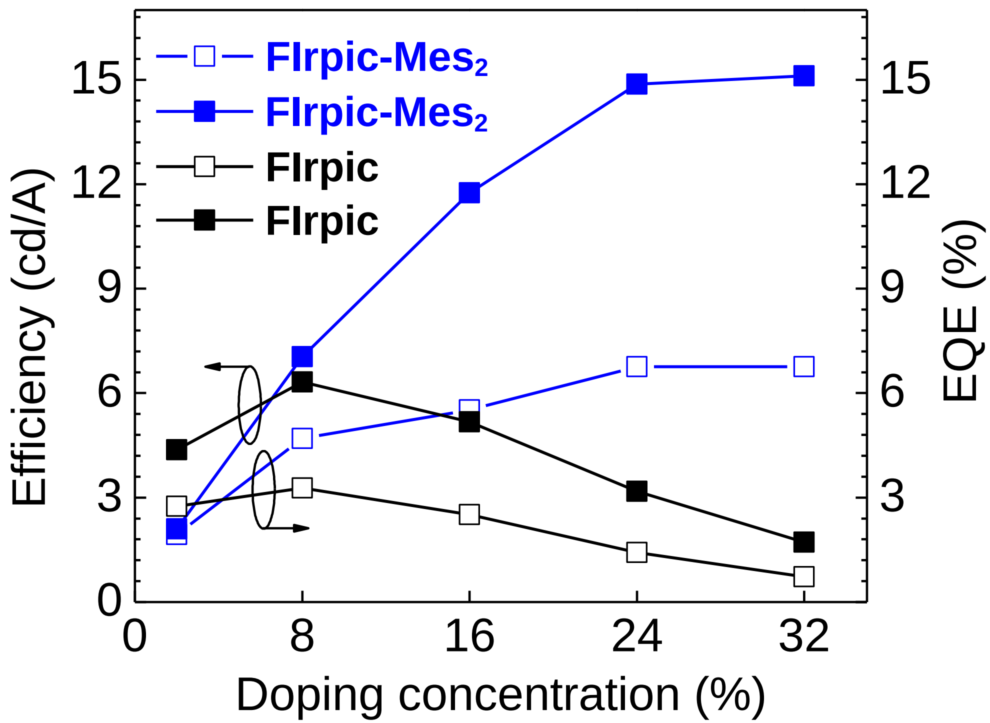
FIrpic

Devices: ITO / PEDOT:PSS / **PVK:OXD-7:Ir complex** / Ba/Al

- *Spin-coated (solution-processed) single emitting layer*
- *Enhanced device performance using **FIrpic-Mes$_2$** due to reduced concentration quenching*

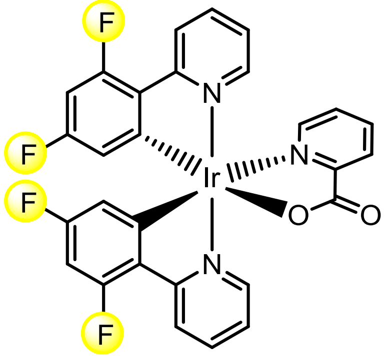


FIrpic-Mes$_2$

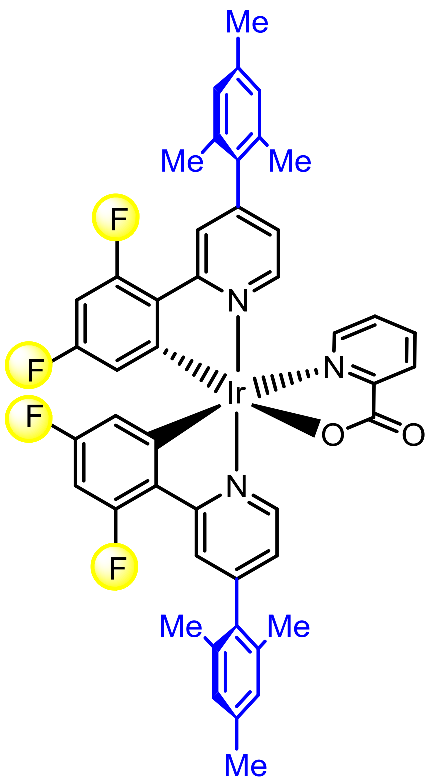


Chem. Mater. **2013**, *25*, 2352

Solution-processable Analogs of FIrpic



FIrpic

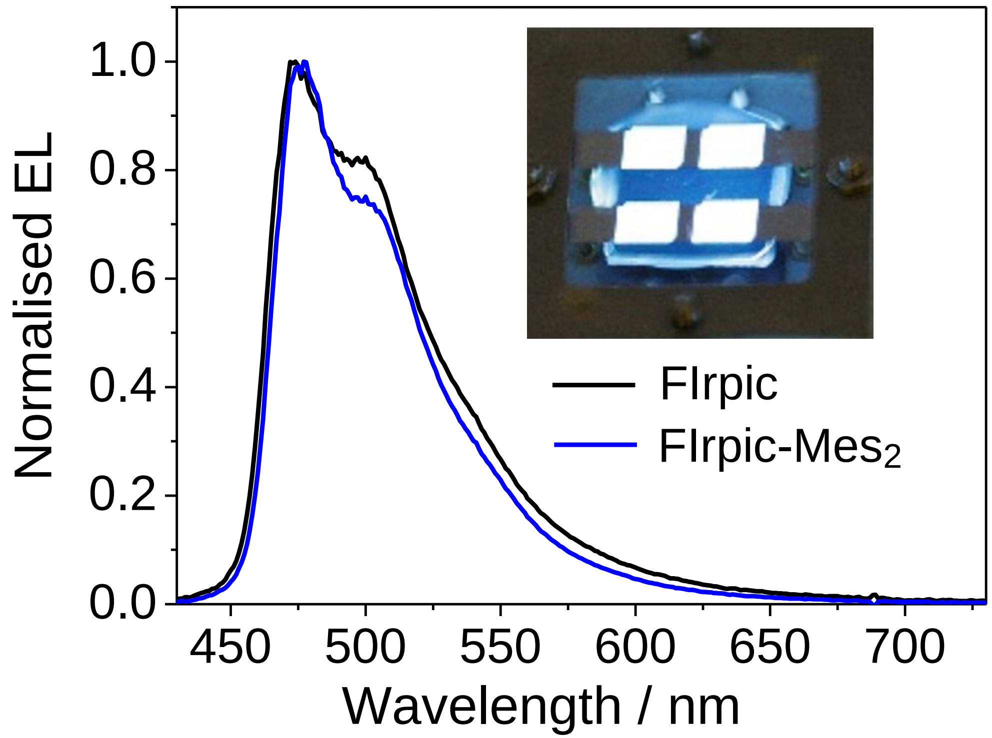


FIrpic-Mes$_2$

Devices: ITO / PEDOT:PSS/ **PVK:OXD-7:Ir complex** / Ba/Al

Spin-coated (solution-processed) single emitting layer

OXD-7 is an electron-transport material

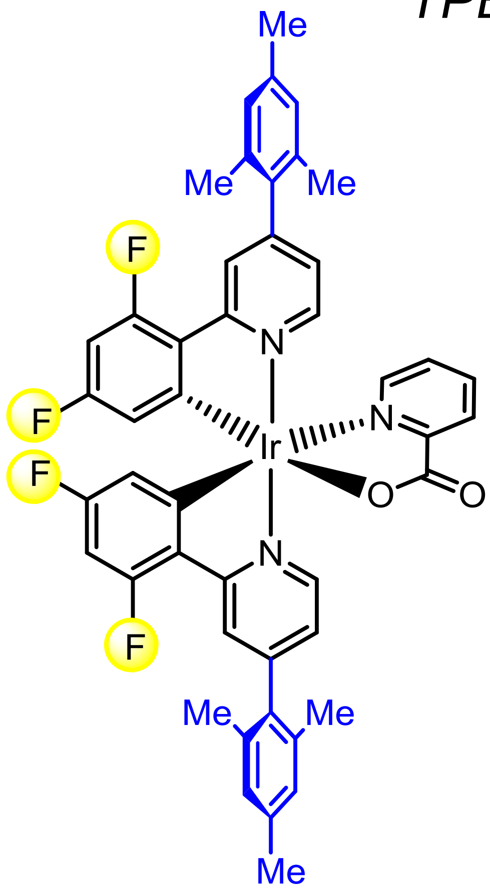


Chem. Mater. **2013**, *25*, 2352

Solution-processable Analogs of FIrpic

Optimized Devices: ITO / PEDOT:PSS / **PVK:Ir complex** / TPBi / LiF / Al

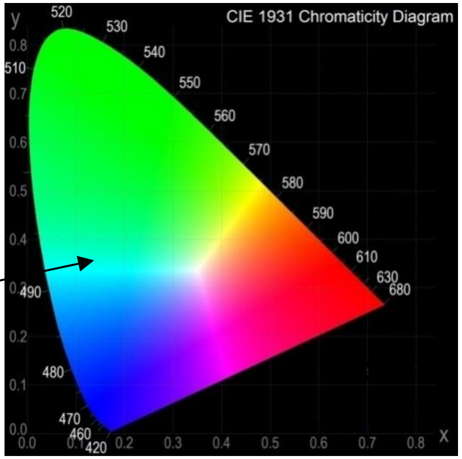
TPBi is a thermally-evaporated electron transport layer



FIrpic-Mes$_2$

EQE :	10.4%
Brightness:	4600 cd m^{-2}
Current efficiency:	23.7 cd A^{-1}
Power efficiency:	12.6 lm W^{-1}
Turn-on (10 cd m^{-2}):	5 V
CIE at 12 V:	0.17, 0.36

x 0.17
y 0.36



Chem. Mater. **2013**, *25*, 2352

Conclusions

Durham University

• New highly-fluorescent, fluorene copolymers have been synthesized and dual emission from local excited states and ICT states has been exploited in OLEDs and SSL

• New Ir(III) complexes of carbazole-based ligands give very high efficiency PhOLEDs, with color tuning by substituent effects (green to orange-red)

• New solution-processable FIrpic analogs are very promising sky-blue emitters in a simple PhOLED architecture

Acknowledgements

Synthesis:
Igor F. Perepichka
Irene I. Perepichka
Kiran T. Kamtekar
Haying Li
Kathryn C. Moss
Mustafa Tavasli
Yonghao Zheng
Tom N. Moore
Valery Kozhevnikov

Photophysics:
Lars-Olof Pålsson
Fernando B. Dias
Helen L. Vaughan
Andrew Beeby
Robert M. Edkins
Vygintas Jankus

Theory: Mark A. Fox

Crystallography: Andrei S. Batsanov

Devices: Andrew P. Monkman
Hameed A. Al-Attar
Gareth C. Griffiths
Khalid Abdullah
Ben Lyons

Funding: EPSRC (UK)
ONE NorthEast
TSB (UK)
Thorn Lighting / Zumtobel

Collaborators: Cambridge Display Technology