Photoactive Molecules for Harvesting & Converting Light

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EaStChem

Example applications of luminescent molecules

- Displays e.g. cathode ray tubes
- Laser systems
- Supramolecular chemistry and sensors
- Biological imaging

Example applications of luminescent molecules

Organic Light-emitting diodes

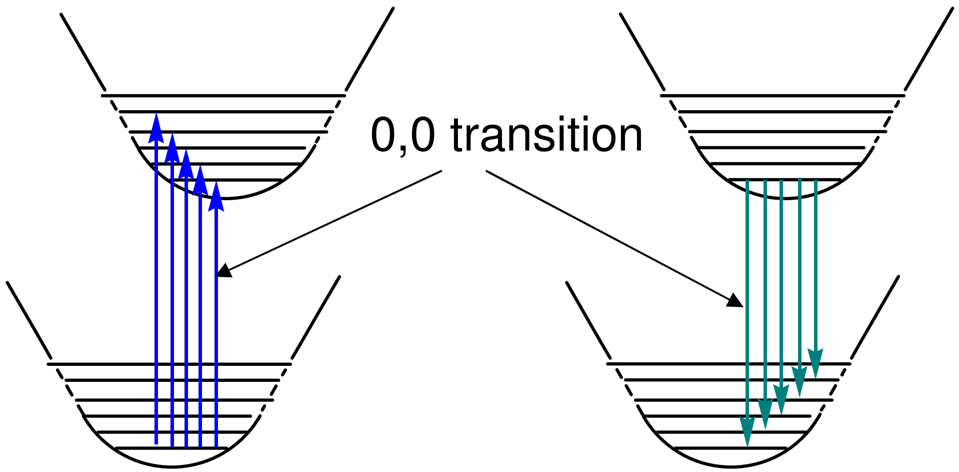
Dye-sensitised solar cells

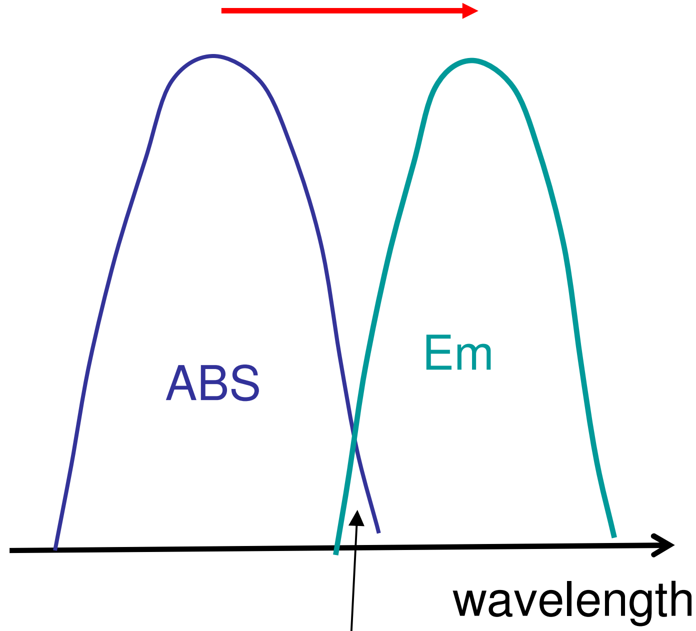
Solar fuels

Important Questions

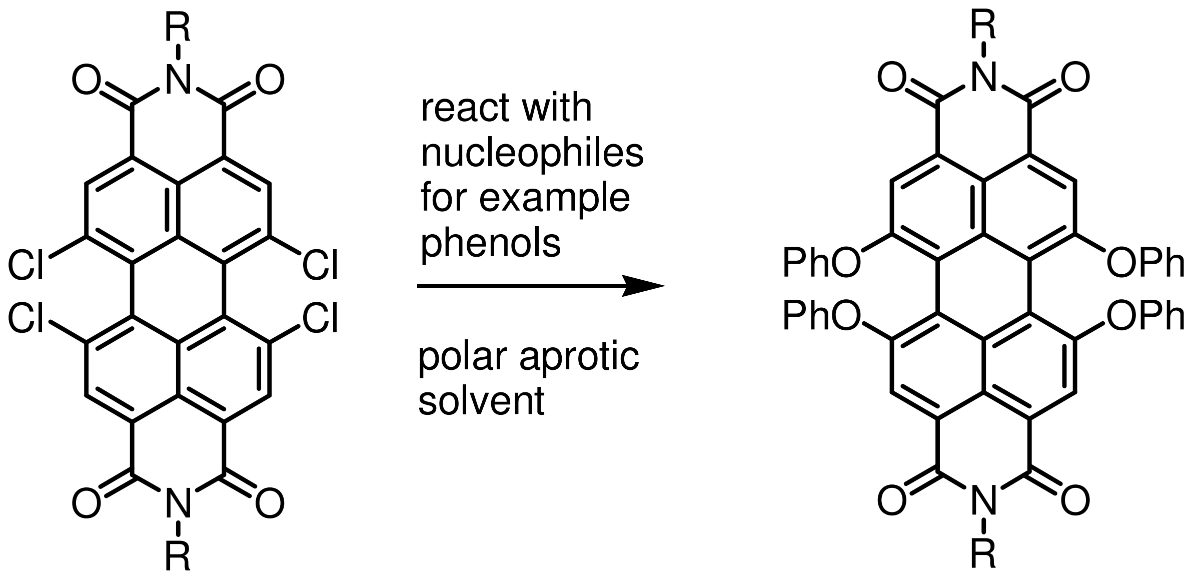
- Wavelength of absoprtion ?
- Wavelength of emission ?
- Character of excited state(s) – singlet and triplet excited states
- Emission quantum yield ?
- Excited-state lifetime ?
- Related factors – e.g. redox properties ?
- Ease of modification ?

Materials – basics of organic fluorophores

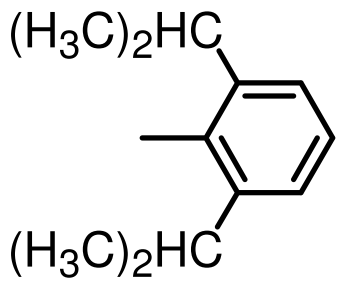




Materials – perylene organic dyes



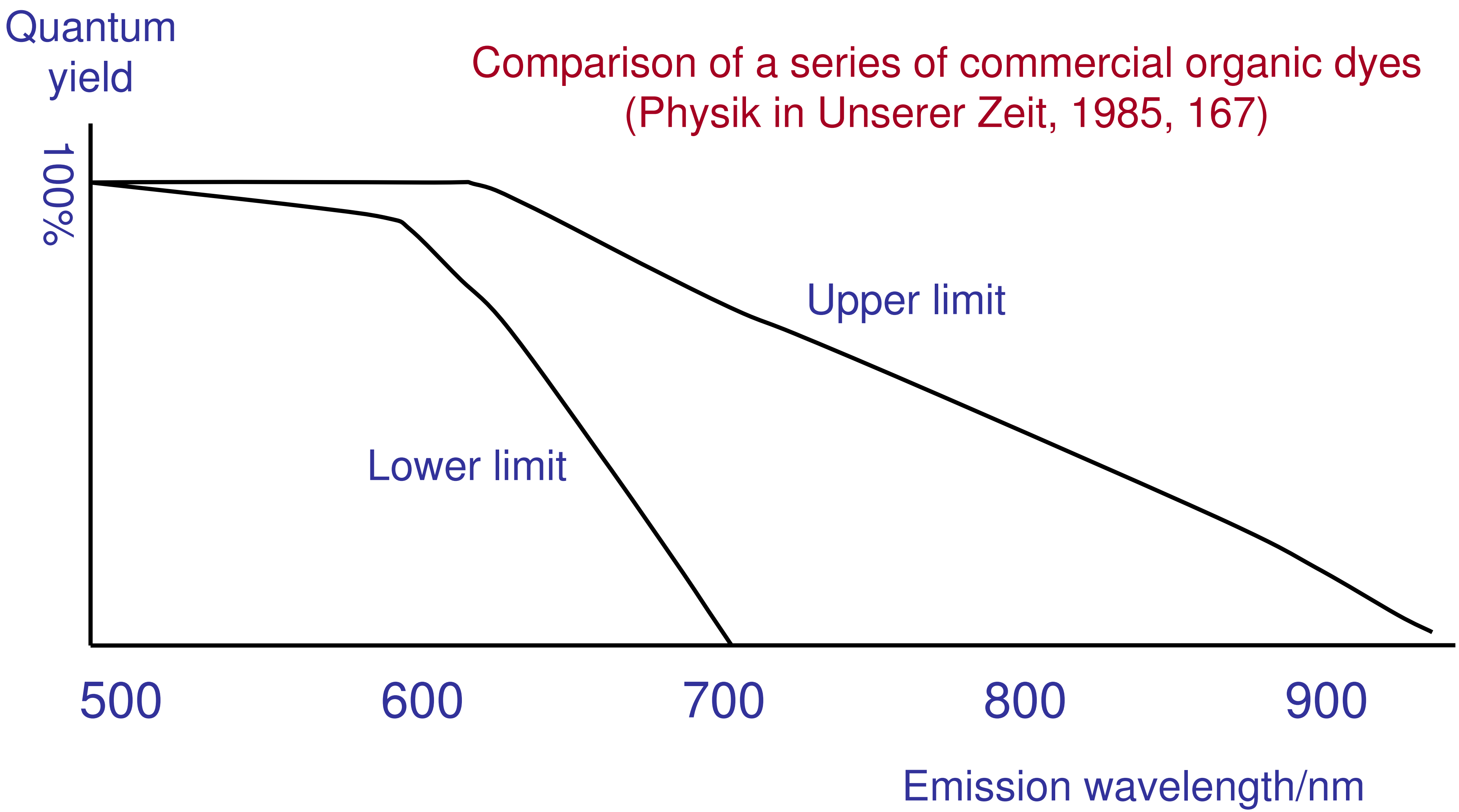
R =



λ_{max} = 578 nm (ε = 44 000); emission max = 613 nm
η_{EQY} = 0.96

- Good long-term stability – 93% of optical density retained after 1.5 years outdoors
- Tremendously improved solubility over Cl analogue

Comparison of a series of commercial organic dyes
(Physik in Unserer Zeit, 1985, 167)



k_r ~ (energy gap)^3

k_{nr} ~ grows exponentially as energy gap falls

Metal-based luminophores

- Transition metals
  - Metal and ligand orbitals
- Lanthanides
  - Metal orbitals, ligand sensitisation
- Metals playing a structural role for organic fluorophore ligands
  - Ligand orbitals

Periodic Table of Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB		VII		IB	IB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110								

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Periodic Table of the Elements

Abundance of Elements in Earth's Crust

http://chemistry.about.com
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About Chemistry

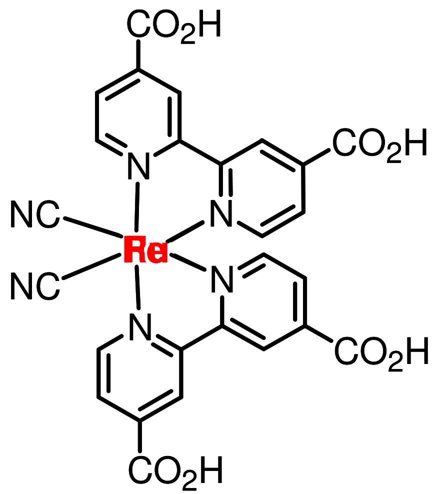
all values are in mg/kg

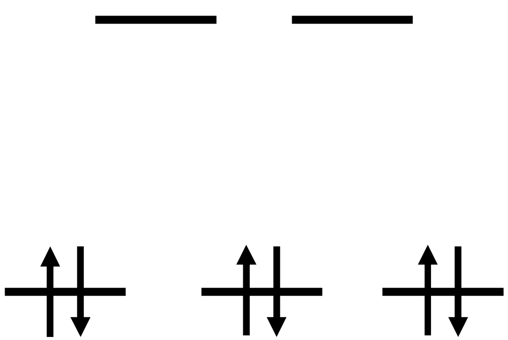
1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1 H 1400 Hydrogen																	2 He 8×10^{-3} Helium
3 Li 20 Lithium	4 Be 2.8 Beryllium											5 B 10 Boron	6 C 200 Carbon	7 N 19 Nitrogen	8 O 461000 Oxygen	9 F 585 Fluorine	10 Ne 5×10^{-3} Neon
11 Na 23600 Sodium	12 Mg 23300 Magnesium											13 Al 82300 Aluminum	14 Si 282000 Silicon	15 P 1050 Phosphorus	16 S 350 Sulfur	17 Cl 145 Chlorine	18 Ar 3.5 Argon
19 K 20900 Potassium	20 Ca 41500 Calcium	21 Sc 22 Scandium	22 Ti 5650 Titanium	23 V 120 Vanadium	24 Cr 102 Chromium	25 Mn 950 Manganese	26 Fe 56300 Iron	27 Co 25 Cobalt	28 Ni 84 Nickel	29 Cu 60 Copper	30 Zn 70 Zinc	31 Ga 19 Gallium	32 Ge 1.5 Germanium	33 As 1.8 Arsenic	34 Se 5×10^{-2} Selenium	35 Br 2.4 Bromine	36 Kr 1×10^{-4} Krypton
37 Rb 90 Rubidium	38 Sr 370 Strontium	39 Y 33 Yttrium	40 Zr 165 Zirconium	41 Nb 20 Niobium	42 Mo 1.2 Molybdenum	43 Tc Technetium	44 Ru 1×10^{-3} Ruthenium	45 Rh 1×10^{-3} Rhodium	46 Pd 1.5×10^{-2} Palladium	47 Ag 7.5×10^{-2} Silver	48 Cd 1.5×10^{-1} Cadmium	49 In 2.5×10^{-1} Indium	50 Sn 2.3 Tin	51 Sb 2×10^{-1} Antimony	52 Te 1×10^{-3} Tellurium	53 I 4.5×10^{-1} Iodine	54 Xe 3×10^{-5} Xenon
55 Cs 3 Cesium	56 Ba 425 Barium	57-71 Lanthanides	72 Hf 3 Hafnium	73 Ta 2 Tantalum	74 W 1.25 Tungsten	75 Re 7×10^{-4} Rhenium	76 Os 1.5×10^{-3} Osmium	77 Ir 1×10^{-3} Iridium	78 Pt 5×10^{-3} Platinum	79 Au 4×10^{-3} Gold	80 Hg 8.5×10^{-2} Mercury	81 Tl 8.5×10^{-1} Thallium	82 Pb 14 Lead	83 Bi 8.5×10^{-3} Bismuth	84 Po 2×10^{-10} Polonium	85 At Astatine	86 Rn 4×10^{-13} Radon
87 Fr Francium	88 Ra 9×10^{-7} Radium	89-103 Actinides	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Uut Ununtrium	114 Uuq Ununquadium	115 Uup Ununpentium	116 Uuh Ununhexium	117 Uus Ununseptium	118 Uuo Ununoctium

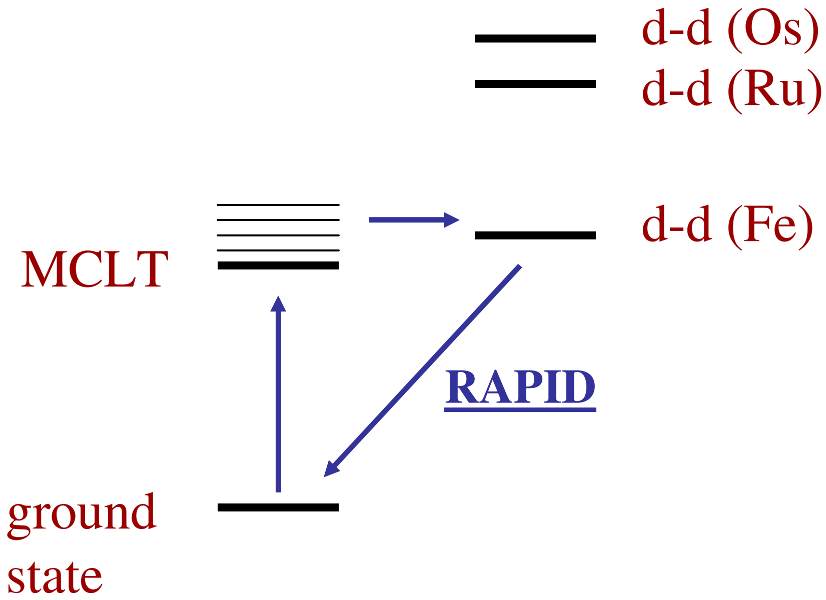
Lanthanides	57 La 39 Lanthanum	58 Ce 66.5 Cerium	59 Pr 9.2 Praseodymium	60 Nd 41.5 Neodymium	61 Pm Promethium	62 Sm 7.05 Samarium	63 Eu 2 Europium	64 Gd 6.2 Gadolinium	65 Tb 1.2 Terbium	66 Dy 5.2 Dysprosium	67 Ho 1.3 Holmium	68 Er 3.5 Erbium	69 Tm 5.2×10^{-1} Thulium	70 Yb 3.2 Ytterbium	71 Lu 8×10^{-1} Lutetium
Actinides	89 Ac 5.5×10^{-10} Actinium	90 Th 9.6 Thorium	91 Pa 1.4×10^{-6} Protactinium	92 U 2.7 Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

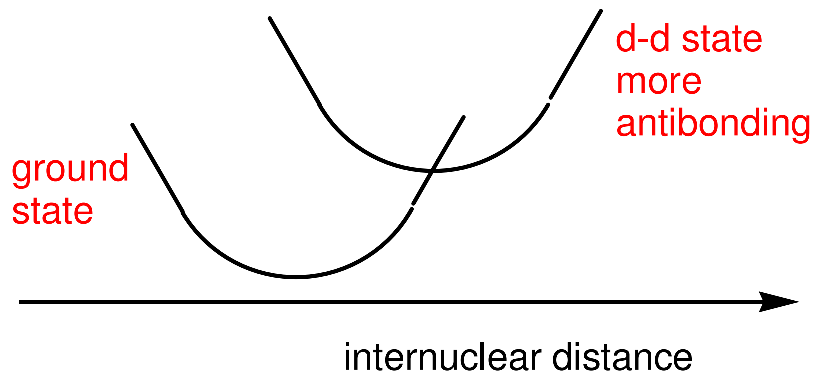
Alkali Metals	Alkaline Earth	Basic Metal	Halogen	Noble Gas	Non Metal	Rare Earth	Semi Metal	Transition Metal

1^{st} row TMs ?

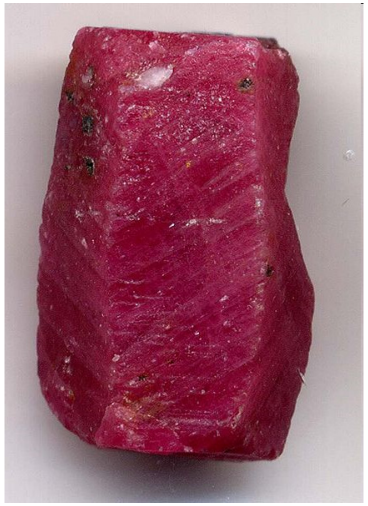

CO2H
CO2H
NC
NC
Ru
N
N
N
N
CO2H
CO2H




d-d (Os)
d-d (Ru)
d-d (Fe)
MCLT
RAPID
ground
state

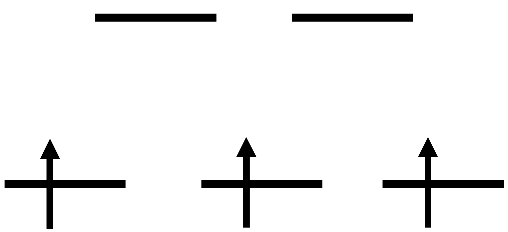

d-d state
more
antibonding
ground
state
internuclear distance

Cr(III) complexes



Ruby - yellow-green absoprtion
- red luminescence

Cr(III) luminescence
- involves d-d states
- ^2E to $^4A_2$ states
- emissive process in ruby laser



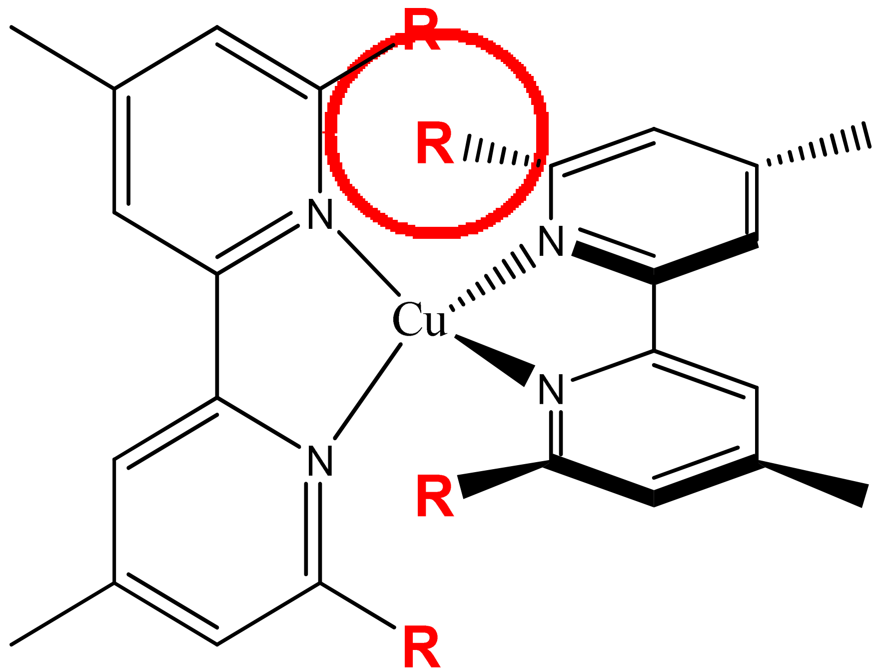
Cu(I) Complexes

Cu(I) d^{10} → no d-d transitions

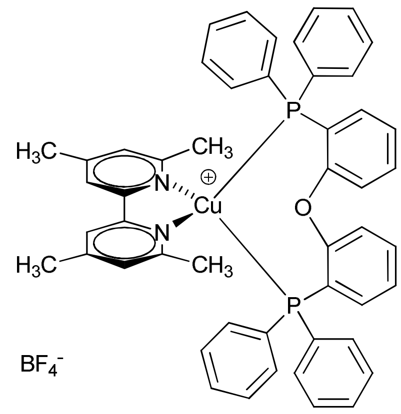
- MLCT in visible region
- Low expense and high abundance

- Cu(I) → Cu(II) geometry change….

Blocking Groups



Cu(POP)(tmbpy) – emission spectra

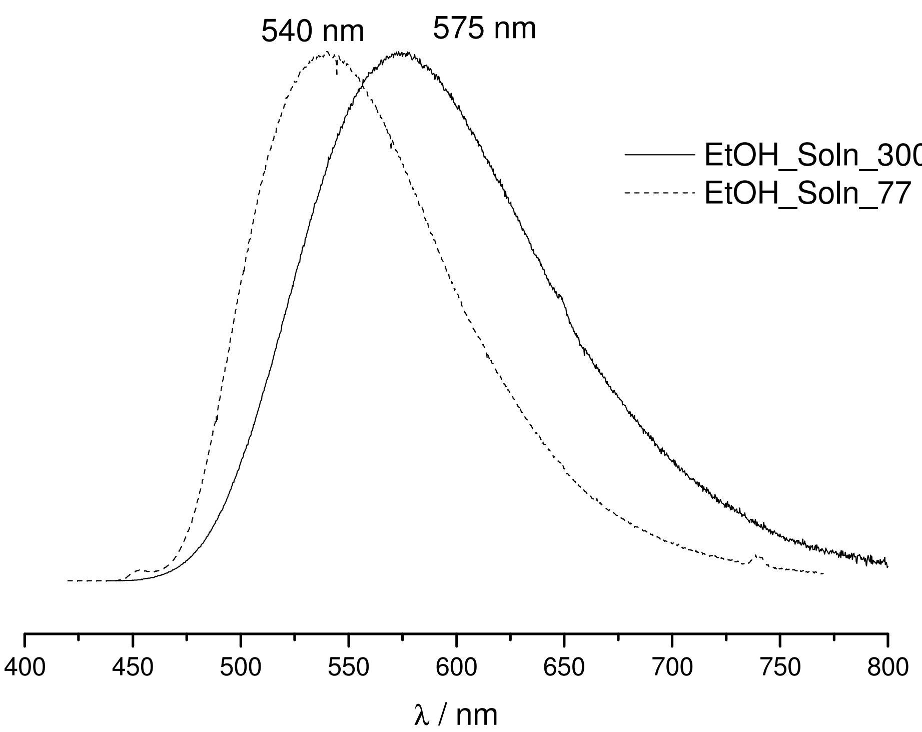


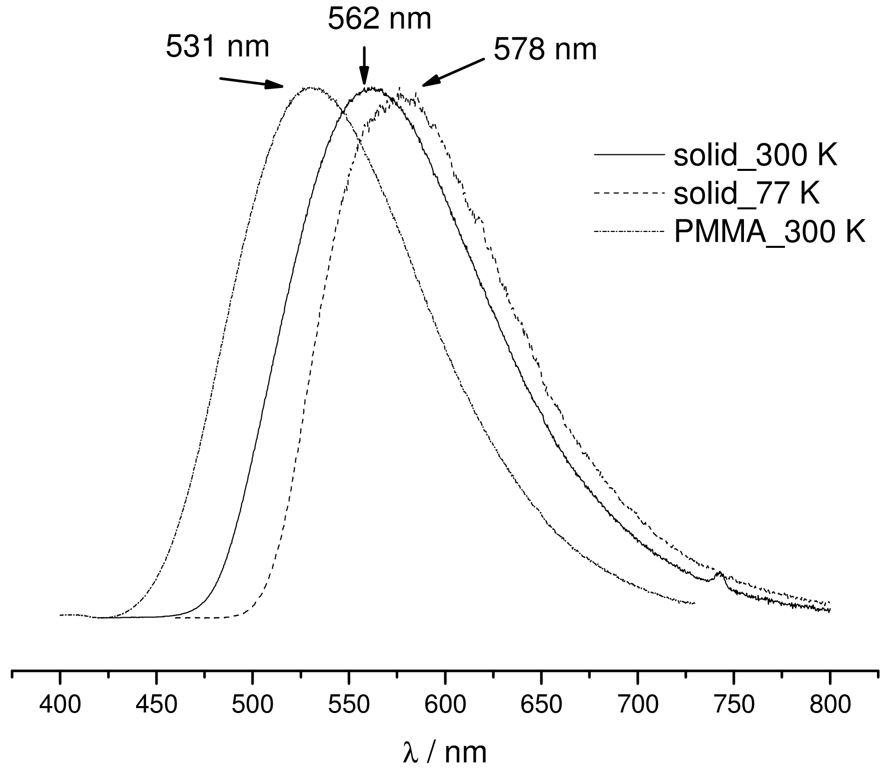
Solution_deaerated_300 K = **5.5 %**

Solid_300 K = **56.5 %**

PMMA_300K = **65.1 %**

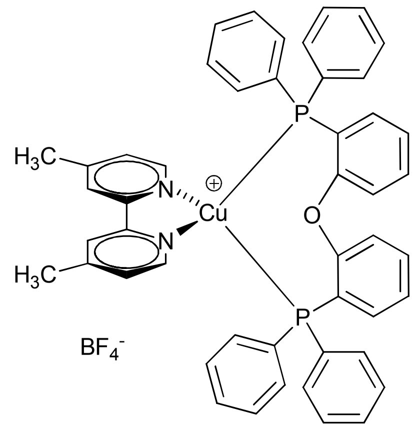
Solid_77K = **87 µs** lifetime



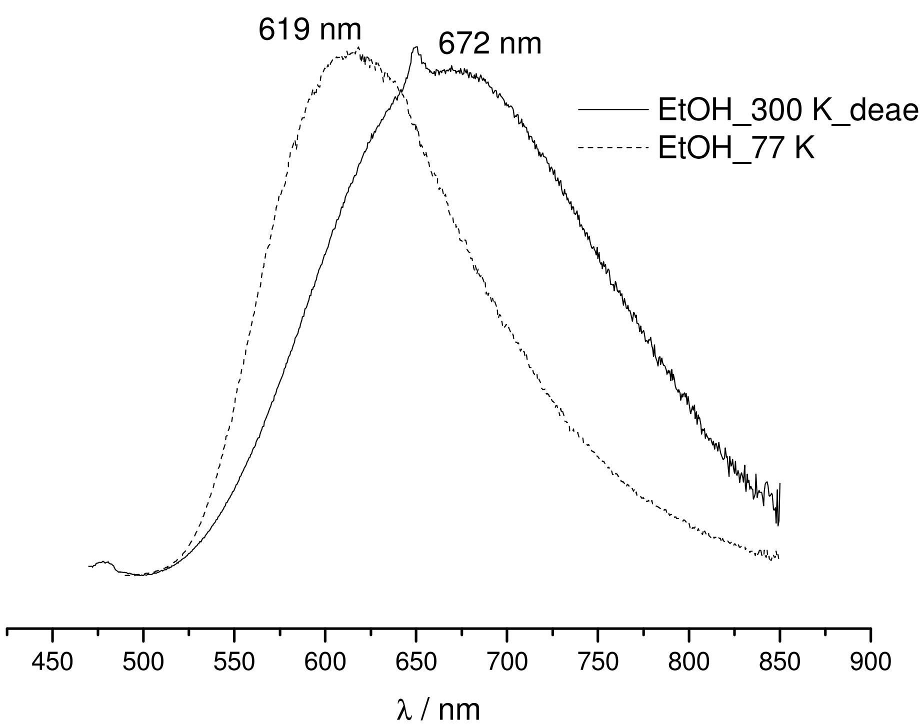


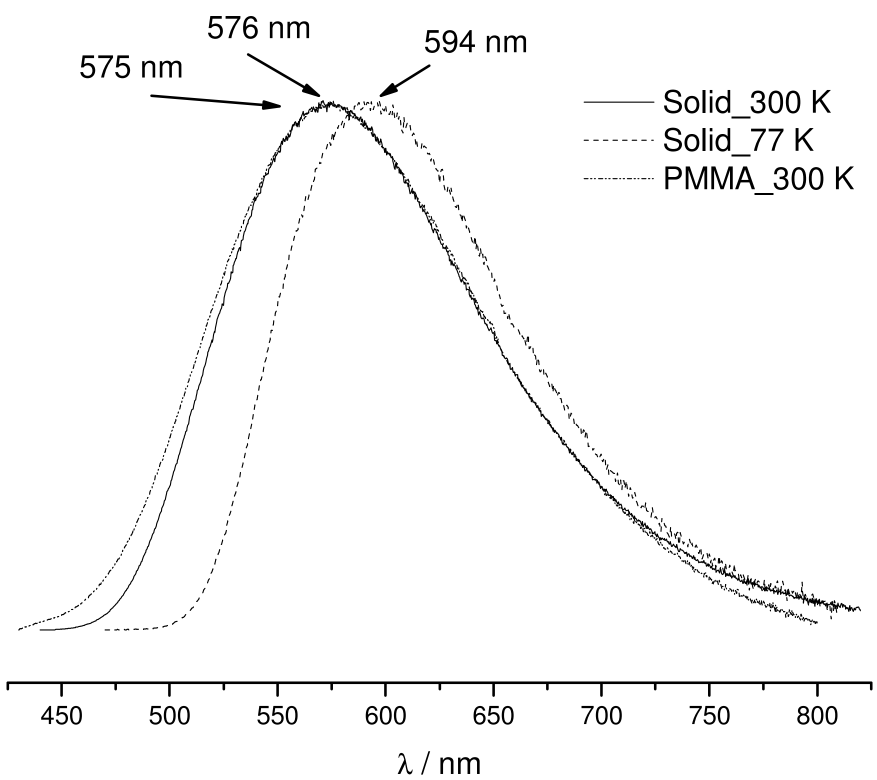
C. L. Linfoot, A. Rausch, H. Yersin, N. Robertson

Cu(POP)(dmbpy) – emission spectra

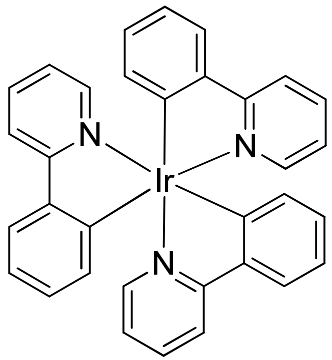


Solution_deaerated_300 K = **too small**
Solid_300 K = **8.1%**
PMMA _300K = **4.65%**
Solid_77 K = **40 μs** lifetime

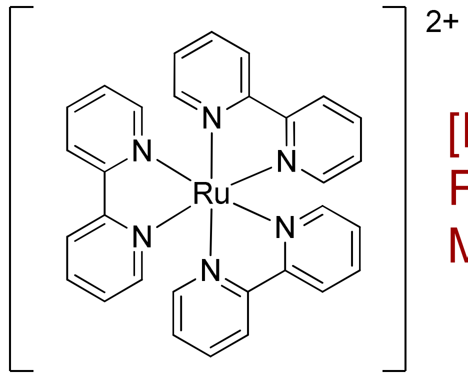




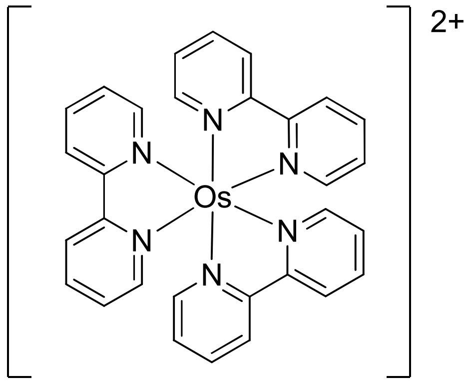
Some important families of emissive $2^{nd}/3^{rd}$ row TM complexes



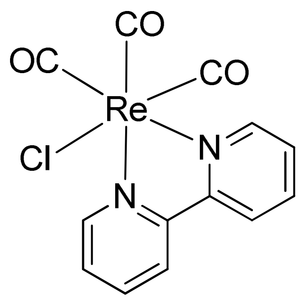
$Ir(ppy)_3$
Ir(III), d^6, low spin
MLCT absorption
(or MLCT-IL)



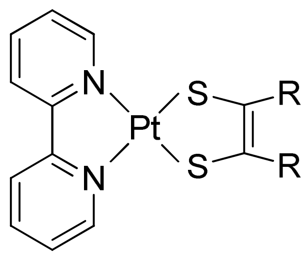
$[Ru(bipy)_3]^{2+}$
Ru(II), d^6, low spin
MLCT absorption



$[Os(bipy)_3]^{2+}$
Os(II), d^6, low spin
MLCT absorption

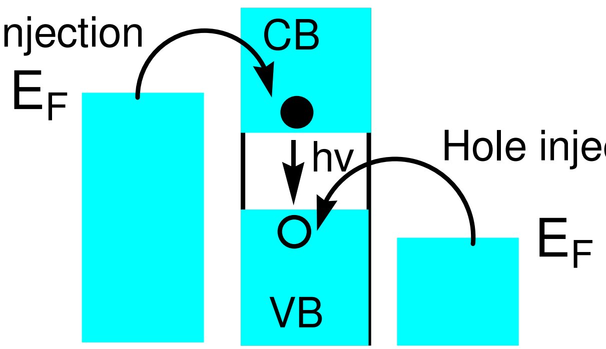


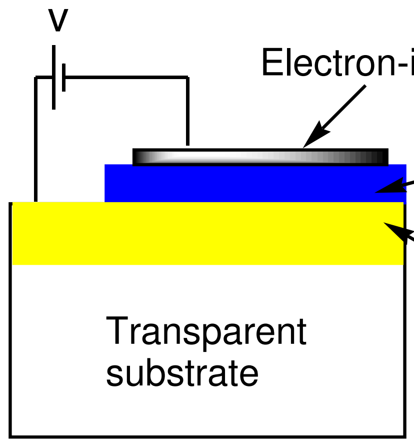
$[Re(bipy)(CO)_3Cl]$
Re(I), d^6, low spin
MLCT absorption
LLCT (Cl→bipy)

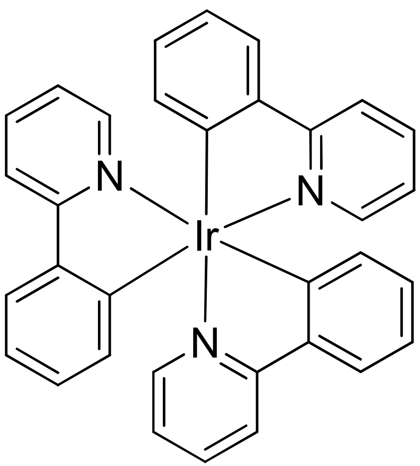


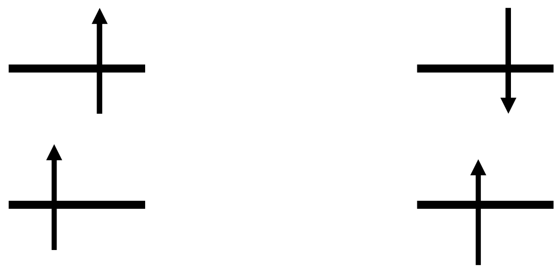
[Pt(diimine)(dithiolene)]
Pt(II), d^8, square planar
LLCT (MMLL′CT) absorption

Iridium Complexes with high emission quantum yield







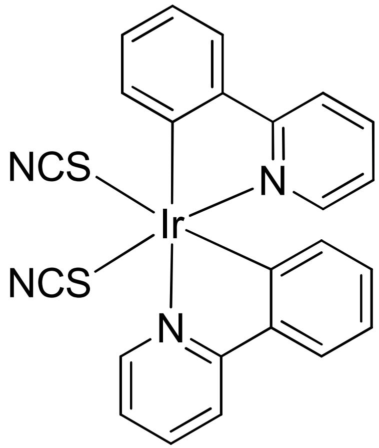


75%
non-emissive

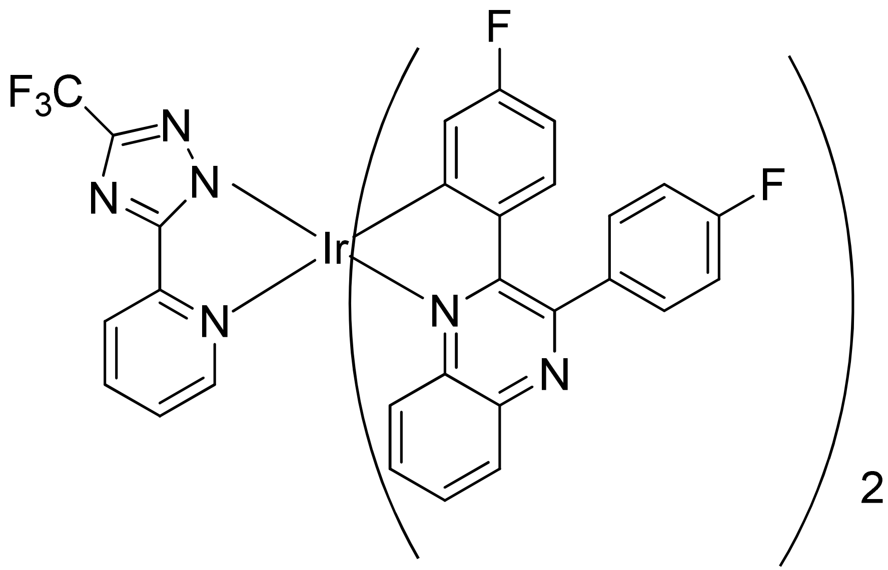
25%
emissive

(For purely organic material)

Dope with triplet-emitter
"PHOLEDS"



Emission at 506, 520 nm
Quantum yield 97%

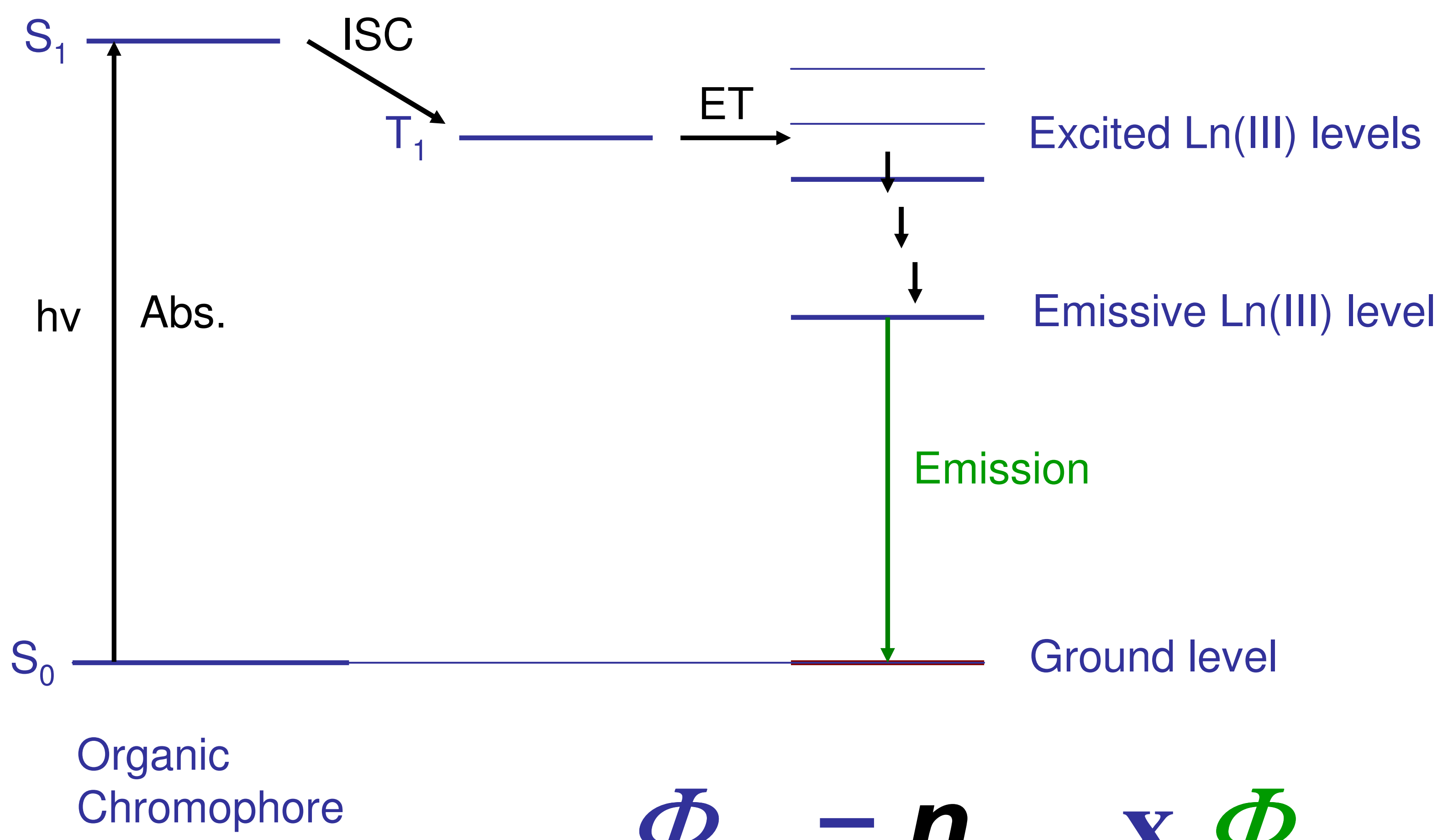


Emission at 622 nm
Quantum yield 85%

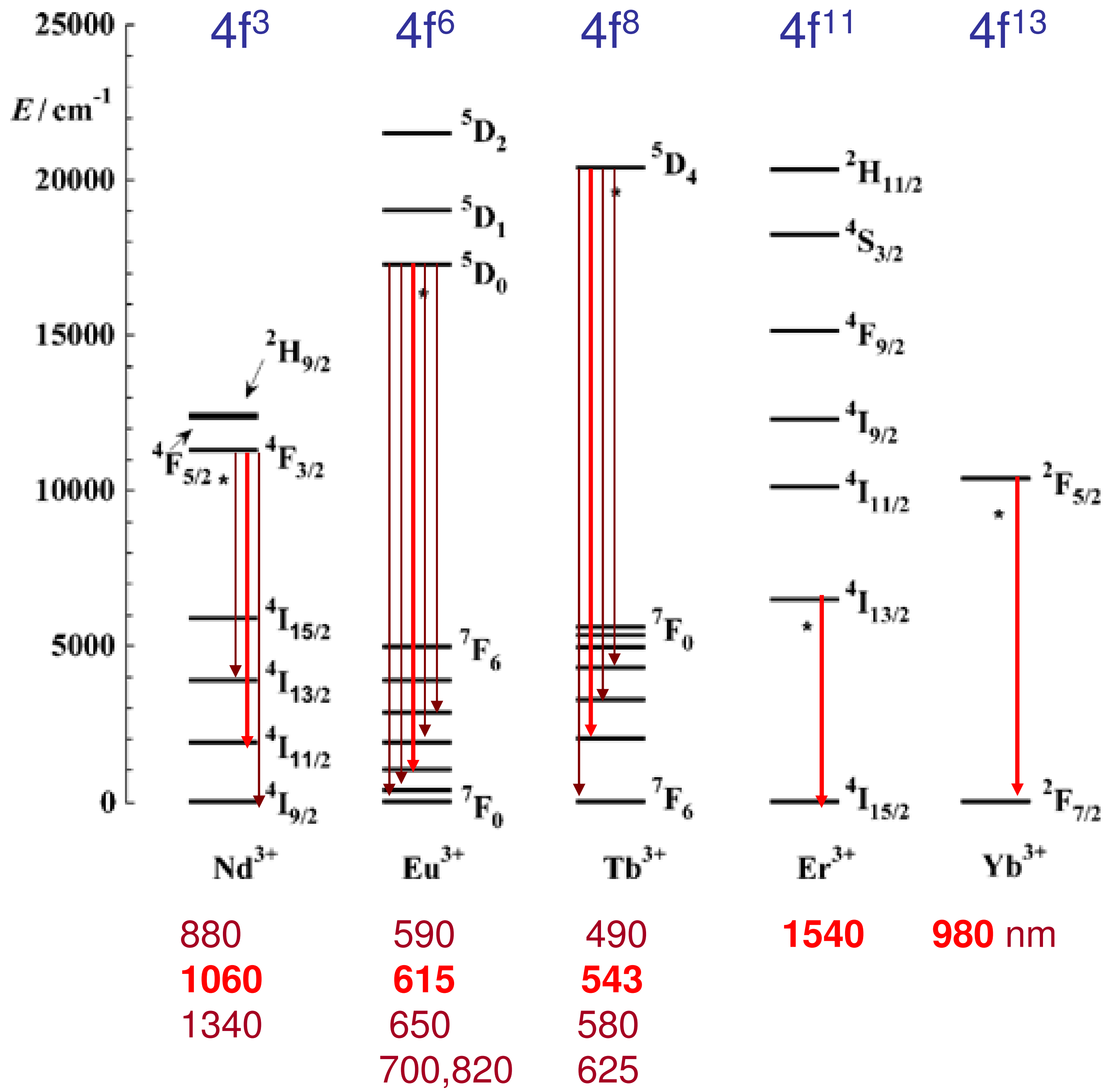
Lanthanides

- Ln(III) can have high η_{EQY} in inorganic matrix
- Yb(III) suitable emission energy for Si solar cells
- Disadvantage – very low oscillator strength – sensitise with organic ligand
- Emission quenched by C-H, N-H, O-H oscillators

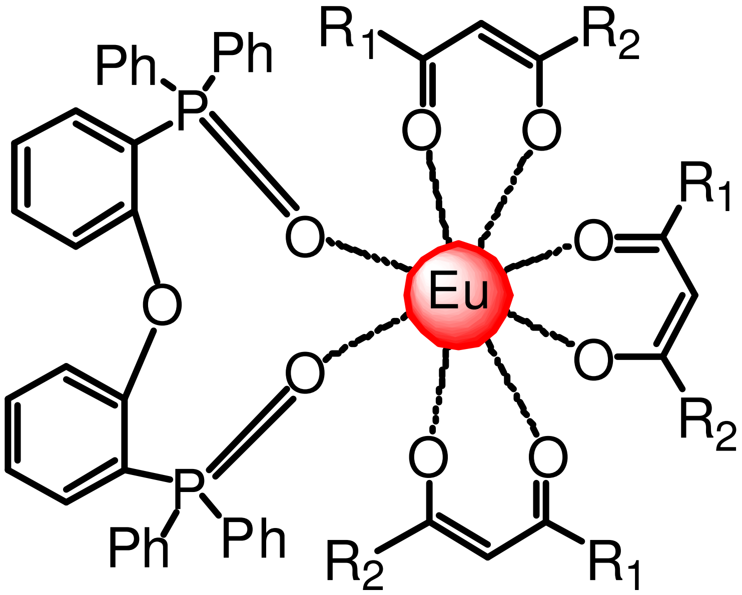
Basics of Lanthanide Sensitisation



$$\Phi_{tot} = \eta_{sens} \times \Phi_{Ln}$$


4f3
4f6
4f8
4f11
4f13
E / cm-1
25000
20000
15000
10000
5000
0
2H9/2
4F5/2 *
4F3/2
4I15/2
4I13/2
4I11/2
4I9/2
5D2
5D1
5D0
7F6
7F0
5D4
7F0
7F6
2H11/2
4S3/2
4F9/2
4I9/2
4I11/2
4I13/2
4I15/2
2F5/2
2F7/2
Nd3+
Eu3+
Tb3+
Er3+
Yb3+
880
1060
1340
590
615
650
700,820
490
543
580
625
1540
980 nm

- Yb
  - Use for visible light harvesting
  - Very efficient quenching by CH, NH, OH
- Eu
  - Use for downshifting UV → Vis
  - Little reporting of total luminescence quantum yield in PMMA

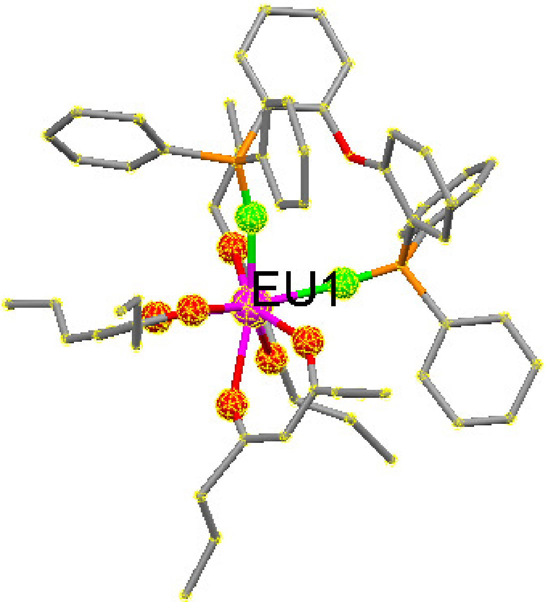


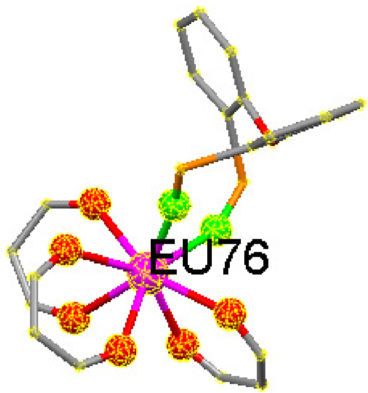
3 $R_1 = CF_3$; $R_2 = CF_3$

4 $R_1 = C_3F_7$; $R_2 = C_3F_7$

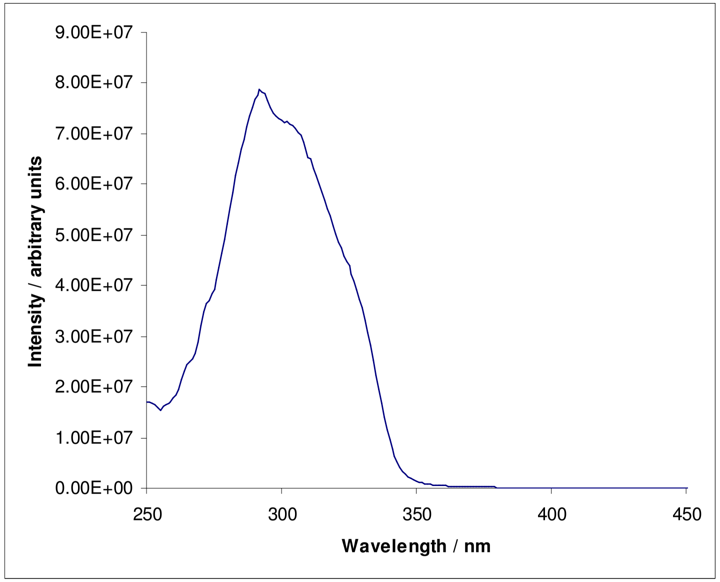
5 $R_1 = {}^tBu$; $R_2 = C_3F_7$

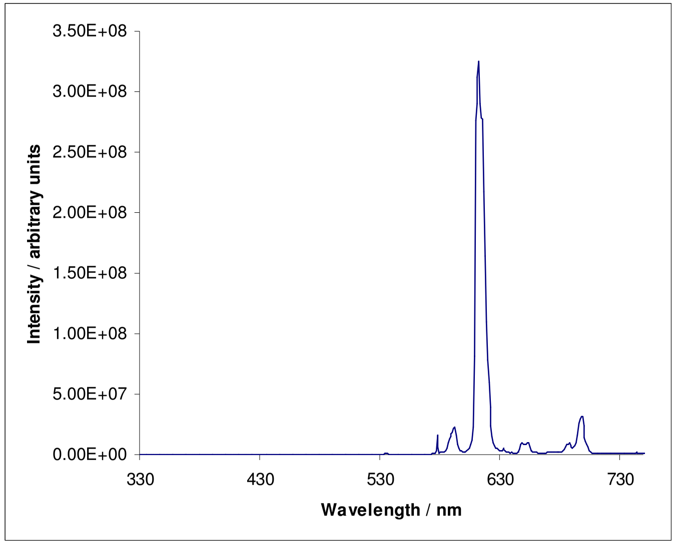
Omar Moudam, Brenda. C. Rowan, Mohammed Alamiry, Patricia Richardson, Bryce. S. Richards, Anita. C. Jones, Neil Robertson, Chem. Commun, 2009, 6649

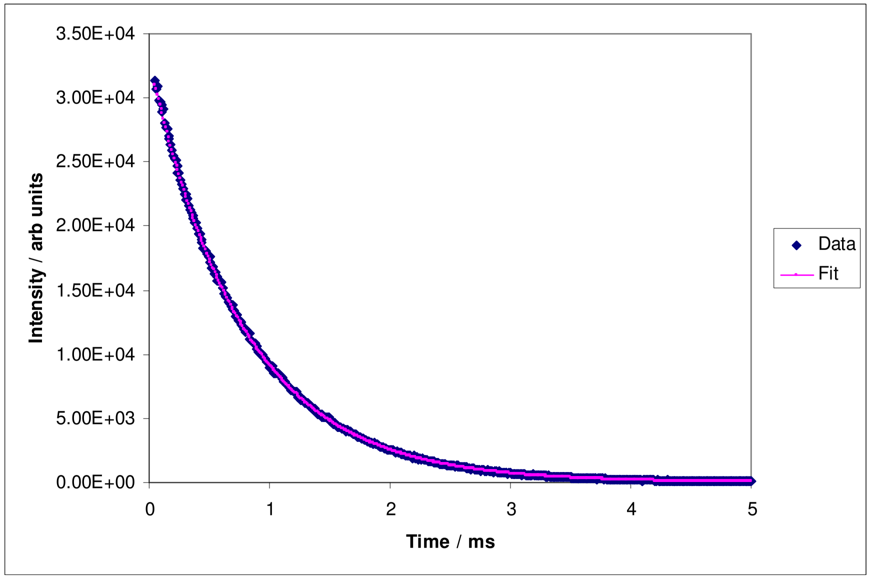




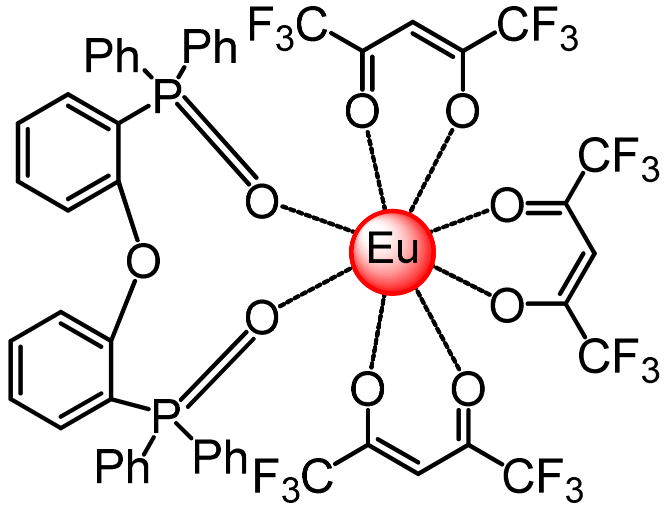
DPEPO, W. Huang, J. Phys. Chem. B., 2006, 110, 3023 (OLED studies)

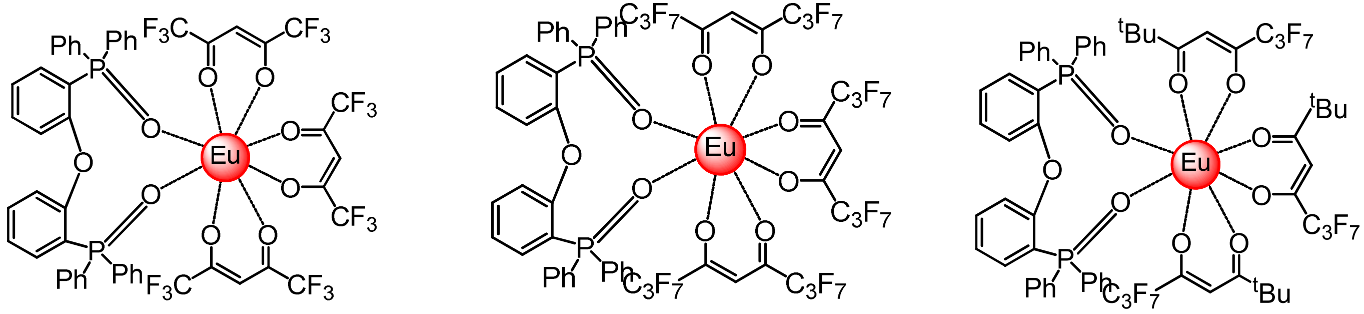






$$\Phi_{tot} = \eta_{sens} \text{ x } \Phi_{Ln}$$

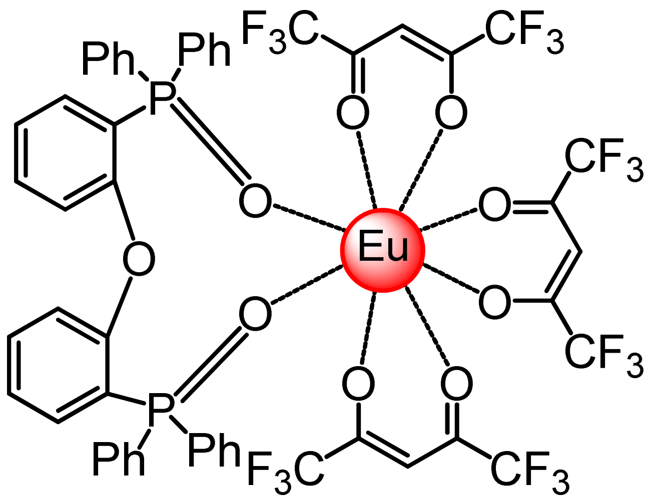


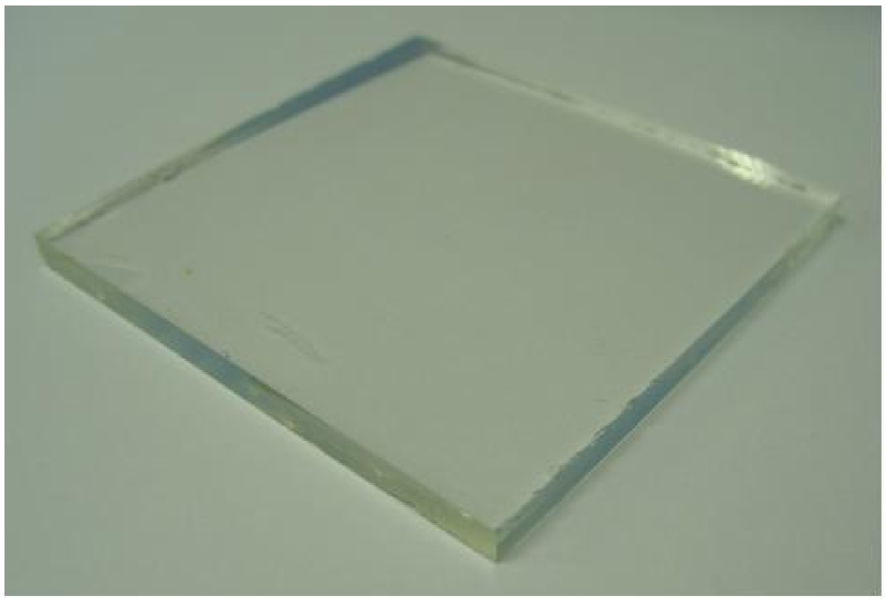


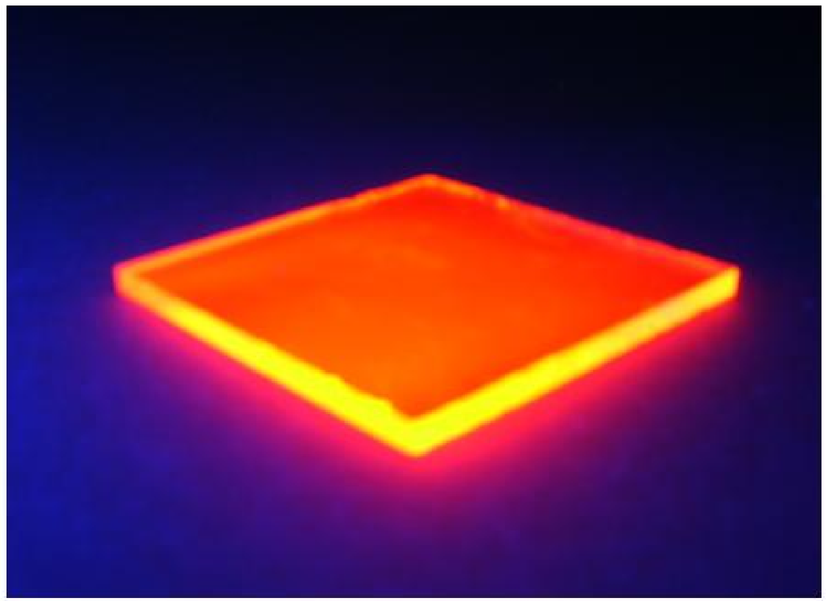
	3	4	5
DCM			
Φ_{Ln}	0.78	0.81	0.80
Φ_{tot}	**0.76**	0.70	0.34
η_{sens}	0.97	0.86	0.43
PMMA			
Φ_{Ln}	0.80	0.75	0.71
Φ_{tot}	**0.85**	0.73	-
η_{sens}	1.0	1.0	-

$$\Phi_{tot} = \eta_{sens} \times \Phi_{Ln}$$

Highest reported total quantum yield in PMMA of around 80 – 85%







Overall Summary

	Org	TM1	TM2/3	Ln
Light harvesting (λ and ε)	**X**	X	**X**	**X**
Large Stokes shift		**X**	**X**	**X**
Quantum yield	X	X	**X**	X
Excited-state lifetime	**X**	X	**X**	
Stability	X		X	X
Cost	**X**	**X**		X
Ease of modification	**X**	**X**	**X**	**X**

There is no dye family that optimises all these at once