Electrophosphorescence

1. OLED efficiency
2. Spin
3. Energy transfer
4. Organic phosphors
5. Singlet/triplet ratios
6. Phosphor sensitized fluorescence
7. Endothermic triplet energy transfer

Lecture by Prof. Marc Baldo

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POWER EFFICIENCY

The eye’s response is wavelength dependent.

The unit of perceived optical power is defined as the lumen (lm).

Power efficiency of LED’s is therefore measured in lumens/Watt.

The maximum photopic response is:
\[ \Phi \sim 20 \text{ lm (blue)} \]
\[ \Phi \sim 680 \text{ lm (green)} \]
\[ \Phi \sim 100 \text{ lm (red)} \]

For an OLED of given color, we must maximize:
- quantum efficiency (\( \eta_Q = \frac{\text{photons out}}{\text{electrons in}} \))
- electrical efficiency (\( \frac{V_\lambda}{V} = \frac{\text{photon energy}}{\text{operating voltage}} \))

\[
\eta_P = \frac{L}{VI} = \Phi \eta_Q \frac{V_\lambda}{V}
\]

Power efficiency = photopic response of eye \( \times \) quantum efficiency \( \times \) electrical efficiency.
Quantum efficiency

is the measure of a luminescent dye’s performance. $\eta_Q = \text{the number of photons emitted per electron injected.}$

\[ \eta_Q = \chi \eta_{\text{out}} \phi_{\text{PL}} \]

$\phi_{\text{PL}}$ is fundamental luminescence efficiency of organic material.

$\eta_{\text{out}}$ is output coupling fraction reduced by absorption losses and wave guiding within the device and its substrate.

$\chi$ is fraction of luminescent molecular excitations (defined by spin selection rules) typically ~ 25%

remaining energy is wasted

\[ \downarrow \]

Imposes a fundamental limit to OLED efficiencies
EXCITON SPIN AND SYMMETRY

Molecular excited states (or excitons) are typically mobile, with binding energy \( \sim 1 \text{eV} \), and spin \( S = 0, 1 \)

Molecular ground state
(spatially symmetric under exchange of electrons)

1st excited state
(spatially anti-symmetric (triplet) or spatially symmetric (singlet))

\[ E \]

\[ \text{LUMO} \]

\[ \psi = | \uparrow \downarrow \rangle \]

\[ \psi = | \uparrow \uparrow \rangle + | \downarrow \downarrow \rangle \quad \text{S=1, triplet} \]

\[ \psi = | \downarrow \downarrow \rangle \]

\[ \psi = | \uparrow \downarrow \rangle - | \uparrow \downarrow \rangle \quad \text{S=0, singlet} \]

\[ \text{HOMO} \]
Fluorescence and Phosphorescence

Fluorescence:
Decay from singlet allowed by symmetry: fast ($10^9$ s$^{-1}$) and often efficient.

Phosphorescence:
Decay from triplet disallowed by symmetry: slow ($> 1$ s$^{-1}$) and inefficient.

Triplet has lower energy because it is spatially antisymmetric under exchange of electrons. (e−e− repulsion lower.)

Intersystem crossing (ISC)

Fluorescence

S$_1$ → T$_1$

Phosphorescence

S$_0$ → Molecular ground state
Efficient phosphorescence

Need to mix singlet and triplet states:
- make both singlet and triplet decay allowed.

Use metal-organic complexes with heavy transition metals:

Spin orbit coupling mixes states: proportional to atomic number

Type I phosphor
Exciton localized on organic

Type II phosphor
Metal-ligand charge transfer exciton

less mixing ~ 100µs triplet lifetime

most mixing ~ 1µs triplet lifetime
Structure and operation of OLEDs

- must transfer energy from host material to luminescent dopant. This determines the quantum efficiency of luminescence.

**A heterostructure OLED**

Assume balanced currents: every hole combines with an electron

Excitons form in host at interface. Ideally energy is transferred to luminescent molecules.
Energy transfer

(a) Förster energy transfer

Exciton non-radiatively transferred by dipole-dipole coupling if transitions are allowed (usually singlet-singlet).

(b) Dexter energy transfer

Exciton hops from donor to acceptor.
A red phosphor:

\[ ^3 \text{latinum octaethylporphyrin} \]

- Triplet lifetime \(~100\text{ms}\)
- Peak external quantum efficiency in Alq\(_3\) \(~4\%\)

![Emission spectrum](image)

- **Device structure**
  - Mg:Ag cathode
  - PtOEP in Alq\(_3\)
  - a-NPD
  - Indium tin oxide

- **Luminance of 6% device (cd/m\(^2\))**

  - 1% PtOEP
  - 6% PtOEP
  - 20% PtOEP

- **Quantum Efficiency (%)**

  - Efficiency roll-off due to triplet-triplet annihilation

- **Loss proportional to square of triplet lifetime**
DOES PTOEP CAPTURE ALQ₃ TRIPLETs?

Put fluorescent dye DCM2 in exciton formation zone.
The singlet/triplet ratio in Alq₃

Device 1 emits from singlets only

Device 2 emits from singlets and triplets

Compare ratio of EL emission from devices to get singlet fraction. After correction for PL efficiency of DCM2 and PtOEP, get:

$$\chi = (22 \pm 3)\%$$
IMPROVED PHOSPHORS

Must reduce triplet lifetime to minimize T-T annihilation. Increase MLCT component of excited state.

The first high efficiency green phosphor was iridium tris(2-phenylpyridine)

Broad green emission at $\lambda \sim 515$ nm. Phosphorescent lifetime, $\tau \sim 1$ ms.
There are many more fluorescent than phosphorescent materials. Can we get high efficiency from a fluorescent dye?

Need to prevent exciting triplet state in fluorescent dye. Want mechanism for triplet-singlet energy transfer.
1. Triplet-singlet hopping transfer is disallowed
2. Triplet-singlet Förster transfer permitted if triplet relaxation on donor is allowed
   \(i.e.\) triplet-singlet transfer is possible from a phosphorescent donor

Predicted by Förster in 1959 (†)
Observed by Ermolaev and Sveshnikova in 1963 (§)

e.g. for triphenylamine as the donor and chrysoidine as the acceptor, in rigid media at 77K or 90K the interaction length is 52Å

IMPLEMENTATION OF TRIPLET-SINGLET ENERGY TRANSFER

host phosphorescent sensitizer fluorescent dye

ISC

S
T

CBP

Ir(ppy)$_3$

DCM2 absorbs in the green
DCM2 fluorescence sensitized by Ir(ppy)$_3$

Roll-off in efficiency is due to charge trapping on DCM2 molecules

Nearly complete energy transfer from Ir(ppy)$_3$ to DCM2
Delayed DCM2 fluorescence confirms sensitizing action of Ir(ppy)$_3$.
**BLUE**

Problem: the most energetic charge transport hosts currently available have blue-green triplets. So to transfer energy to a blue phosphor, exciton transfer must be endothermic.

*Flrpic (blue phosphor)*
- Peak wavelength 470nm
- Triplet lifetime 10 $\mu$s

Flrpic

(2.56 $\pm$ 0.10) eV

CBP

(2.62 $\pm$ 0.10) eV

Flrpic

$\kappa_F$

$\kappa_R$

$\kappa_G$

$\kappa_H$

Possible to get efficient endothermic transfer if decay of host triplet disallowed.

Host CBP triplet lifetime $\sim$ 1s.

Graph showing intensity and CIE coordinates for Flrpic in CBP, CHCl$_3$, and at 460nm.
Transient response of endothermic transfer

Efficiency of luminescence decreases below T=200K as energy transfer to phosphor is frozen out.

Transient response is also consistent with endothermic transfer:
At T=200K, apparent transient lifetime of FIrpic (includes endothermic transfer) >> natural lifetime (~10µs)
Organic materials have broad luminescent spectra. Overcome in red and blue by shifting toward non-visible wavelengths.
OLED SUMMARY

Peak power efficiency in green is 60 lm/W
Peak quantum efficiency is 19%
(corresponds to ~100% internal)

Largest remaining problem is operating voltage

### Table of phosphorescent device operating parameters

<table>
<thead>
<tr>
<th>phosphor</th>
<th>host</th>
<th>Φ (lm/W)</th>
<th>η_p (lm/W)</th>
<th>η_Q_ext</th>
<th>η_Q_int</th>
<th>V_{int}/V</th>
<th>η_p (lm/W)</th>
<th>η_Q_ext</th>
<th>η_Q_int</th>
<th>V_{int}/V</th>
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<tbody>
<tr>
<td>ppy2Ir(acac)</td>
<td>TAZ</td>
<td>530</td>
<td>60</td>
<td>0.19</td>
<td>0.87</td>
<td>0.60</td>
<td>20</td>
<td>0.15</td>
<td>0.68</td>
<td>0.25</td>
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<tr>
<td>btpIr(acac)</td>
<td>CBP</td>
<td>170</td>
<td>4</td>
<td>0.07</td>
<td>0.32</td>
<td>0.34</td>
<td>2.2</td>
<td>0.06</td>
<td>0.27</td>
<td>0.22</td>
</tr>
<tr>
<td>Flrpic</td>
<td>CBP</td>
<td>260</td>
<td>1.3</td>
<td>0.006</td>
<td>0.027</td>
<td>0.83</td>
<td>5.0</td>
<td>0.057</td>
<td>0.23</td>
<td>0.34</td>
</tr>
<tr>
<td>PtOEP</td>
<td>CBP</td>
<td>60</td>
<td>0.3</td>
<td>0.056</td>
<td>0.23</td>
<td>0.09</td>
<td>0.2</td>
<td>0.042</td>
<td>0.19</td>
<td>0.08</td>
</tr>
</tbody>
</table>
PHOSPHORESCENT DEVICE PERFORMANCE

**RED**
- Intensity (arb. units) vs. Wavelength (nm)
- btp$_2$Ir(acac)
- btp$_2$Ir(acac) in CBP

**GREEN**
- Intensity (arb. units) vs. Wavelength (nm)
- ppy$_2$Ir(acac)

**BLUE**
- Intensity (arb. units) vs. Wavelength (nm)
- Flrpic
- Flrpic in CBP

- Power efficiency (lm/W)
- Quantum efficiency (%)
- Current density (mA/cm$^2$)
PHOSPHORESCENT STABILITY

Phosphors should improve OLED stability by rapidly removing triplet excitons and lowering drive current required.

Red: BtpIr(acac) in CBP
Green: (ppy)$_2$Ir(acac) in CBP

Courtesy Ray Kwong and UDC