Microstructure of Thin Films of Ruthenium Bipyridine Derivatives in Organic Light Emitting Devices

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Department of Chemistry and Chemical Biology,
Cornell University
Motivation

Why OLEDs?

• Active emitters
• Higher contrast, greater viewing angles
• Energy-efficient
**Approach**

Transition Metals Complexes: Ruthenium Derivatives

**Electrochemical cell**
- Used of air stable electrodes
- Low operating voltages

**Material**
- Electrochemically active
- Stable in multiple oxidation states
- High quantum efficiency
- Electron and hole transporter

- Efficiency
- Turn-on time
- Color emission

Thin film of transition Metal Complex

Au/Cathode

ITO/Anode
Electrochemical Device Model
Electrochemical Device Model

Recombination layer

Recombination layer

Ru(bpy)$_3^{+n}$  PF$_6^-$  Hopping electron/holes  diffusion of counter ions

h$
u$

h$^+$  ITO  h$^+$

Hopping electron/holes
Energy Level Diagram

- M = Os$^{+2}$
- M = Ru$^{+2}$
- $^1d$-$d^*$
- $^1d$-$\pi^*$
- $^3d$-$\pi^*$
- $^3d$-$d^*$

Increase in stability
M = Os$^{+2}$
M = Ru$^{+2}$

$r$ = radiative
$nr$ = non-radiative

$R = \text{radiative}$
$N = \text{non-radiative}$

Octahedral

Ground State

Color tuning
# Ligand Effects on Efficiency

## $[\text{Ru(L)}_3](\text{PF}_6)_2$ Based Devices

<table>
<thead>
<tr>
<th>Ligands-L</th>
<th>$\lambda_{\text{PL}}$ (nm)</th>
<th>External Quantum Efficiency (%)</th>
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<td><img src="image1.png" alt="Ligand 1" /></td>
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</tr>
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<td>0.25</td>
</tr>
<tr>
<td><img src="image3.png" alt="Ligand 3" /></td>
<td>610</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Quantum Efficiency = $\eta = 100 \times \frac{N_{\text{ph}}}{N_{\text{el}}} \%$

$N_{\text{el}} = \frac{I(A)}{e}$

$N_{\text{ph}} = \frac{L \lambda}{hc}$

$L = \text{energy emitted per time (W)}$
# Ligand Effects on Efficiency

**[Ru(L)₃](PF₆)₂ Based Devices**

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Luminous Efficacy (lm/W) ~**10** (Ir(bpy)(phenbpy)₂ OLED)
Incandescence-**16 lm/W** and Fluorescent-**85 lm/W**
InGaN LEDs (orange/red)-**50 lm/W**
Ruthenium Complexes

- $\left[\text{Ru} (\text{diterbuthylbpy})_3\right]^{+2}$
- $\left[\text{Ru} (\text{ethylphenylbpy})_3\right]^{+2}$
- $\left[\text{Ru} (\text{diethylphenylbpy})_3\right]^{+2}$
- $\left[\text{Ru} (\text{bpy})_2 (\text{dmbpy})_3\right]^{+2}$
- $\left[\text{Ru} (\text{tetra-Me-bpy})_3\right]^{+2}$
- $\left[\text{Ru} (\text{bpy})_3\right]^{+2}$
- $\left[\text{Ru} (2,2'-\text{bpy})_2 (4,4'-\text{bpy})_2\right]^{+2}$
Why grazing incidence?

Taking advantage of the total external reflection phenomena in the X-ray regime we can control the X-ray penetration depth and achieve a surface sensitive analysis. \( q_z = \left(\frac{2\pi}{\lambda}\right) (\sin \alpha + \sin \beta) \)

**Total external reflection**

\[ n = 1 - \delta + i \beta_a, \quad \delta \simeq 10^{-5} \]

\[ \alpha_c = (2\delta)^{\frac{1}{2}}, \quad \alpha_c(\text{ITO}) \simeq 0.4^\circ \]

\[ \delta = \frac{2\pi \rho_a r_0}{k^2} \quad \beta_a = \frac{\mu}{2k} \]
Experimental Set Up

Horizontal Diffractometer

- PSD
- Soller Slit
- $S_1$
- $S_2$

Instrumental Resolution

$\Delta 2\theta = 0.2^\circ$
$\Delta \gamma = 0.08^\circ$

Top View

- ~$10^{13}$ photons/sec
- ~$10^{10}$ photons/sec through a 10mmH x 0.2mmV slit

- Soller Slit (0.2°)

$\Delta E/E = 0.1\%$

Side View

- Surface normal

$\alpha$
$\beta$
$\phi$
$\gamma$
**Experimental Set Up**

**Horizontal Diffractometer**

- PSD
- Soller Slit
- S1
- S2
- Be Laue crystal
- Horizontal diffractometer
- Linear gas detector
- Soller collimator

**Instrumental Resolution**

- $\Delta 2\theta = 0.2^\circ$
- $\Delta \gamma = 0.08^\circ$
Diffraction Geometry

**z-axis geometry***

- $q_x = k \{\cos(\beta)\cos(\psi) - \cos(\alpha)\}$
- $q_y = k \{\cos(\beta)\sin(\psi)\}$
- $q_z = k \{\sin(\alpha) + \sin(\beta)\}$

*The angles coincide with the respective diffractometer axes*

**Pseudo z-axis geometry**

- $q_x = k \{\cos(\gamma)\sin(2\theta)\}$
- $q_y = k \{\cos(\gamma)\cos(2\theta) - 1\}$
- $q_z = k \{\sin(\gamma)\}$

For small $\alpha$, $\gamma$ & arbitrary $2\theta$:

- $\beta = \gamma - \alpha \{\cos(2\theta)\}$

Surface normal
X-ray Reflectivity

XRR map from a Ru(bpy)$_3$ Device

XRR profile from a Ru(bpy)$_3$ Device

Rocking Scan

Integrated Intensity, a.u.

Integrated Intensity, a.u.

-0.1 0.0 0.1 0.2 0.3 0.4 0.5

-0.1 0.0 0.1 0.2 0.3 0.4 0.5

\( \lambda = 1.34 \, \text{Å} \)

FWHM 0.06 deg

Spill over
Reducing the Background

\[ \alpha = 0.13^\circ \]

\[ \alpha = 0.18^\circ \]

\[ \alpha = 0.27^\circ \]

\[ \alpha = 0.4^\circ \]
GIWAXS of OLED devices
(Grazing-Incidence Wide-Angle X-ray Scattering)

**Analysis:**
1. Bragg’s Law - \(2d \sin(\theta/2) = n\lambda\)
   - \(d\) = distance (Å) between diffracting planes → Ru-Ru minimum distance
2. Scherrer Eq. - \(B(2\theta) = 0.89\lambda / L \cos(\theta)\)
   - \(B(2\theta)\) = FWHM
   - \(L\) = average crystal size (Å) (cube)
   - \(\lambda\) = wavelength (Å)
Crystal Structure - Ru(bpy)$_3$ $\text{[Ru(bpy)$_3$]}^{2+}$, $\alpha = 0.13$ deg

Integrated intensity, a.u.

<table>
<thead>
<tr>
<th>2 $\theta$, deg</th>
<th>Measured</th>
<th>Calculated</th>
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<tr>
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<td></td>
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</tr>
<tr>
<td>10</td>
<td></td>
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<tr>
<td>15</td>
<td></td>
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<tr>
<td>20</td>
<td></td>
<td></td>
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<tr>
<td>25</td>
<td></td>
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</table>

$L = 41 \text{Å}$

---

8.29°

---

Space Group $P\overline{3}c1$ (No. 165)

\begin{align*}
& a=b = 10.76 \text{Å} \\
& c = 16.36 \text{Å} \\
& \alpha = \beta = 90^\circ \\
& \gamma = 120^\circ
\end{align*}

---

\[ \bar{1}10 - d=9.32 \text{Å} \]
GIWAXS of OLED devices
(Grazing-Incidence Wide-Angle X-ray Scattering)

ITO device, $\alpha = 0.15$ deg

Integrated intensity, a.u.

$d_1 = 9.4\,\text{Å}$ $L_1 = 41\,\text{Å}$
$d_2 = 6.6\,\text{Å}$ $L_2 = 17\,\text{Å}$
$d_3 = 4.3\,\text{Å}$ $L_3 = 18\,\text{Å}$

[Ru(bpy)$_3$]$^{2+}$ $\alpha = 0.13$

$I$ $2$ $3$

Integarted intensity, a.u.
GIWAXS of OLED devices
(Grazing-Incidence Wide-Angle X-ray Scattering)

[Ru(diethylphenyl-bpy)$_3$]$^{+2}$, $\alpha = 0.15$

Integrated intensity, a.u.

$\beta$, deg

$2 \theta$, deg

$[Ru(diethylphenyl-bpy)_3]^{+2}$ $\alpha = 0.15$

$\beta$, deg

$2 \theta$, deg

$[Ru(ethylphenyl-bpy)_3]^{+2}$ $\alpha = 0.15$

$\beta$, deg

$2 \theta$, deg

$d$ (Å) $L$ (Å)

$d_1 = 12.4\,\text{Å}$ $L_1 = 32\,\text{Å}$

$d_2 = 4.9\,\text{Å}$ $L_2 = 18\,\text{Å}$

$d_1 = 10.1\,\text{Å}$ $L_1 = 28\,\text{Å}$

$d_2 = 5.2\,\text{Å}$ $L_2 = 9\,\text{Å}$
GIWAXS on OLED devices

\( [\text{Ru(dtbutbpy)}_3]^{+2} \alpha = 0.15 \)

\( [\text{Ru(2,2'-bpy)}_2(4,4'-bpy)]^{+2} \alpha = 0.15 \)

\( \beta \) 0.24 to 2.14 deg

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>L (Å)</th>
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<tr>
<td>( d_1 = 11.8\text{Å} )</td>
<td>( L_1 = 33\text{Å} )</td>
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<td>( d_2 = 5.2\text{Å} )</td>
<td>( L_2 = 27\text{Å} )</td>
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<td>( L_1 = 37\text{Å} )</td>
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<td>( d_2 = 6.2\text{Å} )</td>
<td>( L_2 = 8\text{Å} )</td>
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<tr>
<td>( d_3 = 4.2\text{Å} )</td>
<td>( L_3 = 18\text{Å} )</td>
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GIWAXS on OLED devices
(Grazing-Incidence Wide-Angle X-ray Scattering)

[Ru(dmbpy)(bpy)$_2$]$^{+2}$ $\alpha = 0.15$

[Ru(4,4’pentylbpy)(bpy)$_2$]$^{+2}$ $\alpha = 0.15$

[RU(4,4’pentylbpy)(bpy)$_2$]$^{+2}$ $\alpha = 0.15$

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<td>25.86</td>
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<td>10</td>
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<tr>
<td>35.00</td>
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<tr>
<td>40.00</td>
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<td>45.00</td>
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<td>70.00</td>
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<td>75.00</td>
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<tr>
<td>80.00</td>
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<td>13Å</td>
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<td>28Å</td>
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<tr>
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<td>17Å</td>
</tr>
<tr>
<td>4.4Å</td>
<td>18Å</td>
</tr>
<tr>
<td>Molecules</td>
<td>L, ang</td>
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<td>-----------------------------------</td>
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<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>41.4</td>
</tr>
<tr>
<td>[Ru(2,2'-bpy)2(4,4'-bpy)$_2$]$^{2+}$</td>
<td>35.7</td>
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<td>33.4</td>
</tr>
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<td>[Ru(diethylphenyl)$_3$]$^{2+}$</td>
<td>32.1</td>
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Correlation with Device Efficiency (?)
Summary

• We have characterized device-grade thin films with reciprocal space mapping under grazing incidence, and could find various characteristic d-spacings.

• The crystalline order turned out to be short-range, with similar crystallite sizes for all the molecules studied (20-40 ang).

• We observe an increase in the device efficiency as a function of the average Ru-Ru distance (within the range studied), this might suggest that there could be an optimal distance between Ru chromophores that minimizes self-quenching.
Acknowledgements

- Prof. Héctor D. Abreuña
- Prof. Joel D. Brock
- Prof. George G. Malliaras
- Samuel Flores (synthesis-Abruña Lab)
- Alon Gorodetsky and Jason Slinker (Malliaras Lab)

- **G-line students**, G-line staff, CHESS staff, Brian Clasby, Jerry Houghton

**Funding:**

- NSF
- CHESS - G Line
- CCMR
Old Experimental Setup
G2 cave & transfer pipe installed (Aug 03)

Jerry & Brian
G2 mono installation (Summer 04)

Old Mono Setup

New Mono Setup
Incident Beam:
$10^{12}$ photons/sec

Transmitted Beam:
~ 96 %

Reflected Beam:
~ 2.5 %

Be single crystal

0.03° mosaic: $\Delta E/E \approx 0.1\%$
Quantum Efficiency = $\eta = 100 \times \frac{N_{ph}}{N_{el}} \%$

$L = energy\ emitted\ per\ time\ (W)$

$N_{el} = \frac{I(A)}{e}$

$N_{ph} = \frac{L \lambda}{hc}$
Available Energy for Emission

\[- \Delta H^\circ = E^\circ_{\text{oxid.}} - E^\circ_{\text{red.}} - T \Delta S^\circ\]

\[\Delta E \approx 2.57 \text{ eV} \rightarrow 474 \text{ nm}\]

\[\text{[Os(bpy)}_2\text{(dppe)}]^+ 2\]

\[\sigma^* \quad \longrightarrow \quad e_g \quad \downarrow \quad \pi^*\]

\[\Delta E \approx 2.57 \text{ eV}\]

\[\pi \quad \uparrow \uparrow \uparrow \uparrow \quad t_{2g}\]
Efficiency vs. Film Thickness

[Chart showing external quantum efficiency (%) vs. thickness (nm) for [Ru(bpy)$_3$](PF$_6$)$_2$ Films.

Layers indicated: Au, Organic, ITO.