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Organic-complexes and nanoparticles to improve solar cell efficiency

Preliminary findings

Prof. Polizzi Stefano

Dr. Luca Bellotto

Dr. Isidora Freris



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introduction

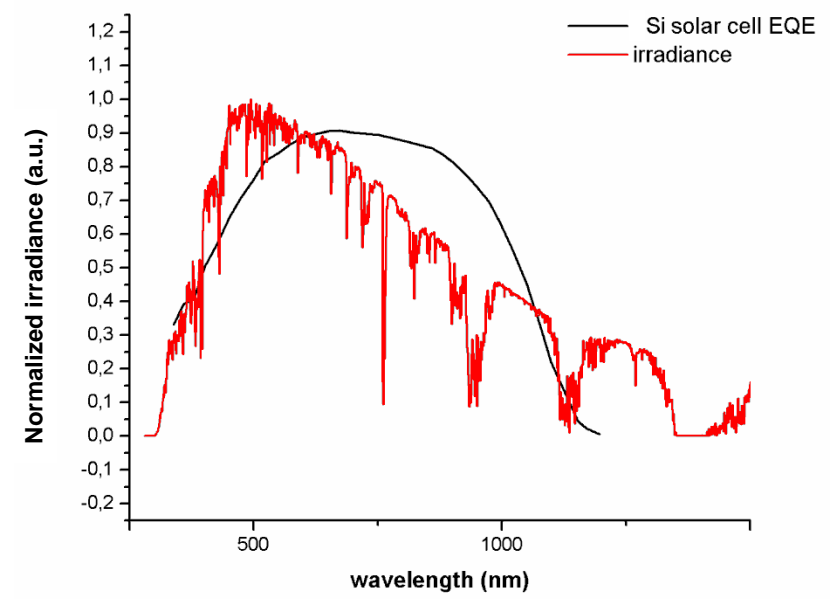
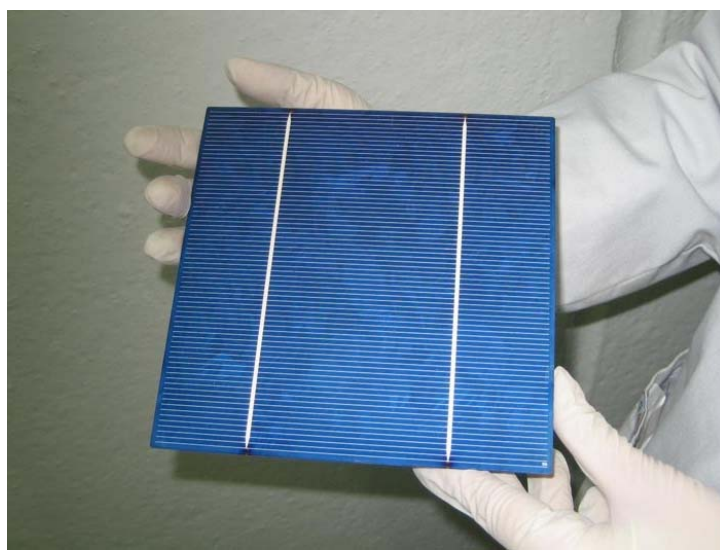
Synthesis
results

spectra

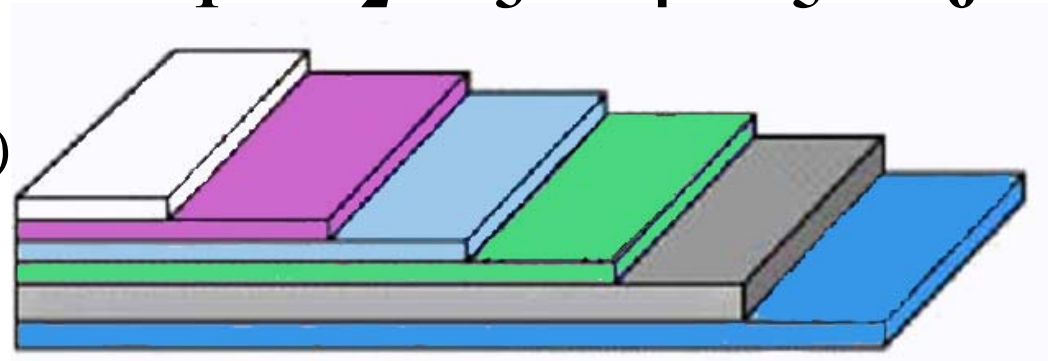
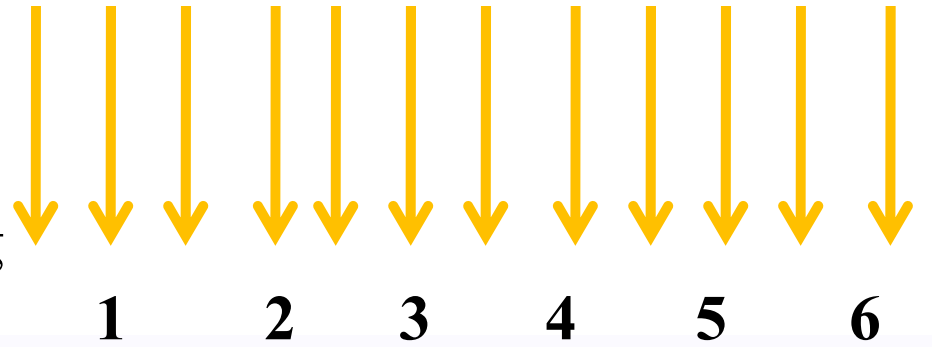
perspective

Organic host
materials

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- 1 Cover glass
- 2 EVA encapsulant
- 3 Antireflecting coating
- 4 Contact grid
- 5 Si (n and p doped)
- 6 Back contact





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Chromophore design

- Emission in the correct region (600-800 nm)
- Tuning of absorption between 300 and 450 nm
- High thermal, chemical and UV stability
- Easy to synthesize and with inexpensive raw materials
- Versatile for use in various matrices

introduction

Synthesis
results

spectra

perspective

Organic host
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Chromophore design

- Use of Eu^{3+} core.
- Use of quinoline based and scorpionate ligands
- Use of O-M ligand
- Full coordination sphere
- Unsaturated chromophores for inorganic matrix

introduction

Synthesis
results

spectra

perspective

Organic host
materials

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introduction

Synthesis
results

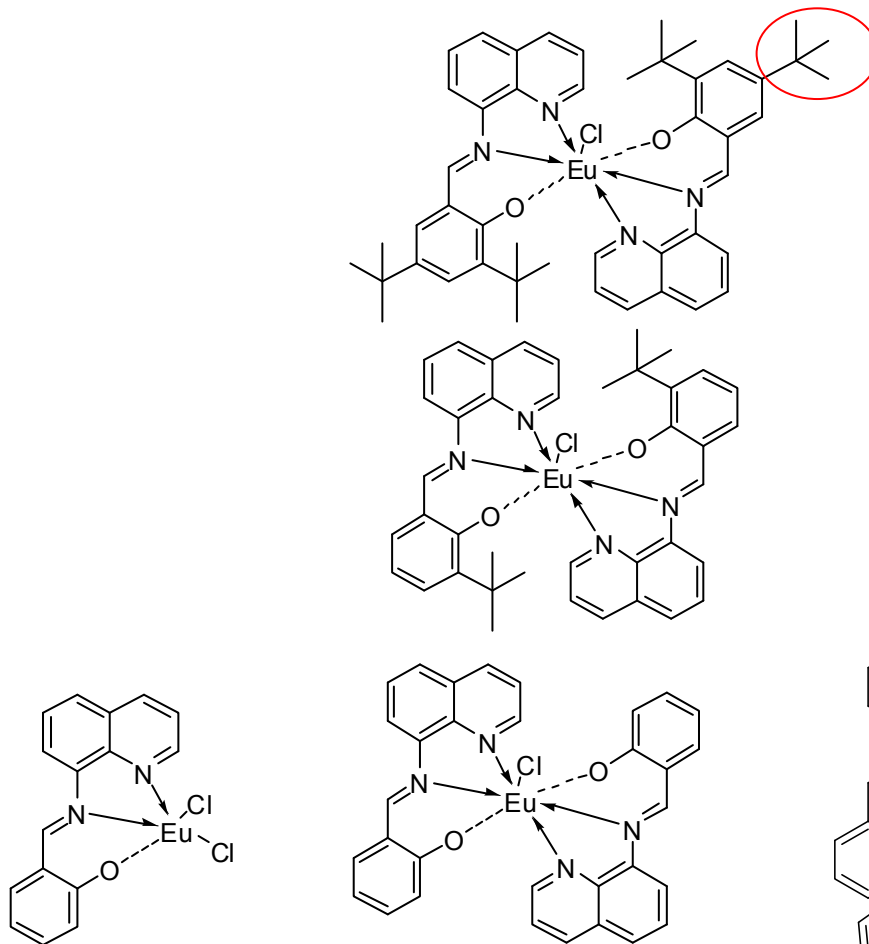
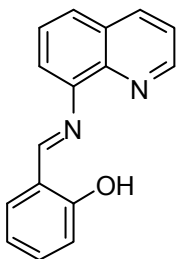
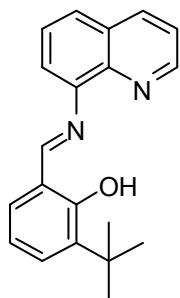
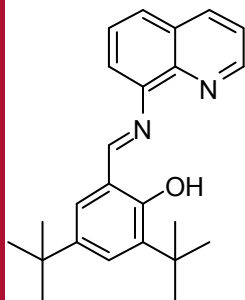
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Quinoline based ligands



Decreasing of tert-butyle

Increasing number of ligands

Scorpionate complexes

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Synthesis
results

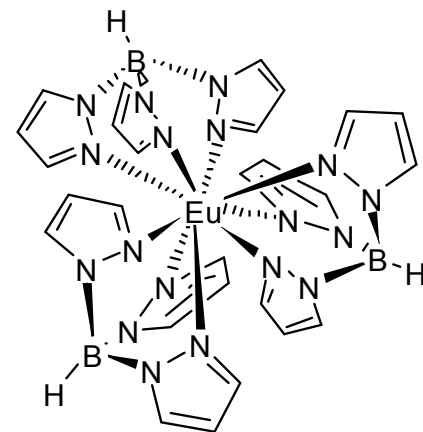
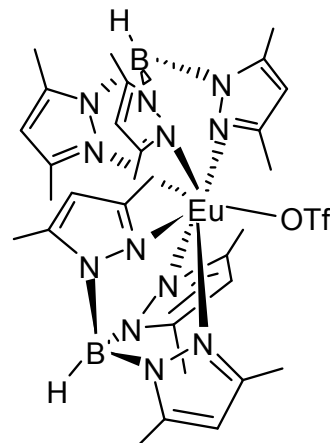
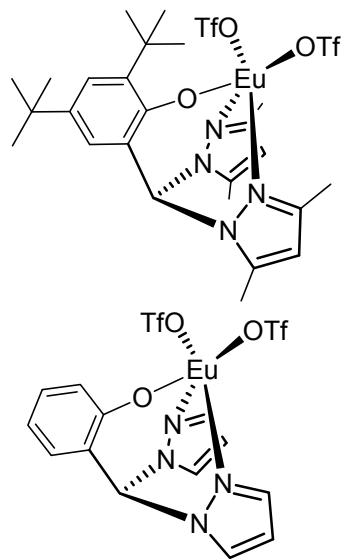
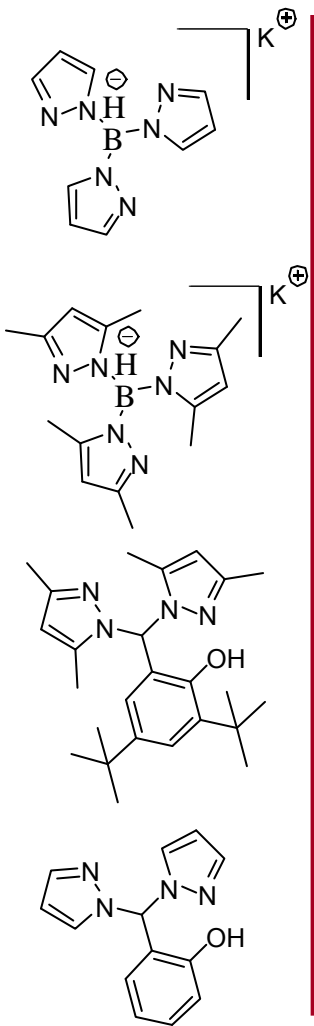
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perspective

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Scorpionate complexes

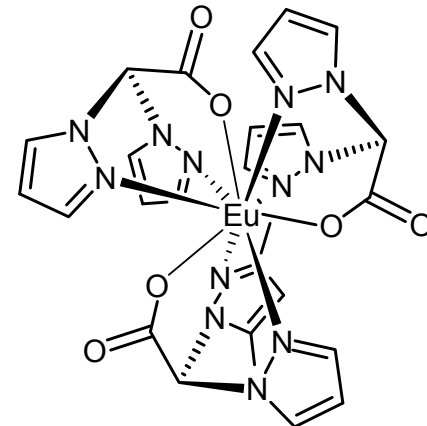
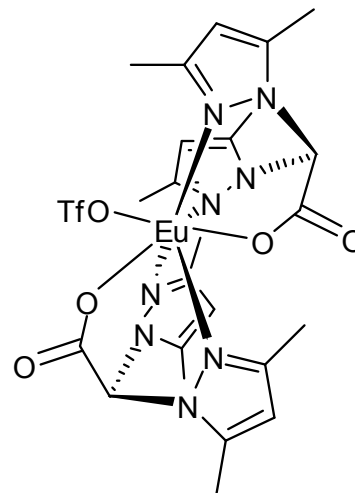
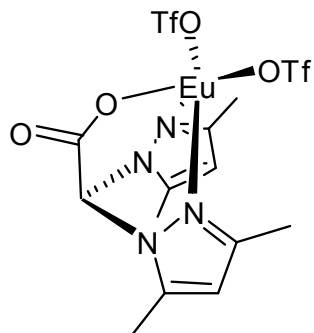
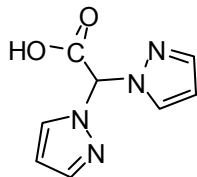
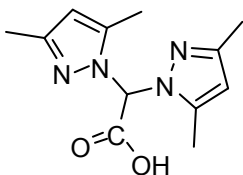
introduction

Synthesis
results

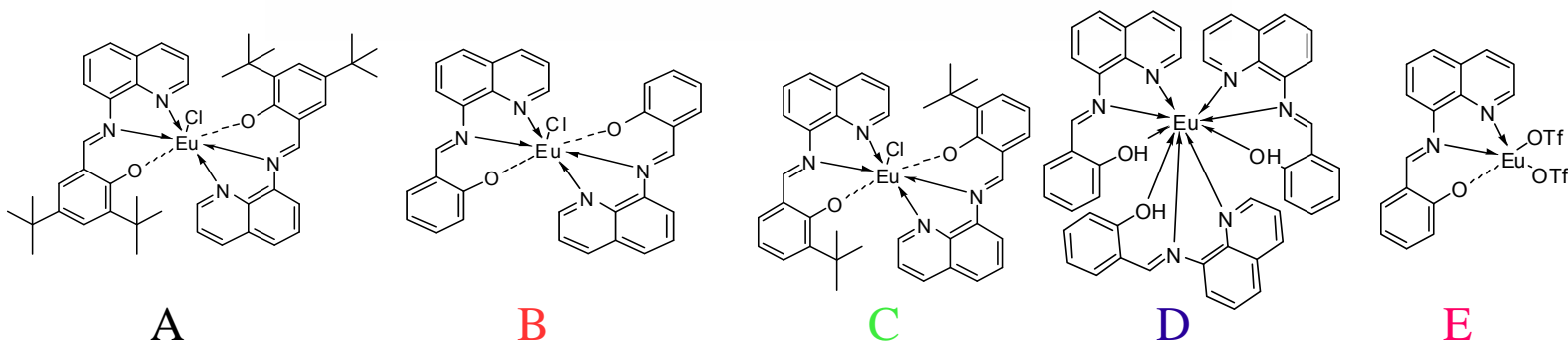
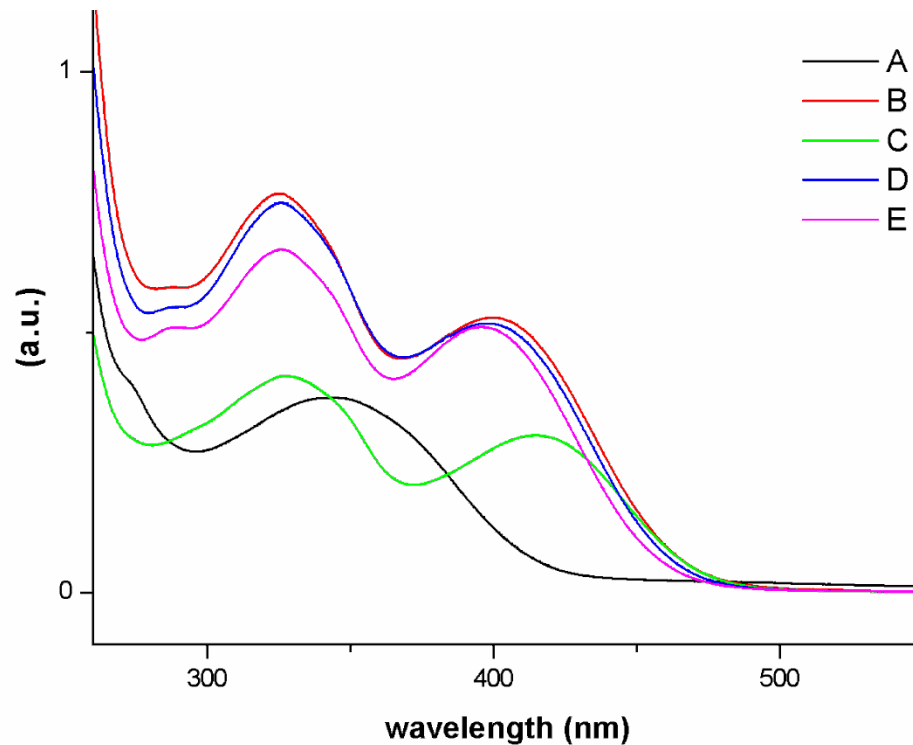
spectra

perspective

Organic host
materials



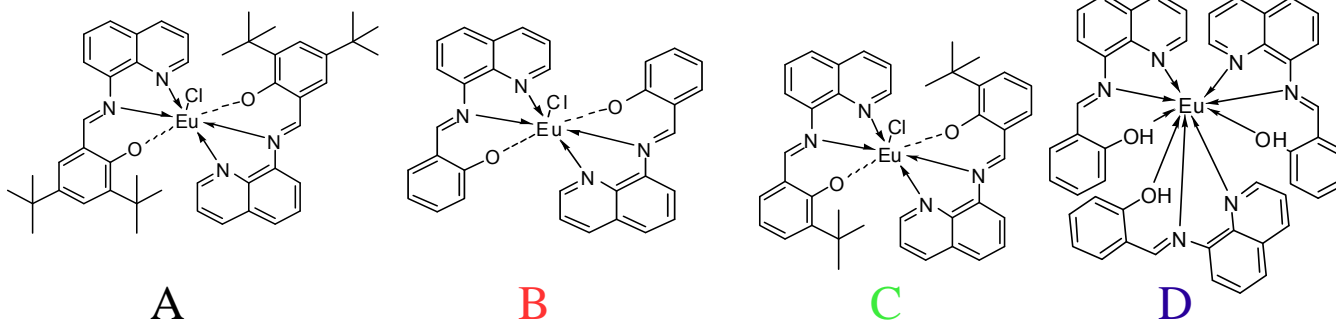
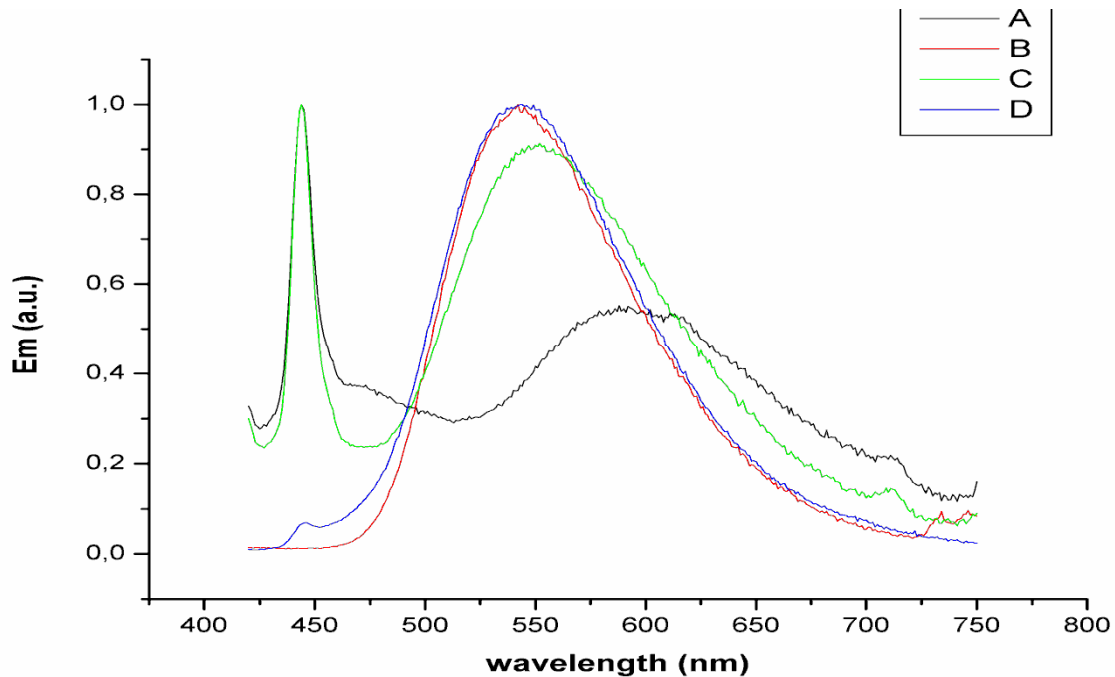
Quinoline complexes Abs.



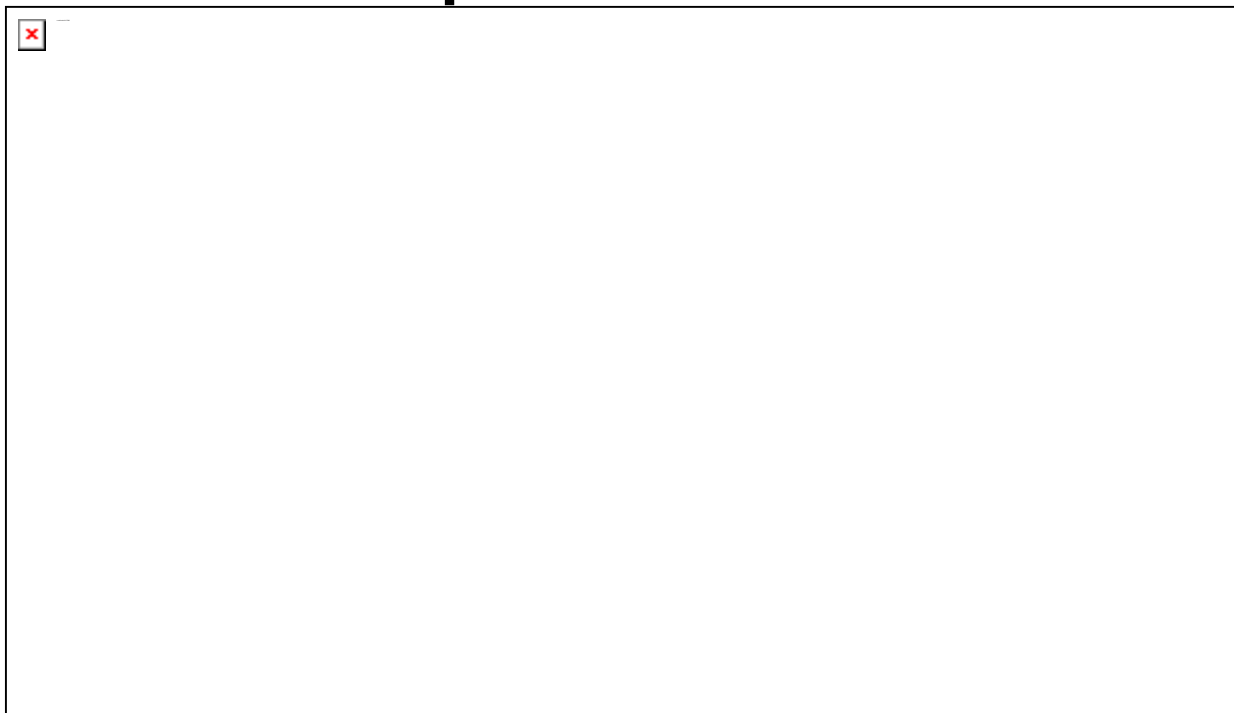


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Quinoline complexes Em.



Scorpionates Abs.



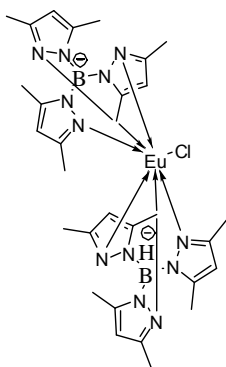
introduction

Synthesis
results

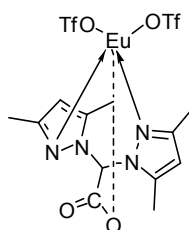
spectra

perspective

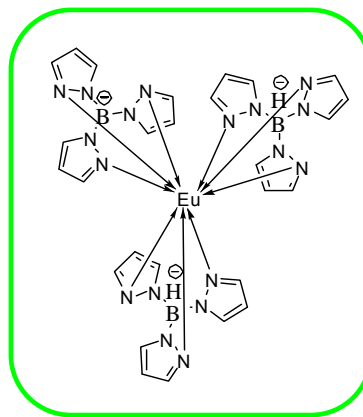
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materials



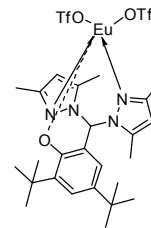
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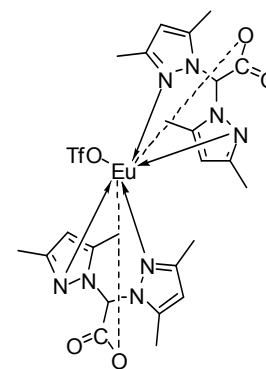
2



3



4



5

Scorpionates Em.

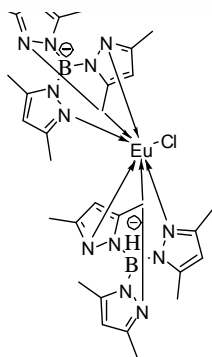
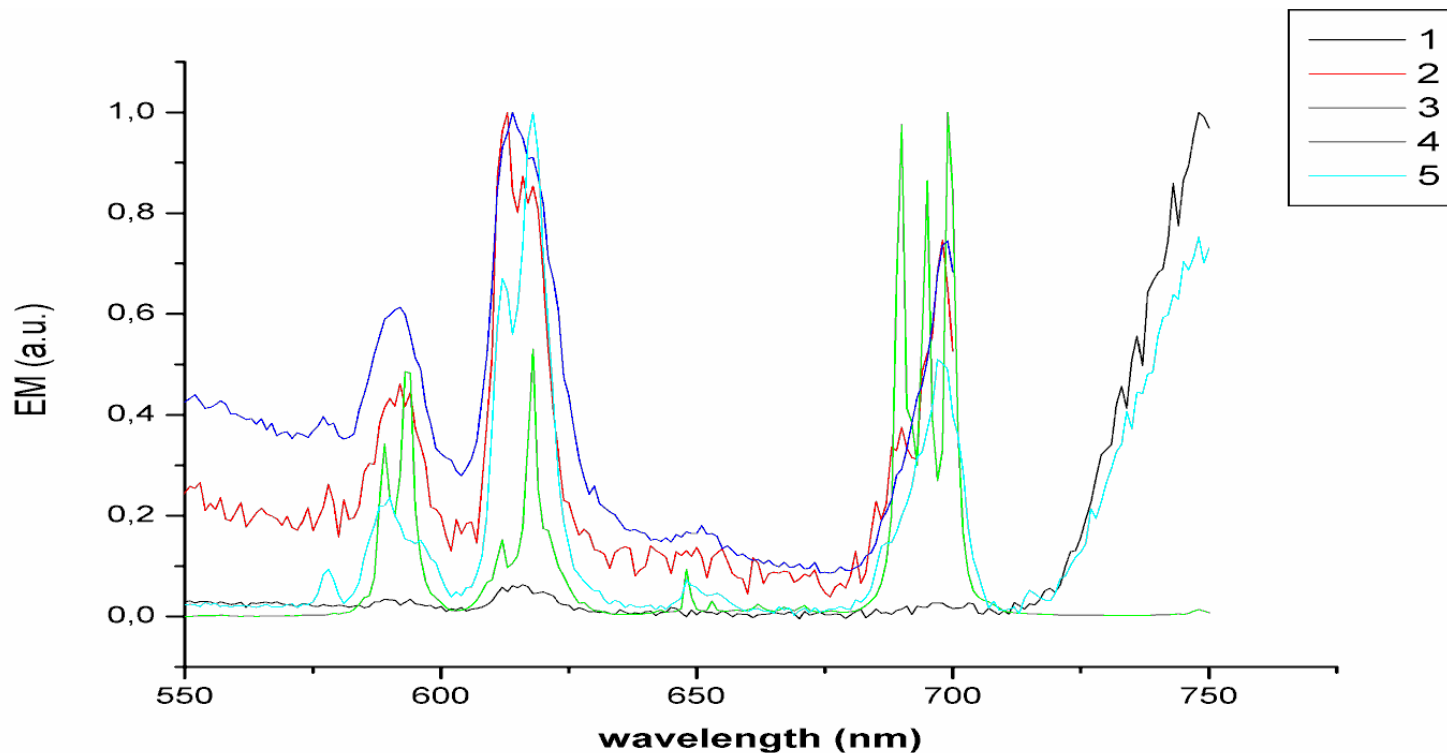
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Synthesis
results

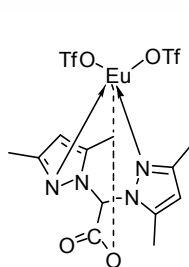
spectra

perspective

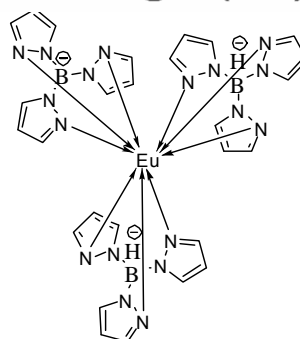
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materials



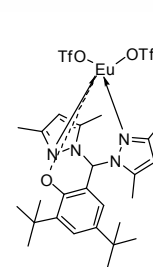
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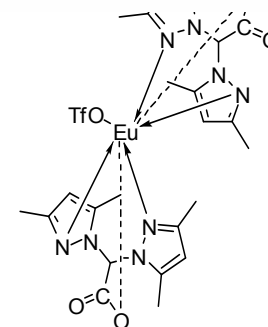
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3



4



5

Work in progress

functionalization of trispyrazolylborate to shift
the Abs. wavelength and/or fix the complex
into various matrices

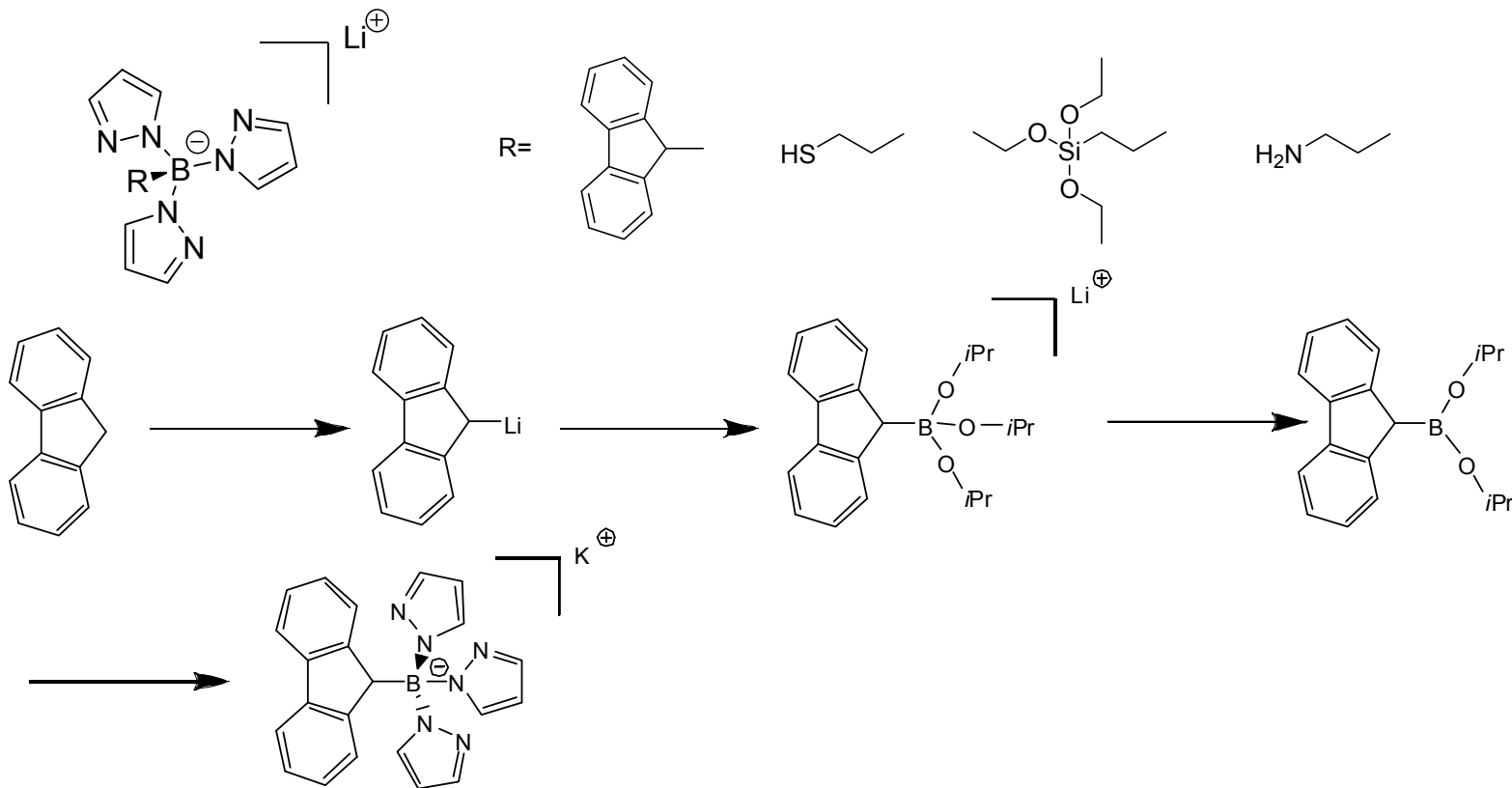
introduction

Synthesis
results

spectra

perspective

Organic host
materials





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Work in progress

Modification of Pyrazol ring in the ligand to
tune the absorption wavelength

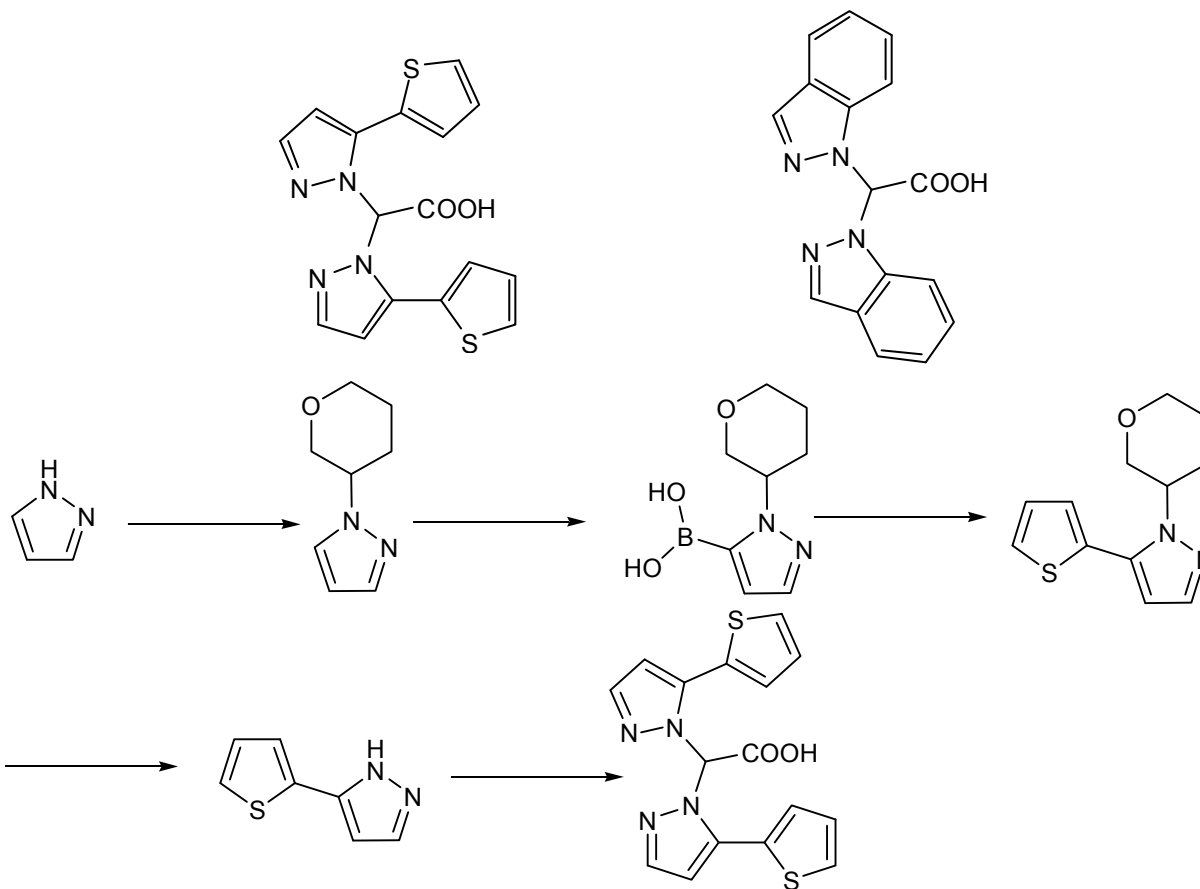
introduction

Synthesis
results

spectra

perspective

Organic host
materials



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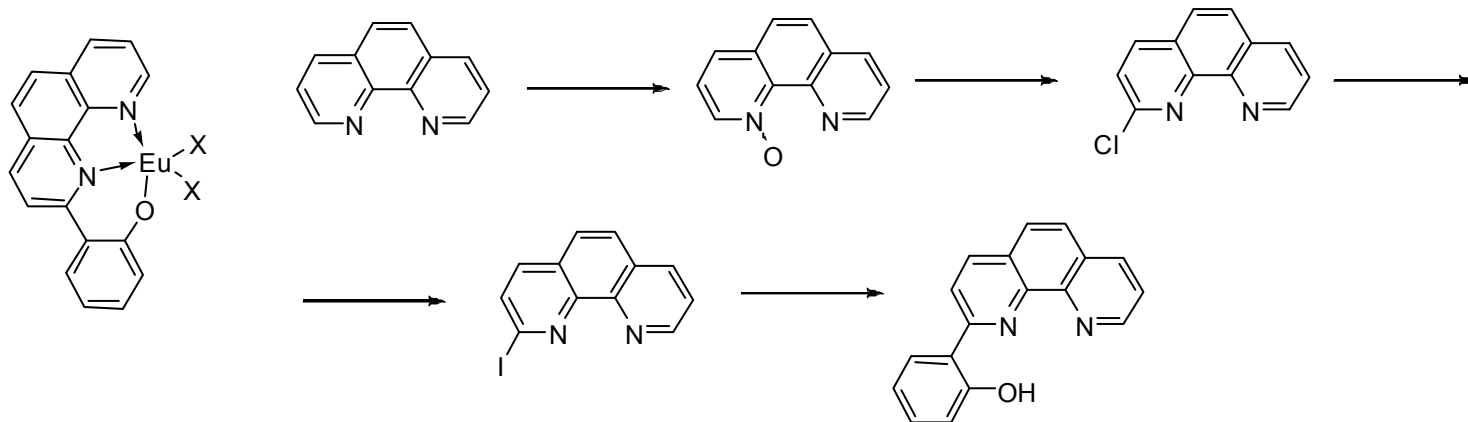
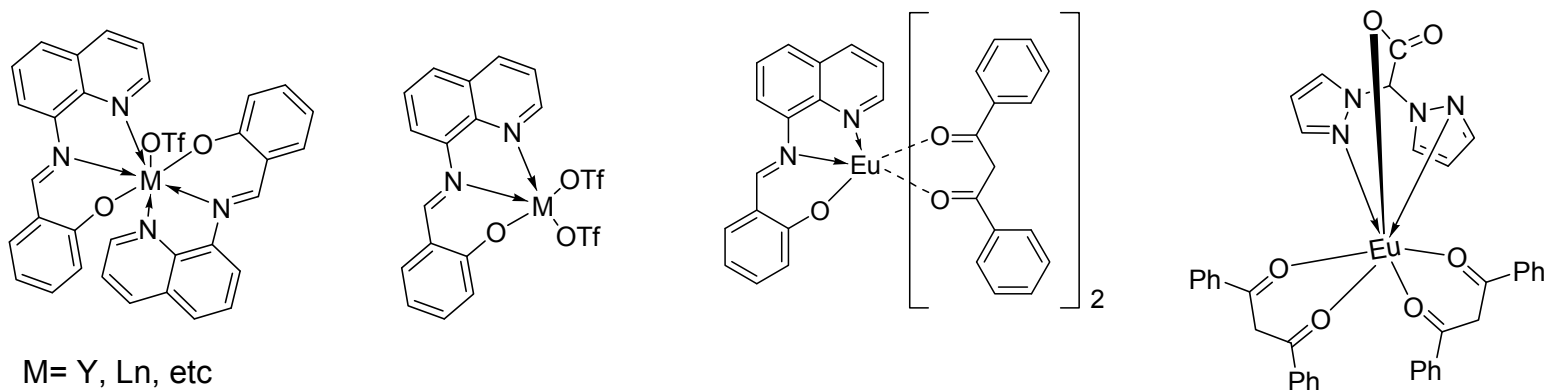
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Work in progress

Use of different metals to modify Abs. and Em.
Wavelength.

Fill coordination sphere with different ligands

New phenanthroline based ligands



introduction

Synthesis
results

spectra

perspective

Organic host
materials



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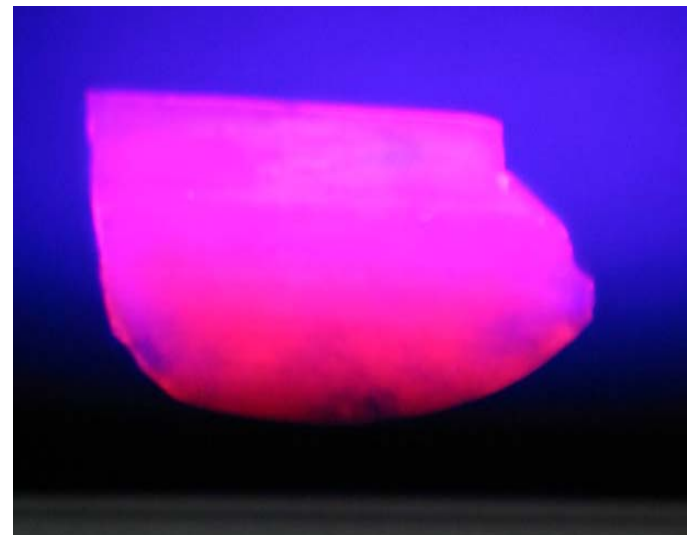
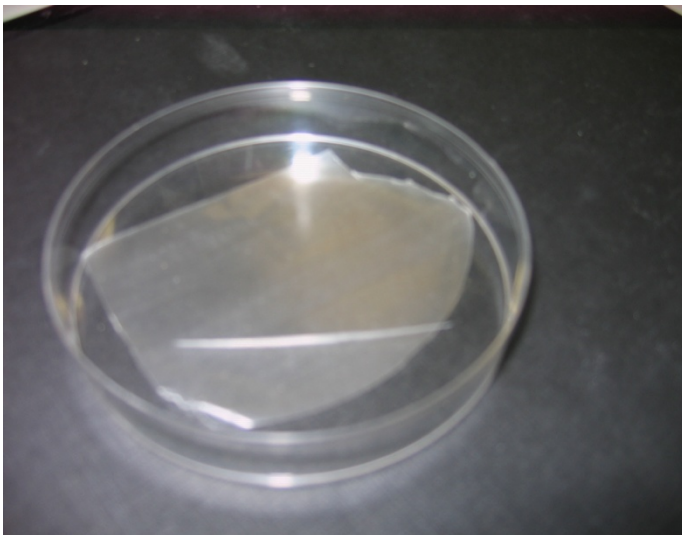
introduction

Synthesis
results

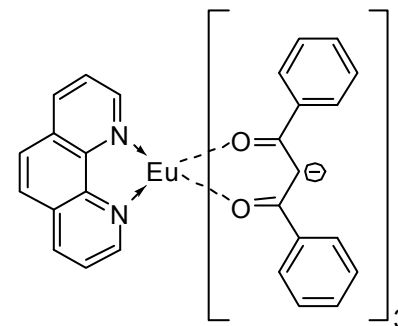
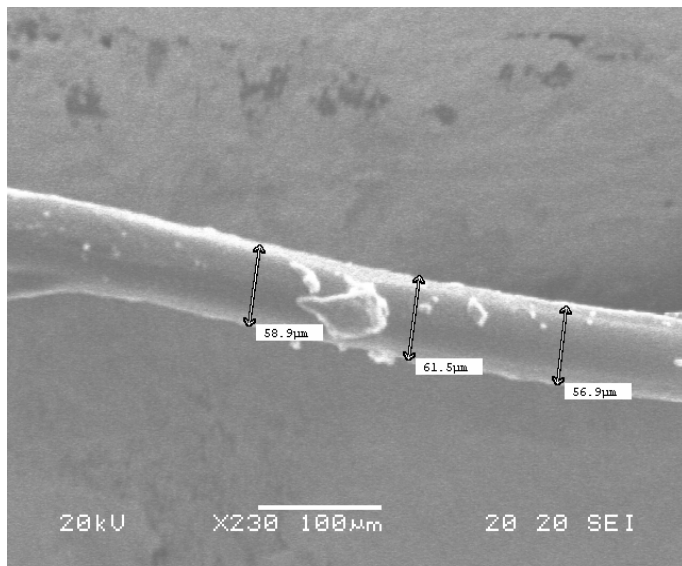
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perspective

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UV light 368 nm



EVA: SP-Sealant (Sekusui-Chemical Co.)
Complex: purchased by Sigma-aldrich

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Inorganic Host Materials

- Glasses / Ceramics
- Rare earth doped
- Oxides
 - Silica (SiO_2)
 - Zirconia (ZrO_2)

Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

Mes.: e.g. 1

Mes.: e.g. 2

Summary

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Host Matrices

Interaction with host:

- Enhanced luminescence
- Increase in quantum efficiency
- Increase in emission lifetimes
- Protective shell – reduced quenching
- Bulk versus nano-structured (confinement effect)

Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

Mes.: e.g. 1

Mes.: e.g. 2

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Inorganic Host Materials

Synthesis

Host Materials

Sol-Gel Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure Directing (SD)

Mes.: e.g. 1

Mes.: e.g. 2

Summary

1. Sol-gel processing
 - Non-porous materials
2. Surfactant templating or Structure directing
 - Porous materials

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Sol-Gel Process

- Hydrolysis and polycondensation of metal complexes or metal alkoxides
- One-pot synthesis (co-condensation)
- Product type depends on pH, temperature and concentration

Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

Mes.: e.g. 1

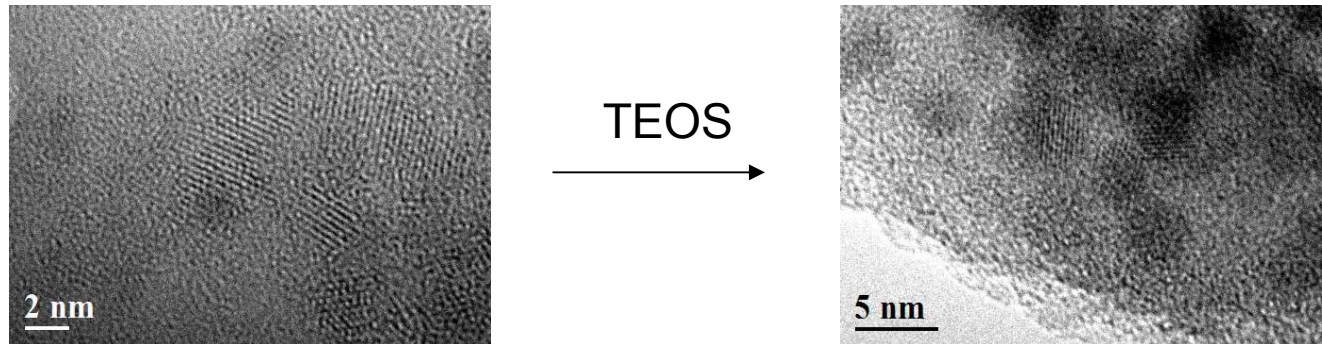
Mes.: e.g. 2

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Sol-Gel Process: Example 1

- Colloidal $\text{ZrO}_2:\text{Eu}^{3+}$ embedded in amorphous SiO_2 matrix



- 5 nm particles dispersed in host matrix
- Narrow Eu emission bands
- High Stokes shift between excitation and emission
- Reduction of concentration quenching and increase of quantum efficiency

Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

Mes.: e.g. 1

Mes.: e.g. 2

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Host Materials

Sol-Gel
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Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

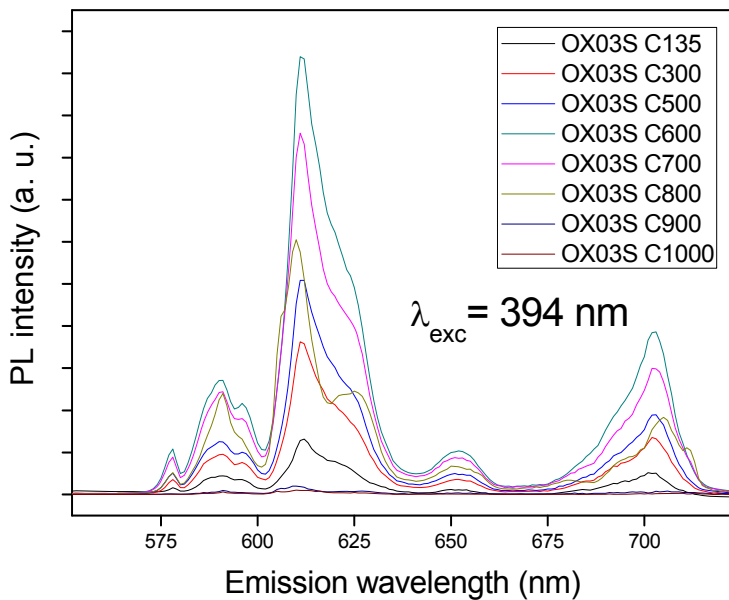
Mes.: e.g. 1

Mes.: e.g. 2

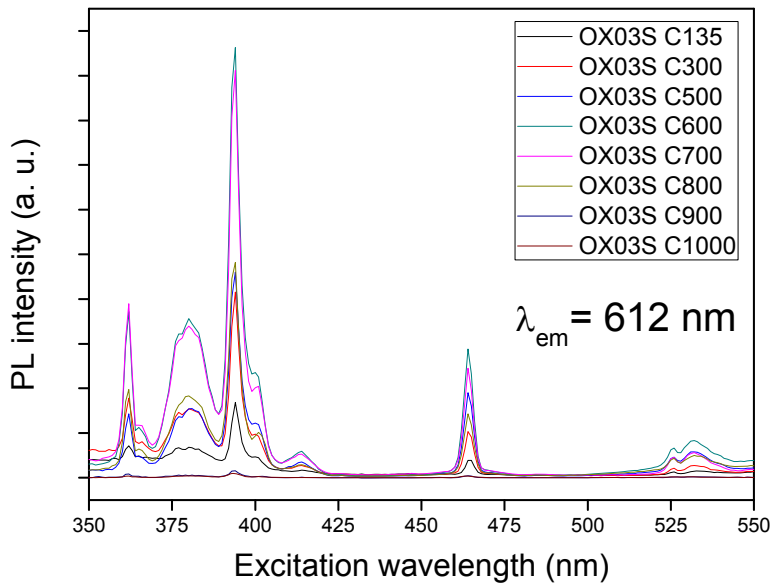
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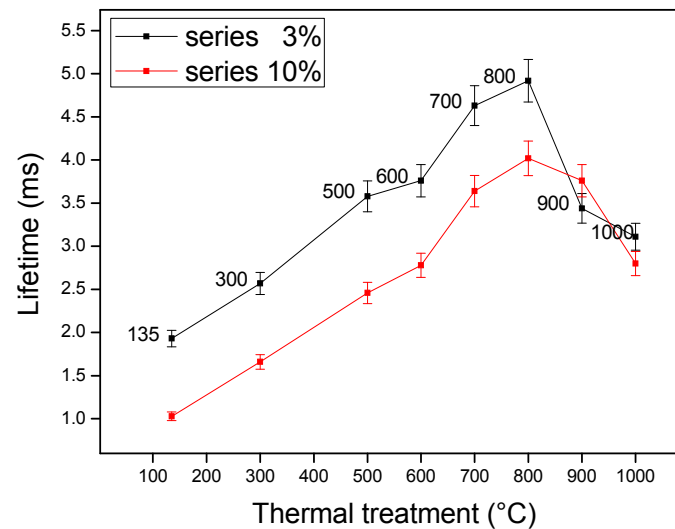
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High Stokes shift



$\langle \tau \rangle$ up to 5 ms





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Sol-Gel Process: Example 2

- Luminescent $\text{ZrO}_2:\text{Eu}^{3+}$ nanoparticles
- $\text{Zr}(\text{OBU})_4$ hydrolysis/condensation with *in situ* Eu^{3+} doping
- Calcination at 700 °C provides polycrystalline material

Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

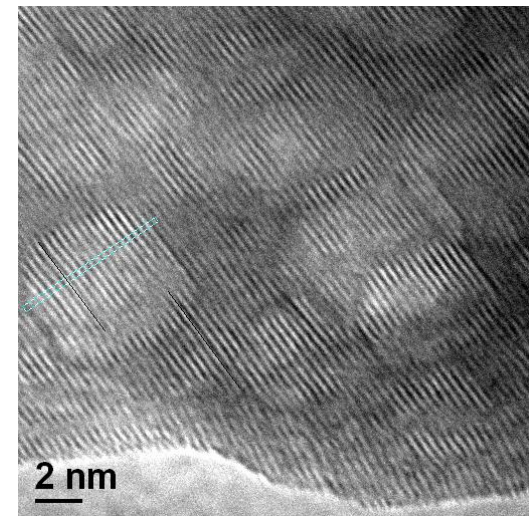
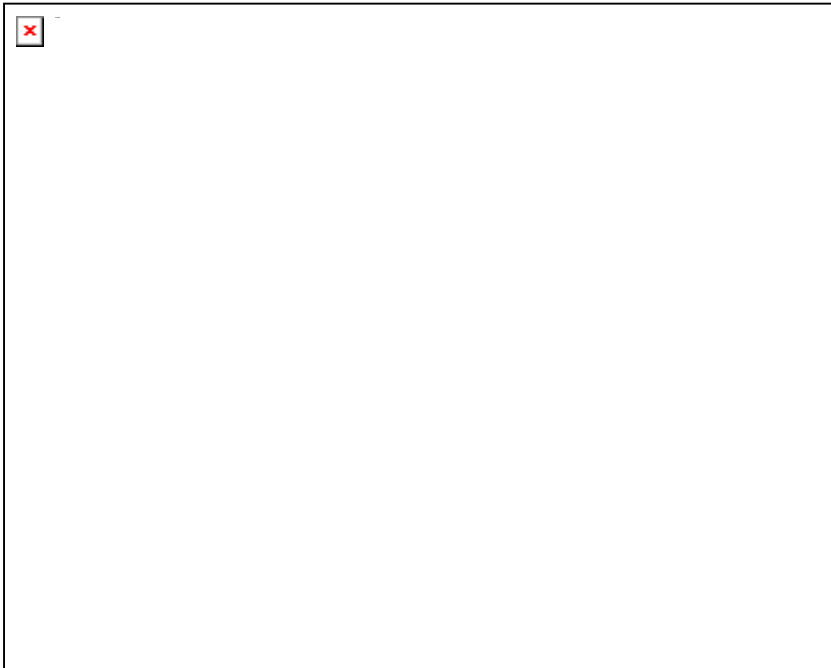
Mes.: e.g. 1

Mes.: e.g. 2

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Sol-Gel Process: Example 2

Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

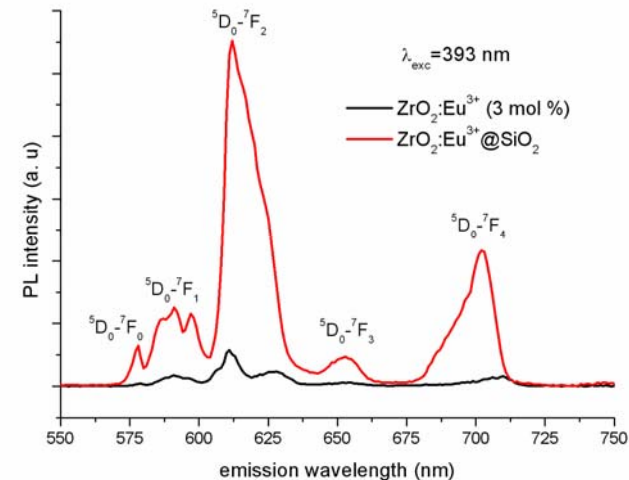
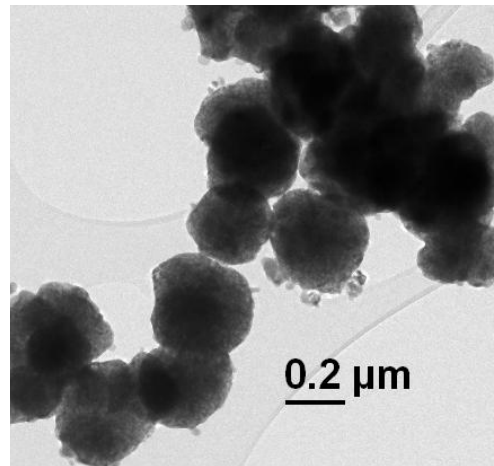
Mes.: e.g. 1

Mes.: e.g. 2

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Sample Composition	Theoretical % Eu ³⁺ ions	612 nm band intensity (5D ₀ →7F ₂)	<τ> ms
ZrO ₂ :Eu ³⁺	3	1.15 x 10 ⁵	1.18
ZrO ₂ :Eu ³⁺ @SiO ₂	3	1.1 x 10 ⁶	1.56
ZrO ₂ :Eu ³⁺ @SiO ₂	3	1.09 x 10 ⁶	1.62
ZrO ₂ :Eu ³⁺	6	2.98 x 10 ⁵	2.76



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Inclusion in Solar Cell?

- Materials could be introduced into transparent glass or polymers
- Thin films could be prepared via spin coating or dip coating
- Reduced scattering for materials with same refractive index

Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

Mes.: e.g. 1

Mes.: e.g. 2

Summary



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Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

Mes.: e.g. 1

Mes.: e.g. 2

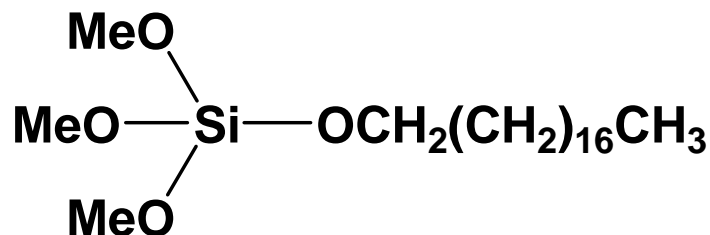
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Surfactant Templating/ Structure Directing Method

- Mesoporous = 2-50 nm pore size
Microporous = < 2 nm pore size
- Sol-gel synthesis in the presence of organic framework:
 - Micelles
 - Silane coupling agents

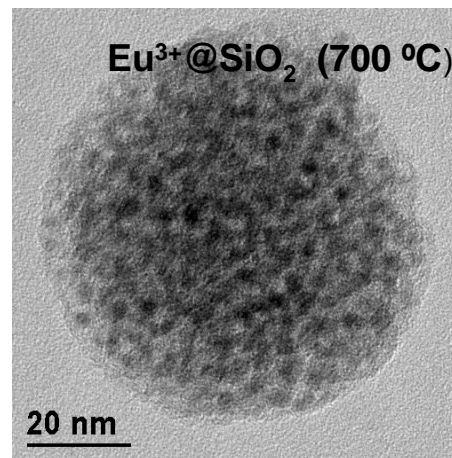
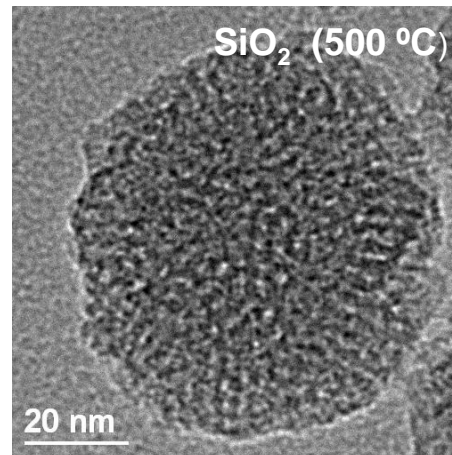




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Mesoporous SiO₂: 1

- Mesoporous SiO₂ nanoparticles via surfactant templating method¹
- Wet impregnation of salt solutions
- Calcination stabilizes solid solution (s.s.) oxide phase



Sample	s.s.	BET Surface area (m ² /g)
SiO ₂ C500	n/a	980
Eu ³⁺ @SiO ₂ C700	Zr _{0.92} Eu _{0.08} O _{1.97}	730
Er ³⁺ @SiO ₂ C1000	Zr _{0.86} Er _{0.04} Yb _{0.1} O _{1.93}	63

1. Huo *et al.*, *Chem. Mater.* **2009**, 21, 3823.

Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

Mes.: e.g. 1

Mes.: e.g. 2

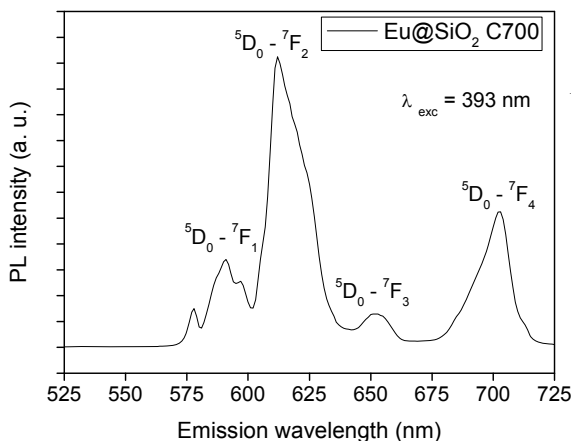
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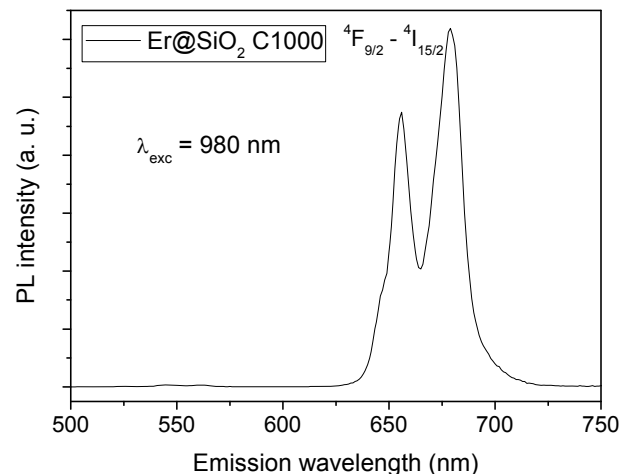
Mesoporous SiO₂: 1

PL emission spectra of impregnated mesoporous silica



- **Europium:** narrow emission bands
- 18.5 wt% s.s. in SiO₂
- 1.05×10^6 for 612 nm band intensity ($^5D_0 \rightarrow ^7F_2$)

- **Erbium:** emission in the visible range by IR excitation (**upconversion**)
- 60 wt% s.s. in SiO₂



Host Materials

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Process

Sol-Gel: e.g. 1

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Mes.: e.g. 2

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Mesoporous SiO₂: 2

- Wet impregnation of tris(dibenzoylmethane) mono(1,10-phenanthroline)europium(III): 5 mM in DCM
- APTES functionalized mesoporous SiO₂

Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

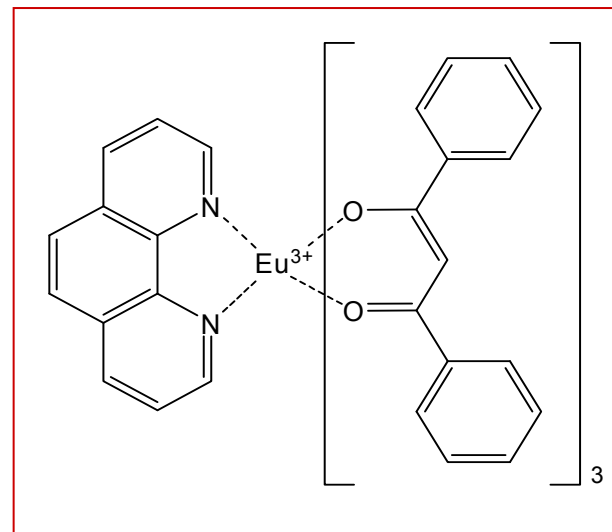
Structure
Directing (SD)

Mes.: e.g. 1

Mes.: e.g. 2

Summary

Sample	612 nm band intensity (⁵ D ₀ → ⁷ F ₂)*	<τ> ms
Complex		0.10
Complex in EVA	5.45 x 10 ⁵	0.18
Mes.2: complex in SiO ₂	1.24 x 10 ⁷	0.65





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Mesoporous SiO₂: 2

Shift to higher wavelength in APTES-functionalized mesoporous SiO₂



Host Materials

**Sol-Gel
Process**

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

**Structure
Directing (SD)**

Mes.: e.g. 1

Mes.: e.g. 2

Summary

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PL Summary

Sample	Amount Eu ³⁺	612 nm band intensity (⁵ D ₀ → ⁷ F ₂)*	<τ> ms
SG.1: ZrO ₂ :Eu ³⁺ (5nm)@SiO ₂	3% Eu C600	2.08 x 10 ⁶	3.76
SG.1: ZrO ₂ :Eu ³⁺ (5nm)@SiO ₂	3% Eu C700	1.72 x 10 ⁶	4.63
SG.2: ZrO ₂ :Eu ³⁺ (250nm)	3 % Eu	5.3 x 10 ⁶	1.18
SG.2: ZrO ₂ :Eu ³⁺ (250nm) coated with SiO ₂	3 % in SiO ₂	1.88 x 10 ⁷	1.56
Mes.1: Zr _{0.92} Eu _{0.08} O _{1.97} in mes. SiO ₂	18.5 % s.s. in SiO ₂	1.05 x 10 ⁶	2.19
Mes.2: complex in SiO ₂	5mM in SiO ₂	1.24 x 10 ⁷	0.65

*measured with same experimental conditions

Host Materials

Sol-Gel
Process

Sol-Gel: e.g. 1

Sol-Gel: e.g. 2

Structure
Directing (SD)

Mes.: e.g. 1

Mes.: e.g. 2

Summary

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