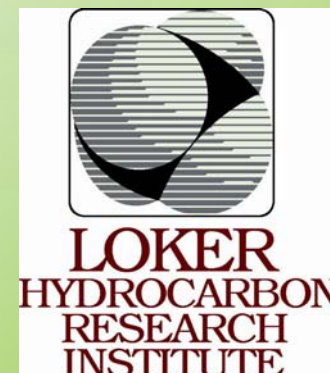
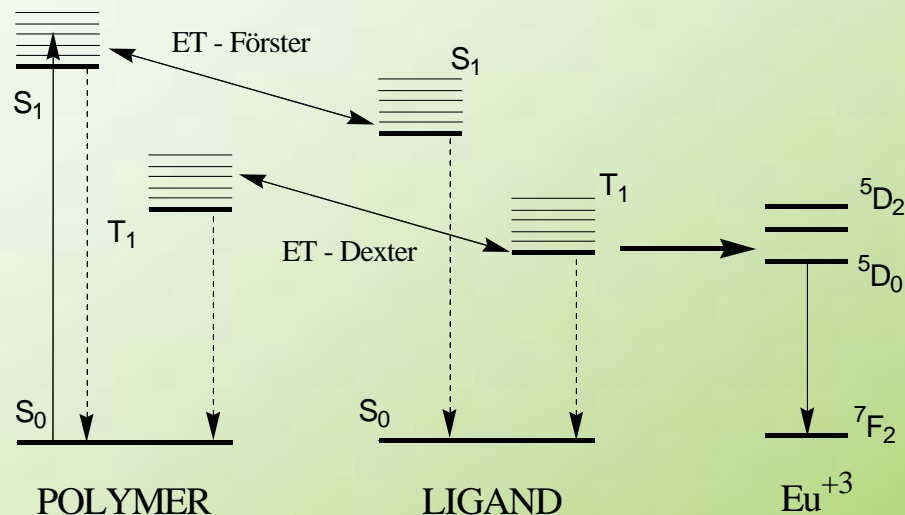


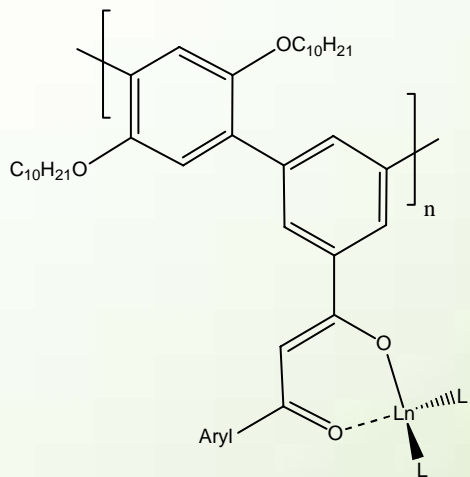
Design and Syntheses of Polymeric Materials for Visible and Near-Infrared Emitting Applications



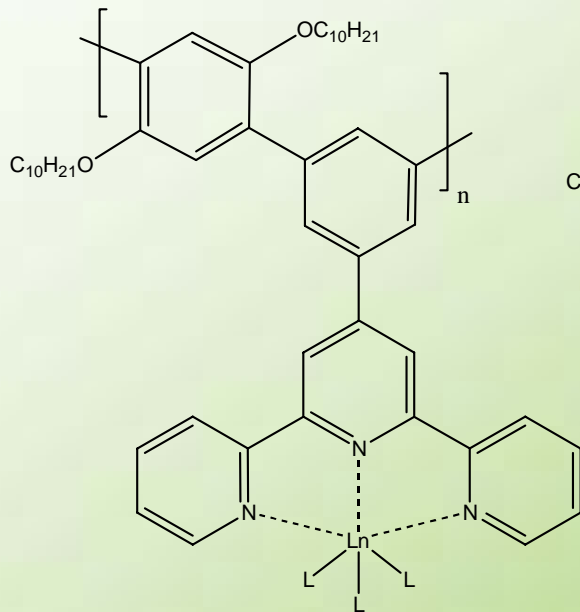
Sean Owen Clancy, Ph.D.

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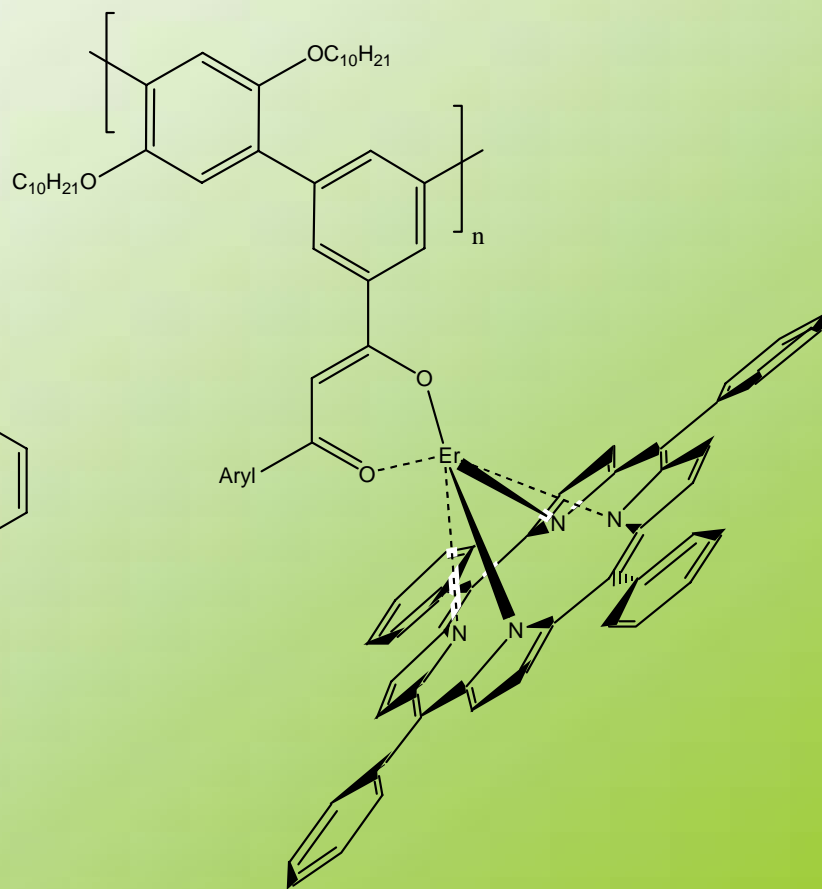
Polymeric Energy Transfer Complexes



• PM_aryl:Ln(L)₂



• PM_trp:Ln(L)₃



• PM_aryl:ErTPP

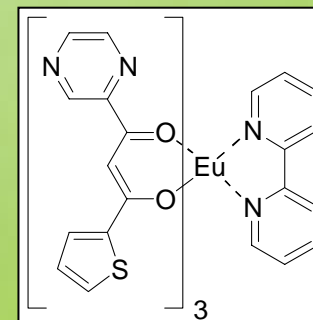
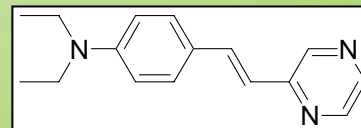
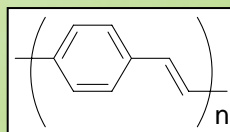
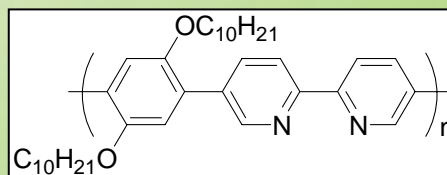
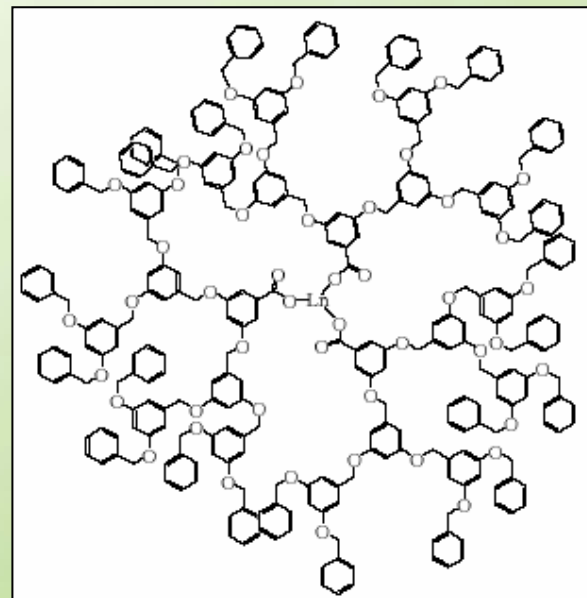
Graduate Research Overview

- Background
 - Harper Group Research
 - Research Goals and Motivation
 - Recent Applications
 - Lanthanides
 - Ligands
 - Color Tuning
 - Polymers Photophysics
 - Energy Transfer
- Visible Emission Resulting from Energy Transfer from Polymers to Ligands to Europium
 - Polymers with Pendant Terpyridines
 - Polymers with Pendant β -Diketonates
- Infrared Emission Resulting from Energy Transfer from Polymers to Ligands to Erbium
- Summary
- Future Work



Harper Group Research

- Energy Transfer Studies
 - Light Harvesting Dendrimers
 - Light Harvesting Polymers
 - Polymer Photophysics
- Lanthanide Complexes
 - β -Diketonate Ligands
 - Dative Bonding Heterocyclic Ligands
- Photonic Materials
 - Lanthanide Containing Materials
 - Organometallic Systems
 - PPV Syntheses
 - Polymer Sensors
 - Photonic Crystals
 - Quantum Dots
 - Two-Photon Dyes



Research Goals and Motivation

Facilitate Tunability and Processing

- Polymers are easier to process than inorganic systems.
- Polymeric device properties can be altered by changing the chemical structure of the polymer.

Increase Efficiencies

- Electrical excitation produces 25% singlets and 75% triplets.¹
- Polymeric devices typically have higher external quantum efficiencies than small molecule devices.^{2,3}
- Electrophosphorescent devices have higher efficiencies than electroluminescent devices.⁴
- Lanthanides exert the “heavy atom effect,” creating more triplet states,⁵ which the lanthanides can harvest and emit as pure colors.
- Improve efficiencies by bringing the donors and acceptors closer to each other.
- Increase dopant/acceptor concentration and prevent aggregation as well.

1. Brown, A. R.; Pichler, K.; Greenham, N. C.; Bradley, D. D.; Friend, R. H.; Holmes, A. B. *Chem. Phys. Lett.*, **1993**, 210, 61.
2. Baldo, M. A.; O'Brien, D. F.; Thompson, M. E.; Forrest, S. R. *Phys. Rev. B*, **1999**, 60, 14422.
3. Wilson, J. S.; Dhoot, A. S.; Seeley, A. J. A. B.; Khan, M. S.; Kohler, A.; Friend, R. H. *Nature*, **2001**, 413, 828.
4. Baldo, M.A.; Lamansky, S.; Burrows, P.E.; Thompson, M.E.; Forrest, S.R. *Appl. Phys. Lett.*, **1999**, 75, 4.
5. Mukherjee, K. K. R. *Fundamentals of Photochemistry*, Wiley Eastern Ltd. India, **1992**.



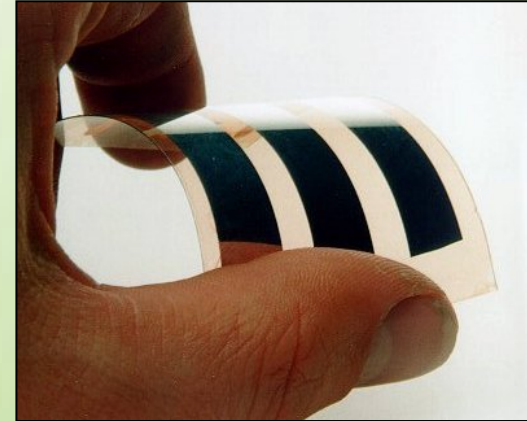
Background – Recent Applications

- Conjugated polymers have many applications:

- Photovoltaics

Flexible photovoltaic diode

http://www.oc.chalmers.se/science/konjug_polymerer.htm



- OLEDs

20" OLED full color display by IBM 2002.

<http://www.zurich.ibm.com/st/display/demo.html>



*Kodak EasyShare Digital Camera
Active-matrix OLED*

<http://www.kodak.com/go/display/>



Background – Lanthanides

- Pure color emission (shielded f orbital transitions)
- Robust metals (will not photobleach)
- Induce heavy atom effect (improves rate of intersystem crossing)
- Triplet harvesters
- Reduce polymer degradation

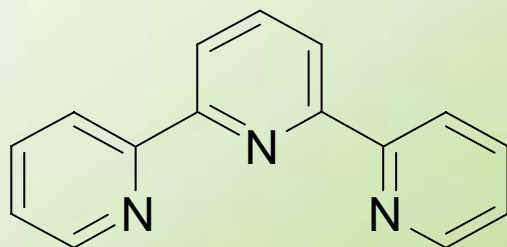
- Eu^{+3} , Sm^{+3} , and Tb^{+3} can be used in visible devices
- Er^{+3} can be used in EDFA (1.55 nm)
- Nd^{+3} and Yb^{+3} can be used in IR-emitting devices

- Direct excitation is inefficient, to overcome
 - Laser source
 - Ligands
- Energy transfer is important
 - Conjugated organic ligands allow for ET
 - Ligands shield lanthanide ion from external environment, such as solvent (mode of energy loss) and other lanthanide ions (self quenching).

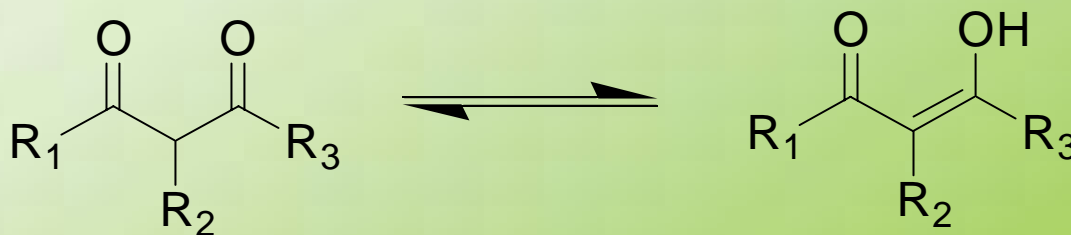


Background – Ligands

- Lanthanides have a high number of coordination sites (from six to twelve).
- Their *f* orbitals are unable to form hybrid orbitals with ligand.
- Need ligands to bind with more than one coordination site (multidentate).
- Dative bonding ligands, such as terpyridine:

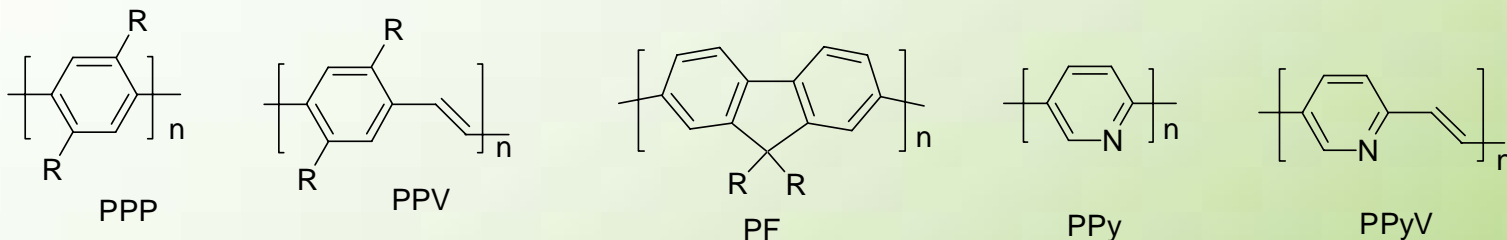


- Bidentate ligands, such as *beta*-diketonates, form both covalent and dative bonds:

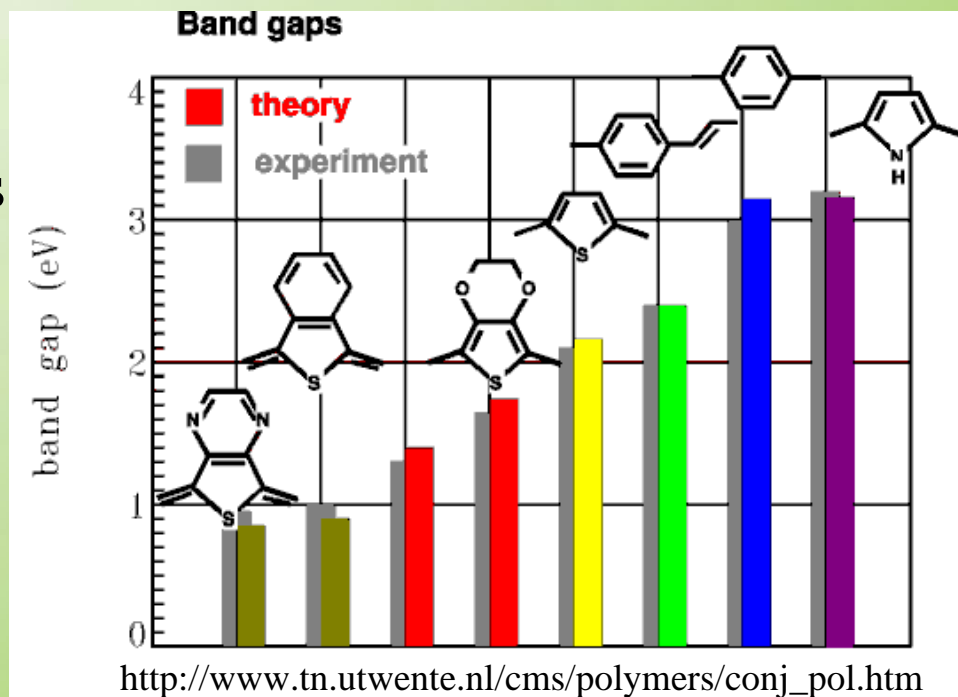


Background – Color Tuning

- *PPV and PPP type polymers are widely used*



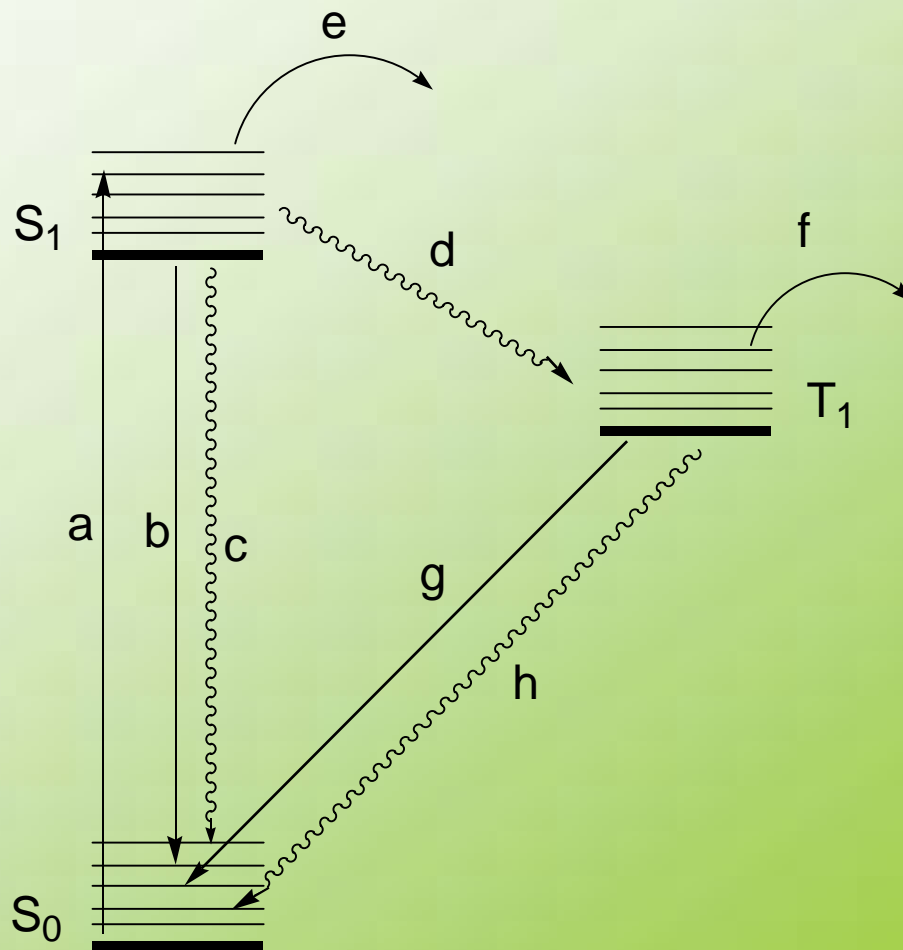
- Mechanical properties
 - Light weight, easy to process
- Infinite π -system
- Give rise to a band structure
- Band gap varies according to structure



Background – Polymer Photophysics

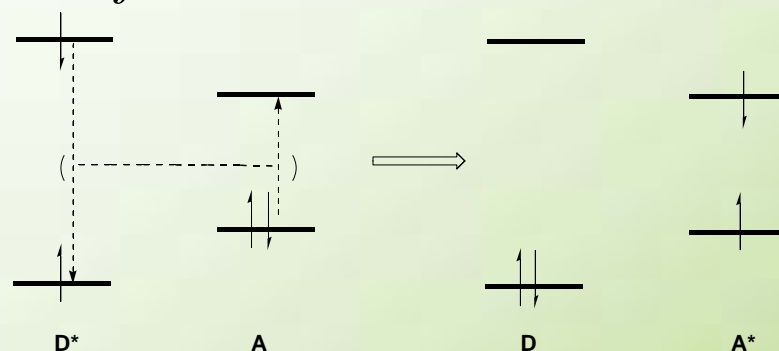
Energy level diagram showing modes of deactivation:

- a – absorbance
- b – fluorescence
- c – nonradiative decay
- d – intersystem crossing
- e – singlet energy transfer
- f – triplet energy transfer
- g – phosphorescence
- h – internal crossing



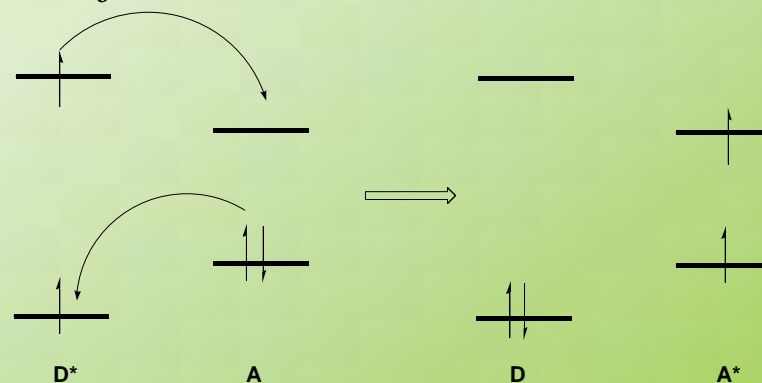
Background – Energy Transfer

Forster Energy Transfer



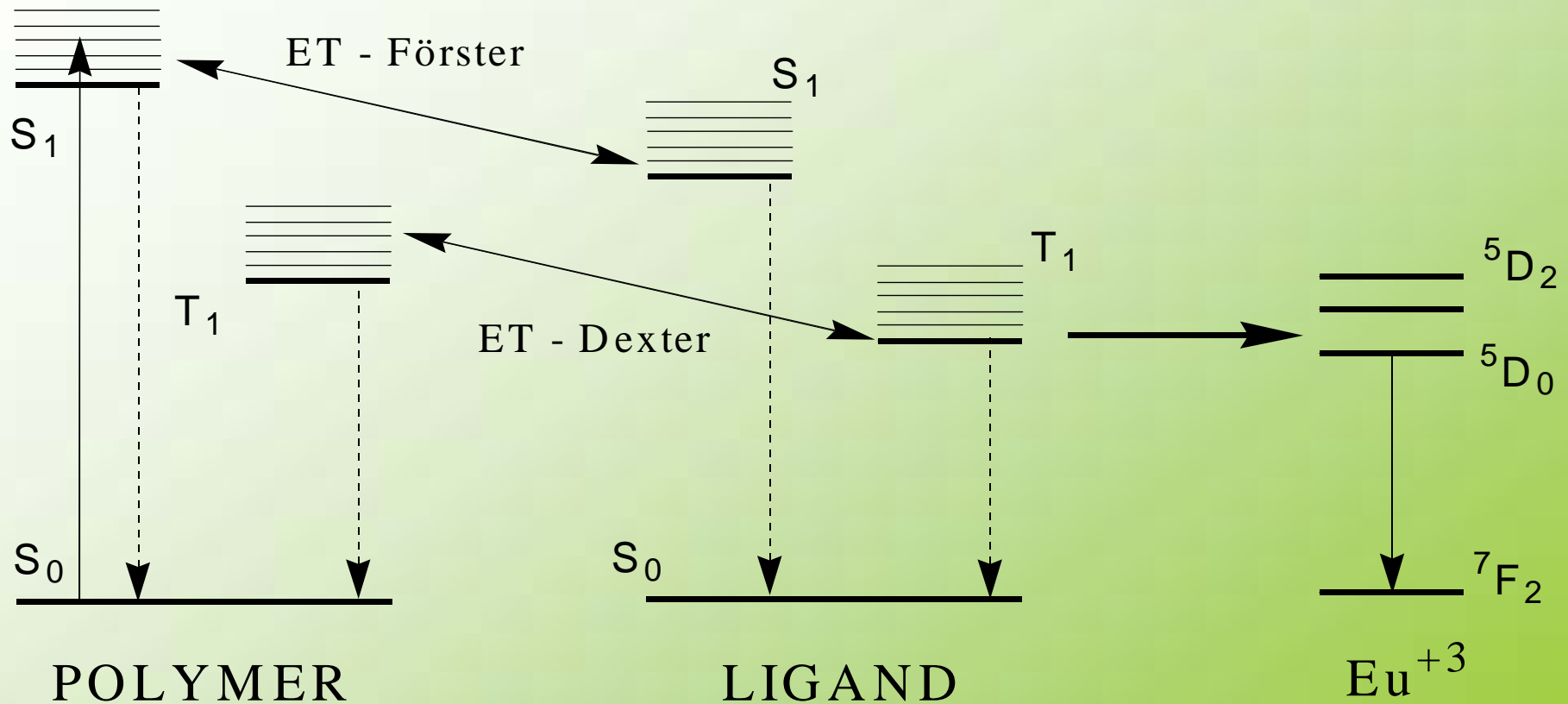
- Singlet to singlet
- Coupled dipole-dipole interaction; through space

Dexter Energy Transfer



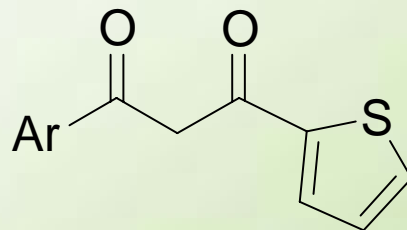
- Triplet to triplet
- Exchange mechanism; through bond

Background – Energy Transfer Polymer to Ligand to Lanthanide

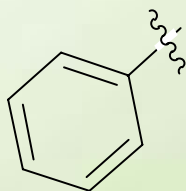


Sensitization of Europium Chelates

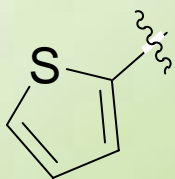
Design and Synthesis of β -Diketone Ligands



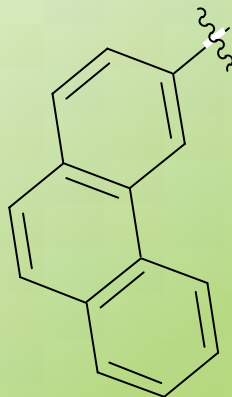
BTM



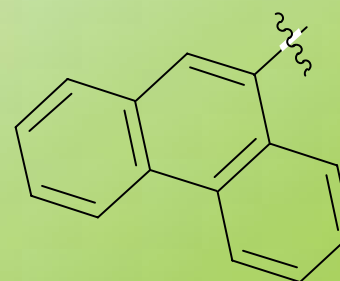
DTM



3-PTM



9-PTM

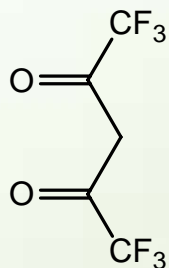


Ar =

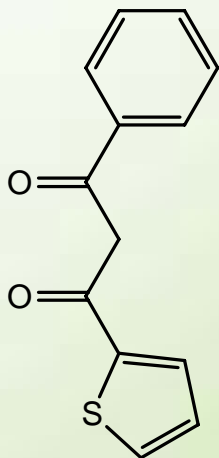
Sensitization of Europium Chelates

Ligand Structures

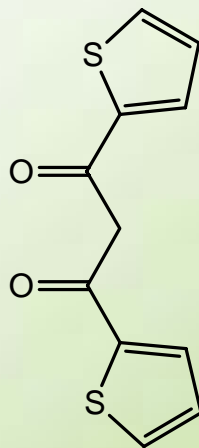
HFA



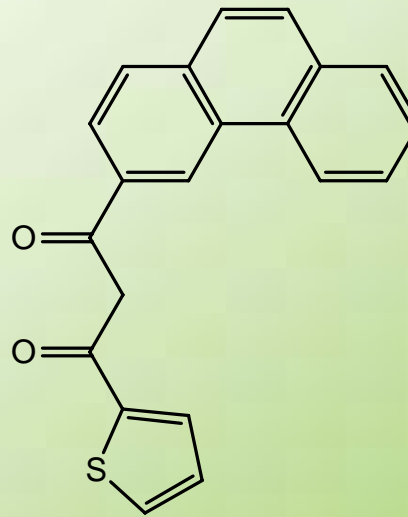
BTM



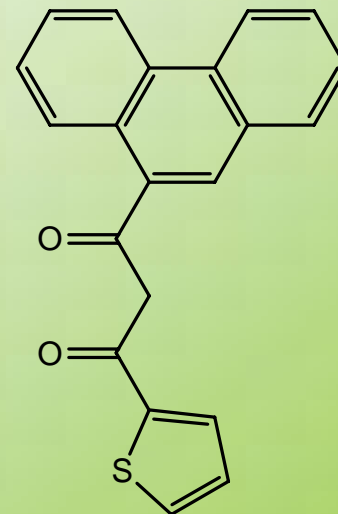
DTM



3-PTM



9-PTM



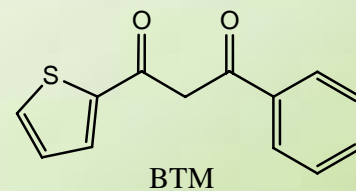
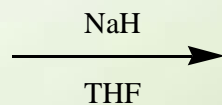
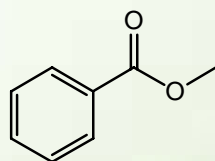
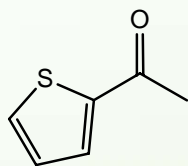
Asymmetric Vs. Symmetric

Asymmetric –
Extent of Conjugation Length

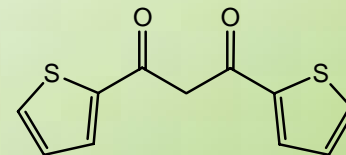
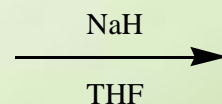
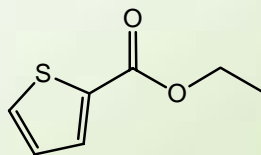
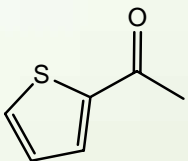
- Asymmetric ligands perturb the ligand field around a lanthanide.
 - The more asymmetric the field, the greater the lanthanide's emission intensity.
- Shorter effective conjugation length increases the energies of a ligand.
 - Larger energy gap will reduce the possibility for back energy transfer.
 - Minimizes a pathway for energy loss.

Sensitization of Europium Chelates

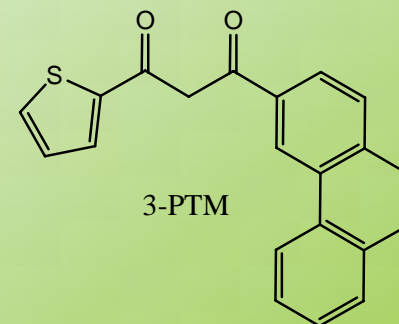
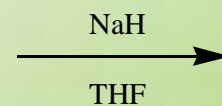
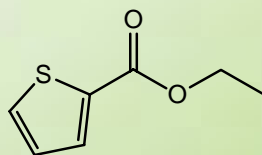
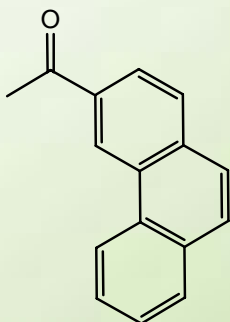
Ligand Syntheses



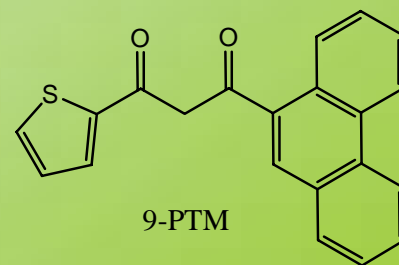
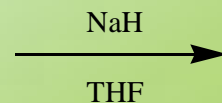
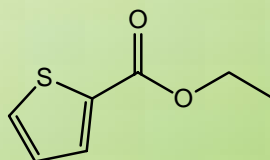
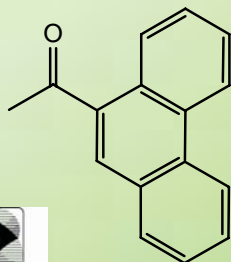
BTM



DTM



3-PTM



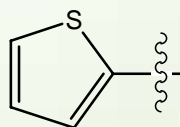
9-PTM

Sensitization of Europium Chelates

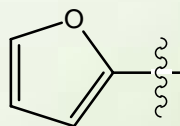
Polymer Structures

Polymer Aryl Group

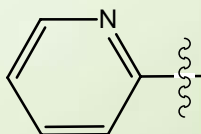
PM_th



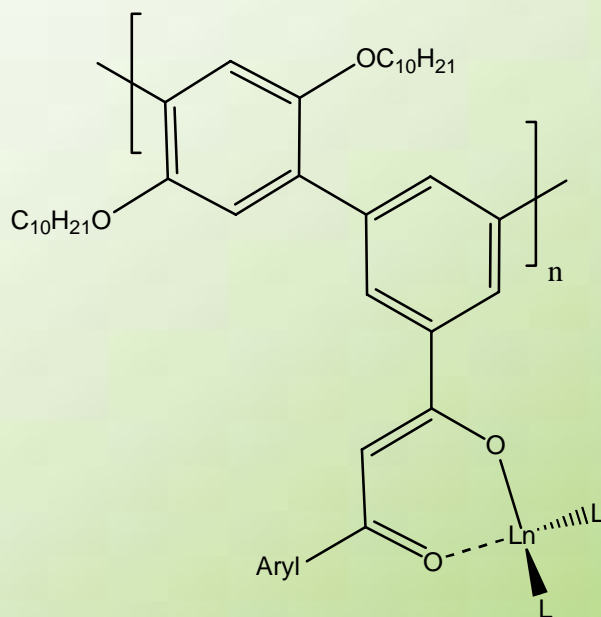
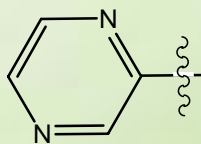
PM_fu



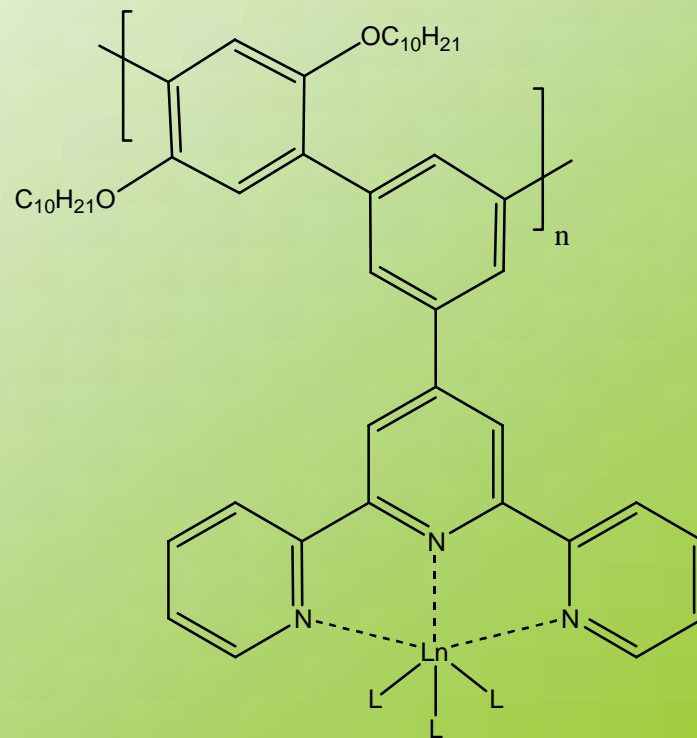
PM_py



PM_pz

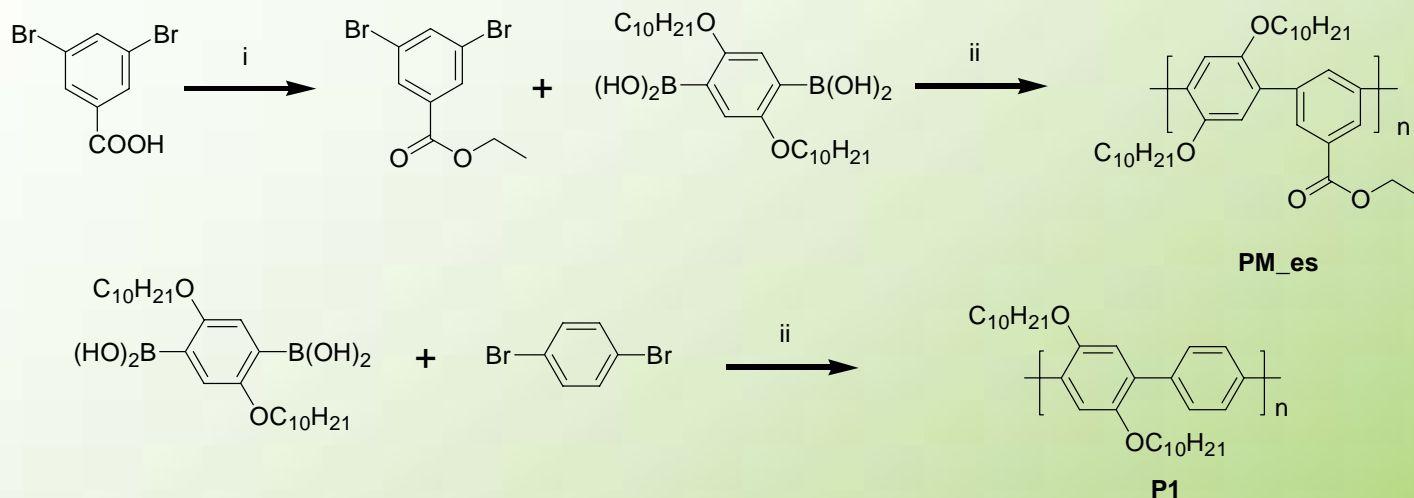


PM_trp



Sensitization of Europium Chelates

Energy Level Tuning of Polyphenylenes – Primary Donors



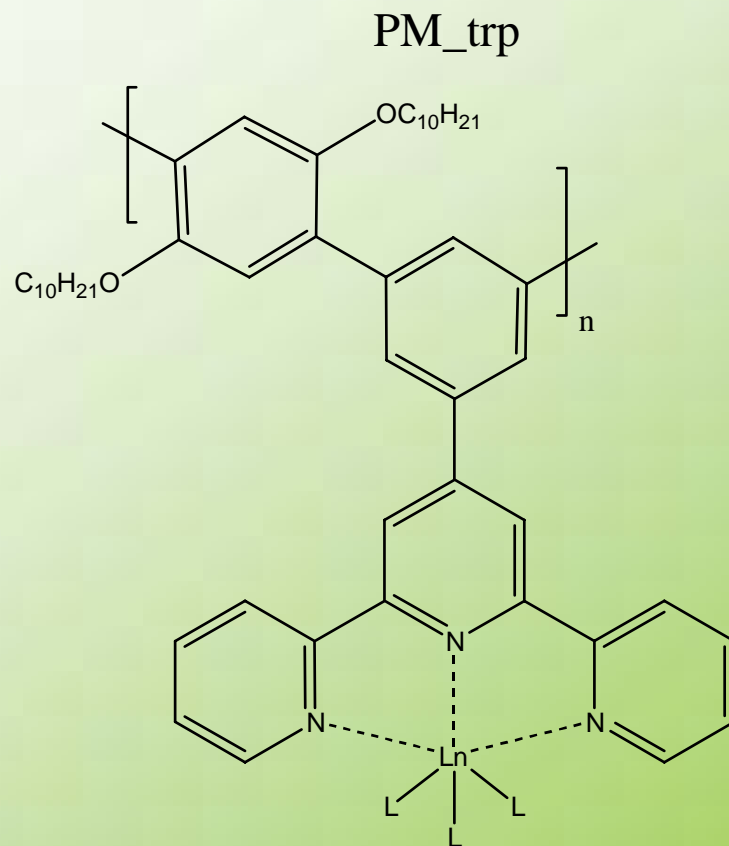
The synthetic route to **PM_{es}** and **P1** (i.) ethanol/ PTSA refluxed 24hrs; (ii.) $Pd(PPh_3)_4$, 2M Na_2CO_3 , toluene, refluxed 72hrs).

Photophysical properties of **P1** and **PM_{es}** in THF.

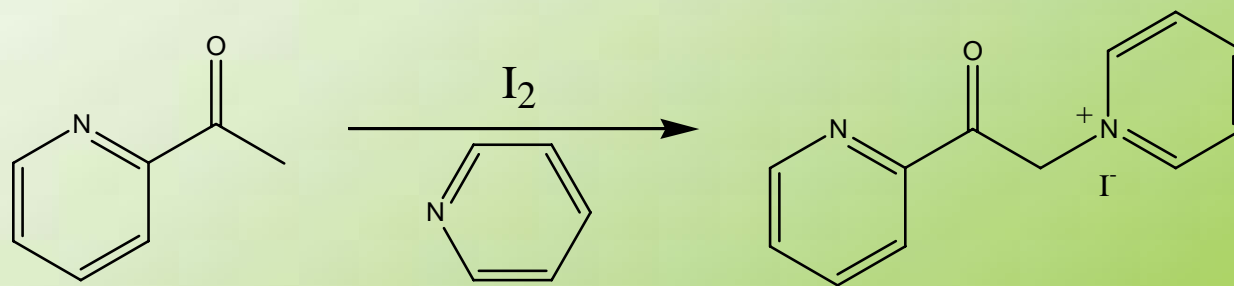
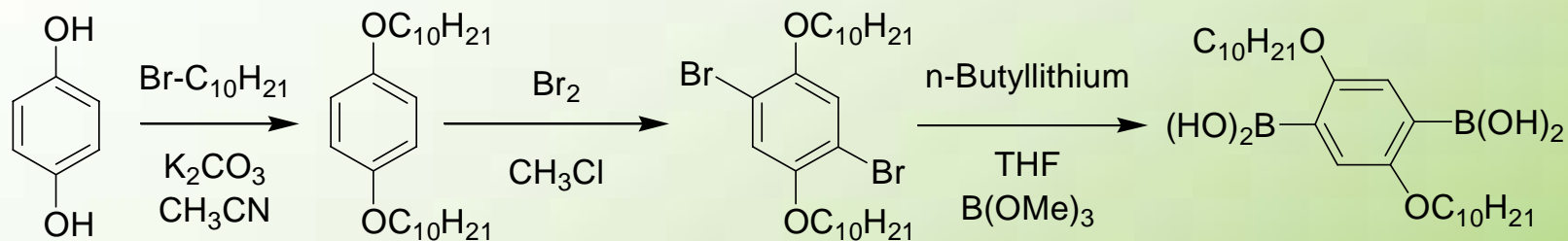
<i>Polymers</i>	Abs. Max (nm)	Emission				Singlet energy (eV)	Triplet energy (eV)
		Max (nm)	FWHM (nm)	ϕ_{FL}	τ (ns)		
<i>P1</i>	350	411	61.5	0.386	0.690	3.24	2.31
<i>PM_{es}</i>	330	392	61.5	0.662	1.665	3.41	2.47

Sensitization of Europium Chelates

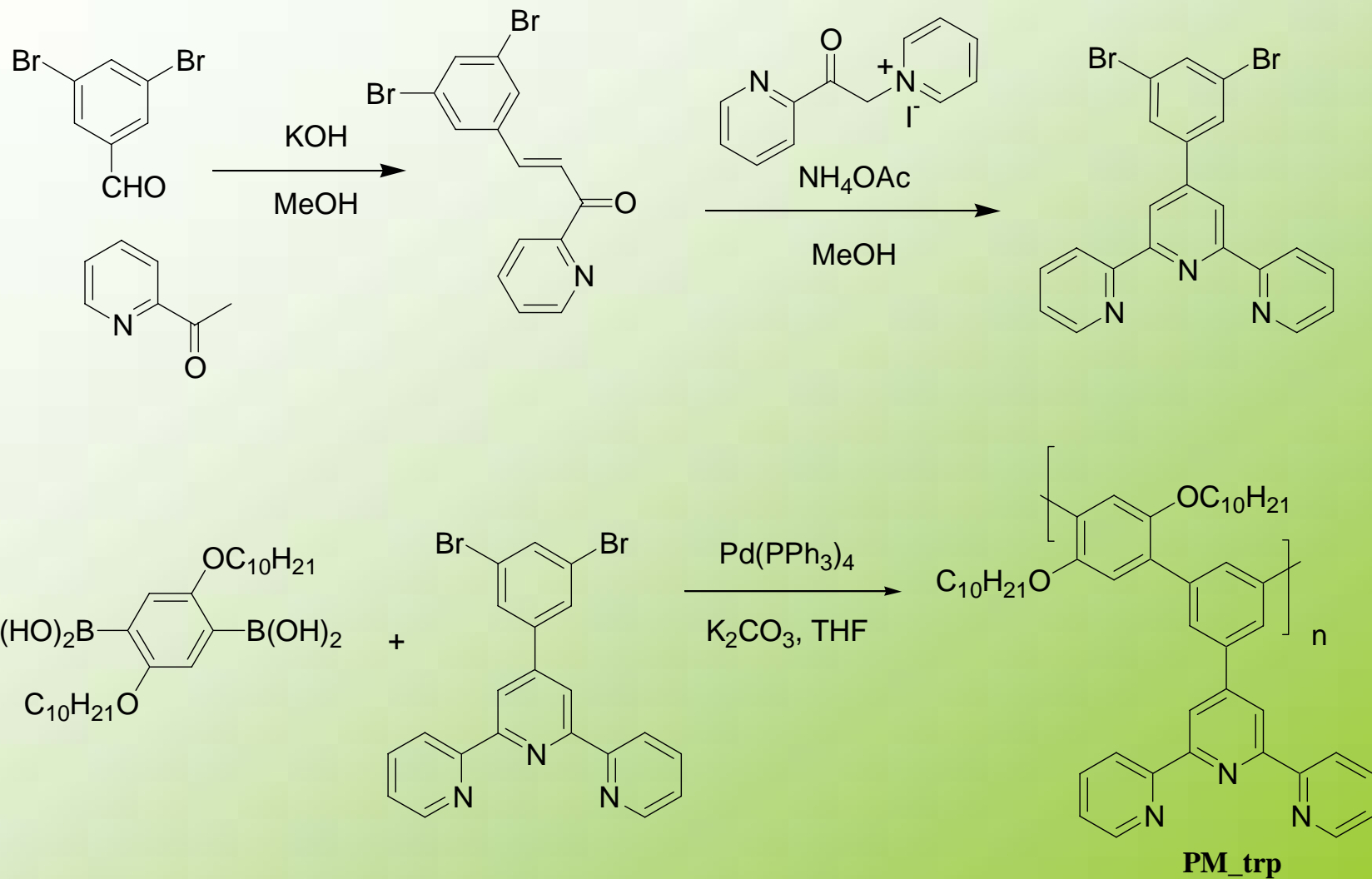
Synthesis of Polymers with Pendant Terpyridines Bound to Europium(III) β -Diketonates



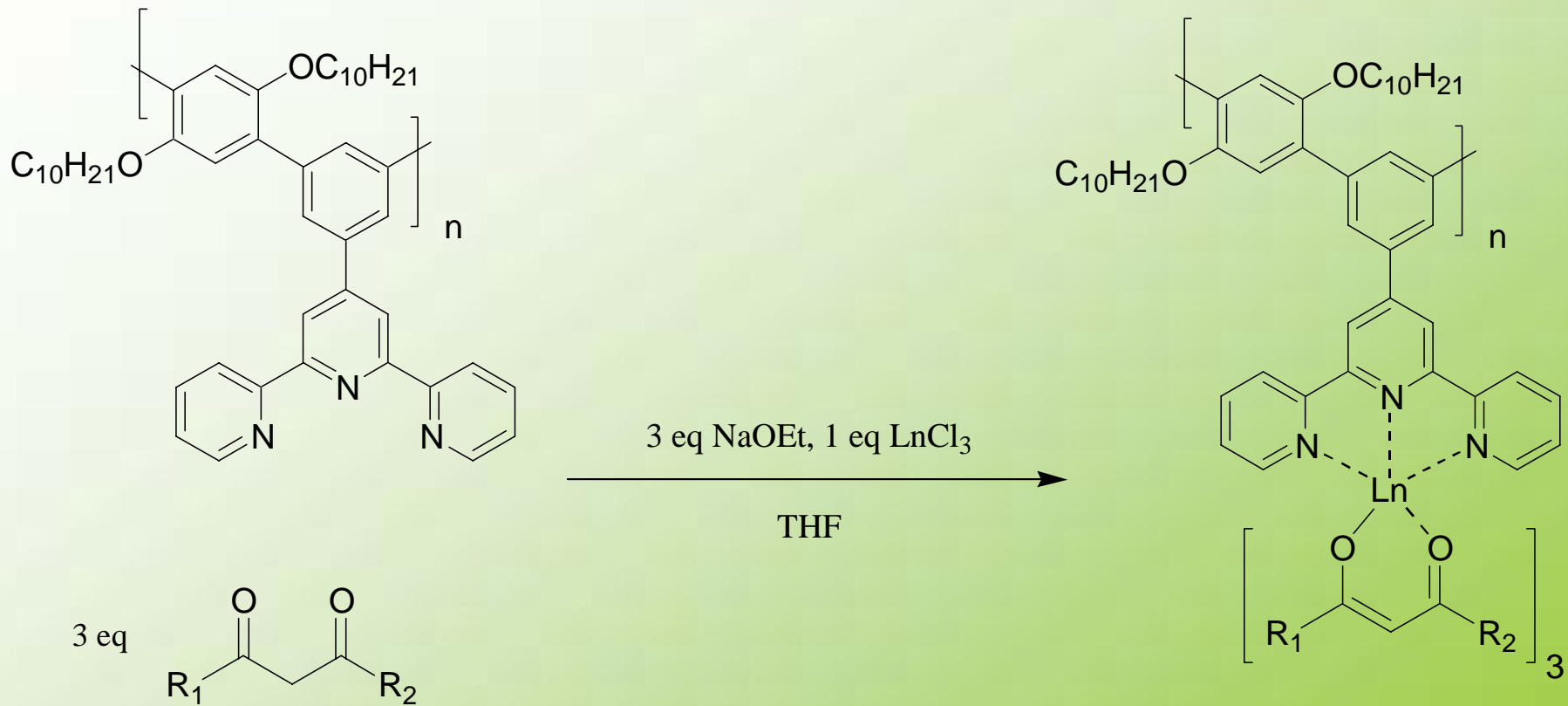
Polymer with Terpyridines Synthesis



Polymer with Terpyridines Synthesis

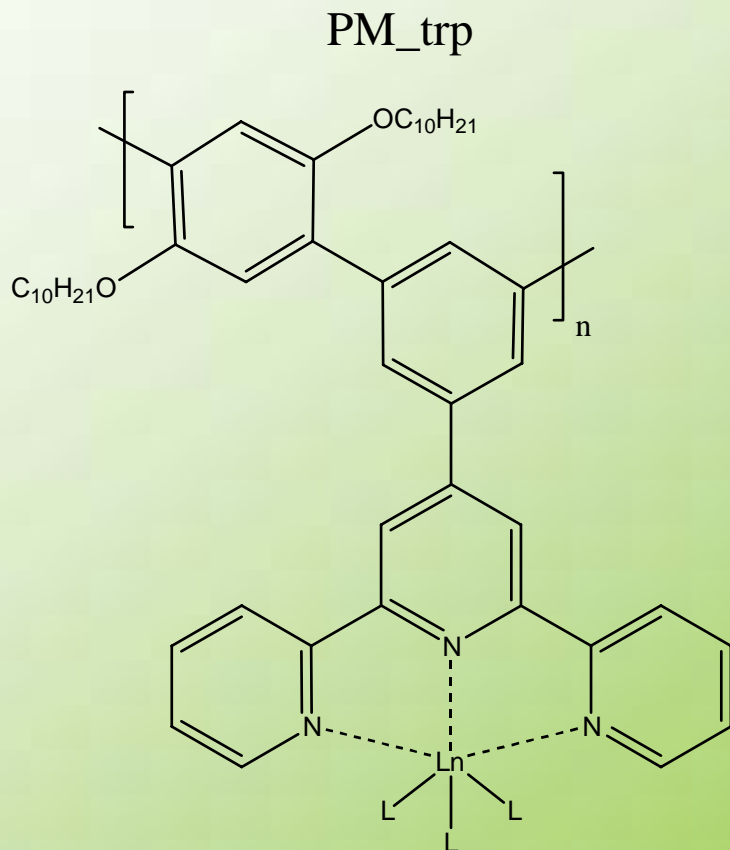


Polymer-Lanthanide Chelate Synthesis



Sensitization of Europium Chelates

Materials Characterization and Photophysical Performance Data



Polymer with Terpyridines Characterization

Polymer molecular weights were determined by gel permeation chromatography (GPC) and multiple angle laser light scattering (MALLS).

Polymer	dn/dc (mL/g)	M_n (g/mol)	M_w (g/mol)	PDI
PM_trp	0.1608	8.669×10^6	1.117×10^7	1.29

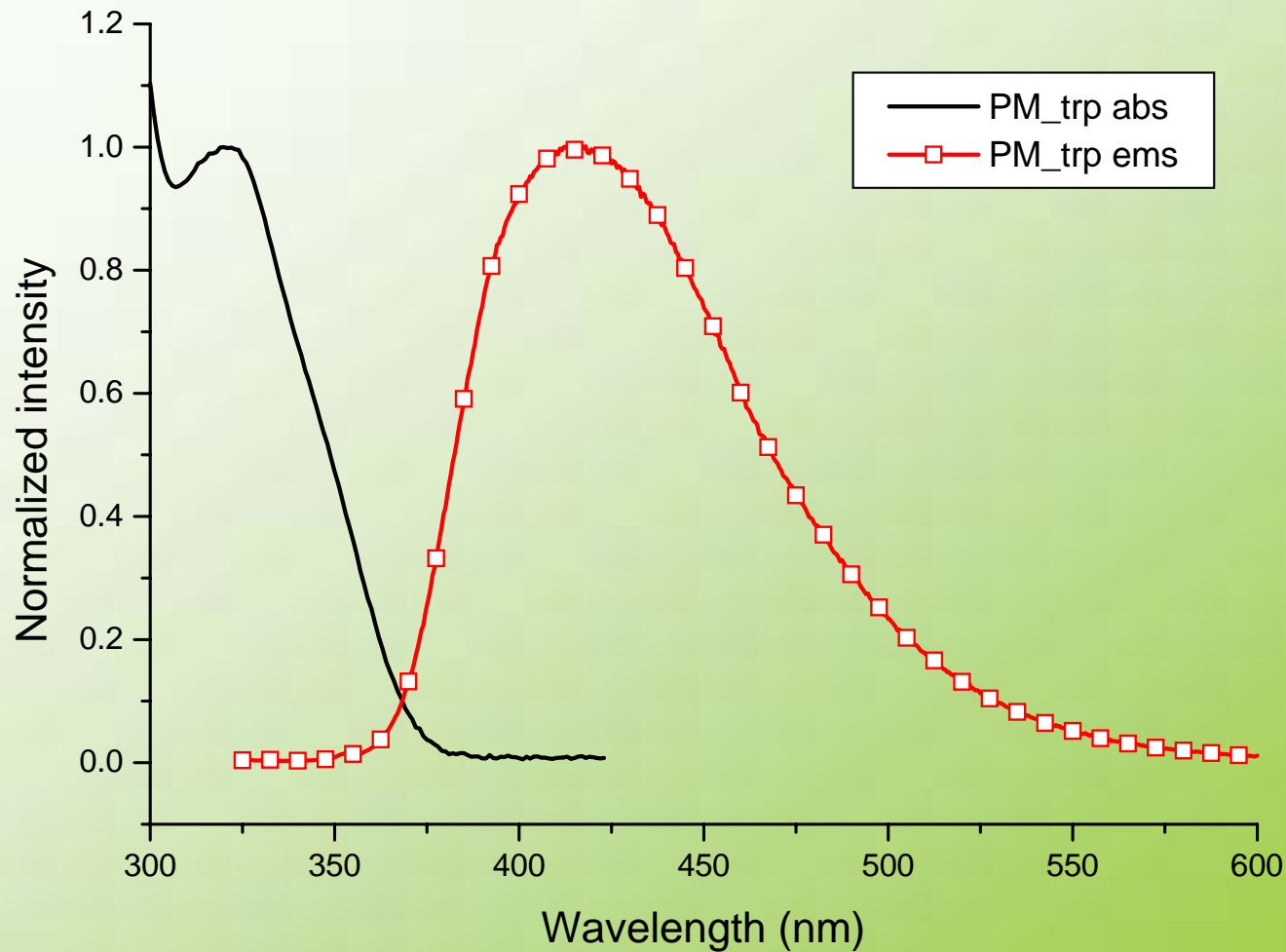
Photophysical properties of polymers PM_trp in THF.

	PM_trp
Absorption maximum	320 nm
Fluorescence maximum	416 nm
FWHM	85 nm
Stokes' shift	$7,212 \text{ cm}^{-1}$
Φ_{FL}	0.062
Lifetime (weighting coefficient)	0.27 ns (0.60) 1.49 ns (0.40)
Singlet energy level (E_s)	3.32 eV
Triplet energy level (E_T)	2.47 eV
Singlet-triplet gap (ΔE_{ST})	0.85 eV

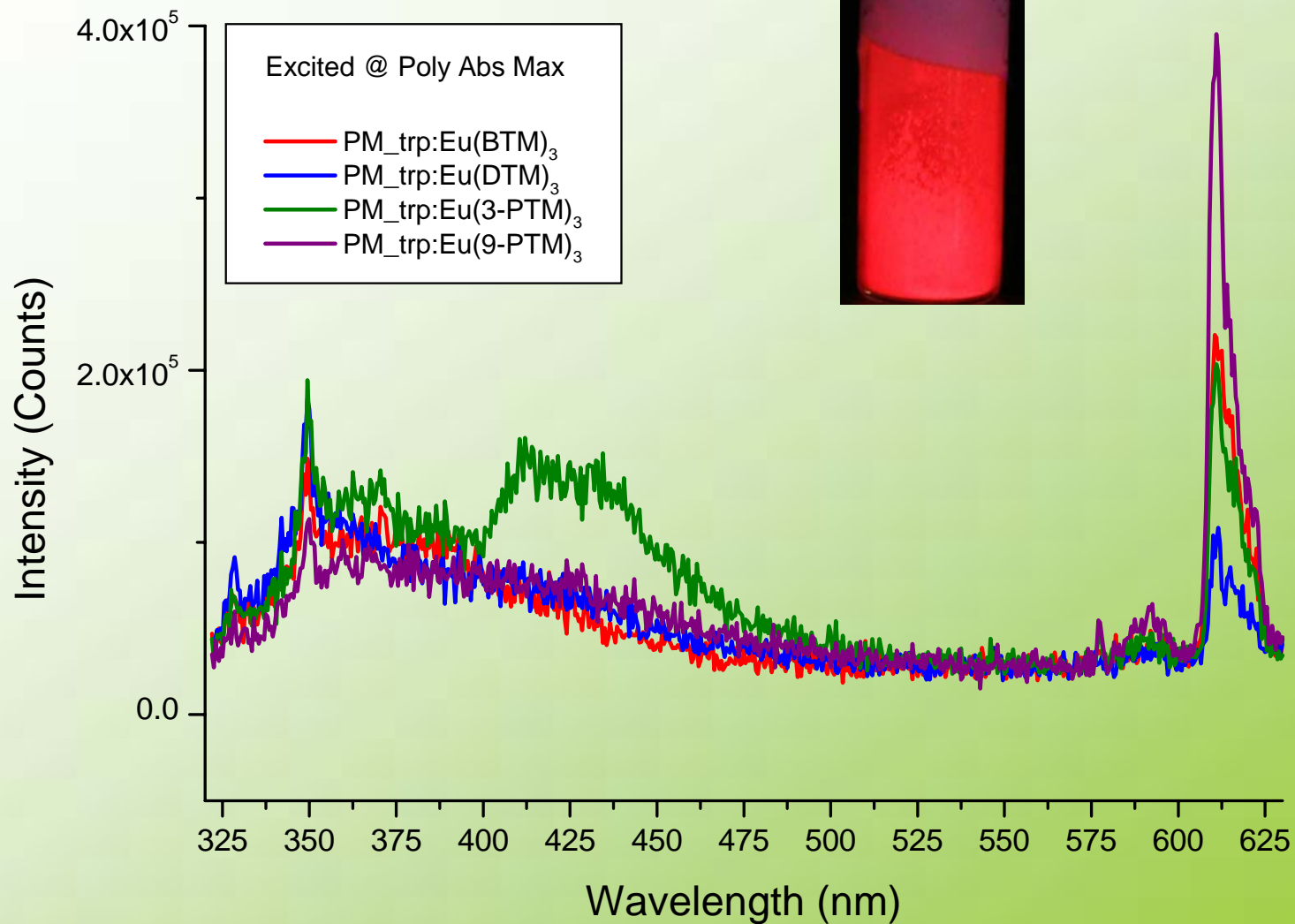


Polymer with Terpyridines Characterization

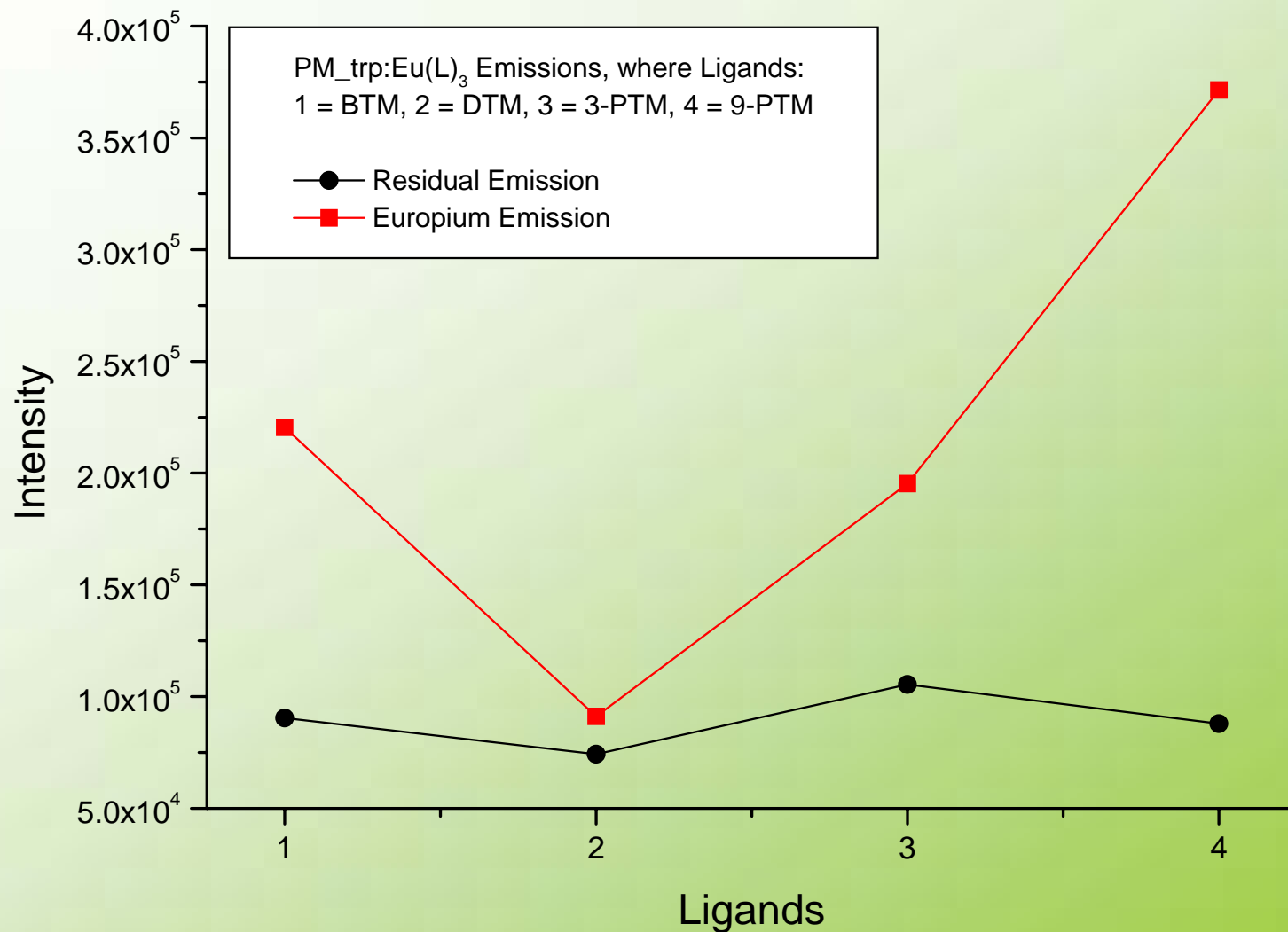
The absorbance and emission spectra of polymer PM_trp in THF (ex = 320 nm).



PM_trp:Eu(L)₃ Emission Spectra

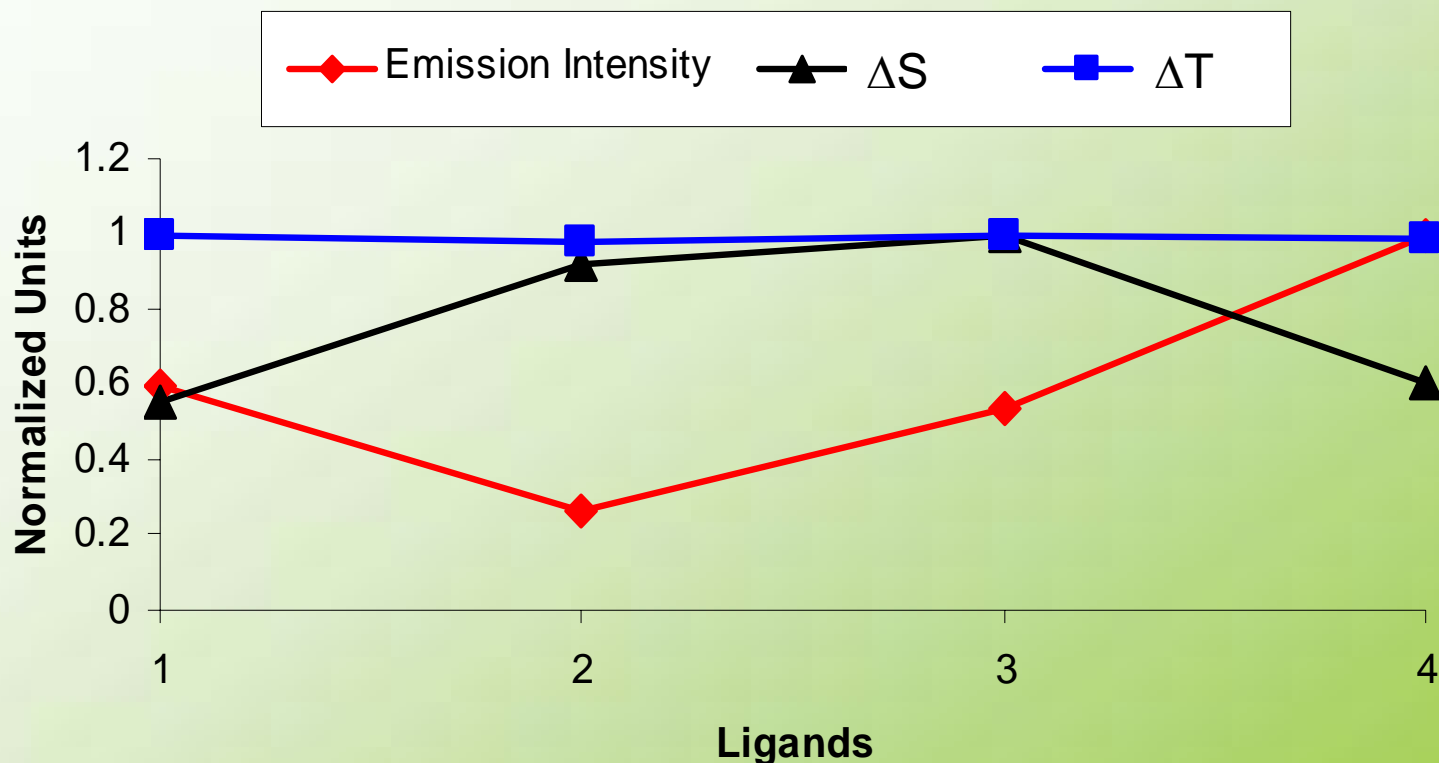


PM_trp:Eu(L)₃ Emission Maxima



PM_{th}:Eu(L)₂ Ligands Versus Energy Parameters

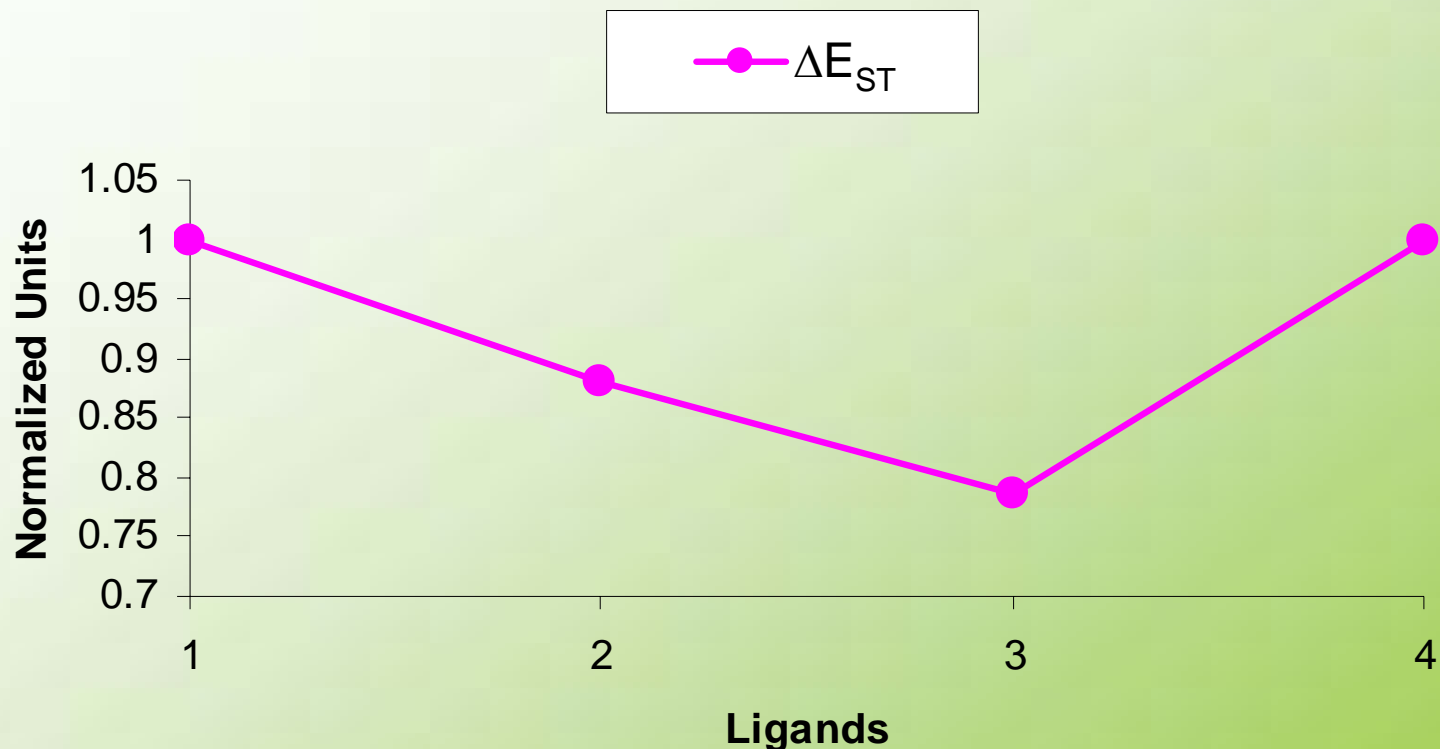
PM_{trp}:Ln(L)₃ Systems, where Ligands: 1 = BTM, 2 = DTM, 3 = 3-PTM, 4 = 9-PTM.



- Smaller distances in singlet energies (ΔS) from polymer to polymer-ligand complexes inversely relate to greater emission intensities from complexes.
- Suggests Forster ET of greater significance than Dexter ET for polymer to ligand ET.

PM_{th}:Eu(L)₂ Ligands Versus Energy Parameters

PM_{trp}:Ln(L)₃ Systems, where Ligands: 1 = BTM, 2 = DTM, 3 = 3-PTM, 4 = 9-PTM.



- Greater distances in singlet to triplet energies for polymer-ligand complexes almost directly relate to greater emission intensities from complexes.
- Suggests back energy transfer led to lower emission intensities for DTM and 3-PTM.
- Forward ISC favored by BTM and 9-PTM.

PM_trp:Ln(L)₃ Systems Characterization

Photophysical properties of PM_trp gadolinium complexes.

	PM_trp: Gd(HFA) ₃	PM_trp: Gd(BTM) ₃	PM_trp: Gd(DTM) ₃	PM_trp: Gd(3-PTM) ₃	PM_trp: Gd(9-PTM) ₃
Abs. Max (nm)	317	358	374	376	358
(cm ⁻¹)	31,546	27,933	26,738	26,596	27,933
Em. Max (nm)	400	410	423	429	410
(cm ⁻¹)	25,000	24,390	23,641	23,310	24,390
Δ (cm ⁻¹)	6,546	3,543	3,097	3,286	3,543
E _S (eV)	3.40	3.21	3.09	3.07	3.20
(cm ⁻¹)	27,397	25,907	24,938	24,722	25,773
E _T (eV)	2.76	2.46	2.43	2.48	2.45
(cm ⁻¹)	22,297	19,841	19,608	20,000	19,763
ΔE _{ST} (eV)	0.64	0.75	0.66	0.59	0.75

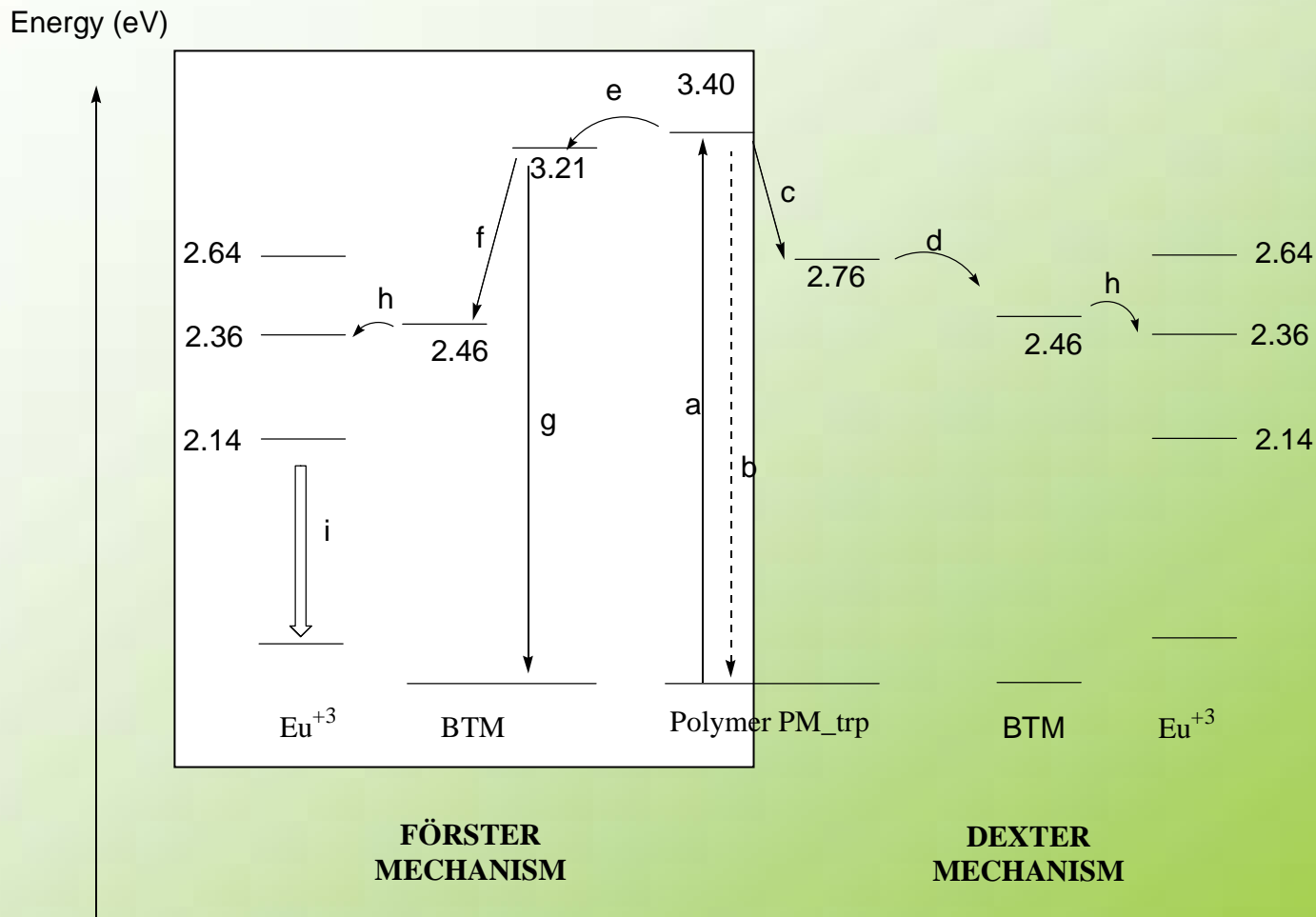
Energy transfer efficiencies from PM_trp to L in PM_trp:Eu(L)₃ systems, where L = BTM, DTM, 3-PTM, and 9-PTM.

	<u>BTM</u>	<u>DTM</u>	<u>3-PTM</u>	<u>9-PTM</u>
<i>PM_trp:Eu(L)₃</i>	0.993	0.994	0.991	0.993



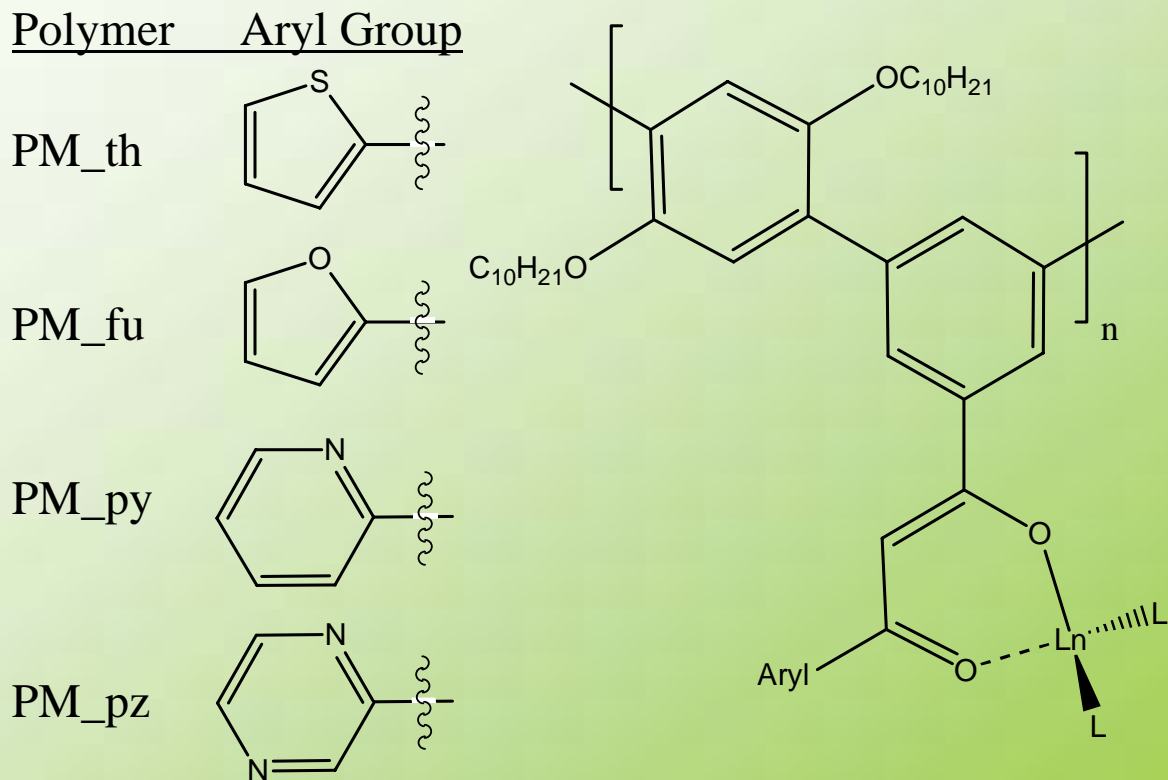
PM_trp:Ln(L)₃ Systems Characterization

The energy transfer mechanism for the PM_trp:Eu(BTM)₃ system.

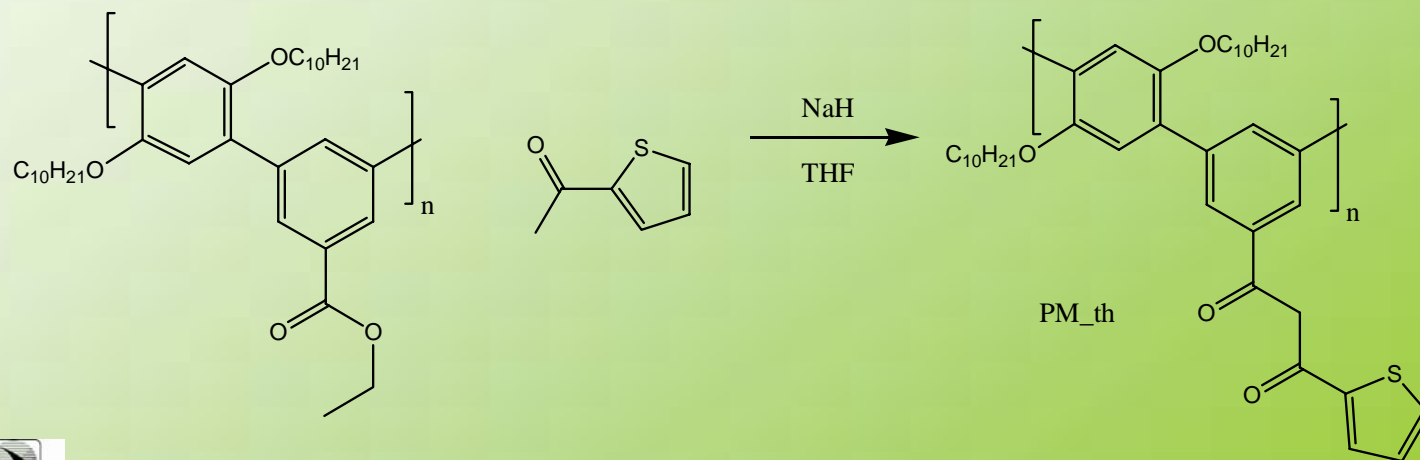
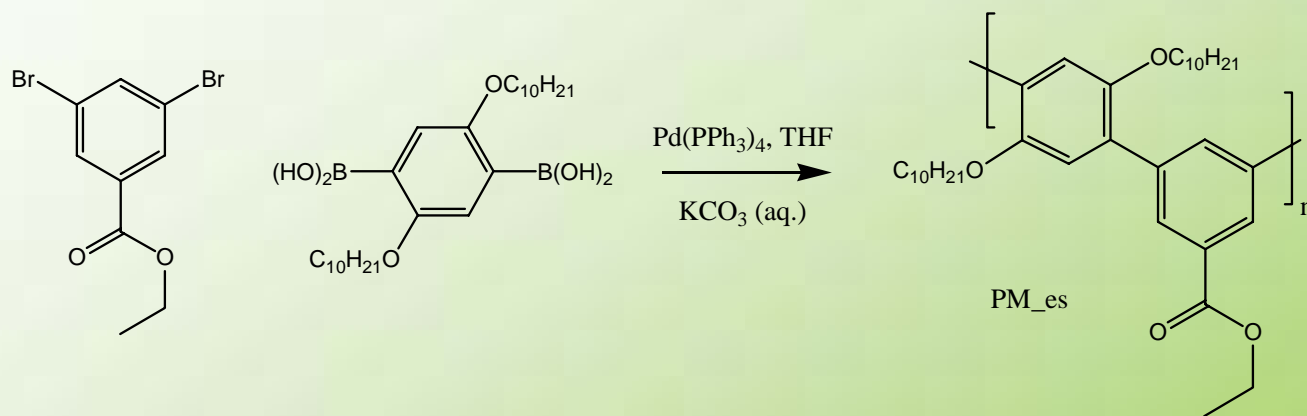
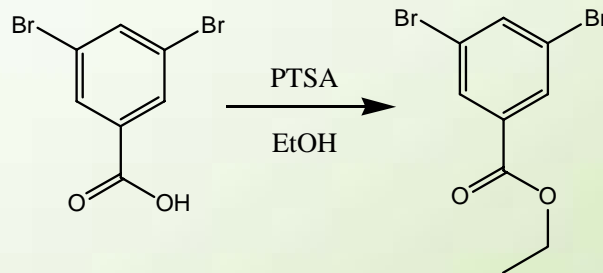


Sensitization of Europium Chelates

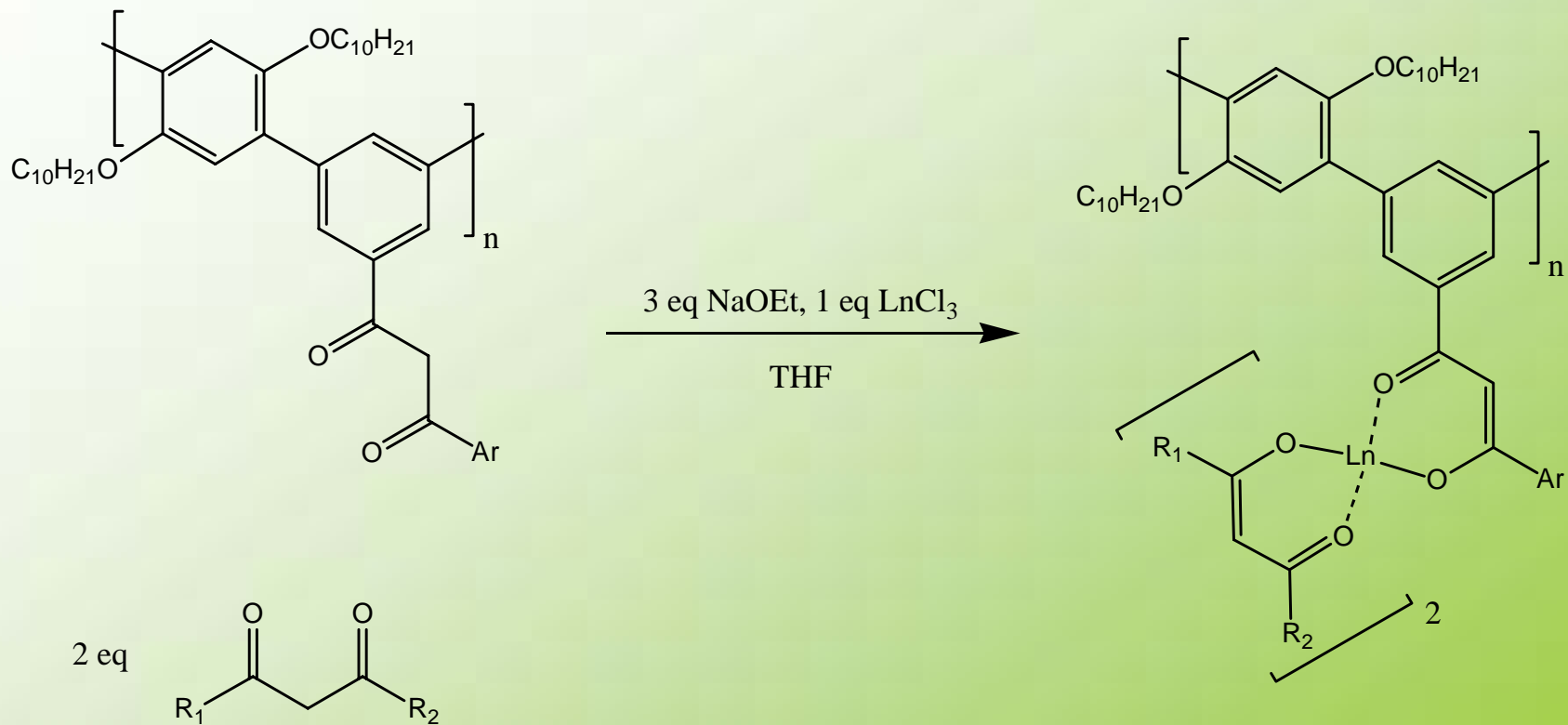
Synthesis of Polymers with Pendant β -Diketonates Bound to Europium(III) β -Diketonates



Polymers with β -Diketones Synthesis

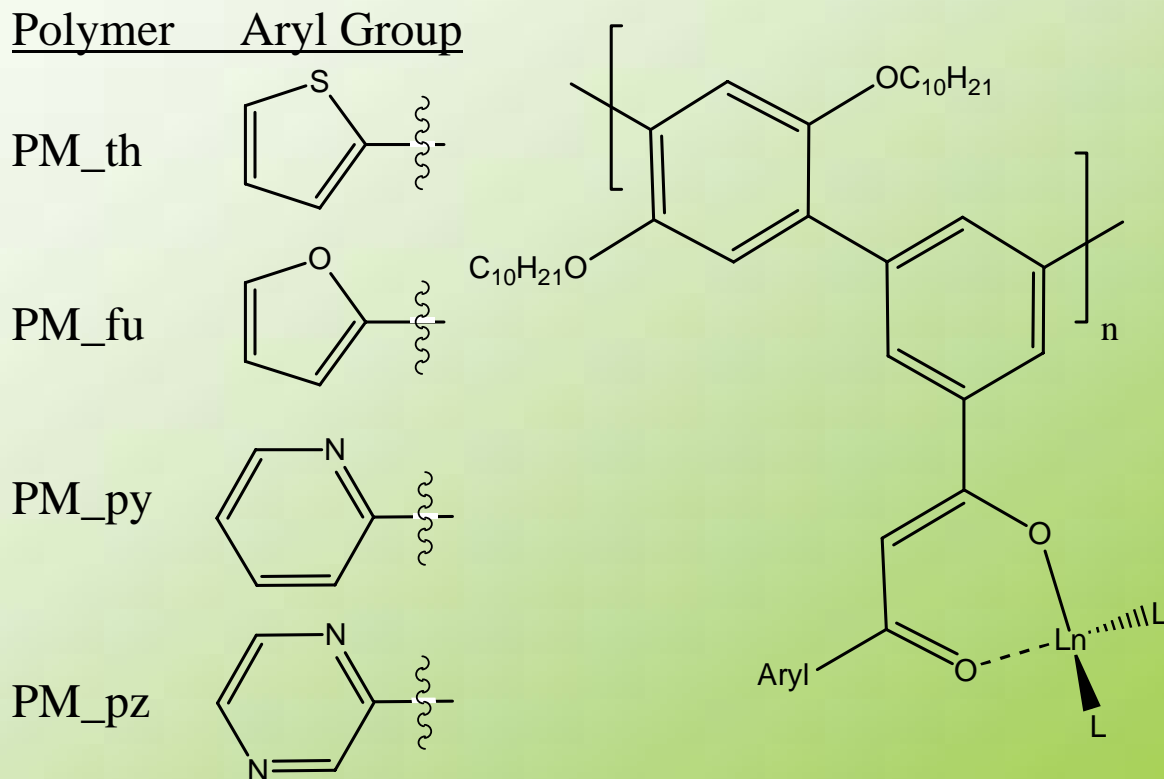


Polymer-Lanthanide Chelate Synthesis



Sensitization of Europium Chelates

Materials Characterization and Photophysical Performance Data



Polymers with β -Diketonates Characterization

Polymer molecular weights determined by GPC and MALLS in CHCl_3 .

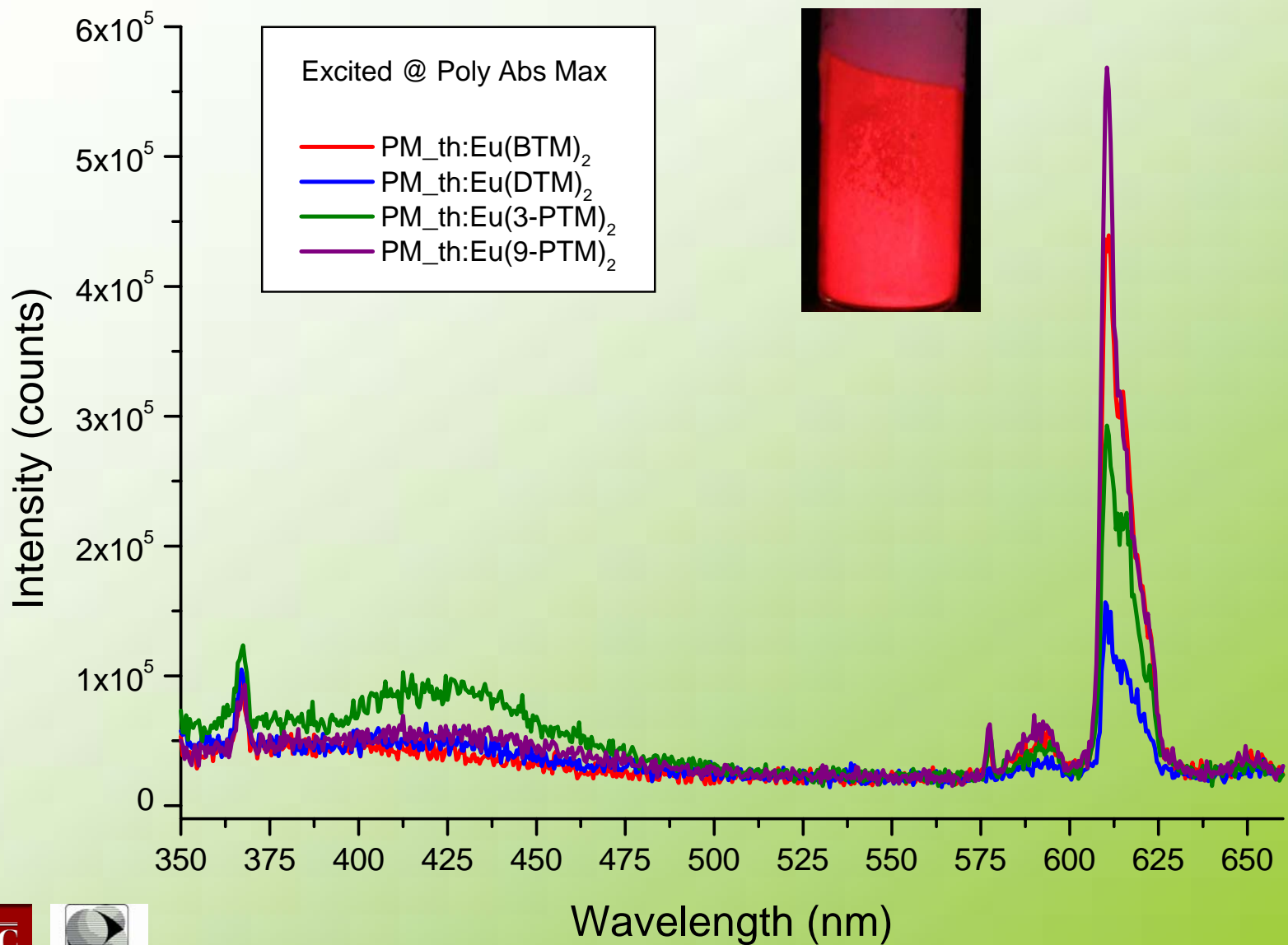
Polymer	dn/dc mL/g	Mn g/mol	Mw g/mol	DP	PDI
PM_es	0.0975	1.27×10^4	1.64×10^4	24	1.28

Photophysical properties polymers with β -diketonate pendant groups.

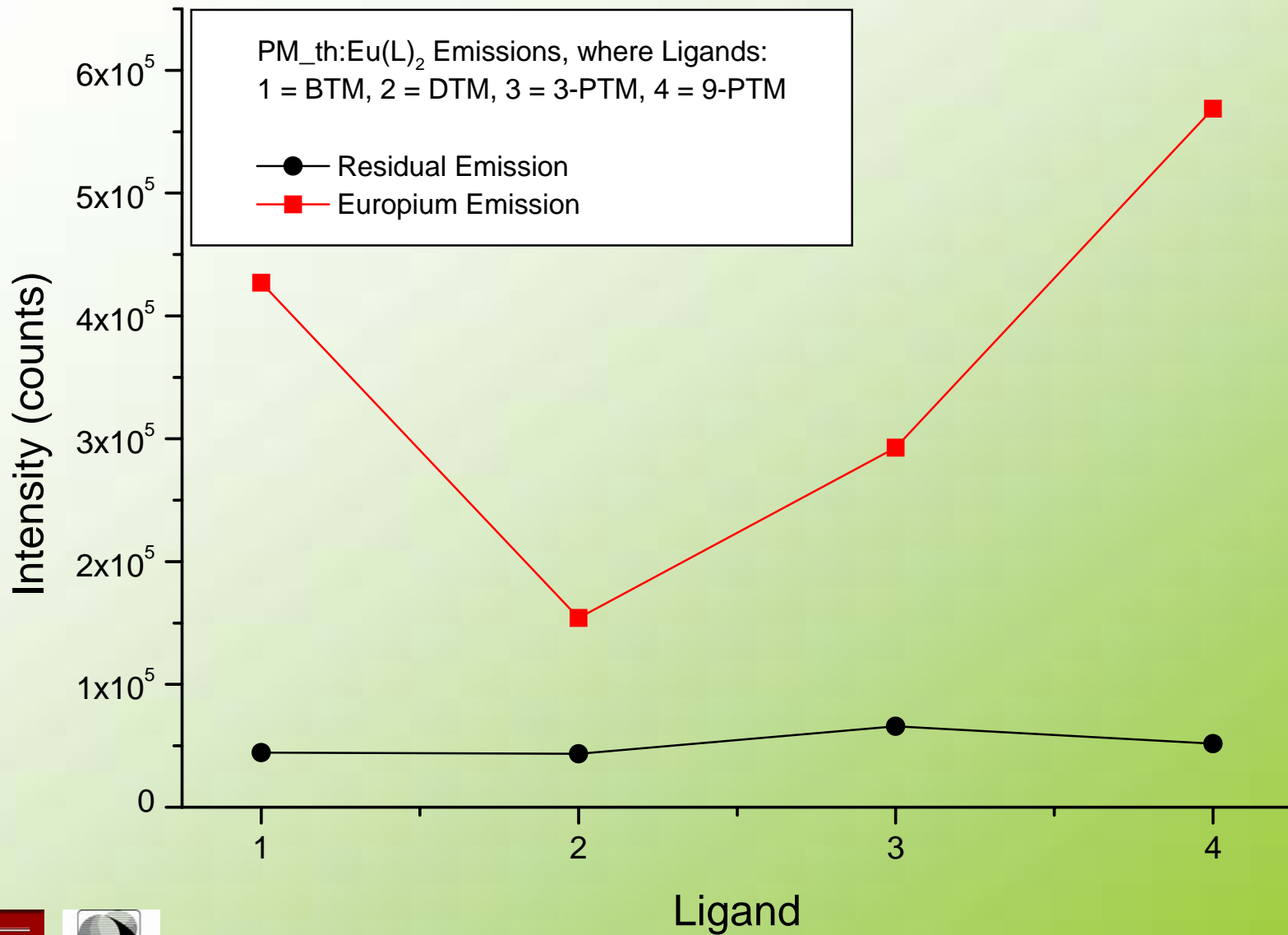
	PM_th	PM_fu	PM_py	PM_pz
Abs. Max (nm)	330	332	330	330
(cm^{-1})	30,300	30,120	30,300	30,300
Em. Max (nm)	396.5	391	391	396
(cm^{-1})	25,220	25,575	25,575	25,250
FWHM (nm)	59	54	54.5	58.4
Δ (cm^{-1})	5,082	4,545	4,728	5,051
QE	0.2121	0.2154	0.1915	0.2134
Life Times (ns)	1.65	1.66	1.52	1.68
k_f (s^{-1})	1.32×10^8	1.32×10^8	1.26×10^8	1.27×10^8
k_{ST} (s^{-1})	4.74×10^8	4.72×10^8	5.31×10^8	4.68×10^8
E_S (eV)	3.40	3.40	3.42	3.40
(cm^{-1})	27,425	27,425	27,585	27,425
E_T (eV)	2.50	2.50	2.50	2.47
(cm^{-1})	20,165	20,165	20,165	19,920
ΔE_{ST} (eV)	0.90	0.90	0.92	0.93



PM_{th}:Eu(L)₂ Emission Spectra

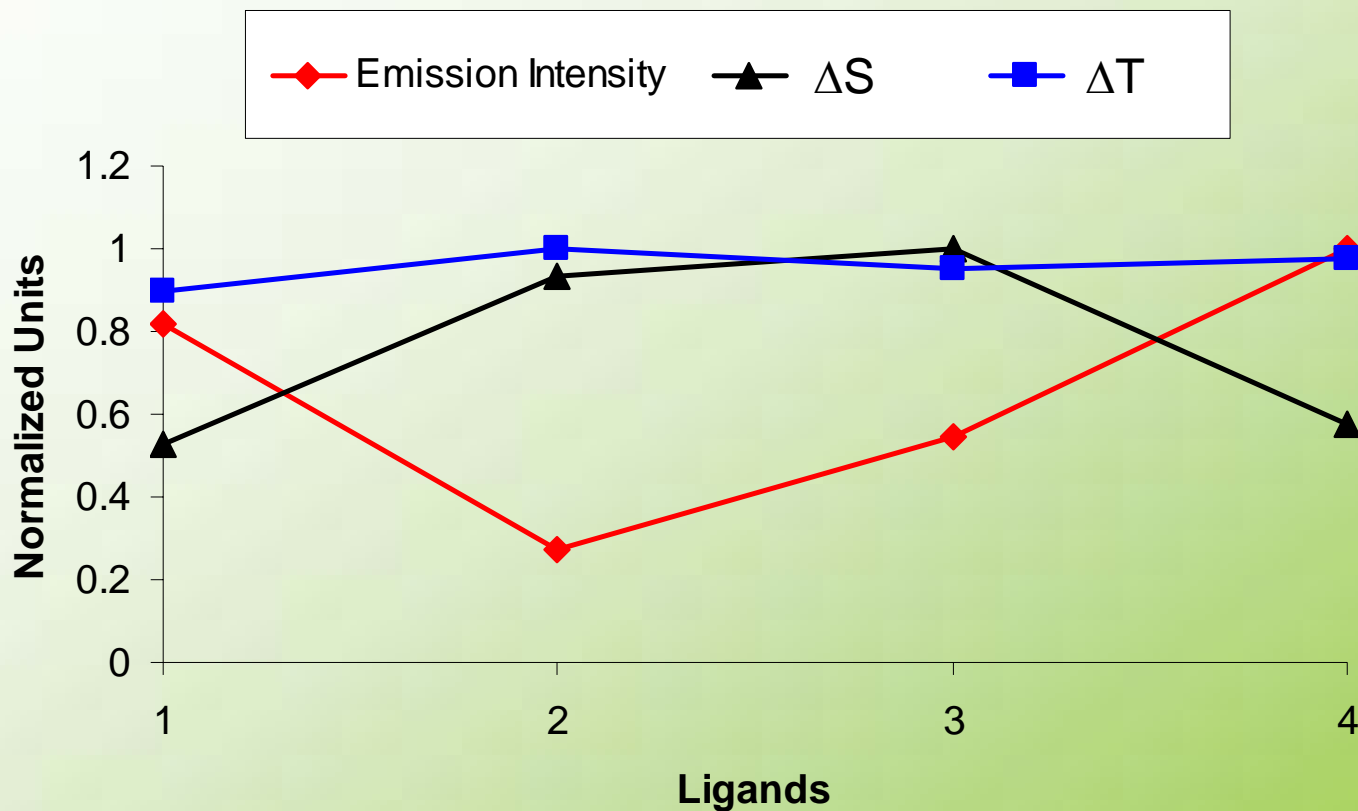


PM_th:Eu(L)₂ Emission Maxima



PM_{th}:Eu(L)₂ Ligands Versus Energy Parameters

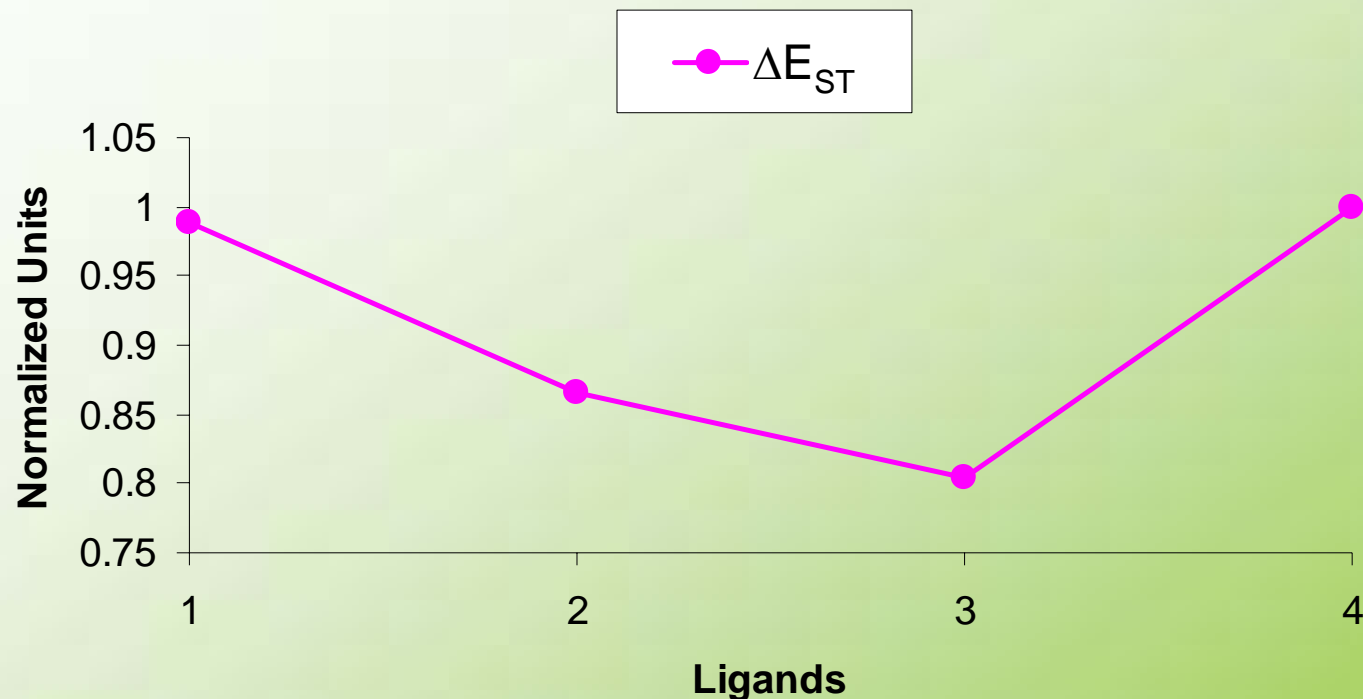
PM_{th}:Ln(L)₂ Systems, where Ligands: 1 = BTM, 2 = DTM, 3 = 3-PTM, 4 = 9-PTM.



- Smaller distances in singlet energies (ΔS) from polymer to polymer-ligand complexes inversely relate to greater emission intensities from complexes.
- Suggests Forster ET of greater significance than Dexter ET for polymer to ligand ET.

PM_{th}:Eu(L)₂ Ligands Versus Energy Parameters

PM_{th}:Ln(L)₂ Systems, where Ligands: 1 = BTM, 2 = DTM, 3 = 3-PTM, 4 = 9-PTM.



- Greater distances in singlet to triplet energies for polymer-ligand complexes almost directly relate to greater emission intensities from complexes.
- Suggests back energy transfer led to lower emission intensities for DTM and 3-PTM.
- Forward ISC favored for BTM and 9-PTM.

PM_{th}:Ln(L)₂ Systems Characterization

Photophysical properties of PM_{th} gadolinium complexes.

	PM _{th} : Gd(HFA) ₂	PM _{th} : Gd(BTM) ₂	PM _{th} : Gd(DTM) ₂	PM _{th} : Gd(3-PTM) ₂	PM _{th} : Gd(9-PTM) ₂
Abs. Max (nm) (cm ⁻¹)	331 30,211	358 27,933	374 26,738	378 26,455	358 27,933
Em. Max (nm) (cm ⁻¹)	391 25,575	416 24,038	421 23,753	427 23,419	405 24,691
Δ (cm ⁻¹)	4,636	3,895	2,985	3,036	3,242
E _S (eV) (cm ⁻¹)	3.42 27,548	3.23 26,042	3.09 24,876	3.06 24,691	3.21 25,907
E _T (eV) (cm ⁻¹)	2.75 22,148	2.42 19,531	2.38 19,231	2.40 19,380	2.39 19,305
ΔE _{ST} (eV)	0.67	0.81	0.71	0.66	0.82

Energy Transfer Efficiencies from Polymer to Ligand to PM_{aryl}:Eu(L)₂ Systems, where L = HFA, BTM, DTM, 3-PTM, or 9-PTM.

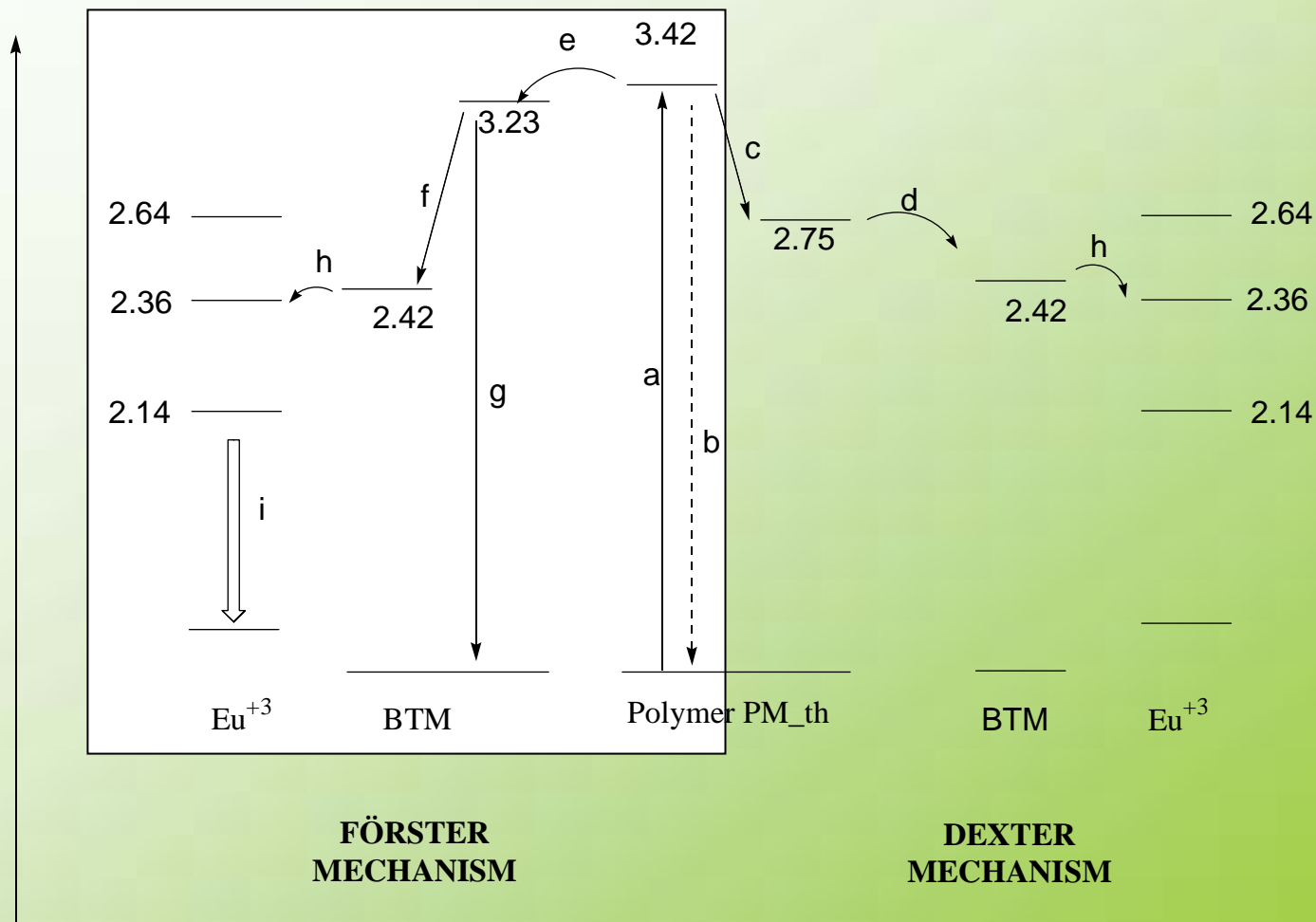
	<u>BTM</u>	<u>DTM</u>	<u>3-PTM</u>	<u>9-PTM</u>
<i>PM_{fu}:Eu(L)₂</i>	0.998	0.998	0.998	0.998
<i>PM_{py}:Eu(L)₂</i>	0.999	0.998	0.998	0.998
<i>PM_{pz}:Eu(L)₂</i>	0.998	0.998	0.997	0.998
<i>PM_{th}:Eu(L)₂</i>	0.998	0.998	0.998	0.998



PM_{th}:Ln(L)₂ Systems Characterization

The energy transfer mechanism for the PM_{th}:Eu(BTM)₂ system.

Energy (eV)



Conclusions – Europium Sensitization Project

- Energy transfer has been shown to occur from polyphenylenes as the energy donors to ligand systems as intermediate acceptors and then to lanthanides as the terminal acceptors.
- Higher intensities of emission from lanthanide were due to:
 - Ligands that were asymmetric and had shorter effective conjugation lengths.
 - Binding acceptor complex directly to donor polymer.
 - Pendant β -diketonates bind complex better than terpyridines.
 - Better matching of energy levels between ligand systems with lanthanides, as illustrated by BTM and 9-PTM being brighter than DTM and 3-PTM.
 - Smaller relative singlet energy distances between polymer and polymer-ligand system (favoring Forster ET).
 - Larger relative singlet to triplet energy gaps on polymer-ligand systems (favoring forward ISC).

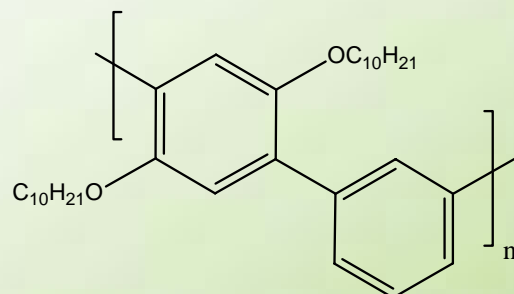
Applications

- Organic / Polymer Light Emitting Diodes
- Methods of Optimizing O/PLEDs
- Sensors



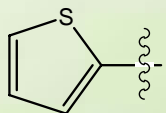
Sensitization of Erbium Chelates

Synthesis of Polymers with Pendant β -Diketonates Bound to Erbium(III) meso-Tetraphenylporphyrinate

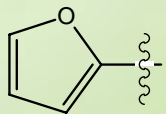


Polymer Aryl Group

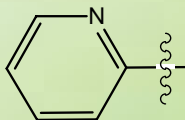
PM_th



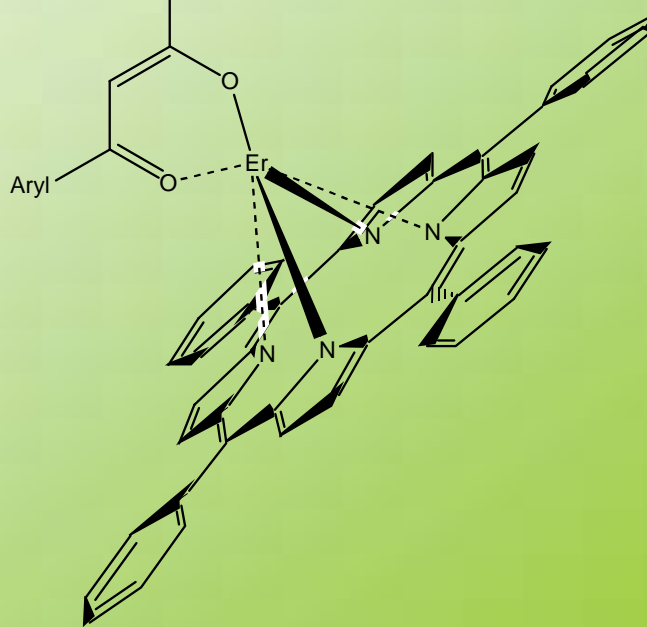
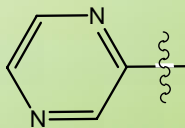
PM_fu



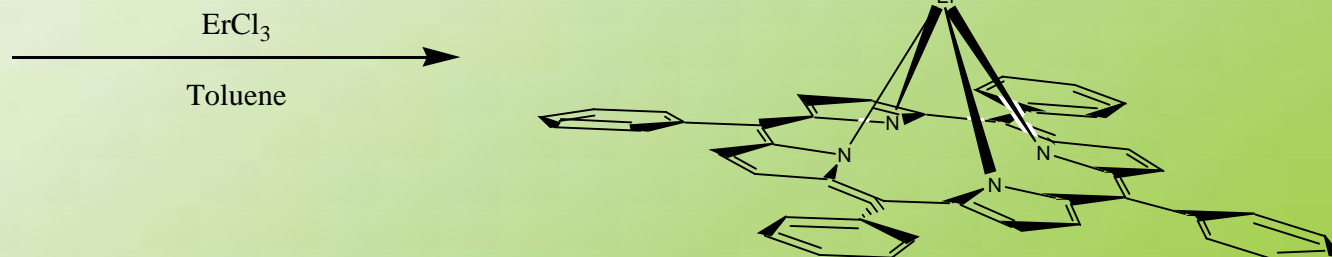
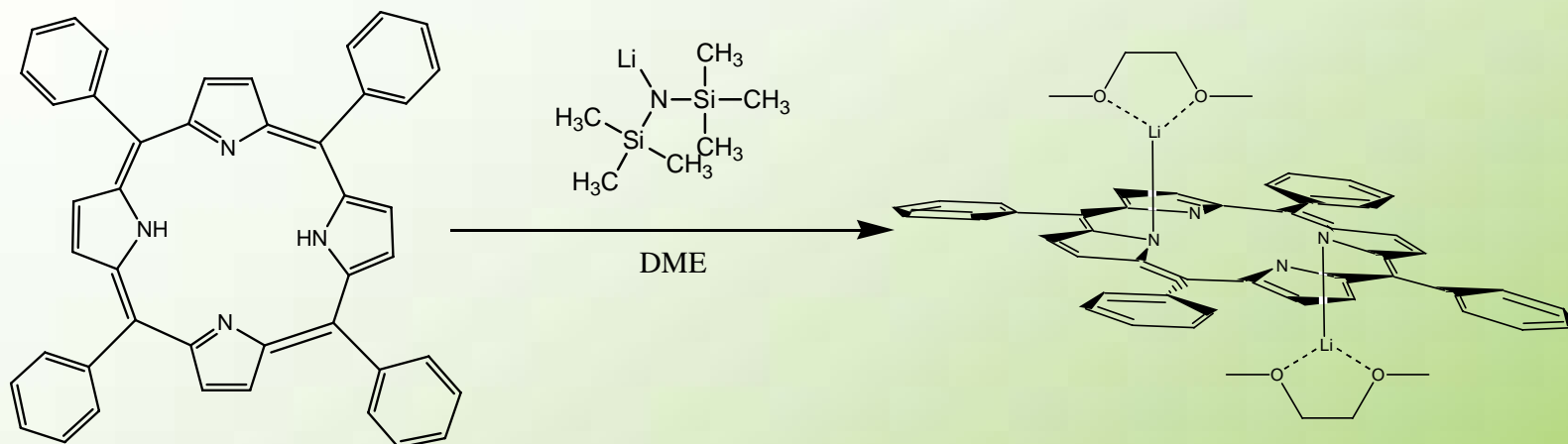
PM_py



PM_pz

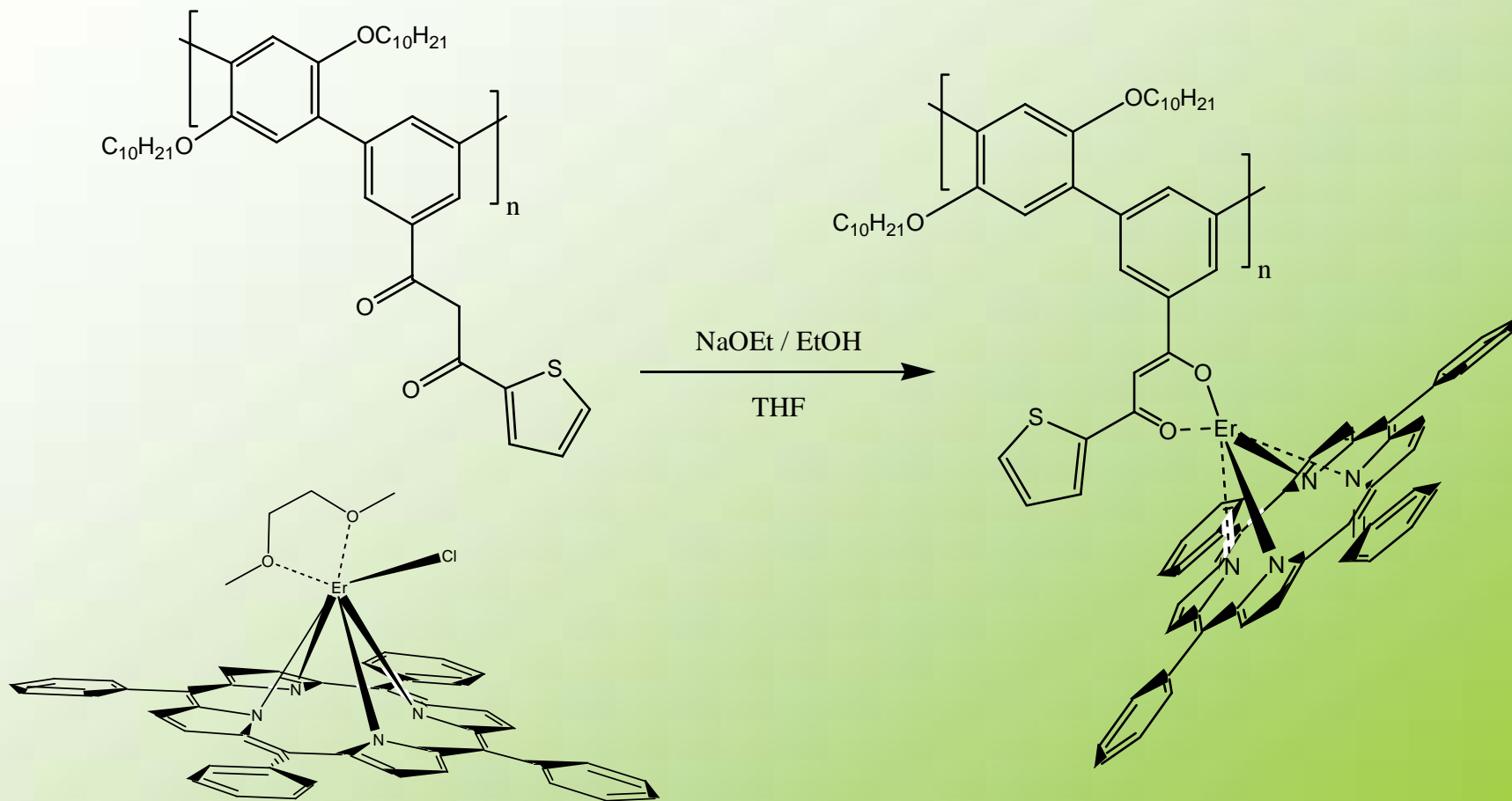


Erbium Porphyrinate Synthesis



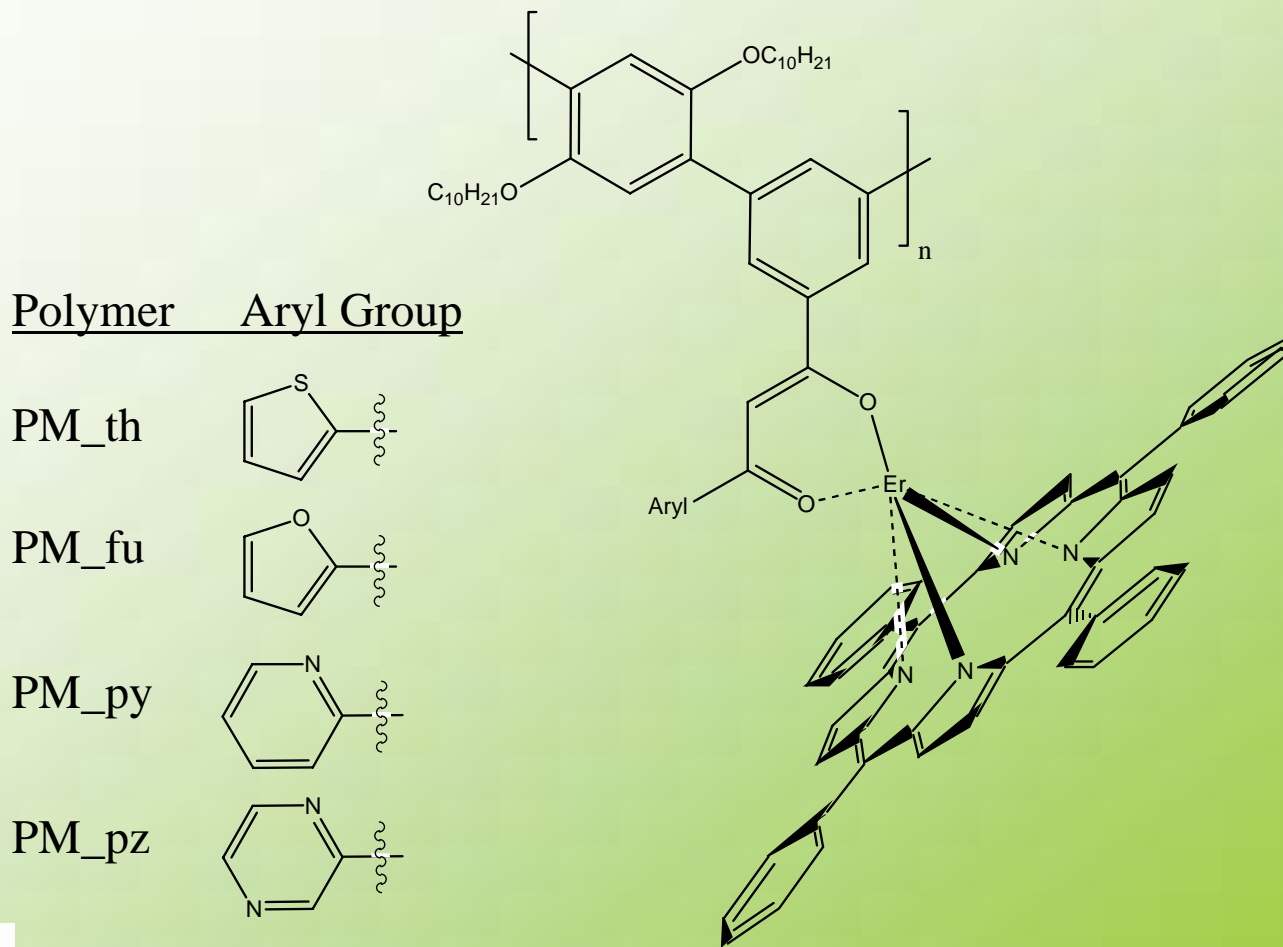
Verified with x-ray crystal.

Polymer Erbium Chelate Synthesis

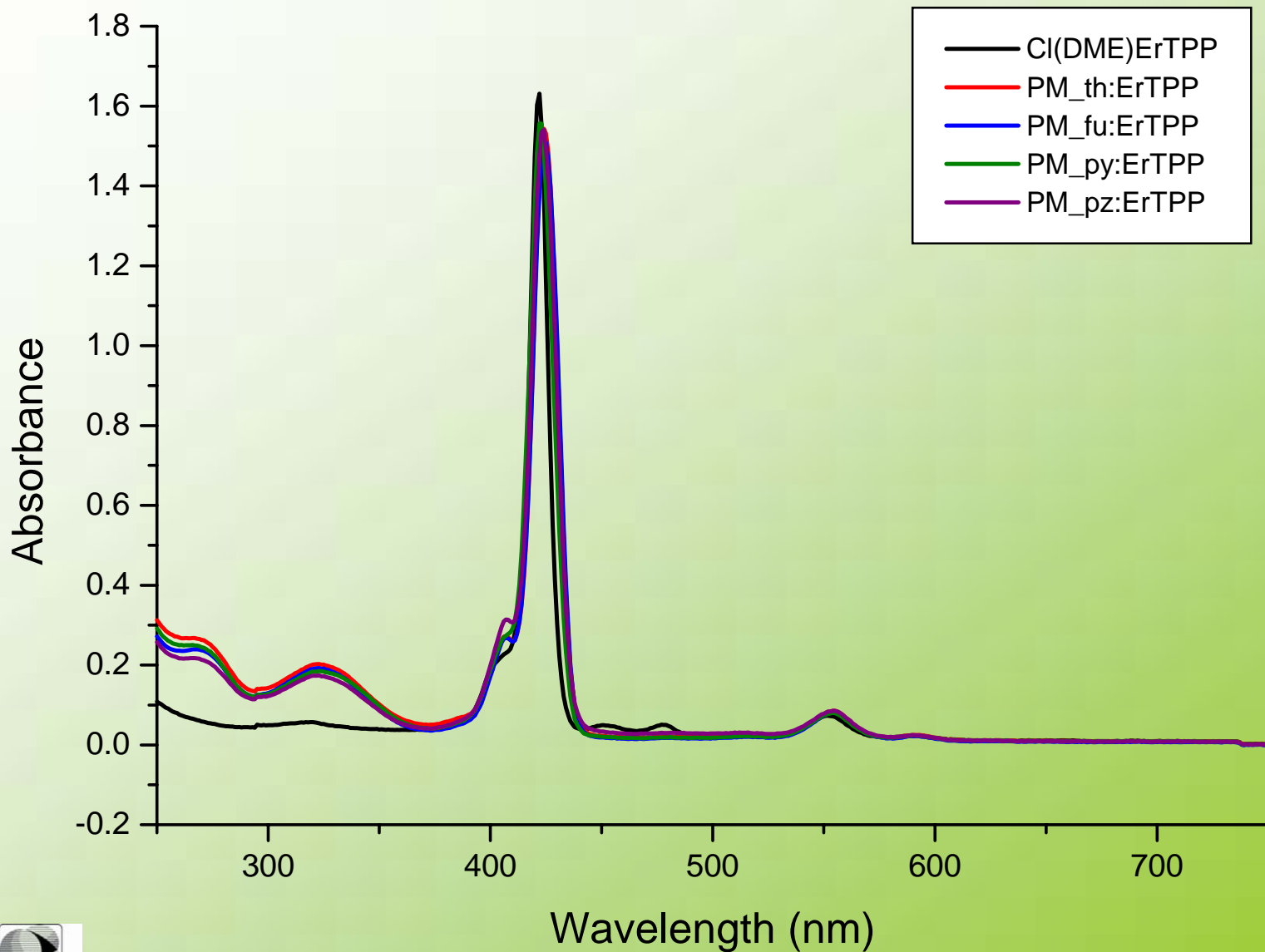


Sensitization of Erbium Chelates

Photophysical Performance Data

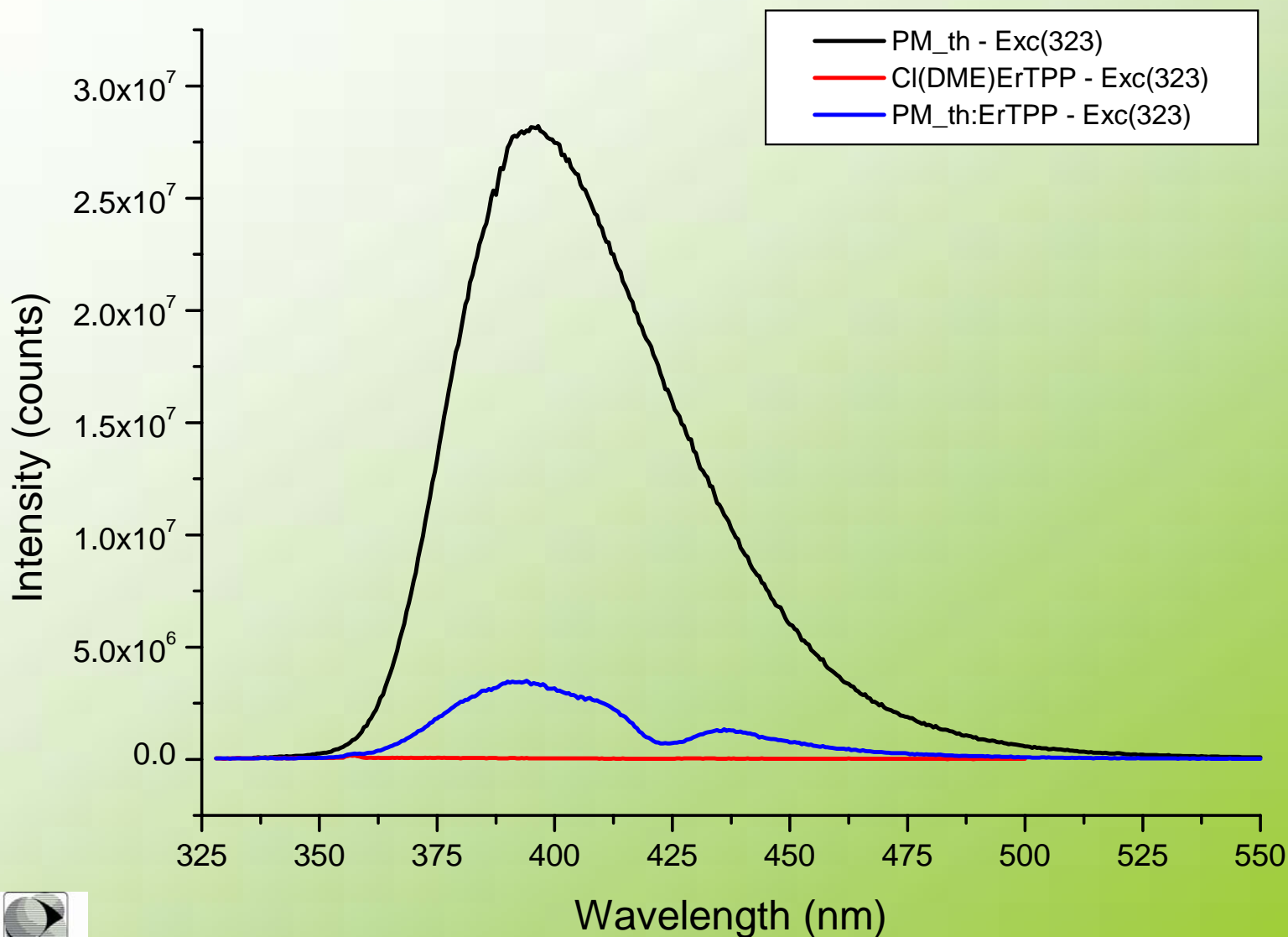


Poly:ErTPP Absorbance Spectra

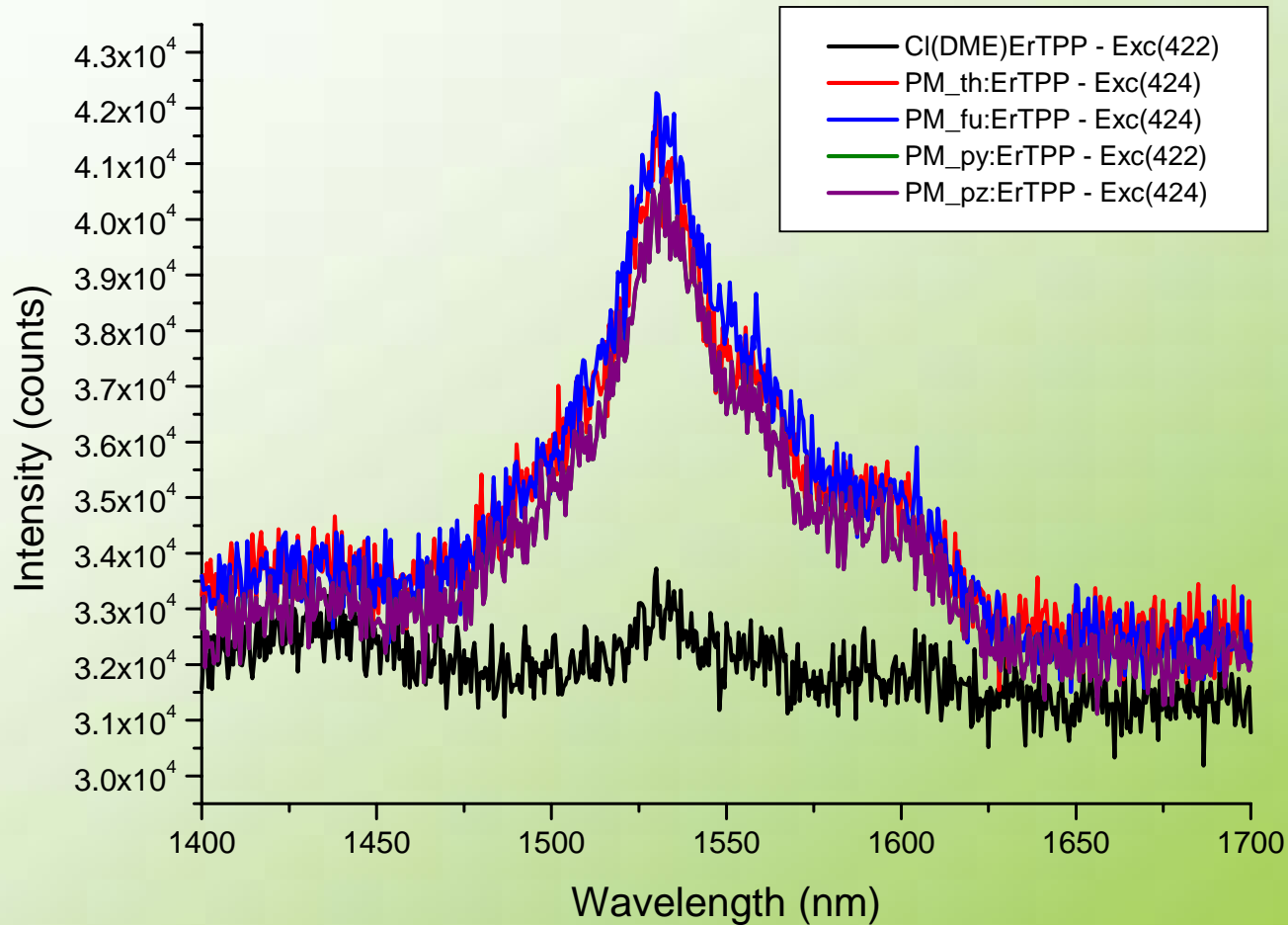


PM_{th}:ErTPP Visible Emission

Exciting @ Poly Max, Relative to PM_{th} and Cl(DME)ErTPP

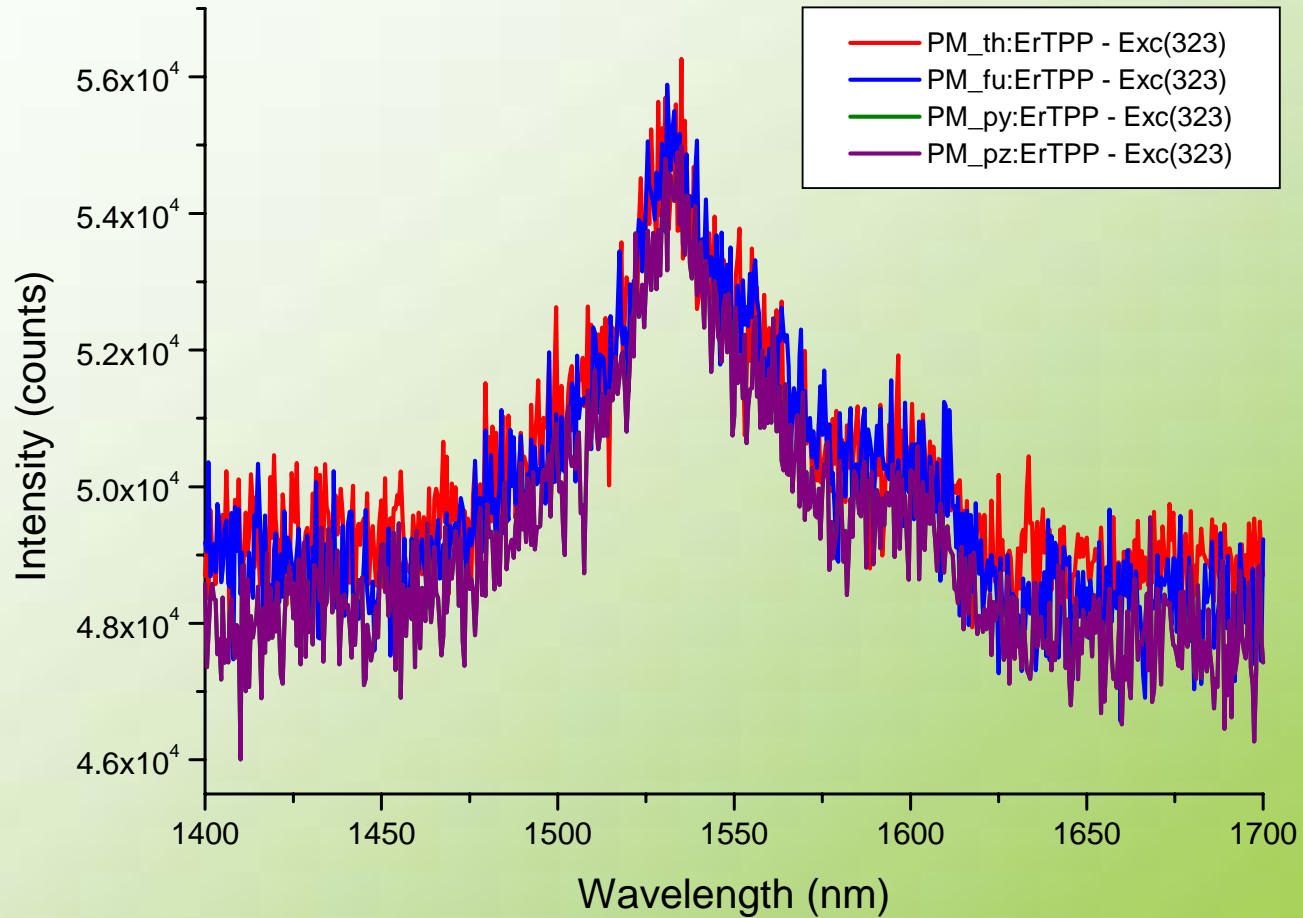


Poly:ErTPP Infrared Emission Exciting at Porphyrin Absorbance Maxima



Room temperature IR emission at 10^{-5} M in degassed, anhydrous THF.

Poly:ErTPP Infrared Emission Exciting at Polymer Absorbance Maxima



Room temperature IR emission at 10^{-5} M in degassed, anhydrous THF.

Conclusions – Erbium Sensitization Project

- Energy transfer has been shown to occur from polyphenylenes as the energy donors to a porphyrin system as an intermediate acceptor and then to erbium as the terminal acceptors.
- Infrared emission from a room temperature solution was shown.
- Intensity of erbium emission indifferent to aryl group identity on beta-diketonate.
- Erbium emission ~33% more intense when excited at porphyrin absorbance max.
- Suggests less than ideal matching of energy levels between polymer and porphyrin ligand.
- Either need to modify polymer to match ligand or modify ligand to match polymer.
- Opportunity to provide higher doping densities when coordinating to polymer.



Summary

- Design and synthesis of polymers with higher singlet and triplet energies.
 - Kink introduced with *para-meta* alternation increased both singlet and triplet energy levels of polyphenylene polymers.
- Design and synthesis of europium complexes with lower triplet energies.
 - Changing the structure of one of the aryl groups on a β -diketonate results in predictable photophysical changes.
 - Shorter conjugation length and higher asymmetry results in higher intensity of lanthanide emission.
- Higher intensity of lanthanide emission produced through the smaller relative singlet energy distances between polymer and polymer-ligand system (favoring Forster ET) and larger relative singlet to triplet energy gaps on polymer-ligand systems (favoring forward ISC).
- Design and synthesis of polymers with the ability to coordinate to lanthanides.
 - Polyphenylene-based polymers with pendant ligand functional groups in the repeat unit are able to donate energy to lanthanide complexes.
 - Europium systems produced visible emission.
 - Erbium systems produced infrared emission.



Future Work

Extending this Research

- Isolating the final complexes and characterizing by crystal structures or other means.
 - Most likely to include model compounds of dimers or trimers of the monomer unit.
- Incorporating these materials into devices and analyzing their performance.
- See if Dexter ET becomes favored via electrophosphorescence, since more triplets should be formed.
- IR-emitting displays for reading while wearing night-vision goggles.
- IR-emitting materials for waveguides and other telecommunication devices.
- Polymer-bound iridium systems for LEDs and related devices.
- Sensors for a variety of analytes: biologicals, inorganics, and organics.



Knowledge, Skills, and Abilities Enhanced or Obtained via this Research

- Design and synthesis of: small molecule organics, organometallic complexes / coordination complexes, and polymers.
- Characterization of materials through a variety of techniques: NMR, mass spectrometry, elemental analysis, x-ray crystallography, absorption spectroscopy, fluorescence and phosphorescence spectroscopy, etc..
- Purification of materials via: column chromatography, preparative thin layer chromatography, medium pressure chromatography, ambient pressure and vacuum distillation, reprecipitation, recrystallization, and sublimation.
- Structure-property / structure-function relationship studies.
- Data analysis using a variety of software: Excel, Igor Pro, Origin, PhotoChemCAD, etc..



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