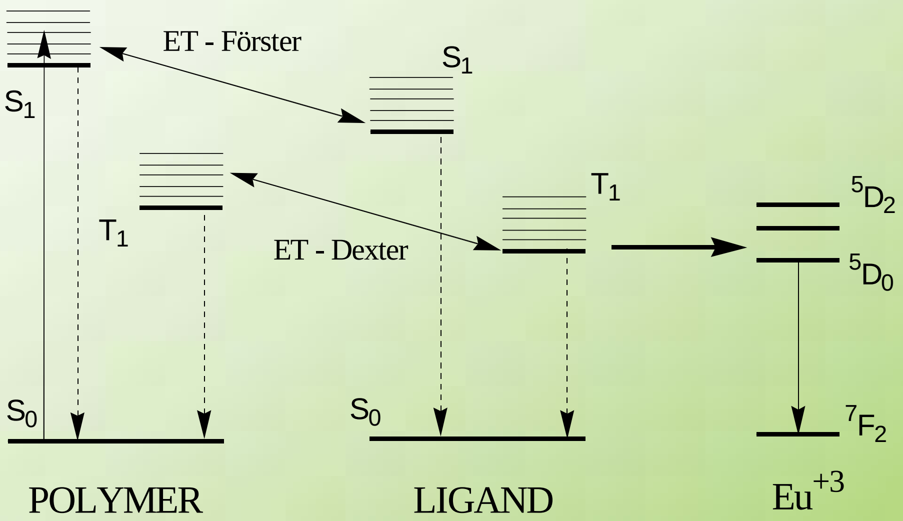
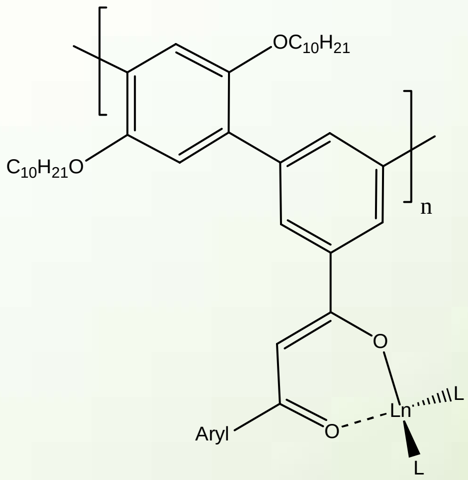
Design and Syntheses of Polymeric Materials for Visible and Near-Infrared Emitting Applications

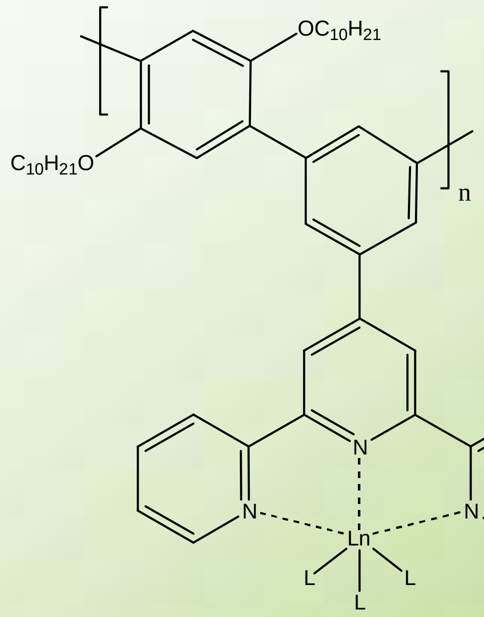


Sean Owen Clancy, Ph.D.

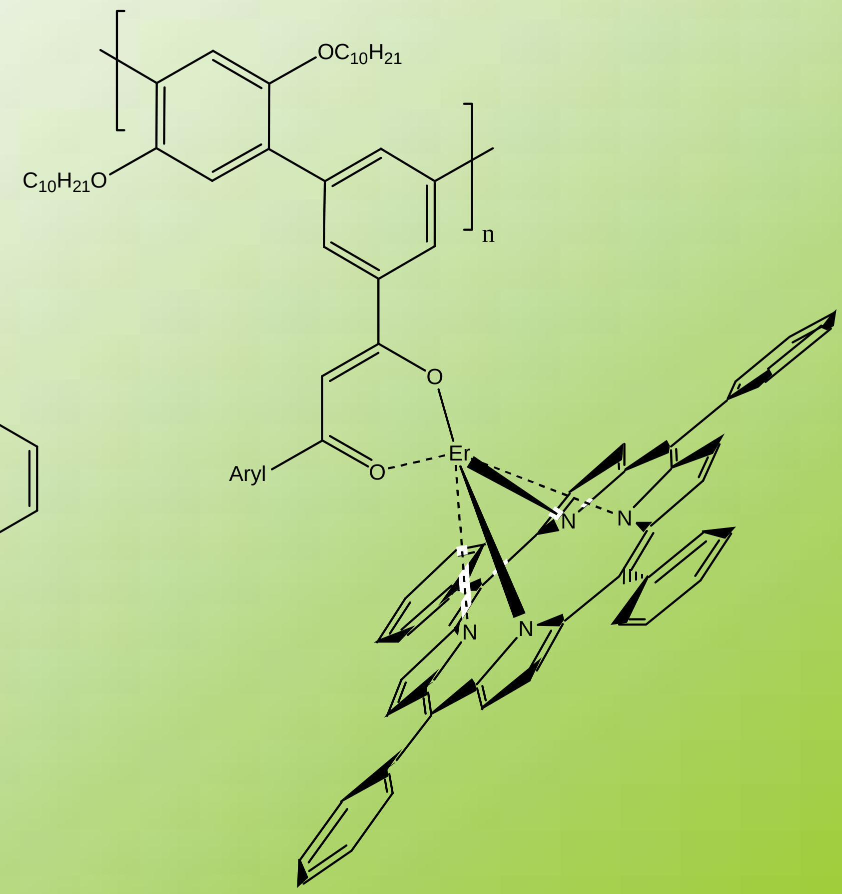
Polymeric Energy Transfer Complexes



• PM_aryl:Ln(L)$_2$



• PM_trp:Ln(L)$_3$



• PM_aryl:ErTPP

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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

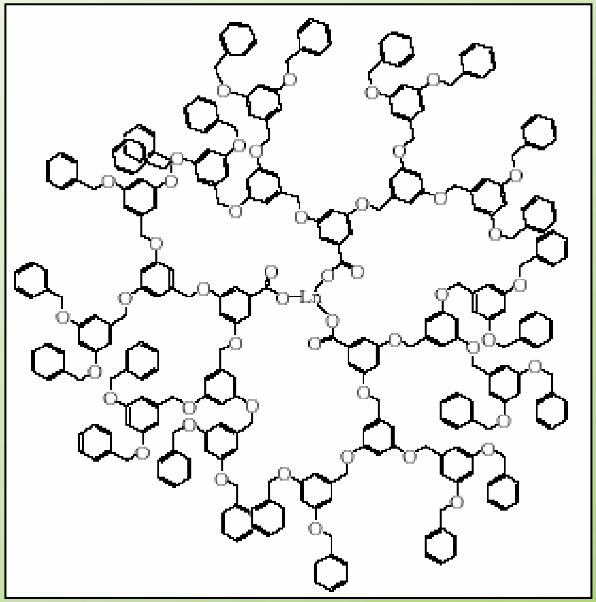
- Future Work

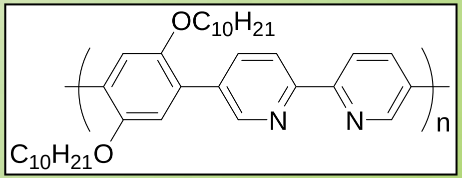
Harper Group Research

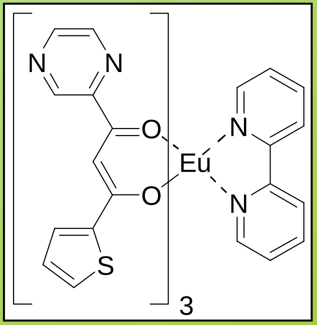
- Energy Transfer Studies
  - Light Harvesting Dendrimers
  - Light Harvesting Polymers
  - Polymer Photophysics

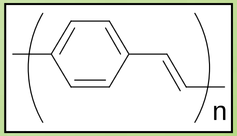
- Lanthanide Complexes
  - *β*-Diketonate Ligands
  - Dative Bonding Heterocyclic Ligands

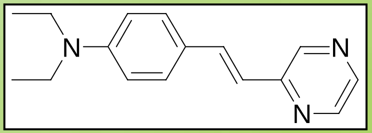
- Photonic Materials
  - Lanthanide Containing Materials
  - Organometallic Systems
  - PPV Syntheses
  - Polymer Sensors
  - Photonic Crystals
  - Quantum Dots
  - Two-Photon Dyes











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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

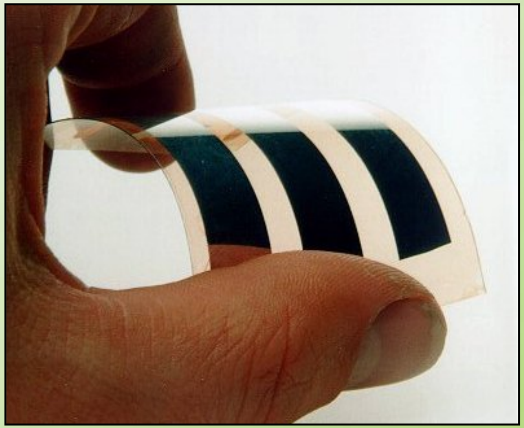
- Electrical excitation produces 25% singlets and 75% triplets.[1]
- Polymeric devices typically have higher external quantum efficiencies than small molecule devices.[2,3]
- Electrophosphorescent devices have higher efficiencies than electroluminescent devices.[4]
- Lanthanides exert the "heavy atom 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

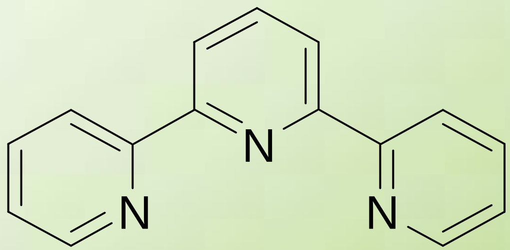
- Pure color emission (shielded *f* orbital transitions)
- Robust metals (will not photobleach)
- Induce heavy atom effect (improves rate of intersystem crossing)
- Triplet harvesters
- Reduce polymer degradation

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

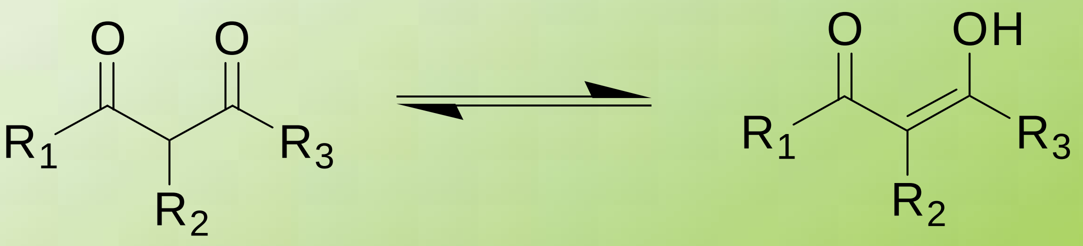
- Direct excitation is inefficient, to overcome
  - Laser source
  - Ligands
- Energy transfer is important
  - Conjugated organic ligands allow for ET
  - Ligands shield lanthanide ion from external environment, such as solvent (mode of energy loss) and other lanthanide ions (self quenching).

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:

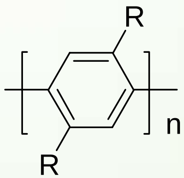


- Bidentate ligands, such as *beta*-diketonates, form both covalent and dative bonds:

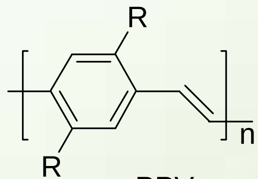


Background – Color Tuning

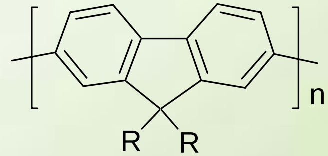
- *PPV and PPP type polymers are widely used*



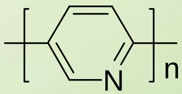
PPP



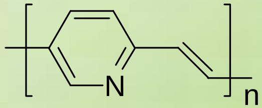
PPV



PF



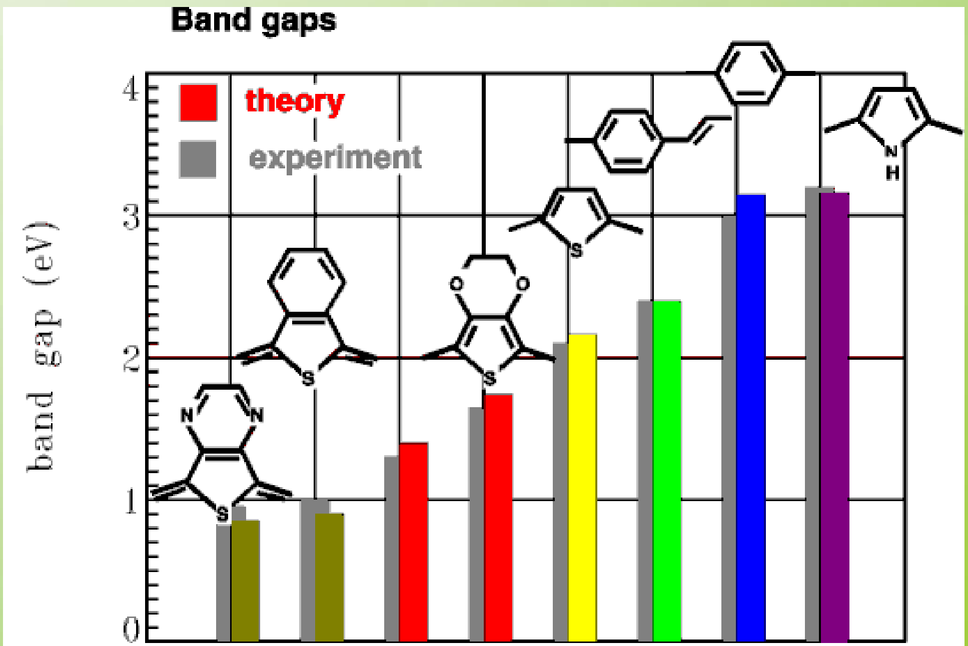
PPy



PPyV

- Mechanical properties

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

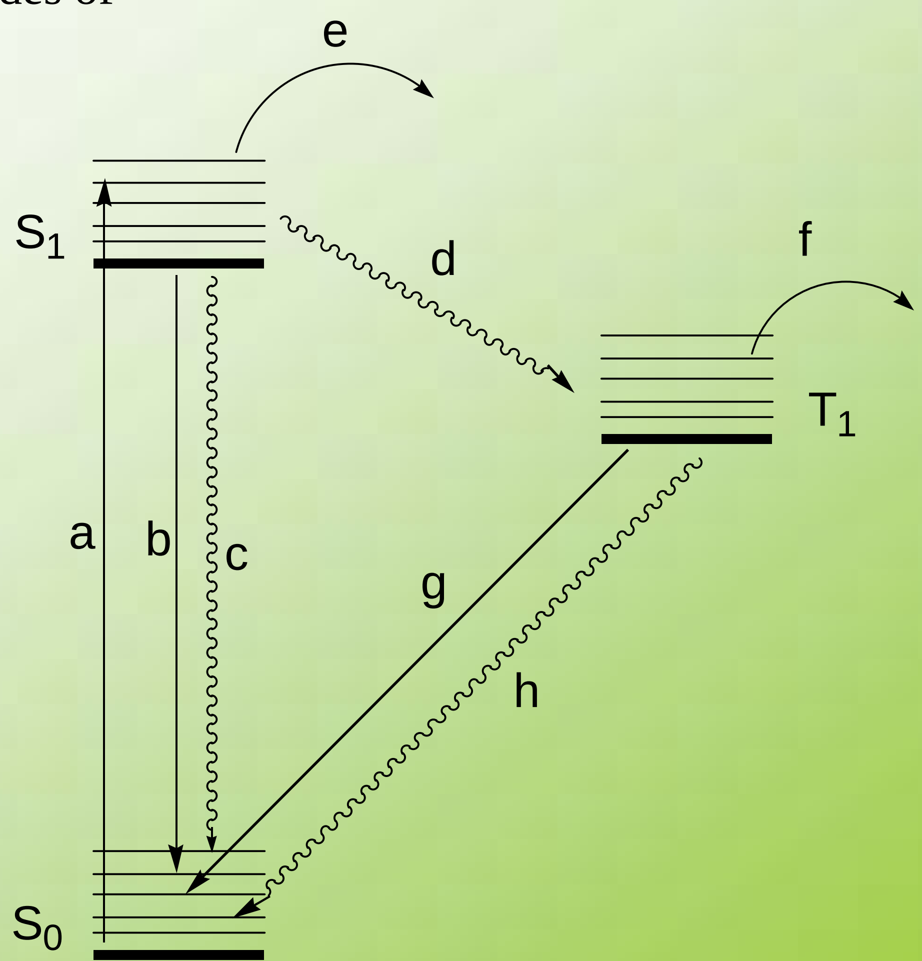


http://www.tn.utwente.nl/cms/polymers/conj_pol.htm

Background – Polymer Photophysics

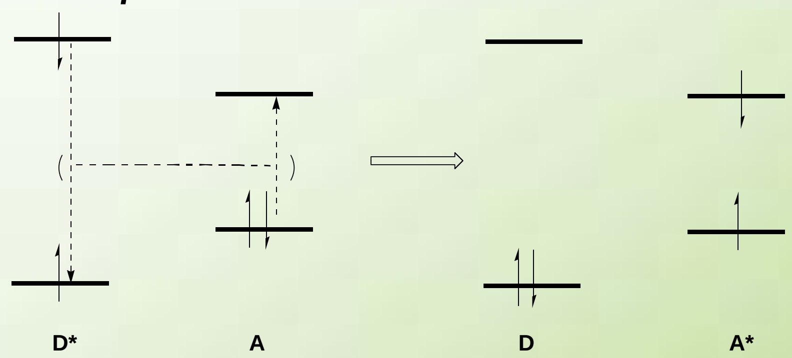
Energy level diagram showing modes of deactivation:

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



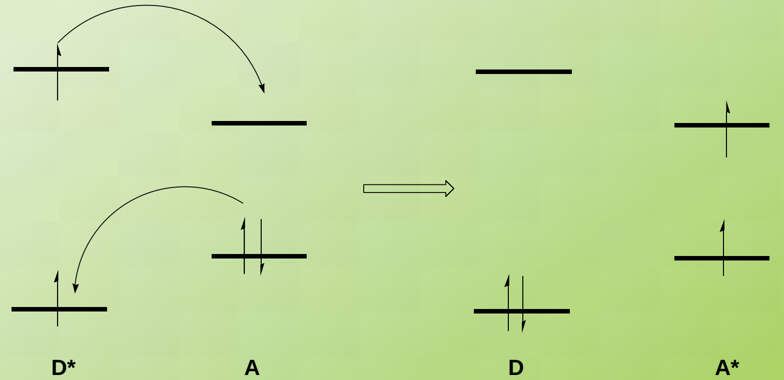
Background – Energy Transfer

Forster Energy Transfer



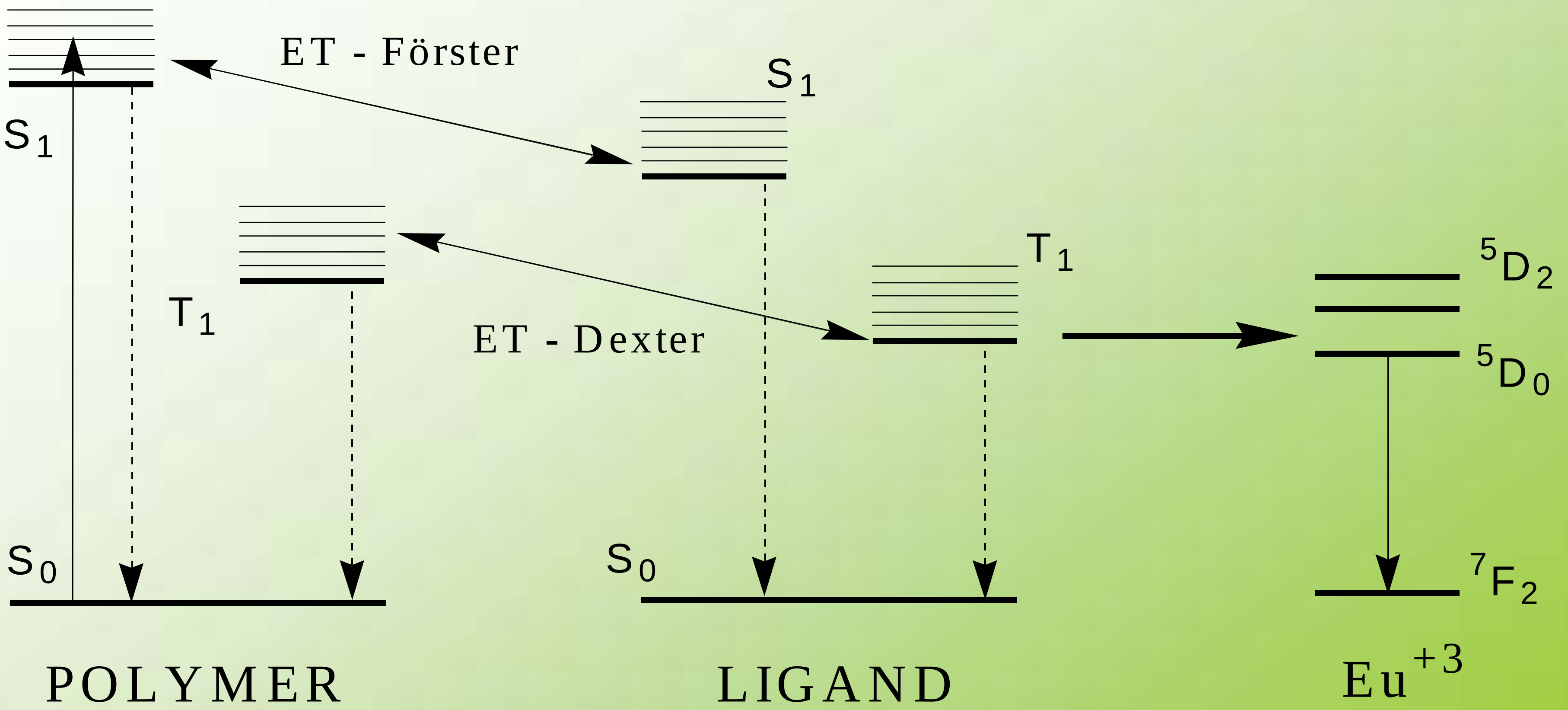
• Singlet to singlet
• Coupled dipole-dipole interaction; through space

Dexter Energy Transfer



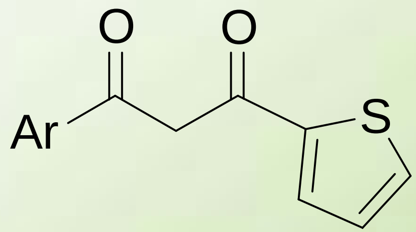
• Triplet to triplet
• Exchange mechanism; through bond

Background – Energy Transfer
Polymer to Ligand to Lanthanide



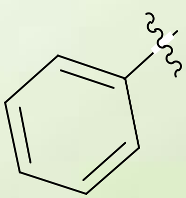
Sensitization of Europium Chelates

Design and Synthesis of β-Diketone Ligands

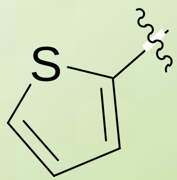


Ar =

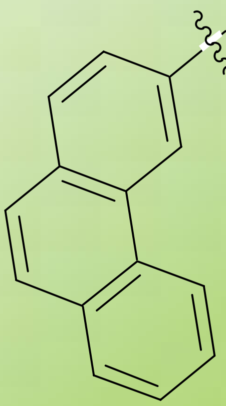
BTM



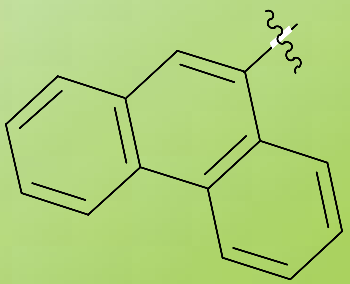
DTM



3-PTM



9-PTM



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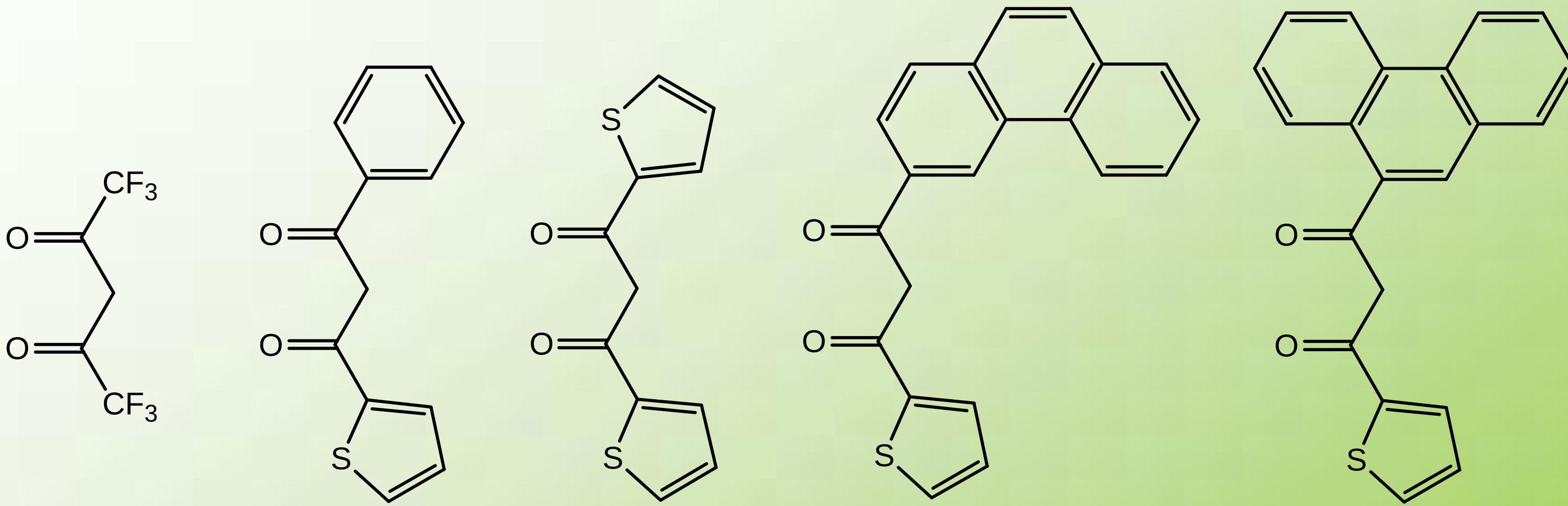
Sensitization of Europium Chelates

Ligand Structures

HFA BTM DTM 3-PTM 9-PTM



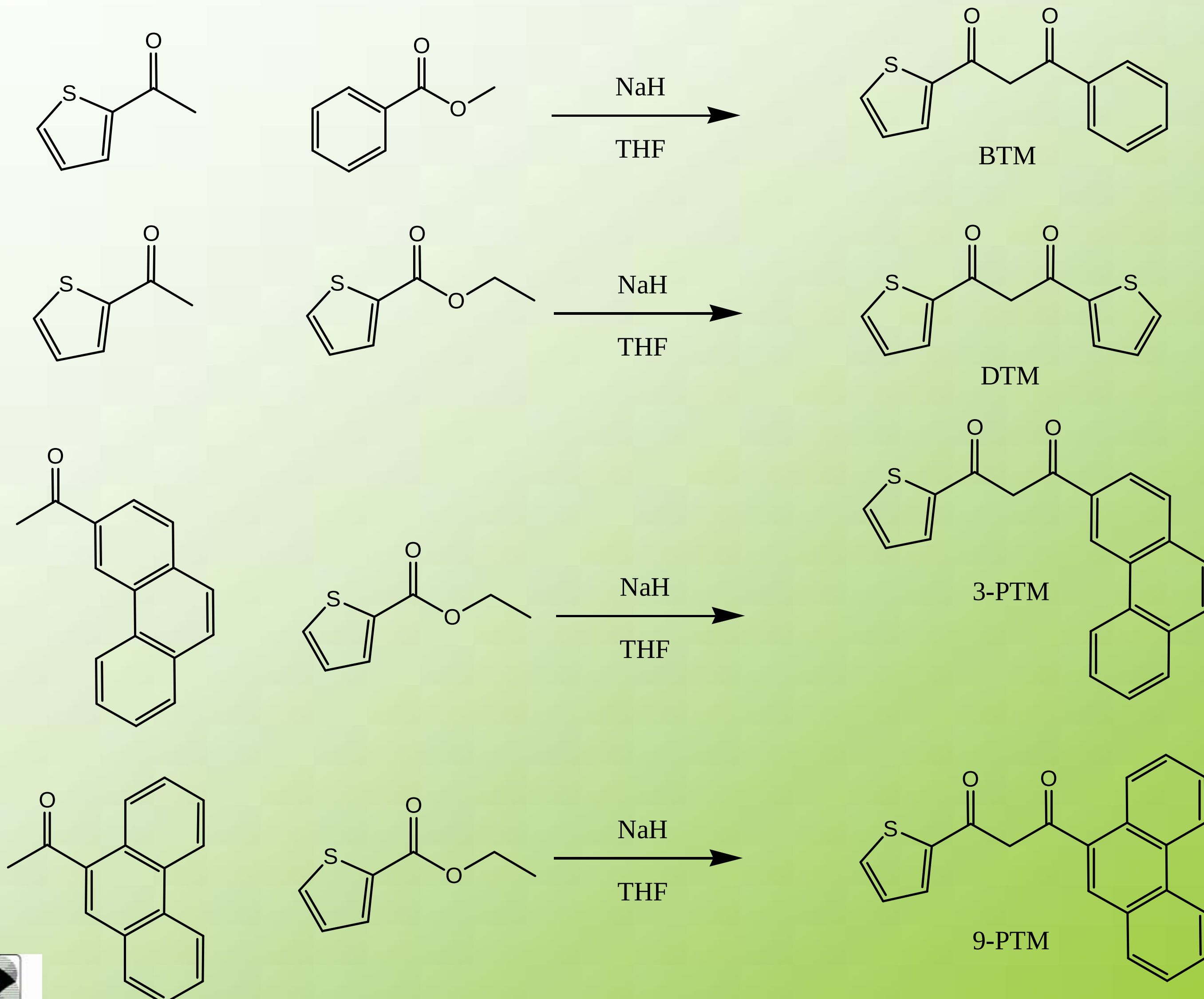
Asymmetric Vs. Symmetric

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.

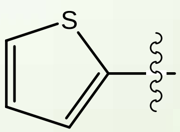
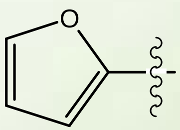
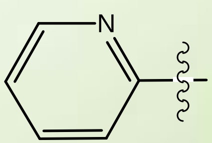
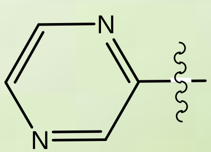
Sensitization of Europium Chelates

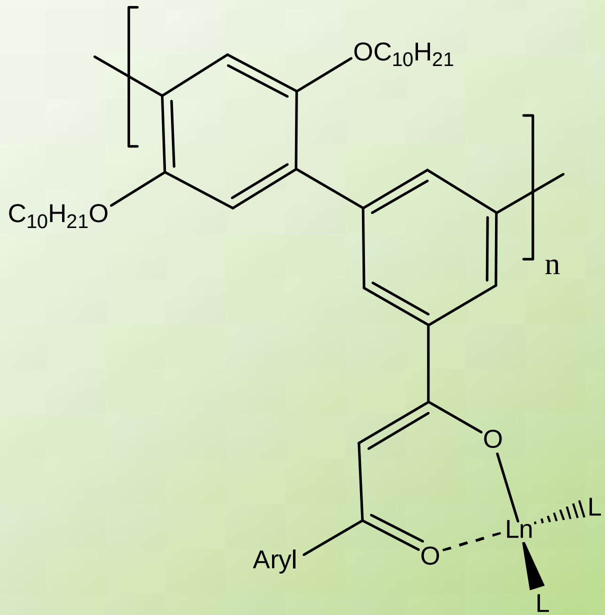
Ligand Syntheses



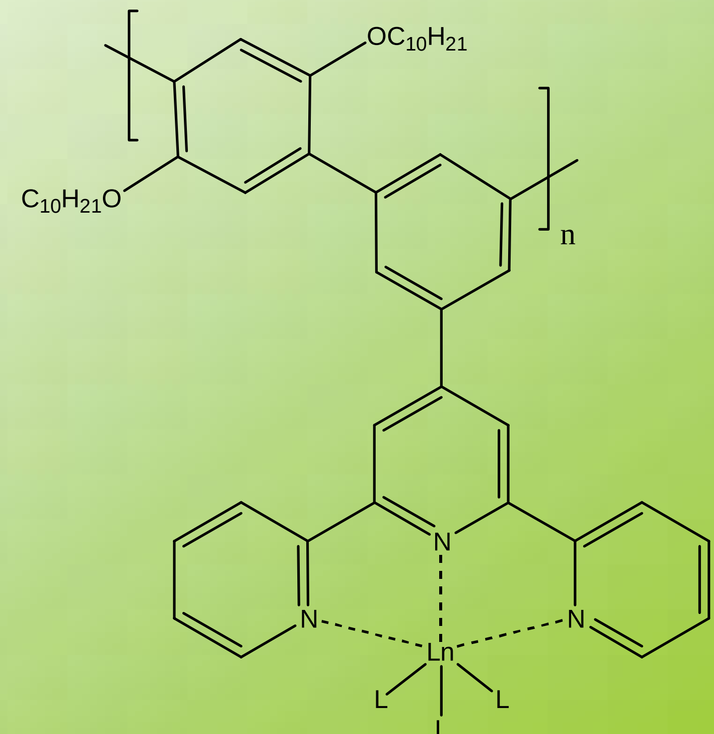
Sensitization of Europium Chelates

Polymer Structures

Polymer	Aryl Group
PM_th	
PM_fu	
PM_py	
PM_pz	

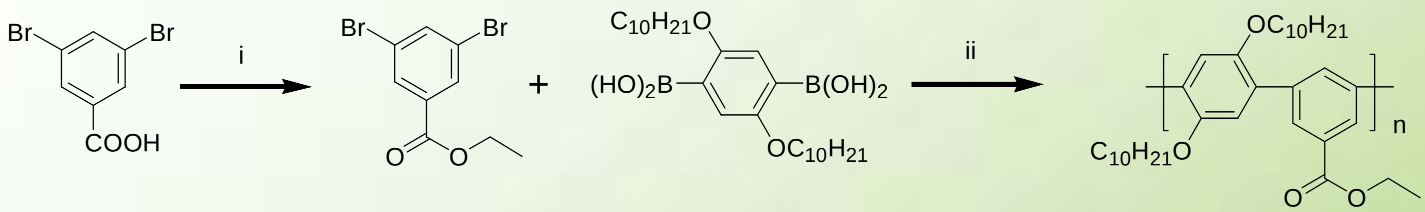


PM_trp

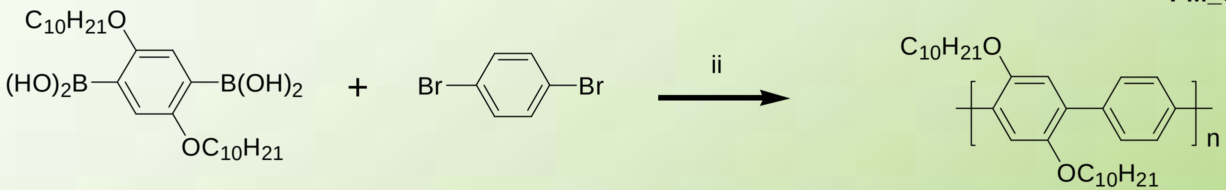


Sensitization of Europium Chelates

Energy Level Tuning of Polyphenylenes – Primary Donors



PM_es



P1

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).

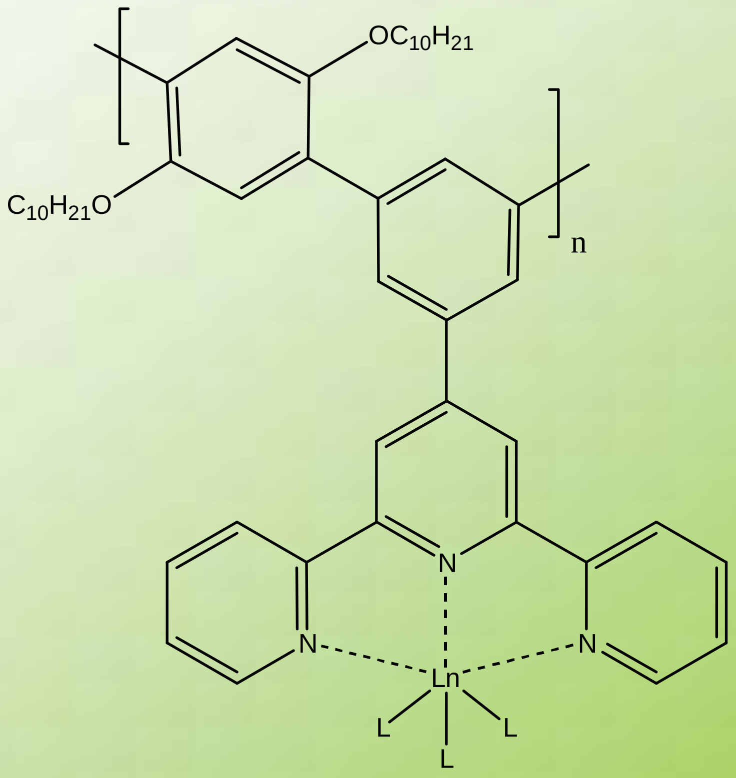
Photophysical properties of P1 and PM_es in THF.

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

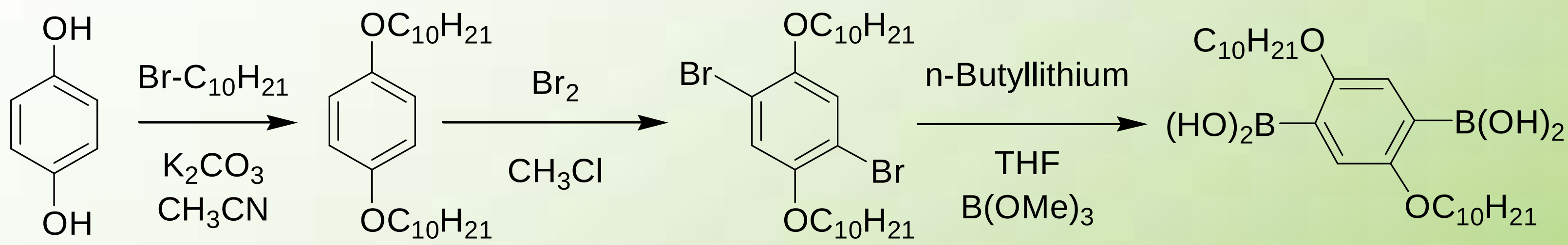
Sensitization of Europium Chelates

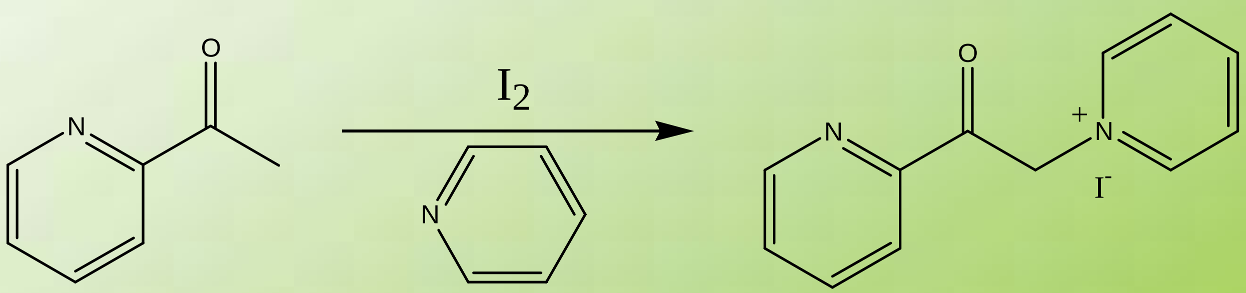
Synthesis of Polymers with Pendant Terpyridines Bound to Europium(III) β-Diketonates

PM_trp

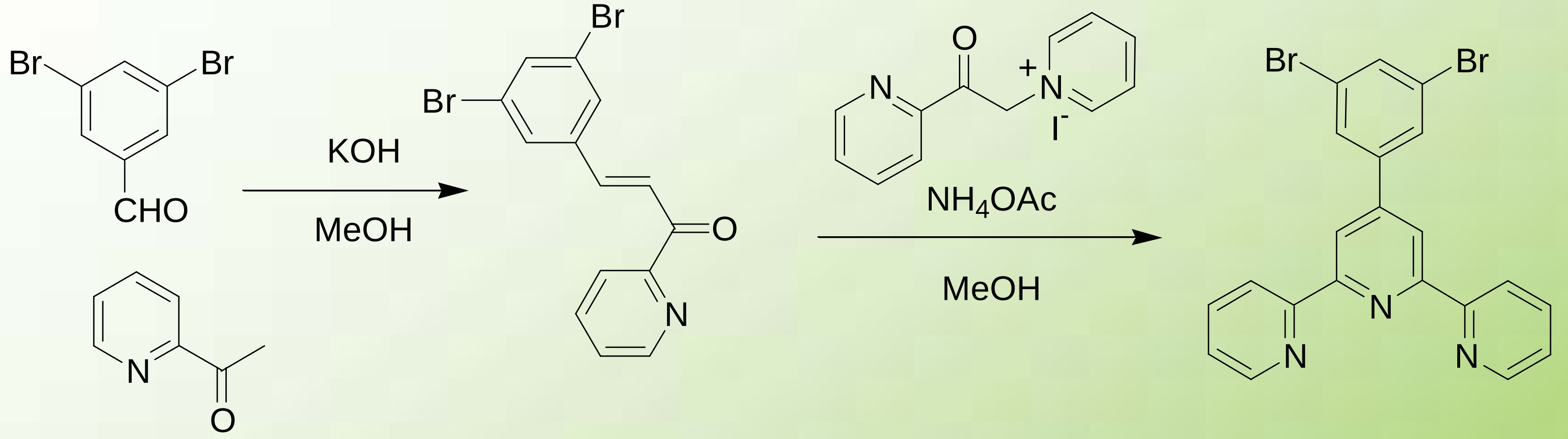


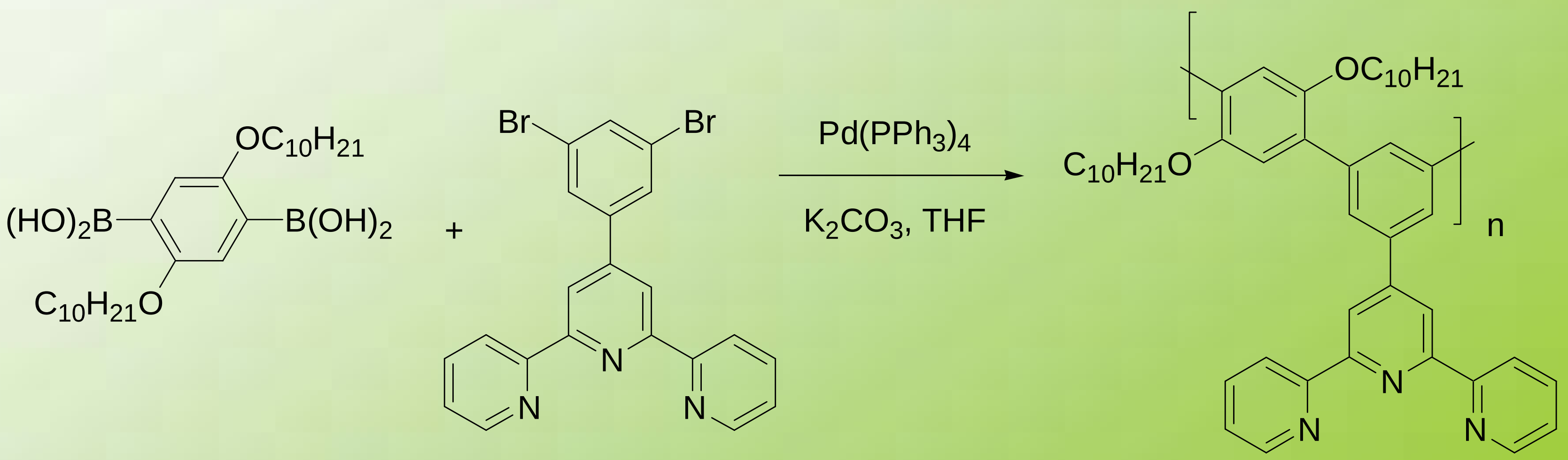
Polymer with Terpyridines Synthesis





Polymer with Terpyridines Synthesis





PM_trp

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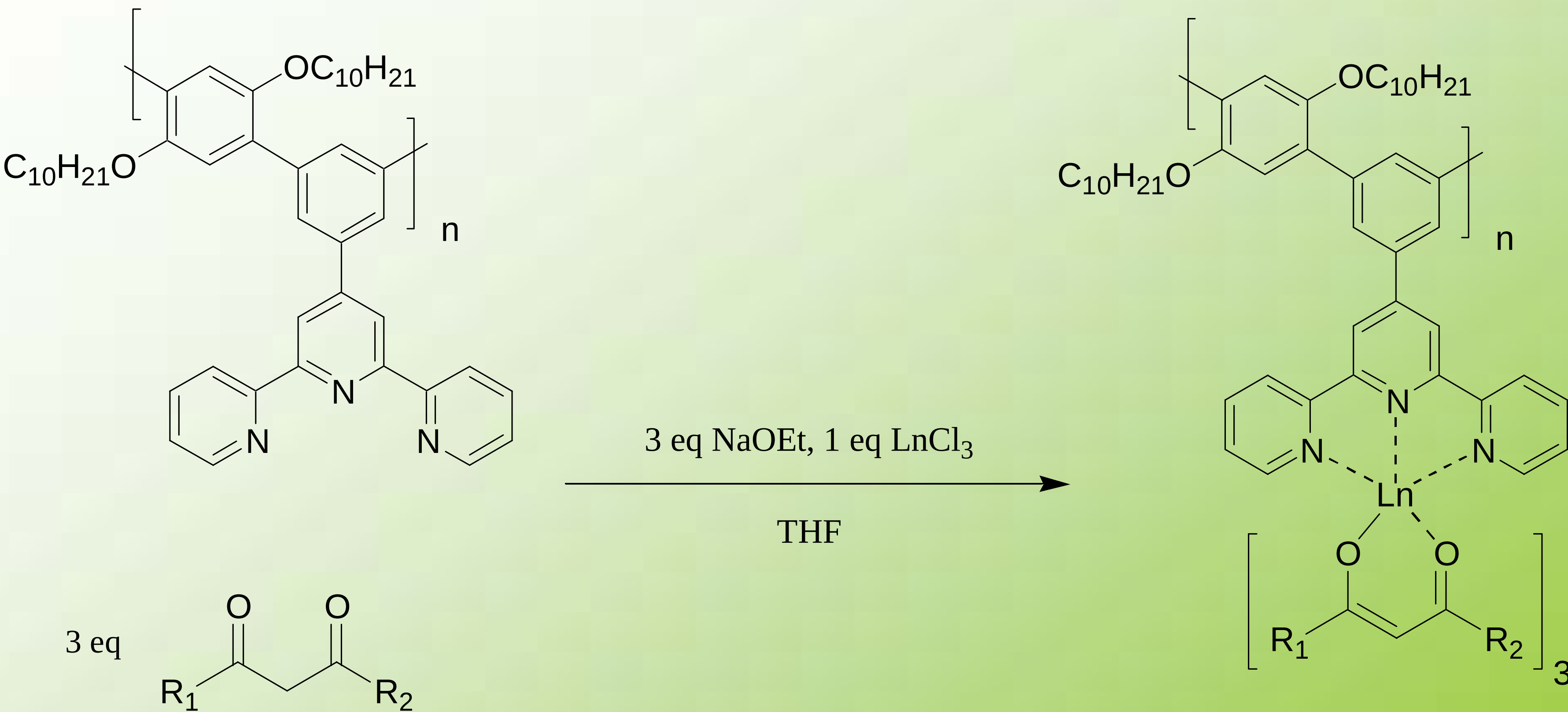
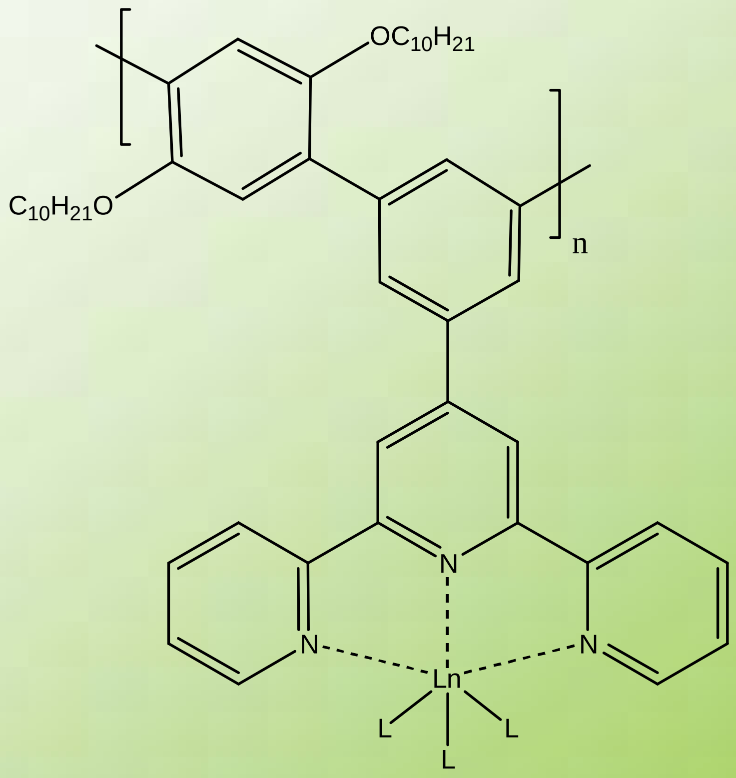
Polymer-Lanthanide Chelate Synthesis



Sensitization of Europium Chelates

Materials Characterization and Photophysical Performance Data

PM_trp



Polymer with Terpyridines Characterization

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

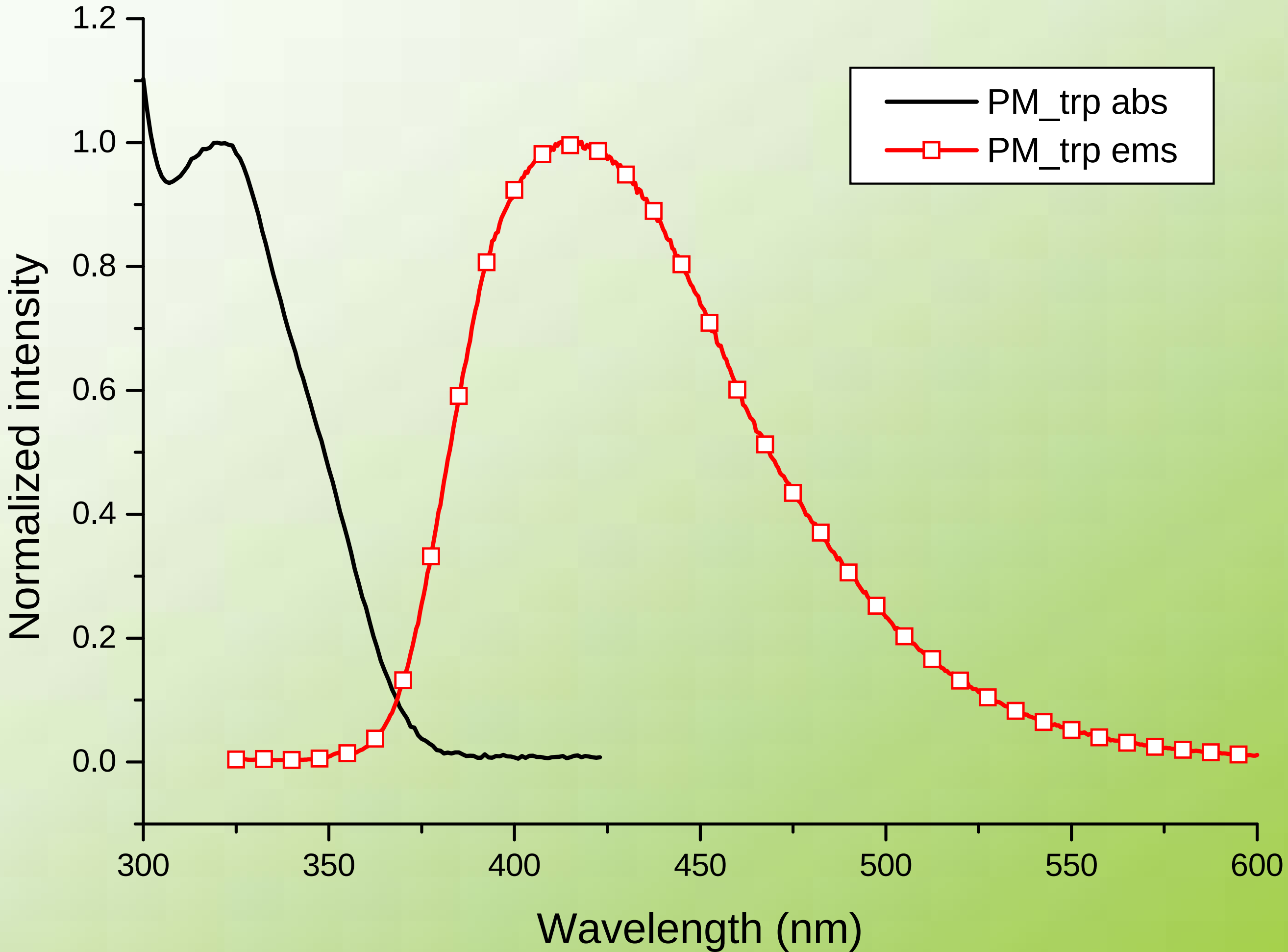
Polymer	dn/dc (mL/g)	M_n (g/mol)	M_w (g/mol)	PDI
PM_trp	0.1608	8.669×10^6	1.117×10^7	1.29

Photophysical properties of polymers PM_trp in THF.

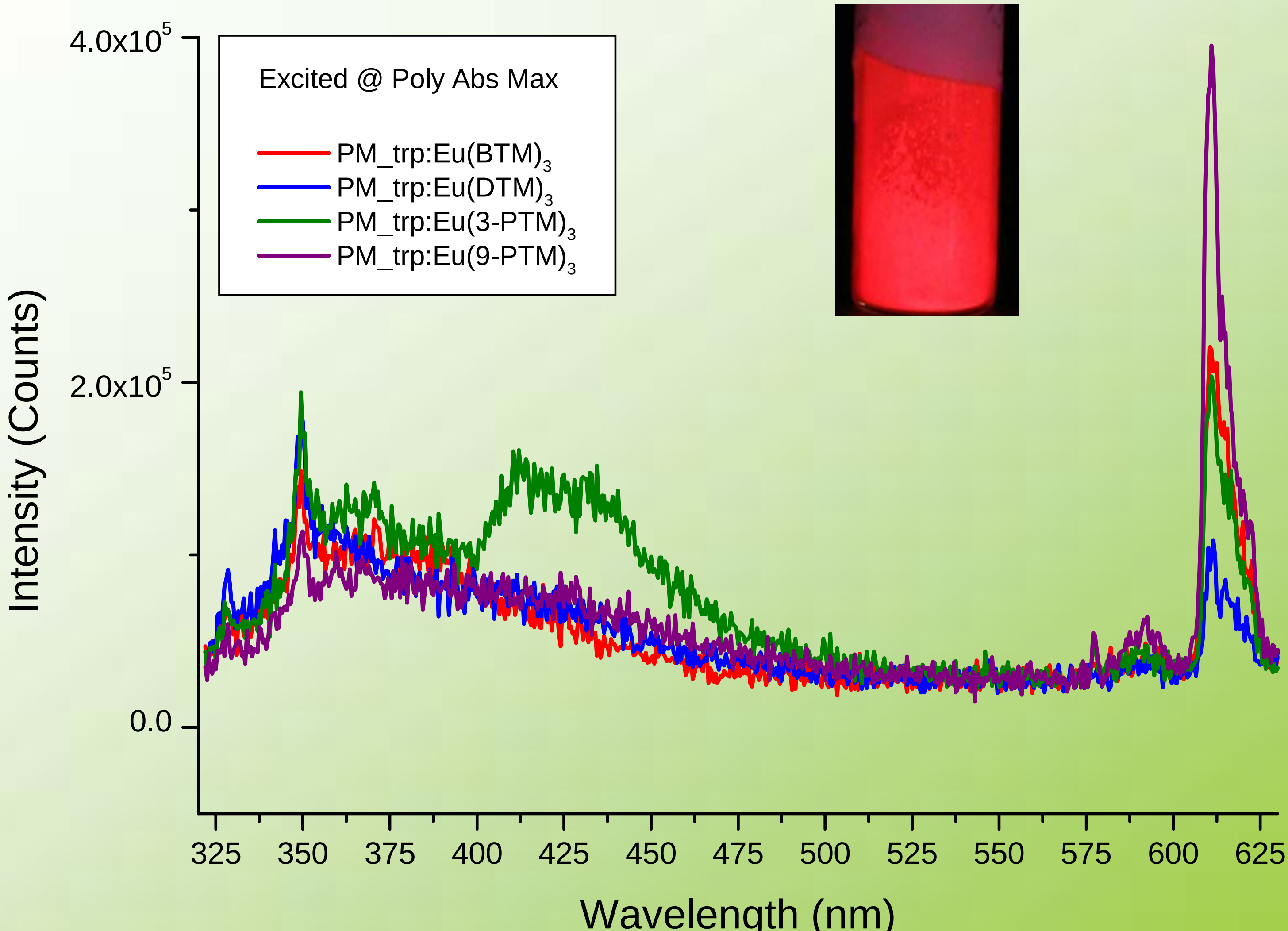
	PM_trp
Absorption maximum	320 nm
Fluorescence maximum	416 nm
FWHM	85 nm
Stokes' shift	7,212 cm^{-1}
Φ_{FL}	0.062
Lifetime (weighting coefficient)	0.27 ns (0.60) 1.49 ns (0.40)
Singlet energy level (E_S)	3.32 eV
Triplet energy level (E_T)	2.47 eV
Singlet-triplet gap (ΔE_{ST})	0.85 eV

Polymer with Terpyridines Characterization

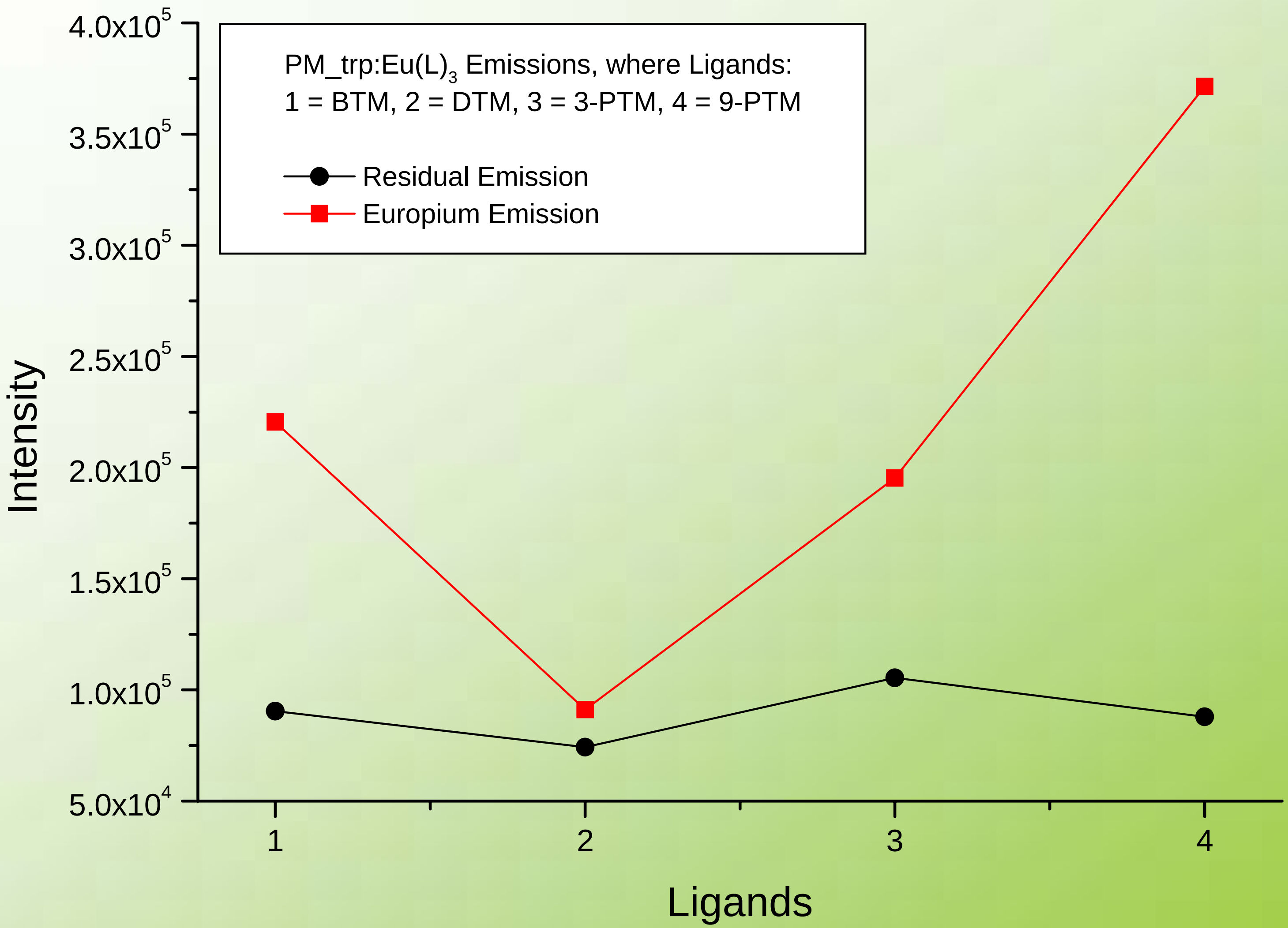
The absorbance and emission spectra of polymer PM_trp in THF (ex = 320 nm).



PM_trp:Eu(L)$_3$ Emission Spectra

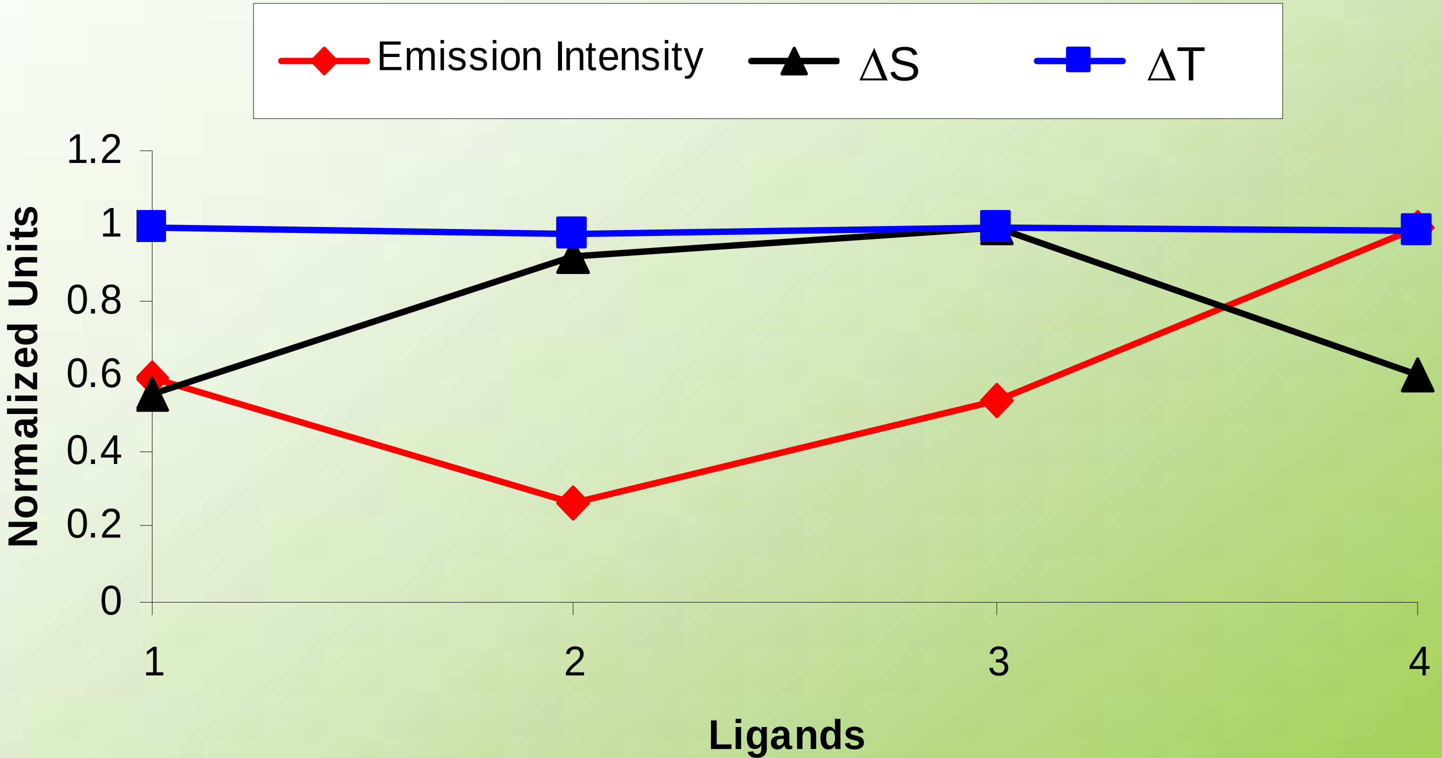


PM_trp:Eu(L)$_3$ Emission Maxima



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.

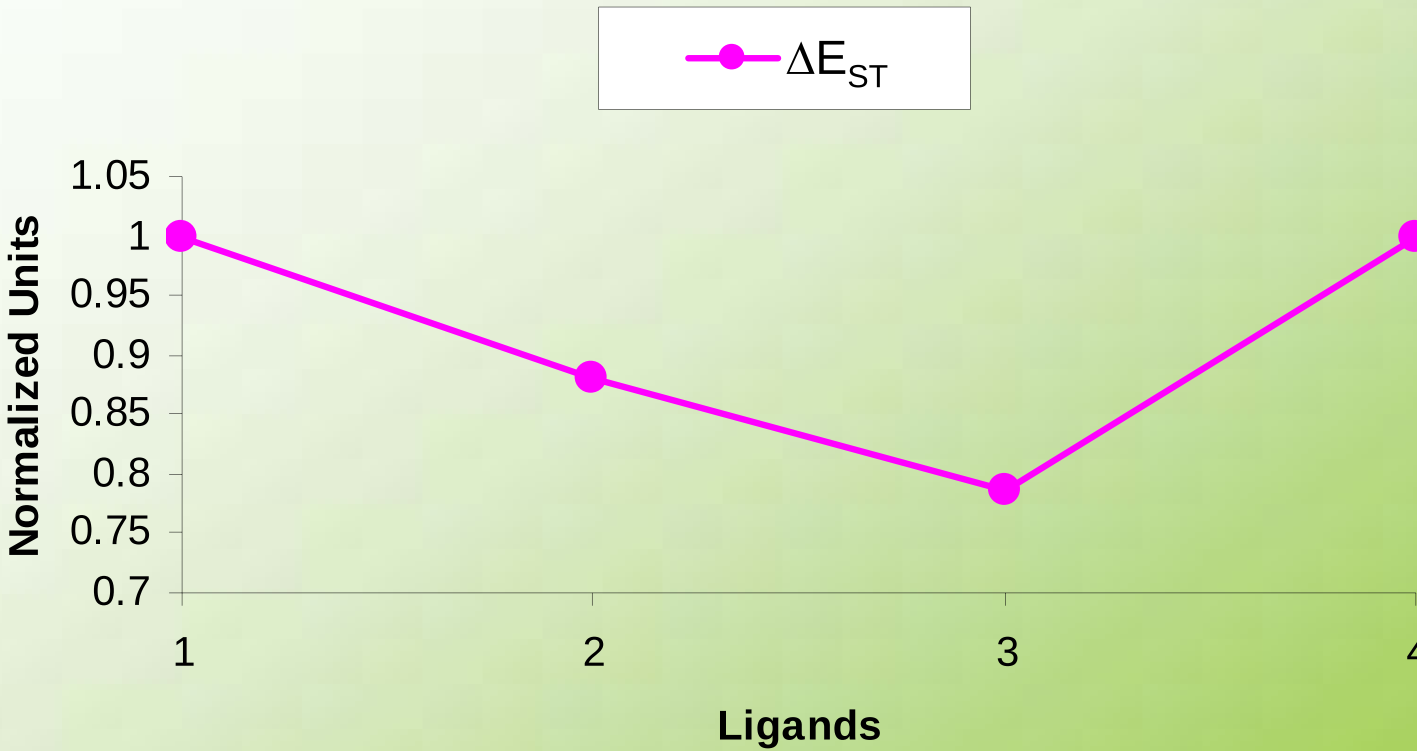


• Smaller distances in singlet energies (ΔS) from polymer to polymer-ligand complexes inversely relate to greater emission intensities from complexes.

• 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.

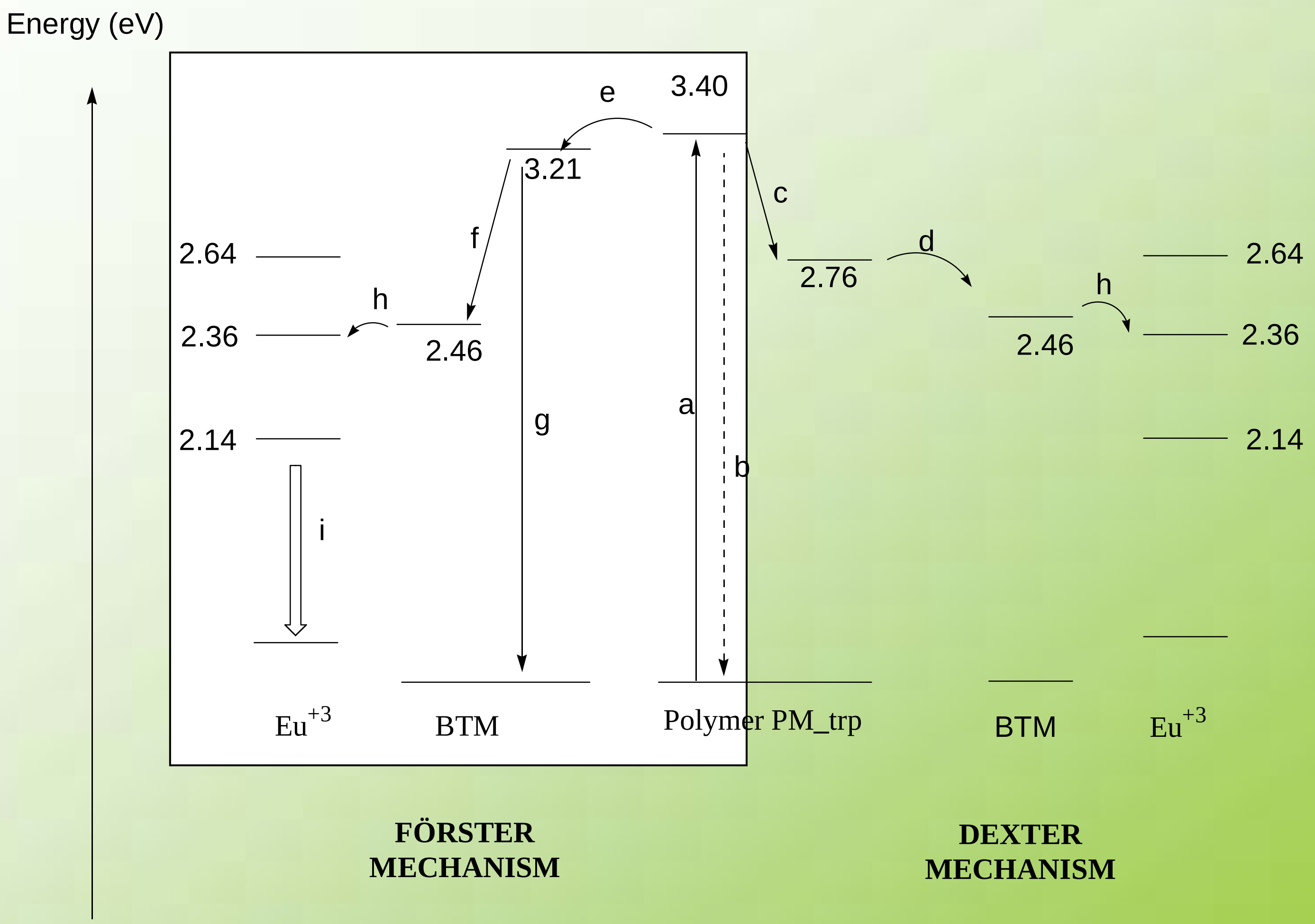
	PM_trp: Gd(HFA)$_3$	PM_trp: Gd(BTM)$_3$	PM_trp: Gd(DTM)$_3$	PM_trp: Gd(3-PTM)$_3$	PM_trp: Gd(9-PTM)$_3$
Abs. Max (nm) (cm^{-1})	317 31,546	358 27,933	374 26,738	376 26,596	358 27,933
Em. Max (nm) (cm^{-1})	400 25,000	410 24,390	423 23,641	429 23,310	410 24,390
Δ (cm^{-1})	6,546	3,543	3,097	3,286	3,543
E_S (eV) (cm^{-1})	3.40 27,397	3.21 25,907	3.09 24,938	3.07 24,722	3.20 25,773
E_T (eV) (cm^{-1})	2.76 22,297	2.46 19,841	2.43 19,608	2.48 20,000	2.45 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.

	BTM	DTM	3-PTM	9-PTM
PM_trp:Eu(L)$_3$	0.993	0.994	0.991	0.993

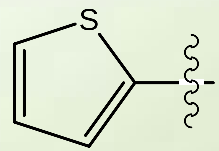
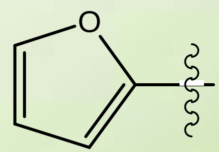
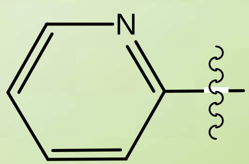
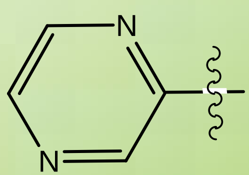
PM_trp:Ln(L)$_3$ Systems Characterization

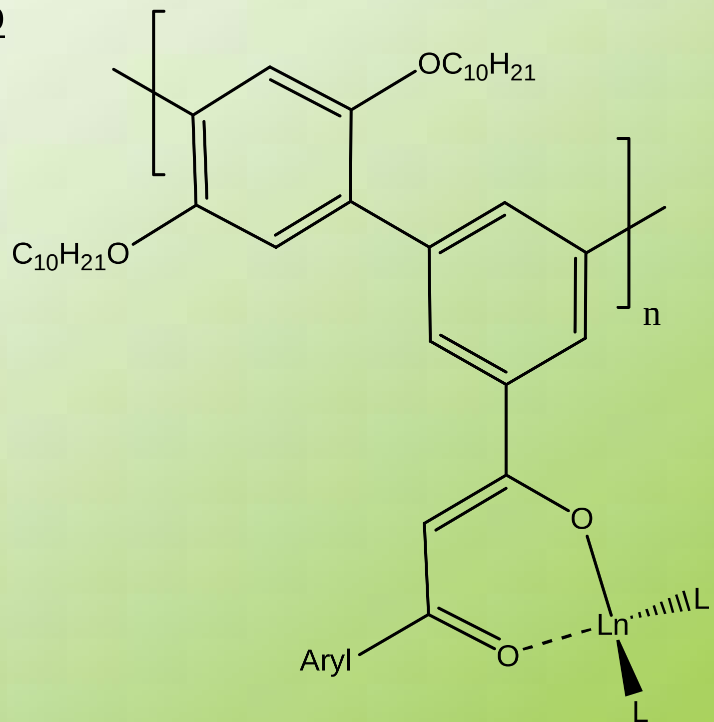
The energy transfer mechanism for the PM_trp:Eu(BTM)$_3$ system.



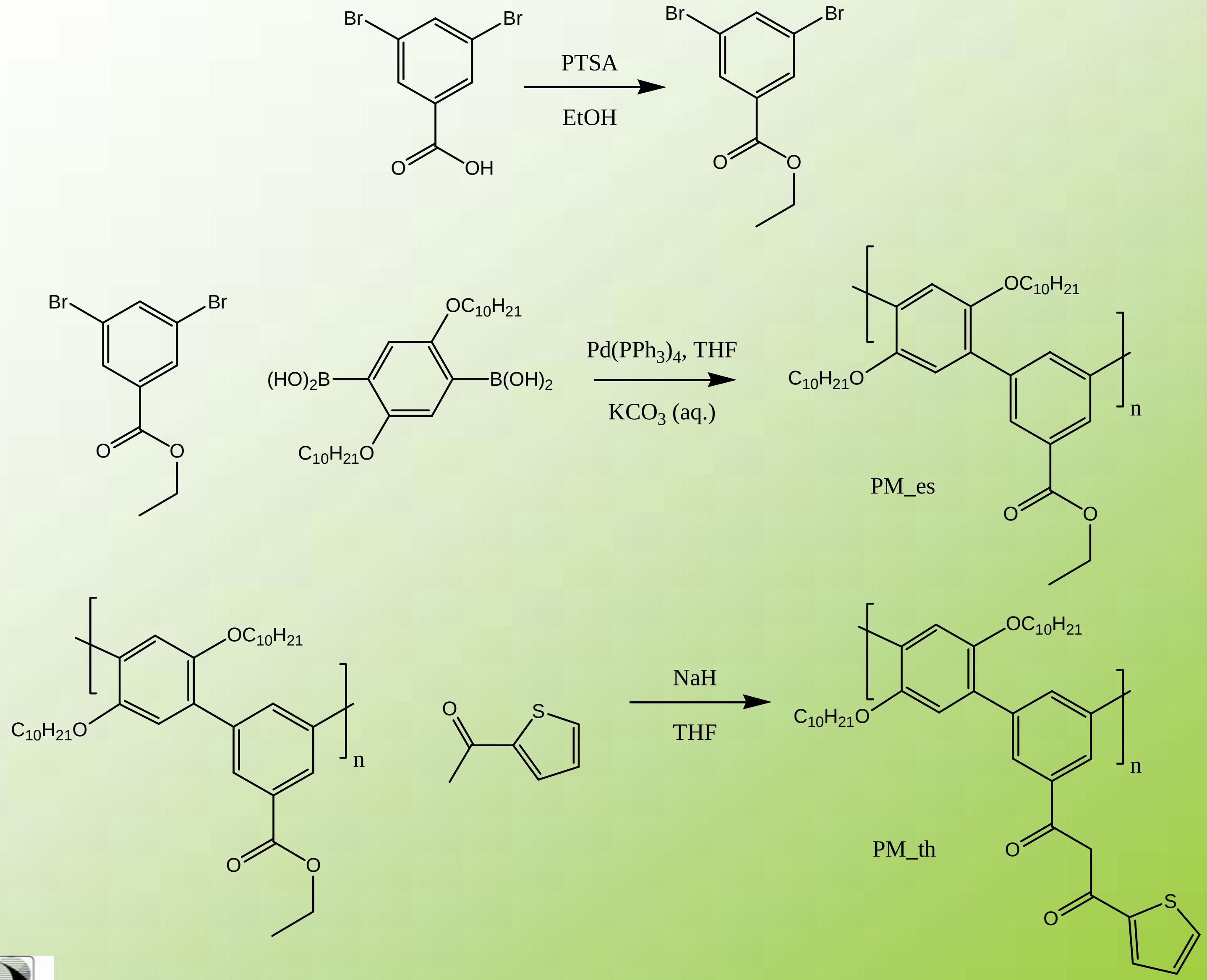
Sensitization of Europium Chelates

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

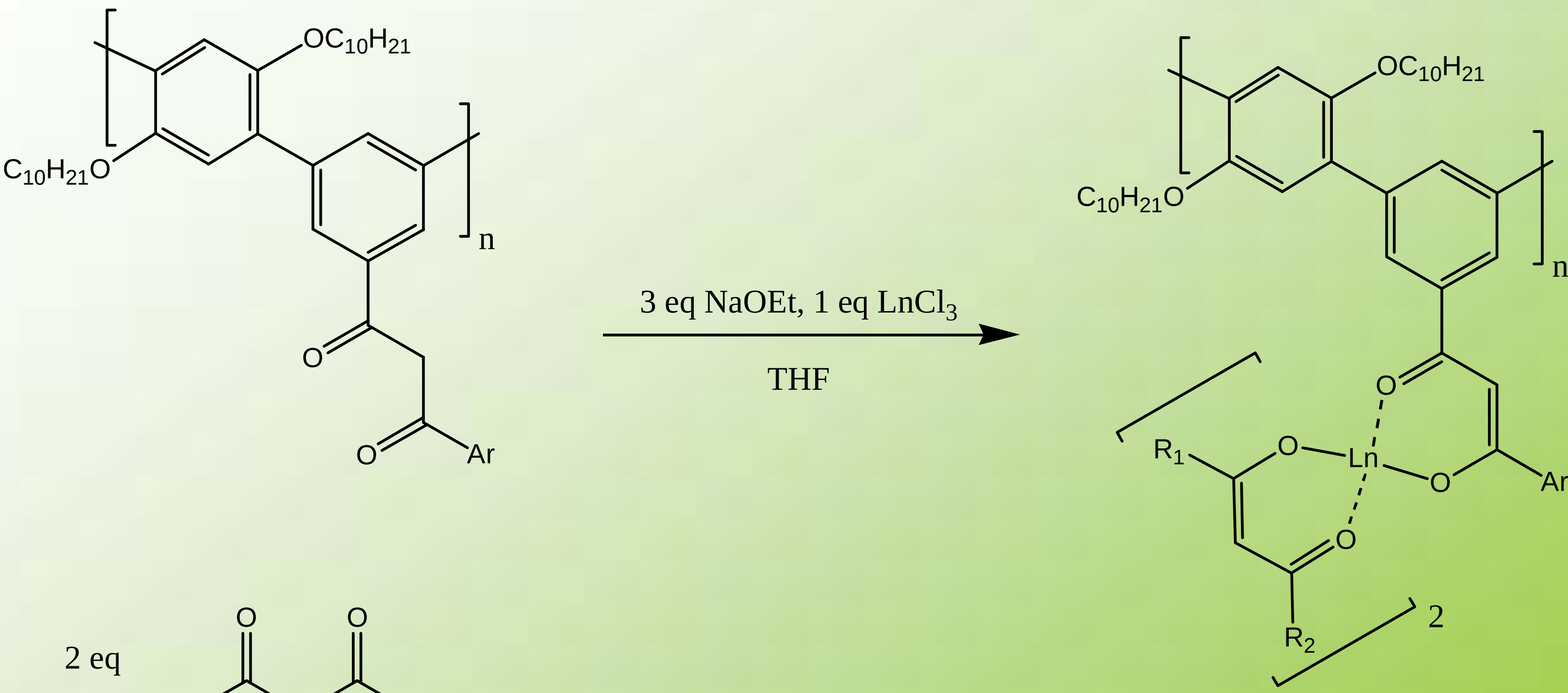
Polymer	Aryl Group
PM_th	
PM_fu	
PM_py	
PM_pz	



Polymers with β-Diketonates Synthesis

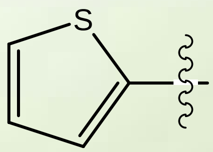
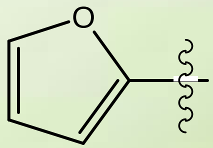
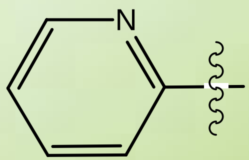
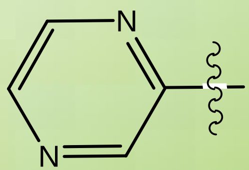


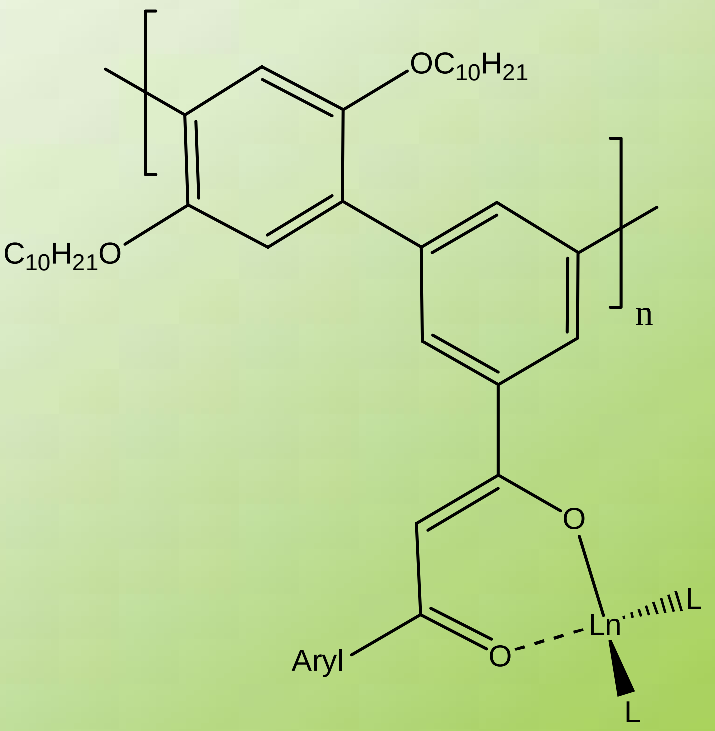
Polymer-Lanthanide Chelate Synthesis



Sensitization of Europium Chelates

Materials Characterization and Photophysical Performance Data

Polymer	Aryl Group
PM_th	
PM_fu	
PM_py	
PM_pz	



Polymers with β-Diketonates Characterization

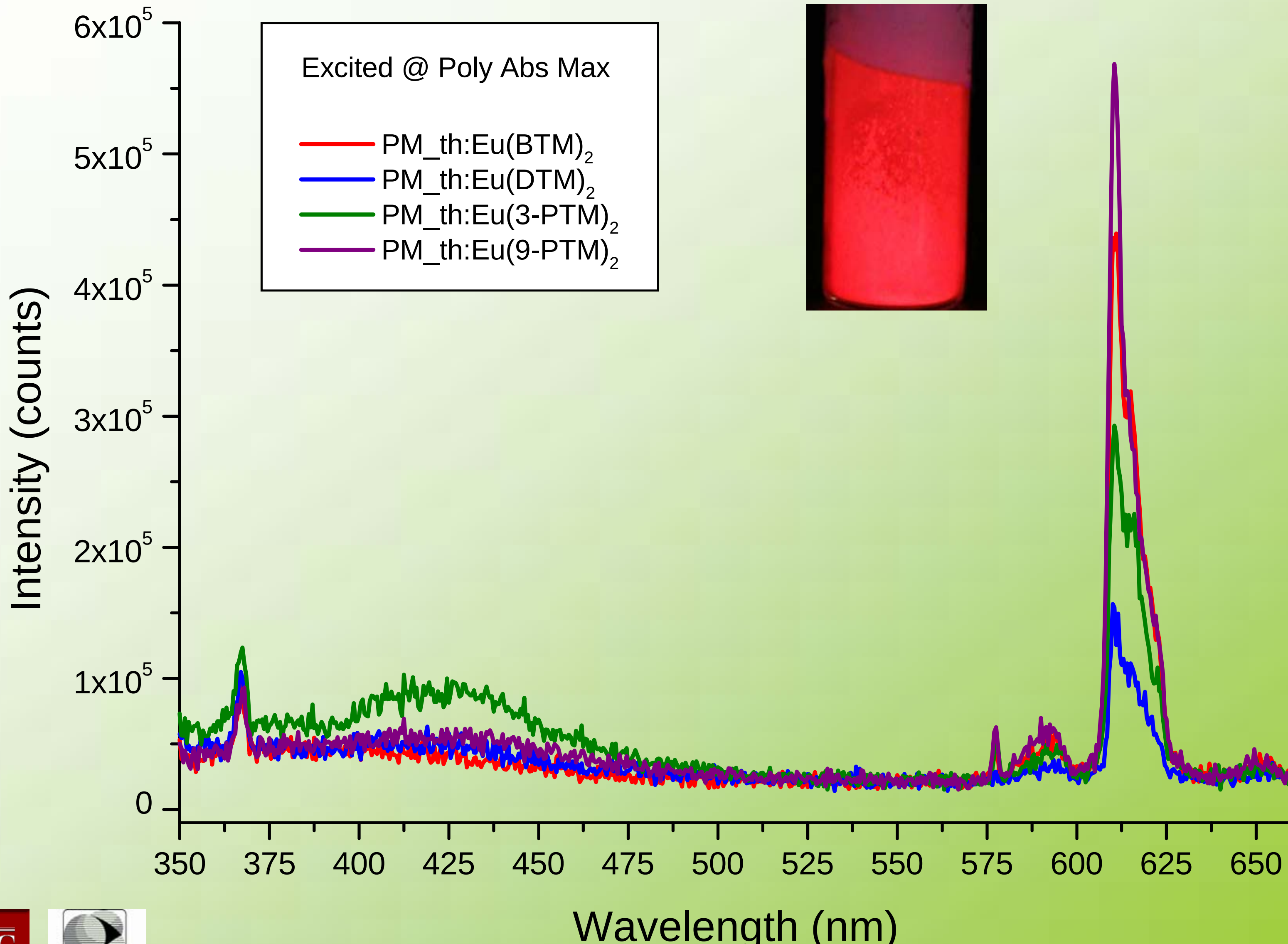
Polymer molecular weights determined by GPC and MALLS in $CHCl_3$.

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

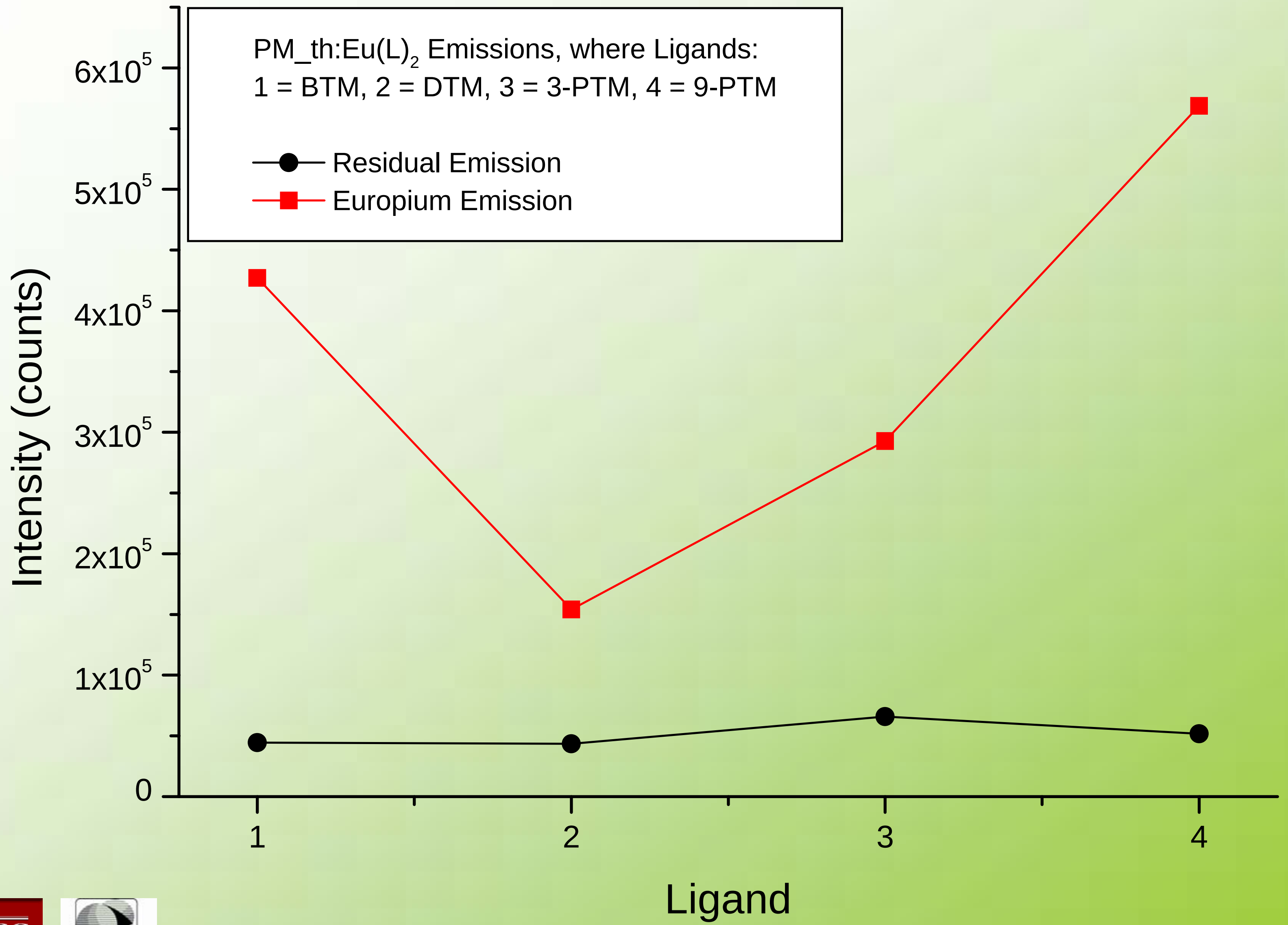
Photophysical properties polymers with β-diketonate pendant groups.

	PM_th	PM_fu	PM_py	PM_pz
Abs. Max (nm) (cm^{-1})	330 30,300	332 30,120	330 30,300	330 30,300
Em. Max (nm) (cm^{-1})	396.5 25,220	391 25,575	391 25,575	396 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) (cm^{-1})	**3.40** 27,425	**3.40** 27,425	**3.42** 27,585	**3.40** 27,425
E_T (eV) (cm^{-1})	**2.50** 20,165	**2.50** 20,165	**2.50** 20,165	**2.47** 19,920
ΔE_{ST} (eV)	0.90	0.90	0.92	0.93

PM_th:Eu(L)$_2$ Emission Spectra

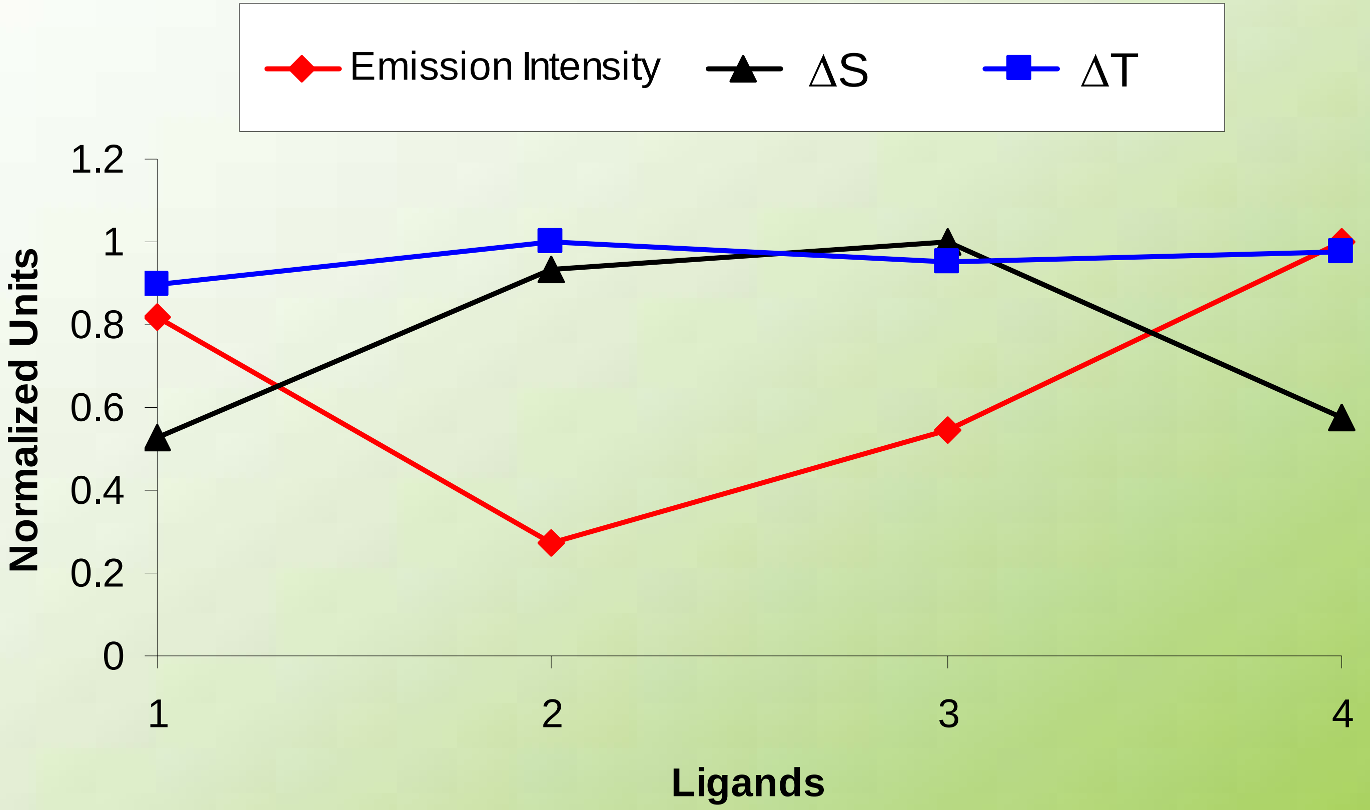


PM_th:Eu(L)$_2$ Emission Maxima



PM_th:Eu(L)$_2$ Ligands Versus Energy Parameters

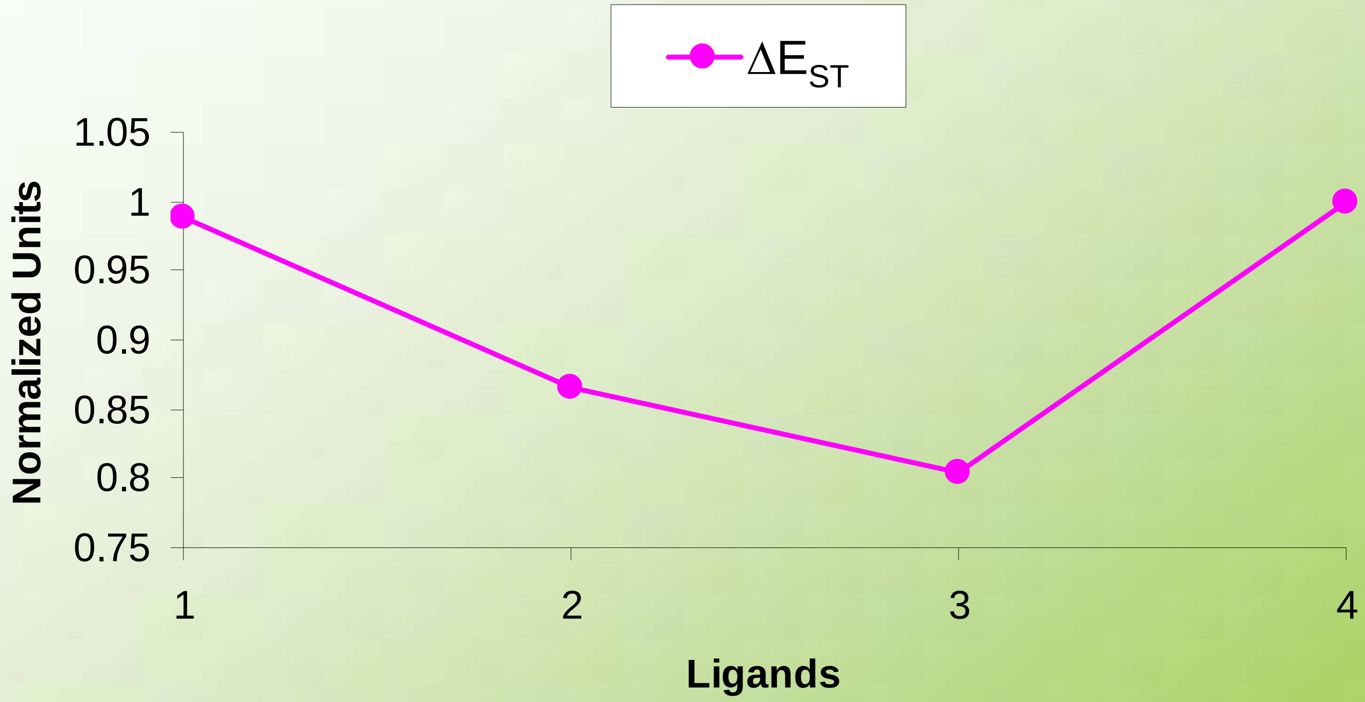
PM_th:Ln(L)$_2$ Systems, where Ligands: 1 = BTM, 2 = DTM, 3 = 3-PTM, 4 = 9-PTM.



- 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.

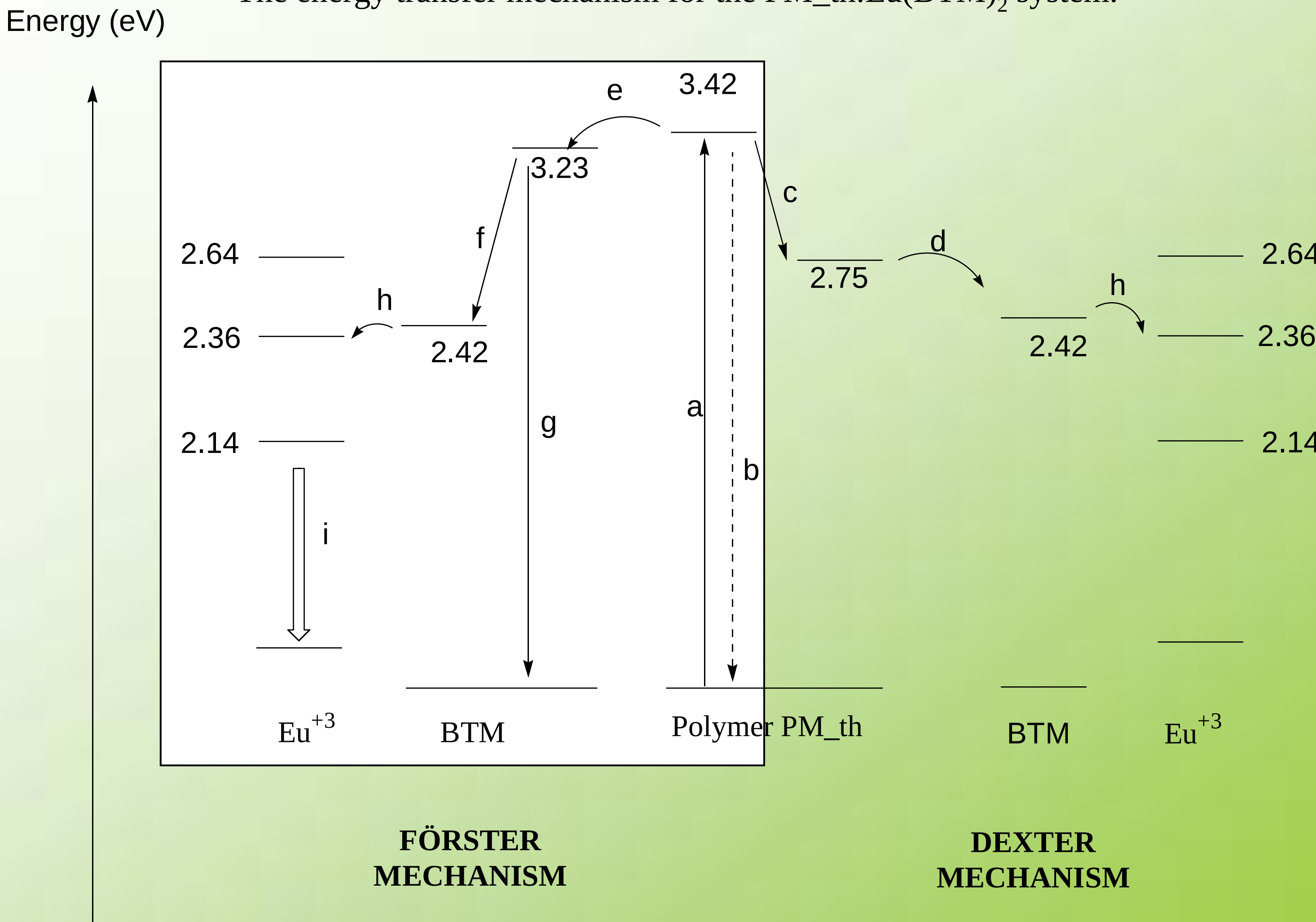
	PM_th: Gd(HFA)$_2$	PM_th: Gd(BTM)$_2$	PM_th: Gd(DTM)$_2$	PM_th: Gd(3-PTM)$_2$	PM_th: Gd(9-PTM)$_2$
Abs. Max (nm) (cm^{-1})	331 30,211	358 27,933	374 26,738	378 26,455	358 27,933
Em. Max (nm) (cm^{-1})	391 25,575	416 24,038	421 23,753	427 23,419	405 24,691
Δ (cm^{-1})	4,636	3,895	2,985	3,036	3,242
E_S (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.

	BTM	DTM	3-PTM	9-PTM
PM_fu:Eu(L)$_2$	0.998	0.998	0.998	0.998
PM_py:Eu(L)$_2$	0.999	0.998	0.998	0.998
PM_pz:Eu(L)$_2$	0.998	0.998	0.997	0.998
PM_th:Eu(L)$_2$	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.



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:

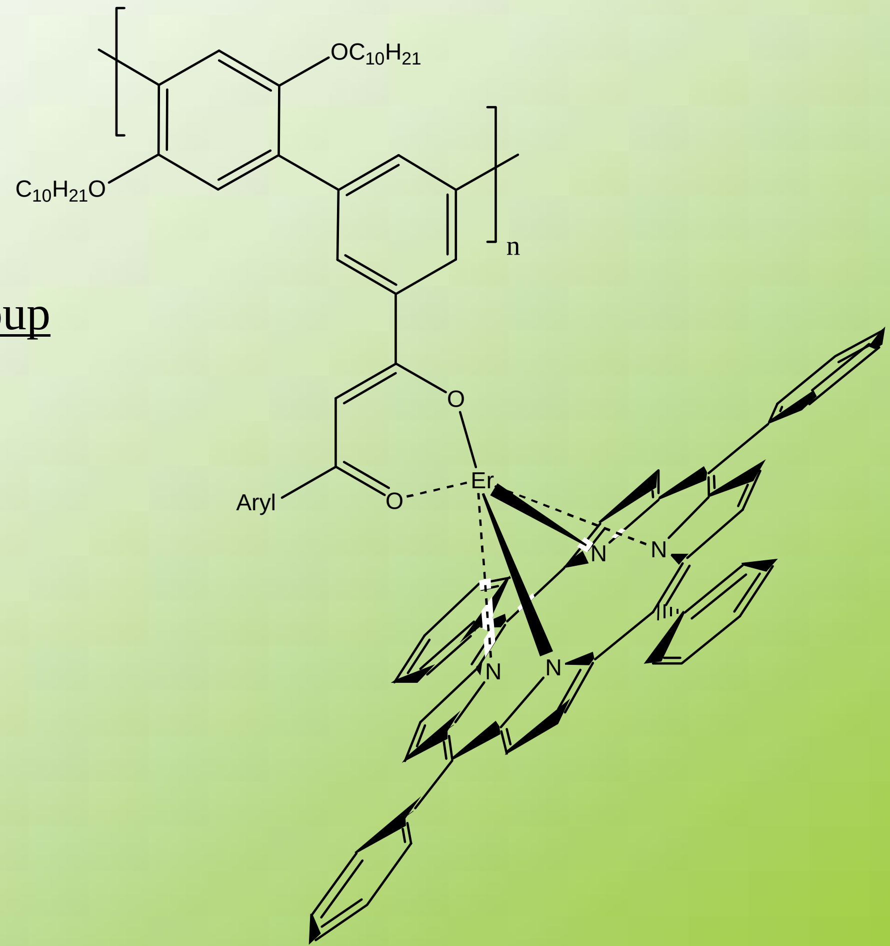
- Ligands that were asymmetric and had shorter effective conjugation lengths.
- Binding acceptor complex directly to donor polymer.
  - Pendant β-diketonates bind complex better than terpyridines.
- Better matching of energy levels between ligand systems with lanthanides, as illustrated by BTM and 9-PTM 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).

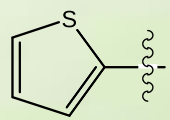
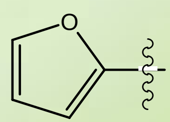
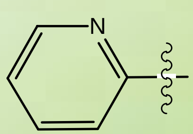
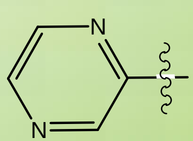
Applications

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

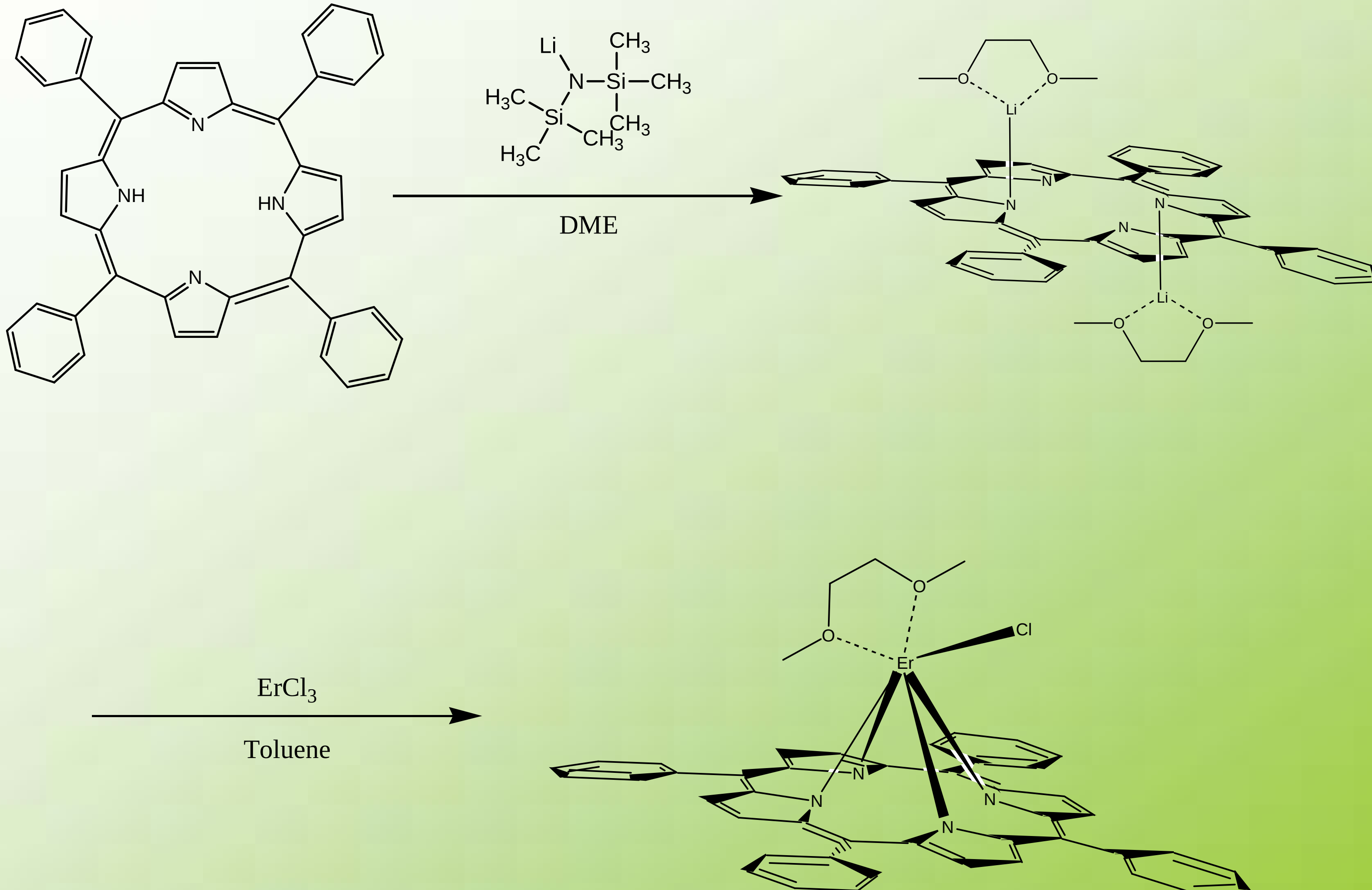
Sensitization of Erbium Chelates

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



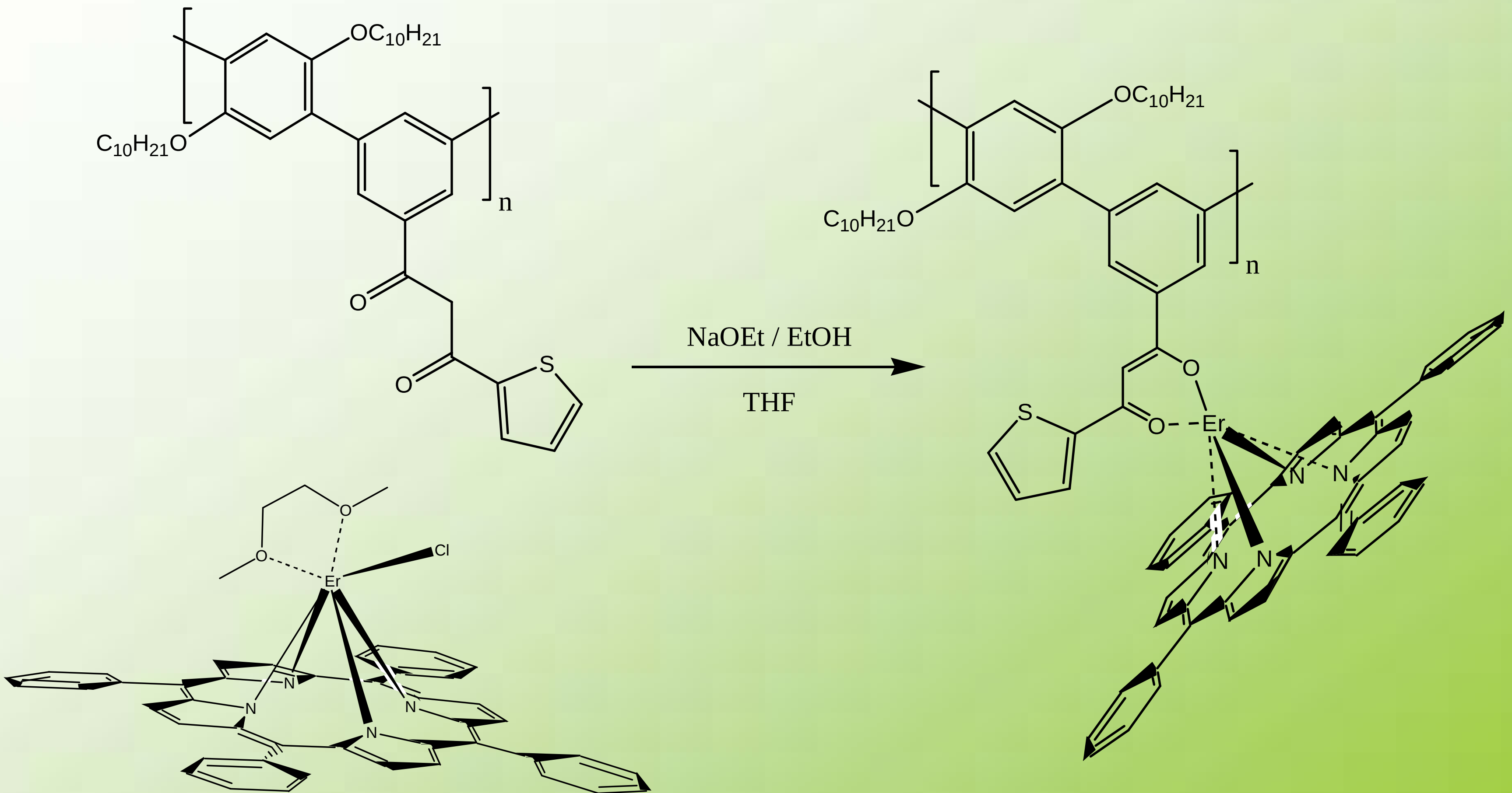
Polymer	Aryl Group
PM_th	
PM_fu	
PM_py	
PM_pz	

Erbium Porphyrinate Synthesis



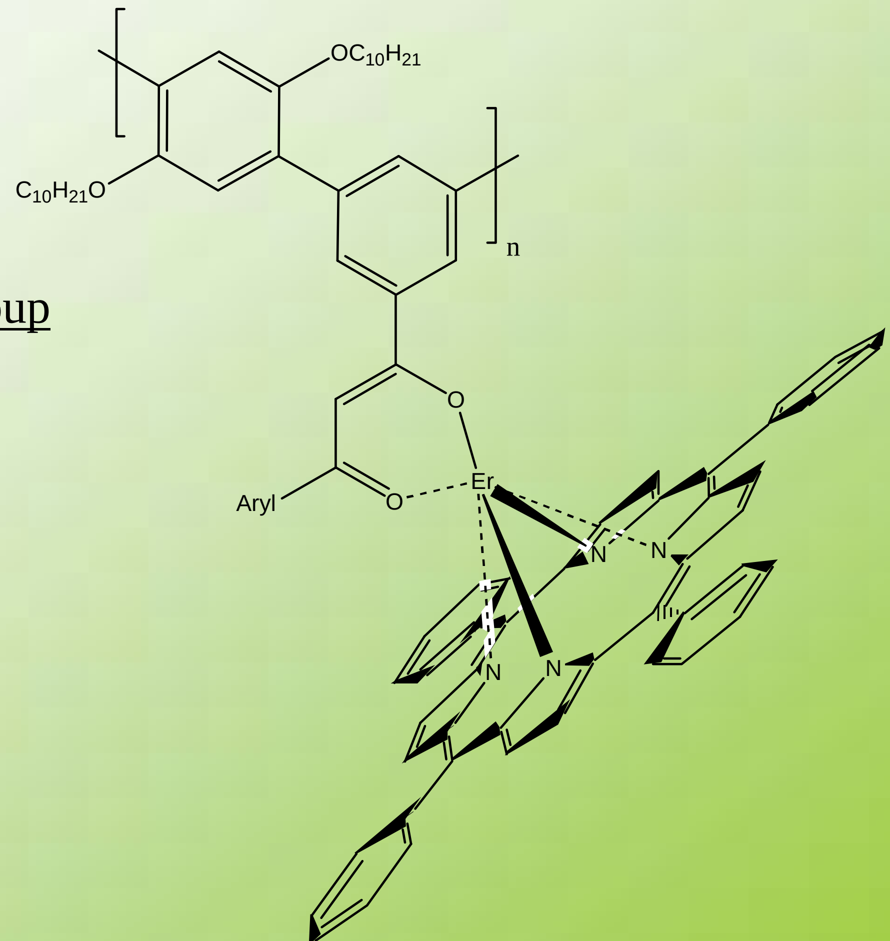
Verified with x-ray crystal.

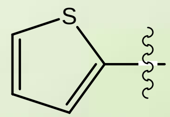
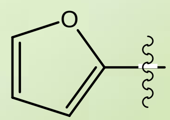
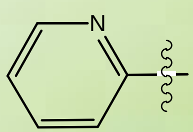
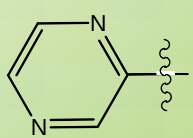
Polymer Erbium Chelate Synthesis



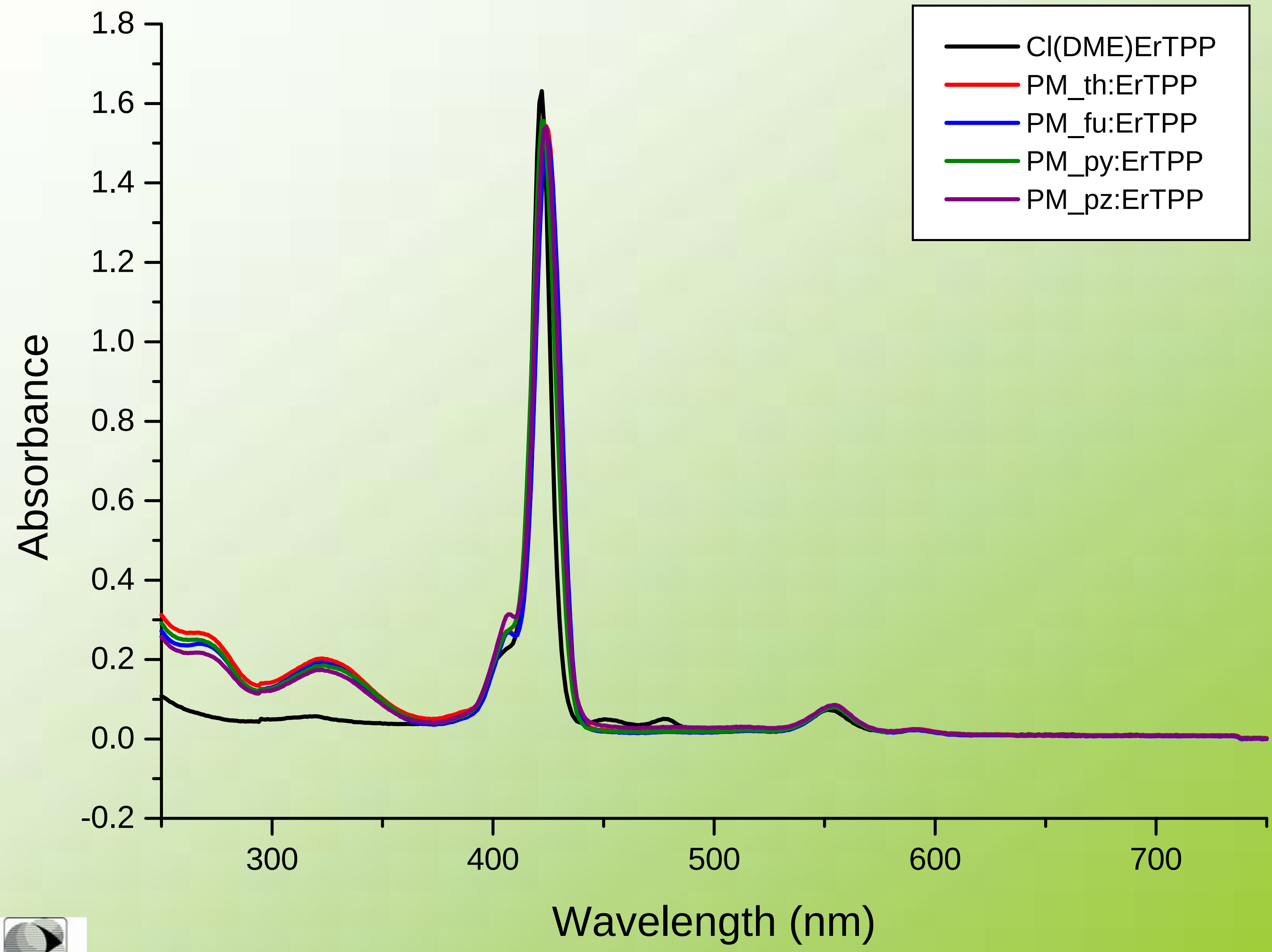
Sensitization of Erbium Chelates

Photophysical Performance Data



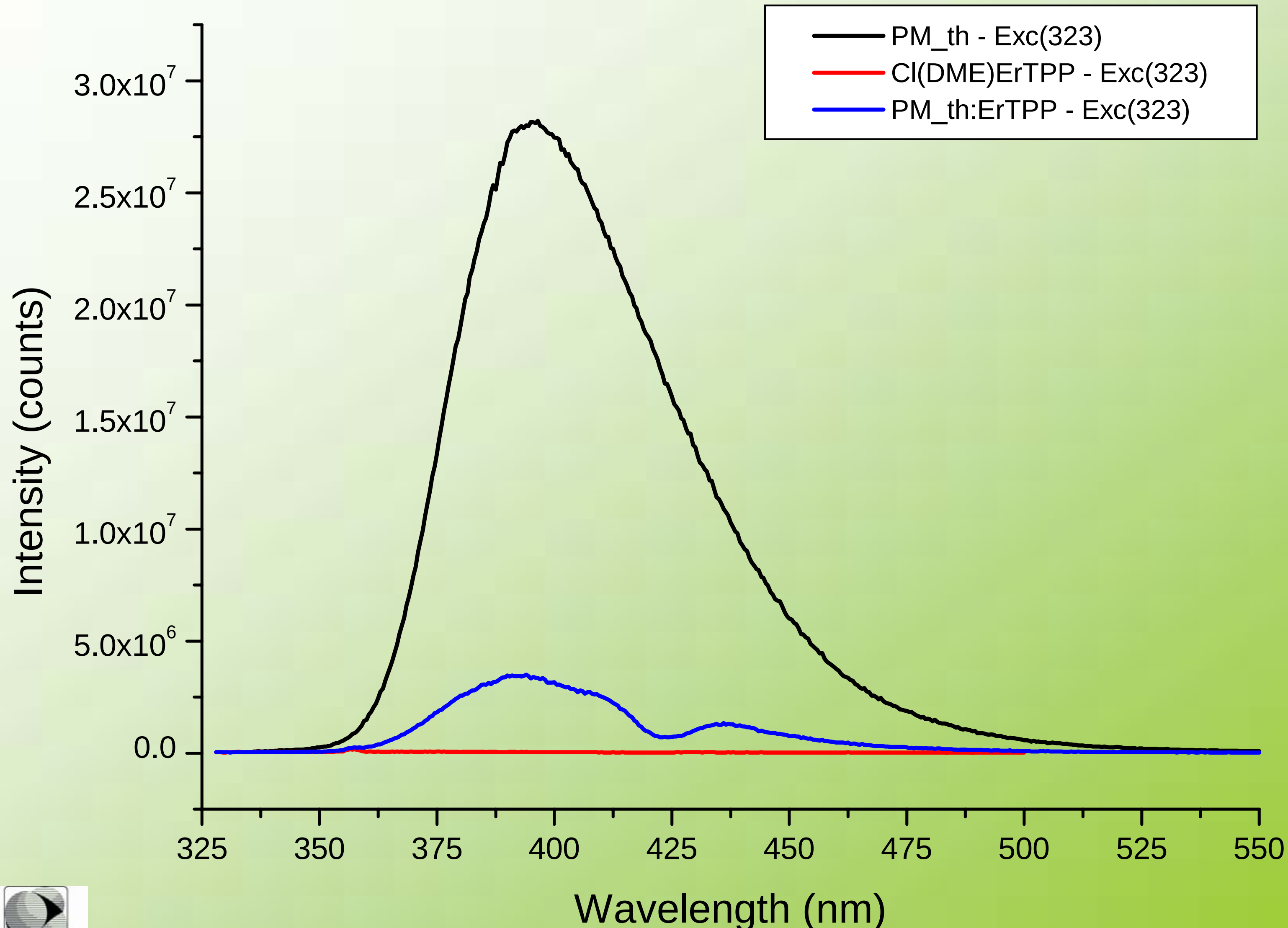
Polymer	Aryl Group
PM_th	
PM_fu	
PM_py	
PM_pz	

Poly:ErTPP Absorbance Spectra



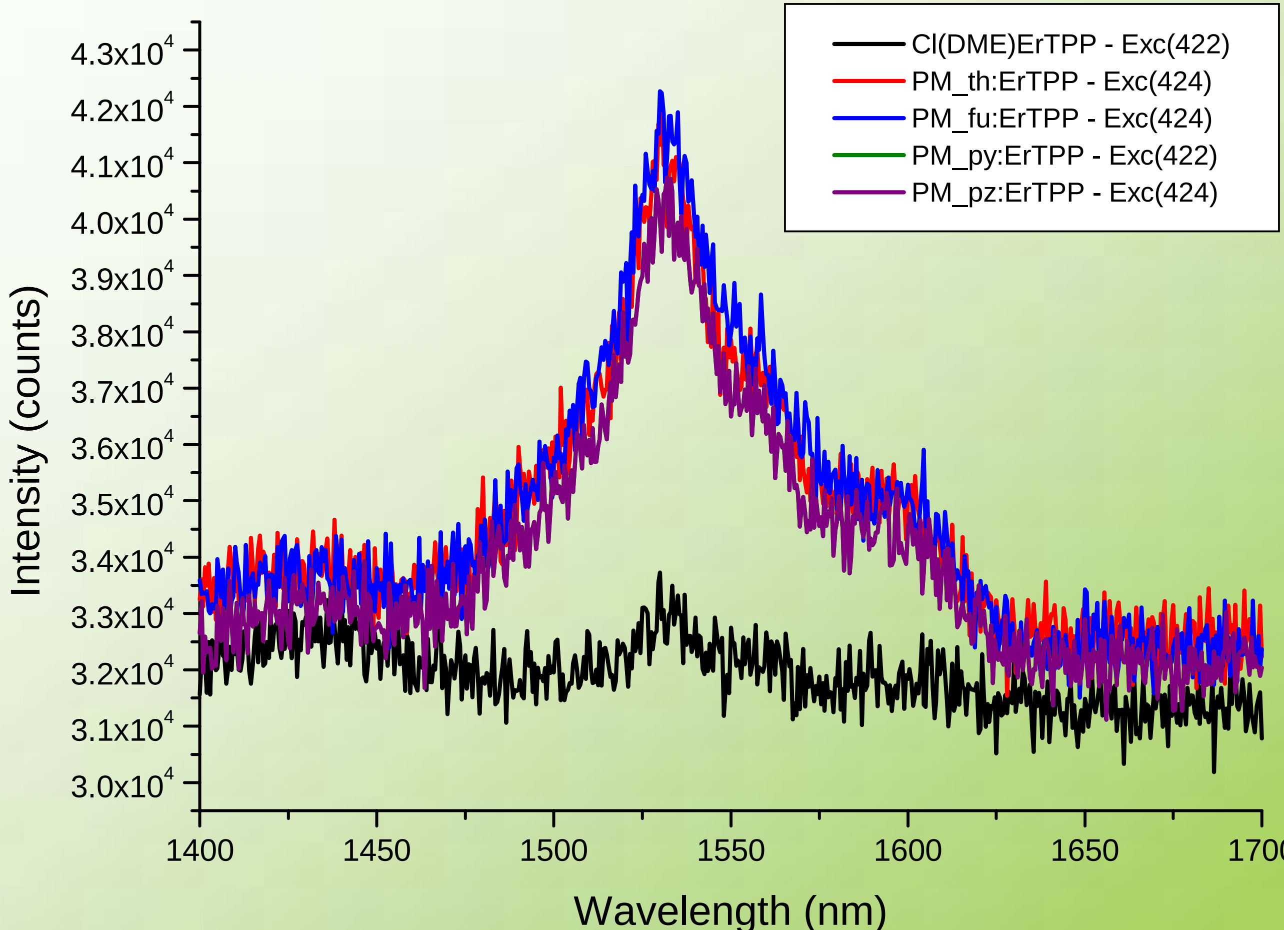
PM_th:ErTPP Visible Emission

Exciting @ Poly Max, Relative to PM_th and Cl(DME)ErTPP



Poly:ErTPP Infrared Emission

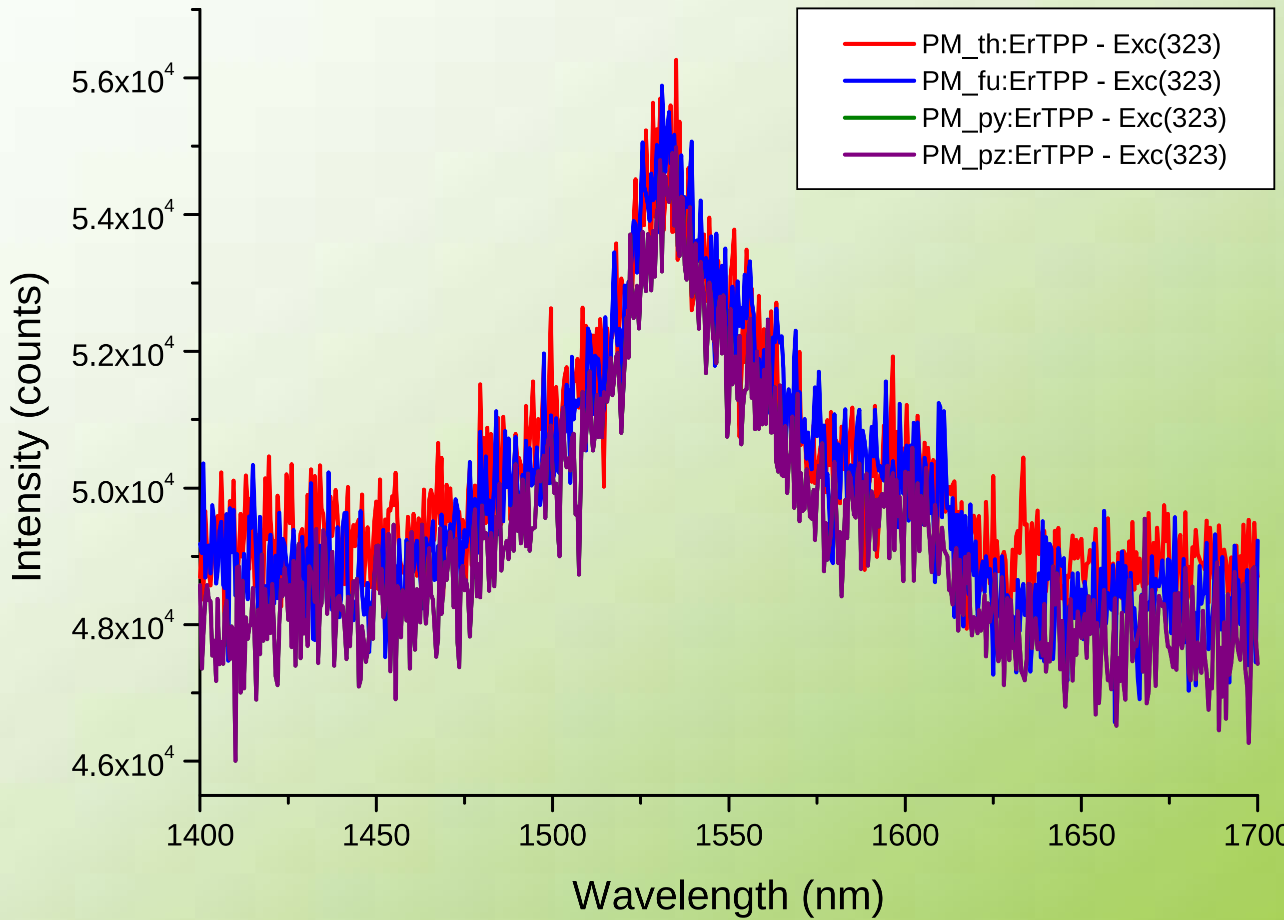
Exciting at Porphyrin Absorbance Maxima



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 though 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 electrophosphosphorescence, 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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