Monitoring chain folding by luminescence using a long-lived ruthenium complex

May 16, 2006

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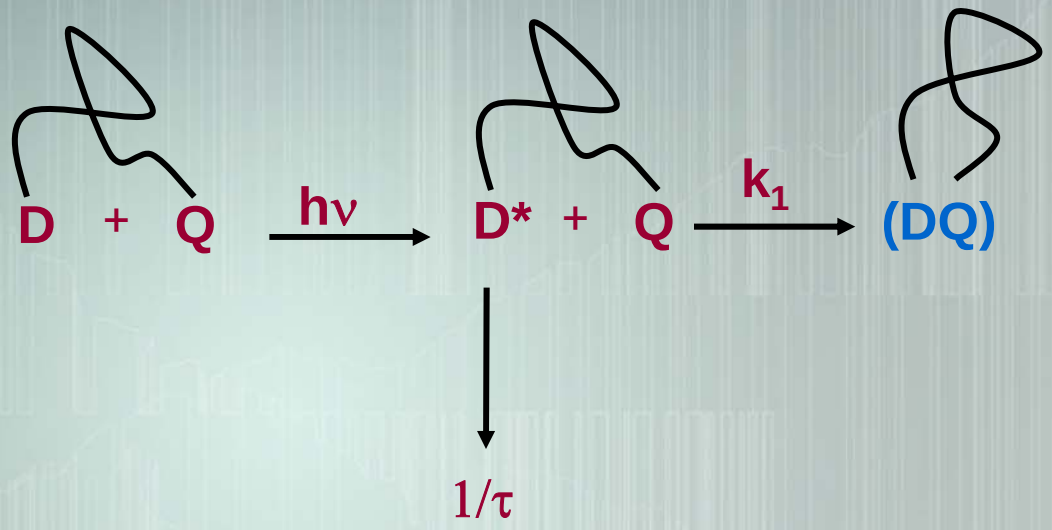
Outline

- Fluorescence to study chain dynamics
- Purpose
- Results
  - Ruthenium bipyridine
  - 3,5-Dinitrobenzylalcohol
  - Polymer
- Future Work

Polymer Dynamics

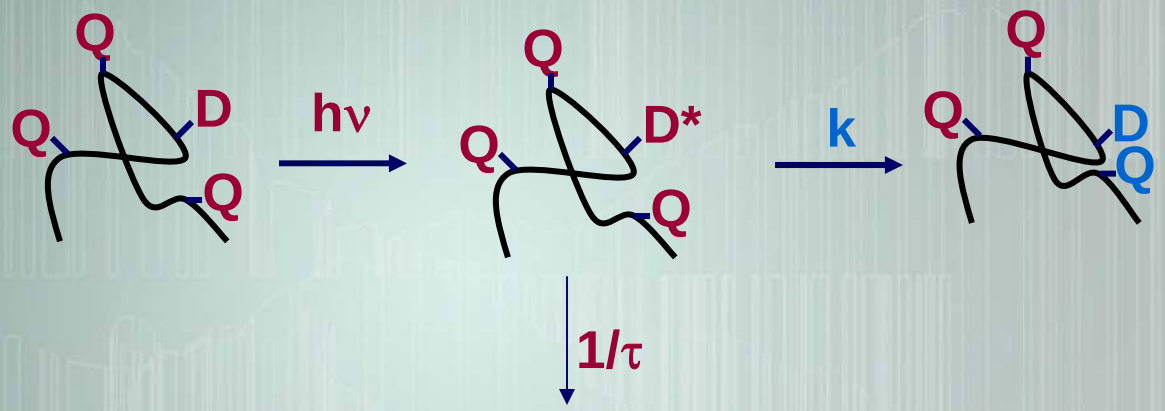
- **End–to–End Cyclization**



- **Problems**
  - **This method is good for end-to-end cyclization but not for chain dynamics.**

Polymer Dynamics

Random Labeling

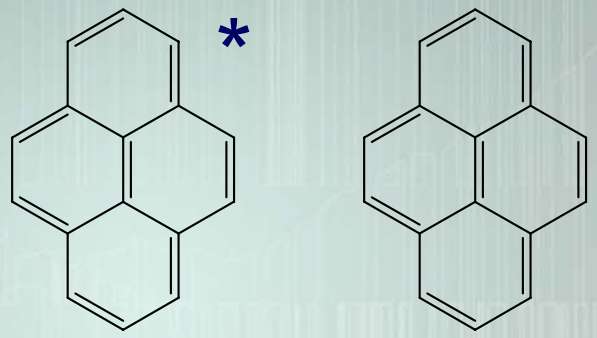


Problems

- Entire backbone monitored but a distribution of rate constants obtained

More Problems

- Hydrophobicity of pyrene causes aggregation of chromophore in aqueous solutions



Chromophore Quencher

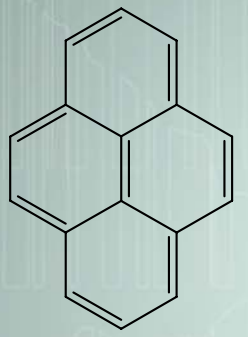
Pyrene

Water solubility

= 7×10^{-7} M

Solution

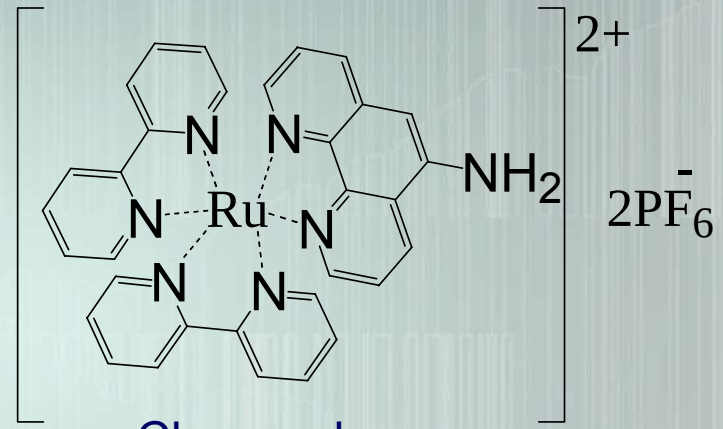
- Use a water-soluble dye and quencher.



Pyrene

Water solubility

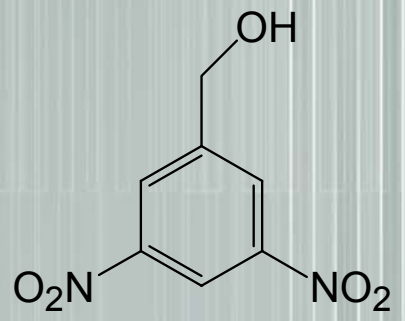
= 7×10^{-7} M



Chromophore

Ruthenium bisbipyridine 5-aminophenanthroline hexafluorophosphate (Ru-bpy).

0.1 M Na_2CO_3 solubility ~ 1×10^{-3} M



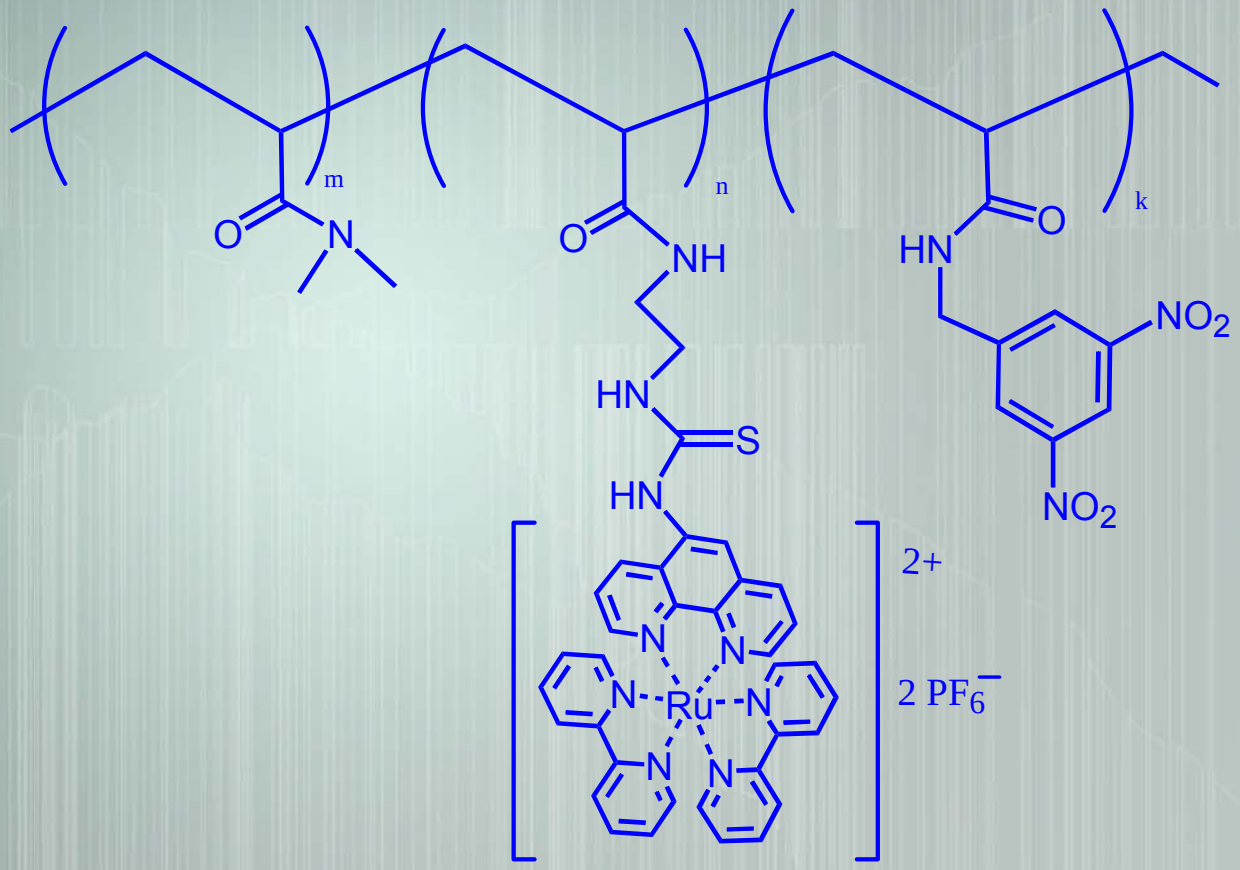
Quencher

Dinitrobenzyl Alcohol

0.1 M Na_2CO_3 solubility ~ 1×10^{-2} M

Goal

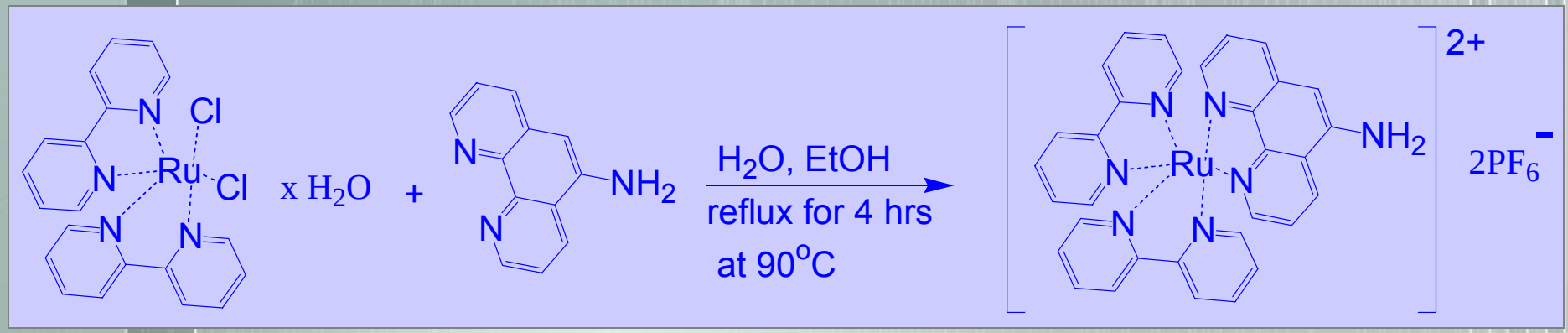
- To label a water-soluble polymer with a water-soluble dye
- To obtain information about polymer dynamics in water



Steps

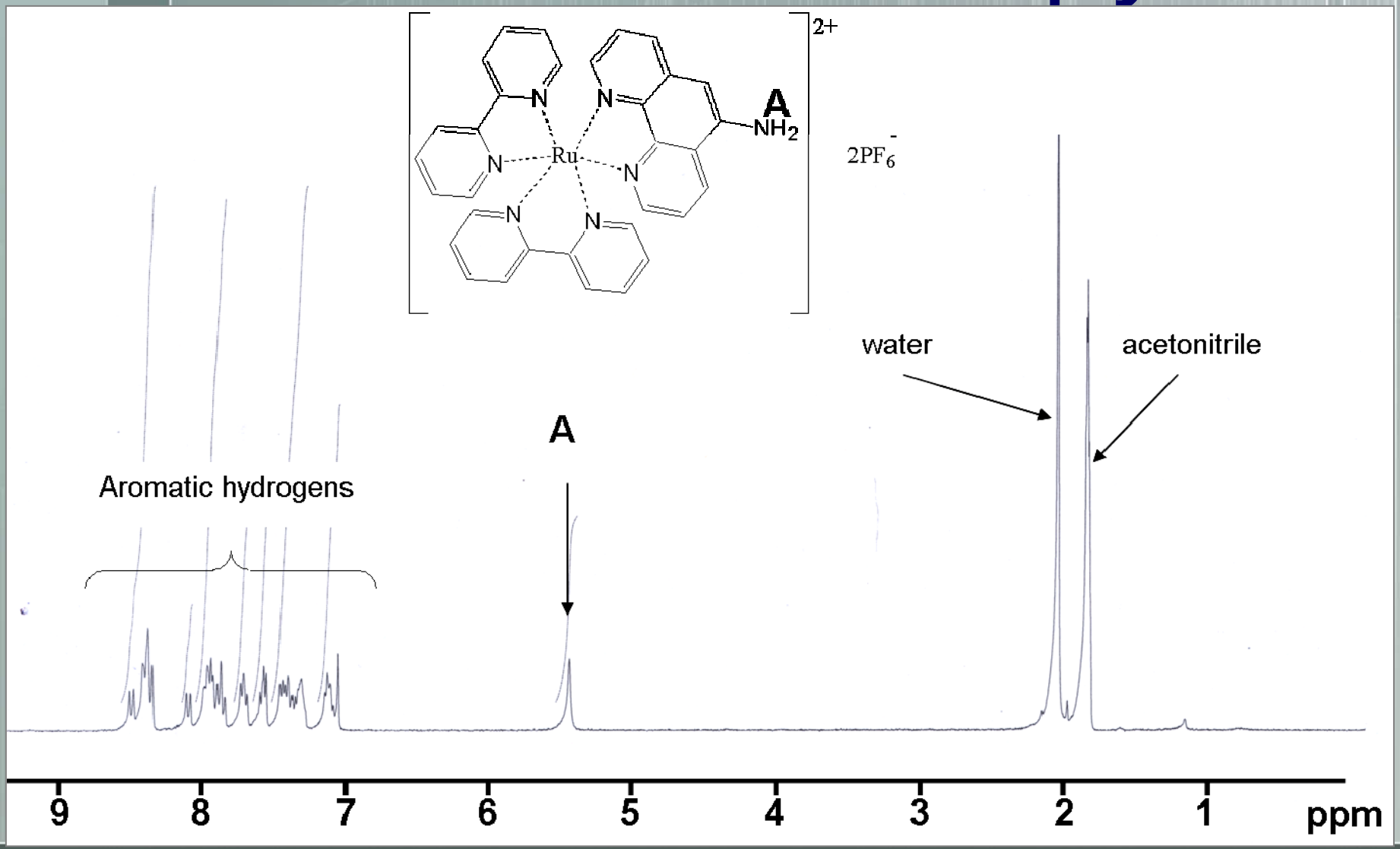
1. Synthesize dye
2. Characterize dye
3. Find a quencher
4. Synthesize Polymer
5. Label Polymer
6. Obtain luminescence experiments

Synthesis of Ru-bpy

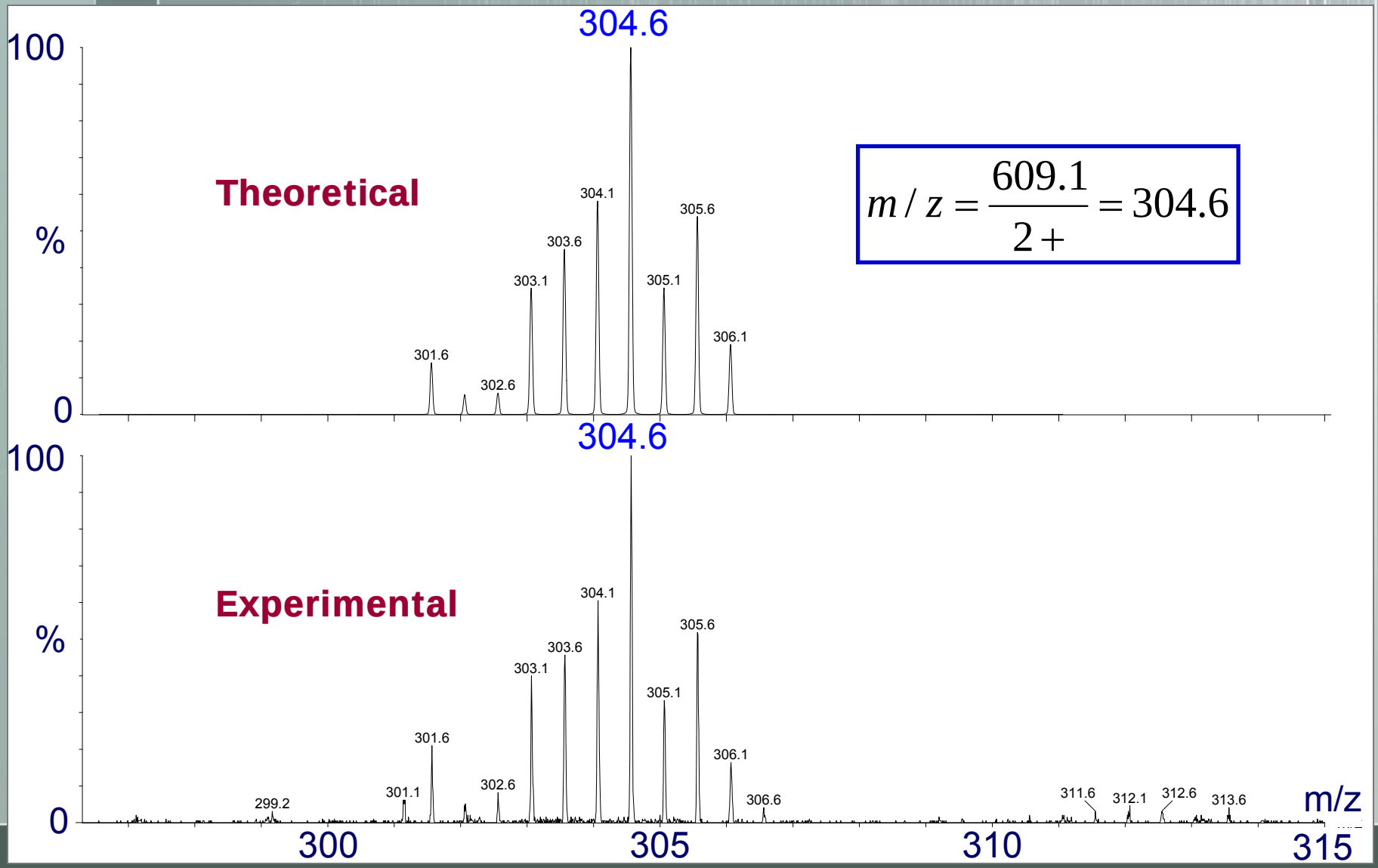


- Refluxed at 75°C under N_2
- Purified by Column Chromatography using alumina and 1:2 toluene/acetonitrile
- ~85% yield

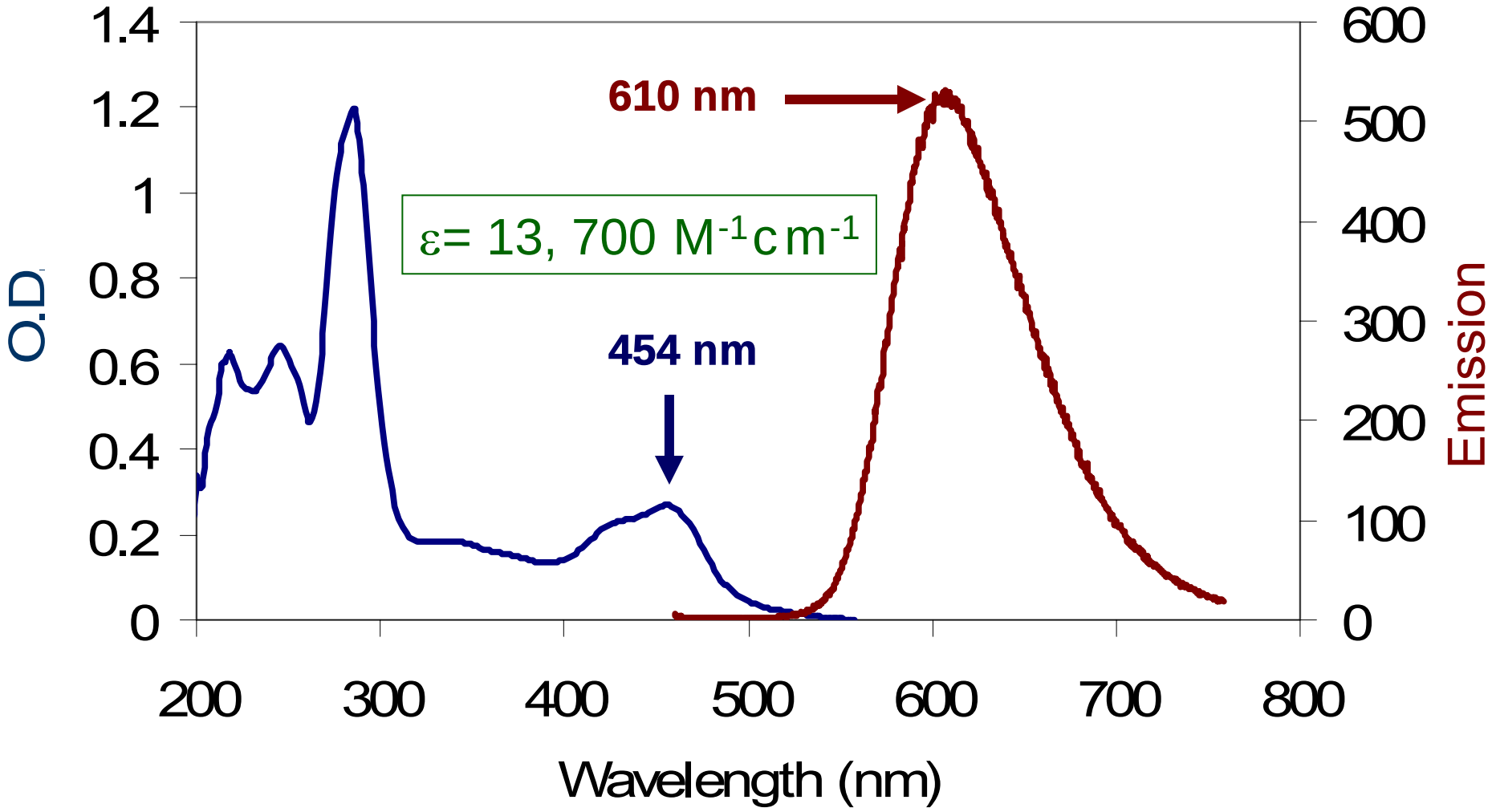
^{1}H NMR of Ru-bpy



ESI-TOF-MS for Ru-bpy



Spectroscopic Characteristics



Decay Measurements

Aerated

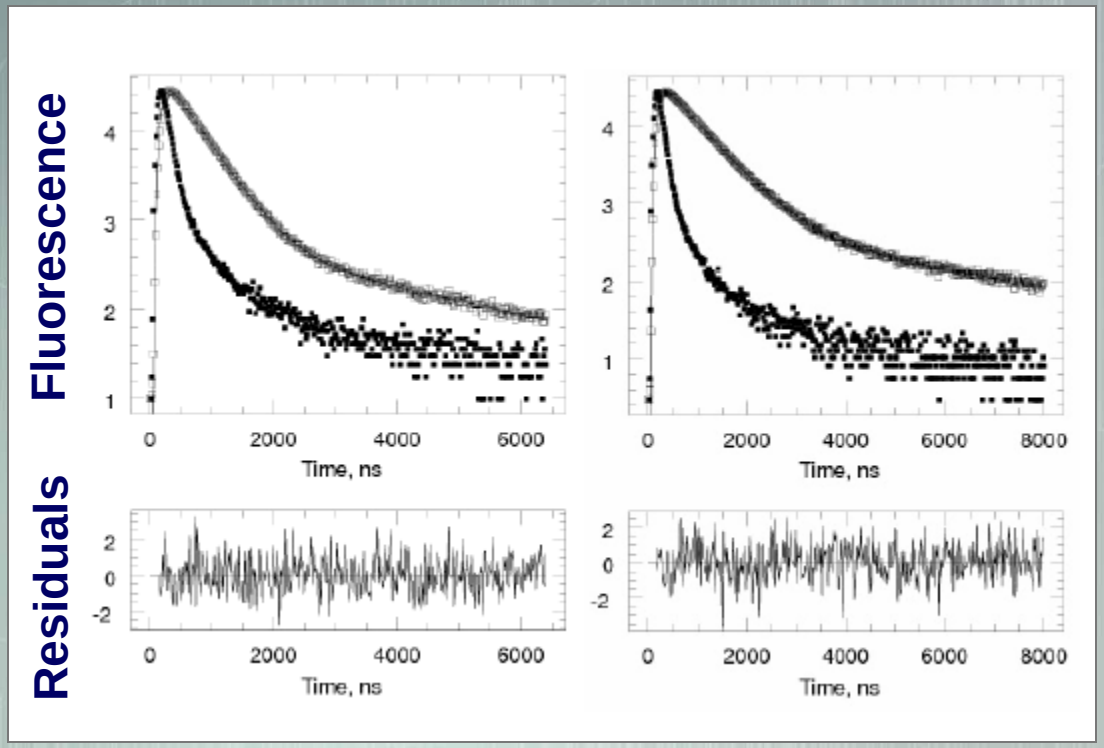
χ^2 =1.07

τ_1 = 385 ns

α_1 = 0.99

τ_2=2800 ns

α_2=0.01



Degassed

χ^2=1.02

τ_1 = 565 ns

α_1 = 0.98

τ_2 = 3500 ns

α_2 = 0.02

8 μM in 0.1 M carbonate solution

λ_{ex}=454 nm

λ_{em}=611nm

$$\frac{[D^*]_t}{[D^*]_0} = \alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2}$$

Steps

1. Synthesize dye
2. Characterize dye
3. Find a quencher
4. Synthesize Polymer
5. Label Polymer
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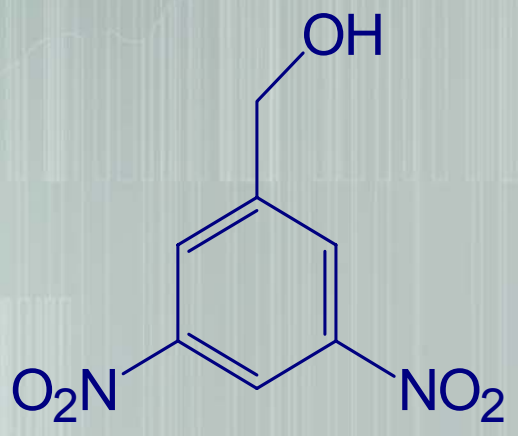
Quencher

Insufficient Quenching

- Triethylamine
- *N,N*-dimethylethanol amine
- Nitromethane
- Iodomethane

Selected Quencher



Dinitrobenzyl alcohol (DNBA)

$k_q = 2.7 \times 10^9\ M^{-1}\ s^{-1}$

Dye Comparison

	Ru-bpy ($0.1\ M\ Na_2CO_3$)	DNBA ($0.1\ M\ Na_2CO_3$)	Pyrenemethanol (water)
Water Solubility (M)	$\sim 1 \times 10^{-3}$	$\sim 1 \times 10^{-2}$	7×10^{-7} (Py)
Molecular Weight	898.6 (608.6)	198.1	232.3
Volume $(Å)^3$	~890	~210	~260
Extinction Coefficient	13,700 ±100	15,150 ± 120	40,000
k_q ($M^{-1}\ s^{-1}$)		2.6×10^9	1×10^9 (I^-)
λ_{ex} (nm)	454	246	344
λ_{em} (nm)	611		374
Lifetime - degassed (ns)	565		
Lifetime - aerated (ns)	385		170

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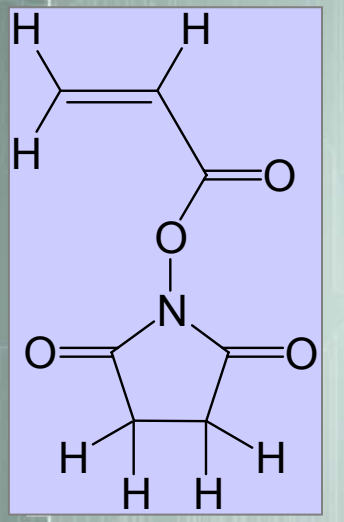
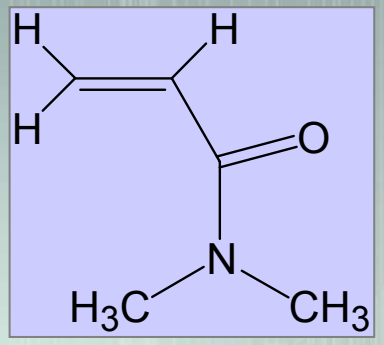
Monomers

Quencher



N-Acryloxysuccinimide

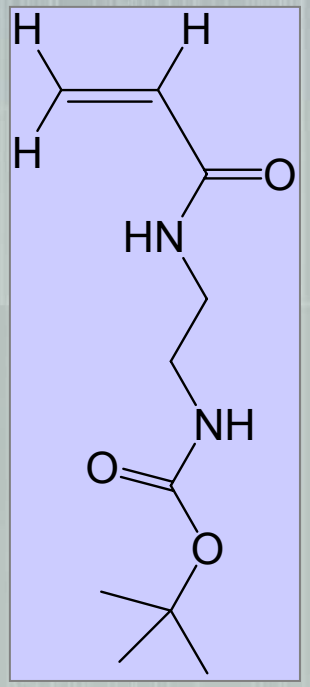
NASI



N,N-dimethylacrylamide

DMA

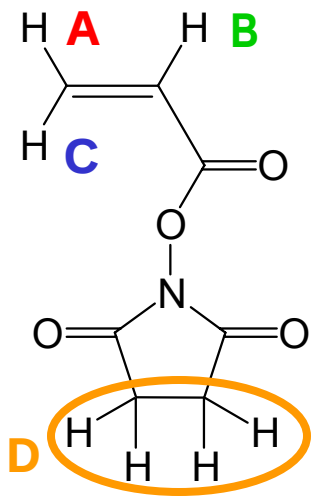
Dye



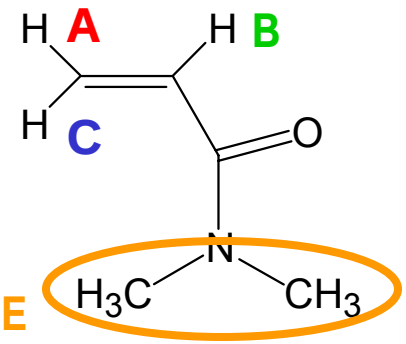
N-Acryloxyethylenediamine

AcEDA

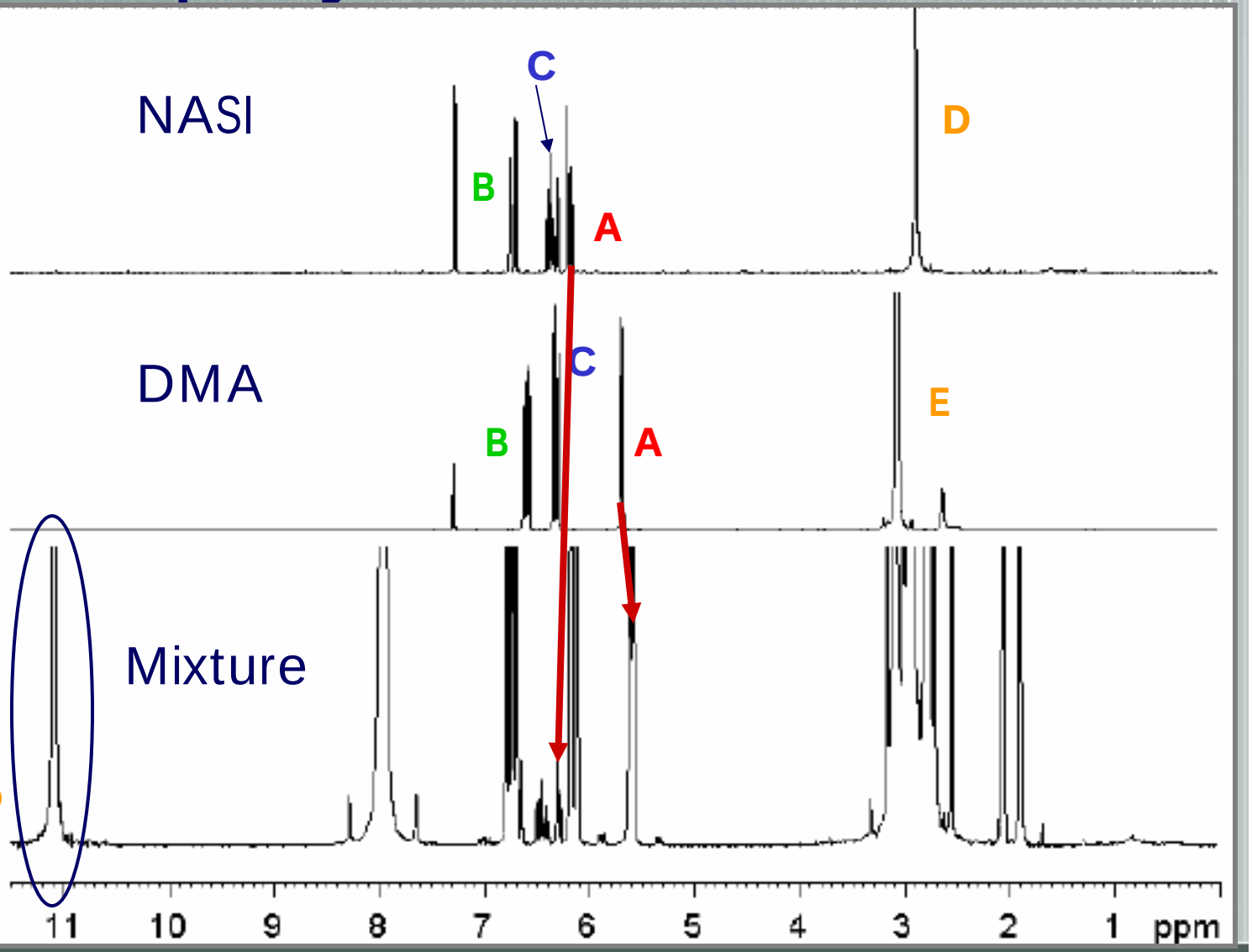
Copolymerization



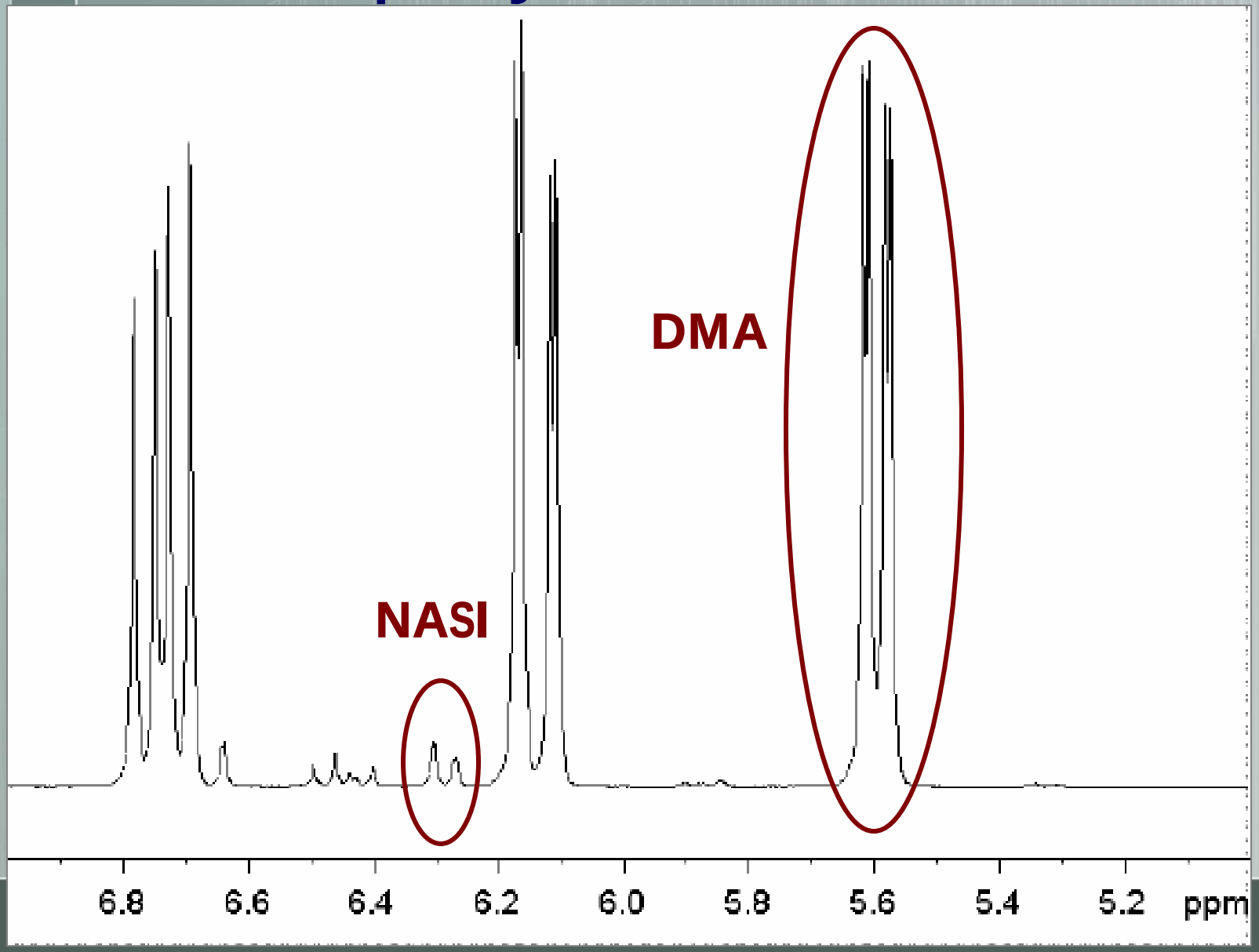
NASI



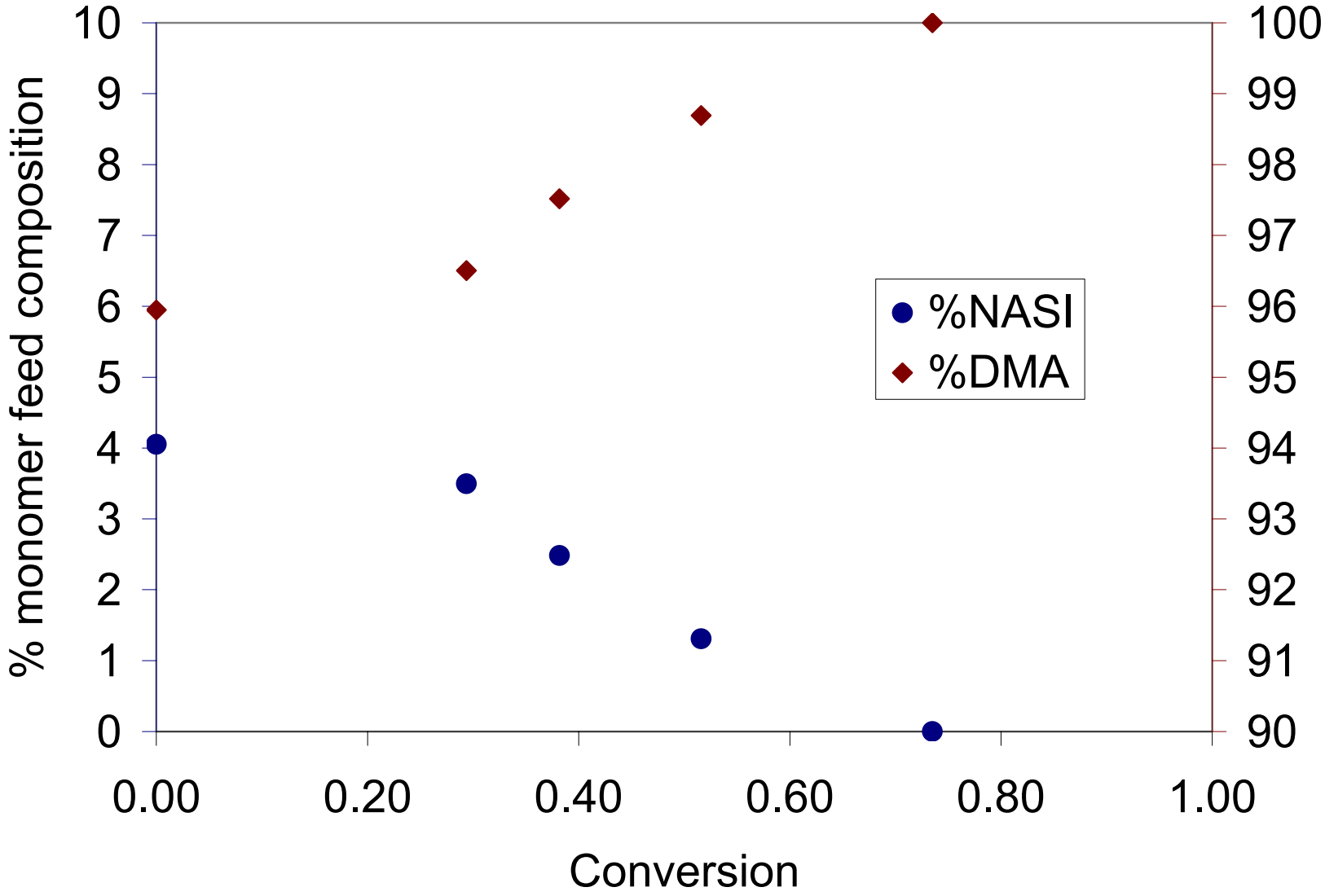
DMA



Copolymerization



Copolymerization



Copolymerization

- Up to 25-30% conversion, both monomers are incorporated randomly.
- After 25-30% conversion, the NASI monomer is preferentially incorportated.

Macromolecules **2003,** *36,* 8119-8129

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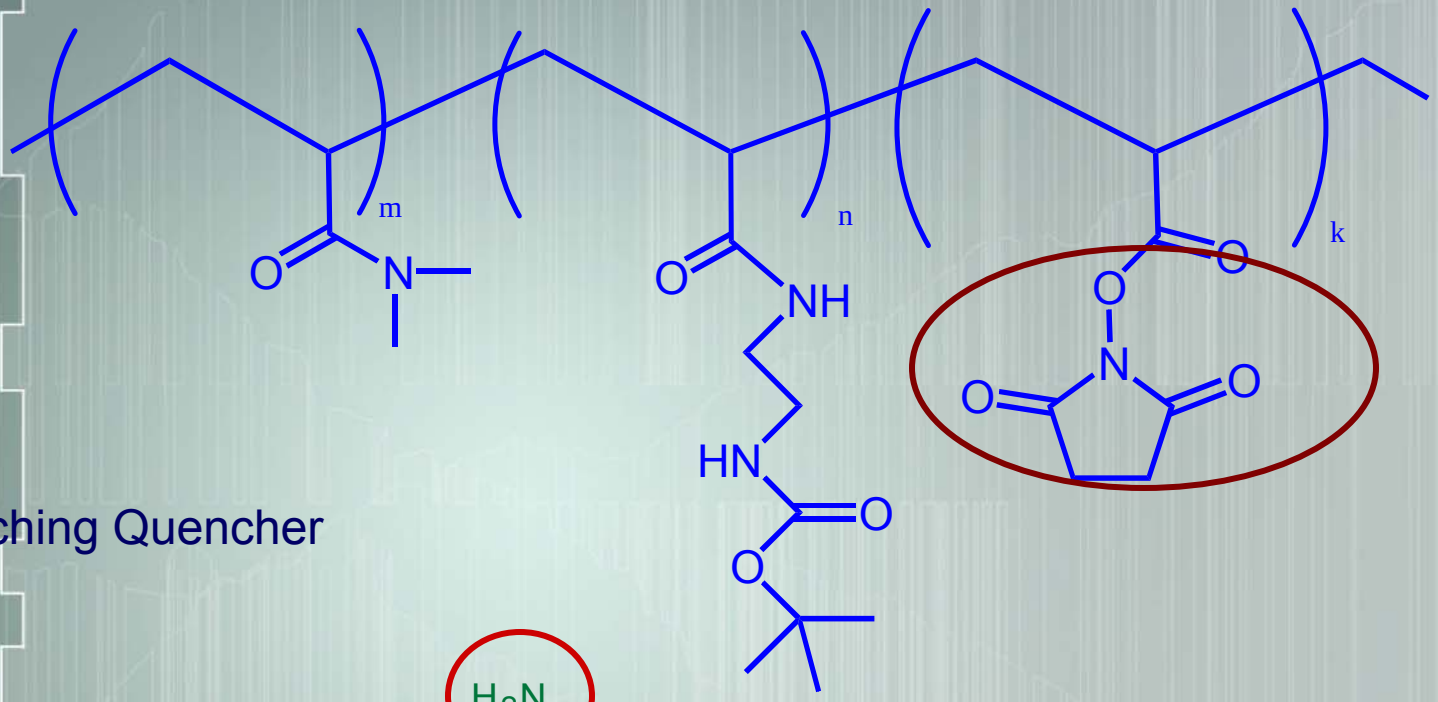
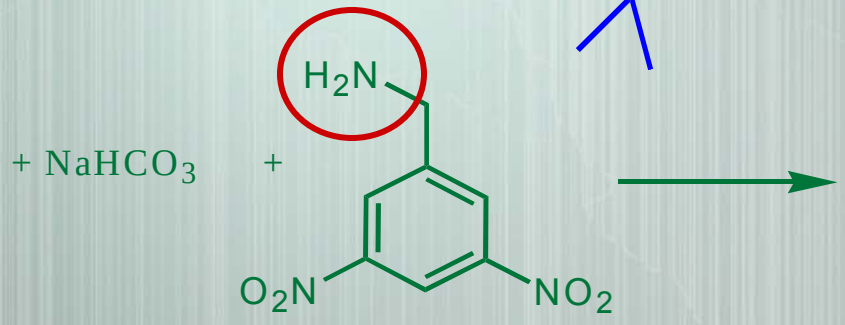
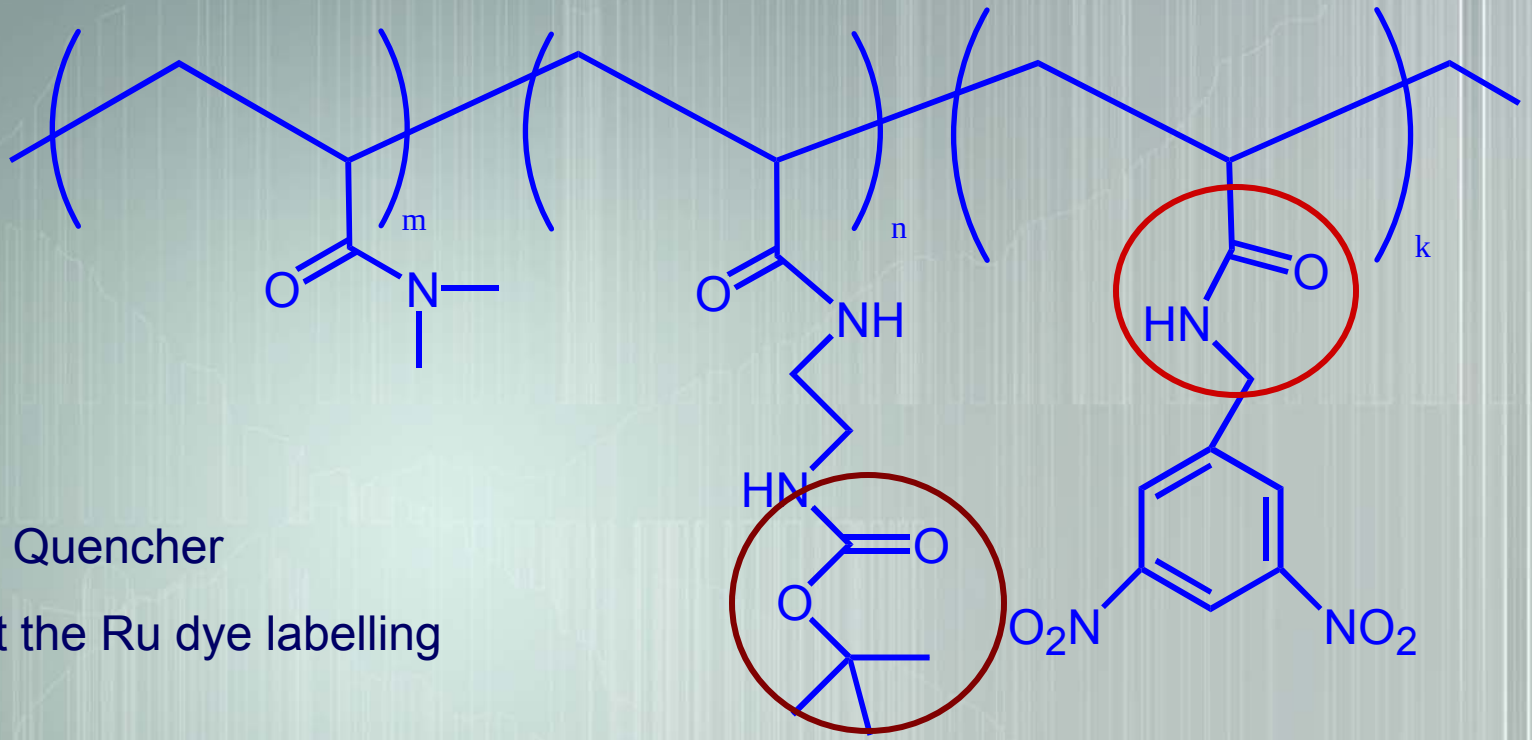
Polymer Labelling Procedure



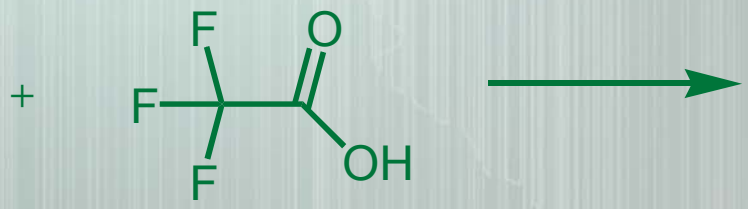
1. Attaching Quencher



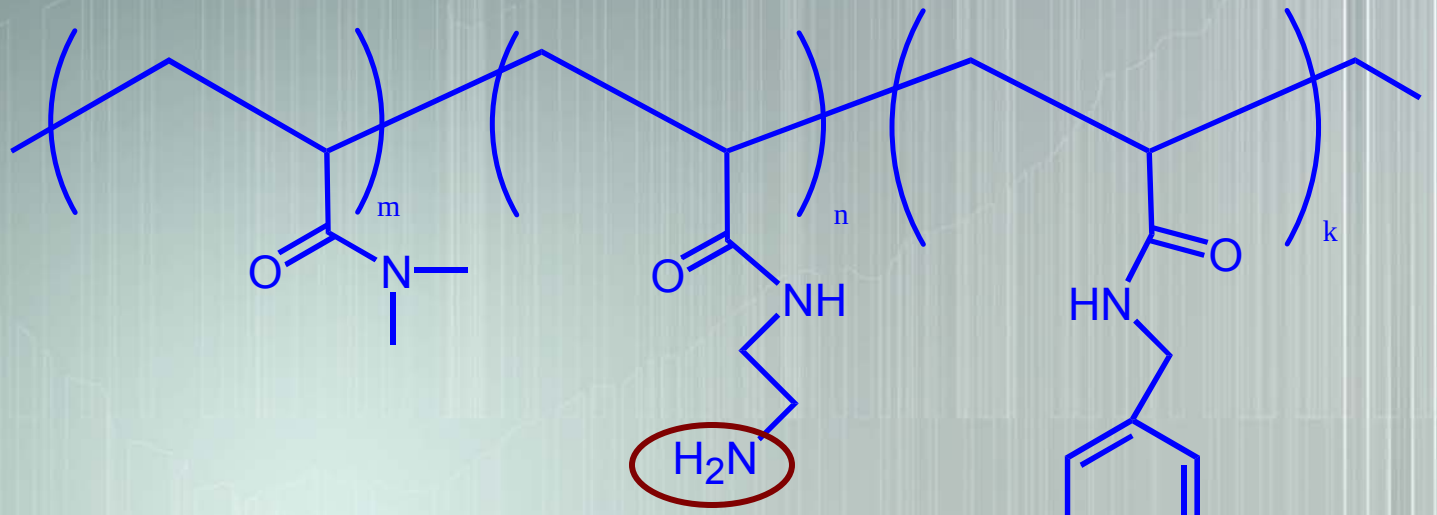
Polymer Labelling Procedure



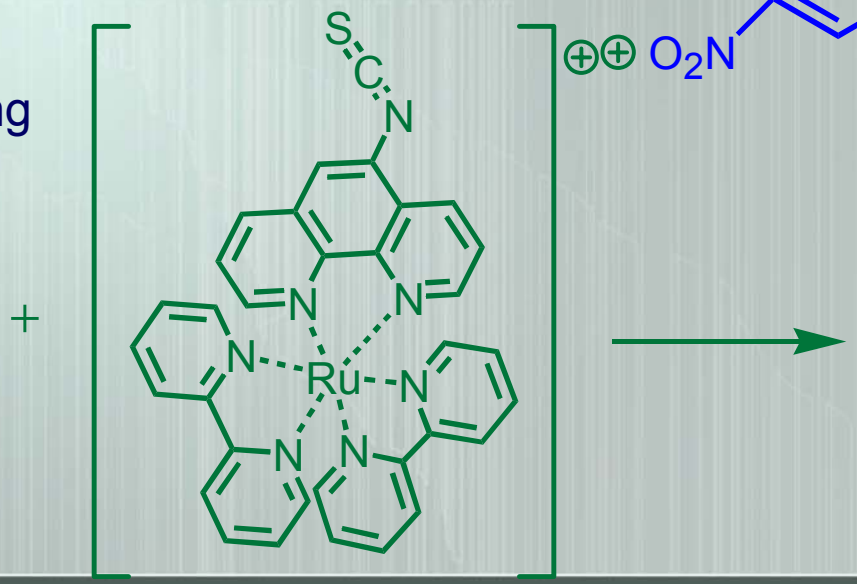
1. Attaching Quencher
2. Deprotect the Ru dye labelling site



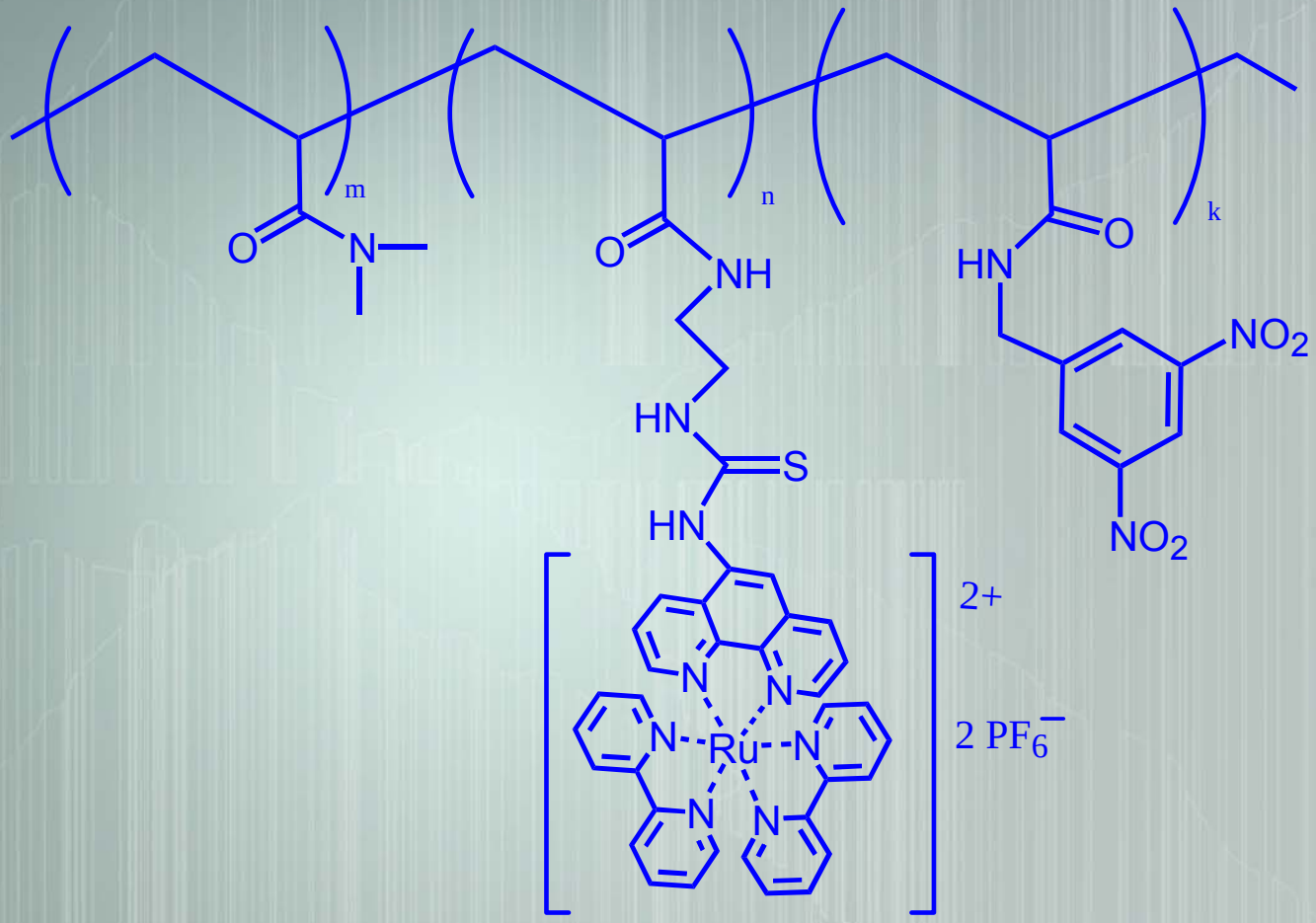
Polymer Labelling Procedure



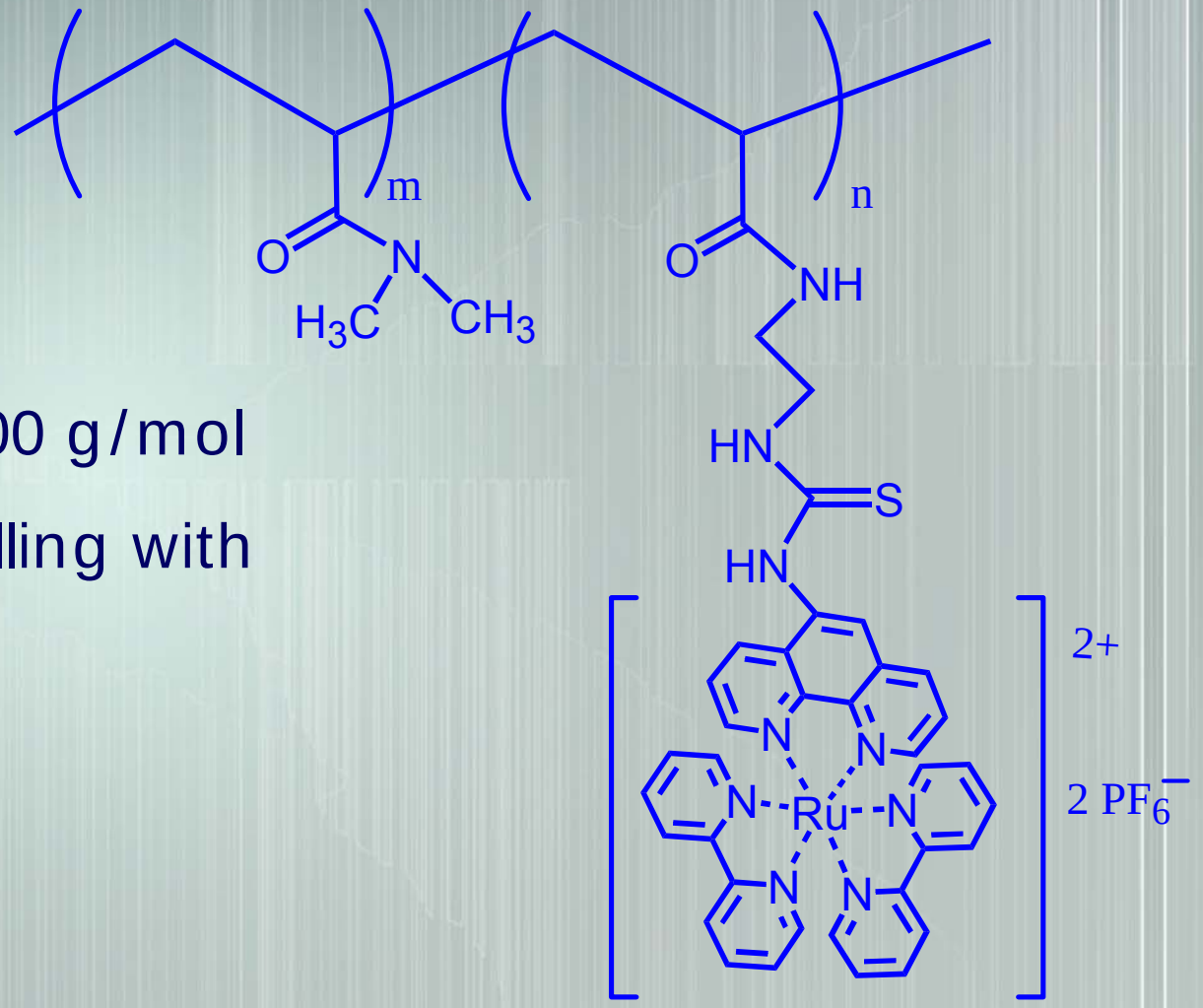
1. Attaching Quencher
2. Deprotect the Ru dye labelling site.
3. Attach Ru dye



Completed Polymer

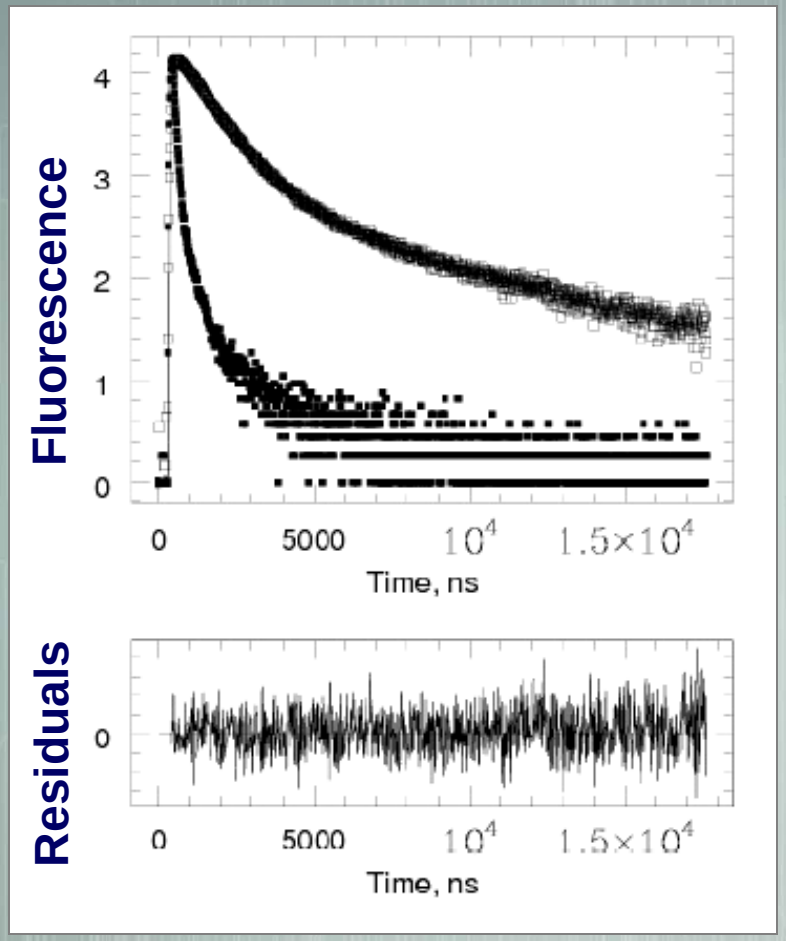


Ru labelled PDMA



- M_W= 400 000 g/mol
- 0.04% labelling with Ru(bpy)

Polymer Lifetime



- **Degassed**
- **9 mM Ru-bpy in 0.1 M Carbonate solution**
- **0.04% labelling**

λ_{ex}=454 nm

λ_{em}=611nm

$\chi^2=1.29$

τ_1 = 850 ns	α_1 = 0.91
τ_2 = 2200 ns	α_2 = 0.07
τ_3 = 6100 ns	α_3 = 0.02

Conclusions

- Water-soluble dye has been synthesized and characterized
- An efficient quencher has been determined, characterized and modified for polymer coupling
- Feasibility of polymer synthesis and labelling has been determined.

Future Work

- Synthesize terpolymer
- Label terpolymer
- Carry out Fluorescence studies

Thank You

- Dr. Jean Duhamel
- Lab colleagues
- OGSST, NSERC