

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

May 16, 2006

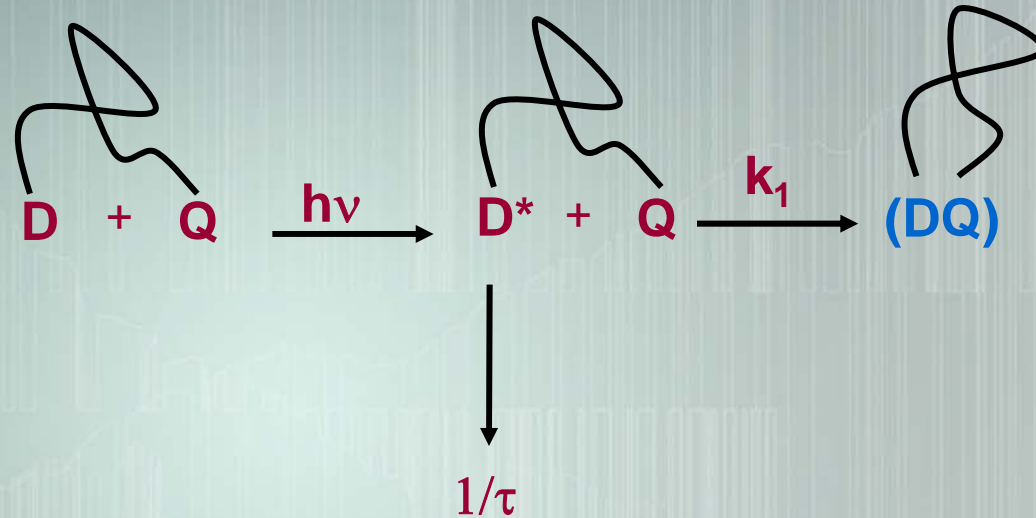
Cristina Quinn  
Institute for Polymer Research  
University of Waterloo

# Outline

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

# Polymer Dynamics

## •End-to-End Cyclization

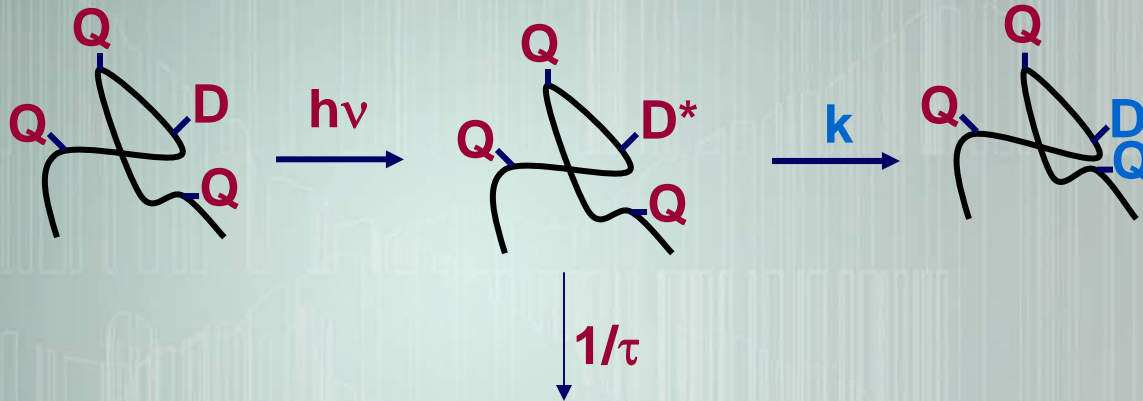


## •Problems

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

# Polymer Dynamics

## Random Labeling

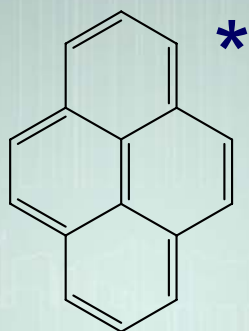


## Problems

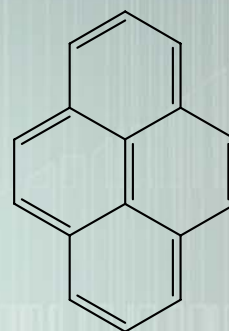
- Entire backbone monitored but a distribution of rate constants obtained

# More Problems

- Hydrophobicity of pyrene causes aggregation of chromophore in aqueous solutions



Chromophore



Quencher

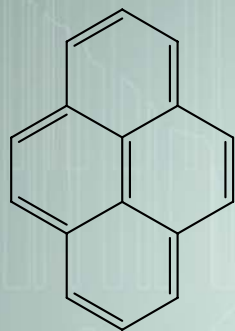
**Pyrene**

Water solubility

=  $7 \times 10^{-7}$  M

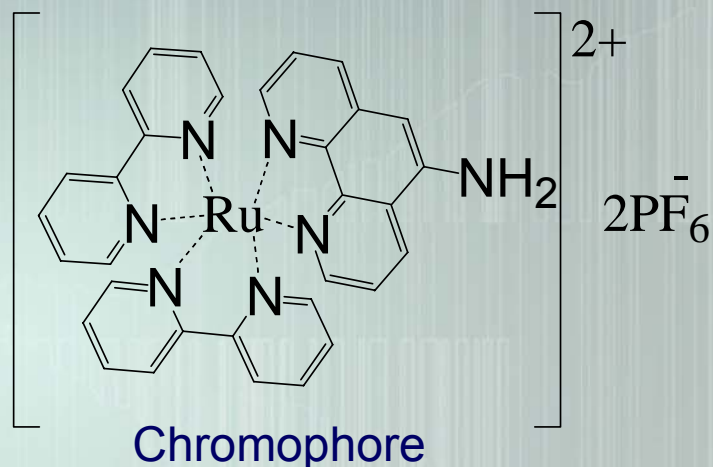
# Solution

- Use a water-soluble dye and quencher.



**Pyrene**

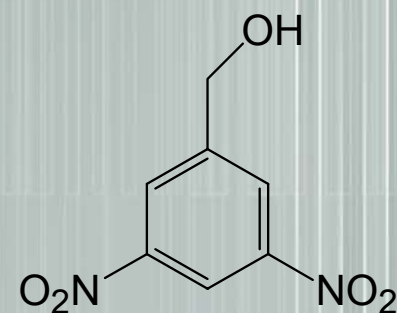
Water solubility  
=  $7 \times 10^{-7}$  M



**Chromophore**

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

0.1 M  $\text{Na}_2\text{CO}_3$   
solubility  
 $\sim 1 \times 10^{-3}$  M



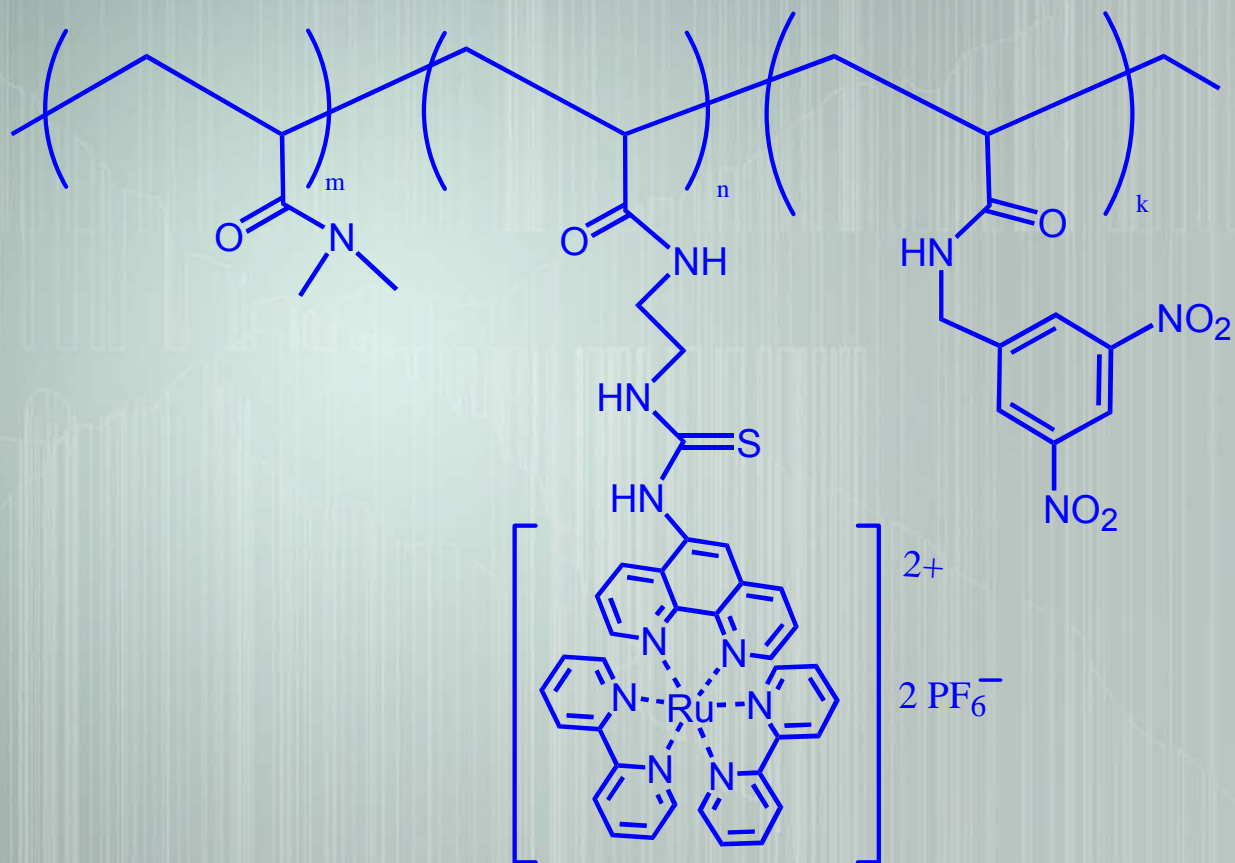
**Quencher**

**Dinitrobenzyl Alcohol**

0.1 M  $\text{Na}_2\text{CO}_3$   
solubility  
 $\sim 1 \times 10^{-2}$  M

# Goal

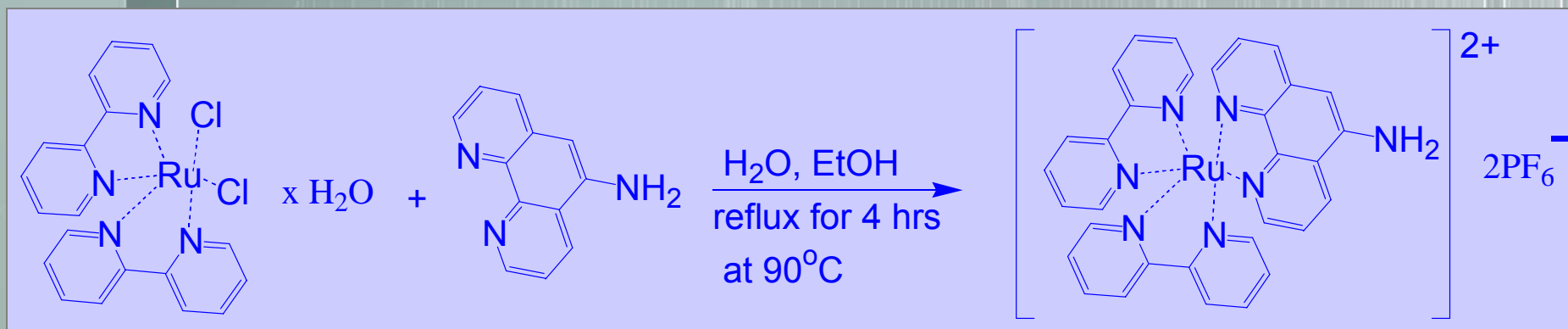
- To label a water-soluble polymer with a water-soluble dye
- To obtain information about polymer dynamics in water



# Steps

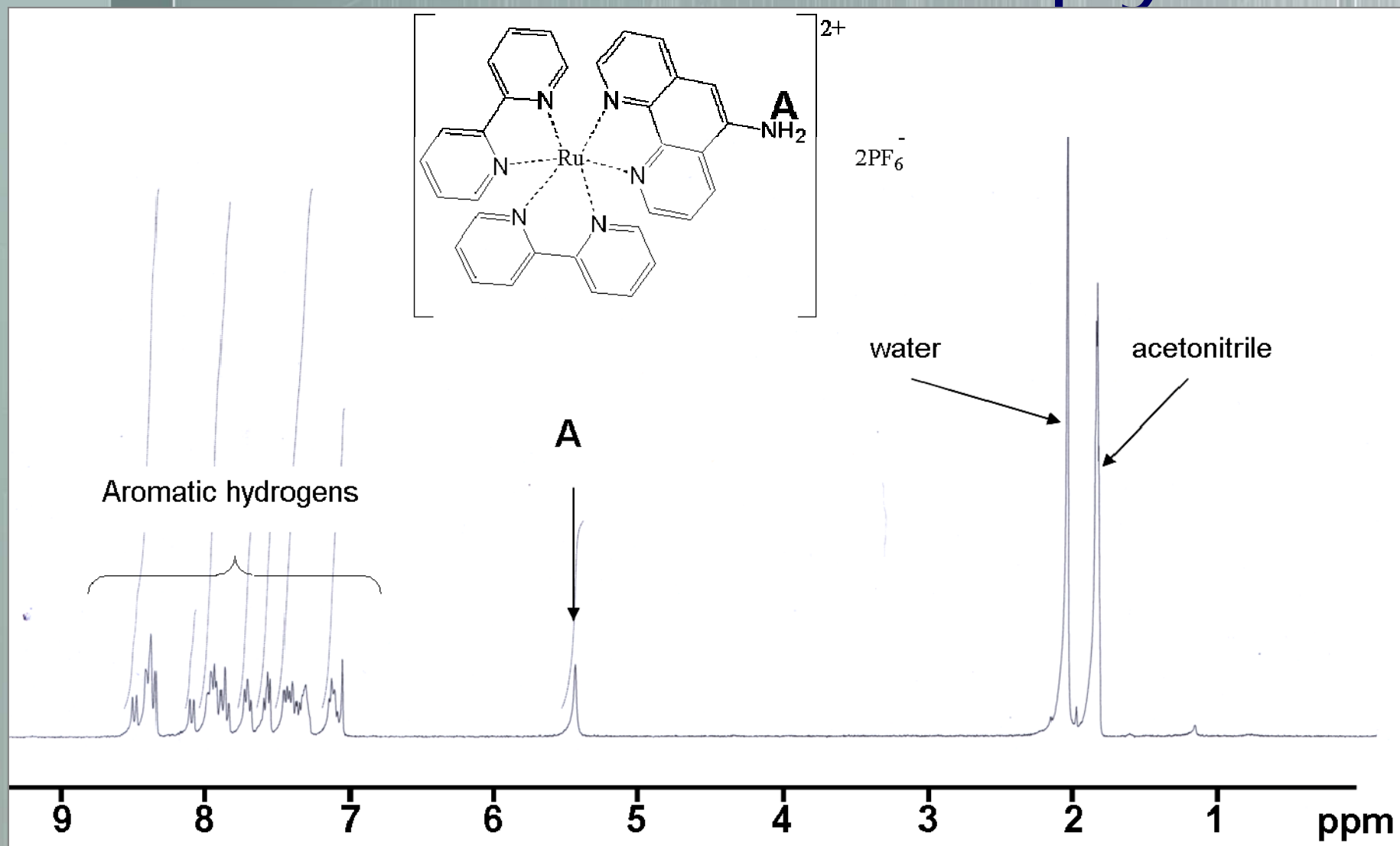
1. Synthesize dye
2. Characterize dye
3. Find a quencher
4. Synthesize Polymer
5. Label Polymer
6. Obtain luminescence experiments

# Synthesis of Ru-bpy

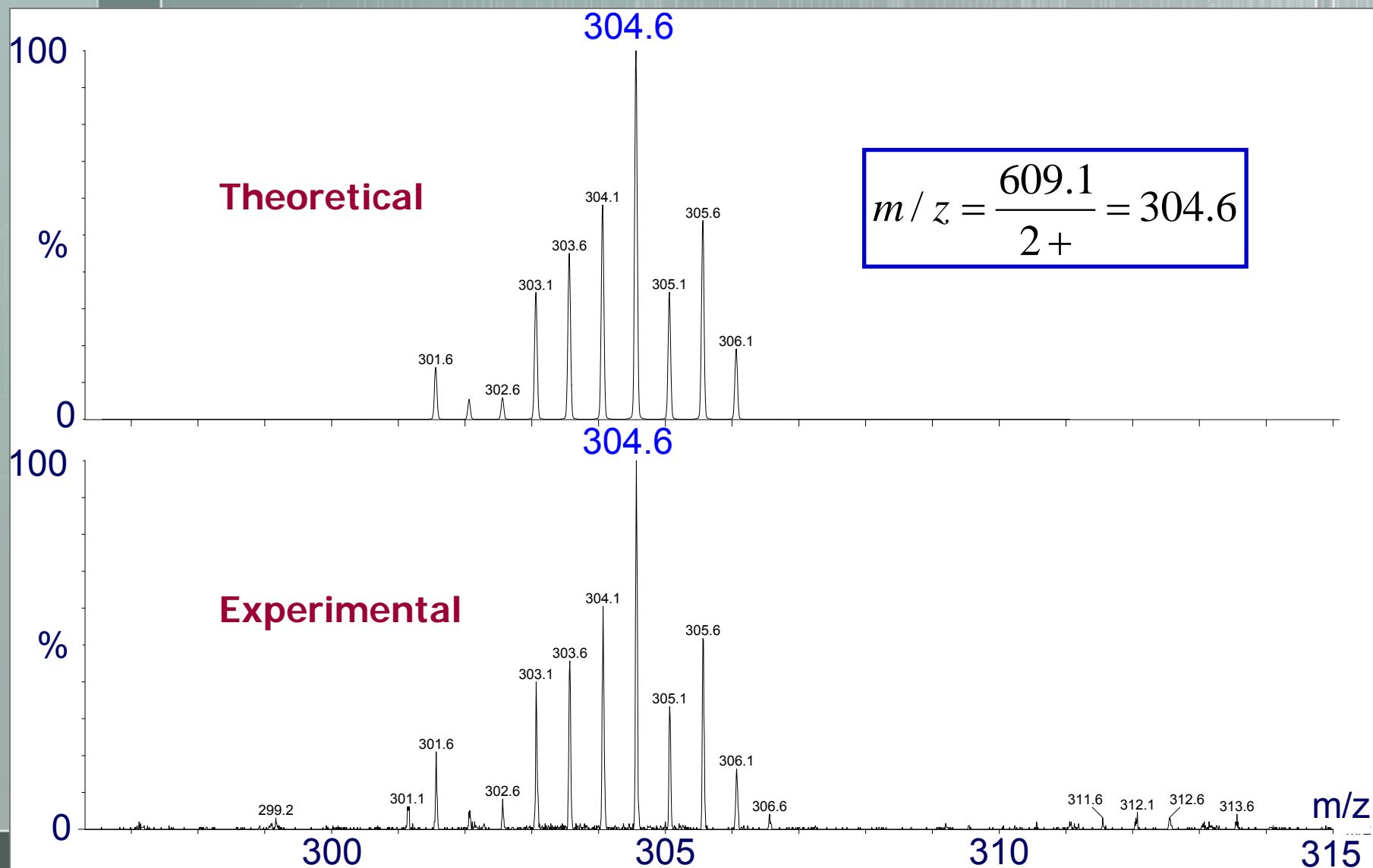


- Refluxed at 75°C under N<sub>2</sub>
- Purified by Column Chromatography using alumina and 1:2 toluene/acetonitrile
- ~85% yield

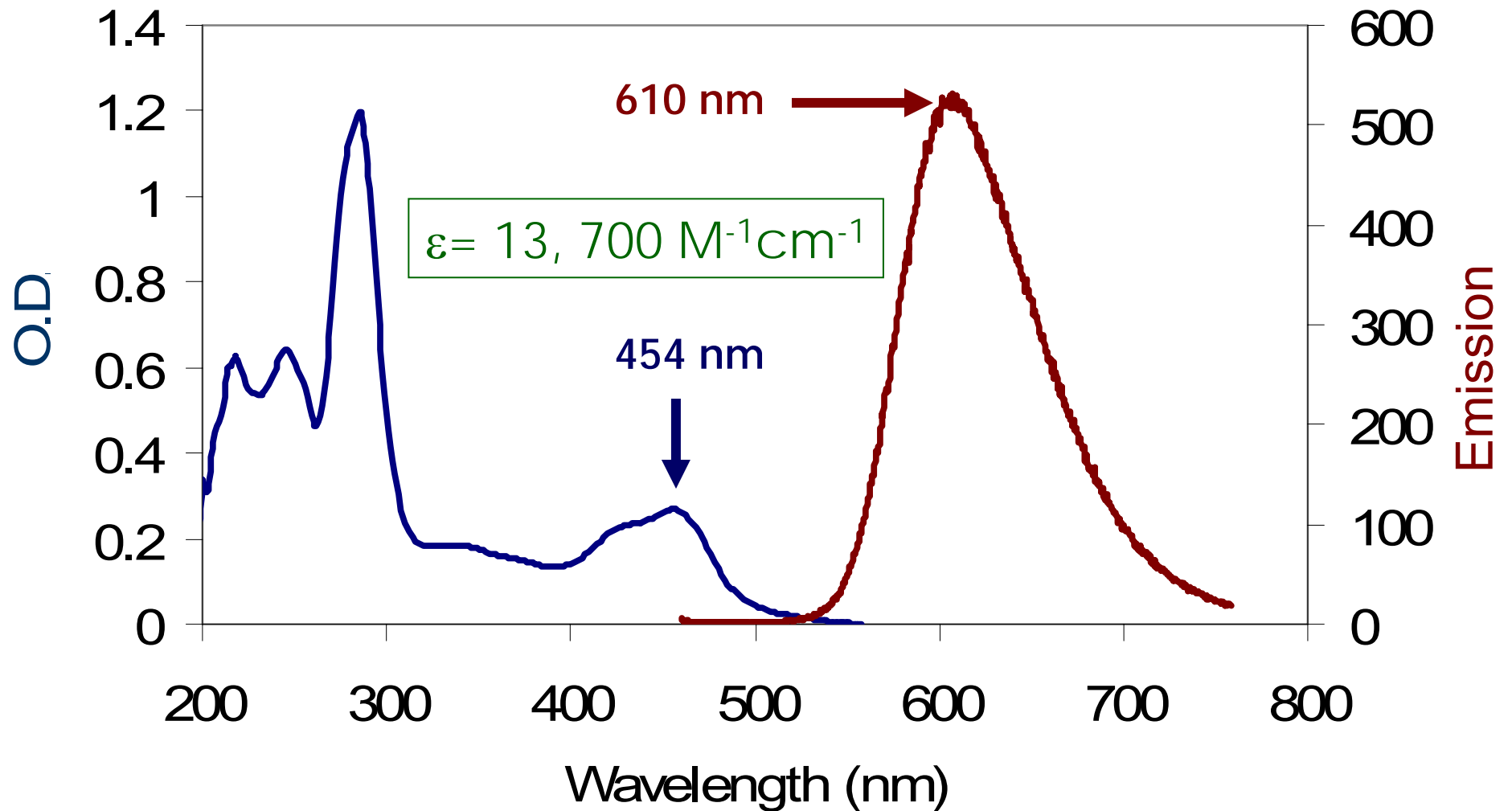
# $^1\text{H}$ NMR of Ru-bpy



# ESI-TOF-MS for Ru-bpy



# Spectroscopic Characteristics



# Decay Measurements

## Aerated

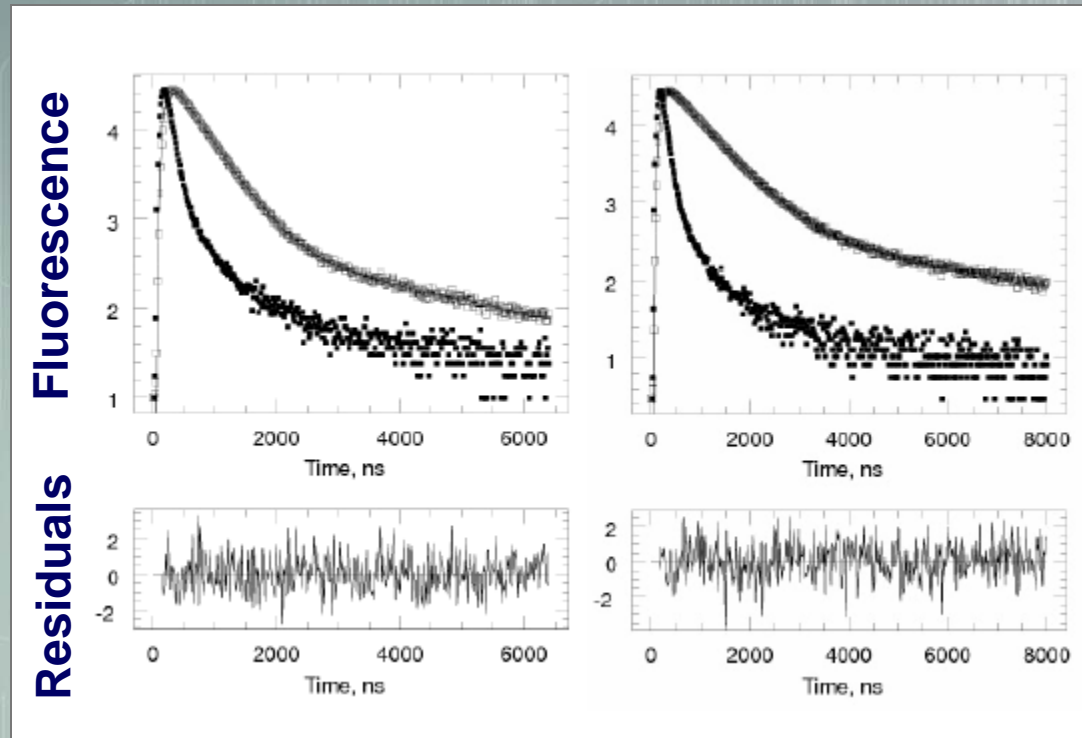
$$\chi^2 = 1.07$$

$$\tau_1 = 385 \text{ ns}$$

$$\alpha_1 = 0.99$$

$$\tau_2 = 2800 \text{ ns}$$

$$\alpha_2 = 0.01$$



## Degassed

$$\chi^2 = 1.02$$

$$\tau_1 = 565 \text{ ns}$$

$$\alpha_1 = 0.98$$

$$\tau_2 = 3500 \text{ ns}$$

$$\alpha_2 = 0.02$$

8  $\mu\text{M}$  in 0.1 M carbonate solution

$\lambda_{\text{ex}} = 454 \text{ nm}$

$\lambda_{\text{em}} = 611 \text{ nm}$

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

# Steps

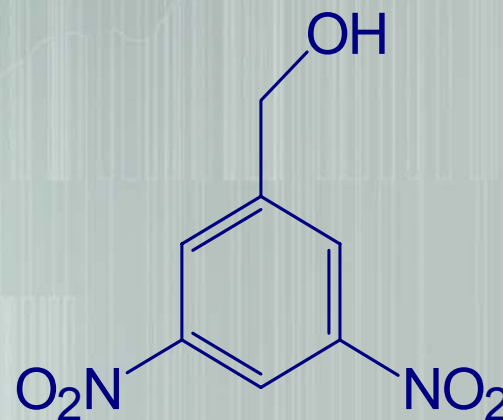
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# Quencher

## Insufficient Quenching

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

## Selected Quencher



Dinitrobenzyl alcohol (DNBA)

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

# Dye Comparison

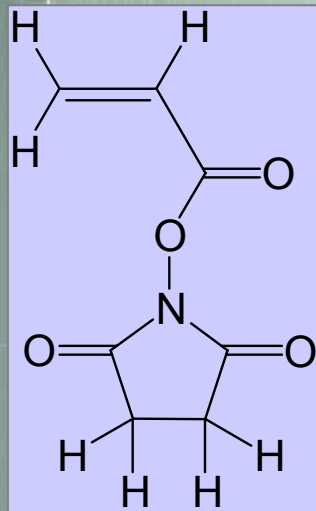
	Ru-bpy (0.1 M Na <sub>2</sub> CO <sub>3</sub> )	DNBA (0.1 M Na <sub>2</sub> CO <sub>3</sub> )	Pyrenemethanol (water)
Water Solubility (M)	$\sim 1 \times 10^{-3}$	$\sim 1 \times 10^{-2}$	$7 \times 10^{-7}$ (Py)
Molecular Weight	898.6 (608.6)	198.1	232.3
Volume (Å) <sup>3</sup>	$\sim 890$	$\sim 210$	$\sim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

# Steps

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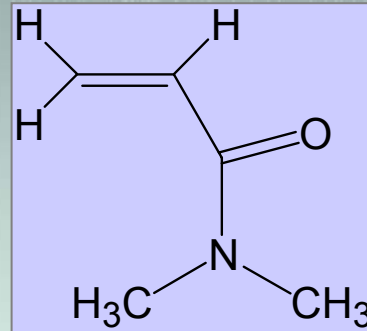
# Monomers

Quencher



N-Acryloxysuccinimide

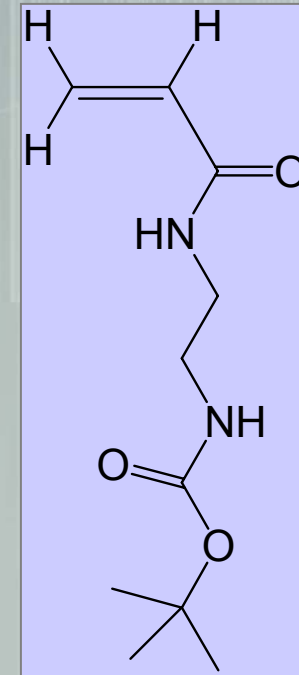
NASI



N,N-dimethylacrylamide

DMA

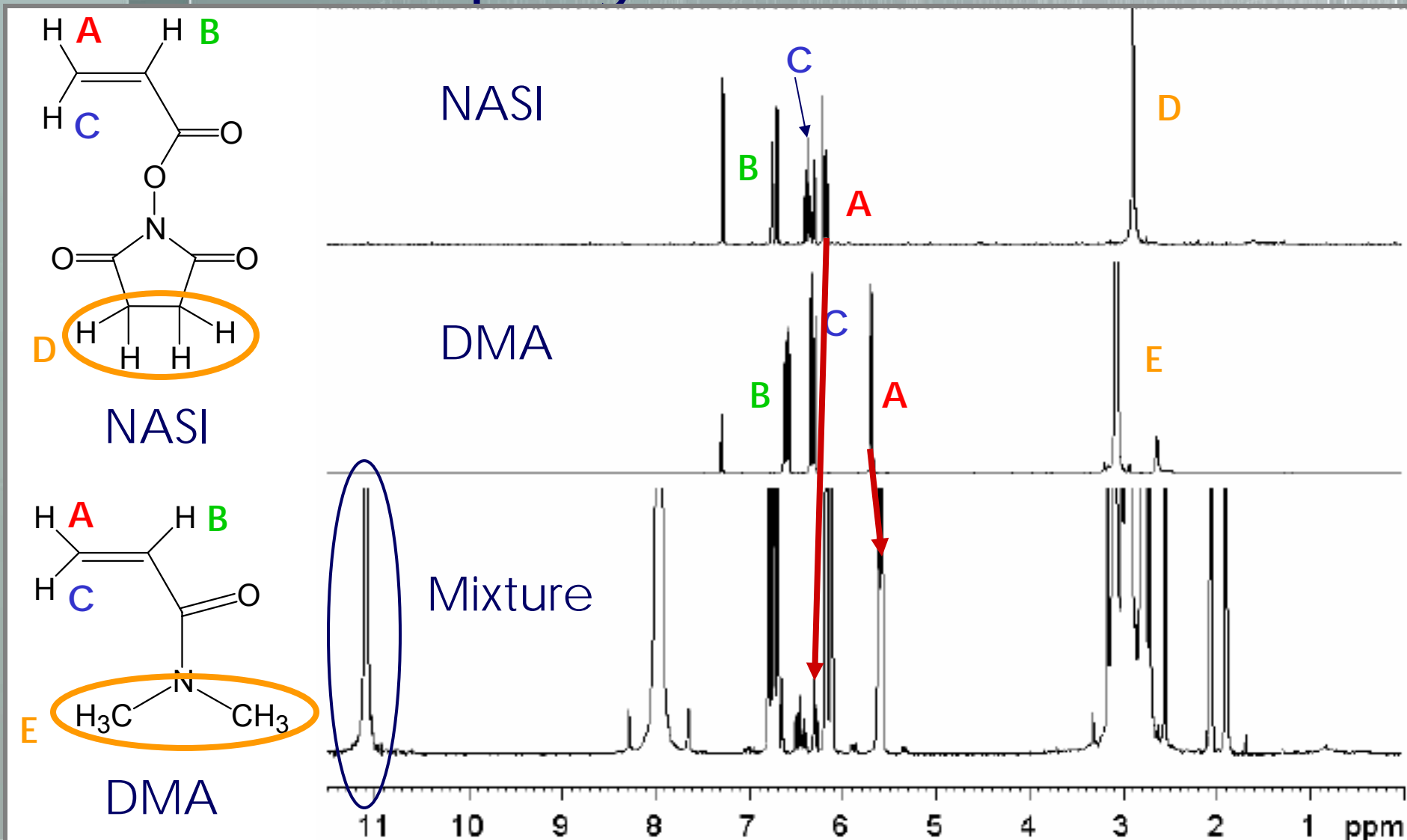
Dye



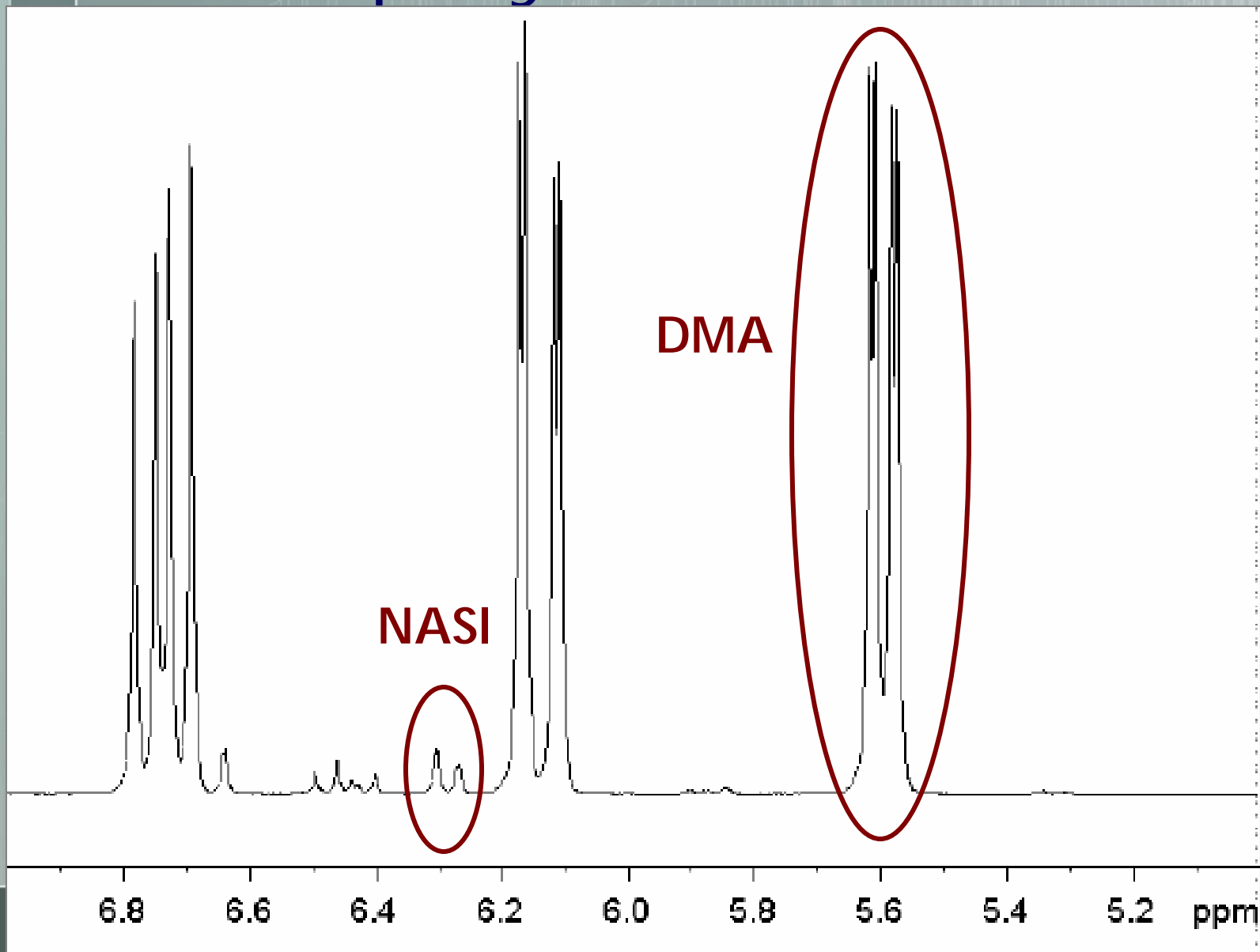
N-Acryloxyethylenediamine

AcEDA

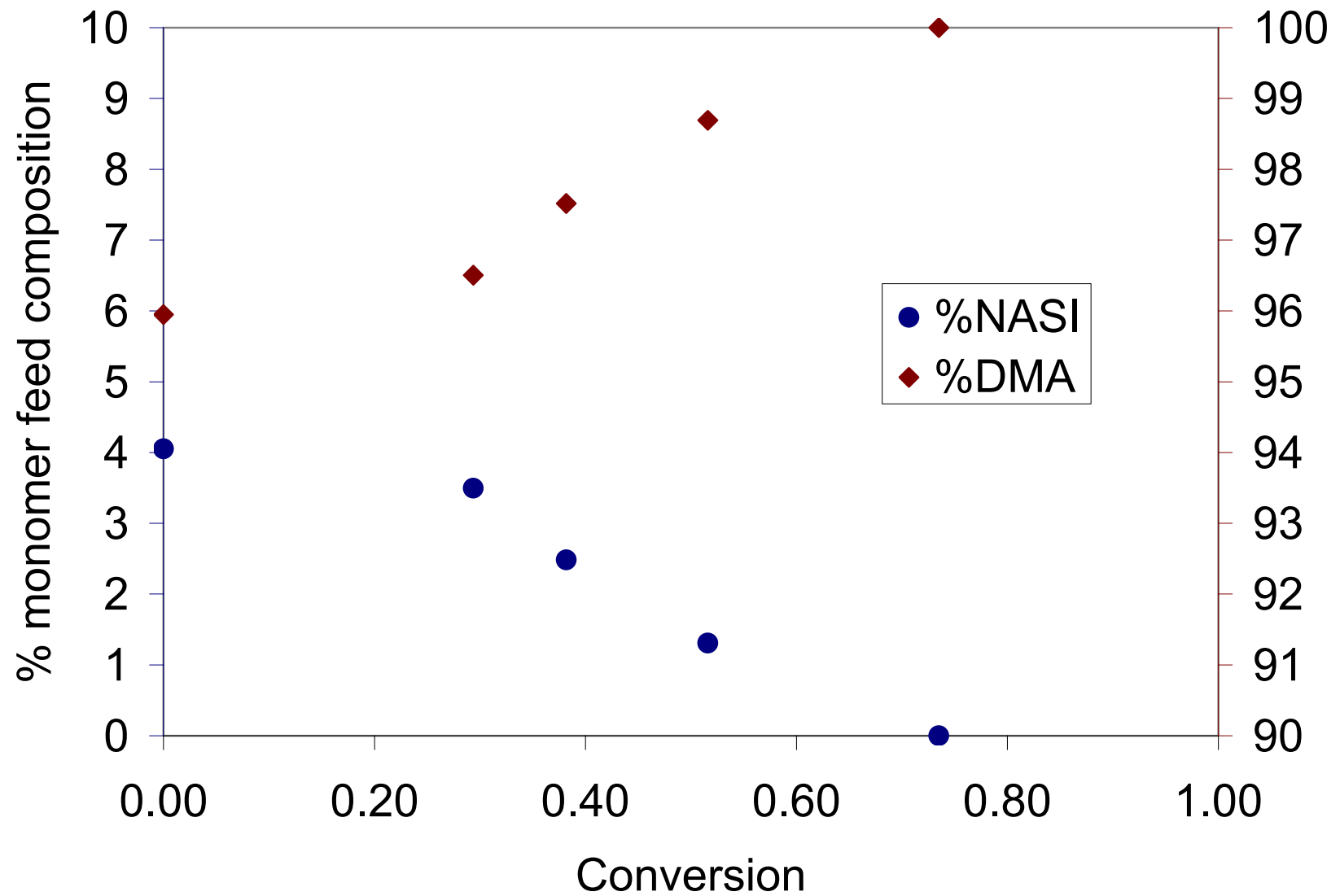
# Copolymerization



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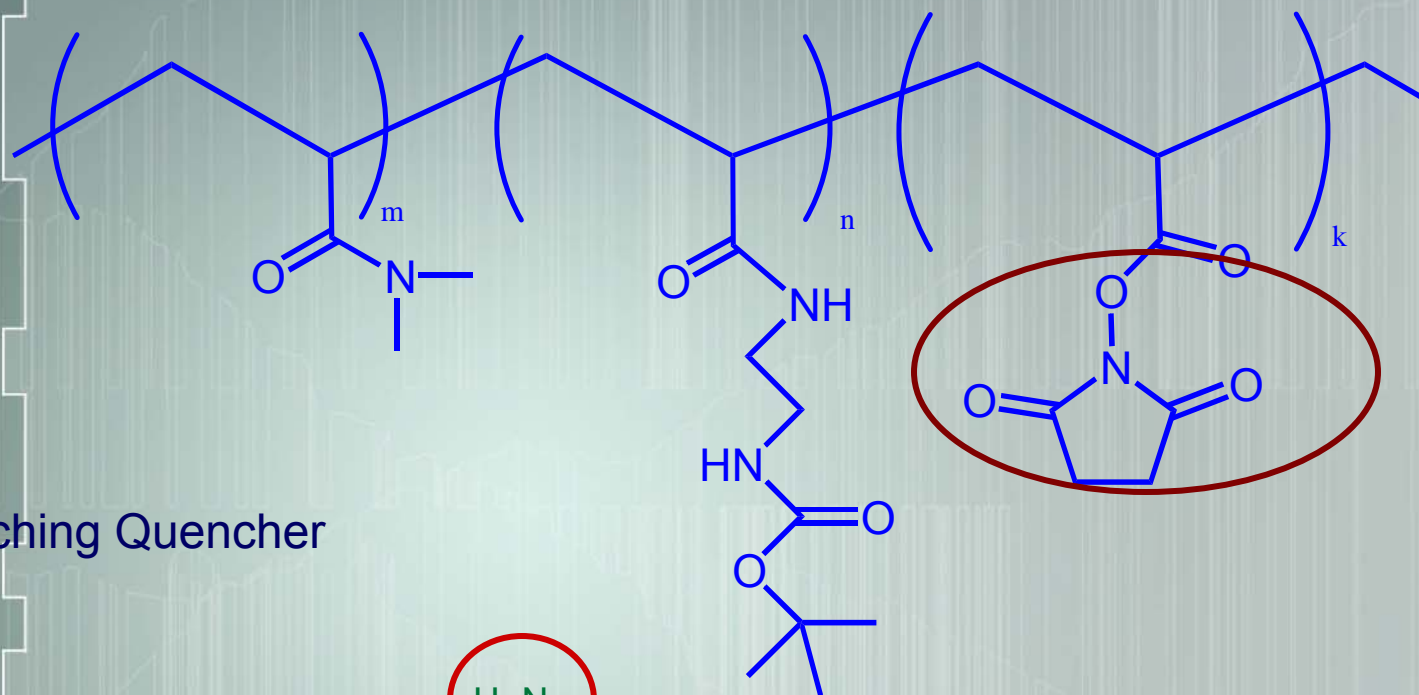
- Up to 25-30% conversion, both monomers are incorporated randomly.
- After 25-30% conversion, the NASI monomer is preferentially incorporated.

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

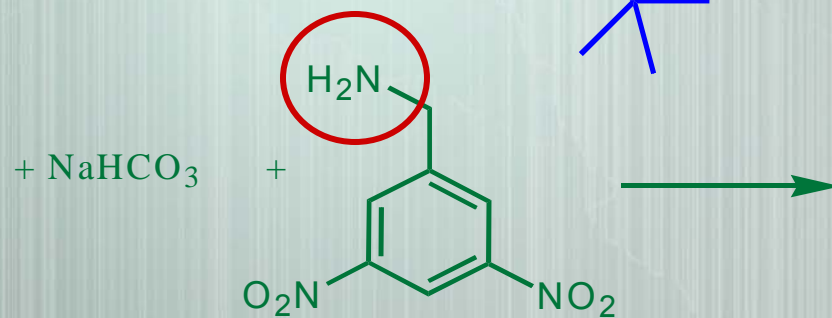
# Steps

1. Synthesize dye
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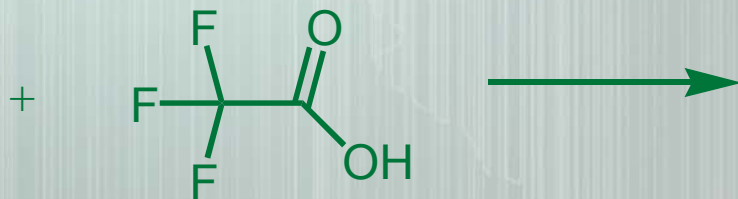
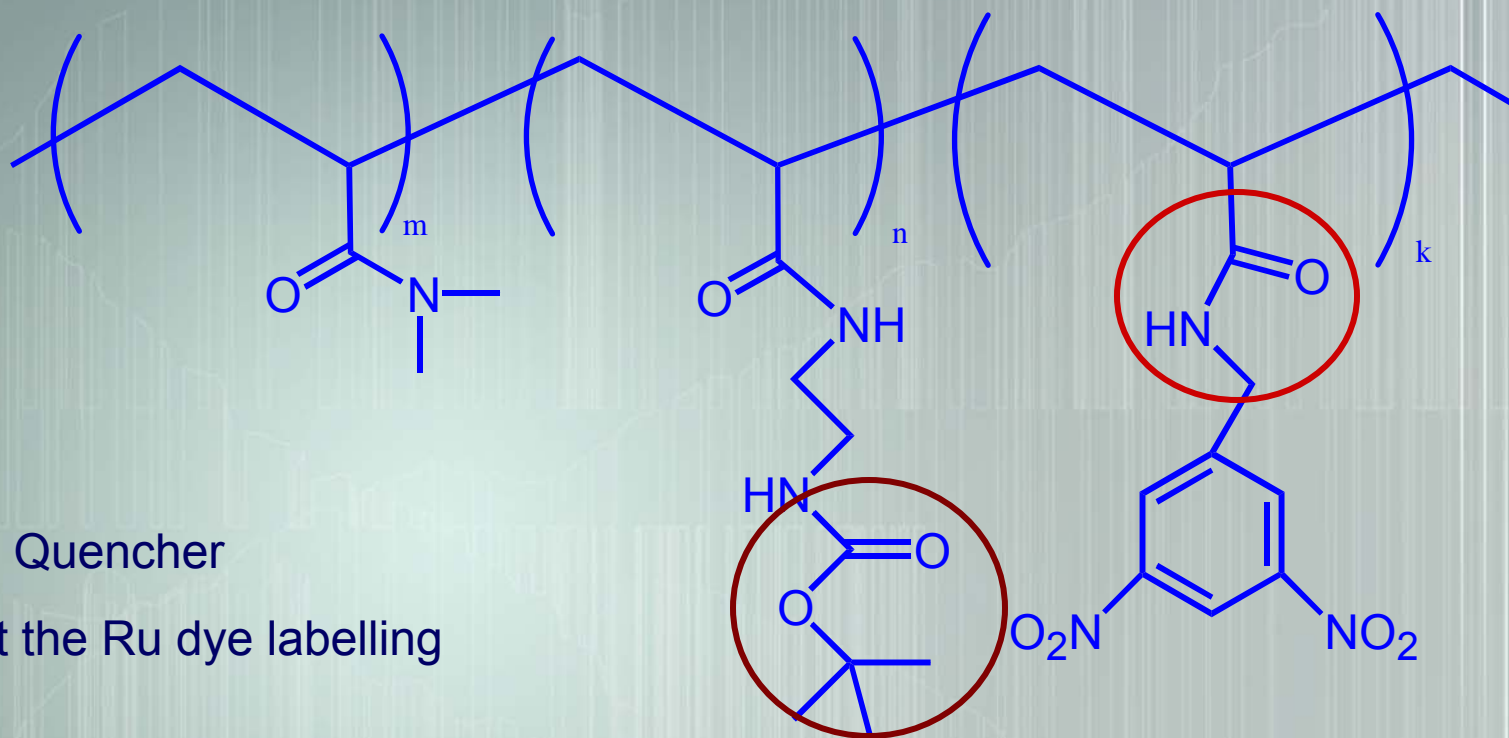
# Polymer Labelling Procedure



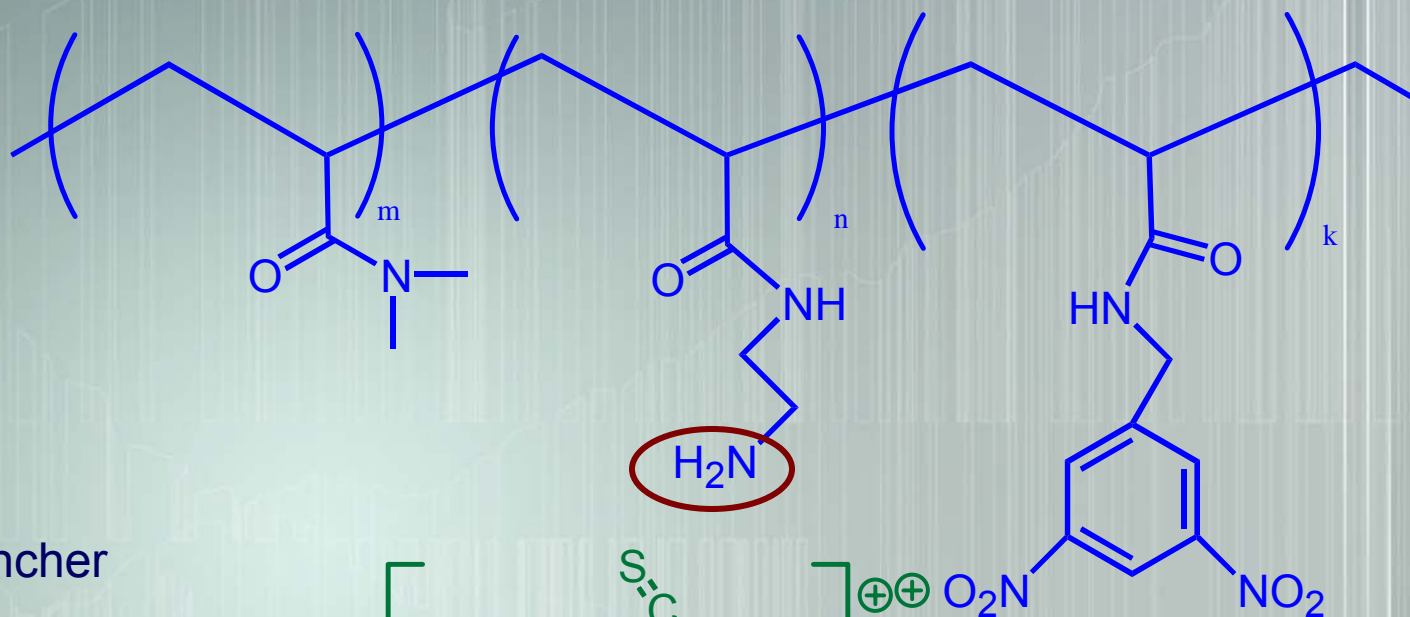
## 1. Attaching Quencher



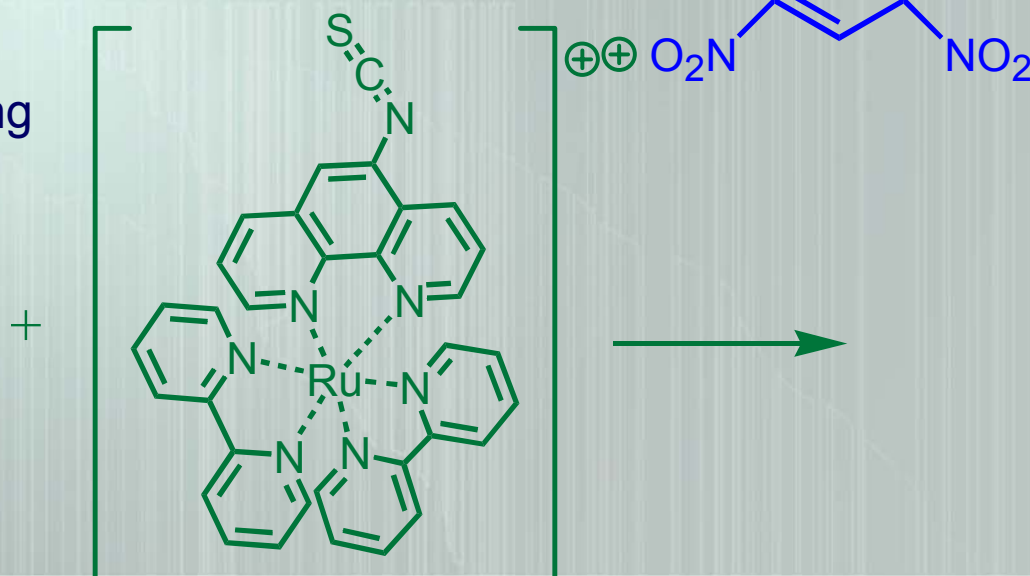
# Polymer Labelling Procedure



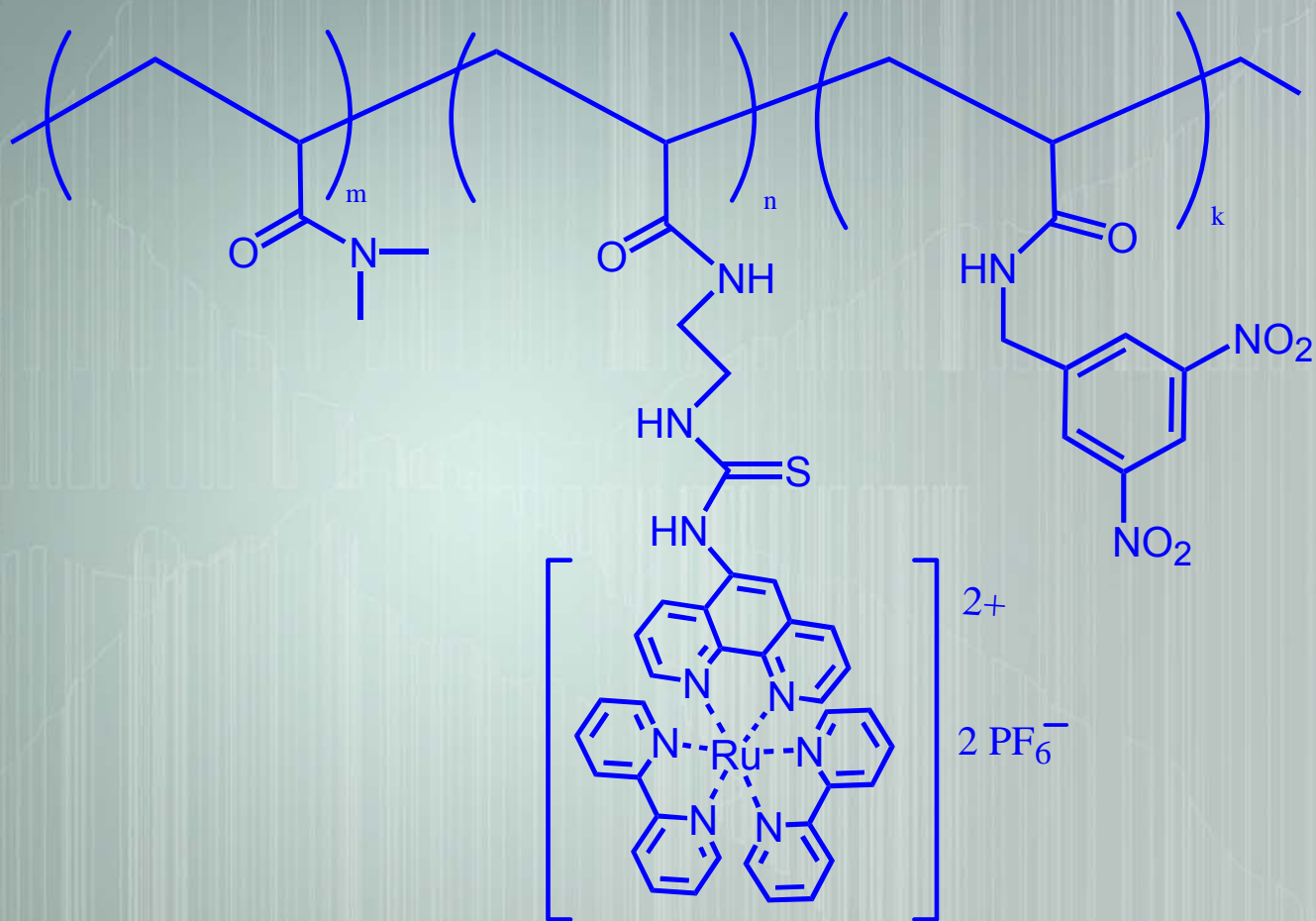
# Polymer Labelling Procedure



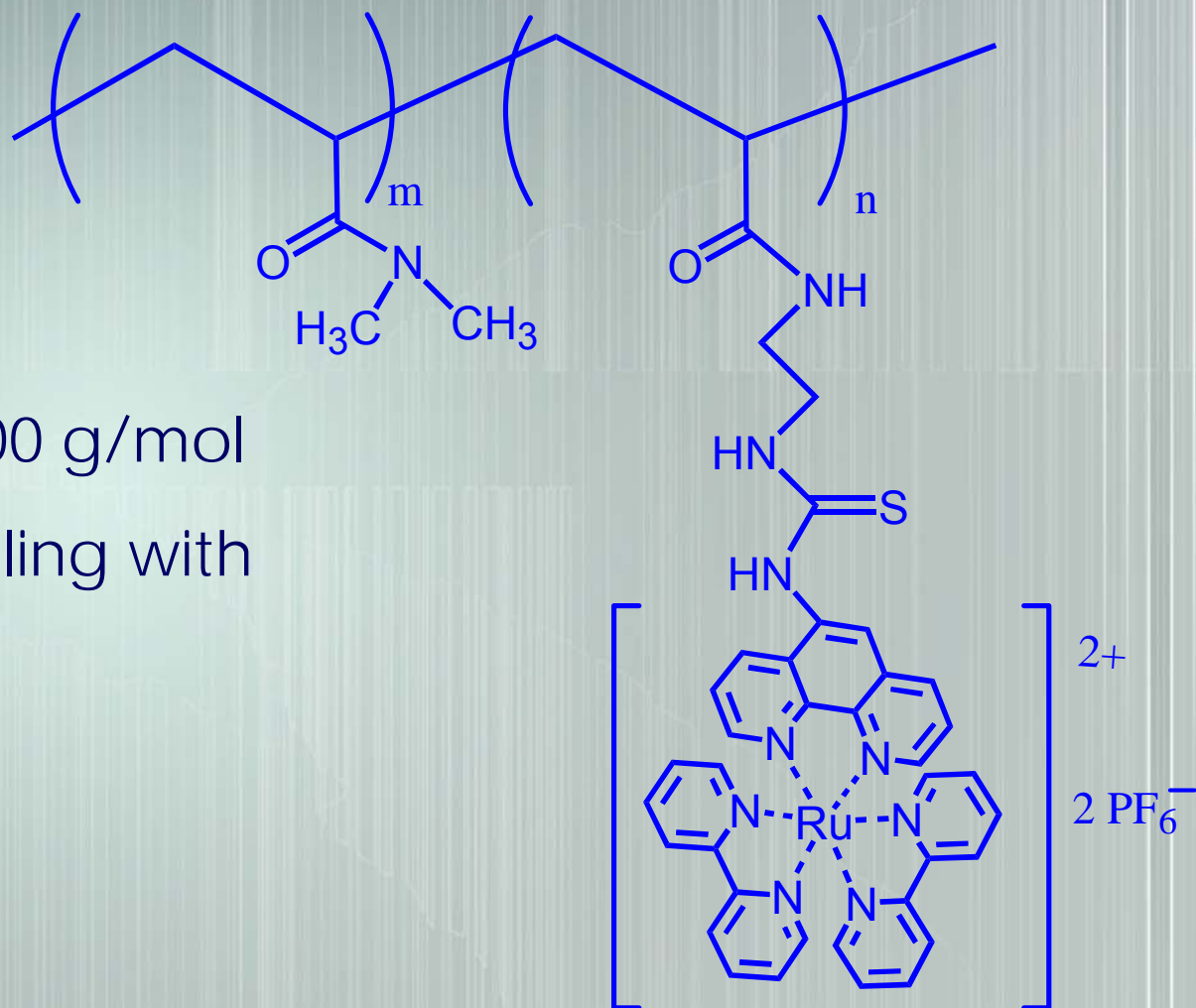
1. Attaching Quencher
2. Deprotect the Ru dye labelling site.
3. Attach Ru dye



# Completed Polymer

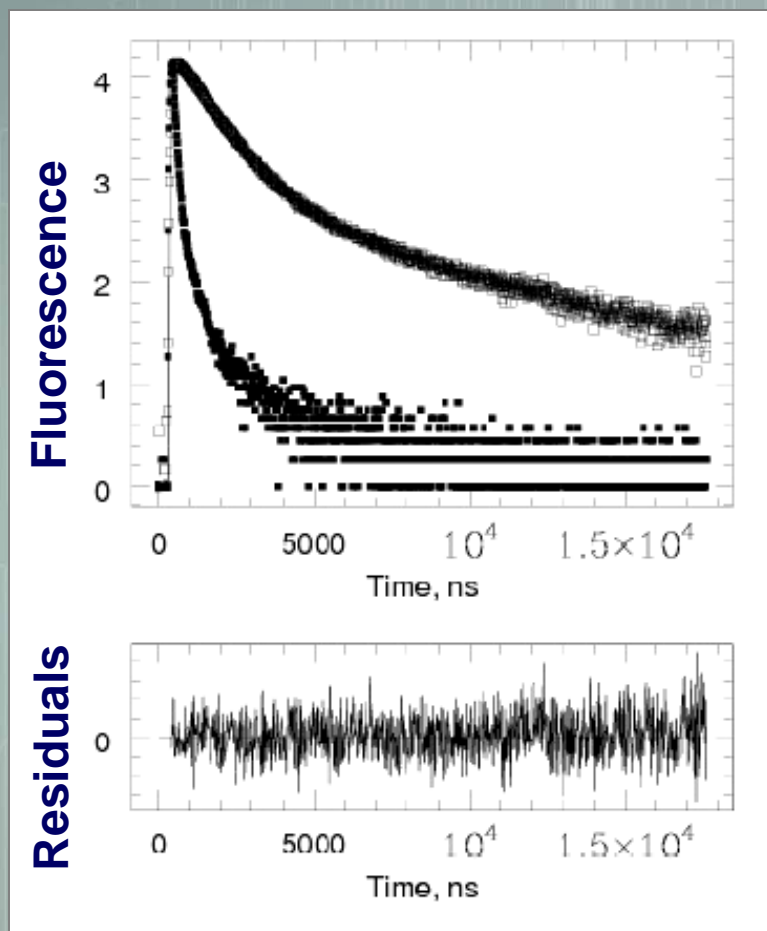


# Ru labelled PDMA



- $M_w = 400\,000$  g/mol
- 0.04% labelling with Ru(bpy)

# Polymer Lifetime



• Degassed

• 9 mM Ru-bpy in 0.1 M Carbonate solution

• 0.04% labelling

$\lambda_{\text{ex}} = 454 \text{ nm}$

$\lambda_{\text{em}} = 611 \text{ nm}$

$$\chi^2 = 1.29$$

$$\tau_1 = 850 \text{ ns} \quad \alpha_1 = 0.91$$

$$\tau_2 = 2200 \text{ ns} \quad \alpha_2 = 0.07$$

$$\tau_3 = 6100 \text{ ns} \quad \alpha_3 = 0.02$$

# 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