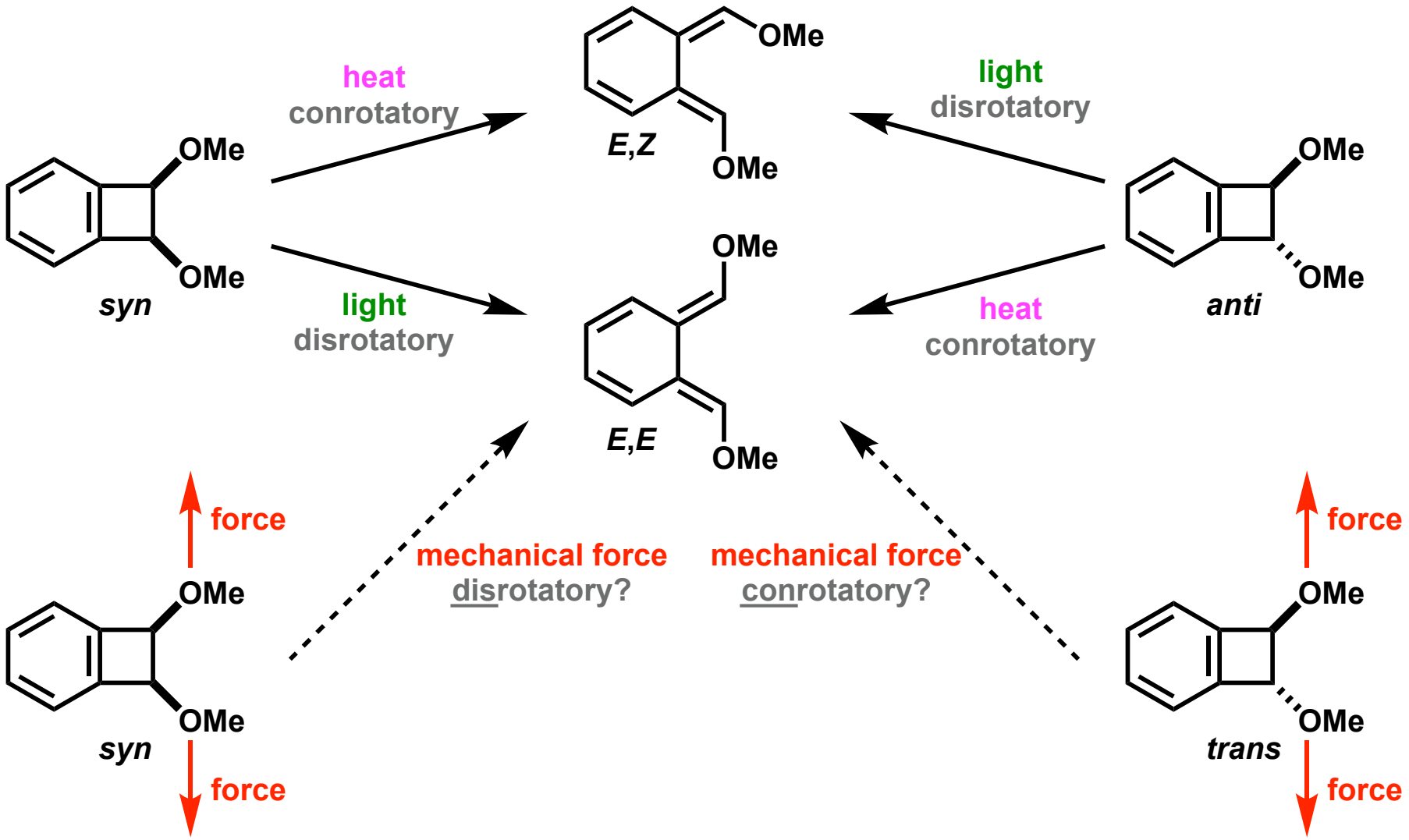
Mechanical Force Cleaves Specific Covalent Bond

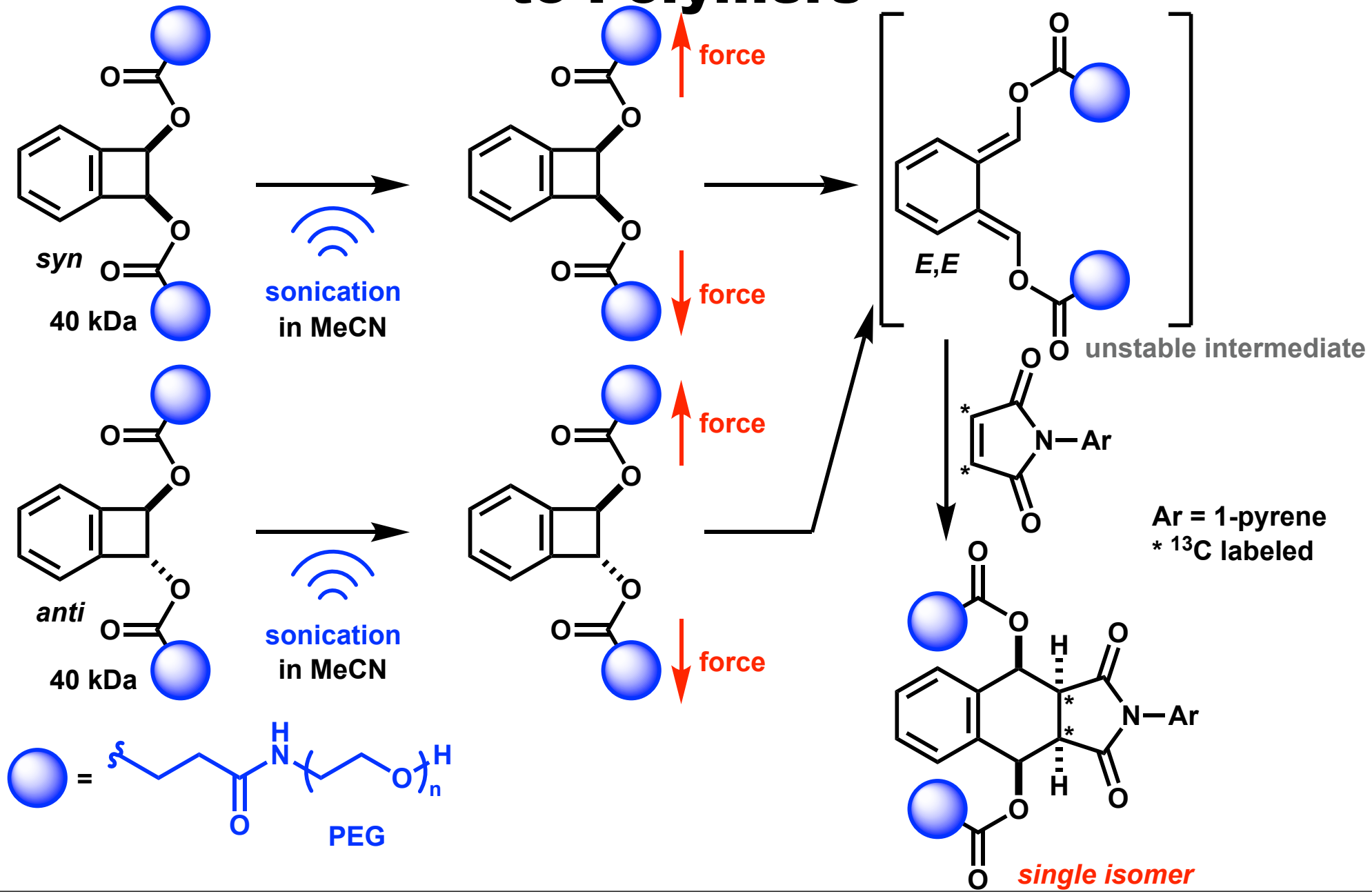
2025.5.31. Literature Seminar
D3 Hibiki Asai

Contents

Can Mechanical Force Overcome Woodward–Hoffmann Rules?

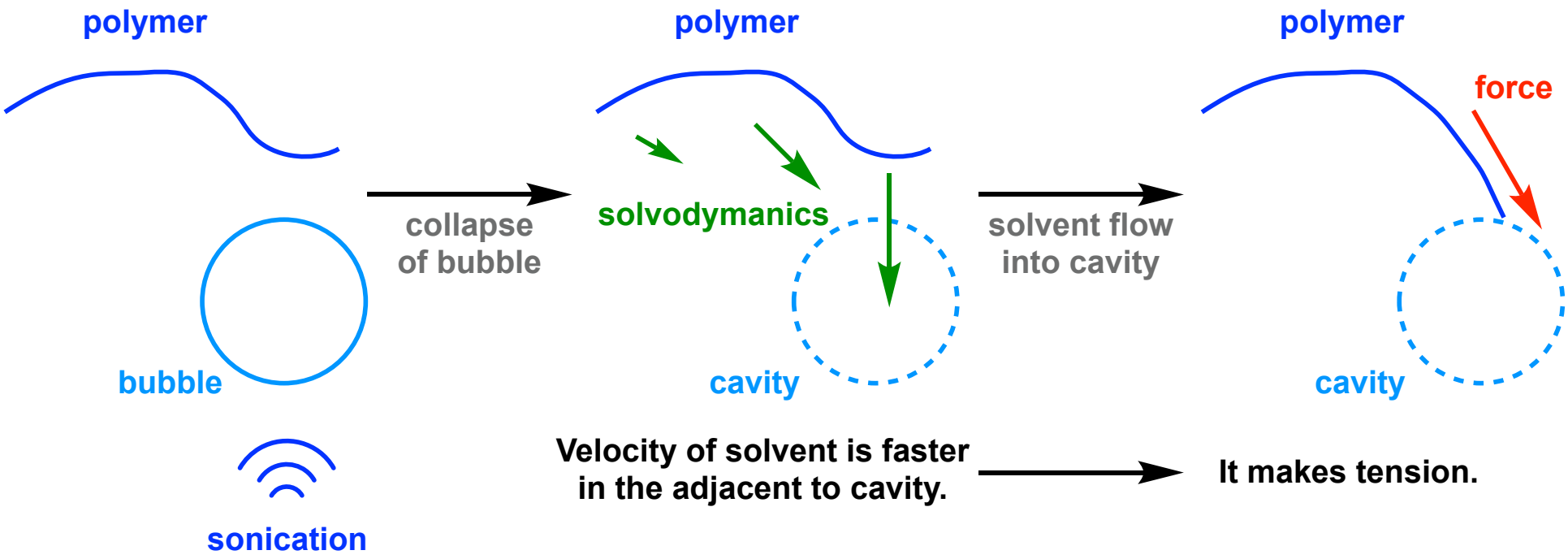


Ultrasound Transmits Mechanical Force to Polymers



Hickenboth, C. R.; Moore, J. S.; White, S.; Sottos, N. R.; Baudry, J.; Wilson, S. *Nature* **2007**, *446*, 423.

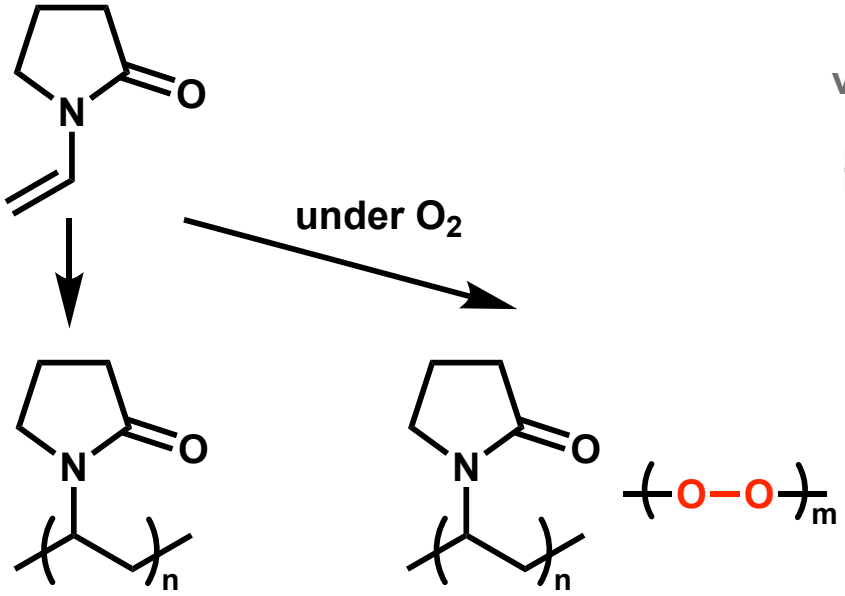
Accepted Mechanism of Polymer Cleavage by Sonication

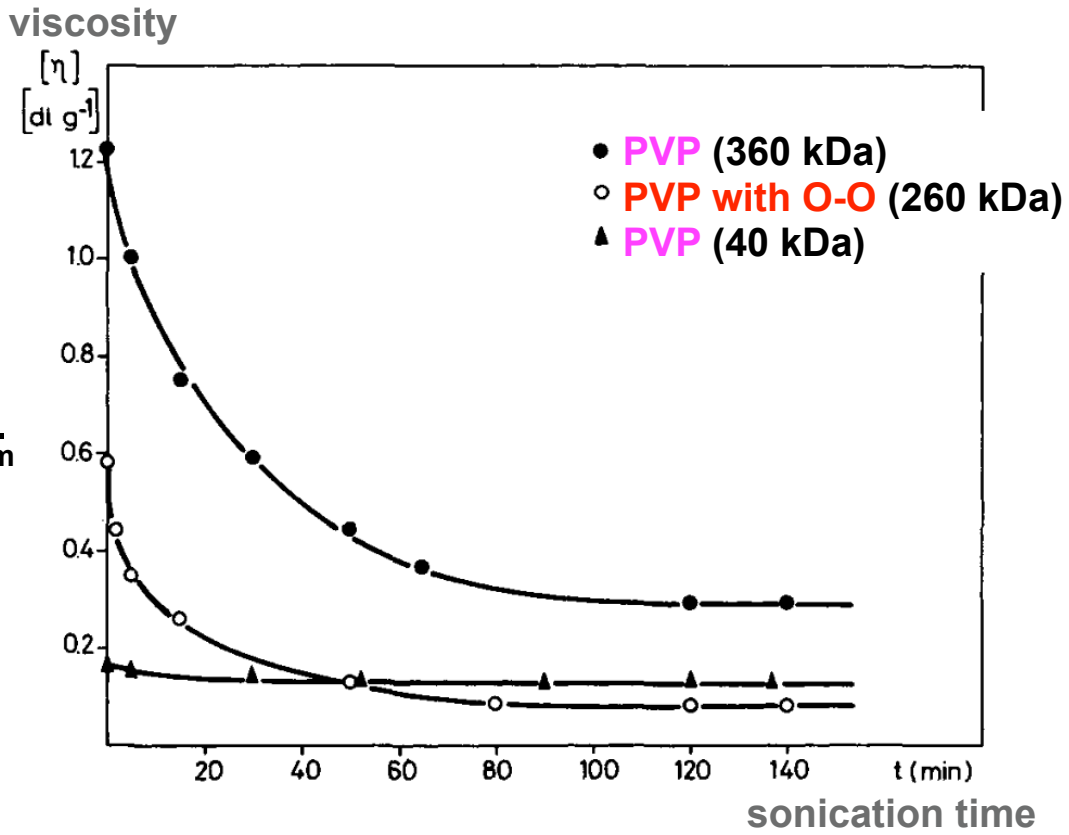


- **Threshold of polymer length: ~30 kDa**
- **Cleavage point: Center of polymer**
- **Efficacy of polymer cleavage: ↑sound intensity, ↓solvent temperature, ↓polymer concentration**

Basedow, A. M.; Ebert, K. H. *Adv. Polym. Sci.* **1977**, *22*, 83.

Ultrasound Cleaves Weak Bond





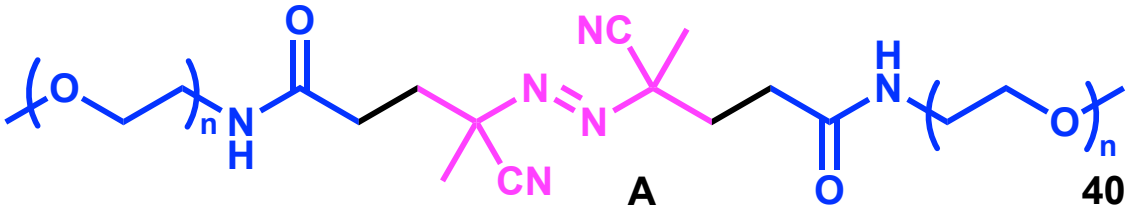
Length of polymer was measured as viscosity of solvent

- PVP with O-O is cleaved faster.
- PVP with O-O has smaller threshold for cleavage.

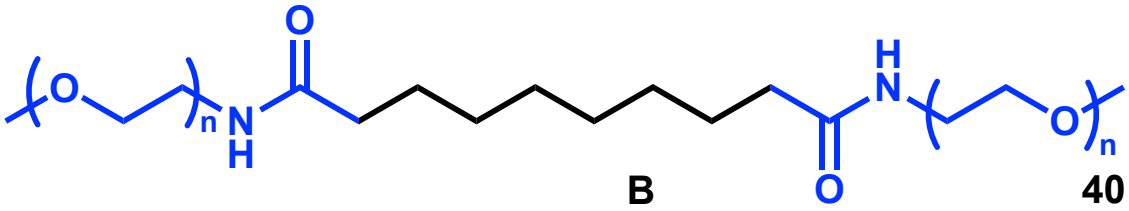
Encina, M. V.; Lissi, E.; Sarasua, M.; Gargallo, L.; Radic, D. *J. Polym. Sci., Plym. Lett. Ed.* **1980**, *18*, 757.

Site-Specific Cleavage by Ultrasound (I)

waek bond at polymer center



A 40 kDa



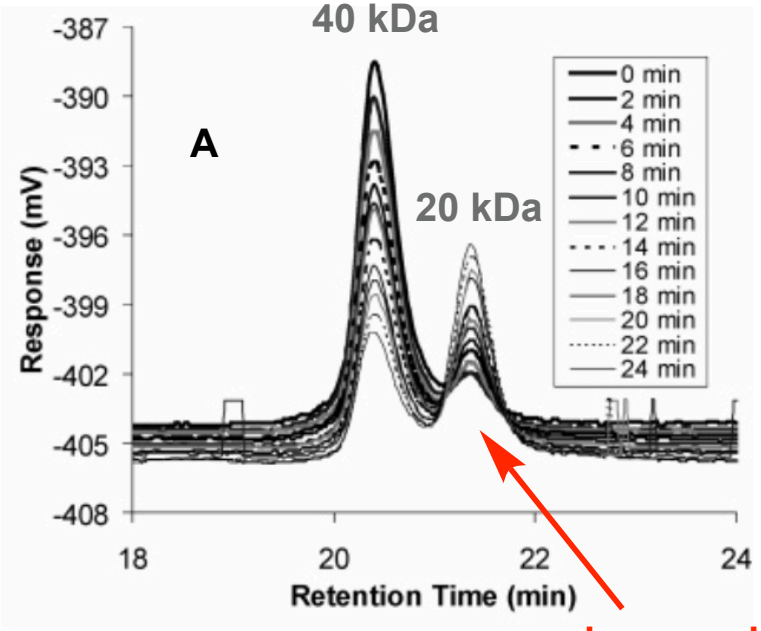
B 40 kDa

20 kHz
8.7 W/cm^2
6~9 °C

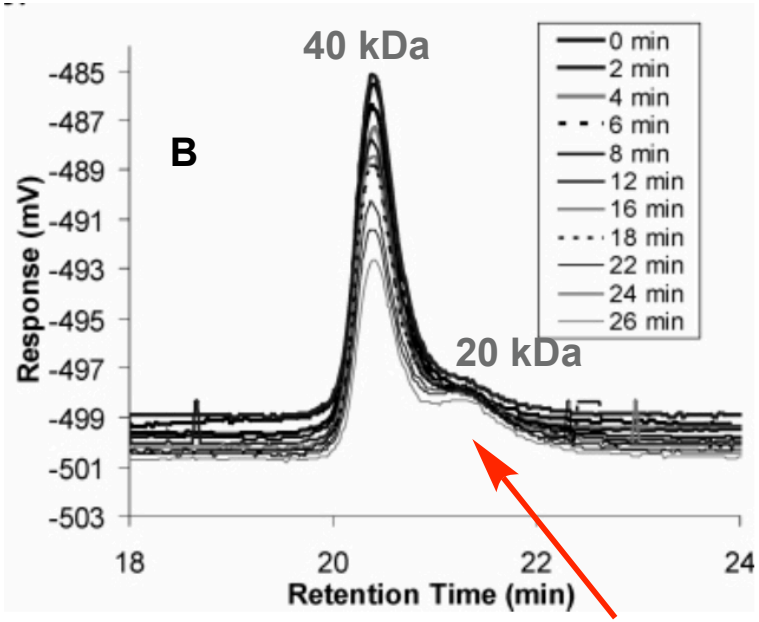
sonication

in MeCN

GPC analysis



sharp peak
→site-specific cleavage

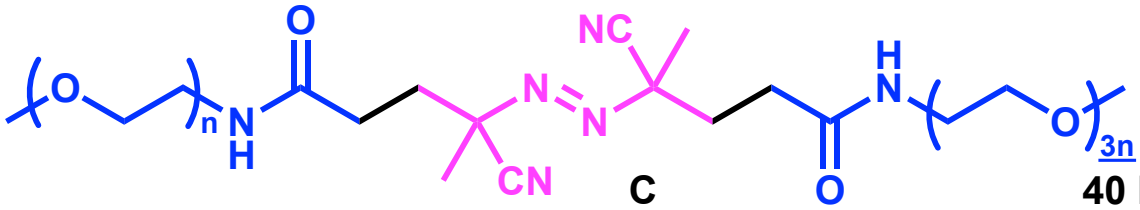


broad peak
→random cleavage

Berkowski, K. L.; Potisek, S. L.; Hickenboth, C. R.; Moore, J. S. *Macromolecules* **2005** *38*, 8975.

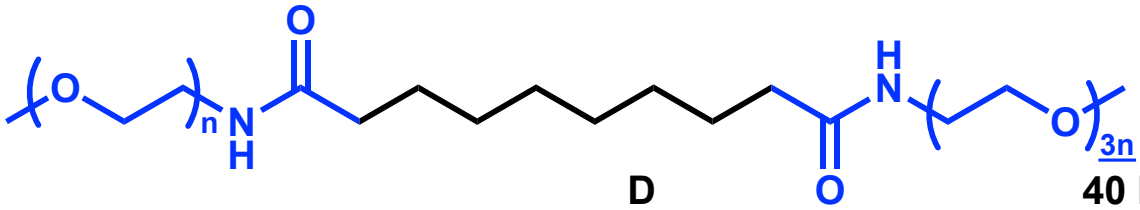
Site-Specific Cleavage by Ultrasound (II)

waek bond at polymer center



C

40 kDa



D

40 kDa

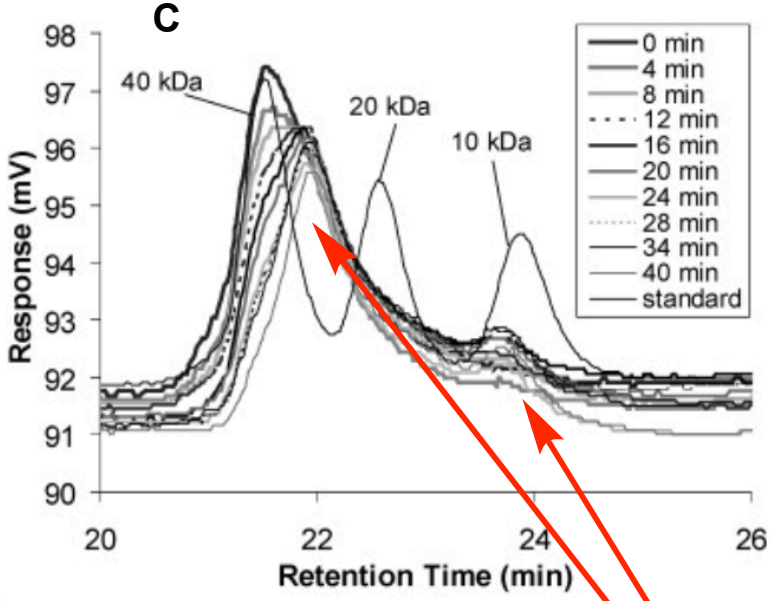
20 kHz
8.7 W/cm^2
6~9 ºC

sonication

in MeCN

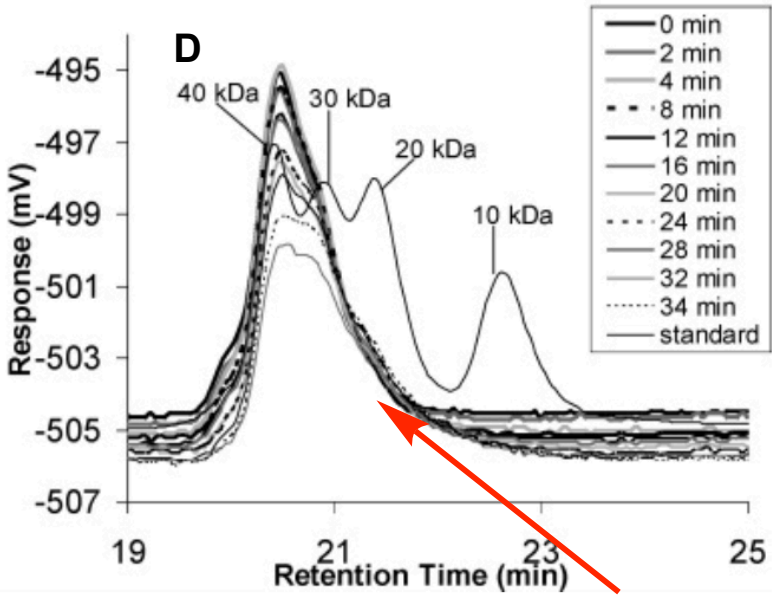
GPC analysis

C



impurity of 30 kDa was included…

D



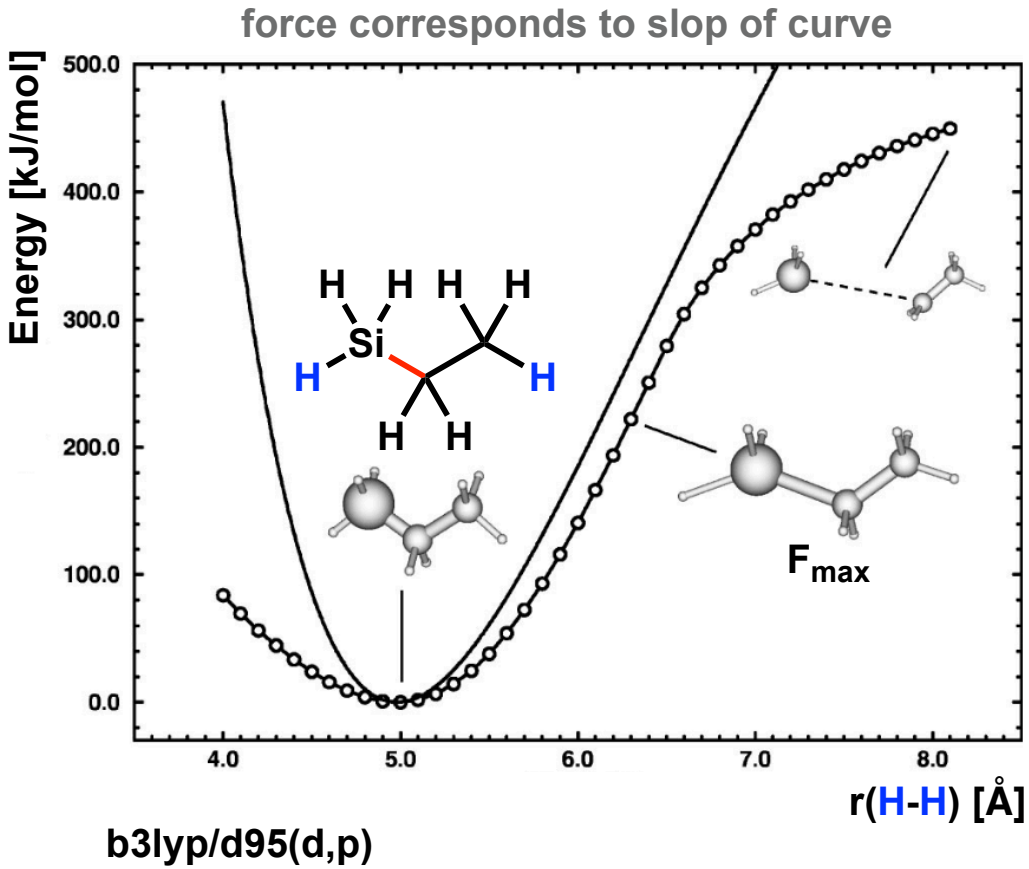
peak of 30 kDa and 10 kDa
→site-specific cleavage

peak of 20 kDa
→cleavage at center

Berkowski, K. L.; Potisek, S. L.; Hickenboth, C. R.; Moore, J. S. *Macromolecules* **2005** *38*, 8975.

Bond “Strength” in Bond Cleavage by Force

	r_0 [Å]	BDE [kcal/mol]	F_{max} [nN]
H—H	0.743	112.7	8.31
Cl—Cl	2.045	50.8	4.60
O=O	1.221	121.6	14.89



	BDE [kcal/mol]	F_{max} [nN]
H_3C—	88.6	6.92
H_3C—O—	82.3	7.56
H_3Si—	80.6	4.78
H_3Si—O—	101.7	5.20
H_3Si—Si(SiH_3)H—H	70.8	3.28

Beyer, M. K. *J. Chem. Phys.* **2000**, *112*, 7307.

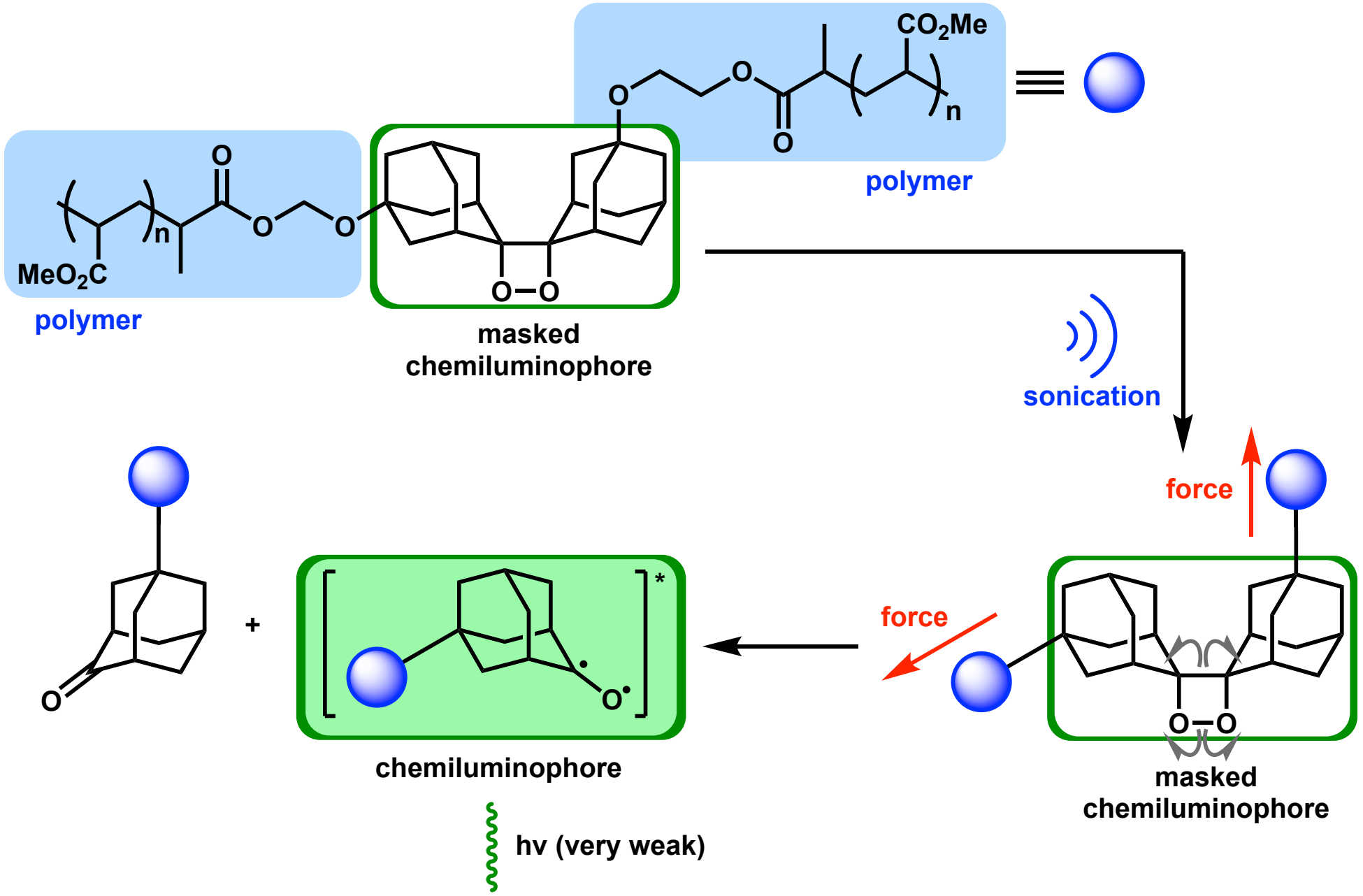
Contents

Introduction of Prof. Maxwell J. Robb

Prof. Maxwell J. Robb
2009 B.S. @ Colorado School of Mines (Prof.)
2014 Ph.D @ University of California (Prof. Craig J. Hawker)
2014~2017 postdoctoral research@ University of Illinois (Prof. Jeffy S. Moore)
2017~2024 Assistant Professor @ California Institute of Technology
2024~ Full Professor @ California Institute of Technology

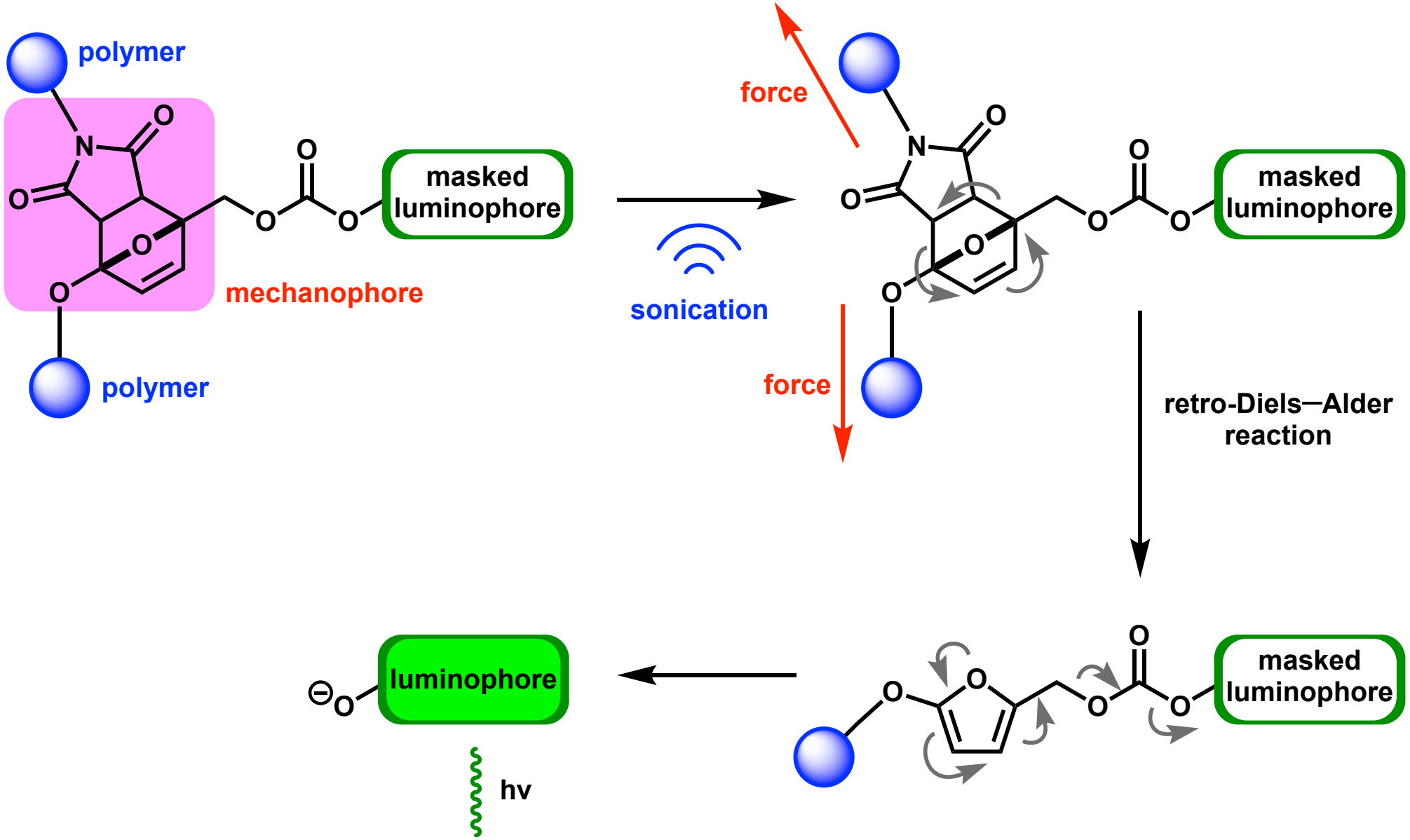
Research topic: Polymer Mechanochemistry

Landmark Report



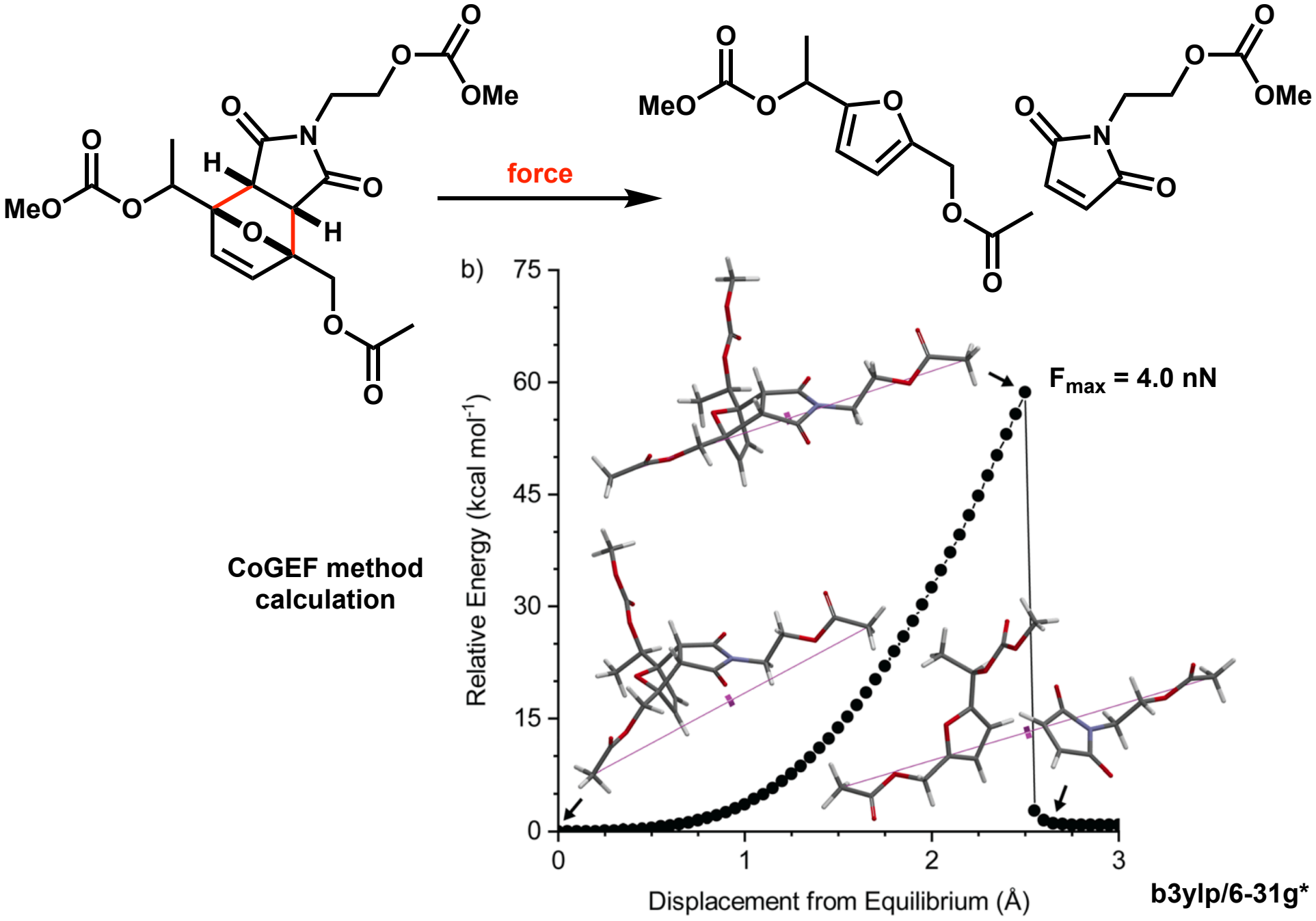
Chen, Y.; Spiering, A. J. H.; Karthikeyan, S.; Peters, G. W. M.; Meijer, E. Q.; Sijbesma, R. P. *Nat. Chem.* **2012**, *4*, 559.

Concept of This Study



Liu, P.; Tseng, Y.-L.; Ge, L.; Zeng, T.; Shabat, D.; Robb, M. J. *J. Am. Chem. Soc.* **2024**, *146*, 22151.

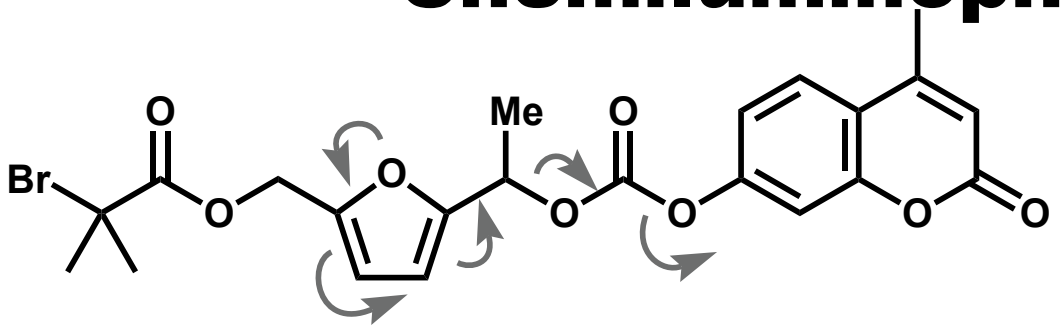
Mechanophore Unit



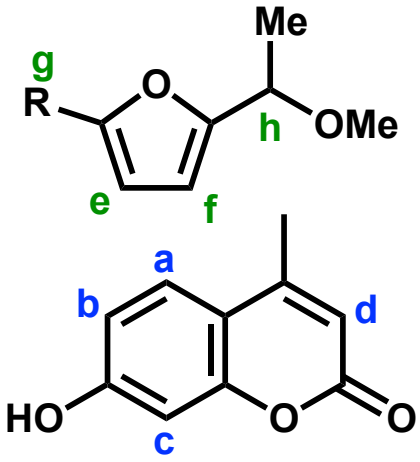
CoGEF method calculation

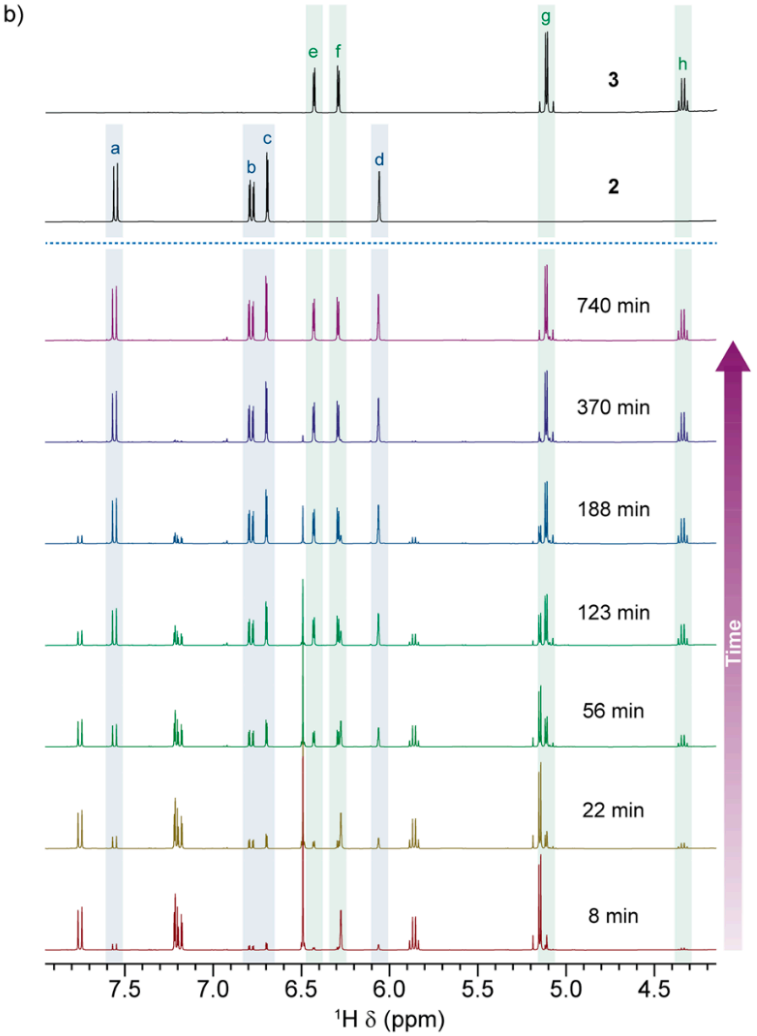
Hu, X.; Zeng, T.; Husic, C.; Robb, M. J. *J. Am. Chem. Soc.* **2017**, *141*, 15018.

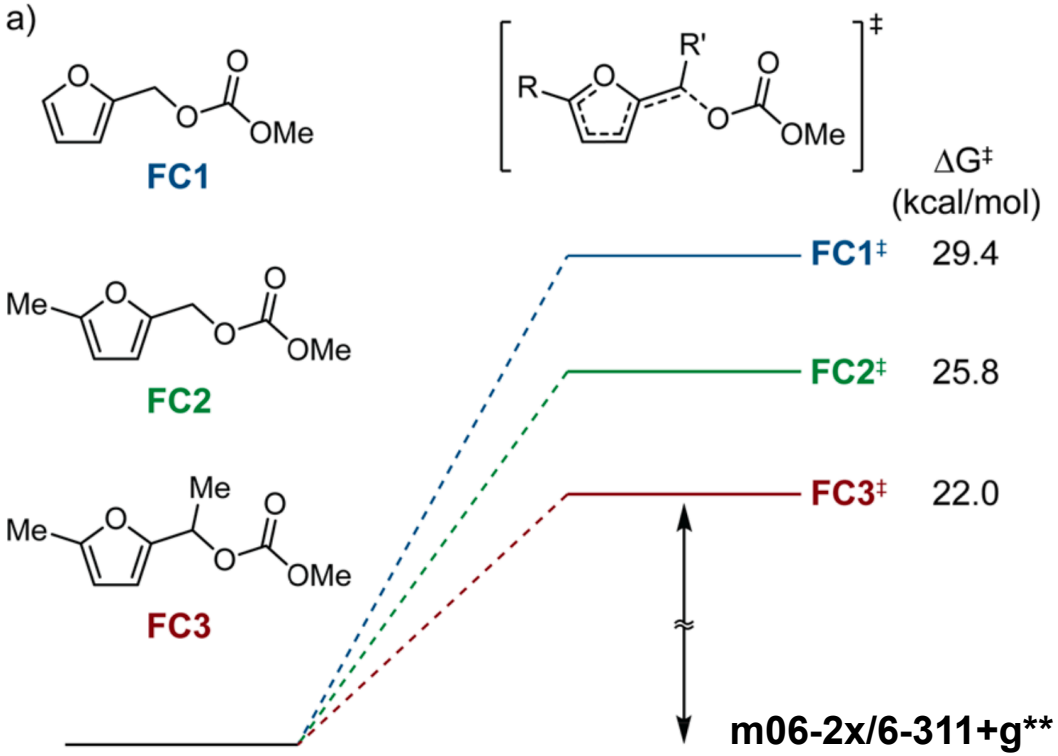
Chemiluminophore Unit (I)



MeCN/MeOH

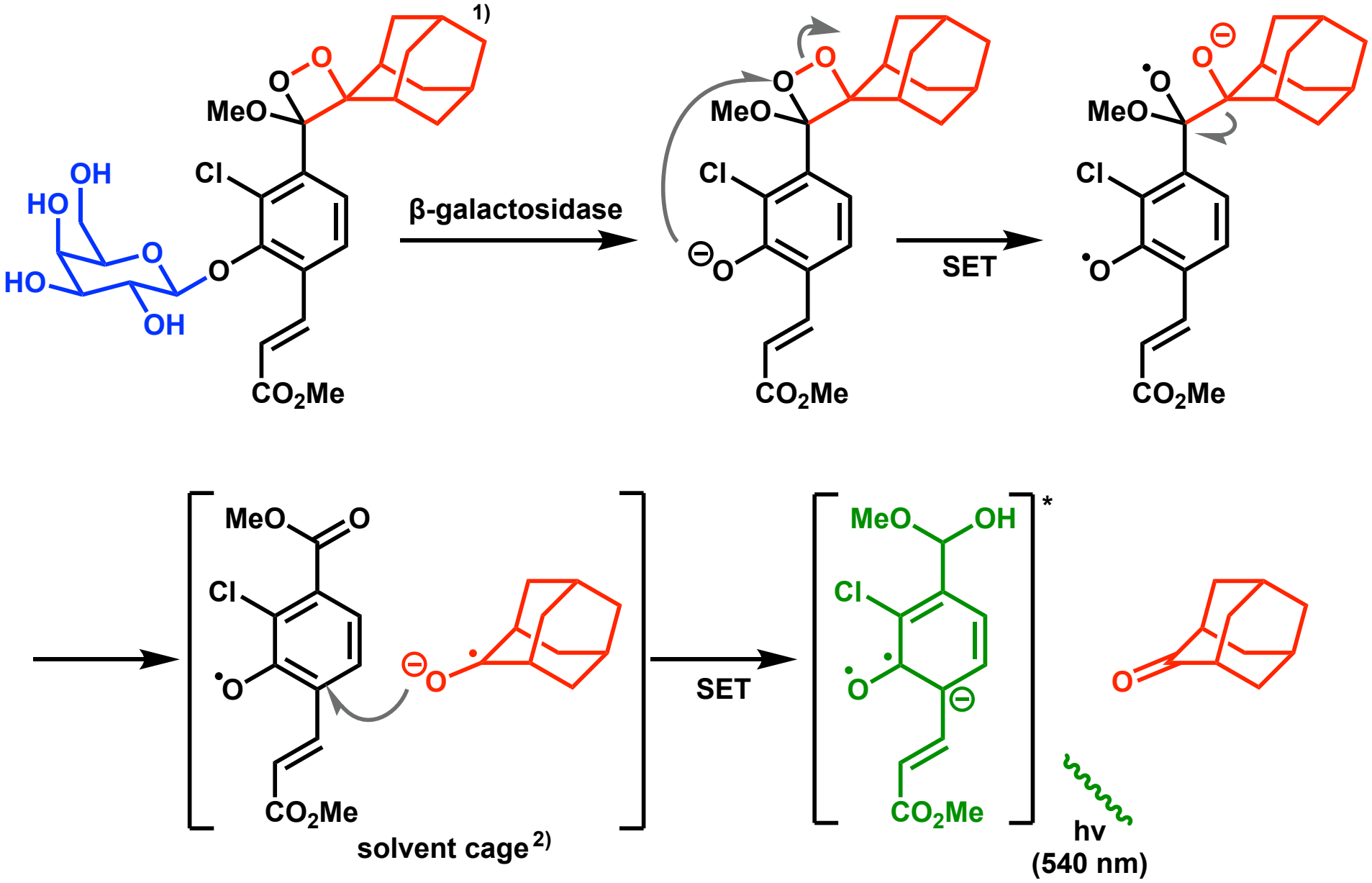






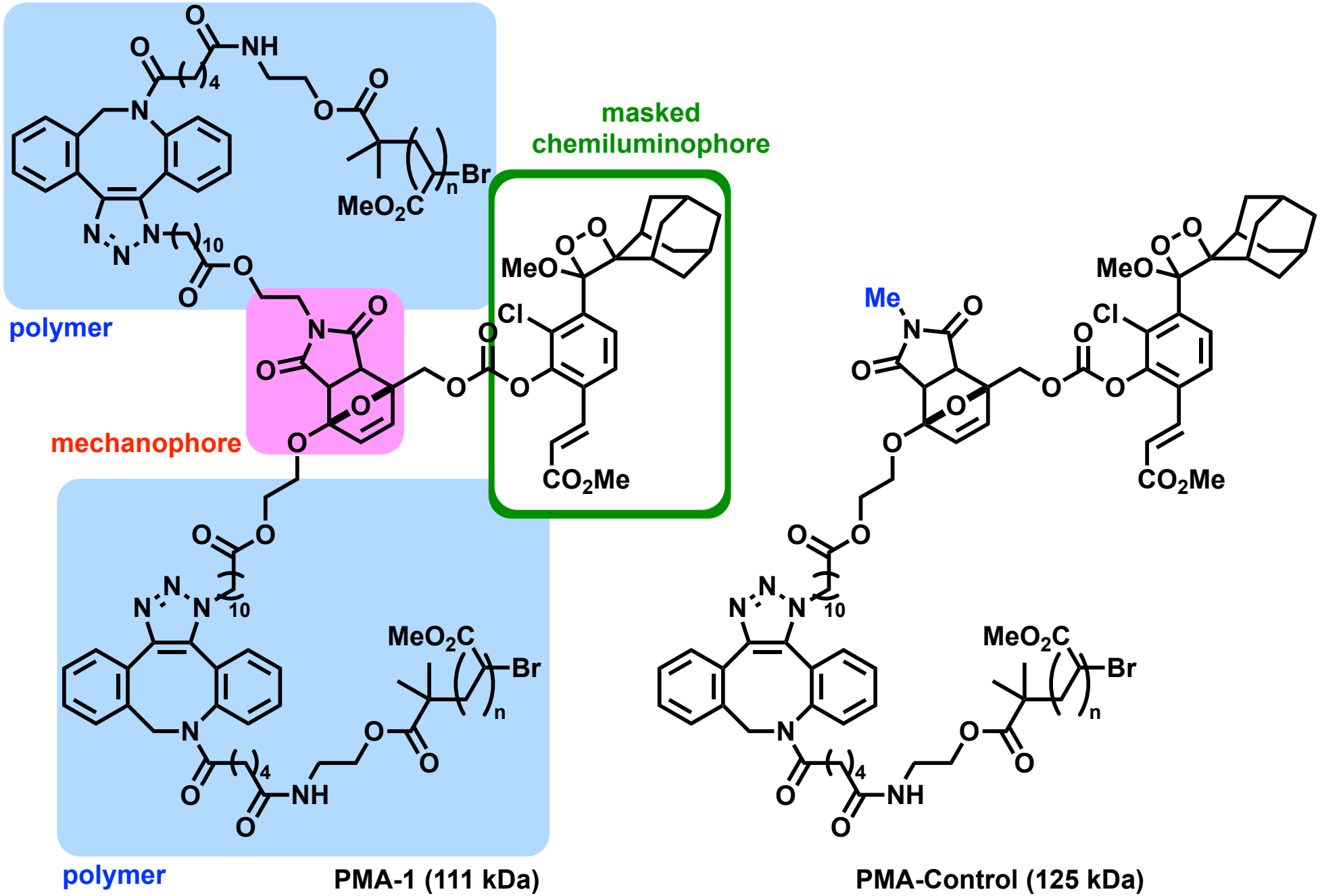
Hu, X.; Zeng, T.; Husic, C.; Robb, M. J. *J. Am. Chem. Soc.* **2017**, *141*, 15018.

Chemiluminophore Unit (II)



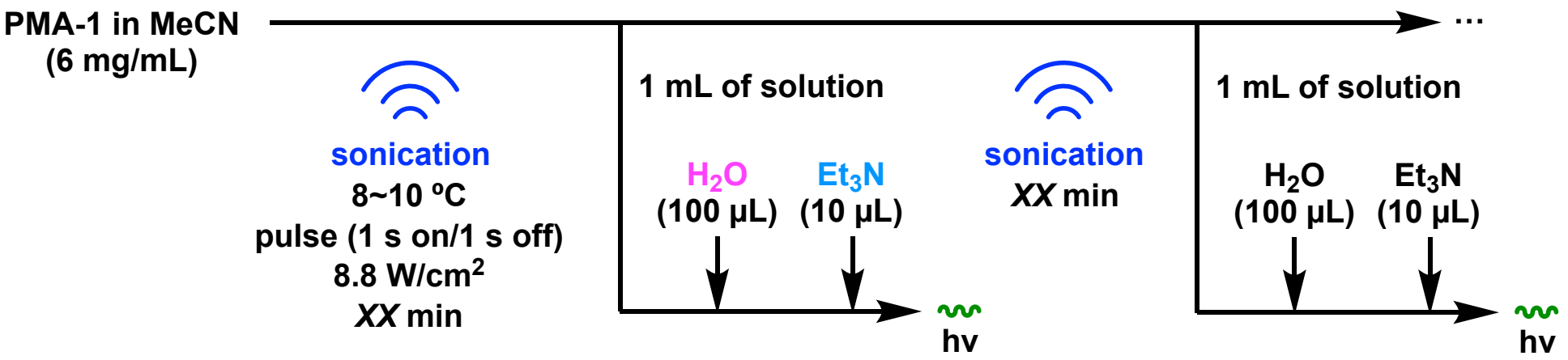
1) Green, O.; Eilon, T.; Hananya, N.; Gutkin, S.; Bauer, C. R.; Shabat, D. *ASC Cent. Sci.* **2017**, *3*, 349.
2) Adam, W.; Bronstein, I.; Trofimov, A. V.; Vasil'ev, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 958.

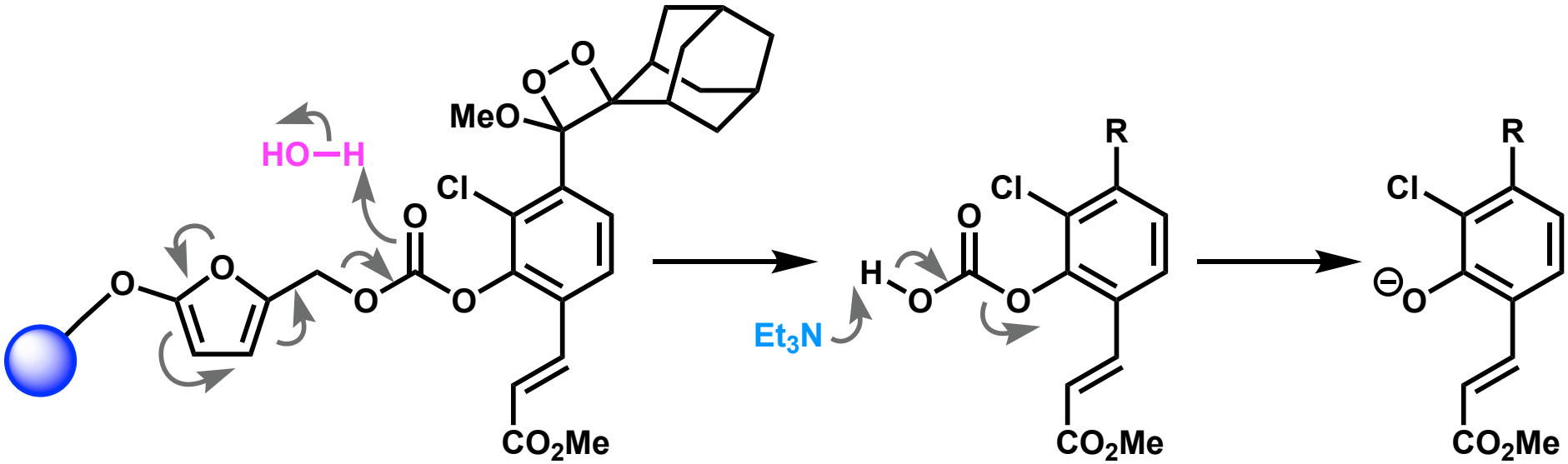
Design of Mechanoluminophore



Liu, P.; Tseng, Y.-L.; Ge, L.; Zeng, T.; Shabat, D.; Robb, M. J. *J. Am. Chem. Soc.* **2024**, *146*, 22151.

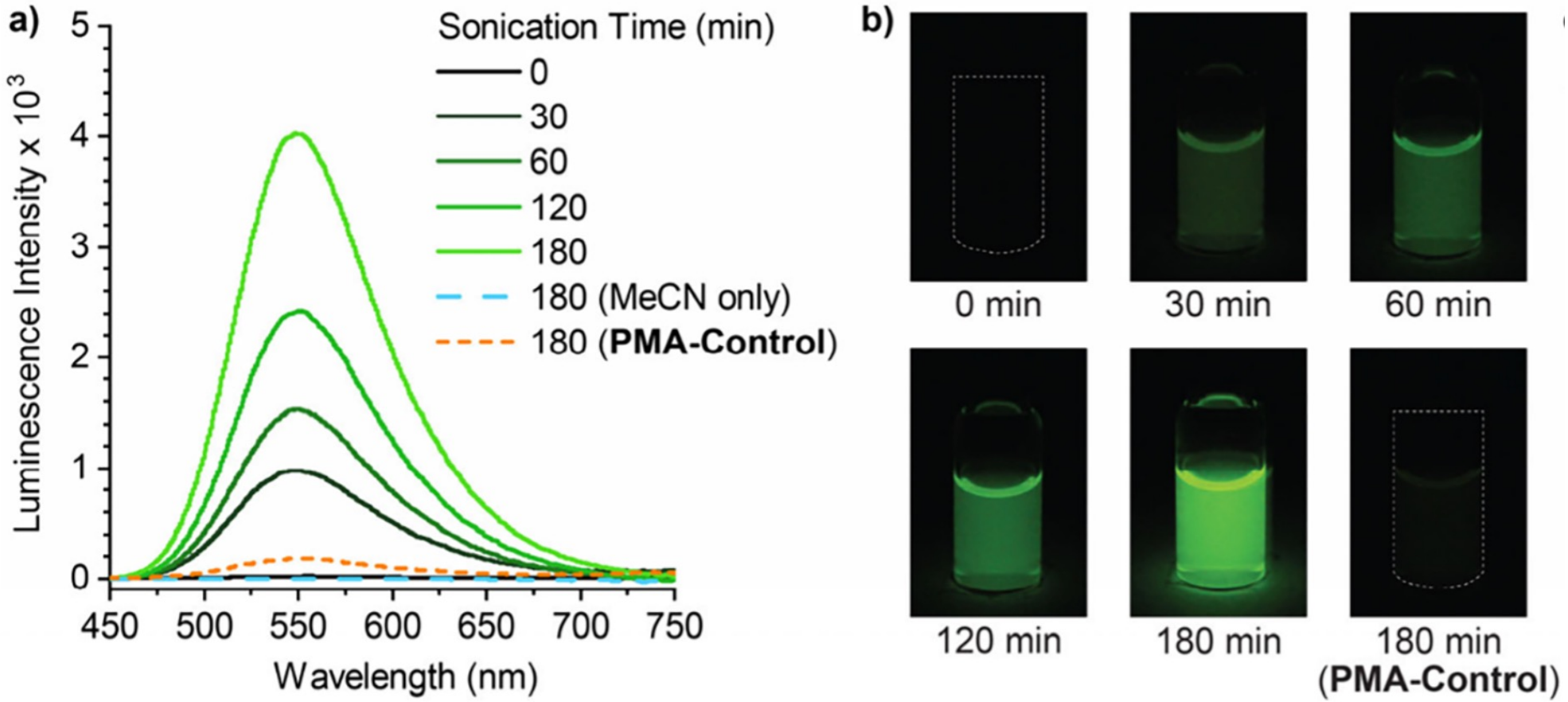
Experiment Procedure





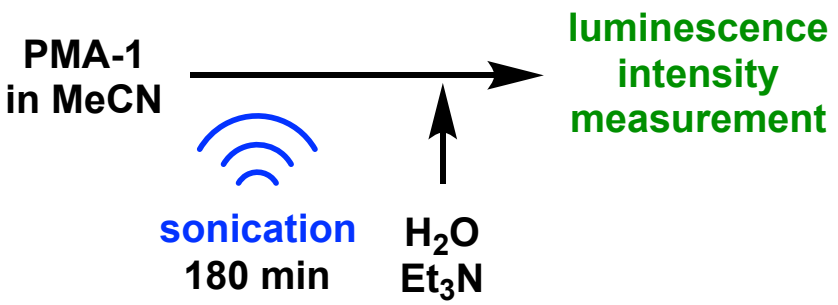
Liu, P.; Tseng, Y.-L.; Ge, L.; Zeng, T.; Shabat, D.; Robb, M. J. *J. Am. Chem. Soc.* **2024**, *146*, 22151.

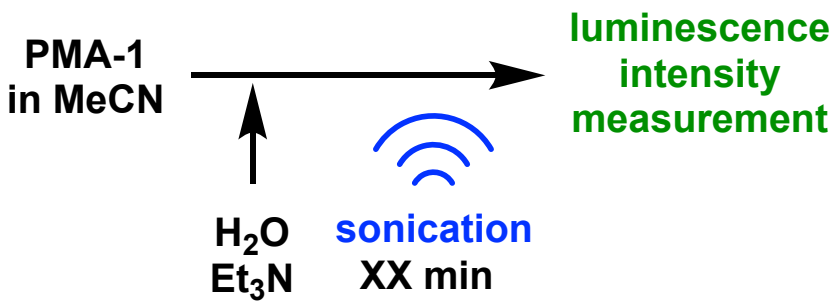
Luminescence Intensity of Each Sonication Time

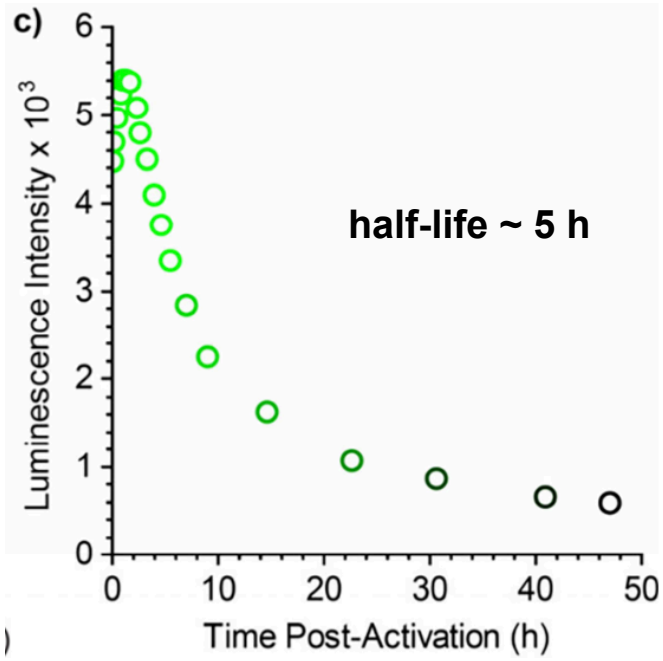


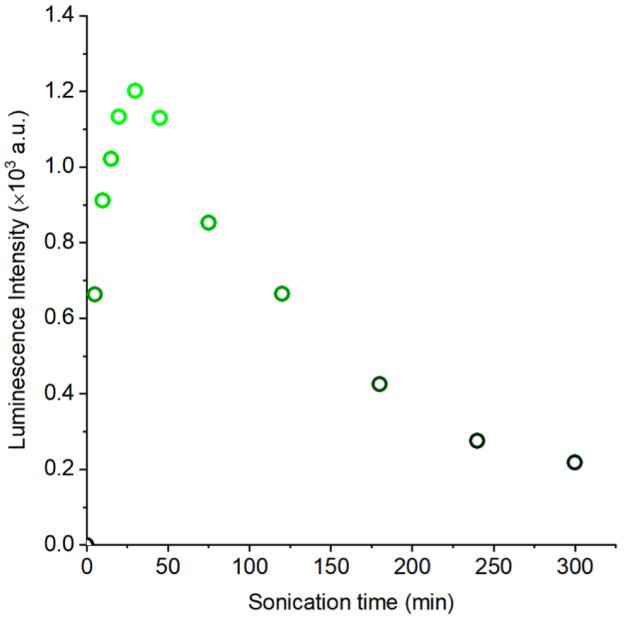
Liu, P.; Tseng, Y.-L.; Ge, L.; Zeng, T.; Shabat, D.; Robb, M. J. *J. Am. Chem. Soc.* **2024**, *146*, 22151.

Luminescence Intensity After of During Sonication



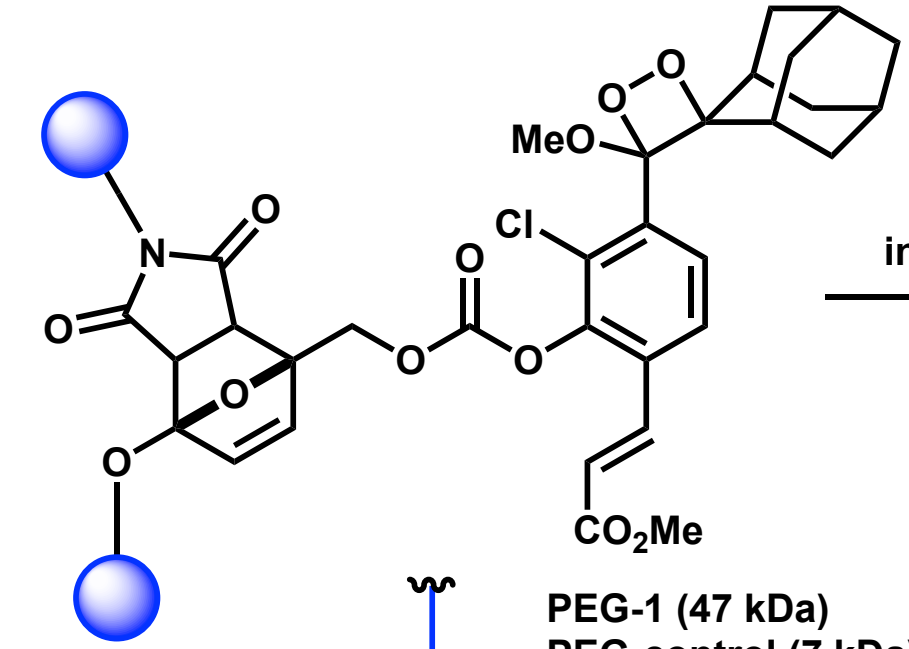






Liu, P.; Tseng, Y.-L.; Ge, L.; Zeng, T.; Shabat, D.; Robb, M. J. *J. Am. Chem. Soc.* **2024**, *146*, 22151.

Mechanoluminescence in Biological Condition

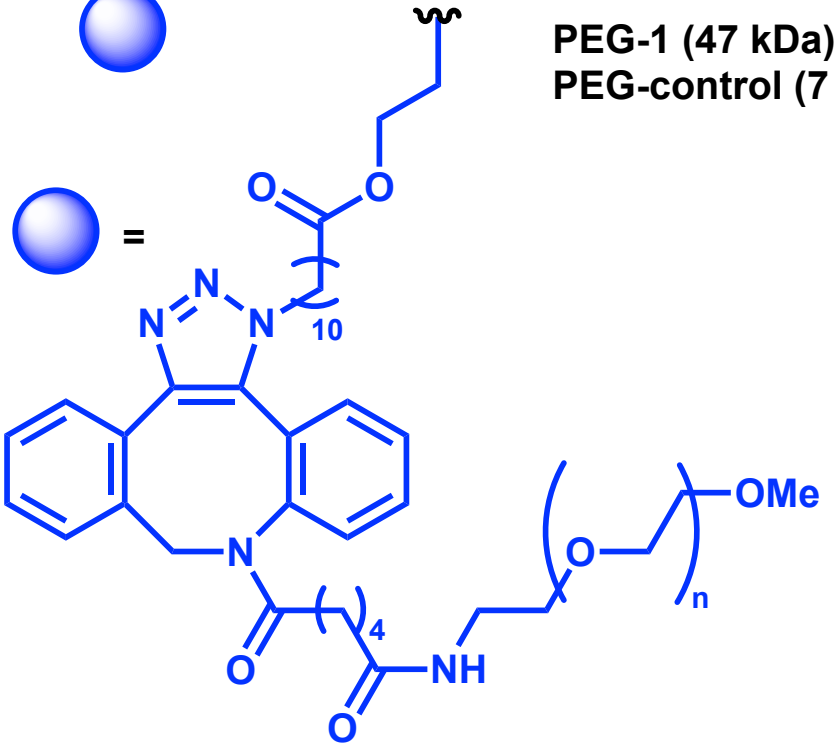


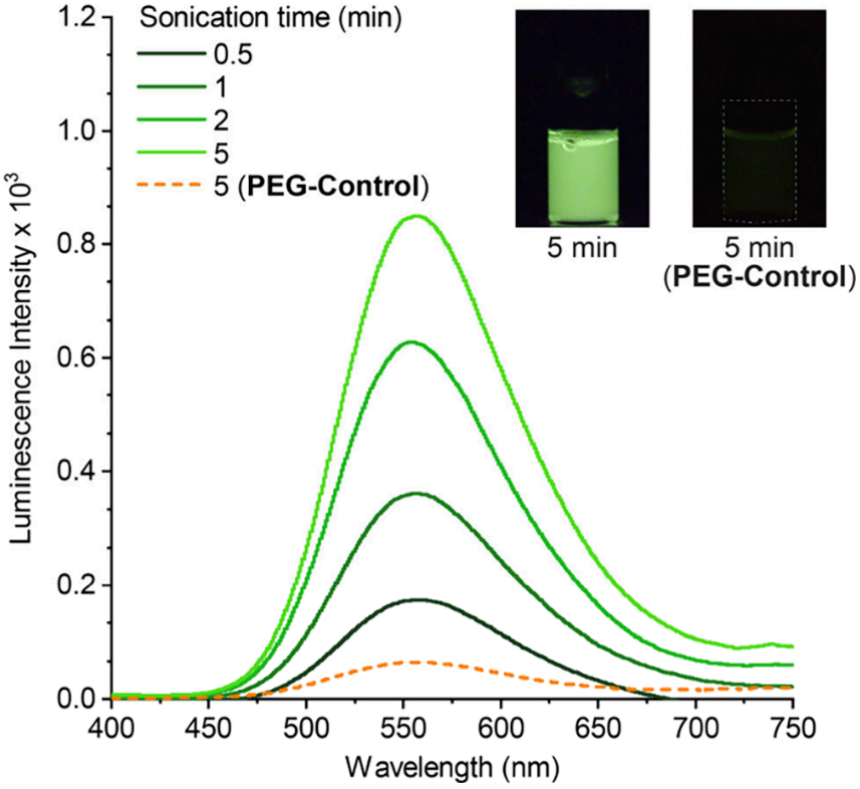
in PBS (pH = 7.4)

sonication
XX min

luminescence intensity measurement

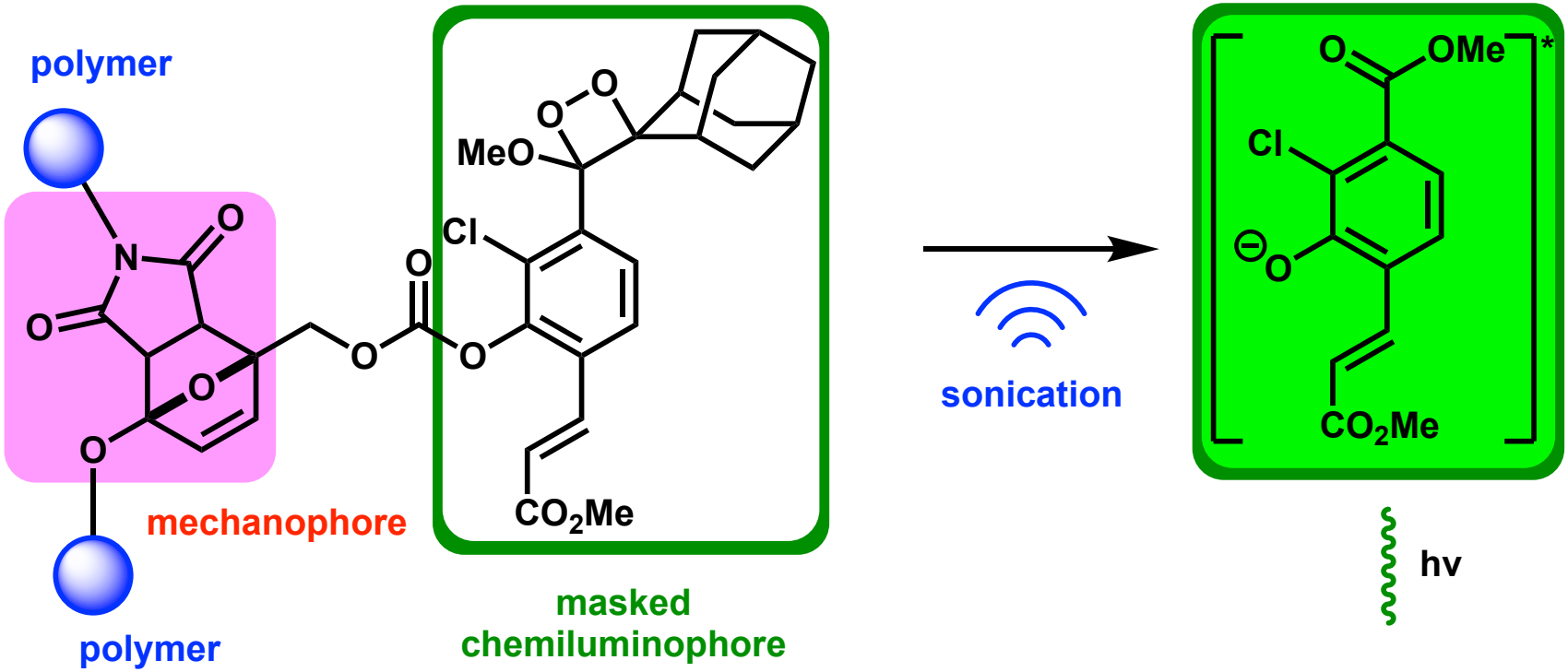
PEG-1 (47 kDa)
PEG-control (7 kDa)





Liu, P.; Tseng, Y.-L.; Ge, L.; Zeng, T.; Shabat, D.; Robb, M. J. *J. Am. Chem. Soc.* **2024**, *146*, 22151.

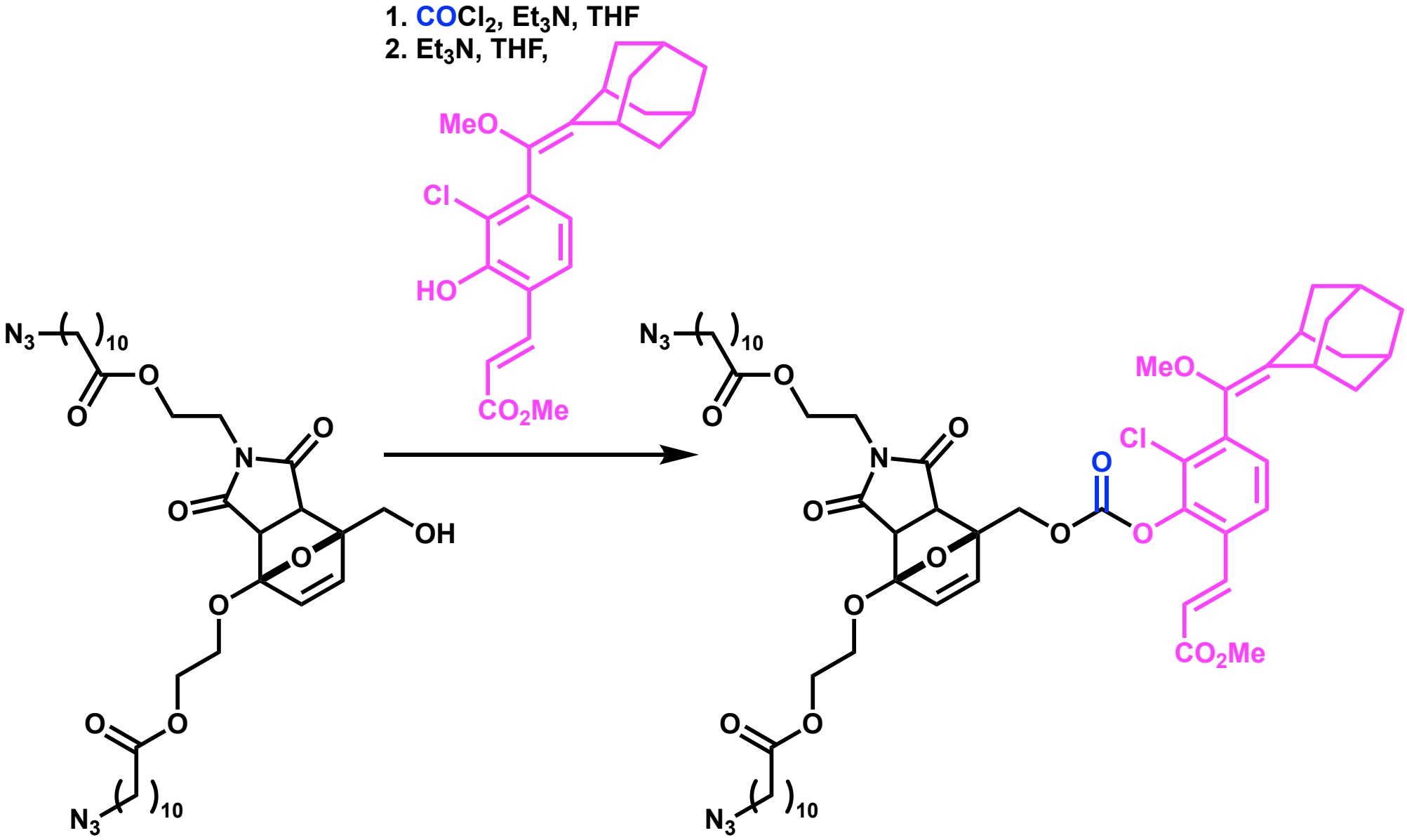
Summary



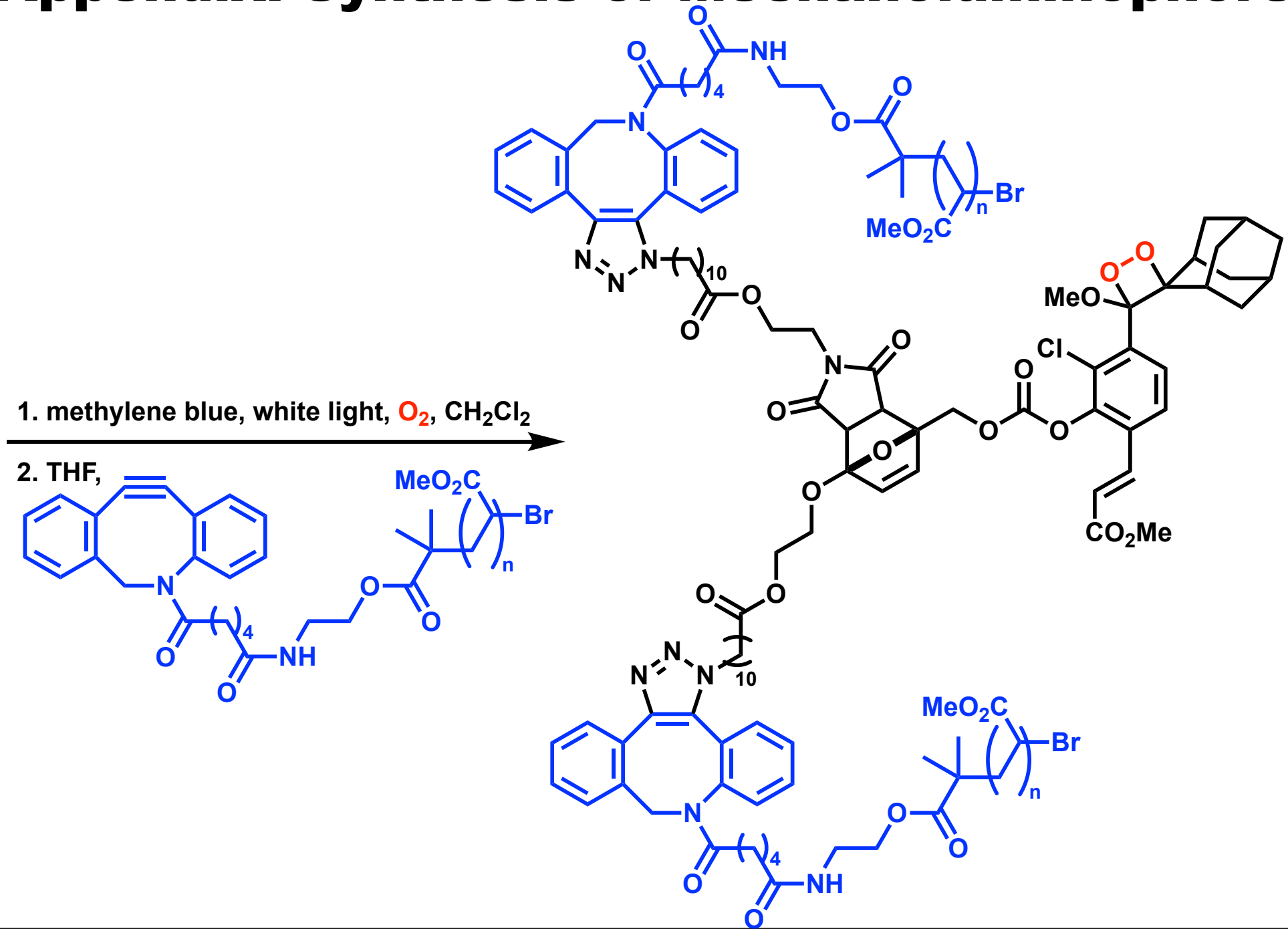
Liu, P.; Tseng, Y.-L.; Ge, L.; Zeng, T.; Shabat, D.; Robb, M. J. *J. Am. Chem. Soc.* **2024**, *146*, 22151.

Apendix

Appendix: Synthesis of Mechanoluminophore



Appendix: Synthesis of Mechanoluminophore



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