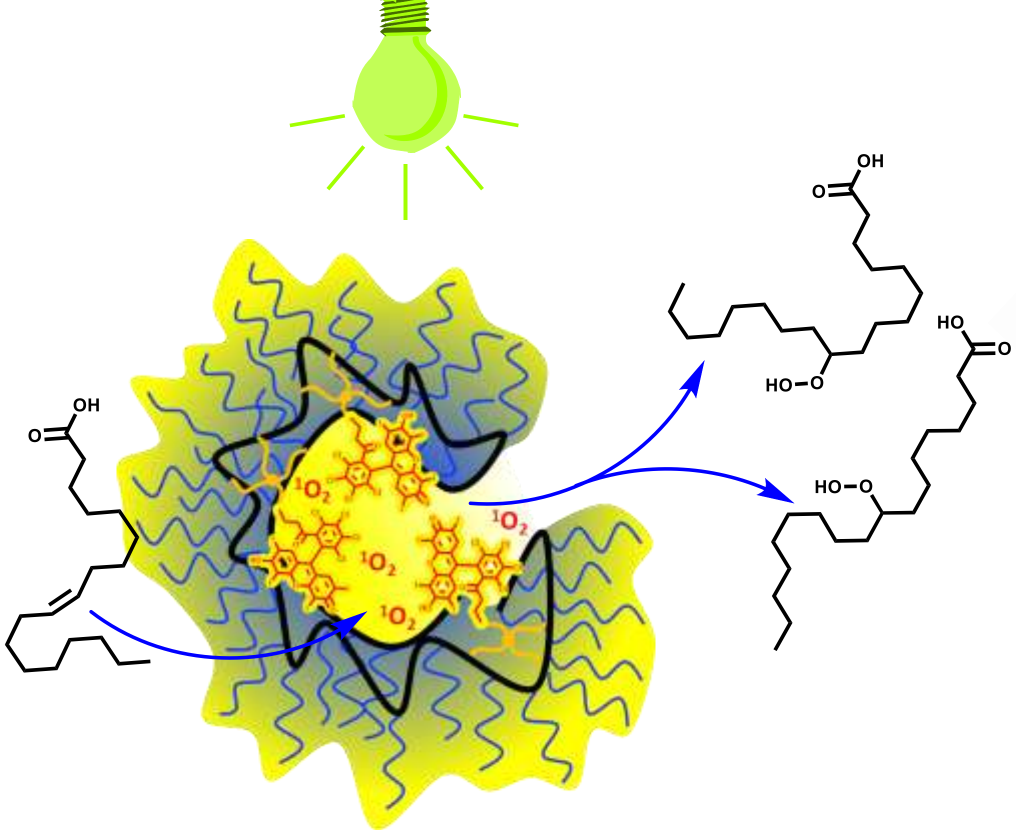
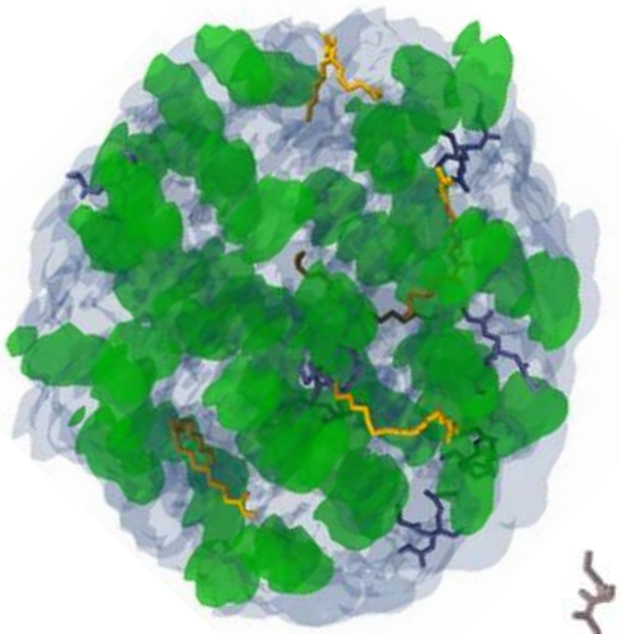
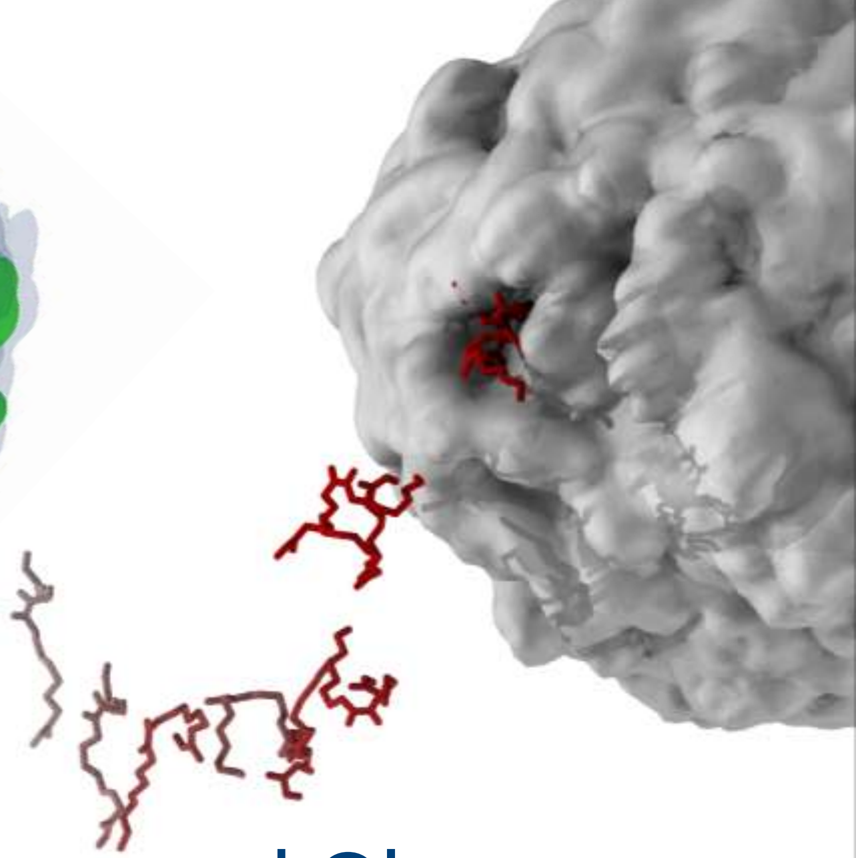






Photoactive “Synthezymes” for Greener and Cleaner Detergents

Kai Mundsinger
k.mundsinger@qut.edu.au
38th APS

Henkel

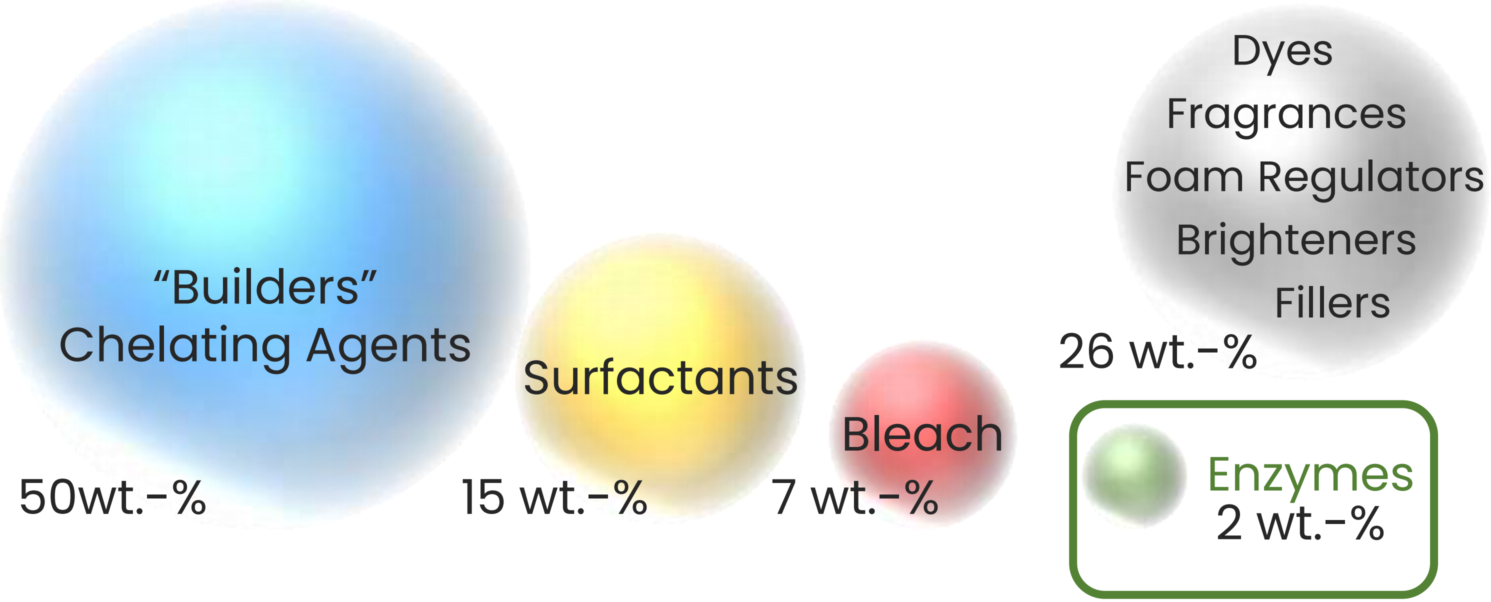
macroarc soft matter materials group

QUT the university for the real world

38APS

Green Light for Greener Chemistry

- Laundry Detergent Composition



- Require Elevated Temperatures
- Require Additives to Create "Safe Environments" for Lipases

- **Can We Use (Visible) Light to Mimic Enzymatic Breakdown of Fatty Acids?**
  - Minimize the Need for Builders, Bleach, Surfactants

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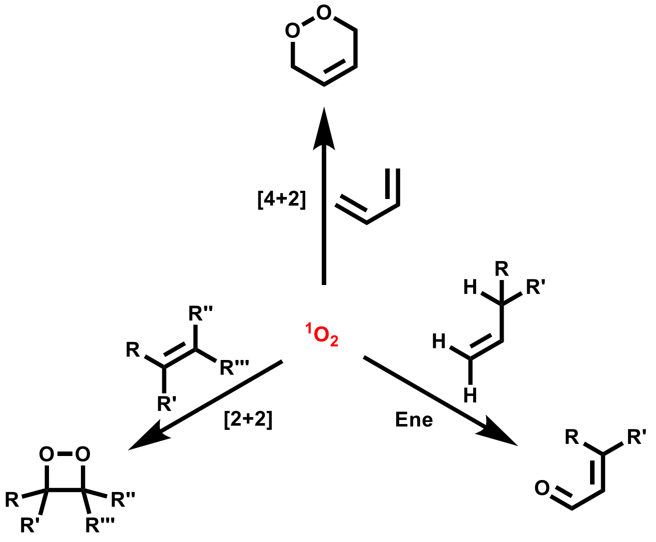
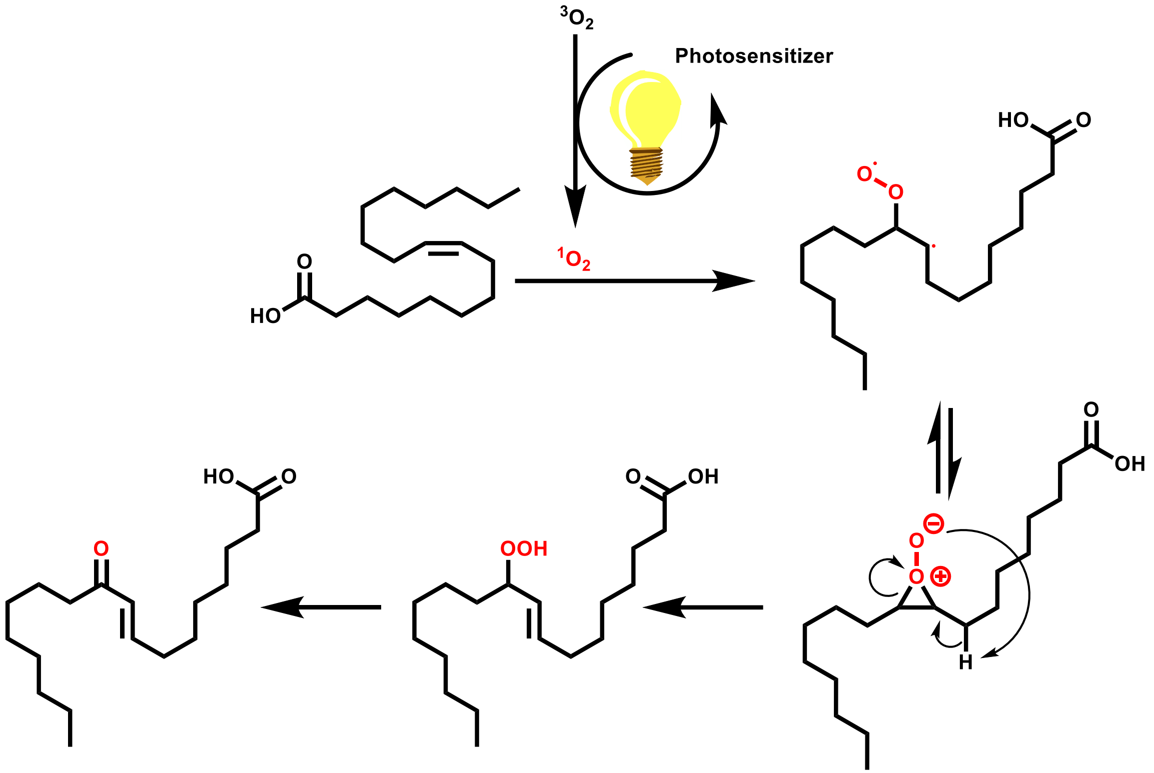
Singlet Oxygen Reactions

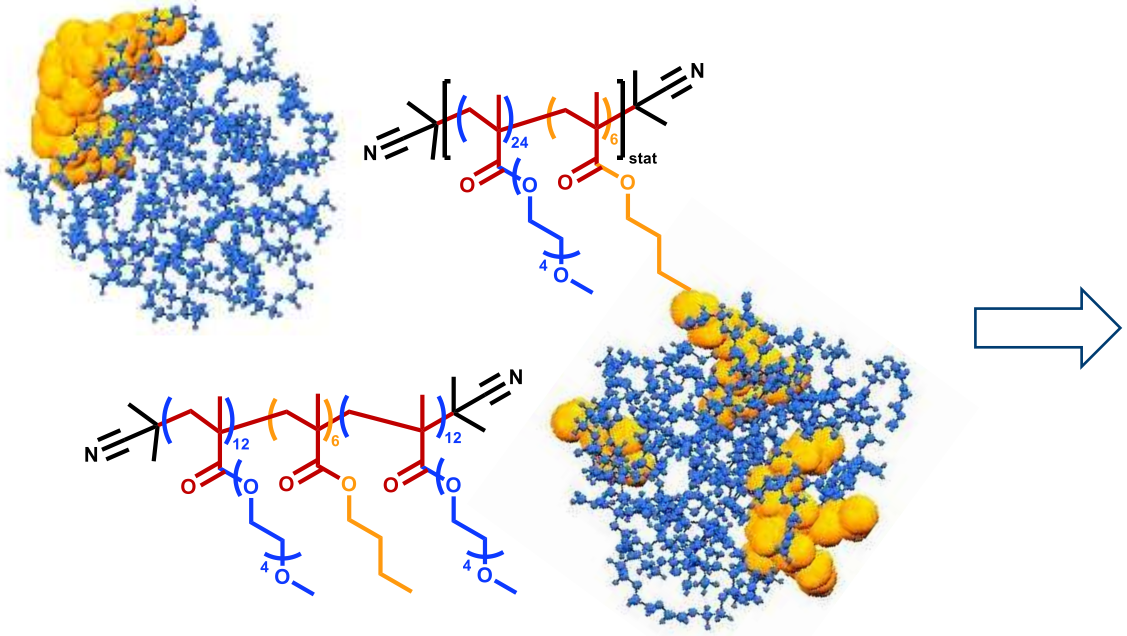




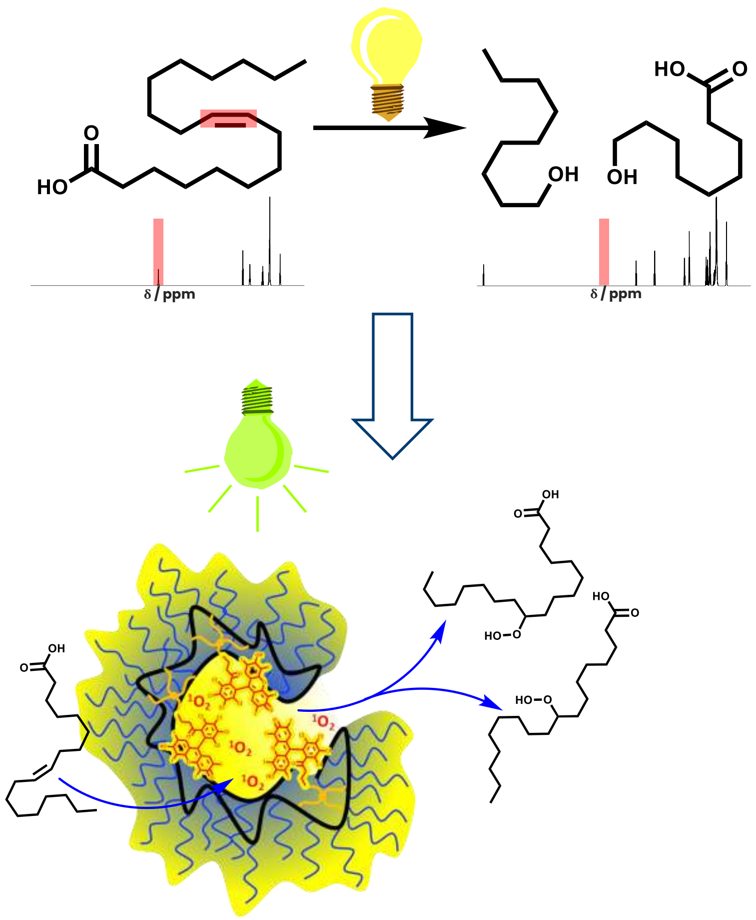
Singleton et al., *J. Am. Chem. Soc.*, **2003**, *125* (5), 1319-1328.
Alberti, M. N.; Orfanopoulos, M., *Chem. Eur. J.*, **2010**, *16* (31), 9414-9421.

Design of the Catalytic System

- Polymer Scaffold
  - Enabling Catalytic Moiety
  - Protecting Catalytic Moiety
  - ➢ Covalent Crosslinks



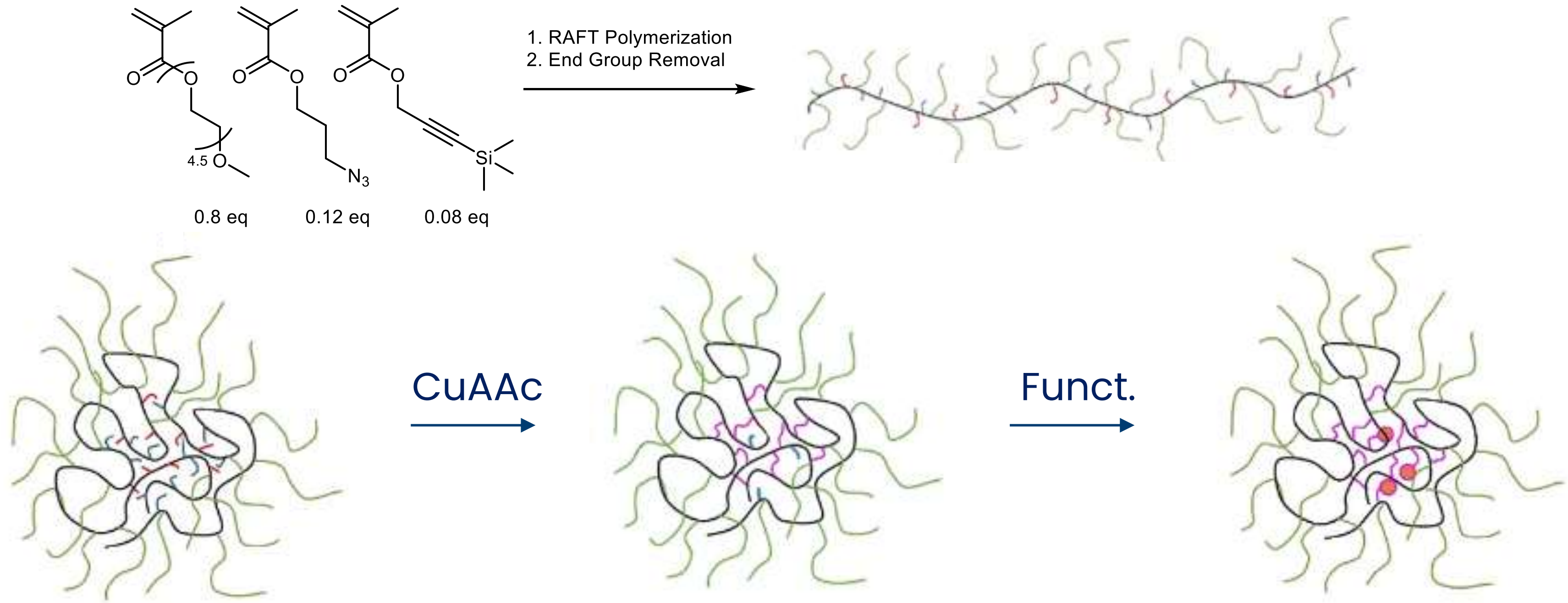
- Active Moiety



Mundsinger, K., Tuten, B., Wang, L., Neubauer, K., Kropf, C., O'Mara, M., Barner-Kowollik, C., *Angew. Chem. Int. Ed.*, **2023,** *62*, e202311734

Polymer Design - SCNP

- Hydrophilicity via Side Chains
- Hydrophobic Backbone



Collapse into Core-Shell Structure in Water

Crosslinked SCNP

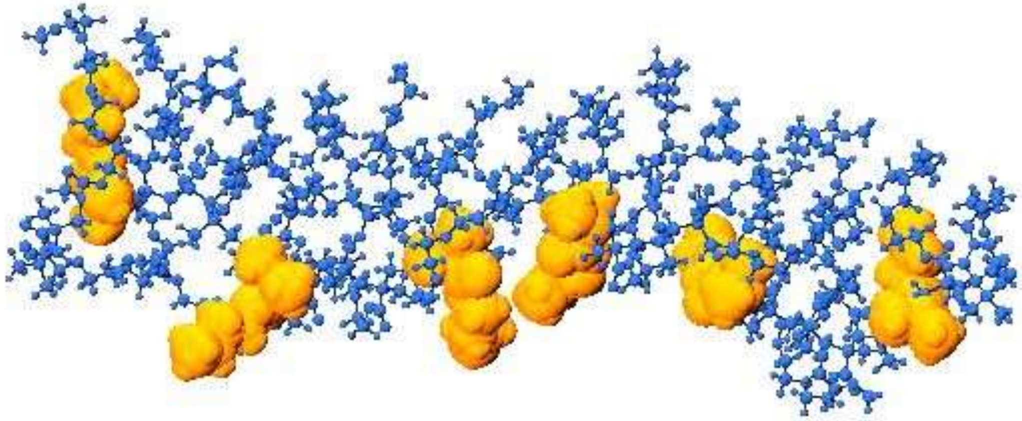
Functionalized SCNP

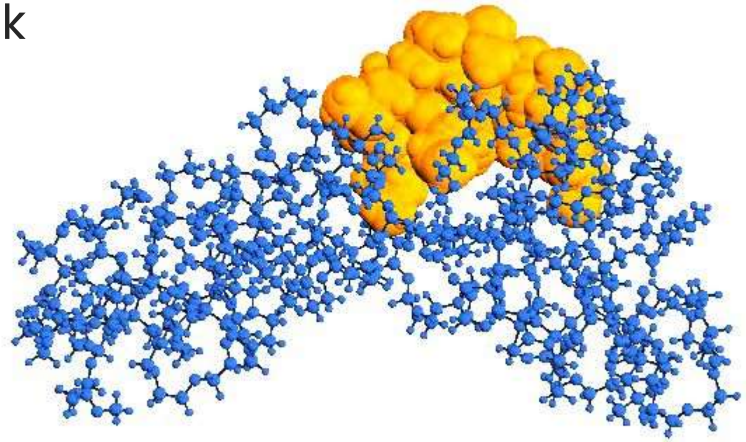
Hoffmann et al., *Angew. Chem. Int. Ed.*, **2021**, *60*, 2-10

Polymer Design – Block vs Stat Copolymer

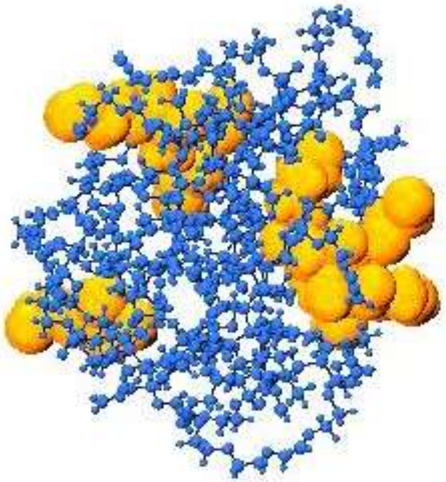
- Stat

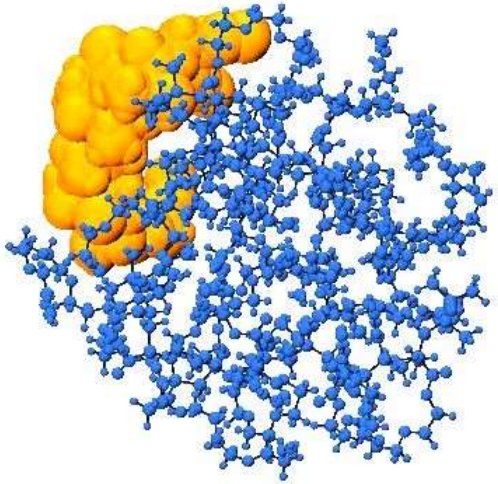
- Block





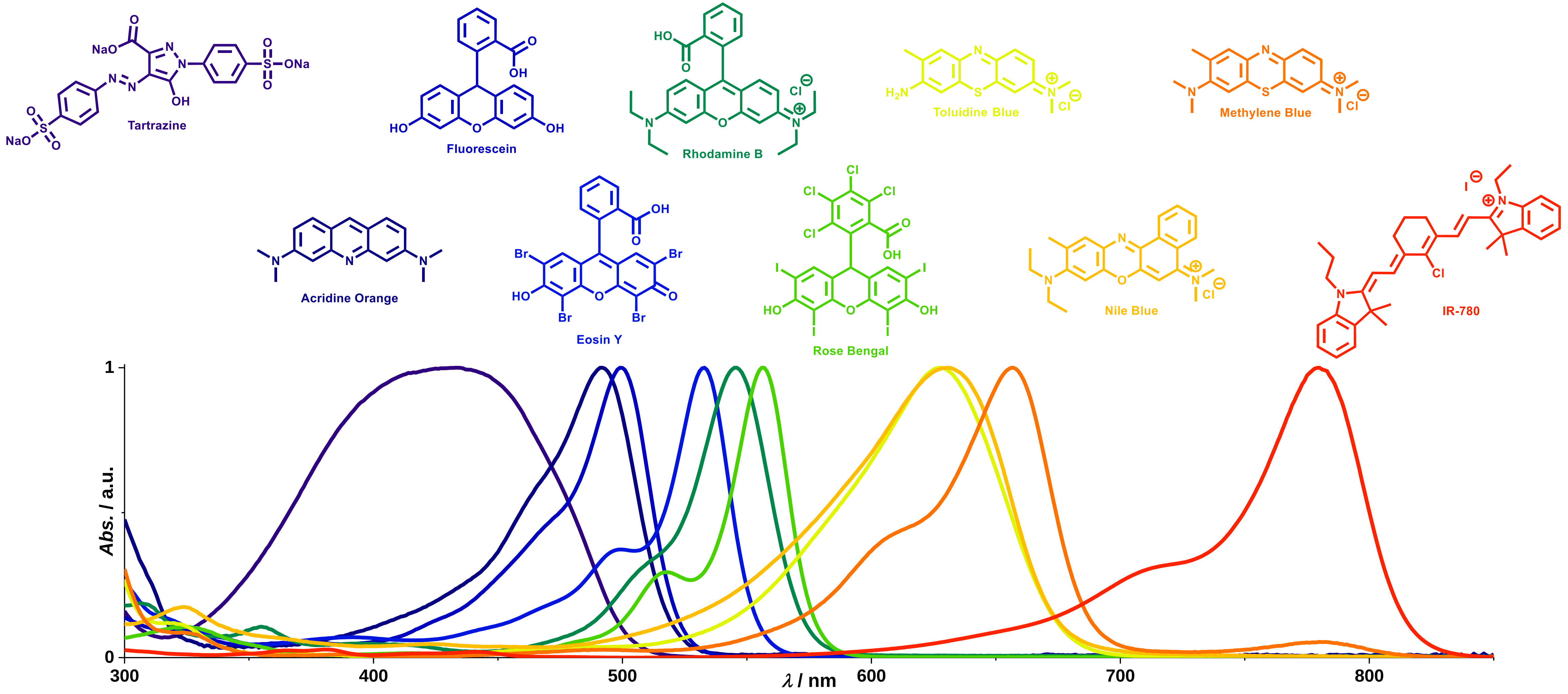
0 ns





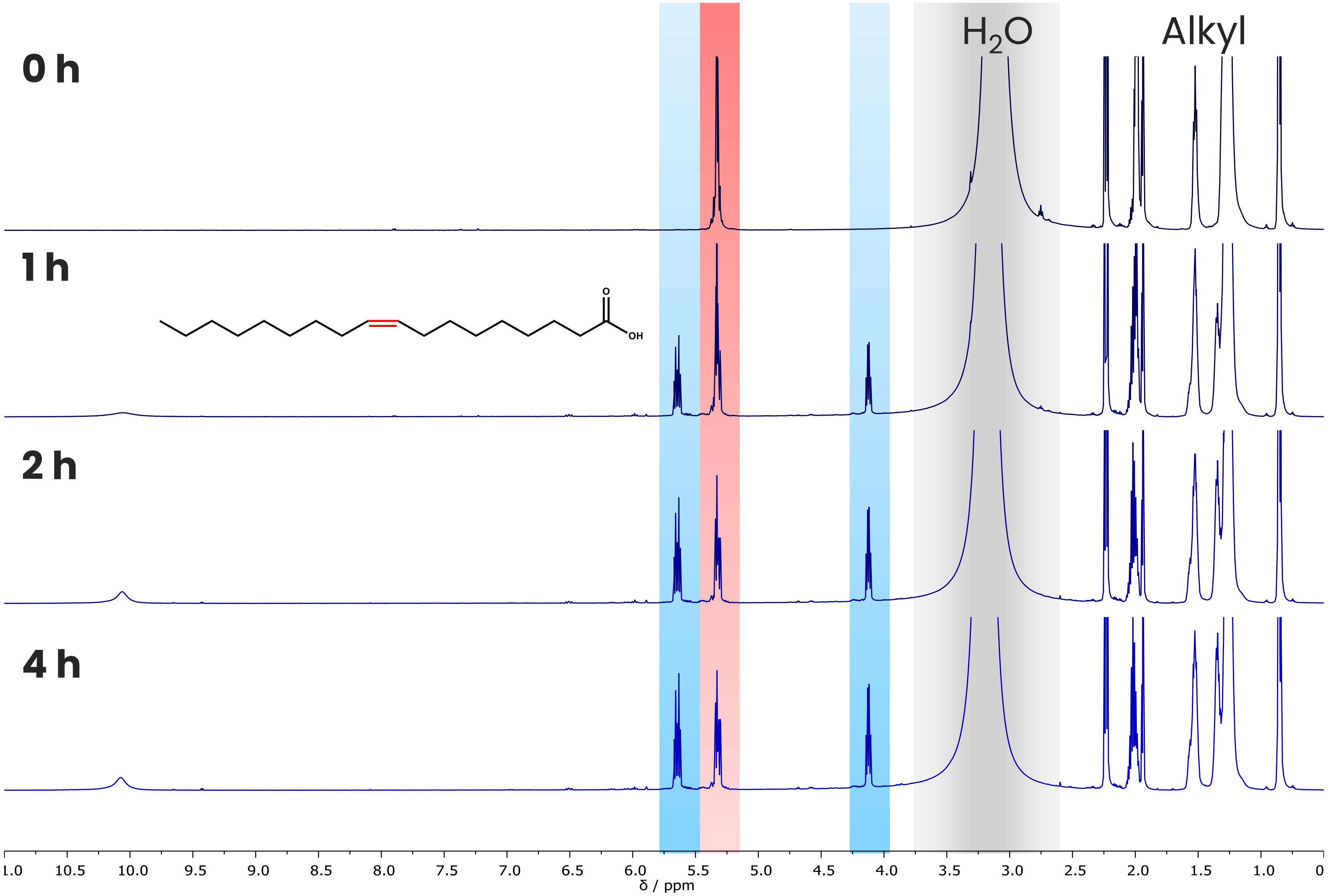
50 ns

Active Centre Selection



Benchmarking Photosensitizers

Acetonitrile
10 % Water
1 % Methylene Blue
λ = 625 nm



Benchmarking Photosensitizers

2.4 mL Acetonitrile/Water (9/1)
80 mg Oleic Acid
0.8 mg Photocatalyst

Irradiation → Air bubbling

Photocatalyst	λ_{max} ACN/H_2O / nm	60 min Conversion$_{NMR}$ / %	Max. Conversion$_{NMR}$ / %
Fluorescein	499	4	4
Eosin Y	533	20	50
Rose Bengal	556	60	60
Nile Blue	631	0	0
Methylene Blue	657	45	65
IR-780	780	0	0

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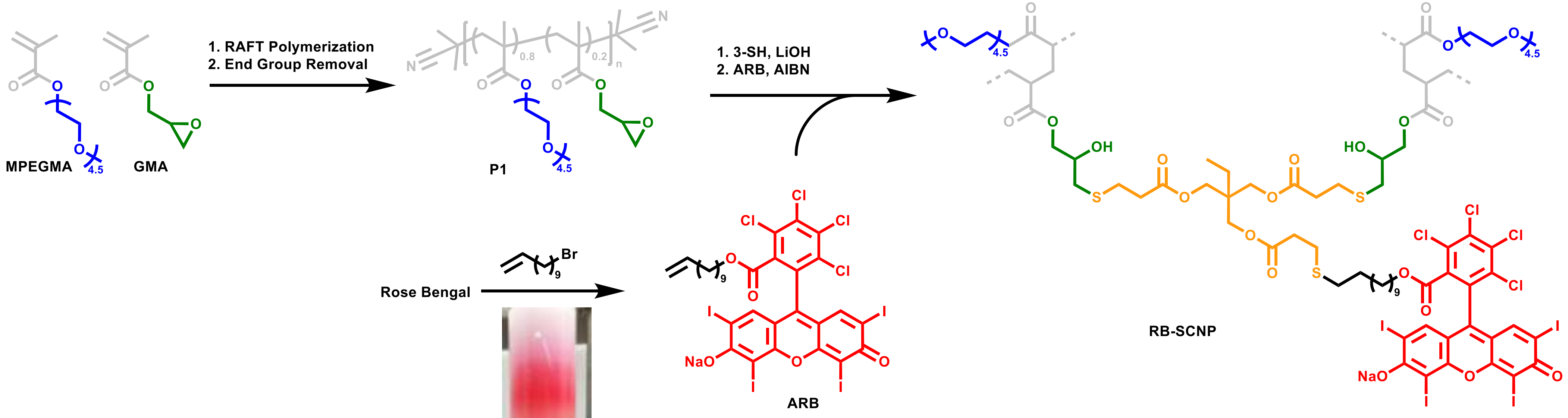
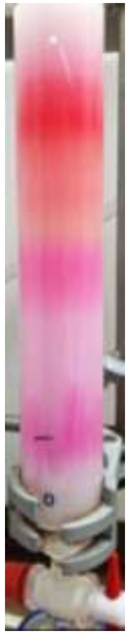
Synthetic Route to RB-SCNP





- RB-SCNP Purified via Prep SEC
- Accessible on 150mg Scale

Mundsinger, K., Tuten, B., Wang, L., Neubauer, K., Kropf, C., O'Mara, M., Barner-Kowollik, C., *Angew. Chem. Int. Ed.*, **2023,** *62*, e202311734

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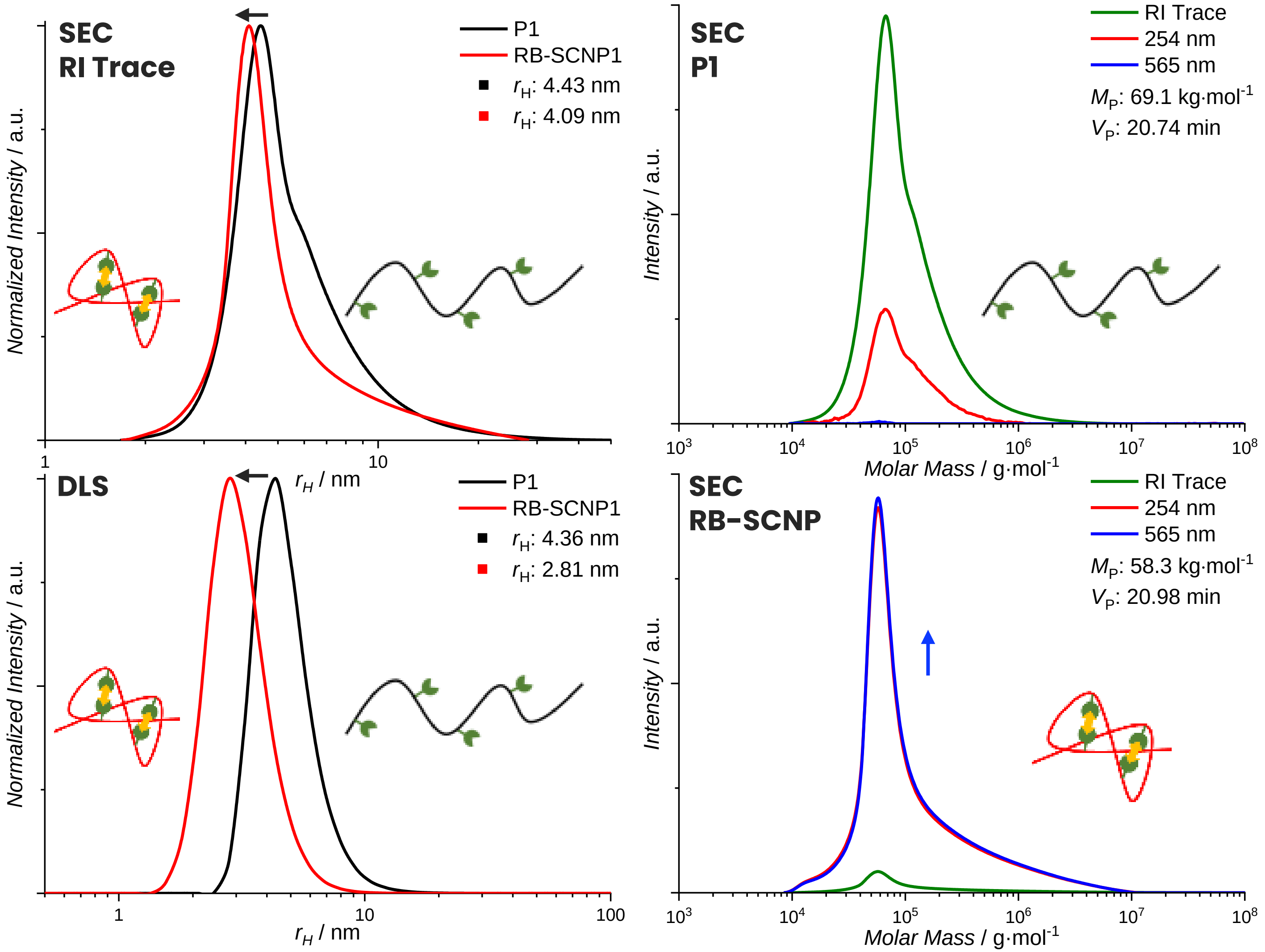
P1 Folding to RB-SCNP

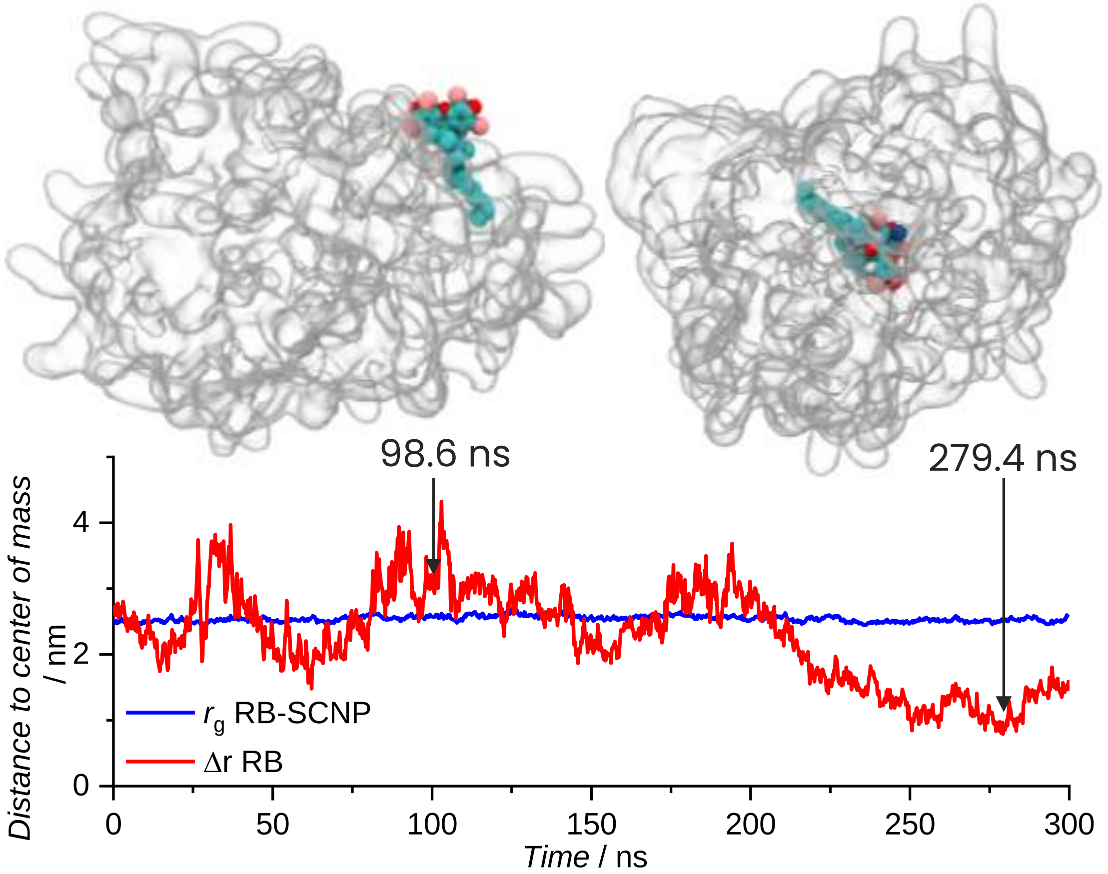


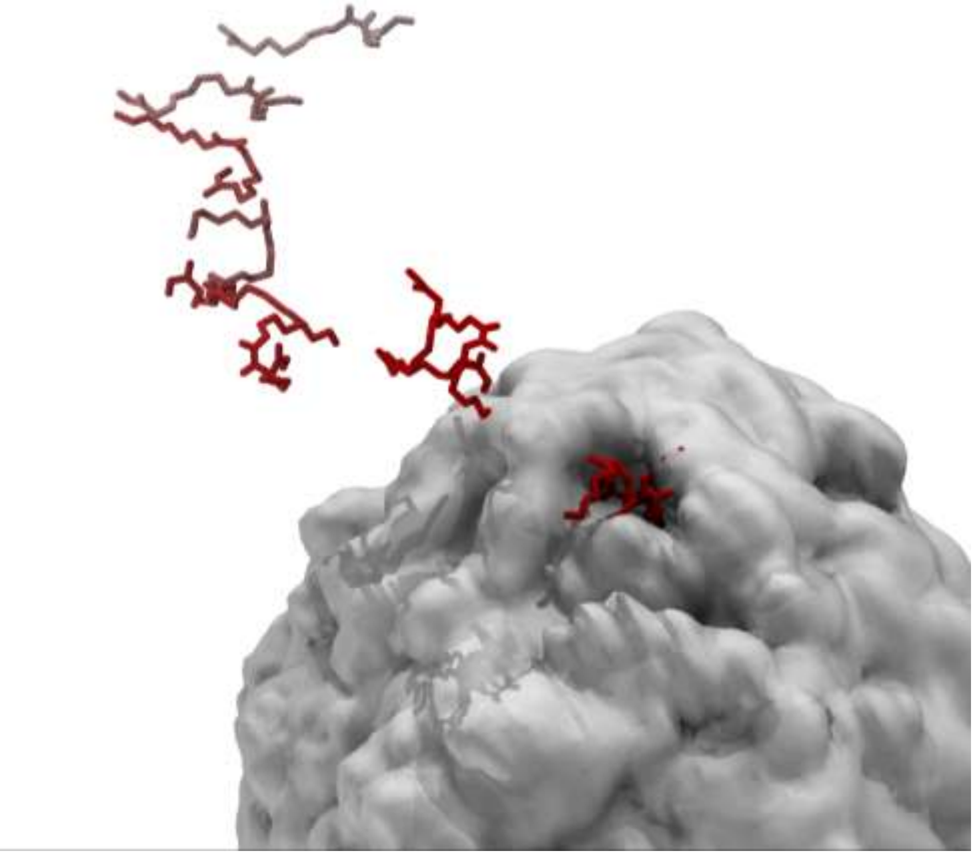
- Reduction of r_H
- Reduction of $Đ$
  - *Successful Folding*
- Increased UV Response
  - *Successful Functionalization*

Mundsinger, K., Tuten, B., Wang, L., Neubauer, K., Kropf, C., O'Mara, M., Barner-Kowollik, C., *Angew. Chem. Int. Ed.*, **2023**, *62*, e202311734

MD Simulation – Active Centres

- RB Residue on SCNP Surface 40% of the Time
- Oleic Acid Collides with RB 5% of the Time





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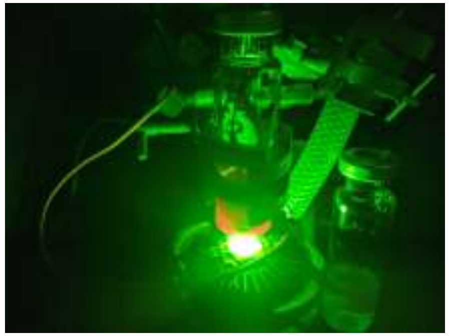
Interplay of Hydrophobicity and Polarity



3.7 μM·L⁻¹ Photoactive Compound

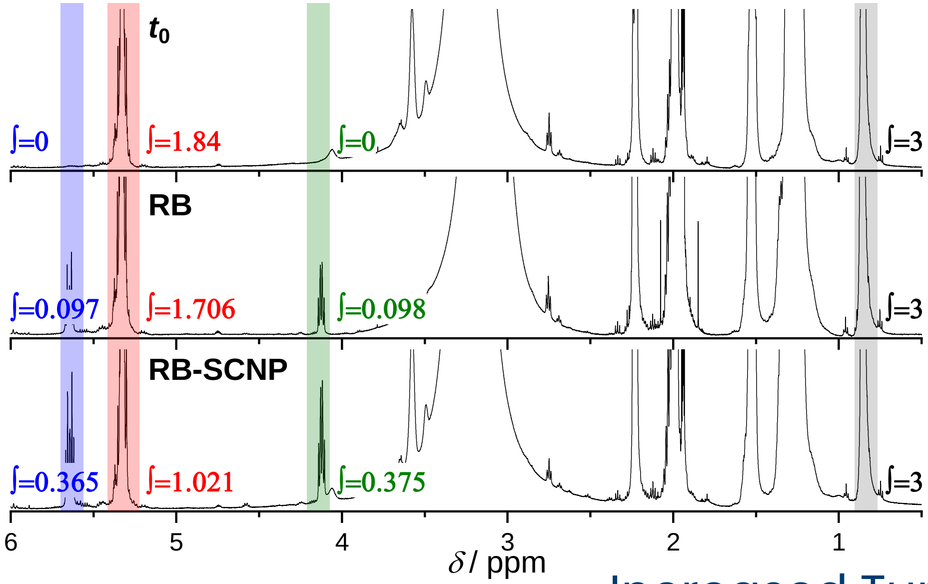
Active Compound	Substrate μmol·mL⁻¹		Conversion / %	mmol	TON
None	OA	24	0	0	**0**
P1	OA	24	0	0	**0**
P1 and RB	OA	24	11.6	5	**700**
RB	OA	24	12.7	6	**800**
RB-SCNP	OA	24	42.9	20	**2800**
RB	OA	143	7.0	20	**2700**
RB-SCNP	OA	143	25.3	72	**9800**
RB	BD	547	1.1	12	**1600**
RB-SCNP	BD	547	1.5	16	**2200**
RB	HA	143	2.0	6	**800**
RB-SCNP	HA	143	1.5	4	**600**

3.5x more efficient

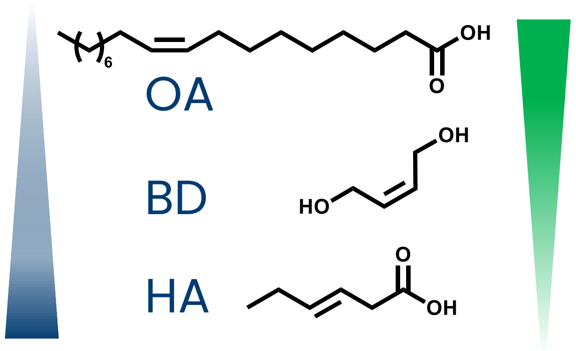
3.5x more efficient

slightly more efficient

less efficient



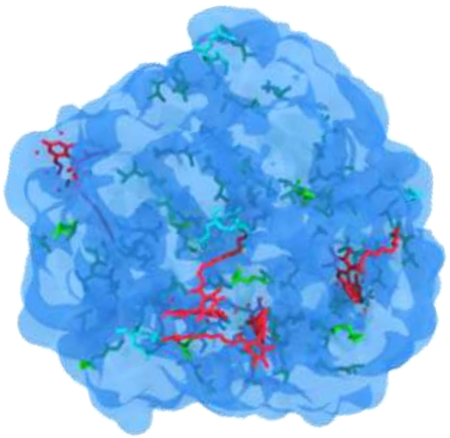
Increased Turnover



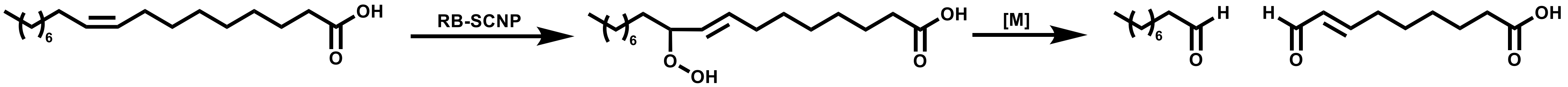
Substrate Polarity

Mundsinger, K., Tuten, B., Wang, L., Neubauer, K., Kropf, C., O'Mara, M., Barner-Kowollik, C., *Angew. Chem. Int. Ed.*, **2023,** *62*, e202311734

Perspective



- Polymeric Scaffolds Enable (Pseudo)Catalytic Behaviour
- (Visible) Light Triggers Conventionally Thermal Transformations
- Standardised Stain Testing Showed Activity at 5.5 nM·L^{-1} @Henkel
- Additional Functionality Enables C–C Bond Scission



Gillhuber, S., Holloway, J., Mundsinger, K., Kammerer, J., Frisch, H., Barner-Kowollik, C., Roesky, P., *Angew. Chem. Int. Ed.*, submitted.
Li et al. *Org. Chem. Front.*, **2022**, *9, 6229-6239*

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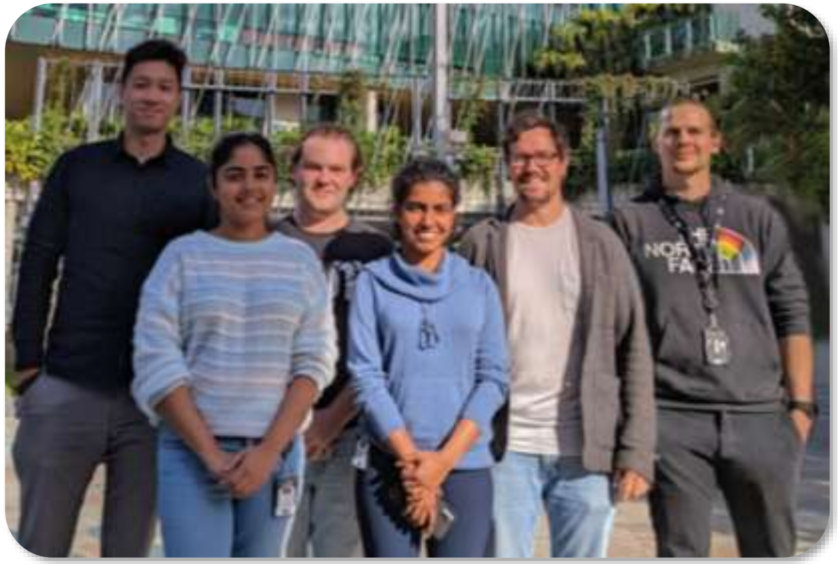

Funding

QUT Centre for Materials Science
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Australian Research Council
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DFG Deutsche Forschungsgemeinschaft
German Research Foundation
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UMONS Université de Mons
THE UNIVERSITY OF SYDNEY

APS Program

Monday 5 pm in Millenium Ballroom

Polymer-membrane interactions as a target for polymeric antivirals

Dr Nathan Boase

Monday 5.15 pm in Tasman 1

Main-chain Macromolecular Hydrazone Photoswitches

Linh-Duy Thai

Tuesday 11.15 am in Tasman 1

Light-triggered Metal-induced Flow Synthesis of Catalytically Active Single-chain Polymer Nanoparticles

Sebastian Gillhuber

APS Program

Tuesday 12.15 pm in Tasman 1

Investigating the impact of olefinic structure in polystyrene-polyisoprene-polystyrene (SIS) triblock copolymers on their performance as flexible electrothermal composite heaters - Hiruni Dedduwakumara

Tuesday 12.45 pm in Tasman 1

Visible-Light-Induced Control over Folding and Unfolding of Fluorescent and Catalytically Active Single-Chain Nanoparticles - Patrick Maag

Tuesday 4 pm in Tasman 1

Dynamic Chalcogen Squares for Material and Topological Control over Macromolecules - Dr Bryan Tuten