

Light-Driven Molecular Motor

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2019/10/03

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1. Introduction

2. Application of Molecular Motor

3. Summary

2016 Nobel Prize in Chemistry

"for the design and synthesis of molecular machines."



Sauvage

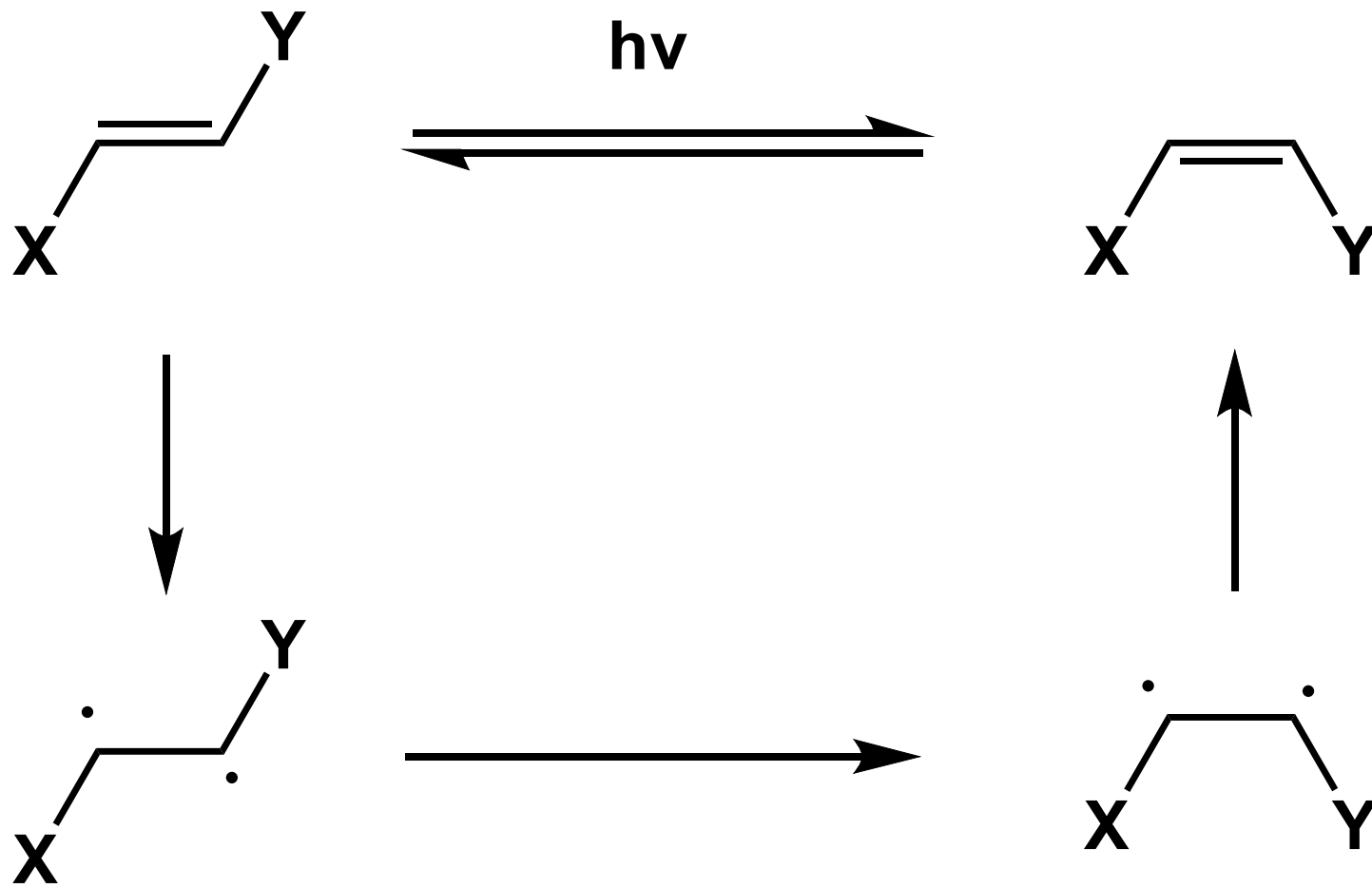


Stoddart

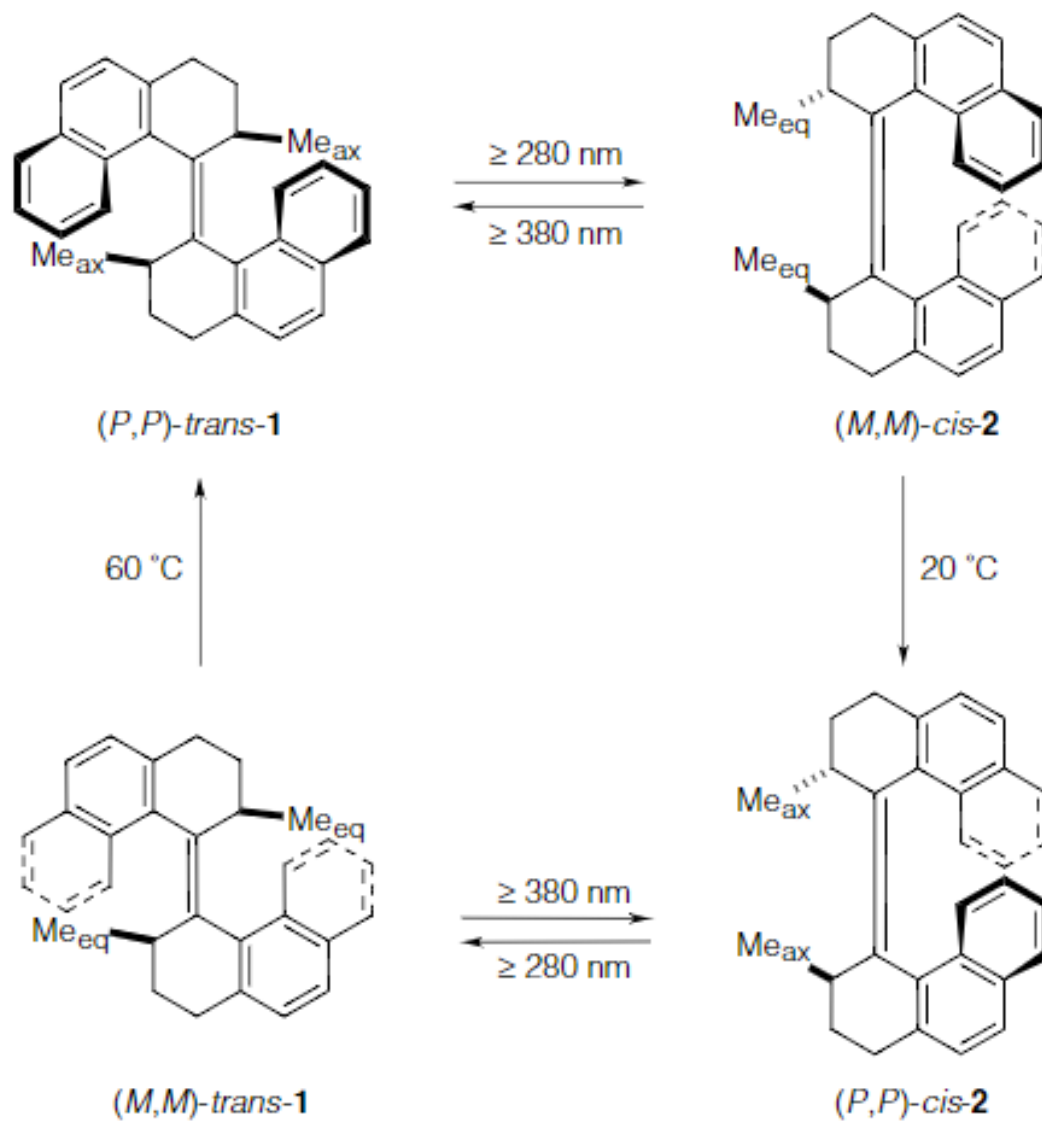


Feringa

Photoisomerization of Alkene

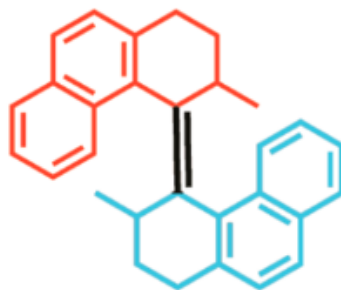
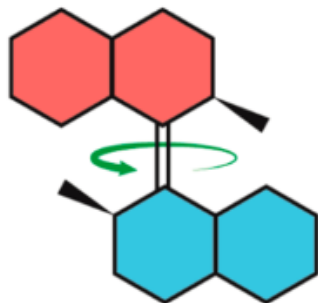


Light-Driven Monodirectional Molecular Motor

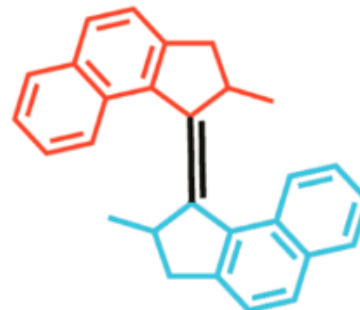


First and Second Generation of Motor

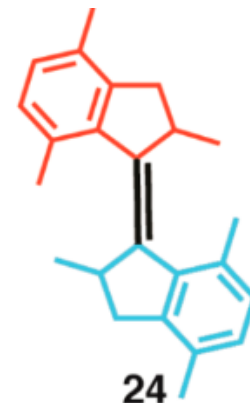
1st generation
two stereocenters



22
 $\tau_{1/2} =$
E 32 min
Z 18 d

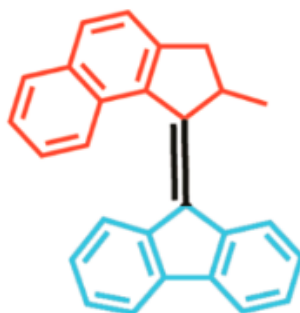
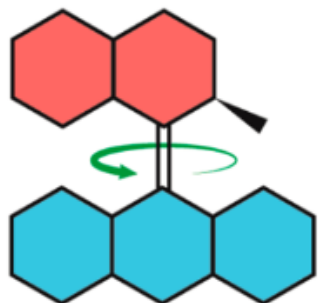


23
 $\tau_{1/2} =$
E 18 s
Z 74 min

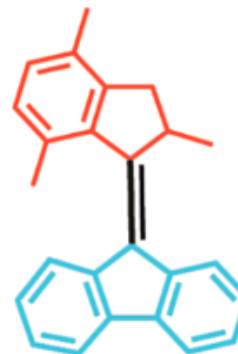


24
 $\tau_{1/2} =$
E 1.2 s
Z > 1.5 d

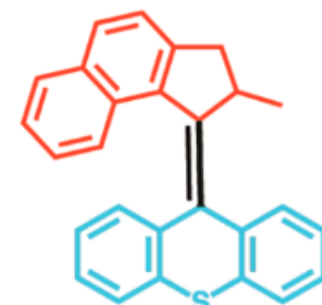
2nd generation
one stereocenter



25
 $\tau_{1/2} =$ 3.2 min

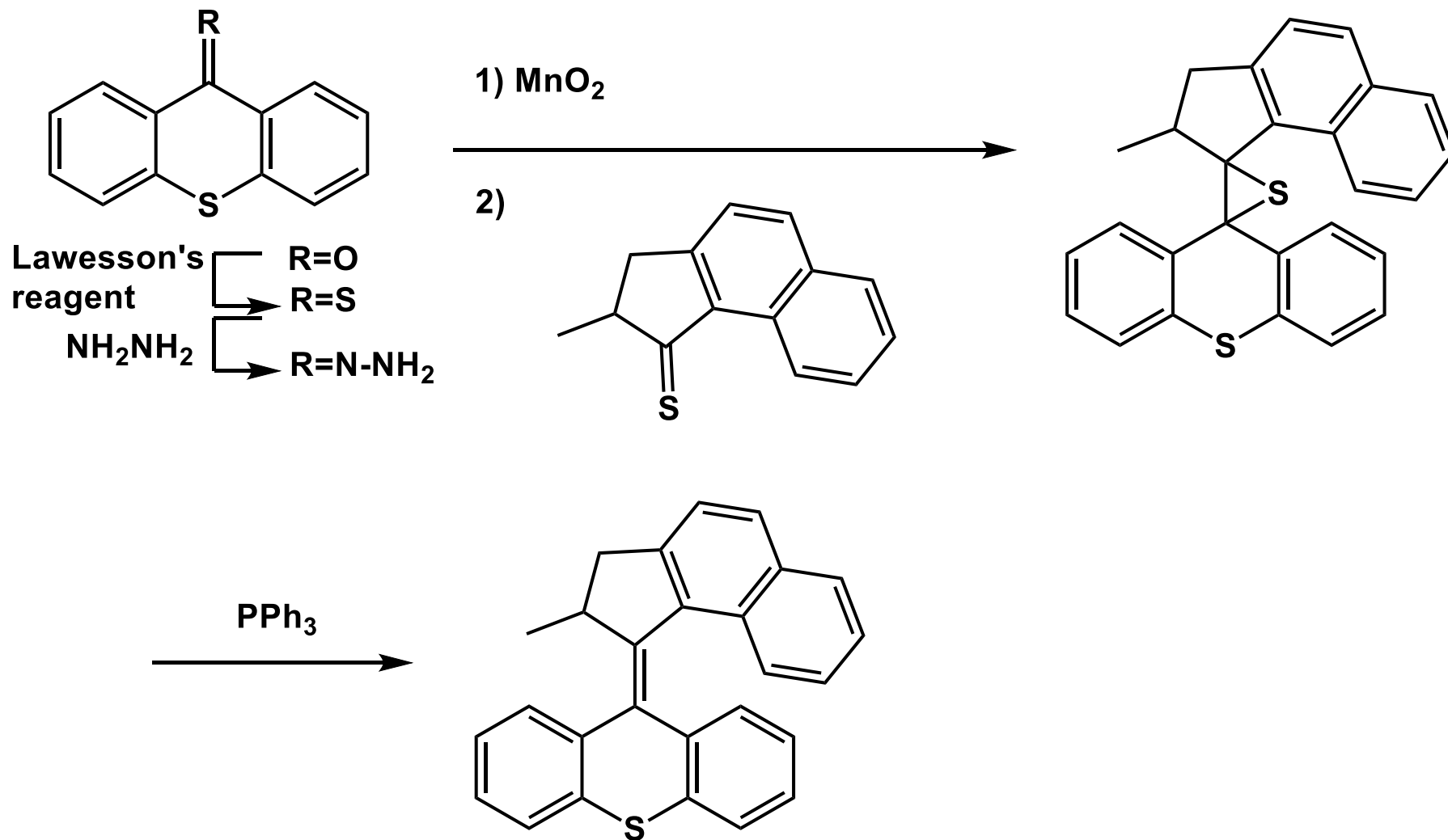


26
 $\tau_{1/2} =$ 15 s



27
 $\tau_{1/2} =$ 0.1 ms

Synthesis of Motor



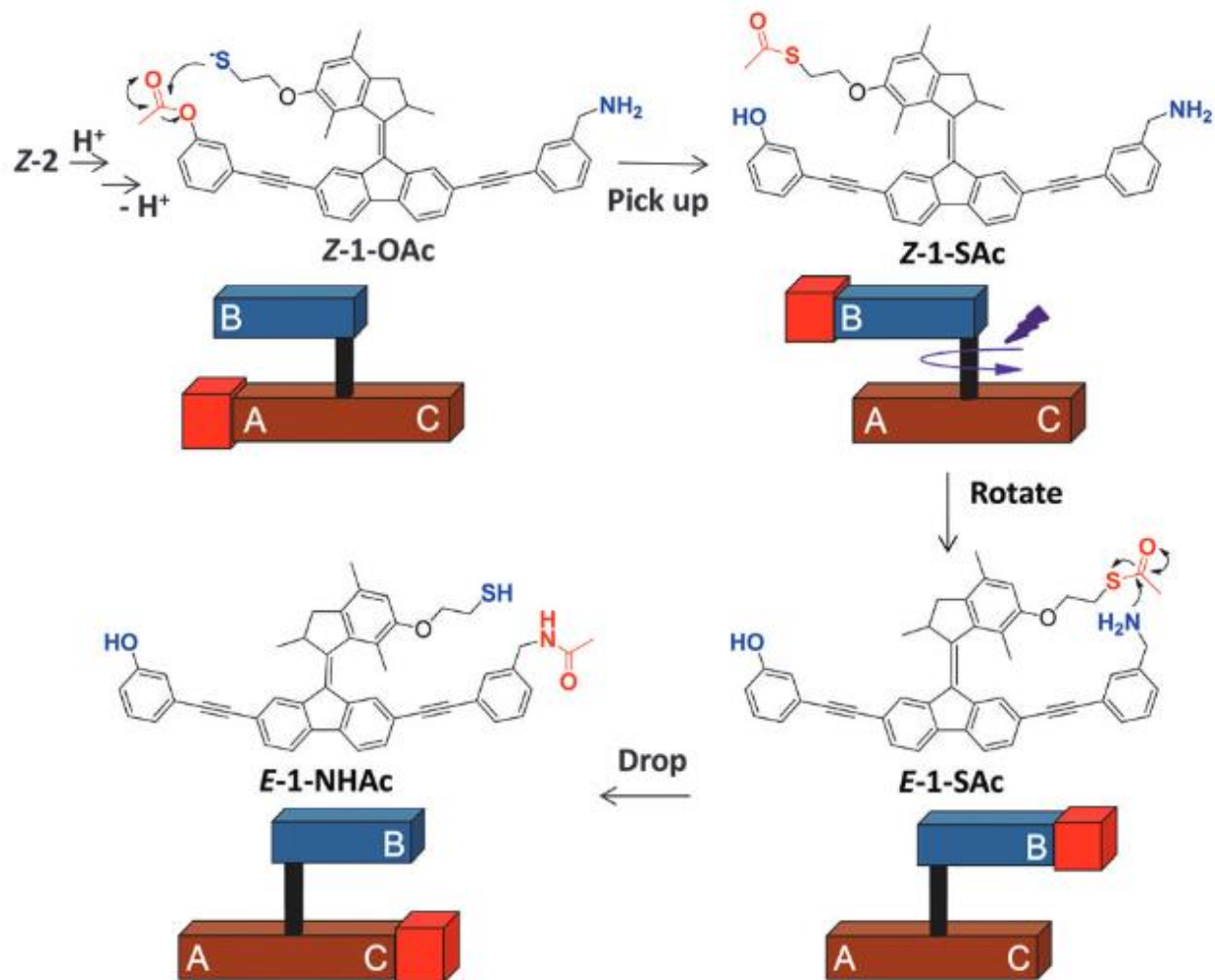
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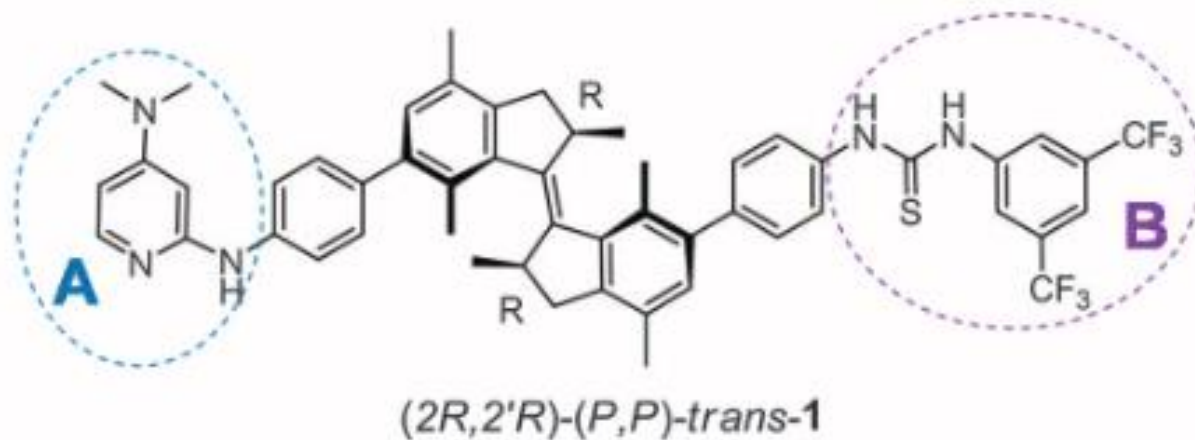
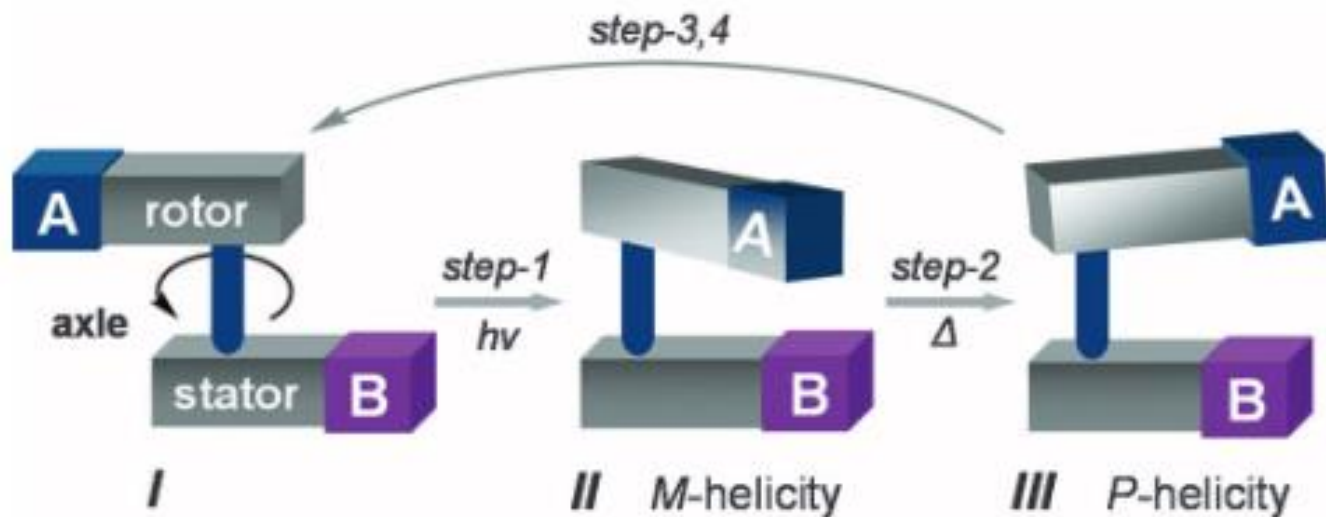
2. Application of Molecular Motor

3. Summary

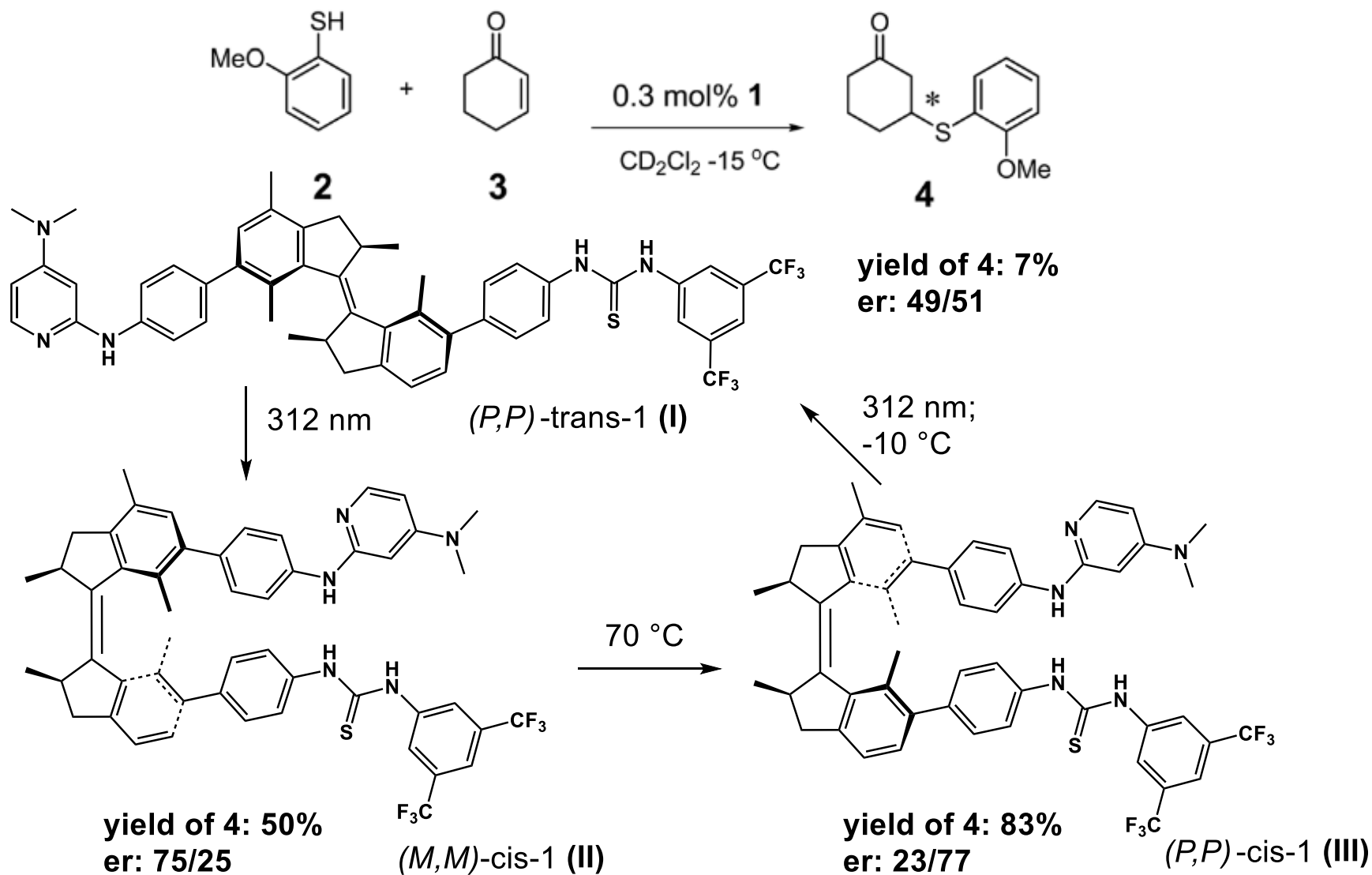
Intramolecular Transport of Acetyl Group



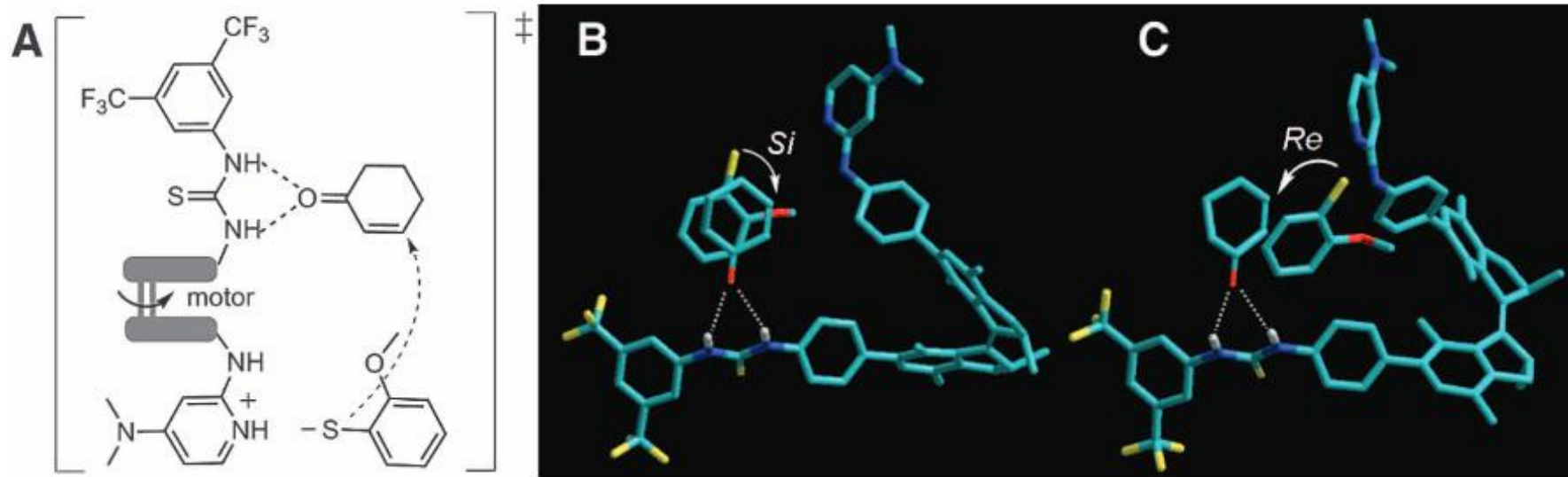
Asymmetric Reaction Control (1)



Asymmetric Reaction Control (1)

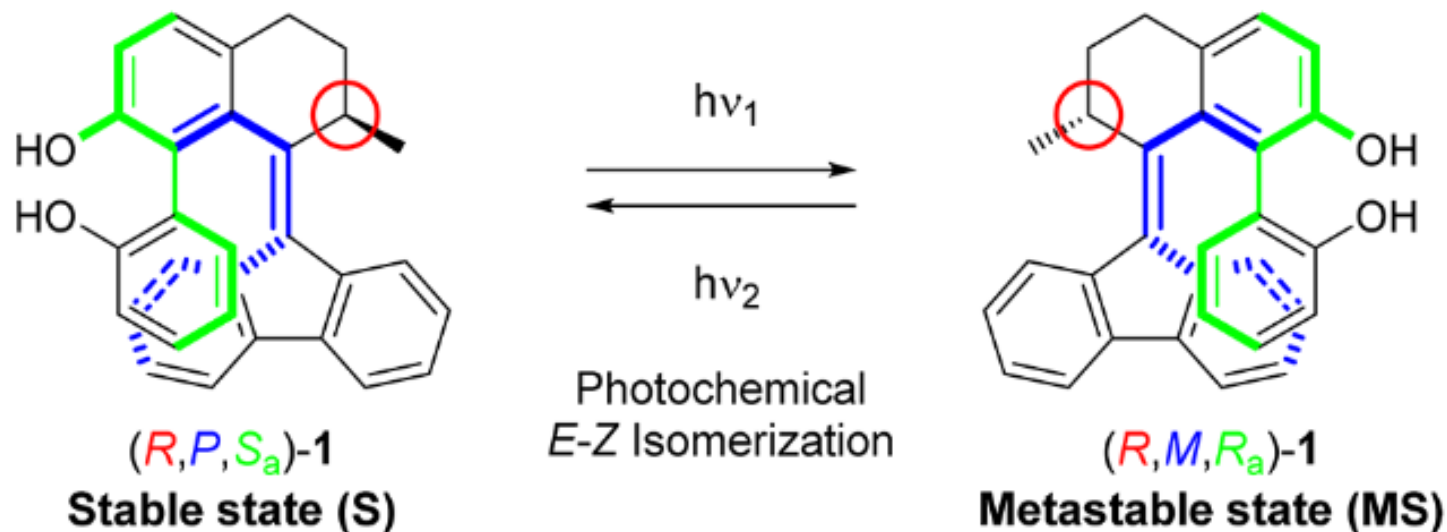


Asymmetric Reaction Control (1)

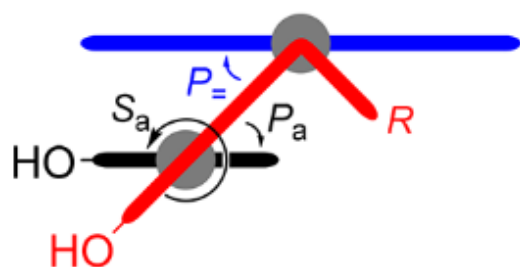


- Hydrogen bonding between enone and thiourea
- Thiol deprotonation by DMAP

Asymmetric Reaction Control (2)

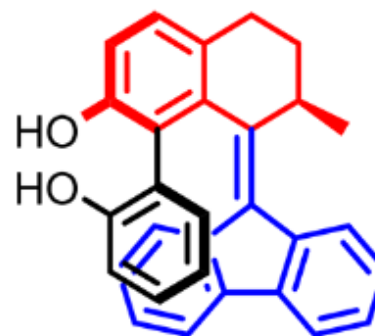


Top-down schematic view

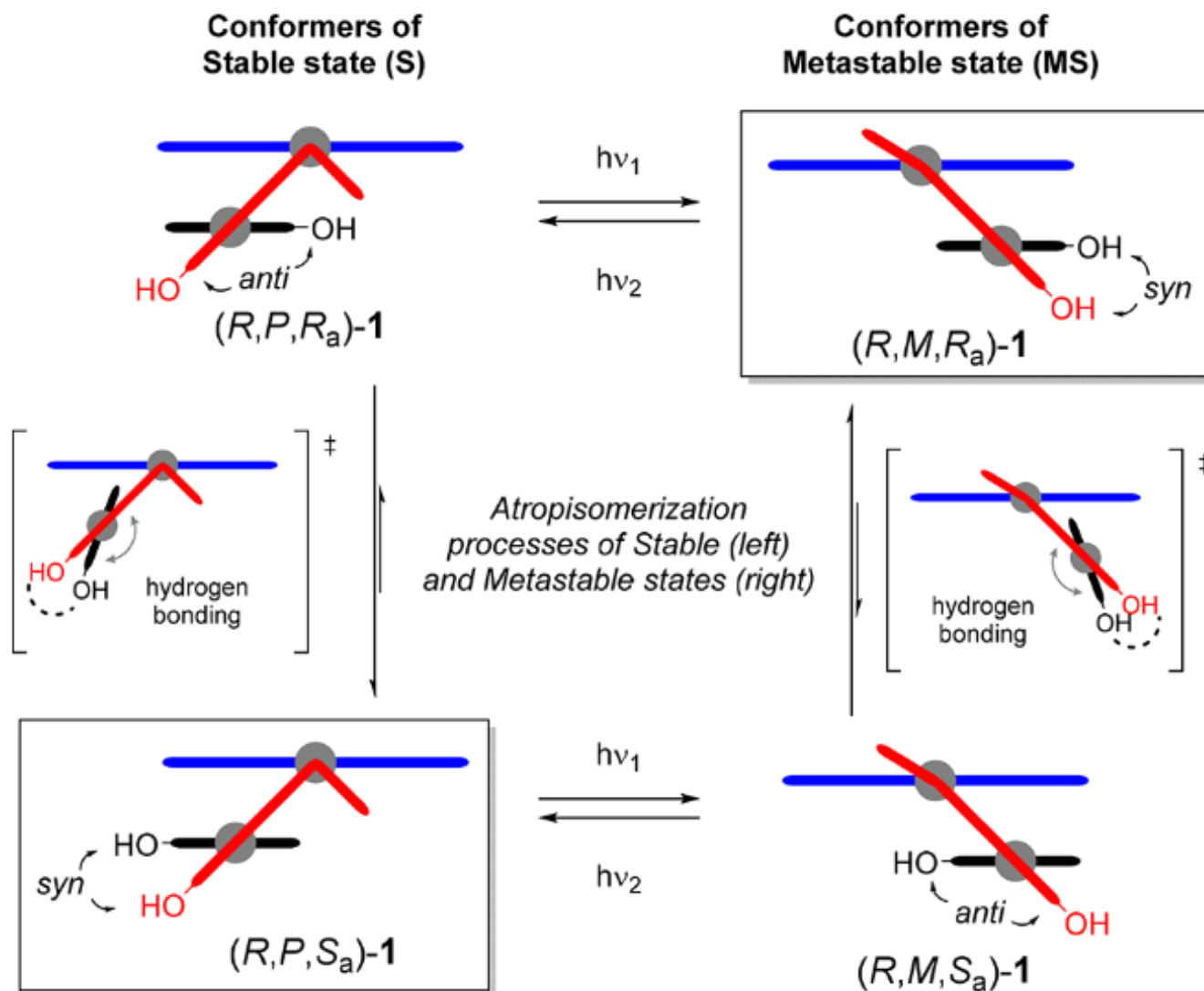


Example: $(R,P_a,P_a,S_a)-1$

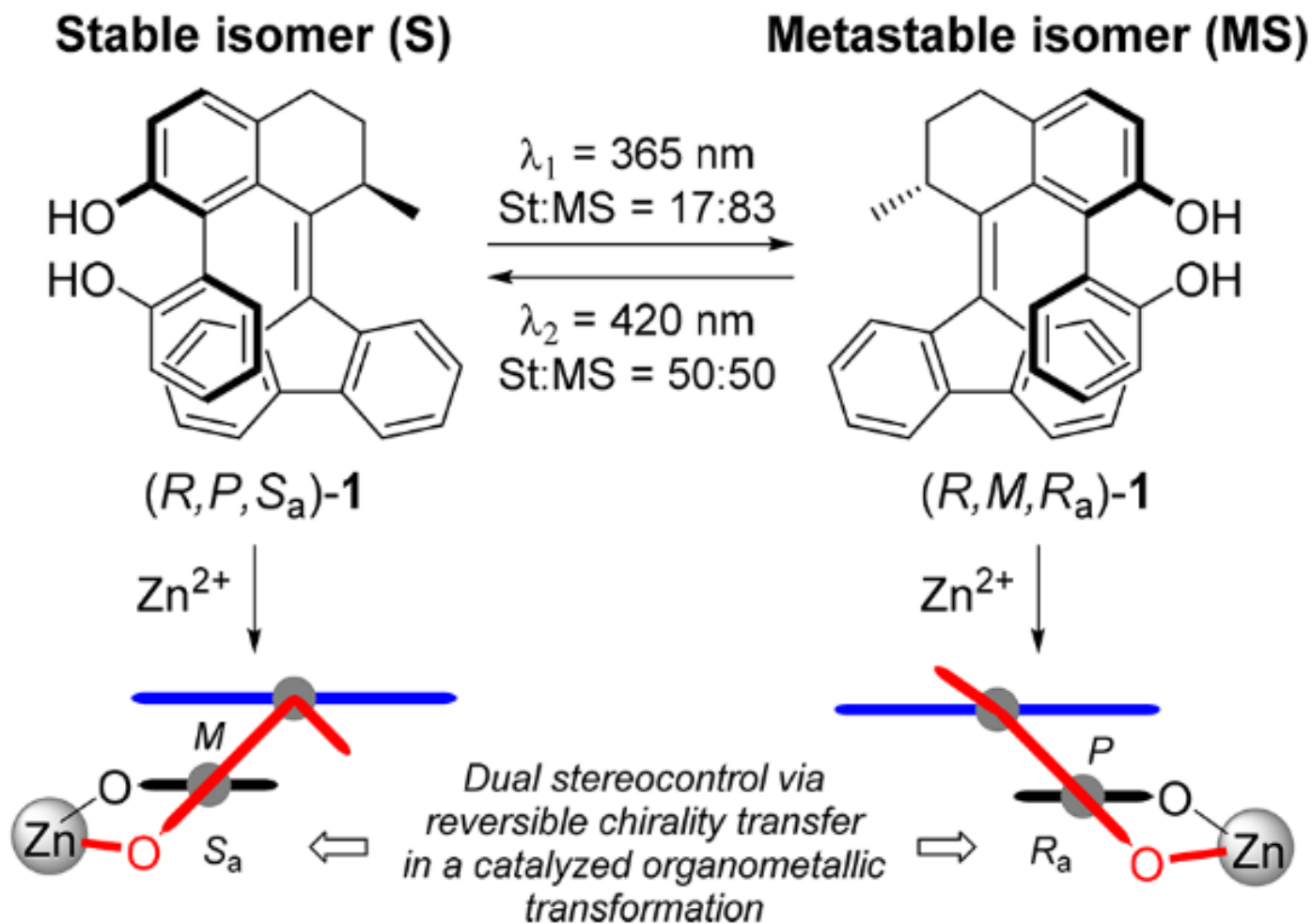
Front structural view



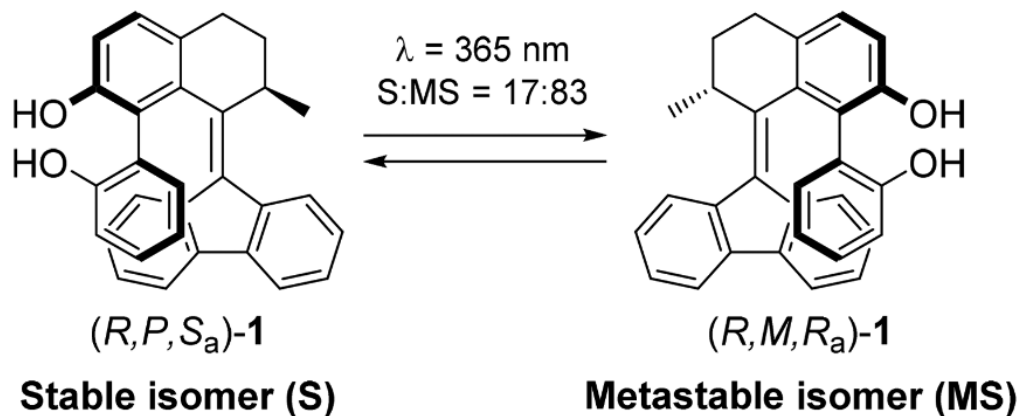
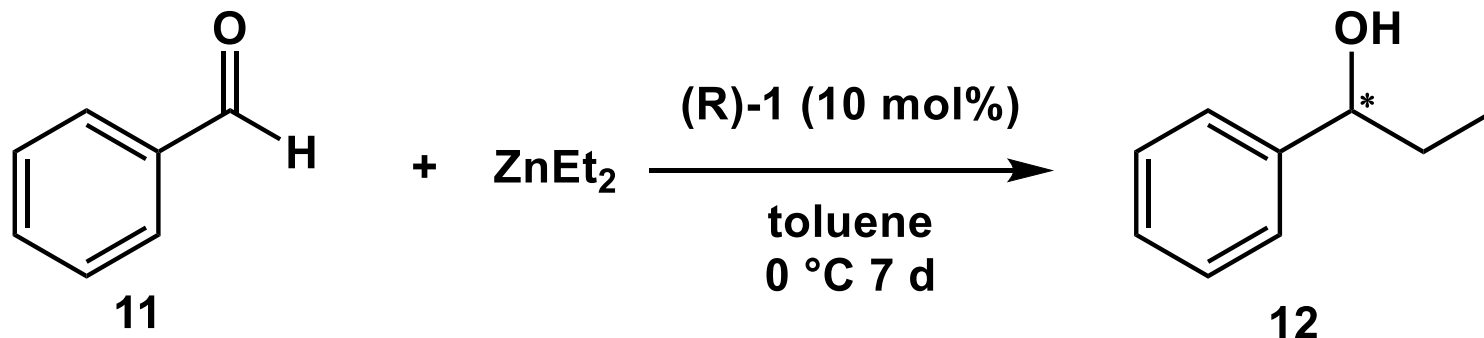
Asymmetric Reaction Control (2)



Asymmetric Reaction Control (2)

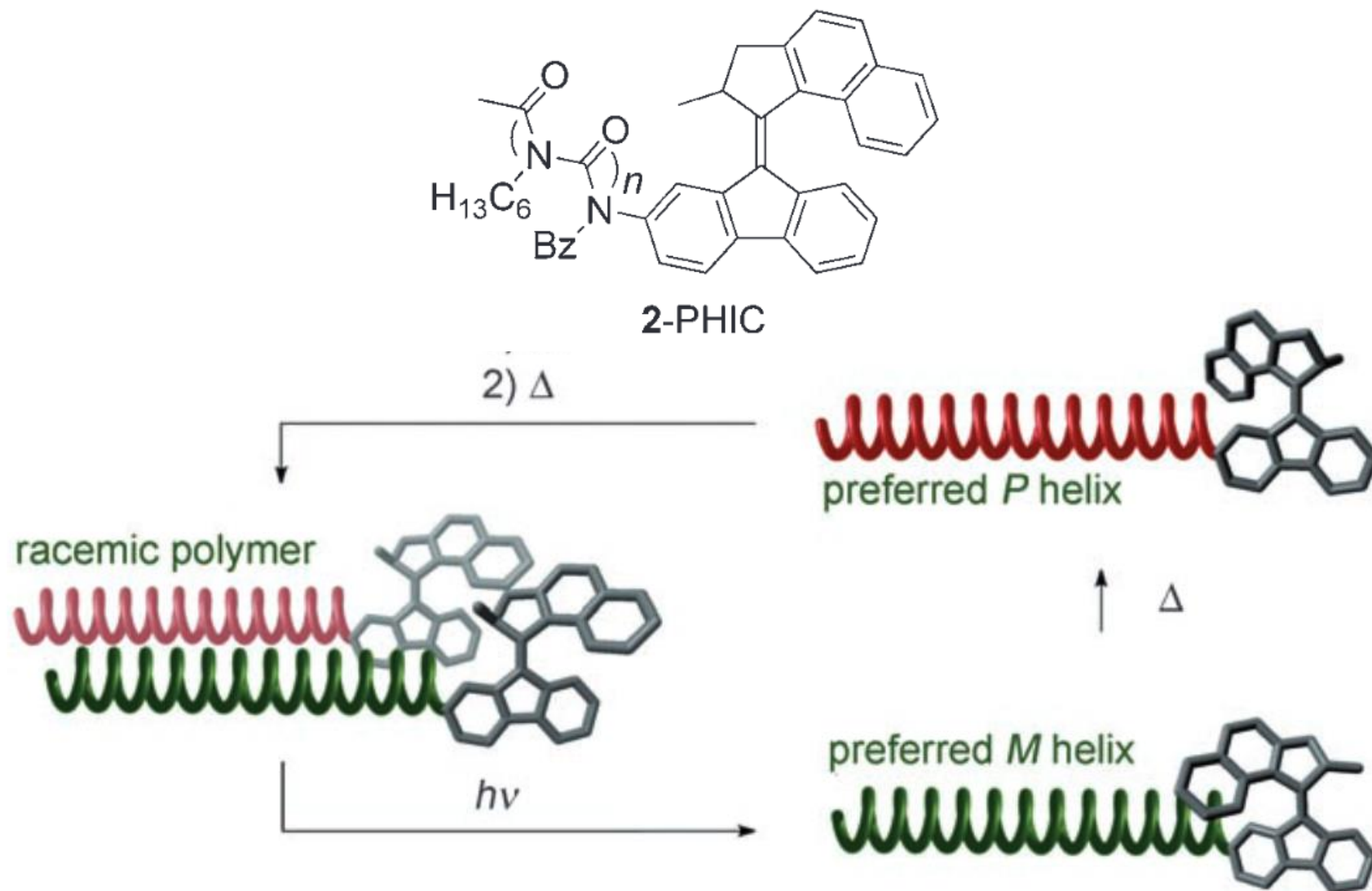


Asymmetric Reaction Control (2)

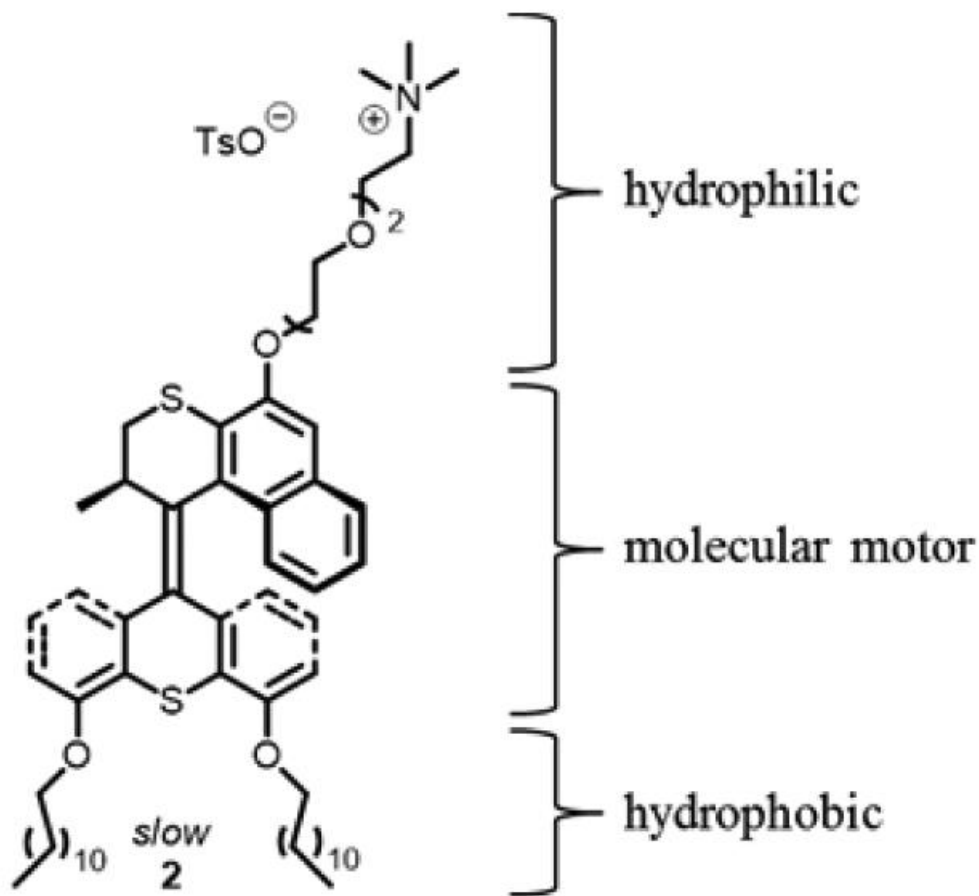


Entry	Catalyst	Yield	ee
1	(R)-1	86%	68% (R)-12
2	(R) + 365 nm	87%	45% (S)-12

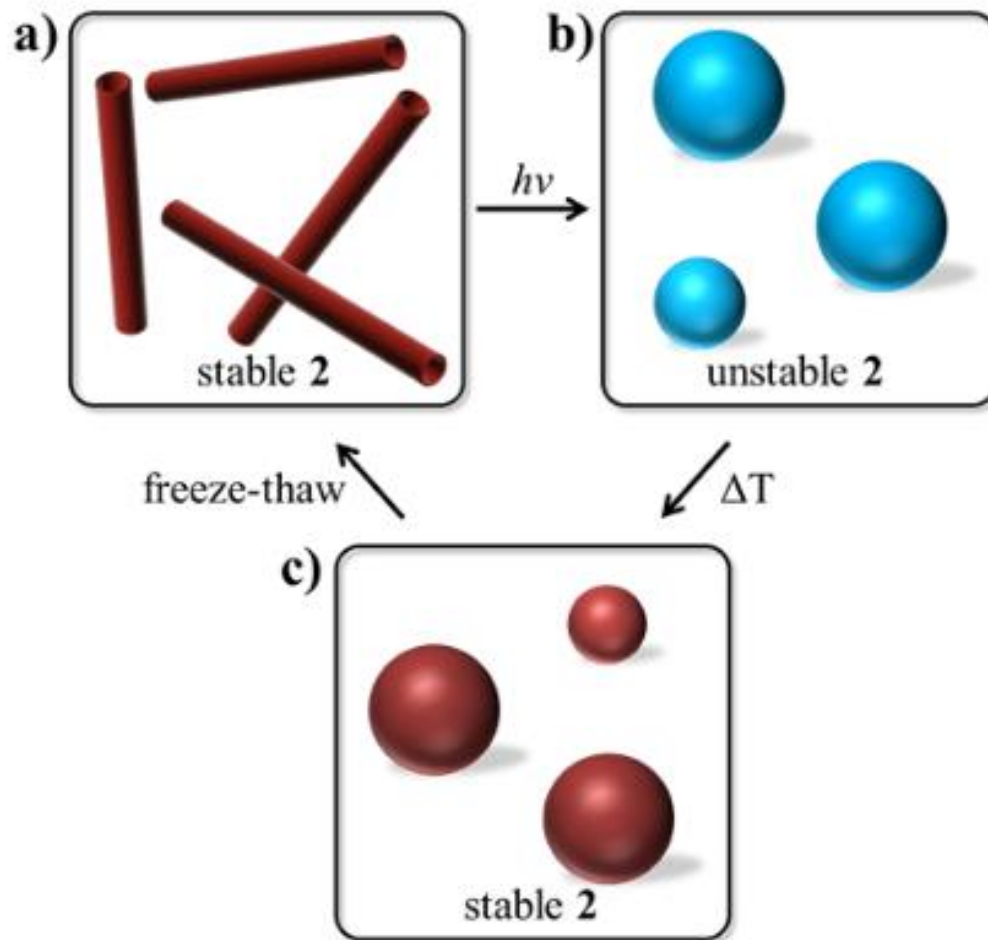
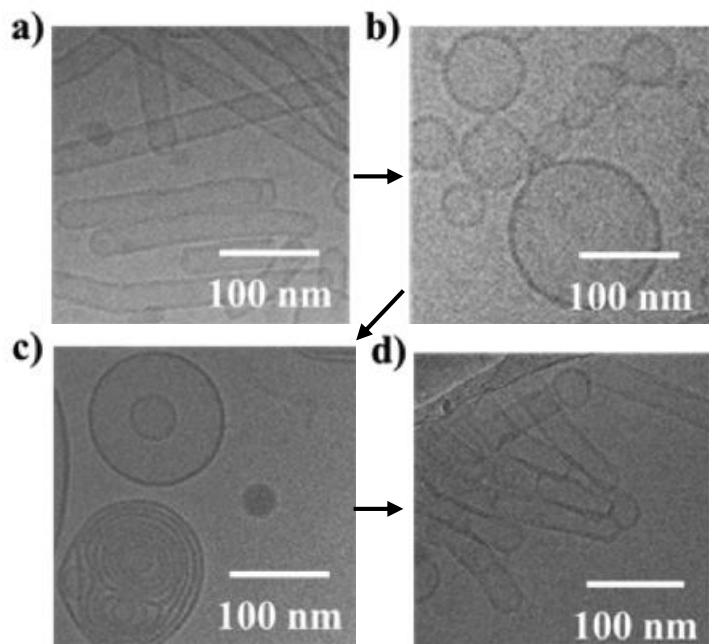
Controlling the Twist Sense of a Helical Polymer



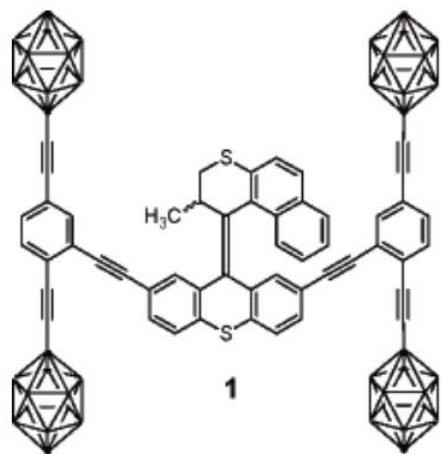
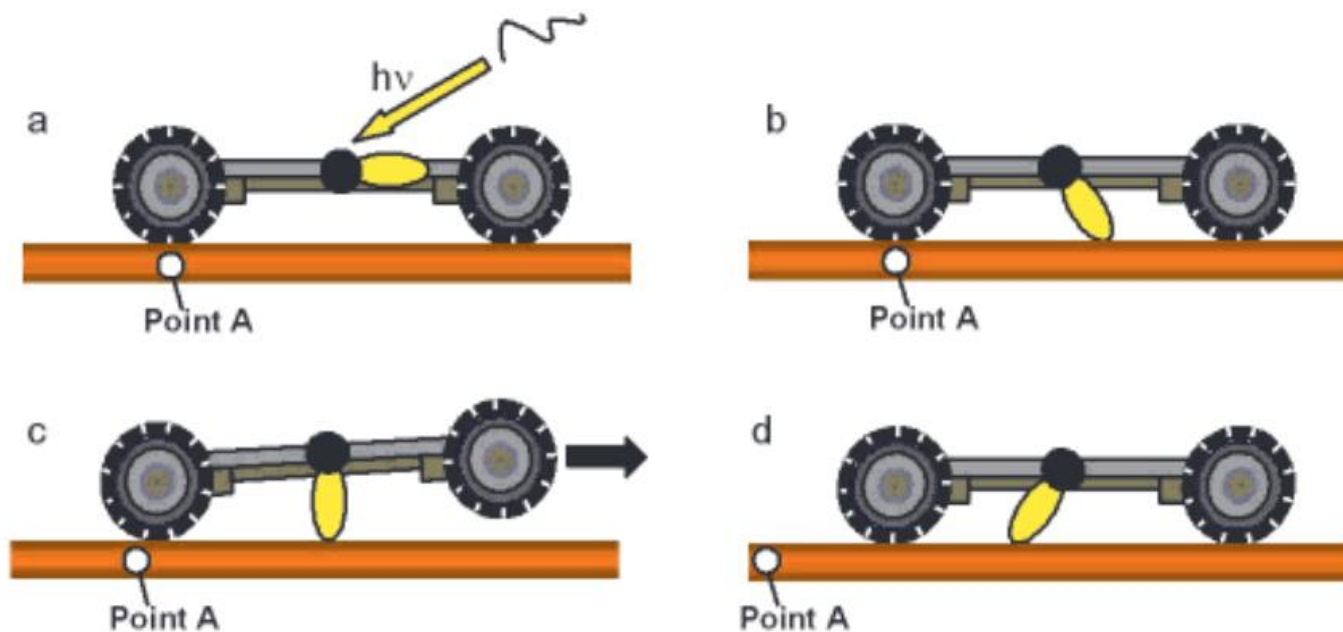
Self-Assembly Supramolecular in Water



Self-Assembly Supramolecular in Water

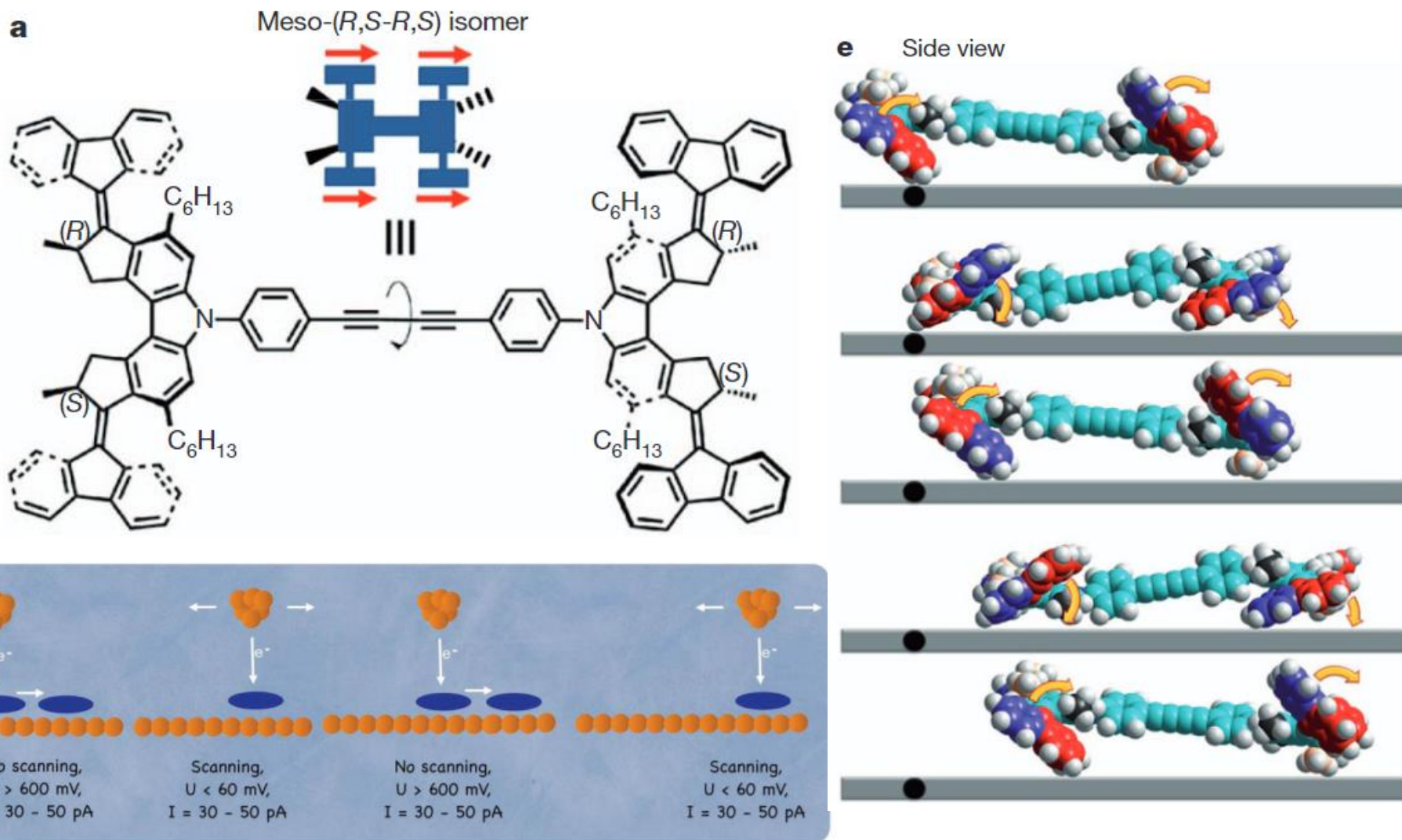


Motorized Nanocar (1)



Unsuccessful – intramolecular quenching of the photoexcited state by fullerene wheels

Motorized Nanocar (2)

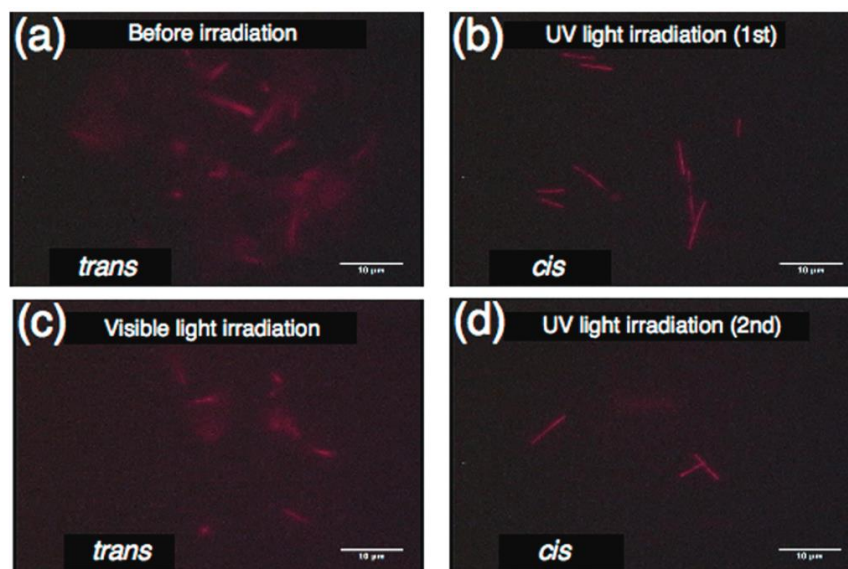
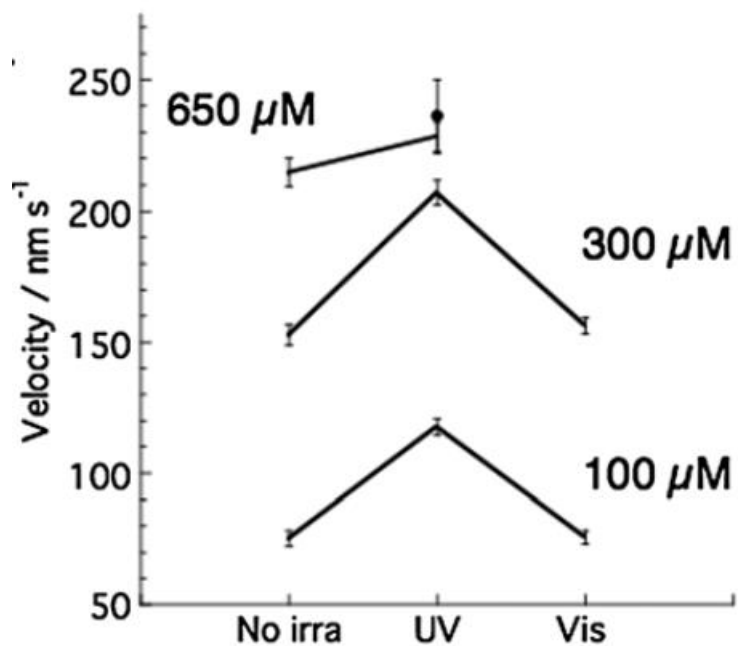
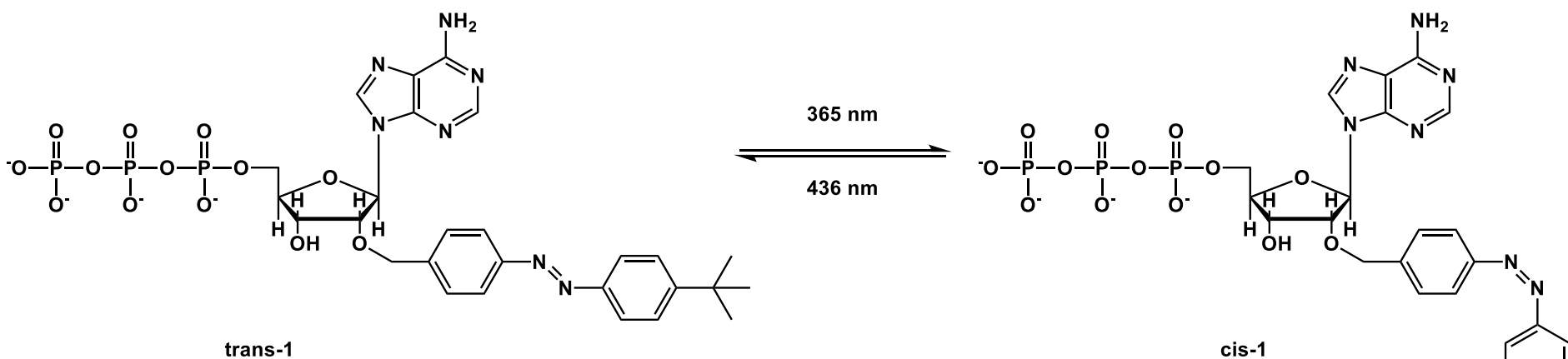


Motorized Nanocar (2)

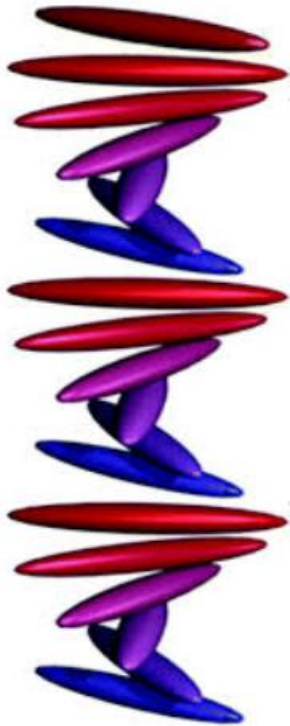
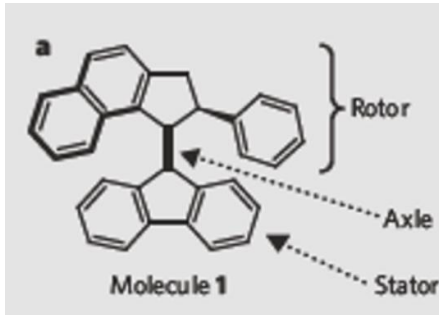


L. Feringa, et al. *Nature*, **2011**, 479, 208–211.

Photo-Switchable ATP analogue



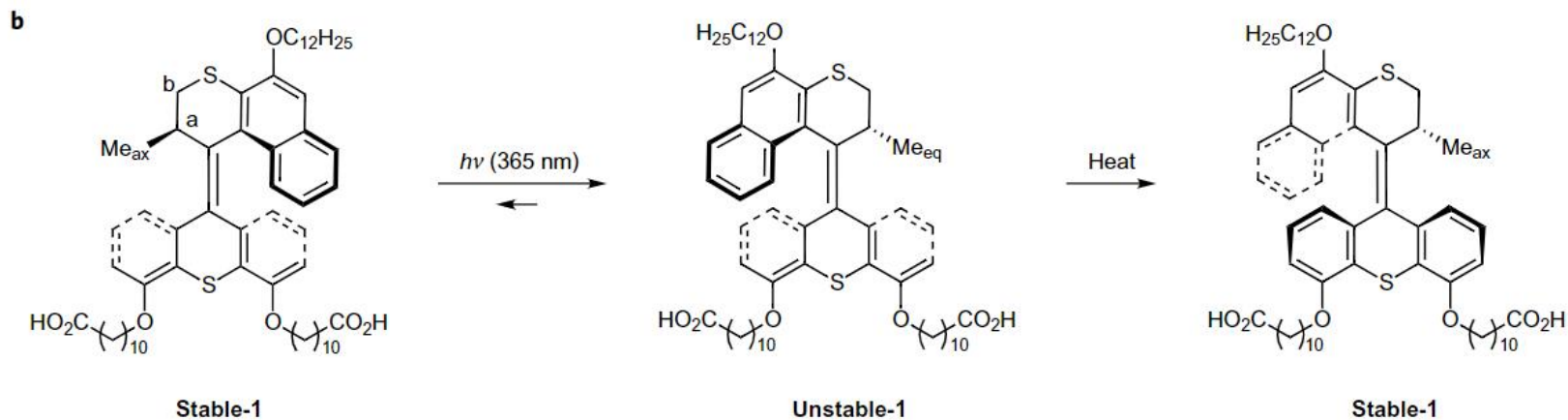
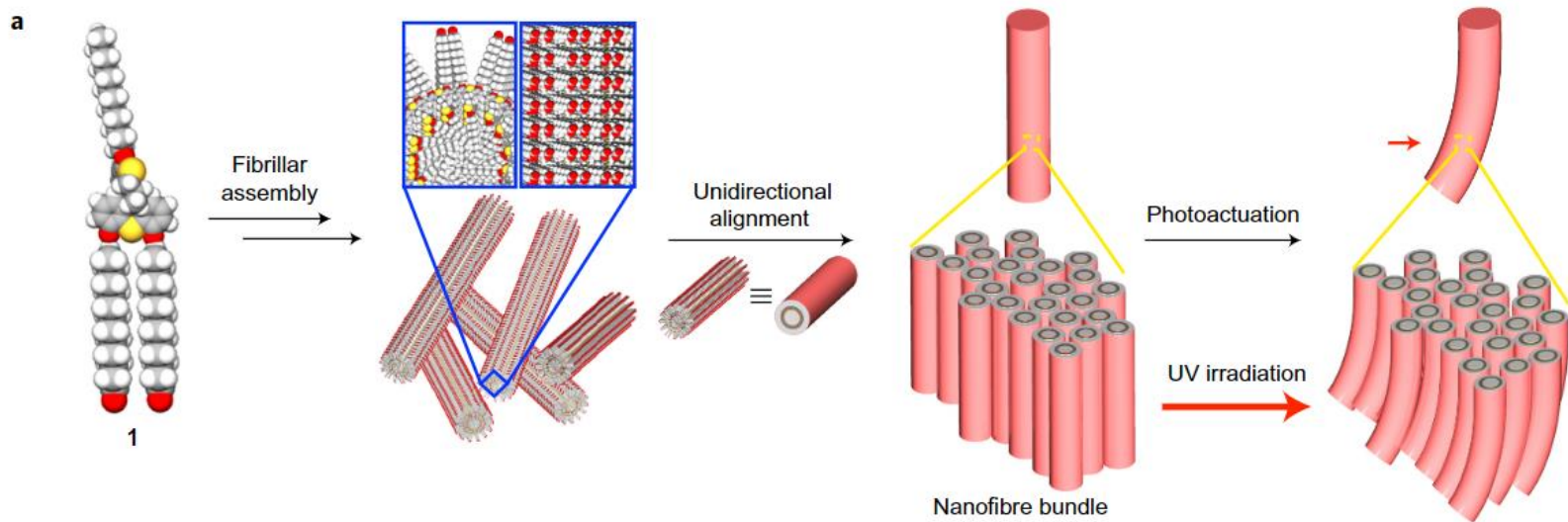
Nanomotor rotates microscale objects



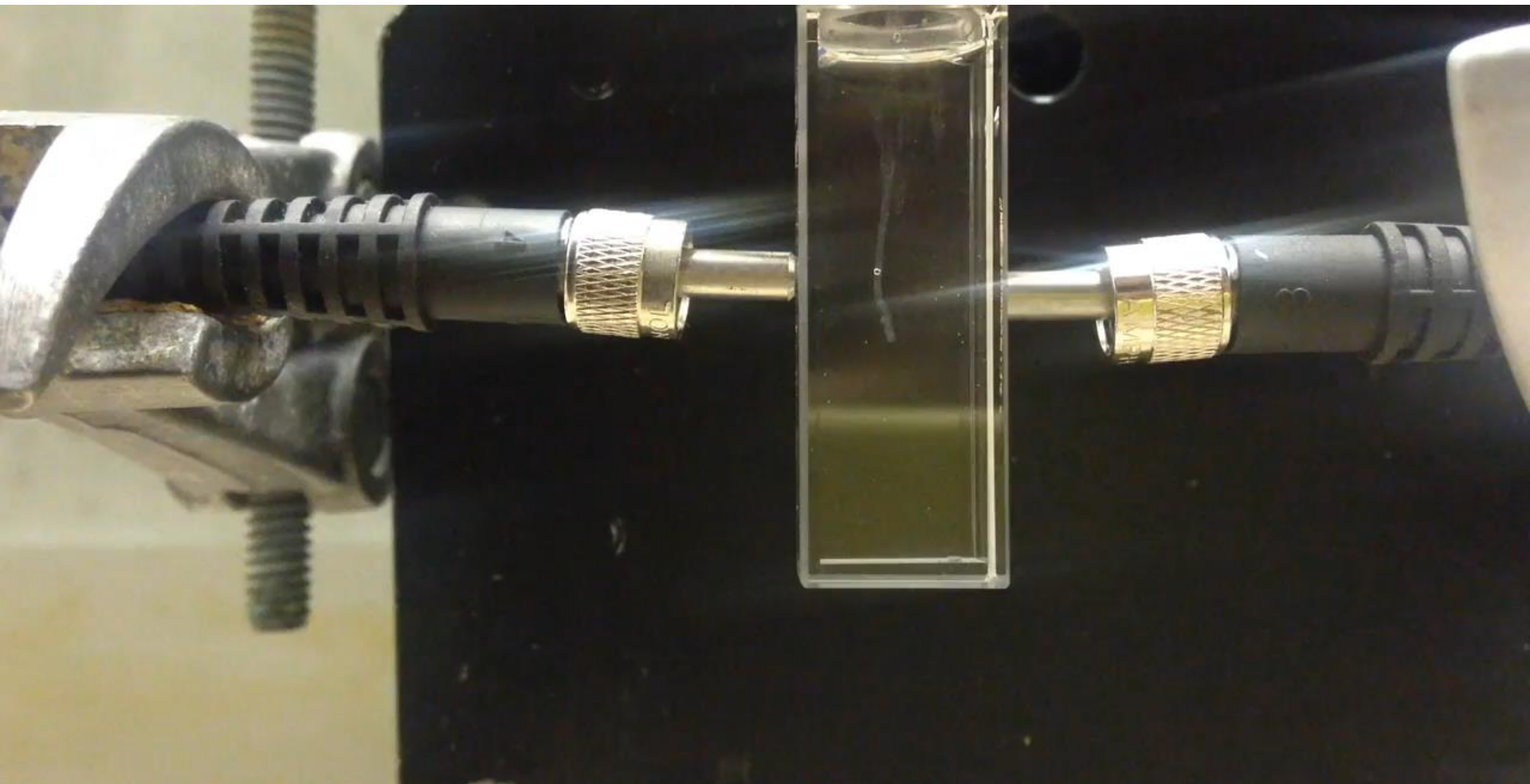
Cholesteric liquid crystal



Artificial Muscle-Like Function



Artificial Muscle-Like Function

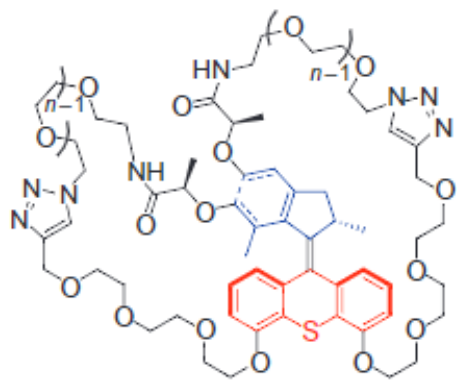


Contraction of Gel

1: $R^1 = \text{CH}_3$, $R^2 = \text{OEt}$

2: $R^1 = \text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{-OCH}_2\text{-C=CH}$, $R^2 = \text{NH-CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_{107}\text{-OCH}_2\text{CH}_2\text{N}_3$

3: $R^1 = \text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{-OCH}_2\text{-C=CH}$, $R^2 = \text{NH-CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_{237}\text{-OCH}_2\text{CH}_2\text{N}_3$

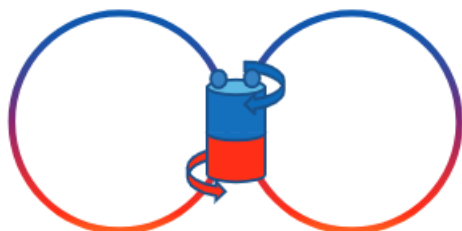


Yields 60-80%

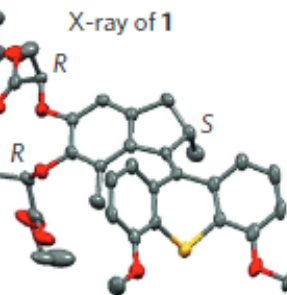
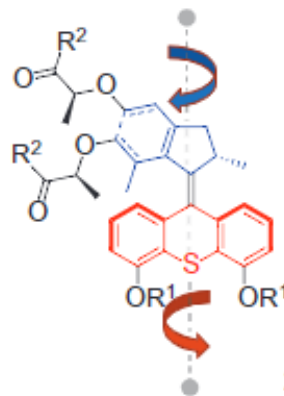
8-shaped-4: $n = 108$

8-shaped-5: $n = 238$

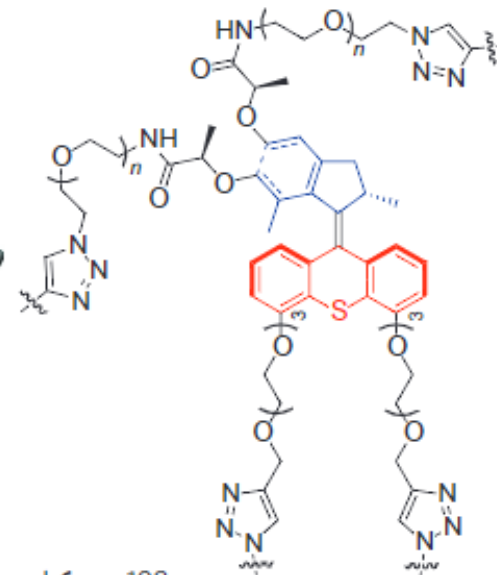
II



(i)
Huisgen 'click'
Diluted solution



(ii)
Huisgen 'click'
Concentrated solution

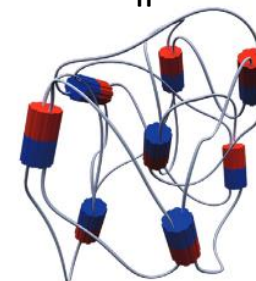


gel-6: $n = 108$

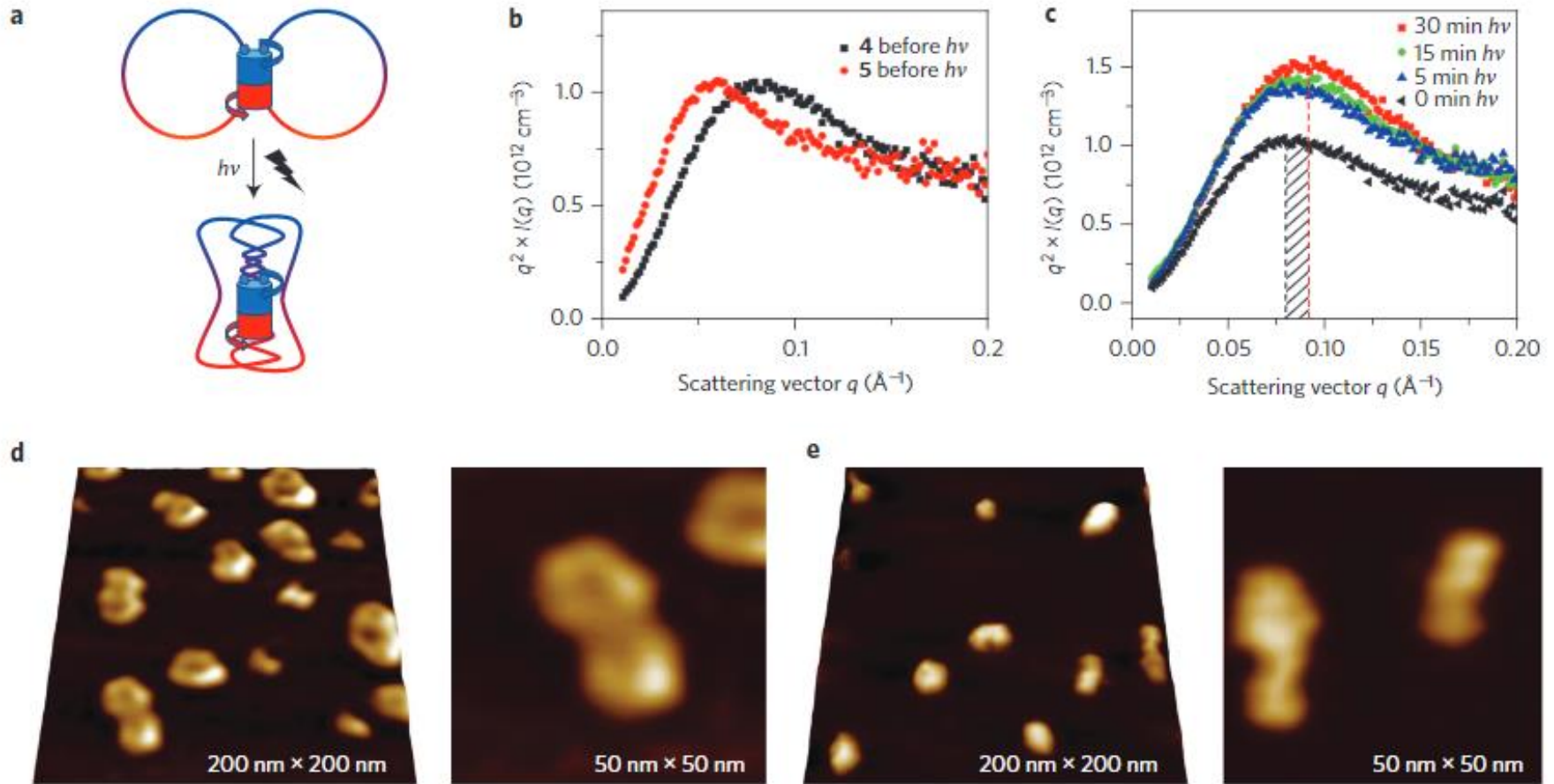
gel-7: $n = 238$

Yields 50-60%

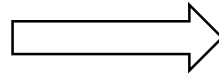
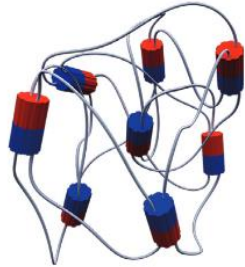
II



Contraction of Gel



Contraction of Gel



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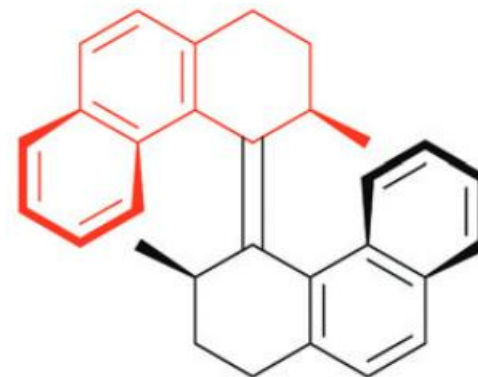
1. Introduction

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Summary

- Light-driven mono directional rotation on double bond



- Many applications –

Asymmetric reaction control, Helical control of polymer,
Nano car, Dynamic control of molecular assembly

Chemical Intramolecular Transport

