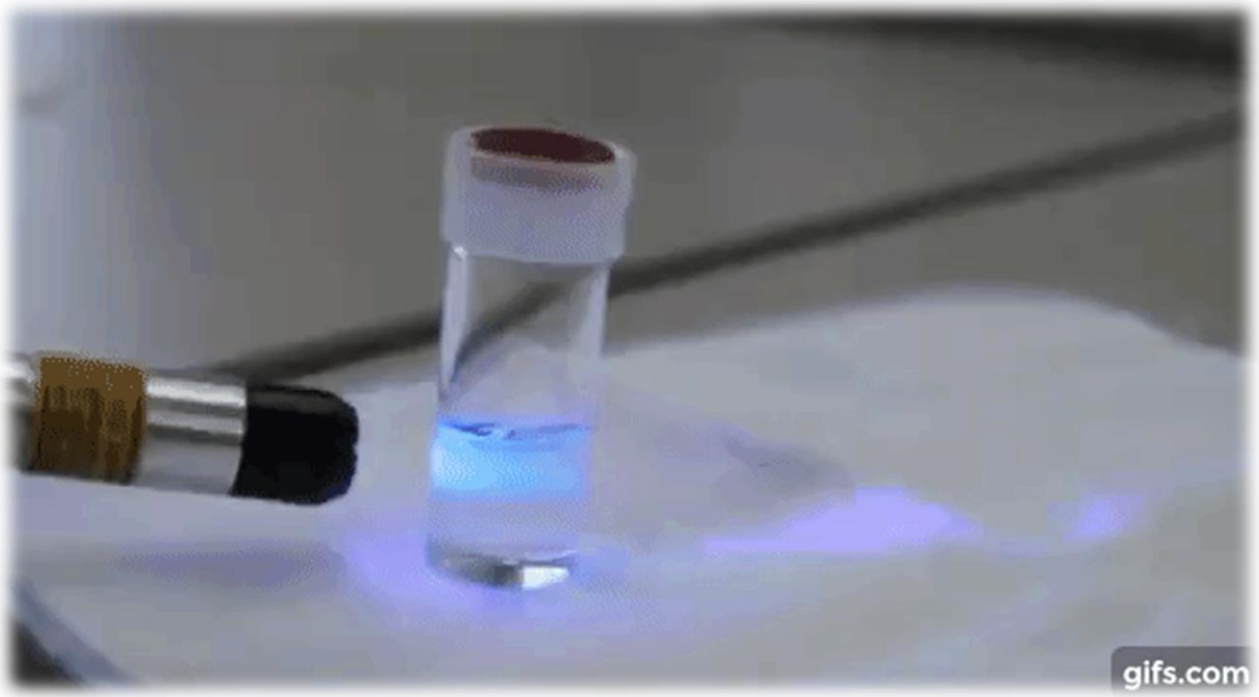
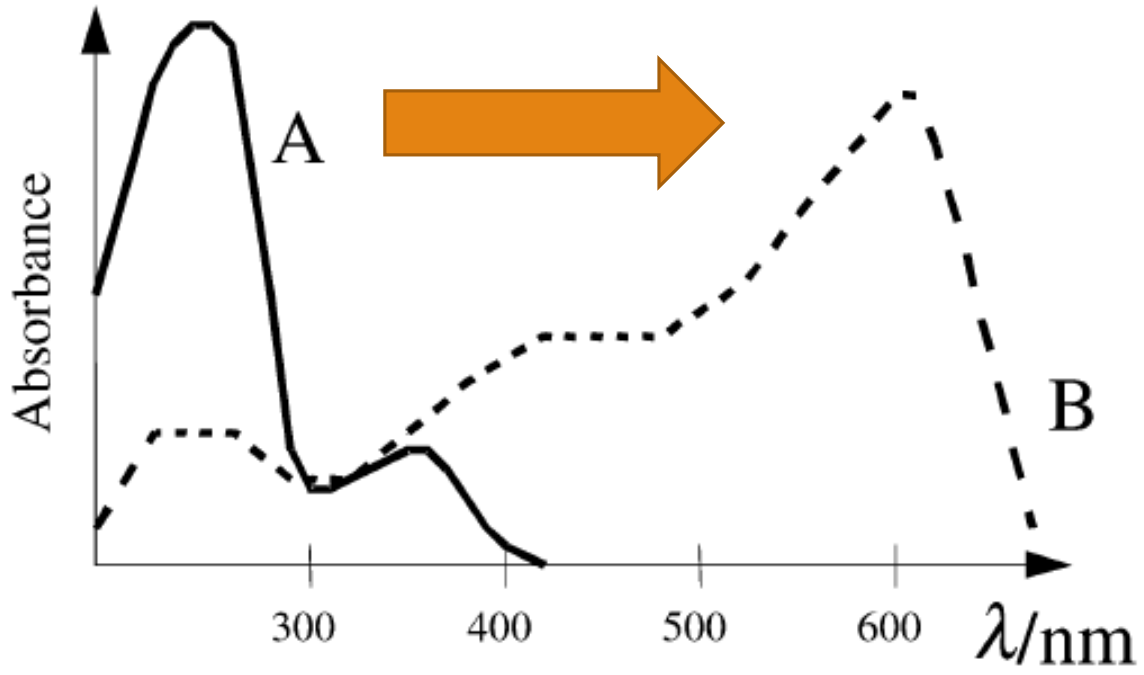


Photochromism

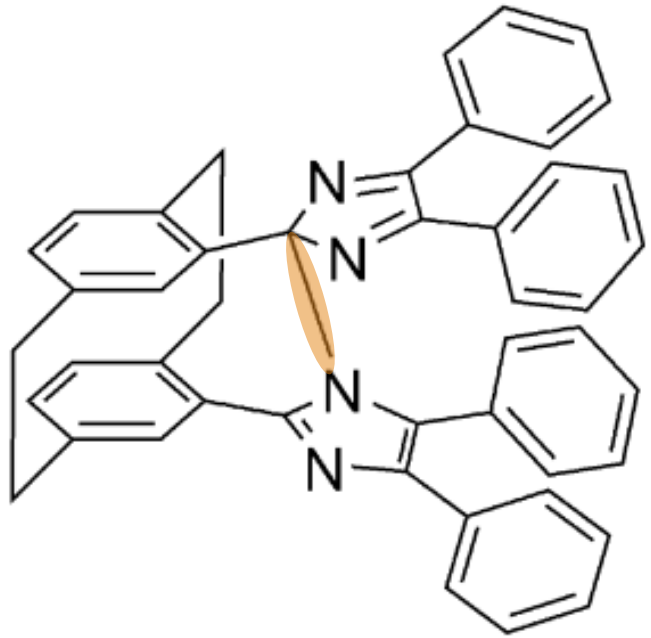
AHIT KAAN TARHAN

30.09.20

J. Am. Chem. Soc. 2009, 131 (12), 4227–4229.

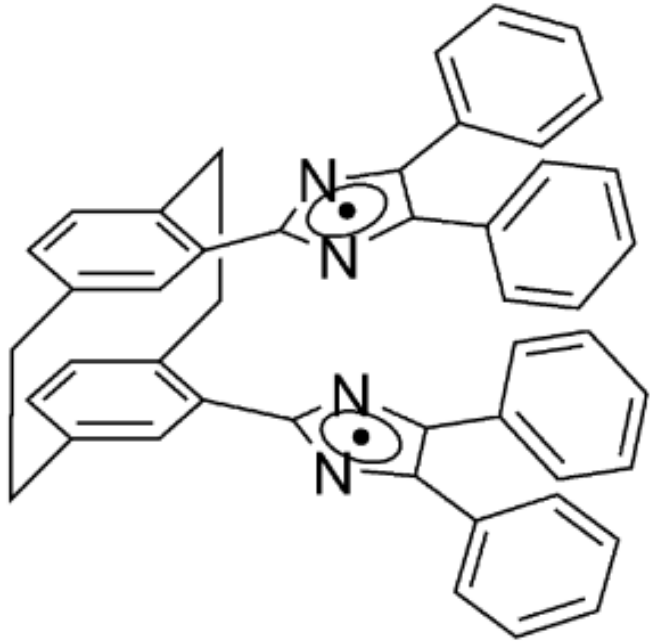


$$A \underset{h\nu_2 \text{ or } \Delta}{\overset{h\nu_1}{\rightleftharpoons}} B$$



$h\nu$

Δ



pseudogem-bisDPI[2.2]PC

transparent

pseudogem-bisDPIR[2.2]PC

blue

Contemporary Photochromism

Contemporary Photochromism

Photochromism of Diarylethene Molecules and Crystals: Memories, Switches, and Actuators

Masahiro Irie*†, Tuyoshi Fukaminato‡, Kenji Matsuda§, and Seiya Kobatake‖

Photochromism into nanosystems: towards lighting up the future nanoworld

Ling Wang and Quan Li*

Coordination Compounds with Photochromic Ligands: Ready Tunability and Visible Light-Sensitized Photochromism

Chi-Chiu Ko†,‡ and Vivian Wing-Wah Yam*,†

Solid Materials with Tunable Reverse Photochromism

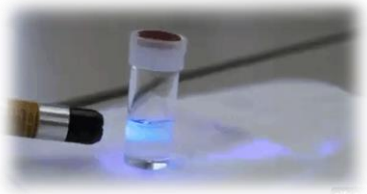
Alex Julià-López, Daniel Ruiz-Molina, Jordi Hernando*, and Claudio Roscini*

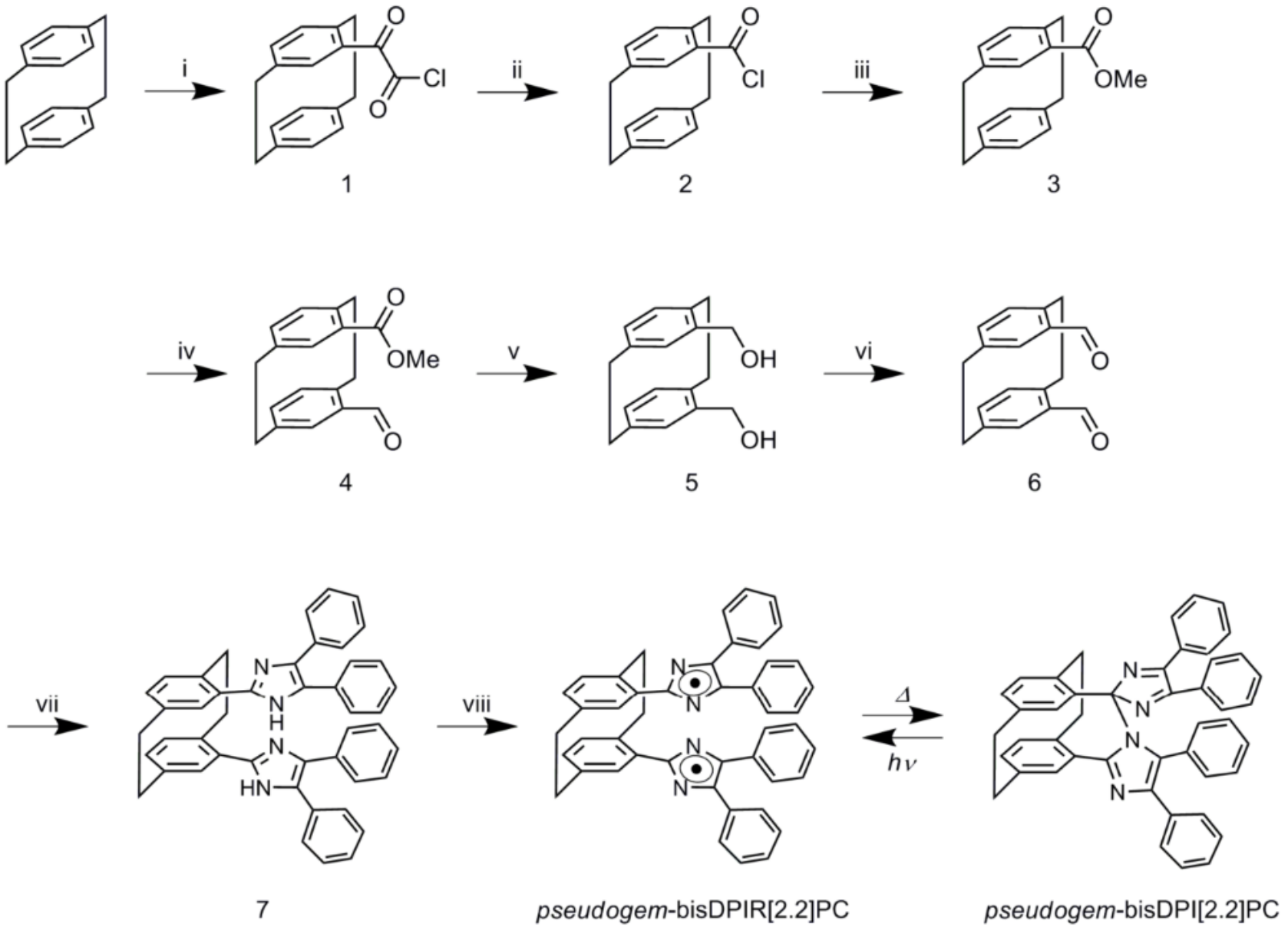
Photochromic Radical Complexes That Show Heterolytic Bond Dissociation

Ryosuke Usui, Katsuya Yamamoto, Hajime Okajima, Katsuya Mutoh, Akira Sakamoto, Jiro Abe*, and Yoichi Kobayashi*

Chem. Rev. 2014, 114 (24), 12174–12277. Chemical Society Reviews 2018, 47 (3), 1044–1097. Acc. Chem. Res. 2018, 51 (1), 149–159. ACS Appl. Mater. Interfaces 2019, 11 (12), 11884–11892. J. Am. Chem. Soc. 2020, 142 (22), 10132–10142.

Synthesis

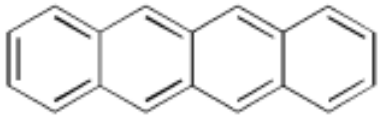



i
ii
iii
iv
v
vi
vii
viii
Cl
OMe
OH
HN
N
H
hν
1
2
3
4
5
6
7
pseudogem-bisDPIR[2.2]PC
pseudogem-bisDPI[2.2]PC

History

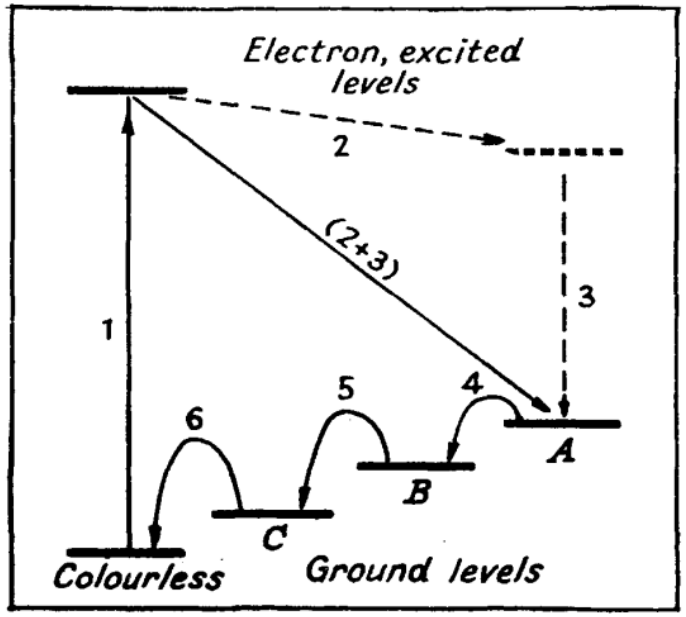
1867

orange $\underset{\text{heat}}{\overset{h\nu}{\rightleftharpoons}}$ colorless

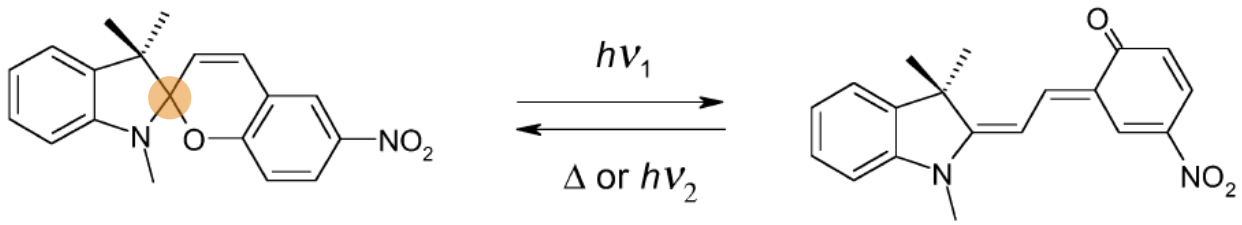


tetracene

1954



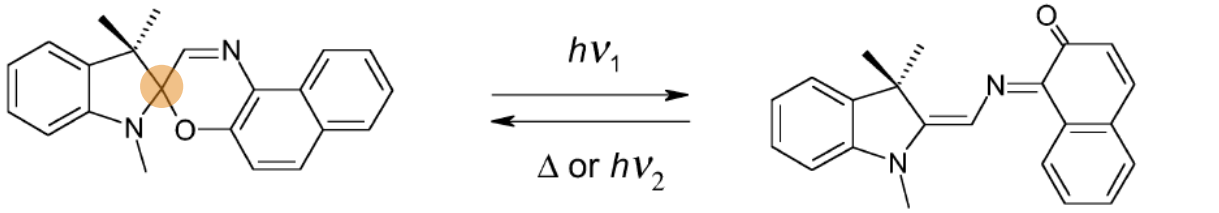
1960s: Spiropyrans



Closed Form

Open Form (Merocyanine)
(Quinonic form)

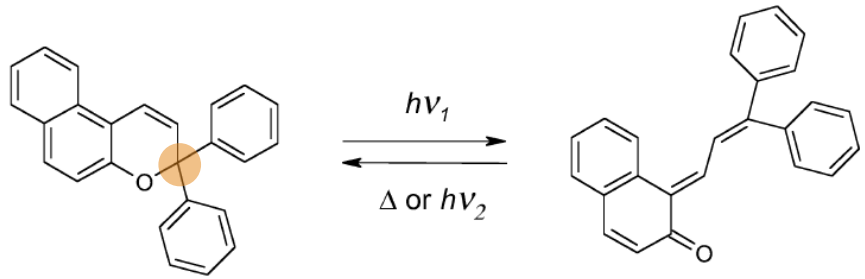
1980s: Spirooxazines



Closed Form

Open Form (Merocyanine)
(Quinonic form)

Chromenes



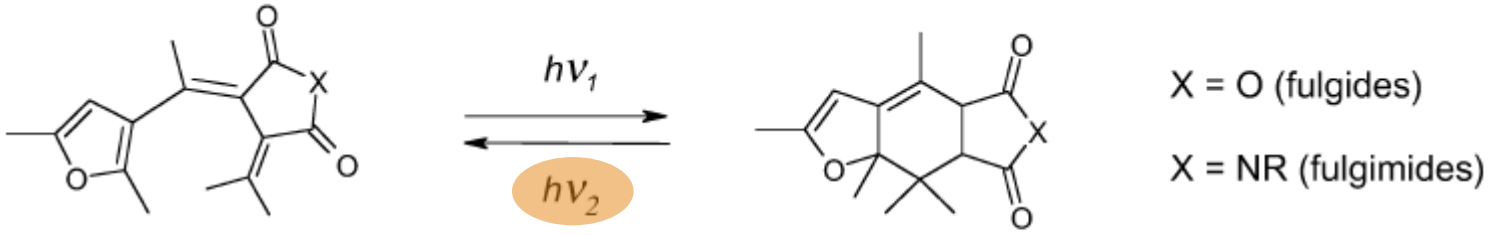
Closed Form

Open Form

Pure and Applied Chemistry 2001, 73 (4), 639–665.

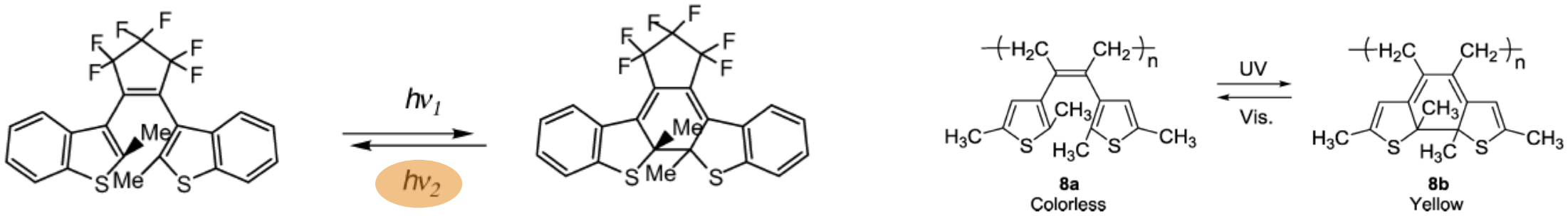
Pure and Applied Chemistry 2001, 73 (4), 639–665.

1980s: Fulgides, Fulgimides



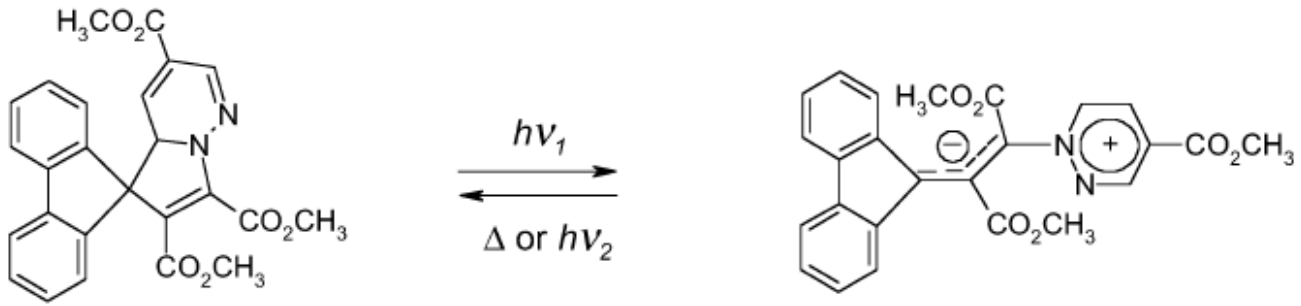
Open Form Closed Form

1990s: Diarylethenes



Open Form Closed Form

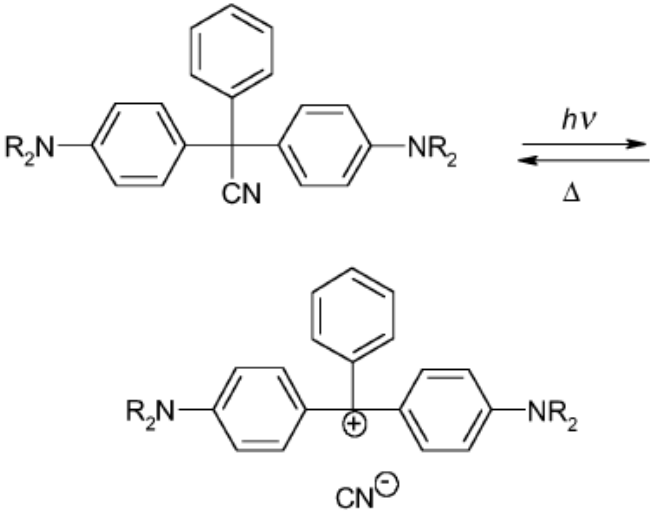
Spirodihydroindolizines: Pericyclic



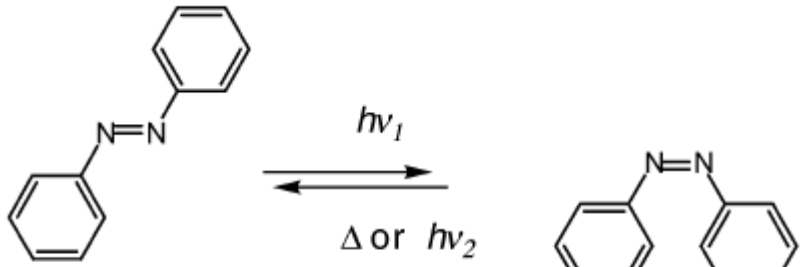
Closed Form

Open Form

Triarylmethanes: σ-bond dissociation



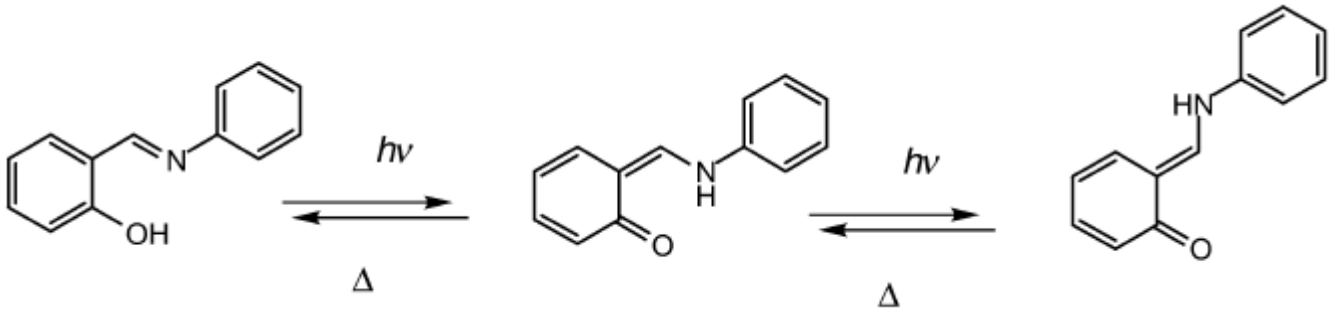
Azobenzenes: (E/Z isomerization)



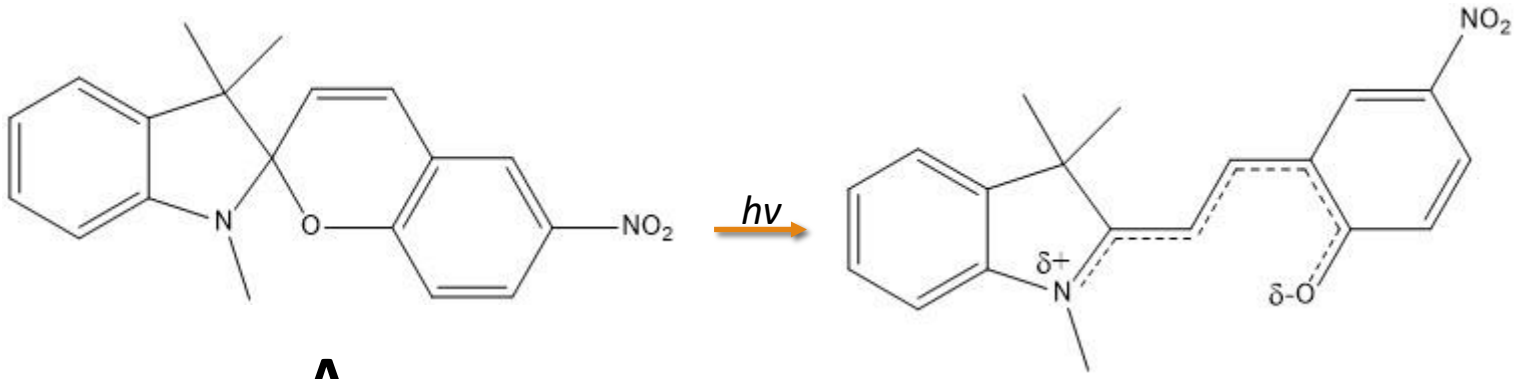
trans (anti)

cis (syn)

Anils: Tautomerization

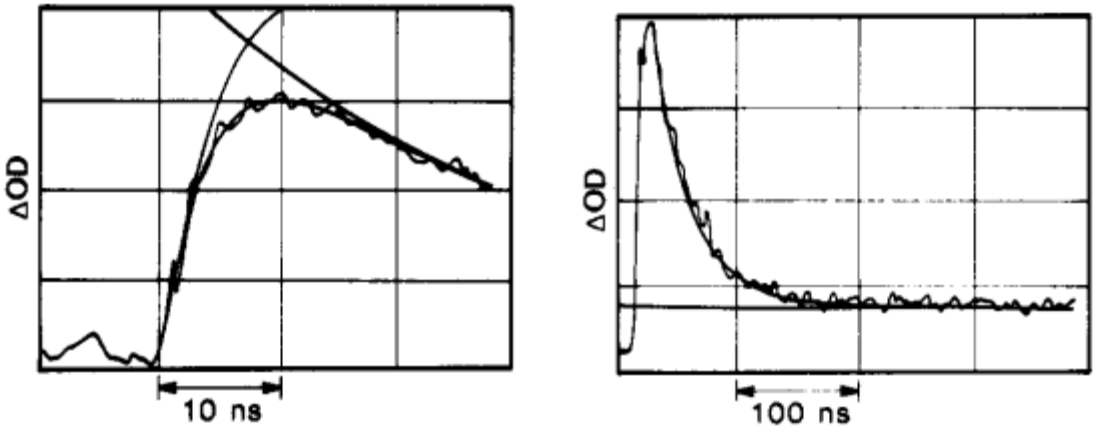


T-type Mechanism

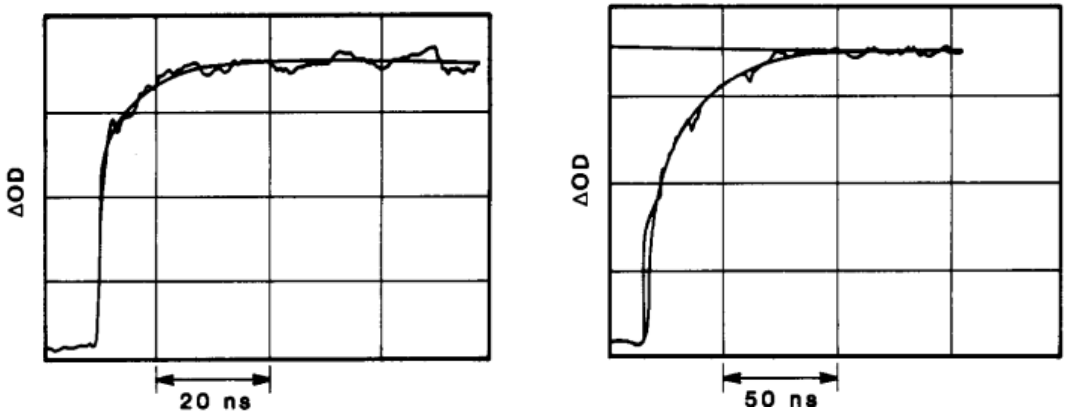


A **B**

Abs 430nm

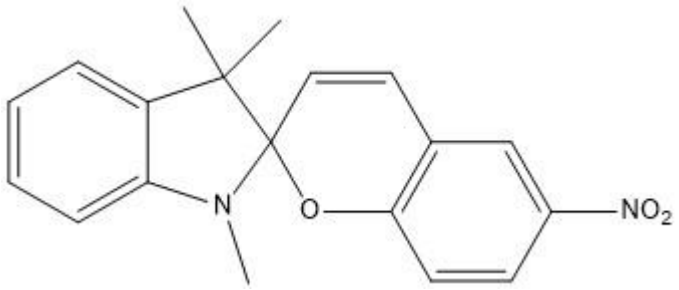


Abs 570nm

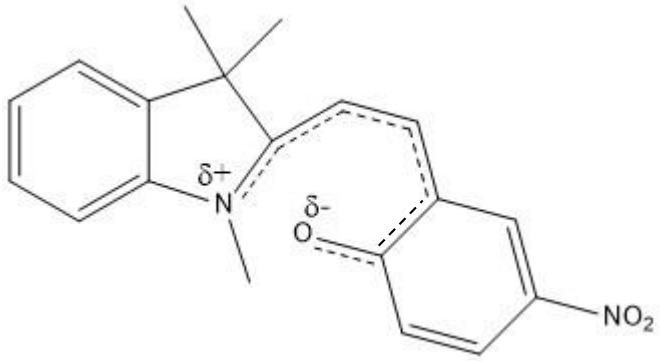


J. Phys. Chem. 1986, 90 (1), 62–65

A —*hv*→ **^{3}A*** —*270 ps*→ **^{3}X** —*10 ns*→ **B**

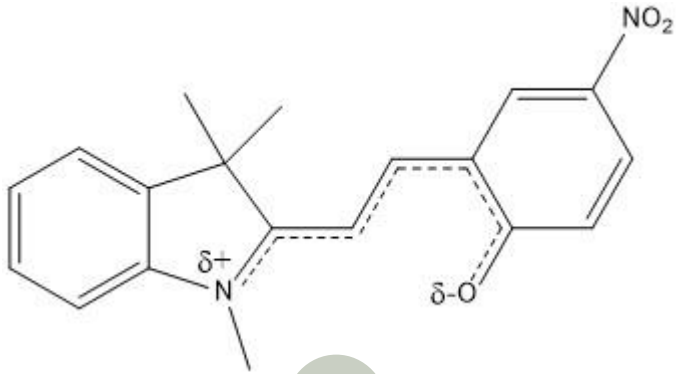


A



^{3}X

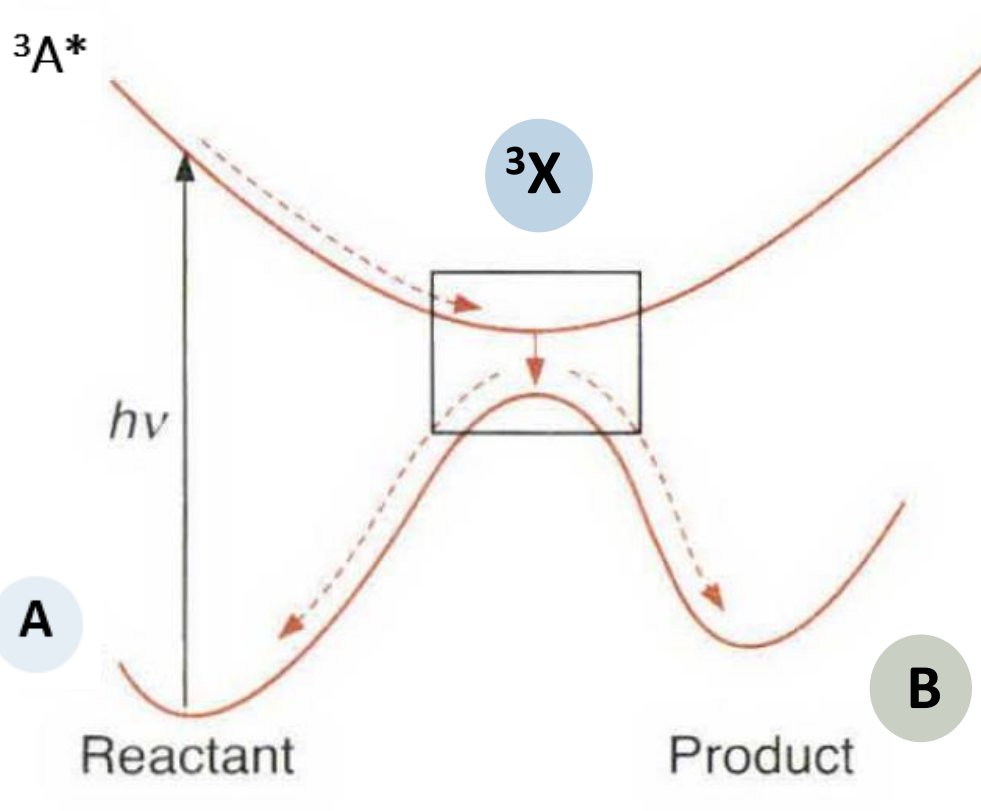
430 nm

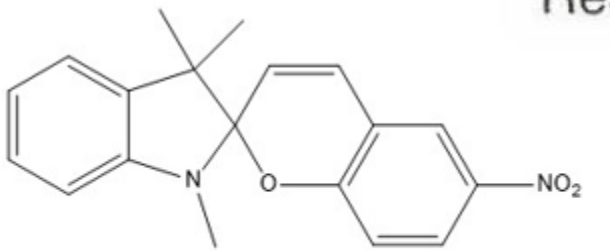


B

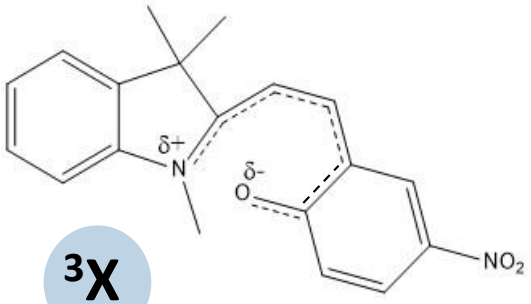
370nm, 530 nm, 570 nm

J. Phys. Chem. 1986, 90 (1), 62–65

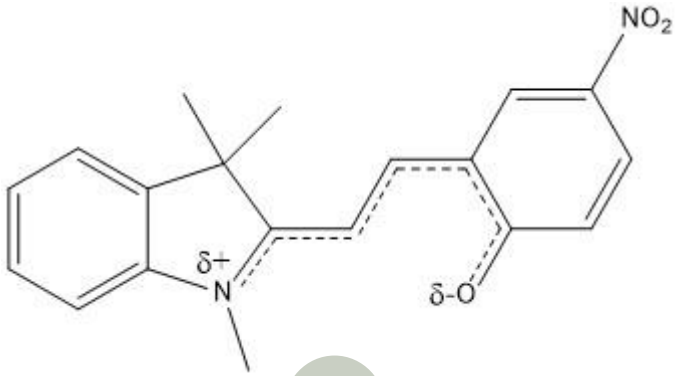

$^3A^*$
^3X
$h\nu$
A
B
Reactant
Product


N
O
NO_2

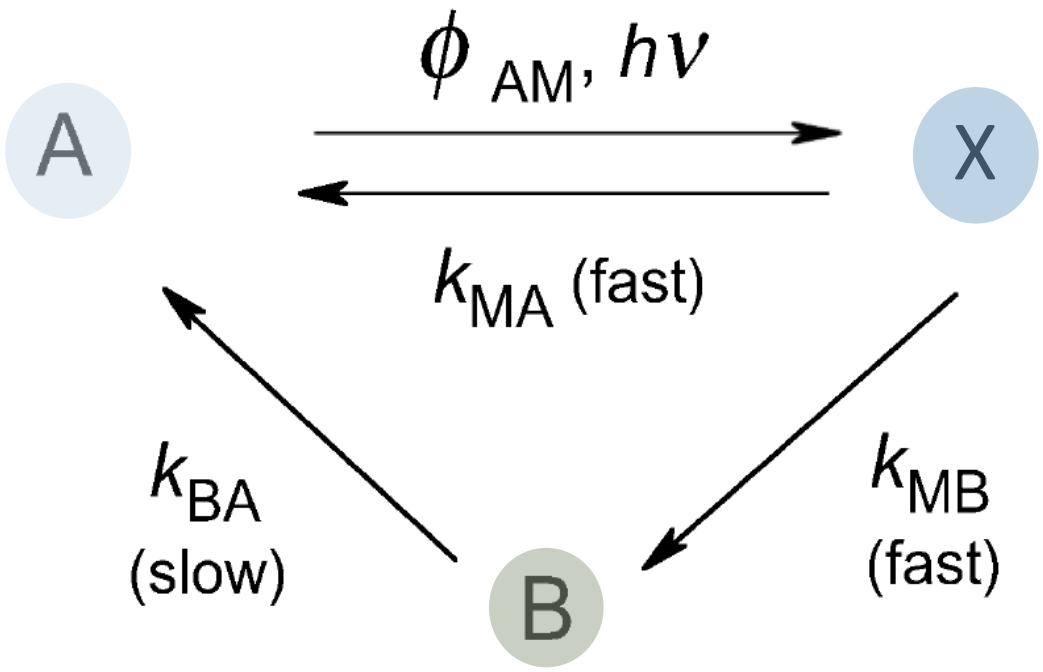
A

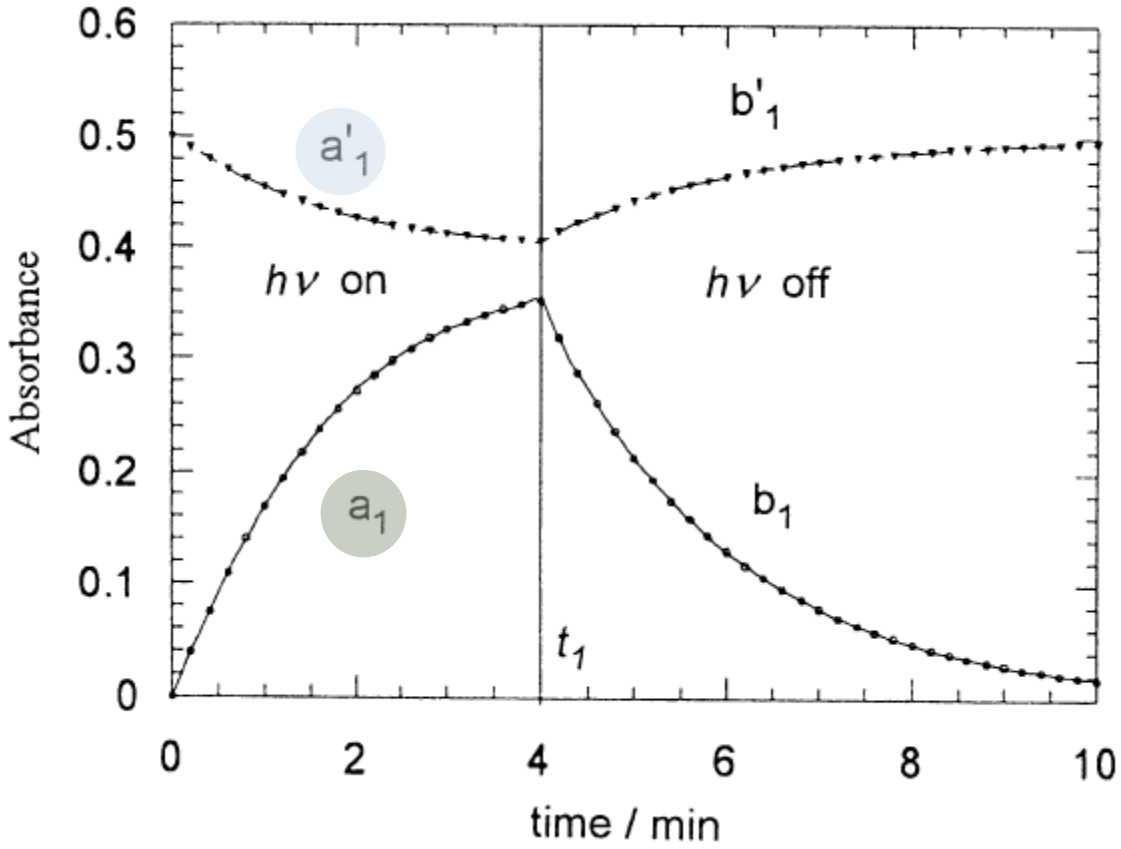

$\delta+$
N
$\delta-$
O
NO_2

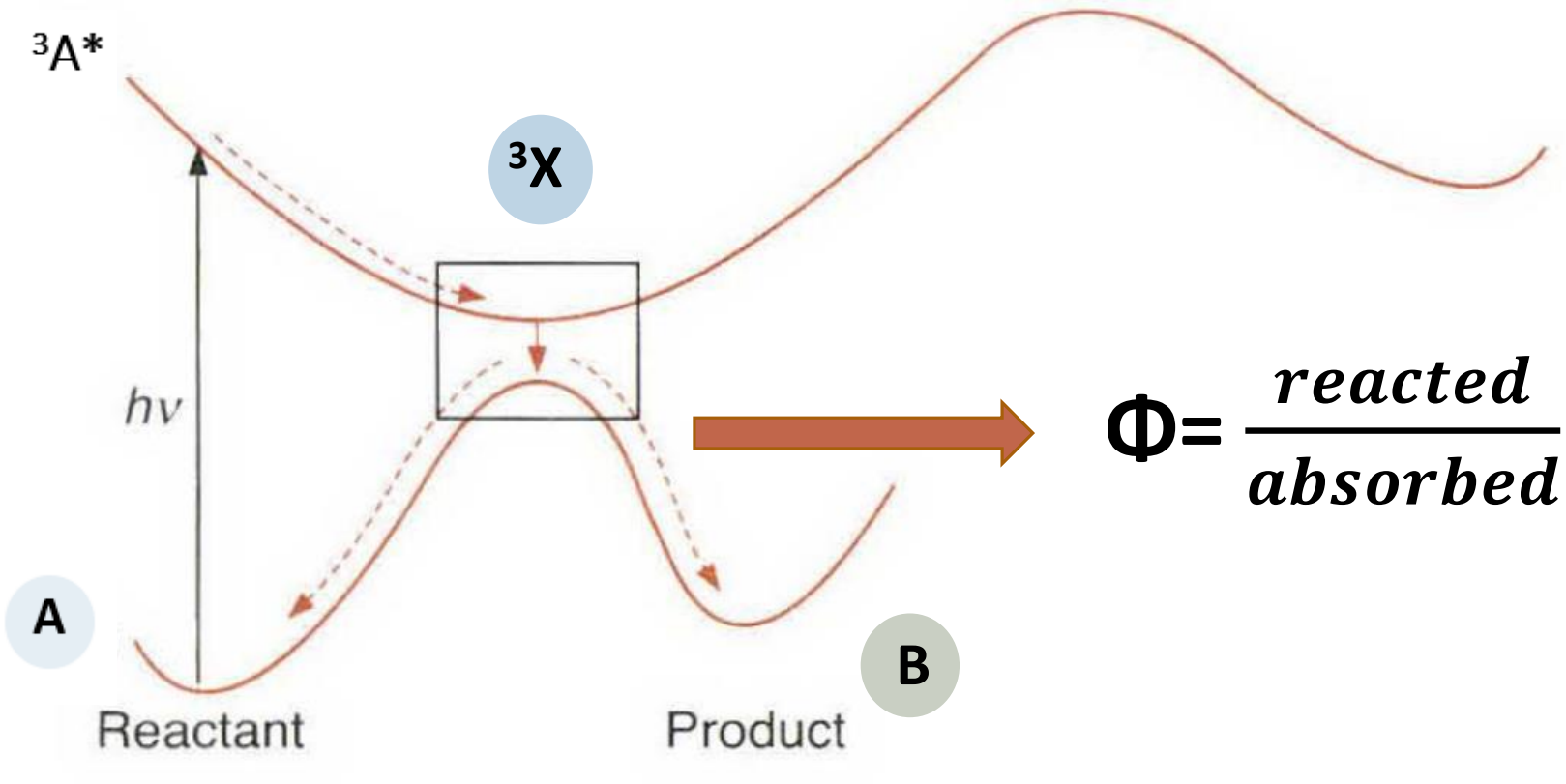
^3X


NO_2
$\delta+$
N
δ-O

B

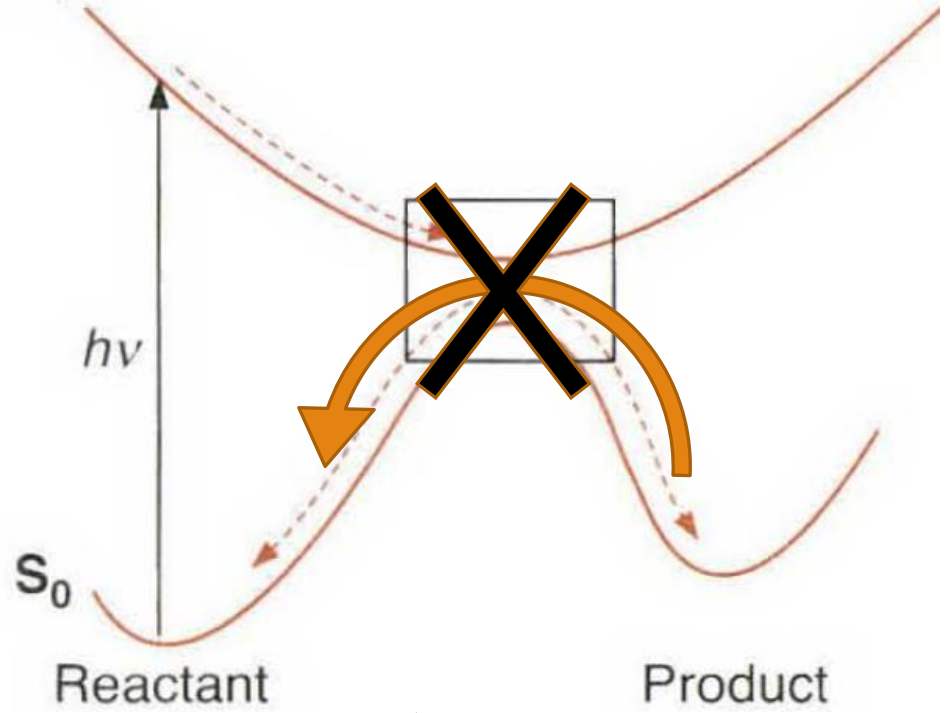

A
X
B
$\phi_{AM}, h\nu$
k_{MA} (fast)
k_{BA} (slow)
k_{MB} (fast)


Absorbance
time / min
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8
10
a'1
b'1
hν on
hν off
a1
b1
t1

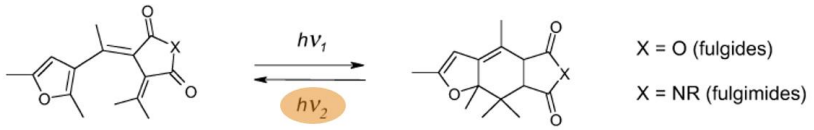


$$\Phi = \frac{reacted}{absorbed}$$

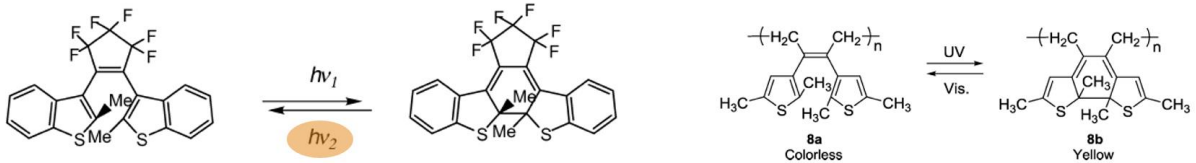
P-type Mechanism



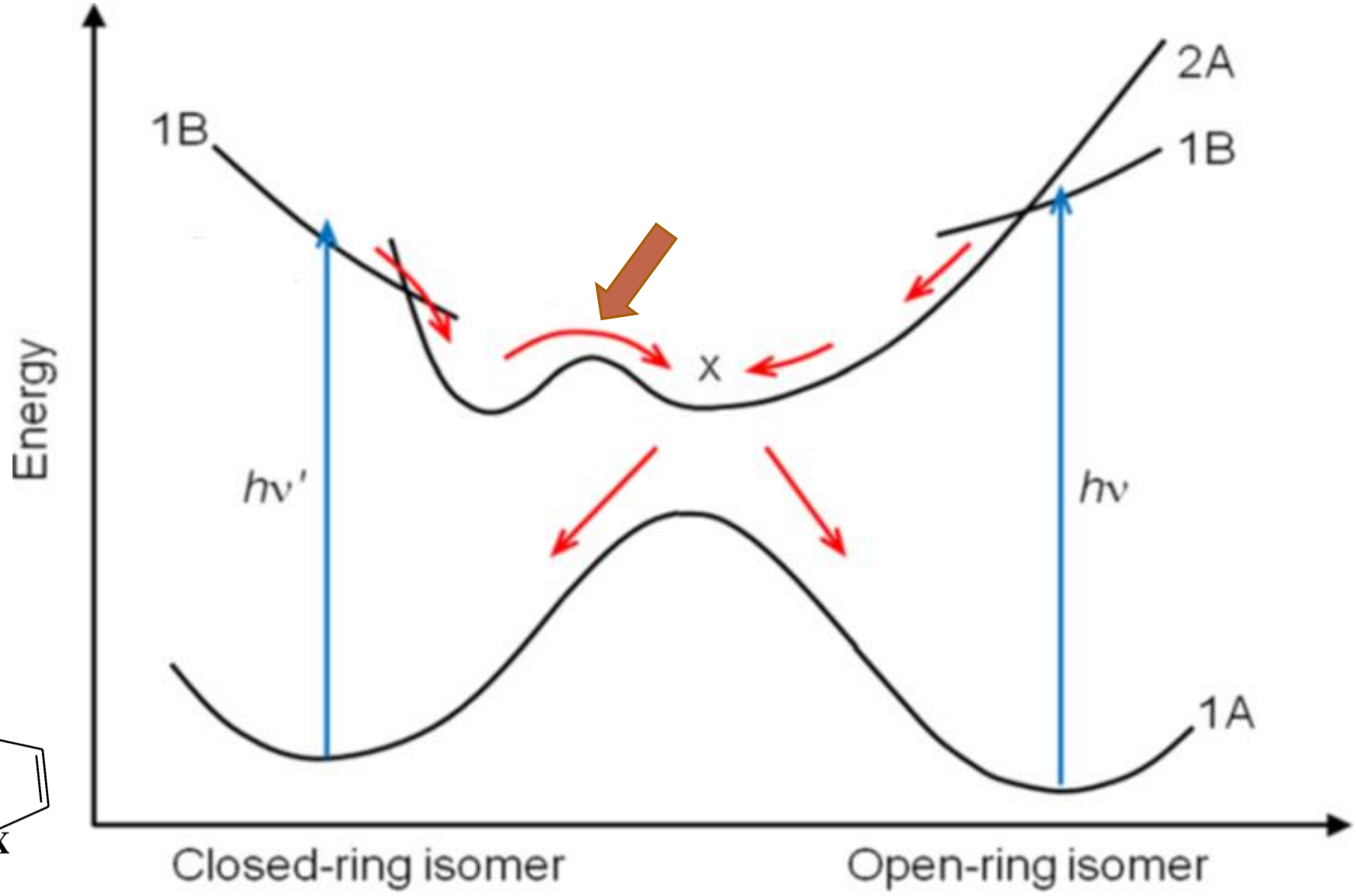
1980s: Fulgides, Fulgimides

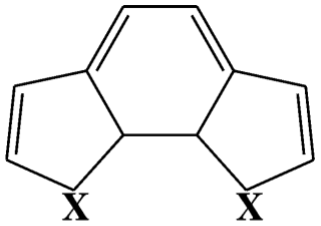


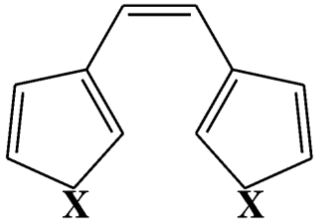
1990s: Diarylethenes



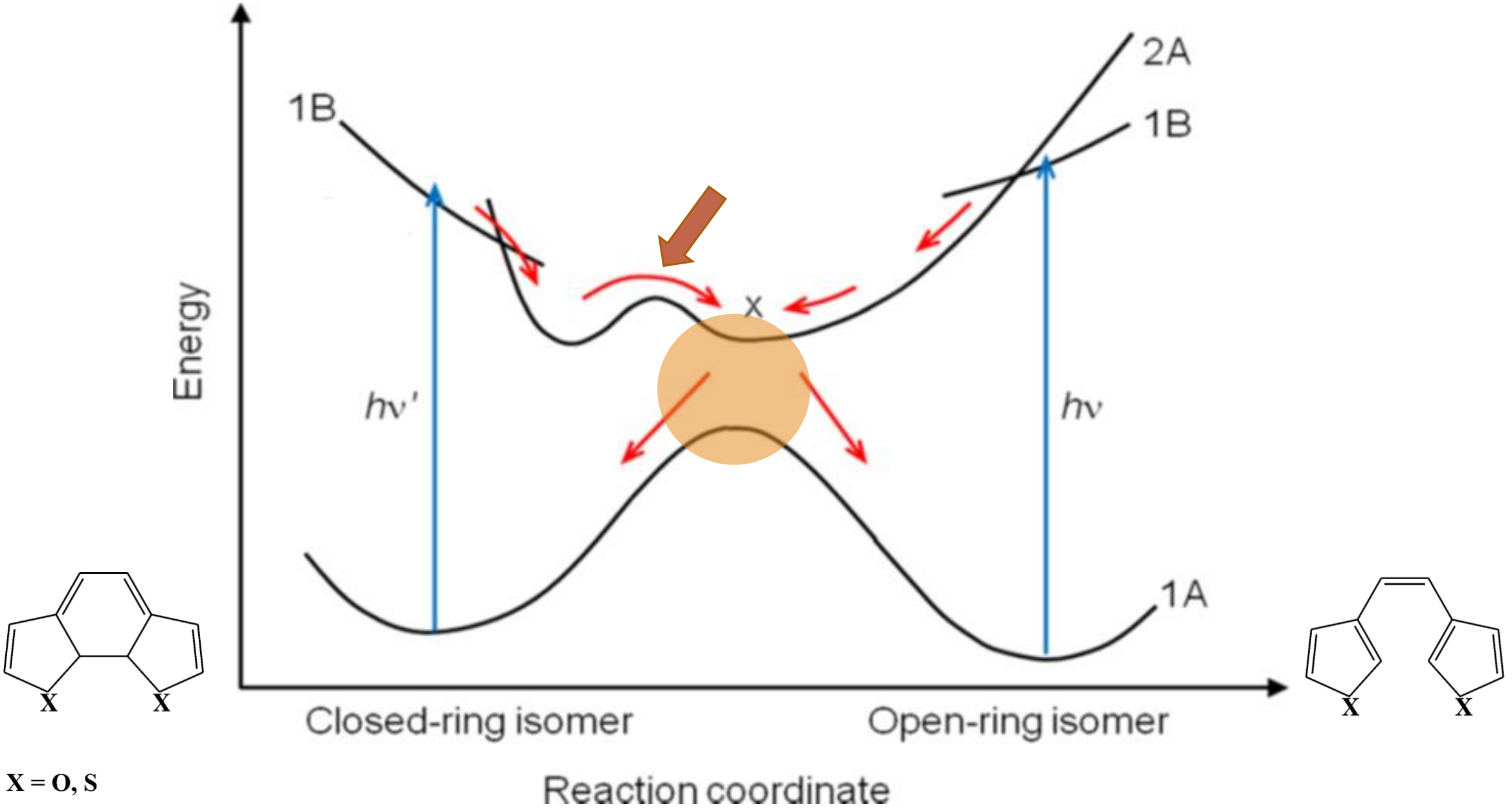
Pure and Applied Chemistry 2001, 73 (4), 639–665. Chem. Rev. 2014, 114 (24), 12174–12277. 9


2A
1B
1B
X
Energy
hν'
hν
1A
Closed-ring isomer
Open-ring isomer
Reaction coordinate


X
X


X
X

X = O, S

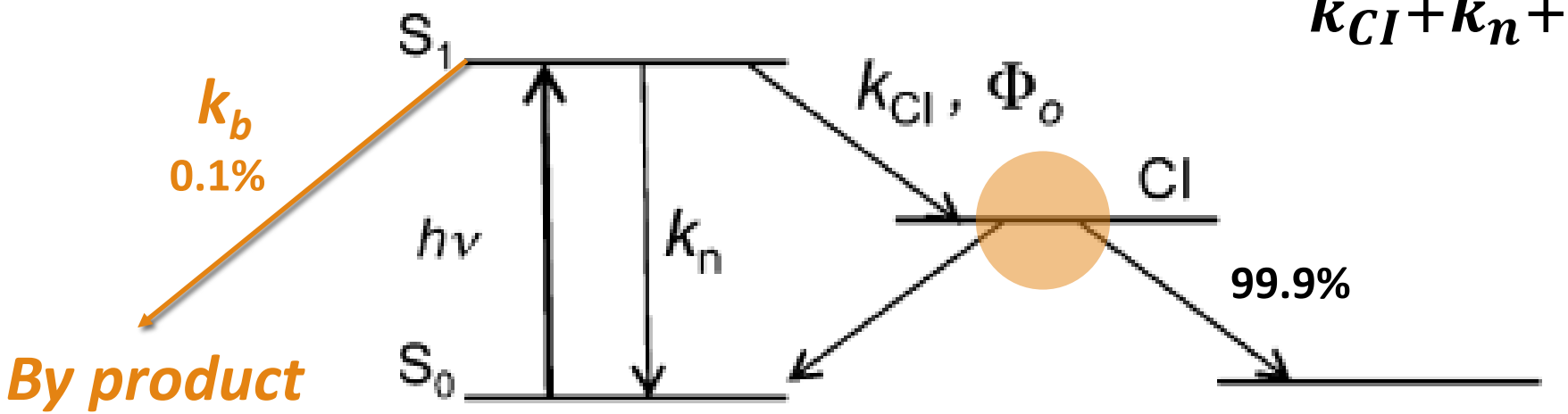

2A
1B
1B
X
Energy
hν'
hν
1A
Closed-ring isomer
Open-ring isomer
Reaction coordinate

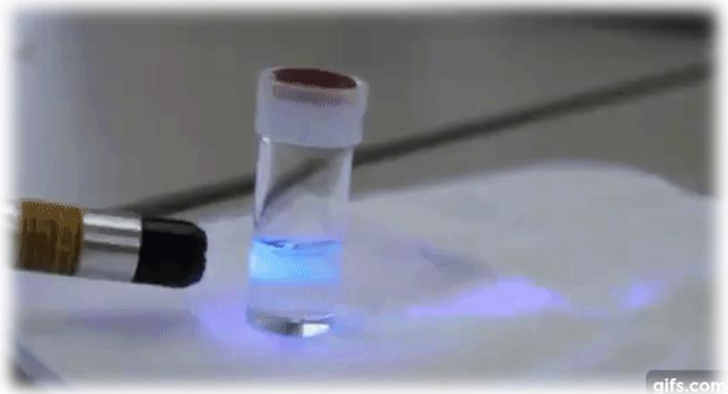
X = O, S

Fatigue ≈10^4

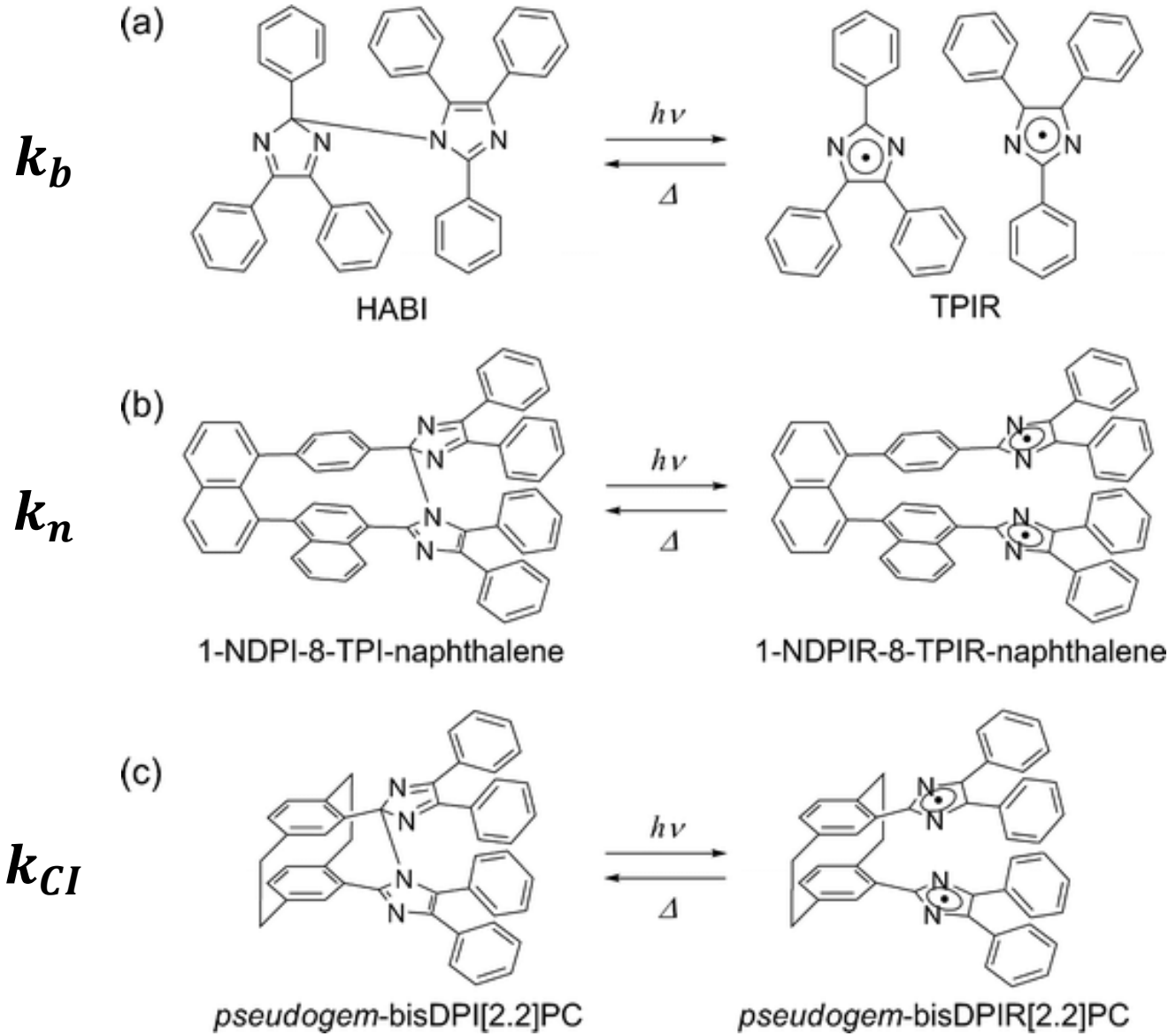
$$\Phi_o = \frac{k_{CI}}{k_{CI}+k_n}$$

$$\Phi = \frac{k_{CI}}{k_{CI}+k_n+k_b}$$

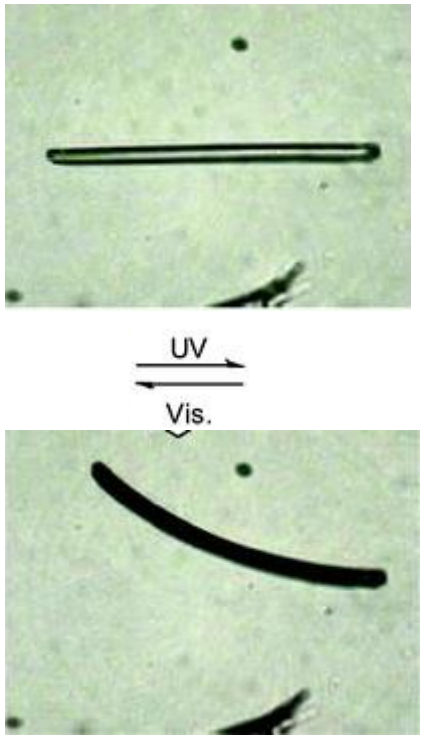


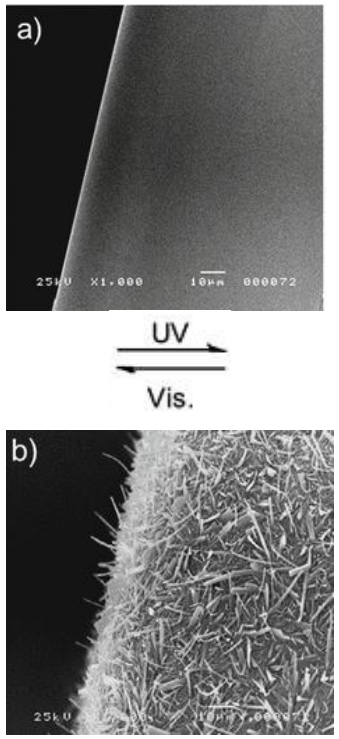


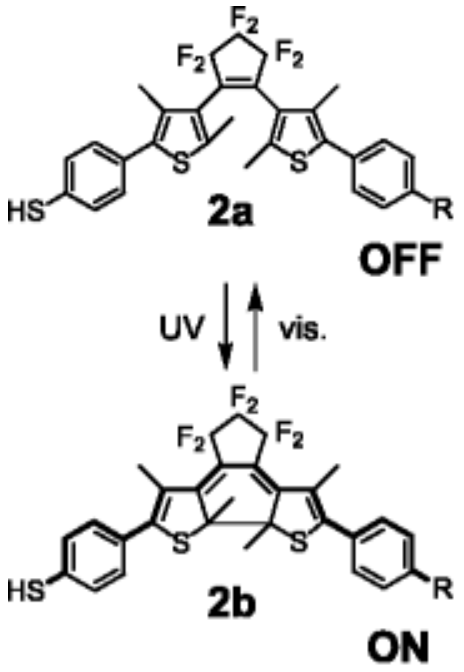
$$\Phi = \frac{k_{CI}}{k_{CI} + k_n + k_b}$$



Applications

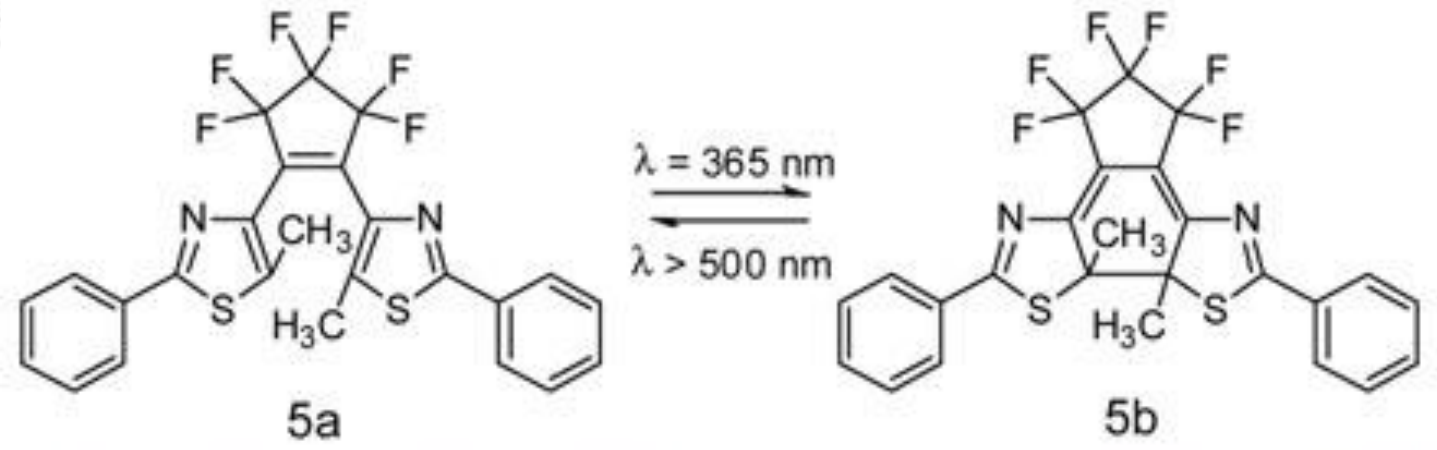


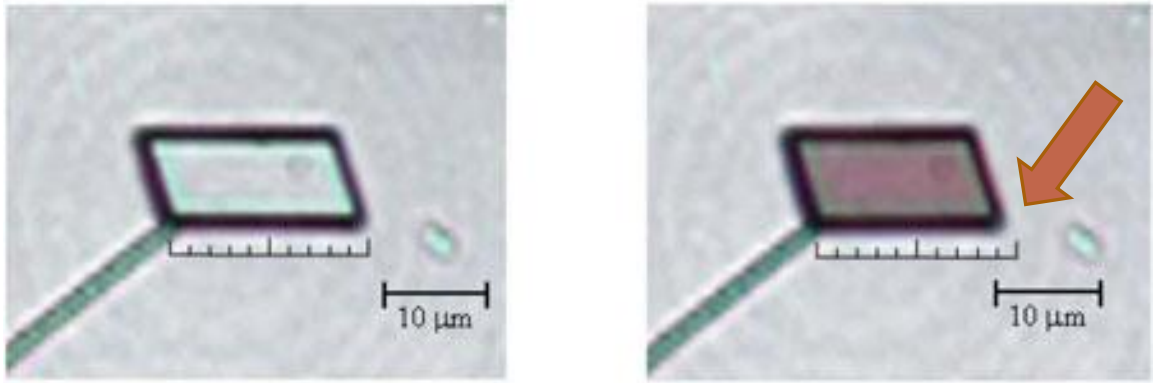


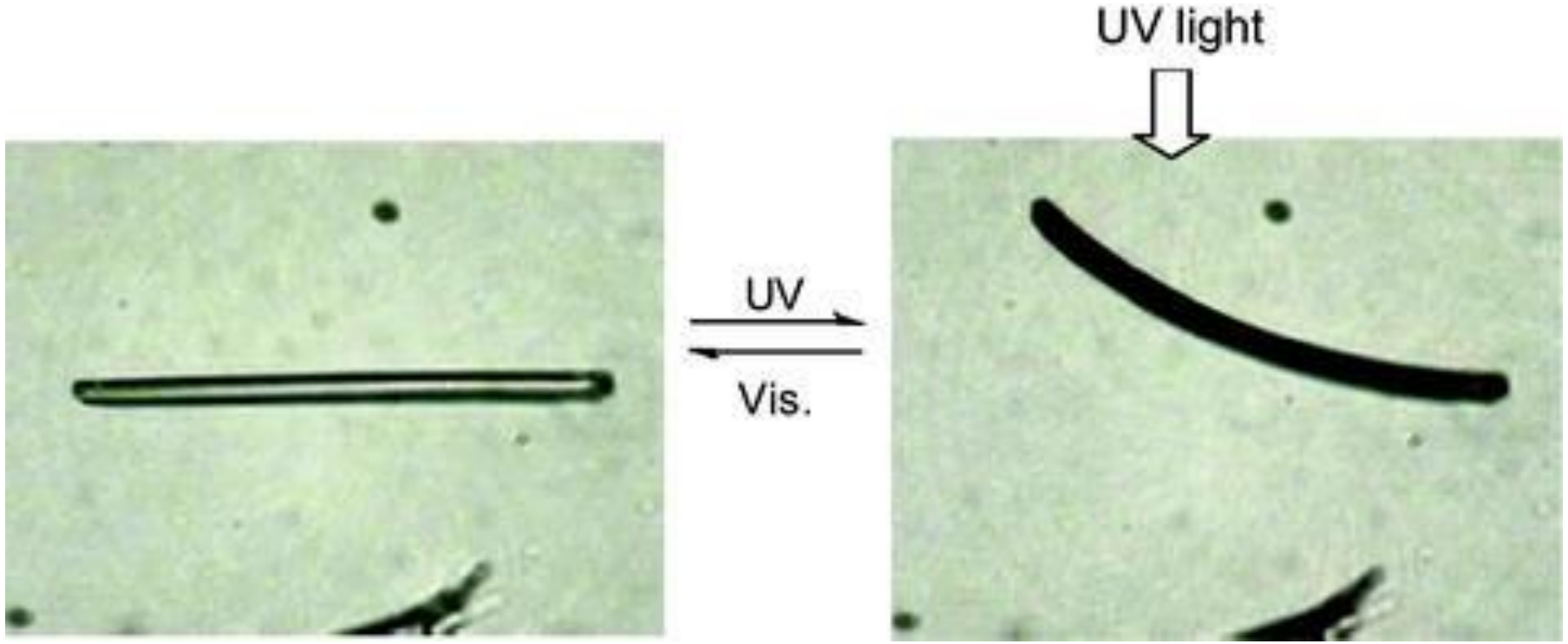


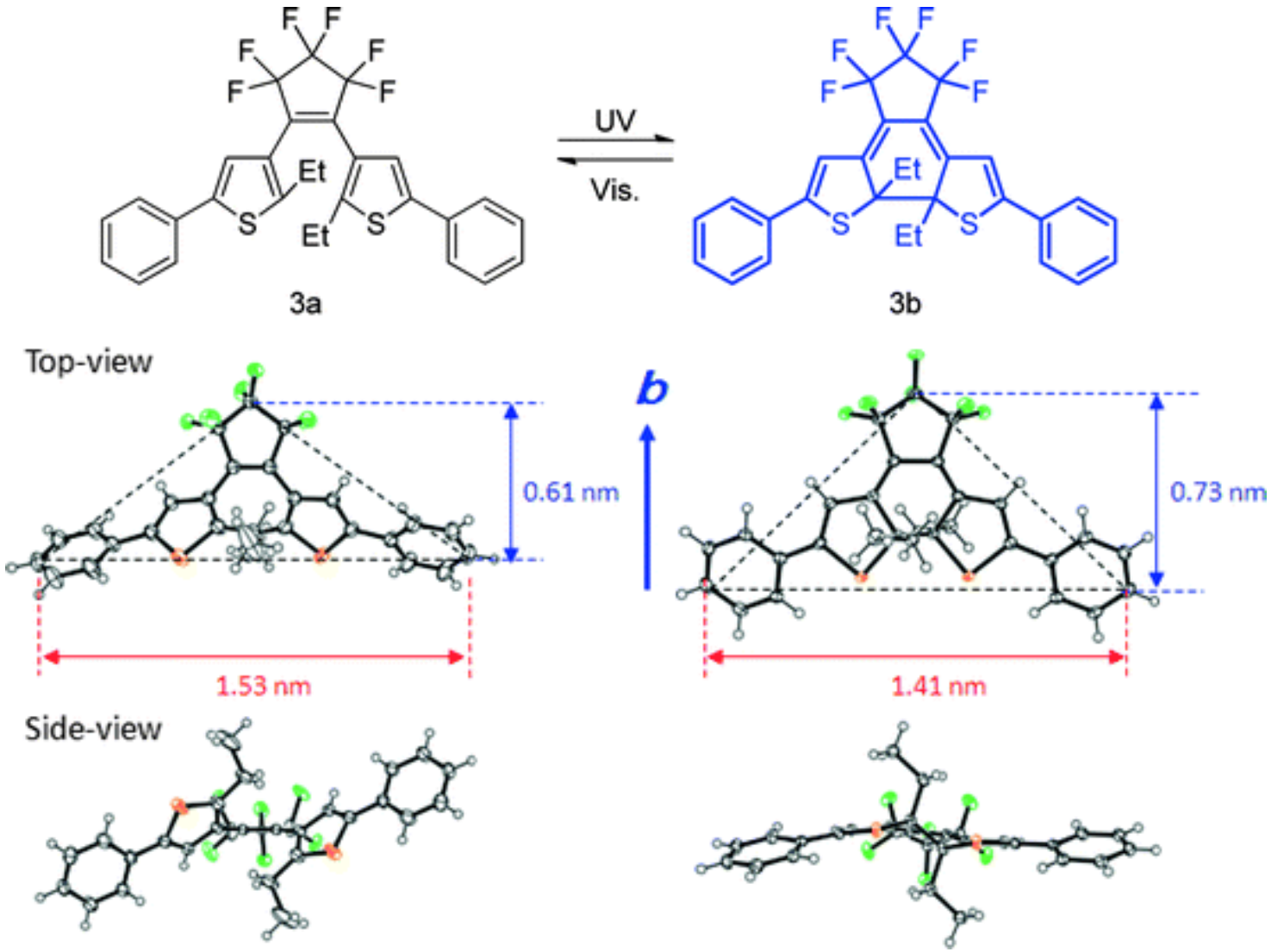
New Frontiers in Photochromism; Springer Japan: Tokyo, 2013; pp 3-19, pp 101-116. Advances in Organic Crystal Chemistry: Springer Japan: Tokyo, 2015; pp 549–568.

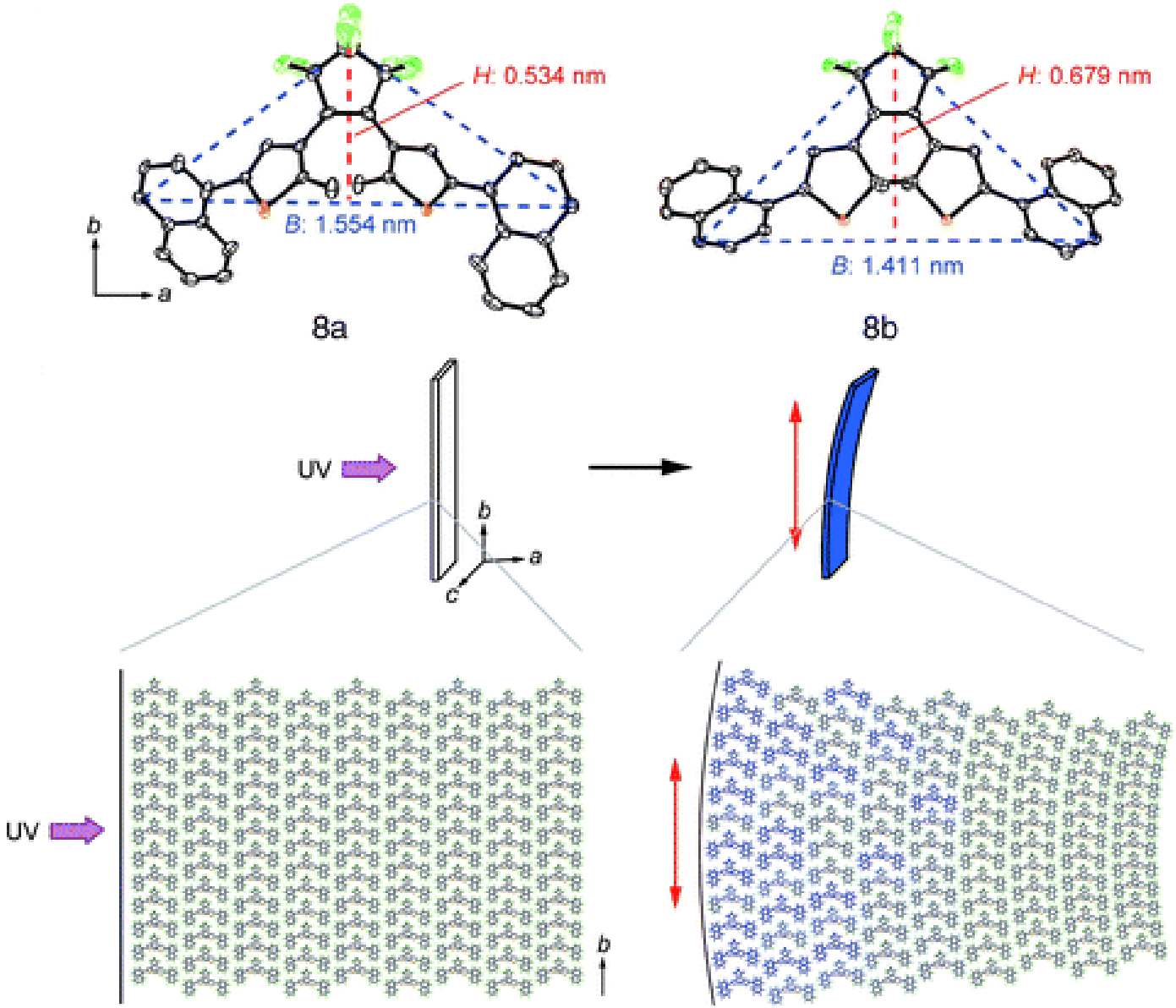
Photomechanical Response of Diarylethene Single Crystals



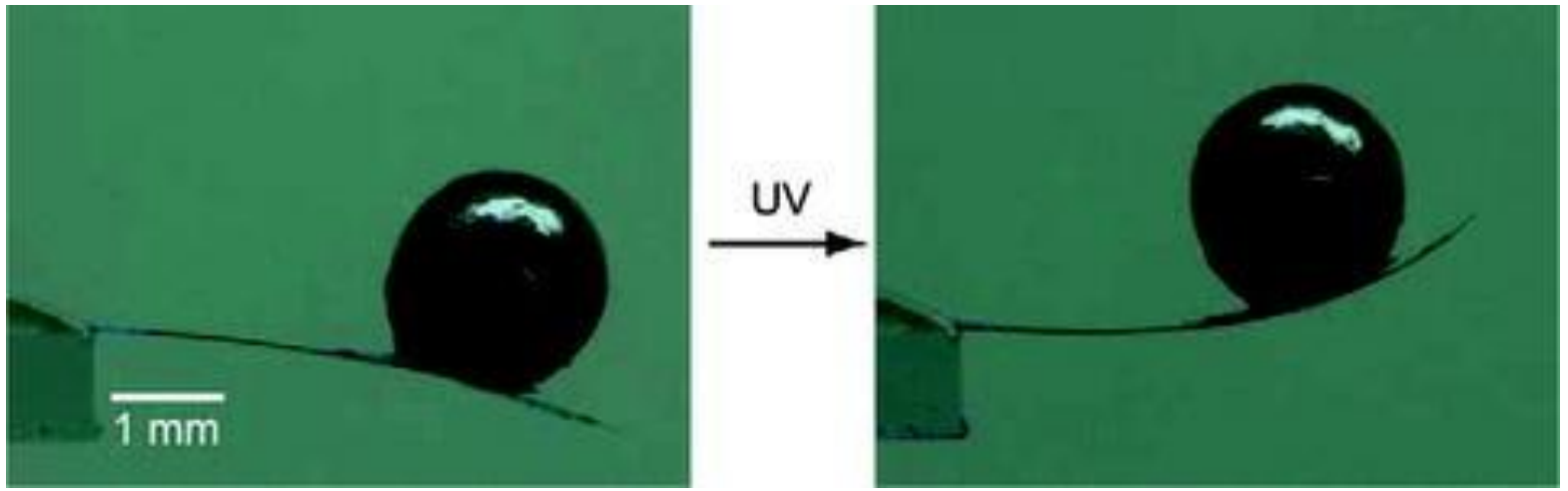



UV light
UV
Vis.

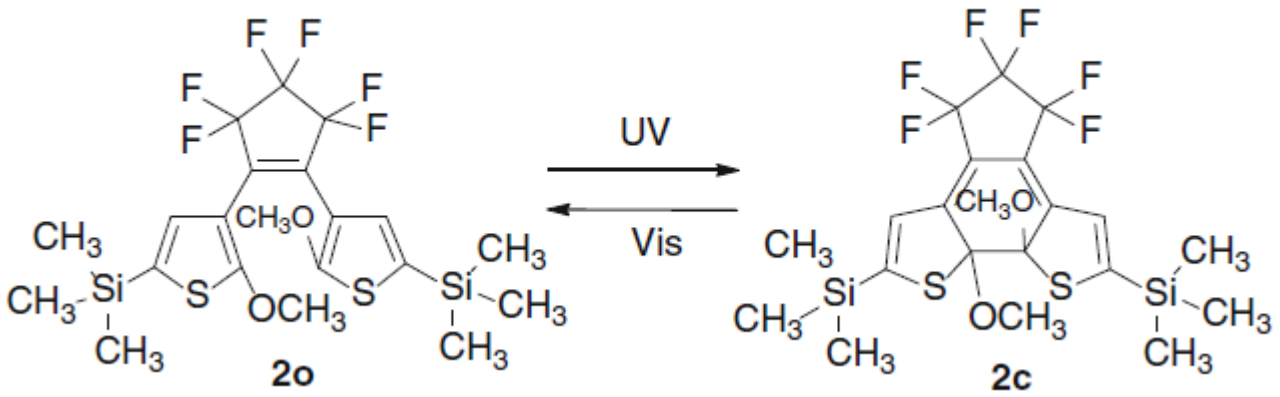

F
F
F
F
F
F
Et
S
Et
S
UV
Vis.
3a
3b
Top-view
0.61 nm
1.53 nm
b
0.73 nm
1.41 nm
Side-view

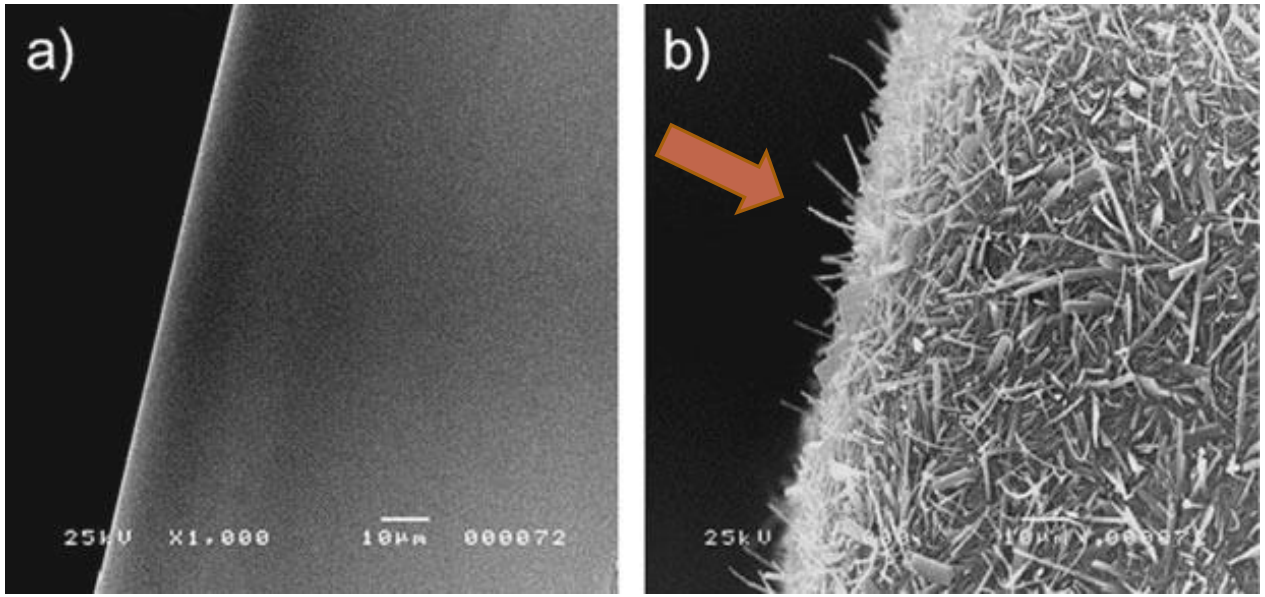

H: 0.534 nm
B: 1.554 nm
b
a
8a
H: 0.679 nm
B: 1.411 nm
8b
UV
b
a
c
UV
b

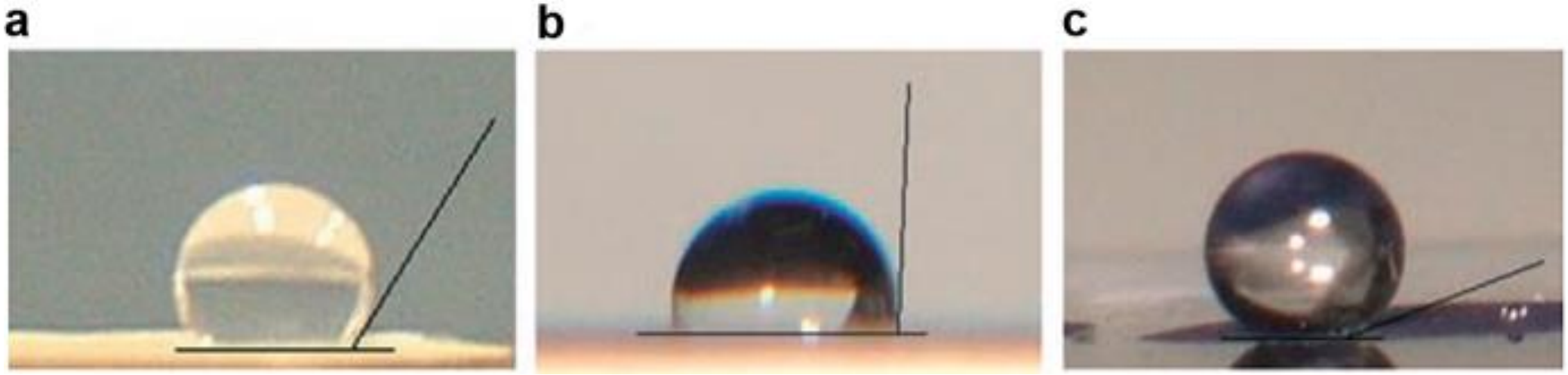
Young's Modulus ← $E = \frac{\sigma}{\varepsilon}$ → *stress* / *strain*



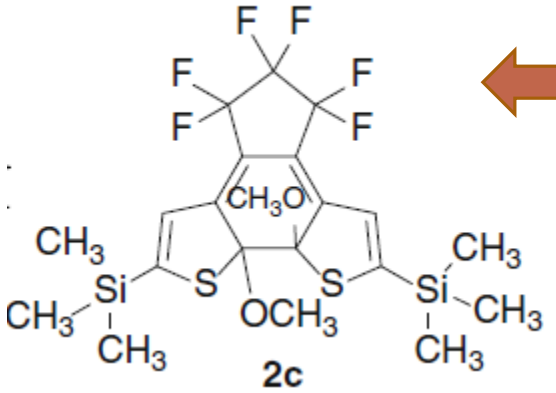
Photoinduced Reversible Topographical Changes of Diarylethene Crystal Surfaces



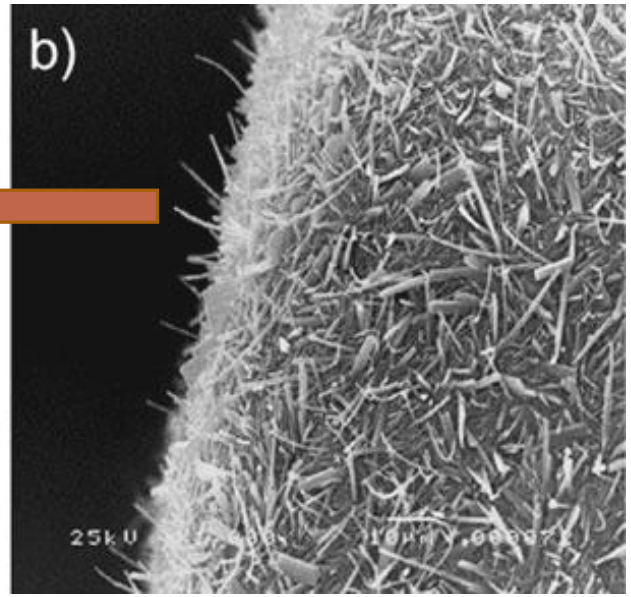


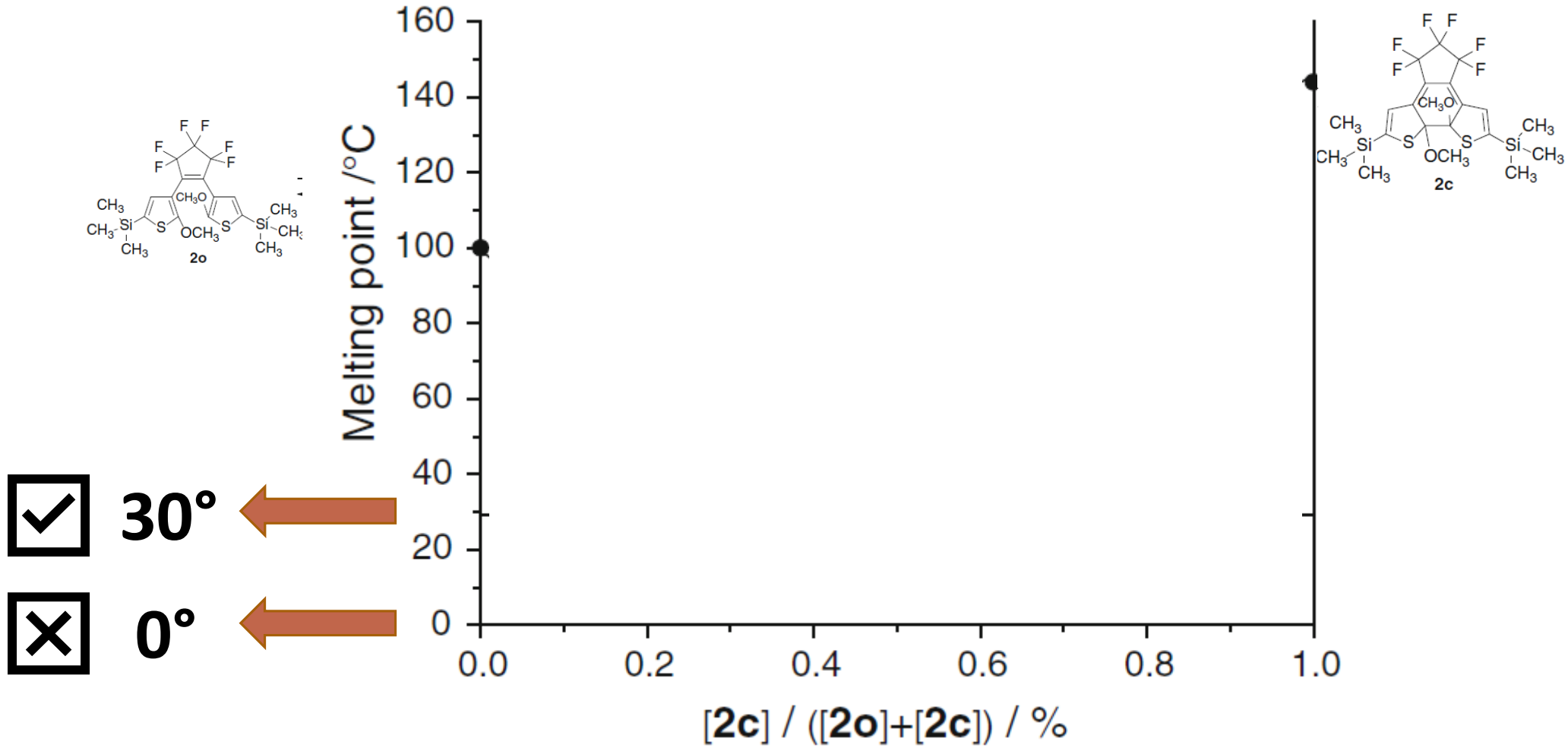


120° **90°** **163°**

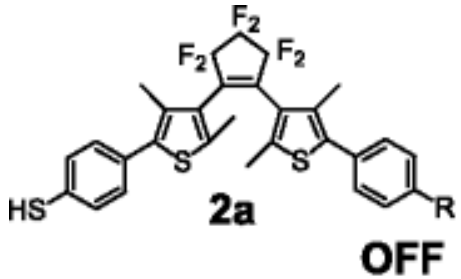


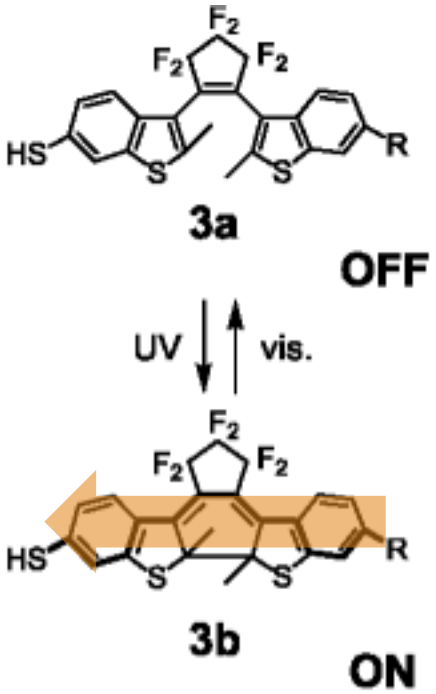
2c





Advances in Organic Crystal Chemistry: Springer Japan: Tokyo, 2015; pp 549–568.


F2
F2
F2
S
S
HS
R
2a
OFF
UV
vis.
2b
ON


F2
F2
F2
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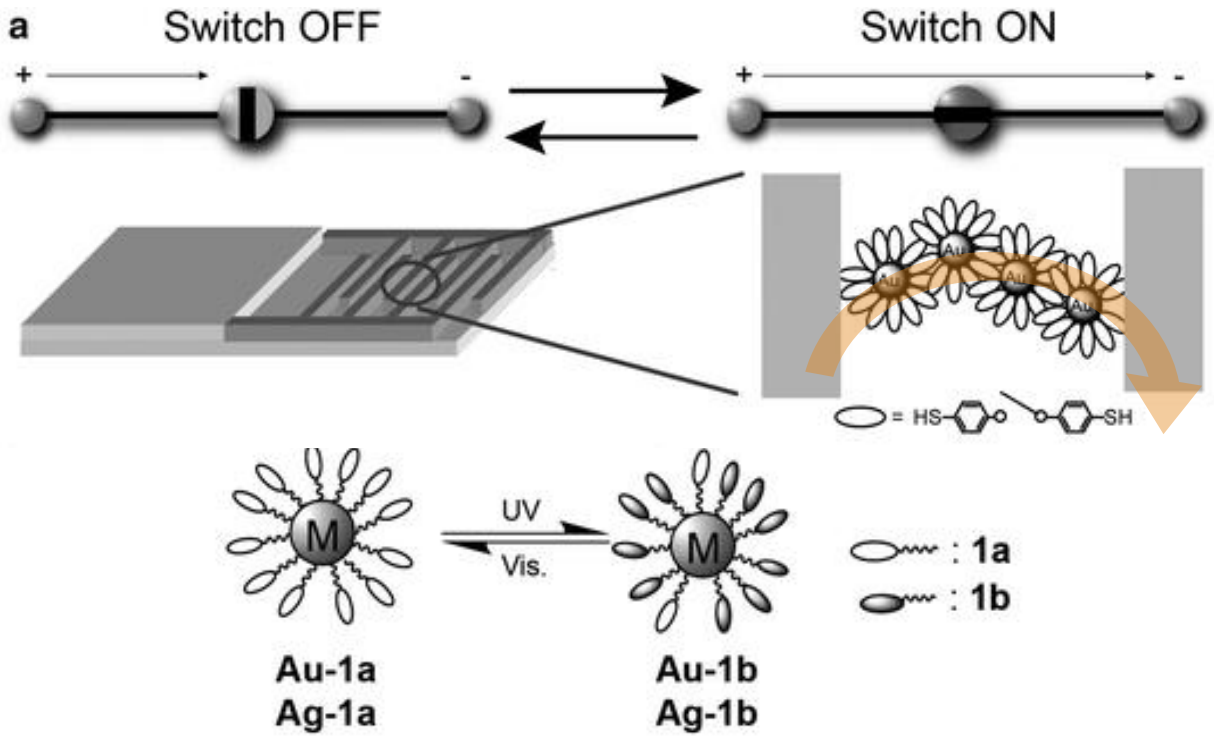
HS
R
3a
OFF
UV
vis.
3b
ON

Conductance Photoswitching of Diarylethene-Gold Nanoparticle Network



Why diarylethenes?

Thermal Stability

High Quantum Yield

Fatigue Resistant

Rapid Kinetics

Solid Phase Photochromism

Thank you for listening!