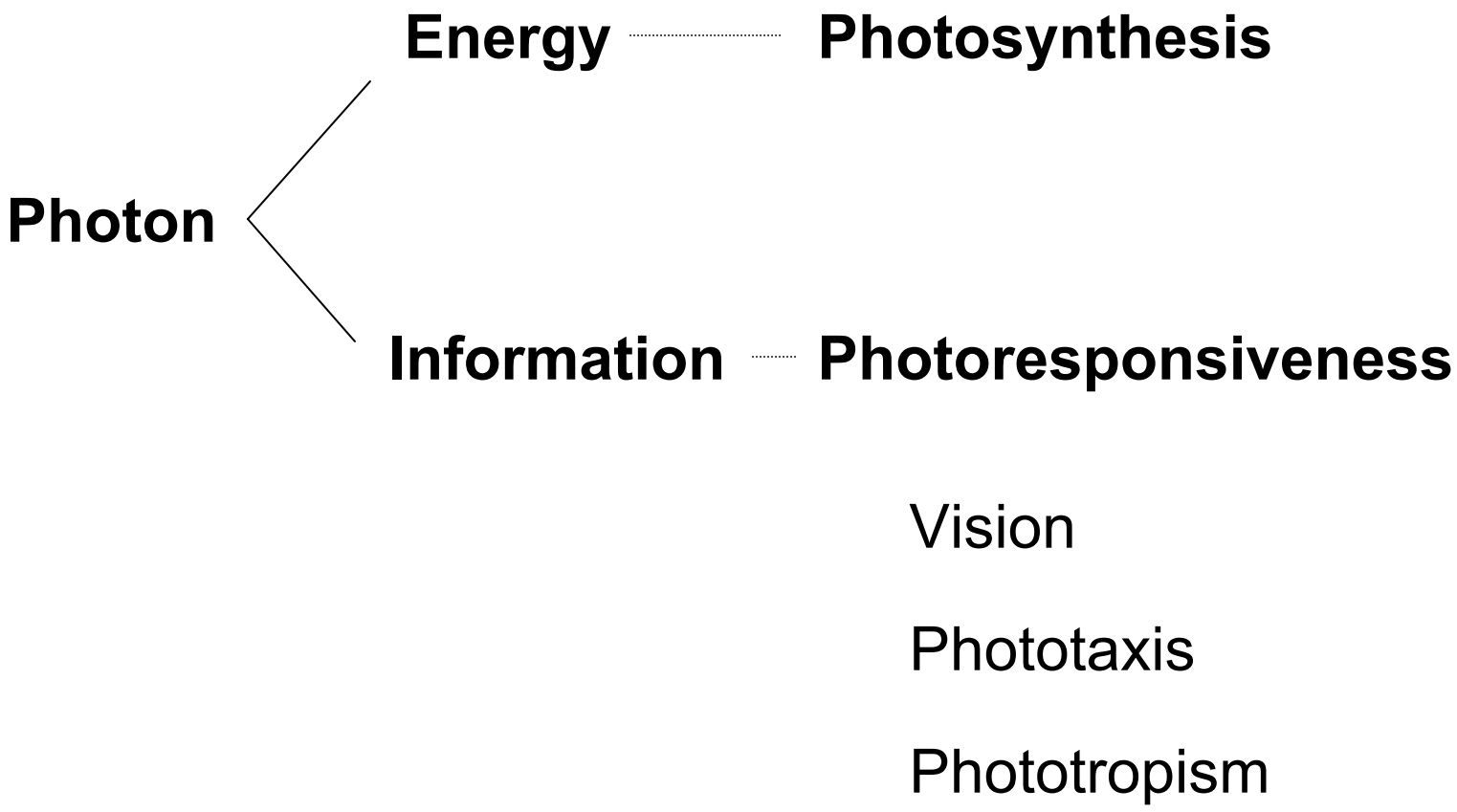
Photochromism

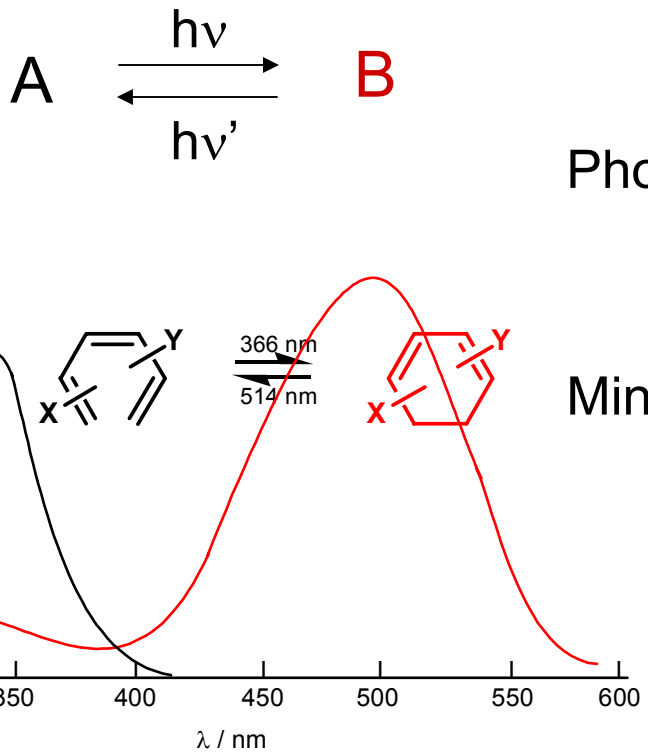
- Fundamentals and Applications -

Masahiro Irie

Department of Chemistry and Biochemistry
Kyushu University, Fukuoka, Japan


Photon
Energy
Photosynthesis
Information
Photoresponsiveness
Vision
Phototaxis
Phototropism

Photochromism



Natural

Photoreceptor : Rhodopsin (Chlamydomonas)
Bacteriorhodopsin
Phytochrome

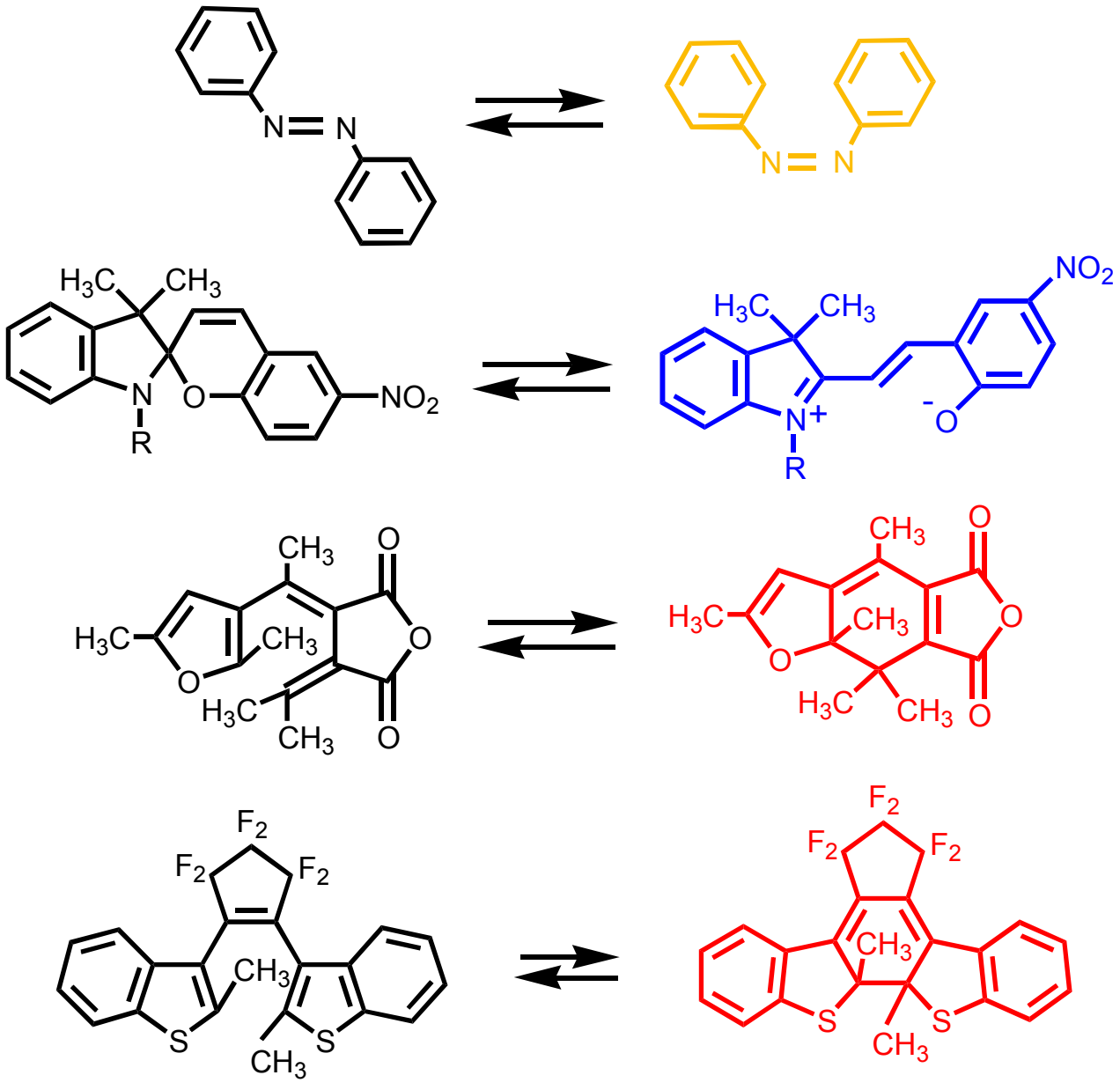
Mineral : Sodalite

Artificial

Dyes : Spirobenzopyran,
Azobenzene・・・

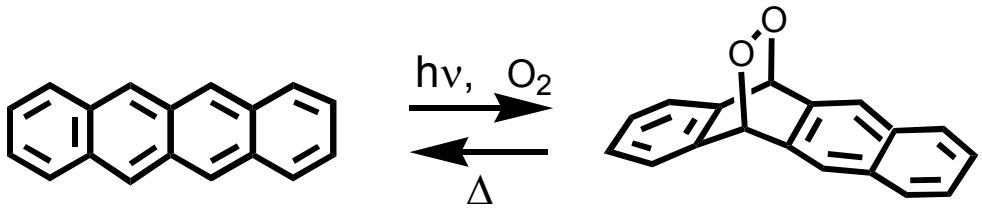
Matel-oxide Glass

Chalcogenide Glass

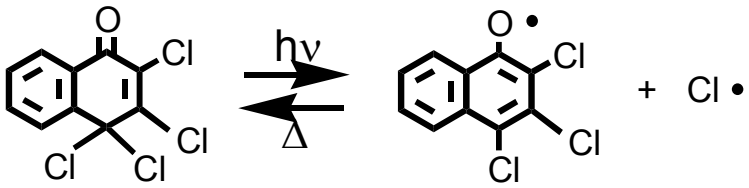

N
N
N
N
H3C
CH3
N
O
NO2
R
H3C
CH3
NO2
N+
O
R
CH3
O
H3C
CH3
O
H3C
CH3
O
CH3
H3C
CH3
O
O
F2
F2
F2
CH3
S
S
CH3
F2
F2
F2
CH3
S
S
CH3

Brief History of Photochromism

1867 M. Fritsche

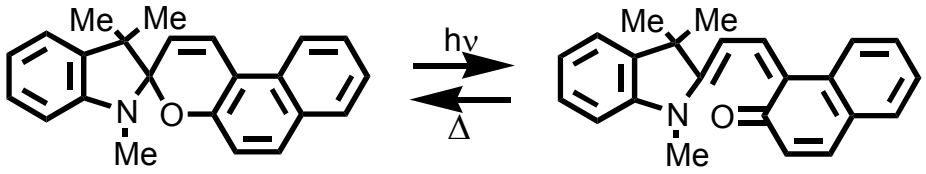


1899 W. Marckwald



(G. Scheibe et al. J. Phys. Chem. **66**, 2449 (1962))

1952 E. Fischer, Y. Hirsberg



(J. Chem. Soc., 4522 (1952))

Self-developing, Dry Photographic Systems

High-speed Printing Materials

Chemical Computer

Camouflage Fabrics

N C R (Spiropyran)

R C A (Indigos)

American Cyanamid (Spiropyrans, Metal Dithizonates)

EG & G (Triarylmethane Leuco Derivatives)

Fuji Film (Spiropyrans)

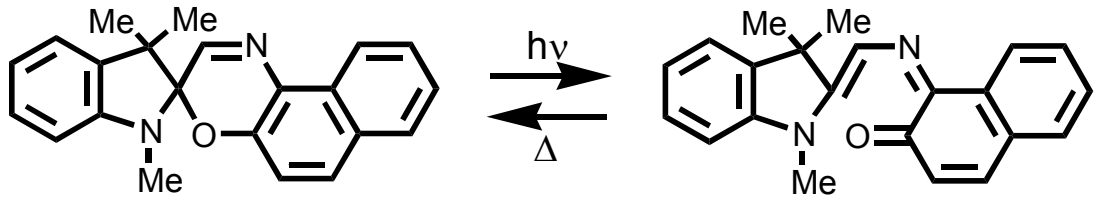
1970 ~ 1980 Dark Ages

Lack of fatigue resistant characteristics
(photo-degradation)

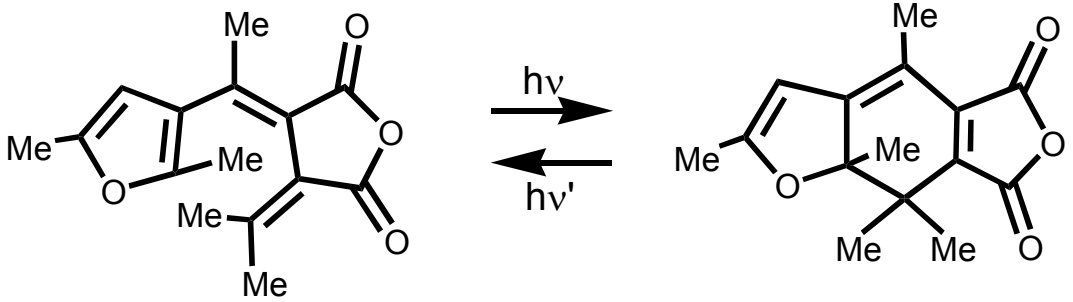
"Photochromism" G. Brown Ed.

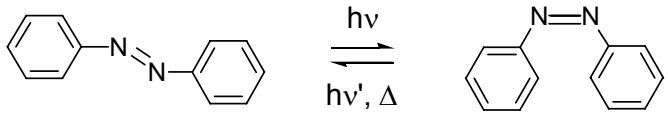
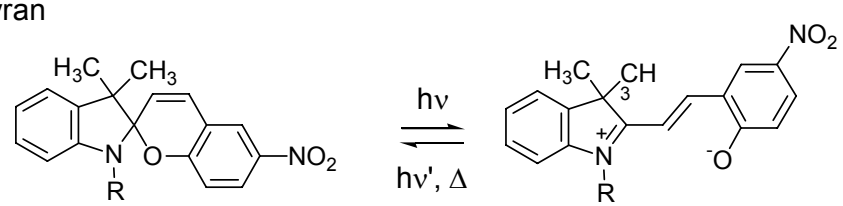
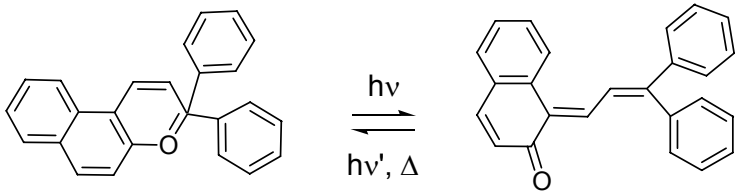
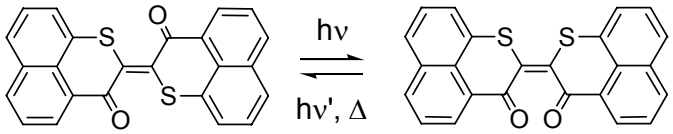
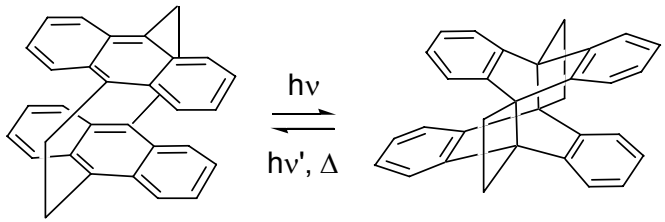
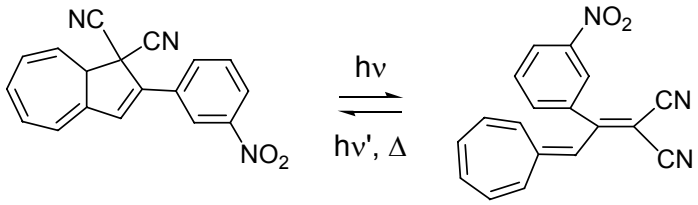
1980 ~ Present Renaissance

Fatigue Resistant Spironaphthoxazine



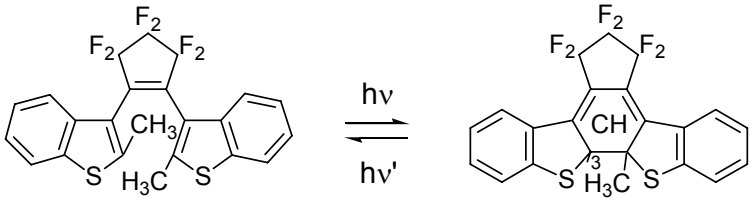
Thermally Irreversible Compounds



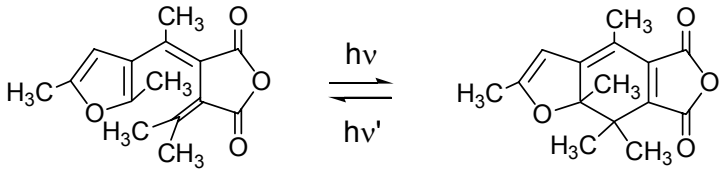
Name	Reaction
Azobenzene	
Spirobenzopyran	
Naphthopyran	
Thioindigo	
Anthracene Dimer	
Dihydroazulene	

Name	Reaction

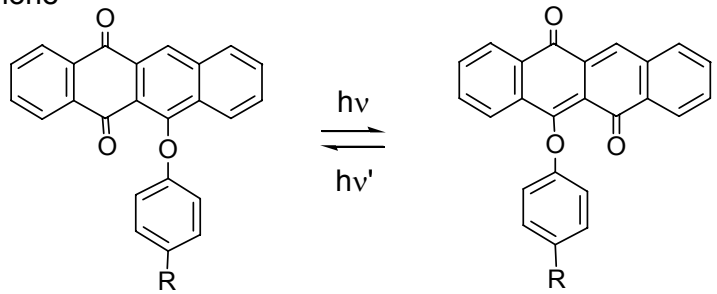
Diarylethene



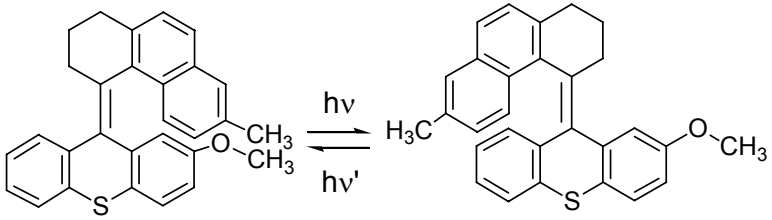
Furyl Fulgide



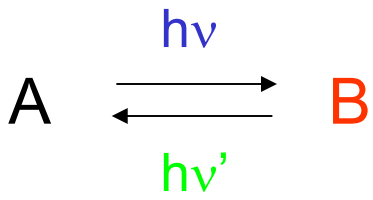
Naphthacene quinone



Stilbene Derivative



Requirements for Photonics Devices



1. *Thermal stability of both isomers*
2. *Fatigue resistant character:*

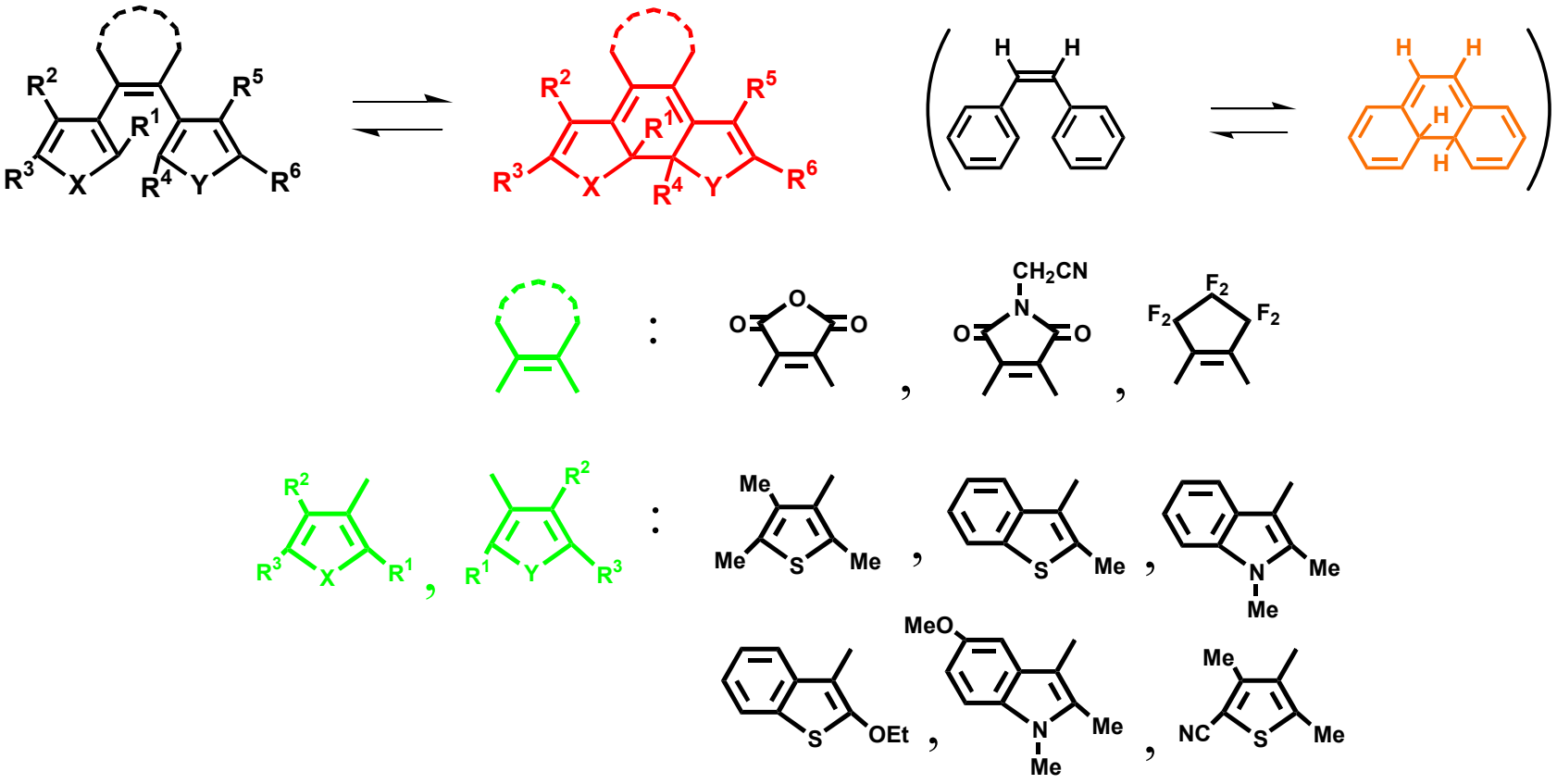
   repeatable cycle number > 10^4
3. *High sensitivity:*

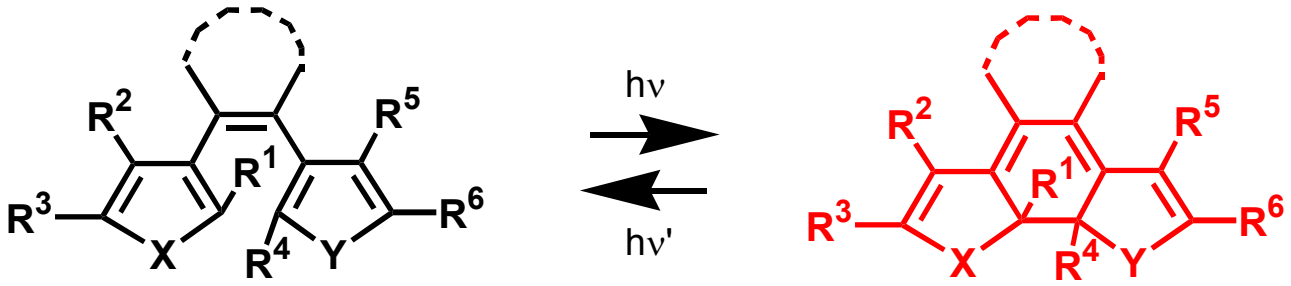
   quantum yield > 0.5
4. *Rapid response*
5. *Reactivity in the solid state*

A New Class of Photochromic Compounds

— Thermally Irreversible and Fatigue Resistant —

— Diarylethenes —





- *Both isomers are thermally stable*

  long term stability :
  470,000 years at 30 ° C

  short term stability : 150 ° C

- *Low fatigue*

  repeatable cycle number : 10^5

- *High sensitivity*

  quantum yield : 0.1 - 1.0

- *Rapid response*

  < 10^{-11} sec

- *Reactivity in the crystalline phase*

- *Sensitivity at visible region*

  forward reaction : 488 nm

  backward reaction : 780 nm

Molecular Design of Diarylethenes

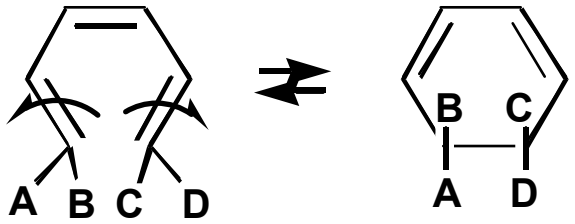
Thermal Stability

Fatigue Resistant Character

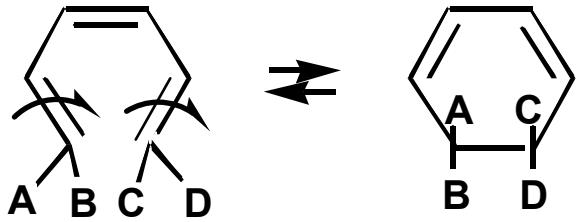
Response Time

Molecular Orbital Calculation

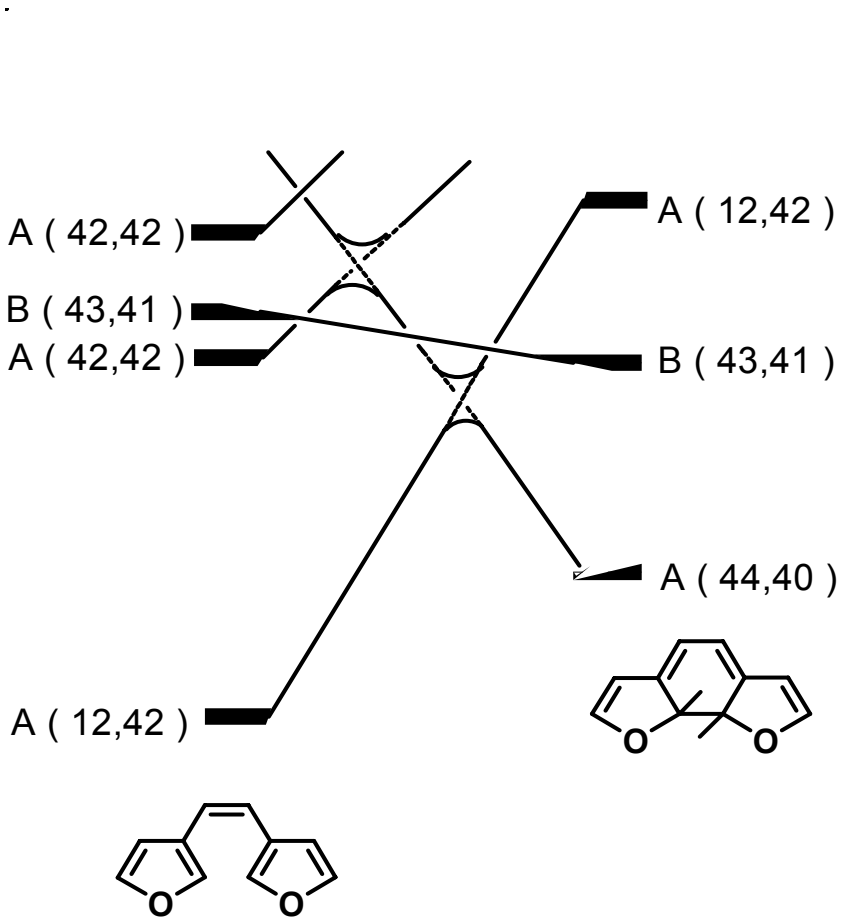
- Thermal reaction - - - disrotatory mode

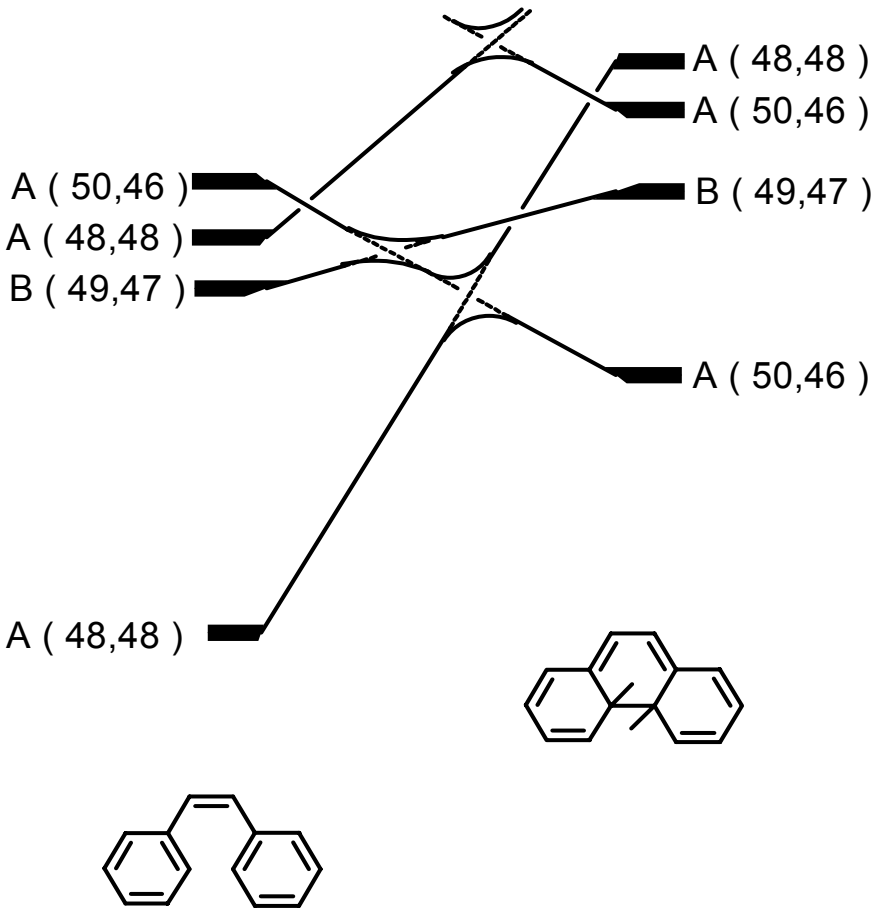


- Photochemical reaction - - - conrotatory mode



Conrotatory Mode - - - Photochemical Reaction Process

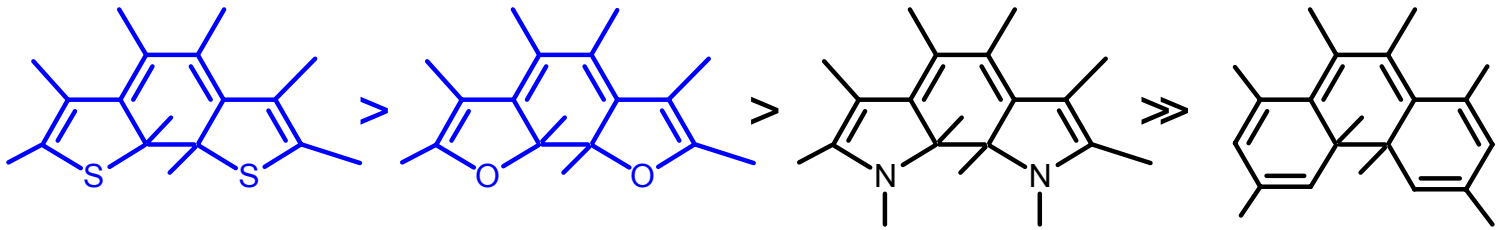




Molecular Design Principle

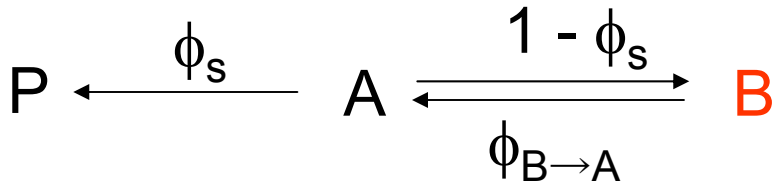
—Thermal Irreversibility—

“ When the compound has aryl groups with low aromatic stabilization energy, both isomers of the diarylethene are thermally stable.”



Stable

Unstable



$\phi_s = 0.001$ ($\phi_{B \rightarrow A} = 1$)

After 10^3 cycles

$[A] \sim 0.37\ [A]_0$

$\phi_s = 0.0001$ ($\phi_{B \rightarrow A} = 1$)

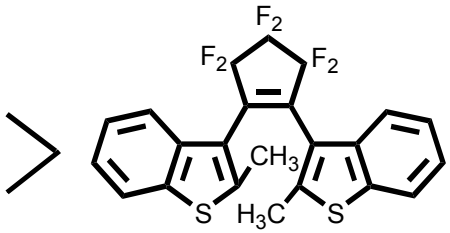
After 10^4 cycles

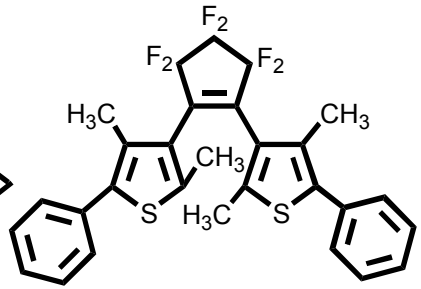
$[A] \sim 0.37\ [A]_0$

Molecular Design Principle

— Fatigue Resistant Character —

Crystalline Systems

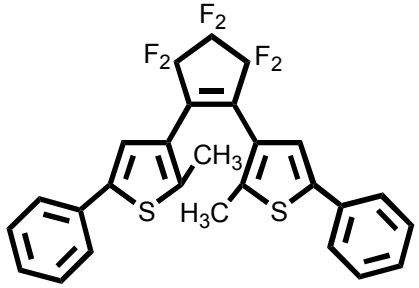


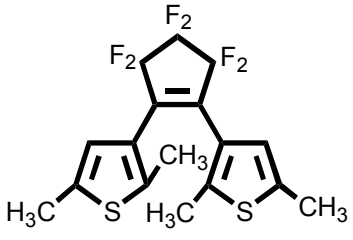


> 100,000

> 10,000

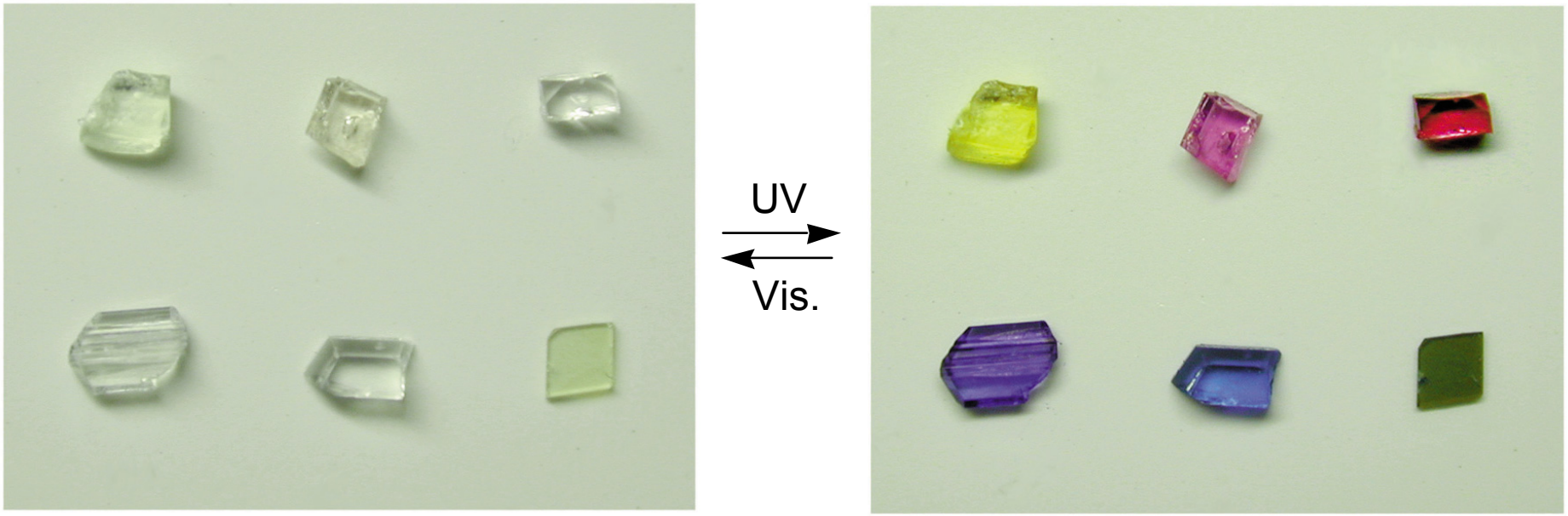
~ 2,000

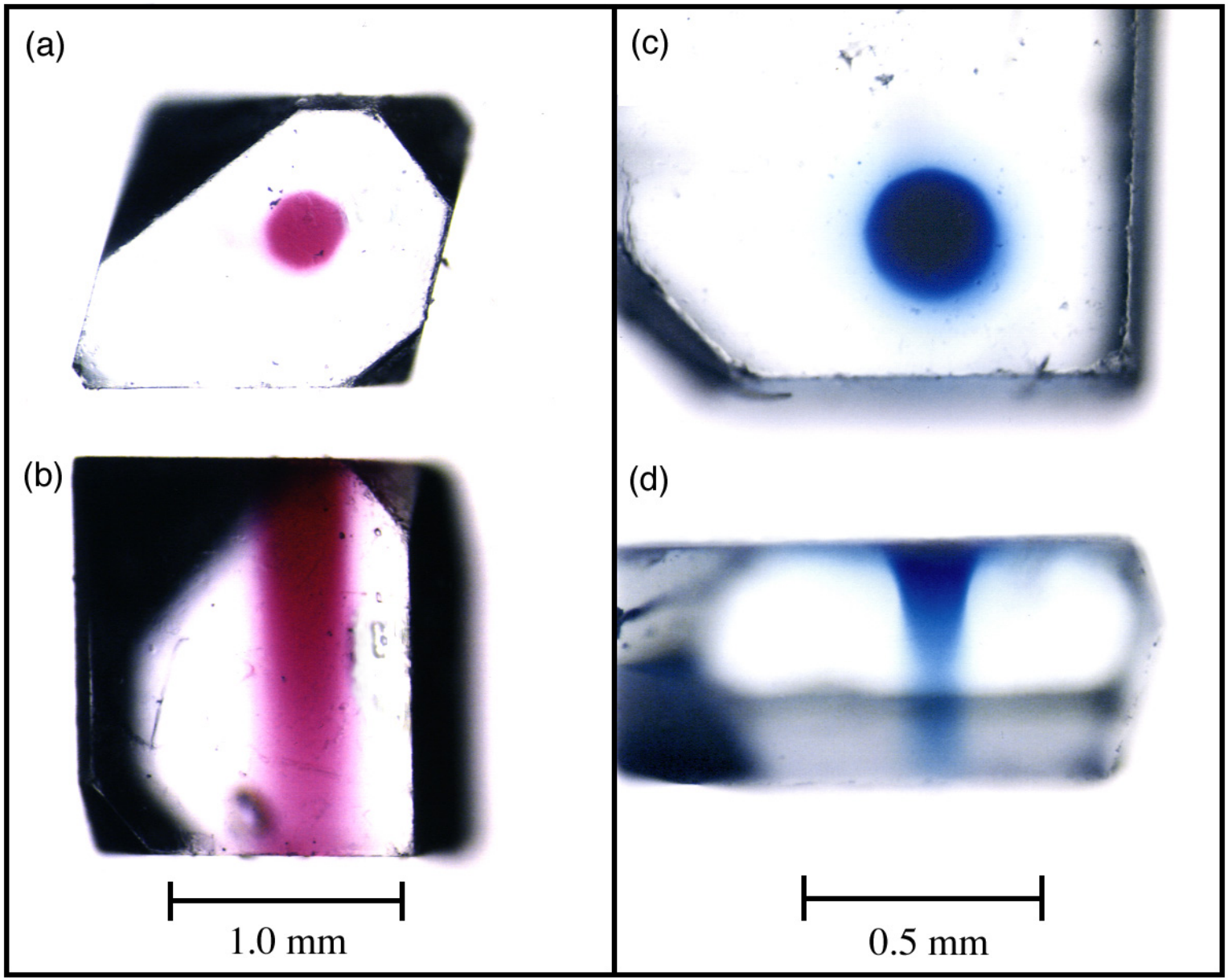




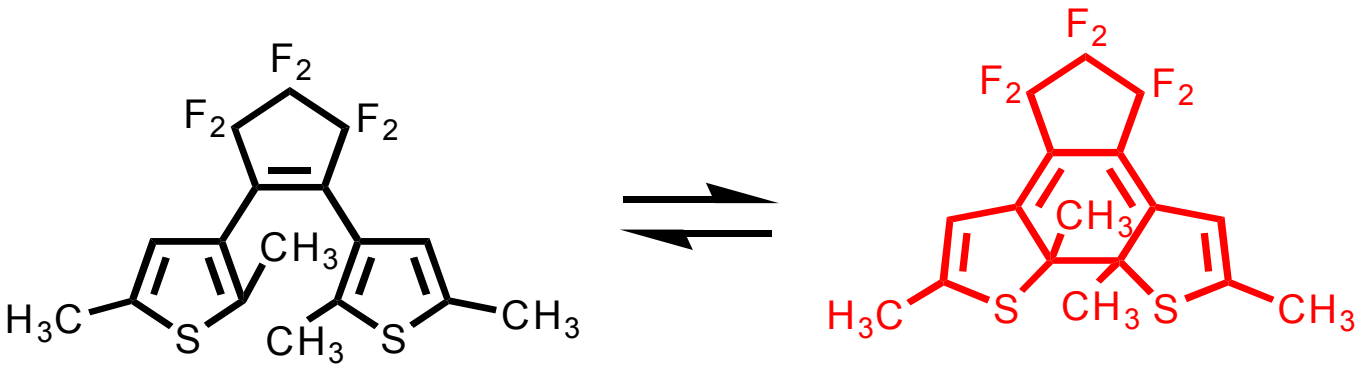
~ 200

~ 80

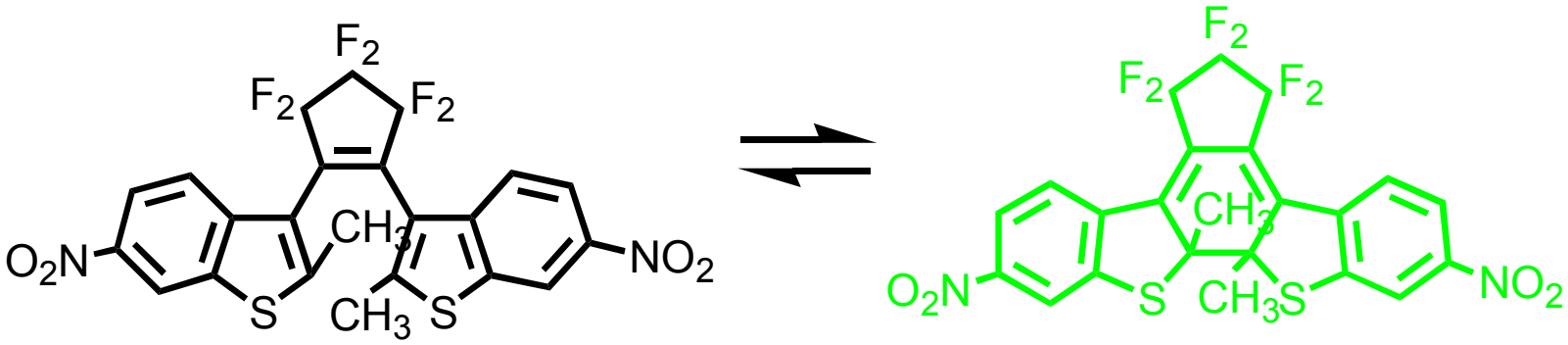

UV
Vis.


(a)
(b)
(c)
(d)
1.0 mm
0.5 mm

Dichroism

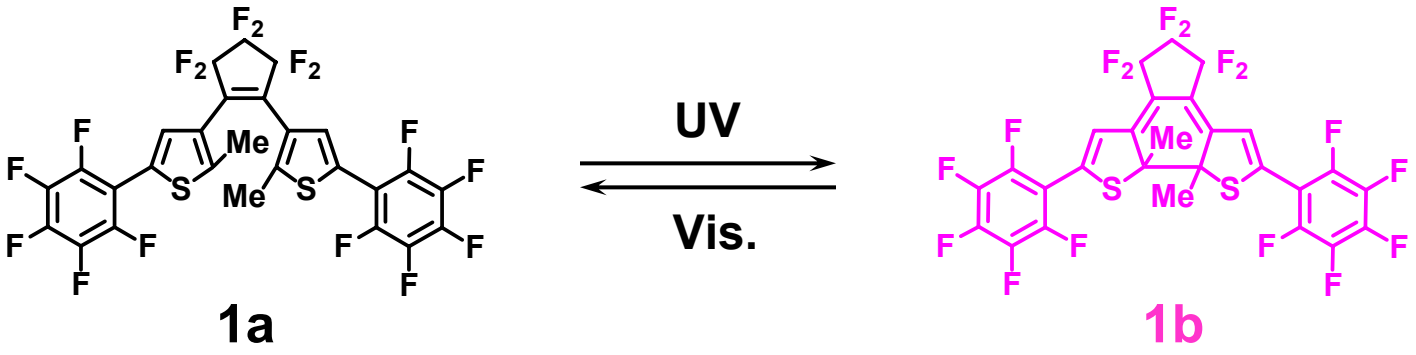


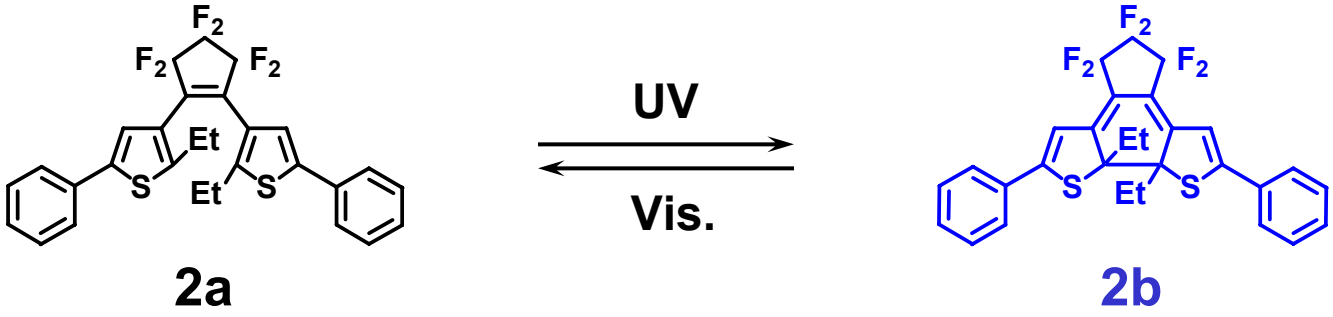
J. Am. Chem. Soc. **121**, 2380 (1999)



J. Am. Chem. Soc. **121**, 8450 (1999)

Nano-layered Structure

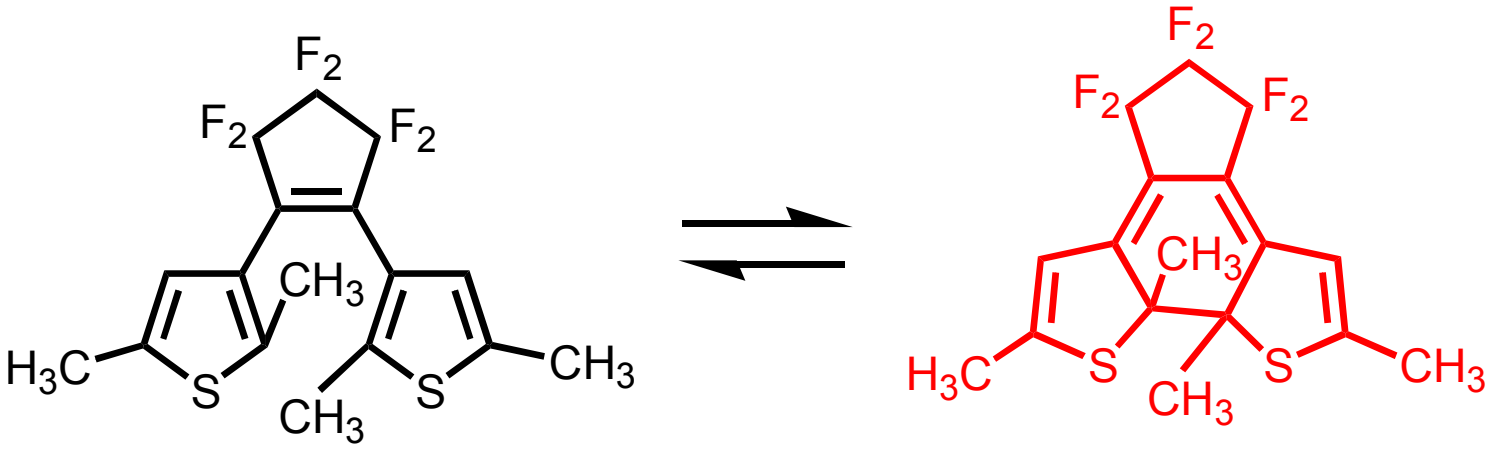




Photochem. Photobio. Sci. 2 ,1088 (2003)

Chem. Rec. **4**, 23 (2004)

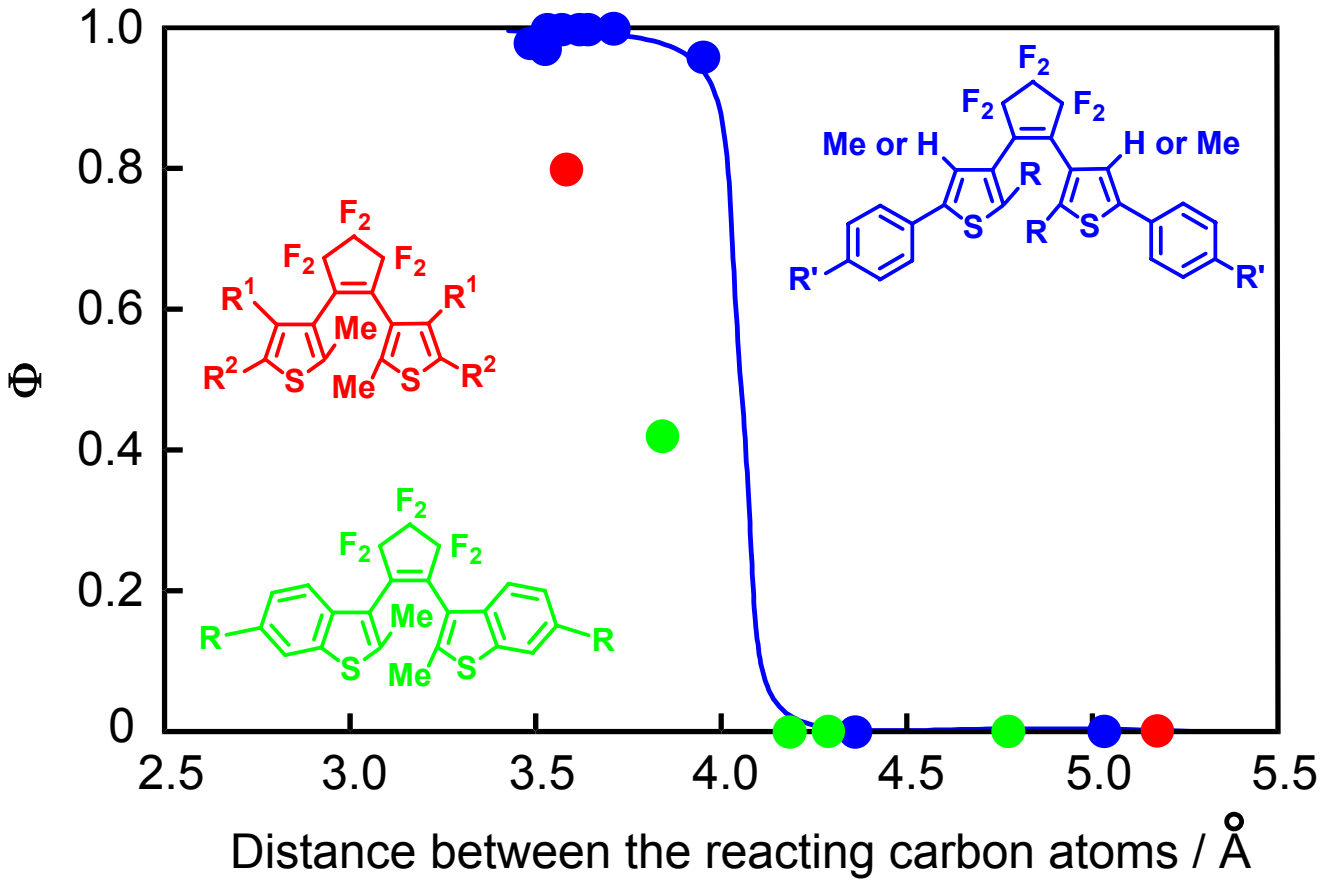
X-ray Crystallographic Analysis



1a 1b

J. Am. Chem. Soc. **122**, 1589 (2000)

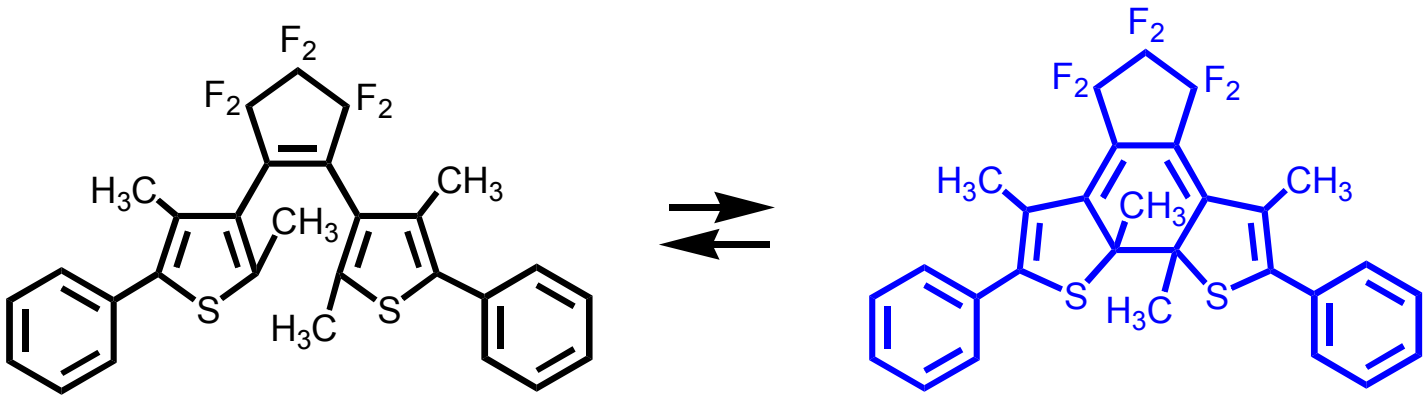
Bull. Chem. Soc. Jpn. **73**, 2179 (2000)



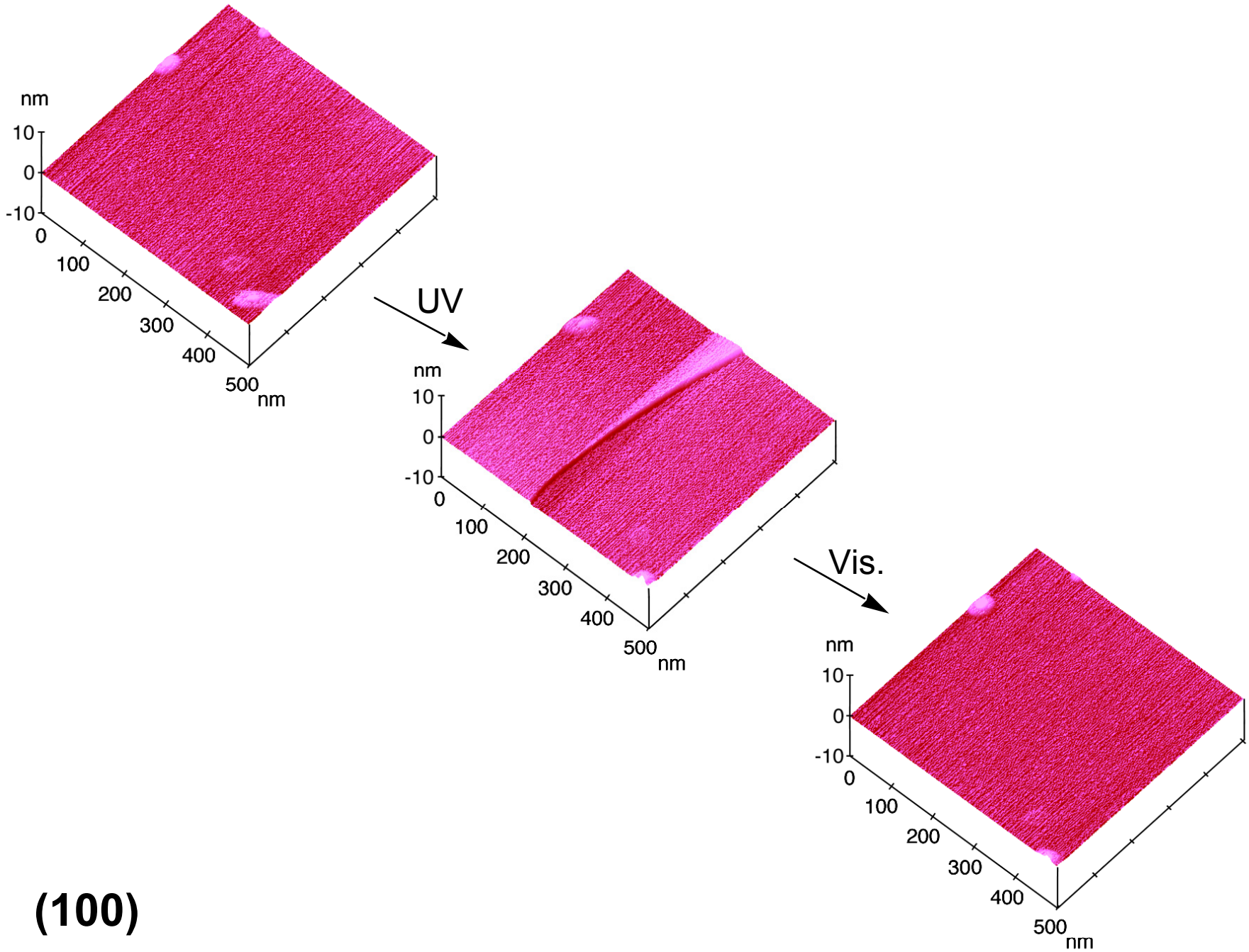
J. Phys. Chem. A. **106**, 209 (2002)

Chem. Commun. 2804 (2002)

Surface Morphology Changes of Single Crystal 1

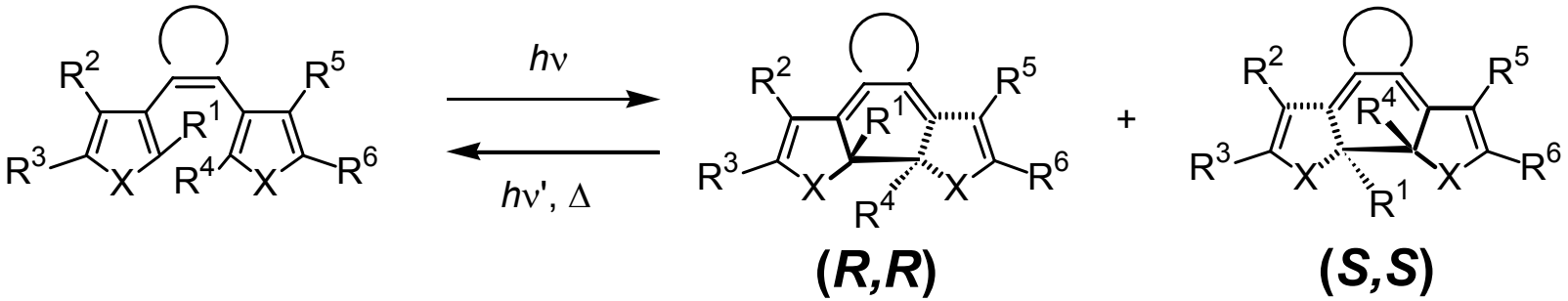


Science, **291**, 1769 (2001)


nm
10
0
-10
0
100
200
300
400
500
nm
UV
nm
10
0
-10
0
100
200
300
400
500
nm
Vis.
nm
10
0
-10
0
100
200
300
400
500
nm

(100)

Absolute Asymmetric Photosynthesis



Ang. Chem. **42**, 1636 (2003)

Tetrahedron Lett. **42**, 7291 (2001)

J. Am. Chem. Soc. **122**, 9631 (2000)