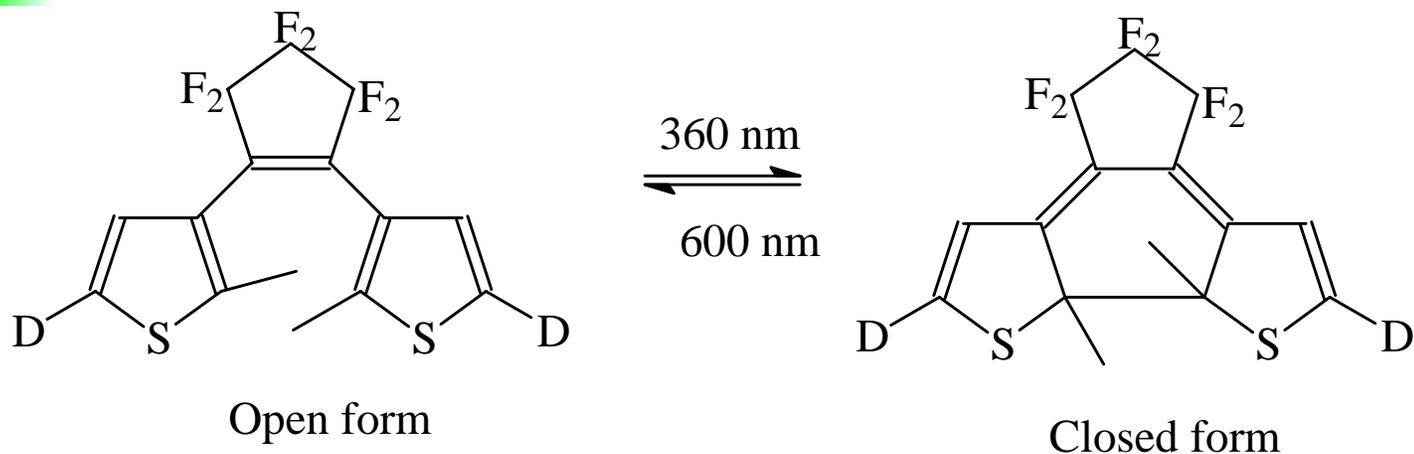


Photochromic materials for fluorescent switch and data storage

He TIAN

*Institute of Fine Chemicals,
East China University of Science & Technology,
Shanghai 200237, P. R. China*



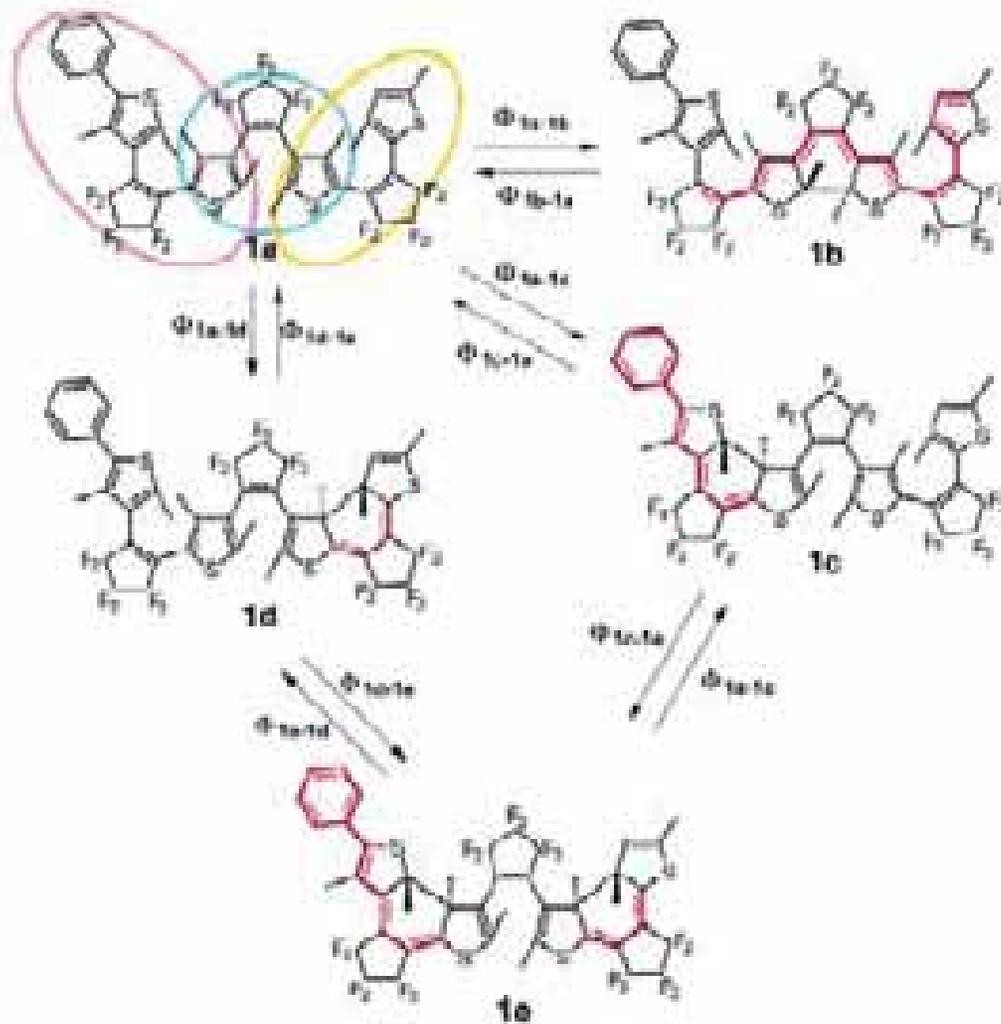
J.M. Lehn, et al., *Chem. Eur. J.*, 1995, **1**, 275

M. Irie, *Chem. Rev.*, 2000, **100**, 1685

H. Tian, et al., *Chem. Soc. Rev.*, 2004, **33**, 85

($\epsilon \sim 5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)

K. Matsuda, Irie M. et al., *JACS.*, 2005, 127, 8922



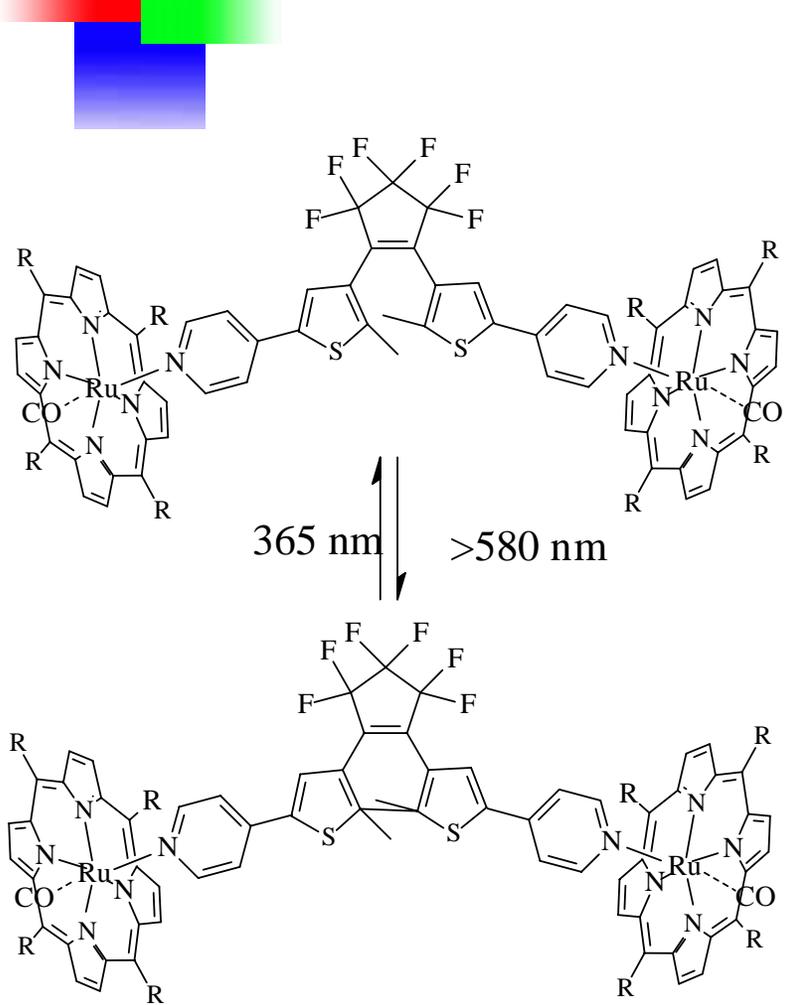
Full color photochromic



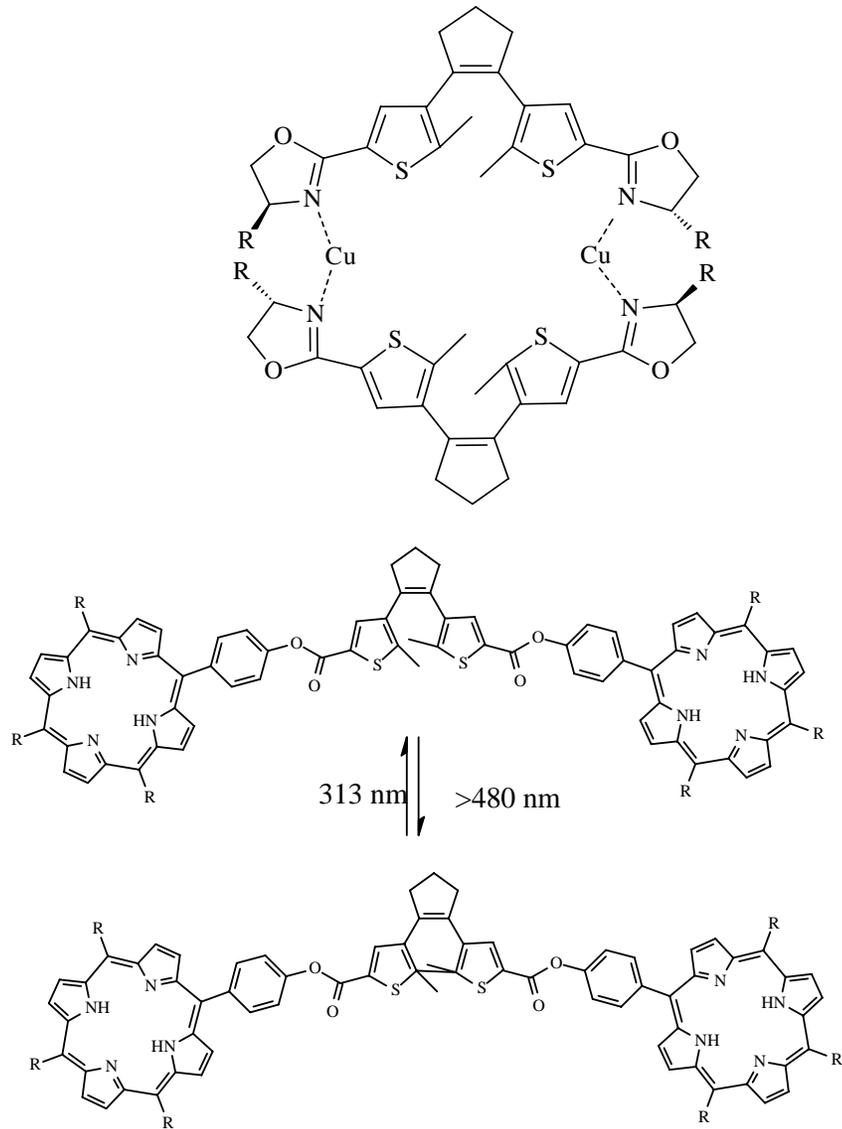
Branda N R. et al., *Angew. Chem. Int. Ed.*, 2001,**40**, 1752

Adv. Mater. 2001, **13**, 347

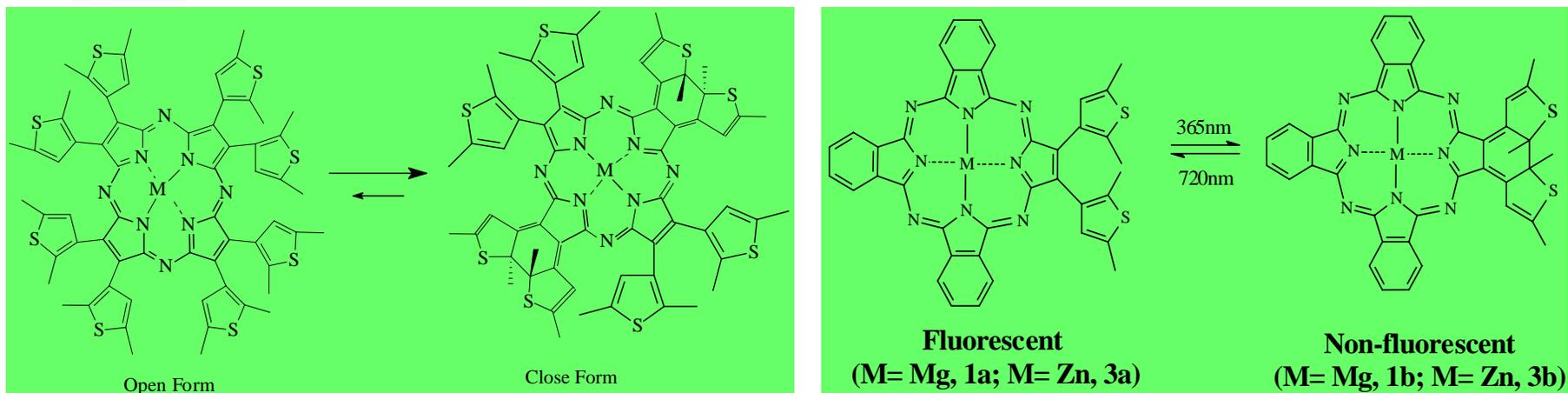
JACS, 2001, **123**, 1784



Fluorescence/phosphorescence switches



Photochromic Materials and Switches



Bisthienylethene-based photochromic tetraaza-porphyrin (BTE-TAPs) switches.

H. Tian, et al., *Adv. Mater.* 14(2002)918

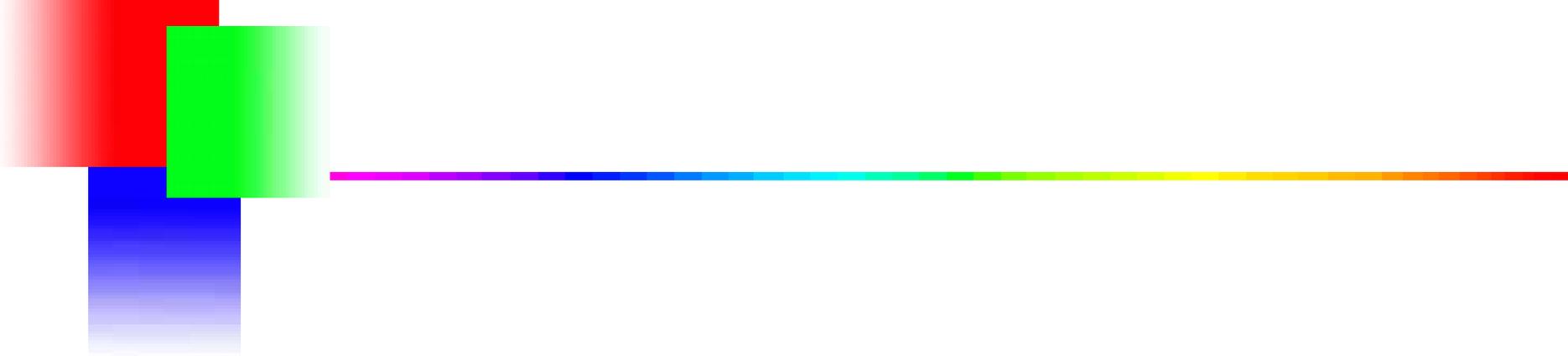
H. Tian, et al., *Advanced Functional Materials*, 13 (2003) 233

H. Tian, et al., *Chem. Commun.*, 2002, 1060

Motivation

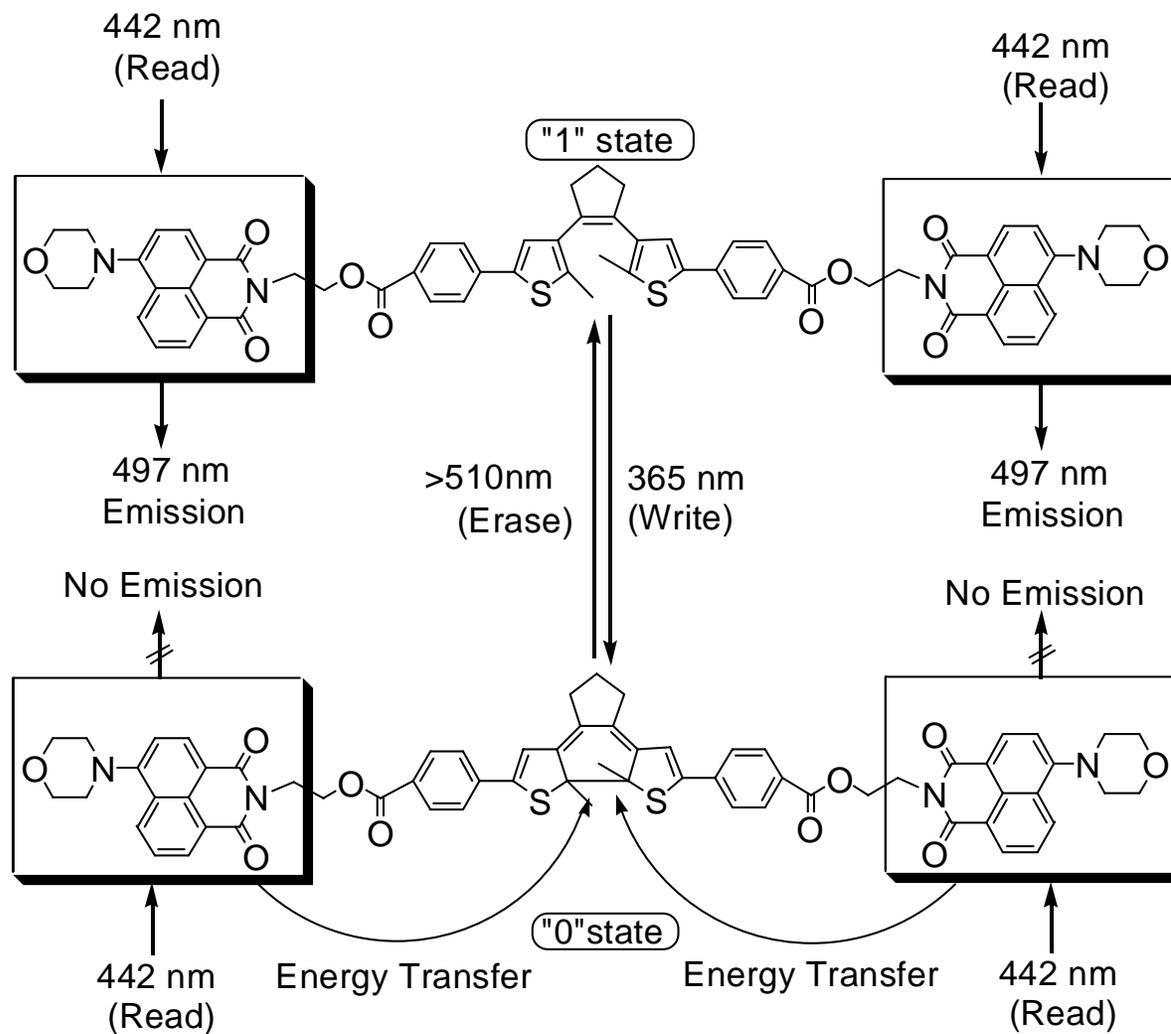


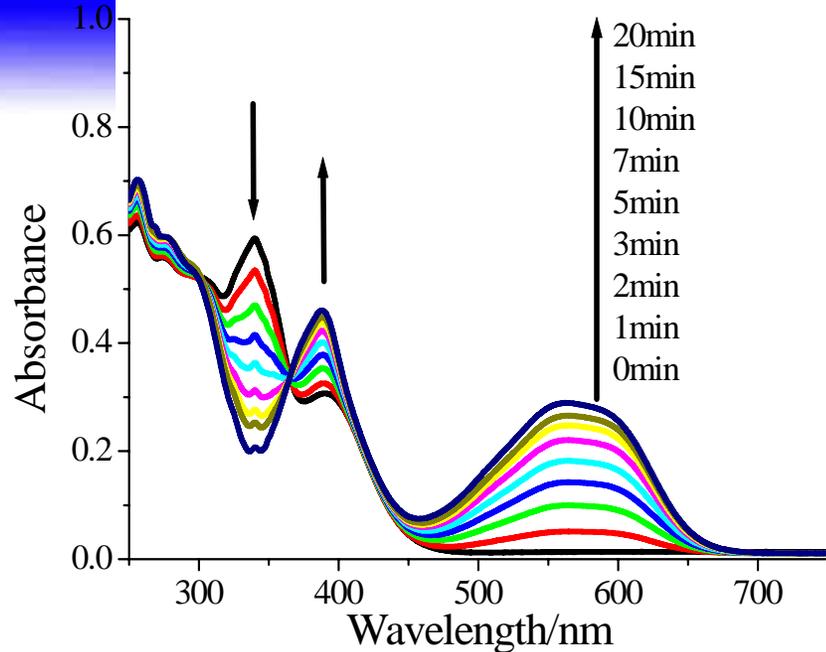
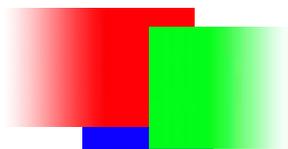
- Highly Fluorescent (Signal) Contrast
- Multiple Switching in One Molecule
- Photochromic Materials (Polymer or Gel)
- High Stability
- Information Storage



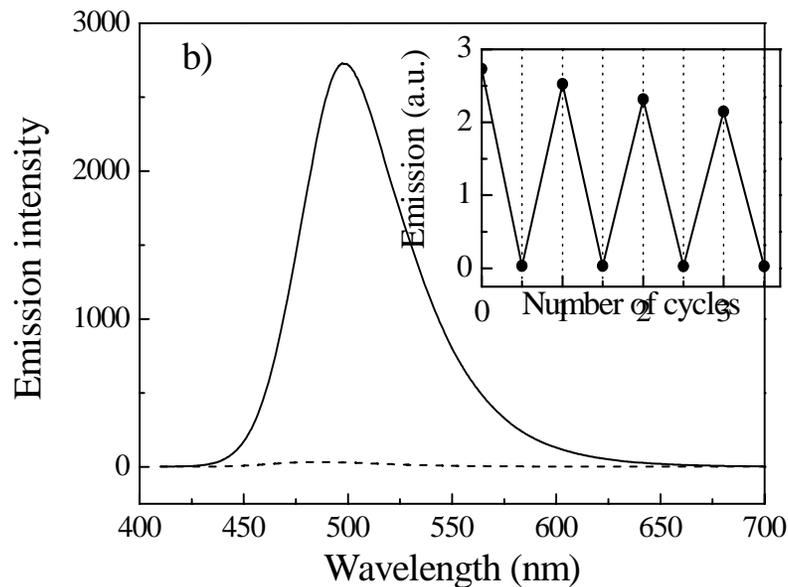
Highly Fluorescent Contrast for
Rewritable Optical Storage based on
Photochromic Bisthiénylene

Y. L. Song, H. Tian, et al., *Chem. Mater.* **18**, 235-237, (2006)

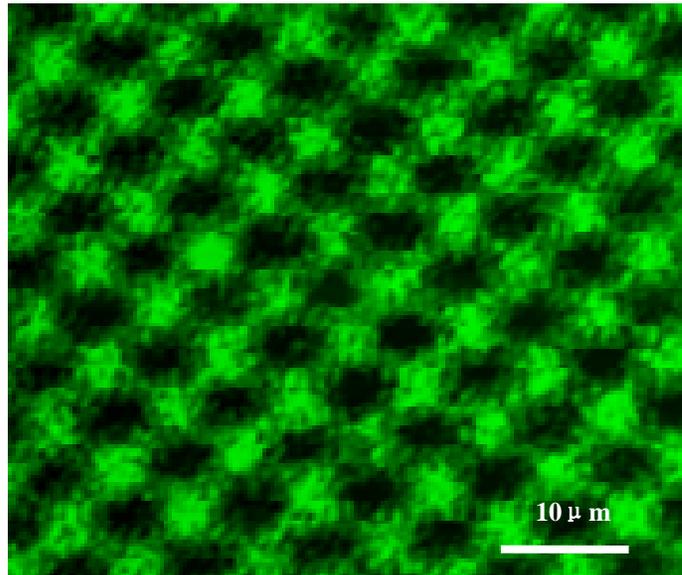




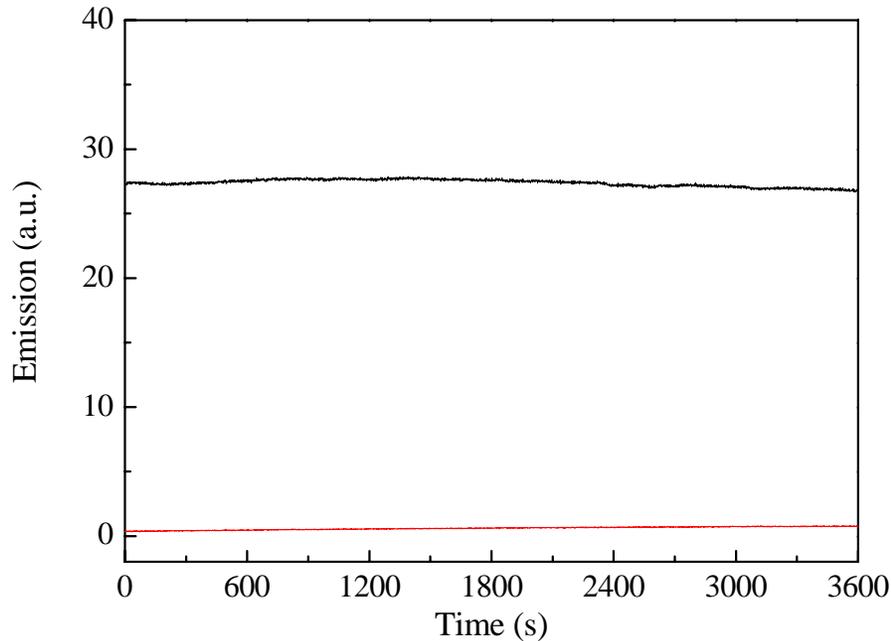
fluorescence on/off ratio 85:1



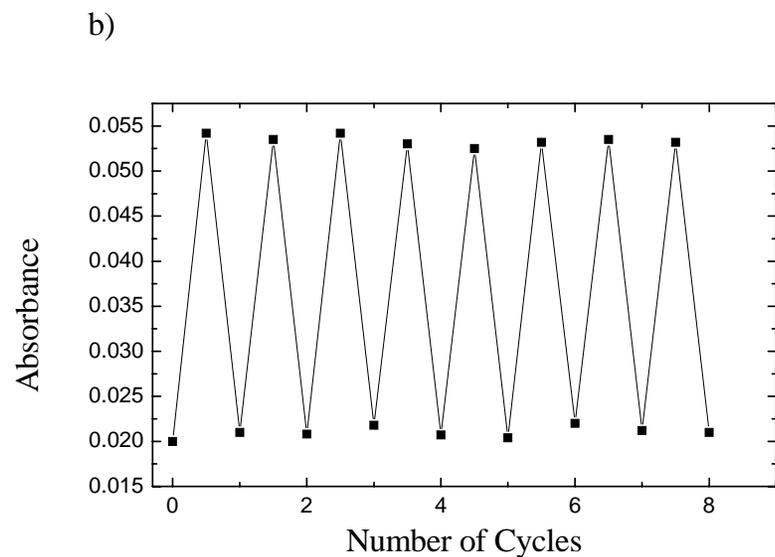
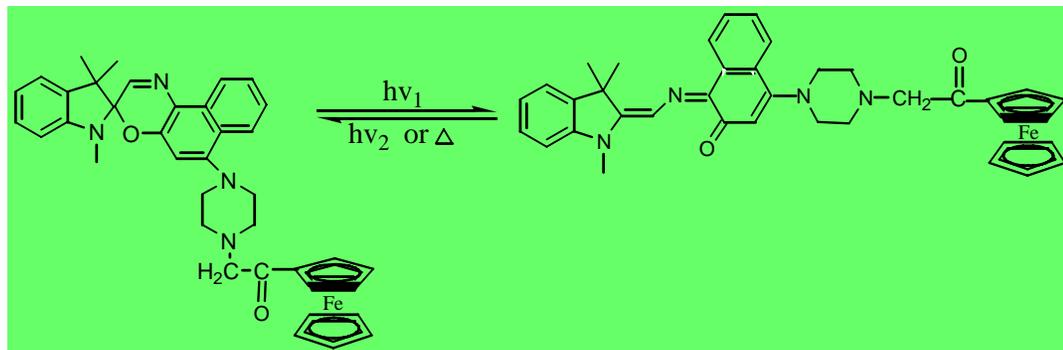
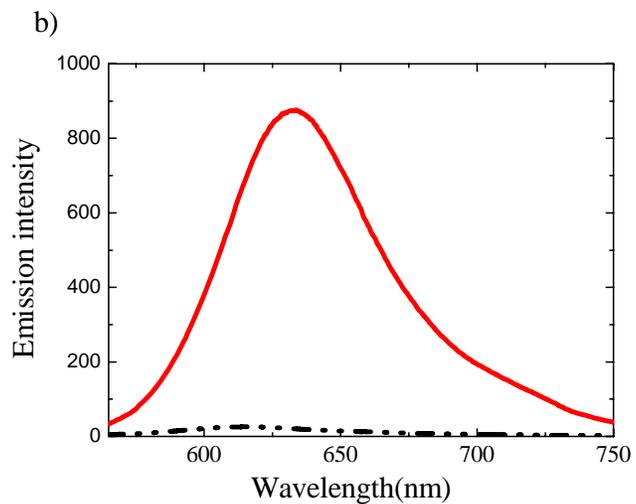
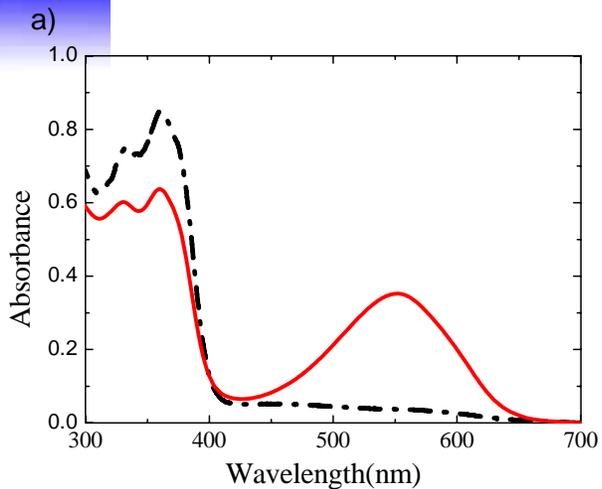
a) Absorption and b) Fluorescence emission spectra change of BTE-NA doped in PMMA before (solid line) and after (dashed line) irradiation with 365 nm light for 5 min at r. t. The inset shows the modulated emission peak intensity (excited at 400 nm) of the sample during alternating irradiation at 365 nm and >510 nm.



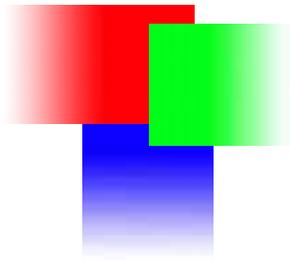
- Fluorescence image generated from 365 nm irradiation (5 min) of BTE-NA doped PMMA film through a dot-patterned contact mask. The light regions indicate luminescence and the dark regions are non-luminescent ($\lambda_{ex} = 442 \text{ nm}$).



- Fluorescence peak intensity vs. time curves of the BTE-NA doped in PMMA thin film, during 1 hr continuous irradiation by $6 \mu\text{W}/\text{cm}^2$ at 442 nm. **Contrast >35:1 @ 442 nm 1hr continuous reading**

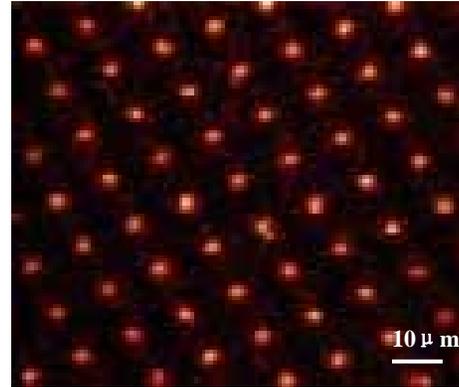


Two-photon 3D memory



SOFC:PMMA (wt : wt % = 1 : 50)

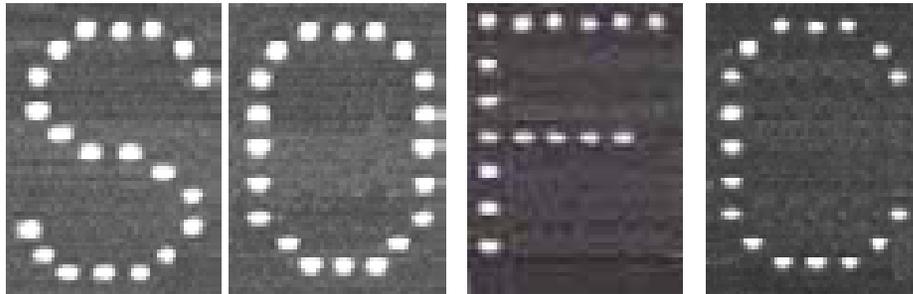
2D



SOFC:PMMA (wt : wt % = 1 : 30)



3D



spacing between adjacent layers: $12 \mu\text{m}$

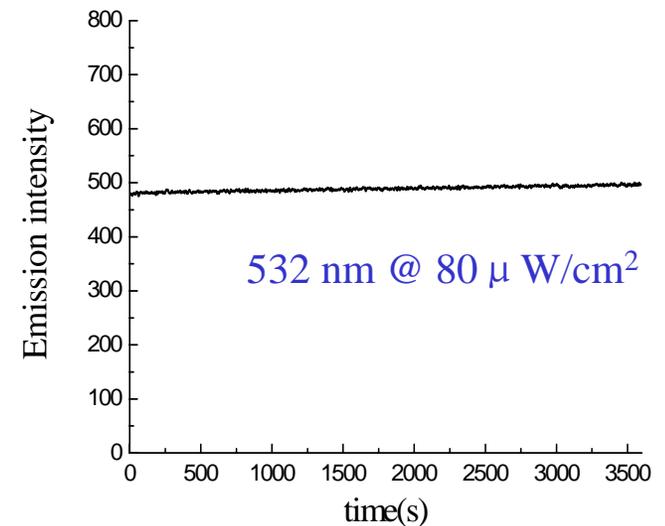
transverse bit separation: $5 \mu\text{m}$

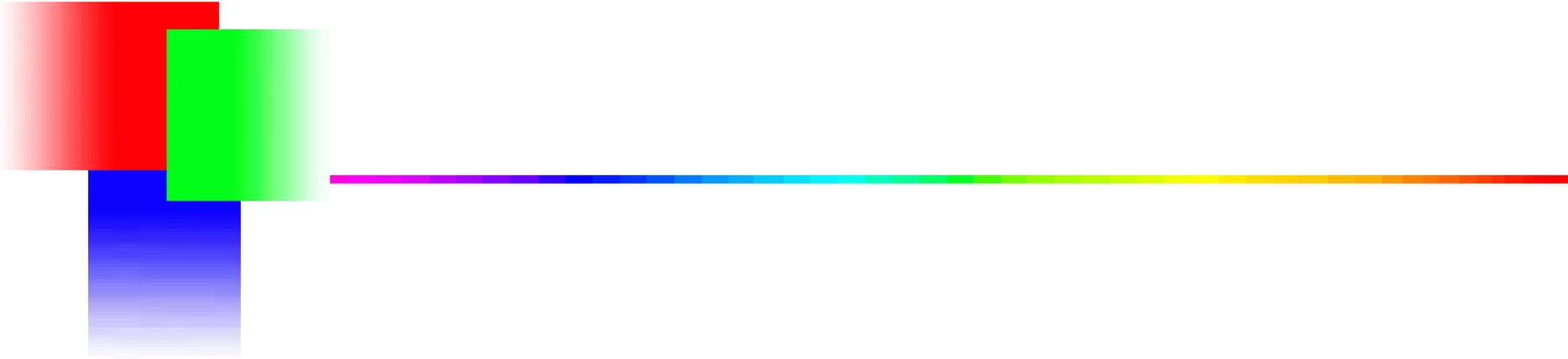


800 nm/80 fs @ repetition rate of 80 MHz

Dichroic mirror

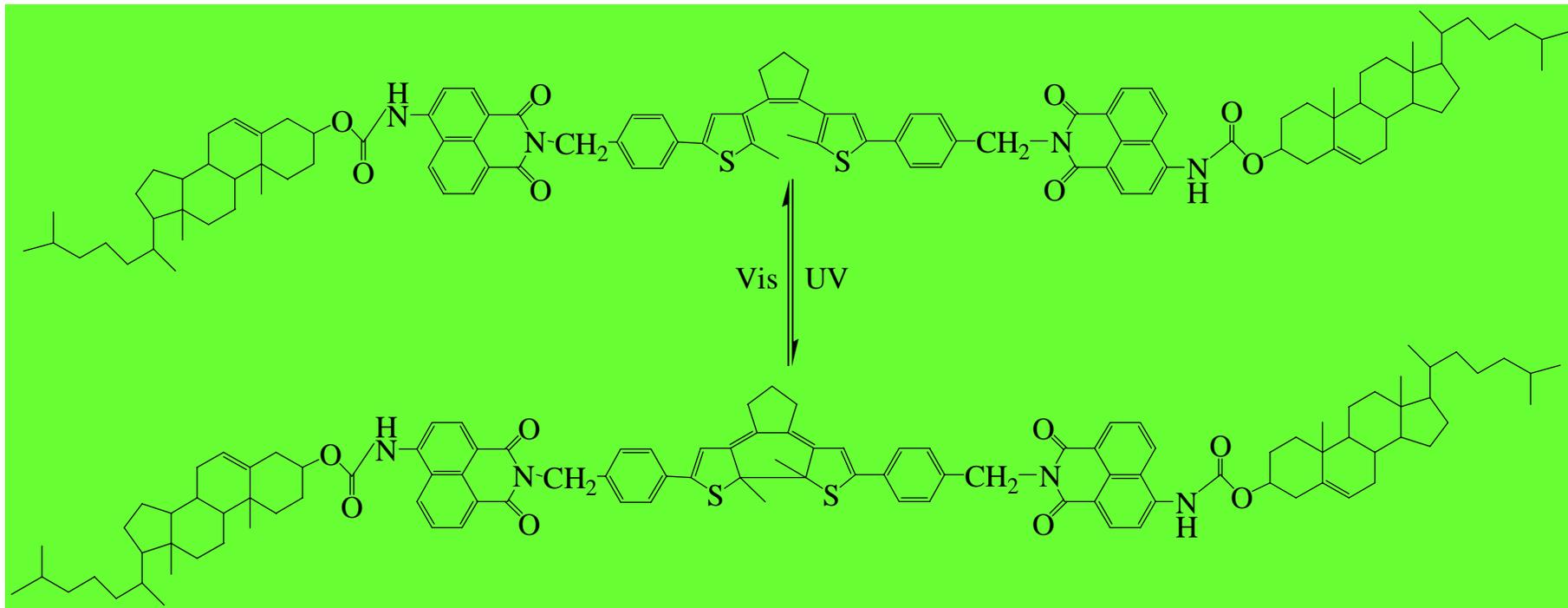
40X objective (NA 0.65)

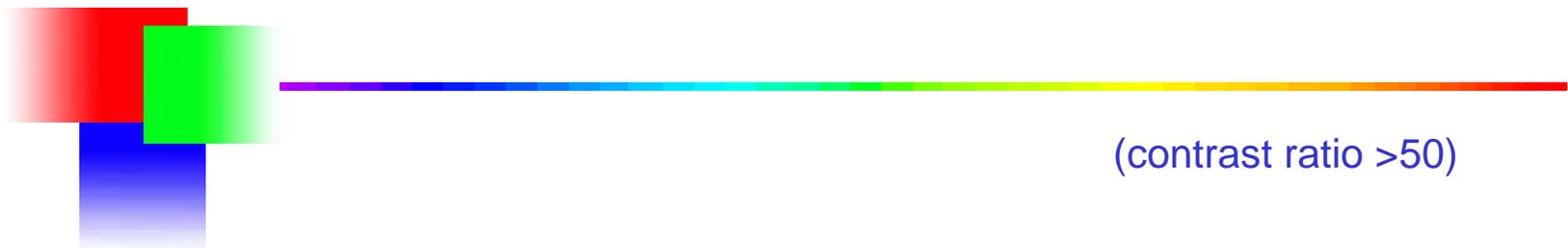




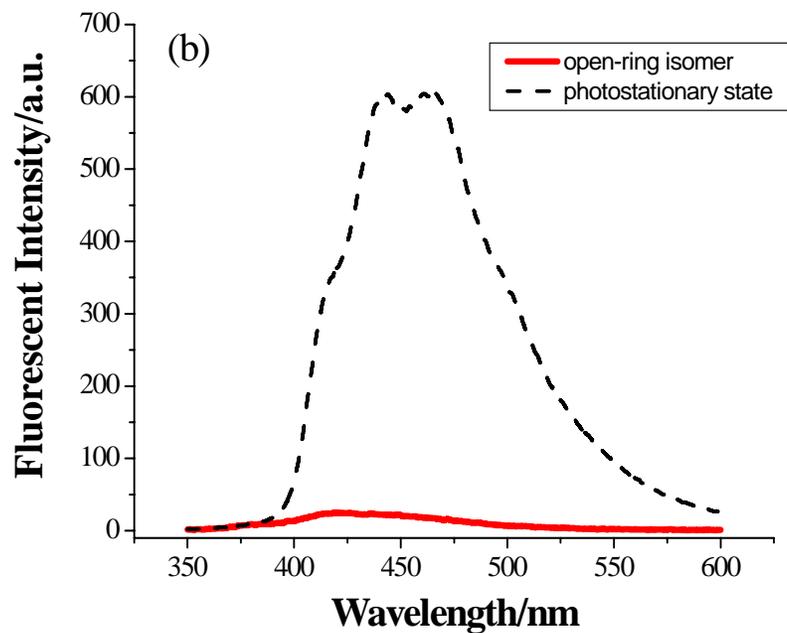
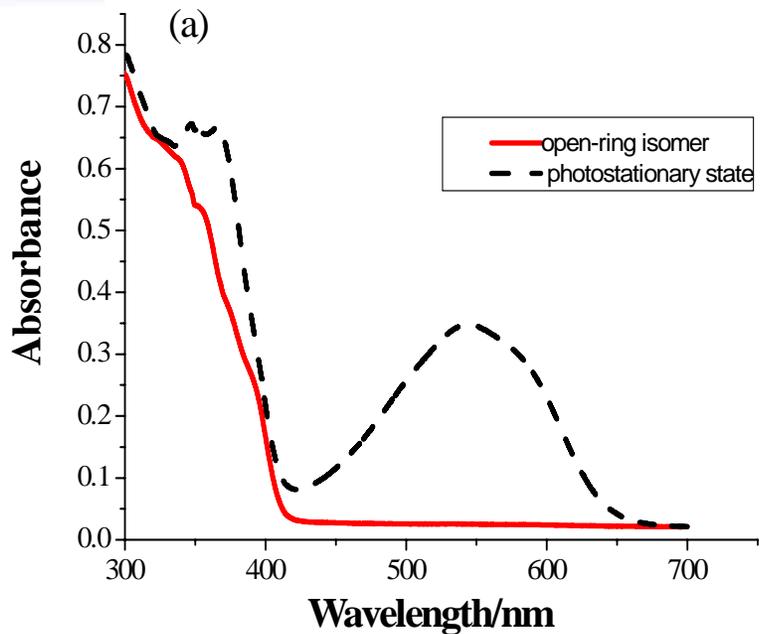
Multiple Switching in a Fluorescent Photochromic Organogel

He Tian, et al., *Chem. Commun.* 1497 -1499, (2006).

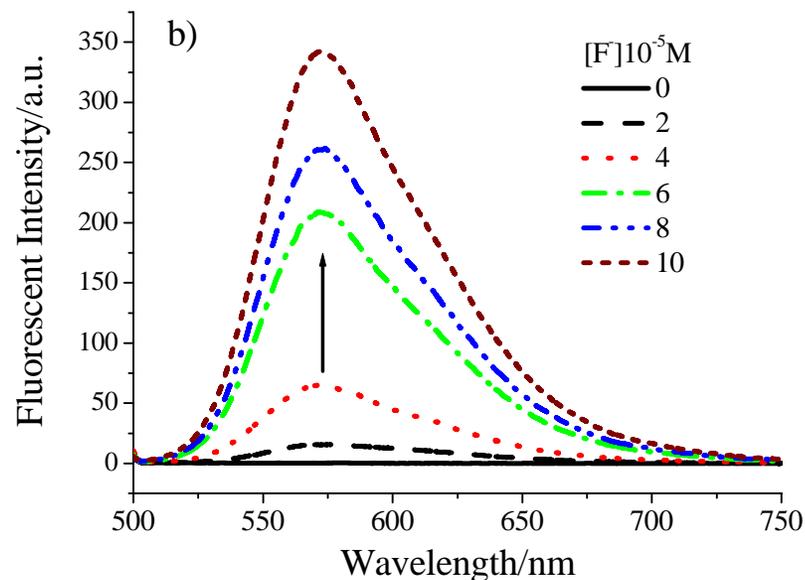
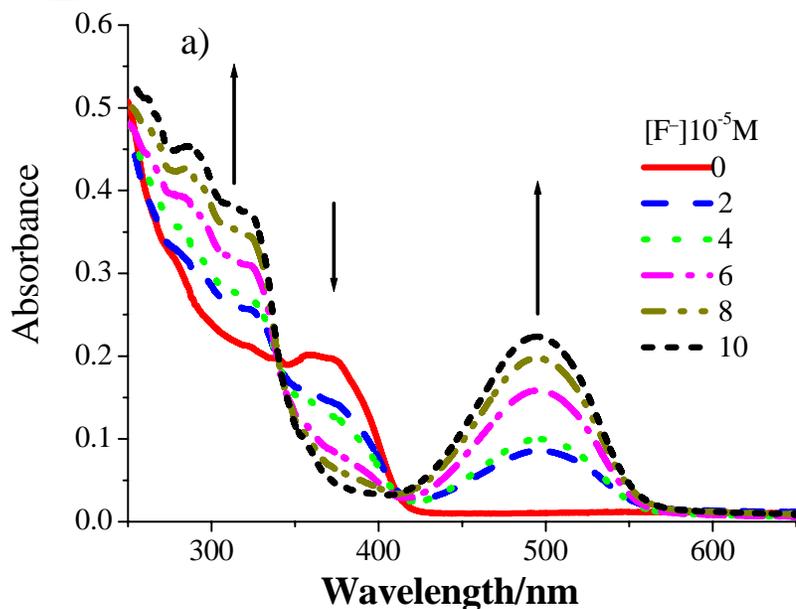
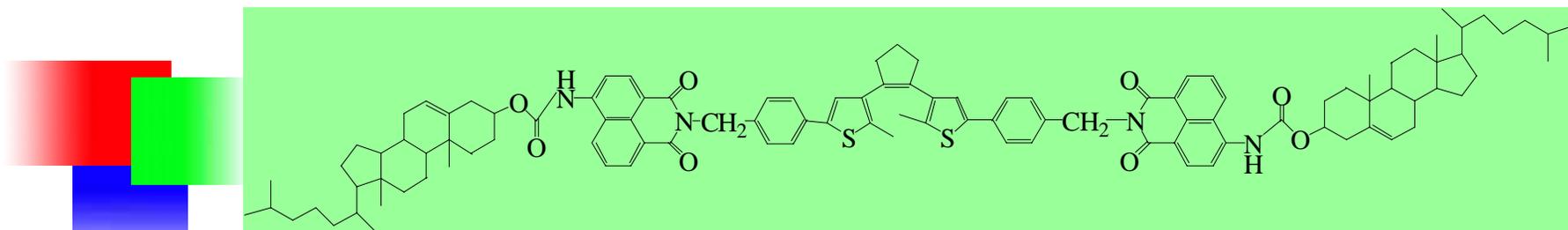




(contrast ratio >50)

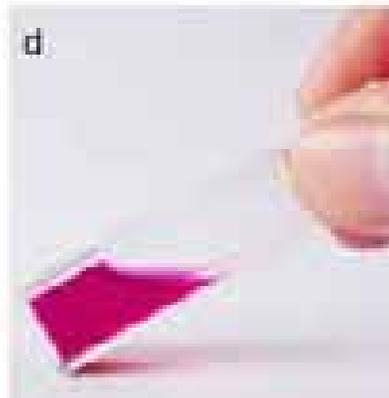
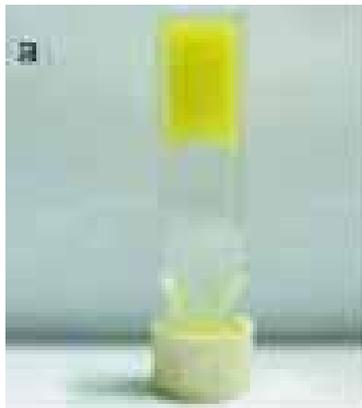


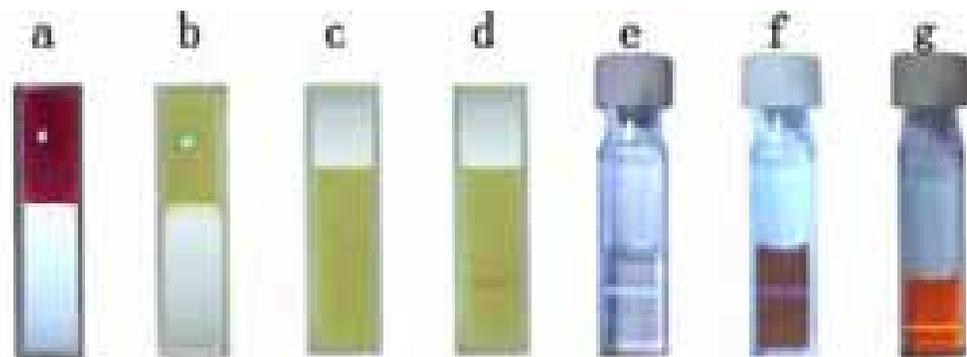
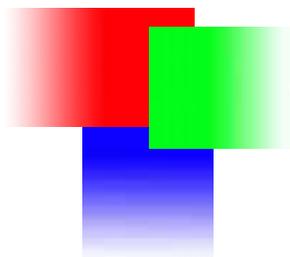
(a) Absorption spectra and (b) Fluorescent spectra (excited at 355 nm) of the open-ring isomer BTE-NA-(chol)₂ (____) and the photostationary state (-----) in toluene (4.0×10^{-5} mol/L) upon irradiation with 365 nm light at r. t.



The changes in absorption and b) the changes in fluorescent spectra (excited at 495 nm) of open form of BTE-NA-(chol)₂ (2.0×10^{-5} mol/L in THF) upon addition of TBAF (tetrabutylammonium fluoride salt) at room temperature

Multi-switching

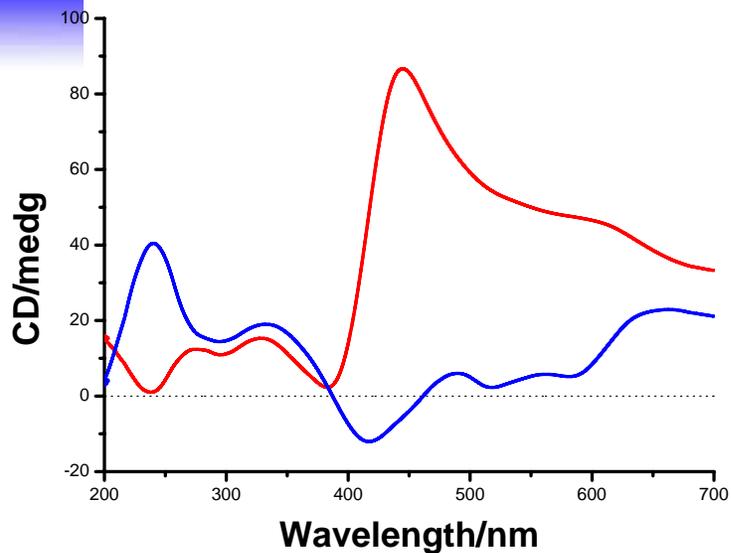
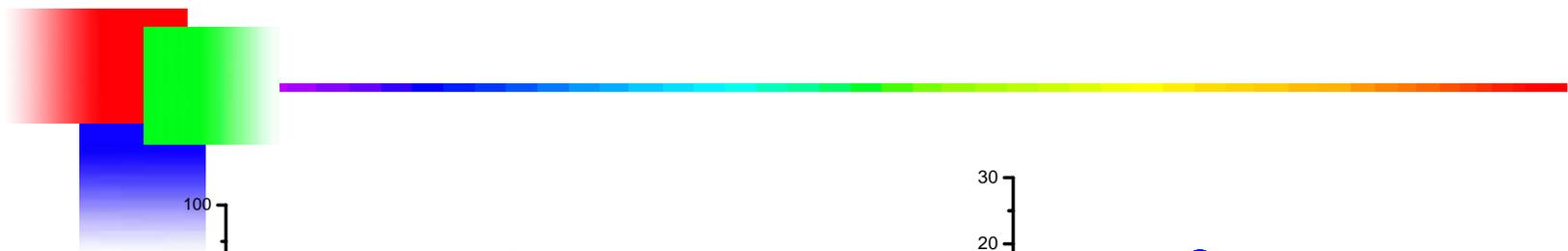




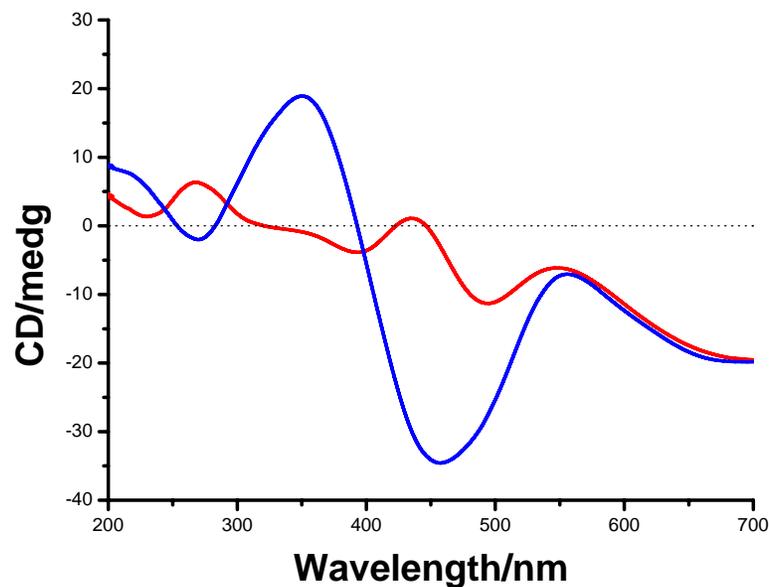
The TPA image of the BTE-NA-(chol)₂ in gel phase and in THF solution (2.0×10^{-4} mol/L), (a) and (b) obtained with the cross focus; (d), (e), (f) and (g) obtained by the parallel configuration. **(a)**: the closed form of BTE-NA-(chol)₂ in gel; **(b)**: the open form of BTE-NA-(chol)₂ in gel; **(d)**: the TPA photochromic of BTE-NA-(chol)₂ in gel **(e)**: the open form of BTE-NA-(chol)₂ in solution; **(f)**: the closed form of BTE-NA-(chol)₂ in solution; **(g)**: the open form of BTE-NA-(chol)₂ titration with F⁻ in solution. **(c)**: the open form of BTE-NA-(chol)₂ with one photon in gel.

- Fluorescent image of the BTE-NA-(chol)₂ gels, the opening isomer (a), in the photostationary state (b) upon irradiation by 313nm light at room temperature.

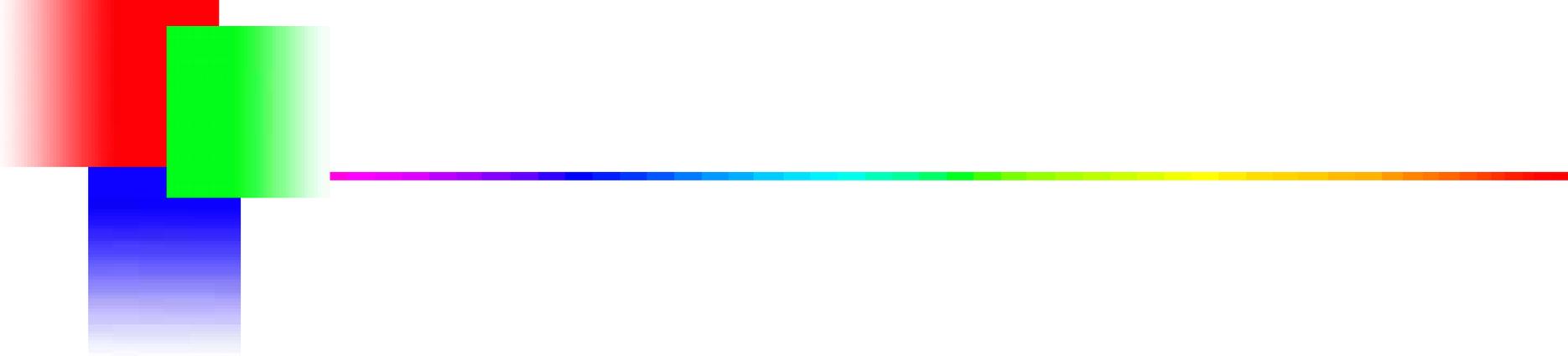




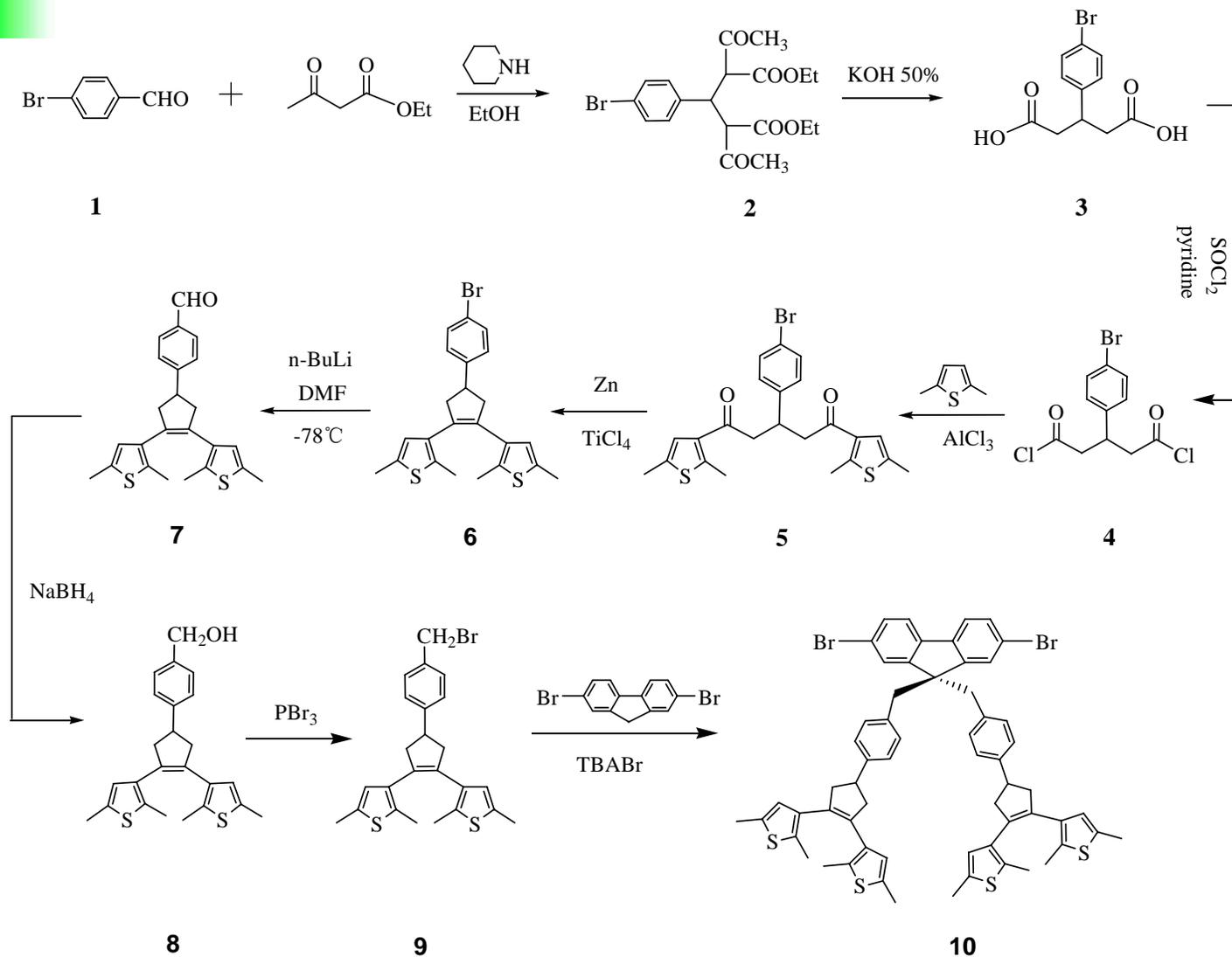
Circular Dichroism spectrum of BTE-NA-(chol)₂ gel, the open-ring isomer (blue line), in the photostationary state (red line) (0.5 wt/v %) upon irradiation by 365nm light at room temperature.



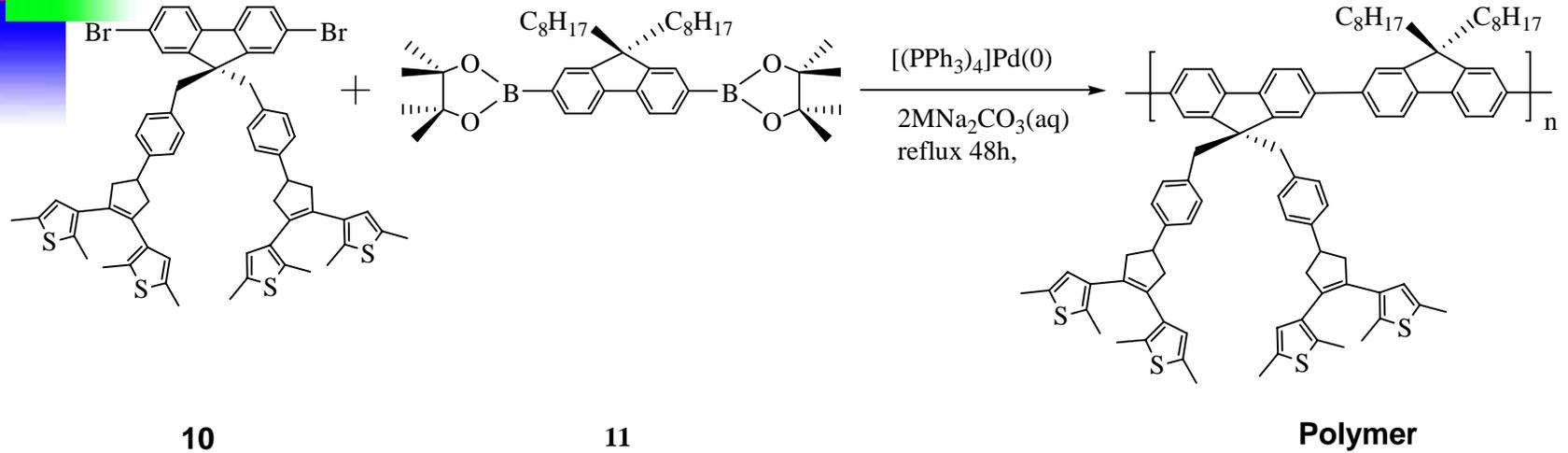
Circular Dichroism spectrum of BTE-NA-(chol)₂ in THF solution (2.0×10^{-5} mol/L), the open-ring isomer (red line), upon addition of TBAF (Tetrabutylammonium fluoride salt) (blue line).



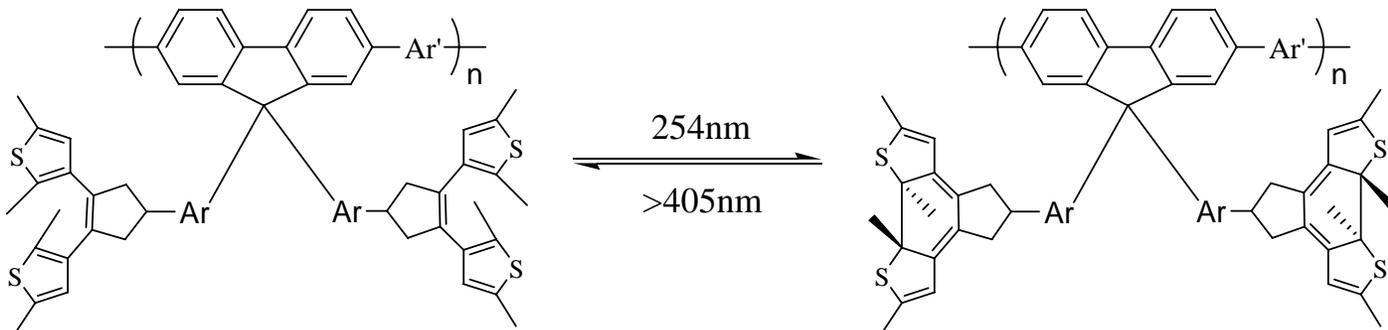
High-Content Pendant Photochromic Copolymers



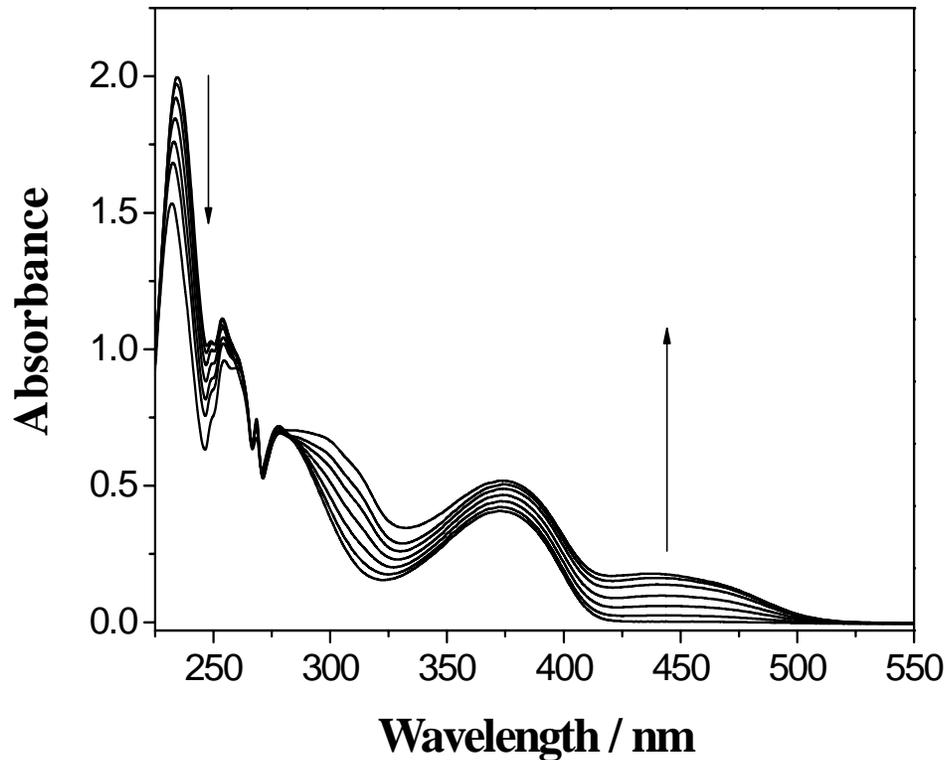
synthesis



weight-average molecular weight **Mw**: 13326 g/mol with a polydispersity of **1.8** Tg: 83.6 °C



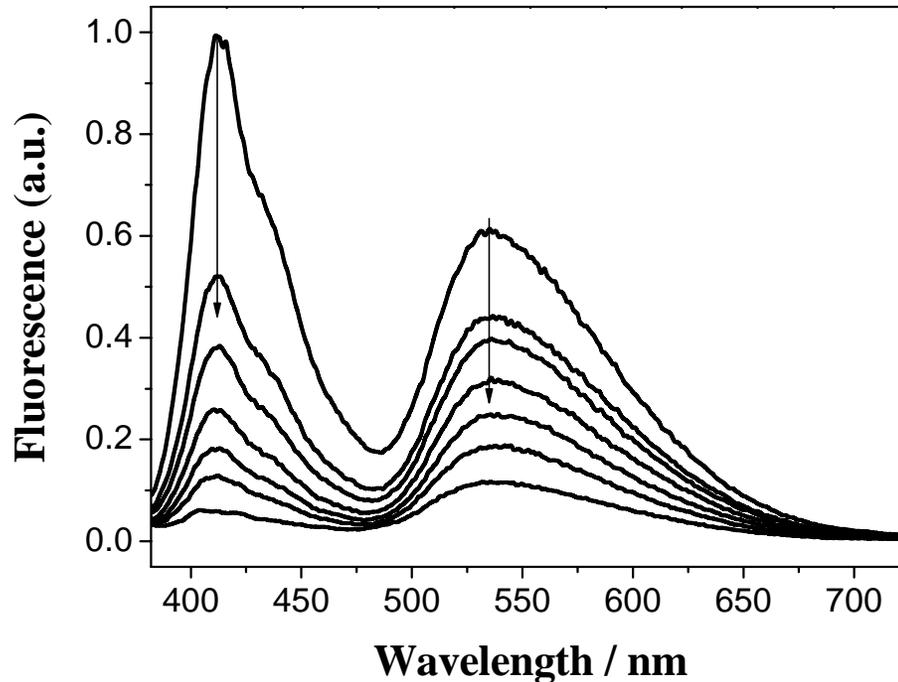
Photochromic polymer film



- Absorbance changes of the polymer net film upon irradiation at 254nm. Irradiation periods are 0, 1, 2, 3, 5, 8, 10min.

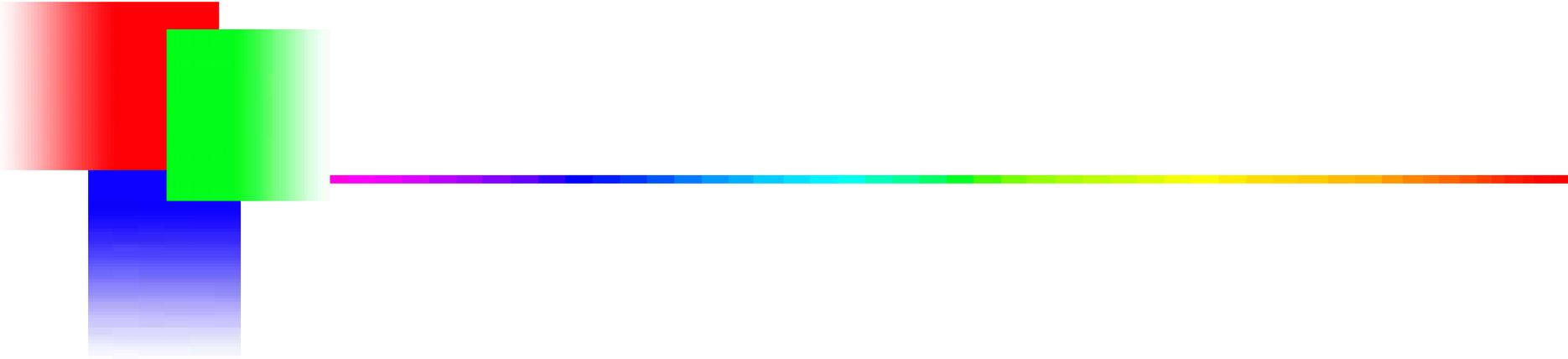
cyclization and cycloreversion quantum yields in THF were determined to be 0.25 and 0.20.

Fluorescence polymer switch



- Fluorescence change of the polymer film excited at 375nm. Irradiation periods are 0, 1, 2, 3, 5, 8, 10min (irradiated at 254nm).

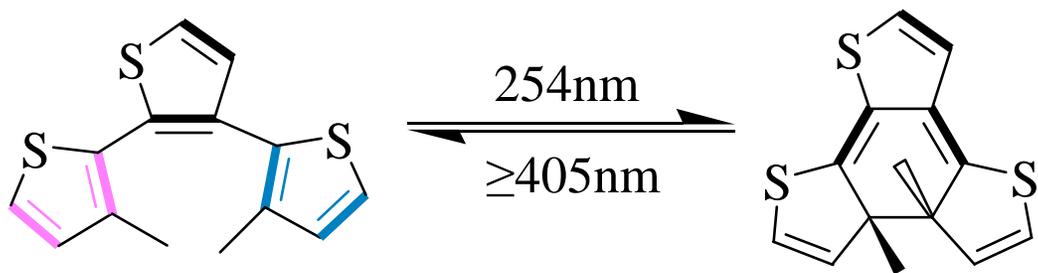
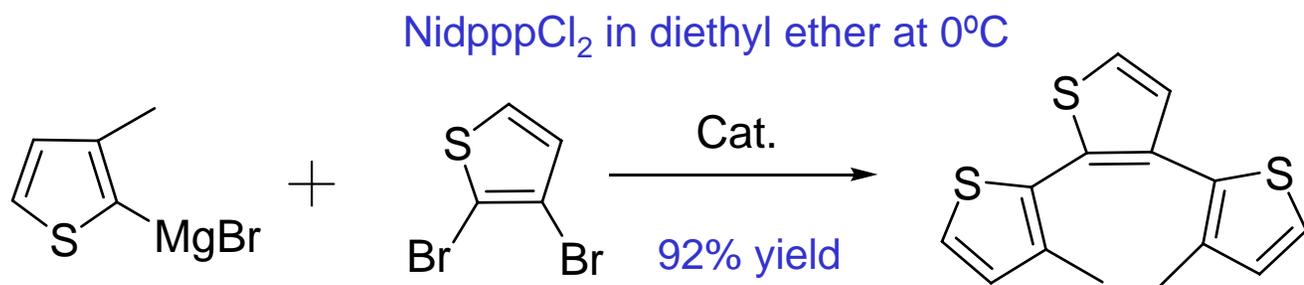
The fluorescence quantum yield of the polymer in THF was measured using anthracene ($\Phi=0.46$) as a reference and determined to be 0.71 .



Effective Synthesis of Photochromic Systems

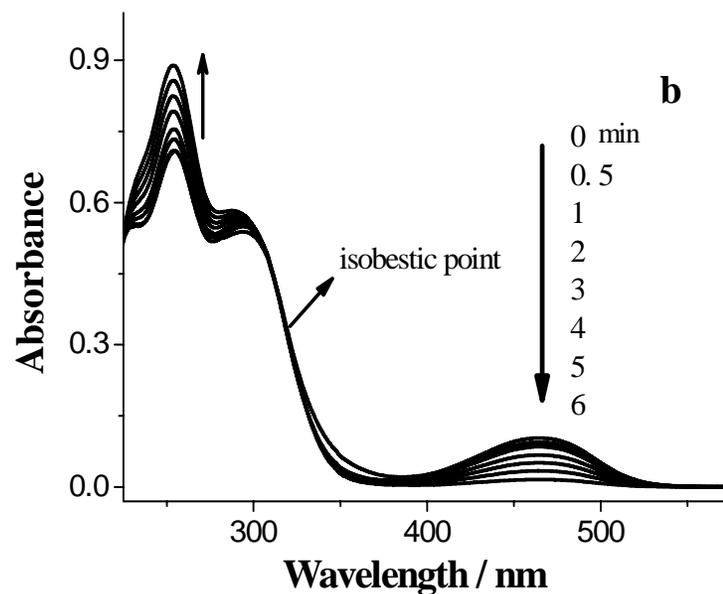
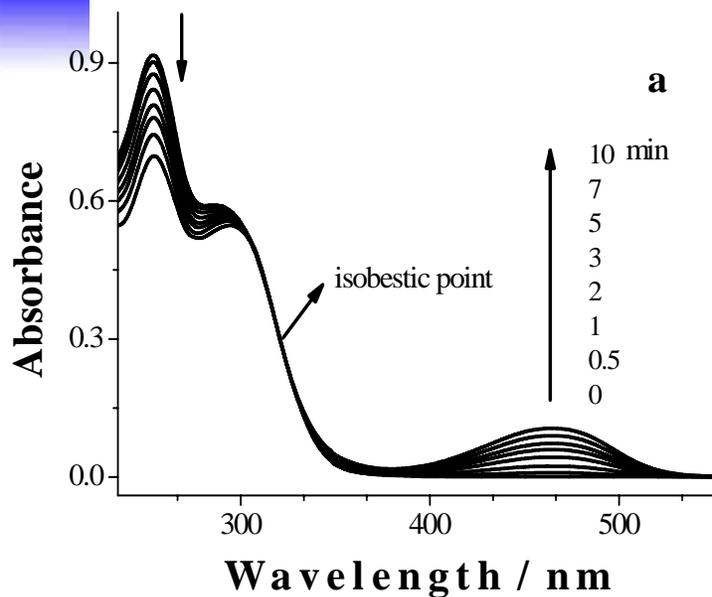
X. C. Li, H. Tian, *Tetrahedron Lett.*, 2005, **46**, 5409

Synthesis of Photochromic Triangle Terthiophene by One Step



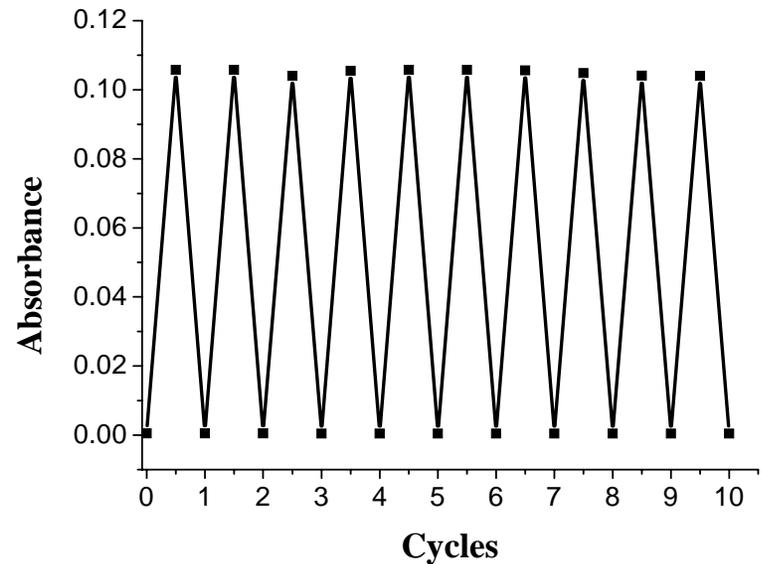
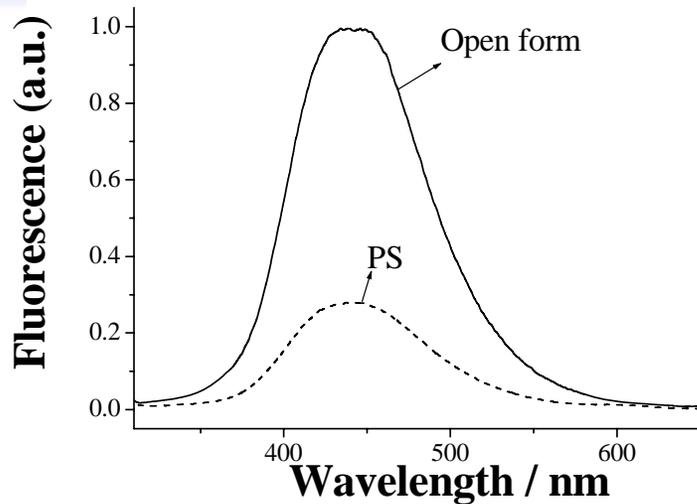
ring-open
(fluorescent)

ring-closed
(non-fluorescent)



- Absorption changes of **TTT** in THF upon irradiation at 254nm (5×10^{-5} M, a) and its photochromic bleaching upon irradiation at ≥ 405 nm (5×10^{-5} M, b)

The cyclization and cycloreversion quantum yields of **TTT** in THF were 0.33 and 0.30.

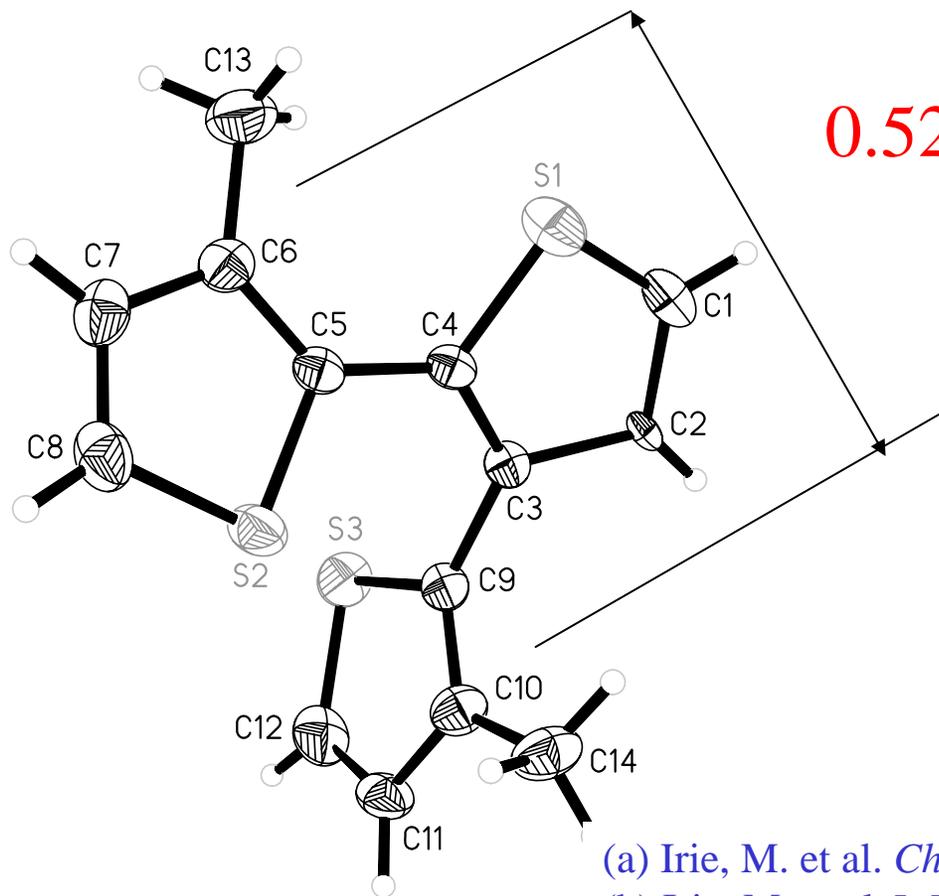


- Fluorescence spectral changes of TTT in THF (5×10^{-5} M, excited at 300 nm) at room temperature: before irradiation with 254nm light (solid line) and after irradiation (dashed line).

Fluorescence quantum yield of **TTT** in THF solution is 0.13. (anthracene as reference)

No cyclization in single crystal, why?

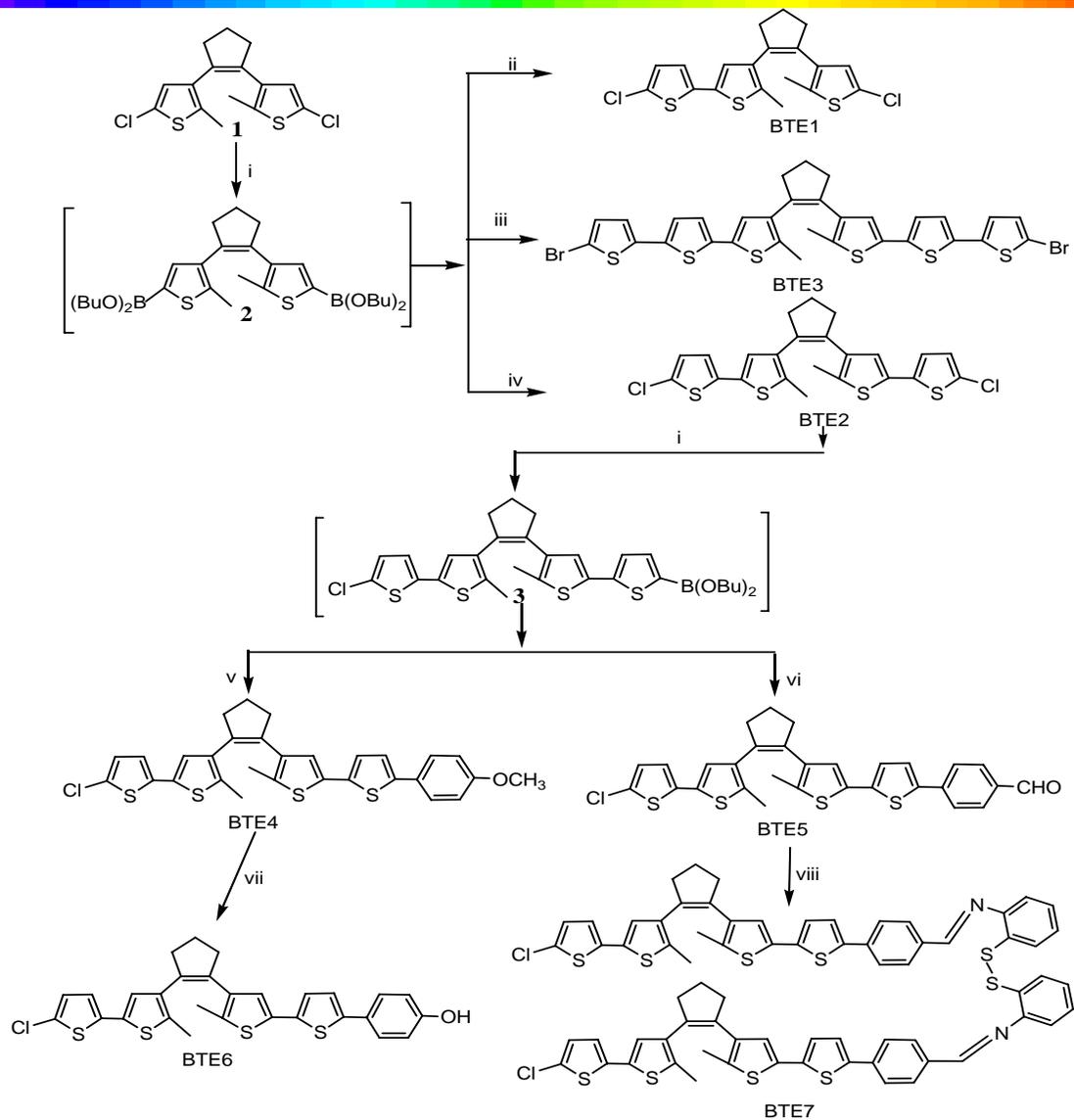
the dihedral angles between the two non-bridging thiophene ring is 80.9°

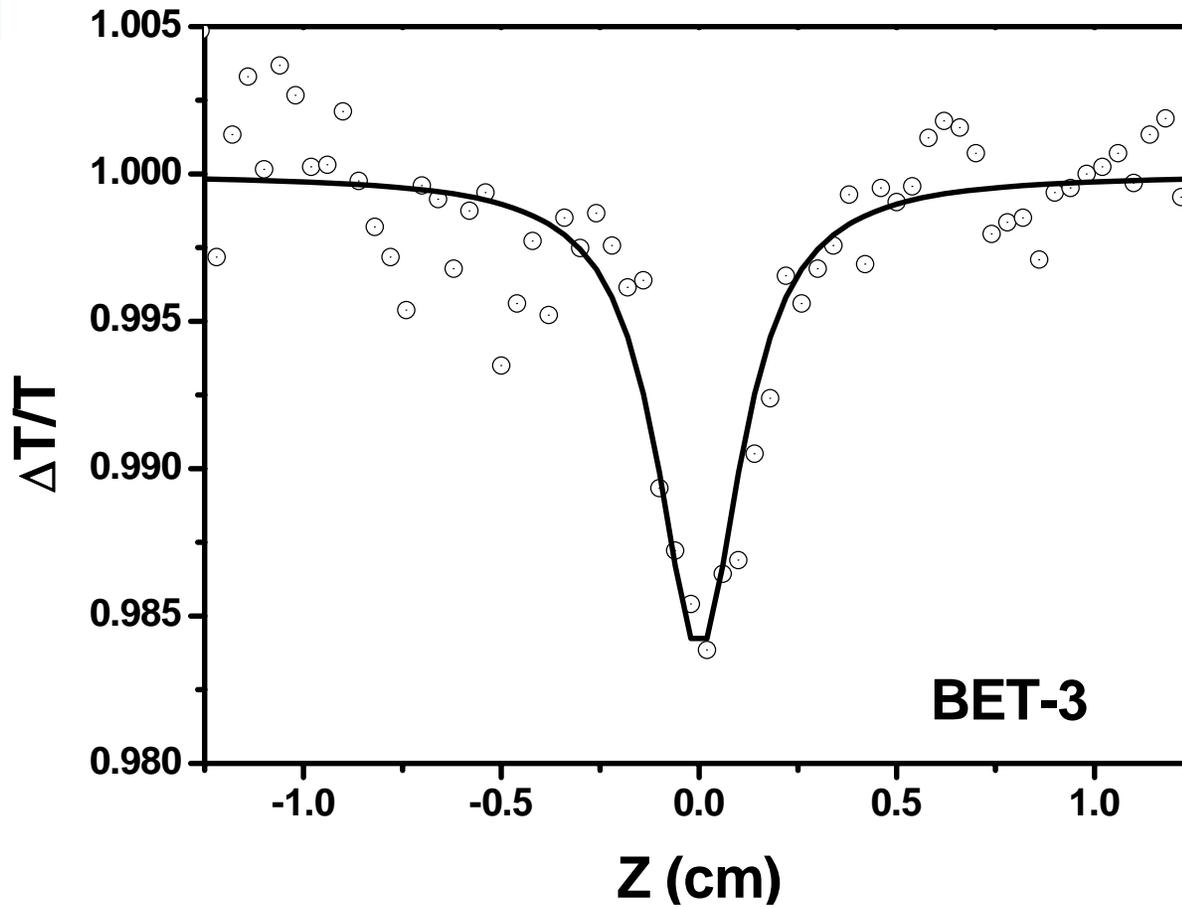


0.524 nm

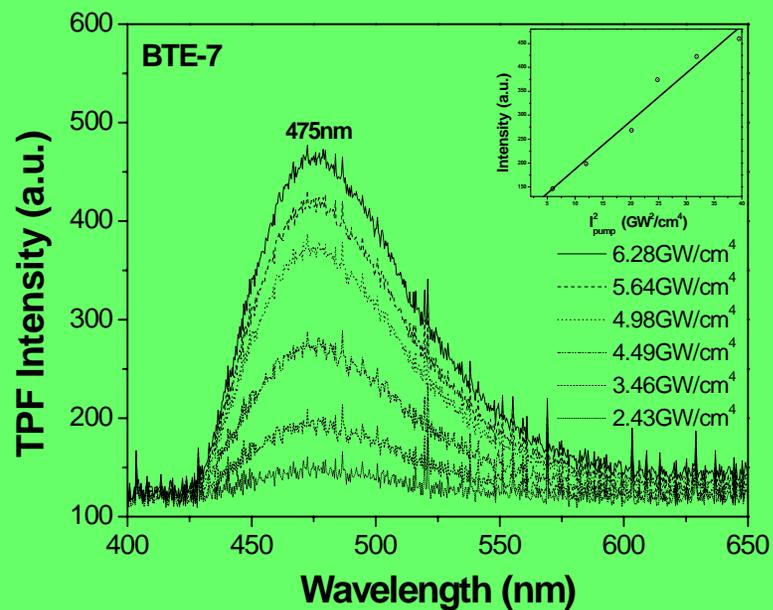
>0.42 nm: -
 ≤ 0.42 nm: +

- (a) Irie, M. et al. *Chem. Commun.* **2002**, 2804.
(b) Irie, M. et al. *J. Phys. Chem. A* **2002**, 106, 209
(c) Irie, M. et al. *Bull. Chem. Soc. Jpn.* **2004**, 77, 195.





Open-Aperture Z-scan trace of BTE3: scattered circle experimental data, straight line theoretic fitted data



BTE2



BTE3



BTE5



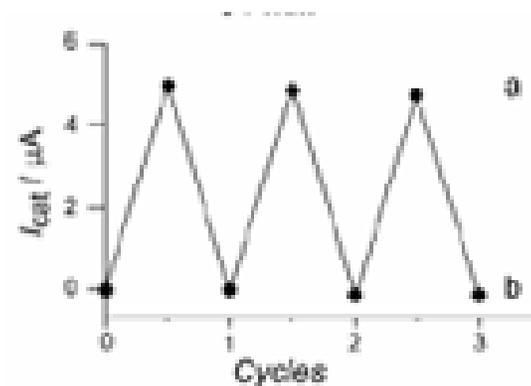
BTE6



BTE7

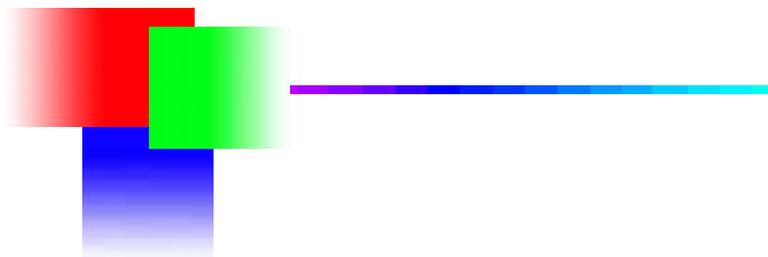
- The fluorescence images of compounds under the excitation of 140 fs, 800 nm pulse

Monolayer “Write-Read-Erase” system based on photochromic compound



Scheme 2 ‘Write-Read-Erase’ photo-electrochemical system based on the electrocyclization of (2a).

I. Willner, H. Tian, et al., *Chem. Commun.* 2006, 2147 - 2149



HOT Paper:

A breakthrough for chemical computers has been achieved by scientists in Israel and China

ChemComm

... the world's no. 1 abstract blend of high quality research from across the chemical sciences



Hot Paper: Information processing encoded

27 February 2008

A breakthrough for chemical computers has been achieved by scientists in Israel and China.

Scientists at the Hebrew University of Jerusalem and East China University of Science and Technology successfully assembled photochemical/photochemical molecules on a solid substrate. The assembly acted as either a logic read-out system, or as a memory element that reversibly increased function.



In recent years, photochemical molecular assemblies have been extensively studied as information storage systems and have become known as chemical computers. The method uses molecules to make systems that function as either switches or logic gates. Daniel Willner and his team realized that integration of the chemical parts with transistors that allow the electrons read-out of the logic operation is essential if any practical use of these systems is going to be achieved.

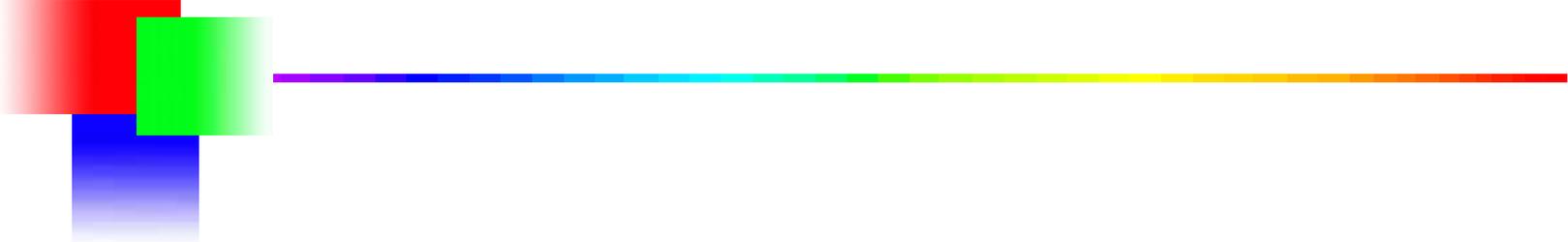
Their new technique couples electrochemical and photochemical inputs which generates a inter-disciplinary information processing system. In addition, they have proven that the chemical interface acts as a memory element, which allows a persistent signal. This breakthrough has the potential to enhance the complexity of information that can be processed by molecular units.

The team believe that input from organic chemists and materials scientists is now needed to further develop this work. They consider that this will lead to a new generation of smart materials that perform logic functions of higher complexity and reliability.

David Willner

Publication

Baron Baran, Aviel Osterberger, Eugene Harel, Oleg Lavrenko, Daniel Willner, Sheng Wang and Pei Tang, Chem Commun, 2008, DOI: 10.1039/b714877a



Thanks

National Science Foundation of China
Shanghai Scientific Committee

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Ms. Yanli Feng, Ms. Lei Sun

Profs. Yanling Song, Daoben Zhu/ ICCAS
Prof. Itamar Willner/ Israel