

Various Sensor Applications Based on Conjugated Polymers

Advanced Photonic Research Institute (APRI)
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미래 광과학기술 연구의 중심지

고등광기술연구소

Advanced Photonics Research Institute



Introduction : Conjugated polymers

Conjugated polymers



Alan J. Heeger



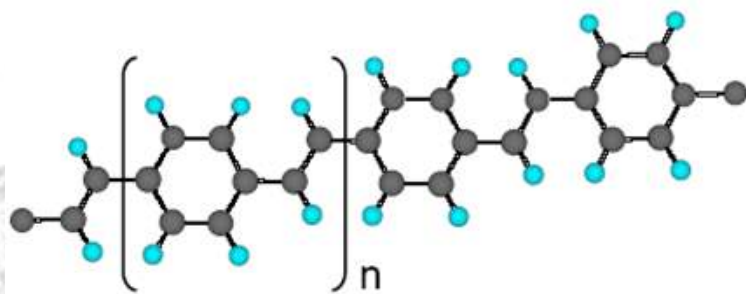
Alan G. MacDiarmid



Hideki Shirakawa



The Nobel Prize in Chemistry 2000 was awarded jointly to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa "for the discovery and development of conductive polymers".



Polyphenylenevinylene

Gwangju Institute of Science and Technology

Attractive due to:

- Integrability with inorganic semiconductors
- Low cost (fabric dyes, biologically derived materials)
- Large area bulk processing possible
- Tailor molecules for specific electronic or optical properties
- Unusual properties not easily attainable with conventional materials

But problems exist:

- Stability
- Patterning
- Thickness control of polymers
- Low carrier mobility

Introduction : Conjugated polymers

Traditional polymers



Plastic case



Plastic panel



Electric wire cover

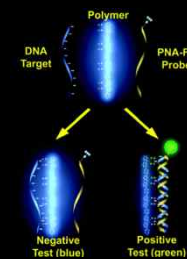


Organic
opto-electronics

Conjugated polymers



Sensors



Organic LED



Photovoltaic

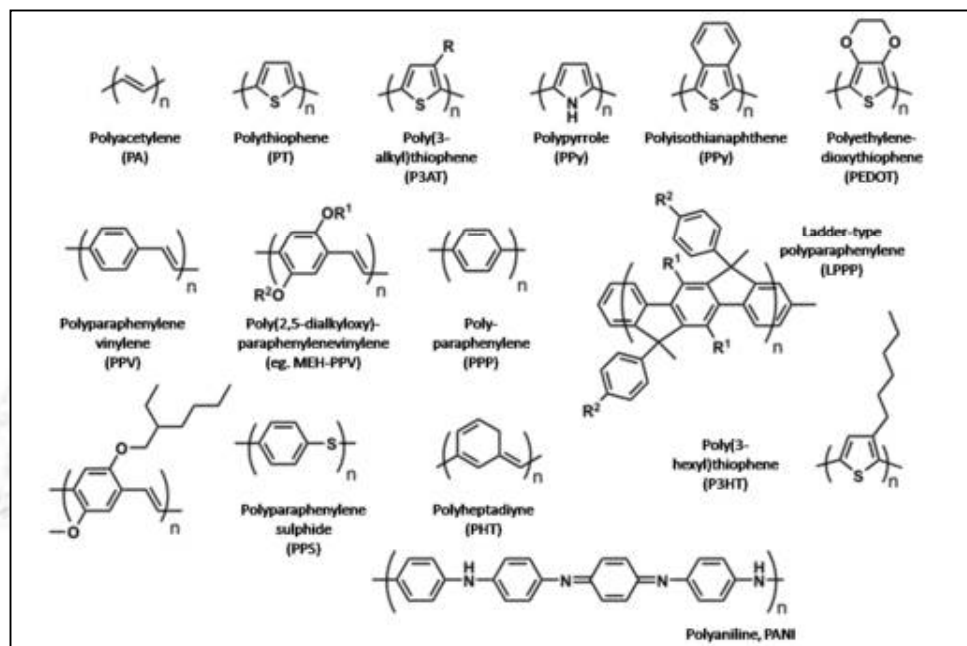


OTFT

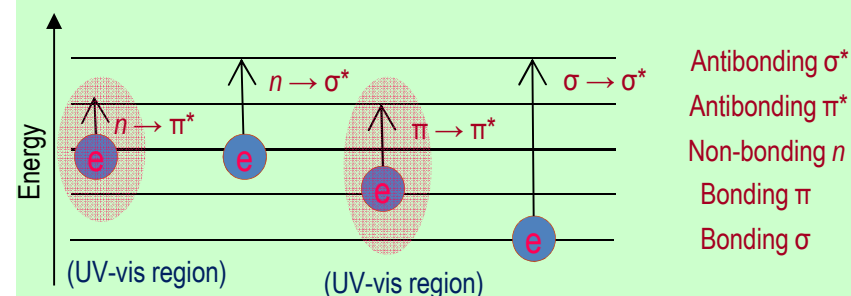


Introduction : Conjugated polymers

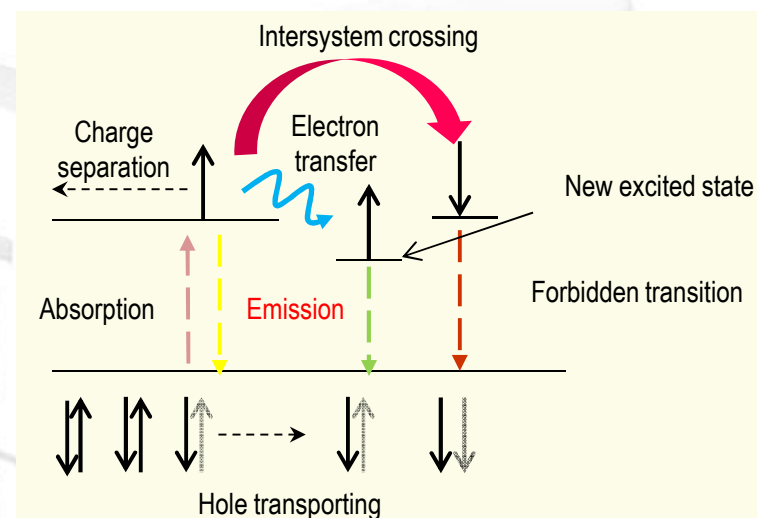
Conjugated polymers



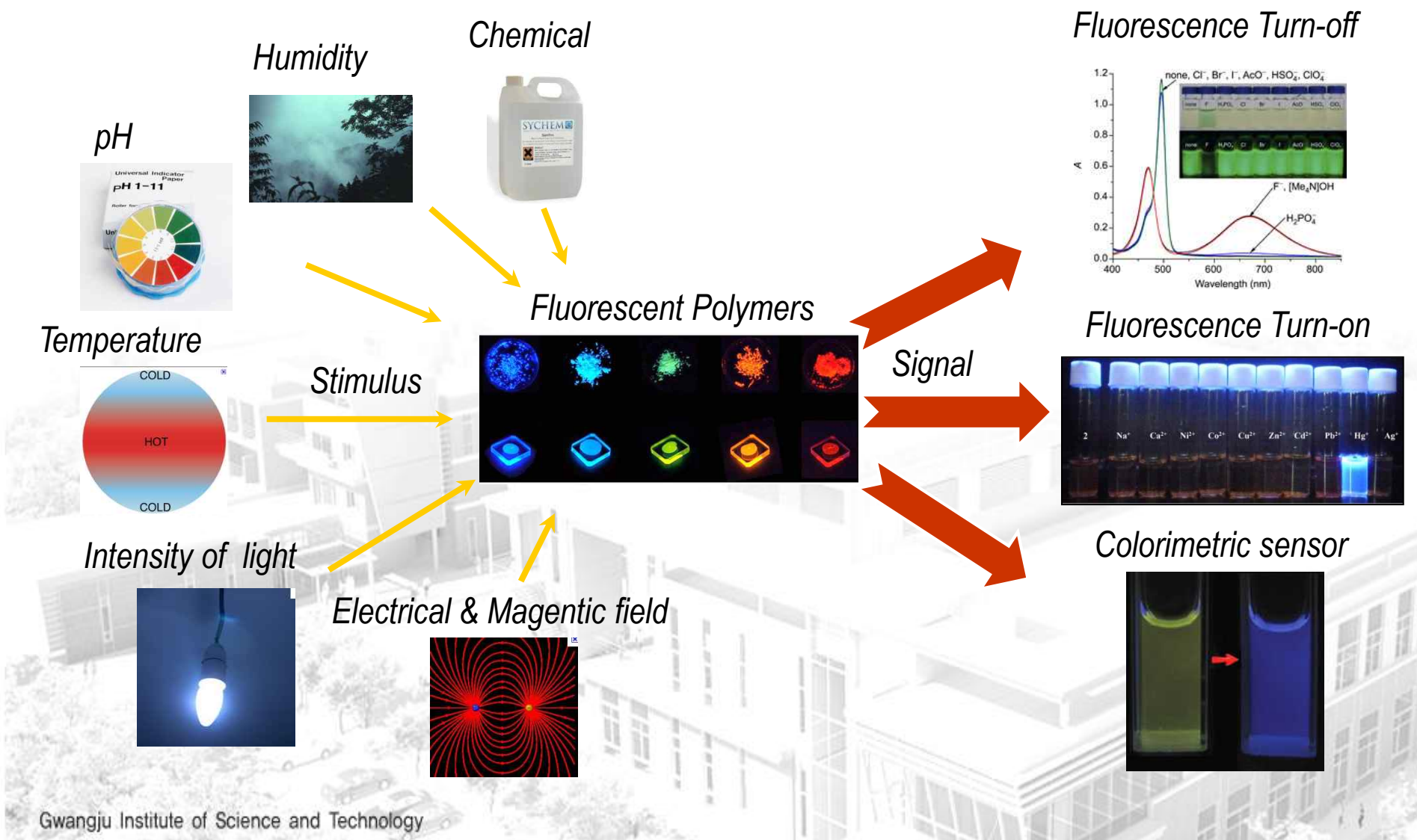
UV-Vis absorption



Fluorescence emission



Introduction : Conjugated polymers

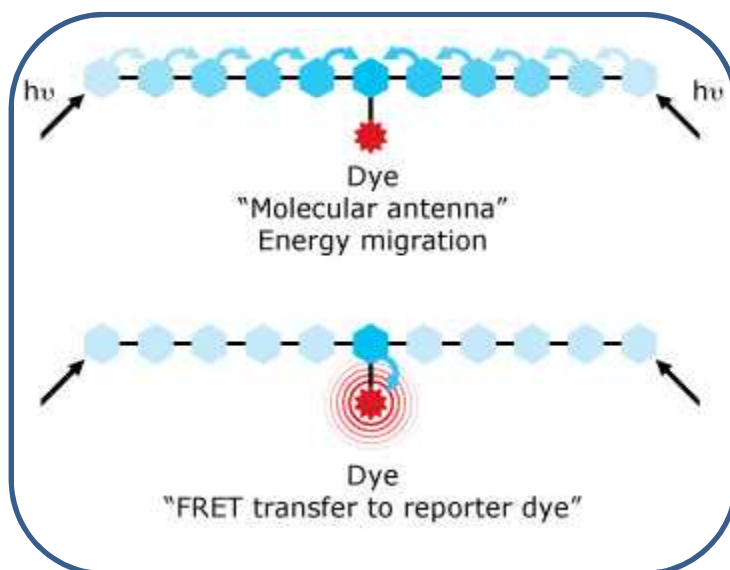


Fluorescence Turn-Off

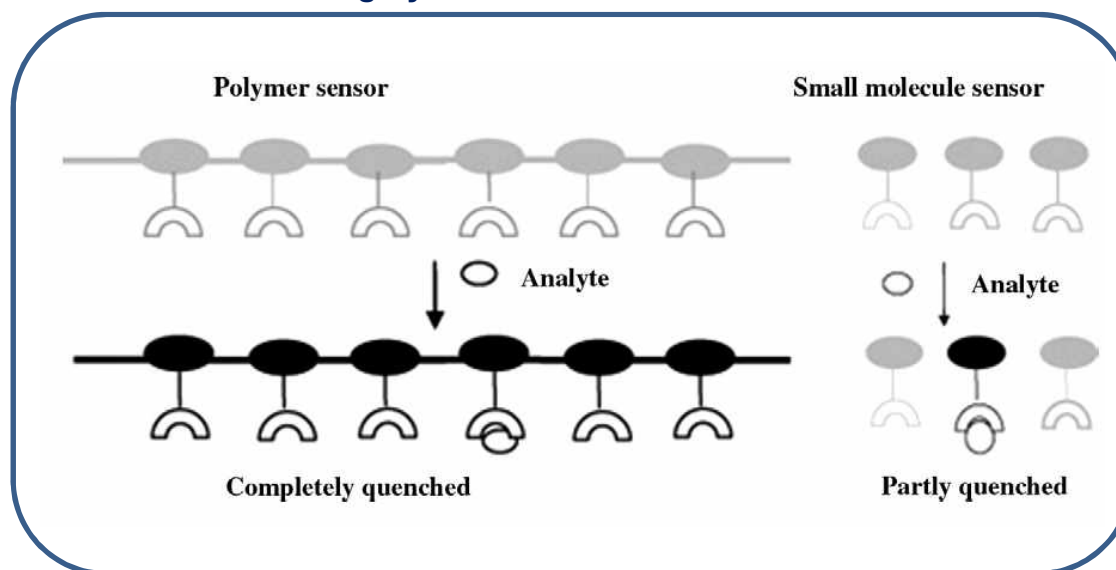
Signal amplification

Fractional binding gives large fluorescence emission changes

Antenna effect



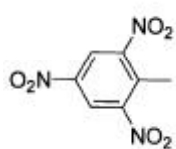
Molecular wiring system



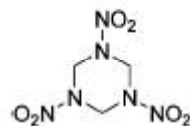
Fluorescence Turn-Off

Quencher :

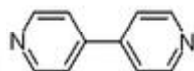
- 1) Electron deficient molecules
ex) Trinitrotoluene (TNT), Viologen
- 2) Heavy metal ions
ex) copper, iron etc.



TNT

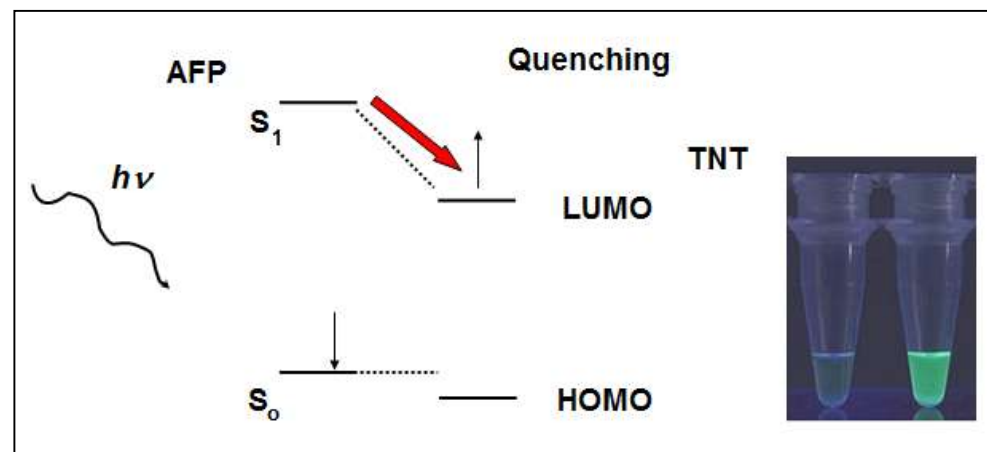
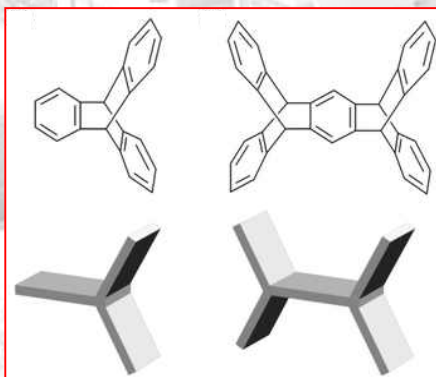


RDX

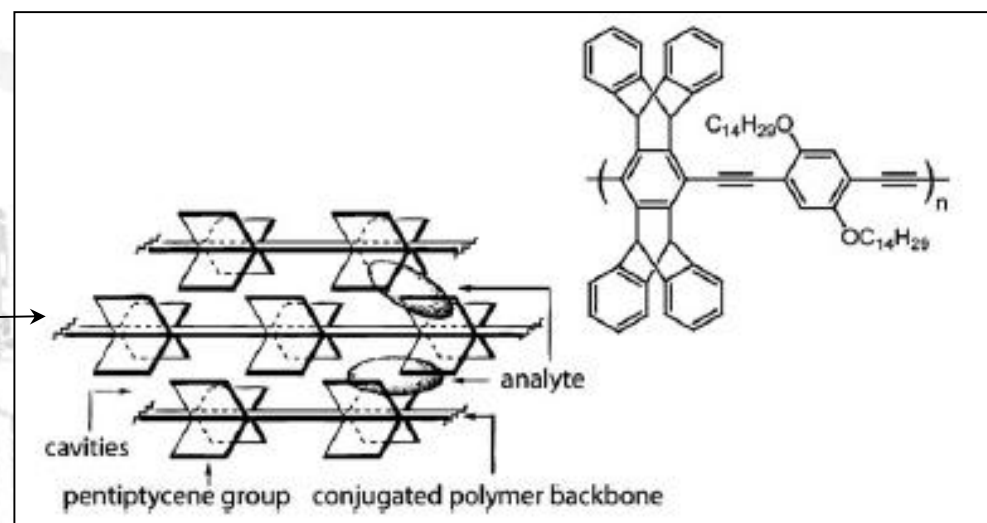


Viologen

Pentapiptycene scaffold



Fluorescent porous polymer film

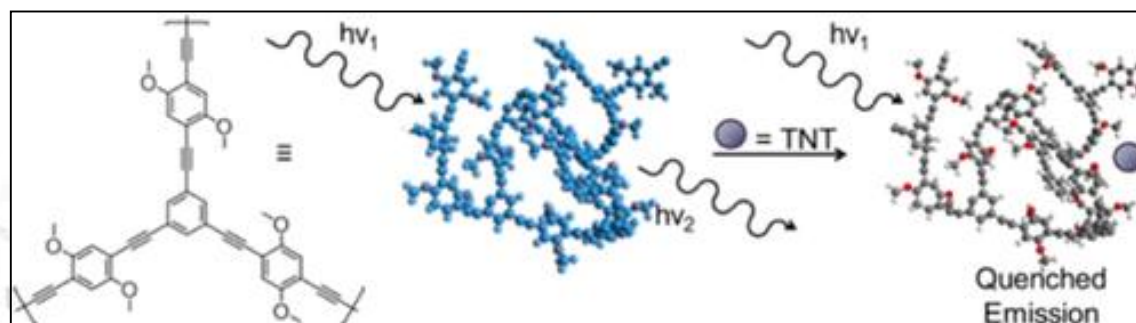


Fluorescence Turn-Off

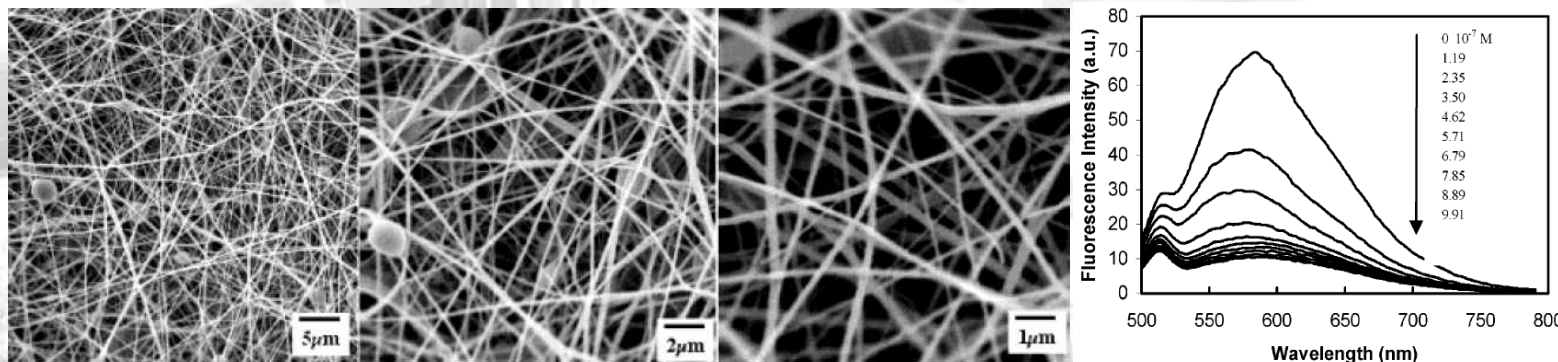
Fluorescent sensors with high sensitivity

High surface area-to-volume ratio leads to efficient interaction between the fluorescent conjugated polymer and analytes.

Conjugated porous polymer network system

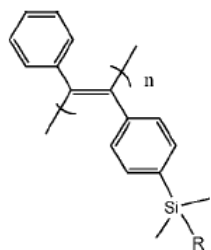
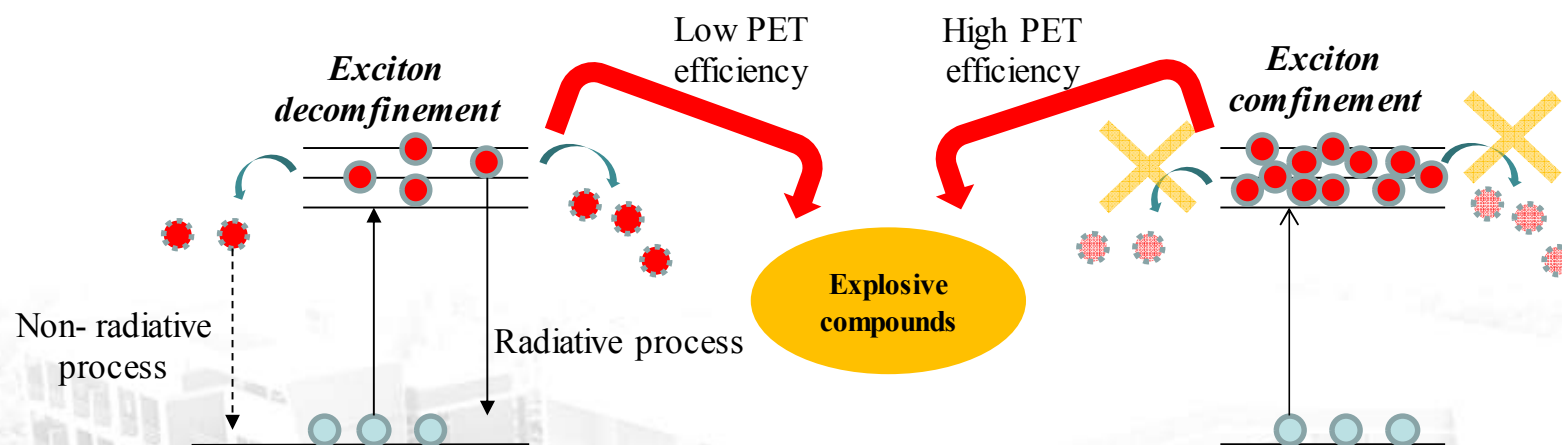


Electrospun nanofibrous membranes for highly sensitive optical sensor



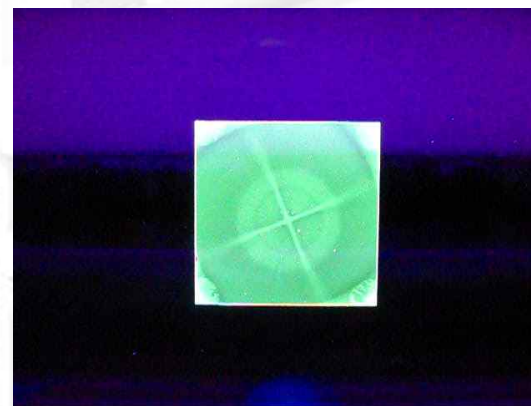
Fluorescence Turn-Off

Conjugated polymer film with high fluorescence quantum efficiency and large fractional free volumes



- High fluorescence quantum efficiency
- Large fractional free volumes.

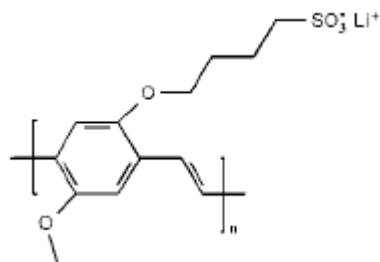
Movie : Fluorescence quenching by TNT vapor and recovery.



Fluorescence Turn-Off

Conjugated polymer biosensor

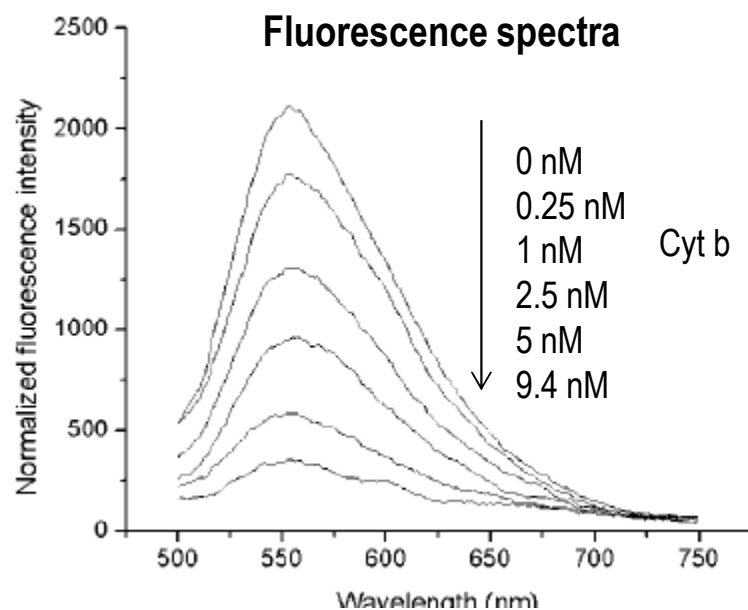
Conjugated polyelectrolyte



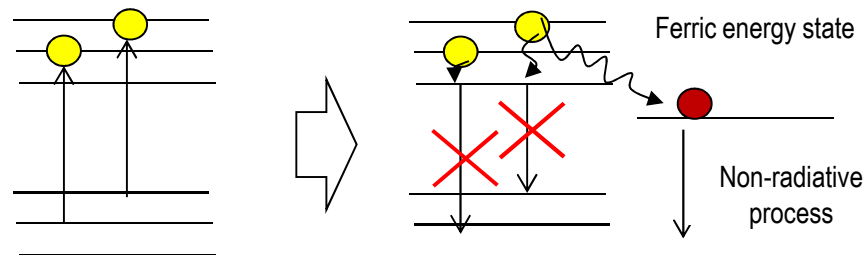
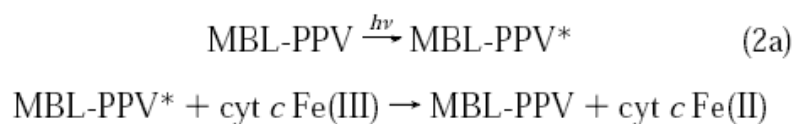
Cytochrome B (cyt b): Mw = 12384 ; isoelectric point = pH 9.6

Myoglobin : Mw = 16951 ; isoelectric point = pH 7.4

Chicken egg white Lysozyme : Mw = 14307 ; isoelectric point = pH 11.4
(50% quenching rate)



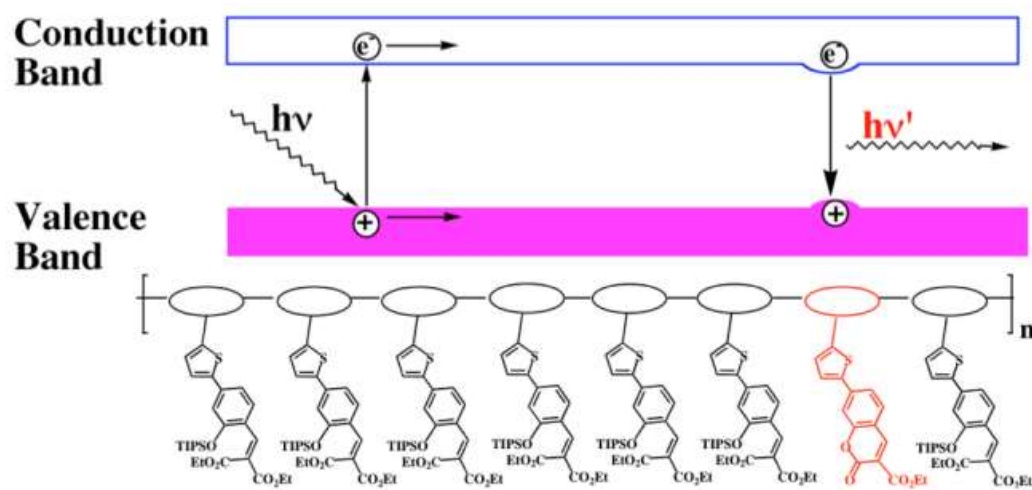
Quenching mechanism



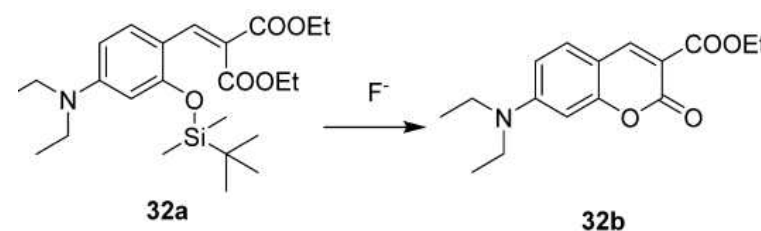
Fluorescence Turn-Off

Detection of fluoride anion

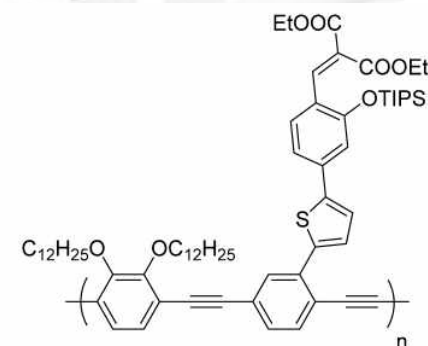
Molecular wiring system



Fluoride-triggered lactonization reaction



Conjugated polymer



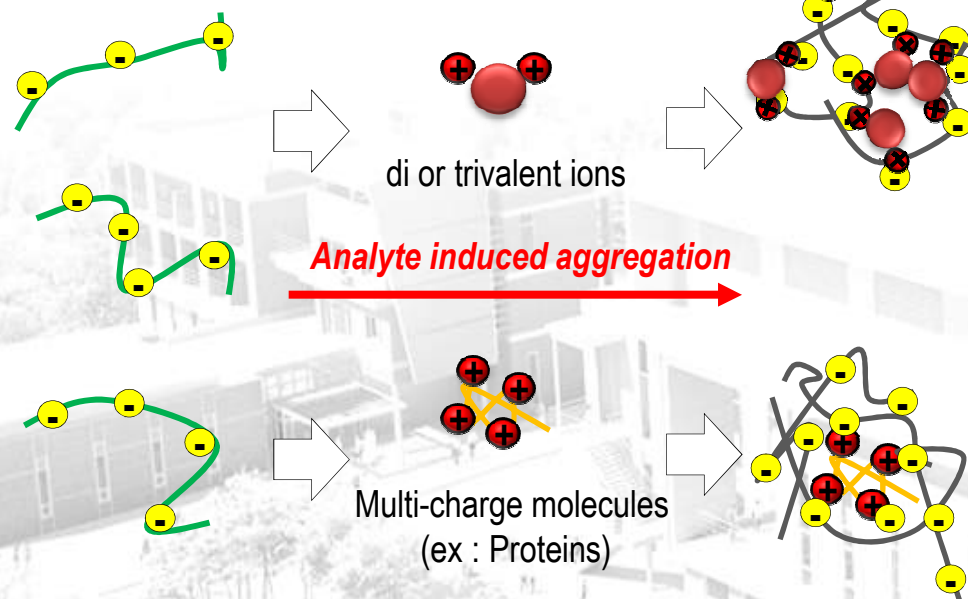
Selective detection of fluoride anion by conjugated polymer was achieved by exploiting the unique reactivity of fluoride with silicon.

Fluorescence Turn-Off

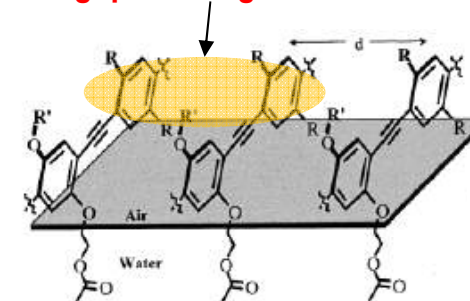
Analyte induced aggregation

Isolated chains :
Strong emission

Aggregated chains :
Weak emission

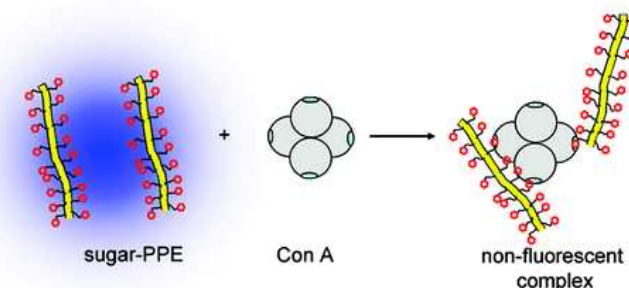


Strong quenching site



JACS 2000, 122, 5885-5886

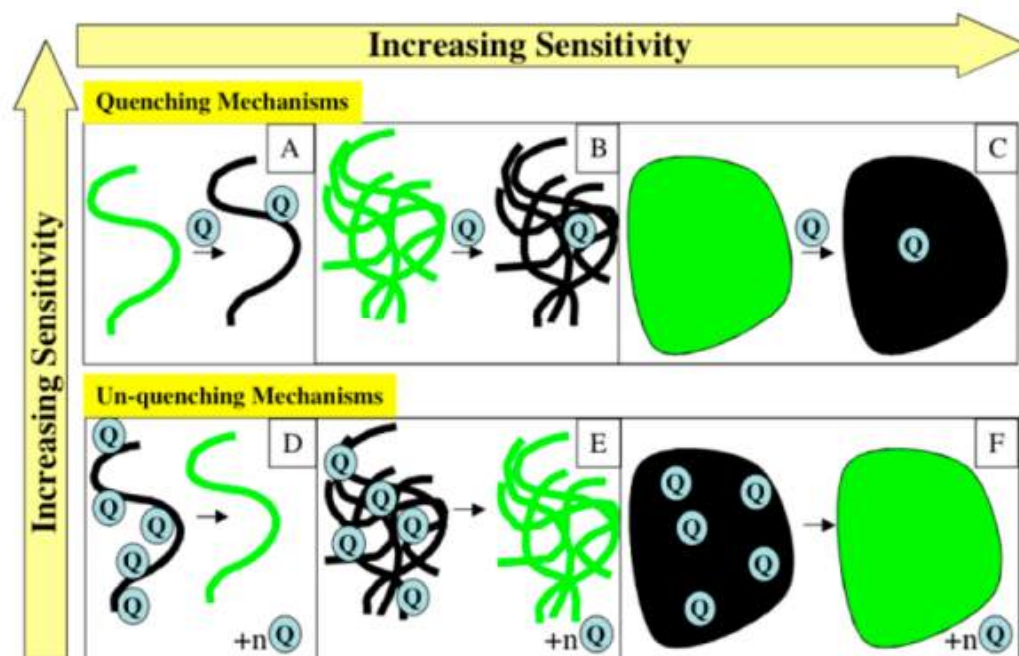
Fluorescence self-quenching mechanism



JACS 2008, 130, 6952-6954

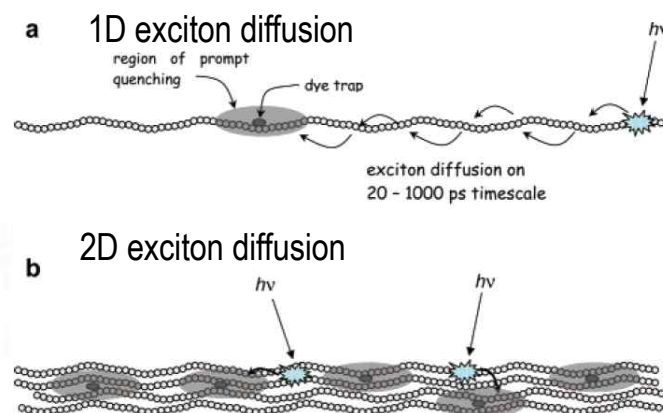
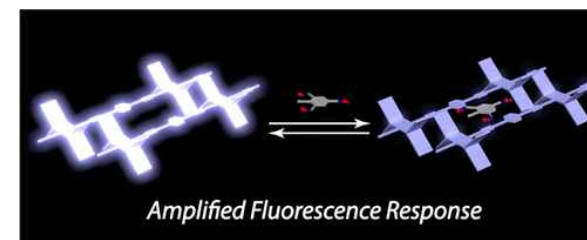
Fluorescence Turn-Off

Effect of dimensionality (D) on (un)quenching mechanisms



Role of mechanism and dimensionality in determining the relative sensitivities of conjugated polymer sensors. Sensitivity increases as polymer chains are assembled into structures that provide the exciton with additional energy migration pathways that exhibit greater efficiency. Unquenching (turn-on) is generally less sensitive than quenching

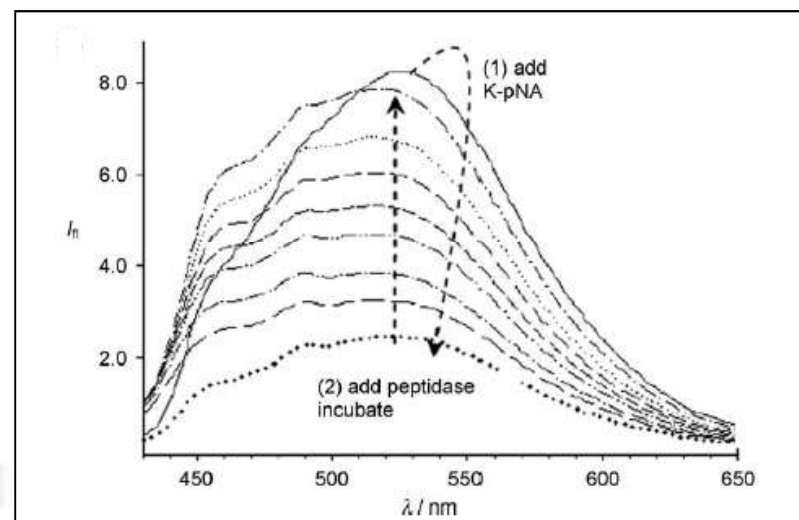
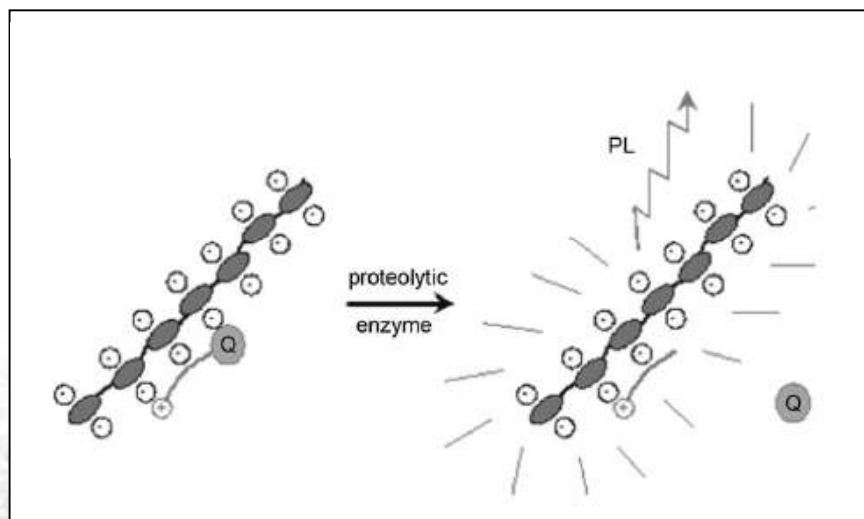
Amplified quenching



a) Nonaggregated polymer chain (1D) at a high polymer/dye ratio
b) Aggregated polymer at a low polymer/dye ratio.

Fluorescence Turn-On

Turn-on mechanism

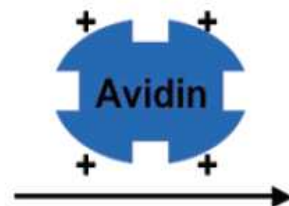
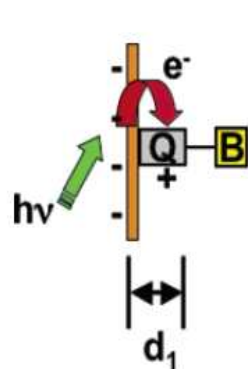


The unquenching process, although a turn-on mechanism, tends to suffer from lower sensitivity because to obtain a highly quenched state, some of the quenching groups will inevitably be located within the exciton diffusion length. However, the mechanism is very useful to develop sensors with high selectivity.

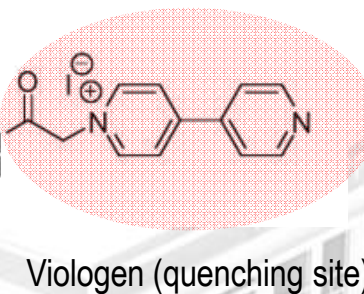
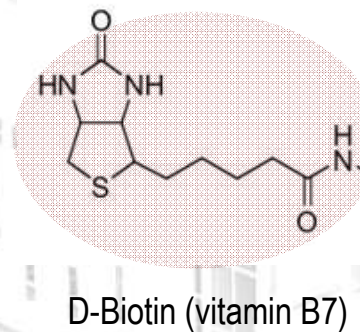
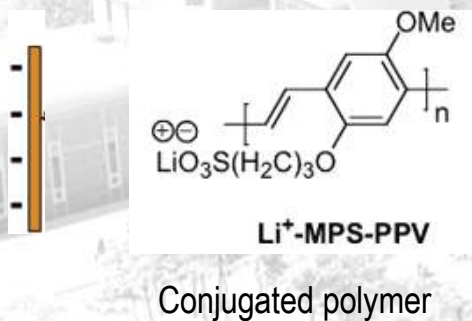
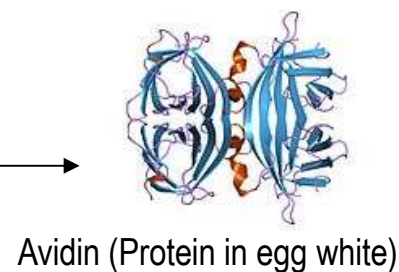
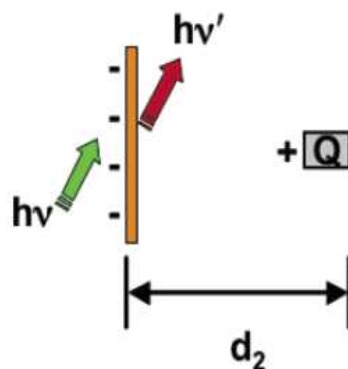
Fluorescence Turn-On

Fluorescence Turn-on type biosensor

Quenched fluorescence

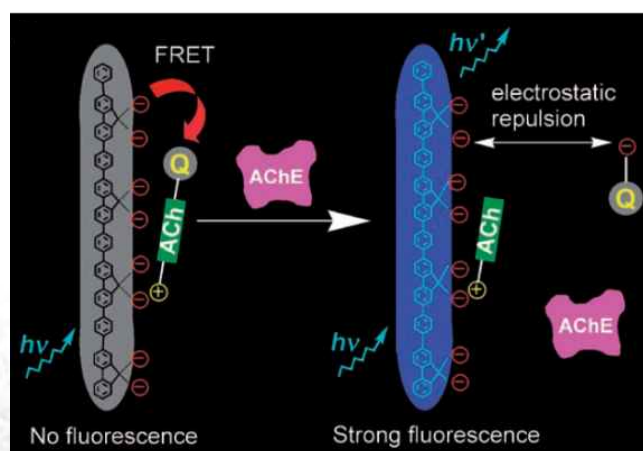


Turn-on!



Fluorescence Turn-On

Continuous Fluorometric Assays for Acetylcholinesterase Activity



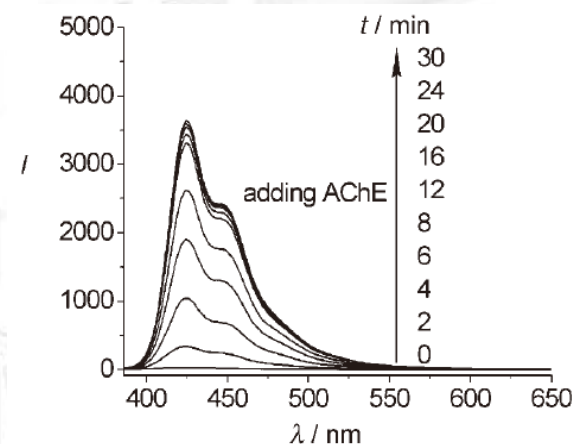
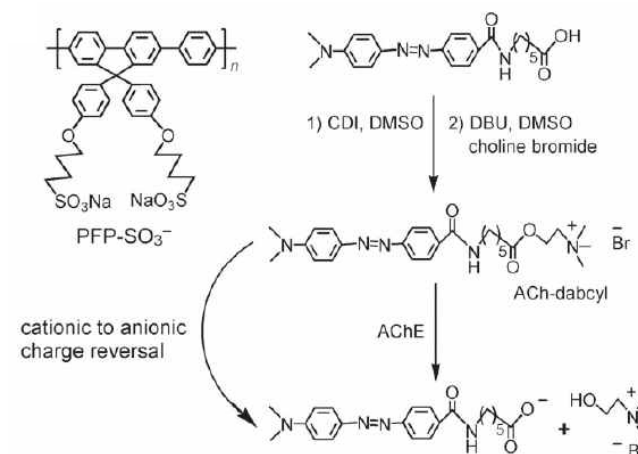
ACh

Acetylcholine (ACh)

AChE

Acetylcholinesterase (AChE)

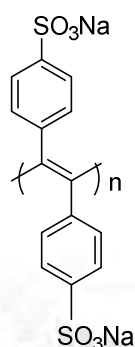
The hydrolytic breakdown of ACh in the brain by AChE can accelerate the assembly of amyloid b-peptides into amyloid fibrils, a process that results in Alzheimer's disease



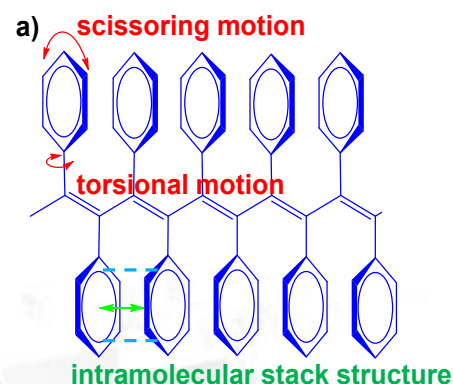
Fluorescence Turn-On

Sensor base on polydiphenylacetylene

Conjugated polyelectrolyte
(CPE) based on PDPA



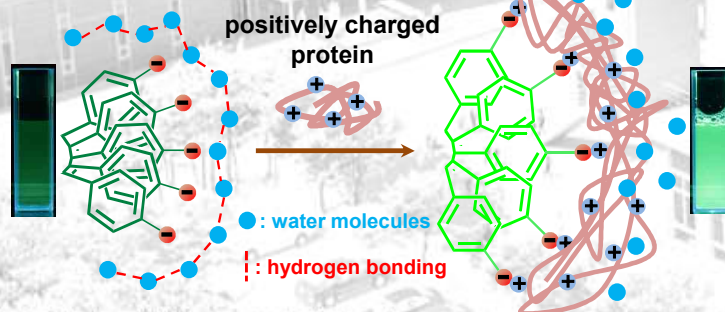
Emissive system :



New fluorescence signal transduction mechanism

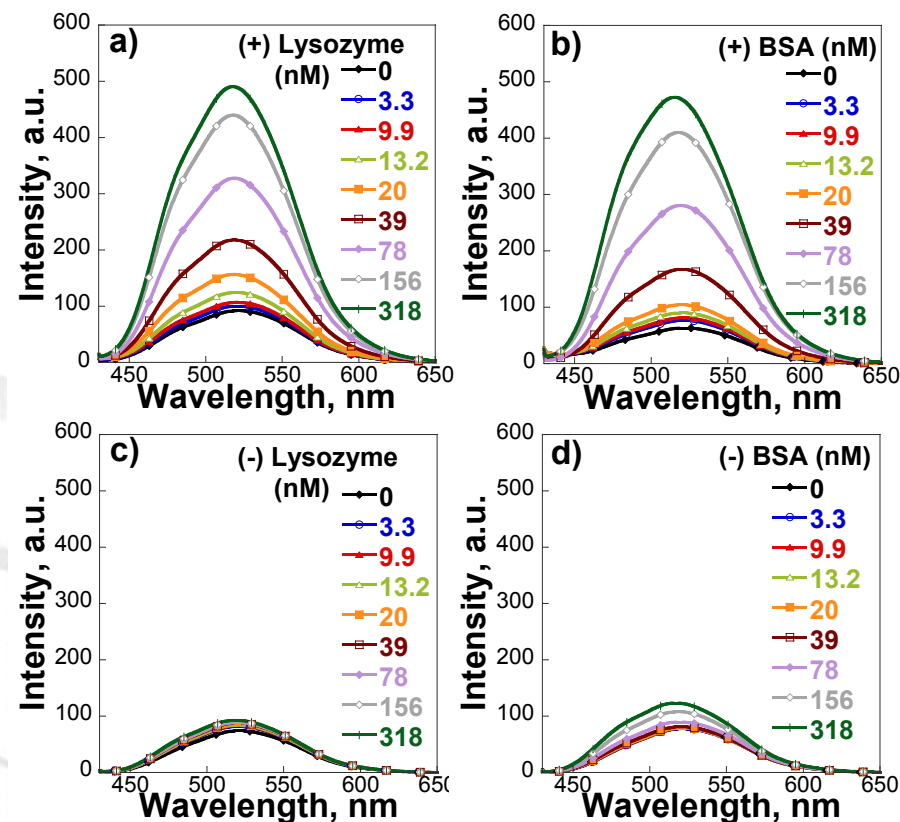
Highly dense IaSS :
low FL emission

Relaxed IaSS :
high FL emission



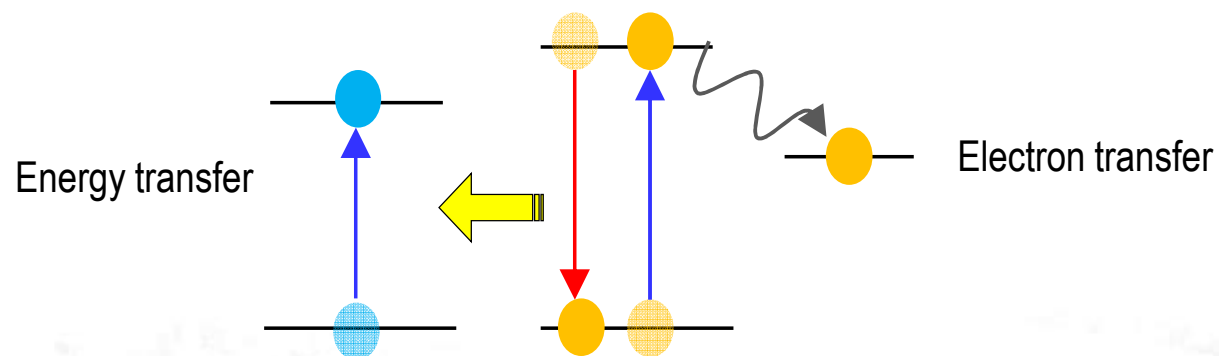
Gwangju Institute of Science and Technology

Fluorescence turn-on response to multi-charged
biomacromolecules



Colorimetric sensors

Fluorescence resonance energy transfer (FRET)



Fluorescence resonance energy transfer

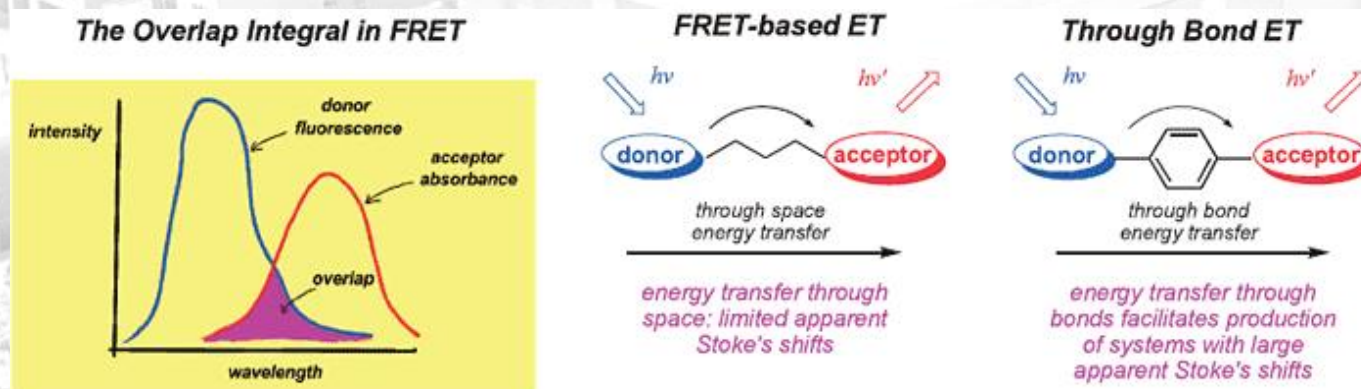
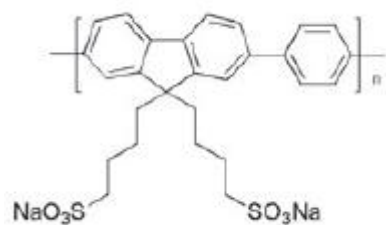


Figure 1. Overlap integral is critical in FRET, and it is the limiting factor in how far to the red a through space energy transfer system can fluoresce for a given donor. Through bond energy transfer systems have no known limitation of this kind.

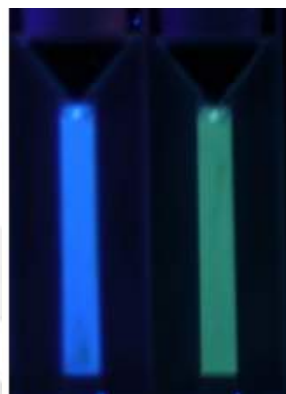
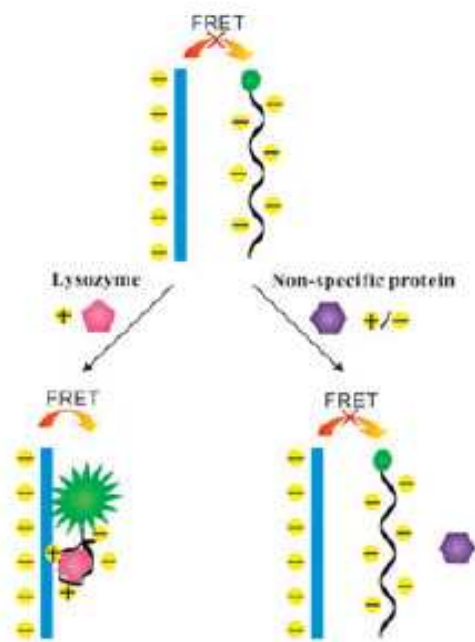
Colorimetric sensors

Chemical structures

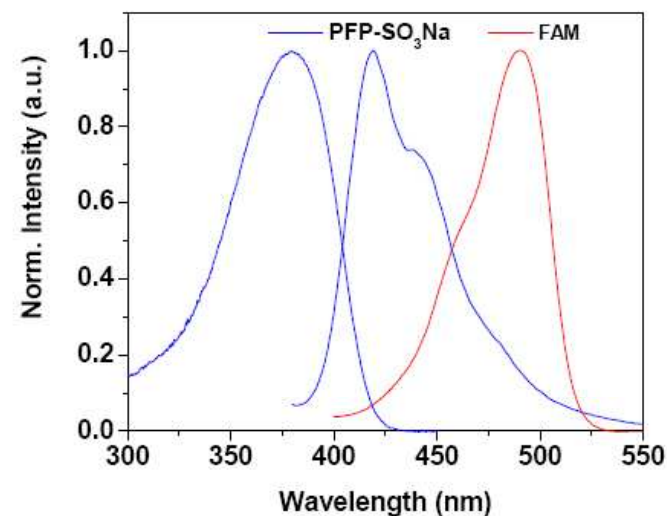


Dye labeled lysozyme :
Dye = 7-carboxyfluorescein (FAM)
isoelectric point = pH 11.4

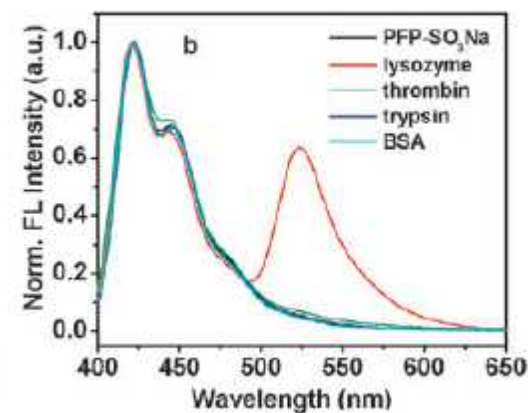
Detection mechanism



Spectra overlap



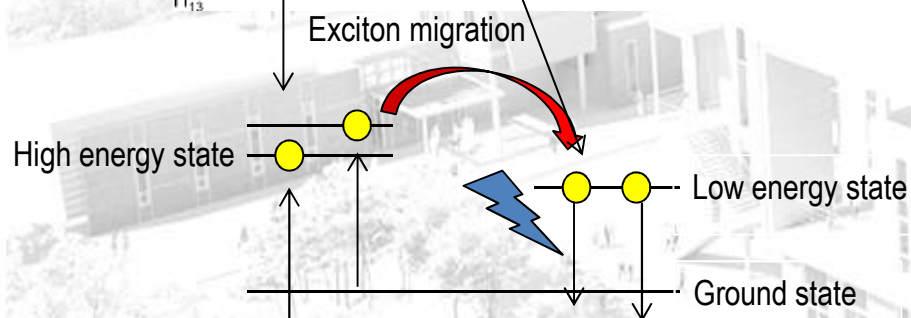
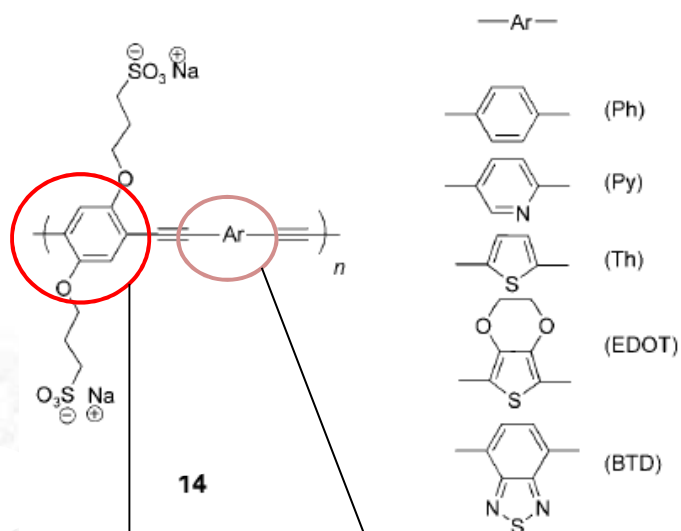
Fluorescence resonance energy transfer



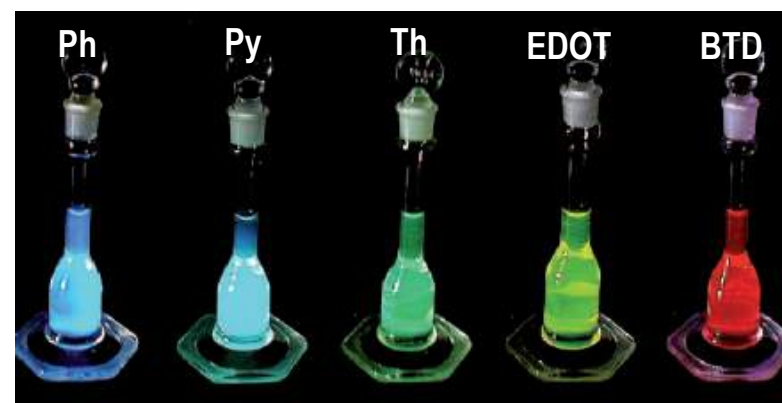
Colorimetric sensors

Aggregation induced fluorescence color changes

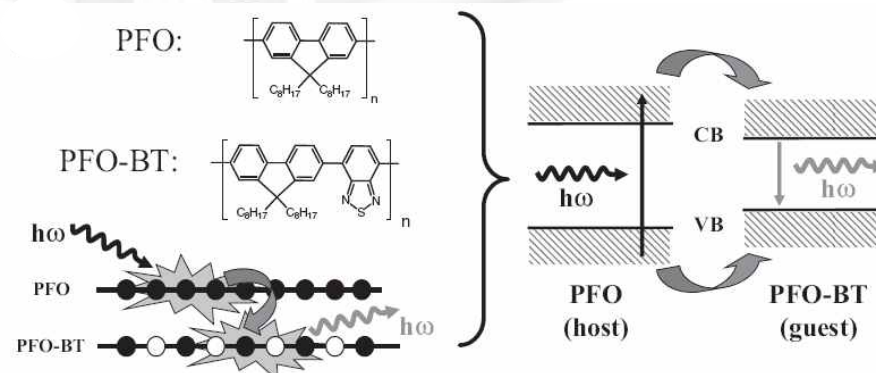
Chemical structures



Fluorescence emission color



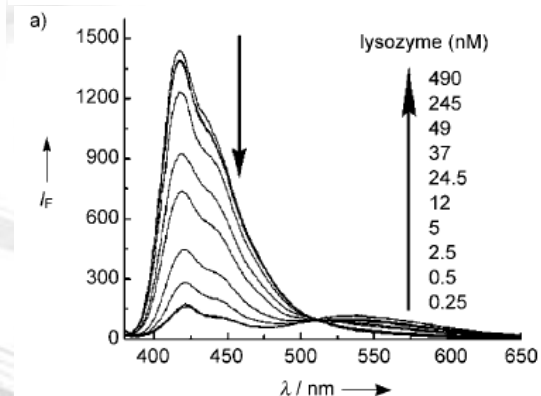
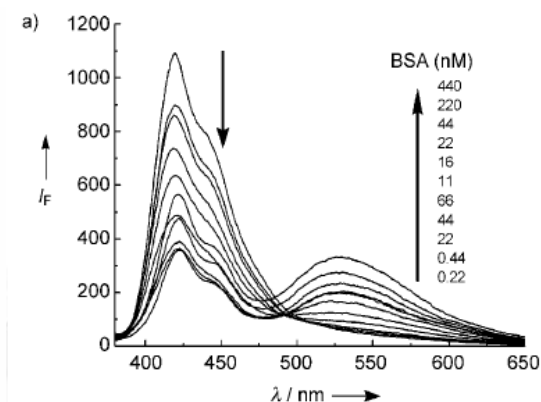
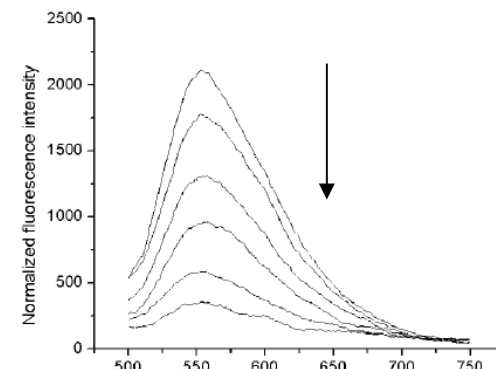
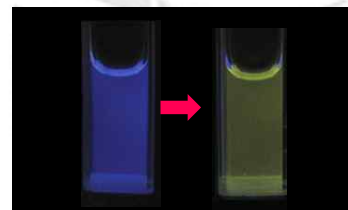
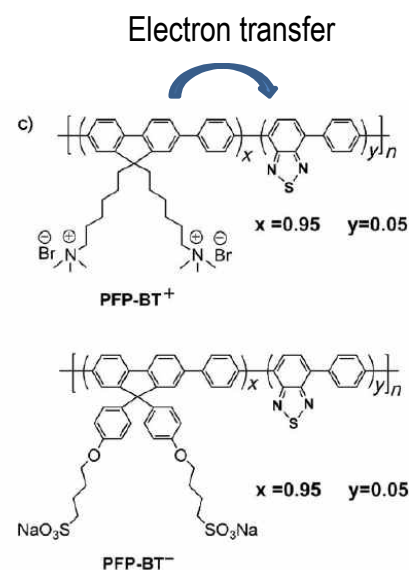
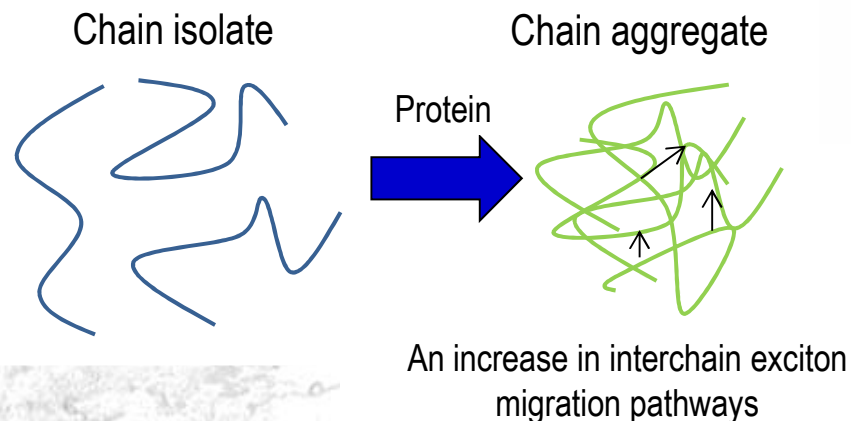
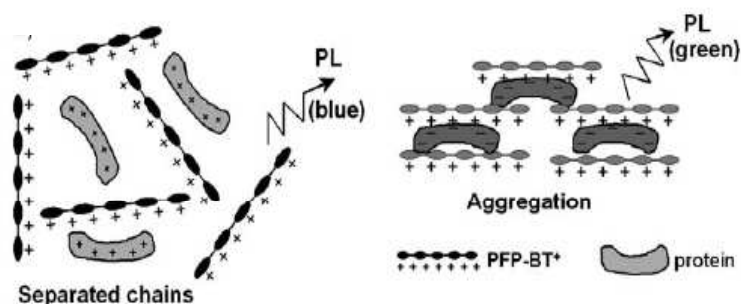
Energy transfer between the band level and a defect state



Colorimetric sensors

Aggregation induced fluorescence color changes

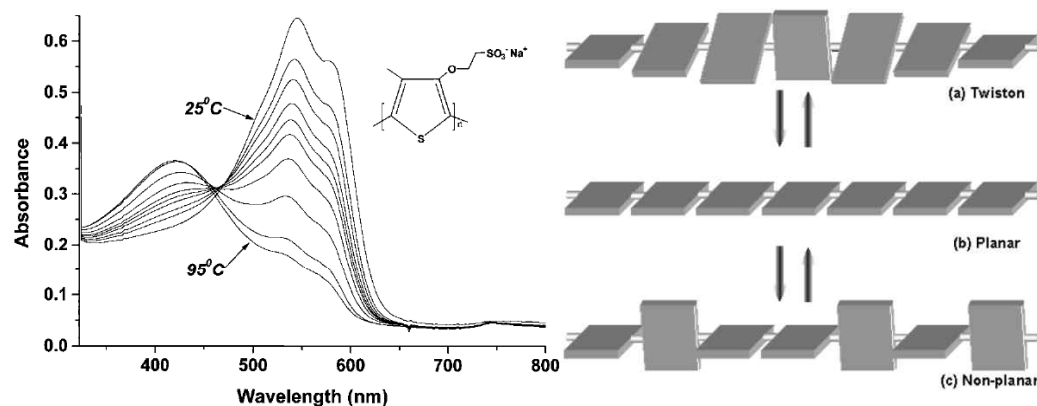
Colorimetric Sensor Based on Analyte-Induced Aggregation



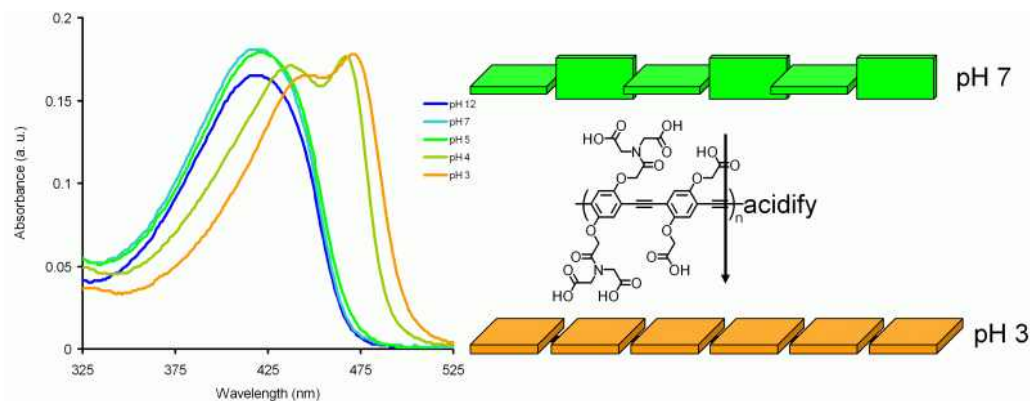
Colorimetric sensors

Conformational effect

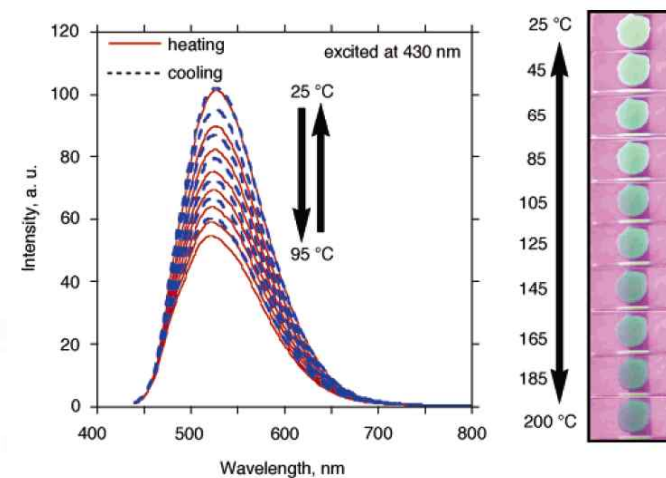
Thermochromism



Halochromism



Temperature dependence of fluorescence intensity



Piezochromism

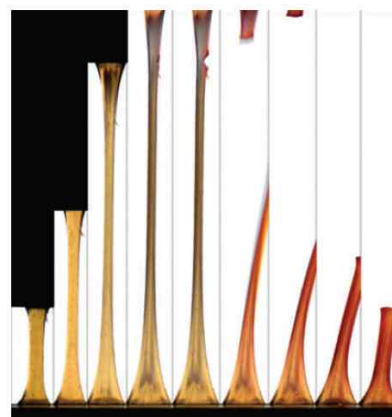
MECHANOCHEMISTRY

Polymers react to stress

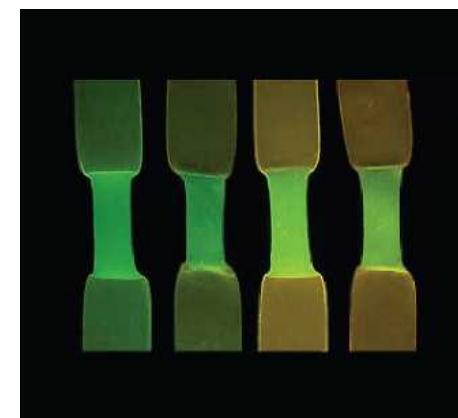
Christoph Weder

The latest polymers are chameleon-like: they change colour on deformation. The transduction mechanism underpinning this effect could be used to make polymers that respond in many other ways to mechanical stress.

Nature 2009,459, 45

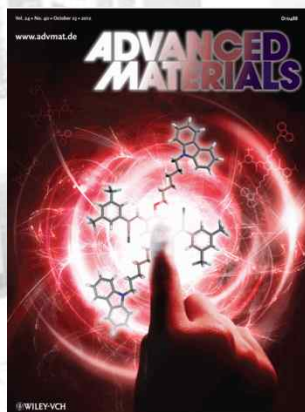


Nature 2009,459, 68

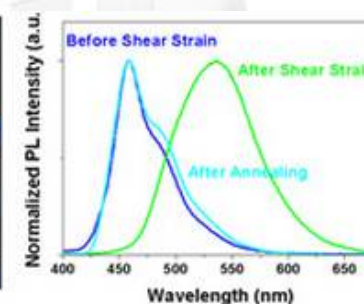
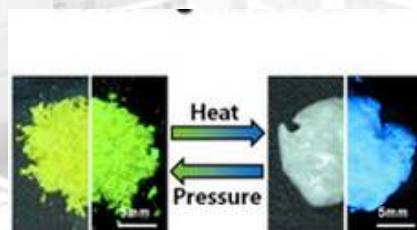


Macromolecules 2007,40, 2400

Piezochromic fluorescence materials



Adv. Mater. 2012,24, 5487 (cover page)

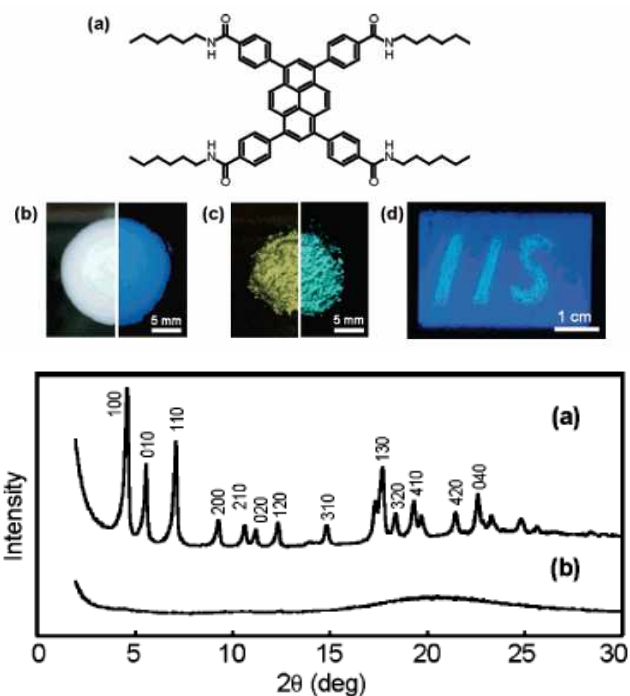
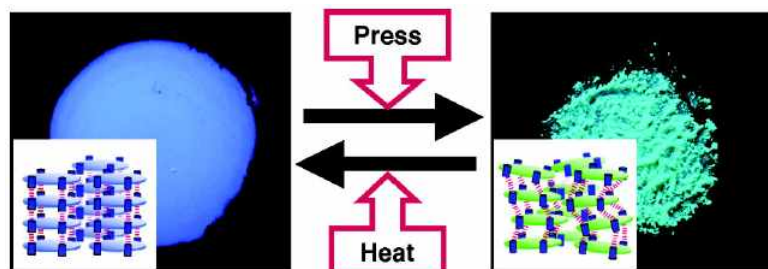


J. Am. Chem. Soc. 2010,132, 13675

Piezochromism

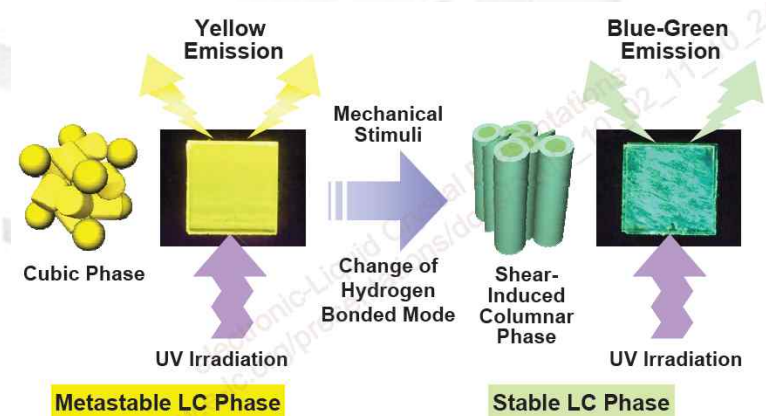
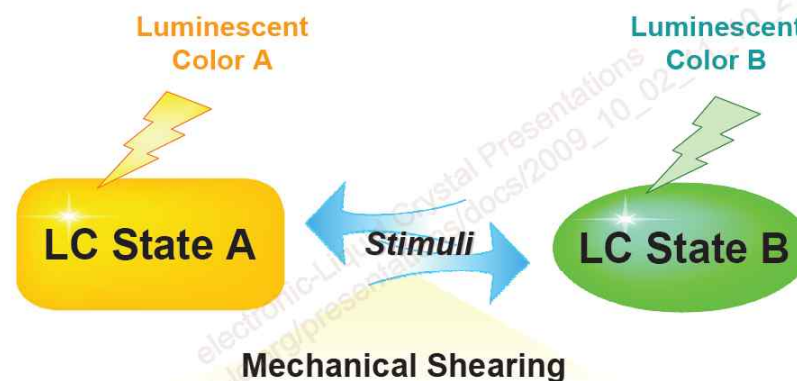
Crystal to amorphous

JACS. 2007,129, 1520



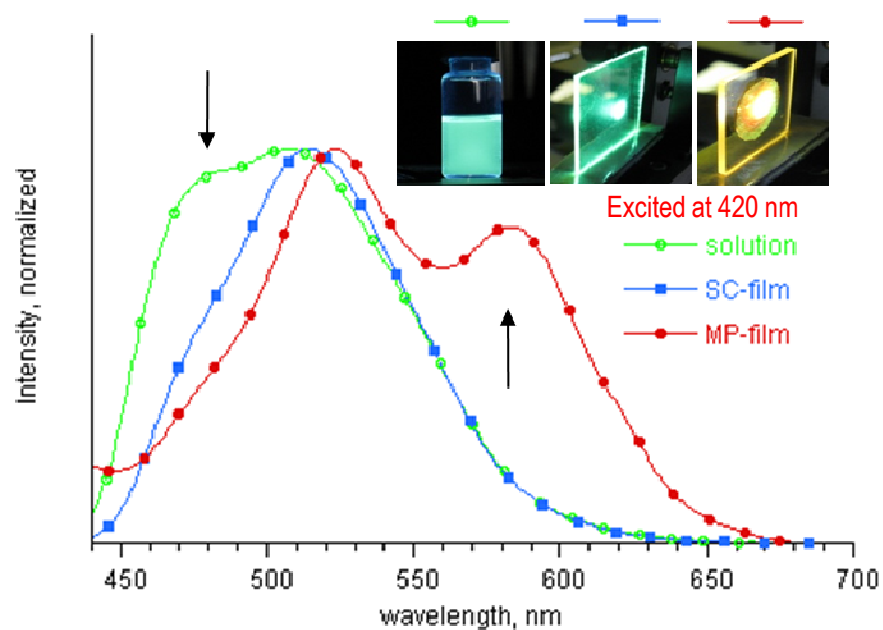
Crystal to crystal

Angew. Chem. Int. Ed. 2008,47, 5175

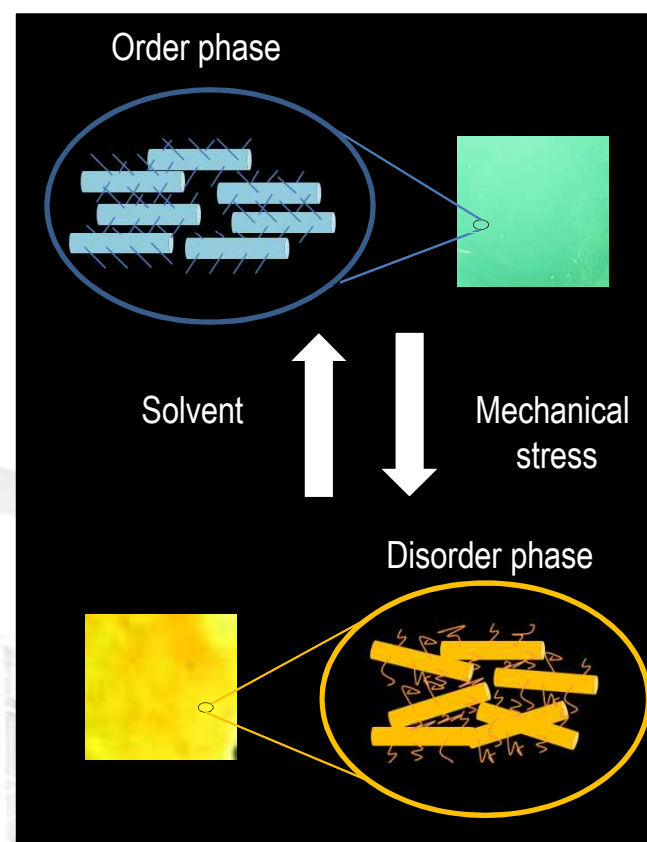


Piezochromism

Fluorescence spectra and photograph



Piezochromic fluorescence mechanism



Conclusion

The conjugated polymer-based sensors have attractive merits as a sensory system and have expanded their applications to various molecular detections

