Iodine-Free Solid-State Dye-Sensitized Solar Cells

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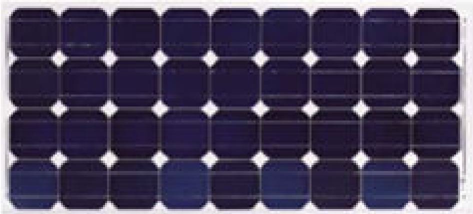
Contents

- Dye-sensitized photocell
- Electrochemical reactions
- Interface engineering
- Double layered DSSC

Energy and Environment
The Natural Solution
"Solar Energy"

- Only 10 minutes of solar irradiation on the Earth's surface is equal to the total yearly human consumption.
- Therefore, if we could accomplish harvesting merely a fraction of the solar energy reaching the Earth, we would solve many problems associated with the energy, and the global environment.

Organic Photovoltaics

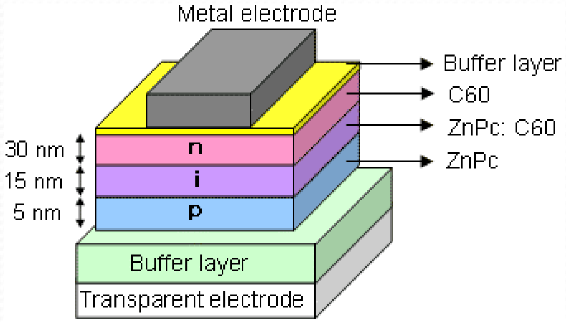


Crystalline silicon

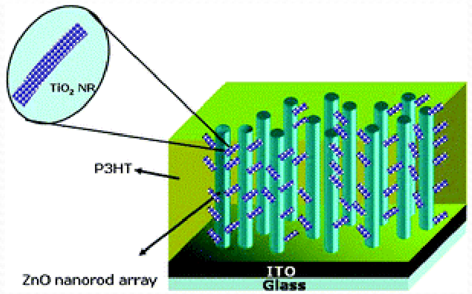
Thin film

Polymers & nanomaterials

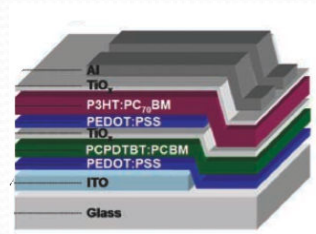
Organic Multilayered Organic Solar Cells



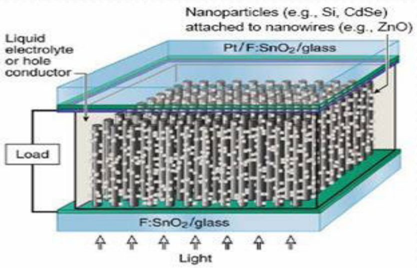
Nanostructured-Oxide Polymer Solar Cells



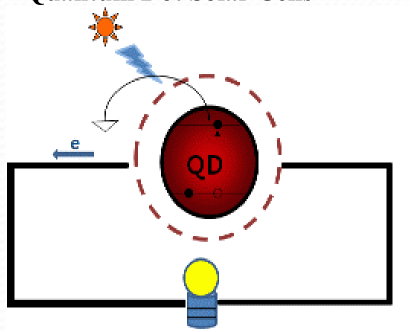
Heterojunction Organic Solar Cells



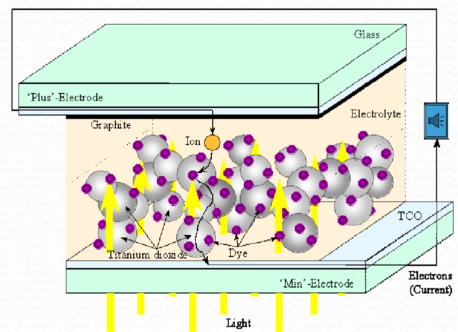
Quantum Dot-Sensitized Solar Cells



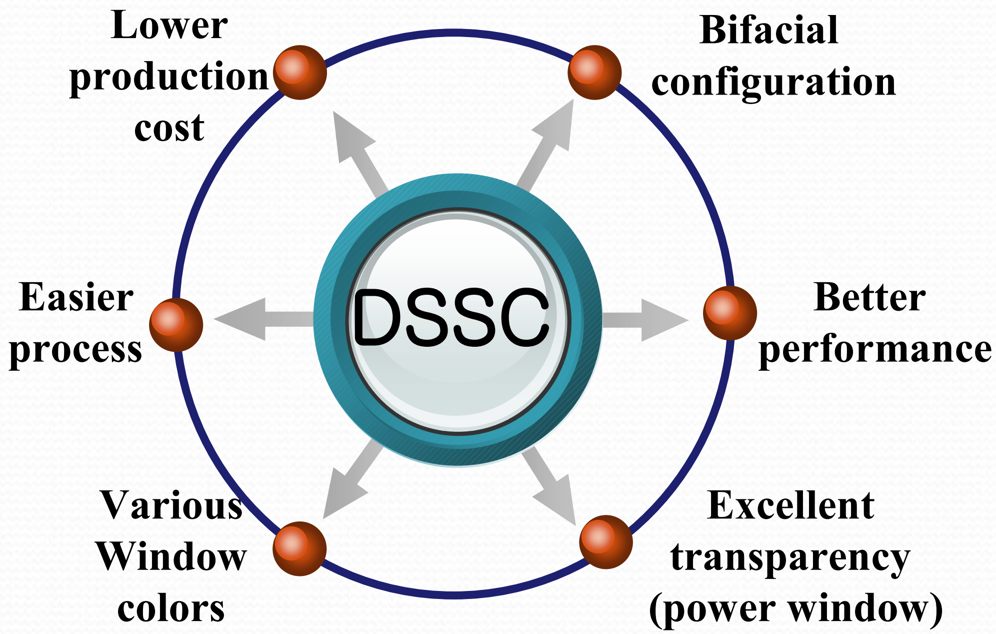
Quantum Dot Solar Cells

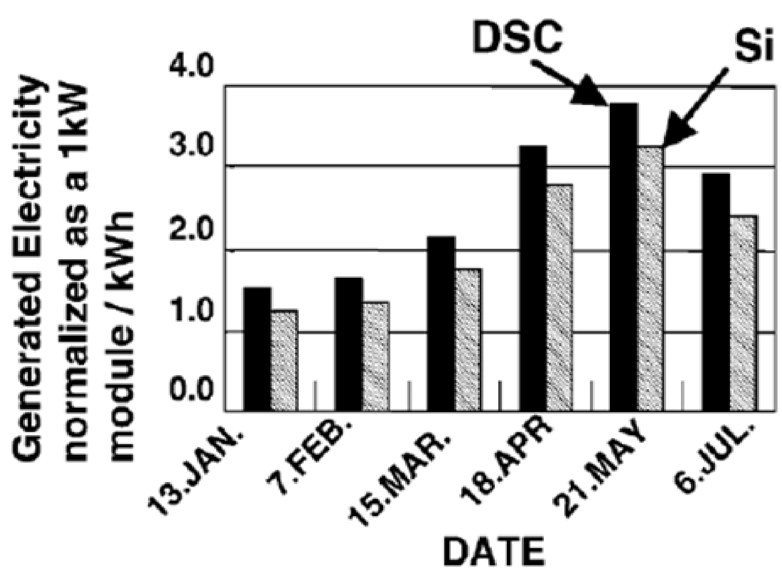


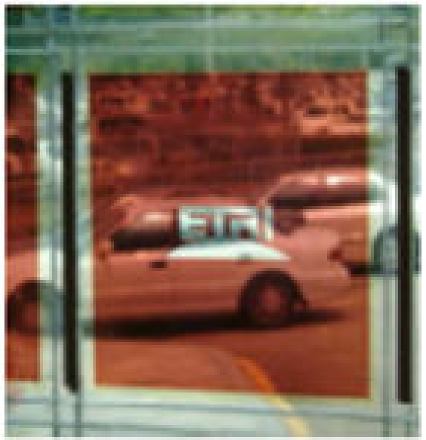
Dye-Sensitized Solar Cells

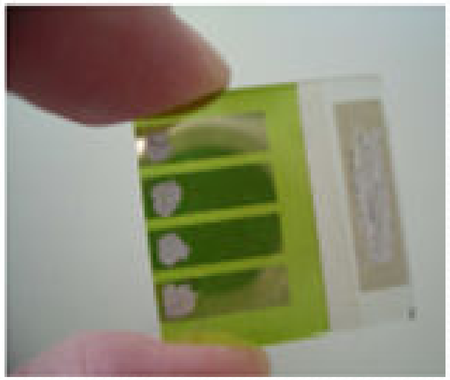


DSSC *vs.* Silicon Cells









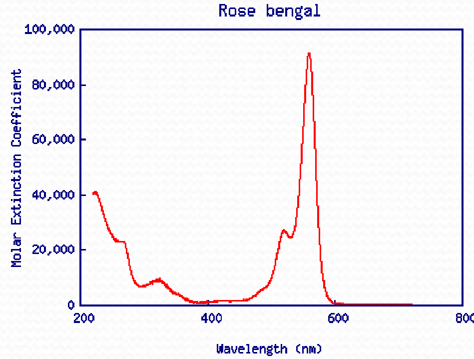
Dye-Sensitized Solar Cells

- Gerischer and Tributsch H. *(Phys. Chem.* **1969**, *73*, 251.)

- Matsumura et. al. (*Bull. Chem. Soc. Japan* **1977**, *50*, 2533.)

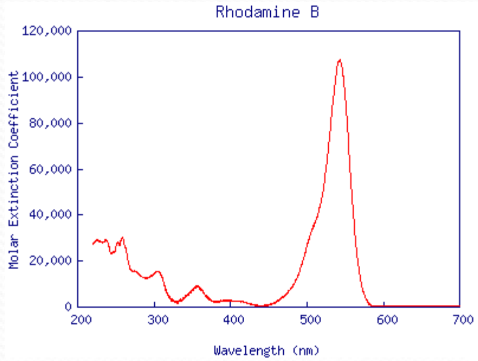
  Sintered ZnO porous disk, Rose Bengal

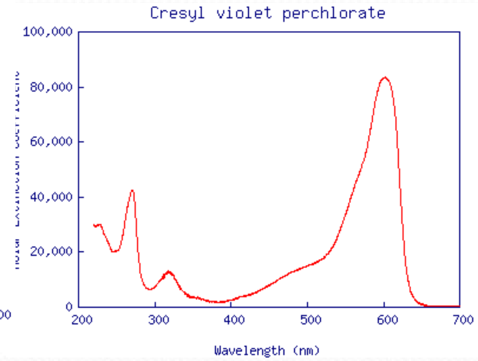
  2.5% at 562 nm



- Alonso et. al. (*Rev. Phys. Appl.* **1981**, *15*, 5.)

  Sintered ZnO, Rhodamine B

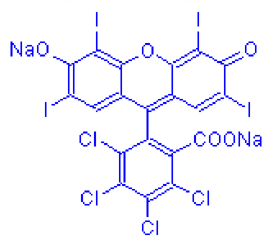


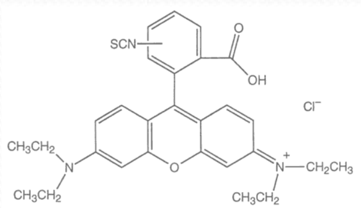


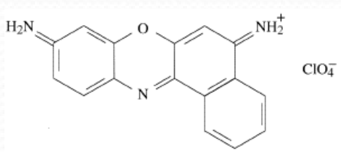
- Pakinson et. al. (*JACS* **1990**, *112*, 2702.)

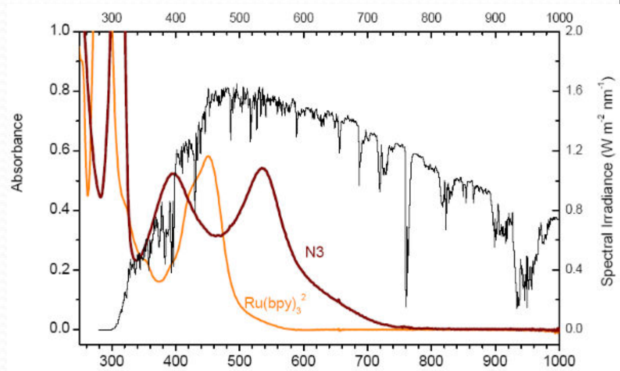
  SnS_2, Cresyl Violet

- chlorophyll, phthalocyanines, coumarins









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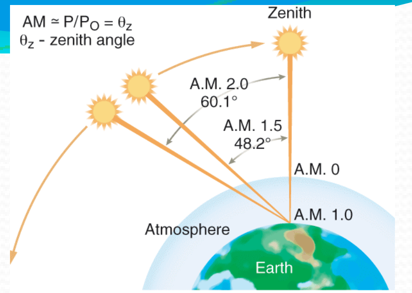
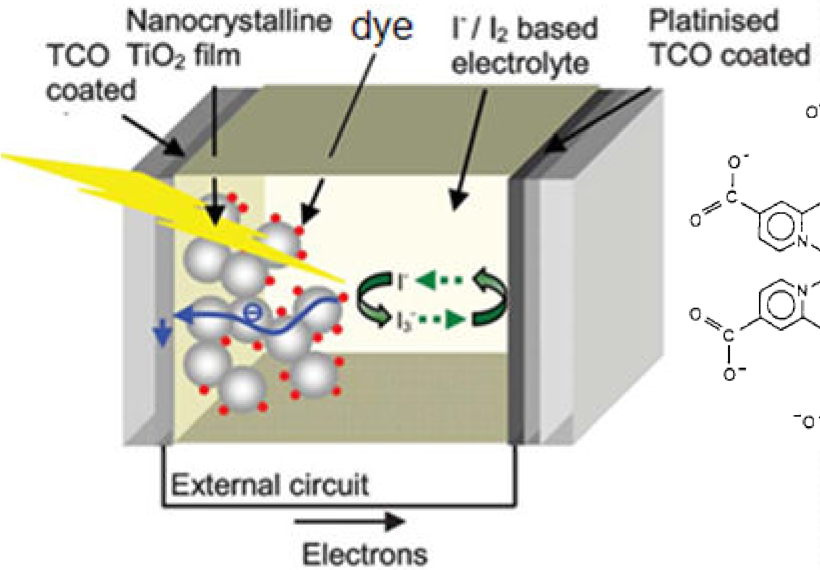
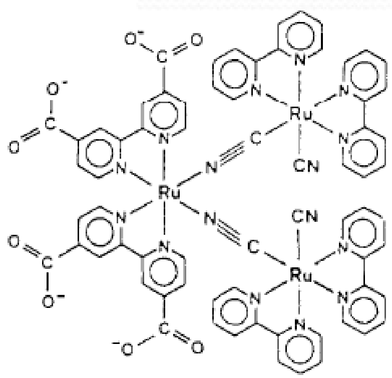
Dye-Sensitized Solar Cells

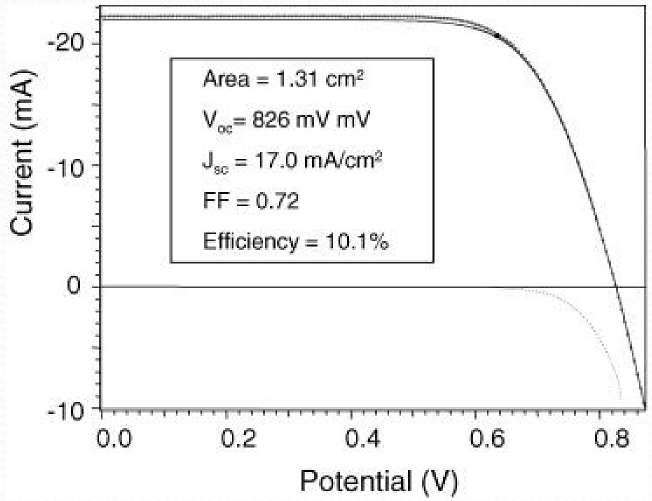


M. Grätzel et al., Nature, 1991, 353, 737

- Ru[porphyrin] complex to harvest light
- Nanocrystalline titania to carry away electrons
- An iodine / triiodide couple in liquid solvent to transport away positive charges







- Dye : N3
- Electrolyte : 0.6M butylmethyl imidazolium iodide
  0.1M GuSCN, 0.03M I_2
- Additive : 0.5M t-butylpyridine(tBP)
- Solvent : acetonitrile/valeronitrile.

η = 7.9% in simulated solar light (1.5 AM)

η = 12 % in diffuse daylight.

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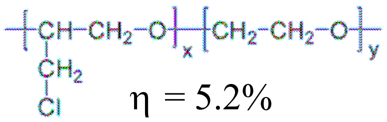
Parameters influencing Real DSSCs

요인	문제점	연구방향
용액 전해질	►고온 불안정성 ►염료 탈착 ►봉합의 누수 ►봉지체와 전해질의 반응 ►요오드의 승화성	►유기물, 고분자 전해질 사용 ►이온성 용매 전해질 사용 ►**유기고분자 전공전달물질 사용**
전자 및 전공의 재결합 반응	►효율 저하의 가장 큰 원인	►TiO_2의 passivation ►유기물 첨가제로 극성 조절 ►염료의 변형을 통한 극성 조절 ►**유기고분자 전공전달물질 사용**
염료	►염료의 고온 분해 ►장파장 영역의 빛 흡수 부족 ►고가의 염료	►새로운 유기물 염료 개발
공정	►고온에서 TiO_2 층 제조 ►제작 과정이 복잡, 장시간 소요 ►잉크젯이나 롤투롤 연속공정 불가	►저온 공정용 TiO_2 개발 ►유연성이 있는 전도성 기판 개발 ►**유기고분자 전공전달물질 사용**

Research for Solid-State DSSC

✓ **Polymer / solid electrolytes** ✓ **Ionic liquid / molten salts**

Poly(epichlorohydrin-co-ethylene oxide)



η = 5.2%

(No TBP)

Control : PEG (100K) η = 2.4%

Polarity & No crystalization

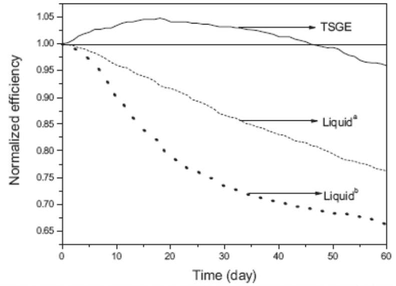
Durrant *et. al. Chem. Commun.*, **2006**, 877.

Poly(acrylic acid)-(ethylene glycol) (PAAPEG)

η = 6.1% *γ-butyrolactone (GBL)*
N-methyl pyrrolidone (NMP)

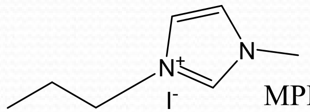
H-bonding & stability

(No TBP)



Wu *et. al. Adv. Mater*. **2007**, *19*, 4006

Poly(ethylene glycol dimethyl ether) + MPII



MPII

N-methyl-benzimidazole (NMBI) (instead of TBP)

Oligomer electrolyte	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	η (%)
250	0.605	13.92	58.4	4.92
500	0.624	11.39	58.0	4.12
1000	0.497	6.40	44.1	1.40
N250	0.665	11.52	65.7	5.03
N500	0.684	10.09	65.2	4.50
N1000	0.604	6.61	46.9	1.87

S.-S. Lee and Y. S. Kang, *J. Power Source* **2007**, *173*, 1029

Summary of Problems in Iodine system

요오드를 사용하는 용액 전해질

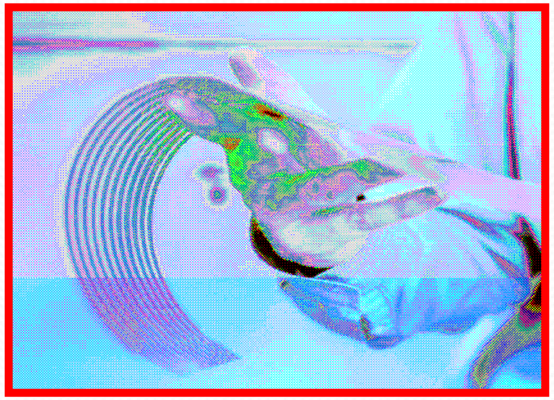
✓고온 불안정성
✓염료의 탈착
✓봉지기술의 문제점
✓요오드와 봉지물질의 반응
✓요오드의 승화성

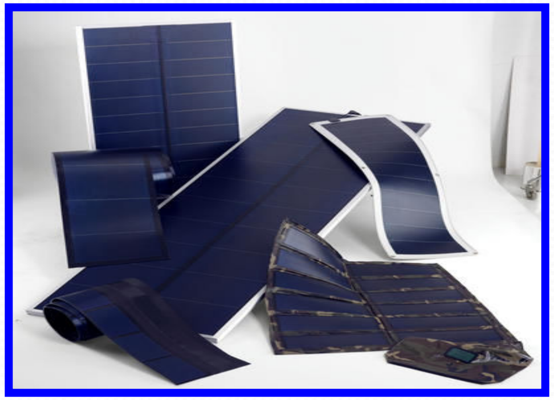
요오드를 사용하는 고분자 겔 전해질

✓낮은 에너지 전환 효율
✓고온에서 고체 전해질의 점도변화
✓여전히 봉지 필요
✓요오드의 승화성

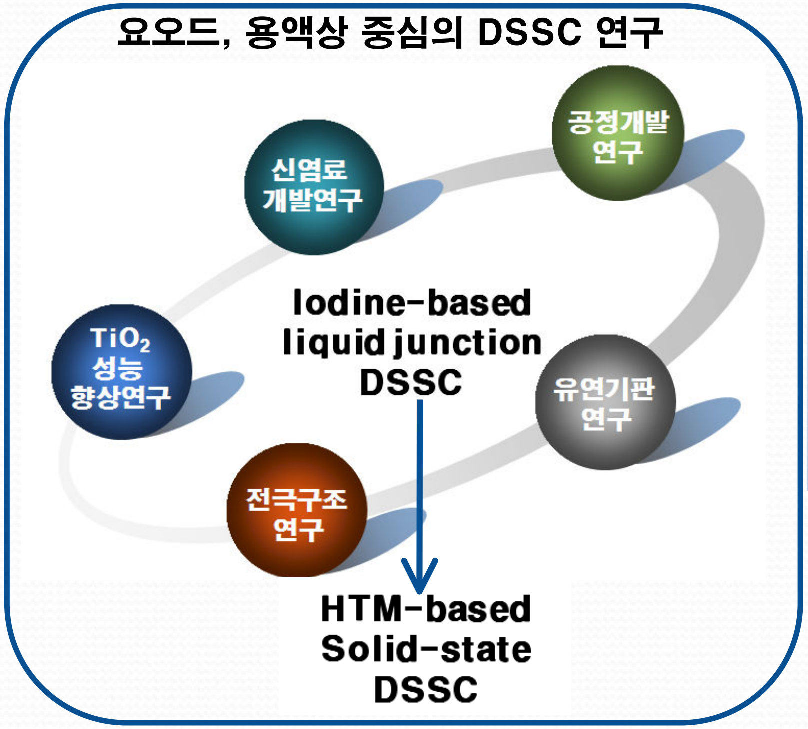
요오드를 사용하지 않는 고분자 HTM

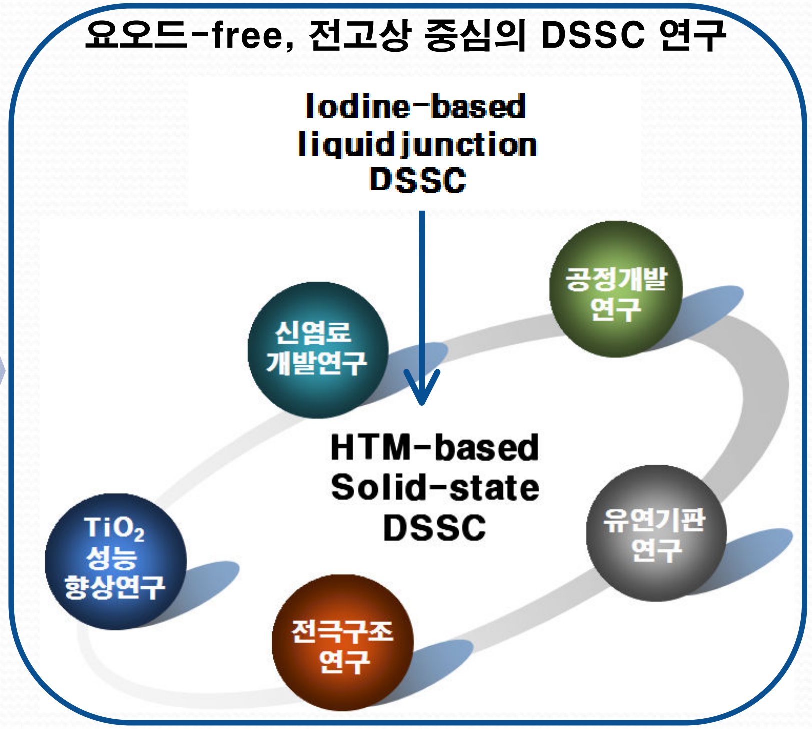
✓가공성
✓대면적화
✓연속공정





Hole transporting materials





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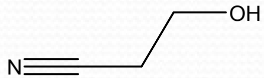
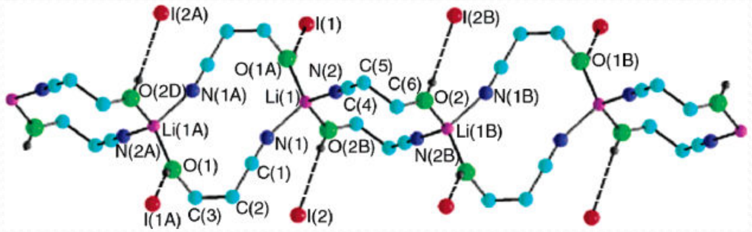
Research for Solid-State DSSC

- ✓ Iodine-free organic/polymeric hole conductors

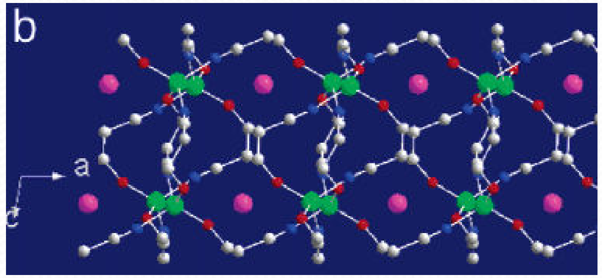
LiI/3-hydroxypropionitrile

+ nano-SiO_2

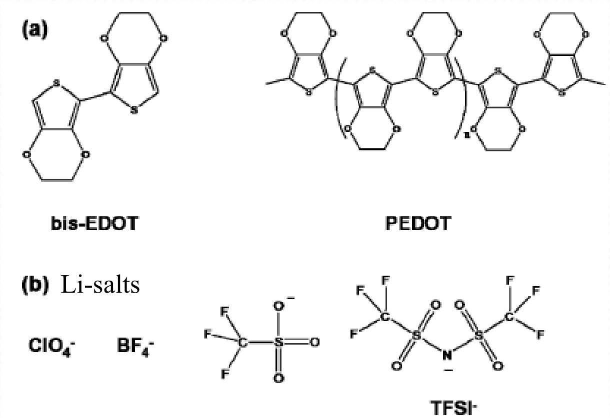




3-D transporting paths for iodine. η = 5.5%



Chen *et.al. JACS* **2005**, *127*, 6394.



(TBP)

doping ions	charge of PEP (mC/cm²)	conductivity S/cm	R_s (Ω)	R_{sh} (kΩ)	η (%)
ClO_4^-	10.7	30	97.2	8.36	1.8 ± 0.1
$TFSI^-$	15.8	130	48.3	25.6	2.85 ± 0.2
$CF_3SO_3^-$	10.7	86	60.4	4.47	2.15 ± 0.1
BF_4^-	9.5	7.5	121	2.65	0.9 ± 0.1

Yanagida *et.al. JACS* **2008,** *130*, 1258.

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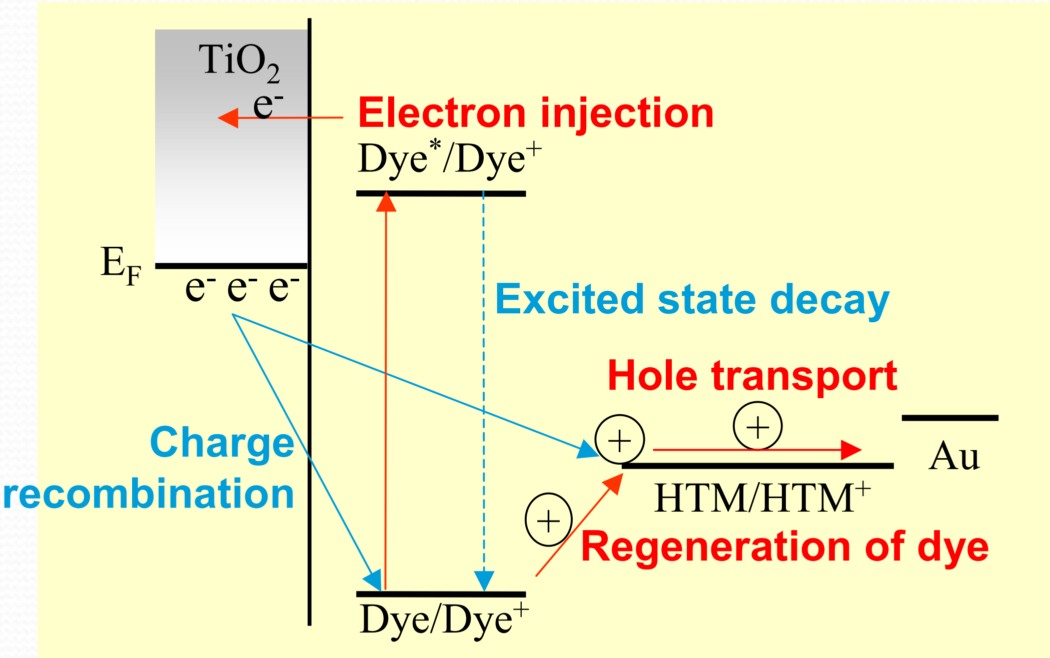
Electrochemical Reactions

Understanding the basic electrochemical reactions at the interfaces of the devices is of importance to design and syntheses of new solid-state redox materials (HTMs) !



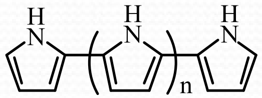
- Electron injection into TiO_2
  $Dye^* \longrightarrow Dye^+ + TiO_2(e^-)$
- Regeneration of cationic dyes (Dye^+)
  $Dye^+ + HTM \longrightarrow Dye + HTM^+$
- Reversible redox process
  $HTM^+ \rightleftarrows HTM$
- Charge transfer to counter electrode
  $HTM^+ + HTM \longrightarrow HTM + HTM^+$

- Excited state decay
- Charge recombination
  $e^-(TiO_2) + Dye^+ \longrightarrow Dye$
  $e^-(TiO_2) + HTM^+ \longrightarrow HTM$

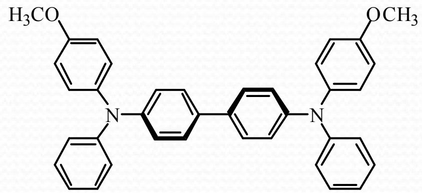
Minimum recombination reaction in the liquid junction DSSC !

Research for Solid-State DSSC

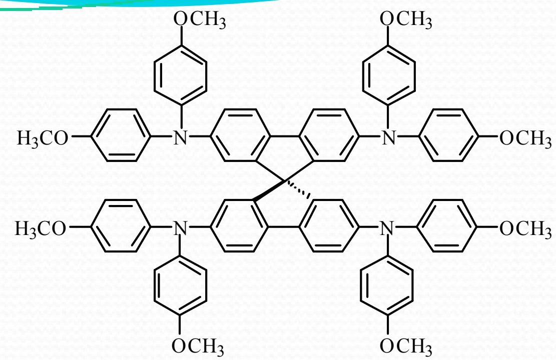
- ✓ Iodine-free organic/polymeric hole conductors



η = 0.1 %



η = 0.2 %

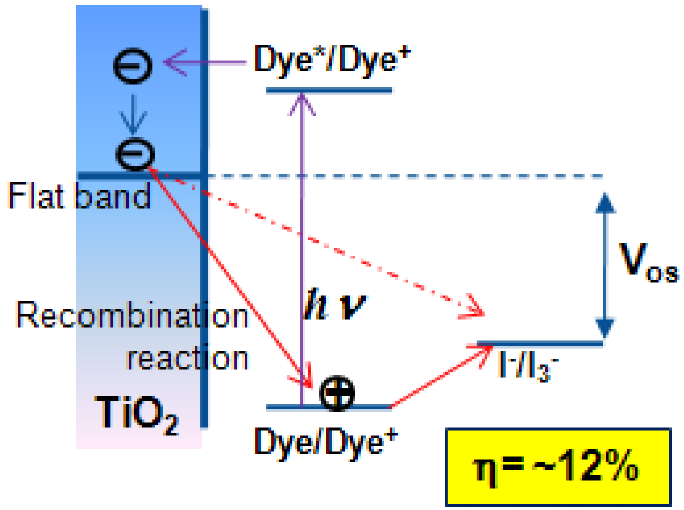


Yanagida et. al., *Chemistry letters* 1997, 471

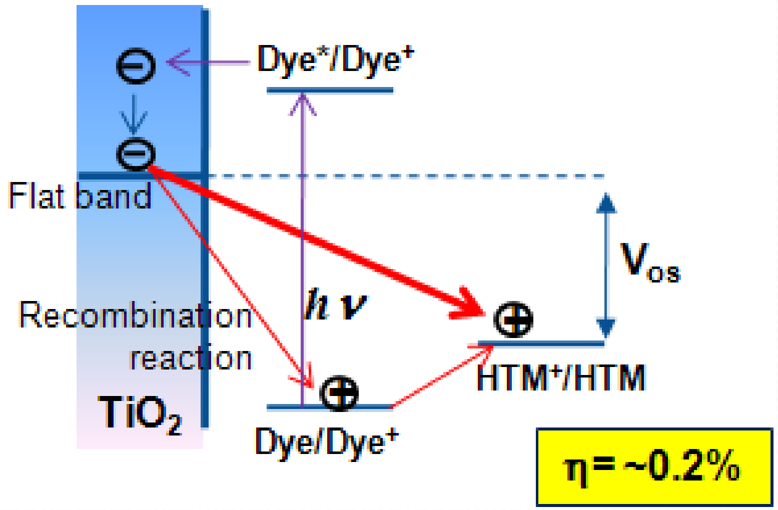
Haarer et. al., *Syn. Met*. 1997, **89**, 215

η = 0.1 %

(a) 요오드와 요오드염을 사용하는 DSSC

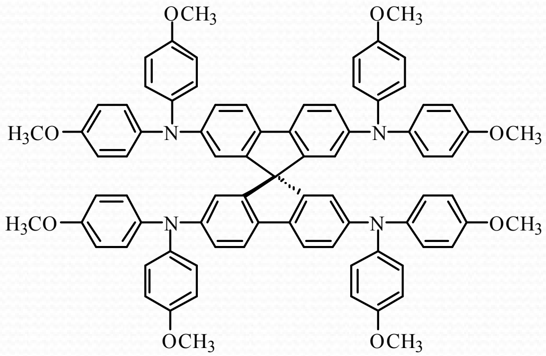


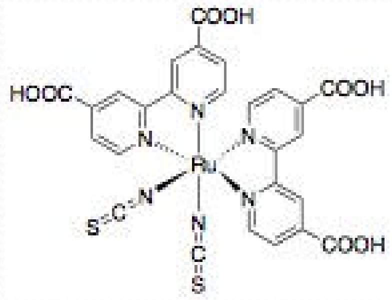
(b) 유기물 HTM을 사용하는 DSSC

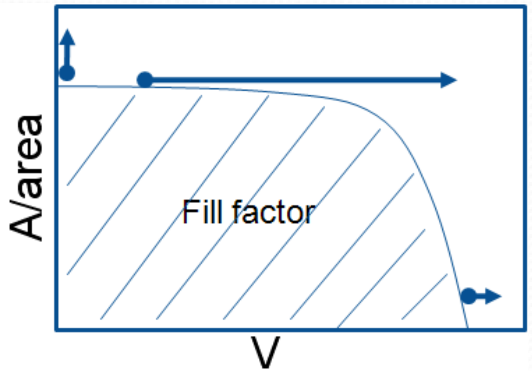


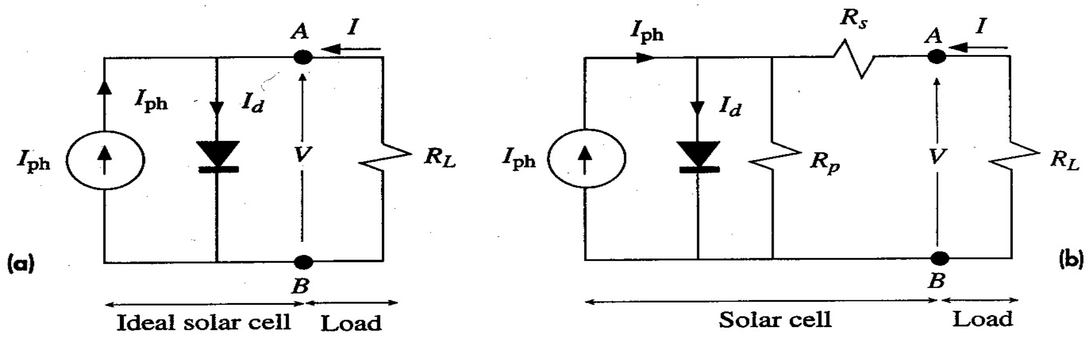
Research for Solid-State DSSC

- ✓ Iodine-free organic/polymeric hole conductors









η = 0.1 %

N(PhBr)$_3$SbCl$_6$ & Li[(CF$_3$SO$_2$)$_2$N]

η = 0.74 %

Grätzel et. al., *Nature* 1998, **395**, 583

^{t}BP & N(PhBr)$_3$SbCl$_6$ & Li[(CF$_3$SO$_2$)$_2$N]

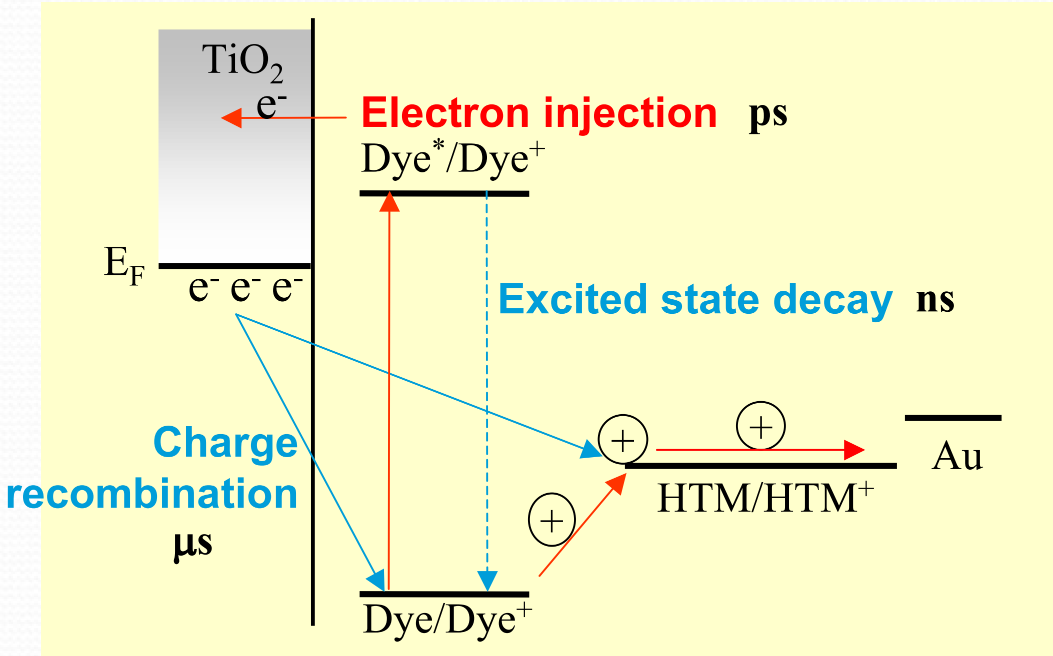
η = 2.56 %

Grätzel et. al., *APL* 2001, **79**, 2085

Interface engineering at the level of single molecules !

Electrochemical Reactions

Understanding the basic electrochemical reactions at the interfaces of the devices is of importance to design and syntheses of new solid-state redox materials (HTMs) !



- **Interfacial electrostatic interactions**

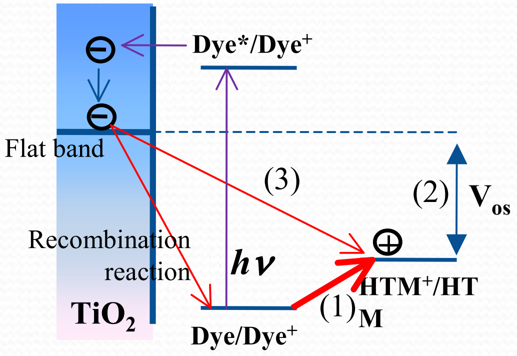
interfacial dipoles & coulombic attractions between the photogenerated charges.

- **Redox reversibility of HTM**
- **High hole mobility and conductivity**
- **Fast reaction and high yield in regeneration of dye**
- **V_{oc}**

M. Grätzel et. al., JASC, 1993, **115**, 6382.
F. Willig et. al., JASC, 1990, **112**, 2702.
J. R. Durrant et. al., J. Phys. Chem. B., 2000, **104**, 538.
M. Grätzel et. al., JASC, 1999, **121**, 7445.

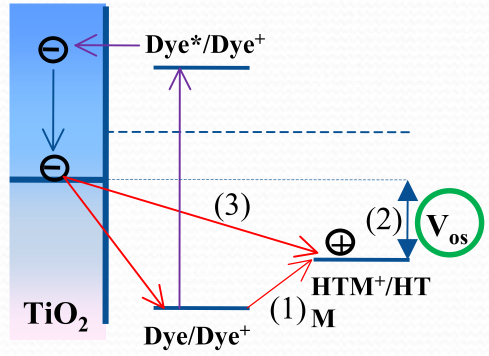
Effects of additives on reactions

(a) 첨가제가 없을 때의 에너지 준위



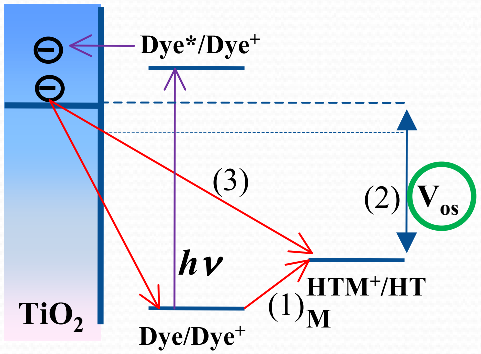
반응 (1) - 염료의 재생반응
반응 (2) - 개방전압
반응 (3) - 전자-정공 재결합 반응

(b) Li^+ 첨가했을 때의 에너지 준위



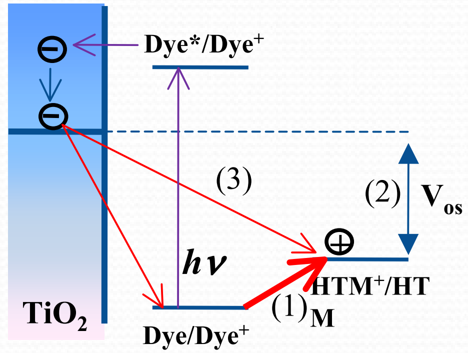
반응 (1) - 효율 감소
반응 (2) - 개방전압 감소
반응 (3) - 재결합 반응 빨라짐

(c) tBP 첨가했을 때의 에너지 준위



반응 (1) - 일정량 이상에서 감소
반응 (2) - 개방전압 증가
반응 (3) - 재결합 반응 지연됨

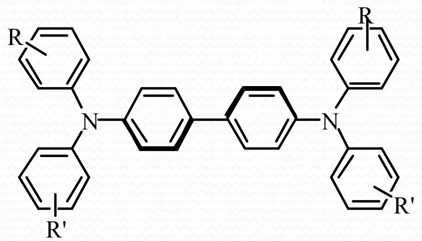
(d) Li^+과 tBP 첨가했을 때의 에너지 준위

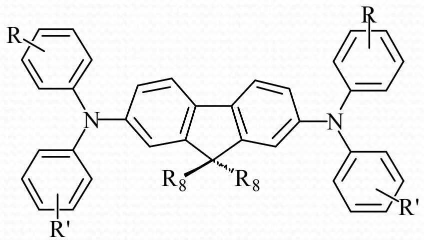


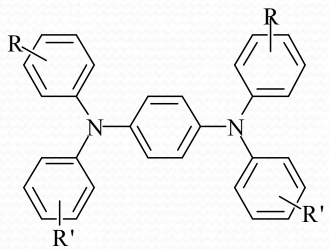
반응 (1) - 효율 변화없음
반응 (2) - 과량의 tBP로 개방전압 증가
반응 (3) - 재결합 반응 지연됨

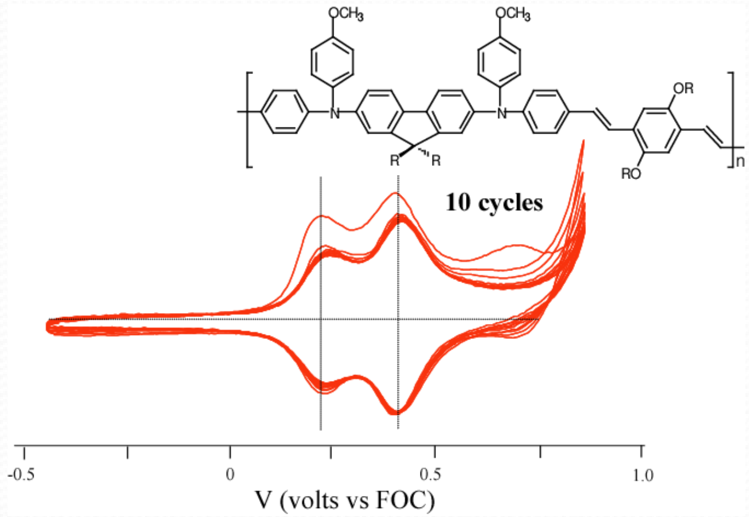
Triarylamines and Conjugated Polymers

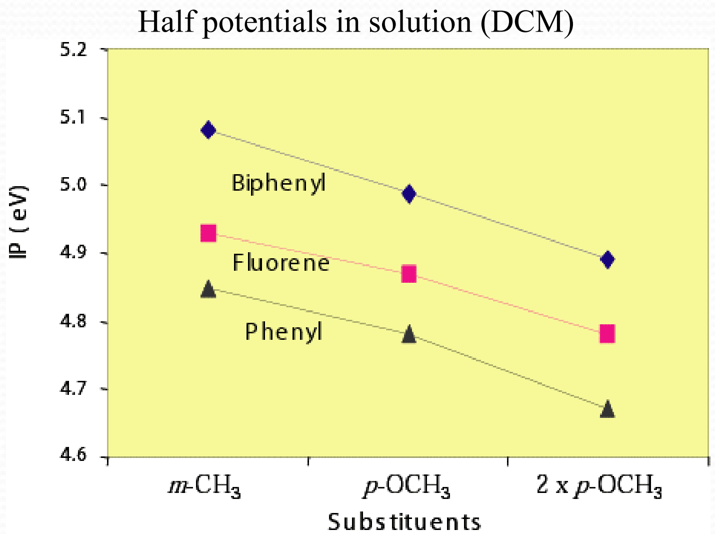
- Reversible oxidation / reduction process.
- Easy functionalization.
- Controllable ionization potentials.
- High hole mobility in amorphous glassy films.







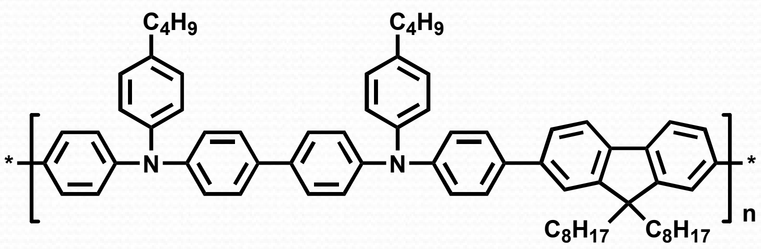


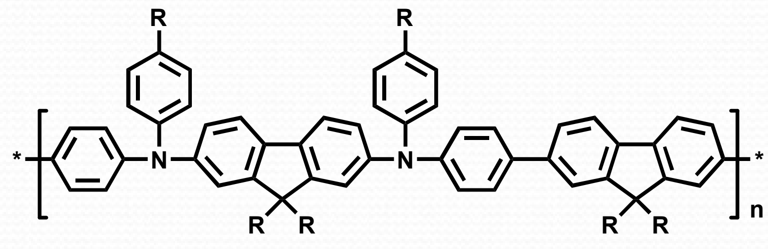


POSTECH

IP Effect on Electrochemical Reactions

• *Transient Absorption Spectrometry*



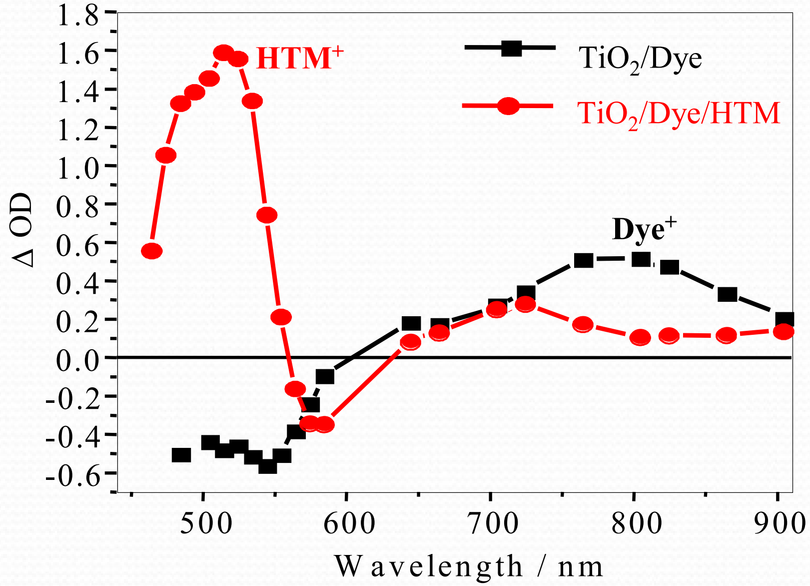


HTM1, 10^{-3} cm²/Vs, 5.27 eV

Φ = 54%

HTM2, 10^{-4} cm²/Vs, 5.11 eV

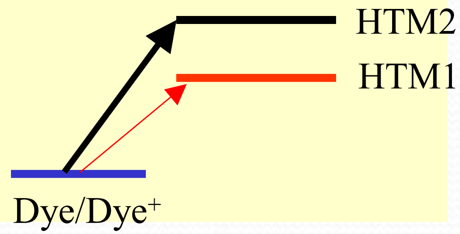
Φ = 72%



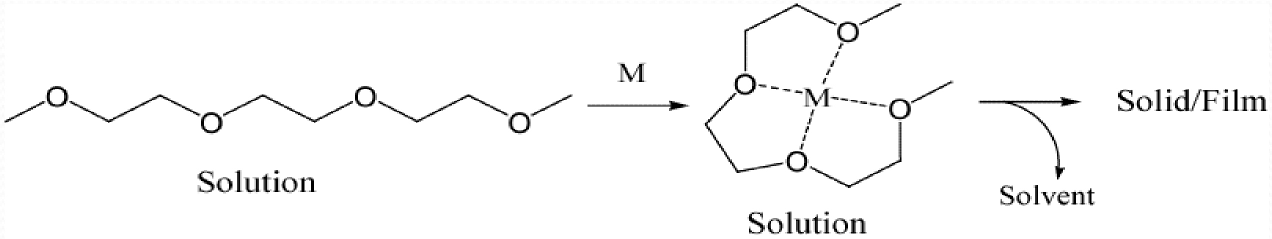
$$|\Delta G_2| = E_{dye} - E_{HTM2}$$

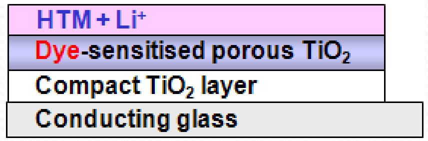
$$\gg$$

$$|\Delta G_1| = E_{dye} - E_{HTM1}$$

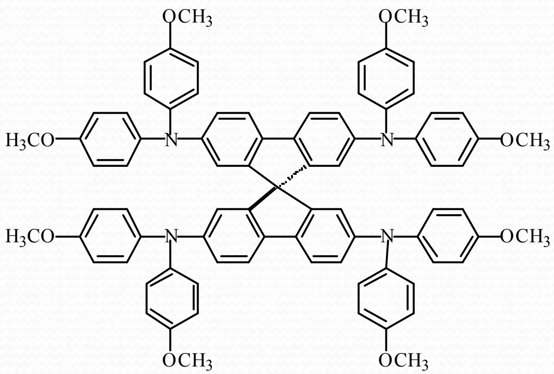


Charge Supporting Groups

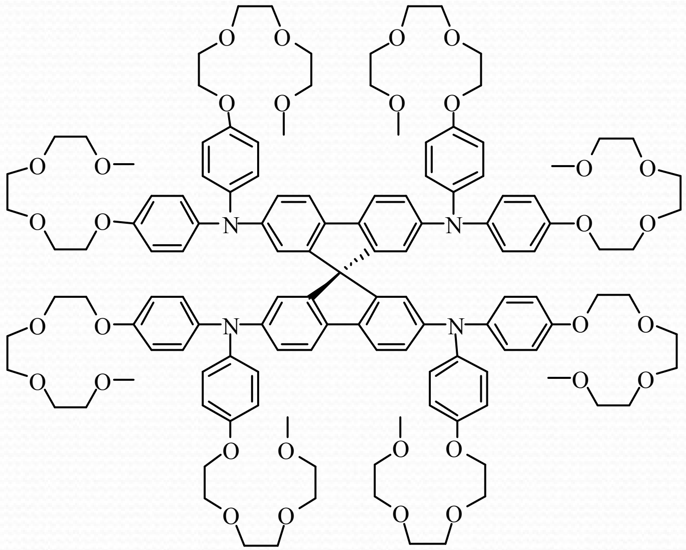




Spiro-OMe



Spiro-TEG



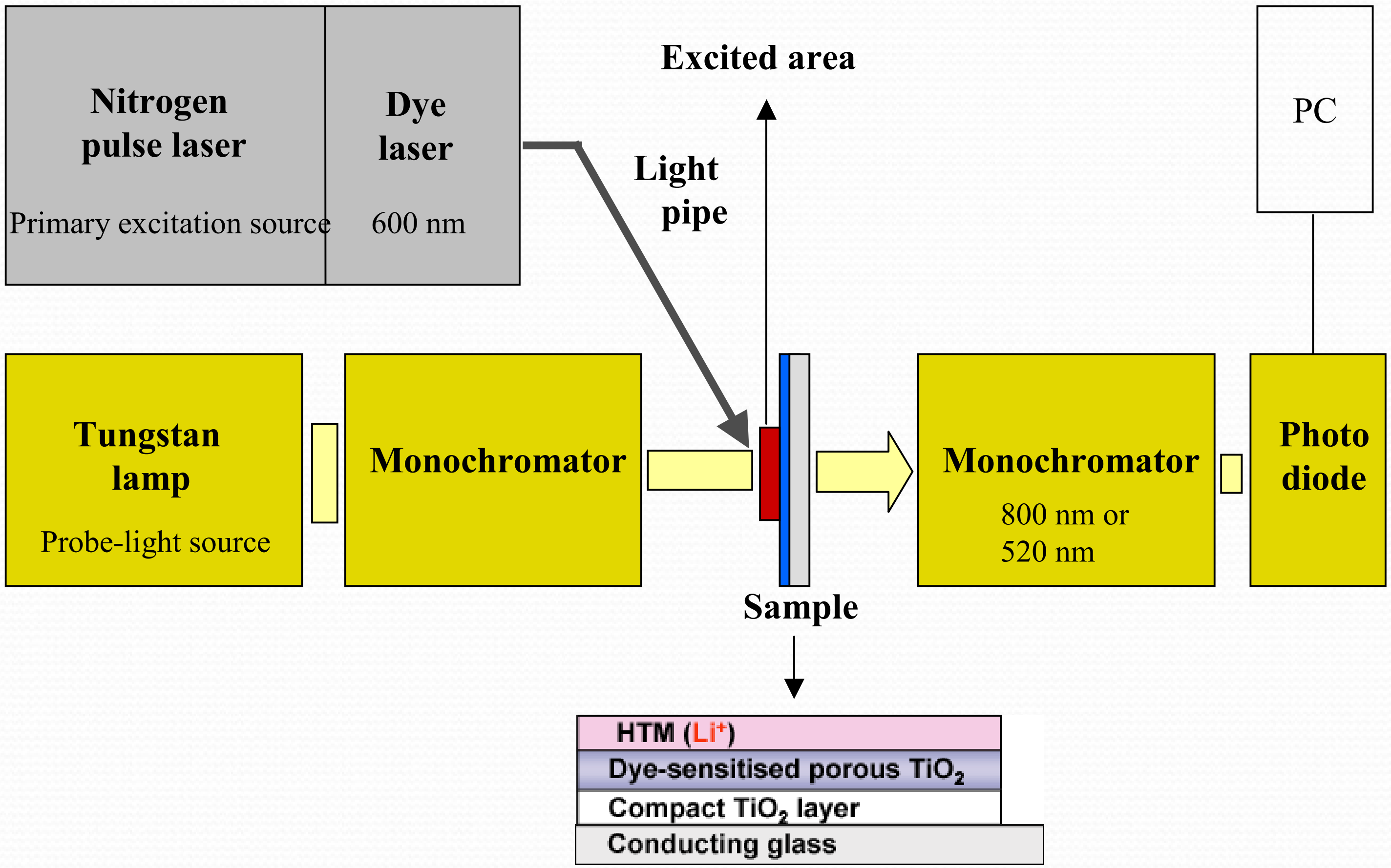
Charge Transfer Yield (TiO2/Dye/HTM:Li$^+$)	< 40%	> 80%

→ Intorduction TEG groups in polymeric HTMs.

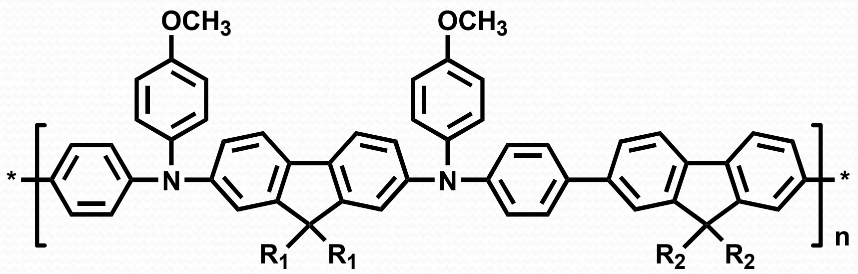
POSTECH

Transient Absorption Spectrometry

Charge transfer quantum yields & Decay kinetics



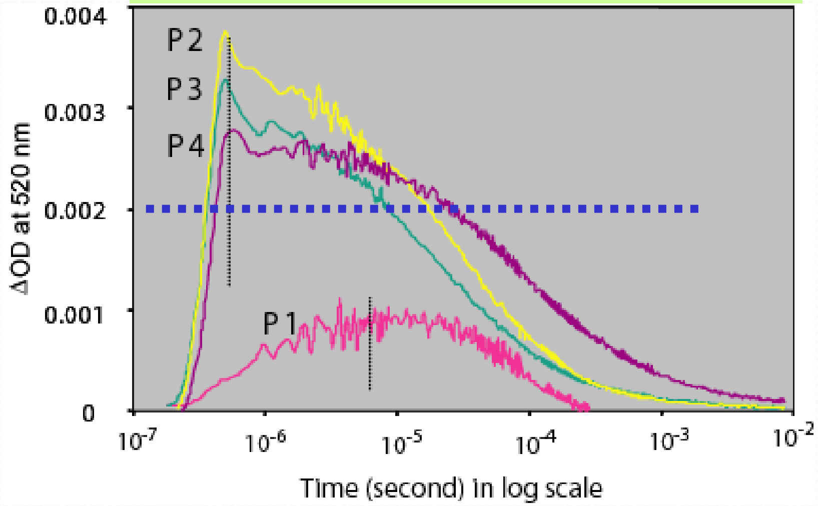
Charge Supporting Groups

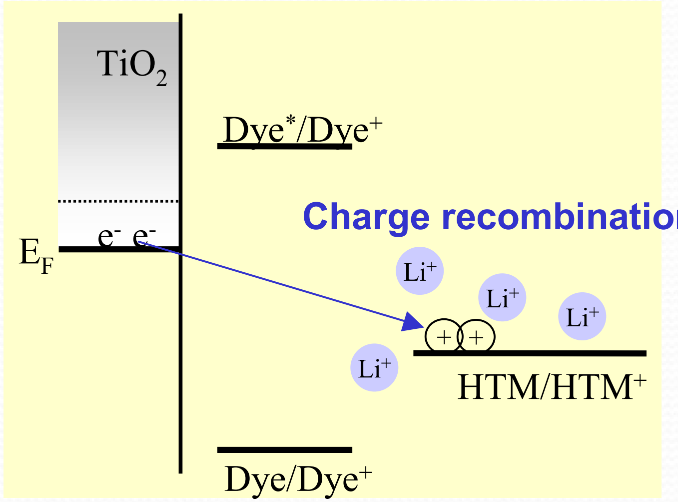


			IP	Φ	Φ (Li+)*
R_1 = -C_8H_{17}	R_2 = -C_8H_{17}	P1	5.11	72	35
R_1 = -C_8H_{17}	R_2 = -TEG	P2	4.96	80	100
R_1 = -TEG	R_2 = -C_8H_{17}	P3	4.96	80	93
R_1 = -TEG	R_2 = -TEG	P4	4.90	73	85

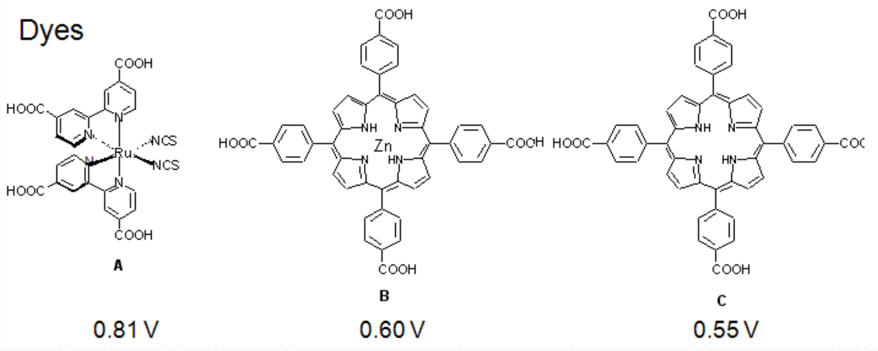
[Li^+ = 0.04]

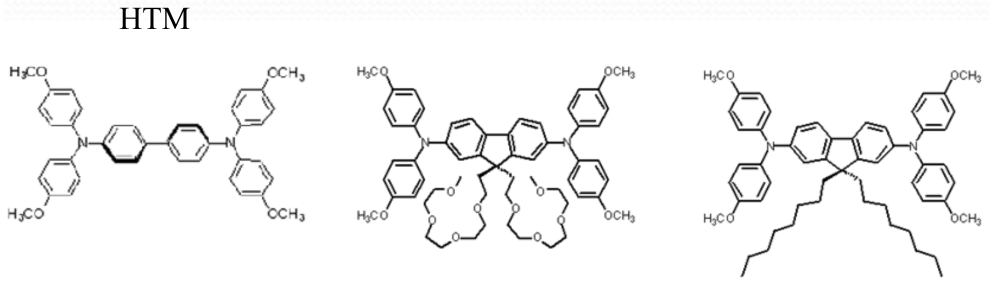
$e^-(TiO_2)$ + HTM^+ ⟶ HTM

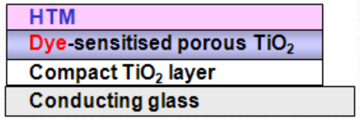


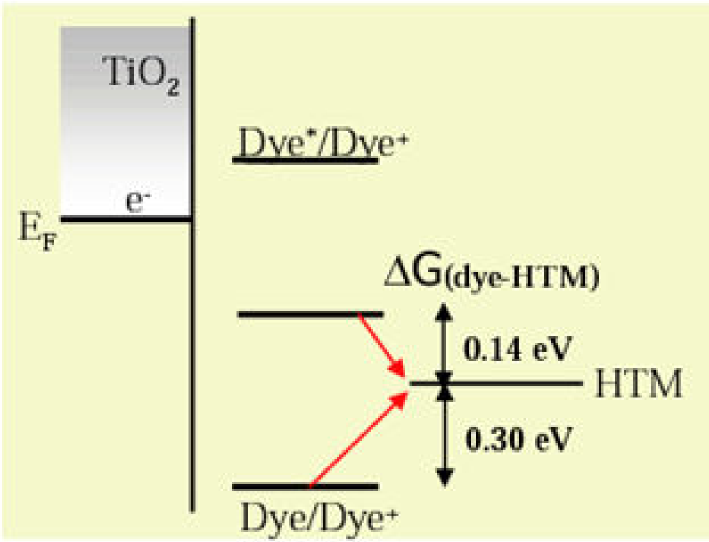


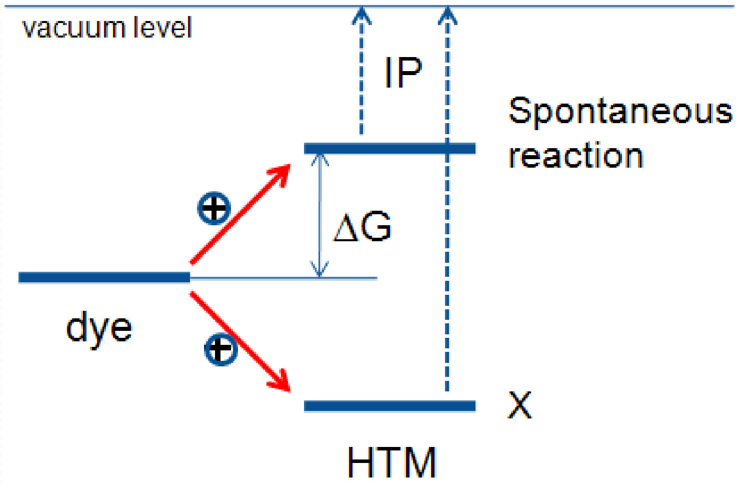
Effect of ΔG and TEG on Quantum Yields











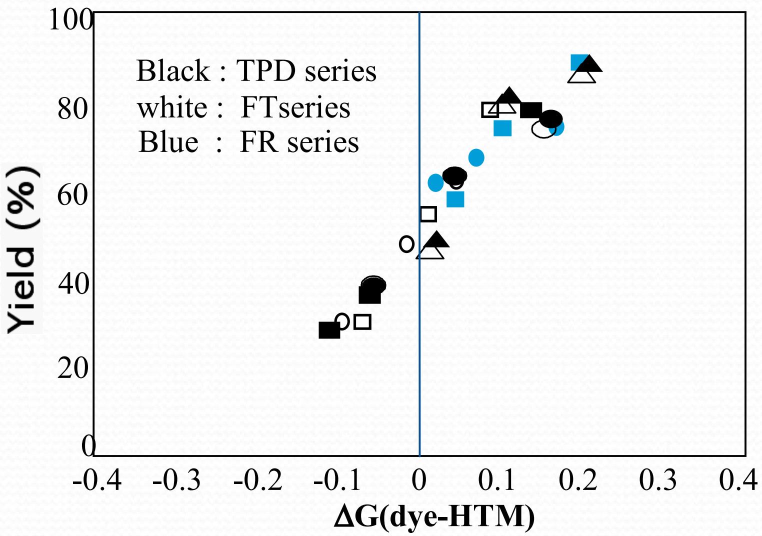
- $\Delta G = E_{dye} - E_{HTM}$

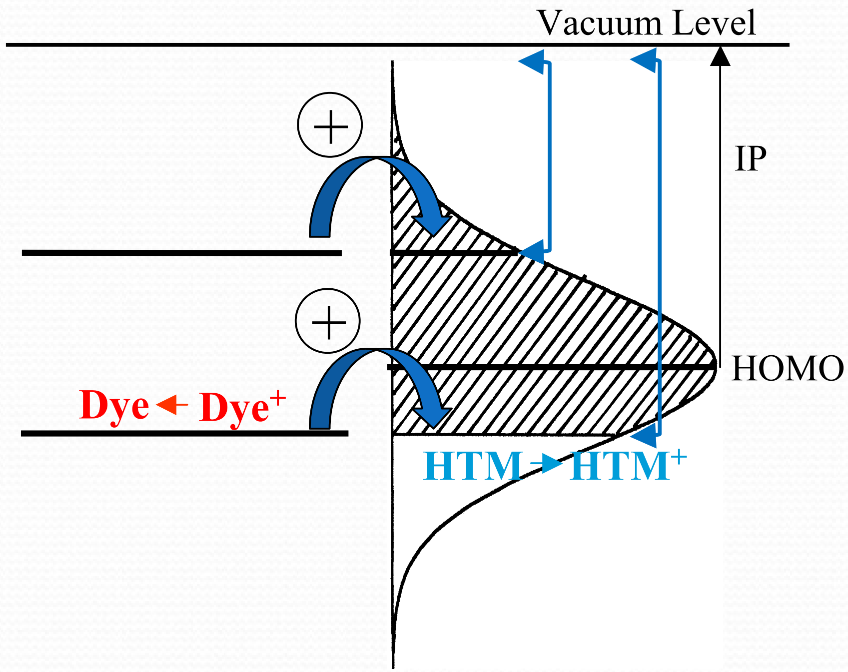
ChemPhyChem, **2003**, 89-93.

Thermodynamic Driving Force

- The yield is controlled not by kinetic competition, but by the thermodynamic driving force for the reacti on, $\Delta G_{(dye\text{-}HTM)}$.

- For a variation in ΔG over a range of 0.4 V, the yield of hole transfer varies from 34 - 90 %.





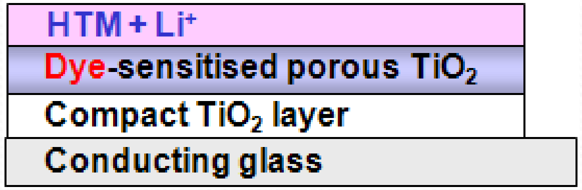
$$\Delta G = -k_bT \ln\left(\frac{[HTM^+]}{[dye^+]}\right)$$

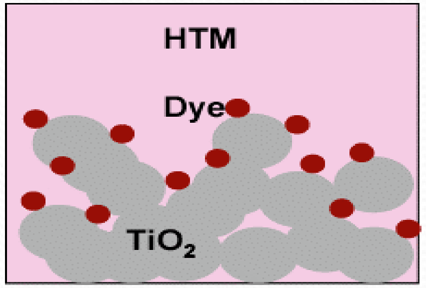
$$\Delta G = -k_bT \ln K$$

$$\text{Yield} \propto \int_{\Delta G}^{\infty} e^{-(E^2/2\sigma^2)}\, dE$$

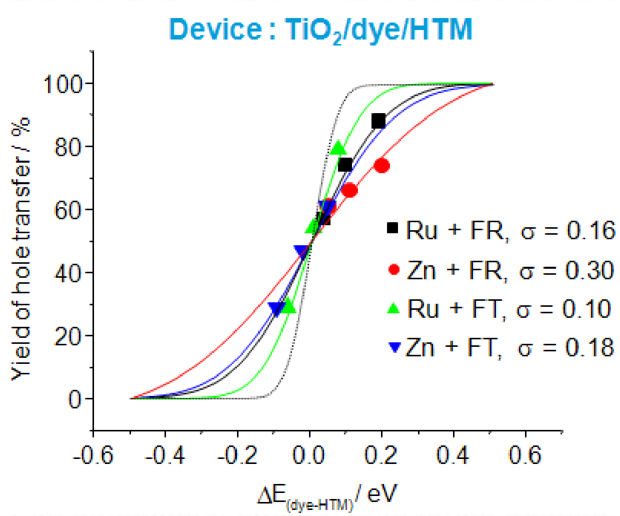
ChemPhyChem, **2003**, 89-93.

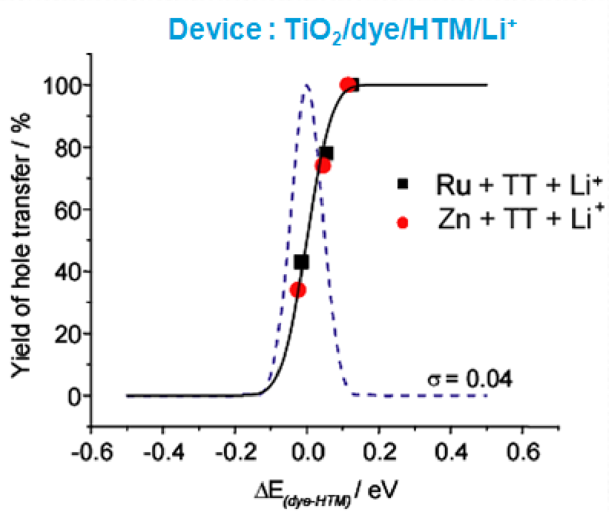
Energetic Homogenous Interface

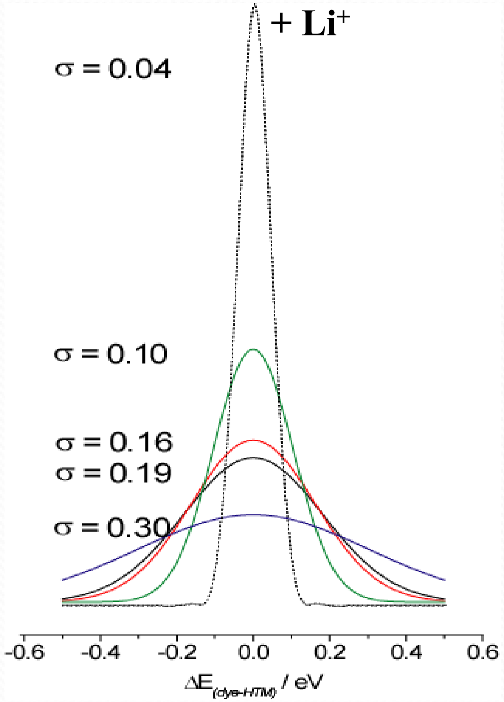




$$\text{Yield } \alpha \int_{\Delta G}^{\infty} e^{-(E^2/2\sigma^2)}\, dE$$

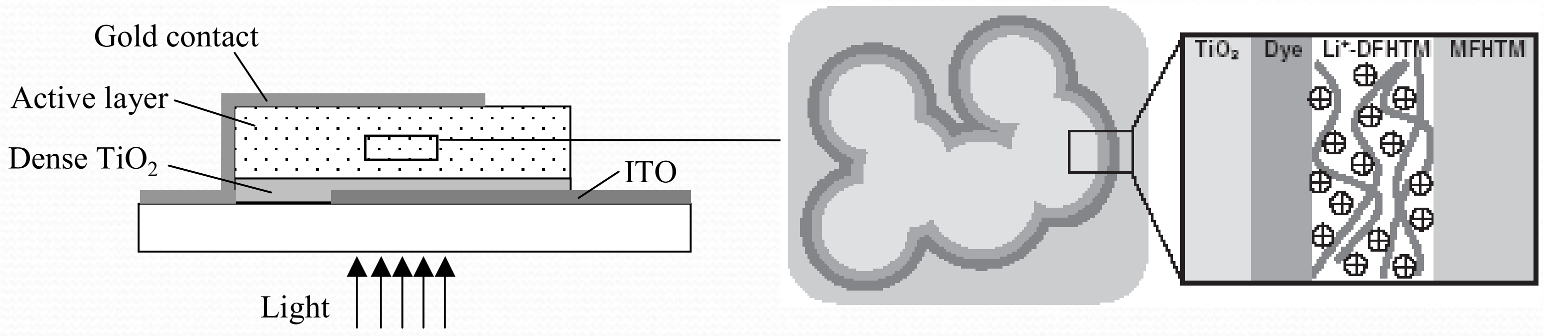




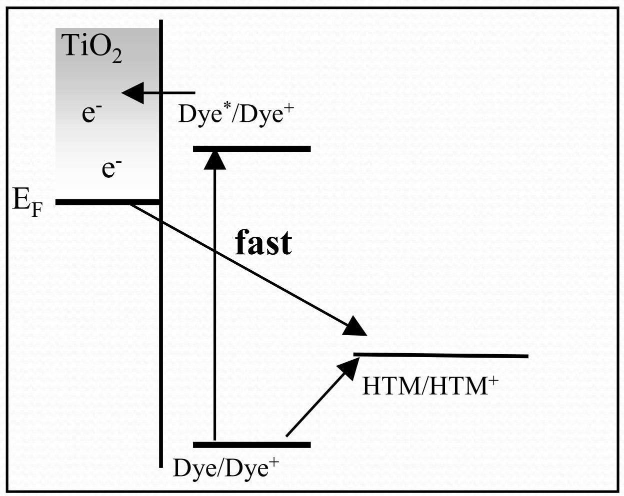


Energetic heterogeneous interface — Interfacial electrostatic interactions → Li^+ — **Energetic homogenous interface**

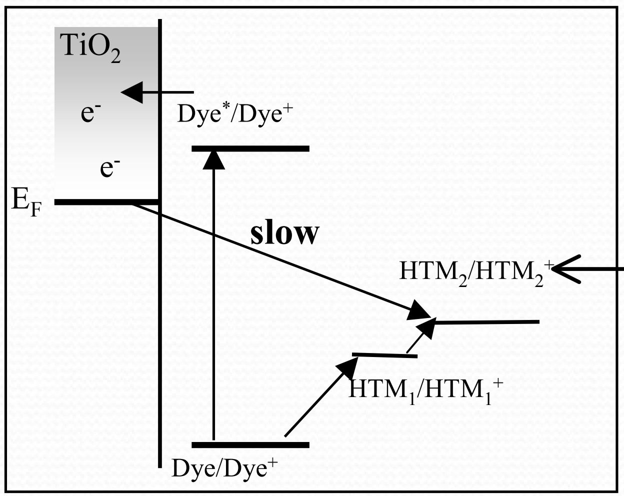
Double Layered Device

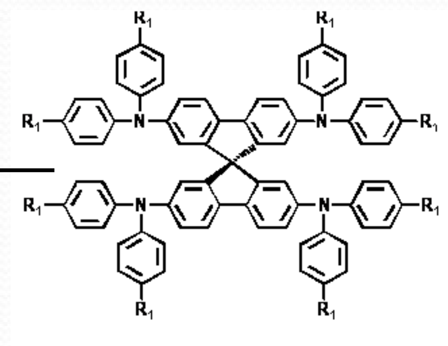


(a) TiO_2 / dye / HTM_1



(b) TiO_2 / dye / HTM_1 / HTM_2

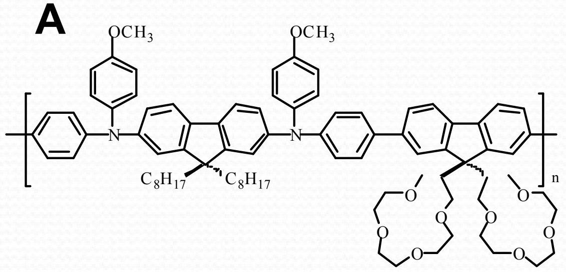




POSTECH

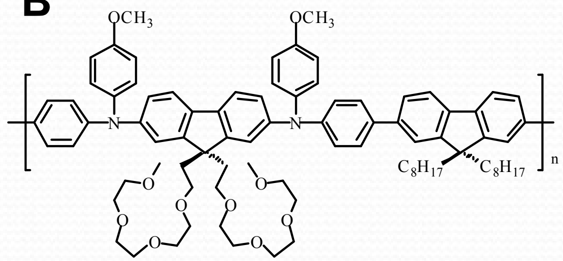
Drift Hole Mobility of the Polymers

A

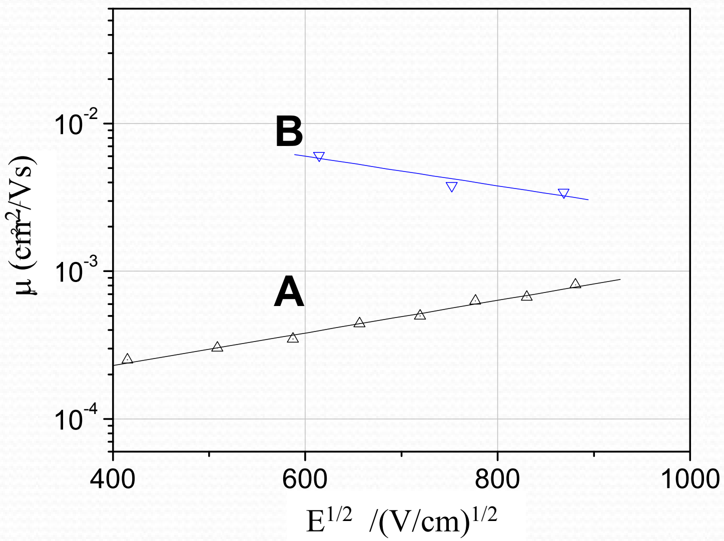


2.3×10^{-4} cm^2/Vs

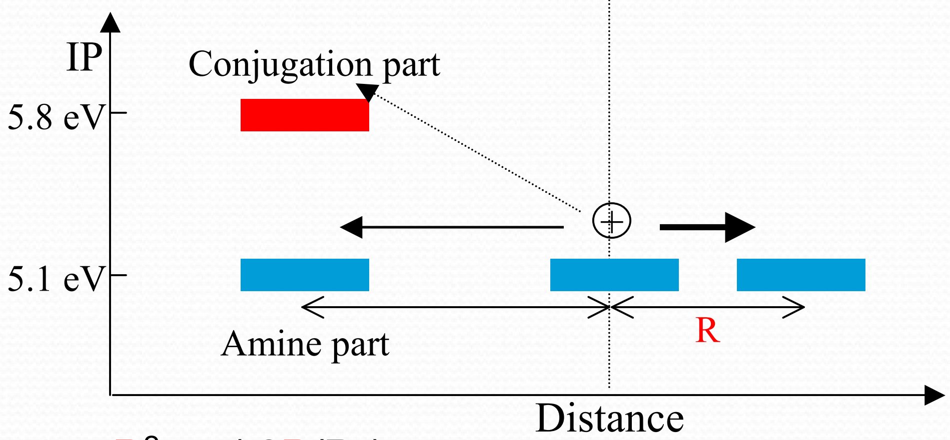
B



2.0×10^{-3} cm^2/Vs



Interpretation



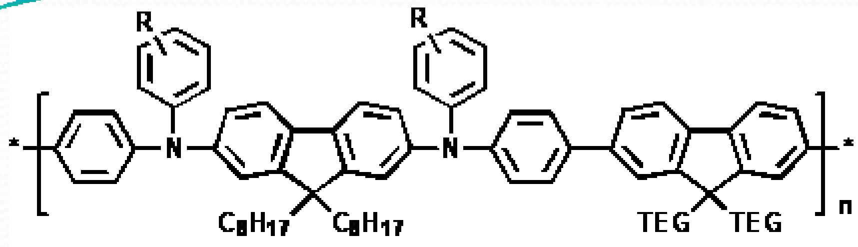
$\mu \propto R^2 \exp(-2R/R_o)$

R : Intersite distance
R_o : Localisation distance

- Major hopping : Closer and lower ionisation potential sites

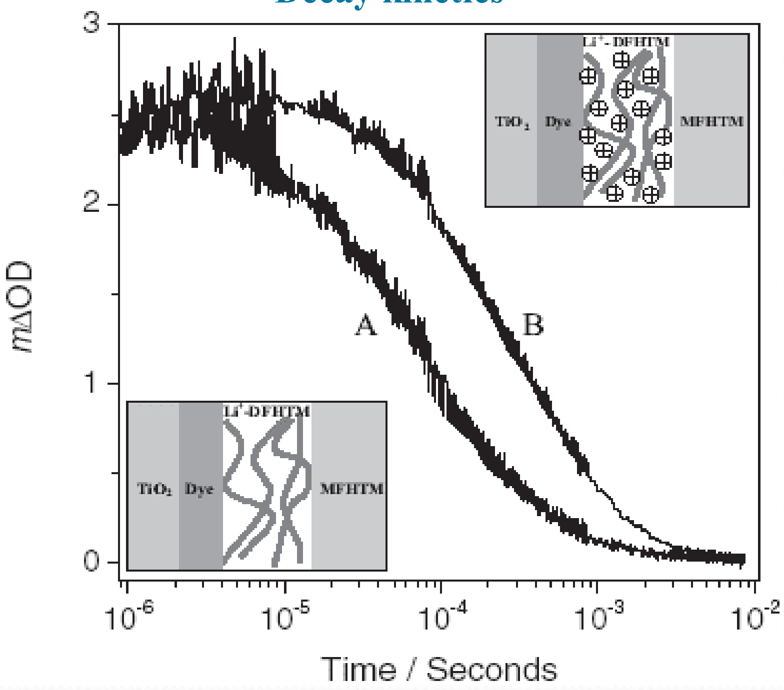
POSTECH

Double Layered Device



R = -H
R = -*p*-F
R = -*p*-OCH_3
R = -3,5-F_2

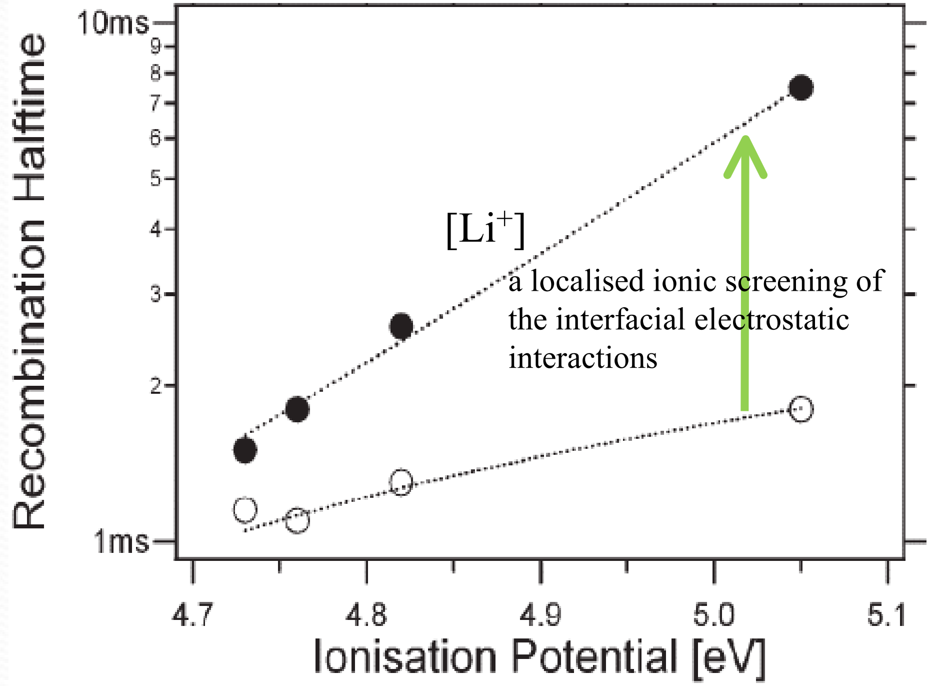
Decay kinetics



$$e^- (TiO_2) + HTM^+ \longrightarrow HTM$$

Adv. Funct. Mater., **2004**, 14, 435.

Formation of an energetic redox cascade



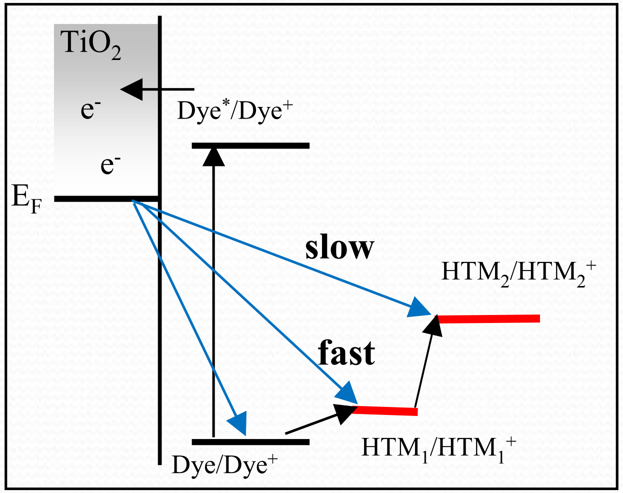
Chem. Commun., **2006**, 535.

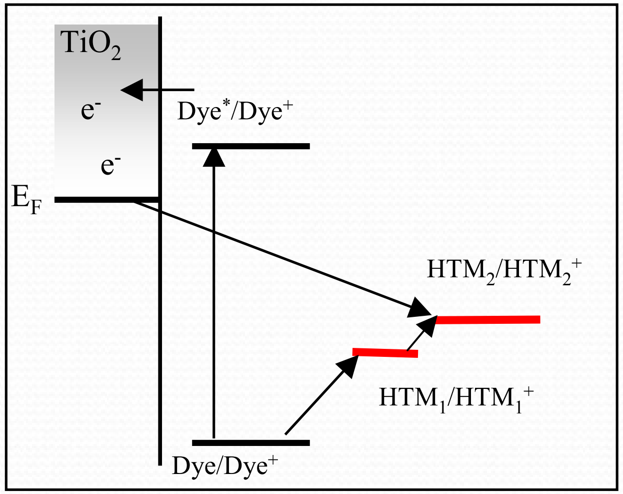
Recombination Reactions

Charge recombination Reactions

(1) $e^-(TiO_2) + Dye^+ \longrightarrow Dye$
(2) $e^-(TiO_2) + HTM_1^+ \longrightarrow HTM_1$
(3) $e^-(TiO_2) + HTM_2^+ \longrightarrow HTM_2$

(a) Higher IP for the first HTM >> (b) Lower IP for the first HTM



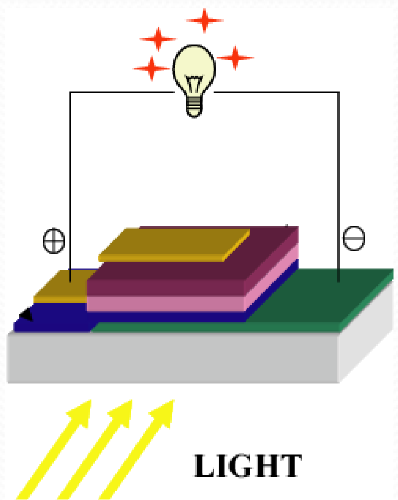


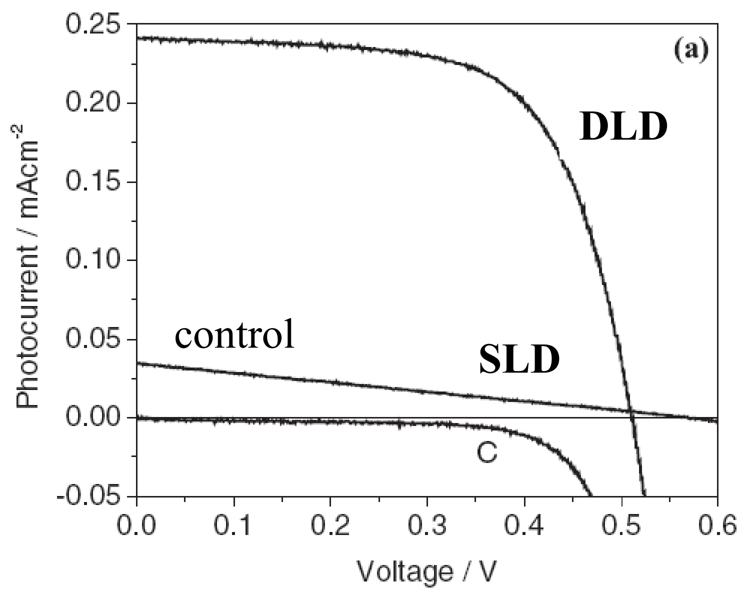
Minimizing the reaction (2) is of importance to improve device efficiency.

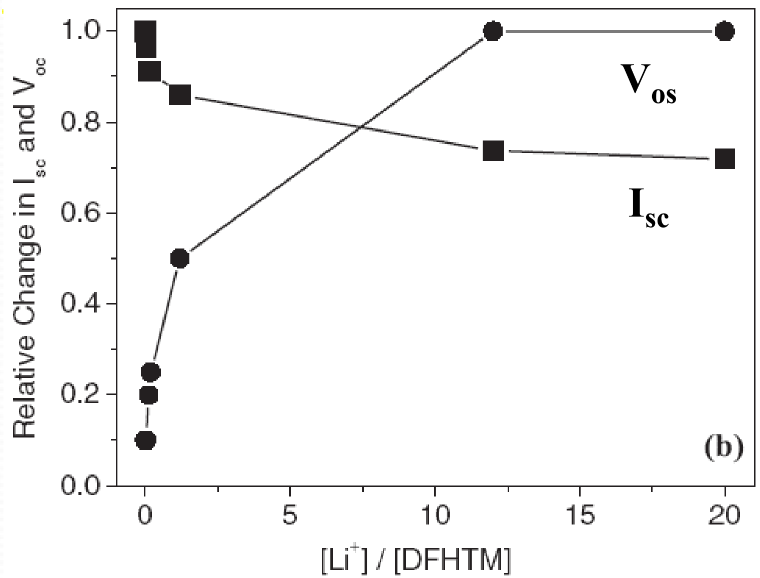
POSTECH

Double Layered Solid State Photocells

•Device efficiency

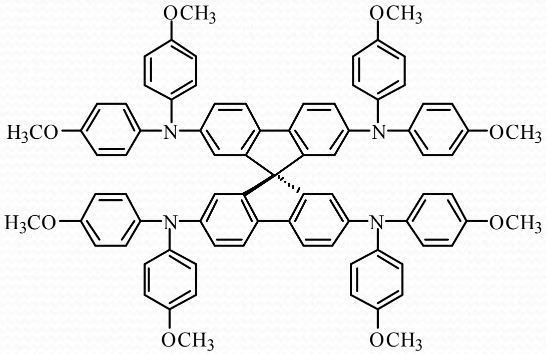






Adv. Funct. Mater. **2004**, 14, 435.

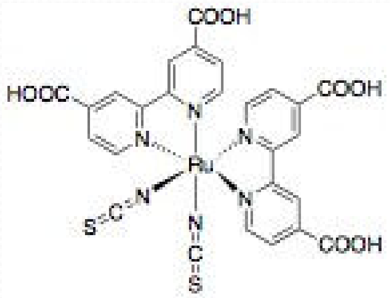
Hydrophobic Buffer Layer



$N(PhBr)_3SbCl_6$ & $Li[(CF_3SO_2)_2N]$

η = 0.74 %

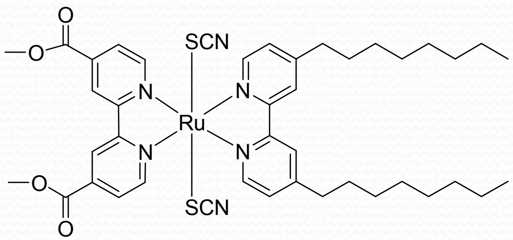
Nature 1998, **395**, 583



^tBP & $N(PhBr)_3SbCl_6$ & $Li[(CF_3SO_2)_2N]$

η = 2.56 %

APL 2001, **79**, 2085



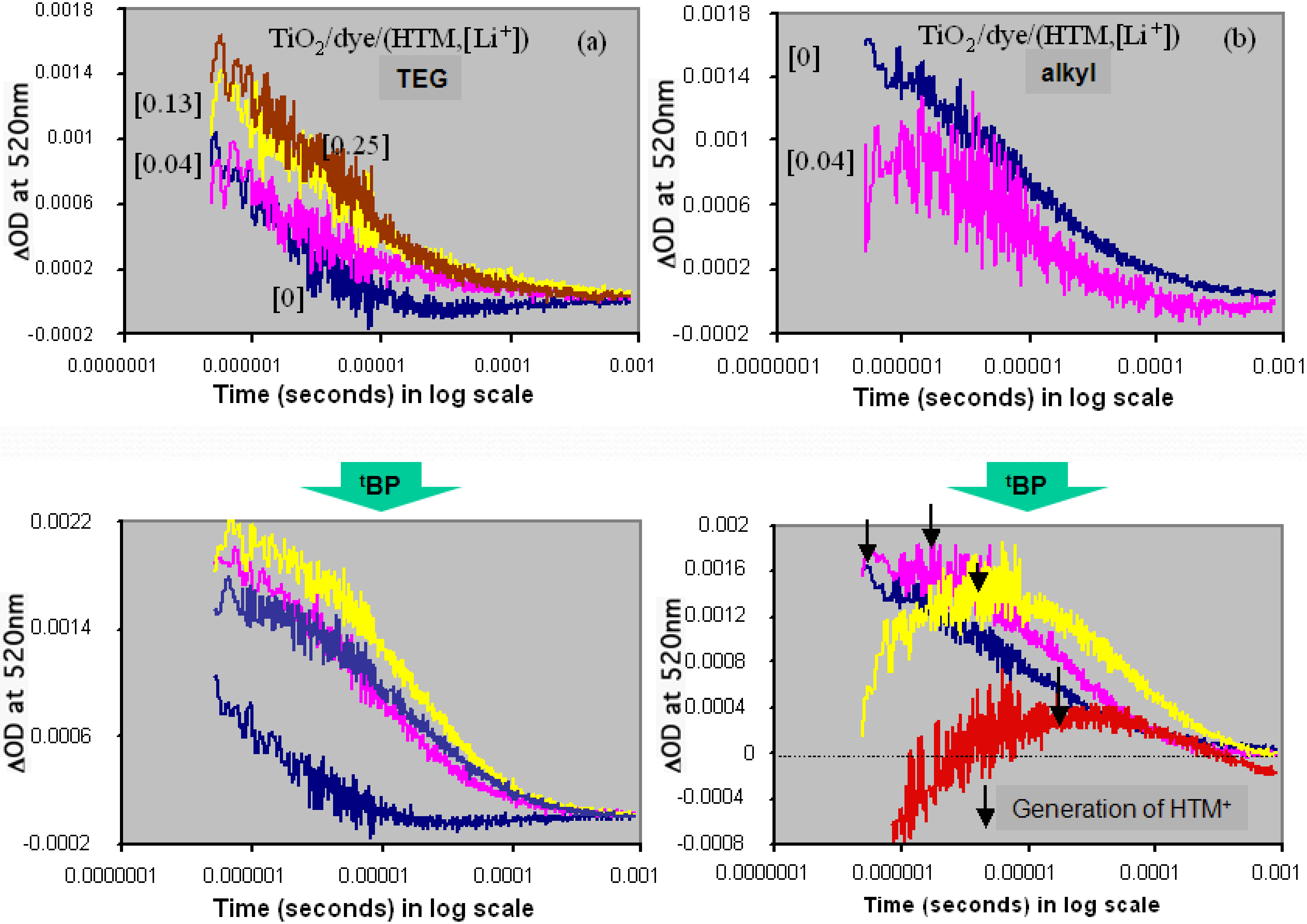
^tBP & $N(PhBr)_3SbCl_6$ & $Li[(CF_3SO_2)_2N]$

η = 4.02 %

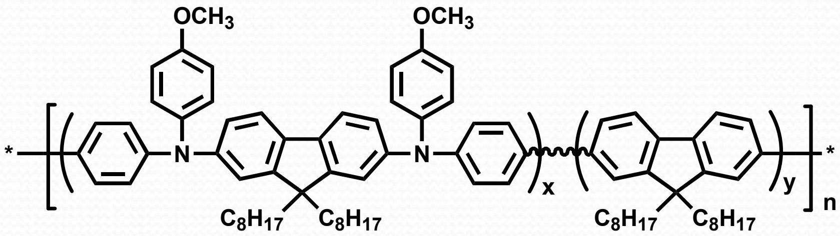
APL 2005, **86**, 013504

POSTECH

Recombination Reactions



Hydrophobic Buffer Layer

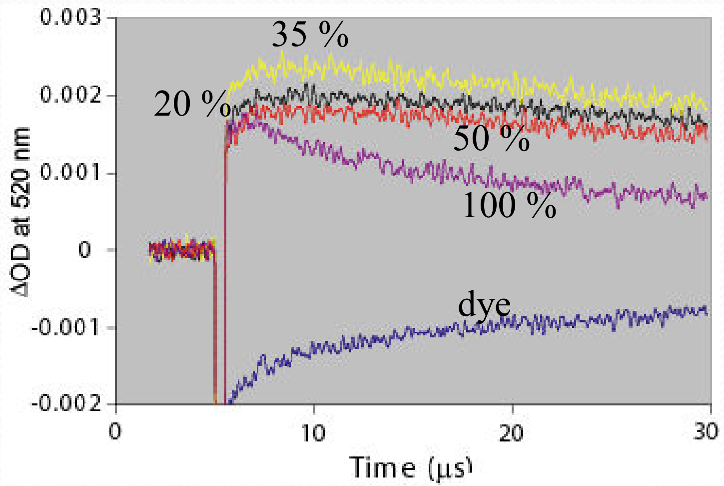


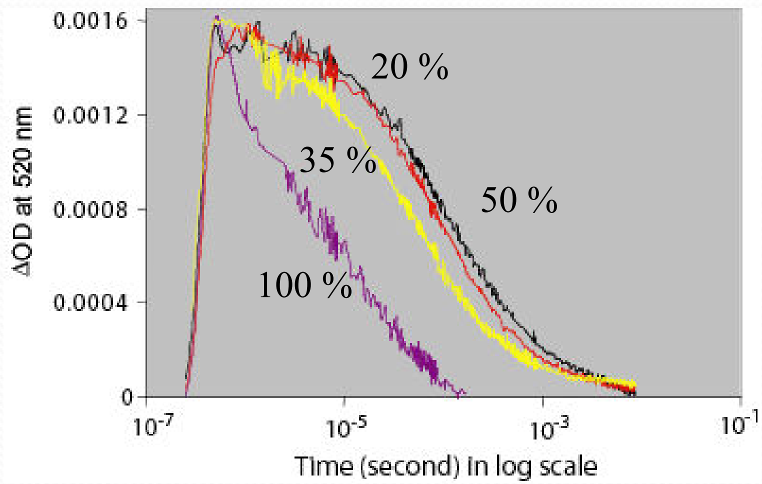
mol % of HTM = 20, 35, 50, 100 %

IP = 5.11 eV

Dye^{+} + HTM ⟶ Dye + HTM^{+}

$e^{-}(TiO_2)$ + HTM^{+} ⟶ HTM





Conclusions

- TEG side groups were introduced, effectively chelating lithium ions resulted to minimize Interfacial electrostatic interactions.

- The formation of an energetic redox cascade was demonstrated at the double layer device.

- A complete solid junction was realized with a double-layered device.

POSTECH