On the Photophysical and Electrochemical Studies of Dye-Sensitized Solar Cells

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Solar cells

Type	Material	Conversion efficiency (%)		Features
		Cell	Module[a]	
Since 1954 Si solar cell	Single crystalline	24	17~18	High efficiency/ matured technology
	Polycrystalline	18	14~15	Excellent for mass-production
	HIT[b]	21	17	Excellent in efficiency and temperature property
	Amorphous thin film	13	9~10	Low efficiency
	Poly/micro crystalline thin film	17	7~16[c]	Next-generation solar cell
Since 1956 Compound solar cell	GaAs	18~30	> 25	For specific use in satellites
	CdTe	17	11~16[c]	For consumer use
	$CuInSe_2$	19	11~18[c]	Promising low-cost thin film solar cell
Since 1970	Dye-sensitized TiO_2 solar cell	10~11	7	Improve efficiency and high-temperature stability, scale up production
	Organic solar cell	6~7[c]	-	Improve stability and efficiency

[a] One module is a panel consisting of multiple solar cells.
[b] Heterojunction with intrinsic thin layer.
[c] Data under R&D stage.

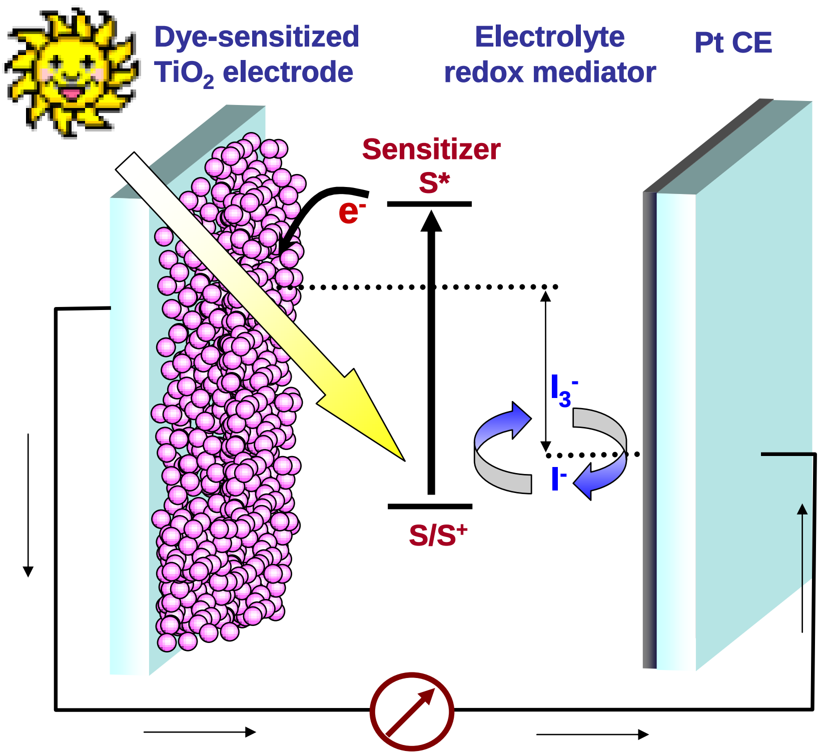
Reference:

KRI Report No. 8 of Phase XVI, KRI, Inc., Japan (2005).

Nature, 1 , 338-3 (2001).

10/23, 2008

Schematic of a Dye-Sensitized TiO_2 Solar Cell



$TiO_2|S + h\nu \rightarrow TiO_2|S^*$ ①

$TiO_2|S^* \rightarrow TiO_2|S^+ + e_{cb}$ ②

$TiO_2|S^+ + e_{cb} \rightarrow TiO_2|S$ ③

$TiO_2|S^+ + 3/2\ I^- \rightarrow TiO_2|S + 1/2\ I_3^-$ ④

$1/2\ I_3^- + e_{(Pt)} \rightarrow 3/2\ I^-$ ⑤

$I_3^- + 2e_{cb} \rightarrow 3\ I^-$ ⑥

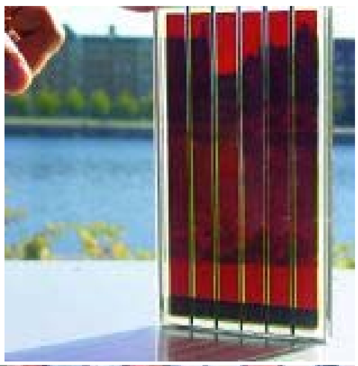
DSSCs technology

Advantages of the DSSC:

- Low cost fabrication of titania cells than that of silicon.
- Compatibility with flexible substrates and a variety of appearances.
- It can be optically transparent or opaque and used as "photovoltaic window."

Disadvantages of the DSSC:

- Low energy conversion efficiency
- Leakage of liquid electrolytes
- Long-term instability



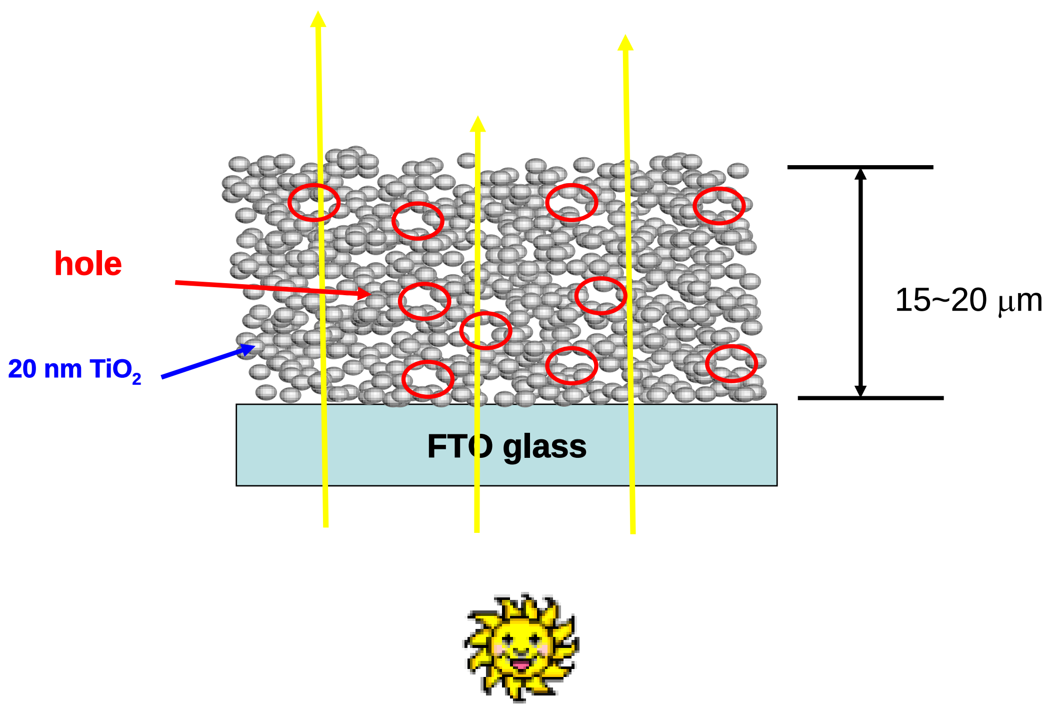
http://www.oja-services.nl/iea-pvps/ar00/aus.htm

http://pubs.acs.org/email/cen/html/07130 135555.html

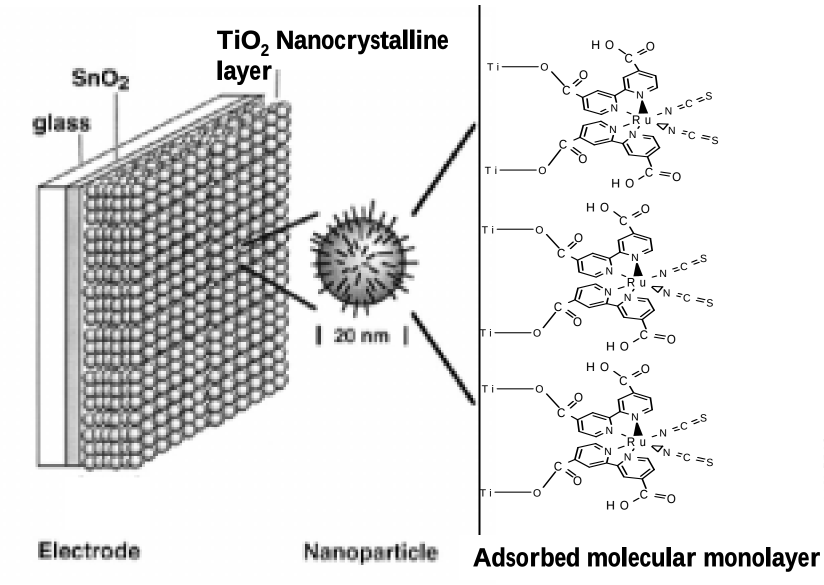
Fabrication of TiO_2 electrodes

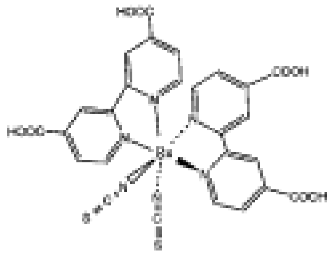
- **The TiO_2 precursor was prepared by sol-gel process. Titanium (IV) isopropoxide was added to a 0.1 M nitric acid solution with constant stirring and heated to 85 ℃ simultaneously for 8 h.**
- **When the mixture was cooled down to room temperature the resultant colloid was filtered and the filtered colloid was heated in an autoclave at 240 ℃ for 12 h in order to allow the growth of the TiO_2 particles.**
- **The TiO_2 colloid was concentrated to 13 wt% and finally 30 wt% (with respect to TiO_2) of PEG (MW=20 000) was added to prevent the film from cracking during drying.**
- **The TiO_2 paste was deposited using the glass rod method on a conducting fluorine-doped tin oxide (FTO) glass.**
- **TiO_2 thin film was dried in air at room temperature. The film was then heated to 500 ℃ at a rate of 10 ℃/min and maintained for 30 min before cooling to room temperature.**
- **The thickness of the TiO_2 film can be controlled by repeating the above process.**

TiO_2 for Light Harvesting

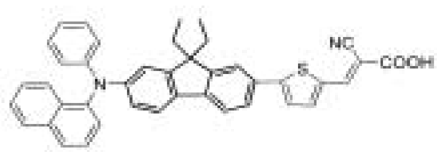


Dye Adsorbed on TiO_2



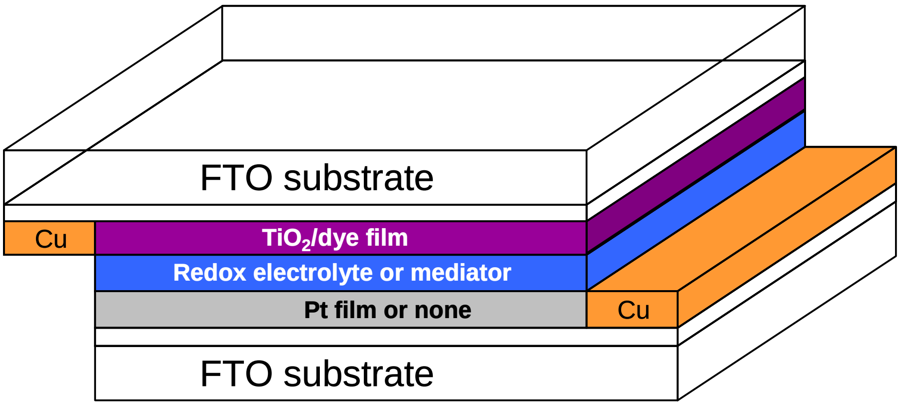


N3
(Gratzel)



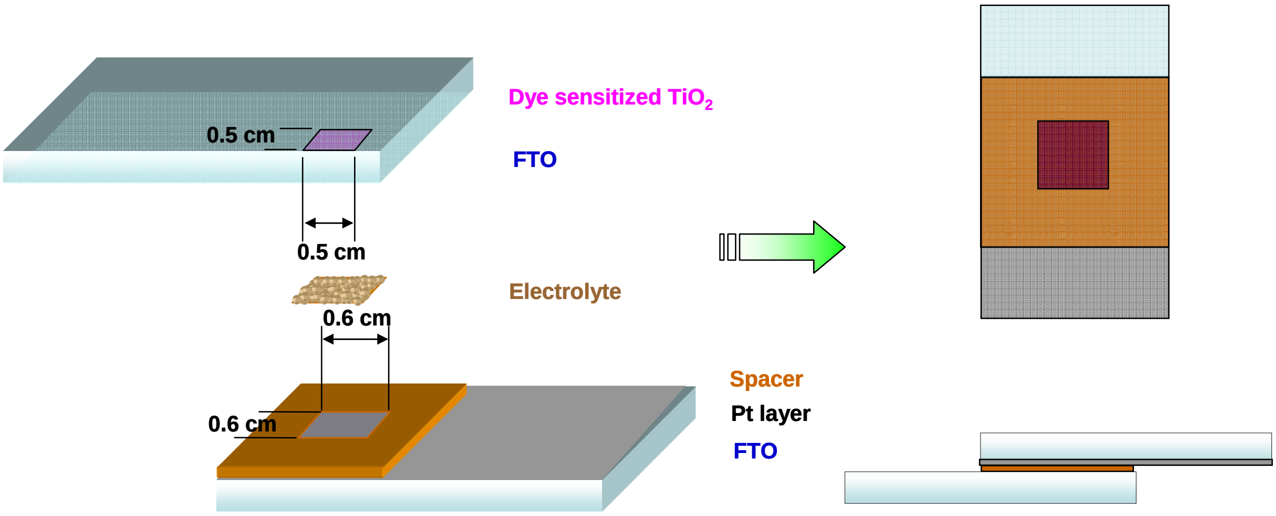
FLDye1
(Academia Sinica)

Configuration of a DSSC



The dye-sensitized TiO_2 photoanode and the redox mediator are investigated in this study.

Our design of a DSSC



Experimental conditions

- **Dye-sensitized TiO_2 photoanode**
  - TiO_2 colloid was prepared by hydrothermal method in a Ti autoclave at 240℃.
  - TiO_2 film was scraped onto a FTO substrate by a glass rod and then was sintered at 450℃.
  - It was immersed into the solution containing 3×10^{-4} M sensitizers for at least 12 h.
- **Mediators**
  - 0.5 M LiI, 0.05 M I_2, and 0.5 M 4-tert-butylpyridine in acetonitrile.
- **Dye sensitizers**
  - Ruthenium dyes: N3, CYC-B1
  - Organic dyes: carbazole dyes; thienyl dyes (S1, S2, S3, and S4); thienylfluorene dyes (FLDye1), all obtained from Prof. Jiann T'suen Lin at Institute of Chemistry, Academia Sinica.
- **Pt counter electrode**
  - Pt film was sputtered on a FTO glass with a thickness of 0.1 μm.
- **Light source**
  - 450 Xe lamp + IR filter + AM 1.5 simulated filter.

Mechanism

➢ Mechanism:

$S + h\nu \rightarrow S^*$

$S^* \xrightarrow{k_{inj}} S^+ + e^-_{CB}$

$k_{inj}=10^{10}\sim10^{12}\ s^{-1}$

$S^* \xrightarrow{k_d} S$

$k_d=10^7\ s^{-1}$

$S^+ + R \xrightarrow{k_m} S + O$

$k_m=10^5\sim10^8\ s^{-1}$

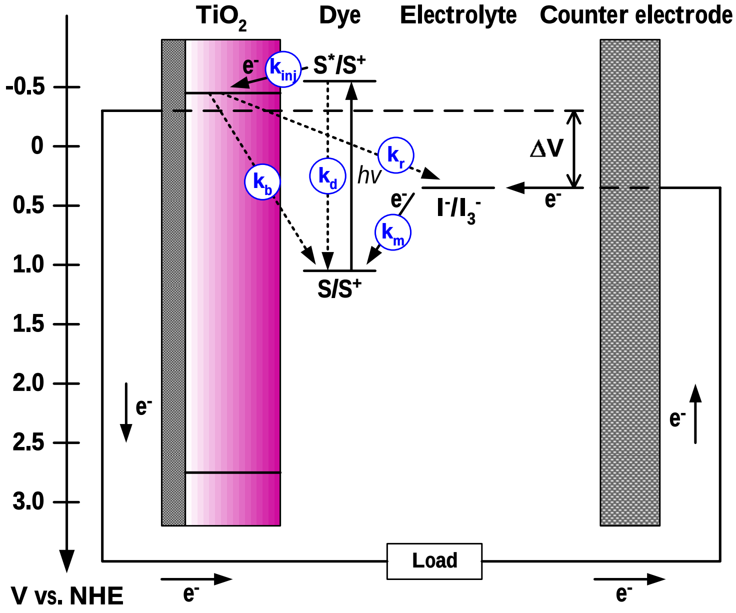
$S^+ + e^-_{CB} \xrightarrow{k_b} S$

$k_b=10^3\sim10^4\ s^{-1}$

$O + e^-_{CB} \underset{k_{-r}}{\overset{k_r}{\rightleftarrows}} R$

$k_r=10^2\ cm\ s^{-1}$

$$\frac{I_{ph}}{qA_g} = \frac{dn_e}{A_g dt} = k_{inj}[S^*] - k_b[S^+] - k_r[O] + k_{-r}[R]$$



Chem. Rev., 95, 9 (1995).

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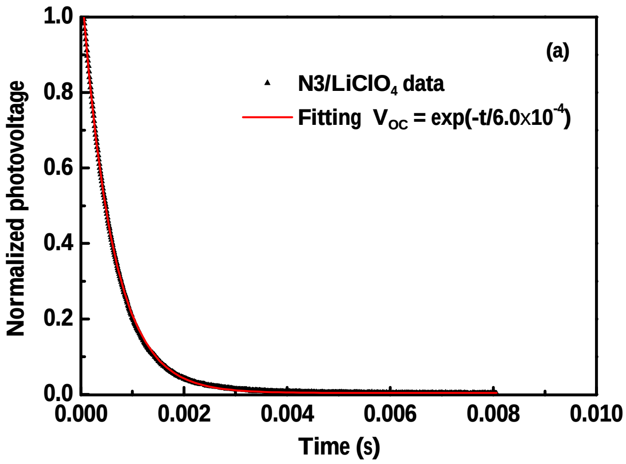
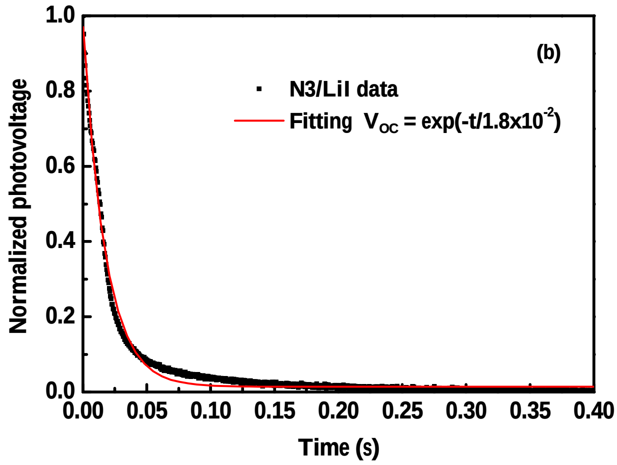
Transient photovoltage

❐ TiO$_2$ / N3 / LiClO$_4$ in CH$_3$CN / Pt



❐ TiO$_2$ / N3 / LiI in CH$_3$CN / Pt



❐ The electron lifetimes (τ_R) increase from 0.6 ms to about 18 ms when LiI was introduced.

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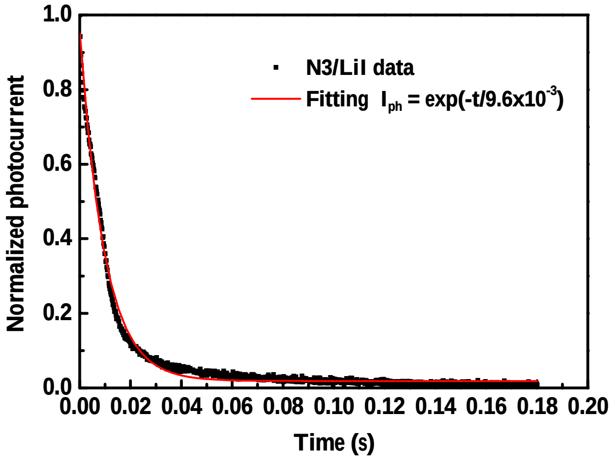
Transient photocurrent (Cont'd)

❐ TiO_2 / N3 / LiI in CH_3CN / Pt



➢ The apparent diffusion coefficient can be estimated:

$$D_e = \frac{w^2}{2.35\tau_C}$$

J. Phys. Chem. B, **105,1119 (2001).**

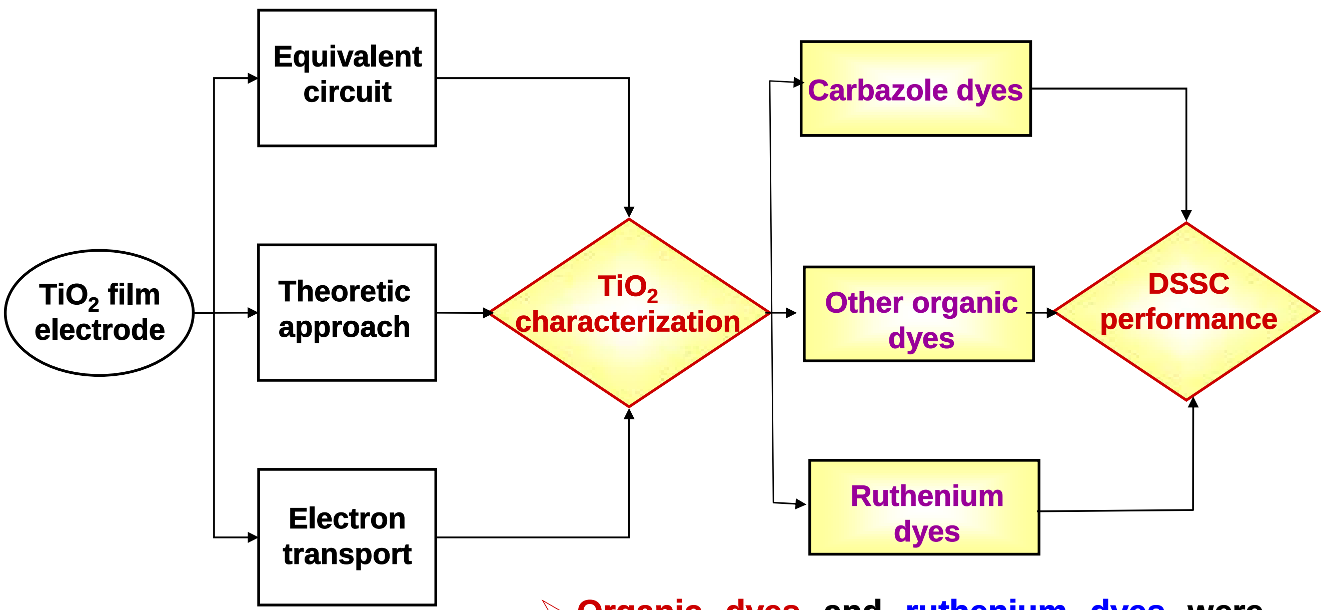
→For a 20 μm TiO_2 film, D_e= 1.8×10^{-4} cm^2/s in 0.5 M LiI solution.

➢ The effective diffusion length (L_e) of photoinjected electron in a TiO_2 film can be calculated from the electron lifetime and the apparent diffusion coefficient as:

$$L_e = \sqrt{D_e \tau_R}$$

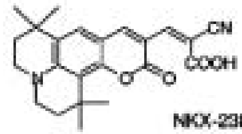
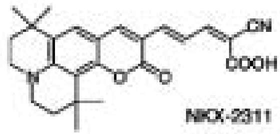
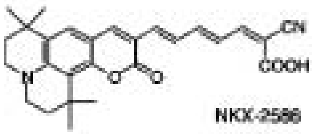
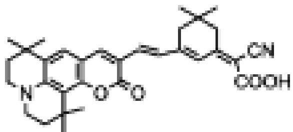
→L_e= 18 μm.
↑ Max. value in LiI solution.

Incorporation with dyes other than N3

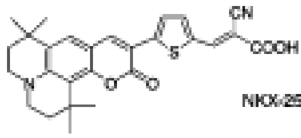
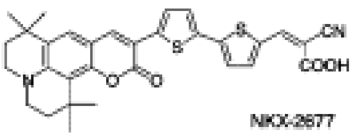
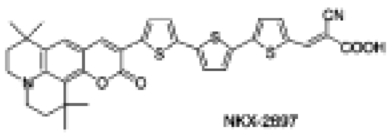


➢ **Organic dyes and ruthenium dyes were obtained from Prof. Jiann T'suen Lin (Institute of Chemistry at Academia Sinica) and Prof. Chun-Guey Wu (Department of Chemistry, National Central University), respectively .**

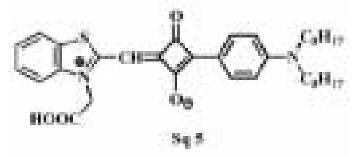
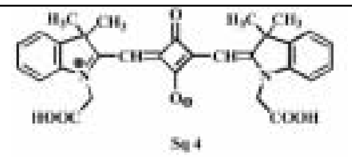
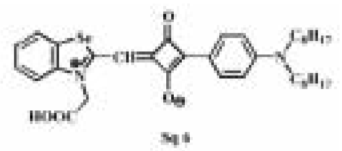
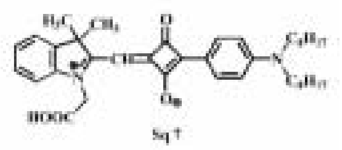
A survey of organic dyes

Coumarin dyes	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Efficiency (%)	Fill factor	Ref.
 NKX-2388	12.9	500	4.1	0.64	H. Arakawa et al.
 NKX-2311	14.0	600	6.0	0.71	H. Arakawa et al.
 NKX-2586	15.1	470	3.5	0.50	H. Arakawa et al.
 NKX-2753	16.1	600	6.7	0.69	H. Arakawa et al.

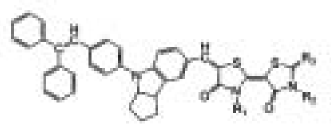
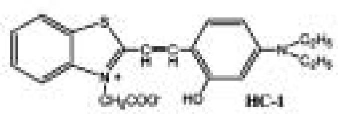
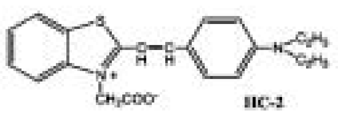
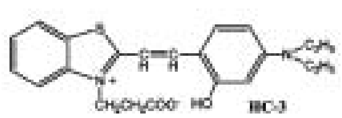
A survey of organic dyes (Cont'd)

Coumarin dyes	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Efficiency (%)	Fill Factor	Ref.
 NKX-2587	12.1	660	5.8	0.73	H. Arakawa et al.
 NKX-2677	13.5	710	7.4	0.77	H. Arakawa et al.
 NKX-2697	14.3	700	6.4	0.64	H. Arakawa et al.

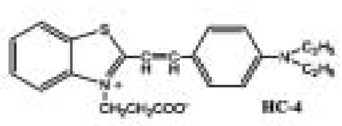
A survey of organic dyes (Cont'd)

Squaraine dyes	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Efficiency (%)	Fill Factor	Ref.
	3.52	530	1.04	0.534	S. Das et al.
	3.94	580	1.25	0.525	S. Das et al.
	3.78	600	1.43	0.605	S. Das et al.
	5.92	640	2.08	0.526	S. Das et al.

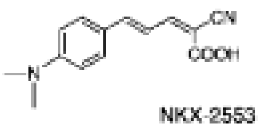
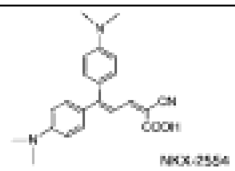
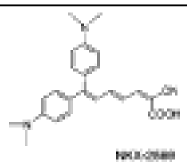
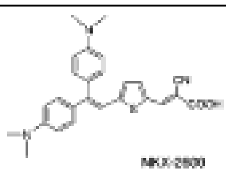
A survey of organic dyes (Cont'd)

Indoline dyes	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Efficiency (%)	Fill Factor	Ref.
	18.50	693	8.00	0.624	T. Horiuchi et al.
Hemicyanine dyes	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Efficiency (%)	Fill Factor	Ref
	13.9	520	5.2	0.57	H. Arakawa et al.
	10.5	448	3.5	0.58	H. Arakawa et al.
	12.7	499	4.4	0.56	H. Arakawa et al.

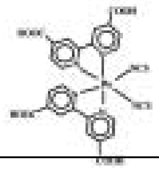
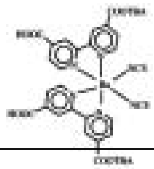
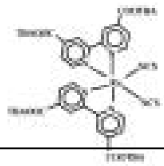
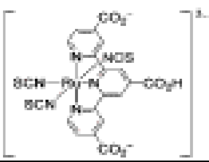
A survey of organic dyes (Cont'd)

Hemicyanine dyes	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Efficiency (%)	Fill Factor	Ref.
 HC-4	8.9	474	3.1	0.59	H. Arakawa et al.
 HC-5	6.1	465	2.0	0.55	H. Arakawa et al.
 HC-6	7.6	452	2.6	0.59	H. Arakawa et al.

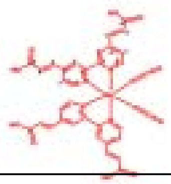
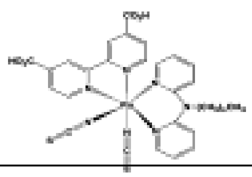
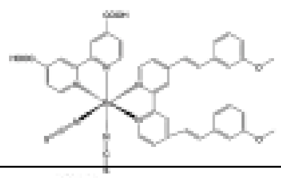
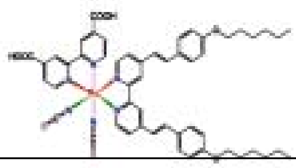
A survey of organic dyes (Cont'd)

Donor-acceptor	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Efficiency (%)	Fill Factor	Ref.
 NKX-2553	10.40	710	5.5	0.74	H. Arakawa et al
 NKX-2554	9.90	740	5.4	0.74	H. Arakawa et al
	12.90	710	6.8	0.74	H. Arakawa et al
	12.5	680	5.9	0.69	H. Arakawa et al

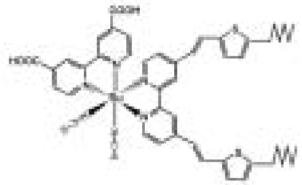
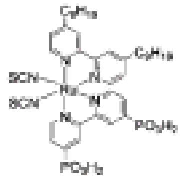
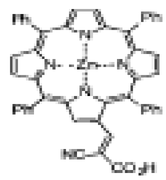
A survey of organic dyes (Cont'd)

Ru dyes	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Efficiency (%)	Fill Factor	Ref
N3 	18.2 (16.8)	720 (865)	10.0 (11.0)	073	M. Gratzel et al.
N719 	17.73	846	11.2	0.75	M. Gratzel et al.
N712 	13.0	900	8.2	0.700	M. Gratzel et al.
Black dye 	20.53	720	10.4	0.704	M. Gratzel et al.

A survey of organic dyes (Cont'd)

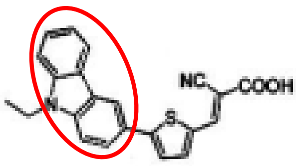
Ru dyes	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Efficiency (%)	Fill Factor	Ref
K-8 	18.0	640	8.6	0.75	M. Gratzel et al.
Z-907 	15.5	756	8.2	0.702	M. Gratzel et al.
Z-910 	17.2	777	10.2	0.764	M. Gratzel et al.
K-19 	14.61	711	7.0	0.671	M. Gratzel et al.

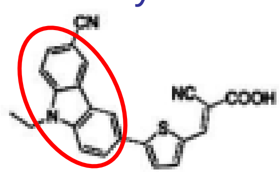
A survey of organic dyes (Cont'd)

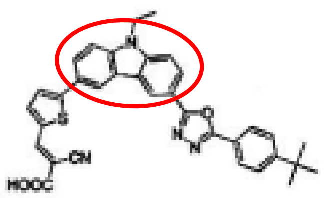
Ru dyes	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Efficiency (%)	Fill Factor	Ref
HRS-1 	20.05	683	9.5	0.69	S. Yanagida et al.
Z-955 	16.37	707	8.0	0.69	M. Gratzel et al.
Zn-3 	13.0	610	5.6	0.70	M. Gratzel et al.

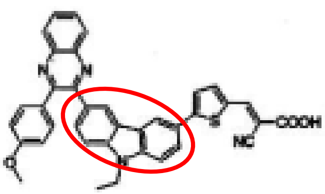
Carbazole based dyes

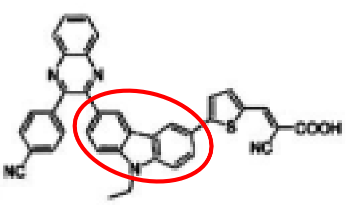
❒ Chemical structures of the Carbazole based dyes.

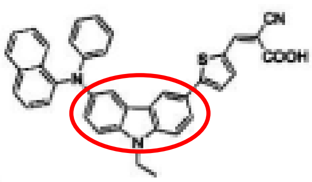

CB1


CB2


CB3


CB4

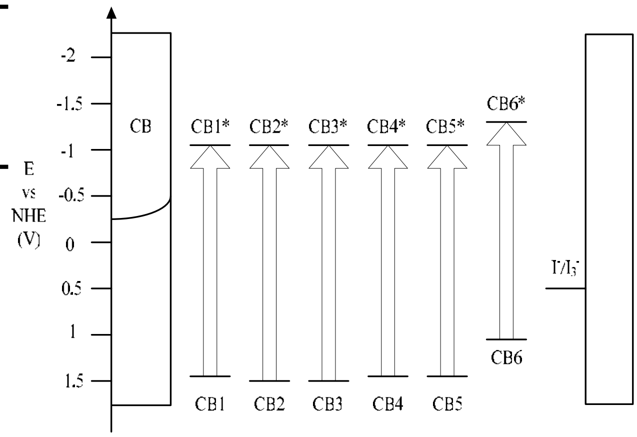

CB5


CB6

Electrochemical and spectral properties

❒ Energy levels:

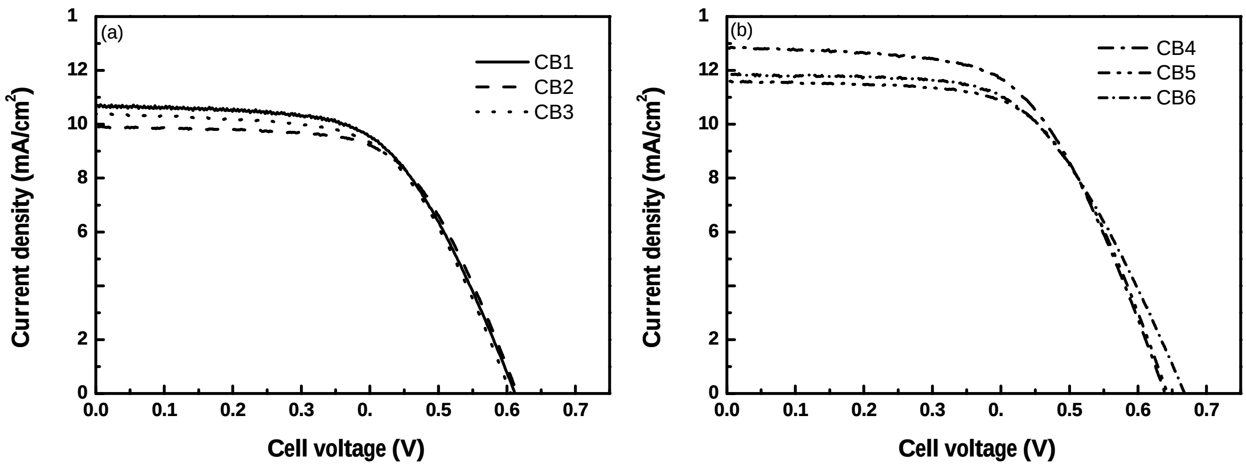
Dye	absorption		E_{0-0}	LUMO	HOMO
	λ_{max}/nm	ε at λ_{max} / M^{-1} cm^{-1}	/eV	/V vs. NHE	E_{ox}/V vs. NHE
CB1	436.5	31713	2.49	-1.05	1.44
CB2	416.2	35766	2.56	-1.06	1.50
CB3	429.7	24827	2.53	-1.05	1.48
CB4	394.0	32680	2.49	-1.05	1.44
CB5	417.2	33400	2.51	-1.05	1.46
CB6	394.4	23966	2.39	-1.33	1.06



❒ E_{LUMO} = oxidation potential (E_{OX}) – excited energy (E_{0-0})

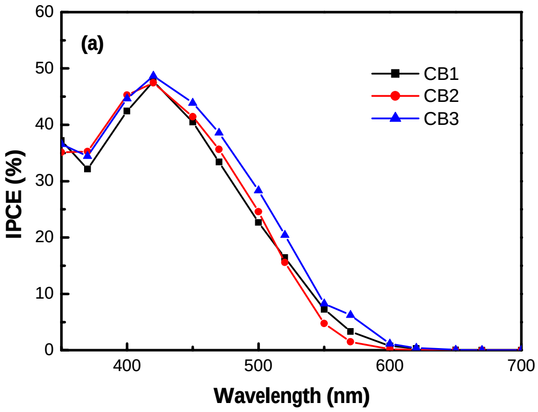
$\approx E_{HOMO} - E_g$

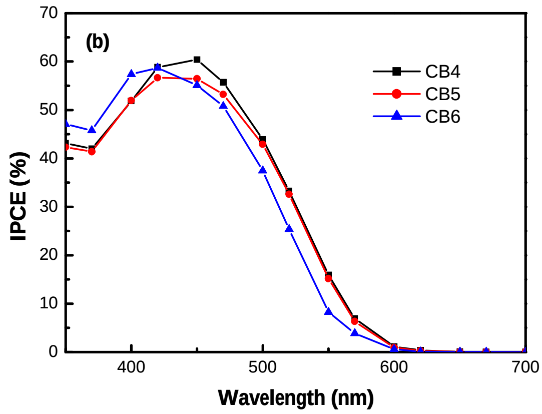
Cell performance

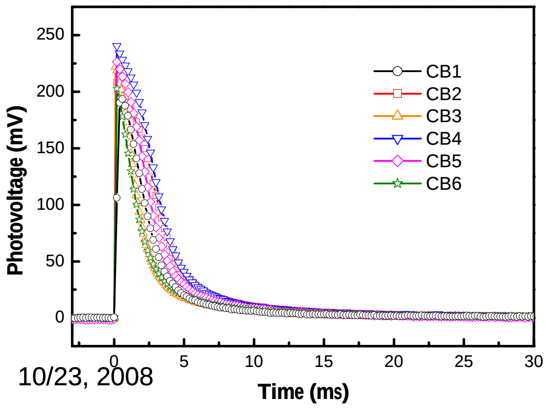


Dye	J_{sc} / mA cm^{-2}	V_{oc} / V	η / %	fill factor
CB1	10.61	0.61	3.850	0.585
CB2	9.89	0.62	3.705	0.625
CB3	10.38	0.61	3.720	0.605
CB4	12.81	0.64	4.705	0.585
CB5	11.59	0.64	4.445	0.600
CB6	11.82	0.67	4.295	0.590
N3	15.73	0.77	6.950	0.570

Photoelectrochemical properties





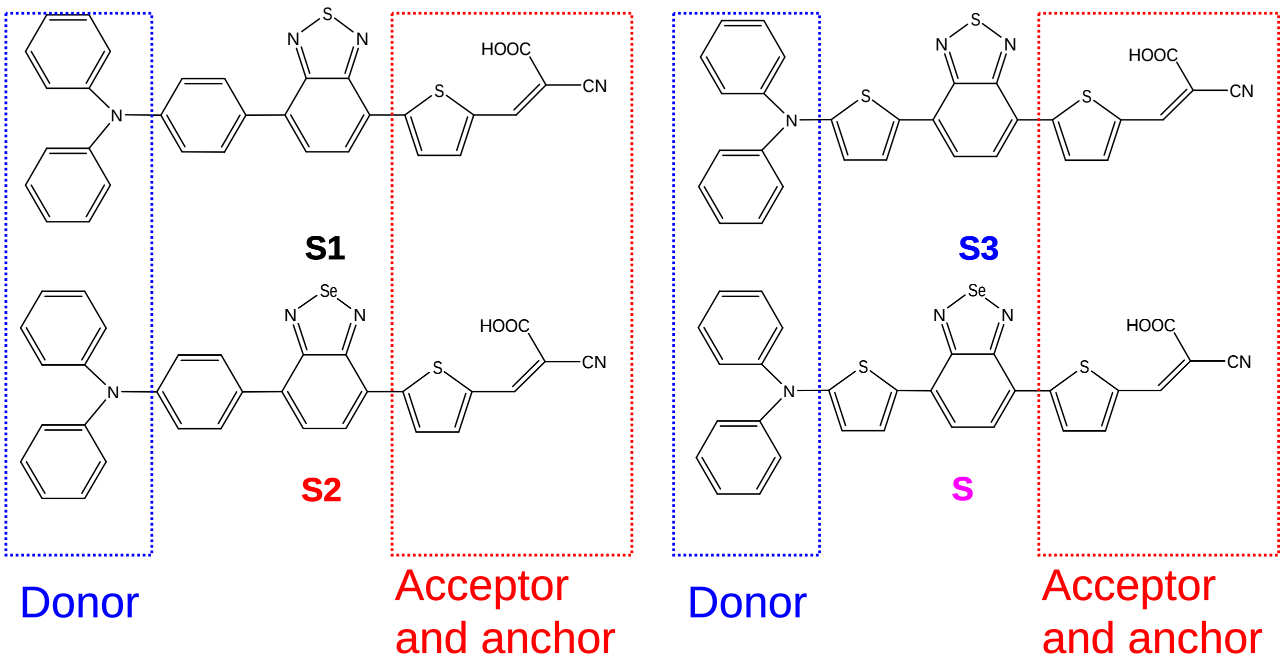


Samples	τ_R (ms)	D_e ($cm^2/s, *10^{-4}$)
CB1	2.02	7.5
CB2	1.81	8.8
CB3	1.81	12.1
CB4	2.99	11.8
CB5	2.52	11.3
CB6	1.92	11.8

τ_R: Electron lifetime; D_e: diffusion coefficient of electron

Thienyl dyes

❒ Benzo(thia/selena)diazole chromophores.



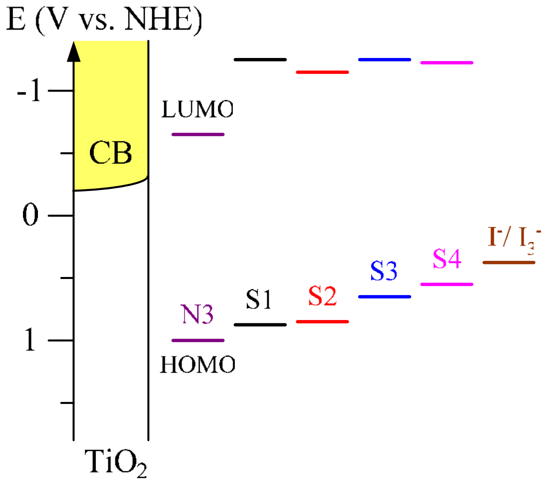
➢ ***Org. Lett.*, 7, 1899 (2005)**

Electrochemical and spectral properties

Dye	Absorption maximum[a] λ_{max} (nm) [ε (10^4 / M cm)]	E_{HOMO} (V vs. NHE)	E_g (eV)
S1	491 [2.75]	0.88	2.12
S2	502 [0.63]	0.86	2.02
S3	541 [2.44]	0.62	1.87
S4	544 [1.32]	0.56	1.77

[a] Measured in THF solution.

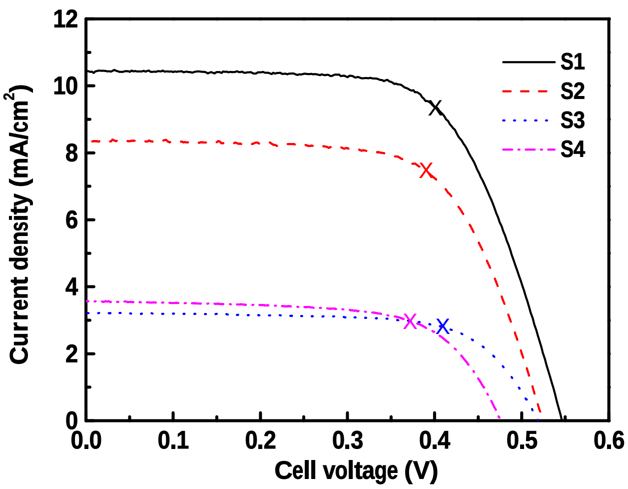
❒ Energy levels:

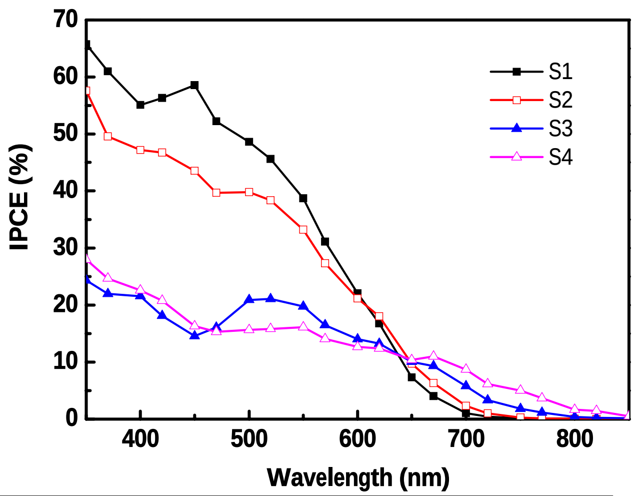


❒LUMO = oxidation potential (E_{OX}) – excited energy (E_{0-0})

$\approx E_{HOMO} - E_g$

Performance of S1 S4





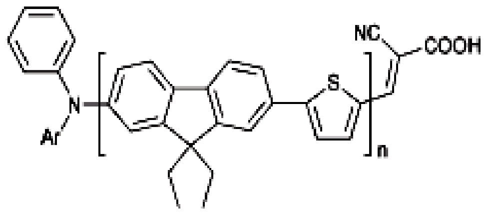
Dye	V_{OC} (V)	I_{SC} (mA/cm²)	η (%)	FF	Thickness δ (μm)	Adsorption (mol/cm²)	Cover area (nm²)
S1	0.55	10.44	3.77	0.66	22	7.83×10^{-7}	0.58±0.04
S2	0.52	8.35	2.91	0.67	21	7.36×10^{-7}	0.57±0.04
S3	0.52	3.21	1.15	0.69	23	8.21×10^{-7}	0.56±0.04
S4	0.47	3.57	1.11	0.66	22	5.98×10^{-7}	0.75±0.05

Lifetime of electrons

Dye	τ_R (ms) LiClO$_4$	τ_R (ms) LiI	τ_C (ms)	L_e (μm)
S1	0.28	6.54	4.68	10.8
S2	0.28	5.73	4.10	10.2
S3	0.23	1.31	0.76	4.9
S4	0.22	1.03	0.63	4.3
N3	0.60	17.65	9.56	17.8

- τ_R: lifetime of the photoinjected electrons.
- τ_C: time constant for electron collection.

Thienylfluorene (FL Dye series)



9 : n = 1; Ar = 1-naphthyl
10 : n = 1; Ar = 9-anthracenyl
11 : n = 1; Ar = 1-pyrenyl
12 : n = 2; Ar = 1-naphthyl
13 : n = 3; Ar = 1-naphthyl

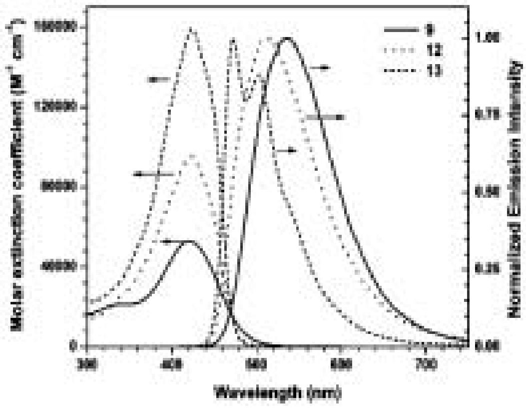
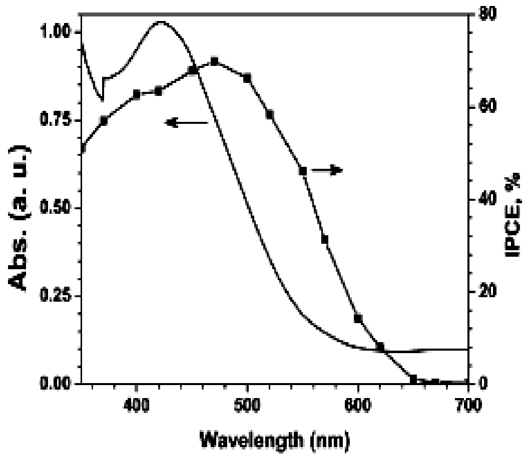


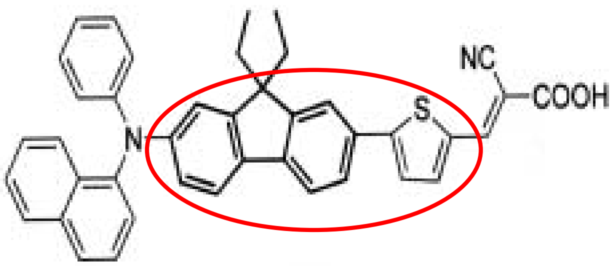
Table 1 Optical, redox and DSSC performance parameters of the dyes[a,b]

Dye	λ_{abs}/nm (ε/M^{-1} cm^{-1})	λ_{em}/nm (Φ_F (%))	E_{ox} (ΔE_p)/mV	V_{OC}/V	J_{SC}/mA cm^{-2}	*ff*	η (%)
9	421 (52 900)	538 (0.28)	509 (82)	0.65	12.47	0.65	5.23
10	421 (46 300)	536 (0.19)	451 (109)	0.57	7.59	0.67	2.86
11	425 (54 500)	537 (0.33)	462 (66)	0.60	8.38	0.67	3.35
12	423 (95 500)	512 (0.26)	447 (59), 613 (61)	0.61	9.83	0.65	3.89
13	423 (159 200)	472, 504 (0.37)	437 (65), 569 (70)	0.61	9.81	0.64	3.80
N3				0.62	13.98	0.63	5.50

***Chem. Commun.*, 098 (2005)**

Performance of FL Dye1

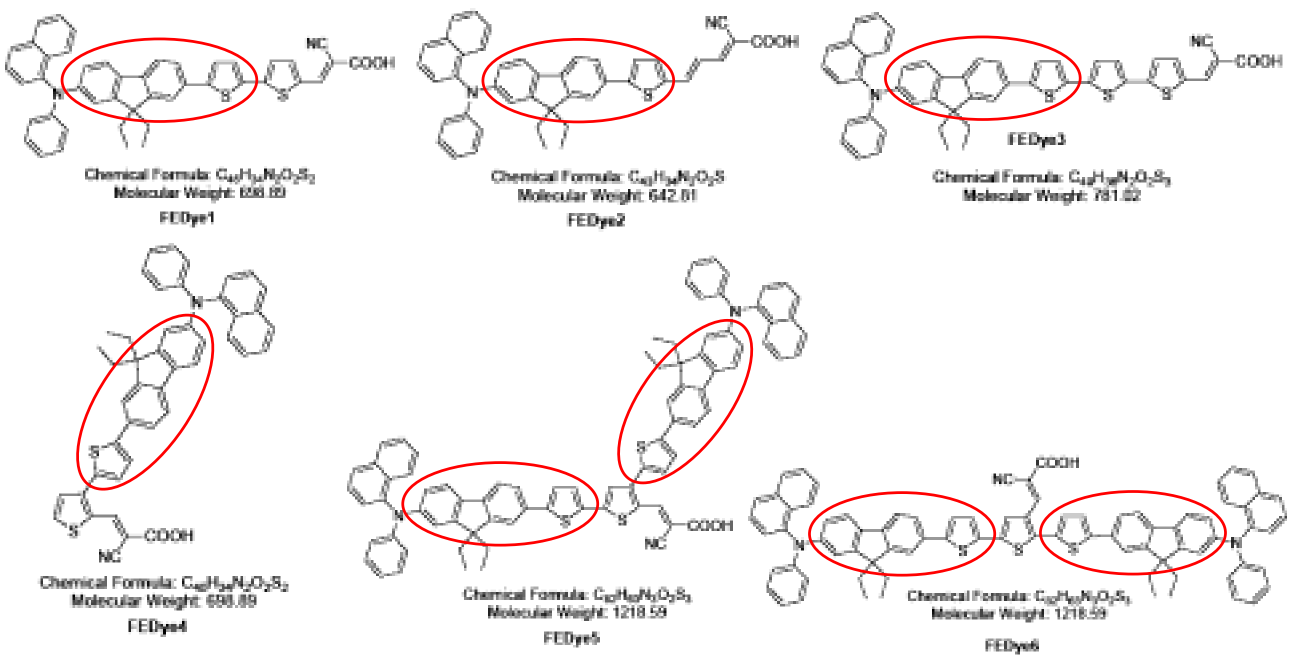




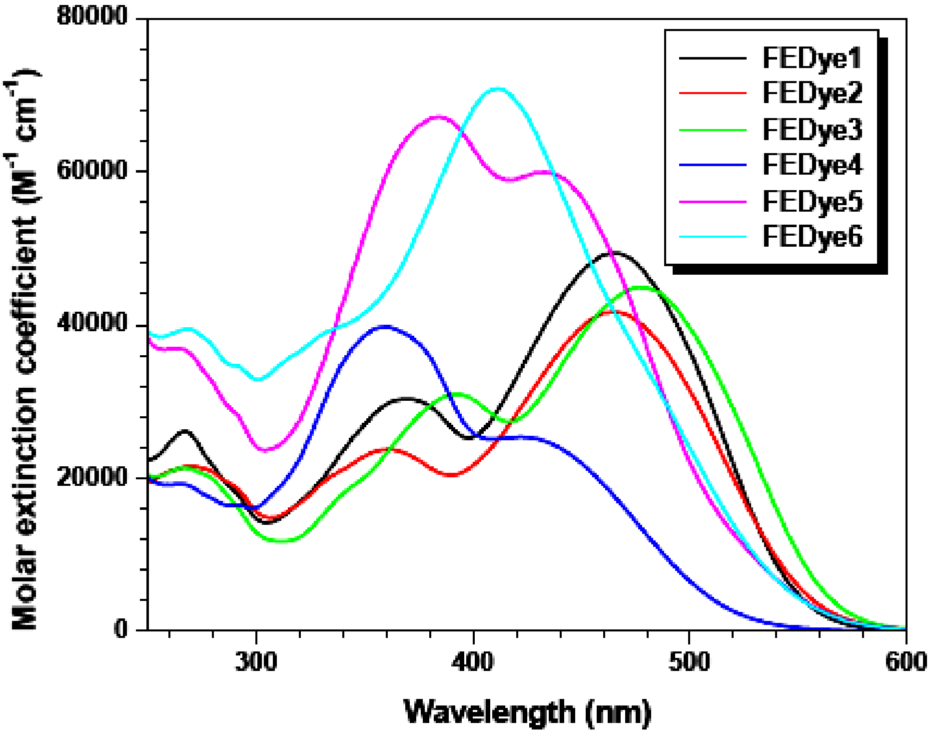
FL Dye1

Samples	Isc(mA)	Jsc(mA/cm²)	Voc(V)	η (%)	FF
FL Dye1	4.24	16.96	0.689	7.19	0.615
N3	4.51	18.04	0.741	7.87	0.589

The structure of FE Dye series



Absorption spectra of FE Dyes

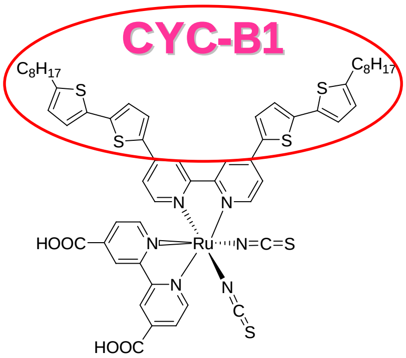


Performances of FE Dyes

Sample	J_{SC}(mA/cm^2)	V_{OC} (V)	η (%)	FF
FE Dye1	16.80	0.639	6.26	0.583
FE Dye2	14.72	0.633	5.86	0.629
FE Dye3	15.56	0.629	5.84	0.596
FE Dye4	8.32	0.587	3.21	0.657
FE Dye5	11.52	0.588	4.00	0.592
FE Dye6	12.76	0.649	4.98	0.601
N3	18.04	0.741	7.87	0.589

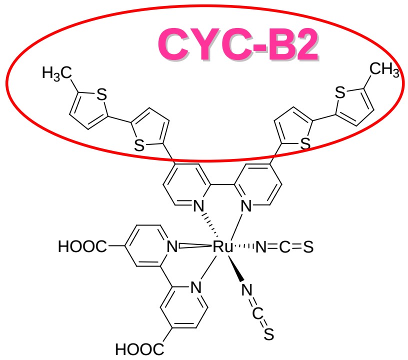
Ruthenium dyes (from Prof. Wu)

CYC-B1



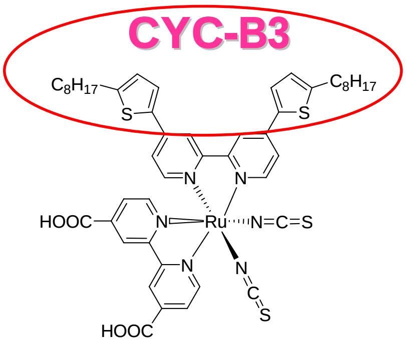
$C_{56}H_{56}N_6O_4RuS_6$
Exact Mass: 1170.1731
Mol. Wt.: 1170.5416

CYC-B2



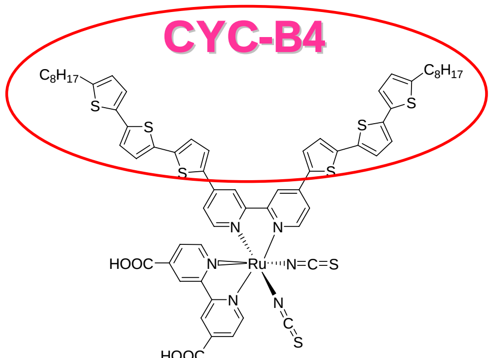
$C_{42}H_{28}N_6O_4RuS_6$
Exact Mass: 973.954
Mol. Wt.: 974.1695

CYC-B3



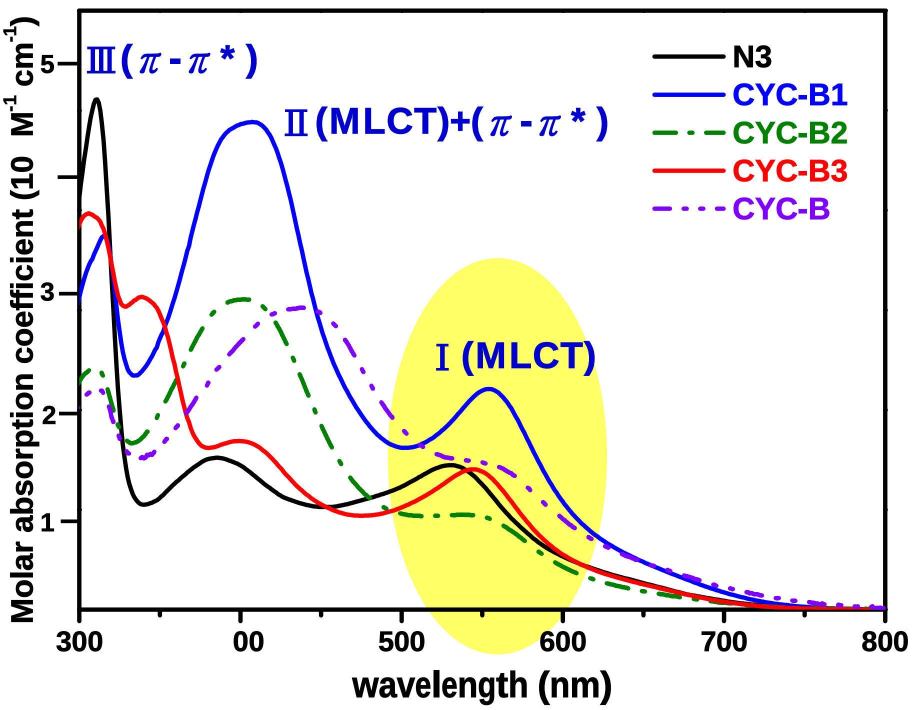
$C_{48}H_{52}N_6O_4RuS_4$
Exact Mass: 1006.1976
Mol. Wt.: 1006.2943

CYC-B4



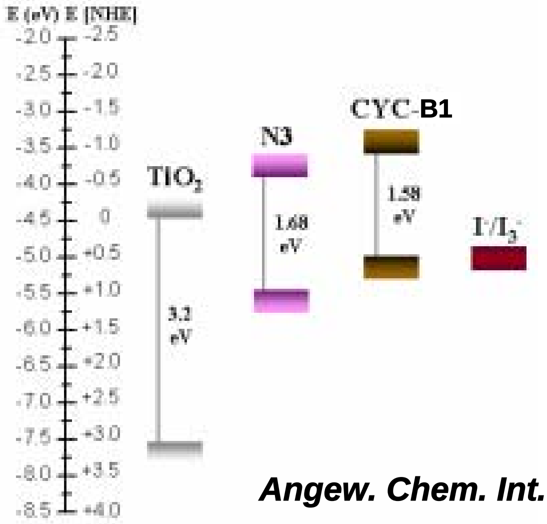
$C_{64}H_{60}N_6O_4RuS_8$
Exact Mass: 1334.1485
Mol. Wt.: 1334.789

Absorption Spectra of CYC Dyes



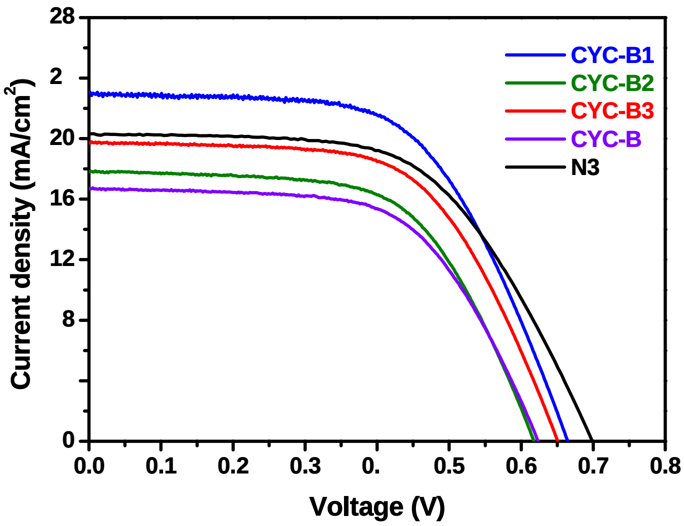
Spectroscopic Properties & Band Structures of CYC B1 & N3

	Absorption coefficient (*10^3 M^{-1} cm^{-1}) π - π *	π - π * (or 4d- π *)	4d- π *	E_g (eV)	HOMO (eV)	LUMO (eV)
N3	51.1 (311)	15.2 (385)	14.5 (530)	1.68	5.52	3.84
CYC-B1	35.8 (312)	46.4 (400)	21.2 (553)	1.58	5.10	3.52



Angew. Chem. Int. Ed., 5, 5822 (2006)

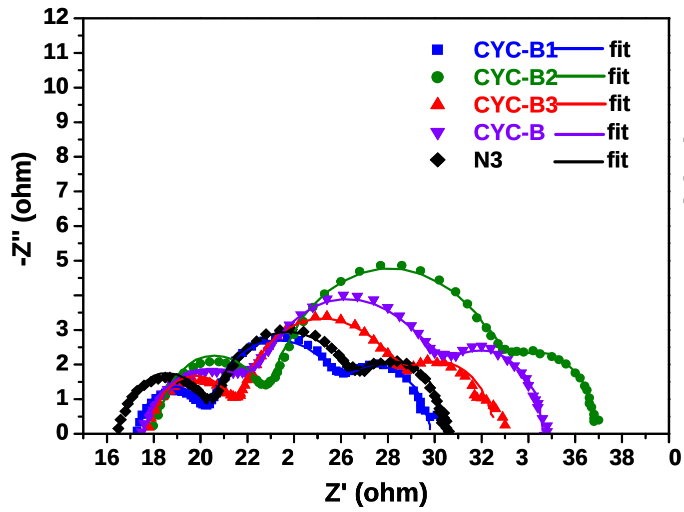
Cell Performance of CYC Dyes

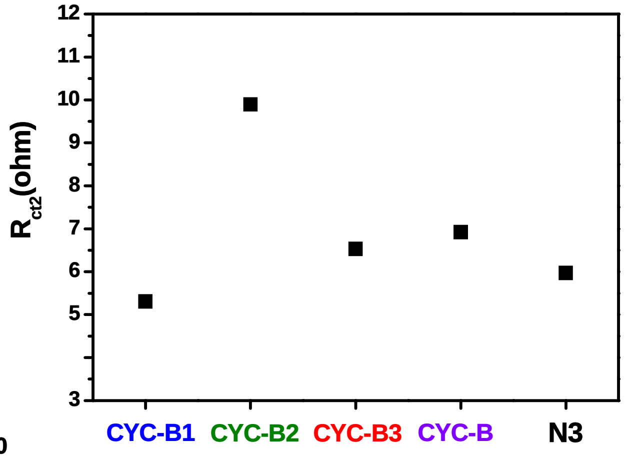


Dye	*I*sc (mA/cm^2)	Voc (V)	FF	η
CYC-B1	22.96	0.66	0.60	9.05
CYC-B2	17.8	0.62	0.61	6.69
CYC-B3	19.76	0.65	0.61	7.78
CYC-B	17.0	0.62	0.61	6.
N3	20. 0	0.71	0.60	8.57

Light intensity: 100 mW/cm^2 FTO: 8 ohm/sq. Area: 0.25 cm^2

AC impedance of N3 and CYC Dyes





System: Glass/FTO/dye-sensitized TiO_2/liquid electrolyte/Pt

Frequency range: 65 kHz~0.01 Hz

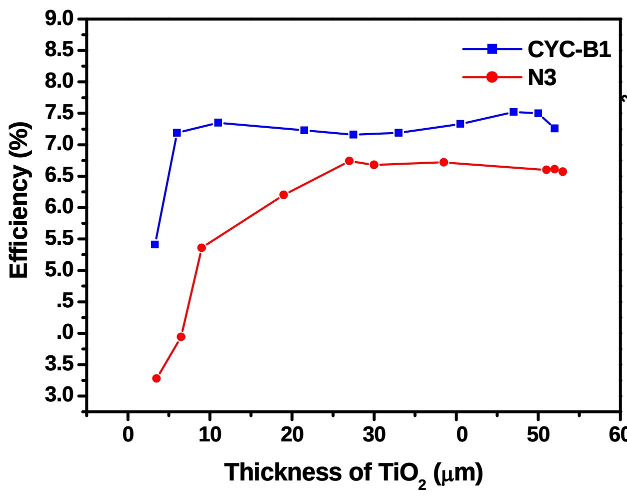
Light intensity: 100 mW/cm^2

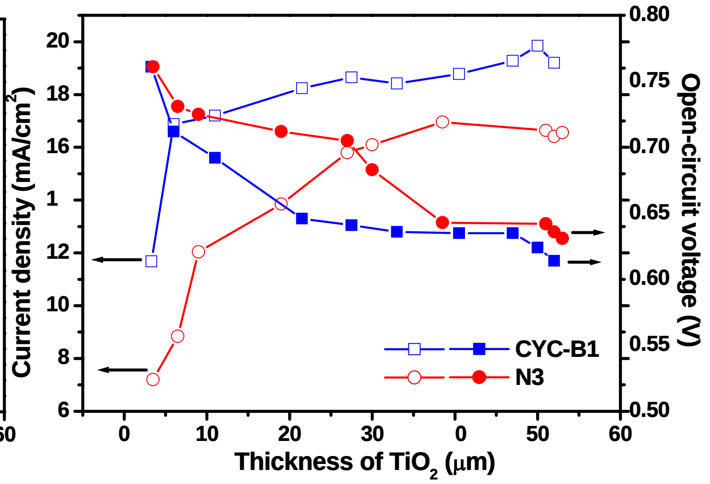
Area: 0.25 cm^2

FTO: 8 ohm/sq.

***Angew. Chem. Int. Ed.*, 5, 5822 (2006)**

TiO_2 Thickness Effect for CYC B1 and N3





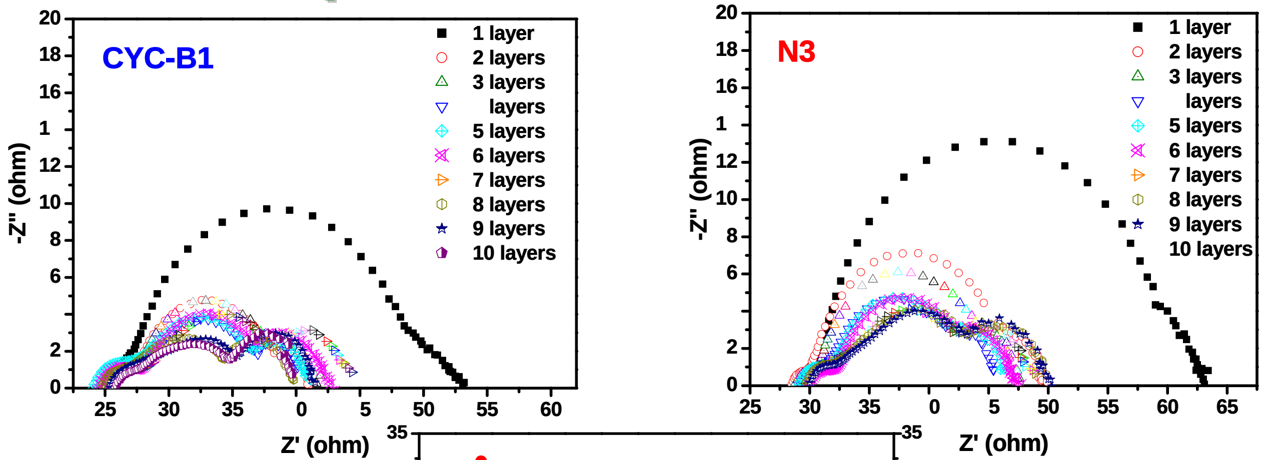
Light intensity: 100 mW/cm^2

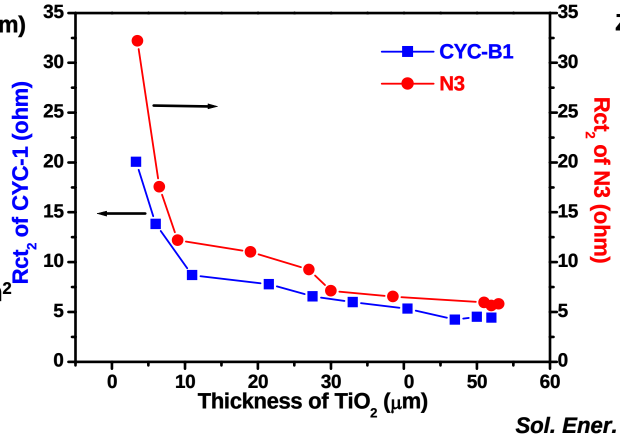
Active area: 0.25 cm^2

TiO_2 paste: 20 μm TiO_2 + 20,000 PEG

***Sol. Ener. Mat. & Sol. Cells* (in press)**

AC Impedance of CYC B1 and N3



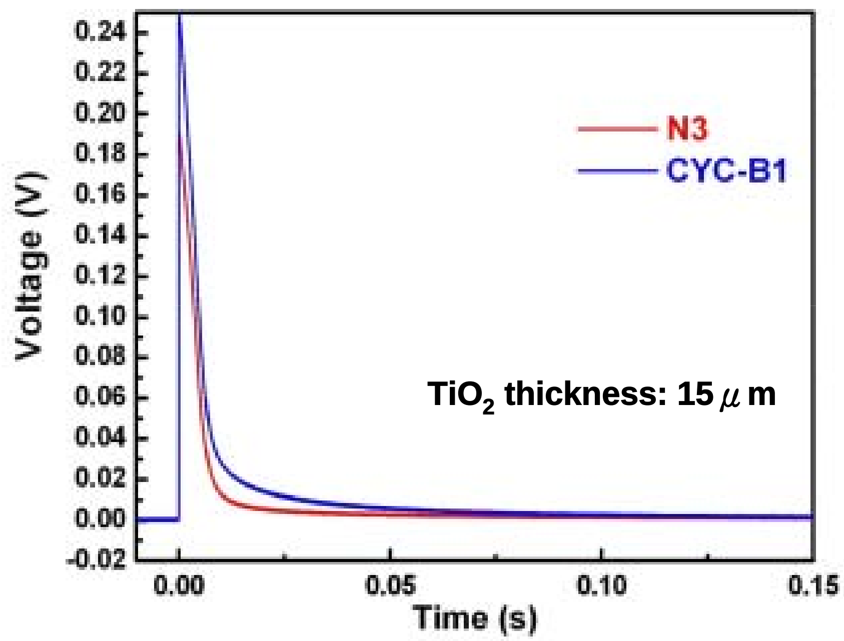


Light intensity: 100 mW/cm²
Area: 0.25 cm²
FTO: 8 ohm/sq.

10/23, 2008

Sol. Ener. Mat. & Sol. Cells **(in press)** 43

Transient Photovoltage



dyes	Electron lifetime, τ_e (ms)
N3	3.96
CYC-B1	.70

10/23, 2008

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Conclusions (1)

1. The transient photovoltage and photocurrent are used to investigate the electron transport and lifetime in dye-sensitized TiO_2 film and help to explain the cell performance.
2. The organic sensitizers that contain diphenylamine donors and cyano acrylic acid acceptors bridged through a phenylene linker and a chromophor ensure charge-transfer and facilitate charge separation.
3. When the phenylene linker (S1 and S2) is replaced by a thiophene unit (S3 and S4), the improvements in donor property and coplanarity causes a red shift in absorption spectrum. However, the quantum efficiency is decreased.

Conclusions (2)

4. The best organic dye tested so far featuring thienylfluorene conjugation, diarylamine donors and 2-cyanoacrylic acid acceptors.
5. Among many novel organic dyes being synthesized at Academia Sinica so far, the best dye (FL Dye1) performs at least 90 % as good as that of N3 in terms of cell efficiency.
6. A new dye CYC-B1 with the highest absorption coefficient known so far for Ru-based photosensitizers. Furthermore, CYC-B1 reported here is a representative of ruthenium complex with high current density and conversion efficiency.
7. It may be possible to find new metal complex sensitizers with higher conversion efficiency by modifying one of the anchoring ligands.

Acknowledgements (1)

- We thank the following researchers for the help in this study

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  Mr. Kun-Mu Lee

  Mr. Jian-Ging Chen

  Mr. Joseph Hwang

  Mr. Chia-Yuan Chen

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