

Innovated Dye Development for DSSC Application

Everlight Chemicals Industrial Corporation

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2009/06/05



EAS4

Fourth East Asia Symposium on Functional Dyes and Advanced Materials

June 2-5, 2009 Osaka, Japan

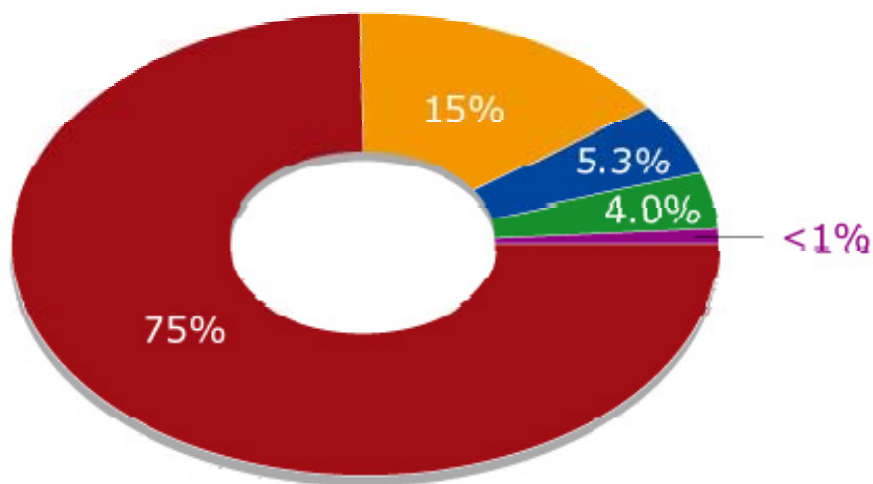
Outline

- **Everlight Group in Brief**
- **Innovated DSSC Dye Development**
 - Organic dye series A
 - Organic dye series B
 - Organic dye series C
 - Novel Ru-Complex
- **Future Concern on DSSC**

Everlight Group in Brief

- Founded in 1972
- 1,200 Employees in world-wide
- Revenue: US \$190 M (2008)

Invests **4%** of Revenue on R&D



- 色料事業 Color Chemicals
- 特化事業 Specialty Chemicals
- 電化事業 Electronic Chemicals
- 醫藥事業 Pharmaceuticals
- 奈米事業 Nano-Materials

PLANT FACILITIES



Plant 1
1976
TaoYuan
大園



Plant 2
1987
TaoYuan
觀音



Plant 3
1992
Taoyuan
觀音



SuZhou
Everlight
2006
China 蘇州SIP



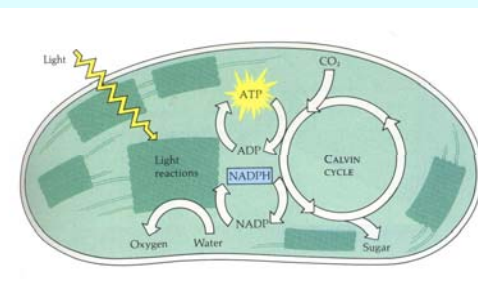
Trend
Tone
Imaging
2005

From Bionics to DSSC

Can laptops run on spinach ?



Spinach photosynthetic power can create electricity.

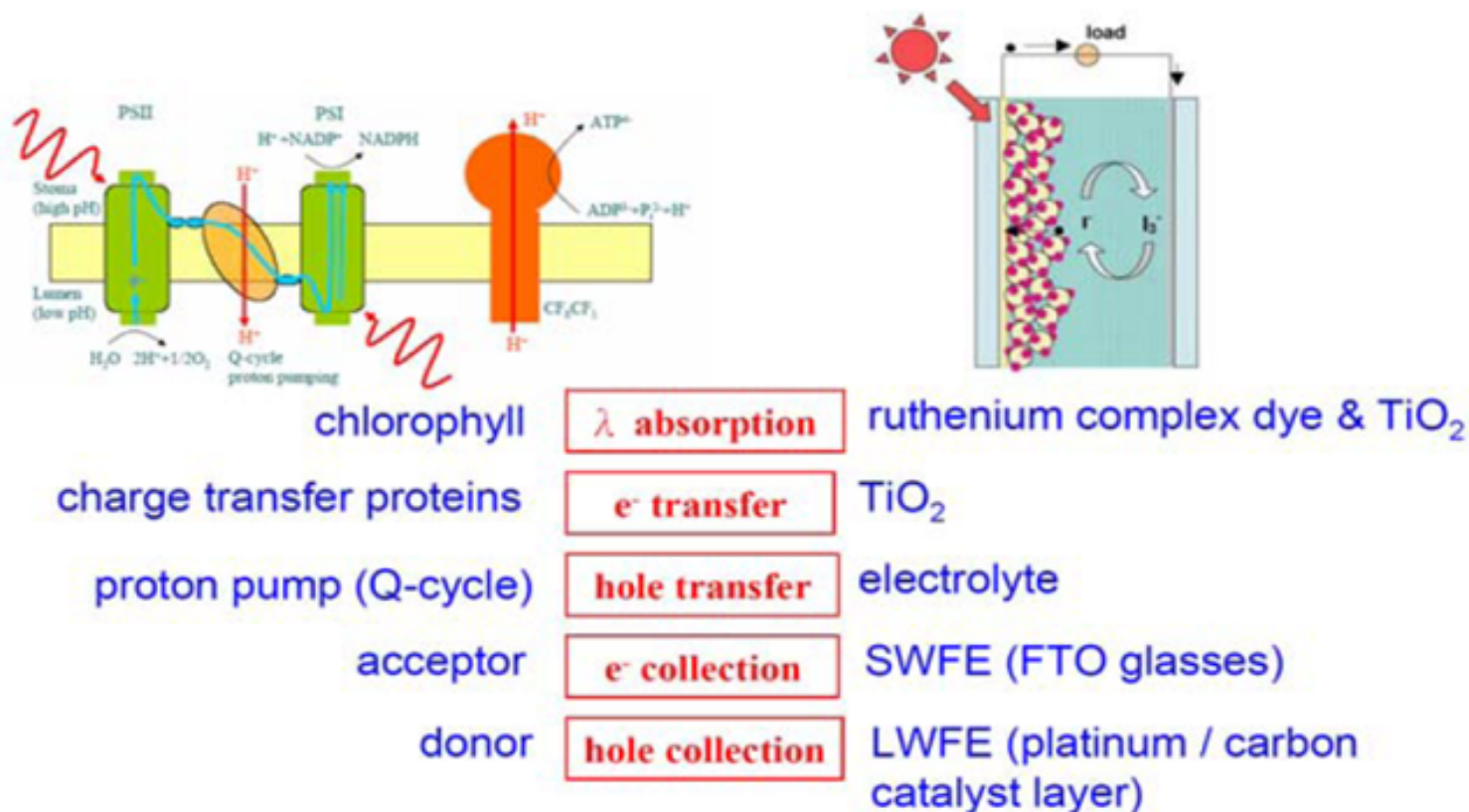


Integration of Photosynthetic Protein Molecular Complexes in Solid-State Electronic Devices

Nanoletters 2004, vol 4, pp 1079 - 1083

Photosynthesis and Biomimicry

Artificial photosynthesis — Grätzel cell



Source : web.ncue.edu.tw/~ccourse/data/Solar%20Cell.pdf

Classification of Dye Sensitizers

- Metal-free Organic Dye :

- ↑ High ϵ , Bright(colors), Flexibility of molecular design

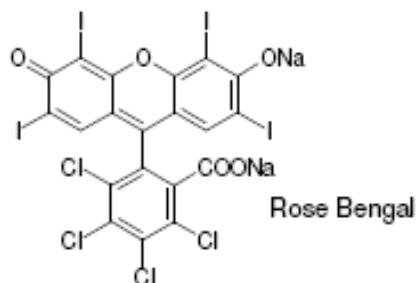
- ↓ Low Voc, Less durability

- Metal Complex Dye :

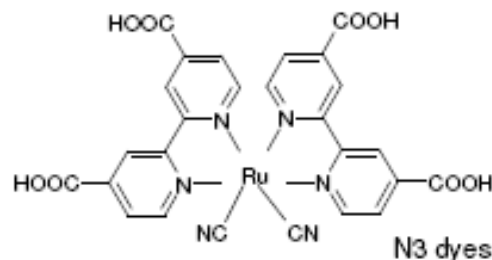
- ↑ Stability, Wide range absorption

- ↓ Noble rare metal, Less flexibility of molecular design

Tsubomura et al., *Nature*, Vol.261, 402(1976)
ZnO + Rose Bengal

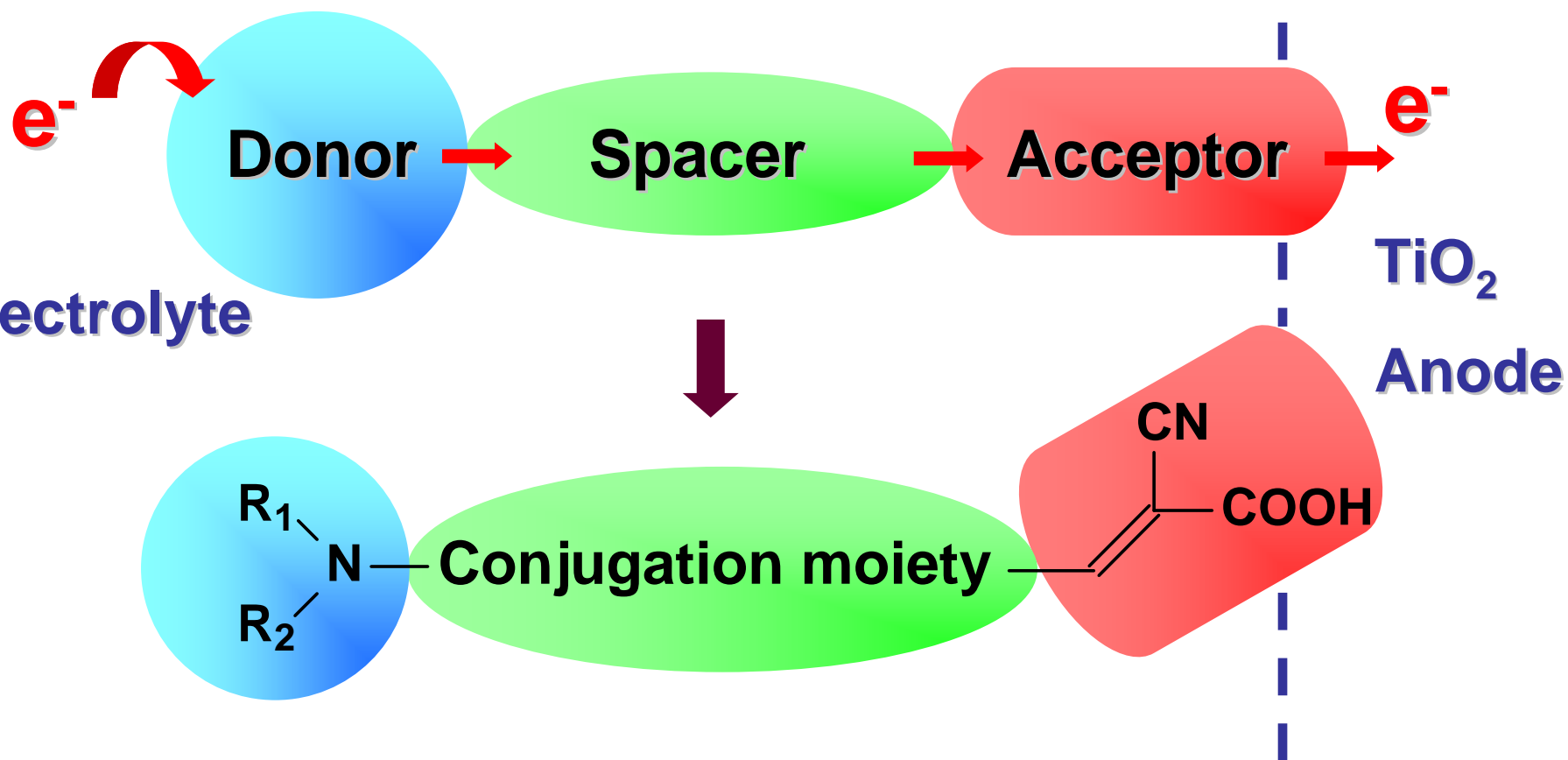


O'Regan et. al., *Nature*, Vol.353, 737(1991)
TiO₂ + Ru Complex

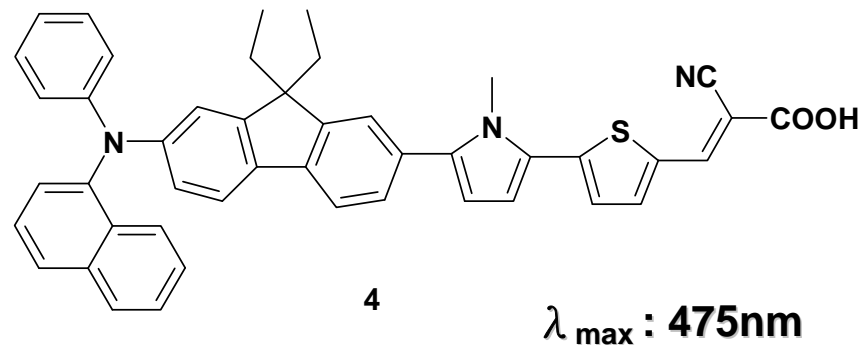
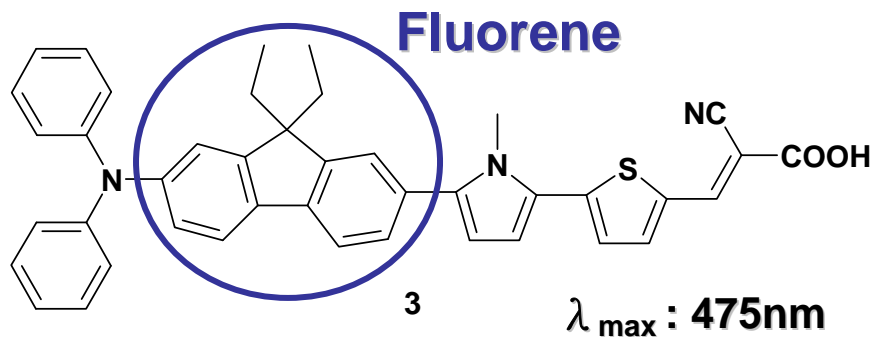
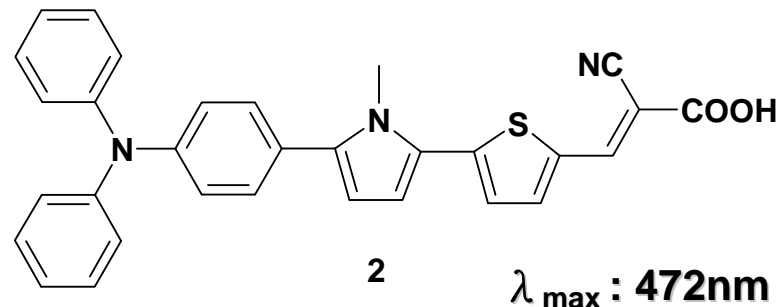
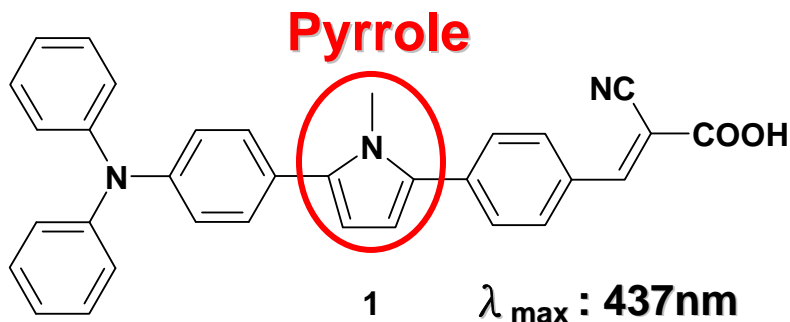


Organic Dye Designed Model

D - π - *A* System



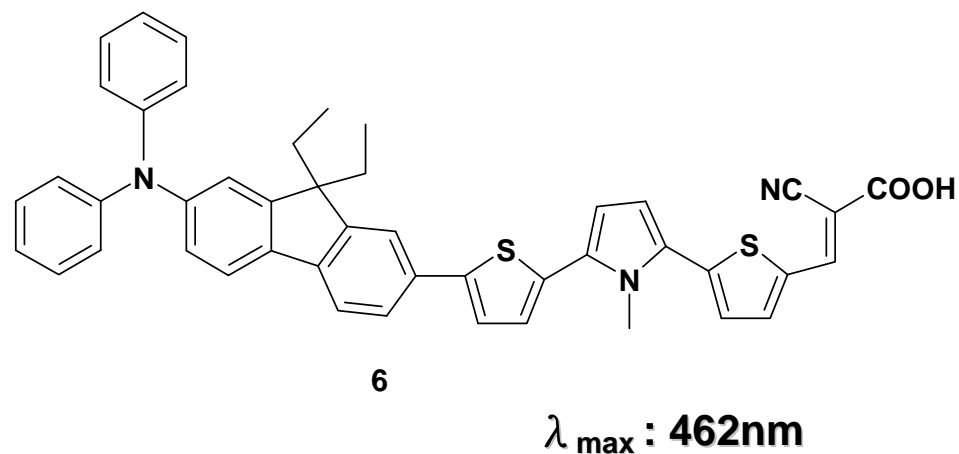
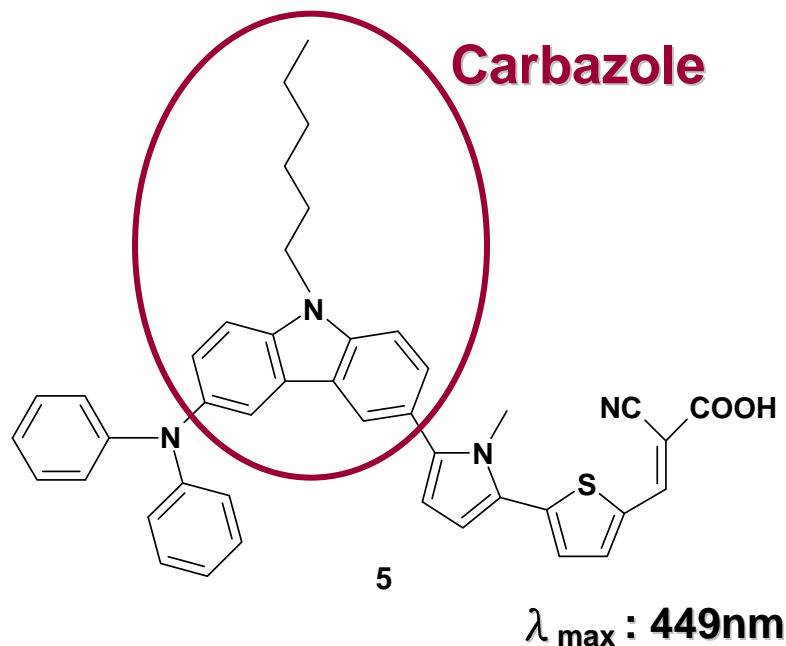
Model A series : Pyrrole-based Spacers



- * Pyrrole's electron-rich property, inducing good charge transfer transition.
- * Fluorene has good electron conductivity and stability.

Pyrrole-based Spacers (cont.)

Carbazole



* Carbazole enable poor electron transition because it's non-linear structure.

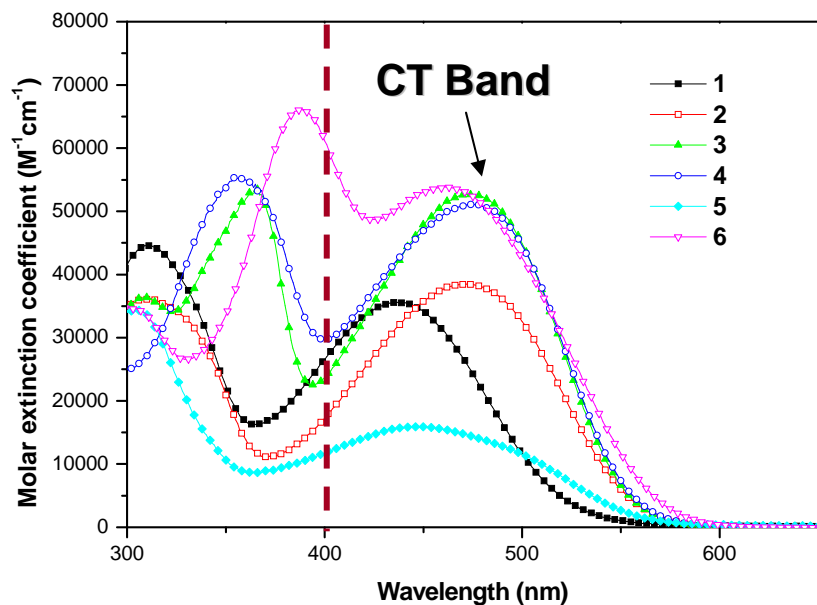
Performance of Model A series Dyes

Dye	Voc (V)	Jsc (mA/cm ²)	FF	η (%)
1	0.60	13.47	0.59	4.77
2	0.57	14.20	0.60	4.79
3	0.61	18.14	0.56	6.16
4	0.64	16.79	0.58	6.18
5	0.58	12.93	0.64	4.80
6	0.60	13.54	0.64	5.25
N719	0.72	16.08	0.63	7.19

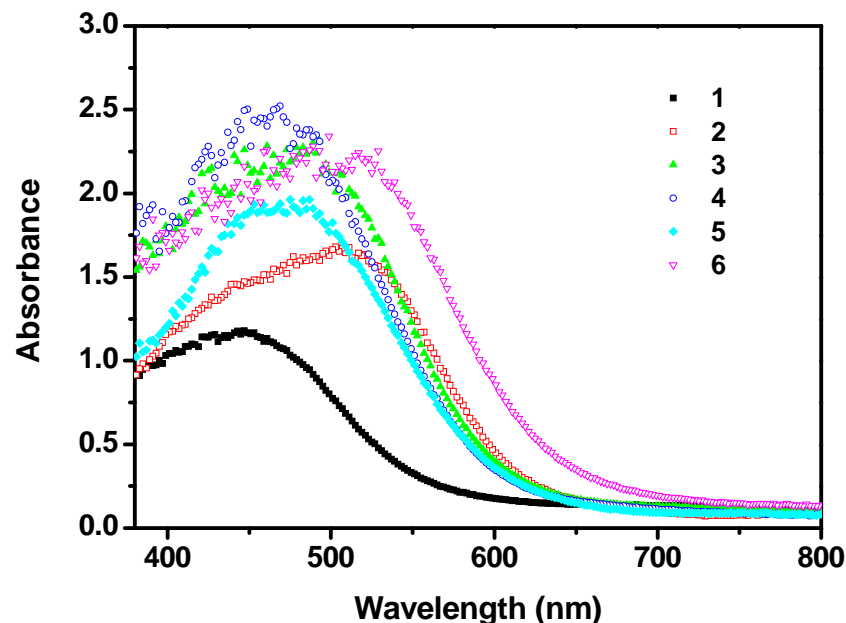
Test conditions:

1. Active area : 0.25 cm²
2. Light source : 100 mW/cm²
3. TiO₂ thickness : 15 μ m
4. 3X10⁻⁴ M in THF
5. I⁻/I₃⁻ Liquid electrolyte

Optical Properties



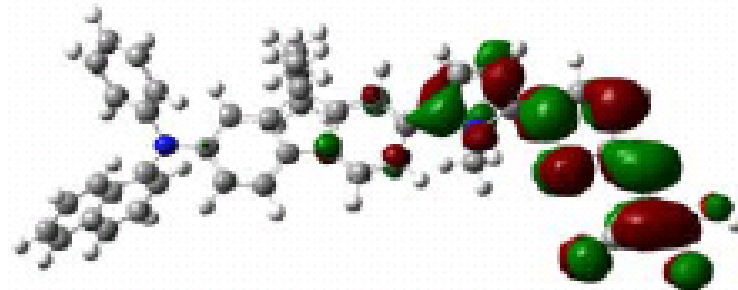
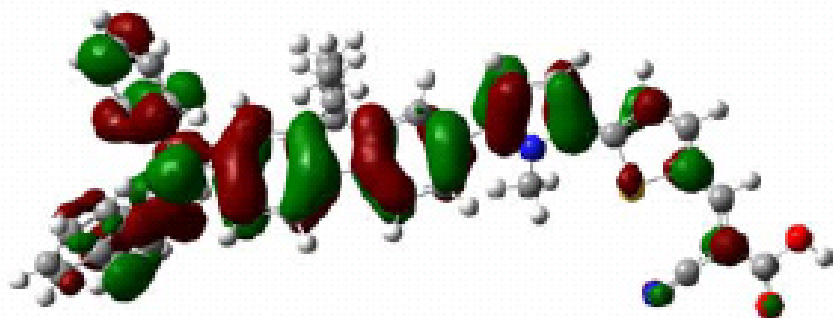
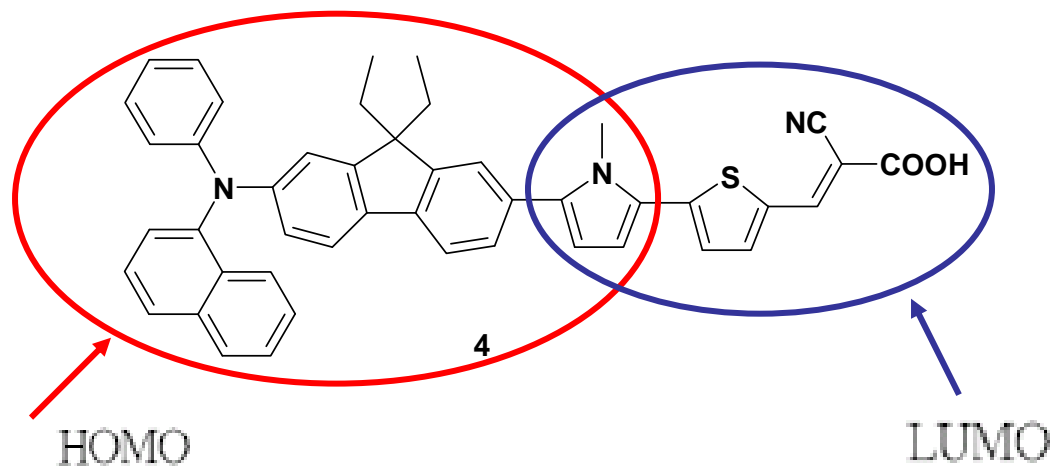
**Absorption spectra of the dyes
recorded in THF**



**UV-vis curves of the dyes on
 TiO_2 electrode**

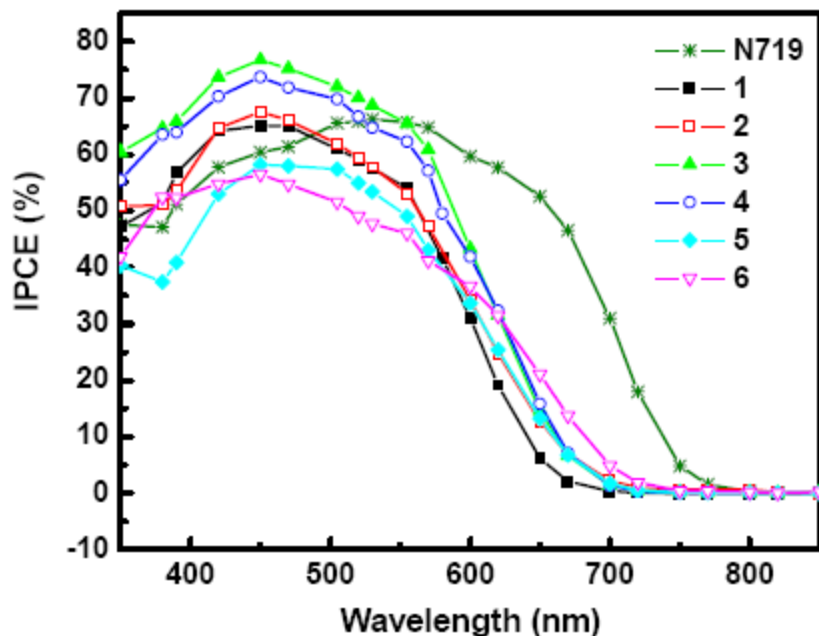
*** Compound 3 , 4 has strong absorption at CT band ,
so they have more better efficiency than other dyes.**

Selected Frontier Orbitals

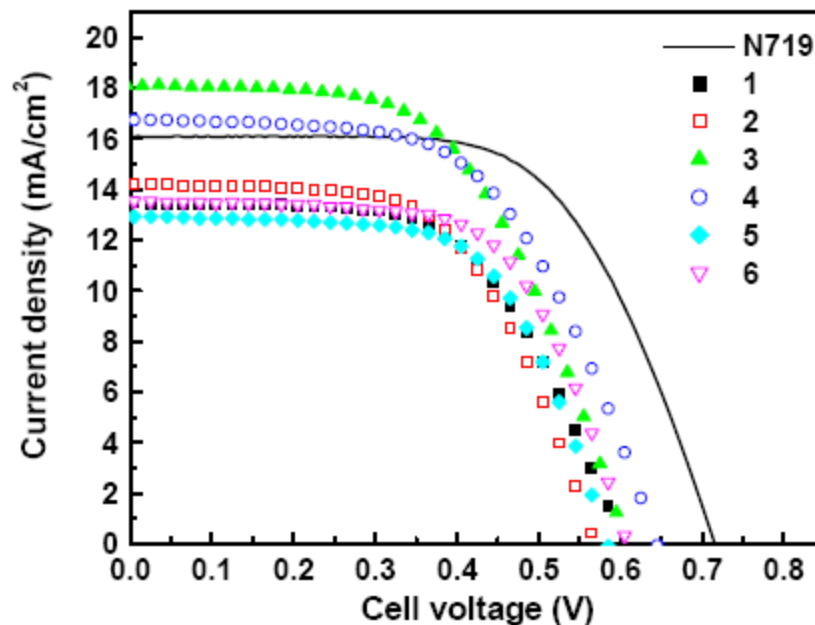


* Excellent charge-shift effect for compound 4 .

Photovoltaic Measurement



IPCE plots for DSSCs



J-V curves of DSSCs based on the dyes

*** Compound 3 , 4 has excellent quantum efficiency (IPCE)**

Conclusion of Model A series Dyes

Dye	Voc (V)	Jsc (mA/cm ²)	FF	η (%)
1	0.60	13.47	0.59	4.77
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N719	0.72	16.08	0.63	7.19

Test conditions:

1. Active area : 0.25 cm²
2. Light source : 100 mW/cm²
3. TiO₂ thickness : 15 μ m
4. 3X10⁻⁴ M in THF
5. I⁻/I₃⁻ Liquid electrolyte

* Pyrrole moiety have larger dihedral angle

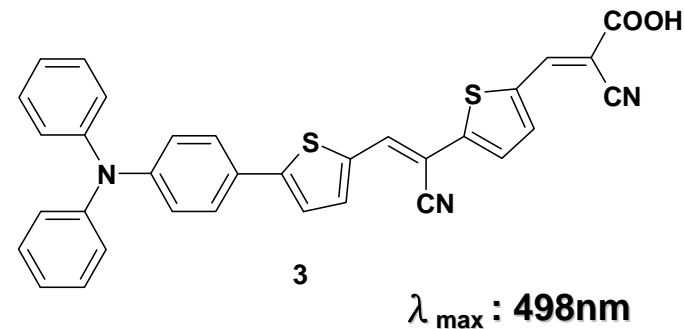
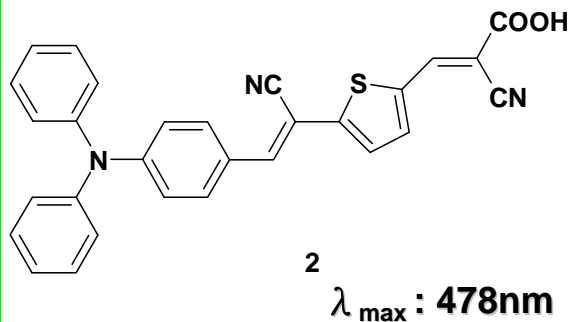
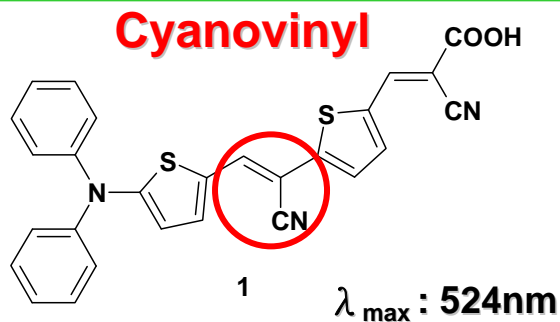
* More efficient light-harvesting capabilities for 3, 4

* Large oscillator strength f for 3,4 (HOMO \rightarrow LUMO transition)

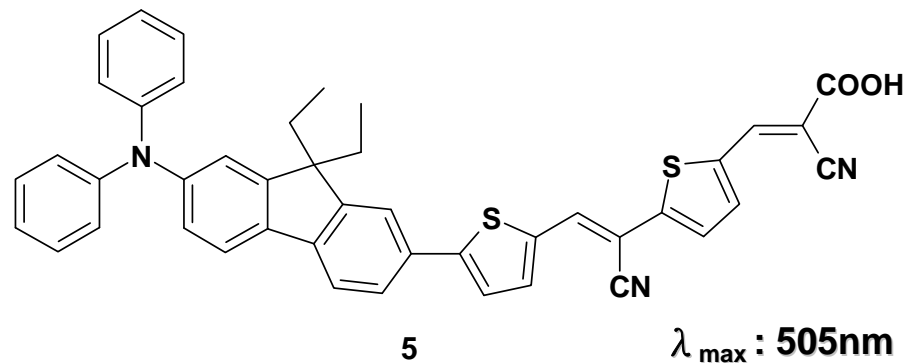
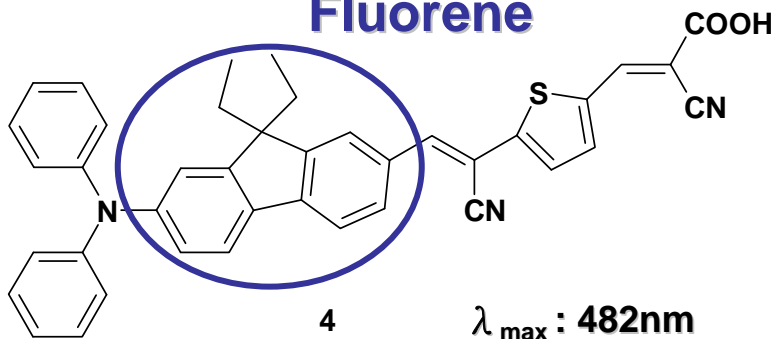
* The efficiencies are 66-- 86% of the standard cell from N719

Model B series : Cyanovinyl Entity Spacers

Cyanovinyl

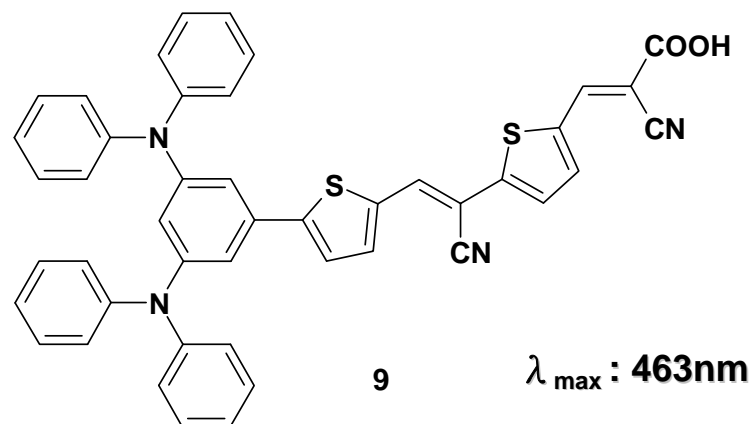
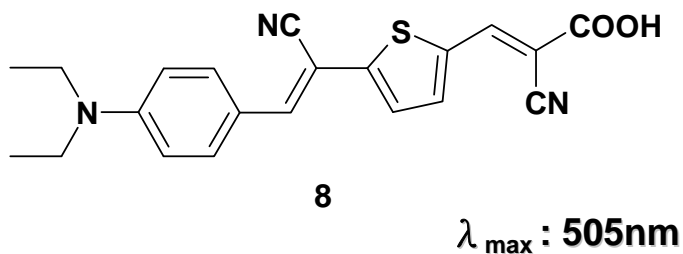
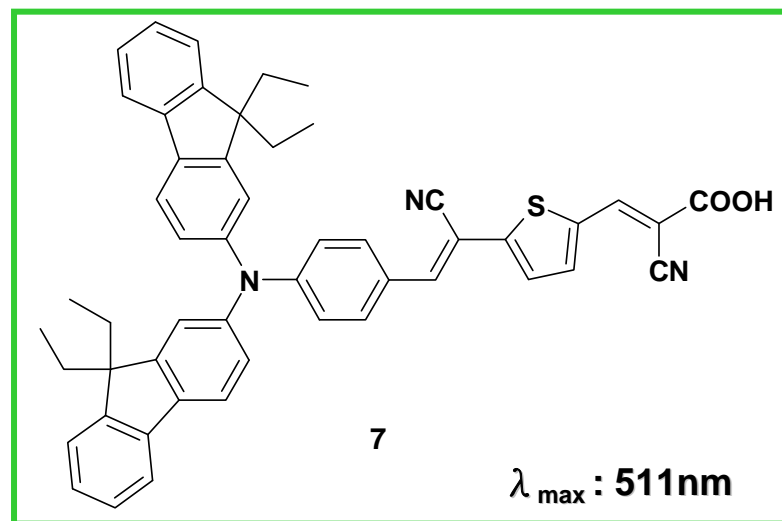
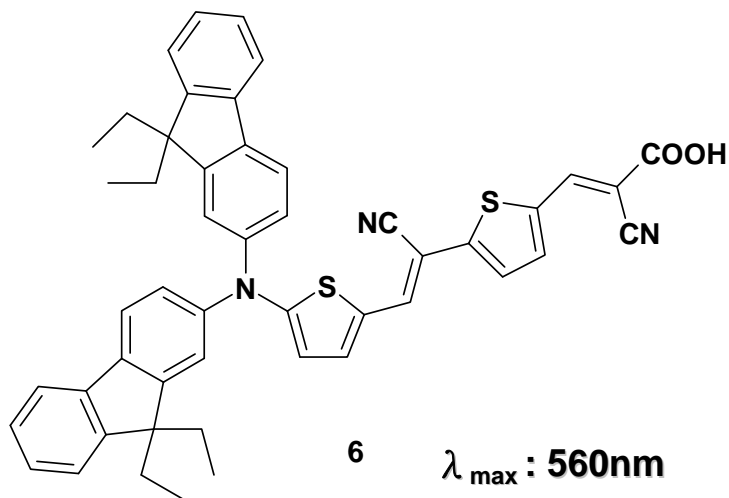


Fluorene



* Cyanovinyl : good electron-pull and charge-trapping effect

Cyanovinyl Entity Spacers (cont.)



Performance of Model B series Dyes

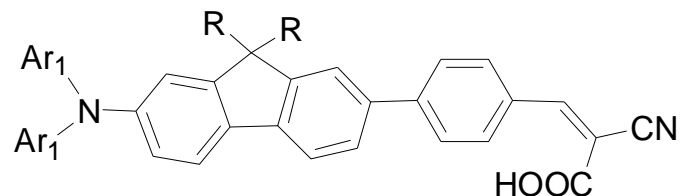
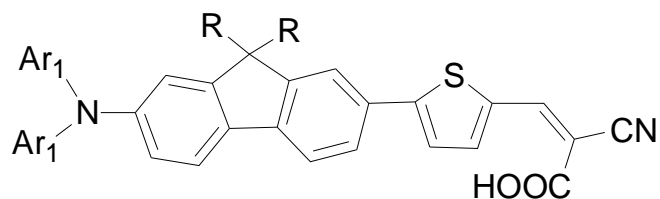
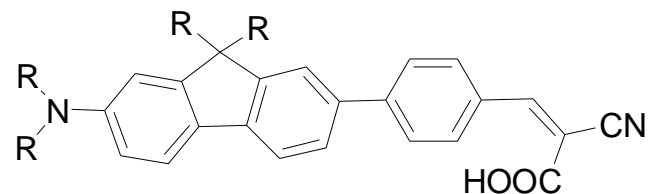
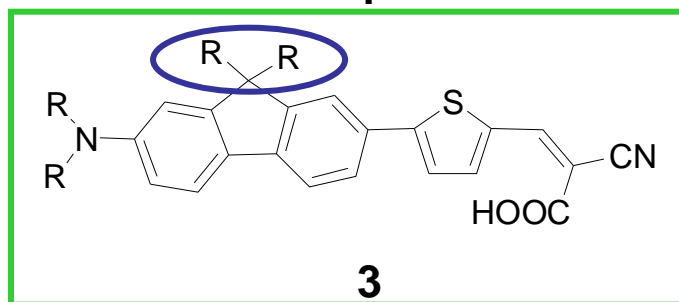
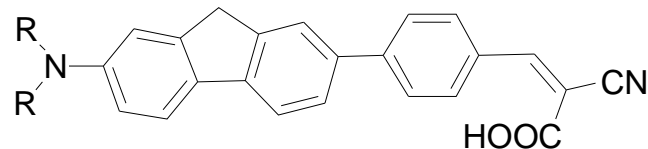
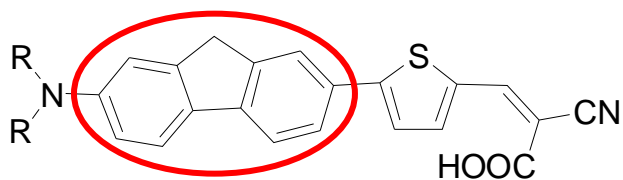
Dye	Voc (V)	Jsc (mA/cm ²)	FF	η (%)
1	0.57	13.43	0.64	4.92
2	0.59	11.40	0.64	4.28
3	0.56	11.43	0.65	4.15
4	0.58	11.00	0.69	4.34
5	0.55	9.56	0.66	3.48
6	0.58	11.96	0.65	4.51
7	0.61	12.48	0.64	4.81
8	0.56	11.56	0.62	4.04
9	0.55	9.24	0.68	3.48
N719	0.70	16.21	0.63	7.16

Test conditions:

1. Active area : 0.25 cm²
2. Light source : 100 mW/cm²
3. TiO₂ thickness : 15 μ m
4. 3X10⁻⁴ M in THF
5. I⁻/I₃⁻ Liquid electrolyte

* The efficiencies are 45-- 70% of the standard cell from N719

Model Series C : Fluorene-based Spacers



R : alkyl group

Ar₁ : aryl group

Performance of Model series C Dyes

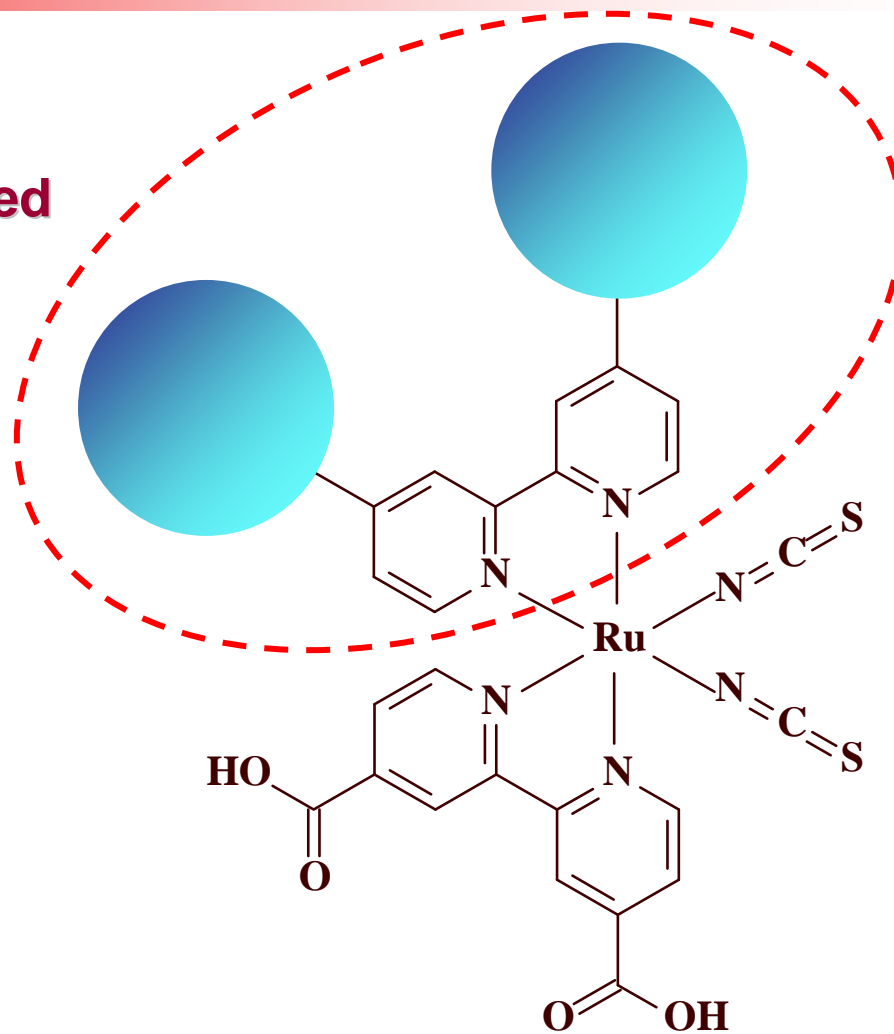
Dye	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
1	6.28	0.61	0.66	2.54
2	8.40	0.60	0.63	3.15
3	13.16	0.69	0.64	5.82
4	11.00	0.68	0.58	4.68
5	10.28	0.69	0.65	4.90
6	10.30	0.70	0.63	4.58
N719	14.12	0.74	0.65	6.81

- Test conditions:
1. Active area : 0.25 cm²
 2. Light source : 100 mW/cm²
 3. TiO₂ thickness : 15 μ m
 4. 3X10⁻⁴ M in THF
 5. I⁻/I₃⁻ Liquid electrolyte

* The efficiencies are 37-- 85% of the standard cell from N719
(Patent filing on 2008)

Novel Ruthenium dye

- * Extend conjugated chain
- * LUMO energy



Performance of New Ruthenium Dyes

Dye	Voc (V)	Jsc (mA/cm ²)	FF	η (%)
ECIC1	0.74	7.44	0.63	3.42
ECIC2	0.75	8.00	0.62	3.74
ECIC3	0.78	8.22	0.64	4.09
N719	0.76	7.36	0.61	3.38

Test conditions:

1. Active area : 0.25 cm²
2. Light source : 100 mW/cm²
3. TiO₂ thickness : 6 μ m
4. 3X10⁻⁴ M in CH₃CN/ t-BuOH
5. I⁻/I₃⁻ Liquid electrolyte

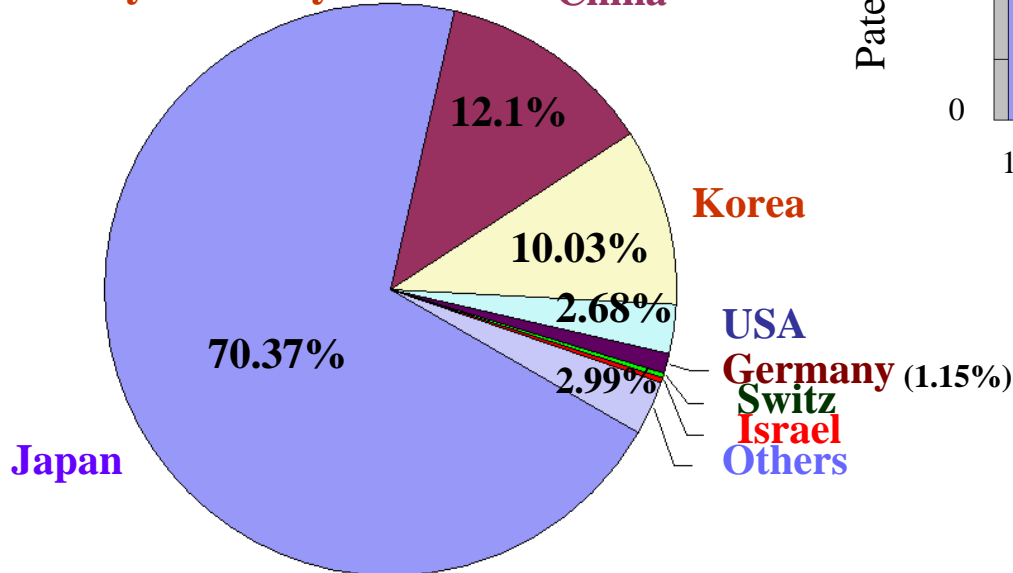
* The efficiencies are 101– 121% of the standard cell from N719
(2 patents filing on 2008)

The Global R&D strength in DSSC

By Institute/Company

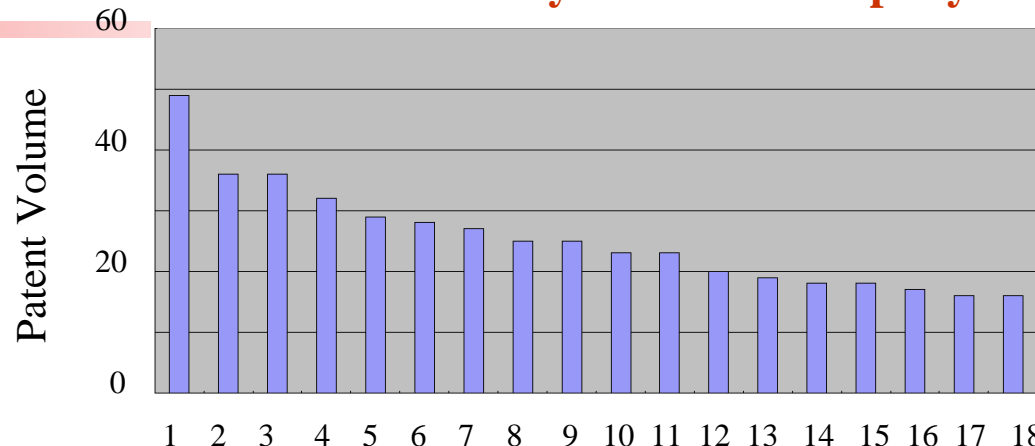
Patent Analysis

By Country



ECIC has 5 patents are filing.

Data analysis : 2009/04 by ECIC



Rank	公司名稱	件數
1	Fujikura Ltd, Japan	49
2	Fuji Photo Film Co Ltd, Japan	36
3	Sharp Corp, Japan	36
4	NGK Spark Plug Co Ltd, Japan	32
5	Mitsubishi Paper Mills Ltd, Japan	29
6	Sekisui Jushi Co Ltd, Japan	28
7	S Korea	27
8	Kyocera Corp, Japan	25
9	Nippon Oil Corporation, Japan	25
10	Bridgestone Corp, Japan	23
11	TDK Corporation, Japan	23
12	Electronics and Telecommunications Research Institute, S Korea	20
13	Toyo Ink Mfg Co Ltd, Japan	19
14	Konica Minolta Business Technologies Inc, Japan	18
15	Konica Minolta Holdings Inc, Japan	18
16	Sony Corp, Japan	17
17	Nippon Kayaku Co Ltd, Japan	16
18	Teijin Du Pont Film Inc, Japan	16

Future concern on DSC

--world -wide cooperation and connection





Thank you!!

Source : www.signallake.com/innovation/DNoceraMITClubOfNY111208.pdf