The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization
IAEA International Atomic Energy Agency

2269-31

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Recent progress in dye-sensitized solar cells - Part II

Jun-Ho YUM
Swiss Federal Institute of Technology, EPFL, Lausanne Switzerland

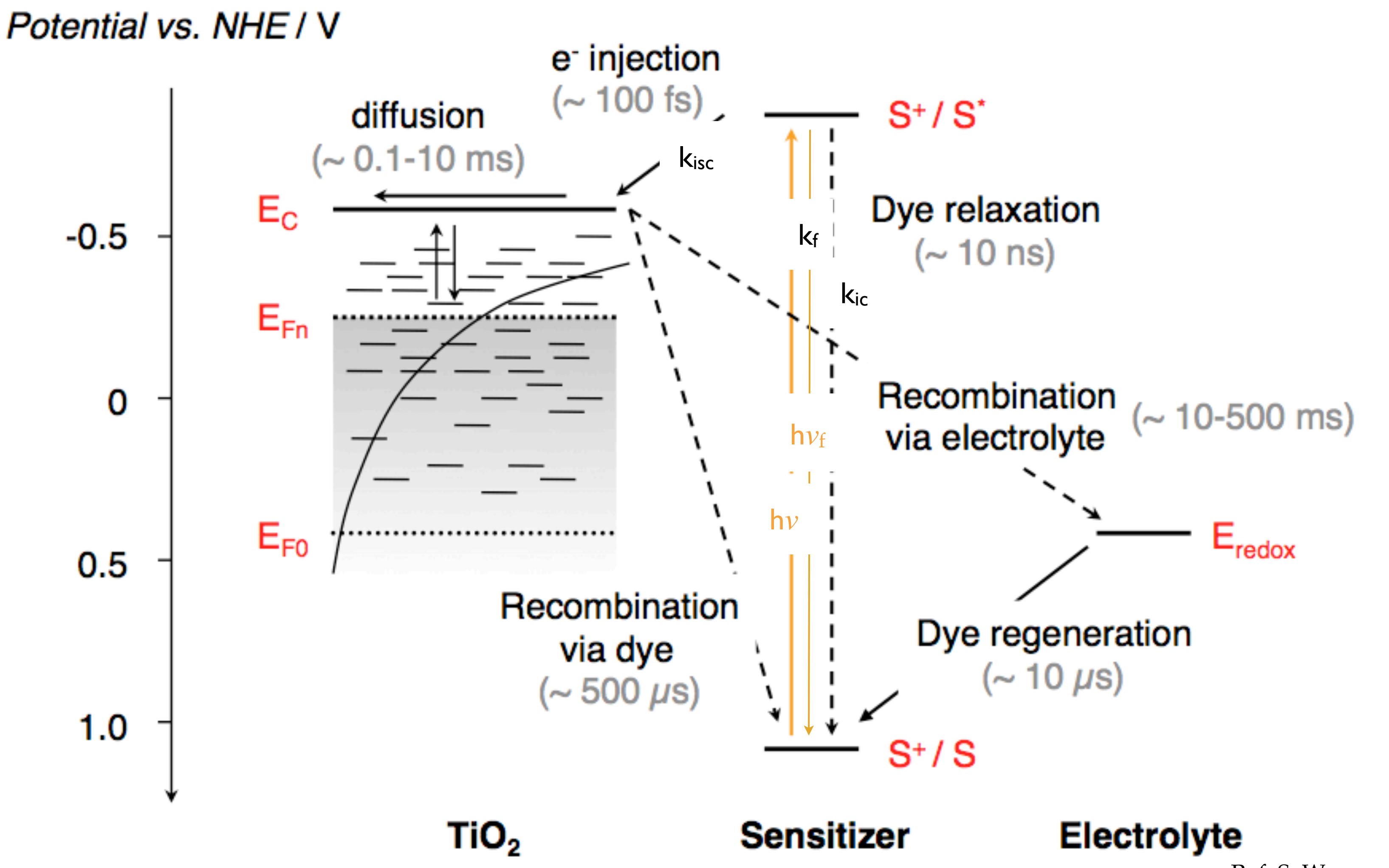
Recent Progress in Dye-Sensitized Solar Cells
Part II

Jun-Ho Yum
junho.yum@epfl.ch
Swiss Federal Institute of Technology Lausanne

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Workshop on New Materials for Renewable Energy, October 20, 2011

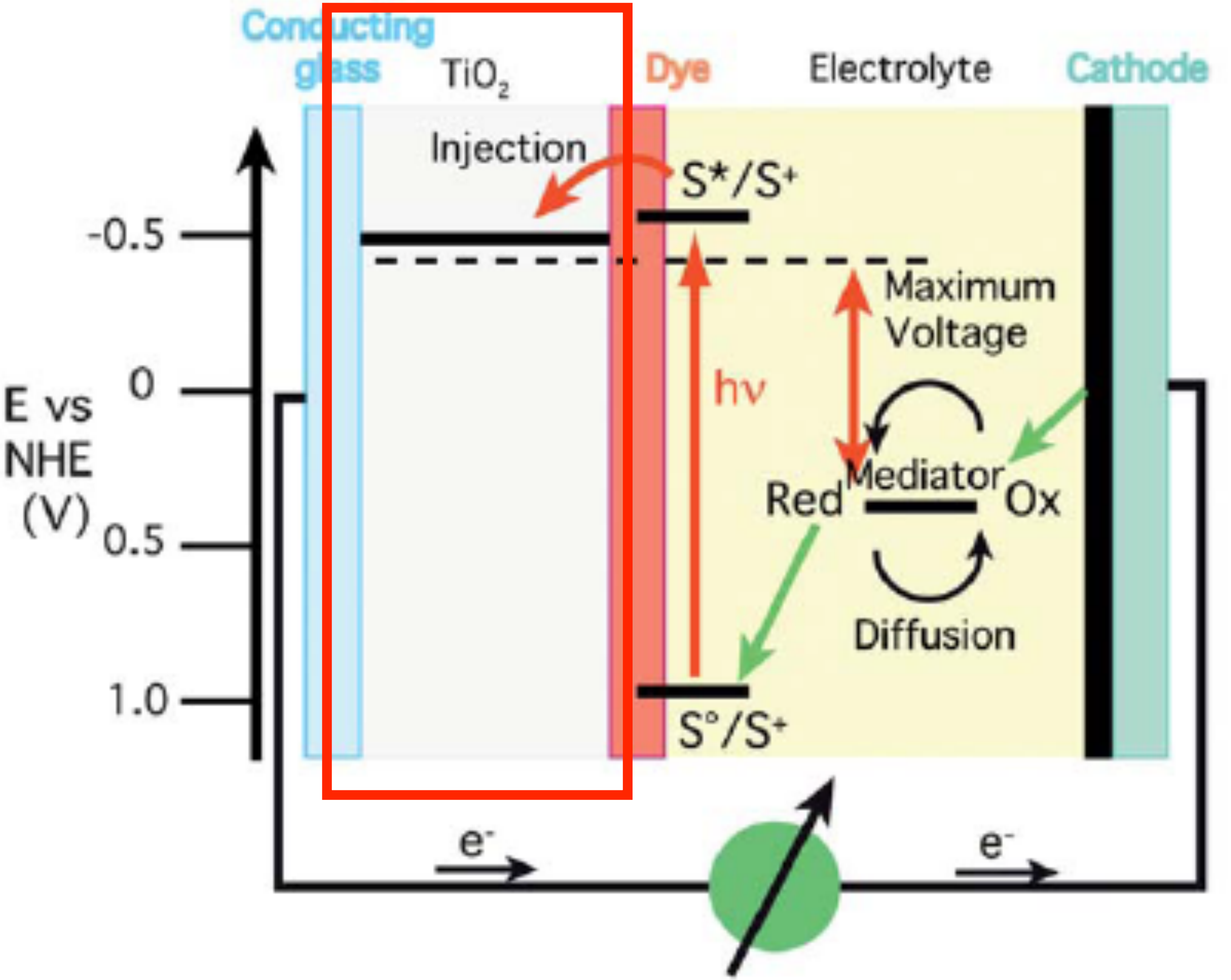
Summary of the key processes involved in the regenerative cycle taking place in a dye-sensitized solar cell under illumination.



Ref: S. Wenger

Ongoing and Future Research

- Advanced meso-structures
- New sensitizers
- New redox mediators
- New counter electrodes


Conducting glass
TiO2
Dye
Electrolyte
Cathode
Injection
S*/S+
-0.5
Maximum Voltage
hν
E vs NHE (V)
0
Mediator
Red
Ox
0.5
Diffusion
1.0
S°/S+
e-
e-

IPCE (EQE) $= \eta_{abs} \Phi_{cg} \eta_{coll}$

η_{ab}: light harvesting efficiency

Φ_{cg}: quantum yield of charge carrier generation

$\Phi_{cg} = \Phi_{\text{injection}} \Phi_{\text{dye regeneration}}$

η_{coll} = efficiency of charge carrier collection

$$\eta_{ab}(LHE) = 1 - 10^{-A} = 1 - 10^{-\sigma\Gamma}$$

σ is the absorption cross section (cm^2/mol) = ε (the molar extinction coefficient $M^{-1}cm^{-1}$) x 1000 (cm^3/L),
Γ is the dye loading per projected surface area of the film,

High ε *and/or* Γ is needed for high LHE.

$$\eta_{ab}(LHE) = 1 - 10^{-A} = 1 - 10^{-\sigma\Gamma}$$

Surface coverage of 10^{-10} mol/cm^2

$\varepsilon = 10^4$

$A = 0.001$,

LHE = 0.23%

$\varepsilon = 10^5$

$A = 0.01$,

LHE = 2.3%

$\Gamma = 10^{-7}$ mol/cm^2

$\varepsilon = 10^4$

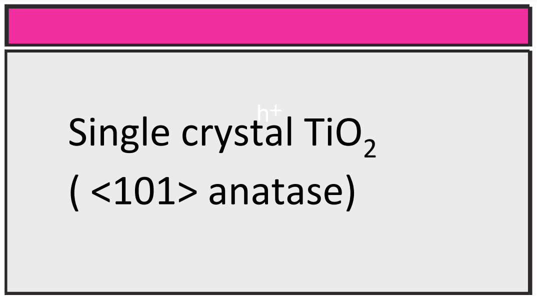
$A = 1$,

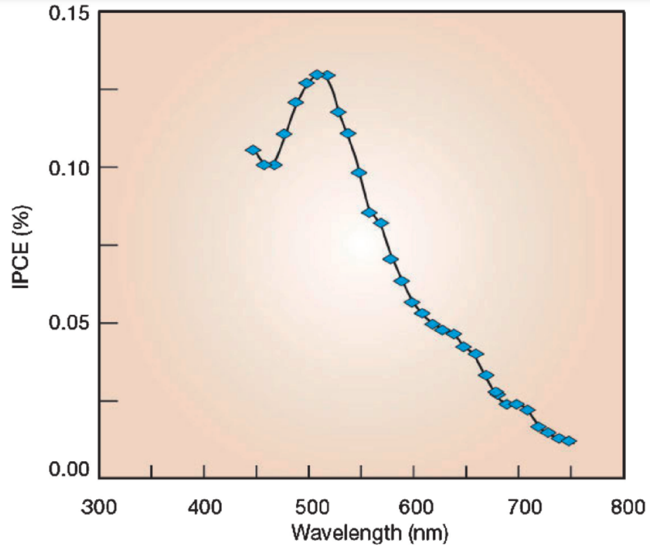
LHE = 90%

Mesoscopic structure improves photocurrent output > 1000 times

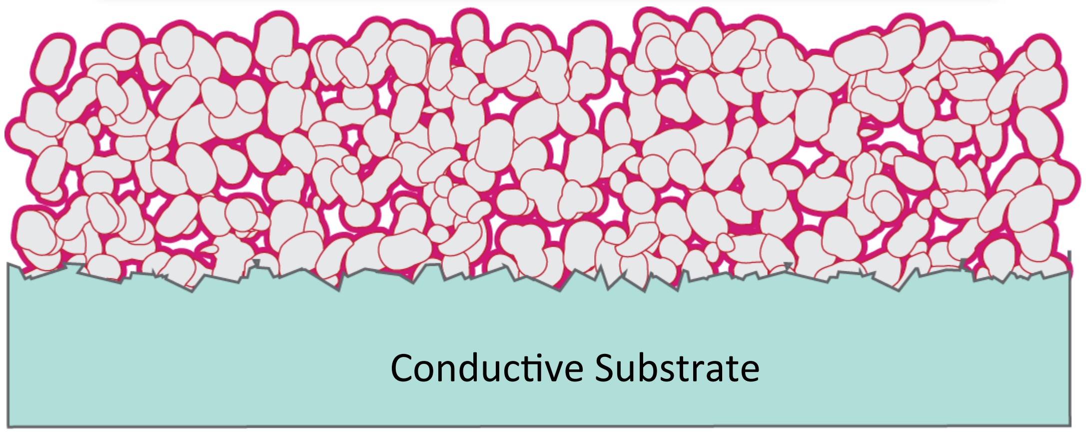
Incident photon to current conversion efficiency (IPCE) increases from 0.12 to 90 %

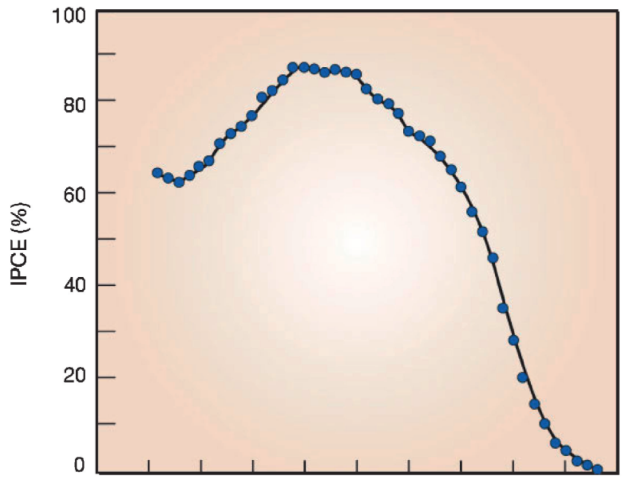
Dye monolayer on flat surface





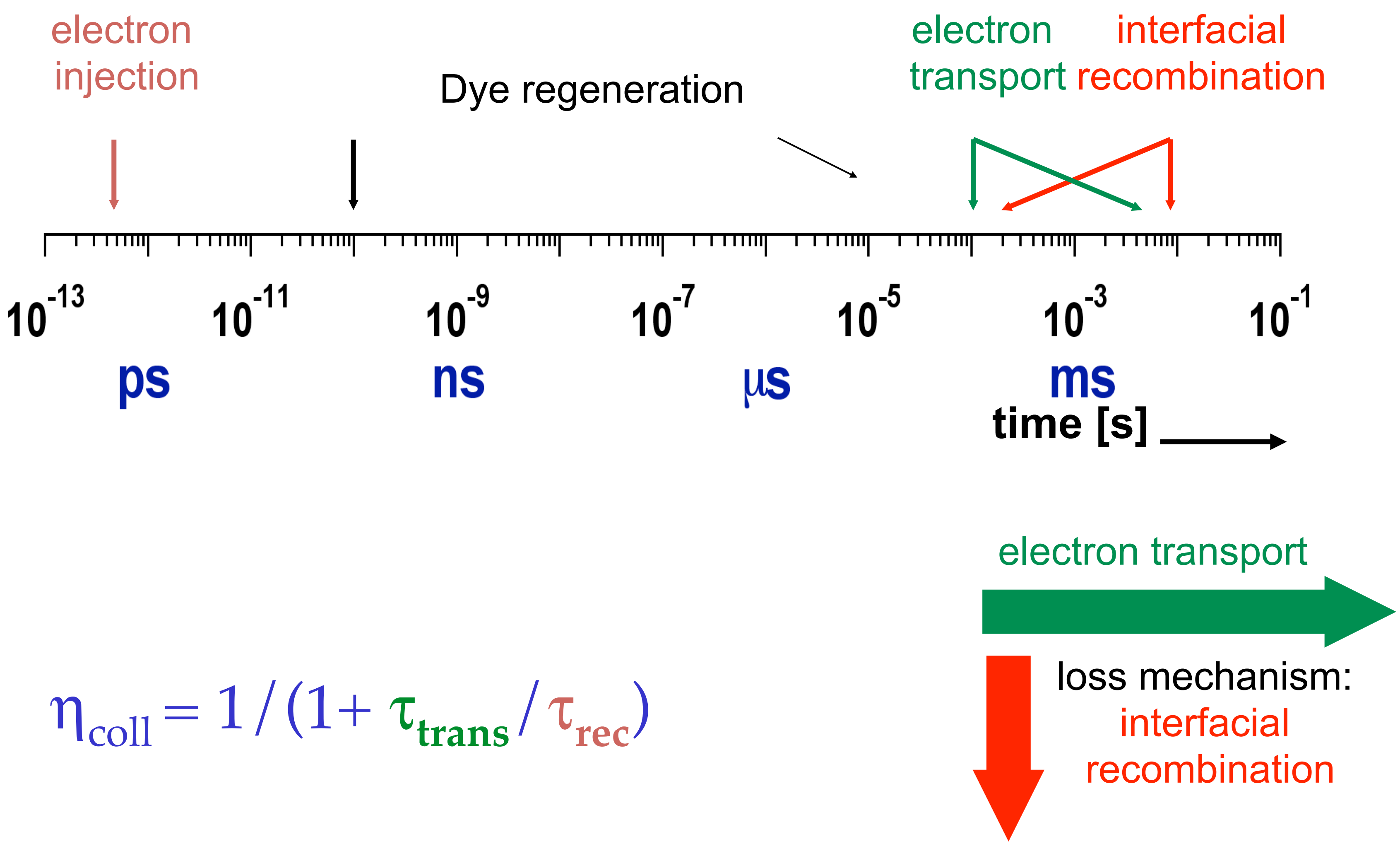
Dye sensitized nanocrystalline TiO_2 film





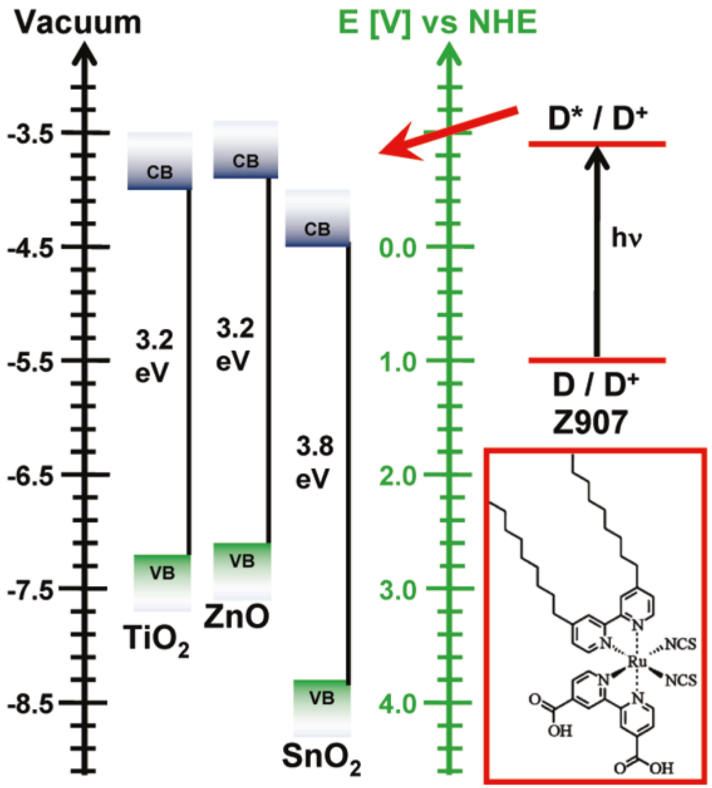
B.O'Regan and M.Grätzel "A Low Cost, High Efficiency Solar Cell based on the Sensitization of Colloidal Titanium Dioxide" *Nature,* 1991, 353, 7377-7380. Cited 6500 times.

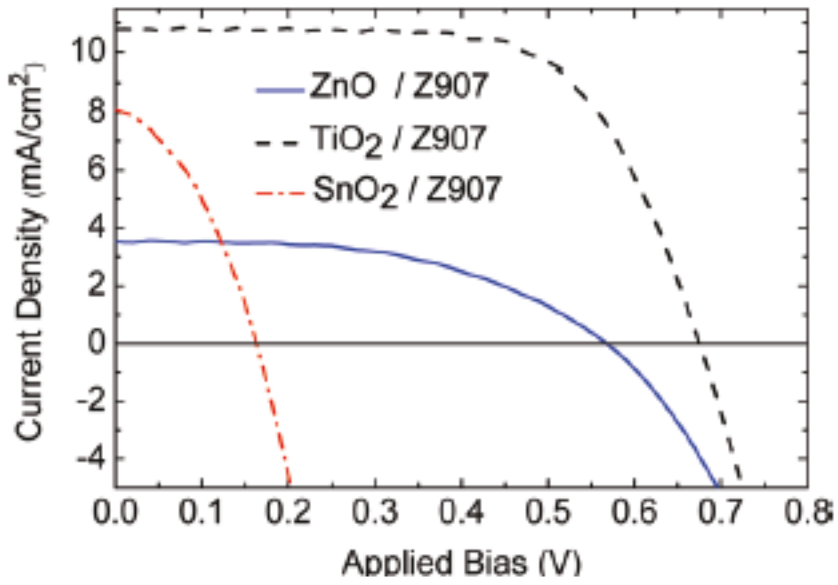
electron transport must be at least 100 x faster than recombination to collect > 99 % of the photo-generated charge carriers



$$\eta_{coll} = 1/(1+\tau_{trans}/\tau_{rec})$$

Semiconductor





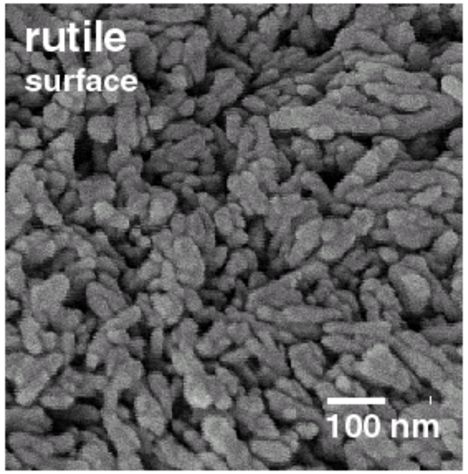
P. Tiwana et al. ACS Nano, 2011, 4, 5158

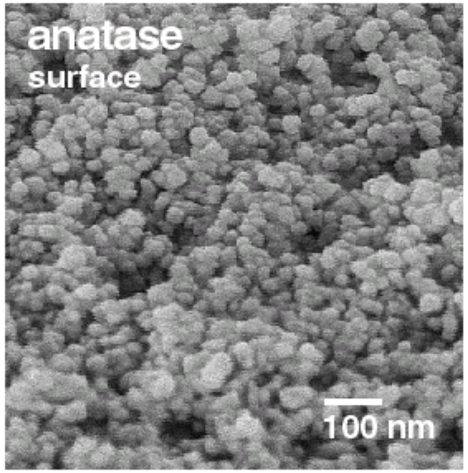
	IPCE (%)	Collection efficiency (%)	Injection efficiency (%)	Device mobility ($cm^2/V.s$)	bulk mobility ($cm^2/V.s$)
ZnO	38	96	47	0.004	200
TiO_2	83	98	100	0.017	1
SnO_2	63	95	79	0.003	250

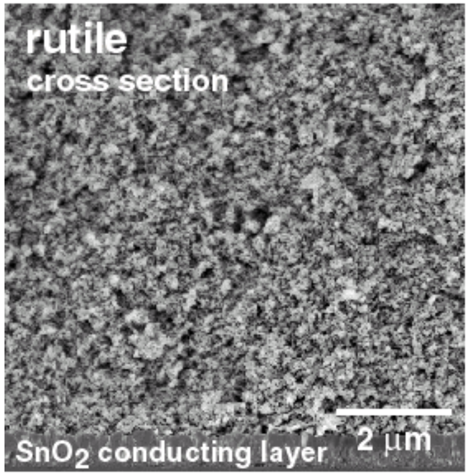
Effect of TiO_2 phase

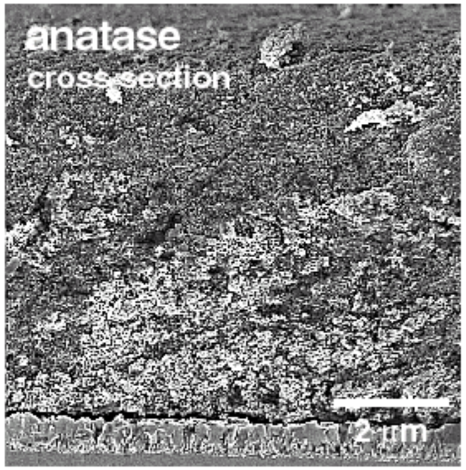
20X80 nm

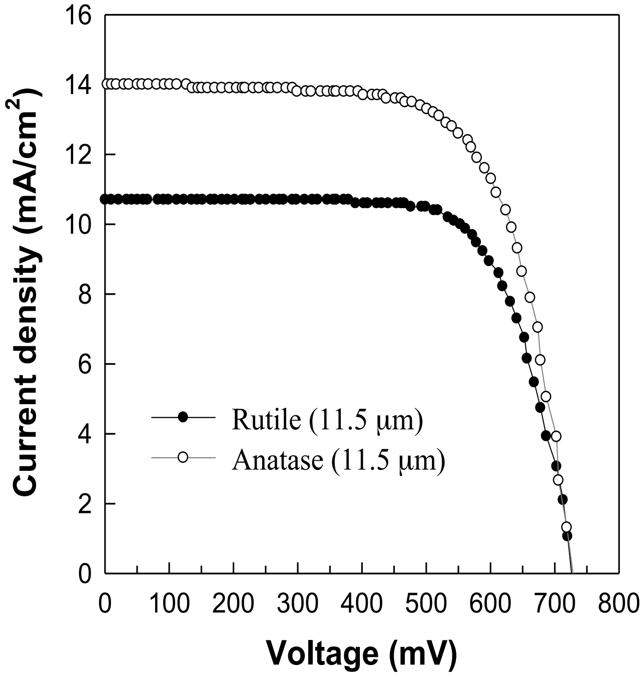
20 nm

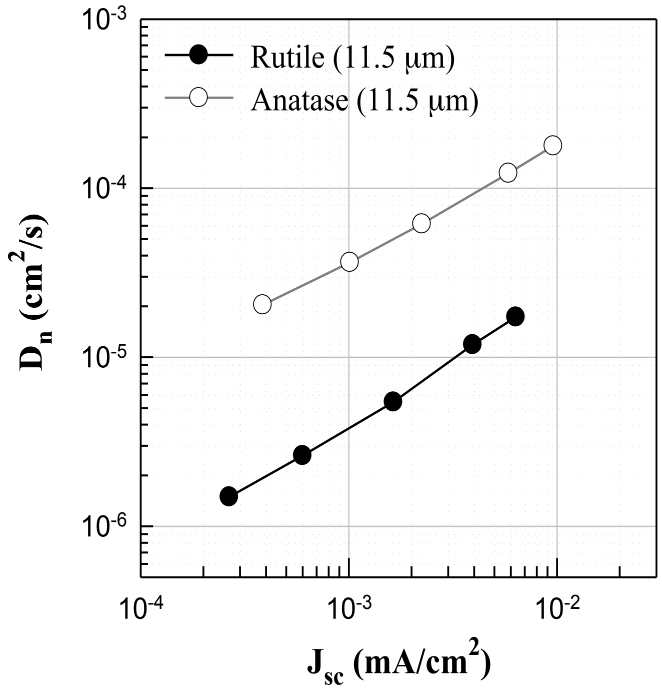












N.-G. Park, et. al, **J. Phys. Chem. B**, 104, 8989 (2000)

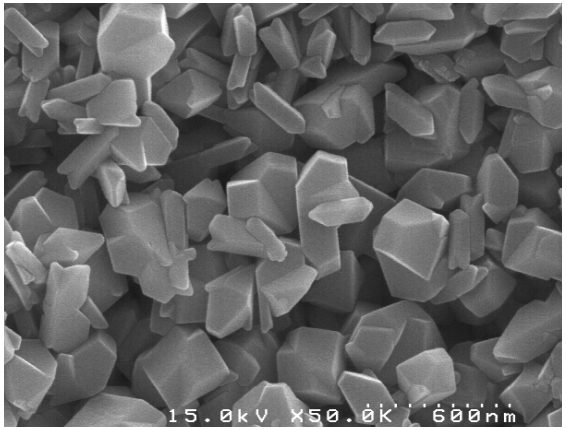
TiO_2 paste preparation

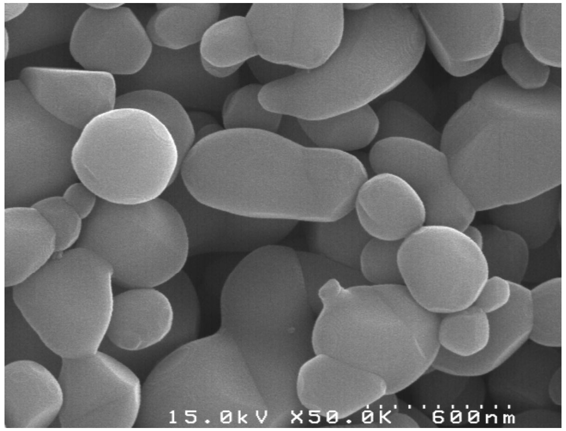
Precursor Preparation	Modify Ti-isopropoxide with acetic acid
Hydrolysis	Rapidly add precursor to water
Peptization	Acidify with HNO3, reflux
Hydrothermal Growth	Autoclave: 12 hours at 230°C
Concentrate Colloid	Rotovap: 45°C, 30mbar
Solvent Exchange, Ethyl Cellulose Addition	Flocculation, centrifuging
Homogenize Paste	3-roll mill, 15 minutes
Screen print films	
Dry and Anneal Films	Anneal: 450°C, 20 minutes

S. Ito et al. Thin Solid Films, **2008**, *516*, 4613.

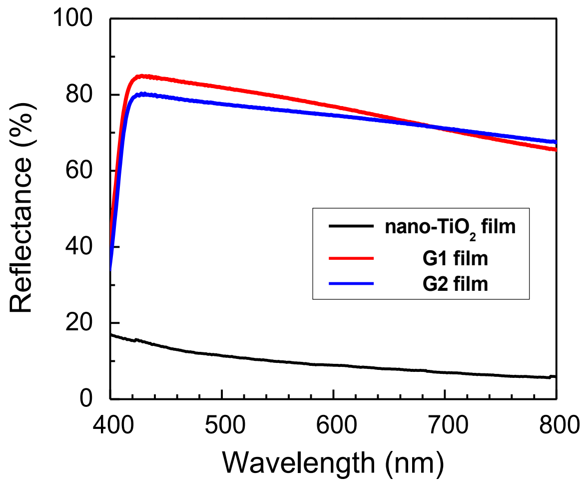
Scattering layer

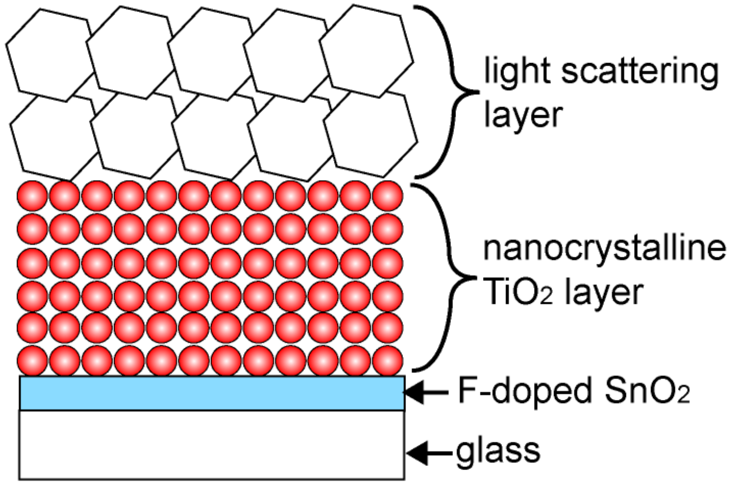
Scattering layer

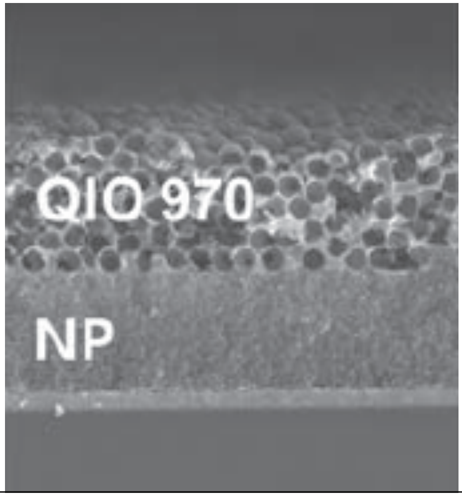




N.-G. Park et al, Inorg. Chim. Acta, (2007)

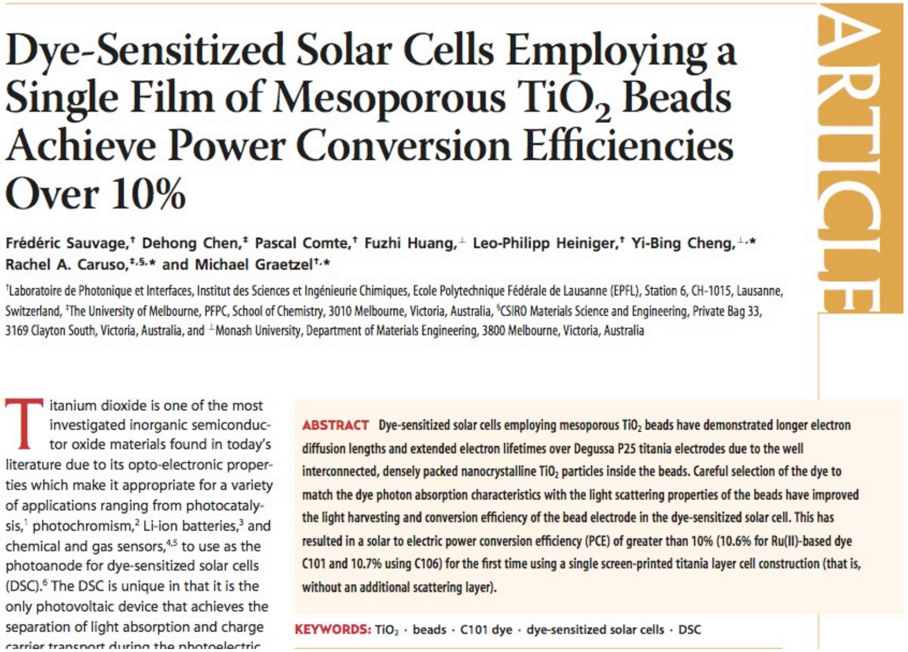






S.H. Han et al., Adv. Energy Mater. (2011)

ACS NANO July, 2010


ARTICLE

Dye-Sensitized Solar Cells Employing a Single Film of Mesoporous TiO_2 Beads Achieve Power Conversion Efficiencies Over 10%

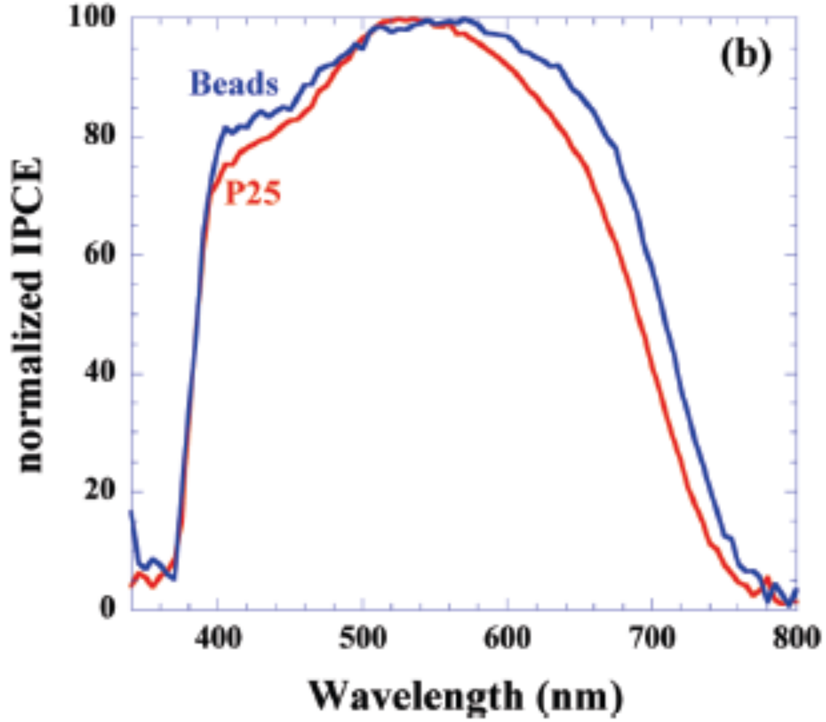
Frédéric Sauvage,[†] Dehong Chen,[‡] Pascal Comte,[†] Fuzhi Huang,[⊥] Leo-Philipp Heiniger,[†] Yi-Bing Cheng,[⊥,*] Rachel A. Caruso,[‡,§,*] and Michael Graetzel[†,*]

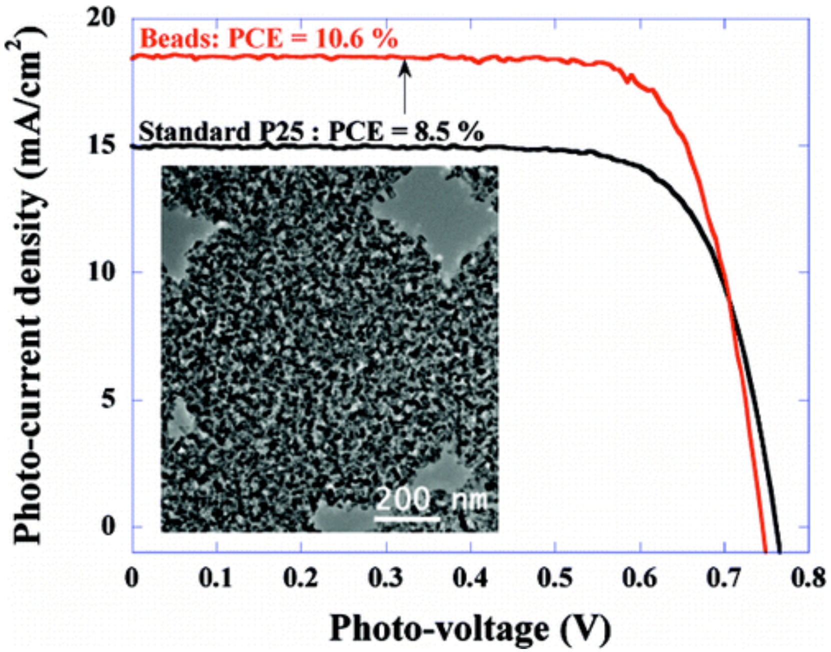
[†]Laboratoire de Photonique et Interfaces, Institut des Sciences et Ingénieurie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), Station 6, CH-1015, Lausanne, Switzerland, [‡]The University of Melbourne, PFPC, School of Chemistry, 3010 Melbourne, Victoria, Australia, [§]CSIRO Materials Science and Engineering, Private Bag 33, 3169 Clayton South, Victoria, Australia, and [⊥]Monash University, Department of Materials Engineering, 3800 Melbourne, Victoria, Australia

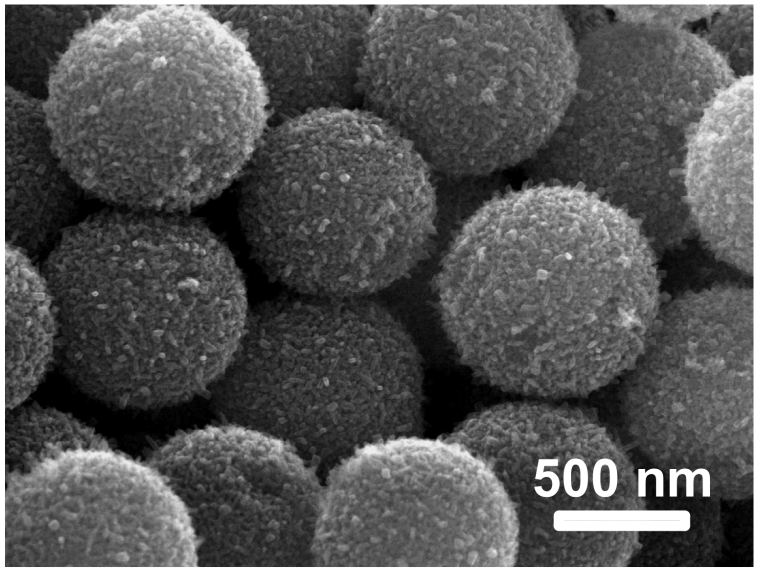
ABSTRACT Dye-sensitized solar cells employing mesoporous TiO_2 beads have demonstrated longer electron diffusion lengths and extended electron lifetimes over Degussa P25 titania electrodes due to the well interconnected, densely packed nanocrystalline TiO_2 particles inside the beads. Careful selection of the dye to match the dye photon absorption characteristics with the light scattering properties of the beads have improved the light harvesting and conversion efficiency of the bead electrode in the dye-sensitized solar cell. This has resulted in a solar to electric power conversion efficiency (PCE) of greater than 10% (10.6% for Ru(II)-based dye C101 and 10.7% using C106) for the first time using a single screen-printed titania layer cell construction (that is, without an additional scattering layer).

KEYWORDS: TiO_2 · beads · C101 dye · dye-sensitized solar cells · DSC

Titanium dioxide is one of the most investigated inorganic semiconductor oxide materials found in today's literature due to its opto-electronic properties which make it appropriate for a variety of applications ranging from photocatalysis,[1] photochromism,[2] Li-ion batteries,[3] and chemical and gas sensors,[4,5] to use as the photoanode for dye-sensitized solar cells (DSC).[6] The DSC is unique in that it is the only photovoltaic device that achieves the separation of light absorption and charge carrier transport during the photoelectric







surface area: 89 m^2/g

Mesoscopic structure

$$\text{IPCE (EQE)} = \eta_{abs}\Phi_{cg}\eta_{coll}$$

η_{ab}: light harvesting efficiency

Φ_{cg}: quantum yield of charge carrier generation

$$\Phi_{cg} = \Phi_{injection}\,\Phi_{dye\ regeneration}$$

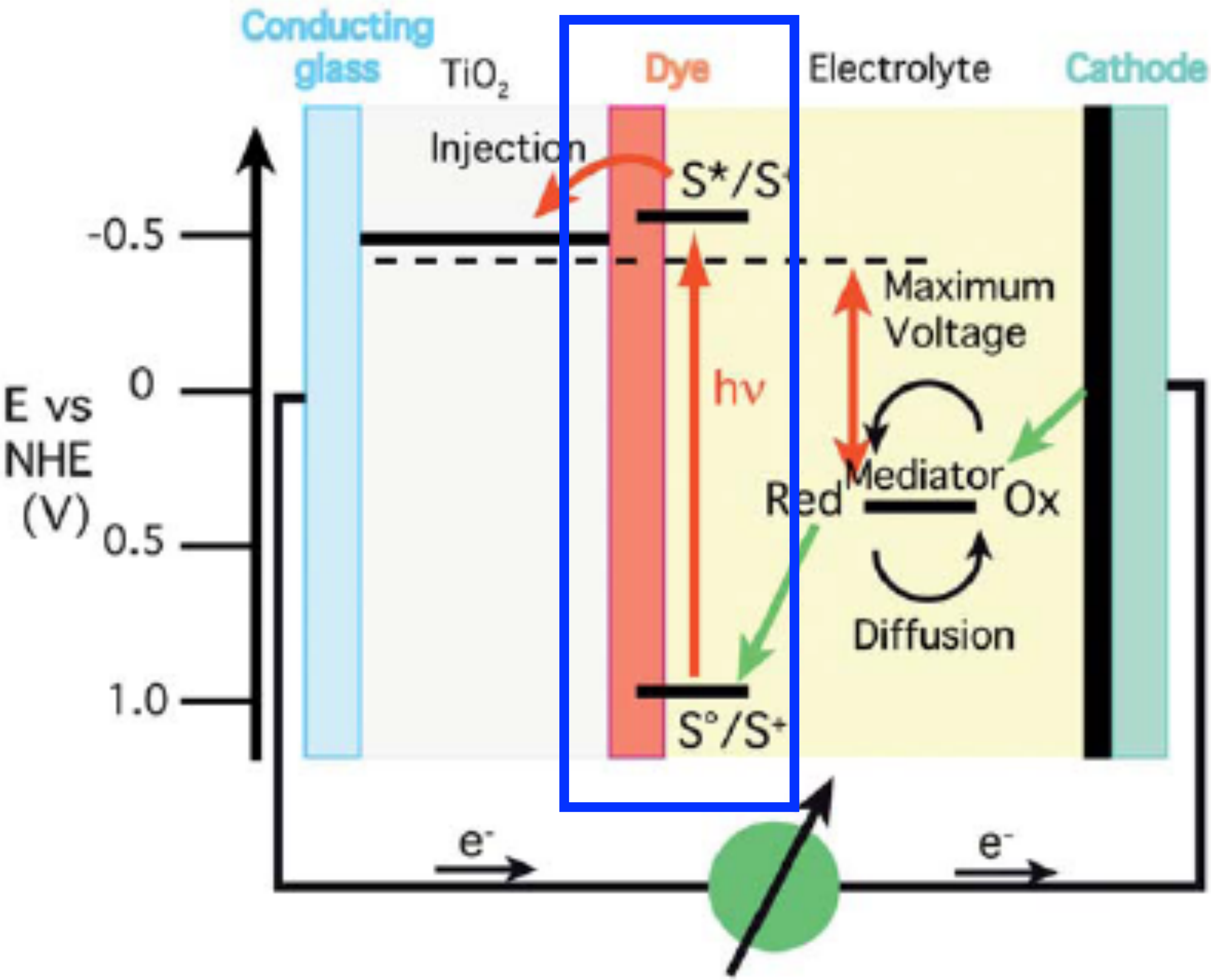
η_{coll} = efficiency of charge carrier collection

Surface Area
Light scattering

Electron percolation

Ongoing and Future Research

- Advanced meso-structures
- New sensitizers
- New redox mediators
- New counter electrodes

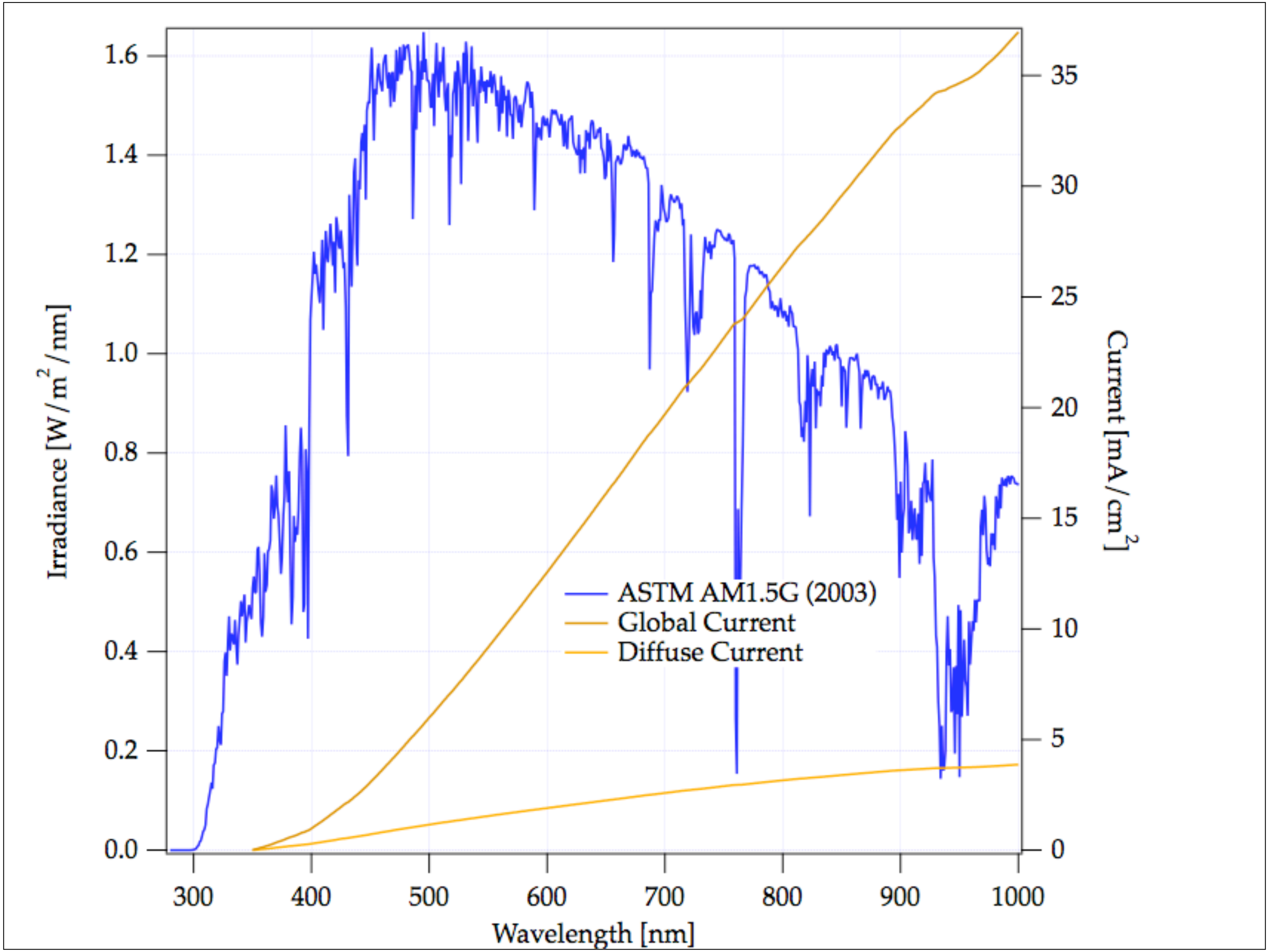

Conducting glass
TiO2
Dye
Electrolyte
Cathode
Injection
S*/S+
-0.5
Maximum Voltage
hν
E vs NHE (V)
0
Mediator
Red
Ox
0.5
Diffusion
1.0
S°/S+
e-
e-

Requirements

1. Distribution on the surface of semiconductor oxide
2. Absorption range (standard global AM 1.5 sunlight to electricity below a threshold wavelength, about 920 nm)
3. Firmly graft to the surface of semiconductor (carboxylate or phosphonate)
4. Quantum yield (injection of electrons into the solid) = 1
5. The energy level

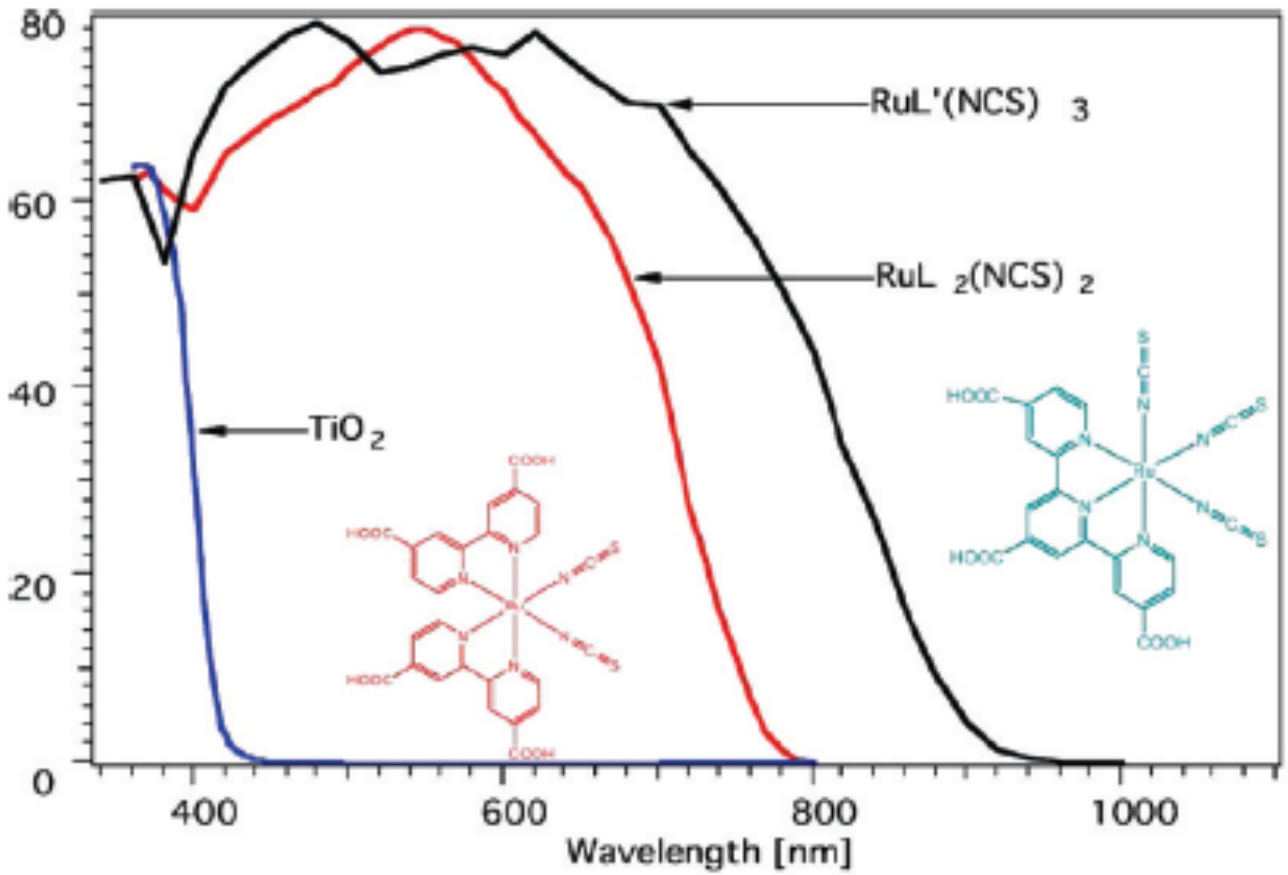
   Excitation state (LUMO) > Conduction band of the oxide

   Ground state (HOMO) < redox potential
6. Stability enough to sustain above 100 millions turnover cycles (= about 20 years of exposure to natural light)



1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Irradiance [W/m^2/nm]
300
400
500
600
700
800
900
1000
Wavelength [nm]
35
30
25
20
15
10
5
0
Current [mA/cm^2]
ASTM AM1.5G (2003)
Global Current
Diffuse Current

Sensitizer Engineering

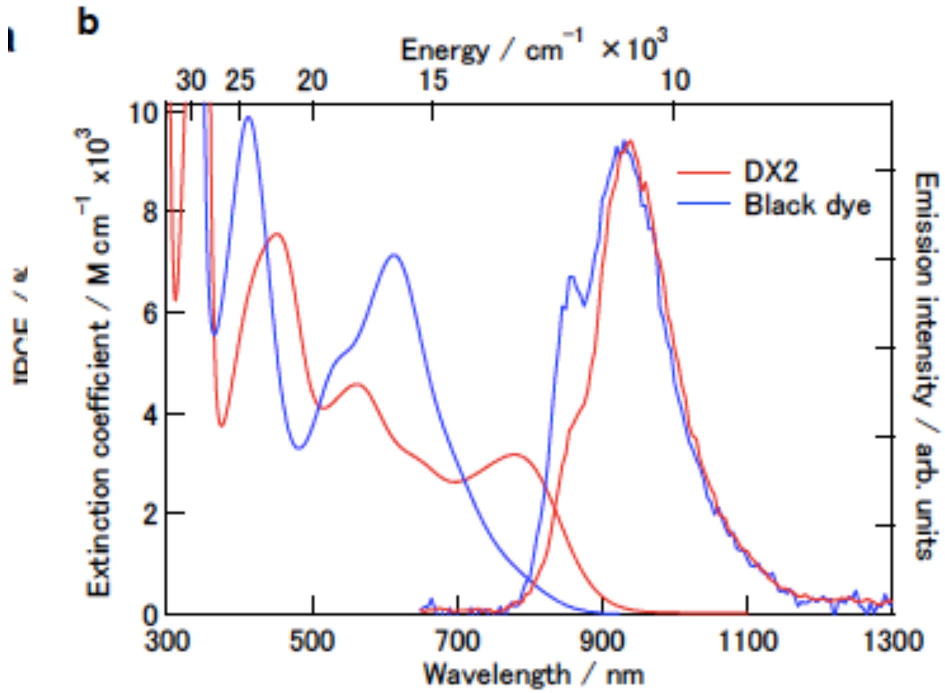


L = 4,4'-COOH-2,2'-bipyridine

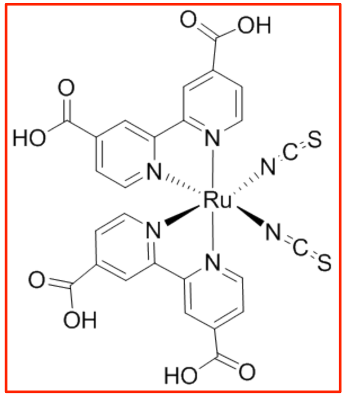
L' = 4,4',4"-COOH-2,2':6',2"-terpyridine

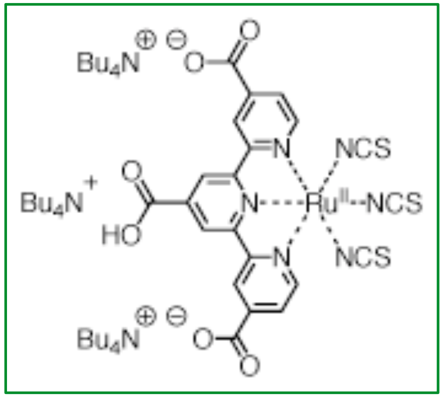
M.K. Nazeeruddin et al., *J. Am. Chem. Soc.* 123, 1613, (2001)

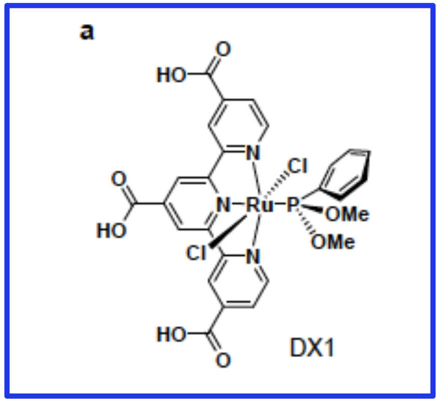
Sensitizer Engineering



	V_{oc} (V)	J_{sc} (mA/cm^2)
GaAs	0.994	**23.2**
nc-Si	0.539	**24.4**
CdTe	0.845	**26.1**
Dye X	0.550	**26.6**
Si module	0.492	**29.7**







DX 1 data presented by Prof. S Uchida,Tokyo University; at NTU Singapore Symposium July 26 2011

IPCE (EQE) = $\eta_{abs}\Phi_{cg}\eta_{coll}$

η_{ab}: light harvesting efficiency

Φ_{cg}: quantum yield of charge carrier generation

$\Phi_{cg} = \Phi_{\text{injection}}\,\Phi_{\text{dye regeneration}}$

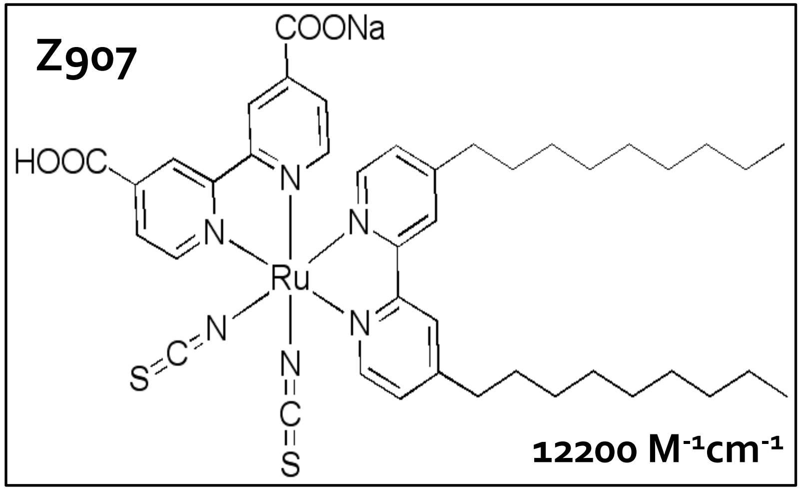
η_{coll} = efficiency of charge carrier collection

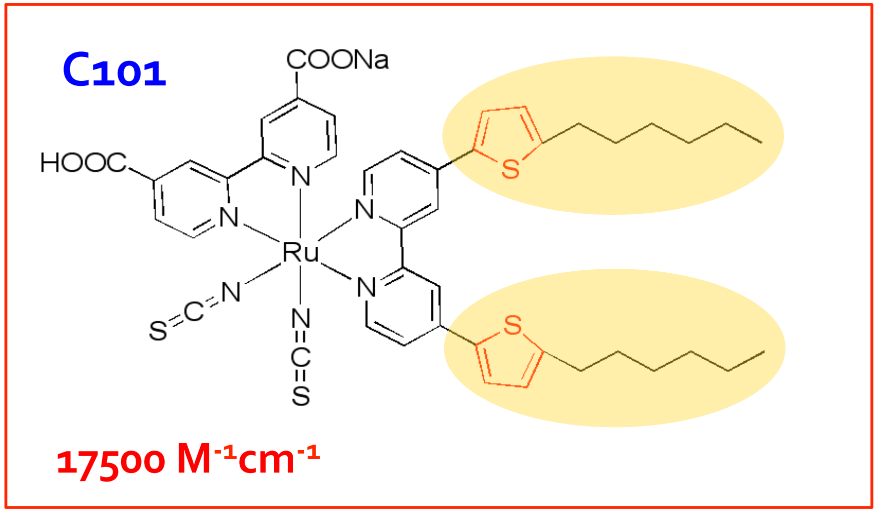
$$\eta_{ab}(LHE) = 1 - 10^{-A} = 1 - 10^{-\sigma\Gamma}$$

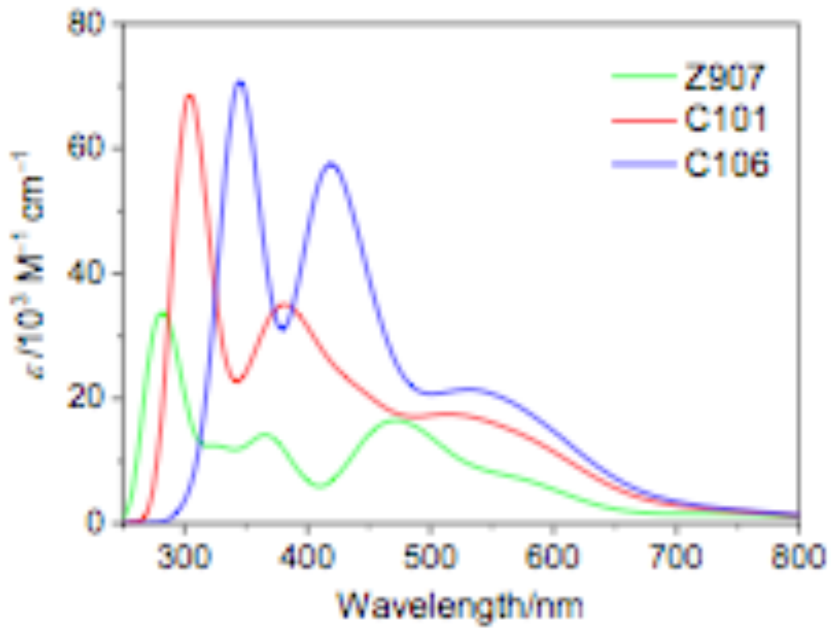
A (the absorption optical density of sensitizer-stained film) > 2
= LHE > 99%

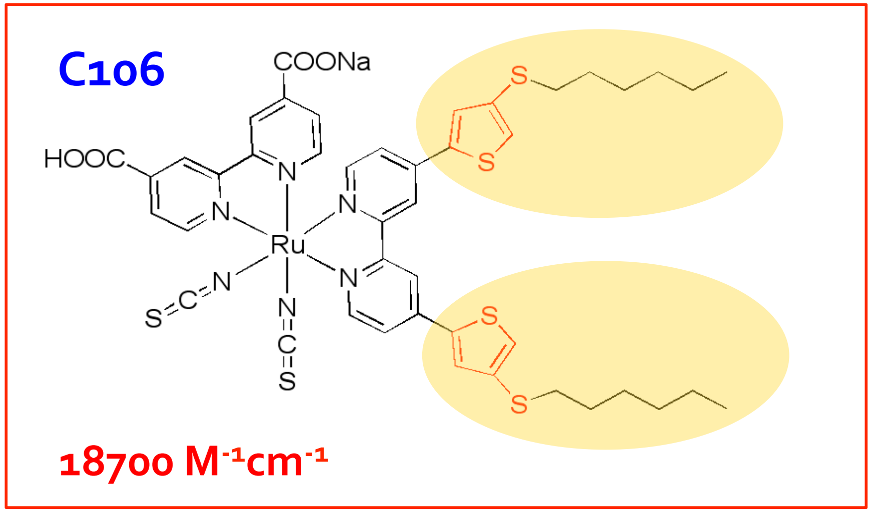
High *ε and/or* Γ is needed for high LHE.

High extinction coefficient Ru dyes

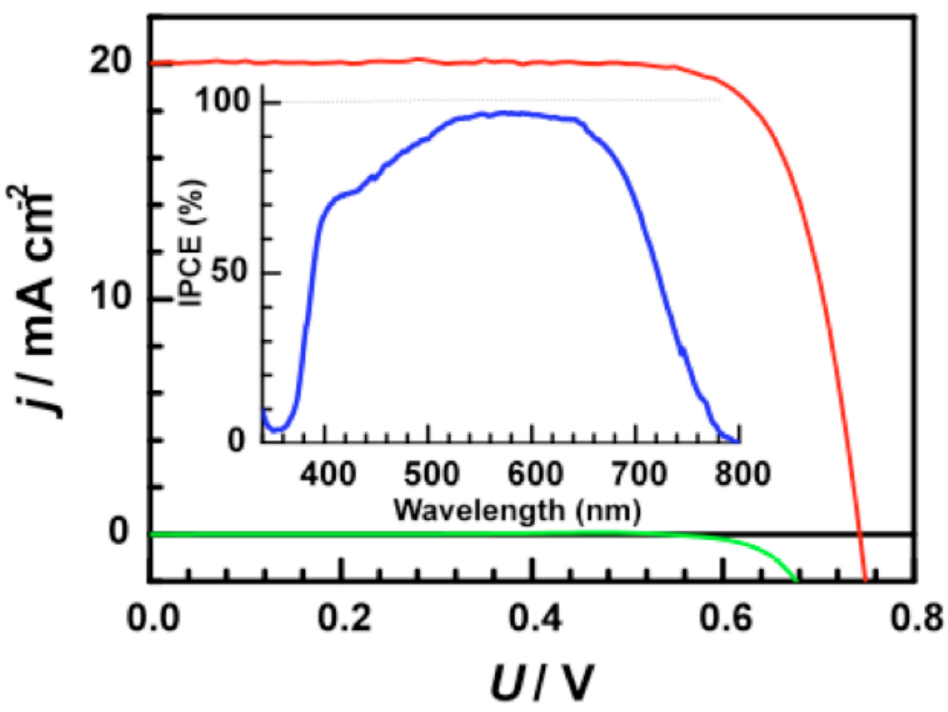




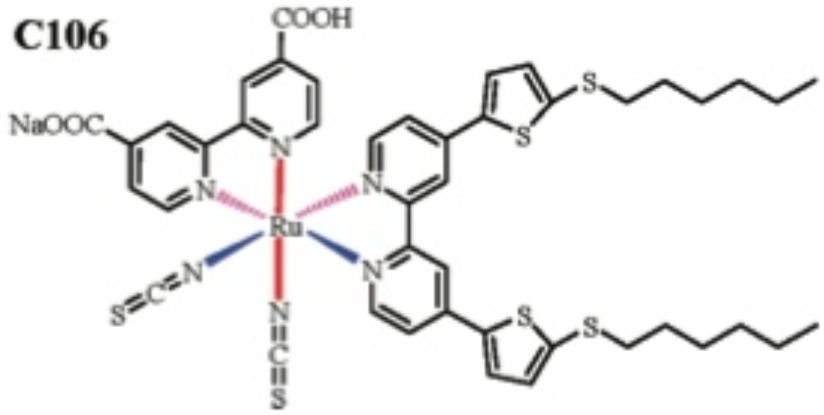




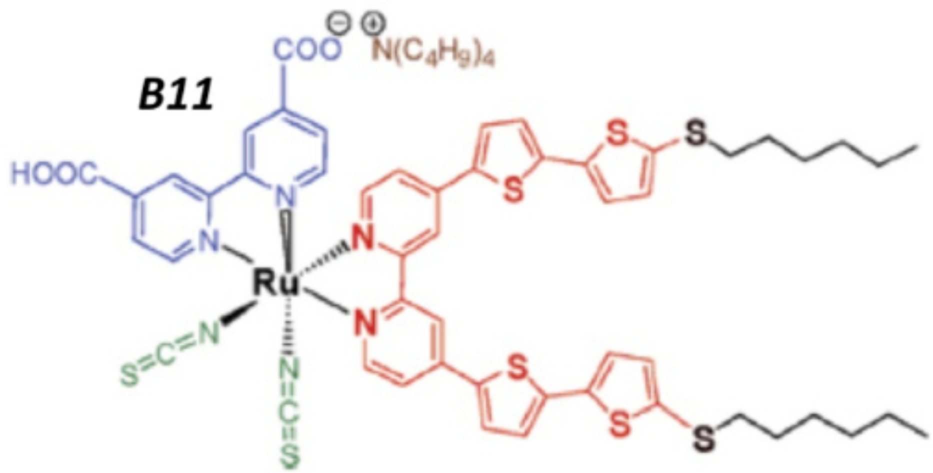
High extinction coefficient Ru dyes



Published PCE: 11.5 %

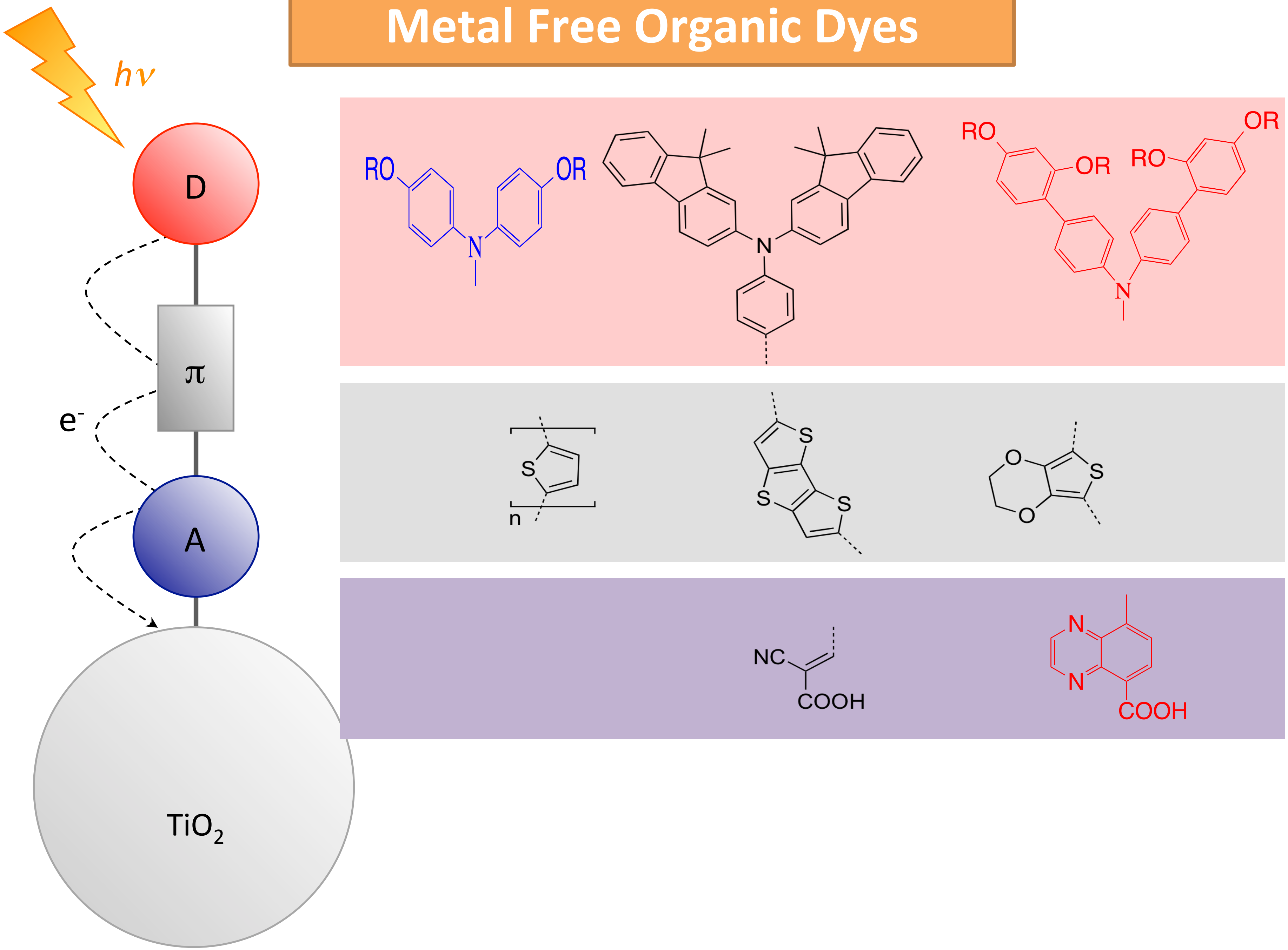


Cao,Y.; Bai, Y.; Qingjiang; C., Y.; Liu, S. Shi, D.; Gao, F; Wang, P.. *J. Phys Chem. C* (2009), 113(15), 6290-6297.

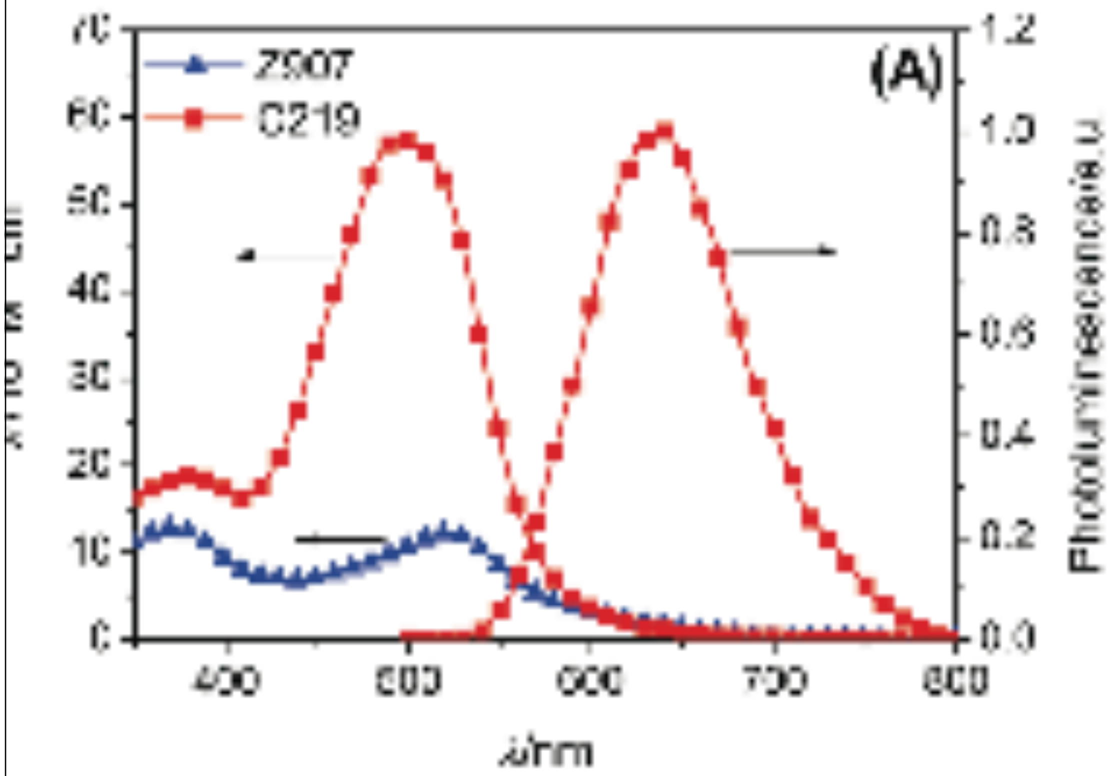


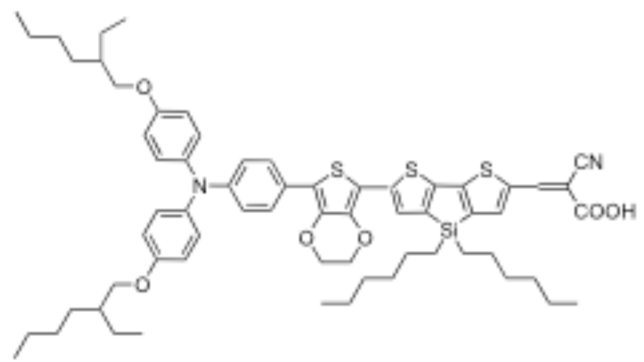
Chen, C.-Y.; Wang, M.; Li, J.-Y.; Pootrakulchote, N.; Alibabaei, L.; Cevey, Le; Decoppet, J.-D.; Tsai, J.-H.; Gratzel, C.; Wu, C.-G.; Zakeeruddin, S. M.; Gratzel, M.l. ACS Nano (2009), 3(10), 3103-3109.

Metal Free Organic Dyes



Absorption and emission spectrum of C219 versus absorption spectrum of Z907 ruthenium dye

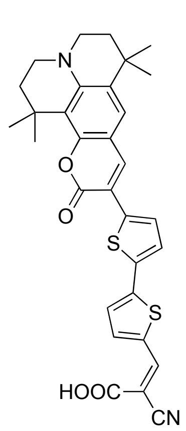




To get >90% LHE,
C219: 2 um
Z907: >10 um

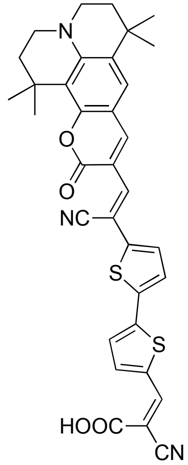
Maximum Molar extinction coefficient of C219 = 5.75 x 10^4 M^{-1} cm^{-1} at 493 nm
Maximum Molar extinction coefficient of Z907 = 1.20 x 10^4 M^{-1} cm^{-1} at 520 nm

W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F.Wang, C. Pan, and P. Wang
Chem. Mater. **2010**, 22, 1915–1925



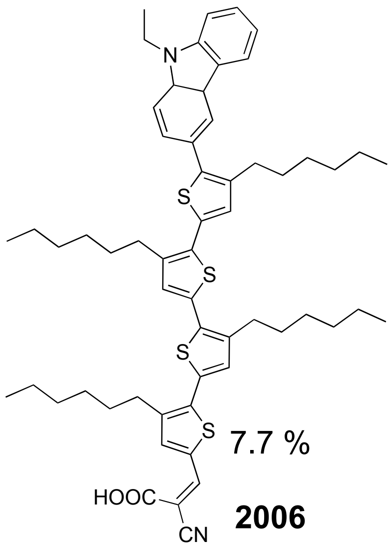
7.7 %

2003



7.6 %
6 % (IL)

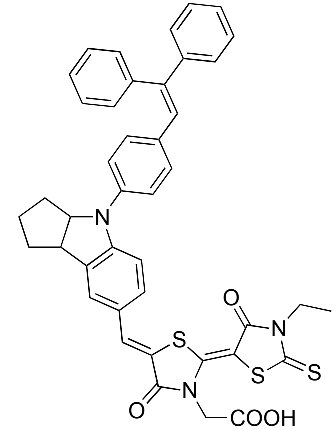
2007



7.7 %

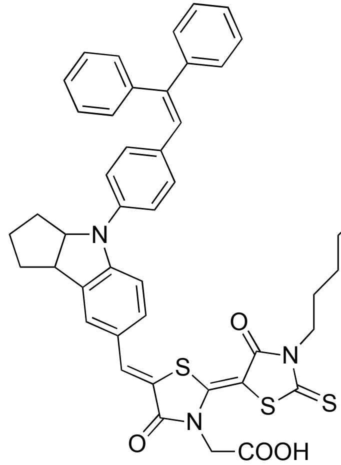
2006

K. Hara et al.,



8 % → 9%

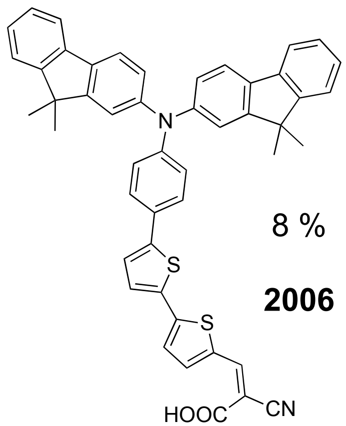
2004 → 2006



> 9%

2008

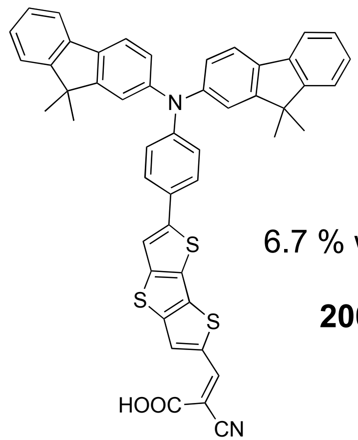
S. Uchida et al., and EPFL



8 %

2006

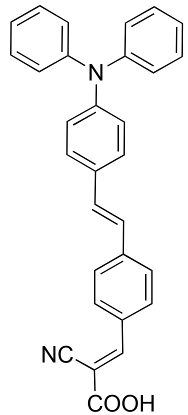
J. Ko et al., and EPFL



6.7 % with IL

2008

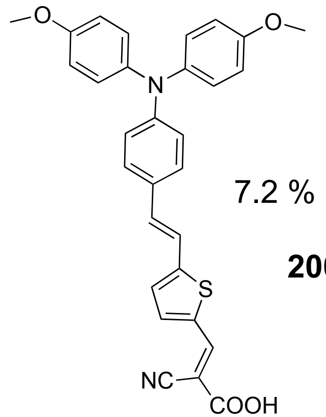
P. Wang et al., and EPFL



9 %

2007

N.-G. Park et al.,
and C. Kim et al.,

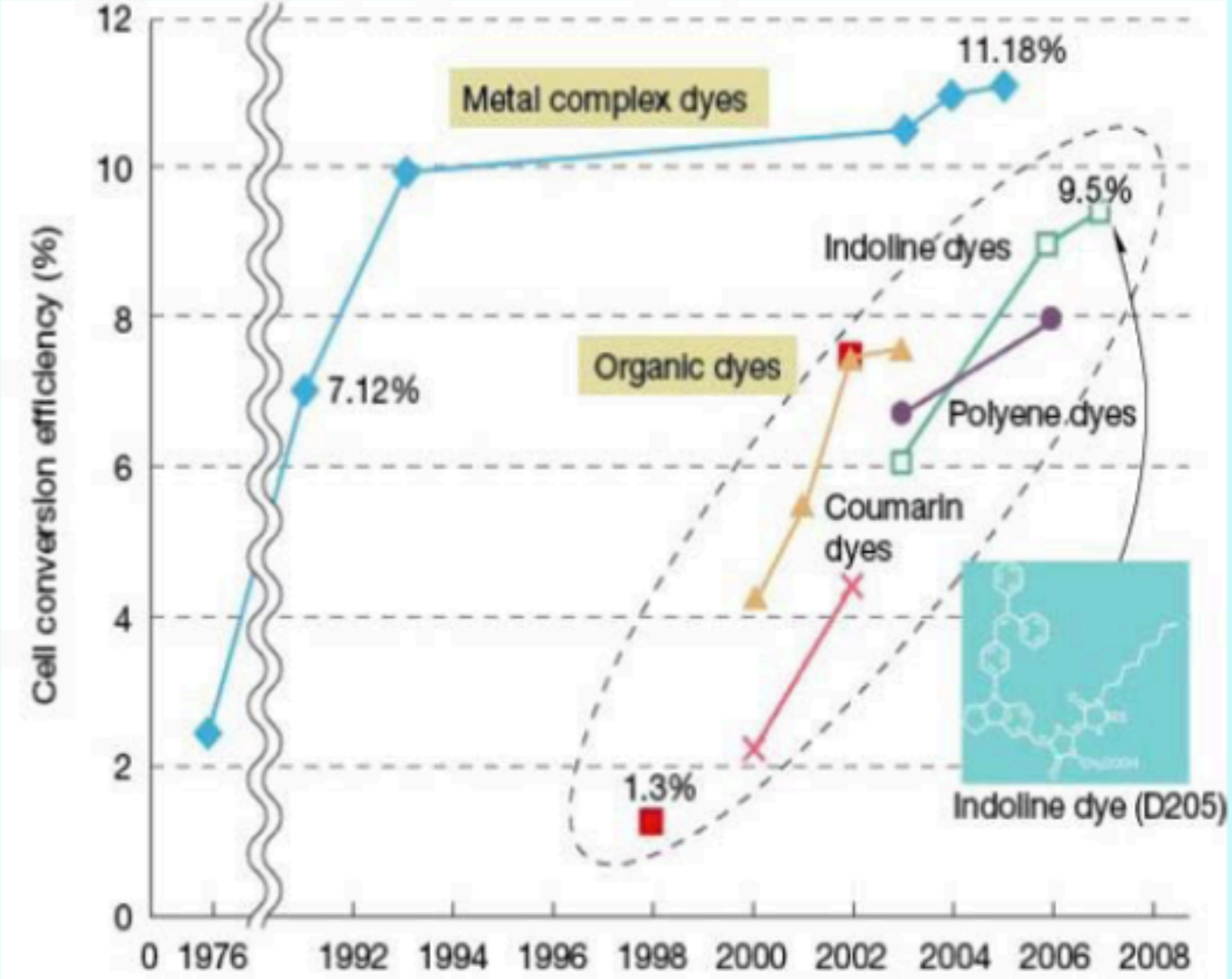


7.2 % Liquid

2007

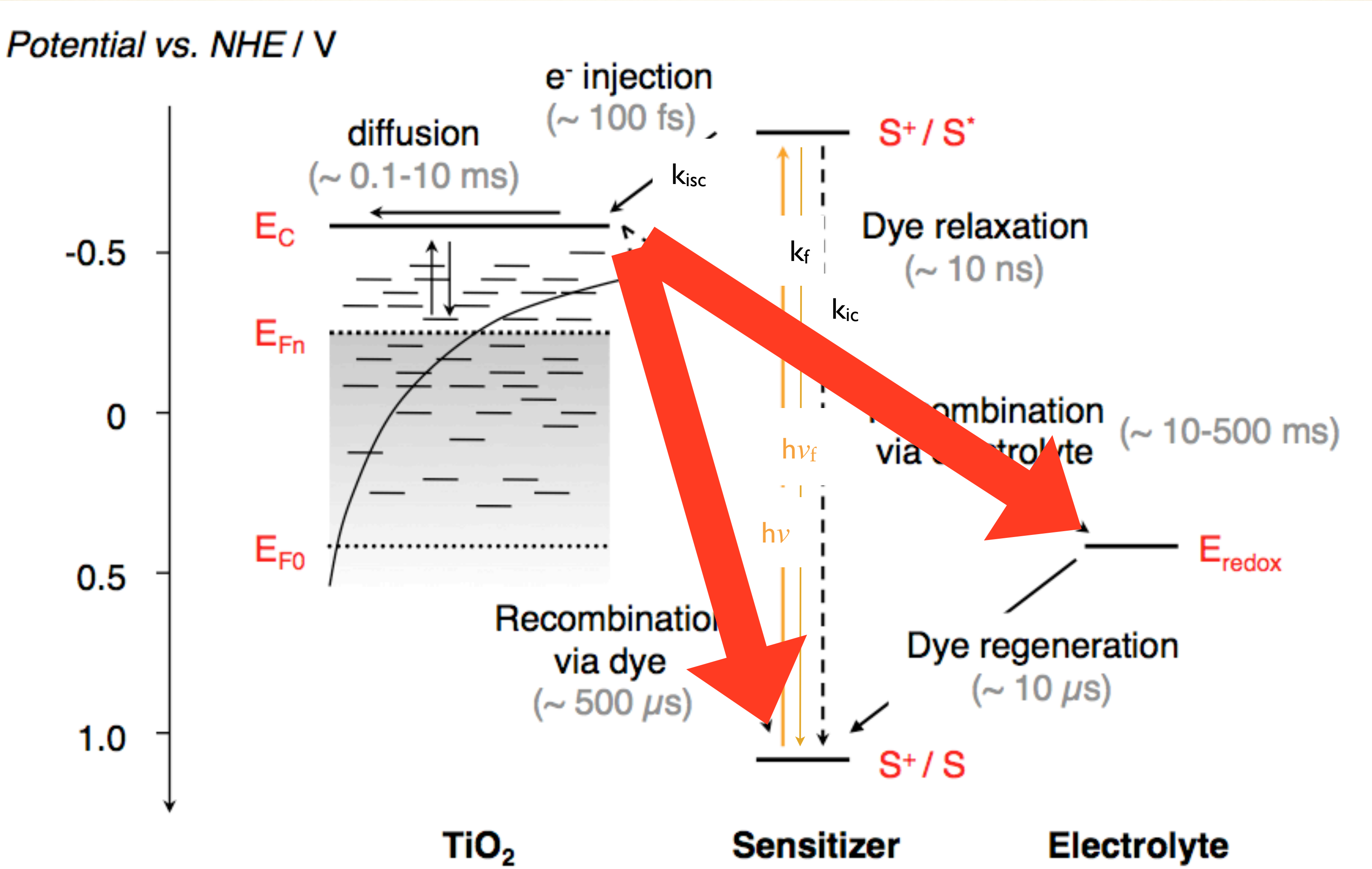
KTH and EPFL

Organic dyes are catching up in conversion efficiency

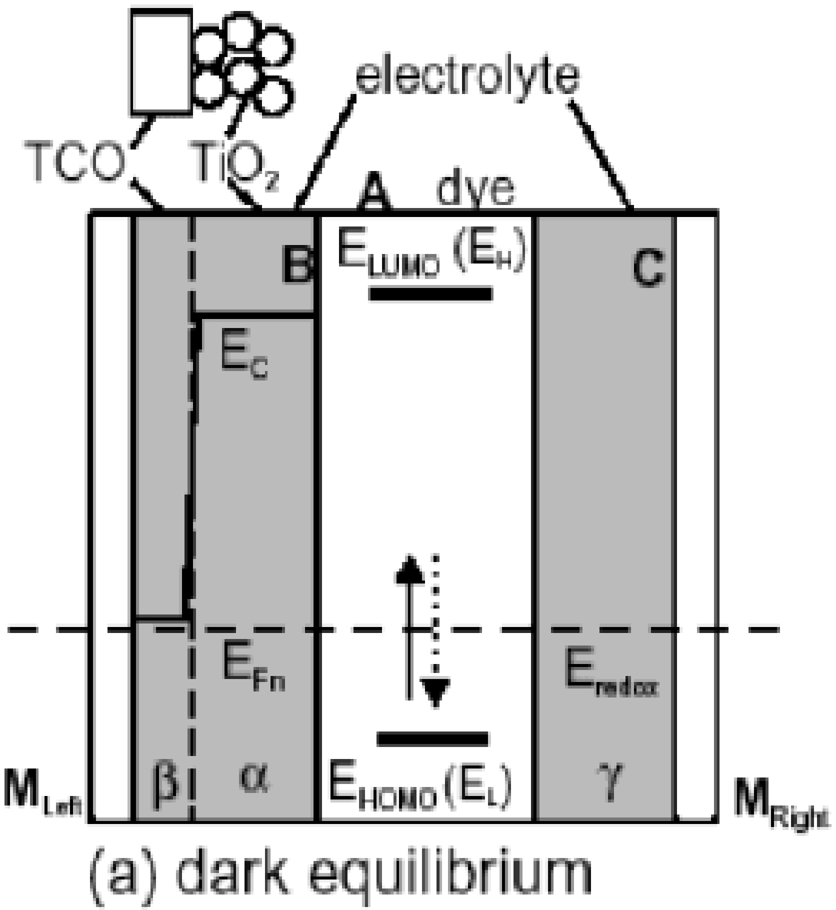


Source: *Tetsuo Nozawa* *Nikkei Electronics Asia* -- July 2008,

Summary of the key processes involved in the regenerative cycle taking place in a dye-sensitized solar cell under illumination.



Ref: S. Wenger



Open circuit voltage

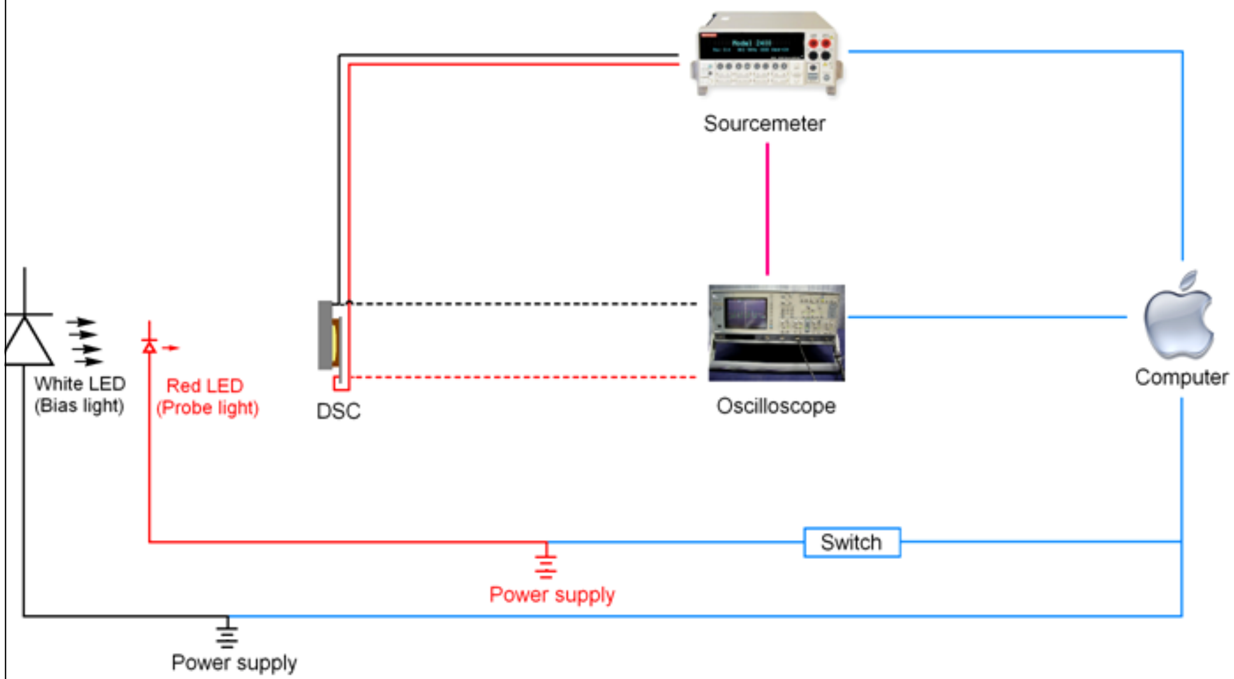
$$qVoc = {}_{n}E_F - E_{F,redox} = kT \ln \frac{n_c}{n_0} = kT \ln \frac{I_0 \tau (1 - e^{-\alpha d_{film}})}{d_{film} n_0}$$

J. Bisquert et. al., J. Phys. Chem. B, 108, 8106 (2004)

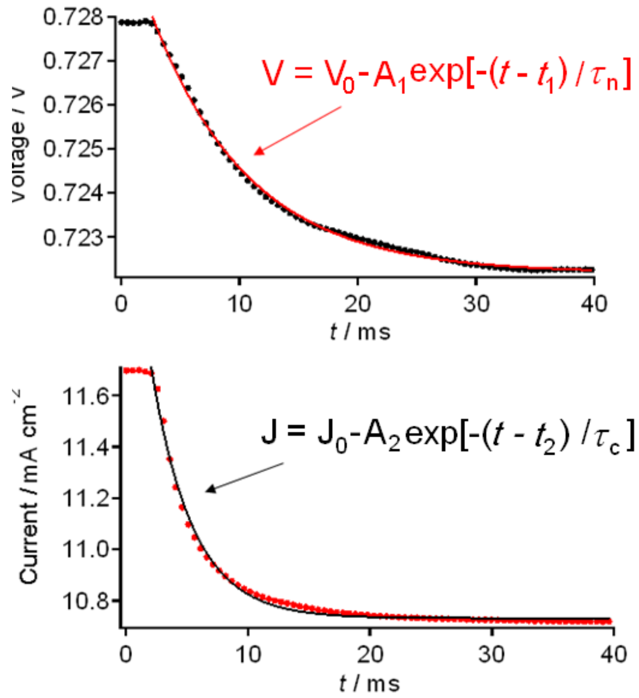
L. M. Peter, J. Phys. Chem. C *111,* 6601 (2007)

Techniques for characterization

Phototransient decay setup

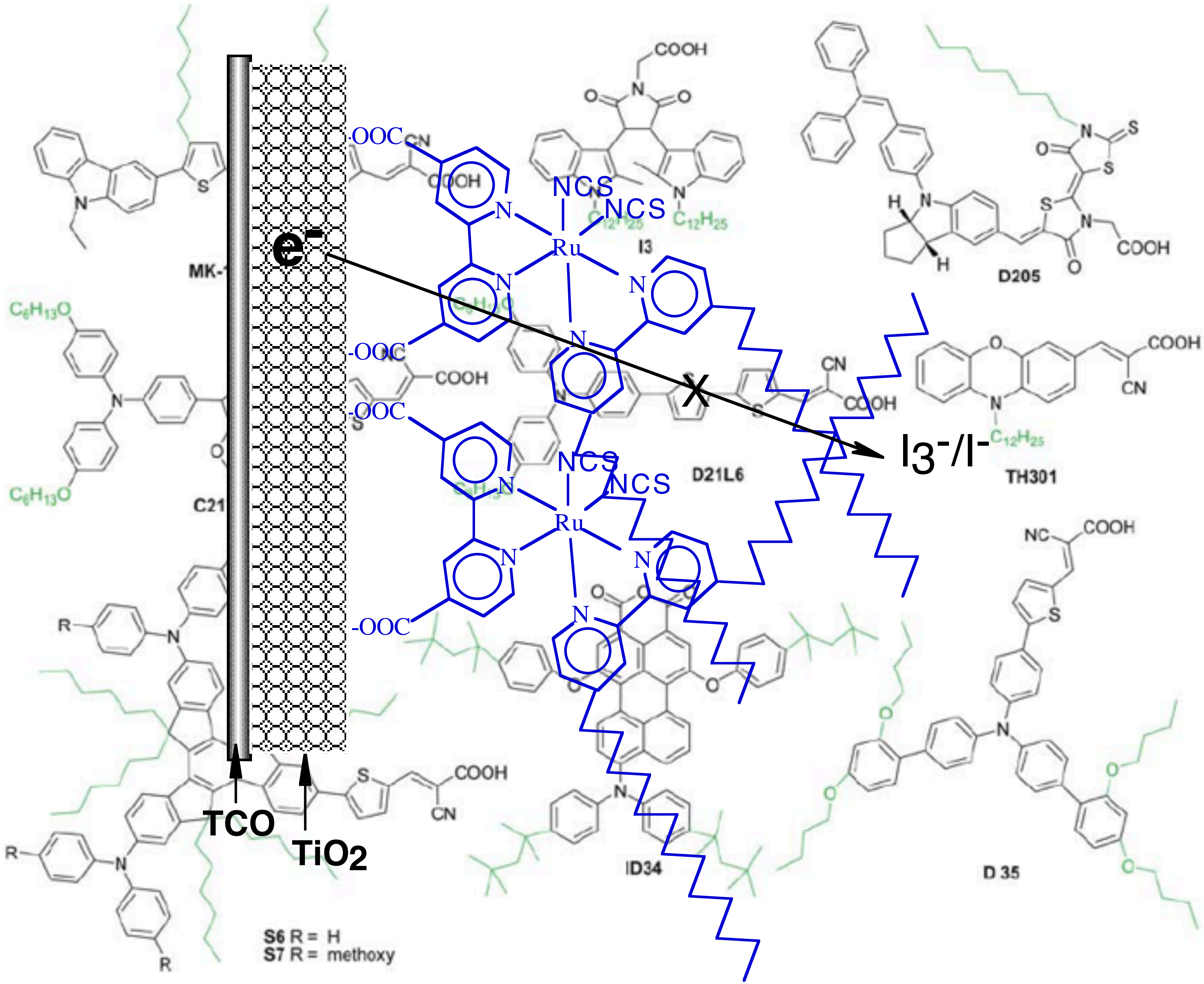


Electron lifetime, τ_n



$$C_\mu = e^2 \frac{d(1-p)N_t}{k_B T_c} \exp\left(\frac{E_{F,redox} - E_c}{k_B T_c}\right) \exp\left(\frac{eV}{k_B T_c}\right)$$

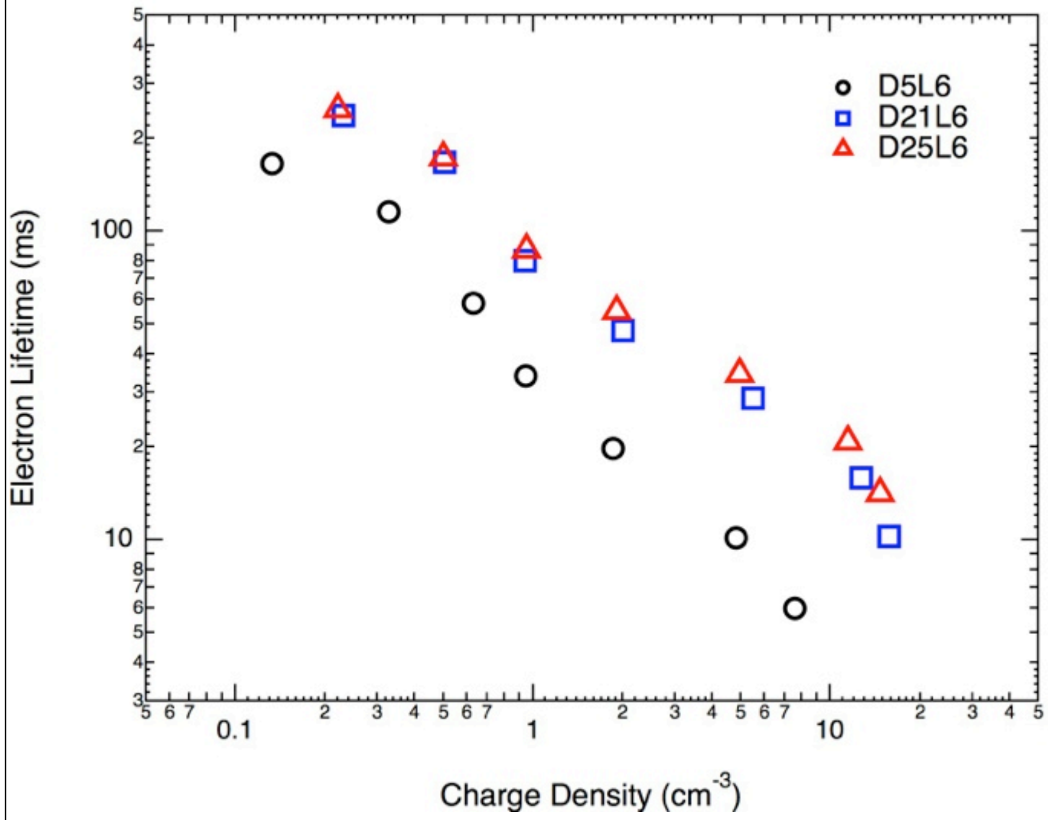
$$D = (L/2)^2/\tau_e$$

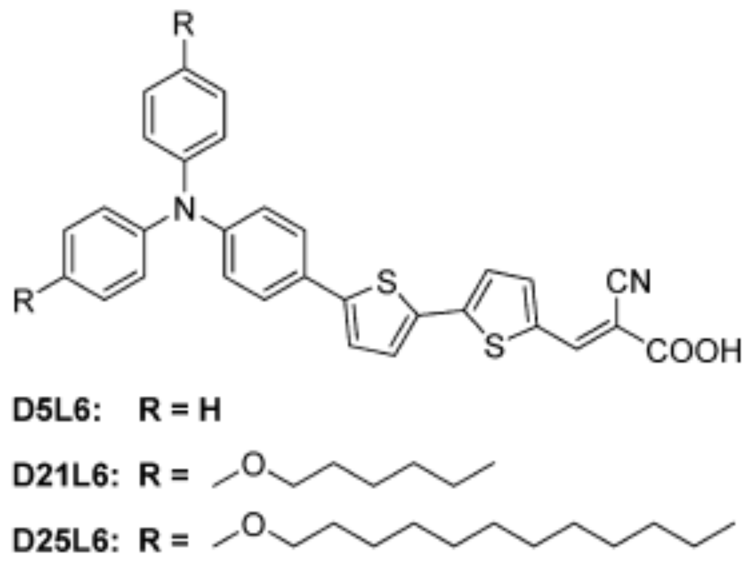


"Molecular Engineering of Sensitizers for Conversion of Solar Energy into Electricity" in Dye-sensitized solar cells, Jun-Ho Yum and Md. K. Nazeeruddin, CRC Press, 2010

Z. Ning et al. Energy & Environmental Science, 2010, 3, 1170

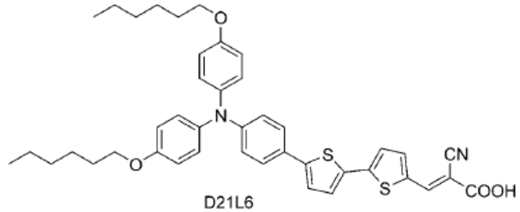
Alkyl chain length effect on Electron Recombination





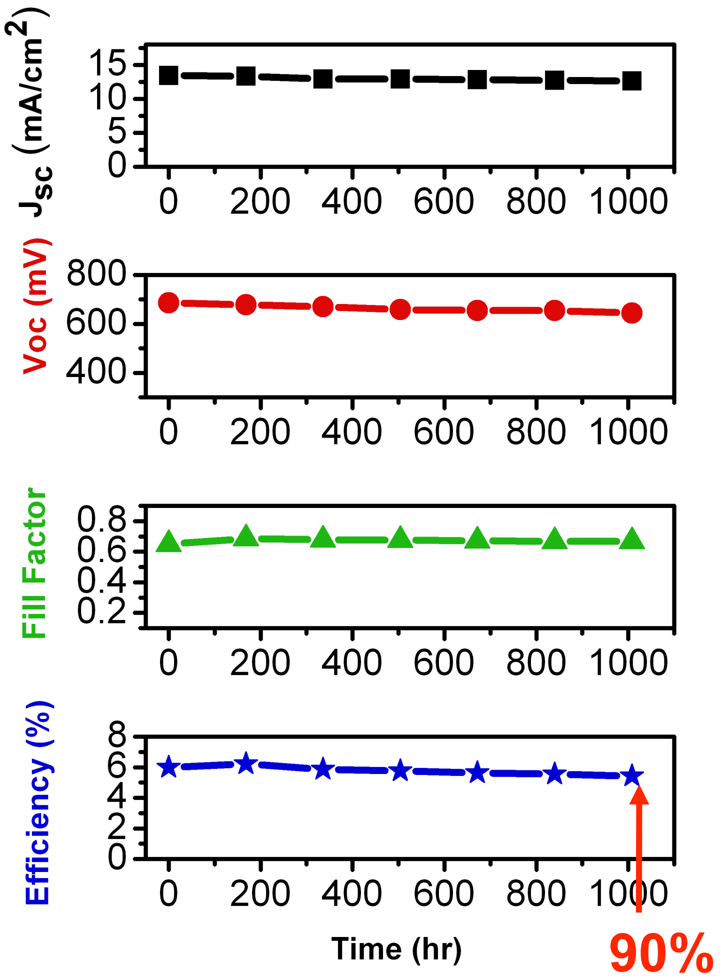
Photovoltage and photocurrent transient used for kinetic measurement

Stability with D21L6

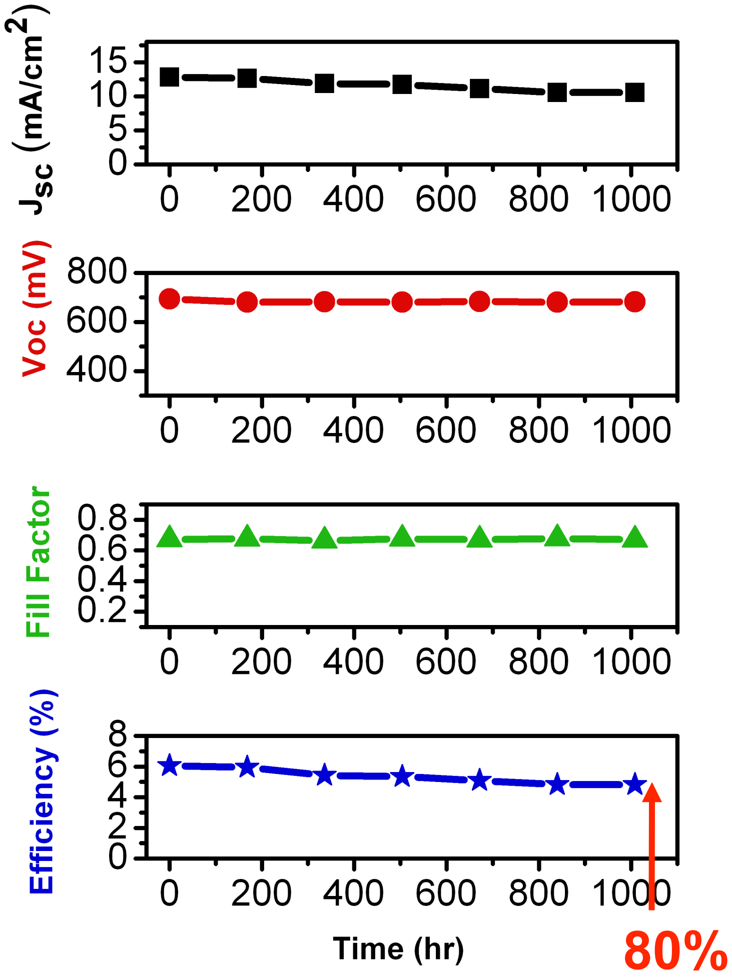


D21L6

Light soaking (1 sun + 60 °C)



Heat stress (dark + 80 °C)

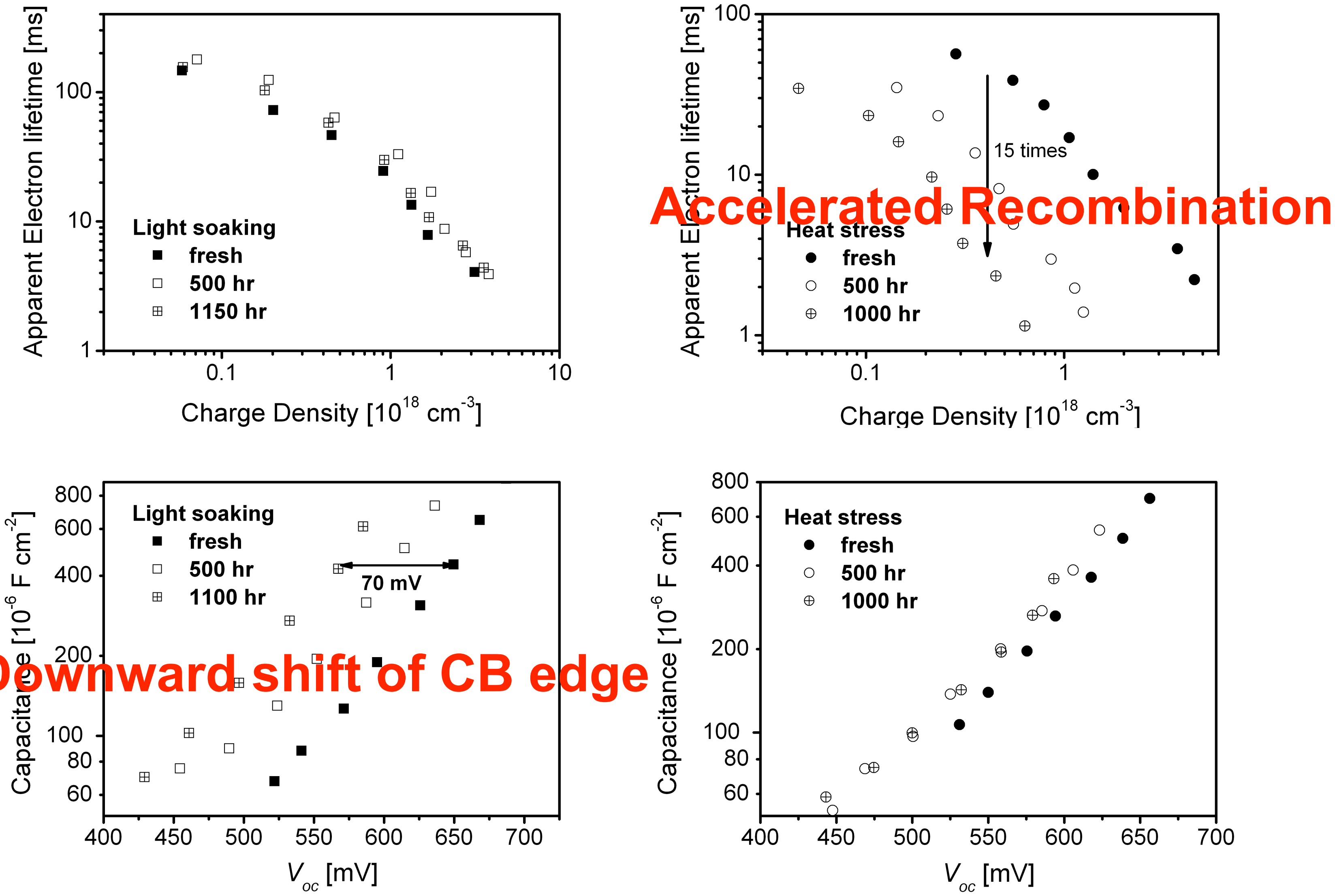


Drop: 42 mV, 0.8 mA/cm^2

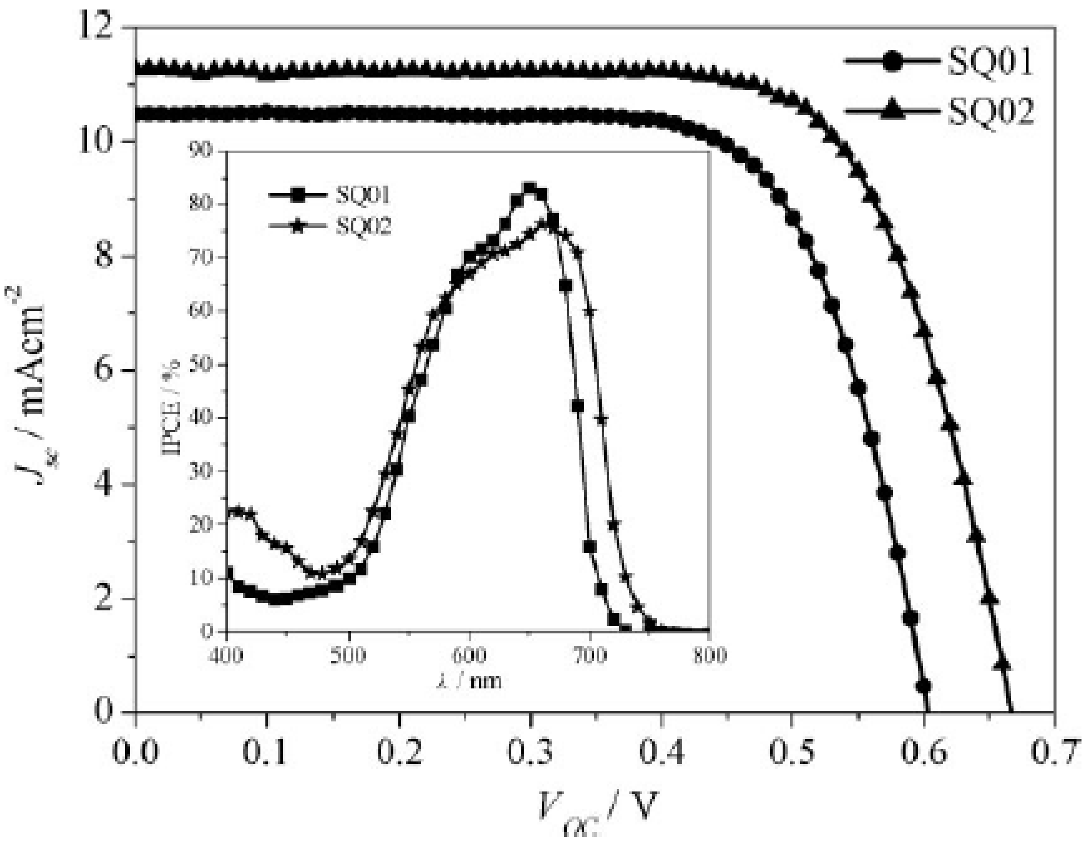
Drop: 12 mV, 2.3 mA/cm^2

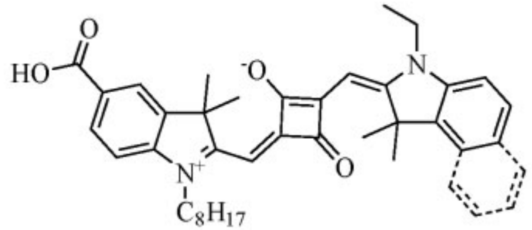
Interfacial Dynamics

Light soaking (1 sun + 60 °C) | **Heat stress (dark + 80 °C)**

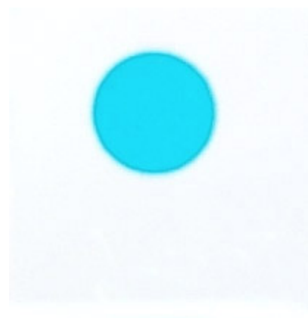


Red and NIR absorbing dyes





SQ01
SQ02 (----)



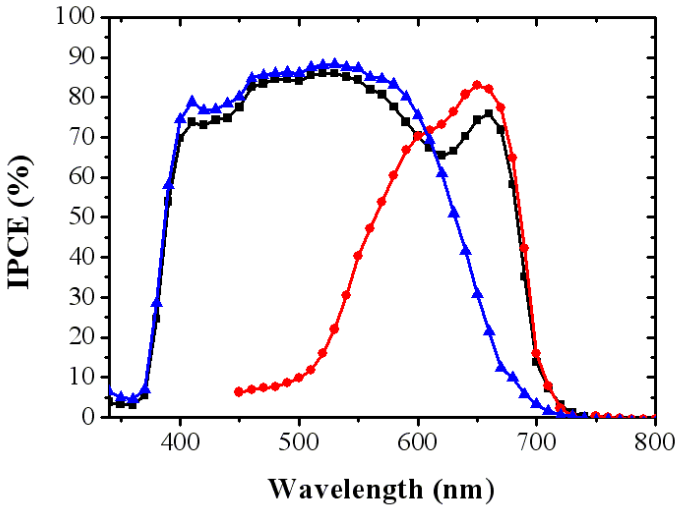
4.5% Sq1 in 2007
5.0% Sq2 in 2010
6.7% YR6 in 2011

J. Am. Chem. Soc., **2007**, *129,* 10320.
Adv. Funct. Mater., **2009**, *19,* 2720.
Angewandt chemie. Int. Ed., **2011,** *50*, 6619

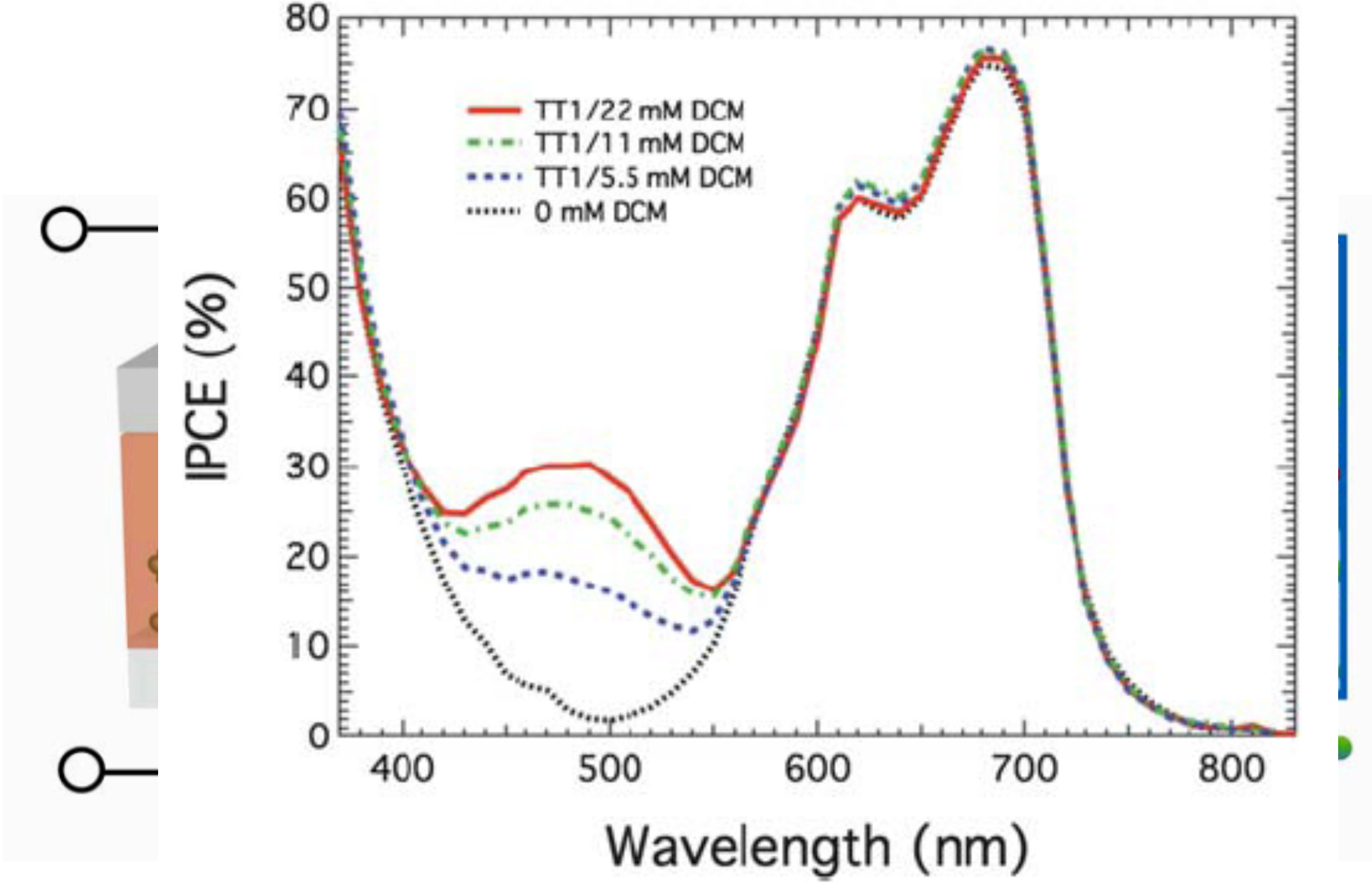
Panchromatic Response

1. Panchromatic dye
2. Co-sensitization
3. Energy transfer: Down or Up conversion

J.H. Yum et al. Energy & Environmental Science, 2011, 4, 842



J.-H. Yum et al., *Chem. Comm.,* **2007**, *4680.*
A. Ehret et al., *J. Phys. Chem. B*, **2001**, 105, 9960.
K. Sayama et al., *Sol. Energy Mater. Sol. Cells*, **2003**, 80, 47.
Y. Chen et al., *New J. Chem.*, **2005**, 29, 773.
V. P. S. Perera et al., *Sol. Energy Mater. Sol. Cells*, **2005**, 85, 91.



EPFL and Stanford University,

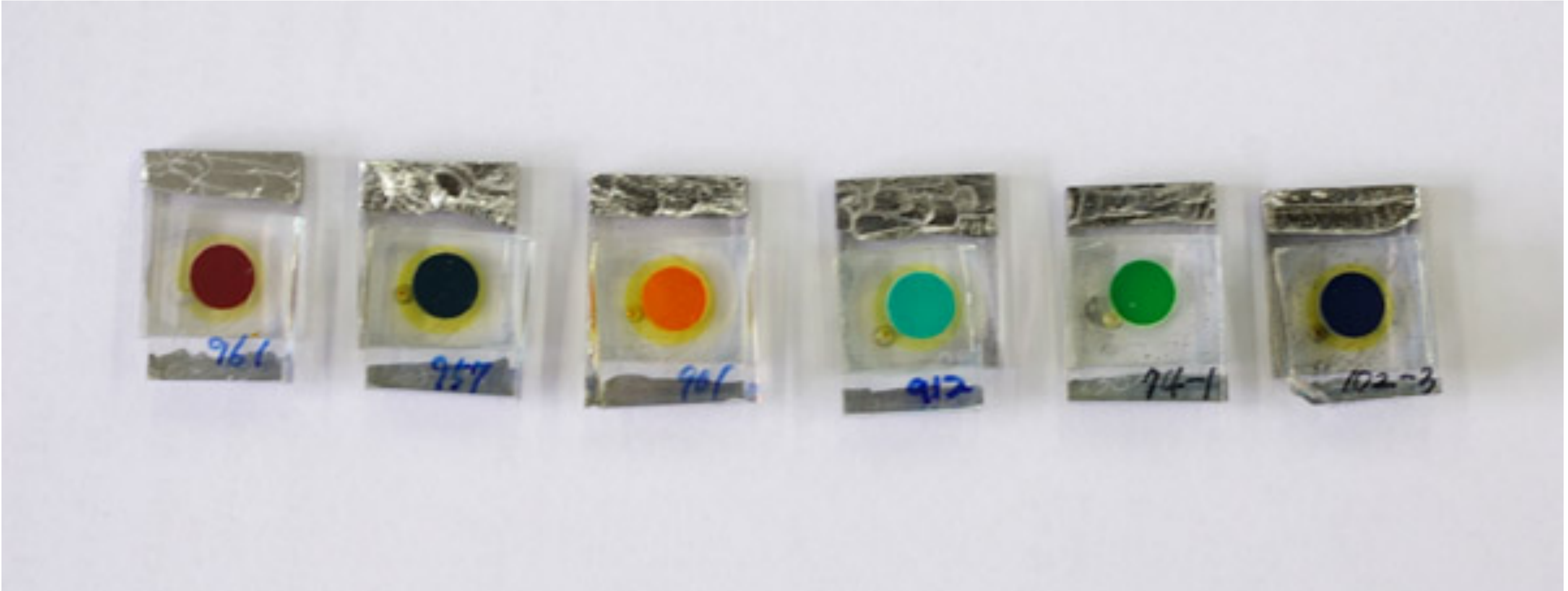
Nature Photonics, **2009**, *3*, *406*

Angewandte Chemie International Edition, **2009**, *48*, *9277-9280*

Energy & Environmental Science, **2010,** *4*, *434-437*

Nano Letters, **2010**, *10*, *3077-3083*

Chemphyschem, **2011**, 12, 657-661



$$\text{IPCE (EQE)} = \eta_{abs}\Phi_{cg}\eta_{coll}$$

η_{ab}: light harvesting efficiency

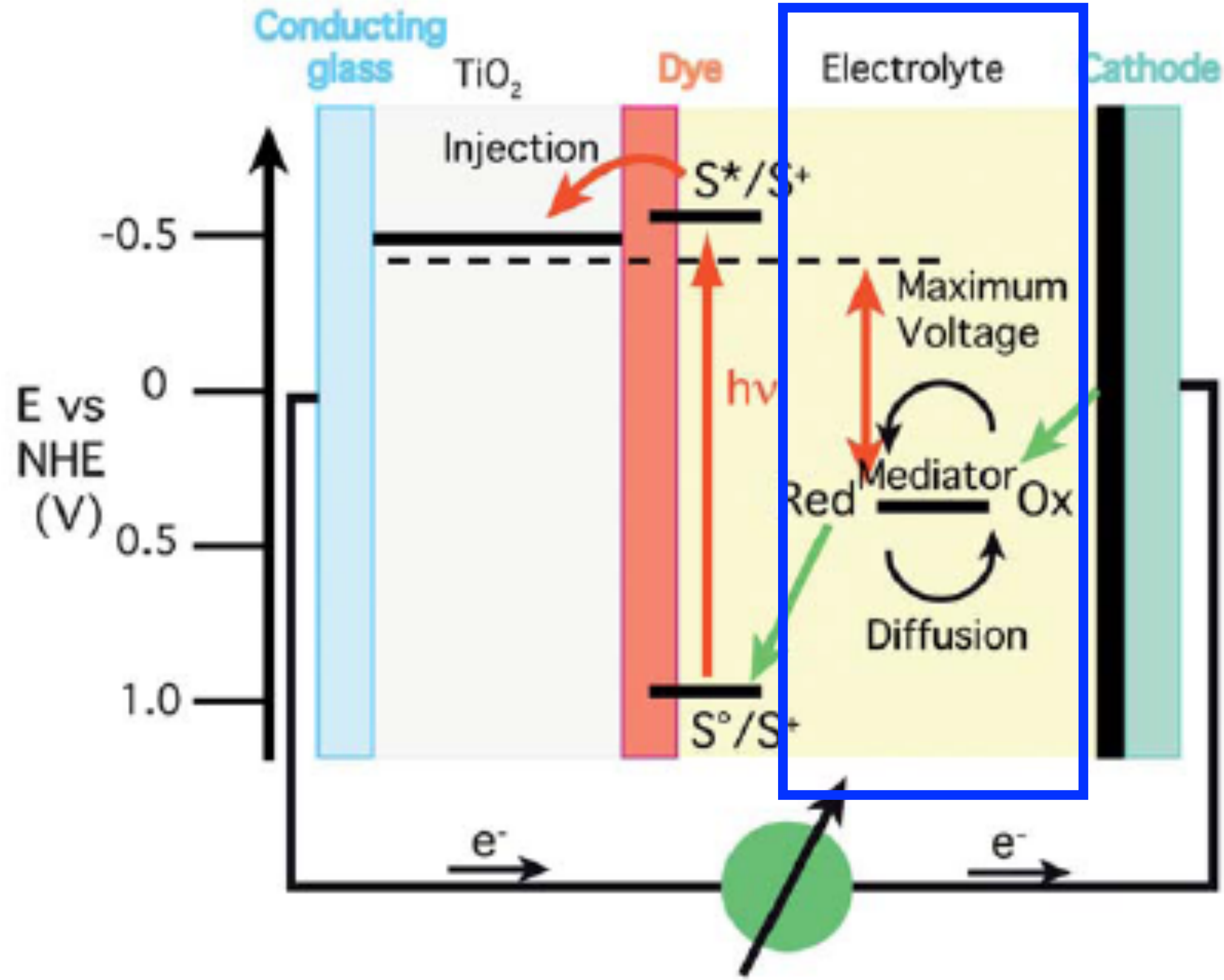
Φ_{cg}: quantum yield of charge carrier generation

$$\Phi_{cg} = \Phi_{\text{injection}}\,\Phi_{\text{dye regeneration}}$$

η_{coll} = efficiency of charge carrier collection

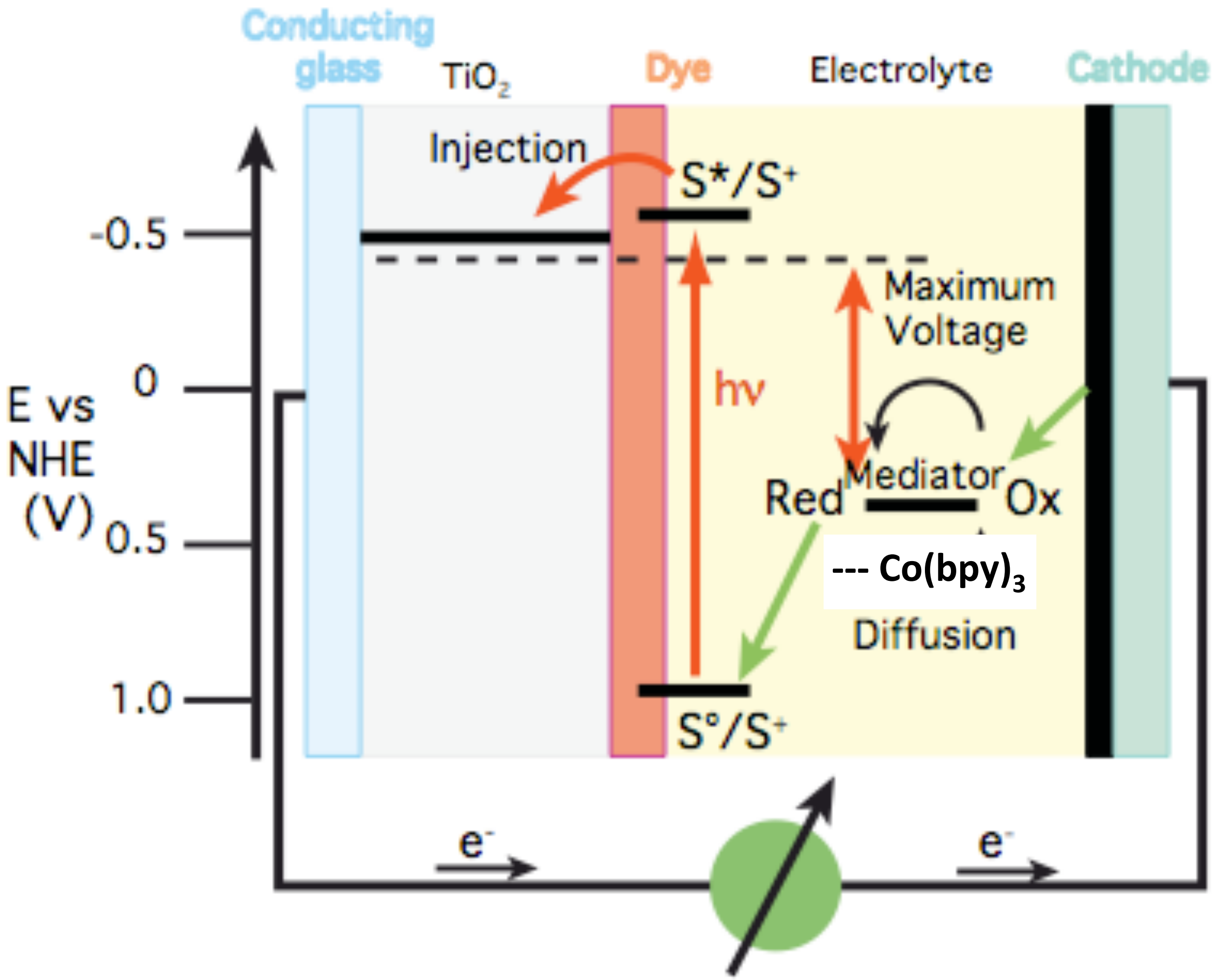
Ongoing and Future Research

- Advanced meso-structures
- New sensitizers
- New redox mediators
- New counter electrodes

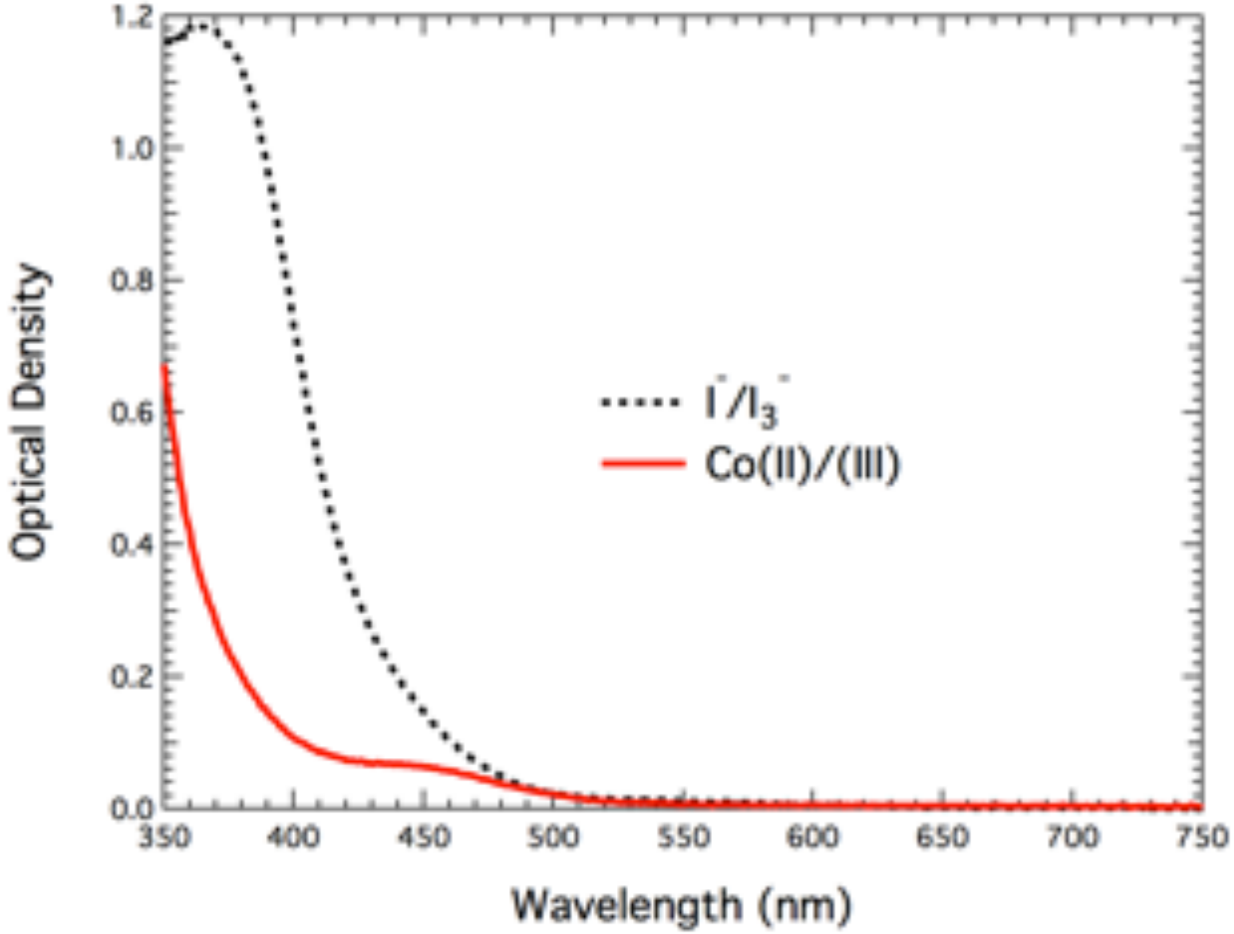


Conducting glass
TiO2
Dye
Electrolyte
Cathode
Injection
S*/S+
-0.5
Maximum Voltage
hv
E vs NHE (V)
0
Red
Mediator
Ox
0.5
Diffusion
1.0
S°/S+
e-
e-

Improvement by matching of energy levels



$$\eta_{global} = \frac{\left(I_{ph} \cdot V_{oc} \cdot FF\right)}{I_s}$$



Absorption spectra of Co(II)/Co(III) and I^-/I_3^- based electrolytes as applied in the DSSCs

$Co^{II}(dbbip)_2^{2+}$ Complex Rivals Tri-iodide/Iodide Redox Mediator in Dye-Sensitized Photovoltaic Cells

Hervé Nusbaumer, Jacques-E. Moser,* Shaik M. Zakeeruddin, Mohammad K. Nazeeruddin, and Michael Grätzel

Laboratory for Photonics and Interfaces, Institute of Physical Chemistry, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Received: May 31, 2001; In Final Form: August 6, 2001

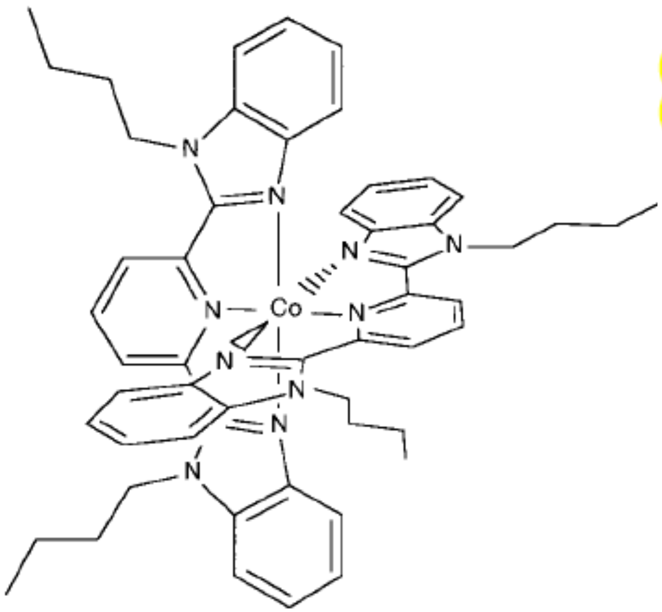
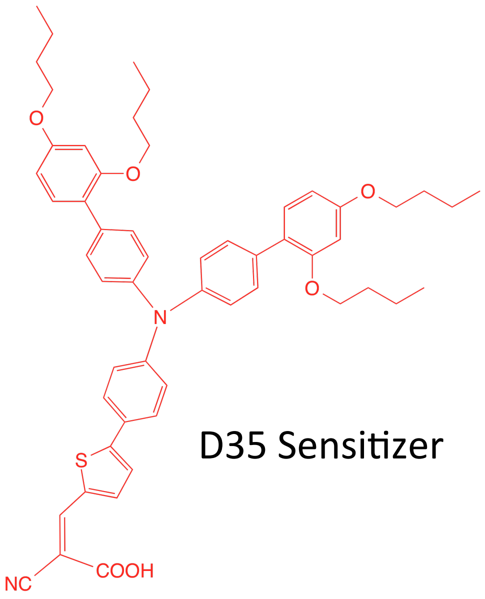


Table 3. Variations in photovoltaic performance parameters at three different illumination levels with an optimized electrolyte.

Power[a] [W m−2]	V_{OC} [mV]	J_{SC} [mA cm−2]	FF	η[b] [%]	IPCE[c] [%]
15	690	0.24	0.77	7.9	74
100	765	1.35	0.73	7.9	74
1000	840	8.40	0.56	3.9	74

[a] Incident illumination levels. [b] Efficiency. [c] IPCE at 540 nm with an illumination of 100 W m−2.



D35 Sensitizer

J|A|C|S ARTICLES

Published on Web 11/03/2010

Design of Organic Dyes and Cobalt Polypyridine Redox Mediators for High-Efficiency Dye-Sensitized Solar Cells

Sandra M. Feldt,† Elizabeth A. Gibson,† Erik Gabrielsson,‡ Licheng Sun,‡ Gerrit Boschloo,*,† and Anders Hagfeldt†

Department of Physical and Analytical Chemistry, Uppsala University, Box 259, 751 05 Uppsala, Sweden and Organic Chemistry, Center of Molecular Devices, Chemical Science and Engineering, Royal Institute of Technology, 100 44 Stockholm, Sweden

Received October 1, 2010; E-mail: gerrit.boschloo@fki.uu.se

Co(bipy)$_3$

Redox couple

Replacing iodide/ triiodide

Abstract: Dye-sensitized solar cells (DSCs) with cobalt-based mediators with efficiencies surpassing the record for DSCs with iodide-free electrolytes were developed by selecting a suitable combination of a cobalt polypyridine complex and an organic sensitizer. The effect of the steric properties of two triphenylamine-based organic sensitizers and a series of cobalt polypyridine redox mediators on the overall device performance in DSCs as well as on transport and recombination processes in these devices was compared. The recombination and mass-transport limitations that, previously, have been found to limit the performance of these mediators were avoided by matching the properties of the dye and the cobalt redox mediator. Organic dyes with higher extinction coefficients than the standard ruthenium sensitizers were employed in DSCs in combination with outer-sphere redox mediators, enabling thinner TiO_2 films to be used. Recombination was reduced further by introducing insulating butoxyl chains on the dye rather than on the cobalt redox mediator, enabling redox couples with higher diffusion coefficients and more suitable redox potential to be used, simultaneously improving the photocurrent and photovoltage of the device. Optimization of DSCs sensitized with a triphenylamine-based organic dye in combination with tris(2,2′-bipyridyl)cobalt(II/III) yielded solar cells with overall conversion efficiencies of 6.7% and open-circuit potentials of more than 0.9 V under 1000 W m^{-2} AM1.5 G illumination. Excellent performance was also found under low light intensity indoor conditions.

DOI: 10.1002/cssc.201100120

Cyclopentadithiophene Bridged Donor–Acceptor Dyes Achieve High Power Conversion Efficiencies in Dye-Sensitized Solar Cells Based on the *tris*-Cobalt Bipyridine Redox Couple

Hoi Nok Tsao, Chenyi Yi, Thomas Moehl, Jun-Ho Yum, Shaik M. Zakeeruddin, Mohammed K. Nazeeruddin, and Michael Grätzel*[a]

The dye-sensitized solar cell (DSSC) is attracting widespread attention as a promising technology for a new generation of photovoltaic (PV) systems. Mimicking the principle of natural photosynthesis, its ecological and economical fabrication processes make it an attractive and credible alternative to conventional PV systems.[1–3] One of the key components of a DSSC is the hole conductor (HC), which transports positive charge carriers from the sensitizer to the back contact of the device. Electrolytes containing the I^-/I_3^- redox system are commonly used as HCs because of their high reliability and good power conversion efficiency (PCE);[3,4] however, the I^-/I_3^- redox couple suffers from a low redox potential, necessitating an excessive thermodynamic driving force for the dye-regeneration reaction. This limits the open-circuit potential of current DSSCs to 0.7–0.8 V. Iodide-containing electrolytes also corrode a number of metals, such as Ag and Cu, which imposes restrictions on the materials that can be used as current collectors in DSSC modules. In this context the development of stable, noncorrosive redox couples with higher redox potentials than I^-/I_3^- is warranted. A wide variety of alternative redox mediators have been investigated in the past, including halogenides[4,5] or pseudohalogenides,[6,7] organic radicals[8] or thiols,[9] and inorganic[10] or organic[11] p-type conductors. So far, all of these redox mediators exhibited inferior PCEs compared to the I^-/I_3^- couple, especially under full sunlight.[9,12,13] This also holds for cobalt polypyridine complexes, the PCE of which remained below 5% under standard AM 1.5G conditions, despite extensive investigations during the last decade.[12,14]

Remarkably, Feldt et al. recently increased the PCE to 6.7% by employing a newly designed donor-π-acceptor (D-π-A) sensitizer, coded **D35**, in conjunction with a cobalt(II/III) tris-bipyridyl redox shuttle.[15] However, **D35** harvests sunlight only below 620 nm, limiting the short-circuit photocurrent (J_{SC}) to 10–11 mA cm^{-2}. Herein, by using judicious molecular engineering, we extend the spectral response of **D35** significantly into the red by introducing a cyclopentadithiophene (CPDT)[16a] bridging unit in the D-π-A structure, as shown in the inset of Figure 1a. Details concerning the synthesis and characterization of the dye are given in the Supporting Information. Owing to its enhanced solar energy harvesting the novel dye 3-{6-{4-[*bis*(2′,4′-dihexyloxybiphenyl-4-yl)amino-]phenyl}-4,4-dihexyl-cyclopenta-[2,1-*b*:3,4-*b*′]dithiphene-2-yl}-2-cyanoacrylic acid, coded **Y123**, exhibits a J_{SC} that is 40% higher than **D35**, reaching almost 15 mA cm^{-2} under full sunlight and an unprecedented PCE of up to 9.6% with the $[Co^{II}(bpy)_3](B(CN)_4)_2/[Co^{III}(bpy)_3](B(CN)_4)_3$ redox couple.

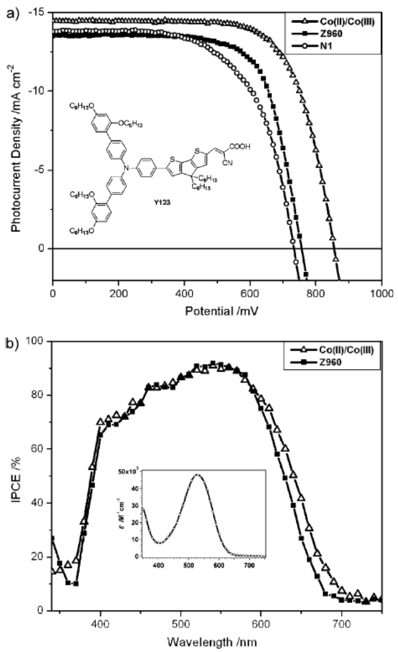
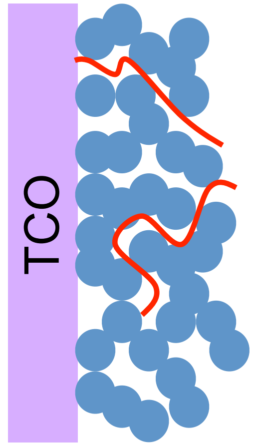


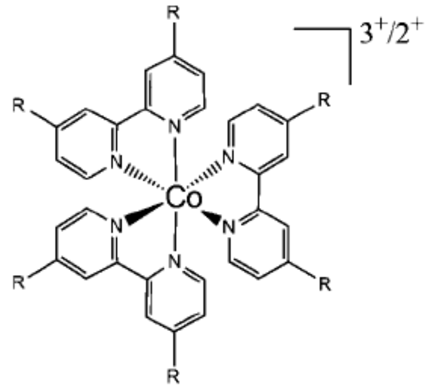
Figure 1. a) Photocurrent–voltage response at simulated full AM 1.5G sunlight employing **Y123** sensitized mesoscopic anatase films together with $[Co^{II}(bpy)_3](B(CN)_4)_2/[Co^{III}(bpy)_3](B(CN)_4)_3$ or I^-/I_3^- based redox electrolytes (inset: chemical structure of **Y123**). b) IPCE spectra of **Y123**-sensitized DSSCs employing $[Co^{II}(bpy)_3](B(CN)_4)_2/[Co^{III}(bpy)_3](B(CN)_4)_3$ and I^-/I_3^- (**Z960**) redox couples. The inset shows the electronic absorption spectrum of **Y123** in $CHCl_3$.

[a] *Dr. H. N. Tsao,+ Dr. C. Yi,+ Dr. T. Moehl, Dr. J.-H. Yum, Dr. S. M. Zakeeruddin, Dr. M. K. Nazeeruddin, Prof. M. Grätzel*
École Polytechnique Fédérale de Lausanne
Institute of Chemical Sciences and Engineering
Laboratory of Photonics and Interfaces
1015 Lausanne (Switzerland)
Fax: (+41) 216936111
E-mail: michael.graetzel@epfl.ch
[+] *These authors contributed equally to this manuscript.*

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201100120.



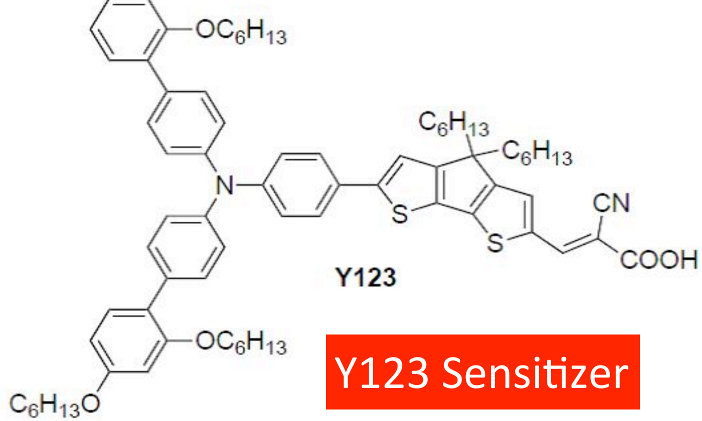
nc TiO_2



Redox shuttle

Enlargement of pore size from 23nm to 32 nm avoids mass transfer limitation of photo current.

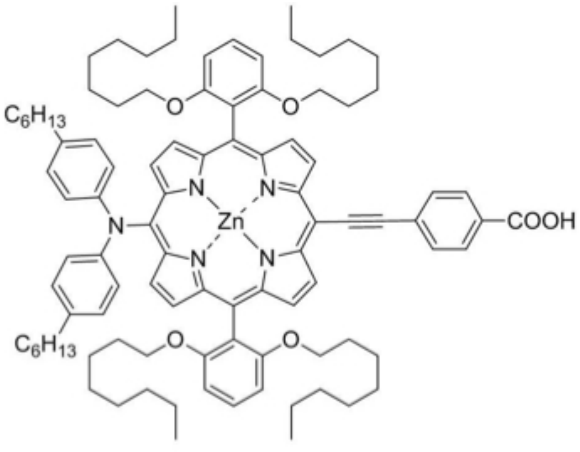
Y123

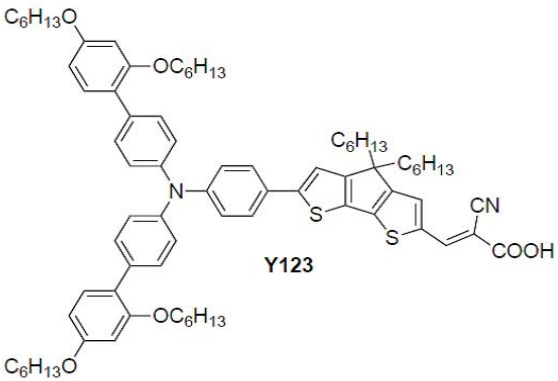


Y123 Sensitizer

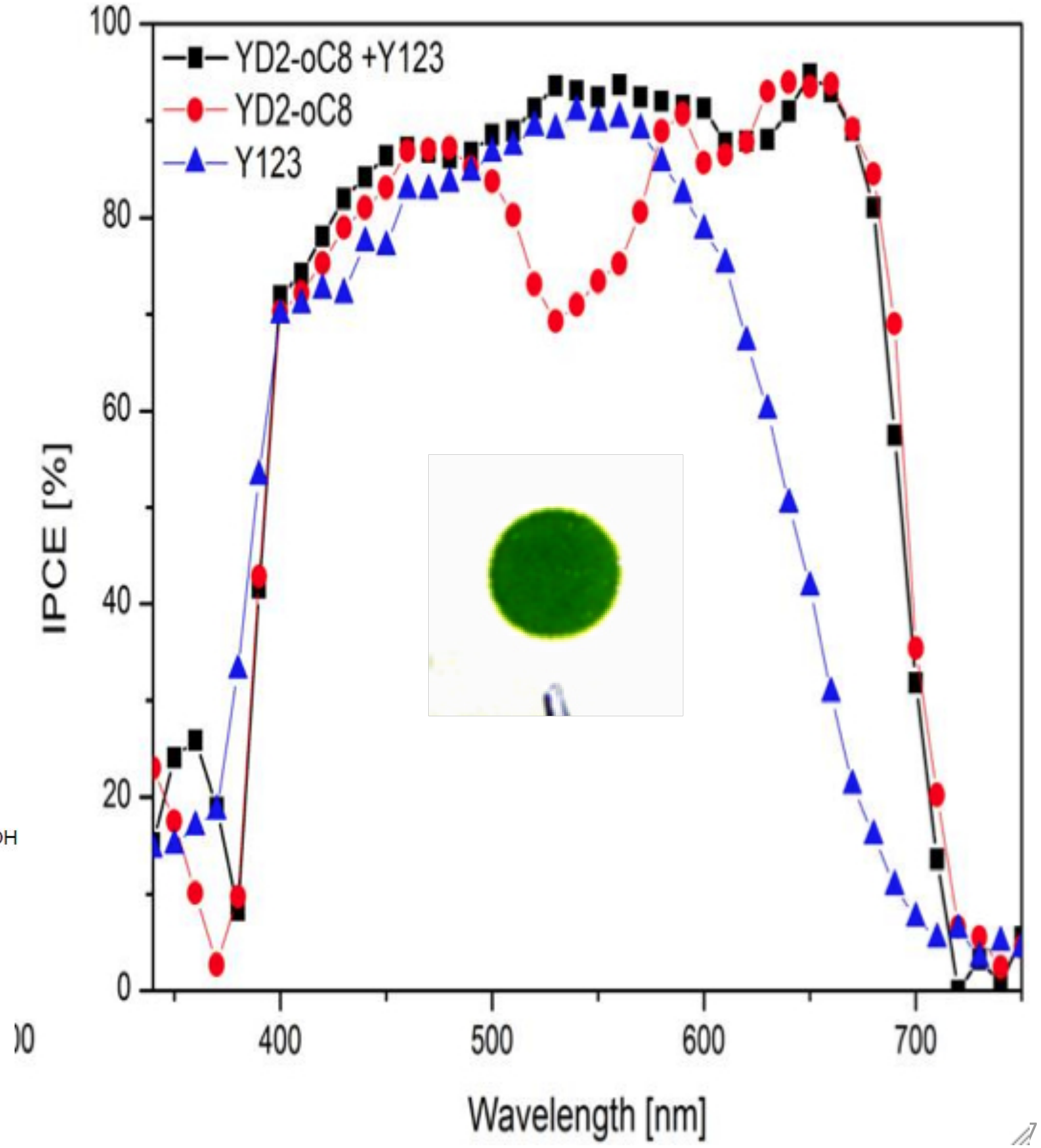
New Record efficiency achieved by Y123/YD2-*o*-C8 co-sensitization

YD2-*o*-C8





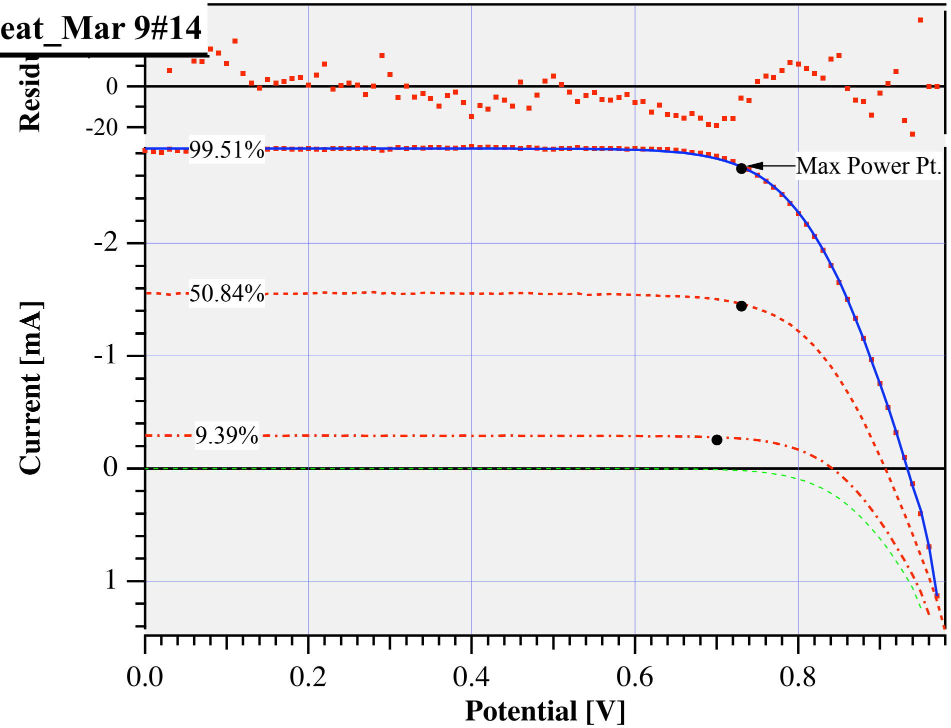
Y123

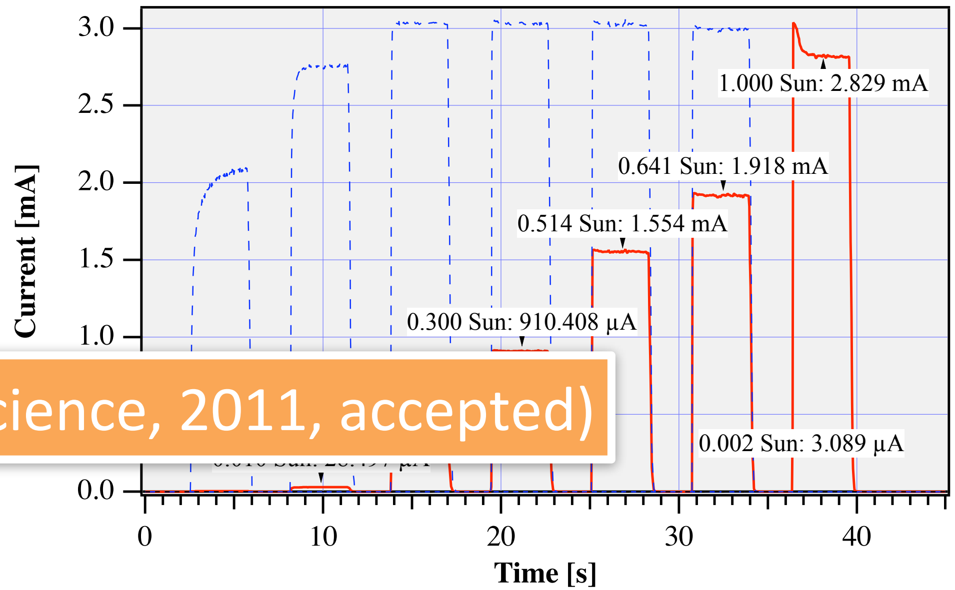


Cell Name: 08032011_YA1074_repeat_Mar 9#14

Measurement Date	: Wed, Mar 9, 2011 / 12:57:13 AM
Type of cell	: AY_Al Back
Cell Active Area	: 0.16 cm^2
Light Source	: Xe 450W @ AM1.5G
Dye Sensitiser	: B11, 0.3mM, tBu/Ac, Dinhop4:1
Additional Remarks	: MG8 + Y123
Electrolyte h+ Conductor	: 3/4 co2 & 1.5 Co3 + 0.8 M TBP
Working Temperature	: 298 K
SemiConductor Layer	: Nok 5/4 + 2.5mL TiCl4
Layer Thickness, Porosity	: 5 µm, 68 %
Working Electrode Glass	: NSG 10/cm
Counter Electrode Type	: LOF 7/Pt
Data File Name	: 08032011_YA1074_repeat_Mar 9#14
Current Compliance	: 2 mA
Settling Time, ΔU, Meas. Delay	: 0.04 s, 10 mV, 0s

	9.4% Sun	**50.8% Sun**	**99.5% Sun**
$Thermopile_{ref}$	-296.576 µSun	-1.597 mSun	-10.273 µSun
$Current_{ref}$	-355.163 µA	-1.923 mA	-3.764 mA
$Power_{in}$	9.391 mW / cm^2	50.841 mW / cm^2	99.515 mW / cm^2
Norm. Std. Dev.	0.25	0.32	0.37
Module U_{oc}	841.56 mV	906.35 mV	933.87 mV
Cell U_{oc}	841.56 mV	906.35 mV	933.87 mV
I_{sc}	-293.243 µA	-1.555 mA	-2.825 mA
J_{sc}	-1.833 mA / cm^2	-9.722 mA / cm^2	-17.659 mA / cm^2
U_{pmax}	702.33 mV	727.91 mV	727.18 mV
I_{pmax}	-1.7 mA / cm^2	-9.2 mA / cm^2	-16.9 mA / cm^2
$Power_{out}$	1.22 mW / cm^2	6.69 mW / cm^2	12.27 mW / cm^2
Total $Power_{out}$	195.59 µW	1.07 mW	1.96 mW
Fill Factor	0.793	0.759	0.744
Efficiency η	13.02%	13.15%	12.33%





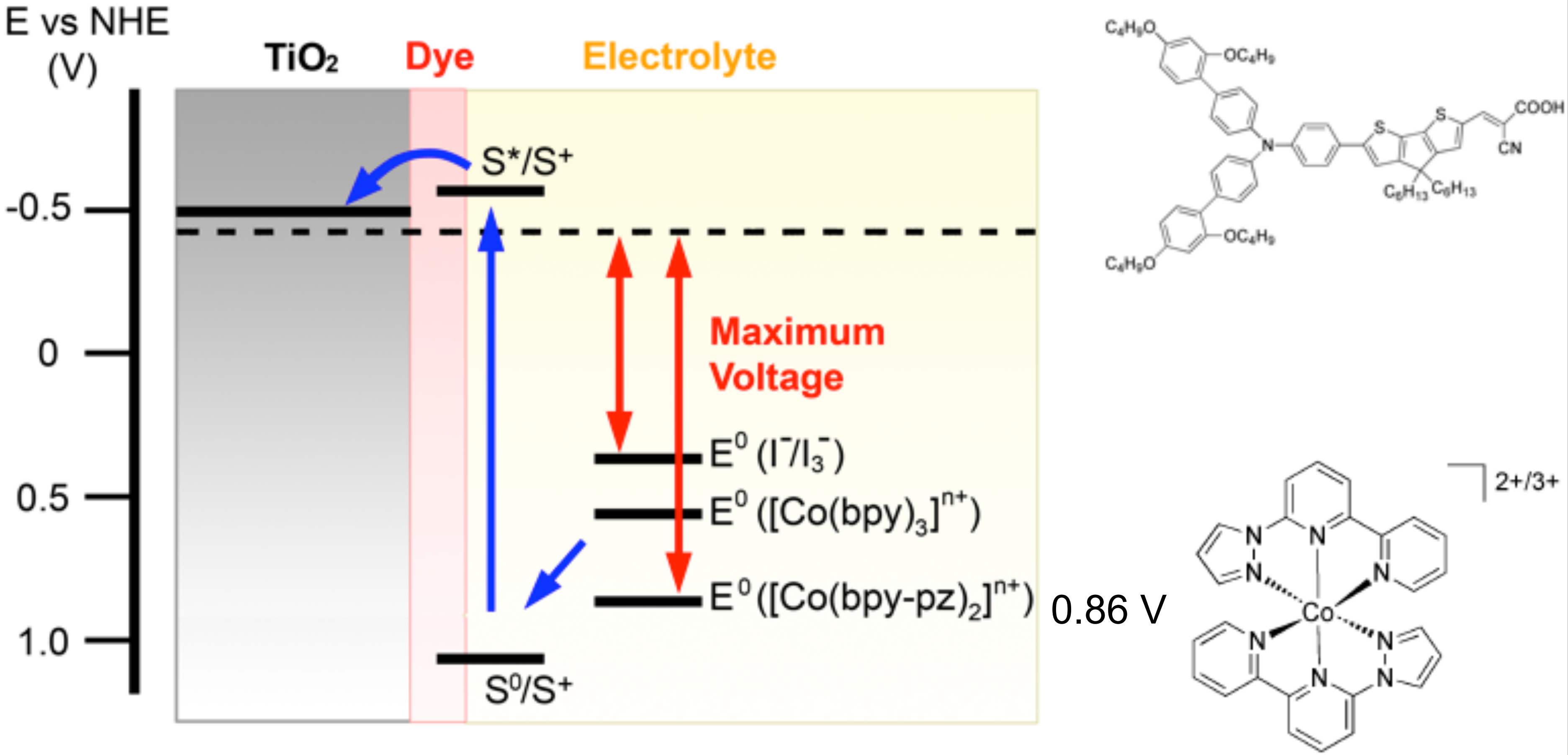
A recent new efficiency record ! (Science, 2011, accepted)

Series Resistance @ 1 Sun: 25.73 ± 1.3 %, (160.83 /cm ^{2})

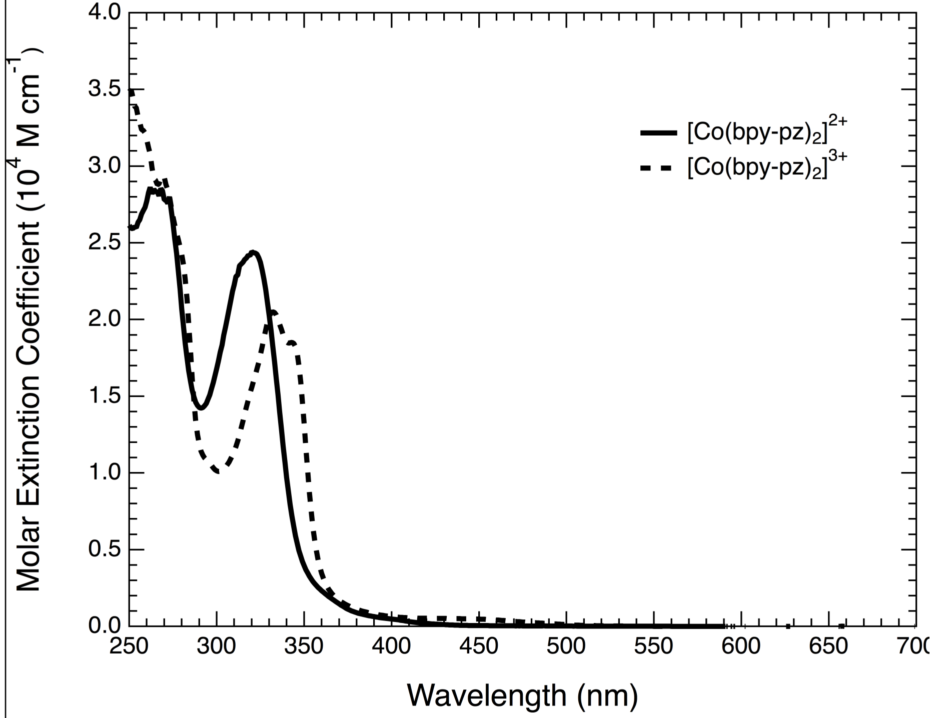
Calibration File: KIDAC: Ref Cell#9, Mon, Jan 14, 2008

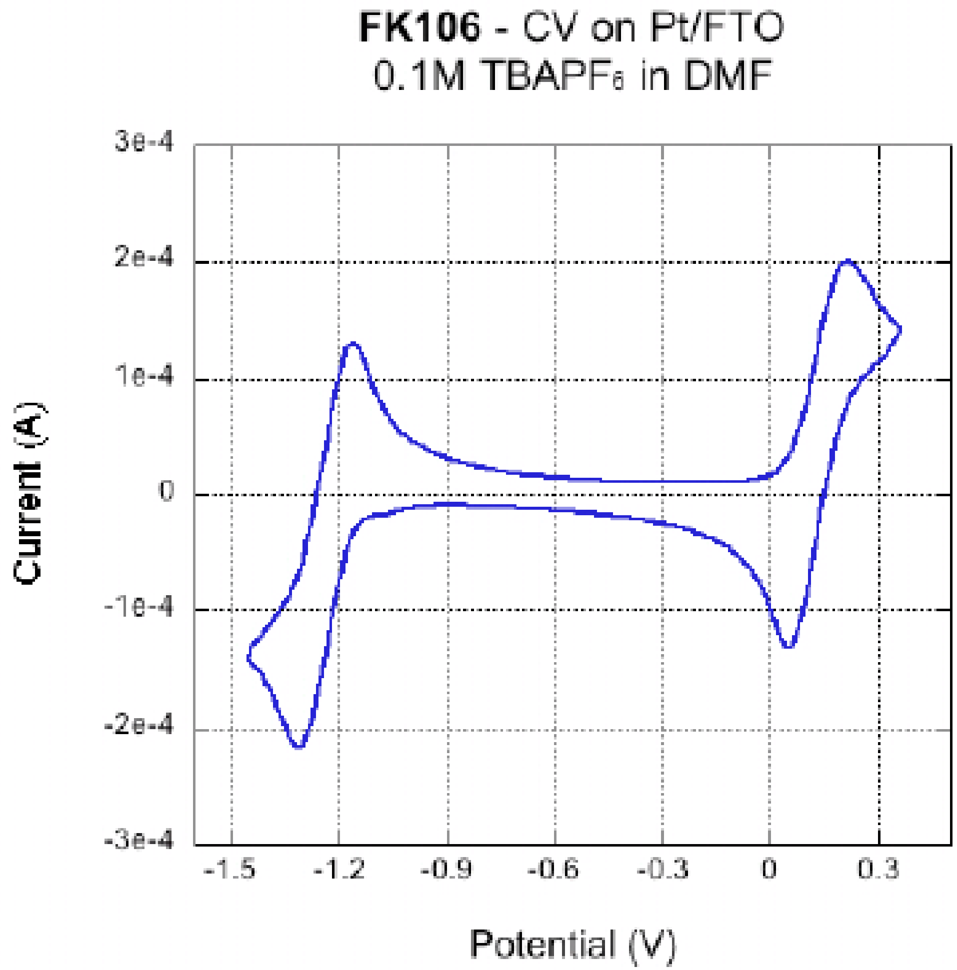
© RAHB: KIDAQX *Measured by Takeru* *Date: Wed, Mar 9, 201*

New Redox Shuttle resulted in over 1000 mV



The high oxidation potential compared to $[Co(bpy)_3]^{2+/3+}$ is ascribed due to the presence of pyrazoles, which stabilize highest occupied molecular orbital's (HOMO) of the metal more than the bipyridine ligand.





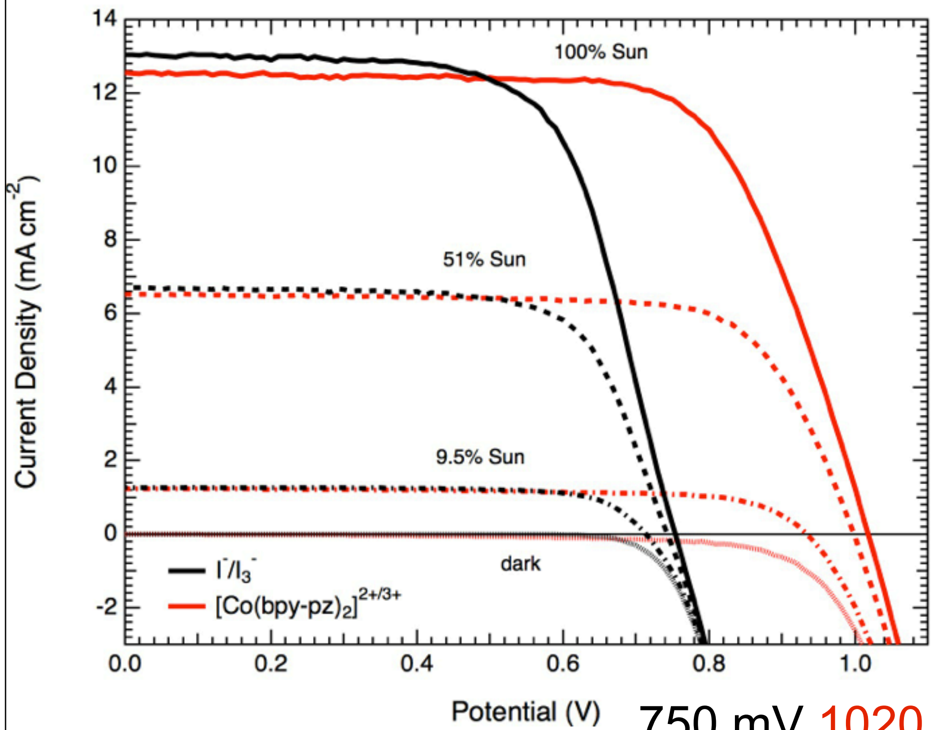
$[Co(bpy\text{-}pz)_2]^{2+/3+}$ system has absorption maxima in the UV region :

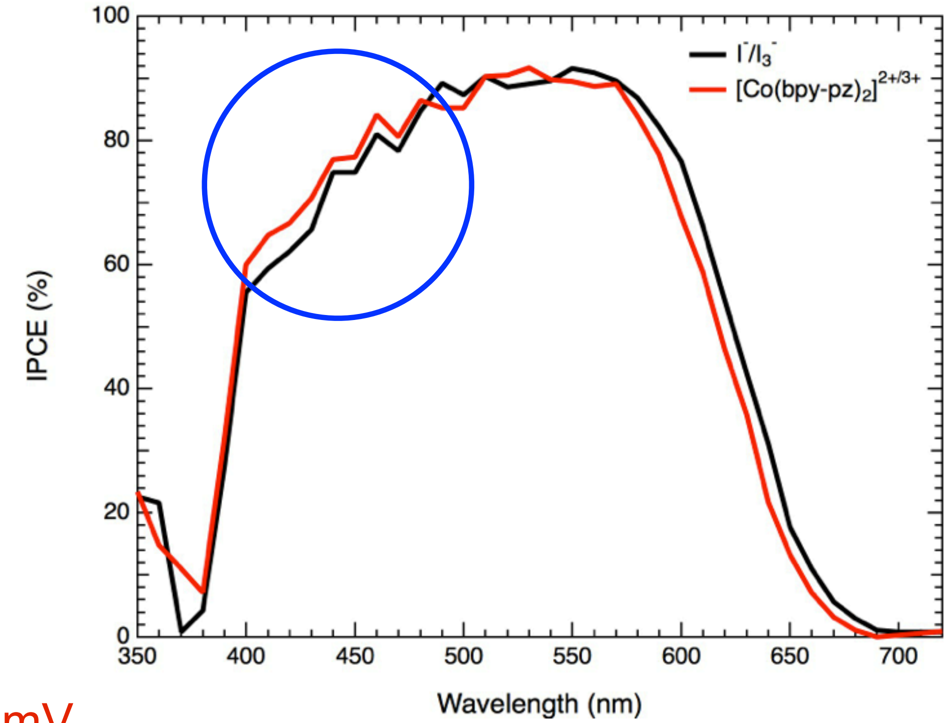
λ_{max} (ε) = 265 (28,300), 320 nm (24,400) for $[Co(bpy\text{-}pz)_2]^{2+}$,

λ_{max} (ε) = 240 (35,500), 276 nm (20,500) for $[Co(bpy\text{-}pz)_2]^{2+}$.

In the visible region, only the weak absorption remains and thus evidently enh ances the blue-response of the photocurrent by the sensitizer.

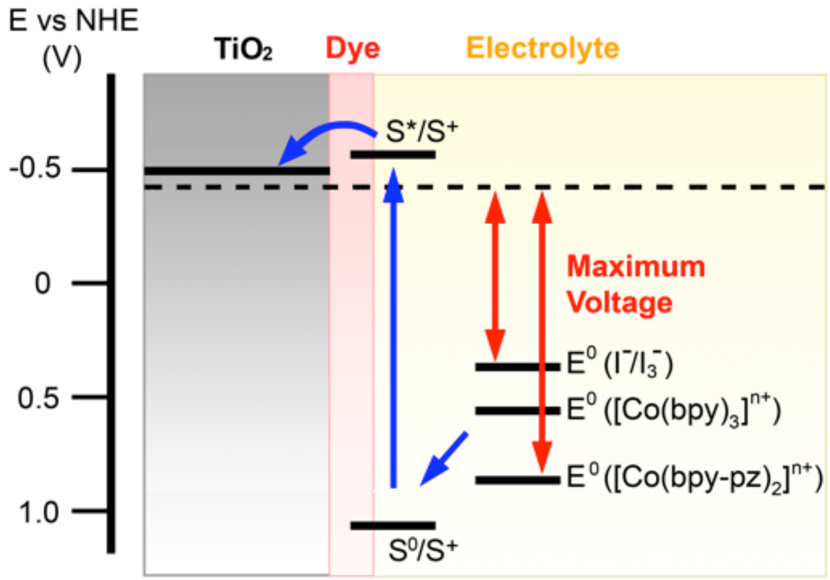
New Redox Shuttle resulted in over 1000 mV





750 mV 1020 mV

J.H. Yum et al., *Nature Communications*, accepted



IPCE (EQE) $= \eta_{abs}\Phi_{cg}\eta_{coll}$

η_{ab}: light harvesting efficiency

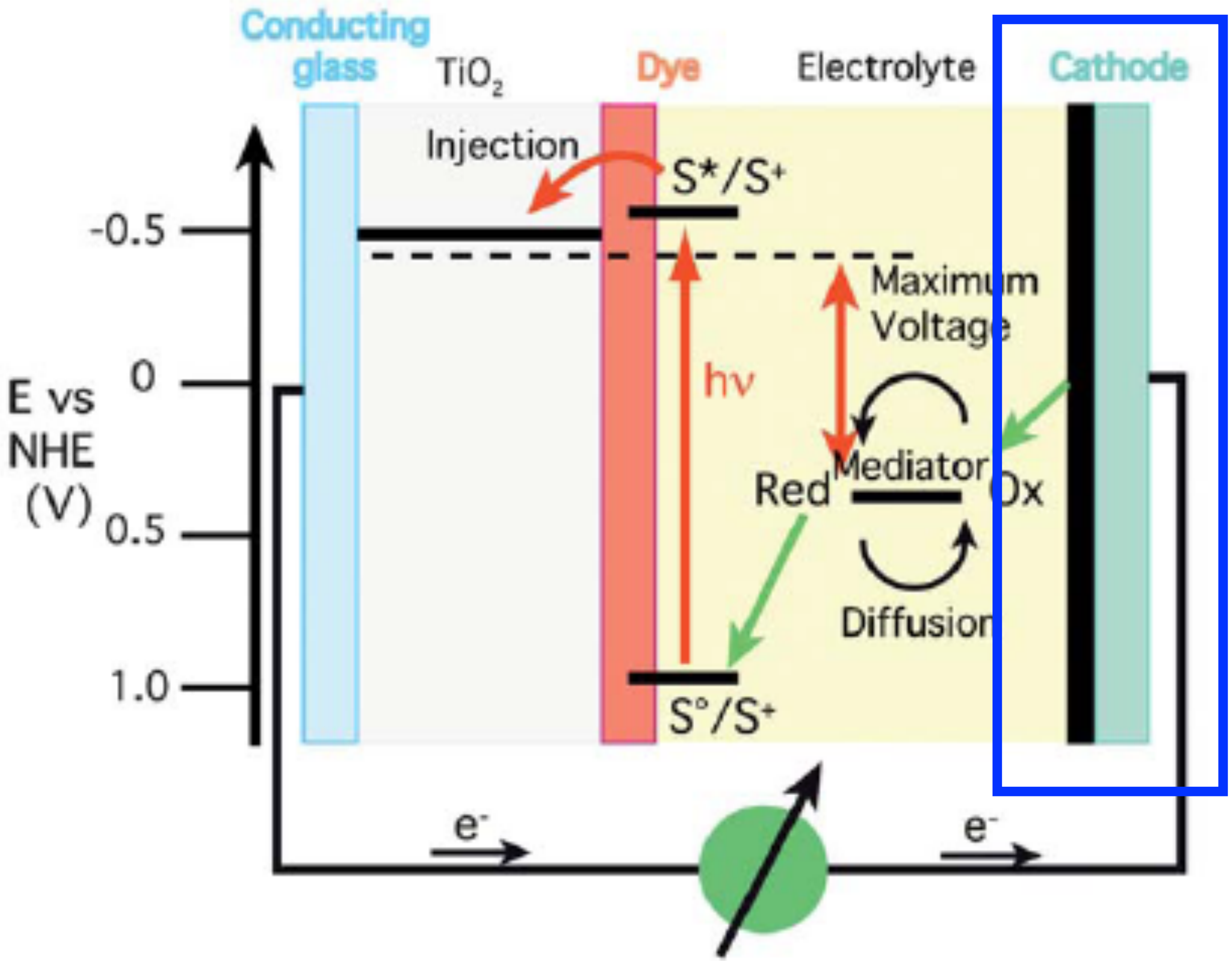
Φ_{cg}: quantum yield of charge carrier generation

$\Phi_{cg} = \Phi_{injection}\ \Phi_{dye\ regeneration}$

η_{coll} = efficiency of charge carrier collection

Ongoing and Future Research

- Advanced meso-structures
- New sensitizers
- New redox mediators
- New counter electrodes

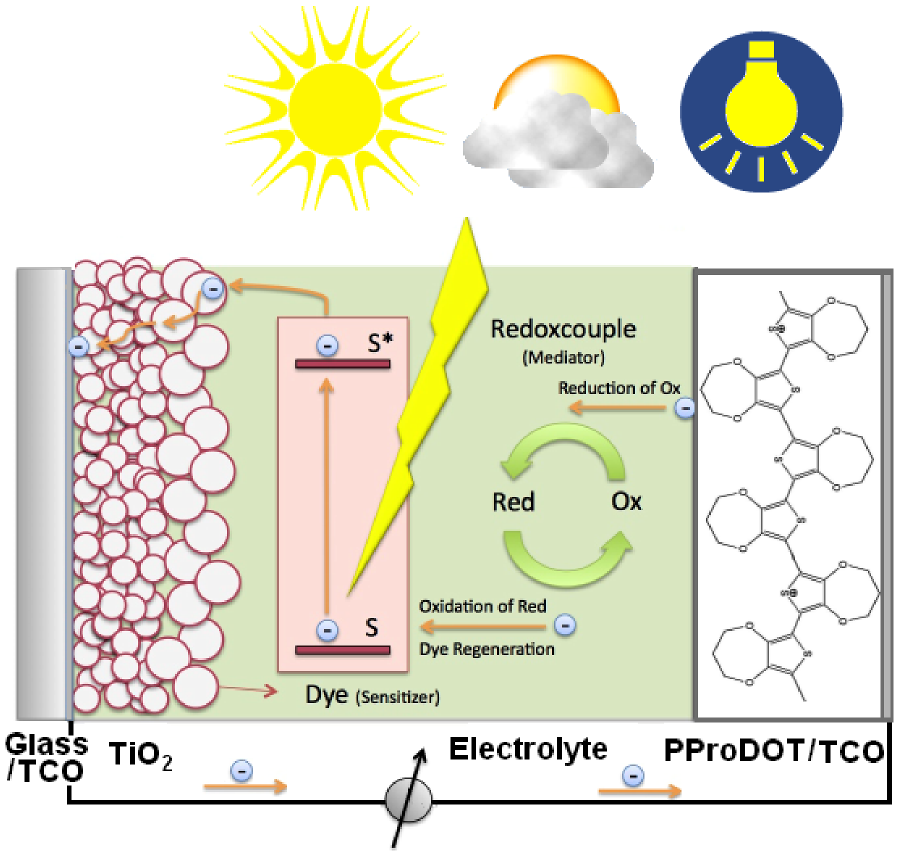

Conducting glass
TiO2
Dye
Electrolyte
Cathode
Injection
S*/S+
-0.5
Maximum Voltage
E vs NHE (V)
0
hν
0.5
Red
Mediator
Ox
Diffusion
1.0
S°/S+
e-
e-

Counter Electrode

1. High electrical conductivity

2. Excellent catalysis on the reduction of oxidized redox

3. Pt: high price and corrosion possibility



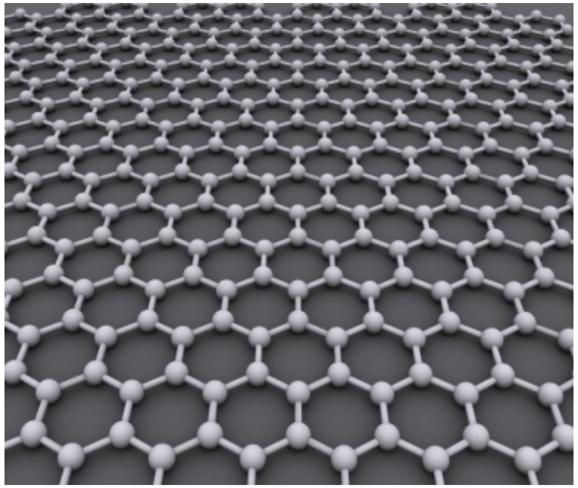
Chemphyschem, **2010**, 11(13), 2814-2819
Journal of Materials Chemistry, **2010**, 20(9), 1654-1658

Graphene/glass: **[4L-G/glass]**

T_{550} = 97.7% [≈ 90%]
R_{CT} ≈ >kΩcm^2 ? [-]
R ≈ 2 kΩ/sq [350 Ω/sq]

intrinsic limit: ≈ 30 Ω/sq (mobility 200 000 cm V^{-1} s^{-1} scattering by the acoustic phonons, not by the substrate)

Li et al. *Nano Lett.* **2009,** 9, 4359.



Andre Geim and Konstantin Novoselov
Nobel Prize 2010

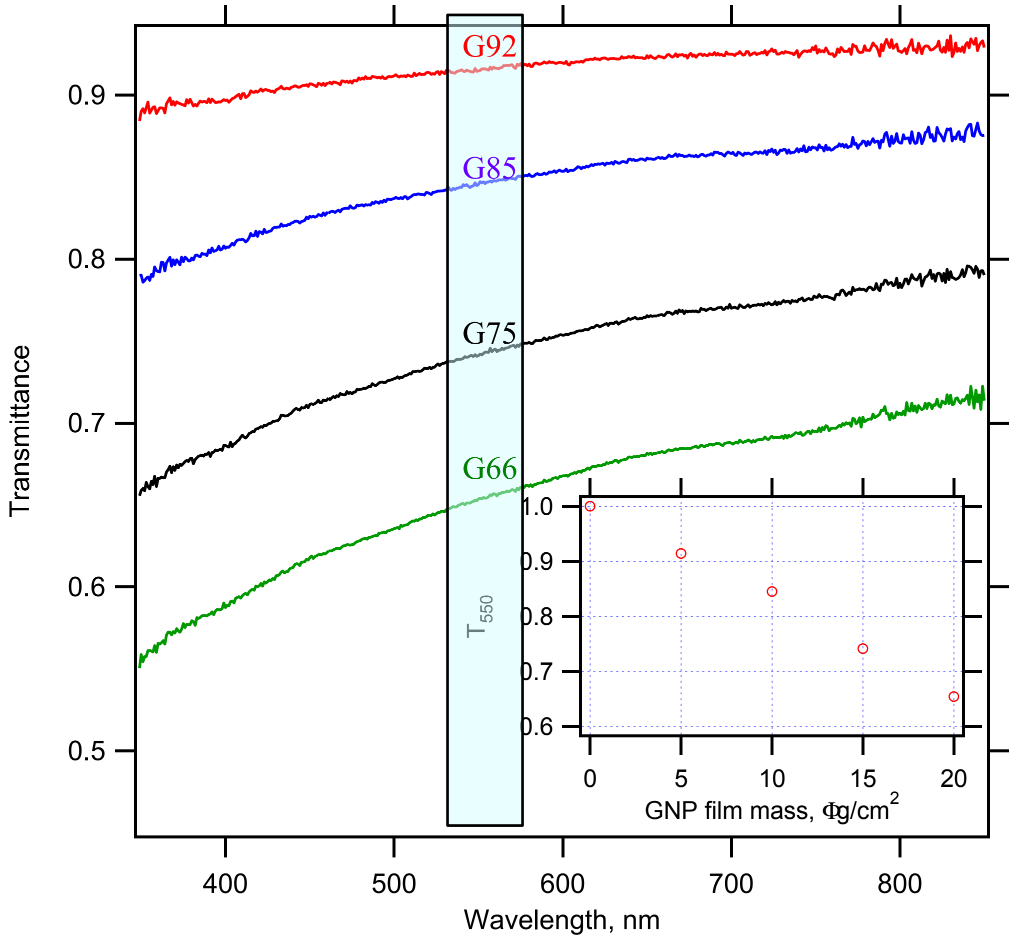
Required for DSC cathode:

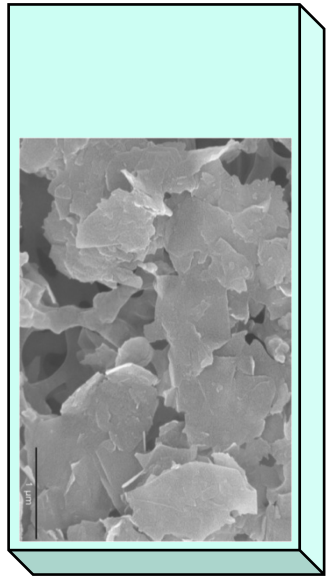
T_{550} = 80%
R_{CT} = 2-3 Ωcm^2
R = 20 Ω/sq

Trancik et al. *Nano Lett.* **2008,** 8, 982.

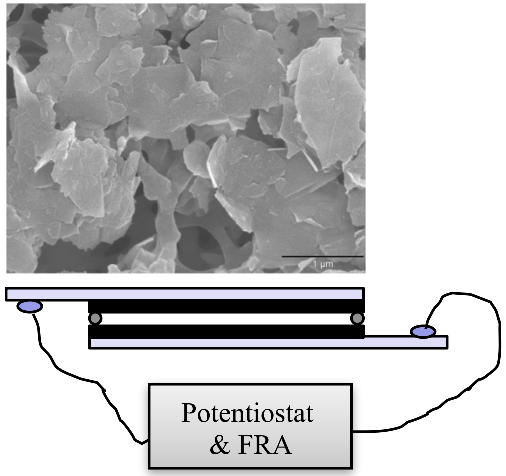
GNP nanoplatelets: several sheets of graphene with an overall thickness of ~ 5 nanometers (ranging from 1 nm to 15 nm) and particle diameters less than 2 microns

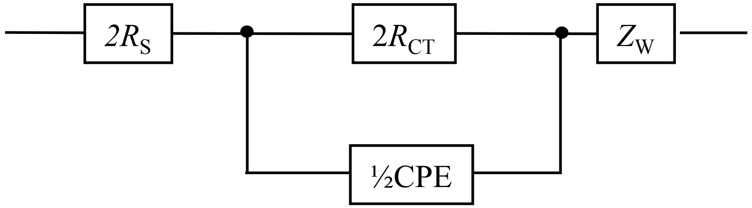
Surface area of 600 - 750 m^2/g





Optical transmittance of GNP films. Inset shows the transmission at a wavelength of 550 nm (T_{550}) as a function of film's mass.

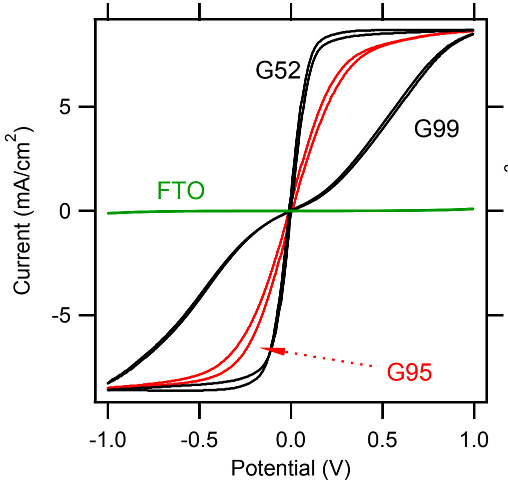


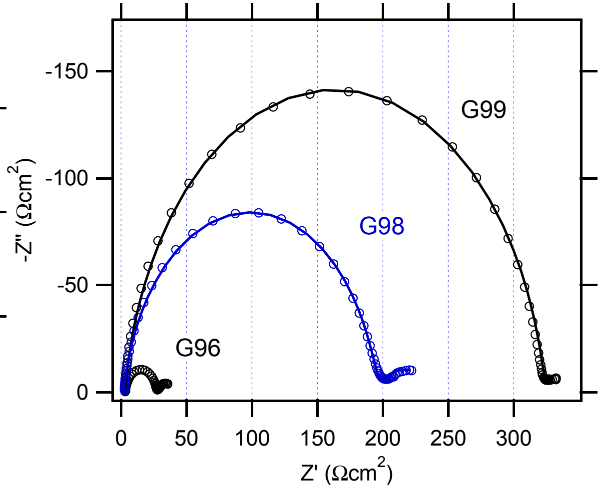


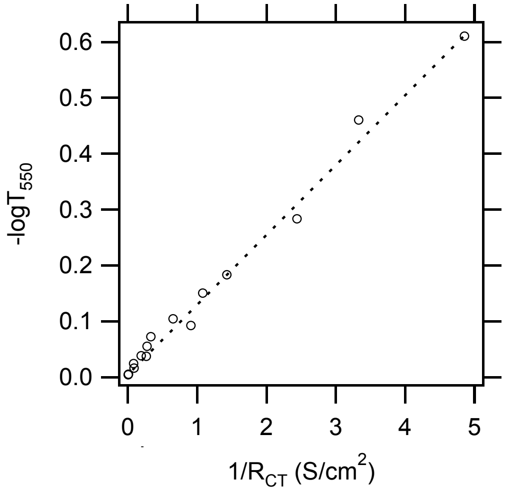
Left top chart: CV; scan rate 10 mV/s.

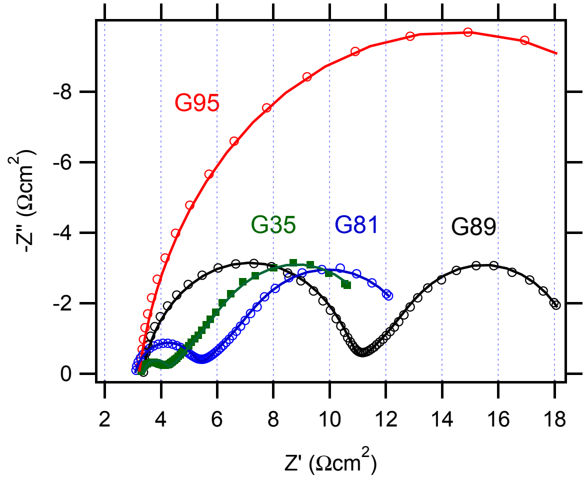
Right top and bottom charts: EIS from 65 kHz to 0.1 Hz (bias 0 V).

Left-bottom: Optical absorbance at a wavelength of 550 nm as a function of inverse charge transfer resistance.



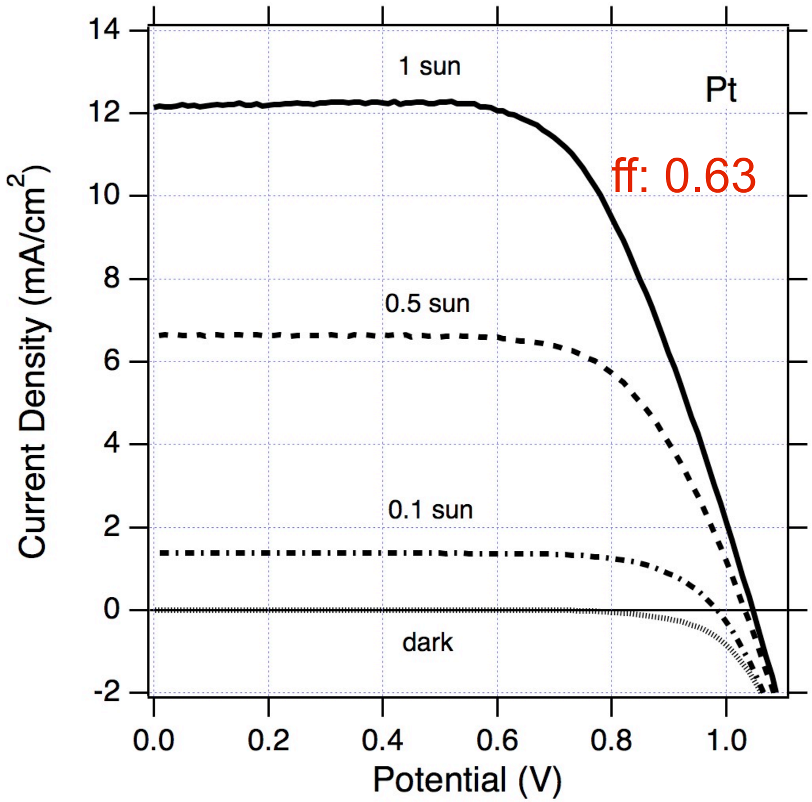




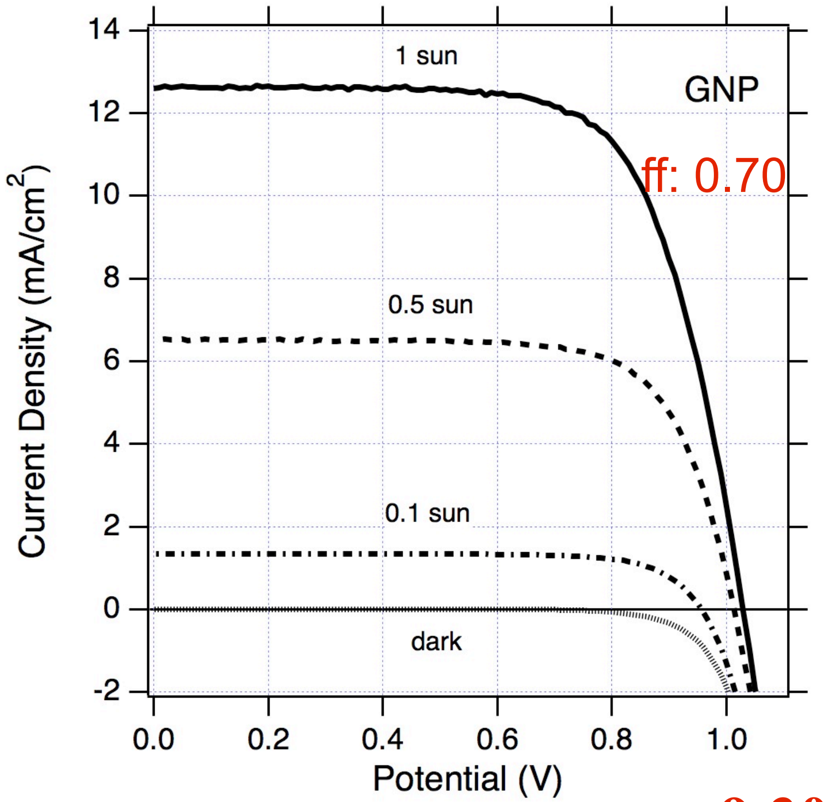


Current-voltage characteristics of dye sensitized solar cells.

Left chart: DSC with Pt-FTO ; Right chart: DSC with GNP (G66).

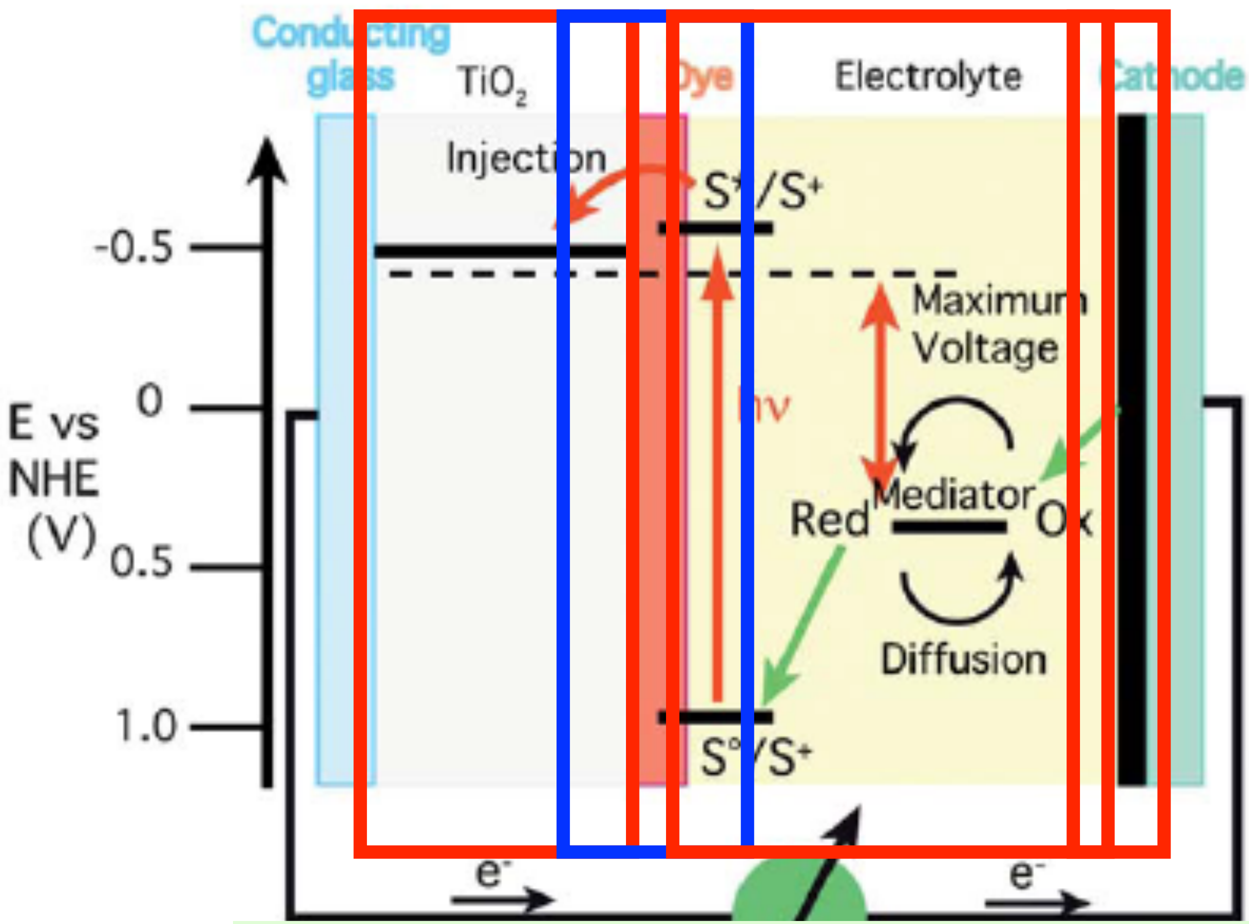


8.1%



9.3%

L. Kavan and J.H. Yum et al., ACS Nano accepted.



IPCE (EQE) $= \eta_{abs} \Phi_{cg} \eta_{coll}$

η_{ab}: light harvesting efficiency

Φ_{cg}: quantum yield of charge carrier generation

$\Phi_{cg} = \Phi_{injection}\, \Phi_{dye\ regeneration}$

η_{coll} = efficiency of charge carrier collection

The members of LPI

- **Michael Grätzel**
- **PhD Students** : Hauke Harms, Philippe Labouchère Adriana Paracchino, Magdalena Marszalek, Jérémie Brillet, Florian Le Formal, Pootrakulchote Nuttapol, Maurin Cornuz, Julian Burschka, Amalie Dualeh, Aravind Kumar Chandiran, Leo Phillip Heininger
- **Postdocs:** Yella Aswani, Celine Leroy, Etienne Baranoff, Takeru Bessho, Takashi Hisatomi, Kevin Sivula, Jun-Ho Yum, Nok Tsao, Chenyi Yi, Peng Gao, Jared Heath Delcamp, Etienne Baranoff, Lioz Etgar, Julien Edouard Frey, Florian Kessler, Il Jung

  Thomas Moehl, Soo-Jin Moon
- **Staff Scientists**: Robin Humphrey Baker, François Rotzinger. Guido Rothenberger, Jaques Moser (titled professor), Peter Pechy, Carole Grätzel, Kuppuswamy Kalyanasundaram, Shaik M. Zakeeruddin, Md. Khaja Nazeeruddin, Paul Liska, Ngoc-Le Cevey, Anne Sophie Chauvin.
- **Technical and administrative staff**: Pascal Comte, Francine Duriaux Arendse, Jean David Décoppet, Manuel Tschumi, Ursula Gonthier, Nelly Gourdou.

We are grateful for funding from

Swiss CTI , CCEM-CH

Swiss National Science Foundation, Swiss Energy Office

US Air Force (European Office of Aerospace Research and Development)

FP7 European Joule Projects: DSC-ROBUST *, NANOPEC, INNOVASOL

European Research Council, Adv. Res. Grant

GRL Korea (with KRICT)

Stanford University, KAUST Center for Advanced Molecular Photovoltaics (CAMP),

Industrial Partners,

MILLENNIUM TECHNOLOGY PRIZE

Technology for humanity


Thank you for attention!!!