Molecular Engineering of Sensitizers for Solar Cell Applications

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Synthesis

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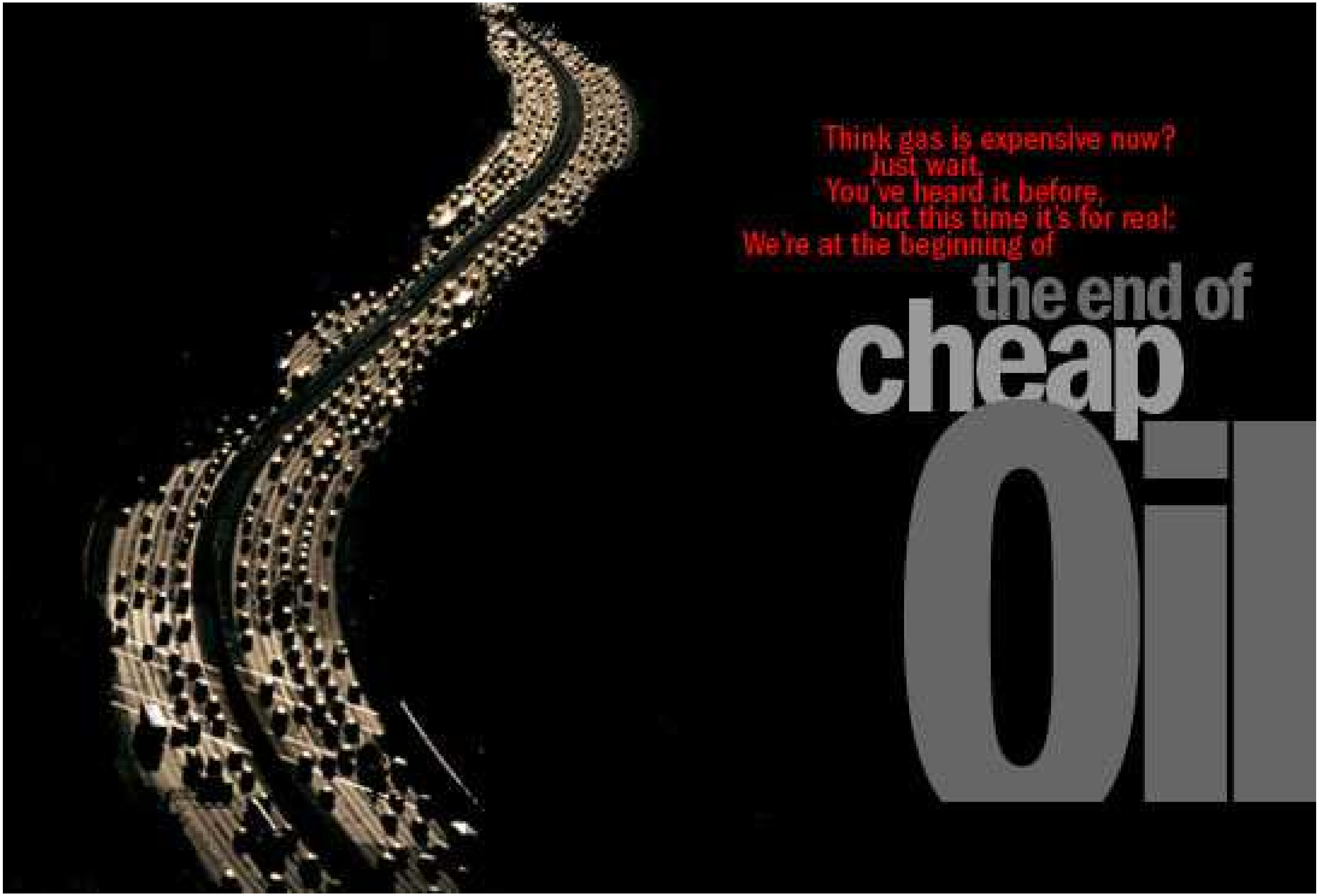


National Geography, June 2004

Real Outdoor Test of DSC Modules

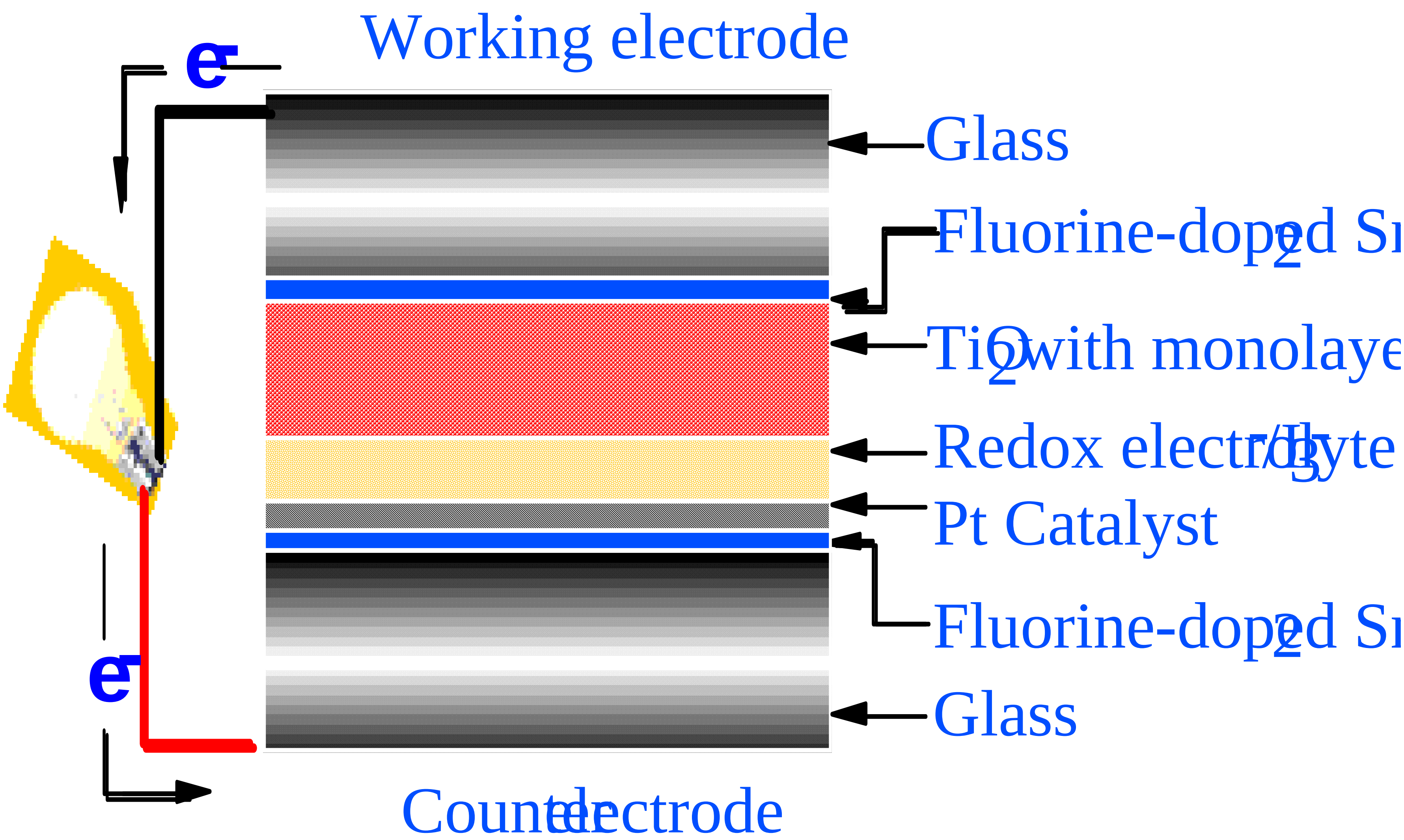
■ Module Unit

Series connected
64 DSC cells

■ Outdoor Test

Kariya City at lat. 35°10’N,
Asimuthal angle: 0°
Facing due south, Tilted at 30°

A cross section of the dye sensitized solar cell



Requirements of the Sensitizers

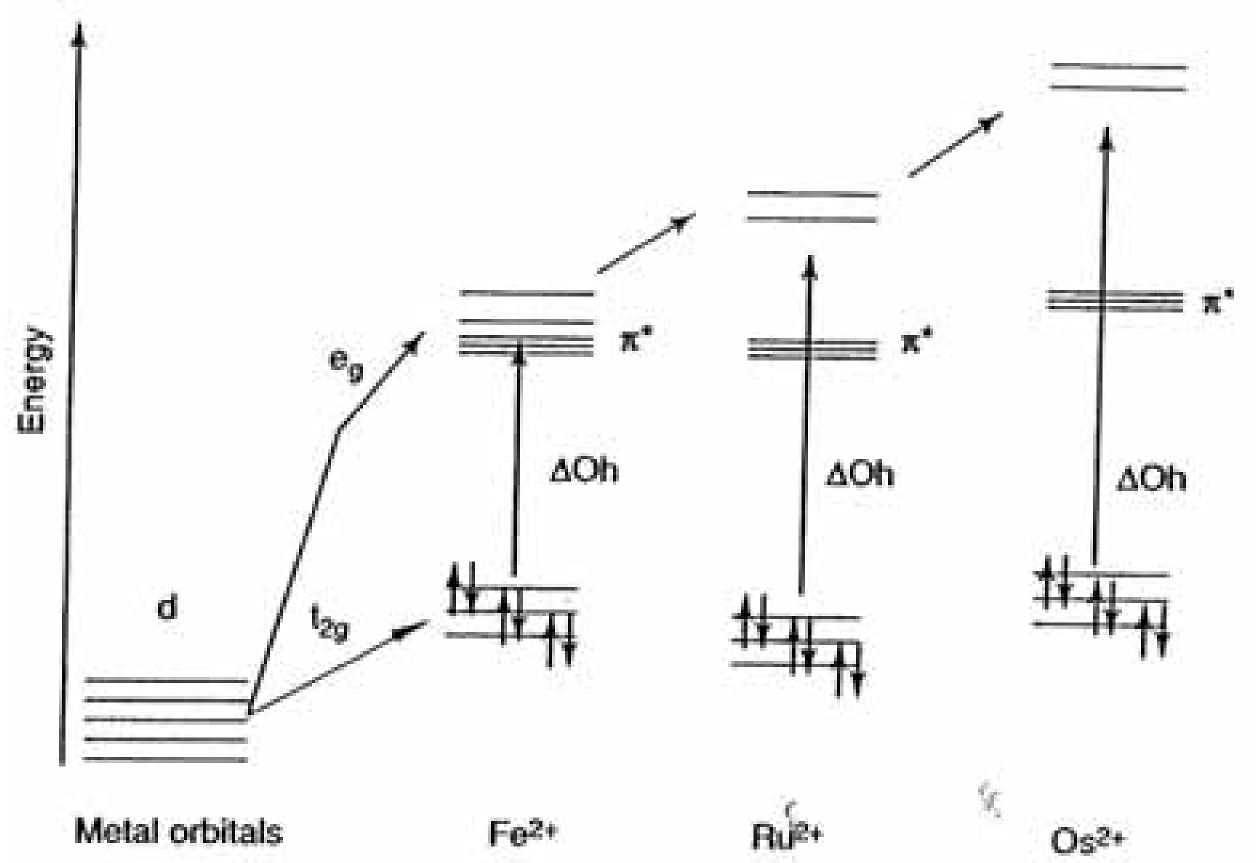
- The optimal sensitizer for the dye sensitized solar cell should be panchromatic, i.e. absorb visible light of all colors.

- It should possess suitable ground- and excited state redox properties (0.5 and -0.8 V vs.SCE)

- It should exhibit thermal and photochemical stability

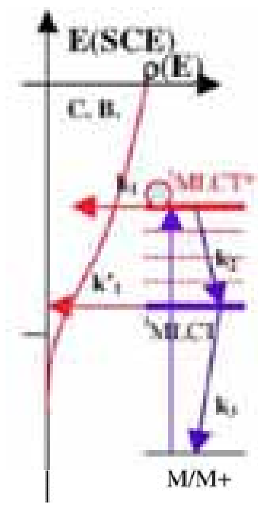
- It must be firmly grafted to the semiconductor oxide surface and inject electrons into the conduction band with a quantum yield of unity.

Splitting pattern of d-orbital in an octahedral field for Fe^{2+}, Ru^{2+} and Os^{2+}



VIIB 8	VIIB 9	VIII 10
26 **Fe** +2 +3 +6 55,85 Geležis	27 **Co** +2 +3 58,93 Kobaltas	28 **Ni** +2 +3 58,69 Nikelis
44 **Ru** +2 +3 +4 +6 +8 101,07 Rutenis	45 **Rh** +2 +3 +4 +5 102,91 Rodis	46 **Pd** +2 +4 106,42 Paladis
76 **Os** +3 +4 +6 +8 190,2 Osmis	77 **Ir** +2 +3 +4 +6 192,22 Iridis	78 **Pt** +2 +4 +6 195,08 Platina

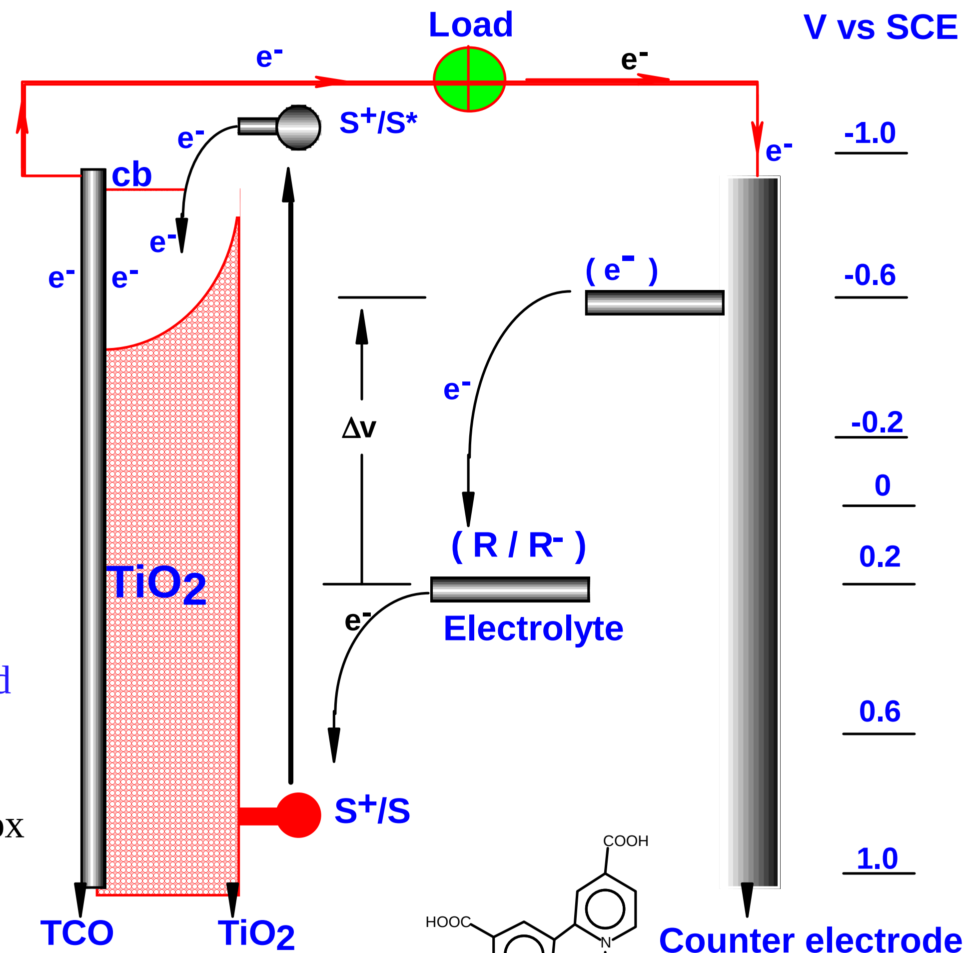
Operating Principles of the Dye-Sensitized Solar Cell

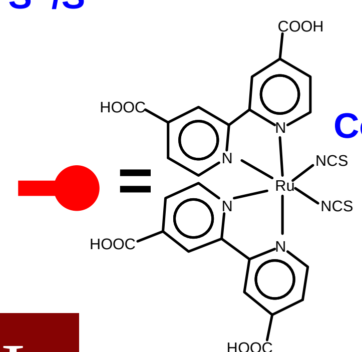


Electron injection from the excited dye into the TiO2 conduction band (CB) is a very fast process *femto*second scale τ1 < 20 fs.

The reduction of the oxidized dye by the redox electrolyte's I- ions occurs in about 10^{-8} seconds.

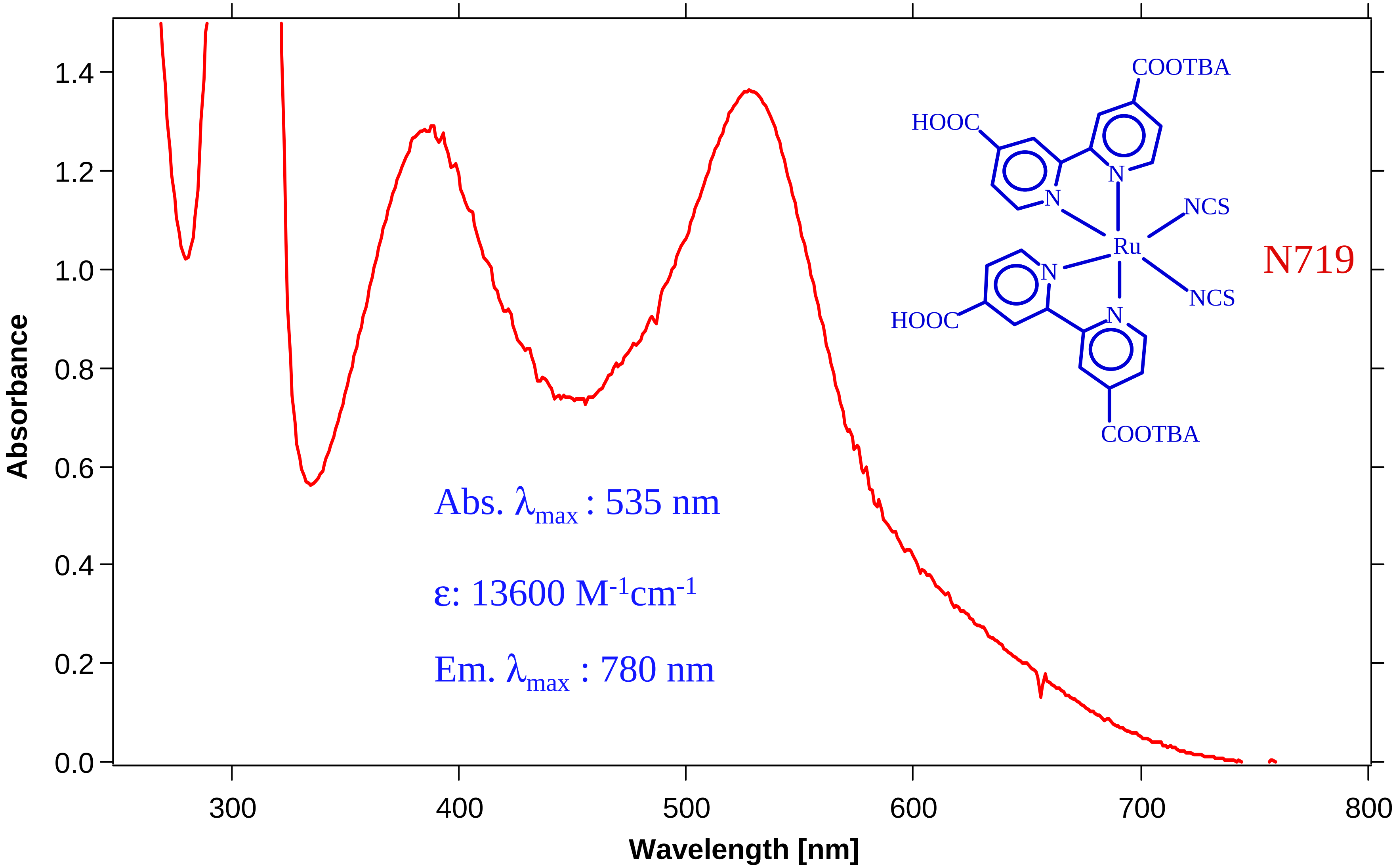
Recombination of photoinjected CB electrons with oxidized dye molecules or with the oxidized form of the electrolyte redox couple (I_3^- ions) occurs in *micro*seconds.



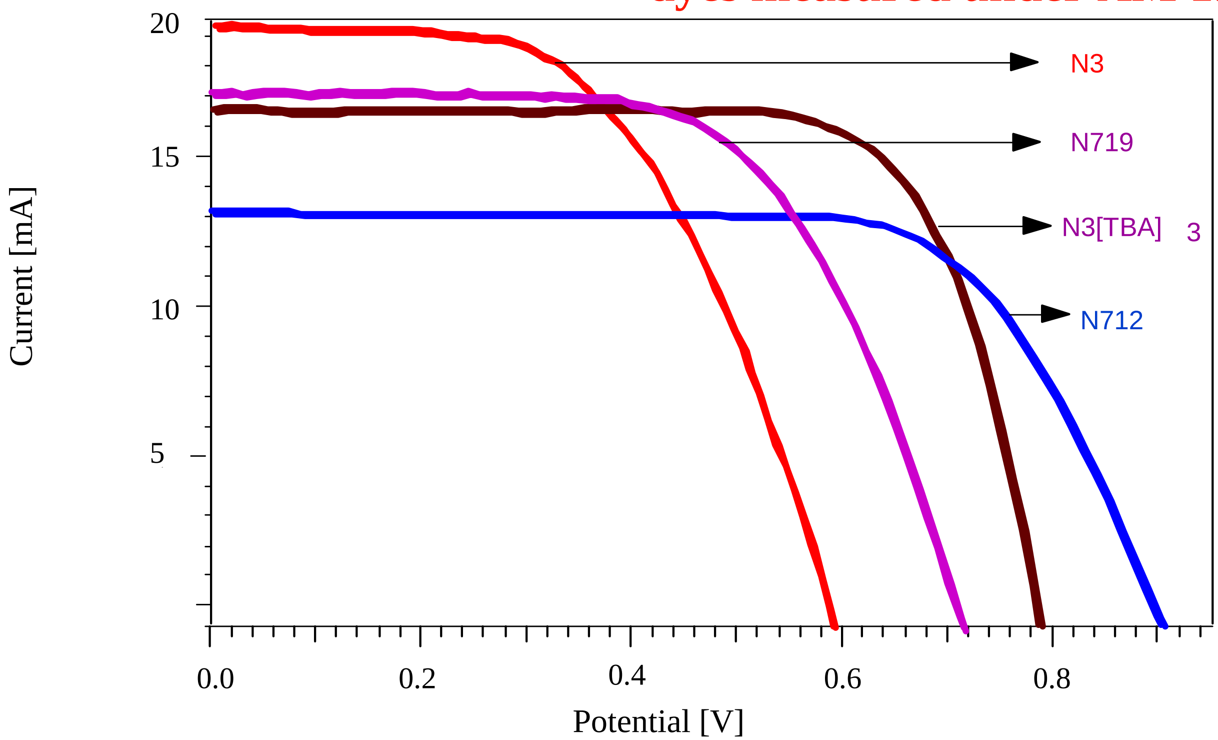


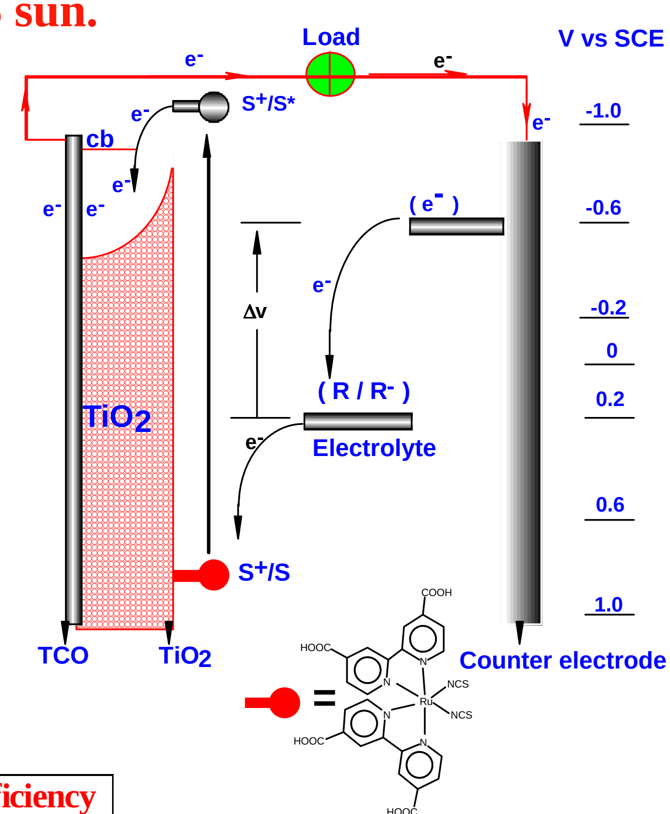
$$\eta = i_{ph} V_{oc} ff / I_s$$

Absorption Spectra of N719 Sensitizer



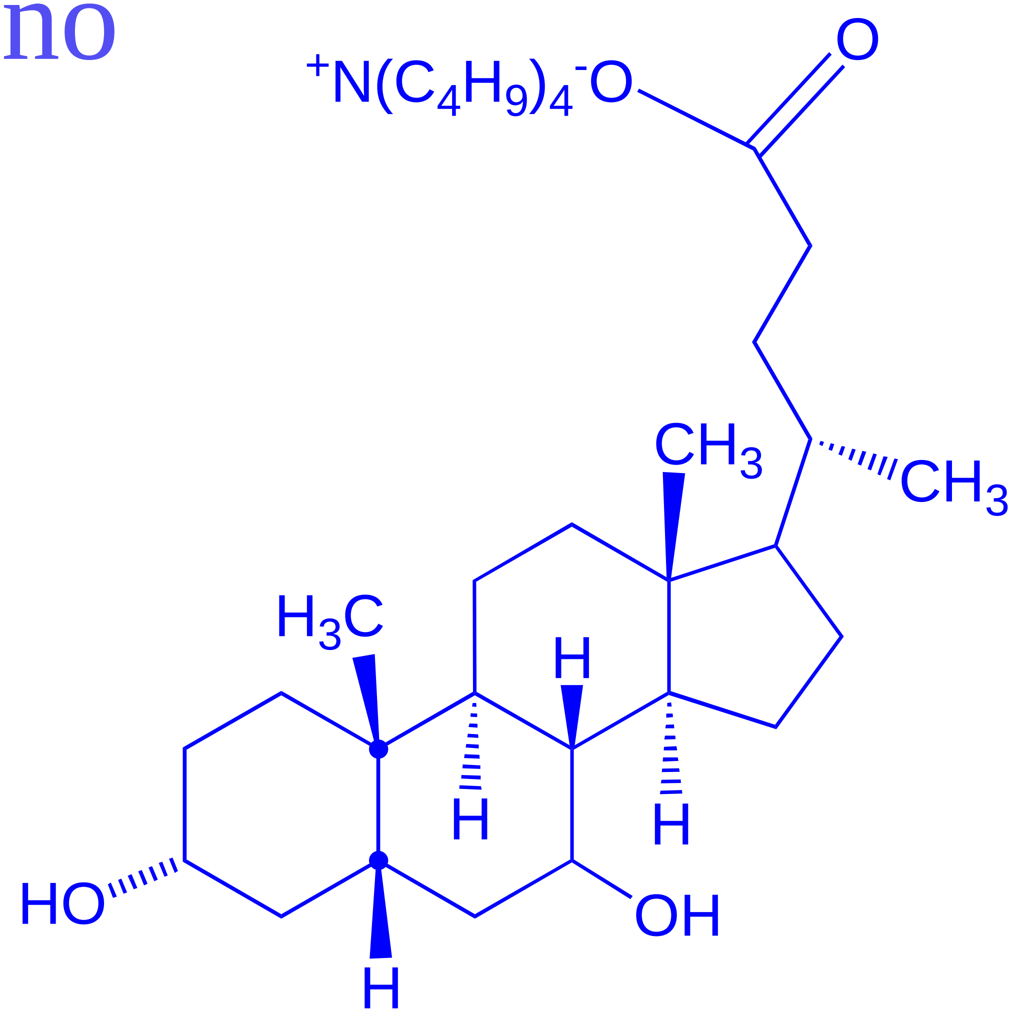
Photocurrent-voltage characteristics of nanocrystalline TiO_2 cell sensitized with N3 (4 protons), N719 (2 protons), N3[TBA]$_3$ (1 proton) and N712 (zero proton) dyes measured under AM 1.5 sun.





Sensitizer	Number of protons	Solvent for dye adsorption	Current mA/cm^2	Potential (mV)	Fill Factor	Efficiency at 1.5 AM
N3	4	1:1 CH_3CN+ *tert*-BuOH	19 ± 0.5	600 ± 30	0.65 ± 0.05	7.4
N719	2	1:1 CH_3CN+ *tert*-BuOH	16 ± 0.5	730 ± 30	0.70 ± 0.05	8.2
N712	0	C_2H_5OH	13 ± 0.5	900 ± 30	0.7 ± 0.05	8.2
N3[TBA]$_3$	1	5:95 CH_3CN +*tert*-BuOH	17±0.5	770 ±20	0.73±0.05	9.56
N3[TBA]	3	1:1 CH_3CN+ *tert*-BuOH	17 ± 0.5	700 ± 20	0.65 ±0.05	7.7

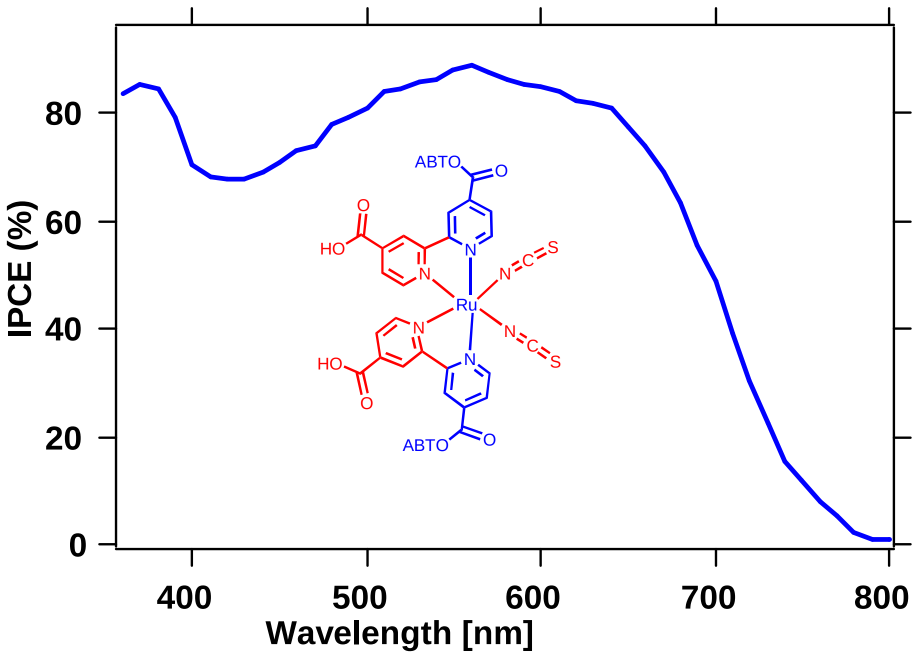
TBA Cheno

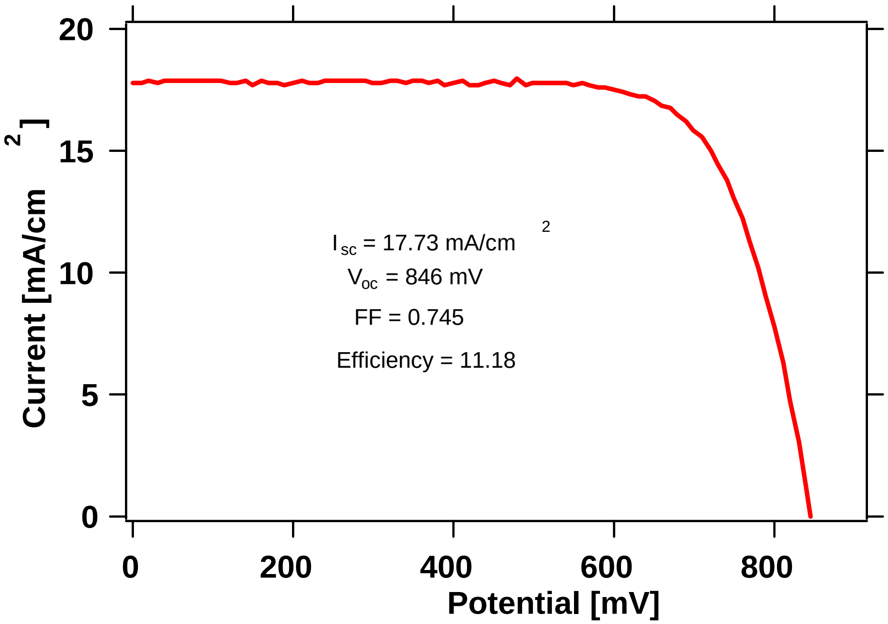


Chenodeoxycholic acid

3α,7α-dihydroxy-5β-cholani cacid

Conversion efficiency of 11.2 % have been reached under AM 1.5 sunlight

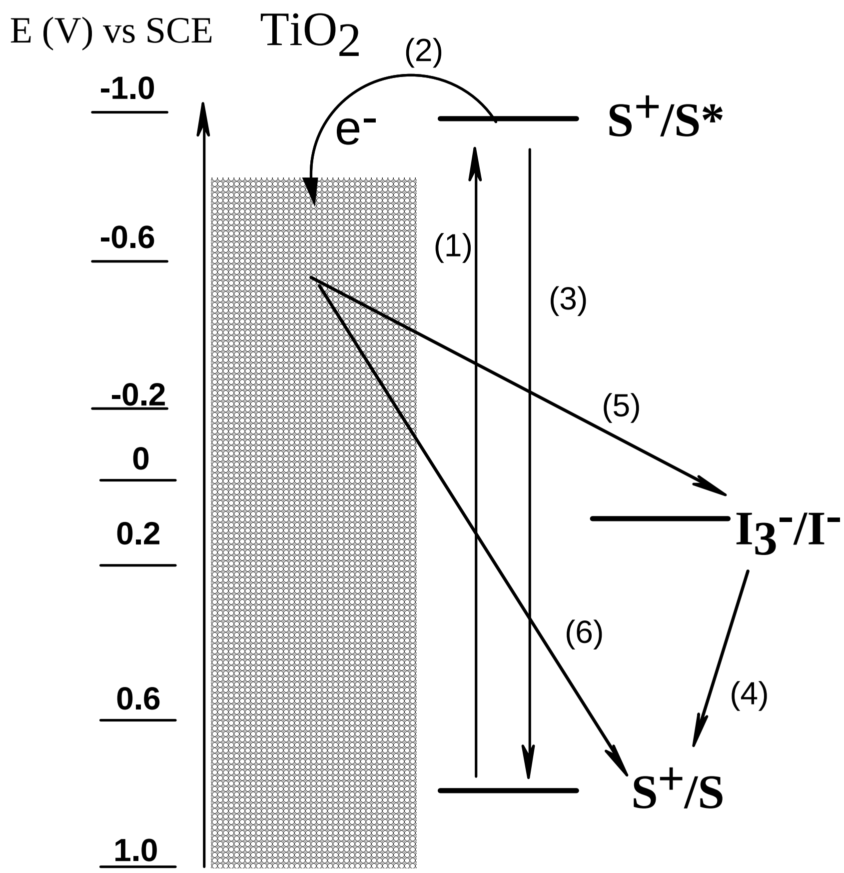




$$\eta = i_{ph} V_{oc} \, ff \, / \, I_s$$

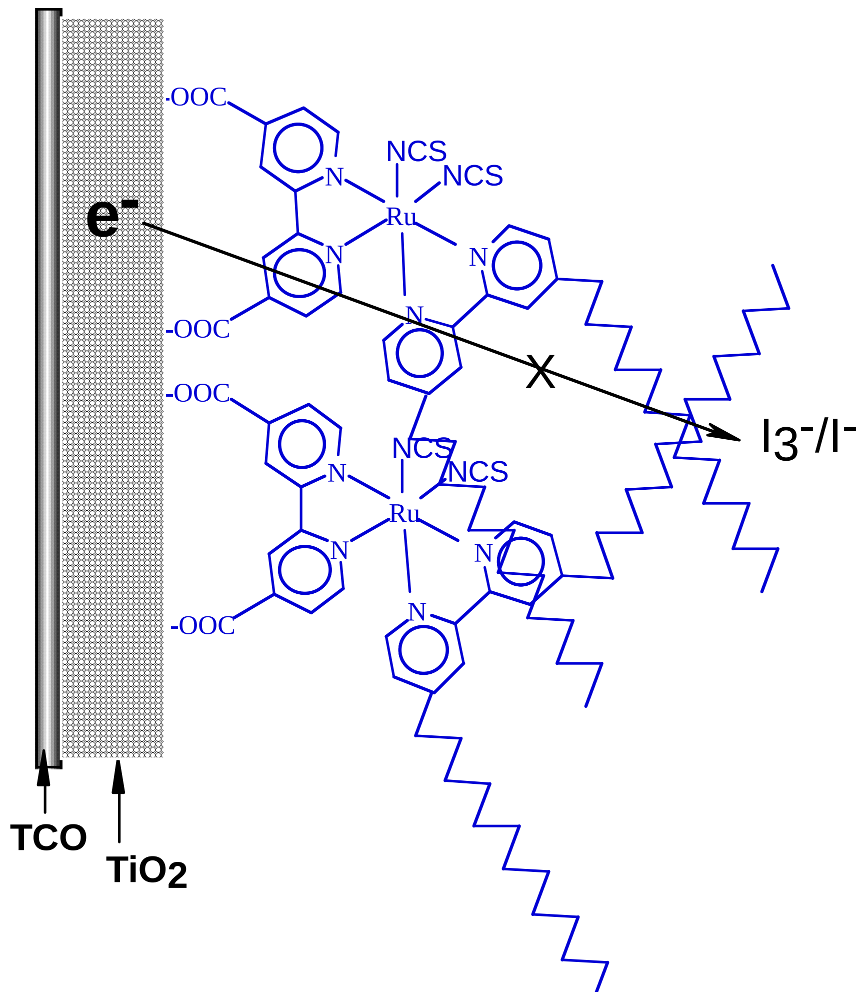
Nazeeruddin, Mohammad K.; De Angelis, Filippo; Fantacci, Simona; Selloni, Annabella; Viscardi, Guido; Liska, Paul; Ito, Seigo; Takeru, Bessho; Graetzel, Michael. JACS, 127, 16835, 2005.

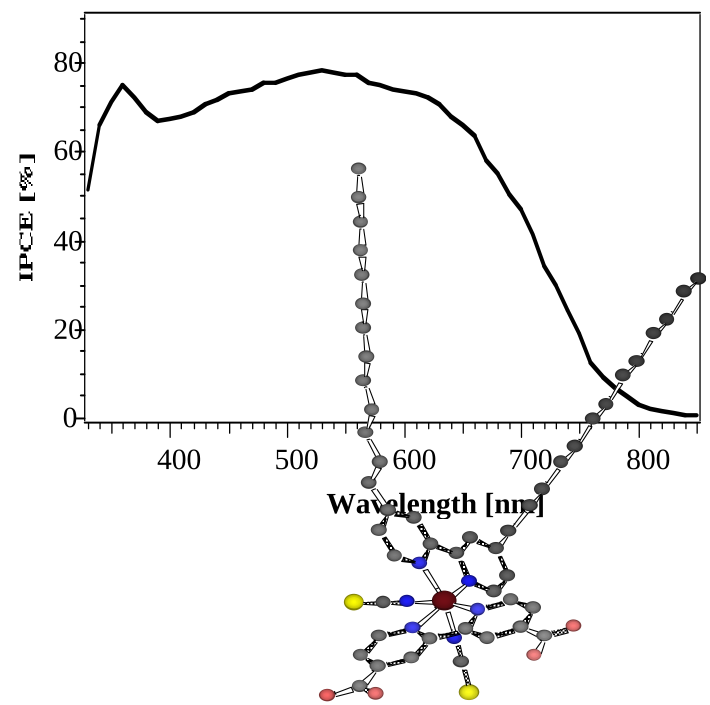
Illustration of the interfacial charge transfer processes in nanocrystalline dye sensitized solar cell.



(1) An excited state. (2) electron injection onto the conduction band of TiO_2. (4) The oxidized sensitizer gets reduced by I^- / I_3^- redox couple. (5) The injected electrons into the conduction band may react either with the oxidized redox couple or with oxidized dye molecule (6).

Pictorial representation of blocking of the oxidized redox couple I_3^- reaching onto the surface of TiO_2 for conduction band electrons using hydrophobic sensitizers, which forms aliphatic net work.



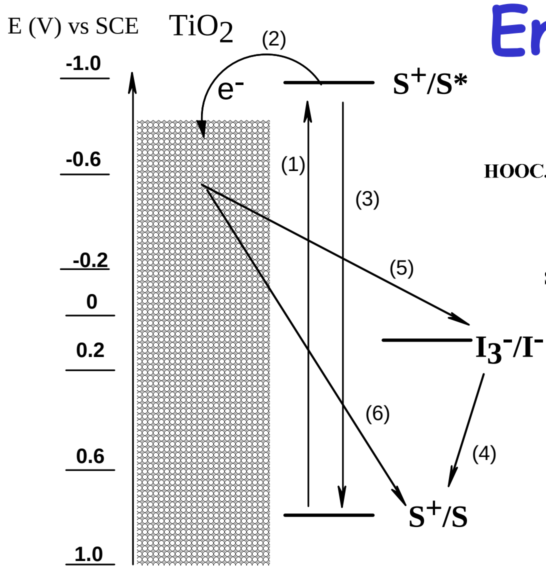


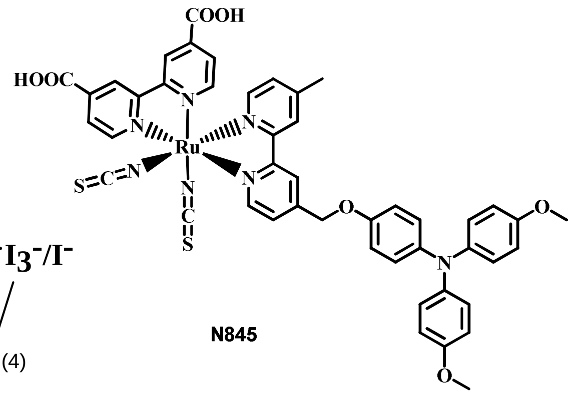
S. M. Zakeeruddin, M. K. Nazeeruddin, R. Humphry-Baker, P. Pechy, P. Quagliotto, C. Barolo, G. Viscardi, M. Grätzel, *Langmuir* 2002, **18**, 952

P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Grätzel, *Nat. Mater.* 2003, **2**, 402

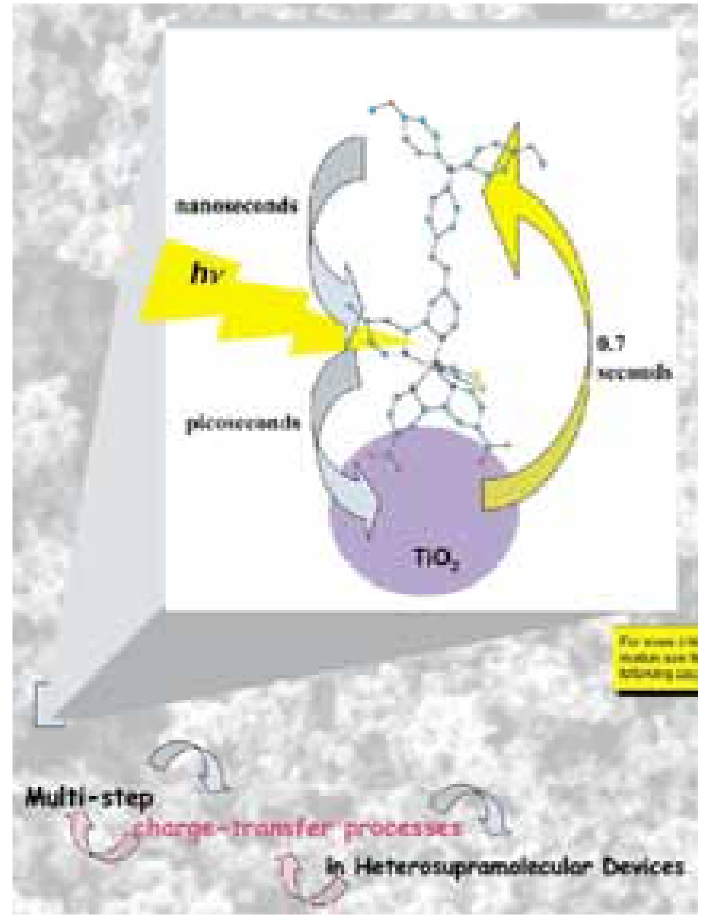
M. K. Nazeeruddin, S. M. Zakeeruddin, J-J. Lagref, P. Liska, P. Comte, C. Barolo, G. Viscardi, K. Schenk, M. Graetzel *Coord. Chem. Rev.* 248 (13-14): 1317-1328 (**2004**)

Enhancing charge separation





N845



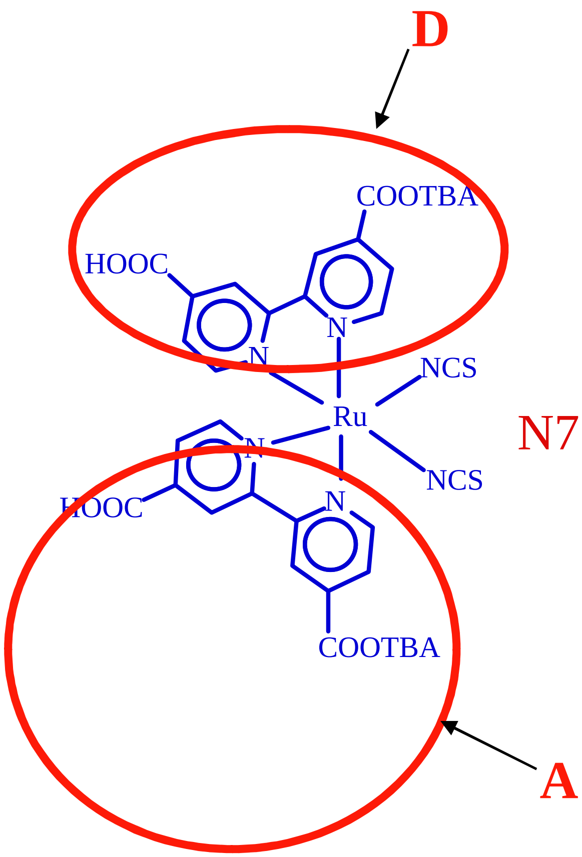
triarylamine moiety

1000-fold retardation of the recombination dynamics in comparison with N-719!

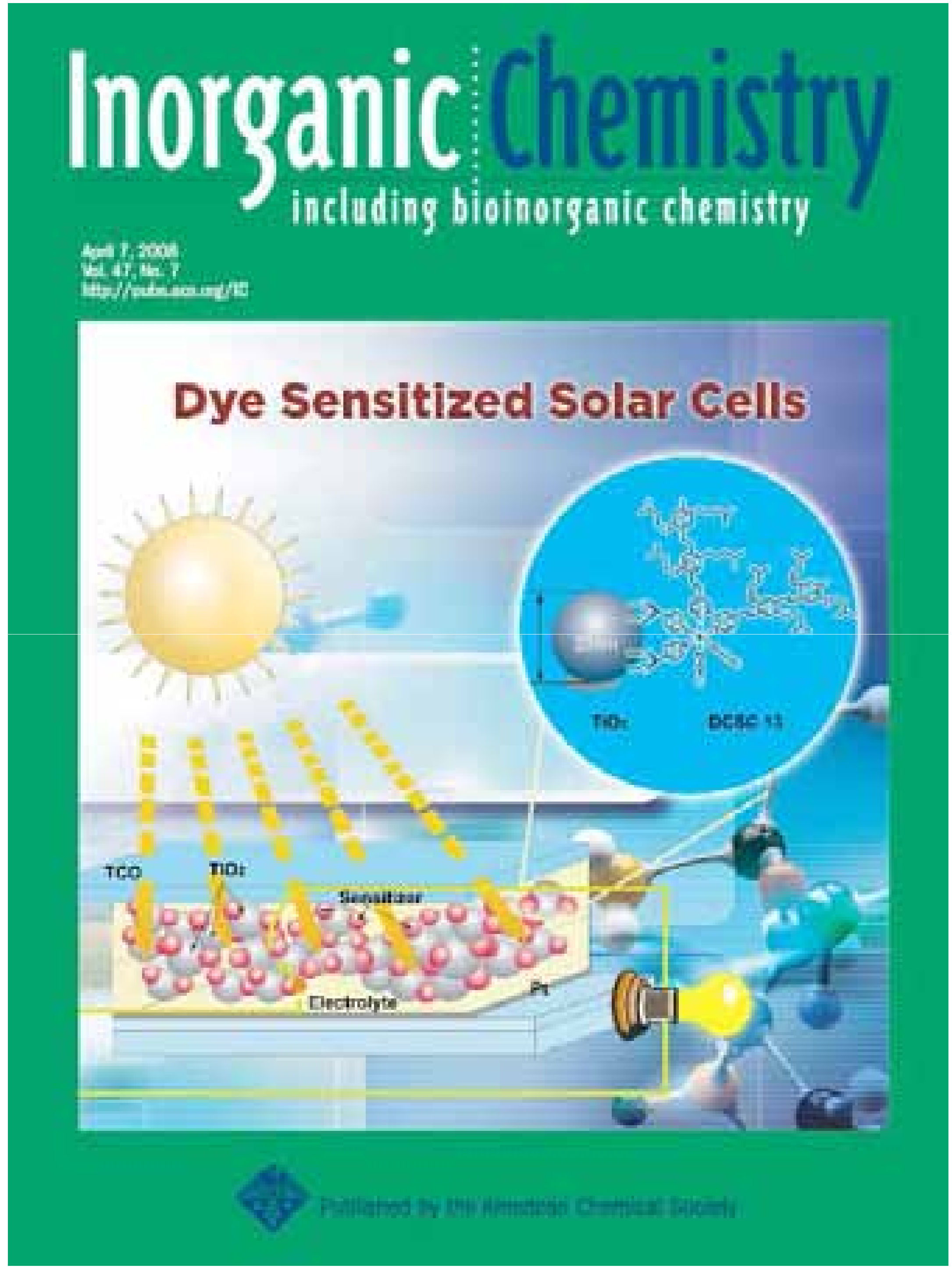
4 Å increase in distance between the cationic center of charge and the TiO_2 surface respect to N-719

N. Hirata, J.-J. Lagref, E. J. Palomares, J. R. Durrant, M. K. Nazeeruddin, M. Graetzel, D. Di Censo, *Chem. Eur. J.* **2004** 10 595

New Sensitizers with π-extended donor ligands

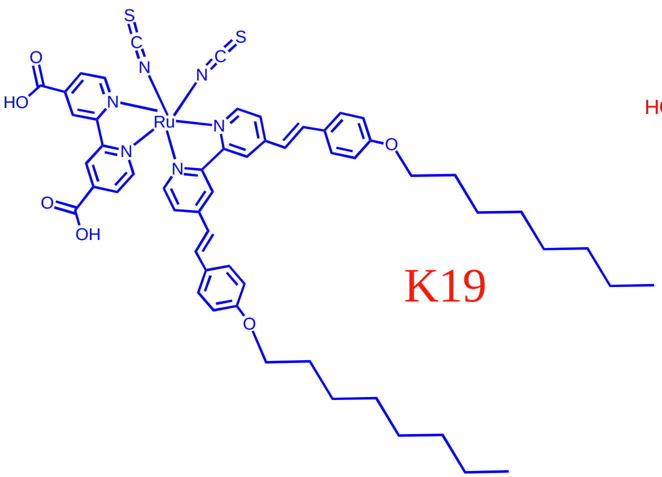


N719

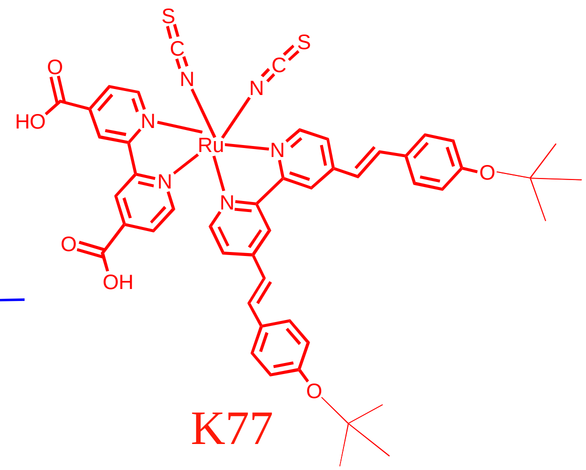


Ko et al. Inorganic Chemistry, Vol. 47, No. 7, **2008**, 2267

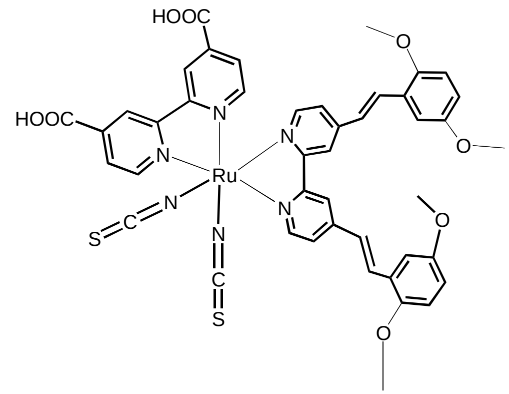
Sensitizers with π-extended donor ligands



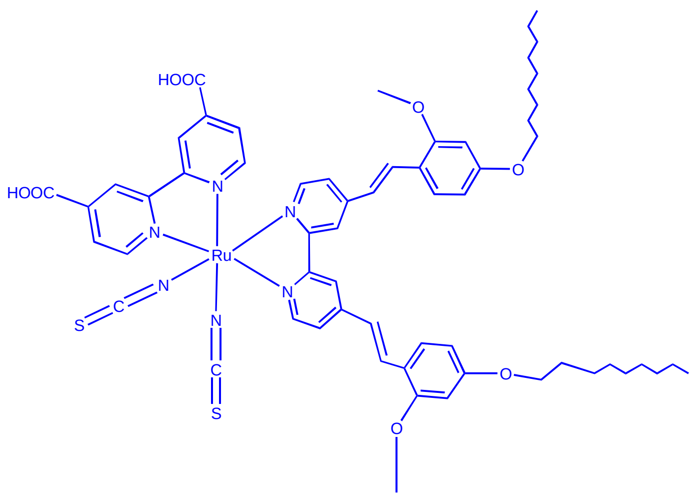
K19



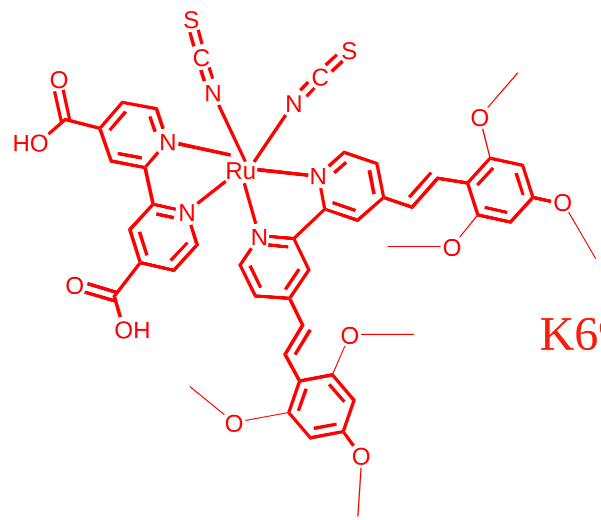
K77



N945



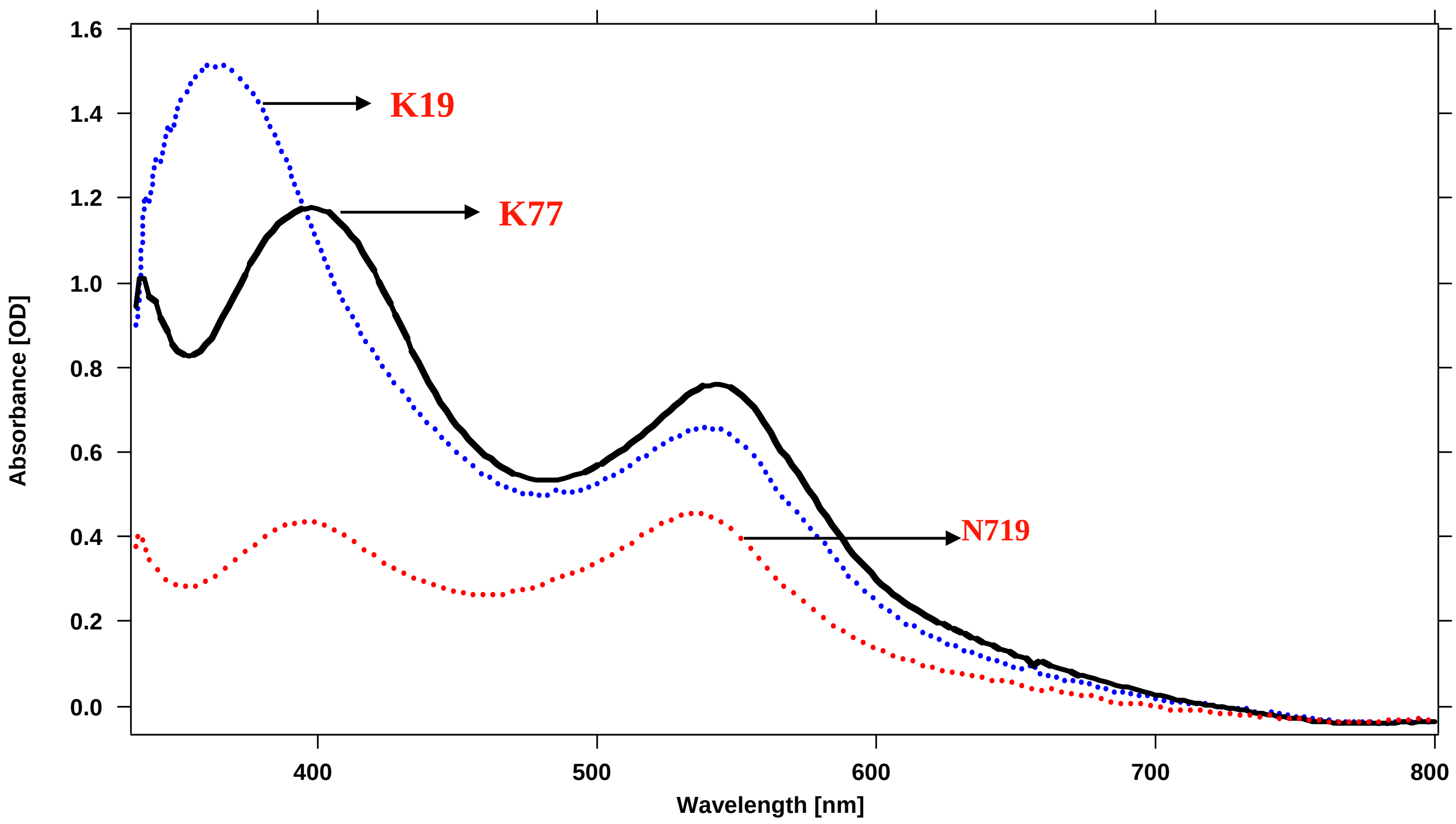
K66



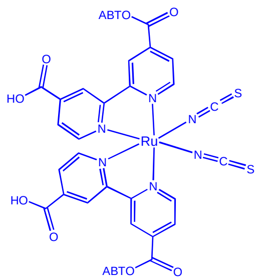
K69

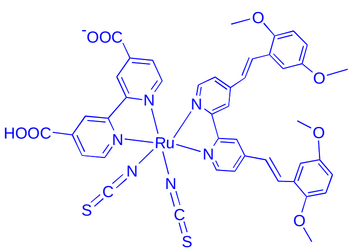
Inorg. Chem. 45, 787-797, 2006.

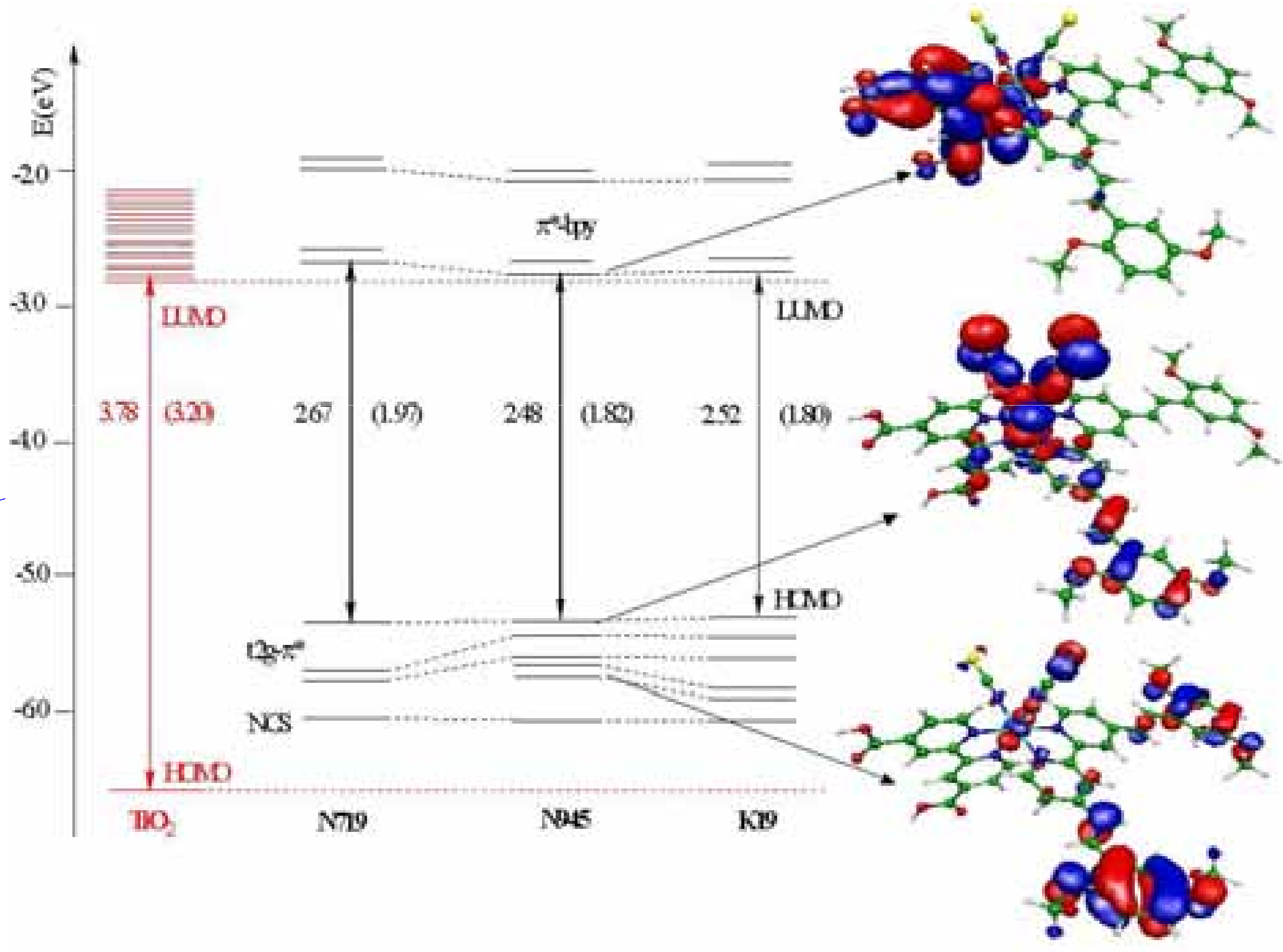
Comparison UV-Vis spectra of N719 (red), K19 (blue) and K77 (black)

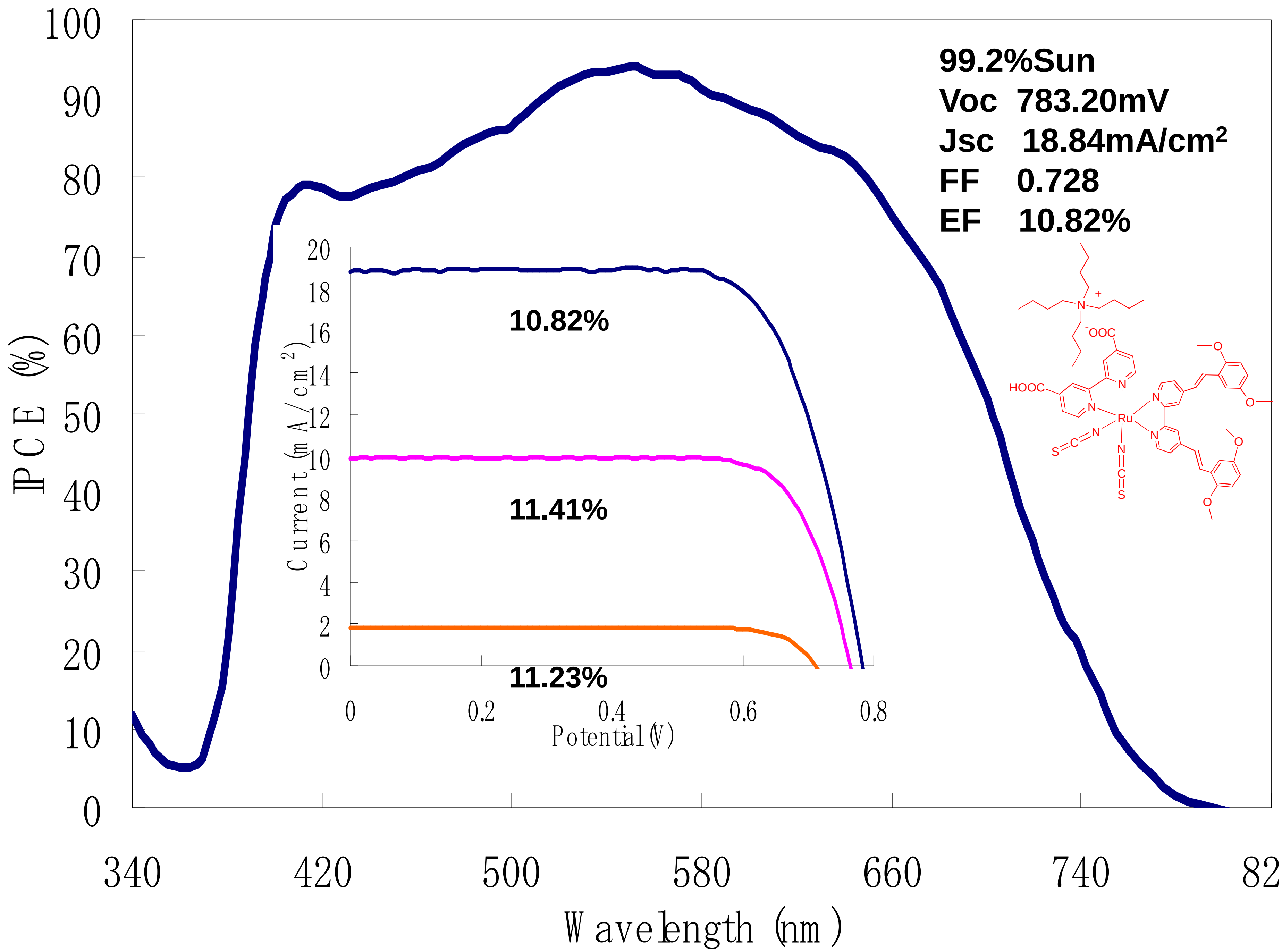


Molecular orbital energy diagram of N719, N945 and K19 compared to that of a TiO_2 nanoparticle model

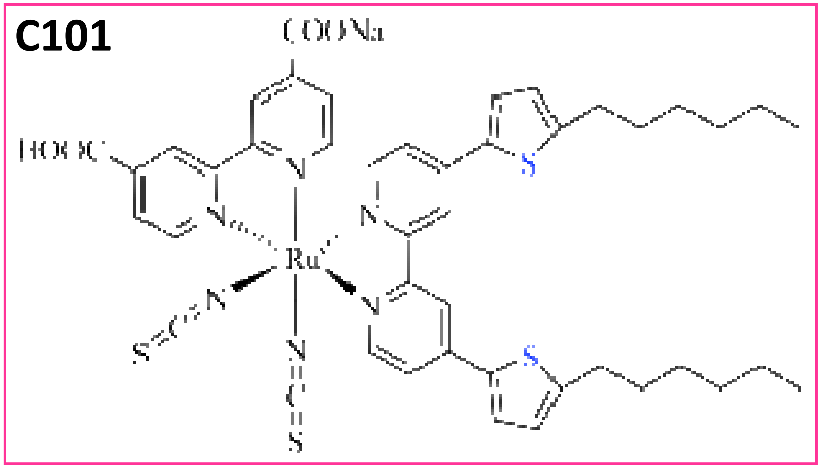


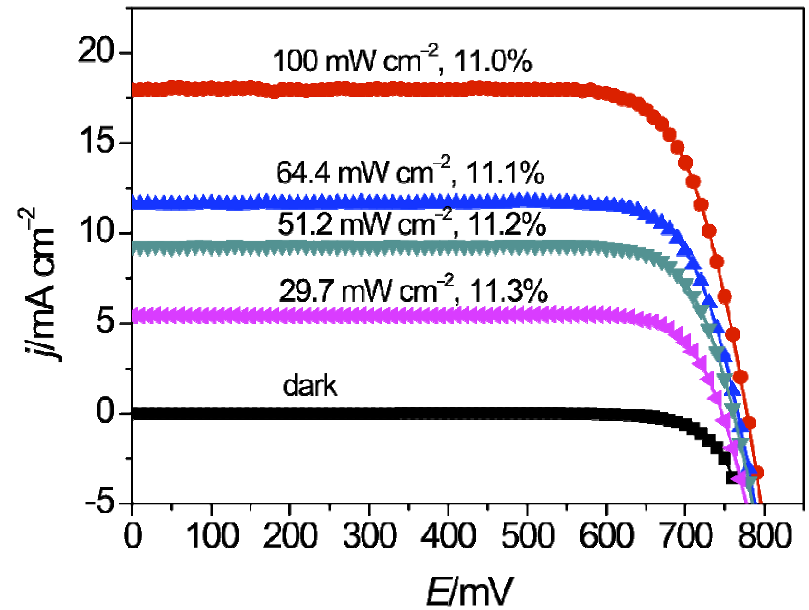






100
90
80
70
60
50
40
30
20
10
0
PCE (%)
340
420
500
580
660
740
820
Wavelength (nm)
99.2%Sun
Voc 783.20mV
Jsc 18.84mA/cm2
FF 0.728
EF 10.82%
20
18
16
14
12
10
8
6
4
2
0
Current (mA/cm2)
10.82%
11.41%
11.23%
0
0.2
0.4
0.6
0.8
Potential (V)
HOOC
-OOC
N
Ru
S=C=N
N=C=S
O



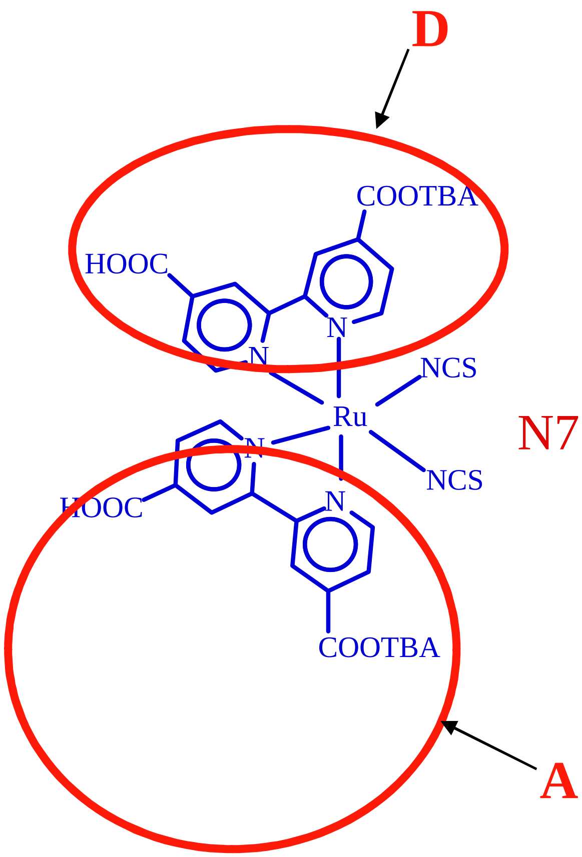


Note: 7+5 film, overnight
Dye solution: 300 μM C101
and 300 μM cheno in AN/t-BuOH
Electrolyte: Z960

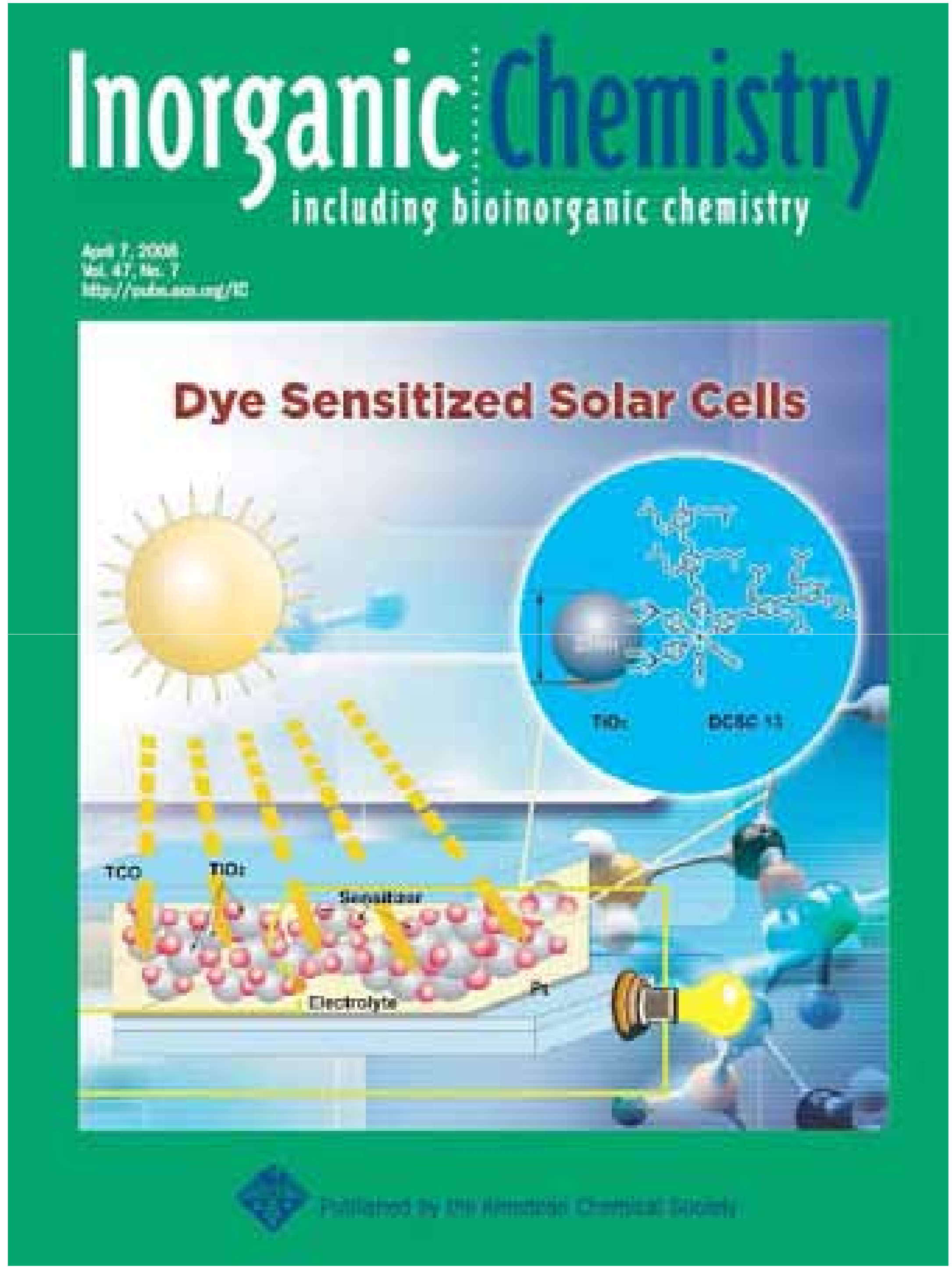
J_{sc}=17.94 mA cm^{-2}
V_{oc}=778 mV
ff=0.785
η =11.0%

Peng Wang et al. J. AM. CHEM. SOC. 2008, *130*, 10720–10728

New Sensitizers with π-extended acceptor ligands

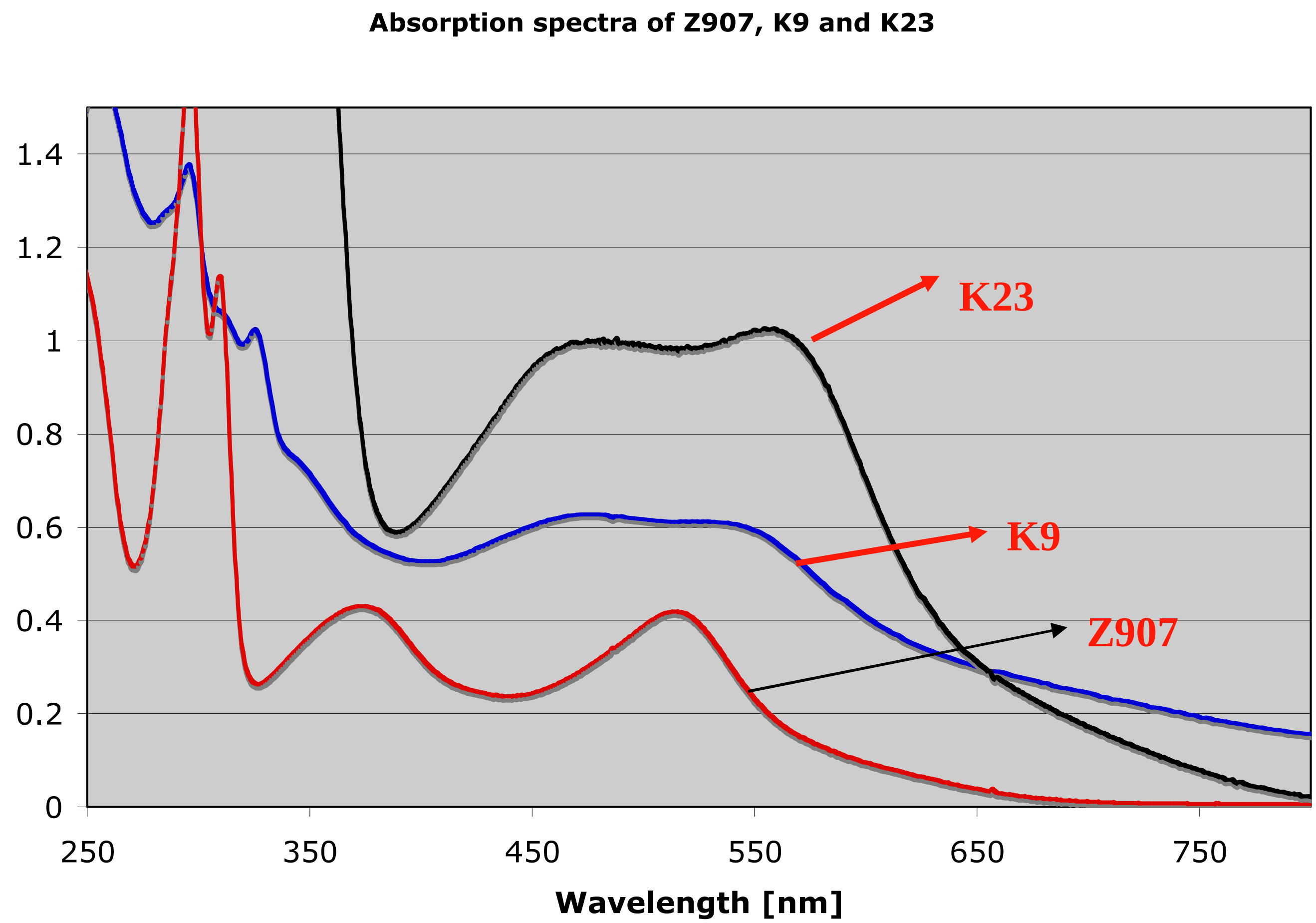


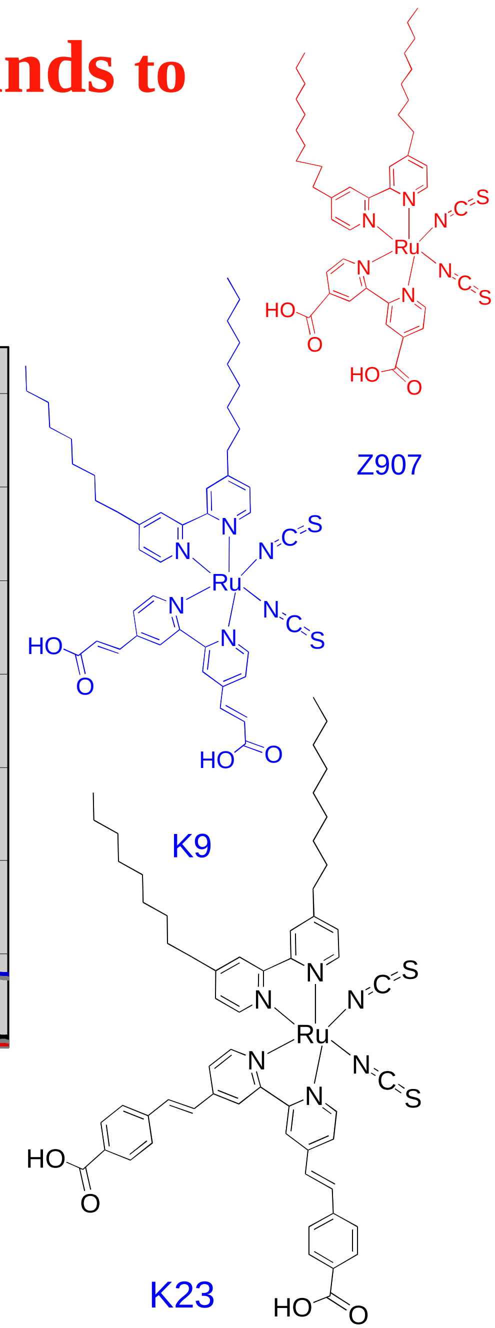
N719



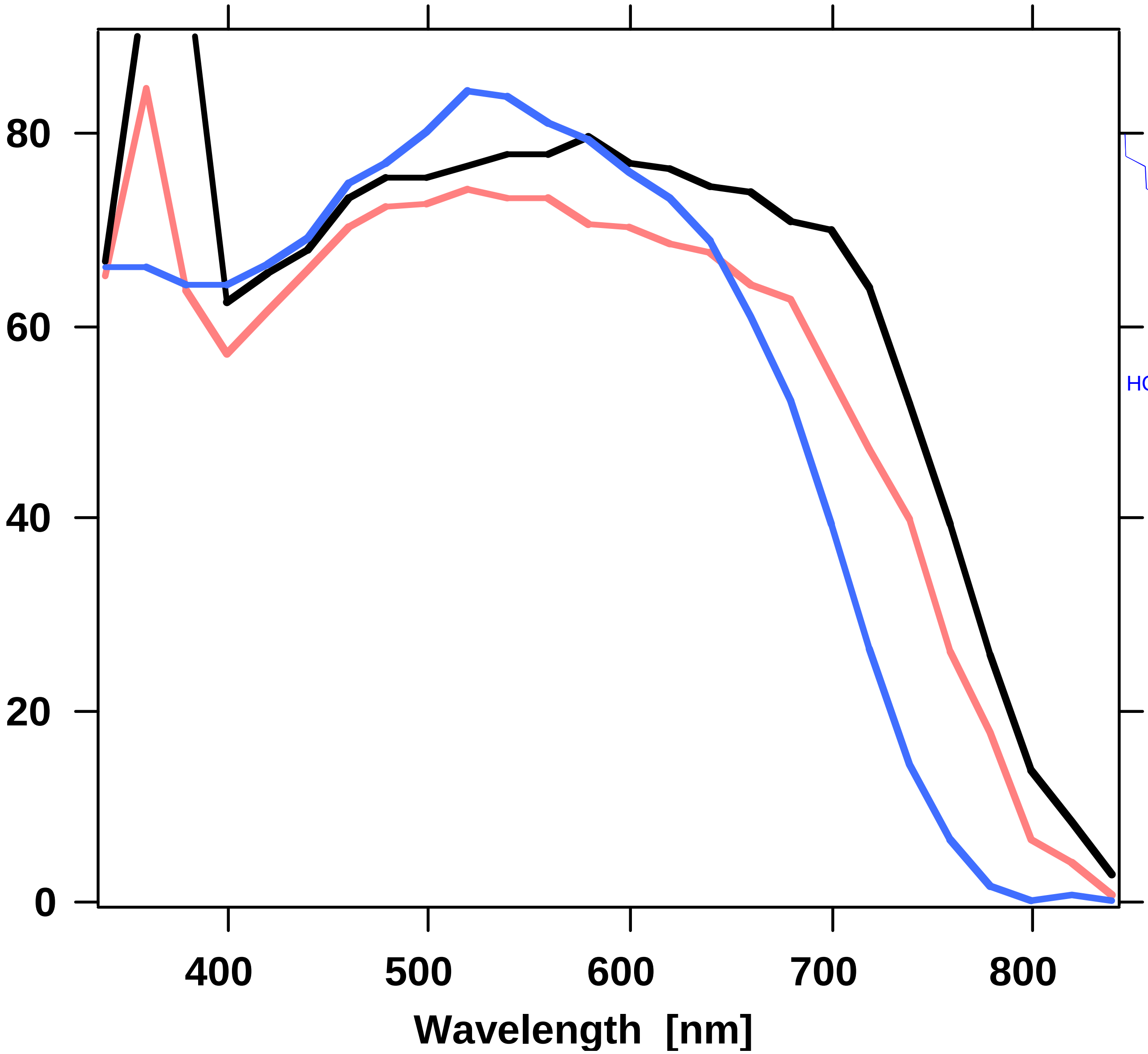
Ko et al. Inorganic Chemistry, Vol. 47, No. 7, **2008**, 2267

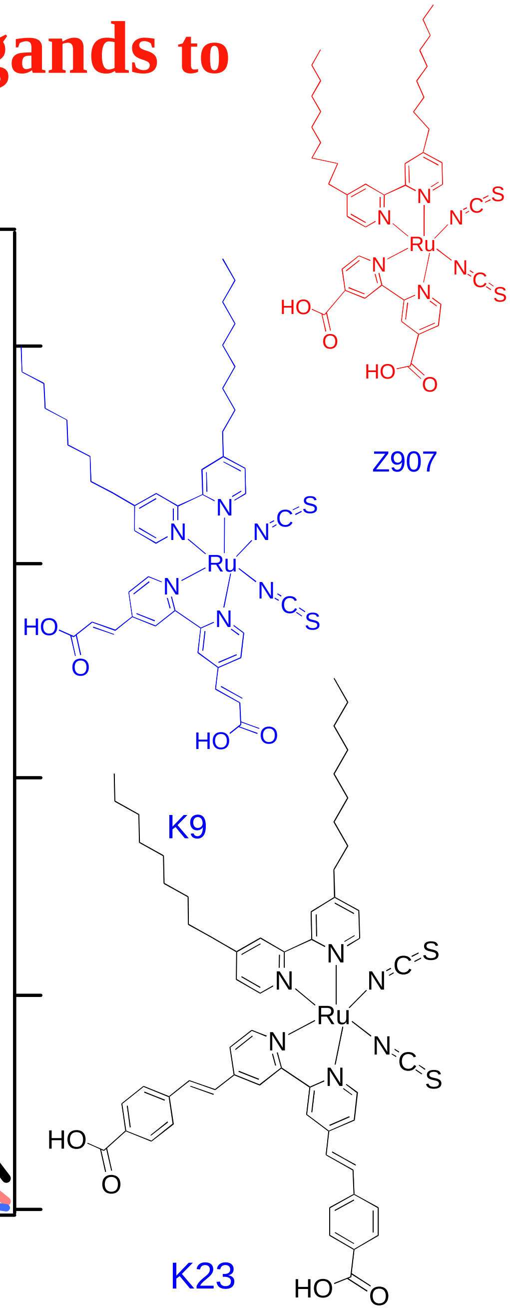
Sensitizers with π-extended acceptor ligands to enhance spectral response



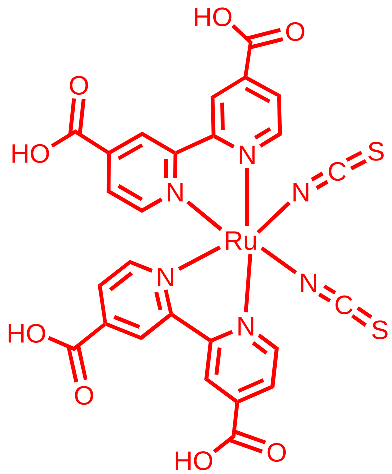


Sensitizers with π-extended acceptor ligands to enhance spectral response





New Sensitizers with extended π-system



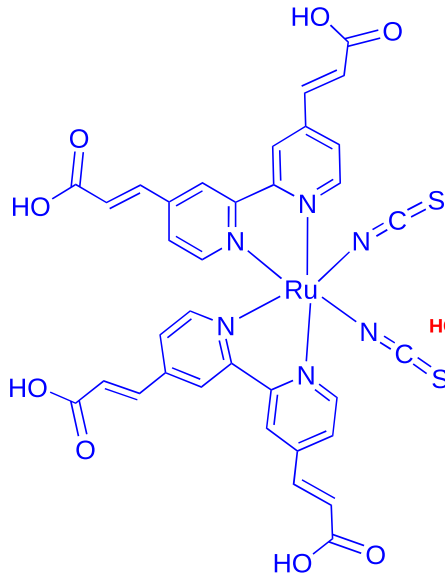
N3

λmax 535 nm

ε= : 13800 $M^{-1}cm^{-1}$

Em. λ_{max} : 780 nm

E_{ox} = 0.85 (irrev)



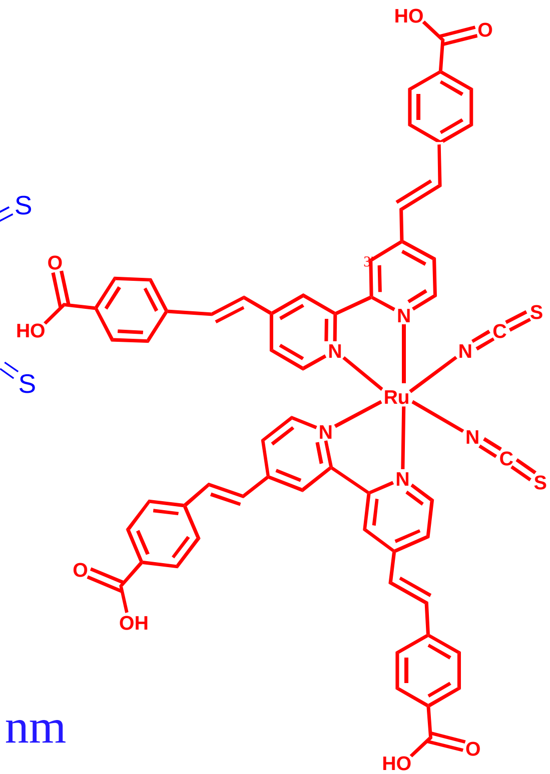
K-8

Abs. λ_{max} : 555 nm

ε: 17600 $M^{-1}cm^{-1}$

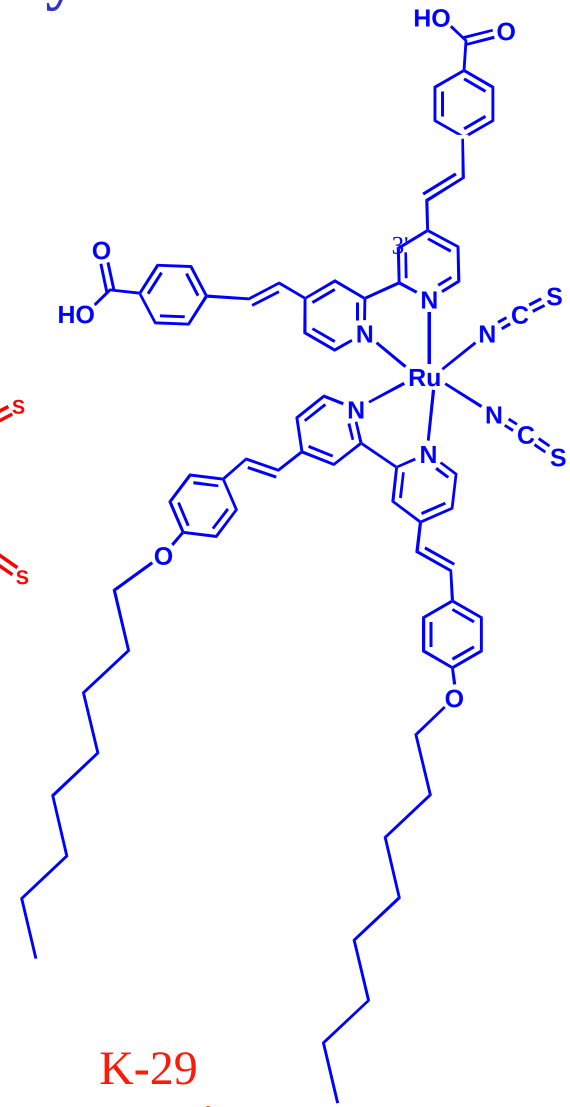
Em. λ_{max} : 840 nm

E_{ox} = 0.77 (rev)



K-27

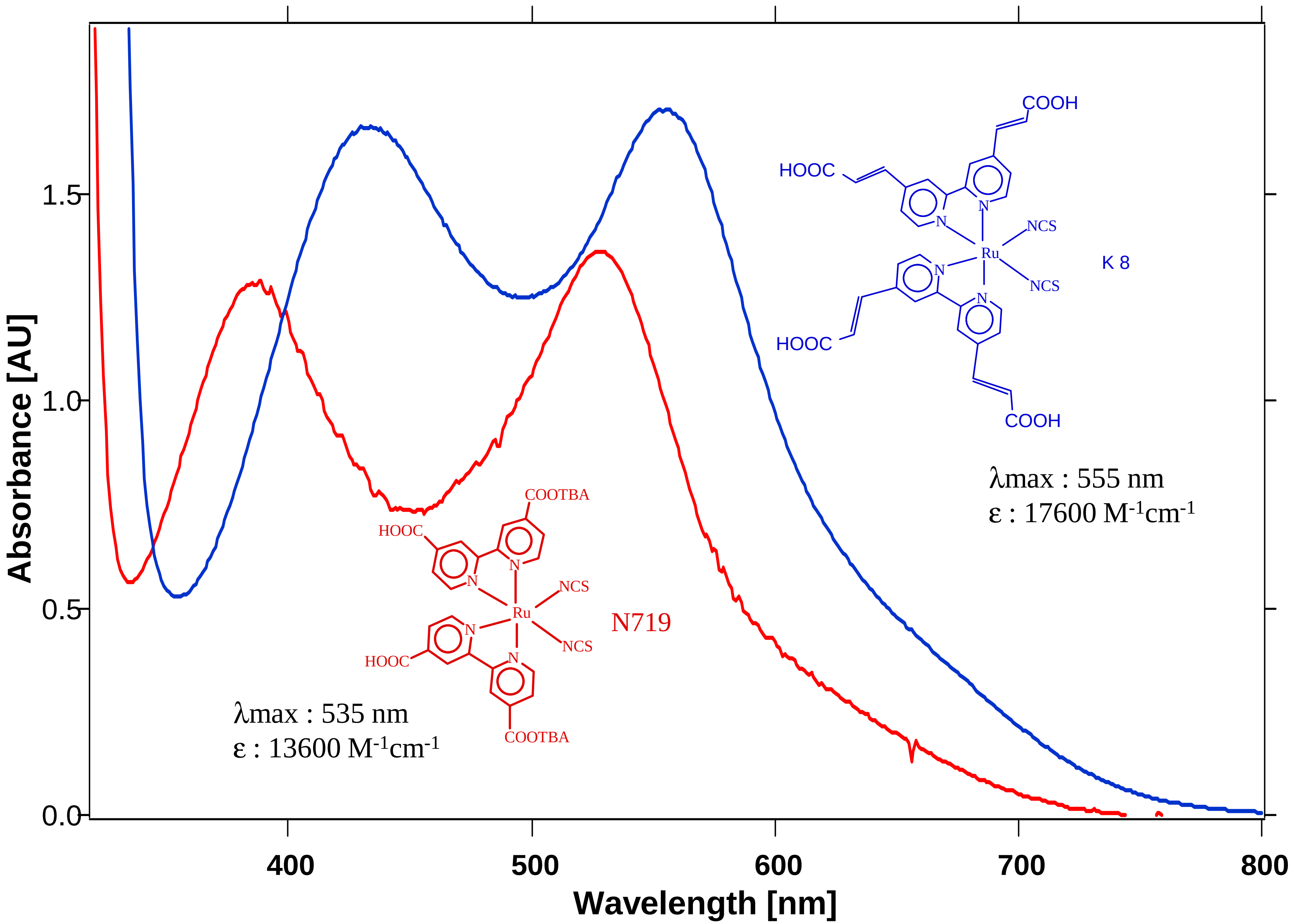
Abs. λ_{max} : 566 nm



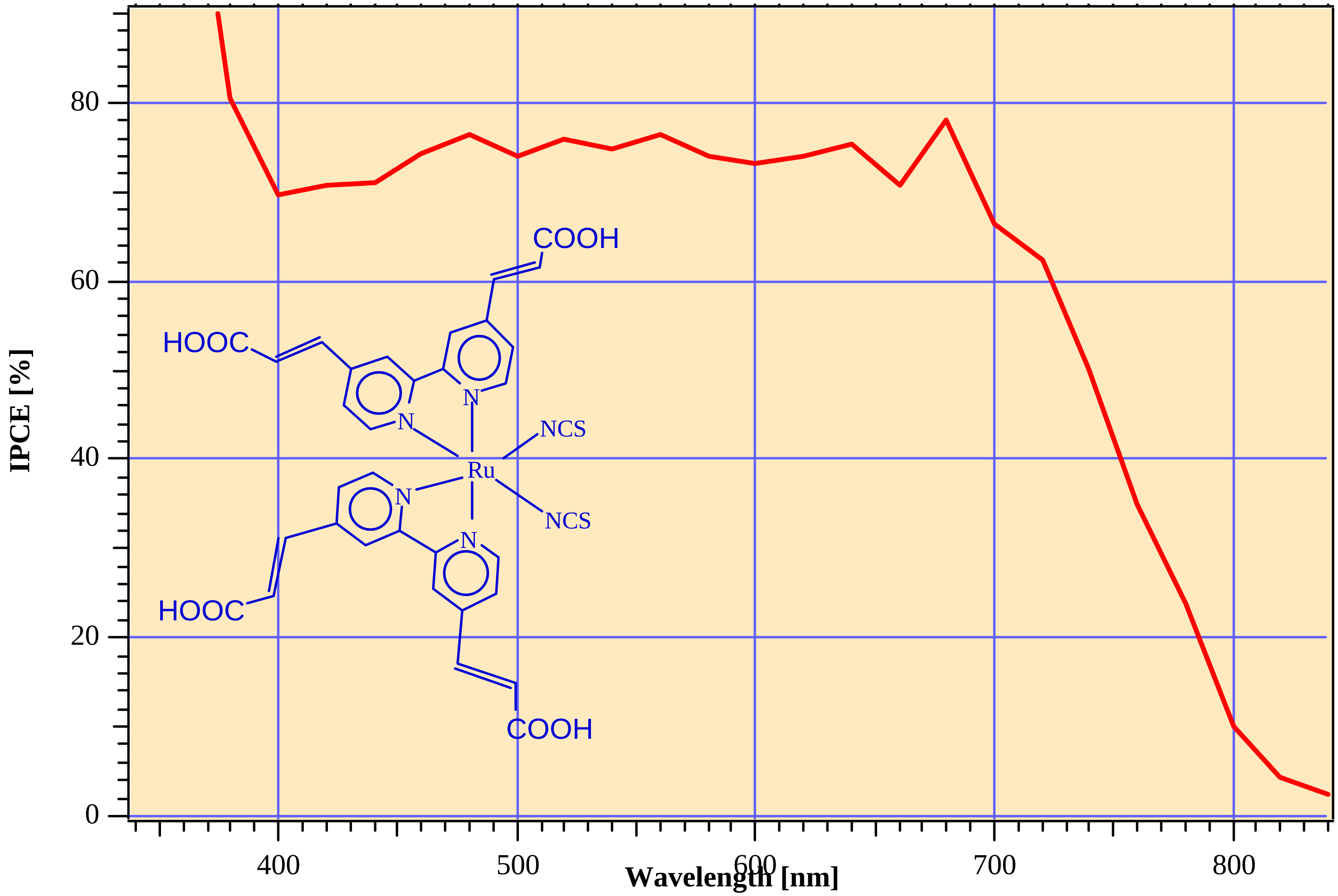
K-29

Abs. λ_{max} : 575 nm

UV/Vis Spectra of N719 and K8 Sensitizers



Incident Photon to Current Conversion Efficiency of K 8 Sensitizer

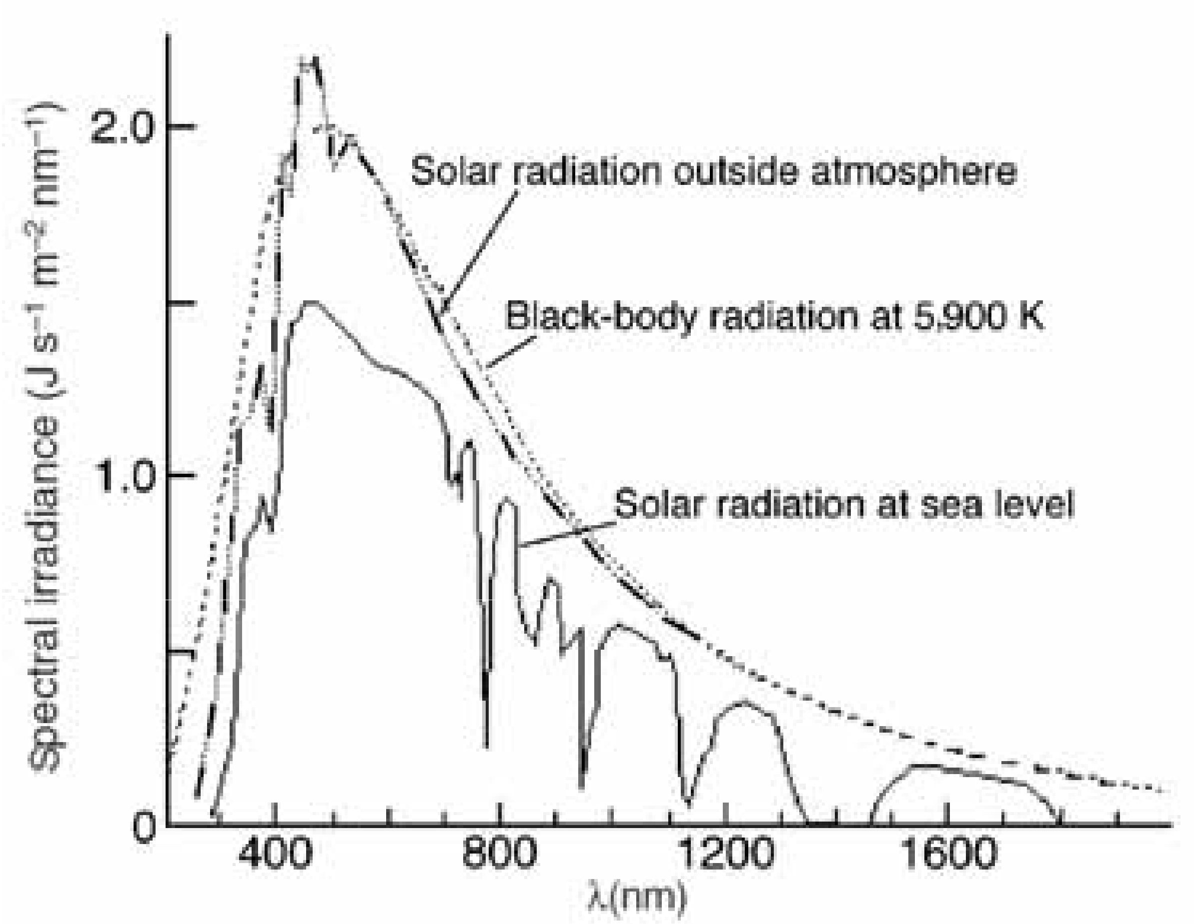


Solar AM 1.5 (1000 W/cm^2) is 18 - 19 mA/cm^2

M. K. Nazeeruddin, C. Klein, P. Liska, M. Graetzel, *Coord. Chem. Rev.* **2005**, 249, 1460

C. Klein, M. K. Nazeeruddin, P. Liska, D. Di Censo, N. Hirata, E. Palomares, J. R. Durrant, M. Graetzel, *Inorg. Chem.* **2005**, 44, 178

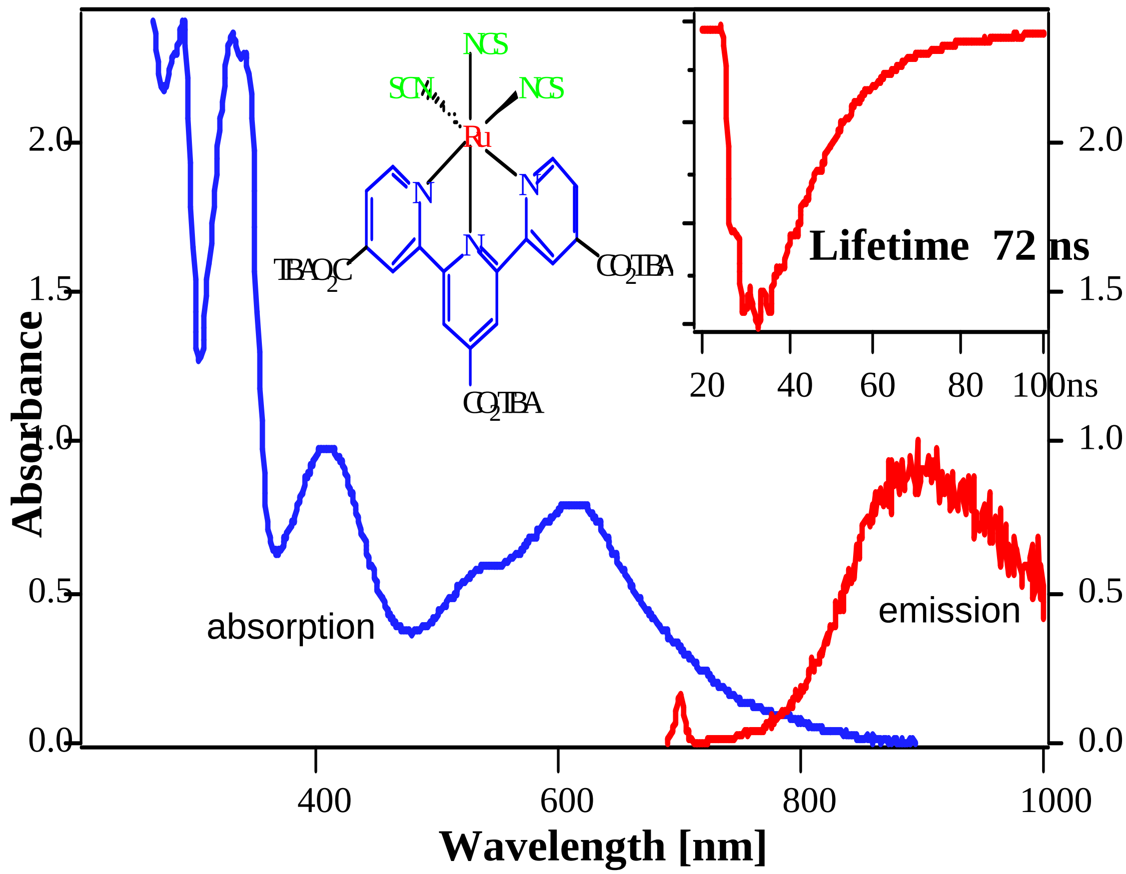
Spectral irradiance of the Sun at mean Earth-Sun separation



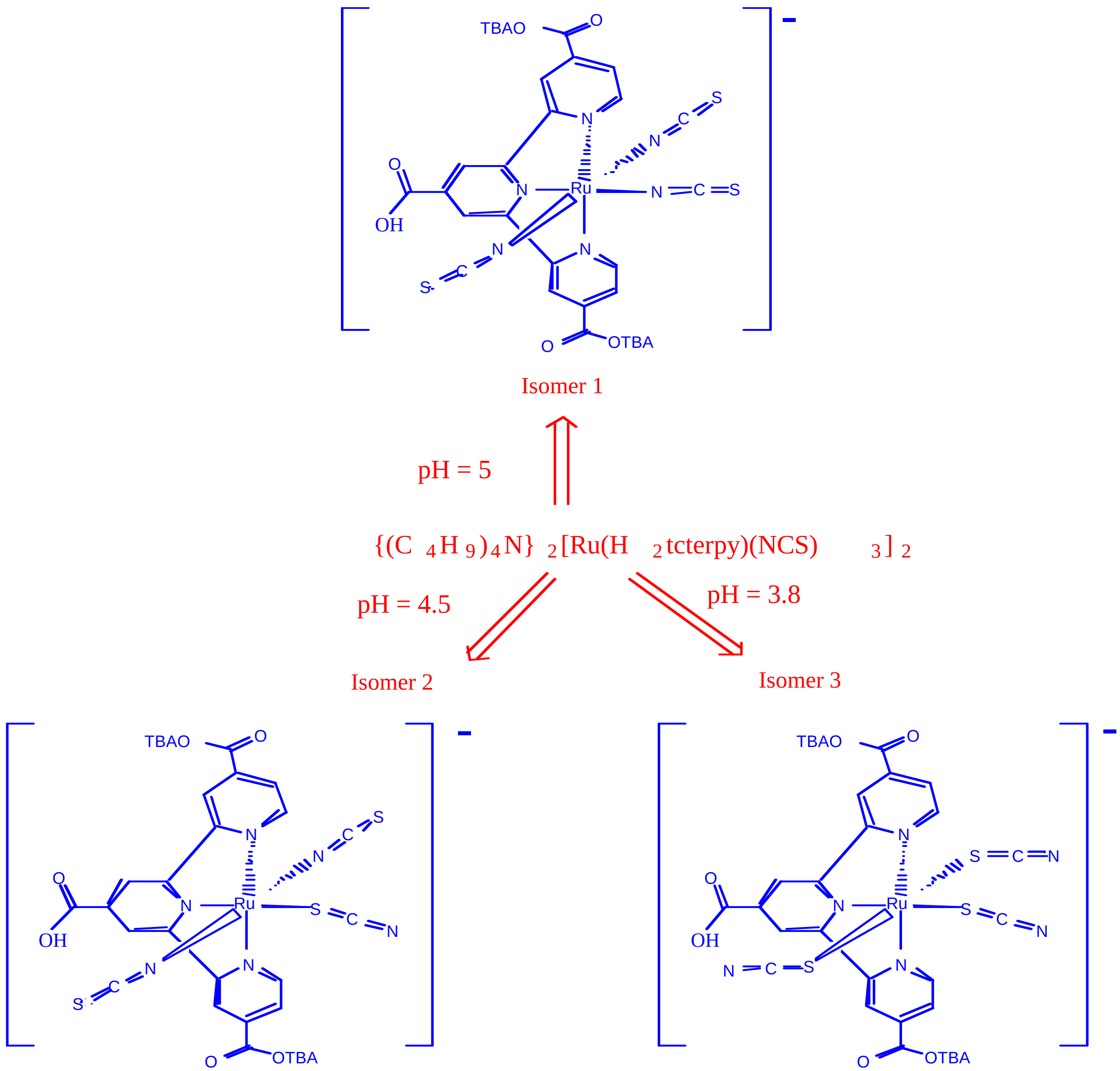
One factor that limiting further improvement of DSC is lack of energy capture by dyes in the IR region.

Half of the sun's energy reaching earth's lies above 700 nm and one third beyond 1000 nm

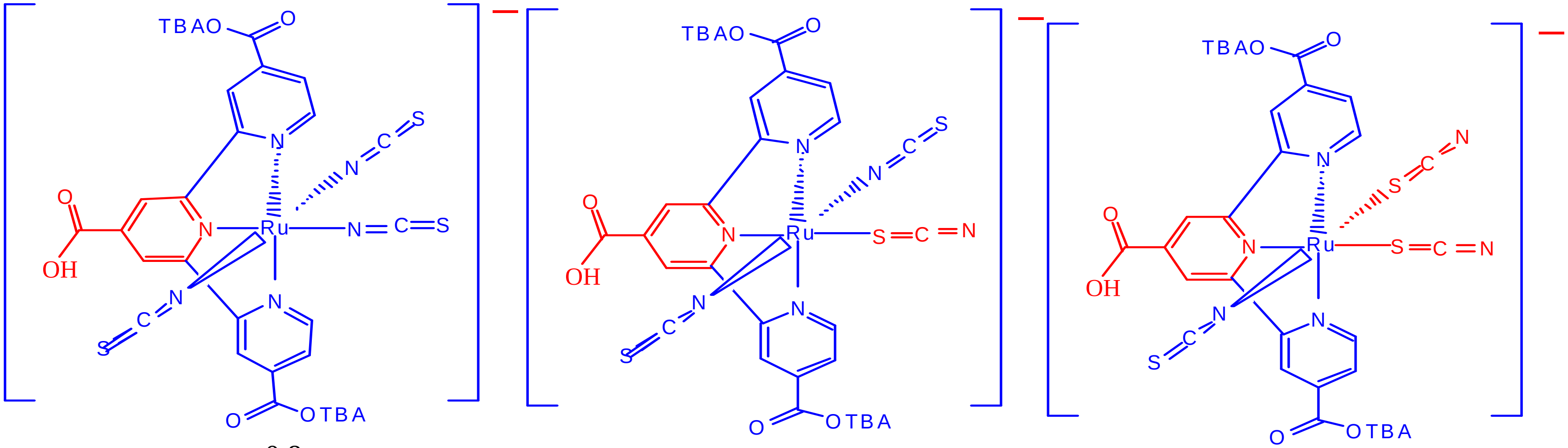
Absorption and Emission (ex = 700 nm) of Trithiocyanato (4,4’,4’’-tricarboxy-2,2’;6,2’’-terpyridine)Ruthenium(II) complex in MeACN

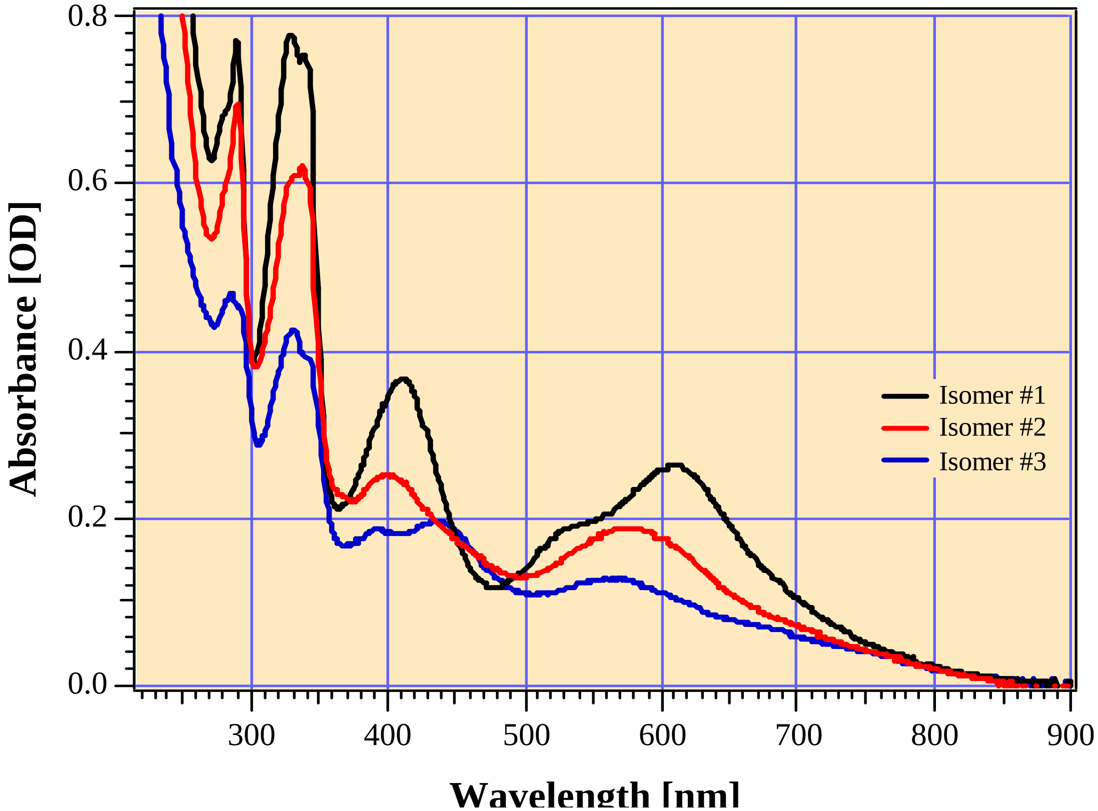


Separation of Linkage Isomers of Trithiocyanato (4,4’,4’’-tricarboxy-2,2’;6,2’’-terpyridine)Ruthenium(II)

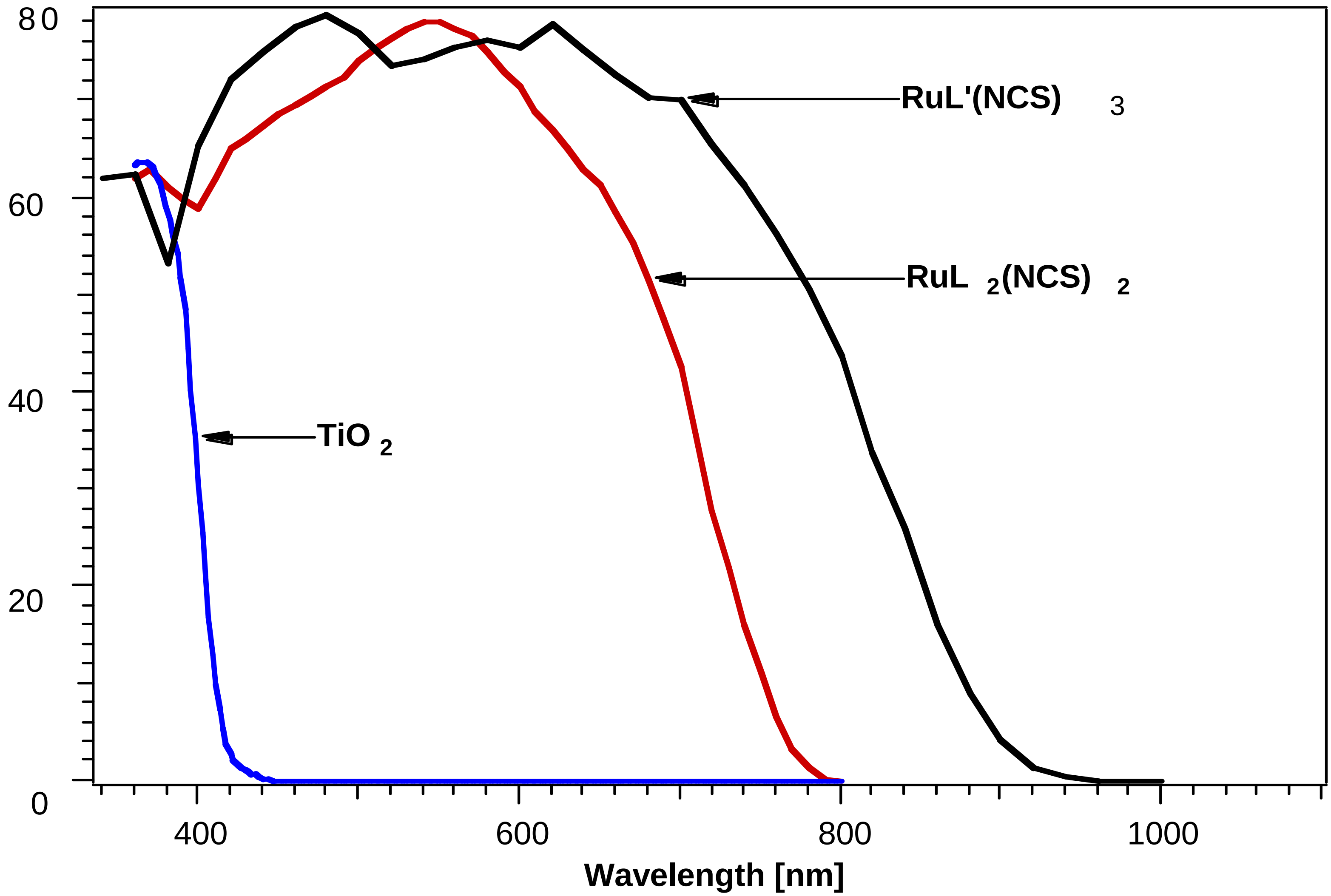


Isomers of the Black dye





Photocurrent action spectrum of different ruthenium complexes attached to nanocrystalline TiO_2 films

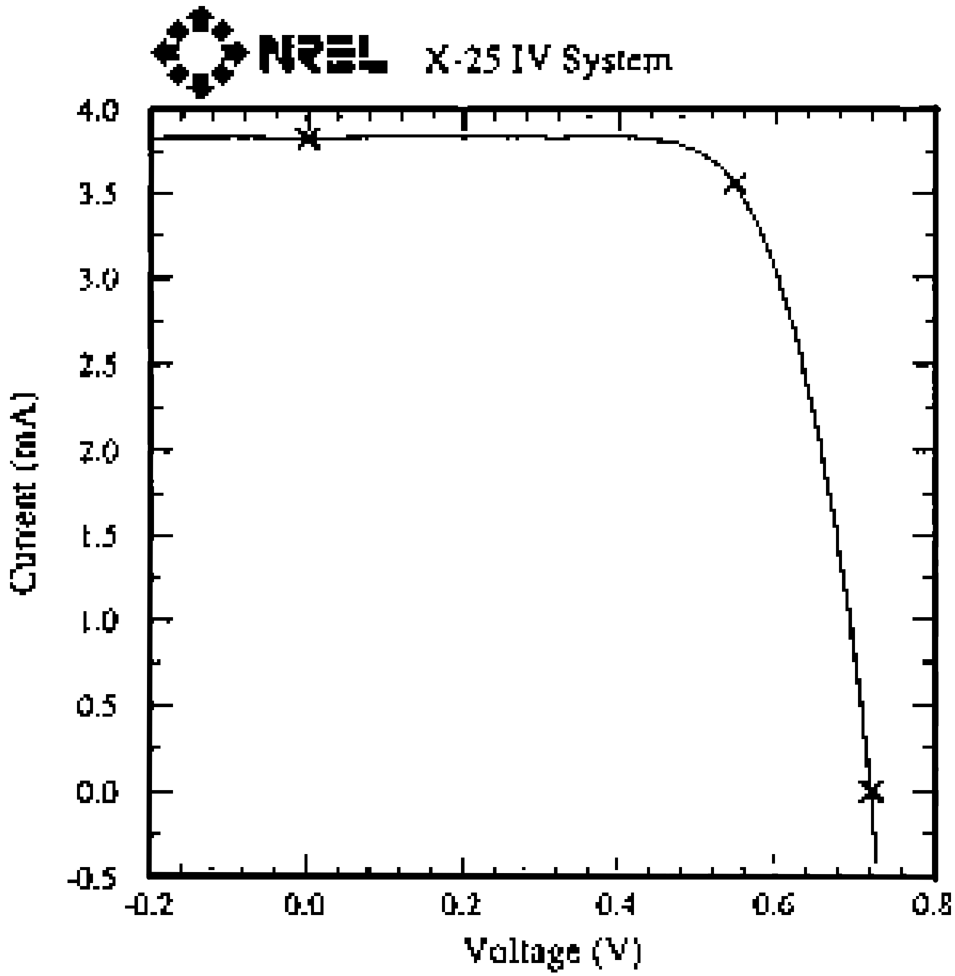


L = 4,4'-COOH-2,2'-bipyridine

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

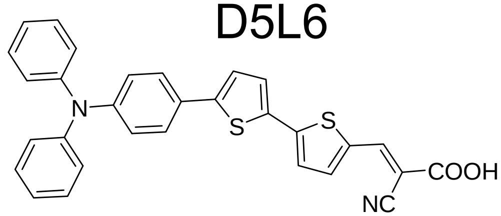
JACS, 2001, 123, 1613

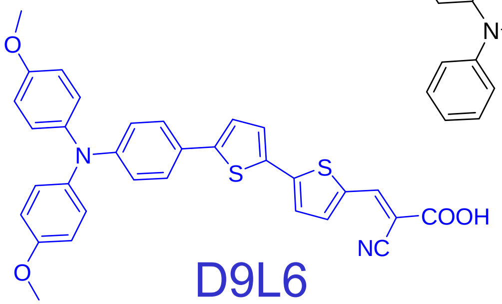
Photocurrent-voltage characteristics of a nanocrystalline photoelectrochemical cell sensitized with the Black Dye



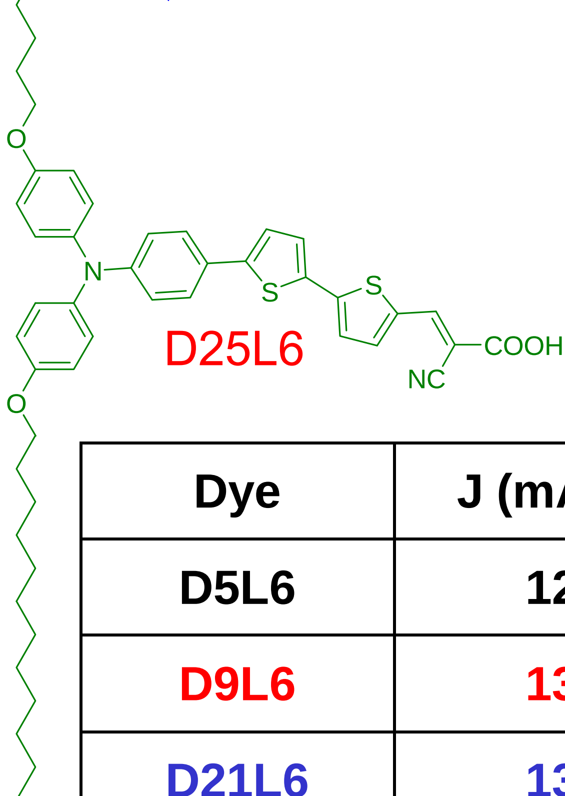
The results were obtained at the NREL calibration laboratory measured with an area of 0.1863 cm2 and irradiance of 1000 Wm-2. V_{oc} = 0.72 V, J_{sc} = 20.53 mAcm-2; fill factor = 70.41%; the efficiency = 10.4.

D5L6

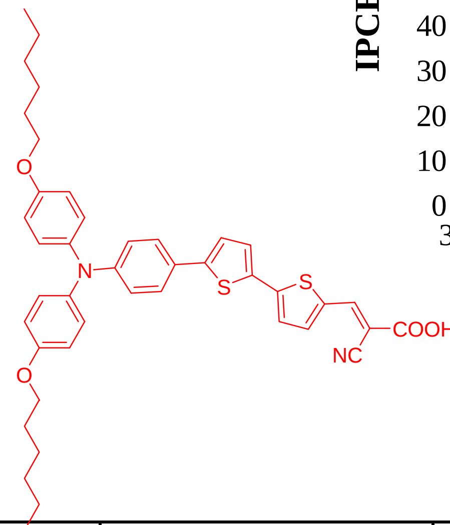




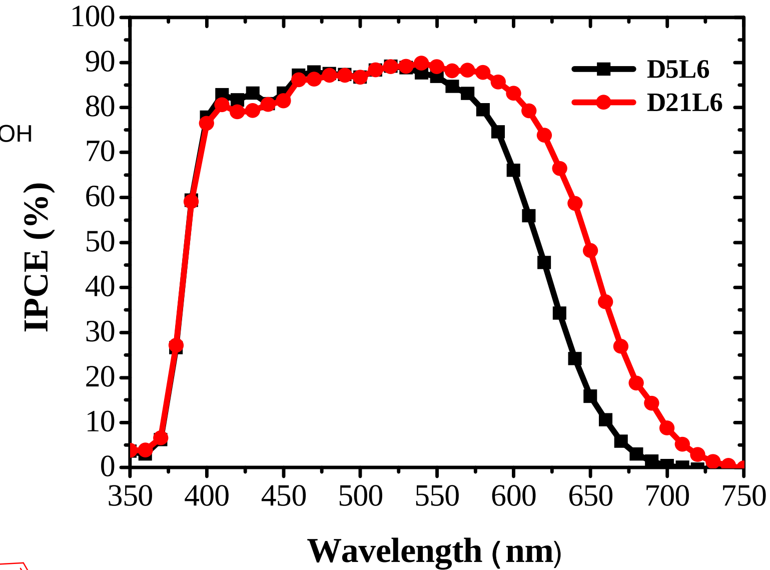
D9L6



D25L6

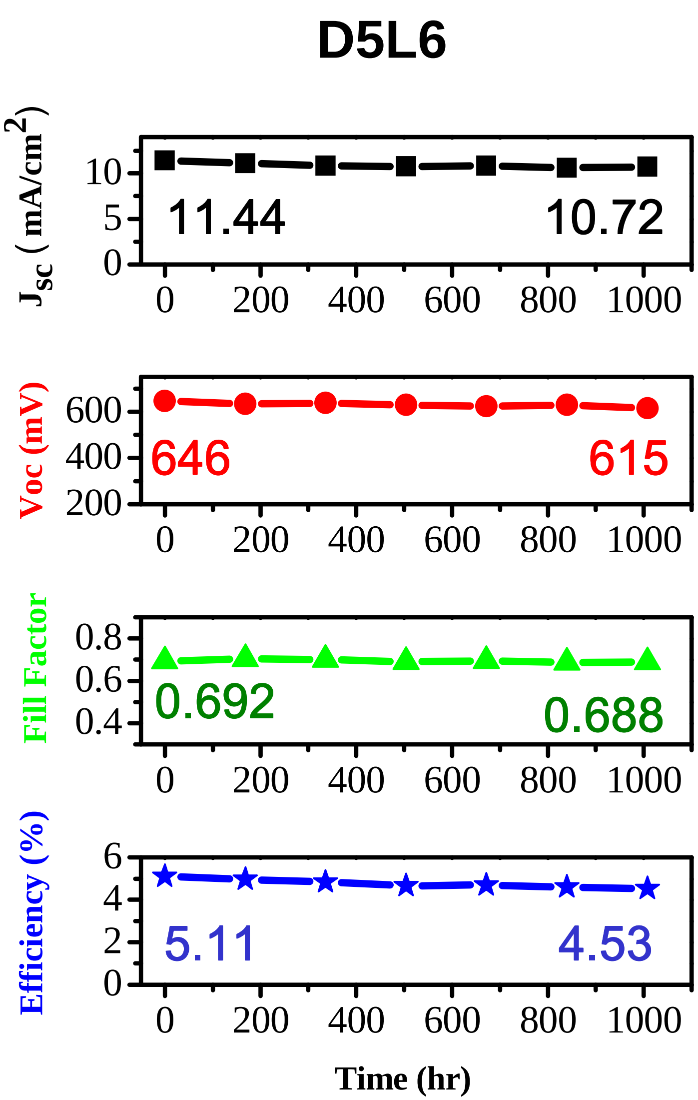


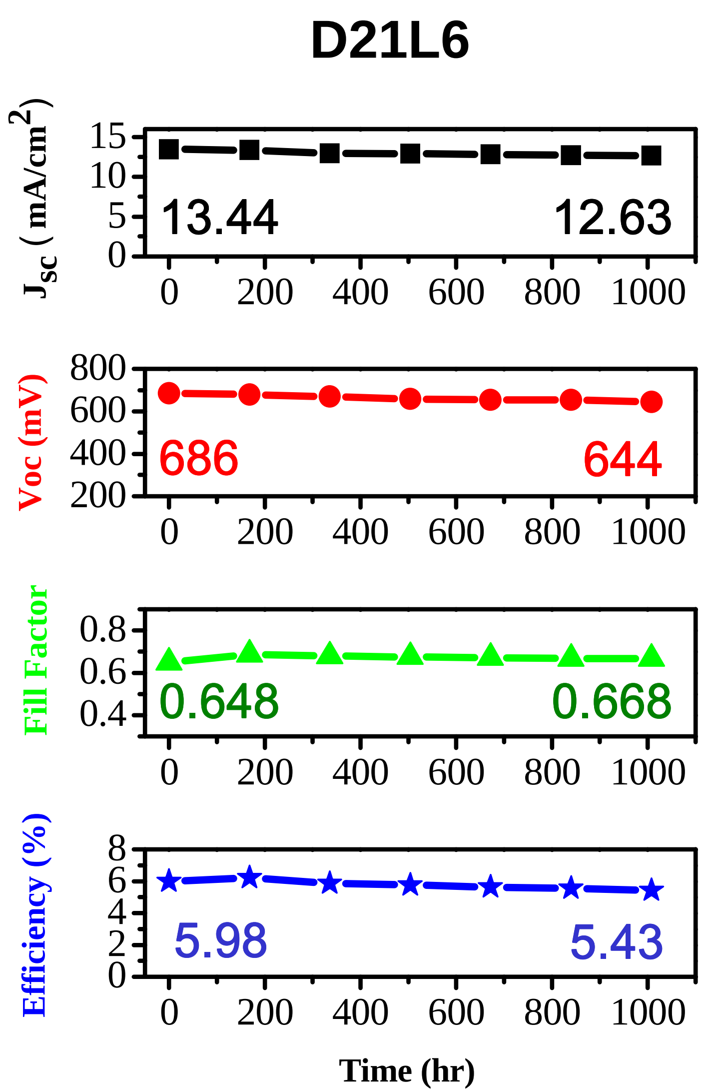
D21L6



Dye	J (mA/cm2)	V (mV)	FF	efficiency
D5L6	12.50	685	0.74	6.29
D9L6	13.36	641	0.70	6.08
D21L6	13.70	733	0.72	7.25
D25L6	13.73	745	0.69	7.05

Stability with IL z655 under light soaking + 60 degree

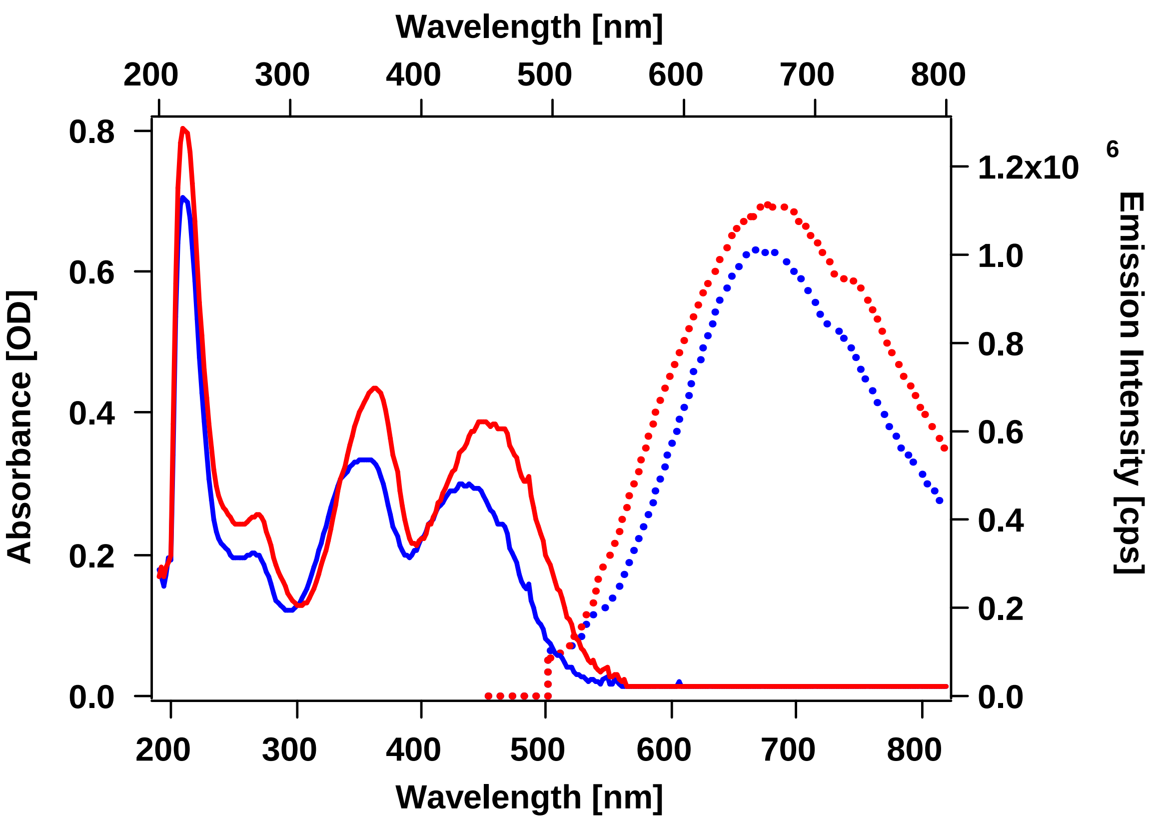


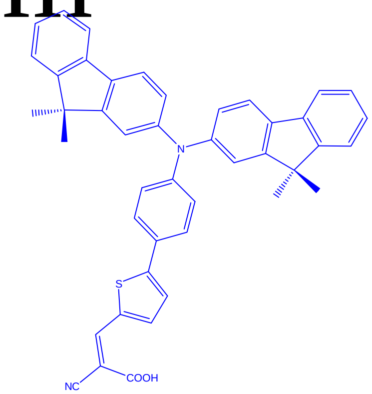


88%

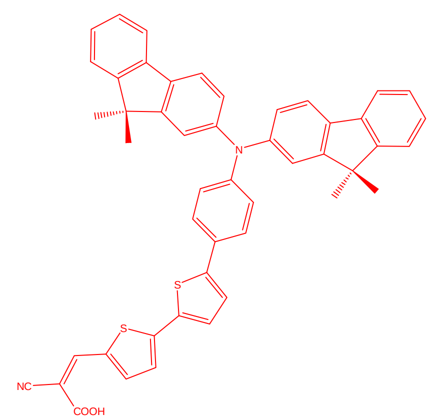
90%

Absorption spectrum



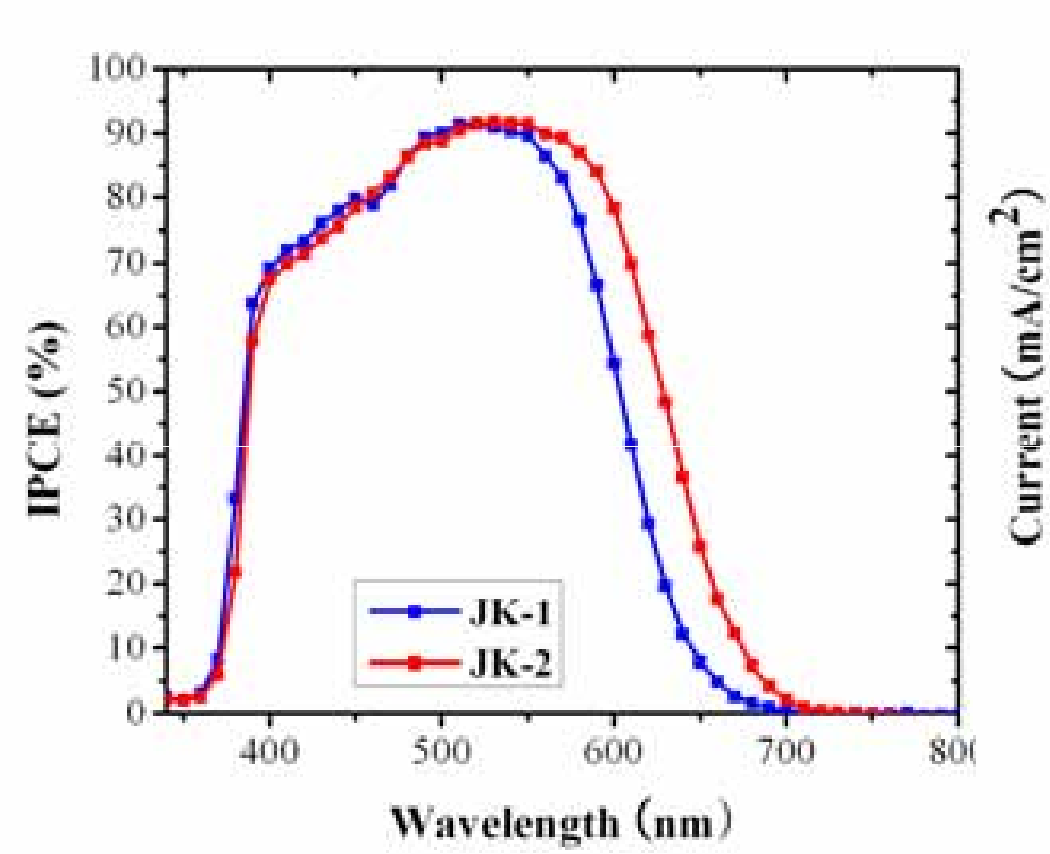


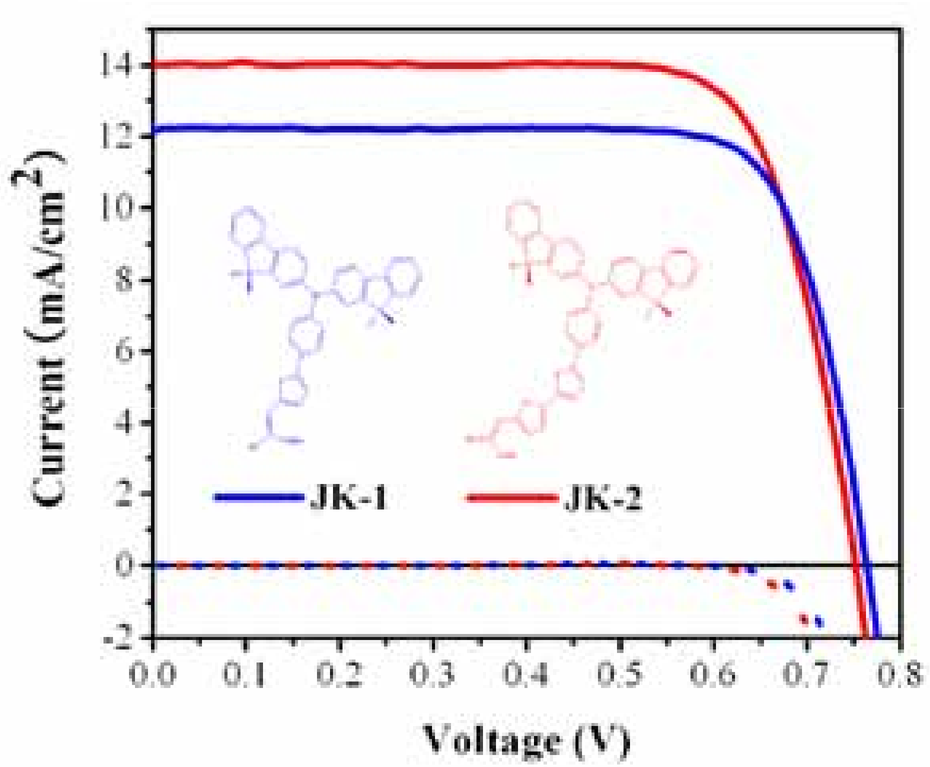
354 nm (ε = **34,000** dm^{3}mol^{-1}cm^{-1})
436 nm (ε = **30,000** dm^{3}mol^{-1}cm^{-1})



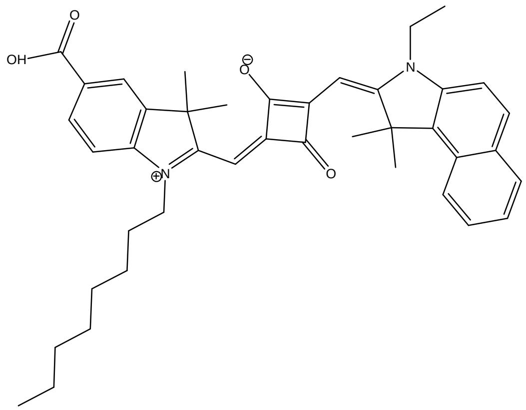
364 nm (ε = **44,000** dm^{3}mol^{-1}cm^{-1})
452 nm (ε = **39,000** dm^{3}mol^{-1}cm^{-1})

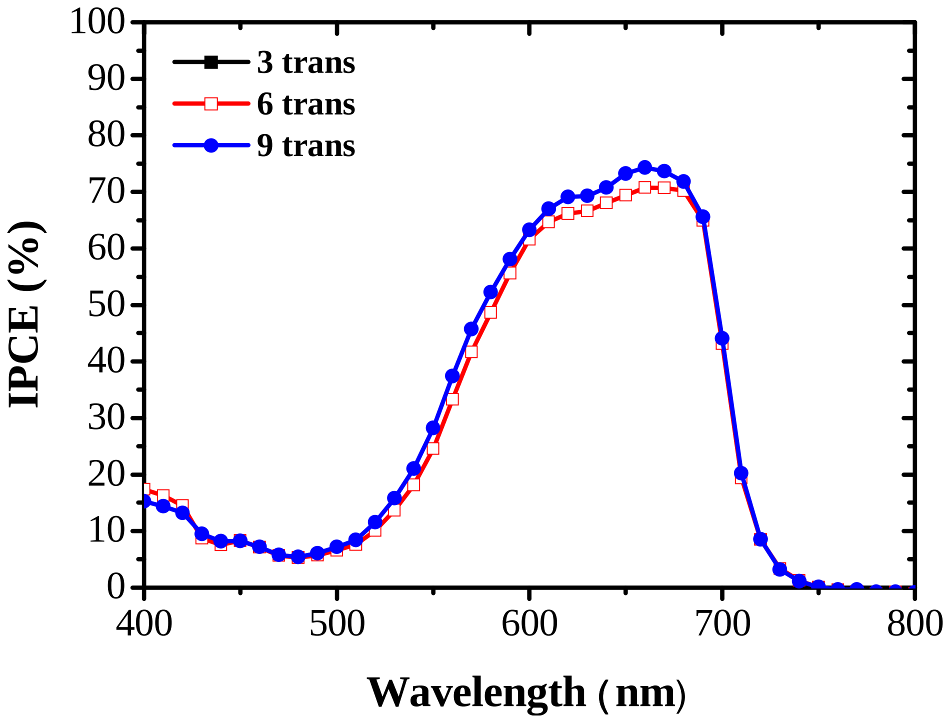
IPCE and IV data of JK1 and JK2 dyes





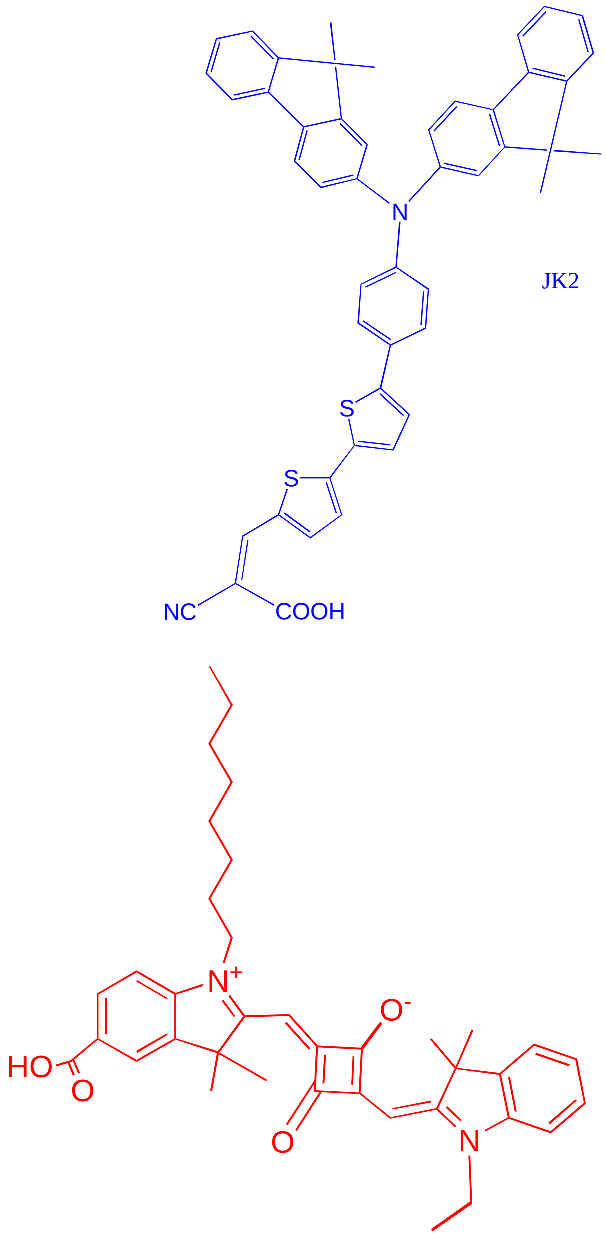
91 % IPCE
power conversion 7.20% (JK-1)
and 8.01% (JK-2)

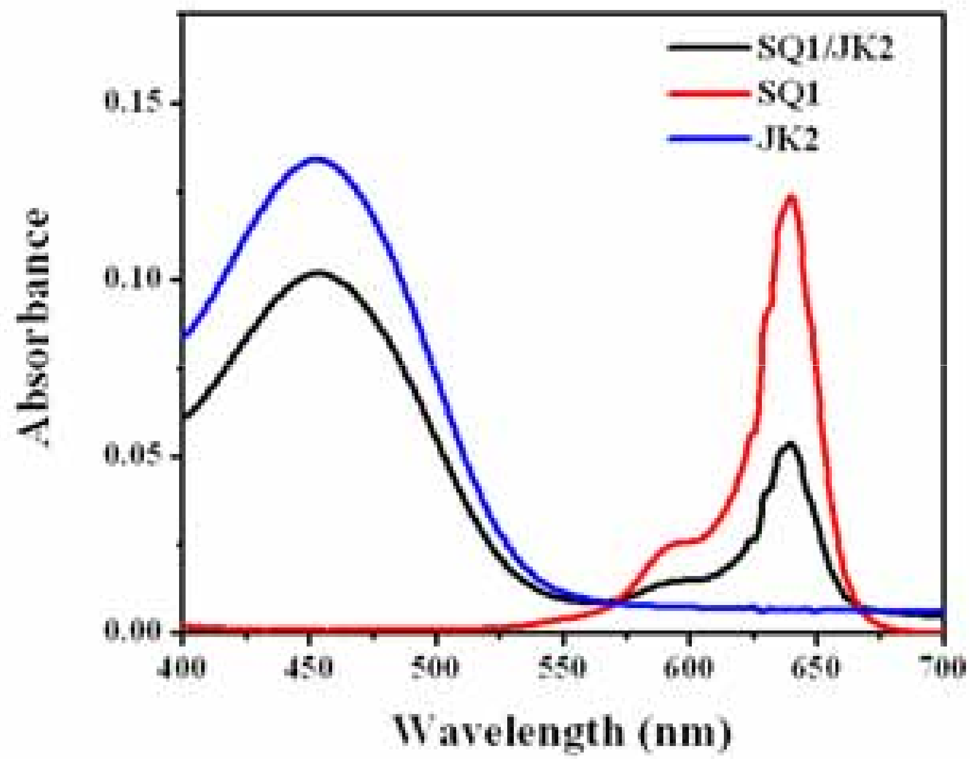


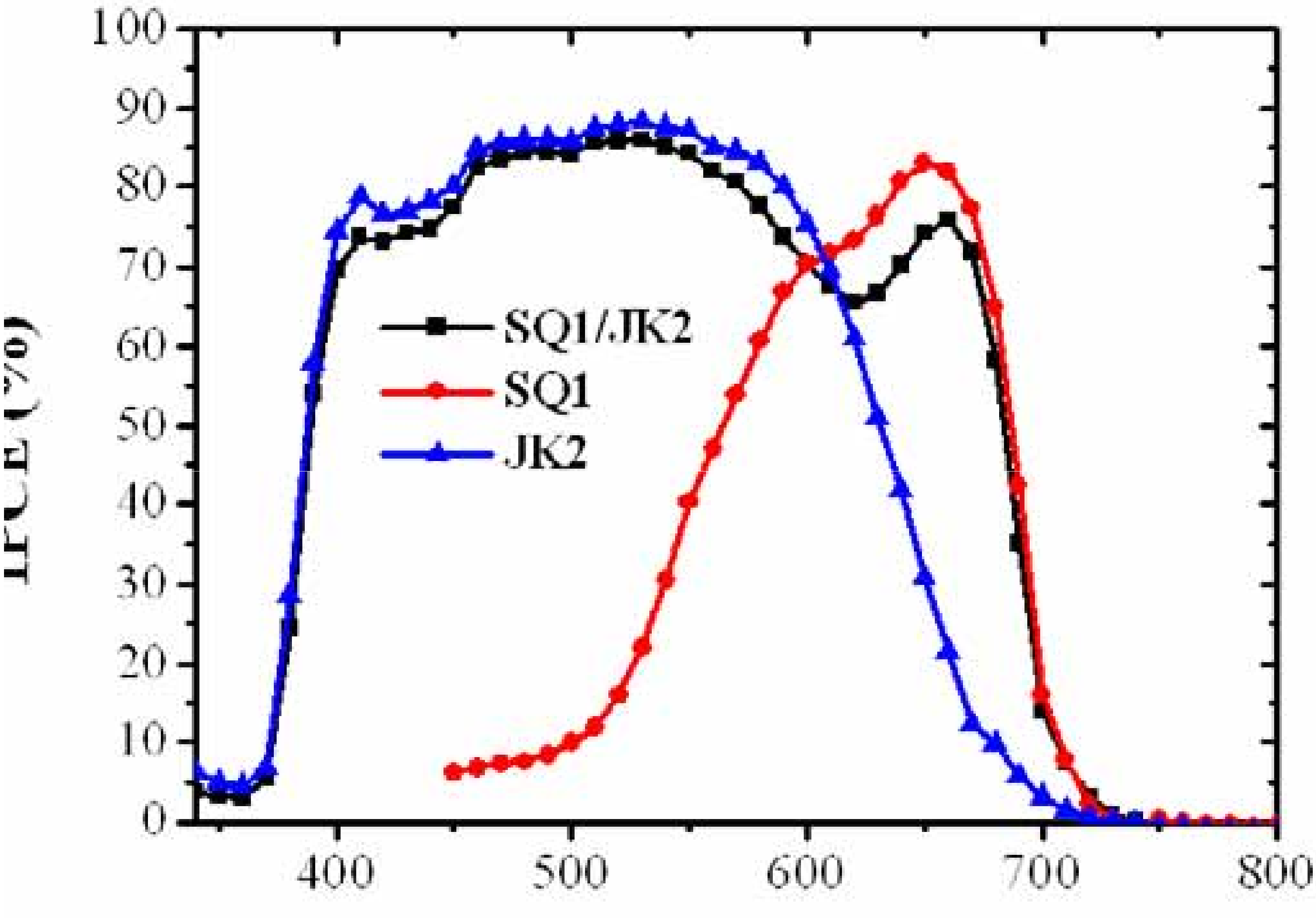


Thickness effect

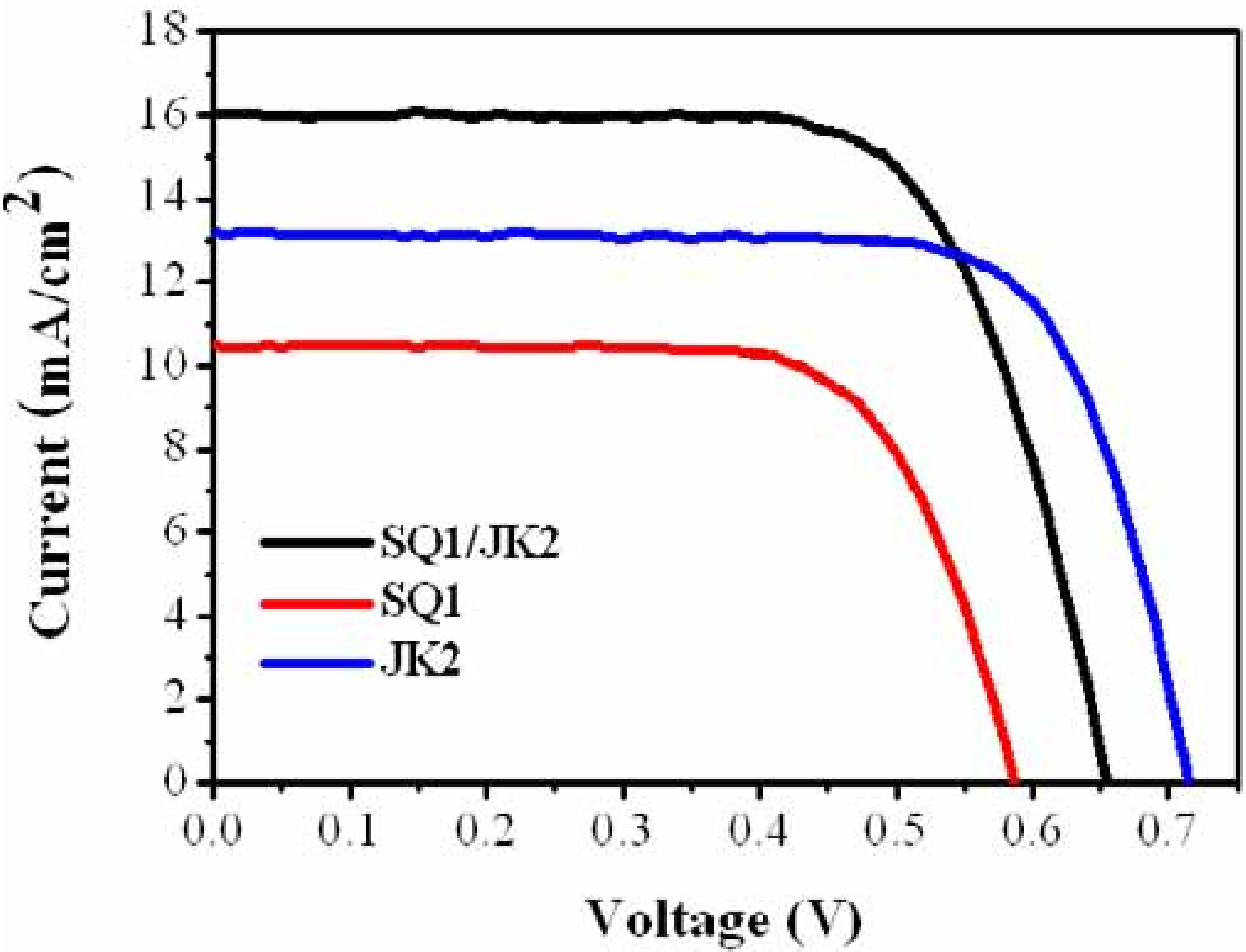
Film (μm)	J (mA/cm2)	V (mV)	FF	efficiency
6 trans	9.31	645	0.661	4.00
9 trans	10.50	621	0.654	4.28
9 +5	11.4	667	0.72	5.40


N
JK2
S
S
NC
COOH
N+
O-
HO
O
O
N


SQ1/JK2
SQ1
JK2
Absorbance
0.15
0.10
0.05
0.00
400
450
500
550
600
650
700
Wavelength (nm)

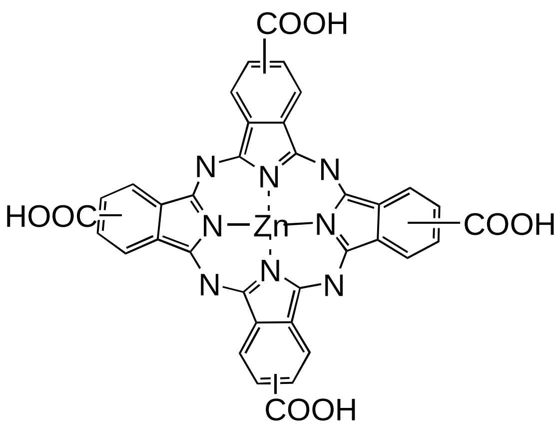


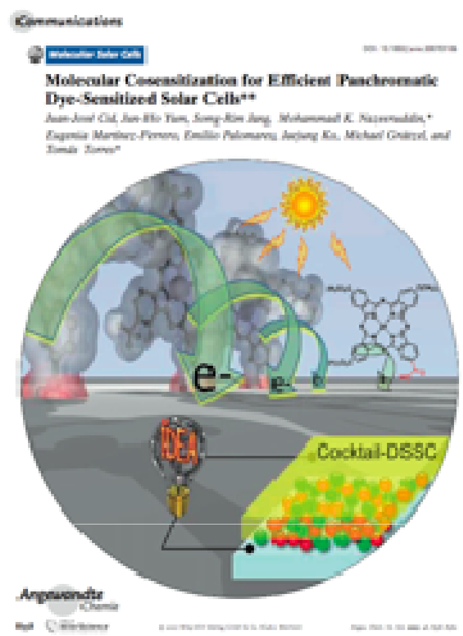
IPCE (%)
100
90
80
70
60
50
40
30
20
10
0
400
500
600
700
800
Wavelength (nm)
SQ1/JK2
SQ1
JK2



18
16
14
12
10
8
6
4
2
0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Current (mA/cm2)
Voltage (V)
SQ1/JK2
SQ1
JK2

Zinc Phthalocyanine

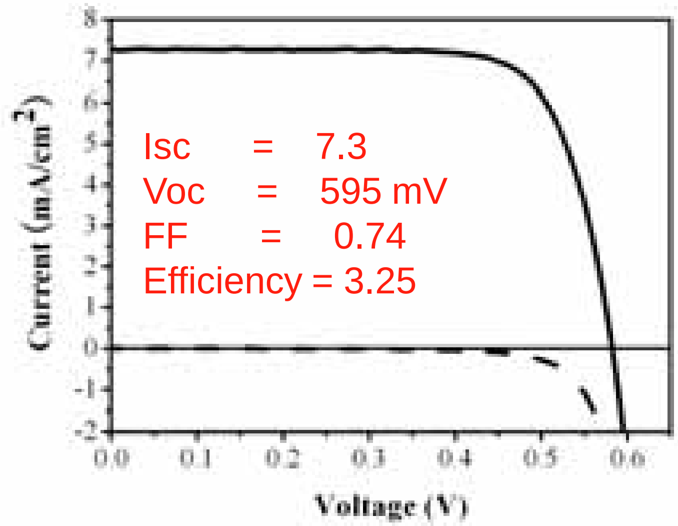


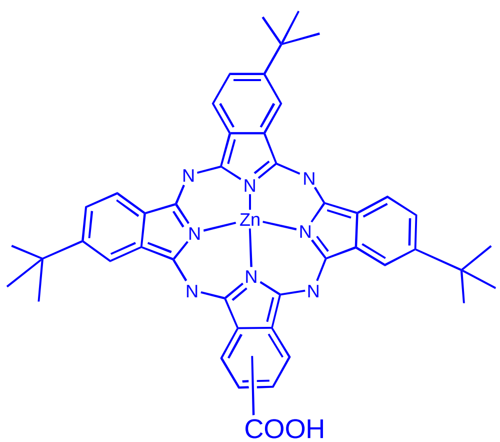

Communications

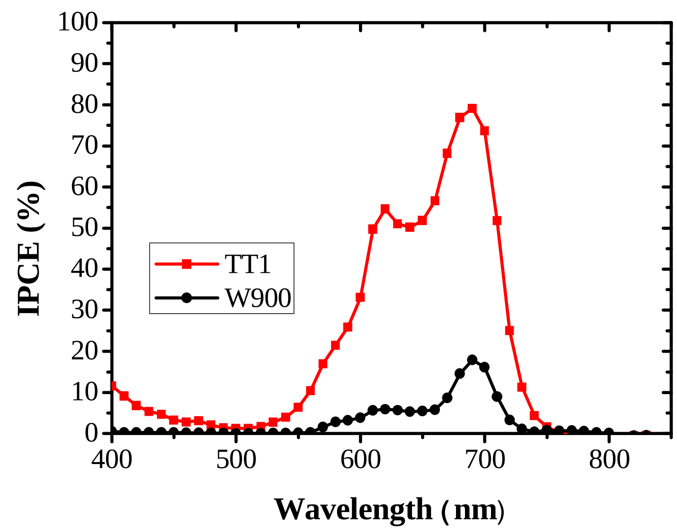
Molecular Solar Cells

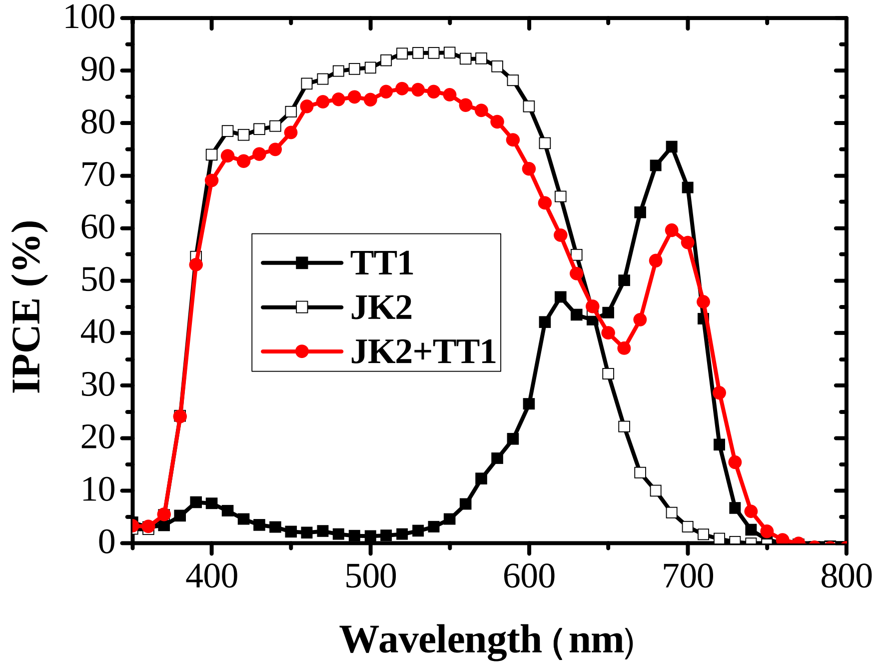
Molecular Cosensitization for Efficient Panchromatic Dye-Sensitized Solar Cells**

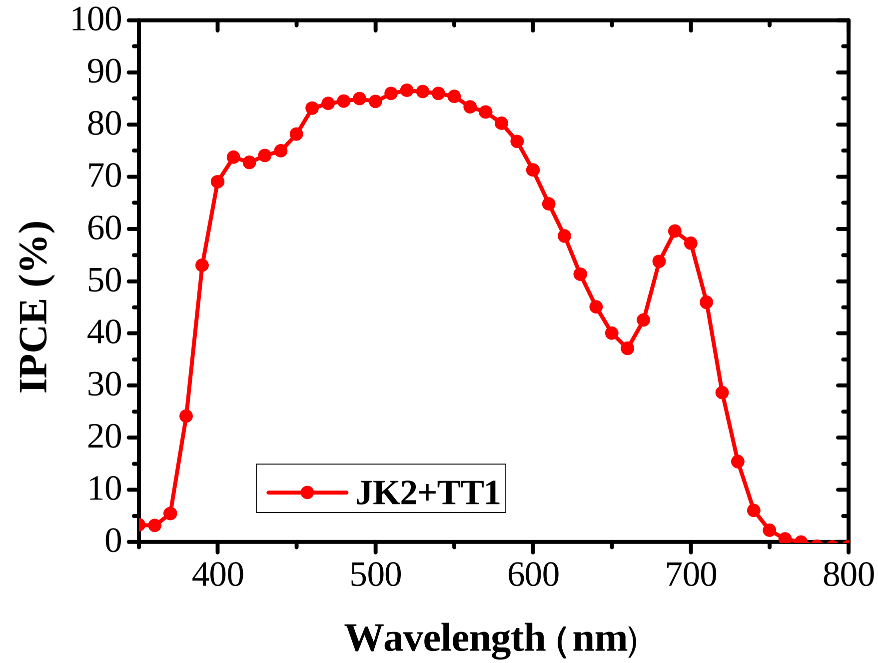
Juan-José Cid, Jun-Ho Yum, Soo-Rim Jang, Mohammad K. Nazeeruddin, Eugenia Martínez-Ferrero, Emilio Palomares, Jaejung Ko, Michael Grätzel, and Tomás Torres**



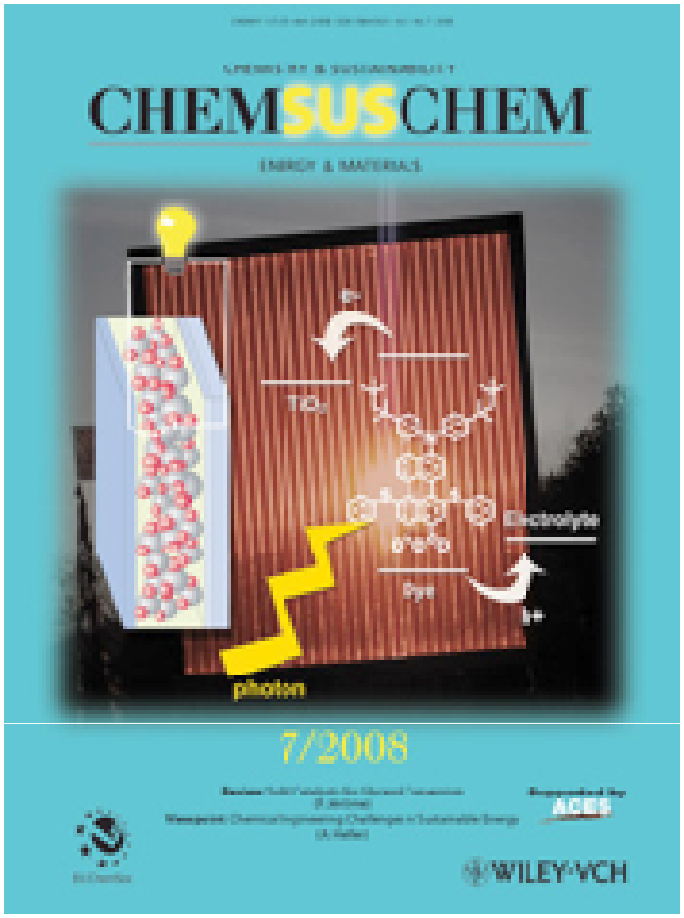


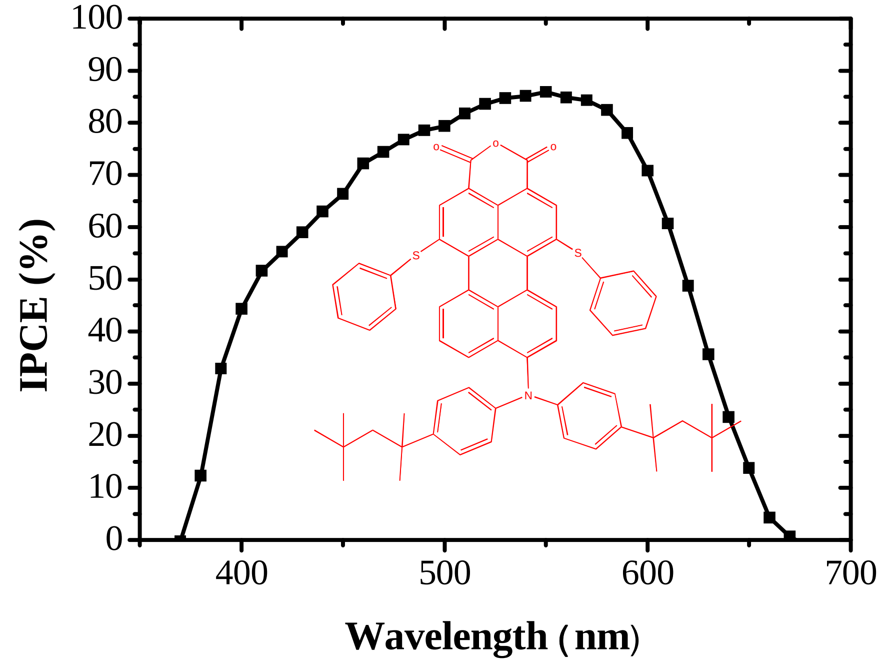




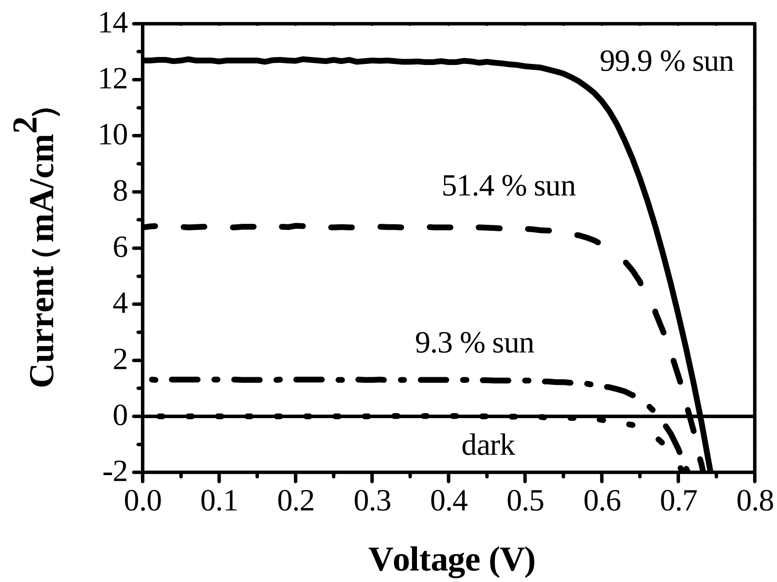


Dye	J (mA/cm2)	V (mV)	FF	efficiency
TT1	6.55	601.5	0.746	2.94
JK2	14.45	690.03	0.709	7.08
JK2+TT1	16.11	650.02	0.7	7.33
after 1 day	15.96	676.82	0.72	7.77





Light Intensity	J (mA/cm2)	V (mV)	FF	efficiency
99.9 %	12.68	728	0.736	6.80
51.4 %	6.74	715	0.766	7.18



Effect of solvent on performance of BASF_ID94 at 1 sun
TIO2: 6+4 μm; electrolyte A7117

Solvent	J (mA/cm2)	V (mV)	FF	efficiency
EtOH	3.75	641.0	0.740	1.77
DCM:AcN	10.30	651.0	0.723	4.85
CB	12.57	725.0	0.708	6.45
DCB	10.52	707.5	0.696	5.18
DMB	2.39	5079	0.725	0.88
BiCH	12.68	728.6	0.722	6.80
toluene	11.55	696.1	0.720	5.79
CCl_4	12.28	718.9	0.714	6.31

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