Dye-Sensitized Solar cells: Basic Science and Commercialization

Royal Society of Edinburgh,

Meeting on zero Carbon Energy 27, May 2015

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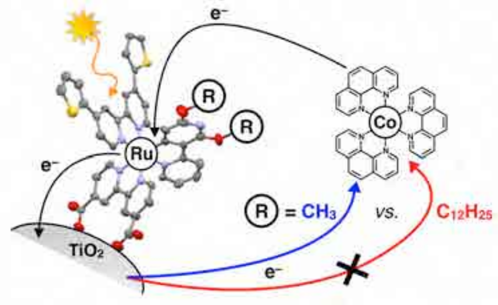

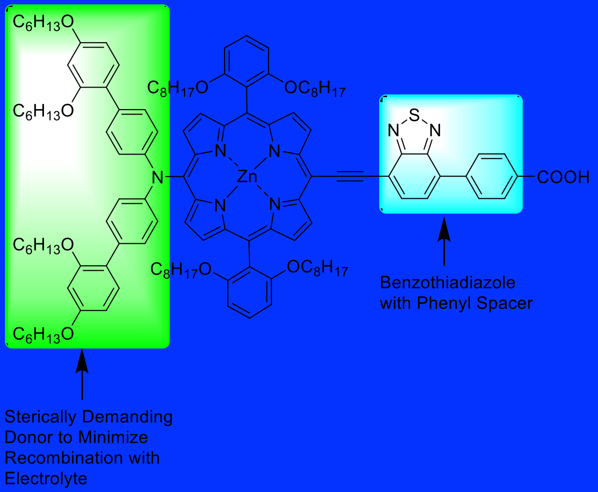

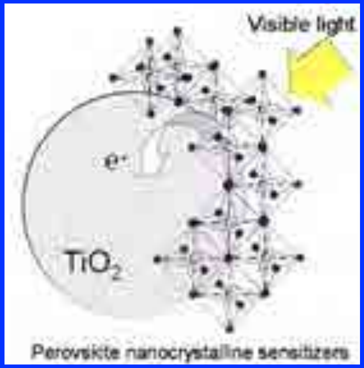

CH3NH3PbI3

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King Saud University

King Abdulaziz University

KOREA UNIVERSITY


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Outline

Molecular engineering of:

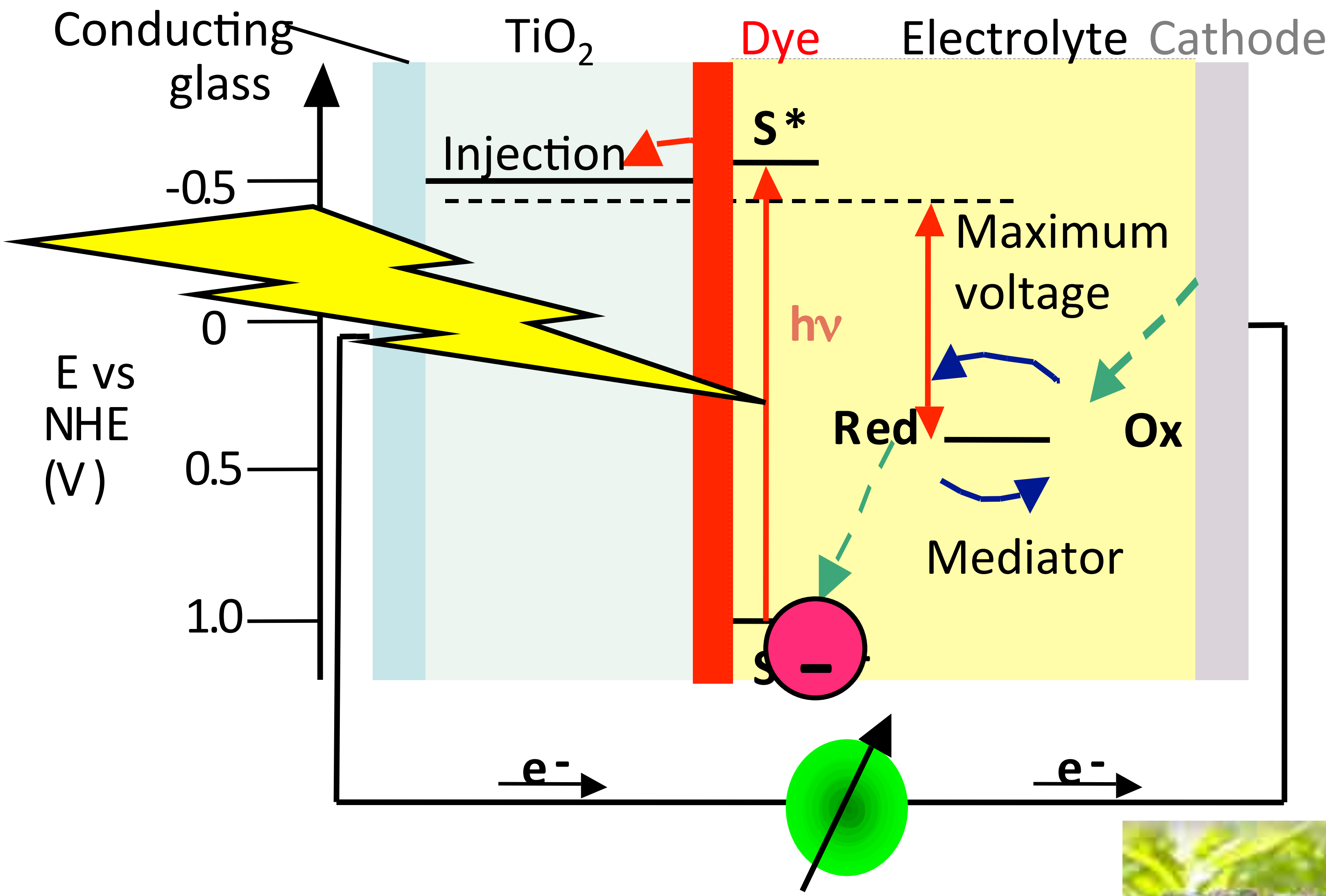
- **Sensitizers**
- **Redox Mediators**

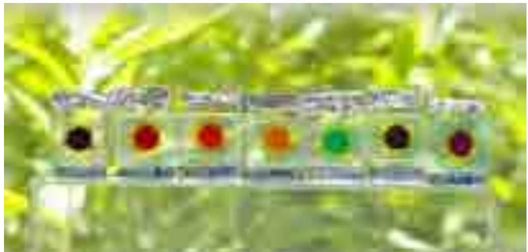
Perovskite Sensitized Solar cells (PSC)

- **Hole Transporting Materials for DSC and PSCs**

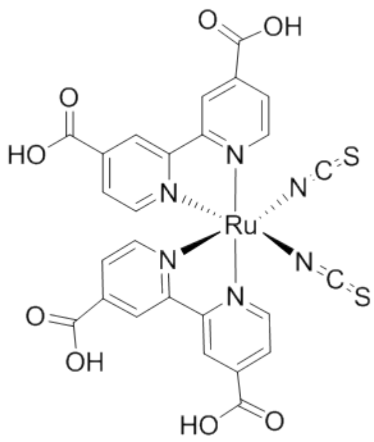
- **First commercial applications of dye sensitized solar cells**

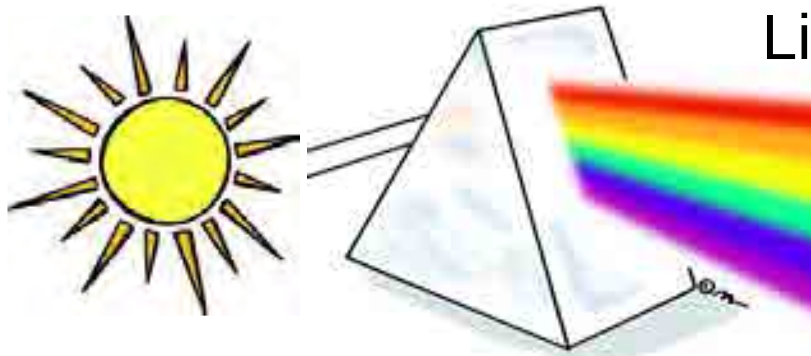
Principle of operation of dye sensitized solar cells





Dye sensitized solar cell

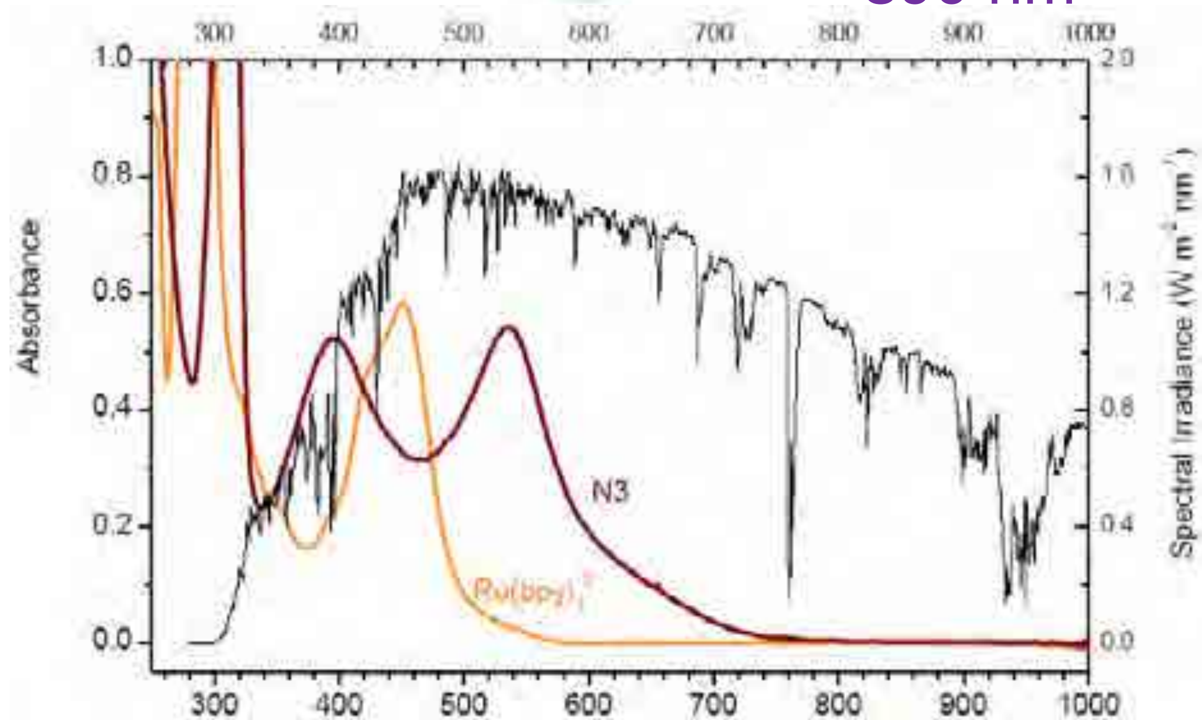




Light wavelength

750 nm

390 nm



wavelength (nm)

Typical Dye (N3)

J_{sc} : 17.73 mA/cm^2
V_{oc}: 0.846 V
FF: 0.74
Eff: 11.2%

JACS, 127, 16835, 2005

Dynamics of electron transfer reactions in sensitized mesoscopic solar cells

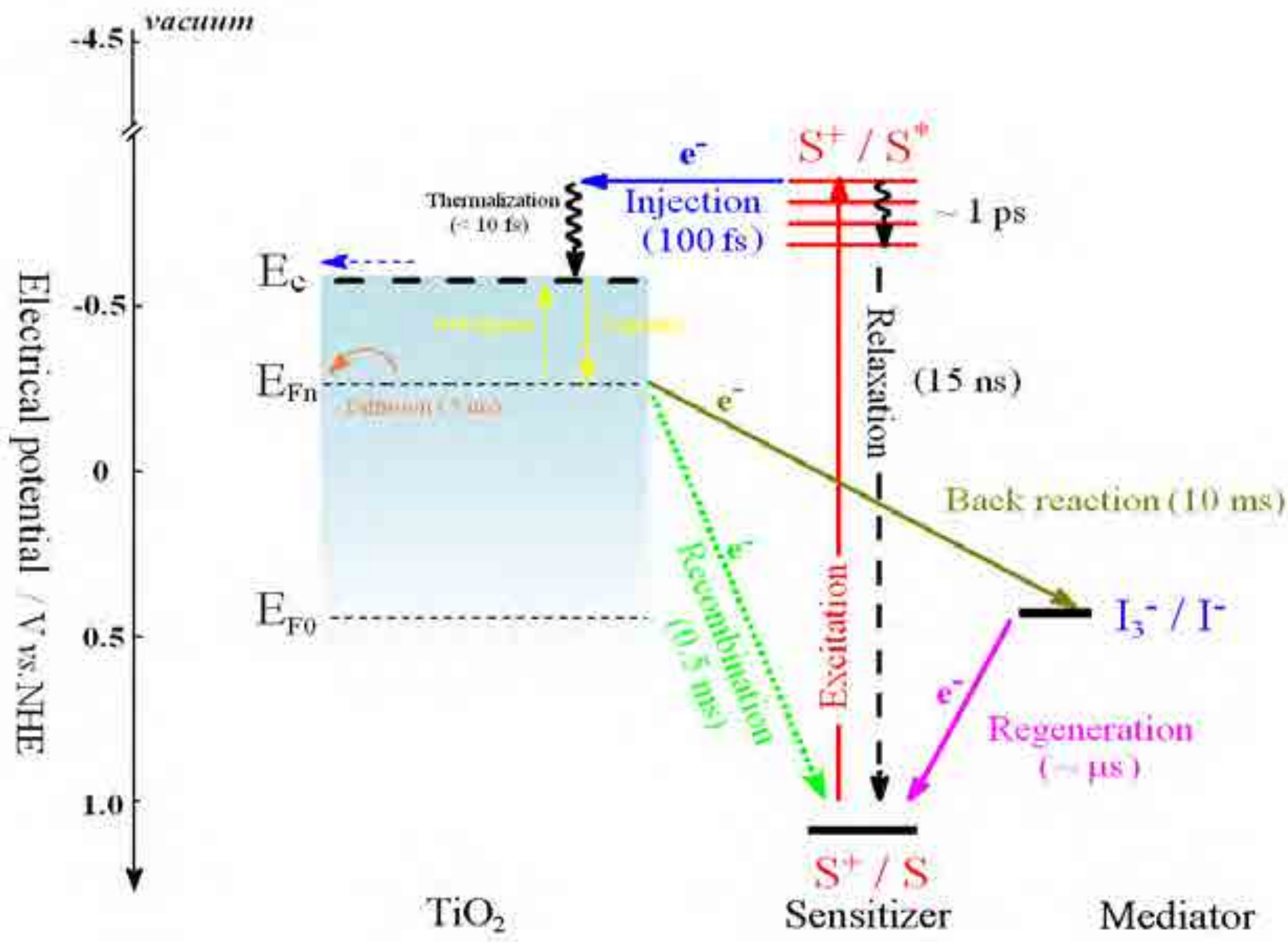
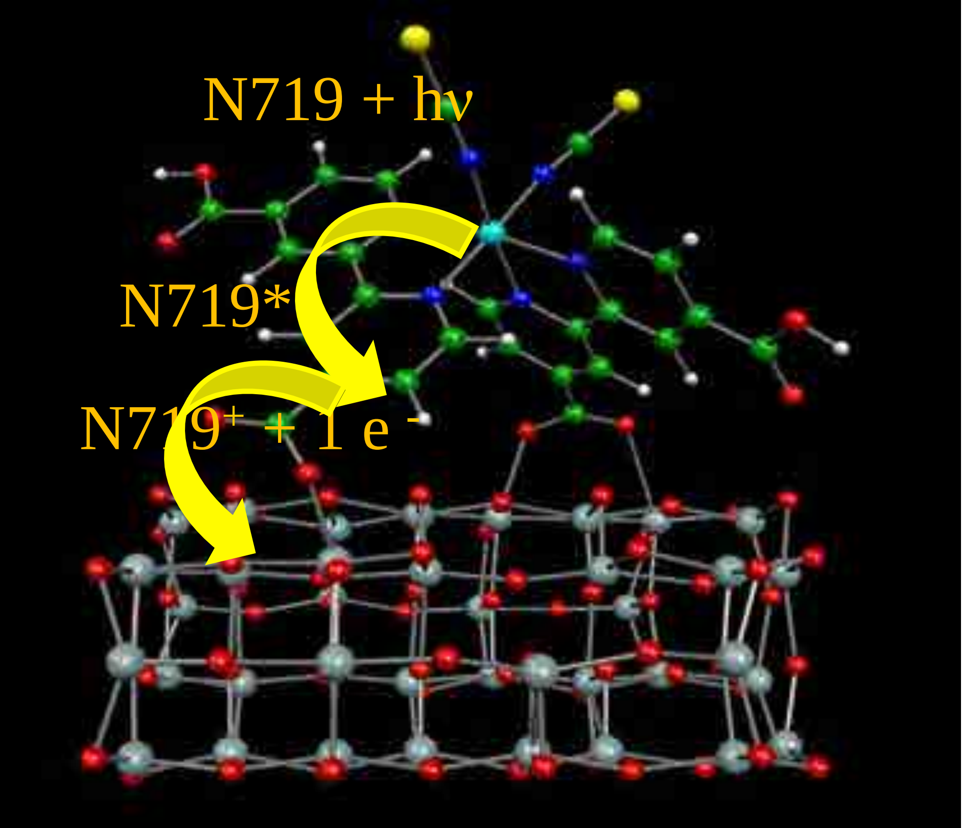
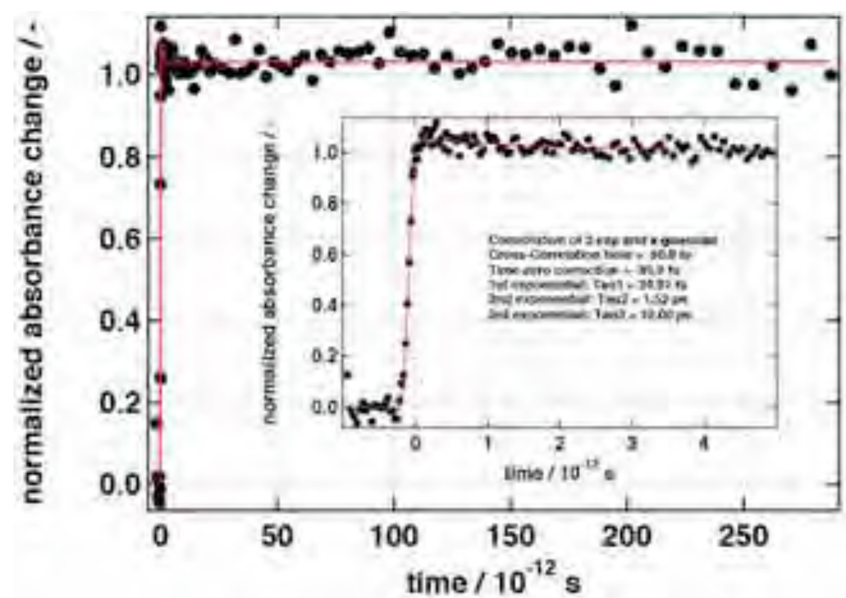
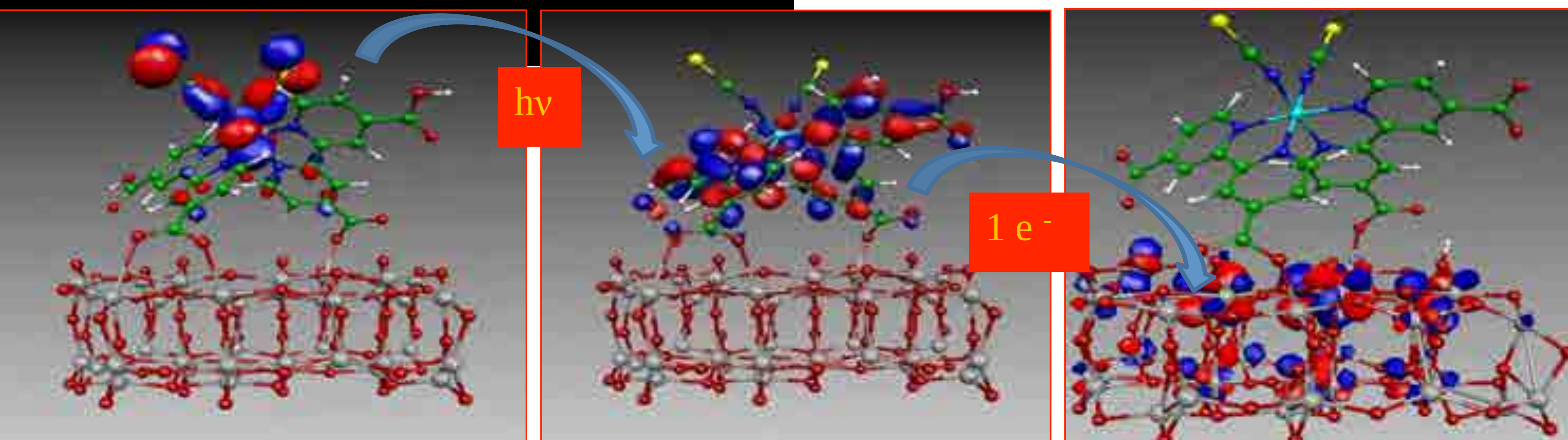


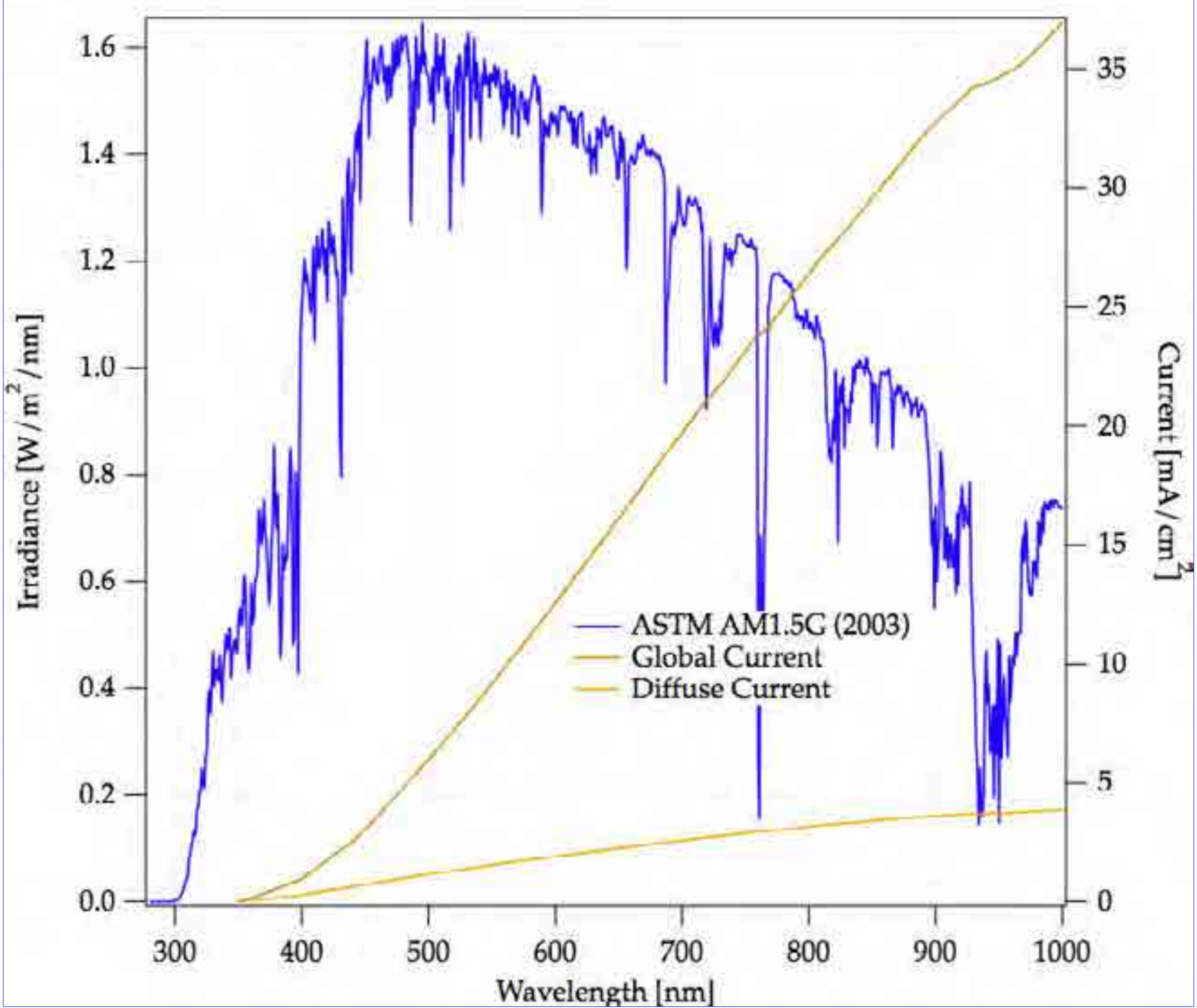
Photo-induced interfacial charge separation occurs within femtosecpnds







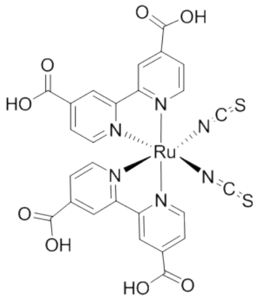
F. F. De Angelis, S. Fantacci, A. Selloni, M. Grätzel *J. Am. Chem. Soc. 2007*

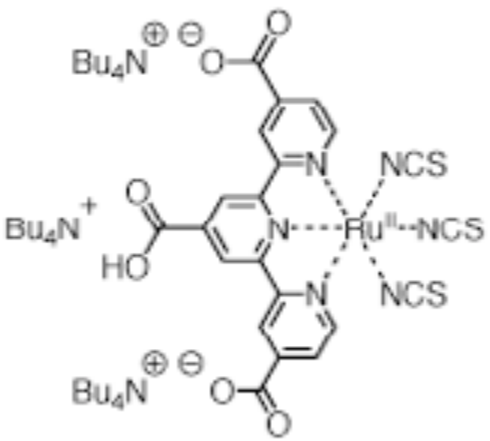


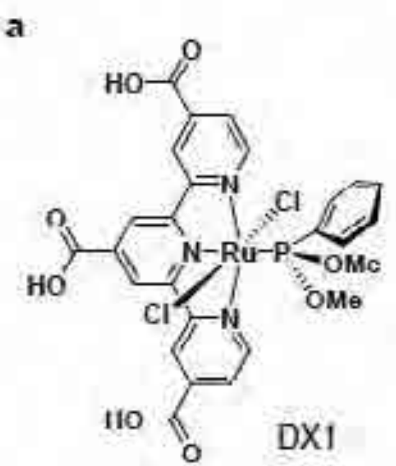
Irradiance [W/m^2/nm]
Current [mA/cm^2]
Wavelength [nm]
ASTM AM1.5G (2003)
Global Current
Diffuse Current
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0
5
10
15
20
25
30
35
300
400
500
600
700
800
900
1000

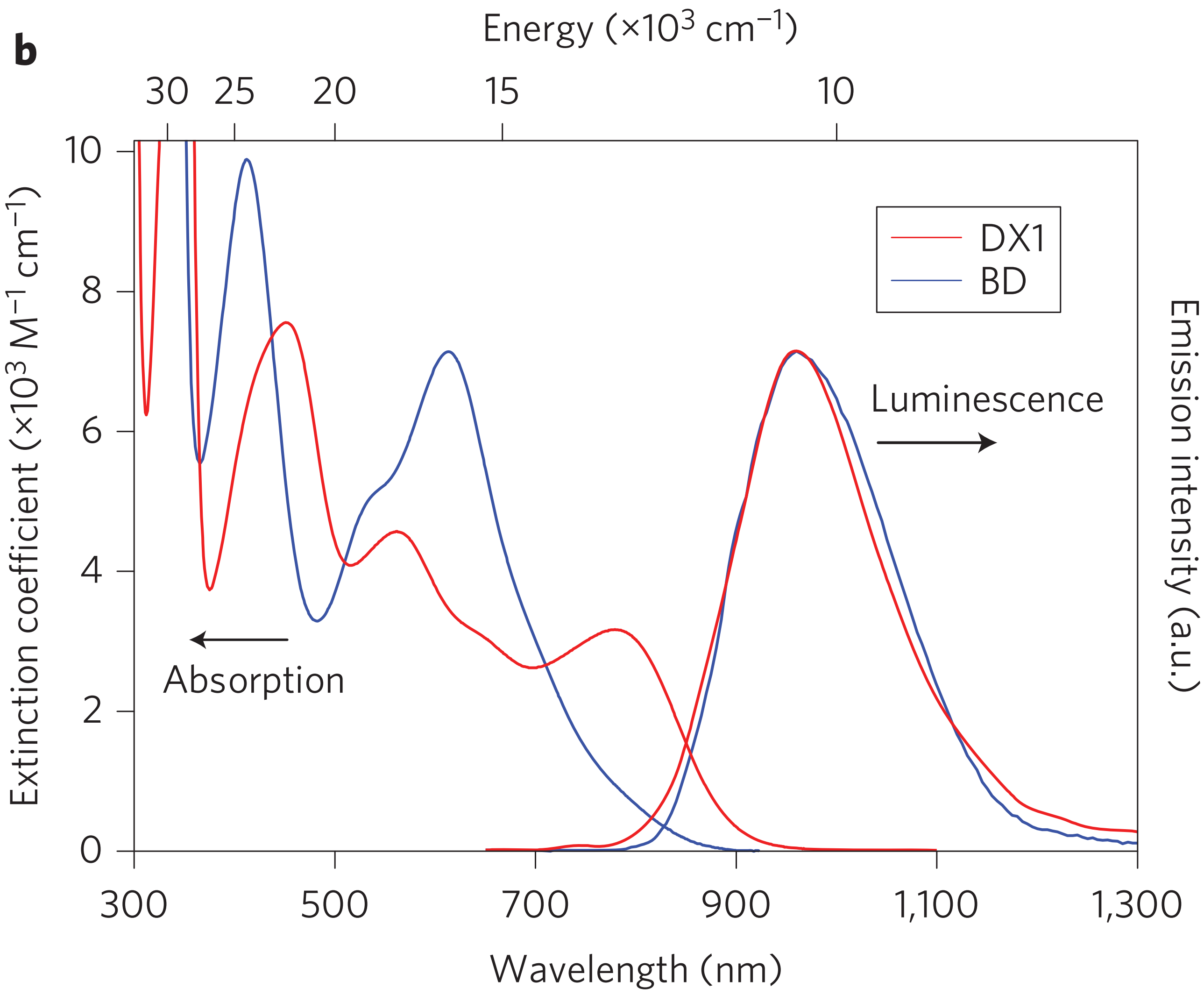
The DX1 dye harvests more near IR light in the 750 -900 nm region than the black dye

Engineering of Triplet Tuning

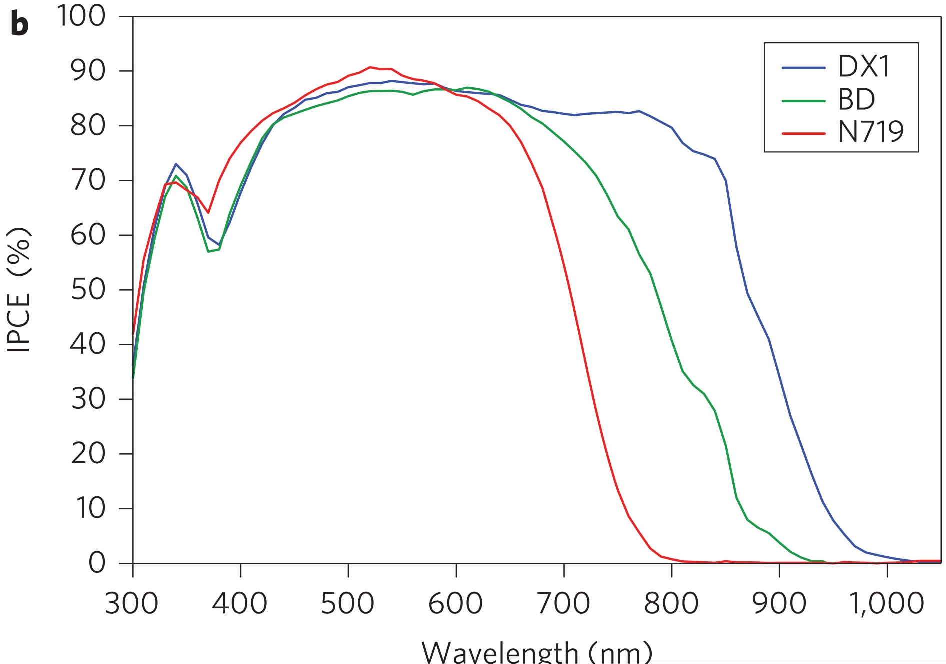


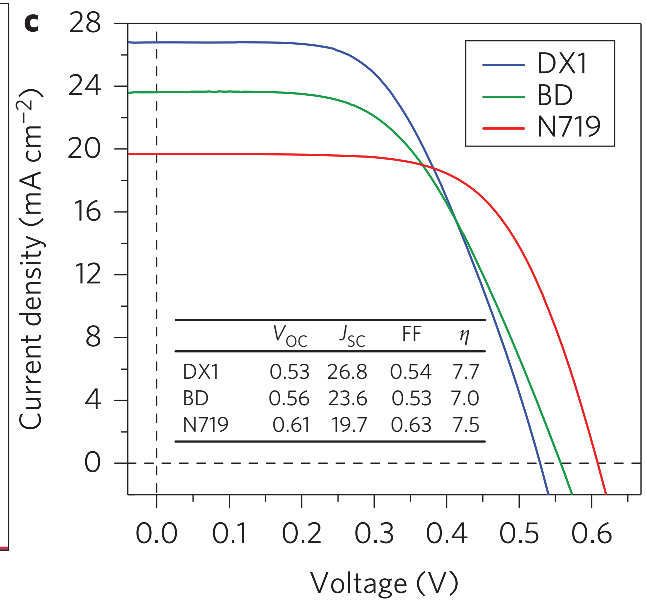






Prof. Segawa et al., Nature Photonics 7, 535–539 (2013)





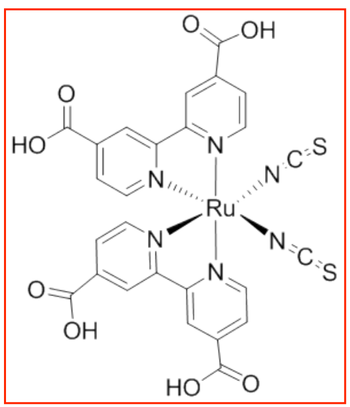
	V_{OC}	J_{SC}	FF	η
DX1	0.53	26.8	0.54	7.7
BD	0.56	23.6	0.53	7.0
N719	0.61	19.7	0.63	7.5

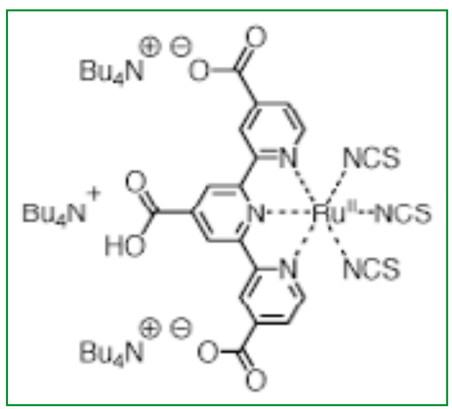
Jsc 19.7 mA/cm2

Jsc 23.6 mA/cm2

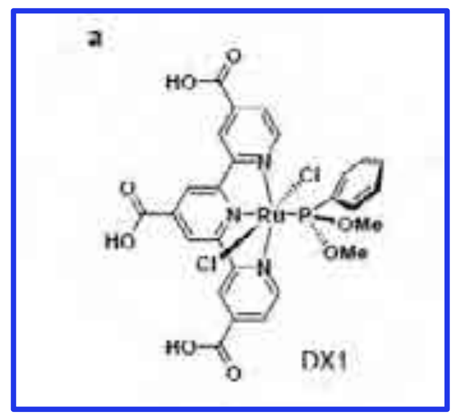
Jsc 26.8 mA/cm2

N719





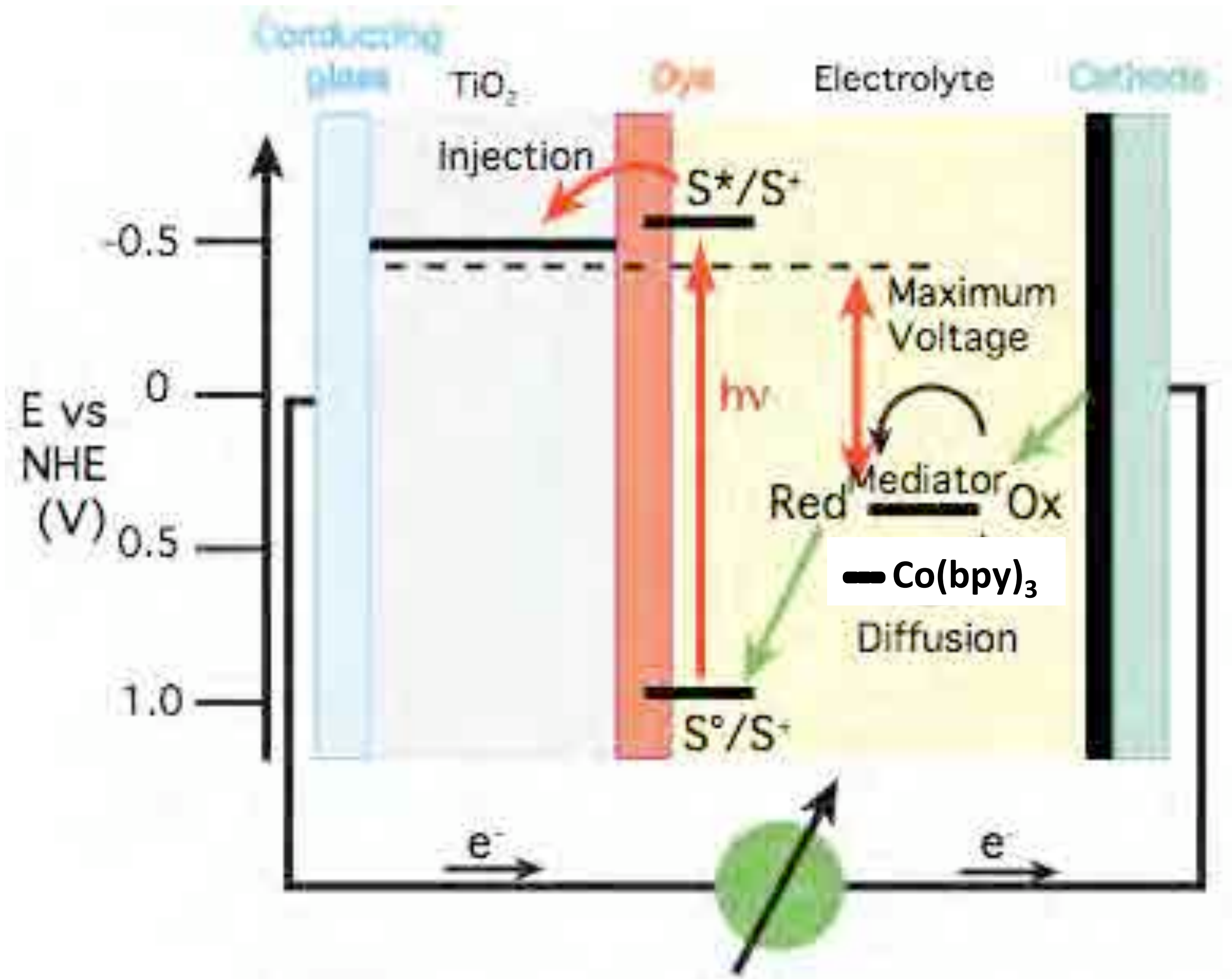
“Black dye” BD



DX1

DOI: 10.1038/NPHOTON.2013.136

Energy level diagram for a typical embodiment of dye sensitized solar cells

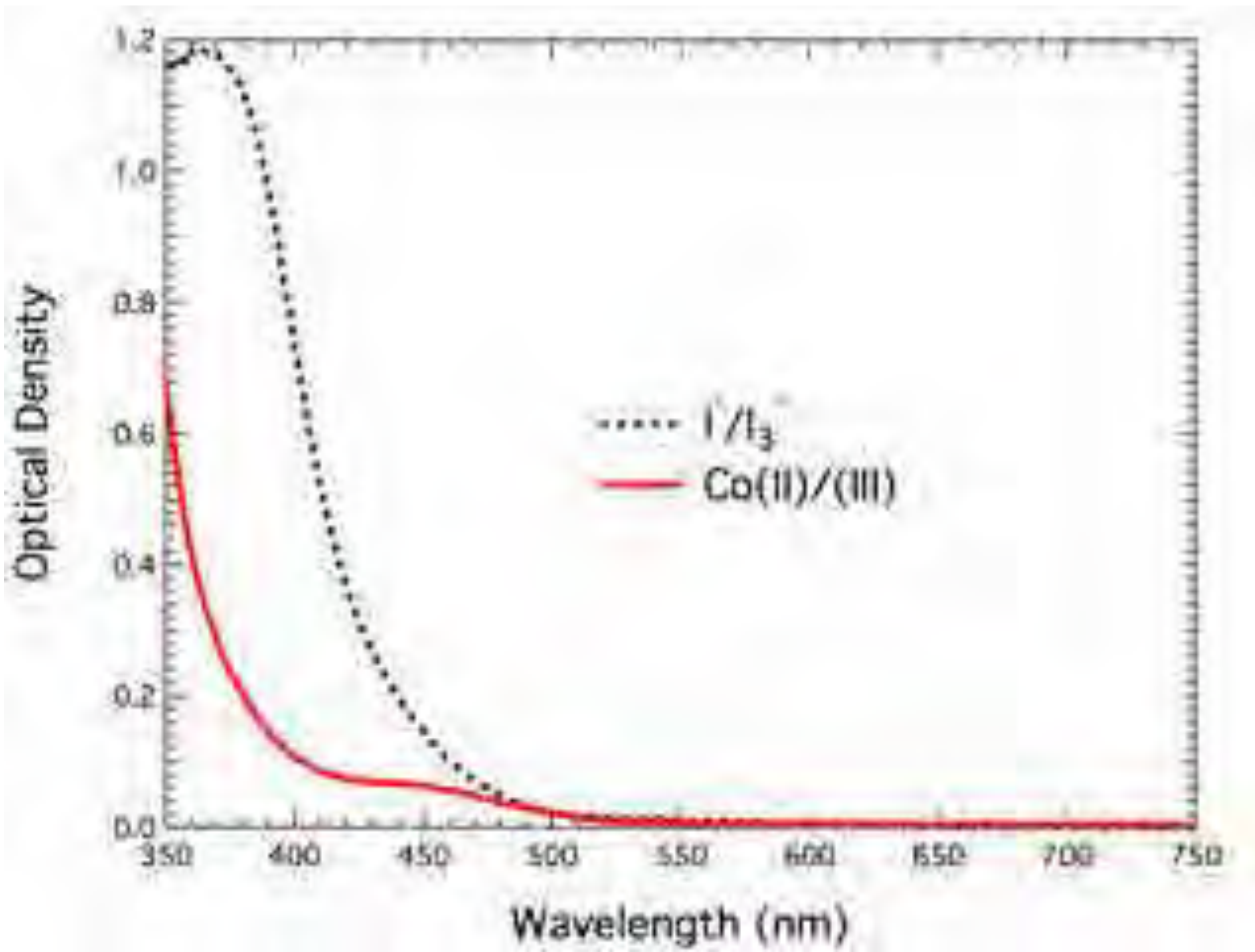


0.35 V

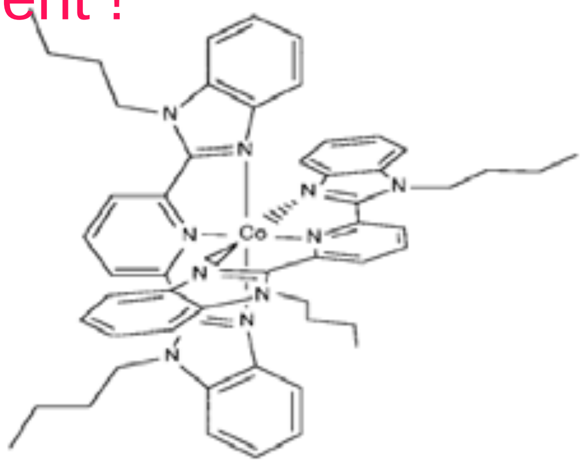
0.56 V

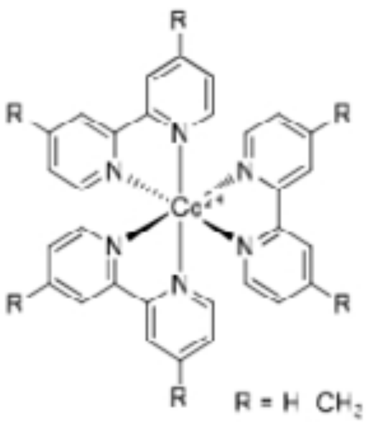
$$\eta_{global} = \frac{\left(I_{ph} \cdot V_{oc} \cdot FF\right)}{I_s}$$

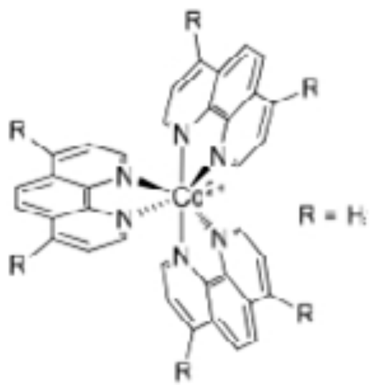
Absorption spectra of Co^{2+}/Co^{3+} and iodide/iodine based electrolytes (diluted 200 times in acetonitrile)

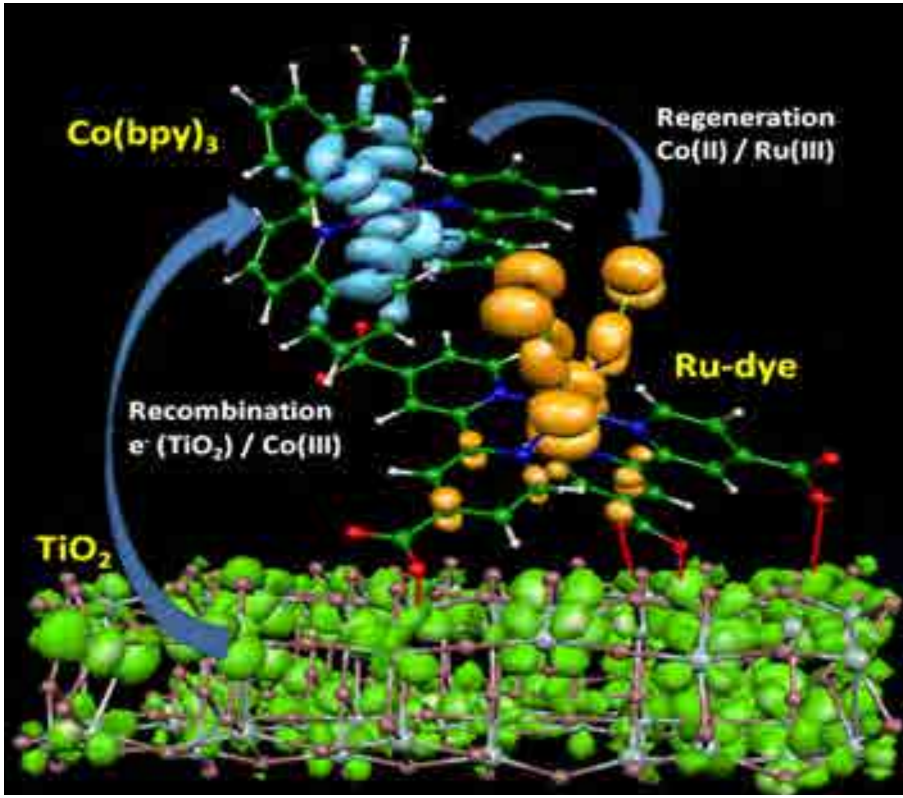


With ruthenium dyes these cobalt complexes are only effective at low light intensities due to ion pair formation leading to charge recombination and diffusion limitation of the photocurrent !



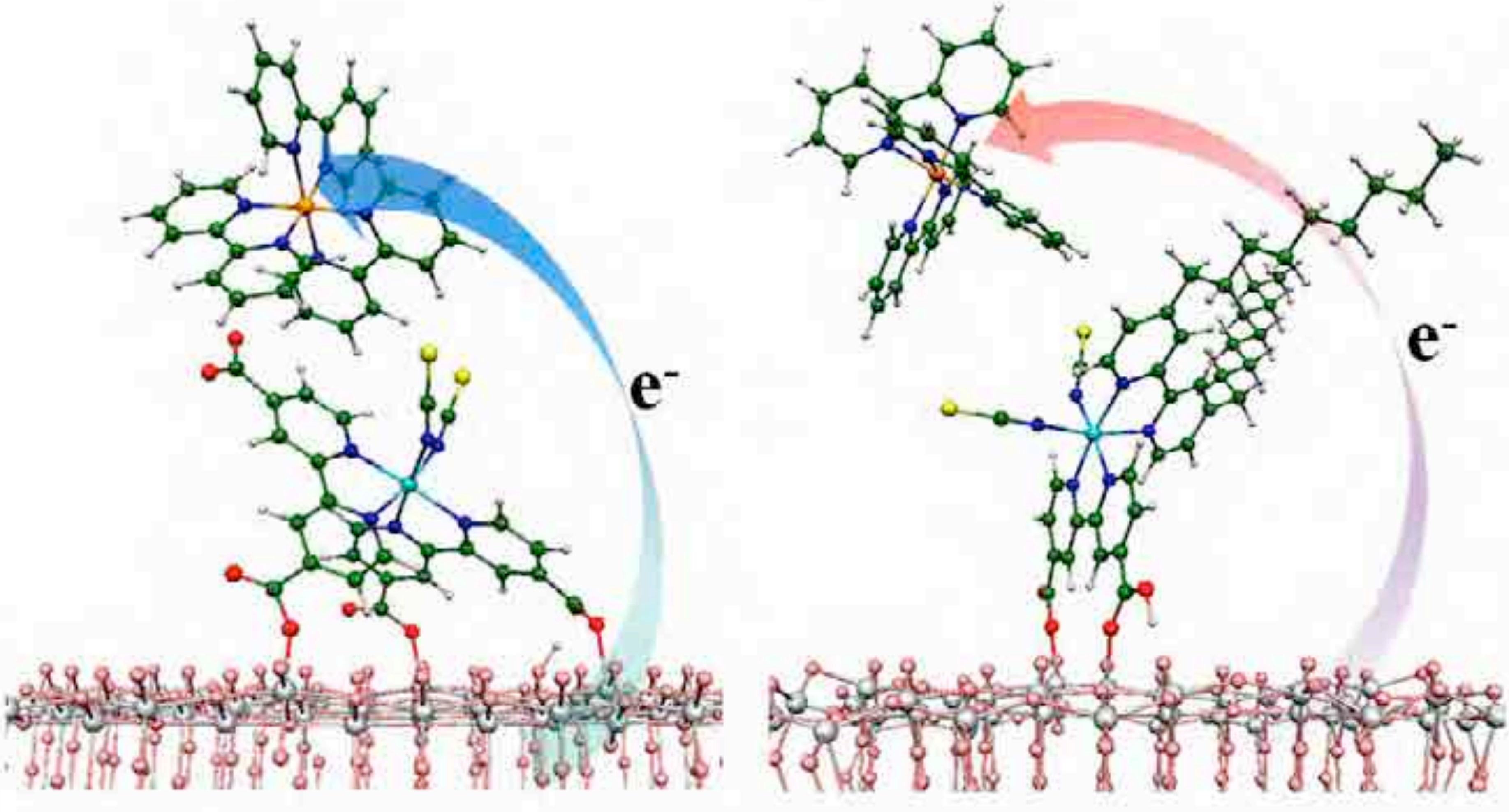






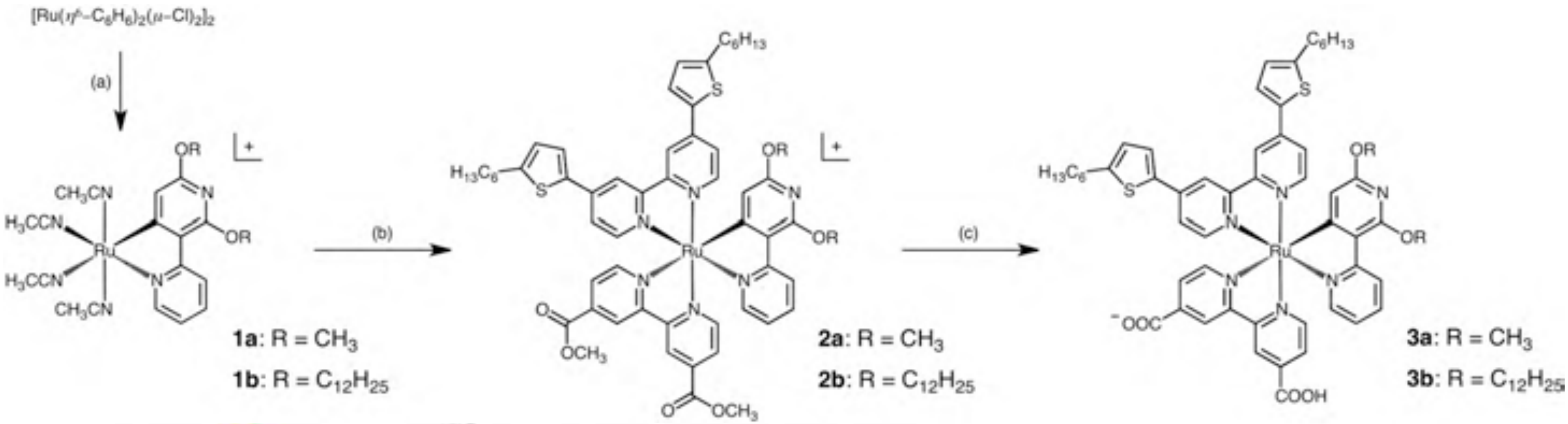
JACS, 134, 19438, 2012. DOI: 10.1021/ja3079016.

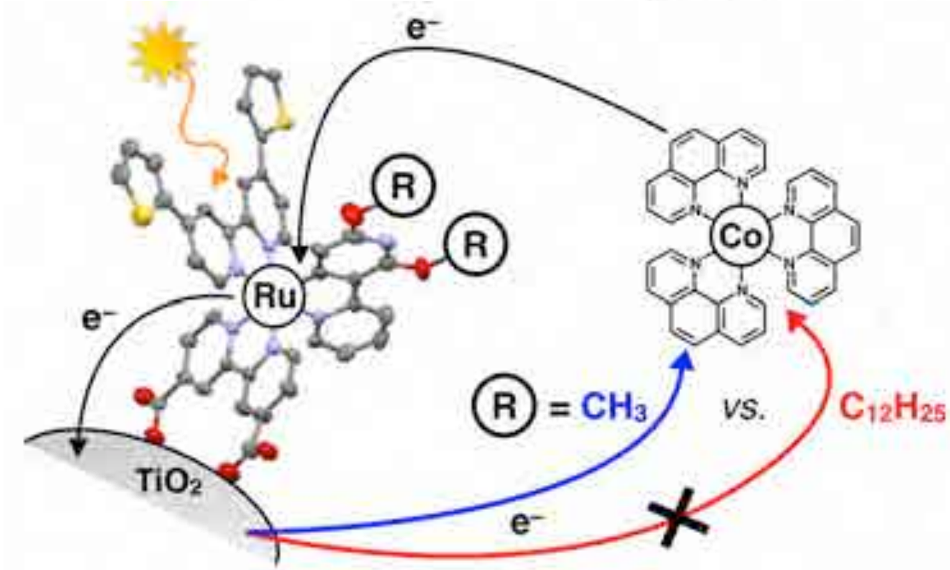
Schematic representation of the higher recombination probability of N719 with respect to the Z907 dye with cobalt electrolyte.



JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 134, 19438, 2012. DOI: 10.1021/ja3079016.

Synthetic scheme leading to complexes 3a and 3b

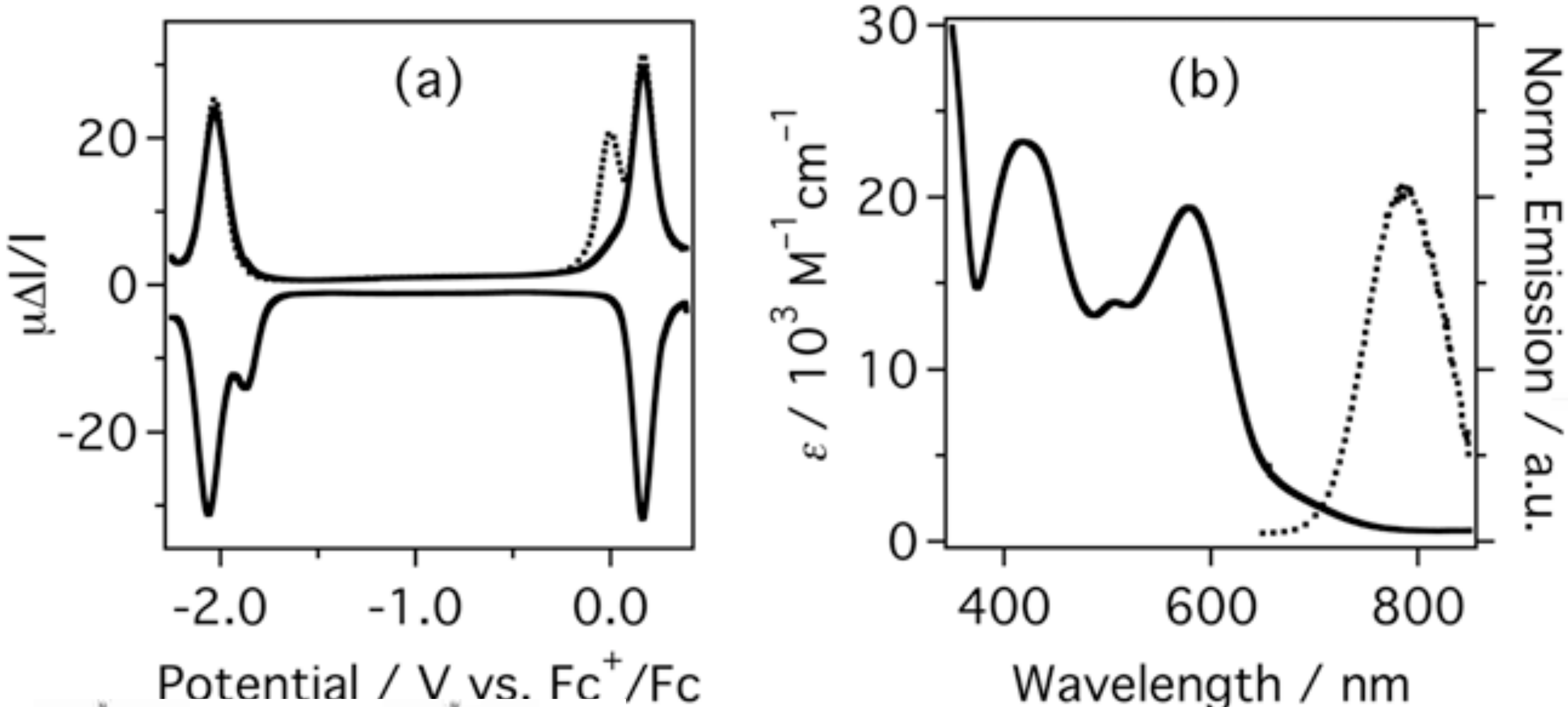


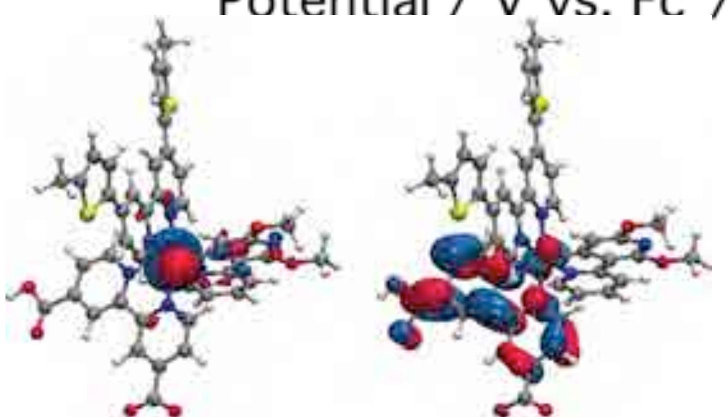


(1) ANGEWANDTE CHEMIE-INTERNATIONAL EDITION, 2013, 52, 8731-8735. DOI: 10.1002/anie.201304608. **(2) ChemSusChem (2014), 7(10), 2930-2938 .**

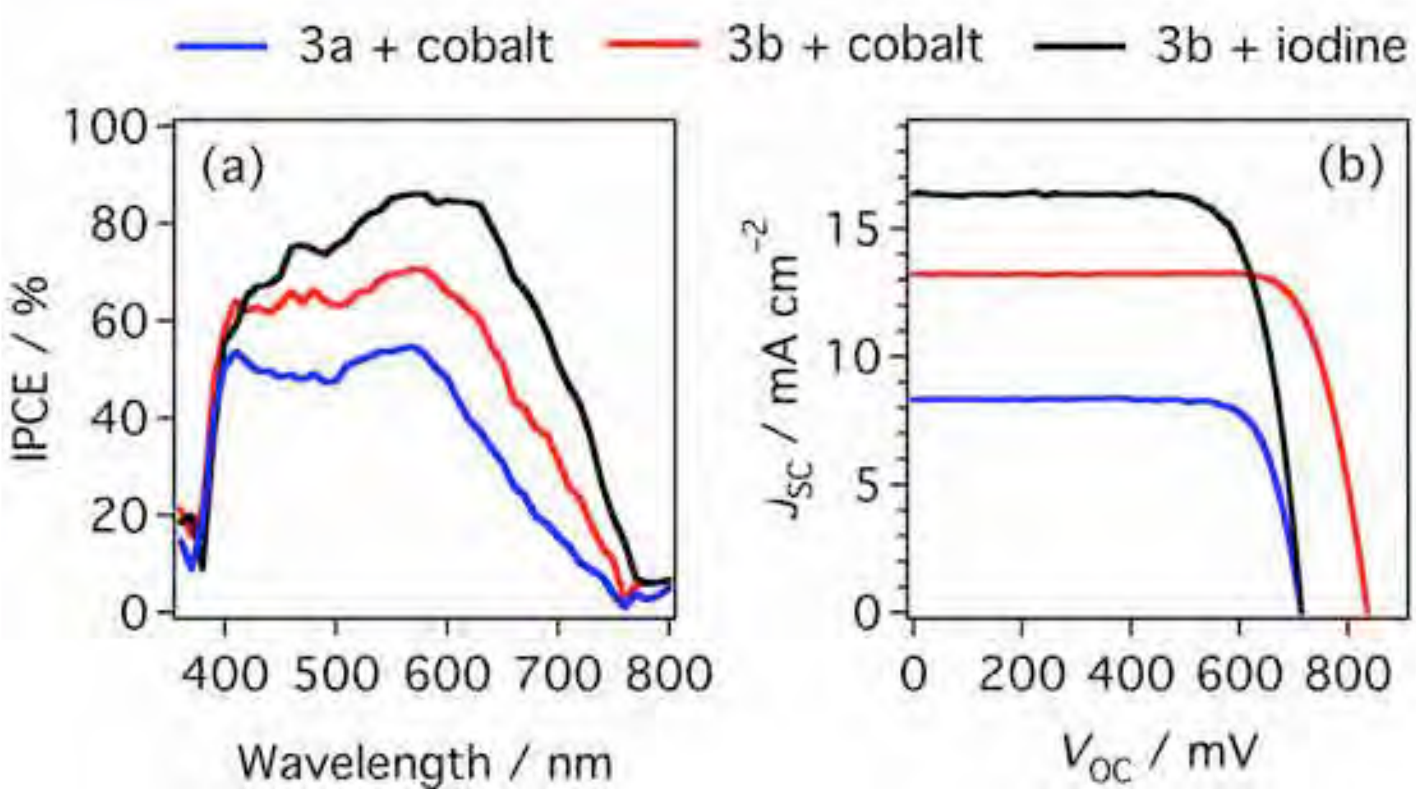
E_{LUMO} = –1.35, and E_{HOMO} = 0.86 V *vs.* NHE

418 (23400 M cm^{-1}) and 580 nm (19600 M cm^{-1})

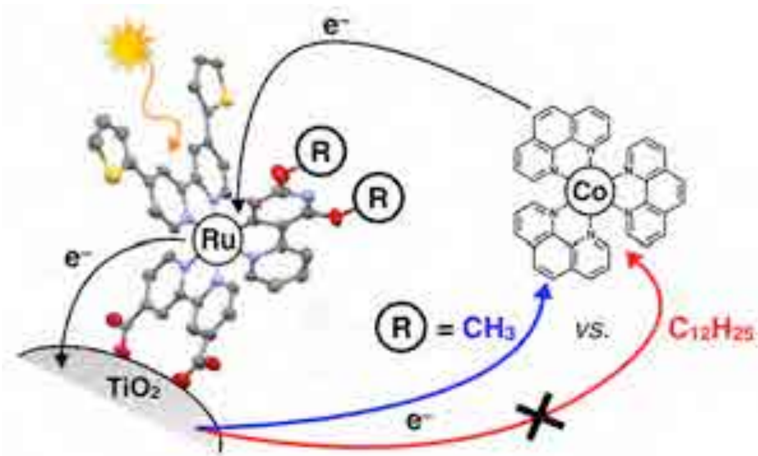


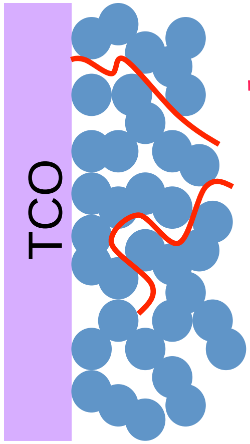


ANGEWANDTE CHEMIE-INTERNATIONAL EDITION Volume: 52 Issue: 33 Pages: 8731-8735 DOI: 10.1002/anie.201304608



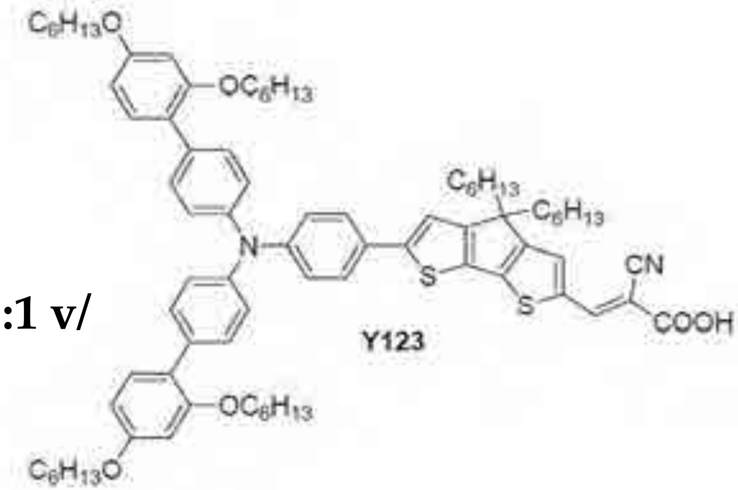
Dye	Electrolyte	J_{SC} / mA cm^{-2}	V_{OC} / mV	FF	η / %
3a	cobalt	8.3	714	0.79	4.7
3b	cobalt	13.2	837	0.78	8.6
3b	iodine	16.3	715	0.75	8.7





Transparent layer: **5μm** of 20nm particle, **32**nm pore size TiO_2

Scattering layer: 5μm 400nm TiO_2



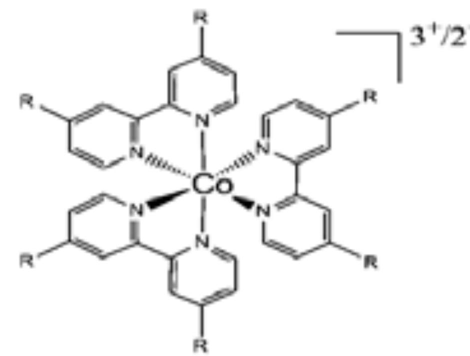
Dye Solution:

0.1mM Y123 in Tert-Butanol / Acetonitrile 1:1 v/v

Electrolyte:

Co2+ = 0.22M, Co3+ = 0.055M,

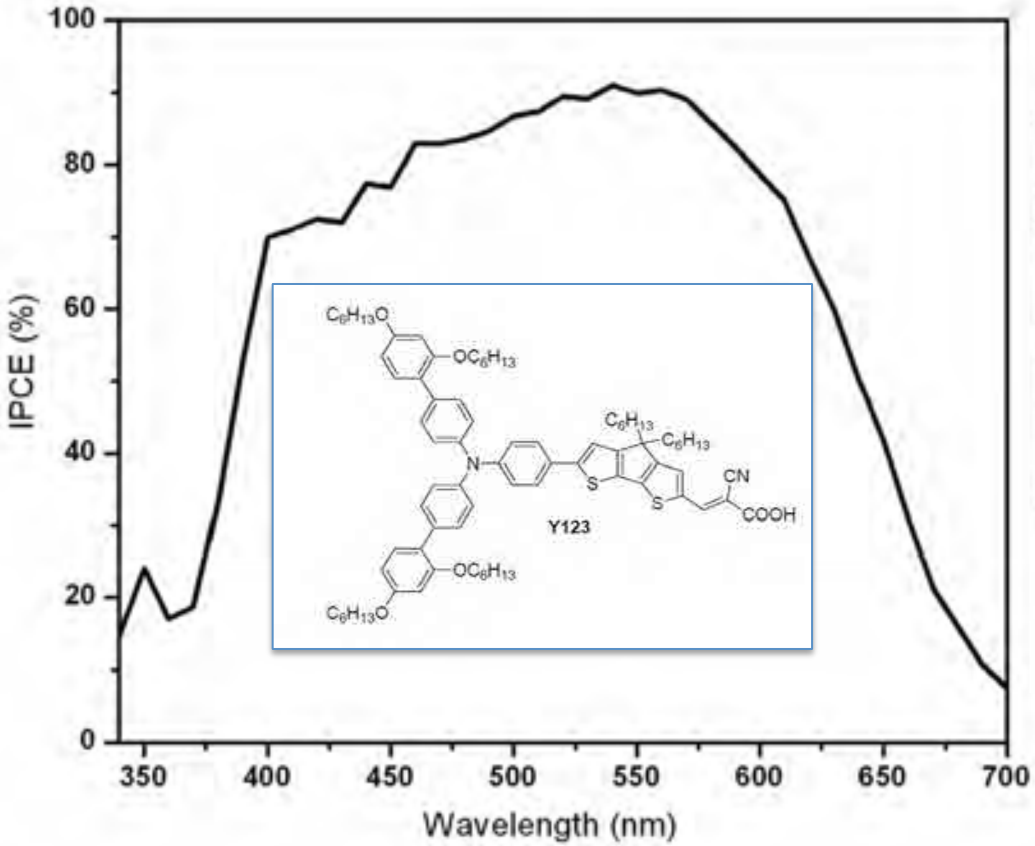
LiClO4 = 0.1M, tbp = 0.2M in ACN

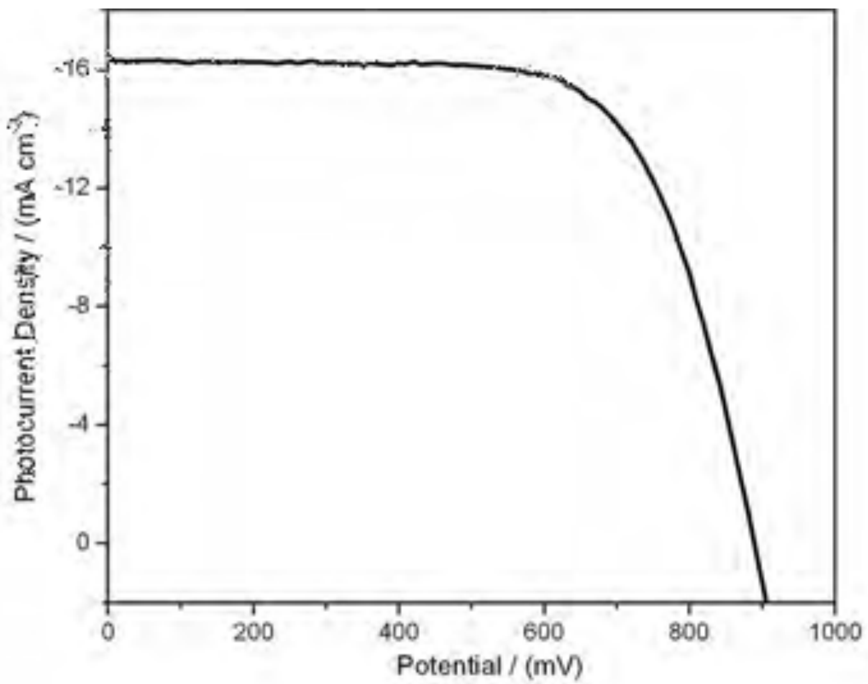


[Co(II/III)(bpy)3](B(CN)4)2/3

ChemSusChem (2011), 4(5), 591-594.

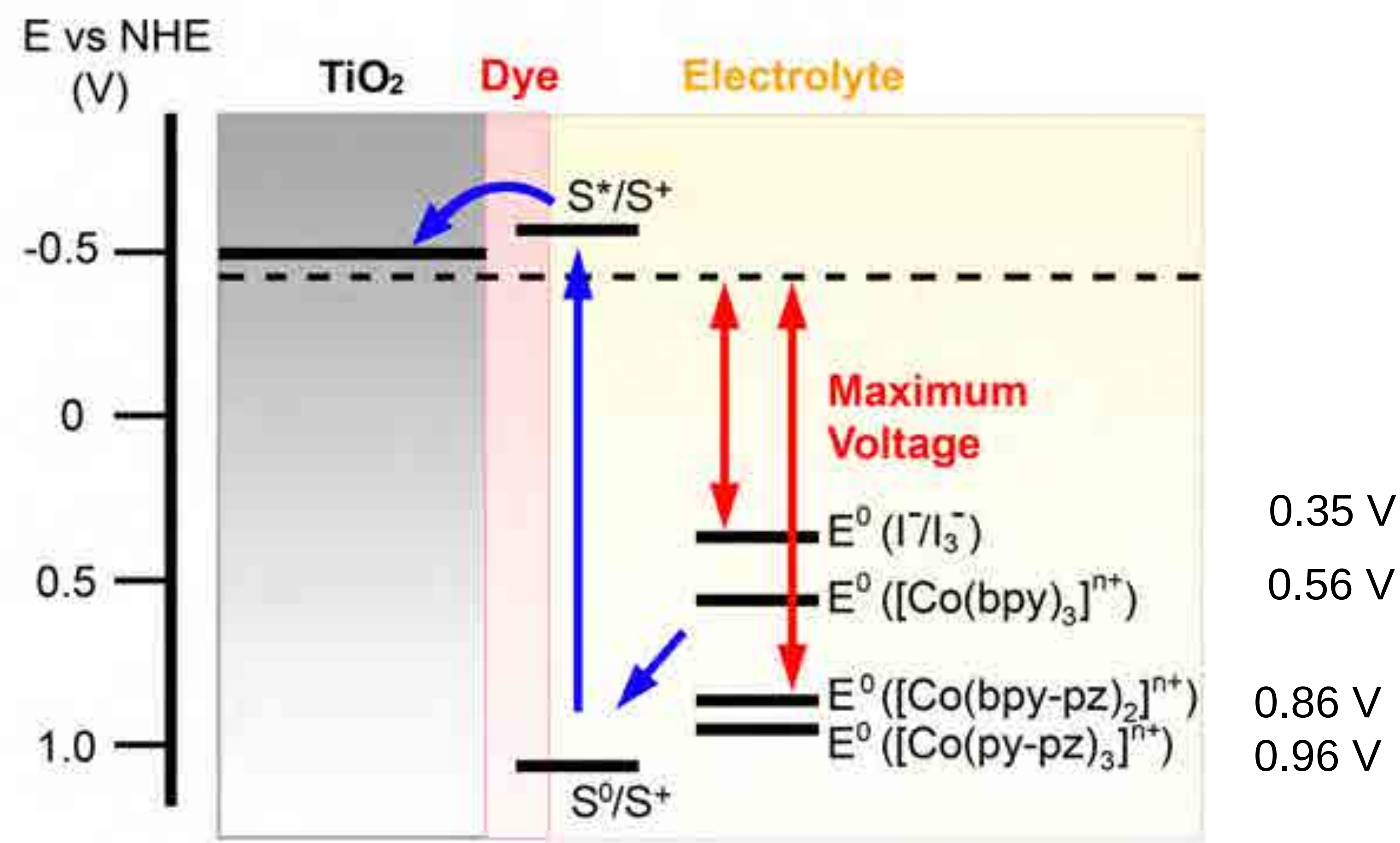
$Co(III(bipy)_3)/Co(II)(bipy)_3$ with Y123 dye





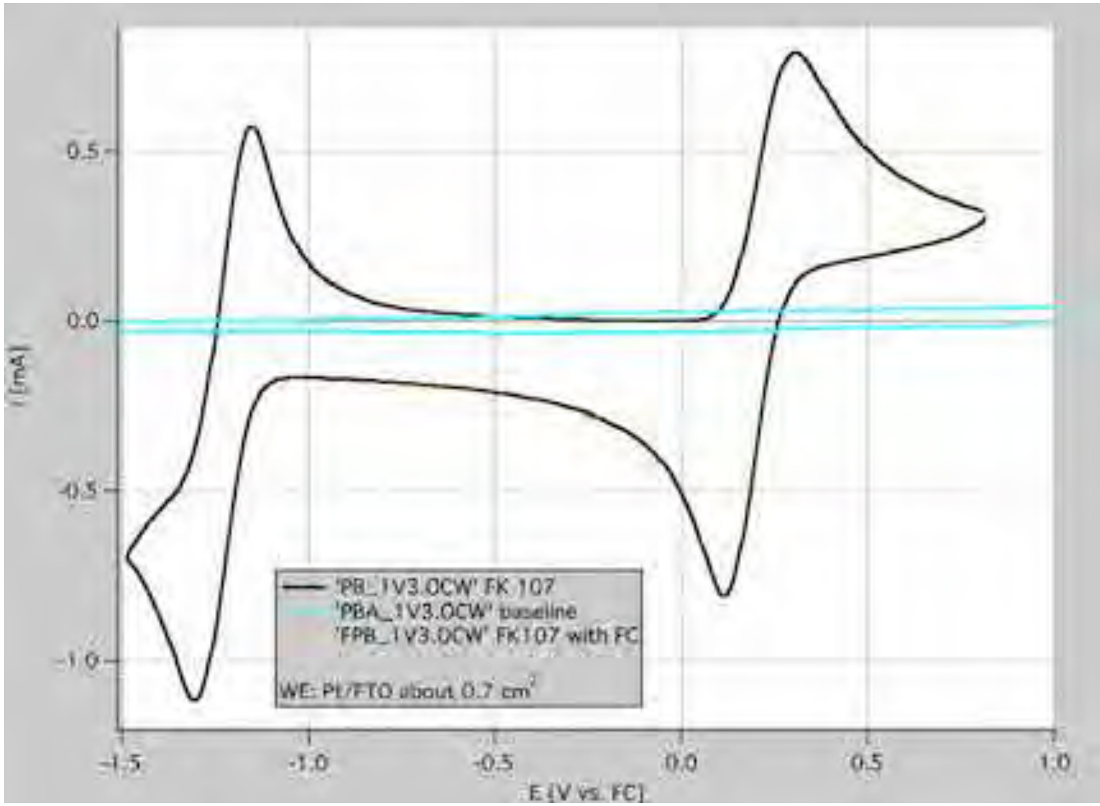
V(oc) mV	J(sc) mA/cm^2	FF	PCE %
889	16.4	0.69	10.02

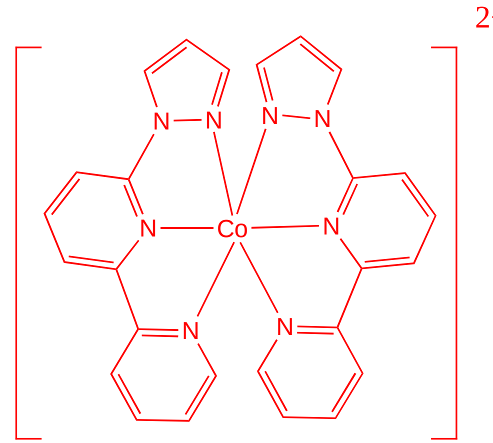
ChemSusChem (2011), 4(5), 591-594.



E vs NHE
(V)
TiO2
Dye
Electrolyte
S*/S+
-0.5
0
0.5
1.0
Maximum
Voltage
E0 (I-/I3-)
E0 ([Co(bpy)3]n+)
E0 ([Co(bpy-pz)2]n+)
E0 ([Co(py-pz)3]n+)
S0/S+
0.35 V
0.56 V
0.86 V
0.96 V

Electrochemical characterization of Co-complexes FK107



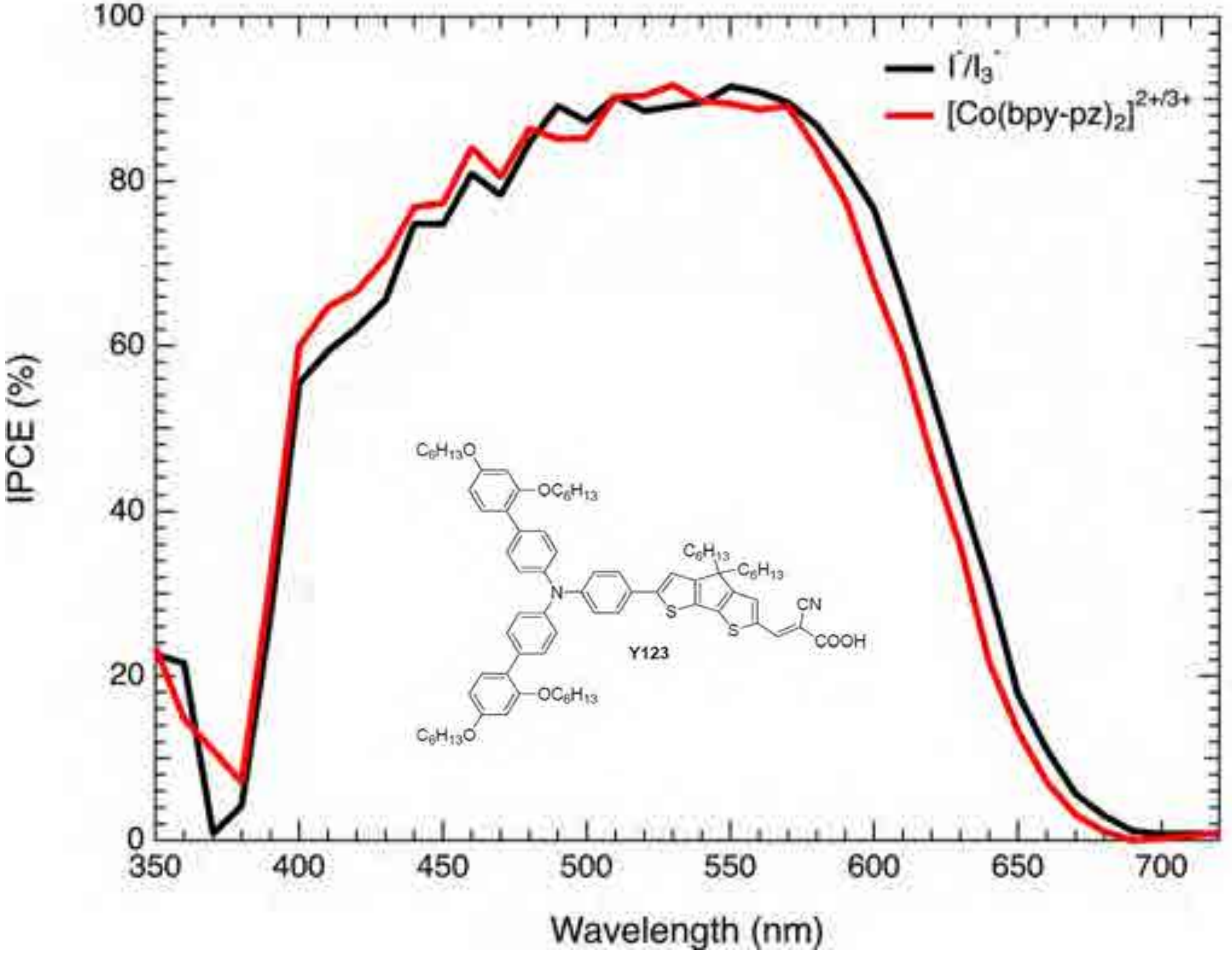


Redox potential: 0.86 V vs. NHE*

*** Fc/Fc⁺ was used as internal standard and +0.64 V**

	Oxidation (Co II->III)	Reduction (Co I -> II)
FK 107 $(Co(bipy\text{-}pz)_2)^{3+}$	0.22	-1.20
FK102 $(Co(py\text{-}pz)_3)^{3+}$	0.32	-1.45

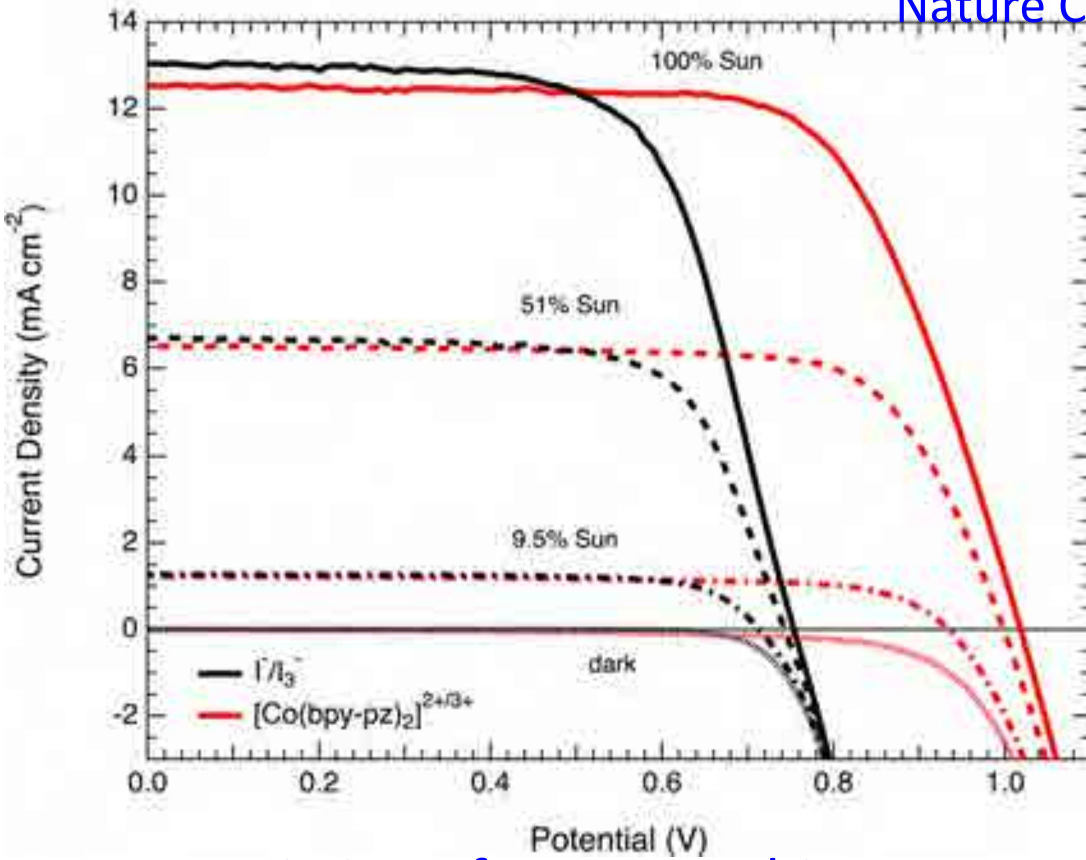
Nature Communications (2012), 3(Jan.), 1655

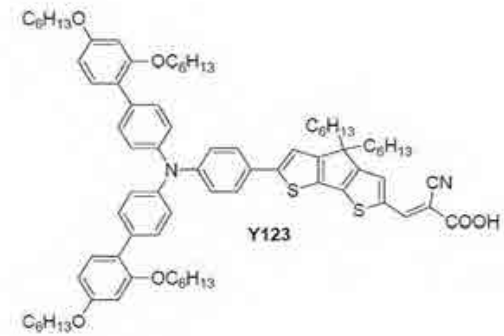


5.6 µm thin transparent nanoporous TiO_2 (anatase) film
Y123 sensitizer

Nature Communications (2012), 3(Jan.), 1655

Nature Communications (2012), 3(Jan.), 1655



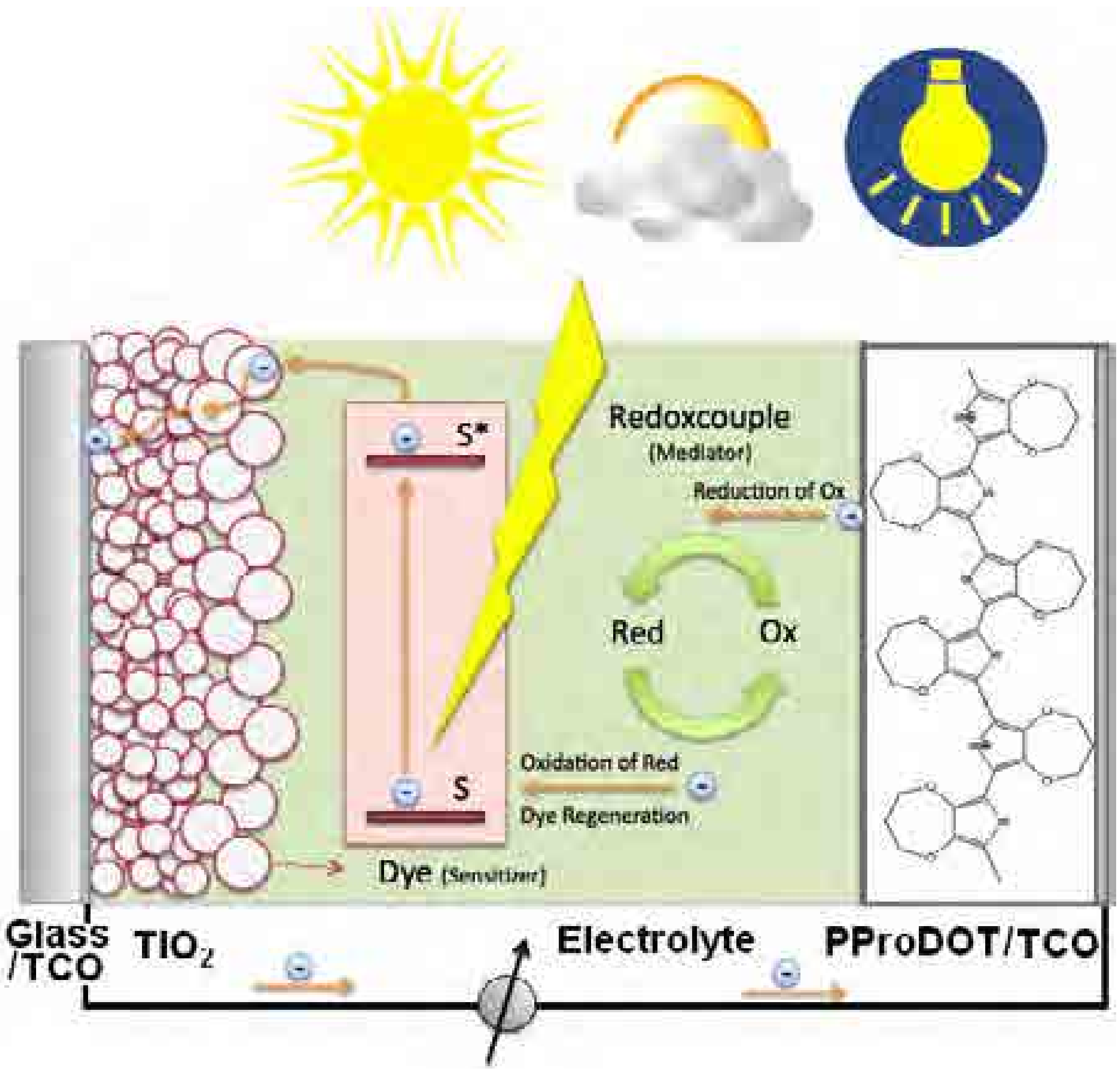


DSCs consisting of a 5.6 μm thin transparent nanoporous TiO_2 (anatase) film, the Y123 sensitizer.

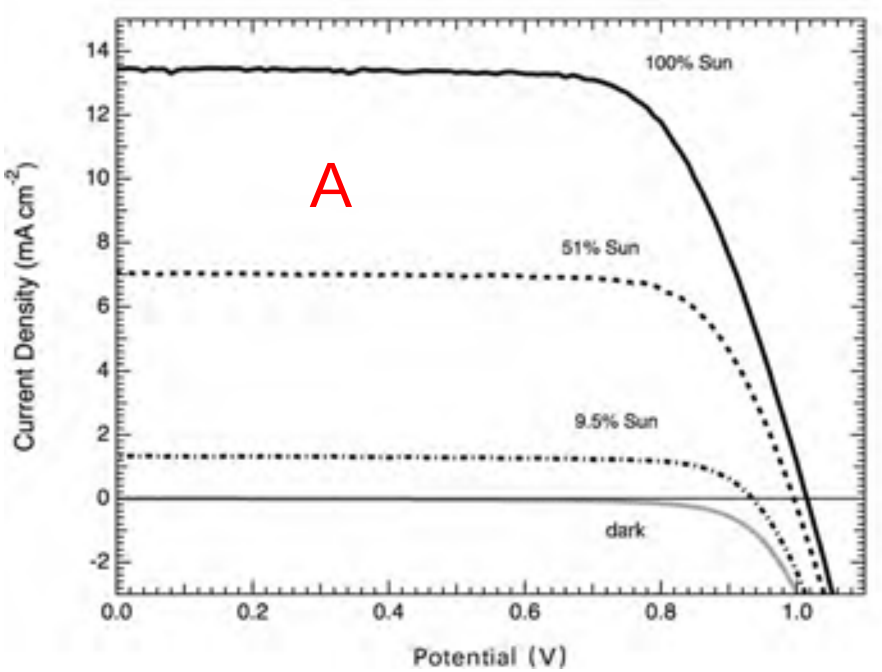
The I^-/I_3^- system resulted in 13.01 mA cm^{-2} J_{sc}, 754 mV *Voc*, and 0.67 *FF*, yielding conversion efficiency of 6.57%.

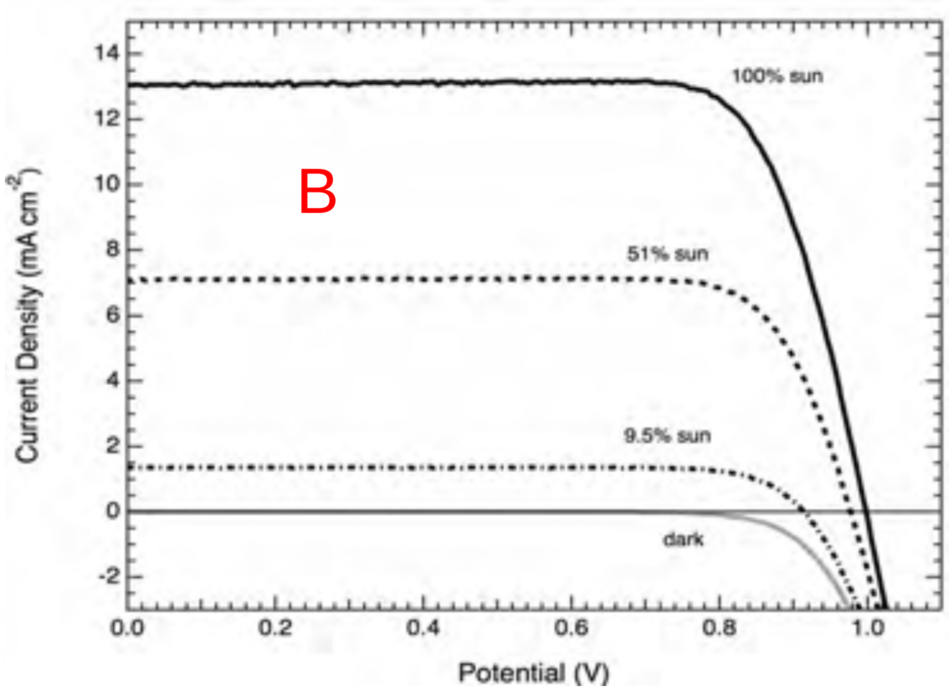
The $[Co(bpy\text{-}pz)_2]^{2+/3+}$ redox system gave J_{sc} 12.54 mA cm^{-2}, V_{oc} 1018 mV, *FF* of 0.69, yielding PCE (η) 8.87%.

Pt free Counter Electrode: PEDOT, PProDOT



Nature Communications (2012), 3, 1655





Photovoltaic characteristics of DSC based on $[Co(bpy\text{-}pz)_2]^{2+/3+}$ system employing the double layered TiO_2 (5.6 + 5 µm) and Pt counter electrode (A), Employing the double layered TiO_2 (4.0 + 4.5 µm) and the PProDOT (B)

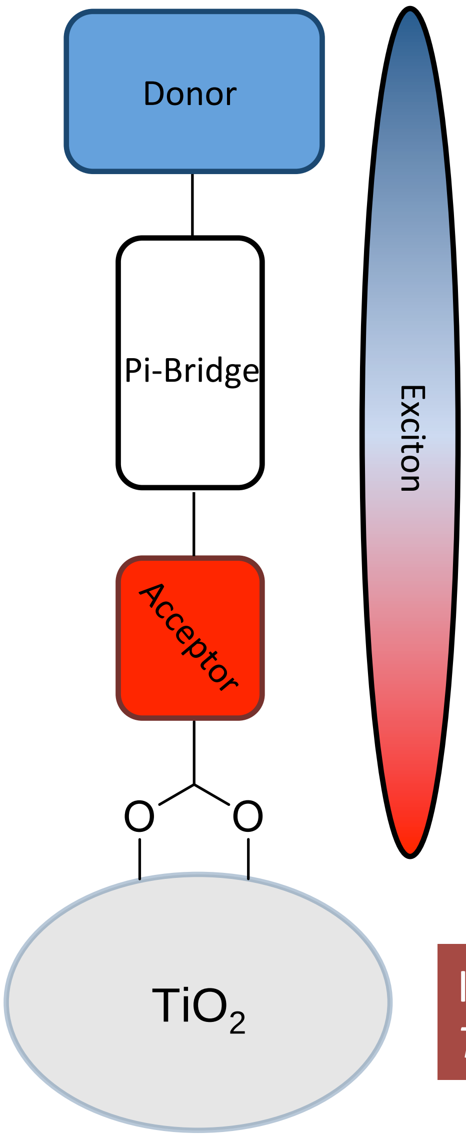
	Pt counter electrode	*PProDOT counter electrode*
J_{sc} (mA cm^{-1})	= 13.45	13.06
V_{oc} (mV)	= 1015	998
FF (%)	= 69.7	77
η (%)	= 9.52	10.08

Nature Communications (2012), 3, 1655

Building-in More Color

Donor -- *Pi-Bridge* -- Acceptor

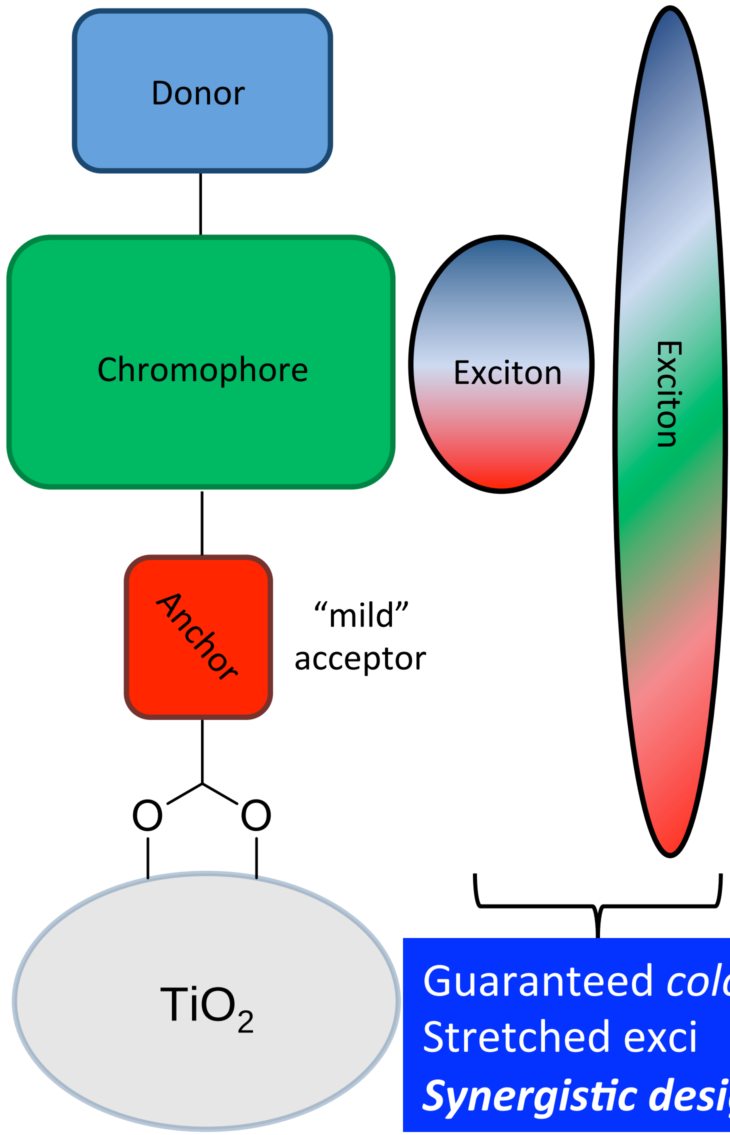
D-*pi*-A



Intrinsic *directionality*
Tunable push-pull

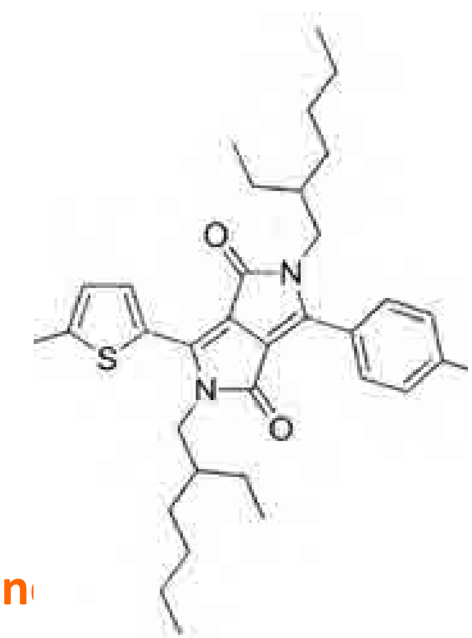
Donor -- *Chromophore* -- Anchor

D-*C*-A



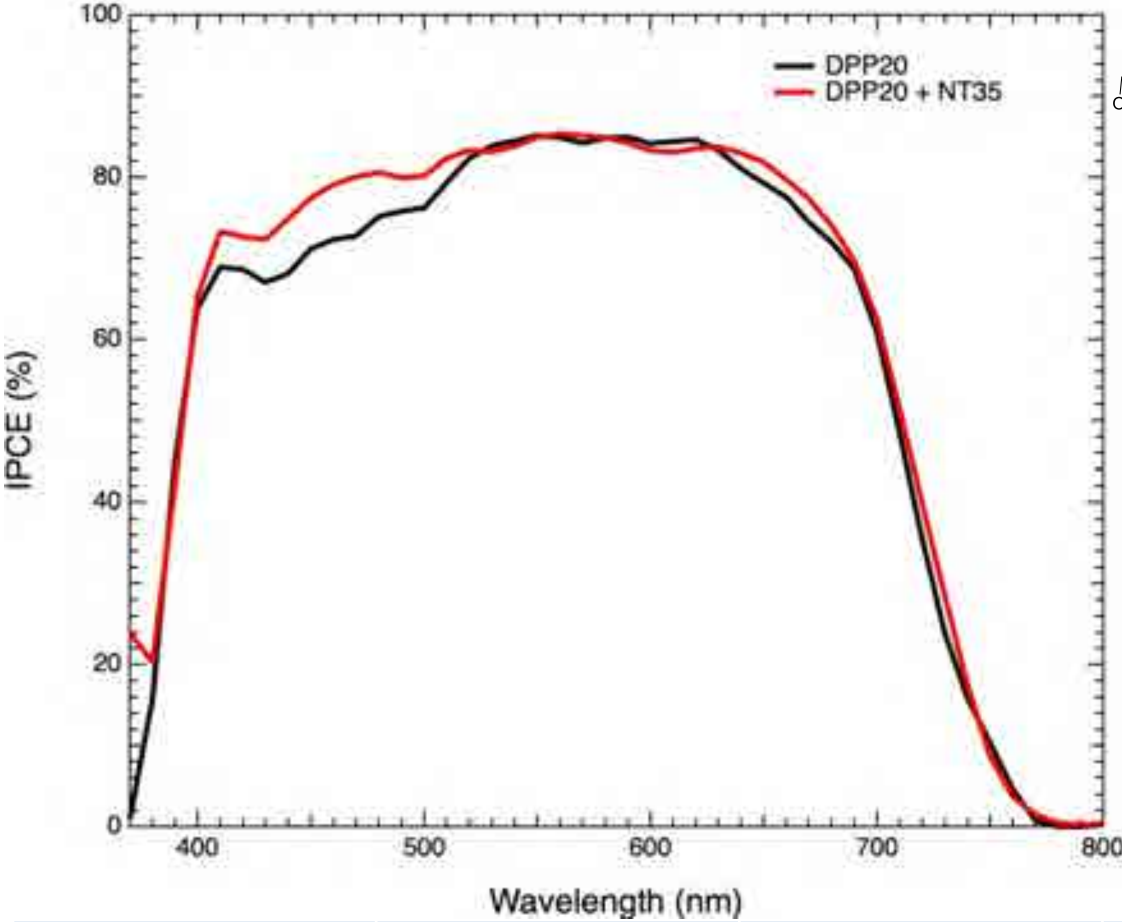
Guaranteed *color*
Stretched exci
Synergistic design

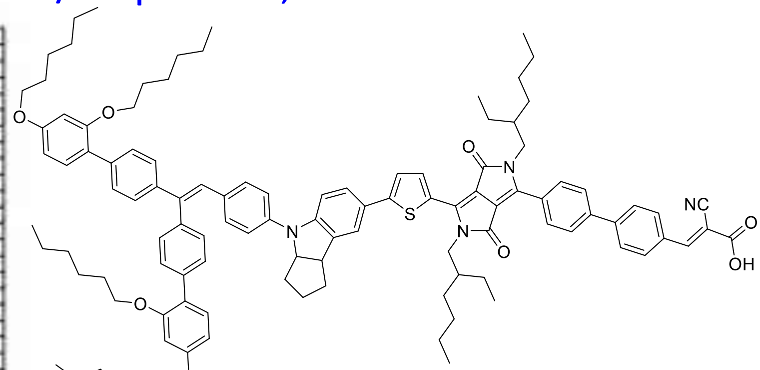
SCIENTIFIC REPORTS Volume: 3 Article Number: 2446 DOI: 10.1038/srep02446

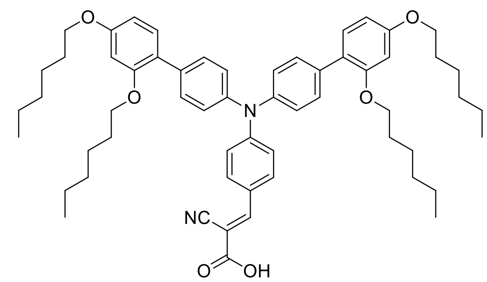


Colour of DPP07, 13, 14, 15, and 17 (from left to right). (a) DPP dyes are dissolved in THF solution (0.025 mM) an are adsorbed on 3 mm thick TiO2 film. Chemistry of Materials (2013), 25(13), 2642-2648

SCIENTIFIC REPORTS | 3 : 2446 | DOI: 10.1038/srep02446, 2013







	Jsc (mA/cm^2)	Voc (mV)	ff	PCE (%)
DPP20	17.3	776	0.75	10.05
DPP20 + NT35	17.9	794	0.73	10.38

On 4+4 um double layer TiO_2 film and the use of the cobalt electrolyte

Science 2011, **334**, 629 – 634.

Porphyrin-Sensitized Solar Cells with Cobalt (II/III)–Based Redox Electrolyte Exceed 12 Percent Efficiency

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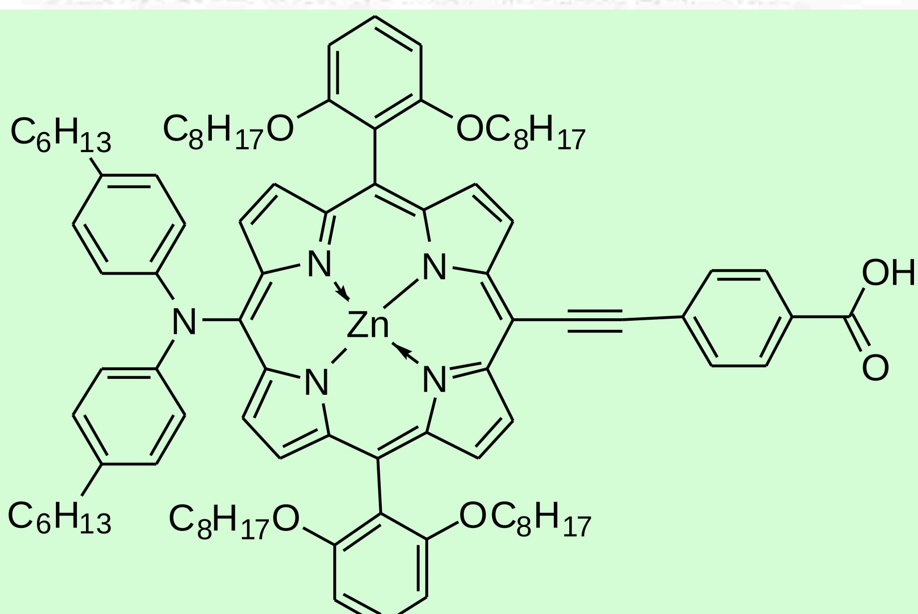

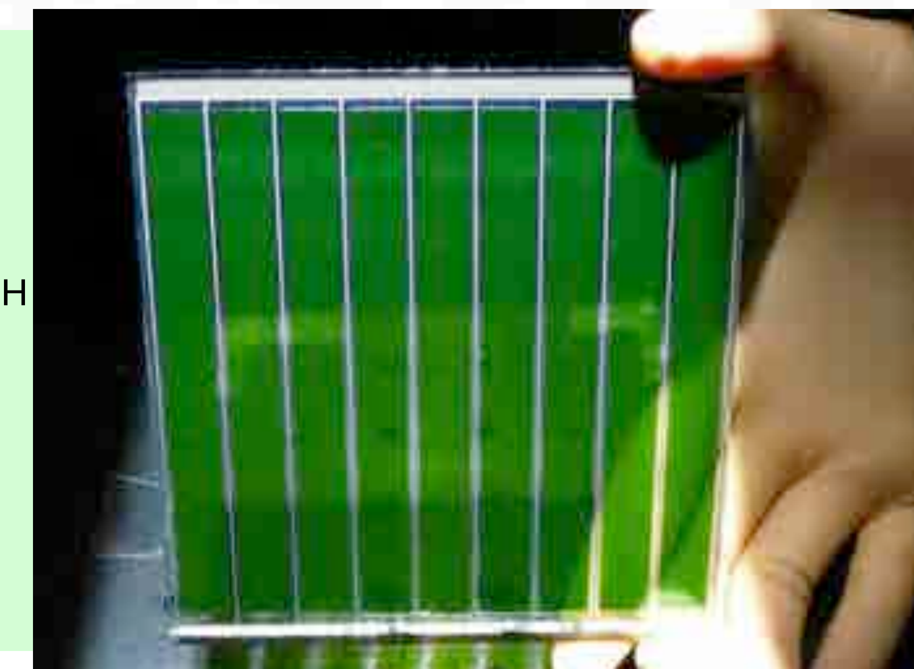

Subtle changes in porphyrine structure produce large effect on PV performance