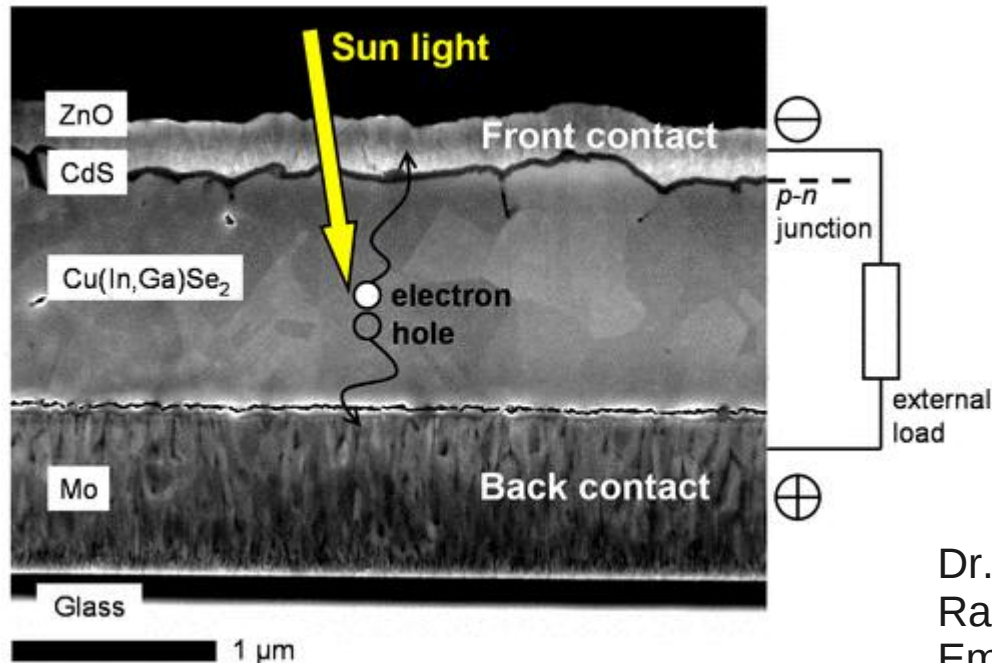
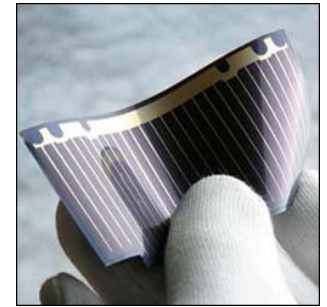
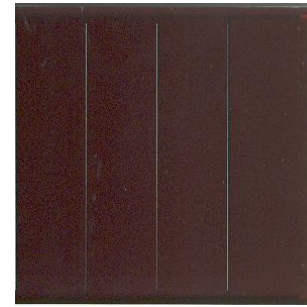


Dye Sensitized Solar Cells (27027-01)


(Dienstag, 8:00-10:00 Departement Physik, Seminarzimmer 3.12)



Dr. Thilo Glatzel
 Raum 3.04
 Email: thilo.glatzel@unibas.ch



Übersicht der Vorlesung

22.02.2011	allg. Einführung in die Solarenergie
01.03.2011	Physikalische Grundlagen der Photovoltaik I
08.03.2011	Physikalische Grundlagen der Photovoltaik II
15.03.2011	(Fastnachtsferien)
22.03.2011	Photochemische und photoelektrische Methoden der Energiewandlung
29.03.2011	Aufbau der Farbstoffsolarzelle, vgl. org. Solarzelle
05.04.2011	TiO ₂ Nanopartikel als Substrat der Farbstoffsolarzelle
 12.04.2011	Geeignete molekulare Farbstoffe zur Sensibilisierung
19.04.2011	Funktionsweise und Alternativen für den Elektrolyten
26.04.2011	(Osterferien)
03.05.2011	(FANAS meeting)
10.05.2011	Experimentelle Methoden zur Solarzellen-Charakterisierung
17.05.2011	Experimentelle Methoden zur Solarzellen-Charakterisierung
24.05.2011	Bau und Charakterisierung eigener Solarzellen
31.05.2011	

Geeignete molekulare Farbstoffe zur Sensibilisierung

Molecular Engineering of Sensitizers for DSSC

- Ruthenium sensitizers
 - Effect of protons
 - Effect of cations
 - Device stability
 - Effect of alkyl chains
 - Molar extinction coefficient
- Organic sensitizers
 - Coumarine
 - Indoline
 - Carotenoides & Anthocyanins
 - SPV measurements

Seminars

Michael Liebetanz

Highly Efficient Light-Harvesting Ruthenium Sensitizer for Thin-Film Dye-Sensitized Solar Cells

Chia-Yuan Chen,[†] Mingkui Wang,[‡] Jheng-Ying Li,[†] Nuttapol Pootrakulchote,[‡] Leila Alibabaei,[‡] Cevey-ha Ngoc-le,[‡] Jean-David Decoppet,[‡] Jia-Hung Tsai,[†] Carole Grätzel,[‡] Chun-Guey Wu,^{†,*} Shaik M. Zakeeruddin,^{*,*} and Michael Grätzel^{†,*}

[†]Department of Chemistry, National Central University, Jhong-Li, 32001 Taiwan, ROC, and [‡]Laboratory for Photonics and Interfaces, Swiss Federal Institute of Technology, CH 1015 Lausanne, Switzerland

Heidi Potts

An element of surprise—efficient copper-functionalized dye-sensitized solar cells[†]

Takeru Bessho,^a Edwin C. Constable,^{*,b} Michael Graetzel,^a Ana Hernandez Redondo,^b Catherine E. Housecroft,^b William Kylberg,^b Md. K. Nazeeruddin,^a Markus Neuburger^b and Silvia Schaffner^b

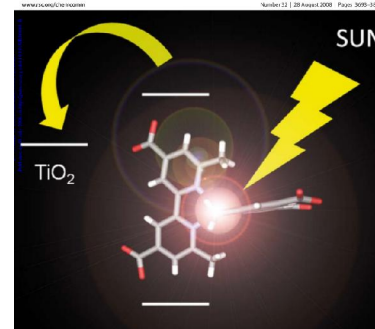
Received (in Cambridge, UK) 20th May 2008, Accepted 24th June 2008

First published as an Advance Article on the web 8th July 2008

DOI: 10.1039/b808491b

ChemComm

Chemical Communications



RSCPublishing

Ruthenium Sensitizers

The dye is one of the key components of DSSCs, **harvesting the solar radiation** and converting it into electric current

- Sensitizer should be **panchromatic** (<920nm)
- **Directionality** of excited state
- **Interlocking groups** for grafting the dye on TiO₂

Most prominent: ruthenium complexes endowed by **thiocyanate ligands**

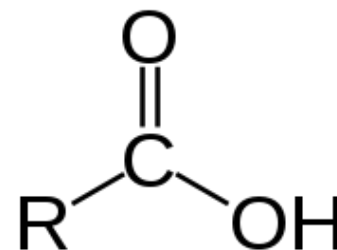


Why ruthenium?

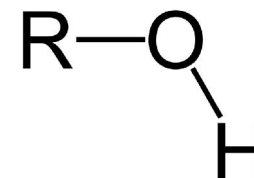
- Octahedral geometry (usage of specific ligands!)
- Tunable properties of the complexes
- Stable and accessible oxidation states

Protonating Ligands

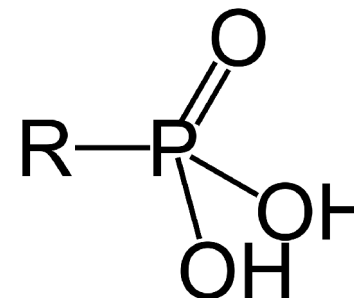
Carboxylic acid (R-COOH)



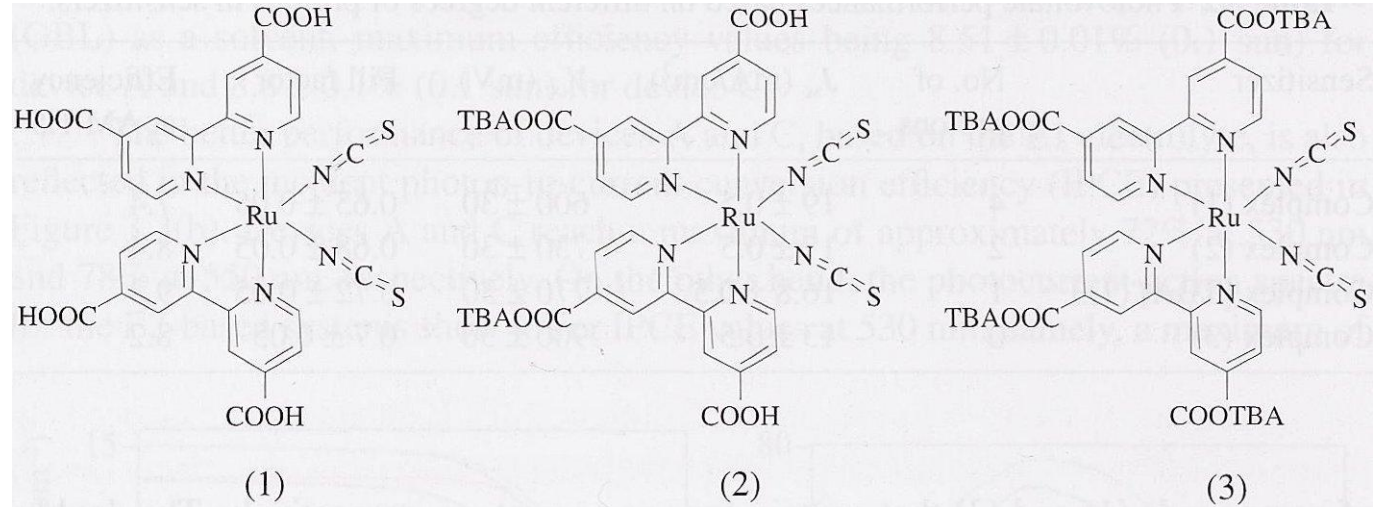
Dihydroxy R-(OH)₂



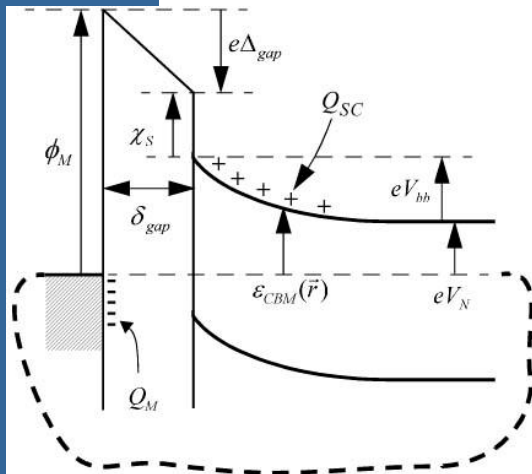
Phosphorous acid (H₃PO₃)



Influence of Protonation



TBA: Tetrabutylammonium (C_4H_9)₄N



- Proton transfer from dye to TiO_2
 - Development of a positive surface charge
 - Electric field (surface dipole) enhances adsorption and current and assists electron injection from excited state
 - Conduction band edge TiO_2 is shifted \rightarrow lower V_{oc}
- \rightarrow optimal degree of protonation

Influence of Protonation

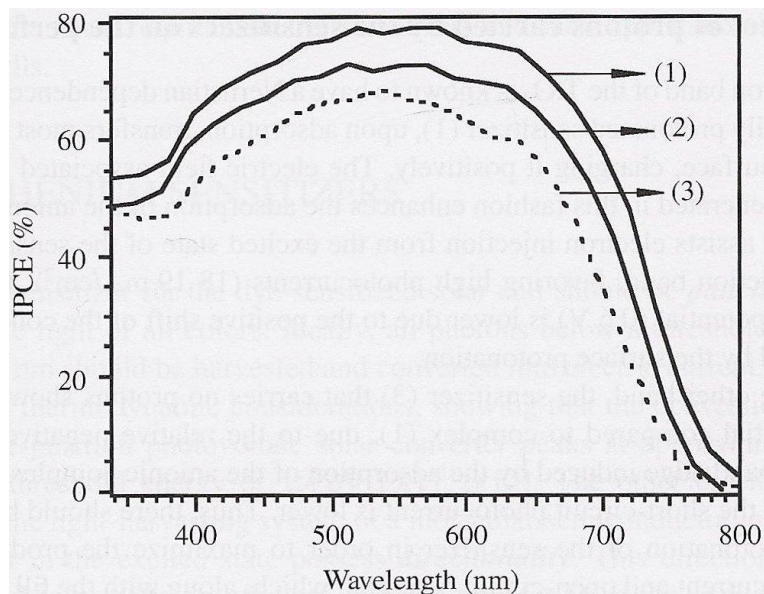
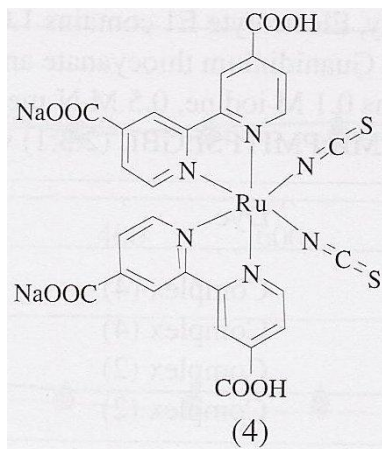


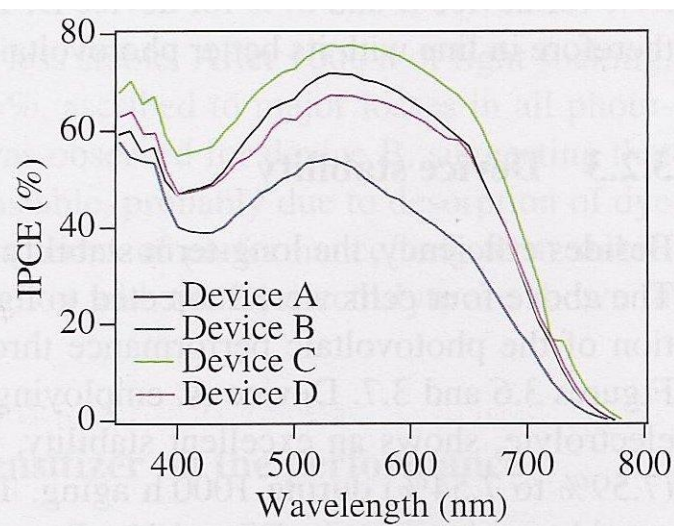
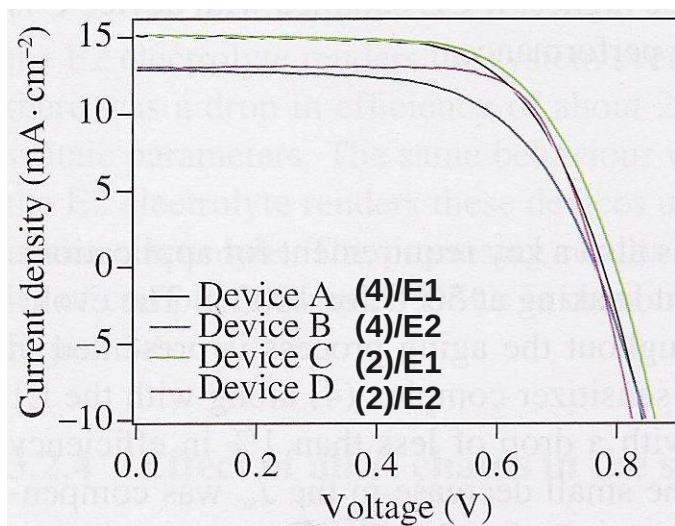
Table 3.2 Photovoltaic performances based on different degrees of protons in sensitizers.

Sensitizer	No. of protons	J_{sc} (mA/cm ²)	V_{oc} (mV)	Fill factor	Efficiency at AM 1.5
Complex (1)	4	19 ± 0.5	600 ± 30	0.65 ± 0.05	7.4
Complex (2)	2	17 ± 0.5	730 ± 30	0.68 ± 0.05	8.4
Complex [TBA] (1)3	1	16.8 ± 0.5	770 ± 30	0.72 ± 0.05	9.3
Complex (3)	0	13 ± 0.5	900 ± 30	0.7 ± 0.05	8.2

Cation Substitution



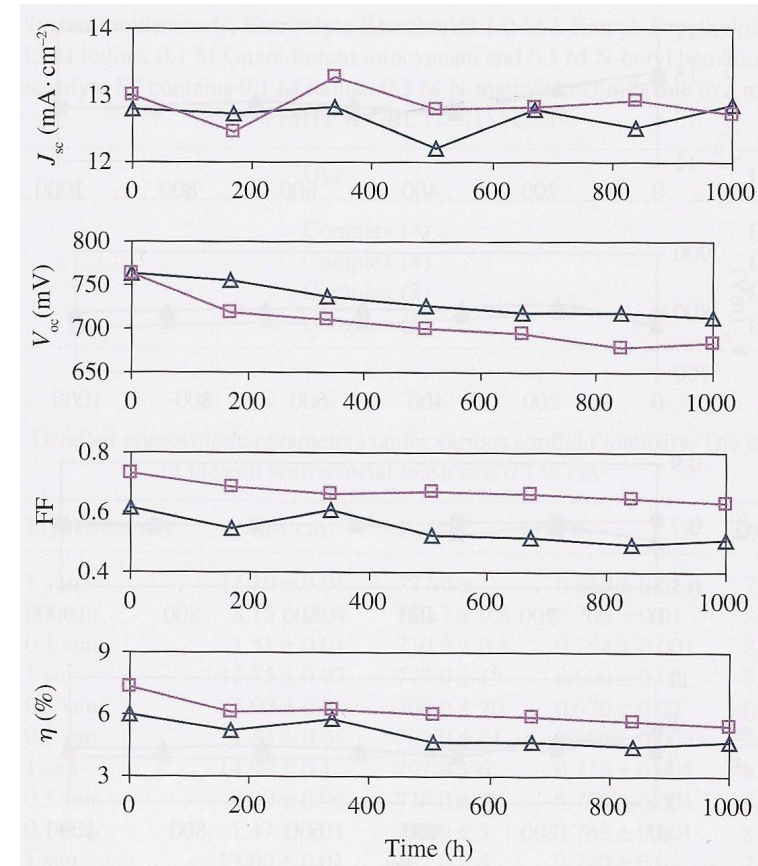
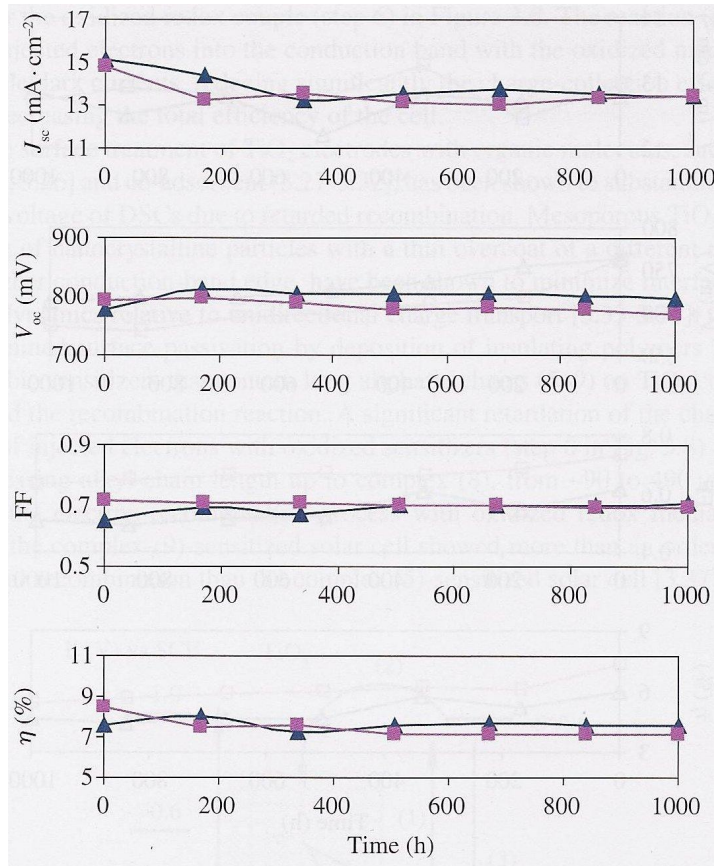
- Substitution of the TBA cations by Na
- Complex (4) shows highest ISC at all intensities
- Strong dependence on the used electrolyte (E1/E2)



Device stability

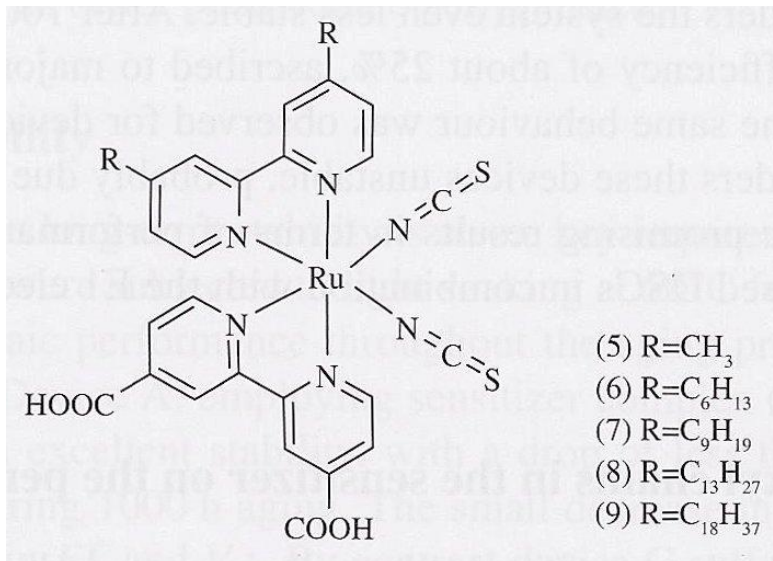
▲ A (4)/E1
■ C (2)/E1

△ B (4)/E2
□ D (2)/E2

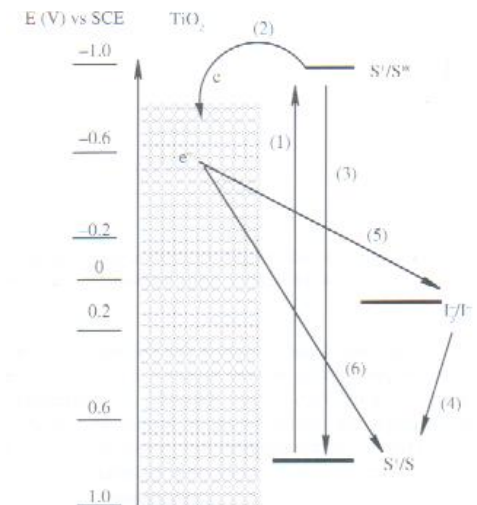
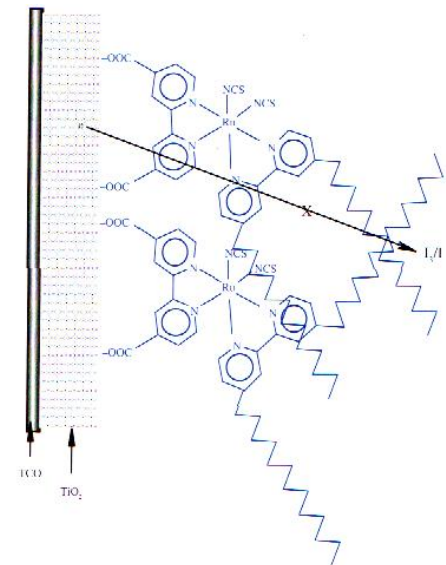


Light soaking: 50°C for 1000h

Effect of Alkyl Chains

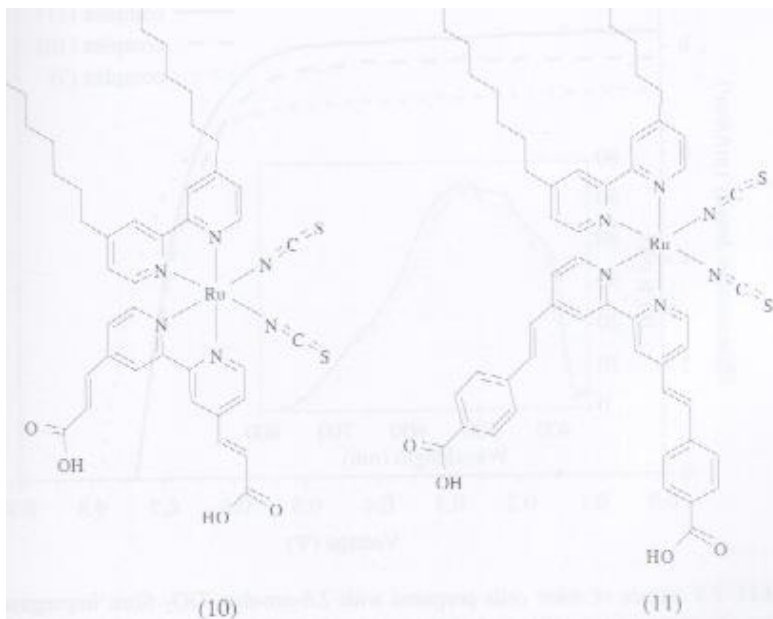


- Problem: water induced desorption
- Solution: hydrophobic ligands
- Also: suppression of recombination (5,6) (preventing triiodide from reaching the TiO_2)
- Negative: retardation of regeneration reaction (4)



Effect of π -conjugated ligands

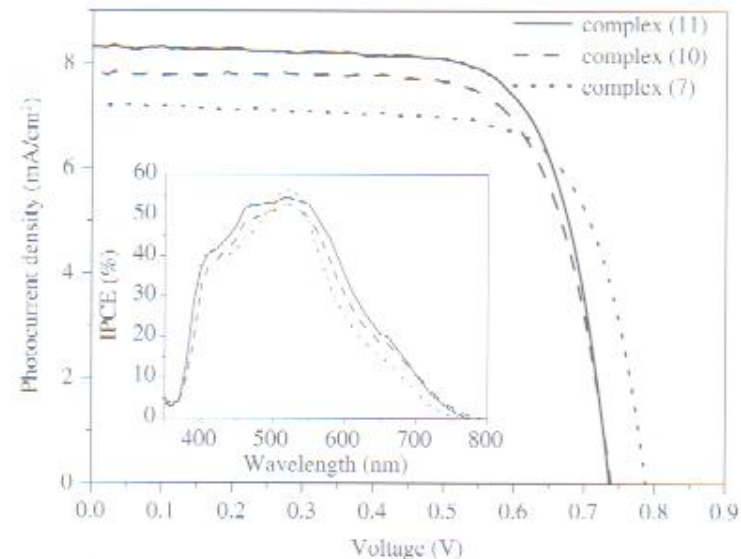
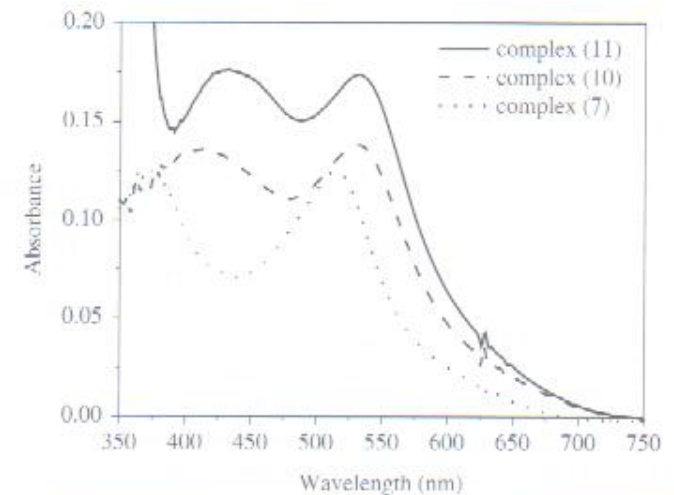
C_6H_{19} plus incorporating π -conjugation bridge between the anchoring groups



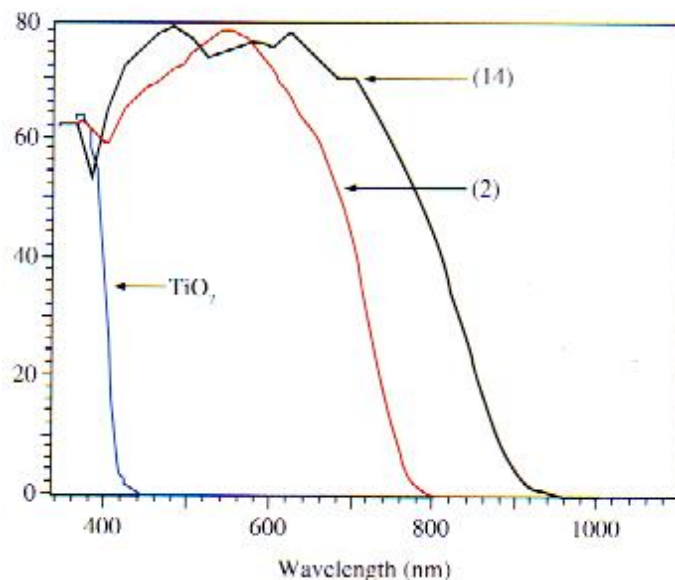
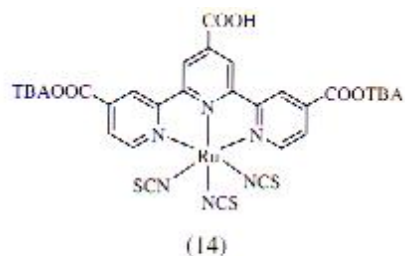
vinyl

phenylethenyl

- Increased molecular extinction coefficients
- Enhanced red response

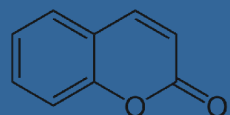


Thiocyanato Ligands

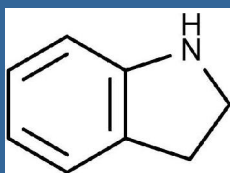


- Tuning the spectral response
- Nearly panchromatic absorption
- With this complex an efficiency of 11.1% was achieved!
- But SCN is still the weakest part of the complex

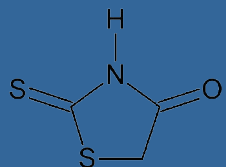
Metal-free Organic Sensitizers



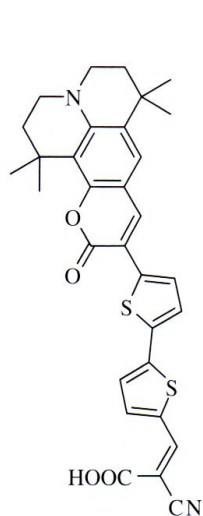
Coumarine



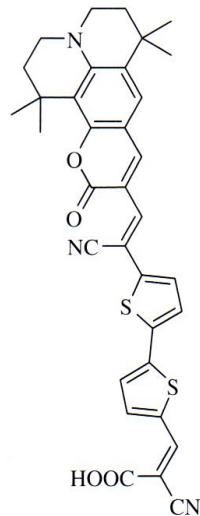
Indoline



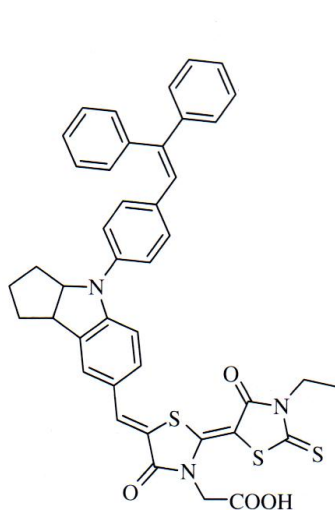
rhodanine



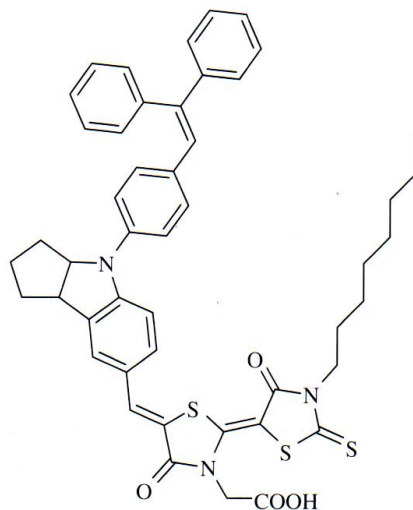
(16)



(17)



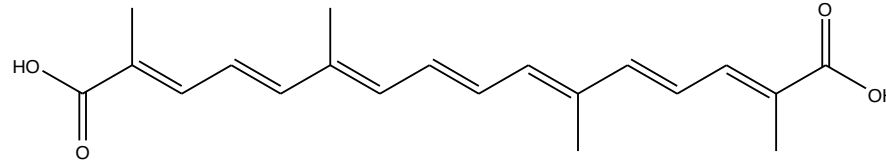
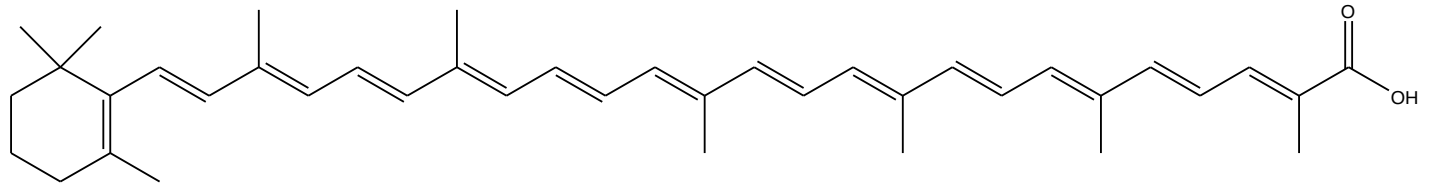
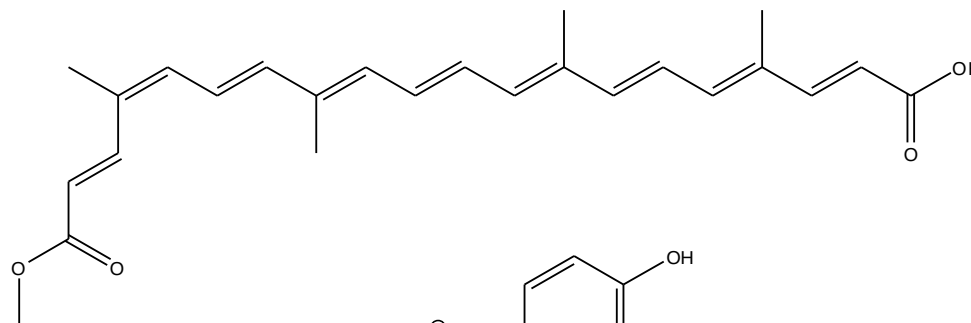
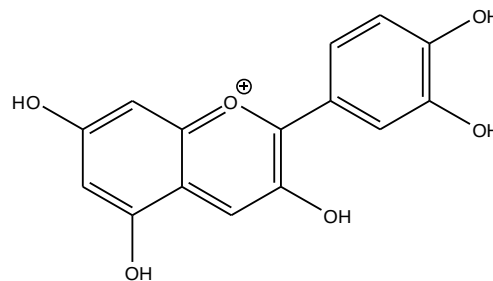
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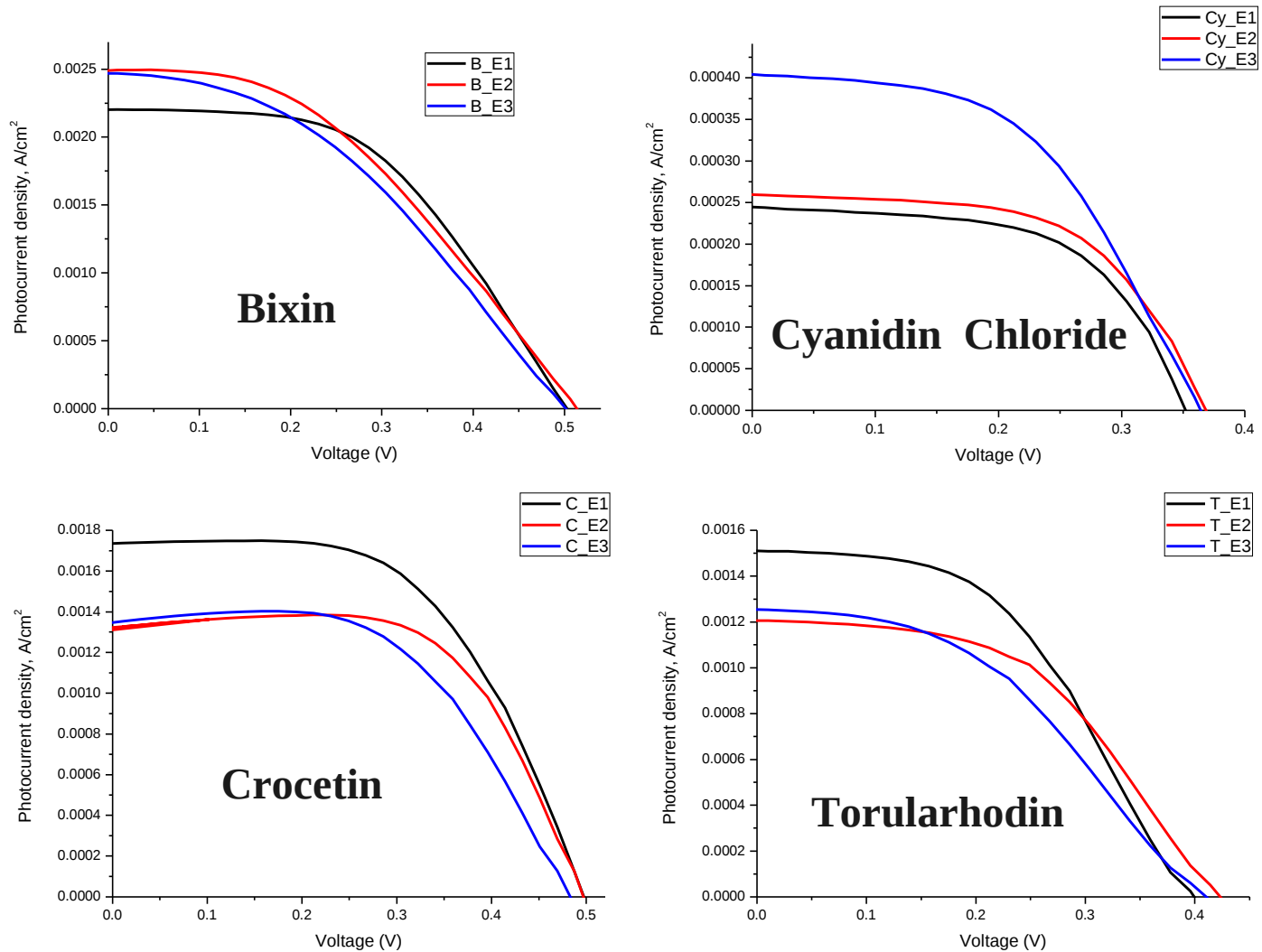
(19)

- Coumarine dyes reach efficiencies up to 7.7%
- Drastically increased molecular extinction coefficients
- Enhanced light harvesting properties due to acceptor CN group
- Indoline dyes reach efficiencies up to 9.03%
- Wide range of absorption (IPCE > 80%)

Structures of Carotenoids and Anthocyanins

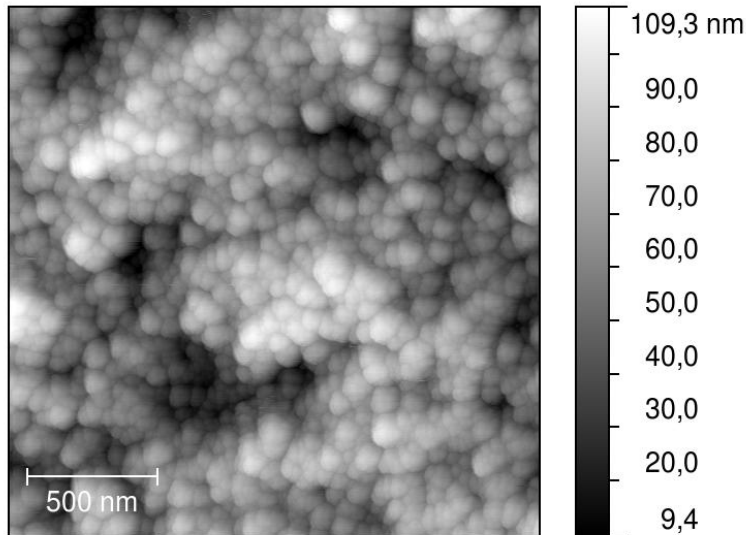
**Crocetin****Torularhodin****Bixin****Cyanidin Chloride**

Effect of Electrolytes on I-V Curves

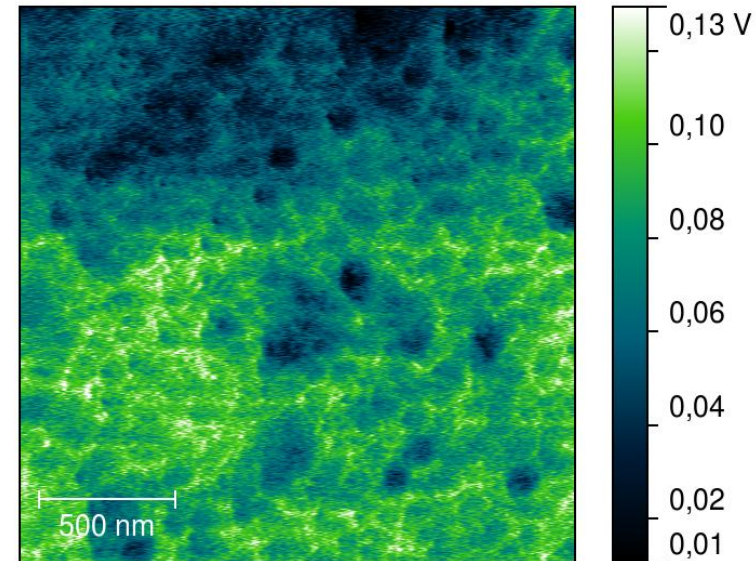


CPD variations on TiO₂

Topography

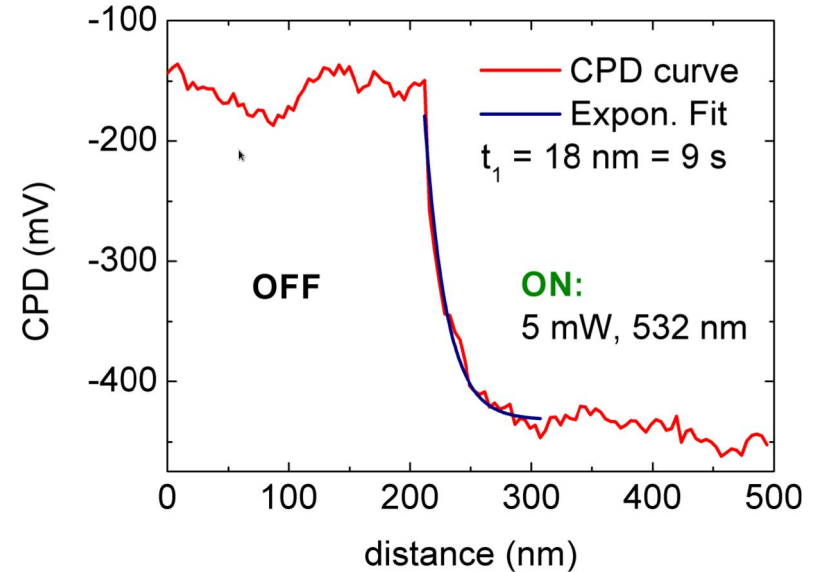
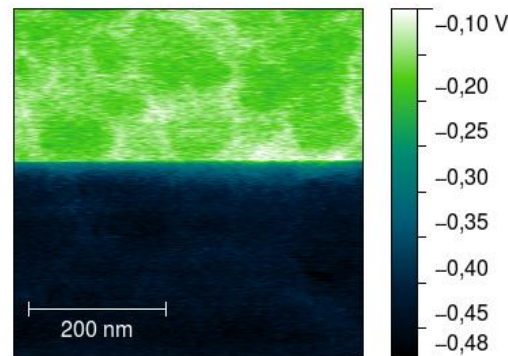
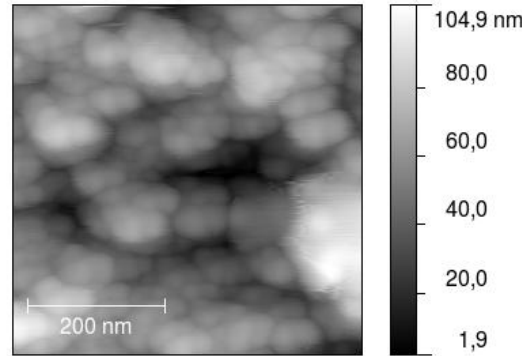


Contact Potential Difference



The nanoporous TiO₂ film deposited on FTO glass shows an inhomogeneous CPD

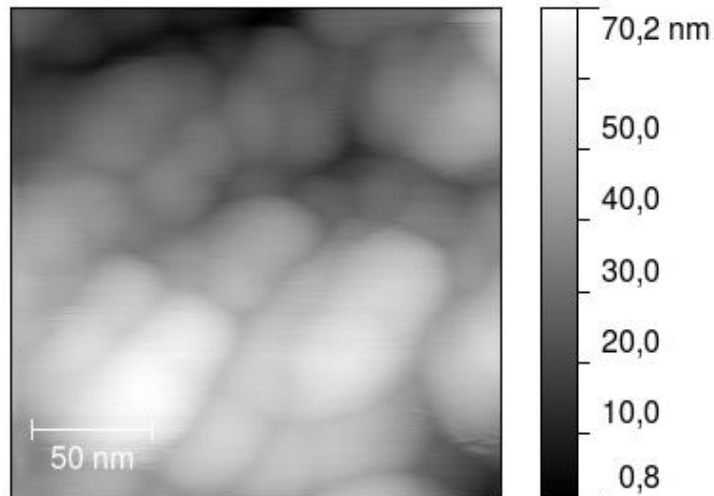
Measurement of the Local Photoactivity



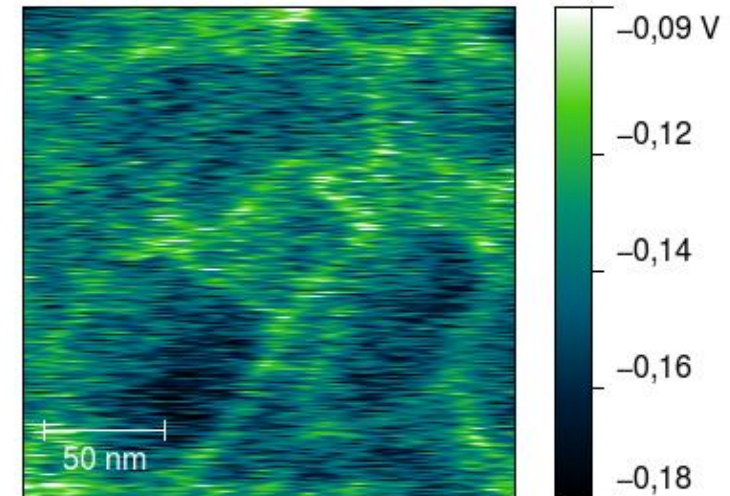
Under illumination (532nm) the CPD drops by 300mV. The process needs roughly 9s to establish an equilibrium. The value corresponds to the V_{oc} measured for the complete solar cell.

CPD Variations at Boundaries

Topography



Contact Potential Difference



Some boundaries between the sensitized TiO₂ particles showing an increased CPD value while others not.