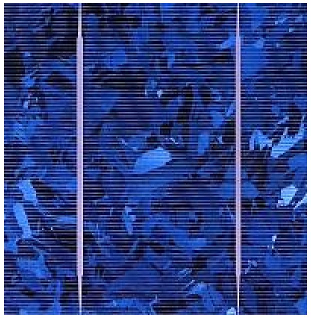
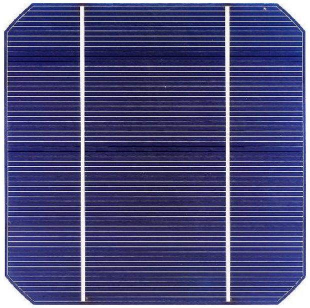
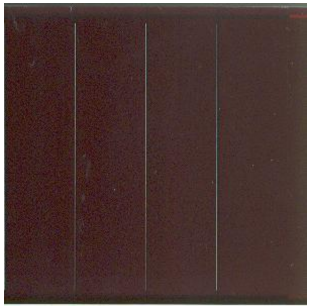
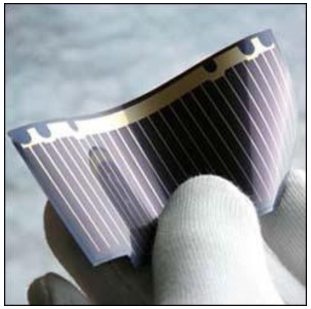
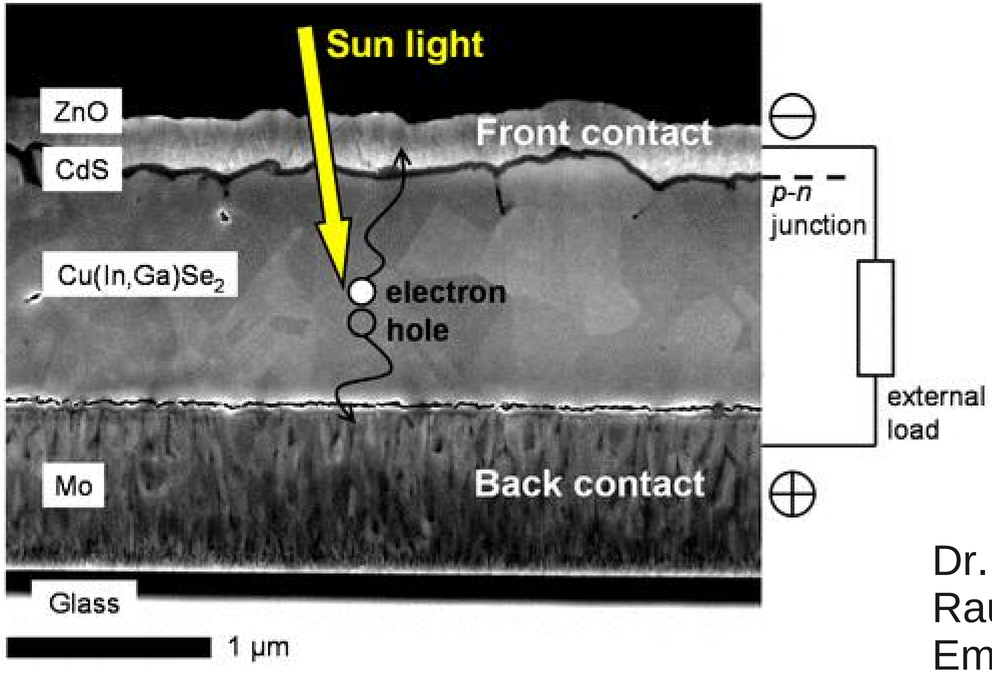
Dye Sensitized Solar Cells (27027-01)

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



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

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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 Frabstoffsolarzelle
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	

Photochemische und photoelektrische Methoden der Energiewandlung

Voltaic -> difference in the chemical potential

- Photosynthesis
  - Chlorophyll & Chloroplast
  - nc-AFM measurements of porphyrins
- Photochemistry
- Photographic Sensitization
- Photoelectrochemical Conversion
  - Photogalvanic cells
  - Semiconductor/liquid junctions
  - Colloids and particulates
- Seminar by E. Berner and M. Martignoni

Seminars

E. Berner

NANO LETTERS

pubs.acs.org/NanoLett

Fast and Scalable Printing of Large Area Monolayer Nanoparticles for Nanotexturing Applications

Sangmoo Jeong,[†] Liangbing Hu,[‡] Hye Ryoung Lee,[†] Erik Garnett,[‡] Jang Wook Choi,[‡] and Yi Cui*[,‡]

[†]Department of Electrical Engineering and [‡]Department of Materials Science and Engineering, Stanford University, Stanford, California 94305

M. Martignoni

PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS
Prog. Photovolt: Res. Appl. 2006; **14**:429–442
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/pip.712

Special Issue

The Advent of Mesoscopic Injection Solar Cells

Michael Grätzel*[,†]
Laboratory for Photonics and Interfaces, Swiss Federal Institute of Technology, Lausanne, Switzerland, CH-1015

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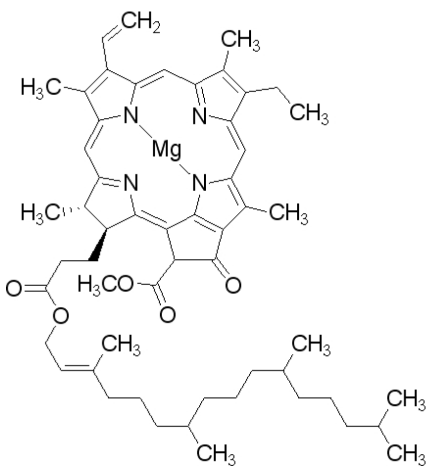
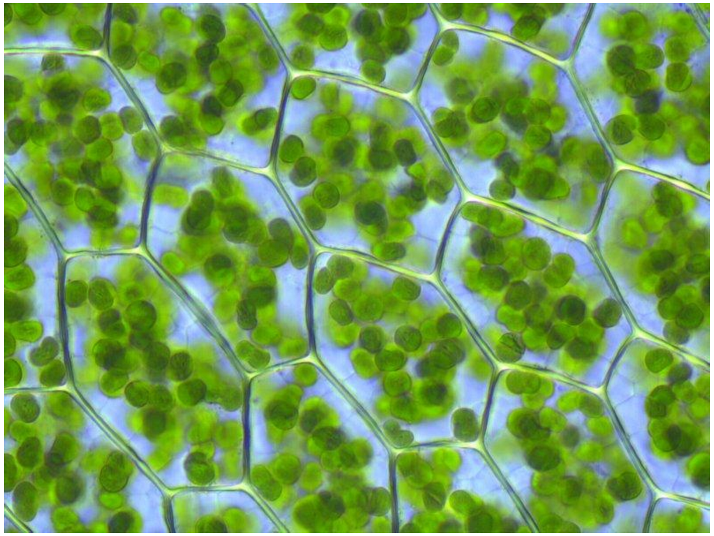
Photosynthesis

Conversion of atmospheric CO_2 to carbohydrates (sugar) by sun light

$$6\,CO_2 + 6\,H_2O\ (+\text{ sun light}) \rightarrow C_6H_{12}O_6 + 6\,O_2$$



Chlorophyll, (antenna + reaction)

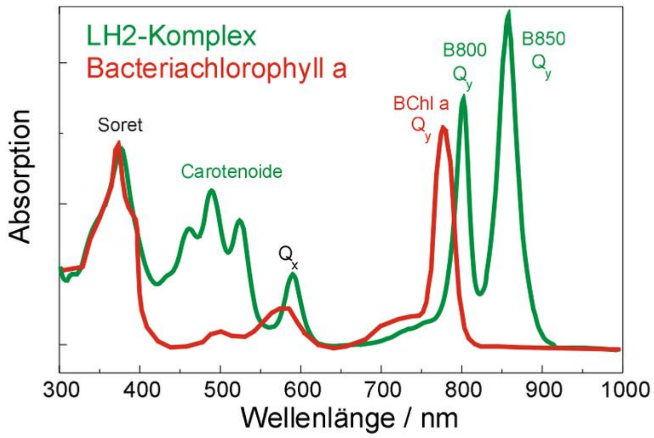


Chloroplasts

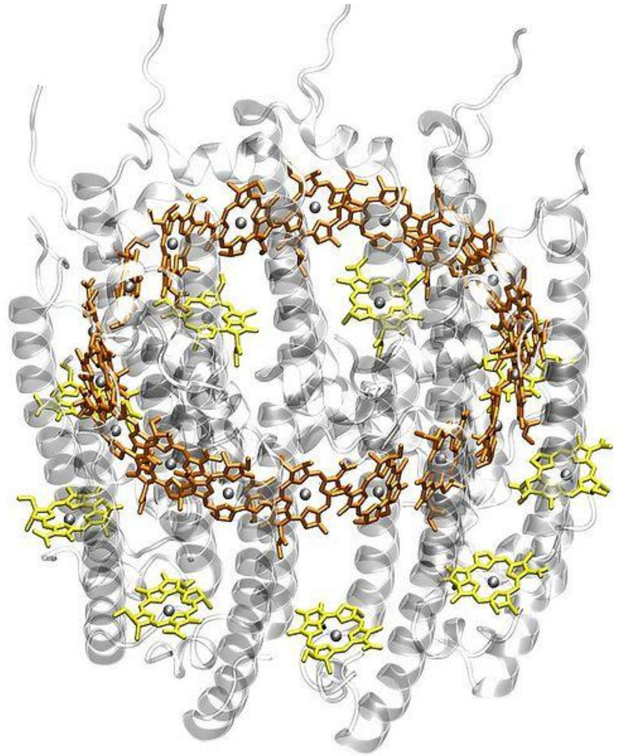
Efficiency (biomass) 3-6%

http://de.wikipedia.org/wiki/Chlorophyll

Photosynthesis
reaction center and antenna complex



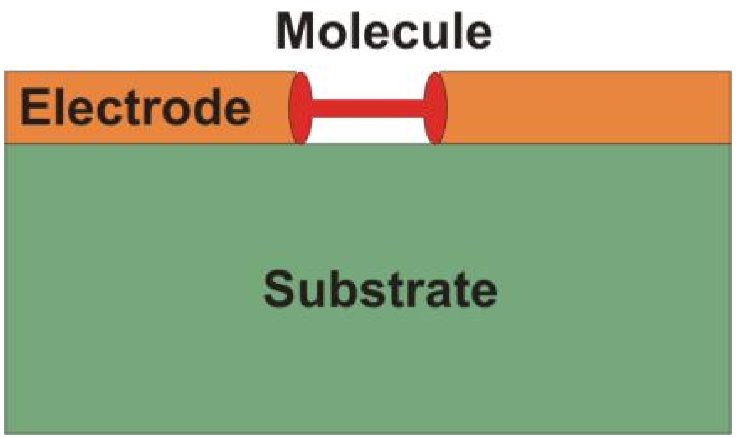
Absorption spectra of BChl a and LH2

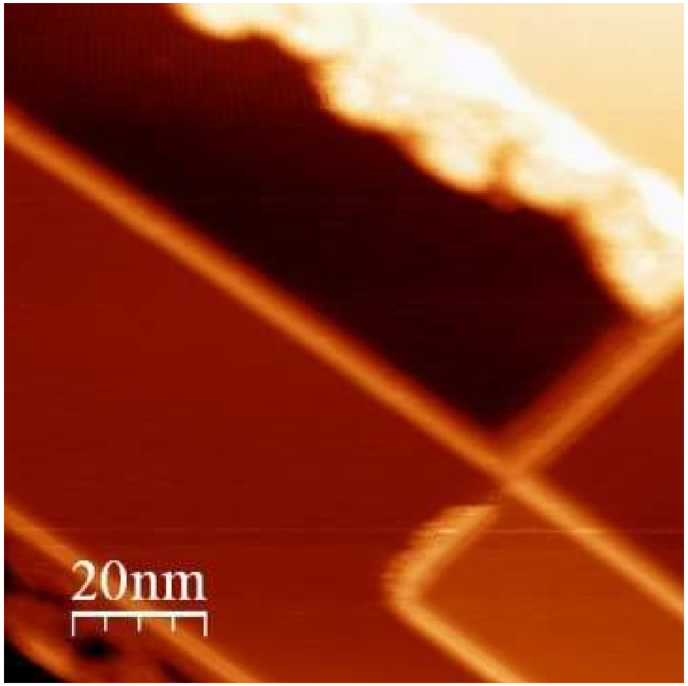


Structure of the antenna complex LH2

http://de.wikipedia.org/wiki/Chlorophyll

Photosynthesis
Molecular electronics



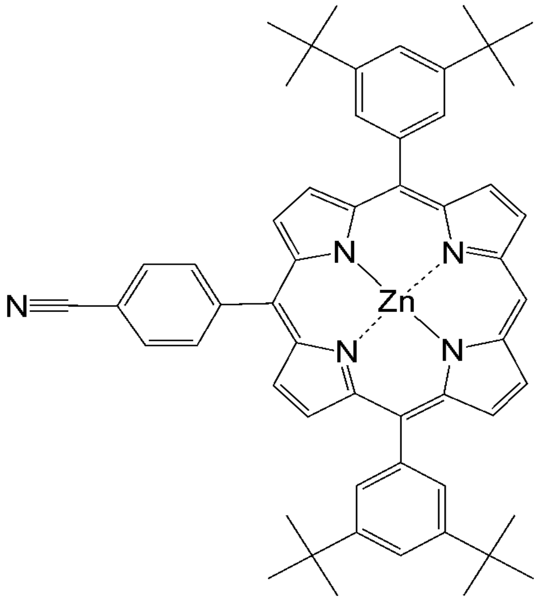


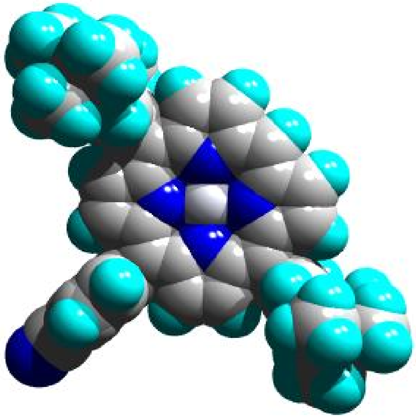
Molecules on Insulators:

- No STM possible – nc-AFM mandatory
- Low diffusion barrier but high intermolecular interaction
- Low temperatures – easier to “fix” molecules but not easy to find applications

Asymmetric Cyano-Porphyrins
Structure

- Able to π–π stack
- Negative charge at the nitrogen atom induces a dipole (p ~ 4.37 D)
- Two 3,5-di(tert-butyl)phenyl-groups act as spacers.



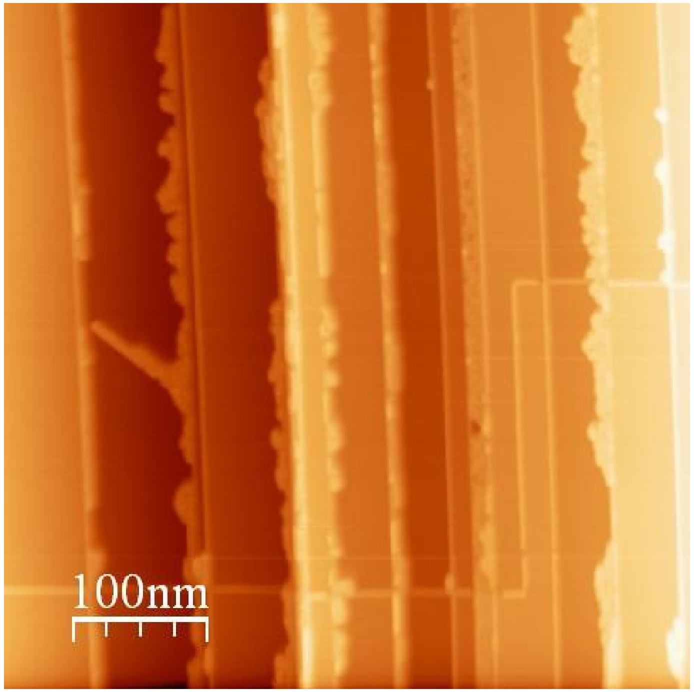


NANO

F. Cheng et al. Chem. Eur. J. 12, 6062-6070, (2006).

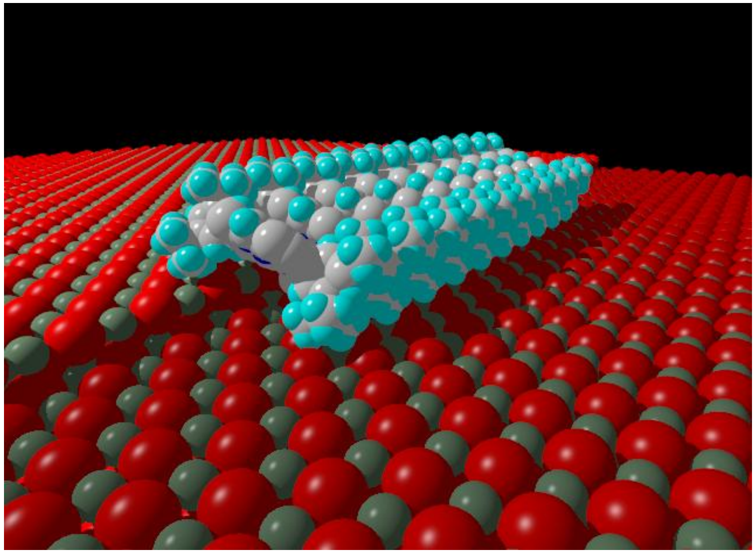
Wire Formation at step edges
Asymmetric Cyano-Porphyrins on KBr(100)

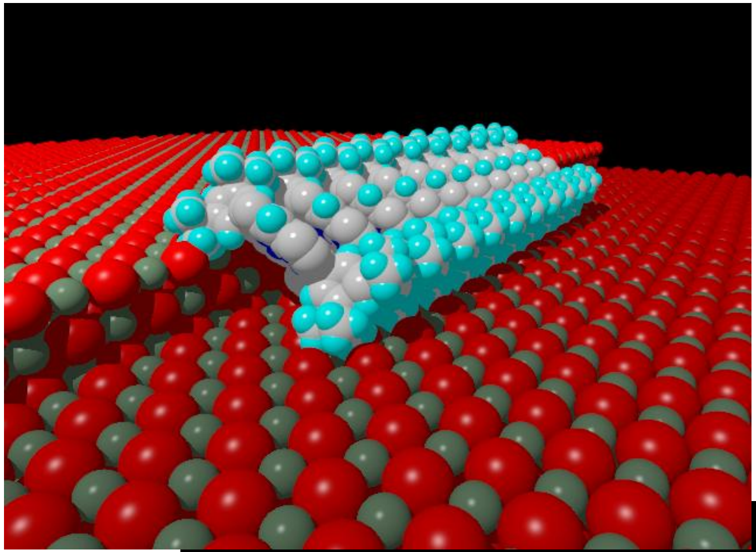
- In situ cleaved KBr with 0.5 ML of molecules
- Steps (< 1nm) are decorated with monowires
- Higher steps act as nucleation sites for structure growth across terraces

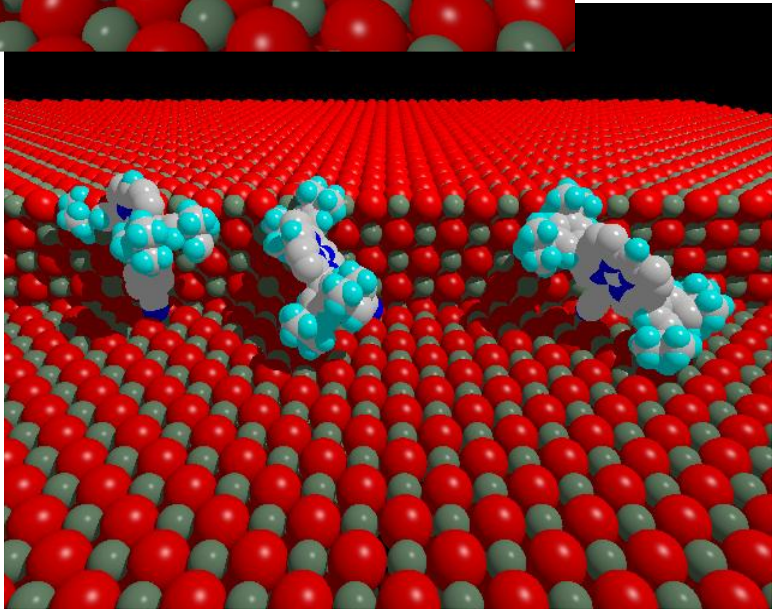


L. Zimmerli, Th. Glatzel et al., J. Phys.: Conf. Ser., 2007, 61, 1357

Wire Formation
Structural model



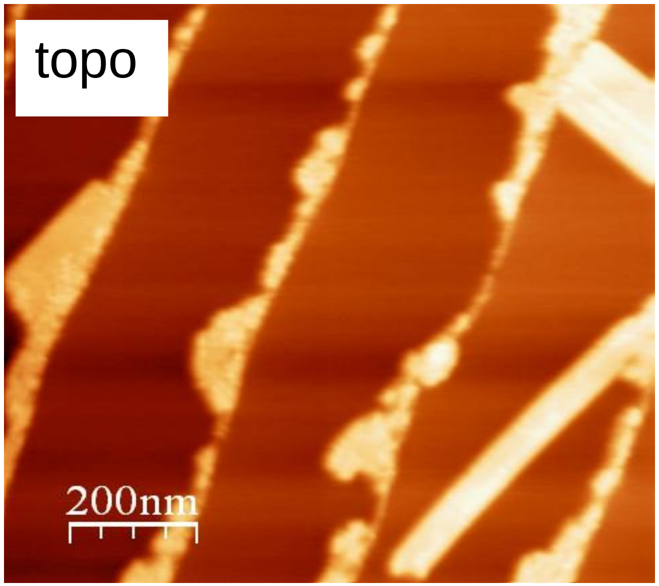




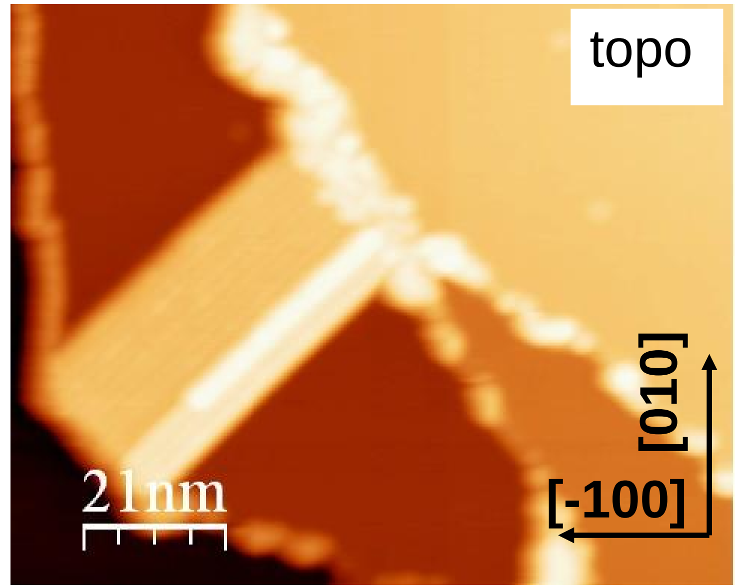
- The tilt angle of the molecules is determined by the side groups, the π–π stacking and the step height.
- Steps higher than 3 ML prevent a π–π stacking.

Th. Glatzel, Uni Basel (2010)

Molecular Assemblies
Multiwires on KBr



$f_0 \approx 174054 Hz, \Delta f = -8 Hz, Q = 15k, A = 5nm$



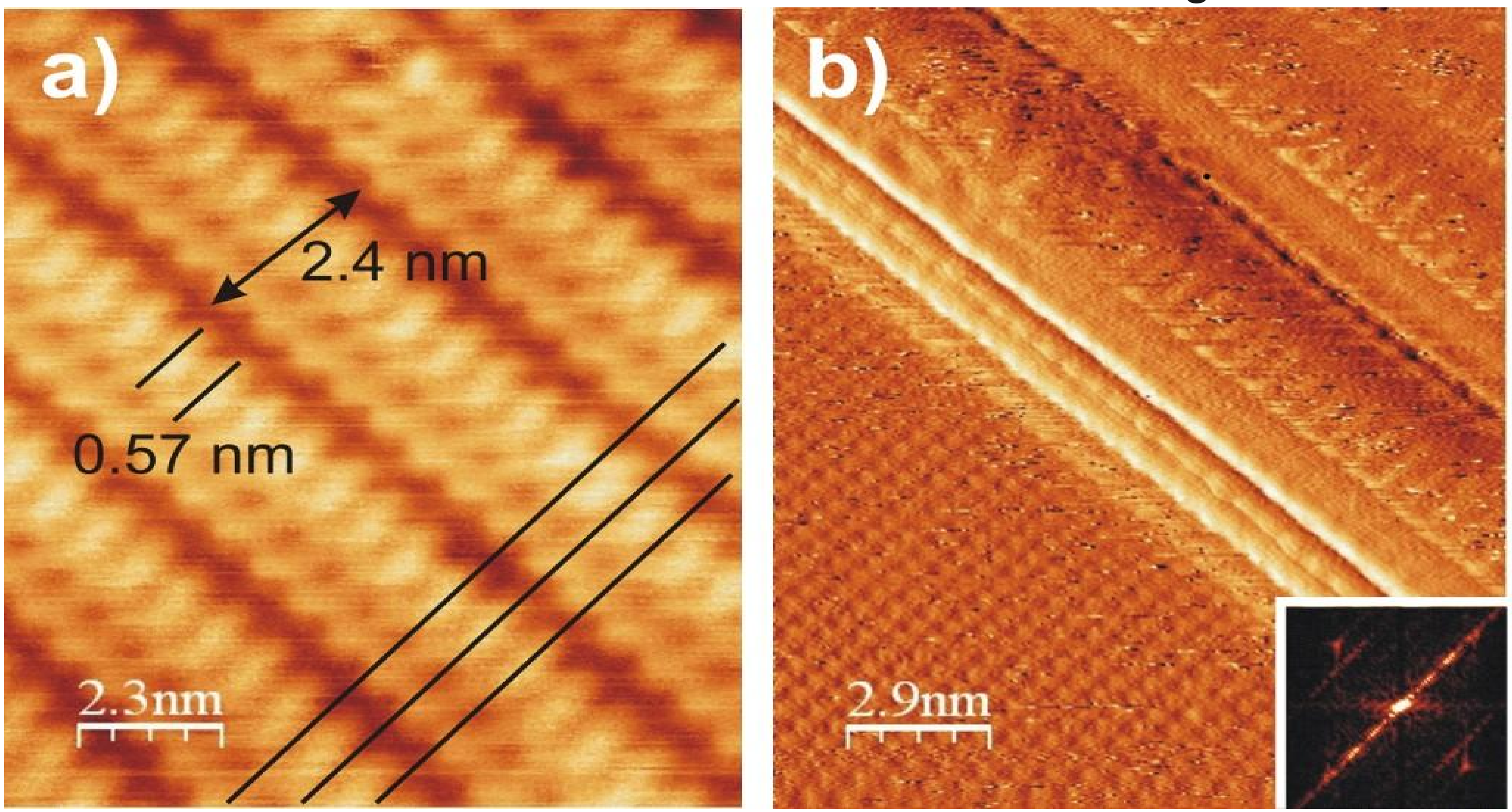
$f_0 \approx 173886 Hz, \Delta f = -52 Hz, Q = 15k, A = 5nm$

- Multiwire growth across terraces
- The <110> directions are preferred
- Different heights are visible

S. Meier, Th. Glatzel et al., Small, 2008, 4, 1115

Molecular Assemblies
High resolution imaging

Incommensurate growth in <110>

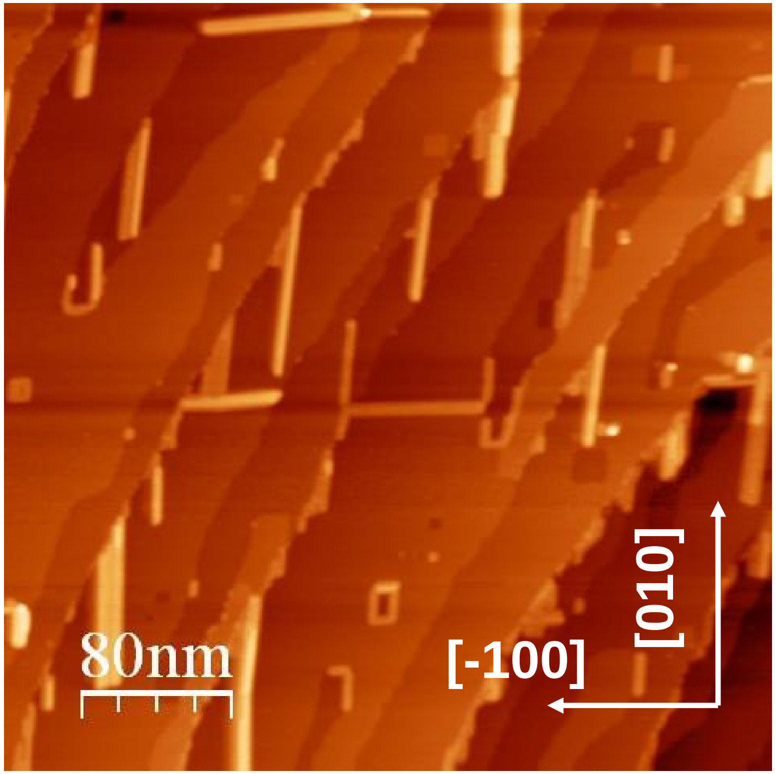


Distance between K^+ ions: <110>: 4.65 Å

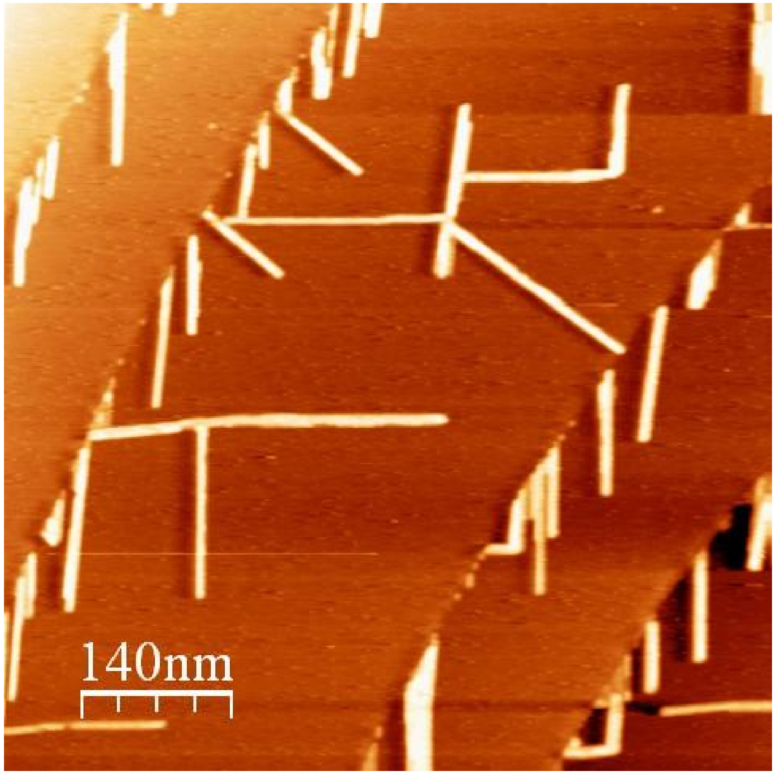
<100>: 6.60 Å

S. Meier, Th. Glatzel et al., Small, 2008, 4, 1115

Molecular Assemblies
Cyano-Porphyrins on NaCl



$f_0 \approx 170992 Hz, \Delta f = -9.5 Hz, Q = 15k, A = 40nm$



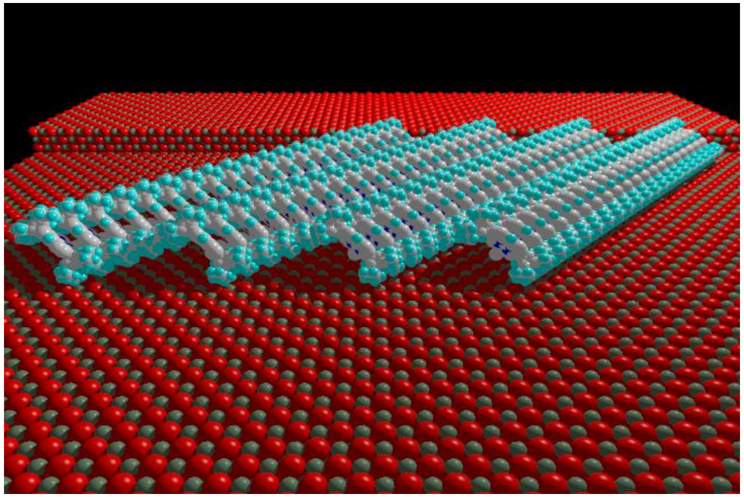
$f_0 \approx 170992 Hz, \Delta f = -11 Hz, Q = 15k, A = 40nm$

NANO

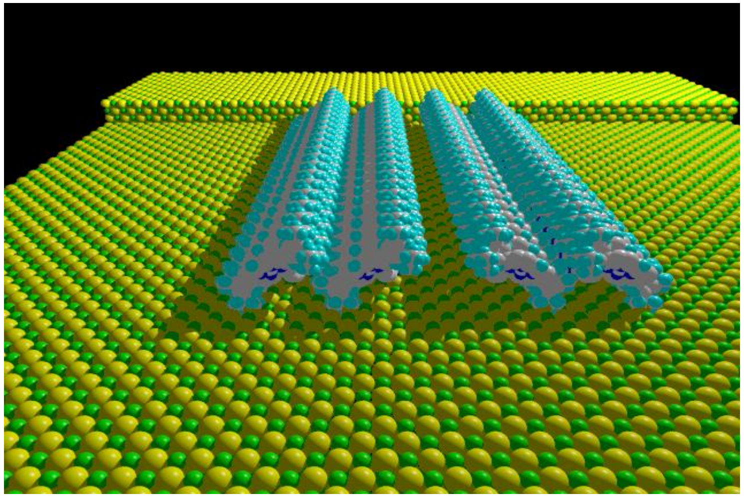
Th. Glatzel et al., Beilstein J. Nanotechnol. 2, 34 (2011)

Molecular Assemblies
Structural model

KBr / NaCl



NaCl

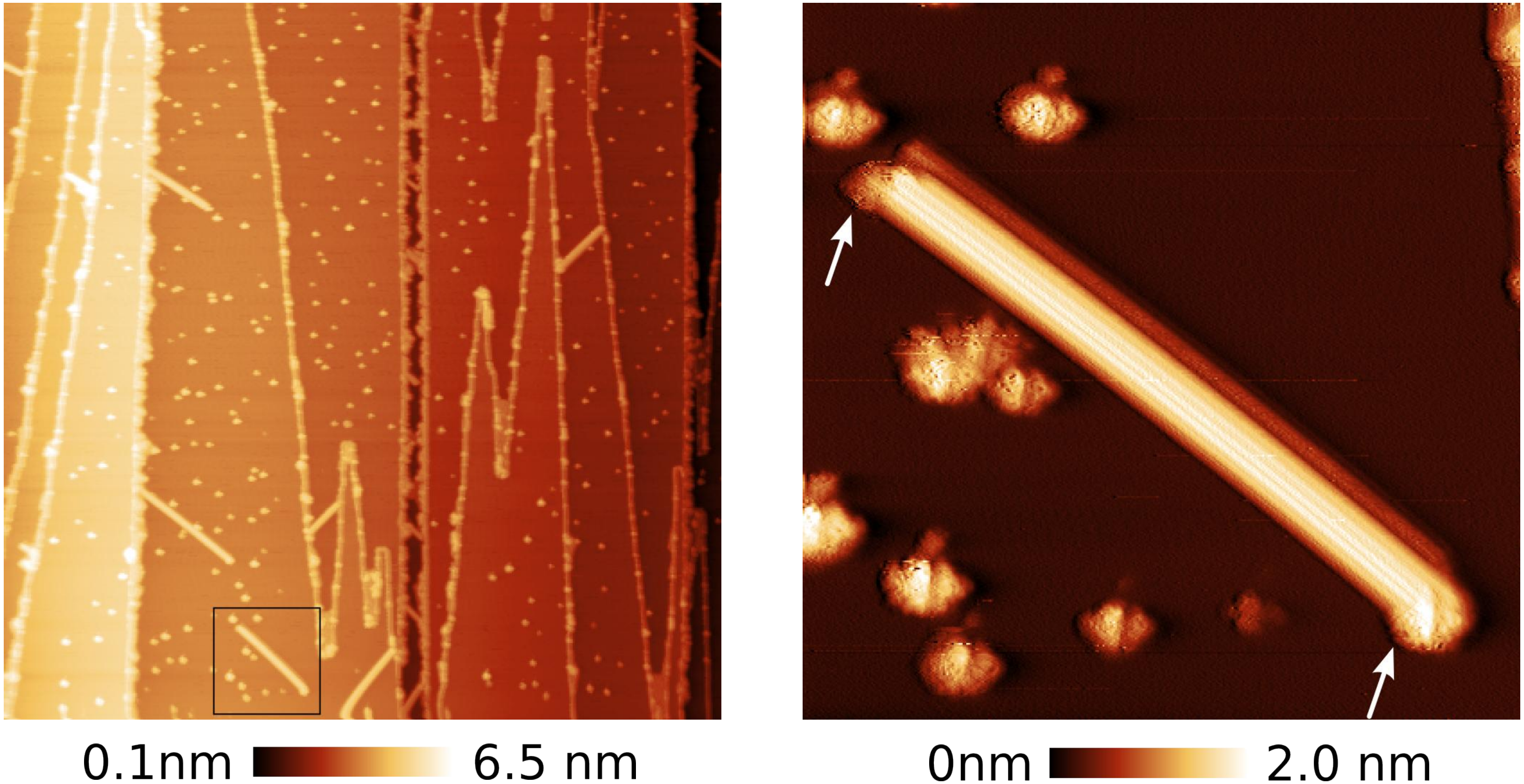


- Inter-molecular equilibrium separation ~ 5.7 Å
- Directed growth by the substrate
- Distance between Na^{+} ions: <110>: 3.99 Å <100>: 5.65 Å
- Distance between K^{+} ions: <110>: 4.67 Å <100>: 6.60 Å

NANO

Th. Glatzel et al., Beilstein J. Nanotechnol. 2, 34 (2011)

Contacting Molecular Assemblies
Au-Molecules-Au

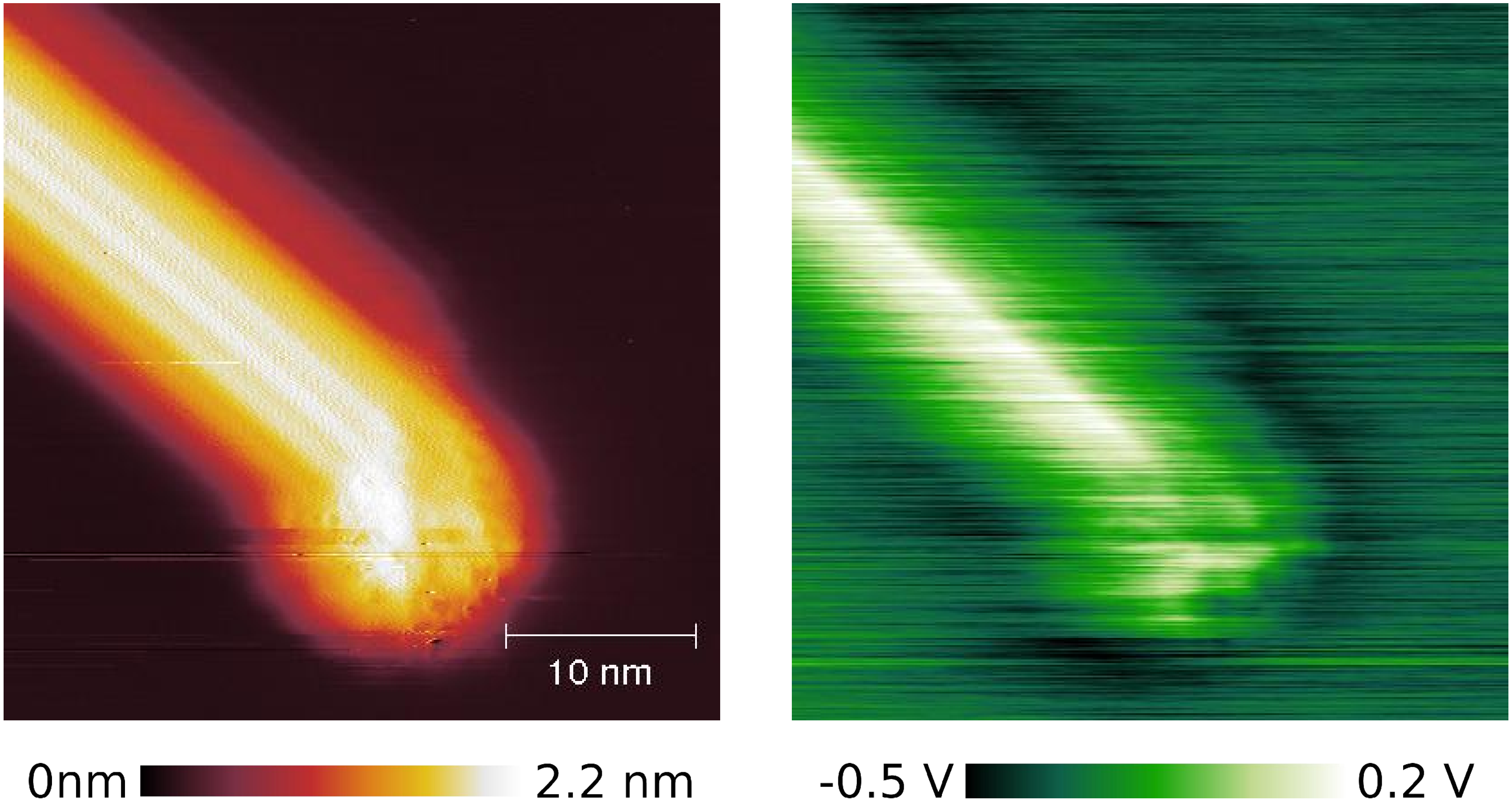


- Molecules arrange at steps and across terraces
- The growth is started/stopped at gold clusters.

NANO

Th. Glatzel et al., APL 94, 063303 (2009)

Interface of Molecules and Au
Topography and Surface Potential

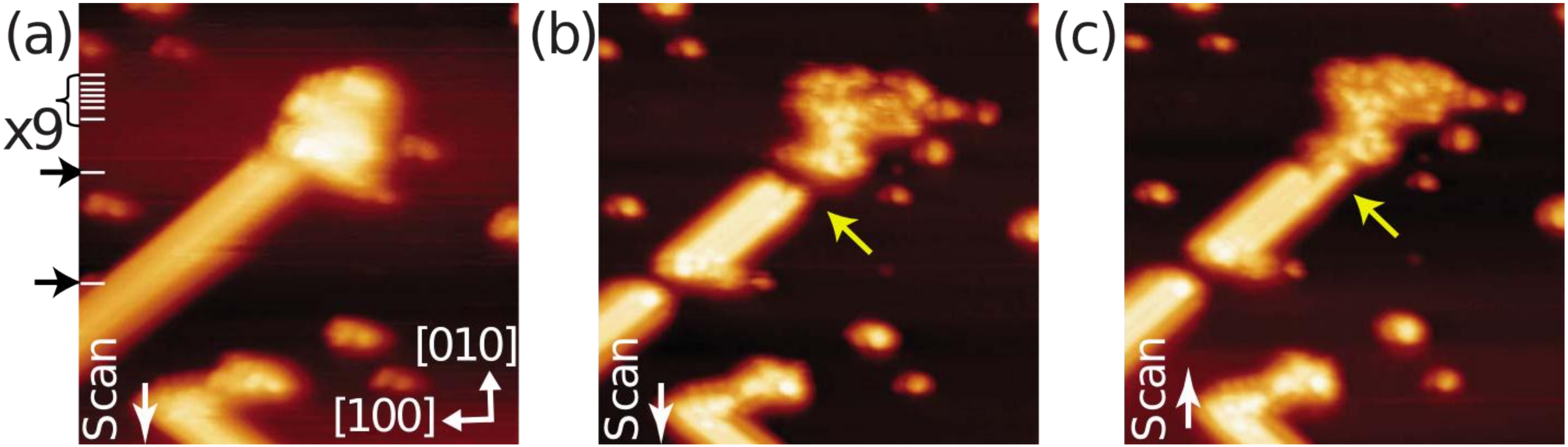


- 250 mV between the KBr surface and the Au nanoclusters
- 220 mV between Au nanocluster and the molecular wire

Th. Glatzel et al., APL 94, 063303 (2009)

Self-Healing of Molecular Wires

Topography

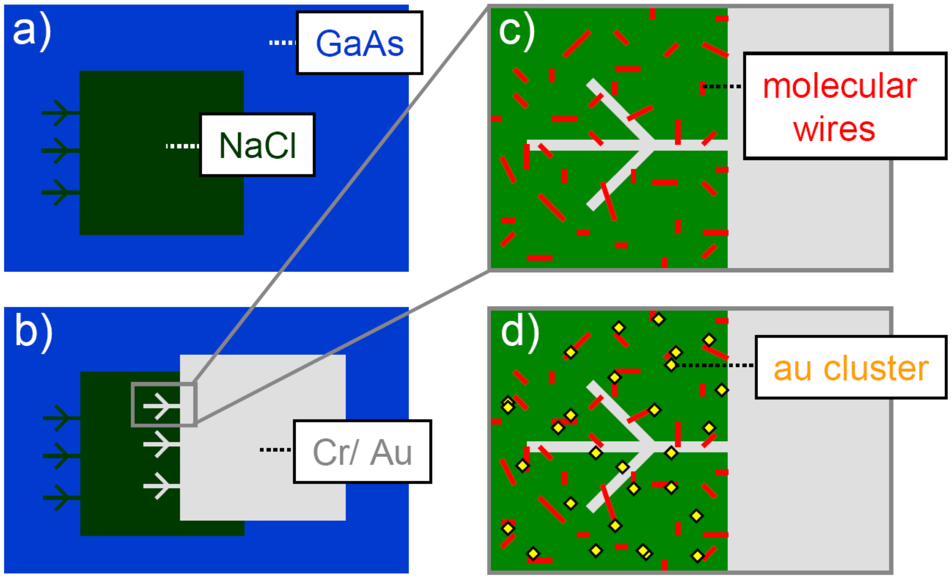


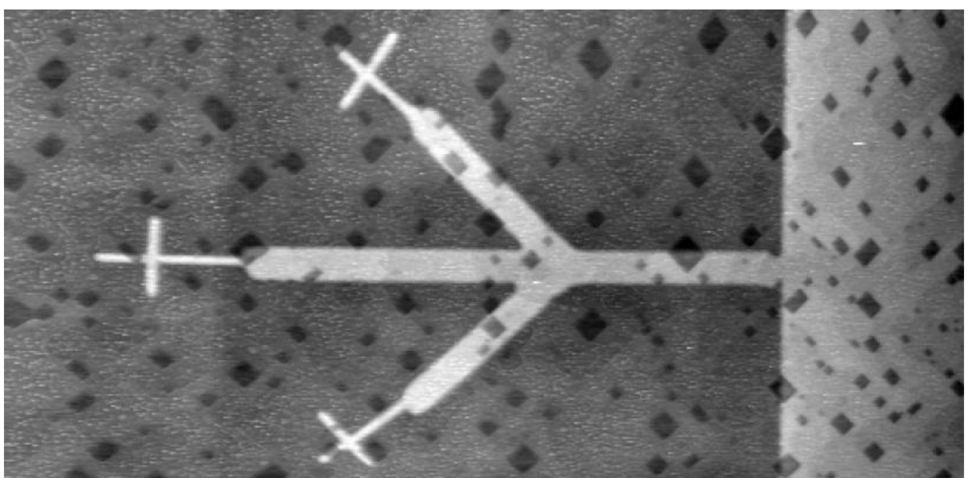
Parameter: $90 \times 90 \text{nm}^2$, $A = 5\text{nm}$, $\gamma = -0.5\text{fN}\sqrt{\text{m}}$, $V_{bias} = 0.43\text{V}$

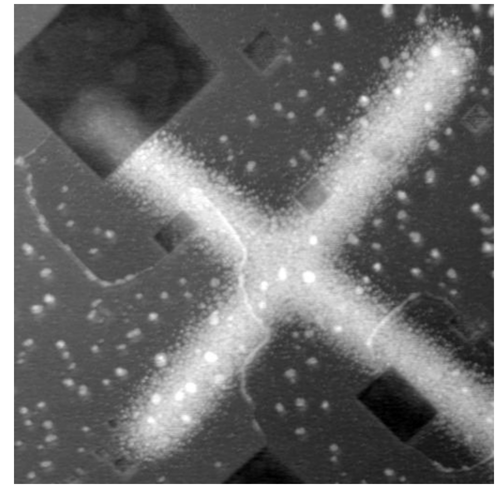
NANO

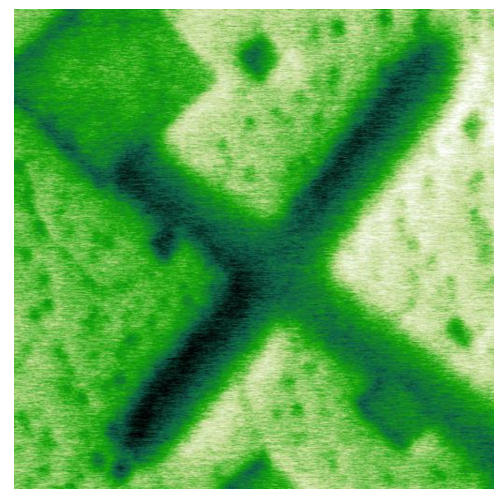
S. Kawai, Th. Glatzel et al., APL 95, 103109 (2009)

Contacting Molecular Assemblies
Nanostencil (IBM Rüschlikon)



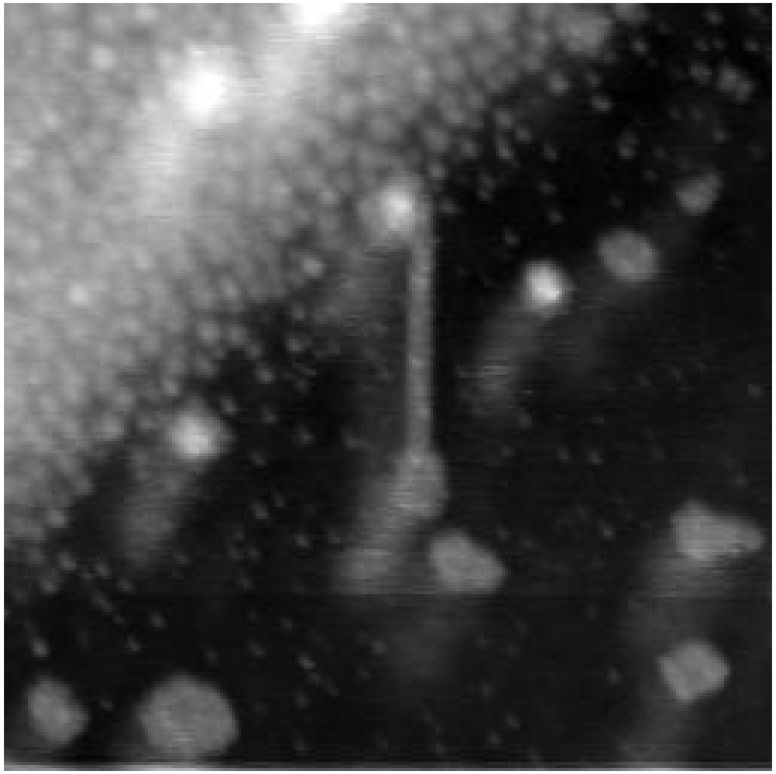




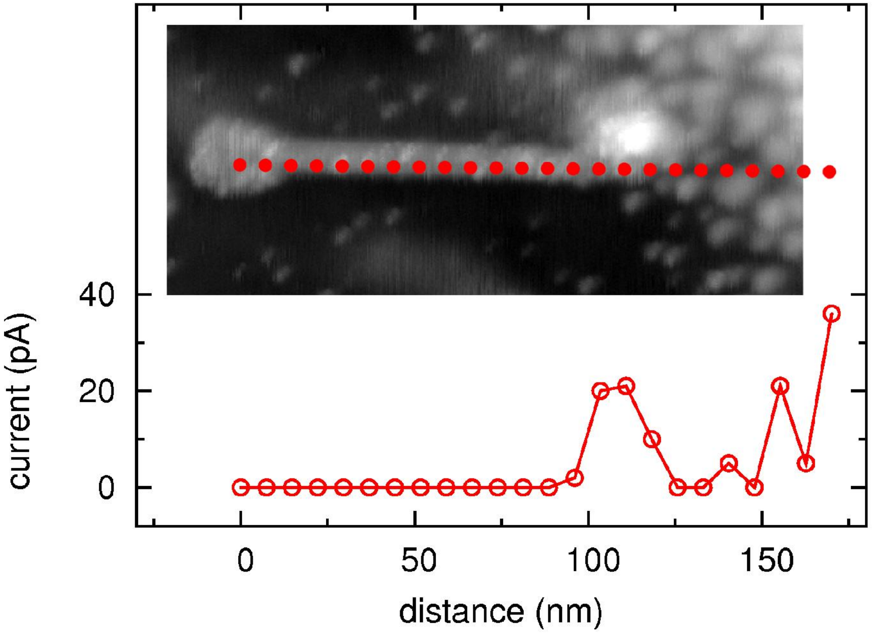


L. Gross, Th. Glatzel et al., J. Vac. Sci. Technol. B, 28, C4D34-C4D39, (2010).

Contacting Molecular Assemblies
Nanostencil (IBM Rüschlikon)



300x300nm^2



L. Gross, Th. Glatzel et al., J. Vac. Sci. Technol. B, 28, C4D34-C4D39, (2010).

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Photochemistry

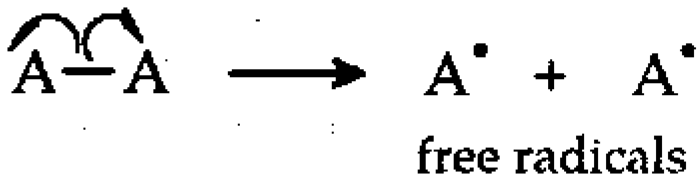
Giacomo Ciamician (20th century) photochemist, Uni Bologna

He proposed to replace “fossil energy” with natural solar radiation in 1912!

Approaches to artificial photosynthesis

- Homolytic bod fission reactions
- Molecular energy conversion-storage systems
- Light-induced electron transfer reactions

Homolytic Bond Fission



- Primary products are free radicals and undergo rapid secondary reactions using full energy stored in the reaction
- Photon energy must be larger than bond energy (< 300kJ/mol) excluding chemical bonds....
- e.g. hydrolysis of NOCl to NO 1/2Cl_2 but very low quantum yield

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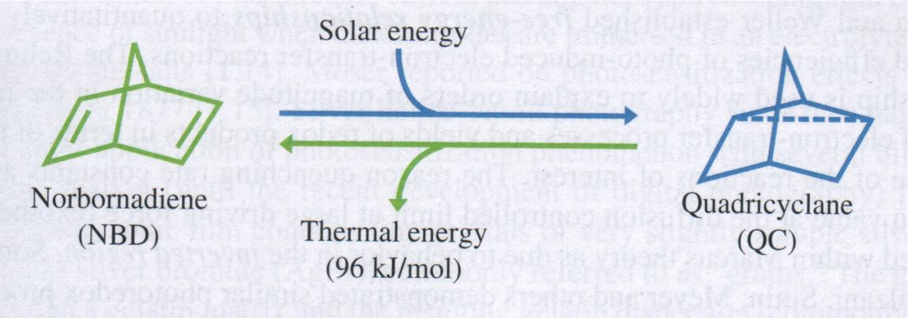
Molecular energy storage reactions



- Formation of new bonds
- Isomerization
- Reorganization of existing bond framework

Problems:
energy in UV region needed
Efficiency less than 1%

Gregory W. Sluggett et al., J. Phys. Chem. A 101, 8834

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Photoinduced electron transfer reactions

$$D + A \text{ (+sun light)} \rightarrow D^+ + A^-$$

Light absorption by donor, acceptor, or third component
Molecules is excited from ground state S to the excited state S^*
Transfer reactions with donor or acceptor molecules

Photoredox reactions

Oxidative $S^* + A \rightarrow S^+ + A^-$
Reductive $S^* + D \rightarrow S^- + D^+$

Photoinduced electron transfer reactions

Back electron reactions

$S^+ + A^- \rightarrow S + A + \text{heat}$

$S^- + D^+ \rightarrow S + D + \text{heat}$

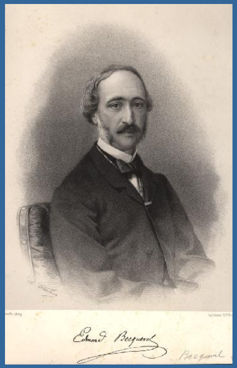
Table 1.1 Some of the chemical reactions with net storage energy [1.2–1.6].

Reaction	# Electrons	ΔE (V)
$H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$	2	1.23
$CO_2(g) \rightarrow CO(g) + \frac{1}{2} O_2(g)$	2	1.33
$CO_2(g) + H_2O(l) \rightarrow HCOOH(l) + \frac{1}{2} O_2(g)$	2	1.48
$CO_2(g) + H_2O(l) \rightarrow HCHO(g) + O_2(g)$	4	1.35
$CO_2(g) + 2H_2O(l) \rightarrow CH_3OH(l) + \frac{1}{3} O_2(g)$	6	1.21
$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$	8	1.06
$N_2(g) + 3H_2O(l) \rightarrow 2NH_3(g) + \frac{1}{2} O_2(g)$	6	1.17
$CO_2(g) + H_2O(l) \rightarrow 1/6\, C_6H_{12}O_6(s) + O_2(g)$	4	1.24

Final goal: generation of fuels like H_2, CH_4, CH_3OH,...

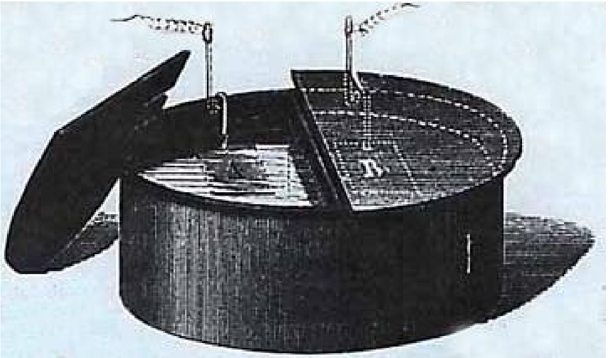
But : most reactants are transparent, external photosensitizers needed

And multi-electron-transfer reduces yield (catalyst needed)



Photographic Sensitization

1839: *Alexandre-Edmond Becquerel* observation of measurable current passing between two platinum electrodes in the presence of sunlight when immersed to an electrolyte containing metal halide grains



$$AgBr \text{ (Grain)} + h\nu \text{ (radiation)} \rightarrow Ag^+ + Br + e^-$$

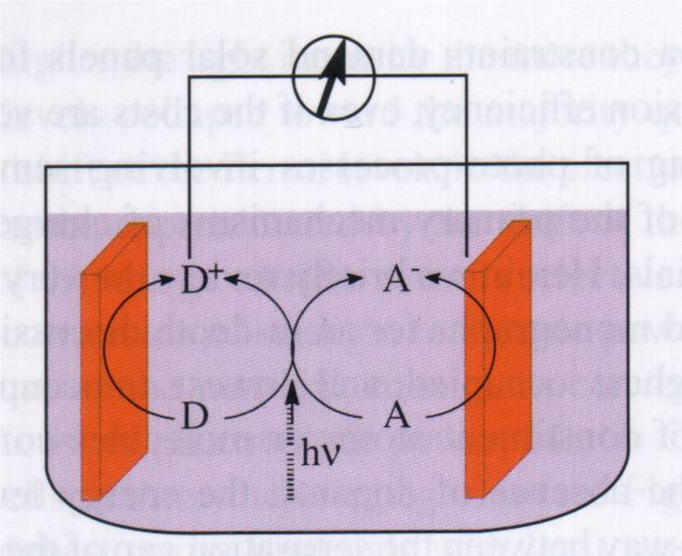
$$Ag^+ + e^- \rightarrow Ag_0$$

silver in grains – latent image
Developers forming free silver, fixing residual silver halide is removed

Photoelectrochemical Conversion

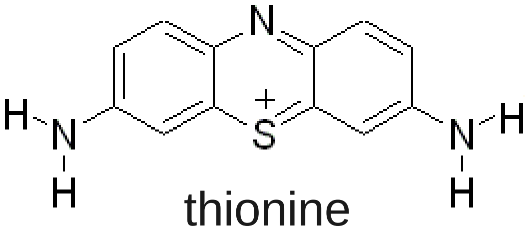
Photogalvanic cells

Two metal electrodes in a Solution of “dye”



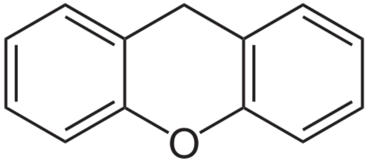
$D^+ + e^- \rightarrow D$ (cathode)

$A^- \rightarrow A + e^-$ (anode)



thionine

+ ferric ions Fe^{3+}



xanthene

Photogalvanic cells

$h\nu \rightarrow e^-$ Most efficient way of solar energy conversion

Theoretical efficiency 5-9%.... but only 0.03% obtained.....

Problems:

- No selectivity of the electrodes
- Only a small fraction of the dye close to the cathode is active (recombination)
- Self quenching of the excited state

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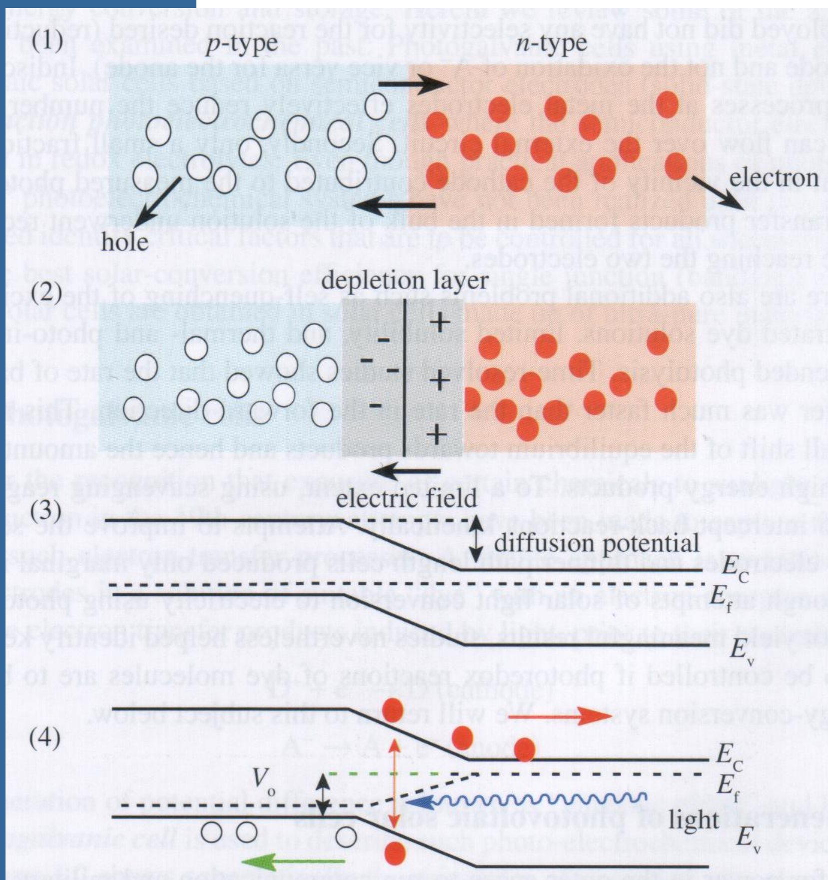
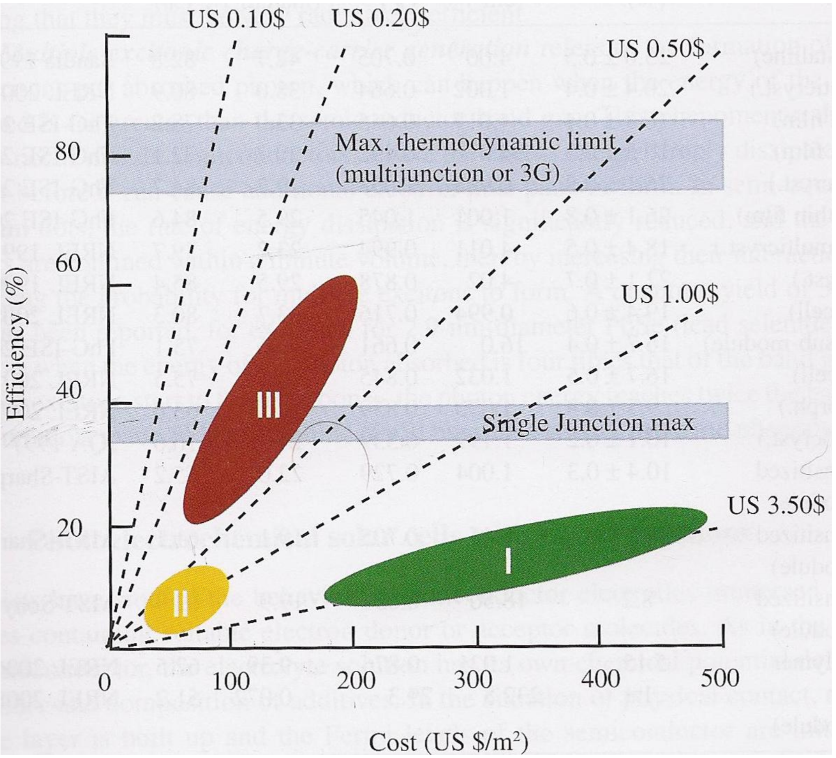
Generation of photovoltaic solar cells



M. Green, major PV categories



1st higest purity materials, expensive
2nd low energy intensive preparation
3rd PV systems above Shockly and Queisser limit

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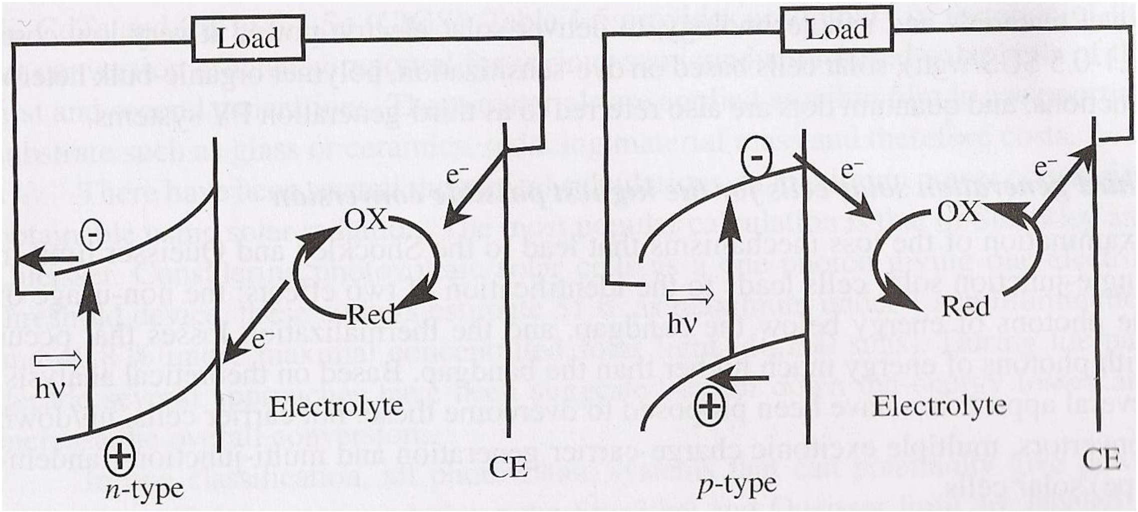
Photoelectrochemical solar cells with liquid junctions

Semiconductor electrodes immersed in electrolytes containing suitable electron donor or acceptor molecules



photoanode photocathode

Space chare layer at the semiconductor/liquid interface
Redox mediator recycled (regenerative solar cell)
Problem: photodecomposition of the semiconductor

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Photoelectrochemical solar cells with liquid junctions

Table 1.7 Light-conversion efficiency of regenerative solar cells based on semiconductor electrodes immersed in redox electrolyte solutions.

Semiconductor	Aqueous redox electrolyte	Solar conv. efficiency (%)	Stability (C/cm^2)	Ref.
n-GaAs	1 M K_2Se, 0.01 M K_2Se_2, 1 M KOH	12.0	35,000	[1.36]
p-InP	0.3 M V^{3+}, 0.05 M V^{2+}, 5 M HCl	11.5	27,000	[1.37]
n-$GaAs_{0.72}P_{0.28}$	1 M K_2Se	11.0	3000	[1.38]
n-WSe_2	1 M KI, 0.01 M KI_3	10.2	40,0000	[1.39]
n-$CuInSe_2$	6 M I^-, 0.1 M Cu^{2+}, 0.1 M In^{3+}	10.1	15,000	[1.40]
n-$CuInSe_2$	I_3^- / I^- mixture, Cu^+	9.5	70,000	[1.41]
n-$MoSe_2$	1 M KI, 0.01 M KI_3	9.4	50,000	[1.42]
n-CdSe	1 M Na_2S_2, 1 M NaOH	7.2	20,000	
n-WS_2	1 M NaBr, 0.01 M Br_2	6.0		
n-CdSe	$Fe(CN)_6^{4+}$	12.4	unstable	

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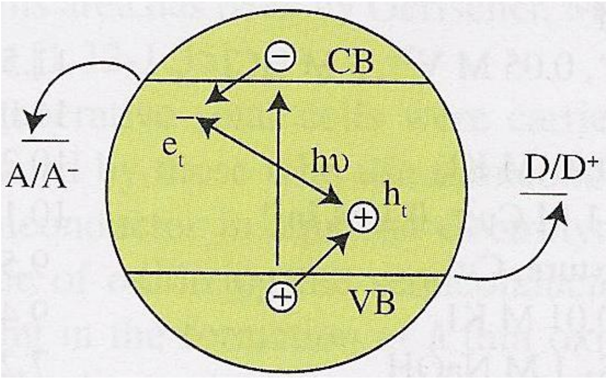
Photoredox reactions of colloidal semiconductors and particulates



Both forms of photo-generated charge carriers rech the surface
Low cost efficent system for degreading toxic waste