

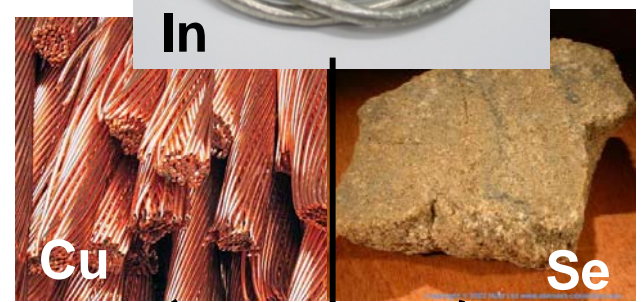
New trends in organic materials based solar cells

*Prof. Frank Nüesch
Funktionspolymere
Empa
8600 Dübendorf*

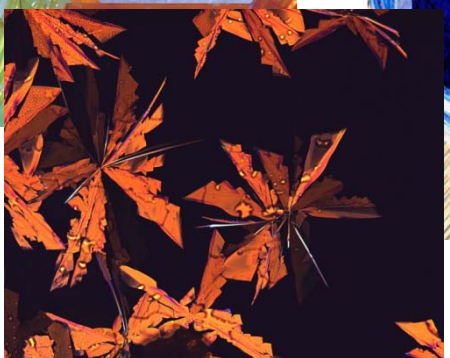
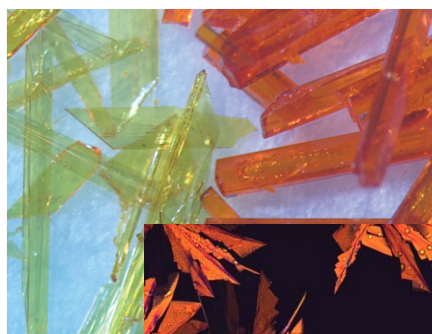


Materials Science & Technology

Semiconductors

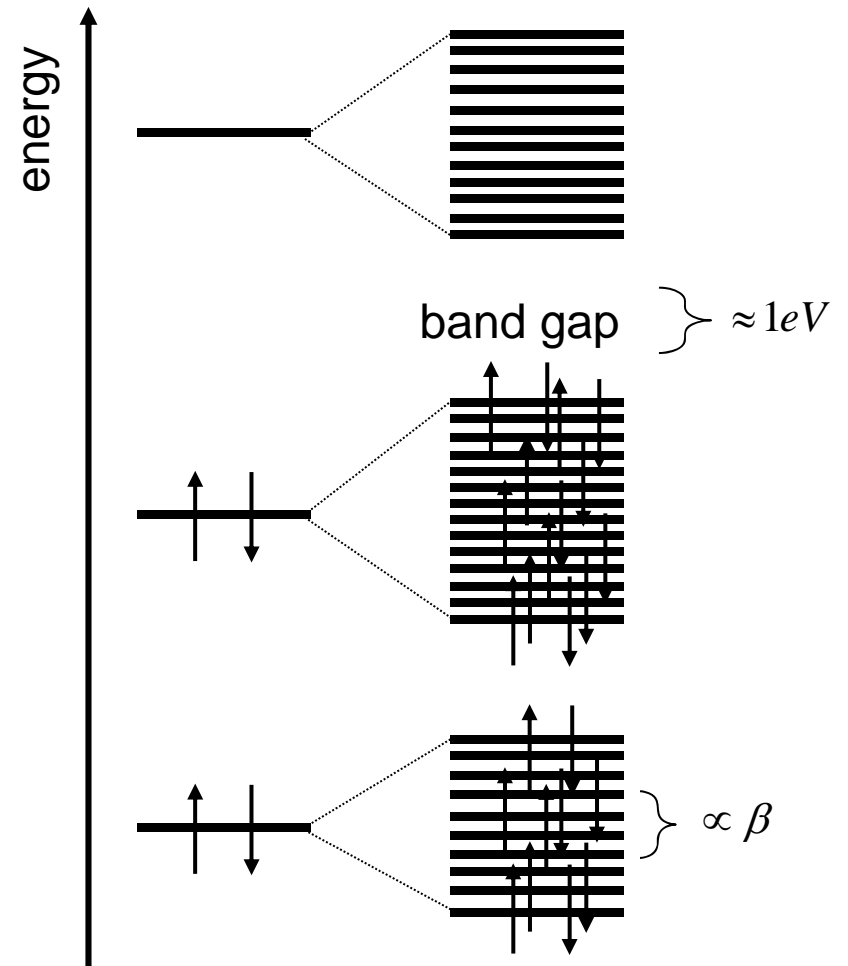
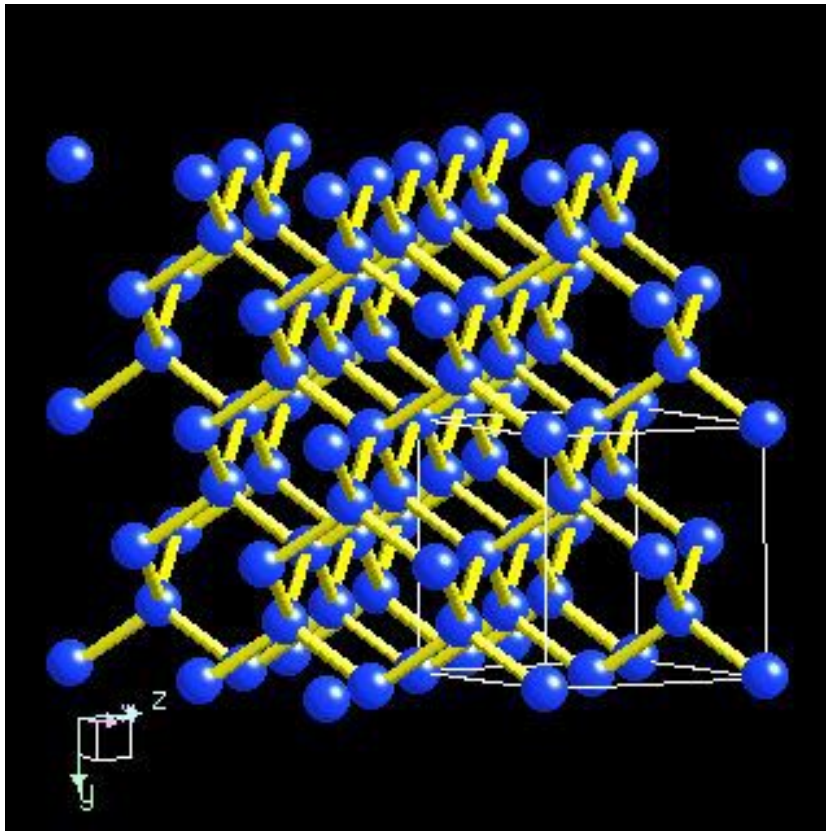


organic single crystals and amorphous powders



Materials Science & Technology

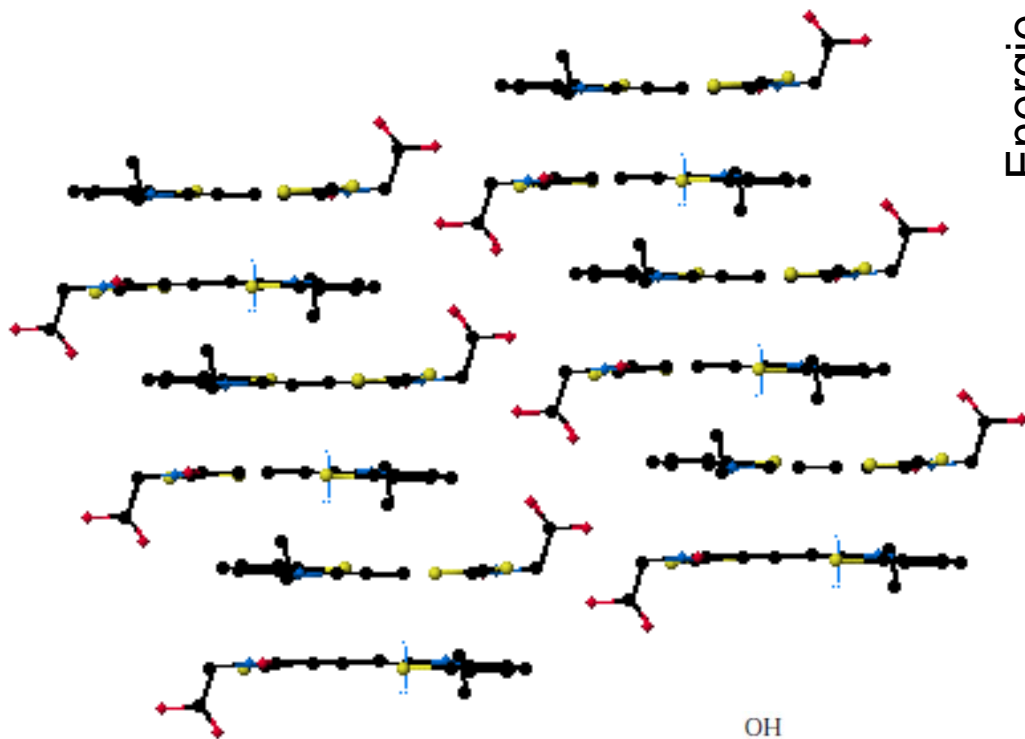
Silicon crystal structure



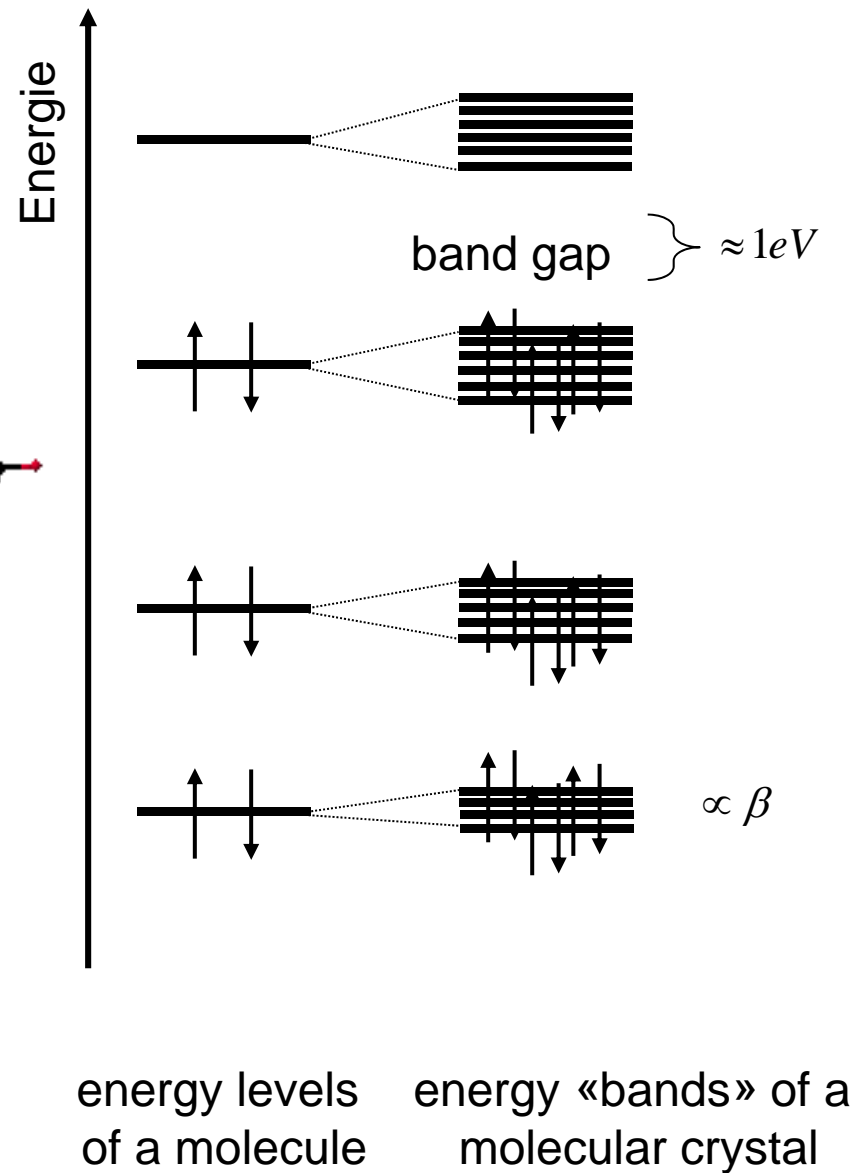
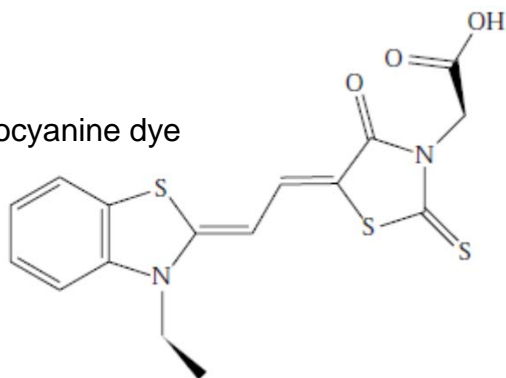
electron energy
levels of a Si atom

energy bands
of a Si crystal

Molecular crystal



merocyanine dye



Properties of organic semiconductors

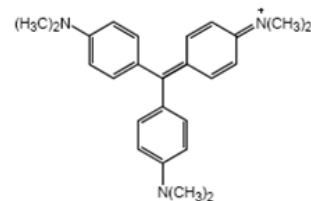
- Organic semiconductors are soft and ductile
- Organic semiconductors have narrow absorption bands
- Organic semiconductors, in particular dyes have high absorption coefficients exceeding those of inorganic semiconductors by 100 times
- The properties of organic semiconductors can be tuned almost arbitrarily (absorption, solubility, crystallinity)
- Organic semiconductors are normally insulators. Conductivity can be achieved by chemical/physical doping.
- Organic semiconductors have a low charge carrier mobility, which is smaller by 3 to 6 orders of magnitude compared to inorganic semiconductors

Organic donor-acceptor junction

HANS MEIER und A. HAUS, Bamberg: *Zum Problem organischer Photodioden* (vorgetr. von H. Meier).

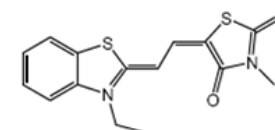
Die Einteilung der photoelektrisch aktiven organischen Farbstoffe in p- und n-Leiter, deren Stromübertragung (wie Messungen der Gasabhängigkeit von Photo- und Dunkelstrom, Thermokraft, Kristallphotoeffekt u. a. beweisen) in der Hauptsache durch Defektelektronen oder Elektronen erfolgt, führte zur Prüfung des organischen pn-Übergangs. In Übereinstimmung zur anorganischen pn-Struktur besitzt ein aus einem p- und n-leitenden Farbstoff zusammengesetztes System (z. B. Merocyanine/Triphenylmethan-Farbstoffe) die Eigenschaft einer Photodiode, die bei Belichtung mit sichtbarer Strahlung einen Kurzschlußstrom I_0 und eine Leerlaufspannung E_{CP} ohne äußere Hilfsspannung ergibt. Charakteristische Merkmale dieser Photoelemente sind: Reversibilität von I_0

Hans Meier, Bamberg 1960



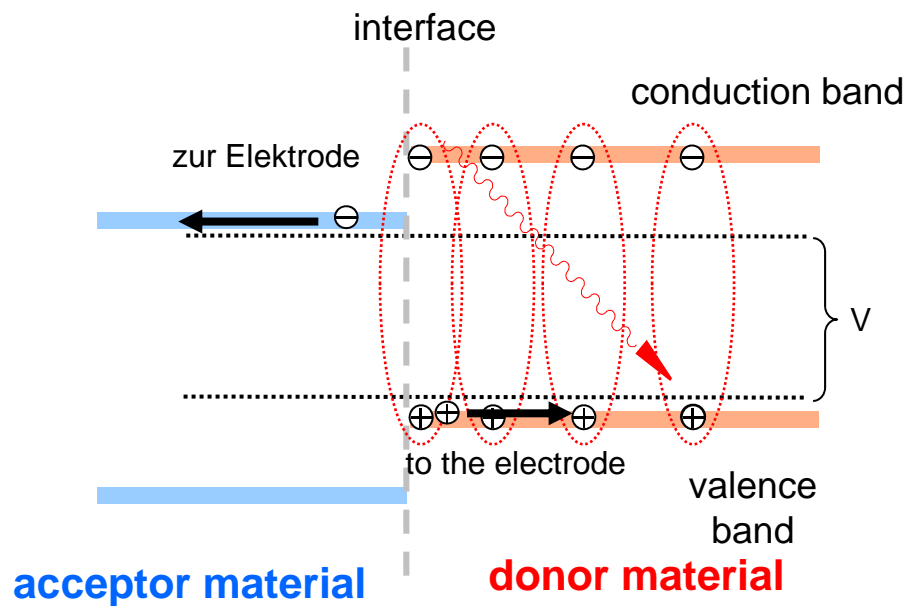
crystal violet

acceptor material



merocyanine

donor material

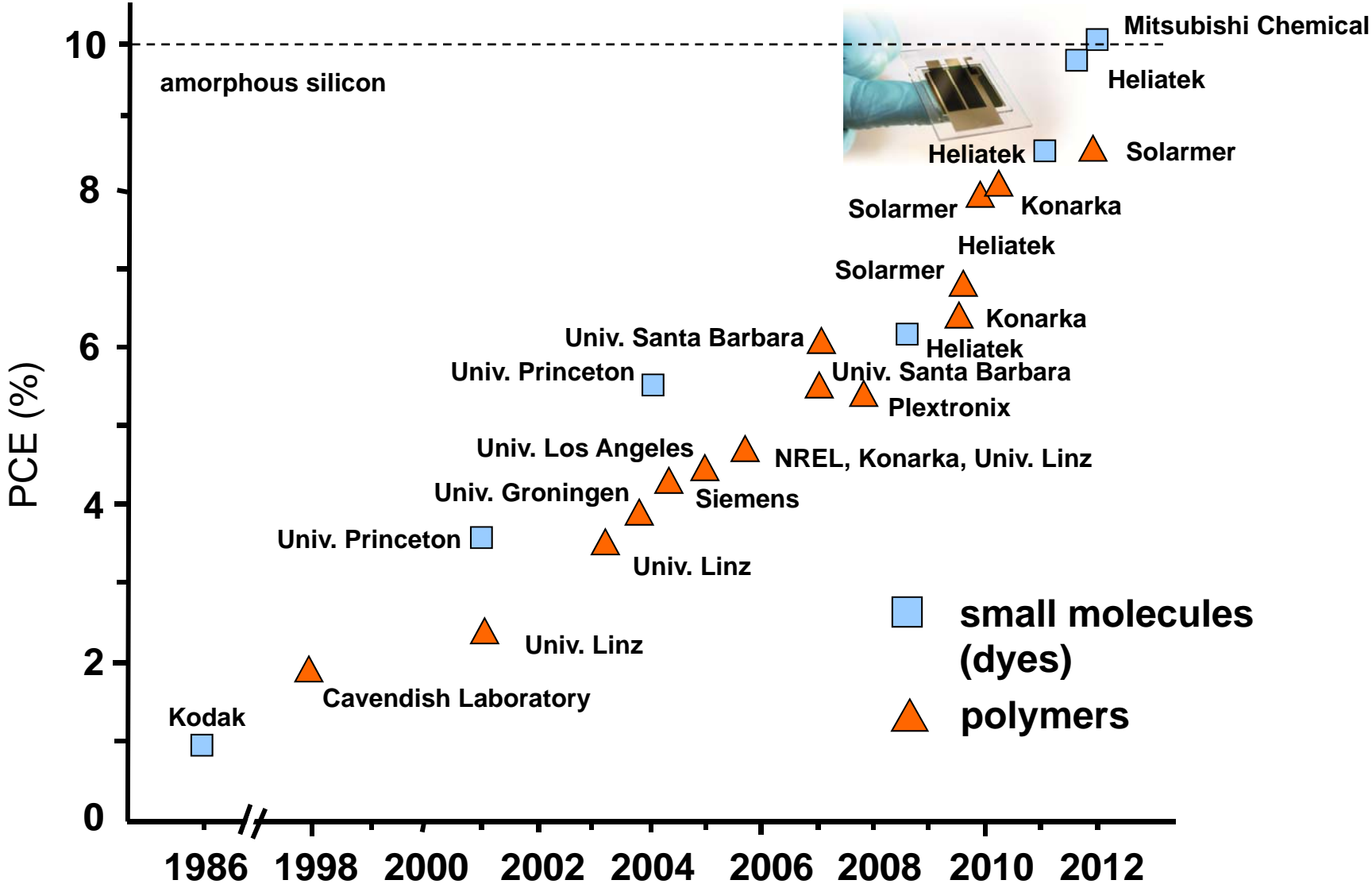


Q. Tang, organic solar cell with 1% PCE (1986)

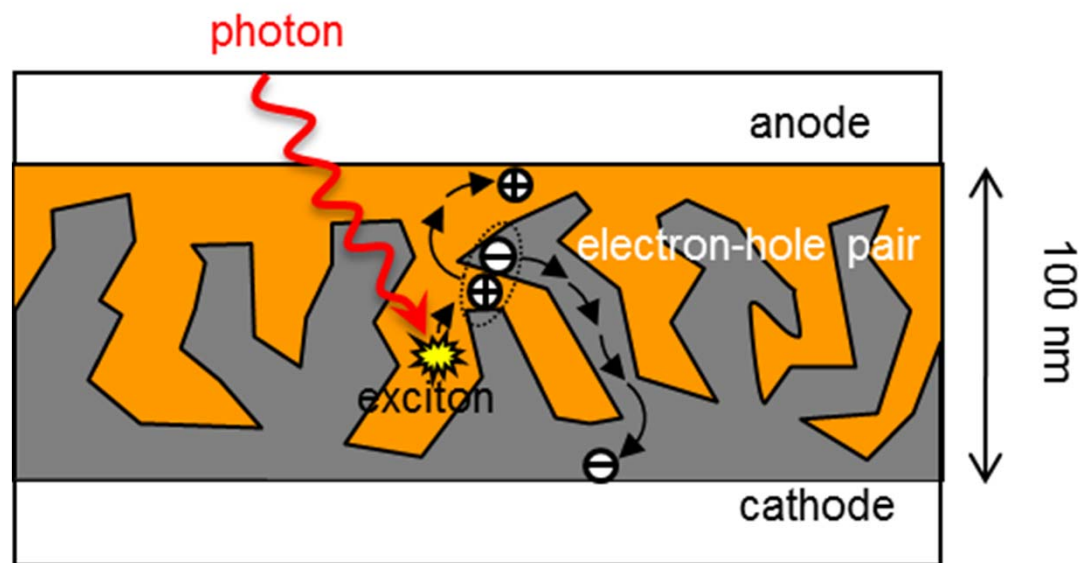


Materials Science & Technology

Development of organic solar cells



Polymer bulk-heterojunction concept



Solarmer

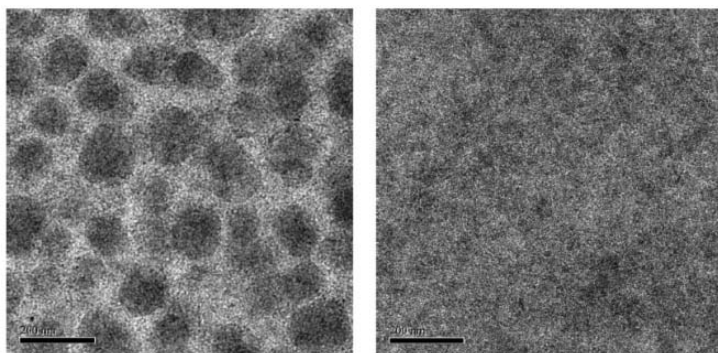
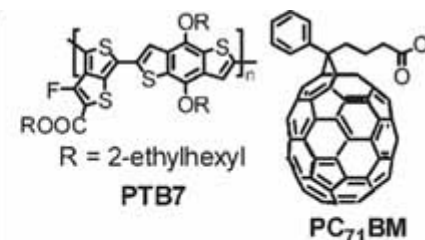
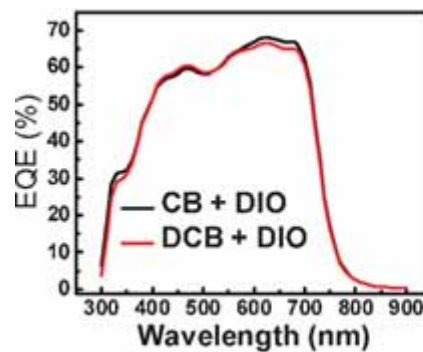


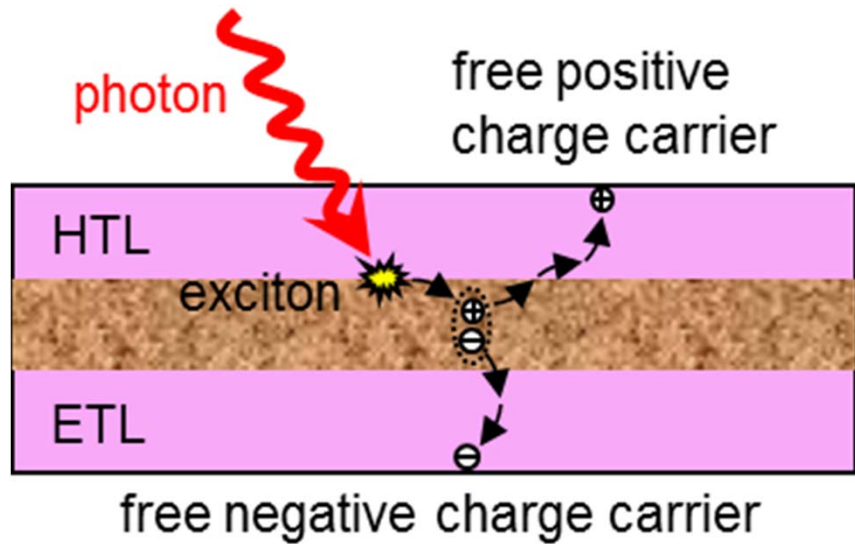
Figure 3. TEM images of PTB7/PC₇₁BM-blend film prepared from CB without (a) and with (b) DIO (the scale bar is 200 nm).



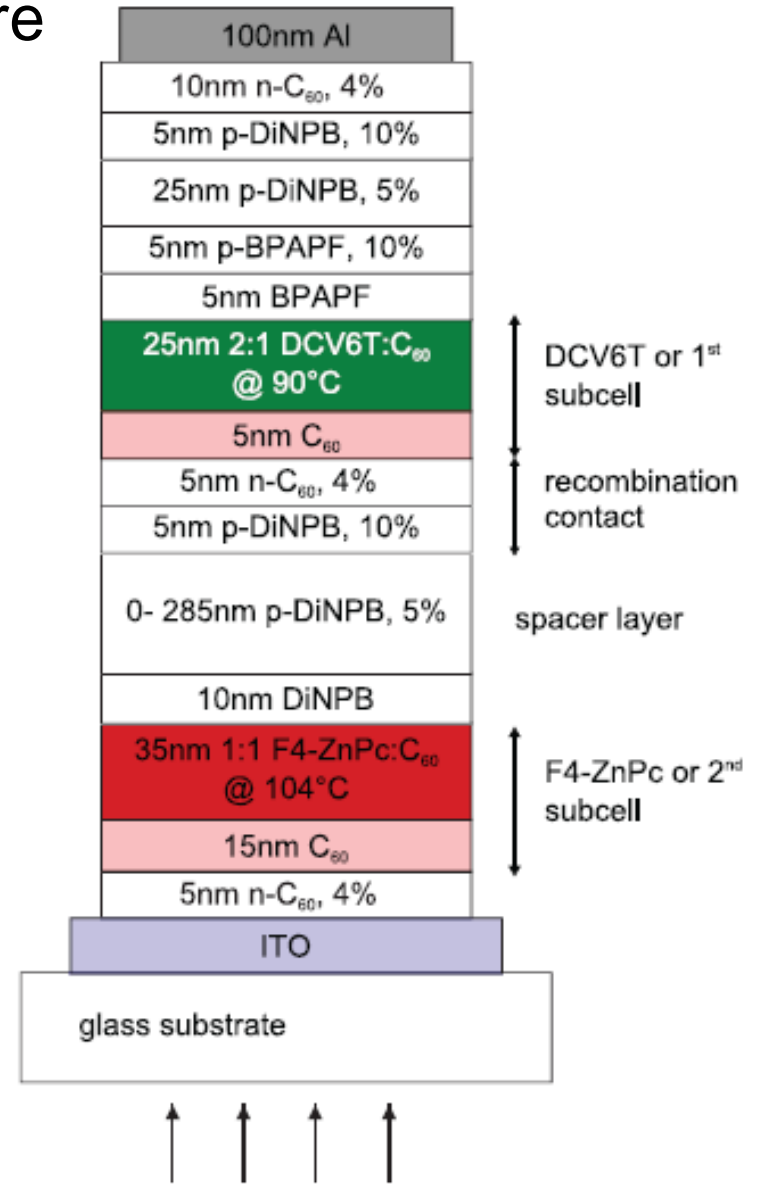
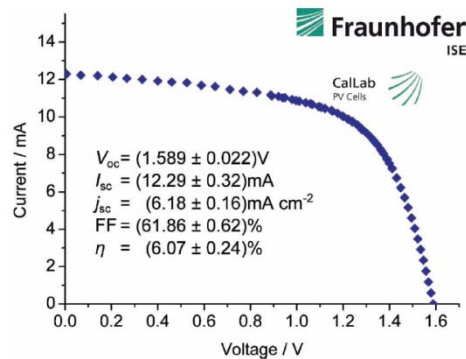
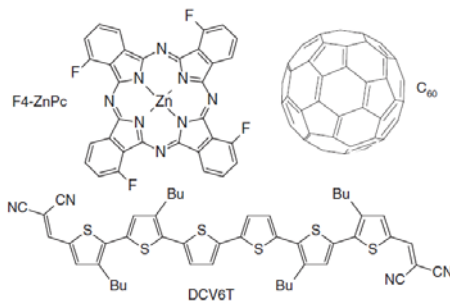
PTB7/PC₇₁BM Solar Cell:
 Voc = 0.74 V, FF = 69.0%
 Jsc = 14.5 mA/cm², PCE = 7.4%



Small molecule multilayer architecture



Heliatek

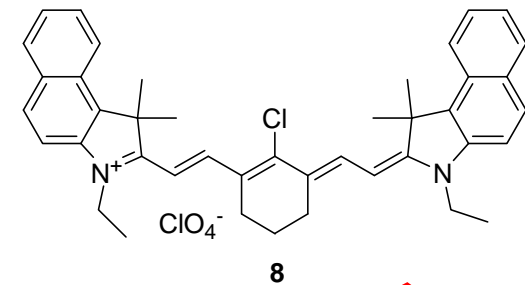
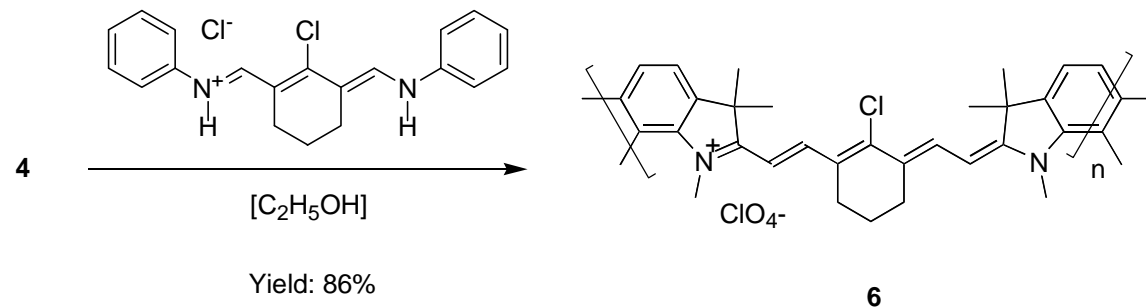
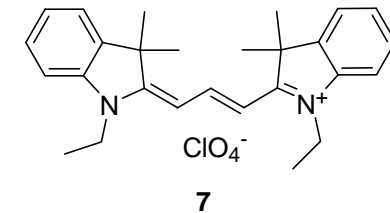
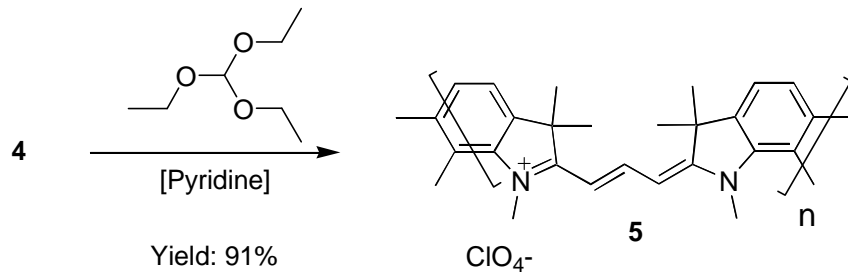
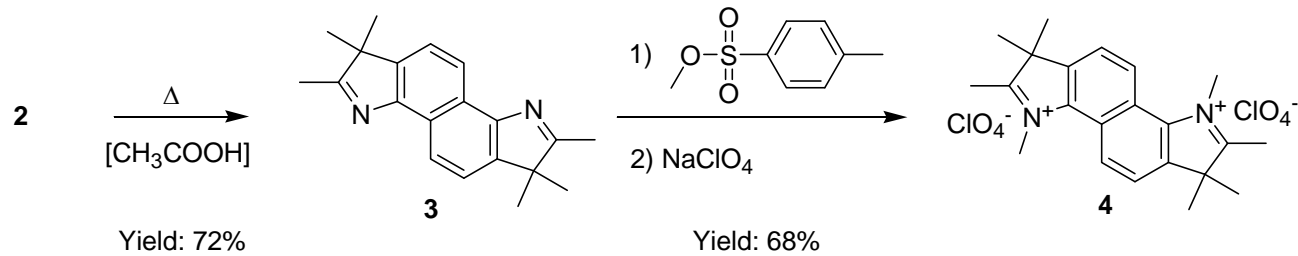
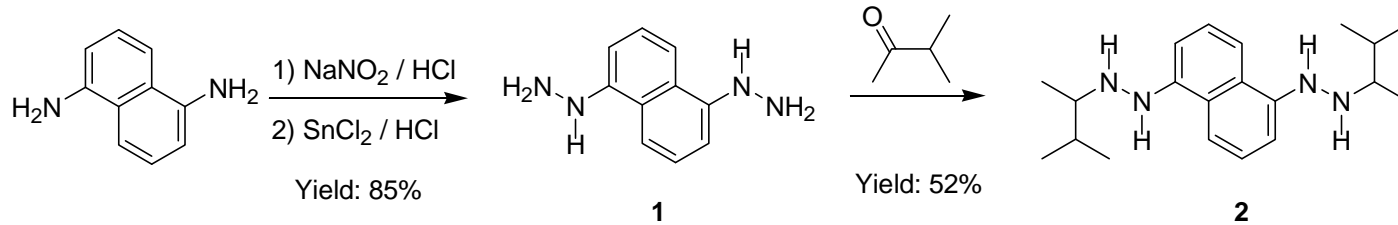


Photographic dyes as organic semiconductors for solar cells

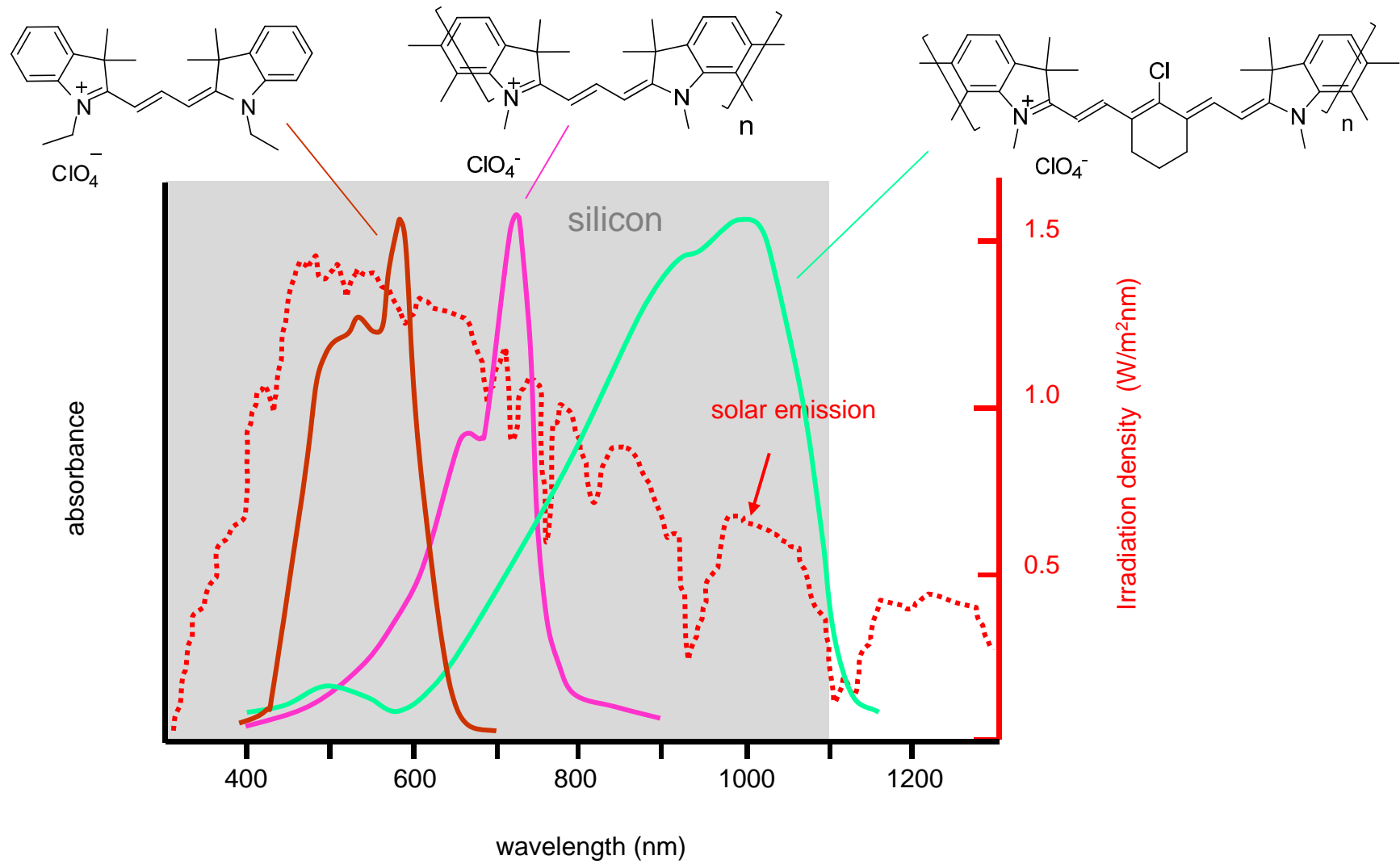
- Extremely strong absorption
- Narrow absorption bands from the UV to the NIR
- Synthesis is known (upscaling possible)
- Cost efficient (about 1% of polymer materials)
- Well soluble (compatible with roll to roll processing)



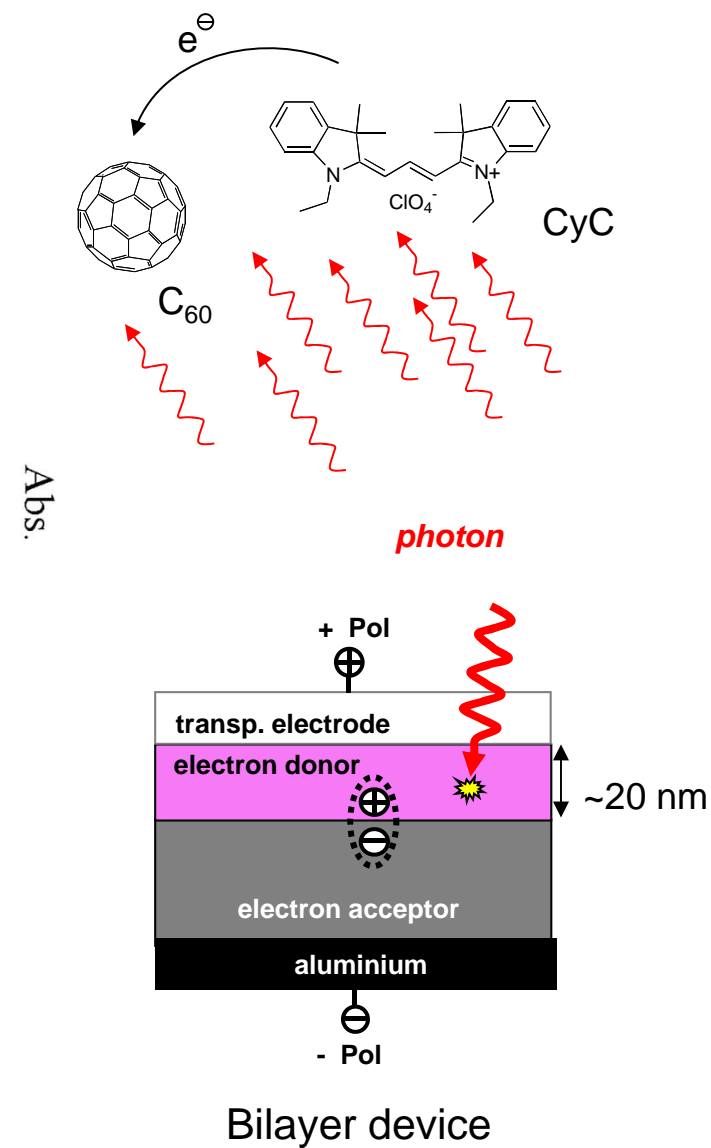
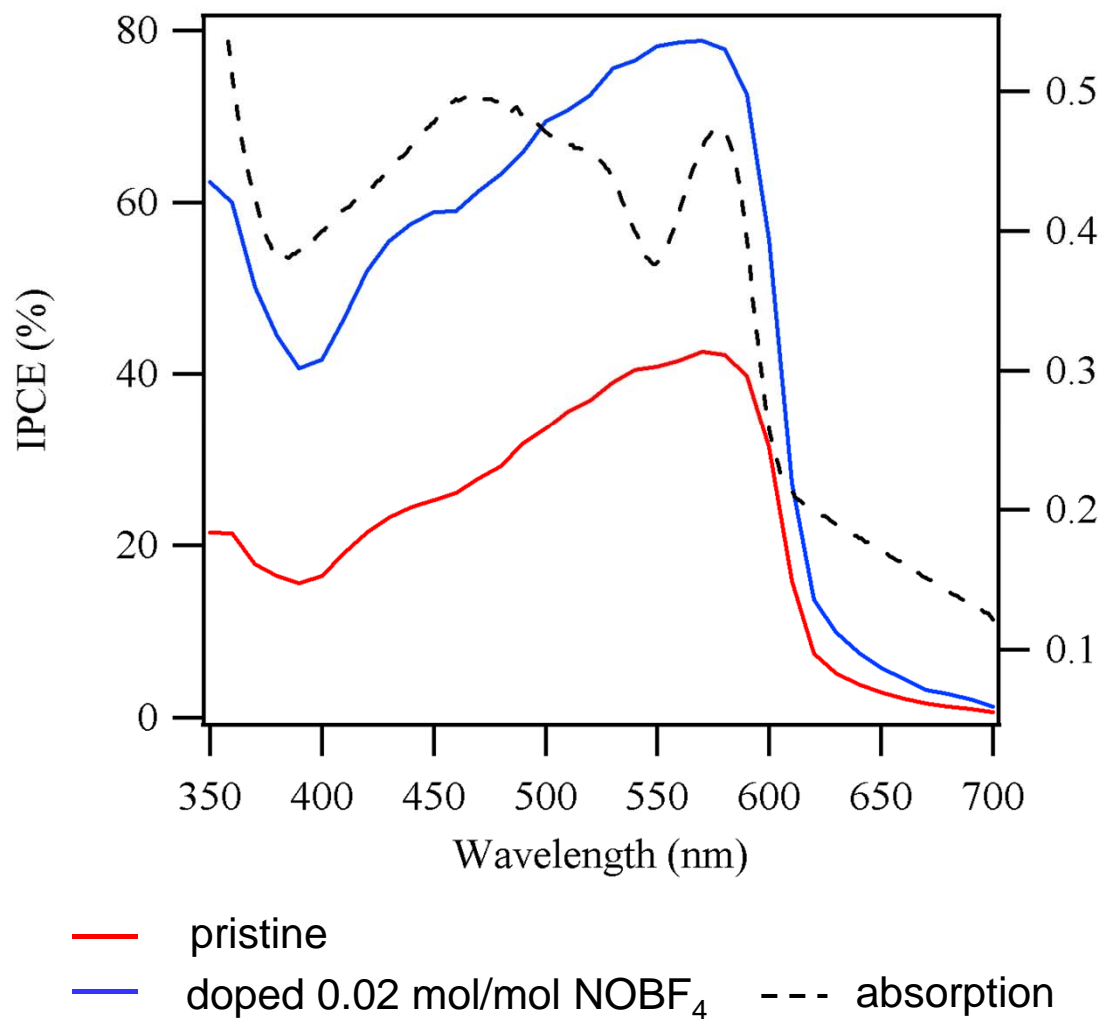
Synthesis of cyanine polymers



Polymeric cyanine dye films



Ultrathin absorber layers



Fan B., Castro F. A., Heier J., Hany R., Nüesch F., *Org. Electron.*, 11, 2010, 583-588
 Hany R. et al., *Prog. Photovoltaics* 2011, 19, 851-857

Ionic dyes for organic solar cells

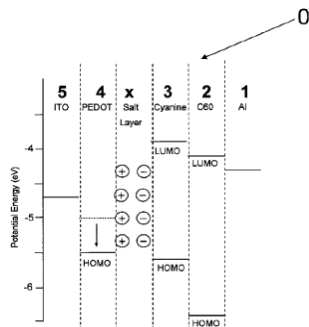
(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)
 (19) World Intellectual Property Organization
 International Bureau
 (43) International Publication Date
 31 March 2011 (31.03.2011)
 PCT
 (10) International Publication Number
 WO 2011/036145 A1

(51) International Patent Classification:
 H01L 51/42 (2006.01) H01L 51/44 (2006.01)
 (21) International Application Number:
 PCT/EP2010/063868
 (22) International Filing Date:
 21 September 2010 (21.09.2010)
 (25) Filing Language:
 English
 (26) Publication Language:
 English
 (30) Priority Data:
 01475/09 24 September 2009 (24.09.2009) CH
 (71) Applicant (for all designated States except US): EMPA
 [CH/CH]; Überlandstrasse 129, CH-8600 Dübendorf
 (CH).
 (72) Inventors: and
 (75) Inventors/Applicants (for US only): FAN, Bin [CN/CH];
 Poststrasse 113, CH-8957 Spreitenbuch (CH). NÜESCH,
 Frank [CH/CH]; Im Fasnachtbuck 1, CH-8602 Wangen
 (CH). HANY, Roland [CH/CH]; Neunbrunnenstrasse
 108b, CH-8050 Zürich (CH).
 (74) Agent: FELDMANN, Clarence P.; Schneider Feldmann
 AG, Beethovenstrasse 49, P.O. Box 2792, CH-8022
 Zürich (CH).

(54) Title: MULTILAYER ORGANIC THIN FILM SOLAR CELL

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
 (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
 Published:
 with international search report (Art. 21(3))

FIG. 3b



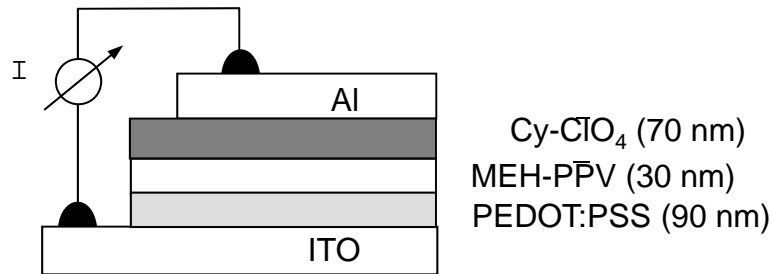
(57) Abstract: The disclosed invention consists of high efficiency organic solar cells (0) with a multi layer structure, consisting of cathode layer (1), organic acceptor layer (2), organic donor layer (3), conductive anode layer (4) and a substrate layer (5), where an adjustment of electronic levels of separated layers is achieved by introduction of at least one intermediate matching layer (x). In conjunction with the selection of active layer (3) consisting of cyanine dyes with appropriate counterions (e.g. hexafluorophosphate), high performance organic solar cells with long lifetimes can be fabricated with a fast and simple manufacturing method.



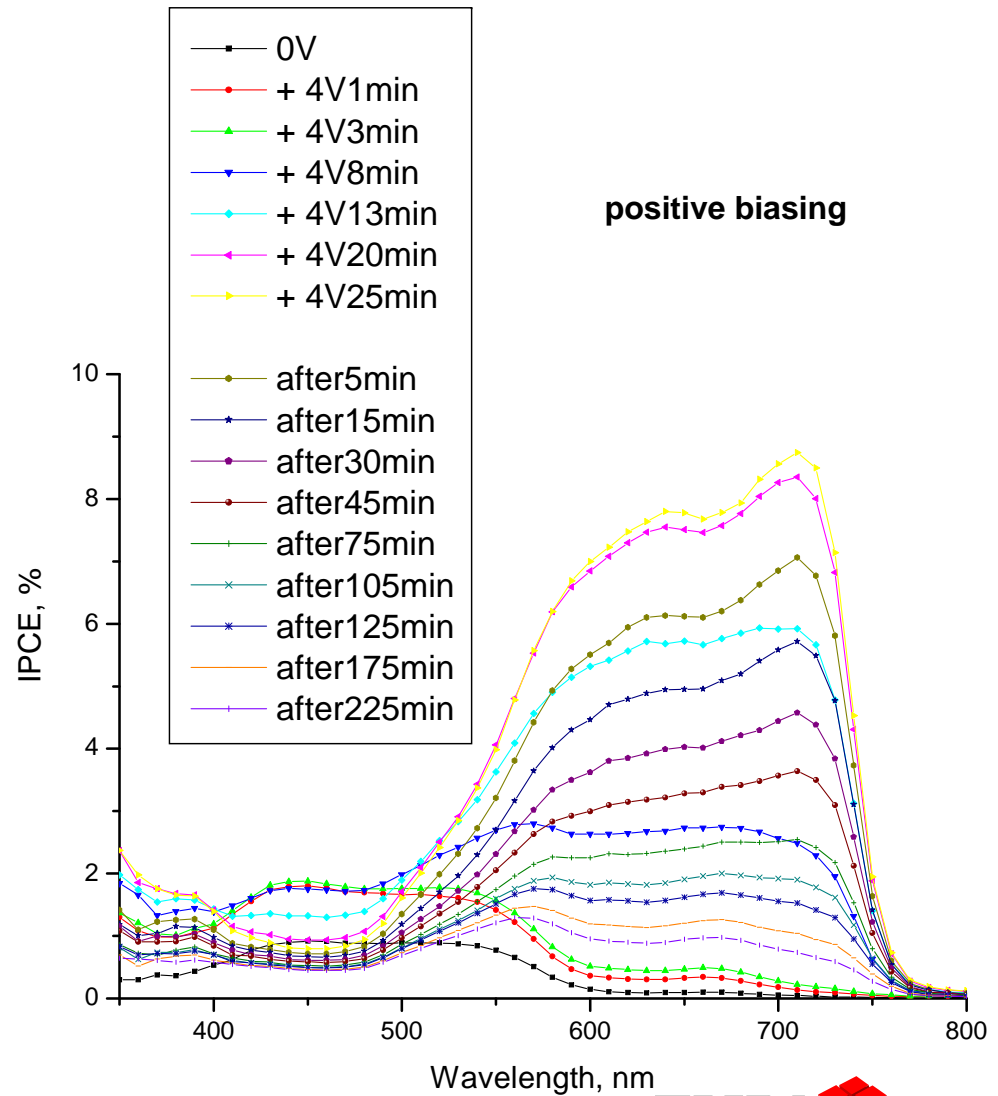
Empa licensed

WO 2011/036145 A1

Effect of counterions in bilayer cyanine devices



The device is biased for a certain time, then IPCE is taken (at V=0)

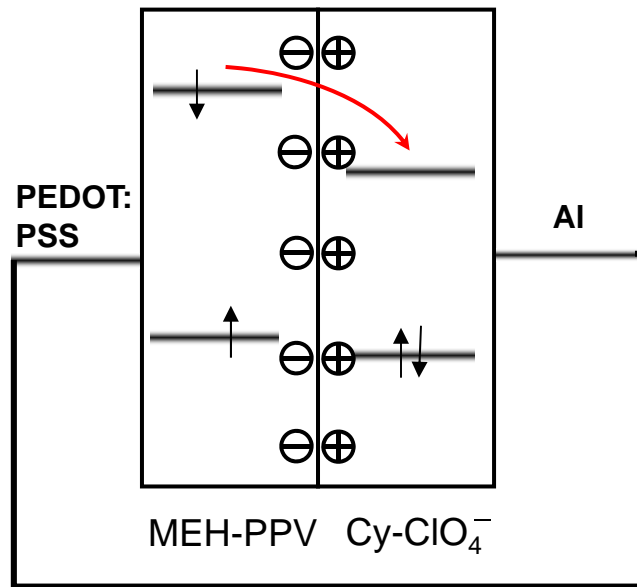


H. Benmansour, F. A. Castro, M. Nagel, J. Heier, R. Hany, F. Nüesch, *Chimia*, 2007, 61 (12) 787.



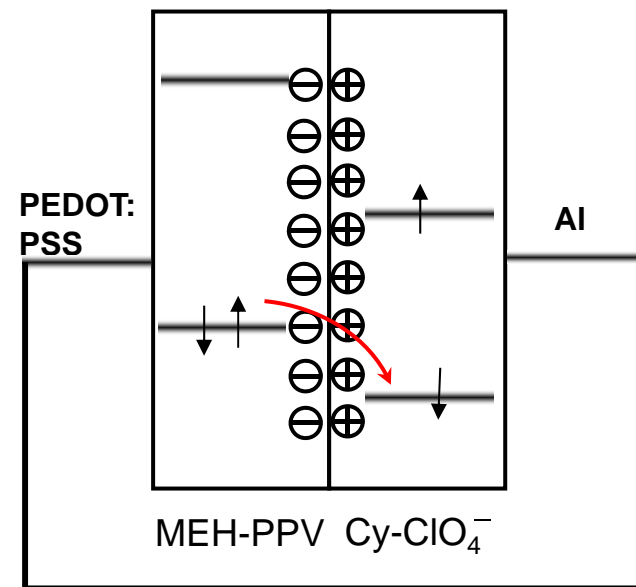
Formation of ionic junctions

no biasing



only reductive charge transfer observed

positive biasing



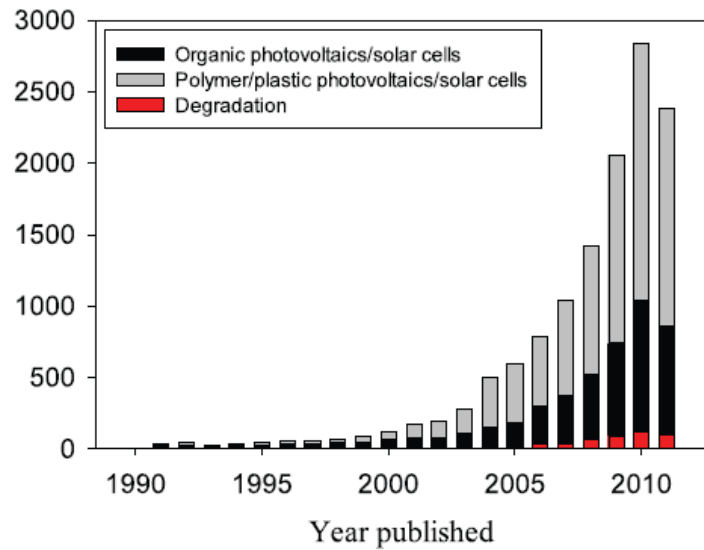
mainly oxidative charge transfer

H. Benmansour, F. A. Castro, M. Nagel, J. Heier, R. Hany, F. Nüesch, *Chimia*, 2007, 61 (12) 787.

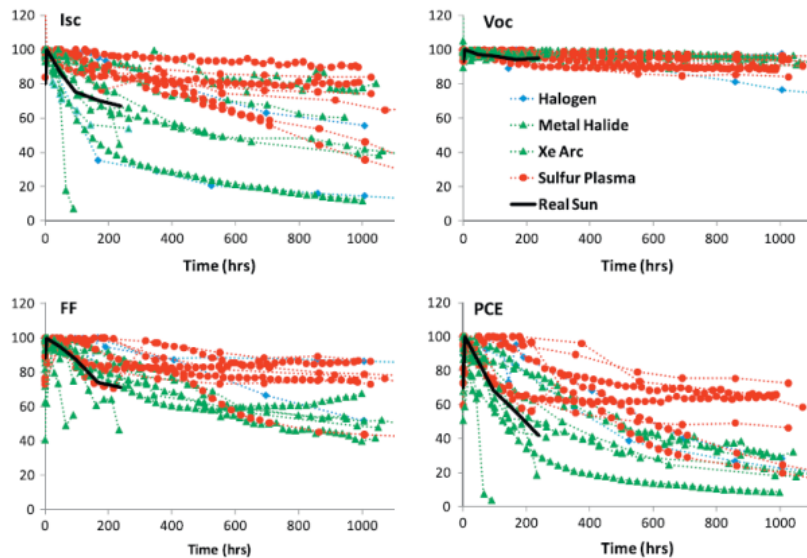


Materials Science & Technology

Lifetime of organic solar cells



M. Jorgensen et al., *Adv. Mater.* **2012**, *24*, 580–612



Suren A. Gevorgyan et al., *Solar Energy Materials & SolarCells*, **95** (2011)1398–1416.



Materials Science & Technology

R2R processing

Low costs by high throughput (small depreciation)

- > R2R fabrication of substrates
- > R2R of the photoactive layers
- > R2R production of encapsulation layers

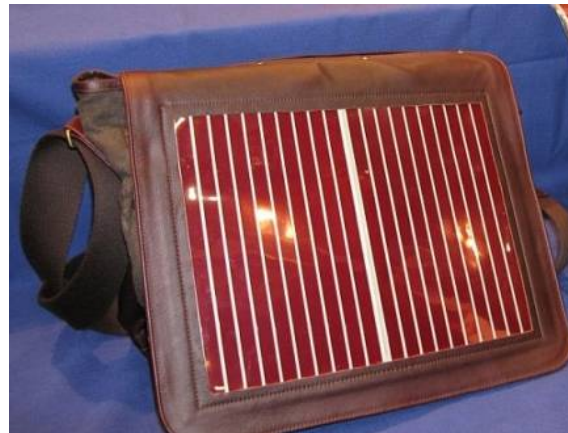


Flexible substrates are needed

- > cheap barrier layers
- > cost efficient, flexible and transparent electrode
- > integrated bus bars



first products: charging bag solar cell from Konarka



Development of fabric electrodes (CTI project)

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro

(43) Internationales Veröffentlichungsdatum
14. Mai 2010 (14.05.2010)

(10) Internationale Veröffentlichungsnummer
WO 2010/051976 A1



(51) Internationale Patenklassifikation:
H01L 31/0392 (2006.01) H01L 51/50 (2006.01)
H01L 51/42 (2006.01)

(21) Internationales Aktenzeichen: PCT/JP2009/007894

(22) Internationales Anmeldedatum:
4. November 2009 (04.11.2009)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(50) Angaben zur Priorität:
10 2008 055 969,5
5. November 2008 (05.11.2008) DE

(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von US): SEIFAR AG [CH]; Freiburg, CH-9425 Thal (CH)

(72) Erfinder: und
(75) Erfinder/Anmelder (nur für US): CHABRECEK, Peter [SK-CH]; Baumgartenweg 11, CH-9306 Freidorf (CH); MEIER, Hanspeter [CH-CH]; Lehn 2545, CH-9112 Schachen (CH); NÜESCH, Frank [CH-CH]; Im Fasnachbühl 1, CH-8602 Wangen (CH); ROSENFELDER, Matthias [CH-CH]; Sonnenbergstrasse 17, CH-9036 Gindis SG (CH); ARAUJO DE CASTRO, Fernando [BR-CH]; Zehnweg 47, CH-8610 Uster (CH)

(74) Anwälte: BEHRMANN, Niels et al.; Hübisch Behrmann Wagner, Muggistrasse 5, Hergau-Tower (10. OG), 78224 Singen (DE)

(81) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare nationale Schutzrechtsart): AF, AG, AI, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KM, KN, KP, KR, KZ, LA, LC, LI, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

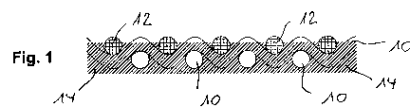
(84) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare regionale Schutzrechtsart): AEPH (BW, GR, GM, KZ, LS, MW, MZ, NA, SD, SI, SZ, TZ, UG, ZM, ZW); europäisches (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM); europäisches (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR); OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Erklärungen gemäß Regel 4.17:
— Erfinderverklärung (Regel 4.17 Ziffer iv)
Veröffentlicht:
— mit internationalem Recherchenbericht (Artikel 21 Absatz 3)
— vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eingehen (Regel 48 Absatz 2 Buchstabe h)



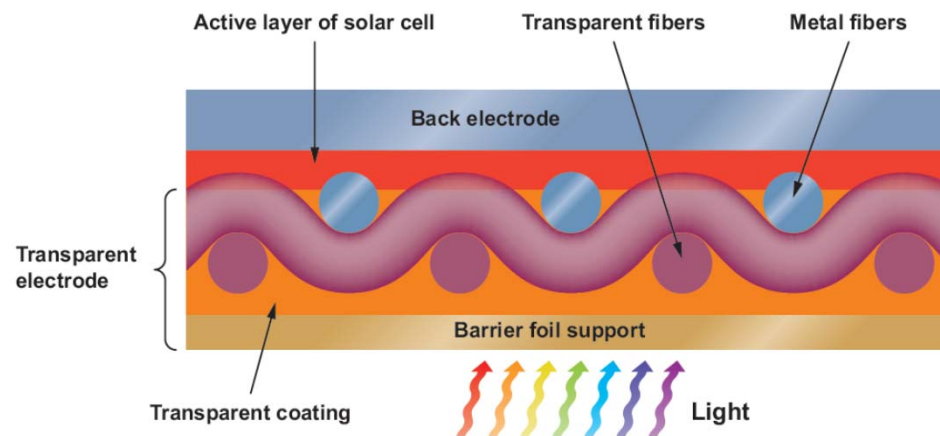
WO 2010/051976 A1

(54) Title: SUBSTRATE FOR AN OPTOELECTRONIC DEVICE
(54) Bezeichnung: SUBSTRAT FÜR FINE OPTOELEKTRONISCH: VORRICHTUNG



(57) Abstract: The invention relates to a substrate for an optoelectronic device, having a fabric made from monofilaments and/or polymer fibers that is designed to implement and/or carry an electrode layer, wherein the fibers have a fiber diameter of between 20µm and 100µm, particularly between 30µm and 80µm, the fabric has mesh openings that realize an open area of 75% to 85% and wherein the fabric is supplied with a transparent, electrically non-conductive polymer material coating so that the fibers are at least partially surrounded by the polymer material.

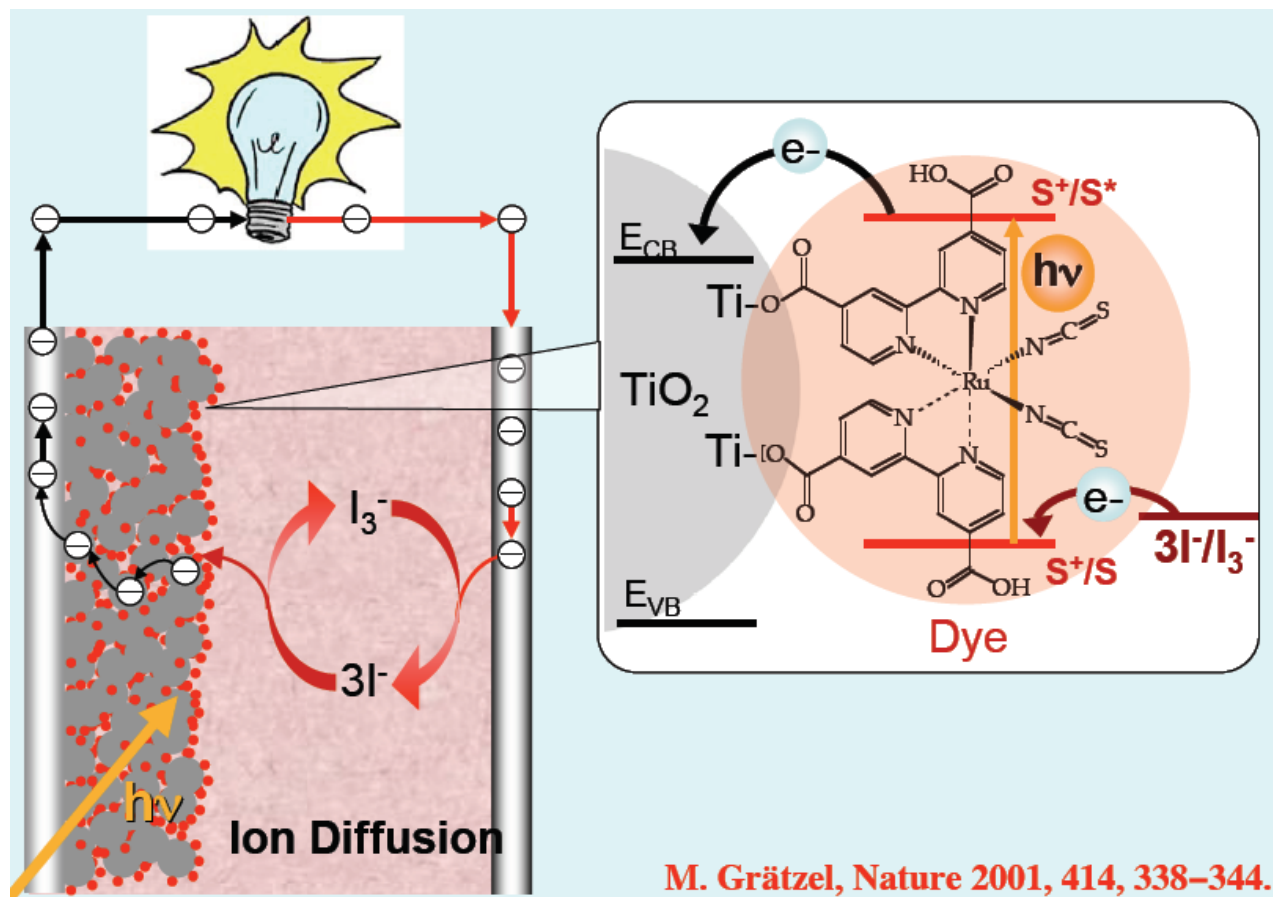
(57) Zusammenfassung: Die Erfindung betrifft ein Substrat für eine optoelektronische Vorrichtung, mit einem Gewebe aus Monofilamenten und/oder ein Polymer aufweisenden Fasern, welches zum Realisieren und/oder Tragen einer Elektroden-schicht ausgebildet ist, wobei die Fasern einen Faserdurchmesser zwischen 20µm und 100µm, insbesondere zwischen 30µm und 80µm aufweisen, das Gewebe Maschenöffnungen aufweist, die eine offene Fläche von 70 % bis 85% realisieren und das Gewebe mit einer transparenten, elektrisch nicht-leitenden Polymermaterial aufweisenden Beschichtung so versehen ist, dass die Fasern zumindest teilweise von dem Polymermaterial umgeben sind.



W. Kylberg, F. A. de Castro, P. Chabrecek, U. Sonderegger, B. Tsu-Te Chu, F. Nüesch, R. Hany,
Advanced Materials 2011, 23, 1015-1019



New developments in dye sensitized solar cells



24.02.12 - The Interdisciplinary Committee of the World Cultural Council has selected Prof. Michael Grätzel as the winner of the ALBERT EINSTEIN World Award of Science 2012

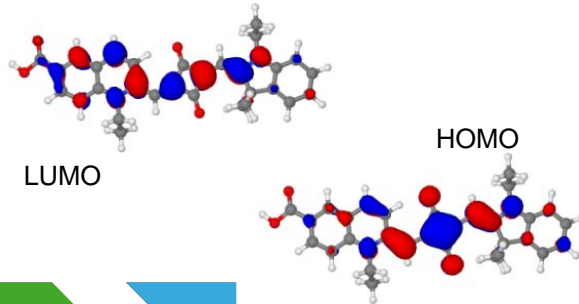
«Transparent" dye sensitized solar cells



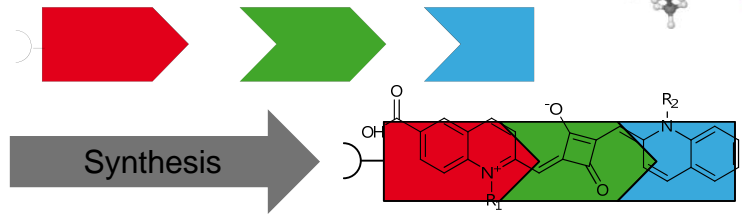
Materials Science & Technology

- photovoltaic windows
- flexible, transparent PV active films
- tandem solar cells

modeling



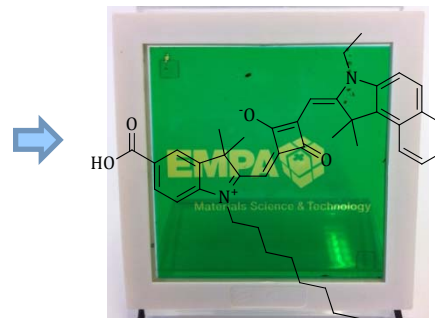
synthesis



solar cell fabrication



visible

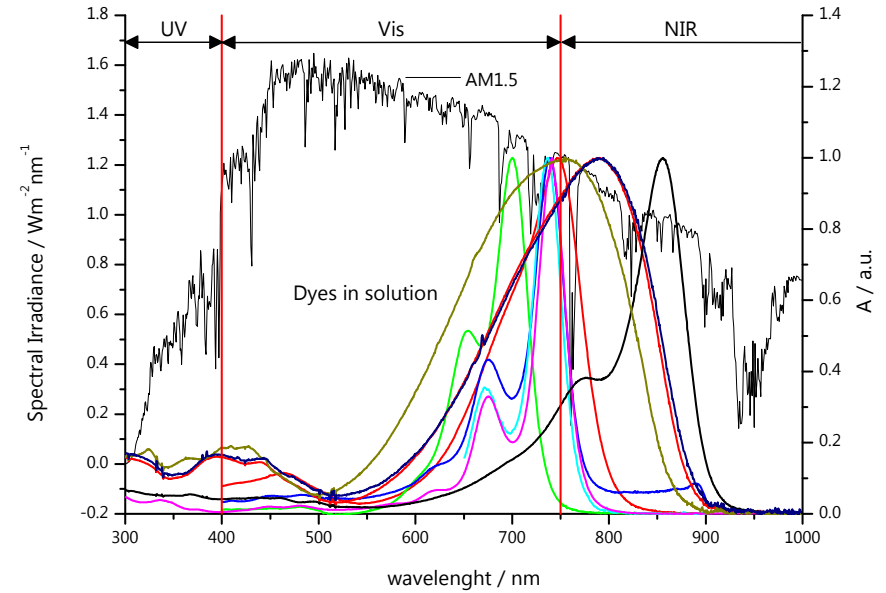


red



NIR

absorption of squaraine dyes



demonstrators

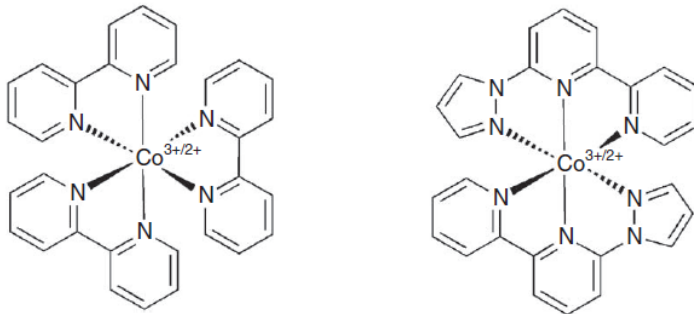
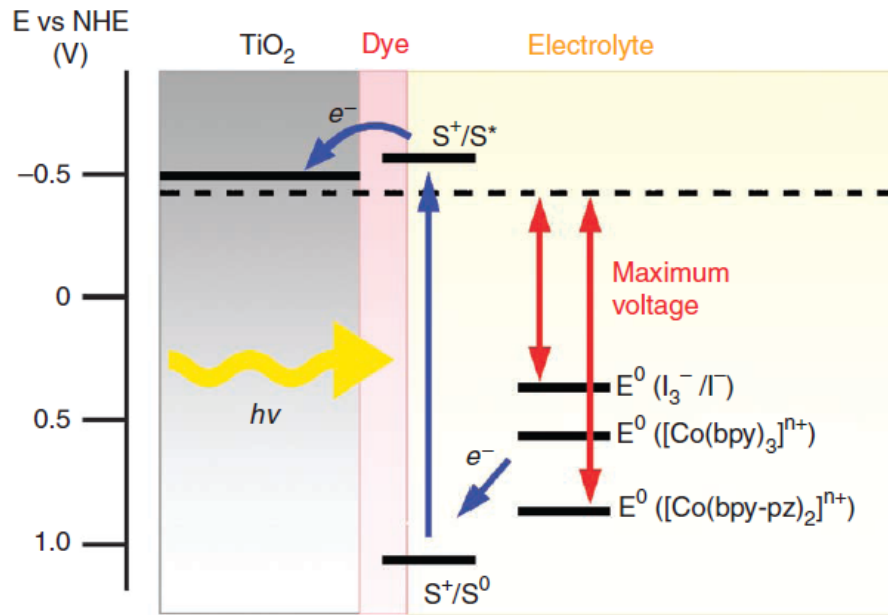


Verkehrshaus der Schweiz (2012)



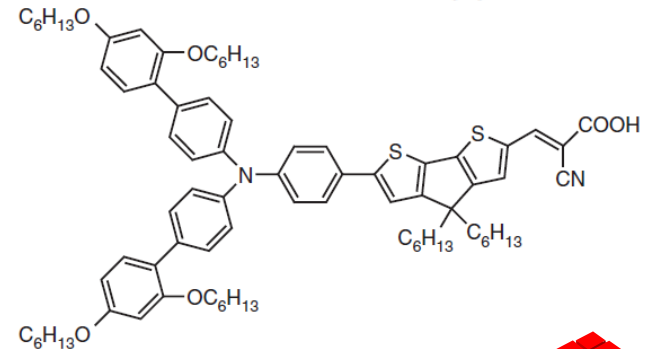
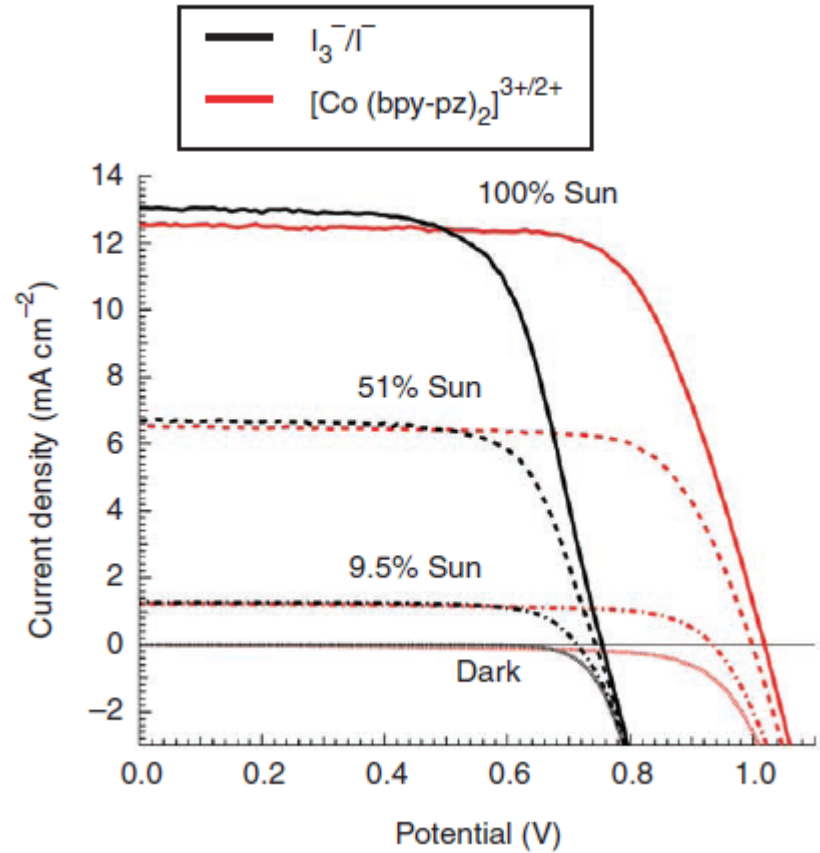
<http://youtu.be/UkLJKqw7zrs>

Novel redox mediators



12.3% using porphyrin dye

Aswani Yella et al., SCIENCE VOL 334 (4), p. 629, 2011



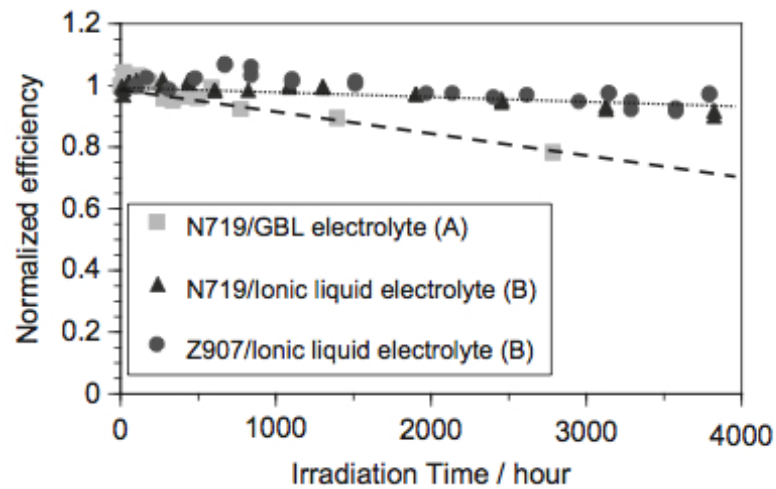
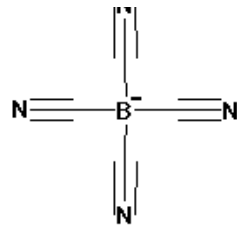
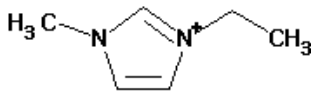
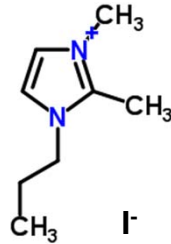
Jun-Ho Yum et al., nature communications | 3:631 | 2011



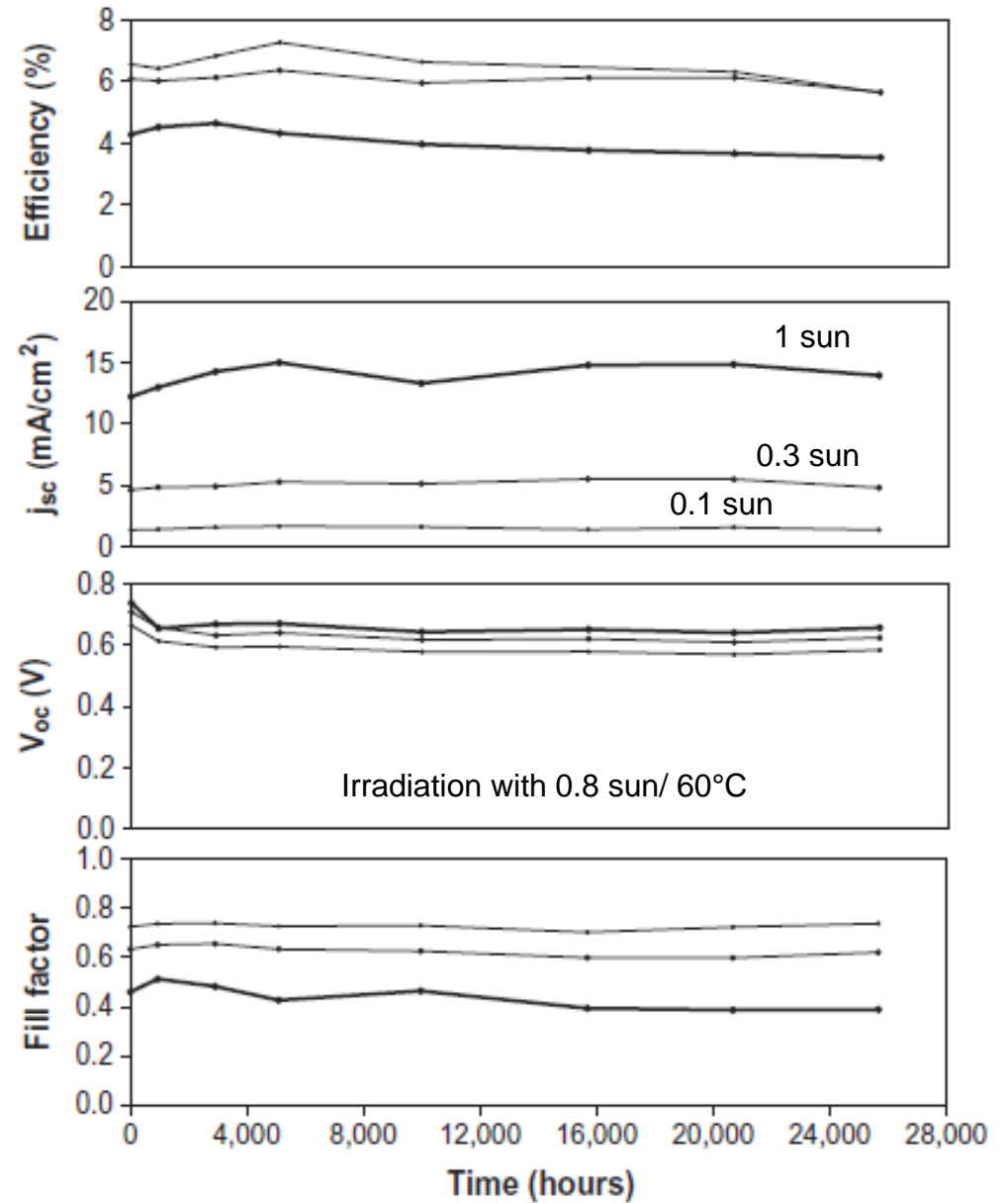
Materials Science & Technology

New electrolyte systems

- liquid
- small vapor pressure
- good ion diffusion



Stability tests at 60°C conducted by Toyota Research(Asin)



R. Harikisun, H. Desilvestro /
Solar Energy 85 (2011) 1179–1188



Materials Science & Technology

APPLICATIONS



- prêt pour les applications en intérieur
- prêt pour les applications en lumière faible
- prêt pour les applications en façade
- prêt pour les applications sur mobilier extérieur



Acknowledgement

Empa (Dübendorf)

Roland Hany

Jakob Heier

Hui Zhang

Gaëtan Wicht

Daniel Rentsch

Matthias Nagel

Hadjar Benmansour (left)

Fernando Castro (left)

William Kylberg (left)

Fan Bin (left)

Thomas Geiger

Iulia Shcherbakova

Fahimeh Nafezarefi

Simon Kuster (left)

Simone Hochleitner (left)

Solaronix

Tobi Meyer

Andreas Meyer

EPFL

Jacques. E. Moser

Jelissa de Jonghe

Michael Grätzel

Yum Ho



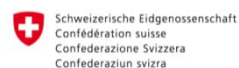
Materials Science & Technology



swiss*electric*
research

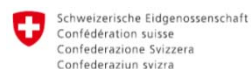


ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE



Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Bundesamt für Energie BFE



Eidgenössisches Volkswirtschaftsdepartement EVD
Bundesamt für Berufsbildung und Technologie BBT
Förderagentur für Innovation KTI

