Chaire Innovation technologique
Liliane Bettencourt 2021-2022

Énergie solaire photovoltaïque et transition énergétique

Mercredi 2 Mars 2022

Technologies émergentes et nouveaux concepts

Daniel LINCOT

Les pérovskites hybrides halogénées: des nouveaux semi-conducteurs adaptés aux défis de photovoltaïque

Emmanuelle DELEPORTE

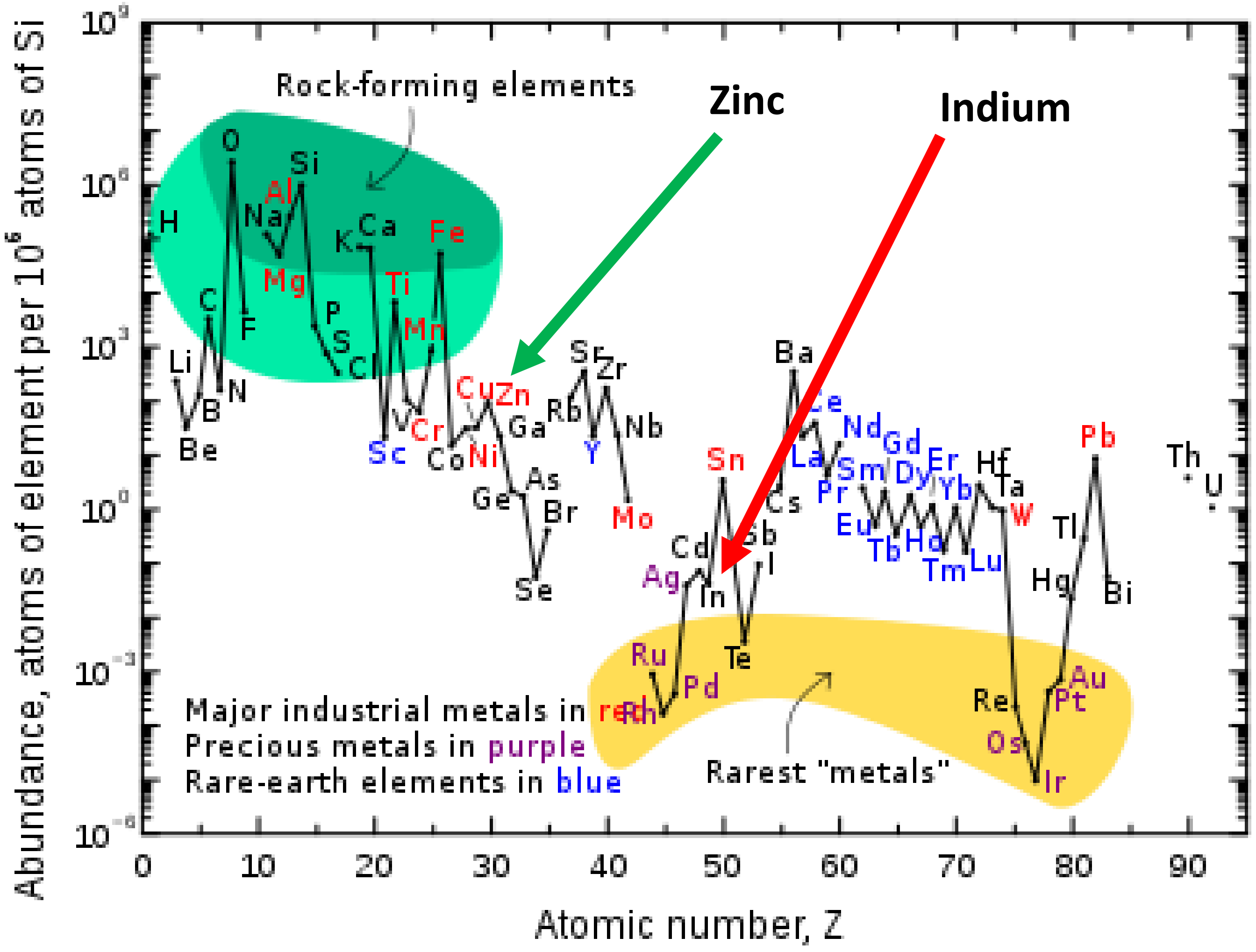
daniel.lincot@cnrs.fr

Retours sur le cours précédent N°5 : technologies couches minces inorganiques

Analyse de cycle de vie technologie CIGS : cas de l'Indium

Daniel Lincot, Collège de France, 2/03/2022

L'indium est rare et critique mais il provient d'une ressource plus abondante : le zinc



1 indium atom for 10^7 Si atoms
64th rank

0.056 ppm in earth crust

but 20-200 ppm in Zinc ores

12.5 Mtons of Zinc in 2018

750 tons of primary In in 2018*
950 tons secondary
1700 tons total in 2018

Only small fraction recovered (1/10 -1/20)

* Indium Corporation

M. Lokanc et al (2015) NREL report "Availablity of Indium : the present, the mid term and the long term"

Sous forme de couches minces (économie d'atomes)
son utilisation à grande échelle est possible dans le photovoltaïque

CIGS Thin Film Photovoltaics for EU's prosperity, energy transition and enabling net zero emission targets

Indium production in Europe is sufficient for more than 100 GW per year PV production with potential to meet TW challenges in a cost effective manner

Coordinated developments are essential for industrialisation and applications of CIGS PV

EU can reach a leading position in future markets

Source: https://cigs-pv.net
Contact: E-Mail: info@cigs-pv.net

pv magazine

Indium supply not an issue for CIGS industry

Scientists Ayodhya Tiwari and Daniel Lincot recently spoke to **pv magazine** about the future of copper indium gallium selenide solar tech, which could play a key role in providing flexible, lightweight products in the building-integrated PV segment.

AUGUST 11, 2021 EMILIANO BELLINI

MODULES & UPSTREAM MANUFACTURING | TECHNOLOGY AND R&D | EUROPE

https://cigs-pv.net/wortpresse/wp-content/uploads/2021/07/Indium_Availability_for_CIGS_thin-film_solar_cells_in_Europe.pdf

https://www.pv-magazine.com/2021/08/11/indium-supply-not-an-issue-for-cigs-industry/

Chaire Innovation technologique
Liliane Bettencourt 2021-2022

Énergie solaire photovoltaïque et transition énergétique

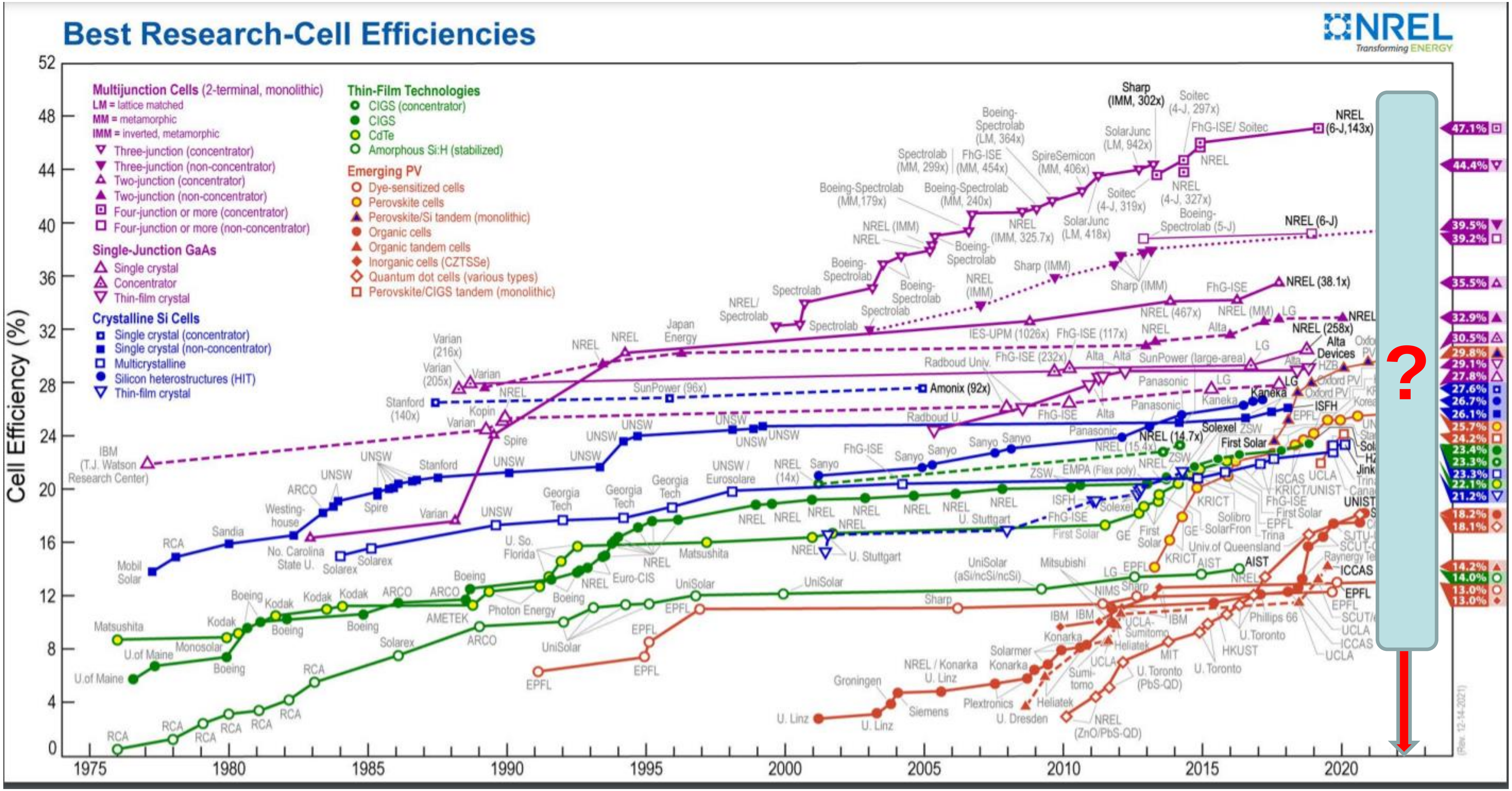
Mercredi 2 Mars 2022

Technologies émergentes et nouveaux concepts

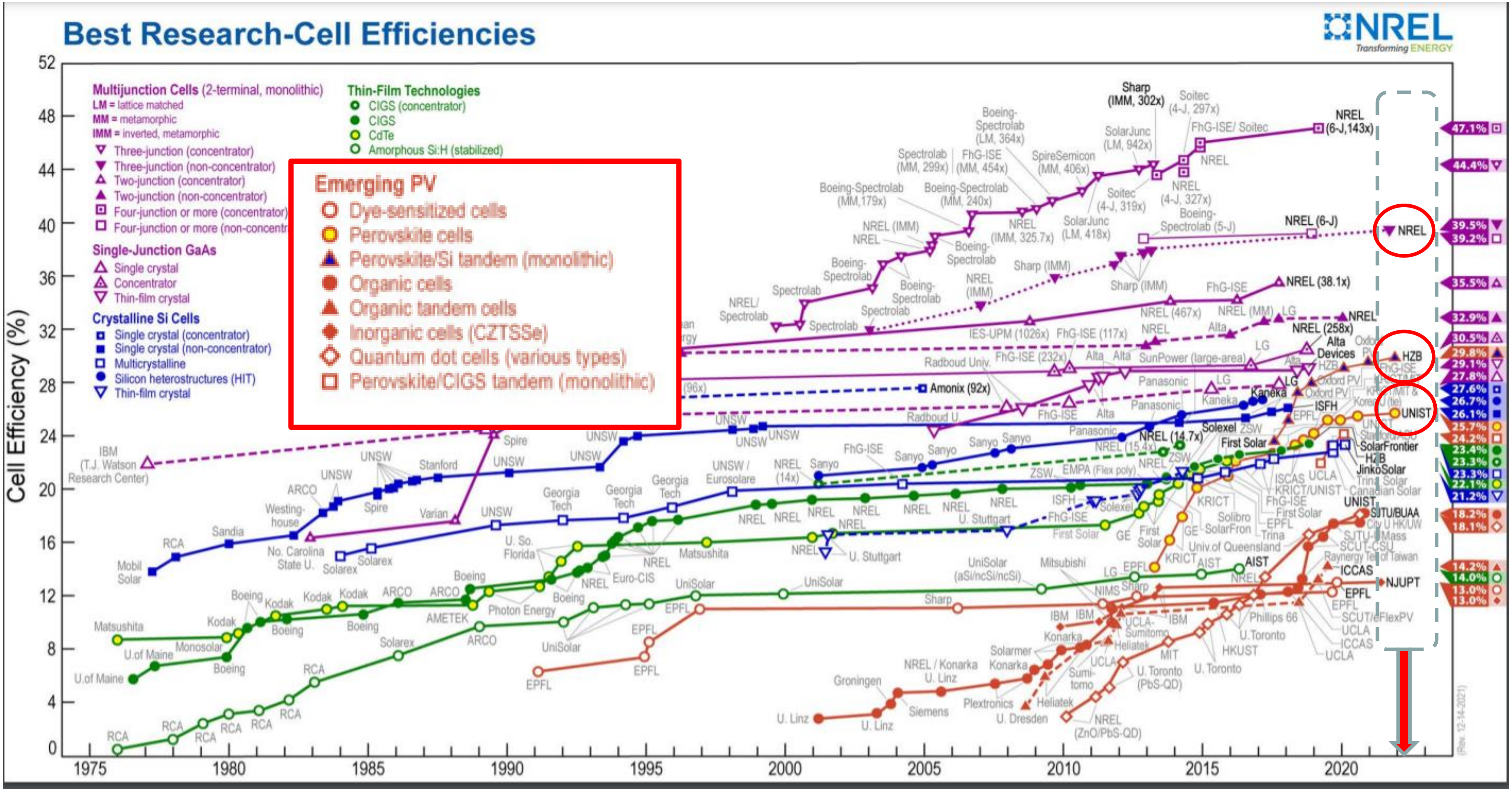
Daniel LINCOT

Remerciements : Jacky Even, Guillaume Wantz, Jean Rousset

daniel.lincot@cnrs.fr

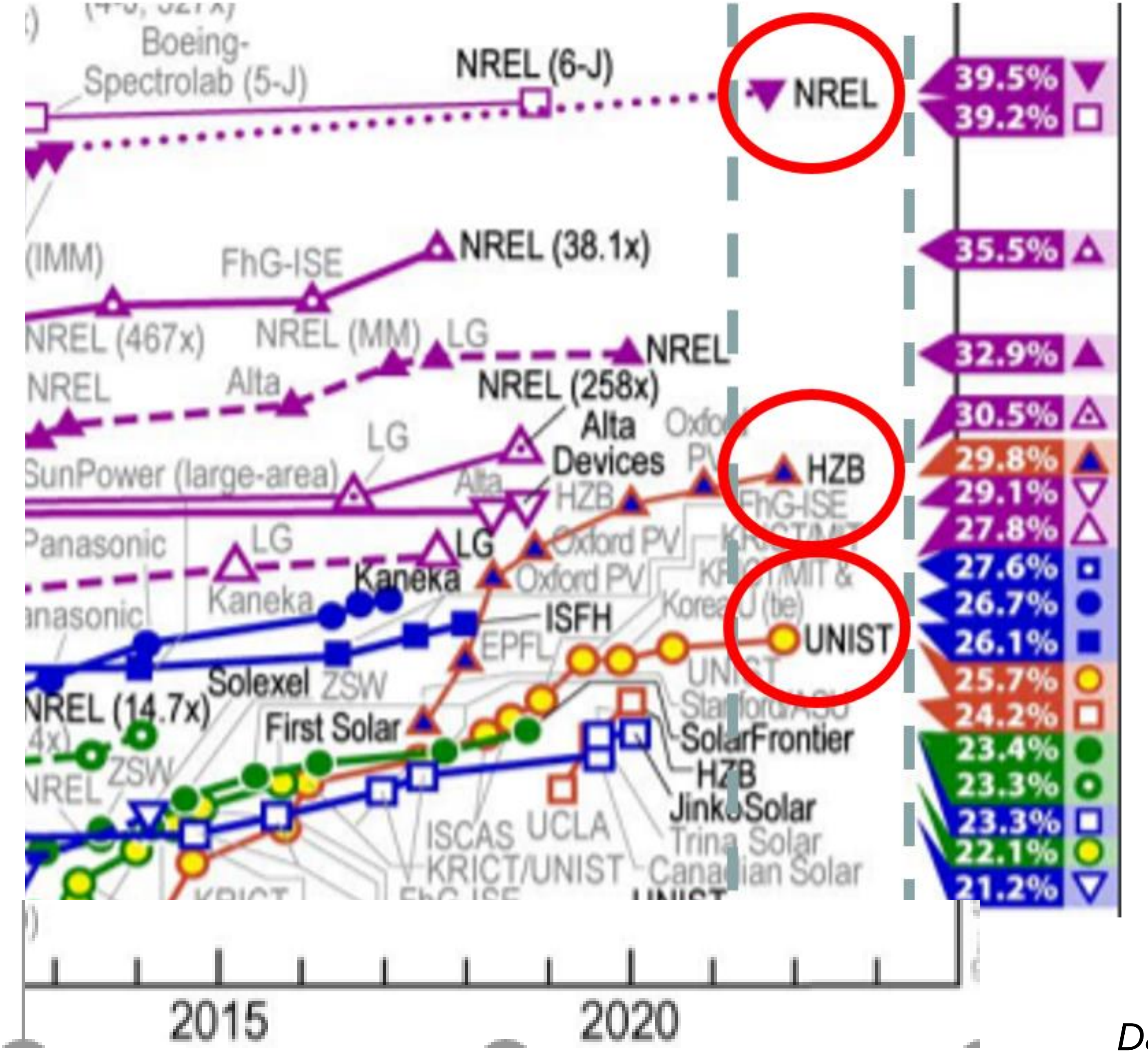


file:///C:/Users/daniel.lincot/Documents/biblio%20record%20efficiency%20tables%20PIP/2022-03-best-research-cell-efficiencies-rev211214.pdf



file:///C:/Users/daniel.lincot/Documents/biblio%20record%20efficiency%20tables%20PIP/2022-03-best-research-cell-efficiencies-rev211214.pdf

Daniel Lincot, Collège de France, 2/03/2022



39,5 % Triple junctions : NREL
→éclairement standard
→Configuration monolytique
→matériaux III V

Elles doublent les 6J

29,8 % tandems Si-perovskite : HZB
→ Éclairement standard
→ Configuration monolytique

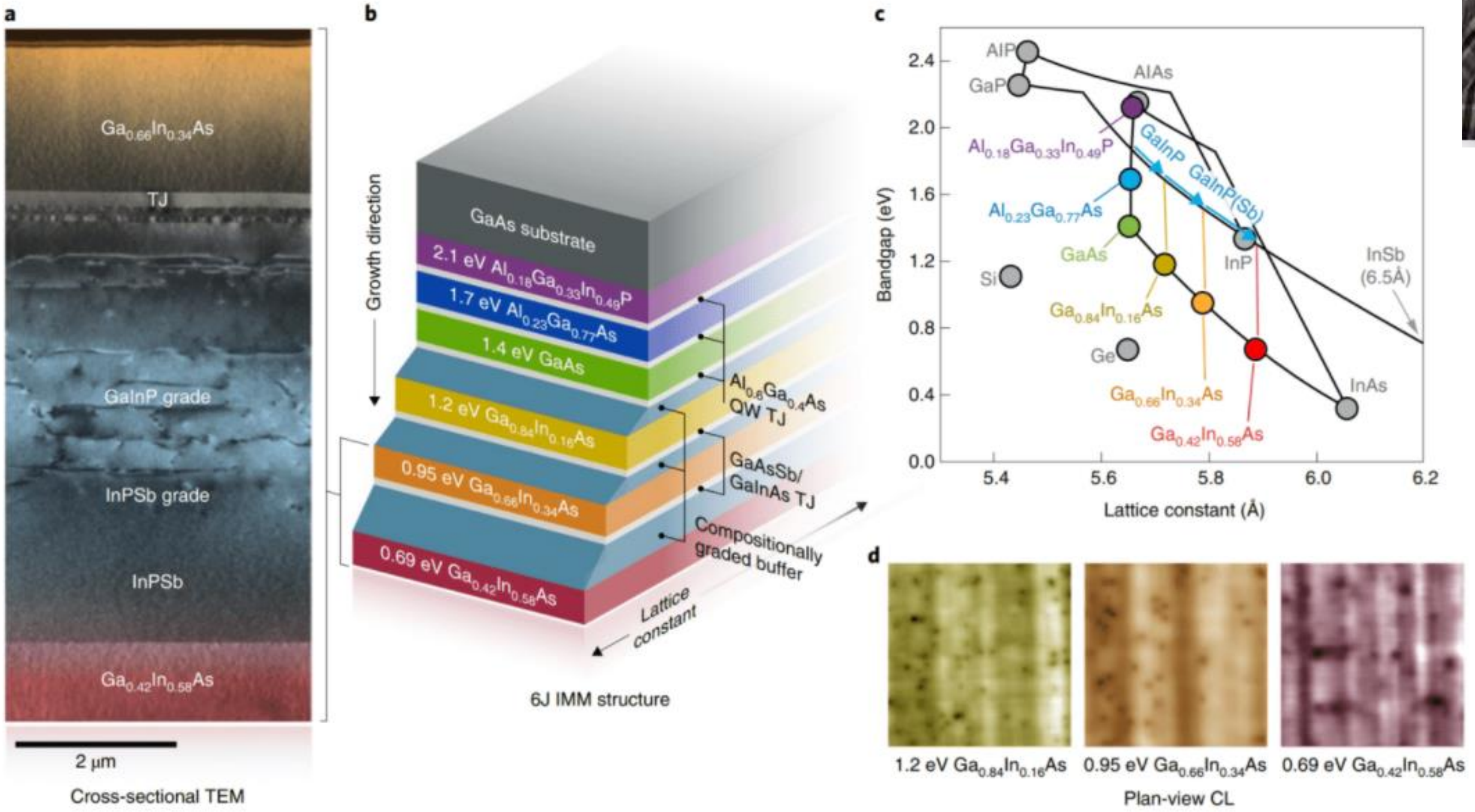
25,7% mono jonction perovskite : UNIST

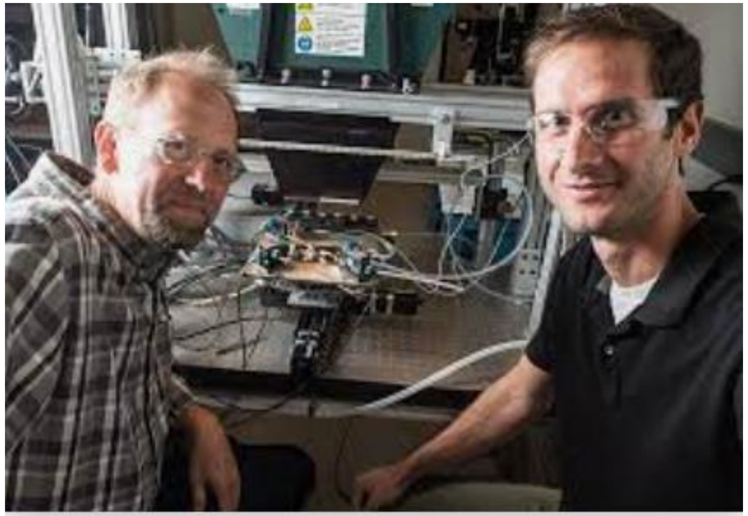
2020

Six-junction III–V solar cells with 47.1% conversion efficiency under 143 Suns concentration

John F. Geisz ✉, Ryan M. France, Kevin L. Schulte, Myles A. Steiner, Andrew G. Norman, Harvey L. Guthrey, Matthew R. Young, Tao Song & Thomas Moriarty

Nature Energy **5**, 326–335 (2020) | Cite this article





Réponse spectrale

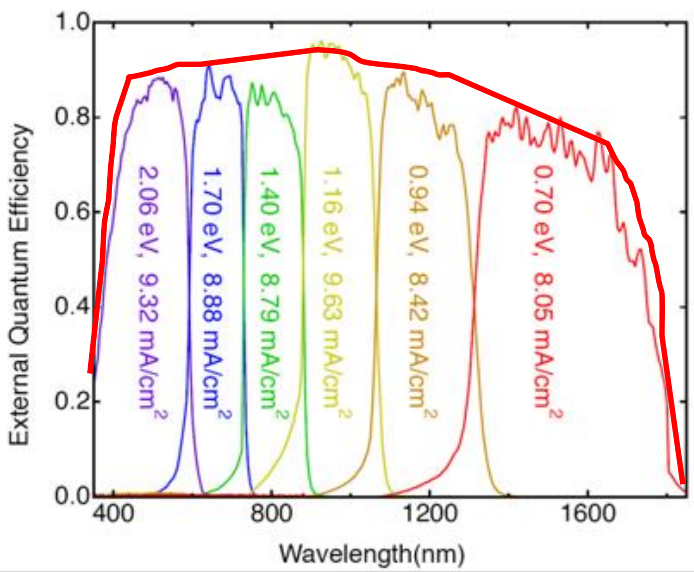


Image: NREL via Nature

L'âge d’or des cellules photo-électrochimiques à semi-conducteurs pour la conversion directe en électricité (1977-1990)

Avant les cellules à colorants

1977

Proc. Natl. Acad. Sci. USA
Vol. 74, No. 10, pp. 4116–4120, October 1977
Chemistry

n-Type Si-based photoelectrochemical cell: New liquid junction photocell using a nonaqueous ferricenium/ferrocene electrolyte

(optical energy conversion/solar energy/photoelectrochemistry/Si photoelectrodes)

KENNETH D. LEGG*, ARTHUR B. ELLIS, JEFFREY M. BOLTS, AND MARK S. WRIGHTON†
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

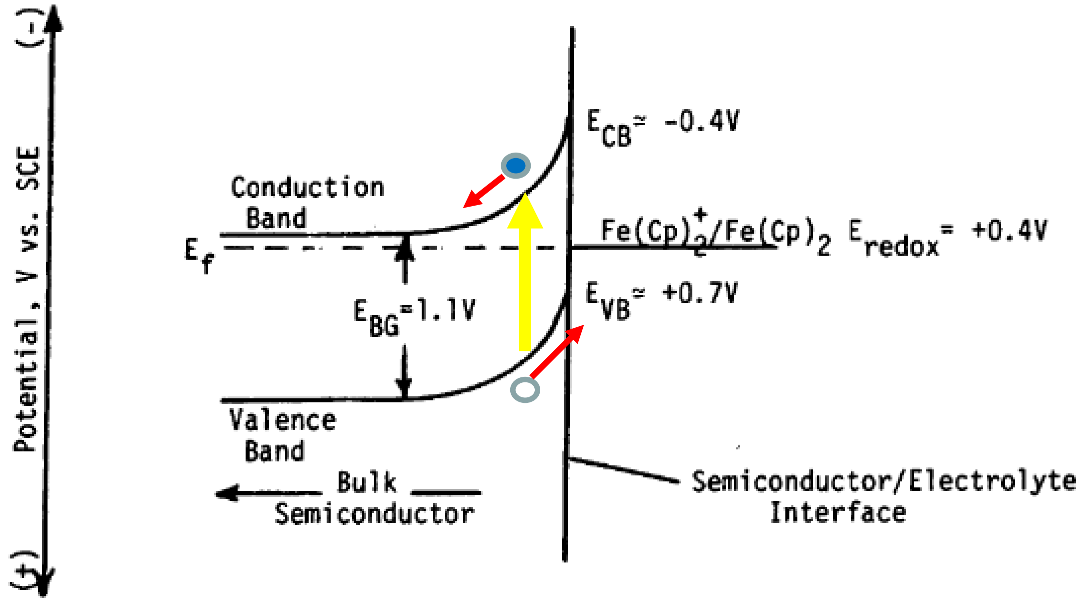


FIG. 4. Interfacial energetics of n-type Si exposed to ethanol solution of $Fe(Cp)_2$ and $Fe(Cp)_2^+$.

Table 2. Output characteristics of Si-based photoelectrochemical cell*

Input power at 632.8 nm, mW	Φ_e at short-circuit	Open-circuit photopotential, mV	η_{max}, %	V at η_{max}, mV
0.41	0.38	300	2.4	200
1.65	0.35	350	2.2	200
4.15	0.37	400	1.4	200

* These data are culled from the current–voltage curves in Fig. 3; the conditions are given in the legend.

$$V_{oc}^{max} = E_{cb} - E_{redox}$$

Daniel Lincot, Collège de France, 2/03/2022

1977

ELECTRODE MATERIALS FOR PHOTOELECTROCHEMICAL DEVICES

A.J. NOZIK
Materials Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960, USA

Journal of Crystal Growth 39 (1977) 200–209

Table 2
Summary of experimental studies on electrochemical photovoltaic cells

Semiconductor electrocyte	Electrode form	Electrolyte	Redox couple	References
n-CdS	Single crystal	$KCl/K_4Fe(CN_6/K_3Fe(CN)_6$	$Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$	[33,32,17]
n-CdS	Single crystal	$NaOH/Na_2S/S$	S^{2-}/S	[34]
	Polycrystalline film	$NaOH/Na_2S/S$	S^{2-}/S	[39,40]
n-CdS	Single crystal	KCl/CH_3OH	–	[36,37]
n-CdTe	Polycrystalline film	$NaOH/Na_2S/S$	S^{2-}/S	[40]
n-CdSe	Single crystal	$NaOH/Na_2S/S$	S^{2-}/S	[34]
n-Bi_2S_3	Polycrystalline film	$NaOH/Na_2S/S$	S^{2-}/S	[40]
n-ZnSe	Polycrystalline film	$NaOH/Na_2S/S$	S^{2-}/S	[40]
n-TiO_2	Polycrystalline film	NaOH, $HClO_4$	H_2O/O_2	[38]
	Single crystal	HCl	H_2O/O_2	[23]
n-GaAs	Single crystal	HCl	–	[37]
p-Si	Polycrystalline and amorphous films	Na_2HPO_4	–	[35]
p-CdTe	Polycrystalline film	$NaOH/Na_2S/S$	S^{2-}/S	[40]

Daniel Lincot, Collège de France, 2/03/2022

1984

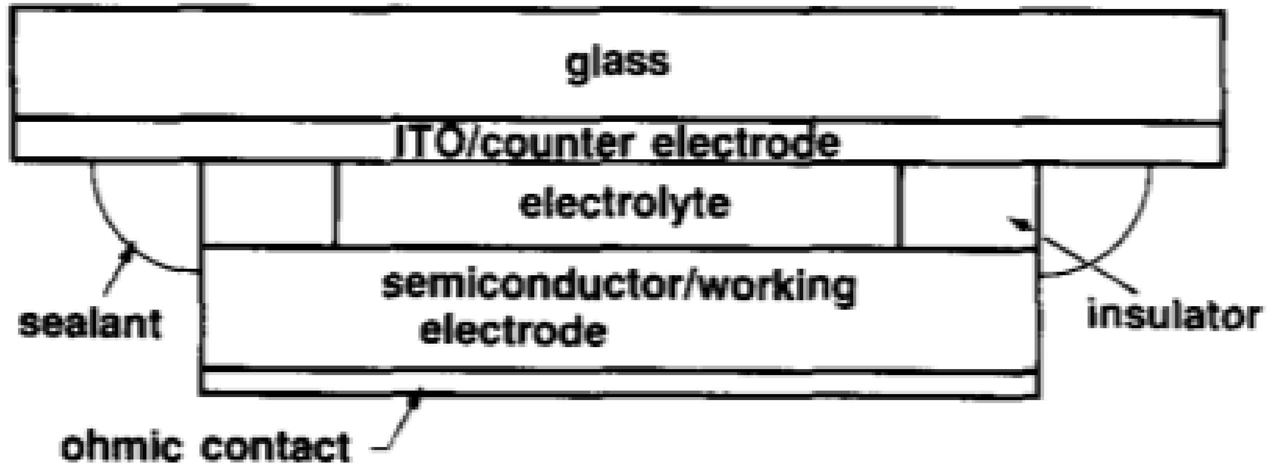
Autres systèmes
GaAs, CdTe, InP, CdSe
X^{2-}/X_2^{2-} : X=S,Se,Te en milieu KOH

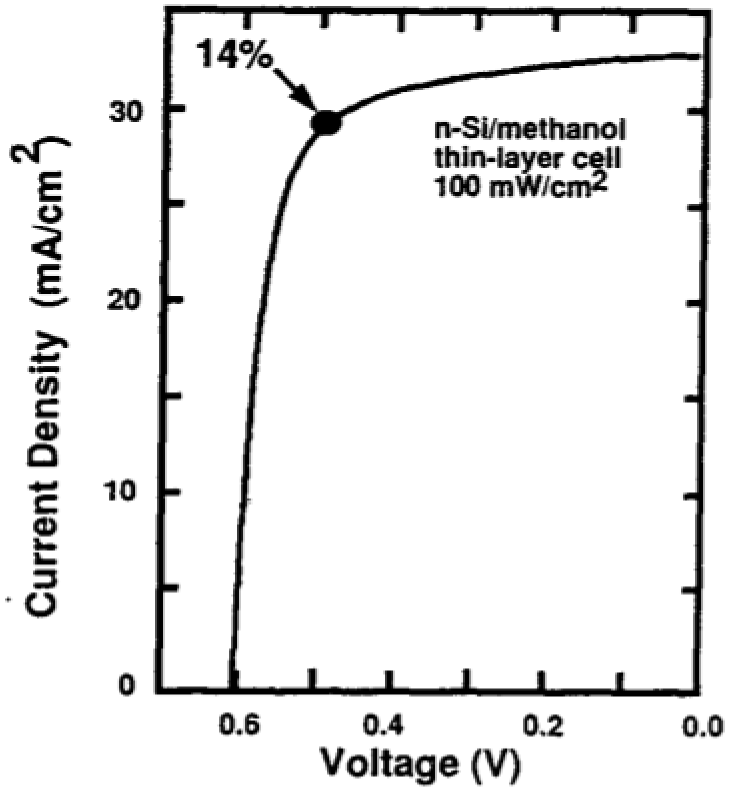
A 14% efficient nonaqueous semiconductor/liquid junction solar cell

James F. Gibbons,[a] George W. Cogan, Chris M. Gronet, and Nathan S. Lewis[b]
SERA Solar Corporation, Santa Clara, California 95054

Appl. Phys. Lett. **45** (10), 15 November 1984 0003-6951

$Si/CH_3OH - Me_2Fc^{+/0}$





Autres systèmes : GaAs, CdTe, InP, CdSe - X^{2-}/X_2^{2-} : X=S,Se,Te en milieu KOH

1978 : 12 %

12 % → N-GaAs : Se^{2-}/Se_2^{2-} KOH avec traitement Ru

A. Heller, B. A. Parkinson, and B. Miller, Appl. Phys. Lett. 33(1978) 512

1987 : 15%

Chemical modification of n-GaAs electrodes with Os^{3+} gives a 15% efficient solar cell

Bruce J. Tufts, Ian L. Abrahams, Patrick G. Santangelo, Gail N. Ryba, Louis G. Casagrande & Nathan S. Lewis*

Department of Chemistry, Stanford University, Stanford, California 94305, USA

NATURE VOL. 326 30 APRIL 1987

N-GaAs : Se^{2-}/Se_2^{2-} KOH avec traitement Os

1988 : étude des mécanismes

ADSORPTION OF TELLURIDE IONS ON CADMIUM TELLURIDE - CONSEQUENCES FOR PHOTOELECTROCHEMICAL CELLS , LINCOT, D; VEDEL, J, JOURNAL OF PHYSICAL CHEMISTRY 92(1988) 4103-4110

1990 : 16,4%

Efficient photoelectrochemical solar cells from electrolyte modification

Stuart Licht & Dharmasena Peramunage

Department of Chemistry, Clark University, Worcester, Massachusetts 01610, USA

NATURE · VOL 345 · 24 MAY 1990

N-CdSe (1,7 eV) : $Fe(CN)_6^{2-/3-}$ -KOH V_{CO} =1,2 V

Les cellules photo-électrochimiques pour la conversion chimique directe -photocatalyse

Electrolyse de l'eau → hydrogène, réduction du CO_2

Vidéo support : la découverte
de l'effet
photovoltaïque (2020)

https://www.youtube.com/watch?v=N20pgyACxL8

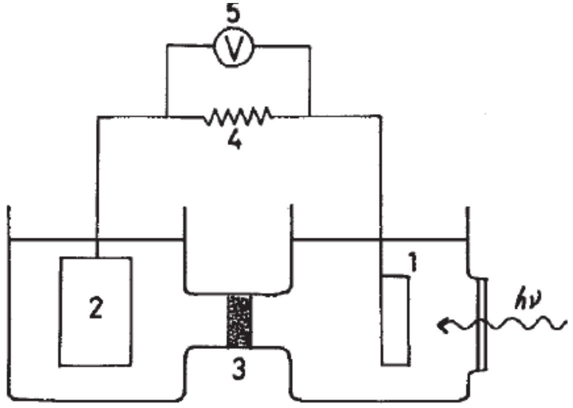
Daniel Lincot, Collège de France, 2/03/2022

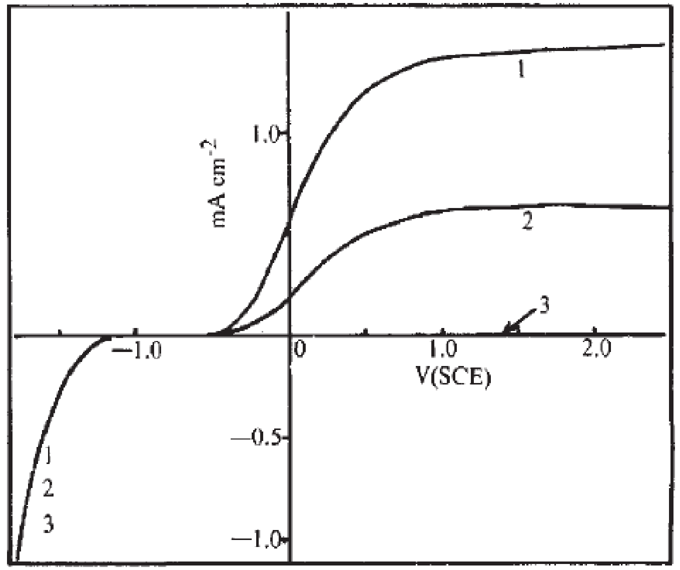
1972

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1148—1150(1971)

Electrochemical Evidence for the Mechanism of the Primary Stage of Photosynthesis[1]

Akira Fujishima and Kenichi Honda
Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo
(Received October 13, 1970)





Electrochemical Photolysis of Water at a Semiconductor Electrode

NATURE VOL. 238 JULY 7 1972 p. 37

$E_{BV} > E_{redox}$

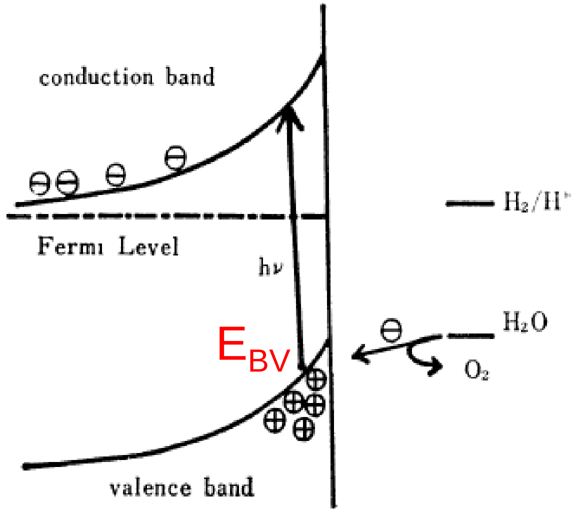


Fig. 2. A mechanistic model of photosensitized electrolytic oxidation.

$$TiO_2 + 2\,h\nu \rightarrow 2\,e^- + 2\,p^+$$
(excitation of TiO_2 by light)

$$2\,p^+ + H_2O \rightarrow \tfrac{1}{2}\,O_2 + 2\,H^+$$
(at the TiO_2 electrode)

$$2\,e^- + 2\,H^+ \rightarrow H_2$$
(at the platinum electrode)

$$H_2O + 2\,h\nu \rightarrow \tfrac{1}{2}\,O_2 + H_2$$

Sujet en pleine renaissance
Photocatalyse, réduction du CO_2

1968

Electrochimica Acta, 1968, Vol. 13, pp. 1509 to 1515. Pergamon Press. Printed in Northern Ireland

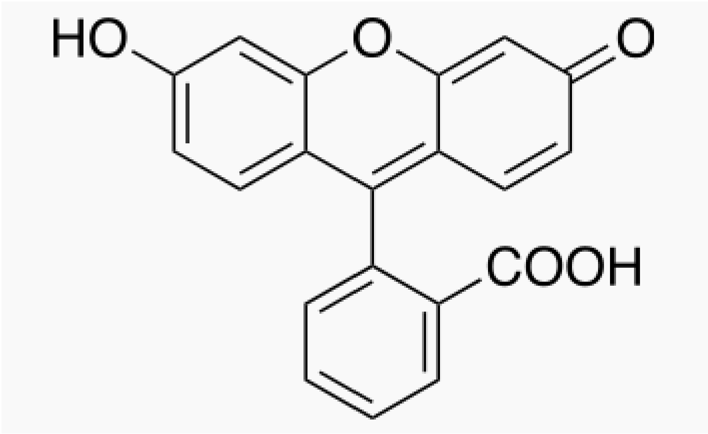
SENSITIZATION OF CHARGE INJECTION INTO SEMICONDUCTORS WITH LARGE BAND GAP*

H. GERISCHER, M. E. MICHEL-BEYERLE,
F. REBENTROST and H. TRIBUTSCH
Institut für Physikalische Chemie der Technischen Hochschule, München, Bundesrepublik Deutschland

Mécanismes précurseurs (<1900) : la photographie avec transfert des trous dans un réducteur adsorbé, permettant de faciliter la réduction de AgCl

Une approche alternative : la sensibilisation de la surface par greffage de molécules, ouvrant la voie aux cellules à colorants

Fluorescéine



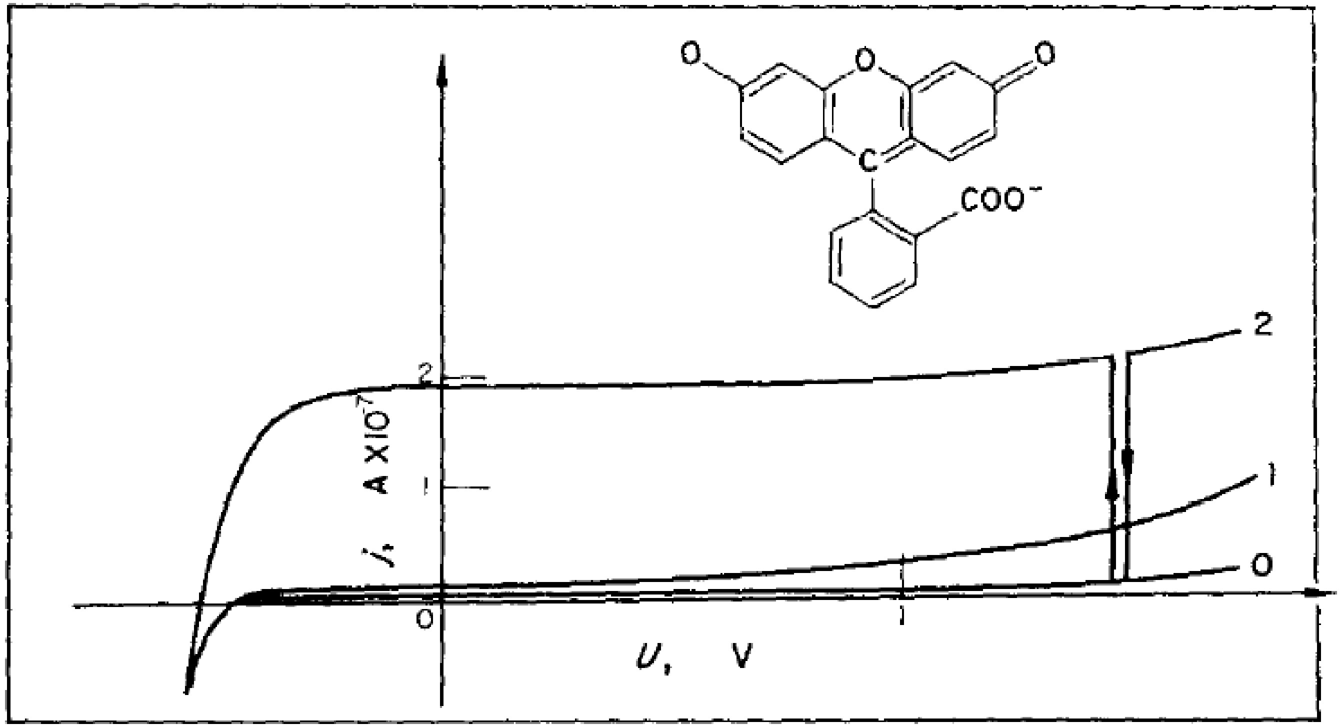
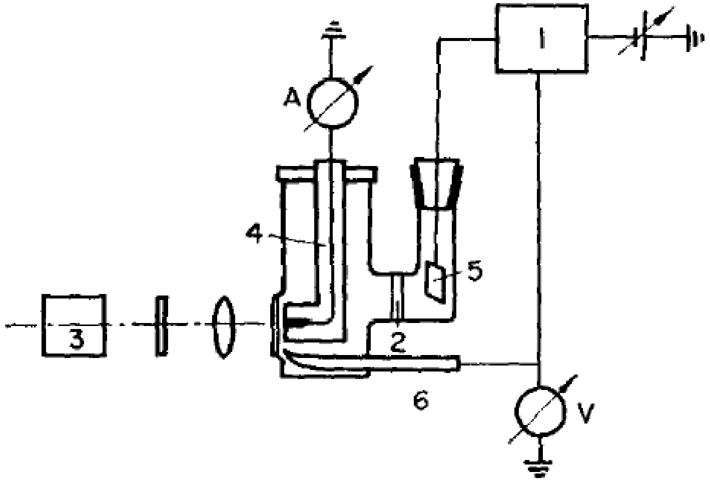


FIG. 2. Current/voltage characteristic for zinc-oxide single-crystal electrode- 0, without illumination and without dye; 1, with illumination and without dye; 2, with illumination and with dye.
Effect of switching off the light is indicated by the arrows.



La molécule de colorant se greffe à la surface (chimisorption)

δ+ δ− δ+ δ− δ+ δ−

surface ---Zn-O-Zn-O-Zn-O---

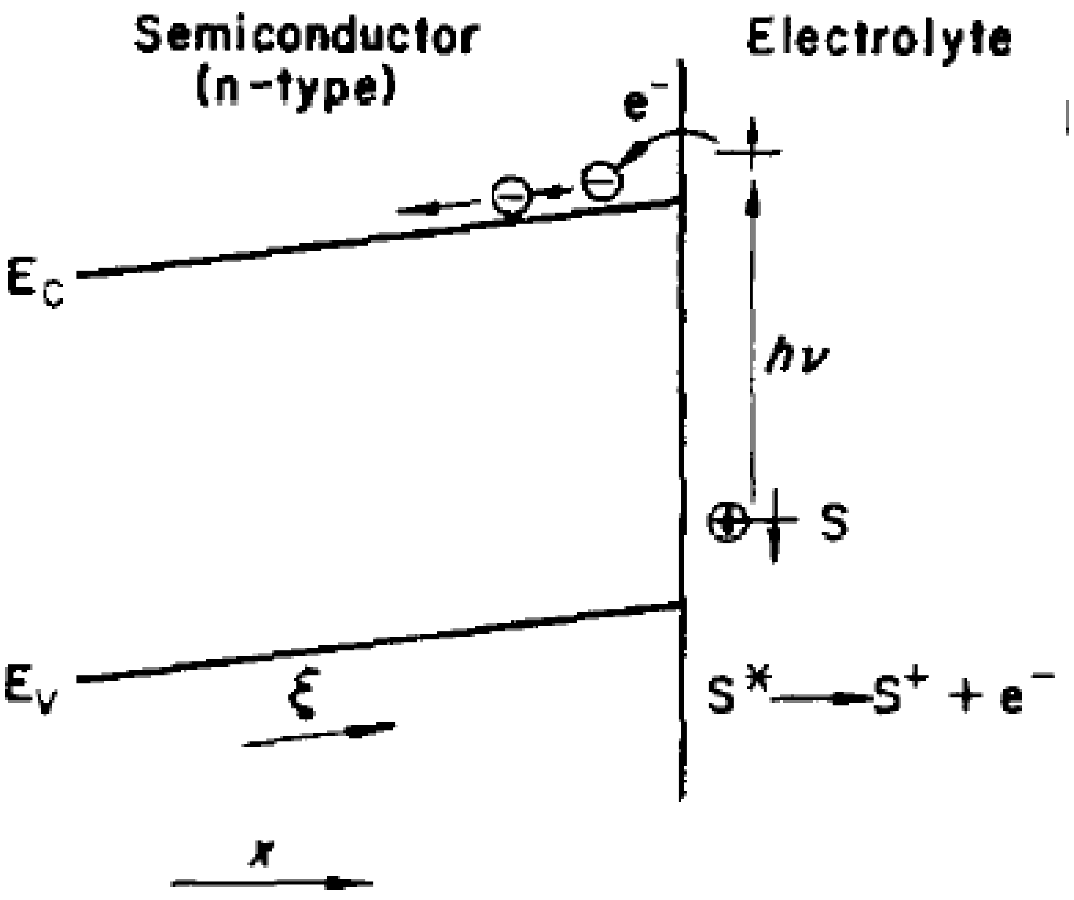
$Zn_S^+ + ACOO^- \rightarrow MOOCA_S$

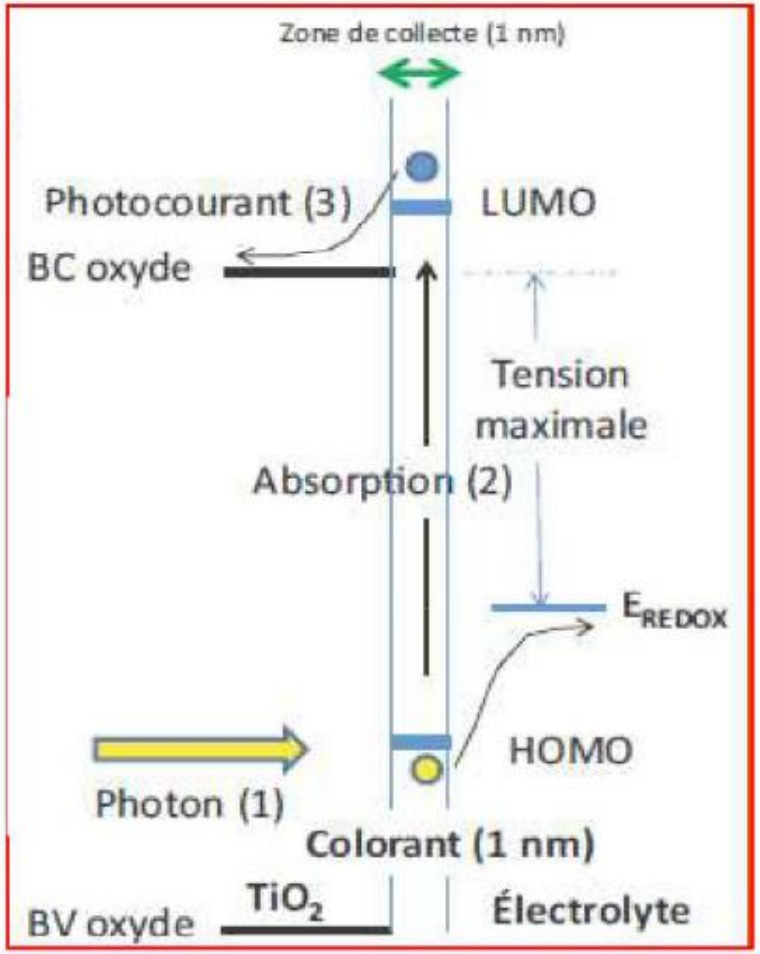
Pont électronique

Daniel Lincot, Collège de France, 2/03/2022

C’est la molécule qui génère le photocourant et non le semiconducteur

On sait enfin se brancher sur une molémolécule !





D. Lincot

128 l’actualité chimique - février-mars 2012 - n° 360-361

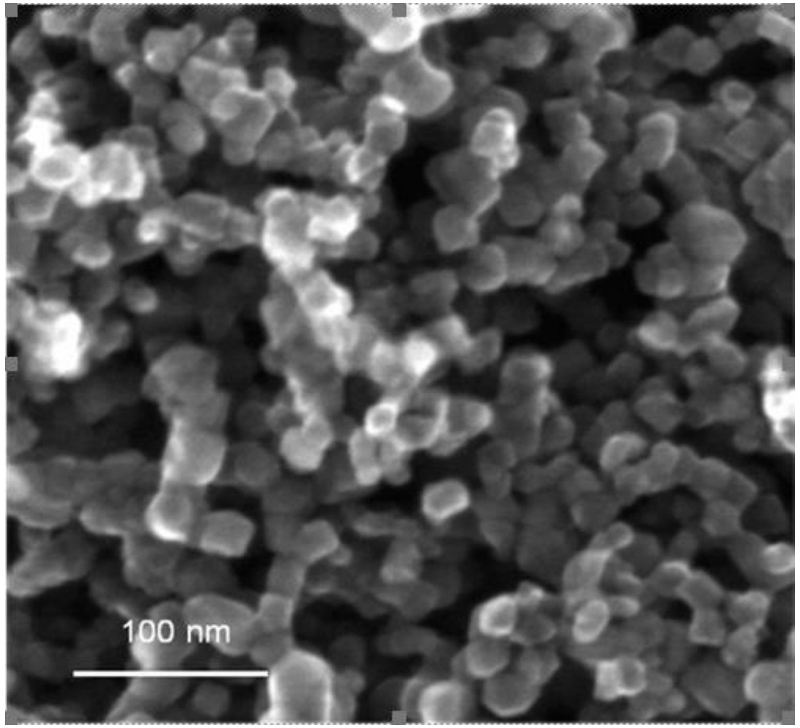
Le semiconducteur n’est plus l’absorbeur !!!!

Daniel Lincot, Collège de France, 2/03/2022

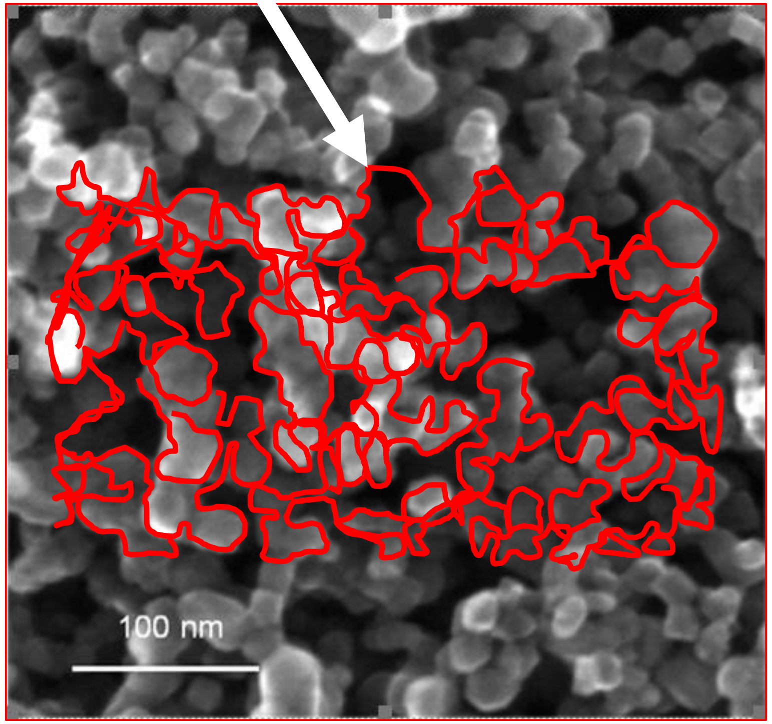
Les cellules à colorants : l'irruption des concepts de la photosynthèse dans le photovoltaïque

→ Photovoltaïque moléculaire
→ Découverte du concept de réseaux interpénétrés

Matrice poreuse de TiO_2

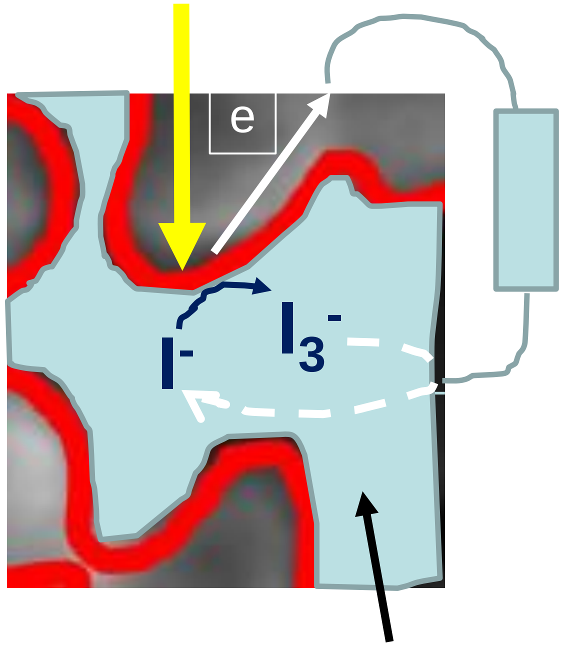


Adsorption d'un colorant



Multiplication de la surface développée
1 cm² → 1000 cm²

Photon



Injection d'un électrolyte iodure

Daniel Lincot, Collège de France, 2/03/2022

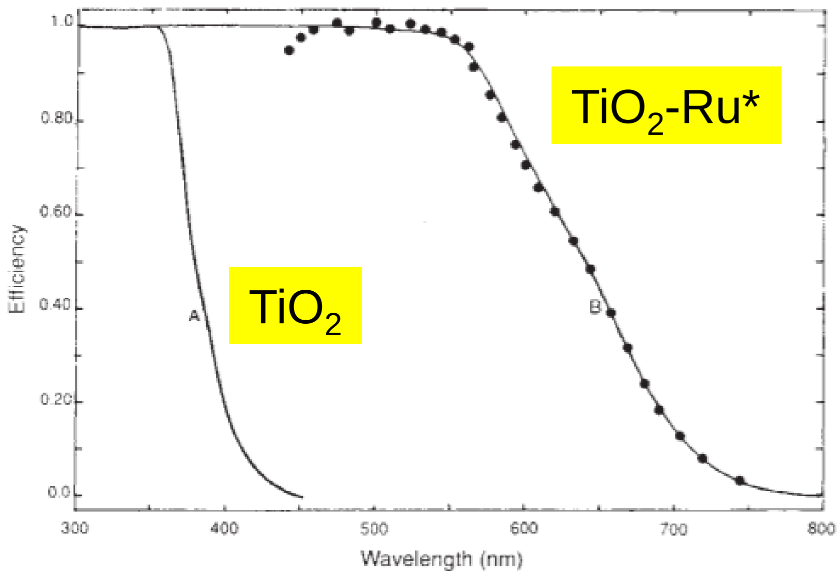
1991

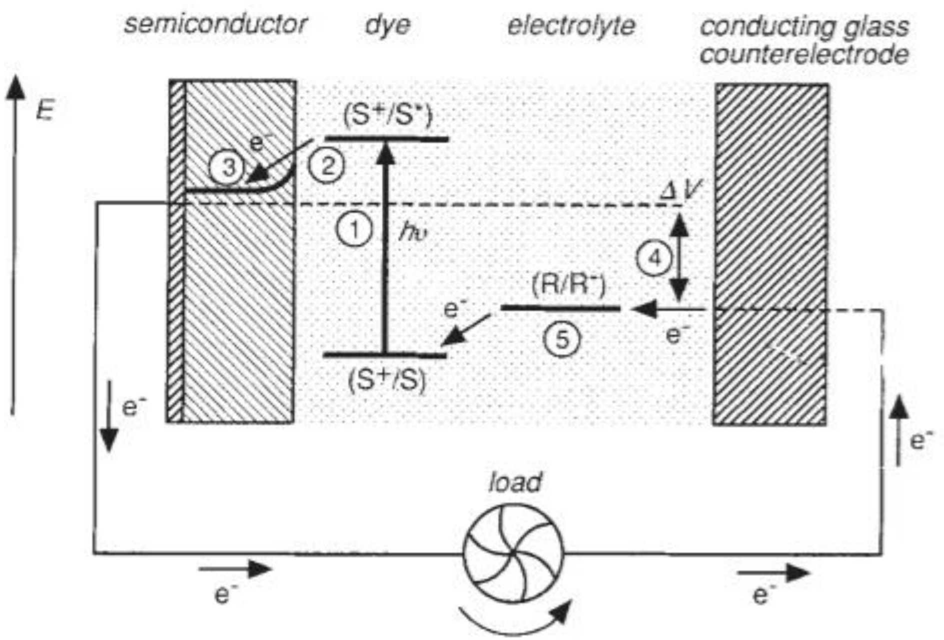
NATURE · VOL 353 · 24 OCTOBER 1991

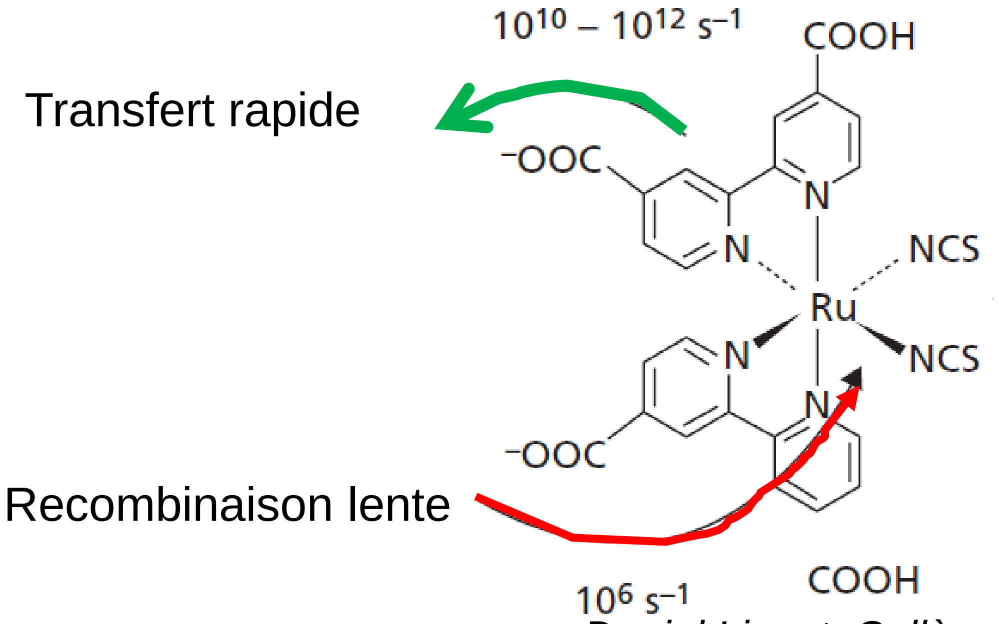
A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films

Brian O'Regan* & Michael Grätzel†

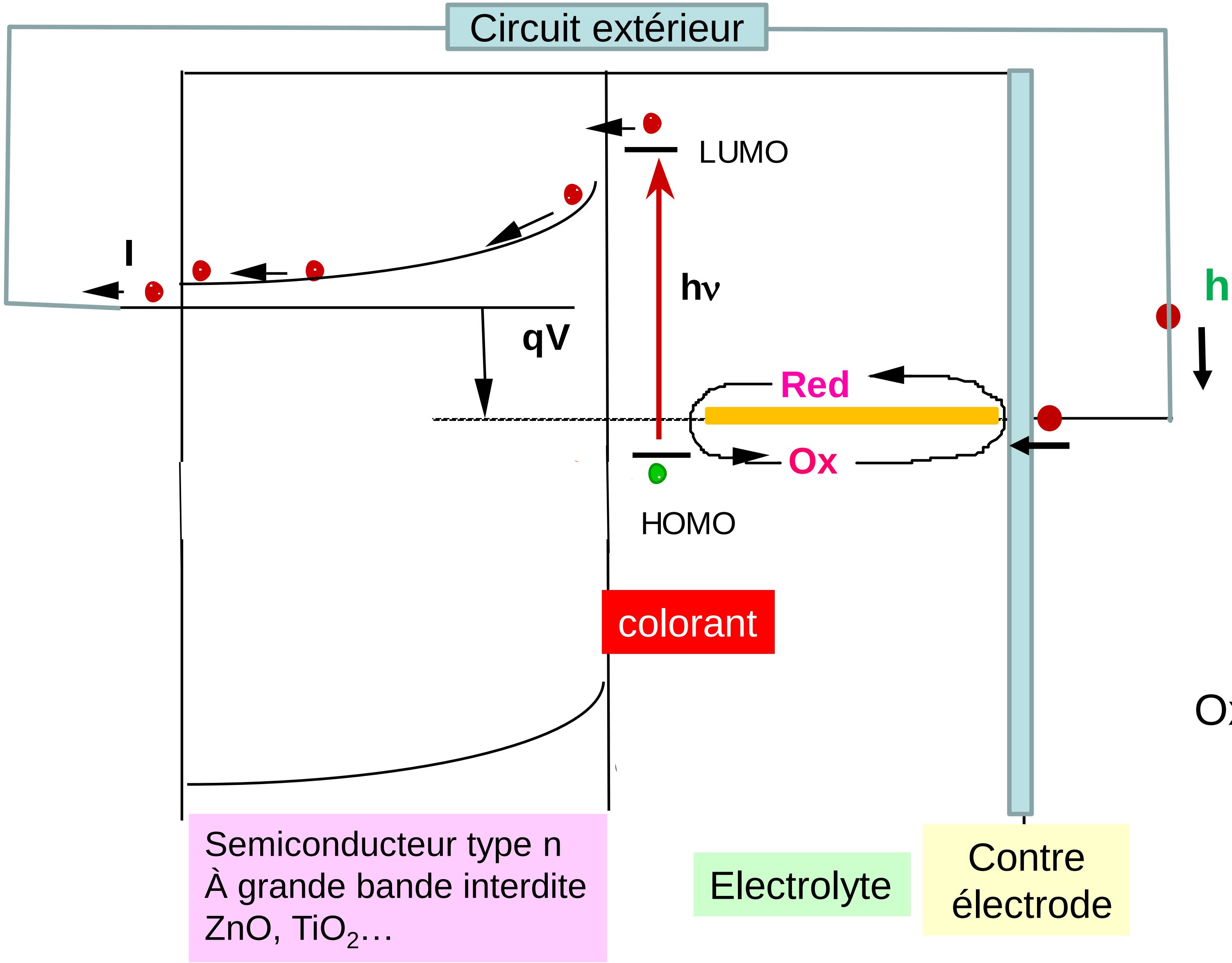
Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland







Récapitulatif



Réactions à l'anode

e_{homo} + hν → e_{lumo} + h_{homo}

e_{lumo} → e_{BC} → e_{ext}

h_{homo} + $Red_{electrode}$ → e_{homo} + $Ox_{contre\ electrode}$

Transport dans l'électrolyte

$Ox_{electrode}$ → $Ox_{contre\ électrode}$

$Red_{contre\ électrode}$ → $Red_{\ électrode}$

Réactions à la cathode

$Ox_{contre\ électrode}$ + e_{ext} → $Red_{\ contre\ électrode}$

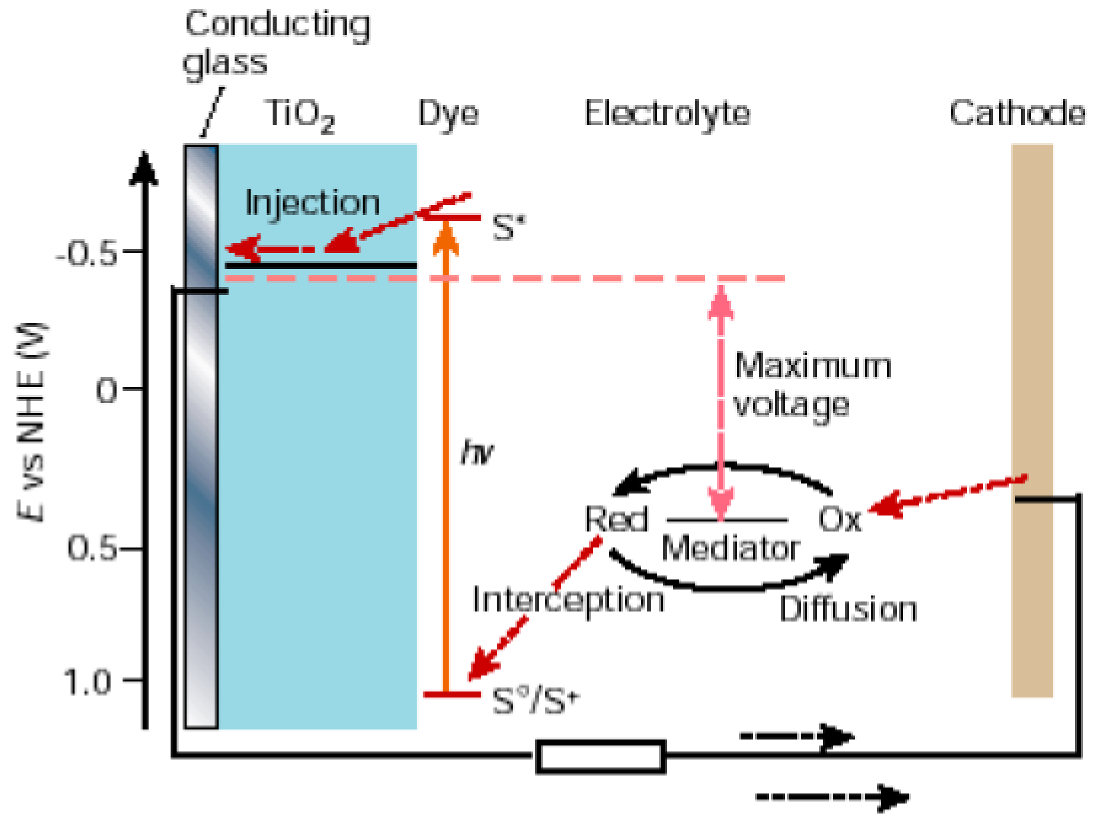
Potentiel redox E_0

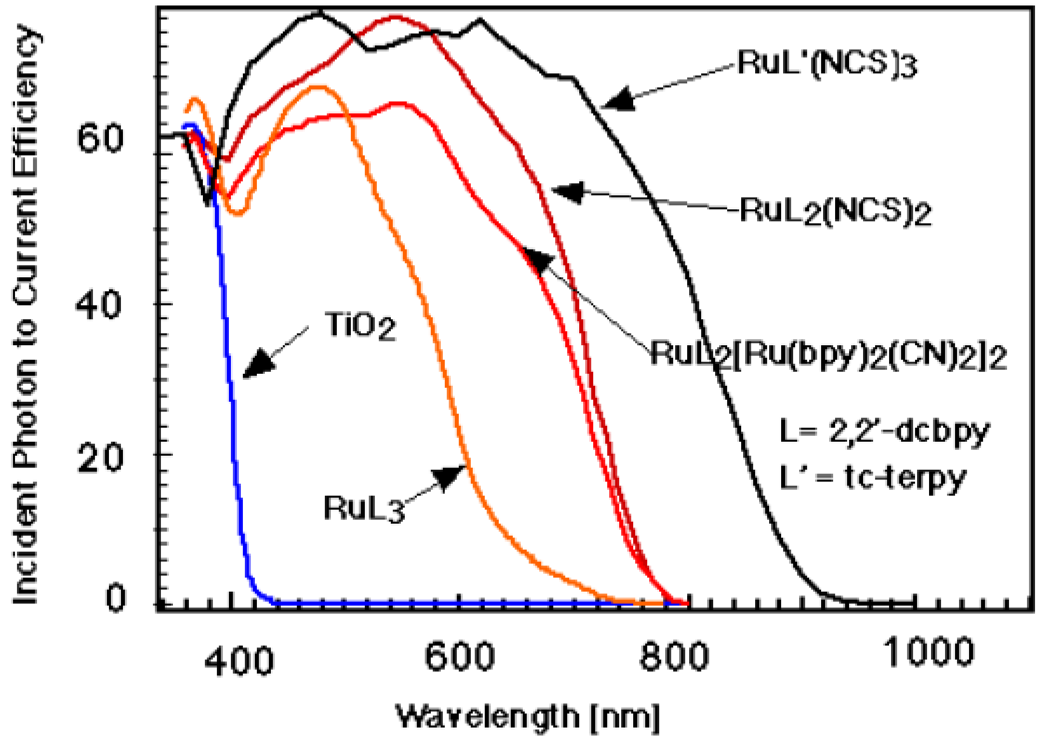
Ox+ e → Red

Voc (max) = E_{BC}-E_{redox}

Daniel Lincot, Collège de France, 2/03/2022

Influence de la nature du colorant (M. Graetzel et al.)





Aux sources du concept (citées par B. O'Regan & M. Graetzel)

1977

Matsumura, M., Nomura, Y. & Tsubomura, H. *Bull. chem. Soc. Japan* **50,** 2533 (1977).

1981

Dye sensitization of ceramic semiconducting electrodes for photoelectrochemical conversion

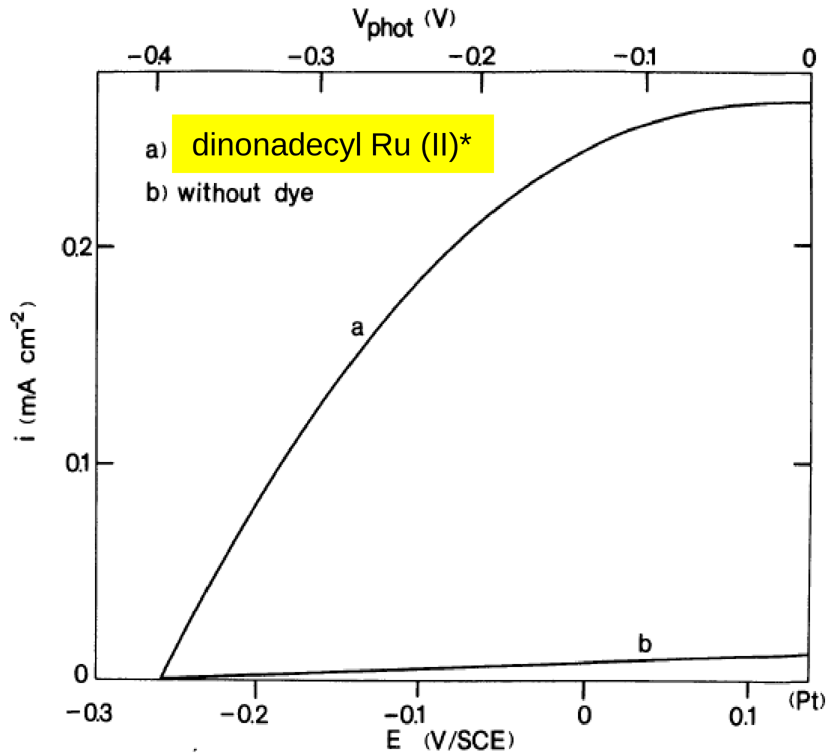
N. Alonso V., M. Beley, P. Chartier

Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Université Louis-Pasteur, 4, rue Blaise-Pascal, 67000 Strasbourg, France

and V. Ern

Institut de Physique (*), Université Louis-Pasteur, 5, rue de l'Université, 67000 Strasbourg, France

Revue Phys. Appl. **16** (1981) 5-10



* *Donné par J.P. Sauvage*

Dans la conclusion

Although it is premature to speculate on any future technological application of such device, it is worthwhile to emphasize that cheap, large scale, production of ceramic oxides is already a well known art in electro-acoustic transducer technology. Moreover**, ceramics have the advantage of increasing the effective electrode area and a better use of diffuse light.**

Et les colorants naturel ?

2010

Dye-sensitized solar cell using natural dyes extracted from spinach and ipomoea

H. Chang[a,*], H.M. Wu[b], T.L. Chen[c], K.D. Huang[d], C.S. Jwo[e], Y.J. Lo[a]

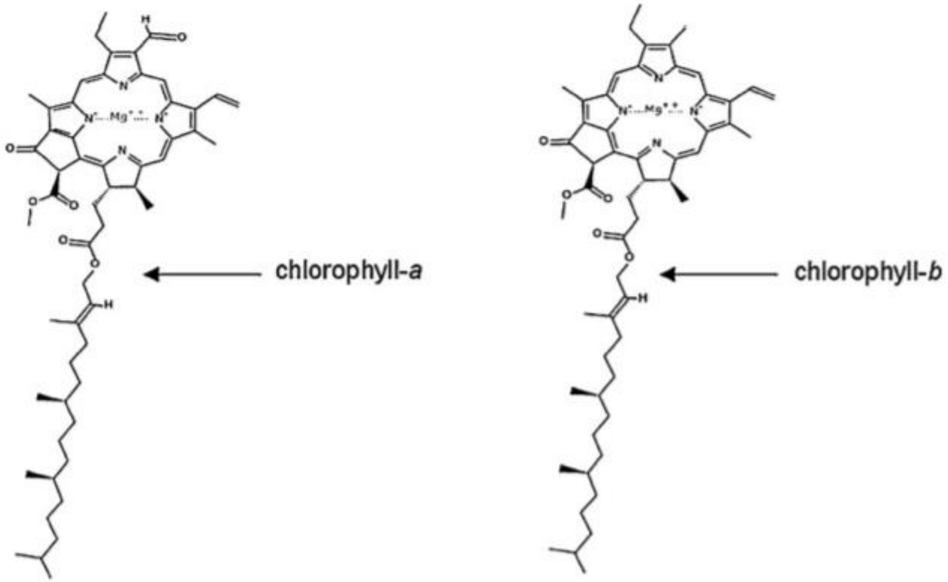
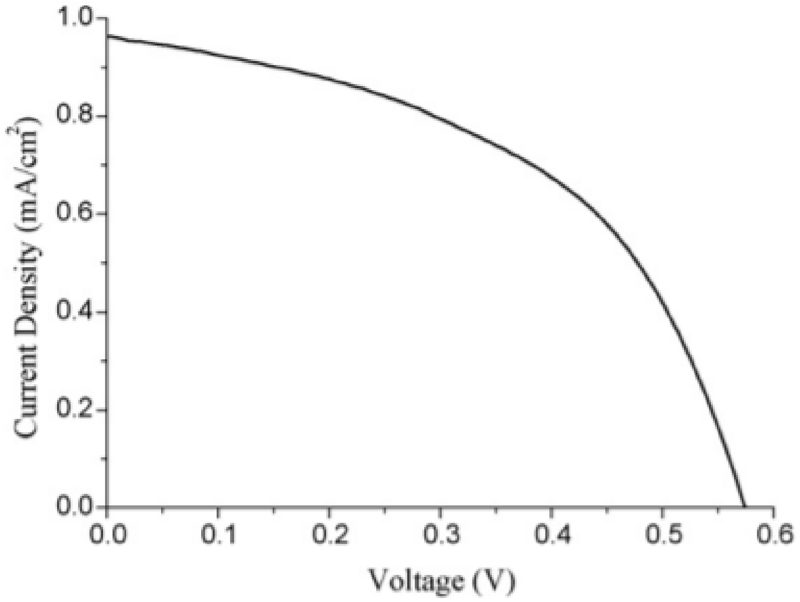


Fig. 8. Chemical structure of chlorophyll-a and chlorophyll-b contained in spinach and in ipomoea leaves.



Photoelectrochemical properties of solar cells with natural extracts.

Dye	V_{oc} (mV)	J_{sc} (mA/cm^2)	P_{max} (mW/cm^2)	FF (%)	Refs.
Spinach	550	0.46	0.25	51	–
Ipomoea	540	0.91	0.36	56.33	–
Skin of Jaboticaba	660	2.6	1.1	62	[16]
Black rice	551	1.14	0.372	52	[4]
Sicilian orange	340	3.84	0.68	50	[23]
Skin of eggplant	350	3.40	0.44	40	[23]

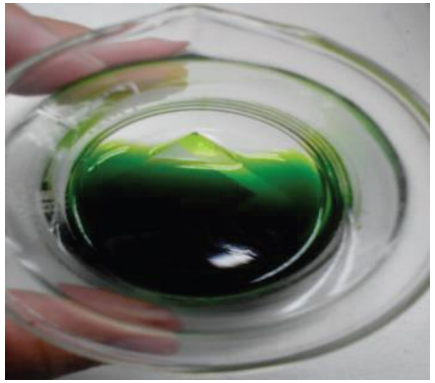
R. Syafinar et al. / Energy Procedia 79 (2015) 896 – 902

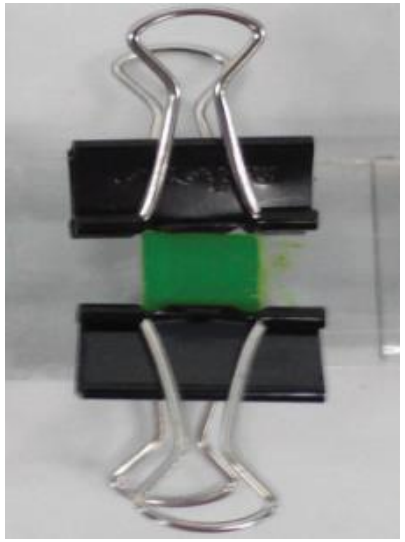
2015 International Conference on Alternative Energy in Developing Countries and Emerging Economies

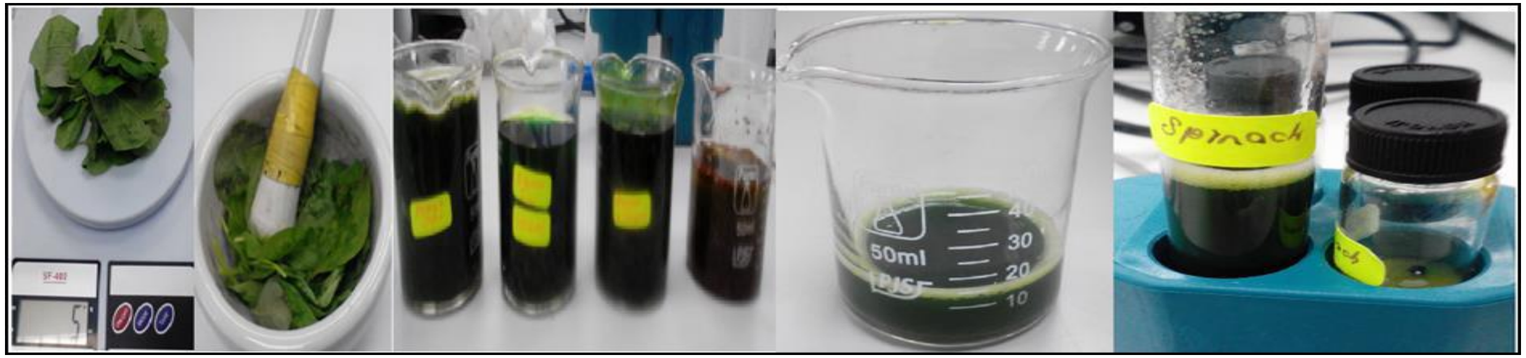
Chlorophyll Pigments as Nature Based Dye for Dye-Sensitized Solar Cell (DSSC)

R. Syafinar[a*], N. Gomesh[a], M. Irwanto[a], M. Fareq[a], Y.M. Irwan[a]

[a]Centre of Excellence for Renewable Energy (CERE), School of Electrical Systems Engineering, Universiti Malaysia Perlis (UniMAP), Malaysia.







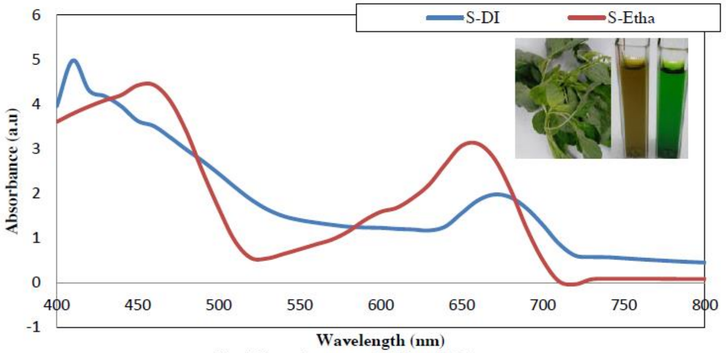


Fig. 4. Absorption spectra of S-Etha and S-DI

Dyes	Extract solvent	V_{oc} (mV)	I_{sc} (mA)	Fill Factor, FF (%)
Spinach	Ethanol	384	0.32	0.36
	DI water	440	0.35	0.49

Renewable and Sustainable Energy Reviews 16 (2012) 208–215

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Review: Dye sensitized solar cells based on natural photosensitizers

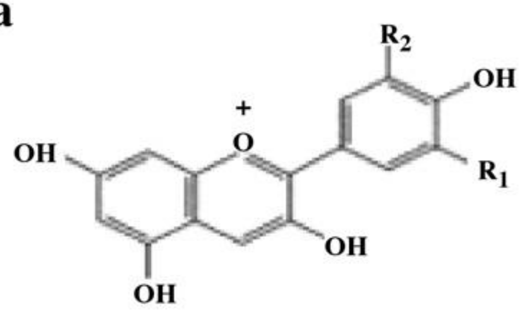
Monishka Rita Narayan

School of Engineering and Information Technology, Faculty of Engineering, Health, Science and Environment, Charles Darwin University, Darwin NT 0909, Australia

2012

anthocyanidins.

a



	R1	R2
Pelargonidin	H	H
Cyandin	OH	H
Peonidin	OCH_3	H
Delphinidin	OH	OH
Petunidin	OCH_3	OH
Malvidin	OCH_3	OCH_3

Pigments in plants.

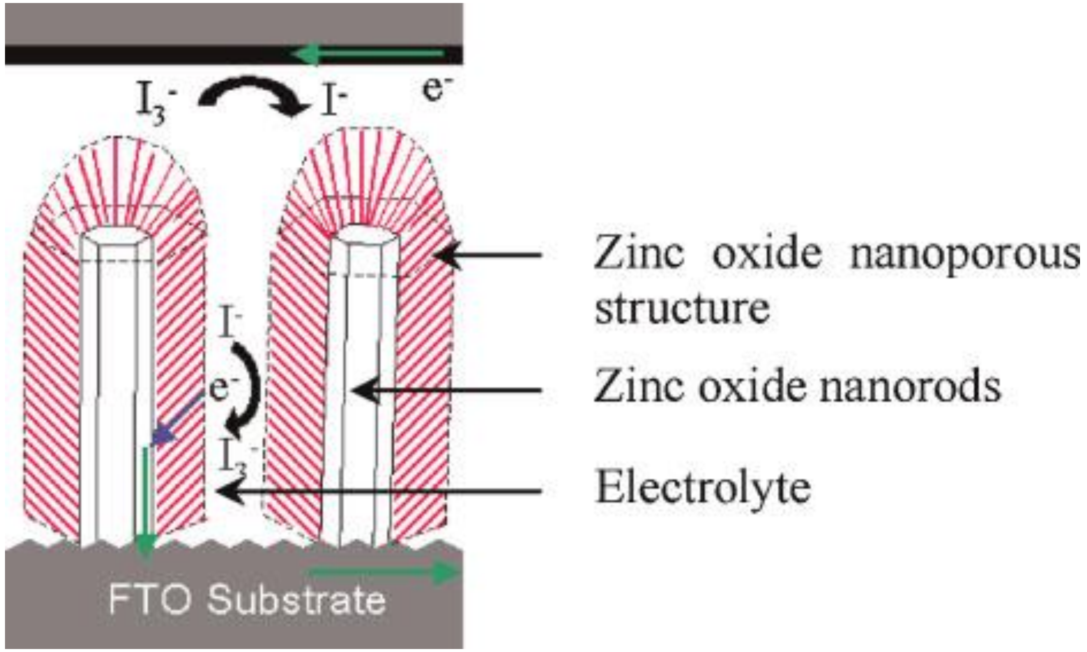
Pigment	Common type	Occurrence
Betalains	Betacyanins Betaxanthins	Caryophyllales and some fungi
Carotenoids	Carotenes	Photosynthetic plants and bacteria
	Xanthophylls	Retained from the diet by some birds, fish and crustaceans
Chlorophyll	Chlorophyll	All photosynthetic plants
Flavonoids	Anthocyanins Aurones Chalcones Flavonols Proanthocyanidins	Widespread and common in plants including angiosperms, gymnosperms, ferns and bryophytes

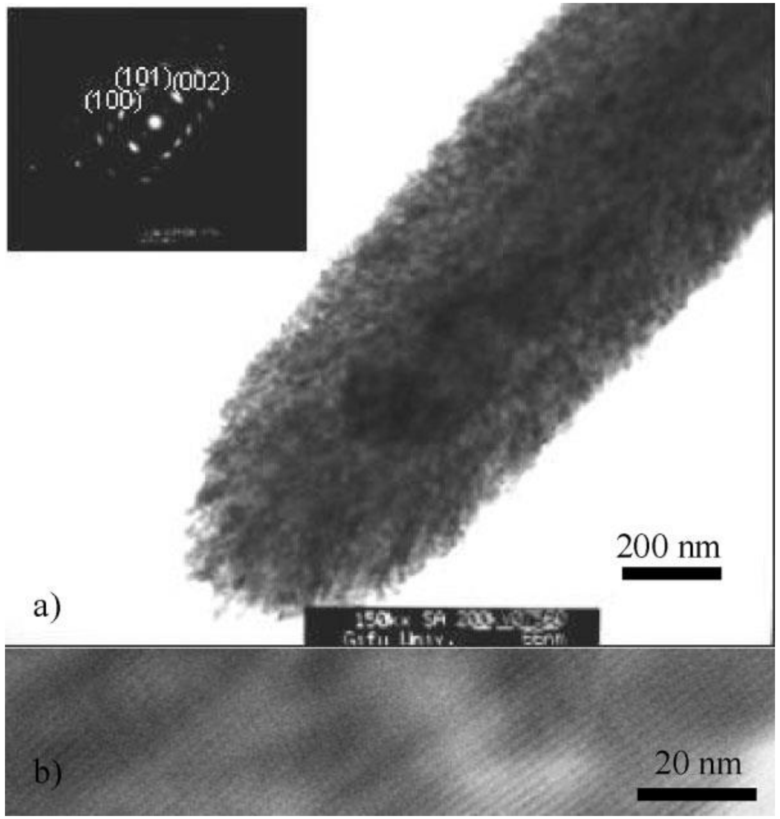
Table 2
Photoelectrochemical parameters of natural dye based DSSCs.

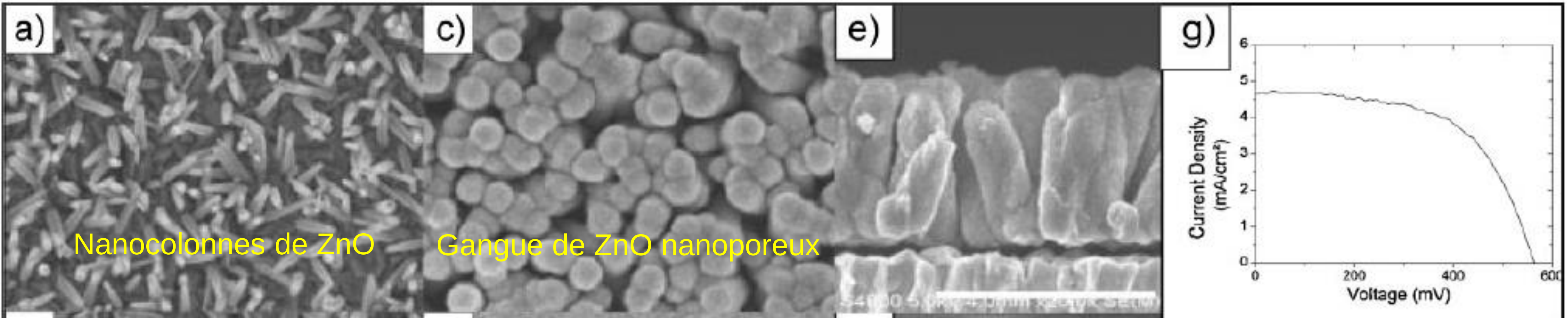
Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)	Reference
Rosella	1.63	0.40	0.57	0.37	[13]
Blue pea	0.37	0.37	0.33	0.05	
Mixed rosella-blue pea	0.82	0.38	0.47	0.15	
Black rice	1.14	0.55	0.52	–	[31]
Capsicum	0.23	0.41	0.63	–	
Rosa xanthina	0.64	0.49	0.52	–	
Kelp	0.43	0.44	0.62	–	
Erythrina variegate	0.78	0.48	0.55	–	
Bixin	1.10	0.57	0.59	0.37	[32]
Annatto	0.53	0.56	0.66	0.19	
Norbixin	0.38	0.53	0.64	0.13	
Crocetin	2.84	0.43	0.46	0.56	[33]
Crocin	0.45	0.58	0.60	0.16	
Fruit of Calafate	6.20	0.47	0.36	–	[34]
Syrup of Calafate	1.50	0.38	0.20	–	
Skin of Jaboticaba	7.20	0.59	0.54	–	
Red Sicilian orange	3.84	0.34	0.50	–	[35]
Purple eggplant extract	3.40	0.35	0.40	–	
Dragon fruit	0.20	0.22	0.30	0.22	[36]
Pomegranate juice	0.20	0.40	0.45	1.50	[37]
Red turnip	9.50	0.43	0.37	1.70	[38]
Wild Sicilian prickly pear	8.20	0.38	0.38	1.19	
Sicilian Indian fig	2.70	0.38	0.54	0.50	
Bougainvillea	2.10	0.30	0.57	0.36	
Shisonin	3.56	0.55	0.51	1.01	[39]
Shisonin and chlorophyll	4.80	0.53	0.51	1.31	
Chlorophyll	3.52	0.43	0.39	0.59	
Hibiscus surattensis	5.45	0.39	0.54	1.14	[28]
Sesbania grandiflora	4.40	0.41	0.57	1.02	
Hibiscus rosasinesis	4.04	0.40	0.63	1.02	
Nerium olender	2.46	0.41	0.59	0.59	
Ixora macrothyrsa	1.31	0.40	0.57	0.30	
Rhododendron arboretum zeylanium	1.15	0.40	0.64	0.29	
Begonia	0.63	0.54	0.72	0.24	[40]
Tangerine peel	0.74	0.59	0.63	0.28	
Rhododendron	1.61	0.59	0.61	0.57	
Fructus lyciia	0.53	0.69	0.47	0.17	
Marigold	0.51	0.54	0.83	0.23	
Perilla	1.36	0.52	0.70	0.50	
Herba artemisiae scopariae	1.03	0.48	0.68	0.34	
China loropetal	0.84	0.52	0.63	0.27	

Nos propres travaux : structure hiérarchique à base de ZnO électrodéposé

2010







S. Haller, T. Suguira, D. Lincot, T. Yoshida, Phys. Stat. Sol. A 207(2010)2252
+ Thèse Servane Haller

nature COMMUNICATIONS

NATURE COMMUNICATIONS | (2021) 12:1777

ARTICLE

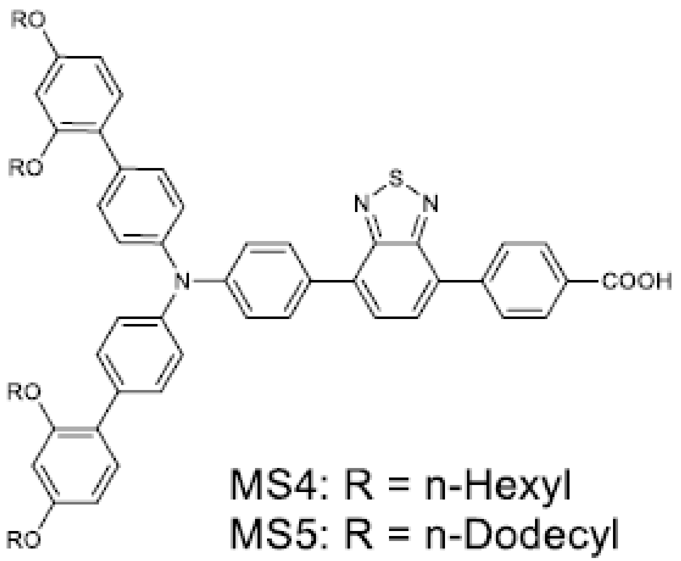
Check for updates

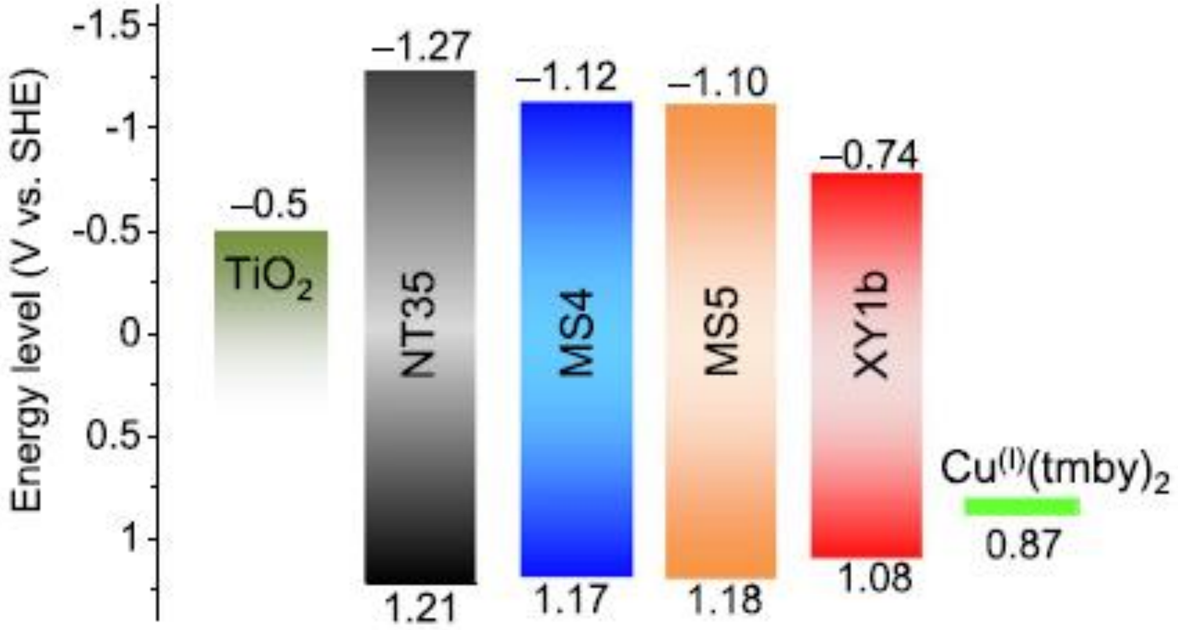
https://doi.org/10.1038/s41467-021-21945-3 OPEN

A molecular photosensitizer achieves a V_{OC} of 1.24 V enabling highly efficient and stable dye-sensitized solar cells with copper(II/I)-based electrolyte

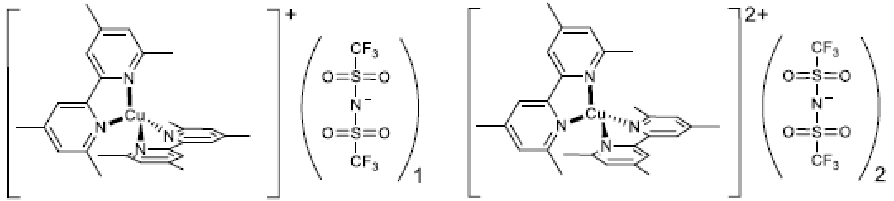
Dan Zhang[1,2,5], Marko Stojanovic[1,5], Yameng Ren[1,5]✉, Yiming Cao[1,4], Felix T. Eickemeyer[1,2]✉, Etienne Socie[3], Nick Vlachopoulos[2], Jacques-E. Moser[3], Shaik M. Zakeeruddin[1], Anders Hagfeldt[2]✉ & Michael Grätzel[1]✉

Daniel Lincot, Collège de France, 2/03/2022

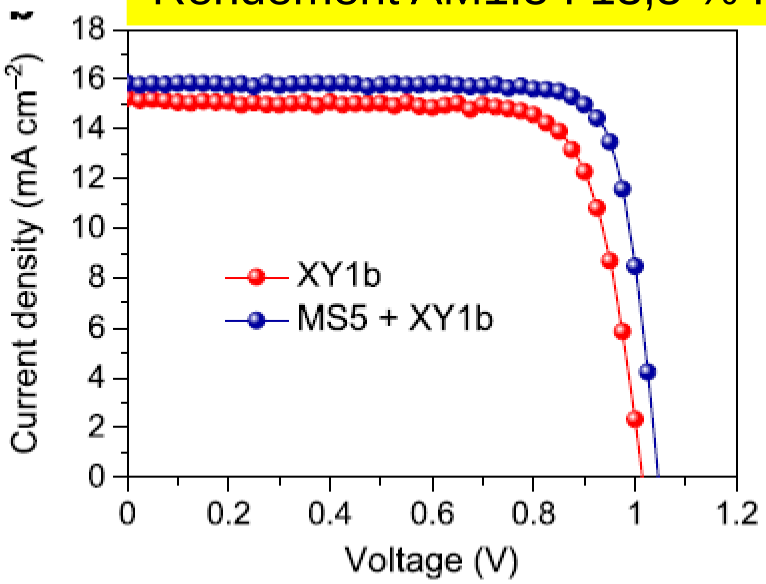


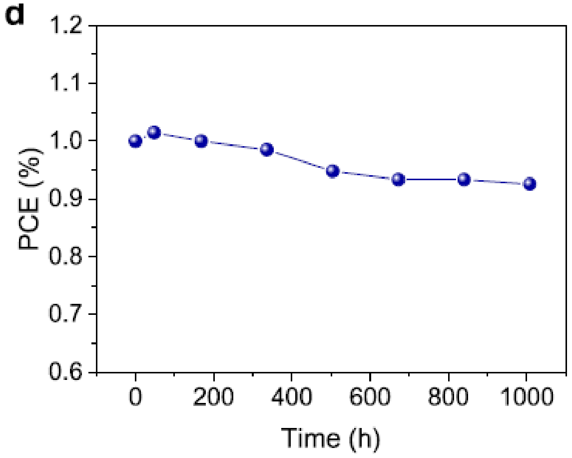


Rendement AM1.5 : 13,5 % Rendement indoor 35%



[Cu$^{(I)}$(tmby)$_2$][TFSI] [Cu$^{(II)}$(tmby)$_2$][TFSI]$_2$



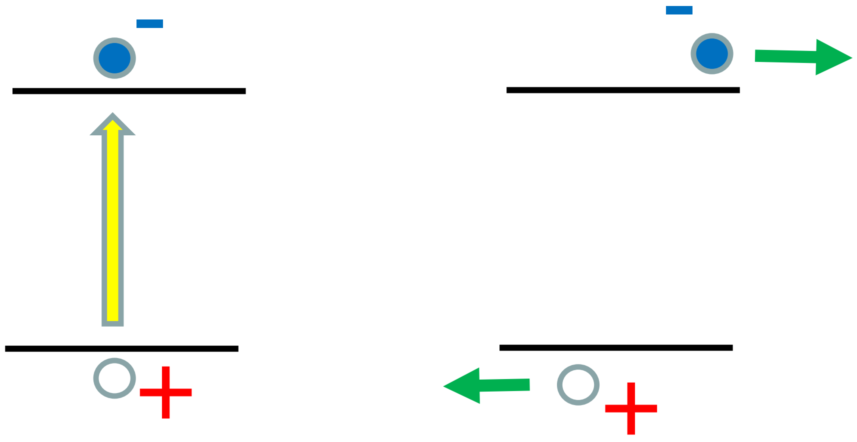


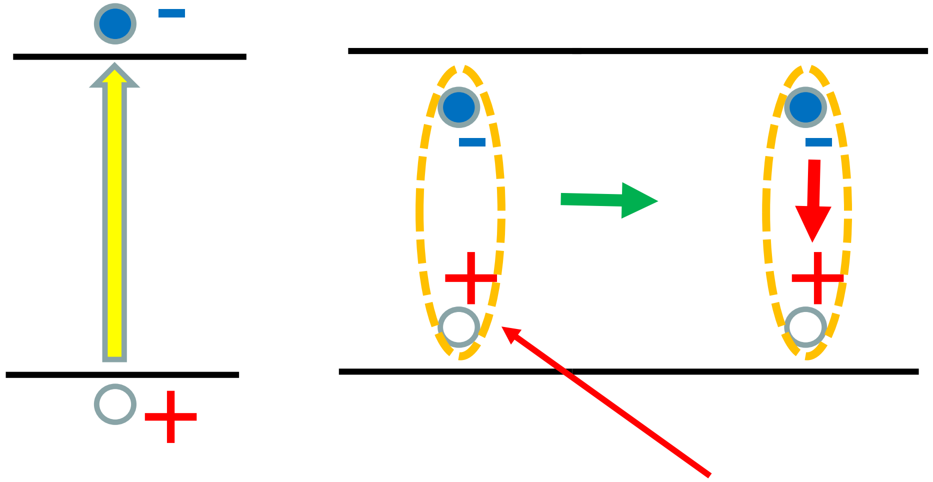
Daniel Lincot, Collège de France, 2/03/2022

Le concept de cellules à réseaux interpénétrés fait décoller le photovoltaïque organique
Irruption des nanostructures dans le photovoltaïque

Semiconducteur

Matériaux organiques, molécules, polymères

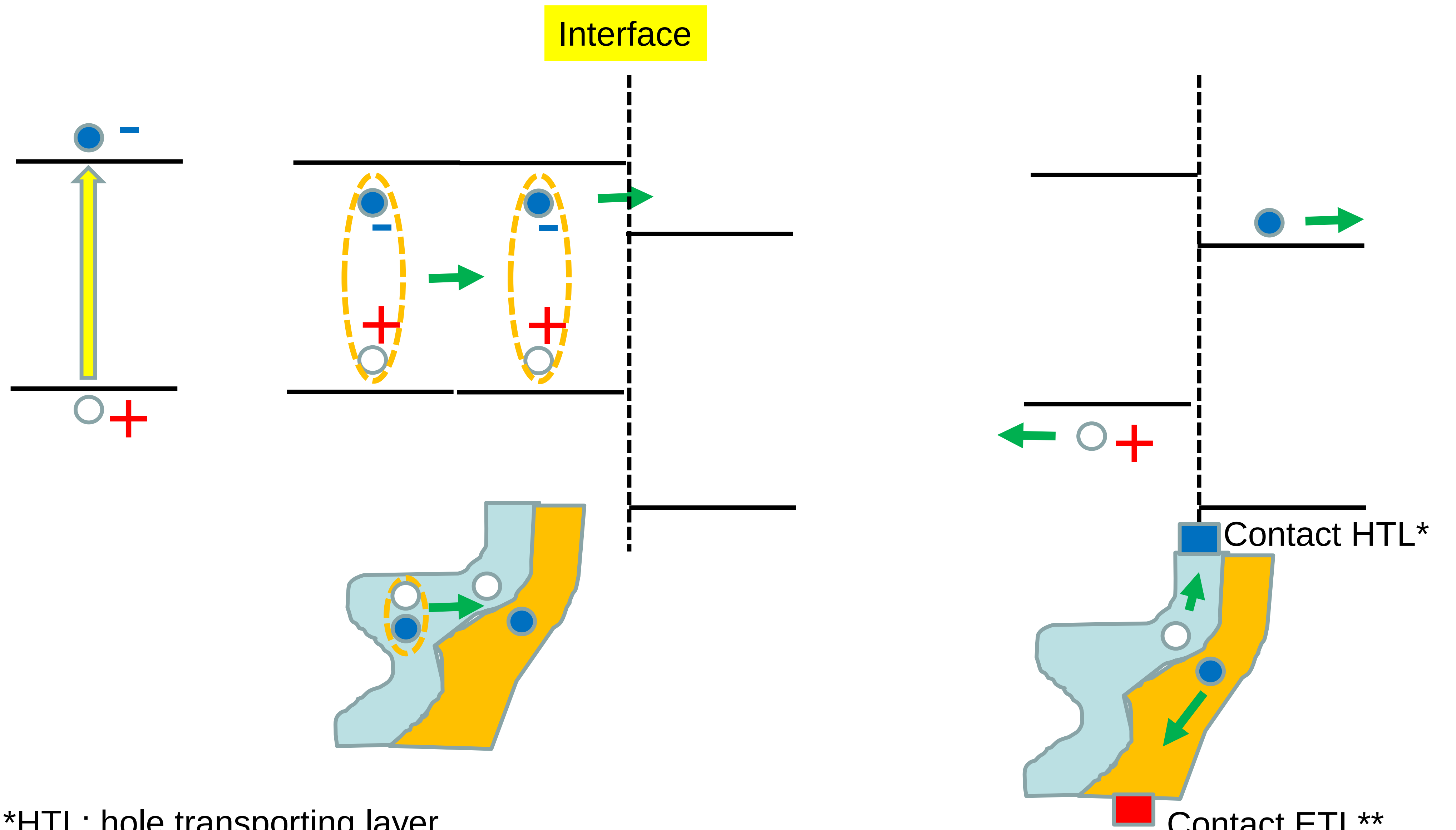




Formation de **paires électron-trou libres**
Grandes longueurs de diffusion (1-500 microns)
→ collecte sur le longues distances
→ Dispositif par couches empilées p-n
→ Photovoltaïque classique

L'électron et le trou restent lés : **EXCITON**
Faible longueur de diffusion (10 -20 nm)
Recombinaison rapide,
pas d'assistance par le champ électrique
Pas le temps d'aller vers des contacts
→ Rendement PV faible avec structure classique (couches)

La dissociation des excitons et la séparation des charges se fait aux INTERFACES

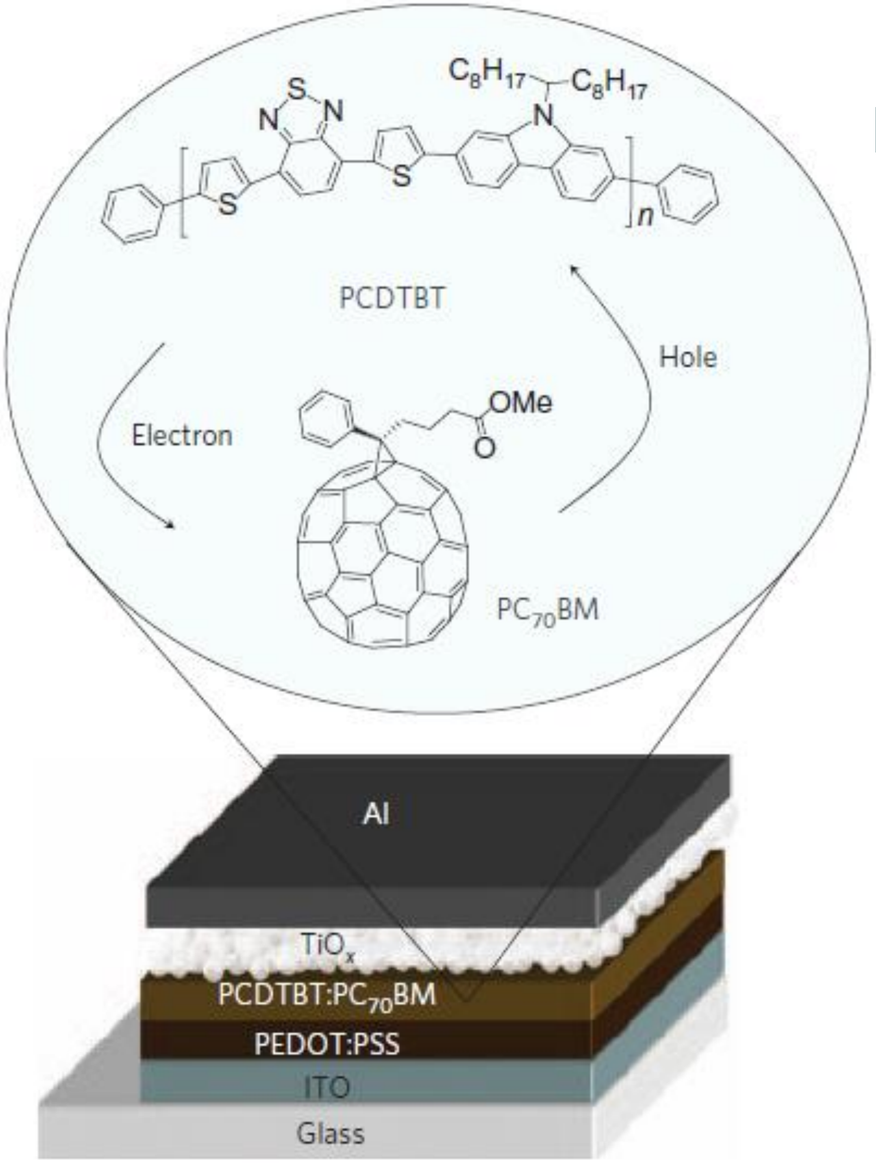


*HTL: hole transporting layer
**ETL: electron transporting layer

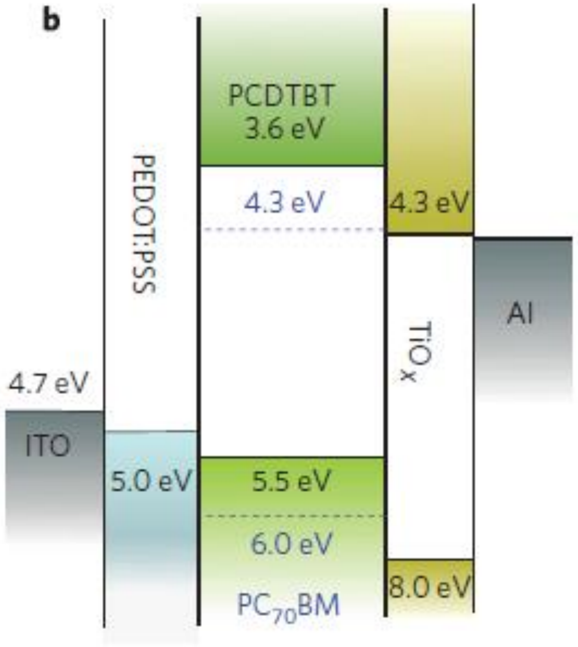
Daniel Lincot, Collège de France, 2/03/2022

Une rupture majeure !

Le photovoltaïque organique (OPV) prend son envol

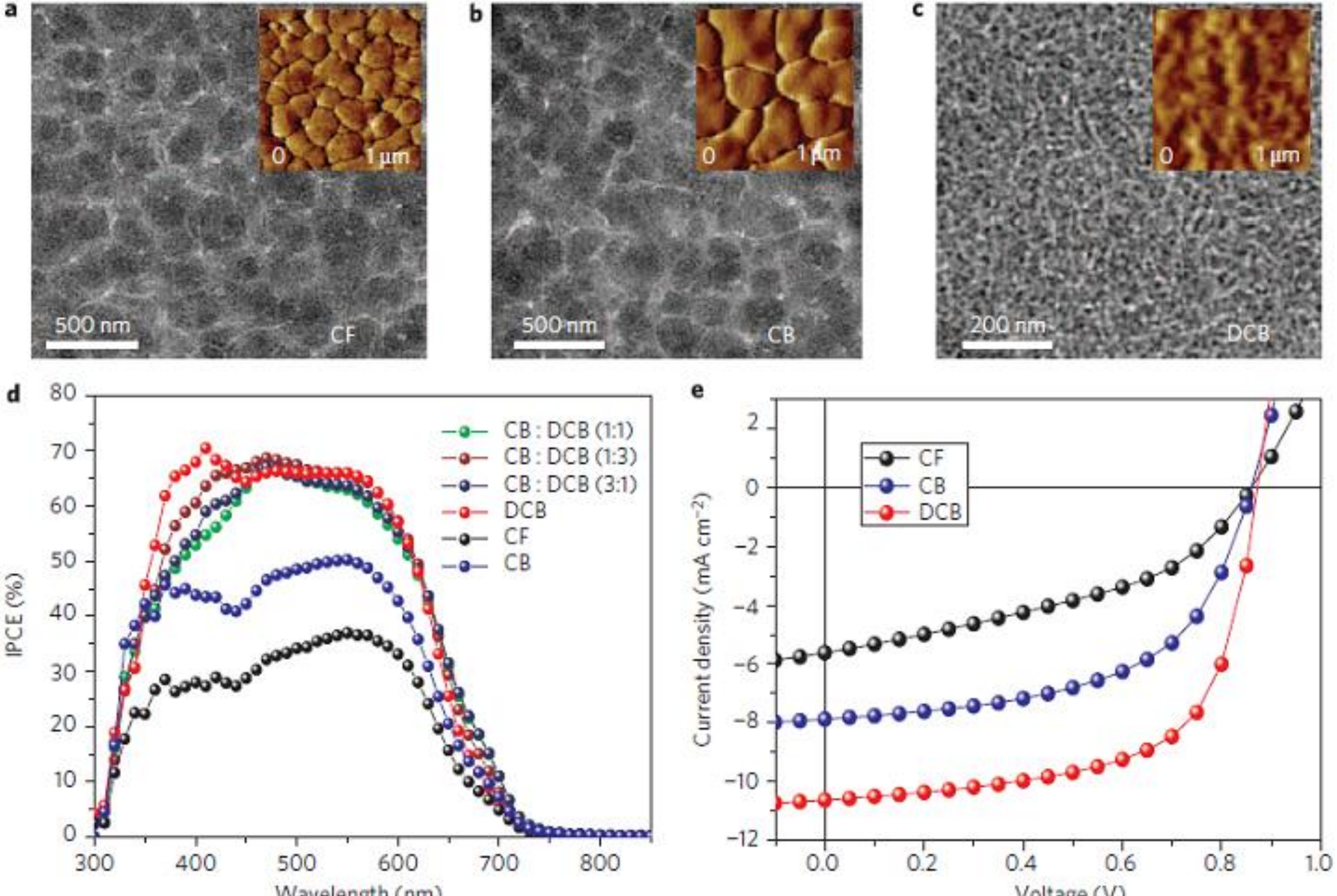


mélange



Park SH, Roy A, Beaupré S, Cho S, Coates N, Moon JS, Moses D, Leclerc M, Lee K et Heeger AJ (2009). Bulk heterojunction solar cells with internal quantum efficiency approaching 100%. *Nature Photonics*, **3** : 297-U5.

L'art du mélange et du séchage : Influence de l'organisation à l'échelle nanométrique des composants d'une cellule organique



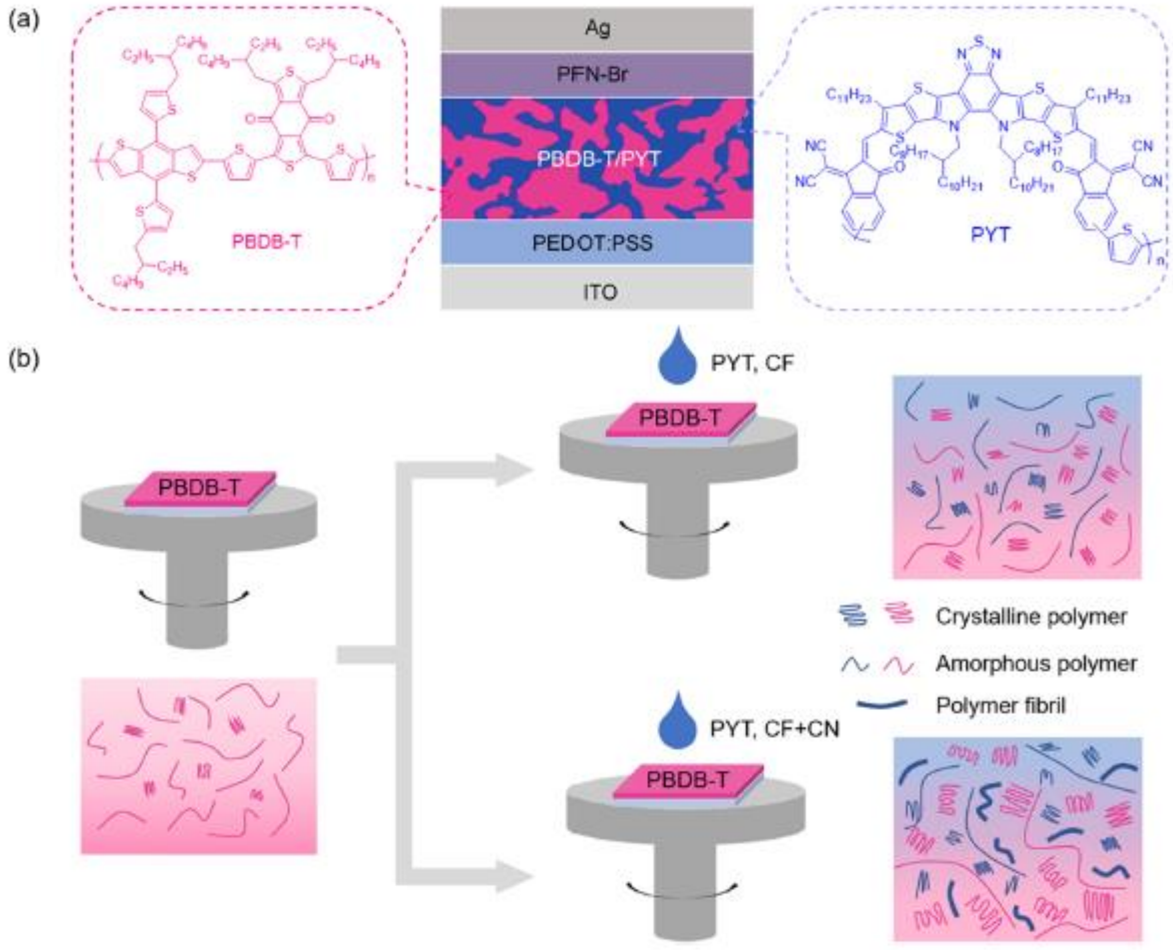
Park et al.
nature photonics
(2009)

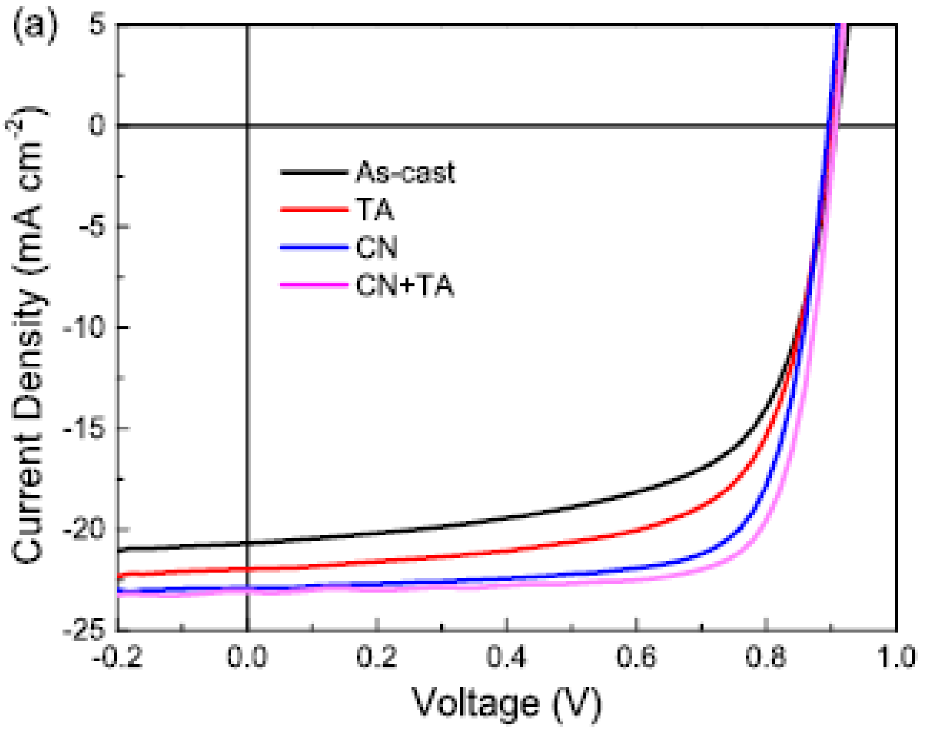
Daniel Lincot, Collège de France, 2/03/2022

Nano Energy 2022

Layer-by-layer processed binary all-polymer solar cells with efficiency over 16% enabled by finely optimized morphology

Yue Zhang [a,1], Baoqi Wu [a,1], Yakun He [b], Wanyuan Deng [a], Jingwen Li [a], Junyu Li [c], Nan Qiao [d], Yifan Xing [d], Xiyue Yuan [a], Ning Li [b], Christoph J. Brabec [b], Hongbin Wu [a], Guanghao Lu [d], Chunhui Duan [a,e,f,*], Fei Huang [a], Yong Cao [a]

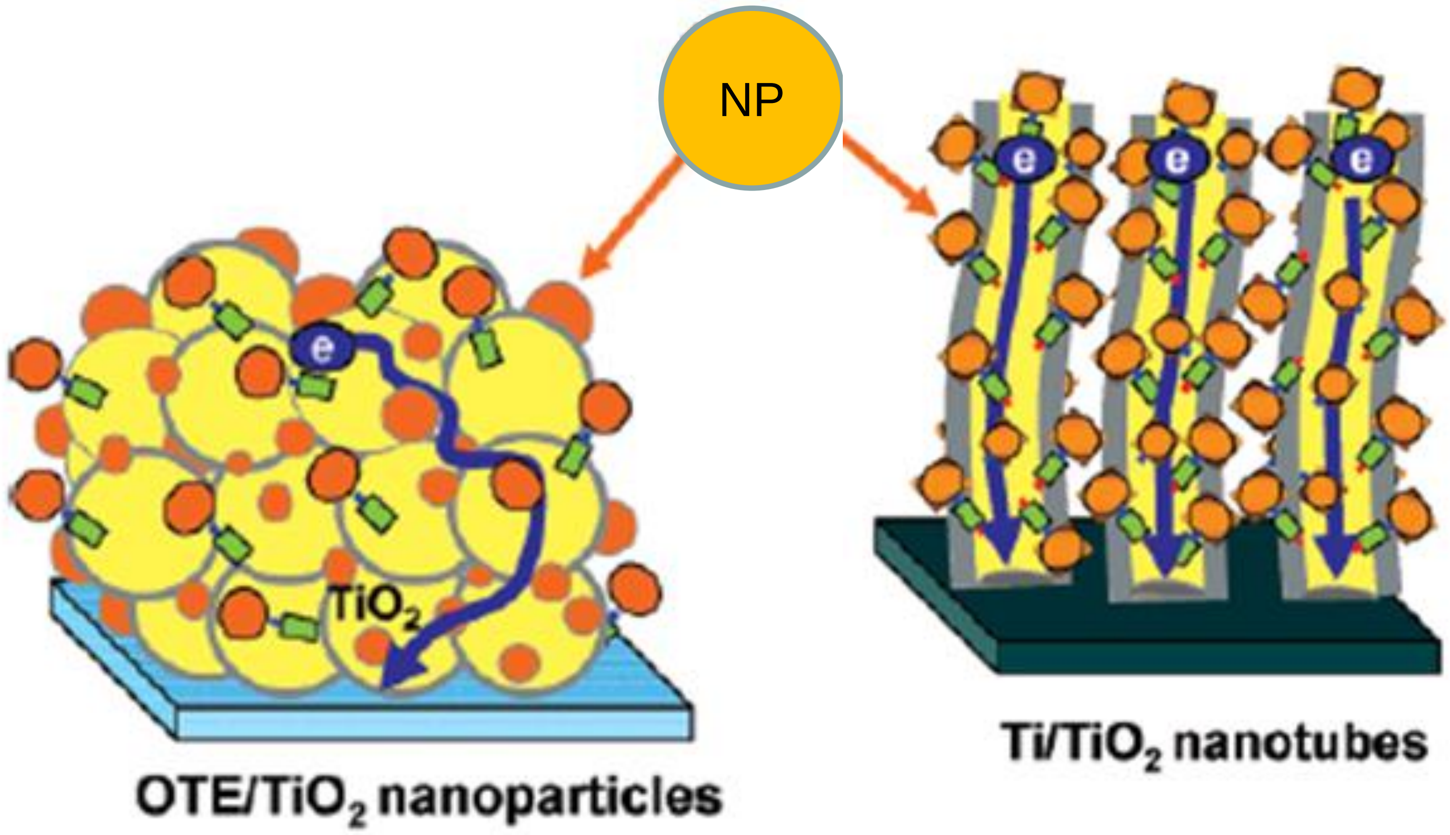




Au sources des cellules perovskites

Remplacer les molécules de colorants par des nanoparticules (quantum dots) dans les cellules à colorants

CdSe, CdS,PbS,InP,InAs : excellentes propriétés de luminescence
Absorption élevée….



Kongkanand A., Tvrdy K., Takechi K., Kuno M., Kamat P.V. (2008). J. Am. Chem. Soc. **130**, 4007.

2009

J|A|C|S COMMUNICATIONS

Published on Web 04/14/2009

Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells

Akihiro Kojima,[†] Kenjiro Teshima,[‡] Yasuo Shirai,[§] and Tsutomu Miyasaka*[,†,‡,∥]

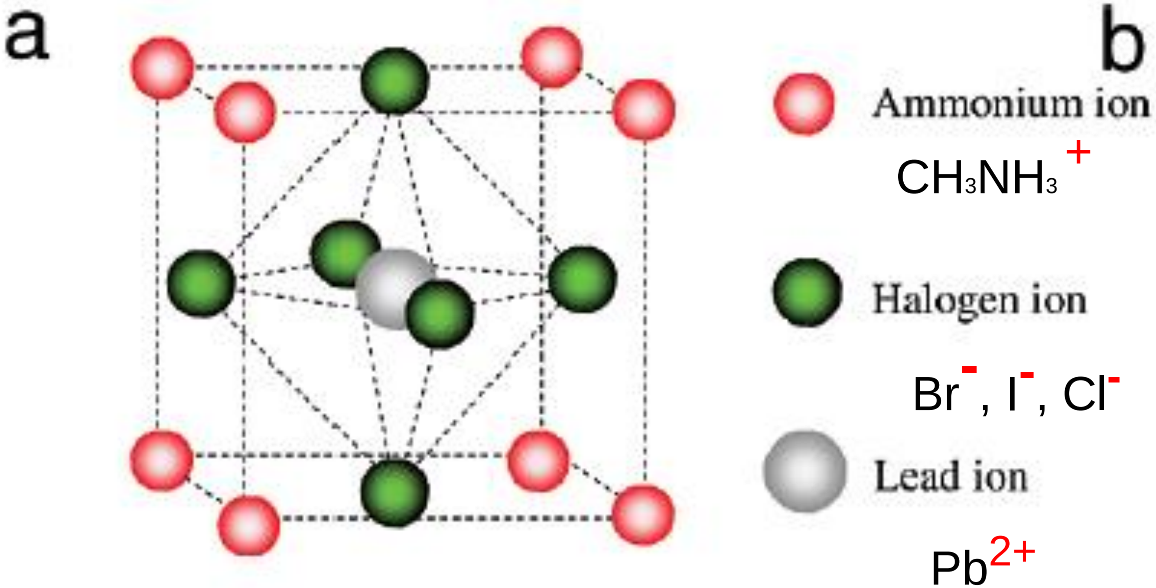
Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan, Graduate School of Engineering, Toin University of Yokohama, and Peccell Technologies, Inc., 1614 Kurogane-cho, Aoba, Yokohama, Kanagawa 225-8502, Japan, and Graduate School of Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan

Received December 9, 2008; Revised Manuscript Received April 1, 2009; E-mail: miyasaka@cc.toin.ac.jp

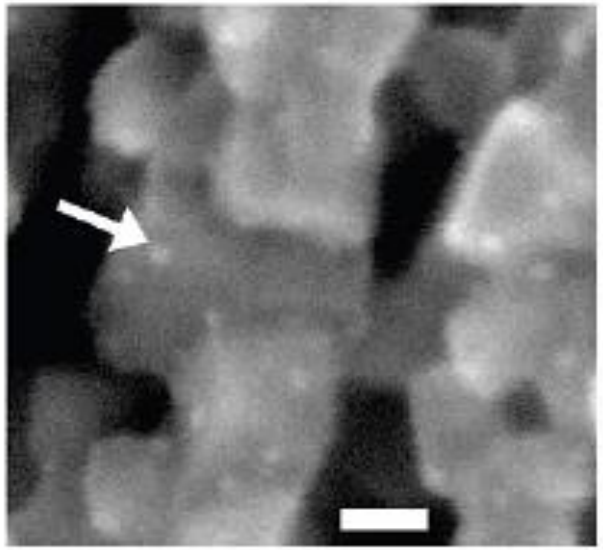
$CaTiO_3$

$(Mg,Fe)SiO_3$

$CH_3NH_3PbBr_3$



b



Daniel Lincot, Collège de France, 2/03/2022

La voie est ouverte

$CH_3NH_3PbI_3/TiO_2$-based cell employed 0.15 M LiI and 0.075 MI_2 dissolved in methoxyacetonitrile.

$CH_3NH_3PbBr_3/TiO_2$-based cell employed an electrolyte of 0.4 M LiBr and 0.04 M Br_2 dissolved in acetonitrile

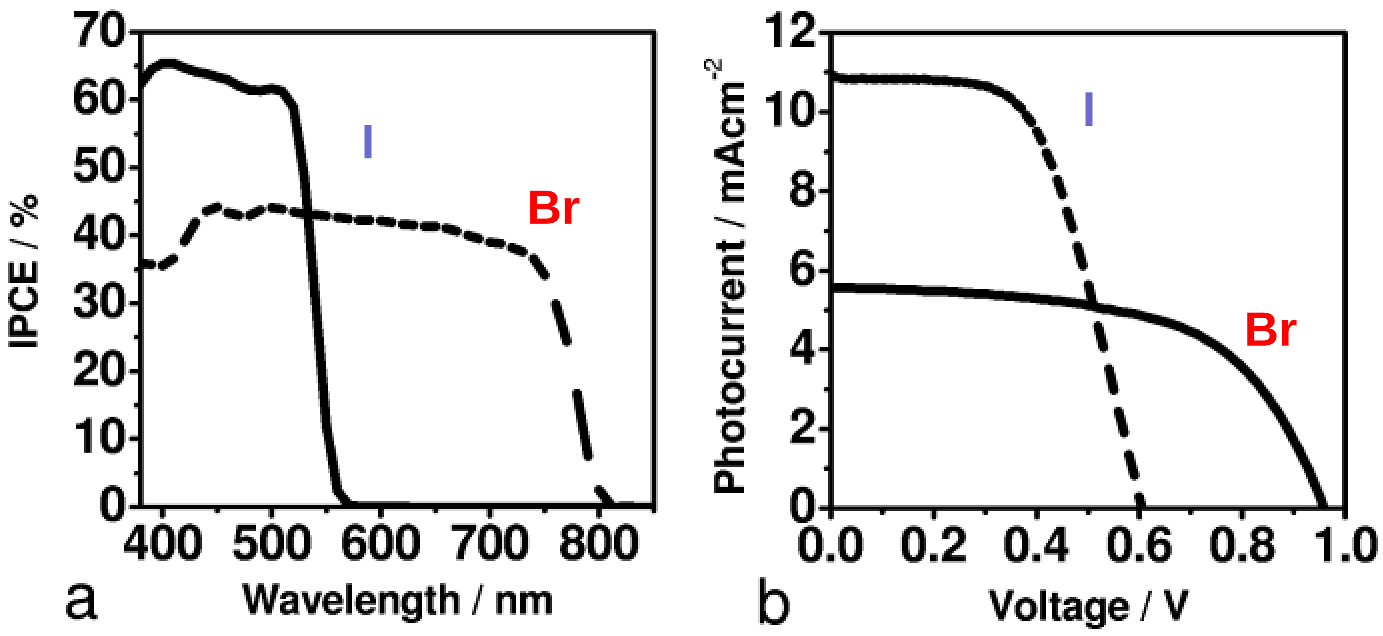


Table 1. Photovoltaic Characteristics of Perovskite-Based Cells[a]

perovskite sensitizer on TiO_2	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
$CH_3NH_3PbBr_3$	5.57	0.96	0.59	3.13
$CH_3NH_3PbI_3$	11.0	0.61	0.57	3.81

Mais

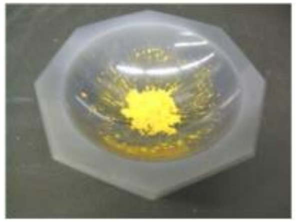
In studies of durability, continuous irradiation caused a photocurrent decay for an open cell exposed to air; this mechanism needs more study to improve the cell lifetime

Grandes possibilités d'ingénierie de bande interdite par substitution anionique ou cationique

Premiers essais dans une architecture de cellule à colorant (DSSC) avec des îlots

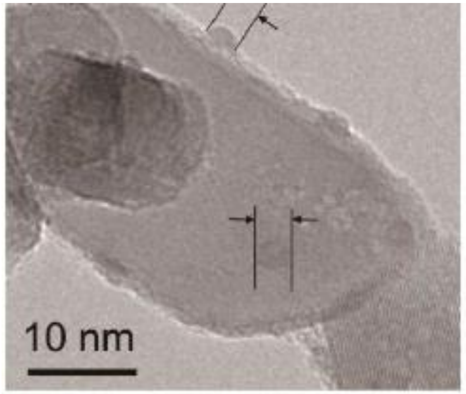
T. Myasaka, Tokyo, 2009

η=3.8%



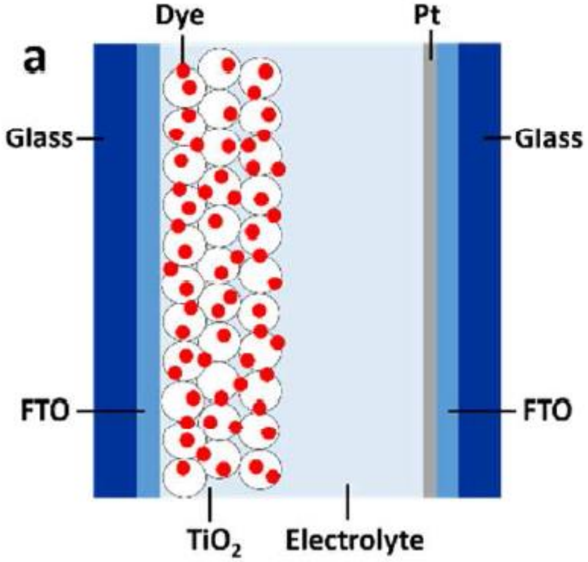
$CH_3NH_3PbBr_3$

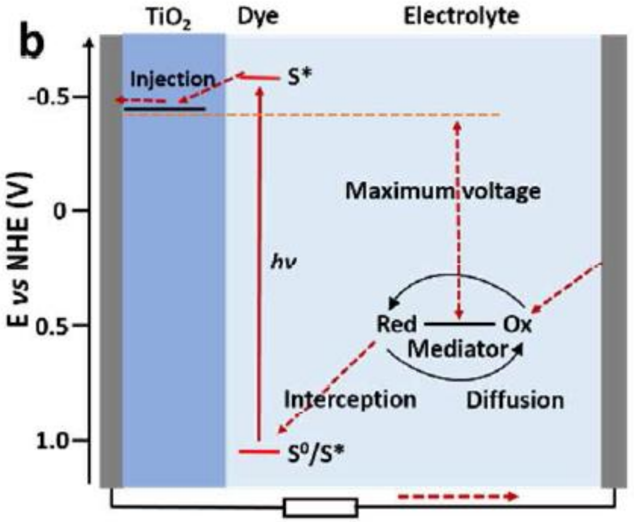
$CH_3NH_3PbI_3$

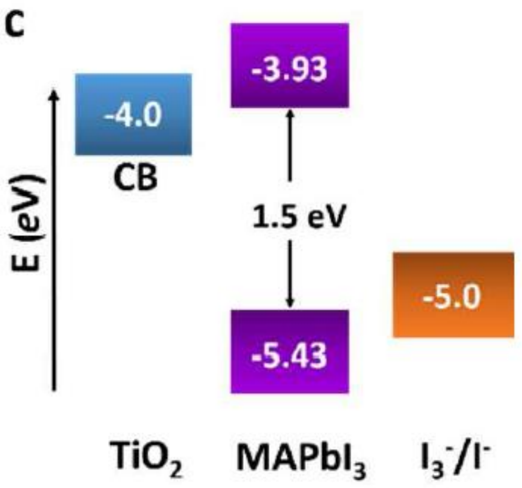


N. G. Park, Corée,2011

η=6.5%







Source : Jacky Even (laboratoire FOTON, Rennes)

Les cellules pérovskites s'affranchissent des cellules à colorants

2012

Les cellules perovskites d'affranchissent des cellules à colorants
→ Nouvelle filière couches minces tout solide
→ Apport des cellules à colorants (contacts mésoscopiques TiO_2) et de l'OPV (couches organiques ETL, HTL)

2012

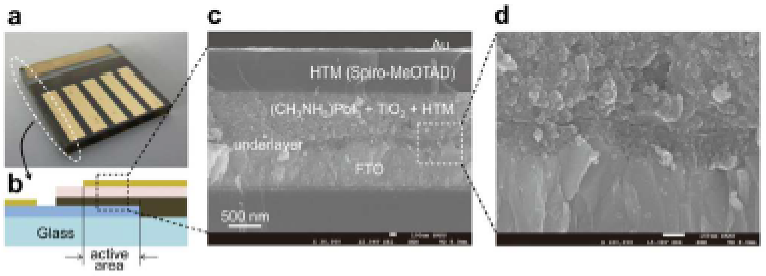
On passe au tout solide !

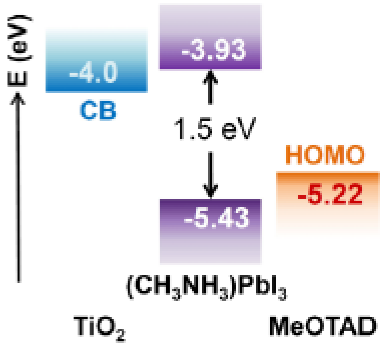
η=9.7%

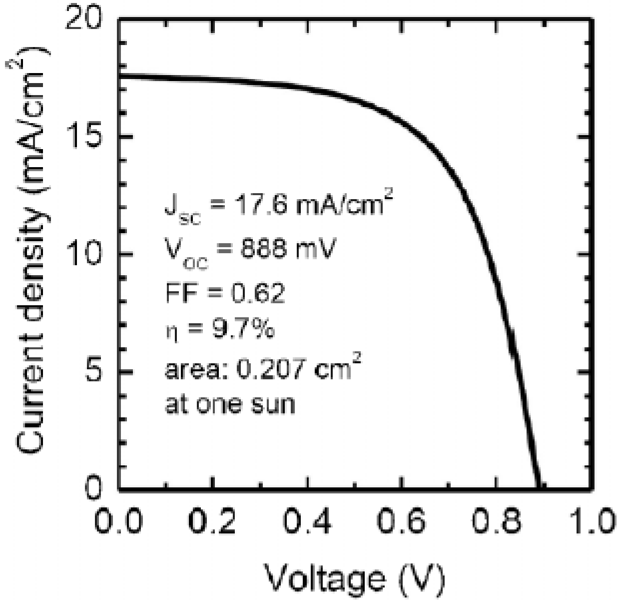
Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%

Hui-Seon Kim[1], Chang-Ryul Lee[1], Jeong-Hyeok Im[1], Ki-Beom Lee[1], Thomas Moehl[2], Arianna Marchioro[2], Soo-Jin Moon[2], Robin Humphry-Baker[2], Jun-Ho Yum[2], Jacques E. Moser[2], Michael Grätzel[2] & Nam-Gyu Park[1]

Scientific Reports 2012







Source : Jacky Even

Comment est il possible que les électrons soient transportés via un isolant (Al_2O_3) ?
Le transport se fait dans la perovskite comme dans un semiconducteur classique !

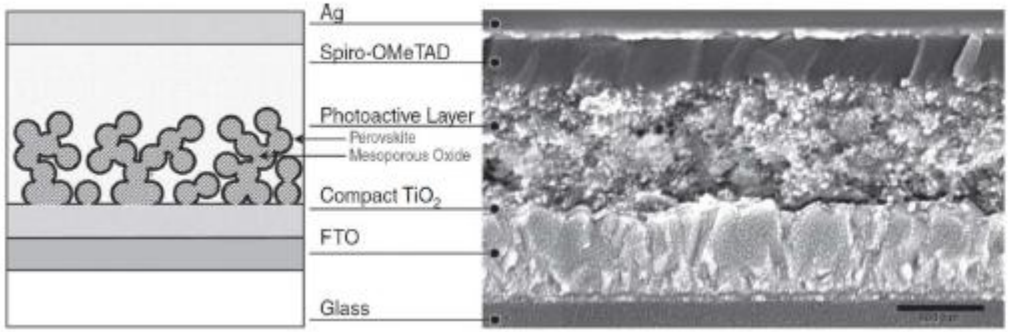
2012

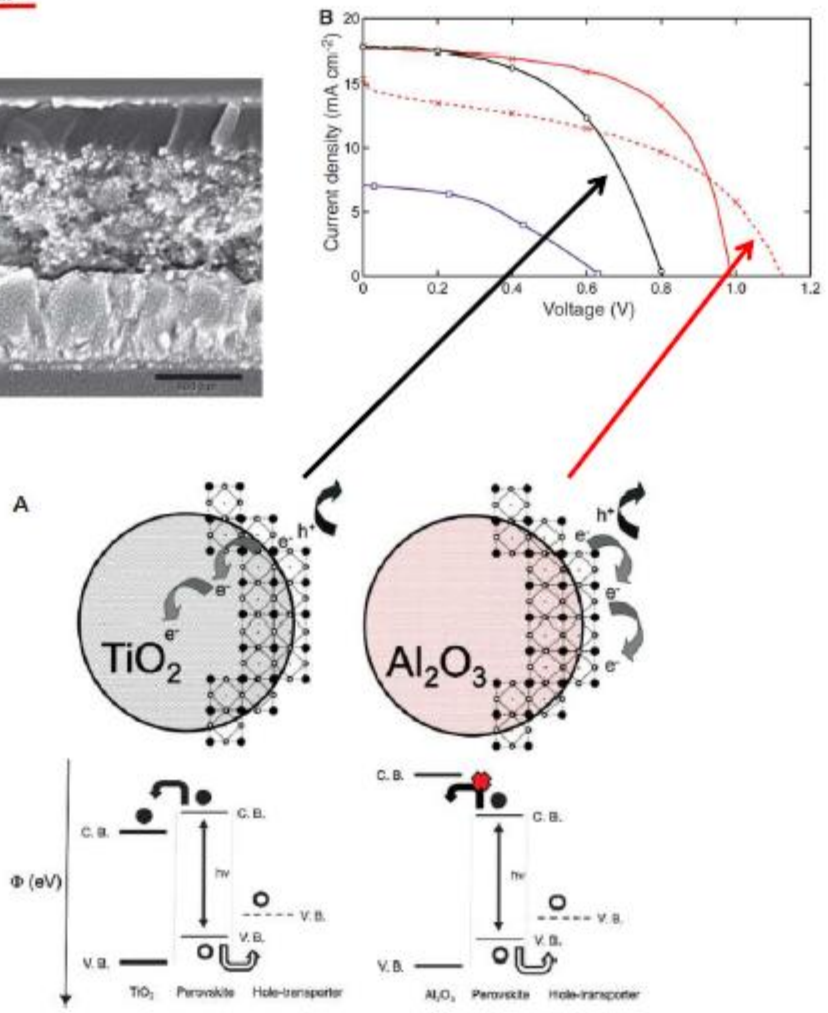
Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites

Science 2012

η=10.9%

Michael M. Lee,[1] Joël Teuscher,[1] Tsutomu Miyasaka,[2] Takurou N. Murakami,[2,3] Henry J. Snaith[1*]



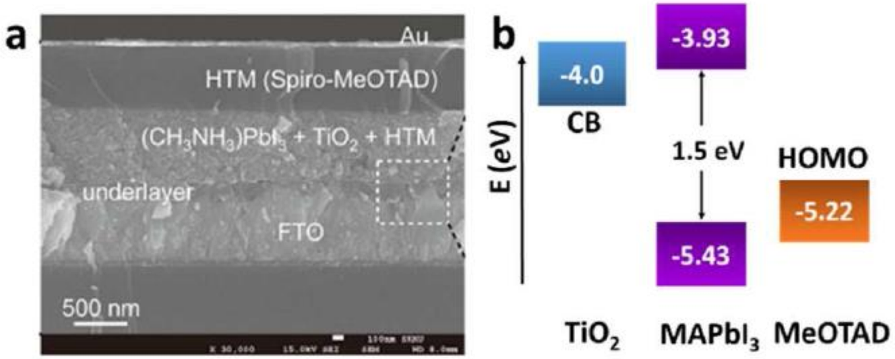


Source: Jacky Even

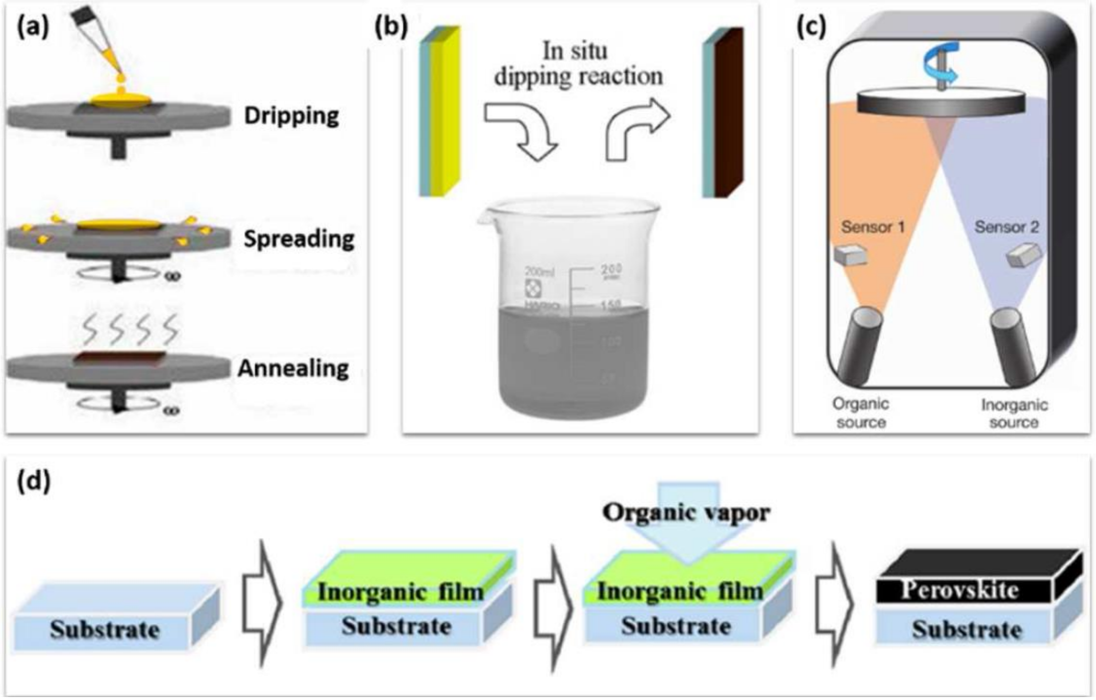
Daniel Lincot, Collège de France, 2/03/2022

Depuis 2012, évolution des concepts de cellules et des procédés

M. Graetzel, Lausanne



H. Snaith, Oxford



a) Dépôt en une étape du précurseur
b) Dépôt séquentiel en deux étapes
c) Dépôt en phase vapeur avec deux sources
d) Dépôt en solution assisté par phase vapeur

Source : Jacky Even

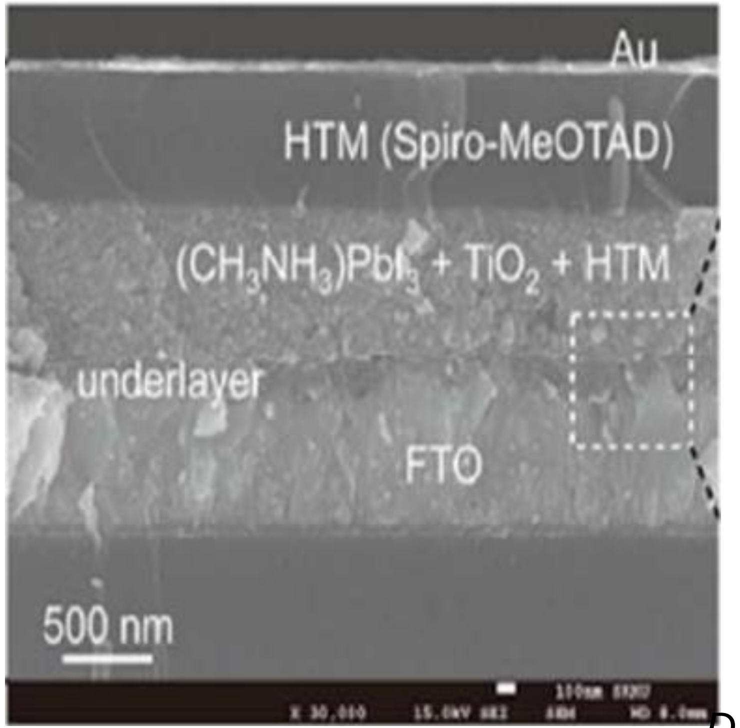
Tsutomu Miyasaka

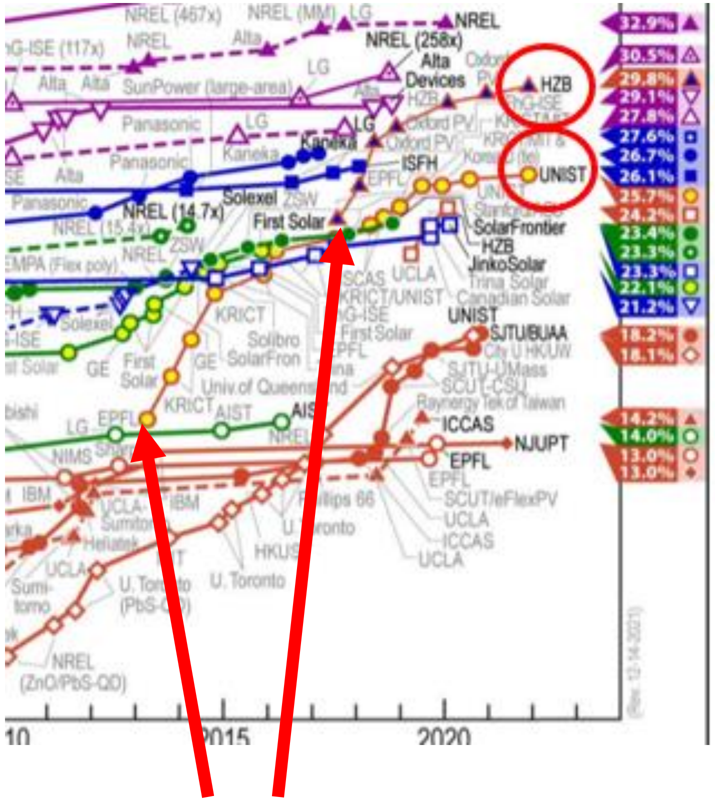
2009 : 3,8 %

$Pb(CH_3NH_3)I_3$

MA : $CH_3NH_3^+$

« MAPI » : $MAPbI_3$





Deux naissances

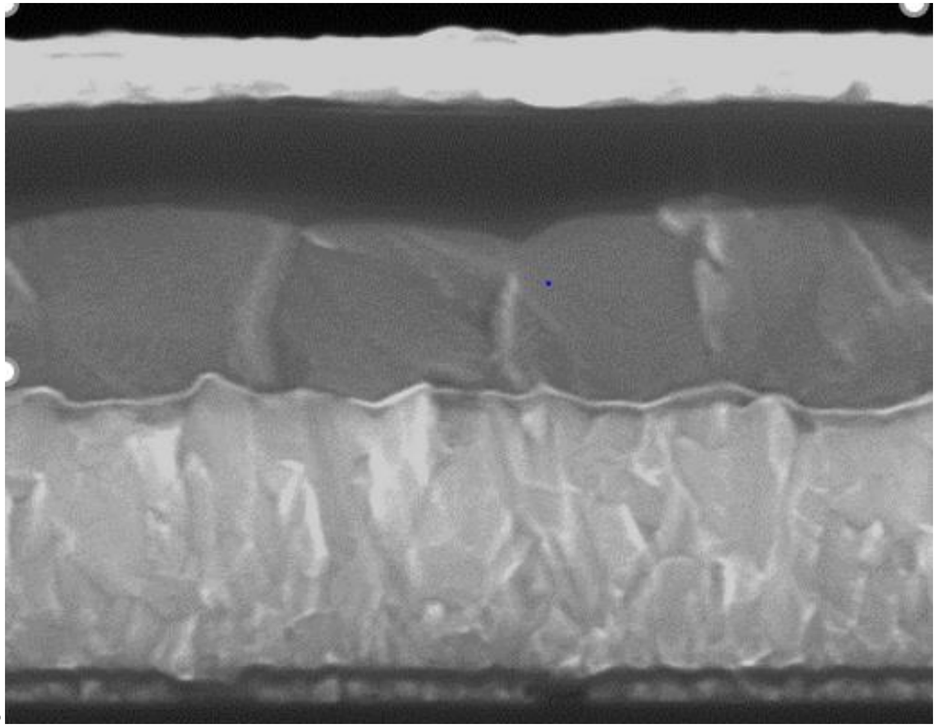
2022 : 25,2 %

$Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$

MA→ FA : $HC(NH_2)_2^+$ → Cs^+, Rb^+,

I→ Br

Pb→ Sn



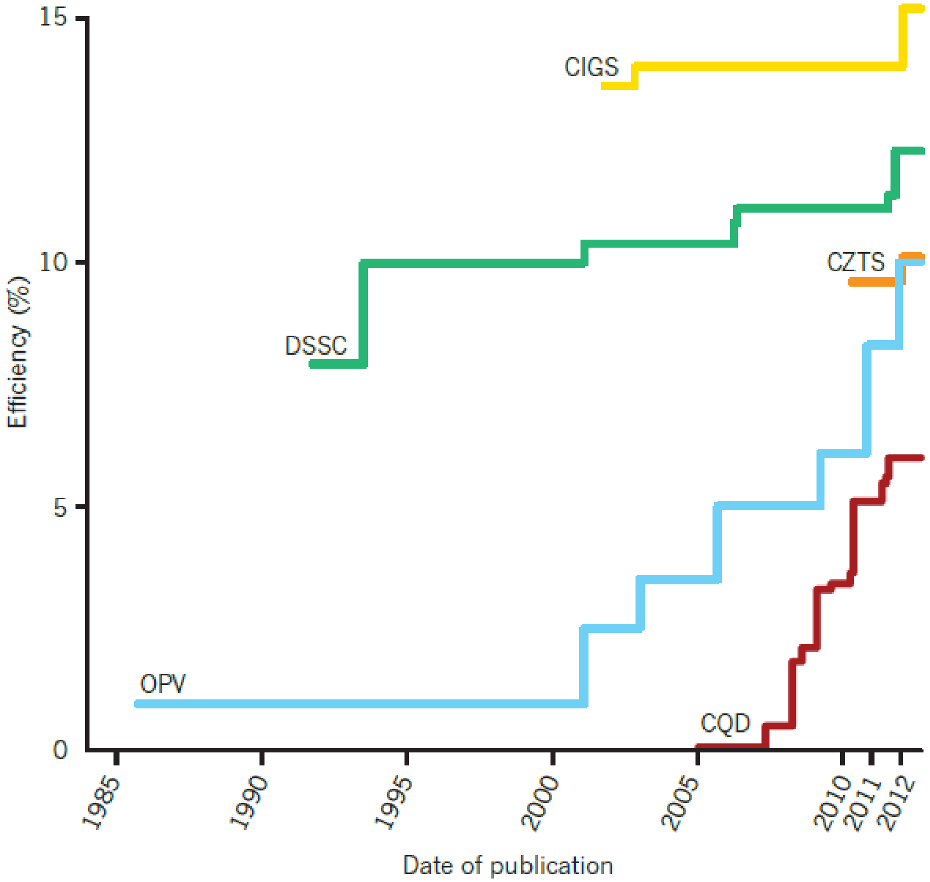
2012

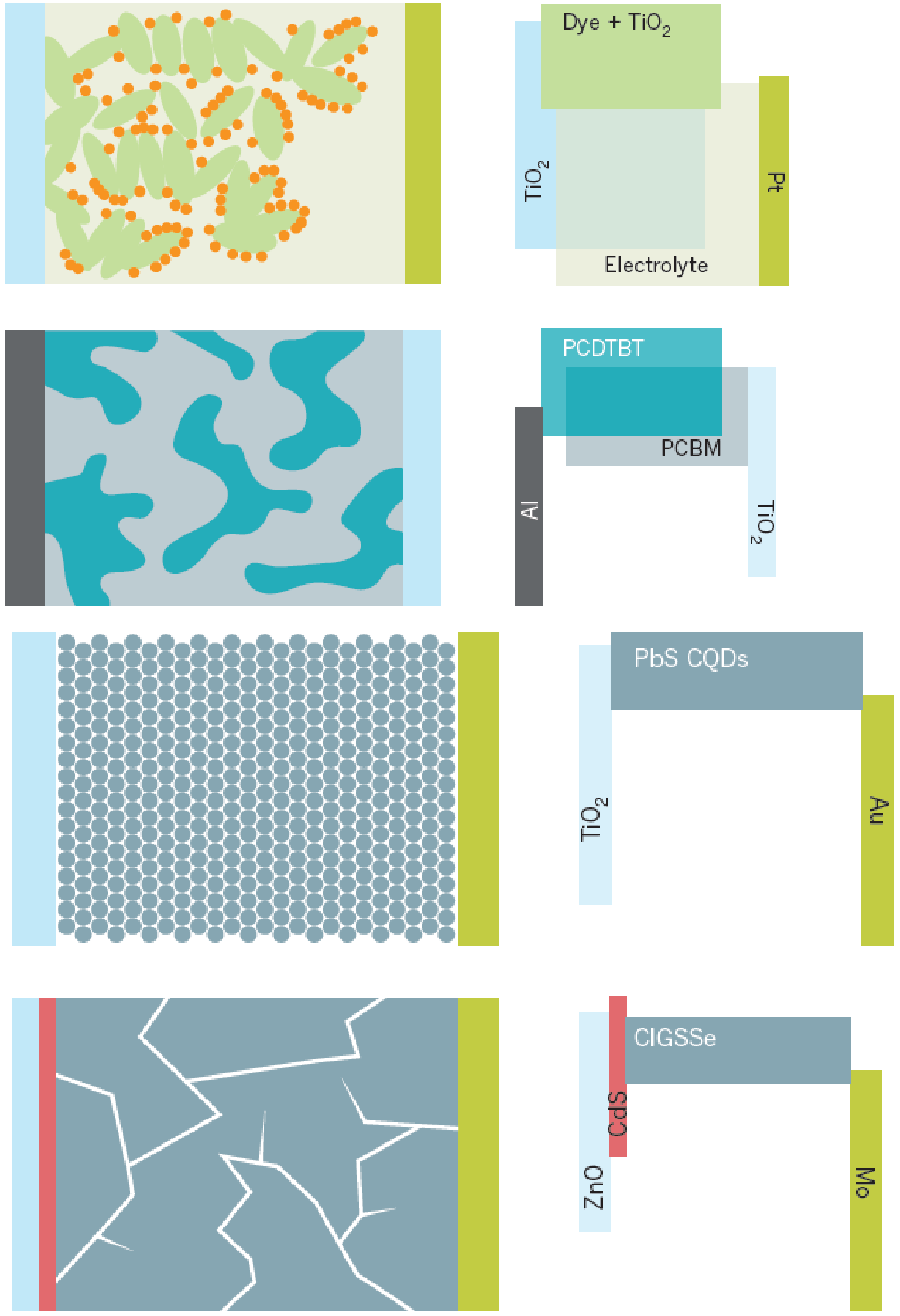
REVIEW

308 | NATURE | VOL 488 | 16 AUGUST 2012

Materials interface engineering for solution-processed photovoltaics

Michael Graetzel[1], René A. J. Janssen[2], David B. Mitzi[3] & Edward H. Sargent[4]





Daniel Lincot, Collège de France, 2/03/2022

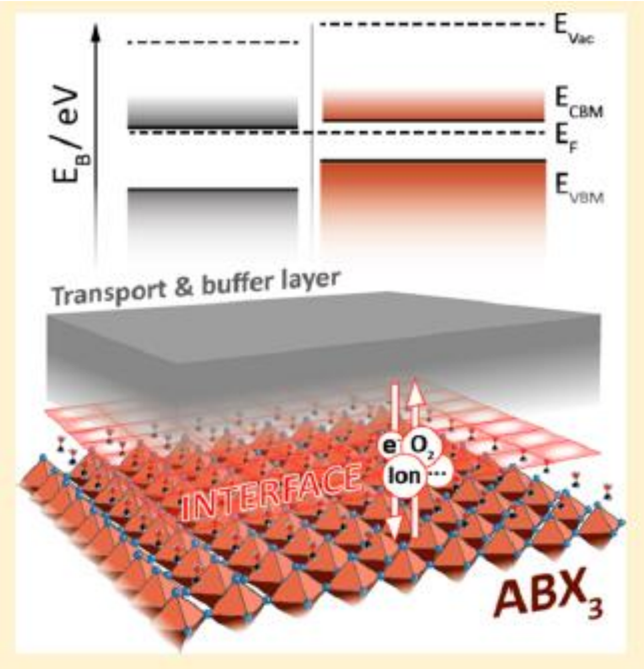
2019

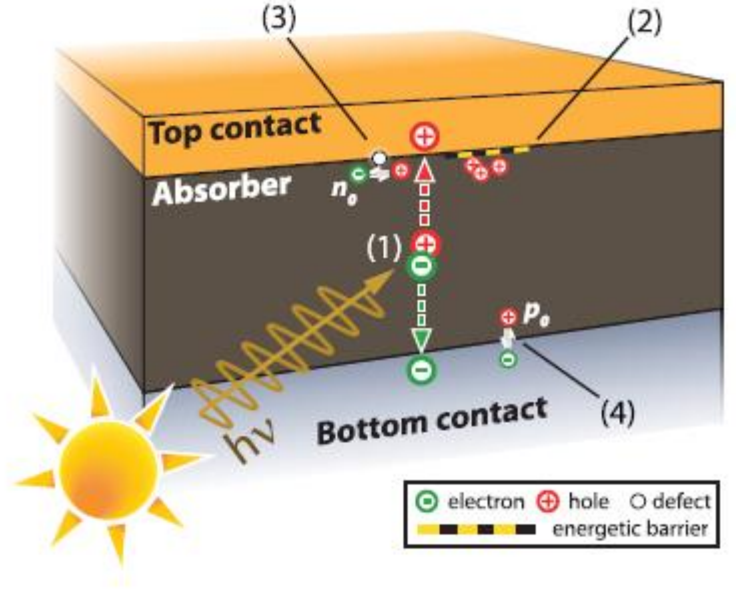
CHEMICAL REVIEWS
Review
Cite This: Chem. Rev. XXXX, XXX, XXX−XXX
pubs.acs.org/CR

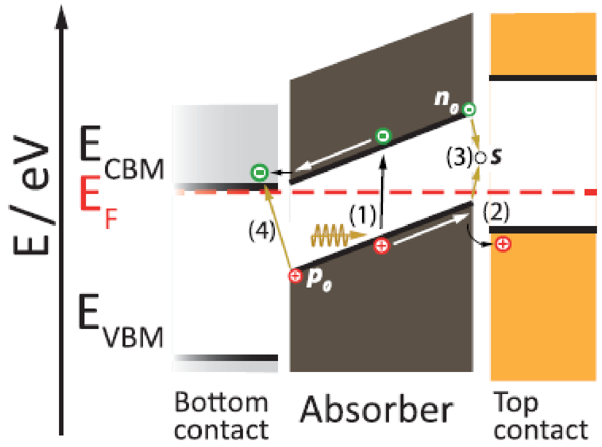
Halide Perovskites: Is It All about the Interfaces?

Philip Schulz,[*,†,‡,∇] David Cahen,[§] and Antoine Kahn[∥]

[†]Institut Photovoltaïque d'Île-de-France (IPVF), 91120 Palaiseau, France
[‡]CNRS, Institut Photovoltaïque d'Île de France (IPVF), UMR 9006, 91120 Palaiseau, France
[∇]National Center for Photovoltaics, National Renewable Energy Laboratory, Golden, Colorado 80401, United States
[§]Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel
[∥]Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544, United States







Interface-related loss mechanisms in a simplified photovoltaic device. After photoexcitation (1) carrier transport to the contact interfaces occurs without significant losses. At the interface, carrier extraction can be impaired by (2) interfacial energy barriers due to inadequate band alignment, (3) defect-induced surface (interface) recombination velocity S, and (4) back recombination of extracted carriers, which still reside in the interface region. E_{CBM}, E_{VBM}, and E_F are the conduction band minimum, valence band maximum, and Fermi level, respectively. Reprinted from ref 57. Copyright 2018 American Chemical Society.

2022 Sous presse

ACS APPLIED MATERIALS & INTERFACES

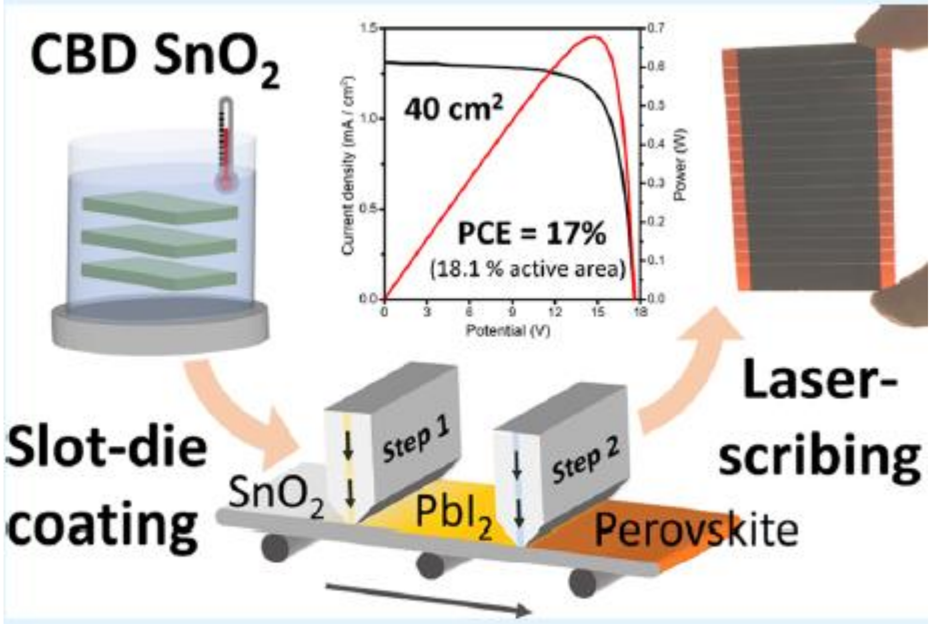
IPVF

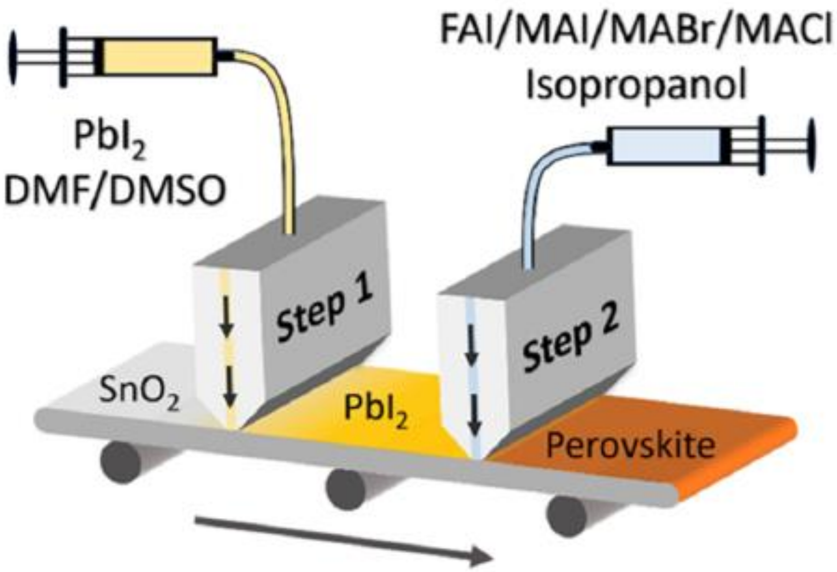
www.acsami.org Research Article

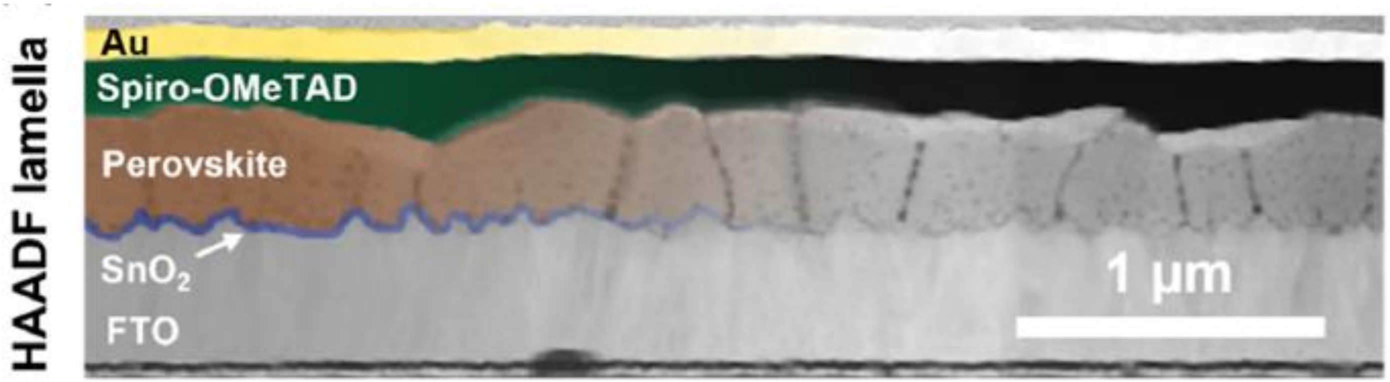
Industrially Compatible Fabrication Process of Perovskite-Based Mini-Modules Coupling Sequential Slot-Die Coating and Chemical Bath Deposition

Iwan Zimmermann,* Marion Provost, Salim Mejaouri, Marc Al Atem, Alexandre Blaizot, Aurélien Duchatelet, Stéphane Collin, and Jean Rousset

Cite This: https://doi.org/10.1021/acsami.1c24558 Read Online





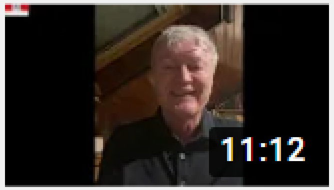


https://www.ipvf.fr/fr/symposium-edmond-becquerel/

Vidéos du Symposium (version française)

Vidéos du Symposium (version anglaise)

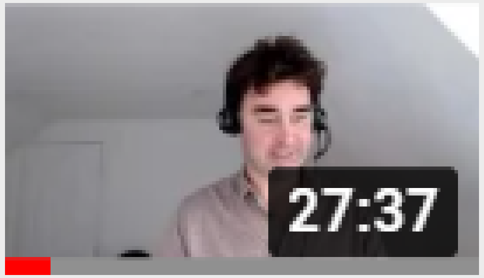
Témoignages Vidéos



Michael Graetzel - Genèse et développement du photovoltaïque moléculaire et des cellules perovskite

Becquerel Day Testimonies

https://www.youtube.com/watch?v=G4w44Al51Ss&list=PL5UqkzFNKba-2yAtWSsilXzEiIuFPk36A&index=8



Henry Snaith - The advent of Perovskite solar cells

Becquerel Day Testimonies

https://www.youtube.com/watch?v=QCy5vjb1FlY&list=PL5UqkzFNKba-csyN3DAazWTEEaNwvX9Wj&index=16

Sources complémentaires

→Pérovskites : Jacky Even

http://foton.cnrs.fr/v2016/article124.html

https://perocube.eu/video-interview-at-jacky-even-for-cnrs/

https://gdr-hpero.cnrs.fr/

→PV organique : Guillaume Wantz

https://www.ims-bordeaux.fr/fr/annuaire/5117-wantz-guillaume

Réseau PV organique

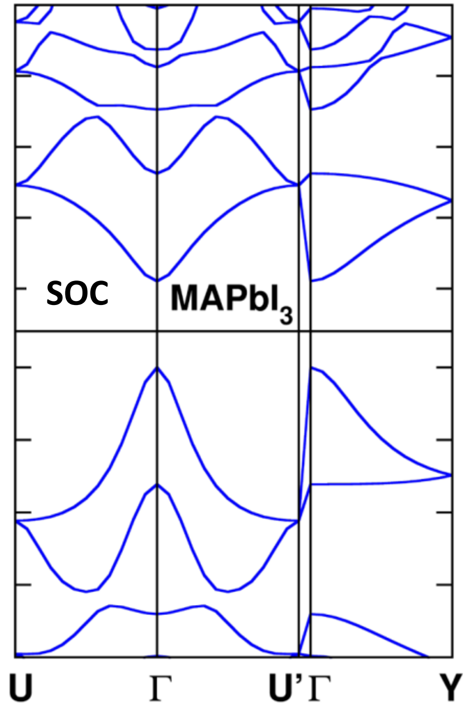
Voir aussi vidéo d'introductionde Guillaume Wantz en 2012

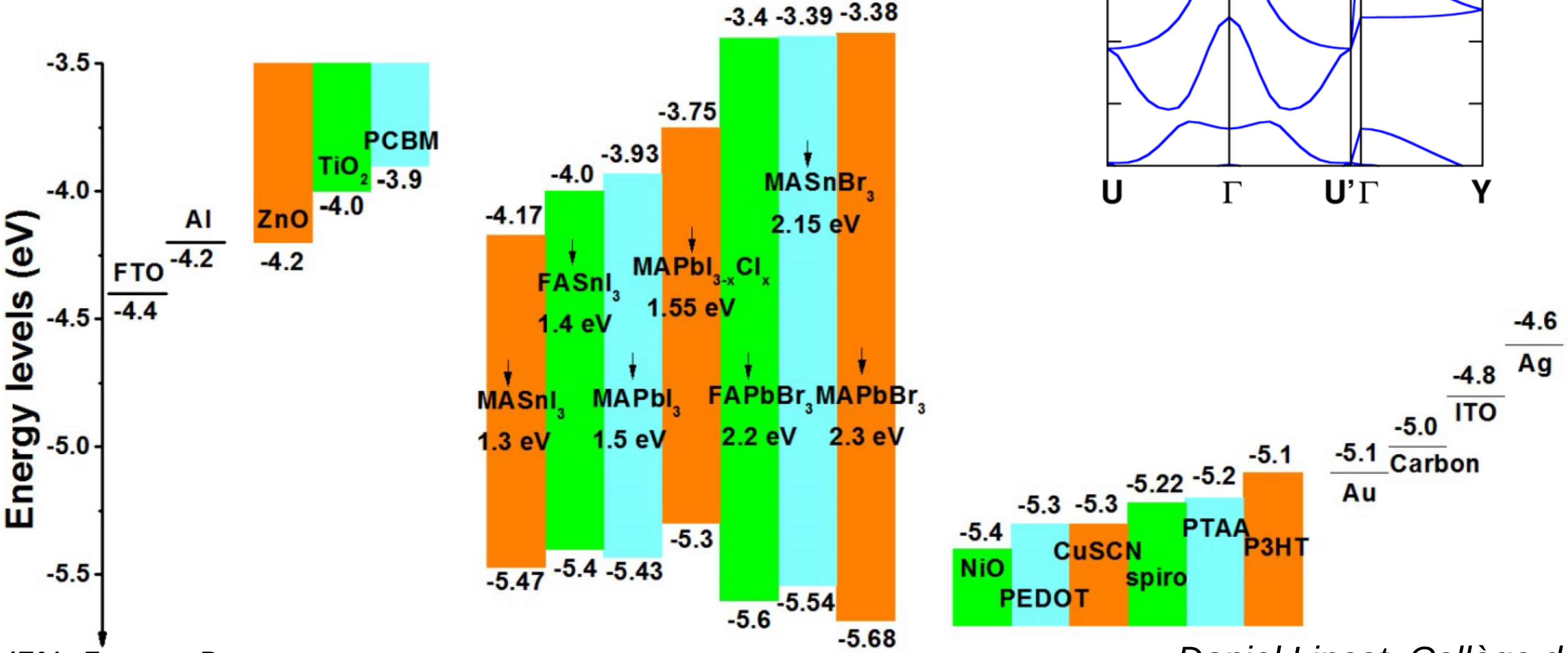
https://www.youtube.com/watch?v=Gros9zotFus

Des propriétés physiques exceptionnelles

https://cv.archives-ouvertes.fr/jacky-even

a) Structure de bandes favorable m_e=0.15, m_h=0.12
b) Quasi-absence de niveaux électroniques profonds
c) Exciton quasi-dissocié à la température ambiante
d) Longueurs de diffusion de 100nm à 1micron
e) Possibilités d'ingénierie de gap optique





Source : Jacky EVEN, Foton, Rennes

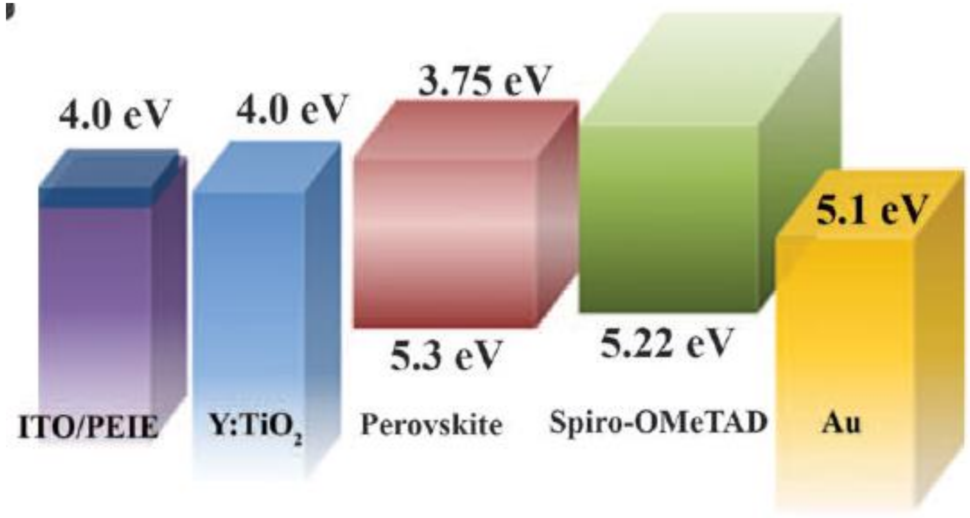
Daniel Lincot, Collège de France, 2/03/2022

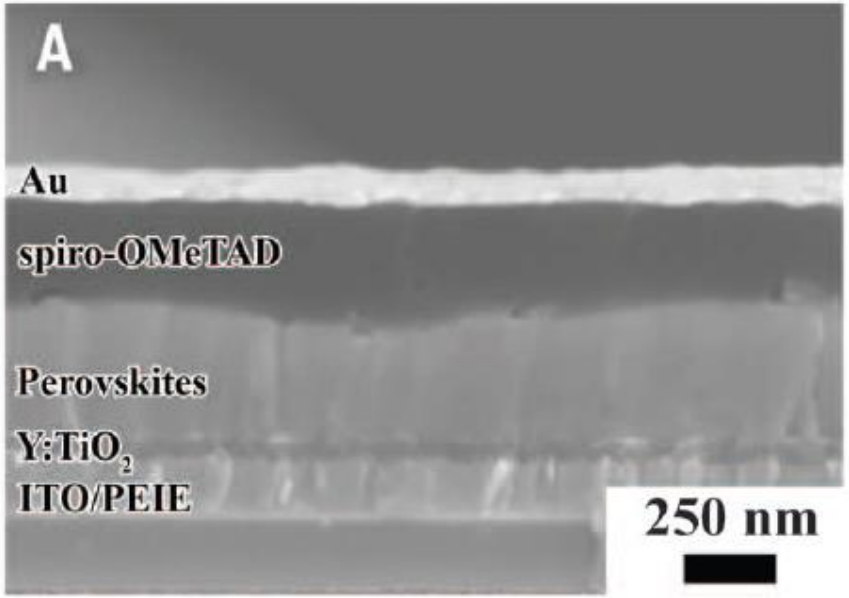
Interface engineering of highly efficient perovskite solar cells

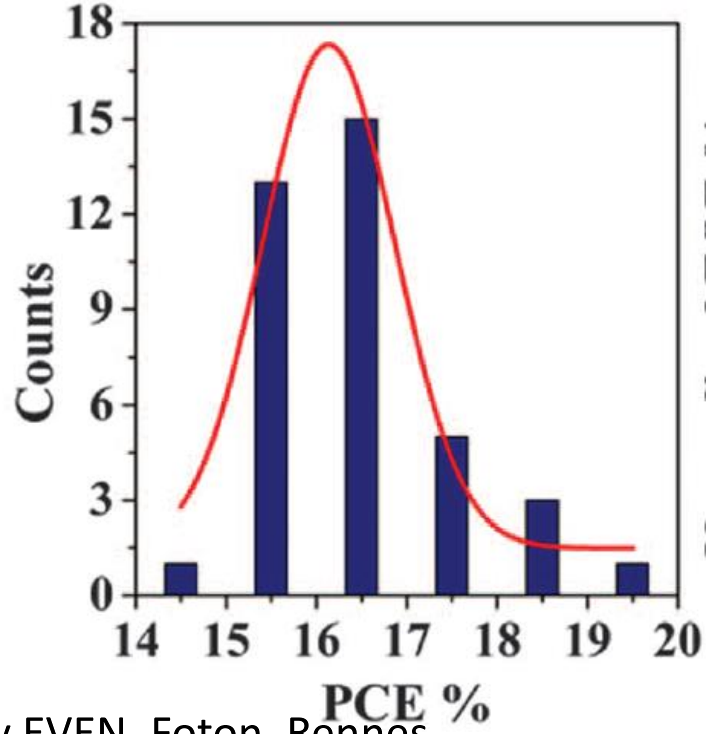
H. Zhou, Qi Chen, G. Li,1 S. Luo, T. Song, H. Duan, Z. Hong, J. You, Y. Liu, Y. Yang UCLA

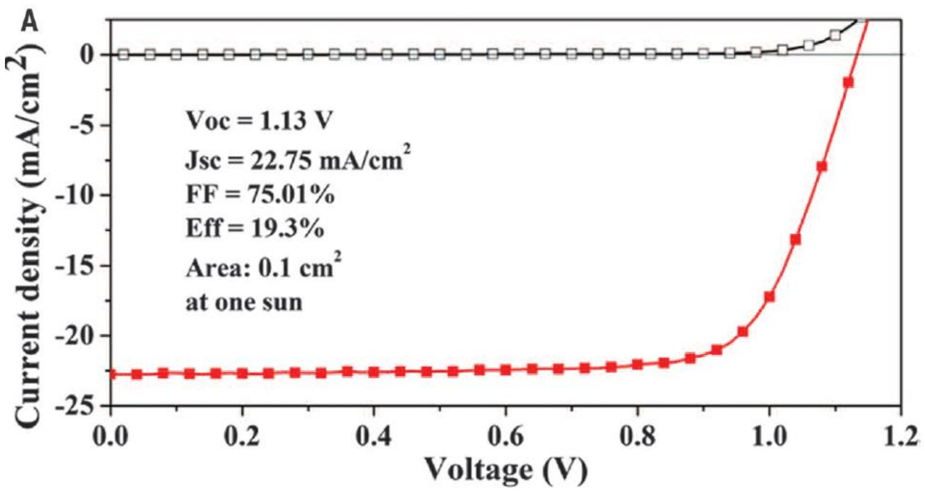
η=19.3%

Science 2014









In the jungle of OPV materials

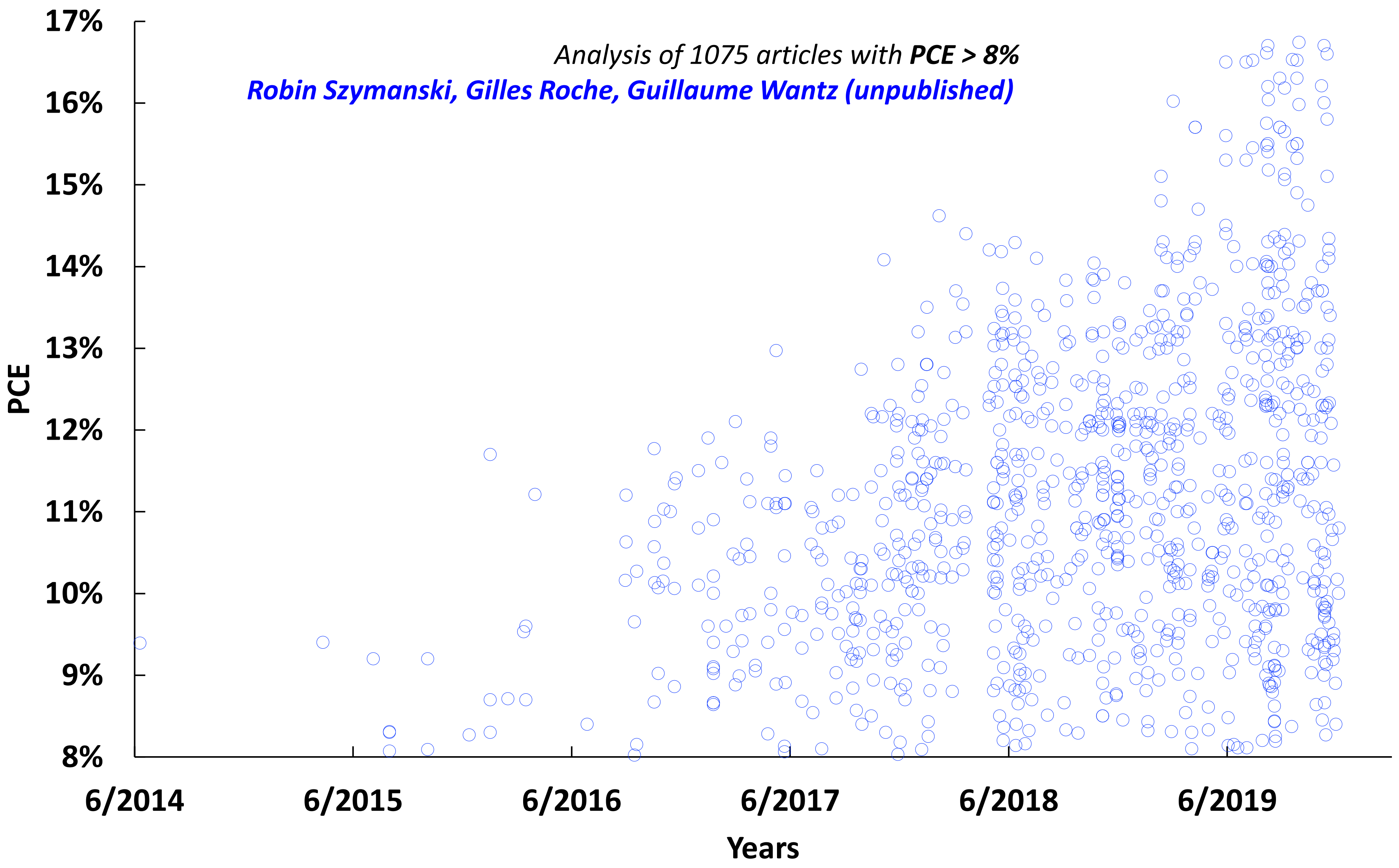
Voir aussi vidéo de Guillaume Wantz en 2012
https://www.youtube.com/watch?v=Gros9zotFus

Guillaume Wantz
guillaume.wantz@ims-bordeaux.fr

Bordeaux INP, ENSCBP, University of Bordeaux
IMS Laboratory (UMR CNRS 5218), FRANCE

Source : Guillaume Wantz

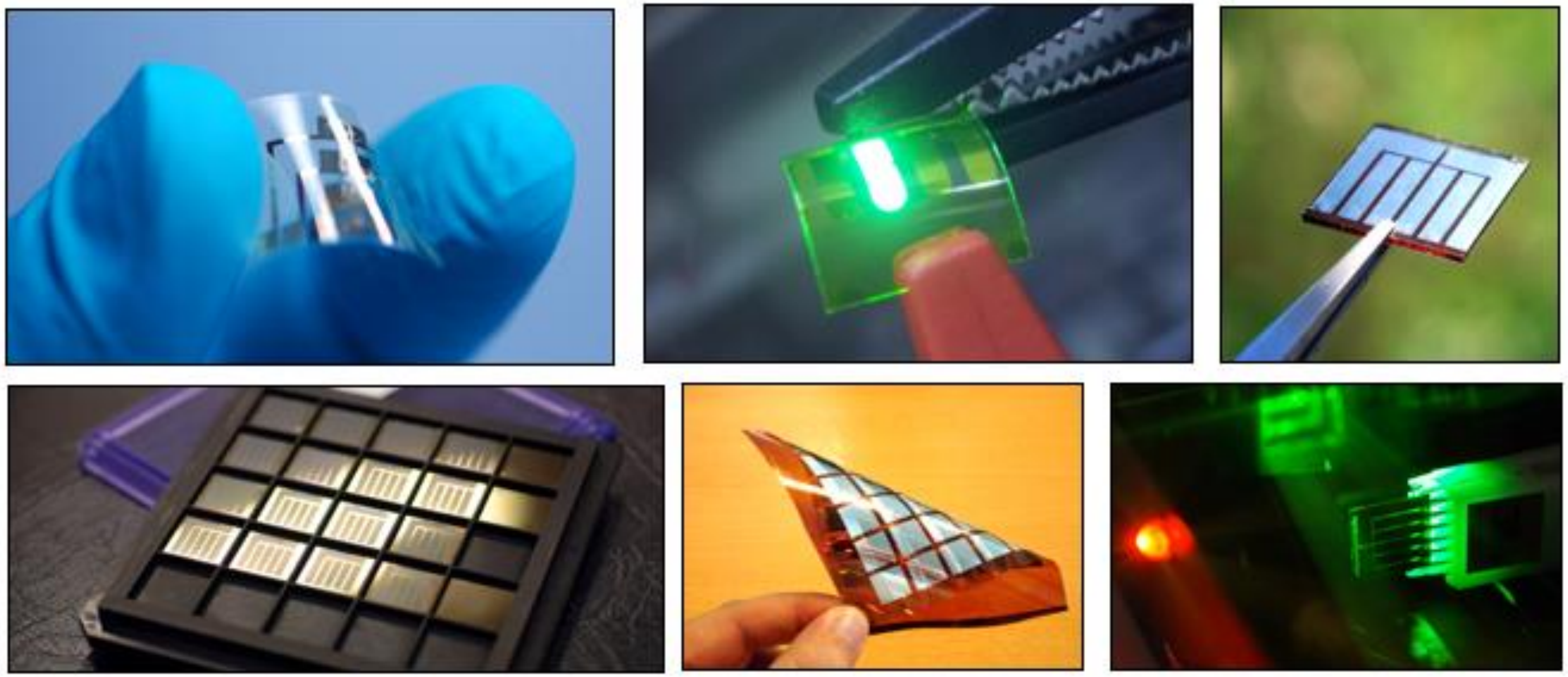
Analyse des publications OPV



université de BORDEAUX

Source : Guillaume Wantz

Organic Electronics Group at Univ. Bordeaux (France)

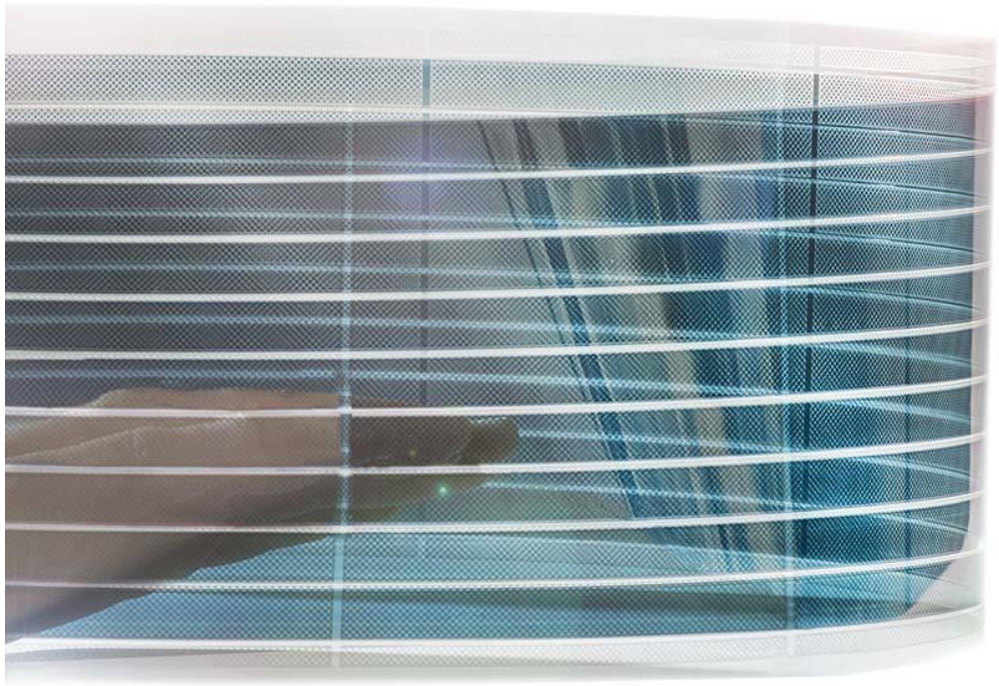


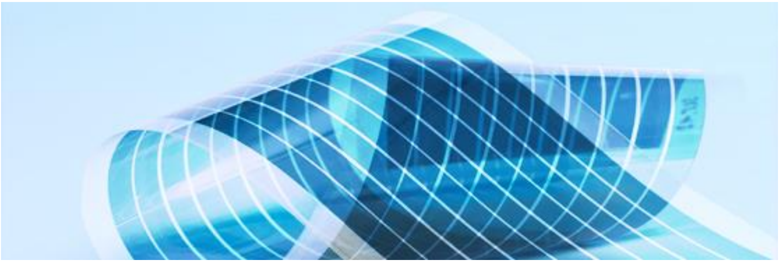
oembordeaux.cnrs.fr

université de BORDEAUX

Source : Guillaume Wantz

OPV: real products !





ARMOR

#MadeInFrance

www.asca.com
www.beautiful-light.eu
www.armor.fr
http://www.beautiful-light-factory.com

2010: R & D and prototyping

↓

2016: Commercialisation of **40 Wp/m²** modules

↓

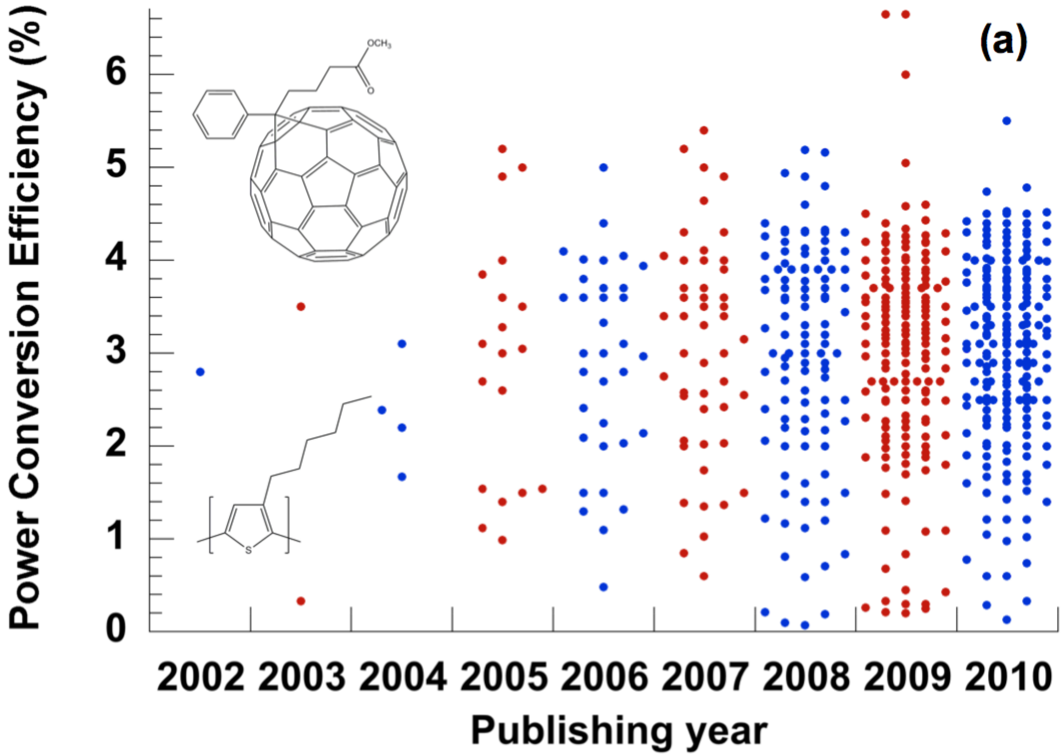
2022: **70 Wp/m²** products to be available

université de BORDEAUX

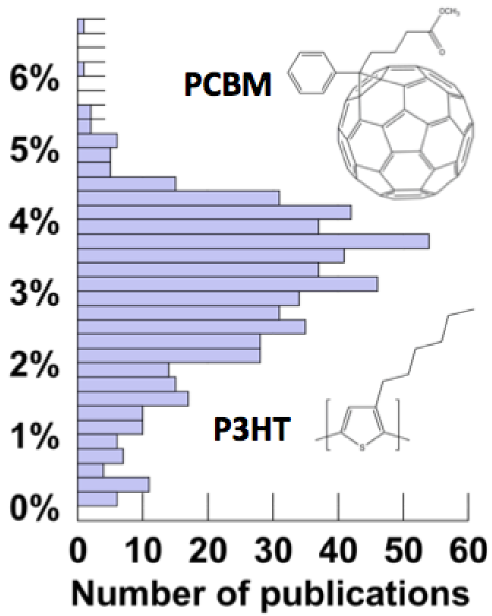
Source : Guillaume Wantz

P3HT:PCBM, the best seller !

Analysis of 579 Papers



- Surface
- Polymer batch
- Purity / Mw
- Illumination power
- Certification ? (NREL, ISE,..)

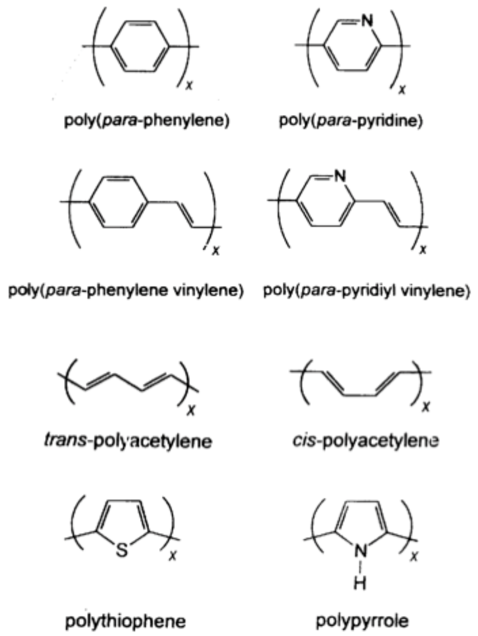


M.T. Dang, L. Hirsch, G. Wantz *Advanced Materials* 23 (**2011**) 3567

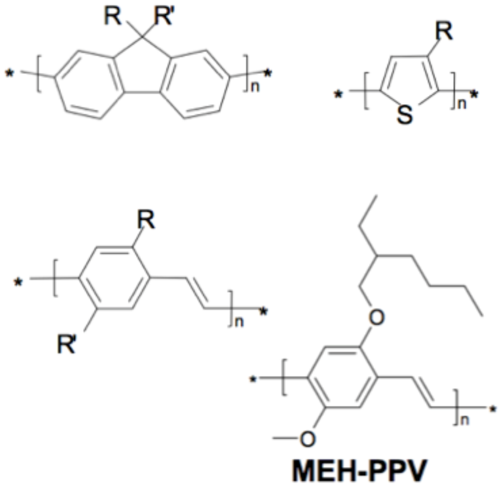
université de BORDEAUX

Source : Guillaume Wantz

3rd Generation
Semiconducting Polymers

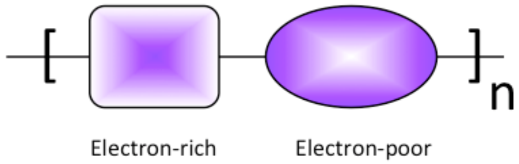


90' s



00' s

Push-pull copolymers

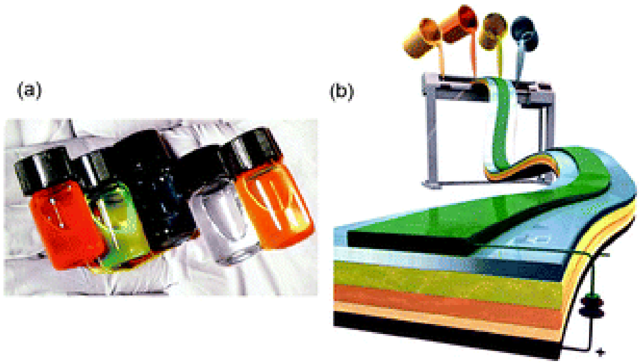


Nobel Prize Chemistry 2000
« *for the discovery of conducting polymers* »


Alan J. Heeger


Alan G. MacDiarmid


Hideki Shirakawa



A.J. Heeger ***Chem. Soc. Rev.*** 39 (**2010**) 2354

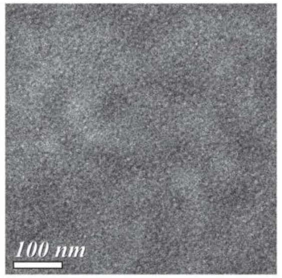
université de BORDEAUX

Source : Guillaume Wantz

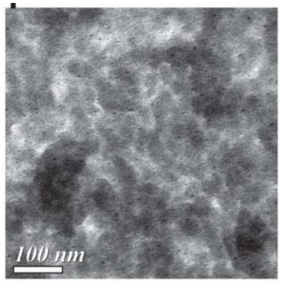
Exemple de problématique OPV
Additive effect: a complex story

PCPDTBT - Increasing phase separation and aggregation of polymer chains

TEM images[1]

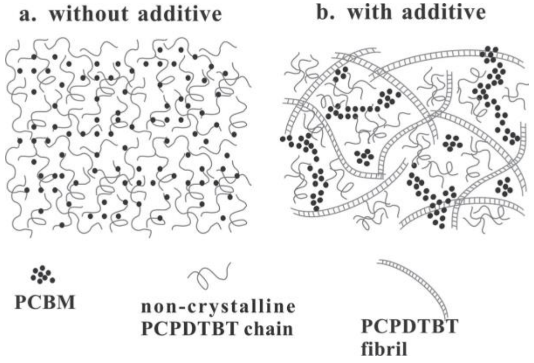


Without DIO



With 3 vol%DIO

Scheme

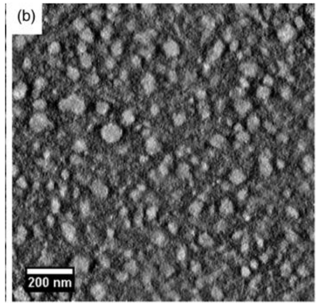


PCEs
Without additive: ~ 3.5%
1,8-octanedithiol : 5.5%
1,8-octanedithiol : 5.5%

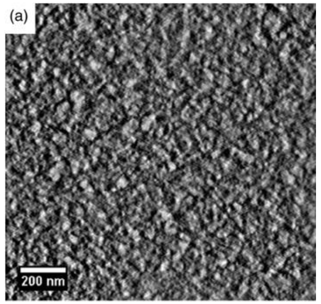
[1] Liao, H.-C. et al. ***Energy & Environmental Science***, *6* (2013)

PTB7 – Decrease of phase separation by preventing the aggregation of the fullerenes

TEM images[2]

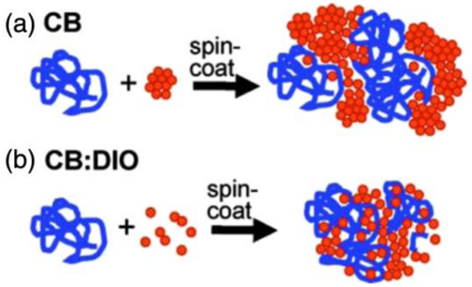


Without DIO



With 3 vol%DIO

Scheme[3]



PCEs
Without additive: 3.9%
1,8-diiodooctane: 7.4%

[2] S.D. Oosterhout et al. ***Nat. Mater.*** 8 (2009)
[3] S. J. Lou et al. ***JACS*** 133 (2011)

université de BORDEAUX

Review of additives for OPV

Table 2 Effects of processing additives on the phase separation of various D:A blends and the efficiency of OSCs based on them.

D:A blend	Additives	Phase separation	Efficiency without-with additive	References
P3HT:$PC_{61}BM$	1,8-octanedithiol	Increase	0.6% to 2.6%	80
P3HT:$PC_{61}BM$	1,6-hexanedithiol	Increase	0.46% to 3.16%	70
P3HT:ICBA[a]	*N*-methyl-2-pyrrolydinone	Decrease	1.15% to 3.45%	86
	1,8-diiodooctane		1.15% to 2.97%	
	1,8-octanedithiol		1.15% to 3.09%	
PCDTBT[b]:$PC_{71}BM$	1,8-diiodooctane	Increase	4.89% to 5.91%	72
PCPDTBT:$PC_{71}BM$	Alkanedithiol	Increase	2.8% to 5.5%	11
	Alkanedithiol	Increase	No PCE reported	82, 84, 87
PCPDTBT:$PC_{71}BM$	1,8-diiodooctane	Increase	2.6% to 4.5%	83
	1,8-diiodooctane	Increase	No PCE reported	81
PCPDTBT:$PC_{71}BM$	1,8-octanedithiol	Increase	3.35% to 4.50%	71
	1,8-diiodooctane		3.35% to 5.12%	
	1,8-dibromooctane		3.35% to 4.66%	
PCPDTBT:$PC_{61}BM$	1,8-diiodooctane	Increase	1.68% to 4.62%	77
	1,8-octanedithiol		1.68% to 3.87%	
	1,8-dichlorooctane		1.68% to 3.45%	
PTB7:$PC_{71}BM$	1,8-diiodooctane	Decrease	3.92% to 7.40%	88
	1,8-diiodooctane	Decrease	No PCE reported	89
DPPT[c]:$PC_{61}BM$	1,8-diiodooctane	Decrease	0.6% to 3.4%	90
DPPBT[d]:$PC_{61}BM$	1,8-diodooctane	Decrease	1.0% to 5.2%	90
PDTSTPD:$PC_{71}BM$	1,8-diodooctane	Decrease	1.0% to 7.3%	91, 92

[a] Indene-C60 bisadduct.
[b] Poly[*N*-11′′-henicosanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)].
[c] Poly(diketopyrrolopyrrole-terthio-phene).
[d] Poly(diketopyrrolopyrrole-quaterthio-phene).

REVIEW

Formulation strategies for optimizing the morphology of polymeric bulk heterojunction organic solar cells: a brief review

Uyxing Vongsaysy,[a,b,c,*] Dario M. Bassani,[a] Laurent Servant,[a] Bertrand Pavageau,[b] Guillaume Wantz,[d] and Hany Aziz[c]

"Review of formulation strategies for optimizing the morphology of polymeric bulk heterojunction organic solar cells"
U. Vongsaysy, D. Bassani, L. Servant, B. Pavageau, G. Wantz, H. Aziz
Journal of Photonics for Energy (**2014**) ASAP

université de BORDEAUX