



Projet de recherche NANODISFLEX

*NANOMatériaux oxydes pour DISpositifs
électrochromes et photovoltaïques FLEXibles*

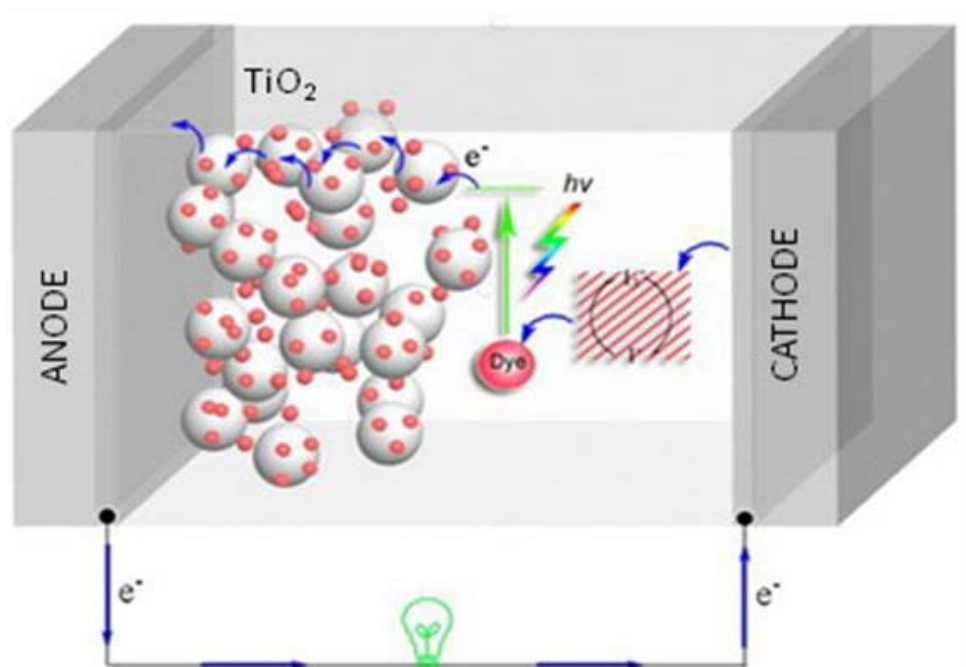
T. Toupance, Y. Nicolas, C. Olivier, ISM, University of Bordeaux 1

G. Campet, M-H. Delville, ICMCB, CNRS Bordeaux

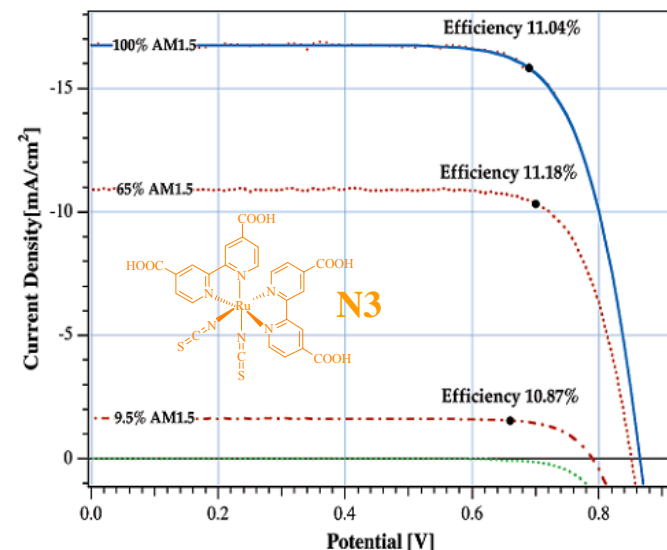
L. Hirsch, IMS, IPB & University of Bordeaux 1



Background



Performances



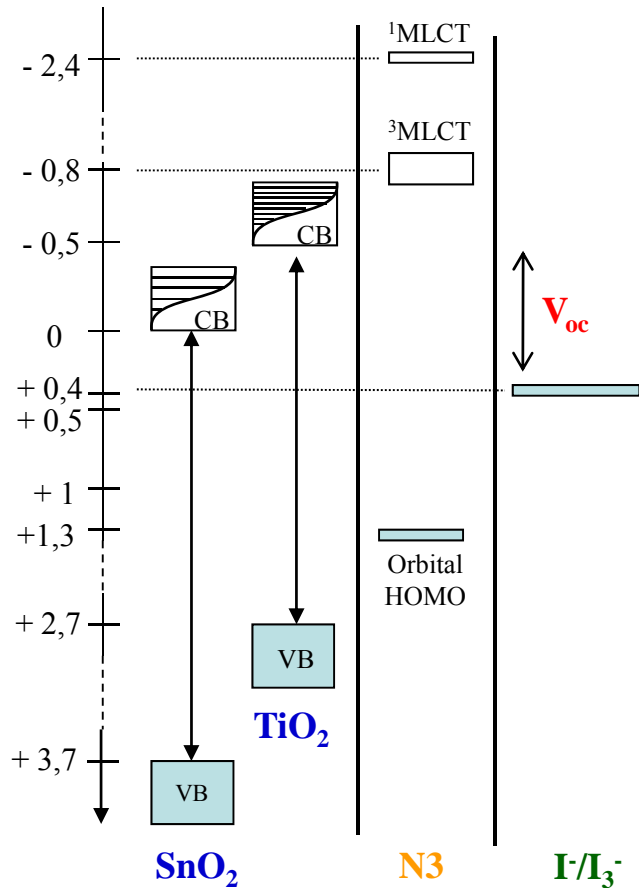
Yield : 11% (0.182 cm²)

Remaining challenges

- New organic dyes for wide light absorption
- Development of low-temperature routes towards nanoporous oxide electrodes
- Morphology of the oxide layers and **other oxides**
- Solid electrolytes

Semiconducting oxides: SnO_2 vs TiO_2

E(V) Semi-conductors Dye Electrolyte (ENH)



TiO_2 : - negative CB, $V_{oc}^{max} = 900$ mV
- high electronic coupling with **N3**

⇒ high efficiency **11.2%** on glass (Grätzel 2005)
7.4% on plastics (Yamaguchi 2007)

- photocatalytic decomposition of the dye
- poor long-term stability

SnO_2 : - more positive CB:
better electron acceptor but $V_{oc}^{max} = 400$ mV
- low electronic coupling with **N3**

⇒ poor efficiency **1.6%** on glass (Sunkara 2008)
no example at low T

- better stability
- no photodecomposition

⇒ **Efficiency of SnO_2 -based DSSCs ?**

⇒ **Low-temperature SnO_2 -based photoanodes ?**

Objectives

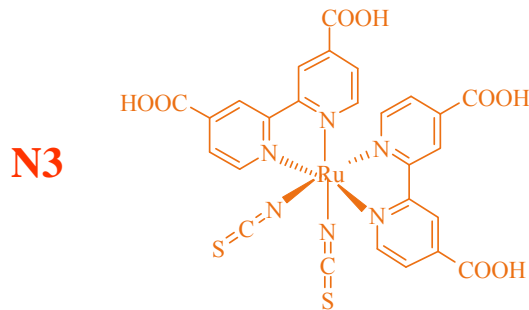
1. Low-temperature processing of semi-conducting oxides

Alternative to the classical approaches, i.e. drying below 150°C, compression, electrophoretic or electrochemical deposition

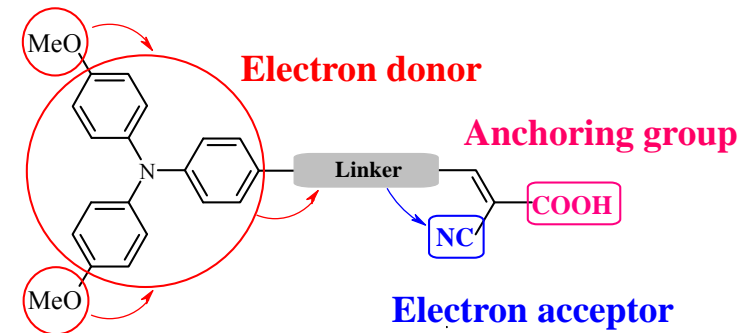
⇒ combination of sol-gel chemistry & UV-illumination for SnO₂, TiO₂ or ZnO

⇒ PLD (Pulsed Laser Deposition) for NiO, Li-NiO, NiO/TiO_{2-x}Zn_x

2. Organic dyes for dye-sensitized solar cells



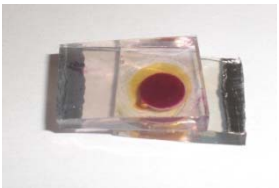
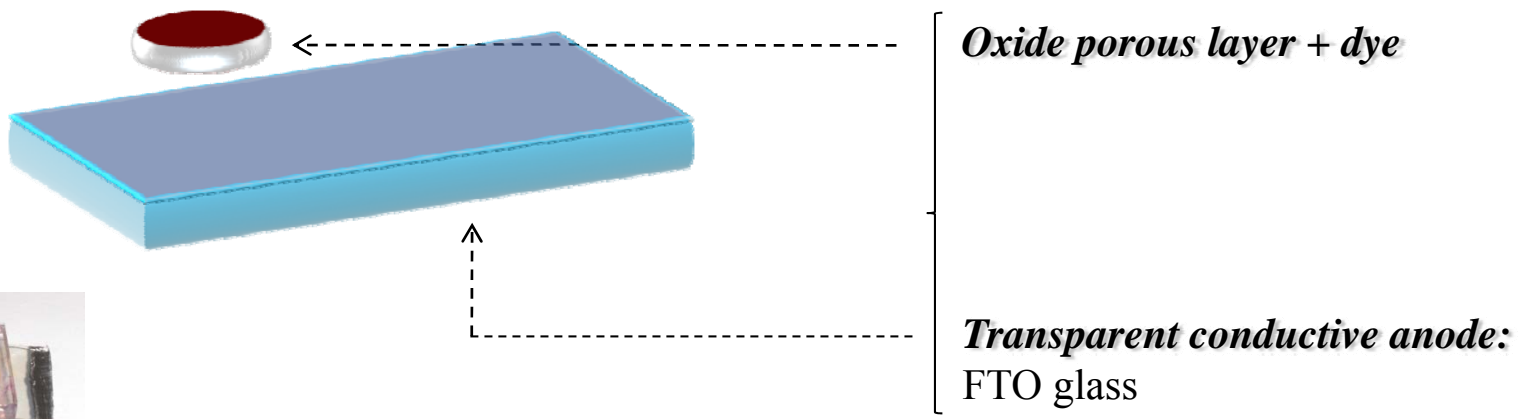
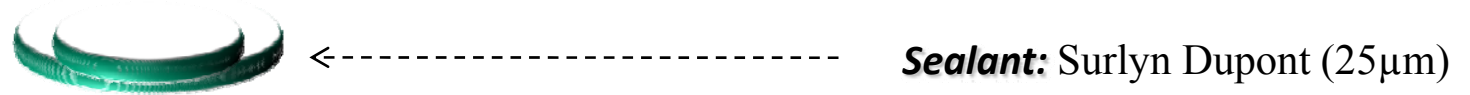
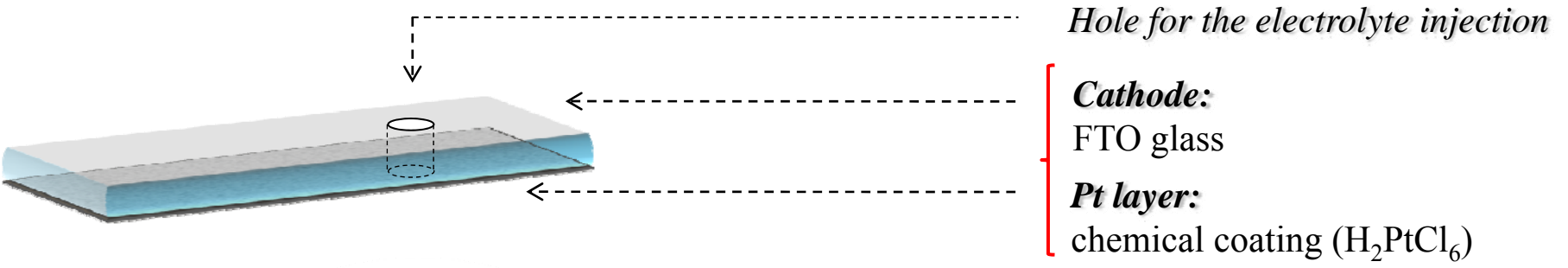
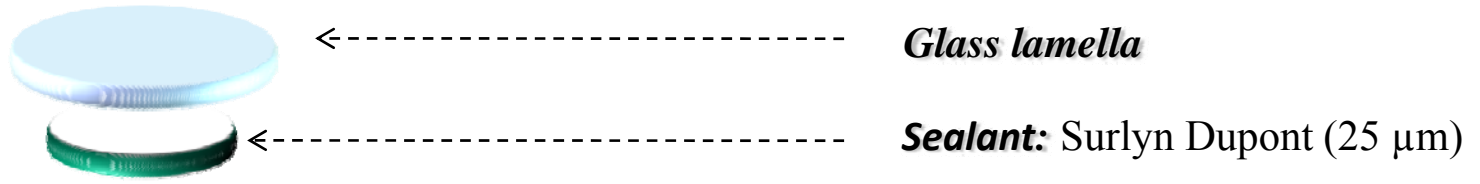
- absorption over wide $\Delta\lambda$
- stable & efficient
- cost and availability of Ru
- low ϵ



- cost effective
 - high ϵ
 - efficient charge carrier separation
- Donor:** improving of delocalization
- Linker:** tuning of the optical properties

3. Devices fabrication and characterization (DSC and electrochromic devices)

Device fabrication



Cells performances

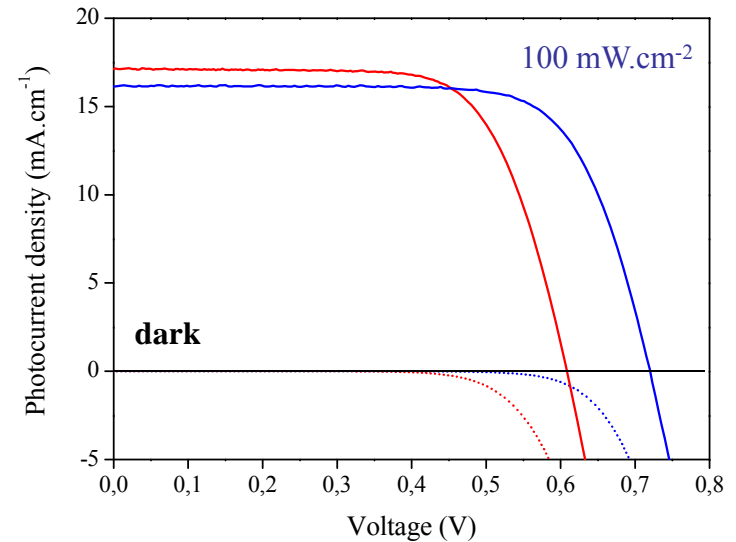
Screen-printed oxide porous layer treated at 450°C

- ✓ Transparent nanocrystalline TiO_2 layer ($\text{Ø}20 \text{ nm} - 9 \mu\text{m}$)
- ✓ Microcrystalline TiO_2 layer ($\text{Ø}400 \text{ nm} - 3 \mu\text{m}$)

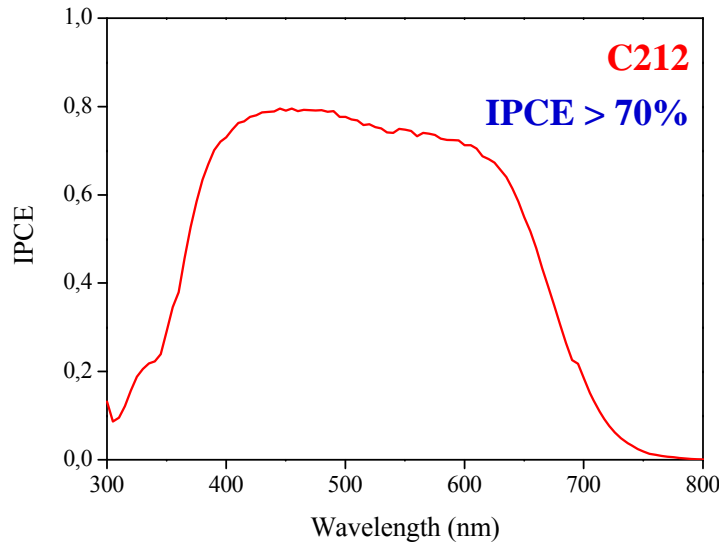
Electrolyte Z960

- ✓ 1.0 M DMII, 0.03 M I_2 , 0.5M TBP, 0.1 M GNCS, 0.05 M LiI in 85/15 (v/v) acetonitrile/valeronitrile

I-V curve AM1.5G



IPCE



N719

$J_{cc} = 16.1 \text{ mA.cm}^{-2}$
 $V_{oc} = 0.72 \text{ V}$
 $FF = 0.73$
Yield = 8.47 %

C212

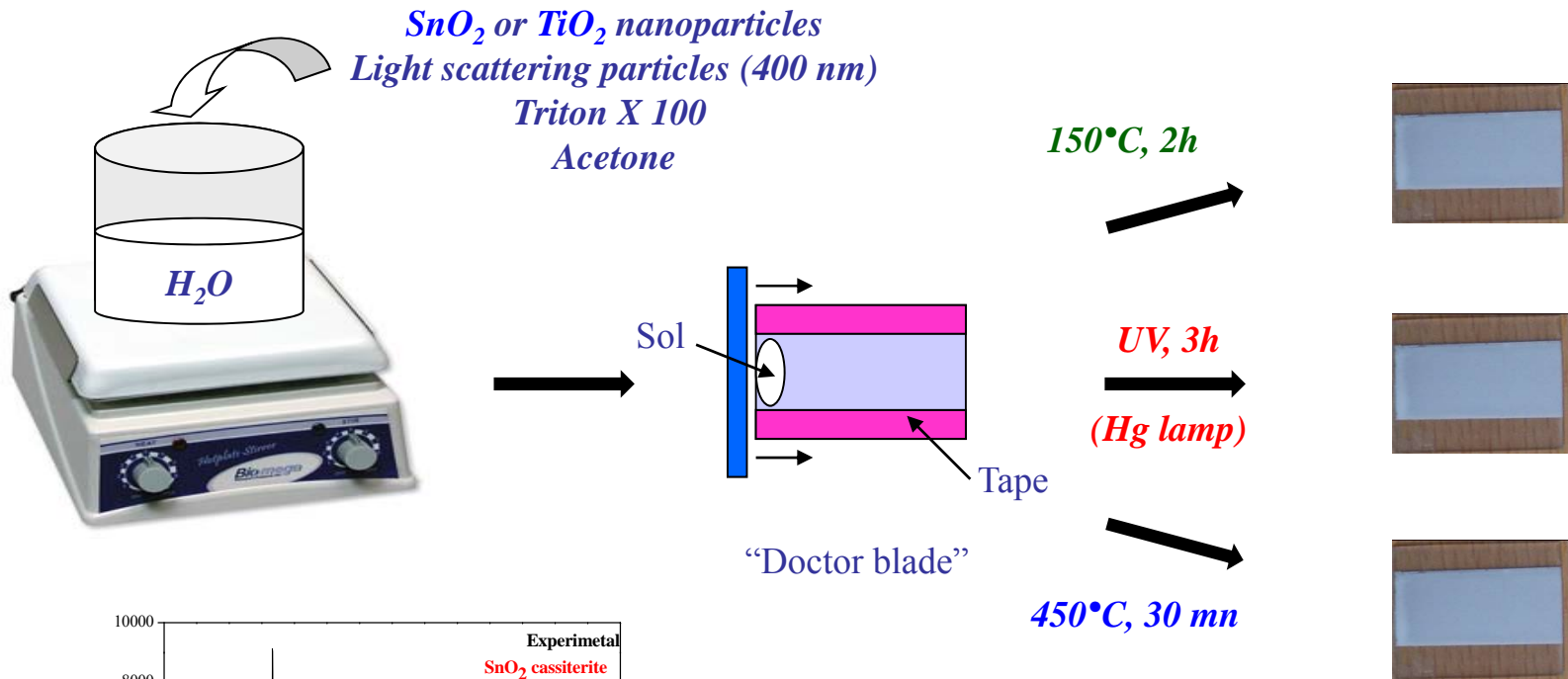
$J_{cc} = 17.1 \text{ mA.cm}^{-2}$
 $V_{oc} = 0.61 \text{ V}$
 $FF = 0.70$
Yield = 7.29 %

Good photovoltaic performances for reference cells (PCE > 7% for 0.16 or 0.2 cm²)

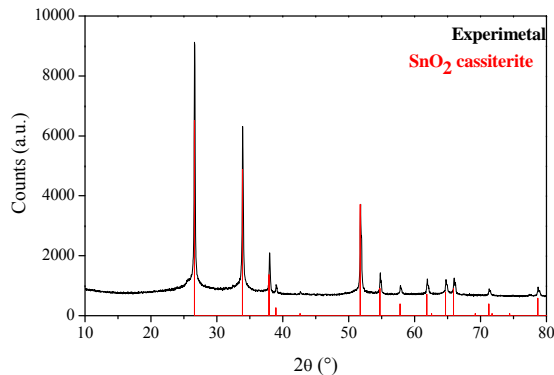
Low-temperature processing: UV-treatment

Challenge: porosity control without high molecular weight polymers

⇒ use of light scattering particles



XRD

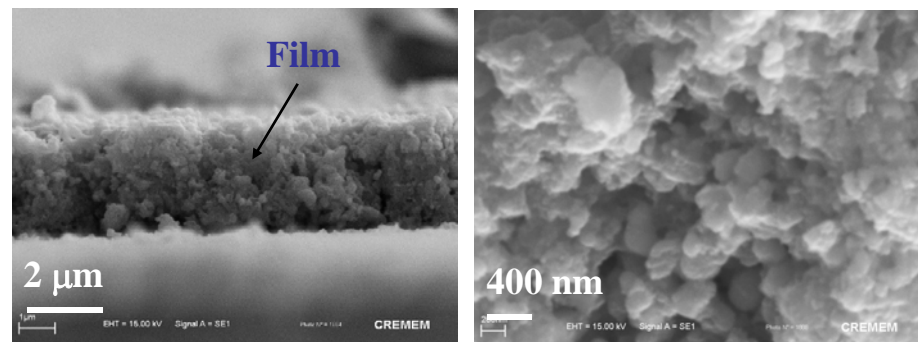


cassiterite SnO₂ films

Structure, texture and morphology of UV-treated SnO_2 films

SEM

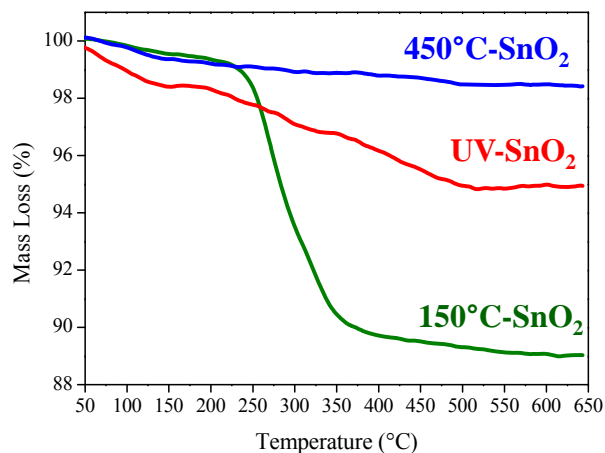
Nitrogen sorption analysis data



Film	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Pore size (nm)
150°C	3	0.02	21
UV	61	0.13	8
450°C	48	0.11	9

Cassiterite SnO_2 nanoporous films thickness : 2-4 μm

TGA



150°C-SnO₂

- poor textural properties
- many remaining organics

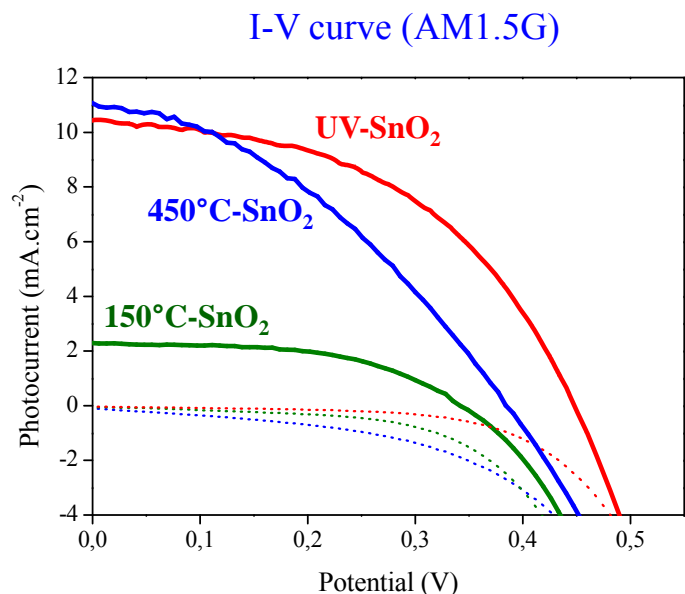
UV-SnO₂

- good textural properties
- few remaining organics



UV-treatment best compromise
for nanoporous nanocrystalline SnO_2 layers

Photovoltaic performances



UV- $\text{SnO}_2/\text{N3}/\text{I}-\text{I}_3^-$
Film thickness 2-4 μm



Conversion yield > 2%
Higher than those reported
for HT- SnO_2 -based materials (Sunkara 2008)

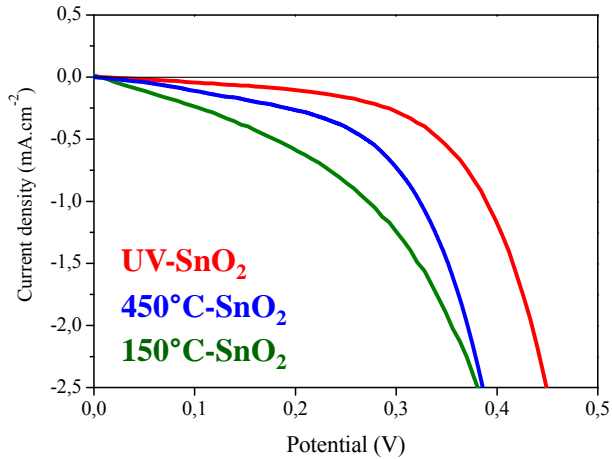


Flexible SnO_2 -based DSC should be accessible

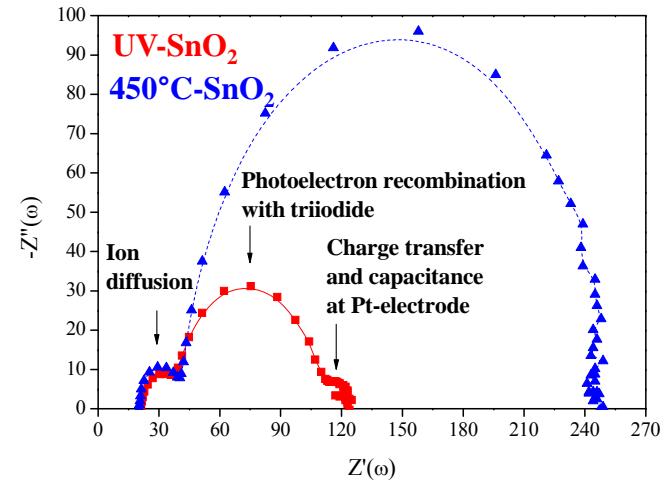
Post-treatment	Area/Power [$\text{cm}^2/\text{mW} \cdot \text{cm}^{-2}$]	J_{sc} [$\text{mA} \cdot \text{cm}^{-2}$]	V_{oc} [mV]	ff	η [%]	Authors
Drying 150°C	0.2/100	2.3	340	0.53	0.4	-
UV	0.2/100	10.5	450	0.48	2.3	-
Calcination 450°C	0.2/100	11.0	380	0.38	1.6	-
Nanowires/575°C	0.25/100	6.3	484	0.53	1.6	Sunkara (2008)

Physical effects induced by the UV-processed SnO_2 films

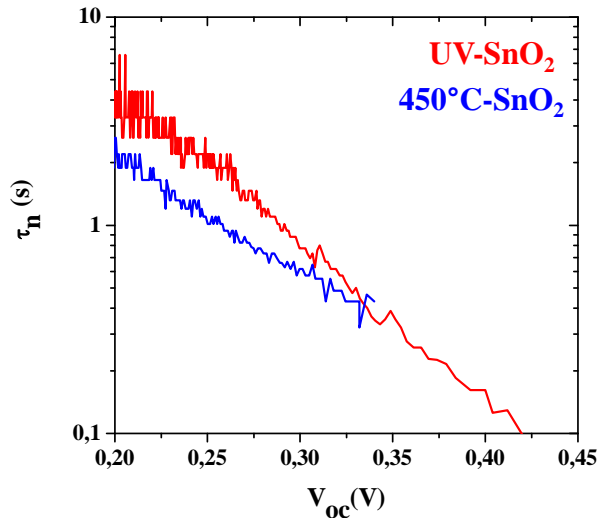
I-V curve: dark current



Impedance spectroscopy



Electron life-time



UV-processed films showed:

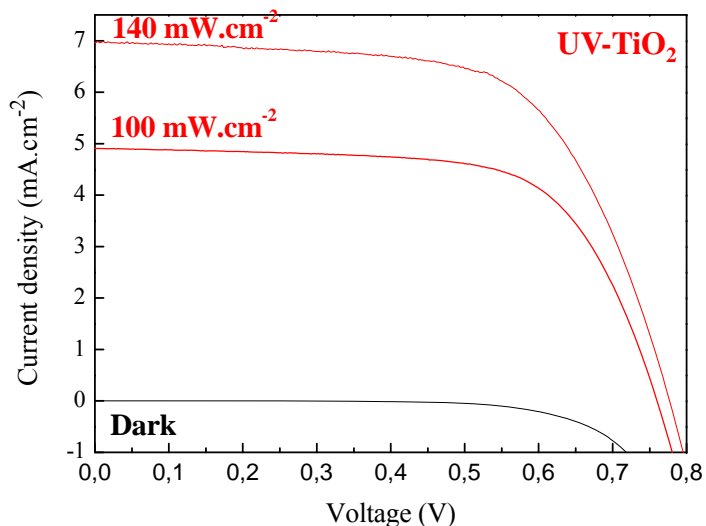
- slower recombination processes
- weaker resistances

↓
higher V_{oc} and FF

↓
UV-treatment improves significantly the photovoltaic responses

Photovoltaic performances

I-V curve (AM1.5G)



UV- TiO_2 /N3/I₃⁻
 Film thickness 2-3 μm



Power conversion efficiencies ~ 2.5%

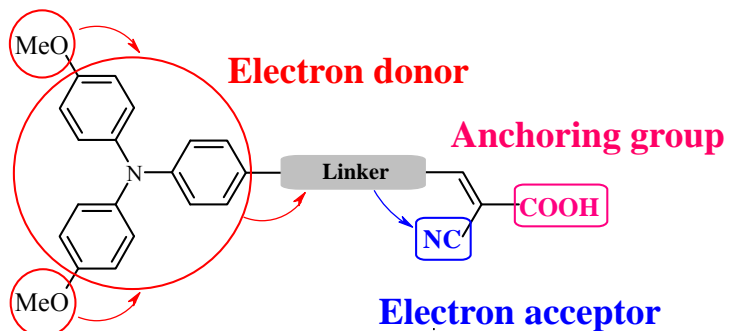


Promising for thickness < 2 μm
 Limitations for reaching thickness > 5 μm

Post-treatment	Area/Power [cm ² /mW.cm ⁻²]	Th [μm]	J _{sc} [mA.cm ⁻²]	V _{oc} [mV]	ff	η [%]
150°C	0.2/140	2.8	4.6	660	0,67	1.3
UV	0.2/140	2.9	7.0	770	0.63	2.5
	0.2/100	2.9	4.9	760	0.67	2.4
450°C	0.2/140	2.9	7.7	700	0.53	2.0

New organic « push-pull » chains for efficient solar light harvesting

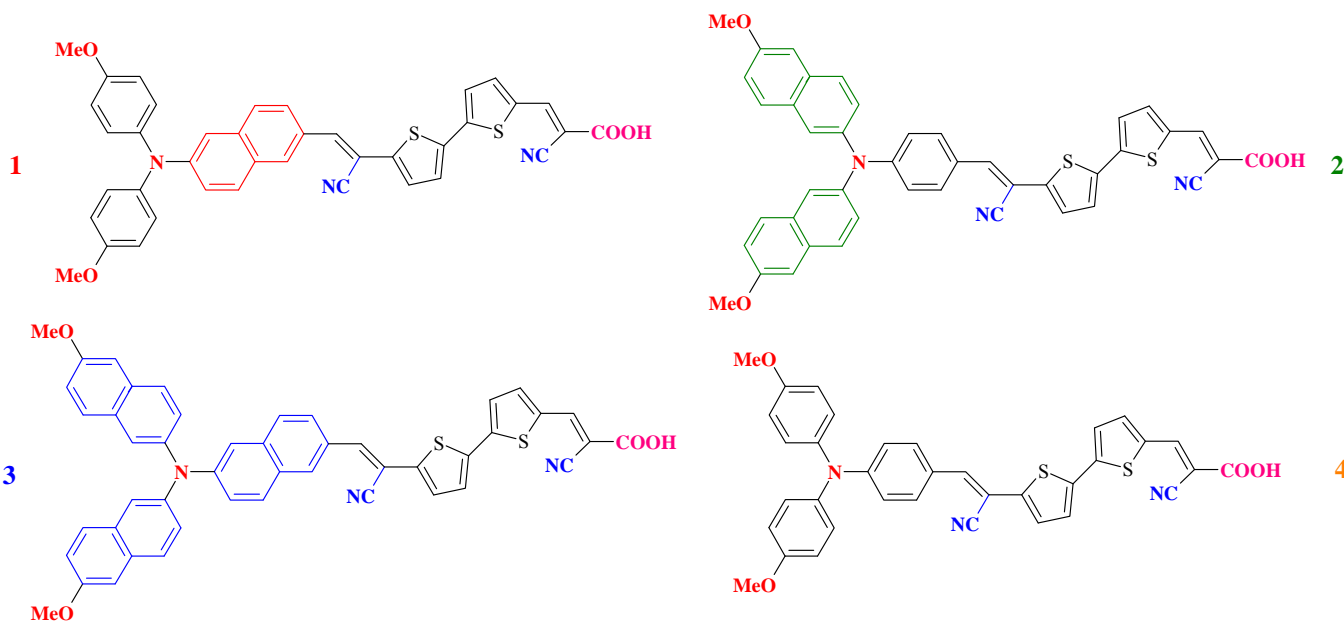
Concept



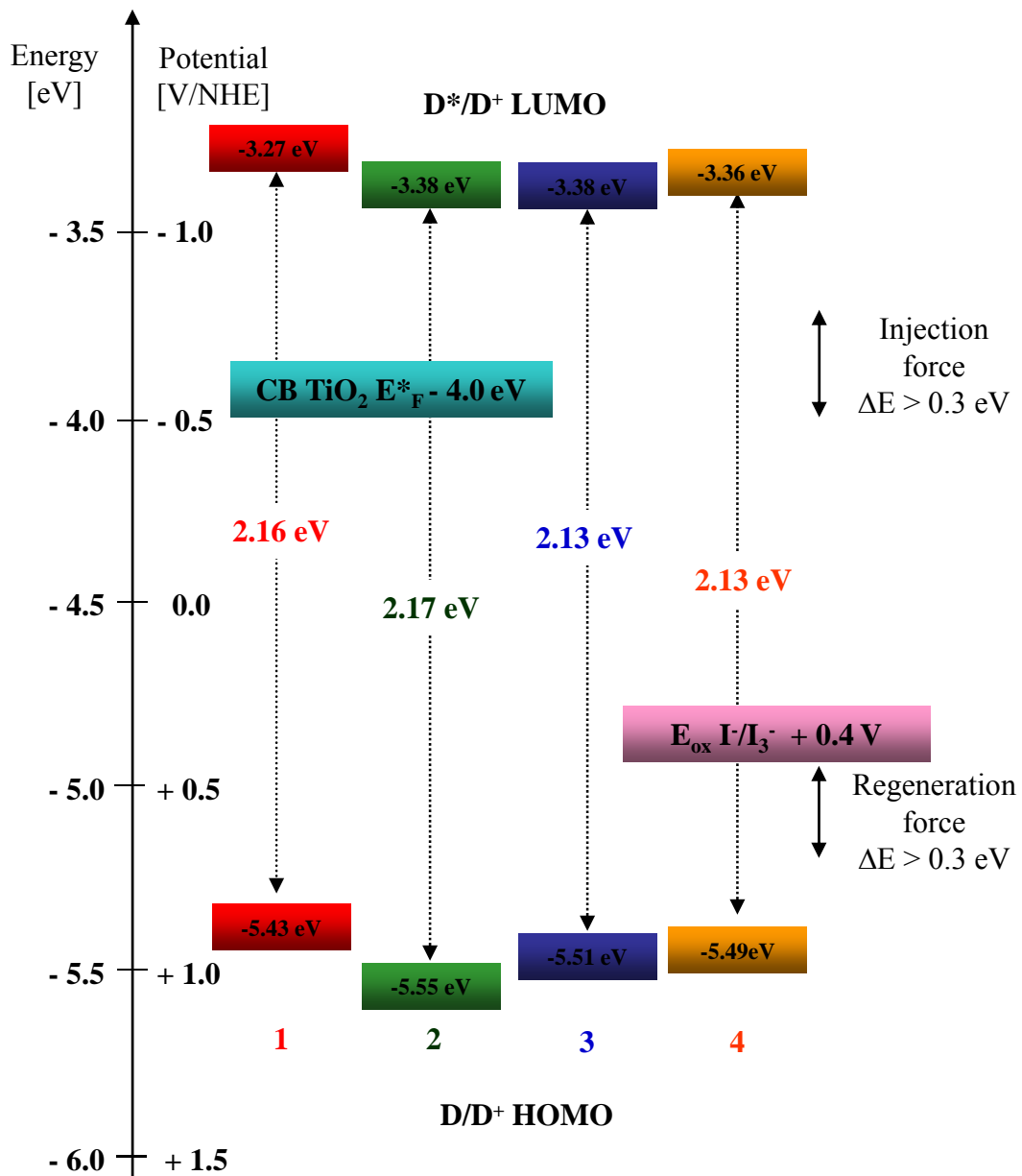
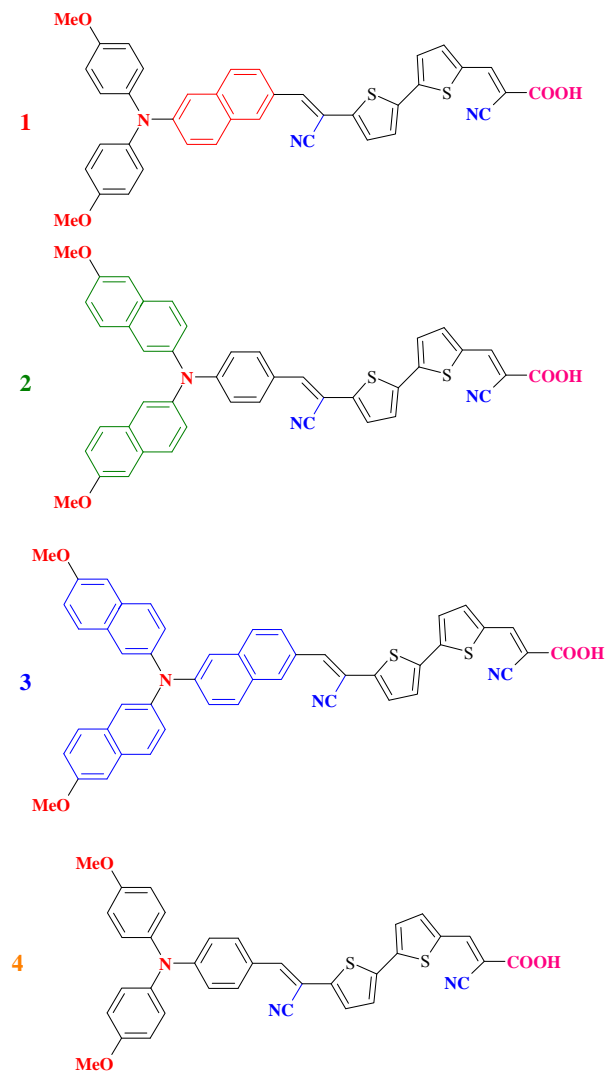
- **Modification of the donor part**
- Tuning the optical properties by varying the linker nature
- Changing the anchoring group

Modification of the donor part

- use of naphthyl units instead of phenyl analogues

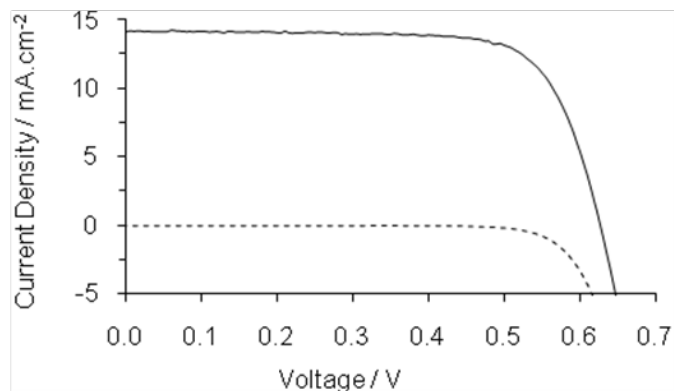


Electronic properties

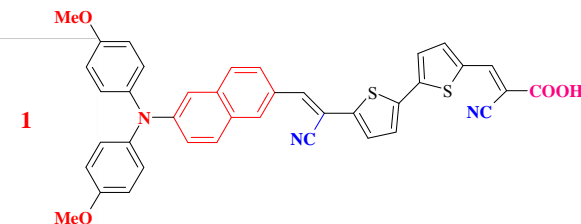
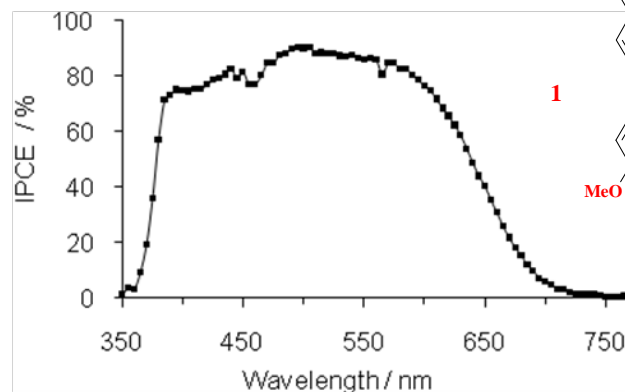


Photovoltaic performances

I-V curve, AM1.5G



IPCE

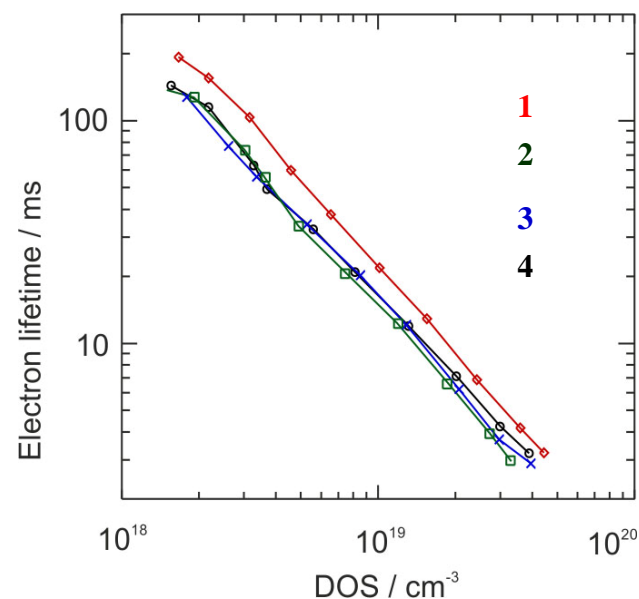
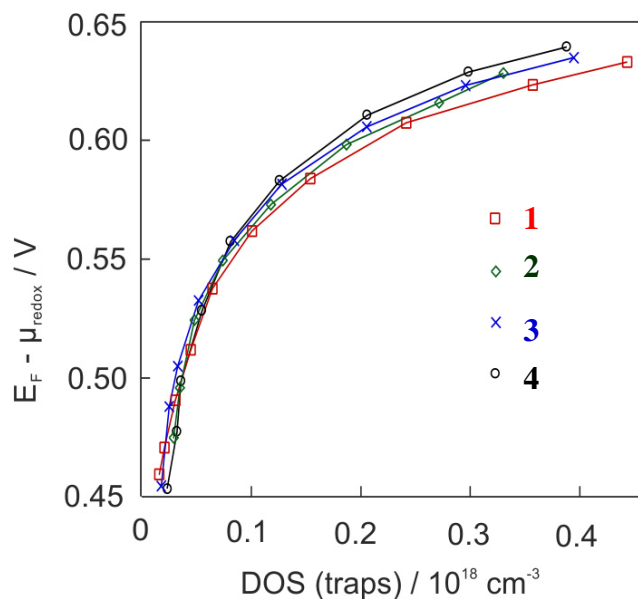


Performances of screen-printing TiO_2 / *Organic Dye* / I^-/I_3^- DSCs (100 mW.cm^{-2})

Dye	Electrolyte	J_{sc} [mA.cm^{-2}]	V_{oc} [mV]	ff	η [%]
4	Z960	13.9	631	74.2	6.5
1	Z960	14.0	627	74.5	6.6
2	Z960	13.9	618	71.7	6.2
3	Z960	13.9	625	73.2	6.4

Physical effects induced by the presence of naphthyl units

Transient photovoltage decay/Charge extraction measurements



Naphthyl units slightly modifies the distribution of traps with a little down-shift in energy

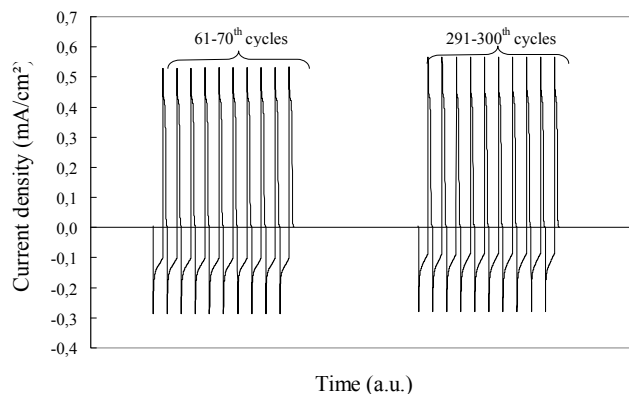
Increase electron life time is observed for **1** \Rightarrow less recombination processes

Naphthyl units have a positive effect when they are introduced in the conjugated bridge

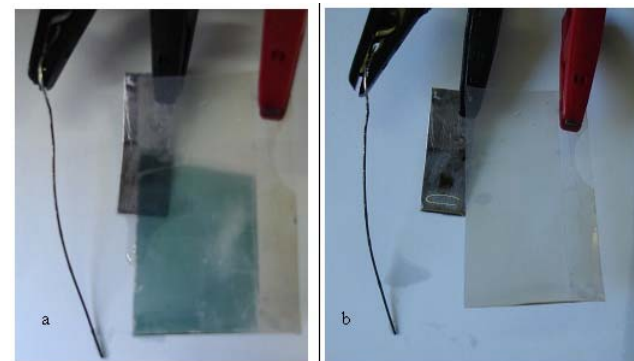
Thin UV-treated nanocrystalline TiO_2 films

Good coloration efficiency along with performances unchanged for > 300 cycles on ITO/PET

Chronoamperometry

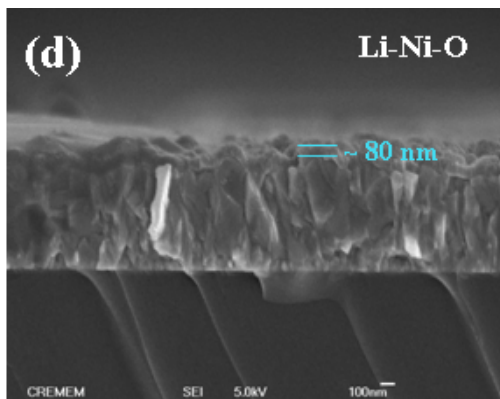


Coloration efficiency

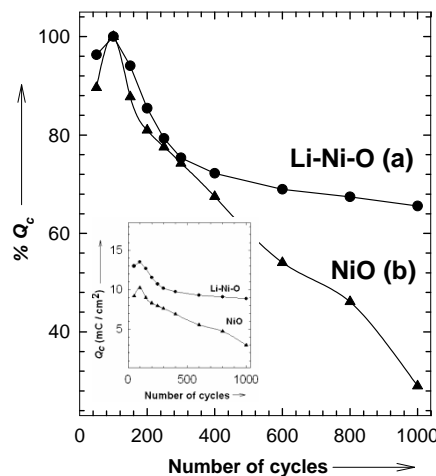


Thin NiO and $Li-NiO$ films prepared by Pulsed Laser Deposition (PLD)

FE-SEM



Coulombic capacity



PLD $Li-NiO$ films showed improved cyclability



Promising materials for brownish electrochromic displays

Conclusion

- UV-irradiation: efficient low-temperature processing of SnO_2 and TiO_2 layers
- In DSC, good photovoltaic responses for layers of thickness lower than $3 \mu\text{m}$
- New promising « push-pull » organic dyes for dye-sensitized solar cells
- Low-temperature processed TiO_2 and Li-NiO thin films for electrochromic applications

Outlooks

- UV-processing of $\text{SnO}_2@ \text{TiO}_2$ or $\text{SnO}_2@ \text{ZnO}$ films to enhance the V_{oc} and FF of SnO_2 -based DSCs
- « push-pull » organic dyes: modification of the donor and the linker nature
- Design and fabrication of a complete flexible electrochromic system combining the blue color of TiO_2 films and the brown one of NiO films.



Acknowledgment



Dr. Y. Nicolas
Dr. C Olivier

Dr. Z. Tebby
T. Uddin
L. Cojocar
S. de Sousa

O. Babot



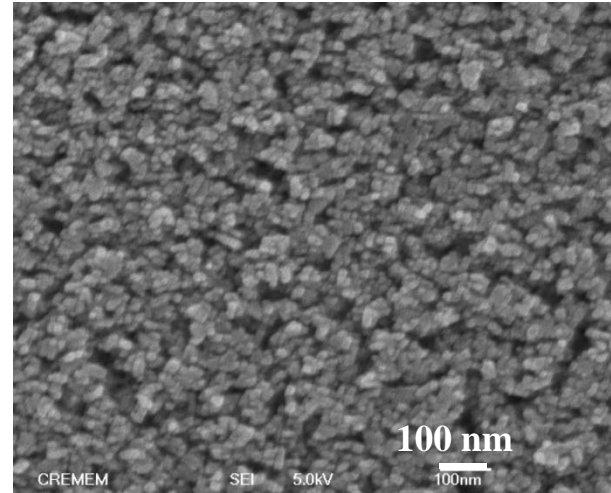
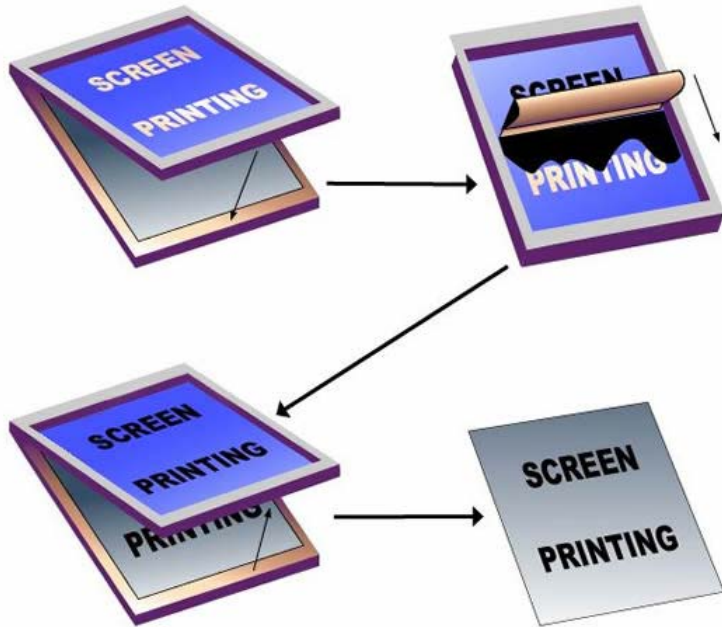
Dr. G. Campet, CNRS Bx
Dr. M-H. Delville, CNRS Bx

Dr. L. Hirsch, IPB

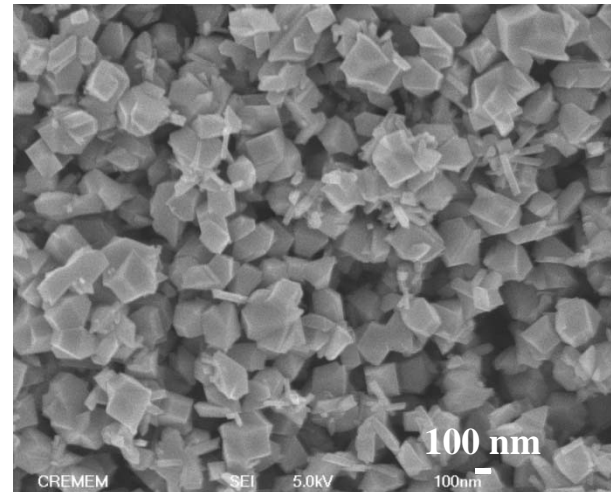
Prof. M. Grätzel, EPFL
Dr. F. Sauvage, EPFL

Surface morphology of the screen-printed nanoporous TiO_2 electrode

SEM



- 9 μm -thick anatase TiO_2 nanoparticulate (20 nm) film



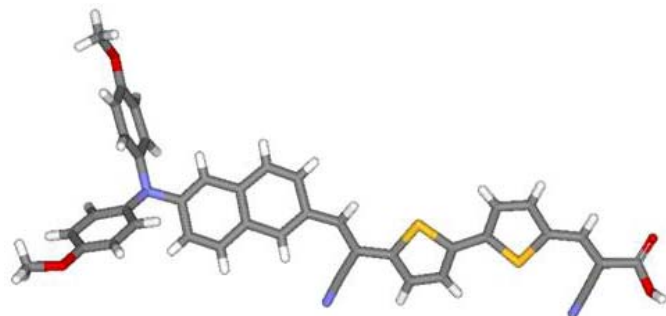
- 9 μm -thick anatase TiO_2 nanoparticulate (20 nm) film + 3 μm -thick light-scattering TiO_2 (400 nm) layer

Towards New « Push-pull » Dyes

C2M research team, ISM, UMR-CNRS 5255, University of Bordeaux 1

Solid-state structure and molecular modeling

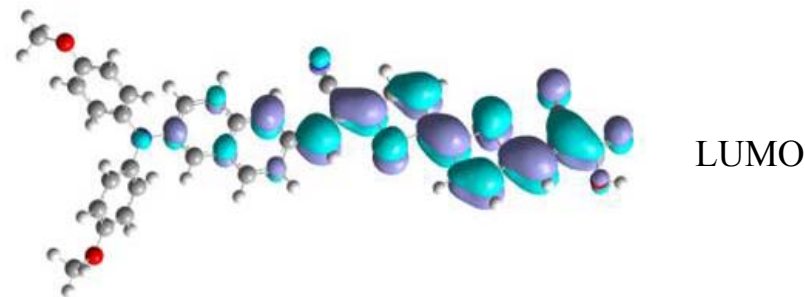
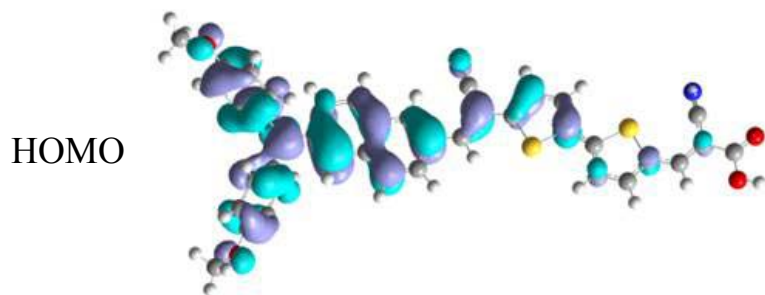
Crystalline structure



- dihedral angle between naphyl and bithiophene rings $< 20^\circ$
- linear, undisrupted and highly conjugated pathway of more than 20 Å

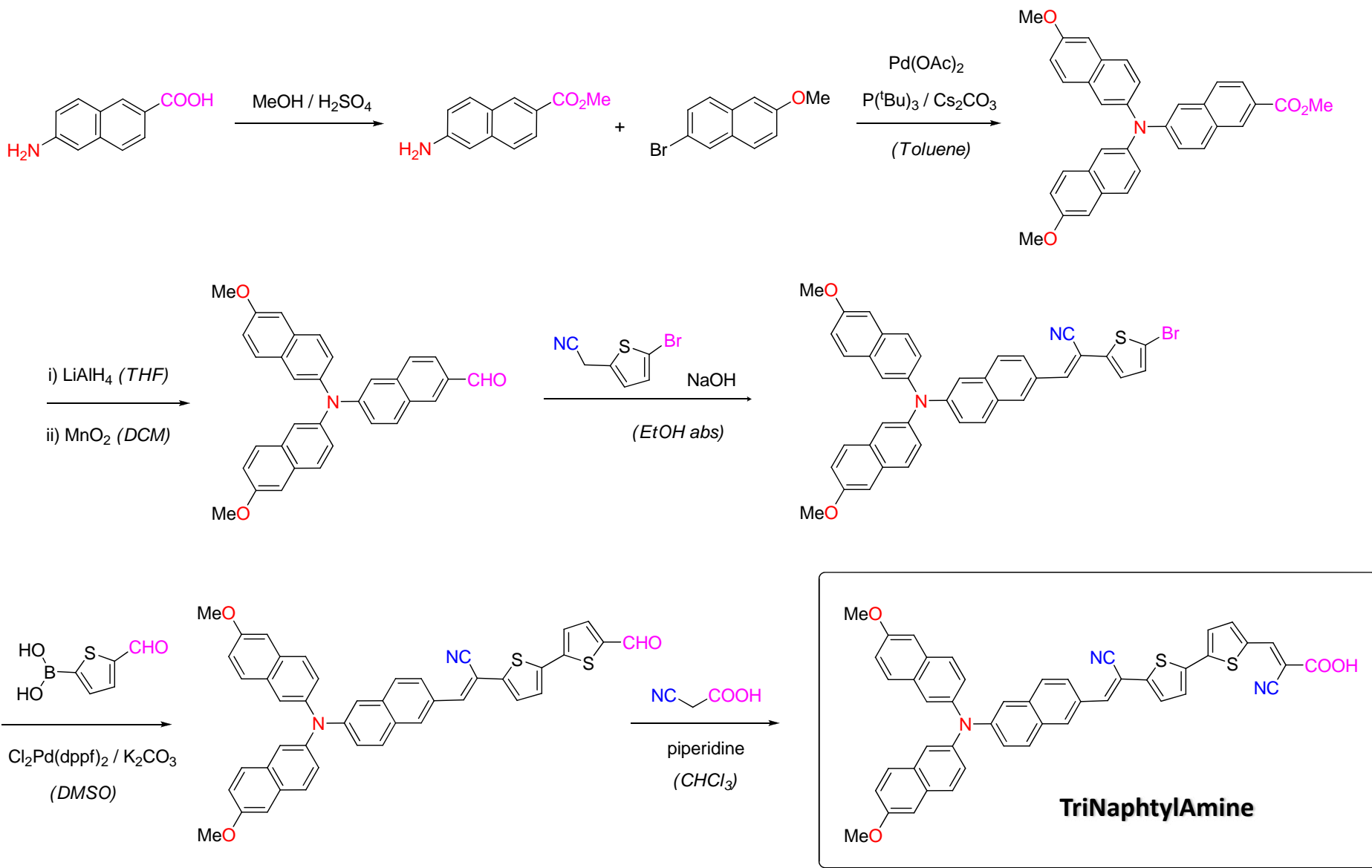
Molecular modeling

DFT calculations (B3LYP/6-31G(d) level in the gas phase)



Excellent directionality in the charge transfer process

Fast electron injection into the conduction band of TiO_2 was expected
Fast regeneration of the oxidized dye should be observed



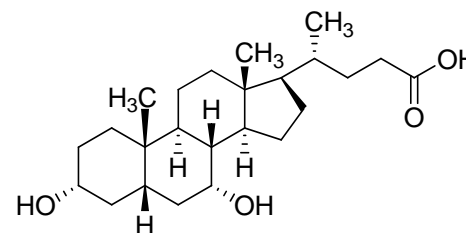
➤ Solution de colorant

Solvant : Acétonitrile / ^tButanol (50/50) **ou** CH₂Cl₂

Colorant organique : 0.3 mM

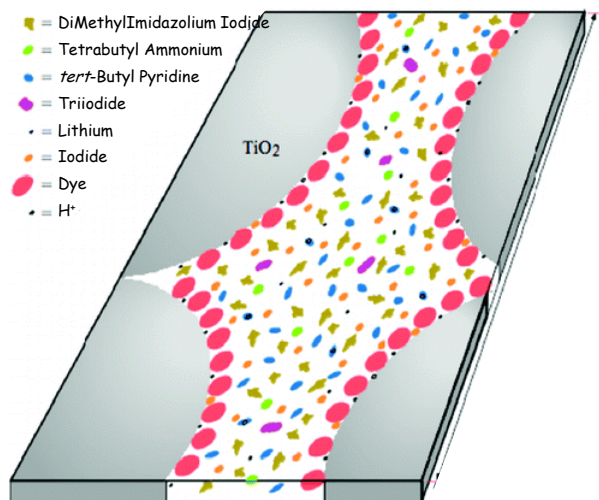
Co-adsorbant (Cheno) : 2 mM

Adsorption : 5H à T° Ambiante



Chenodeoxycholic acid
(acide 3 α ,7 α -dihydroxy-5 β -cholanique)

➤ Electrolyte liquide (Z960)



Solvant : Acétonitrile / Valéronitrile (85 / 15)

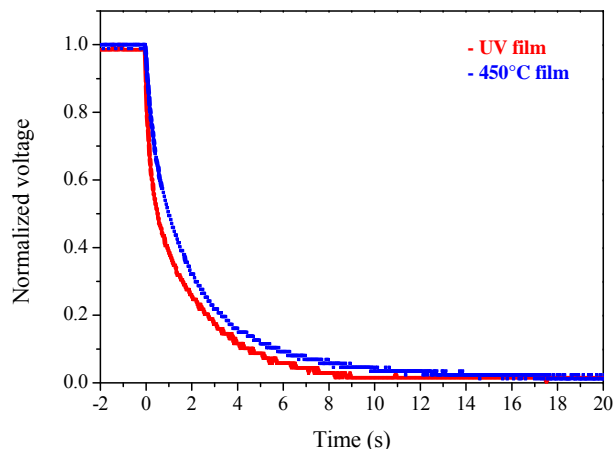
DMII : 1.0 M ; **LiI** : 0.05 M ; **I₂** : 0.03 M

Guanidinium Thiocyanate : 0.1 M

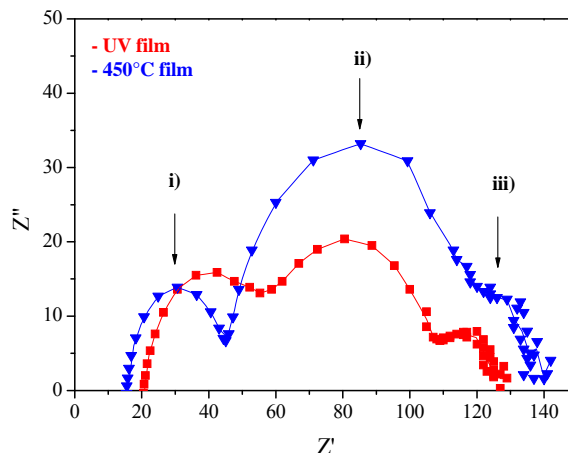
tert-Butylpyridine : 0.5 M

Physical effects induced by the UV-processed TiO_2 films

Open-circuit photovoltage decay



Impedance spectroscopy



i) Diffusion of ions

ii) Photoelectron recombination with triiodide

iii) Charge transfer and capacitance at the Pt-electrode

UV-processed films showed faster recombination processes but also higher V_{oc} and FF



Defects and/or surface hydroxyl groups UV-induced shift the quasi-Fermi level toward higher energies leading to higher V_{oc} and FF



UV-treatment beneficial for good photovoltaic responses

Modeling of the medium frequency feature

Film	Q ($F \cdot s^{n-1}$)	n	R (Ω)	ν (Hz)
UV	$6.0 \cdot 10^{-4}$	0.80	46	14
450°C	$6.1 \cdot 10^{-4}$	0.91	76	5

$$Z(\omega) = (1/Q)(j\omega)^{-n}; t = (RQ)^{1/n}$$

$$t = 1/(2pn); Q: \text{constant}$$

Towards Flexible Solar Cells & Electrochromic Devices

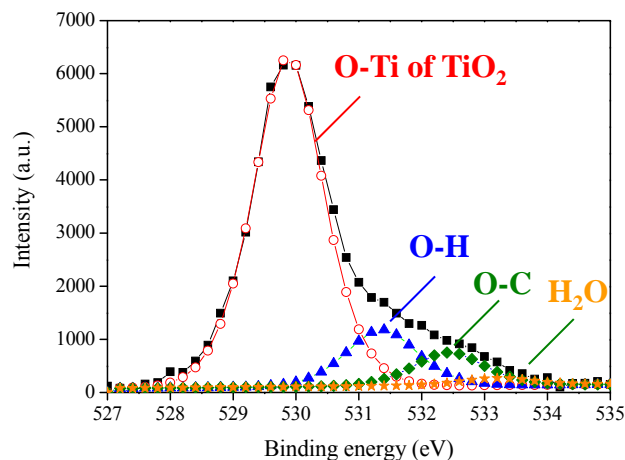
C2M research team, ISM, UMR-CNRS 5255, University of Bordeaux 1

Effect of the atmosphere and treatment on the performances of TiO_2 films

Conditions	Th (μm)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	V_{oc} (V)	FF	Eff (%)
TiO_2 film/UV-treatment air	1.1	4.0	0.79	0.64	1.4
TiO_2 film/Ozone/air	1.1	2.2	0.77	0.63	0.8
TiO_2 film/UV/nitrogen	1.1	2.2	0.66	0.57	0.6

Light source: AM1.5 $140 \text{ mW}\cdot\text{cm}^{-2}$; Th: thickness; J_{sc} : short-circuit photocurrent; V_{oc} : open-circuit voltage
 FF: fill factor; Eff: overall energy conversion efficiency

X-ray Photoelectron Spectroscopy



Film	O-Ti (TiO_2)	O-H	O-C	H_2O
UV	1	0.17	0.10	0.02
450°C	1	0.10	0.07	0.00

Ozone molecules formed by UV-irradiation in air promote the hydroxylation of the oxide surface that induces the particle interconnection and good photovoltaic responses