Functional organic dyes in light harvesting applications

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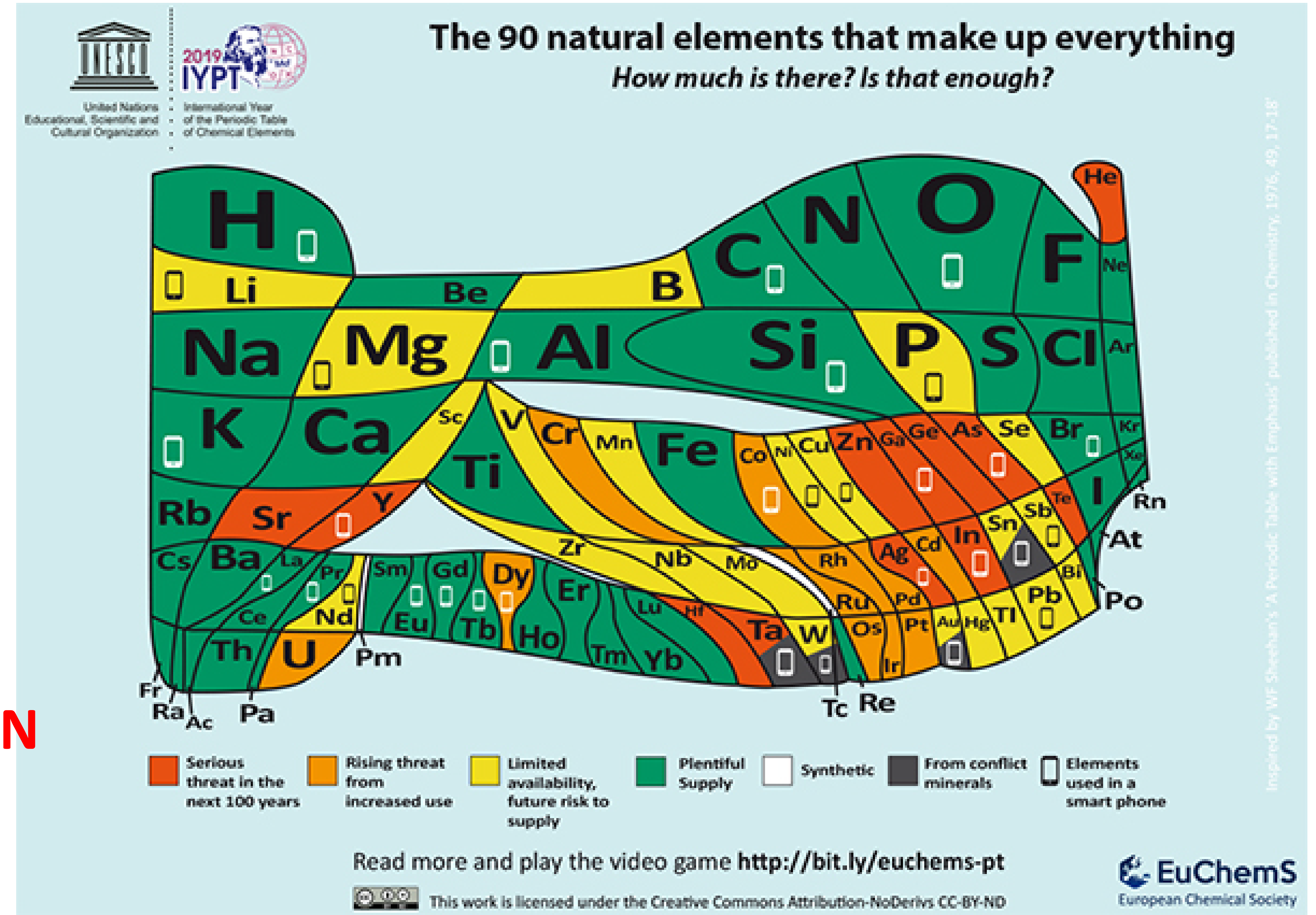
Avogadro Colloquia 2019 _ Roma CNR, 17th -18th December 2019

Elements of the Periodic Table for Energy

in

ENERGY PRODUCTION



United Nations Educational, Scientific and Cultural Organization

2019 IYPT
International Year of the Periodic Table of Chemical Elements

The 90 natural elements that make up everything

How much is there? Is that enough?

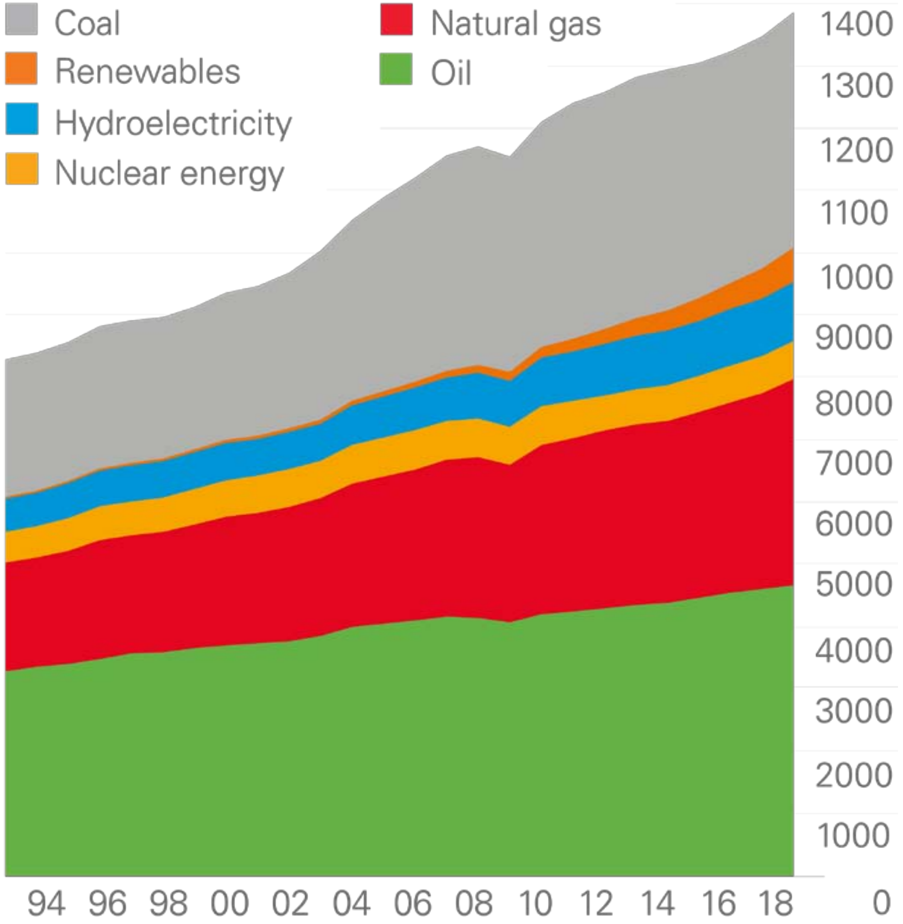
- 🟥 Serious threat in the next 100 years
- 🟧 Rising threat from increased use
- 🟨 Limited availability, future risk to supply
- 🟩 Plentiful Supply
- ⬜ Synthetic
- ⬛ From conflict minerals
- ▯ Elements used in a smart phone

Inspired by WF Sheehan's 'A Periodic Table with Emphasis' published in Chemistry, 1976, 49, 17-18

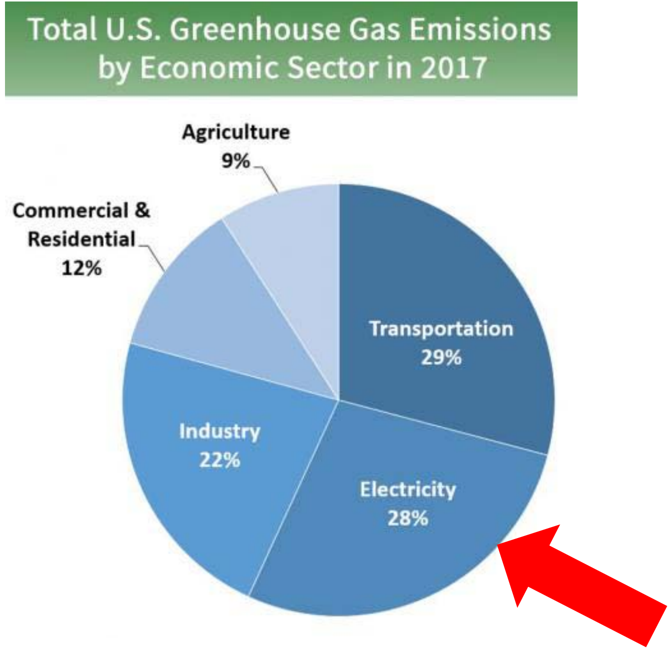
Read more and play the video game **http://bit.ly/euchems-pt**

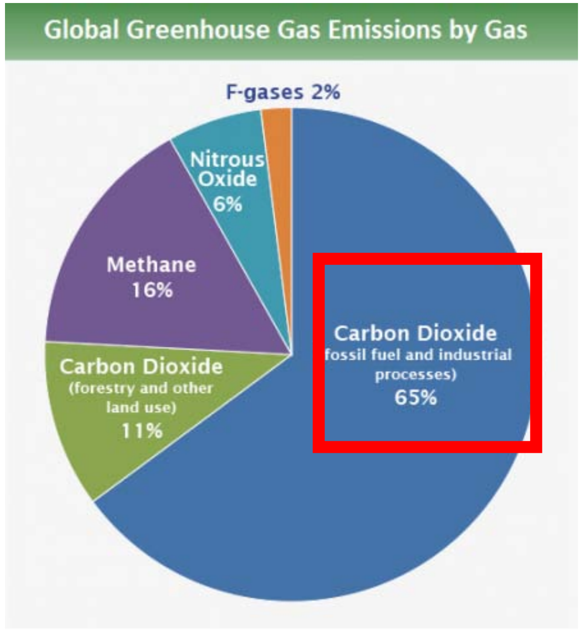
EuChemS
European Chemical Society

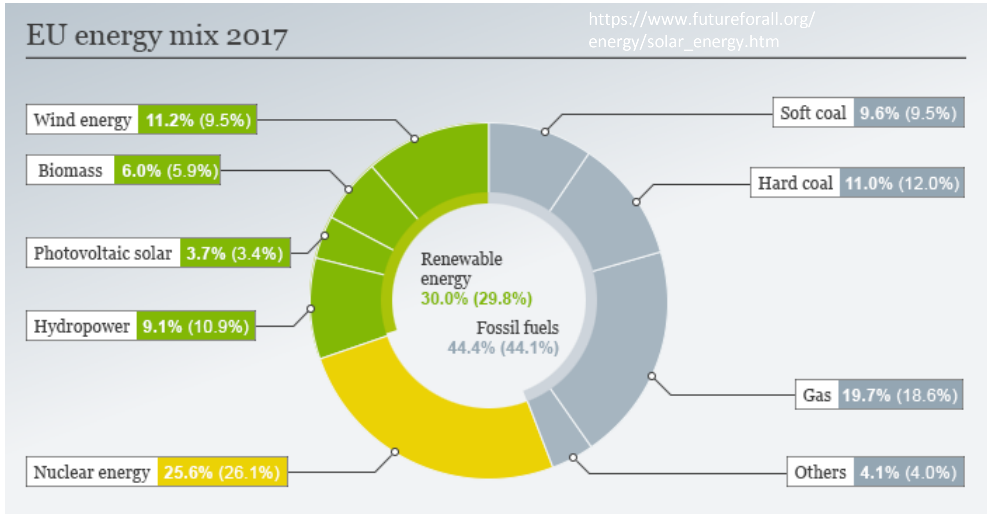
Energy production and use



Primary energy – world consumption (million tonnes oil equivalent)
Source: BP



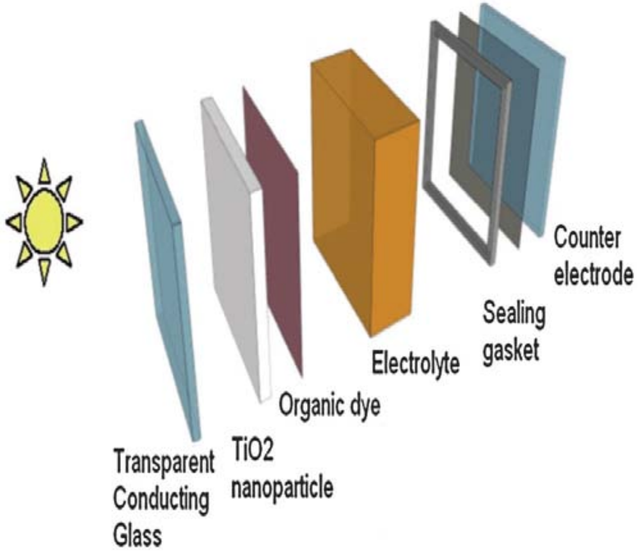


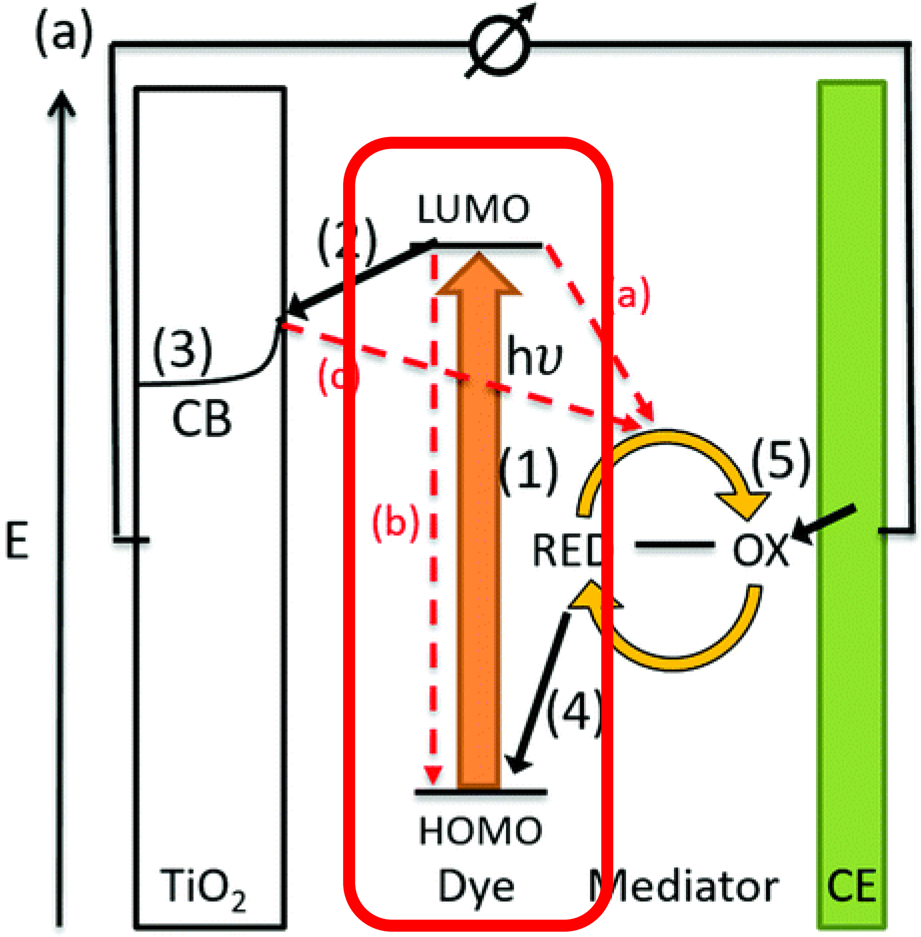


https://www.futureforall.org/energy/solar_energy.htm

Dye-sensitized Solar Cells[1]

- Architectural compatibility
- Environmental compatibility
- Weak / diffuse light
- Indoor / IoT [2]
- Colorful
- Transparency





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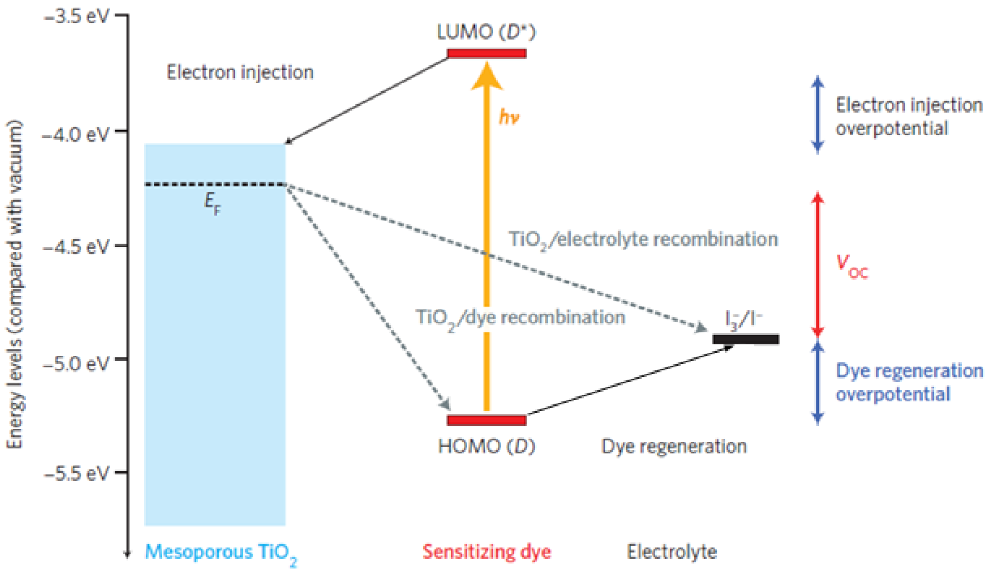
[1] O' Regan, B.; Grätzel, M. Nature 1991, 353, 737; [2] Benesperi,I.; Michaels, H. Freitag, M. J. Mater. Chem. C, 018,6, 11903-11942

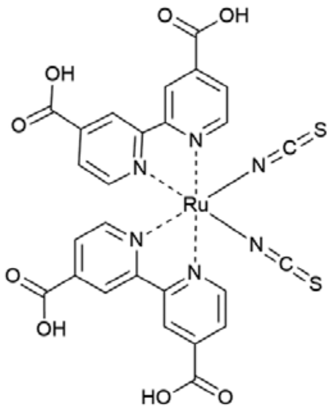
Photosensitizers requirements

- **absorb strongly across the entire visible spectrum**
  - **broad range of wavelengths, high molar extinction coefficient**
- **bind strongly to the semiconductor surface**
  - **(chemical group that can attach to the TiO_2 surface)**
- **have a energy levels at the proper positions**
  - **LUMO high enough in energy for efficient charge injection**
  - **HOMO low enough for efficient regeneration**
- **have a rapid electron transfer to the TiO_2**
  - **in comparison to decay to the ground state of the dye**
- **be stable over many years**
- **have low cost**
- **have simple and reproducible synthesis and purification**

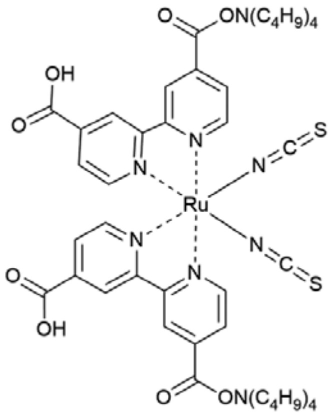


Photosensitizer: a key component in the cell

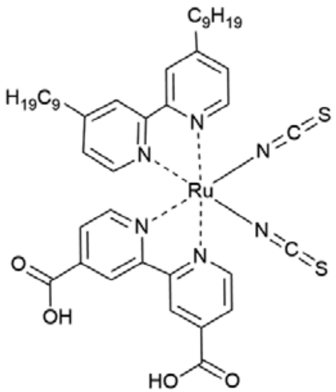
ruthenium-based dyes and metal coordination complexes



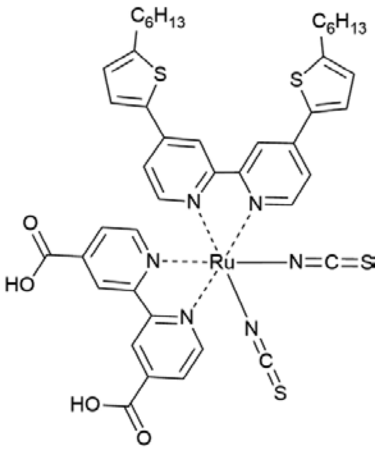
N3



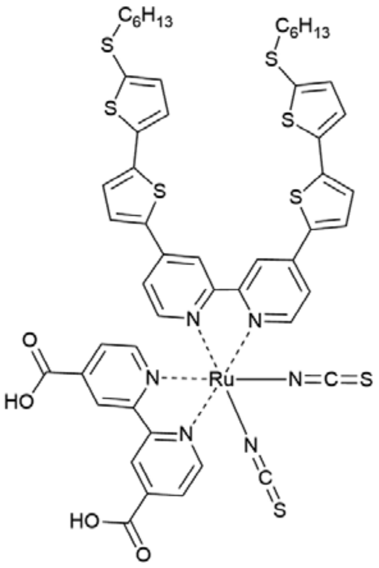
N719



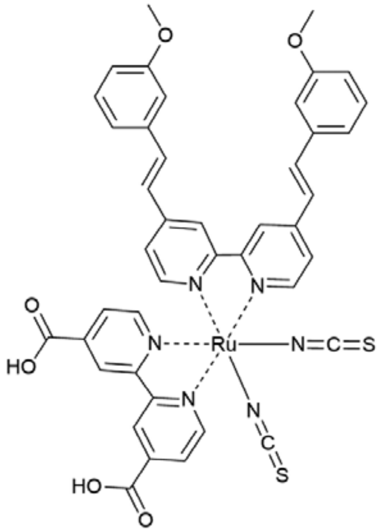
Z907



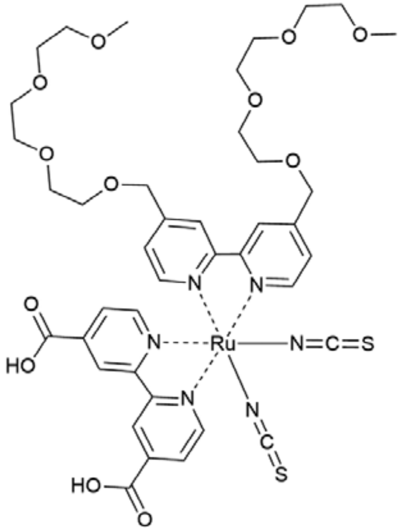
C101



CYC-B11



Z910

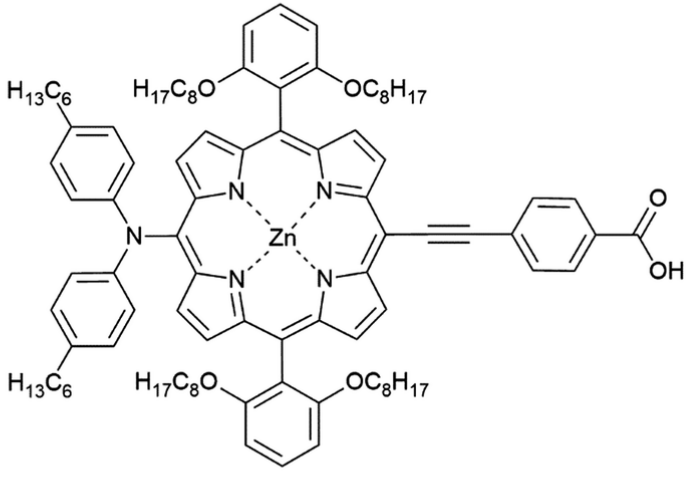


K51

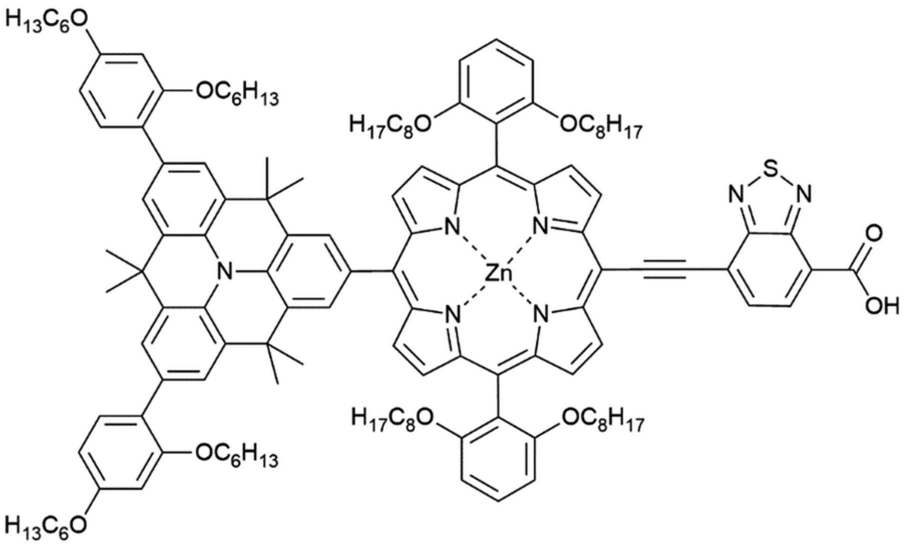
L.-L. Li and E. W.-G. Diau , Chem. Soc. Rev., 2013, 42 , 291 —304

Photosensitizer: a key component in the cell

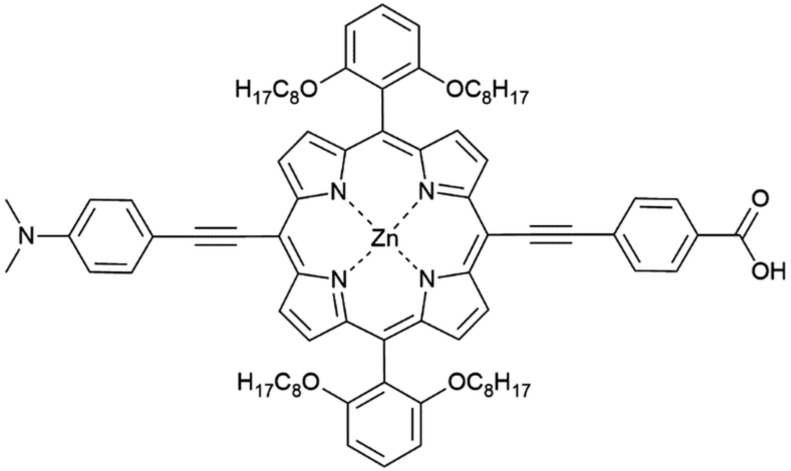
Porphyrin dyes
(meso substitution)



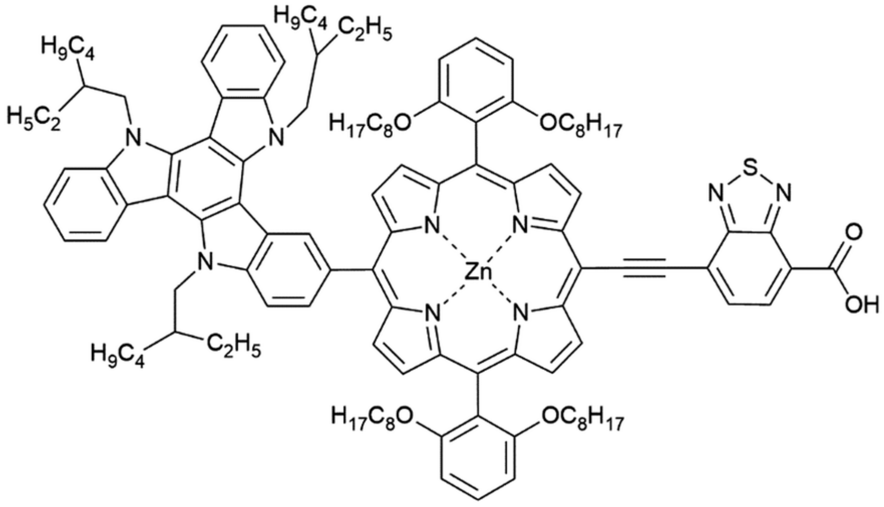
YD2-o-C8



FA



LD14



KS

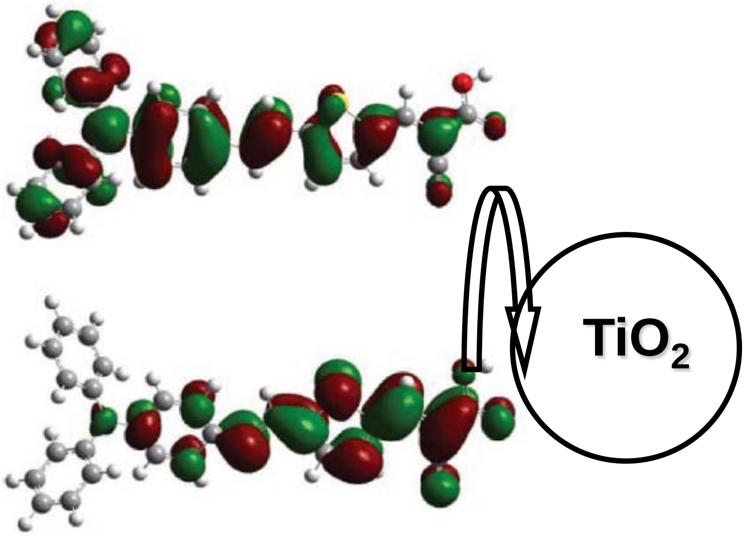
J.-W. Shiu , Y.-C. Chang , C.-Y. Chan , H.-P. Wu , H.-Y. Hsu , C.-L. Wang , C.-Y. Lin and E. W.-G. Diau , J. Mater. Chem. A, 2015, 3 , 1417 —1420

Photosensitizer: a key component in the cell

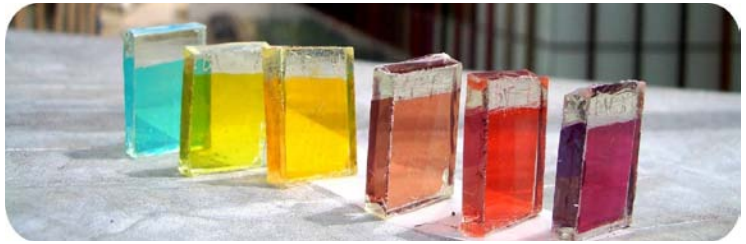
DONOR — π bridge — ACCEPTOR

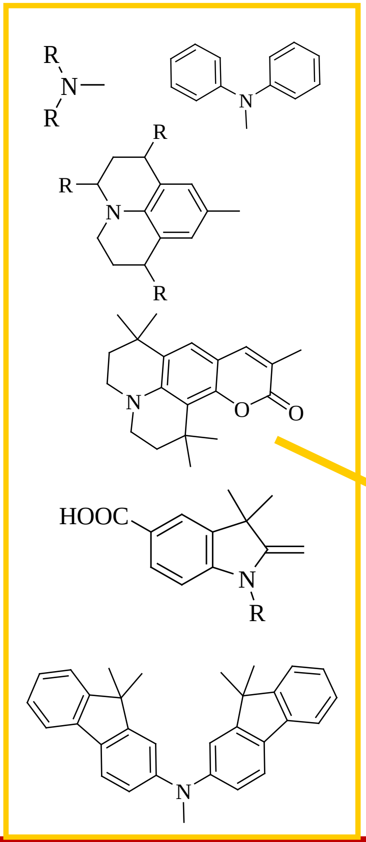
Push → Pull

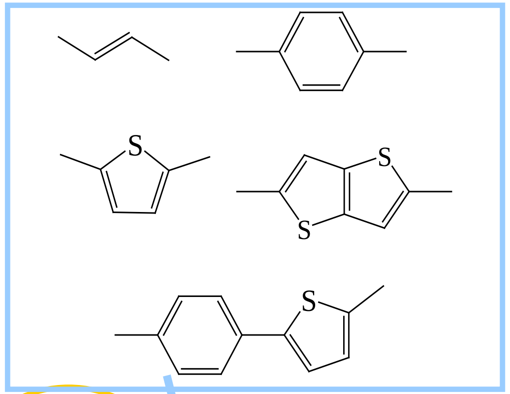
e^-

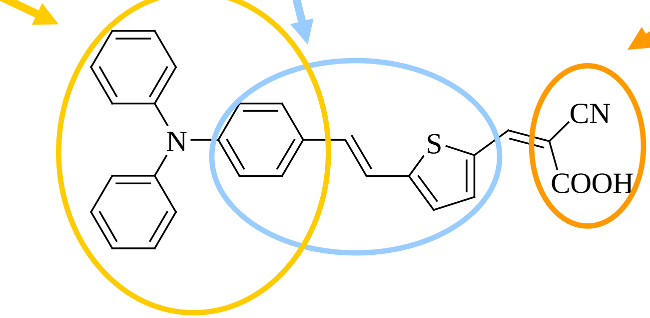


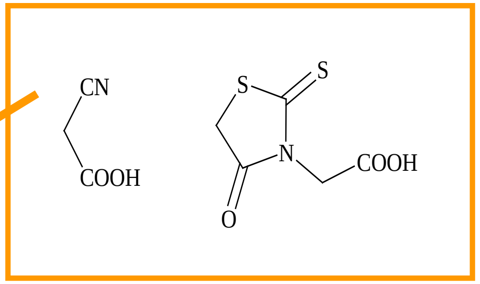
Organic dyes







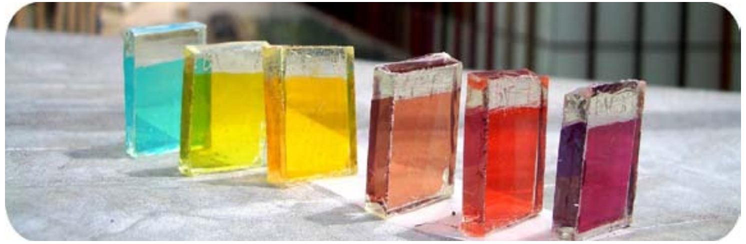




Hagfeldt et al. *Chem.Commun.* 2006 2245-2247

Photosensitizer: a key component in the cell

Organic dyes



LOW COST
- Easy preparation
- Easy purification

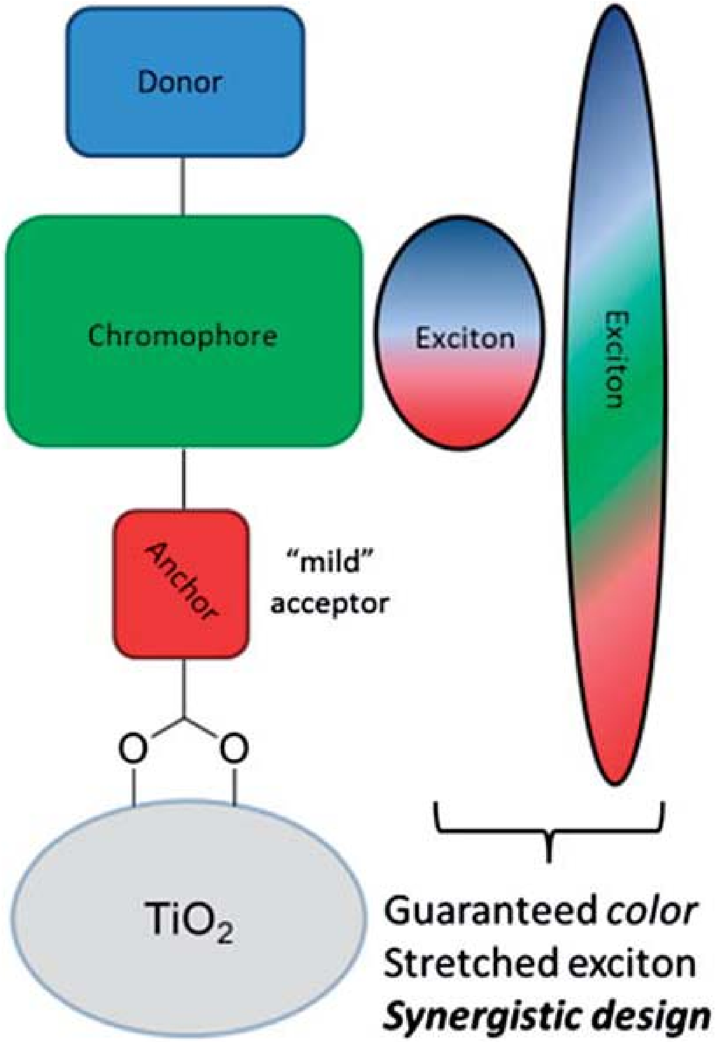
HIGH MOLAR ABSORPTION COEFFICIENT
- Efficient solar light-harvesting

ACCESS TO A WIDE VARIETY OF MOLECULAR STRUCTURES
- Control of photophysical properties
- Control of electrochemical properties

NO RESOURCE LIMITS
- No rare metals used

Donor -- *Chromophore* -- Anchor

D-C-A



Guaranteed *color*
Stretched exciton
Synergistic design

ELECTROCHEMICAL
OPTICAL PROPERTIES
- Electronic effects of D and A units
- Structure / length of the conjugated bridge

INTERMOLECULAR INTERACTIONS OF THE DYE MOLECULES
- Steric effects of substituents (sterically hindering substitutents)

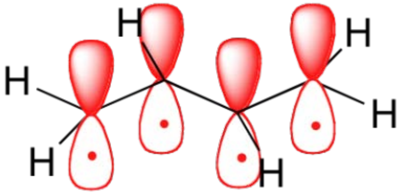
SUPRAMOLECULAR ORGANIZATION OF THE DYE MOLECULES ON TiO_2
- Shape of the dye molecule, Spacers, anchoring groups

Hagfeldt et al. *Chem.Commun.* 2006 2245-2247

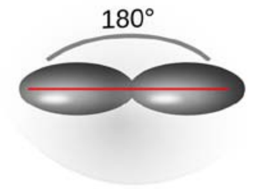
modified from lessons by G.Farinola

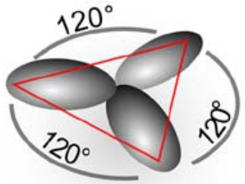
Photosensitizer: key properties to play with

key property of a dye
presence of ***conjugated bonds*** along the carbon backbone



mostly planar structure
that allows to absorb
in the visible





SINGLE MOLECULE PROPERTIES

ELECTRONIC PROPERTIES

- LUMO level of the Dye must be higher than the CB of TiO_2
- HOMO level of the Dye must be lower than the I_3^-/I^- redox potential
- Efficient charge separation

OPTICAL PROPERTIES

- High molar absorption coefficient in the visible/NIR spectrum

CHEMICAL PROPERTIES

- High stability

SUPRAMOLECULAR ORGANIZATION

ANCHORING GROUPS

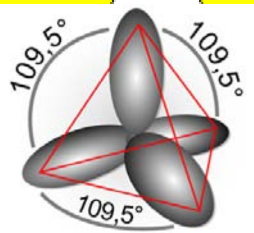
- $-SO_3H$, $-PO_3H_2$, -OH, COOH

INTERMOLECULAR INTERACTIONS

- No aggregation of the dye molecules on TiO_2 surface

INTERMOLECULAR DISTANCES AND ORIENTATION

- Spatial separation of positive moiety of the dye and TiO_2 surface to prevent charge recombination



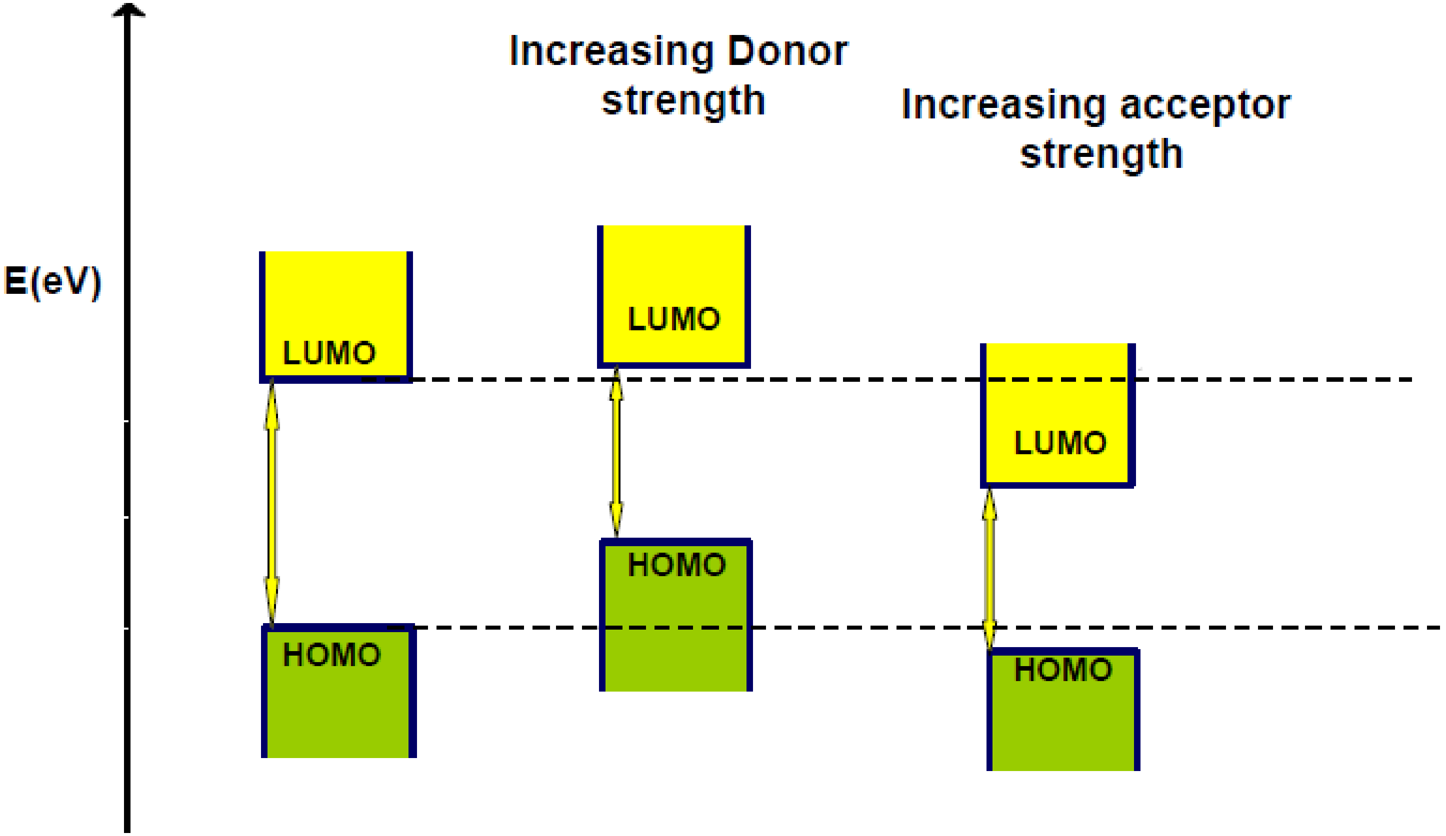
modified from lessons by G.Farinola

Photosensitizer: electronic effects

Dyes:

1) absorb light in the visible spectrum (400–700 nm),
2) have at least one chromophore (colour-bearing group)
3) have a conjugated system, i.e. a structure with alternating double and single bonds
4) exhibit resonance of electrons, which is a stabilizing force in organic compounds

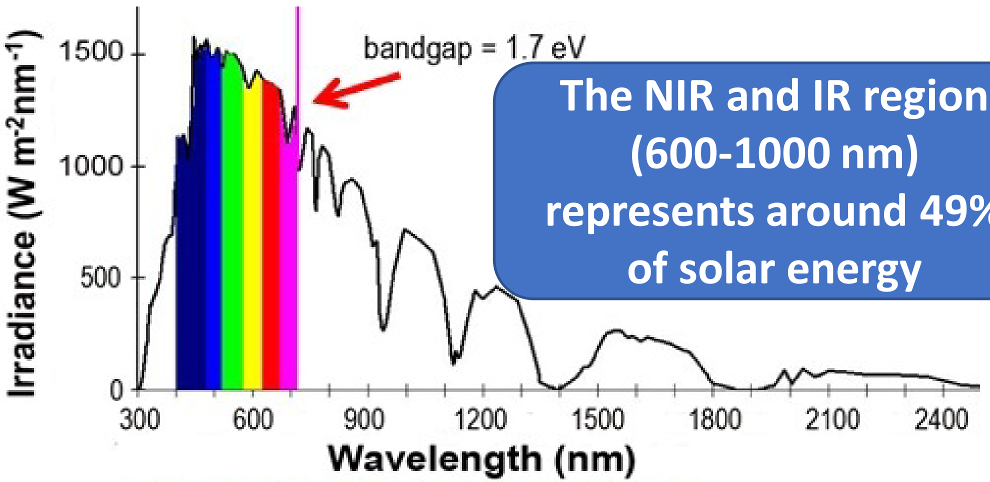
auxochromes: (i.e.: carboxylic acid, sulfonic acid, amino, hydroxyl groups, etc) these are not responsible for colour, their presence can shift the colour of a colourant and they are most often used to influence dye solubility



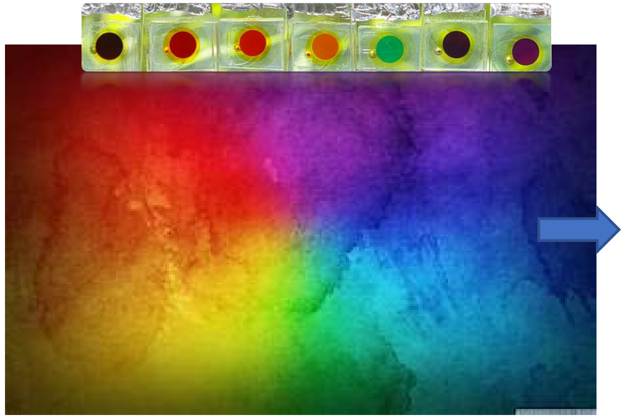
Abrahart EN(1977). *Dyes and their Intermediates*. New York: Chemical Publishing, pp. 1–12

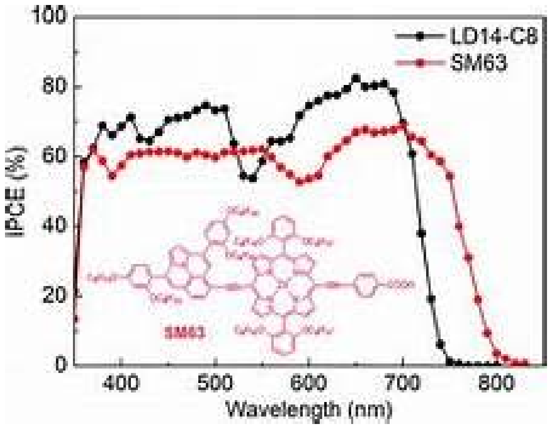
Dye-sensitized Solar Cells: color and transparency

- Architectural compatibility
- Environmental compatibility
- Weak / diffuse light
- Colorful
- Transparency



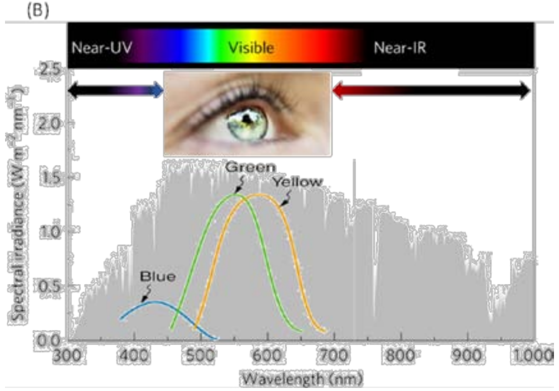
The NIR and IR region (600-1000 nm) represents around 49% of solar energy





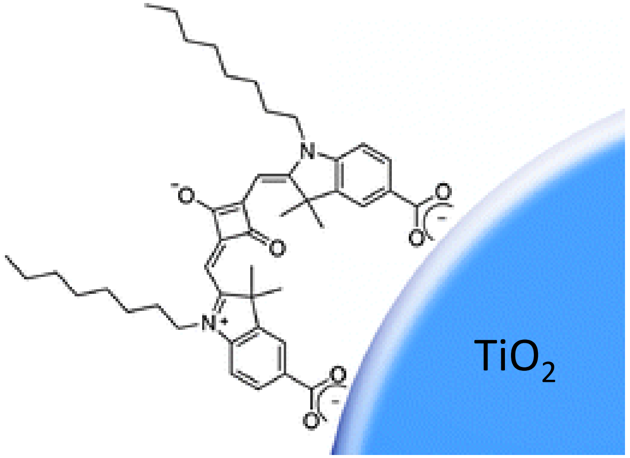
Monochromatic dyes (<u>aesthetic</u>) **Panchromatic dyes (<u>efficiency</u>)**

TRANSPARENT
to visible light dyes ?



Far-red / NIR squaraine dyes @ UNITO

INNOVASOL FP7 PROJECT

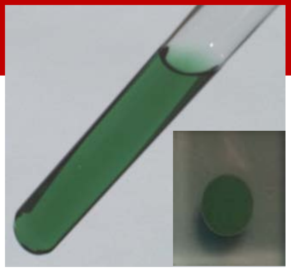


Chem. Commun. **2012**, 48, 2782–2784

η=4.7%
λ $_{max}$ =646 nm

VG1-C8

+ 134 nm



VG5

η=1.1%
λ $_{max}$ =780 nm

Chem. Commun. **2012**, 48, 2406–2408
Renewable Energy **2013**, 60, 672–678

+ 9 nm

VG10-C8

η=6.1%
λ $_{max}$ =655 nm

PCCP **2014**,
16, 24173-24177

- **Central functionalization**
  to prevent *cis-trans* photoisomerization in order to lock the *cis* configuration
- **Increase conjugation**
  (from squaraine to croconine or cyanine dyes)

Chem. Commun. 2012, 48, 2782, Renewable Energy 2013, 60, 672; Energies (2016), 9, 486, PCCP 2014, 16, 24173
Eur. J. Org. Chem. 2016, 13, 2244–2259; ChemSusChem 2017, 10, 2385

Far-red / NIR polymethine dyes

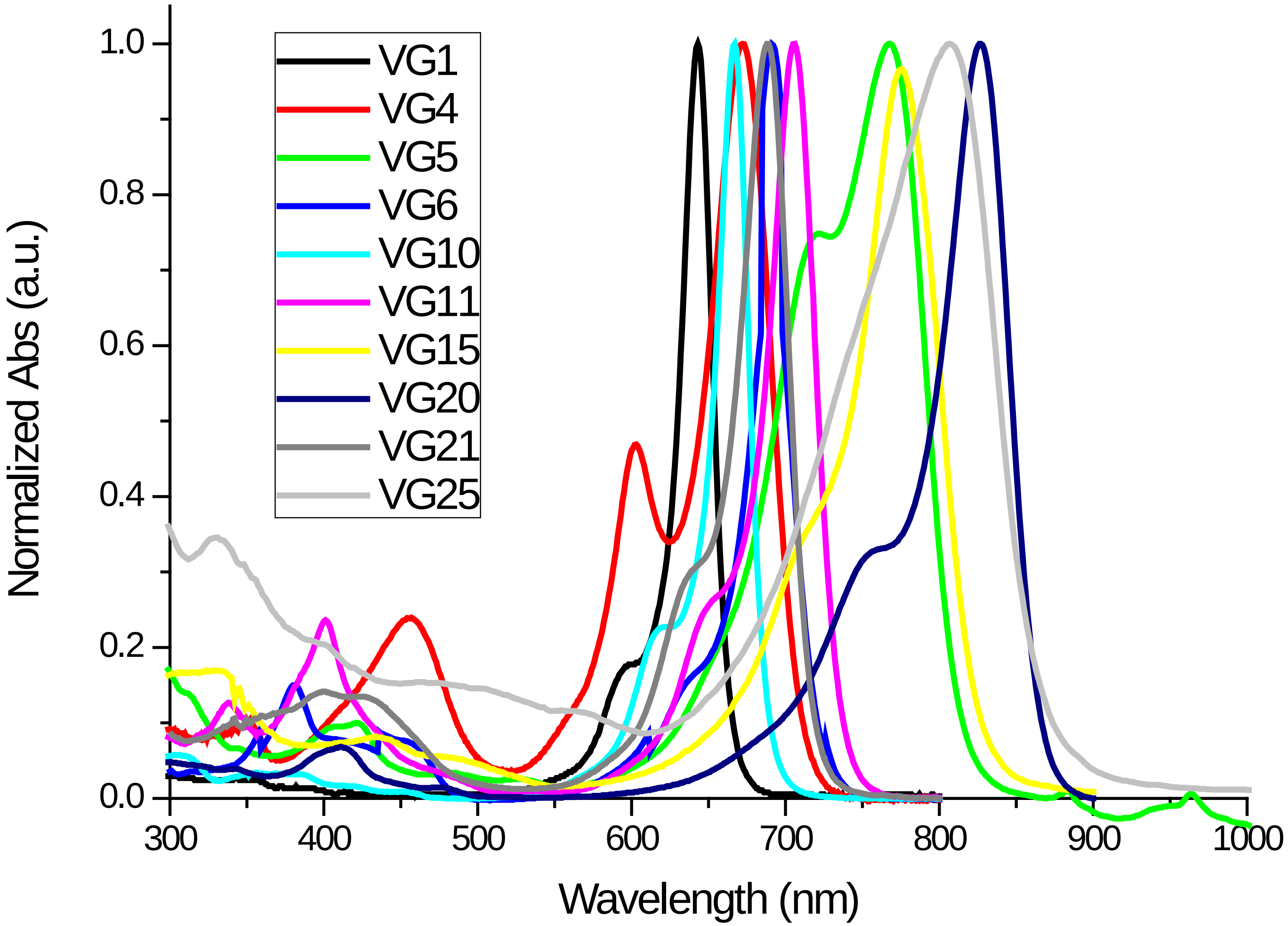
VG1

λ_{max}=646 nm

playing with structures of squaraines

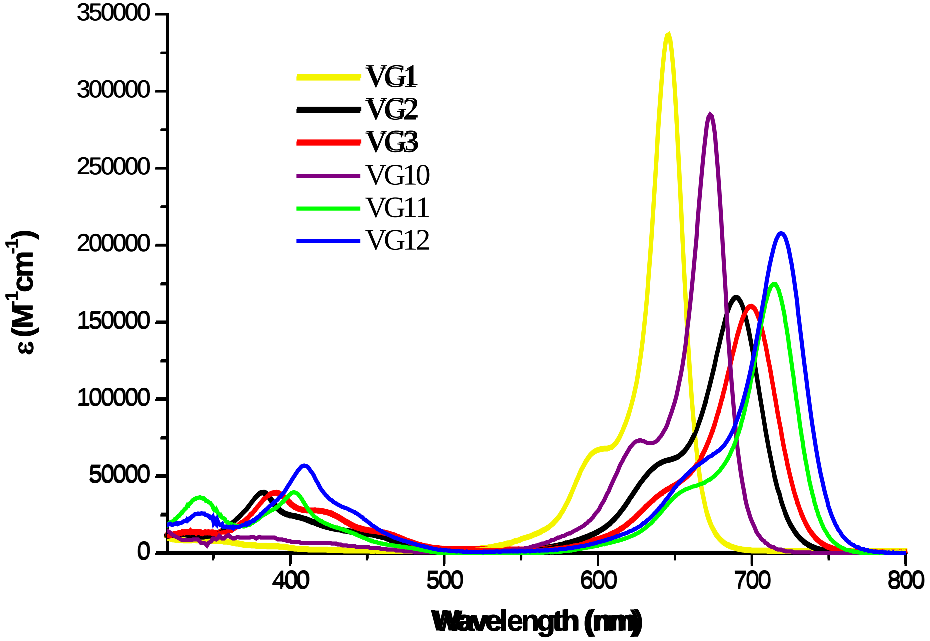
Chem. Commun. 2012, 48, 2782, Renewable Energy 2013, 60, 672; Energies 2016, 9, 486, PCCP 2014, 16, 24173
Eur. J. Org. Chem. 2016, 13, 2244–2259; ChemSusChem 2017, 10, 2385; ChemElectroChem 2017, 4, 2385; Frontiers in Chemistry 2019, 7, 99

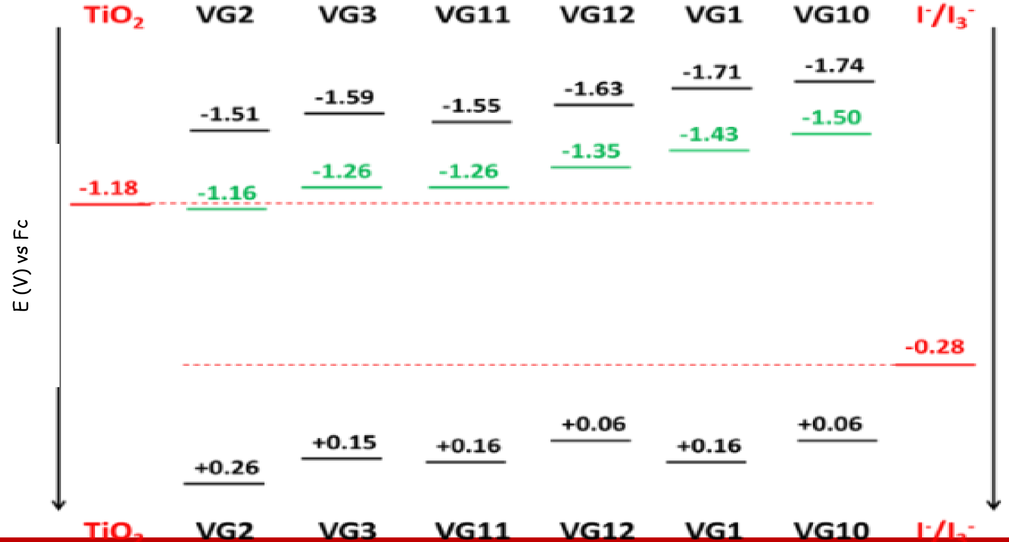
Modulating the conjugated backbone



λ_{max} **from 643 to 827 nm**

Central Functionalized squaraine dyes

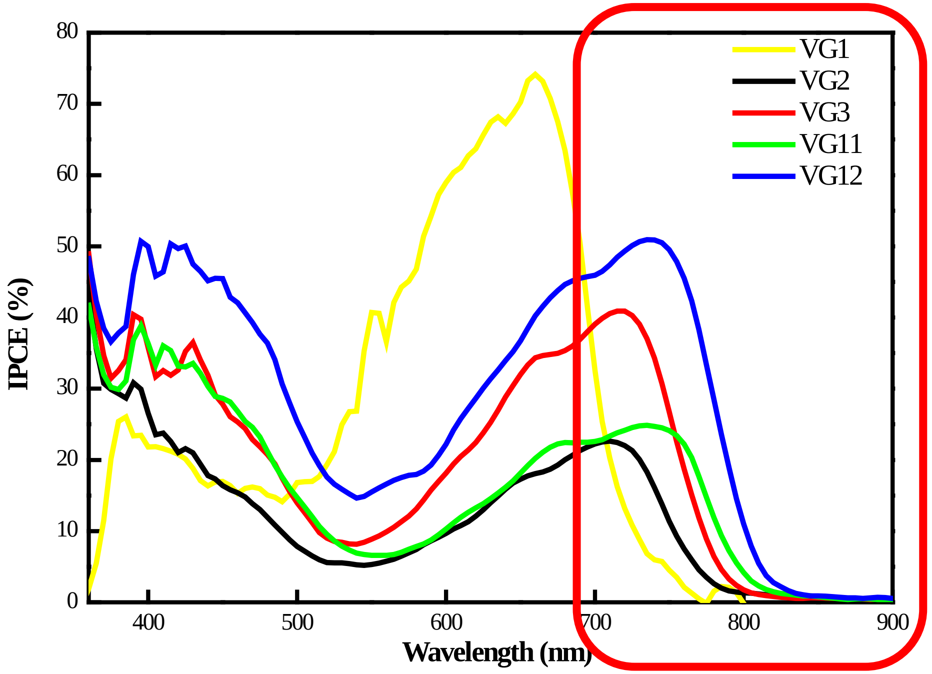


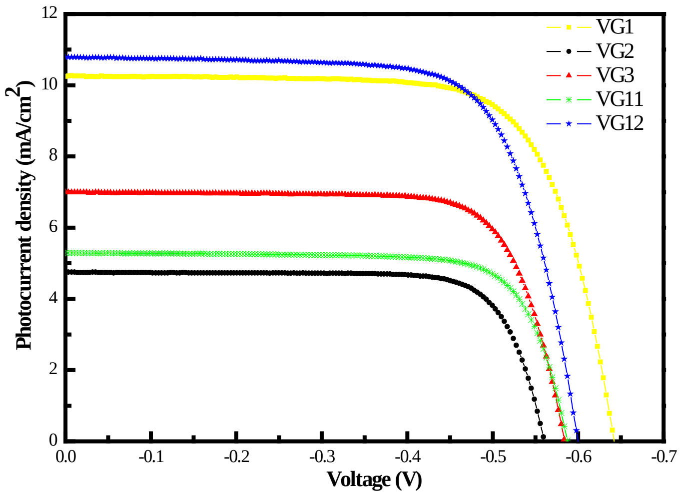


Dye	*λ$_{max}$ (nm)*
VG1	640
VG2	690
VG3	698
VG10	673
VG11	714
VG12	719

Galliano et al. Energies, **2016**, 9, 486

Central Functionalized squaraine dyes: IPCE



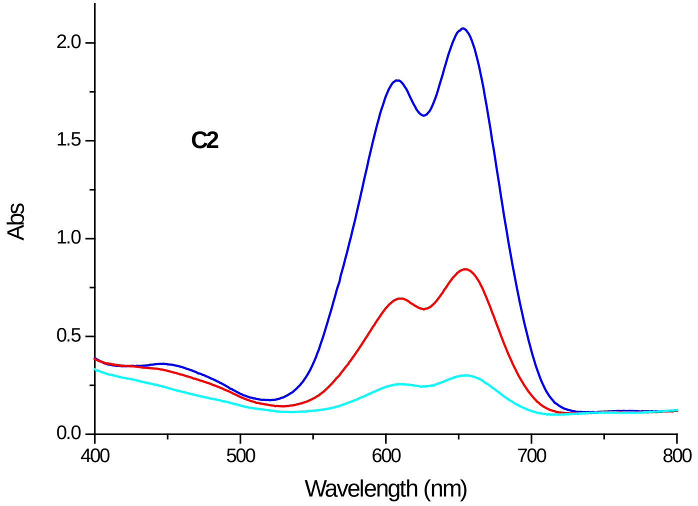


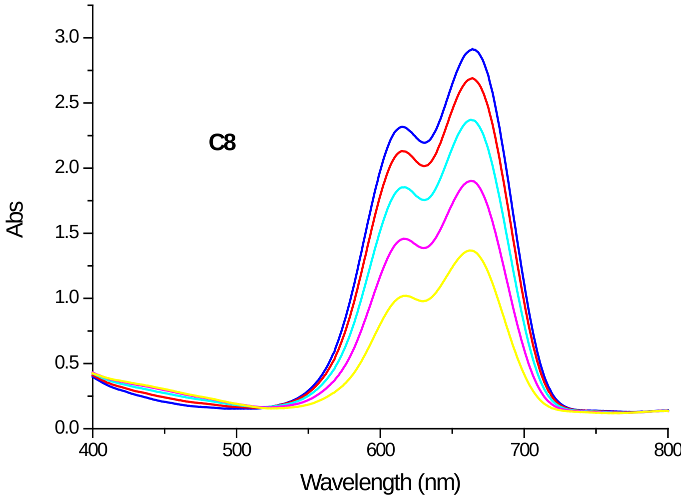
Dye	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	η (%)
VG1	642	10.3	0.72	4.7
VG2	560	4.7	0.77	2.1
VG3	584	7.0	0.75	3.1
VG11	587	5.3	0.76	2.5
VG12	599	10.8	0.71	**4.6**

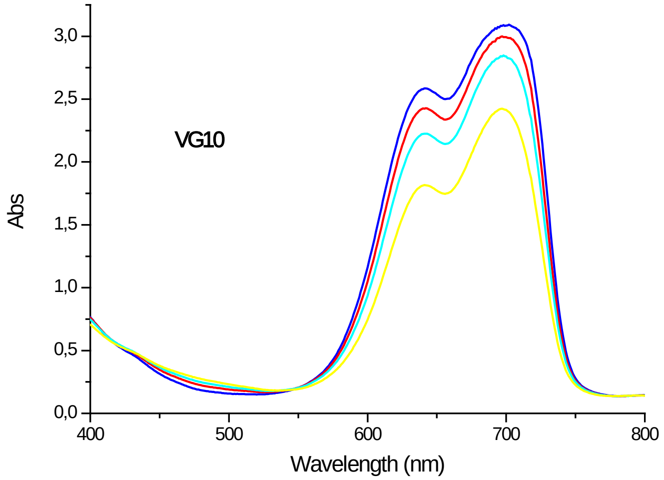
Galliano et al. Energies, **2016**, 9, 486

Symmetric squaraine dyes: effect of alkyl chain

- **higher photochemical stability on irradiated titania electrodes**

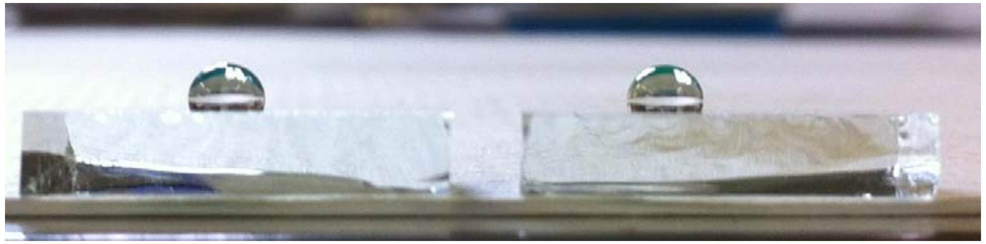






- **highly hydrophobic surface (depending on length and functionalization of the chain)**

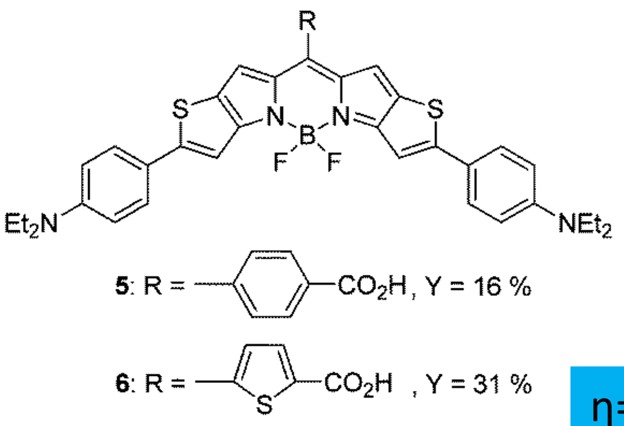
reference



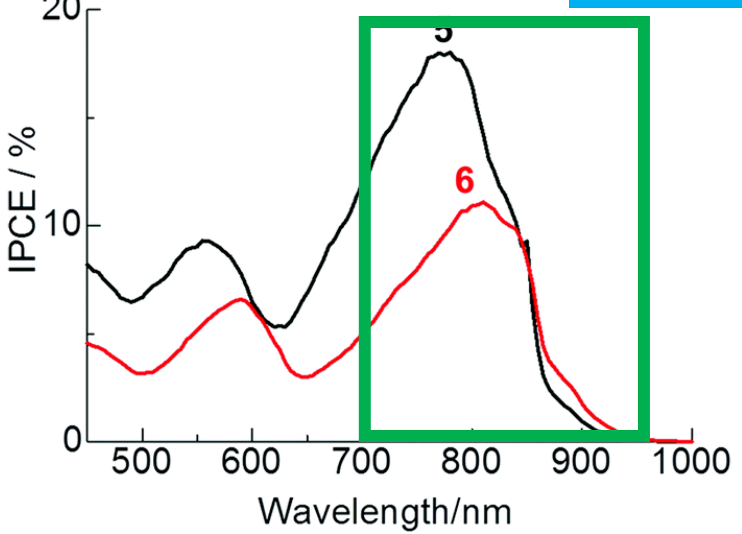
Dyed electrodes

Far-red / NIR dyes in literature (examples)

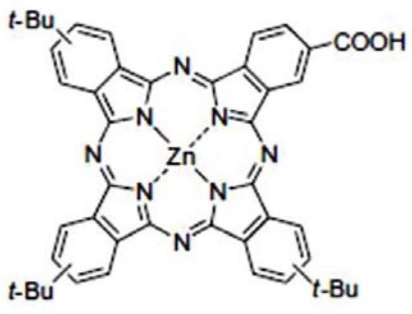
BODIPY



η=1.4%
λ $_{max}$ =746 nm

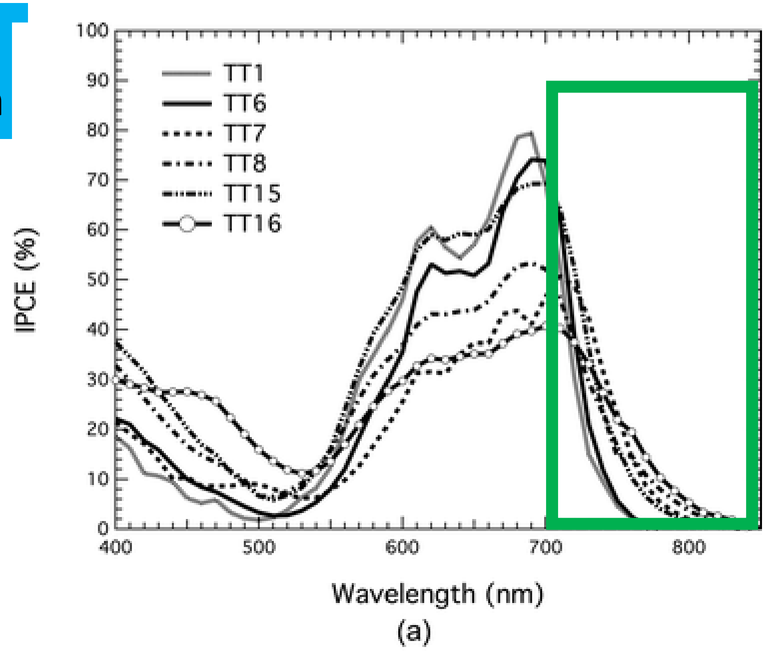


Zn-Phthalo



TT1 (Sensitizing dye)

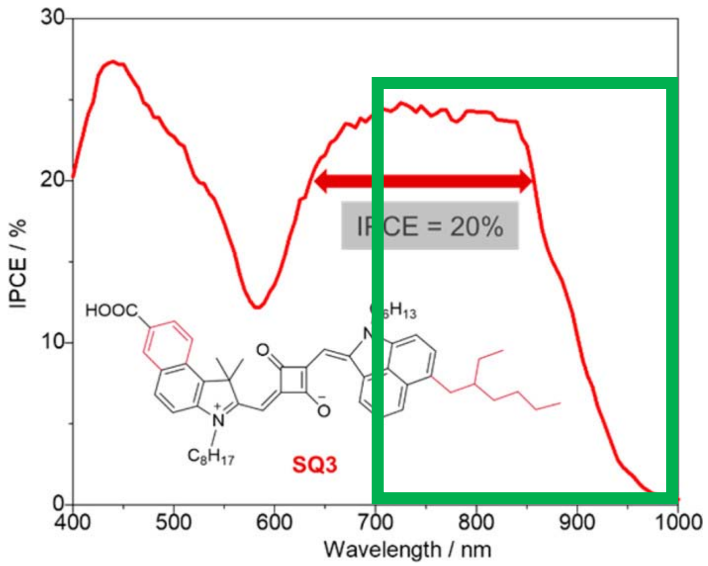
η=3.96%
λ $_{max}$ =680 nm



Reviews:
Polymethine dyes: Eu. JOC, 2016, ***13,*** 2244-2259
Phthalocyanine dyes: Coord Chem Rev, 2019, **381**, 1-64

Squaraine

η=1.3%
λ$_{max}$=850 nm

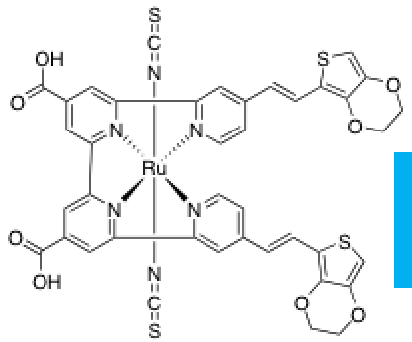


NJC, 2019, **43**, 1156

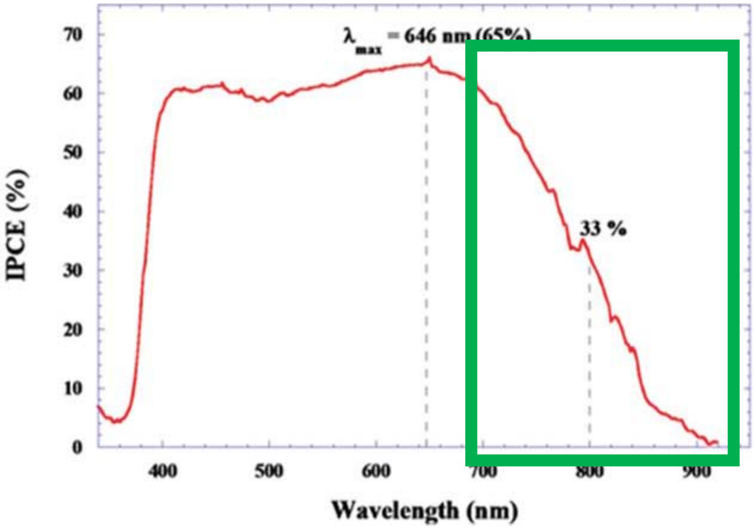
Energy Env Sci. 2011, **4**, 189

J. Org. Chem. 2018, **83** (8) 4389-4401

Far-red / NIR dyes in literature (examples)



η=5.6%
λ_{max} =646 nm



η=2.1%
λ_{max} =811 nm

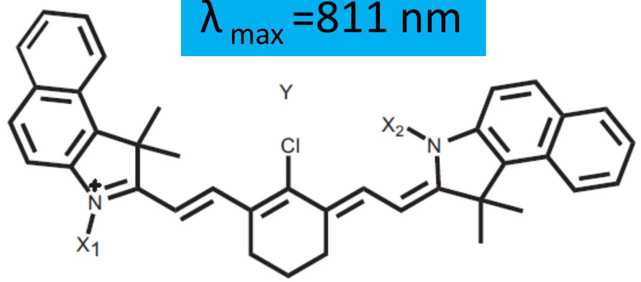
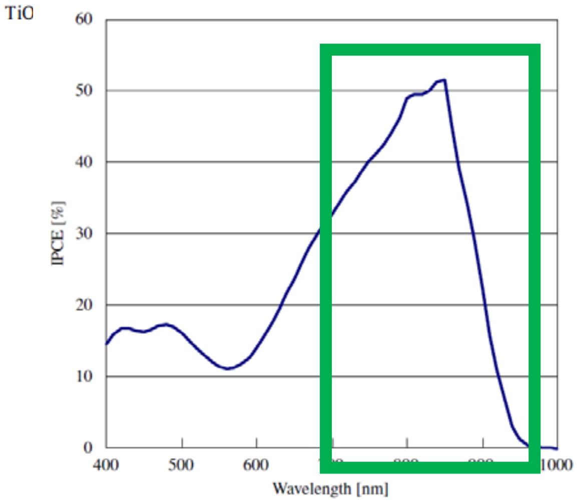
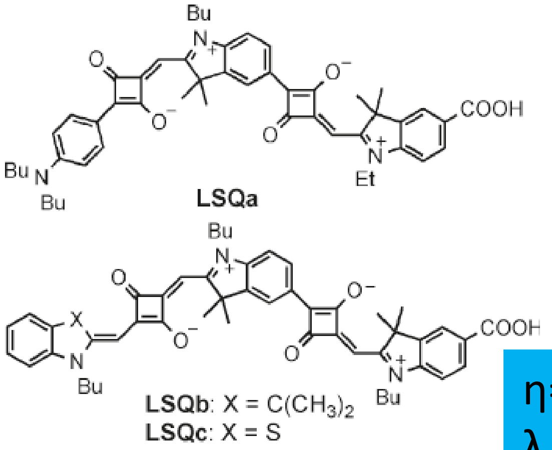


Table 2
Performance of infrared-dye-sensitized solar cells

Infrared dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (–)	Efficiency (%)
NK-4432	0.37	0.40	0.54	0.08
NK-6037	4.2	0.39	0.67	1.10



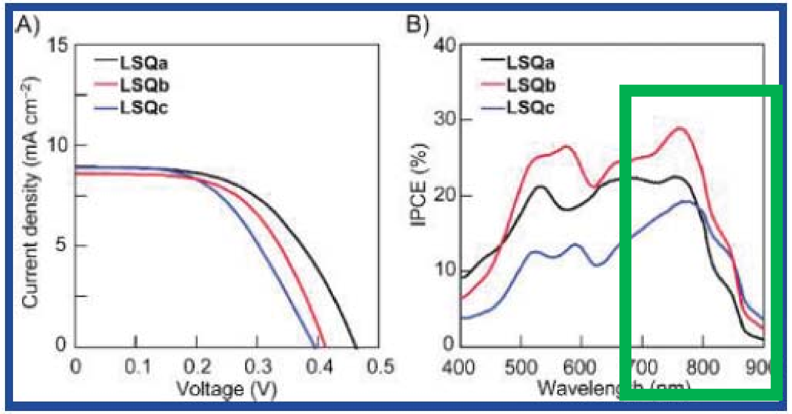


LSQa

LSQb: X = $C(CH_3)_2$
LSQc: X = S

η=2.2%
λ_{max}=777 nm

dye	V_{oc} (V)	J_{sc} (mA)	fill factor	η (%)
LSQa	0.46	9.05	0.54	2.26
LSQb[b]	0.41	8.64	0.57	2.01
LSQc[b]	0.40	9.01	0.51	1.82



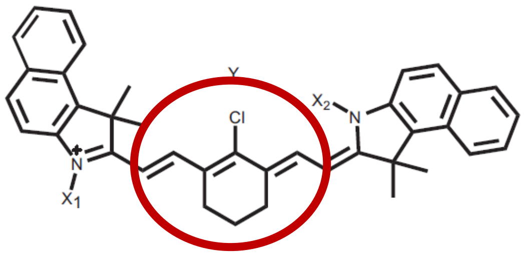
Dalton Trans., 2011, ***40*, 234–242**

Sol. En. Mat. & Solar Cell, 2009, ***93*, 831–835**

Org. Lett., 2011, ***13*, 22**

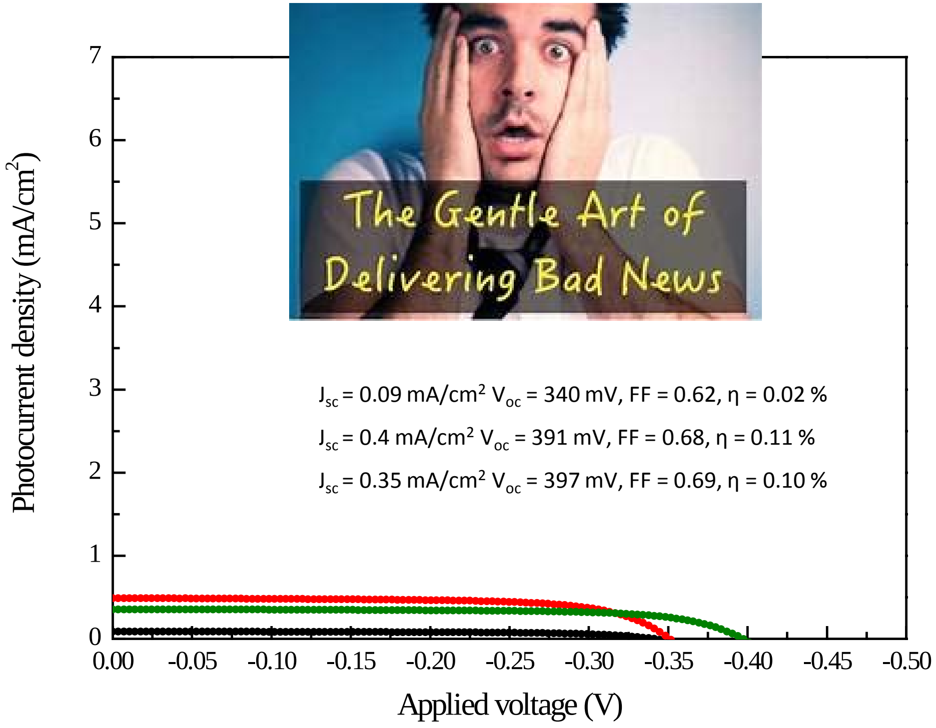
COOH conjugated Cy7

- **Increase conjugation**
  (from squaraine to cyanine dyes)



+

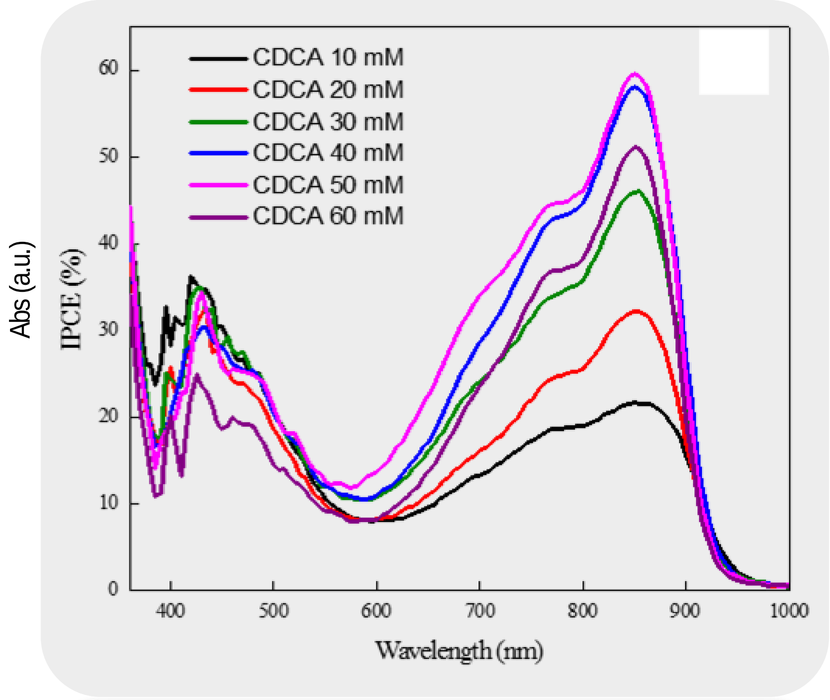
Cyanine VG20



J_{sc} = 0.09 mA/cm^2 V_{oc} = 340 mV, FF = 0.62, η = 0.02 %

J_{sc} = 0.4 mA/cm^2 V_{oc} = 391 mV, FF = 0.68, η = 0.11 %

J_{sc} = 0.35 mA/cm^2 V_{oc} = 397 mV, FF = 0.69, η = 0.10 %



VG20

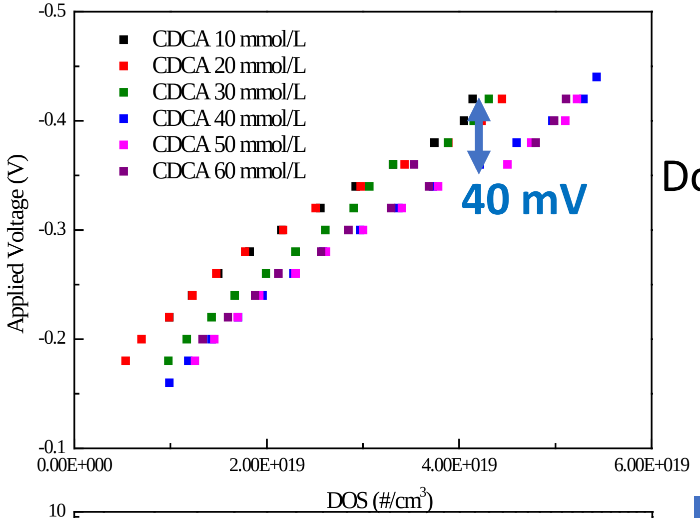
	λ_{max} (nm) in MeOH
VG20	827

NEXT STEPS?

Optics Letters 2014 39(10) 2947-2950 *J. Phys. Chem. C 2018*, **122** (45) 26281-26287 - Biosensors

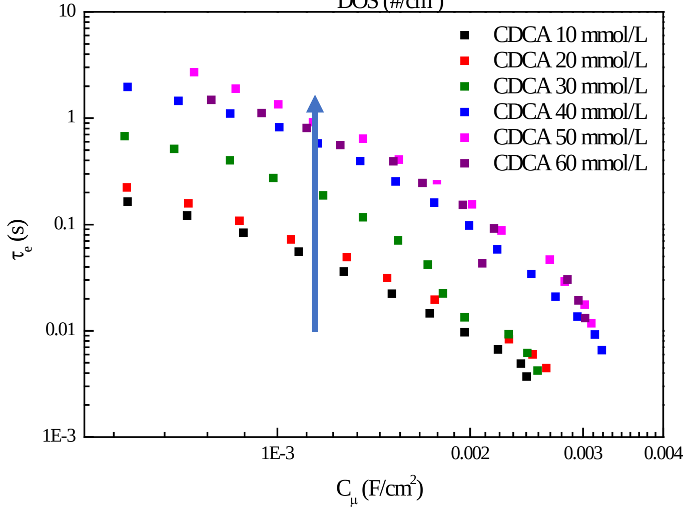
VG20 dye investigation

Evaluation of the kinetic parameters:



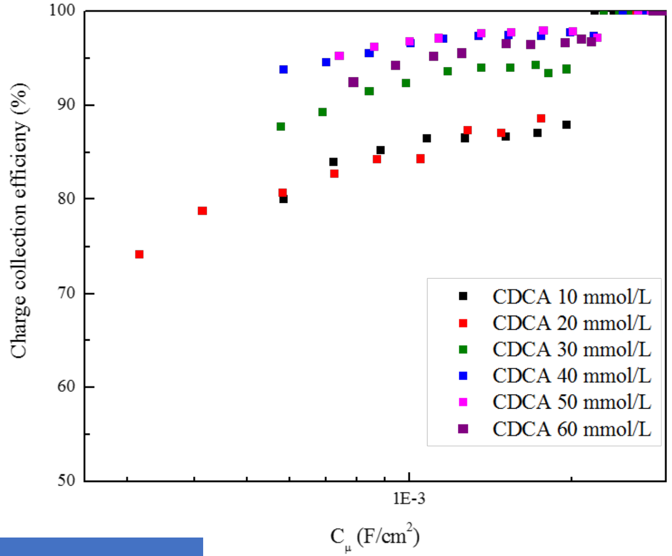
Downshift of traps distribution

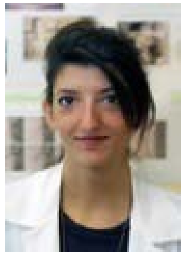
1. Adsorbed dye geometry depends from CDCA ratio
2. CDCA acts as co-absorbent



CDCA acts as a BL towards I_3^-/e^- recombination

e- transport slow down (trapping of e- at low energetic levels)

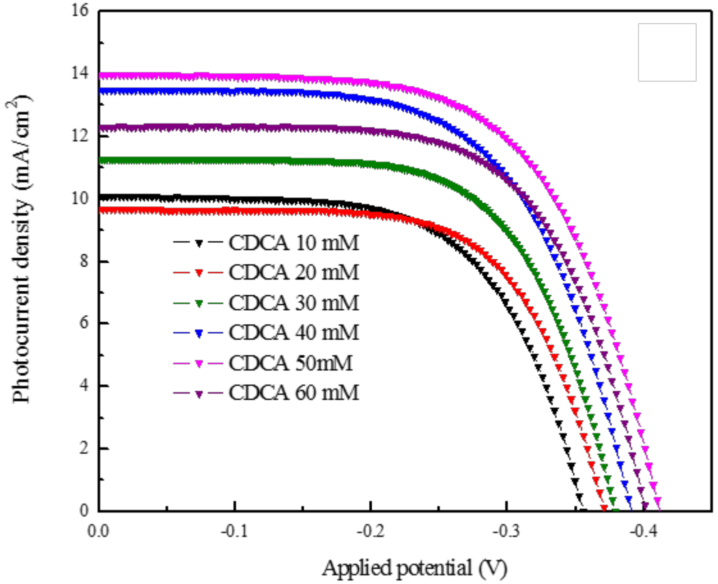




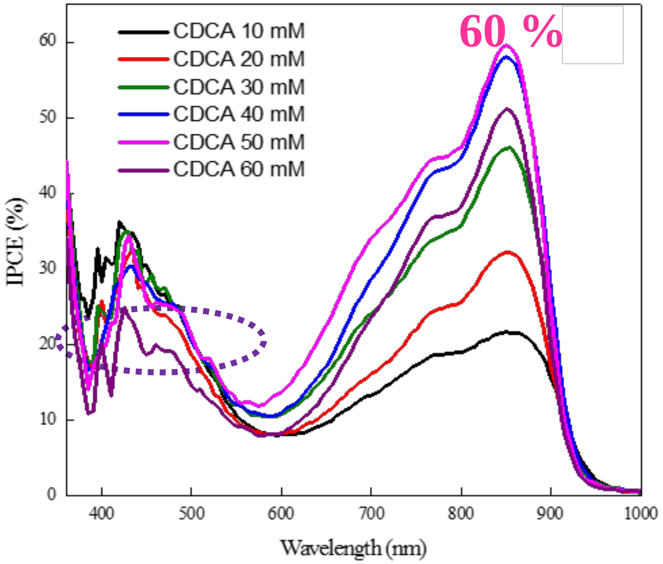
Charge collection efficiency approach 100 % for VG20 with 50 mmol/L CDCA

Optimizing VG20 dye: CDCA effect

By conserving the optimized parameters (thickness, electrolyte, dipping time), CDCA has been added increasing the amount by 10 mmol/L each time.



CDCA	Voc (mV)	Jsc (mA/cm²)	FF	η (%)
10 mmol/L	356	10.1	0.62	2.2
20 mmol/L	371	9.7	0.65	2.3
30 mmol/L	379	11.3	0.64	2.8
40 mmol/L	390	13.5	0.62	3.2
50 mmol/L	412	14.0	0.62	3.6
60 mmol/L	402	12.3	0.64	3.2



NIR part of conversion ($S_0 \rightarrow S_1$ transition) is improved by the CDCA

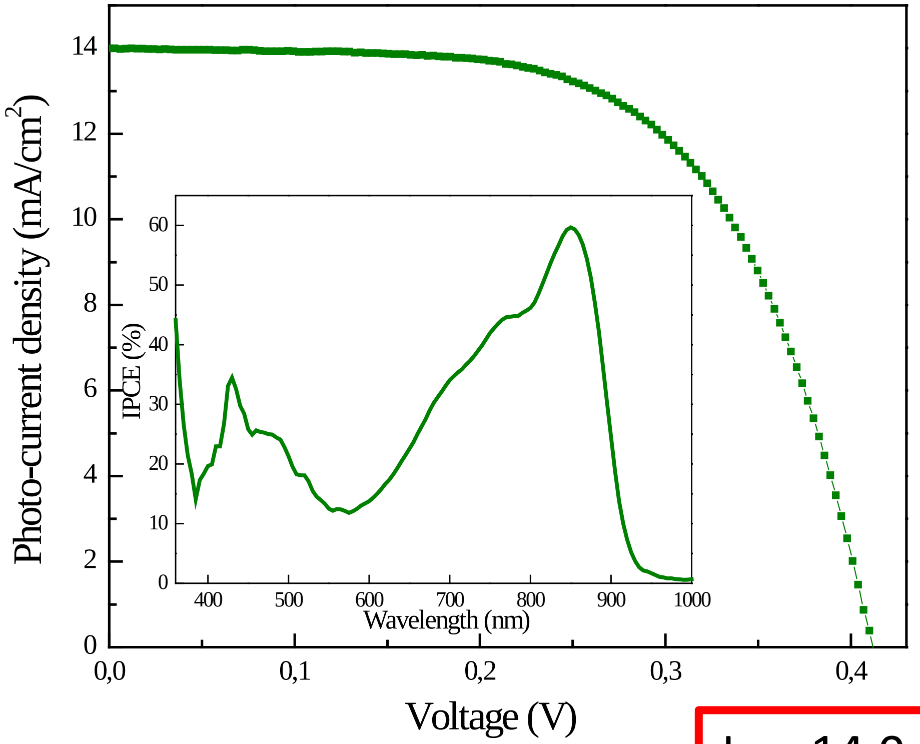
Record of 60 % of IPCE at 850 nm with a tail of conversion up to 920 nm

Optimizing VG20 dye

Conversion up to 950 nm

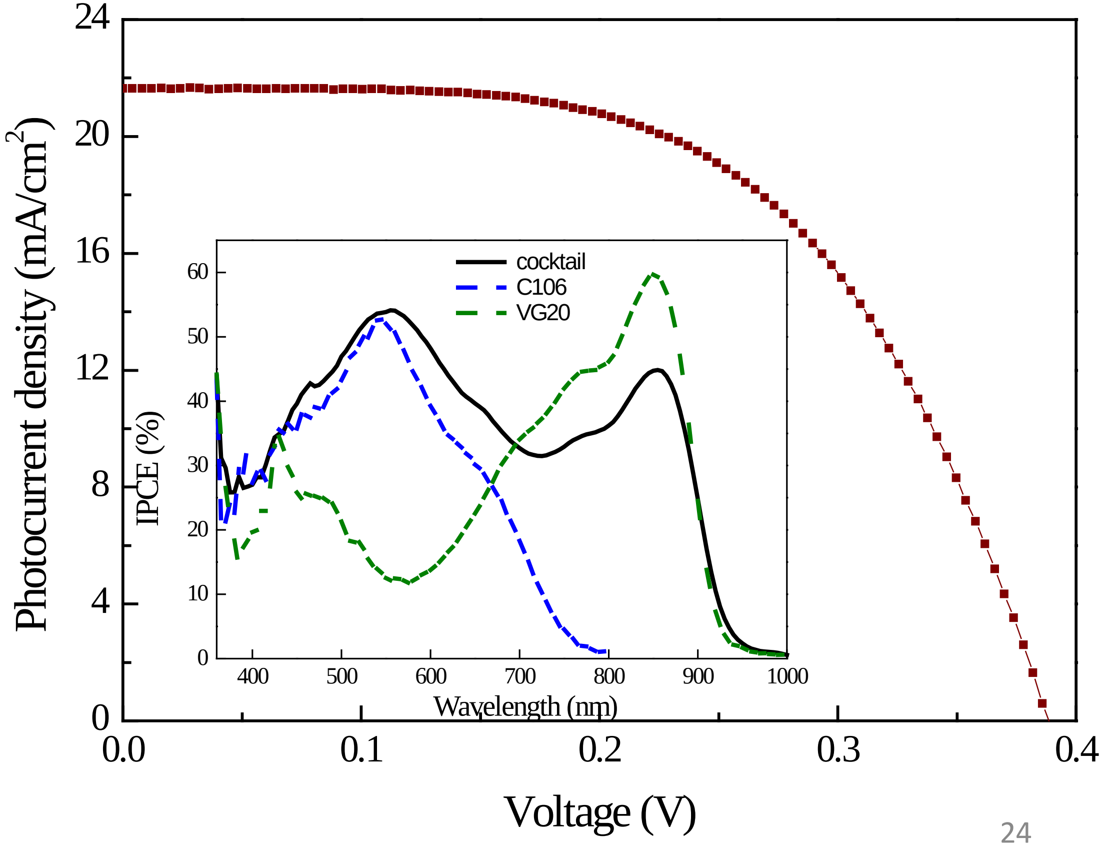
C106
λ=550nm

J_{sc} = 21.6 mA/cm^2
V_{oc} = 389 mV
ff = 0.57
η= 4.9 %



J_{sc} = 14.0 mA/cm^2
V_{oc} = 412 mV
ff = 0.62
η = 3.6 %

Electrolyte: [I_3^-]=50mM; [I^-]=1M; [LiI]=1M
[CDCA]=50mM in 100µM dye solution



Croconines & Cy7

- **Increase conjugation**
  (from squaraine to croconine or cyanine dyes)

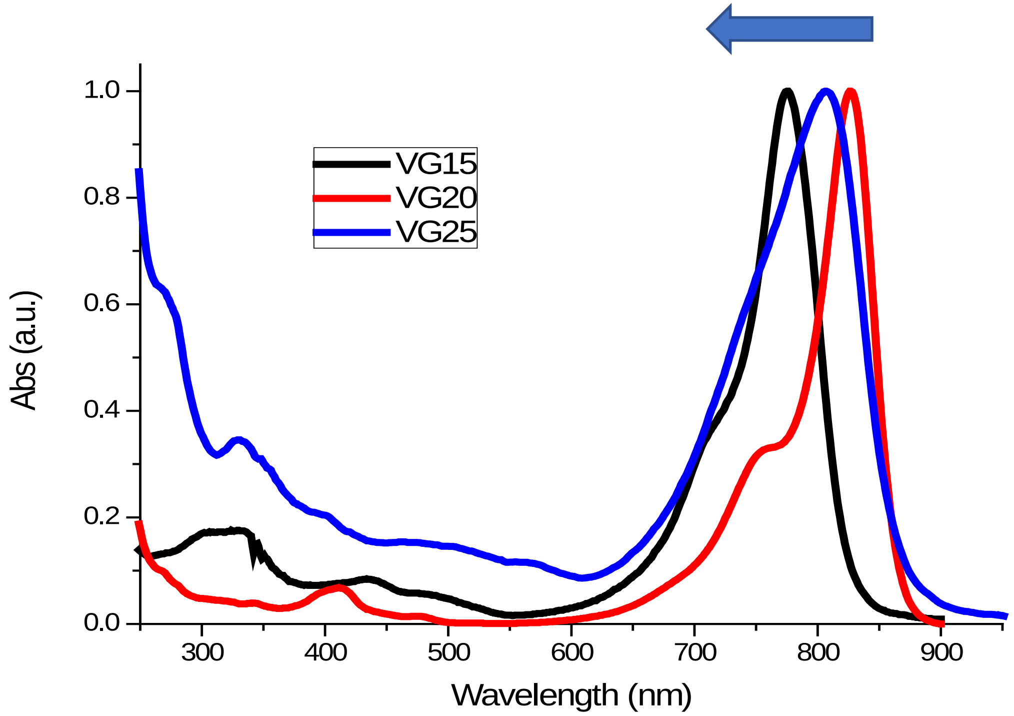
Cyanine VG20

Croconine VG15

Croconine VG25

	λ_{max} (nm) in MeOH
VG15	775
VG20	827
VG25	807

VG15 VG20 VG25

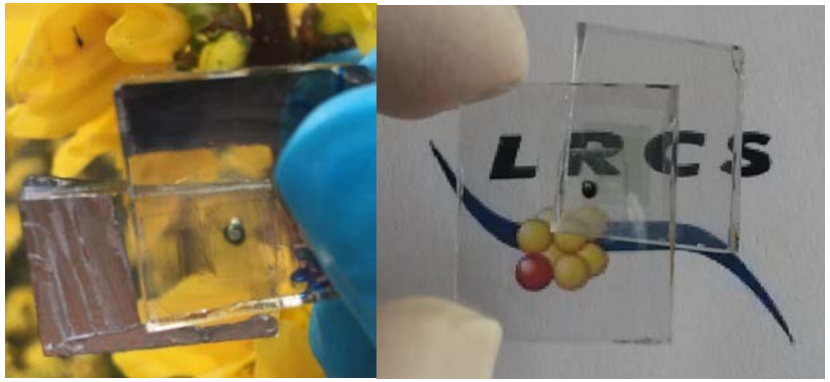


Conclusions (1)

VG20 cyanine-based dyes as NIR colorless working DSSC

Beauty of DSSC: totally non intruisive / active transparent and colourless PV

PCE record of 3.1 %



Low cost synthetic protocols and simple symmetric dyes

Simple synthetic procedure to modulate redox and absorption properties

Substitutions on the skeleton modify the dye behaviour on the surface

impressive

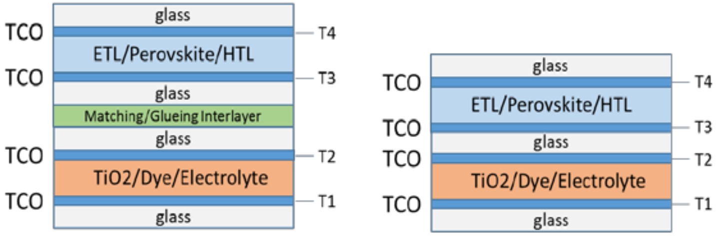
European Commission

H2020-LC-SC3-2018-
Joint-Actions-3

https://impressive-h2020.eu

TARGET PCE = 6%
(320 – 450 nm)

2V
3.6 mA/cm2
0.83 %
AVT = 75 %



Mechanically stacked tandem

Integrated tandem

TARGET PCE = 8%
(700-950 nm)

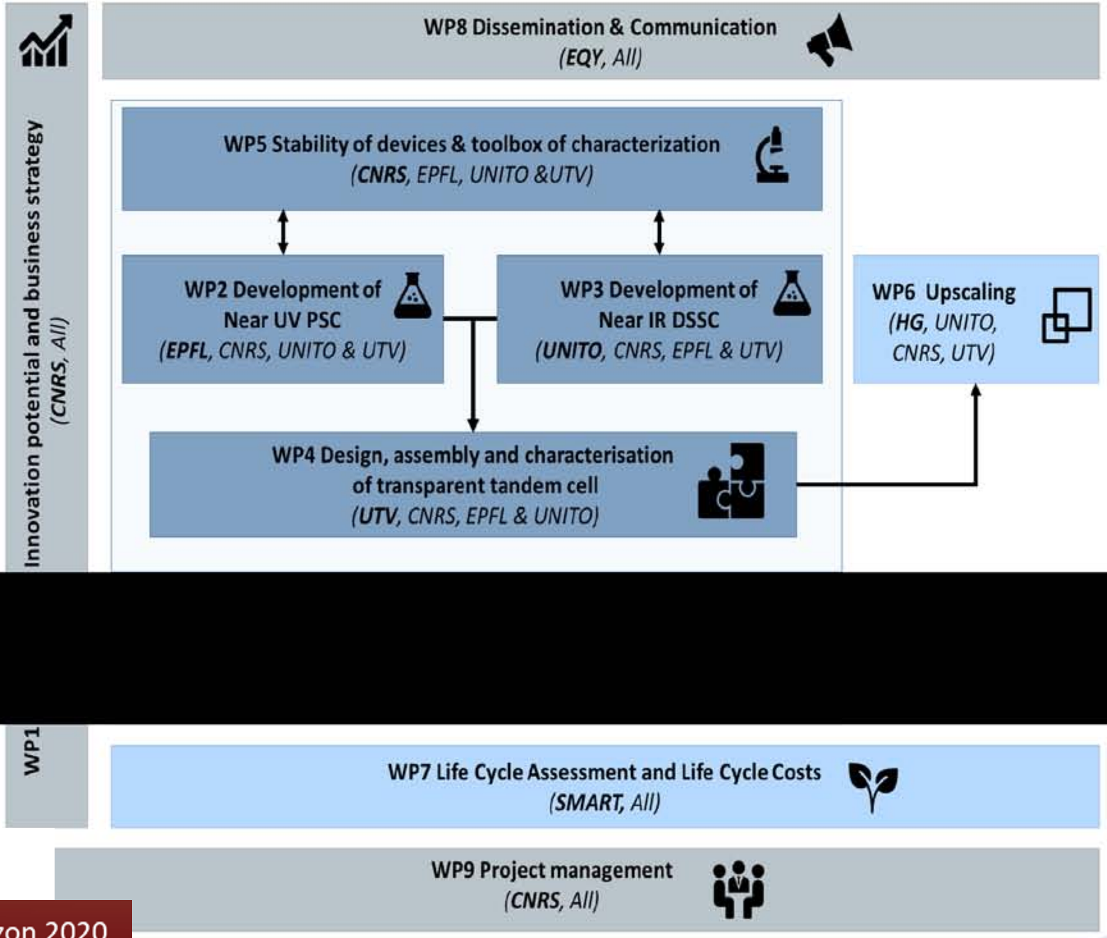
0.76 V
13.5 mA/cm2
0.78 %
AVT = 75%

Prof. Claudia Barolo

Dr. Nadia Barbero

Prof. Michael Graetzel

Dr. Shaik Zakeeruddin



WP8 Dissemination & Communication
(EQY, All)

WP5 Stability of devices & toolbox of characterization
(CNRS, EPFL, UNITO &UTV)

WP2 Development of Near UV PSC
(EPFL, CNRS, UNITO & UTV)

WP3 Development of Near IR DSSC
(UNITO, CNRS, EPFL & UTV)

WP6 Upscaling
(HG, UNITO, CNRS, UTV)

WP4 Design, assembly and characterisation of transparent tandem cell
(UTV, CNRS, EPFL & UNITO)

WP1 Innovation potential and business strategy
(CNRS, All)

[redacted]

WP7 Life Cycle Assessment and Life Cycle Costs
(SMART, All)

WP9 Project management
(CNRS, All)

Università di Roma Tor Vergata

Prof. Aldo Di Carlo

smart GREEN SCANS

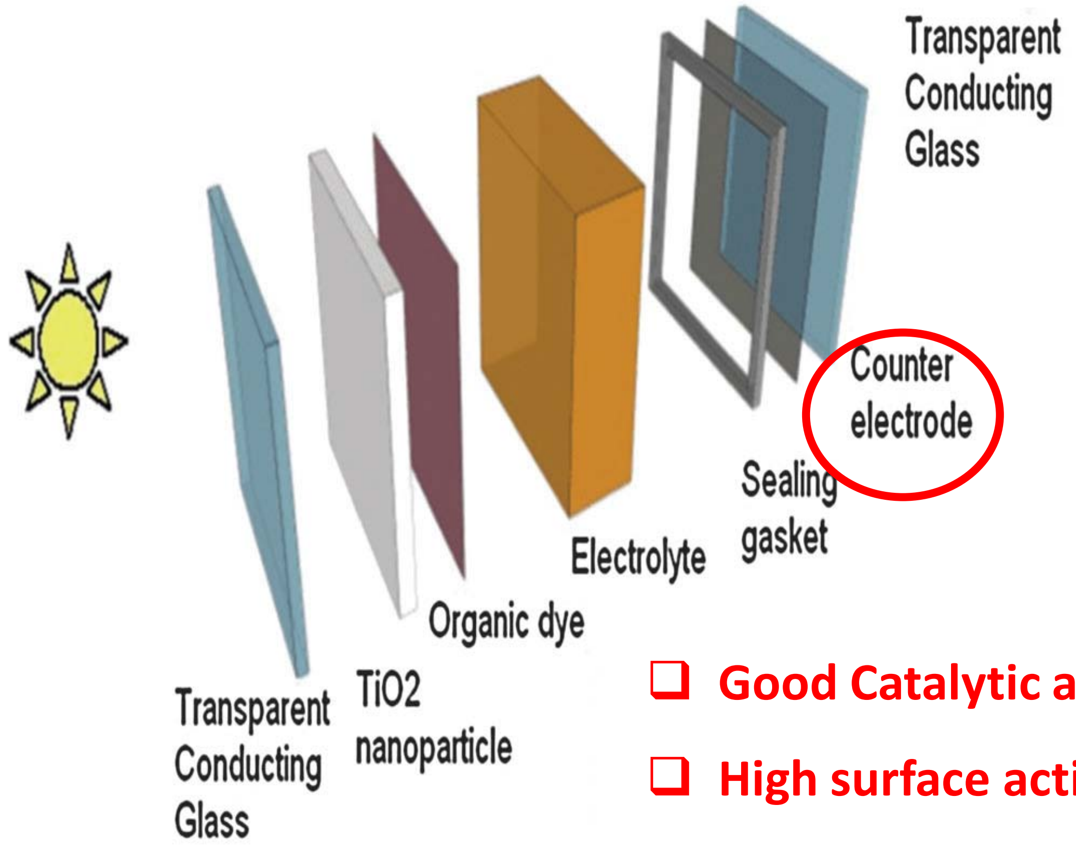
Dr. Mariska de Wild-Scholten

GLASS

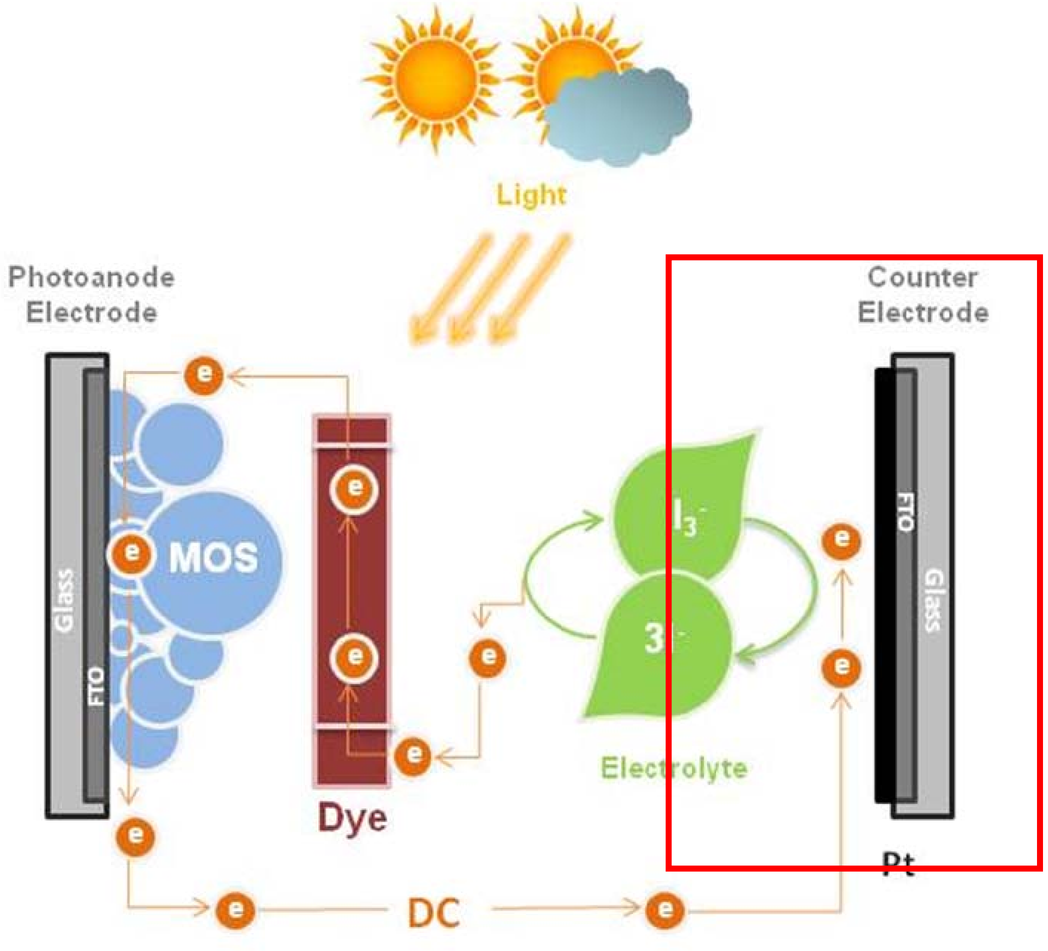
Dr. Yiming Cao
Dr. Thomas Friesen (CTO)

This project has received funding from the European Union's Horizon 2020 research and innovation program under Grant Agreement No 826013

Counter electrode:materials



FUNCTION: Re-generate the oxidized species of the redox couple



- ☐ **Good Catalytic activity**
- ☐ **High surface active area**
- ☐ **(Photo)chemical satbility**
- ☐ **Thermal Stability**

Counter electrode: materials

🙂

Very good catalytic properties

Small amount of material

High efficiency

☹

Easy posionable by electrolyte

Very Expensive

Classified as CRM

? **ALTERNATIVES** ?

🙂

High surface area

Relatively Cheap

Good efficiency

Green and (more) sustainable

☹

Mediocre catalytic properties

Carbonaceous vs polymeric

Green and sustainable
Low cost
Good efficiency

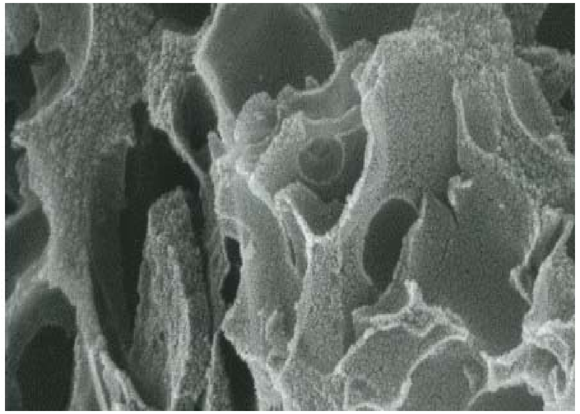
Medium conductivity
(metal doping possible)

High carbonization
temperature (> 800 °C)

Green
No CO_2 release
Very good efficiency

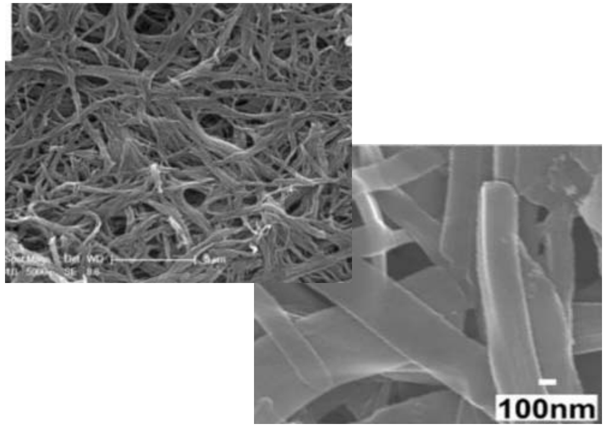
Sutainability still to be proved
Medium cost

Use of harsh solvent
Difficult synthesis



Common Advantages

Possible direct deposition on FTO
Deposition on flexible substrates
Excellent (photo)stability
Good chemical Inertness

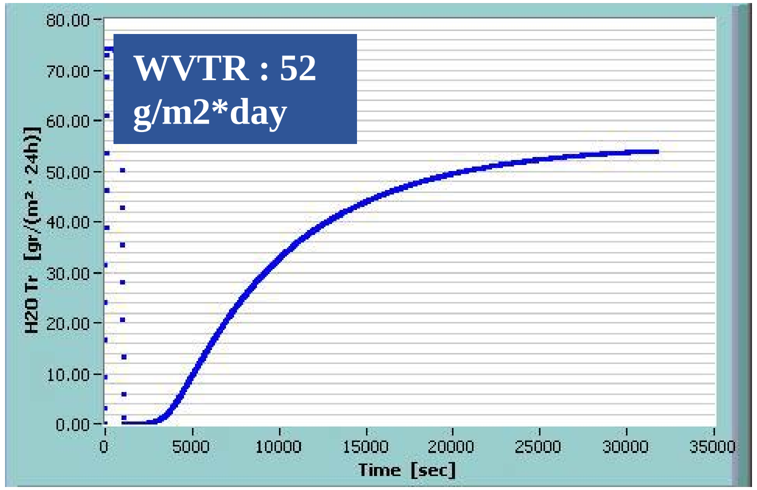


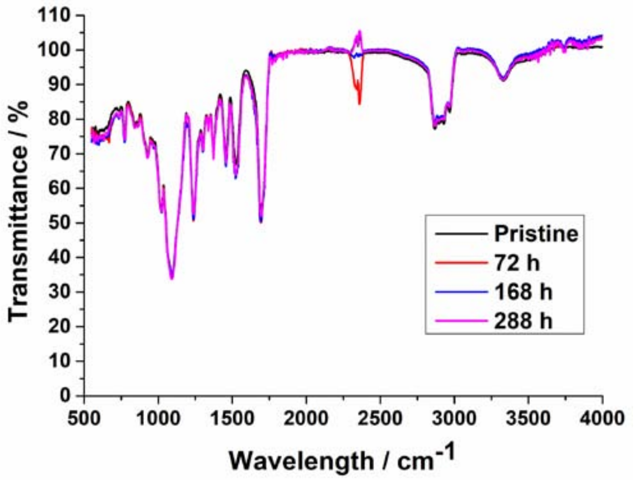
Chung DY *et al.* ACS Appl Mater Interfaces 2017;9:41303–13. doi:10.1021/acsami.7b13799.
Yung S *et al.* Prog Polym Sci 2016;59:1–40. doi:10.1016/j.progpolymsci.2015.10.004.

POLYMERIC ORGANIC NON CONDUCTIVE MATERIALS IN PEROVSKITE SOLAR CELLS?

Unpublished results

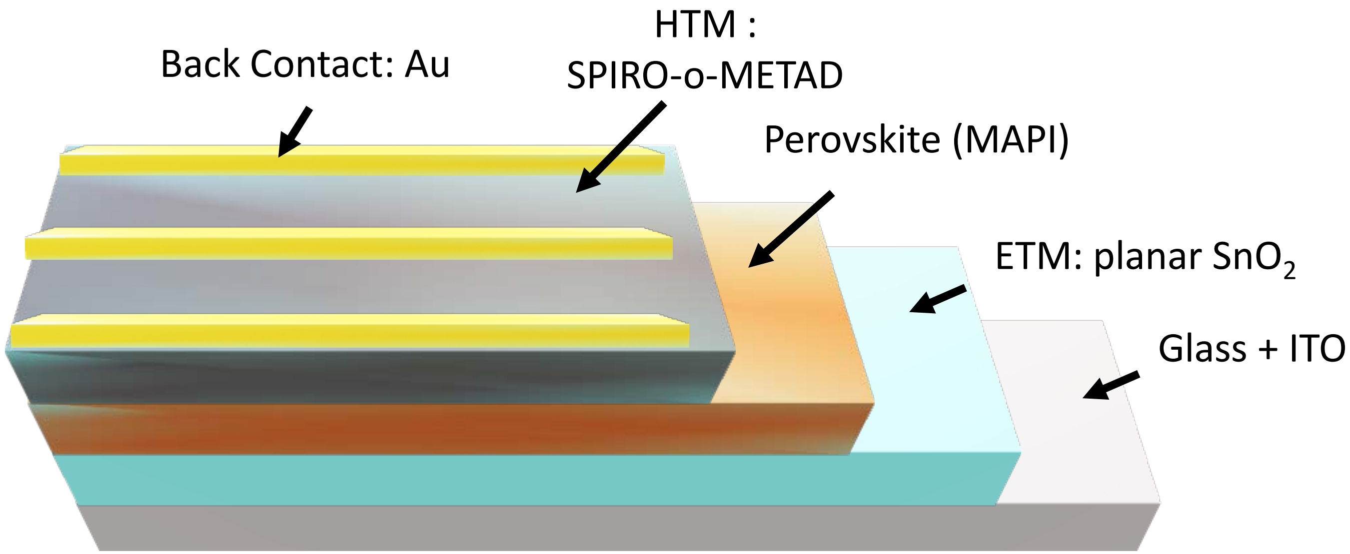
POLYMERIC ENCAPSULATION APPROACH IN PSCs





Good barrier properties

Thermally Stable



Back Contact: Au

HTM :
SPIRO-o-METAD

Perovskite (MAPI)

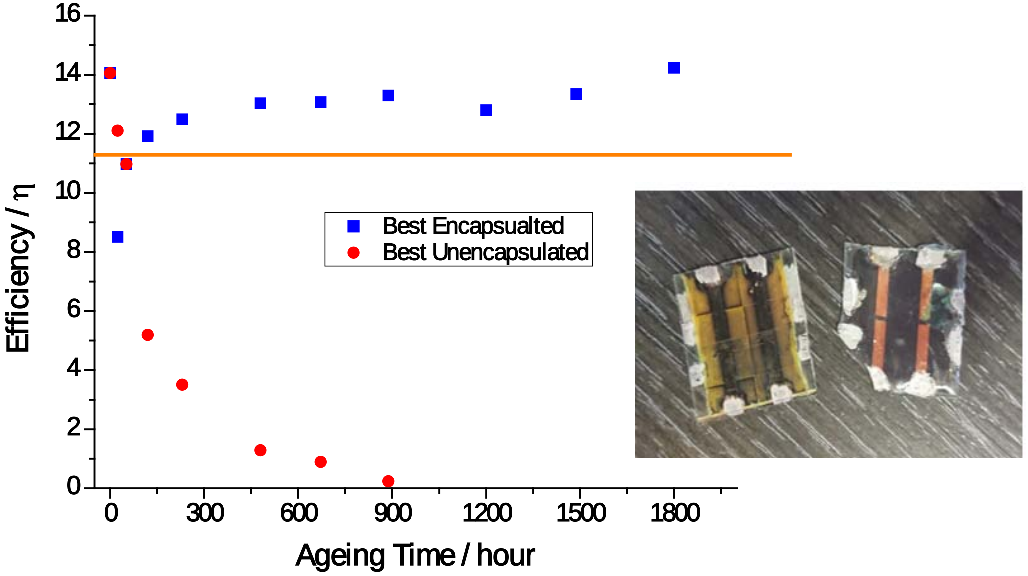
ETM: planar SnO_2

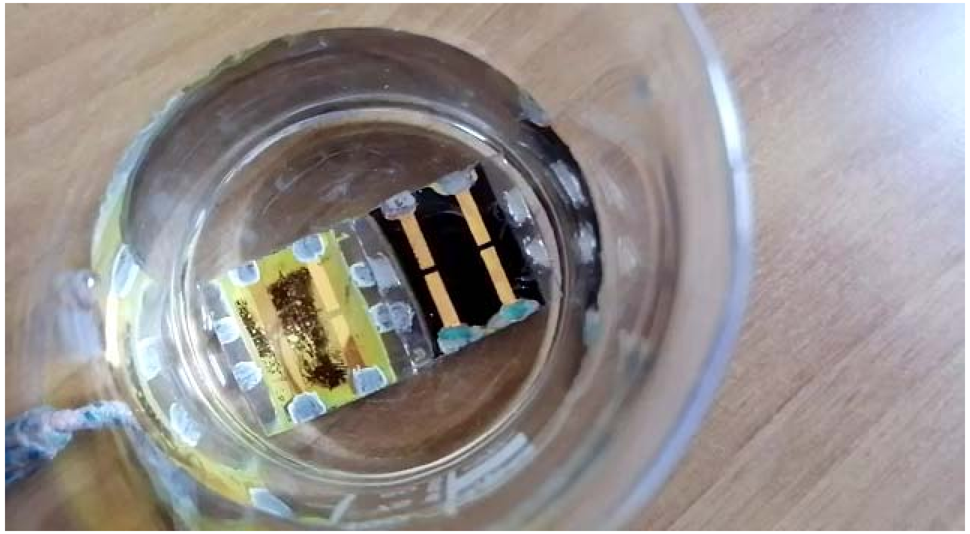
Glass + ITO

Polyurethanes as Encapsulant were manually deposited on the top of the cell: they are in contact with both HTM and Au

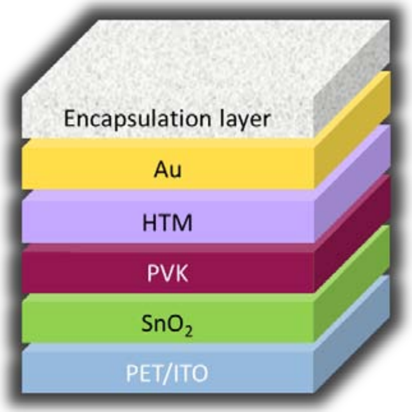
Unpublished results

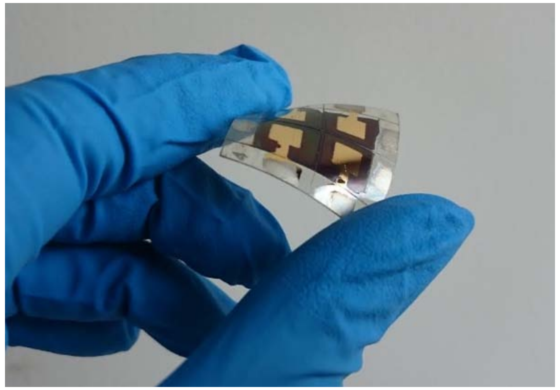
POLYMERIC ENCAPSULATION APPROACH IN PSCs

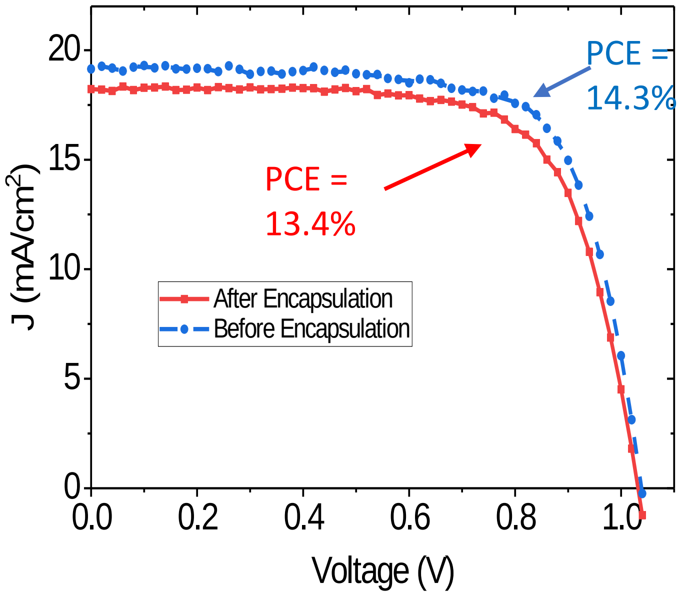




Encapsulation on FLEXIBLE substrate







Unpublished results

Acknowledgments

MOF

UNIVERSITÀ
DEGLI STUDI
DI TORINO

Carbon based CE

POLITECNICO
DI TORINO

F. Bella, C. Ge

Project PEROSKY: PU

agenzia spaziale
italiana

People from

CHOSE

F. Brunetti
B. Taheri
T. Brown
S. Castro-Hermosa
G.Lucarelli
F. De Rossi
A.Di Carlo
A.Reale

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