SOME "SMALL" MOLECULES APPLICATIONS IN PHOTOVOLTAICS

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and

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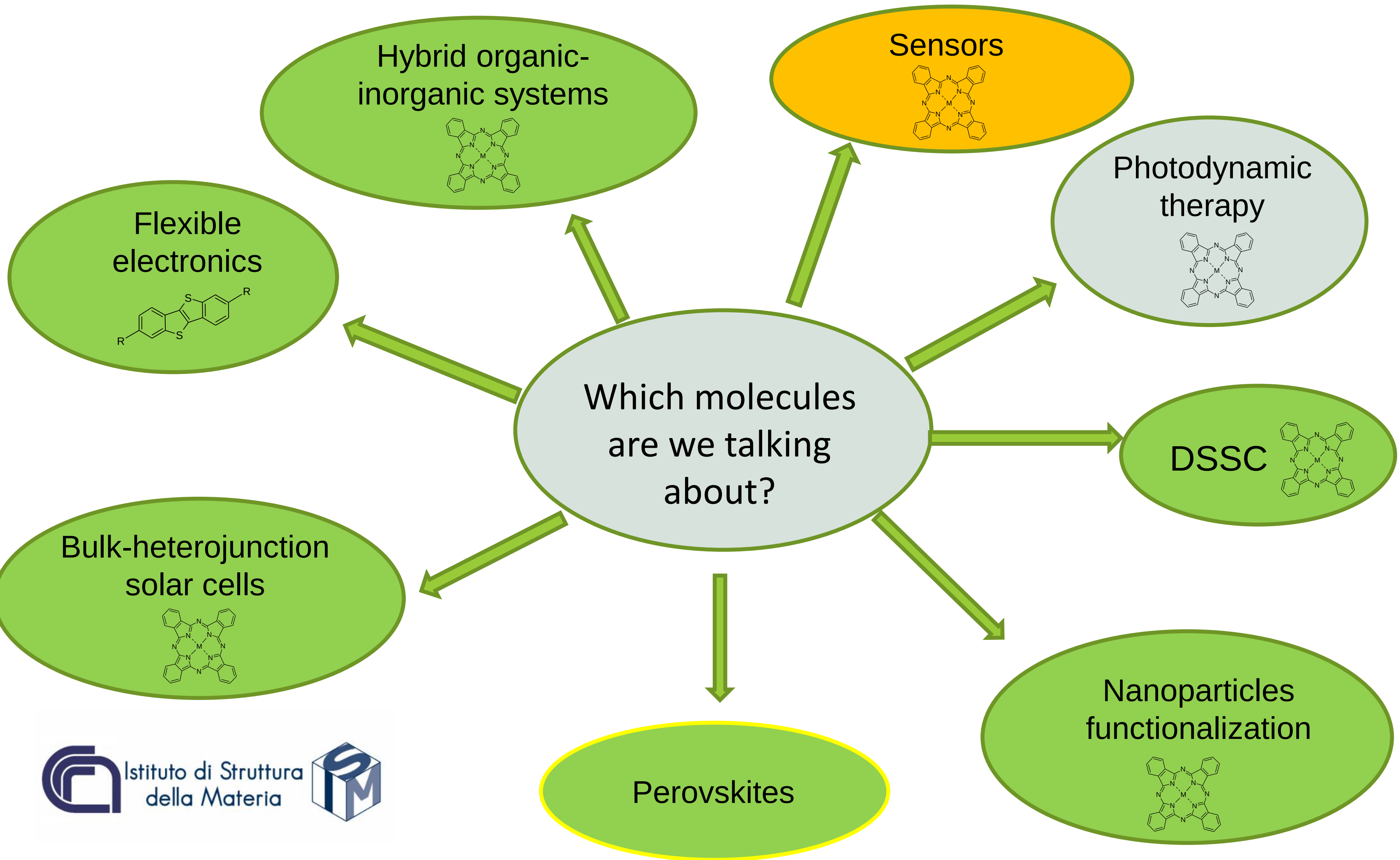
ENEA Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile



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OUTLINE

1. Synthesis of macrocyclic compounds for photovoltaic applications
   1. Phthalocyanines overview
   2. DSSCs
      I. Working principles and dye requirements
      II. State of the art
      III. Our results
   3. Perovskites
      I. Phthalocyanines as potential HTM for perovskite solar cells

Consiglio Nazionale delle Ricerche

2. Long term stability of small-molecules solar cells based on (DBP):C70 planar mixed heterojuncion with (TPBi):C70 electron-filtering cathode buffer layers

Ben-Gurion University of the Negev

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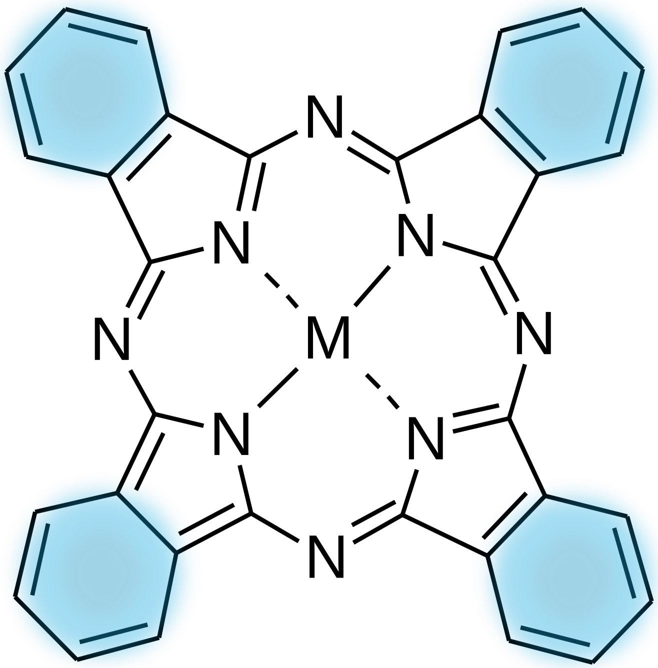
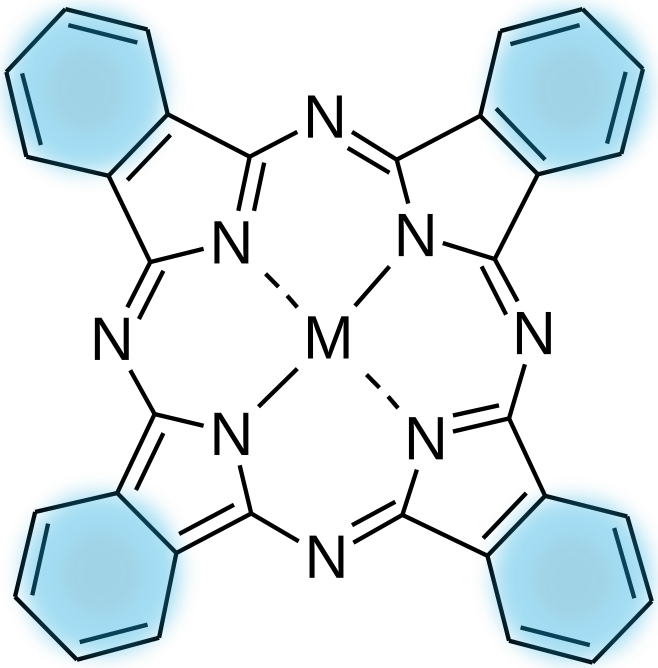
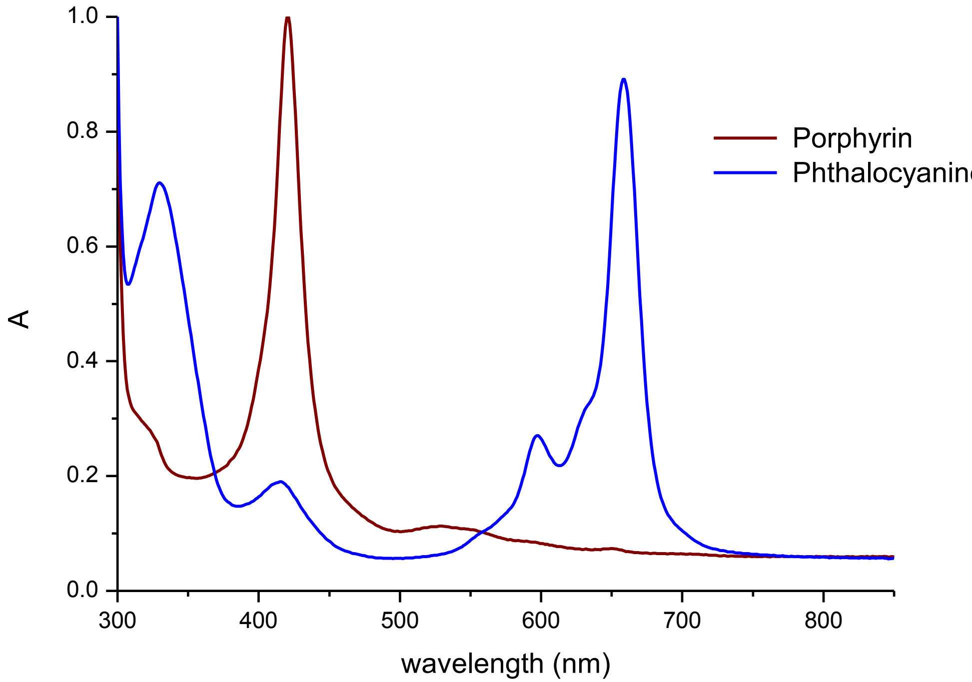
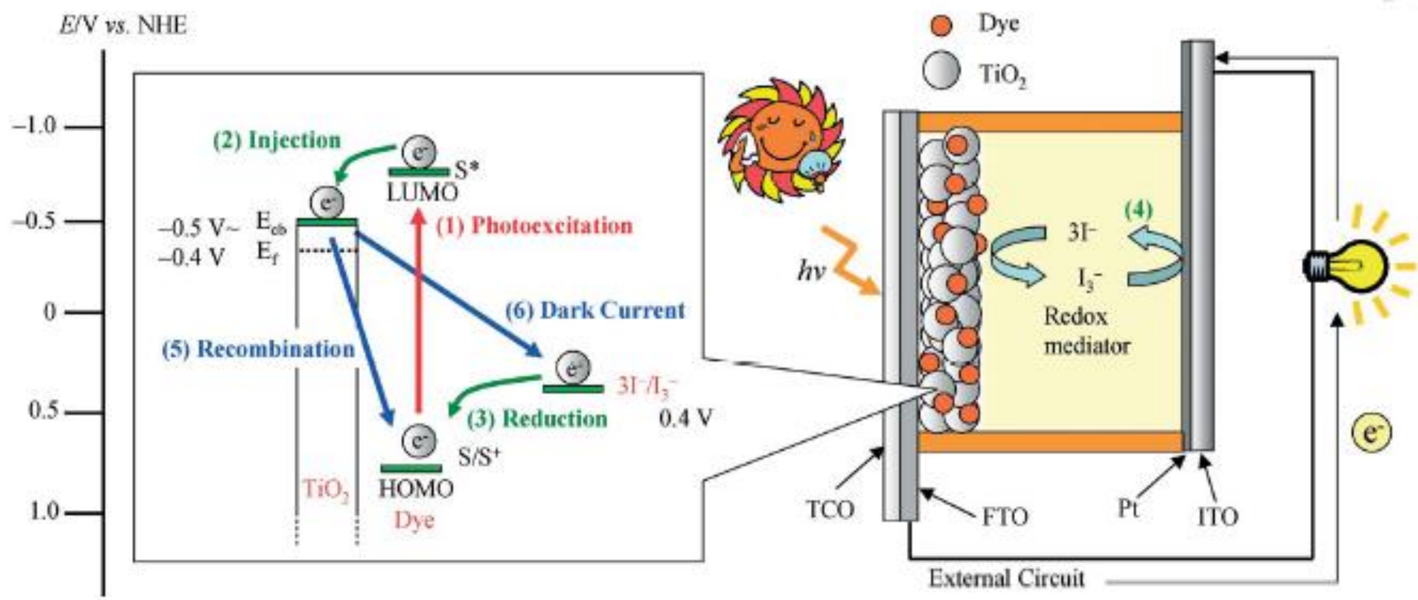


- four isoindole units bridged by four nitrogen atoms that form an inner 16-membered ring
- 18 π-electrons aromaticity
- Central metal in a typical (2+) oxidation state
- Can host 70 different metal ions in a square planar environment





- High chemical and thermal stability
- High molar extinction coefficients ($\varepsilon = 10^5$ $mol^{-1}cm^{-1}$)
- Q band tunability + solubility enhancement by macrocycle functionalization



Eur. J. Org. Chem. **2009**, 2903–2934

❖Strong interaction with the semiconductor surface via chemical bonding. (carboxylic group)

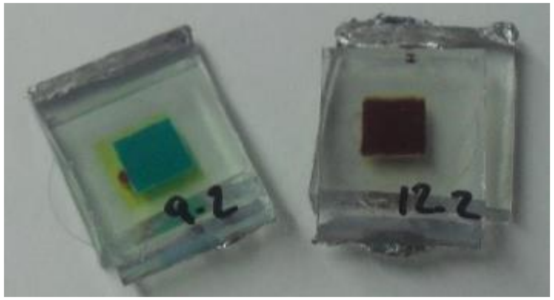
❖Suitable HOMO and LUMO energies

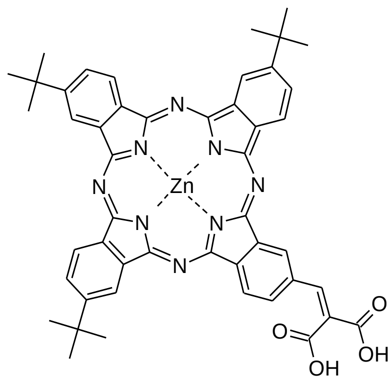
❖Intense absorption in a wide solar spectrum range

❖Negligible aggregation on the TiO_2 surface

❖Processability

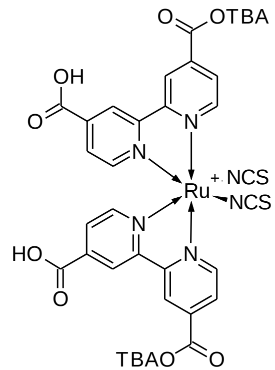
❖Long-term exposure stability to natural sunlight





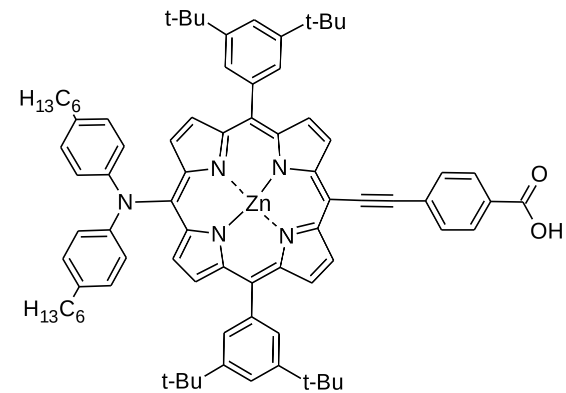
η = 3.96%

J. Chem. Sci., 2009, **121**, 75



N719

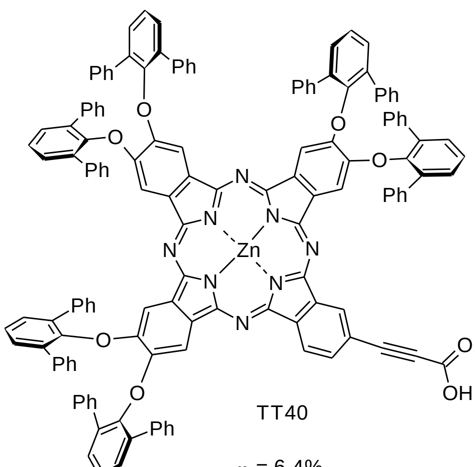
η = 12%



YD2

η = 11%

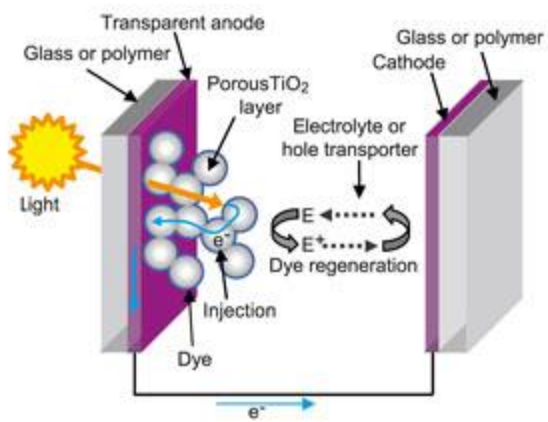
Angew. Chem. Int. Ed. 2010, **49**, 6646 –6649

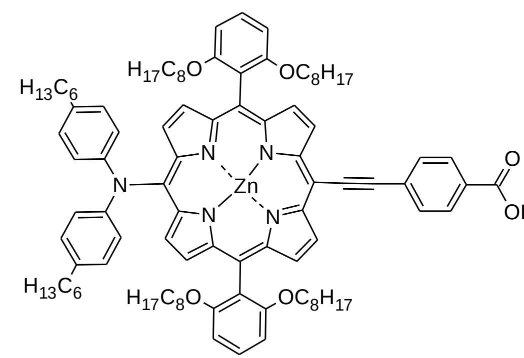


TT40

η = 6.4%

Chem. Commun., 2014, **50**, 1941



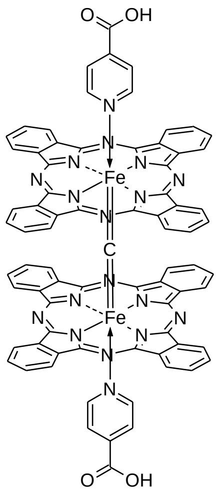


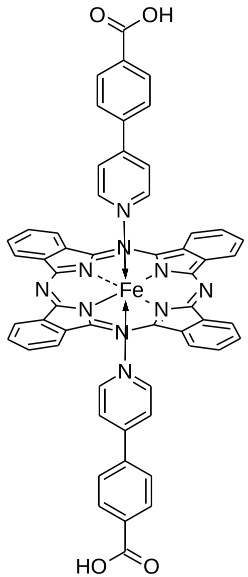
JD2-o-C8

η = 13%

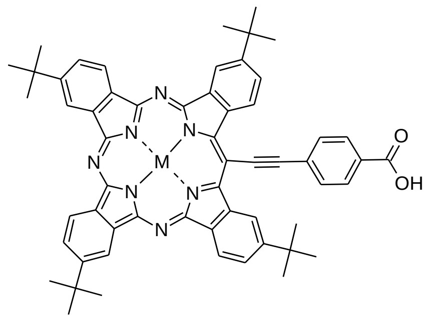
Science. 2011, **334**, 629-634

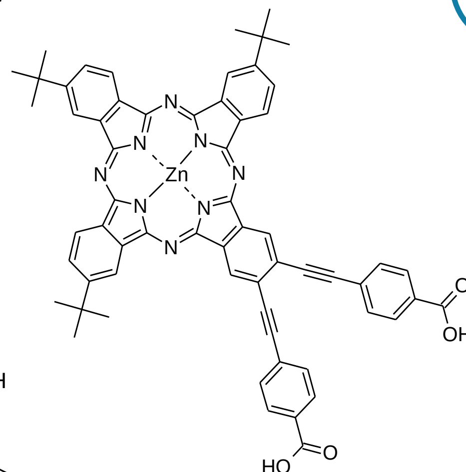
Our results

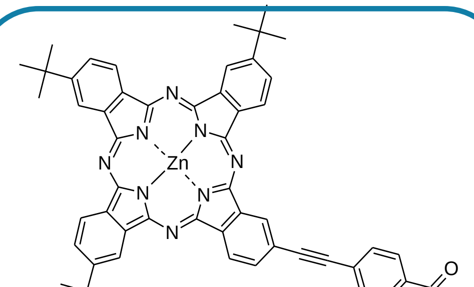




M1b

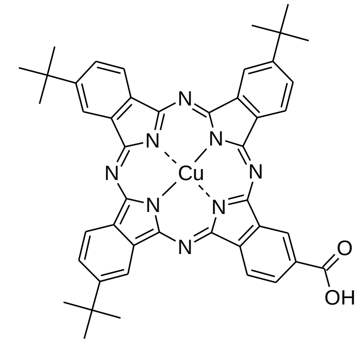


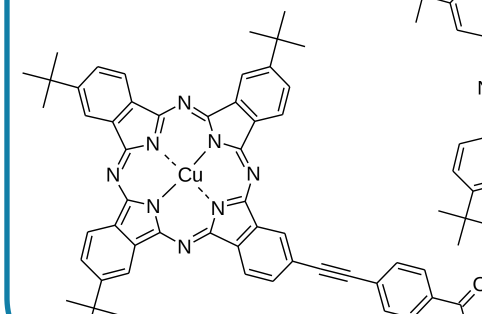




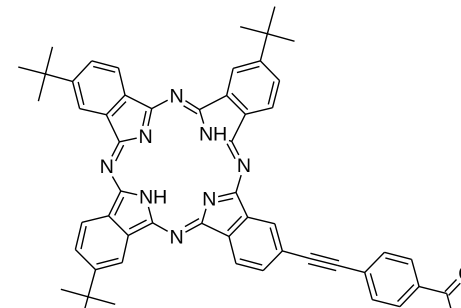
gz3

Zanotti *et al.* Dalton Trans. 2011, **40**, 38



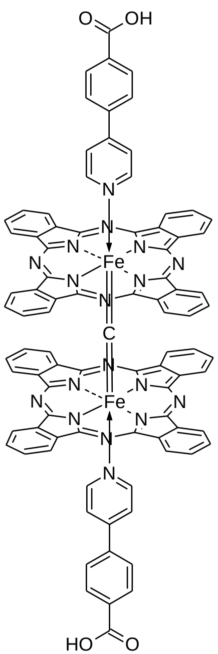


gz230

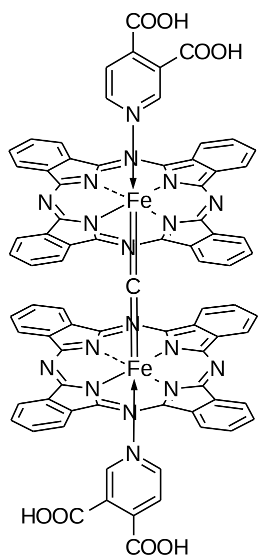


gz231

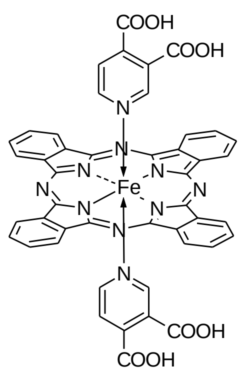
Zanotti et al. Journal of Porphyrins and Phthalocyanines, 2016



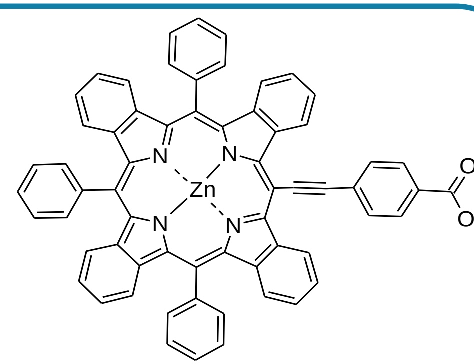
B1b



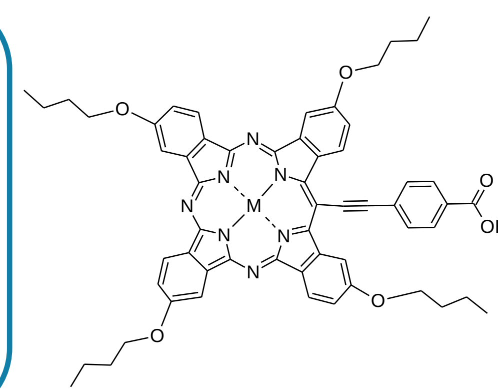
B1c

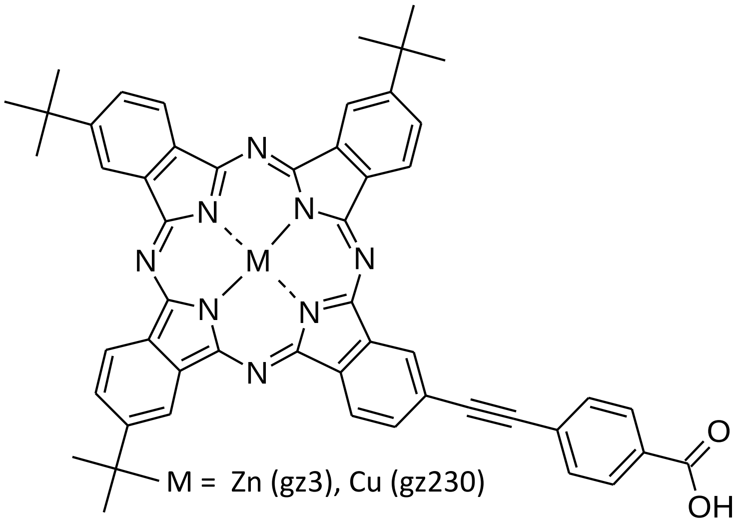


M1c

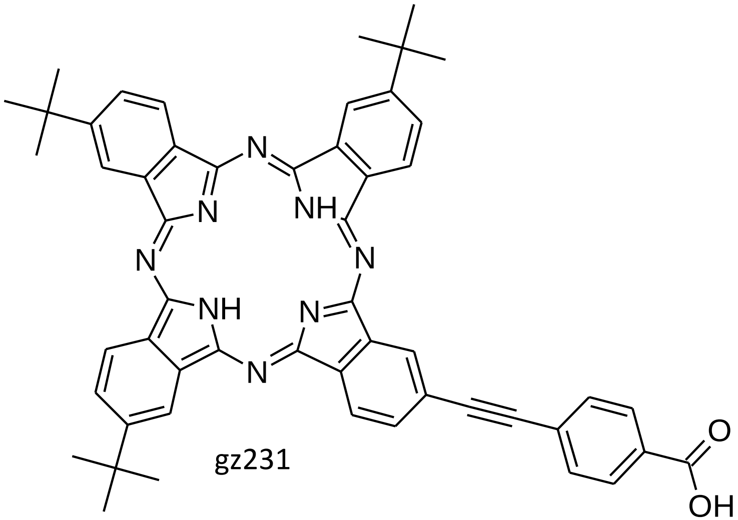


Zanotti et al. RSC Advances 2016, **6**, 5123





Zanotti *et al.* Dalton Trans. 2011, **40**, 38



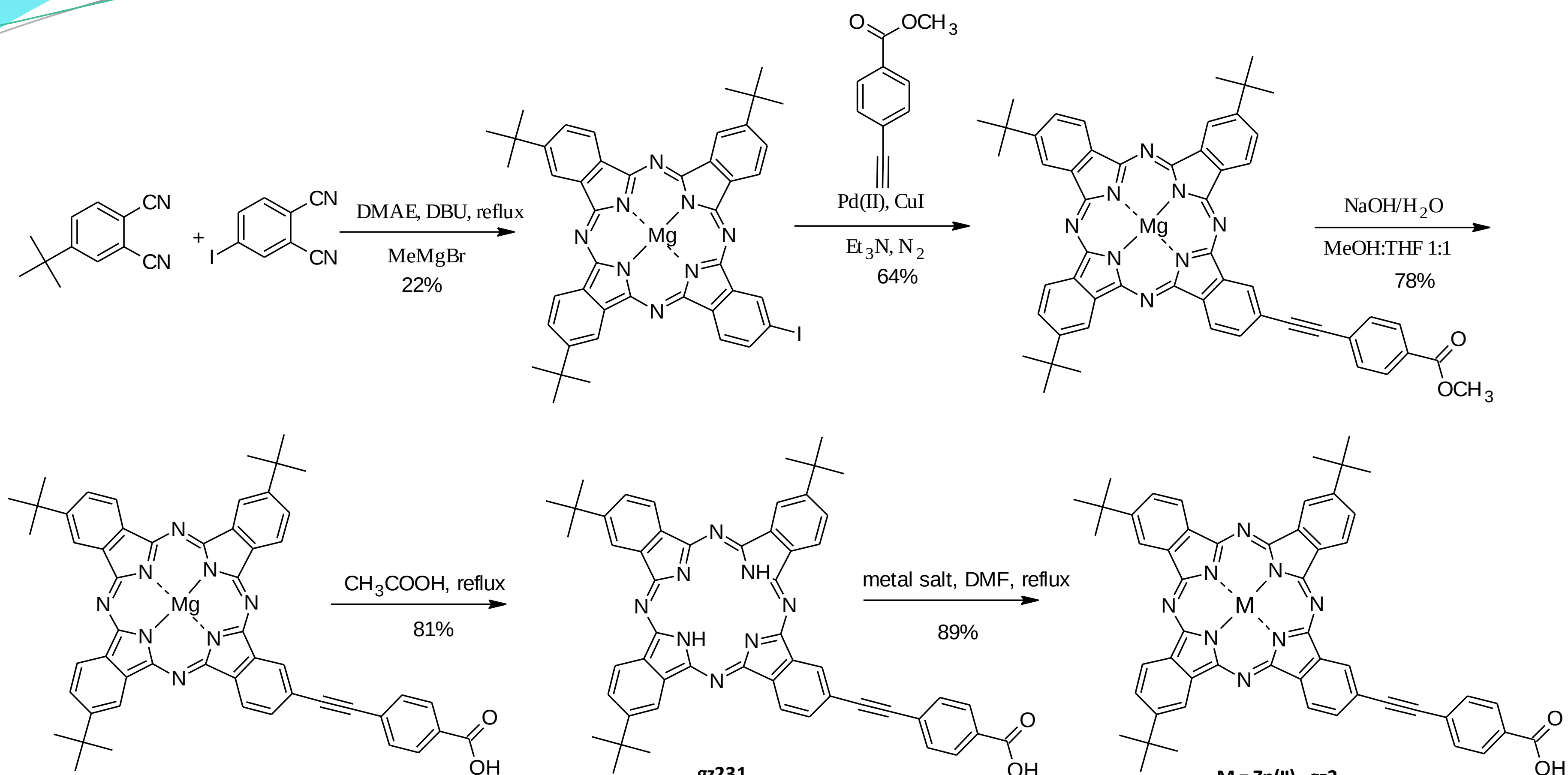
Zanotti et al. Journal of Porphyrins and Phthalocyanines, 2016

❖Pushing groups are useful to: increase the solubility
Redshift the UV-vis spectrum
Diminish the molecular aggregation

❖Copper forms very stable complexes with Pc rings

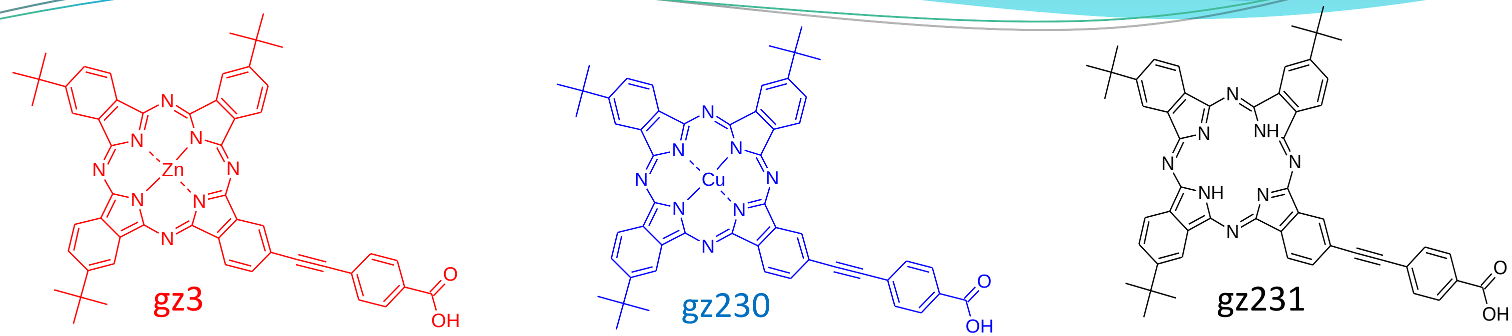
❖Molar extinction coefficients of all the derivatives are very high (10^5)

❖Zinc derivative is greenish-blue, copper and free-base are blue (attractive for Building Integrated Photovoltaics)

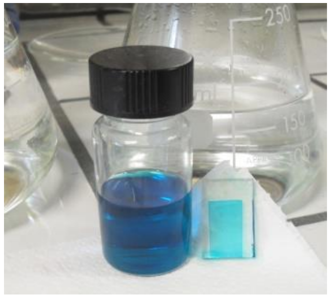


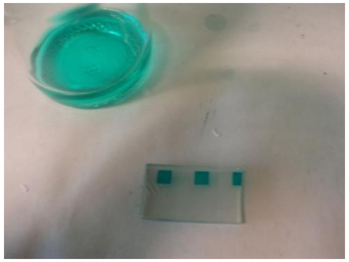
gz231

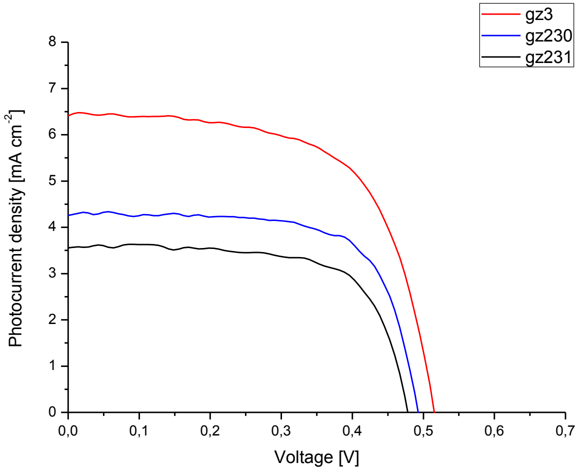
M = Zn(II), gz3
M = Cu(II), gz230



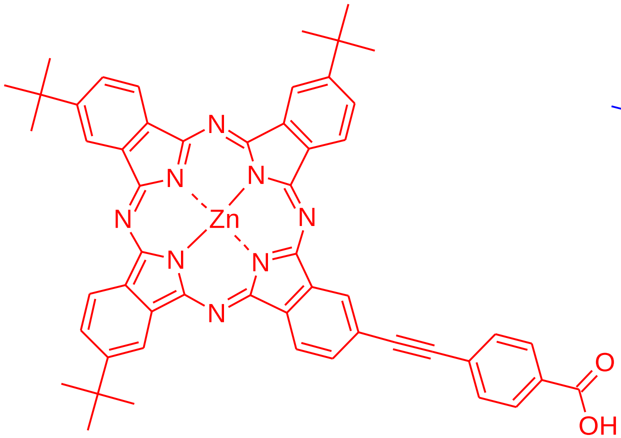
	η %	Voc [V]	Jsc [mA/cm²]	FF	CDCA (mM)	dye loading [mol cm⁻²]
gz231	1.38	0.55	3.59	0.70	-	1.0×10^{-7}
gz231	1.19	0.53	3.11	0.72	2	0.7×10^{-7}
gz230	1.66	0.56	4.24	0.70	-	1.1×10^{-7}
gz230	1.59	0.58	3.65	0.75	2	0.7×10^{-7}
gz3	2.10	0.52	6.43	0.63	-	1.0×10^{-7}
gz3	1.97	0.58	4.79	0.71	2	0.6×10^{-7}
N719	7.64	0.75	14.56	0.70	-	1.5×10^{-7}

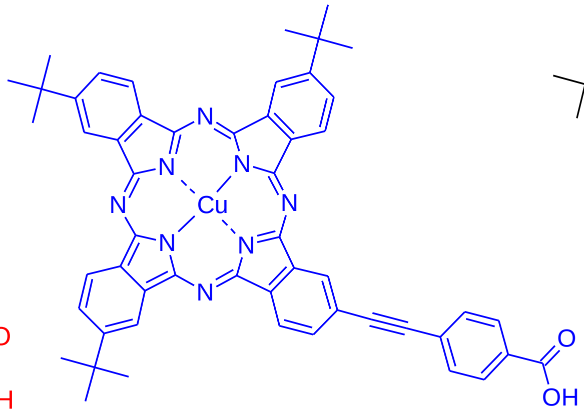


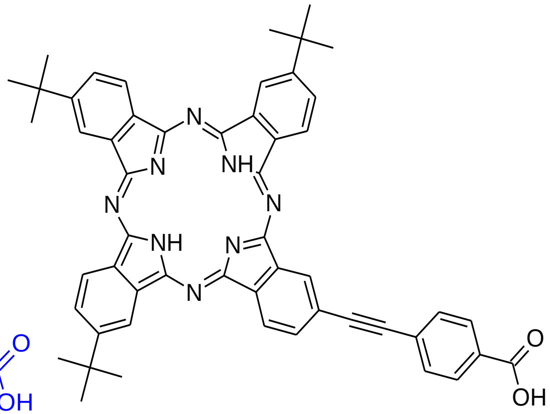


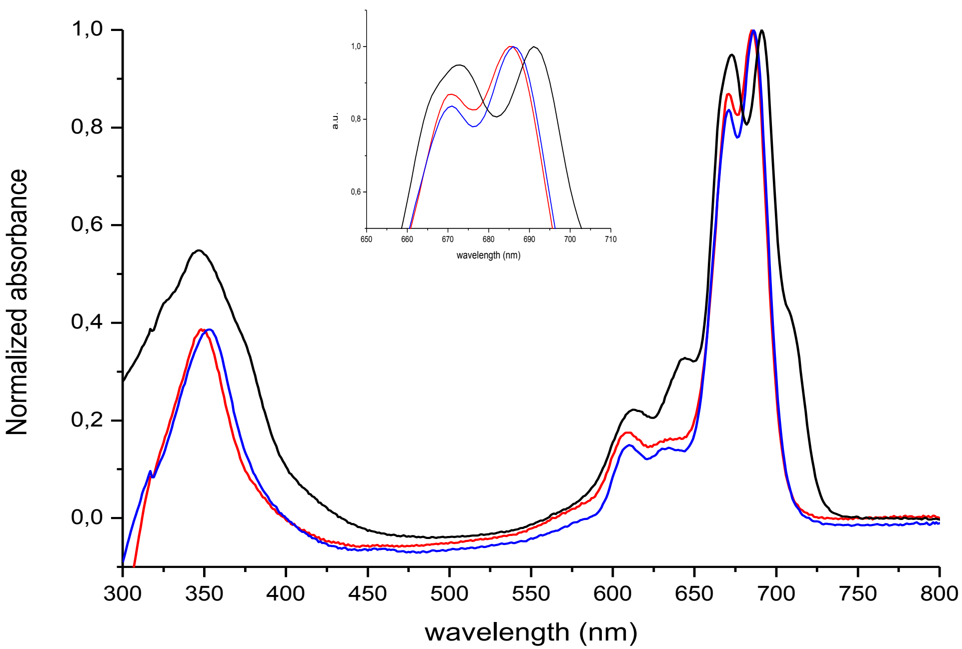


Zanotti et al. Journal of Porphyrins and Phthalocyanines, 2016





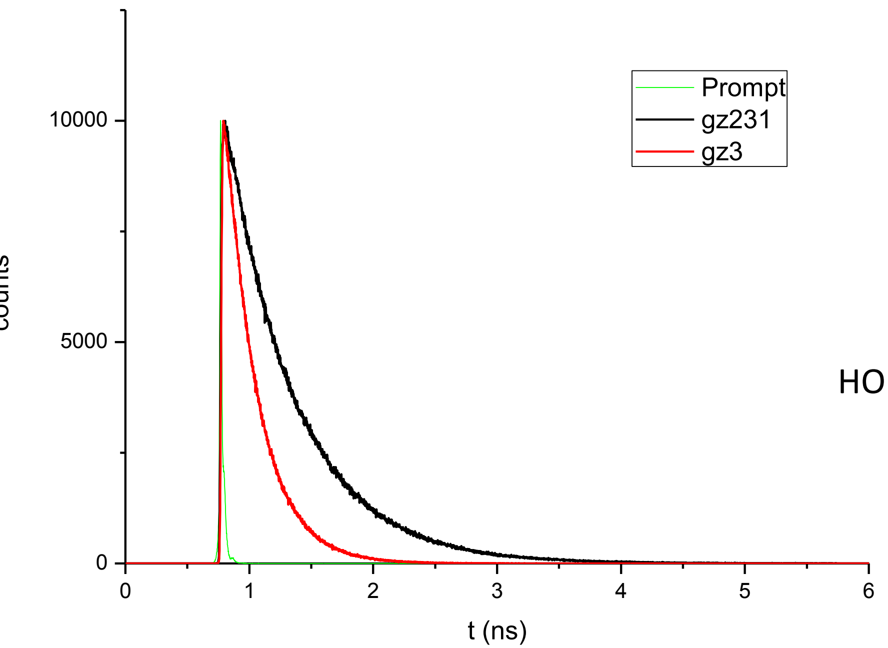




Molecule	λ_{max} (nm)	ε ($cm^{-1}Mol^{-1}$)
gz3	671, 685	1.02 * 10^5 1.15 * 10^5
gz230	671 686	1.08 * 10^5 1.21 * 10^5
gz231	672 692	8.07 * 10^4 8.03 * 10^4

Zanotti et al. Journal of Porphyrins and Phthalocyanines, 2016

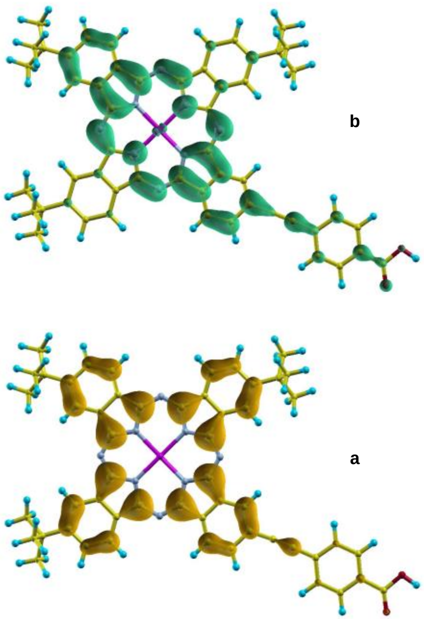
dye	Abs_{max} [nm]	Em_{max} [nm]	$E_{1/2ox}$ [V]vs SCE	$E_{1/2red}$ [V]vs SCE	$\Delta E_{1/2}$ [V]	$E_{(S^+/S)}$ [V]vs SCE	$E_{(0-0)}$ [eV] (Abs/Em)	$E_{(S^+/S^*)}$ [V]vs SCE	HOMO eV	LUMO eV
gz3	687	692	0.75	-	-	0.75	1.8	-1.05	-5.07	-2.99
gz230	685	-	-	-0.83	-	-	-	-	-5.07	-2.96
gz231	671-690	698	1.07	-1.10	2.17	1.07	1.79	-0.72	-5.10	-3.03



Zanotti *et al.* Dalton Trans. 2011, **40**, 38

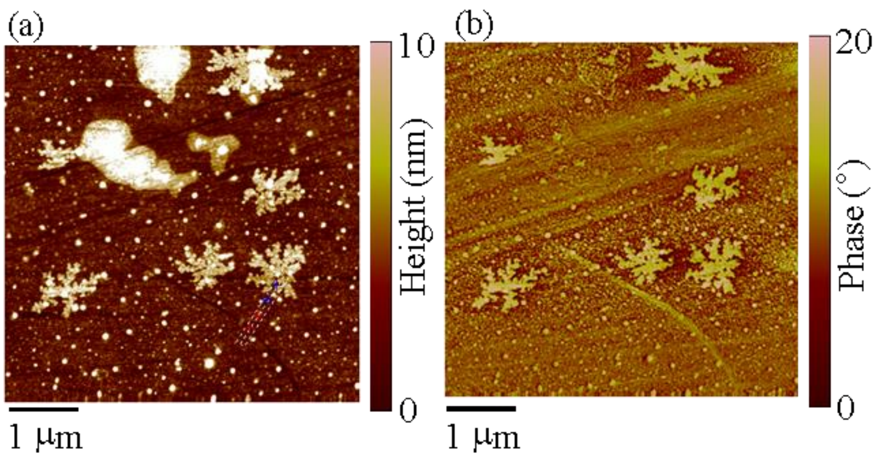
Zanotti et al. Journal of Porphyrins and Phthalocyanines, 2016

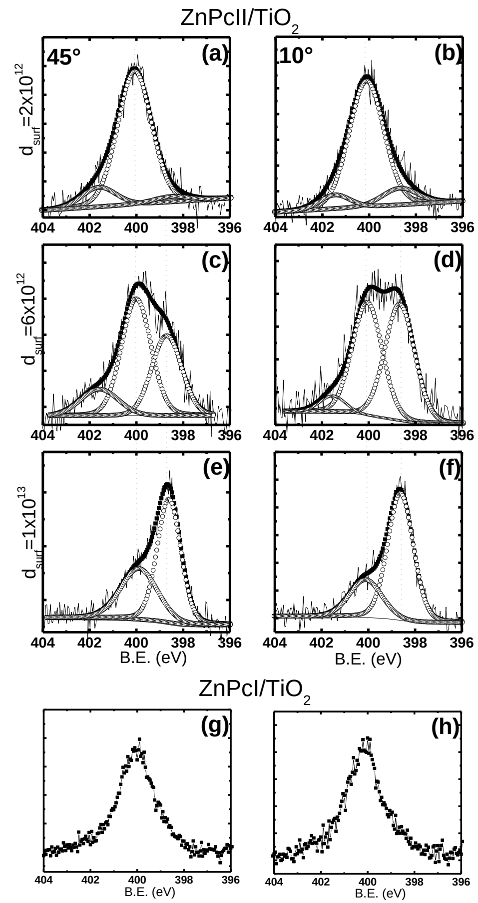
HOMO (**a**) and LUMO (**b**) electron density isosurfaces.



Is there some recombination with TiO_2?

At low surface density (obtained at $M<10^{-6}$) a lying binding geometry (height of ~1.4 nm as estimated by AFM), resulting by the ZnPc aromatic ring-TiO_2 interaction, is achieved, as emerges by the XPS measurements.

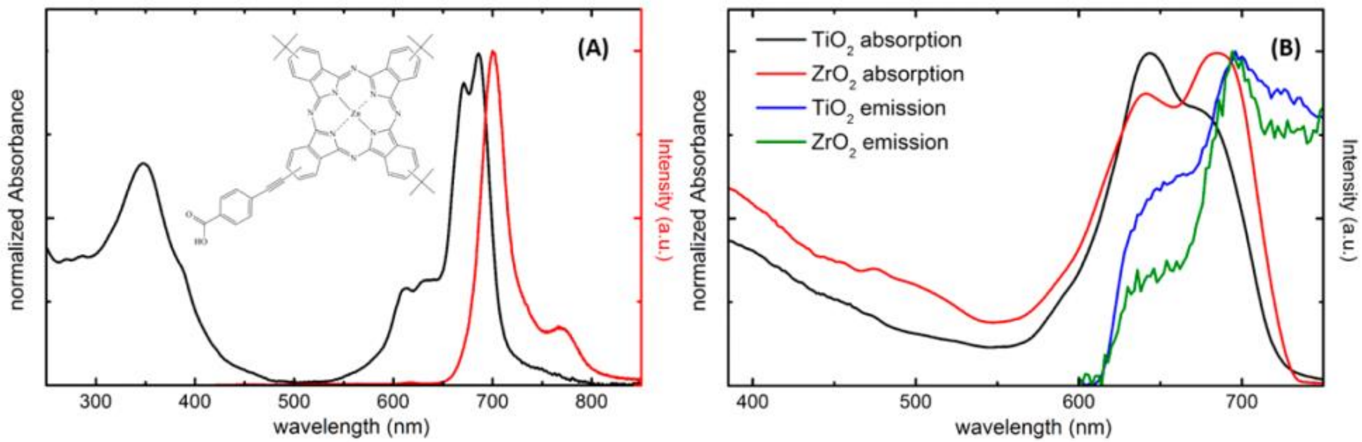




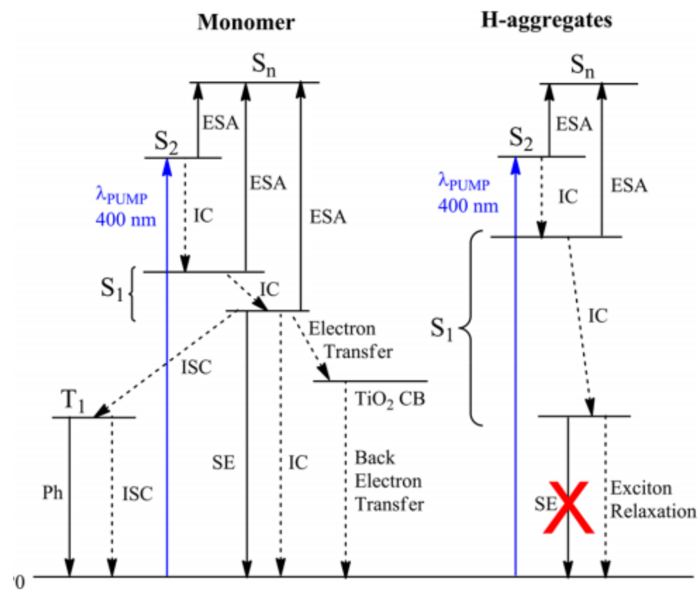
AFM images of the Zn derivative modified TiO_2 surface at $d_{surf} = d=2\times10^{12}$. The simultaneous acquisition of morphologic (a) and phase (b) AFM images indicates that the phthalocyanine/ TiO_2 sample is constituted prevalently by a monolayer of phthalocyanine molecules anchored on the TiO_2 surface

Pellegrino G , Zanotti G et al. *J. Phys. Chem. C*, 2013

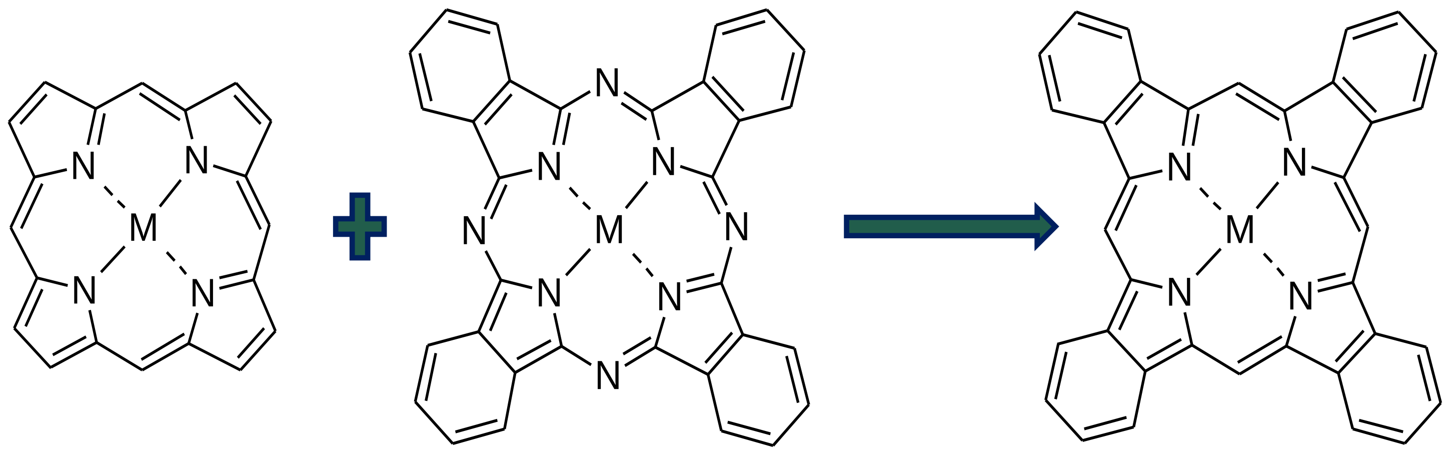
Is there some nonradiative decay due to molecular aggregation?

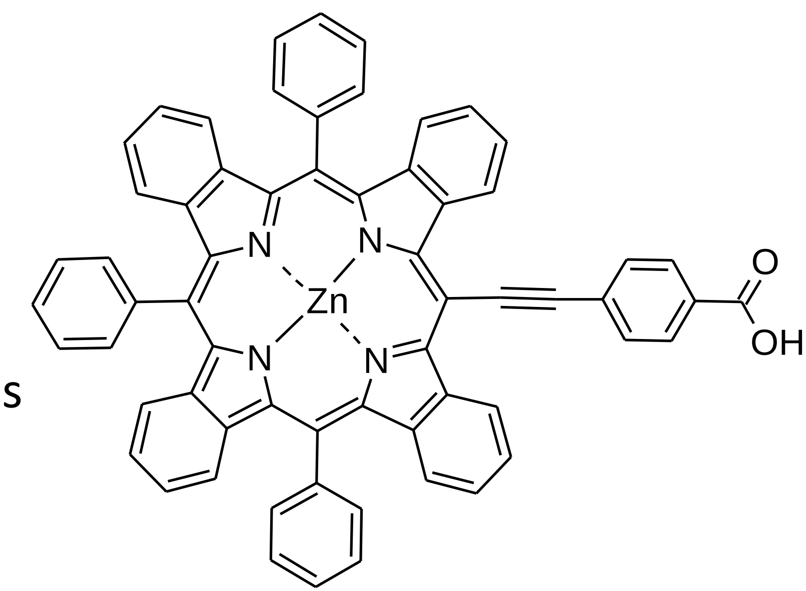


Transient absorption measurements defined the time interval in which nonradiative deactivation occurs in solution and on nanostructured films.



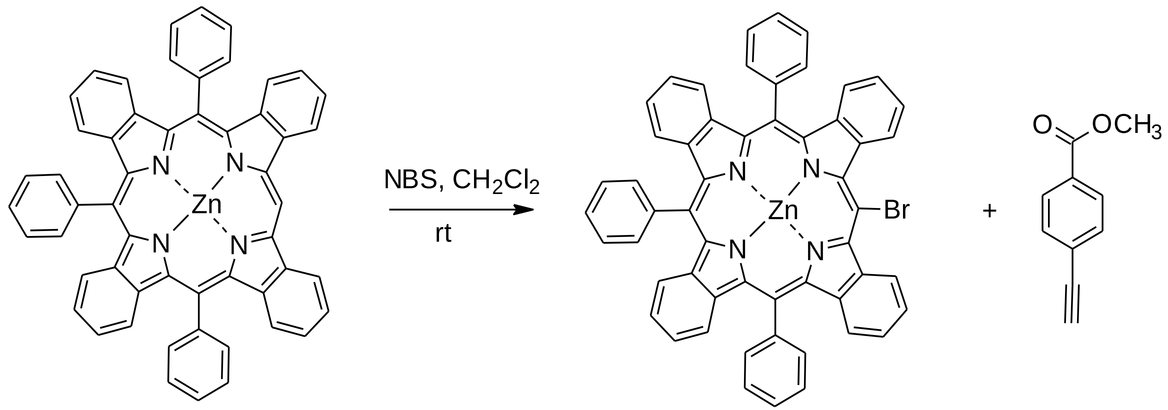
Iagatti A, Zanotti G et al. *J. Phys. Chem. C*, 2015





- **Intense absorption** in visible and near-IR.
- **Increased stability** compared to porphyrins.
- **Substitutions** on the free *meso* and β-positions

Zanotti et al. RSC Advances 2016, **6**, 5123



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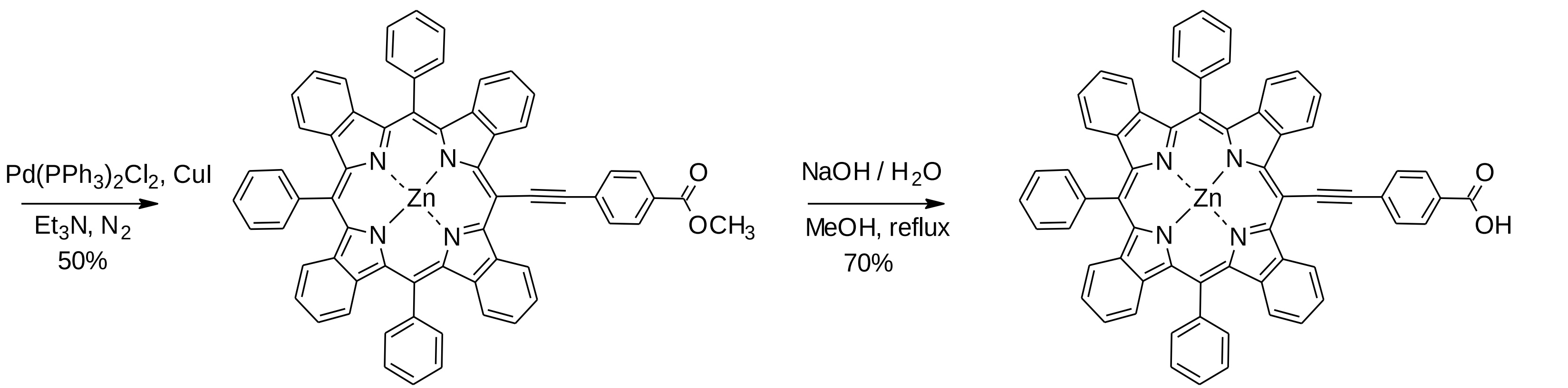

3

PETBP

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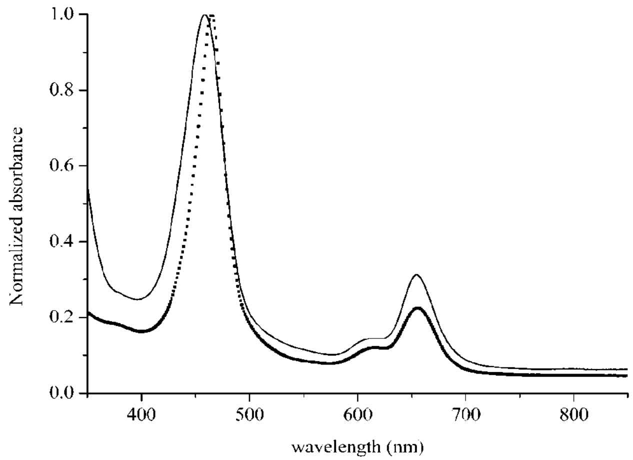
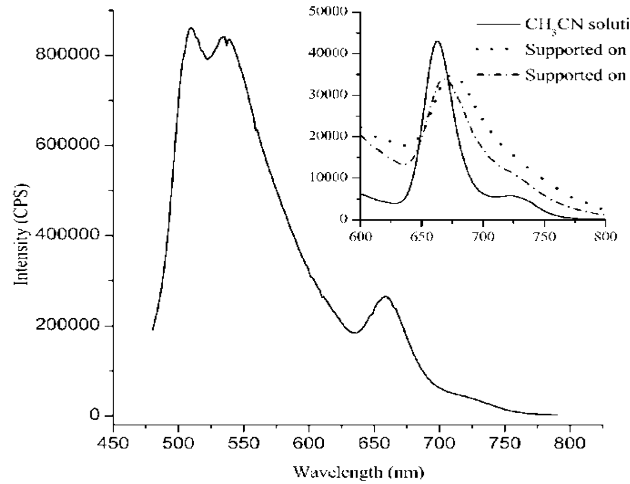
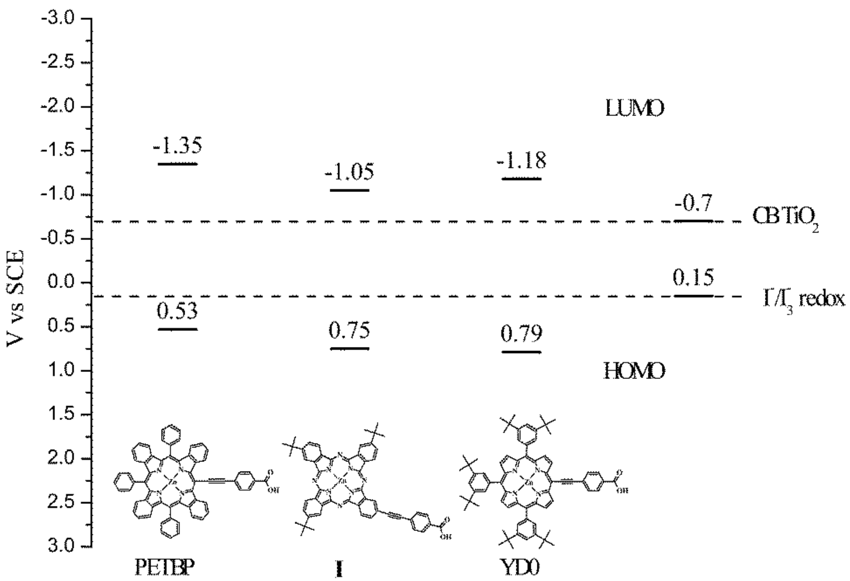
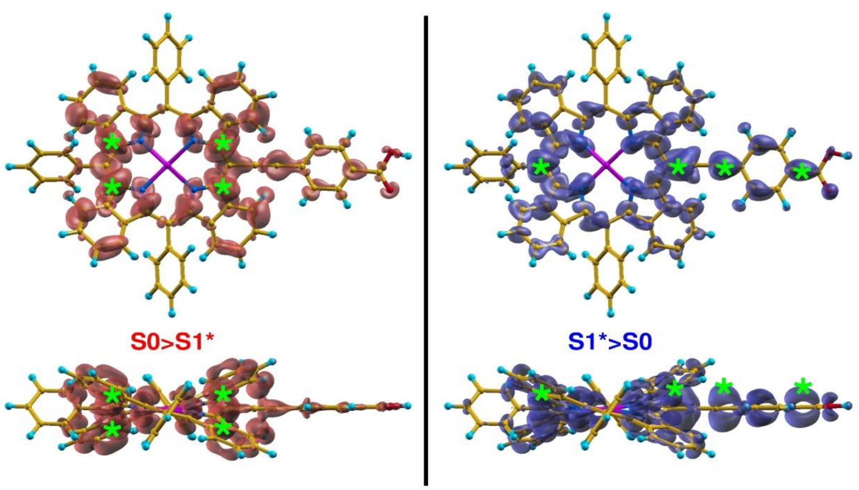


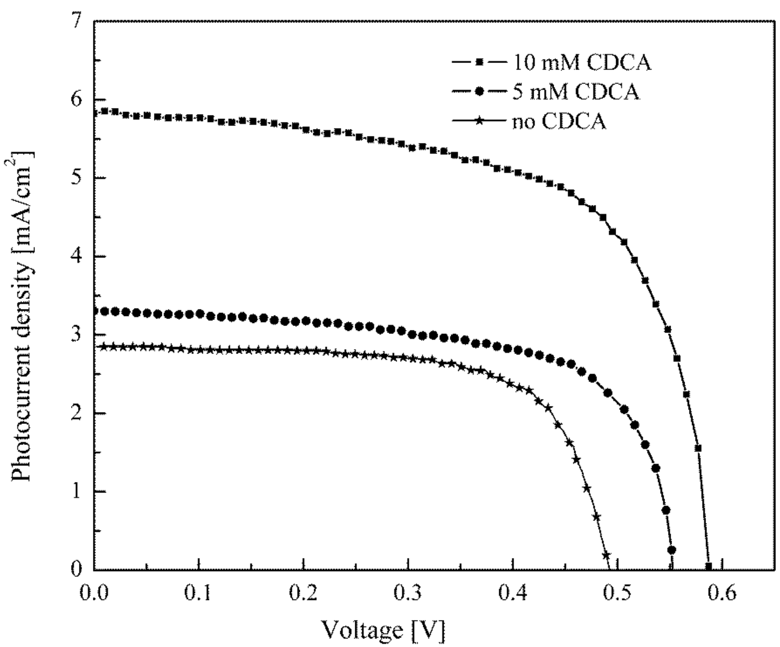


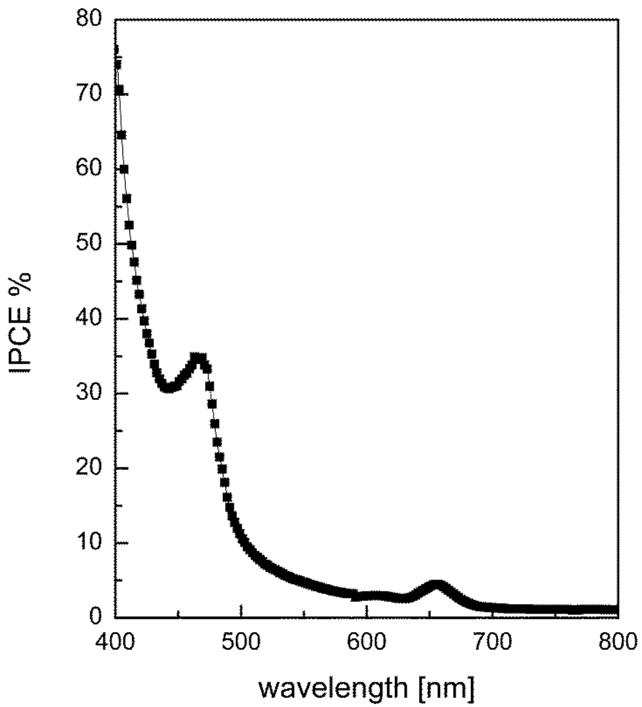




Zanotti et al. RSC Advances 2016, **6**, 5123

	η %	Voc [V]	Jsc [mA/cm^2]	FF	CDCA [Mm]
PETBP	**0.95**	0.493	2.80	0.69	0
	1.27	0.551	3.33	0.69	5
	2.22	0.577	5.83	0.66	10
N719	7.51	0.772	4.79	0.68	0





Zanotti et al. RSC Advances 2016, **6**, 5123

DSSCs: conclusions

- The investigated molecules show lower efficiencies than the state of the art, even if they theoretically fulfil all the dye requirements.
- Side-studies on their transient photochemistry and on their interaction with TiO_2 can explain these results.
- A coadsorbent can be useful to increase the photovoltaic performances, but each case has to be studied independently.

- Multicomponent devices require a careful optimization of all their single element. Changing one of them may require to vary some of the others.

OUTLINE

1. Synthesis of macrocyclic compounds for photovoltaic applications
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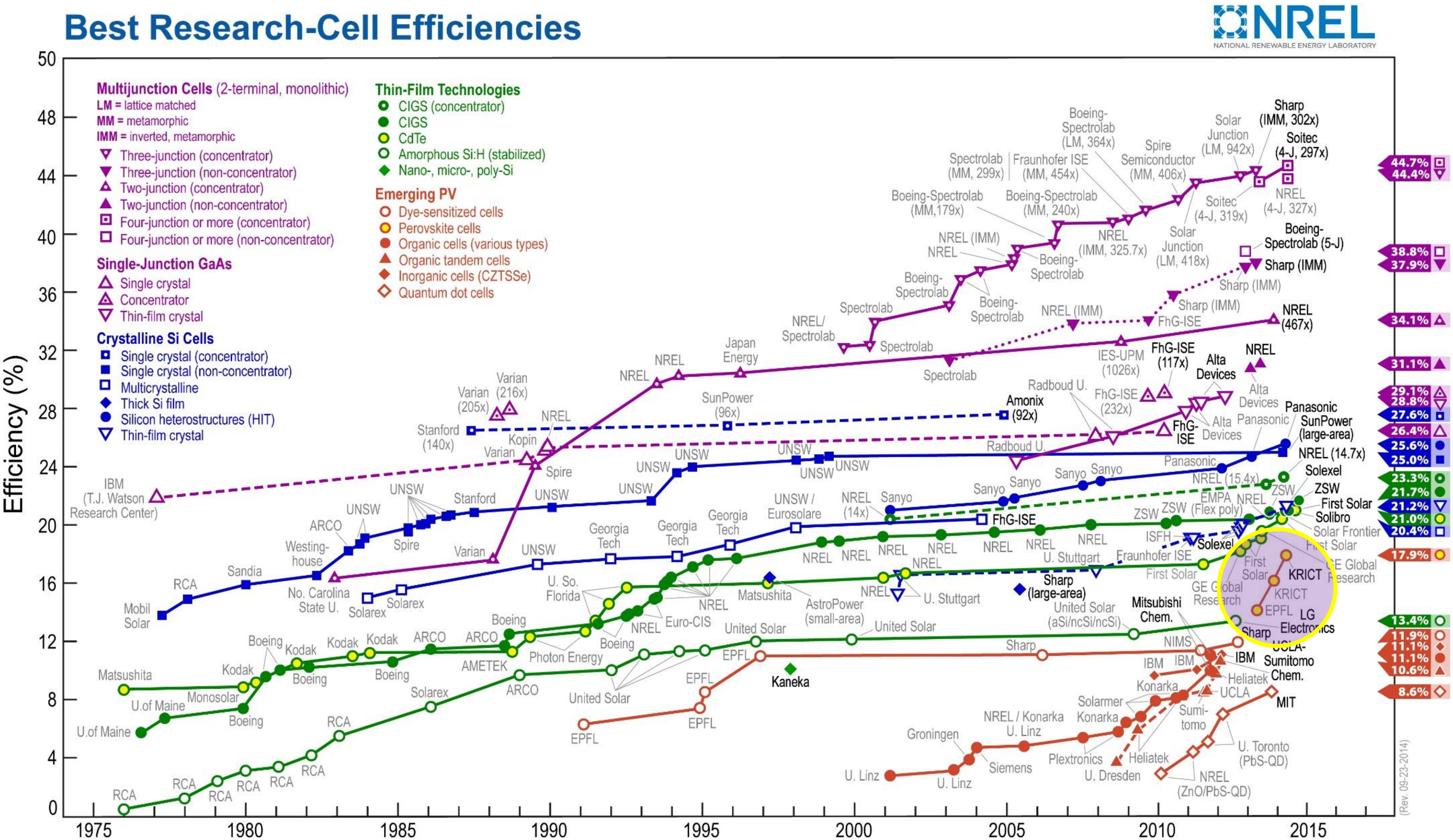
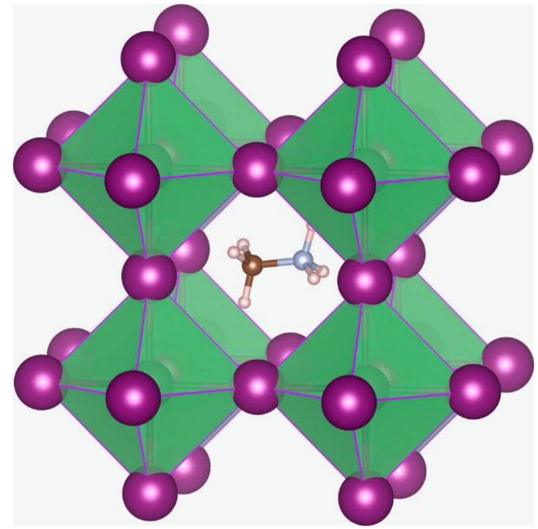
      I. Phthalocyanines as potential HTM for perovskite solar cells

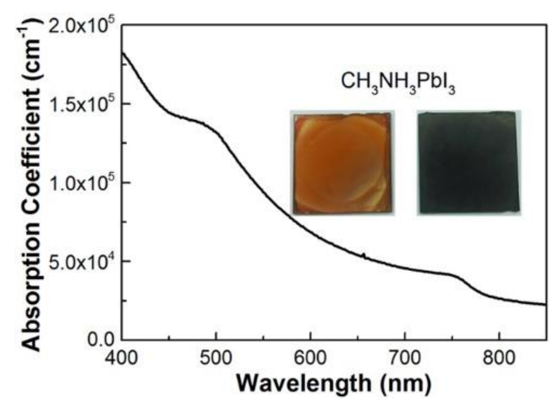
2. Long term stability of OPV devices based on (DBP):C70 planar mixed heterojuncion with (TPBi):C70 electron-filtering cathode buffer layers


Best Research-Cell Efficiencies
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
Efficiency (%)
Multijunction Cells (2-terminal, monolithic)
LM = lattice matched
MM = metamorphic
IMM = inverted, metamorphic
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Two-junction (non-concentrator)
Four-junction or more (concentrator)
Four-junction or more (non-concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin-film crystal
Crystalline Si Cells
Single crystal (concentrator)
Single crystal (non-concentrator)
Multicrystalline
Thick Si film
Silicon heterostructures (HIT)
Thin-film crystal
Thin-Film Technologies
CIGS (concentrator)
CIGS
CdTe
Amorphous Si:H (stabilized)
Nano-, micro-, poly-Si
Emerging PV
Dye-sensitized cells
Perovskite cells
Organic cells (various types)
Organic tandem cells
Inorganic cells (CZTSSe)
Quantum dot cells
44.7%
44.4%
38.8%
37.9%
34.1%
31.1%
29.1%
28.8%
27.6%
26.4%
25.6%
25.0%
23.3%
21.7%
21.2%
21.0%
20.4%
17.9%
13.4%
11.9%
11.1%
11.1%
10.6%
8.6%
KRICT
EPFL
(Rev. 09-23-2014)

PEROVSKITES



AMX_3



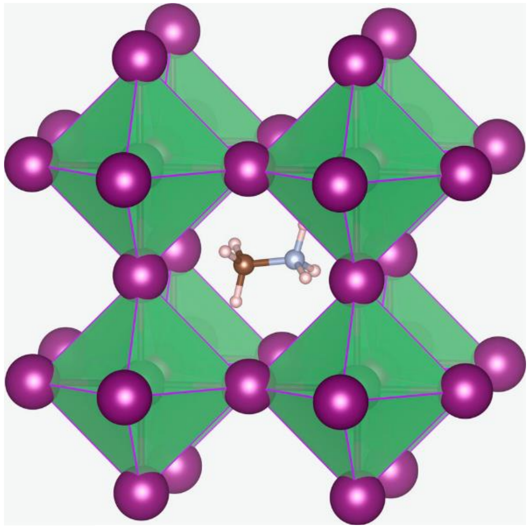
Scientific Reports 5, Article number 14485 (2015)

A organic cation (methylammonium (MA) or formamidinium (FA)) or inorganic monovalent ion (Cs^+)

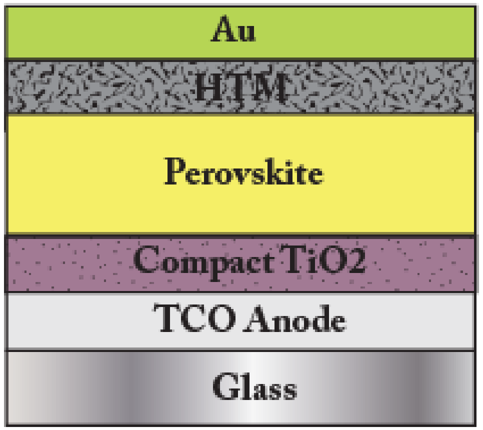
M metal in a +2 oxidation state (Pb^{2+})

X halogen or halogen mixture (Cl^-, Br^-, I^-)

PEROVSKITES



AMX_3

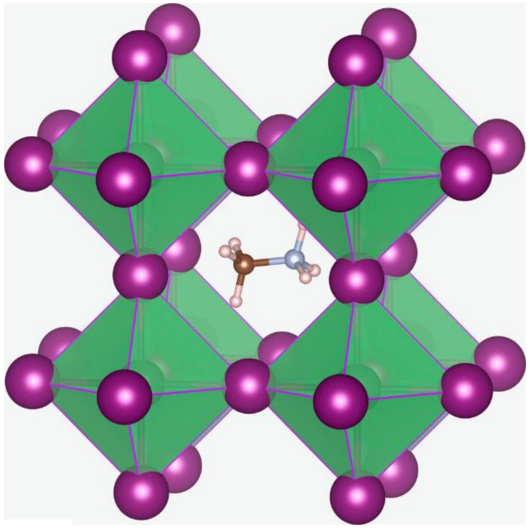


- Synthesis is quite easy
- Absoption spectrum is very good (the material itself is black)
- Outstanding photovoltaic behaviour even in poorly optimized devices

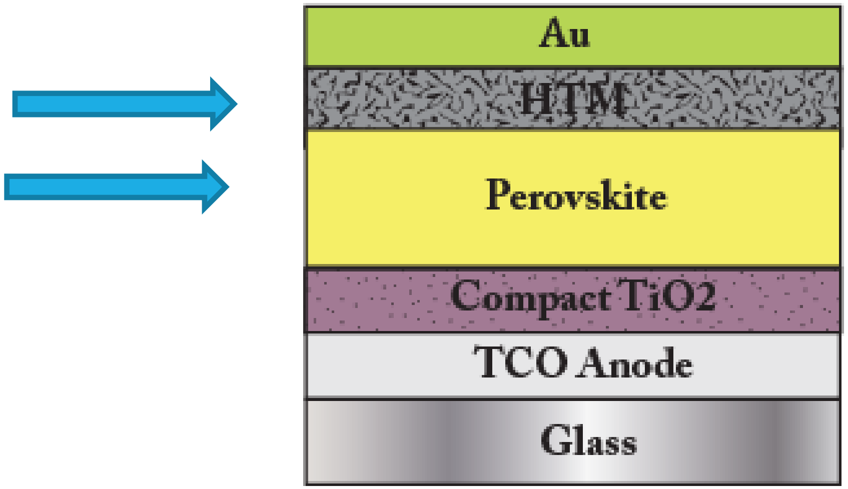
$$(CH_3)NH_3I + PbI_2 \rightarrow (CH_3)NH_3PbI_3$$

J. Fan, B. Jia, M. Gu, *Photon Research*, 2(2014)111-120

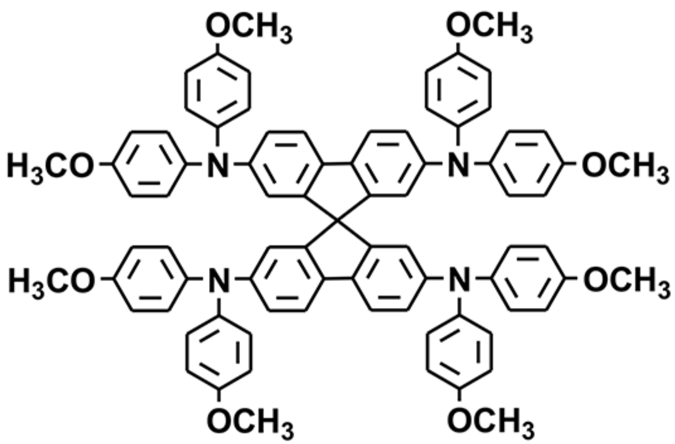
PEROVSKITES



AMX$_3$



J. Fan, B. Jia, M. Gu, *Photon Research*, 2(2014)111-120



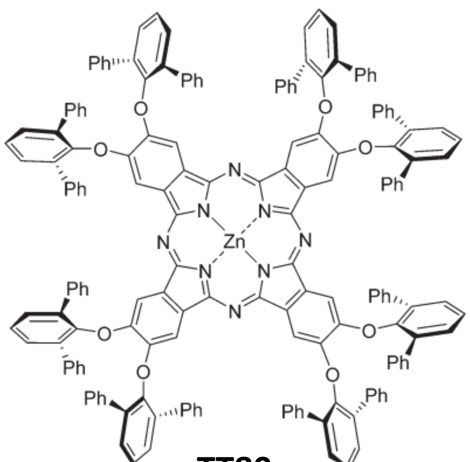
Spiro-OMeTAD

Efficiencies up to 20%

- High cost/multistep synthesis
- Low mobility and conductivity: needs doping to work at its best
- Dopants have to be carefully chosen or the cell may be negatively affected by their presence

Developing novel inexpensive HTMs is an attractive goal

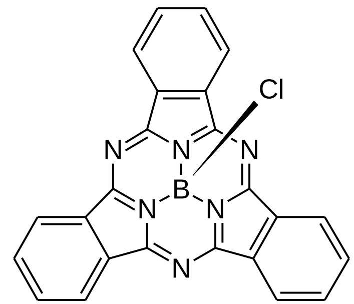
Phthalocyanines as potential HTM for perovskite solar cells



TT80

PCE = 6.7%

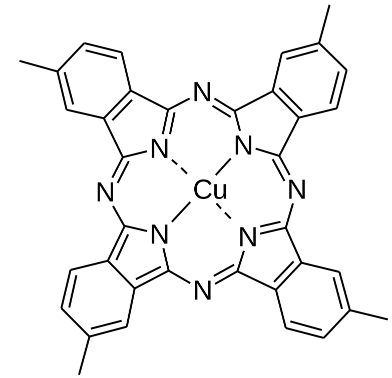
F. Javier Ramos et al. Dalton Trans., 2015, 44, 10847–10851



SubPc

PCE = 6,6%

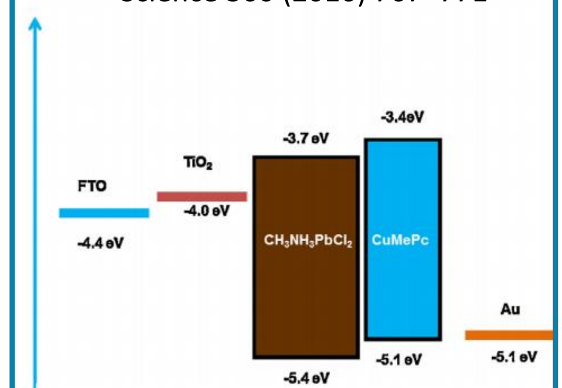
G. Sfyri et al. RSC Advances 2015, 5, 69813



CuMePc

PCE = 5.2%

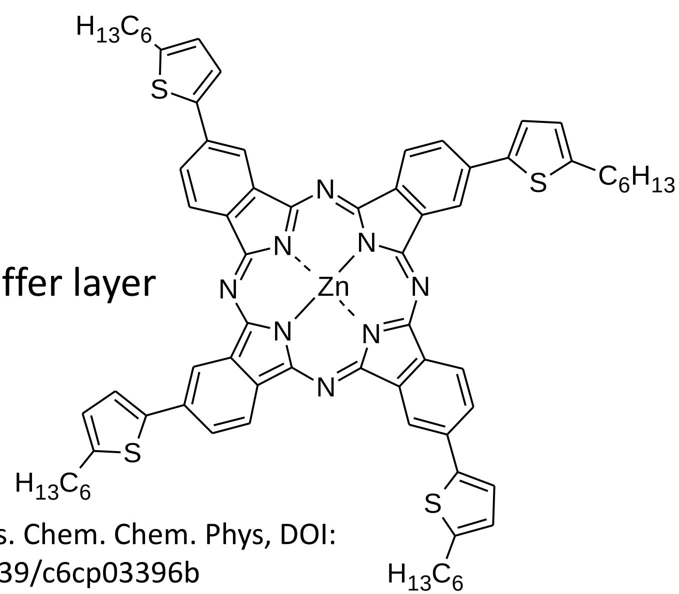
G. Sfyri et al.Applied Surface Science 360 (2016) 767–771



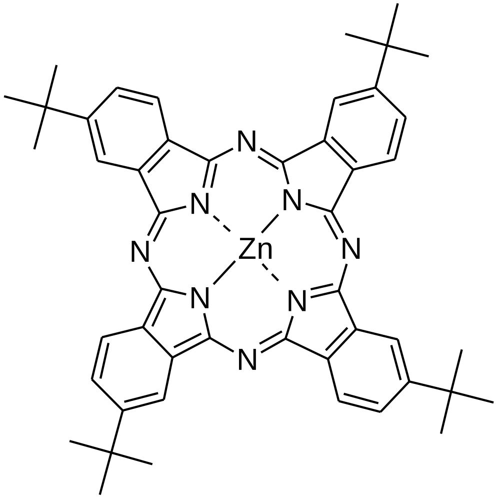
Sym-HTPcH

PCE = 12,8%

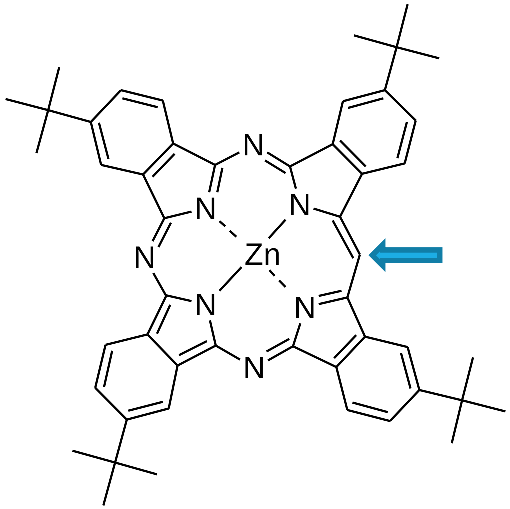
introducing a meso Al_2O_3 buffer layer



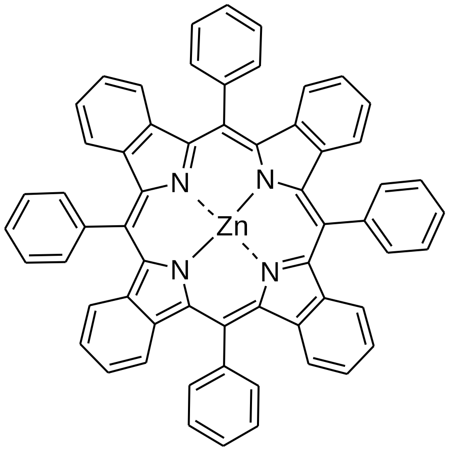
P. Gao et al. Phys. Chem. Chem. Phys, DOI: 10.1039/c6cp03396b



ZnPc



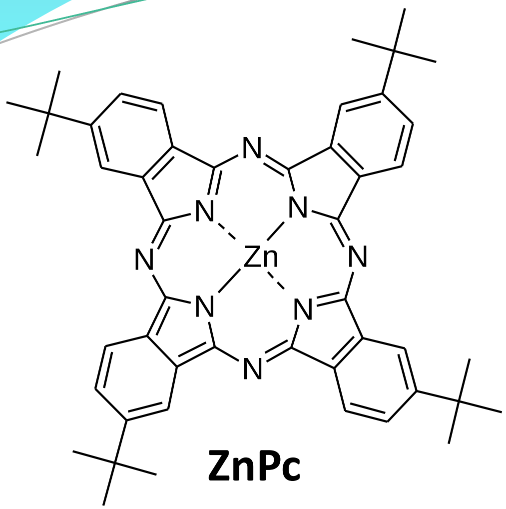
ZnTABP



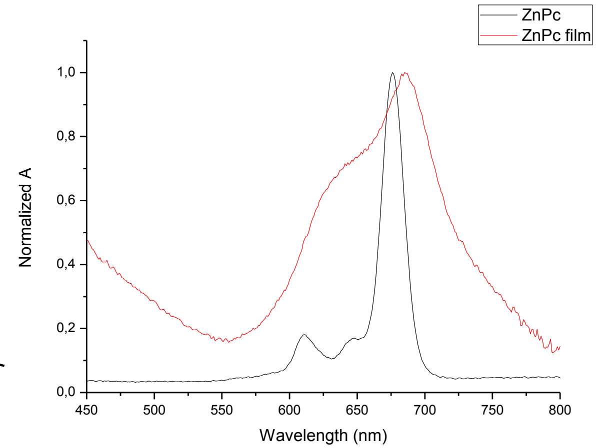
ZnTBP

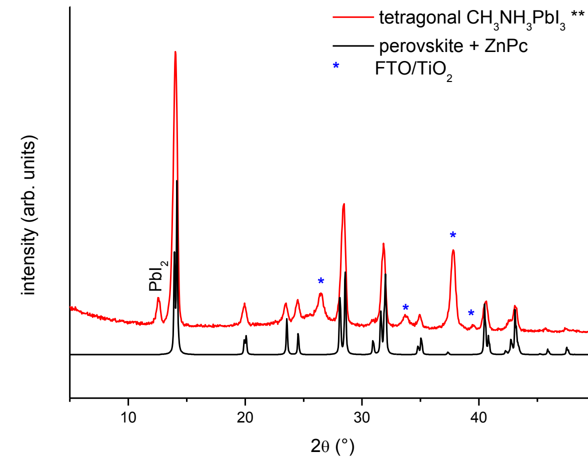
	$E_{1/2ox}$ (V) vs SCE
ZnPc	0.680*
ZnTABP	0,553
ZnTBP	0,629

* Leznoff and Lever, Phthalocyanines properties and application, vol 3,VCH 1993,

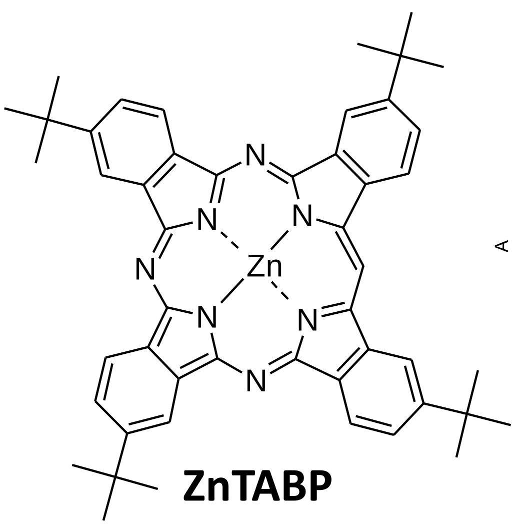


ZnPc

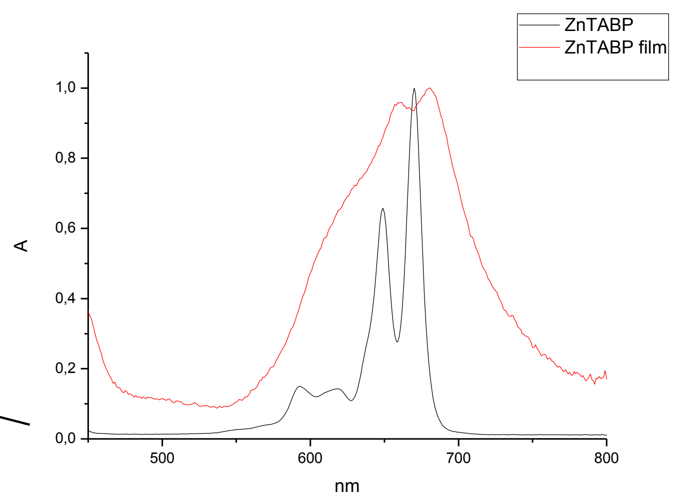


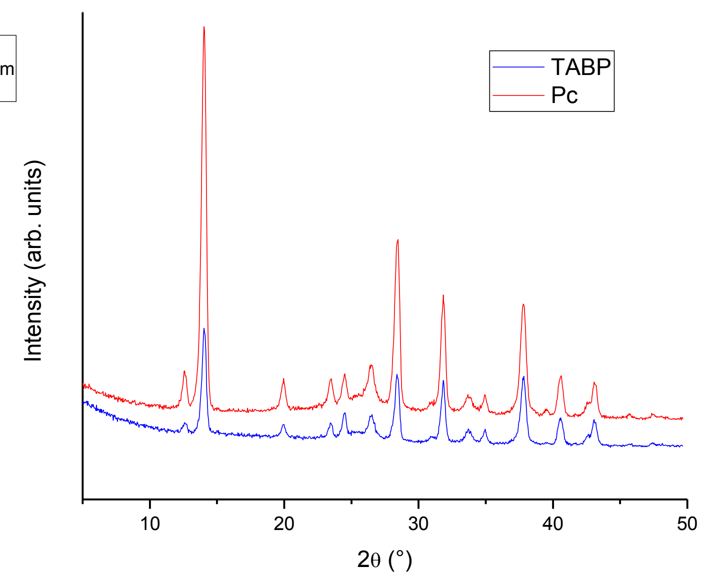


** from: Y. Yamada et al., J. Am. Chem. Soc. 2015, 137, 10456



ZnTABP





ISMN – CNR (Roma):
Optical characterization
(D. Caschera)

Istituto di Struttura della Materia

ISM – CNR (Roma):
X-ray analysis
(P. Imperatori)

IMM – CNR (Catania):
Substrate characterization
(A. Alberti)

ISM – CNR (Roma):
Theoretical modeling
(A. Amore Bonapasta,
G. Mattioli)

NANO – CNR (Lecce):
DSSC characterization
and testing (L. De Marco,
G. Gigli)

INO – CNR (Firenze):
Ultrafast spectroscopic measurements (A. Iagatti, P. Foggi)

- Financial support : **EFOR** project (triennial national research project funded by MInistero dello Sviluppo Economico (MISE))

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Consiglio Nazionale delle Ricerche

2. Long term stability of small-molecules solar cells based on (DBP):C70 planar mixed heterojuncion with (TPBi):C70 electron-filtering cathode buffer layers

In practical applications solar cells must achieve high efficiencies and long-term reliability

$$E_{80} = \int_0^{T_{80}} \mathrm{PCE}(t) \cdot P_{\mathrm{inc}}(t)dt$$

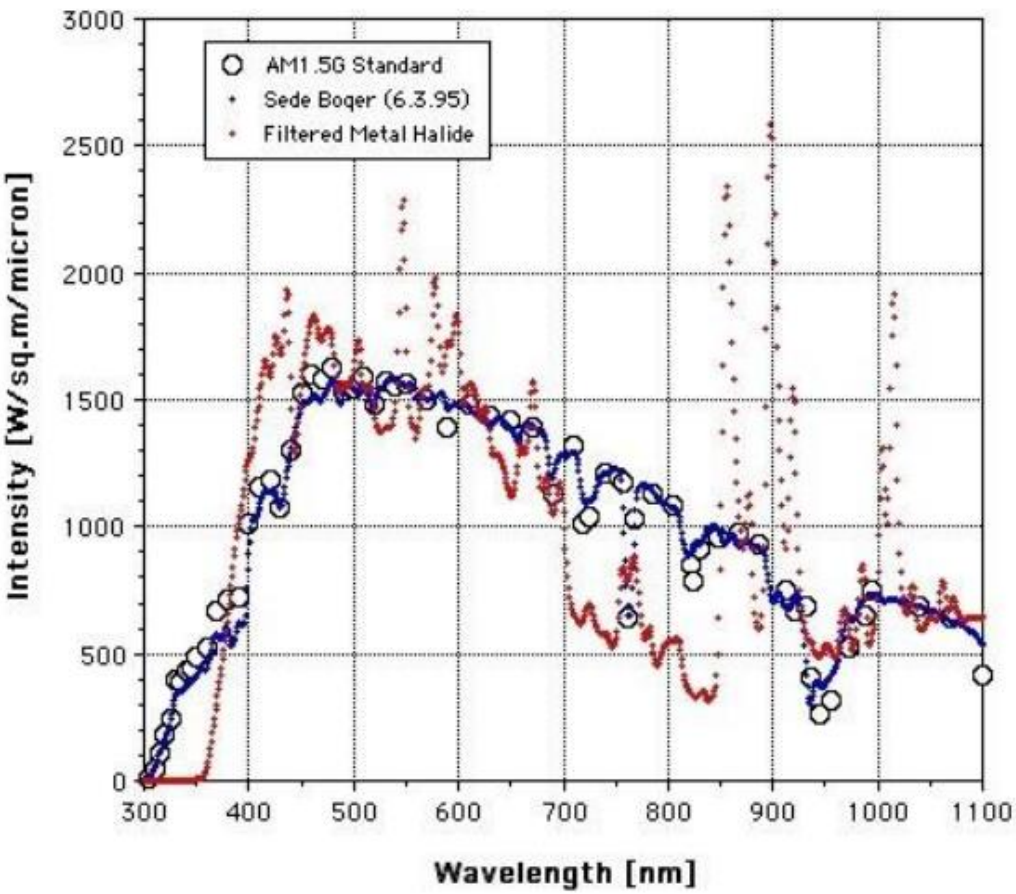
E_{80}: total energy produced by a photovoltaic device prior to failure
T_{80}: time after which a cell has lost the 20% of its initial efficiency
$P_{inc}(t)$= solar irradiance

Testing photovoltaic devices under real-weather condition provides information for the practical application of OPVs for the solar generation of electricity

SEDE BOQER

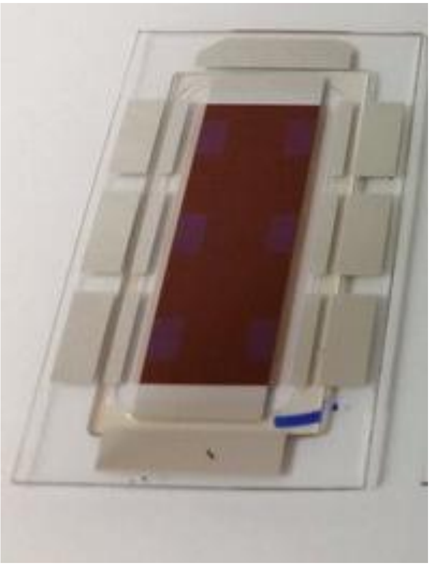
Lat. 30.8N, Lon. 34.8E, Alt. 475 m

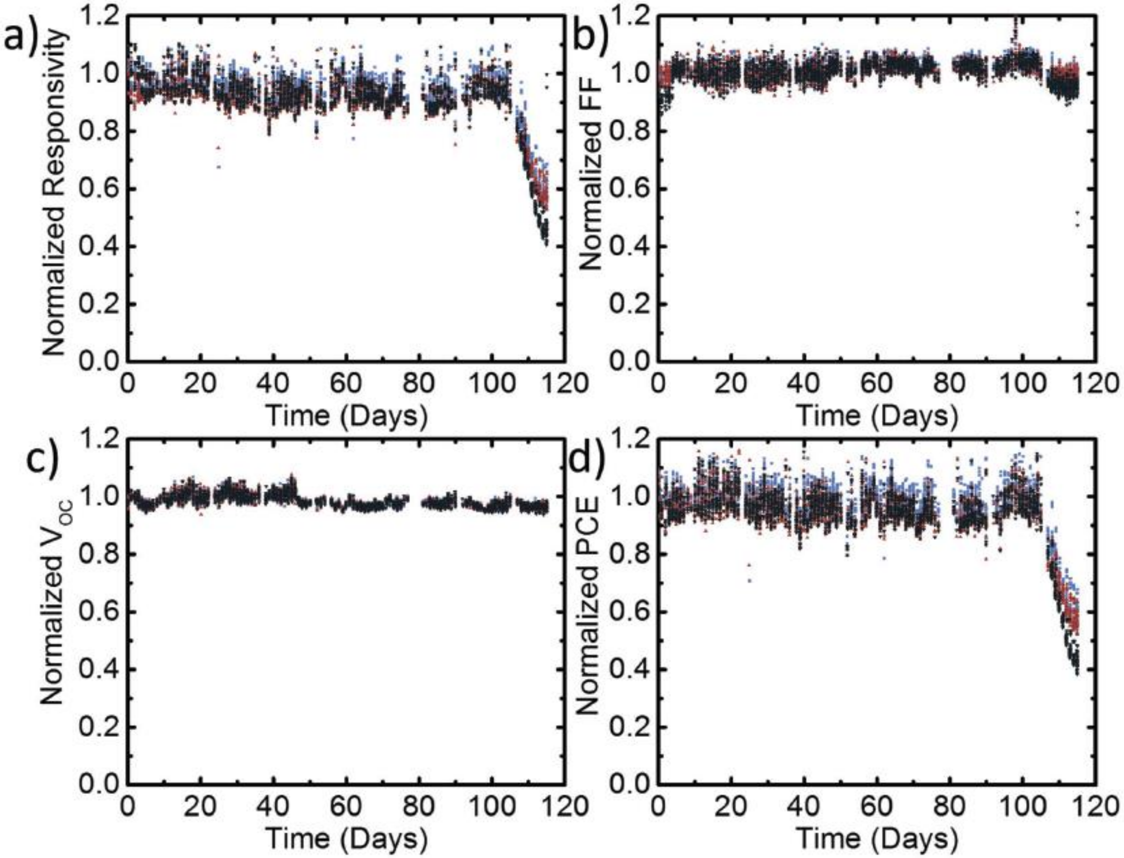
Noontime spectrum on cloudless days is extremely close to the standard 1.5AM solar spectrum.



Berman, D. and Faiman, D. *Solar Energy Materials and Solar Cells*. 1997, **45**, 401-412.

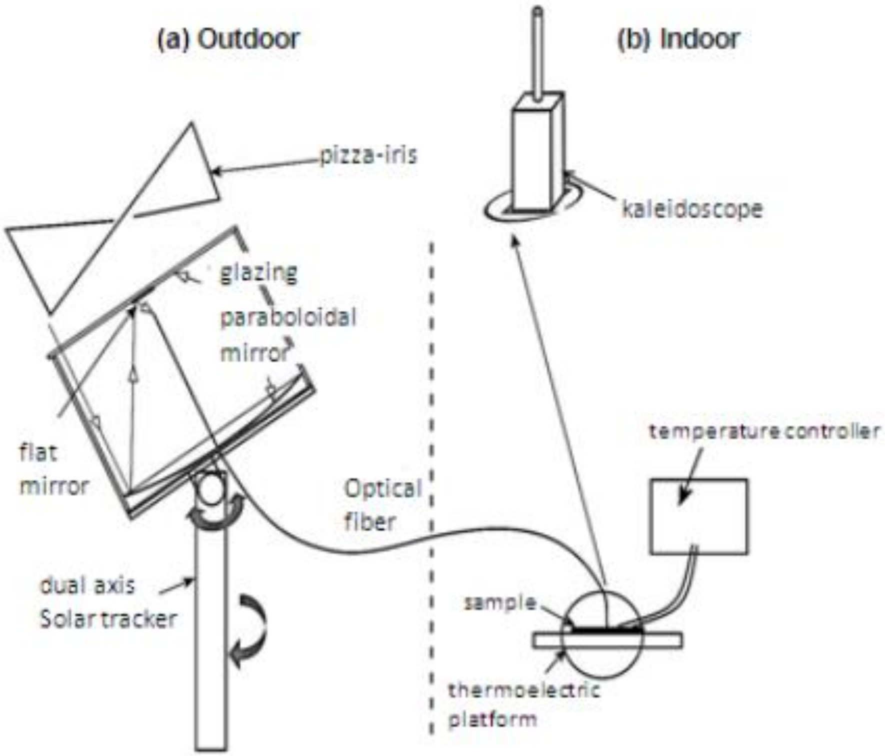
Planar-mixed HJ DBP:C_{70} devices are among the most stable OPV cells to date, with lifetimes of T_{80} > 2500 hr measured under laboratory conditions.





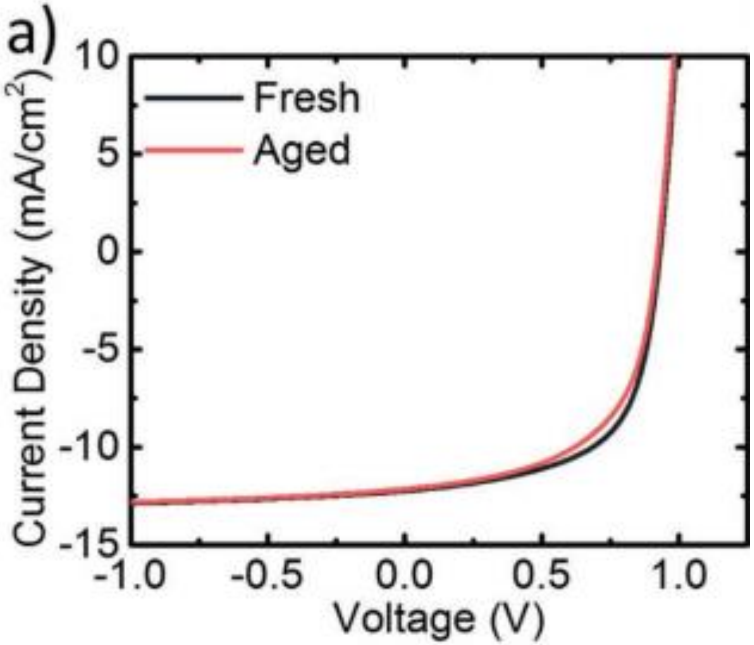
Natural sunlight aging (Nov 15th 2015- Feb 21th 2016) shows no degradation after >100 days, until the encapsulation broke.

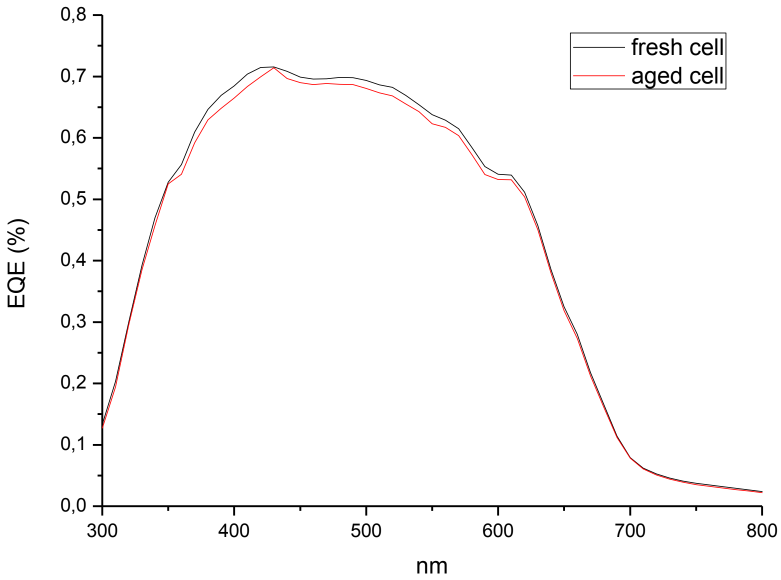
Burlingame, Q.; Song, B.; Ciammaruchi, L.; Zanotti, G.; Hankett, J.; Chen, Z.; Eugene A. Katz, E. A.; Forrest, S. .
Adv. Energy Mater. 2016, 1601094



Katz, E. A.; Gordon, J. M.; Tassew, W.; Feuermann, D.
Photovoltaic Characterization of Concentrator Solar Cells By Localized Irradiation.
J. Appl. Phys. **2006**, 100, 044514 (1-8).

AGING WITH SOLAR CONCENTRATOR

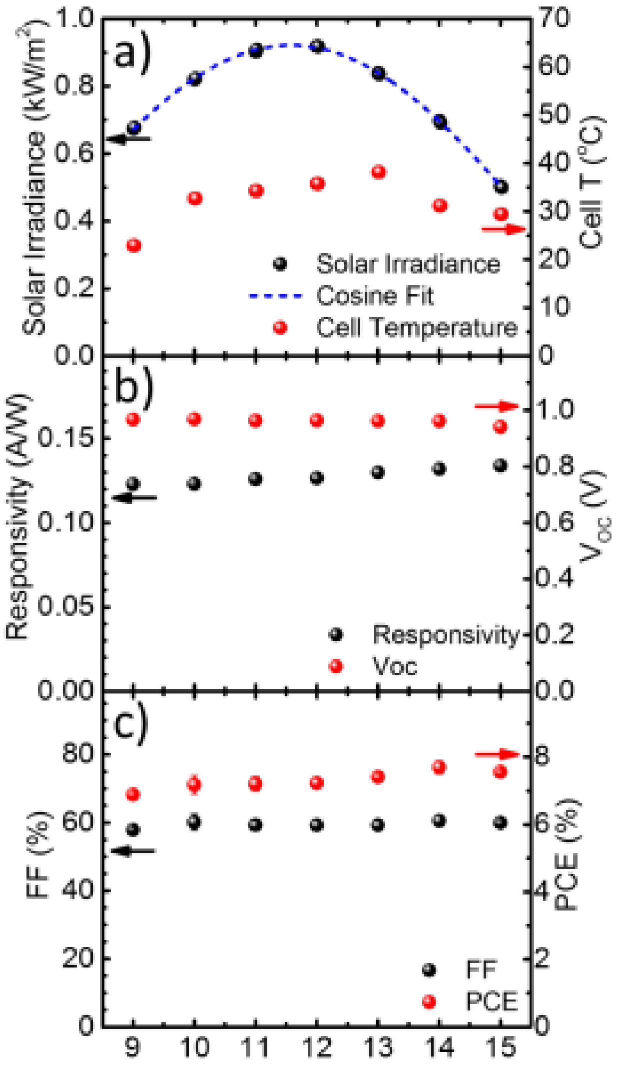




Almost no absorption changes after 5 h under 100-sun intensity

Burlingame, Q.; Song, B.; Ciammaruchi, L.; Zanotti, G.; Hankett, J.; Chen, Z.; Eugene A. Katz, E. A.; Forrest, S. .
Adv. Energy Mater. 2016, 1601094

diurnal dependence of small-molecule planar-mixed HJ DBP:C_{70} OPV cells determined by measuring their performance outdoors



V_{OC} decreases linearly with temperature

PCE has a positive temperature coefficient (0.02 %/°C, absolute) from 15°C to 40°C

J_{SC}, increases because of a broadening of the absorption spectra

At high irradiance, the cell performance was dominated by resistive losses that lead to a reduction in *FF*, and thus *PCE*.

The cells reached their peak efficiency near 40°C and remained within 3% of their maximum *PCE* at 1 sun.

Throughout the day, the variation in all of the photovoltaic operational parameters was <10%.

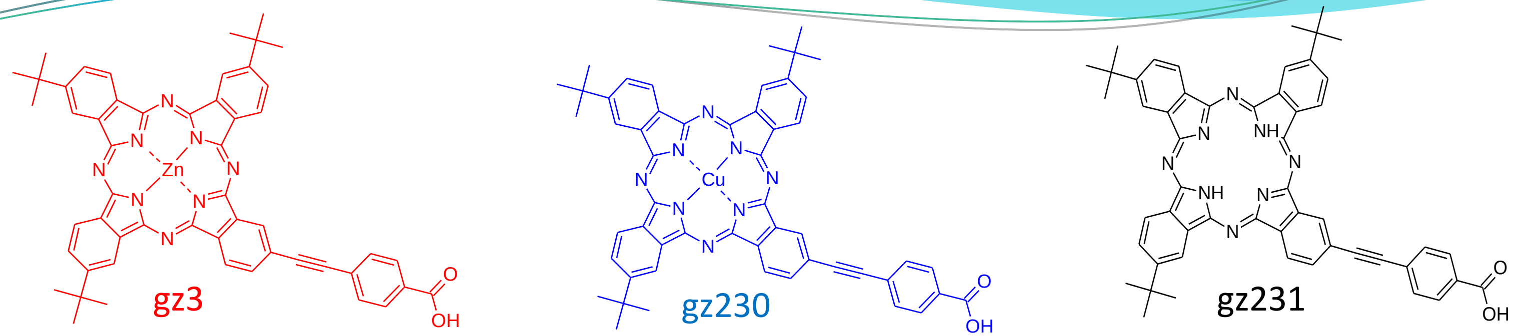
Burlingame et al. manuscript in preparation

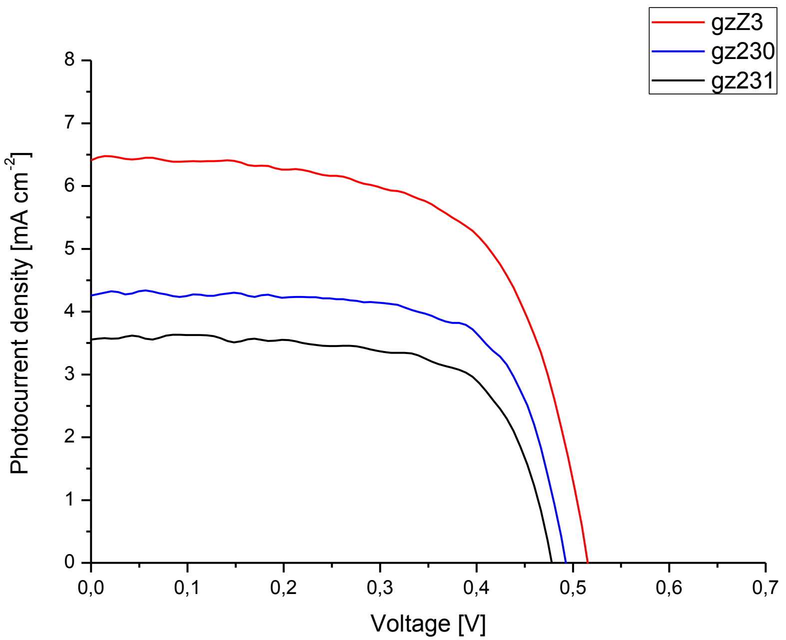
AKNOWLEDGEMENTS

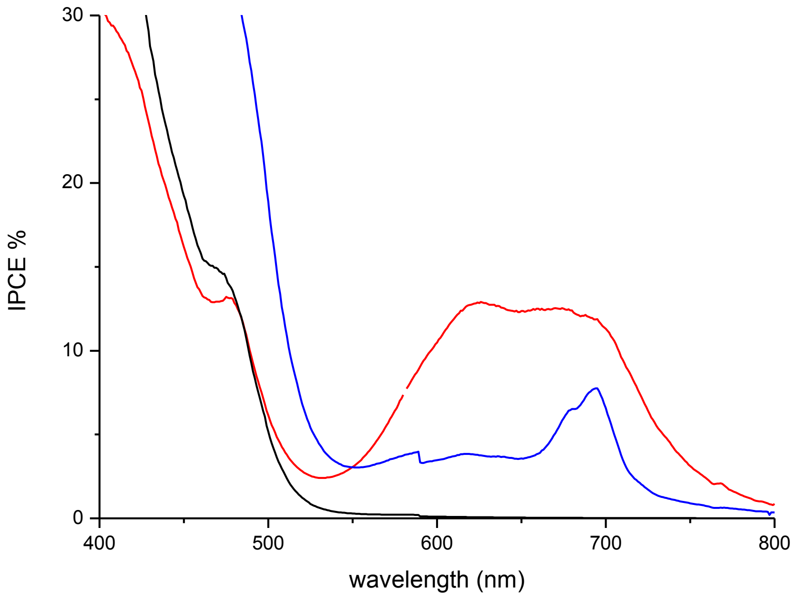
- ***CNR***
  - Dr. Gianna Pennesi
  - Dr. Anna Maria Paoletti
  - Dr. Patrizia Imperatori
  - Dr. Giuseppe Mattioli
  - Dr. Nicola Angelini
  - Sara Notarantonio
  - Dr. Daniela Caschera
  - Dr. Paolo Foggi
  - Dr. Alessandro Iagatti
  - Dr. Alessandra Alberti
  - Dr. Giovanna Pellegrino
- ***BGU- ENEA joint lab***
  - Prof. David Faiman
  - Prof. Eugene Katz
  - Prof. Iris Visoly-Fisher
  - Prof. Daniel Feurmann
  - Dr. Rafi Shikler
  - Dr. Andrea Quintiliani
  - Dr. Francesco Roca
- ***Colleagues from other institutions***
  - Quinn Burlingame
  - Dr. Laura Ciammaruchi
  - Dr. Luisa De Marco
- You all for your kind attention

Istituto di Struttura della Materia

Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile


gz3
gz230
gz231


gzZ3
gz230
gz231
Photocurrent density [mA cm-2]
Voltage [V]


IPCE %
wavelength (nm)