SOME “SMALL” MOLECULES APPLICATIONS IN PHOTOVOLTAICS

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and

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Which molecules are we talking about?

- Flexible electronics
- Bulk-heterojunction solar cells
- Hybrid organic-inorganic systems
- Sensors
- Photodynamic therapy
- DSSC
- Nanoparticles functionalization
- Perovskites
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

2. Long term stability of small-molecules solar cells based on (DBP):C70 planar mixed heterojunction with (TPBi):C70 electron-filtering cathode buffer layers
1. Synthesis of macrocyclic compounds for photovoltaic applications
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2. Long term stability of small-molecules solar cells based on (DBP):C70 planar mixed heterojunction with (TPBi):C70 electron-filtering cathode buffer layers
- four isoindole units bridged by four nitrogen atoms that form an inner 16-membered ring
- 18 $\pi$-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 ($\varepsilon = 10^5 \text{ mol}^{-1}\text{cm}^{-1}$)
- Q band tunability + solubility enhancement by macrocycle functionalization
- 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 TiO₂ surface
- Processability
- Long-term exposure stability to natural sunlight
$\eta = 3.96\%$

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

$\eta = 12\%$

$\eta = 11\%$


$\eta = 6.4\%$

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

$\eta = 13\%$

*Science.* 2011, **334**, 629-634
Our results
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)

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

Our results
<table>
<thead>
<tr>
<th>dye</th>
<th>$\eta$ (%)</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF</th>
<th>CDCA (mM)</th>
<th>dye loading [mol cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>gz231</td>
<td>1.38</td>
<td>0.55</td>
<td>3.59</td>
<td>0.70</td>
<td>-</td>
<td>$1.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>gz231</td>
<td>1.19</td>
<td>0.53</td>
<td>3.11</td>
<td>0.72</td>
<td>2</td>
<td>$0.7 \times 10^{-7}$</td>
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<tr>
<td>gz230</td>
<td>1.66</td>
<td>0.56</td>
<td>4.24</td>
<td>0.70</td>
<td>-</td>
<td>$1.1 \times 10^{-7}$</td>
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<tr>
<td>gz230</td>
<td>1.59</td>
<td>0.58</td>
<td>3.65</td>
<td>0.75</td>
<td>2</td>
<td>$0.7 \times 10^{-7}$</td>
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<tr>
<td>gz3</td>
<td>2.10</td>
<td>0.52</td>
<td>6.43</td>
<td>0.63</td>
<td>-</td>
<td>$1.0 \times 10^{-7}$</td>
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<tr>
<td>gz3</td>
<td>1.97</td>
<td>0.58</td>
<td>4.79</td>
<td>0.71</td>
<td>2</td>
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<tr>
<td>N719</td>
<td>7.64</td>
<td>0.75</td>
<td>14.56</td>
<td>0.70</td>
<td>-</td>
<td>$1.5 \times 10^{-7}$</td>
</tr>
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</table>

Our results


<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (cm$^{-1}$Mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gz3</td>
<td>671, 685</td>
<td>$1.02 \times 10^5$, $1.15 \times 10^5$</td>
</tr>
<tr>
<td>gz230</td>
<td>671, 686</td>
<td>$1.08 \times 10^5$, $1.21 \times 10^5$</td>
</tr>
<tr>
<td>gz231</td>
<td>672, 692</td>
<td>$8.07 \times 10^4$, $8.03 \times 10^4$</td>
</tr>
</tbody>
</table>
### dye | $\text{Abs}_{\text{max}}$ [nm] | $\text{Em}_{\text{max}}$ [nm] | $E_{1/2\text{ox}}$ [V] vs SCE | $E_{1/2\text{red}}$ [V] vs SCE | $\Delta E_{1/2}$ [V] | $E_{(S^+/S)}$ [eV] | $E_{(0-0)}$ (Abs/Em) [V] vs SCE | $E_{(S^+/S^*)}$ [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

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

Zanotti et al. Dalton Trans. 2011, **40**, 38
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$_{\text{surf}}$ = d=2x10$^{12}$. 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.

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.

• **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
Our results

Zanotti et al. RSC Advances 2016, 6, 5123
Zanotti et al. RSC Advances 2016, 6, 5123
<table>
<thead>
<tr>
<th></th>
<th>η %</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF</th>
<th>CDCA [Mm]</th>
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<tbody>
<tr>
<td>PETBP</td>
<td>0.95</td>
<td>0.493</td>
<td>2.80</td>
<td>0.69</td>
<td>0</td>
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<tr>
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<td>1.27</td>
<td>0.551</td>
<td>3.33</td>
<td>0.69</td>
<td>5</td>
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<tr>
<td></td>
<td>2.22</td>
<td>0.577</td>
<td>5.83</td>
<td>0.66</td>
<td>10</td>
</tr>
<tr>
<td>N719</td>
<td>7.51</td>
<td>0.772</td>
<td>4.79</td>
<td>0.68</td>
<td>0</td>
</tr>
</tbody>
</table>

Our results

Zanotti et al. RSC Advances 2016, 6, 5123
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

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

$\text{AMX}_3$

A organic cation (methylammonium (MA) or formamidinium (FA)) or inorganic monovalent ion ($\text{Cs}^+$)

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

X halogen or halogen mixture ($\text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$)

*Scientific Reports 5, Article number 14485 (2015)*
PEROVSKITES

AMX₃

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

(CH₃)NH₃I + PbI₂ → (CH₃)NH₃PbI₃

PEROVSKITES

AMX$_3$

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%

**SubPc**
PCE = 6.6%
G. Sfyri et al. RSC Advances 2015, 5, 69813

**CuMePc**
PCE = 5.2%

**Sym-HTPcH**
PCE = 12.8%
introducing a meso Al₂O₃ buffer layer

ZnPc

ZnTABP

ZnTBP

<table>
<thead>
<tr>
<th></th>
<th>( E_{1/2\text{ox}} ) (V) vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnPc</td>
<td>0.680*</td>
</tr>
<tr>
<td>ZnTABP</td>
<td>0.553</td>
</tr>
<tr>
<td>ZnTBP</td>
<td>0.629</td>
</tr>
</tbody>
</table>

* Leznoff and Lever, Phthalocyanines properties and application, vol 3, VCH 1993,
Phthalocyanines as potential HTM for perovskite solar cells

** from: Y. Yamada et al., J. Am. Chem. Soc. 2015, 137, 10456
IMM – CNR (Catania): Substrate characterization (A. Alberti)

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

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

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

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

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

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

\[ E_{80} = \int_0^{T_{80}} P_{\text{CE}}(t) \cdot P_{\text{inc}}(t) \, dt \]

- \( E_{80} \): 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
- \( P_{\text{inc}}(t) \): 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.

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 15\textsuperscript{th} 2015 - Feb 21\textsuperscript{th} 2016) shows no degradation after >100 days, until the encapsulation broke.

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

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
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• **CNR**
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  - Dr. Paolo Foggi
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  - Dr. Alessandra Alberti
  - Dr. Giovanna Pellegrino

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• You all for your kind attention
Our results