Organic-based light harvesting electronic devices

Maddalena Binda
Organic Electronics: principles, devices and applications
Milano, November 26-29th, 2013
Organic-based light harvesting devices

From signal detection to power generation...

**OPTICAL COMMUNICATIONS**

- Optical Fiber
- Light source
- Photodetector

**SENSORISTICS**

**IMAGING**

- X-rays
- Flat panel X-ray image detector

**REMOTE CONTROL**
Organic-based light harvesting devices

From *signal detection* to *power generation*...

- High speed
- Spectral selectivity
- Bias voltage allowed
- High signal-to-noise ratio
- CW operation
- Broad responsivity
- Bias voltage not allowed
- Hardiness in critical conditions

Photogeneration efficiency: EQE
Light sensors:
Organic PhotoDetectors (OPD)
Light sensors: sensitivity

We want to go from this...

signal

noise

...to this:

High **signal-to-noise ratio** (SNR)

![Diagram]

Increase signal $\rightarrow$ Increase EQE
Reduce parasitic effects like e.g. leakage current

M. Binda et al.
Light sensors: sensitivity

We want to go from this...                             ...to this:

High **signal-to-noise ratio (SNR)**

Increase signal $\rightarrow$ Increase EQE
Reduce parasitic effects like e.g. leakage current

M. Binda et al.  
Light sensors: sensitivity


See also:

Reduced leakage current while EQE is conserved

SNR
Light sensors: response speed

E.g. APPLICATION IN OPTICAL DATA TRANSMISSION

Play with:
• device geometry \(\rightarrow\) Reduced interelectrode spacing
• active material composition

Fast reponse is required!

M. Binda et al., Organic Electronics 10 (2009) 1314–1319

Organic (and hybrid) Solar Cells
Power Conversion Efficiency (PCE)

$\eta_{POWER} = \frac{P_{OUT}}{P_{IN}} = \frac{I_{MPP} \cdot V_{MPP}}{P_{IN}} = \frac{FF \cdot I_{SC} \cdot V_{OC}}{P_{IN}}$

$FF = \frac{V_{mpp} \cdot I_{mpp}}{V_{oc} \cdot I_{sc}}$
Series and Shunt resistance of a solar cell

We want:
- Rs low
- Rsh high

Leakage paths: metal infiltration, pinholes,...

poorly conductive paths in the semiconductor, contact resistance, resistivity of the electrode,...
Power Conversion Efficiency of a solar cell

Power Conversion Efficiency (PCE)

\[
\eta_{\text{POWER}} = \frac{P_{\text{OUT}}}{P_{\text{IN}}} = \frac{I_{\text{MPP}} \cdot V_{\text{MPP}}}{P_{\text{IN}}} = \frac{\text{FF} \cdot I_{\text{SC}} \cdot V_{\text{OC}}}{P_{\text{IN}}}
\]

\[FF = \frac{V_{mpp} \cdot I_{mpp}}{V_{oc} \cdot I_{sc}}\]
Power Conversion Efficiency of a solar cell

Important notes on cell characterization:

1. The solar emission must be reproduced

2. A standard path must be adopted

   air-mass:
   optical path through the Earth atmosphere
   scattering absorption

   **Standard AM1.5 - 1 sun**

   AM1.5 \( z = 48.2^\circ \) (middle latitudes)

   \[ X = \frac{L}{L_0} \approx \frac{1}{\cos z} \]

   \( L_0 \) = zenith path length at sea level
   \( L \) = effective path length

   Es. \( z = 0 \) → AM1

   \[ \approx 1000 \text{W/m}^2 \]
Different parameters must be simultaneously optimized:

\[ PCE = \frac{FF \cdot V_{OC} \cdot I_{SC}}{P_{IN}} \]

But they are indeed strongly correlated!!!
**Open Circuit Voltage ($V_{OC}$)**

Debated...

See:  
Nat. Materials, 8, 904-909, 2009

\[
V_{oc} = \frac{1}{q}(\text{HOMO}_D - \text{LUMO}_A - 0.3)
\]

empirical  
at solar intensity

Open Circuit Voltage ($V_{OC}$): recombination

$V_{oc} = \frac{1}{q}(HOMO_D - LUMO_A - 0.3)$

$J_{net}(x) = 0$

$qVoc = E_{Fh} - E_{Fe}$

$G = R(x)$

$G = R_{geminate}$

$G = R_{Langevin}$

$G = R_{SRH}$

** PHYSICAL REVIEW B 84, 075210 (2011) **

Es. $R = R_{Langevin} = \gamma n_h(x)n_e(x)^*$

$qVoc = E_g + k_B T \ln \left( \frac{G}{\gamma N_h N_e} \right)$

$V_{oc,max} = HOMO_D - LUMO_A$

Recombination -0.2 $\rightarrow$ -0.5

Logarithmic dependence on $G$, often reported in the literature

*Boltzmann approx., no disorder*
Open Circuit Voltage ($V_{OC}$): energetic disorder

*not the complete story...energetic disorder plays a role!!!*

- Recombination via localized states
- Carriers relaxed into the tail of the DOS reduce the quasi-Fermi level splitting

\[
qV_{oc} = const. + mk_B T \ln \left( \frac{G}{\gamma N_i N} \right)
\]

$HOMO_D - LUMO_A - \Delta E$

$m > 1$

Example. PHYSICAL REVIEW B 84, 075210 (2011)

\[
eV_{OC} = E_g + mk_B T ln \left( \frac{G}{\gamma N_i N} \right)
\]

Hp. Langevin modified for disorder, exponential tail distribution
Origin of the $V_{OC}$: role of the electrodes

MIM: Metal Intrinsic Metal model

**Short-circuit condition**

Built-in field due to metals workfunction mismatch

**Open-circuit condition**

or “flat band” condition

No net current flow. $Voc$ given by the difference between the metal workfunctions

$J_{PHOTO}$: photogenerated carriers need a driving force

- Internal Electric Field $\rightarrow$ Drift current
- Charge concentration gradient $\rightarrow$ Diffusion current

ideal BHJ
Origin of the $V_{OC}$: role of the electrodes

MIM: Metal Intrinsic Metal model

**Short-circuit condition**

$$V_{oc,max} = \frac{1}{q}(\Phi_{M1} - \Phi_{M2})$$

Built-in voltage

**Open-circuit condition**
or “flat band” condition

$$V_{oc,max} = \frac{1}{q}(HOMO_D - LUMO_A - \Delta E)$$

- Internal Electric Field $\rightarrow$ Drift current
- Charge concentration gradient $\rightarrow$ Diffusion current

Ideal BHJ
Origin of the $V_{OC}$: role of the electrodes

Contacts have little effect... if I choose them right!

Fermi-level pinning

PHYSICAL REVIEW B 84, 075210 (2011)

<table>
<thead>
<tr>
<th>Cathode</th>
<th>$\varphi_b$ (eV)</th>
<th>$V_{OC}$ (V)</th>
<th>$\Delta V_b$ (V)</th>
<th>$\varphi_b + V_{OC} + \Delta V_b$ (eV)</th>
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<td>LiF/Al</td>
<td>0</td>
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<td>1.28</td>
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<tr>
<td>Ag</td>
<td>0.65</td>
<td>0.84</td>
<td>0</td>
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<td>Au</td>
<td>0.76</td>
<td>0.74</td>
<td>0</td>
<td>1.5</td>
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</table>

0.76eV $\uparrow$ Ag

1.4eV $\downarrow$ Au «effective» due to interf. dipole

Origin of the $V_{OC}$: role of the electrodes

- $V_{oc}$ can exceed the built-in of the contacts if the bulk-heterojunction is not so “ideal”

[Diagram of a heterojunction with donor and acceptor layers]


- Compex, more realistic device architectures provide asymmetry to the system (i.e. blocking layers)

Current flow can be driven by diffusion!
Improving the $V_{OC}$: active material

1. D/A energy level alignment

   | DONOR       | J_{photo} | Voc | ACCEPTOR |

   TRADE OFF with charge dissociation!!

2. Reducing recombinations

   \[ ? \text{material level} ? \]

   Increase phase separation: slow down the rate at which charges meet each other... But TRADE OFF with charge generation (reduced D/A interface)!!!
Improving the $V_{OC}$: device

BLOCKING LAYERS FOR SELECTIVE COLLECTION AT THE ELECTRODES

(b) and (c) diagrams illustrating the concepts of electron and hole transport in organic solar cells.

- **Anode** (hole electrode) and **Acceptor** layers.
- **LUMO** and **HOMO** levels for electron and hole transport.

**Weak electric field case (i.e., high cell voltage):** $J_{\text{diff}} > J_{\text{drift}}$

**Electron blocking layer case (independent of electric field):** $J_{\text{diff}} \approx 0$

Dr. Carvelli
Improving the $V_{OC}$: tandem cells

Large stacks: six-fold junction

17 solution processed layers on top of each other

![Graph showing current density vs. voltage for different junctions.

$V_{oc} = 0.75$ V
$I_{sc} = 3.5$ mA/cm²
FF = 0.48
MPP = 1.3 mW/cm²

Single Junction

$V_{oc} = 1.53$ V
$I_{sc} = 3.0$ mA/cm²
FF = 0.40
MPP = 1.8 mW/cm²

Double Junction

$V_{oc} = 2.19$ V
$I_{sc} = 2.6$ mA/cm²
FF = 0.37
MPP = 2.1 mW/cm²

Triple Junction

$V_{oc} = 3.46$ V
$I_{sc} = 1.6$ mA/cm²
FF = 0.32
MPP = 1.7 mW/cm²

Six-fold Junction

Tandem solar cells for increased $V_{oc}$


Equivalent $V_{oc}$ = sum of single cells $V_{oc}$
Equivalent $J_{sc}$ = $J_{sc}$ of the worst cell in the stack

**REVIEW ART.: Energy Environ. Sci., 2013, 6, 2390-2413**
Short-circuit current ($J_{sc}$)

**EQE**
- Light absorption
- Charge photogeneration efficiency
- Charge transport and collection

$$\text{EQE} = \frac{\text{Number of collected charges}/s}{\text{Number of incoming photons}/s} = \frac{n_c/s}{n_v/s} = \eta_{\text{abs}} \cdot \eta_{\text{ed}} \cdot \eta_{\text{cc}}$$

Active material
Device (architecture) level
Extending the responsivity to low energy photons

As much as half of the energy of the solar spectrum is carried by long wavelengths photons!

\[ \Delta \text{LUMO} \]

\[ \text{Voc} \]

\[ \text{DONOR} \]

\[ \text{ACCEPTOR} \]

Progress in Polymer Science 38 (2013) 1929–1940
Red-light responsivity

**EXAMPLES 1: POLYMERS**

*J. Peet et al., Nature Materials 6, 497 - 500 (2007)*

**PCE>5%**


Other works: Muhlbacher et al., 2006; Kooistra et al., 2006; Yao et al., 2006; Soci et al., 2007; Wang et al., 2008; Hou et al., 2008)
Red-light responsivity

**EXAMPLES 2: SMALL MOLECULES**

**SQUARAINES**

G. Wei et al., ACSNano 4, 4, 2010.

<table>
<thead>
<tr>
<th>SQ:PC_{70}BM ratio</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>$\eta_p$ (%) at $P_0 = 1$ sun</th>
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<td>3:1</td>
<td>0.68(±0.03)</td>
<td>1.79(±0.19)</td>
<td>0.26(±0.01)</td>
<td>0.32(±0.01)</td>
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<td>1:1</td>
<td>0.81(±0.01)</td>
<td>3.61(±0.03)</td>
<td>0.31(±0.01)</td>
<td>0.90(±0.01)</td>
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<td>1:2</td>
<td>0.87(±0.01)</td>
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<td>1:3</td>
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<td>8.83(±0.34)</td>
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<td>1:6</td>
<td>0.89(±0.01)</td>
<td>8.85(±0.22)</td>
<td>0.35(±0.01)</td>
<td>2.7(±0.1)</td>
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</table>

Short-circuit current ($J_{sc}$): light absorption - device

Maximum of the stationary optical field inside the active region

Requirements:
- Transparent
- Electron transporter
- Conduction band lower than LUMO of acceptor and higher than cathode Fermi level

$\eta = 6\%$ (certified by NREL)

Park et al., Nat. Phot. 3 (2009) 297
Short-circuit current ($J_{sc}$): photogeneration and charge transport

BULK-HETEROJUNCTION OPTIMAL FOR EXCITON DISSOCIATION...
...BUT REQUIRES CAREFUL CONTROL OF MORPHOLOGY!

Charges percolation must be allowed!

How?

1. Additives (solvents mixtures):
   
   selective solubility

   One phase still in solution while the other is already in solid state

   Higher degree of phase separation, higher crystallinity

   A. de Sio et al., 95, 3536–3542, 2011.
Short-circuit current ($J_{sc}$): photogeneration and charge transport

BULK-HETEROJUNCTION OPTIMAL FOR EXCITON DISSOCIATION... ...BUT REQUIRES CAREFUL CONTROL OF MORPHOLOGY!

Charges percolation must be allowed!

How?

2. Post deposition treatments: thermal annealing


XRD, increased P3HT crystallinity
No continuous paths between the electrodes for leakage carriers...
  ▫ Higher Shunt resistance
...but continuous and directional paths for photogenerated carriers:
  ▫ Higher mobility
  ▫ Lower recombination
  ▫ Low series resistance

Fill Factor (FF)
Going towards the ideal “comb-like” structure
Hybrid devices: organic/inorganic

Inorganic nanostructured semiconductors exploited in combination with organics for their

Optical properties
CdSe, CdS, PbSe, PbS, ... nanocrystals

- Strong and tunable absorption
- Tunable shape

Morphological and electrical properties
Metal oxides: TiO$_2$, ZnO

- Morphologically stable
- Higher mobilities
- Transparent
- High dielectric constant

1. A.C. Arango et al., Nano Letters 9, 860-863 (2009)

Hybrid devices: organic/inorganic

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solution processed!

Colloidal NCs
- Solubility!

CdSe 4 nm

A.C. Arango et al., Nano Letters 9, 860-863 (2009)
D.M.N.M. Dissanayake, Nanotechnology 20 (2009) 245202
Hybrid devices: heterojunction structure

BHJ

Mimicking comb-like enabled by high morphological stability after thermal post-processing: organic ligands removal, nanoparticles sintering

ZnO, TiO2, Al2O3
Nanocrystals based hybrid solar cells

Optical properties

Quantum confinement effect:

\[ E_n = \frac{\hbar^2}{2m^*} \left( \frac{n\pi}{L_x} \right)^2 \]

Extreme spectral tunability by tuning the dots dimension

MEG? Multiple Exciton Generation

EQE > 100% reported!

Nanocrystals based hybrid solar cells

Charge transport

- Charge trapping at surface states
- Distance between nanocrystals (hopping sites)

interparticle hops
direct transport intra-crystal

careful tuning of capping ligands!
(shorter, conductive,...)

Nano Lett., 2011, 11, 3998 – 4002
# Nanocrystals based hybrid solar cells blended with polymer for extended absorption

## Table 1. A selection of CdSe-based hybrid solar cells

<table>
<thead>
<tr>
<th>Shape</th>
<th>Ligand</th>
<th>Polymer</th>
<th>NCs (wt%)</th>
<th>Light intensity (mW cm(^{-2}))</th>
<th>(J_{SC}) (mA/cm(^2))</th>
<th>(V_{OC}) (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Ref.</th>
<th>Year</th>
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<tbody>
<tr>
<td>NDs</td>
<td>Pyridine</td>
<td>MEH-PPV</td>
<td>90</td>
<td>0.5(^c)</td>
<td>0.01(^{c,d})</td>
<td>0.50(^c)</td>
<td>0.26</td>
<td>0.26(^{c,d})</td>
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<td>89</td>
<td>100</td>
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\(^a\) Abbreviations: \(J_{SC}\) = short-circuit current; \(V_{OC}\) = open-circuit voltage; FF = fill factor; ND = nanodot; NR = nanorod; TP = tetrapod; BA = butylamine; HA = hexanoic acid; tBT = tert-butylthiol; dithiol = benzene-1,3-dithiol. \(^b\) AM 1.5 conditions unless otherwise stated. \(^c\) Monochromatic illumination at 514 nm. \(^d\) Calculated based on the information provided in the original paper. \(^e\) Large size: 7.1 nm. \(^f\) A ZnO layer between the active layer and the cathode was used as the optical spacer and hole-blocking layer. The efficiency was 2.7% without the ZnO layer. \(^g\) Relatively small size: 8 \(\times\) 13 nm. \(^h\) In the form of fibrils. \(^i\) Careful NC washing before pyridine treatment. \(^j\) NDs:NRs = 27:63 by weight.
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Effectiveness of D/A interface? Energy transfer between polymer and NCs? Poor charge transport?

$^a$ Abbreviations: $J_{sc}$ = short-circuit current; $V_{oc}$ = open-circuit voltage; FF = fill factor; ND = nanodot; NR = nanorod; TP = tetrapod; BA = butylamine; HA = hexanoic acid; tBT = tert-butylthiol; dithiol = benzene-1,3-dithiol. $^b$ AM 1.5 conditions unless otherwise stated. $^c$ Monochromatic illumination at 514 nm. $^d$ Calculated based on the information provided in the original paper. $^e$ Large size: 7.1 nm. $^f$ A ZnO layer between the active layer and the cathode was used as the optical spacer and hole-blocking layer. The efficiency was 2.7% without the ZnO layer. $^g$ Relatively small size: 8 × 13 nm. $^h$ In the form of fibrils. $^i$ Careful NC washing before pyridine treatment. $^j$ NDs:NRs = 27:63 by weight.
Metal oxides based hybrid solar cells

Solution processed!

Polymer-MetalOxide

Dye-sensitized

Dye-doped with perovskites

Mesoporous TiO$_2$
Metal oxides based hybrid solar cells
Solution processed!

Polymer-MetalOxide

Dye-sensitized

Dye-doped with perovskites

Mesoporous TiO₂
Metal oxides based hybrid solar cells

polymer - metal oxide

Poor performance: PCE ~ 0.5%

Possible explanation:
- Polymer infiltration inside the mesoporous scaffold
- Poor efficiency of charge generation at D/A interface

Improvement with interlayers chemisorbed onto TiO$_2$ surface to:
- Induce order in the polymer phase at the interface
- Mediate charge transfer process (monolayer of a standard organic acceptor molecule)

PCE ~ 1%
Metal oxides based hybrid solar cells

➢ Dye-sensitized (solid state)  PCE ~ 7%

- No exciton diffusion losses → Extended interface for charge transfer, readily available
- Dye’s charge transport properties are not involved in the process
- High surface mesoporous TiO2 ensures good light absorption from the dye monolayer

Room for improvement: [New dye with higher absorption
Charge transport in TiO2 and HTM]

Metal oxides based hybrid solar cells

- Dye-doped based on perovskites

Organometal halide perovskite

\[ \text{A} = \text{CH}_3\text{NH}_3 \]
\[ \text{B} = \text{Pb} \]
\[ \text{X} = \text{Cl, I} \]

Perovskite layer

TiO\(_2\)/Al\(_2\)O\(_3\)

HTM

PCE ~ 15 %
Record efficiency (not certified)


Solution processed from precursor ➔ Polycrystalline morphology
Metal oxides based hybrid solar cells

➢ Dye-doped based on perovskites

Very new... many things to be understood:
- charge transport: features and mobility values?
- primary photoexcitation: excitonic or not?
- role of morphology
- stability

...but

strong panchromatic absorption +
long range crystallinity (>100 nm)

Efficient migration of the species (excitons, charges)