Dye-Sensitized Solar cells: Basic Science and Commercialization

Royal Society of Edinburgh,
Meeting on zero Carbon Energy 27, May 2015
Prof. Md. K. Nazeeruddin
EPFL, Switzerland
Mdkhaja.nazeeruddin@epfl.ch
Molecular engineering of:

- Sensitizers
- Redox Mediators

Perovskite Sensitized Solar cells (PSC)

- Hole Transporting Materials for DSC and PSCs
- First commercial applications of dye sensitized solar cells
Principle of operation of dye sensitized solar cells

- Conducting glass
- TiO₂
- Dye
- Electrolyte
- Cathode
- Injection
- S*
- Maximum voltage
- Red
- Ox
- Mediator
- e⁻
- E vs NHE (V)

- hν
- S²⁻
- Prussian blue
- e⁻
Dye sensitized solar cell

Typical Dye (N3)

\[ J_{sc} : 17.73 \text{ mA/cm}^2 \]
\[ V_{oc} : 0.846 \text{ V} \]
\[ FF: 0.74 \]
\[ Eff: 11.2\% \]

JACS, 127, 16835, 2005
Dynamics of electron transfer reactions in sensitized mesoscopic solar cells
Photo-induced interfacial charge separation occurs within femtoseconds.
The DX1 dye harvests more near IR light in the 750 - 900 nm region than the black dye
Figure 2 | NATURE PHOTONICS

DX1 is greater than that of BD. This is consistent with the result of each molecular orbital being made on the basis of its composition roughly consistent with the ratio of spin-forbidden intensity (4 mm) printed on FTO substrates. Bottom: comparison with the other dyes: N719 (left), BD (centre) and DX1 (right).

The performances of DSSCs with sensitizers DX1, N719 and BD were estimated to be 27.1 (for DX1), 22.7 (for BD) and 19.4 mA cm\(^{-2}\) (for N719). These results are compared with that of the Ru atom. On the other hand, the 15N resonance observed for BD shifted by a comparatively large amount (231.5 ppm (equator-axial)).

The squared ratio between the intersystem transition and the triplet states, where the calculations were done in Supplementary Table S1, where only the larger contributions were shown (Supplementary Fig. S1). The squared ratio between the contribution of 54–66% in the internal heavy-atom effect.

Therefore, when used in a DSSC, DX1 is expected to have driving forces that are comparable with those of BD for both electron injection into the conduction band (CB) of TiO\(_2\) (shown in Supplementary Table S1, where only the larger contributions were shown) and triplet states, where the calculation may be caused by efficient non-radiative decay via strong spin–orbit coupling. Even this substantially decreased excited-state lifetime (8 ns) of DX1 is still sufficient for electron injection into the CB of TiO\(_2\).

The triplet–singlet transition and triplet–singlet transition of each molecular orbital is made on the basis of its composition 2g character composition of DX1 and BD is ≏ 4–12, and is compared with that of the Ru atom. On the other hand, the 15N resonance observed for BD shifted by a comparatively large amount (231.5 ppm (equator-axial)).

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Energy level diagram for a typical embodiment of dye sensitized solar cells.

\[ \eta_{\text{global}} = \frac{I_{\text{ph}} \cdot V_{\text{oc}} \cdot FF}{I_s} \]
Absorption spectra of $\text{Co}^{2+}/\text{Co}^{3+}$ and iodide/iodine based electrolytes (diluted 200 times in acetonitrile)
With ruthenium dyes these cobalt complexes are only effective at low light intensities due to ion pair formation leading to charge recombination and diffusion limitation of the photocurrent!
Schematic representation of the higher recombination probability of N719 with respect to the Z907 dye with cobalt electrolyte.
Synthetic scheme leading to complexes 3a and 3b

$E_{\text{LUMO}} = -1.35$, and $E_{\text{HOMO}} = 0.86$ V vs. NHE

418 (23400 M cm$^{-1}$) and 580 nm (19600 M cm$^{-1}$)
Dye | Electrolyte | $J_{sc}$ / mA cm$^{-2}$ | $V_{oc}$ / mV | FF | $\eta$ / %
--- | --- | --- | --- | --- | ---
3a | cobalt | 8.3 | 714 | 0.79 | 4.7
3b | cobalt | 13.2 | 837 | 0.78 | 8.6
3b | iodine | 16.3 | 715 | 0.75 | 8.7
Electrolyte:

Co^{2+} = 0.22M, Co^{3+} = 0.055M,
LiClO_{4} = 0.1M, tbp = 0.2M in ACN

Dye Solution:

0.1mM Y123 in Tert-Butanol / Acetonitrile 1:1 v/v

Scattering layer: 5\mu m 400nm TiO_{2}

Transparent layer: 5\mu m of 20nm particle, 32nm pore size TiO_{2}

Co(III(bipy)₃)/Co(II)(bipy)₃ with Y123 dye

<table>
<thead>
<tr>
<th>V(oc) (mV)</th>
<th>J(sc) (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>889</td>
<td>16.4</td>
<td>0.69</td>
<td>10.02</td>
</tr>
</tbody>
</table>

Electrochemical characterization of Co-complexes FK107

Redox potential: 0.86 V vs. NHE*

* Fc/Fc⁺ was used as internal standard and +0.64 V

<table>
<thead>
<tr>
<th></th>
<th>Oxidation (Co II→III)</th>
<th>Reduction (Co I→II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FK 107 (Co(bipy-pz)₂)³⁺</td>
<td>0.22</td>
<td>-1.20</td>
</tr>
<tr>
<td>FK102 (Co(py-pz)₃)³⁺</td>
<td>0.32</td>
<td>-1.45</td>
</tr>
</tbody>
</table>

Nature Communications (2012), 3(Jan.), 1655
5.6 µm thin transparent nanoporous TiO₂ (anatase) film
Y123 sensitizer

Nature Communications (2012), 3(Jan.), 1655
DSCs consisting of a 5.6 μm thin transparent nanoporous TiO₂ (anatase) film, the Y123 sensitizer.

The I⁻/I₃⁻ system resulted in 13.01 mA cm⁻² $J_{sc}$, 754 mV $V_{oc}$, and 0.67 FF, yielding conversion efficiency of 6.57%.

The $[\text{Co(bpy-pz)}_{2}]^{2+/3+}$ redox system gave $J_{sc}$ 12.54 mA cm⁻², $V_{oc}$ 1018 mV, FF of 0.69, yielding PCE (η) 8.87%.
Pt free Counter Electrode: PEDOT, PProDOT

Nature Communications (2012), 3, 1655
Photovoltaic characteristics of DSC based on $[\text{Co(bpy-pz)}_2]^{2+ / 3+}$ system employing the double layered $\text{TiO}_2$ (5.6 + 5 $\mu$m) and Pt counter electrode (A), Employing the double layered $\text{TiO}_2$ (4.0 + 4.5 $\mu$m) and the PProDOT (B)

<table>
<thead>
<tr>
<th>Pt counter electrode</th>
<th>PProDOT counter electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{sc}$ (mA cm$^{-1}$) = 13.45</td>
<td>13.06</td>
</tr>
<tr>
<td>$V_{oc}$ (mV) = 1015</td>
<td>998</td>
</tr>
<tr>
<td>$FF$ (%) = 69.7</td>
<td>77</td>
</tr>
<tr>
<td>$\eta$ (%) = 9.52</td>
<td>10.08</td>
</tr>
</tbody>
</table>

Nature Communications (2012), 3, 1655
Building-in More Color

Donor -- *Pi-Bridge* -- Acceptor

**D-pi-A**

- Donor
- Pi-Bridge
- Acceptor
- TiO$_2$

**Intrinsic directionality**
**Tunable push-pull**

Donor -- *Chromophore* -- Anchor

**D-C-A**

- Donor
- Chromophore
- Anchor
- TiO$_2$

**“mild” acceptor**

**Guaranteed color**
**Stretched exci**
**Synergistic design**
Colour of DPP07, 13, 14, 15, and 17 (from left to right). (a) DPP dyes are dissolved in THF solution (0.025 mM) and are adsorbed on 3 mm thick TiO2 film. Chemistry of Materials (2013), 25(13), 2642-2648
<table>
<thead>
<tr>
<th></th>
<th>Jsc (mA/cm²)</th>
<th>Voc (mV)</th>
<th>ff</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPP20</td>
<td>17.3</td>
<td>776</td>
<td>0.75</td>
<td>10.05</td>
</tr>
<tr>
<td>DPP20 + NT35</td>
<td>17.9</td>
<td>794</td>
<td>0.73</td>
<td>10.38</td>
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On 4+4 um double layer TiO₂ film and the use of the cobalt electrolyte
Porphyrin-Sensitized Solar Cells with Cobalt (II/III)–Based Redox Electrolyte Exceed 12 Percent Efficiency

Aswani Yella,¹ Hsuan-Wei Lee,² Hoi Nok Tsao,¹ Chenyi Yi,¹ Aravind Kumar Chandiran,¹ Md.Khaja Nazeeruddin,¹ Eric Wei-Guang Diau,³ Chen-Yu Yeh,² Shaik M Zakeeruddin,¹ Michael Grätzel¹*
Subtle changes in porphyrine structure produce large effect on PV performance.