Direction for development of near infrared dyes for dye-sensitized solar cells from the view point of electron injection and charge recombination

Shuzi Hayase

Kyushu Institute of Technology (National Institute)
Kitakyushu, Fukuoka, Japan, 808-0196, Japan
Collaborator

Kyushu Institute of Technology
Shyam S. Pandey
Yuhei Ogomi

Nippon Steel & Sumikin Chemical Co., LTD
Yoshihiro Yamaguchi

Universidad de Castilla-La Mancha
Abderrazzak Douhal
Boiko Cohen
Marcin Aiolek
Gustavo de Miguel
Michal Zitnan,
Maria Jose Marchena Barriento,
Sofia Kapetanaki
Dye sensitized solar cells (DSCs)


Electrolyte $I^-/I_3^-$
(Acetonitrile, ethylene carbonate, molten salts, etc.)

TiO$_2$ layer: 10-20 $\mu$m
Electrolyte layer: 30 $\mu$m
Certified efficiency AM1.5G, 1000W/m²

- C-Si: 25.0%
- Poly-Si: 20.4%
- CIGS: 19.6%
- CdTe: 16.7%
- a-Si: 11.9%
- OPV: 10.1%
- Organic PV: 10.7%

Spectrum matching for DSC to sun light spectrum (AM1.5)

Increase in Voc
Increase in Jsc (New dye, or tandem, hybrid)

<table>
<thead>
<tr>
<th>Current Density (mA cm⁻²)</th>
<th>Percentage Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-26</td>
<td>14-15%</td>
</tr>
<tr>
<td>32</td>
<td>18%</td>
</tr>
<tr>
<td>36</td>
<td>20%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Current Density (mA cm⁻²)</th>
<th>Percentage Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR dye</td>
<td></td>
</tr>
</tbody>
</table>

- **Ru dye**
- **IR dye**

- FF: 0.75
- Voc: 0.75

Graph showing the spectral distribution with Ru dye and IR dye.
Efficiency expectation

IPCE 80%, FF 0.75
Cocktail dyes

![Graph showing the IPCE (incident photoelectric conversion efficiency) spectra for different dyes across various wavelengths. The graph compares N-719, a black dye, a conventional Ru dye, and new NIR dyes to be developed. The x-axis represents wavelength (nm), and the y-axis represents IPCE.]
Requirement for development of Near Infrared Dye

How to decrease $\Delta G_1$ and $\Delta G_2$ with maintaining fast electron shift

Collaboration of solar cell researchers with photo-physics researchers
Collaboration of Japan side with Spain side

Douhal group (Time resolved study)
- Time resolved study
- Analyses of electron injection and dye regeneration

Hayase group (Solar cell-based research)
- Molecular orbital calculation
- Dye syntheses
- Solar cell performance evaluation
- Fundamental analyses on solar cells

Samples
- Substrates
- Dynamics

Extraction of items determining solar cell efficiency
Propose high efficiency dyes
Femto-second Transient Absorption: SQ-41

\[ f(x) = A \exp\left(-\frac{t}{\tau}\right)^\beta \]

Electrolyte | Life-time (ps)
---|---
I | 6.7
II | 11.1
III | 4.9
No | 2.5

\[ SQ^* (S_1) + TiO_2 \rightarrow SQ^{\bullet^+} + TiO_2 (e^-) \]
Research Collaboration

✓ Research discussions: 5 times
   March 2010 (Spain), May 2011 (Spain), Aug. 2011 (Japan), Sep. 2011 (Spain), June 2012 (Sweden)

✓ Dr. Gustavo de Miguel visited us in Japan and joined the research in Aug. 2011.

✓ Provided 15 dyes and 15 substrates (encapsulated) to Douhal Lab.
Development of near IR dyes for combination with TiO$_2$ (~900 nm)

- ✔ HOMO-LUMO energy level adjustment
- ✔ LUMO orbital shape
- ✔ Electron injection energy barrier
- ✔ Excitation life time
- ✔ Molecular orbital calculation
- ✔ Dye syntheses tech.
- ✔ Cell structure and cell analyses
- ✔ Time resolved spectroscopy
Simulation results of molecular orbital on organic dye
Model dyes: Sharp absorption spectra

Side chain effect

\[
\begin{align*}
\text{HOOC} & \quad \text{SQ dyes} & \quad \text{COOH} \\
& & \\
N^+ & \quad \text{R} & \quad \text{R} \\
& & \\
& & \\
O & \quad \text{R} & \quad \text{R} \\
& & \\
& & \\
O^- & \quad \text{R} & \quad \text{R} \\
& & \\
& & \\
& & \\
\end{align*}
\]
Designing of molecular structures after MO calculation

SQD-2 (alkyl chain=2)  SQD-4 (alkyl chain=4)  SQD-8 (alkyl chain=8)  SQD-12 (alkyl chain=12)  SQD-18 (alkyl chain=18)

SQD-0 (alkyl chain=0)  SQD-4F3
HOMO-LUMO level of synthesized dyes

HOMO-LUMO level can be controlled within 0.6 eV by varying substituents

Introduction of F alkll decreases HOMO and LUMO
Efficiency vs. Alkyl chain length

Efficiency [%] vs. Alkyl Chain Length

- Efficiency increases as the alkyl chain length increases.
- The data points show a trend of rising efficiency with increasing chain length.
Adsorption scheme for SQ dyes

SQ-2 (alkyl chain=2)  SQ-4 (alkyl chain=4)  SQ-8 (alkyl chain=8)  SQ-12 (alkyl chain=12)  SQ-18 (alkyl chain=18)
Main structure responsible for near IR dyes
Dyes with extended conjugation

SQ-8

SQ-27

(SQD2)

SQ-16

SQ-31

SQ-70

Chemical Formula: C_{36}H_{40}N_{2}O_{4}
Exact Mass: 564.2988

2012/3/16
Electronic spectra
Energy Diagram

Vacuum level [eV]

Conduction band

TiO₂  Model SQ dyes

-7.3  -6.3  -5.3  -4.3  -3.3

HOMO  LUMO  HOMO  LUMO  HOMO  LUMO

I⁻/I₃⁻  Redox potential
One of results of collaboration research
1. Chain length ----- SQ-2 and SQ-4
2. Nature of substituents----SQ-4 and SQ-26
3. Molecular Asymmetry--------- SQ-26 and SQ-41
Electronic Absorption Spectra

\[ \varepsilon = 2-3 \times 10^5 \text{ dm}^3\text{.mole}^{-1}\text{.cm}^{-1} \]
Energy Band Diagram

LUMO change: Electron injection
HOMO change: Dye generation
Anchor group:
Substitution effects:
Photovoltaic Characteristics

Photocurrent Action Spectra

Wavelength (nm)

IPCE

SQ-2
SQ-4
SQ-26
SQ-41

SQ 2
SQ 26
SQ 4
SQ 41
Time-resolved techniques

Femtosecond Transient Absorption Spectroscopy
Nanosecond Flash Photolysis

Experimental Conditions:
- SQ-dyes adsorbed on TiO$_2$
- SQ-dyes adsorbed on ZrO$_2$
  
  To determine the electron injection efficiency!

- Time resolved investigations in the presence of electrolyte
- Time-resolved investigations in the absence of electrolyte
  
  To determine the Dye Regeneration efficiency!
Electron injection
Electron Injection (②)

Relationship between $\Delta G$ and injection rate constant

No apparent relation between $\Delta G_1$ and injection rate constant. Electron injection efficiency is governed by factors other than $\Delta G_1$. 
Electron Injection (②)

Relationship between ΔG and injection rate constant

High electron injection can be realized with lower ΔG1 by using dyes with F atoms.
Dye regeneration
Dye generation (6)

Relationship between $\Delta G_2$ and dye regeneration

- High dye generation with Low $\Delta G_2$
- Better for high efficiency

Common trend

$\Delta G_2$

Gap (redox-HOMO)/eV

Regeneration efficiency

SQ Dye

SQ 2

SQ 4

SQ 41

SQ 26

Better for high efficiency
Possible explanation for high efficiency dye generation with low $\Delta G_2$
\[ R_{rel}(I_3/I) \]

\[ V_{oc} \text{ (V)} \]

- \( I_3^- \) to \( e^- \) transfer
- Dye
- \( TiO_2 \)
- Porous \( TiO_2 \) sheet

<table>
<thead>
<tr>
<th>R1 = R2</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl</td>
<td>SQ4</td>
</tr>
<tr>
<td>Dodecyl</td>
<td>SQ12</td>
</tr>
<tr>
<td>Octadecyl</td>
<td>SQ18</td>
</tr>
<tr>
<td>Trifluorobutyl</td>
<td>SQ4F6</td>
</tr>
<tr>
<td>Methoxybutyl</td>
<td>SQ4O2</td>
</tr>
<tr>
<td>Ethylbutanoate</td>
<td>SQ4O4</td>
</tr>
</tbody>
</table>

Explanation on IPCE (④)

IPCE can be explained by product of electron injection efficiency and regeneration efficiency.

Ei eff: Electron injection efficiency: ②/②+③
Reg eff: Regeneration efficiency: ⑥/④+⑥
Proposed structure realizing high efficiency dye generation with low $\Delta G_2$ and high electron injection with low $\Delta G_1$
Conclusions

- 6 model Squaraine dyes were synthesized to investigate the role of alkyl chain length, nature of substituents and molecular asymmetry on the photovoltaic performance.
- Electron injection and dye regeneration are not always governed by energy gap ($\triangle G$) and influenced by substituents and molecular structure. This suggests that high electron injection with low $\triangle G$ becomes possible.
- Creation of molecular asymmetry and introduction of longer alkyl chain leads to facile electron injection.
- Introduction of electron withdrawing Fluor-alkyl substituent leads to facile dye regeneration.
- Order of IPCE value was explained by the product of charge injection efficiency and dye regeneration efficiency.
List of Publications in Academic Journals:


[13] Effect of anchoring groups on photosensitization behavior in unsymmetrical squaraine dyes’ Gururaj M. Shivashimpi¹, Shyam S. Pandey¹, Rie Watanabe¹, Naotaka Fujikawa¹, Yuhei Ogomi¹, Yoshihiro Yamaguchi², Shuzi Hayase; Synthetic Metals (Submitted).

[14] Real-Time Photodynamics of Squaraine-Based DSSCs with Iodide and Cobalt Electrolytes; Maria Jose; de Miguel, Gustavo; Cohen, Boiko; Hayase, Shuzi; Pandey, Shyam; Douhal, Abderrazzak; Journal of Physical Chemistry-C (Submitted).
Thank you for your attention!