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

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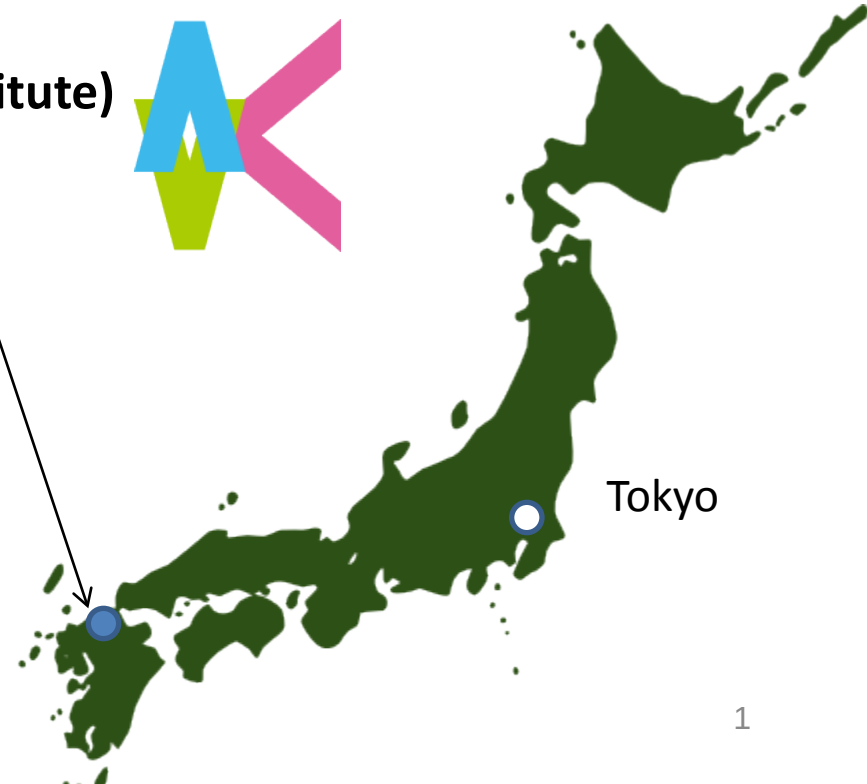

Collaborator

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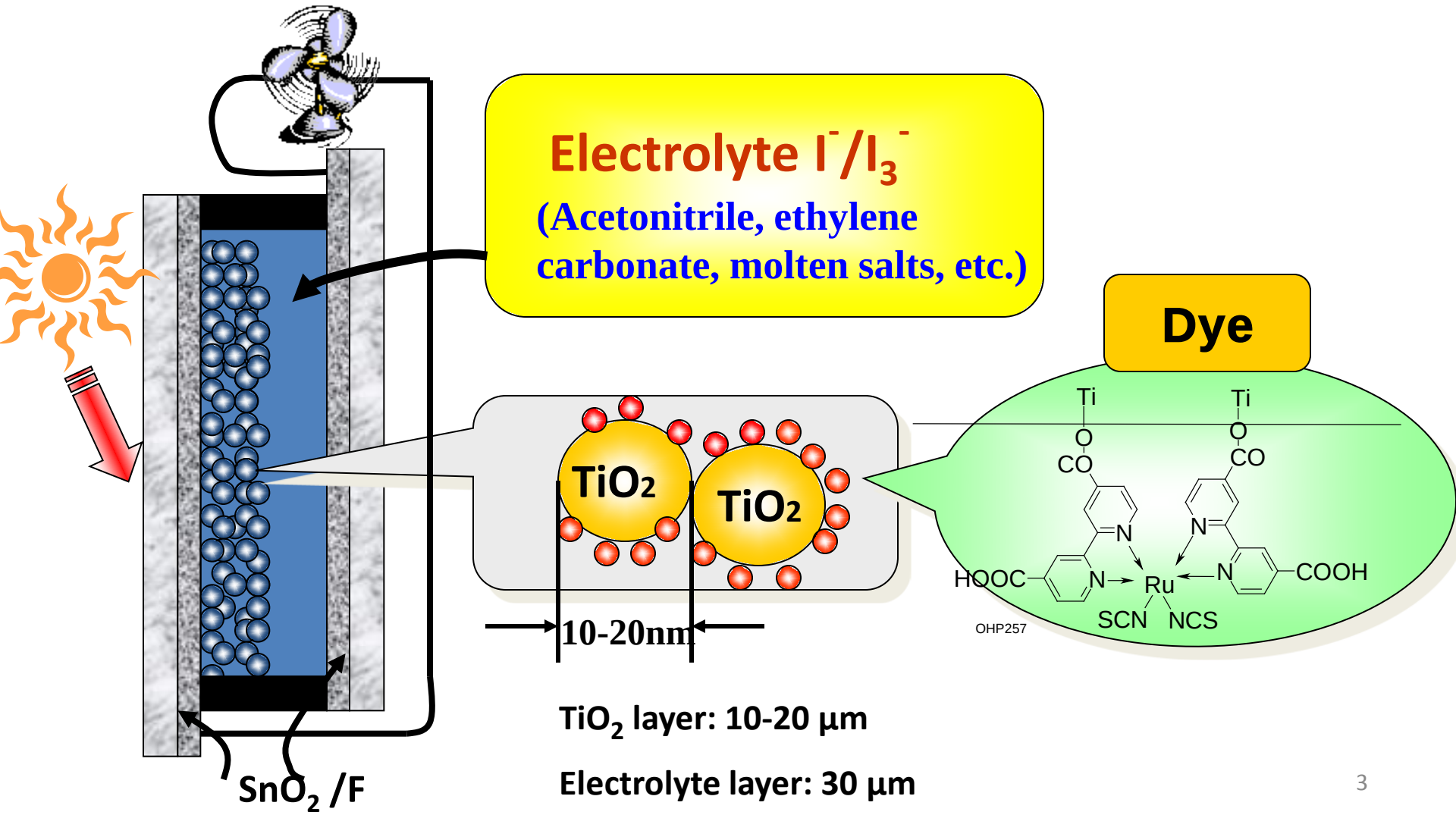
Gustovo de Miguel
Michal Zitnan,
Maria Jose Marchena Barriento,
Sofia Kapetanaki

Dye sensitized solar cells (DSCs)

B. O'Regan and M. Graetzel *Nature*, 1991, *353*, 737

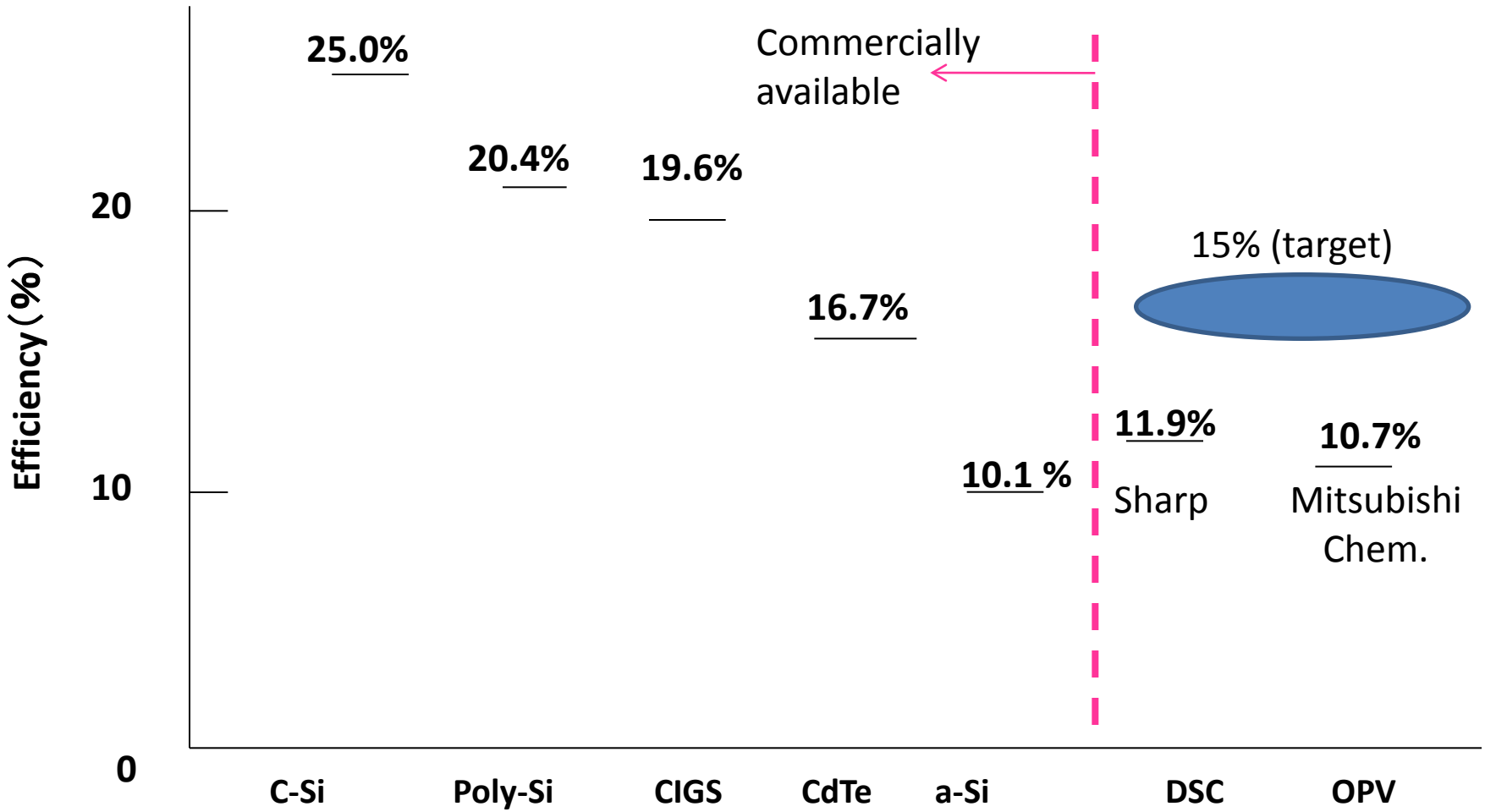


TiO_2 layer: 10-20 µm

Electrolyte layer: 30 µm

Certified efficiency

AM1.5G ,1000W/m^2



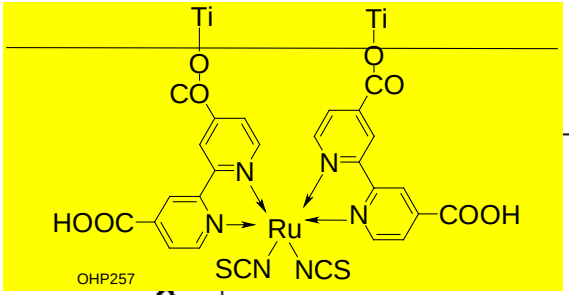
CIGS: CuInGaS(Se)

DSC:Dye-sensitized solar cell

OPV: Organic thin film PV

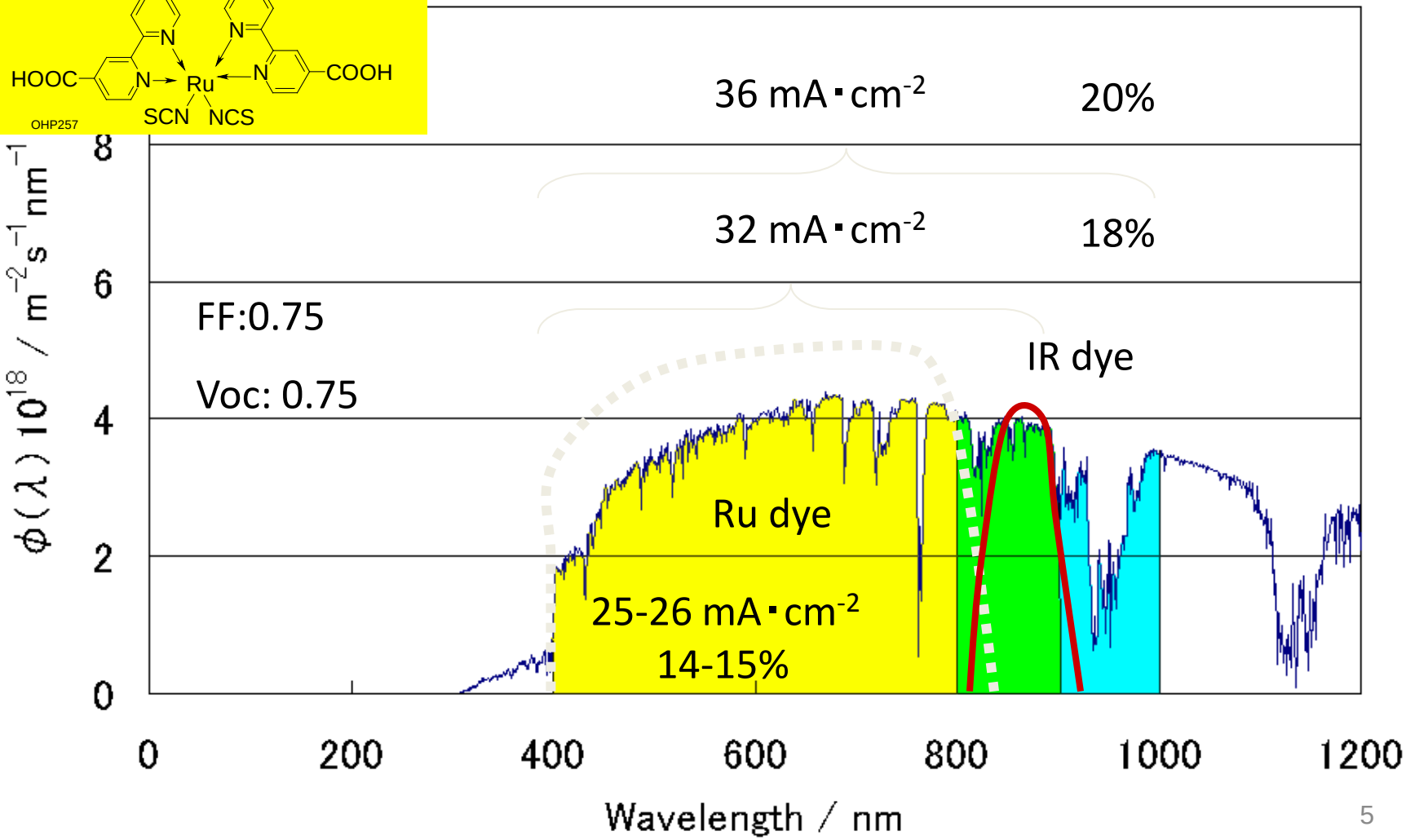
M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, Prog. Photovolt: Res. Appl. 2013; 21:1-11

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



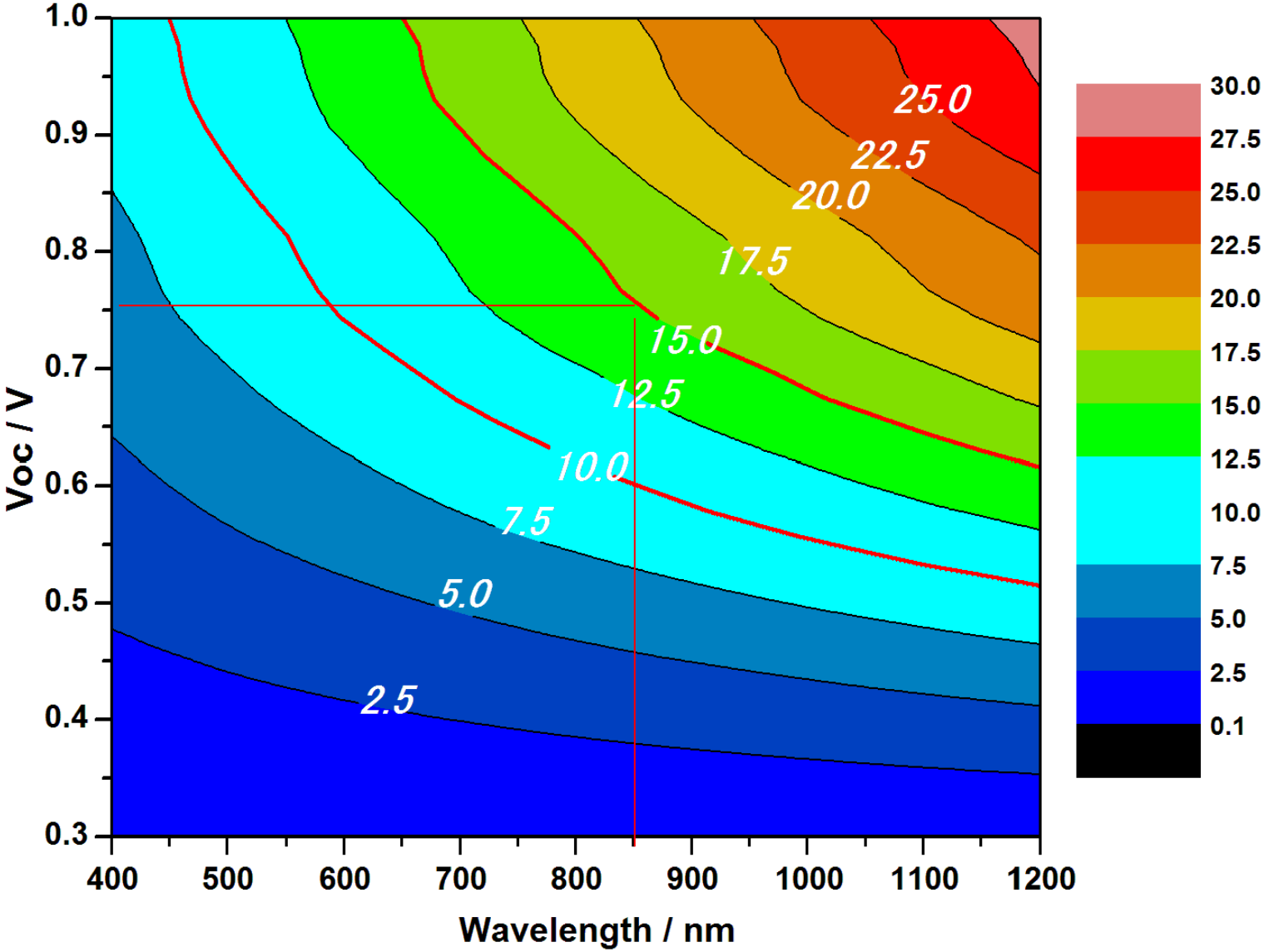
Increase in Voc

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

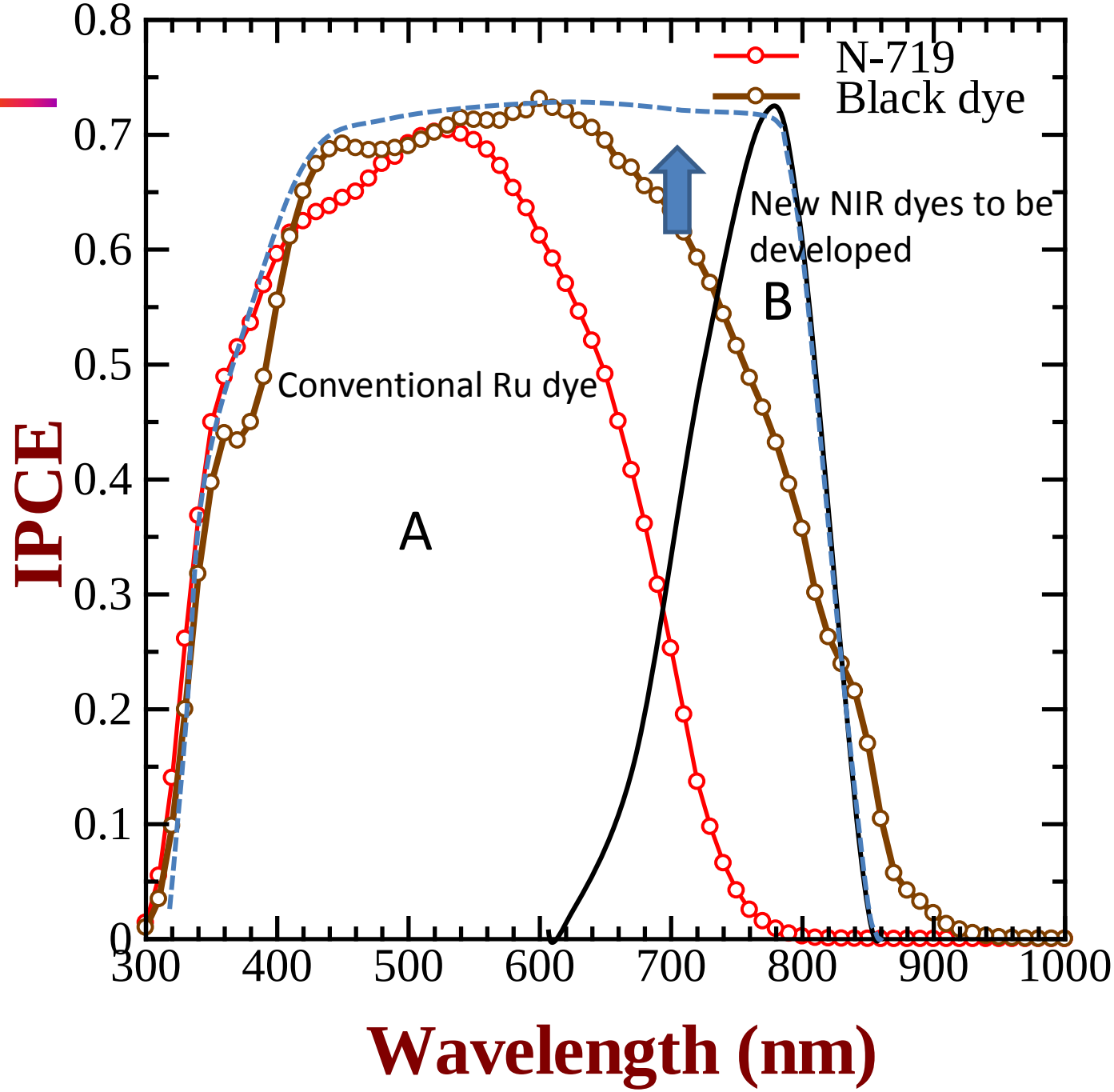


Efficiency expectation

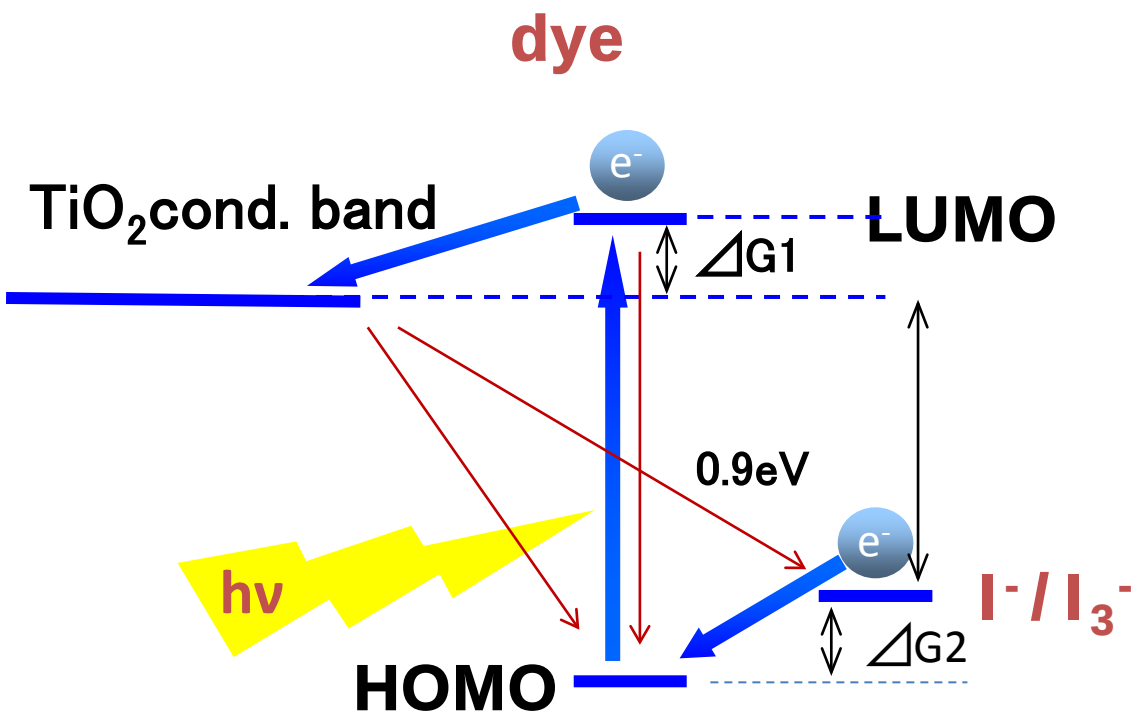
IPCE 80%, FF 0.75



Cocktail dyes



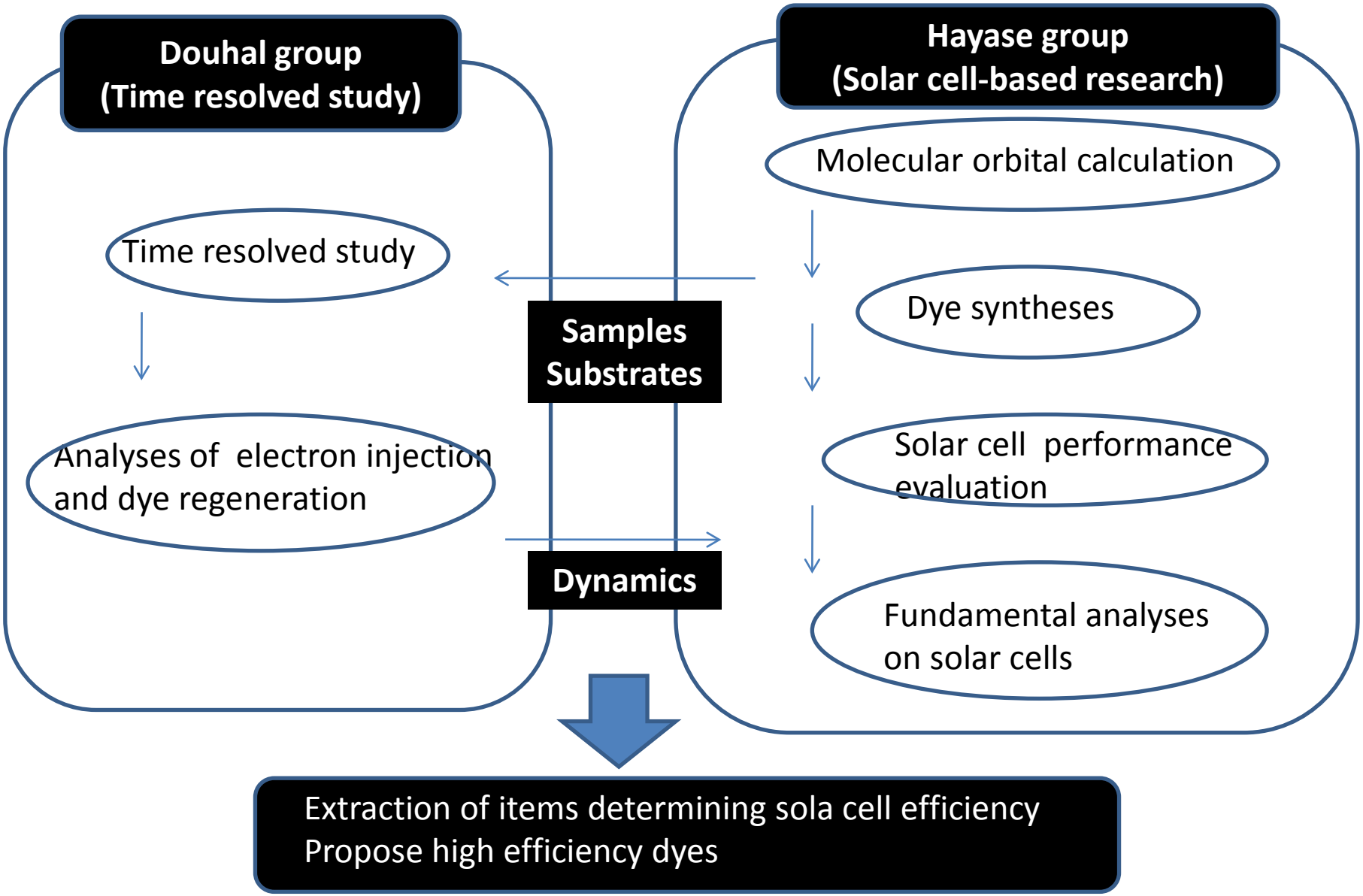
Requirement for development of Near Infrared Dye



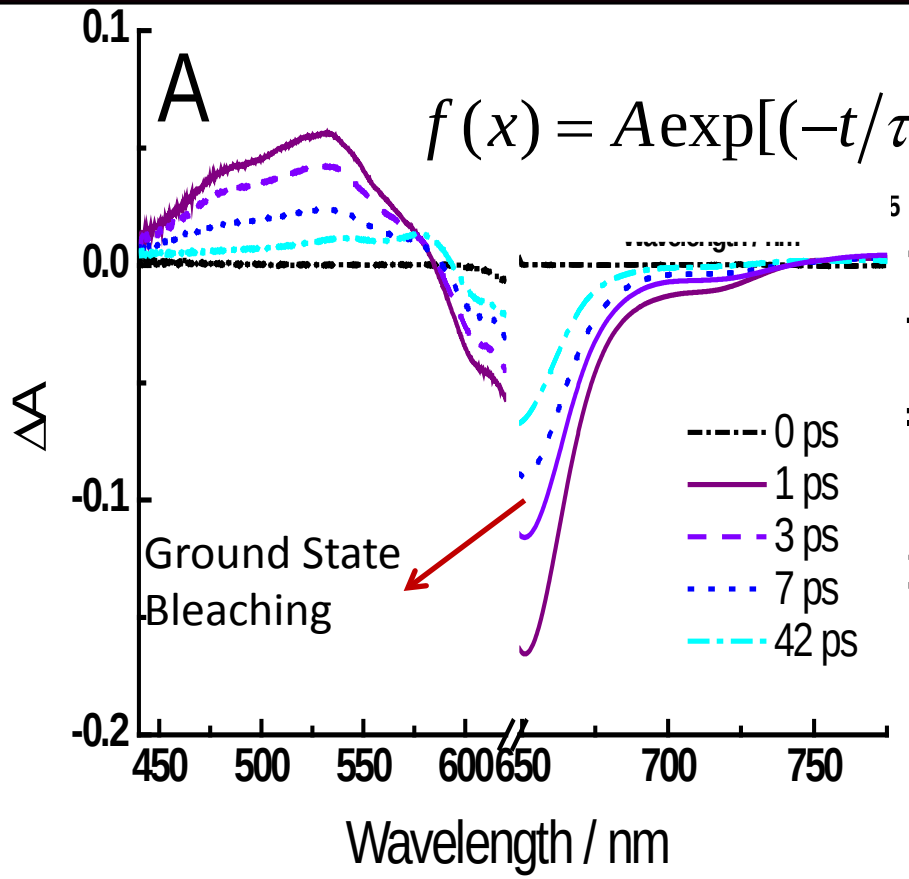
How to decrease ⊿G1 and ⊿G2 with maintaining fast electron shift

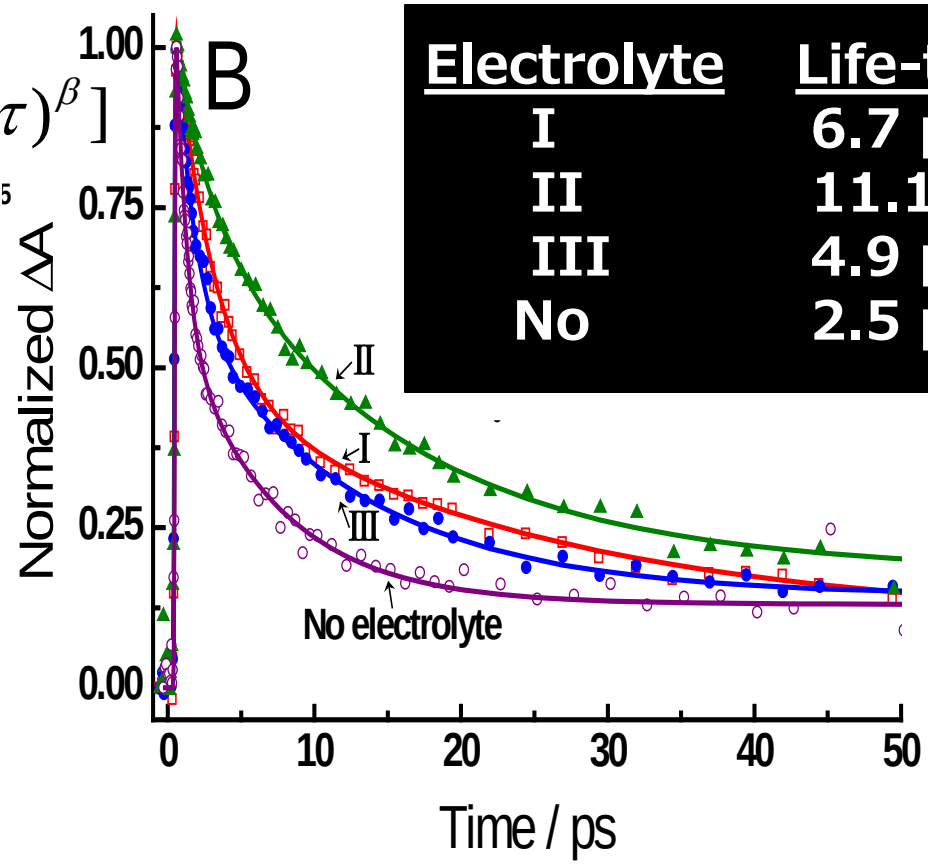
Collaboration of solar cell researchers with photo-physics researchers

Collaboration of Japan side with Spain side



Femto-second Transient Absorption: SQ-41





Electrolyte	Life-ti
I	6.7 ps
II	11.1 p
III	4.9 ps
No	2.5 ps

Change in spectral shape at longer delay.

Signal beyond 2 ns.

SQ radical cation formation;

Electron injection

$$SQ^*(S_1) + TiO_2 \rightarrow SQ^{\bullet +} + TiO_2\ (e^-)$$

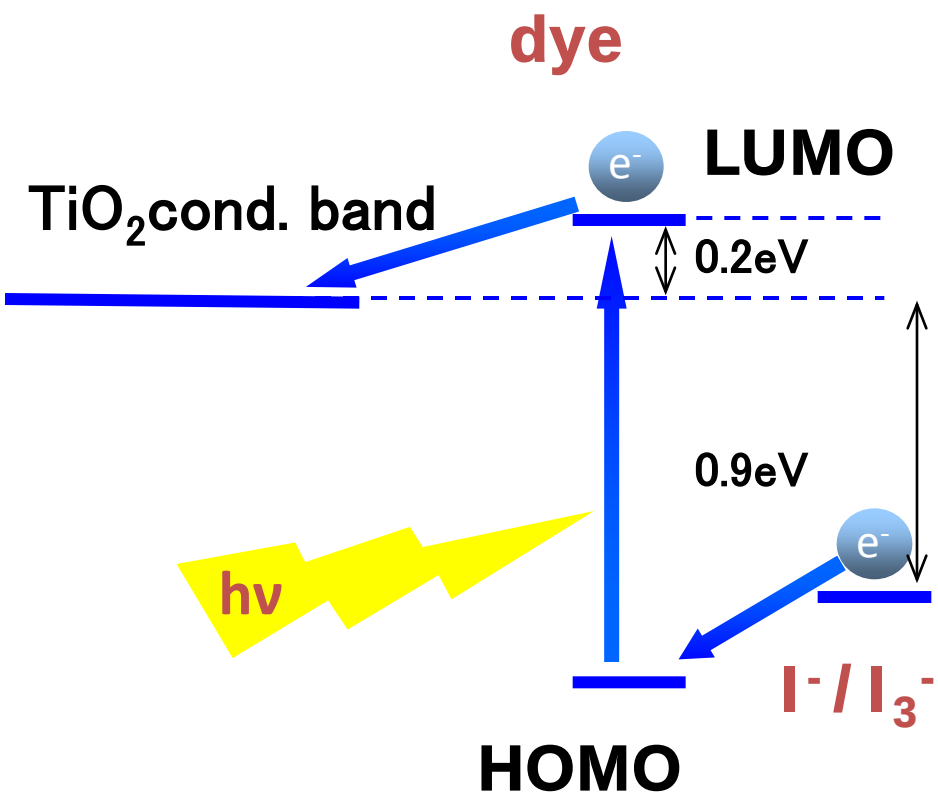
Research Collaboration

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

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

✓ **Provided 15 dyes and 15 substrates (encapsulated) to Douhal Lab.**

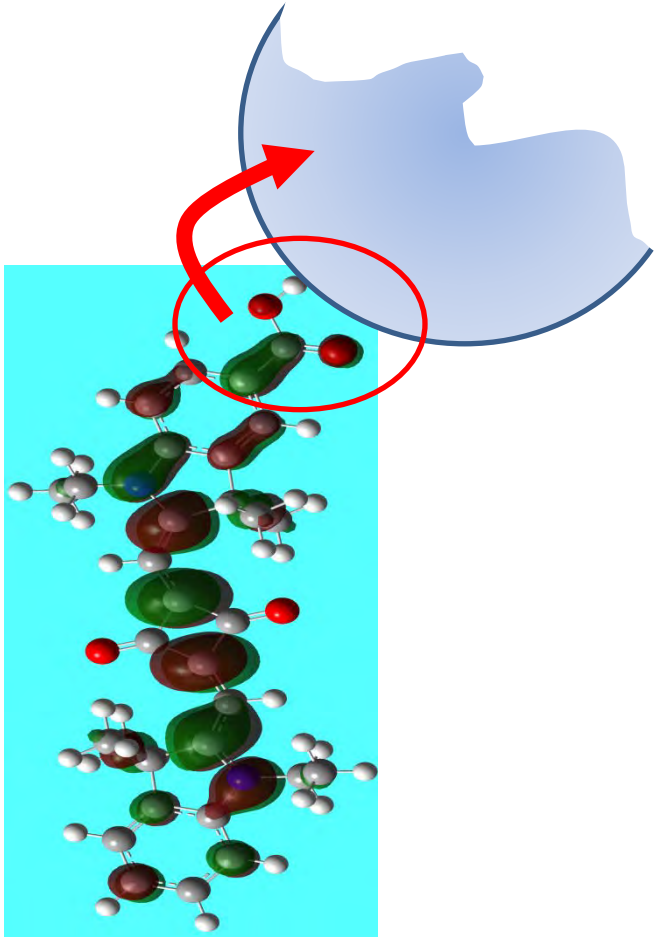
Development of near IR dyes for combination with TiO_2 (~900 nm)



- ✔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

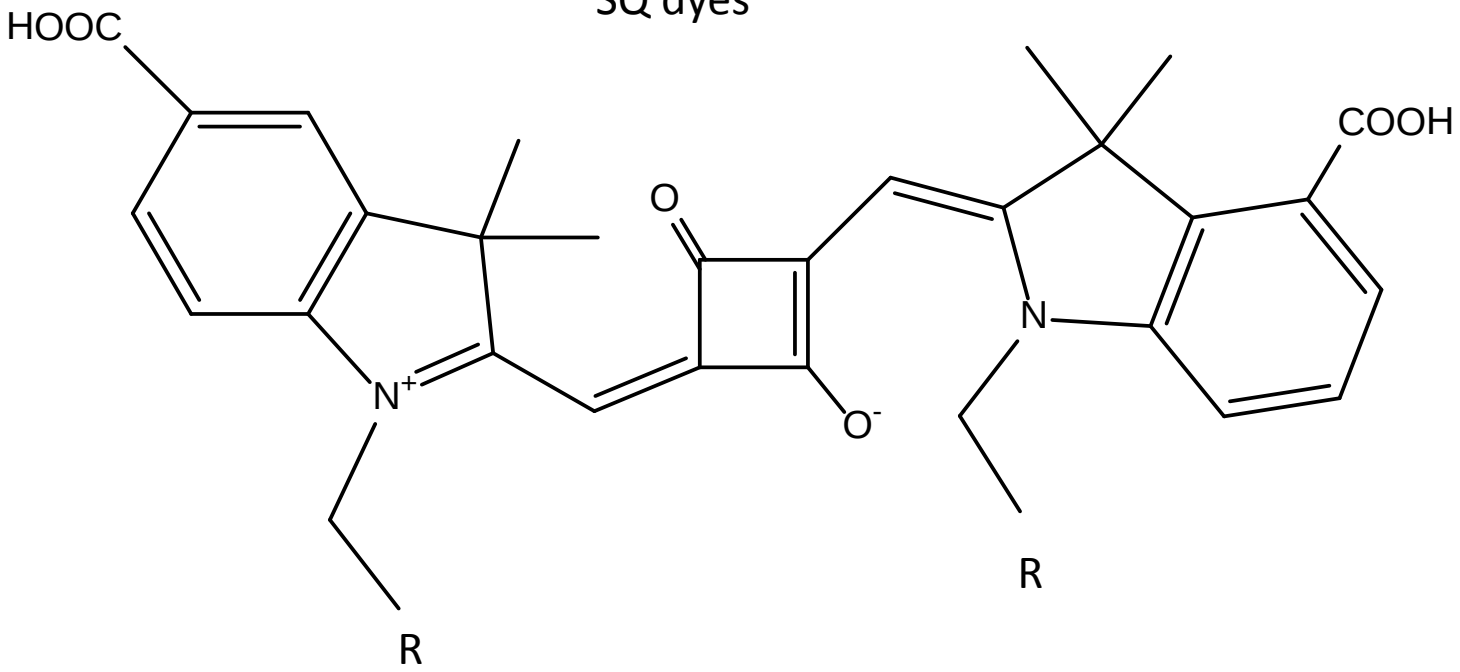
Simulation results of molecular orbital on organic dye



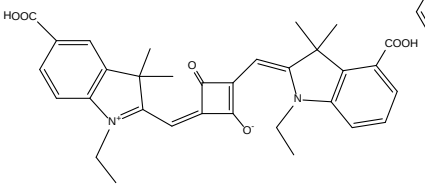
Model dyes: Sharp absorption spectra

Side chain effect

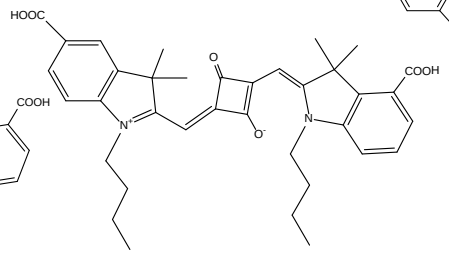
SQ dyes



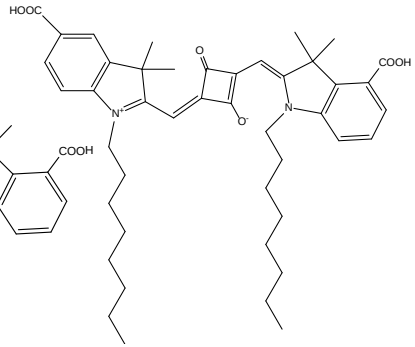
Designing of molecular structures after MO calculation



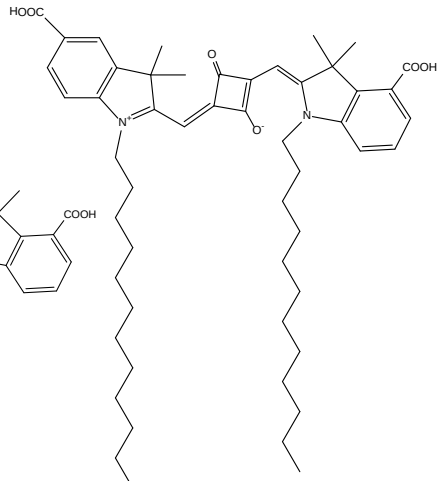
SQD-2
(alkyl chain=2)



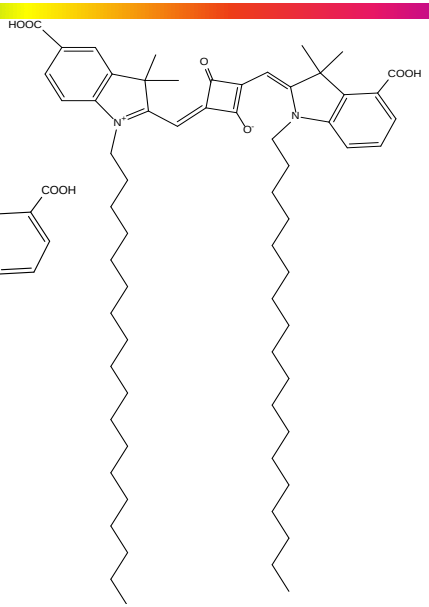
SQD-4
(alkyl chain=4)



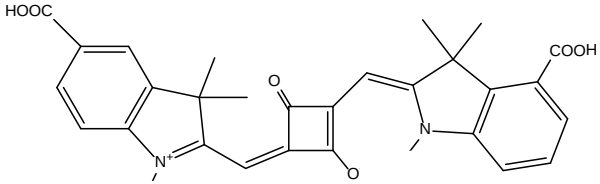
SQD-8
(alkyl chain=8)



SQD-12
(alkyl chain=12)

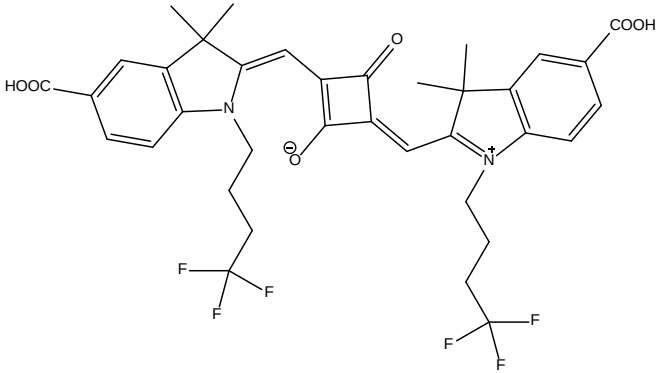


SQD-18
(alkyl chain=18)

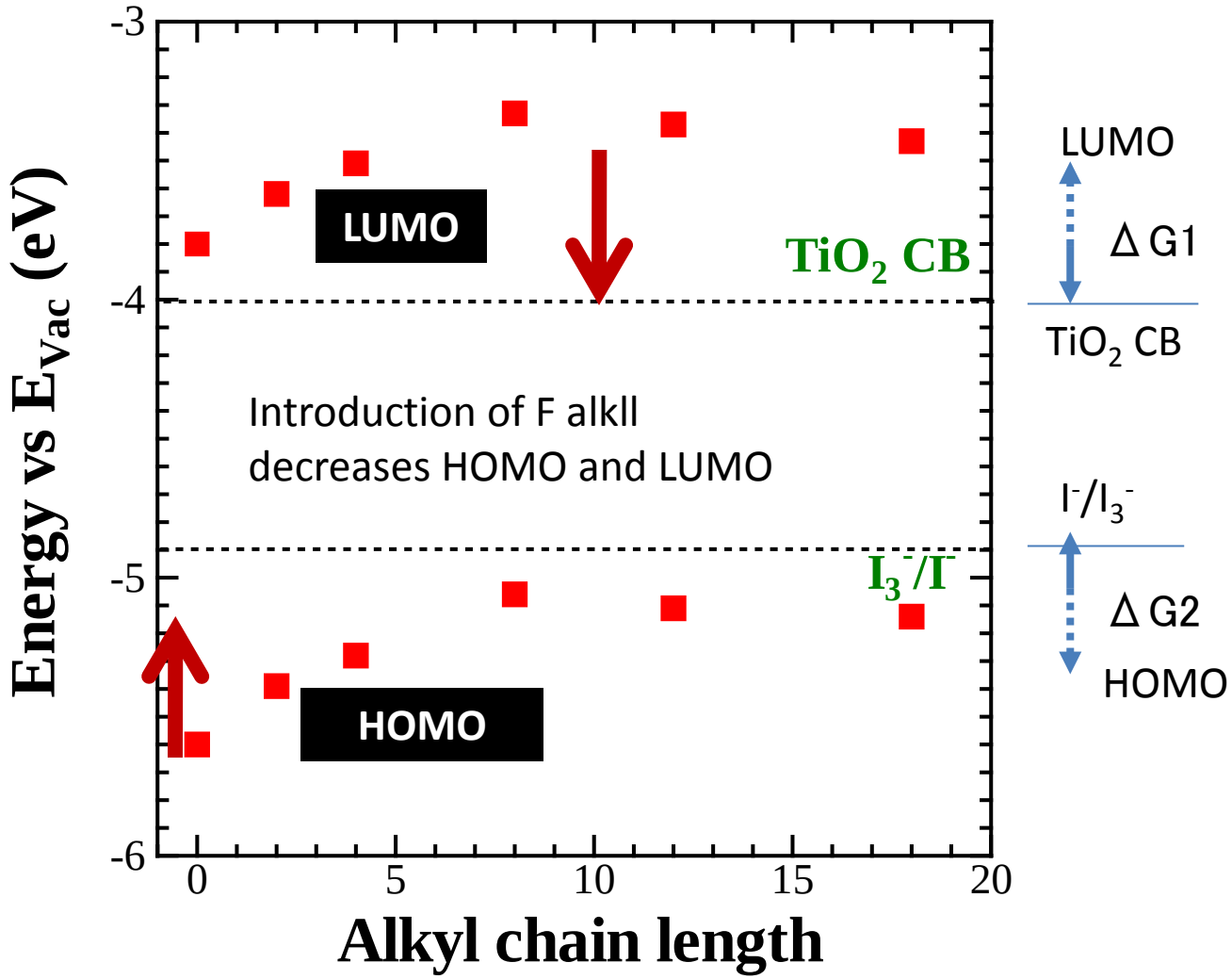


SQD-0
(alkyl chain=0)

SQD-4F3

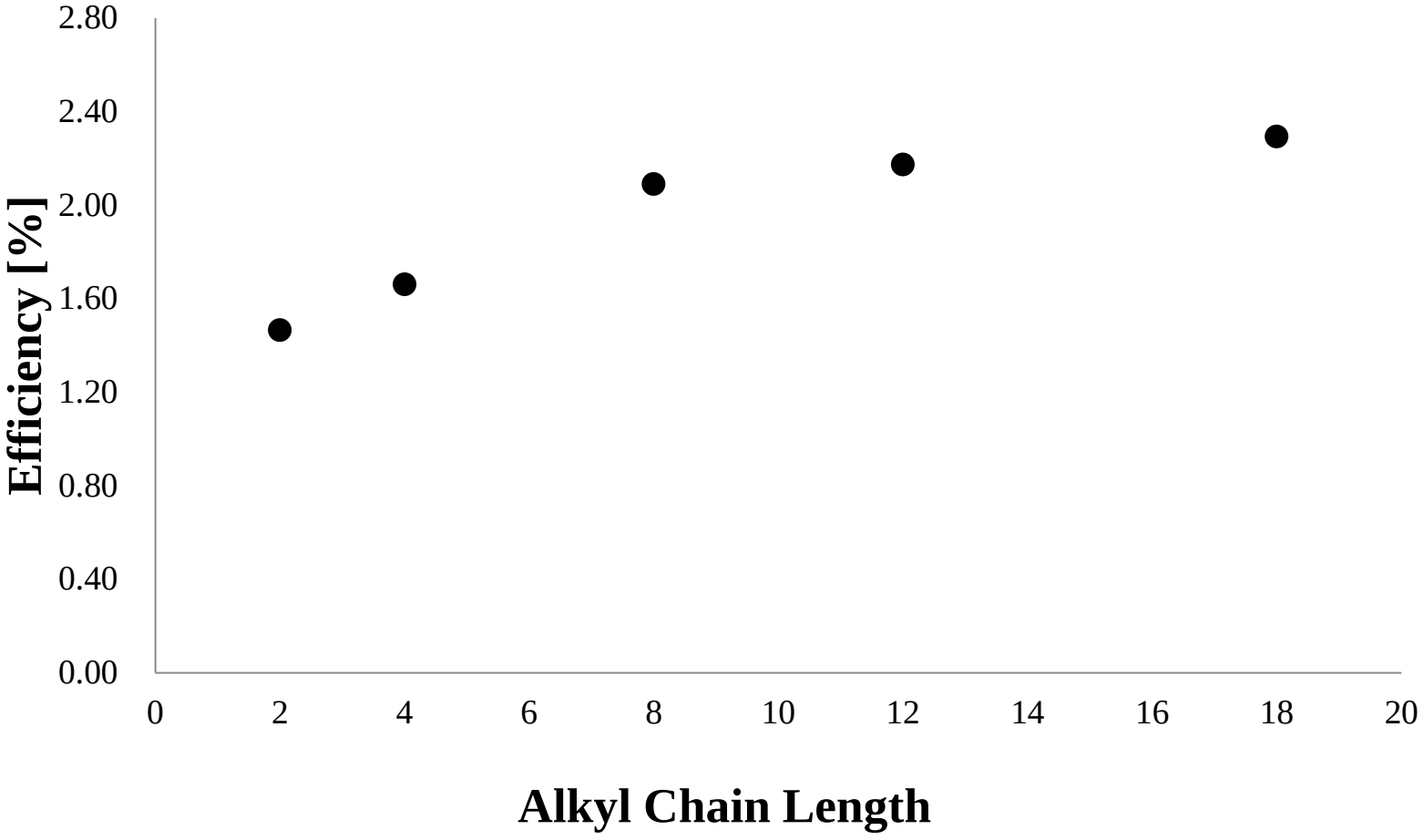


HOMO-LUMO level of synthesized dyes

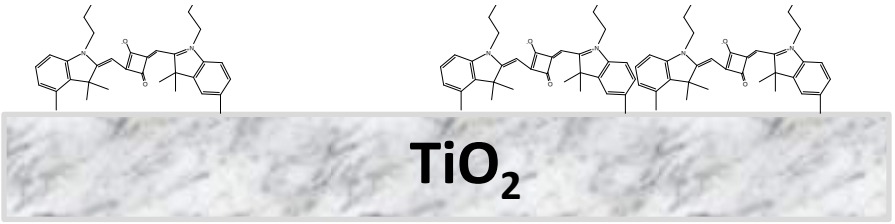


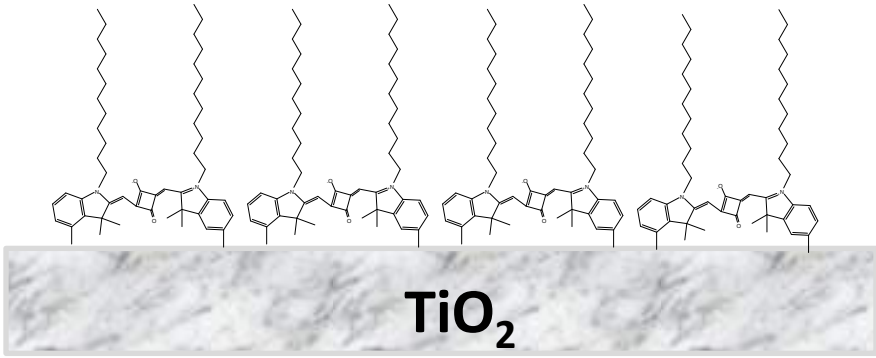
HOMO-LUMO level can be controlled within 0.6 eV by varying substituents

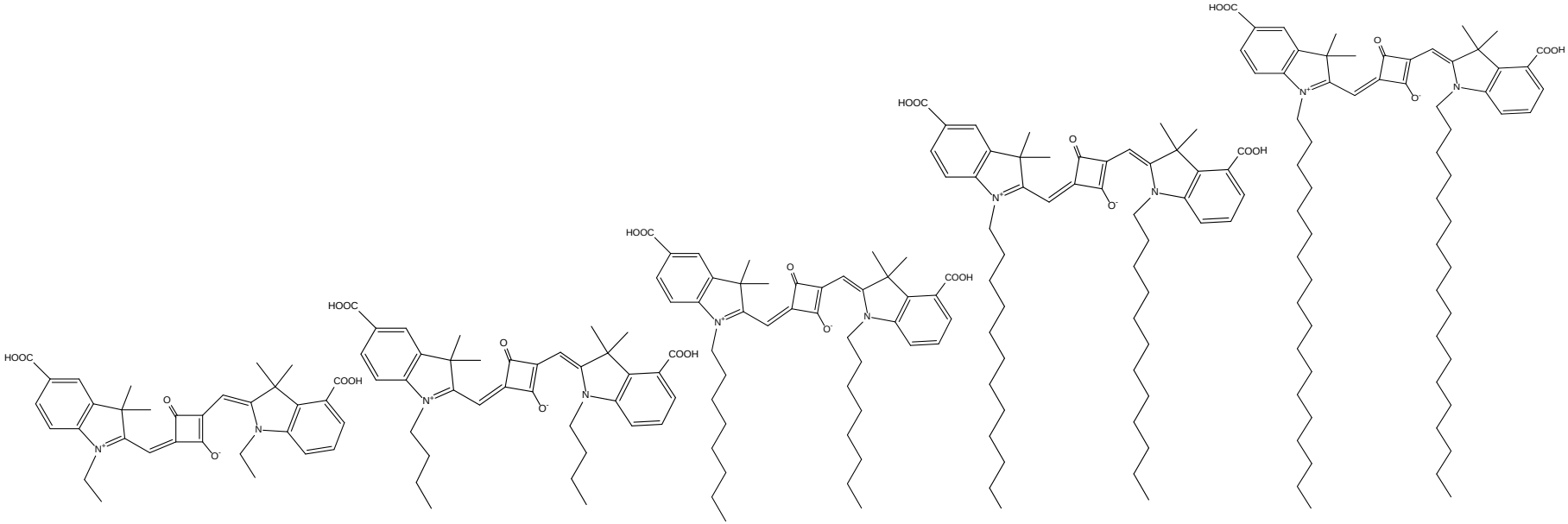
Efficiency vs. Alkyl chain length



Adsorption scheme for SQ dyes



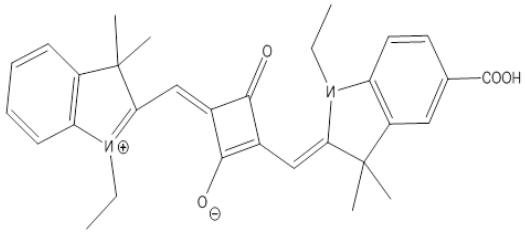




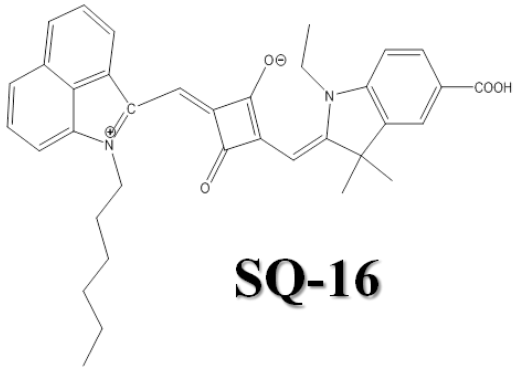
SQ-2 (alkyl chain=2) SQ-4 (alkyl chain=4) SQ-8 (alkyl chain=8) SQ-12 (alkyl chain=12) SQ-18 (alkyl chain=18)

Main structure responsible for near IR dyes

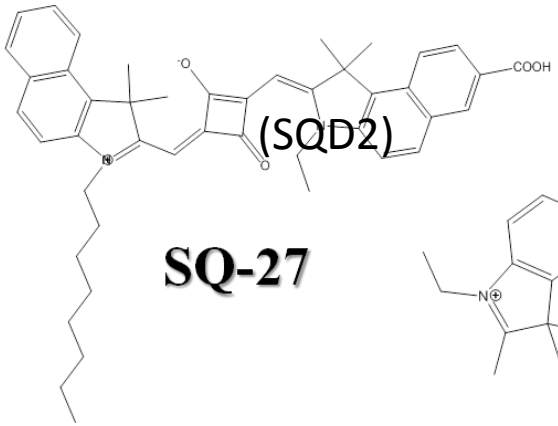
Dyes with extended conjugation



SQ-8

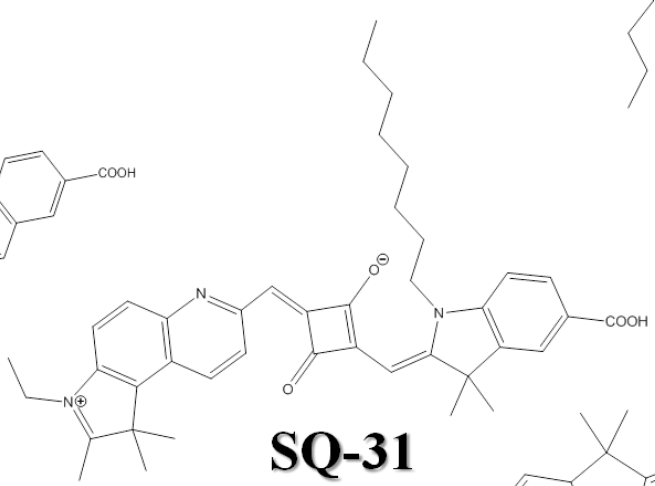


SQ-16

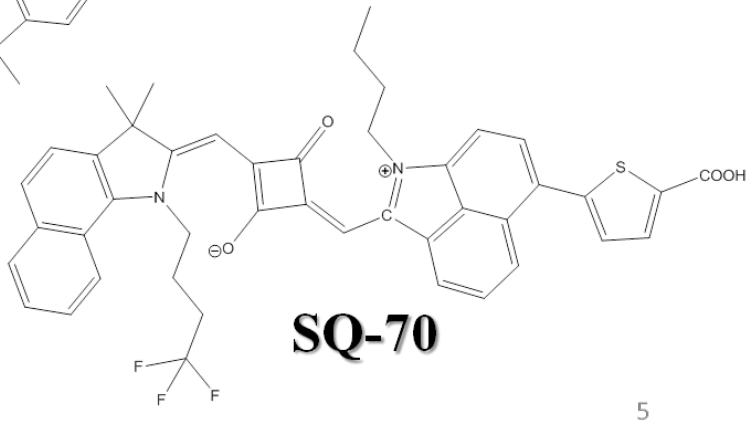


(SQD2)

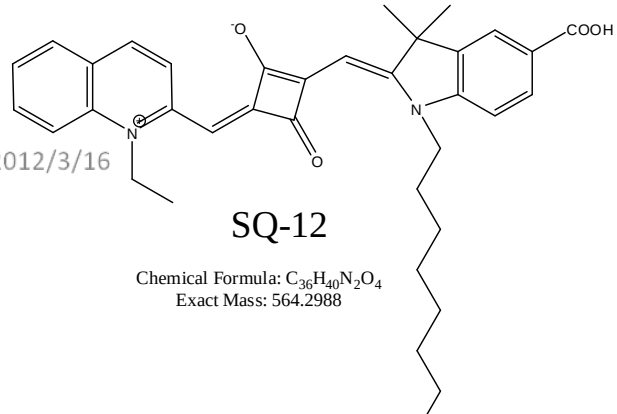
SQ-27



SQ-31



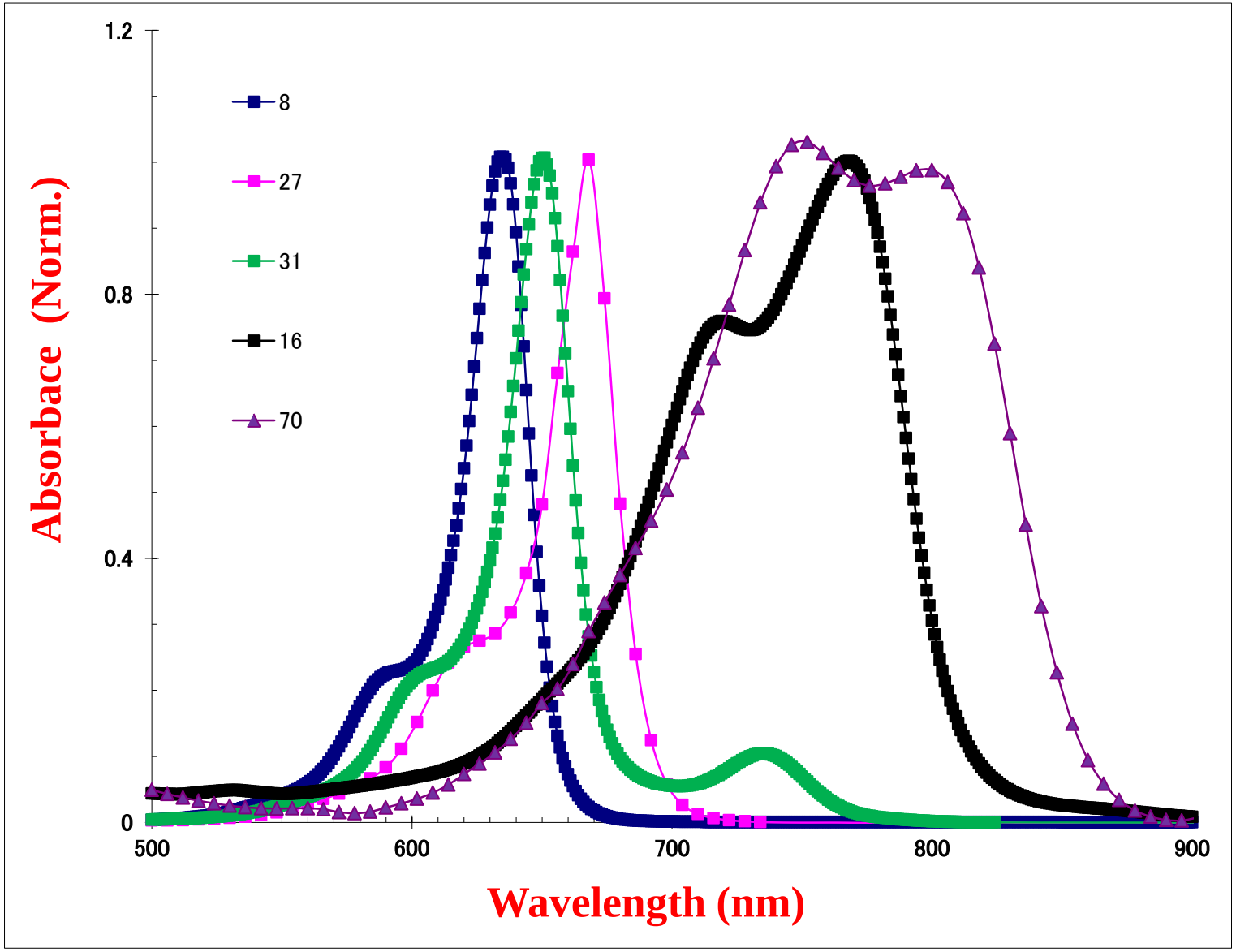
SQ-70



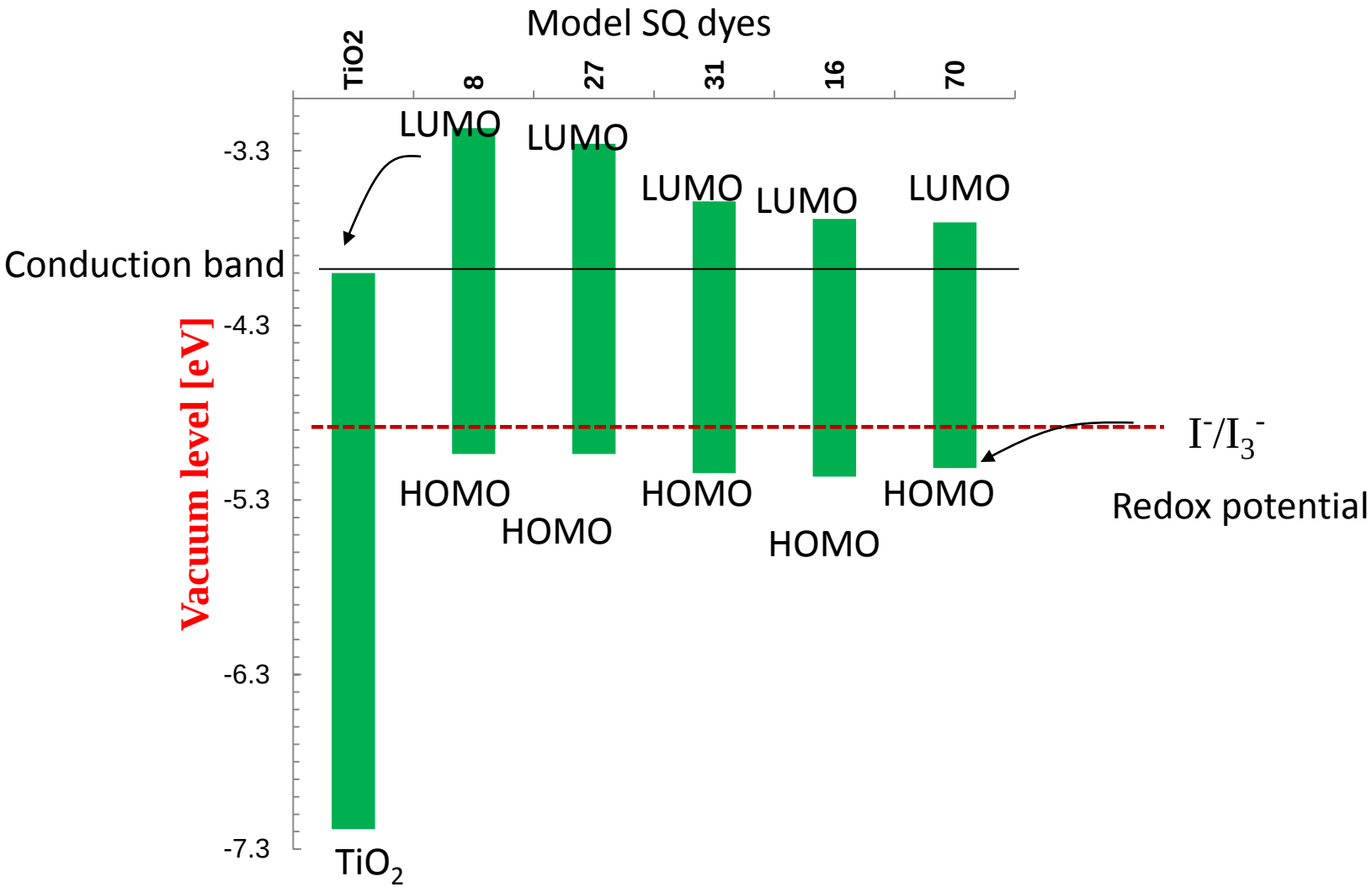
SQ-12

Chemical Formula: $C_{36}H_{40}N_2O_4$
Exact Mass: 564.2988

Electronic spectra

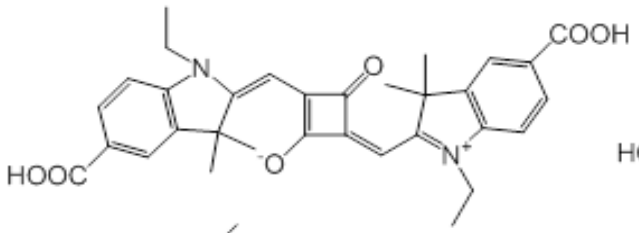


Energy Diagram

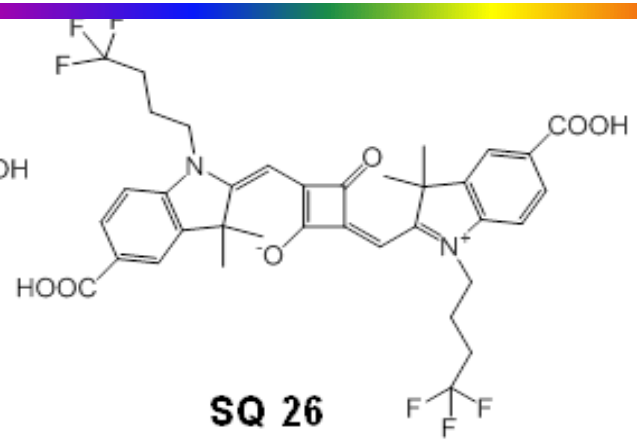


One of results of collaboration research

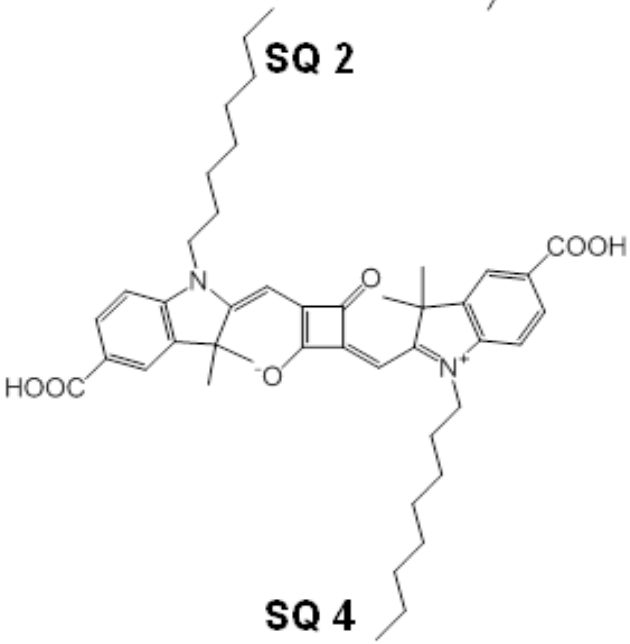
Model Squaraine Sensitizers



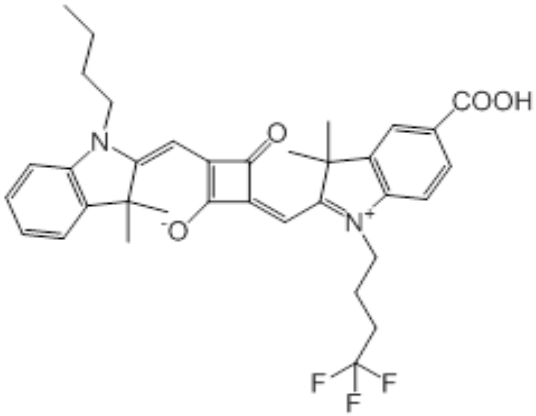
SQ 2



SQ 26



SQ 4

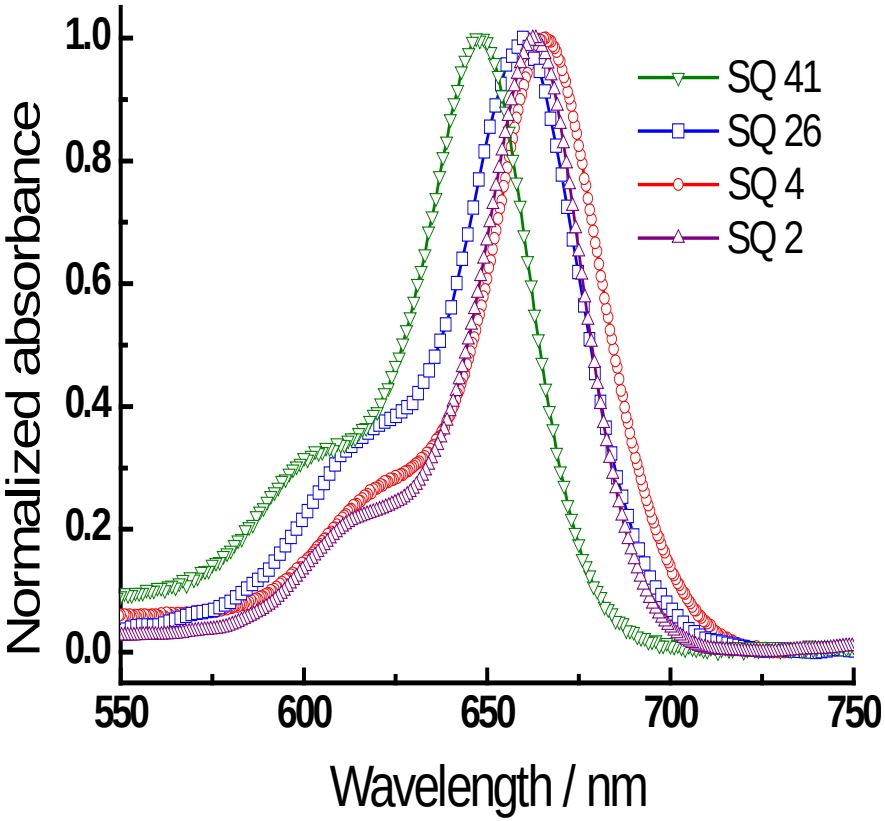


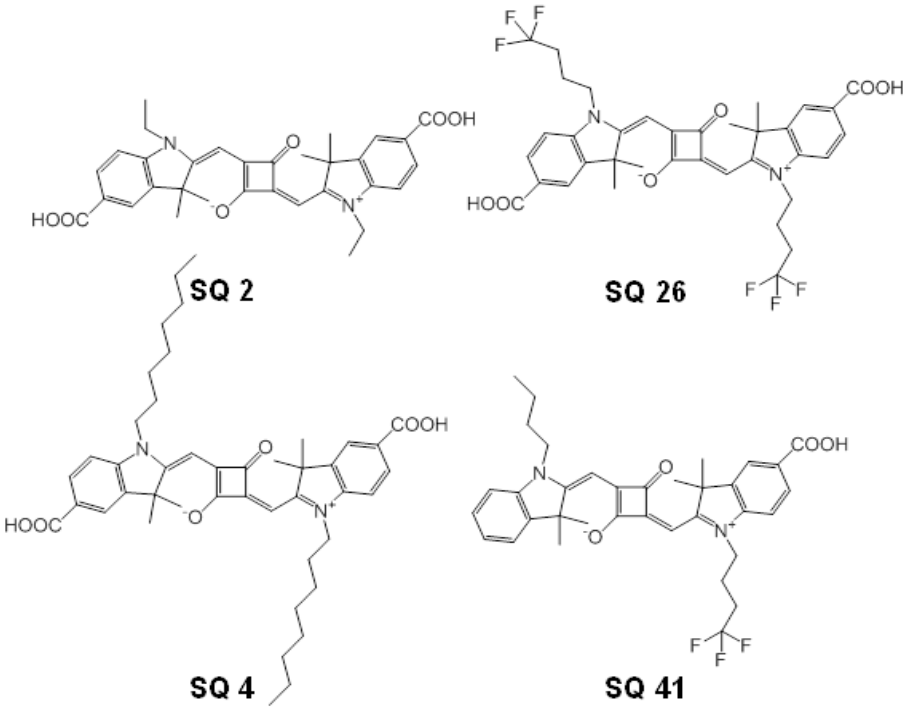
SQ 41

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**

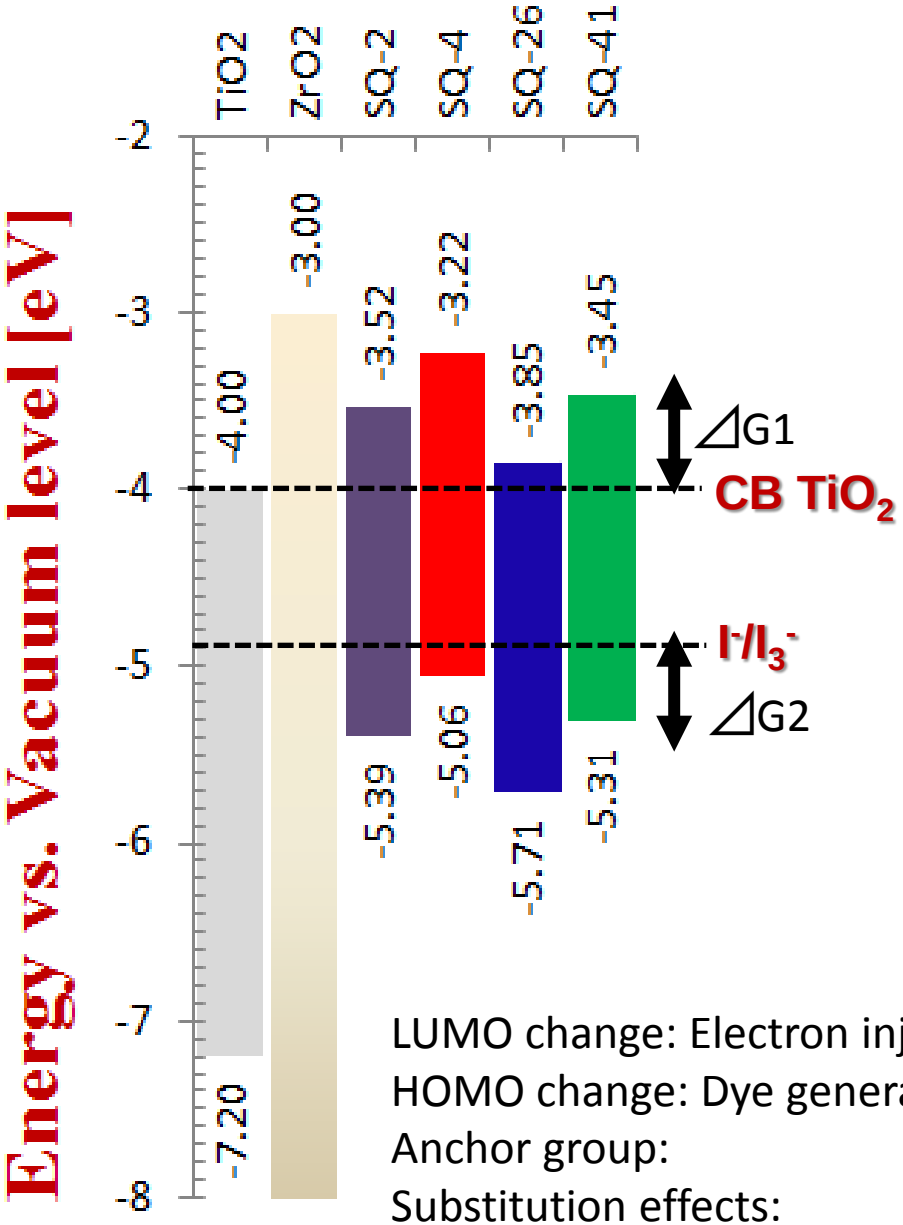
Electronic Absorption Spectra

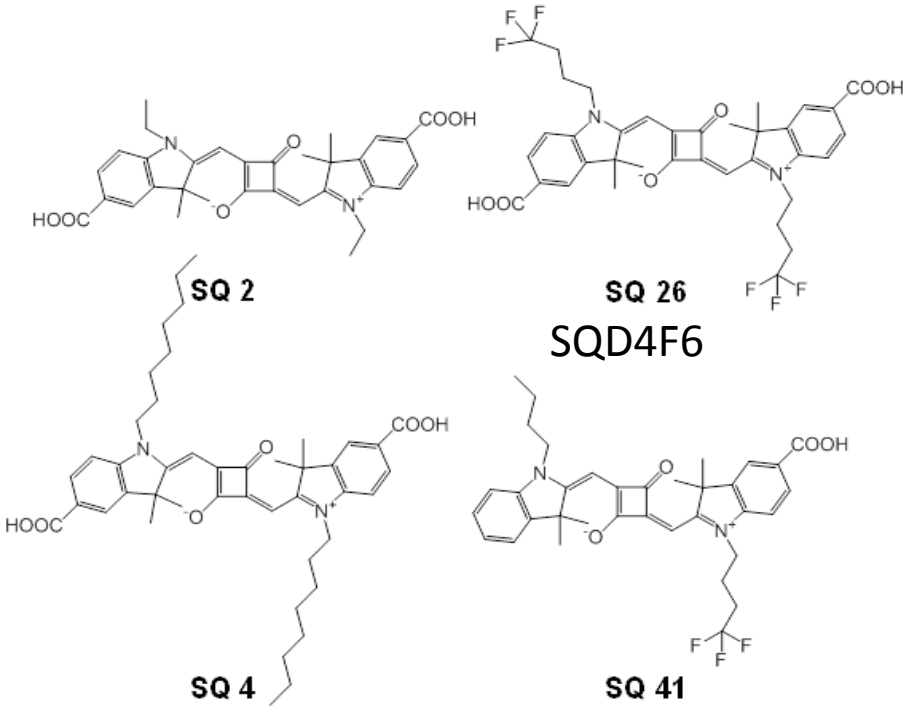
$\varepsilon = 2\text{-}3 \times 10^5\ dm^3.mole^{-1}.cm^{-1}$





Energy Band Diagram





SQD4F6

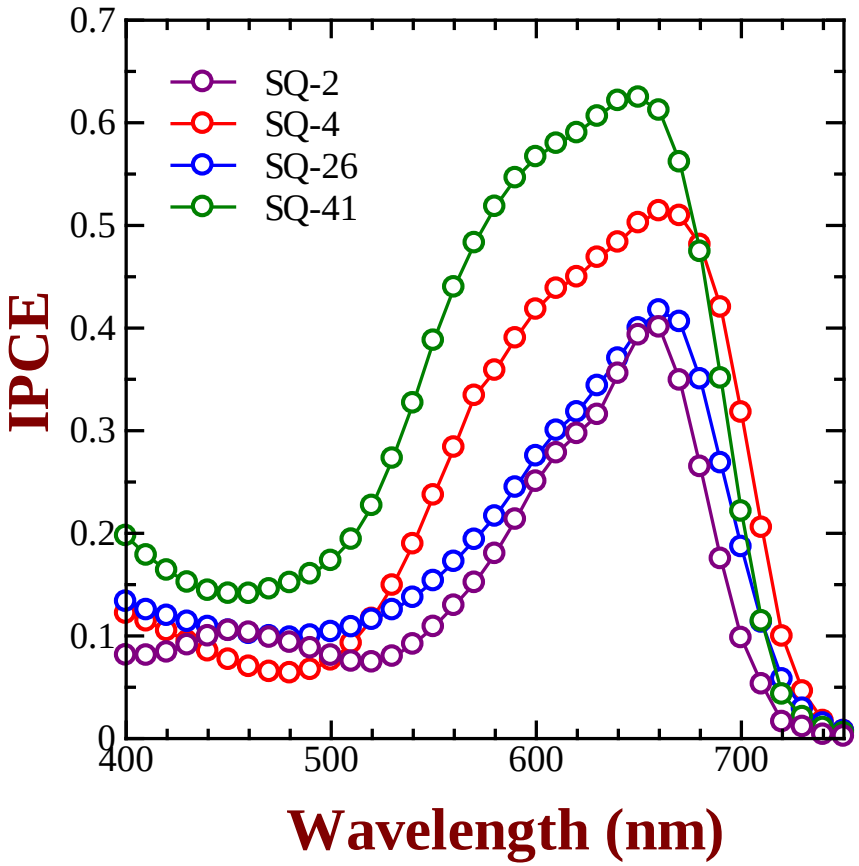
SQD8

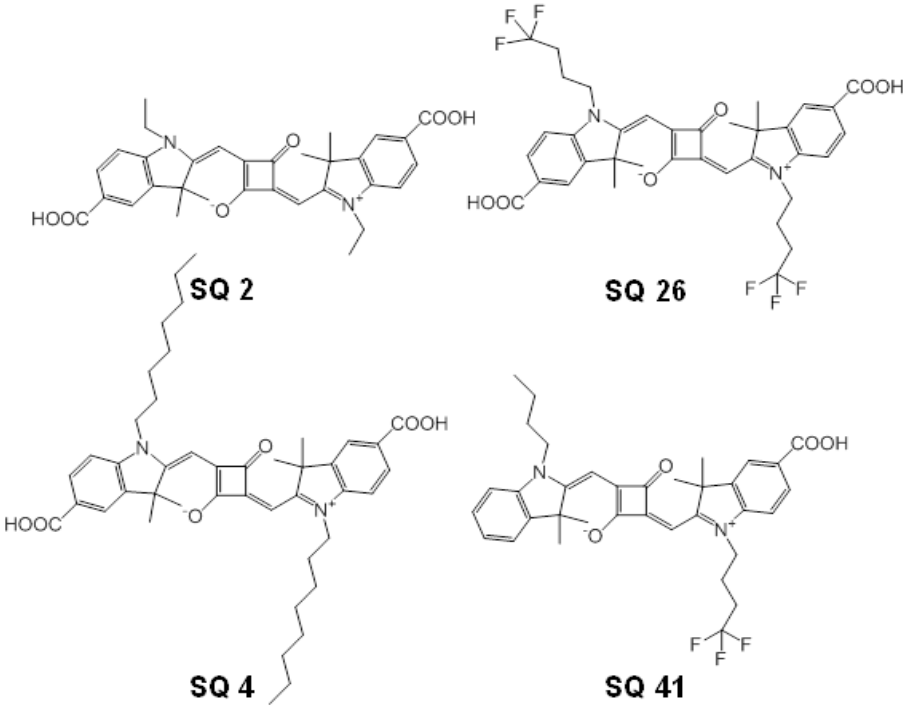
SQ4/4F3

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

Photovoltaic Characteristics

Photocurrent Action Spectra





Time-resolved techniques

Femtosecond Transient Absorption Spectroscopy
Nanosecond Flash Photolysis

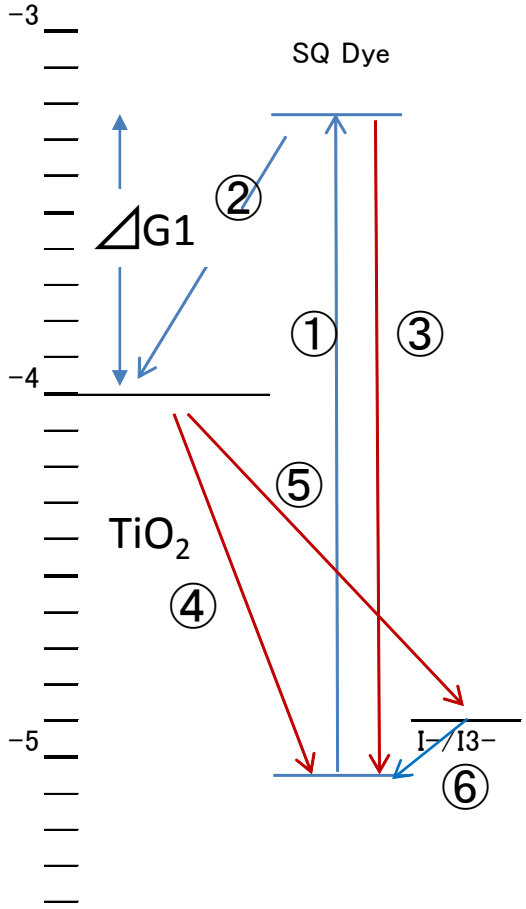
Experimental Conditions:

- **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**

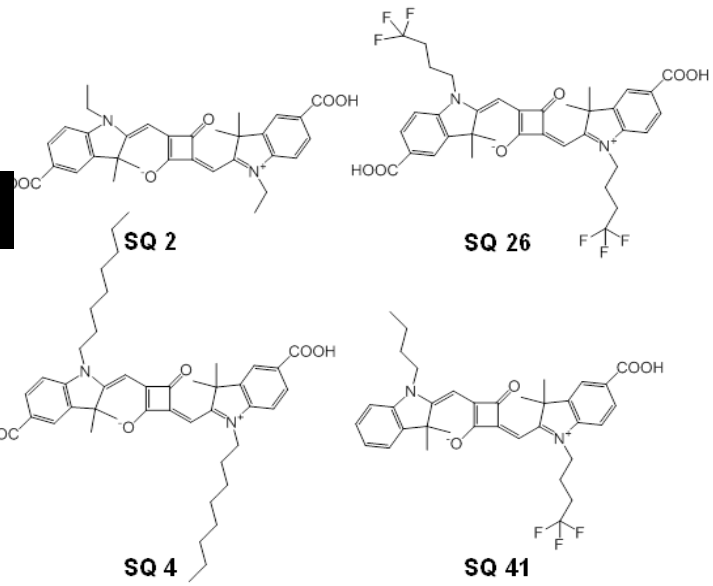
To determine the Dye Regeneration efficiency !

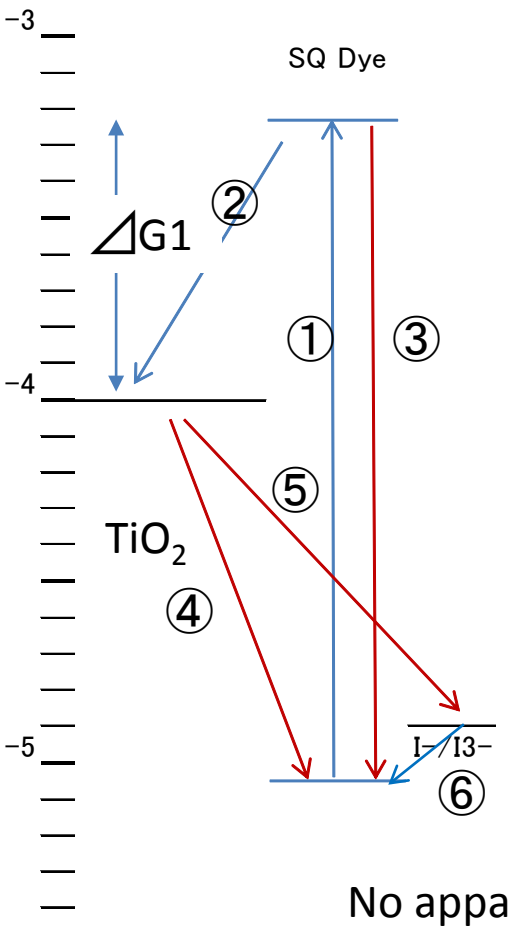


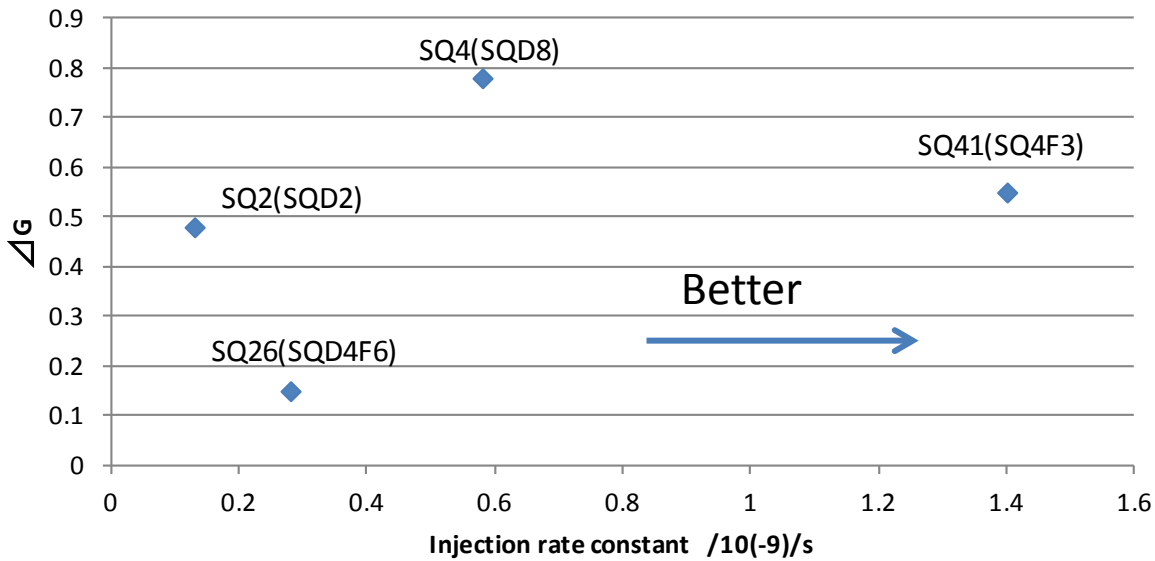
Electron injection

Electron Injection (②)

Relationship between ⊿G and injection rate constant





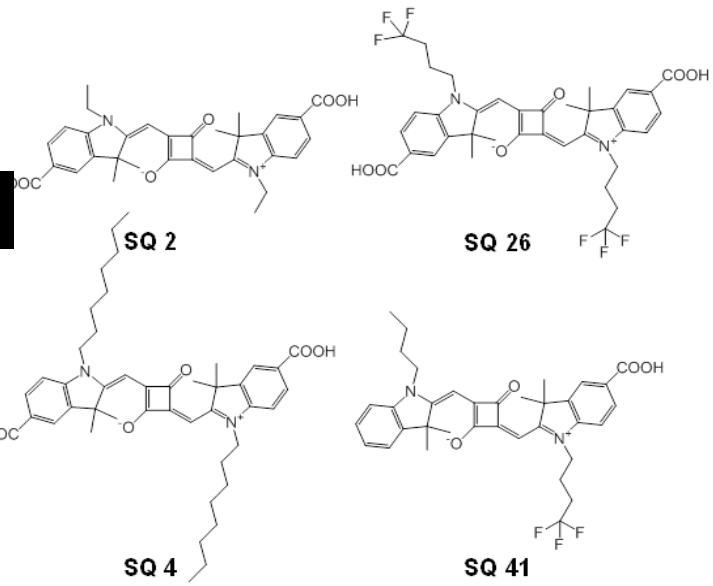


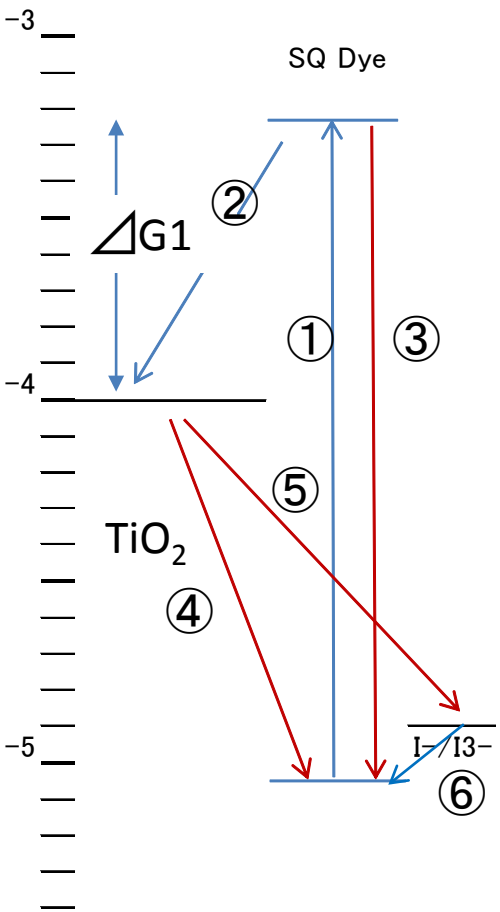
No apparent relation between ⊿G1 and injection rate constant

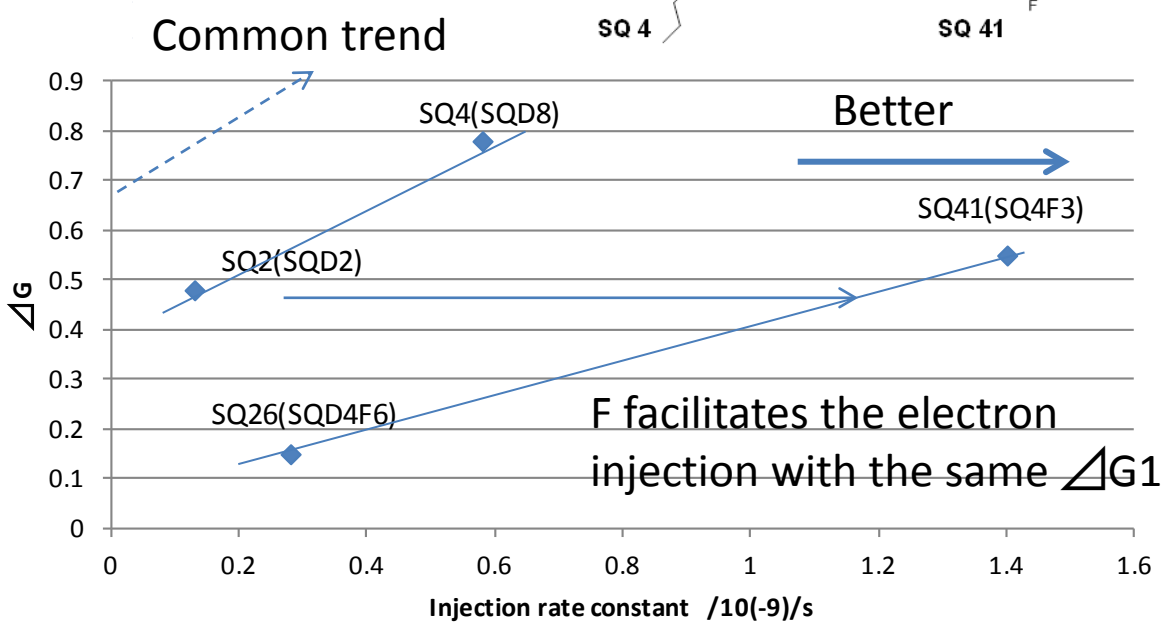
Electron injection efficiency is governed by factors other than ⊿G1

Electron Injection (②)

Relationship between ⊿G and injection rate constant





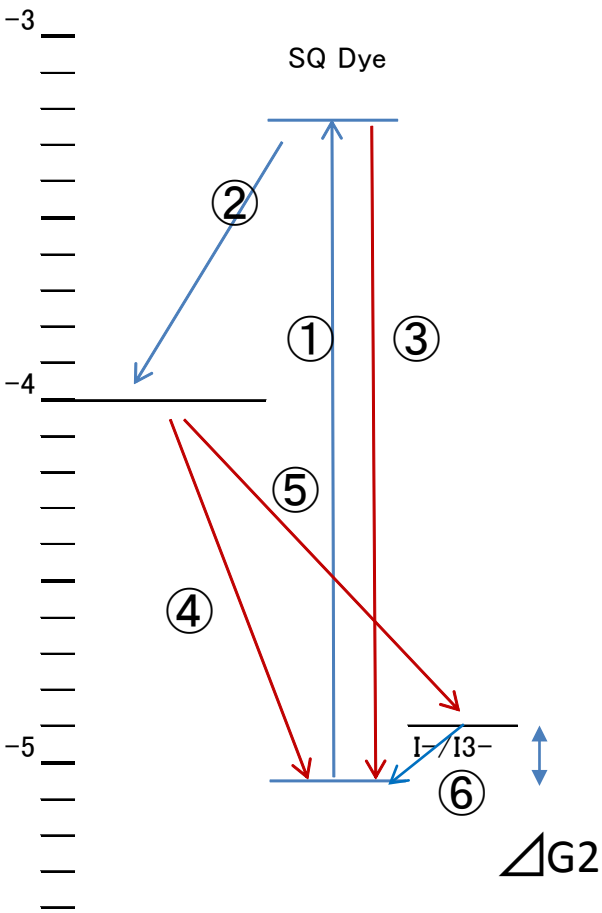


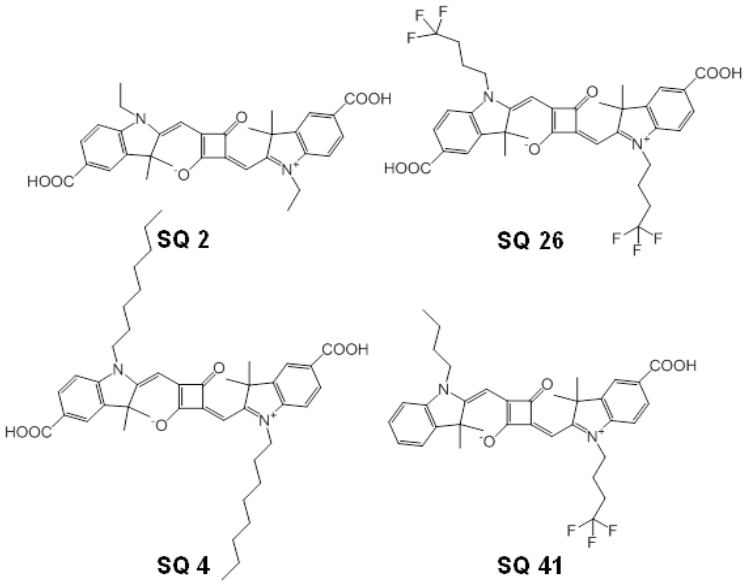
High electron injection can be realized with lower ⊿G1 by using dyes with F atoms

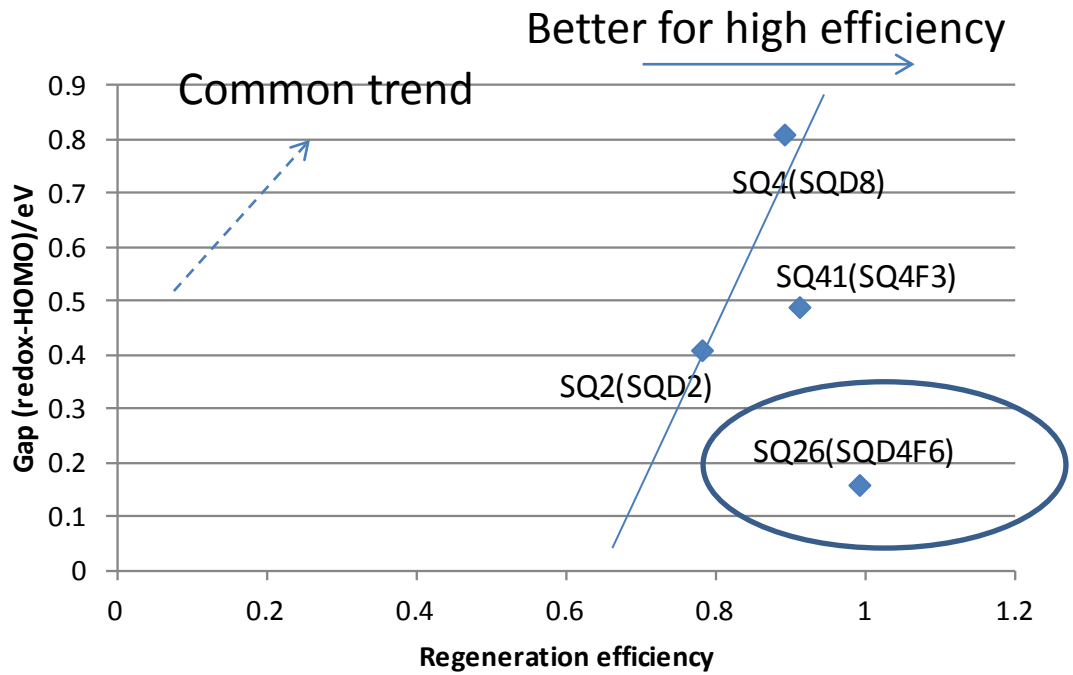
Dye regeneration

Dye generation(⑥)

Relationship between ⊿G2 and dye regeneration

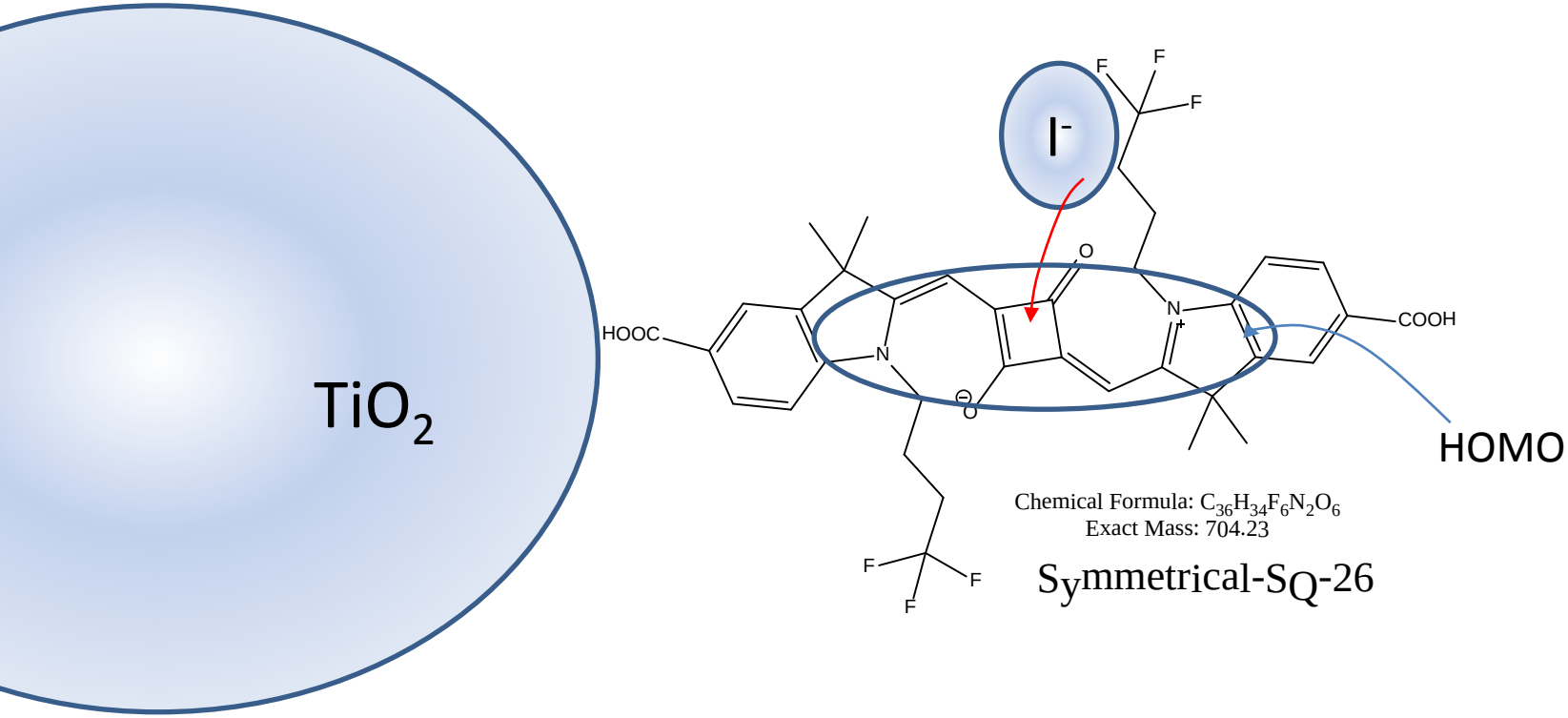


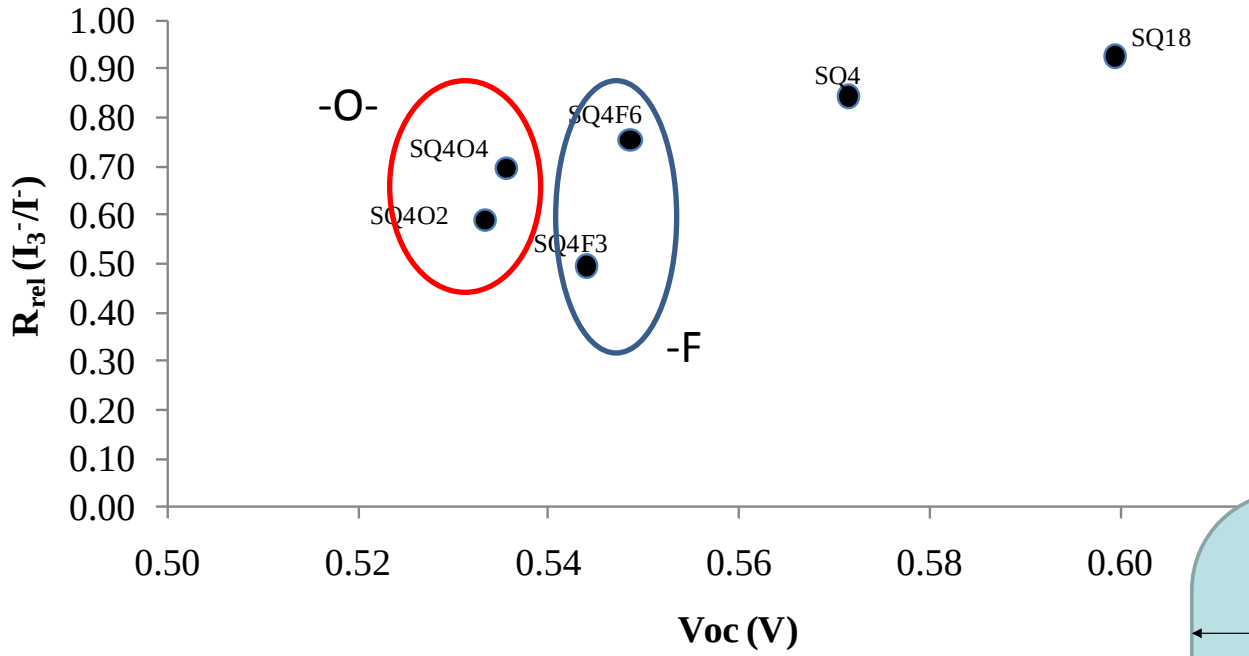


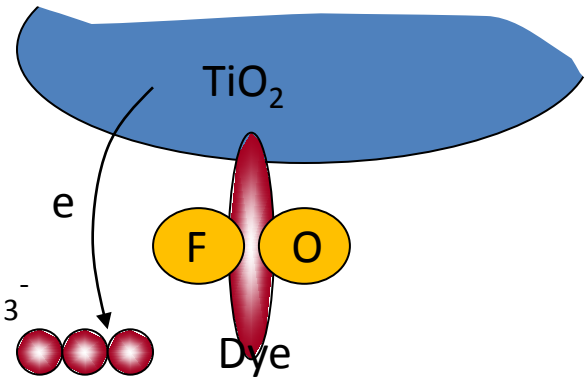


High dye generation with Low ⊿G2

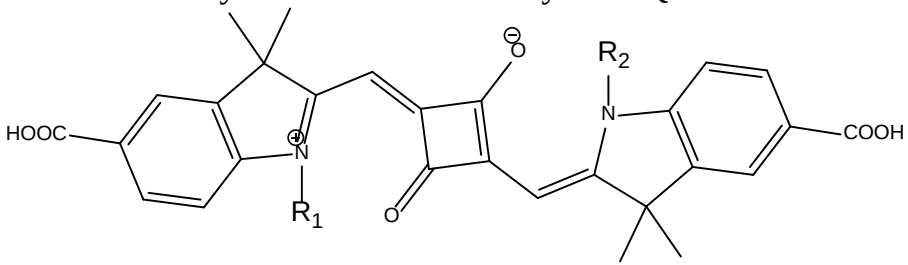
Possible explanation for high efficiency dye generation with low ⊿G2

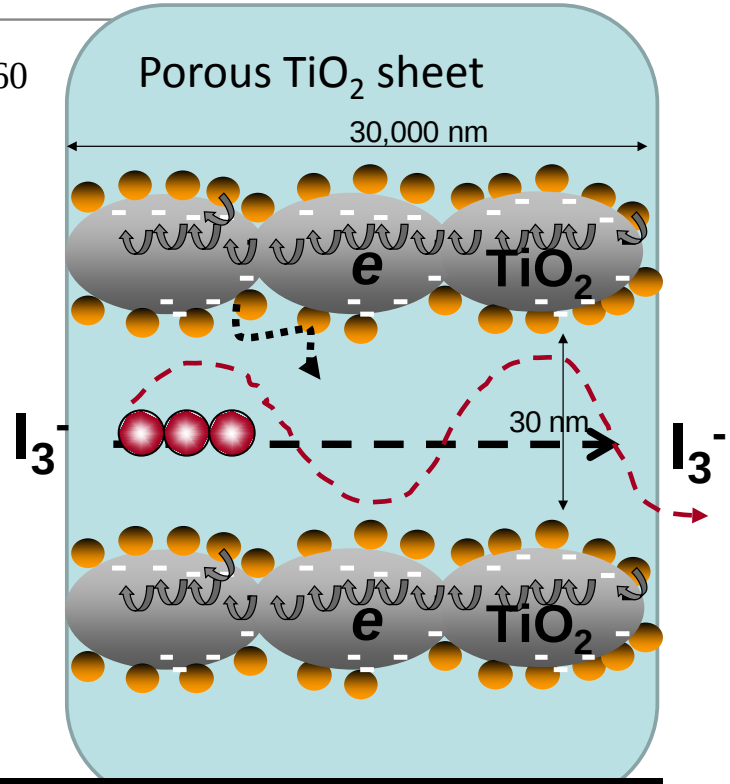






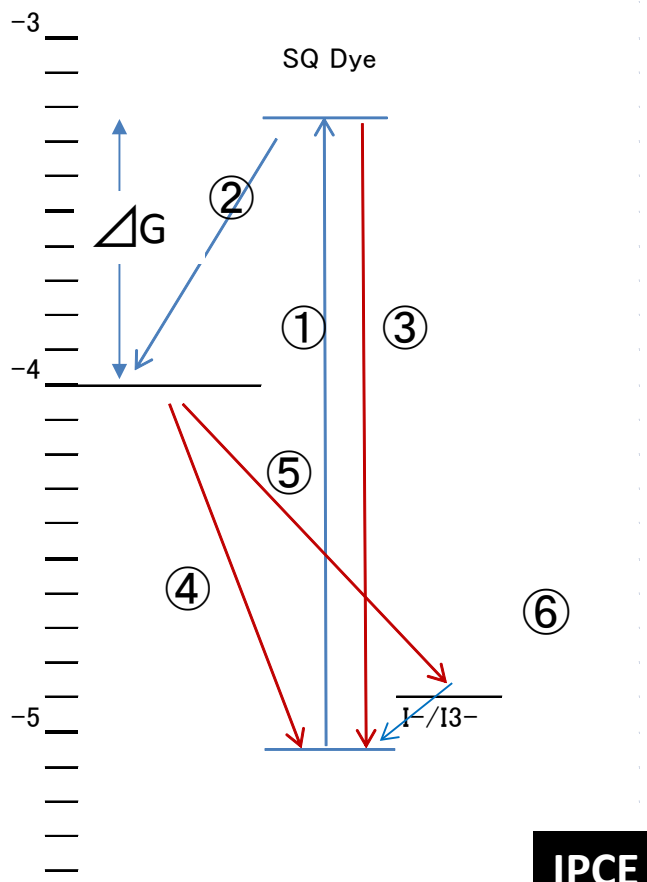
R1 = R2 = Butyl	SQ4
R1 = R2 = Dodecyl	SQ12
R1 = R2 = Octadecyl	SQ 18
R1 = R2 = Trifluorobutyl	SQ 4F6
R1 = R2 = Methoxybutyl	SQ4O2
R1 = R2 = Ethylbutanoate	SQ4O4
R1 =Butyl & R2 = Trifluorobutyl	SQ4F3

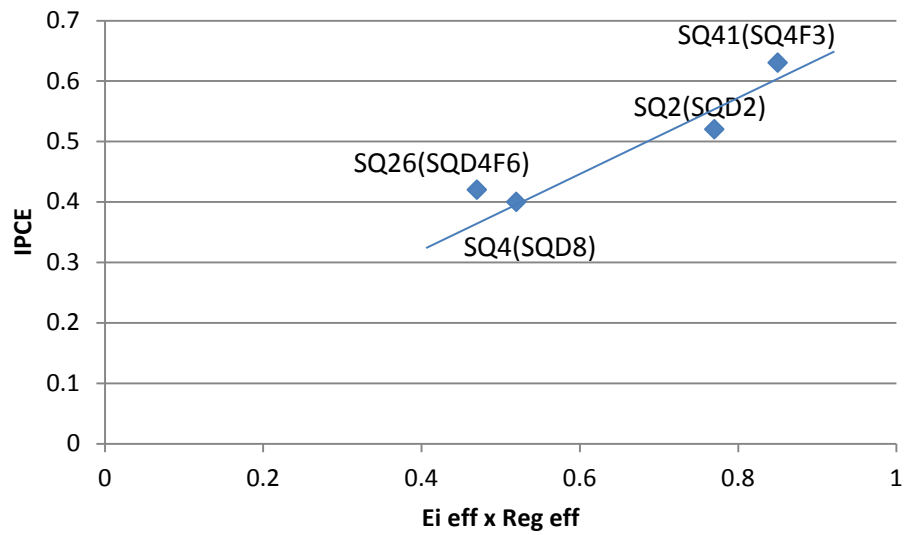




A. Hayat, S. S. Pandey, Y. Ogomi, and S. Hayase, J. Electrochem. Soc., 158, B770-B771 (2011).

Explanation on IPCE (④)



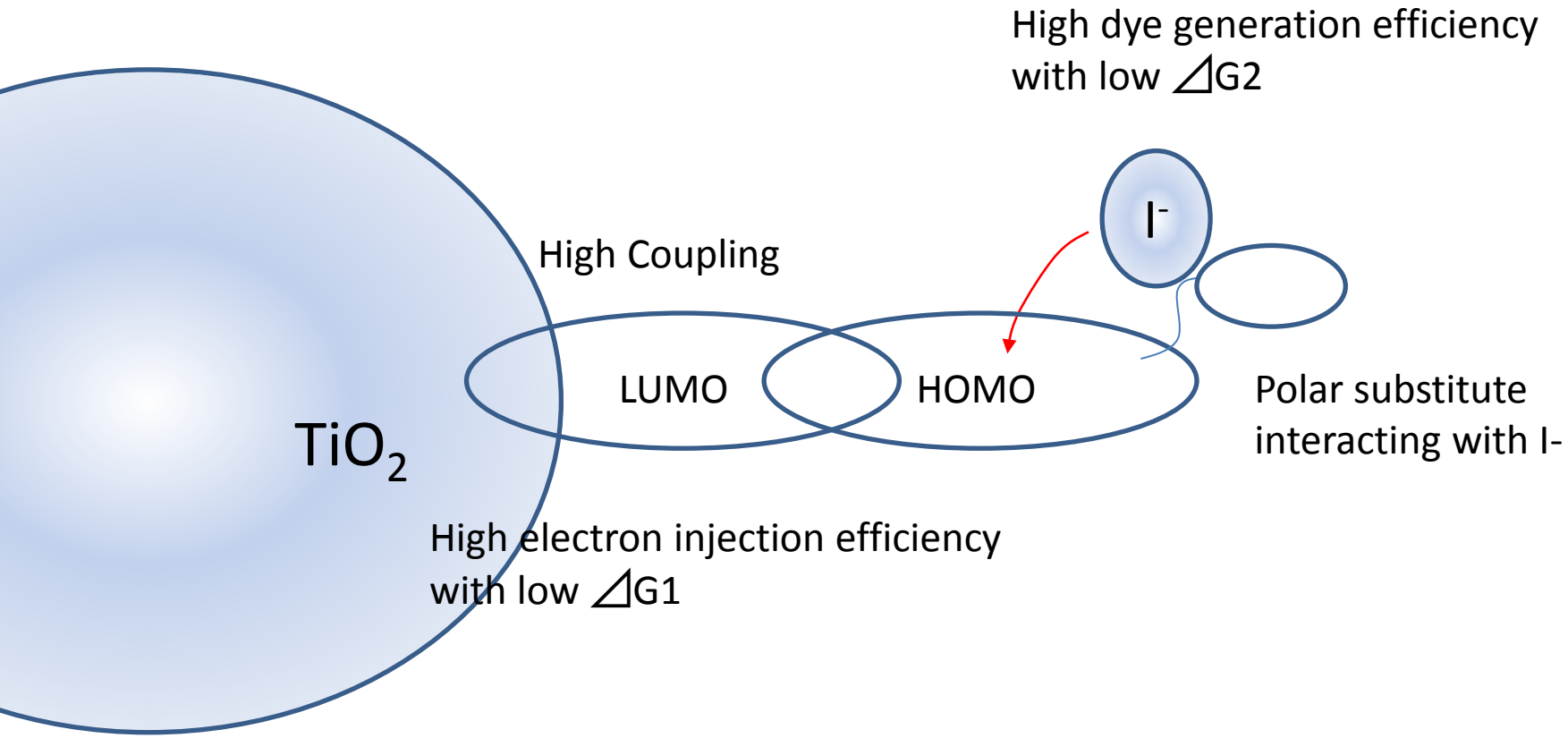


Ei eff: Electron injection efficiency: ②/②+③

Reg eff: Regeration efficiency: ⑥/④+⑥

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

Proposed structure realizing high efficiency dye generation with low ⊿G2 and high electron injection with low ⊿G1



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 (ΔG) and influenced by substituents and molecular structure. This suggests that high electron injection with low ΔG 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:

[1] Alkyl and Fluoroalkyl Substituted Squaraine Dyes: A Prospective Approach Towards Development of Novel NIR Sensitizers; Shyam S. Pandey, Takafumi Inoue, Naotaka Fujikawa, Yoshihiro Yamaguchi and Shuzi Hayase, Thin Solid Films, Vol. 519, pp. 1066-1071 (2010).

[2] Substituent Effect in Direct Ring Functionalized Squaraine Dyes on Near Infra-Red Sensitization of NanocrystallineTiO2 for Molecular Photovoltaics ; Shyam S. Pandey, Takafumi Inoue, Naotaka Fujikawa, Yoshihiro Yamaguchi and Shuzi Hayase, Journal of Photochemistry and Photobiology A: Chemistry, Vol. 214, pp. 269-275 (2010).

[3] Synthesis and characterization of squaric acid based NIR dyes for their application towards dye-sensitized solar cells ; Inoue, Takafumi, Pandey, Shyam S., Fujikawa, Naotaka, Yamaguchi, Yoshihiro, Hayase, Shuzi; JOURNAL OF PHOTOCHEMISTRY AND PHOTOBIOLOGY A-CHEMISTRY Volume: 213 Issue: 1 Pages: 23-29 (2010).

[4] Fine tuning the structure of unsymmetrical squaraine dyes towards the development of efficient dye sensitized solar cells; Shyam S. Pandey, Rie Watanabe, Naotaka Fujikawa, Yuhei Ogomi, Yoshihiro Yamaguchi and Shuzi Hayase; Proc. SPIE Vol. 8111 Page 811116 (2011).

[5] Femto to millisecond observations of indole-based squaraine molecules photodynamics in Solution.; G. de Miguel, M. Marchena, M. Ziolek, M, Zitnan, S. S. Pandey, S Hayase and A. Douhal. Physical Chemistry and Chemical Physics; Vol. 14, Pages 1796-1805 (2012).

[6] Photophysics of H-and J-aggregates of Indole based squaraines in solid state.; G. de Miguel, M. Ziolek, M, Zitnan, J. A. Organero, S. S. Pandey, S Hayase and A. Douhal; Journal of Physical Chemistry-C; Vol. 116, No.-17, Pages 9379-9389 (2012).

[7] Femto to Millisecond Photophysical Characterization of Indole-based Squaraines Adsorbed on TiO_2 Nanoparticle Thin Films. de Miguel, Gustavo; Marchena, Maria Jose; Ziolek, Marcin; Pandey, Shyam; Hayase, Shuzi; Douhal, Abderrazzak; Journal of Physical Chemistry-C; Vol. 116, No.-22, Pages 12137-12148 (2012).

[8] Novel unsymmetrical squaraine dye bearing cyanoacrylic acid anchoring group and its photosensitization behavior; Gururaj M. Shivashimpi, Shyam S. Pandey, Rie Watanabe, Naotaka Fujikawa, Yuhei Ogomi, Yoshihiro Yamaguchi and Shuzi Hayase ; Tetrahedron Letters; Vol. 53, No.40, Pages 5437-5440 (2012).

[9] Relating the Photodynamics of Squaraine-Based Dye-Sensitized Solar Cells to the Molecular Structure of the Sensitizers and to the Presence of Additives; G. de Miguel, M. Marchena, B. Cohen, S. S. Pandey, S. Hayase and A. Douhal; Journal of Physical Chemistry-C; Vol. 116, No.-42, Pages 22157-22168 (2012).

[10] Dye-Sensitized Solar Cells based on Novel Far-red Sensitizing Unsymmetrical Squaraine Dye containing Pyrroloquinoline Moiety.; Shyam S. Pandey, Naotaka Fujikawa, Rie Watanabe, Yuhei Ogomi, Yoshihiro Yamaguchi and Shuzi Hayase; Japanese Journal of Applied Physics; Vol. 51, No.-10, Issue-2, pages 10NE12-1-10NE12-5 (2012).

[11] Solution processable thin film organic photovoltaic cells based on far red sensitive soluble squaraine dye; Shyam S. Pandey, Takafumi Mizuno, Sandeep K. Das, Yuhei Ogomi and Shuzi Hayase; Thin Solid Films; Vol. 522, pages 401-406 (2012).

[12] Effect of extended p-conjugation on photovoltaic performance of dye-sensitized solar cells based on unsymmetrical squaraine dyes; Shyam S. Pandey, Rie Watanabe, Naotaka Fujikawa, Gururaj M. Shivashimpi, Yuhei Ogomi, Yoshihiro Yamaguchi and Shuzi Hayase; Tetrahedron, Vol. 69, No. 12, pages 2633-2639 (2013).

[13] Effect of anchoring groups on photosensitization behavior in unsymmetrical squaraine dyes' Gururaj M. Shivashimpi[1], Shyam S. Pandey[1], Rie Watanabe[1], Naotaka Fujikawa[1], , Yuhei Ogomi[1], Yoshihiro Yamaguchi[2], 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 !