ORGANIC LETTERS

2011
Vol. 13, No. 15
3944–3947

Panchromatic Trichromophoric Sensitizer for Dye-Sensitized Solar Cells Using Antenna Effect

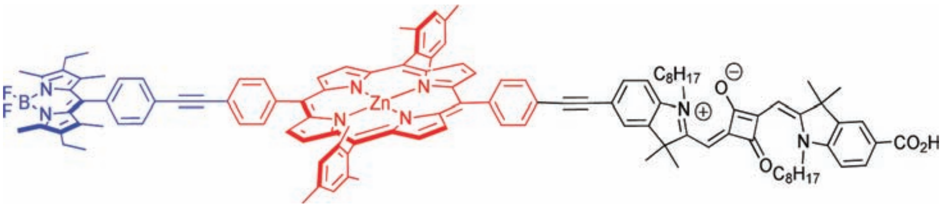
Julien Warnan, Fabien Buchet, Yann Pellegrin, Errol Blart, and Fabrice Odobel*

Laboratoire CEISAM, Equipe d'ingénierie et de photonique moléculaire UMR CNRS 6230 - Bât. 4 Faculté des Sciences et des Techniques de Nantes BP 92208 2, rue de la Houssinière 44322 Nantes cedex 03, France

Fabrice.odobel@univ-nantes.fr

Received May 31, 2011

ABSTRACT



The first trichromophoric sensitizer, consisting of covalently linked boradiazaindacene (BODIPY), zinc porphyrin (ZnP), and squaraine (SQ) units, has been synthesized by Heck alkynylation to obtain a panchromatic dye, for dye sensitized solar cells (DSSCs). Efficient intramolecular energy transfers (ET) were observed between all chromophoric subunits and enhance the overall conversion efficiency by 25%. The antenna effect is demonstrated by the photoaction spectrum which features all of a chromophore's absorption bands.

Dye-sensitized solar cells (DSSCs) have emerged as a realistic low cost technology to convert sunlight into electrical energy. Although ruthenium complexes are still the most efficient sensitizers,[1] the toxicity and the cost of this transition metal have prompted researchers to investigate metal-free dyes.[2] Organic conjugated dyes generally display higher molar extinction coefficients than ruthenium complexes but at a price of narrower absorption bands, leading thus to an incomplete solar spectrum coverage. In response, strategies have been developed to enhance the absorption, wavelength-wise. A mixture of different dyes ("cocktail dye") can be loaded on the semiconductor (SC) surface and gave satisfying results in some instances.[3] Nonetheless, cosensitization requires a tedious optimization step to find suitable chemisorption conditions.[4] Besides, the dye loading on the TiO_2 surface is necessarily reduced, because it is shared with several distinct absorbers. While these difficulties can be handled with success in some cases with two sensitizers, the challenge rapidly increases when more sensitizers are envisioned. The molecules prepared herein aim at developing another concept, that we have previously reported,[5] and which is inspired by the light harvesting antenna found in biological photosynthetic organisms.[6] Indeed, the operation principle of DSSCs is sometimes compared to that of natural photosynthesis, because the light harvesting function is performed by different components (dye) as the charge transport (SC and electrolyte). In the light harvesting antenna, an assembly

---

(1) (a) Polo, A. S.; Itokazu, M. K.; Murakami Iha, N. Y. *Coord. Chem. Rev.* **2004**, *248*, 1343–1361. (b) Cao, Y.; Bai, Y.; Yu, Q.; Cheng, Y.; Liu, S.; Shi, D.; Gao, F.; Wang, P. *J. Phys. Chem. C* **2009**, *113*, 6290–6297.

(2) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474–2499.

(3) (a) Siegers, C.; Hohl-Ebinger, J.; Zimmermann, B.; Würfel, U.; Mülhaupt, R.; Hinsch, A.; Haag, R. *ChemPhysChem* **2007**, *8*, 1548–1556. (b) Lee, C. Y.; Hupp, J. T. *Langmuir* **2009**, *26*, 3760–3765. (c) Bessho, T.; Zakeeruddin, S. M.; Yeh, C.-Y.; Diau, E. W.-G.; Grätzel, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 6646–6649. (d) Yum, J.-H.; Jang, S.-R.; Walter, P.; Geiger, T.; Nuesch, F.; Kim, S.; Ko, J.; Grätzel, M.; Nazeeruddin, M. K. *Chem. Commun.* **2007**, *44*, 4680–4682. (e) Chen, Y.; Zeng, Z.; Li, C.; Wang, W.; Wang, X.; Zhang, B. *New J. Chem.* **2005**, *29*, 773–776.

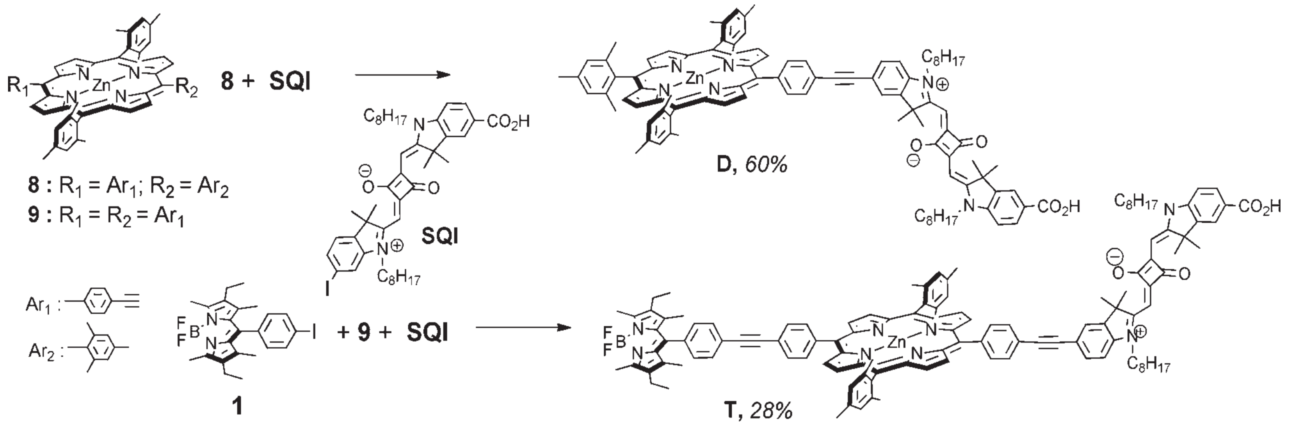
(4) (a) Wrobel, D.; Boguta, A.; Ion, R. M. *J. Photochem. Photobiol. A* **2001**, *138*, 7–22. (b) Otaka, H.; Kira, M.; Yano, K.; Ito, S.; Mitekura, H.; Kawata, T.; Matsui, F. *J. Photochem. Photobiol. A* **2004**, *164*, 67–73. (c) Bandara, J.; Weerasinghe, H. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 864–871.

(5) Odobel, F.; Zabri, H. *Inorg. Chem.* **2005**, *44*, 5600–5611.

(6) (a) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517–521. (b) Pullerits, T.; Sundström, V. *Acc. Chem. Res.* **1996**, *29*, 381–389.

10.1021/ol2014686

Scheme 1. Synthetic Route to the Dyad **D** and the Triad **T**[a]



[a] Coupling conditions: $Pd_2(dba)_3 \cdot CHCl_3$, $AsPh_3$, Et_3N, CH_2Cl_2/MeOH, 4 h, rt.

of different pigments spans complementary absorption spectra to harvest photons over a large spectral window. Then, the incident photonic energy is quantitatively transferred to a final acceptor: the special pair from which a photoinduced electron transfer chain is initiated. The role of the sensitizer anchored to a TiO_2 surface in a DSSC can be considered as similar to that of the SP; therefore a panel of complementary dyes can be used to feed the former in energy. Surprisingly, the utilization of the antenna effect *via* supplementary pigments counts only a few reports in DSSCs.[5,7] In this letter, we describe the synthesis and characterizations of two novel dyes (**D** and **T**) using successfully the antenna effect to improve the photoconversion efficiency of a DSSC (Scheme 1). To realize our light harvesting antenna mimic, we covalently linked chromophoric subunits, acting as antenna, to feed with energy (*via* ET) a sensitizer bearing the anchoring group, the latter acting thus as both a chromophore and reaction center to inject an electron into the conduction band of the semiconductor. We have selected three powerful dyes, a zinc porphyrin (ZnP) and a boradiazaindacene (BODIPY), as light harvesters and a squaraine (SQ) as a sensitizer for electron injection into TiO_2. SQ was reported as a quite efficient sensitizer in DSSCs, and it exhibits a low lying excited state, which makes it well-suited to act as both the final energy acceptor and the electron injector.[8] Moreover, SQ exhibits high molar extinction coefficients in the red ($> 10^5$ $L \cdot mol^{-1} \cdot cm^{-1}$), but they do not display any significant absorbance between 400 and 600 nm whereas the solar flux is particularly high in this region. Individually, these three dyes absorb in a narrow portion of the solar spectrum, but altogether they contribute to a wide spectral coverage (see below).

The unsymmetrical monoiodinated squaraine, 5-carboxy-2-[[3-[(1,3-dihydro-5-iodo-3,3-dimethyl-1-octyl-2*H*-indol-2-ylidene)methyl]-2-hydroxy-4-oxo-2-cyclobuten-1-ylidene]methyl]-3,3-trimethyl-1-octyl-3*H*-indolium (**SQI**), was obtained using modified, previously described methods (synthetic scheme available in Supporting Information (SI)).[9] The two indolium's octyl chains on the SQ enable the increase of solubility, to limit the aggregation and to prevent a close approach of the redox mediator I_3^- to the TiO_2 surface, thus reducing the counterproductive recombination reaction. The dyad **D** was synthesized by a Heck alkynylation reaction between the zinc porphyrin **8** and **SQI** in 60% yield using triphenylarsine, palladium(0) dibenzylideneacetone, and triethylamine as a catalytic system and a mixture of dichloromethane/methanol as solvent (Scheme 1).[10] The zinc(II) 5,10,15-trimesityl-20-(4-ethynylphenyl)porphyrin **8** was easily available in a few steps from a previously described methodology.[11] Despite the copper-free catalytic conditions and the freeze–pump–thaw degassing cycles, the Glaser type homocoupling reaction of the zinc porphyrin occurs and decreases the yield. Alternatively, classical Sonogashira cross-coupling conditions ($Pd(PPh_3)_4$, CuI, Et_3N in THF for 3.5 h) were also tested but furnished **D** with only a 36% yield.

---

(7) (a) Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. *J. Am. Chem. Soc.* **1990**, *112*, 7099–103. (b) Tian, H.; Yang, X.; Pan, J.; Chen, R.; Liu, M.; Zhang, Q.; Hagfeldt, A.; Sun, L. *Adv. Funct. Mater.* **2008**, *18*, 3461–3468. (c) Hardin, B. E.; Hoke, E. T.; Armstrong, P. B.; Yum, J.-H.; Comte, P.; Torres, T.; Frechet, J. M. J.; Nazeeruddin, M. K.; Grätzel, M.; McGehee, M. D. *Nat. Photonics* **2009**, *3*, 406–411. (d) Yum, J.-H.; Hardin, B. E.; Moon, S.-J.; Baranoff, E.; Nüesch, F.; McGehee, M. D.; Grätzel, M.; Nazeeruddin, M. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 9277–9280.

(8) (a) Geiger, T.; Kuster, S.; Yum, J.-H.; Moon, S.-J.; Nazeeruddin, M. K.; Grätzel, M.; Nüesch, F. *Adv. Mater.* **2009**, *19*, 2720–2727. (b) Burke, A.; Schmidt-Mende, L.; Ito, S.; Grätzel, M. *Chem. Commun.* **2007**, *3*, 234–236.

(9) Yum, J.-H.; Walter, P.; Huber, S.; Rentsch, D.; Geiger, T.; Nueesch, F.; De, A. F.; Graetzel, M.; Nazeeruddin, M. K. *J. Am. Chem. Soc.* **2007**, *129*, 10320–10321.

(10) (a) Ljungdahl, T.; Pettersson, K.; Albinsson, B.; Maartensson, J. *J. Org. Chem.* **2006**, *71*, 1677–1687. (b) Odom, S. A.; Webster, S.; Padilha, L. A.; Peceli, D.; Hu, H.; Nootz, G.; Chung, S.-J.; Ohira, S.; Matichak, J. D.; Przhonska, O. V.; Kachkovski, A. D.; Barlow, S.; Brédas, J.-L.; Anderson, H. L.; Hagan, D. J.; Van Stryland, E. W.; Marder, S. R. *J. Am. Chem. Soc.* **2009**, *131*, 7510–7511.

(11) Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941–68.

Besides, the carboxylic acid group seems to also limit the yield of this reaction, since the same reaction with the corresponding ethyl squaric ester instead of **SQI** increased the yield up to 75%. Unfortunately, all the saponification attempts using different conditions (LiOH, NaOH, $Ba(OH)_2$ in various solvent: THF, THF/water, toluene/methanol) caused the degradation of the compounds. This is in line with the strong tendency of cyanine dyes substituted with strong electron-withdrawing groups to react with nucleophiles.[12]

Several strategies were explored to synthesize the triad **T**. Difficulties were linked to the presence of two ethynyl groups. Initially, we prepared a dissymmetric bisalkenyl porphyrin monoprotected by TIPS. Reactions with either **BODIPY-I** or **SQI** enable the two respective bichromophoric molecules to be obtained in good yields. Unfortunately neither **ZnP-SQ** nor **BODIPY-ZnP** were resistant to the tetrabutylammonium fluoride cleavage of the TIPS. **BODIPY**'s deboration by fluoride ions was evidenced as already reported, while the squaraine unit is degraded as evidenced by mass spectrum analysis (data not shown here).[13] Finally, we chose to realize the synthesis of triad **T** according to a statistical mixture by Heck alkynylation coupling in one pot. Zinc porphyrin **9** and an excess of **BODIPY-I** and **SQI** (to reduce homocoupling) were reacted under the same conditions as those for **D**. After column chromatography purification, the triad **T** was obtained pure with 28% yield. To the best of our knowledge, this is the first trichromophoric dye ever reported for TiO_2 sensitization.

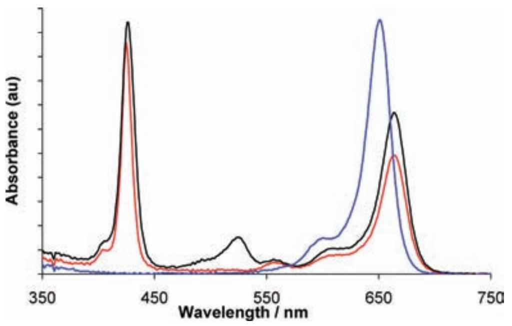


Figure 1. Absorption spectra of **SQI** (blue solid line), **D** (red solid line), and **T** (black solid line) recorded in THF.

The UV−visible spectrum of compounds **D** and **T** is not an exact linear combination of those of their monomeric chromophores since the squaraine's absorption band at 680 nm is red-shifted due to the extended π-conjugation brought by the acetylene link. Interestingly, the three chromophoric subunits display complementary absorption spectra and cover a wide window of the solar spectrum (Figure 1).

Thus, absorption bands at 664 nm, 524 and 426 nm, 556 nm were respectively attributed to the transitions assigned to the squaraine, the BODIPY, and the zinc porphyrin chromophores. The last porphyrin's Q-band overlays with the squaraine transition at 600 nm. To have an efficient energy transfer between all the chromophores, a large overlap between the donor's emission and acceptor's absorption spectrum (Förster mechanism) or between donor and acceptor orbitals (Dexter mechanism) is mandatory. In fact, zinc porphyrin absorption Q-band and BODIPY's emission spectra overlap, while the zinc porphyrin overlap with the squaraine absorption spectrum, thus fulfilling the through-space Förster energy transfer theoretical conditions. Moreover Lindsey and co-workers had already demonstrated an efficient internal ET between ZnP and BODIPY.[14] Interestingly, energy transfer between BODIPY and SQ is inefficient owing to a poor spectral overlap, while ZnP acts as an energy relay between BODIPY and SQ and assists energy migration from BODIPY to SQ. Steady-state fluorescence experiments in solution demonstrate a quantitative quenching of the emission bands of ZnP in **D** and of ZnP and BODIPY in **T** with an exclusive emission from the squaraine unit (Figure 2).

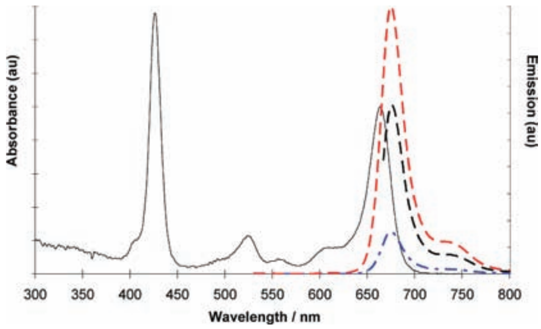


Figure 2. Overlay in THF of the normalized absorption spectrum of dye **T** (black solid line) and respective fluorescence traces upon excitation at 427 nm (Soret band of ZnP, red dashed line), 525 nm (BODIPY, blue point-dashed line), and 665 nm (SQ, black solid line).

The perfect matching of the excitation and the absorption spectra in **D** and **T** also confirm that the energy transfer quantum yield is over 98% from any antenna toward the squaraine (Figure S6 in SI). The squaraine's optical gap was determined by the wavelength at the intersection of the absorption and the emission spectra, and it exhibits a classical value of 1.85 eV. The oxidation potentials of each chromophore were recorded in CH_2Cl_2 by cyclic voltammetry using a saturated calomel electrode (SCE) as reference (Figures S1 and S2 in SI). ZnP and SQ are respectively oxidized at 0.70 V, 0.58 V in the dyad, while BODIPY, ZnP, and SQ are respectively oxidized at 1.01, 0.74, and 0.56 V in the triad. Accordingly, the electron injection and dye regeneration free energies from the squaraine are respectively ~ -0.58 eV and -0.26 eV both in **D** and **T**. Therefore, these processes are thermodynamically allowed and quite unchanged with regard to plain squaraine.[15]

---

(12) Murphy, S.; Yang, X.; Schuster, G. B. *J. Org. Chem.* **1995**, *60*, 2411–2422.

(13) Coskun, A.; Akkaya, E. U. *Tetrahedron Lett.* **2004**, *45*, 4947–4949.

Table 1. *I*/*V* Measure for **SQI**, **D**, **T** under AM 1.5 (1000 W/m^2)

sensitizer	Voc (mV)	Jsc (mA/cm^2)	FF (%)	η (%)
SQI	615	6.6	73	3.0
D	635	8.0	72	3.6
T	625	8.7	71	3.9
N719	745	12.9	73	7.0

Finally, we investigated the photoconversion efficiencies of these new sensitizers in DSSCs and compare them to that of the squaraine **SQI** as a reference (Table 1). The TiO_2 anodes were prepared according to literature procedures (see SI) and stained by the dye for 16 h in the presence of a deoxycholic acid (DCA) as a coadsorbent to avoid aggregation.[16] Optimization of the concentration of DCA was investigated for each dye. As intuitively anticipated, the larger the size of the dye is, the lesser the concentration in coadsorbent is required. The optimum DCA concentration for **SQI** and **D** is 5 mM, whereas it is only 2.5 mM for **T**. Increasing the DCA concentration resulted in a photocurrent decrease, while reducing it diminished the open circuit voltage (see Table S3 in SI). Concerning the optimal TiO_2 thickness, we found that the best performances were collected with a 12 μm thickness (besides diffusive layer), while a plateau was reached for thicker layers, along with reduced Voc (Table S2 in SI). A similar squaraine as **SQI** was recently reported to deliver a 4.5% photoconversion efficiency.[8] The lower performances of **SQI** measured herein (3%) indicate that the preparation of the solar cells was not optimal and that higher photoconversion efficiencies could certainly be reached with more experience to master this technological aspect. However, we were able to give a proof of concept of our design strategy because, within the three sensitizers, the photoconversion efficiency steadily increases in the order **SQI** < **D** < **T** (Table 1). In fact, there is more than 30% photocurrent improvement when we pass from **SQI** to **T**, which is consecutive to the expansion of the absorption spectrum over a broader wavelength frame brought by ZnP and BODIPY dyes.

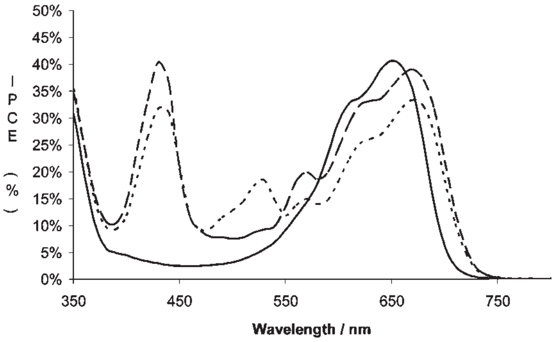


Figure 3. Overlayed IPCE spectrum of dye **SQI** (black solid line), **D** (dashed line), and **T** (point square line).

The contribution of ZnP and BODIPY units to the photocurrent generation is visible on the Incident Photon to Current Efficiency (IPCE, Figure 3) spectra, which also prove that efficient energy transfers from ZnP to SQ in both **D** and **T** and from BODIPY to ZnP in **T** occur on TiO_2 electrodes as the IPCE traces closely match the absorption spectra (Figure S4 in SI). Inspection of the photoaction spectra shows the maximum IPCE on squaraine experienced almost no drop for the dyad **D** or the triad **T** compared to the reference **SQI**, attesting thus that the grafting of the antenna has not significantly diminished its intrinsic photovoltaic performances.

In conclusion, the light harvesting antenna function of the natural photosynthetic systems was implemented in DSSC. We showed that the covalent grafting of three different complementary dyes, acting as light collecting antenna, can effectively boost the performance of a single sensitizer *via* light harvesting antenna. This concept opens new possibilities to develop panchromatic supersensitizers exhibiting high extinction coefficients over a large window of the solar spectrum thanks to the combination of different high absorbing organic dyes.

Acknowledgment. Authors acknowledge ANR Habisol (Asyscol program) and CNRS for fundings.

Supporting Information Available. Synthesis protocols, details of cell construction and characterization, UV/visible spectra on TiO_2, CV data. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(14) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759–9760.

(15) $E(sqi^+/sqi) = 0.61$ V, $E(sq^+/sq^*) = E(sq^+/sq) - E_{00}$, E_{00} was calculed at the intersection of absorption and emission spectra using $E = 1240/\lambda$, TiO_2(CB) = −0.7 V and $I_3^-/I^- = 0.33$ V (vs SCE)

(16) Yum, J. H.; Moon, S. J.; Humphry-Baker, R.; Walter, P.; Geiger, T.; Nuesch, F.; Gratzel, M.; Nazeeruddin, M. d. K. *Nanotechnology* **2008**, *19*, 424005/1–424005/6.