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Dear Editor,

We would be much obliged if you can consider the attached manuscript entitled: **Panchromatic Symmetrical Squaraines: A step forward in molecular engineering of low cost blue-greenish sensitizers for Dye-Sensitized Solar Cells** by J. Park, N. Barbero, J. Yoon, E. Dell'Orto, S. Galliano, R. Borrelli, J.-H. Yum, D. Di Censo, M. Grätzel, Md. K. Nazeeruddin, G. Viscardi and myself for possible publication in *Energy Environmental Science* as COMMUNICATION. Prompt publication in *EES* is justified because it's the best demonstration so far of high efficiency (over 6%) dye sensitized solar cell based on low cost symmetrical **blue-greenish** squaraine.

The literature so far (i.e.: J-Q Jiang et al. *RSC Adv.*, 2014, 4, 32987), has still claimed the superiority of unsymmetrical squaraine structures versus the corresponding symmetrical ones. However, directionality in the charge injection from dye to $TiO_2$ can also be observed in symmetrical structures, if a *cis* conformation of the squaraine on the titania surface is supposed, as we already demonstrated in J. Park et al. *Chem. Commun.*, 2012, **48**, 2782–2784: they act as dibranched sensitizer. The interest in this novel approach is also testified by the very recent publications on NIR symmetrical substituted squaraines, based on a simple modification of the molecule we published, by T. Maeda et al. (*J. Mater. Chem. A*, 2013, **1**, 1303) and L. Han and coworkers (*Adv. Funct. Mater.*, 2014, **24**, 3059).

In the present work, we report the synthesis, spectroscopic, electrochemical and photovoltaic characterization, together with a detailed computational analysis, of a novel series of symmetrical NIR squaraine dyes, coded **VG10**, with excellent photovoltaic performances. In this case, the anchoring groups have been inserted directly on the benzoindolenine moieties, thus obtaining a more conjugated and red-shifted system. The main advantage of these symmetrical structures is the easiness of synthesis and the related lowered costs and possible scale-up. In the DSC, the new symmetrical sensitizers exhibit an efficiency higher of about 10% respect to the unsymmetrical reference. This feature is due to the superior light harvesting both at high and low energies. Spectroscopic data together with computational analyses highlighted the importance of the structural organization of the dibranched molecules on the titania surface.

Although long term stability remains still an issue for NIR dyes, we showed that the presence of two anchoring groups, as well as the long chains and the extending conjugation furnished by the condensed phenyl rings have beneficial effects on photochemical and thermal stability.

We believe our work is in the interest of *EES* readers, because it opens the way to a large number of optimized symmetrical squaraine, whose synthesis can be easily scaled up, and which will become the reference for blue-green colors, especially from the industrial point of view.

Thanking for your attention I send you my best regards.

Claudia Barolo and co-authors

# Journal Name

## COMMUNICATION

# Panchromatic Symmetrical Squaraines: A step forward in molecular engineering of low cost blue-greenish sensitizers for Dye-Sensitized Solar Cells

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**Two novel symmetrical blue squaraine sensitizers were synthesized, which exhibit panchromatic light harvesting and a record efficiency over 6% with $J_{sc}$ exceeding 14 mA/cm$^2$, $V_{oc}$ over 620 mV under 1 sun. Their color, low cost, easiness of synthesis, and relatively high photo and thermal stability, opens up the way for commercial applications.**

Dye-sensitized solar cells (DSCs)[1] provide a significant low-cost alternative to conventional photovoltaics. State-of-the-art DSCs based on molecular dyes are currently characterized by solar-to-electric power conversion efficiencies (PCEs) of 10–13%.[2,3] In DSCs, one of the most critical components is the sensitizer and its spectral response to further increase PCEs. Therefore, it is of paramount importance to molecularly engineer and develop sensitizers, combining easiness of synthesis and increased light-harvesting ability in the near-infrared (NIR) region[4].
A number of metal-free dyes have so far been developed[5] due to high molar extinction coefficient (ε) and the absence of rare and expensive metals. Their chemical structures and relative photovoltaic performance relationships has been examined.[6] NIR dyes could find interesting applications both in photovoltaic windows and in tandem panchromatic solar cells.[7,8] Among them, squaraine dyes are well known for their intense absorption and their relative photo– and thermal stability.[9] The most performing near–IR squaraine dyes reported so far in literature are unsymmetrical structures (**JK216**[10], **YR6**[11], **JD10**[12]), exhibiting panchromatic light harvesting and cell efficiencies around 6–7% (see Figure 1ESI).
However we successfully demonstrated that symmetrical squaraine dyes[13] have similar efficiency in the cell to the related unsymmetrical structures with the evident advantages of easiness of synthesis, purification and possible industrial scale-up due to the inherent low cost. In fact, the syntheses of the previously cited unsymmetrical squaraines require several synthetic steps via difficult and expensive carbon-carbon coupling.

Dibranched symmetrical dyes[14] have been claimed to enhance the stability due to the higher number of anchoring group. Unfortunately, until now, none of these dibranched sensitizers showed an efficient photon-to-current conversion in the NIR region (see Table 1ESI for an overview of the structures and relative photovoltaics records available in literature). Moreover, a symmetrical and conformational locked squaraine structure, due to a *cis* conformation, can lead to a significantly enhanced short-circuit current density as proved by us[13] and more recently by Maeda and Han.[15]
Herein we report the synthesis and optical, electronic, and photovoltaic properties of two simple symmetrical bis(benzoindolenine) squaraine sensitizers coded **VG10–C2** and **VG10–C8** (Figure 1a and Scheme ES1), which incorporate, for the first time, two carboxylic acid each directly conjugated to the benzoindolenine moieties instead of having it in the N-alkyl substituents[16], or on a simple indolenine[17]. The corresponding unknown unsymmetrical squaraine **VG13** was also synthesized for a comparison (Figure 1a and Scheme ESI2). The benzoindoleninium derivative was prepared via a simple and high yields Fischer indole synthesis[18] and a subsequent nitrogen alkylation (see ESI for full details). The benzoindoleninium salt was then reacted with squaric acid to obtain the symmetrical squaraines **VG10–C2** and **VG10–C8**. Very recently, we set up quaternization reactions and the syntheses of indolenine-based squaraine dyes by means of a single mode microwave reactor[19]. This allowed to drastically reduce time (from days to minutes), increase yields (more than two-fold improvement in product yields when compared to conventional methods) and purity. A simple crystallization of the crude symmetrical and unsymmetrical products yielded a very low cost and industrially scalable product (for a detailed account see the synthetic procedures in the ESI).
**VG10** dyes exhibit an absorption maximum around 673 nm in ethanol (Figure 1b) with a very high molar absorption coefficient (around 300000 M$^{-1}$ cm$^{-1}$). A red shift of about 20 nm with respect to the symmetrical **VG1-C8** is consistent with

the expected effect of extending conjugation owing to benzocondensed indoleninium moiety.
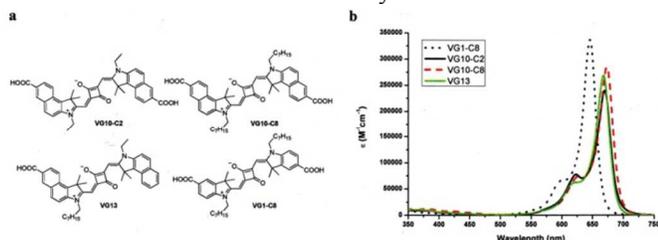


**Figure 1.** a) Structures of symmetrical squaraines **VG10–C2** and **VG10–C8** and unsymmetrical squaraine **VG13**. **VG1-C8** structure is reported for comparison. b) Absorption spectra of **VG10–C2** (solid black line), **VG10–C8** (dashed red line), **VG13** (solid green line) and **VG1-C8** (dotted blue line) in ethanol.

The ground-state oxidation ($E^{(S+/S)}$) and reduction potential ($E^{red}$) of the new symmetrical dyes (**VG10–C2** and **VG10–C8**) were evaluated by cyclic voltammetry to be at same potentials, using ferrocene (Fc) as an internal standard. The ($E^{(S+/S)}$) level (at 0.06 V *vs.* Fc, see Figure 2) indicates that dye regeneration by iodide species is energetically favourable. The $E^{(red)}$ level (at −1.50 V *vs* Fc), being more negative than the conduction band of $TiO_2$, is positioned favourably for efficient electron injection. On the other hand, **VG13** oxidation is very close to Fc redox potential, while the reduction is at -1.60 V *vs.* Fc. Looking at the molecular structure of the different dyes it is evident that symmetrical systems always show more stabilized ground and excited states with respect to the corresponding unsymmetrical structures (**VG1** *vs.* **SQ01**[13] and **VG10** *vs.* **VG13**). On the contrary, the introduction of benzoindolenine moieties instead of indolenine ones induced an unexpected destabilization both of the ground and excited state levels (**VG10** vs. **VG1**) (Figure 2). Electrochemical data are consistent with the bathochromic shifts observed in the spectroscopic analysis (Figure 1b).
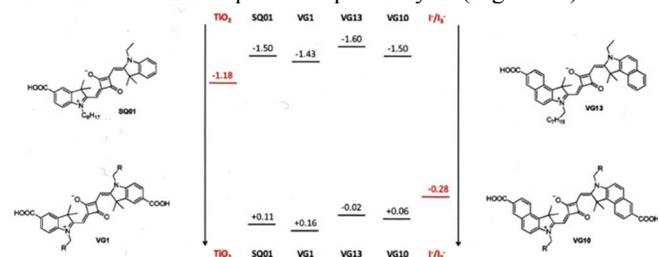


**Figure 2.** Ground state oxidation and reduction potentials *vs.* Fc of the symmetrical and unsymmetrical squaraine dyes.†

In order to elucidate the origin of the spectroscopic properties of the dye we have performed a theoretical analysis using time-dependent density functional theory (TD–DFT) calculations taking into account bulk solvents effects (see ESI, part 5).[20-22] DFT geometry optimization suggests that **VG10–C2** molecule can exist in several stable conformational isomers differing by a rotation of 180° around the double bonds of the polymethine-like chain (Figure 4ESI). The two most stable isomers are shown in Figure 3, the energy of the cis isomer being only 0.7 kcal/mol higher than that of the trans isomer. The computed electronic spectrum of the trans isomer in DMSO shows a strong absorption at 661 nm corresponding to an excitation to the first excited singlet state ($S_1$). The result is in excellent agreement with the observed band at 683 nm (Table 4ESI). The calculated transition energy is higher than the experimental data

by about 0.06 eV, and confirms a trend which has already been reported in previous studies based on TD–DFT.[13,23] The $S_1$ singlet state is described almost entirely by a valence HOMO-LUMO transition, which is in agreement with that relatively small Stoke shifts observed.[24] This can be clearly seen by looking at the isosurfaces of the molecular orbitals displayed in Figure 3. Indeed, the HOMO and LUMO correspond to valence $\pi$ and $\pi^*$ orbitals respectively which mainly involves the squarainic ring and the polymethine-like chain, as also found by other authors.[25,13] Calculations of the absorption spectrum in THF predict a blue shift of the S0-S1 transition to 644 nm, again in good agreement with the experimental value of 676 nm. Similar results hold for the other isomers (see ESI).
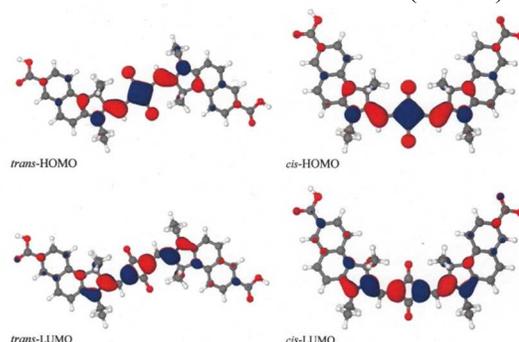


**Figure 3.** Isodensity plots of the HOMO and LUMO molecular orbitals of **VG10–C2** in its *trans* and *cis* conformations.

The above analysis suggests that the excited state of **VG10**, which is involved in the electron injection into the $TiO_2$, has only a minor CT character. Further studies are in progress to understand the nature of the electronic coupling between the dye and the semiconductor.

Dibranched symmetrical squaraine dyes can show a double–anchored linking by the two carboxylic groups.[13,15] The comparison between ATR–FTIR spectra of the dyes alone and absorbed on the electrode (Figure 5ESI) exhibits, in the case of **VG10–C2**, the disappearance of the strong absorption band observed at 1702 cm⁻¹, which can be attributed to the C=O stretching of an aromatic carboxylic acid. On the contrary, the long chain dye (**VG10–C8**) spectrum still shows a non obvious behavior (a peak and a shoulder) which can suggest that the double anchoring mode is not complete. In fact, the conformational changes in solution for the two molecules are strongly affected by the length of the alkyl chains as confirmed by NMR spectra (Figure 6ESI and 7ESI).
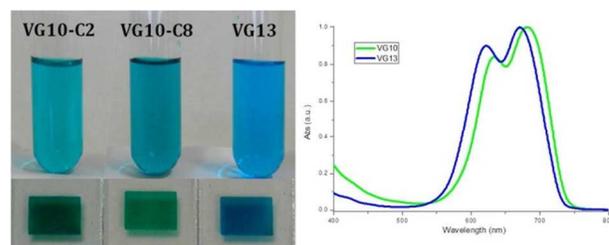


**Figure 4.** Solutions and dipped electrodes of the symmetrical and unsymmetrical dyes (left) and UV-Vis spectra of **VG10** and **VG13** adsorbed on transparent $TiO_2$ electrodes (right).

The double anchoring most likely takes place when the squaraine is in its *cis* configuration. This is further substantiated

by the increase in the absorbance around 400 nm after **VG10** is adsorbed on the electrode, which is not the case for unsymmetrical system (Figure 4). Indeed, results of TD-DFT calculations suggest that the *cis* isomer have the largest absorption in that energy region (Table 4ESI), thus an increase in absorbance would be associated to an increase in the concentration of the *cis* isomer. Analogous results have been recently obtained for the theoretical analysis of the bis(indolenine) squaraine spectral lineshapes.[26]

Table 1 and Figure 5 report photovoltaic performances obtained with the three dyes. Best results from optimized devices showed $J_{sc}$ exceeding 14 mA/cm$^2$, $V_{oc}$ over 620 mV and corresponding efficiencies of 6.18, 6.11 and 5.50% with **VG10–C2**, **VG10–C8** and **VG13** respectively (Table 1). The effect of CDCA[27] addition on the photocurrent is manifest, for the three dyes, in the incident photon–to–current efficiency (IPCE), where a dramatic increase is shown (Figure 5b). The efficiency improvement, highlighted in the presence of co–adsorbent, is higher for the symmetrical systems due to the evident gain in $J_{sc}$ between 400 and 500 nm (see Figure 5b). Due to this particular behaviour, surprisingly both symmetrical dyes result significantly more efficient than the unsymmetrical reference system.

**Table 1.** *J-V* characteristics of **VG10–C2, VG10–C8** and **VG13** sensitized solar cells as CDCA concentration.

| Dye | CDCA (mM) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (mV) | Fill Factor | η (%) |
|---|---|---|---|---|---|
| VG10–C2 | 0[a] | 8.60 | 544 | 0.67 | 3.11 |
| | 10[a] | 14.3 | 623 | 0.69 | **6.18** |
| | 2.5[b] | 13.3 | 617 | 0.71 | 5.81 |
| VG10–C8 | 0[a] | 8.81 | 585 | 0.64 | 3.28 |
| | 10[a] | 13.6 | 641 | 0.70 | 6.10 |
| | 2.5[b] | 14.0 | 634 | 0.69 | **6.11** |
| VG13 | 0[a] | 8.74 | 567 | 0.62 | 3.10 |
| | 10[a] | 12.1 | 665 | 0.68 | **5.50** |
| | 2.5[b] | 12.6 | 640 | 0.68 | 5.44 |

a: 0.1 mM dye concentration. b: 0.025 mM dye concentration. All devices were measured 1 day after being assembled.
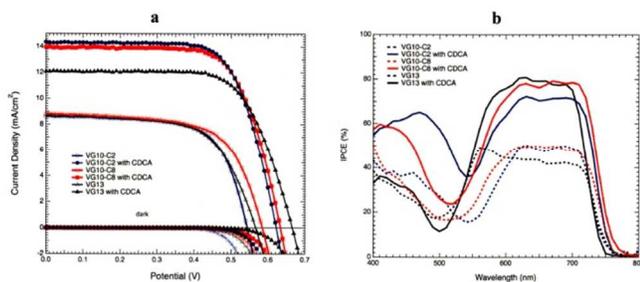


**Figure 5.** a) *J-V* characteristics of **VG10–C2, VG10–C8,** and **VG13** DSCs: **VG10–C2**, **VG10–C8** and **VG13** without and with CDCA. Dotted lines with markers indicate dark currents of devices. b) IPCEs of **VG10–C2**, **VG10–C8**, and **VG13** DSCs: **VG10–C2**, **VG10–C8** and **VG13** without and with CDCA.

Particularly interesting and in line with our previous results[13], unsymmetrical system shows the highest voltage while symmetrical ones the highest current. Moreover, the effect of the length of the chain is also reflected in the $J_{sc}$ and $V_{oc}$ parameters yielding a higher $V_{oc}$ for long chains and slightly higher current for the short ones. A transient study confirmed

that the solar cells in presence of CDCA show increases in the electron lifetime, by one order magnitude, which is in agreement with previous studies[28] (Figure 8aESI). Hence, the higher $V_{oc}$ of **VG10–C8** sensitized solar cell in presence of CDCA is attributed to the enhanced electron lifetime. All chemical capacitances of devices nearly overlap (Figure 8bESI) and this result implies that there is upward or downward shift movement of the TiO$_2$ conduction band (CB) edge. Therefore, the higher $V_{oc}$ of **VG10–C8** compared to those of **VG10–C2** is most likely due to an increase in electron lifetime owing to the presence of a long alkyl chain. The non-obvious behaviour of the symmetrical dyes in presence of CDCA at high energy wavelength can be attributed to the different conformation on the surface, as anticipated from DFT calculation and experimental results on electrode absorption. These features highlight the significance of fundamental studies on sensitizers conformation.[29]

Stability of organic sensitizers, NIR dyes in particular, is still a great challenge in DSC technology.[30] To our knowledge stability reported data on squaraine dyes[10, 15b] used a 420 nm cut–off filter to prevent dye degradation, highlighting that photostability is the main issue for NIR dyes. In our case, looking at the photostability of the different synthesized squaraines directly on the photoelectrode, we realized that symmetrical squaraines are more stable than the corresponding unsymmetrical, even without a cut–off filter, probably due to the dibranched structure. Moreover, as it is evident in Figure 9ESI, also the presence of a benzoindolenine moiety and long chains have a role in the stability of the molecule on the TiO$_2$ surface. Intrigued by these results we also tested the thermal stability (figure 10ESI) that confirm the same behavior. These attractive and promising outcomes deserve an in–depth study to confirm the structure/property relationship.

## Conclusions

We molecularly engineered a series of near–IR squaraine sensitizers (**VG10** and **VG13**), containing the novel benzoindolenine moiety functionalized with COOH as efficient attaching group. These dyes show panchromatic light harvesting in the range between 400 to 800 nm. The obtained efficiency of 6.2%, is an outstanding value considering the easy and efficient low cost synthesis. We note symmetric squaraines show 10% higher efficiency than the corresponding unsymmetrical one, mainly due to the higher photocurrents, derived from the adopted *cis* conformation on the electrode surface, as confirmed by spectroscopic data and TD_DFT computational analysis. The first photo and thermo stability data reveal superior behavior of **VG10** symmetrical molecules. This study opens up a new avenue to a large number of optimized symmetrical squaraine structures.

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## Notes and references

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† The electrode potential of the redox couple is reported to be 0.35 V vs. NHE (*Bull. Chem. Soc. Jpn.*, 1988, **61**, 1735) and $Fc^+/Fc$ is reported as 0.63 V vs. NHE in DMF (*J. Phys. Chem.*, 1972, **76**, 243).

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

2   a) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595; b) Y. Cao, Y. Bai, Q. Yu, Y. Cheng, S. Liu, D. Shi, F. Gao and P. Wang, *J. Phys. Chem. C*, 2009, **113**, 6290; c) W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan and P. Wang, *Chem. Mater.*, 2010, **22**, 1915.

3   A. Yella, H.-W. Lee, H. Nok Tsao, C. Yi, A. K. Chandiran, Md.K. Nazeeruddin, E. Wei-Guang Diau, C.-Y. Yeh, S. M Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629.

4   a) J. Park, G. Viscardi, C. Barolo and N. Barbero, *Chimia*, 2013, **67**, 129; b) C. Barolo, J.-H. Yum, E. Artuso, N. Barbero, D. Di Censo, M. G. Lobello, S. Fantacci, F. De Angelis, M. Grätzel, Md. K. Nazeeruddin and G. Viscardi, *ChemSusChem*, 2013, **6**, 2170; c) J.-H. Yum, T. W. Holcombe, Y. Kim, K. Rakstys, T. Moehl, J. Teuscher, J. H. Delcamp, M. K. Nazeeruddin and M. Grätzel, *Sci. Rep.*, 2013, **3**, 2446.

5   a) A. Mishra, M.K.R. Fischer and P. Bäuerle, *Angew. Chem, Int. Ed.*, 2009, **48**, 2472; b) M. Liang, J. Chen. *Chem. Soc. Rev.*, 2013, **42**, 3453.

6   (a) D. P. Hagberg, J.-H. Yum, H. Lee, F. De Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Grätzel and Md. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2008, **130**, 6259; (b) C. Olivier, F. Sauvage, L. Ducasse, F. Castet, M. Graetzel and T. Toupance, *ChemSusChem*, 2011, **4**, 731.

7   E. Artuso et al., Scaling Up of Dye Solar Cells for Building Integrated PhotoVoltaics (BIPV), 28th EU PVSEC, 30 September **2013**, Paris (France).

8   J.-H. Yum, E. Baranoff, S. Wenger, M. K. Nazeeruddin and M. Grätzel, *Energy Environ. Sci.*, 2011, **4**, 842.

9   L. Beverina and P. Salice, *Eur. J. Org. Chem.*, 2010, **7**, 1207.

10  S. Paek, H. Choi, C. Kim, N. Cho, S. So, K. Song, M. K. Nazeeruddin and J. Ko, *Chem. Commun.*, 2011, **47**, 2874.

11  Y. Shi, R. B. M. Hill, J.-H. Yum, A. Dualeh, S. Barlow, M. Grätzel, S. R. Marder and M. K. Nazeeruddin, *Angew. Chem. Int. Ed.*, 2011, **50**, 6619.

12  J. H. Delcamp, Y. Shi, J.-H. Yum, T. Sajoto, E. Dell'Orto, S. Barlow, M. K. Nazeeruddin, S. R. Marder and M. Grätzel, *Chem. Eur. J.*, 2013, **19**, 1819.

13  a) J. Park, C. Barolo, F. Sauvage, N. Barbero, C. Benzi, P. Quagliotto, S. Coluccia, D. Di Censo, M. Grätzel, Md. K. Nazeeruddin and G. Viscardi, *Chem. Commun.*, 2012, **48**, 2782; b) I. Venditti, N. Barbero, M.V. Russo, A. Di Carlo, F. Decker, I. Fratoddi, C. Barolo and D. Dini, *Mater. Res. Express*, 2014, **1**, 015040.

14  A. Abbotto, N. Manfredi, C. Marinzi, F. De Angelis, E. Mosconi, J.-H. Yum, Z. Xianxi, M. K. Nazeeruddin and M. Grätzel, *Energy Environ. Sci.,* 2009, **2**, 1094.

15  a) T. Maeda, S. Mineta, H. Fujiwara, H. Nakao, S. Yagia and H. Nakazumi, *J. Mater. Chem. A*, 2013, **1**, 1303; b) C. Qin, Y. Numata , S. Zhang, X. Yang, A. Islam, K. Zhang, H. Chen and L. Han, *Adv. Funct. Mater.*, 2014, **24**, 3059.

16  A. Burke, L. Schmidt-Mende, S. Ito and M. Grätzel, *Chem. Commun.*, 2007, 234.

17  a) T. Geiger, S. Kuster, J.-H. Yum, S.-J. Moon, M. K. Nazeeruddin, M. Grätzel and F. Nüesch, *Adv. Funct. Mater.*, 2009, **19**, 2720; b) C. Magistris, S. Martiniani, N. Barbero, J. Park, C. Benzi, A. Anderson, C. Law, C. Barolo and B. O'Regan, *Renew. Energ.*, 2013, **60**, 672; c) S. Martiniani, A. Y. Anderson, C. Law, B. C. O'Regan and C. Barolo, *Chem. Commun.*, 2012, **48**, 2406.

18  J. J. Krutak, W. W. Parham, C. A. Jr. Coates, T.A. Oldfield, W. P. Pruett, S. D. Hilbert and M. A. Weaver, (Eastman Kodak Co., USA), US  5030708, 1991.

19  Barbero et al. submitted

20  T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.

21  R. Borrelli, A. Copobianco and A. Peluso, *J. Phys. Chem. A*, 2012, **116**, 9934.

22  R. Improta, V. Barone, G. Scalmani and M. J. Frisch, *J. Chem. Phys.*, 2006, **125**, 1.

23  J.-H. Yum, P. Walter, S. Huber, D. Rentsch, T. Geiger, F. Nüesch, F. De Angelis, M. Grätzel and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2007, **129**, 10320.

24  P. Salice, J. Arnbjerg, B. W. Pedersen, R. Toftegaard, L. Beverina, G. A. Pagani and P. R. Ogilby, *J. Phys. Chem. A*, 2010, **114**, 2518.

25  R. W. Bigelow and H. J. Freund, *Chem. Phys.*, 1986, **107**, 159.

26  R. Borrelli, S. Ellena and C. Barolo, *Phys. Chem. Chem. Phys.*, 2014, **16**, 2390.

27  J.-H. Yum, S.J. Moon, R. Humphry-Baker, P. Walter, T. Geiger, F. Nüesch, M. Grätzel and Md. K. Nazeeruddin, *Nanotechnology*, 2008, **19**, 424005.

28  J.-H. Yum, S.-R. Jang, R. Humphry-Baker, M. Grätzel, J.J. Cid, T. Torres and Md. K. Nazeeruddin, *Langmuir*, 2008, **24**, 5636.

29  V. Gianotti, G. Favaro, L. Bonandini, L. Palin, G. Croce, E. Boccaleri, E. Artuso, W. van Beek, C. Barolo and M. Milanesio, *ChemSusChem*, 2014, DOI: 10.1002/cssc.201402194.

30  C. Chen, X. Yang, M. Cheng, F. Zhang and L. Sun, *ChemSusChem*, 2013, **6**, 1270.

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