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Polymethine dyes in hybrid photovoltaics: structure-properties relationships

Davide Saccone,^{‡,[a]} Simone Galliano,^{‡,[a]} Nadia Barbero,^[a] Pierluigi Quagliotto,^[a] Guido Viscardi^[a] and Claudia Barolo^{*[a]}

[a] Department of Chemistry and NIS Interdepartmental Center
University of Torino
Via Giuria 7, I-10125 Torino, Italy
E-mail: claudia.barolo@unito.it

‡ These authors equally contributed to this work.

Supporting information for this article is given via a link at the end of the document.

Abstract: Polymethine dyes as photosensitizers for Dye-sensitized Solar Cells (DSCs) are reviewed. The review provides a summary on design strategies, main synthetic routes and optical and photovoltaic properties of polymethine dyes applied in hybrid photovoltaics. In particular, we focused our attention on cyanine and squaraine dyes and their structure-properties relationship, hence highlighting the role of the active molecule design on the device performances.

1. Introduction

Polymethine dyes have been used for the first time in 1873 by Vogel^[1] to sensitize silver halide materials and since early 1920s they have been historically applied in imaging & recording, photographic film development, bio-imaging and printing.^[2–5] Nowadays, this class of dyes still gains a lot of interest in different research fields, including ion and molecular sensors,^[6,7] non-linear optics,^[8,9] photodynamic therapeutical applications (PDT),^[10–12] organic photovoltaics (OPV)^[13–15] and Dye-sensitized Solar Cells (DSCs).^[16,17]

This paper will critically review the use of polymethine dyes in hybrid photovoltaics, i.e. DSCs. The operating principles of this technology are deeply described in two recent reviews on this journal, by Ooyama and Harima^[18] and Manfredi et al.^[19], therefore here we will focus directly on the structure-property relationship between photosensitizers and cell performances.

In a DSC system the photosensitizer has a crucial role, being the component responsible for the solar light harvesting. In order to accomplish this function, some requirements are needed: i) a panchromatic absorption (400 – 920 nm); ii) high molar extinction coefficient; iii) appropriate matching with the energy levels of the semiconductor and the redox mediator; iv) a stable grafting on semiconductor surface; v) high chemical and photo-chemical stability; vi) easy and tunable synthesis with a high efficiency/cost ratio. Different classes of photosensitizers have been proposed so far, ranging from inorganic nanostructures (e.g. quantum dots)^[20] to the more standard organo-metallic,^[21] and organic^[22,23] molecules. However it is difficult to find a sensitizer fulfilling all the above-mentioned requirements. For examples, metal-organic complexes generally show panchromatic absorptions but with low molar extinction coefficients,^[24] while the deeply studied D- π -A organic dyes^[25] have opposite characteristics with narrower absorptions in the visible region. Therefore in this scenario, polymethine dyes can play an important role for their intense absorption in the far red/NIR region.^[26]

2. Polymethine dyes

Polymethines are planar, conjugated, open-chain (sometimes ring) systems of sp²-hybridized carbon atoms (=CH—) with an odd number of methine groups and an even number of π electrons according to the general formula:^[1,27–31]



n = 1,3,5...; R = H or substituents; X and X' = terminal chain atoms (e.g. N,O,P,S) or atom groups (e.g., NR₂, CH=O).

This class of sensitizers, being total organic compounds, is characterized by high absorption coefficients, easy-tunable properties by synthesis and narrow absorption peaks. Among polymethine dyes, this review will be focused on cyanine-type chromogens like cyanines themselves and squaraines. These structures are very interesting for photovoltaic applications since they can harvest near infra-red (NIR) light and convert low-energy frequencies from solar irradiation thanks to their intrinsic structures. In fact Cyanine-type chromogens are characterized by an electronic symmetry that allows a low energy first electronic transition. Symmetrical dyes have equal energy hybrid resonance structures allowing bond equalization, whose length and energy are intermediate between single and double bonds. On the contrary for non symmetric structures, one resonance structure is energetically favored over the others, so the more the hybrid resonance structures are different, the more the dyes will lose peculiar cyanine-type characteristic and acquire charge-transfer characteristics. The edge is represented by merocyanine and hemicyanine^[32] structures that are polymethine dyes for definition, but they have to be considered donor-acceptor chromogens by a theoretical point of view. Moreover these sensitizers, only in very particular case, are able to exceed 700 nm.^[33] For these reasons merocyanines and hemicyanines will not be treated in this review.

Another class of sensitizers that can be considered as cyanine-type polymethines is the croconate dyes, or croconines. This class is characterized by a molecular structure containing an oxyallyl subunit that allows the absorption of NIR light.^[34,35] However to our knowledge, croconate dyes have been rarely used for DSCs application^[36,37] and only one work is reported in literature.^[38] For this reason, this class will not be treated in this review.

NIR conversion is indubitably interesting in order to widen solar harvesting and tune the colours of final devices, in fact at least 25% of the solar light available on earth surface is composed by red/NIR frequencies. Of course, the current conversion expected from red/NIR region (600-1000 nm) is lower with respect to visible region (350-700 nm).^[39]

As regards cyanine sensitizers, the position of the absorption maxima ranges from the near ultraviolet to the near infra-red and embraces a very large portion of electromagnetic spectrum. The color depends most critically on the length of the cyanine bridge and on the nature of the heterocyclic termini.

2.1. Heterocyclic intermediates

A great number of heterocyclic moieties have been used in the synthesis of polymethine dyes, e.g. pyrrolium, pyridinium quinolinium, indolinium, benzoindolinium, benzoxazolium, thiazolium, benzothiazolium and thiazolinium.^[29,40] For DSCs applications, one of the most used heterocycle is represented by dimethylindolenine (Fig. 1) probably due to the higher photostability and the better match of energy levels.^[41] Indolenine derivatives are usually prepared from reaction between para-substituted phenyl hydrazine and 3-methyl-butan-2-one through Fisher mechanism (Figure 1).^[42]

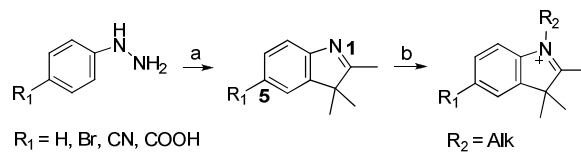


Figure 1. General synthesis of substituted indolenines through Fisher mechanism. a) 3-methyl-butan-2-one in acetic acid; b) alkyl halides in acetonitrile.

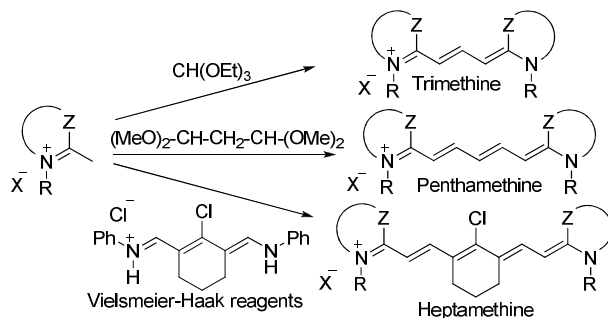
The required grafting group, which allows the binding with the semiconductor surface, is usually introduced in position 1 or 5. Position 1 is generally functionalized through the reaction with alkyl halides^[43] (Fig. 1) and sometimes can also form supramolecular structures with other co-sensitizers, as proposed by Etgar et al.^[44] Usually, for a fast and cheap synthesis, unsubstituted indolenines ($R_1 = \text{H}$ in Figure 1) and 5 carboxy indolenines ($R_1 = \text{COOH}$ in Figure 1) are the most used building blocks. Moreover, starting from para-substituted hydrazines, it is possible to obtain indolenines with different groups in position 5. For example, bromine can be exploited for coupling reactions such as Buchwald-Hartwig or Suzuki for diarylamine^[45] or heteroaryl substitutions,^[46] respectively, while cyano groups can be reduced to aldehydes and then modified through a Knoevenagel reaction, leading to cyanoacetic derivatives.^[47]

As far as the polymethine bridge is concerned, it can greatly influence physical, chemical and optical properties of the dye molecules and it is the structural motif discriminating cyanines from squaraines. For this reason, this topic will be discussed in more details in the following paragraphs.

2.2. Cyanines

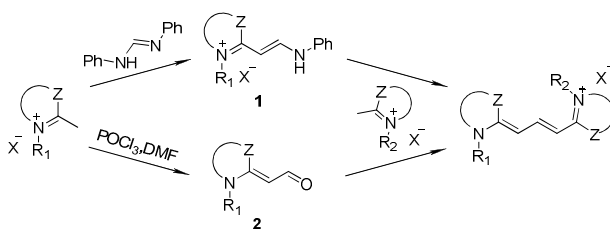
Cyanines (Cy) are cationic molecules in which the nitrogen atoms of two heterocyclic nuclei are linked by a chain of conjugated double bonds, so that this chain necessarily consists of an odd number of carbon atoms. Each compound is therefore regarded as a resonance hybrid of two structures.^[1,48] Cyanine general structures are reported in Figure 2 and their names depend on the number of methine groups in the bridge connecting the two heterocycles (Scheme 1).

Generally, cyanines absorb in visible and NIR region and they can be easily tuned by modifying polyene chains, nitrogen substituents or heterocycles themselves. Except for monomethine structures, the preparation of a symmetric cyanine implies the condensation of quaternary heterocyclic salts, substituted with an activated methyl group, with aldehyde derivatives. Depending on polymethine length, aldehyde derivatives can be represented by orthoesters, malondialdehydes and Vielsmeier-Haak reagents (derived from cyclohexanone) respectively for trimethine (Cy3), pentamethine (Cy5) and heptamethine (Cy7)^[49] cyanines (Scheme 1).



Scheme 1. General synthesis of symmetric cyanine dyes.

Unsymmetrical cyanines can be achieved by a multistep process following the hemicyanine method or the aldehyde method^[50] (Scheme 2).



Scheme 2. Synthesis of unsymmetrical cyanines through

hemicyanine (1) and aldehyde (2) intermediates.

The first one is analogous to the procedure used for symmetric cyanines synthesis, but with different condition of temperature and reagent ratio, in order to obtain a "half-dye" (1 in Scheme 2). Then in a second step, this intermediate reacts with another heterocyclic quaternary salt to achieve the unsymmetrical cyanine. The main drawback in this case is the formation of the symmetrical structure. On the contrary, the aldehyde method concerns the use of methine source reagents with a heterocyclic quaternary salt, in order to obtain an aldehyde (2 in Scheme 2). Subsequently, a second quaternary heterocyclic salt reacts with this intermediate to give the desired unsymmetrical structures. Methine sources depend on the final desired polymethine length. For example, thioethers are used for monomethine carbocyanines, POCl_3 with DMF for trimethine dyes, tetraethoxypropane for pentamethine ones and 1-(dimethylamino)-5-formyl-1,3-butadiene for heptamethines.

General methods and reagents for cyanines preparation have been recently reviewed by Henary - Leviz^[50] and Panigrahi et al.,^[27] including the use of microwave (MW) reactions.^[51,52]

Typically cyanines suffer from undesired phenomena such as molecular aggregation^[53] (see Paragraph 3.4) and photoisomerization. In particular, the *cis/trans* photoisomerization is one of the major side decay pathways of the excited state for methine dyes, affecting the photovoltaic performances. Interesting synthetic improvements have been proposed to prevent it: lengthening^[54] or functionalization^[55] of the polymethine bridge or increasing the steric hindrance of terminal groups by bulky heterocyclic subunits or long alkyl chains.^[56]

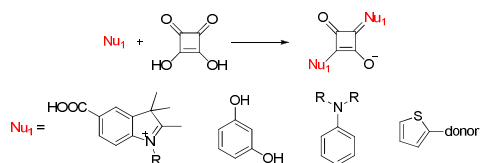
2.3. Squaraines

Squaraine (SQ) dyes can be rationalized within a composite-molecule approach, in which SQ are viewed as Cy bearing an O^- substituent at the *meso* position and a $\text{C}=\text{O}$ substituent bridging the *meso* -1 and the *meso* +1 positions. The *meso* substitutions have opposite effects on molecular orbitals, leading to a close similarity of the HOMO-LUMO transition energies between squaraines and the corresponding cyanines.^[28,57] According to this theory, SQ can be considered as pentamethine cyanines with a four member ring on the methine bridge.^[58-60] This "rigid" squarainic bridge blocks the methine chain towards photoisomerization and oxidation, resulting in a greater inherent stability, compared to cyanines. Minimizing the photoisomerization by squaraine moiety on the bridge, improved electron charge injection and overall photovoltaic performances have been achieved.^[61]

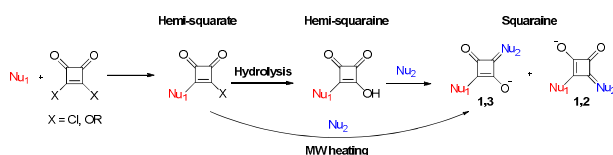
Like cyanines, thanks to Vis-NIR light absorption, easy synthesis, large structural variety and substitution patterns, squaraines are widely used as sensitizers to harvest photons at low frequency. Another main difference with cyanine structures is represented by their overall neutral charge.

The basic structure is formed by a cyclobuten-2,4-dione core conjugated in position 1,3 to two aromatic moieties. First of all, as for cyanine dyes, squaraines can have symmetrical or unsymmetrical structures. Then, we can distinguish between two families which differ from the presence of a methine spacer between the squarainic core and the lateral substituents.

The synthesis of symmetrical squaraines is easier being a one step condensation reaction where two equivalents of the same electron-rich molecule react with squaric acid, generally in polar solvents or high boiling point alcohol (Scheme 3). On the contrary, the synthesis of unsymmetrical structures requires more steps starting with the formation of the hemi-squarate by the condensation of the first electron-rich moiety with a large excess of squaric acid or squaric acid derivatives (such as diethyl squarate or squarylium chlorides) (Scheme 4). The following steps consist in the hydrolysis of the hemi-squarate and the condensation of the second electron-rich molecule.^[58] However, the second step can also lead to 1,2 substituted squaraine, as impurities.

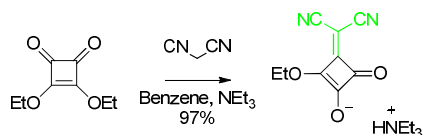


Scheme 3. Synthetic pathway to achieve symmetrical squaraines.



Scheme 4. Synthetic pathway to achieve unsymmetrical squaraines.

Squarate core can be also modified by exchanging one carbonyl on the cyclobutene ring through a Knoevenagel reaction.^[62] Malononitrile is a very used modifying agent as described in Scheme 5, that allows to maintain narrow band gap and tune HOMO – LUMO energy levels.^[63]



Scheme 5. Example of Knoevenagel reaction to modify the squaric core^[64].

Not many considerable innovations have been carried out since the reviews focused on this topic by Beverina et al. in 2010^[58] and 2014^[59] and Hu et al.^[65] in 2013. One of the few improvements about squaraine synthesis is the use of MW heating, in order to speed up reaction time and increase yields. As recently reported by our group,^[66] by exploiting MW heating, it is possible to minimize the need of anhydrous condition and to improve synthetic pathways. Thus, formation of indolenine from hydrazine, quaternization of indolenine nitrogen (as reported also by Winstead et al.^[43]), squaraine formation and even further reaction on the formed squaraine (such as coupling on Br squaraines) have been improved thanks to MAOS (Microwave Assisted Organic Synthesis), that also allows us to reduce reaction steps, avoiding hemisquarate hydrolysis before the unsymmetrical squaraine formation (Scheme 4). The ease of preparation and the possibility of providing a good amount of pure dyes in a short time could lead to the achievement of a large variety of novel structures that can be easily tested in technological applications. Moreover even the synthesis of standard squaraines has been improved in matter of reaction time. For example, the nucleophilic addition on hemisquaraine (Scheme 4) can be done in just few minutes with respect to several hours required by classical thermal heating. We strongly believes that MAOS technology will ease research on this topic and help synthetic efforts to achieve desired structure in less time and better yields.

3. Structure-property relationships

In recent years, squaraine and cyanine sensitizers have attracted great interest in photovoltaic applications due to their simple synthesis and favorable optical and electrochemical properties. An increasing number of novel structures has been proposed in different laboratories all over the world, each one following different theories and synthetic routes. Qin et al.^[67] in 2013 and Jiang et al.^[68] in 2014 have reviewed the application of polymethine dyes in photovoltaic cells following the two excellent general reviews on the design and synthesis of organic dyes in DSCs of Mishra et al.^[22] and Ooyama et al.^[18] in 2009. Nevertheless the identification of the leading principles is lacking. In this scenario, it appears necessary to identify the principles that can guide the molecular design and define the main engineering strategies, in order to increase spectral absorption, photovoltaic performance and stability in DSCs. Therefore, analyzing the literature, we tried to enlighten recent developments about polymethine dyes and identify correlations between molecular structures and device's performances. In order to minimize as much as possible component variables and to report more reliable observations, only dyes that differ for a single structural modification have been compared (i.e. different anchoring moieties or alkyl chain length or donor groups etc...). It is noteworthy that a lower number of cyanine dyes have been studied and published throughout the years with respect to squaraine ones. Consequently, only few structural modifications related to cyanine chromophores have been reported and evaluated in this review. However where it was possible, both squaraine and cyanine structure-property relationships have been evaluated. In these cases, the same behaviors have been observed. Moreover, to have a better understanding of structure-properties relationships, materials^[69] and preparation conditions of devices are also taken into account and reported. In fact, DSCs are a complex multivariate system^[25], with different components and variables, and the only evaluation of the molecular structures and efficiencies can lead to wrong conclusions. For this reason, analogous dyes or series of them can show different, even opposite, behaviors and performances simply by changing characteristics or parameters of the cells. In the following paragraphs the main properties that are influenced by modification of molecular structures are discussed. In order to help the reader, dye structures and performances are reported in Table 1 in the Supporting Information and referred here with the number of the entry ["S#"].

3.1. Increasing orbital coupling between dye and semiconductor

Kamat and co-workers^[70] were the first to investigate the sensitization behavior of squaraine dyes, in 1993, using bis(2,4-dihydroxyphenyl)squaraine **[S1]**. Successively, Zhao et al.^[71] **[S2-4]** (A in Fig. 2) and Sayama et al.^[72] **[S5]** (B in Fig. 2) investigated the effect of different anchoring groups on quaternarized indolenines. On the contrary, Cao's group^[73] **[S9-12]** (C in Fig. 2) worked on aniline-based squaraines with carboxylic moieties (COOH), as anchoring groups. They showed an increase in IPCE and performance, shortening the length of non conjugated alkyl chain and consequently the distance between chromophore and semiconductor.

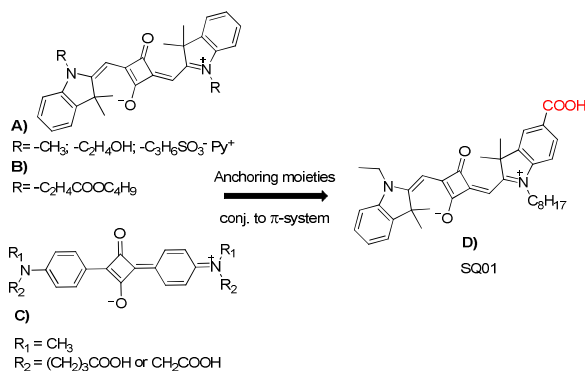


Figure 2. Investigation of different grafting moieties proposed by (A) Zhao et al.,^[71] (B) Sayama et al.,^[72] (C) Cao et al.^[73] and (D) Yum et al.^[74]

The first breakthrough was reached in 2007 when Yum et al.^[74] **[S13]** reported a very interesting 4.5% efficiency with an unsymmetrical squaraine coded SQ01 (D in Fig. 2). A carboxylic acid group was directly attached to the conjugated π -system of the dye. In this way, HOMO-LUMO transition moves the excited electron to acid moiety, anchored on the semiconductor providing a strong electronic coupling between LUMO and conduction band (CB) of TiO₂ layer, significantly increasing charge separation and electron injection. This demonstrated that one of the most important features to fulfill for a dye in DSC application is the ability to form a strong and stable interaction with semiconductor metal-oxide. This effect was also confirmed in 2012 by Yan et al.^[75] with quinoline-based symmetrical squaraines (Fig. 3). When COOH anchoring groups are directly conjugated to quinoline structure **[S15]**, the photocurrent doubles and the overall efficiency increases three times, compared to unconjugated analogous **[S14]**.

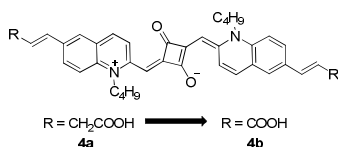


Figure 3. Structures proposed by Yan et al.^[75].

The same structural improvement can be observed on cyanine class. For example, Ehret et al.^[76] reported anchoring moieties not conjugated to the chromophoric structure, while Guo et al.^[77] investigated a series of cyanine dyes with anchored moieties conjugated to the chromophoric structure. Even if these molecular modifications have not been directly compared on cyanine homologous, the same guide-lines observed with squaraines seem to be valid.

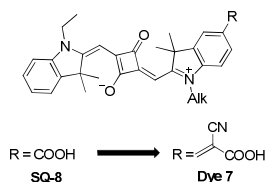


Figure 4. Structures proposed by Hayase et al.^[78].

Different grafting moieties were reported in effort to strengthen the linkage between the dye and the semiconductor surface, to increase their orbital coupling and consequently the electron injection. Moreover the grafting group is responsible of the desorption of the dye from the semiconductor caused by the electrolyte solution. So this modification appears interesting in order to increase the long term stability of the DSCs and also to develop different solvent-based electrolytes.^[79]

As already reported in other classes of organic dyes, one of the most interesting alternative to COOH is the cyanoacetic (CA) group,^[18,22] exhibiting pronounced spectral broadening and enhancement in the photoconversion efficiency. In 2012, Hayase's group^[78] reported a study on unsymmetrical SQ-dye showing that the replacement of a carboxylic [**S18**] (**SQ-8**) with a cyanoacetic [**S19**] (**Dye7**) group greatly increases photocurrent (from 6.4 to 11.5 mA/cm²) and efficiency (from 2.8% to 5.0%) (Fig. 4). Moreover, a small red-shift of absorption peak and a lowering HOMO-LUMO energy levels also occur.

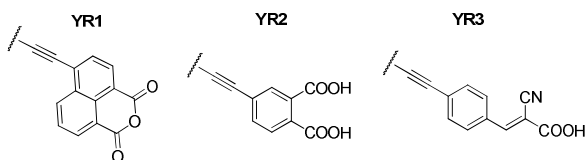


Figure 5. Modifications on SQ01 structure by Delcamp et al.^[80]

Meanwhile, Delcamp et al.^[80] compared cyanoacetic acid [**S23**] (**YR3** dye) with two different binding groups: a naphthalene anhydride (NA) [**S21**] (**YR1** dye) and a phthalic acid (PA) [**S22**] (**YR2** dye) moiety (Fig. 5). Also in this case, CA anchorage demonstrated a significant improvement in η value from about 1% to about 3.5%, through a large gain (about 5 mA/cm²) in photocurrent, also reflected in IPCE spectra.

Finally, in a recent study reported by Jradi et al.^[81] [**S26**, **S28-34**] on a series of unsymmetrical thiophene-based squaraines, cyanoacetic grafting group is compared to cyanophosphonic moiety (CP) (Fig. 6). Electrical impedance measurements showed that CP based dyes may exhibit a slower charge recombination rate between injected electrons and electrolyte, than their CA counterparts. However, femtosecond transient absorption spectroscopy showed that going from CA to CP based dyes, charge injection efficiency is reduced and dye aggregation is increased, yielding lower and narrower IPCE and hence efficiency.

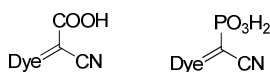


Figure 6. Cyanoacetic (CA) and cyanophosphonic (CP) moieties tested by Jradi et al.^[81]

3.1.1. Symmetric vs unsymmetrical structures

Another molecular modification, which can improve orbital coupling and strengthen dye–SC interaction, is the increase of the number of anchoring groups.^[82] This strategy was adopted since the first studies on DSCs with squaraines and cyanines (Rui Xiao's,^[71] Arakawa's^[72] and Cao's^[73] groups [S2-12]), with symmetrical dianchored dyes. Only in 2005, a series of SQ-dyes with symmetrical and unsymmetrical structures were directly compared in cell by Alex et al. [S11, S35-40] (Fig. 7).^[83] They stated that unsymmetrical dyes showed higher photocurrent and efficiency than symmetrical homologous, thanks to the more efficient charge separation. Moreover cell performances of symmetrical dyes are significantly affected by aggregation on semiconductor surface. The unsymmetrical system can be considered as a hybrid of the two relative symmetric structures and if the electron releasing ability of the terminal nitrogen atoms were identical, they should show no bond alteration. If on the other hand, the two terminal nitrogen atoms of the unsymmetrical dye had appreciable different basicities, the electronic symmetry would be lost and bond alternation would become apparent. This must lead to absorption at shorter wavelength with respect to electronically symmetrical systems, known as Brooker deviation.^[40]

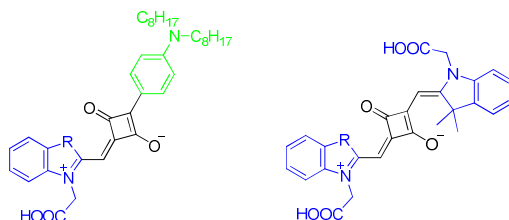


Figure 7. Symmetrical and unsymmetrical structures compared by Alex et al.^[83]

Also in 2010, Pandey et al. observed better performances with alkyl and fluoro-alkyl unsymmetrical squaraine dyes. In particular a symmetrical dye, coded **SQ-A**^[84] or **SQ-3**^[85] (or SQ-1^[86]) [S43], showed lower photocurrent and efficiency when directly compared to its mono anchored analogous (**SQ-D**^[84] or SQ-4^[85]) [S18]) (Fig. 8). The conclusion was that the attachment of an anchoring group in the aromatic ring and the creation of an unsymmetrical molecule facilitate the effective electron injection from photoexcited dye to the conduction band of TiO₂, thanks to unidirectional charge flows, enhancing photovoltaic performance. However, it is observed that addition of CDCA in dipping solution, as coadsorbent, increases efficiencies but it also reduces the difference in performance between the two dyes. This indicates that suppressing the aggregation of symmetrical dyes it is possible to obtain comparable performance with unsymmetrical ones but exploiting easier synthetic pathways.

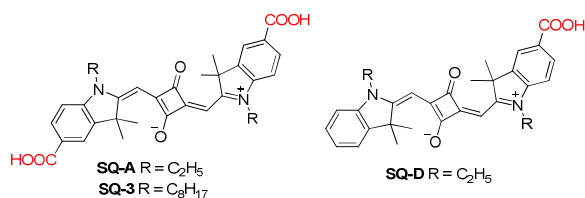
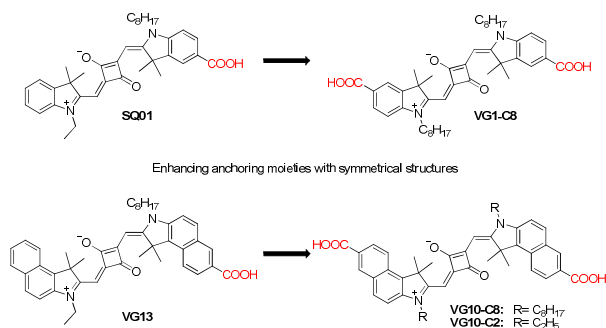


Figure 8. Dianchored and monoanchored homologous tested by Pandey et al.^[84-86]

This was confirmed by our group, first in 2012^[87] and then in 2014,^[88] reporting better efficiencies with symmetrical structures. In particular, **VG1-C8** [S47] in addition with CDCA (until 20 mM) reached a 4.6% efficiency,^[87] comparable with its unsymmetrical standard **SQ01** [S13] ($\eta = 4.2-4.5\%$). A more interesting result was obtained with homologous benzoindolenine dyes, coded VG10.^[88] By increasing the concentration of CDCA, up to 100 times the dye, the aggregation was suppressed and the performances enhanced, reaching a remarkable 6.2% with **VG10-C2** [S50] and **VG10-C8** [S51] (Figure 9). These results exceed over 10% the efficiency of unsymmetrical homologous dye **VG13** [S52] ($\eta = 5.5\%$) and, actually, are the record efficiencies for NIR low cost symmetric sensitizers. Moreover, symmetrical dyes with two anchoring groups show a slight bathochromic shift of the main absorption peak and higher stability (Fig 9). VG1 and VG10 structures have been tested also with ZnO semiconductor showing comparable photocurrent but lower voltage with respect to TiO₂ electrode.^[89]



Viscardi and coworkers (top,^[87] bottom^[88]).

Figure 9. Unsymmetrical and symmetrical structures compared by

Also Maeda et al.^[90] reported a symmetric dicyanovinylene substituted dye (**SQM1a**) [**S53**], bearing two carboxy groups, with increased J_{sc} (14.2 mA/cm²), and efficiency (3.6%), in comparison with mono-anchored homologous **SQM1b** [**S54**] (J_{sc} = 10.3 mA/cm²; η = 2.9%) (Fig. 10 **A**). Similar results were reported by Han's group^[63] on cyano ester substituted squaraines. The dianchored **HSQ4** [**S57**] exhibited a remarkable efficiency (5.66%), 23% better than the mono-anchored **HSQ3** [**S56**] (4.60%), thanks to increased photocurrent density (15.6 mA/cm²) and fill factor. It is noteworthy that in this case, short time of dipping bath in absence of coadsorbent is reported. Moreover, the HSQ4 sensitized solar cell demonstrated an excellent durability under light soaking (with appropriate electrolyte), which is ascribed to the double anchors and the suppression of photoisomerization (Fig 10 **B**).

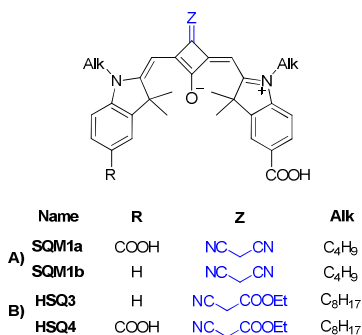


Figure 10. Examples of central substituted squaraines proposed by Maeda et al.^[90] (A) and Han et al.^[63] (B).

These results highlight that by doubling anchor groups the interaction with semiconductor surface increase, leading to higher photocurrent. Moreover, the conformational locking of squaraine dyes in the cis-like form resulted in an increase of the fluorescence quantum yield (ϕ_F) and electron lifetime (τ), thereby reducing the non-radiative decay rates. On the contrary, a slightly decrease in photovoltage occurred, probably due to higher charge recombination between dye and TiO₂. However, these evidences increase the interest in symmetrical SQ-dyes, in addition to their easier synthesis and better stability on the semiconductor surface.

Even for *p*-type DSCs, two structures are compared by Chang et al.^[91] [**S133,134**] in order to test the best way to anchor the sensitizer. Looking at cell performances, unsymmetrical squaraines with two grafting point gave better charge injection and overall efficiency with respect to mono-anchored analogous.

3.2. Extending spectral absorption

Another advantage of central substituted squaraines is the broadening of the absorption spectrum, as reported for the first time by Beverina et al. [**S60**] (Fig. 11).^[92,93] In fact, a merocyanine-like oscillator coming from the delocalization of the negative charge between the oxygen atom and the malononitrile moiety allows to increase absorption at higher energy (400-500 nm).

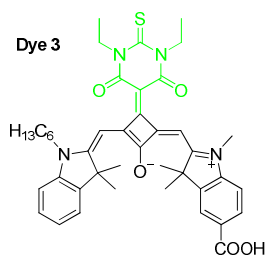


Figure 11. Central substituted squaraine proposed by Beverina et al.^[92]

According to this theory, Maeda^[90] and Han^[94] investigated in 2013 dicyanovinyl and cyanoester substituted squaraines, respectively. In comparison to their non-functionalized homologous (MSQ **[S17]** and SQ01 **[S13]**), central substituted dyes (SQM1b **[S54]** and HSQ1 **[S58]**) exhibited bathochromic shift of absorption spectra (over 50 nm) with the additional second peak at higher energy (400-500 nm), which is reflected in increased IPCE signals. Furthermore, the central substitution forces the molecule in *cis* conformation thanks to steric hindrance and avoids energy loss resulting from photoisomerization. These factors increase mainly the photocurrent densities and the final efficiencies are improved by 30%.

Several other ways to achieve a wider light absorption have been tested in past years, above all extending the π -conjugated delocalization of sensitizers. Firstly, Burke et al.^[95] **[S61]** in 2007 tested benzoindolenine moiety instead of indolenine. Other works followed this thought extending π -conjugation^[96,97] **[S63,64]**, then Geiger and co-workers^[98] synthesized an unsymmetrical squaraine (SQ02 **[S62]**) with extended absorption in the red region, achieving 5.4% efficiency.

Another strategy, proposed by Kuster et al.^[99] (Fig. 12) **[S66]** and then by Maeda and co-workers,^[100,101] **[S67-71]** is to use more than one squarainic core on the same structure. In general the absorption spectra are red-shifted of about 100 nm for each conjugated squarainic ring and TSQ dyes reach 850 nm with improved photocurrent and efficiency. Waman and co-workers tested, both for *n*-type^[102] **[S73,74]** and *p*-type^[103] **[S135,136]**, DSCs multichromophoric sensitizers to obtain panchromatic dyes.

A further strategy to widen absorption has been proposed by Maeda et al.^[104] **[S75-78]** incorporating strongly electron-accepting components, like tetracyanoquinodimethane, via non conjugated linkage.

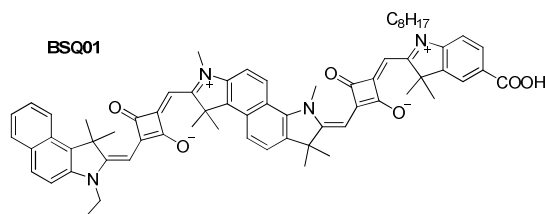


Figure 12. Dye with two squarainic rings proposed by Kuster et al.^[99]

3.2.1. Bathochromic shift

One of the goals in polymethine research applied on DSCs is not only to extend absorption in order to harvest more photons, but specially to capture and convert light in infra-red (IR) and near-IR (NIR) region.^[39] Moreover, it is difficult to harvest this portion of solar irradiation with other classes of dyes and hence to produce blue-greenish devices, desired by architects and market, as recently reviewed by Park et al.^[39] This can be also exploited for co-sensitization and tandem cells. For these reasons, bathochromic shift is commonly searched in dye's absorption to develop NIR sensitizers. This spectral shift has been observed with different structural modifications, above all extending π -conjugation, functionalizing squarainic ring or doubling anchor group. The heterocyclic components could provide an extra-chromophoric conjugation (i.e. outside the fundamental chromogen) that causes a bathochromic shift. Sensitizers based on dimethylindole and benzothiazole heterocycles have comparable absorption and emission wavelengths, while benzoxazole-containing dyes absorb at shorter wavelengths.

Concerning the π -conjugation extension, cyanine-type structures are considered symmetrical electronic systems and hence have a peculiar non-convergent wavelength behaviour. In particular, each extension of chromophore with one vinylene moiety (-CH=CH-) causes a linear bathochromic shift of about 100 nm (Figure 13), as first observed by König in 1925 and so-called vinylene shift.^[28,30,105] This evidence is one of the main differences between polymethine and D- π -A dyes, which instead show a convergent behaviour with a limited achievable absorption wavelength.^[29]

Also in DSCs, the vinylene shift is exploited to achieve bathochromical absorption as reported by e.g. Sayama et al. in a series of cyanines [S6-8].^[72]

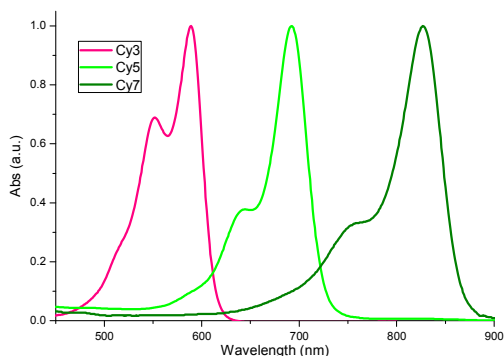


Figure 13. Examples of absorption spectra of tri- (Cy3), penta- (Cy5) and hepta- (Cy7) methine cyanines.

Nowadays, the most “NIR-sensitizers” are represented by cyanines reported in 2009 by Ono et al.^[106] [S79,80], with absorption peaks over 820 nm (Figure 14 A). Other heptamethine structures have been proposed by Geiger et al.^[107] [S81-87] with a series of unsymmetrical cyanines that have maximum absorption around 800 nm.

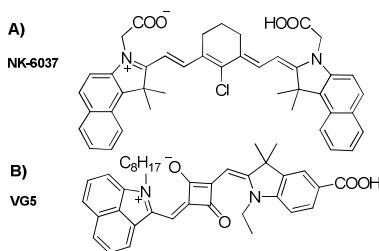


Figure 14. NK-6037 heptacyanine proposed by Ono et al.^[106] (A) and VG5 squaraine designed by Magistris et al.^[108] (B).

We proposed another example of a near infrared squaraine VG5 (Figure 14 B) [S65],^[108,109] that showed IPCE of 36% at 800 nm with a standard TiO₂ layer. Concerning squaraines, several structural modifications led to a bathochromic shift, such as the use of symmetrical structures^[88] (as reported in paragraph 3.1.1) or by exchanging heterocyclic components. Maeda et al.^[110] [S88-91] used electron rich heterocyclic components instead of indolenines and Kim et al.^[111] [S92,93] tested two different thioindolenines.

3.3. Optimizing electronic distribution

A further key feature in sensitization is the electronic distribution of different energy levels of dyes. An ideal sensitizer should have electron density in fundamental state (HOMO) far away from the semiconductor (SC) and, when irradiated, should move it to excited state (LUMO) as near as possible to the SC. This ideal behavior is not easily achievable with a squarainic structure because it is not a classic push-pull system and the squaraine core is a strong withdrawing group. This implies that the LUMO lies on the squaraine core far away from the SC and this evidence rose several questions about excitation mechanism involving probably a HOMO-LUMO+1 transition for electron injection. By the way, the debate about squaraine sensitization's theory is still open, while empiric data show good performing cells with structures far away from the “ideal charge-transfer electronic distribution”. Even if squaraines do not answer to common push-pull theory, several works had the goal to increase the strength of withdrawing and donor groups and to extend π -bridge, in order to space out HOMO-LUMO electron density localizations (Figure 15).

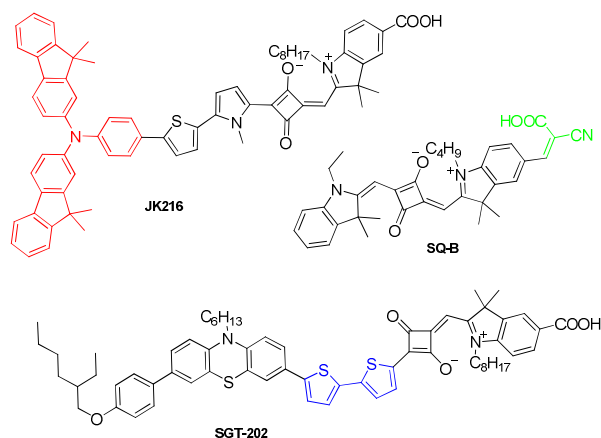


Figure 15. Examples of optimized electronic distribution by: increased donor strength (JK216), risen withdrawing strength (SQ-B) and widen π -bridge (SGT-202).

3.3.1 Tuning energy levels

Due to the working principle of the device, not only the HOMO-LUMO localizations are important but also their energy levels in comparison to the quasi-Fermi level of the SC and the redox potential of the electrolyte mediator (typically I^+/I_3^-). The gap between the *quasi*-Fermi level of the semiconductor and the redox potential of the electrolyte couple, that can be considered as the theoretical V_{OC} , represents the physical limit to the bathochromic shift of the sensitizer, because solar conversion of smaller energy transitions is thermodynamically forbidden. HOMO-LUMO levels are crucial to obtain a good driving force in the injection process and a fast re-oxidation of the dye by the electrolyte. As for polymethine dyes, we commonly consider small band-gap between HOMO and LUMO levels. If on one hand, the small band-gap allows to harness NIR irradiation, on the other hand it reduces the driving force for electron injection or dye oxidation because NIR transitions are closer to the physical limit discussed above. Therefore, small band-gap polymethine dyes are not the right choice if you are just trying to improve photovoltaic efficiency, by the way this class is one of the few that can cover low energetic irradiation.

Concerning polymethine dyes, the close similarity of the HOMO-LUMO transition energies of SQ and the corresponding CY should derive from the fact that, for symmetry reasons, the two substitutions on the methine chain cause opposite effects on molecular orbitals. The *meso*-donor O^- raises the HOMO, stabilizing the excited state, while the acceptor $C=O$ lowers this orbital by virtue of the predominant HOMO-LUMO interaction, stabilizing the ground state.^[28,57] HOMO-LUMO energy positions are determined by the entire structure, and a key role is represented by aryl rings attached to the polymethine bridge. For example a series of heptamethine dyes reported by Matsui et al.^[112] [S94-100] showed increased driving force regeneration and increased efficiency in this series: benzothiazine < benzoxazine < benzoindolenine (Fig. 16).

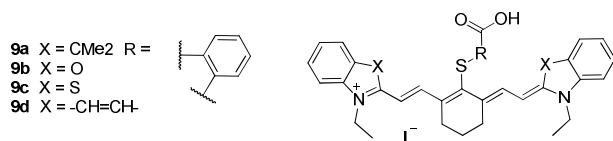


Figure 16. Cyanines reported by Matsui et al.^[112]

The same conclusions can be found for squaraines as recently reported by Maeda et al.^[113] [S101-104] that attributes low performances of pyrylium and thiopyrylium squaraine dyes to high lying HOMOs and thus weaker driving force regeneration (Figure 17).

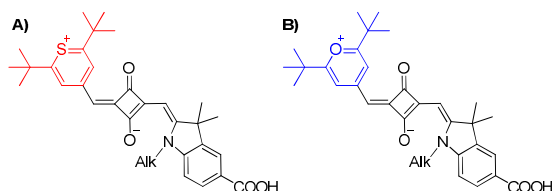


Figure 17. Thiopyrylium (A) and pyrylium (B) squaraines reported by Maeda et al.^[113]

In agreement with Fabian and Hartmann,^[28] also the modification of the carbonyl group (C=O), with a central substitution on the squaric ring, causes HOMO energy variations. In particular, the substitution with electron withdrawing groups lowers the HOMO energy, hence stabilizing it. This was confirmed by the central substituted SQs proposed by Maeda et al.^[90]: the dicyano substitution **[S53,54]** increases the energy oxidation potential (E_{ox}^0) of about 0.1 V compared to the analogues unsubstituted squaraine **[S17]**,

3.3.2 Donor groups

Several research groups designed SQ structures following standard rules of push-pull dyes, attaching electron donor moieties to unsymmetrical dyes far away from the squarainic core. For example, in 2010 Ko and co-workers^[114] **[S105-107]** designed and tested unsymmetrical squaraines containing bulky spirobifluorene units and suggested that the relative high efficiency can be explained as a good match of vectorial electron flow from the HOMO to the LUMO. They noticed wide absorption thanks to a hump in IPCE, caused by the donor group and reduced recombination when hexyl alkyl chains are inserted in donor moieties. Working on these structures, the same group reached in 2011 a new record efficiency of 6.29%,^[115] **[S108,109]** thanks to a further improvement in extended absorption and suppressed aggregation. However these results are comparable to symmetric VG10 performances,^[88] obtained with thinner TiO₂ layer, discrediting the push-pull theory. By the way, JK series (Fig. 18) gives several hints on squaraine aggregation, CDCA effect and reduced recombination, that are crucial to understand the improvement recently obtained, on this topic, by Marder's group.^[81]

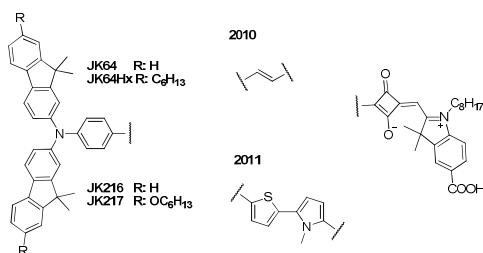


Figure 18. Some structures proposed by Jaejung Ko and co-workers in 2010^[114] and 2011.^[115]

At the same time, Li et al. in two separate papers presented different SQ structures bearing hexyloxyphenyl amino donor moieties. Firstly in 2010,^[116] **[S110,111]** they proposed squaraines which are optimized for panchromatic sensitization of DSCs using the electron-rich 3,4-ethylenedioxythiophene (EDOT) and bithiophene (BT) fragments for improving the light-harvesting capacity. Then in 2012,^[117] **[S112,113]** near-infrared harvesting properties of EDOT based squaraine were further extended by changing indolenines with quinoline heterocycles (Fig. 19).

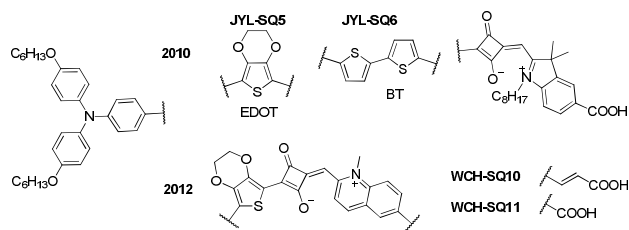


Figure 19. Structures reported by Li et al. in 2010^[116] and

2012.^[117]

Recently, Liu et al.^[118] **[S114-116]** reported different structures featured by diphenylamino donor groups and observed bathochromical shifts and reduced recombination with respect to SQ01.

The same modification has been introduced also in cyanines, in particular unsymmetrical trimethines, by Hua and co-workers in three different papers (Zhan et al. in 2007^[119] **[S117,118]**, Ma et al. in 2008^[120] **[S119,120]** and Wu et al. in 2010^[121] **[S121,122]**) (Fig. 20). Unfortunately, even if a good work on synthesis has been reported, just the last paper can be used for structure-property relationship because the others did not report a proper characterization (unreported TiO₂ thickness, unconventional lamp and impressive high J_{sc} reported). The behavior of these dyes seem to follow the same conclusions taken for squaraines.

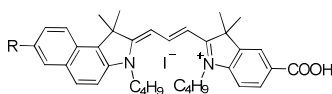


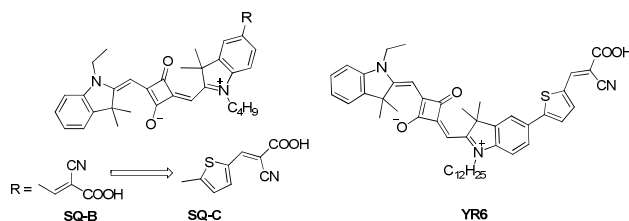
Figure 20. Structures proposed by Hua and co-workers in 2007,^[119] 2008^[120] and 2010.^[121] See SI for the complete structures.

Summarizing the results found in literature for polymethine dyes, the presence of a donor group far away from grafting moieties can help to increase light harvesting properties or reduce dye aggregation and charge recombination. However, the searched unidirectional electrons flow has been just hypotized from theoretical calculation and need to find empirical evidences which have to be confirmed experimentally. Moreover comparing these structures with the simplest one, such as SQ01, electron injection seems not to be so improved because J_{sc} is still comparable, considering the broader light harvesting due to the donor group.

3.3.3 Withdrawing group and π -bridge extension

As already stated, we cannot consider polymethine dyes as push-pull systems. By the way, we could consider half of the dye structure, from the SQ core or the cyanine bridge to the grafting moieties, tunable as a separate system. In this way, even if the chromogen is still a cyanine-type, we could improve the electron charge injection working on half of the dye, as a donor-acceptor system. Thus it is possible to help electrons to move far away from the core to the grafting moieties, by the combination of stronger and stronger withdrawing groups with larger and larger π -bridge. As mentioned, the chromogen-core will remain the same so these modifications will not lead to a bathochromic shift. Subsequent improvements in the device will be ascribed to better IPCE at comparable wavelengths or additional absorption at higher energies, thanks to a new more energetic transition band. Unfortunately this molecular design is not enough to exploit desired NIR region.

Some experimental evidences have already been shown in paragraph 3.1 referred to Hayase group^[78] and Delcamp et al.^[80] In fact, cyanoacetic anchoring moiety is a stronger withdrawing and longer π -spaced with respect to COOH. Hayase and co-workers further investigated in 2014 the possibility of enhancing the π -bridge^[47] **[S19,20]** adding a thiophene between the anchoring moiety and the indolenine (**SQ-B** and **SQ-C** in Fig. 21). Unfortunately, the presence of thiophene lowered all the cell performances.



et al.^[46]

Figure 21. Thiophene π -bridge used by Hayase et al.^[47] and Shi

The same structure modification was proposed for the first time by Marder's group,^[46] but using longer alkyl chain on the indolenine (dodecyl instead of butyl). The dye proposed (**YR6 [S26]**, see Fig. 21) allowed to reach unprecedented conversion efficiency of 6.74%. Bae et al.^[122] have recently reported unsymmetrical structures with increased " π -space" between donor group and squaraine core **[S123-126]** (Fig. 22).

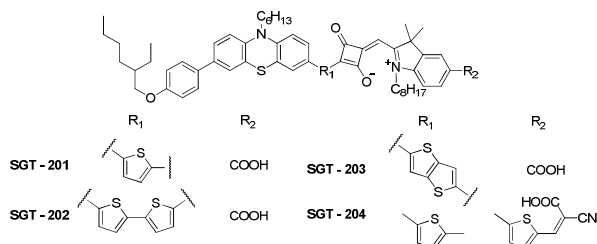


Figure 22. π -bridge extensions tested by Bae et al.^[122]

As a result, the most performing structures carry the smaller π -bridge and the performances decrease with longer distances. Even if results among dyes are comparable we can suppose that π -bridge is more useful when placed

between the dye core and titania. These evidences are in agreement with the “non push-pull dye” behavior and in disagreement with linear electron flow, which until now brought literature to prefer unsymmetrical squaraines with respect to symmetrical ones.

3.4. Decrease recombination and dyes aggregation

The improvement obtained from **SQ01** [S13] to **YR6** [S26] and to **JD10** [S27] (Fig. 23) has not to be attributed simply to a larger π -bridge but it is ascribed to a lower dark current and dye aggregation on the semiconductor surface. This consideration has brought the same group to a further improvement in the structure using bulky 2-ethylhexyl chain next to anchoring groups (**DTS-CA** in Fig. 23 [S33]). These moieties allow to reach an impressive short circuit current (19 mA/cm²) and so a new efficiency record of 8.9% has been recently reported for polymethine dyes in DSC^[81].

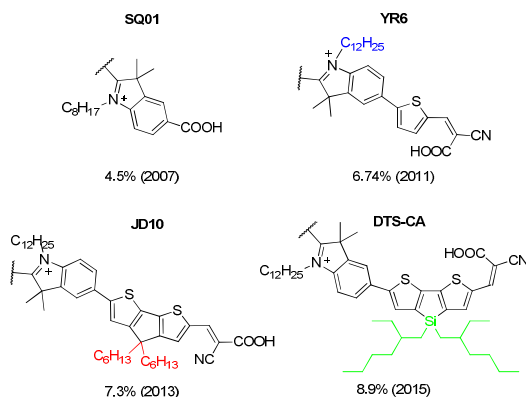


Figure 23. Historical records and progressive hindrance increase of alkyl chain moieties.

The structures summarized in Figure 23, as well as several other papers that evaluated alkyl substitutions on indolenine nitrogen (Pandey et al.^[86] in paragraph 3.1 [S43,S45-49]) or even more hindered groups (like JK series in paragraph 3.3.2), demonstrated that increasing hindrance can achieve good performances. This is due to a worst aggregation among different molecules and at the same time a better coverage of the semiconductor surface. As result, a lower recombination of injected electrons with electrolyte and less self quenching of excited states is observed. These features led to an overall increase in charge injection and to better J_{sc} , commonly low for organic dyes if compared to Ru-complexes^[24]. It is noteworthy that improved efficiencies are correlated with better IPCE in the same spectral region, in fact (as reported in paragraph 3.3.3) the chromogen-core has not been modified. So, more efforts on this topic are still required to improve NIR light conversion.

Another way to reduce aggregation has been proposed by Funabiki et al. [S127,128].^[123] Comparing two heptamethines they reported higher J_{sc} for the cyanine synthesized starting from 2-methyl-3,3-dibutylindolenine respect to 2,3,3-trimethylindolenine (Fig. 24).

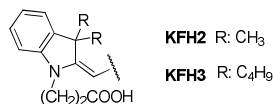


Figure 24. Indolenines reported by Funabiki et al.^[123]

The same group also reported in 2012 two squaraines substituted with the same hindered heterocycle [S129,130] in order to avoid the use of π -spacing groups.^[124]

The importance of aggregation phenomena for this class of dyes is further witnessed by studies on interactions and effect of the use of coadsorbent (i.e. CDCA), during the sensitization procedure. Therefore it will be important for the next research on this topic to consider anti-aggregation coadsorbents for cells optimization.

3.5. p-type design

p-type Dye-sensitized Solar Cells (*p*-DSCs) are based on the sensitization of a wide-band-gap *p*-type semiconductor (i.e. NiO, CuAlO₂), therefore the rules for sensitizers design are inverted with respect to classic *n*-type DSCs. In fact, in

these devices the excited dye has to inject holes from HOMO to the valence band of a *p*-semiconductor.^[125] So the common electron density distribution of squaraines should be more suitable for this kind of sensitization. Even if few structures of polymethine *p*-type sensitizers have been proposed in the past, this class is really interesting thanks to NIR harvesting properties. Development of an efficient NIR *p*-type device would fit with TiO₂ - Ru-complex sensitized anode in order to develop efficient tandem cells. Despite the possibilities to overcome the Shockley-Queisser limit, progresses are still limited by tiny charge collection of *p*-semiconductors that causes mismatching between hole collection and high electron injection in *n*-SC that leads to inefficient tandem devices.^[125]

Mori et al.^[126] were the first who proposed polymethines as *p*-sensitizers [S131,132]. Comparing different cyanines they noted increased performances with higher driving force injection with lower HOMO energy levels. In 2012 Chang et al.^[91] designed non-symmetric squaraines with an inverted electronic distribution in order to help hole injection [S133,134]. They used a triphenylamino moiety carrying the grafting groups in order to push away the electron once taken from the SC (Figure 25). Moreover, they noted better performances with a multi-grafted structure with respect to a mono-anchored one.

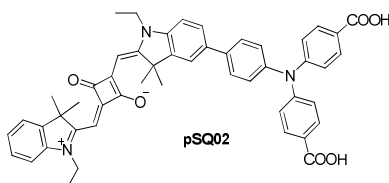


Figure 25. Inverted electronic distribution proposed by Chang et al.^[91]

In 2014, Waman et al.^[103] used squaraines as energy sink component into an energy cascade multichromophoric system and demonstrated through a photophysical study that a simple iodo-squaraine is not sufficiently spatially separated from the NiO surface to maintain a significant lifetime of the radical anion [S135,136].

Also our group spent efforts on *p*-type topic. First of all, the same structures used as *n*-sensitizers have been tested in *p*-type devices, obtained by screen-printed NiO.^[127] VG1-C8 [S47], VG10-C8 [S51], and DS2/35 [S137] were compared on different NiO substrates. The latter structure ([S137] Fig. 26 top) has been designed in the attempt to further increase the anchoring group of pSQ02 [S134] proposed by Chang et al.^[91] From DS2/35 we developed a novel family of *p*-type squaraines comparing symmetric and unsymmetrical structures proving a new guideline for the design of new squaraines [S138-141]. pVGCN4 ([S141] Fig. 26 bottom) showed more interesting results. In fact, dicyano central substitution freezes *cis*-configuration and showed increased surface coverage of NiO semiconductor. This feature reduced recombination with respect to unsubstituted squarainic core homologues which show either *cis/trans* equilibrium.^[45]

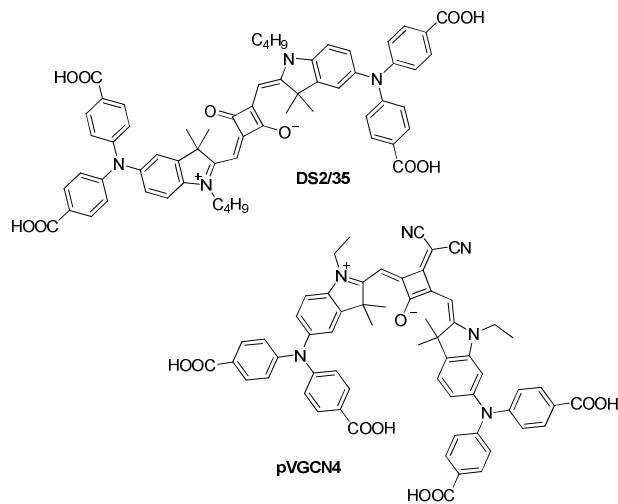


Figure 26. *p*-type squaraines structures which show either an

cis/trans equilibrium (DS2/35) or a frozen *cis* structure (pVGCN4).

3.6. Co-sensitization

Even if polymethine dyes show good performances in DSCs, it is clear that it is extremely tricky to design a single sensitizer with efficient absorption from the visible to the NIR region fulfilling all the requirements necessary to obtain very efficient devices. However, it is possible to design and develop NIR-efficient dyes and to combine them with other sensitizers having different and complementary spectral responses.^[128] Generally, co-sensitized solar cells exhibit extended spectral coverage, showing a greater photocurrent than single dyes and accordingly is expected to exhibit superior performances and efficiencies. For this reason and thanks to their harvesting properties, polymethines are widely investigated in cocktails with more performing red sensitizers. For example, Ru-based dyes, which can be considered as the most common sensitizers in this application, have been mixed with polymethines that can cover lower energy. Qin et al.^[94] mixed N3 dye with two squaraines (SQ01 **[S13]** and HSQ1 **[S58]**) enlarging IPCE over 700 nm. The co-sensitized cells showed increased photocurrents and greater efficiencies than single dye cells: the N3-HSQ1 cocktail achieved $\eta = 8.14\%$. Also Holliman et al. deeply investigated the co-sensitization of SQ01 with N719, testing different soaking conditions and procedures.^[129,130] In particular they achieved an efficiency of 7.9% with a fast soaking in concentrated solution of N3, SQ01 and CDCA. They also reported three-dyes cocktails to improve energy conversion at high frequencies.^[130,131]

Other interesting co-sensitizations are represented by cocktails of only organic sensitizers. Examples of coupled cyanines with a complementary absorption are reported by Ehret et al.^[132] and Guo et al.^[77] For squaraine dyes, noteworthy is to mention the cocktails of D35 with JD10 for solid state^[133] and classic liquid cell,^[80] JK2 with SQ01^[134,135] (or adding also Al₂O₃ layers^[136]) and HSQ5 **[S59]** with Y1 coadsorbent.^[137] Also for *p*-type DSCs, a co-sensitization study on inverted squaraines and P1 chromophore is reported, showing intermediate efficiencies between the individual dyes.^[138]

Other works reported a multi sensitization with more than two dyes to further increase absorption capability and fully cover the 400-700 nm range. Chen et al.^[139] mixed a yellow merocyanine, a red hemicyanine and a blue squaraine achieving 6.3% efficiency. More recently, Cheng et al.^[140] selected three cyanines and tested different sequences and times of TiO₂ adsorption. Under optimal conditions, IPCE increased to 80% in the visible region, with a near doubling in photocurrent ($J_{SC} = 20.1 \text{ mA/cm}^2$) and the power conversion efficiency reaches 8.2%. Meanwhile, Graf et al.^[141] tested squaraine-triphenyldiamine cocktails on solid state DSCs, achieving $\eta = 2.4\%$.

Another type of co-sensitization is the use of inorganic semiconducting quantum dots (QDs) which can absorb energy from NIR to visible region. QDs have attracted attention for their tunable physical and optical properties, controlled by the size-shape ratio of QD particles.^[20] Moreover, they can generate multiple excitons from absorption of a single photon, through an impact ionization mechanism, called multiple exciton generation (MEG effect).^[142,143] Following the idea of built-in QD antennas in DSCs, proposed by Zaban and coworkers,^[144] we reported an example designing a hybrid QDs/dye-sensitized solar cell where donors were CdSe-QDs and the acceptor was a symmetric squaraine (VG1-C10 **[S44]**) in Figure 27).^[44] Exploiting Förster resonance energy transfer (FRET), all photovoltaic parameters are enhanced and the final power conversion efficiency increased by almost 50% compared to SQ-cell. Also Kamat and coworkers investigated the co-sensitization between QDs and squaraine dyes (JK216 **[S108]** and SQSH **[S42]**) enabling the harvesting of NIR light.^[145,146]

All these data show that the co-sensitization is an interesting and promising way to achieve panchromatic and high efficient solar cells, even if some drawbacks still need to be overcome (*i.e.* QD particles degradation when combined with standard I⁻/I₃⁻ redox mediator).

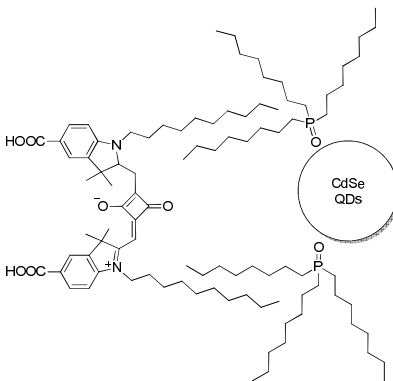


Figure 27. QDs/DSCs reported by Etgar et al.^[44]

4. Summary and outlook

This review has summarized polymethine dyes used so far for DSCs applications. The work has been focused on cyanine-type chromogens highlighting differences with respect to donor-acceptor chromogens like the possibility to harness NIR spectrum. We pointed out that by only comparing dyes structures and efficiencies would drive to wrong conclusions because the sensitizer is just one tiny part of a complex device in which also the semiconductor structure, the electrolyte composition, additives and cell assembling have strong influence on performances. Therefore, just looking at all the data collected in the past by different groups cannot bring to the assumption that one dye is better than another but literature survey allows to show up some trend that can suggest a structure-property relationship for future developments.

First of all in polymethinic dyes, squaraines seem to be an ideal choice thanks to their inherent stability, respect to their cyanine analogues. In these dyes the methine chain is stabilized towards photoisomerization and oxidation by the "rigid" squarainic moiety. However, cyanines and in particular heptacyanines allow to reach low energy absorption being interesting for NIR light conversion.

Among different characteristics, a crucial role is surely represented by aggregation and SC surface coverage. For these reasons, *antiaggregant* co-adsorbent concentration, optimization and design of structures, that can minimize self-aggregation, are fundamental to reach good performances. Moreover the dye must form a strong and stable interaction with the semiconductor surface commonly achieved using carboxylic or cyanoacetic grafting group.

When polymethines were treated as simple push-pull dyes, the design of new molecules not always led to the expected cell performance increase, as it has been shown by Li^[16] and Choi^[15] groups, that used stronger electron donor group to increase the "push strength" of the dye. On the other hand, Shi et al.^[46] and Delcamp et al.^[80] had shown that by increasing the space from the anchoring moieties to the squaraine core leads to a better performance. So the best location of anchoring moieties seems to be far away from squaraine core, bound by conjugate system and "covered protected" by a long alkyl chain. Finally, the prevalent use of unsymmetrical structures is still not justified by experimental evidences. In fact, when properly tested, symmetric structures showed comparable performances but better stability, along with easier and low cost synthesis. Noteworthy they can provide more bathochromical light absorption, particularly interesting to obtain high performance co-sensitized DSCs.

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