

Symmetrical and unsymmetrical squaraine sensitizers for dye-sensitized solar cells: Present day advances and future challenges

Sultan A. Al-horaibi, S.T. Gaikwad, Anjali S .Rajbhoj*

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, Maharashtra 431001, India

*Corresponding author

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Abstract

The requirement for energy is ever increasing in the past few years due to the need for the innovation of clean energy and eco-friendly technologies. Symmetric and asymmetric SQ-dyes have received increasing attention and great potential for use as SQ-sensitizers for application in dye sensitized solar cells (DSSC). This review article gives a synopsis of the advancements on SQ-sensitizers in the domain of DSSC and the chance used to enhance their overall energy conversion efficiency. Specifically, the primary factors in charge of the low values of open-circuit voltage (V_{oc}) short-circuit photocurrent (J_{sc}) and fill factor (FF) are debated in detail. Future orientations in research and expanded absorptions of near-infrared region (NIR) by development organic substances and their applications are suggested from a personal point of view. Copyright © 2018 VBRI Press.

Keywords: Dye-sensitized solar cell; symmetric and asymmetric squaraine dyes; energy conversion.

Introduction

Solar radiation is the plentiful source of energy on earth. Dye sensitized solar cell is one of promising clean energy sources due to the sun which supplies about 120,000 TW of energy to the earth's surface, that means 6,000 times more than the current rate of the world's energy exhaustion. The traditional silicon cells that rely on solar cells are not preferred largely due to the higher cost of production and effective manufacturing techniques. Dye sensitized solar cells (DSSC) have acquired considerable attention because of its environmentally friendly nature, attractive appearance, low cost, ease of manufacture, flexible and it doesn't need to complex fabrication procedures. In 1991, Gratzel and O'Regan presented the notion of low cost, high efficiency DSSC by relying on the mesoporous nanoparticles of TiO_2 [1]. Since the time of, a large number of organometallic and organic dyes which were utilized in DSSC have been designed [2-3] and in a tried endeavor to manufacture solar cells with expand power diversion efficiencies (PCEs) [4]. DSSC have been used tremendous in the previous decade because their potential use in low-cost output of renewable resource and in large-area, colourful, lightweight device [1]. In 1965, Tribes et al [5], first reported about squaraine dyes. Squaraine dyes sensitizers are one of the potential filters due to their sharp and intense absorption to light in near infrared and visible region. They essentially endure a donor- acceptor-donor

(D-A-D) zwitterionic molecular structure having squaric acid center as acceptor. SQ-dyes have wavelength that can be begun from visible light spectrum to near infrared wavelength region relying on wise molecular design with various donor-moieties to extended π -conjugation [6]. DSSC are built of a SQ-dye absorbed broad band gap semicon -ductor such as titanium dioxide (TiO_2) or Zinc oxide (ZnO), liquid electrolyte containing the iodide/triiodide (I/I_3^-) redox, and a Pt-coated counter electrode [7-14], (**Fig.1**). The electron injection into the TiO_2 and dye renewal with hole transport to the redox couple, called sensitizer in DSSC which is one of the most critical component to for the light harvesting and the charge separation process [15].

In the near-IR region the photoelectric conversion efficiency of DSSC is insufficient, so moreover studies are needed to develop new sensitizers to improve light-harvesting in full area of the spectra of sunlight, including visible and NIR regions [16]. Squaraine dyes (SQ) are viewed as one of the best substitutes between the different Ru-free organic dyes available. They have higher molar extinction coefficients and much cheaper Ru-free organic dyes (e.g. extension coefficient of squaraine is $\sim 3 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$) [17-19], than conventional dyes (Ru complexes is $\sim 1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) [20]. They have ability to absorb photons with a long wavelength from 500 to 700 nm. In addition, SQ-sensitizers are utilized to aggregate very easily on the TiO_2 surface, which diminish the solar cell efficiency [21, 22] and their absorption band is very tight

compared to Ru-complexes [17-19]. It will be huge challenge to evolve novel SQ-sensitizers in enhancing and generation of high efficiency DSSC.

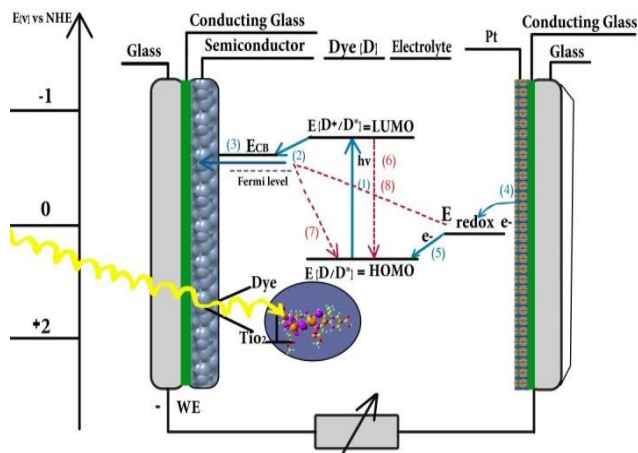


Fig.1 The processes in operational DSSC. Blue arrows indicate beneficial processes and red arrows indicate undesired losses.

Squaraine structures for Dye-sensitized solar cells

SQ-dyes were initially applied in ZnO photoconductors, non-linear optics, and optical data storage [23].

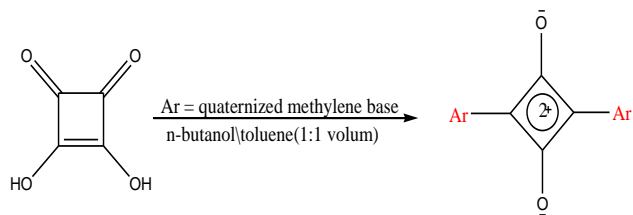
Kamat and co-workers were observed that the initially to investigate the sensitive behaviour of SQ-sensitizers for the cells structure by utilizing these sensitizers had a very low incident photon-to-current transference efficiency [24].

In 1999 Zhao et al introduced symmetrical squaraine as sensitizers dyes in DSSC [25].

Since 2010 there has been wide attention in utilizing SQ-dyes as sensitizers dyes in dye-sensitized solar cells.

Symmetrical squaraine dyes as sensitizers

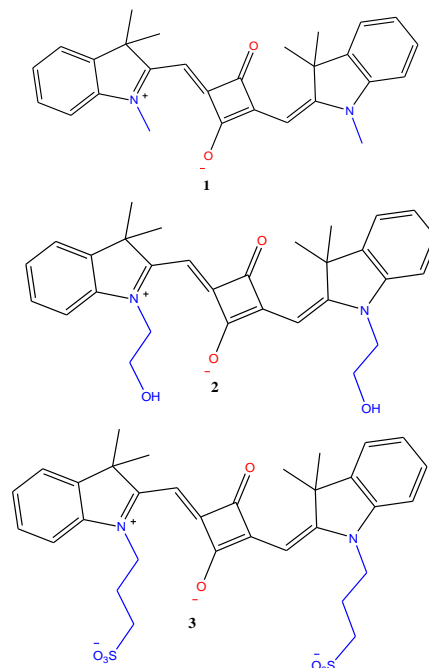
Symmetric SQ-sensitizers are synthetic via intensification of one equivalent of 3,4-dihydroxy -cyclobut-3-ene-1,2-dione (squaric acid) with two equivalents of a quaternized methylene base such as 2-(N-methyl-N-phenylamino) acetic acid and 2-methylbenzo[d]thiazole, indole derivatives (**Scheme 1**). Structure can be achieved by using various precursors of a quaternized methylene base with squaric acid.



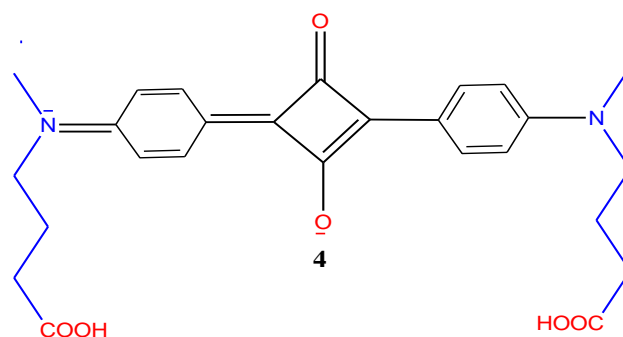
Scheme 1. General method procedure for symmetrical squaraine sensitizers.

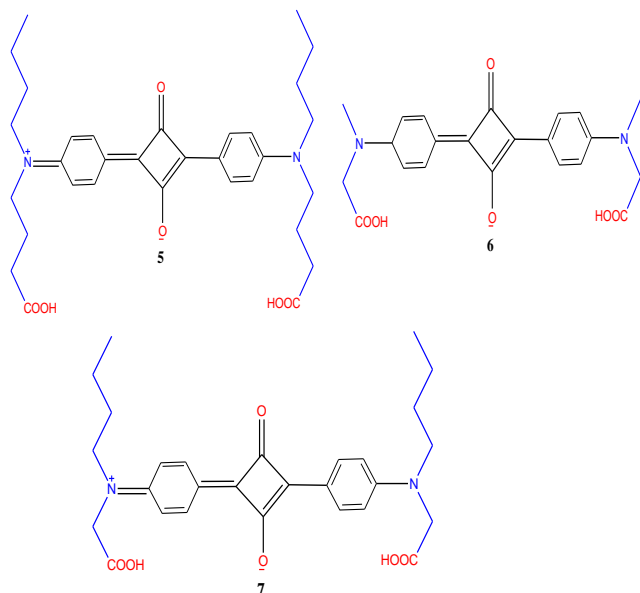
Zhao and co-workers synthetic 3-dyes of SQ-sensitizers **1–3** and utilized them in DSSC. The absorption spectra of SQ-sensitizers were progressi -vely

in the order of $(\text{CH}_2)_3\text{SO}_3\text{Py}^+ > \text{CH}_2\text{CH}_2\text{OH} > \text{CH}_3$ upon changing the substituent on the heterocyclic N-atom. A similar way, the SQ-dye **3** show the performance better than **1** and **2** with a conversion efficiency of 2.16% [26].



The carboxyl groups in four SQ-dyes from **4–7** contain dialkyl-substituted anilines avail as the anchor and donor, and studied the effects of the length of the alkyl halides chain of the dialkyl-aminophenyl unit on the dye-sensitized solar cells performance [27]. They found that the SQ-dyes **6** and **7** have shorter spacer length led to higher IPCE values because their increased absorption intensity and vigorous light harvesting in the near infrared region (NIR), induced by H-aggregation in the green and blue regions of visible light reflecting that the methyl carboxyl acceptors groups dialkyl-substituted anilines may improve the interactions between dye molecules with TiO_2 thus leading to more efficient electron injection.. Also, SQ-dyes **5** and **7** caused to higher V_{OC} due to the restrain of charge recollection between I_3^- and the electrons injected on the TiO_2 by the long alkyl chain on aniline. The SQ-sensitizer **7** based on solar cells has η value of 3.41%, and the incident photon to converted electron value reached up to 72.9% at 671 nm.

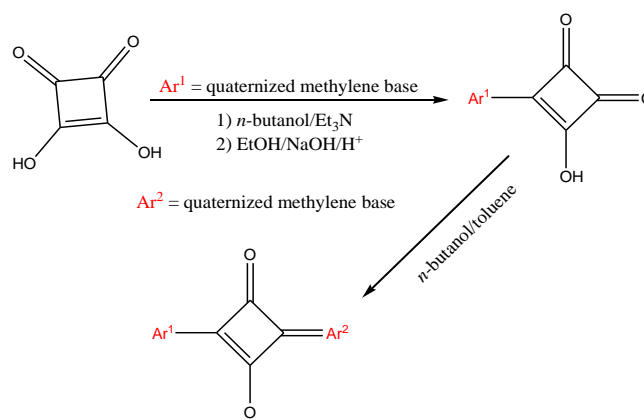




Newly, Yan and his colleagues reported 3-quinoline based on symmetrical SQ-dyes from **8-10** [29]. In these SQ-dyes, the novel acceptor groups are conjugative connected to the quinoline donor moieties. The effect of various acceptor groups and additionally the level of conjugation between -COOH acceptor groups and -CH₃ donor groups on the photo-physical and photo-chemical properties. Maximum absorption of SQ-dye **10** reached up 770 nm among these three SQ-dyes sensitizers because of longest π -electron conjugation length and its highest polarity. In light of experimental and their theoretical that studies quinoline-based SQ-sensitizers with a stronger acceptor group, greater conjugated framework, and higher polarity are valuable for the conversion efficiency of DSSC because of an increase in the driving force for photo-induced electron-injection and a diminishment in electron recombination likelihood. In spite of the best η obtained of result just 0.41% under AM 1.5G solar irradiation, it reveals some SQ-dyes design rules on such sort of sensitizers.

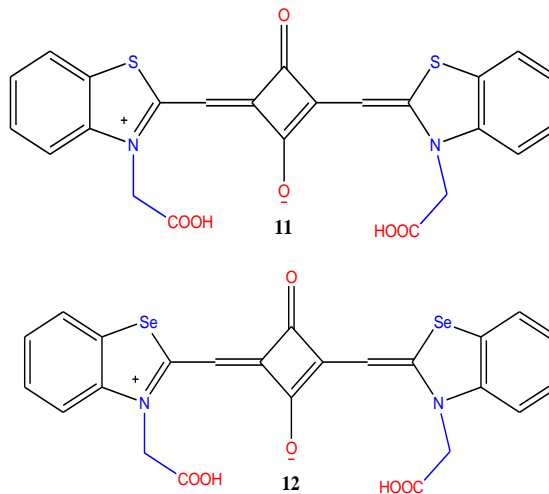
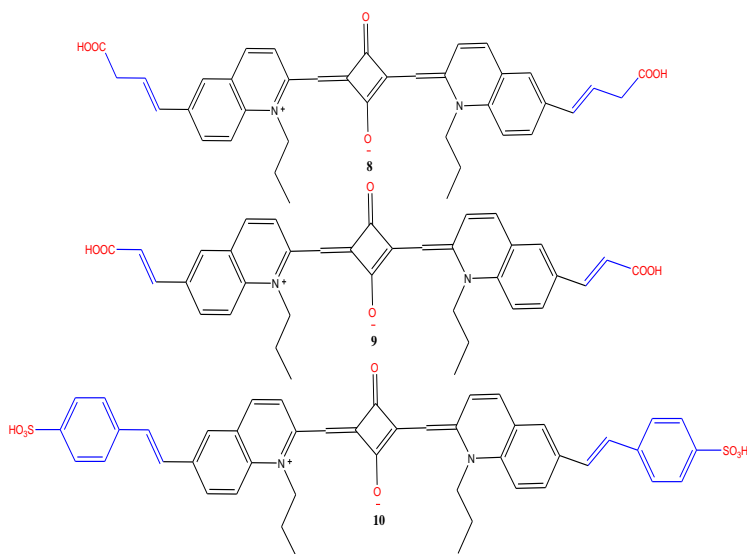
Asymmetrical squaraine dyes as sensitizers

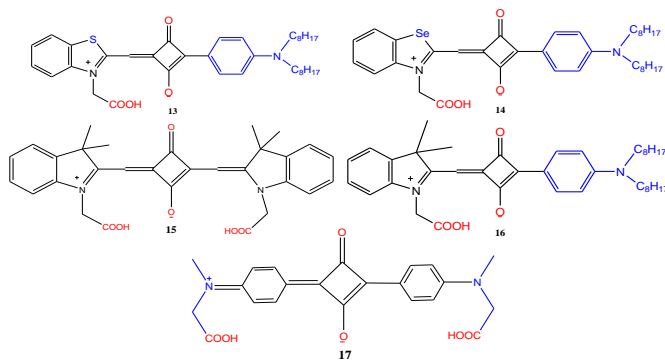
Asymmetrical SQ-sensitizers can be synthetic from dibutyl esquarate by 3-steps (**Scheme 2**). In the initial step the dibutyl esquarate reacts with one equivalent of quaternized methylene base or an aniline derivative with ethanol participation of the triethylamine which act catalyst to give the corresponding monosquaraine. Hydrolysis of the monosquaraine by NaOH and HCl yields mono-squaraine which when reacted with another methylene base leads to corresponding asymmetric SQ-dye.



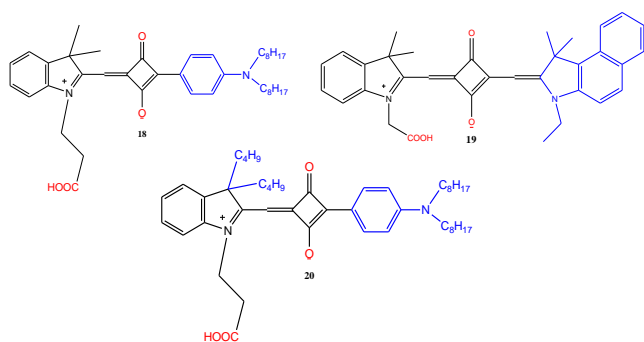
Scheme 2. General synthetic method for unsymmetrical squaraine sensitizers.

In 2005, Alex et al. Methodically studied the variance between different symmetrical and unsymmetrical SQ-sensitizers (**11-17**) [31]. The researchers found that the efficiencies of dye-sensitized solar cells based on asymmetric SQ-sensitizers are better than those symmetrical sensitizers. The aggregation of the symmetrical SQ-sensitizer on the TiO₂ surface lead to decrease the performance of DSSC. Notwithstanding, the electrons of the excited state of asymmetric SQ-sensitizers exhibit in one direction flow that lead to more efficient charge separation and higher performance for DSSC. The DSSC based on SQ-sensitizer **16** showed the best performance with an efficiency up to 2.081%.





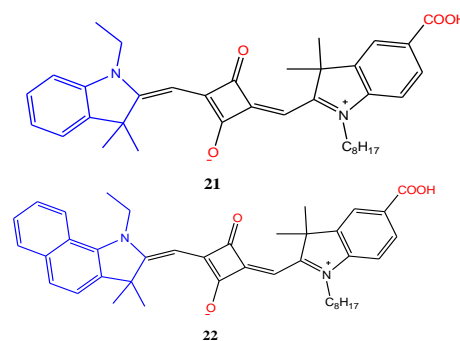
Otsuka and other researchers have modified the structure of asymmetric SQ-dyes by synthesizing 3-dyes (**18-20**) and utilized them in nanocrystalline TiO₂-based DSSC [32]. By introducing long-chain butyl alkyl to the 2, 3, 3-trimethyl-3H-indolium moiety, H-aggregation of SQ-sensitizer **20** led to higher *IPCE* than dye **18** which is based on DSSC. Finally, the DSSC based on **20** as a sensitizer with long carboxylic acid as a co-adsorbent gave a η of 1.51% with a J_{SC} of 4.04 mA cm⁻², a V_{OC} of 0.62 V, and a FF of 0.63, which almost correspond to the efficiencies of the DSSC based on yellow and purple-colored sensitizer dyes.



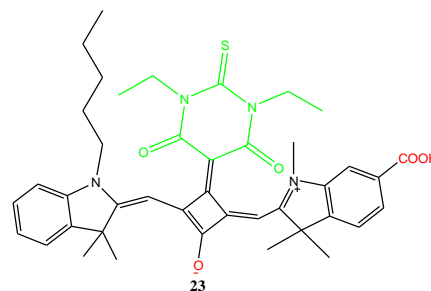
In 2007, Yum et al. reported penetration work on improved asymmetric SQ-sensitizers for implementation in DSSC [33]. They improved and synthesized the novel SQ-dye **21** which contained a novel molecular design to directly link a carboxylic acid group to the 2, 3, 3-trimethyl-3H-indolium moiety. The electron density distributions are useful for electron injection and efficient charge separation. Finally, the DSSC based on **21** exhibits a peak in the IR region at 650 nm, a high *IPCE* up to 85%. The J_{SC} value obtained was 10.50 mA cm⁻². The V_{OC} was 0.603 V, and the FF was 0.72, correspondent to an overall η of 4.52%, which was the highest value reported for a DSSC based on SQ-dye.

Geiger et al. synthesized novel asymmetric SQ-sensitizer dye **22**, which red-shifted the absorption spectrum of SQ-dye **21** by adjusting the molecular structure [34]. In SQ-dye **22**, one of the 1-ethyl-2,3,3-trimethyl-3H-indolium moieties was substituted by a benzindolium moiety which can be displayed on the left side ring of the indolium structure. In spite of it comprises

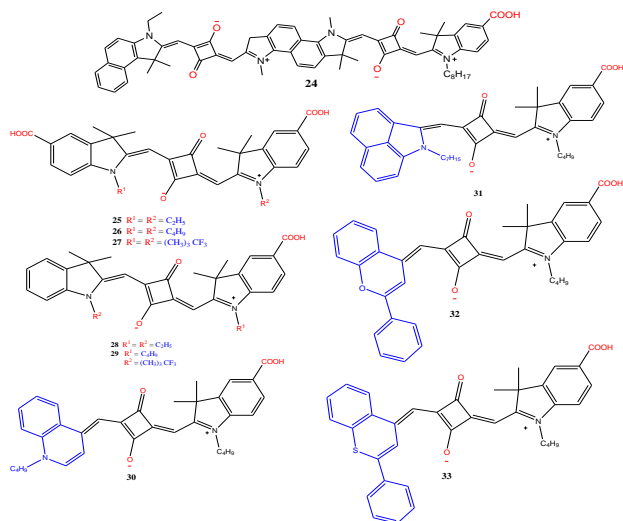
only a short augmentation of the molecular spine, the absorption and molar extinction coefficient were especially enhanced which led to improved light harvesting and expanded *IPCE* range. The excited state electron distribution of **22** is delocalized on the indolium moiety bearing the COOH acceptor group that brought about a strong electronic coupling with the conduction band (CB) of TiO₂ and subsequently a high efficiency of electron-injection. At last, $\eta = 5.40\%$, corresponds to an excess of 21% as contrasted to **21** under the similar conditions. The structural advantages of SQ-dyes lead to their tight absorption at almost 600–800 nm and then it is necessary to increase the absorption intensity in the short-wavelength to enhance the scope of the sun spectrum.



Beverina et al. selected the residues of the diethyl thioarbitres as the electron-pull group instead of an oxygen atom of the SQ-core which provides an additional high energy absorption band and improves the cis-shape SQ-dye sensitizer **23** [35]. The DSSC based on SQ-dye **3** as sensitizer produced a higher J_{SC} value (11.87 mA cm⁻²) than that based on dye **21** (10.5 mA cm⁻²) and an improved η of 4.7% as compared to 4.5% in the dye **21**-based dye-sensitized solar cells. Another strategy is to extend the π -conjugation length of the molecular backbone for bathochromically shifting the absorption spectra of SQ-dyes.



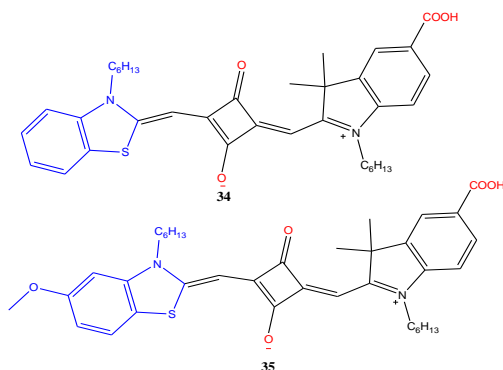
The asymmetrical dimeric SQ-dye **24** reported by Kuster et al. [36]. The absorption of SQ-dye **24** reached up to 725 nm because of the expanded linear π -conjugation, structure and the executed planarity of the naphthalene moiety. Also, the extinction coefficient amounted to 389,000 L mol⁻¹ cm⁻¹, because of the existence of two chromophoric units in the molecule dye **24**. However, the cell performance (1.3%) is small although the excellent absorption spectrum because of intense H-aggregation, that arises from the broadly extended π -backbone.



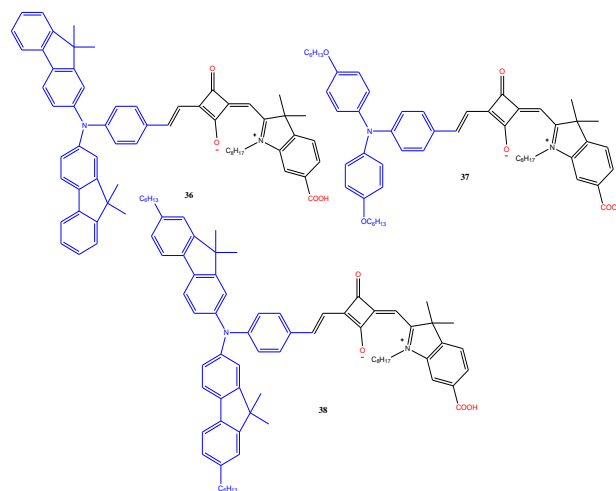
Pandey et al. methodically studied the structure property relationships of asymmetrical and symmetrical SQ-dyes through the integration of various alkyl and fluorinated-alkyl substituents [37]. Dye-sensitized solar cells based on asymmetrical squaraine **28** and **29** gave higher η values than those of **25**, **26** and **27**. The efficiency of SQ-dye **29** (3.35%) is a little greater than the dye **28** (3.1%) because of the utilization of lengthy chain substituent, that effectively suppressed H-aggregation between SQ-sensitizers. In view of the experimental data, the authors proposed that the value of 0.17 eV between the highest occupied molecular orbital (HOMO) and the oxidation/reduction potential. Also between the lowest unoccupied molecular (LUMO) and CB of TiO_2 is adequate for dye regeneration and electron injection, respectively.

Maeda and colleagues joined heterocyclic compounds rich in electrons, for example quinolinium, benz[c,d]indolium, and benzopyrylium groups, into the structure of SQ-dyes to afford dyes **30–33** [38]. In spite of the absorption peaks are broadly red-shifted as contrasted to their parallel dye **21**, the highest general η between the four squaraine dyes (obtained with **34**) was just 1.62% ($J_{SC} = 8.20 \text{ mAcm}^{-2}$, $V_{OC} = 0.41 \text{ V}$, $FF = 0.50$) because of the low IPCE response from the near-infrared (NIR) to the visible region.

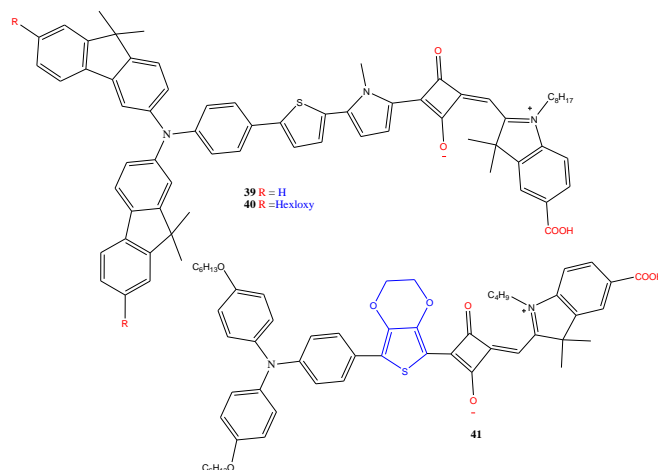
For SQ-dyes **34** and **35**, benzothiazole replacements were introduced into the squaraine sensitizer structure [39]. Solid-state DSSC based on these two-dyes showed total $\eta = 0.90$ and 0.60%, respectively.



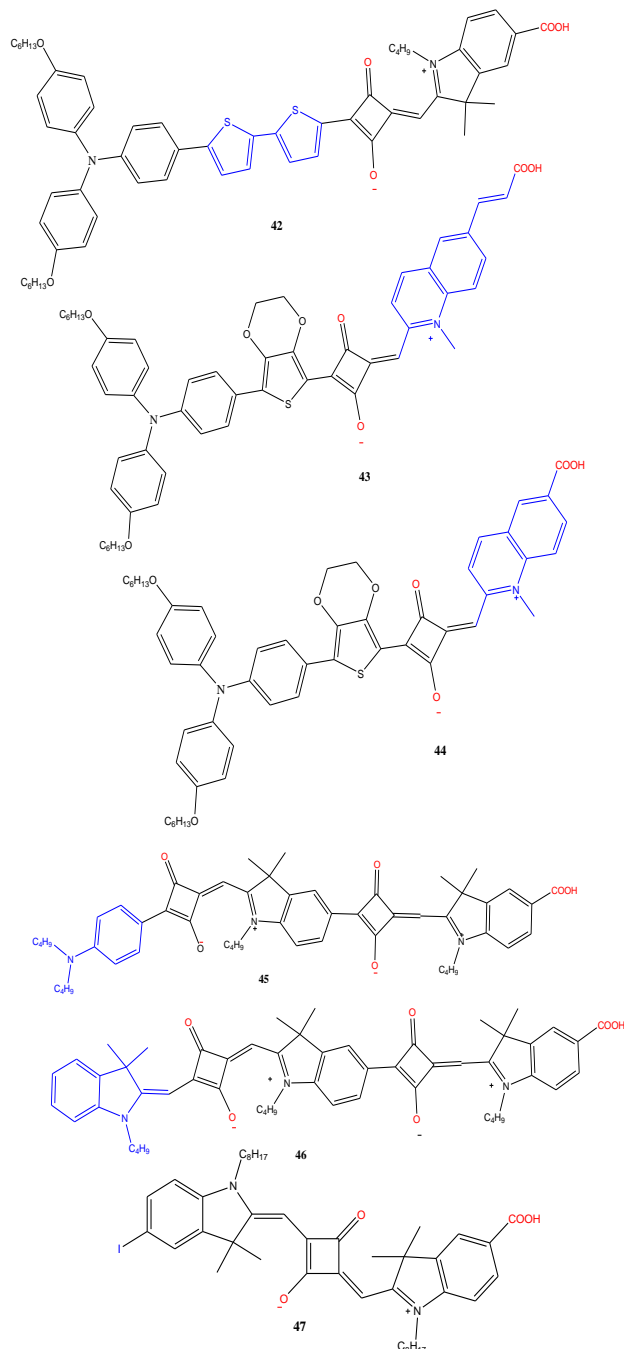
Choi et al. introduced a massive hexyloxyphenyl motif into the SQ-dyes structure and developed three SQ-dyes, **36–38** [40]. Dye aggregation was efficiently stifled because of the introduction of great steric groups. A very high rate of 5.21% was achieved in DSSC based on magnificent J_{SC} of 13.93 mAcm^{-2} .



A similar research group further introduced another π -spacer structure into the SQ-dyes, in this way developing sensitizers **37** and **38** [41]. The absorption peaks of these SQ-sensitizers reached up around 665 nm. By improving the concentration of carboxylic acid and TiO_2 film thickness, DSSC based on dye **37** had an efficiency of 6.29% ($J_{SC} = 13.93 \text{ mAcm}^{-2}$, $V_{OC} = 0.61 \text{ V}$, $FF = 0.74$). The DSSC based on dye **37** achieved an overall η of 1.96%. Both values were between the highest efficiencies obtained at that time utilizing SQ-dyes. In spite of the conversion efficiency of the DSSC based on the dye-**38** dye was less than 37%. The previous cell showed excellent stability over the long term when an ionic liquid was utilized as the electrolyte. Increase efficiency to 3.01% of the initial value of 2.4% after 1000 hours of light soaking at 60°C due to hexyloxy and different equity group dimethylfluorene substituted amino prevent contact of the acceptor with TiO_2 surface resulting in a decrease in the dark current.



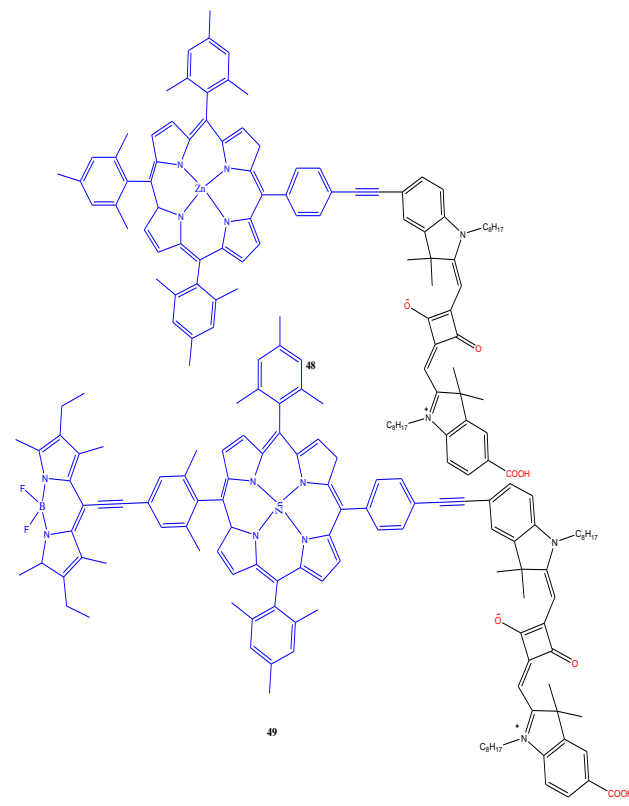
Li et al. A similar strategy was chosen to achieve a panchromatic response of asymmetric SQ-dyes by introducing a rich electron 3,4-ethylenedioxythiophene (EDOT) and bithiophene(BT) units between the center of squaraine and the hexyloxyphenylamino [42]. The resulting dyes **41** and **42** had a maximum absorption at 690 and 655 nm, respectively. A small structural change, which is a 3, 4-ethylenedioxythiophene ring replacement in dye **42** by bithiophene (BT) moiety resulted in a blue-shift of 39 nm and a lower molar extinction coefficient. The higher J_{SC} (11.12mAcm⁻²) and η values (2.61%) of the DSSC based on dye 39 is due to a superior light-harvesting ability. This finding uncovered the impact of spacer groups on the photocurrent and efficiency through improvement of the spectra. Based on the superb light-harvesting performance of **41** as a result of the



introduction of rich electron 3, 4-ethylenedioxy -ythiophene moiety, the authors additionally synthesized two new unsymmetrical SQ-sensitizers, **43** and **44**, by changing the indolium unit to quinoline so as to extend the *IPCE* response into the long-wavelength system [43]. Of course, the *IPCE* response was stretched out to 1050 nm for DSSC based on both of the two SQ-dyes. Nevertheless, the overall η values were low (~1.9%) because of their low V_{OC} and *FF*. Maeda and co-workers created three novel NIR-absorbing SQ-sensitizers (**45**, **46**, and **47**) with a linearly extended π -conjugated structure through Pd-catalyzed cross-coupling reactions utilizing stannylcyclobutenediones [44].

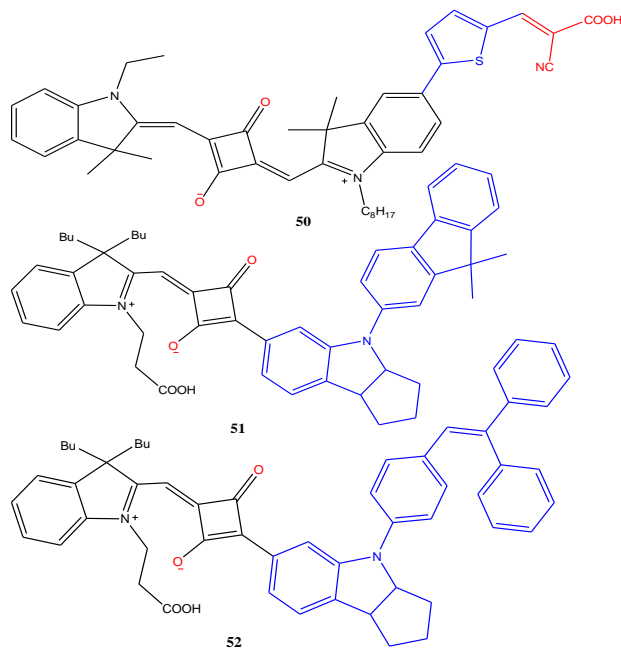
The absorption peaks of these SQ-dyes were situated at 777, 779, and 800 nm, respectively. Nevertheless, the total η values reduced from 2.26% in dye **44**, 2.01% in dye **45**, to 1.82% in dye **46**. The humble efficiency values are due to the decrease in V_{OC} , and electron transfer again and J_{SC} values are unexpectedly low resulting from the aggregation of dye-molecules.

Warnan et al. A novel molecular procedure for obtaining a panchromatic SQ- dye was discovered by covalent linking of squaraine dye and boradiazaindac -ene (BODIPY), which brought about the first tri-chromophoric dye **49**[45]. The SQ-sensitizer **49** has absorption spectra at 660, 520 and 422, and 552 nm, which are set in shifts of the squaraine, and the BODIPY chromophores. The similar states of DSSC creation, the photocurrent and the photo- conversion efficiency showed a progressive increment in the following order **47**<**48**<**49**. In spite of the efficiency of the DSSC by dye**49** was just 3.9%, these outcomes affirmed that such a design strategy to join the covalent three diverse dyes is successful in improve panchromatic SQ-sensitizers.



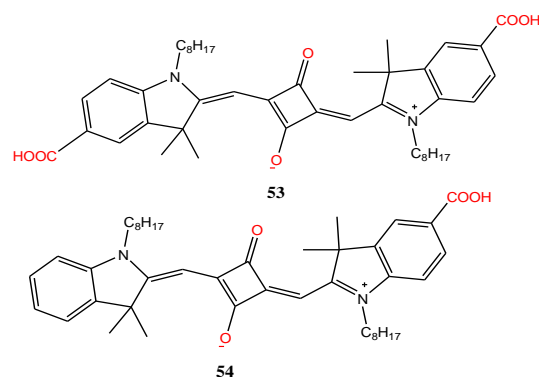
In 2011, Shi and colleagues created an asymmetric bis(indoline) SQ-sensitizer **50** for use in DSSC[46]. In this novel SQ-sensitizer structure, one thiophene unit was covalently connected to an indolium moiety which prompting the band to gain additional power absorption. Besides, utilizing a stronger electron pull the carboxycanoviny group also resulted from the acceptor rather than the COOOH in a very Doppler shift of 23 nm for maximum absorption compared to **20**. The IPCE curve for dye **50** was observed, surpassing 50% in the wavelength range of 425–735 nm and reaches about 67% at 710 nm in a standard iodine-based solution cell. The final η of 6.76% was obtained with a $J_{SC} = 14.7 \text{ mAcm}^{-2}$, a V_{OC} of 0.651 V, and a FF of 0.73. At once, by utilizing the presence of organic hole once, transfer of solids state rather than electrolyte liquid, the efficiency of 2.68% has been achieved. This plan methodology is by all accounts extremely encouraging and indicates that both the maximum absorption of the red shift and the panchromatic absorption can be.

Funabiki et al. synthetic 2-SQ-dyes, **51** and **52**, comprising 2, 3, 3-trimethyl-3H-indole unit as the donator that is directly related to 3, 4-dihydroxycyclo -but-3-ene-1, 2-dione without any linker group [47].



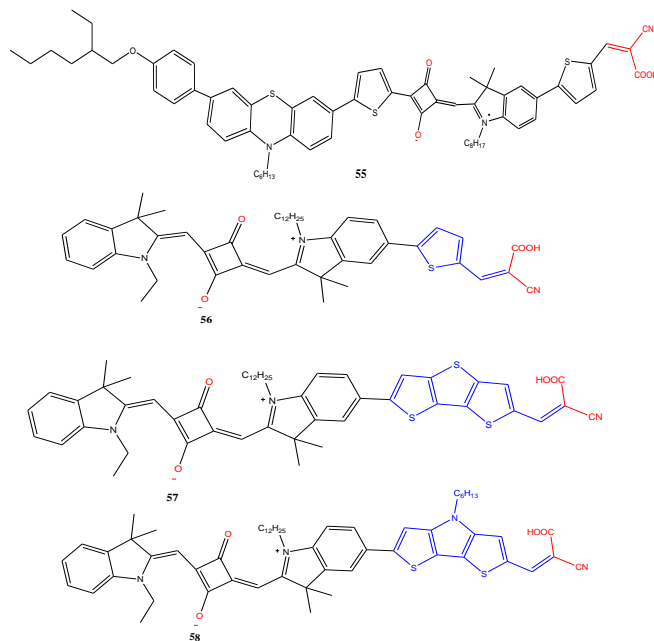
In 2014, Chi Hwan Lee and co-worker reported a new strategy to promote the transfer of charge for SQ-dyes and TiO_2 by increasing the acceptor groups.

Symmetrical (**53**) and asymmetrical SQ-**54** dyes with various anchoring groups. SQ-sensitizer **53** containing a two anchoring groups displays with TiO_2 electronic coupling better than the SQ-sensitizer **54** dye which contain mono-bridge that leads **53** to show better photovoltaic performance. The optimized SQ-**53** sensitized solar cells displays 7.76 mAcm^{-2} of J_{SC} , 0.61V of V_{oc} , and 0.64 of FF , to give overall conversion efficiency of 3.19%, which is approximately 25% higher than the SQ-**54** sensitized solar cells [48].

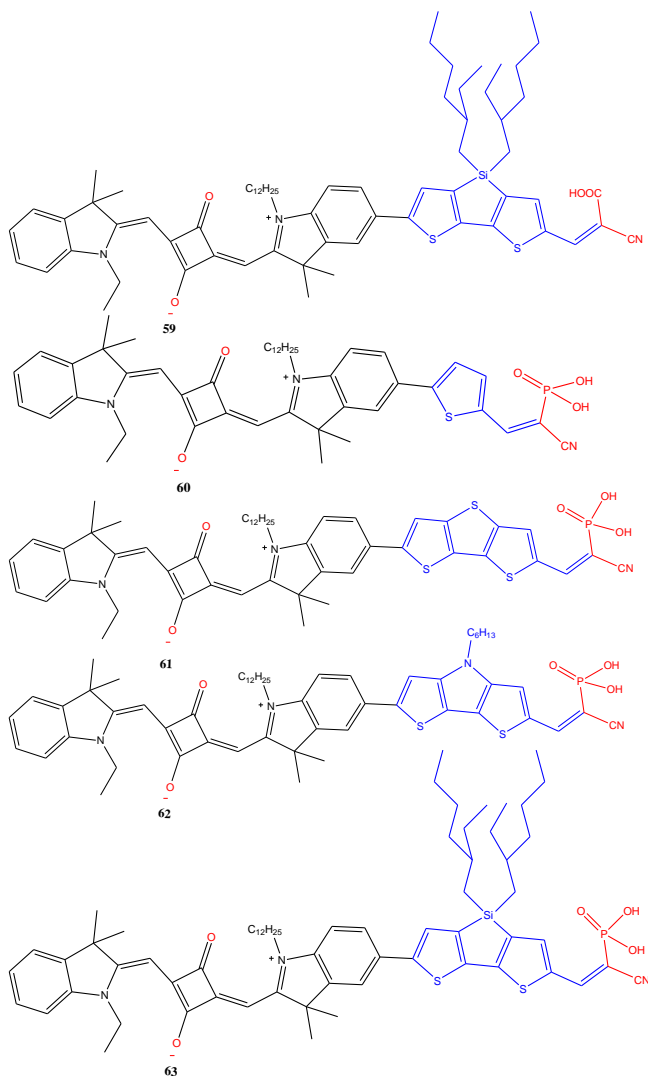


In 2015, Seong Hee Bae *et al* have synthesized asymmetrical SQ-dye **55** and utilized as sensitizers dyes for DSSC with changing π -bridge units, based on the D- π -A SQ-dyes. The phenothiazine was used as a donor group connected to a squaraine center unit by different thiophene derivatives. SQ-sensitizer has a cyanoacrylic acid ($\text{C}_4\text{H}_3\text{NO}$) as an electron accepting group with greater vigor and joined directly to SQ-dye. These SQ-sensitizers showed intense absorption in the NIR region and powerful fluorescence. Consequently, a DSSC based on the SQ-sensitizer dye **55** include a thiophene unit as a π -bridge unit and -COOH group as an electron-anchoring group show the best photovoltaic performance of 6.01 mAcm^{-2} J_{SC} , 447 mV of V_{oc} , and 0.73 of FF to give total conversion efficiency η of 2.01% [49].

Fadi M. Jradi and co-workers reported eight SQ-sensitizers **56-63** with thiophene, π -bridges with cyanoacetic acid **56-59** and cyanophosphonic acid **60-63** contains donor/ acceptor groups synthesized to extend the absorption of SQ-sensitizers. SQ-sensitizers with cyanoacetic acid **56-59** acceptor groups have higher power conversion efficiencies compared to cyanophosphonic acid **60-63**, with the highest being 8.9% for the SQ-sensitizer **59**, this is because of high short



circuit currents (J_{SC}) and increased open circuit voltages (V_{OC}). SQ-sensitizers with cyanophosphonic acid ($\text{CH}_2\text{NO}_3\text{P}$) **60-63** anchoring groups showed lower J_{SC} because of diminished charge injection efficiency, as determined by femtosecond impermanent absorption spectroscopy. This study suggests that out-of plane bulky substituent may increase dye sensitized solar cells performance by increasing open circuit voltages (V_{OC}) and short circuit currents (J_{SC}) through decreased aggregation on $\text{TiO}_2/\text{electrolyte}$ recombination [50].

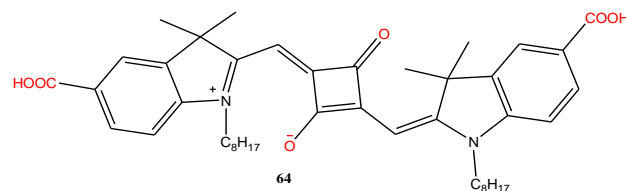


Symmetric versus asymmetric squaraine for DSSC

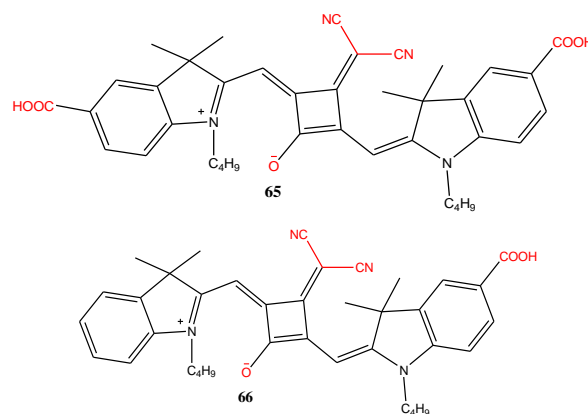
The development of the SQ-dye from the molecular structure of the symmetric to the asymmetric one has been transformed. As previously mentioned, two research groups studied the different effects of asymmetric and symmetric sensors (dyes **13-19** and **27-31**) on the DSSC performance. The two groups concluded that asymmetric structures were helpful for enhancing and improving DSSC performance.

Yum et al. further displayed that the asymmetrical SQ-dye **21** gave good conversion efficiency because of the directional electron transfer in this type of molecular

structure. Nonetheless, modern studies have cast suspicion about the conclusion that asymmetric structures outcome in DSSC with improved performance in comparison with symmetric structures. Park and co-workers accurately compared the symmetrical SQ-dye **64** with its unsymmetrical congener **21** [51]. The researchers found that the symmetric dye **64** generally lead to a higher total $\eta = 4.61\%$ than asymmetric dye **21** $\eta = 4.22\%$ under the same test situations.



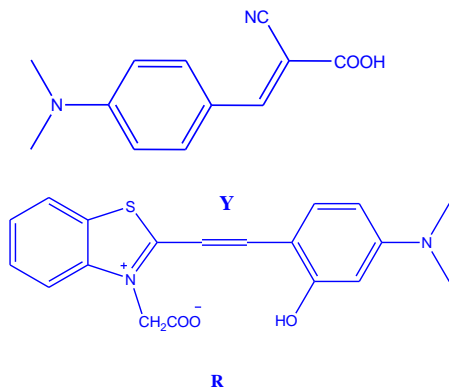
Maeda and co-workers, specified that a symmetric SQ-dye can led to better DSSC performance. The researchers found that the SQ-dye **65** gave a higher total η of 3.58% compared with its asymmetric peer SQ-dye **66** η of 2.8% [52]. The J_{SC} value of the DSSC based on **65** was increased by 35% (from 10.3 - 14.2 mAcm^{-2}) with compared to dye **66**. The researches referred that the increase in J_{SC} not only to the effect of panchromatic absorption but also to the decrease in energy loss caused by the photo isomers. These results have revealed significant effects on DSSC performance by refining the steric structure of the SQ-dyes. From now on, we should continue to consider various variants for the design of new molecules SQ-dye in the future.



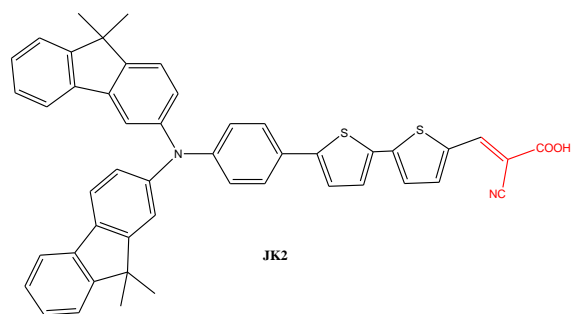
Squaraine dyes for Co-sensitized DSSC

To enhance and evolve the efficiency of DSSC, many researchers have focused their attention on the panchromatic-dyes to expand the absorption of SQ-dyes from 700-2500 nm [53]. The SQ-sensitizer is an excellent promising filter for utilize as a co-sensitizer to expand and increment the light-harvesting at near-infrared wavelengths region as a result of its very high molar extinction coefficient in the long-wavelength region. Below we highlight a few cases in which SQ-sensitizers dyes were utilized as co-sensitizers in DSSC.

Chen and his colleagues co-sensitized SQ-dye **26** with yellow merocyanine ($C_{26}H_{32}N_3NaO_7S$) dye (**Y**) and red hemicyanine fluorescent dye (**R**) [54]. The *IPCE* display high values greater than 70% with a broad band range of 400-800 nm, due to the contribution from three dyes with various absorption properties. This path lead to total η of 6.5% with a J_{SC} = 15.8 $mAcm^{-2}$, a V_{OC} of 0.525 V and a *FF* of 0.63.



Yum et al. mixed SQ-dye **21** with the organic dye **JK2** which exhibits a major absorption band at around 450 nm [55]. The effectiveness of such solar cell awareness participated higher than cells based on the individual sensors because of *IPCE* spectrum resulting from the expansion of the features of the absorption spectra complementary. The securities J_{SC} = 15.5 $mAcm^{-2}$ and volatile organic compounds from 0.684V, and *FF* = 0.70 represents η of 7.43% using liquid electrolytes. It has accomplished greater efficiency of 6.4% based on a similar method utilizing a paired ionic liquid electrolyte dissolved [56].



Conclusions and future perspectives

In the past five years, SQ- dyes based on organic sensitizers have received increasing attention and huge improvements in the structural design. The DSSC performance has been accomplished and efficiency has been reached around 8.9% and there is still much domain for improvement like increasing the *IPCE* in the visible region and/or red-shifting the absorption spectrum to the low energy region. While the synthesis ways required for symmetrical squaraines would still render them promising for their application in dye-sensitized solar cells in the future, efforts are still needed to identify the pros and of our symmetrical vs asymmetrical structures of these dyes.

With the global increasing request for energy saving and alternative energy, technologies, will continue the search for best organic materials for an enhancing and development the DSSC by using SQ- sensitizers. Considered the SQ- dyes sensitizers a very promising candidates due to high absorption coefficients in the near-IR region and stable near-IR absorbing, so should be using in the technology and their applications for constructing integrated photovoltaics. It is important and feasible to search and endeavor to get on more high efficiency SQ-sensitizers for dye sensitized solar cells. So the absorption of panchro -matic with high absorption coefficients of the visible to near-IR spectral area of SQ-sensitizers dyes remains a major challenge for scientists' research in the coming years.

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