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Squaraines as Light Capturing Materials in Photovoltaic Cells

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Photovoltaic cells are considered to be one of the most promising renewable energy sources in 21st century. Among which, dye sensitized solar cells (DSSCs) and organic photovoltaic devices (OPVs) are potentially the most economic and environmentally friendly ones. Squaraine (SQ) has intense absorption at 600-850nm, exactly where sun flux is the most abundant. Furthermore, various substituents on SQ cores provide great possibilities for different molecular design strategies. These characters make SQs ideal candidates for new DSSCs and OPVs. In response to the rapid development of SQ based solar cells, a panorama of these on-going researches is presented here, including the general synthetic routes of SQs and the various SQs used in DSSCs and OPVs. Our discussions are focused on the diverse molecular designs of SQs used in DSSCs and OPVs. The design strategies to acquire better light harvesting abilities are also provided here, as well as the principles behind these strategies.

1. Introduction

Squaraines (SQs) are nucleophilic substitution products of squaric acid, forming π -acceptor- π systems within molecules. They have sharp and intense red-IR absorbance/fluorescence, which is a distinctive feature standing out from other dyes. Besides, the extremely high molar extinction coefficients of SQ absorptions and their wide solid-state absorption window (covering the visible/near-IR region) are all ideal characters for solar energy harvesting.¹

SQs were intensely studied for their good photoconductivity back in 20th century,^{2, 3} as they were promising in applications such as electrophotographic devices and optical recording, however gradually faded of sight after the flourish of phthalocyanine materials.^{4,5} In recent years, SQs have re-emerged as one of the few promising materials of solar cells. The number of the publications on SQs for photovoltaics is increasing rapidly in the last several years (**Fig. 1**).

However the reactivity of the electrophilic cyclobutyl core is so high that most SQs are vulnerable to nucleophiles as well as bases, so their applications are much limited. But these problems are not irrevocable. Thanks to the versatility of core substituents and developments in rotaxane synthesis, these drawbacks have been alleviated. After a short silence in their

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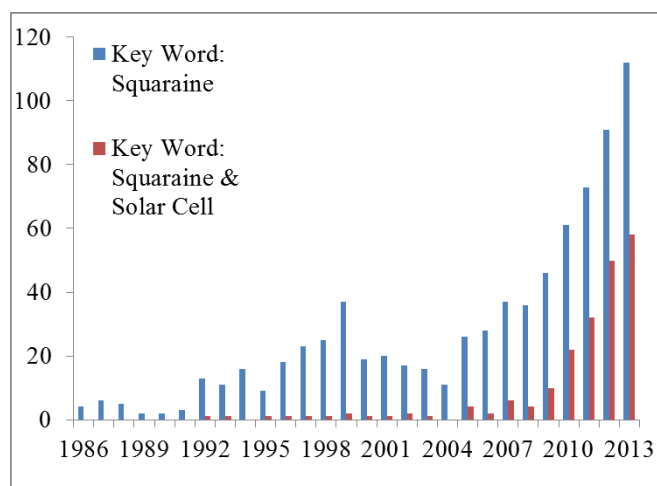


Fig. 1 The reports on SQs are directly collected from Web of Science, ranging from 1986 to 2012. SQ photovoltaics include SQ composited dye sensitized solar cells and organic photovoltaics. Other less intensely studied solar cells are not presented.

on-going study, SQs and their assemblies have found their uses in imaging technologies, photodynamic therapy, biolabeling, and ion detection before long.⁶⁻¹²

Hereinafter, we introduce the synthetic routes for SQs and their various applications in different kinds of solar cells, summarizing recent works as well as providing suggestions for future researches. Our introduction is mainly focused on the molecular modifications of SQ molecules with the purpose of improving their performance in various solar cells.

2. Synthetic routes of SQs

2.1 Condensation of squaric acid with nucleophiles

The most common method to synthesize SQs is the condensation of squaric acid with nucleophiles, which results in symmetrical SQs (**Fig. 2**). During the reaction water resulted from the condensation is usually removed with a Dean-Stark condenser, leaving a solution of SQ behind.^{13, 14}

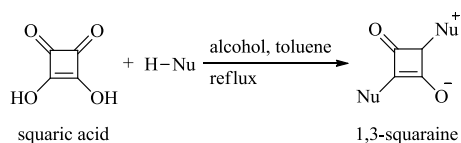


Fig. 2 Synthetic route starts from squaric acid.

2.2 Condensation of squaric acid derivatives with nucleophiles

For the synthesis of unsymmetrical SQs, squaric acid derivatives, such as squaric acid esters and squarylium dichloride, are usually used as the starting materials (**Fig. 3**), which are considerably less reactive than squaric acid. As a consequence, the condensations usually result in semisquaric acid esters/squarylium chlorides. Both of the products can be converted into semisquaric acids after treated with bases and/or acids. Condensation of semisquaric acid with another nucleophile produces unsymmetrical SQs.¹⁵

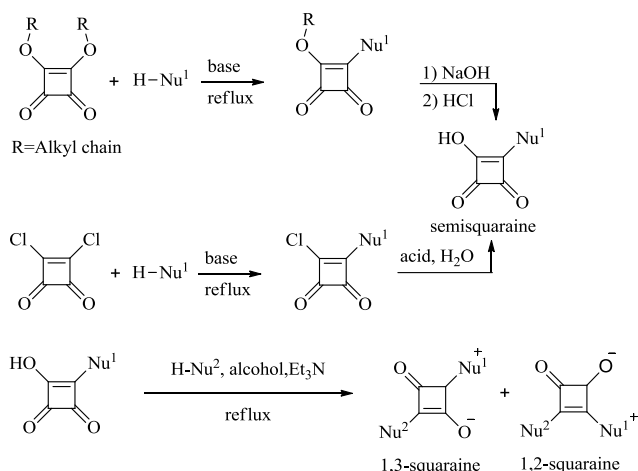


Fig. 3 Synthetic route starts from squaric acid esters & squarylium chloride

2.3 Synthesis of semisquaraine *in situ*

Most of the semisquaraines were synthesized by the condensation of squaric acid derivatives with electron-rich derivatives. The four-member ring of semisquaraines also could be constructed directly.^{16, 17} Thus, chloride **A** was reacted with freshly prepared tetraethoxyethylene in the presence of triethylamine, then the reaction mixture was treated with alumina in hexane to form compound **B**, which was smoothly hydrolyzed to semisquaraine **C** by 18% hydrochloric acid (**Fig. 4**).¹⁶ Using this route, Law and Bailey synthesized a series of aromatic unsymmetrical SQs in 1992 successfully.¹⁷

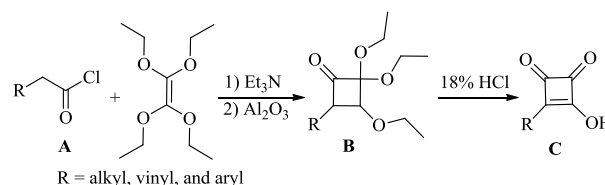


Fig. 4 [2+2] cycloaddition of 2-(4-methoxyphenyl)acetyl chloride and 1,1,2,2-tetraethoxyethene

2.4 Synthesis of 1,2-Squaraines

The condensations of squaric acid yield mainly 1,3-SQs, yet with minor impurity of 1,2-SQs.¹⁸ Thus most studies of SQs are focused on 1,3-isomers, and the selective synthesis of 1,2-SQs is not fully developed. Ronchi *et al.* discovered that exclusive production of 1,2-SQs can only be acquired from condensation of squaric acid esters with highly reactive electron rich precursors (**Fig. 3**). The reaction time, temperature and solvent also play important roles in reducing the 1,3-SQs yields.¹⁹

The above are the four most common strategies to synthesize squaraine compounds. The essence of the prevail synthetic routes is nucleophilic substitution on the squaric acid core. The SQ molecules mentioned below were all synthesized by one of the four methods; therefore their synthetic details are not described. We will focus mainly on their structure-property relation, and their performances in solar cells.

3. SQs sensitizers in dye sensitized solar cells

Dye sensitized solar cells (DSSCs) with the best performances are usually prepared by sensitizing titanium oxide nanocrystals with a ruthenium complex. To date, the best DSSC has a solar-to-electric power-conversion efficiency as high as 13% under standard air mass (AM) 1.5G simulated sunlight

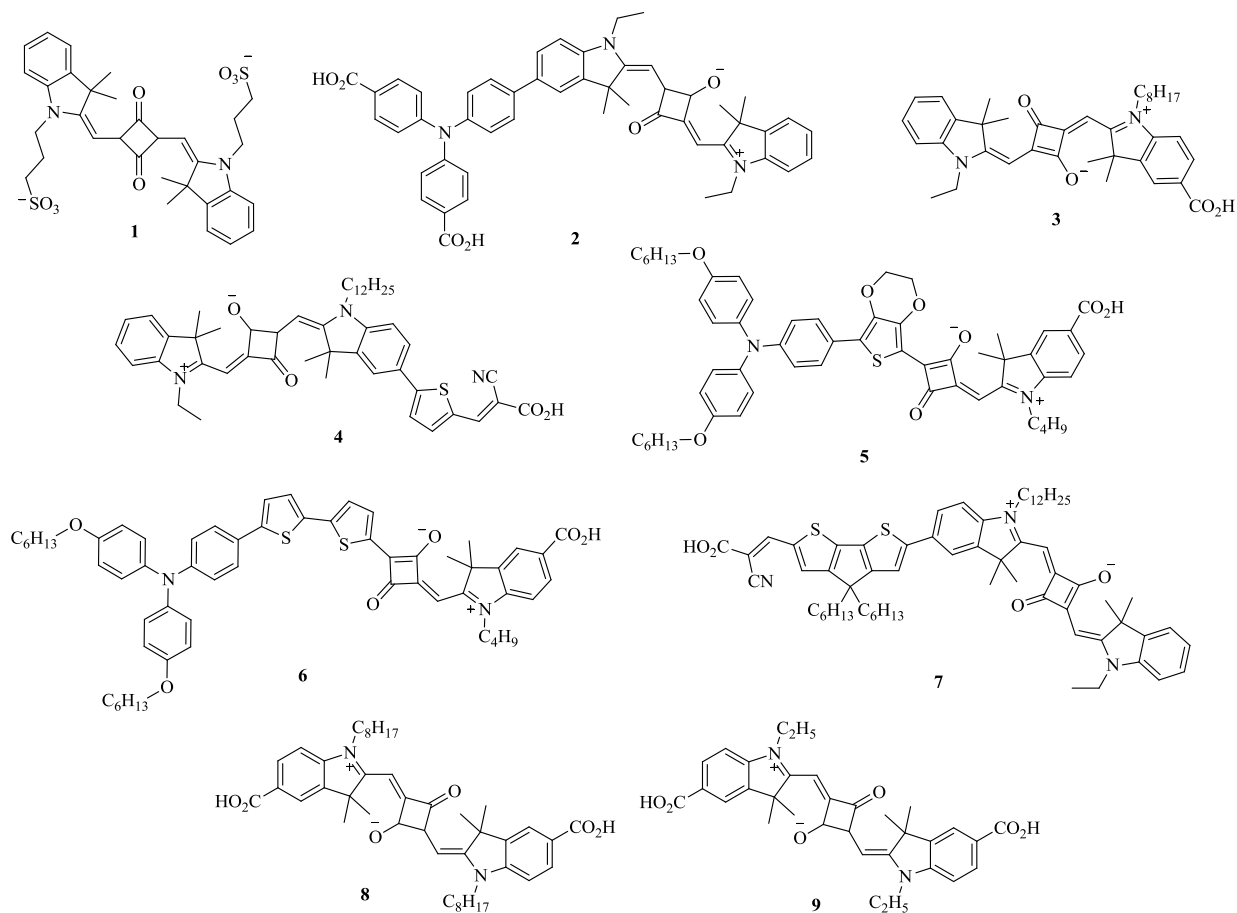


Fig. 5 Squaraines used in DSSC device

(1000 Wm⁻²) using organo-metal sensitizer.²⁰ Though inefficient at present, metal-free organic sensitizers are still under intensive investigation for their high molar absorption and potentially low cost. Moreover, large amount of solar energy are in red/IR region, where Ru(II) complexes are not able to efficiently absorb, while many organic dyes such as SQs have intrinsic strong absorptions at this region.²¹ Thus SQs have been constantly under research as one of the few metal-free sensitizers for metal oxide semiconductors.^{22, 23}

First attempts towards effective sensitization seem to be unsuccessful.^{22, 24} Though the photosensitization process was well understood as the injection of electrons from the excited dye molecules into the conduction band of the large band gap semiconductor, the molecules were not well optimized for such charge injection process. The photo-generated hole and electron were quickly recombined, leading to a poor incident photon-to-current efficiency (IPCE) no higher than 0.1%.

Further researches have taken several approaches to modify the molecular structure in order to improve their efficiency.

3.1 Anchoring groups

Zhao *et al.* introduced anchoring groups into SQs, making a great advance of cell efficiency. They used (CH₂)₃SO₃⁻Py⁺ group to attach SQ onto the TiO₂ surface, reaching a photoelectric conversion efficiency of 2.17% (**1**).²⁵ Adsorption of SQs has dramatic influences on the photovoltaic behaviors. Anchoring group on the heterocyclic nitrogen atom of SQ strongly binds to the active hydroxyl group at the TiO₂ surface, building up electric coupling between the excited state of SQ and the conduction band of TiO₂.

Paterson *et al.* investigated the electron injection process between SQ molecules and TiO₂ surface, providing a further understanding of anchoring group's function.²⁶ They suggested the excited complex will be formed more frequently by anchoring SQs on TiO₂ surface, which will give rise to the electron-transfer rate between SQs and TiO₂.

After the first few trials, great developments have been made to improve the anchoring groups. Carboxyl and cyanoacrylic acids

have become the most frequently used in molecular design.^{27, 28} Firstly, these groups form strong bonds between SQs and TiO₂; secondly, they can be easily introduced to the SQ molecules via synthesis; thirdly they are strong electron withdrawing groups, which will help electron transfer towards TiO₂. In this sense, the increasing polarity of anchoring groups also helps to improve cell performances.²⁹ To achieve better performance, sometimes two anchoring groups were used in one molecule (**2**).³⁰ Anchoring groups intensify the interaction between dye molecules and metal oxides, therefore dyes with two anchors significantly increase the dye loading density. Consequently, higher dye loading density means less metal oxide is exposed to electrolytes, leading to a suppression of dark current.

3.2 Unsymmetrical SQs

In 2004, Alex and coworkers suggested that asymmetry of SQ molecules has great influence upon sensitization efficiency.³¹ They carried out molecular orbital calculations and found that upon excitation, electrons of symmetric SQs tend to concentrate on the center of the molecules, while unidirectional flow of electrons towards the anchoring moiety is favored in unsymmetrical SQs (Fig. 6). This directional flow results in improved charge transfer from the sensitizer to the TiO₂ crystals. Compared to its symmetrical counterpart (molecule **10**), asymmetrical molecule **11** showed improved the power conversion efficiency due to higher dipole moment.

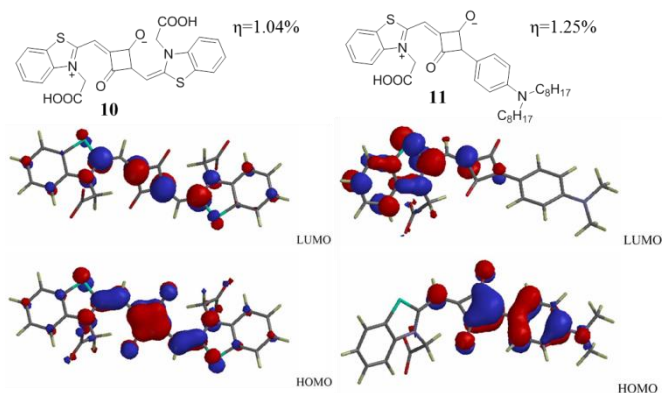


Fig. 6 Frontier molecular orbitals of symmetric SQs and unsymmetrical SQs.³¹

After the first success in theory-assisted design of SQ sensitizers, many SQ molecules have been constructed in this way.³¹

Molecular orbital calculations are now routinely performed to obtain the energy level information related to the excitation process.³²⁻³⁴ In an ideal situation, while the electron cloud is mainly located at the squaraine core or other electron withdrawing groups conjugated to squaraine (which is supposed to be the electronegativity center), the electrons should flow to the anchoring group upon excitation, leading to a more efficient charge transfer to TiO₂.³⁵ This requires electrons concentrate at one end of molecule at ground state and amass around anchoring group at excited state. The asymmetry of electron flow is usually synergized by unsymmetrical molecular structures, thus unsymmetrical SQs are naturally more competent than symmetrical ones. As shown in Fig. 7, this principle has been confirmed by both simulations and experiments. As a result, introduction of asymmetry has become one of the most important design principles for efficient SQ sensitizers.

3.3 Energy level control of SQs

The major breakthrough of SQ sensitized DSSCs power conversion efficiency took place in 2007. Yum *et al.* set three basic rules guiding the construction of an efficient sensitizer: a perfect match between the excited-state redox potential and the energy of the conduction band of the oxide, thus electron injection into TiO₂ crystals is possible; light excitation induced electron flow from the sensitizer toward TiO₂ surface (*vide supra*); and a strong conjugation between the chromophores and the anchoring groups.³² Following these guidelines, they designed a SQ molecule (**3**), with overall conversion efficiency (η) of 4.5% (best at that time).

For the most commonly used DSSCs, where TiO₂ crystal act as an electron accepting semiconductors and I₃⁻/I⁻ pair is used to regenerate ground state dye molecules, the lowest unoccupied molecular orbital (LUMO) should be higher than the conduction band of TiO₂ and the highest occupied molecular orbital (HOMO) of the sensitizer should also match the redox potential of I₃⁻/I⁻.^{33, 36}

3.4 Panchromatic absorption

As mentioned above, SQs' molecular structure can easily be manipulated using different reactants in the condensation reactions. In this sense, SQs' absorption is also possible to be

tuned.²¹ A wider window of absorbance usually leads to an improved IPCE, resulting in better short circuit current (J_{sc}). As coadsorption (see section 3.6) requires screening of different adsorption time of two or more kinds of sensitizers, device construction from a panchromatic absorbing SQ dye is much easier.

Shi and co-workers reported a SQ sensitizer with panchromatic absorption, covering much of the visible region with an IPCE over 50% (**4**).³⁷ Similar attempts have been made by Li *et al.* (**5**, **6**), using electron-rich 3,4-ethylenedioxythiophene or bithiophene linked hexyloxyphenyl amino group and SQ core, they achieved an absorption band across the whole visual spectra, extending to IR absorption as far as 800nm.³³ Dyes being able to absorb red-IR light have intrinsically low LUMO level; therefore the injected electron into the metal oxides has relatively low energy, resulting a low open circuit voltage (V_{oc}) value. This effect was also reflected in the low IPCE maximum of **5** and **6**, resulting a relatively low η of 2.61%.

Antenna effect is also used to achieve panchromatic absorption. Instead of cosensitizing TiO_2 with various dyes, Warnan *et al.* covalently linked boradiazaindacene (BODIPY), zinc porphyrin (ZnP), and SQ unit.³⁸ Different chromophores remained their own absorption nature, yet upon excitation, energy transfers from BODIPY, through ZnP, into SQ, resulting in an enhancement of SQ sensitizer performance.

Most of panchromatic absorbing SQs have an extended π conjugation. Though indeed broadens the absorption window, this strategy also aggravates the π aggregation of SQ sensitizers.²⁷ Some simple strategies such as attaching alkyl groups to the chromophores or coadsorption with chenodeoxycholic acid (CDCA) and may alleviate this problem. The better solution is perhaps twisting the conjugated system; thereby no strong π aggregation could be formed between the molecules. Delcamp and co-workers designed a series of molecules using various structures as π bridges.³⁹ Among which, sensitizer **7** (using di-*n*-hexyl-substituted cyclopentadithiophene (CPDT) as the π bridge) is the most successful one. Due to the out-of-plane substitution groups on CPDT, the aggregation between SQ molecules was successfully hindered, leading to an efficient charge separation and a high-

energy absorption band at the same time. The device fabricated with **7** reached an unprecedented high power conversion efficiency of 7.3%, better than any other reported SQ sensitized DSSCs.

3.5 Effects of alkyl groups

Aggregation of SQ on the TiO_2 electrode often results in decrease of sensitization efficiency, while the monomers of dye molecules can inject electrons into TiO_2 more efficiently.⁴⁰ The π aggregates of SQ usually lead to charge recombination, thus energy captured upon excitation by the sensitizer cannot be transferred to the oxide surface sufficiently.

One of the solutions is the lengthening of alkyl groups attached to the SQ molecules. Longer alkyl chains suppress the electron recombination, improving the V_{oc} of the devices. Also, SQs with longer alkyl chains have higher dye loading density, leading to an enhanced TiO_2 surface trap passivation.^{41,42} Therefore the fabricated DSSCs have broader and more intense IPCE absorption, (*e.g.* molecule **8** has a broader absorption spectra than **9**), leading to a higher J_{sc} value.⁴²

3.6 Coadsorption with other molecules

Another solution to dye aggregation is the coadsorption with other molecules, typically using CDCA.^{36,43} CDCA competes with SQ for adsorption on TiO_2 surface, limiting the growth of SQ aggregates and diminishing the recombination rate.³⁹ Though slightly reducing the load of adsorbed SQs, DSSCs cosensitized with CDCA usually have much better performance (**Fig. 7**).⁴⁴

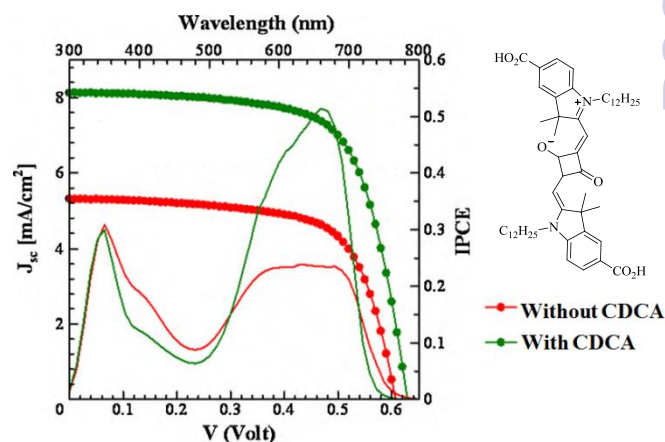


Fig. 7 Effect of CDCA addition on the photovoltaic performance of SQ-4. Thin solid line (action spectra) while line with symbol represents the I–V curve.³⁶

Coadsorption of SQs with other dyes is also used as a convenient method to achieve panchromatic absorption of solar spectrum.⁴⁵ Common SQs have high molar extinction coefficients around red/IR region, while absorption ability at shorter wavelength is relatively low. Synergetic sensitization with other short wavelength absorbing dyes provides rational way to resolve this problem.⁴⁶ Since more photons can be converted into electricity, there is a significant increase in J_{sc} , which is responsible for the increase of the total power conversion efficiency. And in some cases, coadsorbants are doing the double duties both as hole conductor and blue light absorbent in solid state DSSCs, as shown in **Fig. 8**.⁴⁷ Cosensitizing is a good choice when using two dyes, however becomes much more complicated to optimize the blending ratio when using three or more dyes.⁴⁸

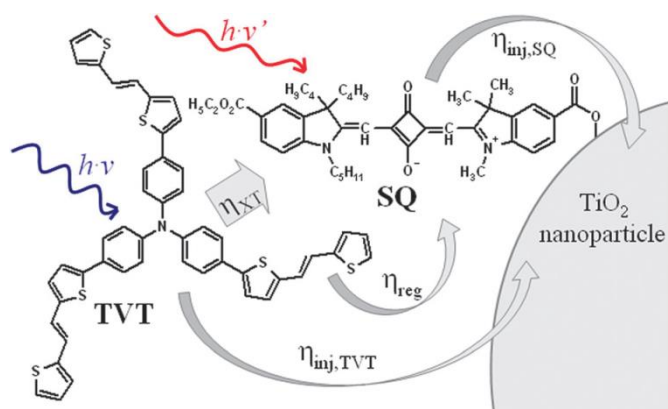


Fig. 8 SQ sensitized titanium oxide undergoes a photoelectric process: With incident light or the energy transferred from other dyes, the excited molecules inject electrons into TiO_2 , creating the driving force of DSSCs. Reproduced from Ref. 47 with permission from the PCCP Owner Societies.

4. SQs in organic photovoltaic cells

Planar-heterojunction solar cells and bulk-heterojunction (BHJ) solar cells are two kinds of widely studied organic photovoltaic (OPV) devices. Both kinds of solar cells typically consist of two or more organic materials. They are commonly fabricated by solution processes; therefore have the potential to be produced cheaply in large scale and on flexible substrates. Their main differences lie in the fabrication processes, while the energy conversion mechanisms

are same. Moreover, in recent literatures BHJ solar cells are more commonly fabricated due to their advantages of having larger interfaces over planar-heterojunction cells, thus BHJ cells are mostly discussed hereinafter.

The vital materials of OPVs are the donor and acceptor organic semiconductors. At present, the most commonly used acceptor materials are fullerene derivatives, such as (6,6)-phenyl C_{61} butyric acid methylester (PC_{61}BM) and (6,6)-phenyl C_{71} butyric acid methylester (PC_{71}BM). Though semiconducting polymers are the main stream of donor materials, small molecule donors also have their intrinsic advantages over the polymers, for example, the good reproducibility and ease of purification. The major drawback of small molecular π -conjugated systems is perhaps the low absorbance in red/IR region of solar spectrum.⁴⁹ And SQ, as a new kind of donor material, having the advantage of high red/IR absorbance, can be used to resolve this problem.⁵⁰ The most urgent problem of SQ donors is that the molecules are planar and strongly interactive to each other; therefore the aggregation within donor phase is almost inevitable. Up to now, the highest power conversion efficiency reached about 6.5%.⁵¹

4.1 Controlling the SQ layer morphology

In a BHJ solar cell device, exciton formation takes place in both donor and acceptor domain as well as at the donor/acceptor interface. All the excitons need to diffuse to the donor/acceptor interface for the charge separation and dissociation to occur. The separated holes and electrons then travel through the semiconducting materials to reach the electrodes. Because both the exciton formation and diffusion processes prefer large donor/acceptor interface, a rough morphology of semiconductor layer that maximize the interface is thought to be beneficial for higher BHJ cell efficiency.^{52, 53} Therefore charge transportation through the semiconducting layer should be less resisted; accordingly charge transfer between the semiconducting molecules is expected to be improved by highly ordered microstructure of both donor/acceptor semiconductors.

In term of charge transportation, morphology of semiconductor layer can be a crucial influencing factor. Thus controlled aggregation of SQ molecules should be studied to tackle this problem. Since SQs are highly polarized planar molecules. They are easy to form crystals in solid state. After deposition, SQ-acceptor blending layer is usually amorphous. The most commonly used way to form ordered

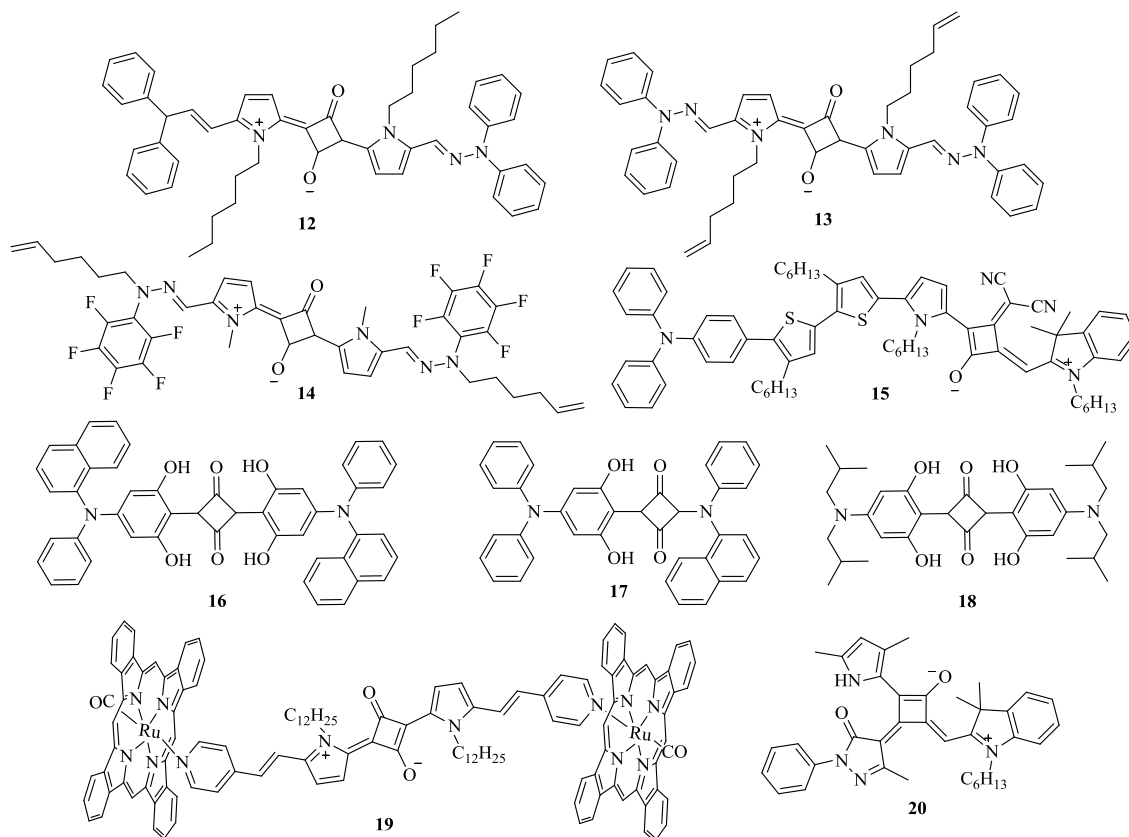


Fig. 9 Squaraines used in OPV devices as electron donors

aggregates is simply to thermally anneal the coating. The SQ molecules will form small crystals due to π - π stacking, enhancing the charge transfer ability of SQ layer. A more detailed study of annealing process was performed by Zimmerman *et al.* According to their experiments, annealing should be performed after the deposition of C_{60} , thereby maintaining the roughness of SQ- C_{60} interface as well as improving order of the SQ bulk.⁵⁴ The disorder of the interfacial molecules will minimize the polaron-pair recombination.⁵⁵

Since SQ molecules can form both H-aggregates and J-aggregates, there should be a difference in solar cell performance between these aggregation states. As illustrated in **Fig. 10**, in J-aggregates, holes can be transferred freely through the SQ domain, and relatively large contact area between SQ and PCBM is also achieved, leading to a significant increase of J_{sc} , and higher power conversion efficiency. Therefore, J-aggregates are generally preferred in BHJ cells.⁵⁶

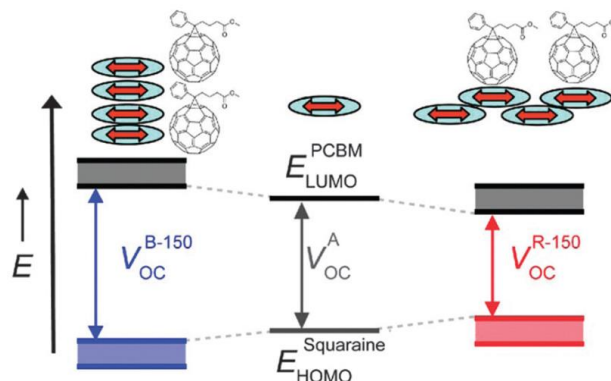


Fig. 10 Both H-Aggregates and J-Aggregates provide sufficient conductance for charge transfer within SQ phases. H-Aggregates of SQ increases the V_{oc} slightly, however inefficient contact between SQ molecules and PCBM dramatically lowers the J_{sc} , resulting in poor PCE. On the other hand, J-Aggregates of SQ secures large contact interface between SQ and PCBM, making great improvements in cell performance. Reproduced from Ref. 56 with permission from the PCCP Owner Societies.

Apart from thermal annealing, molecular design can also improve the aggregation of SQs. Employing arylamine groups on SQ molecules is able to enhance the π - π stacking between the molecules, thereby improving the hole mobility within SQ

Tab. 1 Performances of SQ based solar cell

SQ molecule	Solar cell type	Light source	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	ff (%)	η (%)	reference
1	DSSC	75 mW/cm ^{2*}	4.4	540	56.7	2.17	25
2	DSSC	AM 1.5G	1.92	140	42	0.113	31
3	DSSC	AM 1.5G	10.50	603	71	4.5	32
4	DSSC	AM 1.5G	14.8	642	71	6.74	37
5	DSSC	AM 1.5G	11.12	422	55.7	2.61	33
6	DSSC	AM 1.5G	9.4	432	57.8	2.34	33
7	DSSC	AM 1.5G	16.4	635	70	7.30	39
8	DSSC	AM 1.5G	5.09	600	69	2.09	42
9	DSSC	AM 1.5G	4.03	560	64	1.46	42
12	BHJ	AM 1.5G	7.16	550	37	1.39	59
13	BHJ	AM 1.5G	9.32	570	37	1.99	59
15	BHJ	AM 1.5G	9.05	690	33	2.05	61
16	BHJ	AM 1.5G	10.0	900	64	5.7	53
18	OPV	AM 1.5G	5.58	590	51	1.8	57
19	BHJ	**	1.65	590	28	0.285	68

* The light source is a 250W tungsten halogen lamp

** The experimental conditions are not mentioned in the reference.

domain.^{57, 58} Besides, compared to the SQs with alkyl groups, alkenyl groups substituted SQs forms extra interaction between alkenyl and phenyl groups (**12,13**), enhancing the hole transfer efficiency of the devices.⁵⁹

4.2 Lowering the HOMO of SQs

To achieve a higher V_{oc} value in a SQ based BHJ solar cell, there are two common methods: one is to reduce the charge recombination at the donor-acceptor interface; the other is to lower the HOMO level of SQ donors, therefore increase the band gap between the HOMO of SQ and the LUMO of PCBM. A typical practice is to employ various electron withdrawing groups. Though many substituent groups such as pentafluorophenyl (**14**) and dicyanomethylene (**15**) have been tried, the most success ones by far are the arylamine groups.^{60, 61} Arylamine lowers the HOMO of **16**

to -5.3eV compared to -5.1eV of **18**, and enhances the π - π stacking of SQ molecules at the same time.^{53, 57} While other groups like pentafluorophenyl greatly disrupted the ordered morphology of SQs resulting in even poorer performance than parent SQs. The further modification of arylamine groups is perhaps joining the aryl moieties with conjugations. For example, use carbazole group instead of *N*, *N*-diphenyl groups of molecule **12**. Carbazole group has been used in OLEDs as a hole transporter, suggesting its potential to improve the electronic performances of the SQ donors.^{62, 63} Also it was found to deepen the HOMO of SQs greatly, thus elevating the V_{oc} of the solar cells.⁶⁴

4.3 Panchromatic absorption of SQ donors

A panchromatic absorption is also desired for the improvement of external quantum efficiency, which in turn increases the J_{sc} of the device. Quite alike DSSCs, SQ blends, dye ensembles and asymmetry are used as valid strategies.

As shown in **Fig. 11**, the simplest solution to broaden absorption is blending red-IR harvesting SQs with molecules of higher absorption wavelengths. The Förster resonance energy transfer (FRET) between different donor materials will enable efficient panchromatic energy harvest, increasing the J_{sc} of the device.⁶⁵ However, an efficient FRET between different dye molecules requires the overlap of one dye's emission spectrum and another's absorption spectrum; moreover, both blended molecules (which should be alike in structure with SQ main body) and blending ratio should be carefully controlled, otherwise there won't be any efficient pathway for hole transportation.^{66, 67}

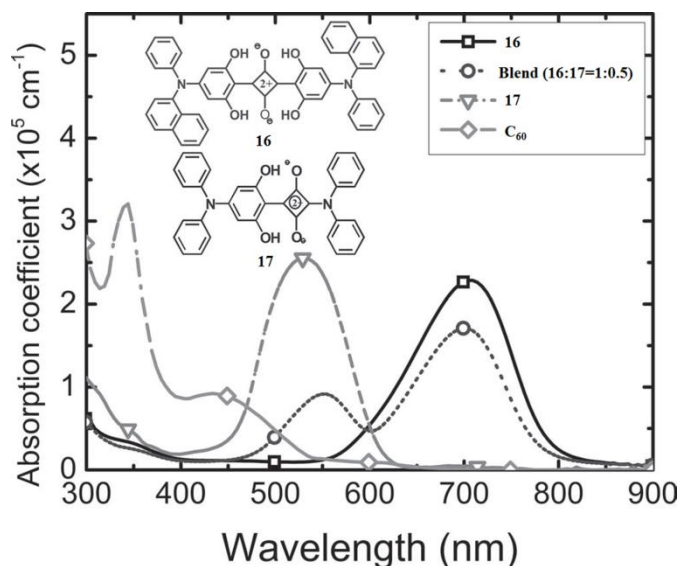


Fig. 11 Blending of SQs to broaden the absorption window of donor materials.⁶⁶

Another feasible method is to assemble SQ with molecules of different absorption bands. Silvestri and coworkers have constructed an ensemble of SQ and phthalocyanine (Pc). Though this ensemble (**19**) has both characteristic absorption of SQ and Pc, the high dark current leads to poor power conversion efficiency.⁶⁸

The most promising solution perhaps lies in the SQ molecule itself. To enhance the absorption of high-energy solar radiation, there should be an electron withdrawing group directly connected to the squaraine core.⁶⁶ Asymmetry formed

by an electron withdrawing group (**20**) can both introduce new short wavelength absorption to the SQ absorption spectrum and broaden the long wave length absorption.⁶⁹

The performances of some representative SQ based solar cells are listed in **Tab. 1**. SQ based OPV solar cells are indeed less efficient than DSSCs, and the design strategies of OPVs are vague and uncertain compared to DSSCs. It is conceivable that OPVs have room for improvements in near future, as OPVs are attracting increasing attentions for new solar cell researches.

5. Summary

SQs have been widely used in DSSCs and OPV solar cells for their intense absorption at red-IR region of solar spectrum. However conventional SQ's absorption band is too narrow for the cells to reach high J_{sc} value, provoking various molecular design and diverse synthetic routes to acquire these molecules in recent years. Much attention was focused on molecular modification of SQs to optimize SQ-based DSSC& OPV devices. Several design strategies of SQ molecules are presented for both kinds of solar cells as guidelines for further researches. However there is no established theory to guide further development of commercially available organic solar cells, thus more attempts should be made to acquire more fundamental insights. Also the importance of device fabrication techniques should not be neglected.

SQs are red-IR absorbing materials; however they themselves are still unable to cover the whole solar spectrum. In this sense, cooperation with other blue-absorbing dyes is an efficient way to improve the performance of SQ-based solar cells. FRET has proven itself an effective way to make this cooperation possible for both kinds of solar cells, but it requires spectra overlap between the different dyes. Meanwhile another energy transfer strategy, i.e. π -bridging, has found its potentials in this field, which does not require spectral overlap, providing more opportunities for the dye combinations. And thanks to the versatility of SQ's core substitution, the formation of π bridges is becoming a feasible way to further exploit the application of SQ molecules in photovoltaic cells.

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