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# Improvement of dye-sensitized solar cells: what we know and what we need to know

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The dye-sensitized solar cell (DSC) has been regarded as one of the most promising next-generation solar cells. Tremendous research efforts have been invested to improve the efficiency of solar energy conversion which is generally determined by the light harvesting efficiency, electron injection efficiency and undesirable charge recombination degree. Recently, charge recombination and electron injection efficiency, that are correlated with the open circuit voltage ($V_{oc}$), have received more and more attention for their crucial roles in the further improvement of the efficiency of DSCs. In this review article, the factors that affect charge recombination and electron injection efficiency systematically discussed in order to formulate basic guidelines and strategies for improving $V_{oc}$ and the overall performance of DSCs is reviewed.

## 1. Introduction

Searching for clean and sustainable energy resources has become an urgent priority for the world. Solar energy is regarded as one of the perfect energy resources. Huge efforts have been invested in developing highly efficient solar energy conversion technologies and the most prospective approach is converting solar energy into electricity. The emerging photovoltaic industry has been growing rapidly in recent years. The price of solar power from the state-of-the-art inorganic silicon technology still significantly exceeds that from the electrical grid, thus prohibiting the large-scale application of silicon-based solar energy. There has been a continuous effort in searching for affordable organic solar energies among which dye-sensitized solar cells (DSCs) thus far demonstrate the highest energy conversion efficiency, and have been regarded as the most prospective technology.[1]

Since the pioneering work of O'Regan and Grätzel in 1991,[2] tremendous efforts were made to improve the performance of DSCs.[3,4] However, ever since the landmark work reporting 10% efficiency in 1993, the maximum efficiency has plateaued over the last 16 years, with a highest efficiency of 11% reached up to now.[3] One important reason for this is that there is lack of efficient panchromatic sensitizers (400 nm–1200 nm), as the absorption spectra of most efficient sensitizers are between 400 nm–800 nm. For the sensitizers that achieved the highest efficiencies up to now, the highest occupied molecular orbital (HOMO) energy level is located at −5.0 eV,[5] which is marginally lower than the HOMO energy level ($E_{HOMO}$) of the redox couple $I^-/I_3^-$ (−4.9 eV).[6] The lowest unoccupied molecular orbital (LUMO) energy level is about −3.5 eV,[5] which is much higher than the $TiO_2$ conduction band (CB) energy level (−4.0 eV),[7] therefore, it seems plausible to broaden the energy conversion region of sensitizers by downshifting the sensitizer LUMO energy level ($E_{LUMO}$). However, one thorny problem is that it will bring down the electron injection efficiency and increase the charge recombination dramatically, which, in turn, reduces the efficiency.[8] Therefore, in order to further improve the efficiency of DSCs, one urgent work is needed to reduce the charge recombination and increase the electron injection efficiency. Additionally, charge recombination and electron injection efficiency are closely correlated with the open-circuit photovoltage ($V_{oc}$), which means $V_{oc}$ becomes the principle factor among many factors accounting for the further improvement of the performance of DSCs.[9,10] Various efforts such as sensitizer modification,[11] usage of additives,[12] co-adsorbents,[13] and novel redox couples[14] were made to improve the $V_{oc}$. Recently, the fast developing organic sensitizers present a new opportunity to enhance the $V_{oc}$ by exquisite molecular design.[15] In addition, in recent years, tandem DSCs received a great deal attention for their great potential to increase the $V_{oc}$ and efficiency of DSCs.[16] In this article, we shall try to review this field systematically in order to formulate basic

### Broader context

Photovoltaic technology is recognized to be one of the most ideal solutions toward the worldwide energy crisis. The dye-sensitized solar cell (DSC) is regarded as the most viable one due to its low-cost and facile fabrication, which has aroused increased interest of industrial sector in recent years. Further improvement of the performance of DSCs is critical to fulfil the purpose of large-scale applications and replacement of traditional fossil fuels. In this perspective article, we analyzed in detail the challenges encountered for the improvement of DSCs and formulated basic guidelines and strategies for improving the devices overall performance.

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guidelines and strategies for improving $V_{oc}$ and the performance of DSCs. The fundamental energy conversion mechanism of the DSC device and the major parameters that characterize the device performance will be described in Section II, to formulate major strategies for improving energy conversion performance. The major strategic methods thus outlined will be fully elaborated in Section III. Finally, conclusions and outlook will be made in Section IV.

## 2. Energy conversion in DSCs

Fig. 1 shows the energy band structure of the DSC device as well as the principal carrier transfer channels.[9] The sensitizer dye absorbs light (*hν*), by which an electron is excited from the HOMO to the LUMO of the dye and the photogenerated electron will be injected from the LUMO of the dye to the CB of $TiO_2$ (channel (a) in Fig. 1). The electron will further transfer to the photoanode fluorine-doped tin oxide (FTO), through the external load, the cathode FTO, the Pt layer, the HOMO of the redox couples, and finally back to the HOMO of the dye (channel (b)). There are many other undesirable carrier transfer channels including charge recombination of the injected electrons from the $TiO_2$ CB (defined as the injected electron) to cations of the dyes (c) and to redox couples (d), and direct decay from the LUMO to the HOMO of the dye (e).

In principle, the energy conversion efficiency of a DSC is the product of the short-circuit photocurrent, $J_{sc}$, the open-circuit photovoltage $V_{oc}$, as well as the fill factor.[4a] Generally speaking, the efficiency of the DSC is largely determined by $J_{sc}$ and $V_{oc}$. $J_{sc}$ is usually correlated with the sensitizer absorption capability and the electron injection efficiency, whereas the factors that affect $V_{oc}$ are much more complicated than $J_{sc}$. Referring to the energy band structure and the carrier transfer processes in Fig. 1, the $V_{oc}$ is calculated by the following equation[17]

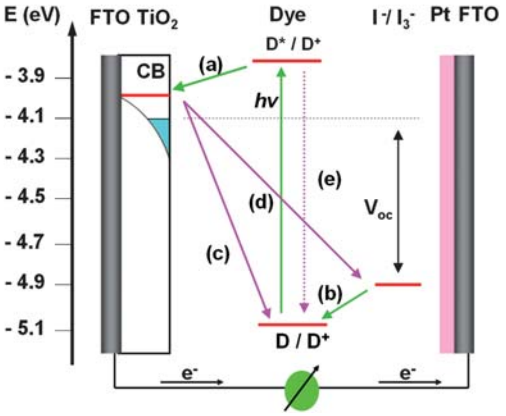
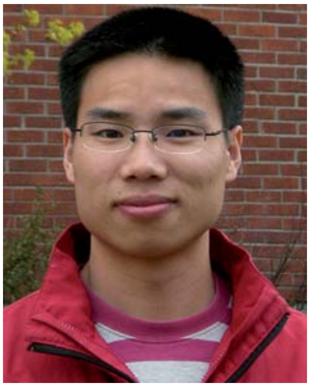


**Fig. 1** Energy band structure and major electron transfer processes in DSCs.

$$V_{oc} = \frac{E_{CB}}{q} + \frac{kT}{q}\ln\left(\frac{n}{N_{CB}}\right) - \frac{E_{redox}}{q} \qquad (1)$$

where $n$ is the number of the electrons in $TiO_2$, $N_{CB}$ is the effective density of states, $E_{redox}$ is the HOMO level of the redox couples, and $q$ is the unit charge. In the above equation, the sum of the first two terms is the quasi Fermi level in $TiO_2$. Eqn (1) thus shows that $V_{oc}$ is the difference between the quasi Fermi level in $TiO_2$ and the $E_{redox}$. Generally, as the number of injected electrons in $TiO_2$, $n$, is smaller than $N_{CB}$, the maximum quasi Fermi level is $E_{CB}/q$, and the maximum $V_{oc}$ becomes $(E_{CB} - E_{redox})/q$, *i.e.*, the difference between the $E_{CB}$ of $TiO_2$ and the $E_{redox}$.[9,10a] According to eqn (1), $V_{oc}$ can be enhanced either by increasing the $TiO_2$ $E_{CB}$ or downshifting the $E_{redox}$.[18] In an open circuit, the



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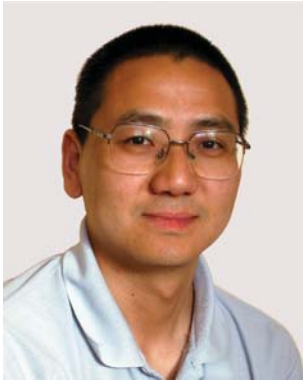

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number of electrons in the $TiO_2$, $n$, is determined by the balance between electron injection and charge recombination. An improvement in the light absorption capability and electron injection efficiency will increase the number of injected electrons in $TiO_2$ and then increase $V_{oc}$, while the charge recombination processes will reduce the electron population in $TiO_2$, and thus cause a decrease in $V_{oc}$.

Corresponding to the factors charge recombination, electron injection, $TiO_2$ $E_{CB}$, and $E_{redox}$ that are listed above, there are six strategic ways to increase $V_{oc}$ as follows: (1) reduce the charge recombination between redox couple and the injected electrons in the $TiO_2$ CB; (2) reduce charge recombination between the oxidized sensitizer and the injected electrons in the $TiO_2$ CB; (3) increase the electron injection efficiency; (4) increase the $TiO_2$ $E_{CB}$; (5) downshift the $E_{redox}$; (6) tandem DSCs. In the following we shall try to elaborate on the details of these strategic methods.

## 3. Strategies for improving $V_{oc}$

### 3.1. Reduce the charge recombination between the redox couple and the injected electrons in the $TiO_2$ CB

**3.1.1 Enhance the blocking effect of the sensitizers.** Recently, organic DSCs have been receiving much attention for the adjustability of their structures, their high molar extinction coefficients, and cost-effective facile preparation processes.[15,19] However, the energy conversion efficiencies of organic sensitizer-based cells are generally lower than those based on ruthenium (Ru) complex sensitizers. The major reason is the relatively low $V_{oc}$ for metal-free DSCs. Mori and coworkers found that at matched electron density, most DSCs using organic dyes showed shorter electron lifetime in comparison to the DSCs using the Ru dyes.[19a] The shorter lifetime (generally, the lower charge recombination degree corresponds to larger charge recombination resistance, longer electron lifetime in $TiO_2$, and smaller dark current) was attributed mostly to the higher $I_3^-$ concentration in the vicinity of the $TiO_2$ surface. One important reason for the higher $I_3^-$ concentration is the lower packing density of organic dyes compared to Ru dyes.[19a] The sensitizer adsorption number affects the $V_{oc}$ and efficiency significantly. For sensitizer **S5** (Fig. 2),[15a] the photovoltage decreased distinctly with the decrease in sensitizer adsorption number, indicating the important role of sensitizer in blocking charge recombination (Fig. 2). A compact sensitizer layer on $TiO_2$ surface is important to reduce the charge recombination between $TiO_2$ and the redox couple.

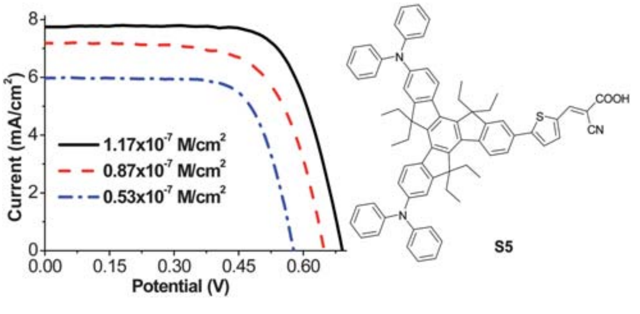

**Fig. 2** Photocurrent–voltage curves of sensitizer **S5** with different adsorption concentrations.

In order to form a compact sensitizer layer on the $TiO_2$ surface, we developed a novel kind of organic sensitizer **S4** (Fig. 3) based on starburst triarylamine, which shows a $V_{oc}$ value higher than **S1** (Fig. 3) based on single triphenylamine.[20] At the same time, Lin's group developed a kind of starburst-type sensitizer (**L1** and **L2**) (Fig. 3).[21] Although there is one more branch on the sensitizer, the total sensitizer adsorption amount did not decrease substantially, which means the sensitizer layer thus formed is more compact than in sensitizers **L3** and **L4** which have rod-like structures. The charge recombination resistance at the $TiO_2$ surface for **L1** and **L2** are significantly larger than their counterparts **L3** and **L4** (Fig. 3). A similar observation was reported by Sun and coworkers.[22] $V_{oc}$ of starburst-triarylamine-based sensitizers **D7** and **D11** (Fig. 3) was increased compared with the simple triarylamine counterparts **D5** and **D9** (Fig. 3). The electron lifetime of the injected electrons of **D7** and **D11** in $TiO_2$ are obviously longer than that of the sensitizers with single triphenylamine units (**D5** and **D9**). These results prove that the starburst sensitizers show better performance than rod-shape sensitizers for blocking charge recombination between the redox couple and $TiO_2$.

Another important strategy to block the approach of the redox couple is to link long alkyl chains onto the sensitizer. There is still some controversy surrounding the mechanism of how the long alkyl chains work. Hara *et. al* speculated that the hydrophobic alkyl chains can suppress the electron recombination by keeping oxidized species in the redox electrolyte at a distance from the $TiO_2$ surface.[23] Mori and coworkers proposed that the alkyl chains themselves will not block the approach of the redox couple, and the main function of the alkyl chains is to facilitate the formation of compact sensitizer layer.[19a] Another possibility is that the alkyl chains reduce intermolecular aggregation and improve the electron injection efficiency.[24] Hara's group reported that the $V_{oc}$ can be improved by connecting alkyl chains on the carbazole based organic dyes (Fig. 4).[23,25] Although the sensitizer adsorption number largely decreased , after the connection of alkyl chains, the electron lifetime in $TiO_2$ increased significantly. Recently, Wang's group[26] and Sun's group[27] developed triarylamine based sensitizers **D21L6** and **C217**, respectively, (Fig. 4) with alkyl chains connected to the triarylamine. The photovoltage and the efficiency were improved significantly compared with sensitizers without the alkyl chains. Müllen and coworkers synthesized perylene sensitizers (**ID34**) (Fig. 4) with multi-alkyl chains attached.[28] The $V_{oc}$ was largely improved as well. Our group developed a kind of cone-shaped dye (**S6**) (see Fig. 4) with several long alkyl chains attached to the linker of the starburst sensitizer.[24] As the sensitizer adsorption number did not decrease obviously, it can be speculated that a more compact blockading layer is formed on the $TiO_2$ surface. Charge recombination between the injected electron and triiodide is effectively reduced, thus explaining the longer transient $V_{oc}$ decay time and the lower dark current. Significantly improved $V_{oc}$ was observed for cone-shaped dyes **S6** and **S7**. Recently, Hagfeldt and Sun *et. al* studied the effect of alkyl chains of several starburst shape sensitizers.[29] Sensitizer **D35** (Fig. 4) can form a compact blocking layer themselves and the addition of extra coadsorbent does not improve the cell performance further. Long alkyl chains were also found to be useful for indoline (such as **D205**) (Fig. 4),[30] benzothiazole merocyanine,[31] squarine,[32] phenoxazine (such as

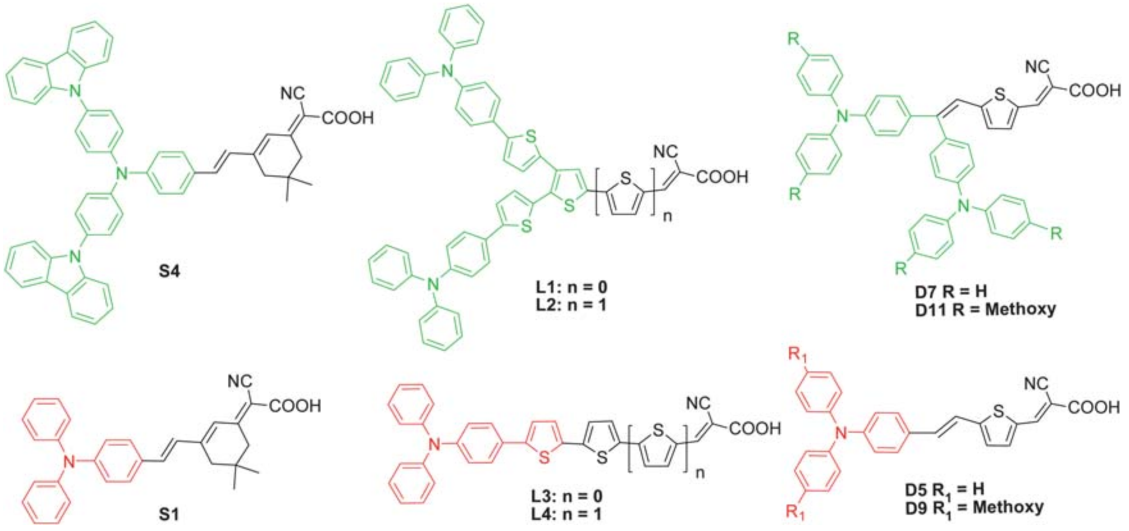

**Fig. 3** Molecular structures of typical starburst structure sensitizers.

**TH301**) (Fig. 4),[33] and bisindoylmaleimide[34] (such as **I3**) (Fig. 4) based sensitizers for improving $V_{oc}$. In conclusion, for organic dyes, the attachment of alkyl chains can reduce effectively charge recombination and enhance $V_{oc}$ and efficiency.

The connection of alkyl chains or triarylamine units was also proved to useful for Ru complexes.[35–39] Durrant *et. al* synthesized a series of Ru complexes (**C1–C13**) (Fig. 5) with alkyl chains of different length.[36] It was found that the injected electron lifetime increased with the increase in the chain length. As with the addition of triphenylamine, the dark current of sensitizer **P–Ru-1** is only half that of **P–Ru-5** (Fig. 5). It was speculated that the connection of the triphenylamine group is favorable for the

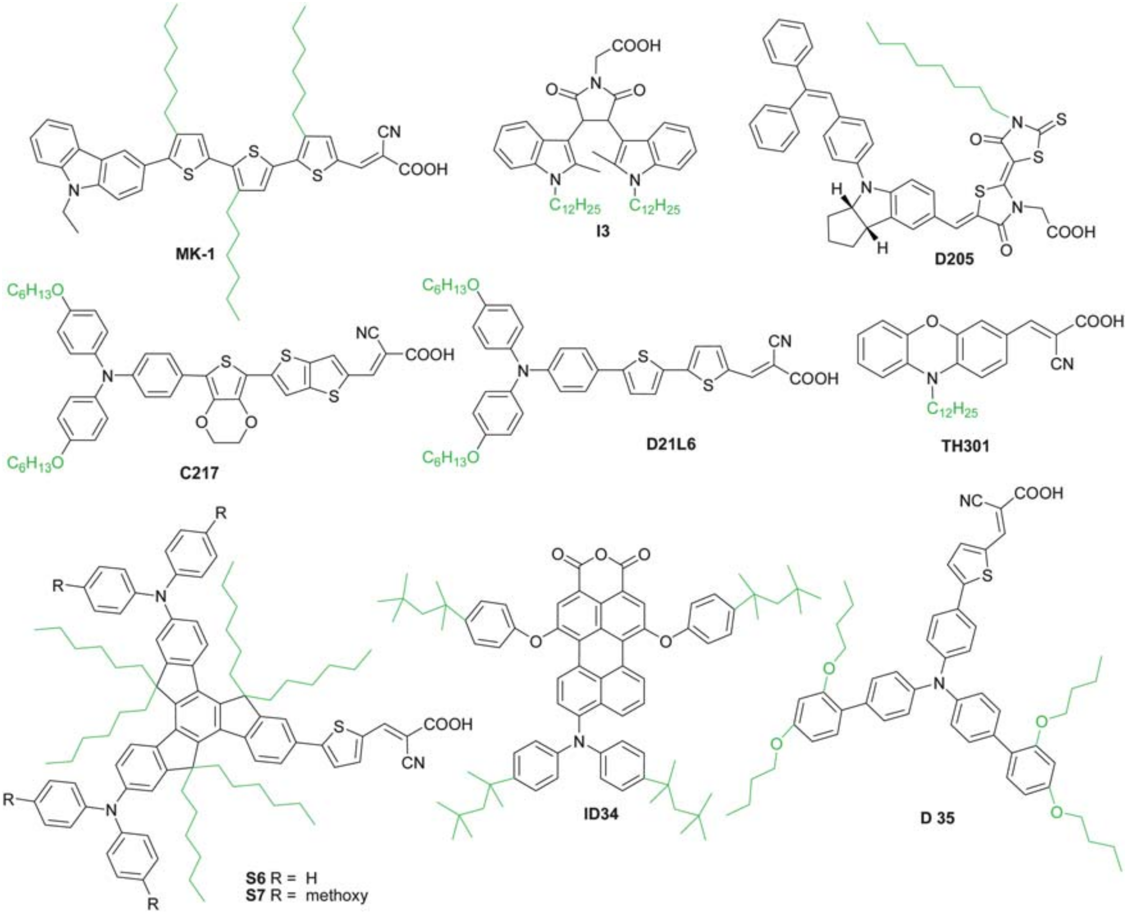

**Fig. 4** Molecular structures of typical dye sensitizers linked with long alkyl chains.

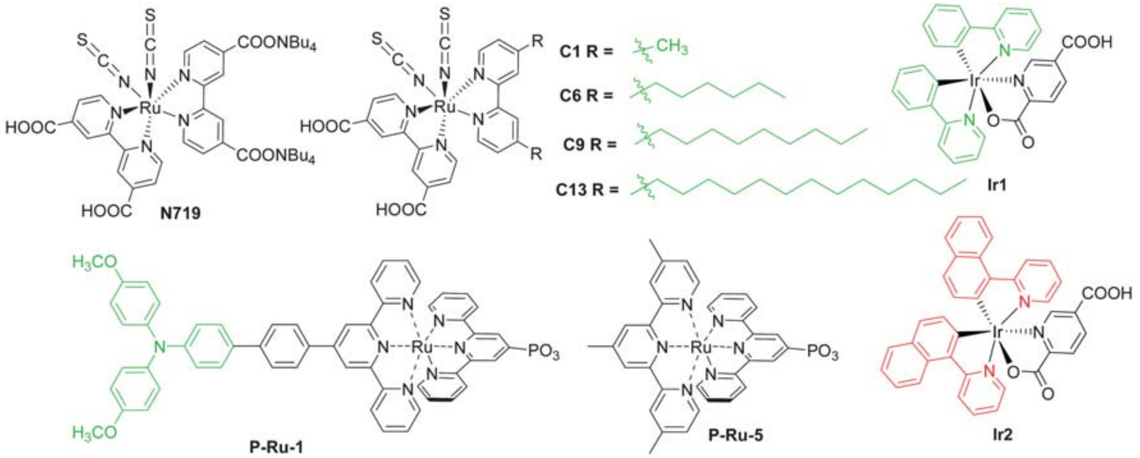

**Fig. 5** Molecular structures of complex sensitizers to reduce charge recombination.

formation of a compact sensitizer layer. However, among all Ru complex sensitizers, sensitizer **N719** (Fig. 5) shows the highest $V_{oc}$ of 0.846 V based on liquid $I^-/I_3^-$ redox couples.[5b] One important reason is its high packing density on the $TiO_2$ surface.[40] Recently, we found sensitizers with phenylpyridine ligands (**Ir1**) showed a much higher $V_{oc}$ than naphthylpyridine ligands (**Ir2**) (Fig. 5), suggesting that the small ligand is beneficial for forming a compact sensitizer layer.[41] The reason might be the large interspaces between the big ligands which are unfavorable for the formation of a compact sensitizer layer.

Apart from the effect of molecular structure, the sensitizer adsorption solution is also important for the formation of the compact sensitizer layer. Sun *et al.* found that for sensitizer **TPC1**, dichloromethane was the best solution to achieve the highest $V_{oc}$.[42] However, acetonitrile and ethanol are better than dichloromethane for some sensitizers.[44] These results indicate that the choice of the optimal adsorption solution varies with each specific sensitizer. A critical factor in the selection procedure of the solution is the sensitizer's solubility. A high enough sensitizer concentration in the solution is required for forming the compact sensitizer layer.

In addition to the blocking effect of the sensitizer, some efforts were made to block carrier recombination by covering the $TiO_2$ surface with a thin layer of a wide-band gap oxide. Zaban and coworkers first found that by sintering a thin film of $Nb_2O_5$ onto the $TiO_2$ surface, carrier recombination was significantly reduced and $V_{oc}$ increased.[43]

#### 3.1.2 Reduce the complexation between the sensitizer and iodide.

In addition to the blocking effect of sensitizer, recently, O'Reagan and coworkers found another potential factor that is crucial to the determination of $V_{oc}$ is that dye molecules have the potential to "catalyze" the recombination reaction between electrons in $TiO_2$ and the electrolyte.[9a] They found sensitizer **RuPc3** (Fig. 6) showed a relatively low photovoltage and short electron lifetime.[45] It was suggested that the phthalocyanine sensitizer can form a complex with iodide, which further complexes with $I_2$ to form $I_3^-$, and accelerates the charge recombination. Recently, they observed that the presence of the amine (–$NH_2$) group in the sensitizer can significantly aggravate charger recombination by its strong iodide binding capability.[46] An amine substituted sensitizer **AR24** (Fig. 6) shows more serious charge recombination than sensitizer without it, while adsorbents **PACA** (Fig. 6) with the amine group substituted by acetyl show a longer electron lifetime than **PABA** with amine substitute (Fig. 6).[9a] Meanwhile, they found that the charge

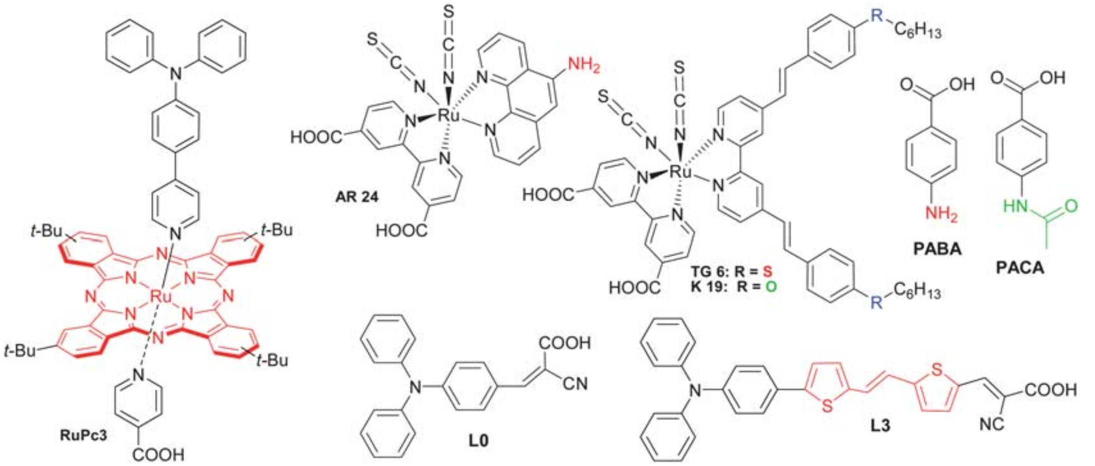

**Fig. 6** Molecular structures of sensitizers that are potential to complex with iodide.

recombination of a sensitizer with an alkyl sulfide substituent (**TG6**) was clearly more serious than the alkoxy group (**K19**).[47] The difference was attributed to the different complexation capability with iodide of the sensitizer.

Recently, Halgfeldt *et. al* investigated the relationship between $V_{oc}$ and molecular structure of a series triarylamine dyes.[17] They found that the interaction between sensitizer and redox couple plays a key role in determining the charge recombination in triarylamine polyene-based sensitizers. **L3** (Fig. 6) dyes showed dramatically enhanced electron recombination in comparison to **L0** (Fig. 6). The electron lifetime in $TiO_2$ in the **L3** dye is even shorter in comparison to bare $TiO_2$. It was suggested that there is an interaction between the **L3** dye molecule and $I_3^-$ and/or $I_2$, and the interaction degree between dyes and electrolyte acceptor species correlated to the increased polarizability of the longer triphenylamine dyes. In order to prevent the approach of the redox couple to the $TiO_2$ surface, it is necessary to reduce the complexation between sensitizer and iodide.

### 3.1.3 Increase the electron injection depth in $TiO_2$.

Apart from the factors discussed above, other potential factors accounting for the charge recombination still need to be clarified. Sensitizers with indoline as the donor and a rhodanine derivative as the acceptor and anchor group are one kind of organic sensitizers with the highest efficiency.[48,49] The photocurrent of some of this kind of sensitizers achieved even higher photocurrent than Ru complex sensitizer **N3**, however, the photovoltage is significantly lower than the Ru complex sensitizer and other organic sensitizers with cyanoacrylic acid as the acceptor.[48] The lower $V_{oc}$ is less likely to be caused by the smaller electron injection efficiency since its higher short circuit photocurrent. Recently, Albinsson and coworkers made a comparison between sensitizers with rhodanine (**A3**) (Fig. 7) and cyanoacrylic acid (**A1**) (Fig. 7) as anchor groups, respectively.[50] It was found for **A1**, electrons are injected farther into the $TiO_2$ nanoparticles, which are less prone to recombine with the electron acceptors. While for **A3**, as the electron density of the sensitizer doesn't show good overlap with the semiconductor, the electrons are more likely to be injected into states close to the $TiO_2$ surface, which greatly enhanced the possibility of charge recombination. Therefore, it can be speculated that the electron injection depth is an important factor that affects the charge recombination.

Besides the factor of the overlap between sensitizer LUMO and $TiO_2$, the sensitizer $E_{LUMO}$ may affect the electron injection depth as well. Our experiments show that methoxy substituted sensitizers (**S7** shown in Fig. 4) have an impressive $V_{oc}$ value which is much higher than the original sensitizers (**S6** shown in Fig. 4).[24] Since the adsorbed amount of **S6** on $TiO_2$ surface is much higher than **S7** and the photocurrent of **S7** is lower than **S6**, the $V_{oc}$ improvement caused by **S7** cannot be explained by the more compact sensitizer layer on the $TiO_2$ surface or higher electron injection efficiency. Meanwhile, the $E_{LUMO}$ was up-shifted with the introduction of methoxy groups, which could be the reason for higher $V_{oc}$. In addition, using magnesium containing $TiO_2$, high $E_{LUMO}$ sensitizer **L0** shows a high $V_{oc}$ of 1.0 V, much larger than that of **N719** at 0.75 V.[51] Since the photocurrent of **N719** is much higher than sensitizer the **L0**, the high $V_{oc}$ is likely to be caused by its high $E_{LUMO}$. It was speculated that the high $E_{LUMO}$ corresponding to deeper electron injection in $TiO_2$ and smaller charge recombination. It should be noted that for organic heterojunction solar cells, it was recently observed that $V_{oc}$ scales linearly with the energy levels of the p-type polymer sensitizer.[52] One can thus speculate that $V_{oc}$ of the DSCs may also correlate with the energy levels of sensitizers, especially $E_{LUMO}$. However, this assumption still needs experimental verification.

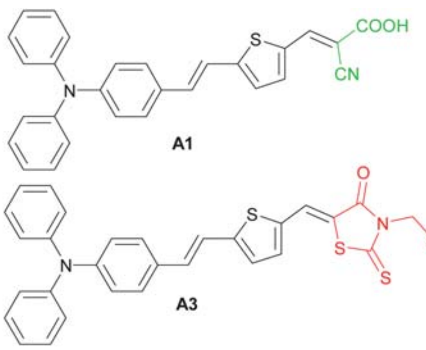

**Fig. 7** Molecular structures of sensitizers with different anchor groups.

As high $E_{LUMO}$ might be favorable for the reduction of charge recombination, it could be beneficial to design a sensitizer with higher $E_{LUMO}$ to enhance the $V_{oc}$. We found that a D-D-π-A sensitizer structure can bathochromically shift the absorption spectra, meanwhile, up-shifting $E_{HOMO}$ and $E_{LUMO}$.[20] Recently, Sun *et. al* added an extra triphenylamine donor on the phenoxazine based sensitizer, by which the absorption spectra was bathochromically shifted and the $E_{HOMO}$ and $E_{LUMO}$ both up-shifted.[33] The conversion efficiency is as high as 7.7% compared with 8.0% of **N719** in the same condition, which might be the highest efficiency of organic sensitizers in comparison with **N719**. Meanwhile, the $V_{oc}$ is higher than the sensitizer without additional donor units and it is even higher than **N719** in the same condition. As the $E_{HOMO}$ of the organic sensitizer is usually lower than the required −5.0 eV, the appropriate uplift of $E_{HOMO}$ can reduce the energy waste between the redox couple and $E_{HOMO}$ of sensitizer and lead to higher efficiency.

## 3.2 Reduce charge recombination between oxidized sensitizer and the injected electrons in $TiO_2$ CB

Besides the charge recombination between the redox couple, the electrons in $TiO_2$ can also recombine with oxidized sensitizer. Durrant *et. al* pointed out that for cell voltages exceeding 0.6 V, the recombination between the injected electrons and the oxidized sensitizer tends to be serious, which will significantly decrease the electron number in $TiO_2$.[53] Much effort was made to reduce this kind of charge recombination by moving the HOMO of the sensitizer away from the $TiO_2$. Bonhôte and coworkers were the first to investigate the charge recombination process in a series of Ru dyes connected with triphenylamine.[39,54] In their model system (without $I^-/I_3^-$ redox couples so that the carrier recombination mostly occurs between the oxidized dye and injected electrons), the lifetime of the injected electrons in $TiO_2$ was enhanced by a significant factor ranging from 10 to 100 times with the introduction of triphenylamine, which increased the distance between the $TiO_2$ surface and the HOMO part of sensitizer. Haque and coworkers reported a novel Ru dye linked

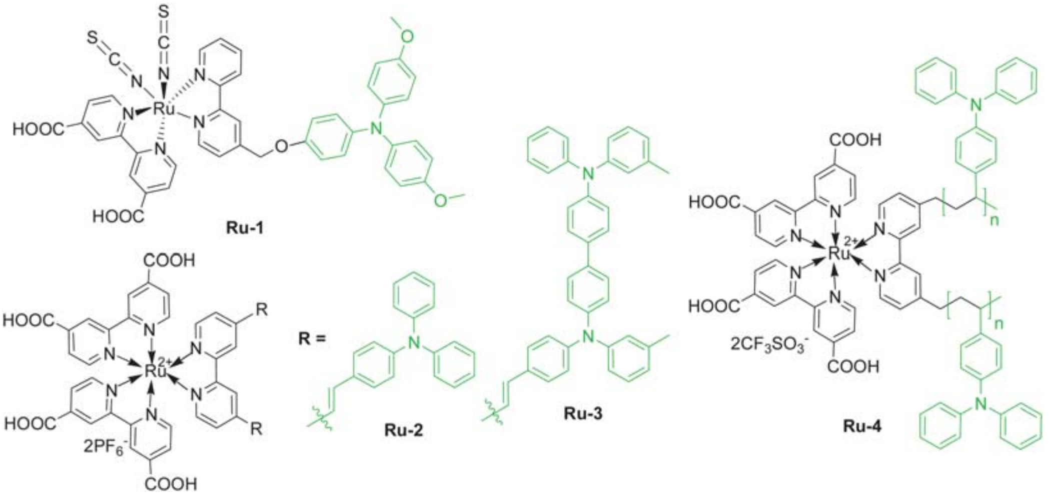

**Fig. 8** Molecular structures of sensitizers with the capability of reducing the charge recombination between $TiO_2$ and oxidized sensitizer.

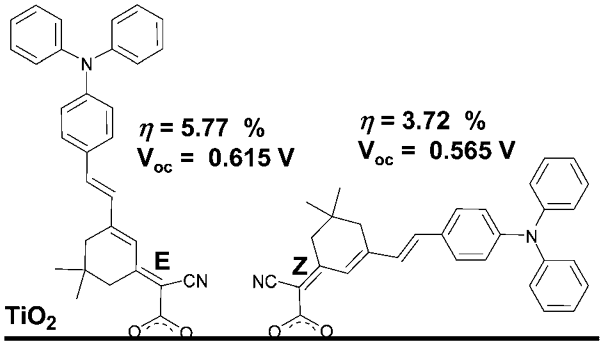

**Fig. 9** Sensitizer configurations of **S1**-E and **S1**-Z on the $TiO_2$ surface.

with antenna-type triphenylamine units (**Ru-2**, **Ru-3** and **Ru-4**) (Fig. 8).[55] The electron recombination halftimes from $TiO_2$ to oxidized sensitizer are 350 μs, 5 ms, and 4 s for **Ru-2**, **Ru-3** and **Ru-4**, respectively, indicating that as the triarylamine substitutes increase, the charge recombination between the oxidized sensitizer decreased dramatically.

For organic sensitizers, as the regeneration of the sensitizer is usually slower than in Ru complexes, the charge recombination between the oxidized sensitizer could be more serious.[19a] Lin *et. al* found the charge recombination between the oxidized sensitizer and $TiO_2$ can be reduced by adopting a multi-branched structure.[21] Recently, we observed two types of configurations denoted as the E-type and the Z-type of cyanoacrylic acid acceptor units for sensitizers with isophorone as linker (Fig. 9).[20] $V_{oc}$ and the efficiency of E-type sensitizers are much higher than the Z-type. It was speculated that the Z-type sensitizer lies down on the $TiO_2$ surface, resulting in more serious charge recombination between oxidized sensitizer and injected electrons, since the donor part is closer to the $TiO_2$ surface.

### 3.3 Increase the electron injection efficiency

**3.3.1 Reduce molecular aggregation.** The dye aggregates formed on the semiconductor surface are considered to be one of the major factors accounting for the low photovoltaic performance of DSCs.[15,56] Aggregation may lead to intermolecular quenching or molecules residing in the system not functionally attached to the $TiO_2$ surface and thus acting as filters, which will decrease the electron injection greatly. In addition, the sensitizer regeneration by redox couple can also be influenced by molecular aggregation.[25a]

To reduce molecular aggregation, one important approach is to design sensitizers with aggregation resistant characteristics. Yeh *et. al* developed a series of aggregation resistant porphyrin sensitizers by connecting the diphenylamine group on the porphyrin unit (**YCY5**, Fig. 10).[57] Li *et. al* synthesized a series of novel perylene based sensitizers with a nonplanar diphenylamine unit on the rear of the sensitizer (**LC5** (Fig. 10)).[58] Sensitizer **LC5** achieved the highest efficiency amongst all the perylene dyes. Thus, for sensitizers with planar structures susceptible to serious aggregation, such as porphyrin and perylene, the introduction of additional nonplanar groups can enhance the $V_{oc}$ and efficiency effectively by giving the dyes aggregation resistant abilities. Sun *et. al* synthesized a series of sensitizers with phenothiazine as donor unit, which can effectively prohibit aggregation by its Y-type nonplanar structure.[59] The $V_{oc}$ of dye **TH208** (Fig. 10) is significantly higher than sensitizers with planar tetrahydroquinoline donor groups. Ko and coworkers synthesized a novel sensitizer with nonplanar spirobifluorene as the linker,[60] the $V_{oc}$ is as high as 0.75 V.

Most organic sensitizers constitute of a donor, linker, and acceptor, which are usually in a rod-shape configuration.[15] Extension of the linker length offers a means to broaden the absorption spectra of the sensitizer, however, aggregation will be aggravated. In order to extend the absorption spectra and prevent aggregation at the same time, we designed and synthesized the starburst triarylamine based sensitizers with D-D-π-A configuration by adding electron donor groups at the periphery of nonplanar triarylamine (Fig. 3).[20] Sensitizer **S4** exhibits broader light absorption region and higher $V_{oc}$ than **S1** (Fig. 2). In addition, to develop sensitizers with broadened absorption spectra free from aggregation, sensitizers with strong electron donor and acceptor groups might be a good substitute for those with extended linkers.

Another strategy to reduce the molecular aggregation and increase the electron injection efficiency is the addition of

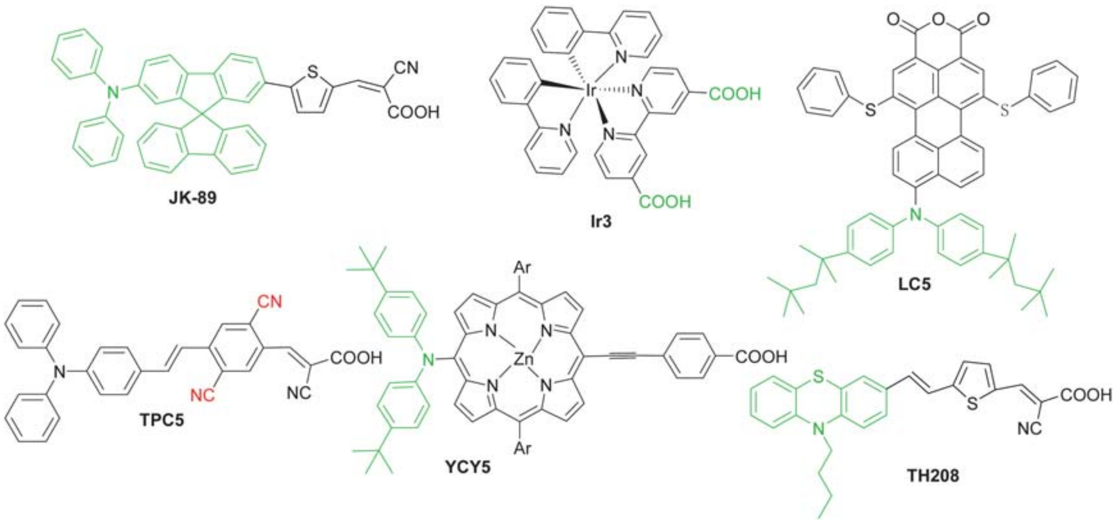

**Fig. 10** Molecular structures of typical dye sensitizers to reduce aggregation.

co-adsorbents during the sensitizer adsorption. Grätzel and coworkers found that using hexadecylmalonic acid (**HDMA**) as co-adsorbents can effectively improve $V_{oc}$ of the cells based on Ru bipyridine complex (**Z907**).[61] The self-assemble of 1-decylphosphlic acid (**DPA**) with **Z907** can reinforce the $V_{oc}$ and stability of the solar cells under long-term irradiation.[13] However, the co-adsorbents do not always result in an increased $V_{oc}$. We investigated the effect of co-adsorbent deoxycholic acid (**DCA**) for several iridium complexes.[41] Sensitizer **Ir1** (Fig. 5) shows decrease in both $V_{oc}$ and the energy conversion efficiency because of the **DCA** co-adsorption. It was suggested that sensitizer **Ir1** itself can prevent molecular aggregation and form a compact sensitizer layer at the same time. The co-adsorption of **DCA** will not further reduce aggregation, on the contrary, will cause the reduction of the sensitizer adsorption amount and injected electrons. Co-adsorbents were also used for metal free organic sensitizers such as coumarin,[62] bisindolymalemide,[34] tetrahydroquinoline,[63] triarylamine,[59b] and indoline dyes.[30,64] $V_{oc}$ and the energy conversion efficiency was effectively enhanced by the co-adsorption procedures when the original sensitizers suffered from aggregation. Meanwhile, the dark current test showed that the carrier recombination between the injected electrons and $I_3^-$ ions was reduced as a result of the co-adsorption.[62] It was suggested that aggregation may result in large interspaces among the clustered dyes and aggravate charge recombination. Due to the co-adsorption of adsorbents, a more compact protection layer can be formed on the $TiO_2$ surface.

### 3.3.2 Increase the overlap between the sensitizer LUMO and $TiO_2$.

Another factor that affects the electron injection efficiency is the overlap between the sensitizer LUMO and $TiO_2$.[34] Recently, Durrant *et. al* investigated the electron injection efficiencies of porphyrin sensitizers with conjugated and non-conjugated linkers between the anchor group and sensitizer LUMO.[65] The performance of the sensitizer with a conjugated link is significantly higher than the one with non-conjugated linker. On the other hand, to keep efficient electron injection, it is better that the electron acceptor is close to the anchor group. Adding extra acceptors on the conjugation linker is a widely adopted approach to broaden the absorption spectra (**TPC5**, Fig. 10),[43,66] however, the $V_{oc}$ and efficiency generally decreased after the modification. In addition, the increase in the number of the anchor groups can enhance the electron injection efficiency. We found that the electron injection efficiency of **Ir3** (Fig. 10) with two carboxyl groups is distinctly higher than **Ir1** and **Ir2** (Fig. 5) with single carboxyl group.[41] It was speculated that multi-anchor units can enhance the electron density overlap between the sensitizer and $TiO_2$. Therefore, it can be concluded that to enhance the electron injection efficiency, it is critical to keep the overlap between the sensitizer LUMO and $TiO_2$.

In addition to the overlap between sensitizer LUMO and $TiO_2$, the sensitizer $E_{LUMO}$ will affect the electron injection as well. Durrant *et. al* found that kinetics of electron injection are strongly dependent upon the relative energy level difference of the dye excited state relative to $TiO_2$ $E_{CB}$, and large differences results in faster electron injection speed.[67] Hence, high $E_{LUMO}$ is also favorable for the enhancement of the electron injection efficiency.

### 3.3.3 Reduce the non-radiative decay of the excited sensitizer.

Recently, we investigated the relationship between the emission intensity and electron injection efficiency of iridium complex sensitizers.[41] It was found that the electron injection efficiency was consistent with the luminescence quantum yield of the sensitizer. Generally, less non-radiative decay guarantees high luminescence quantum yield. Accordingly, in order to enhance the electron injection efficiency, it is important to reduce the non-radiative decay which arises mainly from the molecular vibration. As a result, it is critical to keep the molecular rigidity in order to reduce the non-radiative decay. The ethylene linkage is susceptible to isomerization upon irradiation, which leads to serious energy loss in the form of vibration. For sensitizers with several ethylene units, the $V_{oc}$ and efficiencies are generally low.[17] Hence, in the sensitizer design, the ethylene linkage is not a good candidate for the conjugated link. In addition, a compact sensitizer layer formed on the $TiO_2$ surface is also suggested to be helpful in the effective suppression of the molecular vibration.

### 3.4 Upshift the $TiO_2$ $E_{CB}$

According to Eq (1), the $V_{oc}$ can be increased by the upshift of $E_{CB}$. The adsorption of $Li^+$ on the $TiO_2$ surface was found to downshift the $TiO_2$ $E_{CB}$.[12] Many electrolyte additives have been utilized to adsorb the protons and/or $Li^+$ ions so that these cations were kept from approaching $TiO_2$ surface. Grätzel's group reported that after adding 4-*tert*-butylpyridine (**TBP**) to the electrolyte, $V_{oc}$ was increased from 0.38 V to 0.72 V and the overall conversion efficiency was significantly increased from 7.12% to 10%.[3a] Since then, many nitrogen-containing heterocyclic derivatives including imidadole, triazole, pyrimidine and benzimidazole were tested as additives in the electrolyte.[68–70] However, when the $E_{LUMO}$ of the sensitizer approximates $TiO_2$ $E_{CB}$, the presence of additive will reduce the photocurrent dramatically. Recently, our group synthesized a novel kind of cyanine sensitizers **TJ1** and **TJ2** (Fig. 11),[71] in which the addition of **TBP** will bring down the cell performance significantly because of their low $E_{LUMO}$. The efficiency of **TJ2** is higher than **TJ1** after the addition of **TBP** for the relatively higher $E_{LUMO}$ of **TJ2**. Therefore, it can be concluded that for sensitizers with $E_{LUMO}$ close to $TiO_2$ $E_{CB}$, the upshift of the $TiO_2$ $E_{CB}$ by the usage of additive may not improve their performance.

In addition to the additives, complexation of the sensitizers with cations in the electrolyte can also improve $V_{oc}$. Grätzel and colleagues introduced (triethylene glycol methyl ether) methyl ether substituents to the bipyridyl ligand (Fig. 11), the $V_{oc}$ of which was enhanced compared to the counterpart with alkyl chains.[72] It was proved that (triethylene glycol methyl ether) methyl ether can coordinate with lithium cations ($Li^+$) to block its approach towards the $TiO_2$ surface.

Apart from the above mentioned two approaches, in order to upshift $TiO_2$ $E_{CB}$, some efforts were also made by covering the $TiO_2$ surface with a thin layer of oxide such as $Al_2O_3$, $CaCO_3$, $BaCO_3$, $BaTiO_3$, $SrTiO_3$ and MgO with basic property stronger than $TiO_2$.[73] It was proved that as the adsorption of these oxides on the $TiO_2$ surface, the $E_{CB}$ was effectively upshifted and the $V_{oc}$ was improved. In addition, doping $TiO_2$ with other ingredients such as $Nb_2O_5$ and Mg can upshift the $TiO_2$ $E_{CB}$ as well.[74]

### 3.5 Downshift the $E_{redox}$

As shown by eqn (1), $V_{oc}$ can be increased by replacing the $I^-/I_3^-$ electrolyte with redox couples with lower $E_{redox}$.[75] The energy level of $Br_3^-/Br^-$ is about 0.5 V below $I^-/I_3^-$,[41] which makes $Br_3^-/Br^-$ a potential alternative electrolyte for high $V_{oc}$. However, up to now, only a limited number of sensitizers can be used with $Br_3^-/Br^-$ electrolyte such as the sensitizer Eosin Y.[7] We used $Br_3^-/Br^-$ as an electrolyte for complex **Ir3**, which exhibited a significantly increased $V_{oc}$.[41] Recently, using carbazole based sensitizer and $Br_3^-/Br^-$ electrolyte, $V_{oc}$ of 1.15 V was achieved by Sun *et al.*[76] However, generally, sensitizers are required to have a wide band gap in order to be compatible with the $Br_3^-/Br^-$ electrolyte, which limits the optical absorption in the short wavelength region.

In recent years, organic solid redox couples have received much attention as they can significantly improve the stability of DSCs.[77] In addition, the relatively low $E_{HOMO}$ of such organic hole transporters is favorable for higher $V_{oc}$.[14] The $E_{HOMO}$ of spiro-MeOTAD is about 0.4 V lower than that of $I^-/I_3^-$, which enables the theoretically maximum $V_{oc}$ to reach as high as 1.3 V. The performance of the DSCs based on organic hole transporters was recently shown to be significantly improved in conjugation with the modification of the sensitizers. The introduction of triarylamine and alkyl chains to the sensitizers can reduce the charge recombination in the solid state DSCs (SDSCs).[78–80] Recently, the performance of SDSCs based on metal free triarylamine organic sensitizers has been improved rapidly.[26] The highest $V_{oc}$ is as high as 1.0 V[81] and efficiency is 4.8%.[82]

In order to further increase $V_{oc}$, one can try to utilize sensitizers also as hole transporters (Fig. 12). In this way, the maximum theoretical $V_{oc}$ equals the direct difference between the $TiO_2$ $E_{CB}$ and the $E_{HOMO}$ of the sensitizers (by removing the redox energy levels in Fig. 1 and replacing $E_{redox}$ by the $E_{HOMO}$ of the sensitizers in eqn(1)). In organic light emitting diodes, starburst triarylamine emitters were used simultaneously as hole transporters to simplify the device structure and enhance the device performance.[83,84] We speculate that it is highly possible to find novel DSCs using starburst triarylamine based sensitizers as hole transporters at the same time. Starburst triarylamine based cone shaped sensitizers with several alkyl chains are

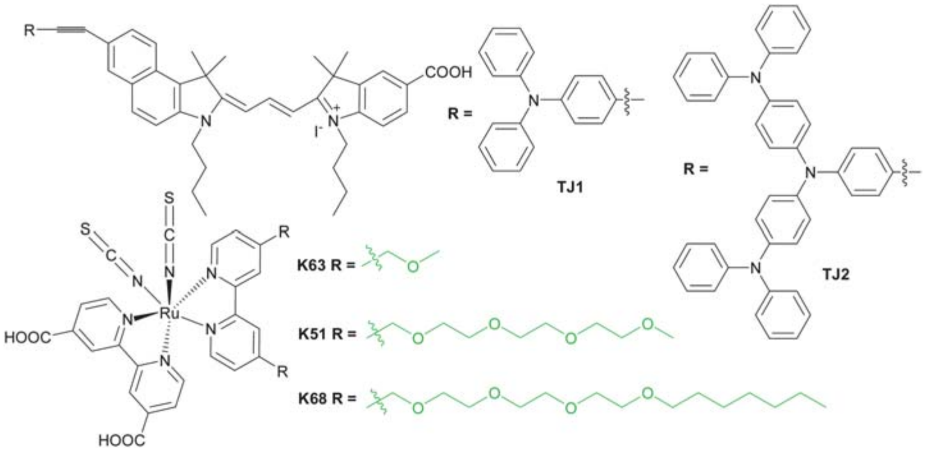

**Fig. 11** The molecular structure of two cyanine dyes and Ru complexes with long chains.

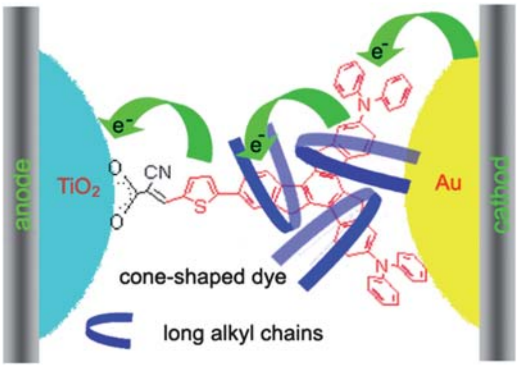

**Fig. 12** The configuration diagram of DSC without redox couples.

expected to be a good candidate because of their good hole transporting properties and the capability of forming a compact sensitizer layer on $TiO_2$.

### 3.6 Tandem DSCs

In order to utilize the full spectrum of solar irradiation and improve the efficiency of DSCs further, another prospective method might be the adoption of tandem DSCs that use $TiO_2$ as the photoanode and NiO as the photocathode. In this way, to achieve the full-wavelength energy conversion of solar irradiation, one can use two kinds of sensitizers with different absorption regions to sensitize the two electrodes, respectively. In this kind of tandem solar cells, as shown in Fig. 13, the maximum $V_{oc}$ equals to sum of $V_1$ (the difference between the $E_{CB}$ of $TiO_2$ and $E_{redox}$) and $V_2$ (the difference between $E_{redox}$ and the valence band of NiO), which can significantly improve the $V_{oc}$.[85] Recently, the performance of p-type DSCs improved considerably with the introduction of triphenylamine-based organic sensitizers by Hagfeldt and coworkers.[85] The good hole-transporting capability of triarylamine might be an important factor for the enhanced efficiency. P-type DSCs based on **P1** (Fig. 14) shows a $J_{sc}$ value of 1.52 mA cm$^{-2}$, a $V_{oc}$ value of 0.11 V, and a ff of 0.31, leading to an efficiency of 0.05%. Using phenyl as the linker (**P4**), the electron will delocalize over more phenylamine units, which can retard the charge recombination on the NiO surface and lead to higher energy conversion efficiency than counterparts with a thiophene linker. Recently, using triphenylamine as the donor, oligothiophene as the linker and perylenemonoimide as the electron acceptor, Bach and coworkers synthesized sensitizer **3** (Fig. 14), which show a light-to-energy conversion efficiency of 0.4%.[86] As with the connection of several alkyl chains on the oligothiophene and the extension of the linker length, the charge recombination was slower by over 10 times. With the combination of the p-type sensitized photoanode and n-type sensitized photocathode, the $V_{oc}$ is as high as 1.08 V, which is almost the sum of the $V_{oc}$ of single p-type and n-type DSCs. This result indicates it is promising to improve the efficiency of DSCs by combining the p-type and n-type DSCs. Another kind of organic tandem solar cell by combining SDSCs with heterojunction solar cells has $V_{oc}$ 1.36 V and an overall conversion efficiency of 6.0%.[87]

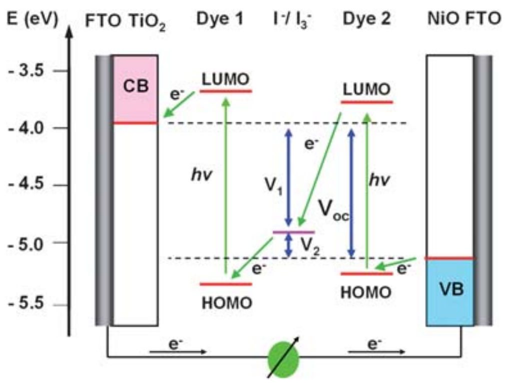

**Fig. 13** Tandem solar cell structure and major electron transfer processes.

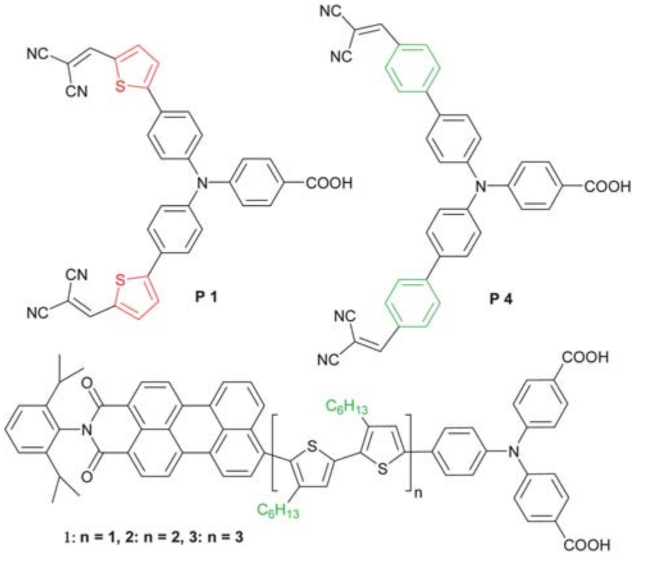

**Fig. 14** The molecular structure of some sensitizers for p-type DSCs.

## 4. Conclusion and perspective

In conclusion, in order to further enhance the energy conversion efficiency of DSCs, it is critical to improve the $V_{oc}$ by reducing the charge recombination and increasing the electron injection efficiency. To reduce charge recombination, the following factors about sensitizers should be considered. First, it should form a compact blocking layer on the $TiO_2$ surface. Secondly, the undesirable complexation between the sensitizer and iodide should be prevented. Thirdly, the electron donor unit should be separated from the $TiO_2$ surface to impede charge recombination between the injected electrons and the oxidized sensitizer. To improve electron injection efficiency, molecular aggregation should be prevented and the LUMO of the sensitizer should overlap well with that of $TiO_2$. Finally, to broaden the absorption spectra of the sensitizer, strong electron donor and acceptor groups might be a good choice. Furthermore, multiple electron donor substituents are encouraged under the condition that the oxidized sensitizer can be reduced effectively by the redox couple. The fast-developing organic sensitizers are promising for reinforcing the $V_{oc}$ and efficiency by exquisite molecular tailoring.

Apart from the modification of sensitizer, increasing the $TiO_2$ $E_{CB}$ and downshifting the $E_{redox}$ present another strategy to enhance $V_{oc}$ under the situation of appropriate sensitizer energy level. A potential method is to develop a hole transporting sensitizer that can be used simultaneously as photon sensitizer and redox couple. In addition, tandem solar cells, which combine the n-type and p-type DSCs, provide a novel opportunity to improve $V_{oc}$ and light-to-energy conversion efficiency.

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