

Recent developments in sensitizers for mesoporous sensitized solar cells

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Abstract Sensitizers have proven to be extremely important in determining the performance of dye-sensitized solar cells (DSCs). The design and understanding of sensitizers, especially D- π -A structured porphyrins, has become a recent focus of DSC research. In this perspective article, advances in the conception and performance of various sensitizers including ruthenium complexes, organic dyes and porphyrins are reviewed with respect to their structure and charge transfer dynamics at the dye-sensitized mesoporous heterojunction interface. In particular, the discussion focuses on the trends that perovskite would be the most effective and most likely to be used in DSCs combining with innovative hole transporting materials.

Keywords solar cells, sensitizer, ruthenium complex, porphyrin, organic dye

1 Introduction

The worldwide energy demand is growing and the development of sustainable power generation becomes a critical issue. Among several possibilities, dye-sensitized solar cells (DSCs), gained much attention since it is a simple and cheap photovoltaic device capable of converting the sunlight into electricity through a regenerative photo-electrochemical process [1–3]. As a promising and environmentally friendly alternative device to the silicon based solar cells, investigations for academic and technological improvement of DSCs are being intensively carried out. Typically, a DSC essentially contains three important components for solar energy conversion (see Fig. 1): 1) a mesocrystalline oxide semiconductor as an electrode, such as TiO₂, responsible for photoelectron collection; 2) dye-sensitizers adsorbed on the TiO₂ surface for light

harvesting and electron generation after being excited by sunlight; and 3) a redox couple for regenerating the excited dye.

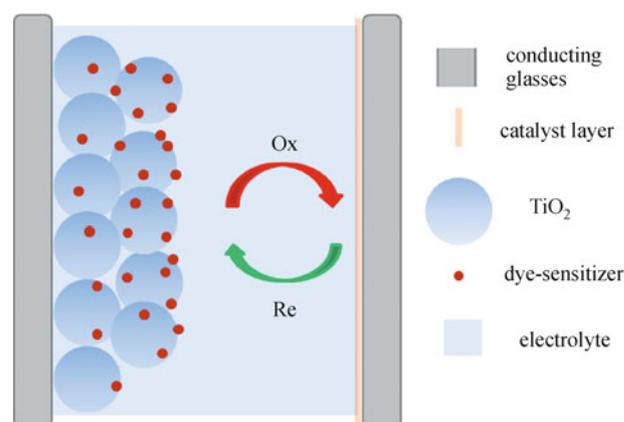


Fig. 1 Schematic structure of dye sensitized solar cell

Chemically, thermally stable, and photo-stable are some of the basic requirements for practical sensitizers in DSCs. The photo-sensitizer should strongly adsorb to the semiconductor. To achieve this strong adsorption, functional groups like carboxylates, sulphonates and phosphates are usually ensured in the dye molecules to chemically binding the dye molecules onto oxide semiconductors. Ideally, a dye molecule should absorb light photons in whole of the visible region and near IR region of solar spectra. The energy level of dye molecules is tunable, which means they can get a suitable absorption spectroscopy for photovoltaic conversion process. In an efficient DSC, the excited state energy level (LUMO) of the dye molecule should be higher than that of the conduction band edge of the semiconductor for an efficient electron transfer process from dye molecules to semiconductor and the oxidized state energy level (HOMO) of dye must be more positive than that of redox electrolyte for efficient regeneration process of dye.

Different kinds of dye molecule have been developed and used in DSCs, the most common ones being ruthenium (Ru) metal complexes, metalloporphyrins, and metal free organic dye molecules. Semiconductor quantum dots with size dependent absorption spectra in visible and near IR region have also been used as sensitizers or as co-sensitizers along with dye. It must be pointed that, at present, nanosized light harvesters, especially organic-inorganic perovskites are gaining much attention.

The most-important component of DSCs is the sensitizer, since it is responsible for the sunlight harvesting and electron injection, the very first steps of energy conversion. Herein, we review on the development of photo-sensitizers and their potential applications in DSCs.

2 Ruthenium complexes for DSCs

Ruthenium complexes have received particular interest as photo-sensitizers in DSCs application due to their favorable photo-electrochemical properties and high stability in the oxidized state, making practical applications feasible [4]. Molecular engineer of ruthenium complex has become one of the essential strategies to improve the performance of DSCs. For example, the well-known N3 and black dye,

due to their outstanding performance in DSCs, have been widely used as models for molecular engineering of new dyes. The molecular structure of the N3 dye consists of two anchoring ligands for connecting to the TiO₂ surface and two NCS for balancing the charge of the Ru metal (see Fig. 2). The carboxylate groups attached to the bipyridyl moiety lower the energy of the ligand π^* orbital, which allows the intimate electronic coupling between the dye-excited state wave function and the semiconductor conducting band.

In an effort to improve the light-harvesting ability of the photo-sensitizer, several modifications in the 2,2'-bipyridine (bpy) moiety were proposed for the high-efficient sensitizers. Some successful variations of substituents in the bpy ligand of Ru sensitizers and their corresponding DSCs photovoltaic properties as well as their metal-to-ligand charge-transfer (MLCT) absorption are listed in Table 1. Compared to the N3 dye, the Z907 sensitizer (cis-Ru(H₂dcbpy)(dnbpy)(NCS)₂, where the ligand H₂dcbpy is 4,4'-dicarboxylic acid-2,2'-bipyridine and dnbpy is 4,4'-dinonyl-2,2'-bipyridine) shows improved stability. The aliphatic chains act as an effective electron donor, and carboxylate group acts as an effective electron withdrawing between the TiO₂ layer and the carboxylate linking TiO₂ layer leading to increasing of electron density

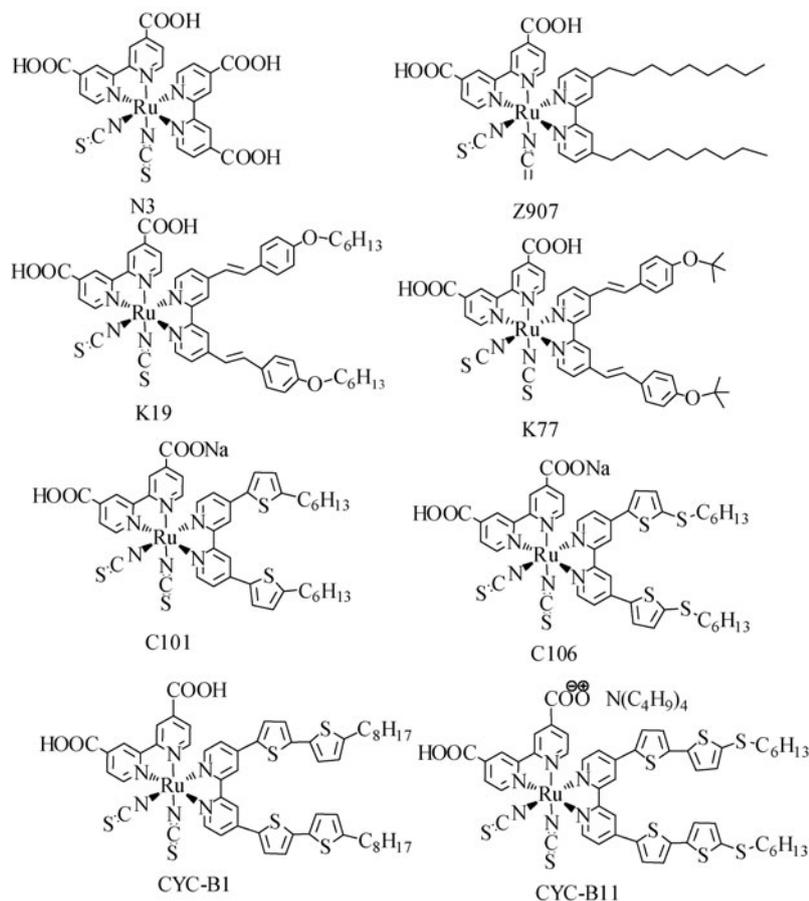


Fig. 2 Molecular structures of N3 dye and derivatives with various ancillary ligands

Table 1 Comparison of devices with various sensitizers compositions

sensitizers	λ_{\max}/nm ($\epsilon/(10^4 \text{ M}^{-1} \cdot \text{cm}^{-1})$)	J_{sc} ($\text{mA} \cdot \text{cm}^{-2}$)	V_{oc} (V)	FF	PCE (%)	reference
N3	534(1.42) ^{a)}	18.2	0.72	0.73	10.0	[4]
Z907Na	526(1.16) ^{a)}	12.5	0.73	0.67	6.1	[5]
K19	543(1.82) ^{b)}	14.6	0.71	0.67	7.0	[6]
K77	546(1.94) ^{c)}	19.2	0.78	0.72	10.5	[7]
C101	547(1.75) ^{c)}	18.6	0.74	0.75	10.5	[8]
CYC-B1	553(2.12) ^{c)}	23.9	0.65	0.55	8.5	[9]
CYC-B11	554(2.42) ^{c)}	20.1	0.74	0.77	11.5	[10]
C106	550(1.87) ^{c)}	19.2	0.78	0.76	11.3	[11]
Ru-TPA-NCS	526(2.45) ^{c)}	4.4	0.77	0.34	1.5	[12]
Ru-TPD-NCS	540(2.67) ^{c)}	9.6	0.76	0.35	3.4	[12]
II-1	536(1.91) ^{c)}	17.6	0.8	0.73	10.3	[13]
Ru-TPA-EO-NCS	524(3.09) ^{c)}	18.3	682	0.72	9.02	[14]
YE05	560(-) ^{c)}	17.0	0.8	0.74	10.1	[15]
TFRS-4	501(2.2) ^{c)}	18.7	0.75	0.73	10.2	[16]
TFRS-63	581(1.9) ^{c)}	17.4	0.74	0.75	9.6	[17]
YD2	644(3.12) ^{a)}	18.6	0.77	0.76	11	[18]
LD4	672(49.8) ^{d)}	19.6	0.71	0.72	10.1	[19]
LD14	667(49.8) ^{d)}	20.4	0.71	0.69	10.1	[20]
LD16	671(58.6) ^{d)}	20.6	0.71	0.70	10.2	[21]
YD2-O-C8/Y123	—(-)	17.7	0.94	0.74	12.3	[22]
BT-I	470(4.07) ^{d)}	15.7	0.78	0.61	7.51	[23]
BT-III	433(3.65) ^{d)}	12.5	0.79	0.61	6.01	[23]
C219	493(5.75) ^{c)}	17.9	0.77	0.73	10.1	[24]
JK-113	490(8.5) ^{c)}	17.6	0.71	0.72	9.1	[25]
D205	532(-) ^{c)}	18.6	0.72	0.72	9.52	[26]
WS-9	536(2.08) ^{d)}	18.0	0.70	0.72	9.04	[27]
T1	—(-)	7.99	0.82	0.76	5.0	[28]
T3	—(-)	13.0	0.84	0.74	8.0	[28]
C220	—(-)	14.8	0.93	0.73	10.1	[29]
(CH ₃ NH ₃)PbI ₃	—(-)	17.0	0.89	0.62	9.7	[30]

Notes: a) In EtOH; b) In 1:1 MeCN-^tBuOH; c) In DMF; d) InCH₂Cl₂; e) In Methanol + 1wt%KOH; f) In THF

at this interface [5]. The use of the amphiphilic Z907Na dye in conjunction with the polymer gel electrolyte was found to result in remarkably stable device performance both under thermal stress and soaking with light [5,6]. The solar cell uses the amphiphilic ruthenium sensitizer Z907Na inconjunction with a quasi-solid-state polymer gel electrolyte, reaching an efficiency of > 6% under full sunlight intensity condition. The cell sustained heating for 1000 h at 80°C, maintaining 94% of its initial performance.

The molar extinction coefficient of the Z907Na is somewhat lower than that of the standard N3 dye (see Table 1). The lower molar absorptivity in the visible region of Z907Na can be understood by the influence of the different de-localized π -systems integrated in the bipyridyl

donor antenna ligands. Thus, complexes prepared with donor-antenna substituents of 2,2'-bipyridine has been an effective approach to improve the light absorption of ruthenium complexes. Another advantage is that the hydrophobic character is enhanced at the same time. The use of aromatic substituents can have this function since the aromaticity increases the light absorption and the existence of the hydrophobic chain allows the protection to dye desorption induced by water. Accordingly, an novel amphiphilic ruthenium complex K19 was reported in 2004 with improved molar extinction coefficients and the desirable stability under thermal stress and light soaking [6]. Compared with the Z907Na, the 4, 4'-bis (*p*-hexyloxystyryl)-2,2'-bipyridine ligand extended this new

dye's conjugated system and maintained the hydrophobicity at the same time. Solar cells employing the K19 dye in combination with a binary ionic liquid electrolyte showed over 7.0% efficiency and maintained excellent stability under light soaking at 60°C for 1000 h [6].

To further improve the photovoltaic performance and stability of DSCs, extensive efforts have been focused on the synthesis of new highly efficient sensitizers. Thus, a most striking breakthrough was achieved in the case of K77 dye [7]. Ru(2,2'-bipyridine-4,4'-dicarboxylic acid) (4,4'-bis(2-(4-tert-butyloxyphenyl) ethenyl)-2,2'bipyridine)(NCS)₂, denoted K77, exhibit high molar extinction coefficient and mesoscopic DSCs with more than 10.5% photoelectrical conversion efficiency were obtained in conjunction with a volatile electrolyte. Highly efficient DSCs (up to 9.5%) exhibiting long-term stability (1000 h) under both light soaking and thermal stressing have been obtained using the K77 sensitizer in combination with a nonvolatile organic solvent-based electrolyte [7].

Electron-rich heteroaromatics such as thiophene and thiophene derivatives were also introduced owing to the higher electron density [8]. The obtained ruthenium(II) sensitizer C101 having a 4,4'-bis(5-hexylthiophen-2-yl)-2,2'-bipyridine ligand possess higher molar absorptivity and higher light harvesting efficiency results in higher IPCE values compared to that of the counterpart Z907Na dye, which consequently improve overall performance of the solar cell (see Table 1). On the basis of the C101 dye, several benchmarks under the illumination of AM 1.5G full sunlight have been reached, such as a 11.0% efficiency along with an acetonitrile-based electrolyte, a long-term stable > 9% device using a low-volatility electrolyte, and a long-term stable about 7.4% device employing an ionic liquid electrolyte. Another important sensitizer employing thiophene derivatives is the CYC-B1 dye, which exhibits a remarkably high light-harvesting capacity of up to $2.12 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ [9]. After the development of the CYC-B1 and C101 dye, several ruthenium dyes were synthesized by incorporating thiophene derivatives into the ancillary ligand and DSC cells based on these dyes exhibited excellent photovoltaic performances [10,11,31–33]. Especially, two new well-designed ruthenium complexes, C106 and CYC-B11 with high molar extinction coefficients, have been synthesized and demonstrated as efficient sensitizers. The CYC-B11-sensitized solar cell presents a high short-circuit photocurrent density (J_{sc}) of $20.1 \text{ mA} \cdot \text{cm}^{-2}$, open-circuit potential (V_{oc}) of 0.74 V, and fill factor (FF) of 0.77, yielding power conversion efficiencies (PCE) of 11.5% [10]. The C106-sensitized solar cell gave a high photocurrent density of $19.2 \text{ mA} \cdot \text{cm}^{-2}$ and $\eta = 11.3\%$ [11]. Therefore, the incorporation of moieties with electron-rich properties onto bipyridine ligands clearly raises the energy levels of the metal center and the LUMO of the ligands [34]. As a consequence, the absorption band resulting from charge transfer from the metal center to the

anchoring ligand is red shifted and the optical absorptivities of mesoporous titania film have been enhanced with these sensitizers due to the extending the π -conjugated system of ancillary ligands.

To obtain bpy donor antenna groups with extended π -electron delocalization, novel ruthenium dyes, Ru-TPA-NCS, and Ru-TPD-NCS (Fig. 3) with electron-donor antenna groups (triphenylamine and tetraphenylbenzidine) were developed [12]. These dyes were applied in all-solid-state dye-sensitized solar cells and displayed remarkably higher efficiencies of 1.5% and 3.4% when compared to the cell fabricated with standard N719 dye (0.7%). Similar to Ru-TPA-NCS dye, a methyl substituted TPA-donor antenna dye IJ-1 showed enhanced ϵ and cell efficiency [13]. Recently, a new heteroleptic ruthenium (II) complex Ru-TPA-EO-NCS was synthesized and characterized for DSC application [14]. The Ru-TPA-EO-NCS dye exhibits a remarkable molar extinction coefficient ($\epsilon = 3.08 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$). The bpy-TPA-EO ligand contributes to the enhancement of light harvesting, rendering a high short-circuit current density of $18.3 \text{ mA} \cdot \text{cm}^{-2}$ at full sun condition ($100 \text{ mW} \cdot \text{cm}^{-2}$). The enhanced molar extinction coefficient benefits for light harvesting yield and a reduction in film thickness. Explored this dye for solid-state solar cell based on $2.0 \mu\text{m}$ thick thin TiO_2 film with organic hole transport material, Spiro-MeOTAD, it turns out to render 3.3% at full sun [14].

The thiocyanate ligands are usually considered as the most fragile part of the ruthenium dyes [35]. At the same time, the HOMO energy level of this ruthenium sensitizer is difficult to tune since it is partially delocalized over the NCS-ligands. Many attempts to replace the thiocyanate donor ligands have been made. It has been shown that these NCS-ligands can be replaced with anionic ligands without a significant decrease in device performance. This thiocyanate-free ruthenium sensitizer builds on a report by Wadman et al. [36], which provides an impetus to investigate this type of compound detailed. An important finding for the field was provided in 2009 when Grätzel and colleagues reported a high DSC efficiency of 10.1% for the cyclometalated Ru dye YE05 [15]. The sensitizer displayed an incident-photon to current conversion efficiency (IPCE) of 83% at 570 nm and produced, at that time, the highest efficiency for any sensitizer devoid of NCS-groups. This novel ruthenium complex presents a promising class of robust and panchromatic sensitizers enabling greatly enhanced DSC performance. Encouraged by this finding, many attempts have been executed to optimize the relevant cyclometalated Ru (II) complexes through modification of their structural and electrochemical properties. Consequently, various NCS-free Ru dcbpy [37–39] and Ru tctpy [40,41], sensitizers were developed and showed conversion efficiencies of over 9%.

Recently, a series of thiocyanate-free Ru(II) sensitizers were synthesized (coded as TFRS series) using a single

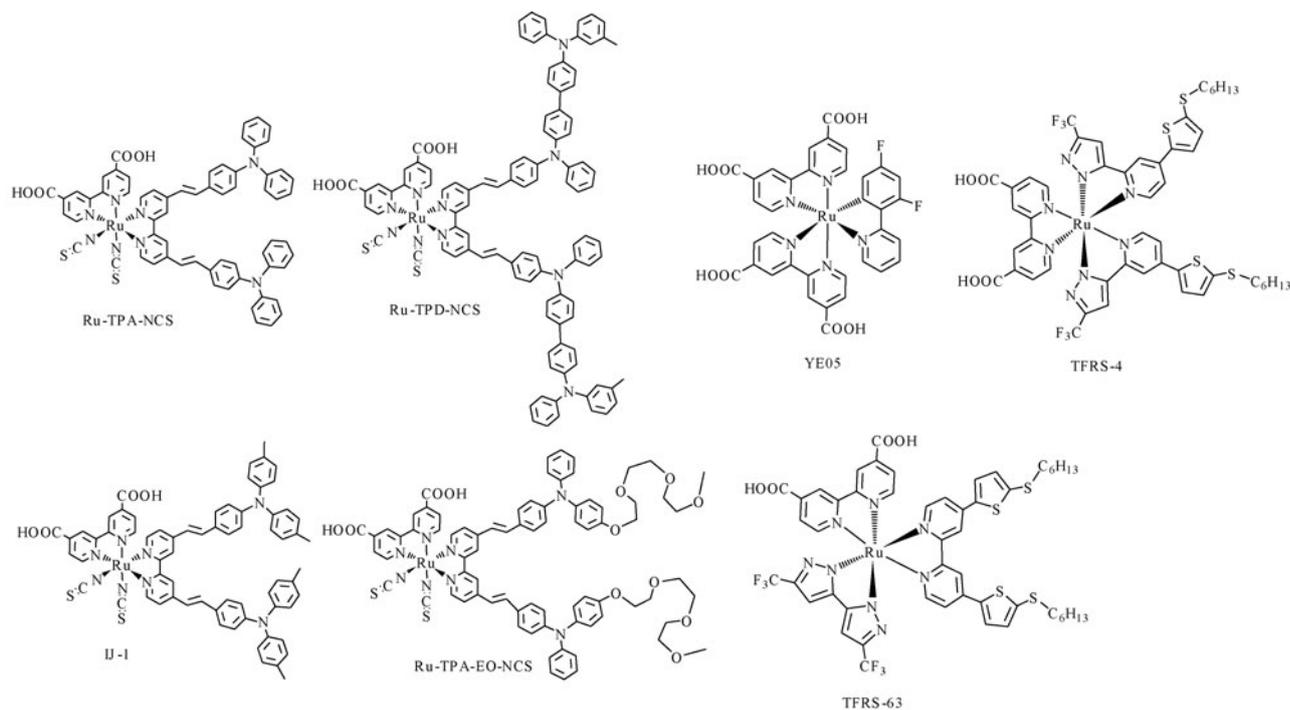


Fig. 3 Molecular structures of ruthenium sensitizers with strong electron-donor groups and thiocyanate-free compounds

4,4'-dicarboxylic acid-2, 2'-bipyridine anchor plus two functionalized pyridyl azolate ancillaries' ligands consisting of pyrazolate or triazolate groups [16]. The TFRS-4 sensitized-device has a short-circuit photocurrent density of $18.7 \text{ mA} \cdot \text{cm}^{-2}$, open-circuit potential of 0.75 V, and fill factor of 0.73, yielding power conversion efficiencies of 10.2%. A molecular design incorporates novel dianionic bipyrazolate or bitriazolate ancillaries to replace the dual thiocyanates in N3 together with the synergistic incorporation of electron-donating thiophene or thiophene-containing appendages to one bipyridine for improved light-harvesting, leads to the achievement of DSCs with a prominent J_{sc} of $17.4 \text{ mA} \cdot \text{cm}^{-2}$ and hence a high photon conversion efficiency of 9.6% using the TFRS-63 dye [17].

3 Porphyrins for DSCs

Porphyrin sensitizers have drawn great interest because of their excellent light-harvesting function mimicking photosynthesis [42–45]. Porphyrin sensitizers exhibit intense spectral response in near-infrared region, owing to their appropriate LUMO and HOMO energy levels and very strong absorption of the Soret band in the 400–450 nm region, as well as the Q-band in the 500–700 nm region [46]. The intrinsic advantages of porphyrin-based dyes are their rigid molecular structures with large absorption coefficients in the visible region and their many reaction

sites, i.e., four meso and eight β positions, available for functionalization. Thus, fine tuning of the optical, physical, electrochemical and photovoltaic properties of porphyrins becomes feasible. Some representative porphyrin sensitizers with high efficiency are collected in Fig. 4 and Table 1. Yeh and coworkers designed and synthesized several meso- or β -derivatized porphyrins with a carboxyl group for DSCs [47]. In 2010, a judiciously tailored porphyrin dye, YD2 with the achievement of an 11% solar-to-electric power conversion efficiency under standard test conditions was reported, and this is the first time that such a high efficiency has been obtained with a ruthenium-free sensitizer [18]. The structure of the YD2 porphyrin is shown in Fig. 4. A diarylamino donor group attached to the porphyrin ring acts as an electron donor, and the ethynylbenzoic acid moiety serves as an acceptor. The porphyrin chromophore itself constitutes the π bridge in this particular D- π -A structure [48]. Due to the strong electron-donating diphenylamine moiety, the HOMO is mainly localized on the diphenylamine and the LUMO is distributed over the porphyrin core and anchoring group.

The most viable way to enhance J_{sc} of a solar cell is to harvest a broader region of the solar spectrum. Generally, there are two approaches to extend the absorption of porphyrin dyes to the near infrared region: one is to introduce a highly conjugated π -extended chromophore coupled with the porphyrin ring, and another is to make fused or dimeric porphyrins [49]. The reported near-

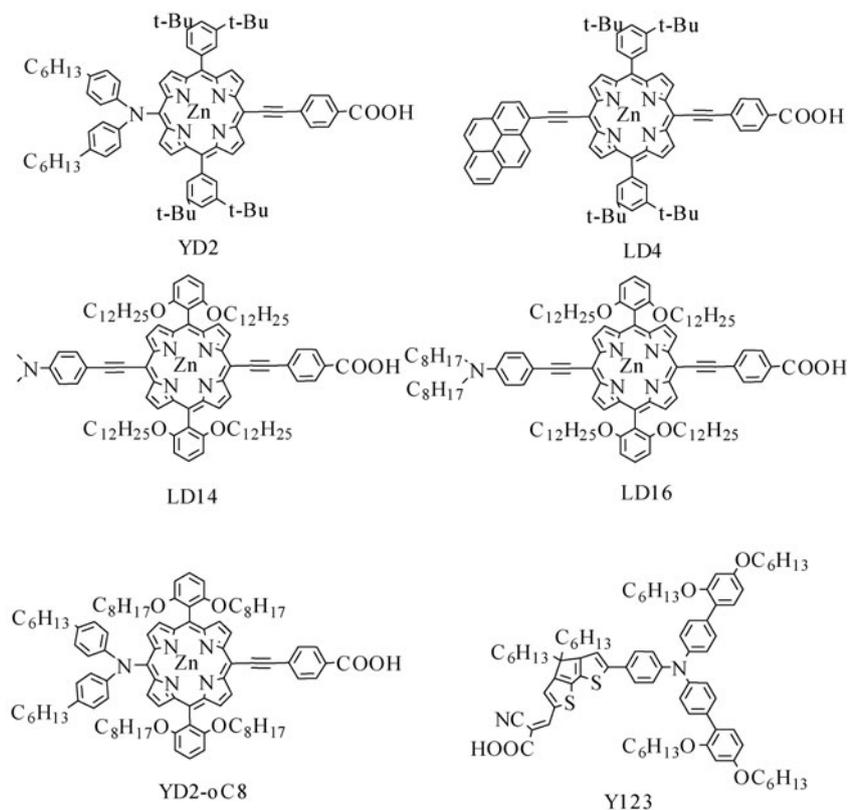


Fig. 4 Molecular structures of zinc porphyrin sensitizers

infrared dyes, such as fused porphyrins [50] and dimeric porphyrins [51,52], have the planar structural feature, which might facilitate the formation of dye aggregates and significantly decrease the efficiency of electron injection. Thus, extending the π -conjugation by functionalizing the target porphyrin at the meso-position becomes a favorite choice. For example, the pyrene-functionalized porphyrin (LD4, Fig. 4) attained $\eta = 10.1\%$ [19], which was superior to that of a N719 dye ($\eta = 9.3\%$) under the same conditions. The superior photovoltaic performance of the LD4 porphyrin based-sensitized solar cells was attributed to its enhanced ability to harvest light with the IPCE action spectrum covering the entire visible spectral region and extending beyond 800 nm, which outperforms N719. But it was found that the electron lifetime of porphyrin-based solar cells was much shorter than that of N719 cells [53]. A new concept was then introduced to design a zinc-porphyrin sensitizer, in which long alkoxy chains were introduced to protect the porphyrin core for retarded charge recombination and also to decrease effectively the dye aggregation for an efficient electron injection. The LD14 and LD16 are two porphyrins with the molecular structures based on this concept, which attained PCE beyond 10%, respectively [20,21]. The long alkoxy chains play a key role to prevent the approach of I₃⁻ in the electrolyte to the surface of TiO₂ so as to retard the electron interception at

the electrolyte/TiO₂ interface, which results in an enhanced V_{oc} of the *ortho*-substituted porphyrins. In 2011, with a structural design involving long alkoxy chains to envelop the porphyrin core to suppress the dye aggregation for a push-pull zinc porphyrin, Grätzel and coworkers reported YD2-OC8 co-sensitized with an organic dye (Y123, Fig. 4) [54] in a cobalt-based redox electrolyte leading to a measured power conversion efficiency of 12.3% under simulated air mass 1.5 global sunlight [22]. Wang and coworkers reported new donor- π -acceptor zinc porphyrin dyes (LW1 and LW2) with a pyridine ring as an anchoring group for applications in DSCs [55]. The investigations demonstrated that the pyridine ring worked effectively as an anchoring group for the porphyrin sensitizers. DSCs that were based on these new porphyrins showed an overall power conversion efficiency of about 4.0% under full sunlight.

4 Organic dyes for DSCs

Generally, donor π -bridge acceptor (D- π -A) structure is the common character of these organic dyes (see Fig. 5). When a dye absorbs light, intra-molecular charge transfer occurs from subunit A to D through the π -bridge. With this construction, it is easy to design new dye structures to

extend the absorption spectra and adjust the HOMO and LUMO levels. To date, many efforts have been made to change the different parts of organic dyes to optimize DSC performance. Hundreds of organic dyes for DSCs have been sensitized and developed, including thiophene-based dyes, carbazole dyes, and indoline dyes [56–59]. Some representative organic dyes with relatively high efficiency are collected in Fig. 5 and Table 1.

Triarylamine unit have prominent electron-donating ability and hole-transport properties, which can be engineered to meet the requirements of ideal donors. Hua and coworkers reported a series of TPA dyes containing bithiazole moieties [23,60]. Despite the long π -bridge of the dye, a high V_{oc} of 778 and 789 mV was achieved by BT-I and BT-III (see Fig. 5). A further study showed that the charge recombination can be retarded by two hexyl chains with substituted bithiazole. Thus, a high J_{sc} was obtained due to a high molar extinction coefficient and a broad photocurrent response. These results indicated that thiophene is superior to benzene in terms of light

harvesting and response of photocurrent, but inferior to the latter in terms of photovoltage. However, the performance of this type of system is still behind the ruthenium dyes owing to lower J_{sc} and V_{oc} . To achieve high J_{sc} , it is necessary to improve the electron-donating ability of TPA and design new push-pull systems for broader and higher IPCE response. Up to now, a variety of 4-substituted TPA derivatives and 4,4'-disubstituted TPA derivatives have been explored [61–64]. In 2010, a promising sensitizer C219 constructed with a binary p-conjugated spacer of EDOT and dihexyl-substituted dithienosilole (DTS) was reported, which is characteristic of an intra-molecular charge-transfer band peaking at 584 nm measured in chloroform [24]. The IPCE exceeds 90% from 500 to 590 nm, reaching a maximum of 95% after coating the cells with an antireflection film. In comparison with the standard ruthenium sensitizer Z907, this metal-free chromophore C219 endowed a nanocrystalline titania film with an evident light-harvesting enhancement, leading to a remarkably high efficiency of 10.0–10.3% (J_{sc} =

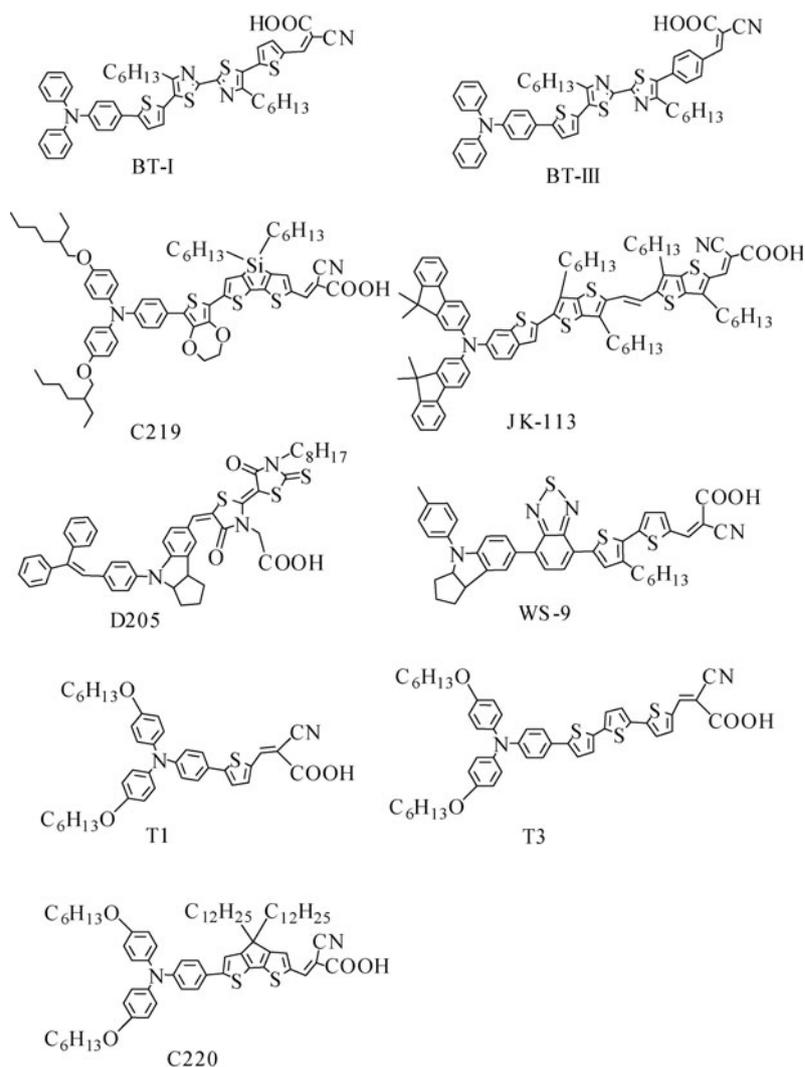


Fig. 5 Molecular structures of metal free organic sensitizers

17.94 mA · cm⁻², $V_{oc} = 770$ mV, $FF = 0.730$) at the AM 1.5 irradiation (100 mW · cm⁻²) for DSC in combination with a highly volatile iodine electrolyte. A solvent-free ionic liquid cell with C219 as the sensitizer showed an impressive efficiency of 8.9% under a low light intensity of 14.39 mW · cm⁻², making it very favorable for the indoor application of flexible DSCs. The fluorene based triarylamine dyes (Fig. 5) were developed as photosensitizers by Ko and coworkers for the first time [65,66]. The tailored dialkylfluoreneaniline moieties in dyes ensure greater resistance to degradation when exposed to light and high temperatures, as compared to simple arylamines. In addition, the nonplanar structure of the dialkylfluoreneaniline suppressed aggregation, disfavoring molecular stacking [67]. Modification of the π -bridge has been made to obtain red-shifted absorption spectra and increase the extinction coefficient. Dye JK-113 consisting of a dimethylfluorenylamino-appended thienothiophene-vinylene-thienothiophene unit with aliphatic chains to maintain the planar geometry of the conjugated linker was synthesized [25]. This type of structure not only increased the light harvesting ability of the sensitizer by extending the π -conjugation of the bridging linker (JK-113, $\lambda_{max} = 490$ nm), but also augmented its hydrophobicity, increasing the stability under long-term light soaking and thermal stress. Under AM 1.5 irradiation (100 mW · cm⁻²), the JK-113-sensitized device gave a J_{sc} of 17.61 mA · cm⁻², a V_{oc} of 0.71 V, and a FF of 0.72, corresponding to a PCE of 9.1%. Further, a JK-113-based solar cell fabricated with a solvent free ionic liquid electrolyte displayed a high conversion efficiency of 7.9% and showed excellent stability under light soaking at 60°C for 1000 h. Dye D205 was designed by utilizing long end alkyl chains on the rhodanine ring to control the aggregation between indoline dye molecules. It was significant that the device based on dye D205 and combination of chenodeoxycholic acid (CDCA) have an improved V_{oc} up to 717 mV, leading to a progressive PCE of 9.52% [26], which is the highest efficiency obtained so far among DSCs based on an indoline dye under AM 1.5 radiation (100 mW · cm⁻²). This dye gave a 7.2% conversion efficiency using an ionic-liquid electrolyte. However, several studies pointed out that these indoline derivatives containing rhodanine-3-acetic acid as the acceptor and anchoring unit maintain short-term stability as a result of dye-desorption. To avoid this problem, Tian and coworkers developed a series of D-A- π -A organic sensitizers (Fig. 5) [27,68,69]. They proposed several favorable characteristics of this type of dyes in the areas of light-harvesting and efficiency: 1) Optimized energy levels, resulting in a large responsive range of wavelengths into the NIR region; 2) A very small blue-shift in the absorption peak on thin TiO₂ films with respect to that in solution; 3) An improvement in the electron distribution of the donor unit to distinctly

increase the photo-stability of the synthetic intermediates and final sensitizers [70]. Remarkable progress has been made on the utilization of low band gap and strong electron-withdrawing units for indoline dye-based DSCs. For example, WS-9 show the maximum absorption peak at 536 nm ($\epsilon = 20800$ M⁻¹ · cm⁻¹) by introduction of a benzothiadiazole unit into the molecular frame, which distinctly decreased the band-gap between the HOMO and the LUMO. And the attached *n*-hexyl chains in the dyes are effective to suppress the charge recombination, resulting in a decreased dark current and enhanced V_{oc} . Without DCA co-adsorption, an 8.15% PCE of WS-9 based DSC device ($J_{sc} = 16.99$ mA · cm⁻², $V_{oc} = 689$ mV, $FF = 0.71$) on a double layer (8 + 5 μ m) TiO₂ film device was obtained. After co-adsorption with 20 mM¹⁾ CDCA, the photovoltaic performance of the WS-9 device was further improved, reaching 9.04% with a high J_{sc} of 18.00 mA · cm⁻² and V_{oc} of 696 mV. The WS-9-based DSC device with an ionic liquid redox electrolyte was stable under AM 1.5 irradiation (100 mW · cm⁻²) for at least 500 h.

Arylamine organic dye-sensitized DSCs employing iodine electrolytes have reached power conversion efficiencies high as 10%–11%, comparable to those of Ru complexes. However, some disadvantages of the iodide/triiodide redox couple limited the performance of the DSCs with the following points. 1) The relatively high over-potential for dye regeneration has led to a noticeable potential loss [71]. 2) The halogen bonding between iodine and some electron-rich segments of dye molecules could cause a larger charge recombination rate at the titania/electrolyte interface [72]. 3) The I₃⁻/I⁻ based redox electrolytes absorb light in the blue part of the spectrum, lowering the short circuit photocurrent and hence the PEC of the devices [73]. Fortunately, astonishing progresses have been made in this area in recent years, especially regarding polypyridyl cobalt redox shuttles. An advantage of the cobalt electrolytes over the iodide/triiodide redox couple is that high V_{oc} can be realized but without sacrificing short circuit photocurrent or fill factor. One of the most astounding findings in arylamine organic dye based DSCs employing cobalt electrolytes is the increment of the cell photovoltage concomitant with an extension of the π -conjugated linker in organic dyes, which is in prominent contrast to the traditional iodine electrolyte system. For example, along with an elongation of the π -conjugated linker from T1 to T3, the V_{oc} in the case of the iodine electrolyte was actually decreased by 43 mV (795 mV vs. 752 mV), while that of the cobalt electrolyte was augmented by 22 mV (815 mV vs. 837 mV) [28]. The dye-iodine interaction was thought to evoke a higher iodine concentration in the vicinity of titania anchored with the T3 dye, rationalizing its faster interfacial charge recombination kinetics. On the other side, the larger steric hindrance of the bulky cobalt (III) complex and the longer π -

1) 1 mM = 1 mmol · L⁻¹

conjugated spacer contributed to slow the interception of photoinjected electrons with cobalt (III) ions. In addition, through elongating the end or side alkyl chains of dye molecules, dye C220 displayed a significantly enhanced V_{oc} of 930 mV, leading to a remarkably high PCE of 10.1% [29].

5 Perovskite absorbers for DSCs

Methylammonium lead halide perovskites were introduced and studied as a light absorber in mesoscopic solar cells due to their broad spectral response and high optical cross section. The optical and electronic properties of this type of perovskites can be tuned by modifying the chemical composition (changes in the alkyl group, metal atom and halide) [74,75]. Perovskite-based hybrids can be synthesized using simple and cheap techniques due to their self-assembling character. Thus, these hybrid materials have the potential as light harvesters for low-cost and high efficiency solar cells.

The basic building block of an organic-inorganic perovskite hybrid has a cubic AMX_3 structure where the M is a metal cation and X is an anion consisting of halide or oxide etc. They form a MX_6 octahedral geometry having M at the center and halides at the corners [75]. The MX_6 octahedral are corner-connected to form a three-dimensional framework (see Fig. 6). The optical and electronic properties of perovskite materials can be tuned to a great extent depending on the size of the metal ion and the organic cation. Perovskite compounds of the general formula $CH_3NH_3MX_3$ where M = Sn, Pb and X = Cl, Br, I has been reported [76–78]. The size, structure, conformation and charge of the organic cations have significant influence on the final structure of the perovskite material and its properties [79–81].

Miyasaka and coworkers reported $(CH_3NH_3)PbI_3$ / $(CH_3NH_3)PbBr_3$ as sensitizers for DSCs with liquid electrolytes to give an open-circuit voltage of 0.61 V and efficiency of 3.8% for a $CH_3NH_3PbI_3$ -based cell. A higher

photovoltage of 0.96 V was obtained with a $CH_3NH_3PbBr_3$ -based cell with 3.1% PCE [82]. However, the perovskite tends to dissolve easily in the electrolytes, which degrades the solar cell performance rapidly. Subsequently, Park and coworkers reported the optimization of the $CH_3NH_3PbI_3$ -based cell, in which J_{sc} of $15.8 \text{ mA}\cdot\text{cm}^{-2}$, V_{oc} of 0.71 V, and fill factor of 0.59 were achieved, giving 6.5% power conversion efficiency [83]. These cells demonstrated good charge separation kinetics and advantage over other crystal structures as sensitizers due to their high light absorption properties and thermal stability. However, it was observed that the perovskite-based DSC device performance decreased by 80% in only a few hours due to the instability of the perovskite material in presence of liquid redox electrolyte. This problem was alleviated by replacing the electrolyte with a solid-state organic hole conductor [30]. In addition, the $(CH_3NH_3)PbI_3$ nanocrystals exhibit a one order of magnitude higher absorption coefficient than the conventional N719 dye. They offer advantages for use in solid state sensitized solar cells, where much thinner TiO_2 layer are employed than in liquid junction devices. A further substantial gain in efficiency pushing the PCE to 8.5% was achieved by combining N719 dye sensitized TiO_2 with the p-type direct band gap semiconductor $CsSnI_3$ perovskite employed as a HTM [84]. Solid-state mesoscopic solar cell employing $(CH_3NH_3)PbI_3$ perovskite nanocrystals as a light absorber and spiro-MeOTAD as a hole-transporting layer, a strikingly high PCE of 9.7% was achieved with submicron thick films of mesoporous anatase under AM 1.5G illumination [30]. The $(CH_3NH_3)PbI_3$ perovskite NPs were produced by reaction of methylammonium iodide with PbI_2 and then deposited onto a submicron-thick mesoporous TiO_2 film. Snaitch and coworkers reported the use of $CH_3NH_3Pb_2Cl$ perovskite as absorber on top of a mesoporous TiO_2 film, employing spiro-MeOTAD as a solid HTM, obtaining nearly about 8% PCE under full sun illumination [85]. Remarkably, replacement of the mesoporous n-type TiO_2 with insulating Al_2O_3 improved the power conversion efficiency to 10.9%. They observed that

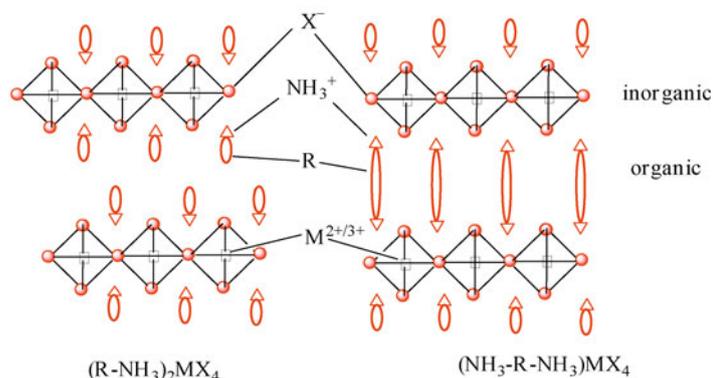


Fig. 6 Schematic representations of single-layer ($n = 1$) $\langle 100 \rangle$ -oriented perovskites with (a) monoammonium ($R-NH_3^+$) or (b) diammonium ($^+NH_3-R-NH_3^+$) organic cations

electron transport through the perovskite layer was much faster than through the *n*-type TiO₂ film. In these devices the electrons are transported through the perovskite layer and the holes are transported through the spiro-MeOTAD layer. It is interesting to note that the perovskite layer can function both as a light absorber as well as *n*-type semiconductor for transporting electronic charges out of the device. Etgar et al. reported on a CH₃NH₃PbI₃ perovskite/TiO₂ heterojunction solar cell using anatase nanosheets with dominant (001) facets as the electron collector and without an additional hole transport material, achieving a PCE of 5.5% under standard AM 1.5 solar light of 100 mW · cm⁻² intensity [86].

6 Current and further developments

For liquid based DSCs, the highest record PCEs were reported on the new designed donor- π -acceptor zinc porphyrins with organic dye as co-sensitizer in combination with cobalt complexes as alternative redox electrolytes. An efficient solar cell must absorb over a broad spectral range, from visible to near-infrared (near-IR) wavelengths, and convert the incident light effectively into charges. Thus, carefully design of sensitizers aiming to extend the absorption to the near infrared region would result in further substantial augmentation of the short circuit photocurrent. At the same time, designing new one-electron outer-sphere redox couples having sufficient driving force suitable for rapid dye regeneration, such as cobalt complexes or a solid-state hole conductor, will boost the device V_{oc} leading to a further enhancement in PCE. For solid-state DSC devices, the use of perovskites as a light harvester sparked a jump in the PCE. These values are now approaching those of their counterpart liquid electrolyte-based DSCs. Further advances in overall power conversion efficiency are expected by extending the absorption onset toward 940 nm, through the implementation of new perovskites or broadening this concept to other solution-processable semiconductors. The exploration of these materials for applications in mesoscopic solar cells has only recently begun, leaving the field wide open to the discovery of new efficient materials for reaching record PCEs in solid-state sensitized mesoscopic solar cells.

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References

1. O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based

- on dye-sensitized colloidal TiO₂ films. *Nature*, 1991, 353(6346): 737–740
2. Bach U, Lupo D, Comte P, Moser J E, Weissörtel F, Salbeck J, Spreitzer H, Grätzel M. Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies. *Nature*, 1998, 395: 583–585
3. Han L Y, Islam A, Chen H, Malapaka C, Chiranjeevi B, Zhang S F, Yang X D, Yanagida M. High-efficiency -sensitized solar cell with a novel co-adsorbent. *Energy & Environmental Sciences*, 2012, 5(3): 6057–6060
4. Kohle O, Grätzel M, Meyer A F, Meyer T B. The photovoltaic stability of, bis(isothiocyanato)ruthenium(II)-bis-2, 2'-bipyridine-4, 4'-dicarboxylic acid and related sensitizers. *Advanced Materials*, 1997, 9(11): 904–906
5. Wang P, Zakeeruddin S M, Moser J E, Nazeeruddin M K, Sekiguchi T, Grätzel M. A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte. *Nature Materials*, 2003, 2: 402–407
6. Wang P, Klein C, Humphry-Baker R, Zakeeruddin S M, Grätzel M. A high molar extinction coefficient sensitizer for stable dye-sensitized solar cells. *Journal of the American Chemical Society*, 2005, 127(3): 808–809
7. Kuang D, Klein C, Ito S, Moser J E, Humphrey-Baker R, Evans N, Durrant J R, Grätzel C, Zakeeruddin S M, Grätzel M. High-efficiency and stable mesoscopic dye-sensitized solar cells based on a high molar extinction coefficient ruthenium sensitizer and nonvolatile electrolyte. *Advanced Materials*, 2007, 19(8): 1133–1137
8. Gao F F, Wang Y, Shi D, Zhang J, Wang M K, Jing X Y, Humphry-Baker R, Wang P, Zakeeruddin S M, Grätzel M. Enhance the optical absorptivity of nanocrystalline TiO₂ film with high molar extinction coefficient ruthenium sensitizers for high performance dye-sensitized solar cells. *Journal of the American Chemical Society*, 2008, 130(32): 10720–10728
9. Chen C Y, Wu S J, Wu C G, Chen J G, Ho K C. A ruthenium complex with superhigh light-harvesting capacity for dye-sensitized solar cells. *Angewandte Chemie International Edition*, 2006, 45(35): 5822–5825
10. Chen C Y, Wang M K, Li J Y, Pootrakulchote N, Alibabaei L, Ngoc-le C H, Decoppet J D, Tsai J H, Grätzel C, Wu C G, Zakeeruddin S M, Grätzel M. Highly efficient light-harvesting ruthenium sensitizer for thin-film dye-sensitized solar cells. *ACS Nano*, 2009, 3(10): 3103–3109
11. Cao Y M, Bai Y, Yu Q J, Cheng Y M, Liu S, Shi D, Gao F F, Wang P. Dye-sensitized solar cells with a high absorptivity ruthenium sensitizer featuring a 2-(hexylthio)thiophene conjugated bipyridine. *Journal of Physical Chemistry C*, 2009, 113(15): 6290–6297
12. Karthikeyan C S, Peter K, Wietasch H, Thelakkat M. Highly efficient solid-state dye-sensitized TiO₂ solar cells via control of retardation of recombination using novel donor-antenna dyes. *Solar Energy Materials and Solar Cells*, 2007, 91(5): 432–439
13. Yum J H, Jung I, Baik C, Ko J J, Nazeeruddin M K, Grätzel M. High efficient donor-acceptor ruthenium complex for dye -sensitized solar cell applications. *Energy & Environmental Sciences*, 2009, 2 (1): 100–102
14. Yum J H, Moon S J, Karthikeyan C S, Wietasch H, Thelakkat M, Zakeeruddin S M, Nazeeruddin M K, Grätzel M. Heteroleptic

- ruthenium complex containing substituted triphenylamine hole-transport unit as sensitizer for stable dye-sensitized solar cell. *Nano Energy*, 2012, 1(1): 6–12
15. Bessho T, Yoneda E, Yum J H, Guglielmi M, Tavernelli I, Imai H, Rothlisberger U, Nazeeruddin M K, Grätzel M. New paradigm in molecular engineering of sensitizers for solar cell applications. *Journal of the American Chemical Society*, 2009, 131(16): 5930–5934
 16. Wang S W, Wu K L, Ghadiri E, Lobello M G, Ho S T, Chi Y, Moser J E, Angelis F D, Grätzel M, Nazeeruddin M K. Engineering of thiocyanate-free Ru(II) sensitizers for high efficiency dye-sensitized solar cells. *Chemical Science*, 2013, 4(6): 2423–2433
 17. Yeh H H, Ho S T, Chi Y, Clifford J N, Palomares E, Liun S H, Chou P T. Ru(II) sensitizers bearing dianionic bisazolate ancillaries: ligand synergy for high performance dye sensitized solar cells. *Journal of Materials Chemistry A*, 2013, 1: 7681–7689
 18. Bessho T, Zakeeruddin S M, Yeh C Y, Diau E W G, Grätzel M. Highly efficient mesoscopic dye-sensitized solar cells based on donor-acceptor-substituted porphyrins. *Angewandte Chemie International Edition*, 2010, 49(37): 6646–6649
 19. Wang C L, Chang Y C, Lan C M, Lo C F, Diau E W G, Lin C Y. Enhanced light harvesting with π -conjugated cyclic aromatic hydrocarbons for porphyrin-sensitized solar cells. *Energy & Environmental Sciences*, 2011, 4(5): 1788–1795
 20. Wang C L, Lan C M, Hong S H, Wang Y F, Pan T Y, Chang C W, Kuo H H, Kuo M Y, Diau E W G, Lin C Y. Enveloping porphyrins for efficient dye-sensitized solar cells. *Energy & Environmental Sciences*, 2012, 5(5): 6933–6940
 21. Chang Y C, Wang C L, Pan T Y, Hong S H, Lan C M, Kuo H H, Lo C F, Hsu H Y, Lin C Y, Diau E W G. A strategy to design highly efficient porphyrin sensitizers for dye-sensitized solar cells. *Chemical Communications (Cambridge)*, 2011, 47(31): 8910–8912
 22. Yella A, Lee H W, Tsao H N, Yi C, Chandiran A K, Nazeeruddin M K, Diau E W G, Yeh C Y, Zakeeruddin S M, Grätzel M. Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. *Science*, 2011, 334(6056): 629–634
 23. He J X, Guo F L, Li X, Wu W J, Yang J B, Hua J L. New bithiazole-based sensitizers for efficient and stable dye-sensitized solar cells. *Chemistry, a European Journal (Weinheim an der Bergstrasse, Germany)*, 2012, 18(25): 7903–7915
 24. Zeng W D, Cao Y M, Bai Y, Wang Y H, Shi Y S, Zhang M, Wang F F, Pan C Y, Wang P. Efficient dye-sensitized solar cells with an organic photosensitizer featuring orderly conjugated ethylenedioxythiophene and dithienosilole blocks. *Chemistry of Materials*, 2010, 22(5): 1915–1925
 25. Choi H, Raabe I, Kim D, Teocoli F, Kim C, Song K, Yum J H, Ko J, Nazeeruddin M K, Grätzel M. High molar extinction coefficient organic sensitizers for efficient dye-sensitized solar cells. *Chemistry, a European Journal (Weinheim an der Bergstrasse, Germany)*, 2010, 16(4): 1193–1201
 26. Ito S, Miura H, Uchida S, Takata M, Sumioka K, Liska P, Comte P, Pechy P, Grätzel M. High-conversion-efficiency organic dye-sensitized solar cells with a novel indoline dye. *Chemical Communications (Cambridge)*, 2008, 41: 5194–5196
 27. Wu Y Z, Marszalek M, Zakeeruddin S M, Zhang Q, Tian H, Grätzel M, Zhu W. High-conversion-efficiency organic dye-sensitized solar cells: molecular engineering on D–A– π -A featured organic indoline dyes. *Energy & Environmental Sciences*, 2012, 5(8): 8261–8272
 28. Zhang M, Liu J G, Wang Y H, Zhou D F, Wang P. Redox couple related influences of π -conjugation extension in organic dye-sensitized mesoscopic solar cells. *Chemical Science*, 2011, 2(7): 1401–1406
 29. Cao Y M, Cai N, Wang Y L, Li R Z, Yuan Y, Wang P. Modulating the assembly of organic dye molecules on titania nanocrystals via alkyl chain elongation for efficient mesoscopic cobalt solar cells. *Physical Chemistry Chemical Physics*, 2012, 14(23): 8282–8286
 30. Kim H S, Lee C R, Im J H, Lee K B, Moehl T, Marchioro A, Moon S J, Humphry-Baker R, Yum J H, Moser J E, Grätzel M, Park N G. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Scientific Reports*, 2012, 2: 591
 31. Li J Y, Chen C Y, Chen J G, Tan C J, Lee K M, Wu S J, Tung Y L, Tsai H H, Ho K C, Wu C G. Heteroleptic ruthenium antenna-dye for high-voltage dye-sensitized solar cells. *Journal of Materials Chemistry*, 2010, 20(34): 7158–7164
 32. Chen C Y, Wu S J, Li J Y, Wu C G, Chen J G, Ho K C. A new route to enhance the light-harvesting capability of ruthenium complexes for dye-sensitized solar cells. *Advanced Materials*, 2007, 19(22): 3888–3891
 33. Chen C Y, Pootrakulchote N, Wu S J, Wang M K, Li J Y, Tsai J H, Wu C G, Zakeeruddin S M, Grätzel M. New ruthenium sensitizer with carbazole antennas for efficient and stable thin-film dye-sensitized solar cells. *Journal of Physical Chemistry C*, 2009, 113(48): 20752–20757
 34. Zhu S S, Kingsborough R P, Swager T M. Conducting redox polymers: investigations of polythiophene-Ru(bpy)₃ⁿ⁺ hybrid materials. *Journal of Materials Chemistry*, 1999, 9(9): 2123–2131
 35. Nazeeruddin M K, Baranoff E, Grätzel M. Dye-sensitized solar cells: a brief overview. *Solar Energy*, 2011, 85(6): 1172–1178
 36. Wadman S H, Kroon J M, Bakker K, Lutz M, Spek A L, Klin G P M, Koten G. Cyclometalated ruthenium complexes for sensitizing nanocrystalline TiO₂ solar cells. *Chemical Communications (Cambridge)*, 2007, 19(19): 1907–1909
 37. Wu K L, Ku W P, Wang S W, Yella A, Chi Y, Liu S H, Chou P T, Nazeeruddin M K, Grätzel M. Thiocyanate-free Ru(II) sensitizers with a 4,4'-dicarboxyvinyl-2,2'-bipyridine anchor for dye-sensitized solar cells. *Advanced Functional Materials*, 2013, 23(18): 2285–2294
 38. Wu K L, Ku W P, Clifford J N, Palomares E, Ho S T, Chi Y, Liu S H, Chou P T, Nazeeruddin M K, Grätzel M. Harnessing the open-circuit voltage via a new series of Ru(II) sensitizers bearing (*iso*-)quinolinyl pyrazolate ancillaries. *Energy & Environmental Sciences*, 2013, 6: 859–870
 39. Bomben P G, Robson K C D, Koivisto B D, Berlinguette C P. Cyclometalated ruthenium chromophores for the dye-sensitized solar cell. *Coordination Chemistry Reviews*, 2012, 256(15-16): 1438–1450
 40. Hsu C W, Ho S T, Wu K L, Chi Y, Liu S H, Chou P T. Ru(II) sensitizers with a tridentate heterocyclic cyclometalate for dye-sensitized solar cells. *Energy & Environmental Sciences*, 2012, 5(6): 7549–7554
 41. Wu K L, Li C H, Chi Y, Clifford J N, Cabau L, Palomares E, Cheng

- Y M, Pan H A, Chou P T. Dye molecular structure device open-circuit voltage correlation in Ru(II) sensitizers with heteroleptic tridentate chelates for dye-sensitized solar cells. *Journal of the American Chemical Society*, 2012, 134(17): 7488–7496
42. Imahori H, Umeyama T, Ito S. Large pi-aromatic molecules as potential sensitizers for highly efficient dye-sensitized solar cells. *Accounts of Chemical Research*, 2009, 42(11): 1809–1818
43. Panda M K, Ladomenou K, Coutsolelos A G. Porphyrins in bio-inspired transformations: light-harvesting to solar cell. *Coordination Chemistry Reviews*, 2012, 256(21–22): 2601–2627
44. Campbell W M, Burrell A K, Officer D L, Jolley K W. Porphyrins as light harvesters in the dye-sensitized TiO₂ solar cell. *Coordination Chemistry Reviews*, 2004, 248(13–14): 1363–1379
45. He H, Gurung A, Si L P. 8-hydroxyquinoline as a strong alternative anchoring group for porphyrin-sensitized solar cells. *Chemical Communications (Cambridge)*, 2012, 48(47): 5910–5912
46. Lammi R K, Wagner R W, Ambroise A, Diers J R, Bocian D F, Holten D, Lindsey J S. Mechanisms of excited-state energy-transfer gating in linear versus branched multiporphyrin arrays. *Journal of Physical Chemistry B*, 2001, 105(22): 5341–5352
47. Lee C W, Lu H P, Lan C M, Huang Y L, Liang Y R, Yen W N, Liu Y C, Lin Y S, Diao E W G, Yeh C Y. Novel zinc porphyrin sensitizers for dye-sensitized solar cells: synthesis and spectral, electrochemical, and photovoltaic properties. *Chemistry, a European Journal (Weinheim an der Bergstrasse, Germany)*, 2009, 15(6): 1403–1412
48. Lu H P, Tsai C Y, Yen W N, Hsieh C P, Lee C W, Yeh C Y, Diao E W G. Control of dye aggregation and electron injection for highly efficient porphyrin sensitizers adsorbed on semiconductor films with varying ratios of coadsorbate. *Journal of Physical Chemistry C*, 2009, 113(49): 20990–20997
49. Li L L, Diao E W G. Porphyrin-sensitized solar cells. *Chemical Society Reviews*, 2013, 42(1): 291–304
50. Tanaka M, Hayashi S, Eu S, Umeyama T, Matano Y, Imahori H. Novel unsymmetrically π -elongated porphyrin for dye-sensitized TiO₂ cells. *Chemical Communications (Cambridge)*, 2007, 20: 2069–2071
51. Liu Y Z, Lin H, Dy J T, Tamaki K, Nakazaki J, Nakayama D, Uchida S, Kubo T, Segawa H. N-fused carbazole–zinc porphyrin–free-base porphyrin triad for efficient near-IR dye-sensitized solar cells. *Chemical Communications (Cambridge)*, 2011, 47(13): 4010–4012
52. Mai C L, Huang W K, Lu H P, Lee C W, Chiu C L, Liang Y R, Diao E W G, Yeh C Y. Synthesis and characterization of diporphyrin sensitizers for dye-sensitized solar cells. *Chemical Communications (Cambridge)*, 2010, 46(5): 809–811
53. Mozer A J, Wagner P, Officer D L, Wallace G G, Campbell W M, Miyashita M, Sunahara K, Mori S. The origin of open circuit voltage of porphyrin-sensitized TiO₂ solar cells. *Chemical Communications (Cambridge)*, 2008, 39: 4741–4743
54. Tsao H N, Yi C Y, Moehl T, Yum J H, Zakeeruddin S M, Nazeeruddin M K, Grätzel M. Cyclopentadithiophene bridged donor-acceptor dyes achieve high power conversion efficiencies in dye-sensitized solar cells based on the tris-cobalt bipyridine redox couple. *ChemSusChem*, 2011, 4(5): 591–594
55. Lu J F, Xu X B, Li Z H, Cao K, Cui J, Zhang Y B, Shen Y, Li Y, Zhu J, Dai S Y, Chen W, Cheng Y B, Wang M K. Zinc porphyrins with a pyridine-ring-anchoring group for dye-sensitized solar cells. *Chemistry, an Asian Journal*, 2013, 8(5): 956–962
56. Mishra A, Fischer M K R, Bruerle P. Metallfreie organische farbstoffe für farbstoffsensibilisierte solarzellen-von struktureigenschaften-beziehungen zu designregeln. *Angewandte Chemie*, 2009, 121(14): 2510–2536
57. Wang X F, Tamiaki H. based molecules for Cyclic tetrapyrroledye-sensitized solar cells. *Energy & Environmental Sciences*, 2010, 3(1): 94–106
58. Ning Z J, Fu Y, Tian H. Improvement of dye -sensitized solar cells : what we know and what we need to know. *Energy & Environmental Sciences*, 2010, 3(9): 1170–1181
59. Fang Z, Eshbaugh A A, Schanze K S. Low-bandgap donor-acceptor conjugated polymer sensitizers for dye-sensitized solar cells. *Journal of the American Chemical Society*, 2011, 133(9): 3063–3069
60. He J X, Wu W J, Hua J L, Jiang Y H, Qu S Y, Li J, Long Y T, Tian H. Bithiazole-bridged dyes for dye-sensitized solar cells with high open circuit voltage performance. *Journal of Materials Chemistry*, 2011, 21(16): 6054–6062
61. Xu W, Peng B, Chen J, Liang M, Cai F S. New triphenylamine-based dyes for dye-sensitized solar cells. *Journal of Physical Chemistry C*, 2008, 112(3): 874–880
62. Zhang G L, Bai Y, Li R Z, Shi D, Wenger S, Zakeeruddin S M, Grätzel M, Wang P. Employ a bithienothiophene linker to construct an organic chromophore for efficient and stable dye-sensitized solar cells. *Energy & Environmental Sciences*, 2009, 2(1): 92–95
63. Liu J Y, Zhou D F, Xu M F, Jing X Y, Wang P. The structure–property relationship of organic dyes in mesoscopic titania solar cells : only one double-bond difference. *Energy & Environmental Sciences*, 2011, 4(9): 3545–3551
64. Zhu X Z, Tsuji H, Yella A, Chauvin A S, Grätzel M, Nakamura E. New sensitizers for dye-sensitized solar cells featuring a carbon-bridged phenylenevinylene. *Chemical Communications (Cambridge)*, 2013, 49(6): 582–584
65. Choi H, Baik C, Kang S O, Ko J, Kang M S, Nazeeruddin M K, Grätzel M. Highly efficient and thermally stable organic sensitizers for solvent-free dye-sensitized solar cells. *Angewandte Chemie International Edition*, 2008, 47(2): 327–330
66. Lim K, Kim C, Song J, Yu T, Lim W, Song K, Wang P, Zu N, Ko J. Enhancing the performance of organic dye-sensitized solar cells via a slight structure modification. *Journal of Physical Chemistry C*, 2011, 115(45): 22640–22646
67. Kim S, Lee J K, Kang S O, Ko J, Yum J H, Frantacci S, Angelis F D, Censo D D, Nazeeruddin M K, Grätzel M. Molecular engineering of organic sensitizers for solar cell applications. *Journal of the American Chemical Society*, 2006, 128(51): 16701–16707
68. Zhu W H, Wu Y Z, Wang S T, Li W Q, Li X, Chen J, Wang Z S, Tian H. Organic D-A- π -A solar cell sensitizers with improved stability and spectral response. *Advanced Functional Materials*, 2011, 21(4): 756–763
69. Wu Y Z, Zhang X, Li W Q, Wang Z S, Tian H, Zhu W H. Hexylthiophene-featured D-A- π -A structural indoline chromophores for coadsorbent-free and panchromatic dye-sensitized solar cells. *Advanced Energy Materials*, 2012, 2(1): 149–156
70. Liang M, Chen J. Arylamine organic dyes for dye-sensitized solar cells. *Chemical Society Reviews*, 2013, 42(8): 3453–3488

71. Boschloo G, Hagfeldt A. Characteristics of the iodide/triiodide redox mediator in dye-sensitized solar cells. *Accounts of Chemical Research*, 2009, 42(11): 1819–1826
72. O'Regan B C, López-Duarte I, Martínez-Díaz M V, Forneli A, Albero J, Morandeira A, Palomares E, Torres T, Durrant J R. Catalysis of recombination and its limitation on open circuit voltage for dye sensitized photovoltaic cells using phthalocyanine dyes. *Journal of the American Chemical Society*, 2008, 130(10): 2906–2907
73. Hagfeldt A, Grätzel M. Light-induced redox reactions in nanocrystalline systems. *Chemical Reviews*, 1995, 95(1): 49–68
74. Mitzi D B. Organic-inorganic perovskites containing trivalent metal halide layers: the templating influence of the organic cation layer. *Inorganic Chemistry*, 2000, 39(26): 6107–6113
75. Grätzel C, Zakeeruddin S M. Recent trends in mesoscopic solar cells based on molecular and nanopigment light harvesters. *Materials Today*, 2013, 6(1-2): 11–18
76. Poglitsch A, Weber D. Dynamic disorder in methylammonium-trihalogenoplumbates (II) observed by millimeter-wave spectroscopy. *Journal of Chemical Physics*, 1987, 87(11): 6373–6378
77. Mitzi D B, Field C A, Schlesinger Z, Laibowitz R B. Transport, optical, and magnetic properties of the conducting halide perovskite $\text{CH}_3\text{NH}_3\text{SnI}_3$. *Journal of Solid State Chemistry*, 1995, 114(1): 159–163
78. Yamada K, Kuranaga Y, Ueda K, Goto S, Okuda T, Furukawa Y. Phase transition and electric conductivity of ASnCl_3 (A = Cs and CH_3NH_3). *Bulletin of the Chemical Society of Japan*, 1998, 71(1): 127–134
79. Mitzi D B, Feild C A, Harrison W T A, Guloy A M. Conducting tin halides with a layered organic-based perovskite structure. *Nature*, 1994, 369(6480): 467–469
80. Billing D G, Llemmerer A. Synthesis and crystal structures of inorganic-organic hybrids incorporating an aromatic amine with a chiral functional group. *CrystEngComm*, 2006, 8(9): 686–695
81. Zhang S J, Lanty G, Lauret J S, Deleporte E, Audebert P, Galmiche L. Synthesis and optical properties of novel organic-inorganic hybrid nanolayer structure semiconductors. *Acta Materialia*, 2009, 57(11): 3301–3309
82. Kojima A, Teshima K, Shirai Y, Miyasaka T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*, 2009, 131(17): 6050–6051
83. Im J H, Lee C R, Lee J W, Park S W, Park N G. 6.5% efficient perovskite quantum-dot-sensitized solar cell. *Nanoscale*, 2011, 3(10): 4088–4093
84. Chung I, Lee B, He J Q, Chang R P H, Kanatzidis M G. All-solid-state dye-sensitized solar cells with high efficiency. *Nature*, 2012, 485(7399): 486–489
85. Lee M M, Teuscher J, Miyasaka T, Murakami T N, Snaith H J. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science*, 2012, 338(6107): 643–647
86. Etgar L, Gao P, Xue Z S, Peng Q, Chandiran A K, Liu B, Nazeeruddin M K, Grätzel M. Mesoscopic $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ heterojunction solar cells. *Journal of the American Chemical Society*, 2012, 134(42): 17396–17399