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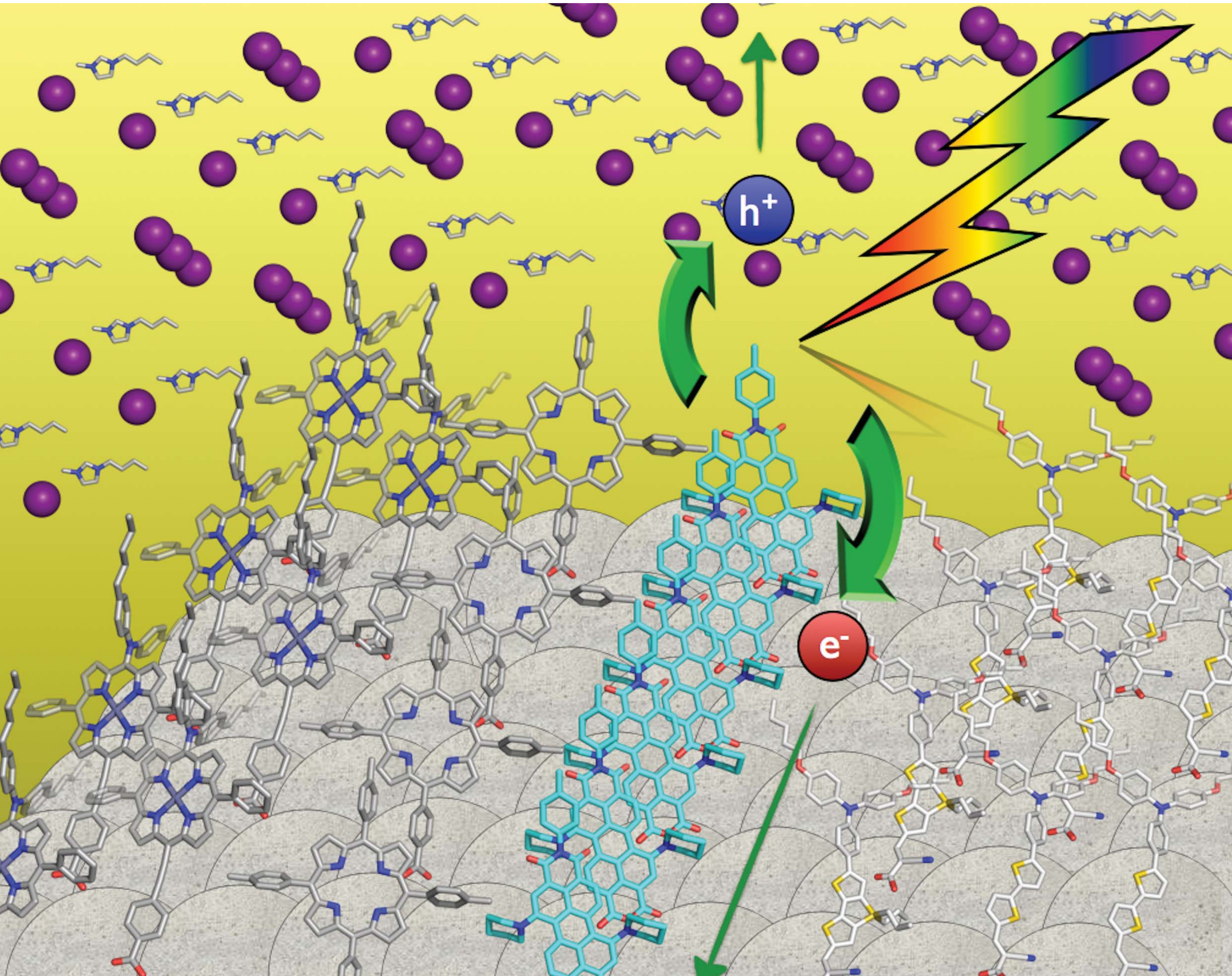

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HIGHLIGHT
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HIGHLIGHT

Advances in high efficiency dye sensitized solar cells based on Ru(II) free sensitizers and a liquid redox electrolyte

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Dye sensitized solar cells (DSCs) are one of the most promising cost effective emerging technologies for clean energy generation using solar radiation. Though many of the highest efficiencies have been associated with Ru(II) polypyridyl sensitizers, Ru(II) free sensitizers have made great progress recently and are now serious alternatives. Indeed the highest efficiency recorded in the literature of 12.05% under standard 100 mW cm^{-2} illumination was obtained using Ru(II) free sensitizers. In this highlight, recent progress in DSCs based on sensitizers such as porphyrins, phthalocyanines, squarines, indolenes, perylenes and donor–(π bridge)–acceptor (D–π–A) dyes is discussed.

Introduction

The best efficiencies for dye sensitized solar cells (DSCs) have historically been recorded with Ru(II) polypyridyl sensitizers.[1–5] These are extremely attractive sensitizers due to their wide absorption range from the visible to the near infrared arising from MLCT bands as well as their well-known thermal and chemical stability. Studies have also revealed that in addition to their sensitizing function they show excellent control over interfacial charge transfer processes that are key to optimized device function.[6–9] The most commonly used and efficient Ru(II) sensitizers include **N719** (ref. 10) and **N749** (ref. 11) (Fig. 1). In recent years, the molecular engineering of bipyridyl ligands has generated several new series of Ru(II) polypyridyl sensitizers. The principal approach is the addition of π-conjugated systems, such as thiophene and its derivatives to the ancillary bipyridyl ligand, as in, for example, **C101** (ref. 2) (Fig. 1). These modifications increase and broaden absorption as well as shift spectra towards the infrared region where generally Ru(II) polypyridyl sensitizers show weak absorption. Another approach to improve absorbance is to completely remove the –NCS ligands altogether using tridendate cyclometalated ligands, as in, for example, **TF-3** (ref. 5) (Fig. 1).

Recently, however, efficiencies for DSCs based on Ru(II) free sensitizers have shown great improvement. In the literature there are now many examples of such sensitizers that show outstanding efficiencies.[12–16] Most of these new

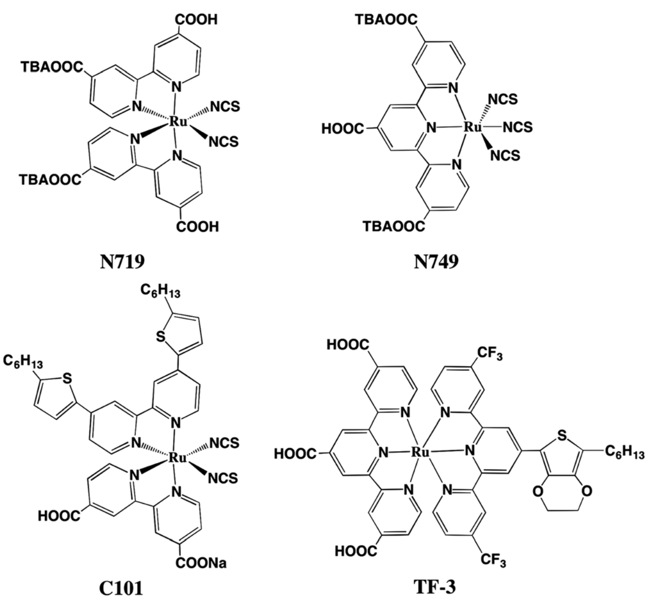

Fig. 1 Molecular structures of Ru(II) polypyridyls **N719**, **N749**, **C101** and **TF-3**.

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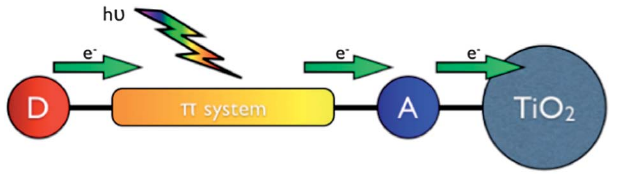


Fig. 2 Structure of D–π–A dyes and the electron transfer processes following illumination.

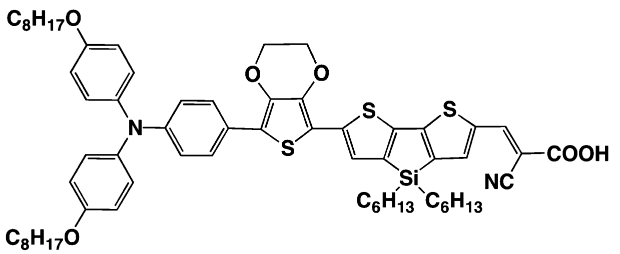


Fig. 3 Molecular structure of D–π–A dye **C219**.

sensitizers are conjugated systems with very high extinction co-efficients, several times larger than the best Ru(II) polypyridyl sensitizers. This makes them perfect candidates as next generation sensitizers for DSCs based on liquid electrolytes other than iodide/tri-iodide (*e.g.* cobalt(II)/cobalt(III)[15] and ferrocene/ferrocene$^+$ (ref. 17) electrolytes) or solid hole-transporting complexes (*e.g.* polymers such as P3HT).[18] In both of these cases the TiO_2 film thickness needs to be thinner to avoid recombination and low voltages, and sensitizers with high extinction co-efficients are therefore required. In addition, many of the new Ru(II) free sensitizers show excellent chemical and photochemical stability whose photochemical and electrochemical properties can be tuned easily.

In this highlight, recent progress in DSCs based on Ru(II) free sensitizers such as porphyrins, phthalocyanines, indolenes, perylenes, squarines and donor–(π bridge)–acceptor (D–π–A) dyes is discussed. Moreover, we discuss how several of these classes of sensitizers appear to function better in DSCs based on electrolytes which are less corrosive than the iodide/tri-iodide electrolyte and how this opens the door for long term stability of DSCs.

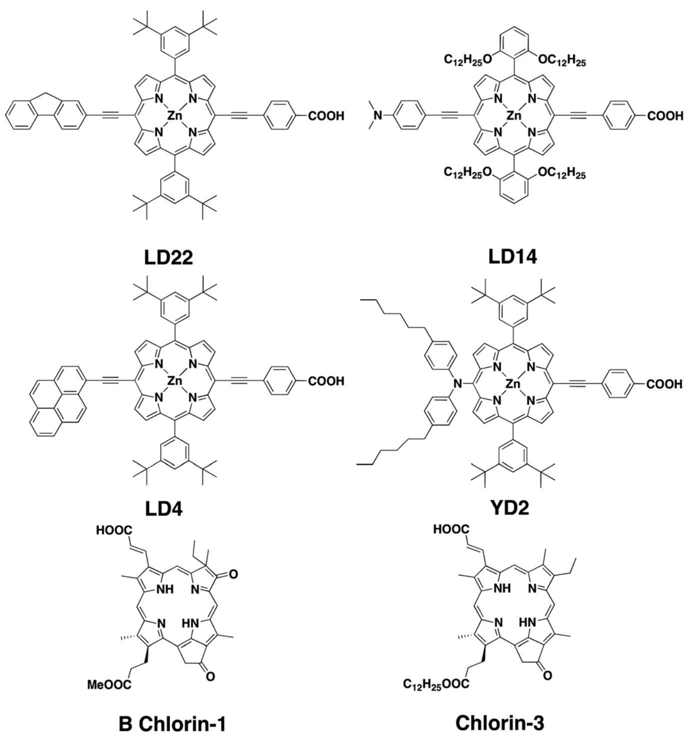


Fig. 4 Molecular structures of **LD22**, **LD14**, **LD4**, **YD2**, **B Chlorin-1** and **Chlorin-3**.

D–π–A complexes

D–π–A dyes, also known as push–pull dyes, consist of electron-donating and electron-withdrawing groups linked covalently through a π-conjugated spacer (Fig. 2).

The photophysical properties of D–π–A dyes are associated with an intramolecular charge transfer from the donor to the acceptor moiety. This transition provides the dye with high molar extinction coefficient and singlet fluorescence. The expansion of the π-conjugated structure, by adding either electron donating or withdrawing groups, can induce a shift in both HOMO and LUMO energy levels, resulting in a change of photophysical properties. Due to the fact that they are easy to tune, D–π–A dyes are considered one of the most promising classes of Ru(II) free sensitizers for DSCs.

Many different kinds of donors, acceptors and π-conjugated spacers have been investigated with ample examples in the literature attesting to this.[19] The most common D–π–A dyes include triphenylamine, thiophene and cyanoacetic acid.[13,16,20–23] The highest efficiency recorded so far for a D–π–A based DSC is 10.3% by Wang and co-workers using the dye **C219** (ref. 13) (Fig. 3). This is also one of the highest efficiencies recorded for a Ru(II) free sensitizer.

Porphyrins and chlorophyll derivatives

Porphyrins are also among the most efficient of the emerging Ru(II) free sensitizers. Porphyrins are fully conjugated aromatic macrocycles characterized by the presence of four modified pyrrole subunits interconnected at their α carbon atoms *via* methine bridges. A typical porphyrin absorption spectrum consists of an intense Soret band centered at 400–450 nm ($\varepsilon \sim 420\,000$ cm^{-1} M^{-1}) and a series of moderately absorbing Q bands at 500–650 nm ($\varepsilon \sim 15\,000$ cm^{-1} M^{-1}).[24]

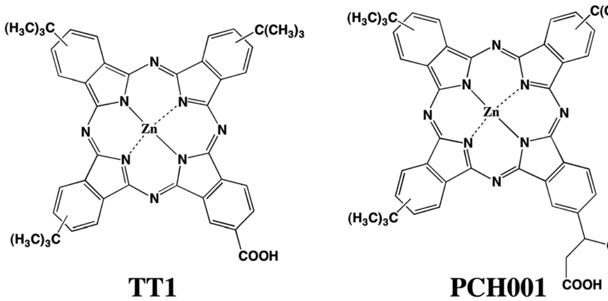


Fig. 5 Molecular structures of **PCH001** and **TT1**.

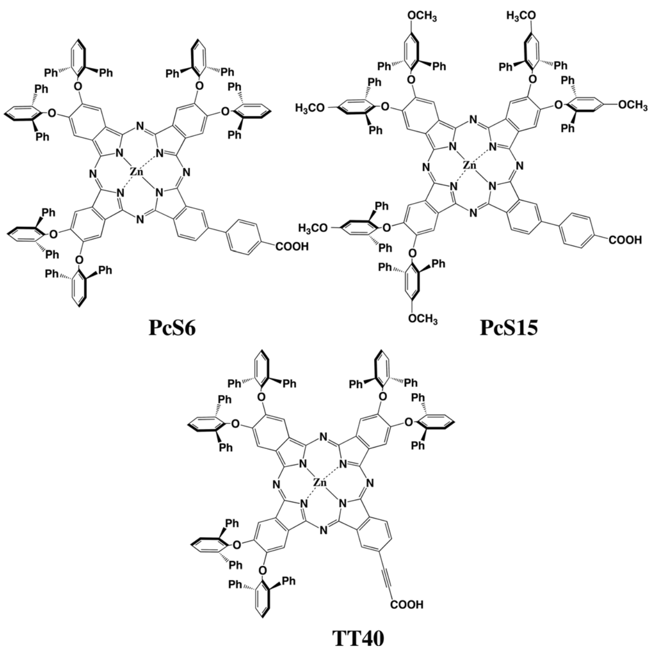


Fig. 6 Molecular structures of **PcS6**, **PcS15** and **TT40**.

Until recently efficiencies for porphyrin based DSCs were rather disappointing[25–27] when compared to those based on Ru(II) polypyridyl sensitizers. This was believed to be due to several reasons including aggregation and a lack of directionality of the excited state due to the symmetry of these structures and therefore poor coupling between the TiO_2 conduction band and the LUMO. However, with the design of push–pull zinc porphyrins containing electron donating and withdrawing groups to improve the directionality of the excited state and bulky groups to reduce aggregation, efficiencies have increased notably. The structures of four such high efficiency push–pull zinc porphyrins are shown in Fig. 4 developed by Lin, Diau, Yeh and co-workers. **LD22**,[28] **LD14**,[29] **LD4** (ref. 30) and **YD-2** (ref. 14) show respectively 8.1, 10.2, 10.1 and 11% efficiency under standard AMG 1.5 illumination conditions. Moreover, the highest DSC efficiency yet recorded of 12.05% was obtained using the porphyrin **YD2-*o*-C8** (ref. 15) (see the final section).

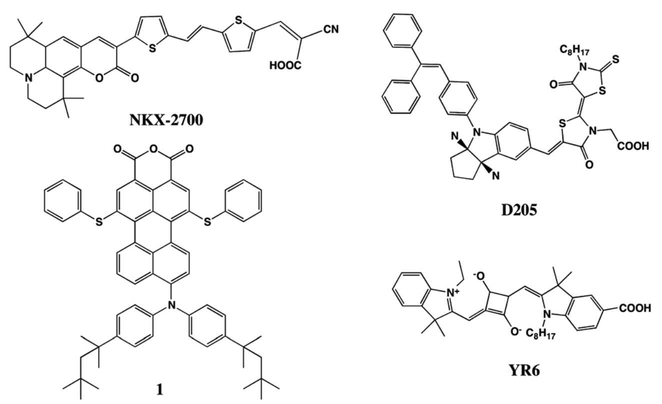


Fig. 7 Molecular structures of coumarine **NKX-2700**, indolene **D205**, perylene **1** and squarine **YR6**.

Chlorophylls and related derivatives have also been used as organic sensitizers in DSCs. The attraction towards these sensitizers is obvious as there is a large number known and their use might make large-scale production of DSCs more economically viable. The highest efficiencies for DSCs fabricated with such sensitizers have been achieved by Wang and co-workers using **B Chlorin-1** (ref. 31) and **Chlorin-3** (ref. 32) (Fig. 4) obtaining 6.6 and 8.0% efficiency respectively.

Phthalocyanines

Phthalocyanines are structurally related to porphyrins but are even more conjugated macrocycles that absorb in the far visible/near-IR region. They have extremely high extinction co-efficients (ε) of over 100 000 M^{-1} cm^{-1} at around 700 nm where ruthenium sensitizers start to tail off in absorbance (IPCE of **C101** at 700 nm is about 60%).[33] Though efficiencies for phthalocyanine based DSCs are still somewhat lower when compared to DSCs based on other Ru(II) free sensitizers, they are transparent over a large part of the UV-visible region, making them attractive for use in "photovoltaic windows".

Just as for porphyrins, until very recently low efficiencies were reported for DSCs based on phthalocyanines (η < 1%)[34,35] which was explained due to reasons such as aggregation, lack of directionality of the excited state due to symmetrical structures and poor coupling between the TiO_2 conduction band and the LUMO. However, a significant breakthrough was made in 2007 when working independently, Nazeeruddin and co-workers developed zinc phthalocyanines **PCH001** (ref. 36) (Fig. 5) showing

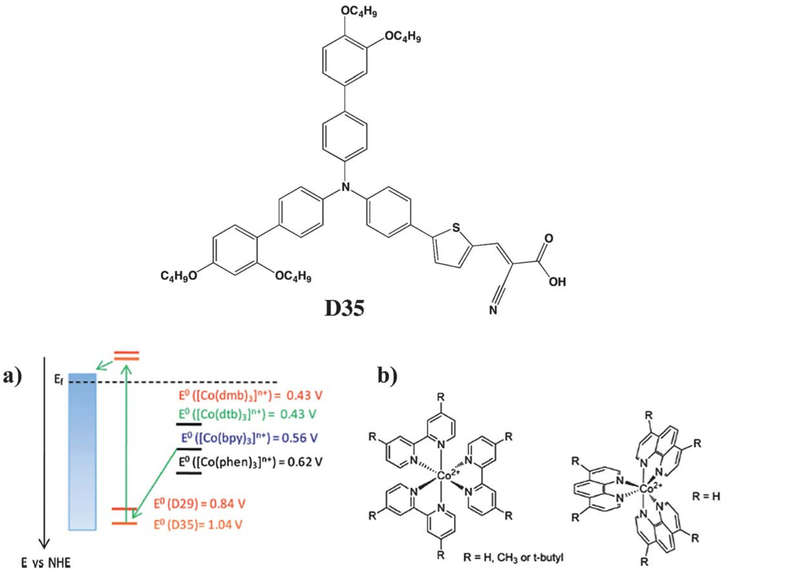


Fig. 8 Top: molecular structure of **D35**. Bottom: (a) energy diagram (*vs.* NHE) of the TiO_2/**D35**/Co(II)/Co(III) interface and (b) structures of the different cobalt redox couples employed. Figure modified from Feldt *et al.*[51]

an efficiency of 3.05% and Torres and co-workers developed **TT1** (ref. 37) (Fig. 5) displaying an efficiency of 3.52%. These structurally very similar phthalocyanines differ only in the number of carboxylic anchoring groups and contain bulky *tert*-butyl groups to improve solubility and reduce aggregation. The unsymmetrical nature of these "push–pull" phthalocyanines helps to improve the directionality of the excited state towards the anchoring groups and therefore the TiO_2, thus improving J_{sc} with IPCE values of over 80% at 700 nm recorded.

By designing the Zn phthalocyanine **PcS6** (ref. 38) containing six 2,6-diphenylphenoxy groups capable of avoiding aggregation even more effectively than *tert*-butyl groups, Mori and co-workers achieved an efficiency of 4.6% (Fig. 6). Indeed, the 2,6-diphenylphenoxy groups are so effective at stopping aggregation that devices were prepared without the need to use the co-adsorbent chenodeoxycholic acid. Mori has since improved upon this, with an efficiency of 5.3% recorded using **PcS15** (ref. 39) (Fig. 6). The introduction of the electron donating methoxy groups in the 2,6-diphenylphenoxy groups improved the photoresponse of **PcS15** from 400–500 nm with respect to **PcS6** with a gain of almost 2 mA cm^{-1} being observed. The record efficiency at present for a phthalocyanine based DSC is 5.5% with **TT40** (ref. 40) (Fig. 6).

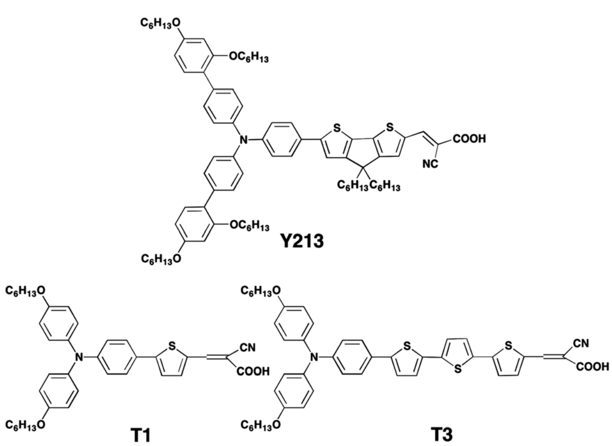


Fig. 9 Molecular structures of D–π–A dyes **Y213**, **T1** and **T3**.

Coumarines, indolenes, perylenes and squarines

Other Ru(II) free sensitizers used in DSCs include coumarines, indolenes, perylenes and squarines. Coumarines were among the best early Ru(II) free sensitizers with efficiencies of over 7% recorded as early as 2003 by Arakawa and co-workers.[41] **NKX-2700** (ref. 42) (Fig. 7) is one of the most efficient with an efficiency of 8.2%. Indolenes also show high efficiencies of up to 9.5% (**D205**,[12] Fig. 7) in DSCs. Highly conjugated perylenes are slightly lower in efficiency with the best efficiency recorded of 6.8% (perylene **1**, Fig. 7).[43] Similar to phthalocyanines, squarines show intense absorption bands in the far visible/near-IR region. The best current efficiency of a squarine in a DSC is 6.7%, with **YR6** (ref. 44) (Fig. 7), making them slightly better than phthalocyanines.

Open circuit voltage (V_{oc}) of DSCs based on Ru(II) free sensitizers with the iodide/tri-iodide electrolyte

A limitation of DSCs based on Ru(II) free sensitizers discussed hitherto is the lower V_{oc} that these often display when using the iodide/tri-iodide electrolyte compared to DSCs based on Ru(II) polypyridyl sensitizers. This has generally been explained in terms of dye–electrolyte interactions, with highly conjugated sensitizers and sensitizers containing groups such as thiophenes strongly binding tri-iodide (or iodine).[45] There are several key studies that show that lower V_{oc} can be correlated with faster e^-_{TiO2}/electrolyte$^+$ recombination lifetimes extracted from transient photovoltage or impedance measurements.[9,46,47] Efforts to minimize dye–electrolyte interactions and e^-_{TiO2}/electrolyte$^+$ recombination include molecular engineering of the sensitizer structure to include alkyl or alkoxy groups and the use of co-adsorbents such as chenodeoxycholic acid.

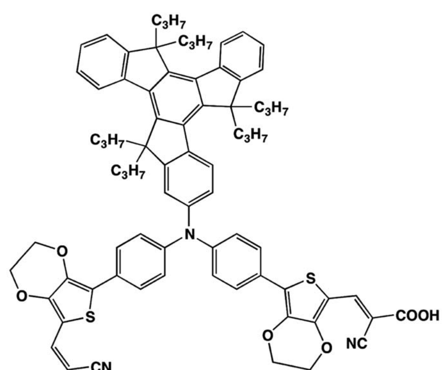
DSCs based on Ru(II) free sensitizers using cobalt(II)/cobalt(III) electrolytes

Despite some notable recent exceptions,[48,49] DSCs based on Ru(II) polypyridyl sensitizers employing cobalt(II)/cobalt(III) electrolytes have generally yielded unsatisfactory results. However, in addition to the breakthroughs already discussed regarding Ru(II) free sensitizers in DSCs using the iodide/tri-iodide electrolyte, they also show much better performances with cobalt(II)/cobalt(III) electrolytes in comparison to Ru(II) polypyridyl sensitizers. Indeed many believe that this has breathed new life into this still nascent technology and it offers exciting new possibilities for the future.[50]

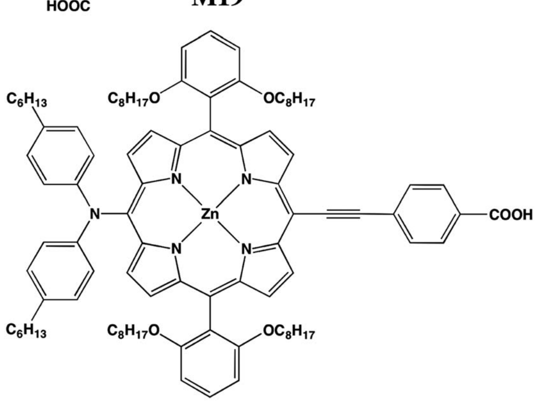
A study reported in 2010 by Feldt *et al.*[51] represents a milestone in efficient DSCs employing cobalt(II)/cobalt(III) electrolytes. In this work various cobalt(II)/cobalt(III) electrolytes were tested using the organic D–π–A dye **D35** (Fig. 8). The use of cobalt(II)/cobalt(III) enables high V_{oc} values to be obtained due to the very positive oxidation potentials of these redox couples (Fig. 8). The outstanding result of 6.7% was obtained with tris(2,2′-bipyridyl)cobalt(II/III), where V_{oc} was 0.92 V. In these devices, faster back electron transfer between the electrons accumulated at the FTO/TiO_2 electrode and the cobalt(II)/cobalt(III) can limit V_{oc} due to the larger driving force ($-\Delta G$) for electron recombination kinetics. Thus, it was of utmost importance to use a thin dense blocking layer (thickness 80–100 nm) on the FTO to reduce recombination under illumination. Moreover, thin mesoporous TiO_2 layers (<5 μm) were employed to eliminate diffusion problems of the cobalt(II)/cobalt(III) through the nanoporous TiO_2 film.

It is worth pointing out that **D5** has long alkoxyl chains incorporated into its structure, as do many outstanding D–π–A dyes with similar structures used in highly efficient DSCs based on iodide/tri-iodide electrolyte (Fig. 3). Nonetheless, the *ortho*- and *para*-positions of the chains in **D5** are different from the usual *para*-position found in the D–π–A dyes (Fig. 3). In another study by Tsao *et al.*[52] employing the dye **Y213** (Fig. 9) which also contains alkoxyl chains at the *ortho*- and *para*-positions, an excellent efficiency of 8.8% was obtained with tris(2,2′-bipyridyl)cobalt(II/III). This may indicate that alkoxyl or alkyl chains at certain positions in the sensitizer structure may facilitate good dye packing on the TiO_2 film leading to high efficiencies and V_{oc} in the presence of the cobalt(II)/cobalt(III) electrolyte. (The **Y213** cell efficiency was improved further to 10.3% by substituting the Pt counter electrode for a poly(3,4-ethylenedioxythiophene) (PEDOT) counter electrode which showed a lower charge transfer resistance to cobalt(III) reduction.)[53] On the other hand, Wang and co-workers[54] carried out an extensive study involving D–π–A dyes **T1** and **T3** (Fig. 9), which have alkoxyl chains at the *para*-positions only on the tri-phenyl amine groups which show efficiencies of 5.0 and 8.0%, respectively, in the tris(1,10-phenanthroline)cobalt(II/III) electrolyte. This study is notable as it shows that the increase in conjugation in **T3** relative to **T1** does not lead to a drop-off in V_{oc} as is typically observed when using iodide/tri-iodide as discussed in the previous section. In this case the **T3** device containing the more bulky and conjugated sensitizer actually shows an improvement of 22 mV in comparison to the **T1** device.

There are other studies which also show that more bulky sensitizers show favourable behaviour in the presence of the cobalt(II)/cobalt(III) electrolyte. Zong *et al.*[55] synthesized a series of truxene dyes bearing polyaromatic moieties and demonstrated that increasing the aromatic structure of the organic dye does not decrease V_{oc} in clear contrast to the experimental results observed for DSC devices using the I^-/I_3^- redox couple. The bulky dye **M19** (Fig. 10) shows the highest V_{oc} and also the longest device electron lifetime indicating that recombination between TiO_2 electron and cobalt(III) is more effectively retarded. This work indicates that increased sensitizer conjugation does not lead to the same problems encountered when employing the iodide/tri-iodide electrolyte. In fact, the highest published efficiency recorded until now of 12.05% was achieved with a Ru(II) free sensitizer, namely the push–pull zinc porphyrin **YD2-*o*-C8** (ref. 15) (Fig. 10).



M19



YD2-*o*-C8

Fig. 10 Molecular structures of **M19** and **YD2-*o*-C8**.

Conclusions

As we hope we have demonstrated in this highlight, DSCs based on Ru(II) free sensitizers have made significant progress in terms of efficiency in the last few years. They have proven themselves to be just as good as Ru(II) polypyridyl sensitizers in devices employing the iodide/tri-iodide redox couple. In addition they have also proven themselves to be even better when employed with other redox couples such as cobalt(II)/cobalt(III) or ferrocene/ferrocene$^+$. As the potentials of such couples can be easily tuned by chemical modification of the polypyridyl and cyclopentadienyl ligands, this allows for DSCs with high V_{oc} to be obtained, thus improving cell efficiency further.

Key to improving the performance of Ru(II) free sensitizers, independent of the electrolyte in question, will be to couple their strong absorbance with panchromatic absorbance (as they often show narrow absorbance bands). Moreover, the stability of DSCs based on Ru(II) free sensitizers using the new electrolytes must be investigated more closely. However Ru(II) free sensitizers offer fresh opportunities for the commercialisation of DSCs in the future.

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