

# Optimizing Dyes for Dye-Sensitized Solar Cells

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dyes/pigments · energy conversion · redox chemistry · semiconductors · sensitizers

**D**ye-sensitized solar cells (DSSCs) have emerged as an important cheap photovoltaic technology. Charge separation is initiated at the dye, bound at the interface of an inorganic semiconductor and a hole-transport material. Careful design of the dye can minimize loss mechanisms and improve light harvesting. Mass application of DSSCs is currently limited by manufacturing complexity and long-term stability associated with the liquid redox electrolyte used in the most-efficient cells. In this Minireview, dye design is discussed in the context of novel alternatives to the standard liquid electrolyte. Rapid progress is being made in improving the efficiencies of such solid and quasi-solid DSSCs which promises cheap, efficient, and robust photovoltaic systems.

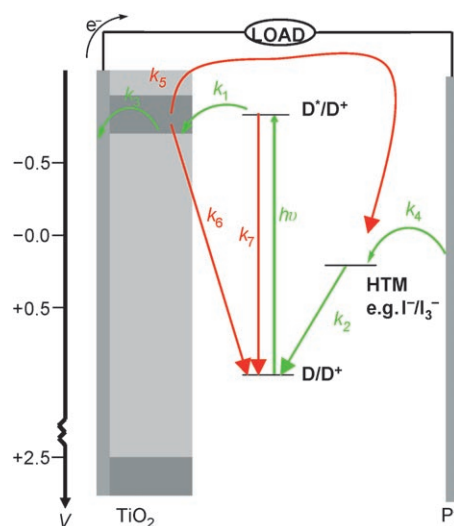
## 1. Introduction

### 1.1. Design of Dye-Sensitized Solar Cells

Increasing energy demands and concerns over global warming have led to a greater focus on renewable energy sources in recent years. The conversion of solar energy is likely to play a key role as one of the technologies that can replace fossil fuels in the generation of mass energy. However, the current high cost of solar panels made from traditional inorganic semiconductors<sup>[1]</sup> imposes a restriction on their mass usage. Alternative cheaper solar energy technologies are therefore under intensive study, and in this context dye-sensitized solar cells (DSSCs) have emerged as an important class of photovoltaic device. DSSCs are currently undergoing rapid development in an effort to obtain robust, efficient, and cheap devices that are suitable for practical use.<sup>[2–4]</sup> An outline of the operation of a DSSC is illustrated in Figure 1. The system comprises a dye that is bound to the surface of an inorganic semiconductor. Typically nanocrystalline TiO<sub>2</sub> is used as it provides a large surface area to which the dye can

adsorb, which is crucial for efficient light harvesting. The porous TiO<sub>2</sub> layer is interpenetrated by a hole-transport material (HTM), which may be a redox electrolyte in solution or a solid-state or quasi-solid-state (gel) material. Excitation of the dye leads

to the injection of electrons from the excited dye to the conduction band of the TiO<sub>2</sub>. The ground state of the dye is regenerated through reduction by the HTM to give the



**Figure 1.** Outline of the operation of a DSSC ( $D$  = dye;  $V$  [V] vs standard calomel electrode (SCE)). The green arrows represent processes required for photovoltaic function:  $k_1$  = charge injection,  $k_2$  = dye regeneration,  $k_3$  = charge collection at the conducting glass electrode, and  $k_4$  = charge collection at the Pt electrode. The red arrows represent loss mechanisms:  $k_5$  = charge recombination with the hole-transport material (HTM; dark current),  $k_6$  = charge recombination with the oxidized dye ( $D^+$ ), and  $k_7$  = decay of the excited state of the dye ( $D^*$ ).

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required charge separation. Charges migrate and are collected at a transparent conducting electrode (electrons) and Pt electrode (holes). A number of parameters are used to characterize the detailed performance of a photovoltaic cell;<sup>[2]</sup> however, in this Minireview discussion is limited mainly to the overall efficiency of conversion of solar-to-electrical energy of the cell ( $\eta$ ) and also to the incident photon to current efficiency (IPCE), which gives a measure of the efficiency as a function of wavelength of the incident light.

Following the initial development of this type of cell by O'Regan and Grätzel,<sup>[5]</sup> there has been further extensive study and optimization of the design, including modifications to the nanocrystalline semiconductor, the redox electrolyte, and the dye. Currently, the most efficient DSSCs show efficiencies of over 10%, which is sufficiently high to be of practical utility. The cells that display the highest efficiency, however, use an HTM comprising an  $I^-/I_3^-$  redox electrolyte solution that gives rise to poor long-term stability and manufacturing complexity.<sup>[6]</sup> The involvement of volatile  $I_2$  and volatile solvent requires the cells to be sealed, and additionally, the  $I^-/I_3^-$  redox electrolyte can be corrosive towards the Pt electrode. Although some commercialization of DSSCs has begun, new aspects of cell design are being intensively explored to continue to address these limitations and open up DSSC technology to much wider exploitation. Thus, a number of alternative redox mediators and electrolyte systems have been explored, including  $I^-/I_3^-$  in either solid polymer,<sup>[7,8]</sup> gel,<sup>[6]</sup> ionic liquid,<sup>[9]</sup> or plastic crystal<sup>[10]</sup> systems; solid inorganic materials;<sup>[11]</sup>  $Co^{II}/Co^{III}$ <sup>[12]</sup> and  $SeCN^-/(SeCN)_3^-$  redox couples;<sup>[9]</sup> and hole-conducting organic polymers<sup>[13]</sup> and small organic molecules.<sup>[14]</sup> However, a reduced efficiency has so far been achieved for such cells; for example, the maximum cell efficiencies observed for the gel-electrolyte systems, organic HTM systems, and ionic liquid systems are around 6, 4, and 8%, respectively. In each of these cases, the efficiencies are less than that for the optimized  $I^-/I_3^-$ /volatile solvent cell as a result of factors such as reduced hole mobility, poorer electron-transfer kinetics, and poorer contact at the dye-HTM interface. Much is now understood concerning loss mechanisms that arise within the system, and key processes are indicated in Figure 1.

Some recent overviews that discuss general aspects of DSSCs<sup>[1,2,4]</sup> have appeared along with a series of articles that give a detailed account of several specific topics within the field.<sup>[3]</sup> The aim of this Minireview is to provide a general



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overview of dye characteristics and illustrate the ways in which dye design has been used to enhance the efficiency of cells. The key challenge at present is to obtain efficiencies that are comparable to that for the optimized  $I^-/I_3^-$ /volatile solvent cell by using an HTM that is more suitable for mass production and long-term stability. The design of dyes will therefore be presented in this context in the quest for photovoltaic (PV) cells that are efficient, robust, and cheap to manufacture.

## 1.2. General Design of Dyes

Progress in the optimization of the dye component of the cell has been made through systematic variation of the ligands, metal, and other substituent groups in candidate transition-metal complexes.<sup>[2,15,16,17]</sup> This systematic study has resulted in the development of mononuclear<sup>[2]</sup> and polynuclear<sup>[18]</sup> dyes based on metals such as  $Ru^{II}$ ,<sup>[19–21]</sup>  $Os^{II}$ ,<sup>[4,22,23]</sup>  $Pt^{II}$ ,<sup>[24,25]</sup>  $Re^I$ ,<sup>[26]</sup>  $Cu^I$ ,<sup>[27]</sup> and  $Fe^I$ .<sup>[28]</sup> Besides transition-metal complexes, a range of organic molecules have been explored, with recent examples including coumarin,<sup>[29]</sup> squaraine,<sup>[30]</sup> indoline,<sup>[31]</sup> hemicyanine,<sup>[32]</sup> and other conjugated donor-acceptor organic dyes,<sup>[33–36]</sup> and the best efficiency reported was 8% (see Figure 7a in Section 2.5).<sup>[31]</sup> Porphyrin dyes<sup>[37,38]</sup> and phthalocyanine dyes<sup>[39]</sup> have also been explored.

The dyes used in DSSC technology must conform to a number of essential design requirements in order to function. They must bind strongly to  $TiO_2$  by means of an anchoring group, typically carboxylic or phosphonic acid groups, to ensure efficient electron injection into the  $TiO_2$  conducting band and to prevent gradual leaching by the electrolyte. The LUMO of the dye must be sufficiently high in energy for efficient charge injection into the  $TiO_2$ , and the HOMO must be sufficiently low in energy for efficient regeneration of the oxidized dye by the HTM. The dye must absorb solar radiation strongly with absorption bands in the visible or near-IR region, preferably covering a broad range of wavelengths. Electron transfer from the dye to the  $TiO_2$  must also be rapid in comparison with decay to the ground state of the dye. Dyes that show emission in the solution state at room temperature have typically been used, although this is not essential.<sup>[40]</sup>

The family of complexes  $[(4,4'-CO_2H)_2(bipy)]_2RuX_2$  ( $bipy = 2,2'$ -bipyridyl;  $X = Cl, Br, I, CN, NCS$ ) perform well;<sup>[19]</sup> for example, the dye  $[(4,4'-CO_2H)_2bipy]_2Ru(NCS)_2$  (**N3**) and the doubly deprotonated analogue (**N719**, Figure 2) give a solar-to-electrical energy conversion efficiency of over 10%. Use of a terpyridyl ligand led to the so-called “black dye” (Figure 2), which gives a very high IPCE across the wavelength range 400–700 nm and a cell efficiency of over 10%.<sup>[21,41]</sup> Dyes are often referred to by codes (as indicated in the figures), which will be used in the remainder of the article.

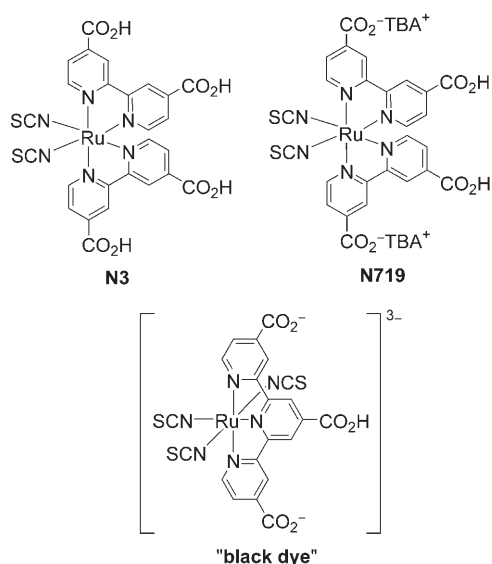
## 2. Current Developments in Dye Design

As previously mentioned, the key limitations of DSSCs arise from the  $I^-/I_3^-$  liquid electrolyte and this has neces-

sitated the exploration of other cell designs that use an alternative HTM. Initial research into these modified cells with novel designs typically used dyes that were previously optimized for a cell with an  $I^-/I_3^-$  solution electrolyte as the HTM (e.g. **N3** or **N719**). As studies develop, however, it is apparent that innovation in transport materials should be carried out in conjunction with the development of new dyes to maximize the improvements in efficiency and stability. Thus, the exploration of new dye designs specifically for solid-state and quasi-solid-state cells is currently an area of high priority that has started to receive increased attention. Key approaches to this area of research are described in Section 2.1–2.5.

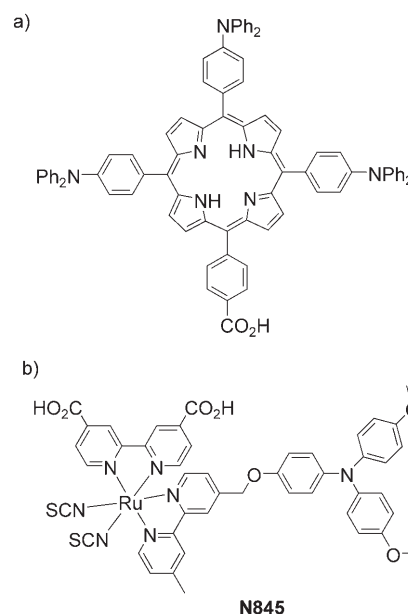
### 2.1. Enhanced Charge Separation in the Dye: Minimizing Charge Recombination

The complex **N3** (Figure 2) is a good illustration of the role that charge separation in the dye plays in controlling the kinetics of electron transfer. Absorption of the dye in the low-energy visible region involves an MLCT (metal-to-ligand charge transfer) transition that places the excited electron on the diimine, which is directly attached to the  $TiO_2$ . The result is ultrafast charge injection (see Section 2.2), however, the positive charge density that remains on the dye is distributed over the metal and also to some extent over the NCS ligands. The resulting spatial separation of the positive charge density on the dye and the injected electrons has the crucial effect of retarding the rate of charge recombination between the injected electrons and the dye cation, which is a key loss mechanism (Figure 1,  $k_6$ ). Indeed, it has been shown that charge-recombination dynamics are closely dependent on this separation and, in contrast, show very little dependence on the thermodynamic driving force for the recombination, as determined by the reduction potential of the dye cation.<sup>[42]</sup>



**Figure 2.** Examples of some Ru-polypyridyl dyes used in DSSCs that give cell efficiencies of over 10%. TBA = tetra-*n*-butylammonium.

Recent work has illustrated that this approach can be extended further and that dyes with attached electron-donor groups can locate the cationic charge at a greater distance from the  $TiO_2$  surface.<sup>[43,44]</sup> For instance, the substituted porphyrin shown in Figure 3a attaches itself to the  $TiO_2$  surface through



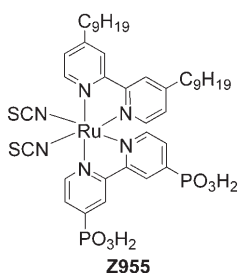
**Figure 3.** Examples of dyes with attached triarylamine electron-donor groups: a) a porphyrin dye<sup>[44]</sup> and b) Ru dye **N845**.<sup>[45]</sup>

its carboxylic acid group, and  $\pi-\pi^*$  photoexcitation leads to charge injection.<sup>[44]</sup> It was found that recombination of the injected electron with the dye was an order of magnitude slower than for a comparable dye that lacked the electron-donor triphenylamine groups. This difference was attributed to the location of the cationic charge largely on the triphenylamine moieties of the dye and the consequently larger physical separation of the cationic charge from the  $TiO_2$  surface. This approach was extended to the ruthenium dye **N845** (Figure 3b), which also contains an appended triarylamine moiety.<sup>[45]</sup> In this case, a 1000-fold retardation of the recombination dynamics was attributed to the 4 Å increase in distance between the cationic center of charge and the  $TiO_2$  surface (as estimated from semi-empirical calculations) in comparison with **N719** (Figure 2).

### 2.2. Methods to Attach the Dye to $TiO_2$

The majority of dyes are linked to the  $TiO_2$  semiconductor through acidic groups—mostly carboxylic acid or, less commonly, phosphonic acid linkers<sup>[46]</sup>—although a variety of other moieties also have been used.<sup>[47,48]</sup> Carboxylic acid groups can form ester linkages with the surface of the metal oxide to provide a strongly bound dye and good electronic communication between the two parts. However, the link can be hydrolyzed through the presence of water, an important factor in terms of the stability of the cell (see Section 2.3). The

dyes that have shown the highest cell efficiencies have used carboxylic acid linkers, although a recent study into phosphonic acid linkers reported the highest efficiency ( $\geq 8\%$ ) for any dye with a non-carboxylic acid linker (**Z955**, Figure 4). In this case, modification of the linker from carboxylic to phosphonic acid groups resulted in an interrelated series of changes in the characteristics of the device; for example, a blue shift of the absorption maxima, good stability of the device, and slower charge-recombination kinetics for **Z955** relative to the analogous dye with carboxylic acid linkers (**Z907**, see Figure 5, Section 2.3). The increased number of protons on the phosphonic acid groups compared with carboxylic acid groups has been suggested as a factor in modifying the performance of the dye, as it has been observed that the efficiency of the solar cell can be influenced by changing the protonation of the acid groups. This is attributed to the effect of the bound dye on the energy of the  $\text{TiO}_2$  conducting band, such that **N719**, which is deprotonated, gives a higher cell efficiency than the protonated analogue **N3** (Figure 2).<sup>[41]</sup>



**Figure 4.** Ru-polypyridyl dye **Z955** with phosphonic acid linker groups.<sup>[46]</sup>

Besides the protonation state of the carboxylic acid group, the position of these linker groups on the bipyridyl moiety has been explored.<sup>[49,25]</sup> The large majority of studies involving bipyridyl groups employ 4,4'-substituted derivatives. The study of a Ru complex with carboxylic acid groups in the 3,3'-positions of the bipyridyl revealed a decreased efficiency of the cell,<sup>[49]</sup> whereas a study of Pt dyes showed the opposite effect with a slightly improved efficiency for the complex with 3,3'-substituted bipyridyl.<sup>[25]</sup> As substitution at the 3,3'-positions necessitates some twisting of the ligand, the consequences of the electronic alteration to the dye when bound to  $\text{TiO}_2$  may be difficult to predict, however, it seems that further study of complexes with 3,3'-substituted bipyridyls is merited.

Charge injection from Ru-polypyridyl dyes linked through carboxylic acid groups is extremely rapid, and for dye-sensitized  $\text{TiO}_2$  covered with an inert solvent it occurs on a femto- to picosecond timescale from the excited singlet and triplet states of the dye, respectively.<sup>[50]</sup> In a complete DSSC,<sup>[51,52]</sup> charge injection occurs on the picosecond timescale, with the composition of the redox electrolyte playing an important role in modifying the energetics of the  $\text{TiO}_2$  conduction band and hence the charge-injection rate. This extremely rapid process leads to injection yields that approach 100% for many dyes. However, as the excited-state lifetime of dyes such as **N3** can be as long as 50 ns, high injection yields may still be achieved with an injection rate that is several orders of magnitude slower than those observed. The unnecessarily rapid charge injection is referred to as "kinetic redundancy" and is important because the rates of charge injection ( $k_1$ ) and the charge-recombination loss process ( $k_6$ ) are correlated, as both are influenced by the strength of electronic communication of the dye with the  $\text{TiO}_2$ .<sup>[52]</sup> For an optimum device kinetic redundancy should be

minimized, with charge injection only just fast enough to compete with excited-state decay such that loss through charge recombination is also minimized. Variation of the nature of the linker group between the dye and the  $\text{TiO}_2$  can play a crucial role in this optimization and hence on the cell efficiencies achieved.

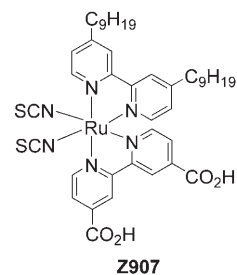
In an attempt to control these interfacial electron-transfer processes, Haque et al. studied an azobenzene dye encapsulated within a cyclodextrin molecule attached to  $\text{TiO}_2$ .<sup>[53]</sup> The cyclodextrin comprises a hydrophilic outer layer, which is suitable for adsorption onto the  $\text{TiO}_2$  surface, and a hydrophobic inner surface. The spatial separation of the dye from the  $\text{TiO}_2$  increased, however, the charge injection yield was comparable with a non-encapsulated dye analogue, in keeping with the kinetic redundancy argument. Importantly, the increased separation also led to a significantly slower rate for  $k_6$ , offering potential gains in cell efficiency. As well as these effects, the encapsulation approach has the possibility to enhance photochemical stability, redox reversibility, and electroluminescent efficiency.

These recent examples illustrate that much is now understood concerning the optimization of kinetic parameters for interfacial electron transfer. These studies, however, have typically involved use of the  $\text{I}^-/\text{I}_3^-$  solution redox electrolyte, and an important next step will involve the exploitation of these ideas in improving the lower efficiencies currently achieved in cells with alternative solid and quasi-solid hole-transport materials.

**2.3. Hydrophobic Dyes**

Dyes attached to  $\text{TiO}_2$  through carboxylic acid groups are susceptible to desorption from the surface under the action of trace quantities of water and has serious consequences on the long-term stability of the resultant solar cells. It has been reported that dyes with attached hydrophobic chains (e.g. **Z907**, Figure 5) can display an enhanced stability towards desorption from  $\text{TiO}_2$  induced by water in the liquid or gel electrolyte.<sup>[54,6]</sup> A cell based on **Z907** using a polymer gel  $\text{I}^-/\text{I}_3^-$  electrolyte was shown to combine a cell efficiency of 6.1% with excellent stability to both prolonged thermal stress and light soaking that matched the criteria required for the outdoor use of solar cells.<sup>[6]</sup> Besides the role played by the gel electrolyte, the stability was attributed to the hydrophobic properties of the dye which enhanced stability towards water-induced desorption. This effect was illustrated with an analogous cell, which used **N719** in place of **Z907** as the dye, that displayed much poorer stability to thermal stress.

A significant loss mechanism involves recombination of electrons from the  $\text{TiO}_2$  conduction band directly with the HTM, known as the dark current ( $k_5$ ). In addition to the above considerations, it has also been suggested that dyes



**Figure 5.** The amphiphilic dye **Z907**.

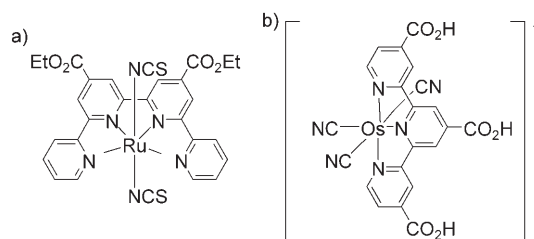
with attached hydrophobic groups can inhibit  $k_5$  by forming a hydrophobic network that impedes the interaction between  $I_3^-$  and the  $TiO_2$  surface and minimizes this loss. Evidence indicates that **N719** itself acts to suppress the dark current by forming a blocking layer on the  $TiO_2$  surface,<sup>[55,25]</sup> and it may be that further addition of steric bulk to the dye might enhance this role.

Another benefit of amphiphilic dyes arises in cells where an organic HTM has been employed to replace the liquid electrolyte. In such cells, there is generally a poor interaction between the dye and the organic HTM<sup>[56]</sup> that leads to weaker electronic communication and slower regeneration kinetics ( $k_2$ ) of the dye. Dyes with attached hydrophobic chains can enhance the wettability of the  $TiO_2$  by the hole-conducting polymer enhancing interaction with the dye. Interfacial contact between the dye and the HTM is also important in the context of solid polymer electrolytes,<sup>[7]</sup> particularly for high-molecular-weight polymers that do not penetrate well into the nanopores of the  $TiO_2$  semiconductor. It is also interesting to note in this context that the typically slower  $k_2$  displayed with an organic HTM may lead to a requirement for dyes that have better long-term stability in their oxidized form.<sup>[23]</sup>

#### 2.4. Extending the Spectral Coverage of Dyes

Currently, sensitizers such as **N3** and **N719** (Figure 2) show comparatively low IPCEs in the red and near-infrared (NIR) region of the electromagnetic spectrum. Control of the HOMO and LUMO levels of a dye is required to develop better red-absorbing dyes, as illustrated by the development of the “black dye” shown in Figure 2. Manipulation of the absorption spectrum of the dye also allows the possibility to develop solar cells that absorb in the NIR and are transparent to visible light, thus allowing their use as photovoltaic windows on buildings. To function as a DSSC, however, the LUMO must remain sufficiently higher than the edge of the conduction band of  $TiO_2$  for efficient charge injection while the HOMO must remain sufficiently below the redox level of the HTM for efficient regeneration of the dye. The lower energy of longer-wavelength photons makes the development of appropriate red-absorbing dyes that adhere to these requirements a challenge, as the HOMO–LUMO gap is narrower. One manner in which this has been approached involves the study of Ru–polypyridyl dyes related to **N3** that are constrained to show *trans* geometry of the NCS ligands (for example, as shown in Figure 6a).<sup>[57]</sup> Such *trans*-Ru–polypyridyl complexes typically show lower-energy absorption in comparison with the *cis* analogues. The use of geometrically restrained ligands is required to prevent photo-induced isomerization of the *trans* form to the *cis* isomer. This approach has led to dyes that show absorption bands across the entire visible and NIR regions of the spectrum, and initial studies have suggested that these dyes may perform better than **N3** once their performance has been optimized.

It has been noted that in osmium complexes, spin-forbidden singlet–triplet MLCT excitation can show significant intensity at low energy as a result of the mixing of some



**Figure 6.** a) Ru complex with *trans* NCS ligands.<sup>[57]</sup> b) Example of an Os complex dye with a good incident photon to current efficiency at long wavelengths.<sup>[23]</sup>

singlet character through the larger spin–orbit coupling in heavier elements (heavy-atom effect).<sup>[23]</sup> For example, for the osmium complex shown in Figure 6b this has led to better IPCE values at longer wavelengths than for a comparable Ru complex dye, although over the whole spectral region the Ru complex performed better.

Another approach to long-wavelength sensitization involves the use of phthalocyanine dyes, which are known to display an intense absorption in the Q band at low energy as well as a higher energy Soret band. However, studies on phthalocyanines are hampered by poor solubility and also by their tendency to aggregate on the  $TiO_2$  surface which leads to deactivation of the excited state of the dye. A recent example employed a titanium phthalocyanine dye with axial ligation to enable binding to  $TiO_2$ . Bulky terminal *tert*-butyl groups were also included to prevent aggregation of the dye and to improve solubility.<sup>[58]</sup> As expected for this class of molecule, an extremely intense Q band absorption ( $\epsilon = 135\,000\text{ cm}^{-1}\text{ M}^{-1}$ ) at  $\lambda_{\text{max}} = 702\text{ nm}$  was observed. Although in practice it was found that this particular dye was not able to efficiently inject electrons following excitation in the Q band, a key observation was the lack of aggregation of the dye when adsorbed onto  $TiO_2$  which opens up the possibility to design other phthalocyanine sensitizers that exploit the intense absorption at low energy.

Similar considerations arise in the case of porphyrin dyes, which also display an intense, low-energy Q band absorption and show kinetics for charge-injection and charge-recombination processes that are comparable to those of the best Ru–polypyridyl dyes. Again a serious limitation arises from the tendency of the dye to aggregate, although poor electronic communication between the dye core and the carboxylate linker may also play a role. Recent reports of porphyrin dyes with a conjugated carboxylate linker revealed negligible evidence of aggregation and, thus, efficiencies of up to 5.6%, the highest known value for any porphyrin dye.<sup>[38]</sup> Significantly, these dyes show comparatively high molar extinction coefficients, for example,  $\epsilon = 18\,500\text{ cm}^{-1}\text{ M}^{-1}$  at  $\lambda_{\text{max}} = 622\text{ nm}$ , suggesting that further optimization of this family may be a fruitful source of novel long-wavelength-absorbing dyes.

The use of several dyes as cosensitizers has been explored to extend the spectral region of the sensitizing layer. In the case of organic dyes, this approach may also overcome the typically narrow absorption bands observed for these dyes. A difficulty of this approach involves the typical decrease in the sensitizing efficiency of the individual dyes upon mixing with

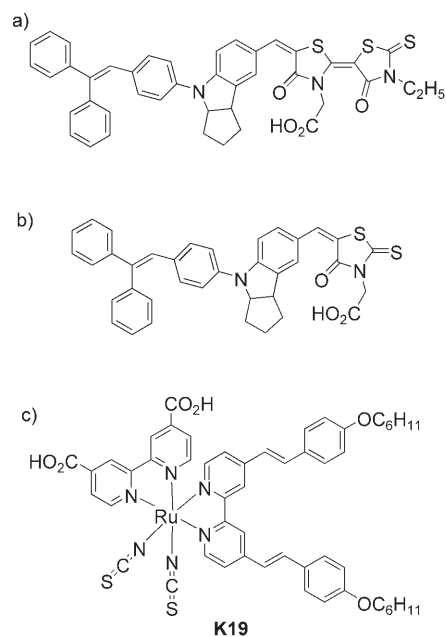
another cosensitizer, as might be expected from simple considerations of the quantity of dye on the TiO<sub>2</sub> surface. A recent report<sup>[59]</sup> demonstrated that cosensitization using three organic dyes with complementary absorption spectra can lead to an overall efficiency of 6.5%. In this case, all three dyes in the mixture actually displayed higher IPCE values in their own spectral region than they did when used alone. Although this appears counterintuitive, it was attributed to two possible effects: 1) more complete packing of the three dyes on the semiconductor surface which blocks the dark current ( $k_s$ ) and 2) an isolating effect that causes a decrease in the aggregation of each dye, thus minimizing loss through the associated deactivation of the excited state. This recent example thus demonstrates that a cosensitization approach can lead to enhanced spectral coverage and better enable the use of organic dyes, which typically display high extinction coefficients (see Section 2.5).

In an alternative approach to co-sensitization, both a Ru–polypyridyl dye and a Ru–phthalocyanine dye were used together, however, in this case a secondary layer of metal oxide was deposited onto the Ru–polypyridyl nanoparticles before attachment of the Ru–phthalocyanine layer.<sup>[60]</sup> This approach allowed near-monolayer coverage of both dyes, rather than a competition between the two for adsorption sites, and resulted in an electron-transfer cascade whereby the charge center of the dye cation was moved away from the TiO<sub>2</sub> surface by transfer between the two dye layers. The observation of efficient current generation through excitation of both dyes indicates that this is an important new approach in the development of panchromatic systems.

### 2.5. Enhancing Molar Extinction Coefficients

The use of dyes with a higher molar extinction coefficient clearly allows increased light harvesting of a given film thickness or, alternatively, thinner dye-sensitized films to be used which results in better efficiencies from decreased losses during charge transport through the nanocrystalline TiO<sub>2</sub>. High extinction coefficients have been achieved by using organic dyes<sup>[34,29]</sup> rather than transition-metal complexes, however, the former typically suffer other disadvantages such as narrow absorption bands that limit the light-harvesting ability (see Section 2.4).<sup>[59]</sup> Enhancement of the extinction coefficient is particularly important in the context of cells that use organic materials as the HTM. For these devices the thickness of the film is crucial, as the limited charge-carrier mobility in the organic HTM leads to significant charge-carrier recombination ( $k_s$ ) and a much lower efficiency. The use of a highly absorbing organic dye (Figure 7b) allowed a reduction in these losses through fabrication of a much thinner device, leading to the greatest efficiency recorded for an organic HTM cell of over 4%.<sup>[61]</sup>

Another recent approach involved the use of extended delocalized ligands for Ru complexes, for example, with the dye **K19** (Figure 7c).<sup>[62]</sup> This dye is related to the analogous amphiphilic dye **Z907** (Figure 5) but comprises additional stilbene units conjugated onto the hydrophobic ligand. Consequently, this dye retains the high stability to thermal



**Figure 7.** a, b) Organic dyes with high extinction coefficient that are used to a) give a high-efficiency DSSC<sup>[31]</sup> and b) make thin DSSCs with organic HTMs.<sup>[61]</sup> c) Ru dye **K19**, which was designed to give an increased extinction coefficient for the MLCT band.<sup>[62]</sup>

stress and light soaking displayed by **Z907** that was attributed to the hydrophobic spectator ligand. In addition, however, **K19** shows a higher extinction coefficient for the low-energy band at  $\lambda = 543$  nm of  $\epsilon = 18200$  cm<sup>-1</sup>M<sup>-1</sup> compared with  $\epsilon = 12200$  and 14000 cm<sup>-1</sup>M<sup>-1</sup> for **Z907** and **N719** (Figure 2), respectively. A comparison of these three dyes demonstrates that under the same conditions **K19** reveals the highest efficiency of 7.0%, and interestingly this was achieved using a low-vapor-pressure electrolyte. A related approach also involved the use of 4,4'-bis(carboxyvinyl)-2,2'-bipyridyl ligands as extended delocalized units that increase the extinction coefficient of the dye. In this case, the extended bipy ligand was used to link to TiO<sub>2</sub> rather than as the spectator ligand.<sup>[63,64]</sup> As well as an increase in extinction coefficient, a red shift of the maxima of the MLCT band was observed and relates to extending the spectral coverage of the dye, as discussed in Section 2.4.

### 3. Summary and Outlook

Recently, much effort has been directed towards the optimization of all aspects of DSSCs, including the inorganic nanocrystalline semiconductor and the hole-transport material. Often, initial studies in this area have involved using the well-established dyes that worked best for previous DSSC designs. The well-known Ru complex dyes **N3**, **N719**, and the “black dye” (Figure 2) exhibit high efficiencies in the standard dye-sensitized solar cell with an I<sup>-</sup>/I<sub>3</sub><sup>-</sup> solution electrolyte, and it is questionable whether in these devices their performance will be significantly bettered. Dye-sensitized solar cells formed with alternative hole-transport

materials, however, may offer different energy levels, different hydrophobicity/hydrophilicity properties, and different electron-transfer kinetics, and show a decrease in hole transport. A need has emerged to optimize the dye in conjunction with other design factors to best exploit and be fully compatible with other cell modifications that have taken place. For example: higher molar extinction coefficients may be crucial to allow thinner cells and the dominance of Ru-polypyridyl sensitizers may be challenged by organic, phthalocyanine, or porphyrin dyes in this type of device; the use of hydrophobic groups to enhance the stability of the device has become well established; near-IR dyes would allow photovoltaic windows to be developed; and cheaper dyes that do not contain expensive transition metals may also become more important in the context of commercialization. Dye-sensitized solar cells are beginning to be exploited as a commercial technology, and further developments in dye design will play a crucial part in the ongoing optimization of these devices.

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