

# Near-infrared Sensitization in Dye-sensitized Solar Cells

Jinhyung Park, Guido Viscardi, Claudia Barolo\*, and Nadia Barbero

**Abstract:** Dye-sensitized solar cells (DSCs) are a low cost and colorful promising alternative to standard silicon photovoltaic cells. Though many of the highest efficiencies have been associated with sensitizers absorbing only in the visible portion of the solar radiation, there is a growing interest for NIR sensitization. This paper reviews the efforts made so far to find sensitizers able to absorb efficiently in the far-red NIR region of solar light. Panchromatic sensitizers as well as dyes absorbing mainly in the 650–920 nm region have been considered.

**Keywords:** Dye-sensitized solar cell (DSC) · Near-IR absorbing dyes · Panchromatic sensitizers

## Introduction

The demand for reliable and economically viable alternatives to fossil fuels and the search for low cost renewable energy sources have boosted the research on new materials for unconventional photovoltaics.<sup>[1]</sup> Nowadays dye-sensitized solar cells (DSCs) represent a technically and economically credible alternative to conventional p-n junction photovoltaic devices.<sup>[2]</sup>

Typically a DSC architecture contains i) a transparent conductive oxide (TCO) on a glass or plastic substrate, ii) a mesoporous nanocrystalline layer of the semiconductor (TiO<sub>2</sub>), iii) a sensitizer monolayer adsorbed on the surface of the semiconductor, iv) an electrolyte with a redox couple (*i.e.* I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) and v) a metal counter-electrode where the redox mediator is regenerated.<sup>[3]</sup> While the total efficiency of the device depends on the optimization of each constituent, the molecular sensitizer has a strategic role in the ability of the cell to gather as many photons from sunlight as possible. In fact a DSC is the only photovoltaic device where the material used for light absorption (sensitizer) is not the same material that has to transport the charges to the electrodes (semiconductor and electrolyte). In brief when the sensitizer is excited by the absorption of a photon, an electron can be injected from the excited level of the molecule in the conduction band of the semiconductor; this electron flows through the semiconductor network up to the back

contact and then to the external circuit finally reaching the counter electrode, where it can reduce the redox mediator, responsible for the regeneration of the oxidized sensitizer (Fig. 1).

State-of-the-art DSCs are currently characterized by solar-to-electric power conversion efficiencies (PCEs), ranging around 350–750 nm, of 10–13%.<sup>[4]</sup> The main limit of these systems is the lack of absorption in the far-red/near-IR region, limiting further improvement in efficiency. In fact looking at the general formula (Eqn. (1)) to obtain the overall energy conversion efficiency of the dye-sensitized solar cell:<sup>[5]</sup>

$$\eta = \frac{(J_{sc} \times V_{oc} \times ff)}{I_0} \quad (1)$$

it can be clearly seen that by increasing the photocurrent density, the conversion

efficiency will be improved. Therefore, a good strategy to improve the performances of DSCs further<sup>[6]</sup> would be to develop effective new NIR sensitizers. In fact red/NIR radiation (600–1000 nm) accounts for about 25% of the solar energy arriving on the Earth's surface, while visible radiation (350–700 nm) accounts for about 45% of solar energy (Fig. 2).

Ideally all the photons below a threshold wavelength of about 920 nm should be harvested and converted into electric power.<sup>[7]</sup> Unfortunately classical sensitizers which have an optical band gap of nearly 1.6–1.7 eV absorb only up to 700 nm, while NIR sensitizers with a band-gap of nearly 1.3–1.4 eV can shift the absorption onset to longer wavelengths.

Moreover, there is a growing interest in the world of architecture for some peculiar characteristics of the DSC, *i.e.* transparency, variety of colors, used in diffuse

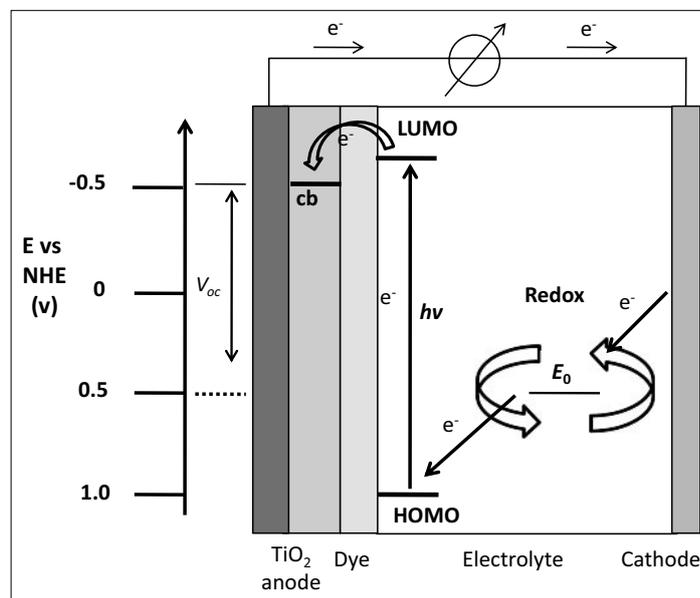


Fig. 1. Energy level diagram of a DSC.

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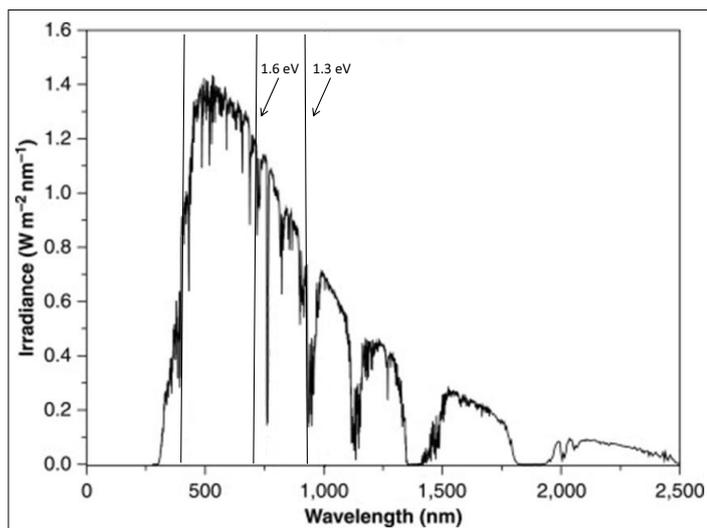


Fig. 2. Solar radiation spectrum on the Earth's surface and classical bandgaps for both classical and NIR sensitizers.

light conditions and as vertical elements. For example DSC glass façades will be the near future at École Polytechnique Fédérale of Lausanne.<sup>[8]</sup> This kind of building-integrated application would be aided by the discovery of efficient and stable far-red NIR sensitizers, not only because of their best photovoltaic performances, but also thanks to the restful colors of the resulting cells.

Over the last few years a number of important contributions have reviewed the synthetic efforts in the search for more efficient dyes and underlined the indispensable requirements<sup>[9]</sup> in the molecular design of photosensitizers for DSCs, such as to have i) at least one anchoring group for adsorption onto the TiO<sub>2</sub> surface, ii) an energy level of the lowest unoccupied molecular orbital (LUMO) higher (more negative) than the conduction band (CB) of the TiO<sub>2</sub> and an energy level of the highest occupied molecular orbital of the oxidized sensitizer lower (more positive) than the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox potential, iii) high molar ab-

sorption coefficients over the wide region of sunlight, iv) good photochemical stability, v) poor aggregation properties, vi) low cost and vii) no toxicity. Unfortunately in both cases of organometallic and metal-free dyes, NIR sensitization still remains a hot topic, which would be worth further investigation.

Several groups have used near-IR dyes as sensitizers in DSCs obtaining rather low conversion efficiencies. This is mainly due to the formation of aggregates and the difficulty to obtain dyes with appropriate energy levels of the excited states, that is with a LUMO sufficiently high in energy to allow for fast electron injection and a HOMO sufficiently low in energy to allow for fast regeneration. This is particularly difficult to achieve for near-IR dyes where the  $\Delta E_{\text{HOMO-LUMO}}$  has to be maintained as small as possible (see for example Fig. 3, where the HOMO and LUMO levels of different NIR sensitizers have been reported with respect to TiO<sub>2</sub> and the iodine/iodide redox couple).

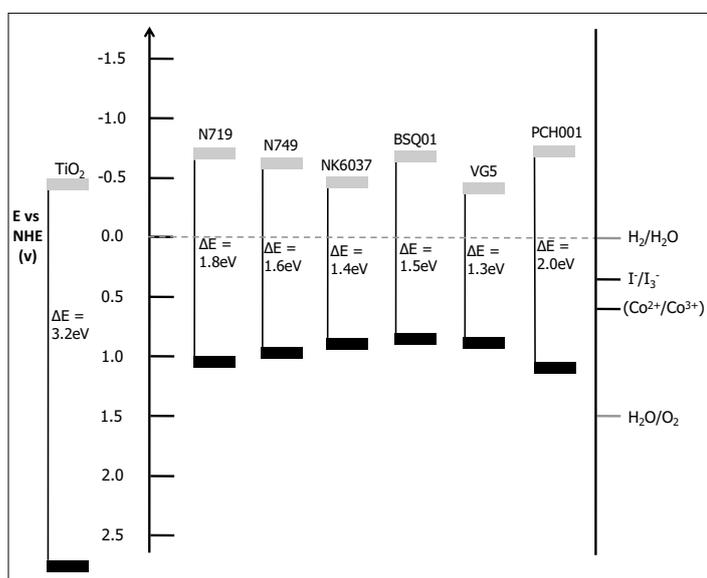


Fig. 3. HOMO (black) and LUMO (grey) band positions of several sensitizers.

Another disadvantage of near-IR dyes is their low stability under thermal stress and in the light-soaking test. Nowadays, molecular engineering of near-IR dyes with a high photovoltaic performance and an enhanced stability is necessary.<sup>[10]</sup>

The present paper aims at reviewing the main means used so far to achieve NIR sensitization in DSCs, looking at panchromatic sensitizers as well as at dyes absorbing mainly in the 650–920 nm region. Metal complex and metal-free sensitizers are discussed, highlighting advantages and drawbacks of the different classes.

## Metal Complex Sensitizers

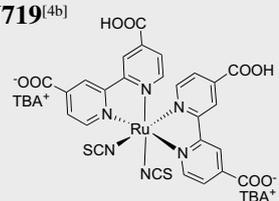
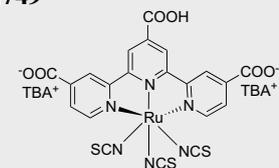
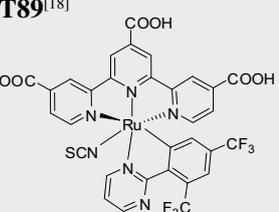
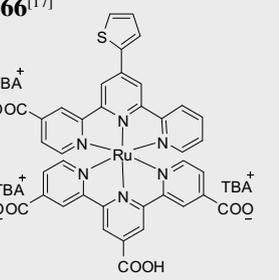
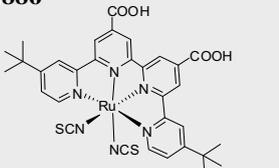
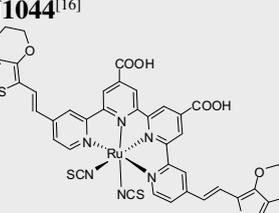
Metal complex dyes are widely used as sensitizers for DSCs and they still hold the record for the most efficient cell.<sup>[4a]</sup> They include ruthenium(II), copper(II) and osmium(II) complexes, but also metal porphyrins and phthalocyanines.

### Panchromatic Ru(II) Complexes

Ru(II) polypyridyl sensitizers<sup>[11]</sup> have been for a long time the most efficient dyes in dye sensitized solar cells.<sup>[4b–d]</sup> They have several merits such as a broad absorption band (metal-to-ligand charge transfer, MLCT), a suitable energy band-gap between ground and excited state, long lifetime in the excited state and good stability, but the main disadvantages are their lack of absorption in the far-red/near-IR region together with their low molar extinction coefficients (rarely above 20000 M<sup>-1</sup> cm<sup>-1</sup>). In recent years, the molecular engineering of bipyridyl ligands has generated several new series of Ru(II) polypyridyl sensitizers.<sup>[12]</sup> The principal approach has been the addition of  $\pi$ -conjugated systems that generally broaden and increase the absorption leading to very powerful cells.<sup>[13]</sup> However, in order to achieve an extended absorption in the far-red NIR region of the solar spectrum, the most successful approach was the introduction of terpyridyl (*i.e.* **N749**<sup>[14]</sup>) and quaterpyridyl ligands (*i.e.* **N886**<sup>[15]</sup> and **N1044**<sup>[16]</sup>). Only in those cases a real panchromatic sensitizer has been obtained, even if a real efficiency enhancement has not been reached for all panchromatic sensitizers. In Table 1 the molecular structures, absorption maxima and photovoltaic data of the cited Ru complexes are shown. **N719** is reported as reference dye for comparison.

**N749**, worldwide known as Black Dye, was specifically designed (the Ru center has three thiocyanato ligands and a terpyridine ligand with three carboxylic acids) in order to shift the absorption to the near-IR region. The red shift in the MLCT band is caused by the decrease in the  $\pi^*$  level of the terpyridine ligand and an increase

Table 1. Molecular structures, absorption maxima and photovoltaic data of a series of panchromatic Ru dyes (N719 is reported as reference dye). % IPCE at three different NIR wavelengths was evaluated from respective references.

Compound	$\lambda_{\max}$ [nm]	$\eta$ [%]	IPCE [% ca.]						
	$\epsilon$ [mol <sup>-1</sup> cm <sup>-1</sup> ]		$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	ff [%]	750 nm	800 nm	850 nm	
<b>N719</b> <sup>[4b]</sup> 	<b>535</b>	<b>11.18</b>	14 000	18.2	0.86	75	11	0	0
	$\epsilon$						$J_{sc}$	$V_{oc}$	ff
<b>N749</b> <sup>[14]</sup> 	<b>570</b>	<b>11.1</b>	7 500	20.9	0.74	72	60	44	21
	$\epsilon$						$J_{sc}$	$V_{oc}$	ff
<b>FT89</b> <sup>[18]</sup> 	<b>556</b>	<b>10.7</b>	11 200	20.8	0.72	71	65	57	22
	$\epsilon$						$J_{sc}$	$V_{oc}$	ff
<b>T66</b> <sup>[17]</sup> 	<b>530</b>	<b>3.05</b>	18 600	9.3	0.53	61	9	2	0
	$\epsilon$						$J_{sc}$	$V_{oc}$	ff
<b>N886</b> <sup>[15]</sup> 	<b>649</b>	<b>5.85</b>	8 400	12.0	0.71	76	35	30	10
	$\epsilon$						$J_{sc}$	$V_{oc}$	ff
<b>N1044</b> <sup>[16]</sup> 	<b>615</b>	<b>5.7</b>	7 500	19.2	0.45	67	47	33	9
	$\epsilon$						$J_{sc}$	$V_{oc}$	ff

in the energy of the  $t_{2g}$  metal orbital. An IPCE spectrum was obtained up to 920 nm. Critical drawbacks of **N749** are the inferior incident-photon-to-current conversion efficiency (IPCE) in the shorter wavelength region, and the presence of three monodentate NCS ligands.

Recently, other terpyridyl Ru(II) complexes have been introduced. Kisserwan *et al.* replaced the NCS ligands with another terpyridyl ligand<sup>[17]</sup> giving the **T66** complex. However, in this case the efficiency and the extension in the absorption region have not been achieved successfully.

Nevertheless Funaki *et al.*<sup>[18]</sup> replaced two thiocyanato ligands with a strong sigma-donating cyclometalating ligand, (**FT89**) obtaining the desired absorption in the NIR region by tuning the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels. This dye presents an unusual absorption band around 650 nm with a distinct shoulder around 750 nm. Its energy conversion efficiency is 10.7% which is even higher than for **N749** (10.1% on standard titania nanoparticles).

Except for terpy complexes, the majority of the polypyridyl ruthenium complexes reported have a *cis* configuration of the NCS ligands, which leads to absorption spectra that are mainly centered in the visible region at around 535 nm. By modifying the geometric isomerism of the reported complexes it is possible to obtain variant optical properties,<sup>[19]</sup> but it is necessary to properly tailor ligands that stabilize the *trans* configuration. Tetradentate quaterpyridines are suitable ligands for this purpose although they are still largely unexplored.<sup>[15]</sup> This is likely due to the long synthetic pathway to prepare these ligands, as well as the repeated purification steps required to obtain the pure corresponding metal complexes.<sup>[16]</sup> Although the highest power conversion efficiency for *trans*-Ru(II)-complexes was so far only 5.85% (AM 1.5) for **N886**, mainly due to the low level of the LUMO position with respect to TiO<sub>2</sub> conduction band (Fig. 3), the interest in this class of dye lies in the possible panchromatic response extending from the NIR to the UV region, with very high current density (for **N1044**) rendering them promising alternative sensitizers with enhanced solar harvesting capability over the conventional bipyridyl-based sensitizers.<sup>[20]</sup>

### Other NIR Absorbing Metal Complexes

Nickel bis(dithiolene) complexes, exhibiting intense absorption bands below 400 nm and broad absorption bands with high molar extinction coefficients in the NIR region (700–1100 nm), were also used as DSCs sensitizers, but their energy conversion efficiencies are in the range of 0.07–0.11%.<sup>[21]</sup>

Osmium complexes are some of the most promising metal complex dyes to absorb up to near-IR region due to the eminent MLCT absorption band. Bigozzi and co-workers reported<sup>[22]</sup> an interesting Os(II) complex, **OspyqCl** (Fig. 4), which exhibits a broad (even if not intense) IPCE spectrum up to 1100 nm.

### Metal Porphyrin and Phtalocyanine Dyes

Porphyrins are aromatic macrocycles bearing four modified pyrrole units inter-

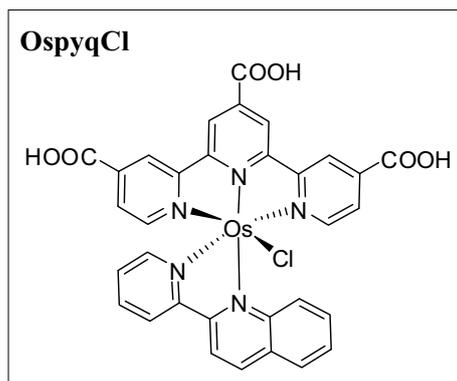


Fig. 4. Structure of the Os(II) complex, **OspyqCl**.

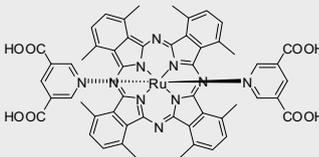
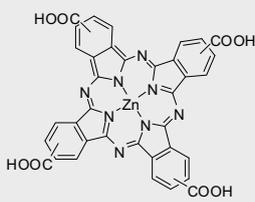
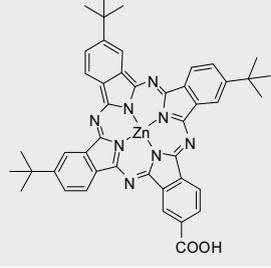
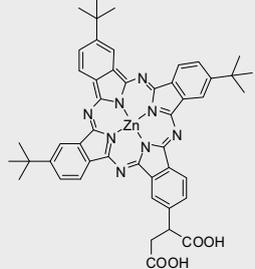
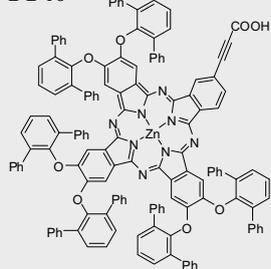
connected *via* methane bridges. They present an intense Soret band at nearly 450 nm and a series of poor absorbing red shifted Q-bands before 650 nm. Zinc porphyrins are among the most promising and efficient ruthenium(II) free sensitizers<sup>[4a]</sup> but, at the moment, they also lack absorption in the NIR region.

In contrast to the metal porphyrins, metal phthalocyanines exhibit absorption maxima near 700 nm (Q-bands), with high molar extinction coefficients. These kinds of dyes have poor solubility and need to be improved by structural optimization. Another critical problem is their aggregation tendency on the semiconductor surface and lack of directionality which has an important role in the energy conversion efficiency of the cell.<sup>[23]</sup> In the first approach to this class, Grätzel and co-workers<sup>[24]</sup> designed a Ru-phthalocyanine dye **JM3306** (Table 2). Later on they also developed a more efficient Zn-phthalocyanine dye,<sup>[23]</sup> with a high IPCE of 45% in NIR region and a 1% of energy conversion efficiency. On the other hand, Nazeeruddin and co-workers<sup>[25]</sup> developed the unsymmetrical Zn-phthalocyanines, **TT1** and **PCH001**. The **TT1** dye in particular shows a high IPCE of 75% and an energy conversion efficiency of 3.0% under AM 1.5. So far, the best phthalocyanine dye is **TT40**, which was introduced by Ragoussi *et al.*<sup>[26]</sup> **TT40**-based cell shows higher efficiency, 5.5%, especially due to the reduced molecular aggregates on the surface of the TiO<sub>2</sub>.

### Metal-free Dyes

Metal-free dyes have been intensively investigated to replace metal-based dyes. They include push-pull dyes, indolines, cumarines and polymethine dyes (squarylium, cyanine and croconate dyes). In general, especially with respect to ruthenium complexes, they show narrower, but more intense absorption bands. For this reason it is quite difficult to find a real panchromatic metal-free dye, while NIR absorbing dyes can be easily found in the class

Table 2. Molecular structures, absorption maxima and photovoltaic data of a series of phthalocyanine dyes. % IPCE at three different NIR wavelengths was evaluated from respective references.

Compound	$\lambda_{\max}$ [nm]	$\eta$ [%]			IPCE [% <i>ca.</i> ]		
		$\epsilon$ [mol <sup>-1</sup> cm <sup>-1</sup> ]	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	ff [%]	750 nm	800 nm
<b>JM 3306</b> <sup>[24]</sup> 	<b>650</b>		<b>&lt;1</b>		10	2	–
	49 000	–	–	–			
<b>Zn-Pht 1</b> <sup>[24]</sup> 	<b>686</b>		<b>1.0</b>		8	1	–
	33 000	5	0.4	49			
<b>TT1</b> <sup>[25a]</sup> 	<b>680</b>		<b>3.52</b>		5	–	–
	191 500	7.8	0.63	77			
<b>PCH 001</b> <sup>[25b]</sup> 	<b>692</b>		<b>3.05</b>		3	–	–
	191 000	6.5	0.64	74			
<b>TT40</b> <sup>[26]</sup> 	<b>698</b>		<b>5.50</b>		10	–	–
	89 000	12.3	0.64	70			

of polymethine dyes. Nevertheless, within these classes of sensitizers the design and development of effective NIR sensitizers is currently a hot topic in DSCs studies.

### Push-Pull Dyes

Push-pull dyes are also known as D- $\pi$ -A dyes, where the donor and the acceptor parts

are conjugated through a  $\pi$ -bridge. However, they have narrow light absorption properties with respect to Ru dyes and, usually, their absorption spectra only lie in the visible part of the solar spectrum. Moreover, efficiencies and stabilities comparable to Ru(II)-based dyes have been researched in recent years with non-corrosive redox me-

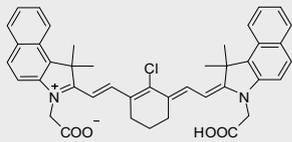
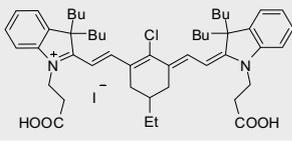
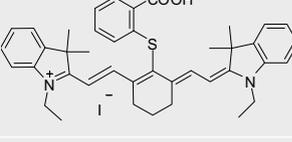
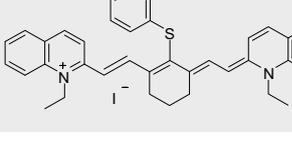
diation.<sup>[9c]</sup> However achieving a panchromatic response in this case is quite rare.<sup>[6]</sup> Very recently, Grätzel's group reported<sup>[27]</sup> a successful diketopyrrolopyrrole (DPP)-based sensitizer which can absorb also in the NIR region (Fig. 5). It provided extended IPCE values up to 800 nm and 4.93% of total energy conversion efficiency. This report could finally open the possibility of synthesizing near-IR sensitizers even with D- $\pi$ -A chromophores.

### Polymethine Dyes

Cyanines as well as squaraines are well known as far-red NIR absorbing dyes with very high molar extinction coefficients, intense and sharp absorption bands. Their uses as photosensitizer in DSCs have been widespread from the beginning<sup>[9a]</sup> especially due to their use as sensitizers in photography. However, the best efficiencies for this class have been reached with a panchromatic absorption that unfortunately does not exceed 750 nm.<sup>[28]</sup>

In order to have a NIR absorption spectrum, an heptamethine chain or a benzo-condensed heteroaromatic unit should be used.<sup>[29]</sup> In Table 3 molecular structures as well as optical and photovoltaic properties of selected dyes of this class are reported. So far, the best NIR cyanine dye is the symmetrical di-anchored **NK-6037**, having a maximum absorption band at around 850 nm.<sup>[30]</sup> An efficiency as high as 2.3% was obtained by adjusting the concentration of deoxycholic acid (DCA) in the dye solution, but that was with a considerably thick (22–26  $\mu\text{m}$ )  $\text{TiO}_2$  electrode with a light confinement effect, while under more standard conditions the efficiency is around 1%. Recently, Funabiki and coworkers<sup>[31]</sup> reported another symmetrical heptamethine cyanine dye, **KFH-3**, for use with porous ZnO prepared at low temperature. An IPCE spectrum almost solely in the near-IR region from 600 nm to 860 nm was obtained. On the other hand, NIR centrally substituted monoanchored cyanine dyes, e.g. **Cy9a** and **Cy9d**, were published by Matsui and coworkers.<sup>[32]</sup> These cyanines exhibit their maximum absorption at 804 and 873 nm, respectively. However, their energy gaps are not large enough to give good efficiencies.

Table 3. Molecular structures, absorption maxima and photovoltaic data of a series of cyanine dyes. % IPCE at three different NIR wavelengths was evaluated from respective references.

Compound	$\lambda_{\text{max}}$ [nm]	$\eta$ [%]			IPCE [% ca.]		
	$\epsilon$ [mol <sup>-1</sup> cm <sup>-1</sup> ]	$J_{\text{sc}}$ [mA cm <sup>-2</sup> ]	$V_{\text{oc}}$ [V]	ff [%]	750 nm	800 nm	850 nm
<b>NK-6037</b> <sup>[30]</sup> 	<b>850</b>		<b>2.3</b>		40	49	52
	146 000	8.9	0.45	58			
<b>KFH-3</b> <sup>[31]</sup> 	<b>787</b>		<b>1.23</b>		23	33	15
	263 000	3.34	0.49	76			
<b>Cy 9a</b> <sup>[32]</sup> 	<b>804</b>		<b>0.16</b>		3	4	–
	246 000	0.73	0.37	55			
<b>Cy 9d</b> <sup>[32]</sup> 	<b>873</b>		<b>0.02</b>		0.05	0.1	–
	169 000	0.08	0.37	60			

### Squaraine Dyes

Squaraine dyes show sharp and intense absorption bands in the visible/NIR regions that are often accompanied by a strong emission in the long-wavelength region. These dyes have been applied successfully as sensitizers for DSCs<sup>[33]</sup> due to their advantageous optical properties and considerable photostability. Nevertheless the simple introduction of a squaric unit in the polymethine chain does not guarantee absorption maxima over 700 nm and the most efficient dyes in this class to date show good IPCE spectra only up to 730 nm.<sup>[34]</sup> In order to reach true NIR sensitization several unsymmetrical squaraine dimers have been synthesized (**BSQ01**,<sup>[35]</sup> **LSQa-c**<sup>[36]</sup>, Table 4), having  $\lambda_{\text{max}}$  in the range between 730 and 800 nm and conversion efficien-

cies up to 2.26%. Wu and coworkers<sup>[37]</sup> introduced an electron-rich 3,4-ethylene-dioxythiophene moiety in the donor part of their unsymmetrical squaraine, **JYL-SQ5**, obtaining a broadening of the absorption band. This dye exhibits IPCE values up to 900 nm and 2.61% of energy conversion efficiency. Recently, a very high IPCE at 750 nm has been reported<sup>[10]</sup> (**JK-217**) by incorporating the nonplanar dimethylfluoreneaniline and unsymmetrical squaraine unit into the organic framework, which not only suppresses aggregation, but also stabilizes device performance under long-term stability. This sensitizer exhibits 45% of IPCE and 6.29% of energy conversion efficiency. Recently, we also synthesized a NIR squaraine dye through the condensation of the classical indole-based emisquaraine with an electron-rich heterocyclic component such as the benzo[cd]indole moiety (**VG5**).<sup>[38]</sup> This sensitizer shows an absorption maximum at 780 nm and 36% of IPCE at 800 nm.

The common belief that unsymmetrical structures perform better in DSCs than their symmetrical counterparts led to the preparation of the reported structures. Very recently, we demonstrated by experimental and computational evidence, that both unsymmetrical and symmetri-

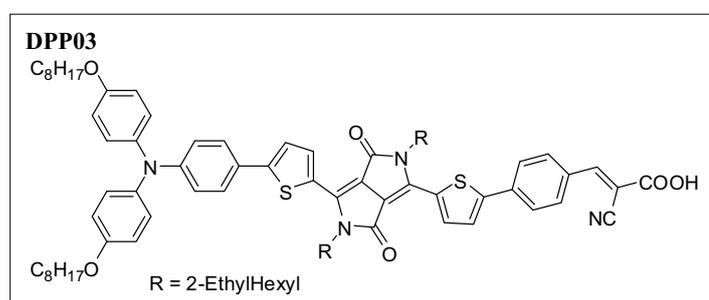
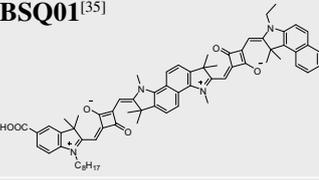
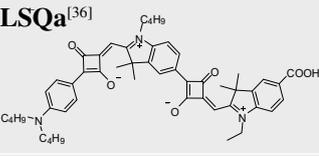
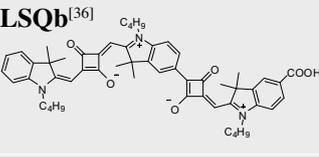
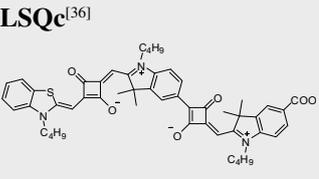
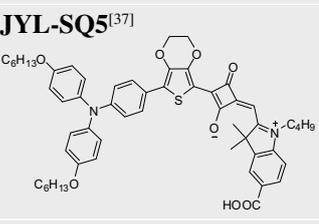
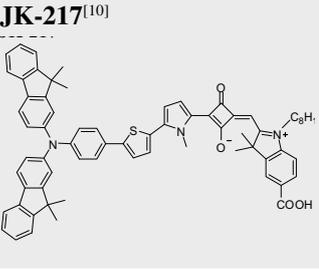
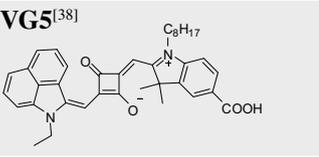
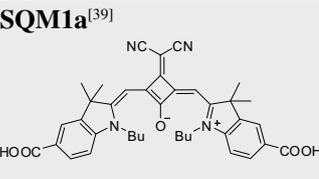
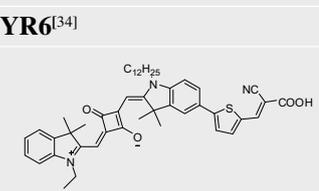


Fig. 5. Structure of the DPP-based dye, **DPP03**.

Table 4. Molecular structures, absorption maxima and photovoltaic data of a series of squaraine dyes. % IPCE at three different NIR wavelengths was evaluated from respective references.

Compound	$\lambda_{\max}$ [nm]	$\eta$ [%]	IPCE [% ca.]				
	$\epsilon$ [mol <sup>-1</sup> cm <sup>-1</sup> ]		$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	ff [%]	750 nm	800 nm
<b>BSQ01</b> <sup>[35]</sup> 	<b>730</b> 389 000	<b>1.3</b> 3.11	<b>0.55</b> 0.55	<b>76</b> 76	17	2	–
<b>LSQa</b> <sup>[36]</sup> 	<b>777</b> 174 000	<b>2.26</b> 9.05	<b>0.46</b> 0.46	<b>54</b> 54	22	17	6
<b>LSQb</b> <sup>[36]</sup> 	<b>779</b> 180 000	<b>2.01</b> 8.64	<b>0.41</b> 0.41	<b>57</b> 57	29	24	8
<b>LSQc</b> <sup>[36]</sup> 	<b>800</b> 189 000	<b>1.82</b> 9.01	<b>0.40</b> 0.40	<b>51</b> 51	19	18	11
<b>JYL-SQ5</b> <sup>[37]</sup> 	<b>691</b> 109 000	<b>2.61</b> 11.12	<b>0.42</b> 0.42	<b>56</b> 56	39	29	15
<b>JK-217</b> <sup>[10]</sup> 	<b>672</b> 77 900	<b>6.29</b> 13.93	<b>0.61</b> 0.61	<b>74</b> 74	45	9	–
<b>VG5</b> <sup>[38]</sup> 	<b>780</b> 77 500	<b>1.1</b> 7.29	<b>0.35</b> 0.35	<b>43</b> 43	32	36	16
<b>SQM1a</b> <sup>[39]</sup> 	<b>705</b> 158 000	<b>3.6</b> 14.2	<b>0.50</b> 0.50	<b>51</b> 51	23	2	–
<b>YR6</b> <sup>[34]</sup> 	<b>659</b> 279 000	<b>6.74</b> 14.8	<b>0.64</b> 0.64	<b>71</b> 71	16	–	–

cal squaraines can be successfully used in DSCs with comparable efficiencies, but with undoubted advantages in the ease of synthesis of symmetrical structures.<sup>[33c]</sup> Moreover, compared to the related unsymmetrical structures, symmetrical dyes showed a red-shift and an increased stability due to their bianchoring mode on the semiconductor surface. This work opened the way to other optimized NIR symmetrical squaraine structures such as **SQM1a**, published by Maeda *et al.*,<sup>[39]</sup> which possesses a dicyanovinylene group attached to the cyclobutene core. This dye shows an overall cell efficiency of 3.6% and about 40% IPCE at 720 nm.

### Croconate Dyes

Croconate dyes (or croconines) are another class of dye that exhibits absorption in the NIR region with a strong solvatochromic effect. The advantages over squaraine dyes are their stronger absorption, greater photostability and better yield.<sup>[40]</sup> However, this class of dye is still under investigation for DSCs. Kamat and co-workers published<sup>[41]</sup> an example of croconate dyes, **CR-1**, which absorbs the light at 865 nm with a maximum IPCE around 1.2% at 650 nm (Fig. 6). This croconine does not show improved behavior with respect to other classes of dyes due to the net charge separation which is poor. Besides, the overall photocurrent conversion efficiency remains rather low. Aggregation is a typical drawback of croconate which has to be solved before implementation in DSCs.

### Conclusions and Perspectives

In this paper an overview of the different approaches used so far to achieve far-red/NIR sensitization by using a molecular sensitizer in a single junction solar cell has been provided. Although a variety of dye classes has been investigated, light harvest, especially in the near IR region, still remains a great challenge, because of non-optimized photocurrent arising from the poor optical response of the dyes in the NIR region (see IPCE percentage at 800 and 850 nm reported in the Tables). Therefore it is necessary to tailor and develop NIR efficient sensitizers, for example to combine them with other dyes to obtain panchromatic systems.<sup>[42]</sup>

Among panchromatic dyes terpyridyl ruthenium complexes are still the best performing class. Even if they do not reach an effective enhancement in efficiency with respect to optimized dipyrindyl-based Ru(II) complexes, they achieved extended absorption in the far-red NIR region of the solar spectrum and they can be used successfully in co-sensitized cells. NIR sensitization can also be achieved with metal-

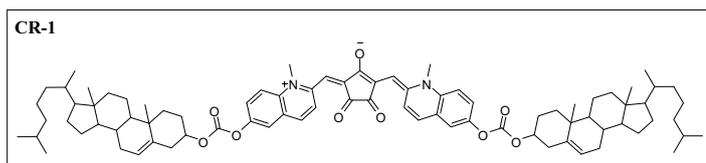


Fig. 6. Structure of the croconate dye, CR-1.

free dyes, phthalocyanine and squaraine dyes in particular, which showed the best cell efficiencies. Moreover, they showed good current values and photochemical properties.

Stability is still a critical issue in this field, in fact long-term stability tests have only been reported for JK-217.<sup>[10]</sup> This topic is important for the industrialization of this kind of cell. We believe that vigorous research on this field will yield promising results in the near future.

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