Metal-Free Sensitizers

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Metal-Free Organic Dyes for Dye-Sensitized Solar Cells: From Structure: Property Relationships to Design Rules

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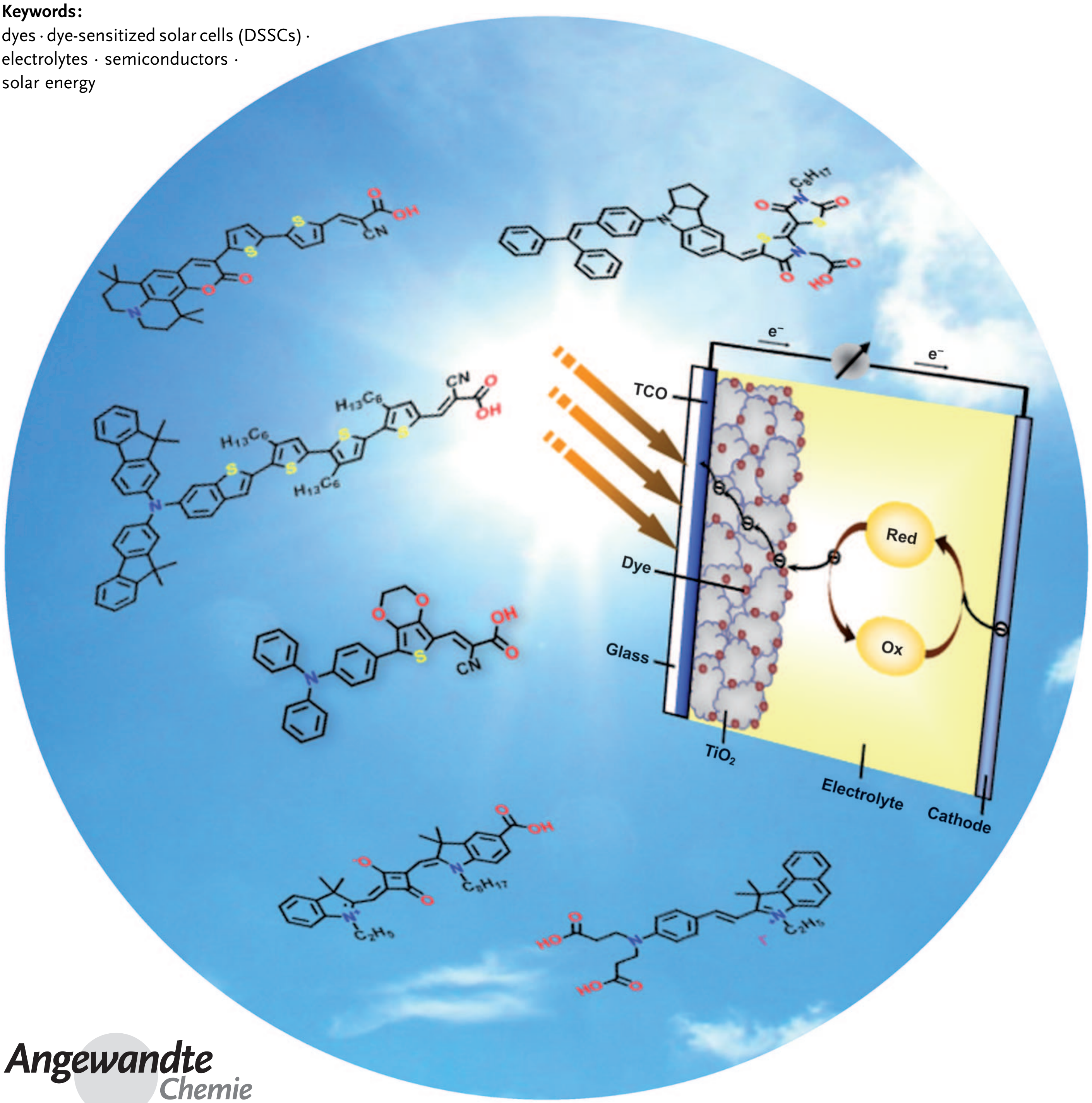
Keywords:
dyes · dye-sensitized solar cells (DSSCs) · electrolytes · semiconductors · solar energy



Angewandte Chemie

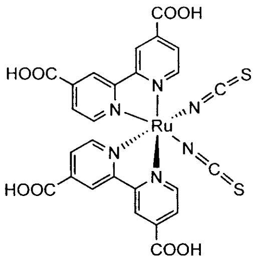
Dye-sensitized solar cells (DSSC) have attracted considerable attention in recent years as they offer the possibility of low-cost conversion of photovoltaic energy. This Review focuses on recent advances in molecular design and technological aspects of metal-free organic dyes for applications in dye-sensitized solar cells. Special attention has been paid to the design principles of these dyes and on the effect of various electrolyte systems. Cosensitization, an emerging technique to extend the absorption range, is also discussed as a way to improve the performance of the device. In addition, we report on inverted dyes for photocathodes, which constitutes a relatively new approach for the production of tandem cells. Special consideration has been paid to the correlation between the molecular structure and physical properties to their performance in DSSCs.

From the Contents

1. Introduction

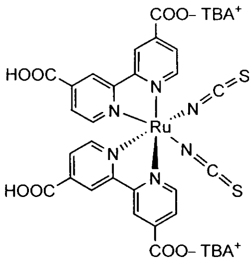
The generation of energy is one of the most important scientific and technological challenges in the 21st century. The commercially available solar cells are currently based on inorganic silicon semiconductors. The demand for silicon will skyrocket within the next decade and the price of silicon will rise dramatically. Organic solar cells, therefore, appear to be a highly promising and cost-effective alternative for the photovoltaic energy sector. In this context, dye-sensitized solar cells (DSSC) have attracted considerable attention in recent years.[1] At present, state-of-the-art DSSCs based on ruthenium(II)–polypyridyl complexes as the active material have an overall power conversion efficiency (η) approaching 11 % under standard (Global Air Mass 1.5) illumination.[2–7]

In the last 15–20 years a lot of effort has been devoted to the synthesis and investigation of materials for DSSCs: Fundamental understanding of the working principles has been gained by means of modeling electrical and optical properties as well as by advanced characterization techniques.[8–15] Efforts in the synthesis of sensitizers for DSSCs can be grouped into two broad areas: 1) Functional ruthenium(II)–polypyridyl complexes such as N3,[16,17] N719 (TBA$^+$ = tetra-*n*-butylammonium),[4,16,18] Z907,[19–21] and black dye;[3,5,22] and 2) metal-free organic donor–acceptor (D–A) dyes. The former class of compounds contains expensive ruthenium metal and requires careful synthesis and tricky purification steps. On the other hand, the second class can be prepared rather inexpensively by following established design strategies. The major advantages of these metal-free dyes are their tunable absorption and electrochemical properties through suitable molecular design.[23]



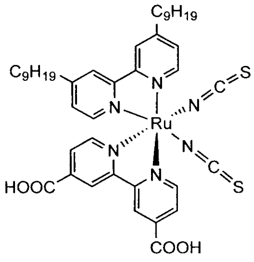
N3

η = 11.03 %



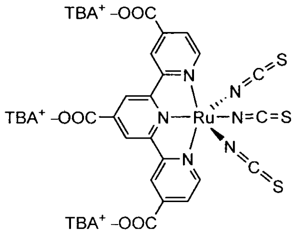
N719

η = 11.18 %



Z907

η = 9.5 %



Black dye

η = 11.1 %

The high efficiencies of the ruthenium(II)–polypyridyl DSSCs can be attributed to their wide absorption range from the visible to the near-infrared (NIR) regime. In addition, the carboxylate groups attached to the bipyridyl moiety lower the energy of the ligand π* orbital. Since the electronic transition is a metal-to-ligand charge transfer (MLCT), excitation energy is effectively channeled to the carboxylate group, from which electron injection into the conduction band of the semiconductor takes place.[24] However, the molar extinction coefficients of these dyes are moderate ($\varepsilon \leq 20000\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ for the longest wavelength MLCT transition). Despite the low absorptivity, the thickness of the

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nanostructured titanium dioxide (TiO_2) layer on top of transparent conductive glass coated with a fluorine-doped tin oxide (FTO) layer can be adjusted to absorb nearly all the incident light. However, high extinction coefficients for all organic donor–acceptor dyes can be achieved from the structure–property relationships well-known in dye chemistry.[25] In contast to ruthenium(II) complexes, different light-absorbing groups can be incorporated into the organic framework to tune the absorption over a broad spectral range and to achieve high extinction coefficents. Remarkable progress has recently been made in the field of highly absorbing metal-free organic dyes, and the highest solar-to-electric power conversion efficiency has exceeded 9%.[26–28] It is feasible to use thin TiO_2 films (4–10 μm) to generate optimal photocurrent and monochromatic incident photon-to-current conversion efficiencies (IPCE) because of their excellent optical properties in the visible region. This is particularly important for electrolyte-free solid-state (ss) DSSCs, where film thicknesses of 2–3 μm are optimal for efficient charge collection.

Conventional DSSCs typically contain five components: 1) a photoanode, 2) a mesoporous semiconductor metal oxide film, 3) a sensitizer (dye), 4) an electrolyte/hole transporter, and 5) a counterelectrode. In DSSCs, the incoming light is absorbed by the sensitizer, which is anchored to the surface of semiconducting TiO_2 nanocrystals. Charge separation takes place at the interface through photoinduced electron injection from the excited dye into the conduction band of the TiO_2. Holes are created at the dye ground state, which is further regenerated through reduction by the hole-transport material (HTM), which itself is regenerated at the counterelectrode by electrons through an external circuit. In principle, for efficient DSSCs the regeneration of the sensitizer by a hole transporter should be much faster than the recombination of the conduction band electrons with the oxidized sensitizer. Additionally, the highest occupied molecular orbital (HOMO) of the dye should lie below the energy level of the hole transporter, so that the oxidized dyes formed after electron injection into the conduction band of TiO_2 can be effectively regenerated by accepting electrons from the HTM. The general operating principle of a dye-sensitized solar cell is depicted in Figure 1.

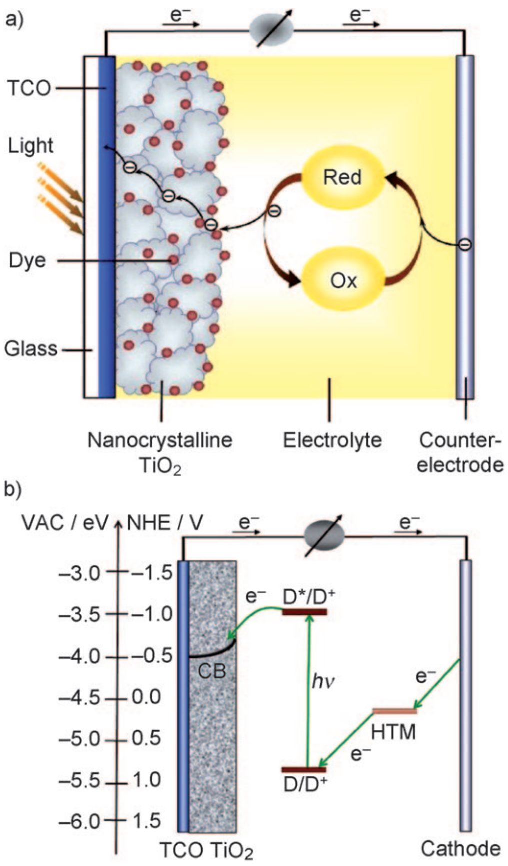


Figure 1. a) Fundamental processes in a dye-sensitized solar cell. b) Energy-level diagram of a DSSC. TCO = transparent conducting oxide.

The research area dealing with DSSCs is expanding very rapidly and attracting scientist from different disciplines: 1) Chemists to design and synthesize suitable donor–acceptor dyes and study structure–property relationships; 2) physicists to build solar cell devices with the novel materials, to characterize and optimize their performances, and to understand the fundamental photophysical processes; and 3) engineers to develop new device architectures. The synergy between all the disciplines will play a major role for future advancements in this area.

Recently, the most prominent class of sensitizers for DSSCs, namely ruthenium(II)–polypyridyl complexes were reviewed by Robertson in *Angewandte Chemie*.[10] This

Amaresh Mishra studied chemistry at the Sambalpur University, India, and obtained his PhD in 2000. In 1999 he joined the group of Prof. G. R. Newkome as a postdoctoral fellow at the University of South Florida and later at the University of Akron. After working at TIFR, Mumbai, as a Visiting Fellow (2002–2004), he joined the group of Prof. P. Bäuerle, University of Ulm, in 2005 as an Alexander von Humboldt Fellow. His research interests include functional oligothiophenes, donor–acceptor dyes, and metal complexes for applications in organic solar cells, molecular electronics, and photonics.

Markus Fischer received his diploma in chemistry in 2005 from the Ludwig-Maximilians University Munich, in the group of Prof. P. Knochel, where he worked on halogen–magnesium exchange reactions. He then joined the group of Prof. P. Bäuerle in 2006 at the University of Ulm for his PhD research. His present research interests are centered on the functionalization of dendritic oligothiophenes and their application in organic photovoltaic devices.

current Review now gives the current state-of-the-art in the field of metal-free organic dyes for DSSCs and describes structure–property relationships. We also discuss new concepts of DSSCs, including different electrolyte systems (liquid, ionic liquid, and solid state), and analyze their perspectives for future developments in research and technology. Cosensitization, to develop new panchromatic sensitizers, is also described. In the last section, recent developments in inverted DSSCs and their prospects for tandem cells are presented.

2. Metal-free Organic Dyes in Dye-sensitized Solar Cells

The molecular structure of the dye plays an important role in DSSCs. After absorption of light, charge separation is generally initiated at the interface between the dye bound to the TiO_2 surface and the hole-transporting material. The performance of DSSCs generally depends on the relative energy levels of the sensitizers and the kinetics of the electron-transfer processes at the interface between the dye bound to the semiconductor surface and the hole-transporting material. Some general principles to construct an efficient dye and efficient DSSCs are as follows: 1) The absorption range of the dye should cover the whole visible and some of the near-infrared region, and its molar extinction coefficient must be as high as possible to enable efficient light harvesting with thinner TiO_2 layers (panchromatic absorption). 2) For efficient electron injection into the anode, the lowest unoccupied molecular orbital (LUMO) of the dye should be localized near the anchoring group (usually a carboxylic or phosphonic acid) and above the conduction band edge of the semiconductor electrode (typically TiO_2). 3) The HOMO of the dye should lie below the energy level of the redox mediator to allow efficient regeneration of the oxidized dye. 4) To minimize charge recombination between the injected electrons and the resulting oxidized dye, the positive charge resulting after electron injection should be localized on the donor part, which is further away from the TiO_2 surface.[29–33] 5) The periphery of the dye should be hydrophobic to minimize direct contact between the electrolyte and the anode to prevent water-induced desorption of the dye from from the TiO_2 surface and consequently enhance the long-term stability. 6) The dye should not aggregate on the surface to avoid nonradiative decay of the excited state to the ground state, which often occurs with thicker films.[34]

Peter Bäuerle received his PhD in organic chemistry from the University of Stuttgart in 1985 with Prof. F. Effenberger. After a post-doctoral year at MIT, Boston (USA), with Prof. M. S. Wrighton, he completed his habilitation (1994) at the University of Stuttgart. After becoming Professor of Organic Chemistry at the University of Würzburg, he became Director of the Institute for Organic Chemistry II and Advanced Materials at the University of Ulm in 1996, and since October 2008 he has served as Dean of the Faculty for Natural Sciences there. He is cofounder of Heliatek GmbH, Dresden/Ulm, which produces organic solar cells.

Besides the design of the sensitizer, another possibility to enhance the performance of DSSCs consists of the use of additives.[3,35,36] For example, cell performances have been improved by the addition of deoxycholic acid (DCA) as a coadsorbent and 4-*tert*-butylpyridine (TBP) as an additive to the electrolyte.[37] DCA was used to prevent aggregation of the dye on the TiO_2 surface, thereby resulting in a high electron-injection yield from the dye into the TiO_2. The photocurrent and photovoltage of the solar cell were also improved even though the amount of adsorbed dye on the TiO_2 surface decreased. The maximum open-circuit voltage (V_{OC}) that can be generated under illumination with a sun simulator (AM 1.5 G, $100\,mW\,cm^{-2}$) corresponds to the difference between the Fermi level of the TiO_2 and the redox potential of the redox couple. The addition of TBP to the electrolyte markedly raised the conduction band edge of the TiO_2 and led to a higher open-circuit voltage (V_{OC}) and fill factor (FF) of the DSSCs, and consequently increased the total efficiency.[38] The improved V_{OC} is probably caused by suppression of the dark current, that is, recombination between the injected electrons and triiodide (I_3^-) ions in the electrolyte. Nevertheless, charge-recombination processes between injected electrons and dye cations and with I_3^- ions in the electrolyte render the actual V_{OC} lower than the theoretical value.[24]

2.1. Neutral Organic Dyes as Sensitizers in DSSCs with Liquid Electrolytes

Significant progress in the use of organic dyes in DSSCs was first made by Hara et al.[39,40] and Yanagida and co-workers[41] using oligoenes **1**–**3** containing dialkylamino-phenyl groups as the donors and cyanoacrylic acid as the acceptor. The use of these dyes as sensitizers in liquid electrolyte systems yielded overall power conversion efficiencies of up to 6.8% (Table 1). During the last few decades, π-conjugated oligothiophenes have played a major role in the development of organic electronic materials because of their well-known high polarizability as well as their tunable spectroscopic and electrochemical properties. They have also been used as core building blocks in the synthesis of a wide variety of novel π systems that are suitable for DSSCs. The use of coumarins[42–47] (**4**–**6**) as donor groups and cyanoacrylic acid as the acceptor linked to an oligoene or oligothiophene core led to efficiencies of up to 8.2%—values comparable to the standard N719 sensitizer. The introduction of a C–C double bond (-CH=CH-) between the cyanoacrylic acid and the coumarin framework increased the π conjugation of dye **4** and resulted in a wide absorption in the visible region. DSSCs based on dye **4** produced a short-circuit current density (J_{SC}) of $14.0\,mA\,cm^{-2}$, with a maximum photon-to-electron conversion efficiency (η) of 6.0%.

Replacement of the C–C double bond by a thienylene-vinylene (in **5**) or by a bithiophene (in **6**) bridge did not change the absorption spectra in solution. In contrast, a

Table 1: Metal-free neutral organic dyes tested in DSSCs with liquid electrolytes.

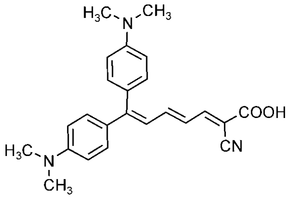
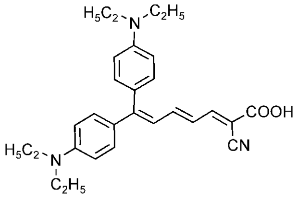
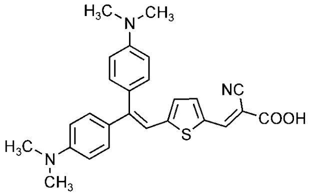
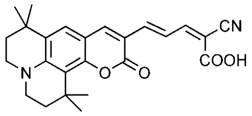
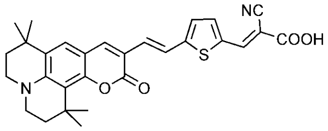
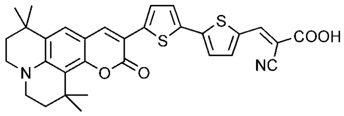
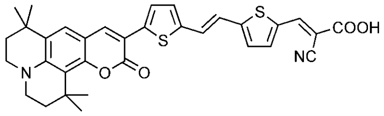
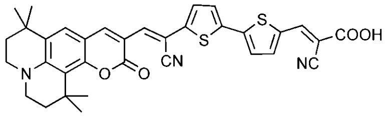
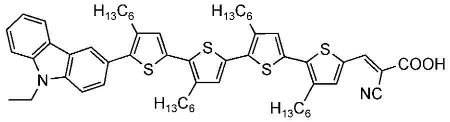
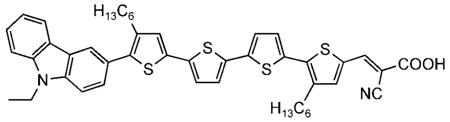
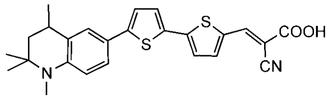
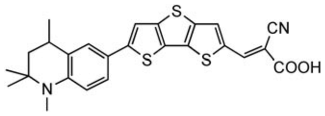
No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
1		12.9	0.71	0.74	6.8	[39, 41]
2		16.4	0.61	0.66	6.6	[39, 41]
3		12.5	0.68	0.69	5.9	[40]
4		14.0	0.60	0.71	6.0	[42–45]
5		14.7	0.67	0.73	7.2	[44]
6		14.3	0.73	0.74	7.7	[37, 44, 46, 47]
7		15.9	0.69	0.75	8.2	[48]
8		18.8	0.53	0.65	6.5	[49]
9		14.0	0.74	0.74	7.7	[50, 51]
10		10.2	0.67	0.64	4.4	[51]
11		12.0	0.60	0.63	4.5	[52, 53]
12		8.8	0.52	0.63	2.9	[52, 53]

Table 1: (Continued)

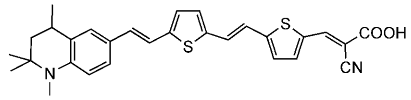
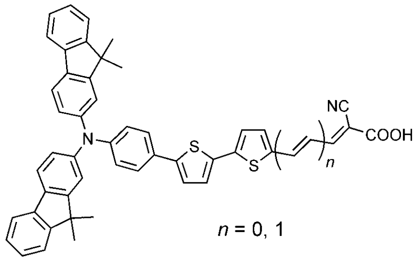
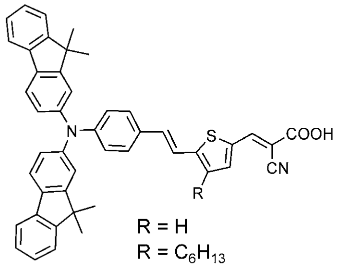
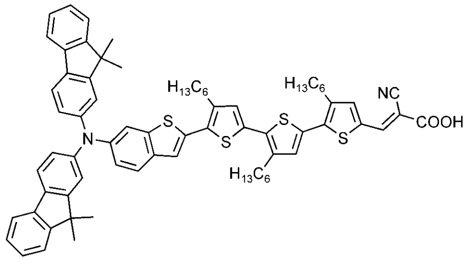
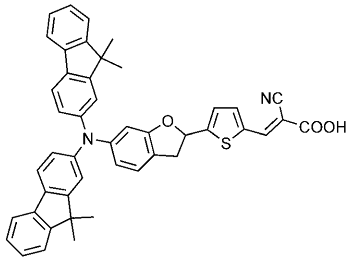
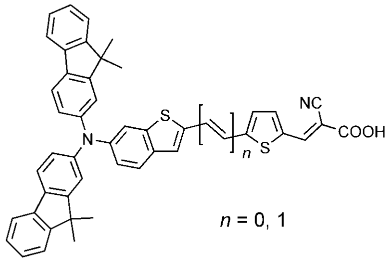
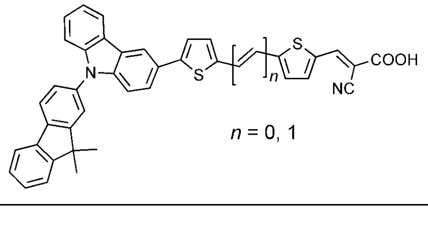
No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
13		7.2	0.54	0.59	2.3	[52, 53]
14		14.0 10.5	0.75 0.64	0.77 0.70	8.0 4.8	[54, 55]
15		15.2 10.6	0.67 0.66	0.75 0.77	7.7 5.4	[56]
16		17.5	0.66	0.74	8.6	[57]
17		14.4	0.70	0.66	6.7	[58]
18		15.3 12.7	0.74 0.67	0.66 0.65	7.4 5.5	[59, 60]
19		11.5 9.1	0.68 0.61	0.66 0.68	5.2 3.8	[61]

Table 1: (Continued)

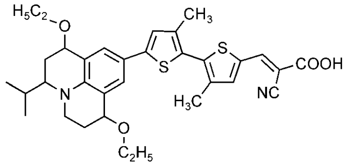
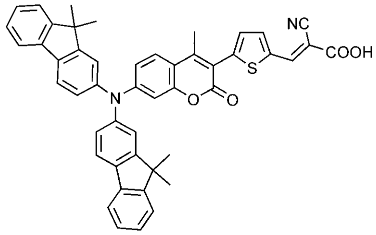
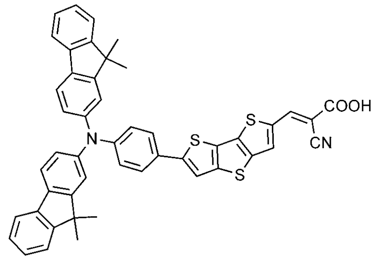
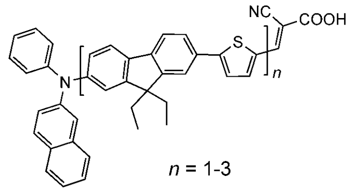
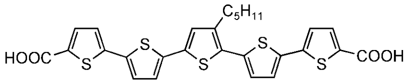
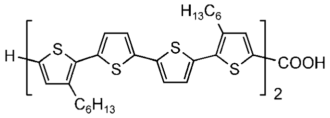
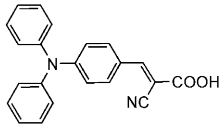
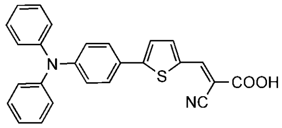
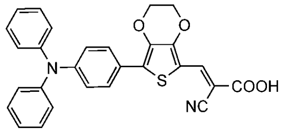
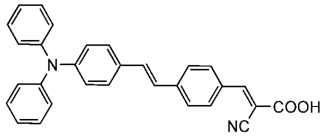
No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
20		6.6	0.61	0.73	3.0	[61]
21		10.1	0.65	0.68	4.5	[62]
22		14.3	0.73	0.76	8.0	[63]
23		12.5	0.65	0.65	5.2	[64]
24		10.6	0.57	0.56	3.4	[65]
25		3.7	0.60	0.58	1.3	[66]
26		6.1	0.60	0.68	2.5	[67, 69]
27		12.8	0.62	0.66	5.2	[68, 69]
28		15.5	0.69	0.68	7.3	[68]
29		18.1	0.74	0.68	9.1	[27]

Table 1: (Continued)

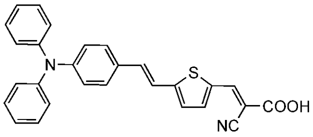
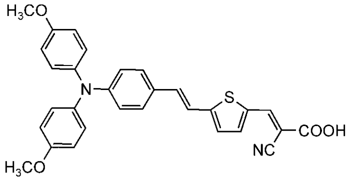
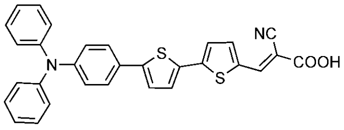
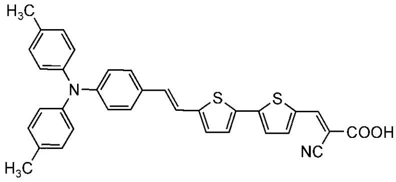
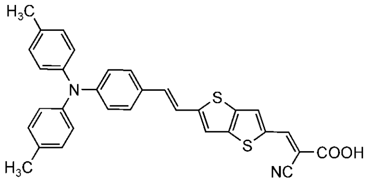
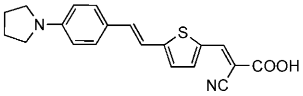
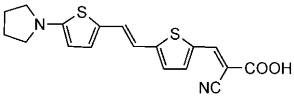
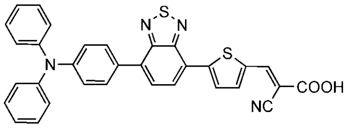
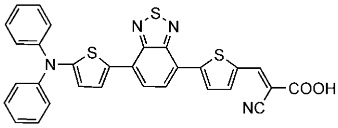
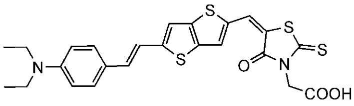
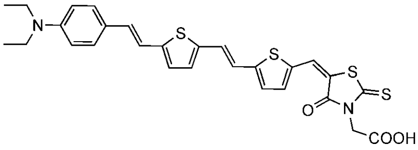
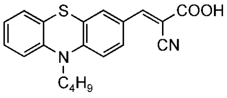
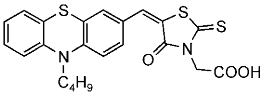
No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
30		12.0	0.69	0.72	5.9	[69–71]
31		14.0	0.69	0.71	6.9	[71]
32		16.0	0.63	0.61	6.2	[72]
33		15.3	0.63	0.73	7.0	[73]
34		15.4	0.61	0.70	6.6	[73]
35		7.6	0.58	0.59	2.3	[74]
36		0.4	0.26	0.45	<0.05	[74]
37		10.4	0.55	0.66	3.8	[76]
38		3.2	0.52	0.69	1.2	[76]
39		15.2	0.56	0.73	6.2	[77]
40		10.6	0.52	0.70	3.9	[77]
41		10.9	0.71	0.71	5.5	[78]
42		4.8	0.53	0.74	1.9	[78]

Table 1: (Continued)

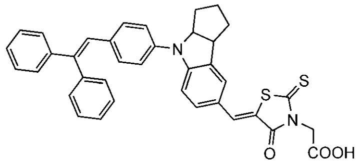
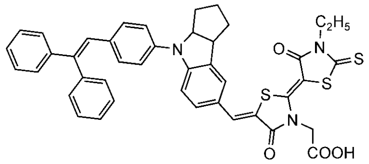
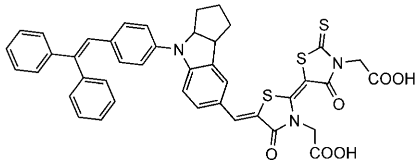
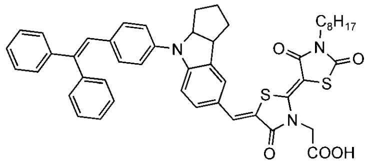
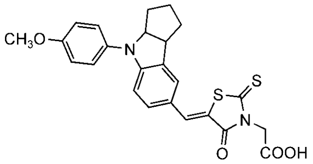
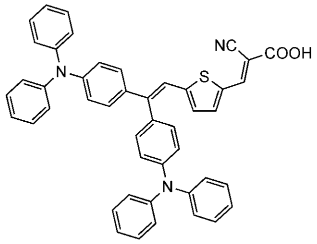
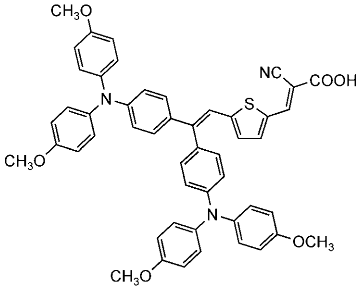
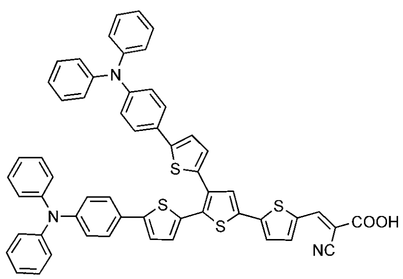
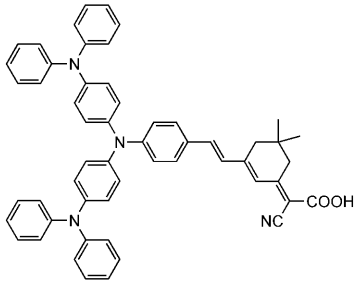
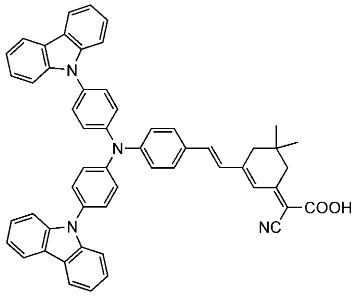
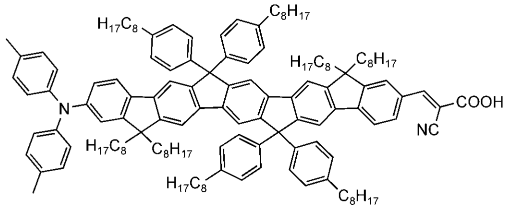
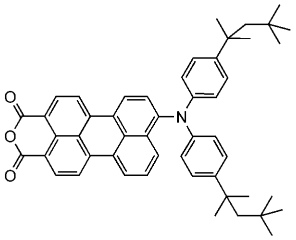
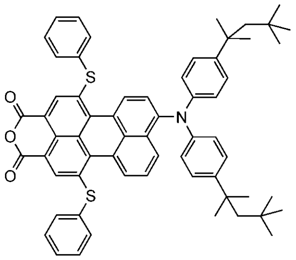
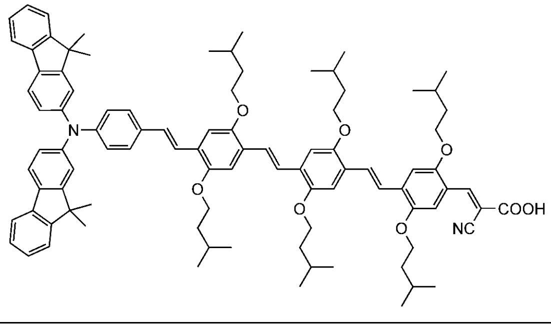
No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
43		17.8	0.60	0.57	6.1	[79]
44		20.0	0.65	0.694	9.0	[26, 80]
45		17.5	0.58	0.538	5.5	[80]
46		18.6	0.72	0.71	9.5	[28]
47		14.8	0.59	0.59	5.1	[81]
48		11.0	0.70	0.71	5.4	[71]
49		13.9	0.74	0.70	7.2	[71]
50		15.6	0.65	0.60	6.0	[72]

Table 1: (Continued)

No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
51		9.0	0.57	0.56	2.9	[82]
52		13.8	0.63	0.69	6.0	[82]
53		8.6	0.52	0.52	2.3	[83]
54		10.4	0.65	0.58	3.9	[84]
55		12.6	0.73	0.74	6.8	[85]
56		14.3	0.70	0.70	7.0	[86]

broadening of the absorption spectrum was observed when dyes **5** and **6** were adsorbed on the TiO_2 surface, leading to an increased photocurrent and overall efficiency. Expansion of the π system in sensitizer **7** by insertion of a C–C double bond red-shifted the absorption maximum relative to that of sensitizer **6**. DSSCs based on **7** generated an efficiency of 5.0% ($J_{SC} = 12.0\ \mathrm{mA\,cm^{-2}}$, $V_{OC} = 0.59$ V, FF = 0.71) without any coadsorbent. The efficiency and photocurrent were significantly improved to 8.2% and $J_{SC} = 15.9\ \mathrm{mA\,cm^{-2}}$, respectively, upon addition of 120 mM DCA to the dye solution before adsorption onto TiO_2. This result is very close to 9.0% for the N719-based DSSC under comparable conditions.[48] Coadsorption of DCA dissociates the π-stacked dye aggregates and also reduces dye coverage on the TiO_2 surface, but improves the electron-injection yield and thus the J_{SC} value. Despite the addition of DCA and TBP, the V_{OC} value for DSSCs based on coumarin dyes is still lower than that of DSSCs with ruthenium(II) complexes because of the significant degree of charge recombination resulting from the strong intermolecular π–π interaction of the dye molecules.

Hara and co-workers synthesized coumarin dye **8**, which absorbs more intensively at longer wavelengths ($\lambda = 552$ nm, $\varepsilon = 97\,400\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) than the similar dye **6** ($\lambda = 511$ nm, $\varepsilon = 64\,300\ \mathrm{L\,mol^{-1}\,cm^{-1}}$).[49] The key to this increase was the introduction of an additional cyanovinylene group to the molecular core which reduced the band gap. In 6 μm thick transparent TiO_2 films, this dyad molecule exhibited near-unity light-harvesting efficiency and an incident photon to current conversion efficiency (IPCE) of greater than 80% in the range 430–660 nm, with the absorption onset at 850 nm. DSSCs based on dye **8** and a nonvolatile electrolyte consisting of 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI), 0.1 M iodine, and 0.1 M *N*-methylbenzimidazole (NMBI) in 3-methoxypropionitrile (MPN) showed a good long-term stability and a power-conversion efficiency of 6.5% under continuous illumination. This kind of redox electrolyte has been reported to be beneficial for the long-term stability, but unfortunately is detrimental to the cell efficiency.[36]

In the case of dye **9**, in which a regioregular hexyl-substituted quaterthiophene bridges a carbazole and a cyanoacrylic acid unit, the increased efficiency over the less-alkylated derivative **10** seems to be due to the longer electron lifetime in the former.[50,51] This longer electron lifetime was attributed to the high hydrophobicity, which improved the packing of the dye on the surface and acted as a barrier preventing hydrophilic I_3^- ions from approaching the TiO_2 surface, thereby retarding electron leakage to the redox electrolyte. This effect accounted for the significant improvement in the V_{OC} value. The efficiency of DSSCs made from **9** dramatically increased to 8.3% ($J_{SC} = 15.22\ \mathrm{mA\,cm^{-2}}$, $V_{OC} = 0.73$ V, FF = 0.75) when the iodine concentration in the electrolyte was increased from 0.05 to 0.2 M.[51] This result is reflected by an improved J_{SC} value, which is attributable to the enhanced electrolyte diffusion and efficient regeneration of the dye. Under comparable conditions, DSSCs based on the dye N719 gave efficiencies of 8.1%.

The overall efficiencies of the cell dramatically dropped when the donor group was replaced by a quinoxaline unit, as in dyes **11**–**13**.[52,53] The use of a dithienothiophene unit in **12** instead of a bithiophene in **11** further reduced the cell efficiency, which was explained by aggregation of the dye. The further reduced efficiency in the case of **13** with thienylenevinylene units was ascribed to possible *cis–trans* photoisomerization of the C=C bonds.

Ko, Grätzel, and co-workers attached bulky difluorenylphenylamine to the oligothiophene core (**14**–**19**) to prevent aggregation of the dyes and to reduce charge-recombination processes.[54–60] In DSSCs, these dyes gave efficiencies in the range from 5.1 to 8.6%. Dye **16**, which contains a head-to-tail coupled oligo(3-hexylthiophene), gave the highest efficiency of the series. The expansion of the π conjugation by insertion of an additional double bond, as in **14** ($n = 1$), **18** ($n = 1$), and **19** ($n = 1$), led to a decrease in the efficiency because of the nonrigid bridging moiety, which causes energy losses by photoisomerization. Replacement of the difluorenylaminophenyl group by julolidine as the donor moiety in **20** decreased the efficiency to 2.95% and thereby also reduced the J_{SC} value to 6.6 $\mathrm{mA\,cm^{-2}}$.[61] This effect was assigned to the lower molar extinction coefficient compared to fluorenylphenylamino-substituted dyes. An increased overall power conversion efficiency of 4.5% was obtained by introduction of a coumarin unit into the fluorenylthiophene backbone of **21**.[62]

Grätzel and co-workers reported an efficiency of 8.0% with dye **22**, which contains a fused dithienothiophene unit with a difluorenylaminophenyl donor and a cyanoacrylic acid acceptor. The cell showed an excellent stability under combined heating and continual illumination.[63]

Lin and co-workers incorporated one to three alternating fluorenylthienyl units between a diarylamine donor and a cyanoacrylic acid acceptor to yield dye **23**. A DSSC prepared from **23** ($n = 1$) gave a good efficiency of 5.2%.[64] The efficiency was reduced to about 3.9% with longer bridges ($n = 2$, 3). Although dyes **23** with two and three repeating units have higher extinction coefficients, the highest efficiency was found for the shortest oligomer ($n = 1$). This finding was attributed to the efficient charge separation. The oxidation potential of the dye is also a crucial factor for their performance in DSSCs. The higher the oxidation potential of the dye, the larger is the driving force for the reduction of the oxidized dye, thereby resulting in a deceleration of the possible back electron transfer from TiO_2 to the dye.

Zhai and co-workers obtained an overall efficiency of 3.4% by using quinquethiophene dicarboxylic acid **24** as the sensitizer.[65] Later, Otsubo and co-workers reported the photovoltaic performance of octithiophene carboxylic acid **25** as the sensitizer with an efficiency of 0.82%. This value is lower than that obtained for **24** (1.29%) with the same cell configuration.[66] The lower efficiency of dye **25** was assigned to the lower J_{SC} value that arose because of a lack of electron injection and/or fast charge-recombination processes. The low effective power conversion efficiency of DSSCs with **24** was partly ascribed to the relatively low V_{OC} value (ca. 0.57 V). It was speculated that two terminal carboxylic acid groups in **24** could force the dye to adsorb flat on the TiO_2 surface, thereby resulting in a lowered photovoltage as a result of an increased dark current.

A triphenylamine-based dye **26** without any substituent gave an efficiency of 2.5% with a 15 μm thick TiO_2 film.[67] Insertion of thiophene and ethylenedioxythiophene (EDOT) as a bridging unit between the donor and acceptor groups in **27** and **28** red-shifted the absorption of the dyes. DSSCs with **27** and **28** on 6 μm thick TiO_2 films generated efficiencies of 5.2 and 7.3%, respectively.[68] Hagfeldt and co-workers reported lower efficiencies of 2.75 and 1.55%, respectively, for sensitizers **26** and **27** with a thinner TiO_2 film (3 μm).[69]

The structurally rather simple triphenylamine-based dye **29** yielded an excellent efficiency of 9.1%.[27] A high short-circuit current density of 18.1 $mA\,cm^{-2}$ was reported. This value seems to be higher than one would expect because of the given spectral response of approximately 80% in the narrow region between 400 and 500 nm. When the phenylenevinylene group was replaced by a thienylenevinylene group as in **30** and **31**, or by bithiophene in **32**, the lower J_{SC} and V_{OC} values led to a reduction in the cell efficiency.[69–72] The slightly higher efficiency obtained for **32** (6.15%) compared to **30** (5.9%) might be due to the higher rigidity of the molecular framework. The presence of additional electron-donating methoxy groups in **31** red-shifted the absorption maximum by 30 nm and gave a better efficiency (6.9%) compared to **30** (5.9%). This finding demonstrates the influence of alkoxy groups on the photovoltage and photocurrent through enhanced spectral response.

Sensitizers **33** and **34** containing di(*p*-tolyl)phenylamine as the electron donor and cyanoacrylic acid as the acceptor linked by a bithiophene or a thienothiophene unit, respectively, showed relatively high photoelectric conversion yields in the range of 6.6 to 7%. Although dye **34** afforded a slightly higher J_{SC} value, the efficiency was lower. This may result from a stronger tendency to aggregate on the TiO_2 surface because of the fused thienothiophene spacer. Aggregation leads to unfavorable back electron transfer and decreases the V_{OC} value of the device.[73]

The introduction of a pyrrolidino group as the donor moiety in sensitizers **35** and **36** significantly reduced the overall efficiency.[74] Furthermore, substituting the phenyl donor group in **35** by a thiophene unit in **36** resulted in a negligible solar cell performance. Such a difference in performance is probably related to a different conformation of the aromatic donor units. Molecular modeling studies have shown that aminophenylene derivative **35** possesses a twisted nonplanar structure, which decelerates the charge recombination in the charge-separated state. Additionally, the reorganization energy required for the decoupled twisted state may be more favorable compared to that for thiophene analogue **36**.[74]

The donor part of a dye molecule has a significant effect on the cell performance, as can be seen for the values for dyes **11**–**13**, **19**, **20**, **35**, and **36**. The major factors for the reduced performance of organic sensitizers in DSSCs are the formation of aggregates on the TiO_2 surface because of planar or sterically less-hindered structures and the recombination of conduction-band electrons with I_3^-.[75] All these studies further suggested that it might be essential to incorporate a bulky conjugated electron-donating group to prevent stacking and a rigid π-conjugative spacer to harvest the solar spectrum effectively.

Lin and co-workers introduced a benzothiadiazole unit into the conjugated backbone of **37** and **38** to shift the absorption band to the near-infrared regime.[76] These dyes showed absorption maxima at 491 and 541 nm, and gave efficiencies of 3.8 and 1.15%, respectively, in DSSCs. A small structural change—namely, the replacement of a benzene ring in **37** by a thiophene ring in **38**—resulted in the conversion efficiency dropping as a consequence of a dramatic decrease in the short-circuit current.

Compounds **39** and **40** containing rhodanine-3-acetic acid as the acceptor and anchoring moiety as well as diethylaniline as the donor showed good efficiencies of 6.2 and 3.9%, respectively.[77] The higher efficiency of **39** suggests that the rigid thienothiophene core in **39** could be an excellent π-conjugated system for light harvesting.

Organic dyes **41** and **42** which are based on phenothiazine chromophores showed broad absorption from 350 to 600 nm, with maxima at 452 and 481 nm, respectively. Efficiencies in DSSCs were measured as 5.5 and 1.9%.[78] DFT calculations have revealed that the LUMO of **41** is located on the cyanoacrylic acid acceptor, but is located on the rhodanine scaffold in **42**. This results in an isolation of the LUMO from the anchoring carboxylic acid group in **42**, thereby preventing efficient electron injection into the conduction band of the TiO_2.

Uchida and co-workers designed indoline-based dyes **43**–**47** for use as sensitizers in DSSCs. An efficiency of 6.5% was obtained with sensitizer **44**; this value was increased to 8.0% by the addition of chenodeoxycholic acid as a coadsorbent and an antireflection (ARF) layer which enhanced the transmittance of the fluorinated tin oxide (FTO) and prevented UV light ($\lambda < 400$ nm) from passing through.[79,80] Grätzel and co-workers achieved a conversion efficiency of 9% with **44** as the sensitizer after optimizing the TiO_2 films with an ARF layer.[26] Similar to the ruthenium(II) dyes N3 and N719, broad IPCEs were observed for **43**, exceeding 80% in the range 410–670 nm and reaching 94.6% at 530 nm. Indoline dye **46**, bearing an octyl chain, exhibited an efficiency of 9.5%, which is the highest value reported so far for DSSCs based on metal-free organic dyes.[28] A conversion efficiency of 5.1% was achieved with dye **47**, compared to 5.75% for ruthenium(II) dye N3 under the same experimental conditions.[81] Although indoline dyes have a narrower absorption band than N3, they show high photocurrents because of the large IPCEs.

Branched organic sensitizers **48** and **49** with triphenylamino or tri(4-methoxyphenylamino) groups as donors were tested in DSSCs.[71] The higher efficiency of **49** (7.2%) than **48** (5.4%) demonstrates the beneficial influence of alkoxy groups on the photocurrent. The lower efficiency of **48**, which contains two triphenylamino groups, in comparison to monosubstituted counterpart **30** (5.9%), was ascribed to the lower J_{SC} value caused by its narrower IPCE spectrum. Furthermore, the disubstituted donor moieties in **48** and **49** prevent recombination of I_3^- ions in the electrolyte with injected electrons in the TiO_2 conduction band, thus leading to increased open-circuit potentials. It was also revealed that electron lifetime, which is important for the open-circuit potential of DSSCs, is longest for methoxy-substituted dyes.

Lin and co-workers further demonstrated that the attachment of triphenylamino groups to the branched oligothiophene backbone of **50** prevents the back electron transfer process and enhances the efficiency of charge transfer in the electronically excited state of the dye. Solar cells with **50** generated an efficiency of 6%.[72]

Recently, it was shown that a bathochromic shift and broadening of the absorption range as well as enhanced absorptivities and high thermal stability can be obtained by incorporating additional arylamine and carbazole units to form D–D–π–A configurations such as **51** and **52**.[82] An improved photovoltaic performance was observed for carbazole-based **52**, which yielded an IPCE value of 85% and an efficiency of 6%. This design strategy seems to be very attractive, and suggests that the HOMO and LUMO energy levels can be tuned by attaching additional donor moieties and simultaneously increasing the hole-transporting ability of the sensitizer.

Müllen and co-workers recently used D–A-substituted fused oligofluorene **53** in DSSCs, but efficiencies of only 2.3% were obtained—probably because the dye absorbed only in the blue region of the spectrum.[83] They also used perylene dyes **54** and **55** as sensitizers, which were adsorbed onto the TiO_2 surface through two carboxylate groups formed by ring opening of the anhydride at the perylene core.[84,85] These dyes showed a more than 100 nm blue-shifted absorption when anchored to the TiO_2. A DSSC prepared from **54** gave an efficiency of 3.9%.[84] On the other hand, dye **55** showed an unprecedented IPCE of 87% and yielded an efficiency of 6.8% under standard AM1.5 solar conditions.[85] The authors explained that the thiophenol donor groups in **55** provide directionality of the electron flow in the excited state, thereby leading to improved device performance.

Dye **56**, which consists of a difluorenylamino donor and a cyanoacrylic acid acceptor bridged by a *p*-phenylenevinylene unit, gave an efficiency of 7.0% and a maximum IPCE value of about 73%.[86] The high efficiency of this dye was explained by the broad and red-shifted absorption band upon binding onto the TiO_2 surface.

2.2. Ionic Dyes as Sensitizers in DSSCs with Liquid Electrolytes

Hemicyanine, merocyanine, squarylium, and cyanine dyes can be regarded as promising sensitizers for DSSCs because of their tunable absorption in the red to near-infrared region as well as their high absorptivities (ca. 10^5 L mol^{-1} cm^{-1}). It is known that some of these dyes have a strong tendency to self-associate in solution or at the solid–liquid interface because of strong intermolecular van der Waals forces between the molecules.[87] The aggregates exhibit distinct changes in their absorption compared to the monomeric species, and three different aggregation patterns of the dyes have been proposed: red-shifted J-aggregates, blue-shifted H-aggregates, and both red- and blue-shifted herringbone aggregates. It was reported that a broadening of the absorption by controlled aggregation can be important to obtain high IPCEs in DSSCs.[88–91] However, these dyes showed rather moderate power conversion efficiencies in solar cells because of formation of aggregates upon adsorption on the TiO_2 surface. In addition, *cis–trans* photoisomerization is one of the major decay pathways for these dyes.[92] Some of the ionic dyes already employed in DSSCs are depicted in Table 2.

Huang and co-workers reported that the maximum IPCE for hemicyanine dyes **57** and **58** can be increased to near unity by pretreatment of the TiO_2 films with hydrochloric acid.[93–95] The binding of these dyes onto the TiO_2 electrode takes place through weak electrostatic interactions between SO_3^- groups and Ti^{4+} ions. However, treatment of the surface with HCl results in the surface of the TiO_2 being protonated and an increase in the number of active sites on the TiO_2 surface for dye adsorption. Additionally, the potential of the TiO_2 was shifted in the positive direction because of the adsorption of protons, which can increase the driving force for electron injection and reduce back electron transfer.[96,97] Dyes **57** and **58** showed efficiencies of 3.1 and 1.3%, respectively, on untreated TiO_2, while the efficiencies increased to 5.1 and 4.8%, respectively, upon treatment with HCl. The acid treatment reduced the open-circuit voltage as a consequence of the smaller difference between the flat-band potential of TiO_2 and the I_3^-/I^- redox couple,[24] which was compensated by the remarkable enhancement in the short-circuit photocurrent.

Hemicyanine dyes **59** and **60**, comprising a naphthothiazolium acceptor and a dialkylamino phenyl donor unit, showed efficiencies of 4.0 and 6.3%, respectively, under 80 mW cm^{-2} illumination.[98] In comparison to dye **59**, hemicyanine **60** contains an additional hydroxy group on the donor unit, which can form hydrogen bonds with the oxygen atom of the TiO_2 nanoparticles. This additional anchoring in cooperation with the RSO_3^- groups increases the contact area between the dye and semiconductor, which eventually led to a decreased number of adsorption sites on the TiO_2 surface. Alternatively, the dual binding mode in **60** largely enhanced the electron injection from the excited state of the dye to the TiO_2 conduction band and increased the overall efficiency. The cell efficiency was reduced to 4.6% when the naphthothiazolium unit was replaced by a benzothiazolium group (in **61**).[99] The lower efficiency for **61** could be due to its higher LUMO level resulting in worse electron injection efficiency.

Tian and co-workers found that D–π–A-based hemicyanine dye **62** generated a high J_{SC} value of 13.8 mA cm^{-2}, while the cell efficiency was only 2.1% because of its relatively low V_{OC} value of 0.36 V and low fill factor of 0.41.[100] Hemicyanine dyes **63** and **64**, in which one or two propionic acid groups were attached to the donor part of the molecule, respectively, showed efficiencies of 4.4 and 4.9%, with short-circuit current densities of 14.5 and 21.4 mA cm^{-2}, respectively, under irradiation with white light from a xenon lamp (90 mW cm^{-2}).[101] The higher efficiency for **64** bearing two carboxylic acid groups was ascribed to a broader absorption of the dye and an increased adsorption on the TiO_2 electrode compared to dye **63**, which contains one carboxylic acid group. Although the adsorption of hemicyanine **64** was three times larger than that of **63**, the J_{SC} value increased by only around 50%. This result was explained by the attachment of

Table 2: Ionic dyes tested in DSSCs with liquid electrolytes.

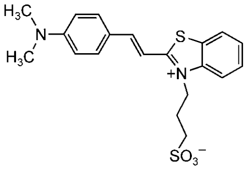
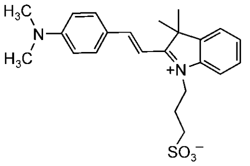
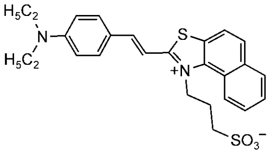
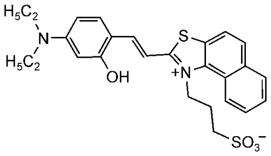
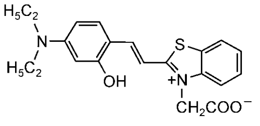
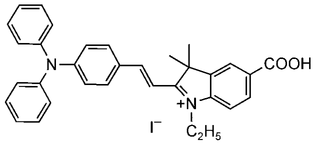
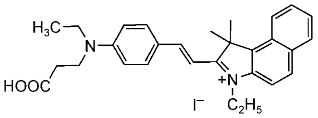
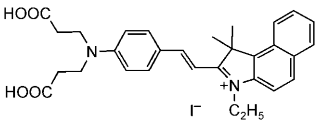
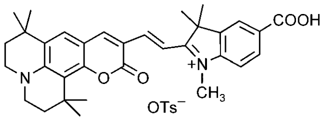
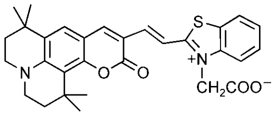
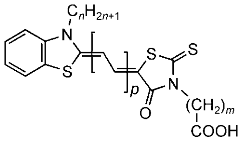
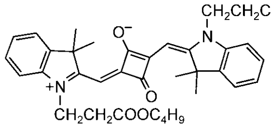
No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
57		16.5	–	–	5.1	[93, 95]
58		15.0	0.44	0.67	4.8	[95]
59		11.1	0.47	0.62	4.0	[98]
60		15.6	0.51	0.63	6.3	[98]
61		12.2	0.51	0.60	4.6	[99]
62		13.8	0.36	0.41	2.1	[100]
63		14.5	0.49	0.56	4.4	[101]
64[a]		21.4	0.42	0.49	4.9	[101]
65		2.7	0.34	0.63	0.6	[43]
66		4.5	0.38	0.63	1.1	[43]
67		11.4	0.60	0.65	4.5	[88, 102, 103]
68		8.1	0.50	0.59	2.4	[103]

Table 2: (Continued)

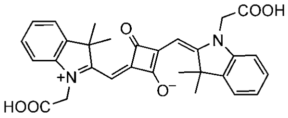
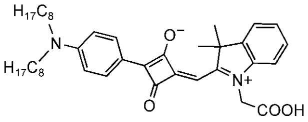
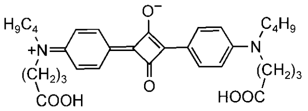
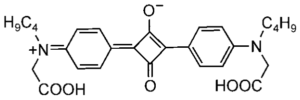
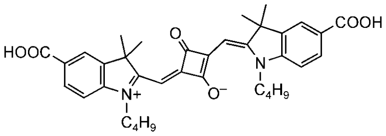
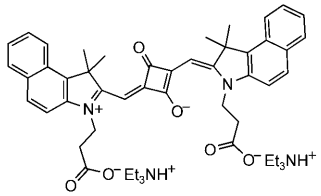
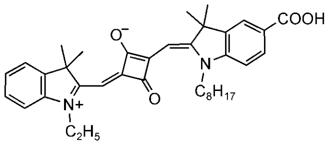
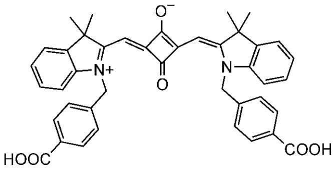
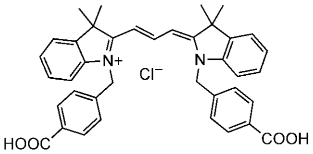
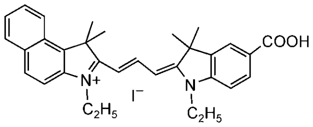
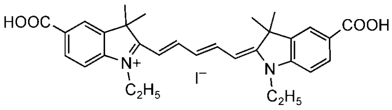
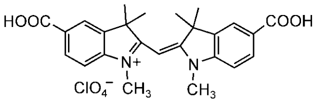
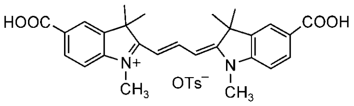
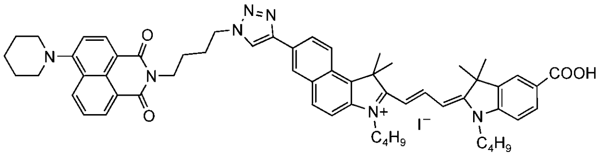
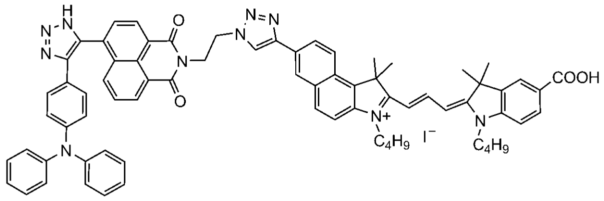
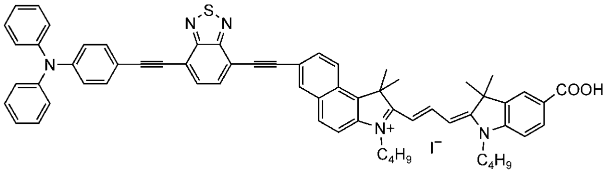
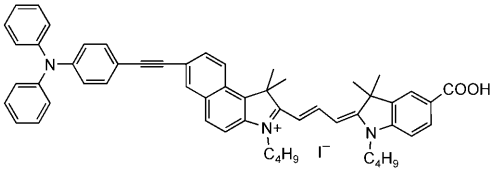
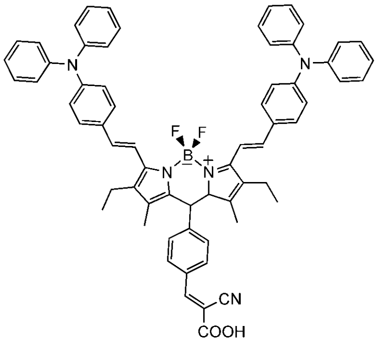
No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
69		3.5	0.53	0.53	1.0	[104]
70		5.9	0.64	0.53	2.1	[104]
71		4.9	0.37	0.53	1.6	[105]
72		10.3	0.38	0.52	3.4	[105]
73		11.6	0.49	0.54	3.9	[99]
74		8.6	0.59	0.73	3.7	[106]
75		10.5	0.60	0.71	4.5	[107]
76		2.8	0.45	0.57	1.7	[108]
77		2.0	0.41	0.53	1.0	[108]
78		5.5	0.47	0.46	2.9	[90]
79		3.85	0.39	0.45	1.3	[90]

Table 2: (Continued)

No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
80		3.0	0.47	0.61	0.9	[103]
81		8.8	0.46	0.56	2.3	[103]
82		14.5	0.50	0.49	4.8	[109, 110]
83		9.7	0.51	0.52	3.5	[109]
84[a]		22.1	0.54	0.48	7.6	[111]
85		15.8	0.57	0.55	6.6	[111]
86		4.0	0.56	0.74	1.7	[112]

[a] The values are not corrected for losses from light reflection and absorption, and hence the efficiencies and current densities can be higher than the actual values.

carboxylic acid groups to the donor side of the molecule reducing the charge separation. At the same time, charge recombination of the injected electrons with the remaining oxidized dye is facilitated and to some extent impedes electron transfer from the redox-active electrolyte to the charged dye. It must be considered that the losses by light reflection and absorption by the conducting glass were not corrected, and hence the reported current density values are larger than expected.

The introduction of indolium and benzothiazolium moieties in conjugation with a coumarin scaffold through a C=C bond led to a positive shift of the reduction potential of the resulting dyes: −0.35 V (versus the normal hydrogen electrode, NHE) for **65** and −0.57 V for **66**. This shift was caused by the strong electron-withdrawing ability arising from the cationic structure of these dyes. DSSCs with **65** and **66** showed rather moderate efficiencies because of their low-lying LUMO levels, which are below or close to the conduction band level of TiO_2.[43]

Arakawa and co-workers studied a series of benzothiazole merocyanines **67** with different alkyl chain lengths and found that the conversion efficiency and the IPCE value increased with an increasing length of the alkyl side chain attached to the benzothiazole ring and with a decreasing number of methylene units between the carboxylic acid group and the dye chromophore.[88,102] The dye with the longest alkyl side chain ($n = 18$; $m = 1$; $p = 1$) was the best sensitizer, generating an efficiency of 4.5 % and a J_{SC} value of 11.4 mA cm^{-2}. Further dyes were prepared with different numbers of C=C double bonds and it was found that an increased length reduced the rate of electron transfer from the excited dye to the conduction band of the TiO_2.[103]

Squarylium dyes have attracted special interest in recent years for use in solar cells. The presence of the rigid squaric acid ring in the methine chain afforded the dyes with high stability towards *cis–trans* photoisomerization and resulted in intense absorption in the red/near-infrared region. Sayama et al. studied the photovoltaic properties of **68**, which showed a sharp absorption at around 630 nm in ethanol. DSSCs with **68** resulted in an effciency of 2.4 % and a maximum IPCE of 37 %.[103]

Das and co-workers synthesized symmetrical dye **69** and unsymmetrical dye **70** as sensitizers for DSSCs.[104] The absorption of the unsymmetrical sensitizer was broad and is blue-shifted by about 20 nm compared to that of the symmetrical counterpart. DSSCs with the unsymmetrical dye **70** produced a higher photocurrent, thus resulting in a higher efficiency of 2.1 % compared to that of symmetrical dye **69** (1 %). This effect was ascribed to the unidirectional flow of electrons, which resulted in favorable charge separation and electron injection into the TiO_2.

In a different approach, Wang and co-workers developed squarylium dyes **71** and **72** with terminal dialkylanilino groups.[105] DSSC devices based on these sensitizers showed that the introduction of a short acetic acid anchoring group to dye **72** resulted in an improved photosensitization compared to **71** with a butyric acid side chain. For the former, a J_{SC} value of 10.3 mA cm^{-2} and an overall efficiency of 3.4 % were determined. A slightly better overall efficiency of 3.9 % and a maximum IPCE of about 65 % at 650 nm was obtained with symmetrical squarylium dye **73**.[99]

More recently, Grätzel and co-workers synthesized squarylium dye **74** with triethylammonium propionate anchoring groups.[106] Upon adsorption on a TiO_2 electrode, the absorption of the dye was broadened and red-shifted with respect to that of the indole analogue **69**. The DSSC showed an increased efficiency of 3.7 % in the presence of chenodeoxycholic acid (CDCA) and a higher V_{OC} value was obtained with *tert*-butylpyridine in the electrolyte. CDCA was used to prevent aggregation of the dye on the surface. More recently, the asymmetric squaraine dye **75** was synthesized in which the carboxylic acid group is directly attached to the chromophore.[107] In an optimized cell with CDCA used as a coadsorbant, a high IPCE of 85 % and a J_{SC} value of 10.5 mA cm^{-2} was obtained, which yielded an overall efficiency of 4.5 %—the highest for squarylium sensitizers. This high overall performance was attributed to two factors: firstly, the direct attachment of the carboxylic acid group to the conjugated π system, which provides strong electronic coupling to the conduction band of TiO_2, and secondly, the asymmetry created by the octyl side chain prevents surface aggregation and minimizes self-quenching of the excited state.

Cai and co-workers used squarylium dye **76** and cyanine dye **77** bearing *N*-(4-carboxy)benzyl anchoring groups as sensitizers in DSSCs and obtained maximum IPCEs of 36 and 46 %, respectively.[108] However, with respect to all the essential parameters regarding cell performance, squarylium dye **76** with an efficiency of 1.7 % was superior to cyanine **77** (1 %). The authors furthermore reported that the similar unsymmetrical cyanine dye **78** gave a higher efficiency (2.9 %) than symmetrical dye **79** (1.3 %).[90]

DSSCs with cyanine dyes **80** and **81** gave efficiencies of 0.9 and 2.3 %, respectively. The lower efficiency of **80** in solar cells was attributed to the worse J_{SC} value arising from the overlap of the absorption of both the dye and the triiodide in the electrolyte.[103]

Tian and co-workers prepared unsymmetrical cyanine dyes **82** and **83** in which a naphthalimide unit was attached at one terminus of the chromophore by a "click" reaction protocol.[109,110] The amount of dye adsorbed on the TiO_2 electrode was higher for **82** than for **83** which resulted in an improved short-circuit photocurrent. DSSCs with **82** and **83** showed good efficiencies of 4.8 and 3.5 %, respectively. The same research group also prepared dyes **84** and **85** containing triphenylamine units, which are complemented by a benzothiadiazole moiety in **84**. Excellent efficiencies of 7.6 and 6.6 % were obtained in DSSCs with **84** and **85**, respectively, under irradiation with white light from a xenon lamp (75 mW cm^{-2}).[111] When anchored to nanocrystalline TiO_2 films, cyanine **84** showed an IPCE of over 80 % in the range 540–590 nm, with a maximum value of 95 % at 560 nm. The maximum IPCE of **85** was 78 % at 560 nm. The unexpectedly high current densities of 15.8 and 22.1 mA cm^{-2} reported for dyes **84** and **85** could be due to uncorrected reflection losses.

Panchromatic boradiazaindacene (Bodipy) **86**, which contains an extended conjugation as a result of the triphenylaminoethenyl donor and phenylcyanoacrylic acid acceptor groups, represents a very promising dye because it absorbs in the visible region, with a maximum absorption at 700 nm. Unfortunately, DSSCs with **86** gave only moderate cell parameters and an efficiency of 1.7 %.[112] The HOMO of the dye is located on the Bodipy unit and the donor groups, whereas the LUMO is confined to the anchoring acceptor group. The rather moderate cell performance was due to the generation of a low photocurrent, thus suggesting an inefficient electron injection from the excited dye to the TiO_2 conduction band.

2.3. DSSCs with Ionic Liquids as Electrolytes

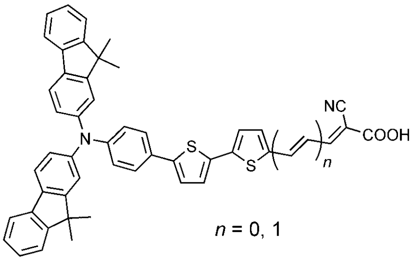
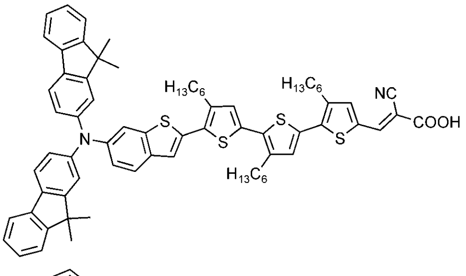
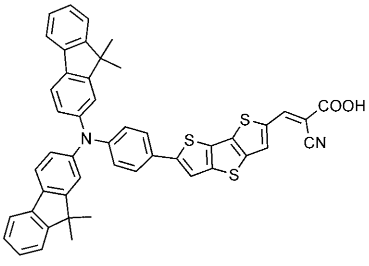
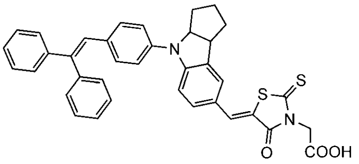
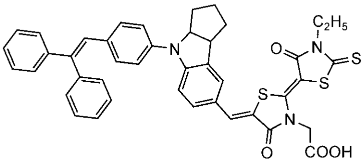
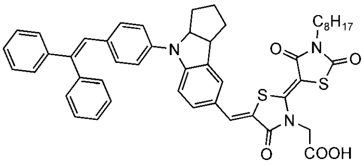
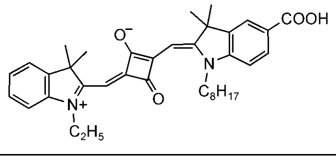
Ionic liquids (ILs) have been developed in recent years as solvents or components of liquid and quasi-solid electrolytes for DSSCs.[12,113–115] The main advantages of ILs over organic solvents is their reduced volatility as a result of negligible vapor pressure, thermal stability, and high ionic conductivity, which result in solar cells with a better long-term stability. Devices with liquid electrolytes tend to show faster degradation in terms of performance compared to cells with ILs. This is a severe problem for practical application. The electrochemical stability is also usually better when ILs are used than liquid electrolytes. The main disadvantage of ILs is the usually lower performance in devices because of their high viscosity, which results in mass-transfer limitations on the photocurrent under full illumination.[116]

Since the diffusion of I^- and I_3^- ions in ILs is slow, because of their high viscosity, a thin nanocrystalline TiO_2 film is necessary to reach high conversion efficiencies. For this reason, metal-free organic dyes with high absorptivities are ideal for DSSCs with ILs (IL-DSSCs). Dyes incorporated in IL-DSSCs are shown in Table 3. These dyes have already been studied in liquid electrolyte systems, therefore, a direct comparison is possible.

Grätzel and co-workers obtained a conversion efficiency of 6% for dye **14** ($n=0$) by using the solvent-free IL electrolyte Z655, which consists of 0.2 M iodine, 0.5 M *N*-butylbenzimidazole (NBB), 0.1 M guanidinium thiocyanate (GuNCS), and 1-propyl-3-methylimidazolium iodide/1-ethyl-3-methylimidazolium tetracyanoboranate (PMII/EMIB(CN)$_4$ 65:35).[117] They further tested dye **16** in a similar IL-electrolyte system of 0.2 M I_2, 0.5 M *N*-methylbenzimidazole (NMBI), and 0.1 M GuNCS in 1-propyl-3-methylimidazolium iodide/1-ethyl-3-methylimidazolium thiocyanate (PMII/EMINCS 65:35), and acquired efficiencies of 7.0%. This result is impressive, but lower than that observed in liquid electrolytes (8.6%).[57] In both cases, the lower efficiencies with the IL electrolyte were mainly due to a decrease in nearly all the cell parameters. In particular, in the case of dye **16**, the J_{SC} value dropped by a third in the IL-electrolyte, whereas the V_{OC} value increased slightly.

By using dye **22** in combination with a solvent-free IL electrolyte based on eutectic melts, the research groups of Grätzel and Wang recently demonstrated a DSSC with an excellent stability and an efficiency of 7%. In this case, the output photocurrent was comparable to that of DSSCs with liquid electrolytes: only the V_{OC} value was slightly lower, and contributed to the reduced efficiency compared to that of the liquid electrolyte system (8%).[63]

Table 3: Metal-free dyes tested in DSSCs with ionic liquids.

No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
14 (n=0)		12.3	0.69	0.71	6.0	[117]
16		11.7	0.76	0.77	7.0	[57]
22		14.1	0.68	0.74	7.0	[63]
43		9.7	0.67	0.74	4.9	[116]
44		12.5	0.71	0.72	6.4	[116]
46		13.7	0.73	0.72	7.2	[116]
75		7.9	0.65	0.74	3.8	[117]

Indoline dyes **43**, **44**, and **46** were examined in IL electrolyte Z655.[26,116] A record efficiency of 7.2 % under full illumination was achieved for dye **46**, with **44** (6.4 %) and **43** (4.9 %) still giving excellent values. The structural changes in this series are rather subtle—for example, the difference between **46** and **44** is only in the length of the alkyl side chain—and indicate that the hydrophobicity of the sensitizer is an important factor for the cell performance. Electrochemical impedance spectroscopy (EIS) analysis revealed longer electron lifetimes for cells sensitized with indoline **46** compared to **43** and **44**, thus indicating a more effective suppression of the dark current. This effect was also reflected in improved J_{SC} and V_{OC} values, and showed that small differences in the dye structure can have a dramatic influence on the cell performance. When compared to liquid electrolytes, the efficiencies of **43** and **44** in IL-DSSCs decreased by about 20 and 26 %, respectively.

The ionic squarylium dye **75** was investigated in IL-DSSCs and achieved an efficiency of 3.8 %.[117] Although the V_{OC} and FF values increased in the IL electrolyte compared to in the liquid electrolyte system the lower efficiency was due to a drop in the J_{SC} value.

2.4. DSSCs with Solid Electrolytes

The construction of solid-state DSSCs (ss-DSSCs) with a solid organic hole-transporting material (HTM) has gained considerable attention as an attractive alternative to DSSCs with liquid electrolytes. Disadvantages such as solvent evaporation and leakage are avoided even better than in IL-DSSCs. A variety of hole-transporting materials have been tested in ss-DSSCs.[118–123] However, the inferior pore filling of porous TiO_2 films by the HTM makes the total efficiencies of ss-DSSCs lower than those for liquid or IL-DSSCs.[122] Solar cells incorporating 2,2′,7,7′-tetrakis-(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-MeOTAD) or a highly conductive ionic polymer solid electrolyte as hole conductors and ruthenium(II)–polypyridyl complexes as sensitizers reached efficiencies of above 5 %.[124–126] The usual device is built up using fluoride-doped tin oxide (FTO) as a transparent electrode which is coated with a mesoporous TiO_2 film and then soaked with the appropriate dye solution for 12–18 h in the dark. Subsequently, a solution of spiro-MeOTAD containing *tert*-butylpyridine and lithium bis(trifluorosulfonyl)imide ($Li[(CF_3SO_2)_2N]$) as additives is spin-coated on the surface. The counterelectrode consists of a vapor-deposited gold layer. The preparation of ss-DSSCs are described in the literature[127–129] and have been reviewed recently.[34,130]

Metal-free organic dyes that have been evaluated in ss-DSSCs are illustrated in Table 4. These dyes exhibit high extinction coefficients and are ideal light-harvesting materials for ss-DSSCs because of their ability to absorb light effectively even in very thin films. For example, with indoline dye **43** an overall efficiency of 4.1 % and an IPCE of about 60 % over a wide range (440–550 nm) were obtained by using a 1.6 μm thick nanoporous TiO_2 film.[128] A comparison of the ss-DSSC with liquid- and IL-DSSCs showed that, corresponding to the electrolyte viscosity, the J_{SC} value drops from 17.8 mA cm^{-2} (liquid) to 9.7 mA cm^{-2} (IL) to 7.7 mA cm^{-2} (ss). The open-circuit voltage in ss-DSSCs is gratifyingly 260 mV higher than that in the liquid cells, probably because of the difference in the energy levels of the different hole-transporting materials.

Indoline dye **44** generated an enhanced IPCE of 70 % between 500 and 650 nm and an efficiency of 4.2 % using a 6 μm thick TiO_2 layer and the inorganic p-type conductor CuI.[131–133] The observed efficiency was higher than for the N3 dye in a similar cell configuration. It was suggested that the formation of nonquenching aggregates and a higher packing density of the indoline dyes are instrumental factors for higher efficiencies.

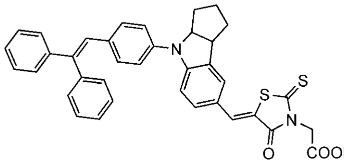
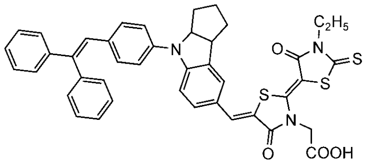
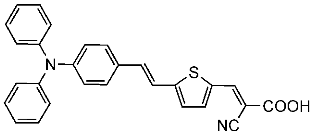
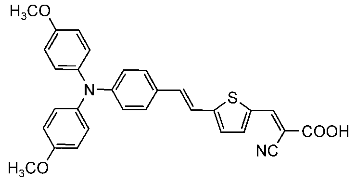
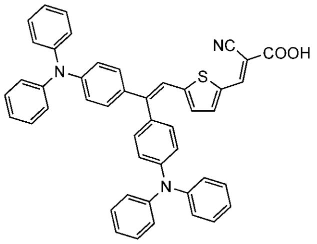
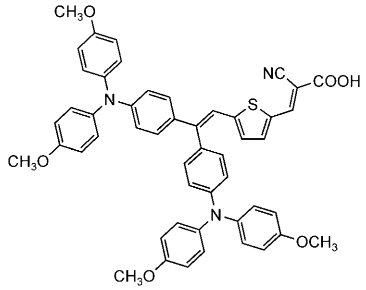
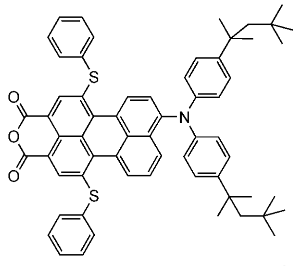
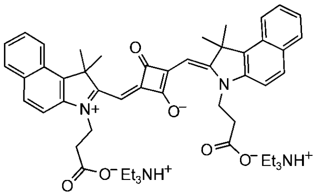
Triarylamine dyes **30** and **31** showed efficiencies of up to 3.3 % in ss-DSSCs.[71] Compared to liquid electrolyte devices more than half of the original efficiency was lost, mainly because of the decrease in the J_{SC} value and a moderate decrease in the V_{OC} value. The use of triarylamine dyes **48** and **49** gave efficiencies of 2.8 and 3 %, respectively, with the methoxy-substituted dye **49** showing a better photovoltaic performance. These results show that the major factors influencing the performance of the ss-DSSCs is the hole-transfer yield, which depends on the extent of penetration of the HTMs into the pores of the nanostructured TiO_2 film and intimate contacts between the dye and the hole conductor.[122]

Nazeeruddin and co-workers obtained a conversion efficiency of 1.8 % with perylene dye **55** as a sensitizer and spiro-MeOTAD as a hole conductor in ss-DSSC.[85] The blue squarylium dye **74** gave an efficiency of 1.5 % in ss-DSSCs, but only 3.7 % in a liquid electrolyte.[106] Compared to the liquid cell, the maximum IPCE is lowered by a factor of four in the ss-DSSC, which can be explained by the increased rate of back electron transfer to the hole-transporting material.

3. Cosensitization Effects in DSSCs

Despite the high absorptivity of organic dyes, the light-to-electricity conversion efficiencies of some dyes are rather modest compared to those of ruthenium(II)–polypyridyl complexes because of their relatively narrow absorption bands in the visible region. One strategy to obtain a broad absorption that extends throughout the visible and near-infrared region is the use of a combination of dyes which complement each other in their absorption properties and do not interfere with the sensitization properties of the other dyes.[135] Spitler and co-workers studied DSSCs with a mixture of cyanine dyes, whose absorptions covered the entire visible spectrum. They found that the J_{SC} value for a solar cell with a 4 μm thick TiO_2 film exceeded that of a cell with the N3 dye.[89] Zhang and co-workers examined the mechanism of the cosensitization with squarylium and N3 dyes by time-resolved spectroscopy.[136] They showed that the squarylium dye is a less-efficient photosensitizer of TiO_2 than is N3 because of its much slower electron transfer to the TiO_2 conduction band. However, when a small amount of squarylium dye (1–2 %) was used as a coadsorbate with N3, both its lowest singlet excited state and ground state can effectively regenerate N3 from N3$^{\bullet+}$ and prevent the TiO_2-to-N3$^{\bullet+}$ back electron

Table 4: Metal-free organic dyes tested in solid-state DSSCs.

No.	Compound	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	η [%]	Ref.
43		7.7	0.87	0.61	4.1	[128, 134]
44		14.1	0.55	0.54	4.2	[133]
30		6.3	0.87	0.57	3.1	[71]
31		7.7	0.76	0.56	3.3	[71]
48		5.0	0.79	0.71	2.8	[71]
49		5.9	0.81	0.63	3.0	[71]
55		2.8	0.84	0.75	1.8	[85]
74		4.2	0.68	0.53	1.5	[106]

transfer. In this way the cell efficiency was improved by more than 10%. The time scale for the squaraine-to-N3 electron transfer reaction was found to be about 300 ps, which is much faster than the reduction of N3$^{\cdot+}$ by the I^-/I_3^- redox couple (ca. 10 ns) or the back electron transfer (in the μs to ms region).

Cosensitization with a mixture of squarylium **68** and cyanine dyes **80** and **81** showed an improved cell performance ($J_{SC} = 11.5$, $\eta = 3.1\,\%$) over DSSCs containing an individual dye (see Table 2 for single dyes).[103] This result suggested that the arrangement of the dyes on the TiO_2 film by, for example, aggregation and ordering of the chromophores, clearly influences the performance of the solar cell. The use of dyes with efficient light-harvesting properties at low energies and negligible intermolecular interactions is important for the development of efficient multidye solar cells.

Guo et al. studied the cosensitization of cyanine dyes **78** and **79**. A combination of the two dyes in a 1:3 ratio was found to cover the entire visible spectrum, thereby generating a conversion yield of 3.4%, which is higher than that of the TiO_2 electrode sensitized with a single dye.[90]

A combination of three dyes such as 4-dimethylaminophenylcyanoacrylic acid, **61**, and **73**, which absorb in the yellow (380 nm), red (535 nm), and blue (642 nm) regions, respectively, were employed as cosensitizers in liquid DSSCs. Although the amount of adsorption of each dye decreased in the cosensitization, because of cooperative interactions, all three dyes exhibited higher IPCEs in their corresponding absorption regions compared to cells without cosensitization. This approach led to an improved efficiency of 6.5%.[99]

Recently, Nazeeruddin and coworkers demonstrated that the combination of dyes **14** ($n = 0$) and **75**, which have complementary absorption properties in the visible region, resulted in a panchromatic response, and yielded an overall efficiency of 7.4%. This value is so far the highest value reported for cosensitized DSSCs with metal-free organic dyes. Under similar conditions, the individually sensitized cells showed efficiencies of 7.0 and 4.2%, respectively.[137] Furthermore, they studied the cosensitization of these two dyes in IL-DSSCs and found enhanced photovoltaic performance compared with that of solar cells containing a single sensitizer, with the cell showing an efficiency of 6.4% and a broad IPCE over the entire visible spectroscopic region (400–700 nm).[117]

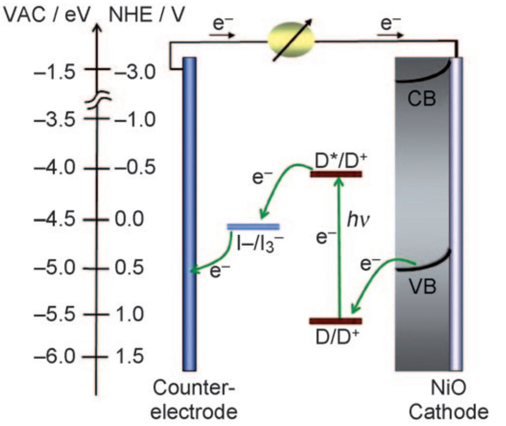
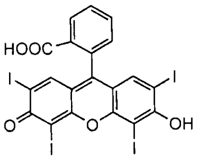
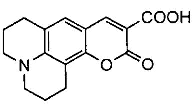


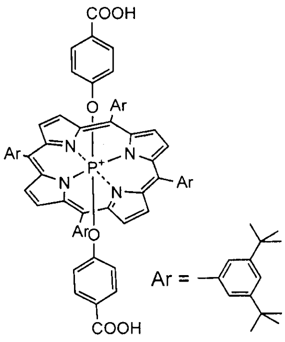
Figure 2. Energy-level diagram of a DSSc with a p-type NiO semiconductor electrode.

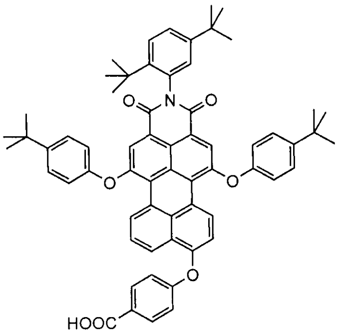
4. Organic Dyes in p-DSSCs with Photocathodes

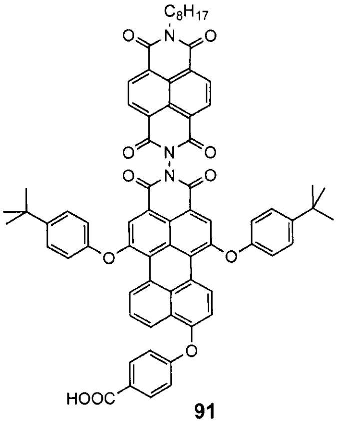
The DSSCs discussed in the previous sections are based on the sensitization of an n-type semiconductor to yield photovoltaic cells with a photoactive anode and a passive cathode. However, dye-sensitized photocathodes can be used in DSSCs in which the sensitizer is immobilized on the electrode surface by an anchoring group connected to the electron-donor part of the dye. In this case, the acceptor unit of the dye molecule should be remote from the photocathode. The basic requirements for the use of this “inverted” type of dye adsorbed on photocathodes are: 1) the HOMO level of the dye must be sufficiently below the valence band of the p-semiconductor; and 2) the LUMO level must be sufficiently higher in energy than the redox potential of the I_3^-/I^- system. Upon excitation with light, the electrons flow from the excited dye to the electrolyte, and the ground state of the dye is regenerated by efficient electron transfer from the valance band of a p-type semiconductor (Figure 2). As a result, the combination of appropriate photocathodes with high-performance photoanodes could lead to highly efficient tandem DSSCs. Only a very limited number of studies describing the sensitization of p-type semiconductors have been reported. To date, nickel(II) oxide (NiO) represents the most successful p-type semiconductor used for the construction of dye-sensitized photocathodes as well as tandem DSSCs because of its good stability and transparency.[138–145] However, at the moment, the reported examples suffer from very low efficiency compared to conventional TiO_2 cells. The major drawback of p-type NiO DSSCs is their low IPCE. Values approach 10% for a sandwich-type cell sensitized with coumarin 343 (**88**).[146]

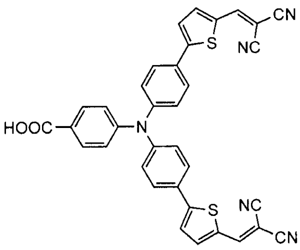

87


88


89


90


91


92

Lindquist and co-workers first demonstrated the generation of cathodic photocurrent with a dye-sensitized, nanostructured NiO cathode coated with erythrosin B (**87**; $J_{SC} = 0.232\ mA\,cm^{-2}$, $V_{OC} = 82.8\ mV$, FF = 0.27, $\eta = 0.008\%$).[138] The cathodic photocurrent is explained by hole injection from the dye to the valence band of the p-NiO electrode. The same research group later demonstrated a tandem DSSC by combining an NiO photocathode coated with erythrosine B and a TiO_2/N3 photoanode. A V_{OC} value of 0.73 V was reported for the tandem cell, a value still lower than that obtained with conventional DSSCs (ca. 0.8 V).[139] Suzuki and co-workers prepared a tandem cell comprising a TiO_2/N3 photoanode and an NiO photocathode coated with merocyanine **67**, which resulted in a J_{SC} value of 3.6 mA cm^{-2} and a high V_{OC} value of 0.92 V.[142]

The dynamics of photoinduced electron transfer in NiO films sensitized with **88** and **89** were studied by transient absorption spectroscopy. The results showed that the major drawback in the development of efficient p-type NiO DSSCs is the fast recombination between the reduced sensitizer and the injected holes in the valence band. As a result, the efficiency of electron collection at the counterelectrode and regeneration of the sensitizer through the redox couple I_3^-/I^- is limited to a large extent.[140,141]

The research groups of Hagfeldt and Odobel studied dyes **90** and **91** on NiO photocathodes in the presence of the I_3^-/I^- redox couple by transient absorption spectroscopy.[144] The study revealed that charge recombination is faster in the case of dye **90** than dyad **91**. This slower charge recombination for **91** was ascribed to the presence of the naphthalenediimide unit, which acts as an electron acceptor and generates a long-lived charge-separated state so that the electron transfer to the electrolyte and hole collection at the photocathode occurs efficiently. This led to a higher IPCE for **91** than for **90**.

Most of the NiO electrodes are prepared by heating $Ni(OH)_2$ sol–gel films at high temperatures. Bach and co-workers recently reported that the performance of such DSSCs can be improved by preparing NiO films from commercial NiO nanopowders.[145] Photovoltaic cells prepared with NiO films coated with dyes **87** and **88** gave J_{SC} values of 0.36 and 0.55 mA cm^{-2}, V_{OC} values of 0.12 and 0.10 V, and efficiencies of 0.01 and 0.02%, respectively. A remarkable enhancement in the photocurrent (J_{SC} = 2.13 mA cm^{-2}) was observed for dye **88** by increasing the iodine concentration to 2 M; unfortunately, the V_{OC} value was reduced by more than 50% and resulted in an efficiency of 0.03%. Under similar conditions, the ruthenium(II) dye N719, the standard dye for n-type DSSCs, showed remarkably strong desensitizing properties (J_{SC} = 8 μA cm^{-2}) when adsorbed onto NiO photocathodes.

Hagfeldt and co-workers synthesized **92**, which consists of a triphenylamine donor and a dicyanovinylene acceptor. The dye was incorporated in p-type DSSCs with NiO photocathodes and a passive anode.[147] The maximum IPCE of 18% in the visible region was obtained for dye **92**, which is so far the highest value for p-type DSSCs. This value is remarkably high, considering that the mesoporous film was only 0.6 μm thick. The cell generated a J_{SC} value of 1.52 mA cm^{-2}, a V_{OC} value of 0.11 V, and a FF of 0.31, thus resulting in an efficiency of 0.05%. Under similar conditions, dye **88** gave a maximum IPCE of 7% at 420 nm and a J_{SC} value of 0.8 mA cm^{-2}, while the classical N3 dye showed a negligible IPCE.

5. Trends and Correlations of the Molecular Dye Structure and Device Performance—Principles for the Design of Organic Dyes for DSSCs

Various functionalized metal-free organic dyes (described in the preceding chapters) have been designed and synthesized not only with the aim of replacing the rather expensive ruthenium(II) complexes, but also to widen the scope of available sensitizers and to extend the electronic properties of the materials. Although their performance in DSSCs is somewhat lower or close to the ruthenium complexes, these metal-free organic dyes can be considered as a new generation of sensitizers. It is therefore important to determine design rules for organic dyes to achieve improved properties and performance so that they may in the future compete or supersede ruthenium(II) sensitizers. Clearly, the development and optimization of materials for organic solar cells in general is not (yet) rational, but rather empirical. This is due to the multiple parameters which have to be taken into account when novel dyes and materials are designed for organic solar cells. The efficiency of the solar cells does not only depend on the molecular structure of the dye, but sometimes even more so on solid-state properties, such as aggregation, morphology, and self-assembly. In the case of DSSCs, the efficiency additionally depends on the type of photoelectrode, anchoring group of the dye, electrolyte, and mediating redox couple.

Therefore, only approximate trends for the design of organic dyes with respect to device performance—one typically looks at the power conversion efficiencies—can be deduced. The general design principle for a dye or sensitizer consists of a donor–acceptor-substituted π-conjugated "bridge" to which the anchoring group to the TiO_2 is attached at the side of the acceptor (Figure 3). Considerable progress has been made in recent years, and the best organic DSSCs are currently running at power conversion efficiencies of 8–9% in liquid DSSCs, approximately 7% in IL-DSSCs, and exceeding 4% in solid-state cells.

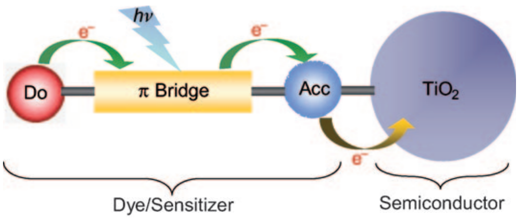


Figure 3. Design principle of an organic dye for TiO_2 photoanodes in DSSCs.

Analysis of the data concerning which type of donor (Do), π bridge, and acceptor (Acc) leads to the most efficient organic dyes in DSSCs (liquid electrolytes $\eta > 8\%$; ionic liquids $\eta > 6\%$; solid state $\eta > 4\%$) reveals that the best donors come from the family of *electron-rich aryl amines*: aminocoumarin, (difluorenyl)phenylamine, triphenylamine, and indoline. The best moieties for the π-conjugated bridge very frequently contain *thiophene* units, such as oligothiophenes, thienylenevinylenes, or dithienothiophene because of their excellent charge-transport properties, or phenylenevinylene. The variation on the acceptor side is rather small, and in most cases a *cyanoacrylic acid* group is used, with the anchoring carboxylic acid group elegantly incorporated into the acceptor moiety. *Rhodanine-3-acetic acid* and dimeric species thereof were used as a second type of acceptor, and their derivatives belong to the most effective dyes.

The same type of compounds and combinations of donor–bridge–acceptor turned out to be the most efficient dyes (indoline and triphenylamine donors, thiophene bridges, and rhodanine and cyanoacetic acid acceptors) in DSSCs with ionic liquids (IL) or solid-state (ss) hole transporters.

In more detail, it was shown that indoline-based dyes **44** and **46** containing rhodanine-3-acetic acid as the acceptor and anchoring unit give the highest overall efficiencies of over 9% in liquid and 7.2% in IL-DSSCs, but the long-term stability of the device was poor as a result of desorption of the dye from the TiO_2 surface. In this respect, the recently reported dithienothiophene dye **22** showed excellent long-term stability in liquid DSSCs and particularly in IL-DSSCs as a consequence of its robust structure.[63] This result marked a milestone, because instabilities and short lifetimes were always the major drawbacks of DSSCs with organic dyes.

Ionic dyes which showed enhanced optical response in the visible and near-infrared region were also tested as sensitizers in DSSCs, but they displayed rather moderate power conversion efficiencies. The best observed values are 6.3% for hemicyanine **60**, 4.5% for squaraine **75**, and 4.8% for cyanine **82**. High efficiencies of 6.7 and 7.6% are reported for cyanines **84** and **85**, but the cells were measured under weaker irradiation, and the data do not seem to be corrected for the reflection losses that can be seen in their IPCE spectra. It has been found for hemicyanines **57** and **58** that simply pretreating TiO_2 with hydrochloric acid was sufficient to significantly improve the energy conversion efficiency. This appears to be due to increased light-harvesting efficiency, electron injection, and/or charge collection.

6. Summary and Future Prospects

The purpose of this Review on metal-free organic dyes and their application in DSSCs was to assess the current status in research and the future developments in this broad and rapidly growing area of technology. The aim has been to provide the science and engineering community with a broad overview of this field and to identify promising design principles for the future development of new molecules. Although remarkable advances have been made with metal-free organic dyes as sensitizers in DSSCs, there is still a need to optimize their chemical and physical properties to further improve the solar cells.

Organic dyes offer infinite possibilities for improving a wide range of properties such as molecular structure and function, efficient light-harvesting ability in different parts of the solar spectrum, control over the molecular energy levels, charge generation and separation, and molecule-to-molecule interactions. The major advantage of organic materials for solar cell applications is their low cost of production. They are easy to design with a very high light-absorbing capacity so that thinner films can be used to generate optimal photovoltaic performance.

Apart from the molecular structure of the sensitizer, electrolytes also play a major role in DSSCs. The highest reported efficiency so far in ss-DSSCs is about 4% with indoline dyes. Although the IL- and ss-DSSCs are less efficient than liquid electrolyte cells, they have long-term stability, and IL-DSSCs have the advantage that leakage of the electrolyte from the cell is minimized. Interfacial charge recombination, which is the major loss mechanism, has to be suppressed to further improve the performance of these devices.

The question of how to improve the efficiency of metal-free organic dyes in DSSCs and how to transform the technology to multijunction solar cells is challenging. In this respect, the combination of highly efficient n-type TiO_2 electrodes and suitable photocathodic p-type NiO_x cells could, in the future, furnish highly efficient tandem solar cells in which both electrodes are photoactive. An appropriate sensitizer for p-type DSSCs should have an inverted arrangement of the donor and acceptor moieties in the dye molecule for efficient hole injection into the photocathode. Another prospective for multijunction DSSCs could be the stacking, on top of one other, of cells which contain dyes with different absorption wavelengths to obtain panchromatic absorption.

Another way to improve efficiencies is by the coadsorption of dyes with additives and by structural modification with bulky substituents which can prevent π–π stacking or dye aggregation. The cosensitization approach is also very appealing for using multiple dyes to obtain panchromatic absorption, but the fine-tuning seems to be quite difficult.

Currently, the efficiency of DSSCs is limited mainly by two factors: 1) non-optimized open-circuit voltage arising from unfavorable dark currents because of interfacial back electron transfer of injected electrons to the redox couple; and 2) non-optimized photocurrent arising from the poor optical response of the dyes in the NIR region. In this respect, novel organic dyes with intermolecular π–π interactions can be designed to obtain a high open-circuit voltage and hence high efficiencies. The π–π interactions help to achieve a closer packing of the dye molecules on the TiO_2 surface and hence better protect the surface from contact with the electrolyte, thereby resulting in a decreased dark current. New highly absorbing NIR dyes need to be designed to improve the photocurrent.

The different classes of dyes presented in this Review can be seen as prototype systems for systematic basic research and represent mosaic pieces for future research and development. Further exploration of structure–property correlations in the context of cell efficiency as well as durability would certainly facilitate widespread utilization of this DSSC technology.

It is clear that there are a number of factors determining the efficiency of solar cells and a multiparameter problem has to be solved. From the synthetic chemists point of view, however, the geometric and electronic structure of the sensitizer play an important role. When all these factors are taken into account, it should be possible to design more sophisticated and appropriate dye structures that satisfy the needs of DSSC technology. DSSC technology undoubtedly has an exciting future and there is still vast opportunities to ameliorate performance. Therefore, the development of a conceptually new design for constructing metal-free dyes is an important and urgent challenge. We also believe that the versatility of the synthetic design concept will continue to inspire research on this topic.

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