DOI: 10.1070/RCR4649

Influence of structural factors on the photovoltaic properties of dye-sensitized solar cells

Ekaterina A. Knyazeva,[a, b] Oleg A. Rakitin [a, b]

[a] *N.D.Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences Leninsky prosp. 47, 119991 Moscow, Russian Federation*
[b] *Education and Research Center for Nanotechnology, South Ural State University prosp. Lenina 76, 454080 Chelyabinsk, Russian Federation*

Data on the structure and photovoltaic properties of organic dye-sensitized solar cells published in the last five years are for the first time collected, systematized and generalized. The data for improved donor – π-spacer – acceptor structures are analyzed. The influence of structural factors in the donor and acceptor moieties and in the π-spacers on the power conversion efficiency of organic dyes containing an additional acceptor group is considered. The design strategies of highly efficient metal-free sensitizers are outlined. The review can be useful for a wide range of researchers working in the field of functional molecular materials.
The bibliography includes 214 references.

Contents

I. Introduction 1146
II. Why the structure of the donor – π-spacer – acceptor organic sensitizers should be improved 1147
III. The donor – acceptor(1) – π-spacer – acceptor(2) organic sensitizers 1147
IV. Donor(1) – donor(2) – π-spacer – acceptor organic sensitizers 1172
V. Other structural types of organic sensitizers 1172
VI. Conclusion 1179

I. Introduction

Increasing demands for green and renewable energy have raised the interest in fabrication of light-to-energy converters in a global scale.[1] Since the publication by Grätzel and O'Regan[2] on manufacturing relatively cheap solar cells (now known as dye-sensitized solar cells, DSSCs) they have represented one of the most promising photovoltaic technologies. In DSSCs, solar light is absorbed by a light-harvesting organic dye which also governs electron transfer to the porous surface of wide-gap metal oxide semiconductor (usually, TiO_2) nanoparticles.[3] The dye molecule acts as sensitizer and injects electrons into the conduction band of the metal oxide by photo-excitation; then, electrons pass to the external electric circuit. The oxidized dye is regenerated by reduction in an electrolyte.[4] There have been increasingly intensive studies aimed at improving the power conversion efficiency of DSSCs. At present, the DSSCs belong to the most promising green power sources owing to high efficiency, ease of fabrication and relatively low cost.[1,5] Clearly, photosensitizers play a key role in the DSSCs because they control the light harvesting on the one hand and the charge generation and separation (electron – hole) on the other hand.[6–10] Among organic sensitizers, impressive results are demonstrated by the ruthenium complexes with organic ligands, namely, the power conversion efficiency (PCE, η), which characterizes the performance of the photovoltaic device, can be as high as 11% under standard conditions.[11–18] The sensitizers based on porphyrins and cobalt electrolyte demonstrate even higher PCE values of up to 13%.[19–23] However, high cost and limited availability of ruthenium resources as well as labour-consuming synthetic methods and difficulties in purification of porphyrin dyes make these materials almost inappropriate for DSSC applications.

E.A.Knyazeva PhD, Junior Researcher of the Laboratory of Polysulfur-Nitrogen Heterocycles at the ZIOC RAS, Research Engineer at the ERC for Nanotechnology, SUSU.
e-mail: katerina_knyazev@mail.ru
O.A.Rakitin Doctor of Chemical Sciences, Professor, Head of the Polysulfur-Nitrogen Heterocycles at the ZIOC RAS, Research Engineer at the ERC for Nanotechnology, SUSU.
Telephone: +7 (499) 135 – 5327, e-mail: orakitin@ioc.ac.ru
Current research interests of the authors: materials chemistry, chemistry of heterocyclic compounds, chemistry of heteroorganic compounds, sulfur nitrogenous heterocycles, polysulfur heterocycles.

Received 29 March 2016
Translation: A.M.Raevskiy

© 2016 Russian Academy of Sciences and Turpion Ltd.

There has been considerable progress in the design of metal-free sensitizers characterized by $\eta > 10\%$ [24–35] and even $\eta = 12.5\%$.[26,29,30,36] The advantages of the metal-free dyes over the ruthenium complexes and porphyrin-based dyes include the low cost, the ease of structure modification and purification, as well as high molar extinction coefficients. Conventional organic sensitizers that have been most intensively studied in recent years (see, *e.g.*,[37–39]) belong to the D–π–A structural type and comprise a donor (D), a π-spacer (π) and an acceptor (A) which acts as an anchor to the electrode (usually, TiO_2) surface. A distinctive feature of these molecules is a high degree of π-electron delocalization, which increases the molecular polarizability and reduces the energy gap between the energy bands corresponding to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of individual molecules (from this point on, the band gap). Such a rational design of molecules enables efficient intramolecular charge transfer from the donor to acceptor.

Although controlled structure modification of the donor, spacer and acceptor allows one to tune the light-harvesting ability of a D–π–A dye, undesired aggregation of dye molecules on the TiO_2 surface and recombination of electron charge are difficult to avoid. π–π-Stacking (aggregation) of the dye molecules can also lead to spontaneous deactivation of the excited state and, consequently, to inefficient photocurrent generation.[40] Thus, the need for structure modification of the D–π–A dyes has become particularly topical in the early 2010s. The aim of the present review is to consider progress in the design of organic metal-free sensitizers in the last five years.

Very recently, a number of reviews on the state of the art in the field of D–π–A- (see Ref. 41) and D–A–π–A-sensitizers have been published.[42] However, these are limited-field surveys. Among numerous reviews on photovoltaic compounds,[43–49] mention should be made of two published in Russian journals. One of them is devoted to a broad range of bulk-heterojunction structures[50] while the other is concerned with conjugated polymers with benzochalcogenadiazole fragments.[51] No review articles presenting very recent data on the design and properties of organic sensitizers of different structure are available. This review mainly covers publications issued in the last five years until February 2016.

II. Why the structure of the donor – π-spacer – acceptor organic sensitizers should be improved

The operating efficiency of an organic photovoltaic device is characterized by the short-circuit current density (I_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF) and the power conversion efficiency (η), the last-mentioned parameter being the most important. For more detailed understanding of these characteristics, the reader is addressed to two recent pertinent reviews.[50,51] The incident photon-to-current efficiency (IPCE) spectrum of the solar cell is also of importance. The lifetime of the photovoltaic device is yet another practically valuable parameter. Improvement of the efficiency of the solar cells also requires good compatibility of their components.

Considerable attention is paid to organic sensitizers, which play a key role in the DSSCs. More exactly, the features of interest include 1) the absorption properties responsible for light harvesting by the DSSCs (the absorption region and the molar extinction coefficient); 2) the molecular orbital energy levels determining the thermodynamics of electron injection and dye regeneration; 3) the configuration and aggregation states on the semiconductor surface (they govern the competition between electron injection and recombination); and 4) photostability and thermal stability, which to a great extent determine the lifetime of the solar cell. In the D–π–A organic sensitizers, the HOMO is mainly localized on the donor group, whereas the LUMO is distributed over the acceptor moiety. It follows that the photons harvested excite a HOMO–LUMO transition, which enables electron transfer from the donor to the terminal acceptor group. Although there has been intensive research on the synthesis and structure modification of the D–π–A organic sensitizers by varying donors, π-linkers and acceptors and corresponding QSPR studies, most of the systems in question are characterized by PCE $< 9\%$.[52–71] Yet another important drawback of these compounds is low photostability. This makes the design of novel structural types of organic sensitizers particularly topical. Improvement of the light-harvesting ability is a necessary condition for more efficient light-to-energy conversion. This can be achieved in different manner by, *e.g.*, (1) extending the π-conjugation system to increase the molar extinction coefficient of the absorption band; 2) improving the electronic properties of the donor and acceptor to broaden the absorption region; and 3) increasing the amount of the dye adsorbed on the TiO_2 surface. Indeed, various design concepts of organic sensitizers were proposed in the last five years. The D–A^1–π–A^2 strategy has been best developed. It assumes the introduction of additional acceptors/spacers (A^1) between the donor and π-spacer. Other approaches to the design of novel types of organic sensitizers are also developed and intensively studied. This review is devoted to systematization of data on these new research avenues in the search for promising DSSCs.

III. The donor – acceptor(1) – π-spacer – acceptor(2) organic sensitizers

In 2011, Zhu *et al.*[72] proposed the 'D–A^1–π–A^2' concept for the design of new-generation efficient and stable organic sensitizers. The essence of the concept is to introduce an additional acceptor group (A^1) between the donor and π-spacer in the D–π–A sensitizer molecule. This not only optimizes the energy levels and the absorption properties and photovoltaic parameters, but also significantly improves the photostability of the sensitizers. Various electron-withdrawing heterocyclic moieties, such as benzothiadiazole, benzotriazole, quinoxaline, phthalimide, diketopyrrole, *etc.* were tested as additional acceptors in the D–A^1–π–A^2 systems. They considerably increase the PCE (from 5% to 10%) and significantly improve the stability of both free sensitizers and those incorporated into the

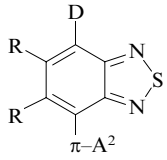
solar cells. It follows that the D – A^1 – π – A^2 motif is suitable for the design of highly efficient and stable photosensitizers that allow one to considerably broaden the absorption domain in the UV spectral region, to increase the molar extinction coefficient and to optimize the net photovoltaic properties. Below we will consider how particular types of the additional acceptor influence the PCE.

III.1. The 2,1,3-benzothiadiazole sensitizers

2,1,3-Benzothiadiazole (BTD) is a promising candidate for the additional acceptor block. This compound belongs to the best studied ones because of its properties and ready availability. It has a positive electron affinity, thus being a strong electron acceptor,[73–77] and a great potential for structural modification by introduction of various groups at four positions of the benzene ring. The introduction of the BTD ring into an organic molecule optimizes the HOMO and LUMO energy levels by narrowing the band gap.[78,79] This is the reason for inexhaustible interest in the synthesis of more and more organic sensitizers for the DSSCs based on this heterocyclic system. Table 1 lists the most efficient sensitizers containing BTD as additional acceptor (compounds **1** – **66**).

Lin and co-workers[80] reported the synthesis of the first representatives of the D – A^1 – π – A^2 organic sensitizers, *viz.*, WS-4 (S-1) (compound **1**) and S-3 (compound **2**) with the 2,1,3-benzothiadiazole ring as the A^1 spacer. In both cases, the A^1 spacer was a thienylcyanoacrylic block, which has been most often used (see Table 1). The only structural difference between compounds **1** and **2** is the π-linker in the donor block, namely, phenyl in the former and thienyl in the latter. It was found that, compared to the WS-4 dye, the thienyl compound S-3 has a 0.255 eV smaller energy difference between the frontier MO, and the charge transfer band in the absorption spectrum undergoes a large bathochromic shift of 50 nm (λ_{max} = 491 and 541 nm for **1** and **2**, respectively). It was assumed that the differences are due to a lower resonance energy and better coplanarity with the adjacent rings, which

Table 1. Power conversion efficiencies of D – A^1 – π – A^2 organic sensitizers with 2,1,3-benzothiadiazole as additional acceptor.



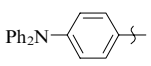
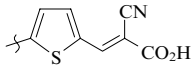
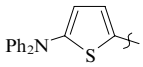
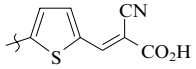
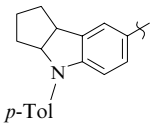
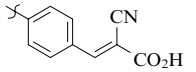
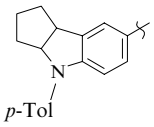
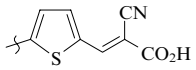
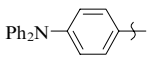
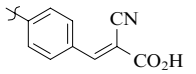
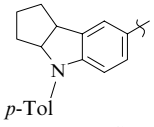
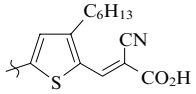
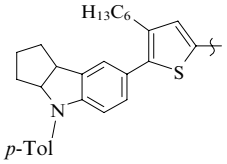
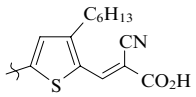
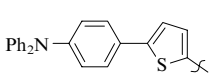
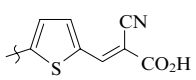
Compound	Code	D	π – A^2	R	η (%)	Ref.
1	WS-4 (S-1)			H	3.77	72, 80
2	S-3			H	1.15	80
3	WS-1			H	5.3	72
4	WS-2			H	8.7	72
5	WS-3			H	4.9	72
6	WS-6			H	7.76	81
7	WS-11			H	4.64	81
8	HKK-BTZ1			H	5.72	82

Table 1 (continued).

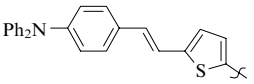
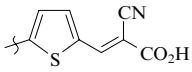
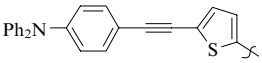
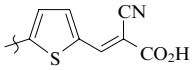
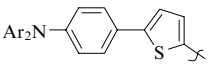
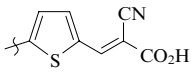
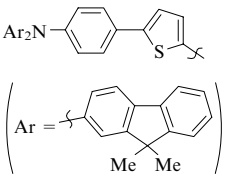
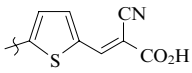
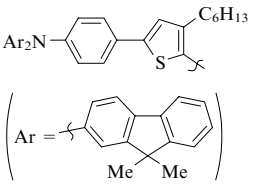
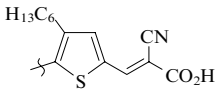
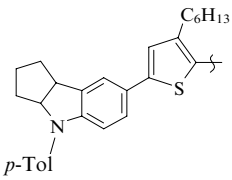
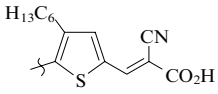
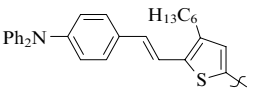
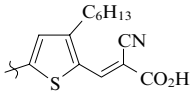
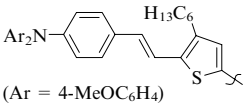
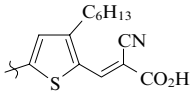
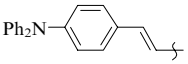
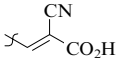
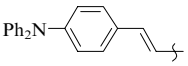
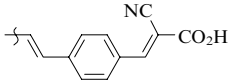
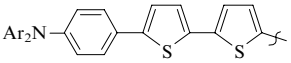
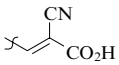
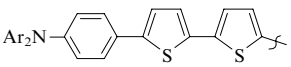
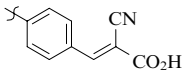
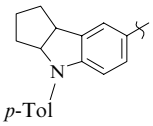
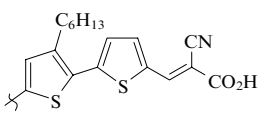
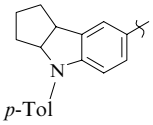
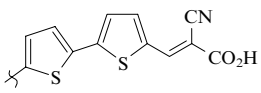
Compound	Code	D	π – A[2]	R	η (%)	Ref.
9	HKK-BTZ2			H	3.37	82
10	HKK-BTZ3			H	4.55	82
11	HKK-BTZ4	 (Ar = 4-[Bu^n(Et)CHCH$_2$O]C$_6$H$_4$)		H	7.30	82
12	JK-68			H	4.66	83
13	JK-69			H	6.61	83
14	WS-13			H	6.45	84
15	BzTCA			H	6.04	85
16	BzTMCA	 (Ar = 4-MeOC$_6$H$_4$)		H	4.68	85
17	K-2			H	2.49	86
18	K-3			H	3.80	86
19	–	 (Ar = 4-C$_6$H$_{13}$OC$_6$H$_4$)		H	1.78	87
20	–	 (Ar = 4-C$_6$H$_{13}$OC$_6$H$_4$)		H	8.21	87
21	WS-9			H	9.04	88
22	WS-23			H	8.15	89

Table 1 (continued).

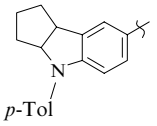
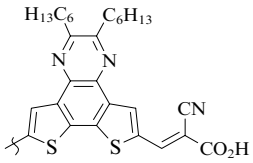
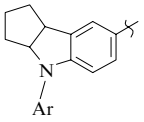
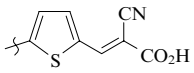
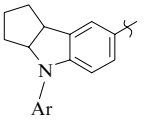
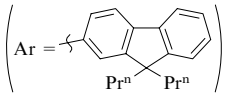
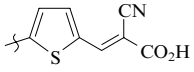
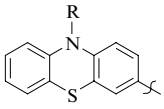
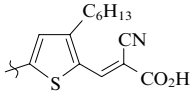
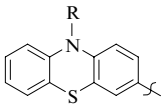
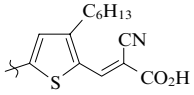
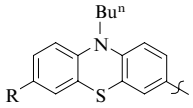
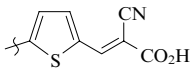
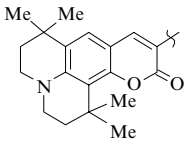
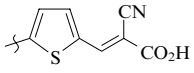
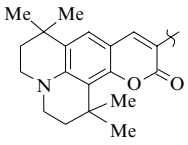
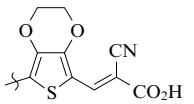
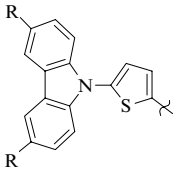
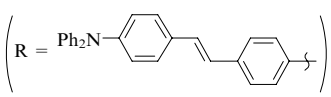
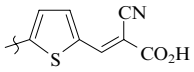
Compound	Code	D	$\pi-A^2$	R	η (%)	Ref.
23	DQ-5			H	7.12	90
24	XS-46	 (Ar = 4-Bu^{t}C$_6$H$_4$)		H	7.05	91
25	XS-45	 		H	7.69	91
26	DX-2	 (R = Bu^n(Et)CHCH$_2$)		H	2.60	92
27	DX-3	 (R = 4-(*p*-Tol)$_2$NC$_6$H$_4$)		H	3.54	92
28	JH-307	 (R = 2,4-(Bu^{n}O)$_2$C$_6$H$_3$)		H	6.4	93
29	HKK-CM4			H	4.82	94
30	HKK-CM5			H	3.93	94
31	H-11	 		H	3.79	95

Table 1 (continued).

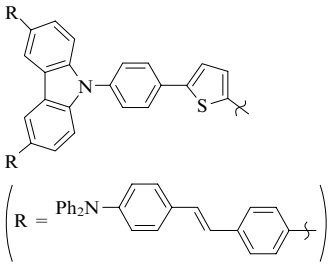
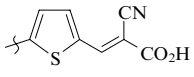
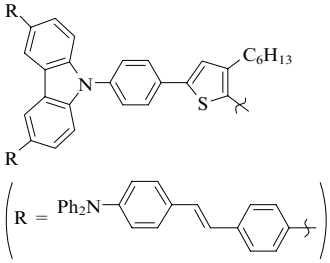
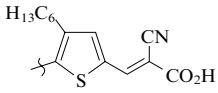
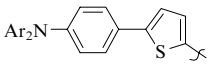
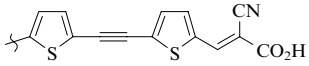
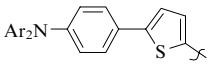
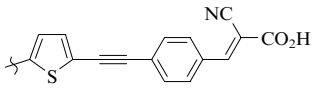
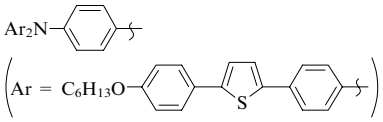
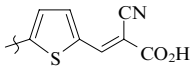
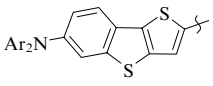
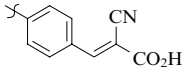
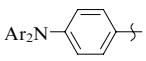
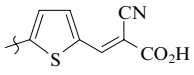
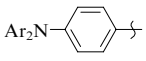
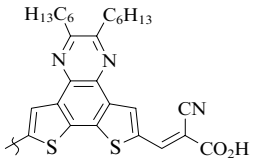
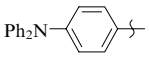
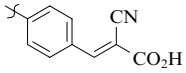
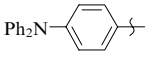
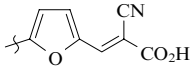
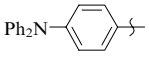
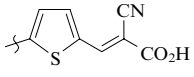
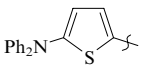
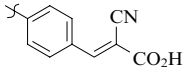
Compound	Code	D	$\pi-A^2$	R	η (%)	Ref.
32	H-12			H	3.97	95
33	H-13			H	5.27	95
34	G-1 [a]	 (Ar = 4-[Bu^n(Et)CHCH$_2$O]C$_6$H$_4$)		H	3.5 6.0	96 97
35	G-2 [a]	 (Ar = 4-[Bu^n(Et)CHCH$_2$O]C$_6$H$_4$)		H	5.1 8.1	96 97
36	OD-9			H	4.7	98
37	SGT-130	 (Ar = 4-[2,4-(C$_6$H$_{13}$O)$_2$C$_6$H$_3$]C$_6$H$_4$)		H	10.47	57
38	CA-III	 (Ar = 4-C$_8$H$_{17}$OC$_6$H$_4$)		H	5.7	99
39	DQ-4	 (Ar = 4-C$_6$H$_{13}$OC$_6$H$_4$)		H	6.78	90
40	DOBT-I			C$_8$H$_{17}$O	3.37	100
41	DOBT-II			C$_8$H$_{17}$O	3.71	100
42	DOBT-III			C$_8$H$_{17}$O	4.24	100
43	DOBT-IV			C$_8$H$_{17}$O	6.66	101

Table 1 (continued).

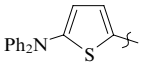
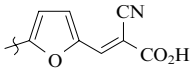
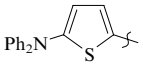
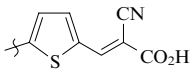
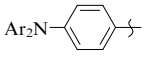
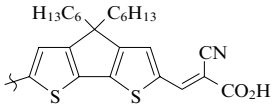
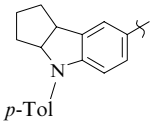
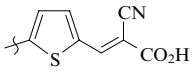
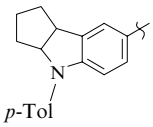
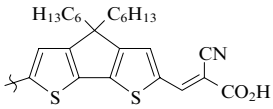
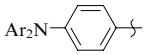
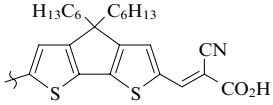
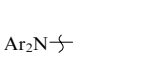
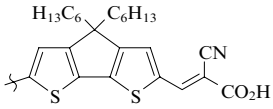
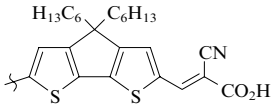
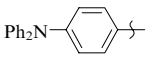
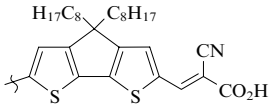
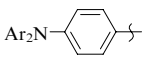
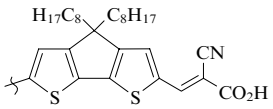
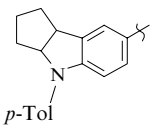
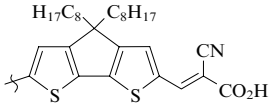
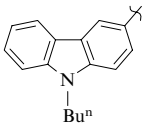
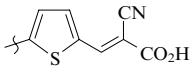
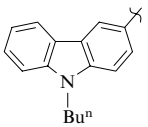
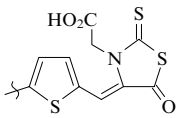
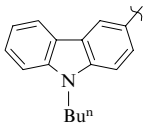
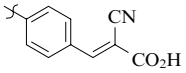
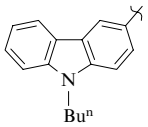
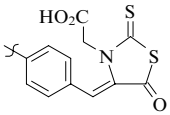
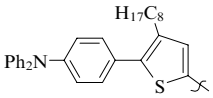
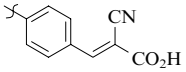
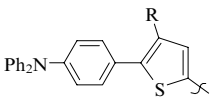
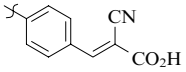
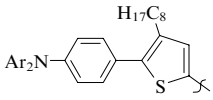
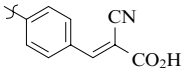
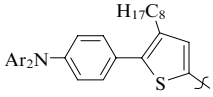
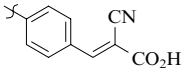
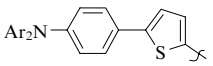
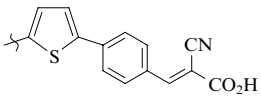
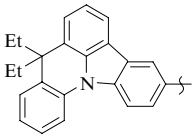
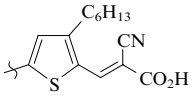
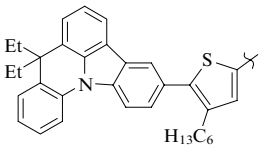
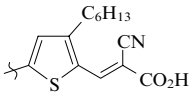
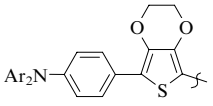
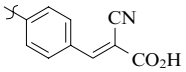
Compound	Code	D	π – A²	R	η (%)	Ref.
44	DOBT-V			$C_8H_{17}O$	7.16	101
45	DOBT-VI			$C_8H_{17}O$	6.19	101
46	AR-II-13	 (Ar = 4-$Bu^nOC_6H_4$)		F	6.6	102
47	JZ-117			F	7.4	103
48	JZ-145			F	9.1	103
49	D-2	 (Ar = 4-$C_6H_{13}OC_6H_4$)		H	7.99	104
50	KM-10	 (Ar = 4-(4-$C_6H_{13}OC_6H_4$)C_6H_4)		H	7.1	105
51	KM-11	(Ar = 4-[2,4-(Bu^nO)$_2C_6H_3$]C_6H_4)		H	8.0	105
52	WS-37			H	8.04	106
53	WS-38	 (Ar = 4-$MeOC_6H_4$)		H	6.27	106
54	WS-51			H	10.1	106
55	ZXY-1			H	5.07	107
56	ZXY-2			H	1.65	107

Table 1 (continued).

Compound	Code	D	π – A[2]	R	η (%)	Ref.
57	ZXY-3			H	5.40	107
58	ZXY-4			H	3.81	100
59	RK-1			H	10.3 [b]	108
60	RK-2	 (R = $Bu^n(Et)CHCH_2$)		H	8.71 [b]	108
61	6RK-1	 (Ar = 4-$C_6H_{13}C_6H_4$)		H	9.67 [b]	108
62	6ORK-1	 (Ar = 4-$C_6H_{13}OC_6H_4$)		H	10.1 [b]	108
63	G-3	 (Ar = 4-[$Bu^n(Et)CHCH_2O$]C_6H_4)		H	8.64	109
64	DIA-9			H	5.20	110
65	DIA-10			H	5.82	110
66	C-321	 (Ar = 4-$C_6H_{13}OC_6H_4$)		H	8.2	111

Note. *p*-Tol is *p*-tolyl; C_nH_{2n+1} groups have normal structure unless otherwise stated. [a] Power conversion efficiencies reported by different authors for the same sensitizer can be appreciably different because they depend on the cell fabrication procedure, the sensitizer layer thickness, *etc*. [b] In the presence of chenodeoxycholic acid (CDCA) additive.

favours not only more efficient conjugation, but also reduction of the barrier to the charge transfer transition. However, experiments with the solar cells based on these two compounds unexpectedly revealed a much higher PCE for WS-4 compared to S-3. Lin and co-workers [80] explained this result as follows: high coplanarity of the S-3 molecule also facilitates nonradiative decay of the excited state accompanied by a decrease in the electron injection efficiency. More recently,[84] it was assumed that the observed behaviour can be due to (1) the higher HOMO level of S-3 (0.259 eV higher than in WS-4) accounts for the insufficient driving force for dye regeneration and (2) high coplanarity of this dye molecule leads to undesired aggregation on the TiO_2 surface (the surface effect can be reduced using appropriate co-adsorbents). Thus, the first representa-

tives of the $D-A^1-\pi-A^2$ sensitizers demonstrated that simple improvement of the spectroscopic and electrochemical properties of the dyes may not be followed by improvement of the photovoltaic properties of the DSSCs based on them and the problem requires in-depth studies of the influence of the structural features of these dyes on the physical and applied properties of the DSSCs.

Further investigations of the effect of the donor block on the properties of organic dyes showed that the introduction of 4-tolyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole [a stronger electron donor than triphenylamine; see Table 1, compounds WS-1 (**3**), WS-2 (**4**), WS-6 (**6**) *vs*. WS-3 (**5**), respectively] as the donor causes a 0.28 eV up-shift of the HOMO level and a bathochromic shift of 36–41 nm for the charge transfer band. Moreover, the use of thiophene ring instead of benzene one as π-linker between the benzothiadiazole ring (A^2) and acceptor (cyanoacrylic acid) leads to an increase in the LUMO energy by 0.16 eV and to broadening of the charge transfer band in the electronic absorption spectrum by 37–42 nm. Also, the band gap in WS-2 (**4**) (one of the most interesting representatives of this series of dyes) reaches the minimum value (1.91 eV), while the absorption band becomes the broadest (λ_{max} = 533 nm).[72] Other photovoltaic parameters of this compound are also record high for this series of dyes. Photovoltaic cells based on compound WS-2 and deoxycholic acid (20 mmol litre^{-1}) as co-adsorbent exhibited η = 8.7%, while researchers from Grätzel's group improved the PCE to η = 9.0% (see a review[84]). These results rejected the assumptions that the introduction of benzothiadiazole as π-spacer can hamper charge transfer from the donor to the terminal acceptor group in the sensitizer molecule and to reduce the efficiency of electron injection into TiO_2. These experimental data were confirmed by the results of the density functional (DFT) calculations, according to which the HOMO and LUMO are to a great extent localized on the benzothiadiazole ring and, consequently, the HOMO–LUMO electron transition is facilitated.

However, it was found that the solar cells based on the dye WS-2 (**4**) exhibit a low open-circuit voltage (V_{oc} = 615 mV) in spite of high η. To increase V_{oc}, attempts were undertaken to introduce long alkyl chains (*e.g.*, hexyl) into the sensitizer molecule. In this case, the n-hexyl group has almost no effect on the electronic configuration of the dye; indeed, compounds WS-2 (**4**) and WS-6 (**6**) are characterized by almost identical molecular energy diagrams and electronic absorption spectra in solutions. However, the alkyl group plays an important role in the adsorption of the sensitizer on the TiO_2 surface, *viz*., it hampers intermolecular aggregation and improves the electron injection efficiency.[112] Moreover, the hydrophobic alkyl chain between TiO_2 and electrolyte can facilitate the formation of a compact dye layer and suppress dark current,[113] thus increasing V_{oc}. For instance, a solar cell based on the WS-6 sensitizer outputs a higher V_{oc} than that based on WS-2 (672 *vs*. 615 mV, respectively). According to electrochemical impedance spectroscopy data, the WS-6 dye suppresses charge recombination between TiO_2 and electrolyte much better than WS-2; this means higher electron injection efficiency of WS-6, higher electron density on TiO_2 and higher V_{oc}. However, it was found that WS-6 is less photostable than WS-2; this fact was explained by the oxidation of the n-hexyl chain.[114]

Further progress in understanding of the role of alkyl groups was achieved in comparing two bis-n-hexyl derivatives, WS-11 and WS-13 (compounds **7** and **14** in Table 1), which only differ in the arrangement of alkyl substituents in two thiophene rings. Large difference between positions of maxima of the charge-transfer bands in the electronic absorption spectra, namely, 557 nm for WS-11 *vs*. 505 nm for WS-13, appeared to be unexpected. Thus, by simply varying positions of alkyl groups one can induce not only a large shift in the absorption band maximum, but also make the band gap wider (*cf*. 1.85 eV for WS-11 and 2.15 eV for WS-13) and, as a consequence, significantly increase the PCE).[84]

The linker between the benzothiadiazole ring and the terminal electron acceptor (cyanoacrylic acid) is of great importance. In particular, compounds with no spacer between these groups, *e.g.*, sensitizers **17** and **19** (see Table 1) exhibit low PCE of 2.49% and 1.78%, respectively. The introduction of a phenylenevinylene or benzene spacers, which increase the distance and improve conjugation between the benzothiadiazole block and terminal group (compounds **18** and **20** in Table 1), causes no bathochromic shift in the electronic spectra of the compounds and position of the maximum of the charge transfer band remains almost unchanged (at 498 nm for compound **17** and at 494 nm for compound **18**).[86] From cyclic voltammetry data it follows that the HOMO and LUMO levels of both dyes in solution almost match each other. To explain significant improvement of the photovoltaic properties of compound **18** compared to dye **17**, the electron injection efficiency was studied by sub-nanosecond transient absorption spectroscopy for both dyes. It was found that compound **18** exhibits a three times more efficient electron transfer to the TiO_2 substrate than compound **17**.

The electronic spectra of dyes **19** and **20** exhibit a 55-nm hypsochromic shift indicating partial violation of conjugation due to the presence of phenylene block. However, the photovoltaic properties of the two compounds are also significantly improved. To explain this result, the dyes were studied by various modern physical methods.[87] It was shown that the solar cells based on dye **19** have high electron injection efficiencies, but the injected electrons undergo unusually fast recombination on the TiO_2 surface which in turn governs the PCE value.

In spite of increased PCE values attained for the sensitizers with phenylene spacers between the benzothiadiazole ring and terminal group, Wu and Zhu[84] believe that thienyl or polythienyl blocks are more appropriate π-spacers because they can not only ensure good electronic conjugation, but also provide a rather long distance to avoid charge recombination between the conduction band in TiO_2 and the oxidized dye.[9] A comparison of the photovoltaic properties of the dyes with mono- and bisthienyl spacers [*cf*. compounds WS-2 (**4**), WS-6 (**6**), WS-9 (**21**) and WS-23 (**22**) in Table 1] shows that increasing the number of thienyl groups has little effect. Taking the solar cells based on the WS-2

and WS-9 dyes as examples, an important role of co-adsorbents was revealed. Optimized amounts of these compounds can favour high PCE (> 9%).

Even more interesting results were obtained when the thienyl spacer was replaced by the di(alkyl)cyclopentadithiophene ring [alkyl = n-hexyl, n-octyl, see compounds JZ-145 (**48**), WS-37 (**52**), WS-51 (**54**), *etc.* in Table 1]. A comparison of the properties of the solar cells based on the WS-2 and JZ-145 dyes revealed some increase in the PCE (from 8.7% to 9.1%) and a considerable increase in the open-circuit voltage (V_{oc}) due to efficient suppression of charge recombination in the di(n-hexyl)cyclopentadithiophene moiety. Besides, the longer-lived excited state and higher electron injection efficiency also lead to an increase in the photocurrent (I_{sc}).[103] At present, di(n-hexyl)cyclopentadithiophene belongs to the most promising π-spacers between the benzothiadiazole unit and the terminal group, *viz.*, it allows the PCE to exceed a value of 10%.[106]

Yet another recently synthesized donor component is thieno[3,2-*b*][1]benzothiophene, which already proved itself.[57] This building block has a planar structure due to rigid junction of three rings that form an efficient electron transfer system. As a result, the SGT-130 dye (compound **37**) exhibited the widest absorption region and high current density. This result is of great theoretical value because it shows how to increase the current density by broadening the absorption band of the organic sensitizer. Besides, solar cells based on the SGT-130 dye possessed the highest open-circuit voltage and, as a result, a very high PCE value of 10.47%.

The sensitizers with *N*-butylcarbazole as terminal electron donor, benzene and thiophene rings as π-spacers, as well as cyanoacrylic acid and rhodanineacetic acid as terminal acceptor groups were compared.[107] In two cases, the sensitizers containing the cyanoacrylic moiety [compounds ZXY-1 (**55**) and ZXY-3 (**57**) in Table 1] exhibited higher efficiencies η than their analogues based on rhodanineacetic acid [compounds ZXY-2 (**56**) and ZXY-4 (**58**)]. This again confirmed the preferableness of cyanoacrylic acid as the terminal group. On the other hand, it was found that compounds with the thiophene π-spacer have the broadest absorption bands and the highest molar extinction coefficients, just like in some cases considered above. However, the presence of benzene rings leads to considerable increase in the open-circuit voltage, which is crucial for the PCE value. The highest efficiency, η = 5.40%, was attained for the carbazole derivative containing the benzene ring and the cyanoacrylic terminal group [compound ZXY-3 (**57**)]; this can be to some extent unexpected in the light of the data considered above.

In the last two or three years, there has been unprecedented progress in the studies of solar cells based on organic sensitizers, and now approaches to the design of solar cells that would meet all the requirements are being developed. Most often, novel research activity is aimed at complicating the structure of both donor and π-spacer; often, this indeed improves the PCE.

At the same time, a family of DSSCs (compounds **59** – **62** in Table 1) synthesized using appropriate co-adsorbents have relatively simple structures and demonstrate not only high PCE values η > 10%, but also outstanding absorption properties in the visible region as well as high photostability upon irradiation with one Sun equivalent at 65 °C (PCE reduced by less than 6% after 3000 h of operation).[108] These solar cells were tested on semitransparent modules with an active surface area of 1750 cm^2 and revealed a power output of 10.5 V m^{-2}, thus confirming a high potential for the building-integrated photovoltaics (BIPV) applications.

The aforesaid suggests that the benzothiadiazole-based $D-A^1-\pi-A^2$ structures are promising for the design of highly efficient organic sensitizers.

III.2. 2,1,3-Benzoxa(selena)diazole sensitizers

The closest analogues to 2,1,3-benzothiadiazole as additional acceptor with appropriate frontier MO energies include the 2,1,3-benzoxadiazole and 2,1,3-benzoselenadiazole. Similarly to BTD, they have positive electron affinities.[77] A number of benzoxa(selena)diazole sensitizers are listed in Table 2 (compounds **67** – **73**).

The results of theoretical calculations as well as experimental data for organic polymeric photovoltaic materials show that benzoxadiazole demonstrates a higher electron-withdrawing ability than benzothiadiazole.[117, 118] The more pronounced electron-withdrawing nature of the additional acceptor leads to a larger bathochromic shift in the absorption spectrum. Of particular importance is the fact that the plateau in the IPCE spectra of such organic sensitizers can extend to the near-IR region (to 860 nm).

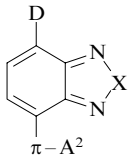
Compared to benzothiadiazole, the introduction of benzoxadiazole, as a stronger electron acceptor, into the molecule indeed causes a larger bathochromic shift in the UV spectrum and a particularly large down-shift of the LUMO level, which is of importance for improving the PCE. It was shown that the introduction of n-hexylthiophene group allows the PCE of compound WS-26 (**70**) to increase to 8.61%.[116] The authors of that study believe that the use of benzoxazole blocks makes it possible to significantly improve the photovoltaic properties; however, it should be noted that the PCE values of the benzothiadiazole derivatives WS-37 (**52**) and D-2 (**49**) (8.04% and 7.99%, respectively, see Table 1) are much higher than those of the other benzoxadiazole derivatives WS-62 (**67**) and WS-64 (**68**) (4.4% and 5.6%, respectively, see Table 2).

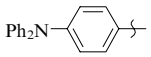
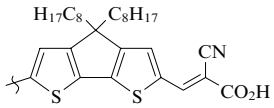
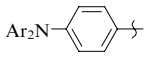
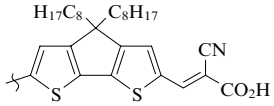
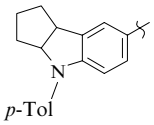
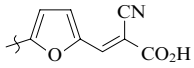
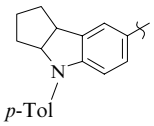
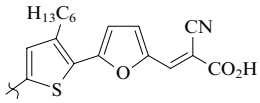
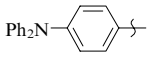
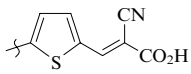
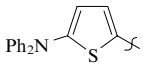
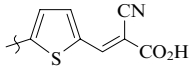
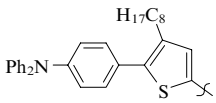
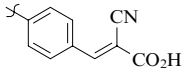
Strange enough, similar relations were also revealed for the benzoselenadiazole ring. This class includes only three compounds at the moment; however, in all cases the PCE values were either close to or much lower than those of the corresponding BTD-containing systems. Experimental data are as follows: η = 1.11% for compound S-4 (**72**) *vs.* η = 1.15% for S-3 (**2** in Table 1) in the former case and η = 2.91% for S-2 (**71**) *vs.* η = 3.77% for WS-4 (**1**, see Table 1) and η = 7.14% for RKSe (**73**) *vs.* η = 10.3% for RK-1 (**59**, see Table 1) in the latter case. Thus, the results obtained suggest that replacement of BTD by corresponding O- and Se-containing analogues deteriorates the photovoltaic properties.

III.3. Sensitizers based on [1,2,5]thiadiazolo[3,4-c]pyridine

[1,2,5]Thiadiazolo[3,4-*c*]pyridine (TP) is successfully used in the design of organic solar cells in both

Table 2. Power conversion efficiencies of D – A^1 – π – A^2 organic sensitizers with 2,1,3-benzoxa(selena)diazole as additional acceptor.



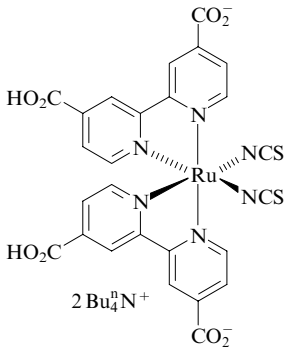
Compound	Code	D	π – A^2	X	η (%)	Ref.
67	WS-62			O	4.4	115
68	WS-64	 (Ar = 4-$C_6H_{13}OC_6H_4$)		O	5.6	115
69	WS-24			O	6.21	116
70	WS-26			O	8.61	116
71	S-2			Se	2.91	80
72	S-4			Se	1.11	80
73	RKSe			Se	7.14	108

monomeric and polymeric forms.[119, 120] This heterocyclic compound is a stronger acceptor than BTD. An important advantage of [1,2,5]thiadiazolo[3,4-*c*]pyridine over BTD is the possibility of extending the absorption band up to the near-IR region. Yet another reason for the use of the thiadiazolopyridine spacer (like all other fused pyridine-containing heterocyclic compounds, see below Section III.6) is the possibility of selective stepwise introduction of the donor and acceptor blocks; this allows one to obtain high yields of end products. Data for a number of sensitizers based on the TP block are presented in Table 3 (compounds **74** – **92**).

Even the pioneering studies[121] showed that the introduction of the TP block allows one not only to vary the HOMO and LUMO energies over a wide range, thus narrowing the band gap, but also to extend the absorption region to deep IR with $\lambda > 800$ nm [compounds H-1 — H-3 (**74** – **76**) in Table 3]; this is comparable with the properties of the established dye N719 (compound **93**).

Then, two series of thiadiazolopyridines were synthesized. The SC-NPyT series includes compounds **77**, **79**, **80**, **82**, **84** and **85** with the donor components closer to the pyridine nitrogen atom while the SC-PyTN series includes compounds **78**, **74**, **81** and **83** with electron

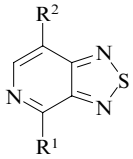
Structure 93



93 (N719)

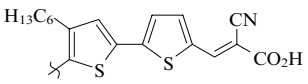
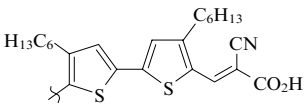
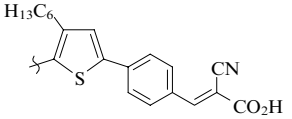
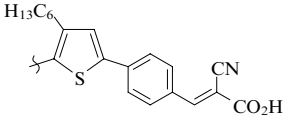
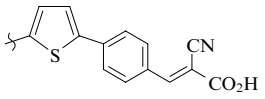
acceptors closer to the pyridine nitrogen atom. Both series of sensitizers are characterized by a large bathochromic shift of the absorption band in the electronic absorption spectrum compared to benzothiadiazole. A comparison of the photovoltaic properties of the two series in question showed that the solar cells based on SC-NPyT are characterized by higher photovoltage and photocurrent and, as a consequence, higher PCE values. However, the η values were at most 4.24%. A possible reason for the relatively low η values is intense

Table 3. Power conversion efficiencies of D – A^1 – π – A^2 organic sensitizers with [1,2,5]thiadiazolo[3,4-*c*]pyridine as additional acceptor.



Compound	Code	D	π – A^2	η (%)	Ref.
74	H-1	R^2 = Ph_2N–	R^1 =	2.63	121
	SC-PyTN2			0.78	122
75	H-2	R^2 = Ar_2N– (Ar = 9,9-dimethylfluorenyl)	R^1 =	3.58	121
76	H-3	R^2 = Ar_2N– (Ar = 4-$C_6H_{13}OC_6H_4$)	R^1 =	4.24	121
77	SC-NPyT1	R^1 = Ph_2N–	R^2 =	0.82	122
78	SC-PyTN1	R^2 = Ph_2N–	R^1 =	0.19	122
79	SC-NPyT2	R^1 = Ph_2N–	R^2 =	1.16	122
80	SC-NPyT3	R^1 = Ph_2N–	R^2 =	3.87	122
81	SC-PyTN3	R^2 = Ph_2N–	R^1 =	2.88	122
82	SC-NPyT4	R^1 = Ph_2N–thienyl	R^2 =	3.06	122
83	SC-PyTN4	R^2 = Ph_2N–thienyl	R^1 =	1.06	122
84	SC-NPyT5	R^1 = Ar_2N– (Ar = 4-$C_6H_{13}OC_6H_4$)	R^2 =	1.26	122
85	SC-NPyT6	R^1 = Ar_2N– (Ar = 4-$C_6H_{13}OC_6H_4$)	R^2 =	0.69	122
86	PT-1	R^1 =	R^2 =	2.1	123
87	PT-2	R^1 =	R^2 = (Alk = $Bu^n(Et)CHCH_2$)	5.1	123

Table 3 (continued).

Compound	Code	D	π – A^2	η (%)	Ref.
88	Y-1	R^1 = Ar_2N– (Ar = 4-$C_6H_{13}OC_6H_4$)	R^2 = 	2.86	124
89	Y-2	R^1 = Ar_2N– (Ar = 4-$C_6H_{13}OC_6H_4$)	R^2 = 	3.84	124
90	Y-3	R^1 = Ar_2N– (Ar = 4-$C_6H_{13}OC_6H_4$)	R^2 = 	4.46	124
91	Y-4	R^1 = Ar_2N– (Ar = 4-$C_6H_{13}OC_6H_4$)	R^2 = 	6.30	124
92	Y-5	R^1 = Ar_2N– (Ar = 4-$C_6H_{13}OC_6H_4$)	R^2 = 	1.32	124

dye aggregation on the TiO_2 surface and the possibility of charge trapping.[122] The introduction of cyclopentadithiophene π-spacer with branched alkyl groups, which suppress the sensitizer aggregation and charge recombination on the TiO_2 surface, led to an increase in PCE to 6.7%. This makes the TP-based compounds promising sensitizers suitable for narrowing the band gap and extending the absorption band to the near-IR region.

However, a comparison of the efficiencies of the BTD derivatives [compounds WS-4 (**1**), η = 3.77%; CA-III (**38**), η = 5.7%; WS-3 (**5**), η = 4.9%; WS-2 (**4**), η = 8.7%; see Table 1] and those of structurally similar thiadiazolopyridine dyes [compounds H-1 (**74**), η = 2.63%; H-3 (**76**), η = 4.20%; SC-NPyT3 (**80**), η = 2.88%; PT-1 (**86**), η = 2.1%; see Table 3] demonstrates that the former always exhibit better (in some cases, much better) properties, so the use of the pyridine-containing building block instead of the benzene-containing one does not improve the photovoltaic properties.

III.4. 2*H*-1,2,3-Benzotriazole sensitizers

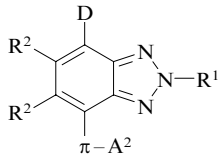
2*H*-1,2,3-Benzotriazole (BTA) is a moderate electron acceptor. In this spacer the sulfur atom of 2,1,3-benzothiadiazole (BTD) is replaced by the N – R group (usually, R = Alk).[125] BTA is widely used as electron acceptor in the semiconducting polymers for bulk heterojunction solar cells.[126, 127] Benzotriazoles are low-cost, commercially available starting compounds widely used for electrochemical coating of surfaces with various metals including silver, copper and zinc. Conjugated polymers based on BTA are also utilized in photovoltaic cells because they are stable against chemical and environmental factors.[127, 128]

The introduction of benzotriazole as additional acceptor into conventional D – π – A sensitizers causes the following beneficial changes in the photovoltaic properties: 1) the band gap becomes narrower because the electron-withdrawing ability of BTA is similar to that of BTD; 2) electron transfer from the donor to the terminal acceptor group is facilitated; 3) the properties of the solar cells can be modified with ease by replacing the substituent in position 2 of the triazole ring; and 4) the open-circuit voltage increases due to the presence of the nitrogen-containing heterocycle. A number of sensitizers with the BTA block are listed in Table 4 (compounds **94** – **109**).

Replacement of methyl group at position 2 of the triazole ring by octyl group causes an increase in the lifetime of electrons on a TiO_2 film and reduces the rate constant for charge recombination by a factor of four.[133] Since the dye films on the TiO_2 surface have similar electronic spectra, a significant increase in the photoelectromotive force is attributed to suppression of charge recombination. This makes it possible to attain high power conversion efficiency and open-circuit voltage (V_{oc} = 0.78 V). Further investigations of the sensitizers with BTA as internal acceptor showed that by varying the donor block one can attain even higher open-circuit voltages [up to V_{oc} = 0.829 V for compound DIA-7 (**106**) in Table 4][104] due to the low position of the HOMO level, long lifetime of an electron and slow charge recombination, and that the introduction of yet another thiophene spacer leads to the best photovoltaic properties (among the DIA compounds) with a PCE of 7.15% [compound DIA-8 (**107**) in Table 4].

The introduction of a more efficient π-spacer, 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT), at the terminal acceptor group led to even better results. The rigid coplanar structure and high electron-donating ability of CPDT causes the band gap to narrow and facilitates intramolecular charge transfer, thus proving

Table 4. Power conversion efficiencies of D – A^1 – π – A^2 organic sensitizers with 2*H*-1,2,3-benzotriazole as additional acceptor.



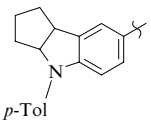
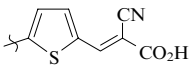
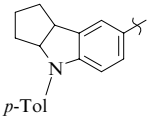
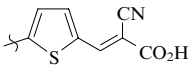
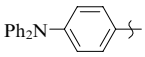
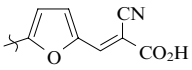
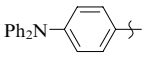
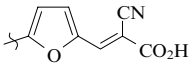
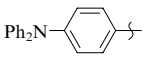
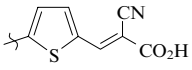
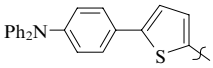
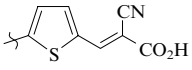
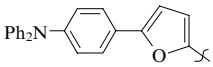
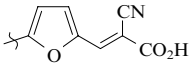
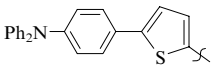
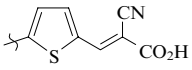
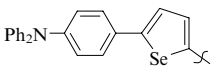
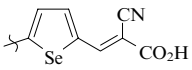
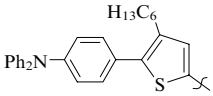
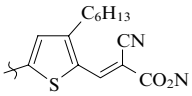
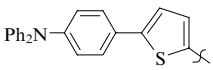
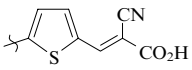
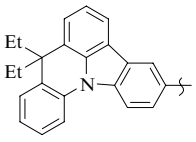
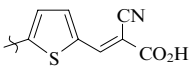
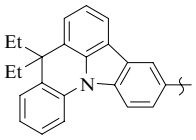
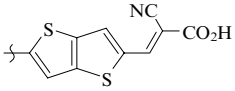
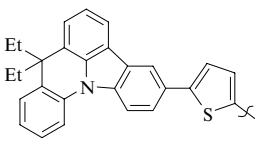
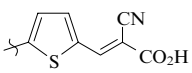
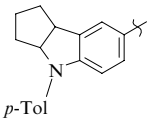
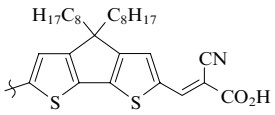
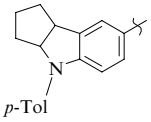
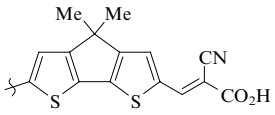
Compound	Code	D	π – A^2	R^1	η (%)	Ref.
94	WS-5			C_8H_{17}	8.38	129
95	WS-8			CH_3	6.74	84
96	BTA-I			C_8H_{17}	6.85	130
97	BTA-II			Alk [a]	6.72	130
98	BTA-III			C_8H_{17}	7.02	130
99	BTA-IV			Alk [a]	7.05	130
100	–			C_6H_{13}	4.37	131
101	–			C_6H_{13}	6.20	131
102	–			C_6H_{13}	5.66	131
103	–			C_6H_{13}	5.89	131
104 [b]	–			C_6H_{13}	6.01	131
105	DIA-6			C_8H_{17}	5.65	110
106	DIA-7			C_8H_{17}	6.23	110
107	DIA-8			C_8H_{17}	7.15	110

Table 4 (continued).

Compound	Code	D	π – A[2]	R[1]	η (%)	Ref.
108	WS-39			C_8H_{17}	9.07	132
109	WS-43			C_8H_{17}	4.74	132

[a] Alk = $CH_2CH(Et)Bu^n$. [b] R^2 = F (in other cases, R^2 = H).

the appropriateness of CPDT for organic photovoltaic applications.[134–136] Besides, the introduction of additional long alkyl chains at the carbon atom may lead to higher solubility of the dye, which is to some extent responsible for weakening of intermolecular interactions in the case of adsorption on TiO_2. The introduction of CPDT block [compounds WS-39 (**108**) and WS-43 (**109**) in Table 4] predetermines a noticeable bathochromic shift in the absorption spectrum compared to that of the thiophene analogue WS-5 (**94**).[132] Studies of the influence of methyl (compound WS-43, **109**) and octyl groups (compound WS-39, **108**) in the CPDT ring unexpectedly revealed significant differences, namely, almost all photovoltaic properties abruptly improved on going to the octyl derivative. Numerical data are as follows: η = 9.07%, I_{sc} = 16.61 mA cm^{-2}, V_{oc} = 770 mV and FF = 0.71 for the dye WS-39 (**108**) *vs.* η = 4.74%, I_{sc} = 10.03 mA cm^{-2}, V_{oc} = 705 mV and FF = 0.67 for compound WS-43 (**109**). Octyl groups at the CPDT block in **108** facilitate electron diffusion and transfer across TiO_2 particles, which leads to generation of maximum photocurrent. Moreover, improvement of the conduction band edge, charge transfer resistance and electron lifetime ensures higher electrical voltage in the solar cells based on WS-39.

Having introduced the benzotriazole spacer into the conjugated sensitizer, one could expect charge recombination similar to that found earlier for some BTD-based sensitizers. In this case, the effect can be to some extent suppressed. In spite of a small hypsochromic shift in the electronic spectra of BTA compared to those of BTD, the introduction of properly chosen alkyl chains at position 2 of BTA can not only improve the solubility of the dye, but also suppress dark current by blocking the electrolyte from immediate contact with the TiO_2 surface.

Summing up, benzotriazole as electron-withdrawing spacer can serve as efficient building block for rational molecular design of sensitizers for solar cells.

III.5. Quinoxaline and pyrazino[2,3-g]quinoxaline sensitizers

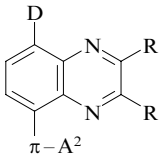
Quinoxaline has a high electron affinity. This heterocyclic compound is also attractive because its structure can be modified with ease. The quinoxaline ring is often investigated as constituent of donor – acceptor conjugated polymers.[137,138] Recently, this block has also been intensively studied as part of organic monomeric sensitizers; some examples are listed in Table 5 (compounds **110** – **132**).

The introduction of a narrow-gap quinoxaline spacer 1) optimizes the energy levels and causes broadening of the absorption band, which leads to efficient photovoltaic power conversion; 2) ensures the possibility of tuning the properties of solar cells in convenient manner by modifying quinoxaline moiety through introduction of alkoxy groups with long alkyl chains; and 3) improves the open-circuit voltage. Generally speaking, other nitrogen-containing heterocycles can also increase the open-circuit voltage; however, which is more important, the quinoxaline ring can significantly facilitate electron transfer from the donor to terminal acceptor group, thus leading to noticeably improved electron distribution over the donor block and to photostability of both intermediates and final sensitizers. As a consequence, this series of sensitizers has high power conversion efficiencies even with unsubstituted pyridazine ring of quinoxaline [compounds FNE-46 (**123**), FNE60 – FNE63 (**119** – **122**), IQ-9 (**124**) and IQ-10 (**125**) in Table 5].

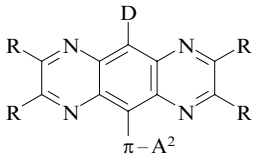
According to electrochemical impedance spectroscopy data, replacement of methoxy group in the dyes IQ-1 (**110**) and TQ-1 (**112**) by octyloxy group [dyes IQ-2 (**111**) and TQ-2 (**113**) in Table 5] causes the lifetime of the injected electron to increase by a factor of 2.4.[139] It follows that the IQ-2 and TQ-2 sensitizers can be used in solar cells even in the absence of co-adsorbents because they successfully suppress charge recombination and dark current and improve the open-circuit voltage. Experiments with a liquid electrolyte based on IQ-2 revealed a high power conversion efficiency which reduced by only 3% after 1000 h of illumination with solar light.

As alkoxyphenyl substituents in the quinoxaline ring were replaced by phenyl ones [compound IQ-4 (**114**) in Table 5], the band gap narrowed, the absorption band broadened and the balance between photocurrent and photovoltage was optimized owing to moderate electron-withdrawing properties of the diphenylquinoxaline moiety. Introduction of two phenyl groups attached to the quinoxaline ring and rotated relative to its plane provides almost perfect morphological control combining suppression of intermolecular aggregation and facilitated formation of a compact

Table 5. Power conversion efficiencies of D – A^1 – π – A^2 organic sensitizers with quinoxaline as additional acceptor.



110 – **130**



131, **132**

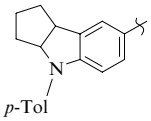
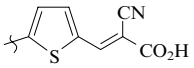
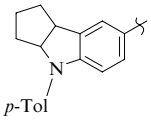
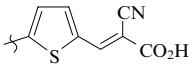
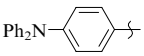
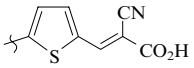
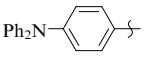
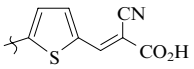
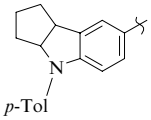
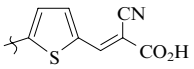
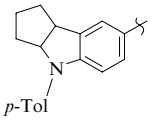
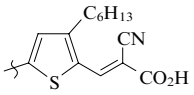
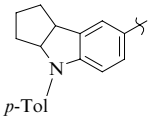
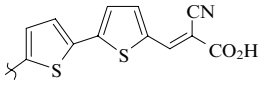
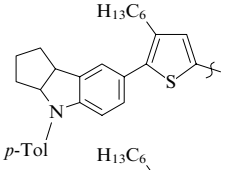
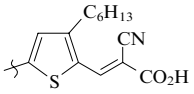
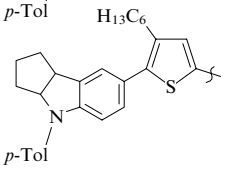
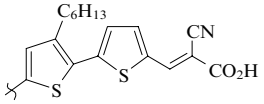
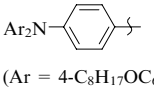
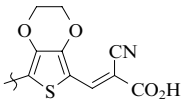
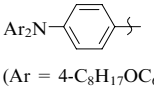
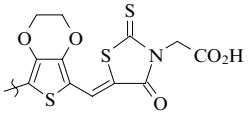
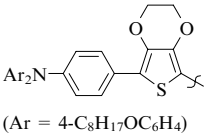
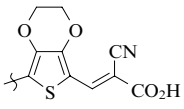
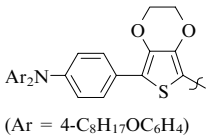
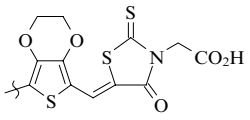
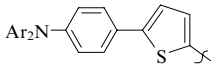
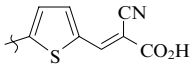
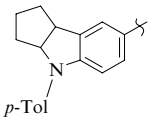
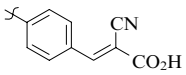
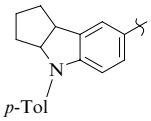
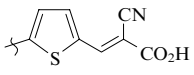
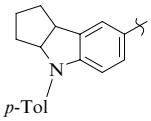
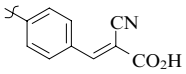
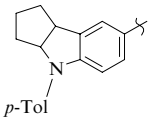
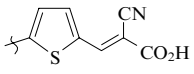
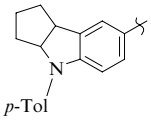
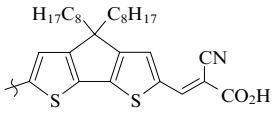
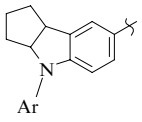
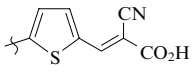
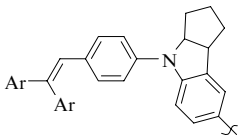
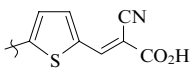
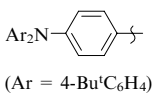
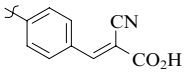
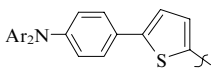
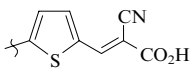
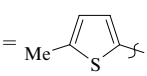
Compound	Code	D	π – A^2	R	η (%)	Ref.
110	IQ-1			Ar^1	6.24	139
111	IQ-2			Ar^2	8.50	139
112	TQ-1			Ar^1	5.19	139
113	TQ-2			Ar^2	7.08	139
114	IQ-4			Ph	9.24	140
115	IQ-5			Ph	8.65	140
116	IQ-8			Ph	7.09	141
117	IQ-6			Ph	7.77	141
118	IQ-7			Ph	6.39	141
119	FNE-60			H	6.1	142
120	FNE-61			H	3.9	142
121	FNE-62			H	8.2	142

Table 5 (continued).

Compound	Code	D	π – A^2	R	η (%)	Ref.
122	FNE-63	 (Ar = 4-$C_8H_{17}OC_6H_4$)		H	4.9	142
123	FNE-46	 (Ar = 4-$C_8H_{17}OC_6H_4$)		H	7.14	143
124	IQ-9			H	2.91	144
125	IQ-10			H	7.75	144
126	IQ-11			Ar^3	6.56	144
127	IQ-12			Ar^3	8.76	144
128	IQ-21			Ph	9.04	145
129	YA-421	 (Ar = 4-[2,4-$(C_6H_{13}O)_2C_6H_3$]C_6H_4)		Ph	9.0	28
130	YA-422	 (Ar = 4-[2,4-$(C_6H_{13}O)_2C_6H_3$]C_6H_4)		Ph	9.22	28
131	PQ-1	 (Ar = 4-Bu^tC_6H_4)		Ar^4	6.86	146
132	PQ-2	 (Ar = 4-Bu^tC_6H_4)		Ar^5	0.34	146

Note. Ar^1 = 4-$MeOC_6H_4$; Ar^2 = 4-$C_8H_{17}OC_6H_4$; Ar^3 = ; Ar^4 = 4-$C_6H_{13}OC_6H_4$; Ar^5 = 4-(iso-$C_8H_{17}O$)C_6H_4.

layer of the sensitizer.[140] For IQ-4, all these improvements made it possible to attain a high power conversion efficiency ($\eta = 9.24 \pm 0.05\%$) using no co-adsorbents. Illumination with solar light under standard conditions over a period of 1000 h at 60 °C caused no changes in the PCE. It is noteworthy that further modification of the structure of the IQ-4 sensitizer by introducing additional thienyl and alkylthienyl rings into the π-linker bonded to the terminal acceptor group and into the donor block [compounds IQ-6 (**117**), IQ-7 (**118**) and IQ-8 (**116**) in Table 5] did not improve the photovoltaic properties of the sensitizers, including the PCE.[141]

The sensitizers with additional 2,3-dithienylquinoxaline acceptor and different π-spacers [compounds IQ-11 (**126**) and IQ-12 (**127**) in Table 5] were compared.[144] It was found that introduction of phenylene spacer strongly violates the planarity of the entire system and deteriorates its properties. However, the introduction of a thiophene spacer leaves system's configuration closer to planar. This extends the absorption region, increases the molar extinction coefficients and suppresses dye self-aggregation and charge recombination. As a result, the dye IQ-12 is characterized by high $\eta = 8.76\%$ and an excellent current/voltage combination, namely, $I_{sc} = 17.97$ mA cm^{-2} and $V_{oc} = 715$ mV. The influence of two thienyl rings in the quinoxaline unit was explained by analogy to that of phenyl substituents (see above).

In order to attain PCE > 10%, Zhu and co-workers[145] used one of the most promising blocks, 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene ring (CPDT), as π-spacer. However, the result obtained for the dye IQ-21 (**128**) was somewhat lower, namely, $\eta = 9.04\%$ *vs.* 9.24% for IQ-4 (see Table 5) in spite of high molar extinction coefficients (to 66 600 litre mol^{-1} cm^{-1}) and broadening of the absorption band. This was explained by a decrease in V_{oc} (711 mV), which is to some extent compensated by improvement of the I_{sc} value (18.3 mA cm^{-2}). A study of the possibility of co-sensitization of the quinoxaline-based dye IQ-21 using a co-adsorbent (in a 3 : 1 ratio) revealed an increase in the PCE of compound IQ-21 (**128**) to $\eta = 10.41\%$, accompanied by improvement of other photovoltaic properties ($I_{sc} = 19.8$ mA cm^{-2}, $V_{oc} = 711$ mV, FF = 0.72). Such a large increase in PCE was explained by well-matched molecular structures and correct choice of the adsorbent/co-adsorbent ratio.

Taking quinoxaline sensitizers as examples, it was shown how their structure can influence the operating characteristics of the solar cells based on these dyes.[28] For instance, the introduction of bulky groups into the indoline donor [compounds YA-421 (**129**) and YA-422 (**130**) in Table 5] leads to high molar extinction coefficients, which in turn allows one to use thinner films for DSSC applications. Charge recombination is considerably retarded owing to the presence of long-chain alkoxy groups in the donor block; the best results were obtained for the cobalt redox electrolyte. The cells using graphene nanoflakes on top of the electrode coated with a gold film increased the PCE to almost a record high value of 10.65% (no co-adsorbents).[28]

An attempt to synthesize pyrazinoquinoxaline dyes was reported.[146] However, variation of substituents in the pyrazinoquinoxaline ring and in the donor unit [compounds PQ-1 (**131**) and PQ-2 (**132**) in Table 5] did not lead to high photovoltaic properties.

III.6. Fused pyridine-containing triazole and pyridazine sensitizers

As shown above (see Section III.3), the use of pyridine ring instead of benzene ring in benzothiadiazoles does not improve the photovoltaic properties. Although pyridothiadiazoles are characterized by a large bathochromic shift in the electronic absorption spectra, the DSSCs based on them demonstrate lower power conversion efficiencies than corresponding benzothiadiazole-based solar cells. Meanwhile, DSSCs containing a benzotriazole block with a long alkyl chain in position 2 of the ring (weaker electron acceptor than BTD) exhibit comparable and, in some cases, higher power conversion efficiencies (*cf.* the data in Tables 1 and 4). This seems surprising to many authors because the UV spectra of benzotriazole dyes exhibit a hypsochromic shift compared to the UV spectra of BTD.[147] Table 6 presents the data for a number of dyes based on triazolopyridines (compounds **133** – **139**) and pyridopyrazines (compounds **140**, **141**).

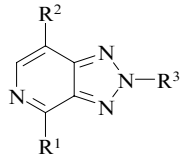
2*H*-[1,2,3]Triazolo[4,5-*c*]pyridines are characterized by much higher power conversion efficiencies than corresponding pyridothiadiazoles [*cf.*, *e.g.*, compounds SC-NPyT1 (**77**), SC-PyTN1 (**78**), SC-NPyT2 (**79**) and SC-PyTN2 (**74**) in Table 3 and compounds NPT-1 (**133**), PTN-1 (**134**), NPT-2 (**135**) and PTN-2 (**136**) in Table 6].[147, 149] Improved properties of triazolopyridines are due to the introduction of long alkyl chains into the donor unit of the sensitizer molecule and into the π-spacer in the acceptor fragment.[147] The most pronounced effect (PCE = 7.92%) was obtained when hexyl substituent was introduced into the π-spacer; this makes triazolopyridine block promising for the design of highly efficient organic sensitizers.

High photovoltaic properties were also demonstrated by the sensitizers based on pyrido[3,4-*b*]pyrazines.[148] The introduction of this additional acceptor (A^1) causes the absorption band to broaden. Taking the dye DT-1 (**140**) as an example, it was shown that the indoline block is more efficient than triphenylamine one: the highest PCE (8.57%) was attained for just this compound **140**. As for the YA-422 sensitizer (**130**, see Table 5), experiments with the cobalt electrolyte led to higher properties compared to the widely used iodide electrolyte.

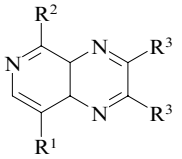
III.7. Diketopyrrolopyrrole sensitizers

Diketopyrrolopyrrole (DPP) is a major structural component of commercially available pigments that are widely used in dyes for automotive industry and in polymeric photovoltaic materials.[150] DPP-based materials usually exhibit valuable properties, such as intense fluorescence and high stability. Very strong electron-withdrawing properties of DPP make the compound attractive as internal acceptor for the D – A^1 – π – A^2 sensitizers. Indeed, pioneering studies by Tian and co-workers (see, *e.g.*, Ref. 151) showed that the introduction of DPP into the D – π – A structure extends the absorption band to the near-IR region. A number of examples are given in Table 7 (compounds **142** – **158**).

Table 6. Power conversion efficiencies of $D-A^1-\pi-A^2$ organic sensitizers with triazolopyridine and pyridopyrazine derivatives as additional acceptors.



133 – 139



140, **141**

Compound	Code	D	$\pi-A^2$	R^3	η (%)	Ref.
133	NPT-1	$R^1 = Ph_2N$–	R^2 =	C_6H_{13}	7.22	147
134	PTN-1	$R^2 = Ph_2N$–	R^1 =	C_6H_{13}	5.45	147
135	NPT-2	$R^1 = Ph_2N$–	R^2 =	C_6H_{13}	6.64	147
136	PTN-2	$R^2 = Ph_2N$–	R^1 =	C_6H_{13}	6.12	147
137	NPT-3	$R^1 = Ph_2N$–	R^2 =	C_6H_{13}	4.92	147
138	NPT-4	$R^1 = Ar_2N$– (Ar = 4-$C_6H_{13}OC_6H_4$)	R^2 =	C_6H_{13}	6.90	147
139	NPT-5	$R^1 = Ph_2N$–	R^2 =	C_6H_{13}	7.92	147
140	DT-1	R^1 = (Ar = 4-{2,4-[Bu^n(Et)$CHCH_2O]_2C_6H_{13}$}C_6H_4)	R^2 =	Ph	8.57	148
141	DT-2	$R^1 = Ar_2N$– (Ar = 4-{2,4-[Bu^n(Et)$CHCH_2O]_2C_6H_3$}C_6H_4)	R^2 =	Ph	7.74	148

However, further investigations showed that DPP-based sensitizers do not provide high power conversion efficiency. For instance, in spite of the bathochromic shift of the absorption band of compound DPP-II (**143**, see Table 7) to 627 nm, the short-circuit current is only 2 mA cm^{-2}. Thus, very strong electron-withdrawing properties of DPP cause a down-shift of the LUMO level to such a low value of 0.56 V that the driving force of electron transfer from the $D-A-\pi-A$ dye to the terminal acceptor group in the conduction band of TiO_2 becomes insufficient.

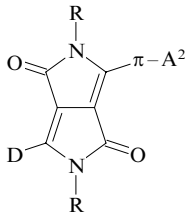
Nevertheless, strong electronic interaction between the donor block and DPP can be to some extent suppressed. Conjugated bridges comprised of five-membered (*e.g.*, thiophene) rings in the donor block are more planar than those built of six-membered (benzene) rings.[72] This can be exemplified by compound YCD-01 (**147**) where the introduction of thiophene instead of benzene ring suppressed electronic interaction between the donor and DPP and improved the PCE to 7.43%.[153] It follows that by varying the structure of the π-spacer between the donor and acceptor one can control the bathochromic shift of the absorption band, the HOMO and LUMO levels and the IPCE.

Although recent studies revealed the possibility of improving the efficiency of the $D-A^1-\pi-A^2$ sensitizers to PCE > 8% by tuning the design of the donor, acceptor and spacer blocks as well as using co-adsorbents and the cobalt(II/III) electrolyte,[156, 157] it must be admitted that strong internal acceptors provide no way to achieve record high PCE values.

III.8. Other $D-A^1-\pi-A^2$ organic sensitizers

Various heterocycles moieties were tested as additional acceptors. Examples are presented in Table 8 (compounds **159 – 203**).

Table 7. Power conversion efficiencies of D – A^1 – π – A^2 organic sensitizers with diketopyrrolopyrrole as additional acceptor.



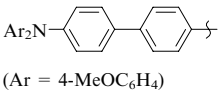
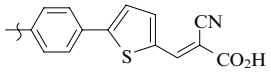
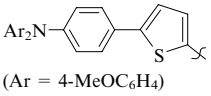
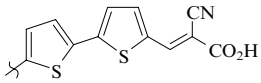
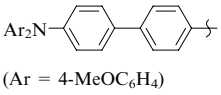
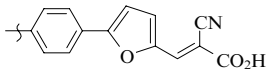
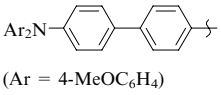
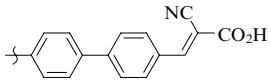
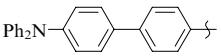
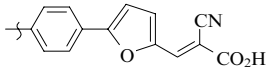
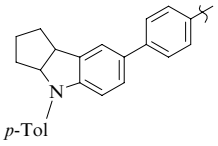
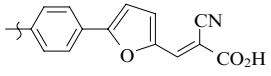
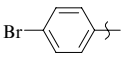
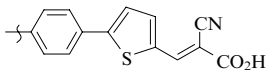
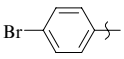
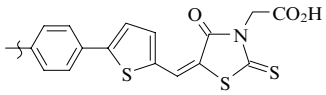
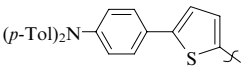
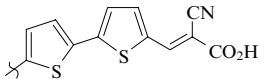
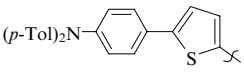
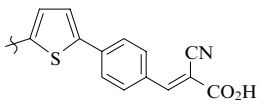
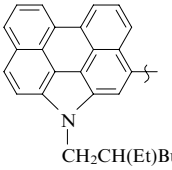
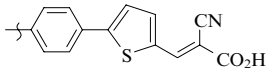
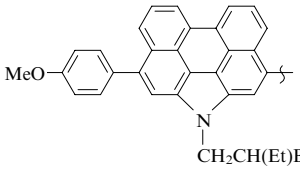
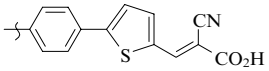
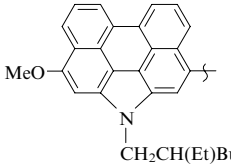
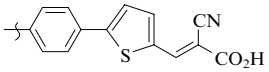
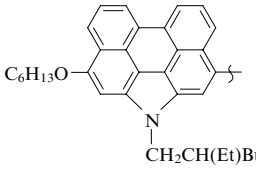
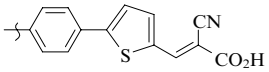
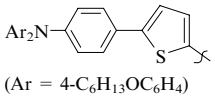
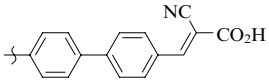
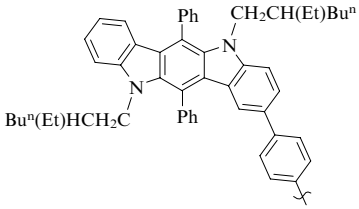
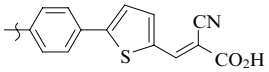
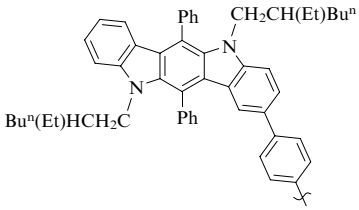
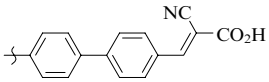
Compound	Code	D	π – A^2	R [a]	η (%)	Ref.
142	DPP-I	 (Ar = 4-$MeOC_6H_4$)		Bu^n	3.44	151
143	DPP-II	 (Ar = 4-$MeOC_6H_4$)		Bu^n	0.43	151
144	–	 (Ar = 4-$MeOC_6H_4$)		Bu^n	5.65	152
145	–	 (Ar = 4-$MeOC_6H_4$)		Bu^n	6.03	152
146	TD-01			Bu^n	5.18	153
147	YCD-01	 *p*-Tol		Alk	7.43	153
148	DPP-1			Alk	3.33	154
149	DPP-2			Alk	0.63	154
150	TDPP1			Alk	4.81	155
151	TDPP-2			Alk	3.42	155
152	ND-01	 $CH_2CH(Et)Bu^n$		Alk	7.46	156

Table 7 (continued).

Compound	Code	D	π – A[2]	R [a]	η (%)	Ref.
153	ND-02			Alk	8.30	156
154	ND-03			Alk	6.69	156
155	ND-04			Alk	7.01	156
156	DPP-07			Alk	7.30	157
157	T-1			Alk	8.24	158
158	T-2			Alk	7.83	158

[a] Alk = $CH_2CH(Et)Bu^n$.

1,3-Thiazole exhibits the properties of a moderate strength electron acceptor. Structure modification studies of carbazole sensitizers with the donor connected to the thiazole π-linker through the nitrogen or carbon atom were carried out. However, no high power conversion efficiency was achieved.[159] Nevertheless, it was established that the addition of carbazole ring at the carbon atom is more preferable. Two sensitizers with planar structure, LT-2 and LT-3 (compounds **160** and **161** in Table 8), were characterized by broad absorption bands and improved short-circuit current density, photoelectromotive force and, eventually, higher PCE values.

A series of sensitizers with bisthiazole block as internal acceptor (compounds **172** – **176**) were synthesized.[163, 164] Careful design of the donor moiety made it possible to achieve high V_{oc} (745 – 810 mV) and moderate power conversion efficiencies (η = 4.20% – 6.63%).

Researchers from Italy synthesized [165, 166, 173] a series of thiazolo[5,4-*d*]thiazole sensitizers (compounds **177** – **183**, see Table 8). It was shown that bulky electron-rich bis(pentyl)propylenedioxythiophene (ProDOT) groups near the electron-deficient thiazolothiazole block provide almost optimum physicochemical properties of the sensitizer, including a strong, broad absorption band in the visible region and very high molar extinction coefficient (9.67×10^{-4} litre mol^{-1} cm^{-1}). This makes the dyes very attractive for thin-film (3.0 – 6.5 μm) DSSC applications. Solar cells based on these dyes using CDCA as cosensitizer demonstrated PCE values to 7.71%. The dyes based on thiazolothiazoles are high stable, *viz.*, the PCE values remained almost unchanged after illumination of the solar cells over a period of 1000 h at 85 °C.

It should be noted that the introduction of benzene ring between two thiazole rings in the benzo[1,2-*d*:4,5-*d*]bisthiazole dyes BBZ-1 (**184**) and BBZ-2

Table 8. Power conversion efficiencies of other D – A^1 – π – A^2 organic sensitizers.

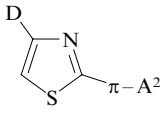
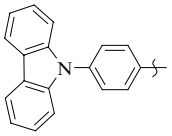
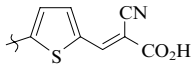
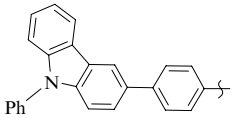
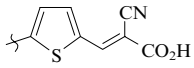
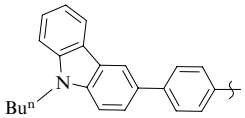
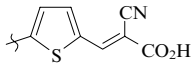
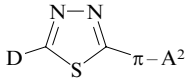
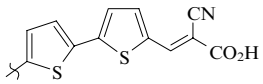
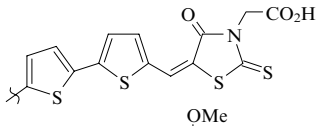
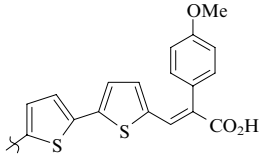
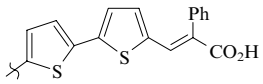
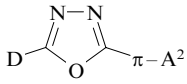
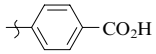
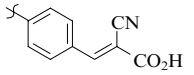
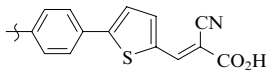
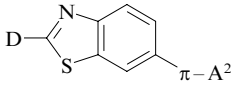
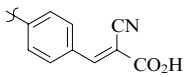
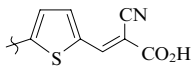
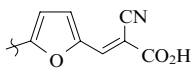
Compound	Code	D	π – A^2	η (%)	Ref.
					
159	LT-1			2.01	159
160	LT-2			4.72	159
161	LT-3			4.47	159
					
162	–	Ar_2N– (Ar = 4-$Bu^tC_6H_4$)		4.12	160
163	–	Ar_2N– (Ar = 4-$Bu^tC_6H_4$)		1.95	160
164	–	Ar_2N– (Ar = 4-$Bu^tC_6H_4$)		2.74	160
165	–	Ar_2N– (Ar = 4-$Bu^tC_6H_4$)		3.10	160
					
166	OD-1	Ph_2N–		0.80	161
167	OD-2	Ph_2N–		1.76	161
168	OD-3	Ph_2N–		2.72	161
					
169	Z-1	Ar_2N– (Ar = 4-$MeOC_6H_4$)		3.15	162
170	Z-2	Ar_2N– (Ar = 4-$MeOC_6H_4$)		4.16	162
171	Z-3	Ar_2N– (Ar = 4-$MeOC_6H_4$)		4.12	162

Table 8 (continued).

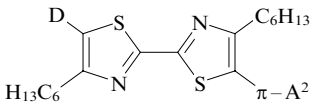
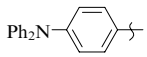
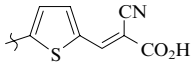
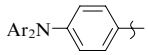
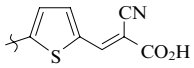
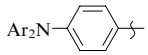
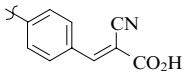
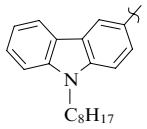
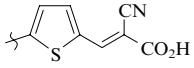
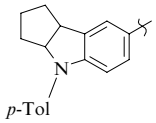
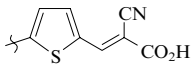
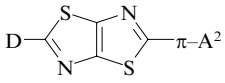
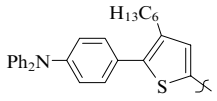
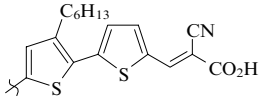
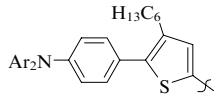
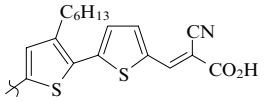
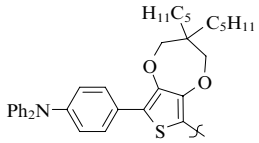
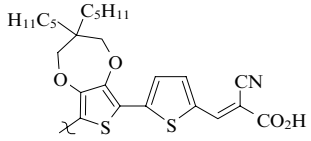
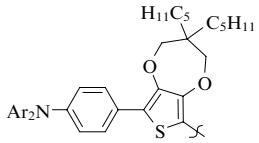
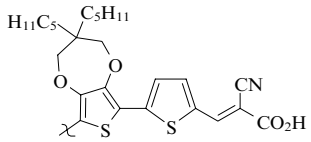
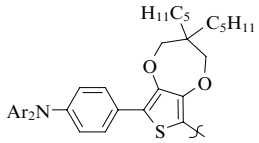
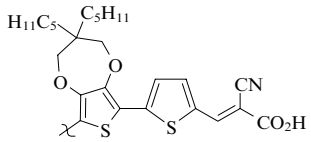
Compound	Code	D	π – A²	η (%)	Ref.
					
172	T1 BTT-II			5.73 6.19	163 164
173	T3	 (Ar = 4-MeOC$_6$H$_4$)		4.48	163
174	T4	 (Ar = 4-MeOC$_6$H$_4$)		4.20	163
175	BTT-I			5.53	164
176	BTT-III			6.63	164
					
177	TTZ-1			3.53 [a]	165
178	TTZ-2	 (Ar = 4-MeOC$_6$H$_4$)		2.53 [a]	165
179	TTZ-3			6.54 [a]	166
180	TTZ-4	 (Ar = 4-C$_6$H$_{13}$SC$_6$H$_4$)		5.71 [a]	166
181	TTZ-5	 (Ar = 4-C$_6$H$_{13}$SC$_6$H$_4$)		7.71 [a]	166

Table 8 (continued).

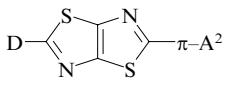
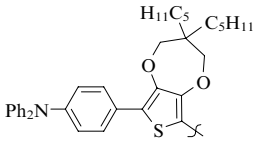
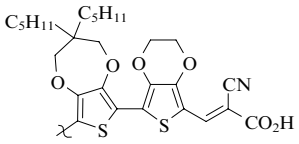
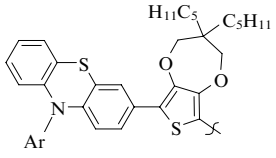
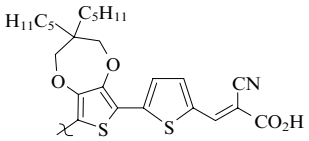
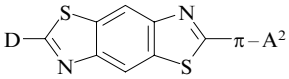
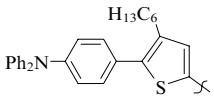
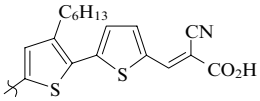
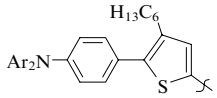
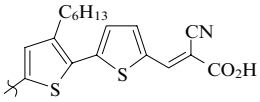
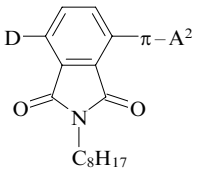
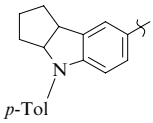
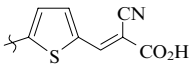
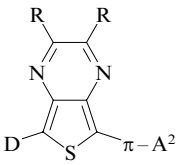
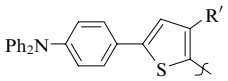
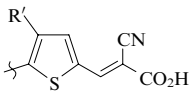
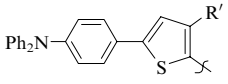
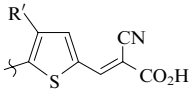
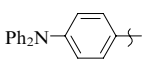
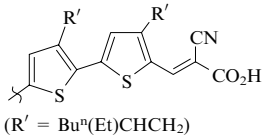
Compound	Code	D	π – A²	η (%)	Ref.
					
182	TTZ-6			5.03 [a]	166
183	TTZ-7	 (Ar = 4-MeOC$_6$H$_4$)		6.94 [a]	166
					
184	BBZ-1			2.32 [a]	165
185	BBZ-2	 (Ar = 4-MeOC$_6$H$_4$)		1.67 [a]	165
					
186	LS-2			5.11	129
					
187	FNE-32 (R = H)	 (R′ = Bu^n(Et)CHCH$_2$)		3.66	167
188	FNE-34 (see [b])	 (R′ = Bu^n(Et)CHCH$_2$)		5.30	167
189	FNE-36 (see [b])		 (R′ = Bu^n(Et)CHCH$_2$)	4.93	167

Table 8 (continued).

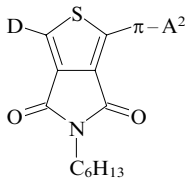
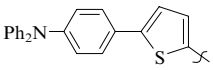
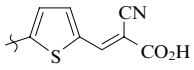
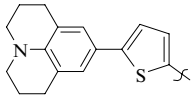
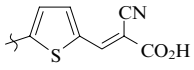
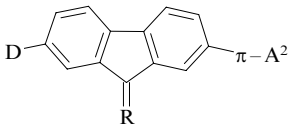
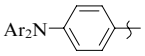
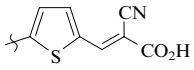
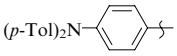
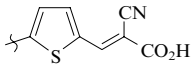
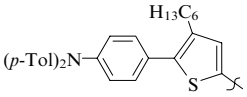
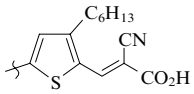
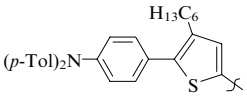
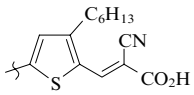
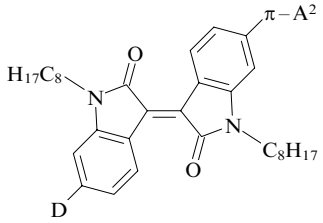
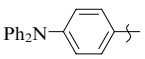
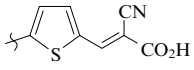
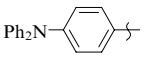
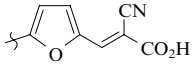
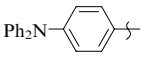
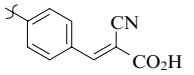
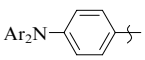
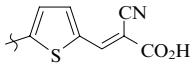
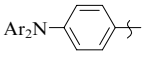
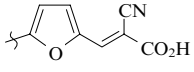
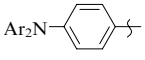
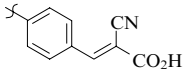
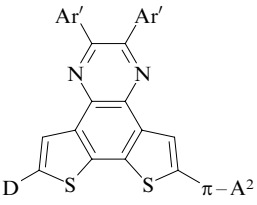
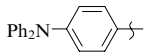
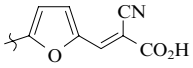
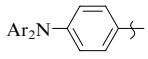
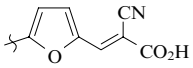
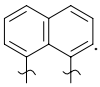
Compound	Code	D	π – A^2	η (%)	Ref.
					
190	FNE-38			5.16 [a]	168
191	FNE-39			2.99 [a]	168
					
192	HIQF-1 (R = O)	 (Ar = 4-[Bu^n(Et)CHCH$_2$O]C$_6$H$_4$)		6.26	169
193	HIQF-2 (R = O)			5.66	169
194	Dye-1 (R = O)			5.33	170
195	Dye-2 (R = C(CN)$_2$)			1.25	170
					
196	ID-1			3.52	171
197	ID-2			3.92	171
198	ID-3			3.33	171
199	ID-4	 (Ar = 4-MeOC$_6$H$_4$)		4.36	171
200	ID-5	 (Ar = 4-MeOC$_6$H$_4$)		4.41	171
201	ID-6	 (Ar = 4-MeOC$_6$H$_4$)		5.35	171

Table 8 (continued).

Compound	Code	D	π – A²	η (%)	Ref.
		 ($Ar' = 4\text{-}C_6H_{13}OC_6H_4$)			
202	QBT-4			8.41 [a]	172
203	QBT-5	 ($Ar = 4\text{-}MeOC_6H_4$)		8.08 [a]	172

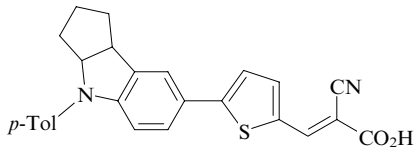
[a] In the presence of CDCA additive. [b] R – R = .

(**185**) led to abrupt decrease in the power conversion efficiency to 1% – 3% even in the presence of CDCA as co-adsorbent.[165]

Phthalimide is a strong electron acceptor. Structure modification of this molecule is possible at the imido nitrogen atom. However, only one phthalimide-based sensitizer, the dye LS-2 (**186**, see Table 8) was synthesized.[129] It was found unexpectedly that the absorption band in the UV spectrum of this compound undergoes a hypsochromic shift even compared to the spectrum of compound LS-1 (**204**) whose structure contains no additional acceptor. According to DFT calculations, the indoline donor and thienyl spacer deviate from the phthalimide ring plane owing to steric hindrance due to the phthalimide carbonyl groups. Thus, the introduction of phthalimide acceptor into the D – π – A molecule causes no broadening of the absorption band and does not improve the photocurrent voltage. It follows that phthalimide is inappropriate for the synthesis of highly efficient D – A¹ – π – A² sensitizers.

Thieno[3,4-*b*]pyrazine is also a strong acceptor.[174] Wang and co-workers[167] introduced it into the structure of three organic sensitizers, FNE-32 (**187**), FNE-34 (**188**) and FNE-36 (**189**) (see Table 8). This led to a considerable bathochromic shift from $\lambda_{max} = 596 - 625$ nm to the near-IR region with $\lambda > 800$ nm. Of particular interest is the fact that the DSSCs based on compound **188** exhibited efficient photon-to-electron conversion throughout the visible region and in the near-IR region (> 900 nm); this is comparable with the data obtained for the established ruthenium sensitizer N719 (**93**). However, the thienopyrazine sensitizer FNE-34 has the same band gap as the inefficient DPP-based dyes (see Section III.7). It was concluded that careful optimization of the HOMO and LUMO levels is critical to narrow-band sensitizers.

Structure 204



204 (LS-1, $\eta = 4.42\%$)

Wang and co-workers[175] used thieno[3,4-*c*]pyrrole-4,6-dione (TPD) as internal acceptor and found that the influence of the TPD block on the absorption spectra to a great extent depends on the donor moiety. For instance, no large bathochromic shift of sensitizer's charge transfer band ($\lambda_{max} = 485$ nm) occurs when triphenylamine is used as donor [compound FNE-38 (**190**) in Table 8], whereas the introduction of 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline as donor [compound FNE-39 (**191**) in Table 8] leads to a considerable broadening of the absorption band to λ_{max} 510 nm. Nevertheless, although the TPD block retards charge recombination at the TiO_2/dye/electrolyte interfaces and improves the photovoltaic properties, the photocurrent in the solar cells based on the TPD sensitizers decreases rather than increases. Besides, like in the case of phthalimide, TPD causes the donor and terminal acceptor blocks to deviate from the TPD ring plane owing to steric interaction with the TPD carbonyl groups.

Fluorenone- and 9-(dicyanomethylene)fluorene-based photosensitizers were synthesized.[169, 170] The fluorenone-base compounds HIQF-1 and HIQF-2 [**192** and **193** in Table 8, respectively] have a strong charge transfer band (~500 nm) both in solution and on the TiO_2 surface. Both dyes efficiently sensitize nanocrystalline TiO_2 in the region from 300 to 700 nm and exhibit a 80% plateau in the IPCE spectrum in the most part of the visible region. As a result, the fluorenone dyes are characterized by $\eta = 5\% - 7\%$. It should be noted that the introduction of dicyanomethylene unit instead of ketone group causes an abrupt, more than fourfold, decrease in η. This was explained by violation of excited state delocalization between the strong acceptor blocks (dicyanomethylenofluorene and cyanoacrylic acid), which influences the efficiency of electron transfer from the dye to the conduction band of TiO_2.

High power conversion efficiencies were obtained upon introduction of dithieno[3,2-*f*:2′,3′-*h*]quinoxaline as internal acceptor [compounds QBT-4 (**202**) and QBT-5 (**203**) in Table 8].[172] Both compounds have a broad absorption band (λ_{max} = 368 – 487 nm) with high molar extinction coefficient (~40 000 litre mol^{-1} cm^{-1}). It is believed that in this case dye aggregation in the film favours an increase in photocurrent, which leads to high PCE values (~8%).

Thus, the introduction of internal additional acceptor to optimize the energy levels and to broaden the absorption band significantly improves the photovoltaic properties and photostability of DSSCs. It was established that the additional acceptor bonded to the electron donor can considerably enhance the overall 'push-pull' effect in the molecule by varying positions of the frontier MO levels and the absorption properties of the $D-A^1-\pi-A^2$ sensitizers. Charge transfer can be significantly facilitated when electrons follow a consecutive pathway from the donor to the A^1 acceptor and then to the terminal acceptor A^2. When choosing an appropriate additional acceptor, one should strike a compromise between efficient absorption and the frontier MO energy levels. Therefore, strong electron acceptors like diketopyrrole are undesirable because they can violate the overall π-conjugation system. The π-spacer also plays an important role in this configuration, *viz.*, a properly chosen π-spacer should not only broaden the absorption band, but also reduce recombination losses. An important advantage of the internal acceptor is that it can participate in charge distribution and act an anti-aggregation unit. It should be noted that the $D-A^1-\pi-A^2$ configuration can be used not only for metal-free sensitizers, but also for, *e.g.*, porphyrin dyes that allow one to attain a record high PCE of 13%.[20] Taken altogether, these undoubtful advantages make the $D-A^1-\pi-A^2$ system highly attractive for researchers.

IV. Donor(1) – donor(2) – π-spacer – acceptor organic sensitizers

Unlike well-studied structures of the $D-A^1-\pi-A^2$ type, a few data on the $D^1-D^2-\pi-A$ structures are available at the moment. Compared to the $D-\pi-A$, this type of sensitizers is characterized by a bathochromic shift in the absorption spectrum, high molar extinction coefficients and high thermal stability.[176] A number of examples (compounds **205** – **232**) are presented in Table 9. Also, by varying substituents in the distant donor group (D^1) one can control the HOMO and LUMO energies. However, this does not always obey the laws characteristic of the $D-A^1-\pi-A^2$ structures. In particular, the sensitizer P-2 (**206**, see Table 9) with the triphenylamine terminal donor group unexpectedly demonstrated a higher power conversion efficiency than the corresponding dye P-1 (**205**) with *p*-methoxyphenyl groups and the sensitizer P-3 (**207**) with the diphenylethylene moiety.[177]

Nevertheless, the internal donor D^2 governs the photovoltaic properties of dyes. It was established that the use of phenothiazines as internal donors significantly improves the stability of dyes and enhances π-conjugation in chromophores, thus improving the photovoltaic properties (compounds **205** – **209**, see Table 9).[177, 178]

Dyes with carbazole internal donor blocks also proved themselves.[179, 180] All of them are characterized by high molar extinction coefficients of the charge transfer bands and appropriate HOMO and LUMO energies; this facilitates electron transfer from the excited sensitizer to the conduction band of TiO_2 and regeneration of the oxidized dye with an electrolyte. Compared to the sensitizers **223** – **225** with the carbazole terminal donors connected through the phenylene linker, the dyes in question demonstrated better light harvesting ability. The main drawback of these systems is that radical cations produced upon the loss of electrons are unstable.[186] They can be stabilized by introducing certain groups to increase the donor strength of carbazole into the carbazole ring.[187, 188] Even better results were obtained using two carbazole rings as successively arranged donors (compounds **211** – **214** and **217** – **220** in Table 9).[180]

The $D^1-D^2-\pi-A$ concept was then developed by Zhu and co-workers,[183] who used indoline as internal donor. Note that indoline was also employed in the design of the $D-A^1-\pi-A^2$ dyes (see Section III). It was found that the thiophene or furan π-spacers improve all photovoltaic properties including the open-circuit voltage, suppression of charge recombination and the photostability.

Two sensitizers, DT-3 (**232**) and DW-3 (**231**), are of particular interest as belonging to starburst dyes.[27] Structure modification by introducing biscarbazolyl(triphenylamine) or bis(diphenylaminophenyl)carbazole as donors led to improvement of almost all photovoltaic properties, especially, the open-circuit voltage. Mixed dithiophene and 3,4-ethylenedioxythiophene (EDOT) blocks made it possible to delocalize the electron density in the intermediate radical species. This improved the stability of the dyes on the one hand, and increased the bathochromic shift of the absorption maximum and the molar extinction coefficient, on the other hand. The introduction of two long alkyl chains into the bithiophene spacer caused suppression of dye aggregation and enhancement of the dye solubility and the ability to form dense self-assembling layers to prevent recombination of injected electrons. These two sensitizers exhibited excellent photostability on the TiO_2 surface. The best of them, DT-3, demonstrated very high PCE values in liquid DSSCs. Taken altogether, these data are indicative of great prospects for targeted molecular design using starburst organic sensitizers.

V. Other structural types of organic sensitizers

Various donor/acceptor combinations to design organic sensitizers have been proposed in the last decade. This review concerns only the dyes with the terminal acceptor groups that can anchor to the TiO_2 surface, namely, the $A-\pi-D-\pi-A$ and $A-D-\pi-D-A$ systems.

V.1. The A –π– D – π – A organic sensitizers

Recently, there has been increasing interest in the sensitizers with multiple terminal groups (so-called 2A dyes). These systems can anchor to the TiO_2 surface at

Table 9. Power conversion efficiencies of $D^1-D^2-\pi-A$ organic sensitizers.

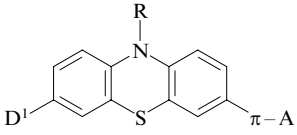
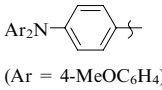
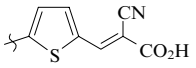
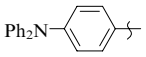
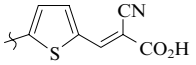
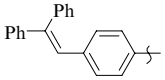
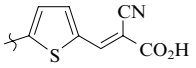
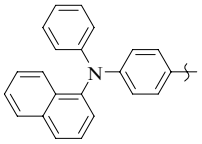
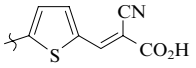
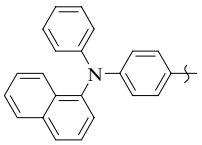
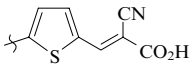
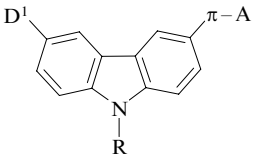
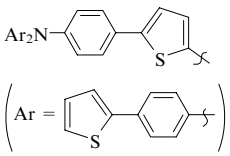
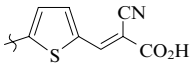
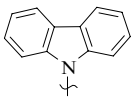
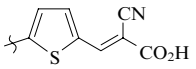
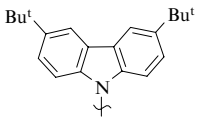
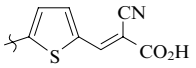
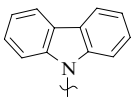
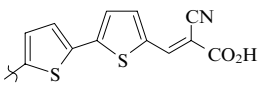
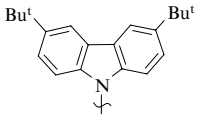
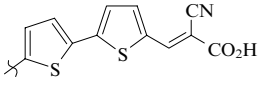
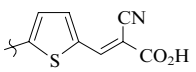
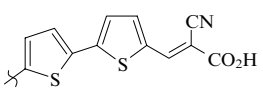
Compound	Code	D^1	$\pi-A$	R	η (%)	Ref.
						
205	P-1			C_8H_{17}	3.78	177
206	P-2			C_8H_{17}	4.41	177
207	P-3			C_8H_{17}	2.48	177
208	NPtS-C_6			C_6H_{13}	2.04	178
209	NPtS-T			Ar′ (see [a])	4.24	178
						
210	TTC-104			Et	6.37	179
211	–			Bu^n	4.22	180
212	–			Bu^n	4.95	179
213	–			Bu^n	6.04	180
214	–			Bu^n	5.48	180
215	C-1	Ph_2N		Bu^n	6.05	181
216	C-2	Ph_2N		Bu^n	6.83	181

Table 9 (continued).

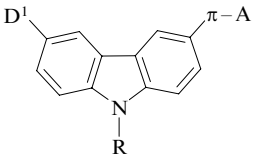
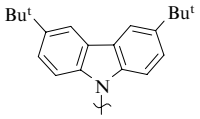
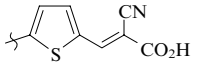
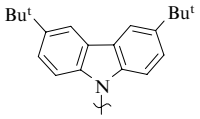
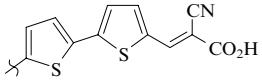
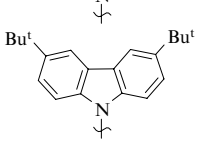
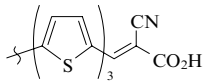
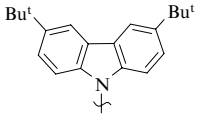
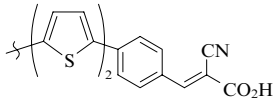
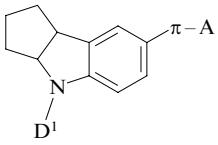
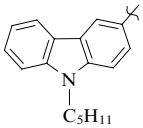
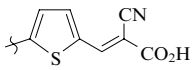
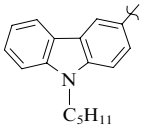
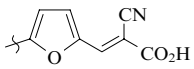
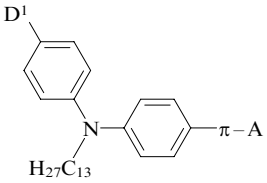
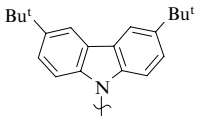
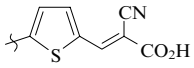
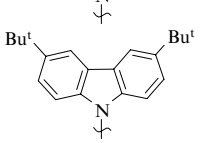
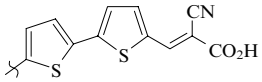
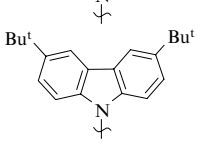
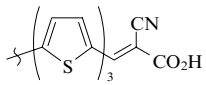
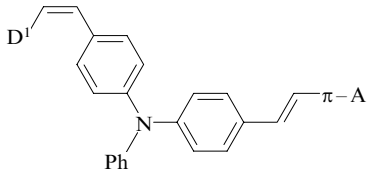
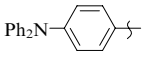
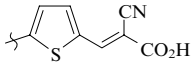
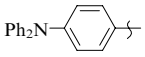
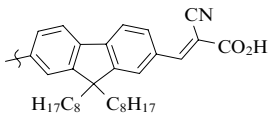
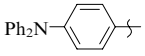
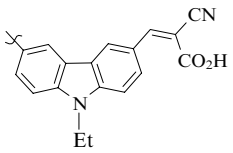
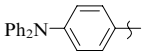
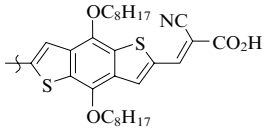
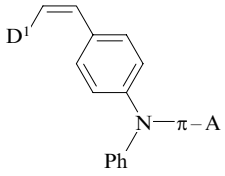
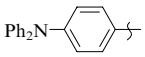
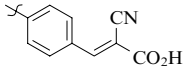
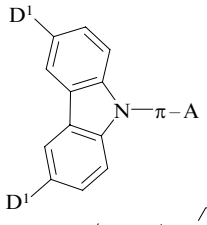
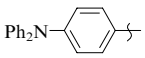
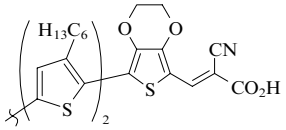
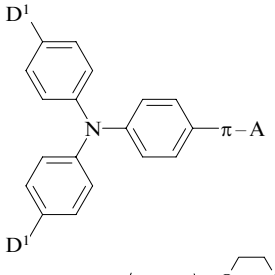
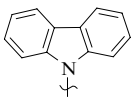
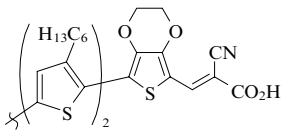
Compound	Code	D^1	π – A	R	η (%)	Ref.
						
217	CCT1A			$C_{12}H_{25}$	3.64	182
218	CCT2A			$C_{12}H_{25}$	4.80	182
219	CCT3A			$C_{12}H_{25}$	5.69	182
220	CCT2PA			$C_{12}H_{25}$	4.82	182
						
221	WBS-1T				9.29	183
222	WBS-1F				9.49	183
						
223	UB-1				3.52	184
224	UB-2				4.10	184
225	UB-3				5.12	184

Table 9 (continued).

Compound	Code	D[1]	π – A	R	η (%)	Ref.
						
226	TPAM-2				4.83	185
227	TPAM-3				5.41	185
228	TPAM-4				2.26	185
229	TPAM-5				3.39	185
						
230	TPAM-1				5.67	185
						
231	DW-3				10.03 [b]	27
						
232	DT-3				9.15 [b]	27

[a] Ar′ = 4-(*p*-Tol)$_2$NC$_6$H$_4$. [b] In the presence of a liquid electrolyte.

two sites, thus increasing the number of electron injection channels to improve the photocurrent and stability of the associates.[26, 189 – 195] The A – π – D – π – A dyes with two anchor/acceptor groups exhibit a higher photocurrent[196, 197] than their D – π – A precursors with one acceptor group owing to better light harvesting, *i.e.*, a broader absorption band and more intense absorption. Often, the introduction of two terminal groups leads to high molar extinction coefficients in the visible region, which in turn contributes to the short-circuit current.[198, 199] The main advantage of such compounds is that the efficiency typical of thicker nanostructured semiconductor films can be attained using thinner films; this is of paramount importance for the DSSC applications.[200] However, no higher photovoltage is often generated because the extra protons released from the A – π – D – π – A molecules cause the Fermi level of TiO_2 to down-shift and lead to inefficient suppression of dark current. Therefore, in this review we will consider only the very recent data concerning this type of sensitizers. Some examples are presented in Table 10 (compounds **233** – **249**).

A series of 2,3,4-trisubstituted thiophene-based sensitizers DA1 – DA3 (**236** – **238**) exhibited the power conversion efficiencies exceeding a value of 7%.[202] These dyes increase the electron injection efficiency and more effectively suppress dark current compared to their D – π – A congeners.[202]

Considerable advances were made in the studies of sensitizers based on phenothiazine and cyanoacrylic acid as terminal groups.[203, 204] Two terminal groups favour charge generation and transfer to the TiO_2 surface, while the introduction of hexyl chains into the π-spacer efficiently suppresses dye aggregation and charge recombination, thus increasing the power conversion efficiency to 7.31%. Even higher photovoltaic parameters were attained upon introduction of 2,6-bis(alkoxy)phenyl substituent at the phenothiazine nitrogen atom [compounds HL5 – HL7 (**241** – **243**) in Table 10]. A bathochromic shift of the absorption band of the dye and better suppression of dark current and dye aggregation on the TiO_2 surface led to a power conversion efficiency exceeding a value of 8% for compound HL-7; this is comparable with the results obtained for the solar cells based on the N719 complex (**93**).[204]

A series of imidazole-based sensitizers (compounds **245** – **249** in Table 10) were synthesized recently.[205] However, attempts to attain a high power conversion efficiency by varying the structure of the donor fragment and by introducing long alkyl chains failed (η = 3.21% – 3.54%; the addition of co-adsorbents improves the PCE to 4.11%). Interesting data were obtained for the NH-sensitizer TL-5 (**249**) with properties superior to those of the N-alkyl compound TL-1 (**245**).[205] This unexpected result was explained by electron injection from the photo-excited dye molecule on the TiO_2 surface.

V.2. The A – D – π – D – A organic sensitizers

V.2.a. Symmetrical A – D – π – D – A-sensitizers

The introduction of a dithienopyrrole unit as donor linker into the molecule enhances not only the charge carrier mobility, but also the light-harvesting ability of the dye.[206] The main advantage of compounds FD1 – FD3 (**250a** – **c**) is a very high molar extinction coefficient (up to 145 000 litre mol^{-1} cm^{-1}), which significantly improves the parameters of the DSSCs.

Two sensitizers, DP-1 (**251**) and DP-2 (**252**), containing *N*-octylphenothiazine as donor, cyanoacrylic acid as acceptor and 9,9-dihexylfluorene and 2,2′-(9,9-dihexylfluorene-2,7-diyl)dithiophene as donor linkers, exhibited high molar extinction coefficients and a bathochromic shift of the absorption band; this improves the short-circuit current.[207] The introduction of two thiophene rings into the DP-2 molecule further extends the conjugation system, thus increasing the molar extinction coefficient. However, this is accompanied by π-aggregation of the dye on the TiO_2 surface and, as a consequence, by a decrease in the electron injection efficiency and power conversion efficiency (η = 4.21%).

Table 10. Power conversion efficiencies of symmetrical A – π – D – π – A organic sensitizers.

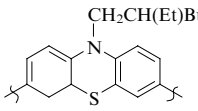
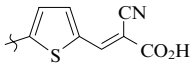
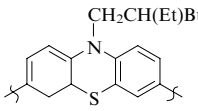
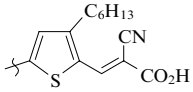
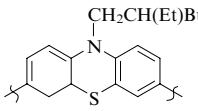
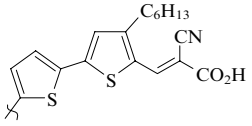
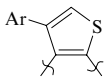
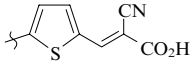
Compound	Code	D	π – A	η (%)	Ref.
233	HL-2			5.53	198
234	HL-3			6.85	198
235	HL-4			7.31	198
236	DA-1	 (Ar = 4-$Ph_2NC_6H_4$)		6.33	197

Table 10 (continued).

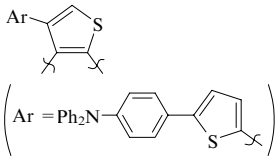
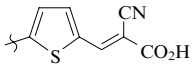
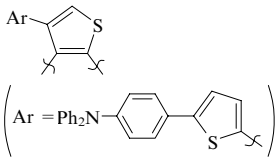
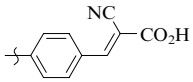
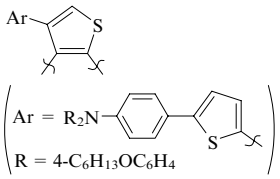
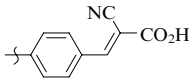
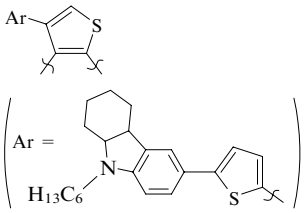
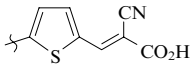
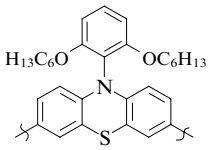
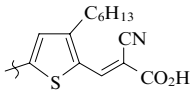
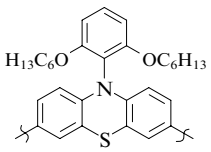
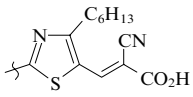
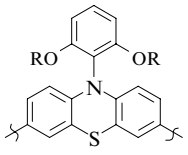
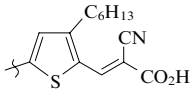
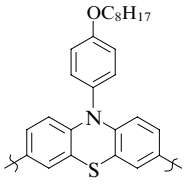
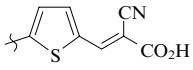
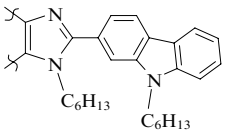
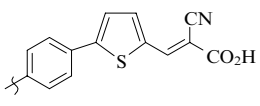
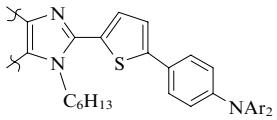
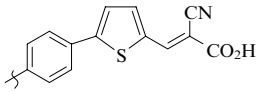
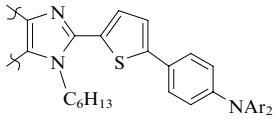
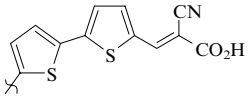
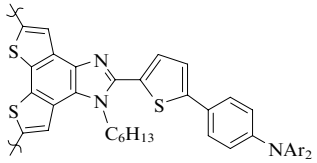
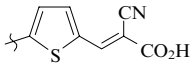
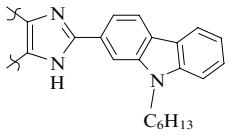
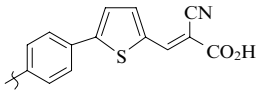
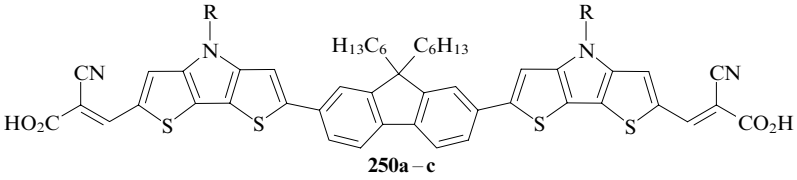
Compound	Code	D	π – A	η (%)	Ref.
237	DA-2			7.02	197
238	DA-3			5.56	197
239	DA-4			2.60	197
240	DA-5			7.28	197
241	HL-5			7.80	199
242	HL-6			7.43	199
243	HL-7			8.32	199
244	PTDA			6.82	200
245	TL-1			3.21	201

Table 10 (continued).

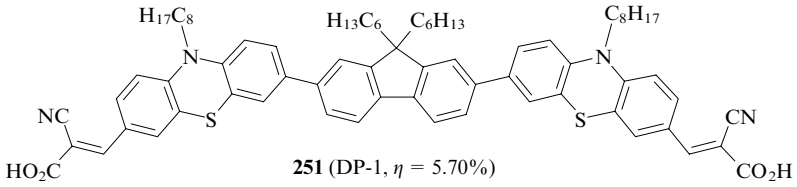
Compound	Code	D	π – A	η (%)	Ref.
246	TL-2	 (Ar = 4-$C_6H_{13}OC_6H_4$)		3.29	201
247	TL-3	 (Ar = 4-$C_6H_{13}OC_6H_4$)		3.34	201
248	TL-4	 (Ar = 4-$C_6H_{13}OC_6H_4$)		3.54	201
249	TL-5			4.11	201

Structures 250 – 254

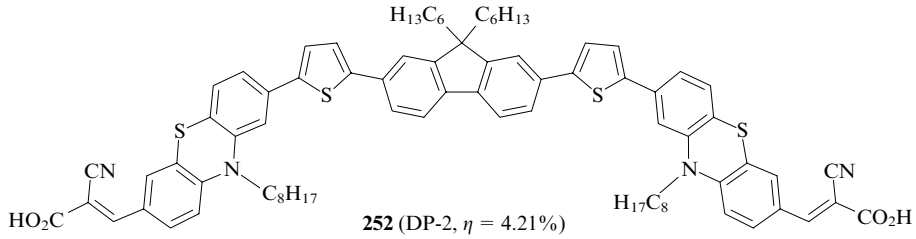


250a – c

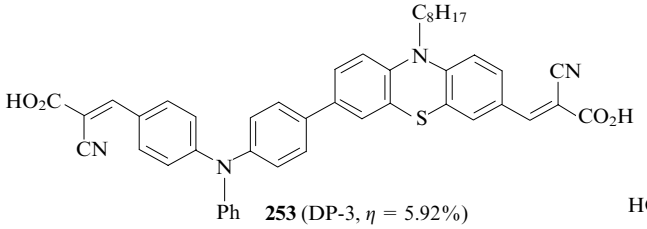
R = C_6H_{13} (**a**, FD-1; η = 5.66%),
4-$MeOC_6H_4$ (**b**, FD-2; η = 6.36%),
4-(*p*-Tol)$_2NC_6H_4$ (**c**, FD-3; η = 4.95%)



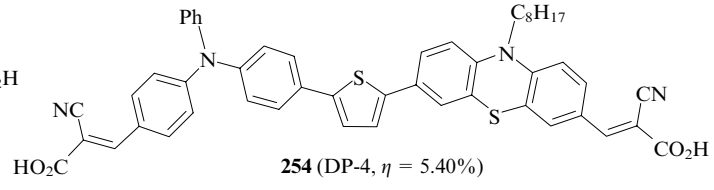
251 (DP-1, η = 5.70%)



252 (DP-2, η = 4.21%)



253 (DP-3, η = 5.92%)



254 (DP-4, η = 5.40%)

V.2.b. Asymmetrical A – D – π – D – A-sensitizers

Among structures with two terminal acceptor groups used to attain high photovoltaic parameters, symmetrical compounds are mainly studied (see Section V.2.a). Asymmetrical structures have been investigated since very recently [208] because these compounds are difficult to synthesize. Researchers from China synthesized asymmetrical sensitizers DP-3 (**253**) and DP-4 (**254**) containing phenothiazine and triphenylamine as donors and cyanoacrylic acid as acceptor.[209] The thiophene ring in compound DP-4 acts as a π-spacer. Similarly to the symmetrical dyes with two terminal acceptor groups (see above), these asymmetrical compounds demonstrated a broader absorption region, high molar extinction coeffcients and IPCE and the short-circuit current density. However, the power conversion efficiency appeared to be low (< 6%). The introduction of additional thienyl π-spacer unexpectedly deteriorated the properties of the sensitizer (compound DP-4). Thus, the advantages of asymmetrical dyes still remain a moot question because the synthesis of these compounds is labour-consuming.

VI. Conclusion

In this review we considered the influence of structural factors on the photovoltaic properties (first of all, the PCE) of the modified structures of the D – π – A organic sensitizers. Usually, structure modifications involve the introduction of additional donor and acceptor groups or π-spacers. A very popular research avenue is to introduce linkers between the donor and the π-spacer to obtain two structural types, $D-A^1-\pi-A^2$ and $D^1-D^2-\pi-A$. However, it is still unclear which is holds more promise, since both have their benefits and disadvantages. A promising alternative in the search for efficient sensitizers is to synthesize starburst dyes. This class of compounds was only touched upon because we restricted ourselves to analysis of the structural types mentioned in the Introduction. Although being beyond the scope of our review, starburst dyes deserve particular consideration.

A common drawback of many studies is that their authors strive to synthesize structurally complicated compounds by introducing a large number of additional donors and π-spacers. Often, this does not significantly improve the photovoltaic properties but makes the synthesis labour-consuming, thus excluding the dyes in question from candidate materials for the DSSC applications. One should keep in mind that one of the main potential advantages of metal-free organic sensitizers over organometallic ones is their low cost and the possibility of being used in practice.

The title field makes very rapid progress. Indeed, a period of a few weeks since we completed the list of references was marked by a number of new publications on the structural types in question.[210 – 214]

Unfortunately, the available methods for calculating the power conversion efficiency are not credible; therefore, it is difficult to predict the pathways of the design and synthesis of organic sensitizers. This field of science is in the early stage of its development. We hope that the materials presented above will be useful for chemists and physicists to gain a deeper insight into the structural features of the known organic dyes and to choose their own, the only right way for future research.

The review has been written with the financial support from the Russian Science Foundation (RSF Project No. 15-13-10022).

References

1. M Graetzel, R A J Janssen, D B Mitzi, E H Sargent *Nature (London)* **488** 304 (2012)
2. B O'Reagen, M Gritzel *Nature (London)* **353** 737 (1991)
3. W-Q Wu, H-L Feng, H-S Rao, Y-F Xu, D-B Kuang, C-Y Su *Nat. Commun.* **5** Art. No. 3968 (2014)
4. M Gritzel *J. Photochem. Photobiol. C* **4** 145 (2003)
5. A Hagfeldt, G Boschloo, L Sun, L Kloo, H Pettersson *Chem. Rev.* **110** 6595 (2010)
6. C Grätzel, S M Zakeeruddin *Mater. Today* **16** 11 (2013)
7. Z-Z Sun, Q-S Li, P-P Sun, Z-S Li *J. Power Sources* **276** 230 (2015)
8. H Cheema, L Ogbose, A El-Shafei *Dyes Pigm.* **113** 151 (2015)
9. Z Ning, Y Fu, H Tian *Energy Environ. Sci.* **3** 1170 (2010)
10. T Mohr, V Aroulmoji, R S Ravindran, M Müller, S Ranjitha, G Rajarajan, P M Anbarasan *Spectrochim. Acta, Part A* **135** 1066 (2015)
11. C-C Chou, F-C Hu, H-H Yeh, H-P Wu, Y Chi, J N Clifford, E Palomares, S-H Liu, P-T Chou, G-H Lee *Angew. Chem., Int. Ed.* **53** 178 (2014)
12. Y Chiba, A Islam, Y Watanabe, R Komiya, N Koide, L Han *Jpn. J. Appl. Phys.* **45** L638 (2006)
13. F Gao, Y Wang, D Shi, J Zhang, M Wang, X Jing, R Humphry-Baker, P Wang, S M Zakeeruddin, M Gritzel *J. Am. Chem. Soc.* **130** 10720 (2008)
14. C-Y Chen, M Wang, J-Y Li, N Pootrakulchote, L Alibabaei, C-h Ngoc-le, J-D Decoppet, J-H Tsai, C Grätzel, C-G Wu, S M Zakeeruddin, M Grätzel *ACS Nano* **3** 3103 (2009)
15. Y Cao, Y Bai, Q Yu, Y Cheng, S Liu, D Shi, F Gao, P Wang *J. Phys. Chem. C* **113** 6290 (2009)
16. F Sauvage, J-D Decoppet, M Zhang, S M Zakeeruddin, P Comte, M Nazeeruddin, P Wang, M Grätzel *J. Am. Chem. Soc.* **133** 9304 (2011)
17. W-Q Wu, Y-F Xu, H-S Rao, C-Y Su, D-B Kuang *J. Am. Chem. Soc.* **136** 6437 (2014)
18. M K Nazeeruddin, P Péchy, T Renouard, S M Zakeeruddin, R Humphry-Baker, P Comte, P Liska, L Cevey, E Costa, V Shklover, L Spiccia, G B Deacon, C A Bignozzi, M Grätzel *J. Am. Chem. Soc.* **123** 1613 (2001)
19. A Yella, H-W Lee, H N Tsao, C Yi, A Chandiran, M K Nazeeruddin, E W-G Diau, C-Y Yeh, S M Zakeeruddin, M Gritzel *Science* **334** 629 (2011)
20. S Mathew, A Yella, P Gao, R Humphry-Baker, B F E Curchod, N Ashari-Astani, I Tavernelli, U Rothlisberger, M K Nazeeruddin, M Grätzel *Nat. Chem.* **6** 242 (2014)
21. A Yella, C-L Mai, S M Zakeeruddin, S-N Chang, C-H Hsieh, C-Y Yeh, M Grätzel *Angew. Chem., Int. Ed.* **53** 2973 (2014)
22. J Luo, M Xu, R Li, K-W Huang, C Jiang, Q Qi, W Zeng, J Zhang, C Chi, P Wang, J Wu *J. Am. Chem. Soc.* **136** 265 (2014)
23. S M Feldt, E A Gibson, E Gabrielsson, L Sun, G Boschloo, A Hagfeldt *J. Am. Chem. Soc.* **132** 16714 (2010)
24. W Zeng, Y Cao, Y Bai, Y Wang, Y Shi, M Zhang, F Wang, C Pan, P Wang *Chem. Mater.* **22** 1915 (2010)

25. Y Cao, N Cai, Y Wang, R Li, Y Yuan, P Wang *Phys. Chem. Chem. Phys.* **14** 8282 (2012)
26. M Zhang, Y Wang, M Xu, W Ma, R Li, P Wang *Energy Environ. Sci.* **6** 2944 (2013)
27. L-L Tan, J-F Huang, Y Shen, L-M Xiao, J-M Liu, D-B Kuang, C-Y Su *J. Mater. Chem. A* **2** 8988 (2014)
28. J Yang, P Ganesan, J Teuscher, T Moehl, Y J Kim, C Yi, P Comte, K Pei, T W Holcombe, M K Nazeeruddin, J Hua, S M Zakeeruddin, H Tian, M Grätzel *J. Am. Chem. Soc.* **136** 5722 (2014)
29. Z Yao, M Zhang, H Wu, L Yang, R Li, P Wang *J. Am. Chem. Soc.* **137** 3799 (2015)
30. Z Yao, M Zhang, R Li, L Yang, Y Qiao, P Wang *Angew. Chem., Int. Ed.* **54** 5994 (2015)
31. N Zhou, K Prabakaran, B Lee, S H Chang, B Harutyunyan, P Guo, M R Butler, A Timalsina, M J Bedzyk, M A Ratner, S Vegiraju, S Yau, C-G Wu, R P H Chang, A Facchetti, M-C Chen, T J Marks *J. Am. Chem. Soc.* **137** 4414 (2015)
32. Q Qi, X Wang, L Fan, B Zheng, W Zeng, J Luo, K-W Huang, Q Wang, J Wu *Org. Lett.* **17** 724 (2015)
33. X Jia, W Zhang, X Lu, Z Wang, G Zhou *J. Mater. Chem. A* **2** 19515 (2014)
34. H-W Lin, Y-S Wang, P-F Yang, K-T Wong, L-Y Lin, F Lin *Org. Electron.* **14** 1037 (2013)
35. S-R Li, C-P Lee, P-F Yang, C-W Liao, M M Lee, W-L Su, C-T Li, H-W Lin, K-C Ho, S-S Sun *Chem. – Eur. J.* **20** 10052 (2014)
36. K Kakiage, Y Aoyama, T Yano, T Otsuka, T Kyomen, M Unno, M Hanaya *Chem. Commun.* **50** 6379 (2014)
37. A Mishra, M K R Fischer, P Bäuerle *Angew. Chem., Int. Ed.* **48** 2474 (2009)
38. T-D Kim, J-W Kang, J Luo, S-H Jang, J-W Ka, N Tucker, J B Benedict, L R Dalton, T Gray, R M Overney, D H Park, W N Herman, A K-Y Jen *J. Am. Chem. Soc.* **129** 488 (2007)
39. F Kajzar, K S Lee, A K-Y Jen *Adv. Polym. Sci.* **161** 1 (2003)
40. Z-S Wang, N Koumura, Y Cui, M Takahashi, H Sekiguchi, A Mori, T Kubo, A Furube, K Hara *Chem. Mater.* **20** 3993 (2008)
41. T-D Kim, K-S Lee *Macromol. Rapid Commun.* **36** 943 (2015)
42. Y Wu, W-H Zhu, S M Zakeeruddin, M Grätzel *ACS Appl. Mater. Interfaces* **7** 9307 (2015)
43. O A Abdulrazzaq, V Saini, S Bourdo, E Dervishi, A S Biris *Particul. Sci. Technol.* **31** 427 (2013)
44. N Yeh, P Yeh *Renew. Sustain. Energy Rev.* **21** 421 (2013)
45. N Kaur, M Singh, D Pathak, T Wagner, J M Nunzi *Synth. Met.* **190** 20 (2014)
46. C W Lee, O Y Kim, J Y Lee *J. Ind. Eng. Chem.* **20** 1198 (2014)
47. M-E Ragoussi, T Torres *Chem. Commun.* **51** 3957 (2015)
48. C-P Lee, R Y-Y Lin, L-Y Lin, C-T Li, T-C Chu, S-S Sun, J T Lin, K-C Ho *RSC Adv.* **5** 23810 (2015)
49. T C Parker, D G (Dan) Patel, K Moudgil, S Barlow, C Risko, J-L Brédas, J R Reynolds, S R Marder *Mater. Horiz.* **2** 22 (2015)
50. G V Bulavko, A A Ishchenko *Russ. Chem. Rev.* **83** 575 (2014)
51. A V Akkuratov, P A Troshin *Polym. Sci., Ser. B* **56** 414 (2014) [*Vysokomol. Soedin., Ser. B* **56** 371 (2014)]
52. Y Ooyama, K Uenaka, M Kanda, T Yamada, N Shibayama, J Ohshita *Dyes Pigm.* **122** 40 (2015)
53. X Zhou, X Li, Y Liu, R Li, K Jiang, J Xia *Org. Electron.* **25** 245 (2015)
54. H Jiang, K Oniwa, A Islam, J Zhao, L Han, Y-J Sun, M Bao, N Asao, Y Yamamoto, T Jin *Tetrahedron* **71** 6534 (2015)
55. K S V Gupta, S Prakash Singh, A Islam, L Han, M Chandrasekharam *Electrochim. Acta* **174** 581 (2015)
56. D D Babu, H Cheema, D Elsherbiny, A El-Shafei, A V Adhikari *Electrochim. Acta* **176** 868 (2015)
57. Y K Eom, I T Choi, S H Kang, J Lee, J Kim, M J Ju, H K Kim *Adv. Energy Mater.* **5** 1500300 (2015)
58. V Mallam, H Elbohy, Q Qiao, B A Logue *Int. J. Energy Res.* **39** 1335 (2015)
59. A Gupta, A Ali, M Gao, Th B Singh, A Bilic, S E Watkins, U Bach, R A Evans *Dyes Pigm.* **119** 122 (2015)
60. M Paramasivam, R K Chitumalla, S P Singh, A Islam, L Han, V J Rao, K Bhanuprakash *J. Phys. Chem. C* **119** 17053 (2015)
61. K Narayanaswamy, T Swetha, G Kapil, S S Pandey, S Hayase, S P Singh *Electrochim. Acta* **169** 256 (2015)
62. G Sorohhov, C Yi, M Grätzel, S Decurtins, S-X Liu *Beilstein J. Org. Chem.* **11** 1052 (2015)
63. X Qian, Y-Z Zhu, W-Y Chang, J Song, B Pan, L Lu, H-H Gao, J-Y Zheng *ACS Appl. Mater. Interfaces* **7** 9015 (2015)
64. A J Huckaba, F Giordano, L E McNamara, K M Dreux, N I Hammer, G S Tschumper, S M Zakeeruddin, M Grätzel, M K Nazeeruddin, J H Delcamp *Adv. Energy Mater.* **5** 1401629 (2015)
65. F Wu, S Zhao, L T L Lee, M Wang, T Chen, L Zhu *Tetrahedron Lett.* **56** 1233 (2015)
66. A Baheti, K R J Thomas, C-T Li, C-P Lee, K-C Ho *ACS Appl. Mater. Interfaces* **7** 2249 (2015)
67. A Diac, D Demeter, M Allain, I Grosu, J Roncali *Chem. – Eur. J.* **21** 1598 (2015)
68. V Srinivasan, M Panneer, M Jaccob, N Pavithra, S Anandan, A Kathiravan *Phys. Chem. Chem. Phys.* **17** 28647 (2015)
69. Y K Eom, S H Kang, I T Choi, E Kim, J Kim, M J Ju, H K Kim *RSC Adv.* **5** 80859 (2015)
70. M-D Damaceanu, M Mihaila, C-P Constantin, S Chisca, B-C Serban, C Diaconu, O Buiu, E M Pavelescu, M Kusko *RSC Adv.* **5** 53687 (2015)
71. Z Yang, C Shao, D Cao *RSC Adv.* **5** 22892 (2015)
72. W Zhu, Y Wu, S Wang, W Li, X Li, J Chen, Z-s Wang, H Tian *Adv. Funct. Mater.* **21** 756 (2011)
73. L S Konstantinova, E A Knyazeva, O A Rakitin *Org. Prep. Proced. Int.* **46** 475 (2014)
74. Z V Todress *Chalcogenadiazoles: Chemistry and Applications* [London: CRC Press (Taylor and Francis), 2012]
75. P A Koutentis, in *Science of Synthesis* Vol. 13 (Eds R C Storr, T L Gilchrist) (Stuttgart: Thieme, 2003) p. 297
76. P A Koutentis, n *Comprehensive Heterocyclic Chemistry III* Vol. 5 (Eds A R Katritzky, C A Ramsden, E F V Scriven, R J K Taylor) (Oxford: Elsevier, 2008) p. 516
77. A V Lonchakov, O A Rakitin, N P Gritsan, A V Zibarev *Molecules* **18** 9850 (2013)
78. K R J Thomas, J T Lin, M Velusamy, Y-T Tao, C-H Chuen *Adv. Funct. Mater.* **14** 83 (2004)
79. J-M Raimundo, P Blanchard, H Brisset, S Akoudad, J Roncali *Chem. Commun.* 939 (2000)
80. M Velusamy, K R J Thomas, J T Lin, Y-C Hsu, K-C Ho *Org. Lett.* **7** 1899 (2005)
81. Y Wu, X Zhang, W Li, Z-S Wang, H Tian, W Zhu *Adv. Energy Mater.* **2** 149 (2012)

82. D H Lee, M J Lee, H M Song, B J Song, K D Seo, M Pastore, C Anselmi, S Fantacci, F De Angelis, M K Nazeeruddin, M Grätzel, H K Kim *Dyes Pigm.* **91** 192 (2011)
83. J-J Kim, H Choi, J-W Lee, M-S Kang, K Song, S O Kang, J Ko *J. Mater. Chem.* **18** 5223 (2008)
84. Y Wu, W Zhu *Chem. Soc. Rev.* **42** 2039 (2013)
85. Z-M Tang, T Lei, K-J Jiang, Y-L Song, J Pei *Chem. – Asian J.* **5** 1911 (2010)
86. S Kim, H Lim, Kwang Kim, C Kim, T Y Kang, M J Ko, Kyung Kim, N-G Park *IEEE J. Select. Top. Quantum Electron.* **16** 1627 (2010)
87. S Haid, M Marszalek, A Mishra, M Wielopolski, J Teuscher, J-E Moser, R Humphry-Baker, S M Zakeeruddin, M Grätzel, P Bäuerle *Adv. Funct. Mater.* **22** 1291 (2012)
88. Y Wu, M Marszalek, S M Zakeeruddin, Q Zhang, H Tian, M Grätzel, W Zhu *Energy Environ. Sci.* **5** 8261 (2012)
89. H Zhu, W Li, Y Wu, B Liu, S Zhu, X Li, H Ågren, W Zhu *ACS Sustain. Chem. Eng.* **2** 1026 (2014)
90. Z-S Huang, X-F Zang, T Hua, L Wang, H Meier, D Cao *ACS Appl. Mater. Interfaces* **7** 20418 (2015)
91. L Wang, M Liang, Y Zhang, F Cheng, X Wang, Z Sun, S Xue, *Dyes Pigm.* **101** 270 (2014)
92. X Liu, J Long, G Wang, Y Pei, B Zhao, S Tan *Dyes Pigm.* **121** 118 (2015)
93. X Yang, J Zhao, L Wang, J Tian, L Sun *RSC Adv.* **4** 24377 (2014)
94. K D Seo, I T Choi, Y G Park, S Kang, J Y Lee, H K Kim *Dyes Pigm.* **94** 469 (2012)
95. W Lee, J y Seng, J-I Hong *Tetrahedron* **69** 9175 (2013)
96. R Grisorio, L De Marco, R Agosta, R Iacobellis, R Giannuzzi, M Manca, P Mastrorilli, G Gigli, G P Suranna *ChemSusChem* **7** 2659 (2014)
97. V Roiati, R Giannuzzi, G Lerario, L De Marco, R Agosta, R Iacobellis, R Grisorio, G P Suranna, A Listorti, G Gigli *J. Phys. Chem. C* **119** 6956 (2015)
98. J Lu, Y-C Chang, H-Y Cheng, H-P Wu, Y Cheng, M Wang, E W-G Diau *ChemSusChem* **8** 2529 (2015)
99. J Mao, X Zhang, S-H Liu, Z Shen, X Li, W Wu, P-T Chou, J Hua *Electrochim. Acta* **179** 179 (2015)
100. L Chen, X Li, W Ying, X Zhang, F Guo, J Li, J Hua *Eur. J. Org. Chem.* 1770 (2013)
101. X Zhang, L Chen, X Li, J Mao, W Wu, H ngren, J Hua *J. Mater. Chem. C* **2** 4063 (2014)
102. X Kang, J Zhang, A J Rojas, D O'Neil, P Szymanski, S R Marder, M A El-Sayed *J. Mater. Chem. A* **2** 11229 (2014)
103. X Kang, J Zhang, D O'Neil, A J Rojas, W Chen, P Szymanski, S R Marder, M A El-Sayed *Chem. Mater.* **26** 4486 (2014)
104. X Wang, J Yang, H Yu, F Li, L Fan, W Sun, Y Liu, Z Y Koh, J Pan, W-L Yim, L Yan, Q Wang *Chem. Commun.* **50** 3965 (2014)
105. M Katono, M Wielopolski, M Marszalek, T Bessho, J-E Moser, R Humphry-Baker, S M Zakeeruddin, M Grätzel *J. Phys. Chem. C* **118** 16486 (2014)
106. Q Chai, W Li, J Liu, Z Geng, H Tian, W-H Zhu *Sci. Rep.* **5** Art. No. 11330 (2015)
107. L Han, X Zu, Y Cui, H Wu, Q Ye, J Gao *Org. Electron.* **15** 1536 (2014)
108. D Joly, L Pellejà S Narbey, F Oswald, T Meyer, Y Kervella, P Maldivi, J N Clifford, E Palomares, R Demadrille *Energy Environ. Sci.* **8** 2010 (2015)
109. R Grisorio, L De Marco, C Baldisserri, F Martina, M Serantoni, G Gigli, G P Suranna *ACS Sustain. Chem. Eng.* **3** 770 (2015)
110. X Hu, S Cai, G Tian, X Li, J Su, J Li *RSC Adv.* **3** 22544 (2013)
111. C-F Du, L Jiang, L Sun, N-Y Huang, W-Q Deng *RSC Adv.* **5** 37574 (2015)
112. Z Ning, Q Zhang, H Pei, J Luan, C Lu, Y Cui, H Tian *J. Phys. Chem. C* **113** 10307 (2009)
113. N Koumura, Z -S Wang, S Mori, M Miyashita, E Suzuki, K Hara *J. Am. Chem. Soc.* **128** 14256 (2006)
114. M Jurgensen, K Norrman, S A Gevorgyan, T Tromholt, B Andreasen, F C Krebs, *Adv. Mater.* **24** 580 (2012)
115. H Li, Y Wu, Z Geng, J Liu, D Xu, W Zhu *J. Mater. Chem. A* **2** 14649 (2014)
116. H Zhu, Y Wu, J Liu, W Zhang, W Wu, W-H Zhu *J. Mater. Chem. A* **3** 10603 (2015)
117. D G (Dan)Patel, F Feng, Y-y Ohnishi, K A Abboud, S Hirata, K S Schanze, J R Reynolds *J. Am. Chem. Soc.* **134** 2599 (2012)
118. N Blouin, A Michaud, D Gendron, S Wakim, E Blair, R Neagu-Plesu, M Belletête, G Durocher, Y Tao, M Leclerc *J. Am. Chem. Soc.* **130** 732 (2008)
119. X Liu, Y Sun, L A Perez, W Wen, M F Toney, A J Heeger, G C Bazan *J. Am. Chem. Soc.* **134** 20609 (2012)
120. Y Sun, G C Welch, W L Leong, C J Takacs, G C Bazan, A Heeger *Nat. Mater.* **11** 44 (2012)
121. Y Hua, H Wang, X Zhu, A Islam, L Han, C Qin, W-Y Wong, W-K Wong *Dyes Pigm.* **102** 196 (2014)
122. S Chaurasia, C-Y Hsu, H-H Chou, J T Lin *Org. Electron.* **15** 378 (2014)
123. J Mao, J Yang, J Teuscher, T Moehl, C Yi, R Humphry-Baker, P Comte, C Grätzel, J Hua, S M Zakeeruddin, H Tian, M Grätzel *J. Phys. Chem. C* **118** 17090 (2014)
124. Y Hua, J He, C Zhang, C Qin, L Han, J Zhao, T Chen, W-Y Wong, W-K Wong, X Zhu *J. Mater. Chem. A* **3** 3103 (2015)
125. A Tanimoto, T Yamamoto *Macromolecules* **39** 3546 (2006)
126. L Zhang, C He, J Chen, P Yuan, L Huang, C Zhang, W Cai, Z Liu, Y Cao *Macromolecules* **43** 9771 (2010)
127. S C Price, A C Stuart, L Yang, H Zhou, W You *J. Am. Chem. Soc.* **133** 4625 (2011)
128. Z Zhang, B Peng, B Liu, C Pan, Y Li, Y He, K Zhou, Y Zou *Polym. Chem.* **1** 1441 (2010)
129. W Li, Y Wu, Q Zhang, H Tian, W Zhu *ACS Appl. Mater. Interfaces* **4** 1822 (2012)
130. J Mao, F Guo, W Ying, W Wu, J Li, J Hua *Chem. – Asian J.* **7** 982 (2012)
131. Y-S Yen, C-T Lee, C-Y Hsu, H-H Chou, Y-C Chen, J T Lin *Chem. – Asian J.* **8** 809 (2013)
132. Q Chai, W Li, Y Wu, K Pei, J Liu, Z Geng, H Tian, W Zhu *ACS Appl. Mater. Interfaces* **6** 14621 (2014)
133. Y Cui, Y Wu, X Lu, X Zhang, G Zhou, F B Miapeh, W Zhu, Z-S Wang *Chem. Mater.* **23** 4394 (2011)
134. L Ying, B B Y Hsu, H Zhan, G C Welch, P Zalar, L A Perez, E J Kramer, T-Q Nguyen, A J Heeger, W-Y Wong, G C Bazan *J. Am. Chem. Soc.* **133** 18538 (2011)
135. M Horie, J Kettle, C-Y Yu, L A Majewski, S-W Chang, J Kirkpatrick, S M Tuladhar, J Nelson, B R Saunders, M L Turner, *J. Mater. Chem.* **22** 381 (2012)
136. M Zhang, J Zhang, Y Fan, L Yang, Y Wang, R Li, P Wang *Energy Environ. Sci.* **6** 2939 (2013)
137. L Huo, Z Tan, X Wang, Y Zhou, M Han, Y Li *J. Polym. Sci. A* **46** 4038 (2008)

138. C Li, M Liu, N G Pschirer, M Baumgarten, K Müllen *Chem. Rev.* **110** 6817 (2010)
139. K Pei, Y Wu, W Wu, Q Zhang, B Chen, H Tian, W Zhu *Chem. – Eur. J.* **18** 8190 (2012)
140. K Pei, Y Wu, A Islam, Q Zhang, L Han, H Tian, W Zhu *ACS Appl. Mater. Interfaces* **5** 4986 (2013)
141. K Pei, Y Wu, A Islam, S Zhu, L Han, Z Geng, W Zhu *J. Phys. Chem. C* **118** 16552 (2014)
142. T Lan, X Lu, L Zhang, Y Chen, G Zhou, Z-S Wang *J. Mater. Chem. A* **3** 9869 (2015)
143. X Lu, Q Feng, T Lan, G Zhou, Z-S Wang *Chem. Mater.* **24** 3179 (2012)
144. H Zhu, B Liu, J Liu, W Zhang, W-H Zhu *J. Mater. Chem. C* **3** 6882 (2015)
145. K Pei, Y Wu, H Li, Z Geng, H Tian, W-H Zhu *ACS Appl. Mater. Interfaces* **7** 5296 (2015)
146. L-P Zhang, K-J Jiang, G Li, Q-Q Zhang, L-M Yang *J. Mater. Chem. A* **2** 14852 (2014)
147. S Chaurasia, J-S Ni, W-I Hung, J T Lin *ACS Appl. Mater. Interfaces* **7** 22046 (2015)
148. X Zhang, J Mao, D Wang, X Li, J Yang, Z Shen, W Wu, J Li, H Ågren, J Hua *ACS Appl. Mater. Interfaces* **7** 2760 (2015)
149. S Chaurasia, W-I Hung, H-H Chou, J T Lin *Org. Lett.* **16** 3052 (2014)
150. S Qu, H Tian *Chem. Commun.* **48** 3039 (2012)
151. S Qu, W Wu, J Hua, C Kong, Y Long, H Tian *J. Phys. Chem. C* **114** 1343 (2010)
152. S Qu, B Wang, F Guo, J Li, W Wu, C Kong, Y Long, J Hua *Dyes Pigm.* **92** 1384 (2012)
153. S Qu, C Qin, A Islam, Y Wu, W Zhu, J Hua, H Tian, L Y Han *Chem. Commun.* **48** 6972 (2012)
154. J Warnan, L Favereau, Y Pellegrin, E Blart, D Jacquemin, F Odobel *J. Photochem. Photobiol., A* **226** 9 (2011)
155. S P Singh, M S Roy, A Thomas, K Bhanuprakash, G D Sharma *Org. Electron.* **13** 3108 (2012)
156. X Li, Z Zheng, W Jiang, W Wu, Z Wang, H Tian *Chem. Commun.* **51** 3590 (2015)
157. T W Holcombe, J-H Yum, Y Kim, K Rakstys, M Grätzel *J. Mater. Chem. A* **1** 13978 (2013)
158. G Tian, S Cai, X Li, H Ågren, Q Wang, J Huang, J Su *J. Mater. Chem. A* **3** 3777 (2015)
159. T Li, J Gao, Y Cui, C Zhong, Q Ye, L Han *J. Photochem. Photobiol., A* **303 – 304** 91 (2015)
160. G S Kumar, K Srinivas, B Shanigaram, D Bharath, S P Singh, K Bhanuprakash, V J Rao, A Islam, L Han *RSC Adv.* **4** 13172 (2014)
161. S B Mane, C-F Cheng, A A Sutanto, A Datta, A Dutta, C-H Hung *Tetrahedron* **71** 7977 (2015)
162. J Zeng, T L Zhang, X F Zang, D B Kuang, H Meier, D R Cao *Sci. China Chem.* **56** 505 (2013)
163. J He, W Wu, J Hua, Y Jiang, S Qu, J Li, Y Long, H Tian *J. Mater. Chem.* **21** 6054 (2011)
164. F Guo, J He, S Qu, J Li, Q Zhang, W Wu, J Hua *RSC Adv.* **3** 15900 (2013)
165. A Dessì, G B Consiglio, M Calamante, G Reginato, A Mordini, M Peruzzini, M Taddei, A Sinicropi, M L Parisi, F F de Biani, R Basosi, R Mori, M Spatola, M Bruzzi, L Zani *Eur. J. Org. Chem.* 1916 (2013)
166. A Dessì, M Calamante, A Mordini, M Peruzzini, A Sinicropi, R Basosi, F F de Biani, M Taddei, D Colonna, A di Carlo, G Reginato, L Zani *RSC Adv.* **5** 32657 (2015)
167. X Lu, G Zhou, H Wang, Q Feng, Z-S Wang *Phys. Chem. Chem. Phys.* **14** 4802 (2012)
168. Q Feng, W Zhang, G Zhou, Z-S Wang *Chem. – Asian J.* **8** 168 (2013)
169. C Qin, A Islam, L Han *J. Mater. Chem.* **22** 19236 (2012)
170. L Wang, P Shen, Z Cao, X Liu, Y Huang, C Liu, P Chen, B Zhao, S Tan *J. Power Sources* **246** 831 (2014)
171. W Ying, F Guo, J Li, Q Zhang, W Wu, H Tian, J Hua *ACS Appl. Mater. Interfaces* **4** 4215 (2012)
172. J-S Ni, W-S Kao, H-J Chou, J T Lin *ChemSusChem* **8** 2932 (2015)
173. A Dessì, M Calamante, A Mordini, M Peruzzini, A Sinicropi, R Basosi, F F de Biani, M Taddei, D Colonna, A Di Carlo, G Reginato, L Zani *Chem. Commun.* **50** 13952 (2014)
174. S C Rasmussen, R L Schwiderski, M E Mulholland *Chem. Commun.* **47** 11394 (2011)
175. Q Feng, X Lu, G Zhou, Z-S Wang *Phys. Chem. Chem. Phys.* **14** 7993 (2012)
176. Z Ning, Q Zhang, W Wu, H Pei, B Liu, H Tian *J. Org. Chem.* **73** 3791 (2008)
177. W Wu, J Yang, J Hua, J Tang, L Zhang, Y Long, H Tian *J. Mater. Chem.* **20** 1772 (2010)
178. C-J Yang, Y J Chang, M Watanabe, Y-S Hon, T J Chow *J. Mater. Chem.* **22** 4040 (2012)
179. M-D Zhang, H-X Xie, X-H Ju, L Qin, Q-X Yang, H-G Zheng, X-F Zhou *Phys. Chem. Chem. Phys.* **15** 634 (2013)
180. A Venkateswararao, K R J Thomas, C-P Lee, C-T Li, K-C Ho *ACS Appl. Mater. Interfaces* **6** 2528 (2014)
181. A Venkateswararao, K R J Thomas, C-P Lee, K-C Ho *Tetrahedron Lett.* **54** 3985 (2013)
182. T Sudyoadsuk, S Pansay, S Morada, R Rattanawan, S Namuangruk, T Kaewin, S Jungsuttiwong, V Promarak *Eur. J. Org. Chem.* 5051 (2013)
183. B Liu, B Wang, R Wang, L Gao, S Huo, Q Liu, X Li, W Zhu *J. Mater. Chem. A* **2** 804 (2014)
184. S Namuangruk, R Fukuda, M Ehara, J Meeprasert, T Khanasa, S Morada, T Kaewin, S Jungsuttiwong, T Sudyoadsuk, V Promarak *J. Phys. Chem. C* **116** 25653 (2012)
185. C A Echeverry, R Cotta, E Castro, A Ortiz, L Echegoyen, B Insuasty *RSC Adv.* **5** 60823 (2015)
186. K Brunner, A van Dijken, H Börner, J J A M Bastiaansen, N M M Kiggen, B M W Langeveld *J. Am. Chem. Soc.* **126** 6035 (2004)
187. C Teng, X Yang, S Li, M Cheng, A Hagfeldt, L-z Wu, L Sun *Chem. – Eur. J.* **16** 13127 (2010)
188. W Lee, N Cho, J Kwon, J Ko, J-I Hong *Chem. – Asian J.* **7** 343 (2012)
189. A Abbotto, N Manfredi, C Marinzi, F De Angelis, E Mosconi, J-H Yum, X Zhang, M K Nazeeruddin, M Grätzel *Energy Environ. Sci.* **2** 1094 (2009)
190. J Liu, J Zhang, M Xu, D Zhou, X Jing, P Wang *Energy Environ. Sci.* **4** 3021 (2011)
191. H-C Chu, D Sahu, Y-C Hsu, H Padhy, D Patra, J-T Lin, D Bhattacharya, K-L Lu, K-H Wei, H-C Lin *Dyes Pigm.* **93** 1488 (2012)
192. S Ramkumar, S Manoharan, S Anandan *Dyes Pigm.* **94** 503 (2012)
193. Y Ooyama, N Yamaguchi, I Imae, K Komaguchi, J Ohshita, Y Harima *Chem. Commun.* **49** 2548 (2013)
194. Y S Yang, H D Kim, J-H Ryu, K K Kim, S S Park, K-S Ahn, J H Kim *Synth. Met.* **161** 850 (2011)
195. S S Park, Y S Won, Y C Choi, J H Kim *Energy Fuels* **23** 3732 (2009)

196. R Sirohi, D H Kim, S-C Yu, S H Lee *Dyes Pigm.* **92** 1132 (2012)
197. X Ren, S Jiang, M Cha, G Zhou, Z-S Wang *Chem. Mater.* **24** 3493 (2012)
198. J Mao, N He, Z Ning, Q Zhang, F Guo, L Chen, W Wu, J Hua, H Tian *Angew. Chem., Int. Ed.* **51** 9873 (2012)
199. S Cai, G Tian, X Li, J Su, H Tian *J. Mater. Chem. A* **1** 11295 (2013)
200. D Heredia, J Natera, M Gervaldo, L Otero, F Fungo, C-Y Lin, K-T Wong *Org. Lett.* **12** 12 (2010)
201. Y-S Yen, J-S Ni, T-Y Lin, W-I Hung, J T Lin, M-C P Yeh *Eur. J. Org. Chem.* 7367 (2015)
202. R Y-Y Lin, F-L Wu, C-H Chang, H-H Chou, T-M Chuang, T-C Chu, C-Y Hsu, P-W Chen, K-C Ho, Y-H Lo, J T Lin *J. Mater. Chem. A* **2** 3092 (2014)
203. W-I Hung, Y-Y Liao, C-Y Hsu, H-H Chou, T-H Lee, W-S Kao, J T Lin *Chem. – Asian J.* **9** 357 (2014)
204. W-I Hung, Y-Y Liao, T-H Lee, Y-C Ting, J-S Ni, W-S Kao, J T Lin, T-C Wei, Y-S Yen *Chem. Commun.* **51** 2152 (2015)
205. Z Iqbal, W-Q Wu, H Zhang, L Han, X Fang, L Wang, D-B Kuang, H Meier, D Cao *Org. Electron.* **14** 2662 (2013)
206. H Zhang, J Fan, Z Iqbal, D-B Kuang, L Wang, H Meier, D Cao *Org. Electron.* **14** 2071 (2013)
207. X-X Dai, H-L Feng, Z-S Huang, M-J Wang, L Wang, D-B Kuang, H Meier, D Cao *Dyes Pigm.* **114** 47 (2015)
208. V Leandri, R Ruffo, V Trifiletti, A Abbotto *Eur. J. Org. Chem.* 6793 (2013)
209. X-X Dai, H-L Feng, W-J Chen, Y Yang, L-B Nie, L Wang, D-B Kuang, H Meier, D Cao *Dyes Pigm.* **122** 13 (2015)
210. S Irie, S Fuse, M M Maitani, Y Wada, Y Ogomi, S Hayase, T Kaiho, H Masui, H Tanaka, T Takahashi *Chem. – Eur. J.* **22** 2507 (2016)
211. K Y Chiu, V Govindan, L-C Lin, S-H Huang, J-C Hu, K-M Lee, H-H G Tsai, S-H Chang, C-G Wu *Dyes Pigm.* **125** 27 (2016)
212. G S Selopal, H-P Wu, J Lu, Y-C Chang, M Wang, A Vomiero, I Concina, E W-G Diau *Sci. Rep.* **6** Art. No. 18756 (2016)
213. F Guo, X Liu, Y Ding, F Kong, W Chen, L Zhou, S Dai *RSC Adv.* **6** 13433 (2016)
214. M-D Zhang, C-Y Huang, M-X Song, D-X Zhao, H Cao, M-D Chen *Mendeleev Commun.* **26** 288 (2016)