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Cross-coupling reactions: Some applications to the synthesis of thiazolothiazole- and benzobisthiazole-based dyes for new generation solar cells (DSSC)

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ABSTRACT

Dye-sensitized solar cells (DSSCs) have received considerable attention in the last decade because of their good efficiency coupled with low cost of production. To increase the performances of such devices it is important to develop effective organic photosensitizers with optimal chemical structures and, to this end, compounds featuring D– π –A architectures have been found very promising. Many classes of D– π –A dyes have been developed so far and cross-coupling reactions have emerged as an unique tool for designing flexible synthetic strategies. The aim of this microreview is to highlight the application of cross-coupling reactions in the preparation of such dyes, which is exemplified by the synthesis of a new class of thiazolothiazole- and benzobisthiazole-based dyes.

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Cross-coupling reactions combine two molecular fragments, coming respectively from an organic reagent bearing a good leaving group and an organometallic species, leading to the formation of a new bond. To do that efficiently, an organometallic transformation needs to occur, which is mediated by a transition-metal complex acting as a catalyst. This protocol is widely recognized as one of the most straightforward and general methods not only for the formation of carbon–carbon bonds but also for the introduction of new functional groups, both carbon- or heteroatom-based, and has long attracted the attention of both academia and industry [1,2]. Since the seminal studies by Heck, Negishi and Suzuki on palladium-catalyzed cross-coupling reactions that led to the award of the Nobel Prize in Chemistry in 2010 [3], much work has been done in this field and many improvement have been achieved, including a deeper mechanistic understanding, the expansion of the substrate scope, a better functional group tolerance, lower catalyst loadings, higher yields in milder conditions. Despite the enormous number of very elegant and efficient examples which illustrate the ability of this modern synthetic tool, research in this area is still very active and particular attention has been devoted to the development of new and more efficient catalytic systems. Pd

complexes have been for long time recognized as the most general and effective catalysts for cross-coupling processes, however, during the past decade, remarkable progresses have been achieved also with different transition metals like Fe, Ni, Co, Cu, which have been extensively studied and successfully used in synthetic applications. The use of suitable ligands or ligand precursors such as bulky trialkylphosphines, *N*-heterocyclic carbenes (NHC), bidentate or tridentate amines, olefins, and dienes has allowed various metals to play important roles as catalysts in such reactions, to activate poorly reactive substrates, to make possible catalysts recycling, to find more environmentally benign reactions conditions. As a result, many highly efficient and mild protocols have emerged, which have found a wide application for the construction of complex structures in several fields such as natural products synthesis, supramolecular chemistry, organic materials and polymers, medicinal chemistry.

Among others, a very recent and stimulating field in which this class of transformations has found successful application is the design and synthesis of new photosensitizers for dye-sensitized solar cells (DSSCs) [4]. Since the first report by O'Regan and Grätzel in 1991 [5], DSSCs have been investigated extensively as promising candidates for energy production from renewable sources. Their working principle is inspired to natural photosynthesis, as light harvesting is carried out by a dye which is absorbed on a thin-layer of a mesoporous semiconductor (usually TiO₂). Indeed, DSSCs are made of few simple components (Fig. 1): (a) a

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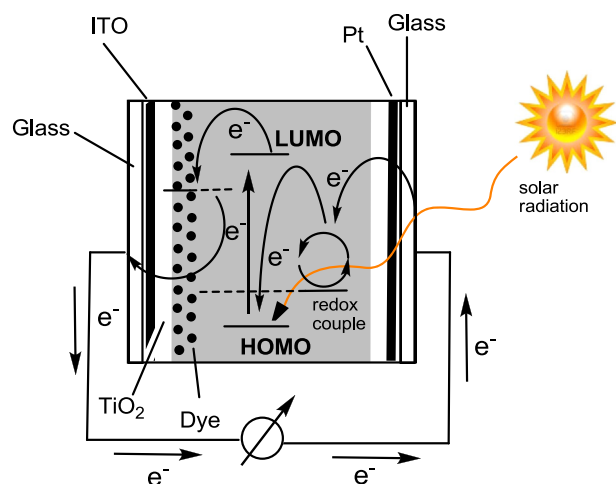


Fig. 1. Simple scheme of the working principle of a DSSC.

photoanode, constituted by a layer of an inorganic semiconductor (typically nanocrystalline TiO_2) deposited on conductive ITO-glass and a light-absorbing dye (sensitizer) which is adsorbed on the surface of the semiconductor nanoparticles to harvest light; (b) a suitable electrolyte, which can be either a liquid solution or a gel containing a redox couple (most often the I^-/I_3^- couple), or a solid hole-conducting material; (c) a metal cathode (usually made of a thin-layer of platinum) able to efficiently catalyze the reduction of the electrolyte. When sunlight hits the dye, an electron is promoted from the sensitizer's HOMO to its LUMO, and from there it is transferred to the conduction band of nc- TiO_2 ("injection"). The resulting positive charge on the sensitizer (hole) is then transferred to the redox mediator, which is thus converted in its oxidized form. Meanwhile, the electron travels through the external circuit (generating an electric current) and is collected at the cathode, where the reduction of the oxidized redox mediator takes place, closing the circuit.

The light-harvesting dye is certainly one of the most important components of a DSSC, being involved both in the light absorption and charge separation processes. Until recently, the most efficient DSSCs described in the literature incorporated polypyridyl complexes of Ru(II) as sensitizers [6] which allowed to reach power conversion efficiencies (PCE, defined as the ratio between the electrical power produced by the cell and the power of incident light) exceeding 11% [7]. Unfortunately, these dyes suffer from some important drawbacks, such as difficult purification procedures, low molar extinction coefficients and high cost of the metal precursors. Alternatively, PCEs superior to 12% have been also demonstrated for DSSCs based on a zinc porphyrin dye [8], but in this case a rather laborious synthesis was required to access the sensitizer. As a

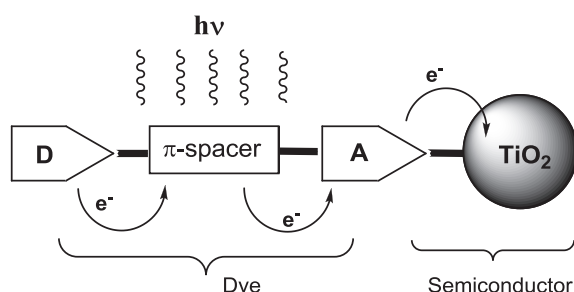


Fig. 2. General structure of a (D- π -A) dye.

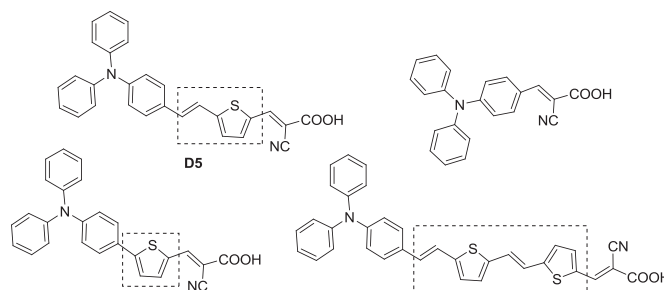


Fig. 3. Structure of **D5** and some related (D- π -A) dyes.

consequence, metal-free organic dyes have recently been at the center of intense research efforts due to their high molar absorptivities, low cost, and easy molecular tailoring and synthesis [9]. Many organic dyes exhibiting relatively high DSSC performances have been designed and developed [10] and the relationship between their chemical structures and photovoltaic performances has been examined.

In particular, dyes based on donor-acceptor π -conjugated (D- π -A) architectures represent one of the most promising class of organic sensitizers. The general structure of such dyes is shown in Fig. 2 and features an electronrich donor group (D) which is connected through a conjugated π -spacer to an electron withdrawing acceptor (A), usually also responsible for the anchoring of the dye to the nanocrystalline semiconductor [11].

The photophysical, electrochemical and photovoltaic properties of a (D- π -A) dye strongly depend on the electron-donating and the electron-accepting ability of the D and A units, respectively, as well as on the effective photoinduced intramolecular charge transfer which should be allowed by the π -conjugated spacer. Thus, each component should be strategically tunable through chemical modification to optimize the structure for efficient DSSCs.

In many cases such push-pull type metal-free sensitizers have a triarylamine unit as the electron donor. This choice is due to the excellent stability and aggregation resistance (resulting from a non-planar molecular configuration) of triphenylamine (TPA), properties which are expected to be retained in the final sensitizers. Furthermore, the suitable electron-donating ability of such moiety can be easily tuned with substituents on the phenyl rings [9f,g]. 2-Cyanoacrylic acid is used very often as the electron acceptor/anchoring group due to the electron withdrawing effect of the cyanoacrylic moiety and the strong interaction of the carboxy group with TiO_2 . As an example, in Fig. 3 the structure of compound **D5** and some related dyes is shown. This is one of the most well-characterized organic photosensitizers, and was reported to give a solar-to-electric conversion efficiency of approximately 5%, to be compared with the conventional Ru-based **N719** dye (6% under the same conditions) [12].

In this series of dyes the π -conjugated systems between the donor (triphenylamine moiety) and the acceptor (cyanoacrylic acid moiety) were systematically extended to adjust the molecular HOMO and LUMO energy levels of the dyes, hence red-shifting and broadening the absorption spectra according to the extent of π -conjugation. Many other kinds of different spacers have been

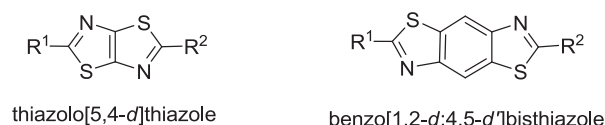


Fig. 4. The thiazolo[5,4-*d*]thiazole and benzo[1,2-*d*:4,5-*d'*]bisthiazole ring systems.

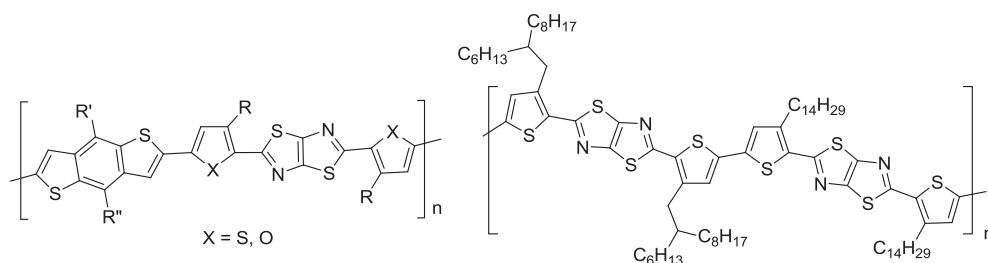


Fig. 5. Thiazolothiazole-containing donor/acceptor polymers for bulk heterojunction (BHJ) solar cells.

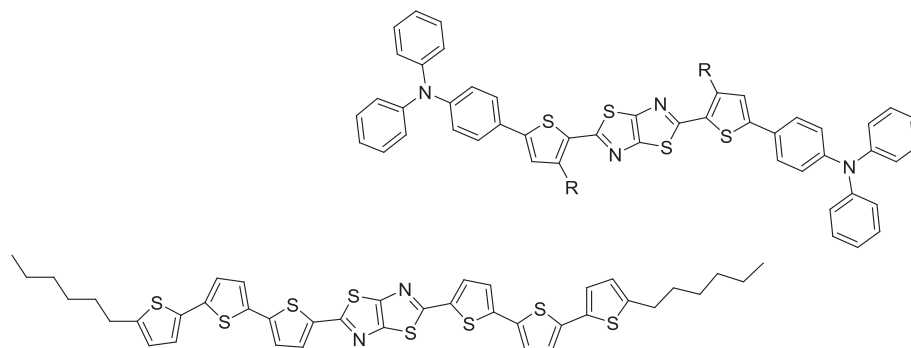


Fig. 6. Thiazolothiazole-containing small molecules as light absorbing/donor materials for bulk heterojunction (BHJ) solar cells.

introduced, all of them featuring a conjugated system where the electrons can flow easily from the donor to the acceptor [13].

To build this sort of structures different approaches are available, but it clearly appears that, being cross-coupling reactions probably the most efficient and general method for C–C (sp) and (sp²) bond formation, for arylation and for C–N bond generation, such methodology is a privileged synthetic tool for accessing different classes of dyes and introduce molecular diversity. For instance, the synthesis of a triarylamine-based donor can be performed by *N*-arylation of aniline using Ullman coupling with a copper salt as the catalyst [14] or using the milder and more efficient Pd-catalyzed amination of aryl halides, the so-called Buchwald–Hartwig reaction. It is well known how using such protocol a variety of aryl- [15b], heteroaryl- [15c], and alkylamines [15d] can be introduced onto an aromatic or heteroaromatic ring. Very good results have been obtained using palladium complexes with sterically hindered alkylphosphine ligands (e.g., RP(*t*-C₄H₉)₂) and RP(cyclo-C₆H₁₁)₂) as catalysts. Furthermore the nature of both the leaving group and the starting materials, has been greatly broadened (e.g., to halides, pseudo-halides, hindered or functionalized substrates, etc.), thanks to the impressive range of ligands which have been developed in recent years [15e–h].

Concerning the π -scaffold of the dye, in many instances, the synthetic strategy needs the assembling of conjugated double bonds. Although this moiety can be introduced by a Wittig reaction using a phosphine ylide, as we have already outlined, cross-coupling reactions are an alternative remarkable tool which strongly changed the approach for forming carbon–carbon bonds between sp and sp² C-atoms. Among these powerful transformations, the Suzuki–Miyaura cross-coupling, generally defined as the transition-metal-catalyzed cross-coupling between an organo-boron compound and an organic electrophile, become one of the most attractive approach because of the mild reaction conditions and the broad functional group tolerance [16]. Furthermore many aryl and heteroarylboranes are air and moisture stable, are commercially available or can be easily synthesized

by various ways [16]. Due to the mild transmetalation conditions which result in a high chemoselectivity, the Stille reaction, in which transition-metal-catalyzed cross-coupling occurs between an organo-tin compound and an organic electrophile, has also found wide application [17]. In both cases, the palladium-based catalysts have been the most frequently investigated ones and very good results have been achieved by the optimization of ligand design and reaction conditions. The substrate scope for either coupling partner has been substantially expanded, thus sterically congested substrates, less reactive aryl chlorides and sulfonates could be successfully employed under very mild conditions [18]. In many instances, microwave activation provided very good results leading to increased yields and remarkably decreased reaction times.

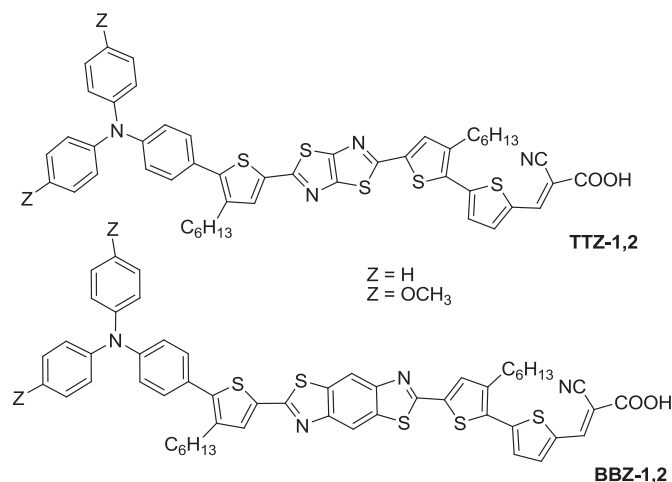
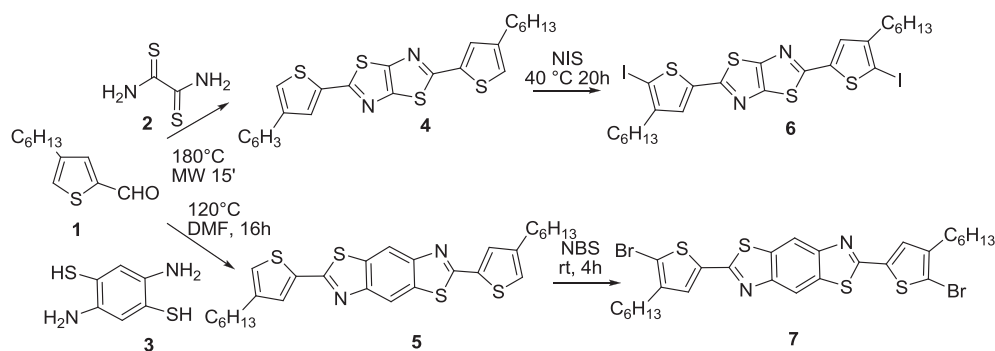


Fig. 7. Structures of [5,4-*d*]thiazole and benzo[1,2-*d*:4,5-*d'*]bisthiazole-containing dyes.



Scheme 1. Synthesis of key intermediates dihalides for the preparation of TTZ and BBZ dyes.

As an example of the application of such synthetic approach in the field of DSSC sensitizers, we have recently developed a series of new dyes based on thiazolo[5,4-*d*]thiazoles and benzo[1,2-*d*:4,5-*d'*]bisthiazoles as spacer units. Thiazolo[5,4-*d*]thiazoles are a class of heterocyclic compounds endowed with a rigid and coplanar bicyclic scaffold giving rise to a highly extended π -electron system (Fig. 4).

The first compound of this class was prepared in 1891 by Ephraim [19], but its correct structure was established only in 1960 by Johnson and Ketcham [20], who were the first to establish a general synthetic procedure. Thiazolo[5,4-*d*]thiazoles have been especially used as spacer units in semiconducting organic materials for polymer light-emitting diodes (PLEDs) and organic field-effect transistors (OFETs), but more recently, the thiazolothiazole unit has been incorporated in donor/acceptor polymers used as the photoactive components of organic bulk heterojunction (BHJ) solar cells [21]. The synthesis of such compounds is traditionally accomplished by means of cross-coupling/polymerization reactions between appropriate symmetrical bifunctional monomers, with Suzuki [22] and Stille [23] couplings being the preferred options. A couple of examples of this kind of structures, where the thiazolothiazole moiety is combined with diverse (hetero)cyclic unit, are presented in Fig. 5.

In the last two years, BHJ solar cells having thiazolothiazole-containing small molecules as light absorbing/donor materials have also been published [24]. In most cases, such compounds present a symmetric structure with a central electron deficient core flanked by conjugated chains ending with electron rich units, most often triphenylamines. Also in this case, the linkage between the central heteroaromatic system and the donor units was realized by means of Suzuki [24a,d] or Stille [24b,c] couplings. Two examples of this kind of molecules are presented in Fig. 6.

In various instances, thiazolothiazole-based compounds gave solar cells with high power conversion efficiencies in the 5.0–5.9% range, with those measured using small molecules-based BHJ being

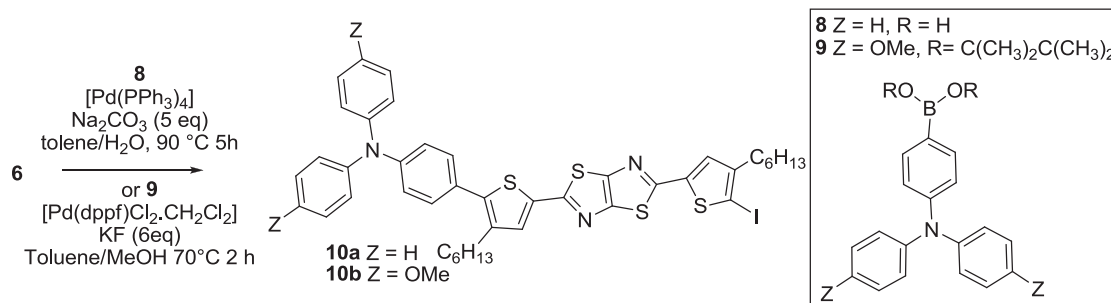
currently lower than those recorded with polymers. In analogy with thiazolothiazoles, benzo[1,2-*d*:4,5-*d'*]bisthiazoles have been extensively investigated for their applications in non-linear optics and organic (opto)electronics [25], and have also been incorporated in photoactive polymers used in BHJ solar cells [26].

Despite these interesting results, the employment of thiazolo[5,4-*d*]thiazoles and benzo[1,2-*d*:4,5-*d'*]bisthiazoles as photosensitizers for DSSCs had not yet been described. Therefore, we decided to prepare new organic dyes containing these two scaffolds as spacer units and to assess their potential as DSSC sensitizers, with the goal of determining whether the properties of high planarity, good electronic conductivity and oxidative stability of these heterocycles could be beneficial for such an application [27].

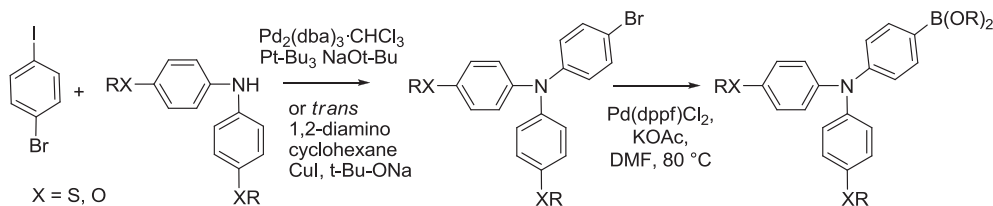
The structures of the thiazolothiazole-containing DSSC sensitizers we designed are shown in Fig. 7. Compounds **TTZ-1,2** and **BBZ-1,2** featured the well-characterized triarylamine and cyanoacrylate groups as the donor and acceptor/anchoring moieties, thiophene rings next to the central heterocyclic core to extend the overall conjugation of the molecule and long alkyl chains on the thiophene rings to improve the solubility of the final compounds and to suppress dye aggregation on the semiconductor surface [28].

Compounds **TTZ-1,2** and **BBZ-1,2** were prepared starting from 4-hexylthiophene-2-carbaldehyde **1**, which was reacted in the presence of dithiooxamide (**2**) or 2,5-diaminobenzene-1,4 dithiol-bis-hydrochloride(**3**) to provide thiazolothiazole **4** or benzobis-thiazole **5** in good yield (Scheme 1).

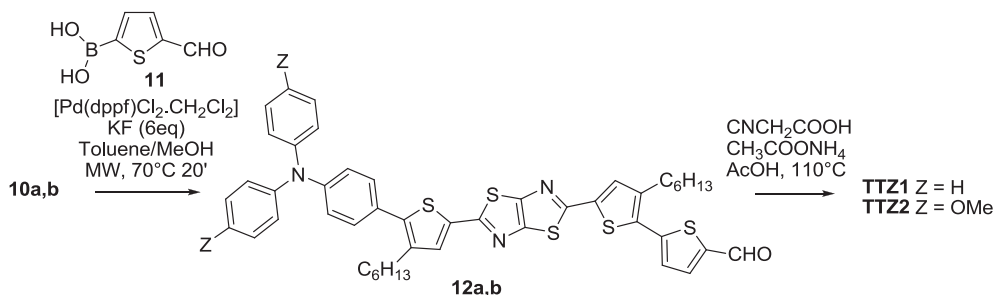
Condensation with dithiooxamide (**2**) was performed in solvent-free conditions at 180 °C under microwave heating, giving the desired product in good yield [29]. Remarkably, this procedure provided a general way for preparing the thiazolothiazole ring system, thus allowing the easy introduction of molecular diversity on the π -scaffold of the dye. Halogenation by treatment with *N*-iodosuccinimide(NIS) at 40 °C overnight, or *N*-bromosuccinimide (NBS), gave the *bis*-halo intermediates **6** or **7** in good yields.



Scheme 2. Arylation of the scaffold via Pd-catalyzed Suzuki cross-coupling.



Scheme 3. Preparation of triarylamine boranes via Buchwald amination/borylation.



Scheme 4. Insertion of the formyl moiety via MW activated Suzuki coupling.

Compounds **6** and **7** are suitable substrates to be elaborated via cross-coupling reactions. Indeed compound **6** underwent a selective Pd-catalyzed Suzuki coupling to introduce the triarylamine donor moiety (Scheme 2). Two different organo-boron compounds were employed for this transformation: commercially available 4-(diphenylamino)benzenboronic acid (**8**) was used to prepare triphenylamino-derivative **10a** ($R = H$), while boronic ester **9** was used for the synthesis of *bis*-methoxy-substituted analog **10b** ($R = MeO$) (Scheme 3). Careful monitoring of the reaction progress ensured a good conversion of the starting materials and minimization of the double coupling products. Although the reactions could not be driven to completion providing products **10a,b** only in moderate yields, recovery and recycling of the unreacted starting material were possible.

Again, this procedure allows to introduce easily structural differentiations on the triphenylamino moiety, as the required boronic acid (or ester) can be prepared *via* amination of 4-bromo-iodobenzene [30] and subsequent Pd-catalyzed borylation [31], as outlined in Scheme 3.

At this stage, a second Pd-catalyzed Suzuki coupling with commercially available 5-formyl-2-thiopheneboronic acid (**11**) was used to introduce the formyl group, leading to compounds **12a–b**. The latter transformation was necessary as the direct formylation of compounds **10a,b** using *n*-BuLi/DMF was a sluggish reaction which required too harsh conditions for our substrates (Scheme 4).

On the contrary, cross-coupling with boronic acid (**11**) proceeded well and with good yields, especially when KF was employed as the base and heating was performed by microwave irradiation. Finally, compounds **12a–b** were converted in good yields to sensitizers **TTZ-1,2** by Knoevenagel condensation. The same sequence was used for preparing the two dyes of the benzobisthiazole series **BBZ-1,2**.

Very recently, the synthesis and application of very similar thiazolothiazole–thiophene-based dyes **FNE71–74** (Fig. 8) has been independently reported and a very similar synthetic approach has been used. Indeed, also in this case, the connection between the thiophene–thiazolothiazole center and the TPA unit was established *via* a Suzuki coupling [32].

The two series of compounds had very similar chemical and photophysical properties, with absorption maxima in the visible

region between 470 and 490 nm. Unfortunately, due to the different fabrication procedures employed, the power conversion efficiencies of the resulting DSSCs cannot be directly compared. Nevertheless, it can be observed that compound **FNE74**, featuring long alkyl chains on the donor moiety, was the best-performing sensitizer among its series, giving a maximum PCE of 5.10% in combination with a quasi-solid state I^-/I_3^- electrolyte. On the other hand, **TTZ1**, bearing unsubstituted phenyl rings, performed better than the corresponding methoxy-substituted analog **TTZ2**, giving a maximum PCE of 3.53% in the presence of a classic liquid electrolyte.

We have also reported a different thiazolothiazole-containing sensitizer (**13**), which was based on a rather unconventional π –D–A architecture (Scheme 5) [33]. The dye was prepared following a procedure similar to **TTZ1–2**, but performing a Vilsmeier–Haack formylation after the Suzuki coupling step: the resulting structure presents a heteroaromatic conjugated unit placed in terminal position rather than between the donor and the acceptor moieties.

Remarkably, such compound presented a red-shifted absorption compared to a similar molecule lacking the heteroaromatic section, indicating that the latter was capable to enhance light harvesting in the visible region. In addition, DSSCs built using dye **13** showed a good V_{oc} value of 0.712 V and yielded a power conversion efficiency of 2.55%, a result which was still significant, since it demonstrated that also dyes based on uncommon structural designs could be employed to fabricate working dye-sensitized solar cells.¹

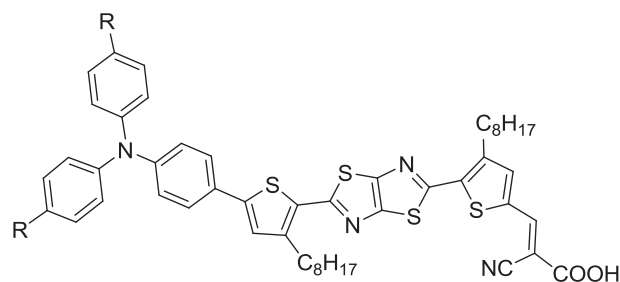
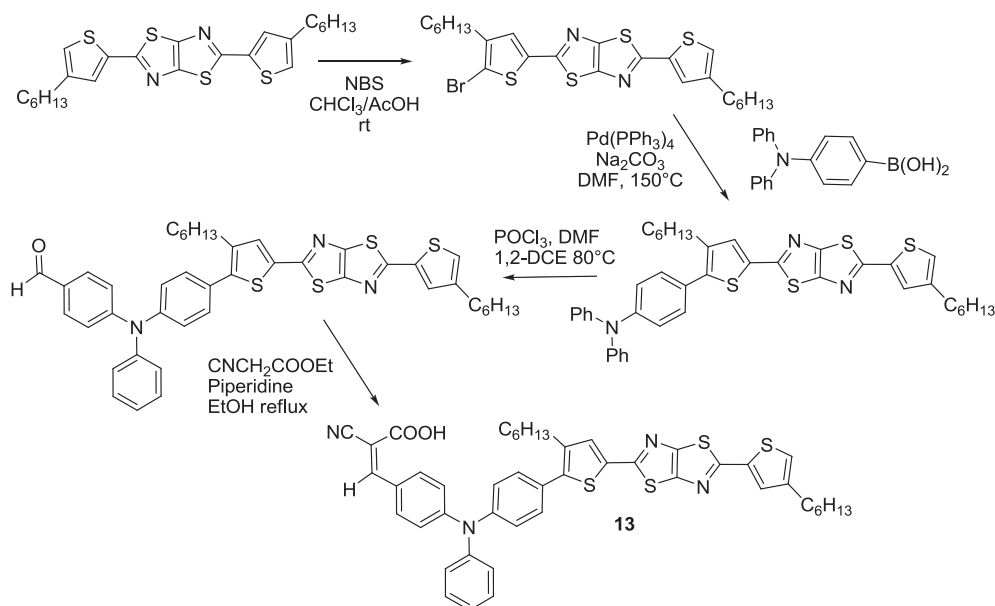


Fig. 8. Structure of FNE type dyes.



Scheme 5. Synthetic scheme of dye **13** featuring an unconventional π -D-A architecture.

1. Conclusions

Cross-coupling reactions have found a wide application for the construction of complex structures in the field of organic materials and polymers. Very recently they have emerged as an unique tool for designing flexible synthetic strategies for new sensitizers for DSSC. The application of cross-coupling reactions in this new and very stimulating area has been exemplified in this microreview by the synthesis of a new class of thiazolothiazole and benzobisthiazole containing dyes. These molecules, designed on the basis of previously successful applications of the relative heterocyclic cores in optoelectronic devices, displayed interesting photoelectronic properties and satisfactory efficiency parameters.

References

- [1] (a) A. deMeijere, F. Diederich (Eds.), *Metal-catalyzed Cross-coupling Reactions*, Wiley-VCH, Weinheim, 2004; (b) E. Negishi, A. de-Meijere (Eds.), *Handbook of Organopalladium Chemistry for Organic Synthesis*, Wiley, New York, 2002.
- [2] C.C.C. Johansson Seechurn, M.O. Kitching, T.J. Colacot, V. Snieckus, *Angew. Chem. Int. Ed.* 51 (2012) 5062–5085 (and ref. cited therein).
- [3] Nobel Lecture, see: (a) A. Suzuki, *Angew. Chem. Int. Ed.* 50 (2011) 6722–6737; (b) E. Negishi, *Angew. Chem. Int. Ed.* 50 (2011) 6738–6764.
- [4] See for instance: Y. Ooyama, Y. Harima *Eur. J. Org. Chem.* (2009) 2903–2934.
- [5] B. O'Reagen, M. Grätzel, *Nature* 353 (1991) 737–740.
- [6] (a) M. Grätzel, *Acc. Chem. Res.* 42 (2009) 1788–1798; (b) Y. Cao, Y. Bai, Q. Yu, Y. Cheng, S. Liu, D. Shi, F. Gao, P. Wang, *J. Phys. Chem. C* 113 (2009) 6290–6297; (c) A. Hagfeldt, G. Boschloo, L.C. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* 110 (2010) 6595–6663.
- [7] 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 (2010) 3103–3109.
- [8] A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.-G. Diau, C.-Y. Yeh, S.M. Zakeeruddin, M. Grätzel, *Science* 334 (2011) 629–634.
- [9] Selected examples: (a) B.S. Chen, D.Y. Chen, C.L. Chen, C.W. Hsu, H.C. Hsu, K.L. Wu, S.H. Liu, P.T. Chou, Y. Chi, *J. Mater. Chem.* 21 (2011) 1937–1945; (b) D. Zhou, N. Cai, H. Long, M. Zhang, Y. Wang, P. Wang, *J. Phys. Chem. C* 115 (2011) 3163–3171; (c) W. Zhu, Y. Wu, S. Wang, W. Li, X. Li, J. Chen, Z.S. Wang, H. Tian, *Adv. Funct. Mater.* 21 (2011) 756–763; (d) Z. Ning, Q. Zhang, H. Pei, J. Luan, C. Lu, Y. Cui, H. Tian, *J. Phys. Chem. C* 113 (2009) 10307–10313; (e) Y.S. Yen, H.-H. Chou, Y.-C. Chen, C.Y. Hsu, J.T. Lin, *J. Mater. Chem.* 22 (2012) 8734–8747; (f) W. Xu, B. Peng, J. Chen, M. Liang, F. Cai, *J. Phys. Chem. C* 112 (2008) 874–880; (g) H. Tian, X. Yang, J. Pan, R. Chen, M. Liu, Q. Zhang, A. Hagfeldt, L. Sun, *Adv. Funct. Mater.* 118 (2008) 3461–3468; (h) Y. Hua, S. Chang, D. Huang, X. Zhou, X. Zhu, J. Zhao, T. Chen, W.-Y. Wong, W.-K. Wong, *Chem. Mater.* 25 (2013) 2146–2153; (i) S. Chang, H. Wang, Y. Hua, Q. Li, X. Xiao, W.-K. Wong, W.Y. Wong, X. Zhu, T. Chen, *J. Mater. Chem. A* 1 (2013) 11553–11558.
- [10] (a) A. Mishra, M.K.R. Fischer, P. Bäuerle, *Angew. Chem. Int. Ed.* 48 (2009) 2474–2499; (b) Y. Wu, W. Zhu, *Chem. Soc. Rev.* 42 (2013) 2039–2058; (c) C. Qin, W.-Y. Wong, L. Han, *Chem. Asian J.* 8 (2013) 1706–1719.
- [11] Z. Chen, F. Li, C. Huang, *Curr. Org. Chem.* 11 (2007) 1241–1258.
- [12] (a) D.P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, L. Sun, *Chem. Commun.* (2006) 2245–2247; (b) D.P. Hagberg, T. Marinado, K.M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun, *J. Org. Chem.* 72 (2007) 9550–9556.
- [13] Y. Ooyama, Y. Harima, *Chem. Phys. Chem.* 13 (2012) 4032–4080.
- [14] J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* 102 (2002) 1359–1470.
- [15] (a) J.P. Wolfe, S. Wagaw, J.-F. Marcoux, S.L. Buchwald, *Acc. Chem. Res.* 31 (1998) 805–818; (b) J.P. Wolfe, H. Tomori, J.P. Sadighi, J. Yin, S.L. Buchwald, *J. Org. Chem.* 65 (2000) 1158–1174; (c) M. Kienle, S.R. Dubbaka, K. Brade, P. Knochel, *Eur. J. Org. Chem.* (2007) 4166–4176; (d) Q. Shen, T. Ogata, J.F. Hartwig, *J. Am. Chem. Soc.* 130 (2008) 6586–6596; (e) E.A.B. Kantchev, C.J. O'Brien, M.G. Organ, *Ald. Acta* 39 (2006) 97–110; (f) M.G. Organ, M. Abdel-Hadi, S. Avola, I. Dubovyk, N. Hadei, E.A.B. Kantchev, C.J. O'Brien, M. Sayah, C. Valente, *ChemEur J.* 14 (2008) 2443–2452; (g) D.S. Surry, S.L. Buchwald, *Angew. Chem. Int. Ed.* 47 (2008) 6338–6361; (h) J.F. Hartwig, *Acc. Chem. Res.* 41 (2008) 1534–1544.
- [16] N. Miyaura, A. Suzuki, *Chem. Rev.* 95 (1995) 2457.
- [17] V. Farina, V. Krishnamurthy, W.J. Scott, *The Stille Reaction*, John Wiley and Sons, New York, 2004.
- [18] For recent reviews, see: (a) R. Jana, T.P. Pathakand, M.S. Sigman, *Chem. Rev.* 111 (2011) 1417–1492; (b) C. Valente, S. Çalimsiz, K.H. Hoi, D. Mallik, M. Sayah, M.G. Organ, *Angew. Chem. Int. Ed.* 51 (2012) 3314–3332; (c) A.F. Littke, G.C. Fu, *Angew. Chem. Int. Ed.* 41 (2002) 4176–4211; (d) S. Wurtz, F. Glorius, *Acc. Chem. Res.* 41 (2008) 1523–1533 (selected examples); (e) M. Huffman, N. Yasuda, *Synlett* (1999) 471–473; (f) H. Nguyen, X. Huang, S.L. Buchwald, *J. Am. Chem. Soc.* 125 (2003) 11818–11819; (g) D. Steinhuebel, J.M. Baxter, M. Palucki, I.W. Davies, *J. Org. Chem.* 70 (2005) 10124–10127; (h) L. Zhang, T. Mengand, J. Wu, *J. Org. Chem.* 72 (2007) 9346–9349; (i) B. Bhayana, B.P. Forsand, S.L. Buchwald, *Org. Lett.* 11 (2009) 3954–3957; (j) S.P.H. Mee, V. Lee, J.E. Baldwin, *Angew. Chem. Int. Ed.* 43 (2004) 1132–1136; (k) J.-H. Li, Y. Liang, D.-P. Wang, W.-J. Liu, Y.-X. Xie, D.-L. Yin, *J. Org. Chem.* 70 (2005) 2832–2834; (l) H. Huang, H. Jiang, K. Chen, H. Liu, *J. Org. Chem.* 74 (2009) 5599–5602;

- (m) R. Lerebours, A. Camacho-Soto, C. Wolf, *J. Org. Chem.* 70 (2005) 8601–8604.
- [19] J. Ephraim, *Ber. Dtsch. Chem. Ges.* 24 (1891) 1026–1031.
- [20] J.R. Johnson, R. Ketcham, *J. Am. Chem. Soc.* 82 (1960) 2719–2724.
- [21] (a) I.H. Jung, J. Yu, E. Jeong, J. Kim, S. Kwon, H. Kong, K. Lee, H.Y. Woo, H.-K. Shim, *Chem. Eur. J.* 16 (2010) 3743–3752;
 (b) Q. Shi, H. Fan, Y. Liu, W. Hu, Y. Li, X. Zhan, *J. Phys. Chem. C* 114 (2010) 16843–16848;
 (c) M. Yang, B. Peng, B. Liu, Y. Zou, K. Zhou, Y. He, C. Pan, Y. Li, *J. Phys. Chem. C* 114 (2010) 17989–17994;
 (d) S.K. Lee, J.M. Cho, Y. Goo, W.S. Shin, J.-C. Lee, W.-H. Lee, I.-N. Kang, H.-K. Shim, S.-J. Moon, *Chem. Commun.* (2011) 1791–1793;
 (e) J. Peet, L. Wen, P. Byrne, S. Rodman, K. Forberich, Y. Shao, N. Drolet, R. Gaudiana, G. Dennler, D. Waller, *Appl. Phys. Lett.* 98 (2011) 043301;
 (f) M. Zhang, X. Guo, Y. Li, *Adv. Energy Mater.* 1 (2011) 557–560;
 (g) S. Subramanian, H. Xin, F.S. Kim, S. Shoaee, J.R. Durrant, S.A. Jenekhe, *Adv. Energy Mater.* 1 (2011) 854–860;
 (h) T.M. Clarke, D. Rodovsky, A.A. Herzing, J. Peet, G. Dennler, D. DeLongchamp, C. Lungenschmied, A.J. Mozer, *Adv. Energy Mater.* 1 (2011) 1062–1067;
 (i) L. Huo, X. Guo, S. Zhang, Y. Li, J. Hou, *Macromolecules* 44 (2011) 4035–4037;
 (j) S. Subramanian, H. Xin, F.S. Kim, S. Jenekhe, *Macromolecules* 44 (2011) 6245–6248;
 (k) T.M. Clarke, J. Peet, P. Denk, G. Dennler, C. Lungenschmied, A.J. Mozer, *Energy Environ. Sci.* 5 (2012) 5241–5245;
 (l) Y.-M. Hwang, J. Ohshita, Y. Harima, T. Mizumo, Y. Ooyama, Y. Morihara, T. Izawa, T. Sugioka, A. Fujita, *Polymer* 52 (2011) 3912–3916;
 (m) Z.-G. Zhang, J. Min, S. Zhang, J. Zhang, M. Zhang, Y. Li, *Chem. Commun.* 47 (2011) 9474–9476;
 (n) M. Zhang, X. Guo, X. Wang, H. Wang, Y. Li, *Chem. Mater.* 23 (2011) 4264–4270;
 (o) I. Osaka, M. Saito, H. Mori, T. Koganezawa, K. Takimiya, *Adv. Mater.* 24 (2012) 425–430;
 (p) S. Van Mierloo, A. Hadipour, M.-J. Spijkman, N. Van den Brande, B. Rutters, J. Kesters, J. D'Haen, G. Van Assche, D.M. de Leuw, T. Aernouts, J. Manca, L. Lutsen, D.J. Vanderzande, W. Maes, *Chem. Mater.* 24 (2012) 587–593;
 (q) H. Xin, S. Subramanian, T.-W. Kwon, S. Shoaee, J.R. Durrant, S.A. Jenekhe, *Chem. Mater.* 24 (2012) 1995–2001;
 (r) Y.-X. Xu, C.-C. Chueh, H.-L. Yip, C.-Y. Chang, P.-W. Liang, J.J. Intemann, W.-C. Chen, A.K.-Y. Jen, *Polym. Chem.* 4 (2013) 5220–5223;
- (s) T. Earmme, Y.-J. Hwang, N.M. Murari, S. Subramanian, S.A. Jenekhe, *J. Am. Chem. Soc.* 135 (2013) 14960–14963.
- [22] Q. Peng, J.-B. Peng, E.T. Kang, K.G. Neoh, Y. Cao, *Macromolecules* 38 (2005) 7292–7298.
- [23] I. Osaka, G. Sauvè, R. Zhang, T. Kowalewski, R.D. McCullough, *Adv. Mater.* 19 (2007) 4160–4165.
- [24] (a) P. Dutta, W. Yang, S.H. Eom, S.-H. Lee, *Org. Electron.* 14 (2012) 273–282;
 (b) Q. Shi, P. Cheng, Y. Li, X. Zhan, *Adv. Energy Mater.* 2 (2012) 63–67;
 (c) P. Cheng, Q. Shi, Y. Lin, Y. Li, X. Zhan, *Org. Electron.* 14 (2012) 599–606;
 (d) M. Nazim, S. Ameen, M.S. Akhtar, Y.-S. Lee, H.-S. Shin, *Chem. Phys. Lett.* 574 (2013) 89–93.
- [25] (a) J.A. Osaheni, S.A. Jenekhe, *Chem. Mater.* 4 (1992) 1282–1290;
 (b) J.A. Osaheni, S.A. Jenekhe, *Chem. Mater.* 7 (1995) 672–682;
 (c) S.-H. Lee, A. Otomo, T. Nakahama, T. Yamada, T. Kamikado, S. Yokoyama, S. Mashiko, *J. Mater. Chem.* 12 (2002) 2187–2188;
 (d) M.M. Alam, S.A. Jenekhe, *Chem. Mater.* 14 (2002) 4775–4780;
 (e) H. Pang, F. Vilela, P.J. Skabara, J.J.W. McDouall, D.J. Crouch, T.D. Anthopoulos, D.D.C. Bradley, D.M. de Leeuw, P.H. Horton, M.B. Hursthouse, *Adv. Mater.* 19 (2007) 4438–4442;
 (f) I. Osaka, K. Takimiya, R.D. McCullough, *Adv. Mater.* 17 (2010) 4993–4997.
- [26] (a) E. Ahmed, F.S. Kim, H. Xin, S.A. Jenekhe, *Macromolecules* 42 (2009) 8615–8618;
 (b) E. Ahmed, S. Subramanian, F.S. Kim, H. Xin, S.A. Jenekhe, *Macromolecules* 44 (2011) 7207–7219.
- [27] A. Dessi, G. Barozzino Consiglio, M. Calamante, G. Reginato, A. Mordini, M. Peruzzini, M. Taddei, A. Sinicropi, M.L. Parisi, F. Fabrizi de Biani, R. Basosi, R. Mori, M. Spatola, M. Bruzzi, L. Zani, *Eur. J. Org. Chem.* (2013) 1916–1928.
- [28] N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, *J. Am. Chem. Soc.* 128 (2006) 14256–14257.
- [29] A. Dessi, M. Calamante, A. Mordini, L. Zani, M. Taddei, G. Reginato, *RSC Adv.* 4 (2014) 1322–1328.
- [30] (a) C. Lambert, J. Schelter, T. Fiebig, D. Mank, A. Trifonov, *J. Am. Chem. Soc.* 127 (2005) 10600–10610;
 (b) A. Proń, G. Zhou, H. Norouzi-Arasi, M. Baumgarten, K. Müllen, *Org. Lett.* 11 (2009) 3550–3553.
- [31] L. Chen, B. Zhang, Y. Cheng, Z. Xie, L. Wang, X. Jing, F. Wang, *Adv. Funct. Mater.* 20 (2010) 3143–3153.
- [32] W. Zhang, Q. Feng, Z.-S. Wang, G. Zhou, *Chem. Asian J.* 8 (2013) 939–946.
- [33] L. Zani, G. Reginato, A. Mordini, M. Calamante, M. Peruzzini, M. Taddei, A. Sinicropi, M.L. Parisi, F. Fabrizi de Biani, R. Basosi, A. Cavallaro, M. Bruzzi, *Tetrahedron Lett.* 54 (2013) 3944–3948.