



Surprising characteristics of D–A-type functional dyes by introducing 4-alkoxythiazoles as the donor-unit



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ABSTRACT

In this study, we report on the syntheses of novel donor–acceptor molecules. These new dyes comprised benzo[c][1,2,5]thiadiazole and pendants with one or two 4-alkoxythiazoles as donor parts, which were introduced without Pd-catalyzed cross coupling reactions. The optical and electrochemical properties were studied via absorption, emission spectroscopy and cyclovoltammetric measurements. We experimentally found surprising small band gaps from HOMO to LUMO of 2.4 eV and 2 eV, respectively, which were also investigated using DFT calculations.

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1. Introduction

Since the development of the organic photovoltaic (OPV) devices, there is a great interest in novel semiconductive materials, such as the light harvesting unit.^{1–3} Thereby, the solar energy conversion is realized by two fundamental devices: heterojunctions (HJ) and dye sensitized solar cells (DSSCs). The active layer in the first case is realized via π -conjugated polymers or small molecules as the donor materials and mostly fullerenes as the acceptor.^{4–8} The efficiencies of small molecule bulk-HJ (BHJ) have recently been raised significantly. Thus, novel small molecules became attractive because of their good reproducibility, charge carrier mobilities and monodispersity for usage in BHJ.^{9–11} In comparison, OPVs working on the DSSC approach only use small molecules to convert light into electricity.^{12–14} New semiconductive materials are also important for the development of organic field effect transistors. Therefore, high charge carrier mobilities and small reorganization energies are necessary.¹⁵ In summary, such functional materials offer a wide range of possible applications. By using functional dyes as the active layer, such as merocyanines, squaraines or porphyrines, which are established in DSSC devices, they,

furthermore, offer an utilization as the emitting unit in organic light emitting diodes.¹⁶

The band gap (energy difference between HOMO and LUMO) and specific energy level of these single molecules could be influenced very strongly using the donor–acceptor (D–A) approach.^{17–19} Since the HOMO is mainly determined by the donor part, while the LUMO relies on the acceptor unit, their energy levels could be tuned by selecting the building blocks carefully. Moreover, D–A type dyes are often featured by intramolecular charge transfer (ICT) processes. The ICT not only lowers the band gap, but also enhances charge carrier mobility.

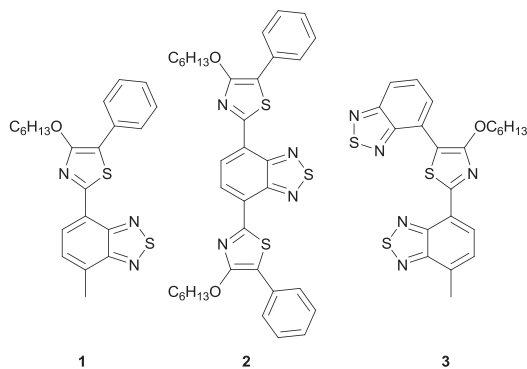
The greatest advantage of organic dyes regarding inorganic or polydispers semiconductors is the possibility of simple and manifold derivatization.²⁰ Furthermore, a good solubility and well-defined morphology could be realized easily and is important for receiving good processabilities.

The reactivity, derivatization and the usage of benzo[c][1,2,5]thiadiazole (BT) as an electron acceptor has been studied intensively over the last few years.^{21–23} It is used in many different D–A type copolymers, but rather in D–A type small molecules^{24–31} and especially in D–A–D type dyes showing two-photon absorption.^{32,33} Thereby, the electron-donating units are mostly based on thiophene or triarylamine, which were introduced via Pd-catalyzed cross-coupling reactions.

We here present a D–A, D–A–D and an A–D–A type system (see Scheme 1), where 4-alkoxythiazoles are used as the electron-

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donating moieties, while the established BTs are utilized as the electron-accepting units. Starting at BT, it is possible to synthesize these structures via five steps and without expensive Pd-catalyzed cross-coupling reactions. We obtained well-soluble functional dyes by fusing two kinds of established substructures, which could act as model substances for forthcoming studies.



Scheme 1. Structures of the D–A type dyes **1**, **2** and **3**.

2. Results and discussion

2.1. Syntheses and structures

Knowing the synthesis and especially the purification of mono brominated BT is elaborate,³⁴ we decided to start with 4-methyl-BT **13**, which is easy accessible via sulphurisation of 3-methyl-1,2-phenylenediamine **15** (see Scheme 2).²⁴ Bromination of **13** gave the mono-brominated species **11** in good yields, and the treatment of BT (**14**) with an excess of bromine leads to 4,7-dibromo-BT **12**.³⁴

The nitrile functions should be introduced via nucleophilic substitution of bromine. According to the literature,³⁵ the mononitrile **9** could be obtained in moderate yield. The synthesis of **10** occurred with more difficulty, but the dinitrile was accessible via the slightly optimised procedure of Garo et al.^{36,37} The subsequent addition reactions between hydrogen sulphide and the nitriles **9** and **10** were realized via freshly prepared *O,O'*-diethylthiophosphate, which is able to release H₂S.³⁸ For the preparation of target compound **3**, we also had to synthesize the cyclization partner **16**. This was realized beginning with the α -bromination of **13** by means of NBS.³⁹ Nucleophilic substitution of bromine (see compound **20**) by CN⁻ was carried out subsequently,⁴⁰ followed by hydrolysis of the isolated nitrile to obtain the BT-substituted acetic acid **18**. After the esterification and renewed bromination of the α -carbon atom, the desired, racemic product **16** was obtained as yellowish oil in moderate yield. Hantzsch cyclization was carried out via, by our group, optimized reaction conditions to introduce the thiazole substructures.^{41–43} The thioamides **7**, **8** on addition of ethyl α -bromophenylacetate **21** or compound **16**, respectively, gave the 4-hydroxythiazoles **4**, **5** and **6** under alkaline conditions. Williamson type etherifications were carried out to introduce the hexyl side chains and gave the desired well-soluble products.

The structures were determined by elemental analysis, mass spectrometry and NMR experiments. We were also able to obtain single crystals suitable for single crystal X-ray analysis via slow evaporation of a solution of **1** in a mixture of *n*-heptane and chloroform. It is noteworthy that 0.5 molecules of CHCl₃ co-crystallized in the packing of compound **1**. Due to this, we obtained an alternating packing of two kinds of structures in the single crystal analysis (as depicted in Fig. 1). While one molecule of thiazole **1** appears strictly planar and interacts via H-bonds to the neighboring molecules (molecule distance of about 3.4 Å), the phenyl residue of

the other kind is, due to the interaction to CHCl₃ (distance of about 3.6 Å), twisted by about 27° relative to the BT-thiazole plane.

2.2. Photophysical and electrochemical properties

The UV–vis absorption and fluorescence spectra of BT-thiazoles **1**, **2** and **3** are depicted in Fig. 2. All derivatives show intense absorption in the visible region and two strong bands. In the case of **1**, the maxima of the absorption are located at $\lambda_{\text{max}}=316$ nm and 452 nm. Due to the second electron donating moiety in **2**, the absorption bands entail a significant bathochromic shift to $\lambda_{\text{max}}=365$ nm and 545 nm. The UV–vis absorption spectrum of derivative **3**, compared to that of compound **1**, is only slightly bathochromic shifted, but the A–D–A type dye **3** exhibits a more intense absorption with maxima at $\lambda_{\text{max}}=315$ nm and 470 nm. The absorption spectra of all dyes are low structured with broad absorption bands, but all compounds exhibit high oscillator strengths with log ϵ between 4.0 and 4.5. All donor–acceptor dyes possess high Stoke's shifts of about $\nu=5500$ cm⁻¹ (**1**), $\nu=3600$ cm⁻¹ (**2**) and $\nu=4900$ cm⁻¹ (**3**) as the maxima of the fluorescence spectra appear, after excitation at the appropriate absorption maximum, in the orange and red region of visible light at $\lambda=602$ nm for **1**, $\lambda=667$ nm for **2** and $\lambda=609$ nm for **3**, respectively.

Fluorescence measurements in different solvents showed a positive fluorescence solvatochromism (see SI, Figs. 1–3). Thus, the change from nonpolar (cyclohexane) to polar solvents, such as acetone, leads to a bathochromic shift of the fluorescence maxima (**1**: $\Delta\lambda=55$ nm $\hat{=}$ 1580 cm⁻¹; **2**: $\Delta\lambda=34$ nm $\hat{=}$ 793 cm⁻¹; **3**: $\Delta\lambda=51$ nm $\hat{=}$ 1430 cm⁻¹). Furthermore, we examined the fluorescence quantum yields in cyclohexane to $\Phi_{\text{F}}=0.5$ E·mol⁻¹ for **1**, $\Phi_{\text{F}}=0.3$ E·mol⁻¹ for **2** and $\Phi_{\text{F}}=0.1$ E·mol⁻¹ for **3**, respectively.^{44,45}

Cyclic voltammetry was performed to investigate the redox potential; the voltammograms are depicted in Fig. 3. Thiazole **1** exhibits a reduction at a potential of $E_{1/2}=-1.8$ V and an irreversible oxidation at $E=0.82$ V. Thus, we determined the HOMO and LUMO energy via the onset potential of the oxidation and reduction. The band gap is $E_{\text{Gap}}^{\text{CV}}=2.44$ eV, which is in good agreement with $E_{\text{Gap}}^{\text{opt}}=2.35$ eV, ascertained via the energy of the longest wavelength absorption band at 10% intensity. We achieved different results in case of bis-thiazole **2**, which could be oxidized twice, while the first step at $E_{1/2}=0.67$ V seems to be reversible, the second one at $E=0.93$ V is irreversible. A reversible reduction step is located at $E_{1/2}=-1.5$ V at the reduction wave. Through this, the reduction of our dyes relies, as expected, on the BT unit and the oxidation takes place at the thiazole moiety, since bis-thiazole **2** could be oxidized twice. Furthermore, it is remarkable that the introduction of a second thiazole moiety leads to a significantly lowered LUMO energy of about 0.4 eV (**2**, see Table 1), in comparison to the structure containing only one donating unit (**1**), while the HOMO is nearly unaffected. This results in a smaller band gap for **2** of $E_{\text{Gap}}^{\text{CV}}=2.06$ eV, which correlates well with the optical band gap, examined via absorption spectroscopy, of $E_{\text{Gap}}^{\text{opt}}=1.97$ eV. Derivative **3** exhibits a similar behavior like the D–A type dye **1**. The A–D–A dye **3** is featured by an irreversible oxidation at a potential of: $E=1.25$ V and a reversible reduction at $E_{1/2}=-1.8$ V, with respect to the limit of cyclic voltammetry measurements in THF. Due to the second BT unit compound **3** should be able to accept two electrons, but possibly the second reduction occurs at a potential beyond the limits of the appropriate solvents. However, we were able to examine the energies of HOMO and LUMO which lead to a band gap of $E_{\text{Gap}}^{\text{CV}}=2.44$ eV that concurs to the optical gap of $E_{\text{Gap}}^{\text{opt}}=2.28$ eV.

In order to gain more detailed insight into the electronic characteristics of the herein presented target compounds density functional theory (DFT) calculations have been performed. The effects of solvation (THF) have been addressed for ground properties

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