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Synthesis and characterization of non-symmetrical photoswitchable DTE(OMe) sensitizers

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ABSTRACT

DTE-BODIPY 2 and **BTD-DTE 3** were designed for reversible light modulation of electron- and energy-transfer processes on TiO₂, and showed almost complete ring closure. In **BTD-DTE 3** the BTD is an acceptor group in the open form (OF), and an energy donor group in the closed form (CF), but this property is depending on the solvent. Quantum yields for ring closure decreased (**BTD-DTE 3**: factor 5; **DTE-BODIPY 2**: factor 12) compared to **DTE 1**, because of π -system elongation in OFs, and also cycloreversion quantum yields became smaller (**BTD-DTE 3**: factor 1.4; **DTE-BODIPY 2**: factor 2.2).

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1. Introduction

Photoswitches connected to energy- and/or electron-donating molecular units provide unique insights into transfer mechanisms within these conjugates by using ultrafast transient absorption spectroscopy. Typically, dithienylethenes (DTEs) can be switched reversibly between a thermally stable open (OF) and a closed (CF) form by irradiation with light of different energy.¹ Another possibility to switch DTEs is by electrochromism, whereby the substitution pattern of the DTE core is controlling if the OF or CF can be obtained by redox processes.² With the attachment of fluorophores, DTEs became well investigated for applications in on/off-switching of chemical reactivity³, microscopy⁴ and material science⁵.

Our recent approach⁶ to switch electron transfer by energy transfer between a fluorescent BODIPY-moiety (**BCP-18**, Fig. SI-6) and a DTE photoswitch on the semiconductor material TiO₂ showed an electron transfer with a detectable BODIPY cation signature in the open form (DTE-o), which competed with the intramolecular energy transfer of the S₁ fluorophore state to the DTE in the closed form (DTE-c). Furthermore, transient absorption spectroscopy revealed the formation of a DTE-c cation. However, **BCP-18** containing a dimethyl-DTE had a decreased ratio of isomers in the

photostationary state (pss, CF:OF = 60:40). Therefore, a new design for the DTE photoswitch was chosen. Dimethoxy-DTE-systems, e.g. **DTE 1** (Fig. 1), were developed by Irie for single molecule applications in matrices and had a uniquely reduced cycloreversion quantum yield of factor 1000 compared to dimethyl-DTEs.⁷

The herein presented systems **DTE-BODIPY 2** and **BTD-DTE 3** (Fig. 1) contain the dimethoxy-DTE unit and carry a benzoic acid anchor group for the attachment to TiO₂. Both compounds should allow to investigate the molecular processes influencing electron- and energy transfer processes in the open (OF) and closed forms (CF, pss). The BTD unit is well suited for improving the formation of a detectable photoproduct by an electron transfer reaction and usage in an on/off-switchable scenario.⁸ Benzoic acid directly coupled to the BTD-unit is known for being twisted around 33° and for hindering the charge recombination.⁹ The **DTE-BODIPY 2-o** is designed as a donor- π -acceptor-system and **BTD-DTE 3-o** as a donor- π -acceptor- π -acceptor molecule. Literature known systems with D-A- π -A design containing BTD showed a significant charge separated state.¹⁰ Furthermore, the bithiadiazole (BTD) unit is an electron withdrawing group and also an efficient fluorophore for energy transfer processes.¹¹

2. Results and discussion

2.1. Preparation

The novel conjugates **DTE-BODIPY 2** and **BTD-DTE 3** and the

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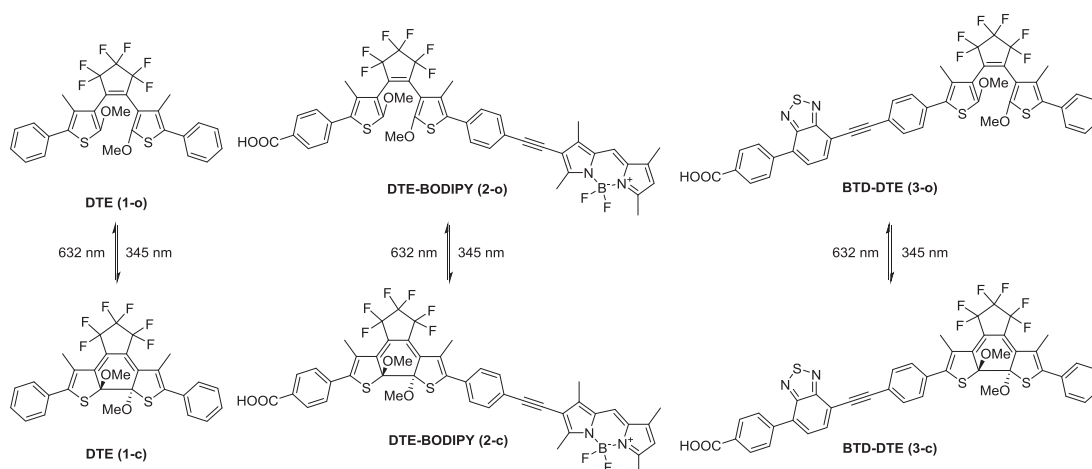


Fig. 1. Structures of the new conjugates **DTE 1**, **DTE-BODIPY 2** and **BTD-DTE 3** in open (OF) and closed (CF) forms.

literature known compound **DTE 1** were synthesized (procedures in SI, Fig. SI-4). The synthetic route to **DTE-BODIPY 2** is shown in Fig. 2 and the synthesis of thienylethene **5** and chloro-thiophene **4** are given in the SI (Figs. SI-2 and 3).

Chemoselective lithiation of chloro-thiophene **4** in 4-position and reaction with the thienylethene **5** led to **DTE 6**. Dimethoxy-DTE-c compounds showed decomposition under standard conditions in the laboratory upon treatment with base. Therefore all reactions, workups and chromatographies were carried out in the dark to prevent switching. Because of the reactivity of the chlorine substituent of compound **6** lithiation and boronation were readily achieved for the following SUZUKI-coupling with iodo-benzoic acid ester (Fig. 2). Starting from compound **7** TMS- and ester-deprotection in aqueous base (Fig. 2) and SONOGASHIRA-coupling with iodo-BODIPY **15** (Fig. 3) yielded **DTE-BODIPY 2**.

The BTD-conjugate **BTD-DTE 3** was synthesized by a similar approach, from the lithiated intermediate of compound **9** and thienylethene **5** as shown in Fig. 4. TMS-deprotection, SONOGASHIRA-coupling with BTD-benzoic acid ester **23**, followed by ester cleavage furnished **BTD-DTE 3**.

2.2. Spectroscopy

The UV/Vis- and fluorescence spectra were recorded at room temperature in acetonitrile after degassing under argon for 15 min. Irradiations were carried out with LEDs (M340L4 and M625L3 from Thorlabs, emission spectra are given in Fig. SI-1) in a stirred and temperature controlled environment. Conversions to the pss were determined by LCMS (reversed phase) at the isosbestic points (Table 1).

The absorption spectra of **DTE 1** (Fig. SI-7) showed in the OF (**DTE 1-o**) a dominant absorption band at 287 nm. Irradiation at

345 nm (2.0 mW/cm²; HW = 11 nm) converted the OF into the CF (**DTE 1-c**) with further absorption bands at 624 nm and 404 nm, while the absorption band of the DTE shifted to 296 nm (dynamics of OF to CF conversions of **DTE 1**, **DTE-BODIPY 2** and **BTD-DTE 3**, and vice versa are given in Fig. SI-8-SI 10). All cycloreversion reactions towards the OFs were done with excitation at 632 nm (250 mW/cm²; HW = 18 nm). **DTE 1** did not show photodegradation in 5 cycles in acetonitrile and could be switched quantitatively. Literature known photodegradation during switching upon irradiation of **DTE 1** with 313 nm in acetonitrile could not be detected.⁴ The decreased quantum yields of **DTE 1** ($\epsilon_{345 \text{ nm}} = 5.4 \cdot 10^3 \text{ Lmol}^{-1}\text{cm}^{-1}$, Table 1) for ring closure in comparison to the literature (0.46^4 , $\epsilon_{313 \text{ nm}} = 1.5 \cdot 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$) can be explained by the extinction coefficient at the excitation wavelength for the ring closure and the broad emission characteristics of the used LEDs towards lower energy (Fig. SI-1).

With the attachment of BODIPY to the dimethoxy-DTE unit in **DTE-BODIPY 2**, the strong absorption band of BODIPY at 530 nm is the most dominant change in the UV/Vis spectra compared to **DTE 1** (Fig. 5). The absorption of OF shifted bathochromic to 331 nm and showed a shoulder at 401 nm. The latter band should be a combination of DTE and BODIPY absorption (stacked spectra of **8**, BODIPY **14** and **DTE-BODIPY 2** in OF and CF(pss) are shown in Fig. SI-13). In the pss of **DTE-BODIPY 2** for CF the typical band at 636 nm was formed, while the other absorption band of OF was blue shifted to 321 nm. **DTE-BODIPY 2** did not show photodegradation in 3 cycles in acetonitrile and could be switched quantitatively. One of the most remarkable properties of BODIPYs is their small Stokes shift and their sharp absorption and emission bands (tetramethyl-BODIPY **14** in acetonitrile, $QY_{\text{Fl}} = 0.96^{12}$, has a Stokes shift of 5 nm, absorption and emission spectra of **14** are shown in Fig. SI-11).¹³ In Fig. 5 the emission band of **DTE-BODIPY 2** at 530 nm is shown for

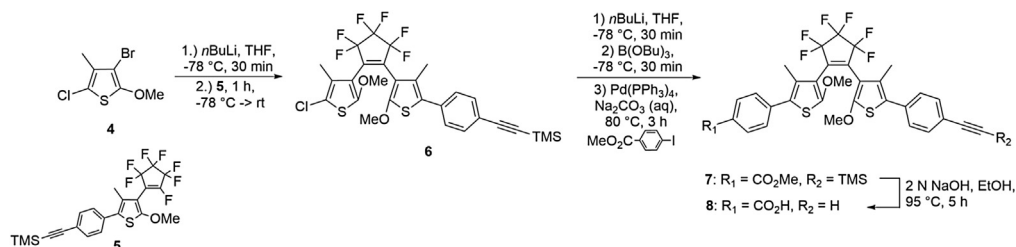


Fig. 2. Synthesis of unsymmetrically substituted **DTE 8**.

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