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4-Methoxy-1,3-thiazole based donor-acceptor dyes: Characterization, X-ray structure, DFT calculations and test as sensitizers for DSSC

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ABSTRACT

Four donor-(π -conjugated-bridge)-acceptor type dyes **A-D** were designed and synthesized. These new compounds use an unconventional 4-hydroxy-1,3-thiazole building block as an additional chromophore for light harvesting and to extend the π -conjugated system of the molecules. The synthetic route involved a double *N*-arylation Hartwig–Buchwald reaction using Pd(dba)₂ as precatalyst and P(^tBu)₃ as ligand. Two different triarylamines and a 4-methoxyphenyl group were used as electron donor moieties. The electron acceptor (anchoring) group was 2-cyanoacrylic acid for all dyes, whereas the π -spacer was varied and the influence was investigated. The dyes were thoroughly characterized using photophysical and electrochemical methods and by density functional theory calculations. Additionally, they were evaluated in nanocrystalline TiO₂-based dye-sensitized solar cells (DSSCs). The DSSCs were prepared with and without deoxycholic acid (DCA) as a co-adsorbent to inhibit dye aggregation. The efficiencies obtained were low for DSSCs fabricated without DCA, but were significantly improved for DCCS with co-adsorbed DCA. Additionally, the X-ray structure of dye **D** was obtained, demonstrating the stereochemistry and planar geometry of the molecule. The DSSC based on dye **A** showed an efficiency of $\eta = 1.70\%$ ($J_{sc} = 4.49$ mA cm⁻², $V_{OC} = 0.61$ V, FF = 0.62) under 100 mW cm⁻² simulated AM 1.5 G solar irradiation compared to $\eta = 4.1\%$ of the standard N₃ obtained under same conditions.

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1. Introduction

The 4-hydroxy-1,3-thiazoles are a well known type of heterocyclic compounds [1]. This building block was revived from our group due to the similarity to the naturally occurring luciferine, the light-emitting dye of fireflies, and their interesting optical properties. Since then, they have received interest due to their use as light harvesting ligands in Ru(II) polypyridyl complexes [2], as blueemitting dyes in polymers [3], and because of their tuneable absorption and emission spectra [4], high quantum yields and extinction coefficients, and easy functionalization [5].

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In this paper, new thiazole dyes were designed, that consist of a donor-(π -conjugated-bridge)-acceptor structure (D $-\pi$ -A), *e.g.* a main prerequisite of sensitizers in dye-sensitized solar cells (DSSCs). Molecules with this special structural architecture have attracted attention since they can be used as emissive materials in molecular electronics [6,7], as fluorescent probes in biochemical applications [8], as nonlinear optical (NLO) materials [9,10], in organic light-emitting diodes (OLEDs) [11] and of course, in DSSCs.

DSSCs have received considerable attention as one possibility to convert solar energy into electricity. Numerous compounds have been tested [12–15] since their description by Grätzel et al. in 1991 [16], and the efficiency was driven up to 11.1% for small DSSCs sensitized with N₃ and up to 10.3% for DSSCs sensitized by an organic-dye [17,18]. Recently, a new record was obtained from Yella et al. using a porhpyrine dye as sensitizer and a cobalt (II/III) redox electrolyte instead of the commonly used iodide/triiodide (I^-/I_3^-) redox couple, exceeding an efficiency of 12% [19]. The advantages of organic sensitizers toward Ru(II) polypyridyl complexes, such as N₃, N719, and the black dye, are higher molar absorption coefficients,

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often simpler synthesis procedures and structure varieties and, naturally, lower costs for the production of a DSSC [20]. The record mentioned for a DSSC with an organic sensitizer was set by a dye containing a triarylamine-based donor. This moiety is extraordinarily promising in various fields of organic dyes [21–26] and was, therefore, predominantly used in this study.

One important possibility to tune the optical properties of organic sensitizers is by alternating the π -conjugated bridge which typically consists of thiophenes and corresponding derivatives (e.g. bithiophene, ethyldioxythiophene). They proved to be more advantageous than an oligoene bridge, which undergoes cis-trans isomerisation or oxidation reactions [27]. In this contribution, we substituted the commonly used thiophene unit with a novel etherified 4-hydroxy-1,3-thiazole chromophore to build up D- π -A dyes with high molar extinction coefficient and to expand the absorption spectra further into the solar spectral region. Dyes with a similar structure already proofed to be effective as sensitizers in DSSCs [28,29]. Consequently, two different triarylamines and one 4-methoxyphenyl unit were used as electron donors and the influence of the length of the conjugated bridge was verified. 2cyanoacrylic acid was used as the electron acceptor/anchoring group for the nanocrystalline TiO₂ surface. The dyes obtained were characterized by UV/Vis and emission spectroscopy, electrochemical measurements, and quantum chemical methods. Furthermore, they were tested regarding their application as sensitizers in DSSCs.

2. Experimental section

2.1. General procedures and spectroscopic measurements

¹H, ¹³C NMR and the corresponding correlation spectra were recorded on a Bruker AC-250 (250 MHz) and AC-400 (400 MHz) spectrometer. Chemical shifts (δ) are given relative to solvents and all coupling constants are given in Hz. UV/Vis data of the compounds were collected on a Lambda 19 from PERKIN-ELMER and fluorescence spectra were measured on a Jasco FP 6500. Optical absorption spectra of the adsorbed dyes were recorded by using a Cary 300 UV/ Vis spectrophotometer operated at a resolution of 1 nm. The absorption spectra of the electrodes were measured in a reflection arrangement and the absorption of pure TiO₂ nanoparticles was subtracted. Measurements of the fluorescence intensity were carried out on a Perkin Elmer lambda16 UV/VIS spectrometer in the perpendicular excitation-emission geometry, at excitation conditions where the absorbance in the most red-shifted absorption was <0.05. The emission quantum yields were determined by comparing the corrected emission spectra with the reference spectrum of quinine sulfate ($\Phi = 0.55$). All compounds were excited in their absorption maximum. The fluorescence lifetimes of the thiazoles were obtained by time-correlated single photon counting (TCSPC) after excitation with a frequency-doubled Ti-sapphire laser (Tsunami, Newport Spectra-Physics GmbH), *i.e.* $\lambda_{ex} = 650$ nm. The repetition rate of the laser was adjusted to 0.8 MHz by a pulse selector (Model 3980, Newport Spectra-Physics GmbH). The emission of the thiazoles was detected using a streak-camera in TCSPC mode. Elemental analysis was carried out on a Leco CHNS-932. Mass spectra were measured either on a Finnigan MAT SSQ 710 (EI) or MAZ 95 XL (FAB) system. MALDI-TOF MS was performed on a Bruker Ultraflex TOF/TOF mass spectrometer equipped with a 337 nm nitrogen laser operated in the reflectron mode using an acceleration voltage of 25 kV, and dithranol (Bruker, #209783) was used as matrix. Electrochemical measurements were performed on a Metrohm Autolab PGSTAT30 potentiostat with a standard threeelectrode configuration. The experiments were carried out in degassed solvents containing 0.1 M Bu₄NPF₆ salt. At the end of each measurement ferrocene (Fc/Fc⁺) was added as an internal standard. Starting materials were commercially obtained from Sigma–Aldrich and used as received. TLC was from Merck (Polygram SIL G/UV254, aluminum oxide 60 F254). The material for Column chromatography was also obtained from Merck (Silica gel 60).

2.2. Synthesis of the compounds

2.2.1. 5-(4-Nitrophenyl)-2-(thiophen-2-yl)thiazol-4-ol (1)

A mixture of thiophene-2-carbothioamide (2.50 g, 17.5 mmol) and ethyl 2-bromo-2-(4-nitrophenyl)acetate (5.46 g, 19.0 mmol, 1.1 equiv) in 100 mL toluene was heated under reflux for 24 h, and an orange precipitate occurred. After the reaction was cooled down to 50 °C, pyridine (5 mL) was added and stirring was continued for additional 30 min. The mixture was cooled to 0 °C, filtered through a glass frit, washed with cold EtOH and pentane, and dried in vacuo. The orange product was pure in terms of elemental analysis and used without further purification (3.57 g, 11.7 mmol, 67%). mp 279 °C (decomp.). ¹H NMR (250 MHz, DMSO- d_6): δ 7.19 (dd, J = 4.0 Hz, J = 4.8 Hz, 1H), 7.69 (d, J = 3.2 Hz, 1H), 7.78 (d, J = 5.0 Hz, 1H), 7.87 (m, 2H), 8.20 (m, 2H), 12.53 (s, 1H). ¹³C NMR (63 MHz, DMSO-*d*₆): δ 160.42, 156.86, 144.09, 138.77, 136.05, 129.949, 128.76, 127.60, 125.63, 124.19, 104.65. MS-EI: m/z 304 (M⁺⁺, 100%), 110 (M⁺⁺ - C₈H₄NO₃S, 60%). Anal. Calc. for C₁₃H₈N₂O₃S₂: C, 51.30; H, 2.65; N, 9.20; S, 21.07. Found: C, 51.43; H, 2.84; N, 9.16; S, 20.92. UV/Vis (DMSO): λ_{max} (log ε): 325 (3.78), 429 (4.10), 611 (4.39).

2.2.2. 4-Methoxy-5-(4-nitrophenyl)-2-(thiophen-2-yl)thizaole (2)

A mixture of **1** (1.86 g, 6.11 mmol) and KOH (0.41 g, 7.33 mmol, 1.2 equiv) in DMSO (50 mL) was stirred for 30 min followed by the addition of CH₃I (1.04 g, 7.33 mmol, 1.2 equiv). The deep blue mixture was stirred for 24 h at room temperature. The solution was poured into H₂O (150 mL) and was extracted with CHCl₃ $(3 \times 50 \text{ mL})$. The combined organic phases were additionally washed with H_2O (3 \times 50 mL) to remove the DMSO, dried over MgSO₄ and concentrated *in vacuo* to give a brown oil which was further purified by a short gel filtration (silica, CHCl₃) to yield the ether as an orange solid (1.3 g, 4.09 mmol, 67%). mp 144–145 °C. ¹H NMR (250 MHz, CDCl₃): δ 4.22 (s, 3H), 7.10 (dd, J = 3.8 Hz, J = 5.0 Hz, 1H), 7.44 (dd, J = 1.1 Hz, J = 5.1 Hz, 1H), 7.54 (dd, J = 1.1 Hz, J = 3.7 Hz, 1H), 7.81 (m, 2H), 8.20 (m, 2H). ¹³C NMR (63 MHz, CDCl₃): δ 161.00, 157.02, 145.14, 138.48, 137.18, 128.63, 128.17, 126.71, 126.24, 124.12, 107.81, 58.12. MS-EI: *m*/*z* 318 (M⁺⁺, 100%), 288 (M⁺⁺ - CH₂O, 10%). Anal. Calc. for C₁₄H₁₀N₂O₃S₂: C, 52.82; H, 3.17; N, 8.80; S, 20.14. Found: C, 52.67; H, 2.90; N, 9.11; S 20.02. UV/Vis (CH₂Cl₂): λ_{max} (log ε): 254 (3.80), 413 (4.30).

2.2.3. 4-(4-Methoxy-2-(thiophen-2-yl)thiazol-5-yl)aniline (3)

 N_2H_5OH (1.7 mL, 18.7 mmol, 5 equiv, solution 80% in H_2O) was added to a suspension of 2 (1.18 g, 3.73 mmol) and freshly prepared Raney nickel (catalytic amounts) in MeOH (100 mL) at 50 °C. The suspension turned green and became clear as the reaction proceeded. After the reaction had finished, as indicated by TLC (if the conversion was not complete, more hydrazine was added), the mixture was diluted with CH₂Cl₂ (100 mL) and filtered through a frit on which a 2 cm-thick silica bed was applied to efficiently remove the Raney nickel. The mixture was concentrated till dryness and the crude product was either purified using flash chromatography (silica, CHCl₃/EtOAc 5:1) or by recrystallization from heptane/ CH₂Cl₂ by slow evaporation of the CH₂Cl₂, yielding the pure amine as a yellow solid (1.02 g, 3.54 mmol, 95%). mp 114–115 °C. ¹H NMR (250 MHz, CDCl₃): δ 7.56–7.47 (m, 2H), 7.44 (ddJ = 3.7 Hz, *J* = 1.1 Hz, 1H), 7.34 (dd, *J* = 5.1 Hz, *J* = 1.1 Hz, 1H), 7.06 (dd, *J* = 5.1, J = 3.7 Hz, 1H), 6.77–6.64 (m, 2H), 4.12 (s, 3H), 3.73 (s, 2H).¹³C NMR (63 MHz, CDCl₃): δ 157.86, 152.60, 145.36, 138.27, 128.22, 127.99, 126.98, 125.20, 121.92, 115.35, 111.55, 57.93. MS-EI: *m/z* 288 (M⁺⁺, 70%), 136 (M⁺⁺ - C₇H₆NOS, 100%). Anal. Calc. for C₁₄H₁₂N₂S₂O: C, 58.31; H, 4.19; N, 9.71; S 22.24. Found: C, 57.98; H, 4.12; N, 9.51; S, 22.01. UV/Vis (CH₃CN): λ_{max} (log ε): 233 (4.05), 248 (4.03), 283 (3.92), 397 (4.35).

2.2.4. 4-(4-Methoxy-2-(thiophen-2-yl)thiazol-5-yl)-N,N-dip-tolylaniline (**3a**)

To a solution of 3 (740 mg, 2.57 mmol) in dry and degassed toluene (30 mL) were added Pd(dba)₂ (74 mg, 0.128 mmol, 5 mol%), $P(^{t}Bu)_{3}$ (130 µL of a 1 M solution in toluene, 0.130 mmol, 5 mol%), pbromotoluene (970 mg, 5.70 mmol, 2.2 equiv) and KO^tBu (633 mg, 5.70 mmol, 2.2 equiv). The mixture was degassed for 30 min and heated to 90 °C for 2 days till no educt and monosubstituted product was left as indicated by TLC (silica, $CHCl_3$ /heptane 3:1 R_f educt = 0.2, R_f monosubstituted product = 0.6, R_f disubstituted product = 0.7). After the reaction was finished, the mixture was allowed to cool down to RT, was washed with H₂O (3 \times 50 mL), dried over MgSO₄ and concentrated in vacuo till dryness. Purification using column chromatography yielded the product as a yellow solid (1.10 g, 2.34 mmol, 91%). mp 174–175 °C. ¹H NMR (250 MHz, CDCl₃): δ 2.32 (s, 6H), 4.12 (s, 3H), 7.13–6.96 (m, 11H), 7.35 (dd, J = 5.1 Hz, J = 1.0 Hz, 1H), 7.45 (dd, J = 3.7 Hz, J = 1.1 Hz, 1H), 7.57-7.49 (m, 2H). ¹³C NMR (63 MHz, CDCl₃): δ 158.21, 153.04, 146.70, 145.05, 138.01, 132.64, 129.87, 127.87, 127.41, 127.03, 125.24, 124.65, 124.51, 122.47, 110.83, 57.77, 20.79. MS-EI: m/z 468 (M⁺⁺, 100%), 316 (M $^{\cdot +}$ - C7H6NOS, 90%). Anal. Calc. for C28H24N2OS2: C, 71.76; H, 5.16; N, 5.98; S, 13.68. Found: C, 71.98; H, 5.18; N, 5.82; S, 13.44. UV/Vis (CHCl₃): λ_{max} (log ε): 311 (4.23), 417 (4.35).

If the reaction was aborted earlier (after 2 h), the monosubstituted product, 4-(4-methoxy-2-(thiophen-2-yl)thiazol-5-yl)-*N*-*p*-tolylaniline, was obtained in 70% yield after purification. ¹H NMR (250 MHz, CDCl₃): δ 7.58 (d, *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 3.4 Hz, 1H), 7.35 (d, *J* = 4.9 Hz, 1H), 7.21–6.89 (m, 2H), 5.69 (s, 1H), 4.14 (s, 1H), 2.32 (s, 1H). MS-EI: *m*/*z* 378 (M⁺⁺, 70%), 226 (M⁺⁺ - C₇H₆NOS, 100%).

2.2.5. 4-Methoxy-N-(4-(4-methoxy-2-(thiophen-2-yl)thiazol-5-yl) phenyl)-N-(4-methoxyphenyl)aniline (**3b**)

The procedure was similar to that for **3a**. **3** (170 mg, 0.59 mmol), Pd(dba)₂ (10.2 mg, 0.018 mmol, 3 mol%), P(${}^{t}Bu$)₃ (30 μ L of a 1 M solution in toluene, 0.030 mmol, 5 mol%), p-bromoanisole (243 mg, 1.29 mmol, 2.2 equiv), KO^tBu (146 mg, 0.29 mmol, 2.2 equiv), toluene (10 ml). After purification (silica, $CHCl_3/heptane 3:1 R_f$ educt = 0.2, R_f monosubstituted product = 0.7, R_f disubstituted product = 0.8), the product was obtained as an orange oil which solidified after a few hours (266 mg, 0.53 mmol, 90%). mp 131–132 °C. ¹H NMR (250 MHz, CDCl₃): δ 7.56–7.47 (m, 2H), 7.45 (dd, J = 3.7 Hz, J = 1.0 Hz, 1H), 7.34 (dd, J = 5.1 Hz, J = 1.0 Hz, 1H),7.13–7.02 (m, 5H), 6.93 (dJ = 8.8 Hz, 2H), 6.89–6.79 (m, 4H), 4.12 (s, 3H), 3.81 (s, 6H).¹³C NMR (63 MHz, CDCl₃): δ 158.19, 156.04, 152.88, 147.40, 140.86, 138.18, 128.00, 127.55, 127.10, 126.67, 125.31, 123.59, 120.73, 114.84, 111.15, 57.90, 55.62; HRMS Micro-ESI: m/z 500.123743 (calc. for C₂₈H₂₄N₂O₃S₂: 500.12283). UV/Vis (CH₃CN): λ_{max} (log ε): 238 (4.20), 302 (4.30), 414 (4.42).

2.2.6. 4-(2-(2,2'-Bithiophen-5-yl)-4-methoxythiazol-5-yl)-N,Ndip-tolylaniline (**3c**)

To a solution of **3a** (600 mg, 1.28 mmol) in dry THF (15 mL) at -78 °C under a nitrogen atmosphere was added *n*-BuLi (0.615 mL, 1.54 mmol, 1.2 equiv, 2.5 M solution in hexanes) and the mixture was stirred for 30 min. After warming up to room temperature and additional stirring for 30 min, the mixture was cooled again to -78 °C and tributyltin chloride (625 mg, 1.92 mmol, 1.5 equiv) was added, and stirring was continued for 30 min more,

followed by warming up to room temperature and stirring for 24 h. The mixture was concentrated and dried in vacuo and used without further purification. The tin organyl thereby obtained was dissolved in dry DMF (15 mL) and the mixture was degassed for 15 min. To this solution, 2-bromothiophene (313 mL, 1.92 mmol, 1.5 equiv) and freshly prepared Pd(PPh₃)₄ (60 mg, 0.052 mmol, 4 mol%) were added, and the mixture was heated to 95 °C for 16 h till no educt was left, as indicated by TLC (silica, CHCl₃/heptane 5:2, R_f educt = 0.6, R_f product = 0.8). The mixture was concentrated and directly applied to column chromatography yielding the product as a red solid (578 mg, 1.05 mmol, 82%). mp 161–162 °C. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: δ 7.58 (d, I = 8.7 Hz, 2H), 7.34 (d, I = 3.9 Hz, 1H), 7.27 (d, J = 4.4 Hz, 2H), 7.20–7.01 (m, 12H), 4.17 (s, 3H), 2.37 (s, 6H).¹³C NMR (75 MHz, CDCl₃): δ 158.37, 152.55, 146.76, 145.13, 138.96, 137.02, 136.46, 132.72, 130.00, 128.10, 127.49, 125.91, 125.12, 124.78, 124.60, 124.35, 124.29, 122.52, 111.02, 57.84, 20.94. HRMS Micro-ESI: *m*/*z* 551.12687 (calc. for C₃₂H₂₆N₂OS₃ + H⁺: 551.12855). UV/Vis (CH₃CN): λ_{max} (log ε): 240 (3.93), 304 (4.15), 442 (4.36).

2.2.7. 5-(5-(4-(Dip-tolylamino)phenyl)-4-methoxythiazol-2-yl)thiophene-2-carbaldehyde (**4a**, general procedure)

To a solution of **3a** (626 mg, 1.34 mmol) in dry THF (10 mL) at $-78 \circ C$ under a nitrogen atmosphere, was added *n*-BuLi (0.59 mL, 1.47 mmol, 1.1 equiv, 2.5 M solution in hexanes) and the mixture was stirred for 30 min. After warming up to room temperature and additional stirring for 30 min, the mixture was cooled again to -78 °C and approx. Dry DMF (1 mL) was added and stirring was continued for 30 min followed by warming up to room temperature and further stirring for 1 h. The mixture was neutralized with saturated NH₄Cl solution, diluted with CHCl₃ (50 mL) and washed with $H_2O(3 \times 50 \text{ mL})$. The organic phase was dried over MgSO₄ and concentrated in vacuo. Column chromatography (silica, CHCl₃ to CHCl₃/EtOAc 3:1) yielded the product as a red solid (600 mg, 1.21 mmol, 90%). mp 151–152 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.90 (s, 1H), 7.69 (d, J = 4.0 Hz, 1H), 7.54 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 4.0 Hz, 1H), 7.08 (d, J = 8.3 Hz, 4H), 7.05–6.97 (m, 6H), 4.13 (s, 3H), 2.33 (s, 6H).¹³C NMR (100 MHz, CDCl₃): δ 182.59, 159.00, 150.45, 147.41, 146.60, 144.84, 143.33, 136.55, 133.01, 129.95, 127.66, 125.00, 124.93, 123.55, 121.96, 114.30, 57.88, 20.81. MS-EI: m/z 496 (M^{·+}, 100%), 468 (M^{·+} - CO, 20%), 316 (M^{·+} - C₈H₆NO₂S, 70%). Anal. Calc. for C₂₉H₂₄N₂O₂S₂: C, 70.13; H, 4.87; N, 5.64; S, 12.91; Found: C, 70.08; H, 4.68; N, 5.92; S, 13.04. UV/Vis (CHCl₃): λ_{max} (log ε): 311 (4.29), 332 (4.18), 485 (4.39).

2.2.8. 5-(5-(4-(Bis(4-methoxyphenyl)amino)phenyl)-4-methoxythiazol-2-yl)thiophene-2-carbaldehyde (**4b**)

The procedure was similar to that for **4a**. **3b** (249 mg, 0.50 mmol), THF (10 mL), *n*-BuLi (0.22 mL, 0.55 mmol, 1.1 equiv), DMF (1 mL). After purification (silica, CHCl₃), the product was obtained as a deep red solid (230 mg, 0.44 mmol, 87%). mp 90–91 °C. ¹H NMR (250 MHz, CDCl₃): δ 9.89 (s, 1H), 7.68 (d, J = 4.0 Hz, 1H), 7.55–7.47 (m, 2H), 7.45 (d, J = 4.0 Hz, 1H), 7.13–7.00 (m, 4H), 6.96–6.88 (m, 2H), 6.88–6.78 (m, 4H), 4.12 (s, 3H), 3.80 (s, 6H).¹³C NMR (63 MHz, CDCl₃): δ 182.79, 158.98, 156.27, 150.29, 148.05, 146.79, 143.35, 140.56, 136.81, 127.79, 126.93, 125.06, 122.64, 120.21, 114.90, 114.62, 58.01, 55.63. MALDI-TOF: 528.1 (M·⁺). Anal. Calc. for C₂₉H₂₄N₂O₄S₂: C, 65.89; H, 4.58; N, 5.30; O, 12.11; S, 12.13. Found: C, 65.87; H, 4.54; N, 5.30; S, 12.13. UV/Vis (CH₃CN): λ_{max} (log ϵ): 298 (4.29), 331 (4.18), 476 (4.41).

2.2.9. 5'-(5-(4-(Dip-tolylamino)phenyl)-4-methoxythiazol-2-yl)-2,2'bithiophene-5-carbaldehyde (**4c**)

The procedure was similar to that for **4a**. **3c** (390 mg, 0.715 mmol), THF (5 mL), *n*-BuLi (0.37 mL, 0.93 mmol, 1.1 equiv), DMF (1 mL). After purification (silica, CHCl₃), the product was

obtained as a black solid (380 mg, 0.66 mmol, 93%). mp 193–194 °C. ¹H NMR (250 MHz, CDCl₃): δ 2.33 (s, 6H), 4.13 (s, 3H), 7.03 (m, 10H), 7.27 (d, *J* = 4.3 Hz, 2H), 7.33 (d, *J* = 4.0 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 4.0 Hz, 1H). ¹³C NMR (63 MHz, CDCl₃): δ 182.29, 158.44, 151.38, 146.93, 146.35, 144.88, 141.99, 139.16, 137.21, 136.83, 132.78, 129.89, 127.42, 126.72, 125.76, 124.76, 124.48, 123.99, 122.14, 112.10, 57.77, 20.80. MS-EI: *m*/*z* 578 (M⁺⁺, 100%), 316 (M⁺⁺ - C₁₂H₈NO₂S₂, 80%). Anal. Calc. for C₃₃H₂₆N₂O₂S₃: C, 68.48; H, 4.53; N, 4.84; S, 16.62. Found: C, 68.46; H, 4.65; N, 4.77; S, 16.40. UV/Vis (CHCl₃): λ_{max} (log ε): 263 (4.13), 313 (4.32), 376 (4.24), 486 (4.50).

2.2.10. 2-Cyano-3-(5-(5-(4-(dip-tolylamino)phenyl)-4-

methoxythiazol-2-yl)thiophen-2-yl)acrylic acid (**Dye A**, general procedure)

To a solution of 4a (143 mg, 0.29 mmol) and cyanoacetic acid (27 mg, 0.32 mmol, 1.1 equiv) in CH₃CN (5 mL) was added piperidine (cat. amounts, one drop). The deep red mixture was heated to reflux under a nitrogen atmosphere for 4 h till no starting material was left as indicated by TLC. After cooling down to room temperature, the suspension was diluted with CHCl₃ (20 mL) and washed with H₂O (3 \times 20 mL). The organic phase was dried over MgSO4, concentrated in vacuo and the residue was purified by flash chromatography (silica, CHCl₃ to CHCl₃/MeOH 5:1) to yield the product as a glasslike black solid (123 mg, 0.22 mmol, 76%). mp 190 °C (decomp.). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.25 (s, 1H), 7.77 (d, J = 4.0 Hz, 1H), 7.65 (d, J = 4.0 Hz, 1H), 7.50 (d, J = 8.7 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 4H), 6.91 (d, *J* = 8.3 Hz, 4H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.04 (s, 3H), 2.26 (s, 6H). ¹³C NMR (100 MHz, DMSO- d_6): δ 163.43, 158.35, 150.87, 146.75, 144.24, 142.38, 141.84, 137.67, 137.47, 132.74, 130.07, 127.51, 126.39, 124.63, 122.98, 121.32, 117.93, 112.72, 106.36, 57.88, 20.37. MS-EI: *m*/*z* 563 (M⁺⁺, 10%), 519 (M⁺⁺ - CO₂, 30%). Anal. Calc. for C₃₂H₂₅N₃O₃S₂: C, 68.18; H, 4.47; N, 7.45; S, 11.38. Found: C, 68.27; H, 4.31; N, 7.49; S, 11.31. IR (ATR, cm⁻¹): 2970 (br), 2360 (m), 2330 (m), 1730 (s), 1560 (s), 1550 (s), 1495 (s), 1365 (s), 1320 (m), 1270 (m), 1230, (m), 1090 (w). UV/Vis (CHCl₃): λ_{max} (log ε): 308 (4.32), 360 (4.16), 517 (4.38). UV/Vis (THF): λ_{max} (log ε): 302 (4.36), 354 (4.15), 520 (4.43).

2.2.11. 3-(5-(5-(4-(Bis(4-methoxyphenyl)amino)phenyl)-4methoxyth-iazol-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (**Dye B**)

The procedure was similar to that for **Dye A. 4b** (163 mg, 0.31 mmol), cyanoacetic acid (29 mg, 0.34 mmol, 1.1 equiv), CH₃CN (5 mL), piperidine. After purification, the product was obtained as a black solid (164 mg, 0.28 mmol, 89%). mp 220 °C (decomp.). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.16 (s, 1H), 7.67 (t, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 4.0 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.03–6.98 (m, 4H), 6.93–6.87 (m, 4H), 6.75 (d*J* = 8.8 Hz, 2H), 4.03 (s, 3H), 3.73 (s, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 158.05, 155.96, 150.77, 147.45, 140.90, 140.84, 139.64, 137.94, 136.46, 127.48, 126.83, 126.23, 121.69, 119.07, 118.72, 115.00, 112.59, 109.27, 57.87, 55.25. MALDI-TOF: 595.1 (M⁺⁺). Anal. Calc. for C₃₂H₂₅N₃O₅S₂: C, 64.52; H, 4.23; N, 7.05; O, 13.43; S, 10.77. Found: C, 64.36; H, 4.20; N, 7.12; O, 13.32; S, 10.82. IR (ATR, cm⁻¹): 3030 (w), 2940 (br), 2840 (w), 2350 (m), 2325 (m), 1741 (s), 1600 (m), 1500 (s), 1370 (s), 1240 (s), 1090 (m), 1030 (m). UV/Vis (THF): λ_{max} (log ε): 300 (4.37), 364 (4.16), 505 (4.46).

2.2.12. 2-Cyano-3-(5'-(5-(4-(dip-tolylamino)phenyl)-4methoxythiazol -2-yl)-2,2'-bithiophen-5-yl)acrylic acid (**Dye C**)

The procedure was similar to that for **Dye A**. **4c** (230 mg, 0.40 mmol), cyanoacetic acid (37 mg, 0.44 mmol, 1.1 equiv), CH₃CN (10 mL), piperidine. After purification, the product was obtained as a black solid (230 mg, 0.36 mmol, 90%). mp 243 °C (decomp.). ¹H NMR (250 MHz, DMSO-*d*₆): δ 8.05 (s, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.60 (d, *J* = 4.0 Hz, 1H), 7.58–7.43 (m, 4H), 7.12 (d*J* = 8.2 Hz, 4H), 6.99–6.81 (m,*J* = 8.6 Hz, 6H), 4.04 (s, 3H), 2.26 (s, 6H). ¹³C NMR

(63 MHz, DMSO-*d*₆): δ 163.50, 157.98, 151.22, 146.55, 146.11, 144.61, 144.33, 141.28, 137.79, 136.44, 134.67, 132.71, 130.14, 128.01, 127.43, 125.84, 125.82, 124.62, 123.26, 121.48, 116.53, 111.41, 98.71, 57.84, 20.45. MS-Micro-ESI (neg.): *m/z* 644 (M⁺⁺). Anal. Calc. for C₃₆H₂₇N₃O₃S₃: C, 66.95; H, 4.21; N, 6.51; O, 7.43; S, 14.90. Found: C, 66.87; H, 4.31; N, 6.40; S, 15.01. IR (ATR, cm⁻¹): 3030 (w), 2930 (br), 2350 (m), 2315 (m), 1600 (s), 1500 (s), 1380 (s), 1320 (s), 1270 (s), 1080 (m). UV/Vis (THF): λ_{max} (log ε): 278 (4.13), 307 (4.24), 400 (4.23), 490 (4.50).

2.2.13. 5-(4-Methoxyphenyl)-2-(thiophen-2-yl)thiazol-4-ol (5)

To a solution of thiophene-2-carbothioamide (3.25 g, 22.7 mmol) in DMF (50 mL) was added ethyl 2-bromo-2-(4methoxyphenyl)acetate (9.30 g, 34.1 mmol, 1.5 equiv). The solution was heated to 50 °C and maintained there for 24 h under continuous stirring. After cooling down to RT, H₂O (100 mL) was added and the product precipitated as a yellow solid. The mixture was stirred for additional 30 min. The product was filtered off, washed thoroughly with EtOH and Et₂O, and dried in vacuo. The light yellow solid was used without further purification (4.6 g, 15.9 mmol, 70%). mp 227–228 °C. ¹H NMR (250 MHz, DMSO-*d*₆): δ 3.75 (s, 3H), 6.96 (d, J = 8.77 Hz, 2H), 7.15 (dd, J = 4.73 Hz, J = 3.98 Hz, 1H), 7.65–7.54 (m, 3H), 7.68 (d,J = 4.93 Hz, 1H), 11.41 (s, 1H). ¹³C NMR (63 MHz, DMSO-*d*₆): δ 157.56, 156.64, 152.51, 136.71, 128.46, 128.33, 127.12, 125.98, 123.96, 114.23, 106.58, 55.05. MS-EI: *m*/*z* 289 (M⁺⁺, 100%), 274 (M⁺⁺ - CH₃, 15%). Anal. Calc. for C₁₄H₁₁NO₂S₂: C, 58.11; H, 3.83; N, 4.84; S, 22.16. Found: C, 58.27; H, 4.08; N, 4.47; S, 21.80. UV/Vis (DMSO): λ_{max} (log ε): 394 (4.12).

2.2.14. 4-Methoxy-5-(4-methoxyphenyl)-2-(thiophen-2-yl)thiazole (6)

The procedure was similar to that for **2**. **5** (1.67 g, 5.78 mmol), DMSO (40 mL), K₂CO₃ (96 g, 6.93 mmol, 1.2 equiv, red solution), CH₃I (0.98 g 6.93 mmol, 1.2 equiv), After purification, the product was obtained as a yellow solid (1.01 g, 3.33 mmol, 58%). mp 75–76 °C. ¹H NMR (250 MHz, CDCl₃): δ 7.63 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 3.2 Hz, 1H), 7.35 (d, *J* = 4.9 Hz, 1H), 7.11–7.01 (m, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.13 (s, 3H), 3.83 (s, 3H). ¹³C NMR (63 MHz, CDCl₃): δ = 158.48, 158.19, 153.35, 138.10, 128.21, 128.00, 127.19, 125.41, 124.19, 114.30, 110.62, 57.92, 55.45. HRMS Micro-ESI: *m/z* 304.04572 (calc. for C₁₅H₁₃NO₂S₂ + H⁺: 304.0466). UV/Vis (CHCl₃): λ_{max} (log ε): 252 (3.98), 385 (4.26).

2.2.15. 5-(4-Methoxy-5-(4-methoxyphenyl)thiazol-2-yl)thiophene-2-carbaldehyde (**7**)

The procedure was similar to that for **4a. 6** (477 mg, 1.57 mmol), THF (20 mL), *n*-BuLi (0.69 mL, 1.73 mmol, 1.1 equiv), DMF (2 mL). After purification (silica, CHCl₃), the product was obtained as an orange solid (389 mg, 1.17 mmol, 75%). mp 128–129 °C. ¹H NMR (250 MHz, CDCl₃): δ = 9.91 (s, 1H), 7.69 (d, *J* = 4.0 Hz, 1H), 7.68–7.61 (m, 2H), 7.48 (d, *J* = 4.0 Hz, 1H), 7.01–6.87 (m, 2H), 4.15 (s, 3H), 3.82 (s, 3H).¹³C NMR (100 MHz, CDCl₃): 182.69, 158.90, 150.80, 146.53, 143.41, 136.60, 130.64, 128.35, 125.09, 123.44, 114.30, 113.80, 57.91, 55.35. MS-EI: *m/z*: 331 (M⁻⁺, 50%), 316 (M⁻⁺ - CH₄, 10%), 151 (M⁻⁺ -C₈H₆NO₂S, 70%). Anal. Calc. for C₁₆H₁₃NO₃S: C, 57.99; H, 3.95; N, 4.23; S, 19.35. Found: C, 58.16; H, 3.99; N, 4.23; S, 19.36.

2.2.16. 2-Cyano-3-(5-(4-methoxy-5-(4-methoxyphenyl)thiazol-2yl)th-iophen-2-yl)acrylic acid (**Dye D**)

The procedure was similar to that for **Dye A**. **7** (324 mg, 0.98 mmol), cyanoacetic acid (92 mg, 1.08 mmol, 1.1 equiv), CH₃CN (15 mL), piperidine. The product precipitated as a red solid during the reaction. The mixture was diluted with CHCl₃ (50 mL) and washed with H₂O (3 \times 50 mL). The organic phase was dried over MgSO₄ and concentrated *in vacuo*. The crude product was

recrystallized from a mixture THF/EtOH by slow evaporation of the THF, yielding a deep red-black fine crystalline compound (351 mg, 0.88 mmol, 90%). mp 260 °C (decomp.). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.47 (s, 1H), 7.96 (d, *J* = 4.1 Hz, 1H), 7.75 (d, *J* = 3.9 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 4.08 (s, 3H), 3.78 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 163.25, 158.63, 158.38, 150.54, 145.94, 143.98, 140.50, 136.33, 128.03, 126.58, 122.53, 116.35, 114.49, 113.32, 99.99, 57.96, 55.19. MS-EI: *m/z* 398.5 (M⁺⁺, 50%), 354.4 (M⁺⁺ - CO₂, 60%), 151.5 (M⁺⁺ - C₁₁H₇N₂O₃S 100%). Anal. Calc. for C₁₉H₁₄N₂O4S₂: C, 57.27; H, 3.54; N, 7.03; S, 16.09. Found: C, 57.31; H, 3.49; N, 6.82; S, 16.06. IR (ATR, cm⁻¹): 3000 (w), 2970 (m), 2930 (w), 2360 (m), 2320 (m), 1730 (s), 1580 (w), 1500 (m), 1420 (m), 1370 (s), 1230 (s), 1215 (s), 1200 (s). UV/Vis (THF): λ_{max} (log ε): 278 (4.11), 338 (4.00), 478 (4.60).

2.3. Preparation of the DSSC

TiO₂ nanopowder (5 g, AEROXIDE[®] TiO₂ P25, Evonik) was suspended in HNO₃ (1 N, Fluka) to prepare a suitable TiO₂ paste. This suspension was heated at 80 °C for 24 h. The HNO3 was evaporated and the TiO₂ solid was dried for three days at 100 °C. Finally, the TiO₂ solid was treated with 25 mL H₂O, acetylacetone (2.5 g, 25.0 mmol, Merck), Triton X-100 (1.25 g, 1.92 mmol, Avocado), and polyethylene oxide (M.W. 100 000, Alfa Aesar). Aluminoborosilicate glass, coated with fluorine doped tin oxide (FTO, SnO₂:F), was used as a conducting, transparent substrate (resistance ~ 10 Ω/cm^2 , Solaronix SA, Switzerland). The active area was masked with scotch tape and was coated with TiO₂ suspension by using a glass scraper and dried at 80 °C for 10 min. After removal of the scotch tape, approx. 11 µm were measured as deposit thickness. This primed photo electrode was sintered in a muffle furnace for \sim 45 min at 450 °C. The TiO₂ electrode was then immersed in the dye solution (0.2 mM in THF) for 24 h at room temperature. A thin platinum layer was spread on the FTO coating of the counter electrode (Platisol, Solaronix SA, Switzerland). A few drops of the active redox couple iodine/iodide (0.1 M LiI (Fluka), 0.05 M I₂ (Aldrich), 0.6 M Bu₄NI (Aldrich) and 0.5 M 4-tert-butylpyridine (Aldrich) in CH₃CN) were added to the photoelectrode. Finally, the counter electrode was clamped to the photoelectrode/electrolyte system.

2.4. Measurements

Measurements of the wavelength dependence of the short circuit current density (J_{SC}) were carried out in a light-proof box with a 70 W Xenon lamp (Oriel, Germany) and a grating monochromator (Zeiss, Germany) in the spectral range of 300–800 nm with a resolution of 1 nm. The light intensity incident (I_{inc}) on the electrode was measured with a power meter (Coherent, USA). The IPCE was calculated using the following expression:

$$IPCE(\%) = \frac{J_{SC}[A \text{ cm}^{-2}]1240}{\lambda[nm]I_{inc}[W \text{ cm}^{-2}]}100$$

The photocurrent-voltage (I–V) curves were measured using a focused 120 W Xenon lamp (Oriel, Germany) and a special filter to simulate solar irradiation (100 mW cm⁻², 1 sun, 1.5 air mass (AM) global). The fill factors (FF) and overall efficiencies (η) were calculated according to following equations.

$$FF = \frac{MPP[W \text{ cm}^{-2}]}{J_{SC}[A \text{ cm}^{-2}]V_{OC}[V]}$$

$$\eta(\%) = \frac{J_{\text{SC}}[\text{A cm}^{-2}]V_{\text{OC}}[\text{V}]\text{FF}}{I_{\text{inc}}[\text{W cm}^{-2}]}100$$

Here MPP is the "maximum power point" and V_{oc} the opencircuit voltage [30].

2.5. Computational methods

All calculations were performed with the GAUSSIAN 09 program [31] in the presence of solvent (tetrahydrofuran, $\varepsilon = 7.4257$, n = 1.4070) via the integral equation formalism of the polarizable continuum model [32]. The ground state equilibrium structures were optimized with the long-range corrected CAM-B3LYP XC functional [33] and the 6-31G(d,p) double- ξ basis set. [34]. Harmonic vibrational frequencies at the same level of theory proved that the stationary points obtained corresponded to the minima of the potential energy surfaces. Excited state properties, such as excitation energies, oscillator strengths and excited states geometries, were computed via TDDFT and the same XC functional and basis set as was employed for the ground state. The absorption spectra in the FC region were simulated by the first ten singlet excited states. According to Kasha's rule fluorescence occurs from the lowest excited singlet state [35], the S₁ state was optimized to obtain the emission energies from the S₁.

3. Results and discussion

3.1. Synthesis and structure of the dyes

The synthetic route and molecular structures of the triarvlaminebased dves are depicted in Scheme 1. The starting material, 5-(4nitrophenyl)-2-(thiophen-2-yl)thiazol-4-ol (1), was synthesized using a Hantzsch cyclization of thiophene-2-carbothioamide with ethyl 2-bromo-2-(4-nitrophenyl)acetate. The 4-hydroxy-1,3-thiazole obtained was alkylated following a Williamson-type etherification with K₂CO₃ as the base and methyl iodide as the nucleophile to yield the 4-methoxy-5-(4-nitrophenyl)-2-(thiophen-2-yl)thiazole (2). The reduction of the nitro group was realized following a standard protocol using freshly prepared Raney nickel and hydrazine hydrate solution as the hydrogen source in ethanol to almost quantitatively yield the amine 4-(4-methoxy-2-(thiophen-2-yl)thiazol-5yl)aniline (3). The crucial step in the synthetic route was the Hartwig–Buchwald coupling of the aryl amine 3 with an appropriate aryl halide using a Pd-catalyst. Although thoroughly described in literature, this type of coupling is difficult and strongly depends on the nature of the catalysts, ligands and reaction conditions [36,37]. In addition, the coupling has to take place twice to obtain the desired product. This double N-arylation of primary amines is not often described in literature. Examples exist for simple triarylamines basically consisting of tolyl or anisole groups [38], or for a catalytic process with a second, intramolecular coupling to generate different types of carbazoles [39, 40]. Tri-*tert*-butylphosphine ($P(^{t}Bu)_{3}$) was chosen as a promising ligand, which has already been successfully applied in the synthesis of different indole derivatives [41]. For the coupling reaction, bis(dibenzylideneacetone) palladium(0)(Pd(dba)₂) was used as the precatalyst, KO^tBu as the base to deprotonate the amine in the catalytic cycle and toluene as solvent. The aryl halides chosen were p-bromotoluene and p-bromoanisole because of a better stability of the corresponding triarylamines toward oxidative coupling reactions in para-position after excitation and radical formation (charge separation), which is well known for these radicals [42,43]. Surprisingly, the coupling reaction with $P(^{T}Bu)_{3}$ as ligand (several attempts using, for example, triphenylphosphine or 1,1'*bis*(diphenylphosphino)ferrocene as ligands failed completely) produced the coupling products in very good yields (>86%). Furthermore, the two-step process of the reaction was confirmed and the monosubstituted product formed was isolated and identified for **3a** (see experimental section). A noteworthy observation was that



Scheme 1. Synthesis and structure of the triarylamine-based dyes A-C.

when a high excess of coupling agent together with longer reaction times were applied, an additional spot (TLC) eluting in front of the coupling products, occurred. This by-product was identified (MS) as the coupling product of the thiophene moiety at the electron rich 5position with the aryl halide.

In order to vary the conjugation lengths of the dyes, a further thiophene ring was introduced in **3a** *via* a Stille coupling with 2-bromothiophene to yield 4-(2-(2,2'-bithiophen-5-yl)-4-methoxyt-

hiazol-5-yl)-*N*,*N*-di-4-tolylaniline (**3c**) in very good yields (86%). The introduction of the aldehyde group *via* a Vilsmeier–Haack reaction with DMF and POCl₃ was not successful. Therefore, the thiophene was deprotonated with *n*-BuLi followed by the addition of DMF and quenching with saturated NH₄Cl solution to give the corresponding aldehydes in excellent yields (>87%). No side product due to a possible directed *ortho*-metalation at the 4-methoxyphenyl ring for **3b** was observed if *n*-BuLi was added very slowly at -78 °C and the excess was

kept small. The last step, the introduction of the 2-cyanoacrylic acid acceptor group, was achieved by a Knoevenagel condensation of the aldehyde group with cyanoacetic acid and catalytical amounts of piperidine in acetonitrile to give the dyes A-C in moderate to good yields (>75%) Similar to the synthesis of **1**, the starting material for **D**, 5-(4-methoxyphenyl)-2-(thiophen-2-yl)thiazol-4-ol (5). was obtained by a cyclization reaction of the thiophene-2-carbothioamide and ethyl 2-bromo-2-(4-methoxyphenyl)acetate. The reaction in toluene only resulted in a sluggish conversion to 5, therefore a second method, with DMF as the solvent and slightly elevated temperature was used, which gave the product in a satisfactory yield (70%). All the following reactions (alkylation, introduction of the aldehyde and Knoevenagel condensation) were similar to that for dyes A-C and the synthetic route is depicted in Scheme 2.

3.2. X-ray structure of dye D

Single Crystals suitable for X-ray structure analysis were obtained from a mixture ethylene glycol/THF in an NMR tube by slow evaporation of the THF. The presented structure is a rare example in this field, because of the weak crystallization tendency of this D- π -A type compounds. Usually, crystallization leads to amorphous precipitates or very thin plates because of the planarity of the molecules (aggregation).

The crystal structure of **D** is depicted in Fig. 1 and a more detailed look, selected bond lengths and angles in comparison with the calculated values and additional crystallographic data are given in the ESI (S1 and S2). The structure reveals the almost planar arrangement of the dye. Two hydrogen bonds between the carboxylic acid groups of two adjacent molecules lead to the formation of a dimer. The distance between the two oxygens forming the hydrogen bonds is 2.593(3) Å. The cyano group of the 2-cyanoacrylic acid acceptor unit is in cis-position to the sulfur of the thiophene moiety. The NMR spectrum of **D** shows only one signal for the ethylene hydrogen bound to C16. (ESI, S3). Therefore, it can be considered that the presented isomer is exclusively formed in the Knoevenagel condensation reaction. This is similar to one infrequent literature example where the cyano group is also in cis-position to the sulfur of the thiophene moiety [44]. As expected, the conjugation pathway of the molecule shows an almost planar geometry. The distance between two layers formed form the dimers is only 3.5 Å, which is typical for strong π -stacking interactions between the molecules [45]. The torsion angles between the three aromatic rings and the anchoring group are 4.47(2) (C20-C8-C7-S2), 7.21(2) (N1-C5-C4-S1) and 8.99(2) ° (S1-C1-C16-C17). This planarity allows an electron flow from the donor to the acceptor group.



Scheme 2. Synthesis and structure of the 4-metoxyphenyl-based dye D.



Fig. 1. Ortep plot of dye D. Ellipsoids are at 50% probability level. Shown are the numbering scheme (above) and the two hydrogen bonds to form the dimer (below).

3.3. Photophysical properties

The UV/Vis spectra of the protonated and deprotonated dyes are depicted in Fig. 2 and the spectroscopic data are summarized in Table 1. The small unmodified etherified 4-hydroxy-1,3-thiazoles usually show an intense band in the region of 380 nm (see experimental section for **2**, **3** and **6**) due to π - π * transition of the thiazole moiety. These λ_{max} of absorption were successfully shifted bathochromically after the formation of the electron-donating triarylamine moieties for 3a and 3b, furthermore, after the introduction of the electron accepting aldehyde and up to 505 nm for **B** after the generation of the electron-accepting cyanoacrylic acid group due to an intense intramolecular charge transfer (ICT) transition. The absorption maximum of A-C is at moderate longer wavelengths compared to very similar triarylamines using thiophenes and oligothiophenes [46], thiophenes and 3,4-ethylenedioxythiophene [47], and thiophenes and 3,4- thienothiophene [23] instead of 4methoxy-1,3-thiazoles units as a π -spacer. This is promising in terms of the light harvesting properties of the dyes presented. The influence of the 4-methoxy group at the triarylamine moiety for B compared to the tolyl group (A) resulted in a bathochromic shift of



Fig. 2. UV/Vis spectra of the protonated and deprotonated dyes A-D in THF solution at room temperature.

| Table 1 |
|---|
| Spectroscopic properties, and redox potentials of the protonated and deprotonated (dep) dves A-D . |

| Dye | $\lambda_{Abs}(nm)[\epsilon(10^2M^{-1}cm^{-1})]$ | $\lambda_{Fl}(nm)^a$ | Stokes S. (cm ⁻¹) ^b | τ (ns) ^c | Φ (%) | $E_{1/2} \operatorname{Ox} (V)^d$ | $E_{1/2}$ red (V) ^d | $E_{0-0}\left(eV\right) ^{e}$ | $E (S^+/S^*) vs \text{ NHE } (V)^f$ |
|---------|--|----------------------|--|--------------------------|-------|-----------------------------------|--------------------------------|--------------------------------|-------------------------------------|
| Α | 305 [220], 355 [133], 503 [247] | 611 | 3500 | 2.5 | 4 | 0.35, 0.59 ^g | -1.95 | 2.30 | -1.32 |
| A (dep) | 277 [400], 457 [295] | 592 | 5000 | | | _ | _ | | |
| В | 300 [230], 363 [145], 505 [289] | 640 | 4200 | 1.1 | < 1 | 0.20, 0.56 ^g | -1.93 | 2.35 | -1.52 |
| B (dep) | 297 [280], 450 [460] | 558 | 4300 | | | _ | _ | | |
| С | 307 [175], 400 [170], 490 [320] | 622 | 4300 | 1.4 | 1 | 0.28, 0.68 ^g | -1.99 | 2.23 | -1.32 |
| C (dep) | 309 [210], 474 [360] | 598 | 4400 | | | _ | | | |
| D | 277 [130], 339 [100], 477 [400] | 599 | 4300 | 2.9 | 54 | 0.69 | -1.53 | 2.34 | -1.02 |
| D (dep) | 276 [150], 433 [390] | 507 | 3400 | | | _ | | | |

^a Excitation at the longest wavelength absorption.

^b Relative to maximum of the absorption.

^c Excitation at $\lambda = 650$ nm.

^d $E_{1/2} = (E_{pa} - E_{pc})/2 \ vs \ Fc/Fc^+$.

^e Calc from the onset (10%) of the photoluminescence spectra.

^f The excited-state oxidation potential $E(S^+/S^*) = E_{1/2}$ (first oxidation) - E_{0-0} with Fc/Fc⁺ vs NHE = 0.63 V.

^g Peaks are irreversible, *E* derived from differential pulse polarographic (DPP) measurements.

only 2 nm (0.01 eV), which is in accordance with the quantum chemical calculations. In the energetic representations of the HOMO, it can be seen that participation of the 4-methoxy groups is very small and, therefore, the influence to the ICT is negligible (see Fig. 5 dye B). Surprisingly, the extension of the conjugation length for C did not lead to a bathochromic shift of the absorption maximum. This is contrary to the literature examples mentioned and can be attributed to an insufficient ICT transition, which is also in accordance with the quantum chemical calculations (see Fig. 5 dye C). The bands in the UV-A region at 300-310 nm with extinction coefficients (ϵ) from 17 500 to 23 000 M⁻¹ cm⁻¹ correspond to a mixture of $\pi - \pi^*$ transitions in triarylamines and ICT states (see ESI, S11). Accordingly, this band is missing in the spectra of **C**, which only shows a weak UV absorption at 277 nm due to the 4-methoxyphenyl ring. The extinction coefficients of the absorption bands in the visible region are up to 40 000 M^{-1} cm⁻¹. which is characteristic for an ICT and 2½ times higher than those of Ru(polypyridyl) complexes [48]. Deprotonation of the dyes was carried out by adding the appropriate amount (1.1 equiv) of a tetrabutylammonium hydroxide (TBAOH) solution directly to the cuvette, followed instantaneously by the measurement.

The longest wavelength absorptions for all dyes are hypsochromically shifted (46 nm or 0.25 eV for **A**, to 16 nm or 0.09 eV for **C**). The energy acceptor strength (electronegativity) of the cyanoacrylic acid after deprotonation is lowered, which leads to



The large Stokes Shift is typical for these D- π -A dyes. In accordance with the UV/Vis spectra, the emission is also hypsochromically shifted after deprotonation. The fluorescence lifetimes vary from 1.1 to 2.9 ns for **B** and **D**, respectively. The dye emissions showed the expected monoexponential decay curves, which are presented in the ESI (S4). The values obtained are consistent with the measured fluorescence quantum yields (Φ) of the dyes. They are very low for the triarylamines **A-C** (below 4%) and higher for the 4-methoxyphenyl-based dye **D** (54%).

3.4. Electrochemical properties

In order to gain deeper insights into the electrochemical properties of the dyes, cyclic voltammetry (CV) and differential puls polarography (DPP) measurements were applied. They were



Fig. 3. Emission spectra of the protonated and deprotonated dyes **A-D** in THF solution at room temperature after excitation in the longest wavelength absorption band.



Fig. 4. Cyclic voltammetry spectra of dyes **A-D** in THF; experimental conditions: 0.1 M TBAPF₆, $c \approx 10^{-4}$ M, 25 °C, scan rate 200 mV s⁻¹, RE: Ag/AgCl, WE: carbon, AE: platinum.



Fig. 5. Frontier orbitals of the four dyes optimized at the CAM-B3LYP/6-31G(d,p) level of theory.

carried out in THF with 0.1 M TBAPF₆ at 25 °C with a scan rate of 200 mV s⁻¹, with Ag/AgCl as the reference, carbon as the working and platinum as the auxiliary electrode. Ferrocene was added as the internal standard after every measurement. All potentials discussed here are given relative to the normal hydrogen electrode (NHE) with Fc/Fc⁺ vs NHE = 0.63 V [50]. The cyclic voltammetry spectra of the compounds are depicted in Fig. 4 and data are summarized in Table 1.

The dyes **A-C** show a reversible first oxidation wave, caused by the oxidation of the triarylamine donor in the region from 0.98 to 0.83 V for **A** and **B**, respectively. This suggests that the first oxidized state of these dyes is stable, which is one prerequisite for a good long term stability of DSSCs [13]. The oxidation potential for **B** is lowered by 0.15 V compared to **A** due to the introduction of the electron-donating 4-methoxy group at the triarylamine core, which facilitates the oxidation of the amine. Additional, compound **C** is oxidized more easily than **A** after the incorporation of the thiophene unit in the conjugation pathway, leading to an increase of the electron density of the aromatic linker which, consequently, lowers the oxidation potential of the end-capped amine unit [51]. The oxidation wave for compound **D** is superimposed by the oxidation of the solvent and, therefore, it is not possible to assign if the oxidation process is reversible or not.

Nonetheless, due to the missing triarylamine moiety, the oxidation occurs at a significant higher potential (1.32 V) compared to the dyes **A-C**, but it could not be clarified where the oxidation and radical formation takes place.

The first reduction peaks appear to be irreversible for all dyes. They are very similar for the triarylamines $(-1.30 \text{ for } \mathbf{B} \text{ to } -1.33 \text{ V} \text{ for } \mathbf{C})$ and shifted to a higher potential for compound \mathbf{D} (-0.90 V). In a water-free environment, it could be attributed to the reduction of the double bond forming a radical which then undergoes dimerization or hydrodimerization reactions (if traces of water are present) [52,53]. This would explain the overall irreversible nature of the process. The higher potential for \mathbf{D} is in agreement with the lower ICT character and a reduced dipole moment, which leads to a less pronounced electron density at the cyanoacrylic acid group, which makes it easier to reduce [54].

In order to judge the possibility for efficient charge injection in the conducting band of TiO₂, the excited-state oxidation potential

E (S⁺/S^{*}) was calculated from the first oxidation potential and the zero–zero transition energy E_{0-0} , which was determined from the onset (10%) of the emission spectra ($E(S^+/S^*) = E_{1/2} \text{ Ox} - E_{0-0}$). A schematic representation of the energy levels is given in the ESI (S5). The calculated potentials vary from -1.52 to -1.02 V for **B** and **D**, respectively. They are sufficiently more negative ($\Delta E > 0.2$ V) [55] than the conducting band (CB) edge of the TiO₂ (standard potential $E_{CB} = -0.5$ V *vs* NHE) [56] and electron injection should be possible. The regeneration of the oxidized dyes is also energetically favored. The oxidation potential, the energy of the HOMO, lies in the range of 1.32 V (**D**) to 0.98 (**A**), which is high enough for an efficient reduction by the I^-/I_3^- redox couple (E = 0.35 V *vs* NHE) [57]. Thus, electron injection of the oxidized species is energetically permitted. This allows the application of the dyes in DSSC.

3.5. Computational results

In order to gain more detailed insight into the structural and the spectroscopic properties of the chromophores, density functional theory (DFT) and its time-dependent version (TDDFT) was applied. The four dyes were investigated in the protonated form and in the trans-arrangement of the nitrile group to the thiophene. TDDFT calculations on both the trans and the cis-isomer were performed and details are summarized in the ESI. It was shown that both isomers exhibit very similar photophysical properties. Therefore an influence of the different isomers on the spectroscopic properties can be neglected. The ground state equilibrium geometries of the protonated species show similar structural features. The conjugated π -system from the bridge to the anchoring group is planar in all dyes. The phenyl groups of the triphenylamine fragment (**A-C**) are twisted out of planarity due to sterical hindrance. All dyes exhibit a torsionated phenyl ring connected to the 4-methoxy-1,3thiazole fragment, with a dihedral angle independent of the length of the bridge, as well as of the size of the donor system. It varies only marginally from 18.3 (C) up to 20.4° (D). The analysis of the harmonic vibrational modes corresponding to the torsion indicates a shallow minimum in this normal coordinate. Wavenumbers of ca. 30 cm⁻¹ have been determined for this vibrational mode for all compounds. For this reason, a thermal distribution in this coordinate is to be expected. According to the low frequencies, the HOMOs show a non-constructive overlap of the π -systems from the 4-methoxy-1,3-thiazole and the adjacent phenyl moiety leading to a single bond in these positions.

The optimized geometries of the S₁ states hold similarities to the ground state equilibrium structures. The reason is the $\pi - \pi^*$ nature of the S₁ and the partial occupation of the LUMOs. Therefore, the excited state structures show only minor shifts in the bond lengths and angles. However, the 4-methoxy-1,3-thiazole-phenyl fragments are planarized as a result of the bonding character of the LUMOs in these positions. The most important molecular orbitals involved in the electronic excitations are shown in Fig. 5. The absorption spectra of the four dyes were calculated using the Franck-Condon (FC) geometry and the first ten singlet excited states. Table 2 collects vertical and adiabatic excitations from the S1 state. The absorption energies to higher excited states, together with an overlay of the experimental and calculated absorption spectra and the molecular orbitals contributing to those states, are summarized in the ESI (S6-S11). In all dyes the S₁ is assigned to a $\pi - \pi^*$ excitation, with the main transition occurring from the HOMO to the LUMO. The main contribution to the HOMO of A, B and **C** is due to the π -systems of the donor and thiazole fragments, while in the case of **D**, the donor and the entire bridge contribute to the HOMO. The LUMO for all dyes is spread over the anchoring group and the bridge. Hence, an ICT from the donor to the acceptor occurs.

The expansion of the aromatic π -system tends to increase the weight of further configurations. The HOMO/LUMO transition for **D** has a weight of 88%, while the implementation of the N.N-di-4-tolvl (A) and N,N-bis(4-methoxyphenyl) (B) donor groups decreases the weight to 72 and 71%, respectively. The weight is decreased further to 54% by the introduction of an additional thiophene moiety (C). As a consequence, the S₁ of C features a less pronounced ICT leading to an increase of the excitation energy and, consequently, to a hypsochromic shift of the λ_{max} of the absorption compared to **A** and **B**. Additionally, **D** shows a blueshift of the S₁. The reason is the more local π - π ^{*} transition between the frontier orbitals. The wavelength dependency of the first absorption band is in good agreement to the experiment. In general, the excitation energies of the S_1 are marginally overestimated (A: 0.12, B: 0.09, C: 0.11, and D: 0.16 eV), showing that the CAM-B3LYP functional is very well suited to describe ICT in these dyes. By comparing the oscillator strengths (f) with the experimentally obtained molecular extinction coefficients, a general trend of increasing absorption is obvious for A, B and C.

Table 2

Calculated absorption/emission (fluorescence) properties to/from the first excited state S₁. Main contributions to the wavefunction (weight), vertical (absorption) or adiabatic (emission) excitation energies (ΔE^e in eV and nm), oscillator strengths (*f*) and deviations from experimental values (ΔE_{Exp}). H = HOMO, L = LUMO.

| Transition | | Weight (%) | ΔE^{e} | | f | $\Delta E_{\rm Exp}~({\rm eV})$ | |
|------------|-----------------------|------------|----------------|------|-------|---------------------------------|--|
| | | | (eV) | (nm) | | | |
| Abso | orption | | | | | | |
| А | $H \rightarrow L$ | 72 | 2.58 | 479 | 1.511 | 0.12 | |
| | $H-1 \rightarrow L$ | 20 | | | | | |
| В | $H \rightarrow L$ | 71 | 2.54 | 487 | 1.502 | 0.09 | |
| | $H-1 \rightarrow L$ | 20 | | | | | |
| С | $H \rightarrow L$ | 54 | 2.64 | 470 | 1.958 | 0.11 | |
| | $H-1 \rightarrow L$ | 26 | | | | | |
| | $H \rightarrow L + 1$ | 12 | | | | | |
| D | $H \rightarrow L$ | 88 | 2.75 | 451 | 1.364 | 0.16 | |
| Emission | | | | | | | |
| Α | $H \leftarrow L$ | 91 | 1.91 | 650 | _ | -0.02 | |
| В | H←L | 89 | 1.88 | 658 | _ | -0.06 | |
| С | $H \leftarrow L$ | 85 | 1.85 | 669 | _ | -0.15 | |
| D | $H \leftarrow L$ | 95 | 2.12 | 586 | - | 0.01 | |

The first absorption band of **D** exhibits the largest measured molecular extinction coefficient, while the calculated oscillator strength is considerably too small. This is caused by the more local HOMO/LUMO transition for **D**, and the fact that CAM-B3LYP tends to underestimate the oscillator strength of such systems.

The adiabatic emission spectra were obtained using the optimized geometry of the first excited singlet state. The measured and simulated fluorescence wavelengths are also collected in Table 2. A comparison of the theoretical and experimental fluorescence spectra, as well as the molecular orbitals contributing to the relevant transitions, can be found in the ESI (S12 and S13). In agreement with the configurations of the S₁ in the ground state equilibrium structure, the weight of the LUMO/HOMO transitions decreases with the enhancement of the π -system. Nevertheless, the weight is significantly increased (**A**: 91, **B**: 89, **C**: 85, and **D**: 95%) compared to the vertical excitations in the FC region. The emission wavelengths obtained are in excellent agreement with the experimental data. Only minor deviations of -0.02, -0.06 and 0.01 eV for **A**, **B** and **D**, respectively, were generated, while **C** shows a slight underestimation of -0.15 eV.

3.6. Photovoltaic devices and solar cell performance

In order to test the dyes for a possible application as sensitizers, DSSCs with nanocrystalline TiO₂ (70% anatase, 30% rutile) were prepared. The exact protocol is given in the experimental part and the results, together with the standard N3 (*cis*-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)), are summarized in Table 3. The incident photon-to-current conversion efficiencies (IPCE) spectra obtained are shown in Fig. 6. Only moderate IPCEs were achieved, with values varying from 25 (D) to 13% (C) for the absorption maximum of the dyes, though several different preparation conditions (different solvents, dye concentrations) were utilized. IPCEs of up to 80% are usually expected for these types of compounds [12,23]. Therefore, it can be assumed that the electron injection efficiency in the electron acceptor states of the TiO₂ is low. The amount of dyes adsorbed on the TiO₂ was determined by measuring the absorption spectra of a solution of the corresponding dye before and after soaking of the TiO₂ plate. After correlation with the measured extinction coefficient, the adsorbed amount was calculated to be 5.0×10^{-8} (**A** and **B**), 6.6×10^{-8} (**D**) and 4.0 \times 10⁻⁸ mol cm⁻² for the largest sensitizer **C**. The values correspond very well with the size of the molecules and are in good agreement with literature examples and cannot account for the low IPCEs [58,59]. The absorption spectra of the adsorbed dyes are depicted in the ESI (S18). They were similar to the absorption spectra of the dyes in solution. The main difference is the broadening of the longest wavelength ICT band (absorption from approx. 370–700 nm compared to 425–600 nm for the dyes in solution)

Photovoltaic performance of DSSCs based on dyes A-D without and with the addition of DCA (10 mM) as a co-adsorbent.

Table 3

| Dye | $J_{\rm sc}$ (mA cm ⁻²) | V _{oc} (mV) | FF | η (%) | | | |
|-------------|-------------------------------------|----------------------|------|-------|--|--|--|
| Without DCA | | | | | | | |
| Α | 1.81 | 519 | 0.46 | 0.44 | | | |
| В | 1.42 | 558 | 0.51 | 0.41 | | | |
| С | 1.37 | 524 | 0.47 | 0.36 | | | |
| D | 1.03 | 468 | 0.52 | 0.25 | | | |
| N3 | 11.73 | 690 | 0.51 | 4.1 | | | |
| With DCA | | | | | | | |
| Α | 4.49 | 612 | 0.62 | 1.70 | | | |
| В | 3.55 | 611 | 0.50 | 1.08 | | | |
| С | 3.27 | 616 | 0.51 | 1.02 | | | |
| D | 2.23 | 511 | 0.52 | 0.61 | | | |



Fig. 6. Spectra of the incident photon-to-current conversion efficiencies obtained for nanocrystalline TiO_2 solar cells sensitized by the dyes **A-D** without (—) and with $(-\blacksquare -)$ co-adsorption of DCA (10 mM).

due to the absorption on the TiO₂ surface. This ensures a sufficient light harvesting over a broad wavelength range. Two reasons can be assumed for this broadening: Firstly, the energy of the π^* level is lowered due to interaction of the carboxylic acid with the Ti⁴⁺ ions on the TiO₂ surface, which consequently leads to a bathochromic shift of the absorption spectra [60], and (more important) secondly, unfavorable dye aggregation and excimer formation (J-aggregates) would lead to this behavior [61,62]. The DSSCs prepared only showed a low short circuit photocurrent density J_{SC} (Fig. 7) from 1.81 to 1.03 mA cm⁻² for **A** and **D**, respectively. Because of the low J_{SC} , the maximum power outputs (MPP = $J_{mp} \cdot V_{mp}$) and, consequently, the fill factors (FF) were small. The resulting solar energy-to-electricity conversion yield (η) is low and follows the trend **A** > **B** > **C** > **D** with values from 0.44 to 0.25%.

Two possible reasons for the weak solar cell performance can be: (i) an electron accepting property of the 4-methoxy-1,3thiazole, which can effect an efficient electron injection in the CB of TiO₂ as observed for anthraquinone-based dyes [63] or (ii) the formation of aggregates leading to a loss of excitation energy through intermolecular processes [64,65]. The first fact is supported from the TDDFT calculations. The LUMO is not only spread over the anchoring group, but also includes contribution from the thiophene and also the thiazole moieties, leading to an insufficient electron injection. In order to verify the second reason as crucial for the low performance, DSSCs were prepared using deoxycholic acid (DCA) as a co-adsorbent. It has been proven several times that coadsorption of either DCA or chenodeoxycholic acid (CDCA) can efficiently suppress dye aggregation [61,66,67]. Therefore, DCA (10 mM in THF) was chosen for the preparation of more elaborated DSSCs (Table 3). The IPCE values (Fig. 6) were improved by about the factor two (from 14 to 30% for **A** and up to 35% for **D**) at the longest wavelength absorption band. Consequently, the short circuit photocurrent densities and the open-circuit voltages were also significantly improved (Fig. 7). The FF was increased by 35% for **A** (FF = 0.62), whereas they remained almost unchanged for the other dyes. A reason for the poor FFs of all dyes can be a poor performance of the counter electrode, which was made of TiO₂ P25. This will affect the I-V characteristics of the DSSC and, consequently, lowering the FF. For further experiments mesoporous anatase TiO₂ beads will be used to improve the cell performance as described in literature [68]. The overall efficiencies of the optimized DSSCs obtained varied from 0.61 to 1.7% for **D** and **A**, respectively.



Fig. 7. Photocurrent-voltage characteristics for **A-D** sensitized DSSCs under illumination of simulated solar light (100 mW cm⁻², 1.5 AM global) without (—) and with $(-\blacksquare -)$ co-adsorption of DCA (10 mM).

This equals a remarkable increase of a factor 4 of the efficiency in the case of dye **A**. Keeping in mind that the efficiency of a DSSC prepared from the standard N3 with the preparation technique described was 4.1%, the best performance DSSC using **A** as sensitizer achieved reasonable 42% of this value. The trend of the efficiencies of the cells equals the trend without co-adsorbed DCA. For **A** and **B** the efficiency is very similar, whereas for **C** it is decreased. Most likely electron recombination is enhanced for compound **C** due to the extended bridge and, therefore, electron injection in the CB of TiO₂ is less favored leading to lower IPCE values [69]. Most likely due to the missing strong electron donor and the low ICT character of the first excited state, DSSCs sensitized with **D** showed the lowest performance.

In summary, the dyes tend to aggregate on the surface of TiO₂. This effect was more pronounced for the triarylamine-based dyes than for **D**. Further improvements to overcome this aggregation could be the introduction of long alkyl chains [70,71], for example, *via* the alkylation reaction or by bridging two dye molecules [72]. Also the introduction of the strong electron-withdrawing benzo-thiadiazole unit in the conjugation pathway to further shift the absorption maximum will be considered in the construction of novel dyes [73]. Also photophysical experiments, like electrochemical impedance spectroscopy (EIS) and electron lifetime measurement of the adsorbed dyes, have to be carried out to account the photovoltaic properties further [74,75].

4. Conclusion

A series of donor- π -acceptor dyes were successfully synthesized. Instead of the commonly used thiophene derivatives, an unconventional chromophore based on a 4-hydroxy-1,3-thiazole was used in the conjugation pathway of the dyes, to efficiently shift the absorption maximum toward longer wavelengths compared to similar triarylamines. A double *N*-arylation Hartwig–Buchwald reaction, rarely described in literature, was successful applied in the synthetic route for the triarylamine-based dyes. All dyes have been fully characterized including a series of spectroscopic and theoretical methods. The quantum chemical TDDFT calculations used proofed to be well suited to reproduce the experimental values as supported by the X-ray structure of the **D** and the absorption and emission characteristics. Electrochemical measurements and DFT calculations approved a possible application of the synthesized dyes as sensitizers in DSSCs. The efficiencies obtained of DCCSs without co-adsorption of DCA proved to be very low. Nevertheless, the performance was significantly increased after the addition of DCA. This demonstrated the distinct tendency of the dyes to form aggregates on the surface of nanocrystalline TiO₂. The best performance solar cell sensitized with dye **A** achieved 42% of the performance of a DSSC prepared with the standard N3 dye. In further investigations, the NLO properties of this class of molecules will be reviewed. For molecules of type **D** this property has already been proven in experiment. Furthermore, the use as fluorescent probes, bearing a reactive –OH group instead of the methoxy ether to interact with biological systems, will be the subject of further research.

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Appendix. Supporting information

Supplementary data related to this article can be found online at 10.1016/j.dyepig.2012.02.014.

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