

Synthesis, Electrochemical, and Optical Properties of New Fluorescent, Substituted Thieno[3,2-b][1]Benzothiophenes

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Abstract The synthesis, electrochemical and optical properties of three fluorescent substituted thieno[3,2-b][1]benzothiophenes (TBT) derivatives, including 3-methoxythieno[3,2-b][1]benzothiophene (3-MeO-TBT), 2,3-dimethylthieno[3,2-b][1]benzothiophene (2,3-diMe-TBT), and 6-methoxythieno[3,2-b][1]benzothiophene-2-carboxylate (6-MeO-TBT-2-

COOMe), were investigated. The oxidation potential values varied between 1.40 and 1.20 V/SCE according to the electronic substituent effect, and electropolymerization attempts, performed in 0.1 M LiClO₄ acetonitrile solution, led to the formation of very thin films of poly(3-MeO-TBT) and poly(2,3-di-Me-TBT). Electronic absorption spectra, fluorescence excitation and emission spectra, fluorescence quantum yields (Φ_F), lifetimes (τ_F), and other photophysical parameters of the three new TBT derivatives were measured in DMSO solutions at room temperature. For the methyl- and methoxy-substituted TBT derivatives, the fluorescence emission peak were slightly red shifted relative to that of unsubstituted TBT ($\Delta\lambda_{em}=1-12$ nm) whereas, in the case of 6-MeO-TBT-2-COOMe, a rather strong red-shift ($\Delta\lambda_{em}=73$ nm) was attributed to the existence of a “push-pull” electronic interaction of the MeO and COOMe groups. All Φ_F values were rather high, varying between 0.11 and 0.35, according to the substituent effect. Fluorescence decays were mono-exponential and τ_F values were very short, ranging between 0.11 and 0.30 ns for the substituted TBT derivatives until study.

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Introduction

As reported in our previous studies, the electropolymerization and physicochemical properties of simple thiophenes [1–6] and condensed benzothiophenes [7, 8] are significantly influenced by their substituents. Nowadays, interest for the fused heterocycles is marked because of their important applications such as in films transistors [9] and

photoluminescent systems [10]. It is also important to study optical properties in order to explain the electronic and electrochemical phenomena occurring in conducting polymers. For example, the formation of polarons and bipolarons (caused by elimination of electrons of the conjugated π system in the polymer) was explained by using the UV-VIS absorption spectra [11]. Luminescence spectrometry was also applied to elucidate the oxydo-reduction processes and solute-solvent interactions [12–14].

In the last few years, we have demonstrated that fused heterocycles such as various thieno[1]benzothiophene (TBT) and benzothienoindeole (BTI) derivatives were characterized by remarkable ferroelectric liquid crystal [15, 16] and luminescence properties [7, 8, 17–19], and could also lead to the electrosynthesis of conducting oligomers with interesting luminescent applications. Indeed, we have found that these oligomers generally possessed a strong fluorescence emission maximum, occurring in the visible part of the spectrum, which was dramatically red shifted relative to the corresponding monomers.

Also, we have recently carried out a detailed study on the optical and electrochemical characteristics, and electropolymerization of 2-Me-TBT and 3-MeTBT in acetonitrile as well as in a partially-aqueous SDS-containing micellar medium [8]. The corresponding polymer films [poly(2-MeTBT) and poly(3-MeTBT)] were electrochemically and spectroscopically characterized in both media, and exhibited a satisfactory electroactivity. Our FT-IR and MALDI-TOF mass spectral results demonstrated that these films had a molecular structure constituted of short-chain oligomers, obtained by couplings essentially taking place on the phenyl ring (6- and 8- positions) for poly(2-MeTBT), and partly on the thiophene ring (2-position) and on the phenyl ring (6-position) in the case of poly(3-MeTBT). Moreover, poly(2-MeTBT) and poly(3-MeTBT) presented a relatively strong fluorescence emission band in organic solution, as well as in the solid state, which could lead to applications for the fabrication of luminescence diodes since the solid-state fluorescence appeared in the visible region. Finally, small variations observed between the optical and electrochemical properties of 2-MeTBT and 3-MeTBT, and of the corresponding polymers, due to the placement of the methyl group at the α or β position of the thiophene ring, were attributed to the occurrence of a difference of electronic delocalization.

The main goal of this work was to describe the synthesis, and investigate the electrochemical and optical properties of three new fluorescent substituted TBT derivatives, including 2,3-dimethylthieno[3,2-b][1]benzothiophene (2,3-diMeTBT), 3-methoxythieno[3,2-b][1]benzothiophene (3-MeOTBT) and methyl 6-methoxythieno[3,2-b][1]benzothiophene-2-carboxylate (6-MeOTBT-2-COOMe). In order

to better evaluate the substituent effects on these optical and electrochemical properties, we also compared the present results with some data that we previously obtained for other TBT derivatives and their oligomers.

Experimental

Chemicals and synthesis procedures

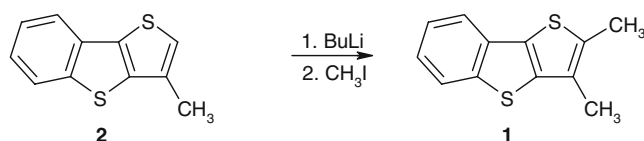
Melting points were determined on a Leica VM TG block and were uncorrected. Elemental analyses were carried out on a Perkin-Elmer 2400 spectrometer. NMR spectra were measured on a Varian Gemini 300 HC spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C). Deuteriochloroform and DMSO (dimethyl sulfoxide)- d_6 were used as solvents, and the NMR solvent signals served as internal standards.

Preparation of 2,3-dimethylthieno[3.2-b][1]benzothiophene (1)

To a solution of 3-methylthieno[3.2-b][1]benzothiophene (**2**) [8] (0.729 g; 3.57 mmol) in dry THF (40 ml) was added drop wise 3.7 ml of a 2 M solution of butyl-lithium in hexane (7.4 mmol). The mixture was stirred at -78°C for 5 min, the cooling bath was removed and stirring was continued at room temperature for 45 min. After cooling again to -78°C , iodomethane (2.3 g; 16 mmol) was added and the solution was stirred at room temperature for 2 h, and then evaporated (Scheme 1). The residue was dissolved in dichloromethane (100 ml) and washed with a saturated aqueous solution of ammonium chloride (30 ml), brine, and dried with anhydrous magnesium sulfate. After evaporation, the residue was purified by column chromatography (silica gel, elution with hexane) to afford 0.71 g (91%) of **1**, m.p. $79.6\text{--}81.0^\circ\text{C}$ (methanol). For $\text{C}_{12}\text{H}_{10}\text{S}_2$ (218.34) calcd.: C 66.01%, H 4.62%, S 29.37%; found: C 65.90%, H 4.49%, S 29.22%. ^1H NMR (CDCl_3 , δ): 7.83 d (1 H, $J=8.0$, H-5), 7.75 d (1 H, $J=8.0$, H-8), 7.38 ddd (1 H, $J_1=8.0$, $J_2=1.1$), 7.28 ddd (1 H, $J_1=8.0$, $J_2=1.1$), 2.51 s (3 H, CH_3 -2), 2.28 s (3 H, CH_3 -3).

Preparation of methyl 3-[(methoxycarbonyl)methyl] sulfanyl} benzo[b] thiophene-2-carboxylate (5)

To a slurry of 50% sodium hydride (2.90 g, 121 mmol) in dry DMF (70 ml) was added under stirring dropwise methyl



Scheme 1 Preparation reaction of 2,3-diMeTBT

thioglycolate (16.6 g, 136 mmol) at 0 °C in nitrogen atmosphere (Scheme 2). After 10 min, the easily accessible chloro ester **4** (10.0 g; 43 mmol) [20] was added in one portion, and the mixture was stirred at room temperature for 16 h and then poured on 500 ml of cold water. The deposited precipitate was filtered, washed thoroughly with water (3×50 ml) and dried. Crystallization from hexane afforded 10.57 g (83%) of diester **5**, m.p. 84–86 °C. Elemental analysis for C₁₃H₁₂O₄S₂ (296.37): calcd. C 52.69, H 4.08, S 21.64; found C 52.64, H 3.99, S 21.47. ¹H NMR (300 MHz, CDCl₃, δ): 3.52 (s, OCH₃), 3.76 (s, CH₂), 3.97 (s, OCH₃), 7.48 (dt, *J*₁=8.2, *J*₂=2.0, 1 H), 7.52 (dt, *J*₁=8.2, *J*₂=2.0, 1 H), 7.85 (dd, 1 H), 8.19 (dd, 1 H).

Preparation of methyl 3-hydroxythieno[3,2-*b*][1]benzothiophene-2-carboxylate (**6**)

Diester **5** (5.24 g, 17.7 mmol) was added to a solution of sodium methoxide (1.19 g, 22 mmol) in methanol (100 ml). The mixture was stirred and heated to reflux for 1 h, after cooling to room temperature, acidified with 5% aq. hydrochloric acid (20 ml). The formed precipitate was filtered, washed with water (50 ml) and dried. 4.55 g (97%) of ester **6** was obtained, m.p. 158–160 °C. Elemental analysis for C₁₂H₈O₃S₂ (264.32): calcd. C 54.53, H 3.05, S 24.26; found C 54.39, H 3.03, S 24.11. ¹H NMR (300 MHz, CDCl₃, δ): 3.96 (s, OCH₃), 7.46 (m, 2 H), 7.88 (m, 2 H), 10.05 (bs, OH).

Preparation of methyl 3-methoxythieno[3,2-*b*][1]benzothiophene-2-carboxylate (**7**)

Ester **6** (4.0 g, 15.1 mmol) was added in one portion to a solution of sodium methoxide (1.70 g; 31.5 mmol) in dry

DMF (150 ml), and the solution was stirred in nitrogen atmosphere at room temperature for 30 min. Iodomethane (10.7 g, 75.5 mmol) was added, and stirring was continued for 16 h, the reaction mixture was diluted with water (300 ml), and washed with chloroform (3×75 ml). The combined organic solution was washed with brine, and dried with anhydrous magnesium sulfate. Evaporation of the filtrate left the crude product, which was purified by column chromatography (silica gel, elution with toluene) to afford 3.27 g (78%) of methoxy ester **7**, m.p. 154.5–156.5 °C (ethyl acetate). Elemental analysis for C₁₃H₁₀O₃S₂ (278.35): calcd. C 56.10, H 3.62, S 23.04; found C 55.98, H 3.47, S 22.76. ¹H NMR (300 MHz, CDCl₃, δ): 3.91 (s, OCH₃), 4.32 (s, OCH₃), 7.45 (m, 2 H), 7.87 (m, 2 H).

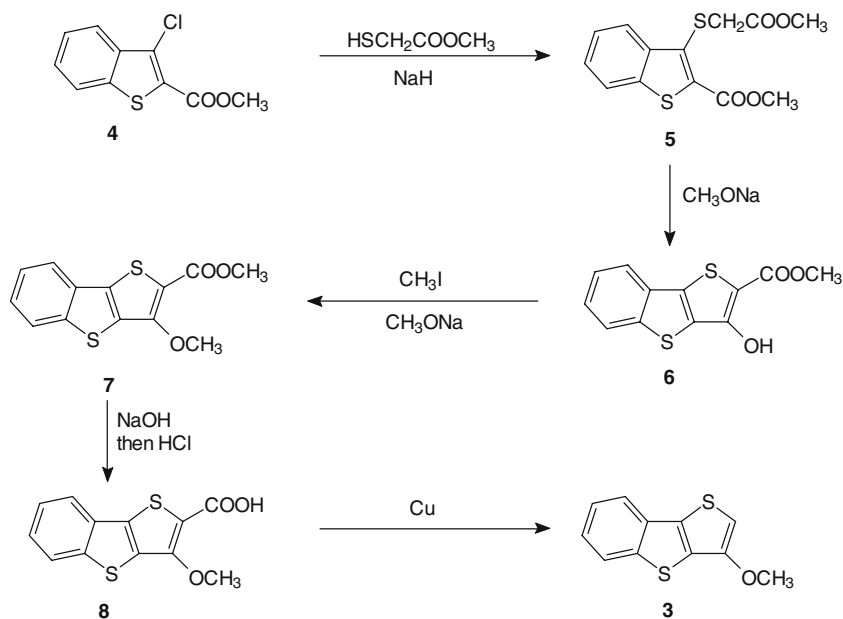
Preparation of 3-methoxythieno[3,2-*b*][1]benzothiophene-2-carboxylic acid (**8**)

A mixture of ester **7** (2.05 g, 7.36 mmol), sodium hydroxide (3.2 g, 80 mmol), methanol (100 ml) and water (60 ml) was stirred and heated to reflux for 6 h, and then acidified with conc. hydrochloric acid (10 ml). The precipitate was filtered and washed thoroughly with water. 1.83 g (94%) of acid **8** was obtained, m.p. 243–245 °C (dec.). Elemental analysis for C₁₂H₈O₃S₂ (264.32): calcd. C 54.53, H 3.05, S 24.26; found C 54.37, H 3.11, S 24.01. ¹H NMR (300 MHz, DMSO-*d*₆, δ): 4.20 (s, OCH₃), 7.53 (m, 2 H), 8.09 (m, 2 H).

Preparation of 3-methoxythieno[3,2-*b*][1]benzothiophene (**3**) (Scheme 2)

Copper bronze (0.56 g, 8.8 mmol) was added to acid **8** (1.83 g; 6.92 mmol) in freshly distilled quinoline

Scheme 2 Five-step synthesis procedure of 3-MeOTBT



(40 ml), and the mixture was heated to 200 °C for 30 min in nitrogen atmosphere. The dark solution was poured on a mixture conc. hydrochloric acid (36 ml) and ice (300 ml). The water phase was extracted with hexane (3×50 ml), and the combined hexane solution was washed successively with cold water (20 ml), saturated aq. sodium hydrogencarbonate solution, brine, and then dried with anhydrous magnesium sulfate. The solution was concentrated to approx. 15 ml and cooled. The deposited crystals were filtered and washed with cold hexane to afford 1.14 g (75%) of **3**, m.p. 75–77 °C. Elemental analysis for C₁₁H₈OS₂ (220.31): calcd. C 59.97, H 3.66, S 29.11; found C 59.67, H 3.53, S 28.97. ¹H NMR (300 MHz, CDCl₃, δ): 3.96 (s, OCH₃), 6.38 (s, H-2), 7.35 (dt, *J*₁=8.2, *J*₂=2.2, 1 H), 7.40 (dt, *J*₁=8.2, *J*₂=2.2, 1 H), 7.81 (dd, 1 H), 7.83 (dd, 1 H). ¹³C NMR (75 MHz, CDCl₃, δ): 57.6 (OCH₃), 97.9, 120.5, 124.0, 124.4, 124.6, 128.9, 132.8, 133.0, 142.0, 151.3.

Electrochemical measurements

Electrochemical measurements were carried out in a one-compartment three-electrode cell, using an EG&G Parr 362 potentiostat/galvanostat. A Pt disk (disk area = 19.6×10⁻² cm²) and/or a Pt-coated glass plate were used as working electrodes. The counter-electrode was a stainless grid, and a saturated calomel electrode was utilised as potential reference.

Electropolymerization was performed by cyclic voltammetry in 0.1 M LiClO₄ acetonitrile solutions containing, respectively, 5×10⁻² M of 3-MeOTBT and 6-MeOTBT-2-COOMe, and 2×10⁻² M of 2,3-diMeTBT.

Optical measurements

UV-visible absorption spectra of TBT derivatives were recorded in DMSO (Dimethyl sulfoxide) as solvent with a Lambda 2 Perkin Elmer UV-VIS absorption spectrometer. Their fluorescence excitation and emission spectra were also obtained in DMSO, using a Perkin Elmer LS 50 Luminescence spectrometer. The fluorescence quantum yields were measured on a Perkin Elmer LS 50 Luminescence spectrometer by comparing the integrated area of the emission spectra of the compounds under study to that of tryptophan, used as a standard, recorded in 0.05 M H₂SO₄ aqueous solution. All spectral measurements were performed at room temperature. Fluorescence lifetimes were measured with a femtosecond 8-MHz laser excitation at 300 nm, using TCSPC technique at 3.1 ps per channel [21]. Fluorescence decays were analysed by the Maximum Entropy Method.

Results and discussion

Synthesis of the new substituted TBT derivatives

*Synthesis route of 2,3-dimethylthieno[3,2-*b*][1]benzothiophene(2,3-diMeTBT) (1)*

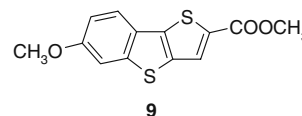
2,3-Dimethylthieno[3,2-*b*][1]benzothiophene (**1**) was easily obtained from 3-methylthieno[3,2-*b*][1]benzothiophene (**2**) (Scheme 1), preparation of which we described elsewhere [8]. Lithiation of **2** with butyl-lithium proceeded selectively in position 2, and then the formed lithium salt was alkylated with iodomethane into **1** in 91% yield.

*Synthesis route of 3-methoxythieno[3,2-*b*][1]benzothiophene (3-MeOTBT) (3)*

3-Methoxythieno[3,2-*b*][1]benzothiophene (**3**) was synthesized in a five-step procedure (Scheme 2) starting with the easily accessible chloro ester **4** [20]. Unlike the previously published procedure utilizing t-BuONa as base in DMF [22], we first substituted the chloro atom of **4** in mild conditions with the anion of methyl thioglycolate in methanol to afford the diester **5** in 83% yield, which in the next step was cyclized with sodium methoxide in methanol into the hydroxy ester **6** (yield 97%). The hydroxylic group of **6** was then alkylated with iodomethane to form the 3-methoxy ester **7** (yield 78%). This alkylation protocol turned out to be more efficient than a recently-reported procedure [23]. The ester group was saponified with a sodium hydroxide aqueous methanolic solution, and, in the last step, the carboxylic group of the acid **8** was removed by heating with copper bronze in quinoline at 200 °C. Overall yield of preparation of **3** based on **4** was 39%.

*Synthesis route of methyl 6-methoxythieno[3,2-*b*][1]benzothiophene-2-carboxylate (6-MeOTBT-2-COOMe) (9)*

Methyl 6-methoxythieno[3,2-*b*][1]benzothiophene-2-carboxylate (**9**) (Scheme 3) was obtained by a procedure that we reported previously [24].



Scheme 3 Molecular structure of 6-MeOTBT-2-COOMe

Electrochemical studies

Electrochemistry of monomers and electropolymerization attempts

Acetonitrile solutions of 3-MeO-TBT, 2,3-diMeTBT and 6-MeOTBT-2-COOMe containing 10^{-3} M of monomer and 0.1 M LiClO₄ were used for the investigation of the electrochemical behaviour of these three compounds. Cyclic voltammograms (CV) were performed from -0.3 to 1.5 V/SCE at scan rates (v) ranging from 10 to 200 mV/s for the three compounds. In the case of 3-MeO-TBT, the CV exhibited one oxidation peak (E_{ox}) at 1.20 V/SCE, and one reduction peak at -0.10 V/SCE. Due to the important electron-donating effect of the methoxy group, the oxidation potential was lowered by about 200 mV/SCE relatively to un-substituted TBT (1.40 V/SCE) [24]. Very probably, this electron-donating effect stabilizes the formed radical-cation, which facilitates the oxidation of monomer. For 2,3-diMeTBT, the CV presented one anodic peak at about 1.30 V/SCE. The E_{ox} value for this monomer is smaller by about 100 mV than that of un-substituted TBT, but only slightly smaller than those of 2-MeTBT and 3-MeTBT (respectively 1.35 and 1.32 V/SCE) [8]. This E_{ox} relatively weak decrease for 2,3-diMeTBT could result from the occupation of the two reactive sites of the thiophene ring by methyl groups, which would make more difficult the oxidation of this monomer, in spite of the increased electron-donating effect of two methyl groups. In the case of 6-MeOTBT-2-COOMe, the CV were characterized by the presence of one anodic peak at about 1.35 V/SCE and one cathodic peak at approximately -0.15 V/SCE. The E_{ox} value of this monomer is smaller than that of un-substituted TBT by only 50 mV. This E_{ox} slight decrease probably results from the electron-withdrawing effect of the COOMe group, which partly compensates the methoxy group electron-donating effect. A similar behaviour was observed in the case of other substituted thieno[1]benzothiophenes and of thieno-indoles, for which the electron-donating effects of methoxy and methyl groups contribute to decrease significantly the oxidation potential of the parent molecule [24, 25].

Following our previous electrosynthesis studies of poly(TBT)s [7, 8], we attempted to electropolymerize the three, new substituted TBT derivatives by CV, upon scanning repetitively the potential between -0.3 and 1.5 V/SCE at 100 mV/s, in 0.1 M LiClO₄ acetonitrile solutions containing 10^{-2} M to 5×10^{-2} M monomer concentrations. The electropolymerization behaviour varied with the compound.

In the case of 3-MeOTBT, when using a monomer 10^{-2} M concentration, a poly(3-MeOTBT) thin film was electro-

deposited by CV on Pt electrode, but was quasi-instantaneously dissolved, which is probably due to the formation of very soluble oligomers [8]. In contrast, with a more concentrated acetonitrile solution ($[3\text{-MeOTBT}] = 5 \times 10^{-2}$ M), the CV were characterized by the presence of anodic and cathodic peaks, respectively located at about 1.2 and -0.1 V/SCE, and a very thin, adhesive, violet polymer film was progressively electrodeposited. The anodic peak can be attributed to the oxidation of the formed oligomers, accompanied by insertion in the film of ClO₄⁻ doping anions, whereas the cathodic wave corresponds to the film reduction process during which the expulsion of ClO₄⁻ anions are taking place [26]. In addition, the current intensity of the anodic peak decreased significantly upon increasing the number of cycles, which suggests a phenomenon of passivation of the electrodeposited poly(3-MeOTBT) films, as already reported for poly(2-MeTBT) [8]. Also, the poly(3-MeOTBT) films, electrodeposited by CV, were found to be electroactive.

Attempts to perform by CV the electropolymerization of a 2×10^{-2} M 2,3-diMeTBT, acetonitrile solution led to the formation of a very thin, greenish polymer film at the Pt electrode surface. The CV were characterized by an anodic peak located at 1.25 V/SCE, progressively decreasing of intensity with the number of scans, which indicates a phenomenon of film passivation. We also attempted to electropolymerize by CV a 5×10^{-2} M 6-MeOTBT-2-COOMe, acetonitrile solution. The voltammograms exhibited anodic and cathodic peaks, respectively occurring at about 1.30 and -0.1 V/SCE, which decreased slightly with the number of cycles. It appeared a greenish colour very close to the Pt electrode, probably corresponding to the formation of soluble oligomers, but no film was obtained on the electrode.

Comparative study of the electrochemical properties of substituted TBT

In order to investigate the substituent effects on the electrochemical properties of TBT derivatives, we decided to compare the oxidation potential (E_{ox}) and reduction potential (E_{red}) values of the three above-described compounds to those of other substituted TBT previously reported. Table 1 summarizes the E_{ox} and E_{red} values for the various TBT derivatives, as well as the available information on the electrodeposited polymer films. It leads to the following remarks:

- The E_{ox} values of all substituted TBT derivatives are lower than that of un-substituted TBT (1.4 V/SCE) [24].

- The E_{ox} lowest values are obtained for 3-MeOTBT and 6-MeOTBT, because of the methoxy group strong electron-donating effect. The TBTBT similar E_{ox} value can be attributed to the increased electronic delocalization resulting from the presence of an additional, fused thiophenyl group in the TBTBT molecular structure.
- The 2-MeTBT, 3-MeTBT and 2,3-diMe-TBT E_{ox} values are comprised between those of un-substituted TBT and of 3-MeOTBT and 6-MeOTBT, which can be explained by the methyl electron-donating effect lower than that the methoxy one.
- The 6-MeOTBT-2-COOMe E_{ox} value is only 50 mV lower than that of un-substituted TBT, which can be attributed to the partial compensation of the methoxy electron-donating effect by the strong electron-withdrawing effect of the COOMe group.
- Except for TBTBT, the E_{red} values do not significantly vary with the nature of the substituent, and ranged between -0.1 and -0.20 V/SCE.

Concerning the electropolymerization behaviour, Table 1 shows that polymer films can be electrodeposited on Pt electrode from all TBT derivatives, except for 6-MeOTBT-2-COOMe. In most cases, these films are characterized by a passivation phenomenon [8]. Also, it is worthwhile to note that the physicochemical properties of the electrosynthesized polymer films, such as the colour, thickness, electroactivity, passivating character, widely vary with the nature and position of substituents on the thiophene and/or phenyl ring of TBT derivatives.

Optical properties

In order to study the substituent effects on the optical properties of substituted TBT derivatives, we have measured in diluted DMSO solutions at room temperature the electronic (UV-VIS) absorption and fluorescence spectra, as well as the fluorescence quantum yields (Φ_{F}) and lifetimes (τ_{F}), of the three newly-synthesized TBT derivatives (3-MeOTBT, 2,3-diMeTBT and 6-MeO-TBT-2-COOMe), and we have compared them to those of other TBT derivatives

and oligomers [8, 17, 19]. We have also calculated from these experimental data several important photophysical kinetic parameters for the fluorescence and intersystem crossing processes. All our experimental data and calculations are gathered in Tables 2 and 3.

UV-VIS absorption spectra

The electronic (UV-VIS) absorption spectra of the TBT derivatives under study were recorded in diluted DMSO solutions (concentration: 10^{-5} M) at room temperature (Table 2). All substituted TBT derivatives, displayed rather similar spectra, characterized by the presence of two strong, well-resolved bands (or shoulders) with maximums located at around 255–279 nm and 286–294 nm, and shoulders or secondary peaks occurring at longer wavelength in the 312–337 nm region, according to the compound (Fig. 1).

In the case of the three newly-synthesized TBT derivatives, two different spectral behaviours can be distinguished. Two of these compounds, including 3-MeOTBT and 2,3-diMeTBT, presented two strong, short-wavelength bands located, respectively, at 274–279 nm (maximum molar absorption coefficient $\epsilon_{\text{max}}=1.70 \times 10^4$ – 3.24×10^4 $\text{M}^{-1} \text{cm}^{-1}$) and 291–294 nm ($\epsilon_{\text{max}}=1.78 \times 10^4$ – 3.16×10^4 $\text{M}^{-1} \text{cm}^{-1}$), and weaker shoulders or secondary peaks appearing in the 305–319 nm region ($\epsilon_{\text{max}}=7.9 \times 10^3$ – 2.5×10^4 $\text{M}^{-1} \text{cm}^{-1}$) (Table 2 and Fig. 1). The two short-wavelength bands were attributed, respectively, to ${}^1\text{B}$ ($\lambda_{\text{A}}=274$ – 279 nm) and ${}^1\text{L}_a/{}^1\text{L}_b$ ($\lambda_{\text{A}}=291$ – 294 nm) $\pi \rightarrow \pi^*$ aromatic electronic transitions, whereas the shoulders or bands observed at longer wavelengths and having smaller ϵ_{max} values than the corresponding, short-wavelength bands for the same compound were ascribed to the presence of n, π^* electronic transitions, belonging to the thiophene rings, and partially overlapped by π, π^* bands. A similar assignment was proposed previously for other fused benzothiophene derivatives [7, 8, 17]. Introduction of an electron-donating substituent, such as methyl and methoxy, in the fused rings produced a very weak red-shift of the bands in the 291–294 and 305–319 nm regions relative to the corresponding bands of un-substituted TBT. Moreover,

Table 1 Electrochemical properties of TBT derivatives and electrodeposited polymer films

| Compound | E_{ox} (V/SCE) | E_{red} (V/SCE) | Formation of film | Passivation of film |
|-----------------------|-------------------------|--------------------------|-------------------|---------------------|
| TBT ^a | 1.40; 1.80 | – | yes | no |
| 2-MeTBT ^b | 1.35 ; 1.60 | -0.20 | yes | yes |
| 3-MeTBT ^b | 1.32 ; 1.60 | -0.15 | yes | yes |
| 2,3-diMeTBT | 1.30 | – | yes | yes |
| 3-MeOTBT | 1.20 | -0.10 | yes | yes |
| 6-MeOTBT ^a | 1.20; 1.80 | – | yes | no |
| 6-MeOTBT-2-COOMe | 1.35 | -0.15 | no | – |
| TBTBT ^{c,d} | 1.20 | -0.50 | yes | no |

^a Reference [24]

^b Reference [8]

^c Reference [7]

^d TBTBT = 1-thiophen-2-yl[1]benzo-thieno[3,2-b][1]benzothiophene

Table 2 Electronic absorption spectral properties of TBT derivatives and their oligomers under study in DMSO solution at room temperature^a

| Compound | λ_A /nm (log ϵ) |
|-------------------------------|--|
| TBT ^{b,c} | 291(3.5), <u>304</u> (3.34), 314 (3.15) |
| 2-MeTBT ^{d,e} | 262 (4.65), <u>274</u> (4.72), 294 (4.66), 306 (4.60) _{sh} , 312 (4.42) _{sh} |
| 3-MeTBT ^{d,e} | 261 (4.76) <u>270</u> (4.83) 292 (4.77) 304 (4.62) _{sh} , 314 (4.43) |
| 2,3-diMeTBT ^f | 255 (4.30), <u>274</u> (4.51), 294 (4.50), 305 (4.41) _{sh} 315 (4.14) _{sh} |
| 3-MeOTBT ^f | 260 (4.02), <u>279</u> (4.23), <u>291</u> (4.25), 306 (3.95) _{sh} , 319 (3.90) |
| 6-MeOTBT ^{b,c} | 252 (4.57), <u>274</u> (4.72), 298 (4.46), 319 (4.12) |
| 6-MeOTBT-2-COOME ^f | 257(4.14), 276 (4.14) _{sh} , 286(4.39), <u>337</u> (4.51) |
| Poly (2-MeTBT) ^d | 260 (4.68), <u>274</u> (4.70), 294 (4.63), 307 (4.59), 314 (4.52) _{sh} , 345 (4.28) _{sh} |
| Poly (3-MeTBT) ^d | 258 (4.22), <u>271</u> (4.28), 293 (4.22), 314 (4.16) _{sh} , 348 (4.07) _{sh} |

^a The monomer concentrations were 10^{-5} M, and the oligomer ones were 5×10^{-6} repeat unit (r.u.) L^{-1} , unless otherwise noted - λ_A = absorption band wavelengths. The logarithms of molar absorption coefficients ϵ (in $M^{-1} cm^{-1}$) are given in parenthesis. The underlined wavelength values correspond to the absorption maxima. sh = shoulder. Wavelength precision = ± 1 nm

^b Reference [17]

^c Concentration = 2×10^{-6} M

^d Reference [8]

^e Concentration = 1.5×10^{-5} M

^f This work

Table 3 Fluorescence spectral properties, fluorescence quantum yields (Φ_F) and lifetimes (τ_F), and other photophysical parameters of theTBT derivatives under study, in DMSO solution at room temperature^a

| Compound | λ_{ex} (nm) | λ_{em} (nm) | Φ_F^b | τ_F^c (ns) | k_F^d (s^{-1}) | Φ_{ISC}^e | k_{ISC}^f (s^{-1}) |
|-------------------------------|---|--------------------------------|-------------------|---------------------|-----------------------|-------------------|--------------------------|
| TBT ^{g,h} | <u>298</u> | 323, <u>333</u> | 0.15 ^k | — | — | — | — |
| 2-MeTBT ⁱ | 274, <u>294</u> , 304 | <u>334</u> | 0.11 | 0.11 ^j | 1.0×10^{9j} | 0.89 ^j | 8.09×10^{9j} |
| 3-MeTBT ⁱ | 273, <u>292</u> , 302 _{sh} , 316 _{sh} | 323, <u>335</u> | 0.17 | 0.30 ^j | 5.7×10^{8j} | 0.83 ^j | 2.77×10^{9j} |
| 2,3-diMeTBT ^j | 273 _{sh} , <u>302</u> | <u>336</u> | 0.19 | 0.11 | 1.73×10^{9j} | 0.81 ^j | 7.36×10^{9j} |
| 3-MeOTBT ^j | <u>291</u> , 304 319 | 331 _{sh} , <u>345</u> | 0.21 | 0.16 | 1.31×10^{9j} | 0.79 ^j | 4.94×10^{9j} |
| 6-MeOTBT ^{g,h} | <u>273</u> | <u>341</u> | 0.56 ^k | — | — | — | — |
| 6-MeOTBT-2-COOME ^j | 285, <u>336</u> | <u>406</u> | 0.35 | 0.24 | 1.46×10^{9j} | 0.65 ^j | 2.71×10^{9j} |
| Poly(2-MeTBT) ⁱ | 268, <u>306</u> , 336 | <u>378</u> | 0.25 | 0.33 ^{j,1} | 7.57×10^{8j} | 0.75 ^j | 2.27×10^{9j} |
| Poly(3-MeTBT) ⁱ | 268, <u>300</u> , 334 | 334, <u>380</u> | 0.28 | 0.21 ^{j,1} | 1.33×10^{9j} | 0.72 ^j | 3.43×10^{9j} |

^a The monomer concentrations were 10^{-6} M, and the oligomer ones were 10^{-6} r.u. L^{-1} , unless otherwise noted - λ_{ex} = fluorescence excitation peak wavelengths. λ_{em} = fluorescence emission peak wavelengths. The underlined wavelength values correspond to the fluorescence excitation or emission maxima. sh = shoulder. Wavelength precision = ± 1 nm

^b Φ_F = fluorescence quantum yield

^c τ_F = fluorescence lifetime

^d k_F = fluorescence rate constant

^e Φ_{ISC} = intersystem crossing quantum yield—Calculated from the relationship $\Phi_{ISC} = 1 - \Phi_F$, by assuming that the phosphorescence quantum yield Φ_P is nil at room temperature and neglecting the contribution of internal conversion

^f k_{ISC} = intersystem crossing rate constant

^g Reference [17]

^h Concentration = 2×10^{-6} M

ⁱ Reference [8], unless otherwise mentioned

^j This work

^k Φ_F values measured using quinine sulfate as reference compound

¹ Fluorescence lifetime mean value, including several components in the fluorescence decay curve

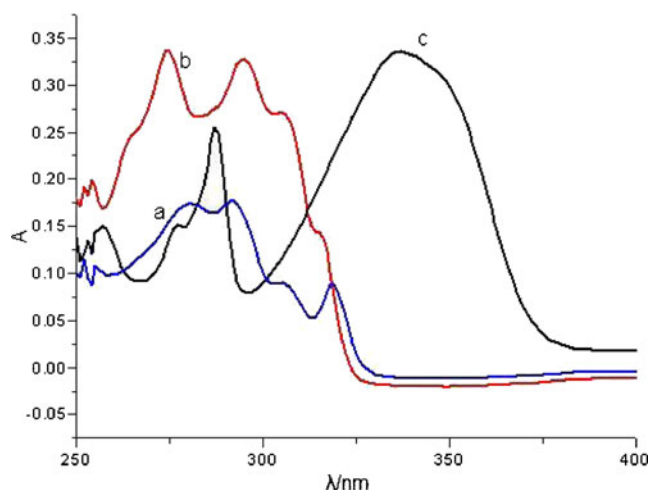
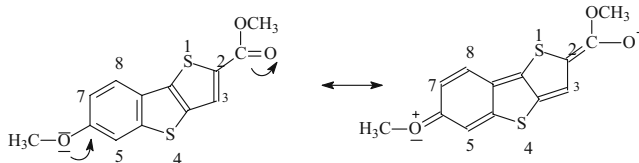


Fig. 1 UV–VIS absorption spectra of 10^{-5} M 3-MeOTBT (a), 2,3-diMeTBT (b) and 6-MeOTBT-2-COOMe (c) in DMSO at room temperature

for all substituted TBT under study, except 6-MeO-TBT-2-COOMe, the absorption wavelength values of the various bands were only slightly shifted ($\Delta\lambda_A=7-8$ nm) by the electronic effect and the position of the various substituents on the heterocyclic system (Table 2), and no significant change in the shape of the substituted TBT spectra occurred.

In contrast, the absorption spectrum of 6-MeOTBT-2-COOMe was characterized by an unusual behaviour, since, besides two short-wavelength bands appearing at about 276 and 286 nm and weakly-perturbed relative to the corresponding peaks of the other TBT derivatives, it also presented a strongly red-shifted ($\Delta\lambda_A=33$ nm, relative to the un-substituted TBT absorption maximum wavelength), structureless, very broad, and very intense long-wavelength band ($\lambda_{max}=337$ nm, $\epsilon_{max}=3.24 \times 10^4$ M $^{-1}$ cm $^{-1}$). This later band was attributed to an absorption transition towards an intramolecular charge-transfer (ICT) state. This ICT state was assumed to result from a “push-pull” electronic effect, related to the direct resonance interaction occurring between the methoxy and methyl acetate substituents which possess antagonistic effects. In Scheme 4, we have presented the 6-MeOTBT-2-COOMe ICT state mesomer forms that might take into account this spectral phenomenon.



Scheme 4 Mesomer forms of the 6-MeOTBT-2-COOMe ICT state involved in the push-pull electronic effect

The UV-visible absorption spectra of poly(2-MeTBT) and poly(3-MeTBT) were also recorded in DMSO diluted solutions (concentration = 5.10^{-6} r.u. L $^{-1}$) at room temperature (Table 2). It was observed that, relatively to the corresponding monomers, the oligomer absorption peaks were wider, but their maximum wavelengths were not significantly shifted. Moreover, broad, additional shoulders appeared for both compounds, and were attributed to the existence of oligomers of various size, in which an important π electronic delocalization took place because of the existence of an increased number of conjugated segments [8].

Fluorescence spectra

The fluorescence excitation and emission spectral properties of substituted TBT derivatives were obtained in diluted DMSO solutions (concentration = 10^{-6} M) at room temperature (Table 3). For most substituted TBT derivatives, the fluorescence excitation spectra possessed several bands located in the 273–294 and 304–319 nm regions, whereas their fluorescence emission spectra were characterized by the presence of only one maximum appearing between 334 and 345 nm (Figs. 2 and 3).

Excitation spectra of TBT derivatives contained bands generally occurring at wavelength values very close to those of the corresponding absorption ones, which indicates that the excited fluorescent species are practically identical to the absorbing species (Fig. 2).

Again, like in the case of the absorption spectra, two different spectral behaviours were distinguished for the fluorescence excitation spectra of the three newly-synthesized TBT derivatives. Two of these compounds, i.e.

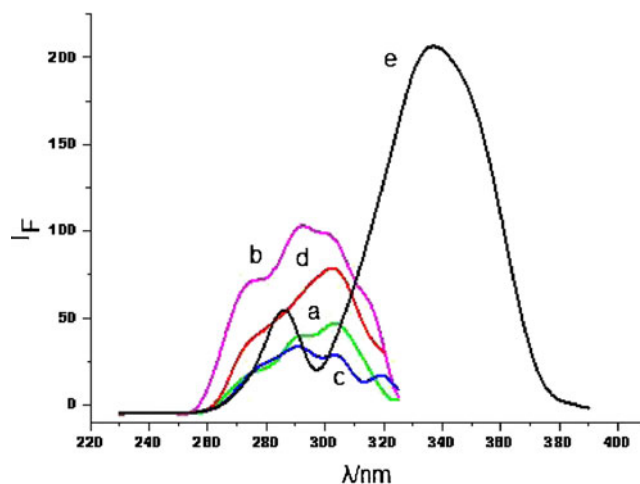


Fig. 2 Fluorescence excitation spectra of 10^{-6} M 2-MeTBT (a), 3-MeTBT (b), 3-MeOTBT (c), 2,3-diMeTBT (d) and 6-MeOTBT-2-COOMe (e) in DMSO at room temperature. Excitation spectra were performed by using the maximum emission wavelength value corresponding to the compound under study

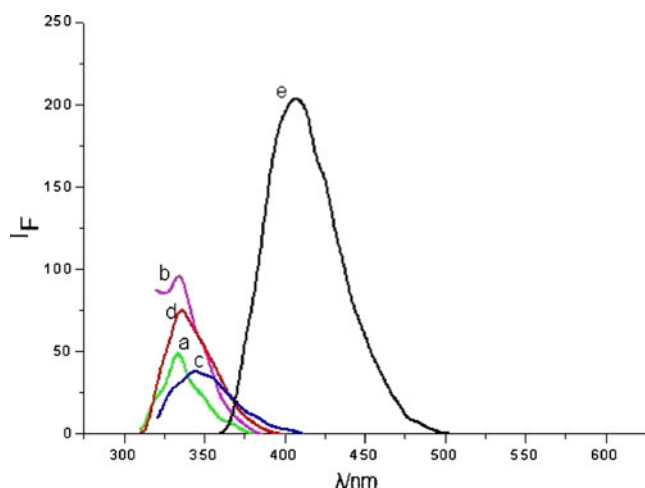


Fig. 3 Fluorescence emission spectra of 10^{-6} M 2-MeTBT (a), 3-MeTBT (b), 3-MeOTBT (c), 2,3-diMeTBT (d) and 6-MeOTBT-2-COOMe (e) in DMSO at room temperature. Emission spectra were performed by using the maximum excitation wavelength value corresponding to the compound under study

3-MeOTBT and 2,3-diMeTBT, presented excitation maximums at 291 and 302 nm, respectively, and secondary peaks or shoulders in the 273–319 nm region. Their excitation spectra were of relatively weak intensity and looked very much like those of the other substituted TBT derivatives that we have previously studied [8, 17] (Table 3). In contrast, the third compound, 6-MeOTBT-2-COOMe, displayed, besides a secondary peak at 285 nm, a very intense, red-shifted excitation band located at 336 nm, occurring at practically the same wavelength than the absorption maximum (Fig. 2). The later band was attributed to a transition towards an intramolecular charge-transfer (ICT) state, presumably due to the already-mentioned “push-pull” electronic effect, resulting from a direct resonance interaction between the methoxy and methyl acetate groups (Scheme 4).

The emission spectra of all substituted TBT derivatives did not change with the excitation wavelength value, which shows that there is only one fluorescent species for each compound. To the notable exception of 6-MeOTBT-2-COOMe, the fluorescence emission spectra of the substituted TBT derivatives under study possessed one maximum located in the 334–345 nm region. This peak was slightly red shifted relative to unsubstituted TBT ($\Delta\lambda_{em}=1-12$ nm) (Table 3 and Fig. 3). For 2,3-diMeTBT, the red-shift of the emission maximum was only 3 nm, a value comparable to those found for 2-MeTBT and 3-MeTBT. In contrast, for 3-MeOTBT as well as for 6-MeOTBT, the red-shift values were a little larger ($\Delta\lambda_{em}=8-12$ nm) because of the methoxy electron-donating effect stronger than the methyl one, which would result into a more important electronic delocalization in their singlet excited state (S_1) and a lowering of the S_1 energy level.

In the particular case of 6-MeOTBT-2-COOMe, a very intense, broad, considerably red-shifted ($\Delta\lambda_{em}=73$ nm)

emission peak appeared at 406 nm (Table 3 and Fig. 3). This band, occurring in the violet-blue part of the spectrum, can be attributed to the existence of an ICT state, related to the already-noted “push-pull” electronic interaction of the MeO and COOMe groups, which would be significantly enhanced in the singlet excited state.

The fluorescence excitation and emission spectra of poly (2-MeTBT) and poly(3-MeTBT) were also measured in DMSO solutions (concentration = 10^{-6} r.u. L^{-1}) at room temperature (Table 3). Comparatively to the corresponding monomers, poly(2-Me-TBT) and poly(3-Me-TBT) presented significant red-shifts of the fluorescence excitation ($\Delta\lambda_{ex}=8-12$ nm) and emission ($\Delta\lambda_{em}=44-45$ nm) maximums [8]. The rather strong emission bathochromic shifts implied an important π electronic delocalization in the oligomer singlet excited state, resulting from the presence of well-conjugated segments in the oligomer chains of poly (2-MeTBT) and poly (3-MeTBT), and a decrease of the oligomer singlet excited state energy levels relative to those of the corresponding monomers [8, 17, 18].

Fluorescence quantum yields

The fluorescence quantum yields (Φ_F) of the substituted TBT derivatives were measured in DMSO diluted solutions at room temperature (Table 3). Owing to its convenient spectral absorption and fluorescence emission properties, tryptophane ($\Phi_F=0.13$ in 0.05 M H_2SO_4 aqueous solution) was used as the reference compound for most substituted TBT derivatives [27]. The fluorescence quantum yield (Φ_F) values were rather high, varying between 0.11 and 0.35 for the differently substituted TBT derivatives. Also, the Φ_F values were found to be larger for poly (2-MeTBT) ($\Phi_F=0.25$) and poly (3-MeTBT) ($\Phi_F=0.28$) than for their corresponding monomers, which was ascribed to the π electronic system delocalization in the polymers, due to the presence of short-chain conjugated oligomers similarly to the case of other, recently investigated TBT and benzothienoindole (BTI) derivatives (17, 18). It is worthwhile to note that 6-MeOTBT-2-COOMe again presented a peculiar behaviour, with the highest quantum yield value relative to tryptophane ($\Phi_F=0.35$), which can be attributed to the existence of the above-mentioned “push-pull” electronic interaction of both substituents. These results would make this particular TBT derivative suitable for future applications to the development of strongly-luminescent materials and devices.

Fluorescence lifetimes

The fluorescence lifetimes (τ_F) of the substituted TBT derivatives were determined in the same experimental

conditions (Table 3). The fluorescence decays of all TBT derivatives under study were found to be monoexponential, which confirms that each compound possesses only one fluorescent species. The lifetimes of TBT derivatives presented very short values ranging between 0.11 and 0.30 ns. No significant substituent effect upon the lifetime values could be noted, except for 3-MeTBT which exhibited a notably greater lifetime than the other substituted TBT derivatives. All these fluorescence decay values were comparable to the lifetime values of about 0.2 ns, obtained for 4-methoxy-benzo[*b*]thiophene in different media [28], and of generally below 1 ns, measured for a series of polycyclic benzo-fused thiophene compounds [29–31]. An exception was thieno[2,3-*f*:5,4-*f'*] bis[1]benzothiophene which possessed a longer fluorescence lifetime of 4.6 ns [31]. In contrast, some less strongly condensed hetero-aromatic molecules, such as alkoxy benzo[*b*]thiophenes, namely 5-methoxy benzo[*b*]thiophene (5MBT) and 5-methoxymethyl benzo[*b*]thiophene (5MMBT), had longer fluorescence lifetimes of, respectively, 11.8 and 17.2 ns [32]. Also, a benzo[*b*]thiophene—containing rhodamine dye compound presented a fluorescence lifetime of 3.0 ns in DMSO vs. 3.7 ns for the rhodamine 101 reference molecule [33].

Contrarily to the monomers, poly (2-MeTBT) and poly (3-MeTBT) were characterized by very complex and heterogeneous fluorescence decays, which can be fitted to four and five exponential curves, ranging respectively from a few tens of picoseconds to around 1 ns. The existence of these multiple, very short-lived components in the fluorescence decays of poly (2-MeTBT) and poly (3-MeTBT) might be explained by the occurrence of several fluorescent oligomers of various conjugated chain lengths in the polymer films [8]. The fluorescence lifetime mean values of oligomers, comprised between 0.21 and 0.33 ns, were relatively close to the lifetime values obtained for the corresponding monomers.

Other photophysical parameters

We also calculated from our experimental results several photophysical parameters of TBT derivatives, such as the fluorescence rate constants (k_F), the quantum yields of intersystem crossing (Φ_{ISC}) and the intersystem crossing rate constants (k_{ISC}), by using the classical kinetic relations which are characteristic of fluorescence emission [34]. The k_F values were rather high, ranging between about 5.7×10^8 and 1.7×10^9 s⁻¹, according to the compound. 2,3-diMeTBT and 6-MeOTBT-2-COOMe presented the largest k_F values, indicating a rapid radiative deactivation rate from the S₁ state of both compounds. The Φ_{ISC} values were comprised between 0.65 and 0.89, which demonstrates an important efficiency of the non-radiative transition from the

S₁ to the first triplet excited state (T₁) of the TBT derivatives. Accordingly, the k_{ISC} values were found to be large, going from about 2.8×10^9 to 8.1×10^9 s⁻¹, depending on the compound.

The above-mentioned photophysical parameters were also calculated for poly(2-MeTBT) and poly(3-MeTBT). The k_F values decreased upon going from 2-MeTBT ($k_F = 1.0 \times 10^9$ s⁻¹) to poly (2-MeTBT) ($k_F = 7.6 \times 10^8$ s⁻¹), while they increased from 3-MeTBT ($k_F = 5.7 \times 10^8$ s⁻¹) to poly (3-MeTBT) ($k_F = 1.3 \times 10^9$ s⁻¹). A similar behaviour was observed when comparing the k_{ISC} values of monomers and oligomers, whereas the Φ_{ISC} values were found to decrease from 0.89 to 0.83 for both monomers to 0.75–0.72 for the oligomers.

Conclusion

We can conclude from this work that we were able to synthesize three new differently-substituted TBT derivatives, namely 2,3-diMeTBT, 3-MeOTBT and 6-MeOTBT-2-COOMe, following simple, rapid and efficient routes. In the electrochemical study, these compounds were characterized by oxidation potential values lower than that of unsubstituted TBT, due to the electron-donating effect of the methyl and methoxy substituents, and the electropolymerization attempts led to only electrodepositing very thin films for poly(3-MeOTBT) and poly(2,3-diMeTBT). In contrast, all these new substituted TBT derivatives displayed very interesting optical properties. Their fluorescence emission maximum wavelength values were found to depend on the electronic effect of substituents, and rather high fluorescence quantum yield values were obtained, the oligomers being characterized by an enhancement of fluorescence. Moreover, all these TBT derivatives presented the particularity to possess very short mono-exponential decays in the range of a few hundreds ps, whereas the oligomers had rather complex fluorescence decays that we were able to fit with a multi-exponential model. In the future, some of these TBT derivatives should have a potential usefulness for the development of novel luminescent materials.

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References

1. Gningue-Sall D, Dieng MM, Aaron JJ, Lacaze PC (1999) Phys Chem Chem Phys 1:1731

2. Fall M, Assogba L, Aaron JJ, Dieng MM (2001) *Synth Met* 123:365
3. Fall M, Aaron JJ, Dieng MM, Jouini M, Aeiyaeh S, Lacroix JC, Lacaze PC (1998) *J Chim Phys* 95:1559
4. Fall M, Aaron JJ, Sakmeche N, Dieng MM, Jouini M, Aeiyaeh S, Lacroix JC, Lacaze PC (1998) *Synth Met* 93:175
5. Sakmeche N, Aeiyaeh S, Aaron JJ, Jouini M, Lacroix JC, Lacaze PC (1999) *Langmuir* 15:2566
6. Sakmeche N, Bazzouai EA, Fall M, Aeiyaeh S, Jouini M, Lacroix JC, Aaron JJ, Lacaze PC (1997) *Synth Met* 84:191
7. Lô C, Adenier A, Chane-Ching K, Maurel F, Aaron JJ, Kosata B, Svoboda J (2006) *Synth Met* 156:256
8. Lô C, Adenier A, Maurel F, Aaron JJ, Kosmik V, Svoboda J (2008) *Synth Met* 158:6
9. Li XC, Sirrighaus H, Garnier F, Holmes AB, Moratti SC, Feeder N, Clegg W, Teat SJ, Friend RH (1998) *J Am Chem Soc* 120:2206
10. Pasini M, Destri S, Botta C, Porsio W (1999) *Tetrahedron* 14:985
11. Brédas JL, Street GB (1985) *Acc Chem Res* 18:309
12. Aaron JJ, Fall M (2000) *Spectrochim Acta A* 56:1391
13. Fall M, Aaron JJ, Gningue-Sall D (2000) *J Fluoresc* 10:107
14. Balaei S, Aaron JJ, Desbène-Monvernay A, Lacaze PC (1992) *Synth Met* 53:95
15. Cernovska K, Svoboda J, Stibor I, Glagarova M, Vanek P, Novotna V (2000) *Ferroelectrics* 241:231
16. Kosata B, Kosmik V, Svoboda J, Novotna V, Vanek P, Glogarova M (2003) *Liq Cryst* 30:603
17. Aaron JJ, Mechbal Z, Adenier A, Parkanyi C, Kosmik V, Svoboda J (2002) *J Fluoresc* 12:231
18. Aaron JJ, Mezlova M, Capochichi M, Svoboda J, Brochon JC, Guiot E (2006) *Luminescence* 21:330
19. Lô C, Aaron JJ, Svoboda J, Brochon JC, Na L (2008) *Luminescence* 23:240
20. Wright WB Jr, Barabander HJ (1971) *J Heterocycl Chem* 8:711
21. Deprez E, Tauc P, Leh H, Mouscadet JF, Auclair C, Hawkins ME, Brochon JC (2001) *Proc Natl Acad Sci USA* 98:10090
22. Moretto AF, Kirincich SJ, Xu WX, Smith MJ, Wan Z-K, Wilson DP, Follows BC, Binnun E, Joseph-McCarthy D, Foreman K, Erbe DV, Zhang YL, Tam SK, Tam SK, Lee J (2006) *Bioorg Med Chem* 14:2162
23. Fontana-Urbe BA, Heinze J (2006) *Tetrahedron Lett* 47:4635–4640
24. Fouad I, Mechbal Z, Chane-Ching K, Adenier A, Maurel F, Aaron JJ, Vodička P, Černovská K, Kozmik V, Svoboda J (2004) *J Mater Chem* 14:1711
25. Mezlova M, Aaron JJ, Svoboda J, Adenier A, Maurel F, Chane-Ching K (2005) *J Electroanal Chem* 581:93
26. Bidan G, Genies EM, Lapokovski M (1989) *Synth Met* 31:327
27. Chen RF (1967) *Anal Lett* 1:35
28. Maiti M, Sinha S, Deb C, De A, Ganguly T (1999) *J Lumin* 82:259
29. Seixas de Melo J, Rodrigues LM, Serpa C, Arnaut LG, Ferreira ICFR, Queiroz M-JRP (2003) *Photochem Photobiol* 77:121
30. Berlman IB (1971) *Handbook of fluorescence spectra of aromatic molecules*. Academic, New York
31. Wex B (2005) Ph.D. thesis, Bowling Green State University, Photochemical Sciences
32. Misra T, Ganguly T, Kamila S, Basu C, De A (2001) *Spectrochim Acta A* 57:2795
33. David E, Lejeune J, Pellet-Rostaing S, Schülz J, Lemaire M, Chauvin J, Deronzier A (2008) *Tetrahedron Lett* 49:1860
34. Valeur B (2002) *Molecular fluorescence. Principles and applications*. Chap.3. Wiley-VCH, Weinheim (FRG)