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# The structure – opto-electronical properties investigation of substituted 2,2'-bithiophenes as $\pi$ -building blocks. A joint experimental and theoretical study.

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**Electronic Supplementary Information** 

#### 1. SYNTHESIS AND CHARACTERIZATION OF INTERMEDIATES AND PRODUCTS

All commercially available chemicals were used as received without further purification. Solvents were purified by standard methods and dried if necessary. Reactions were monitored by thin layer chromatography (TLC) on plates precoated with silica gel (Merck 60 F254) and visualized using a UV hand lamp operating at 254/365 nm wavelengths. Melting points were recorded on a Kofler block and are uncorrected. Elemental analyses were measured by means of Carlo Erba Elemental Analyzer 1108. NMR spectra (<sup>1</sup>H at 300 and/or 400 MHz, <sup>13</sup>C at 75 and/or 100 MHz) were obtained in CDCl<sub>3</sub> on the VARIAN VXR-300 spectrometer operating at 300 MHz for <sup>1</sup>H NMR and 75 MHz for <sup>13</sup>C NMR using tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm). Coupling constants are reported in Hertz (Hz). Splitting patterns are designated as s: singlet, d: doublet, t: triplet m: multiplet.



#### **Reagents and conditions**

 $\label{eq:constraint} \begin{array}{l} \textit{i} \ (CH_3CH_2CO)_2O, \ Mg(ClO_4)_2.2H_2O, \ 80^\circ C, \ 4h \ for \ synthesis \ of \ \textbf{2a,b}; \\ \textit{ii} \ D_{13}H_{27}COCI, \ AICI_3, \ benzene, \ 80^\circ C, \ 30 \ min \ for \ \textbf{2c} \ and \ C_3H_7COCI, \ AICI_3, \ benzene, \ 80^\circ C \ for \ \textbf{2d}; \\ \textit{iii} \ POCI_3, \ DMF, \ 90^\circ C, \ 1.5 \ h; \ \textit{iv} \ ) \ SHCH_2COOCH_3, \ MeONa, \ MeOH, \ 0^\circ C, \ 1 \ h, \ then \ RT, \ 16h. \end{array}$ 

Scheme S1. Synthetic pathway towards bithiophenes BT1-BT4.

#### 1.1 FRIEDEL-CRAFTS ACYLATION - SYNTHESIS OF ACYLATED THIOPHENES 2a-d

**Procedure A:** Mixture of thiophene (**1a**) or 5-chlorothiophene (**1b**) [1] (0.1 mol), propionic anhydride (0.15 mol, 19.5 g, 19.0 mL) and Mg(ClO<sub>4</sub>)<sub>2</sub>.2H<sub>2</sub>O (1.0 mmol, 260 mg) was heated at 80°C for four hours under inert atmosphere of nitrogen. After the reaction was completed, the reaction mixture was cooled to RT and poured into water (100 mL) and quenched with saturated solution of Na<sub>2</sub>CO<sub>3</sub> (accompanied with the CO<sub>2</sub> leakage). The resulting mixture was extracted with dichloromethane (DCM, 3 x 30 mL) and dried on MgSO<sub>4</sub>. The solvent was evaporated under reduced pressure and the residue was purified by distillation under reduced pressure or by combined distillation and subsequent crystallisation from ethanol. By this manner intermediates **2a** and **2b** were obtained.

**Procedure B**: A flame-dried round-bottom flask equipped with the nitrogen inlet tube was charged with starting substituted thiophene derivatives **1b**,**c** (50.0 mmol) and appropriate acyl chloride (62.5 mmol) in benzene (100 mL). Then anhydrous AlCl<sub>3</sub> (62.5 mmol, 8.3 g) was added in portions, with stirring for 30 min. The resulting black solution was heated at the boiling point of benzene (80 °C) for further 30 min and cooled down to RT. The reaction was quenched by cold aqueous solution of HCl (150 mL of 1M solution) affording a yellow slurry which was separated from aqueous layer. The organic phase was washed with aq. HCl (2 x 100 mL of 1M solution) and with H<sub>2</sub>O (2 x 100mL). The solvent was evaporated under reduced pressure and the residue was purified by crystallisation from ethanol. By this manner intermediates **2c** and **2d** were obtained.

**1.1.1** *1-(Thiophene-2-yl)propan-1-one* (**2a**):The reaction was performed starting from thiophene (**1a**, 0.1 mol, 8.4 g). Crude product was distilled under the reduced pressure affording 13.6g (96%) of colourless liquid, b.p. =  $107-110^{\circ}C$  / 1.46 kPa. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 1.02 (t, *J* = 7.5 Hz, 3H), 2.89 (q, 2H), 7.13 (d, *J* = 4.0 Hz, 1H), 7.62 (d, *J* = 4.0 Hz, 1H), 7.72 (d, *J* = 3.5 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 18.5, 41.5, 128.3, 131.9, 133.6, 144.8, 193.6.Elemental anal. Calc. (%) for C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>S (142.18 g.mol<sup>-1</sup>): C 50.69, H 4.25, S 22.55; found: C 50.72, H 4.54, S 22.75.

**1.1.2** *1-(5-Chlorothiophene-2-yl)propan-1-one* (2b): The reaction was performed starting from 5-chlorothiophene [1] (1b, 0.1 mol, 11.8 g, 12.0 mL). Crude product was distilled under the reduced pressure and subsequently crystallized from cold ethanol affording 16.6 g (94%) of white solid, b.p. = 132-133°C/ 2 kPa, m.p. = 46-48°C (ethanol). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 1.15 (t, *J* = 7.2 Hz, 3H), 2.80 (q, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 3.9 Hz, 1H), 7.42 (d, *J* = 3.9 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)

δ: 8.2, 31.6, 126.2, 130.9, 138.9, 142.6, 192.7.Elemental anal. Calc. (%) for C<sub>6</sub>H<sub>5</sub>ClO<sub>2</sub>S (176.62 g.mol<sup>-1</sup>): C 40.80, H 2.85, S 18.15; found: C 40.94, H 2.80, S 18.30.

**1.1.3** *1-(5-Chlorothiophene-2-yl)-1-tetradecanone* (2c): The reaction was performed starting from 5-chloro-thiophene [1] (**1b**, 50.0 mmol, 6.0 g) and tetradecanoyl chloride (62.5 mmol, 15.5 g). Crude product was crystallised from ethanol affording 14.5g (84%) of white solid, m.p. 65-69 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 0.88 (t, 3H), 1.26 (m, 18H), 1.46 (m, 2H), 1.71 (q, 2H), 2.80 (t, 2H), 6.96 (d, *J* = 4.0 Hz, 1H), 7.49 (d, *J* = 4.0 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 14.5, 23.1, 25.1, 29.6, 29.7, 29.8, 29.8, 30.0, 32.3, 39.2, 122.6, 131.5, 132.1, 146.4, 192.8. Elemental anal. Calc. (%) for C<sub>18</sub>H<sub>29</sub>ClO<sub>2</sub>S (328.94 g.mol<sup>-1</sup>): C 62.68, H 8.47, S 9.30; found: C 62.72, H 8.68, S 9.25.

**1.1.4** *1-(5'-Chloro-3-methyl-[2,2']bithiophene-5-yl]-1-butanone* (2d): The reaction was performed starting from 5'-chloro-3-methyl-[2,2']bithiophene [2] (**1c**, 50.0 mmol, 7.0 g) and propionyl chloride (62.5 mmol, 6.0 g). Crude product was crystallised from ethanol affording 13.0g (87%) of yellow solid, m.p. =  $81-82^{\circ}$ C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 1.00 (m, 3H), 1.76 (m, 2H), 2.37 (s, 3H), 2.81 (t, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 3.9 Hz, 1H), 7.01 (d, *J* = 3.9 Hz, 1H), 7.45 (s, 1H,). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ :9.4, 14.8, 24.1, 69.5, 120.8, 122.8, 128.5, 133.0, 136.2, 144.3, 148.0, 190.3 Elemental anal. Calc. (%) for C<sub>13</sub>H<sub>13</sub>ClO<sub>2</sub>S<sub>2</sub> (300.82 g.mol<sup>-1</sup>): C 51.90, H 4.36, S 21.32; found: C 52.12, H 4.54, S 21.26.

Table S1. Reaction conditions of the Friedel-Crafts electrophilic substitution, molecular structures and the yields of the intermediates **2a-d**.

Substrate	Acetylating reagent / catalyst	Structure of product	Yield (%) / Mehod
1a: thiophene	(CH <sub>3</sub> CH <sub>2</sub> CO) <sub>2</sub> O / Mg(ClO <sub>4</sub> ) <sub>2</sub> .2H <sub>2</sub> O	2a: $S \to O \in H_3$	96 % / Method A
1b: 5-chlorothiophene	(CH <sub>3</sub> CH <sub>2</sub> CO) <sub>2</sub> O / Mg(ClO <sub>4</sub> ) <sub>2</sub> .2H <sub>2</sub> O	2b:	94 % / Method A
1b: 5-chlorothiophene	C <sub>13</sub> H <sub>27</sub> COCI / AICI <sub>3</sub>	2c: $CI$ $S$ $O \in G_{13}H_{27}$	84 % / Method B
<b>1c:</b> 5'-chloro-3-methyl-[2,2']bi- thiophene	C <sub>3</sub> H <sub>7</sub> COCI / AICI <sub>3</sub>	2d: H <sub>3</sub> C S CI	87 % / Method B

#### 1.2 VILSMEIER- HAACK HALOFORMYLATION REACTION – SYNTHESIS OF METHYLACRYLADEHYDES 3a-d

**General procedure**: Haloformylating agent was prepared by slow addition of  $POCl_3$  (5.0 eqv., 0.15 mol) to dimethylformamide (DMF, 6 eqv., 0.18 mol) at 0-5 °C and stirred at RT for 30 min. Appropriate acylated compound **2a-d** (1 eqv., 0.03mol) was added to this reagent slowly during 15 min. The reaction mixture was then stirred at 45°C for 90 min and for further 90 min at 90°C. After the reaction was completed the mixture was cooled down with ice, neutralised with aqueous solution of NaHCO<sub>3</sub> and extracted with diethyl ether (3 x 30 mL). The solvent was evaporated under reduced pressure and the residue was used as the mixture of *E/Z* isomers without purification to final reaction step. The ratio of the geometric isomers is evaluated from <sup>1</sup>H NMR.

**1.2.1** *3-Chloro-2-methyl-3-(thiophen-2-yl)acrylaldehyde (3a)*: Reaction was performed with the 1-(thiophen-2-yl)propan-1one (**2a**, 0.03 mol, 4.3 g) affording 4.7 g (84 %) of brownish oil ( $C_8H_7ClOS / 186.66 \text{ g.mol}^{-1}$ ), *E/Z* isomeric ratio = 5/1.

(*E*)-*3-Chloro-2-methyl-3-(thiophen-2-yl)acrylaldehyde*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ: 2.08 (s, 3H, CH<sub>3</sub>), 7.05 (d, *J* = 3.6 Hz, 1H), 7.19 (m, 1H), 7.56 (d, *J* = 4.8 Hz, 1H), 9.70 (s, 1H, CHO). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ: 13.8, 126.9, 130.4, 132.1, 136.9, 137.6, 146.1, 189.5 (d, CHO).

(*Z*)-*3-Chloro-2-methyl-3-(thiophen-2-yl)acrylaldehyde*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ:2.14 (s, 3H, CH<sub>3</sub>); 7.16 (m, 1H); 7.62 (d, *J* = 3.9 Hz, 2H); 10.36 (s, 1H, CHO). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ: 14.1, 127.4, 130.8, 131.6, 136.9, 137.6, 162.3, 191.4.

**1.2.2** *3-Chloro-3-(5-chlorothiophene-2-yl)-2-methylacrylaldehyde (3b)*: Reaction was performed with 1-(5-chlorothiophene-2-yl)propan-1-one (**2b**, 0.03 mol, 5.3 g) affording 6.2 g (94%) of white solid ( $C_8H_6Cl_2OS / 221.10 \text{ g.mol}^{-1}$ ), m.p. 65-67°C, *E/Z* isomeric ratio= 25/1

(*E*)-*3-Chloro-3-(5-chlorothiophene-2-yl)-2-methylacrylaldehyde*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ: 2.08 (s, 3H, CH<sub>3</sub>), 6.89 (d, *J* = 3.9 Hz, 1H, H-4), 6.97 (d, *J* = 3.9 Hz, 1H, H-3), 9.72 (s, 1H, CHO). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ: 14.1, 126.3, 131.6, 135.9, 136.4, 137.8, 145.0, 189.3.

(**Z**)-**3-Chloro-3-(5-chlorothiophene-2-yl)-2-methylacrylaldehyde**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ:2.12 (s, 3H, CH<sub>3</sub>), 6.99 (d, *J* = 4.2 Hz, 1H, H-4), 7.43 (d, *J* = 3.9 Hz, 1H, H-3), 10.34 (s, 1H, CHO). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ:14.1, 126.9, 131.2, 136.3, 137.2, 138.0, 139.7, 191.5.

**1.2.3** *3-Chloro(5-chlorothiophen-2-yl)dodecylpropenal (3c)*: Reaction was performed with the 1-(5-chlorothiophene-2-yl)-1-tetradekanone (**2c**, 0.03 mol, 10.0 g)affording 8.1 g (72%) of yellowish waxy material ( $C_{19}H_{28}Cl_2OS$  / 375.40 g.mol<sup>-1</sup>), *E/Z* isomeric ratio = 25/1

(*E*)-*3-Chloro(5-chlorothiophen-2-yl)dodecy|propenal*: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ: 0.94 (t, *J* =6.9 Hz, 3H), 1.26 (m, 20H), 2.54 (t, *J* =6.9 Hz, 2H), 6.86 (d, *J* = 3.9 Hz, 1H), 6.95 (d, *J* = 3.9 Hz, 1H), 9.67 (s, 1H, CHO). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ 11.2, 21.1, 24.8, 28.0, 31.1, 33.4, 122.8, 124.2, 132.5, 138.0, 148.2, 165.7.

(**Z**)-3-Chloro(5-chlorothiophen-2-yl)dodecylpropenal: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ: 0.94 (t, *J* =6.9 Hz, 3H), 1.26 (m, 20H), 2.54 (t, *J* =6.9 Hz, 2H), 6.86 (d, *J* = 3.9 Hz, 1H), 6.95 (d, *J* = 3.9 Hz, 1H), 10.30 (s, 1H, CHO).

**1.2.4** (*E*)-**3-Chloro-3-(5'-chloro-3-methyl-[2,2']bithiophene-5-yl)-2-ethyl-propenal (3d**): Reaction was performed with the 1-(5'-chloro-3-methyl-[2,2']bithiophene-5-yl)-1-butanone (**2d**, 0.03 mol, 8.1 g) affording 8.6 g (87%) of brown oily material ( $C_{14}H_{12}Cl_2OS_2 / 331.28 \text{ gmol}^{-1}$ ), isolated as the *E* isomer only. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 1.08 (t, *J* = 5.1 Hz, 3H), 2.35 (s, 3H), 2.59 (q, *J* = 5.1 Hz, 2H), 6.91 (d, *J* = 3.9 Hz, 1H), 6.96 (d, *J* = 3.93 Hz, 1H), 6.97 (s, 1H), 9.75 (s, 1H, CHO), 10.32 (s, 1H, CHO). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 12.0, 14.2, 120.8, 124.4, 126.8, 128.0, 130.4, 135.5, 141.4, 148.0, 148.8, 168.5.

Structure of the intermediate E/Z ratio Yield % Substrate **2**a 3a: 5/1 84 % сно 2b 3b: 25/1 94 % H<sub>3</sub>C сно ςι CI 3c: 25/1 72 % 2c C12H25 сно С 3d: 87 % 2d H₃C сно CI

Table S2. Structures, yields and the E/Z isomeric ratioof the intermediates – methylacryladehydes 3a-3d.

# **1.3 SYNTHESIS OF TARGET BITHIOPHENES BT1-BT4**

Sodium methoxide (MeONa, 0.033 mol, 1.8 g) was dissolved in methanol (70 mL) and the solution was cooled in ice bath to 0 °C. The methylthioglycolate (0.03 mol, 3.2 g, 2.7 mL) was added in one portion to the solution of sodium methoxide, followed by the dropwise addition of the corresponding methyacrylaldehyde **3a-d** (0.03 mol) in 10 mL of methanol for 15 min. The reaction mixture was then left to stir at 0 °C for 1 hour. Later, the ice bath was removed and the reaction mixture was stirred at RT for further 16 hours and when this time was over other amount of MeONa (0.033 mol, 1.8 g) in methanol (35 mL) was added and stirred for additional 4 hours. When the reaction was completed, diluted acetic acid (200 mL of 2% aqueous solution) was added. The resulting precipitate was filtered off and purified by crystallisation.

**1.3.1** *3-Methyl (3-methyl-[2,2']bithiophene-5-carboxylic acid methyl ester (BT1):* The reaction was performed starting from (*E,Z*) 3-chloro-2-methyl-3-(thiophen-2-yl)acrylaldehyde (**3a**, 0.03 mol, 5.6 g).The crude product was crystallised from methanol affording 6.7g (79%) of cream-coloured solid, m.p. = 59-60°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 2.39 (s, 3H), 3.88 (s, 3H), 7.09 (d, *J* = 5.2 Hz, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.37 (d, *J* = 5.1 Hz, 1H), 7.57 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 15.5, 52.1, 126.4, 126.6, 127.7, 129.5, 134.3, 135.5, 137.3, 138.4, 162.5. Elemental anal. Calc. (%) for C<sub>11</sub>H<sub>10</sub>O<sub>2</sub>S<sub>2</sub> (238.33 g.mol<sup>-1</sup>): C 55.44, H 4.23, S 26.91; found: C 55.60, H 4.44, S 26.74.

**1.3.2** *5'*-*Chloro-3-methyl-[2,2']bithiophenyl-5-carboxylic acid methyl ester* (**BT2**): The reaction was performed starting from (*E,Z*) 3-chloro-3-(5-chlorothiophene-2-yl)-2-methylacrylaldehyde (**3b**, 0.03 mol, 6.6 g). The crude product was crystallised from methanol affording 6.3 g (77%) of cream-coloured solid, m.p. =  $62-64^{\circ}$ C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 2.33 (s, 3H), 3.85 (s, 3H), 6.88 (d, *J* = 3.9 Hz, 1H), 6.97 (d, *J* = 3.9 Hz, 1H), 7.53 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 15.3, 52.1, 125.8, 126.7, 127.4, 133.9, 134.6, 137.3, 137.3, 146.3, 162.5. Elemental anal. Calc. (%) for C<sub>11</sub>H<sub>9</sub>ClO<sub>2</sub>S<sub>2</sub> (272.77 g.mol<sup>-1</sup>): C 48.44, H 3.33, S 23.51; found: C 48.56, H 3.42, S 23.70.

**1.3.3** *5'*-*Chloro-3-dodecyl-[2,2']bithiophenyl-5-carboxylic acid methyl ester*(BT3): The reaction was performed starting from (*E,Z*) 3-chloro(5-chlorothiophen-2-yl)dodecylpropenal(**3c**, 0.03 mol, 11.3g). The crude product was crystallised from hexane affording 10.0 g (78%) cream-coloured solid ( $C_{22}H_{31}ClO_2S_2$  / 427.06 g.mol<sup>-1</sup>), m.p. = 39-41°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ :0.94 (t, *J* = 6.2 Hz, 3H), 1.25 (m, 16H), 1.57 (m, 2H), 1.64 (m, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 6.88 (d, *J* = 3.92 Hz, 1H), 6.95 (d, *J* = 3.92 Hz, 1H), 7.60 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  12.8, 23.6, 24.8, 28.6, 31.0, 33.4, 52.2, 124.4, 126.0, 128.5, 131.3, 133.0, 136.7, 142.2, 160.2. Elemental. anal. Calc. (%) for  $C_{22}H_{31}ClO_2S_2$  (427.06 g.mol<sup>-1</sup>): C 61.87, H 7.32, S 15.02; found: C 61.94, H 7.60, S 15.40.

**1.3.4** *5*<sup>''</sup>*-Chloro-3-ethy-l4*'*-methyl-[2,2';5',2'']terthiophene-5-carboxylic methyl ester* (**BT4**): The reaction was performed starting from (*E*) 3-chloro-3-(5'-chloro-3-methyl-[2,2']bithiophene-5-yl)-2-ethyl-propenal(**3d**, 0.03 mol, 9.5 g). The crude product was crystallised from a mixture of hexane-ethylacetate (80 : 20) to afford 8.5 g (74 %) of white solid, m.p 78-80°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 1.27 (t, 3H), 2.35 (s, 3H), 2.75 (q, 2H), 3.87 (s, 3H), 6.87 (d, *J* = 3.9 Hz, 1H), 6.91 (d, *J* = 3.9 Hz, 1H), 6.97 (s, 1H), 7.64 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 10.2, 16.8, 17.4, 54.4, 120.2, 124.0, 128.6, 130.0, 136.6, 139.4, 140.0, 144.2, 145.1, 165.4. Elemental anal. Calc. (%) for C<sub>17</sub>H<sub>15</sub>ClO<sub>2</sub>S<sub>3</sub> (382.95 g.mol<sup>-1</sup>): C 53.32, H 3.95, S 25.12; found: C 53.42, H 3.90, S 25.20.

Substrate		Structure of bithiophene	Partial yield % (cyclisation)	Overal yield %
3a	BT1:	S H <sub>3</sub> C	79 %	86 %
3b	BT2:	CI S H <sub>3</sub> C	77 %	88 %
3c	BT3:		78 %	78 %
3d	BT4:		74 %	82 %







Figure S2.  $^{1}$ H NMR spectrum of **BT2** (300 MHz, CDCl<sub>3</sub>).



Figure S3. <sup>1</sup>H NMR spectrum of **BT3** (300 MHz, CDCl<sub>3</sub>).



Figure S4.  $^{1}$ H NMR spectrum of **BT4** (300 MHz, CDCl<sub>3</sub>).

# 2. DENSITY FUNCTIONAL THEORY (DFT) AND TIME-DEPENDENT FUNCTIONAL THEORY (TD-DFT) CALCULATIONS

The geometry optimization and electronic states calculation of neutral single molecules were performed using DFT method with B3LYP exchange-correlation functional [3] and 6-31G(d) localized basis set. Excitations in UV-Vis absorption spectra were determined by time dependent DFT (TD-DFT) approximation. Absorption spectra have been plotted from determined oscillator strength of electronic transitions for pure gas phase and solvent environmental model regarding the relaxed dyes molecular structures and with the same basis set. For performing the TD-DFT simulation of excitations several flavours of DFT functionals were examined in order: hybrid-GGA PBE0 and B3LYP, range separated CAMB3LYP, and meta-GGA TPSSH and M06-2X as introduced in theoretical study of [4]. To describe the influence of  $CH_2Cl_2$  solvent on dyes molecular states the conductor-like polarizable continuum model (C-PCM) was considered [5]. All calculation procedures were performed with GAMESS program suite [6]. Contour plots of frontier molecular orbitals were drawn at isosurface value = 0.03 using the VxMacMolPlt program utility [7].

#### 2.1 ELECTRONIC STATES AND OPTICAL PROPERTIES IN UV-VIS SPECTRA

To get insight into the dyes molecular structure, its electronic properties and excitations, we have calculated the system of energy levels of relaxed molecule and estimated its HOMO-LUMO energy gap, which represents an approximation for the investigation of excitations and optical properties. The B3LYP and TPSSH gas phase results for electronic system match measurements qualitatively the best. The main differences between calculated and experimental **CV** energy gaps is within 20% (B3LYP) and 2% (TPSSH) for bithiophene compounds **BT1** and **BT2** (Table S6). Computed energy gaps of both organic dyes **BT1** and **BT2** are quite similar in value ~ 3.8 eV (B3LYP) and ~ 3.3 eV (TPSSH) but not differ more than 0.07 eV.

More feasible view on the basic system of electronic excitations in molecule provide optical absorption UV-vis spectra measurement. To elucidate its characteristics theoretically the TD-DFT method for electronic excitations calculation was applied along with exploiting several DFT functionals – PBE0, B3LYP, CAMB3LYP, TPSSH and M06-2X. Both the molecule in gas phase and placed in CH<sub>2</sub>Cl<sub>2</sub> C-PCM solvent model were investigated. Absorption maxima wavelengths  $\lambda_{max}$ , optical energy gaps E<sub>o</sub>, and electronic states oscillator strengths fgp have been computed with selected functionals and are sorted in Tables S4, S5 and S7, S8. The ocillator strengths parameters for excited states allow modeling of the molar absorption coefficients and extinction directly. The experimental oscillator strenghts were roughly estimated from integration of gaussian shaped measured absorption curves [8] with UV band half-width (HW) ~ 5400 cm<sup>-1</sup>. From comparison of the BT1 TD-DFT/B3LYP gas phase results with UV-Vis measurement follows that calculated  $\lambda_{max}$  and oscillator strength  $f_{gp}$  reproduce experimental range of dyes absorption parameters in solvent environment in good accordance. In the case of BT2 compound the calculated f<sub>solv</sub> values are somehow 2.5 times larger than experimental intensity. For the dyes measured in the CH<sub>2</sub>Cl<sub>2</sub> solvent, the  $\lambda_{max}$  values are best matched by M06-2X functional for BT1 and by CAMB3LYP for BT2 sample. The overview of evaluated by different DFT functionals and experimental molar absorption coefficients in CH<sub>2</sub>Cl<sub>2</sub> solvent are shown in Tables S4, S5 and S7, S8. Again, BT1 theoretical gas phase results for log care closer to experimental values than calculated for CH<sub>2</sub>Cl<sub>2</sub> solvent (Table S7). For BT2 the log ɛ-s appears to be larger than in case of experimental absorption what follows from TD-DFT oscillator strengths (Table S8).

Functional								
	PBEO	B3LYP	CAM-B3LYP	TPSSH	M06-2X	exp. (CH <sub>2</sub> Cl <sub>2</sub> )		
λ <sub>max</sub> (nm)	333	341	320	345	315			
E <sub>ogp</sub> (eV)	3.720	3.634	3.879	3.598	3.939			
$f_{gp}$	0.581	0.568	0.576	0.562	0.572			
λ <sub>max</sub> (nm)	359	368	341	372	336	330		
E <sub>osolv</sub> (eV)	3.456	3.368	3.632	3.329	3.692	3.757		
f <sub>solv</sub>	0.808	0.792	0.794	0.793	0.796	0.58		

Table S4. Compound **BT1**: TD-DFT/6-31G(d) calculated first excitation energies and oscillator strengths  $f_{gp}$  in the gas phase ( $E_{ogp}$ ) and  $CH_2Cl_2$  solvent ( $E_{osolv}$ ) (with exp. HW ~ 5400 cm<sup>-1</sup> a crude estimation [8]).

Table S5. Compound **BT2**: TD-DFT/6-31G(d) calculated first excitation energies and oscillator strengths  $f_{gp}$  in the gas phase ( $E_{ogp}$ ) and  $CH_2Cl_2$  solvent ( $E_{osolv}$ ). (with exp. HW ~ 5400 cm<sup>-1</sup> [8]).

	Functional						
	PBE0	B3LYP	CAM-B3LYP	TPSSH	M06-2X	exp. (CH <sub>2</sub> Cl <sub>2</sub> )	
λ <sub>max</sub> (nm) E <sub>ogp</sub> (eV)	333 3.727	342 3.630	320 3.934	345 3.569	311 3.984		
$f_{gp}$	0.619	0.600	0.634	0.580	0.627		
λ <sub>max</sub> (nm) E <sub>osolv</sub> (eV)	353 3.516	363 3.418	332 3.735	369 3.357	327 3.786	335 3.701	
f <sub>solv</sub>	0.829	0.807	0.835	0.739	0.834	0.29	

Table S6. Comparisonal data for HOMO and LUMO and energy band gap DFT calculations.

BT1	HOMO	LUMO	Eg (eV)	HOMO-1	BT2	HOMO	LUMO	Eg (eV)	HOMO-1
CV exp.	-5.50	-2.20	3.30		CV exp.	-5.52	-2.28	3.24	
B3LYP	-5.55	-1.73	3.82	-6.78	B3LYP	-5.73	-1.85	3.88	-6.91
CAMB3LYP	-6.94	-0.69	6.25	-8.34	<b>CAMB3LYP</b>	-7.14	-0.81	6.33	-8.47
M06-2X	-6.90	-1.02	5.88	-8.27	M06-2X	-7.09	-1.13	5.96	-8.40
TPSSH	-5.36	-2.07	3.29	-6.54	TPSSH	-5.53	-2.19	3.34	-6.67
PBEO	-5.91	-1.75	4.16	-7.17	PBEO	-6.09	-1.87	4.22	-7.30

Table S7. Molar absorption coefficients valued as  $\log \varepsilon$  of **BT1** (mol<sup>-1</sup>.L.cm<sup>-1</sup>) calculated in TD-DFT/6-31(g) for gas phase and CH<sub>2</sub>Cl<sub>2</sub> solvent and compared with measurement.

		PBEO	B3LYP	CAM-B3LYP	TPSSH	M06-2X	exp. (CH <sub>2</sub> Cl <sub>2</sub> )
Gas phase	λ <sub>max</sub> (nm) log ε	333 4.37	341 4.36	315 4.37	347 4.36	315 4.37	
Solvent	λ <sub>max</sub> (nm) log ε	359 4.51	368 4.51	341 4.51	372 4.51	336 4.51	330 4.39

Table S8. Molar absorption coefficients valued as  $\log \varepsilon$  of **BT2** (mol<sup>-1</sup>.L. cm<sup>-1</sup>) calculated in TD-DFT/6-31(g) for gas phase and CH<sub>2</sub>Cl<sub>2</sub> solvent and compared with measurement.

		PBEO	B3LYP	CAM-B3LYP	TPSSH	M06-2X	exp. (CH <sub>2</sub> Cl <sub>2</sub> )
Gas phase	λ <sub>max</sub> (nm) log ε	333 4.40	342 4.39	315 4.41	347 4.37	311 4.41	
Solvent	λ <sub>max</sub> (nm) log ε	353 4.53	363 4.51	332 4.53	369 4.47	328 4.53	335 4.08

# 3. CYCLIC VOLTAMMETRY

Cyclic voltammetry measurements were performed in solution, under nitrogen atmosphere with a computer controlled Amel 2053 (with Amel 7800 interface) electrochemical workstation in a three electrode single-compartment cell using platinum electrodes and SCE as standard electrode, with  $Fc/Fc^+$  redox couple as internal standard. The electrolyte is a 0.1 M tetrabutylammoniumtetrafluoroborate solution in  $CH_2Cl_2$  and the scan rate is 50 mV/s (Figure S5).

# 4. OPTICAL PROPERTIES OF BITHIOPHENES BT1-BT4

## 4.1 GENERAL METHODS.

Absorption spectra of the solutions of **BT1-BT4** with concentration 1.10<sup>-5</sup> mol.L<sup>-1</sup> in toluene (TOL), dichloromethane (DCM), methanol (MeOH) and acetonitrile (MeCN) and in polymer matrices – polymethylmetacrylate (PMMA), polystyrene (PS) and polyvinylchloride (PVC) with concentration of the compound in appropriate matrix 0.02 kg.L<sup>-1</sup> and 0.002 kg.L<sup>-1</sup>were measured on a UV 1650PC spectrometer (Shimadzu, Japan). Emission spectra of the same samples were recorded on a RF-5301PC spectrofluorophotometer (Shimadzu, Japan). The fluorescence of the solutions was measured in 1 cm cuvette in a right-angle arrangement. The fluorescence of the polymer films was measured in a front-face arrangement on the solid sample holder. The quantum yields were determined relative to anthracene. The quantum yields of anthracene fluorescence in different media, which were determined by comparing the fluorescence of anthracene in cyclohexane (QY = 0.25 [9]) to that in the media used in this study, were determined to be 0.20 in methanol and acetonitrile, 0.16 in toluene and 0.11 in dichloromethane. In the polymer matrices, the quantum yields were assumed to be 0.20 in PMMA, 0.16 in PS and 0.11 in PVC. The quantum yields in the solutions and films were corrected to different absorptions at the excitation wavelength [10]. The fluorescence spectra were obtained by exciting into the maximum of the longest wavelength absorption band.

# 4.2 UV-VIS AND EMISSION SPECTRA OF INVESTIGATED BITHIOPHENES BT1-BT4

All data obtained according to experimental evaluations of the absorption and the fluorescence spectra are collected in Table S9 and in graphical form on Figures S6-S21.

	$\lambda$ max Absorption (nm) / log $\varepsilon$ (mol <sup>-1</sup> .L.cm <sup>-1</sup> )											
	DCM	TOL	MeCN	MeOH	PMMA	PMMA	PVC	PVC (0.02)	PS (0.002)	PS(0.02)		
					(0.002)	(0.02)	(0.002)					
BT1	330/4.39	329/4.26	328/4.28	329/4.18	330/4.12	330/5.17	338/4.23	338/5.21	332/4.04	334/5.05		
BT2	335/4.08	333/4.00	331/4.09	331/4.06	334/3.48	333/4.99	340/3.99	342/5.01	337/3.86	336/4.82		
BT3	331/4.17	330/4.15	331/4.11	327/3.98	336/4.23	329/5.13	335/4.14	341/4.84	330/4.10	-		
BT4	370/4.36	367/4.26	364/4.12	361/4.41	368/4.26	369/5.00	-	-	363/4.21	381/5.43		
λmax Emission (nm) / Δν (cm <sup>-1</sup> ) / QY												
	DCM	TOL	MeCN	MeOH	РММА	PMMA	PVC	PVC (0.02)	PS (0.002)	PS (0.02)		
					(0.002)	(0.02)	(0.002)					
BT1	405/5611/	393/4949/	404/15897	414/6240/	407/5917/	395/4986/	409/5833/	405/4894/	398/4994/	412/5668		
	0.175	0.144	/0.016	0.845	0.320	0.109	0.027	0.248	0.102	/0.094		
BT2	413/5637/	407/5460/	412/5939/	418/6288/	405/5248/	417/6049/	411/5058/	417/5258/	407/5103/	412/5490		
	0.094	0.058	0.107	0.261	0.027	0.014	0.125	0.110	0.075	/0.052		
BT3	412/5939/	407/5733/	414/6056/	417/6600/	405/5070/	423/6754/	423/5098/	437/6442/	409/5853/	426/6465		
	0.138	0.073	0.120	0.197	0.023	0.010	0.075	0.026	0.016	/0.005		
BT4	463/5428/	442/5475/	463/5874/	472/6286/	462/5528/	463/5501/	471/5015/	477/6508/	464/5996/	477/5282		
	0.043	0.041	0.032	0.051	0.006	0.003	0.018	0.011	0.032	/0.01		

Table S9. Detailed data of the optical characterisations of bithiophenes BT1-BT4.

4.3 Graphical presentation of the measured/obtained data







Figure S5. CV graphs of BT1-BT4 electrolyte using 0.1 M tetrabutylammonium tetrafluoroborate solution in  $CH_2Cl_2$  with the 50 mV/s scan rate.



Figure S6. UV-Vis spectra of **BT1** in solutions (1.10<sup>-5</sup> mol.L<sup>-1</sup>).



Figure S7. UV-Vis spectra of **BT1** in matrix (0.02 kg.L<sup>-1</sup>, 0.002 kg.L<sup>-1</sup>).



Figure S8. UV-Vis spectra of **BT2** in solutions  $(1.10^{-5} \text{ mol}.\text{L}^{-1})$ .



Figure S9. UV-Vis spectra of **BT2** in matrix (0.02 kg.L<sup>-1</sup>, 0.002 kg.L<sup>-1</sup>).



Figure S10. UV-Vis spectra of **BT3** in solutions  $(1.10^{-5} \text{ mol.L}^{-1})$ .



Figure S11. UV-Vis spectra of **BT3** in matrix (0.02 kg.L<sup>-1</sup>, 0.002 kg.L<sup>-1</sup>).



Figure S12. UV-Vis spectra of **BT4** in solutions (1.10<sup>-5</sup> mol.L<sup>-1</sup>).



Figure S13. UV-Vis spectra of **BT4** in matrix (0.02 kg.L<sup>-1</sup>, 0.002 kg.L<sup>-1</sup>).



Figure S14. Fluorescence of **BT1** in solutions ( $1.10^{-5}$  mol.L<sup>-1</sup>).



Figure S15. Fluorescence of BT1 in matrix (0.02 kg.L<sup>-1</sup>, 0.002 kg.L<sup>-1</sup>).



Figure S16. Fluorescence of **BT2** in solutions  $(1.10^{-5} \text{ mol.L}^{-1})$ .



Figure S17. Fluorescence of **BT2** in matrix (0.02 kg.L<sup>-1</sup>, 0.002 kg.L<sup>-1</sup>).



Figure S18. Fluorescence of **BT3** in solutions ( $1.10^{-5}$  mol.L<sup>-1</sup>).



Figure S19. Fluorescence of **BT3** in matrix (0.02 kg.L<sup>-1</sup>, 0.002 kg.L<sup>-1</sup>).



Figure S20. Fluorescence of **BT4** in solutions ( $1.10^{-5}$  mol.L<sup>-1</sup>).



Figure S21. Fluorescence of **BT4** in matrix (0.02 kg.L<sup>-1</sup>, 0.002 kg.L<sup>-1</sup>).



Figure S22. Demonstration of the fluorescent properties in the solid / liquid sample of BT1.

## 4.3 PREPARATION OF POLYMER MATRICES DOPPED WITH BITHIOPHENES BT1-BT4

**General procedure**: Polymer films doped with the bithiophenes**BT1-BT4** with the concentrations of 0.02 mol.kg<sup>-1</sup> and 0.002 mol kg<sup>-1</sup> were prepared by casting from solution. Films of polystyrene (PS) (ChemischeWerkeHuels, Germany) and poly(methyl methacrylate) (PMMA) (Diacon, ICI, England) were prepared by casting 0.002 or 0.02 mg of probe in 1 mL of a chloroform solution of polymer (5 g / 100 mL) on a glass plate ( $25 \times 40$  mm). To ensure slow evaporation of the solvent, the glass plates were covered with Petri dishes. Films of poly(vinylchloride) (PVC) (Neralit, SpolanaNeratovices.e., CR) were prepared in a similar fashion by casting from tetrahydrofuran solution (5 g / 100 mL).



Figure S23. Example of the polymer thin film doped with **BT1** in PMMA (0.002 mol.kg<sup>-1</sup>), transparency and the visibility through the polymer film (left), storage of the polymer film (right).

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