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Toward multi-addressable molecular systems: Efficient synthesis and photochromic performance of unsymmetrical bisthienylethenes

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ABSTRACT

Various synthetic routes have been compared to access to unsymmetrical 1,2-bisthienylperfluorocyclopentenes having one electro-withdrawing formyl group. The strategy based on key monosubtituted cyclopentenes appears to be the most reliable and versatile synthetic approach. Applying this controlled sequential synthesis to appropriate thiophenic building blocks leads to the preparation of π-conjugated extended push–pull system where photochromic performance were characterised.

1. Introduction

Multi-addressable organic materials stimulated by light is currently a very active research topic and such systems are expected to be of great importance for optical computing as logic gates, field-effect transistors and high density data storage systems. [1–5] The design and synthesis for functional molecules that could serve as molecular devices for sensing, switching, and signal transduction from optical inputs are areas of intense activity and tremendous potential significance. The goal is a miniaturization of functional elements down to the molecular level, which could result in a markedly increased performance as a consequence of ultra-high density of the functional elements compared to current devices and in that regard organic photochromic compounds are targeted candidates because of the light-induced reversible isomerization between two isomers having different absorption spectra acting as a binary system. Several attempts to prepare multi-photochromic switches have been reported recently. [6–10] In the course of our programme to prepare photoinduced NLO-phores [11–13] we demonstrated that 1,2-bisthienylethenes [14] hereafter named BTE for convenience bearing an electronically withdrawing group are key intermediates to the route for covalently linked BTE to indolinoxazolidines which exhibit promising tunable hyperpolarisabilities. In this article, we describe the synthesis along the photochromic performance of four unsymmetrical bisthienylethenes **1**–**4** (Scheme 1) bearing a formyl group on position 5 as a strong electro-withdrawing group that can be used as intermediates for the preparation of multi-addressable systems based on bisthienylethene–indolinooxazolidine hybrid [15] or azacrown and bisthienylethene. [16]

2. Discussion

2.1. Synthesis

As a synthetic route to prepare an unsymmetrical substituted BTE containing one aldehyde function from a symmetrical compound has been reported to proceed efficiently [17], we tried to synthesize the targeted unsymmetrical BTE starting from the diiodinated dithienylethene **5**. This latter compound was selected as a common intermediate since iodine is a suitable prerequisite for either a carbon–carbon coupling reaction, following Sonogashira or Suzuki procedures, or a formylation using n-butyllithium and DMF as reagents. A symmetrical compound presents the advantage of using the same intermediate for all the desired target molecules. Compound **5** was prepared in 87% yield by double lithiation of the well-known dichlorinated dithienylethene **6** [14] using n-butyllithium subsequently followed by a substitution on iodine as depicted on Scheme 2.

The reaction has repeated several times and we found that this approach is unsuccessful either for the formylation as well as the carbon–carbon coupling reaction. Indeed, the reaction of **5** with 1

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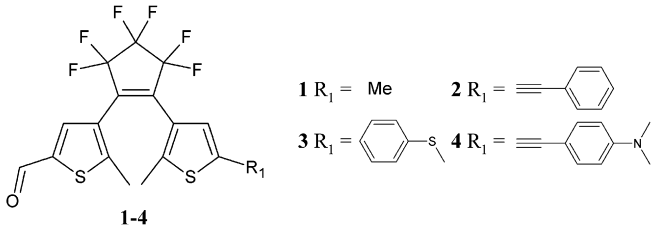


Scheme 1. Targeted unsymmetrical BTE **1**–**4**.

equivalent of n-butyllithium followed by an addition of DMF afforded an interesting mixture of the diformylated compound and the starting material in a 1:1 ratio (Scheme 3) where no significant amount of desired unsymmetrical BTE was obtained. As a confirmation of the lack of selectivity, the Sonogashira coupling with 1 equivalent of phenylacetylene gave a mixture of three compounds which were difficult to purify due to their similar polarities and which were identified as the starting material, the monosubstituted and disubstituted compounds.

An other synthetic route involving a monosubstituted perfluorocyclopentene has to be considered: the unsymmetrization is performed from the beginning and the molecule is built step-by-step starting from thiophene building blocks. The synthetic strategy relies on the reaction of the halogenated key synthon **10** with different conveniently substituted thiophenes to first obtain chlorinated BTEs which were subsequently exchanged with lithium using n-butyllithium and reacted with DMF to afford the targets possessing a formyl group Scheme 4.

The synthesis of **10** was performed as previously described [18] and thiophenes **11** and **13** were synthesized through a palladium-catalyzed Sonogashira coupling reaction in the presence of copper iodide starting from the diiodiated compound **14** and phenylacetylene derivatives in good yield. A copper-free method [19] could also be used to prepare thiophene **11** in 64% yield (Scheme 5).

The diiodination of 2-methylthiophene gave a mixture of two regioisomers, i.e. 2,4-diiodo-5-methylthiophene **14** and 2,3-diiodo-5-methylthiophene in 84% and 12% yield respectively. These two isomers could not be separated neither by chromatography on silica gel nor by distillation under vacuum. The purification was realized during the next step as the reaction of the undesired and minor isomer was not observed during the Sonogashira coupling reaction using phenylacetylene. Suzuki coupling of the boronic acid **15** [20] with 4-iodothioanisole **16** afforded thiophene **12** in 72% yield. The compound **16** was prepared in 88% yield by a lithiation of 1,4-diiodobenzene to afford the lithium thiophenolate which reacted on methyl iodide as depicted on Scheme 6.

The chlorinated dithienylethenes **7**–**9** result from the lithiation of the thiophenes **11**–**13** with n-butyllithium which react on the key synthon **10** in moderate to good yield. Finally, the dithienylethenes **2**–**4** were obtained from the formylation with n-butyllithium/DMF of the chlorinated compounds **7**–**9**. BTE **1** was prepared by acid hydrolysis of the compound **17** which results from the reaction of the monosubstituted perfluorocyclopentene **18** [21] with the acetal **19** [17] as shown in Scheme 7. The electron-withdrawing formyl group of thiophene **20** was protected with 2,2-dimethylpropane-1,3-diol [22] to give the acetal **19** in 89% yield.

Despite the strong acidic conditions (trifluoroacetic acid in a mixture of THF and water), the acetal **19** could not be deprotected at room temperature, this protecting group is known to be a robust one. This result was already observed during the deprotection of diacetal-substituted dithienylethene **21** to give the symmetrical diformyl-substituted one **22**. [17] We found that the deprotection of diacetal **1** was almost quantitative when the reaction was carried out with aqueous hydrochloric acid in refluxing methanol (Scheme 8).

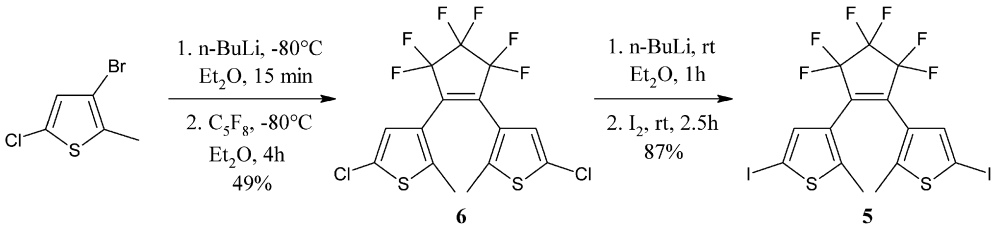
2.2. Experimental section

2.2.1. 1,2-bis(5-chloro-2-methyl-3-thienyl)perfluorocyclopentene *6*

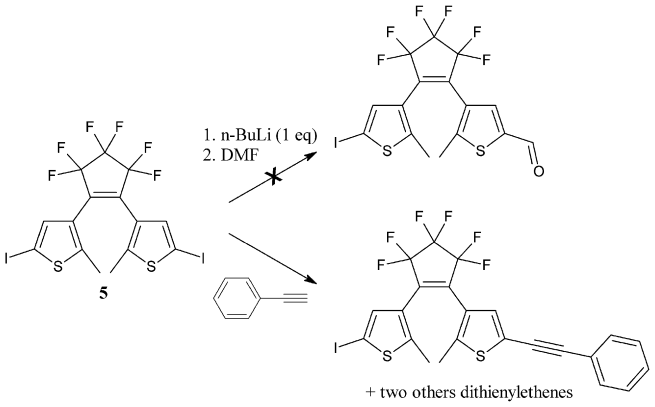
To a stirred solution of 3-bromo-5-chloro-2-methylthiophene (13.79 g, 65.21 mmol) in anhydrous diethyl ether (140 mL) was added dropwise n-butyllithium (42.8 mL, 1.6 M in hexanes, 68.48 mmol) at −80 °C under nitrogen atmosphere and the solution was stirred for 15 min. Perfluorocyclopentene (4.4 mL, 32.61 mmol) was added and the mixture was stirred for 4 h at −80 °C. The mixture was diluted with diethyl ether (100 mL) and the reaction was quenched with an aqueous solution of hydrochloric acid (1% v/v, 200 mL). The aqueous layer was extracted with diethyl ether (3 × 70 mL) and the organic layers were washed with an aqueous solution of $NaHCO_3$ (75 mL), water (2 × 70 mL), brine (70 mL), dried over Na_2SO_4, filtered and the solvent was evaporated. The crude product was washed with methanol to afford 7.0 g of compound **6** as a white solid in 49% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.89 (s, 2H, ArH), 1.89 (s, 6H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 140.7; 128.2; 125.6; 124.2; 91.7; 14.5. LRMS (EI), *m*/*z* (%): 438 (M + 2, 74), 436 (M^+, 100), 403 (23), 401 (53), 386 (75), 366 (60), 343 (26), 332 (44), 78 (18), 61 (28), 59 (30), 45 (19).

2.2.2. 1,2-bis(5-iodo-2-methyl-3-thienyl)perfluorocyclopentene *5*

To a stirred solution of 1,2-bis(5-chloro-2-methyl-3-thienyl) perfluorocyclopentene **6** (2.91 g, 6.66 mmol) in anhydrous diethyl ether (150 mL) was added dropwise n-butyllithium (10.4 mL, 1.6 M in hexanes, 16.64 mmol) the solution was stirred for 1 h at room temperature under nitrogen atmosphere. Iodine (5.08 g, 19.97 mmol) was added and the mixture was stirred 2 h at room temperature. The solution was diluted with diethyl ether (100 mL) and the organic layer was washed with an aqueous solution of $Na_2S_2O_3$ (10% w/v, 100 mL), water (2 × 50 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was flash chromatographed on silica gel (pentane) to afford 3.6 g of compound **5** as a slightly pink solid in 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.19 (s, 2H, ArH), 1.89 (s, 6H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 147.8; 136.1; 126.7; 70.9; 14.5.



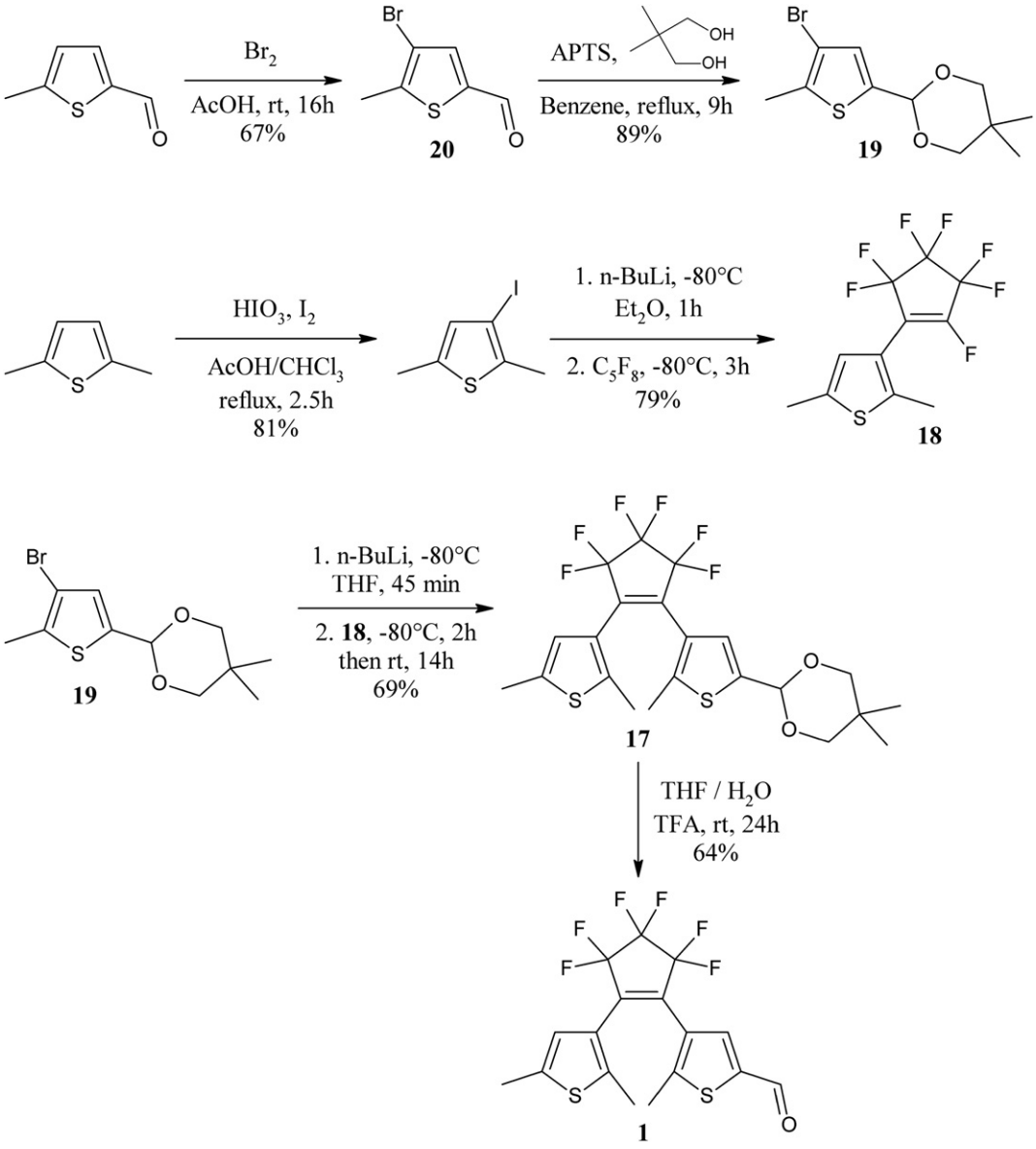
Scheme 2. Synthetic pathway for diiodinated BTE **5**.



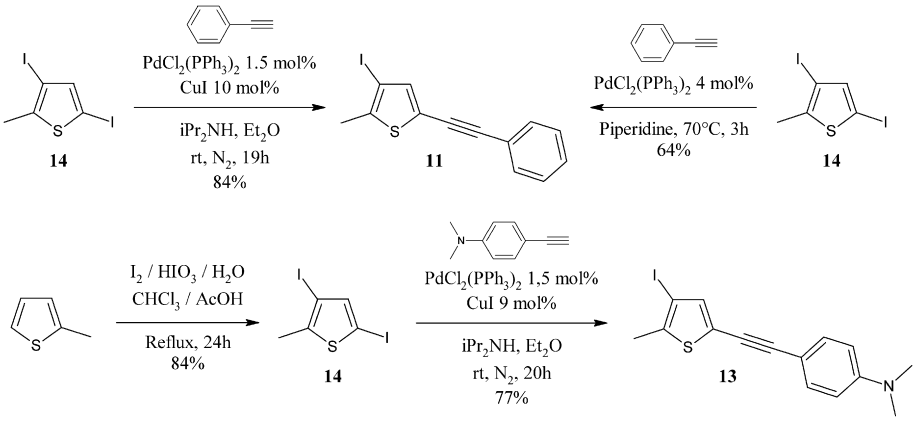
Scheme 3. Attempt to prepare unsymmetrical BTE from dihalogenated BTE.

*2.2.3. (5-chloro-2-methyl-3-thienyl)perfluorocyclopentene **10***

To a stirred solution of 3-bromo-5-chloro-2-methylthiophene (8.0 g, 37.82 mmol) in anhydrous diethyl ether (120 mL) was added dropwise n-butyllithium (26.0 mL, 1.6 M in hexanes, 41.61 mmol) at −80 °C under nitrogen atmosphere and the solution was stirred for 15 min. Perfluorocyclopentene (10.2 mL, 75.65 mmol) was added and the mixture was stirred for 4 h at −80 °C. The reaction was quenched with an aqueous solution of hydrochloric acid (1% v/v, 150 mL) and the aqueous layer was extracted with diethyl ether (4 × 40 mL). The organic layers were washed with an aqueous solution of $NaHCO_3$ (5% w/v, 50 mL), water (2 × 50 mL), brine (50 mL), dried over Na_2SO_4, filtered and the solvent was evaporated. The crude product was flash chromatographed on silica gel (pentane) to afford 10.0 g of compound **10** as a yellow liquid in 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.92 (bs, 1H, ArH), 2.40 (d, J = 3.4 Hz, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 153.5 (m, CF); 149.5 (m, CF_2); 142.5 (s); 128.5 (s); 125.7 (s); 119.2 (s); 118.4 (m), 114.3 (m, CF_2); 110.8 (m, CF_2); 107.1 (m); 14.6 (s, CH_3). LRMS



Scheme 4. General route.



Scheme 5. Synthesis of thiophenes **11** and **13** via a Sonogashira coupling reaction.

(EI), *m/z* (%): 326 (M + 2, 47), 324 (M^+, 100), 305 (14), 289 (97), 269 (19), 219 (23), 189 (21), 170 (13), 145 (13), 131 (22), 69 (21), 45 (16).

*2.2.4. 2,4-diiodo-5-methylthiophene **14***

2-methylthiophene (20.0 g, 0.204 mol), iodine (49.12 g, 0.194 mol), iodic acid (16.13 g, 0.092 mol) were dissolved in a mixture of water (50 mL), chloroform (150 mL) and acetic acid (150 mL) and the mixture was refluxed for 24 h. After cooling down to room temperature, the solvent was evaporated and the residue was dissolved in chloroform (200 mL). The organic layer was washed with an aqueous solution of $Na_2S_2O_3$ (10% w/v, 150 mL), a solution of $NaHCO_3$ (5% w/v, 2 × 50 mL), brine (50 mL), dried over Na_2SO_4, filtered and the solvent was evaporated. The crude product was dissolved with pentane and passed through a silica gel column to afford a mixture composed of 60.0 g of compound **14** in 84% yield and 9.0 g of 2,3-diiodo-5-methylthiophene in 12% yield as a orange liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.07 (s, 1H, ArH), 2.42 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 145.1; 143.2; 80.4; 70.8; 18.1. LRMS (EI), *m/z* (%): 350 (M^+), 223 (52), 96 (76), 67 (18).

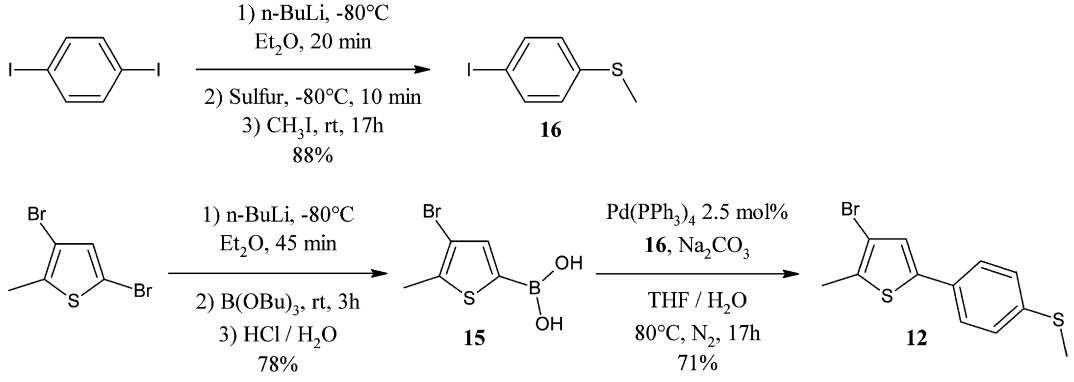
*2.2.5. 3-iodo-2-methyl-5-(phenylethynyl)thiophene **11***

To a degassed solution of 2,4-diiodo-5-methylthiophene **14** (5.22 g, 14.92 mmol), copper(I) iodide (0.293 g, 1.543 mmol), bis (triphenylphosphine)palladium(II) chloride (0.184 g, 0.257 mmol) in a mixture of anhydrous diethyl ether (20 mL) and diisopropylamine (25 mL) was added phenylacetylene (1.9 mL, 17.15 mmol). The mixture was stirred for 19 h at room temperature under nitrogen atmosphere. Then, the solvent was evaporated, the residue was dissolved with diethyl ether and the solution was sonicated. The beige precipitate was filtered and washed with diethyl ether. The organic layer was evaporated and the crude product was flash chromatographed on silica gel (pentane) to afford 4.1 g of compound **11** as a white solid in 84% yield.

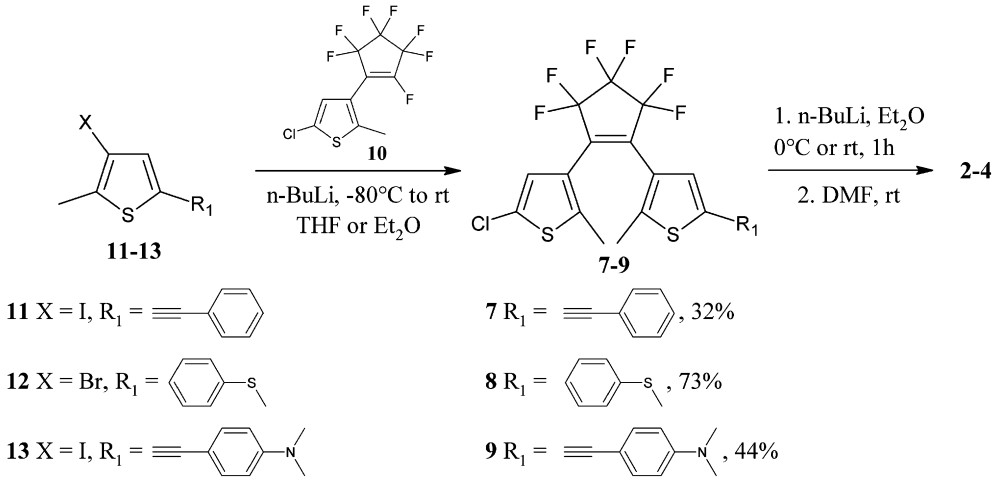
2.2.5.1. Free-copper method. 2,4-diiodo-5-methylthiophene **14** (8.7 g, 24.86 mmol), bis(triphenylphosphine)palladium(II) chloride (0.698 g, 0.944 mmol) and phenylacetylene (2.81 mL, 26.11 mmol) were dissolved in piperidine (7.4 mL) and the solution was stirred for 3 h at 70 °C. After cooling down to room temperature, the mixture was diluted with diethyl ether (50 mL) and water (50 mL), and the aqueous layer was extracted with diethyl ether (4 × 50 mL). The organic layers were washed with an aqueous solution of hydrochloric acid (1% v/v, 2 × 50 mL), water (3 × 50 mL), brine (50 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was flash chromatographed on silica gel (pentane) and washed with methanol to afford 5.1 g of compound **11** as a white solid in 64% yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.53–7.48 (m, 2H, ArH), 7.38–7.34 (m, 3H, ArH), 7.15 (s, 1H, ArH), 2.43 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 140.8 (*C*–CH_3); 139.1 (CH thiophene); 131.5 (CH phenyl); 128.7 (CH phenyl); 128.5 (CH phenyl); 122.7 (Cq phenyl); 122.6 (Cq thiophene); 93.9 (Cq); 81.7 (Cq); 80.2 (C–I); 18.2 (CH_3). LRMS (EI), *m/z* (%): 324 (M^+), 197 (M-I, 40), 152 (24), 145 (18), 98 (21).

*2.2.6. 4-[(4-iodo-5-methylthiophen-2-yl)ethynyl]-N,N-dimethylaniline **13***

To a degassed solution of 2,4-diiodo-5-methylthiophene **14** (6.10 g, 17.43 mmol), copper(I) iodide (0.344 g, 1.804 mmol), bis



Scheme 6. Synthesis of thiophene **12**.



Scheme 7. Synthesis of targeted BTE **1**.

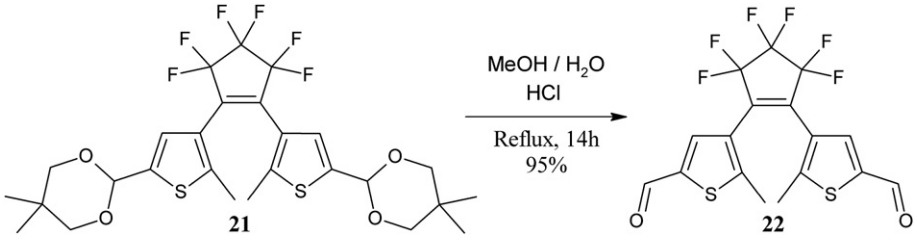
(triphenylphosphine)palladium(II) chloride (0.211 g, 0.301 mmol) in a mixture of anhydrous diethyl ether (25 mL) and diisopropylamine (30 mL) was added 4-ethynyl-N,N-dimethylaniline (2.91 g, 20.04 mmol) and the solution was stirred for 20 h at room temperature under nitrogen atmosphere. Then, the solvent was evaporated, the residue was dissolved in diethyl ether (100 mL) and sonicated. The brown precipitate was filtered, washed with diethyl ether. The organic layers were washed with an acidulated aqueous solution (100 mL), water (2 × 100 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was chromatographed on silica gel (petroleum ether/dichloromethane: 1/1) to afford 4.94 g of compound **13** as a yellow solid in 77% yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.38 (d, J = 8.8 Hz, 2H, ArH), 7.08 (s, 1H, ArH), 6.65 (d, J = 8.8 Hz, 2H, ArH), 2.99 (s, 6H, CH_3), 2.42 (s, 3H, CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm) = 150.3; 139.6; 137.8 (CH); 132.7 (CH); 123.7; 111.8 (CH); 109.2; 95.3; 80.0; 79.6; 40.2 (CH_3); 18.2 (CH_3). LRMS (EI), *m/z* (%): 367 (M^+, 100), 240 (M-I, 6), 196 (25), 120 (25). HRMS (ESI), (M + H^+) calcd for $C_{15}H_{15}NSI$: 367.9964, found: 367.9965.

2.2.7. 4-iodothioanisole ***16***

To a stirred solution of 1,4-diiodobenzene (19.62 g, 59.50 mmol) in anhydrous diethyl ether (500 mL) was added dropwise n-butyllithium (39.0 mL, 1.6 M in hexanes, 62.40 mmol) at −80 °C under nitrogen atmosphere and the solution was stirred for 20 min. Sulfur (2.10 g, 65.40 mmol) was added and the mixture was stirred until the disappearance of the precipitate. Then, methyl iodide was added (7.40 mL, 118.90 mmol), the cooling bath was removed and the solution was stirred for 17 h at room temperature under nitrogen atmosphere. The reaction was quenched with an aqueous solution of ammonium chloride (10% w/v, 300 mL) ant the aqueous layers were extracted with diethyl ether (2 × 100 mL). The organic layers were washed with water (3 × 150 mL), brine (150 mL), dried over $MgSO_4$, filtered and the solvent was evaporated to afford 13.1 g of compound **16** as a slightly yellow solid in 88% yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.56 (d, J = 8.4 Hz, 2H, ArH), 6.96 (d, J = 8.4 Hz, 2H, ArH), 2.44 (s, 3H, CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm) = 138.6; 137.6; 128.2; 89.3; 15.7. LRMS (EI), *m/z* (%): 250 (M^+, 100), 235 (M-CH_3, 55), 123 (M-I, 22), 108 (58), 77 (24), 45 (35).

2.2.8. 3-bromo-2-methyl-5-[4-(methylsulfanyl)phenyl] thiophene ***12***

3-bromo-2-methyl-5-thienylboronic acid **15** (4.87 g, 22.05 mmol), 4-iodothioanisole **16** (5.51 g, 22.05 mmol), tetrakis(triphenylphosphine)palladium (0.637 g, 0.551 mmol) and sodium carbonate (8.88 g, 83.79 mmol) were dissolved in THF (200 mL) and water (20 mL), and the solution was stirred 17 h at 80 °C under nitrogen atmosphere. After cooling down to room temperature, the solvent was evaporated and the residue was dissolved in dichloromethane (50 mL) and water (50 mL). The aqueous layer was extracted with dichloromethane (2 × 50 mL) and the organic layers were washed with water (4 × 100 mL), brine (50 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was flash chromatographed on silica gel (pentane/dichloromethane: 80/20) to afford 4.7 g of compound **12** as a white solid in71% yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.41 (d, J = 8.5 Hz, 2H, ArH), 7.23 (d, J = 8.5 Hz, 2H, ArH), 7.07 (s, 1H, ArH), 2.50 (s, 3H, CH_3), 2.41 (s, 3H, CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm) = 140.7; 138.4; 133.4; 130.4; 126.9; 125.7; 125.2; 109.9; 15.8; 15.0. LRMS (EI), *m/z* (%): 300 (M + 2, 96), 298 (M^+, 100), 283 (M-CH_3, 70), 285 (68), 219 (M-Br, 14), 204 (16), 203 (18), 172 (13), 171 (35), 109 (16), 108 (8).



Scheme 8. Synthesis of BTE **22**.

*2.2.9. 4-bromo-5-methylthiophene-2-carbaldehyde **20***

To a stirred solution of 5-methyl-2-thiophenecarboxaldehyde (39.2 g, 0.311 mol) in acetic acid (320 mL) was added dropwise a solution of bromine (19.2 mL, 0.373 mol) in acetic acid (150 mL) over 1 h in the absence of light and at room temperature. The reaction mixture was stirred vigorously in the dark for 16 h at room temperature and then the reaction was quenched adding carefully and slowly a saturated solution of $NaHCO_3$ (3 L). The mixture was extracted with diethyl ether (2 × 500 mL) and the organic layers were washed with a solution of $NaHCO_3$ (5% w/v, 5 × 150 mL), water (2 × 150 mL), brine (150 mL), dried over Na_2SO_4, filtered and the solvent was evaporated. The brown crude product was recrystallized from hexane to afford 43 g of compound **20** as a yellow solid in 67% yield. mp = 56.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.74 (s, 1H, CHO), 7.56 (s, 1H, ArH), 2.45 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 181.6; 145.8; 140.1; 138.7; 111.2; 15.9. LRMS (EI), *m*/*z* (%): 206 (M + 2, 83), 205 (M+1, 100), 204 (M^+,82), 175 (M-CHO, 18), 125 (M-Br, 26), 96 (43), 69 (17).

*2.2.10. 2-(4-Bromo-5-methylthiophen-2-yl)-5,5-dimethyl-1,3-dioxane **19***

4-bromo-5-methylthiophene-2-carbaldehyde **20** (20.0 g, 0.098 mol), 2,2-dimethylpropane-1,3-diol (15.3 g, 0.146 mol) and para-toluenesulfonic acid monohydrate (3.08 g, 0.015 mol) were dissolved in benzene (150 mL) and the mixture was refluxed for 9 h. After cooling down to room temperature, the reaction mixture was diluted with dichloromethane (150 mL) and washed with a solution of $NaHCO_3$ (5% w/v, 150 mL), water (2 × 150 mL), brine (150 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was recrystallized form hexane to afford 25.3 g of the compound **19** as a beige solid in 89% yield. mp = 72.1–72.8 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.94 (s, 1H, ArH), 5.52 (s, 1H, CH), 3.73 (d, J = 11.0 Hz, 2H, CH_2), 3.60 (d, J = 10.7 Hz, 2H, CH_2), 2.37 (s, 3H, CH_3), 1.25 (s, 3H, CH_3 acetal), 0.78 (s, 3H, CH_3 acetal). ^{13}C NMR (75,5 MHz, $CDCl_3$): δ (ppm) = 138.6 (s, *C*–CH); 134.9 (s, *C*–CH_3); 128.1 (s, CH); 108.7 (s, C–Br); 97.9 (s, CH acetal); 72.2 (s, CH_2–O); 30.5 (s, Cq acetal); 23.3 (s, CH_3); 22.1 (s, CH_3); 15.1 (s, CH_3). LRMS (FAB-LSIMS), *m*/*z*: 291 (M + H^+); HRMS (FAB-LSIMS), (M + H^+) calcd for $C_{11}H_{16}BrO_2S$: 291.00543, found: 291.00535.

*2.2.11. 1-(2,5-dimethyl-3-thienyl)-2-(5-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)-2-methyl-3-thienyl)perfluorocyclopentene **17***

To a solution of 2-(4-bromo-5-methylthiophen-2-yl)-5,5-dimethyl-1,3-dioxane **19** (4.51 g, 15.49 mmol) in anhydrous THF (90 mL) was added dropwise n-butyllithium (11.62 mL, 1.6 M in hexane, 18.59 mmol) at −80 °C under nitrogen atmosphere and the mixture was stirred for 45 min. The resulting solution was added dropwise over 10 min to a solution of (2,5-dimethyl-3-thienyl)perfluorocyclopentene **18** (4.72 g, 15.49 mmol) in anhydrous THF (50 mL) and the mixture was stirred for 2 h at −80 °C. The cooling bath was removed and the stirring was carried on for 14 h at room temperature. Then an aqueous solution of hydrochloric acid (0.5% v/v, 200 mL) was added and the mixture was extracted with diethyl ether (4 × 75 mL). The organic layers were neutralized with water (6 × 100 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The yellow brown syrup was chromatographed on silica gel (heptane then dichloromethane/heptane: 1/1) to afford 5.28 g of the compound **17** as a slightly orange solid in 69% yield. mp = 102–103 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.10 (s, 1H, ArH), 6.70 (s, 1H, ArH), 5.56 (s, 1H, CH acetal), 3.76–3.72 (m, 2H, CH_2–O), 3.63–3.60 (m, 2H, CH_2–O), 2.41 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.26 (s, 3H, CH_3 acetal), 0.79 (s, 3H, CH_3 acetal). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 142.4; 139.9; 139.5; 137.9; 125.1; 124.7; 124.6; 124.4; 116.3; 98.0; 77.6; 30.3; 23.1; 21.9; 15.2; 14.5. LRMS (FAB-LSIMS), *m*/*z*: 496 (M+); HRMS (FAB-LSIMS), (M^+) calcd for $C_{22}H_{22}O_2F_6S_2$: 496.0965, found: 496.0985.

*2.2.12. 1-(2,5-dimethyl-3-thienyl)-2-(5-formyl-2-methyl-3-thienyl)perfluorocyclopentene **1***

To a solution of 1-(2,5-dimethyl-3-thienyl)-2-(5-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)-2-methyl-3-thienyl)perfluorocyclopentene **17** (1.9 g, 3.83 mmol) in THF (300 mL) and water (75 mL) was added trifluoroacetic acid (35 mL) and the mixture was stirred for 24 h at room temperature. Then the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (350 mL) and the mixture was extracted with diethyl ether (3 × 100 mL). The organic layers were washed with an aqueous solution of $NaHCO_3$ (2% w/v, 2 × 150 mL), water (3 × 150 mL), dried over Na_2SO_4, filtered and the solvent was evaporated. The crude product was washed with cold methanol and recrystallized from hexane to afford 1.0 g of the compound **1** as a slightly yellow solid in 64% yield. mp = 117–118 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.84 (s, 1H, CHO), 7.74 (s, 1H, ArH), 6.70 (s, 1H, ArH), 2.42 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.83 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 182.2; 151.9; 141.8; 140.0; 138.6; 136.5; 126.9; 124.5; 124.1; 15.5; 15.2; 14.4. LRMS (FAB-LSIMS), *m*/*z*: 409 (M–H^+); HRMS (FAB-LSIMS), (M–H^+) calcd for $C_{17}H_{11}OF_6S_2$: 409.0156, found: 409.0146.

*2.2.13. 1-(5-chloro-2-methyl-3-thienyl)-2-(2-methyl-5-phenylethynyl-3-thienyl)perfluorocyclopentene **7***

To a solution of 3-iodo-2-methyl-5-(phenylethynyl)thiophene **11** (4.29 g, 13.245 mmol) in anhydrous THF (130 mL) was added dropwise n-butyllithium (10.0 mL, 1.6 M in hexane, 15.894 mmol) and the solution was stirred for 1 h at −80 °C under nitrogen atmosphere. (5-chloro-2-methyl-3-thienyl)perfluorocyclopentene **10** (3.35 g, 10.331 mmol) dissolved in anhydrous THF (15 mL) was added and the mixture was stirred for 2 h at −80 °C. The cooling bath was removed and the solution was stirred for 15 h at room temperature. An aqueous solution of hydrochloric acid (1% v/v, 100 mL) was added and the aqueous layer was extracted with diethyl ether (2 × 50 mL). The organic layers were washed with an aqueous solution of $NaHCO_3$ (5% w/v, 50 mL), water (2 × 50 mL), brine (70 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was flash chromatographed on silica gel (petroleum ether) and washed with methanol to afford 2.7 g of the compound **7** as a white solid in 51% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.53–7.50 (m, 2H, ArH), 7.38–7.34 (m, 3H, ArH), 7.25 (s, 1H, ArH), 6.91 (s, 1H, ArH), 1.95 (s, 3H, CH_3), 1.88 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 143.4; 140.7; 131.6; 131.4; 128.9; 128.6; 128.1; 125.7; 124.9; 124.3; 122.5; 122.1; 119.4 (CF_2); 116.0 (CF_2); 94.2; 81.5; 14.6. LRMS (EI), *m*/*z* (%): 504 (M + 2, 44), 502 (M^+, 100), 467 (M-Cl, 42), 452 (41), 419 (20), 243 (25), 226 (68), 145 (60), 121 (24), 59 (20).

*2.2.14. 1-(5-formyl-2-methyl-3-thienyl)-2-(2-methyl-5-phenylethynyl-3-thienyl)perfluorocyclopentene **2***

To a solution of 1-(5-chloro-2-methyl-3-thienyl)-2-(2-methyl-5-phenylethynyl-3-thienyl)perfluorocyclopentene **7** (2.0 g, 3.97 mmol) in anhydrous diethyl ether was added dropwise n-butyllithium (3.22 mL, 1.6 M in hexane, 5.16 mmol) and the solution was stirred for 1 h at room temperature under nitrogen atmosphere. Anhydrous DMF (0.92 mL, 11.90 mmol) was added and the mixture was stirred for 0.5 h at room temperature. The reaction was quenched with an aqueous solution of hydrochloric acid 1 M (50 mL) and the mixture was extracted with diethyl ether (3 × 50 mL). The organic layers were washed with an aqueous solution of $NaHCO_3$ (5% w/v, 70 mL), water (3 × 70 mL), brine (70 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was flash chromatographed on silica gel (pentane then dichloromethane) to

afford 0.93 g of the compound **2** as a yellow solid in 47% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.85 (s, 1H, CHO), 7.75 (s, 1H, ArH), 7.52–7.48 (m, 2H, ArH), 7.38–7.34 (m, 3H, ArH), 7.24 (s, 1H, ArH), 2.06 (s, 3H, CH_3), 1.91 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 182.2 (CH); 152.0 (Cq); 143.3 (Cq); 142.0 (Cq); 136.2 (CH); 131.6 (CH); 131.1 (CH); 129.0 (CH); 128.6 (CH); 126.4 (Cq); 124.6 (Cq); 122.5 (Cq); 122.4 (Cq); 94.4 (Cq); 81.3 (Cq); 15.7 (CH_3); 14.6 (CH_3). LRMS (EI), *m/z* (%): 496 (M^+, 100), 481 (37), 452 (12), 419 (15), 226 (36), 145 (45), 121 (17), 59 (17).

2.2.15. 1-(5-chloro-2-methyl-3-thienyl)-2-(2-methyl-5-[4-(methylsulfanyl)phenyl]-3-thienyl)perfluorocyclopentene **8**

To a solution of 3-bromo-2-methyl-5-[4-(methylsulfanyl) phenyl]thiophene **12** (4.47 g, 14.92 mmol) in anhydrous THF (300 mL) was added dropwise n-butyllithium (10.3 mL, 1.6 M in hexane, 16.42 mmol) and the solution was stirred for 1 h at −80 °C under nitrogen atmosphere. (5-chloro-2-methyl-3-thienyl)perfluorocyclopentene **10** (5.12 g, 15.77 mmol) dissolved in anhydrous THF (15 mL) was added and the mixture was stirred 2 h at −80 °C then 15 h at room temperature. The solvent was evaporated and the residue was dissolved in a mixture of diethyl ether (200 mL) and an aqueous solution of hydrochloric acid (1% v/v, 100 mL). The aqueous layer was extracted with diethyl ether (2 × 70 mL) and the organic layers were washed with an aqueous solution of $NaHCO_3$ (5% w/v, 70 mL), water (2 × 70 mL), brine (70 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was flash chromatographed on silica gel (pentane/dichloromethane: 80/20) to afford 5.7 g of compound **8** as a slightly purple solid in 73% yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.46 (d, J = 8.4 Hz, 2H, ArH), 7.26 (d, J = 8.4 Hz, 2H, ArH), 7.22 (s, 1H, ArH), 6.95 (s, 1H, ArH), 2.51 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.88 (s, 3H, CH_3).

2.2.16. 1-(5-formyl-2-methyl-3-thienyl)-2-(2-methyl-5-[4-(methylsulfanyl)phenyl]-3-thienyl)perfluorocyclopentene **3**

To a solution of 1-(5-chloro-2-methyl-3-thienyl)-2-(2-methyl-5-[4-(methylsulfanyl)phenyl]-3-thienyl)perfluorocyclopentene **8** (3.88 g, 7.39 mmol) in anhydrous diethyl ether (200 mL) was added dropwise n-butyllithium (5.54 mL, 1.6 M in hexane, 8.87 mmol) and the solution was stirred for 1 h at 0 °C under nitrogen atmosphere. Anhydrous DMF (1.43 mL, 18.48 mmol) was added and the solution was stirred 1 h at room temperature. The reaction was quenched with an aqueous solution of hydrochloric acid 1 M (50 mL) and the aqueous layer was extracted with diethyl ether (50 mL). The organic layers were washed with an aqueous solution of $NaHCO_3$ (5% w/v, 70 mL), water (3 × 70 mL), brine (70 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was flash chromatographed on silica gel (pentane/dichloromethane: 30/70 then dichloromethane) to afford 2.63 g of compound **3** as a green solid in 69% yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 9.85 (s, 1H, CHO), 7.78 (s, 1H, ArH), 7.44 (d, J = 8.3 Hz, 2H, ArH), 7.24 (d, J = 8.3 Hz, 2H, ArH), 7.20 (s, 1H, ArH), 2.50 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 1.92 (s, 3H, CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm) = 182.2 (CHO); 152.0; 142.6; 141.9 (CH); 141.1; 139.0; 137.7 (m); 136.4 (CH); 134.7 (m, CF_2); 129.8; 128.9 (CH); 126.8 (CH); 126.6; 126.0 (CH); 125.3; 116.1 (m, CF_2); 111.1 (m); 15.7 (CH_3); 15.6 (CH_3); 14.6 (CH_3). HRMS (ESI), (M + H^+) calcd for $C_{23}H_{17}OF_6S_3$: 519.0340, found: 519.0359.

2.2.17. 1-(5-chloro-2-methyl-3-thienyl)-2-(2-methyl-5-[4-ethenyl-N,N-dimethylaniline]-3-thienyl)perfluorocyclopentene **9**

To a solution of 4-[(4-iodo-5-methylthiophen-2-yl)ethynyl]-N,N-dimethylaniline **13** (3.60 g, 9.803 mmol) in anhydrous diethyl ether (150 mL) was added dropwise n-butyllithium (7.4 mL, 1.6 M in hexane, 11.763 mmol) and the solution was stirred for 1 h at −80 °C under nitrogen atmosphere. (5-chloro-2-methyl-3-thienyl)perfluorocyclopentene **10** (2.88 g, 8.874 mmol) dissolved in anhydrous diethyl ether (15 mL) was added and the mixture was stirred 1 h at −80 °C then 16 h at room temperature. An aqueous solution of hydrochloric acid (1% v/v, 100 mL) was added and the aqueous layer was extracted with diethyl ether (2 × 70 mL). The organic layers were washed with a solution of $NaHCO_3$ (5% w/v, 100 mL), water (2 × 100 mL), brine (100 mL), dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was chromatographed on silica gel (petroleum ether/dichloromethane : 70/30) then recrystallized from methanol to afford 2.12 g of the compound **9** as slightly green solid in 44% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.38 (d, J = 9.0 Hz, 2H, ArH), 7.17 (s, 1H, ArH), 6.92 (s, 1H, ArH), 6.65 (d, J = 9.0 Hz, 2H, ArH), 3.00 (s, 6H, CH_3), 1.93 (s, 3H, CH_3), 1.88 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 150.5; 142.3; 140.7; 132.8 (CH); 130.1 (CH); 128.0; 125.7 (CH); 124.7; 124.3; 123.2; 111.9 (CH); 108.9; 95.6; 79.5; 40.2 (CH_3); 14.6 (CH_3). LRMS (EI), *m/z* (%): 547 (M + 2, 45), 545 (M^+, 100), 265 (13), 247 (34), 188 (28). HRMS (ESI), (M + H^+) calcd for $C_{25}H_{19}NF_6S_2Cl$: 546.0546, found: 546.0554.

2.2.18. 1-(5-formyl-2-methyl-3-thienyl)-2-(2-methyl-5-[4-ethenyl-N,N-dimethylaniline]-3-thienyl)perfluorocyclopentene **4**

To a solution of 1-(5-chloro-2-methyl-3-thienyl)-2-(2-methyl-5-[4-ethenyl-N,N-dimethylaniline]-3-thienyl)perfluorocyclopentene **9** (1.70 g, 3.109 mmol) in anhydrous diethyl ether (70 mL) was added dropwise n-butyllithium (2.53 mL, 1.6 M in hexane, 4.042 mmol) and the solution was stirred for 1 h at 0 °C under nitrogen atmosphere. Anhydrous DMF (0.61 mL, 7.773 mmol) was added and the mixture was stirred for 1 h at room temperature. The reaction mixture was diluted with diethyl ether (50 mL) and a solution of hydrochloric acid 1 M (50 mL) was added. The aqueous layer was

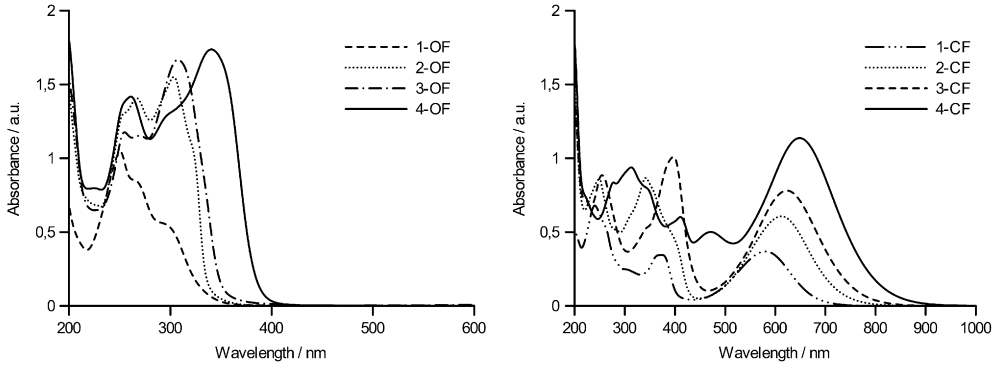


Fig. 1. Absorption spectra of dithienylethenes **1**–**4** in acetonitrile, $C = 5 \times 10^{-5}$ mol L^{-1}; Open forms (Left) and photostationnary state after irradiation with 254 nm light (Right).

Table 1
UV–Visible spectroscopic data of the open and closed (PSS) forms of the compounds **1**–**4**.

Compound	R_1	Concentration (mol L^{-1})	λ_{max} open form (nm)	λ_{max} PSS (nm)
1	Me	5.10×10^{-5}	250	374, 580
2	C_2Ph	6.04×10^{-5}	267, 303	361, 612
3	PhSMe	3.03×10^{-5}	255, 308	397, 623
4	$C_2PhN(Me)_2$	4.08×10^{-5}	261, 340	411, 472, 649

extracted with diethyl ether (2×50 mL) and the organic layers were washed with a solution of $NaHCO_3$ (5% w/v, 70 mL), water (3×50 mL), brine (50 mL), dried over $MgSO_4$, filtered ant the solvent was evaporated. The crude product was chromatographed on silica gel (petroleum ether/dichloromethane : 1/1) to afford 1.35 g of the compound **4** as a green solid in 80% yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 9.84 (s, 1H, CHO), 7.75 (s, 1H, ArH), 7.37 (d, J = 8.9 Hz, 2H, ArH), 7.16 (s, 1H, ArH), 6.64 (d, J = 8.9 Hz, 2H, ArH), 3.00 (s, 6H, CH_3), 2.05 (s, 3H, CH_3), 1.89 (s, 3H, CH3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 182.2 (CHO); 152.0; 150.5; 142.2; 141.9; 136.3 (CH); 132.8 (CH); 129.9 (CH); 126.5; 124.4; 123.6; 111.8 (CH); 108.8; 95.9; 79.3; 40.2 (CH_3); 15.6 (CH_3); 14.5 (CH_3). LRMS (EI), m/z (%): 539 (M^+, 100), 262 (6), 248 (30), 240 (10), 188 (21), 172 (7), 59 (4). HRMS (ESI), ($M + H^+$) calcd for $C_{26}H_{19}NOF_6S_2$: 539.0806, found: 539.0812.

2.3. UV–Visible absorption spectroscopy

Absorption spectra were recorded in non degassed acetonitrile solutions at room temperature. Upon irradiation with 254 nm light, the colourless open form of the dithienylethenes **1**–**4** was converted to the closed form, this photochromic reaction was characterised by a colour change of the solutions from sky blue to purple due to an extension of the conjugation on the whole molecule. The ring-closing of the dithienylethenes was accompanied by a decreasing of the absorption bands in UV range and the appearance of new broad bands in the visible region which are ascribed to closed-ring isomer. The effect of the substituents R_1 bearing by the dithienylethenes **1**–**4** on their electronic properties was investigated. More the substituent extend the conjugation and more the absorption band of the closed forms is red-shifted. On another aspect, the effect of the substituents R_1 is more pronounced for the open-ring forms in which the maximum absorption band varies from 250 nm (**1**, R_1 = Me) to 340 nm (**4**, R_1 = 4-ethynyl-N,N-dimethylaniline) than for the closed-ring forms for which we observed an bathochromic shift of 69 nm, the maximum absorption band being centred at 580 and 649 nm for respectively for **1** and **4** (Fig. 1).

The irradiation times needed to reach the photostationnary state and therefore the quantum yields are quite similar for dithienylethenes **1**–**3** and the determined values are in the range of previously described BTE, i.e. $0.3 < \phi < 0.4$. On the contrary the ring closure electrocyclisation efficiency is strongly affected for compound **4** for which the quantum yield has been found to be as low as 0.07. This huge difference can be explained by the strong electron-donating character of the 4-ethynyl-N,N-dimethylaniline which decreases the efficiency of the electrocyclization reaction. [14] The presence of isobestic points clearly states for the good fatigue resistance of the molecules during the photochromic process. All the closed forms are thermally stable at room temperature and they do not come back to the open forms when stored in the dark. The reversibility of this process was demonstrated by irradiation with visible light and the original absorption spectra were recovered in all cases. The UV–Visible spectroscopic data of the open and closed (photostationnary state) forms of the dithienylethenes **1**–**4** are summarized in Table 1. This behaviour has been observed even after numerous UV/Vis. irradiation cycles.

3. Conclusion

Unsymmetrical 1,2-bisthienylperfluorocyclopentenes bearing a formyl group as an electro-withdrawing group on one side and various π-conjugated extended susbtituents on the other side were prepared using a sequential synthetic strategy. This versatile approach would allow the design of photocontrolled push-pull NLO-phores. The photochromic performance has been investigated and it has been demonstrated that the π-conjugated susbtituents deeply modify the absorption spectra of the both isomeric forms whereas keeping the excellent P-type properties. The bathochromic shift for the open-ring isomers has been determined to as high as 90 nm.

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