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Synthesis, properties, and electrochemistry of a photochromic compound based on dithienylethene and ProDOT

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Abstract: The synthesis, photochromic features, and electrochemistry of a novel material based on dithienylethene (DTE) and 3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (didecyl-ProDOT) units are described. It is noteworthy that 1,2-bis(5-(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-2-methylthiophen-3-yl)cyclopent-1-ene can be efficiently switched between open and closed states by light in both solution and in the solid poly(methyl metacrylate) (PMMA) matrix. It is also found that the emission of this novel compound can be switched on and off upon irradiation.

Key words: Dithienylethene, photochromism, electrochemistry, ProDOT

1. Introduction

The design and synthesis of novel functional organic compounds have attracted considerable attention since they lead to a variety of advanced technological applications in the field of molecular electronics and photonics, sensors, machines and devices, light emitting diodes, photovoltaics, transistors, electrochromics, data processing, and storage media.[1] Among functional organic compounds, photochromic dithienylethene (DTE) derivatives are highly valuable materials due to their unique properties such as thermal stability and high fatigue resistance, which are indispensable for optoelectronic applications.[2,3] However, some other properties of DTEs such as fast switching, high quantum yield, and large differences between the absorption wavelengths of 2 isomers have also contributed to the ever increasing popularity of these compounds, which have found diverse applications as smart materials (e.g., molecular switches, optical data processing and storage devices, molecular probes, machines, and imaging agents) in both bio- and nanotechnological sciences as well as in materials science.[4–10] In spite of the fact that excellent molecular DTE systems,[11–21] which hold great promise for applications in the field of molecular electronics and optics, have been created so far, photochromic conducting polymers[22,23] based on DTE systems are still rare.[24–27]

In continuation of our work on the design of novel photochromic materials,[22,23] we recently described the synthesis and properties of 2,5-dithienylpyrrole (SNS) derivative with a pendant photochromic DTE unit, **SNS-DTE**[28] (Chart). We found that **SNS-DTE** can be efficiently switched between open and closed isomers.

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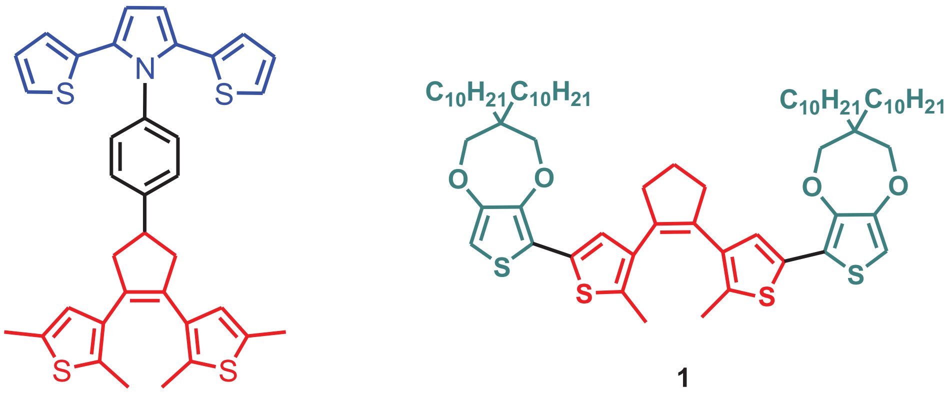
Furthermore, it can be smoothly polymerized by electrochemical means. Although **SNS-DTE** did not retain its photochemical switching properties after polymerization, it was noted that the polymer exhibited remarkable electrochromic features; it can be switched from green in the neutral state to violet state under applied external potentials without disturbing the photochromic units.[28] These results stimulated us to design and investigate the fate of a new combination of DTE. We envisaged that the incorporation of the DTE unit in the main chain would not only tailor the electronic structure due to the increased conjugation when compared to **SNS-DTE**, but also provide a switchable polymeric photochrome. For that reason, we designed a novel photochrome, **1**, which is based on DTE and didecyl-ProDOT units (Chart). In this combination, the didecyl-ProDOT[29−31] unit was the choice as the electroactive donor part due to its electron-rich nature and low oxidation potential, which staves off the detrimental effects (i.e. degradation) of high potentials. Moreover, didecyl units,[32,33] which increase the solubility of the photochrome **1** in organic solvents, might enable a solution processable photoconductive material, which provides access to dual (photo and electro) chromism.



SNS-DTE

1

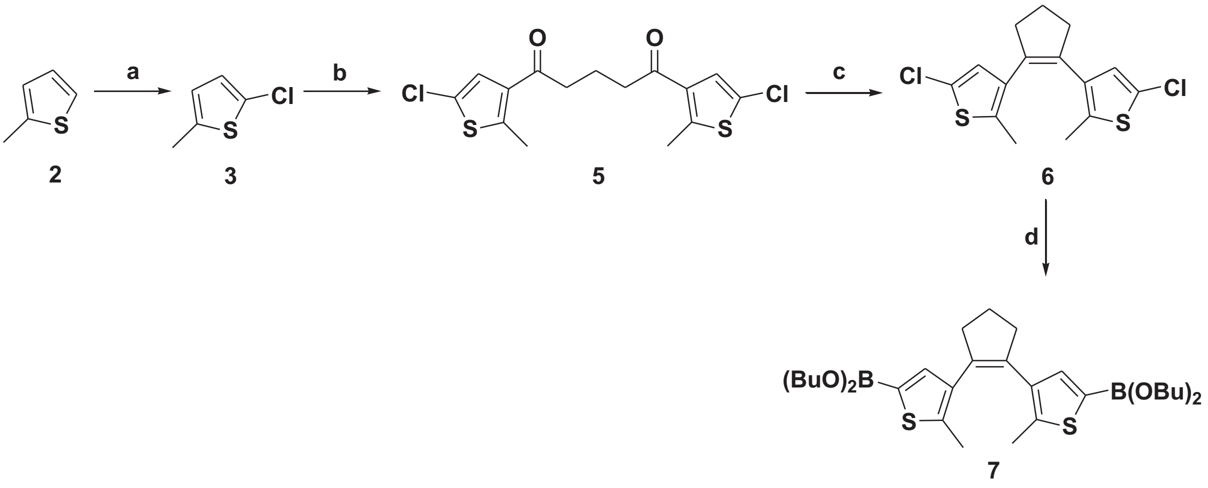
Chart. The structures of **SNS-DTE** and compound **1**.

Herein we wish to report the design, synthesis, photochromic features, and electrochemistry of a novel compound, **1**, viz. 1,2-bis(5-(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-2-methylthiophen-3-yl)cyclopent-1-ene. It is noteworthy that the system **1** can be efficiently switched between open (**1o**) and closed (**1c**) states by light both in solution and in the solid poly(methyl metacrylate) (PMMA) matrix. It was also found that the emission of **1** could be switched on and off upon irradiation.

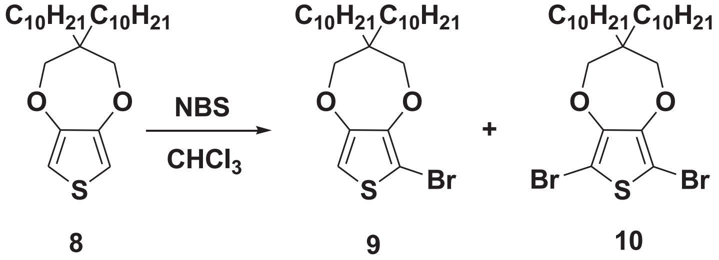
2. Results and discussion

In order to obtain the target compound **1**, initial efforts were directed to the synthesis of a DTE scaffold according to the method developed by Feringa and co-workers.[34] For this purpose, 2-methylthiophene (**2**) was treated with N-chlorosuccinimide (NCS) to give **3**, which was followed by Friedel–Crafts acylation with glutaryl dichloride (**4**) (Scheme 1). Diketone **5** was converted to DTE **6** by McMurry coupling reaction using $TiCl_3(THF)_3$ complex in the presence of zinc in dry THF albeit in low yield (35%). Subsequent borylation of **6** with n-BuLi and $B(OBu)_3$ afforded **7**, which was directly used in the next step due to its instability.[34]

After the construction of the DTE unit, bromination of didecyl-ProDOT **8**[29−31] was carried out with N-bromosuccinimide (NBS), which resulted in the formation of a mixture of compounds **9** and **10** (Scheme 2). This mixture was separated by flash column chromatography to afford each of **9** and **10** as analytically pure substances in 50% and 30% yield, respectively. The products were characterized by ^{1}H and ^{13}C NMR spectral data along with the elemental analysis.

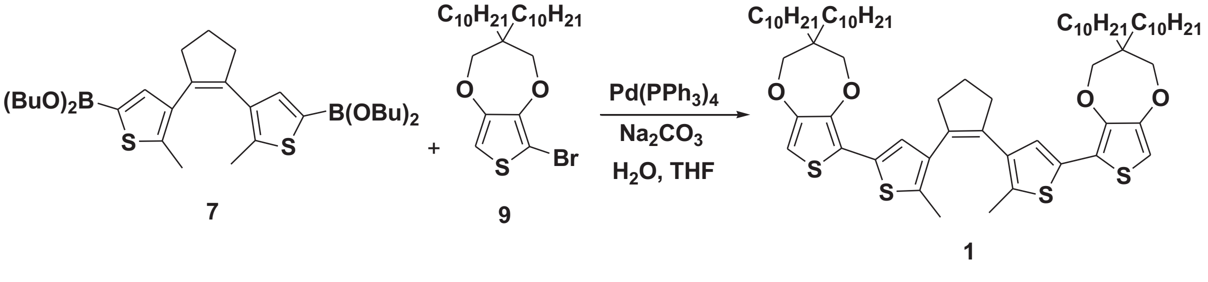


Scheme 1. Synthesis of DTE unit. Reagents: a) NCS, HOAc, C_6H_6, 84%; b) glutaryl dichloride (**4**), $AlCl_3$, CS_2, 83%; c) Zn, $TiCl_3(THF)_3$, THF, 35%; d) nBuLi, $B(OBu)_3$, THF, 70%.



Scheme 2. Bromination of **8**.

Finally, the synthesis of the target compound **1** was implemented by the application of a Suzuki coupling reaction of DTE **7** with **9** in a yield of 60% (Scheme 3). Initial characterization of compound **1** was based on ^{1}H and ^{13}C NMR spectral data along with MALDI TOFF analysis, which confirmed the structure.



Scheme 3. Synthesis of the novel photochrome **1**.

In the ^{1}H NMR spectrum of **1**, the signals of aromatic protons of thiophene and didecyl-ProDOT units appeared at 6.90 (s, 2H) and 6.24 (s, 2H) ppm as singlets, respectively. Methylenic protons of didecyl-ProDOT resonated also as a singlet at 3.89 (s, 4H) and 3.84 (s, 4H) ppm along with the protons of the cyclopentene ring of the DTE unit at 2.80 (t, $J = 8$ Hz, 4H) and 2.05 (p, $J = 8$ Hz, 2H) ppm as a triplet and a pentet. Methyl protons attached to the thiophene unit gave rise to a singlet at 1.93 (s, 6H) ppm, whereas the protons of the decyl chain gave a triplet and a multiplet at 0.88 (t, $J = 8$ Hz, 12H) and 1.40–1.26 (m, 72H) ppm, respectively. Moreover, ^{13}C NMR, whose signals appeared at 150.01, 144.69, 135.37, 134.39, 133.67, 130.80, 123.72, 117.16, 100.74, 77.78, 43.86, 38.54, 31.92, 31.79, 30.49, 29.65, 29.63, 29.54, 29.35, 22.80, 22.69, 14.21, and 14.12 ppm, and MALDI TOFF mass data also proved the structure.

The absorption profile of compound **1** was examined in n-hexane solution. The UV-Vis spectrum of **1o** was characterized by broad bands between 220 and 370 nm (λ_{max} = 325 nm) with a molar extinction coefficient (ε_m) of 63,860 M^{-1} cm^{-1}. On the other hand, it was noted that **1o** induced blue emission with a λ_{max} of 380 nm when excited by 325 nm light. When the photochemical switching behavior of compound **1** was investigated in solution, it was found that **1** underwent efficient photochemical ring closing and opening in solution upon irradiation with UV (313 nm) and visible (>400 nm) light, respectively (Figure 1a; Scheme 4). The absorption changes could also be detected by the naked eye (Figure 1b). By irradiating the colorless open isomer (**1o**) with UV light, the purple closed isomer (**1c**) is formed by electrocyclization.

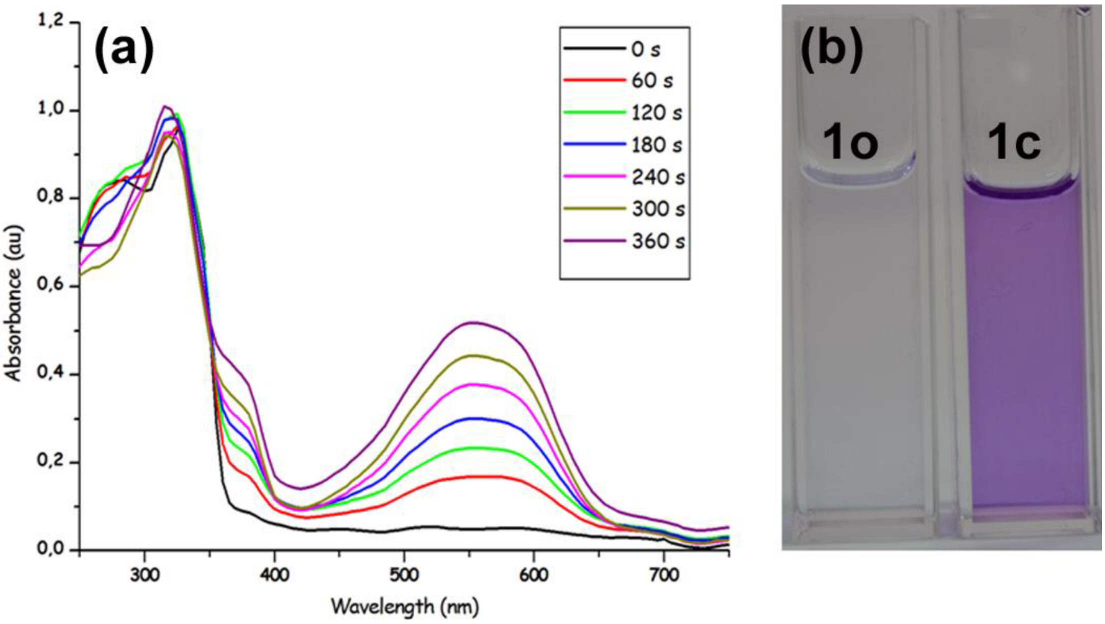
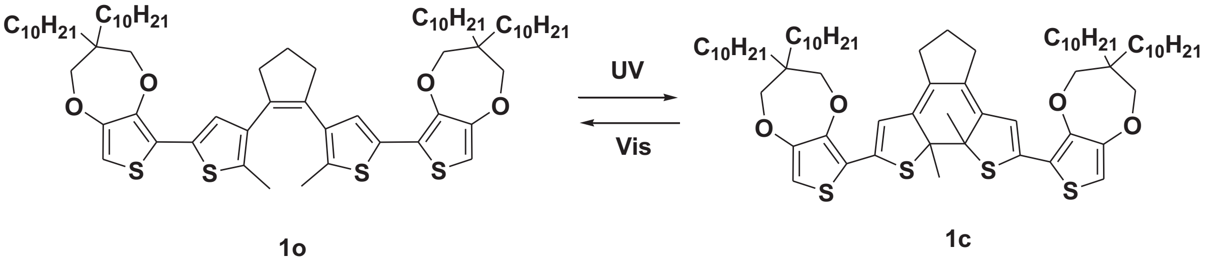


Figure 1. a) UV-Vis absorption spectra of **1** (15 μM in n-hexane) in the open (**1o**) and closed (**1c**) state upon irradiation with UV (313 nm) and visible (>400 nm) light. b) The photographs of compound **1** in hexane before (**1o**) and after (**1c**) irradiation.

Figure 2 illustrates the photochromic film, which was prepared by the introduction of this novel photochromic system **1o** in the PMMA matrix as dopant. After the preparation of the film (Figure 2a), it was homogeneously irradiated with UV light through a patterned mask (Figure 2b). The color change was quite prominent in the regions that were exposed to UV light (Figure 2c). It should be noted that the system **1** can be efficiently switched by light both in solution and in the solid (film) state (Figure 2).

It was also noted that the open isomer (**1o**) of compound **1** is highly fluorescent and gives a broad emission band between 350 nm and 500 nm (λ_{max} = 390 nm) when excited (λ_{exc}) at 325 nm in $n-$hexane solution (Figure 3, black line, t = 0 s). Figure 3 depicts the irradiation time dependent emission spectral changes of compound **1**. The data indicate that the emission intensity changes dramatically from one isomer to another by time during the irradiation (high emission intensity with **1o** and low emission intensity with **1c**). This observation is in close agreement with the photoisomerization of compound **1**: **1o** mainly isomerizes to **1c** by irradiation with light (ca. after 360 s, Figure 3, yellow line). The lower emission intensity is probably due to nonradiative decay of the excited state in the closed form (**1c**) when compared to the open form (**1o**). On the basis of the above data, it is also safe to conclude that the emission of **1** can be switched on and off upon irradiation.



Scheme 4. Photochemical switching of **1o**/**1c** in *n*-hexane with UV (313 nm) and visible light (>400 nm).

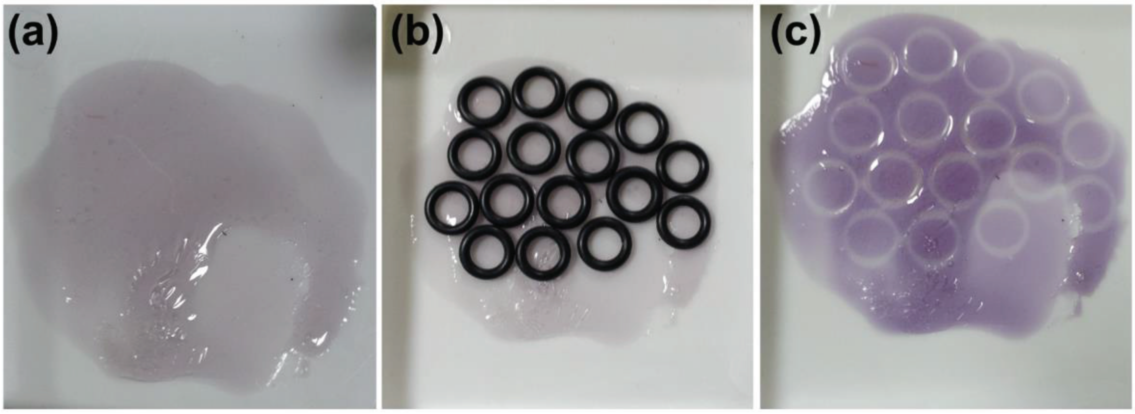


Figure 2. Images of **1** in PMMA matrix a) and b) before and after (c) irradiation.

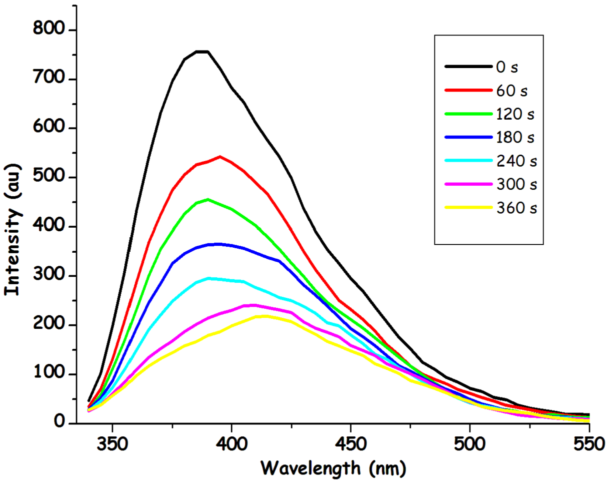


Figure 3. Emission spectral changes of **1** (15 μM) during irradiation in *n*-hexane, (λ_{exc} = 325 nm).

Kim and co-workers described the electro(co)polymerization of 2-methyl-1-benzothiophen-3-yl]perfluorocyclopentene-based systems with EDOT and/or ProDOT units.[35,36] Unfortunately, however, we were unable to make a comparison of our system **1** with those molecules due to the lack of data concerning the UV-Vis, fluorescence, and electrochemistry of the monomers. To reveal the electrochemical properties of **1o**, the redox behavior was investigated in solution by cyclic voltammetry between 0.0 and 2.0 V (vs. Ag/AgCl). It was found that **1o** (3.0×10^{-3} M) induced multiple oxidation peaks at 1.03, 1.12, 1.22, and 1.84 V in an electrolyte solution consisting of 0.1 M TBAH dissolved in CH_3CN at a scan rate of 100 mV/s (vs. Ag/AgCl) (Figure 4). The first peak at 1.03 V was attributed to the oxidation of the ProDOT unit and the others were probably due to the overoxidation of oligomeric species formed at 1.03 V or oxidation of the DTE unit.

At this stage the electropolymerization of **1o** was also explored. Unfortunately, all attempts to obtain an electroactive polymer film via cyclic and/or constant potential electrolysis methods met with failure. Although a new oxidation peak at around 1.10 V was observed along with slight increases in the current density during electrochemical scanning (Figure 5), there was no film formation on the electrode surface. This was mainly ascribed to the solubility and/or mechanical instability of the product under the given conditions.

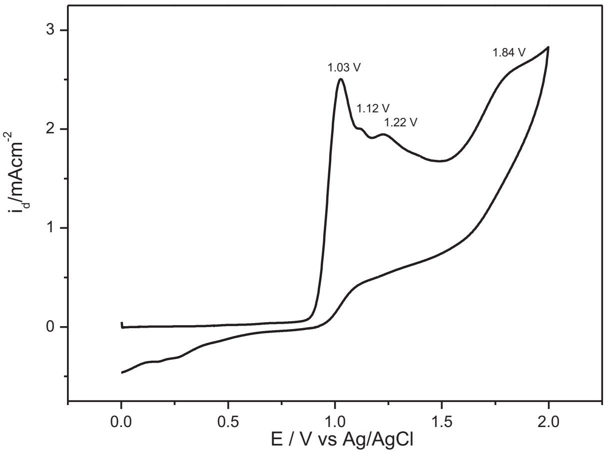


Figure 4. Cyclic voltammogram of **1o** (3.0×10^{-3} M) in an electrolyte solution consisting of 0.1 M TBAH dissolved in CH_3CN at a scan rate of 100 mV/s.

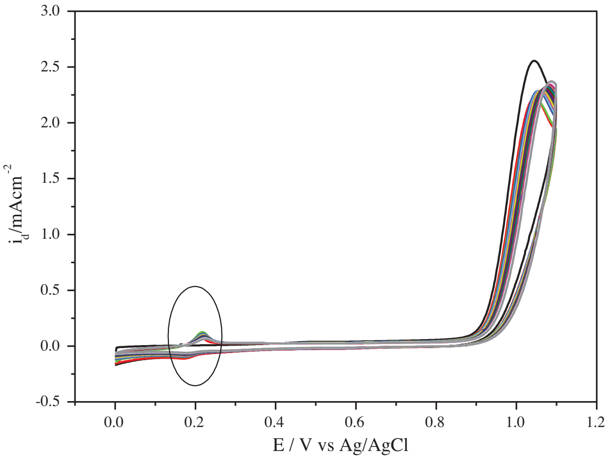


Figure 5. Cyclic voltammogram of **1o** (3.0×10^{-3} M) during attempted polymerization in an electrolyte solution consisting of 0.1 M TBAH dissolved in CH_3CN at a scan rate of 100 mV/s.

3. Conclusion

In summary, the synthesis, photochromic features, and electrochemistry of a novel material based on DTE and ProDOT units were disclosed. It is noteworthy that the system **1** can be efficiently switched between open (**1o**) and closed (**1c**) states by light both in solution and in the solid PMMA matrix. It was also found that the emission of **1** could be switched on and off upon irradiation. Interestingly, this novel photochrome **1** did not undergo polymerization by electrochemical means under the given conditions. Further work on macromolecular photochromic systems based on **1** is currently underway in our laboratories and the results will be reported in due course.

4. Experimental section

4.1. General methods

All chemicals were purchased from Sigma Aldrich or Merck and used as received unless otherwise noted. FTIR spectra were recorded on a PerkinElmer Spectrum 100 model FTIR with an attenuated total reflectance (ATR). ^{1}H (400 or 300 MHz) and ^{13}C (100 or 75 MHz) NMR spectra were recorded on a Bruker DPX-400 or Ultrashield 300 NMR spectrometer. Combustion analyses were carried out by using a LECO CHNS-932 analyzer. Mass spectra were recorded on Bruker Daltonics model MALDI TOF MS analyzer. UV-Vis and fluorescence measurements were recorded on Varian Cary 50 and Varian Cary Eclipse spectrophotometers, respectively. Melting points were determined on a Schorrp MPM-H2 model apparatus and are uncorrected. Column chromatography was performed on silica gel (60–200 mesh) from Merck. TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. The synthesis of compounds **3**, and **5**–**7**[34] was carried out according to previously published procedures.

As electrolyte solution 0.1 M Bu_4NPF_6 dissolved in acetonitrile was used. A platinum button (0.02 cm^2) and a platinum wire were used as working and counter electrodes, respectively, as well as a Ag/AgCl reference electrode (calibrated externally using 10 mM solution of ferrocene/ferrocenium couple, which is an internal standard calibrated to be 0.44 V in acetonitrile solution vs. Ag/AgCl).

4.1.1. 2-Chloro-5-methylthiophene (3)

2-Methylthiophene (**2**, 10 mL, 0.103 mol) and *N*-chlorosuccinimide (15.2 g, 0.113 mol) were added to a stirred solution of benzene (40 mL) and acetic acid (40 mL). The suspension was stirred for 30 min at room temperature; then, after 1 h of heating at reflux, the cooled mixture was poured into a 3 M aq. NaOH solution (30 mL). The organic phase was washed with a 3 M aq. NaOH solution (3 × 30 mL), dried over Na_2SO_4, filtered, and the solvent evaporated in vacuo to yield a slightly yellow liquid, 11 g, 84% yield, bp 55 °C (19 Torr). ^{1}H NMR (400 MHz, $CDCl_3$)δ/ppm: 6.66 (d, $J = 4.0$ Hz, 1H), 6.50–6.48 (dq, $J = 4.0$–1.5 Hz, 1H), 2.38 (d, $J = 1.5$ Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 138.5, 128.3, 125.8, 124.4, 15.5.

4.1.2. 1,5-Bis(5-chloro-2-methylthien-3-yl)pentane-1,5-dione (5)

To an ice-cooled solution of **3** (3.23 mL, 29.8 mmol) and glutaryl dichloride (**4**, 1.88 mL, 15 mmol) in CS_2 (30 mL) was added $AlCl_3$ (4.8 g, 36 mmol) in portions under vigorous stirring. After addition of $AlCl_3$, the reaction mixture was stirred for 2 h at room temperature. Then ice-cold water (100 mL) was carefully added to the reaction mixture and the water layer was extracted with diethyl ether (3 × 100 mL). The combined organic phases were washed with water (100 mL), dried over Na_2SO_4, filtered, and the solvent was evaporated in vacuo to yield a brown tar (4.5 g, 83%). This tar was further purified by flash chromatography (hexane/ethyl acetate, 9:1) to provide a white solid (2.0 g, 37% yield), mp 83-84 °C (lit. 82–85 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.20 (s, 2H), 2.87 (t, $J = 6.8$ Hz, 4H), 2.68 (s, 6H), 2.08 (p, $J = 6.8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 194.21, 147.41, 134.79, 126.65, 125.26, 40.31, 18.04, 15.90.

4.1.3. 1,2-Bis(5-chloro-2-methylthien-3-yl)cyclopentene (6)

A mixture of **5** (1.13 g, 3.13 mmol), $TiCl_3(THF)_3$ (2.32 g, 6.26 mmol), Zn dust (0.82 g, 7.8 mmol), and dry THF (30 mL) was stirred under nitrogen at 40 °C for 1 h. The mixture was cooled to room temperature and poured through a glass filter containing silica gel that had been pretreated with petroleum ether. The silica was rinsed with petroleum ether. After evaporation of the solvent, a yellow solid (0.97 g, 94%) remained. Pure **6** was obtained as a white solid (0.34 g, 35%) after purification by chromatography on silica gel (petroleum ether), mp 77–78 °C (lit. 75–78 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.57 (s, 2H), 2.71 (t, J = 7.5 Hz, 4H), 2.03 (p, J = 7.5 Hz, 2H), 1.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 134.8, 134.4, 133.3, 126.7, 125.2, 38.3, 22.8, 14.1.

4.1.4. 1,2-Bis[5-(dibutoxyboryl)-2-methylthien-3-yl]cyclopentene (7)

First, **6** (1.75 g, 5.30 mmol) was dissolved in anhydrous THF (12 mL) and nBuLi (4.5 mL of 2.5 M solution in hexane, 11.2 mmol) was added dropwise under nitrogen at room temperature by using a syringe. This solution was then stirred for 30 min at room temperature; next $B(OBu)_3$ (4.3 mL, 16 mmol) was added in 1 portion. This reddish solution was stirred for 1 h at room temperature and was then used in the next step directly.

4.1.5. Bromination of 3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (8)

A solution of NBS (0.178 g; 1 mmol) in $CHCl_3$ (20 mL) was added dropwise to a magnetically stirred solution of **8** (0.437 g; 1 mmol) in $CHCl_3$ (20 mL) at room temperature under nitrogen flow. After the addition, the mixture was allowed to stand overnight while stirring magnetically. The solvent was removed and the residue was subjected to column chromatography on silica gel by eluting with hexane.

4.1.6. 6-bromo-3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (9)

colorless liquid, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.42 (s, 1H), 3.91 (s, 2H), 3.83 (s, 2H), 1.39–1.23 (m, 72H), 0.88 (t, J = 8.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 148.87, 147.68, 104.09, 92.56, 77.88, 77.73, 43.92, 31.93, 30.45, 29.63, 29.36, 22.78, 22.71, 14.1; FTIR (cm^{-1}): 2954, 2922, 2853, 1490, 1456, 1366, 1172, 1042, 1006, 948, 859, 837, 722, 676. Anal. Calcd for $C_{27}H_{47}BrO_2S$: C, 62.89; H, 9.19; S, 6.22. Found: C, 62.87; H, 9.18; S, 6.22. MS (MALDI-TOF (m/z)) calcd for $C_{27}H_{47}BrO_2S$: 514.25, found: 515.71 $[M+H]^+$.

4.1.7. 6,8-dibromo-3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (10)

colorless liquid, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 3.92 (s, 4H), 1.37–1.28 (m, 72H), 0.88 (t, J = 6.7 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 147.15, 90.64, 78.01, 44.0, 31.92, 31.60, 30.40, 29.64, 29.63, 29.52, 29.35, 26.24, 22.71, 22.47, 14.14. Anal. Calcd for $C_{27}H_{46}Br_2O_2S$: C, 54.55; H, 7.80; S, 5.39. Found: C, 54.53; H, 7.82; S, 5.36.

4.1.8. 1,2-bis(5-(3,3-didecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-2-methylthiophen-3-yl)cyclopent-1-ene (1)

First, **9** (0.516 g, 1 mmol) was dissolved in toluene (10 mL), $Pd(PPh_3)_4$ (0.04 g, 0.03 mmol) was added, and the resulting solution was stirred for 15 min at room temperature. Then aqueous Na_2CO_3 (2.3 mL, 2 M) and 3 drops of ethylene glycol were added. This 2-phase system was heated in an oil bath just below reflux at a temperature of 60 °C and the solution of **7** (0.293 g, 0.5 mmol) was added dropwise via a syringe over a short period (approximately 5 min). Subsequently, the mixture was refluxed for 2 h and cooled to room temperature, after which diethyl ether (50 mL) and H_2O (50 mL) were added. The organic layer was separated and dried over Na_2SO_4. After concentration, the compound was purified by column chromatography on silica (hexane) to give the product as colorless oil (0.39 g, 60%). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 6.90 (s, 2H), 6.24 (s, 2H), 3.89 (s, 4H), 3.84 (s, 4H), 2.80 (t, $J = 8.0$ Hz, 4H), 2.05 (p, $J = 8.0$ Hz, 2H), 1.93 (s, 6H), 1.40–1.26 (m, 72H), 0.88 (t, $J = 8.0$ Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 150.01, 144.69, 135.37, 134.39, 133.67, 130.80, 123.72, 117.16, 100.74, 77.78, 43.86, 38.54, 31.92, 31.79, 30.49, 29.65, 29.63, 29.54, 29.35, 22.80, 22.69, 14.21, 14.12; FTIR (cm^{-1}): 2954, 2922, 2852, 1543, 1499, 1457, 1447, 1413, 1373, 1309, 1202, 1165, 1037, 1005, 968, 825, 749, 722, 706, 683. Anal. Calcd for $C_{69}H_{108}O_4S_4$: C, 73.35; H, 9.63; S, 11.35. Found: C, 73.37; H, 9.66; S, 11.38. MS(MALDI-TOF (m/z)) calcd for $C_{69}H_{108}O_4S_4$: 1128.71, found: 1126.68 $[M-2H]^+$.

Acknowledgments

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