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Electrosynthesis of a Low Band Gap π-Conjugated Polymer from a Multibridged Dithienylethylene

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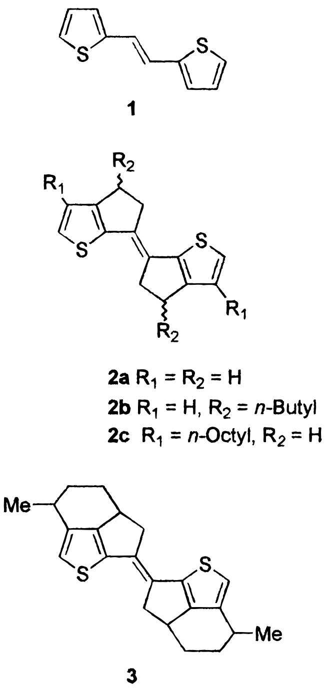
Linear π-conjugated molecular or polymeric systems (LCSs) are the focus of a considerable current research interest owing to their inherent optoelectronic properties and their potential applications ranging from electronic devices[1] to nonlinear optics[2] or light-emitting diodes.[3] Since the intrinsic electronic properties of LCSs are related to the width of the HOMO−LUMO gap of the molecule (ΔE) or band gap of the material (E_g), the structural control of these parameters has become one of the main challenges for chemists involved in the field of organic conductors.[4]

During the past decade the synthesis of small gap LCSs has been essentially pursued through two main strategies[4] namely (i) the increase of the quinonoid character of the π-conjugated system to the detriment of its aromaticity[5] and (ii) the introduction of electron-withdrawing groups at selected sites of the π-conjugated system.[6]

Recently, we have shown that rigidification of the π-conjugated system by partial or full covalent bridging[4,7] represents an efficient alternative approach allowing considerable gap reduction especially for fully rigid oligomers.[7b,c] However, application of this strategy to the synthesis of precursors for electrochemical polymerization comes up against the dramatic decrease of solubility resulting from rigidification of the precursor which considerably limits the efficiency of the electropolymerization process.[7c] We have shown already that introduction of solubilizing alkyl chains on bridged dithienylethylene (DTE) as done in **2b** (Chart 1) significantly improves the efficiency of electropolymerization.[8] However, due to the presence of two asymmetric carbons, compound **2b** is obtained as a mixture of diastereomers. To circumvent this obstacle, we recently synthesized compound **2c** in which the alkyl chains are introduced at the 4,4′-positions of thiophene. However, attempts to electropolymerize this substrate remained unsuccessful, presumably because steric interactions between octyl chains hinder the formation of a fully planar π-conjugated system.[9]

Chart 1



2a $R_1 = R_2 = H$
2b $R_1 = H$, $R_2 =$ *n*-Butyl
2c $R_1 =$ *n*-Octyl, $R_2 = H$

The synthesis of the bridged DTEs **2** by a McMurry reaction implies the preparation of a precursor cyclic ketone by intramolecular Friedel−Crafts acylation (Scheme 1). In the course of the synthesis of ketone **5**, i.e. the precursor of **2b**, the hitherto unknown ketone **6** was isolated in appreciable yield. Owing to its highly constrained structure, this compound represents an interesting building block for the preparation of a multibridged DTE (**3**). We report here the synthesis and characterization of this new precursor and its electropolymerization into a low band gap conjugated polymer.

Ketone **6** has been isolated in the conditions depicted in Scheme 1. Intramolecular Friedel−Crafts acylation of the acid chloride **4**[8] in the presence of $AlCl_3$ followed by column chromatography gave the expected ketone **5** as main product and the multicyclic ketone **6** in 11% yield. A possible mechanism for the formation of ketone **6** via Wagner−Meerwein (WM) rearrangement of carbocation[10] in the presence of $AlCl_3$ is shown in Scheme 2.

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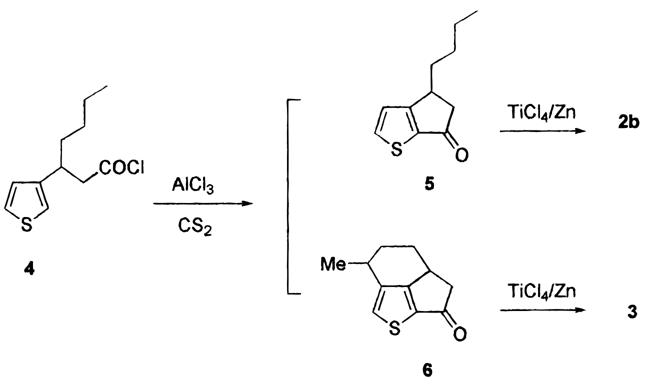
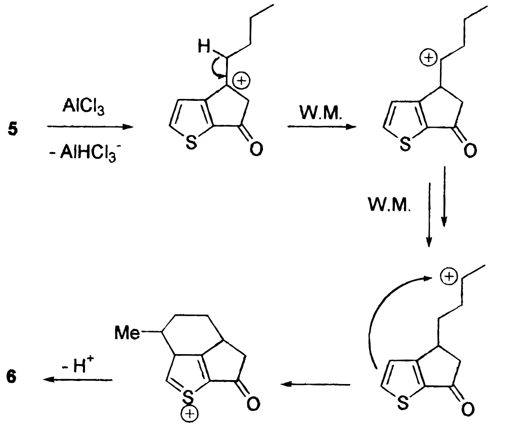
Scheme 1



Scheme 2



This interpretation is consistent with the fact that reaction of ketone **5** with $AlCl_3$ produces traces of ketone **6**. On the other hand, the fact that no product of intramolecular cyclization is detected when 3-octylthiophene is reacted with $AlCl_3$ suggests that formation of the six-membered ring of compound **6** requires the presence of the acyl chloride (or that of the resulting carbonyl group) on the molecule. However, further work is required to determine which of the acylation or the six-membered ring formation takes place at first.

Due to the presence of two asymmetric carbons, compound **6** is obtained as a mixture of two diastereomers as confirmed by ^{1}H NMR. The X-ray structure of a single crystal of **6** obtained by recrystallization in ethanol[11] is shown in Figure 1. This crystal corresponds to the diastereomer of configuration 7*S*,10*S*. The presence of the six-membered ring induces a deformation of the thiophene nucleus with in particular a shortening of the C_4-C_5 bond distance (1.386 Å for compound **6** vs 1.409 Å for **2b**).[8]

The multibridged compound **3** was prepared by McMurry self-coupling[12] of ketone **6**. Due to the presence of four asymmetric carbons, column chromatography gave two fractions containing a mixture of several diastereomers. As expected, the UV−vis spectra of both fractions are identical and show a well-resolved vibronic fine structure with a 0−0 transition at 373 nm and two vibronic replicas at 337 and 354 nm. Comparison with the data for unbridged DTE (**1**) and its bridged analogues (**2a**−**c**) reveals a bathochromic shift of the three maxima for compound **3** (Table 1). While it is evident that this red shift is caused by the additional six-membered ring, comparison with the data for **2c** substituted at the 4,4′ positions of the thiophenes shows that this shift is not due to the simple +I effect of the alkyl group. A further support to this conclusion is provided by the 20 mV negative shift of the first anodic peak potential (E_{pa1}) between **2c** and **3**. On the other hand this potential shift is noticeably smaller than the corresponding energy decrease of the 0−0 transition (0.05 eV). Since E_{pa1} and λ_{0-0} are related to the energy level of the HOMO and to ΔE respectively,[13] this difference suggests that the additional bridging in compound **3** induces a slight decrease of the LUMO level.

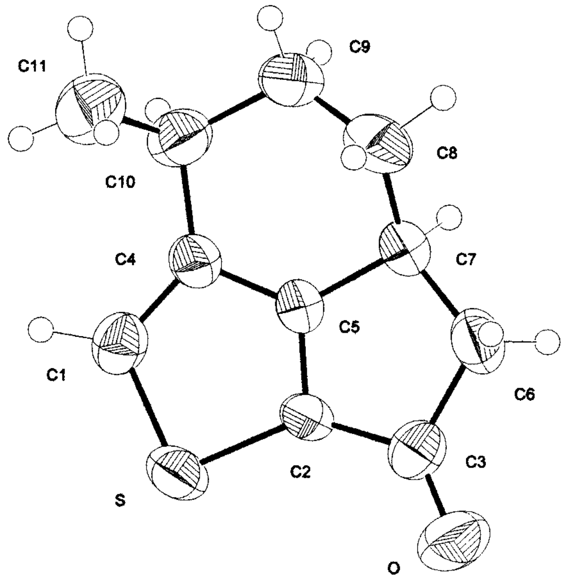


Figure 1. ORTEP view of ketone **6**.

Table 1. UV−Visible[a] and Electrochemical[b] Data for Compounds 1, 2,[c] and 3

compd	λ_{max} (nm)			E_{pa1} (V/SCE)
1	330	341	360	1.10
2a	331	348	367	0.72
2b	332	349	369	0.72
2c	331	348	368	0.68
3	337	354	373	0.66

[a] In CH_2Cl_2. [b] In 0.10 M Bu_4NPF_6/CH_3CN, scan rate 100 mV s^{-1}. [c] From ref 8b.

Previous AM1 calculations based on X-ray data for compound **2b** have shown that the bridging of the DTE molecule results in a decrease of bond length alternation along the π-conjugated path which produces a ca. 0.40 eV decrease of ΔE.[8] On the basis of these previous results, the X-ray data for ketone **6** suggest that the further narrowing of ΔE observed between **2c** and **3** might be related to a decrease of the resonance energy of the thiophene ring resulting from its deformation by multiple bridging.

Figure 2 shows the CVs corresponding to the potentiodynamic electropolymerization of **3**. Application of

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[11] Crystal data for **7**: $C_{11}H_{12}OS$, $M = 192.28$; colorless prismatic crystals, $0.6 \times 0.5 \times 0.4$ mm^3; monoclinic, $P2_1/n$; $a = 8.109(3)$, $b = 9.315(3)$, $c = 13.022(5)$ Å; $\beta = 100.70(3)$ Å; $V = 966.5(6)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.321$ g cm^{-3}; λ(Mo Kα) = 0.710 73 Å; 2750 reflections ($2.5 < \theta < 30°$) were collected at 298 K from which 949 were independent with $I > 3\sigma(I)$, 118 refined parameters; $R = 0.065$, $R_w = 0.069$.

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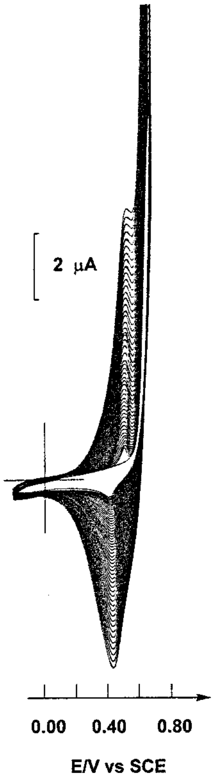

Figure 2. Potentiodynamic electropolymerization of **3** (1(10^{-3} M) in 0.10 M Bu_4NPF_6/CH_3CN, Pt electrodes, scan rate 100 mV s^{-1}.

recurrent potential scans leads to the development of a new redox system associated with the oxidation and reduction of the growing polymer. This steady electropolymerization contrasts strikingly with the unsuccessful attempts to electropolymerize the parent compound **2c**. Since the very close oxidation potentials of **2c** and **3** indicate a comparable reactivity for the corresponding cation radicals, these contrasting behaviors may reflect differences in the steric interactions between precursor molecules upon the cation radical coupling step. A previous analysis of the electropolymerization of 3,4-dimethylthiophene and cyclopenta[*c*]thiophene has shown that cyclization between the 3 and 4 positions of thiophene drastically limits the steric interactions between substituents on adjacent monomers thus leading to a considerable increase of the effective conjugation of the polymer.[14] On this basis, the above results suggest that the fastening of the free alkyl chain of compound **2c** into the fused six-membered ring of compound **3** reduces the steric hindrance, thus allowing cation radical coupling.

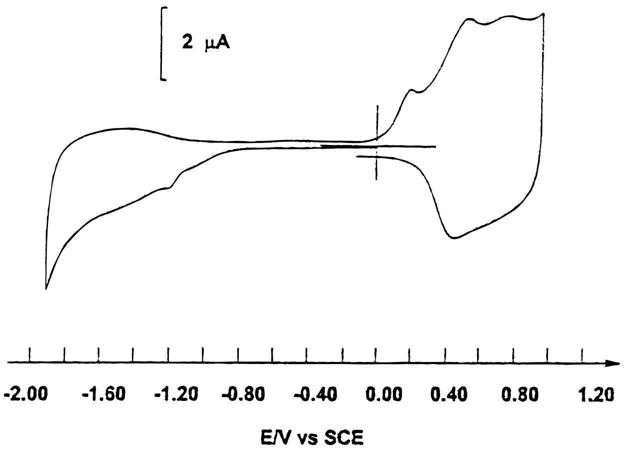

Figure 3. Cyclic voltammogramm of poly(**3**) in 0.10 M Bu_4NPF_6/CH_3CN, scan rate 100 mV s^{-1}.

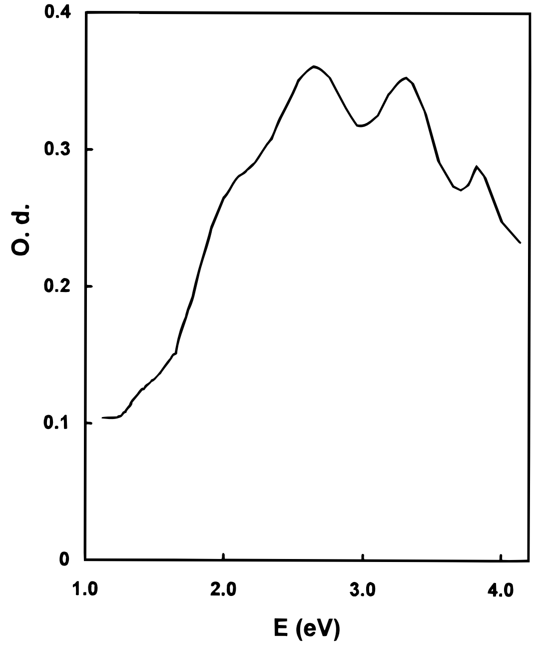

Figure 4. Electronic absorption spectrum of undoped poly(**3**) on ITO.

The CV of poly(**3**) exhibits two anodic peaks at 0.51 and 0.72 V. The first peak, already observed in Figure 3, corresponds to the oxidation of the longest conjugated chains, while the second one can be ascribed to the oxidation of precursor molecules trapped in the film during electrodeposition, as already observed for poly(terthienyls).[15] In the negative potential region, the CV exhibits a broad reduction wave between −1.00 and −1.90 V corresponding to the reduction (or n-doping) of the polymer. The smaller area under these latter redox waves shows that the n-doping level is lower that the p-doping one, while the dissymmetry of the cathodic and anodic waves indicates a limited reversibility. The weak shoulders observed at +0.20 and −1.20 V upon repetitive cycling are due to residual n- and p-doping, respectively. The potential difference between the threshold for hole (p-doping) and electron injection (n-doping) leads to an estimated band gap of ca. 1.40 eV.

The optical spectrum of undoped poly(**3**) on ITO (Figure 4) shows a shoulder at 620 nm, a main band with λ_{max} at 466 nm, and a less intense band at 375 nm attributed to the trapped precursor **3**. The long wavelength absorption edge leads to an estimated band gap of 1.60−1.70 eV, in satisfying agreement with CV data. While the spectrum of poly(**3**) is reminiscent of that of the polymers derived from compounds **2**,[8] the 10−20 nm blue shift of λ_{max} together with the slightly larger E_g value and the presence of unreacted substrate in the polymer suggest a less complete polymerization and/or a less planar polymer chain. These results thus reveal that in addition

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to a stabilization of the cation radical, the additional six-membered ring induces some steric hindrance to conjugation in the resulting polymer.

To summarize, a new rigidified DTE **3** has been synthesized by McMurry coupling of the multibridged ketone **6**. The presence of the additional six-membered ring induces a deformation of the thiophene ring which might be responsible for the smaller ΔE value of **3** compared to simply bridged systems. This further bridging of the DTE system allows a significant decrease of the steric hindrance associated with substitution of the 4,4′ positions of thiophene, thus allowing the electropolymerization of **3** into a new low electroactive polymer. On the other hand, the results obtained on the molecule itself show that this novel system represents an interesting building block for the synthesis of monodisperse rigid oligomers or as π-conjugating spacer in NLO chromophores.

Experimental Section

Electrochemistry was carried out with a PAR 273 potentiostat in single-compartment cells equipped with Pt microelectrodes of 7.8 × (10^{-3} cm^2 area, a Pt wire counter-electrode, and a saturated calomel reference electrode (SCE). Acetonitrile was distilled over CaH_2 before use, and Bu_4NPF_6 (Fluka puriss) was used as received. The electrolytic medium involved 1×10^{-3} M monomer in 0.10 M Bu_4NPF_6/CH_3CN. Films for optical characterization were grown on indium−tin oxide coated glass electrodes (ITO) by repetitive potential sweeps between −0.25 and +0.70 V and electrochemically reduced.

4-Butyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophene-6-one (5) and 2-Methyl-11-thiatricyclo[7.2^{1,8}.0^{1,9}0^{5,9}]undeca-1(10),8-dien-7-one (6). The crude acid chloride **4** (7.58 g, 32.88 mmol) synthesized according to the already reported procedure[8b] was dissolved in CS_2 (100 mL), and this solution was added dropwise to a mixture of $AlCl_3$ (6.50 g, 48.75 mmol) in CS_2 (100 mL) under N_2. After 4 h of reflux, the mixture was cooled to 20 °C and poured into a mixture of concentrated HCl (100 mL) and ice−water (200 mL). The aqueous phase was extracted with CH_2Cl_2, and the organic phase was washed with water, dried ($MgSO_4$), and evaporated in vacuo. The residue was first subjected to a rapid filtration (silica gel, CH_2Cl_2) and then chromatographed (silica gel, 4:1 petroleum ether/Et_2O) which allowed the separation of ketones **5** (2.63 g, 40%)[8] and **6** (0.75 g, 11%) as a mixture of two diastereomers (60:40). The latter was obtained as an oil which slowly crystallized, mp 73−77 °C. ^{1}H NMR ($CDCl_3$): δ 1.18−1.38 (m), 1.20 (d, 3H, ^3J = 7.3 Hz, 2nd diastereomer), 1.34 (d, 3H, ^3J = 6.8 Hz, 1st diastereomer), 1.42−1.60 (m), 1.69−1.79 (m), 1.96−2.24 (m), 2.61−2.72 (m), 2.75−2.89 (m), 3.00−3.20 (m), 7.54 (d, 1H, ^4J = 1.2 Hz, 2nd diastereomer), 7.55 (d, 1H, ^4J = 1.4 Hz, 1st diastereomer). ^{13}C NMR ($CDCl_3$): δ 21.50, 23.54, 25.28, 28.44, 29.14, 30.98, 32.20, 34.20, 35.50, 35.92, 50.47, 50.51, 135.03, 135.43, 135.68, 135.86, 139.33, 140.20, 174.70, 174.87, 195.56, 195.71. MS (EI): *m*/*e* 192 (M^+, 100). IR (NaCl): 1695 cm^{-1} (C═O). UV−vis (CH_2Cl_2) [λ_{max} nm (log ϵ)]: 271 (4.16). Anal. Found: (calcd) for $C_{11}H_{12}OS$: C, 68.65 (68.71); H, 6.27 (6.29); S, 16.68 (16.67).

Bis(2-methyl-11-thiatricyclo[7.2^{1,8}.0^{1,9}0^{5,9}]undeca-1(10),8-dien-7-ylidene) (3). After dropwise addition of $TiCl_4$ (0.60 mL, 5.47 mmol) to 20 mL of anhydrous THF at 0 °C under N_2 atmosphere, zinc dust (0.68 g, 10.40 mmol) was added in one portion. The mixture was then refluxed for 0.5 h and cooled to 0 °C. A solution of ketone **6** (0.5 g, 2.60 mmol) in THF (35 mL) was addded dropwise, and the mixture was refluxed for 4 h. After cooling to room temperature and addition of water, the mixture was extracted with CH_2Cl_2. The combined organic phases were washed with water, dried ($MgSO_4$), and evaporated in vacuo. After chromatography (silica gel, 95:5 petroleum ether/CH_2Cl_2), two fractions F1 (0.11 g, R_f = 0.61, white solid) and F2 (0.08 g, R_f = 0.46, slightly yellow oil) were separated; both of them corresponded to a mixture of several diastereomers. F1: mp 180−183 °C; ^{1}H NMR ($CDCl_3$) δ 1.16−1.76 (m), 1.93−2.20 (m), 2.67−2.95 (m), 2.97−3.20 (m), 3.25−3.43 (m), 6.88−6.96 (m); MS (EI) *m*/*e* 352 (M^+, 100); UV−vis (CH_2Cl_2) [λ_{max} nm (log ϵ)] 373 (4.48), 354 (4.54), 337 (4.34). Anal. Found (calcd) for $C_{22}H_{24}S_2$: C, 75.03 (74.95); H, 6.68 (6.86).

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Supporting Information Available: Tables of X-ray data for compound 6 (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS: see any current masthead page for ordering information.

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