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Synthesis, Optical and Electrochemical Characterization Of Inter-ring Bridged Tetramers Based On Thiophene

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Abstract Tetramers based on thiophene and phenylene residues in which the torsion angles between thiophene rings are locked by a chemical bridge have been synthesised by organosynthetic routes. The effect of locking on photoluminescence and absorption in solution has been studied. An enhanced tendency of doubly locked tetrathiophene to aggregate together with its facile decomposition upon light exposure greatly influence the luminescence properties. © 1999 Elsevier Science Ltd. All rights reserved.

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Introduction

The synthesis of oligothiophenes has received a great deal of attention because of their extensive π-electron conjugation which makes them interesting for a large number of optoelectronic applications as active layers in field effect transistors[1-3] and light emitting diodes.[4] On the other hand, using molecular design they can be easily modified and used as model compounds in the study of the spectroscopic properties related to structural features of different parent polythiophenes.

In particular, the coexistence in solution of a variety of non-planar conformations of oligothiophenes, due to torsional mobility around the interring C-C bond, greatly influences the degree of conjugation and therefore the optical properties, i.e. absorption and emission. Indeed the absorption spectrum in solution of tetrathiophene (**5**), for example, is blue-shifted with respect to the data obtained from solid state samples and does not show any vibronic structure.[5]

In order to control the molecular conformation and aiming to increase the planarity of thiophene based oligomers in solution, we have synthesized and studied three molecules formed by four aromatic rings. The first molecule **1**, see Scheme 1, is constitued by thiophene moieties only and two methylene bridges on the β position of the rings prevent any rotation between the first and second rings and between the third and the fourth rings. In order to enhance the solubility of **1**, which shows a high tendency to aggregation,[6] the analogous tetrabutyl substituted compound **2** has been synthesised. In the third compound **3** of scheme 1

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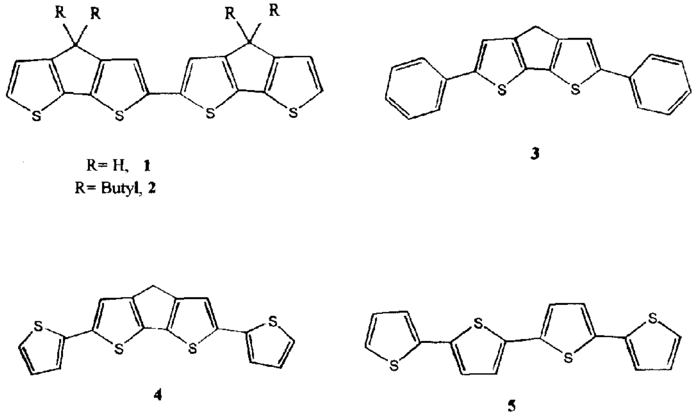
the thiophene residues, which are bridge-locked, constitute the middle while two phenyl rings having conformational freedom end the molecule. This last compound has been synthesised to compare the effect of phenyl ring with respect to thienyl group on the stability of bridged bithiophene.

The optical and electronic properties of **1**, **2** and **3** in solution have been studied by using absorption and photoluminescence spectroscopies. Moreover the comparison between these molecules and **4** and **5**[7] compounds, also reported in scheme 1, allows us to obtain information about the effect of the conformational mobility on the luminescence properties.

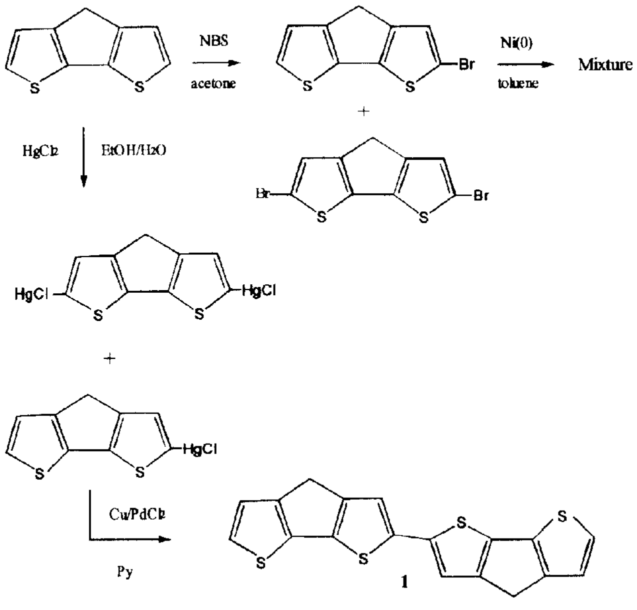


SCHEME 1

Results and discussion

The synthesis of 2,2'-bis-4H-cyclopenta[2,1-b;3,4-b']bithiophene (**1**) was firstly tried by coupling the bromo derivative in α position of 4H-cyclopenta[2,1-b;3,4-b']bithiophene (**6**) with Ni(0) in situ prepared as a catalyst (see Scheme 2). Indeed the preparation of mono bromo derivative turned out to be troublesome because of the difficulty of obtaining the compound free from the dibromo derivative even working with a molar deficiency of bromine. A good separation was obtained using inverse phase flash-chromatography, but sometime during purification and handling, the brominated mixture yielded a bluish-black solid which was insoluble. Infra-red characterisation of this black solid is in agreement with a mixture of oligomers of **6** polymerised mostly in β position, hence completely amorphous from XRD analysis. The coupling with Ni(0) failed due to the acidic hydrogen atoms of the bridge which destroy the catalyst and a mixture of **6** and both mono and dibromo derivatives were recovered at the end of the reaction even when the starting monoderivative was rigorously pure. Only traces of **1** attributable to a thermal coupling were detected by using GCMS.

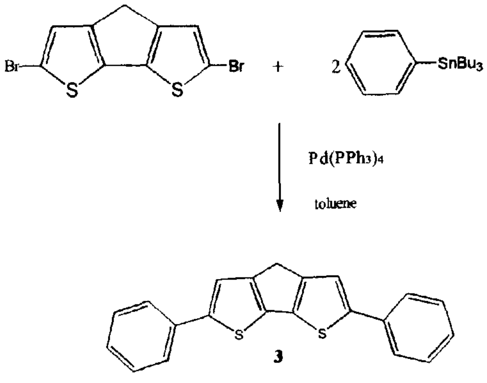
For these reasons we followed the suggestions of Curtis and McClain[10] and prepared the arylmercuric chloride which undergoes a Pd-catalysed coupling reaction assuring α-α' links (Scheme 2).



SCHEME 2

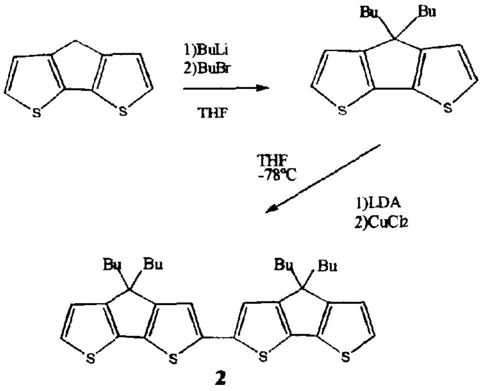
A coupling based on chloromercuration can be considered complementary to chemical coupling reactions that involve strongly basic or nucleophilic reagents such as organolithium or Grignard reagents. In this way an organometallic compound in the α position of **6** can be prepared also in the presence of strongly acidic protons such as those of the bridge, making this α position reactive toward the Pd catalyst and allowing the coupling even if the yields are much lower than those found by the authors in thiophene polymerisation. There may be several reasons for this; firstly the presence of an amount of the dimercuric chloride derivative which should give a polymer in the coupling reaction, indeed a black insoluble precipitate was recovered at the end of the reaction. Unfortunately both the mono and the dimercuric chloride were insoluble in any solvent save pyridine, so it is impossible to carry out any separation. The addition of some water permits a certain control of the degree of the substitution by limiting the solubility of monomercuric chloride. Secondly we can not rule out also some reaction of acidic protons with Pd, in fact with respect to lithiation they prove more reactive than a bromine in α position.[11]

The dibromo derivative of **6** was use in a Stille[12] reaction with tributylphenyltin in order to synthesise **3** (see Scheme 3).



SCHEME 3

The alkylation with butylbromide of 4-lithium derivative of **6** following the literature procedure[13] was used to overcome the problem of the acidity of protons of the bridge. In this way the lithiation of **6** in α-position of thiophene ring becomes possible and also the subsequent homocoupling by using $CuCl_2$ as a catalyst (see Scheme 4).



SCHEME 4

The electron-rich character of 4,4-dibutyl derivative of **6** accounts for the reduced yield of dimer with respect to that obtained in the same reaction from simple bithiophene.[14] In fact a significant amount of 2-formyl-4,4-dibutyl derivative of **6** was observed.

The optical absorption and photoluminescence (PL) spectra of, **1**,**2**, **5** and **3** solutions are presented in Fig.1.

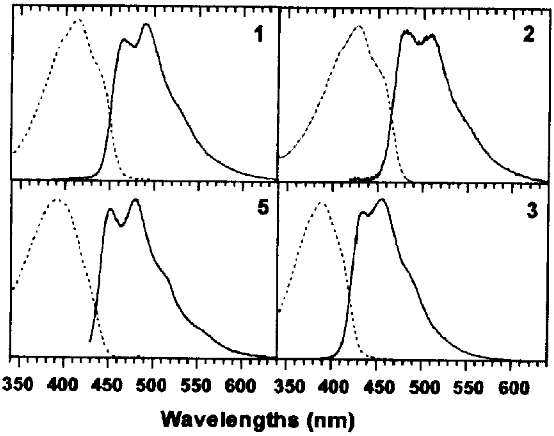


Fig.1 Optical absorption (dotted lines) and photoluminescence (solid lines) of the molecules in dilute THF solutions.

The double chemical bridge in **1** induces a 23 nm red shift of the optical absorption with respect to **5**, while a smaller shift is observed for the PL spectrum. This behaviour is consistent with a higher planarity of the **1** molecule in the ground state with respect to **5**. Photoexcitation produces a planarization of the **5** molecule in the excited state. This effect accounts for the smaller red-shift observed in the PL spectra with respect to the absorption spectra upon chemical bridging.[7] The optical spectra of the **2** molecule are slightly red shifted with respect to these of **1**, in agreement with the increased conjugation induced by the alkyl substitution. The conjugation of the thiophene only based oligomers is higher than that of **3**, whose absorption and PL spectra are in fact blue shifted as compared with the former spectra. The PL quantum yields (QY) of **1** and **3** in dilute THF solutions are 14% and 27%, respectively. The relatively low PL QY of the thiophene oligomer, with respect to the value (24%) obtained for **4**[7], is probably related to the poor solubility of **1**. In fact in CH_2Cl_2 solutions, for which a better solubility is observed, the QY of **1** slightly increases reaching the value of 16%. However the low value may also be related to an higher tendency of **1** to decompose during the PL measurement exciting at 360 nm. As a matter of fact a subsequent PL measurement with 260 nm excitation, revealed the presence of **6** emission. The presence of four butyl chains in **2** imparts good solubility to the molecule, hence preventing the formation of aggregates in THF solution. Unfortunately the electron-donor effect of alkyl chains further destabilises the molecule which tends to decompose quicker than **2**. After the PL measurement an intense luminescence of 4,4-dibutyl derivative of **6** was observed and also an absorption band at higher energy, which can be attributed to the same species, undetectable before the excitation at 260 nm. A further exposure of the solution in air produces a complete oxidation of **2**, via formation of epoxide, hydroxyl and carbonyl groups, detected by FTIR analysis. No absorption peak was observed in the UV-vis. spectrum after 3-hour exposure. The measured QY of 9% is therefore reduced by degradation during the measurements. The higher QY of **3**, with respect to **4**, despite its lower conjugation, is in agreement with the higher PL efficiency of phenyl rings with respect to thiophenes.[15-16]

Table 1 reports the oxidation potentials (E°) together with the maxima of absorption and emission of the tetramers in solution. The stability of the tetramers can be related to the oxidation potential which decreases on going from the unbridged compound to the doubly bridged one and is further lowered by the addition of alkyl chains. The tetramer with terminal phenyl rings is the most stable and displays the highest oxidation potential. This fact is in agreement with the absence of detectable decomposition products in PL measurements and can be related to the ability of phenyl group with respect to the thienyl one (well known as an electron rich ring) to delocalize an excess of electronic charge.

Table 1: Absorption and emission maxima and oxidation potentials (E°) of tetramers in solution.

Tetramers	Absorption max (nm)		Emission max (nm)	E°(V)	[scan rate (Vs^{-1})]
	$CHCl_3$	THF solution	THF solution		
5	391		451	0.65	1
4	408		458	0.35;0.75	>1
1	416	414	467	0.27;0. 57	>1
2	427	428	479	0.22;0.50	>1
3	389	388	435	0.49;1.04[a]	0.1

[a] Peak potential of irreversible process

Conclusions

Three tetramers of oligothiophenes having cyclopentadithienyl building blocks were synthesised and optically characterised. A strong tendency to aggregation is found in the unsubstituted molecule constituted only by locked thienyl residues together with a fast degradation upon light exposure. Such a degradation, due to oxidation, becomes also faster for the tetramer bearing butyl substitution on the bridges, yielding carbonyl groups, quencher of photoluminescence. These facts account for the reduced solution quantum yield values of the doubly locked tetramers with respect to the expected values considering the increased planarity of these stiff molecules, having less conformers through which the excitation can decay non-radiatively. .

On the contrary, in the case of end phenyl rings, the bridge presence seems to negligibly affect the optical properties.

Experimental section

Materials and Instruments

N-bromosuccinimide (NBS), $Pd(PPh_3)_4$ hydroquinone, $PdCl_2$ (Aldrich) were used as received, pyridine, toluene, tetrahydrofuran (THF) and dimethylformamide (DMF) (Aldrich) were freshly distilled. 4H-cyclopenta[2,1-b;3,4-b']bithiophene (**6**) and 4,4-dibutylcyclopenta[2,1-b;3,4-b']bithiophene (**7**) were prepared according to literature procedures.[8-9]

FTIR spectra were recorded on a Bruker IFS 48 instrument. ^{1}H NMR spectra were obtained at 270 Mhz on a Bruker instrument. MS measurements were carried out on a GC-MS Hewlett-Packard 5985B instrument, operating in electron impact mode (EI) at 70 eV. Melting point determinations were obtained using a Mettler FP5 hot stage coupled with a Reichert optical microscope.

Cyclic voltammetries of all the compounds were performed in acetonitrile except for the less soluble **2** which was dissolved in a mixture of acetonitrile and methylene chloride, at room temperature under nitrogen in three electrode cells using a Amel apparatus. The counter electrode was platinum; reference electrode was a silver/0.1M silver perchlorate in acetonitrile (0.34V vs SCE).

The optical absorption was measured with a Varian-Cary 2400 spectrometer. The photoluminescence was measured with a SPEX 270M monochromator equipped with a CCD detector by exciting with a monochromatic Xe lamp. Photoluminescence quantum yields were obtained by using quinine sulphate as a reference.

Synthesis of 2-bromo-4H-cyclopenta[2,1-b;3,4-b']bithiophene.

The reaction was carried out in the dark. **6** (64.8 mg, 0.364 mmol) together with hydroquinone (4.95 mg, 0.045 mmol) were dissolved in acetone (1.5 ml) with stirring and a solution of NBS (63.7 mg, 0.36 mmol) in 5.5 ml of acetone was slowly added dropwise (45 min.) maintaining the temperature in a range of 15-18°C. Immediately after the end of addition the solvent was removed by evaporation in vacuo at low temperature obtaining a pale yellow solid which was washed with 5 ml of water. The purification, performed by flash chromatography (reversed phase using methanol/water 9/1), gave 35% of starting product **6**, 37% of a white solid, monobromo derivative, and 26% of a pale-green solid, dibromo compound.

2-Bromo-4H-cyclopenta[2,1-b;3,4-b']bithiophene: FTIR (cm^{-1}) 3110, 3070, 1080, 990, 825, 815, 690; ^{1}H-NMR ($CDCl_3$, ppm) 7.18, 7.07 (2H, AB system $J_{A,B}$ = 4.89 Hz), 7.08 (s, 1H), 3.52 (s, 2H); Mp: decomposition before melting at 80°-82°C.[Found: C, 42.07%; H, 1.9; S, 25.01; Br 31.00. Calcd for $C_9H_5S_2Br$: C, 42.04; H, 1.96; S, 24.93; Br, 31.07].

2,6-Dibromo-4H-cyclopenta[2,1-b;3,4-b']bithiophene: FTIR (cm^{-1}) 3070, 800; ^{1}H-NMR ($CDCl_3$, ppm) 7.08 (s, 2H), 3.51 (s, 2H). Mp: decomposition before melting at 143°-145°C. [Found : C, 32.2%; H, 1.12; S, 19.52; Br, 47.4. Calcd for $C_9H_4S_2Br_2$ C, 32.17; H, 1.20; S, 19.08; Br, 47.55].

Synthesis of 2,2'-bis-4H-cyclopenta[2,1-b;3,4-b']bithiophene (**1**).

6 was mercurated according to the method of Steinkopf.[8] (49.8 mg, 0.28 mmol) of **6**, mercuric chloride (38.0 mg, 0.14 mmol) and sodium acetate (22.9 mg, 0.28 mmol) were stirred in 30% aqueous ethanol (15 ml) at room temperature, light repaired. After a few minutes a white precipitate appeared which was collected by filtration after 1 h (56% yield). After another hour a second solid was collected (38% yield). Both the solids were washed with hot ethanol and water. Only the first precipitate was used for coupling reaction in order to reduce the amount of oligomeric products. The mercurated compound **6** (63.6 mg, 0.154 mmol), Cu powder (39.4 mg, 0.62 mmol) and $PdCl_2$ (1.7 mg, 0.01 mmol) were added in a Schlenk flash in the dark , evacuated and nitrogen backfilled repeatedly. Dry pyridine (4.6 ml) was transferred by a syringe into the flask and the mixture was refluxed for 5 h, meanwhile the colour changed from yellow to brown. The hot solution was filtered through Celite, trapping the excess of Cu and the formed Hg and the Celite was rinsed several times with chloroform. To completely remove Cu^+ , the organic solution was washed several times using a saturated solution of NH_4Cl, then with aqueous HCl and finally with brine. After drying over $MgSO_4$, the solvent was removed by rotary evaporation to obtain a solid that was subsequently purified by sublimation at 180°C, pressure 4×10^{-2} torr, giving the title compound **1** as a yellow powder (44% yield).

MS(EI): m/z 354 [M^+]; FTIR (cm^{-1}) 3092 and 3060 α and β protons C-H stretching, 1376, 1262, 802; ^{1}H-NMR ($CDCl_3$, ppm) 7.19, 7.08 (4H, AB system $J_{A,B}$ = 4.76 Hz), 7.16 (s, 2H), 3.55 (s, 4H); UV_{CHCl3} λ_{max} 416 nm.; Mp: progressive darkening from 200 °C to 260 °C without melting.[Found: C, 59.52%; H, 2.9; S, 37.56. Calcd for $C_{17}H_{10}S_4$ C, 59.62; H, 2.94; S, 37.44].

Synthesis of 2,6-diphenyl-4H-cyclopenta[2,1-b;3,4-b']bithiophene (**3**).

2,6-Dibromo-4H-cyclopenta[2,1-b;3,4-b']bithiophene (100.7 mg, 0.3 mmol) in 6 ml of toluene was added dropwise over 30 min at room temperature to a toluene solution (2 ml) of tributylphenyltin (202 mg, 0.6 mmol) and $Pd(PPh_3)_4$ (16.2 mg, 0.014 mmol, 2.4 mol %). The reaction was carried out under nitrogen and in the dark. After addition the brown solution was refluxed for 4.5 h, then poured into 10 ml of HCl 2N. The aqueous layer was extracted many times with chloroform. All the organic phases were collected, filtered through Celite, neutralized with $NaHCO_3$ and water, then dried over Na_2SO_4. The evaporation in vacuo provided a pale yallow solid that was triturated in toluene and completely purified by sublimation at 140 °C, pressure 2×10^{-3} torr giving a white powder (yield 57%).

MS(EI): m/z 330 [M$^+$]; FTIR(cm^{-1}) 3058 β proton C-H stretching, 1596, 1572, 1514 benzene ring, 750, 686 monosubstituted phenyl ring, 824 thiophene ring; ^{1}H-NMR (CDCl$_3$, ppm) 7.63-7.61 (4H, m, o-phenyl protons), 7.41-7.37(4H, m, m-phenyl protons), 7.35 (2H, s, thiophene protons), 7.28-7.25 (2H, m, p-phenyl protons), 3.63 (s, 2H); UV$_{CHCl_3}$ λ_{max} 389 nm; Mp: decomposition above 290 °C without melting.

[Found: C, 76.3%; H, 4.25; S, 19.48. Calcd for $C_{21}H_{14}S_2$ C, 76.33; H, 4.27; S 19.4].

Synthesis of 4,4,4',4'-tetrabutyl-2,2'-bis-4H-cyclopenta[2,1-b;3,4-b']bithiophene (**2**).

n-Butyllithium (1.6 M) in hexane (0.14 ml, 0.22 mmol) was added dropwise to a stirred solution of diisopropylamine (22.4 mg, 0.22 mmol) in dry THF (0.5ml) at -78 °C under nitrogen. The mixture was stirred at -78 °C for 20 min, at 0 °C for 15 min, then cooled again to -78 °C. A solution in THF (0.5 ml) of **7** (26 mg, 0.43 mmol) prepared under nitrogen and in the dark, was added dropwise, the mixture was stirred during 30 min at -78 °C, then anhydrous $CuCl_2$ (30.5 mg, 0.23 mmol) dissolved in dry DMF (0.5 ml) was added using a syringe. The solution was stirred in the dark for 1 h at -78 °C and allowed to warm to room temperature over 0.5 h under stirring. After addition of 3% aqueous HCl, the organic layer was extracted with ether and rinsed several times with water, then was dried over Na_2SO_4 and concentrated by rotary evaporation. All handling operations were carried out in the dark. Flash chromatography on silica gel using n-heptane before and then n-heptane: ethylacetate (80:20) as eluents resulted in the separation of the starting monomer of which 46.2 mg were recovered, the title dimer **2**, as an orange solid obtained in 52% yield, and the formyl derivative of the monomer **7** (48% yield), which is an oil.

2 MS(EI): m/z 488 [M$^+$]; FTIR(cm^{-1}): 3062 β protons C-H stretching, 1368, 1262, 796, 700; ^{1}H-NMR (CDCl$_3$, ppm): 7.17, 6.93 (4H, AB system $J_{A,B}$ = 4.86 Hz), 7.02 (s, 2H), 1.85 (t, 8H),1.22-1.14 (m,16H), 0.79 (t,12H); UV$_{THF}$ λ_{max} 427 nm; Mp = 111-112 °C. [Found C, 70.44%; H 7.3; S, 22.26. Calcd for $C_{34}H_{42}S_4$ C, 70.54; H, 7.31; S, 22.15].

2-formyl-4,4-dibutyl4H-cyclopenta[2,1-b;3,4-b']bithiophene MS(EI): m/z 318 [M$^+$]; FTIR (cm^{-1}): 1656 C=O stretching, 1384, 1226, 796; ^{1}H-NMR (CDCl$_3$, ppm): 9.83 (s, 1H, aldehydic proton), 7.57 (s, 1H), 7.40, 6.93 (2H, AB system $J_{A,B}$ = 4.92 Hz), 1.89-1.84 (2t overlapped, 4H), 1.18-1.14 (m, 4H), 0.93-0.88 (m, 4H), 0.77 (t,6H); UV$_{THF}$ λ_{max} 377nm. [Found: C, 67.7%; H 6.9; S 20.3. Calcd for $C_{18}H_{22}S_2O$ C, 67.88; H, 6.96; S, 20.14].

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