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Synthesis of conjugated 2-arylethynyl and 2-arylethenyl thiophene structures with optical properties

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Abstract—Conjugated mono(arylethynyl)oligothiophene structures have been obtained starting with (*E*)-[1-(2′-thienyl)-2-(*p*-phenyl)]ethyne (*E*)-**7** and 2-[*p*-(iodophenyl)ethynyl]thiophene **8**. Conjugated nanostructures were synthesized by oxidative coupling between the terminal acetylenes (*E*)-**7** and **8** to give, respectively, 1,4-di[(2-*p*-(iodophenyl)ethynyl)thienyl]-1,3-butadiyne and 1,4-di[(2-*p*-iodophenylethynyl)thienyl]-1,3-butadiyne. All the thiophene derivatives synthesized show an important fluorescence radiation emission, with a bathochromic shift, which increases with the conjugation of the chain.

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1. Introduction

One strategy used to improve the nonlinear optical properties is the insertion of five-member heteroaromatic rings in the conjugate backbone by increasing the first molecular hyperpolarizability β. It has been shown that highest β-values can be achieved by replacing benzenoid rings with easily delocalizable thiophene moieties.[1]

The thiophene-based compounds have attracted great attention, mainly because they show intrinsic electronic properties such as: luminescence,[2] redox,[3] and charge-transport.[4] Thiophene oligomers emit light across the entire visible range. Moreover, the compounds are very stable, easy to functionalize, and soluble in most organic solvents.[5] Thienyl oligomer dendrimers with π-extended conjugate chains have shown that the π–π^* electronic conduction band decreases from periphery to heart with an increase in the fluorescence quantum yield.[6]

Conjugated thienyl systems have been recently developed with enhanced thermal and chemical stability.[7] In the area of electro-optical applications, the improvement in electronic strength effect was obtained by varying the classical donor and acceptor groups on the conjugate system,[8] and by the extension of the conjugation between donor and acceptor moieties.[9,10]

The 2-ethynyl and 2,5-di(ethynyl)thiophene units are good starting candidates for preparing end-capped thienyl oligomers and conjugated structures with angular geometry (about 155°). The *para*-connection of two acetylene units guarantees the conjugate electronic communication. Cyclic oligomers with nanometric diameter, integrated by 2,5-thienyl and *para*-phenylethynyl rings, have been recently reported.[11] A series of 2-thienyl polyenes has been synthesized and analyzed spectroscopically in *n*-alkane solutions at liquid helium temperature.[12]

We now report the synthesis of conjugate 2-thienyl ring end-capped structures, which are attractive and promising by their fluorescence properties.

2. Results and discussion

We carried out the syntheses of (*E*,*E*)-1,4-di(2′-thienyl)-1,3-butadiene, (*E*,*E*)-**2** and 1,4-di(2-thienyl)-1,3-butadiyne (**4**),[13] which permit a comparison between the polarity and polarizability effect of the conjugate thienyl systems formed by double or triple bonds.

Compound (*E*,*E*)-**2** was obtained in good yield (72%) by the homocoupling reaction of 2-(2′-chlorovinyl)thiophene (**1**), catalyzed by zero-valent nickel complexes.

Keywords: Arylethynyl and arylethenylthiophene structures; π-Extended conjugation; Fluorescence analysis; Eglinton–Glaser, Cadiot–Chodkiewicz and Sonogashira reaction.

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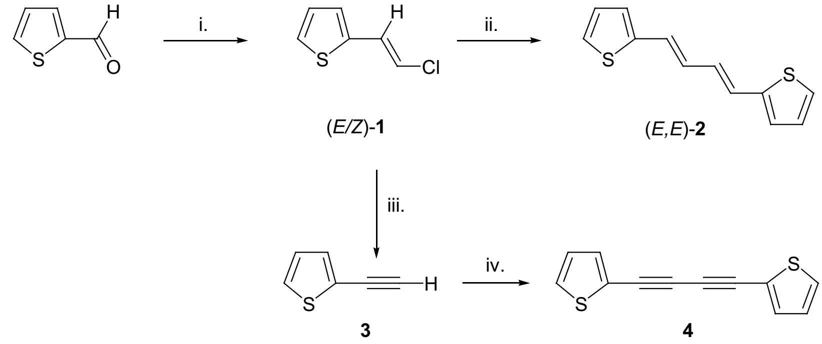


Scheme 1. Reagents and conditions: (i) $Cl_2CH_2PPh_3$, KO^tBu; (ii) $Cl_2Ni(PPh_3)_2$, Zn, THF, rt, 2 h; (iii) KO^tBu, THF; (iv) Cu_2Cl_2/O_2, pyridine.

The 2-chlorovinylthiophene, as the (*E*/*Z*)-**1**[14] mixture (57:43), was prepared in good yield by the Wittig reaction between the (chloromethyl)(triphenyl)phosphonium ylide and 2-thiophenecarboxaldehyde. The homocoupling reaction of the (*E*/*Z*)-**1** mixture was carried out in the presence of the zero-valent nickel complex, prepared in situ by reaction of dichloro bis[(triphenyl)phosphine] nickel and powdered zinc in tetrahydrofuran, giving 1,4-di(2-thienyl)-1,3-butadiene **2**, as a brown solid, mp 140–143 °C, hexane, only as the (*E*,*E*) isomer in good yield (82%; Scheme 1).

In the same way, 2-ethynylthiophene (**3**) was obtained in good yield starting with the (*E*/*Z*)-**1** mixture in THF treatment with potassium *tert*-butoxide at room temperature (brown oil, 87%).[15]

The synthesis of compound **4** has been reported by means of the Glaser homocoupling of the acetylene **3** in the presence of Cu_2Cl_2 in pyridine under an oxygen atmosphere, giving 1,4-di(thienyl)-1,3-butadiyne (**4**) (yellow solid, mp 92–93 °C, hexane), in excellent yield (91%; Scheme 1).

The 1,3-diene derivative (*E*,*E*)-**2** shows a fluorescence radiation with a low quantum yield, while the 1,3-diyne (**4**) does not show appreciable fluorescence emission in dichloromethane solvent (Table 1).

The conjugated 2-(*E*)-phenylethenyl- and phenylethynyl-thiophene structures were obtained starting of 2-[*p*-(iodophenyl)-2′-ethenyl]thiophene *E*-**5** and the ethynyl analogue **8**. Compound *E*-**5** was prepared by the Wittig reaction between *p*-(iodobenzyl)(triphenyl)phosphonium ylide and 2-thiophenecarboxaldehyde, giving a (*E*/*Z*)-**5** mixture (50:50),[16] which was completely isomerized to *E*-**5**, by exposure to sunlight in the presence of a few iodine crystals (Scheme 2).

Table 1. Wavelengths for the first absorption and fluorescence emission maxima for the compounds **2**, **7**, **10**, **12**, **13** and **14** in CH_2Cl_2 at room temperature[19]

Compd.	UV–vis λ_{max}, nm	ε ($M^{-1}\,cm^{-1}$)	Fluorescence λ_{max}, nm	Φ_f
2	381	25,100	431	0.02
7	341	28,400	420, 450	0.13
10	337	30,000	392, 410	0.14
12	382	78,300	427, 454	0.29
13	359	81,250	421	0.36
14	352	57,100	390, 410	0.30

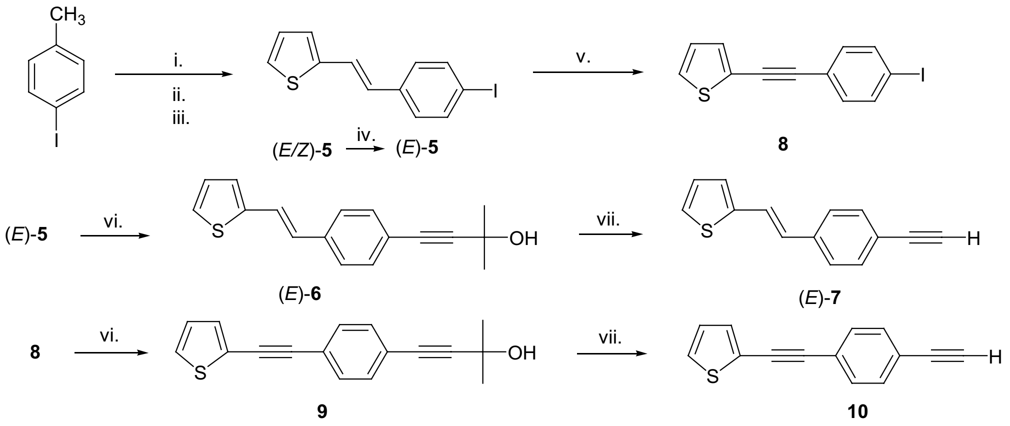
Fluorescence quantum yield was determined relative to 2-aminopyridine in 0.1 N H_2SO_4.

The heterocoupling of (*E*)-**5** with 2-methyl-3-butyn-2-ol in the presence of dichloro bis[(triphenyl)phosphine] palladium and cuprous iodide, in diethylamine at room temperature, gives the propargyl derivative (*E*)-**6** in excellent yield (brown solid, mp 144–147 °C, 94%). By treatment of (*E*)-**6** with powdered sodium hydroxide in dry toluene at reflux temperature, the terminal acetylene (*E*)-**7**, was obtained in excellent yield (pale-yellow solid, mp 117–119 °C, hexane, 92%).

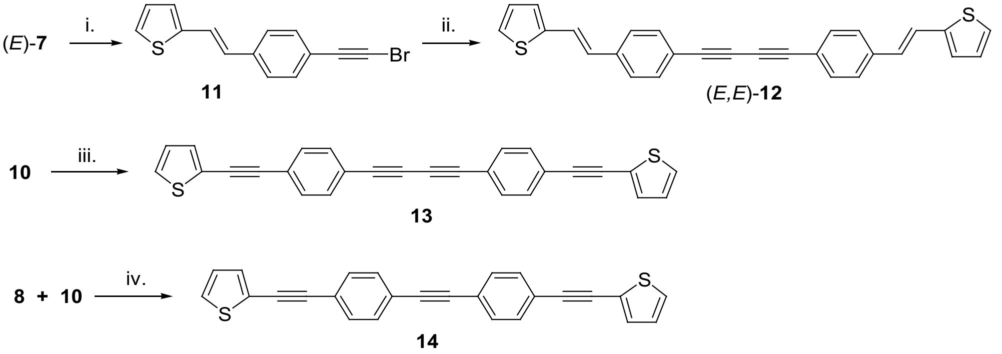
2-(*p*-Iodophenylethynyl)thiophene (**8**) (white solid, 89–91 °C, hexane), was prepared in quantitative yield from (*E*)-**5** by bromine addition followed by treatment with potassium *tert*-butoxide. The heterocoupling reaction of **8** with 2-methyl-3-butyn-2-ol, catalyzed by the palladium/copper system, gave propargyl intermediate **9** in good yield (white solid, mp 102–105 °C, 85%), which by subsequent treatment with powdered sodium hydroxide in dry toluene afforded terminal acetylene **10**,[10] yellow solid, mp 90–92 °C, hexane in excellent yield (94%).

The oxidative homocoupling of alkynes (*E*)-**7** or **10** afforded (*E*,*E*)-**12** or **13**, respectively, with an extended conjugation through the 1,3-butadiyne chain. The oxidative homocoupling of compound (*E*)-**7** in presence of cuprous chloride, under the Glaser (or Eglinton) conditions, failed. In this case, the 1,3-butadiyne (*E*,*E*)-**12** was obtained by means of the Cadiot–Chodkiewicz reaction. Thus, the oxidative bromination of compound (*E*)-**7** in situ with potassium hypobromide gave (*E*)-**11** in good yield, which in the presence of cuprous chloride, furnished (*E*,*E*)-**12** as a yellow solid, mp > 300 °C, in moderate yield (40%, Scheme 3).

In contrast, the 1,3-butadiyne derivative **13** was obtained in good yield by oxidative homocoupling reaction of the terminal acetylene **10** by the Eglinton–Glaser reaction, catalyzed by cuprous chloride in pyridine at room temperature under oxygen atmosphere (yellow solid, mp 239–240 °C, dichloromethane, 71%, Scheme 3). The different behaviour of (*E*)-**7** seems to be due to



Scheme 2. Reagents and conditions: NBS/CCl_4; (ii) PPh_3; (iii) KO^tBu, Furfural, toluene; (iv) EtOH, sunlight, I_2; (v) Br_2, CCl_4, KO^tBu; (vi) $PdCl_2(PPh_3)_2$, CuI, 2-methyl-3-butyn-2-ol; (vii) NaOH, toluene, at reflux.



Scheme 3. Reagents and conditions: KOBr, H_2O/THF; (ii) (*E*)-**6**, Et_2NH, $NH_2OH{\cdot}HCl$, Cu_2Cl_2, MeOH; (iii) Cu_2Cl_2, O_2, pyridine; (iv) $PdCl_2(PPh_3)_2$, Cu_2I_2, $HNEt_2$.

coordination of the double bond to the cuprous salt catalyst thus inhibiting the intermediate cuprous acetylide formation.[17]

The 1,3-diyne **13** was analyzed by mass spectrometry (MALDI-TOF technique) using a laser radiation at 337 nm, in a complete volatilization of the sample. Hence, at the laser irradiation time, the topo-oligomerization of **13** was detected on the mass spectrum,[18] giving a mixture of oligomers together with the 1,3-diyne monomer **13** (73%), in the following distribution: dimer 21%; trimer 4%; tetramer 1% and the 1,3-diyne pentamer in traces.

A conjugate homologous structure **14** was synthesized as a conjugate reference structure to compare the optical properties of the mono-yne and the 1,3-diyne structure **13**. Compound **14** was obtained by heterocoupling reaction of **8** with the terminal acetylene **10**, catalyzed by the palladium/copper system, in low yield (yellow solid, mp 210–212 °C, dichloromethane, 48%, Scheme 3).

The ethynyl conjugate 1,3-diyne molecule **13** shows a unique fluorescence emission band at 421 nm with higher quantum yield than the ethenyl conjugate 1,3-diyne **12**, which displays two emission bands at 427 and 454 nm (Table 1). This fact contrasts with the low quantum yield observed in the 1,3-diene (*E*,*E*)-**2** versus the 1,3-diyne **4** (no emission fluorescence). The conjugated mono-yne molecule **14** shows two fluorescence emission bands at 390 and 410 nm with a considerable quantum yield although lower than that of 1,3-diyne **13**. Hence, the conjugated 2-ethynylthiophene 1,3-diyne (**13**) exhibits a higher than expected quantum yield of the fluorescence emission as compared with 2-ethenylthiophene 1,3-diyne (*E*,*E*-**12**) or the mono-yne compound (**14**), (Table 1).

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19. All the new compounds give satisfactory elemental analyses. Selected spectral data for the new nanostructure are given (^{1}H NMR was registered in $CDCl_3$ at 300 MHz, and the chemical shifts are given in δ with TMS as an internal reference and constants coupling J are given in Hz). Compound **2**, ^{1}H NMR: 7.17 (d, 2H, $J = 4.4$ Hz); 7.02 (d, 2H, $J = 6.9$ Hz); 6.99 (dd, 2H, $J = 6.9$ and 4.4 Hz); 6.78 and 6.68 (d, 2H, $J = 17.0$ Hz). Compound **7**, ^{1}H NMR: 7.40 (d, 2H, $J = 8.6$ Hz); 7.39 (d, 2H, $J = 8.6$ Hz); 7.24 (d, 1H, $J = 16.1$ Hz); 7.22 (d, 1H, $J = 5.0$ Hz); 7.08 (d, 1H, $J = 3.4$ Hz); 7.00 (dd, 1H, $J = 5.0$ and 3.4 Hz); 6.88 (d, 1H, $J = 16.1$ Hz); 3.15 (s, 1H). Compound **10**, ^{1}H NMR: 7.46 (s, 4H); 7.32 (d, 1H, $J = 4.8$ Hz); 7.30 (d, 1H, $J = 3.2$ Hz); 7.03 (dd, 1H, $J = 4.8$ and 3.2 Hz); 3.19 (s, 1H). Compound **12**, ^{1}H NMR: 7.45 (d, 2H, $J = 8.6$ Hz); 7.40 (d, 2H, $J = 8.6$ Hz); 7.24 (d, 1H, $J = 16.1$ Hz); 7.21 (d, 1H, $J = 5.0$ Hz); 7.09 (d,1H, $J = 3.4$ Hz); 7.01 (dd, 1H, $J = 5.0$ and 3.4 Hz); 6.88 (d, 1H, $J = 16.1$ Hz). Compound **13**, ^{1}H NMR: 7.49 (s, 8H); 7.33 (d, 2H, $J = 5.4$ Hz); 7.30 (d, 2H, $J = 3.8$ Hz); 7.03 (dd, 2H, $J = 5.4$ and 3.8 Hz). Compound **14**, ^{1}H NMR: 7.49 (s, 8H); 7.33 (d, 2H, $J = 5.2$ Hz); 7.30 (d, 2H, $J = 3.7$ Hz); 7.03 (dd, 2H, $J = 5.2$ and 3.7 Hz).