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Synthesis and optical properties of conjugated *N*,*N*-dimethyl and thienyl end-capped 2,5-(arylethynyl)thiophene oligomer structures

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Abstract—End-capped (*N*,*N*-dimethylaminophenyl) and 2′-thienylethynyl 2,5-thiophene oligomer structures were synthesized by heterocoupling between the terminal acetylenes such as: *p*-(*N*,*N*-dimethylaminophenyl)ethyne (**3**) [or 1-(*p*-(*N*,*N*-dimethylaminophenyl)-2-*p*-(ethynylphenyl)ethyne, **4**]; *p*-(β-ethenyl-2′-thienyl)phenylethyne (*E*-**9**) [or *p*-(β-ethynyl-2′-thienyl)phenylethyne, **11**], and 2,5-diiodothiophene, catalyzed by the $Cl_2Pd(PPh_3)_2$/CuI system, in good to excellent yields. The 2,5-di[(3′,5′-di(trimethylsilylethynyl)-phenyl]$_x$-1-ethynyl]thiophene oligomers were prepared by heterocoupling between 3′,5′-di[(trimethylsilylethynyl)phenyl]$_x$-1-ethyne ($n = 0$–2) terminal acetylenes and 2,5-diiodothiophene, in excellent yields. The terminal acetylenes were efficiently prepared by a specific protection-deprotection methodology. All the ethynylphenyl compounds obtained show fluorescence radiation emission, with a bathochromic shift of the wavelength that increases with the chain conjugation.

1. Introduction

The insertion of thiophene in the linear ethynylphenyl conjugated chain, gives a higher electron delocalization to the molecule.[1] In general, the conjugated molecules, integrating the thiophene rings and the end-capped *N*,*N*-dimethylaminophenyl moiety, of precise length and constitution, exhibit high thermal stability[2,3] and show intrinsic electronic properties such as: luminescence,[4] redox,[5] and charge transport.[6] Moreover, the compounds are very stable, easy to functionalize, and soluble in most organic solvents.[7] The improvement of electronic strength effect was obtained by varying the classical donor and acceptor groups on the conjugated system,[8] and 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 compounds for preparing end-capped thienyl oligomers and conjugated structures with angular geometry. The *para*-connection of two acetylene units guarantees the conjugated electronic communication. Thus, cyclic oligomers with nanometre diameter, integrated by 2,5-thienyl and *para*-phenylethynyl rings, can be prepared.[11]

We now report the synthesis of conjugated 2,5-thiophene ring with the end-capped 2-ethenyl, 2-ethynyl thienyl and *N*,*N*-dimethylaminophenyl moieties, which are attractive and promising by their fluorescence properties.

2. Results and discussion

The syntheses of 2,5-di(phenylethynyl)thiophene structures with π-extended conjugation having the *N*,*N*-dimethylamino donor group has been undertaken. Hence, the linear terminal acetylenes *p*-(*N*,*N*-dimethylaminophenyl)ethyne (**3**) and 1-(*p*-*N*,*N*-dimethylaminophenyl)-2-(*p*-ethynylphenyl) ethyne (**4**) were prepared, starting of *p*-(*N*,*N*-dimethylamino)iodobenzene (**1**).

Compound **1** was obtained by reductive amination with formaldehyde and sodium cyanoborohydride in acetic acid, in practically quantitative yield (mp 105–107 °C, Scheme 1). The heterocoupling reaction between the iodoarene **1** and 2-methyl-3-butyn-2-ol, in triethylamine at room temperature, catalyzed by the palladium/copper system, gives the propargyl derivative **2** in good yield

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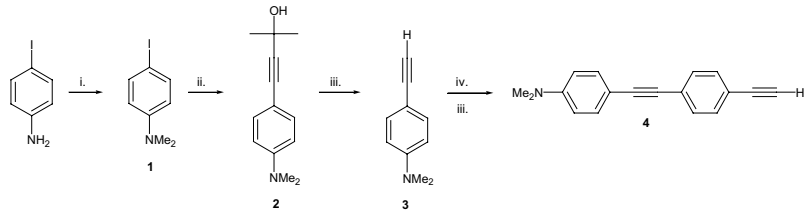


Scheme 1. Reagents and conditions: (i) $NaCNBH_4$, formaldehyde, AcOH; (ii) 2-methyl-3-butyn-2-ol, $Cl_2Pd(PPh_3)_2$, CuI, NEt_3; (iii) NaOH, toluene at reflux; (iv) 4-(*p*-iodophenyl)-2-methyl-3-butyn-2-ol, $Cl_2Pd(PPh_3)_2$, CuI, NEt_3.

(mp 71–73 °C, 85%).[12] Finally, compound **2** was treated with powdered sodium hydroxide in toluene at reflux temperature, giving the terminal acetylene **3** in practically quantitative yield (mp 51–53 °C).[12]

In the same way, the heterocoupling reaction between the acetylene **3** and 4-(*p*-iodophenyl)-2-methyl-3-butyn-2-ol, in the presence of the palladium/copper catalyst system, and successive deprotection with powdered sodium hydroxide, in toluene at reflux temperature, gave **4** as a white solid, mp 138–140 °C, in practically quantitative yield (Scheme 1).

Now, the terminal acetylenes **3** and **4** serve to prepare the end-capped (*N*,*N*-dimethylaminophenyl)-ethynyl-2,5-thiophene oligomers.

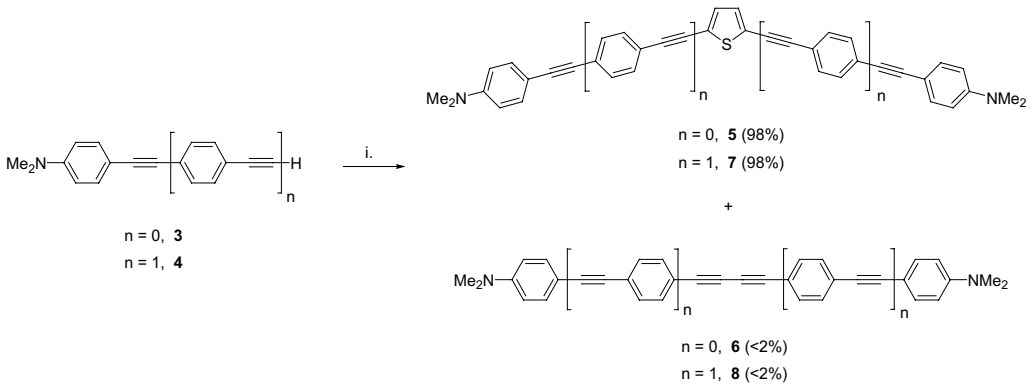
Thus, the syntheses of the 2,5-disubstituted thiophene conjugated compound **5**, was carried out by heterocoupling between the terminal acetylene **3** and 2,5-di(iodo)thiophene, in triethylamine at room temperature, in the presence of the palladium/copper catalyst system, providing 2,5-di(*p*-*N*,*N*-dimethylaminophenylethynyl)thiophene (**5**), as a yellow solid, mp 181–183 °C, in excellent yield (98%, Scheme 2); 1,3-butadiyne **6** (2%), was also isolated as a yellow solid, mp 233–234 °C. Compound **6** results by oxidative homocoupling of the terminal acetylene **3** in the presence of the catalyst system.[13]. The same heterocoupling reaction between the terminal acetylene **3** and 2,5-dibromothiophene as the haloarene, only gives the 1,3-butadiyne derivative **6**.

The heterocoupling reaction between 2,5-di(iodo)thiophene and the terminal acetylene **4**, catalyzed by the palladium/copper system, in triethylamine at room temperature, gives 2,5-di[(*p*-*N*,*N*-dimethylaminophenylethynyl)-*p*-(phenylethynyl)]thiophene (**7**) as an orange solid, mp 227–230 °C, in excellent yield (98%, Scheme 2). The oxidative homocoupling product **8**, brown solid, mp > 260 °C, was detected in very low yield (<2%).

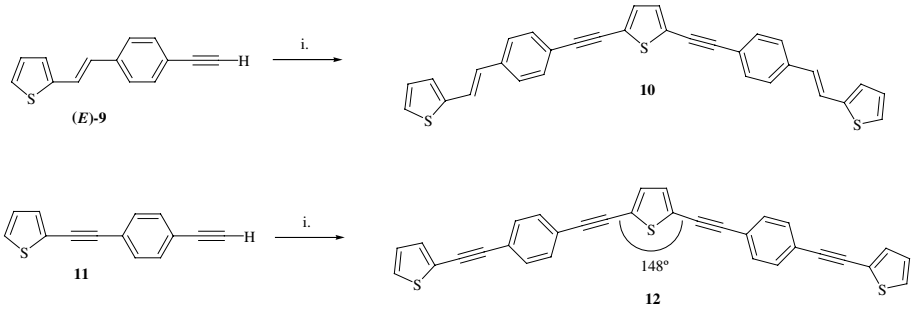
On the other hand, the end-capped thienyl conjugated chains were also prepared. The heterocoupling reaction between the thienylethenyl terminal acetylene (*E*)-**9**,[14] (or the thienylethynyl terminal acetylene **11**[14]) and 2,5-diiodothiophene, in triethylamine, in the presence of the palladium/copper catalyst system, afforded conjugated 2,5-thiophene structure **10**, as a yellow solid, mp 261–262 °C (65%) (or 2,5-di(thienylethynyl)thiophene **12**, yellow solid, mp 234–235 °C, 85%) in good yield (Scheme 3). Compounds **5**, **7**, **10** and **12** exhibit angular geometry with an interchain angle about 148°.[15]

Moreover, the heterocoupling between the conjugated terminal acetylenes **13**–**15** (trigonal–linear geometry) and 2,5-diiodothiophene was carried out.[16] Hence, the heterocoupling between the terminal acetylene **13** ($n = 1$), (or **14**, $n = 2$, or **15**, $n = 3$) and 2,5-di(iodo)thiophene, in triethylamine at room temperature, catalyzed by the palladium/copper system, gives the conjugated compound **16**, as a yellow solid, mp 139–140 °C (97%), in excellent yield, (or **17**, yellow solid, mp 218–220 °C, 95%, or **18**, yellow solid, mp 291–293 °C, 95%, Scheme 4).

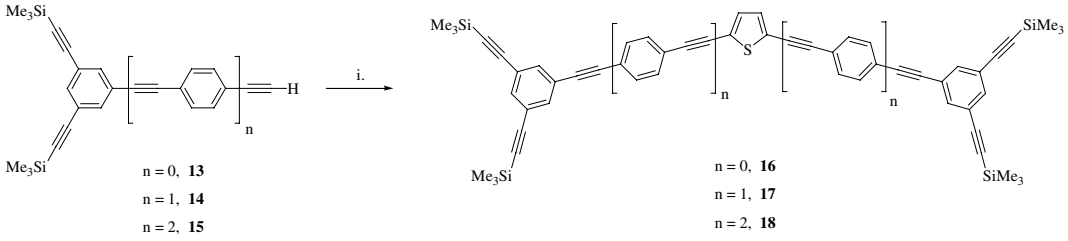
The UV–visible spectra of the conjugated compounds **5** and **7**, **10** and **12** and **16**–**18** show a bathochromic effect on the absorption wavelength and a strong increasing on



Scheme 2. Reagents: (i) 2,5-Diiodothiophene, $Cl_2Pd(PPh_3)_2$, CuI, NEt_3.



Scheme 3. Reagents: (i) 2,5-Diiodothiophene, $Cl_2Pd(PPh_3)_2$, CuI, NEt_3.



Scheme 4. Reagents: (i) 2,5-Diiodothiophene, $Cl_2Pd(PPh_3)_2$, CuI, NEt_3.

the molar extinction coefficient (ε), Table 1. Moreover the 2,5-thiophene ring included in the linear ethynylphenyl conjugated chain shows slightly higher ε values but an important decreasing of the quantum yield with respect to the linear 1,4-phenyl ring included in the conjugated ethynylphenyl chain.[16]

All the 2,5-disubstituted thiophene conjugated structures show fluorescence radiation emission, the wavelength and quantum yield are summarized in Table 1. Some considerations can be remarked: (a) There are a significant increase in the quantum yield of the radiation emission with the ethynylphenyl units in the chain, compounds **5** and **7** and **16**–**18**; (b) There is an important increase in the quantum yield for the triple versus double bond connecting with the thiophene ring unit, compounds **12** and **10**, respectively; (c) The ethynylphenyl chains show two fluorescence wavelength emission bands (compounds **12** and **16**–**18**), while the 1,4-(*N*,*N*-dimethylaminophenyl)ethynyl and the ethenylphenylethynyl chains show a unique emission band (compounds **5**, **7** and **10**); (d) The emission wavelength bands for the 1,4-(*N*,*N*-dimethylaminophenyl) (**5**, **7**) and for the 3,5-di(trimethylsilylethynyl)phenyl end-capped homologous exhibit a bathochromic shift for each ethynylphenyl unit in the conjugated chain, respectively.

Table 1. Wavelengths for the first absorption and fluorescence emission maxima for the compounds **5**, **7**, **10**, **12**, **16**, **17** and **18**[17] in CH_2Cl_2 at room temperature

Compd	UV–vis λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	Fluorescence λ_{max} (nm)	Φ_f
5	385	57,500	456	0.23[a]
7	393	104,320	512	0.30[b]
10	367	21,850	440	0.10[a]
12	379	44,000	398, 423	0.34[a]
16	355	46,900	391, 410	0.20[a]
17	379	78,900	421, 447	0.42[a]
18	377	113,000	429, 454	0.54[a]

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

[b] Fluorescence quantum yield was determined relative to quinine sulfate in 1 N H_2SO_4.

Hence, new 2,5-di(ethynylphenyl)thiophene conjugated oligomers were satisfactorily obtained by means of the Sonogashira reaction using a 2,7-dihalothiophene (Br, I). The yields are excellent and the iodo derivative shows highest versatility. All the conjugated compounds show fluorescent properties.

Acknowledgements

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References and notes

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17. All new compounds were recrystallized in dichloromethane and give satisfactory spectral and elemental analyses. Selected spectral data 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 **5**, ^{1}H NMR: 7.38 (d, 4H, $J = 8.0$ Hz); 7.05 (s, 2H); 6.64 (d, 4H, $J = 8.0$ Hz); 2.99 (s, 12H). Compound **7**, ^{1}H NMR: 7.46 (br s, 8H); 7.43 (d, 4H, $J = 8.0$ Hz); 7.16 (s, 2H); 6.66 (d, 4H, $J = 8.0$ Hz); 3.00 (s, 12H). Compound **10**, ^{1}H NMR: 7.45 (s, 8H); 7.35 (d, 1H, $J = 4.8$ Hz), 7.27 (d, 2H, $J = 15.9$ Hz); 7.15 (d, 2H, $J = 3.8$ Hz), 7.10 (s, 2H); 7.02 (dd, 2H, $J = 4.8$ and 3.8 Hz), 6.90 (d, 2H, $J = 15.9$ Hz). Compound **12**, ^{1}H NMR: 7.49 (s, 8H); 7.32 (d, 2H, $J = 4.8$ Hz); 7.31 (d, 2H, $J = 4.3$ Hz); 7.18 (s, 2H); 7.03 (dd, 2H, $J = 4.8$ and 4.3 Hz). Compound **16**, ^{1}H NMR: 7.55 (d, 4H, $J = 1.6$ Hz); 7.53 (t, 2H, $J = 1.6$ Hz); 7.14 (s, 2H); 0.24 (s, 36H). Compound **17**, ^{1}H NMR: 7.56 (d, 4H, $J = 1.6$ Hz); 7.53 (t, 2H, $J = 1.6$ Hz); 7.51 (d, 4H, $J = 8.7$ Hz); 7.46 (d, 4H, $J = 8.7$ Hz); 7.18 (s, 2H); 0.24 (s, 36H). Compound **18**, ^{1}H NMR: 7.56 (d, 4H, $J = 1.6$ Hz); 7.53 (t, 2H, $J = 1.6$ Hz); 7.52 (br s, 8H); 7.51 (d, 4H, $J = 8.9$ Hz); 7.47 (d, 4H, $J = 8.9$ Hz); 7.18 (s, 2H); 0.25 (s, 36H).