Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron 62 (2006) 3112–3122
Tetrahedron

Synthesis of conjugated 2 and 2,5-(ethenyl) and (ethynyl)phenylethynyl thiophenes: fluorescence properties

J. Gonzalo Rodriguez,* Jorge Esquivias, Antonio Lafuente and Laura Rubio

Dpto. Química Orgánica, Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain

Received 21 November 2005; revised 20 December 2005; accepted 10 January 2006

Available online 13 February 2006

Abstract—Nano conjugated thienylethenyl and thienylethynyl compounds with controlled structure and dimensions have been efficiently prepared, by heterocoupling reaction between 1,4-(thienylethynyl)phenylacetylene (or thienylethenyl)phenylacetylene and 2- or 2,5-dihalothiophene. Conjugated 1,4-di(2-thienylethynylphenyl)- (or 2-thienylethenylphenyl)-1,3-butadiyne were obtained by the homocoupling of the terminal acetylenes in excellent yield. The end-capped (*N*,*N*-dimethylaminophenyl)- and [3,5-di(trimethylsilylethynyl)-1-ethynyl]-2,5-di(phenylethynyl)$_n$thiophene were obtained by the heterocoupling between the corresponding terminal acetylene and 2,5-di(iodo)thiophene, catalyzed by the bis(triphenylphosphine)palladium and cuprous iodide system in excellent yield.

1. Introduction

Nanometer-sized molecules of precise length showing π extended conjugation, exhibit in general high thermal stability and can present electroconductive, magnetic and optical properties.[1] Several potential applications such as artificial photosynthesis,[2] photocatalysis,[3] molecular photovoltaic cells,[4] molecular informatics,[5] and optoelectronic devices[6,7] are beginning to emerge from this new field of research.

Earlier studies on the heteroaromatic systems containing the thiophene ring shows three significant details: (i) an increasing of the first molecular hyperpolarizability (β)[8] (ii) the substitution of the thiophene ring by an aryl one, changes the donor versus the acceptor effect, [9] (iii) the electronic nature of the heteroaromatic ring affects the donor or acceptor strength through the inductive effects.[9]

Therefore, polythiophene has been obtained as a conjugated polymer with many interesting optical and electronic properties such as electrochromism and near-metallic conductivity.[10] Oligomers of thiophene are also technologically important materials and have been used in prototype organic thin-film transistors.[11] Interest in materials with these properties has directed substantial efforts towards the preparation of conjugated substituted oligo- and polythiophenes,[12] which exhibit an electronic conductivity that was dependent on the resonance along the polymeric chain.[10] Thiophene dendrimers with π-extended conjugated chains, shown that the π–π* conduction band decreases from the periphery to the heart, increasing the fluorescence quantum yield.[13] The conjugated thiophene chains show interesting solvatochromic properties.[14]

Recently, we have developed π-extended conjugated structures with important optical properties.[15] Now, we report the synthesis of conjugated end-capped (*N*,*N*-dimethylaminophenyl)- and [3,5-di(trimethylsilylethynyl)-1-ethynyl]-2,5-di(phenylethynyl) molecules containing the thiophene ring. Moreover, the conjugation effect through the double or triple bond linking the thiophene ring and the conjugated chains are also considered.

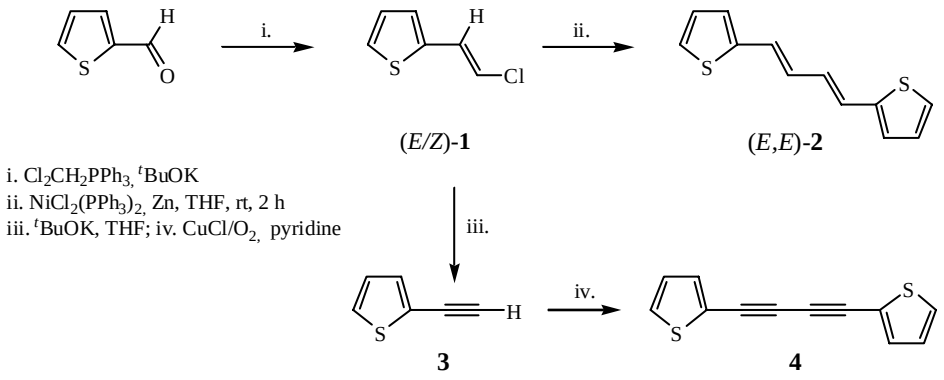
2. Results and discussion

The synthesis of (*E*,*E*)-1,4-di(2′-thienyl)-1,3-butadiene, (*E*,*E*)-**2**[16] and 1,4-di(2-thienyl)-1,3-butadiyne (**4**),[17] was carried out to compare the polarity-polarizability produced by the double or triple bond of the thiophene conjugated systems.

Thus, compound (*E*,*E*)-**2** was obtained by the homocoupling reaction of 2-(2′-chlorovinyl)thiophene (**1**), catalyzed by the zerovalent nickel(triphenylphosphine)$_n$ complexes. The mixture (*Z*/*E*)-2-chlorovinylthiophene (**1**),[18] (*Z*/*E*, 43:57), was obtained by the Wittig reaction between furfural and

Keywords: Arylethynylthiophenes; π-Extended conjugation; Eglinton–Glaser reaction; Cadiot–Chodkiewicz reaction; Sonogashira reaction; Fluorescence.
* Corresponding author. Tel.: +34 914974715; fax: +34 914973966; e-mail: gonzalo.rodriguez@uam.es

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.01.032



Scheme 1.

the (chloromethyl)(triphenyl)phosphonium ylide, in good yield. The homocoupling reaction of the (*Z*/*E*)-**1** mixture was catalyzed by the zerovalent nickel complexes, prepared in situ by reaction of dichloro bis[(triphenyl)phosphine]-nickel and powdered zinc in tetrahydrofuran giving (*E*,*E*)-1,4-di(2-thienyl)-1,3-butadiene **2** as the unique isomer in good yield (62%), Scheme 1.

Moreover, the (*Z*/*E*)-**1** mixture was treated with potassium *tert*-butoxide, at room temperature, giving 2-ethynylthiophene (**3**) in good yield (77%).[19] The oxidative dimerization of the terminal acetylene **3** was catalyzed by cuprous chloride in pyridine, under oxygen atmosphere, affording 1,4-di(thienyl)-1,3-butadiyne (**4**), in excellent yield (91%), Scheme 1.

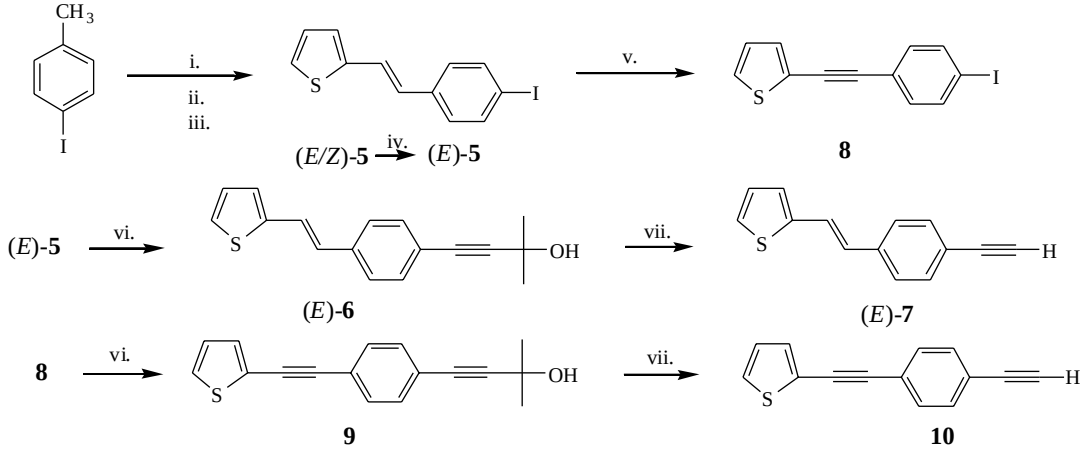
2.1. Synthesis of the terminal acetylenes

The previous synthesis of terminal acetylenes are necessary for the construction of the π extended conjugated thienyl-(*p*-ethynylphenyl) structures. Thus, the conjugated units of 2-(*E*)-phenylethenyl- and phenylethynyl- for the thiophene structures were prepared by heterocoupling between 2-[*p*-(iodophenyl)-2′-ethenyl]thiophene (*E*)-**5** and the ethynyl analogue **8**. Compound (*E*)-**5** was prepared by the Wittig reaction between furfural and *p*-(iodobenzyl)(triphenyl)-phosphonium ylide, giving the (*Z*/*E*)-**5** mixture (50:50).[20] The complete isomerization of (*Z*/*E*)-**5** to (*E*)-**5** was carried out by sunlight exposure in presence of iodine crystals, Scheme 2.

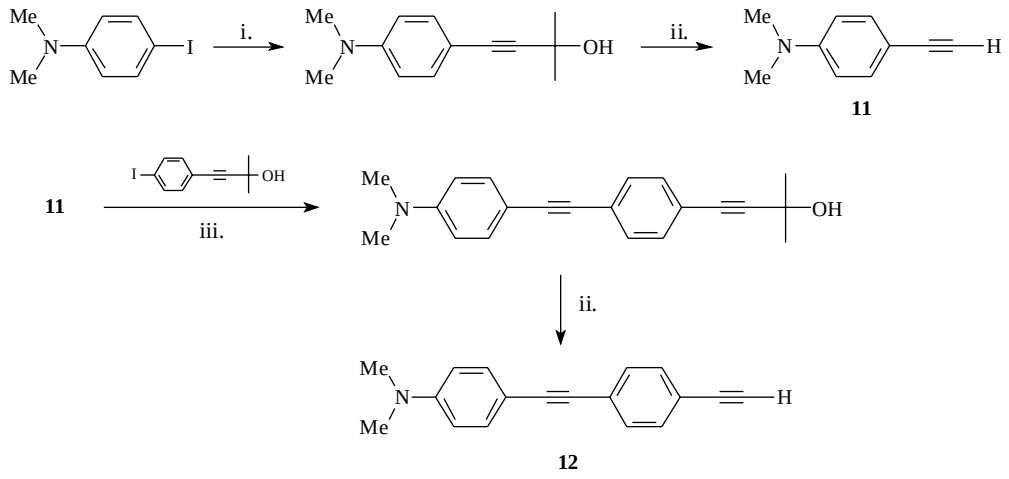
Now, the heterocoupling of (*E*)-**5** with 2-methyl-3-butyn-2-ol in presence of dichloro bis[(triphenyl)phosphine]palladium and cuprous iodide catalyst system, in diethylamine at room temperature, gives the propargyl compound (*E*)-**6**, which by treatment with powdered sodium hydroxide in dry toluene at reflux temperature gives the terminal acetylene (*E*)-**7** in good yield.

The 2-(*p*-iodophenylethynyl)thiophene (**8**) was prepared from (*E*)-**5** by bromine addition and successive elimination with potassium *tert*-butoxide in quantitave yield. The heterocoupling reaction between **8** and 2-methyl-3-butyn-2-ol, in presence of the palladium–copper catalyst, affords the propargyl intermediate **9** in good yield (85%), which was treated with powdered sodium hydroxide in dry toluene, giving the terminal acetylene **10**.

Thus, the heterocoupling between the acetylene **11** and 4-(hydroxyl-3-methyl-1-butyn)-1-iodobenzene gives an



Scheme 2.



i. 2-Methyl-3-butyn-2-ol, CuI, $PdCl_2(PPh_3)_2$, NEt_3; ii. NaOH, toluene at reflux; iii. CuI, $PdCl_2(PPh_3)_2$, NEt_3.

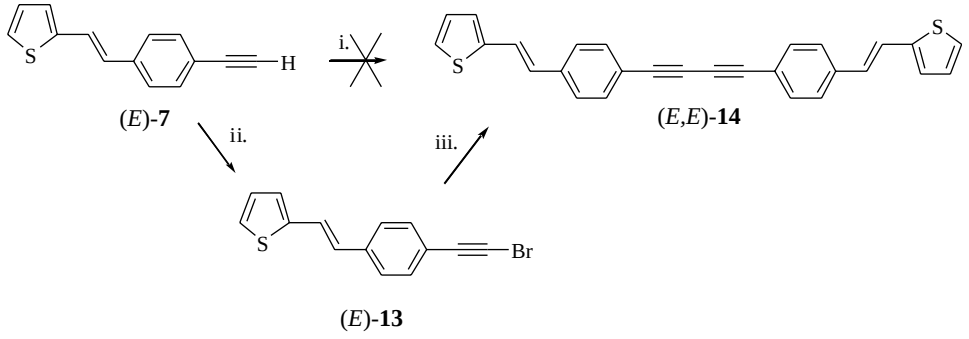
Scheme 3.

intermediate propargyl derivative, which by treatment with sodium hydroxide in dry toluene at the reflux temperature yields compound **12**, as a red solid, in excellent yield (90%), Scheme 3.

2.2. Oxidative dimerization of the terminal acetylenes

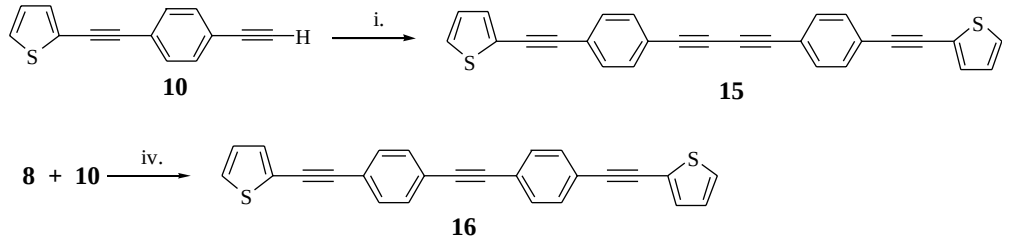
To extend the conjugation of the terminal acetylenes (*E*)-**7** and **10** were transformed by catalytic oxidative dimerization in (*E*,*E*)-**14** and **15**, respectively. Thus, the oxidative homocoupling of (*E*)-**7** was carried out in presence of cuprous chloride and under the Glaser (or Eglinton) conditions fails. The 1,3-butadiyne (*E*,*E*)-**14** was obtained by the Cadiot–Chodkiewicz reaction. Thus, through the oxidative bromination of compound (*E*)-**7**, which was carried out in situ with potassium hypobromide giving (*E*)-**13** in good yield, which in presence of cuprous chloride gives (*E*,*E*)-**14** in moderate yield, Scheme 4.

In contrast, the 1,3-butadiyne derivative **15** was obtained by oxidative homocoupling reaction of the terminal acetylene **10**, catalyzed by cuprous chloride in pyridine, at room temperature, under oxygen atmosphere, Scheme 5. The different reactive behavior of (*E*)-**7**, seems to be due to



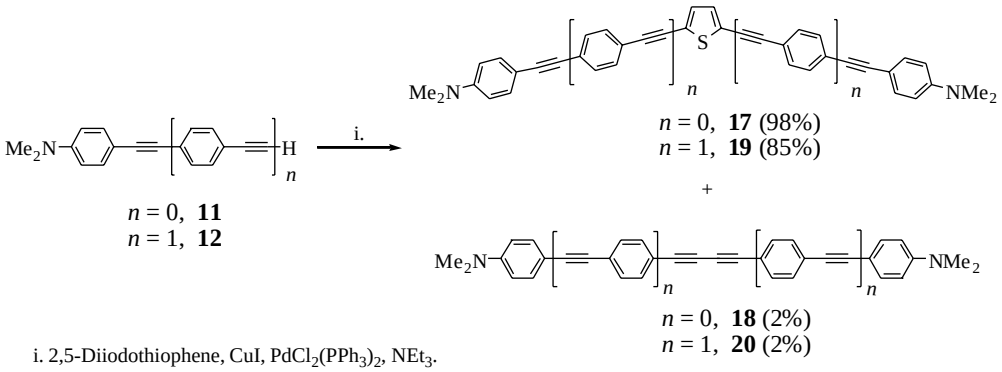
i. CuCl, O_2, pyridine; ii. KOBr, H_2O/THF; iii. (*E*)-**6**, Et_2NH, $NH_2OH{\cdot}HCl$, CuCl, MeOH.

Scheme 4.



i. CuCl, O_2, pyridine; ii. $PdCl_2(PPh_3)_2$, CuI, 2-methyl-3-butyn-2-ol.

Scheme 5.



i. 2,5-Diiodothiophene, CuI, $PdCl_2(PPh_3)_2$, NEt_3.

Scheme 6.

the double bond coordination to the cuprous salt catalyst, avoiding the intermediate cuprous acetylide formation.[21]

The 1,3-diyne **15** was analyzed by mass spectrometry (MALDI-TOF technique) using a laser radiation at 337 nm, with complete volatilization of the sample. During the laser irradiation the topo-oligomerization products were detected in the mass spectrum,[22] in the following ratio: dimer (21%); trimer (4%); tetramer (1%) and pentamer (in traces).

The conjugated structural homologue **16** was synthesized as a conjugated reference to compare their optical properties with the 1,3-diyne structure **15**. Compound **16** was obtained by the heterocoupling reaction between **8** and the terminal acetylene **10**, catalyzed by the palladium–copper system, in good yield (78%), Scheme 5.

2.3. Synthesis of the conjugated arylethynyl-2,5-thiophene structures

The heterocoupling reaction between 2,5-di(iodo)thiophene and the terminal acetylene **11**, in presence of the palladium–copper catalyst, provides 2,5-[di(*p*-*N*,*N*-dimethylamino)-phenylethynyl]thiophene (**17**) (98%) and the 1,3-butadiyne derivative **18** (2%). Compound **18** seems to be formed by the oxidative dimerization of the terminal acetylene, resulting from the Eglinton–Glaser behavior of the catalyst. At this point, it is remarkable the high reactivity of 2,5-di(iodo)thiophene compared with 2,5-dibromothiophene, that gives only the 1,3-butadiyne derivative (**18**).

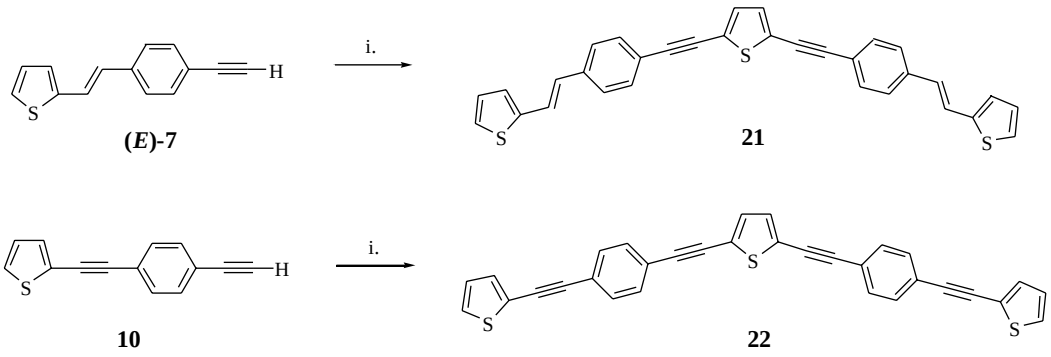
Similarly, 2,5-[di(*p*-*N*,*N*-dimethylamino)(phenylethynyl)(phenylethynyl)]thiophene (**19**) was obtained in good yield (85%) by the heterocoupling reaction between 2,5-di(iodo)thiophene and the terminal acetylene **12**, catalyzed with the palladium–copper system. In this reaction was also detected the oxidative dimerization product **20** in very low yield (2%), Scheme 6.

On the other hand, compounds **17** and **19** exhibit the conjugated chains on 2,5 positions of the thiophene ring forming a high-angle structure. High-angle structures containing the end-capped thiophene ring were also synthesized.

Thus, the heterocoupling reaction between 2,5-di(iodo)thiophene and the thienylethenyl terminal acetylene (*E*)-**7** (or the thienylethynyl terminal acetylene **10**) affords the conjugated high-angle structure **21** as a yellow solid in a 65% yield (or **22**, 85%), Scheme 7.

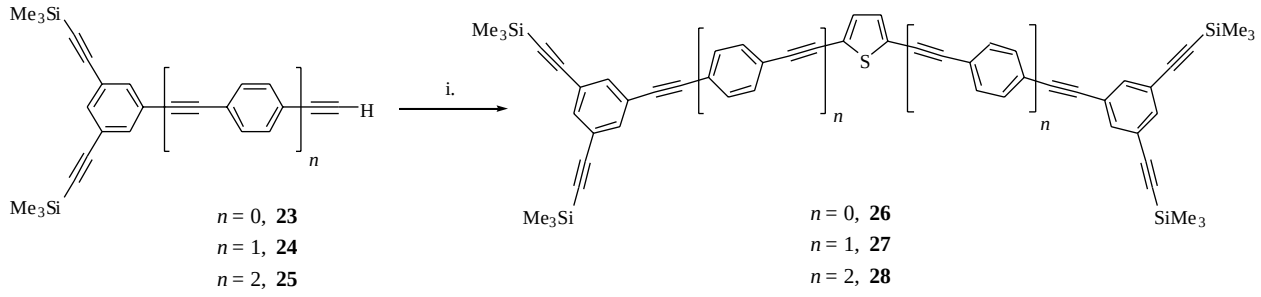
Finally the synthesis of high-angle 2,5-(ethynylphenyl)thiophenes, with trigonal-linear 3,5-di(trimethylsilylethynyl)-1-phenylethynyl structure, was carried out by the heterocoupling reaction between 2,5-di(iodo)thiophene and the terminal acetylenes **23** ($n=1$), **24** ($n=2$) or **25** ($n=3$), previously prepared,[14b] catalyzed by the palladium–copper system, giving the conjugated compounds **26** (97%), **27** (95%) and **28** (95%), respectively, Scheme 8.

The oxidation potential of compounds **26**–**28** was determined by cyclic voltammetry resulting of 1.04, 1.08 and



i. 2,5-Diiodothiophene, $PdCl_2(PPh_3)_2$, NEt_3, CuI.

Scheme 7.



n = 0, **23**
n = 1, **24**
n = 2, **25**

n = 0, **26**
n = 1, **27**
n = 2, **28**

i. 2,5-Diiodothiophene, $PdCl_2(PPh_3)_2$, CuI, NEt_3.

Scheme 8.

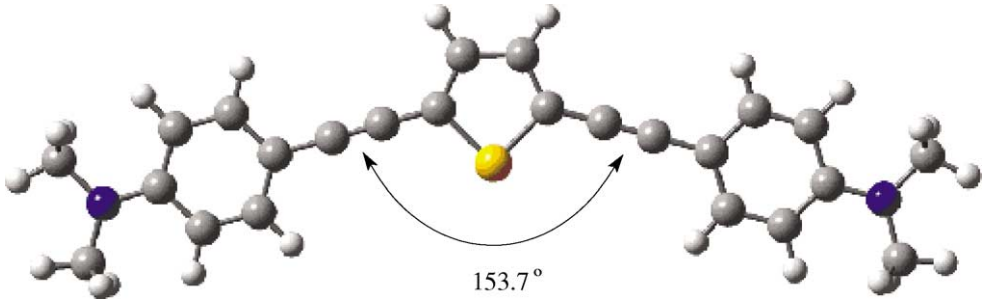


Figure 1. Computed analysis of compound **17**.

1.08 V, respectively, as irreversible oxidizable peaks. Hence, no dependence of the oxidative potential on the chain conjugation must be expected.

Compounds **17**, **19**, **21**, **22** and **26–28** exhibit the referred high-angle geometry for the linear chain on 2,5- positions of the thiophene ring. The internal angle for compound **17** reaches a value of 153.7°, calculated by theoretical computational methods[23] (Fig. 1), which agrees well with the data obtained by X-ray diffraction analysis.[24]

2.4. Fluorescent properties

The UV–vis absorption and fluorescent emission radiation of the terminal acetylenes, 1,3-butadiynes and conjugated arylethynyl-2,5-thiophene structures were analyzed.

All the 1,3-butadiynes and terminal acetylenes show fluorescence emission radiation in solution of dichloromethane. In a general analysis, it is noticeable that (*E*,*E*)-1,4-di(thienyl)-1,3-diene (*E*,*E*)-**2**, exhibits a fluorescent radiation with very low quantum yield, while 1,4-di(thienyl)-1,3-diyne (**4**) does not show appreciable fluorescence emission radiation in dichloromethane, Table 1.

The terminal *N*,*N*-dimethylamino compounds, such as the ethynyl conjugated 1,3-diyne **15** shows an unique fluorescence emission band at 421 nm while that their ethenyl conjugated 1,3-diyne analogue **14**, shows two emission bands at 427 and 454 nm (Table 1). Similarly, the terminal *N*,*N*-dimethylamino triyne conjugated **16** also exhibits two fluorescence emission bands at 390 and 410 nm with practically, the same quantum yield while their 1,3-diyne **15** shows only an emission band at 421 nm with higher quantum yield, Table 1.

The terminal *N*,*N*-dimethylamino 2,5-thiophene conjugated structures (compounds **17** and **19**) show fluorescent emission radiation with important quantum yields (Table 2). There is a significant increase of the radiation quantum yield with the conjugation by the number of

Table 1. UV–vis absorption and fluorescence emission radiation for compounds **2**, **4**, **7**, **10**, and **14–16** in CH_2Cl_2 at room temperature

Compound	UV–vis λ_{max} (nm)	ε (M^{-1} cm^{-1})	Fluorescence λ_{max} (nm)	Φ_f[a]
2	381	25,100	431	0.02
4	364	26,300	—	—
7	341	28,400	420, 450	0.13
10	337	30,000	392, 410	0.14
14	382	78,300	427, 454	0.29
15	359	81,250	421	0.36
16	352	57,100	390, 410	0.30

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

Table 2. UV–vis absorption and fluorescence emission radiation for the compounds **17**, **19**, and **21–22** in CH_2Cl_2 at room temperature

Compound	UV–vis λ_{max} (nm)	ε (M^{-1} cm^{-1})	Fluorescence λ_{max} (nm)	Φ_f
17	385	57,500	456	0.23[a]
19	393	104,320	512	0.30[b]
21	367	21,850	440, 462	0.10[a]
22	379	44,000	398, 423	0.34[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 sulphate in 1 N H_2SO_4.

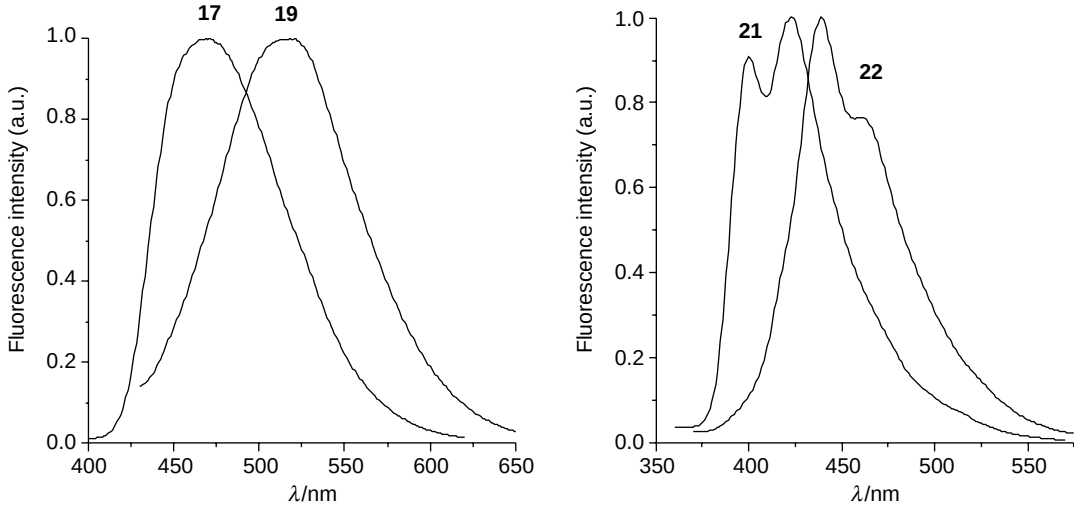


Figure 2. Normalized fluorescence emission spectra for compounds **17**, **19** and **21**–**22** in dichloromethane at room temperature.

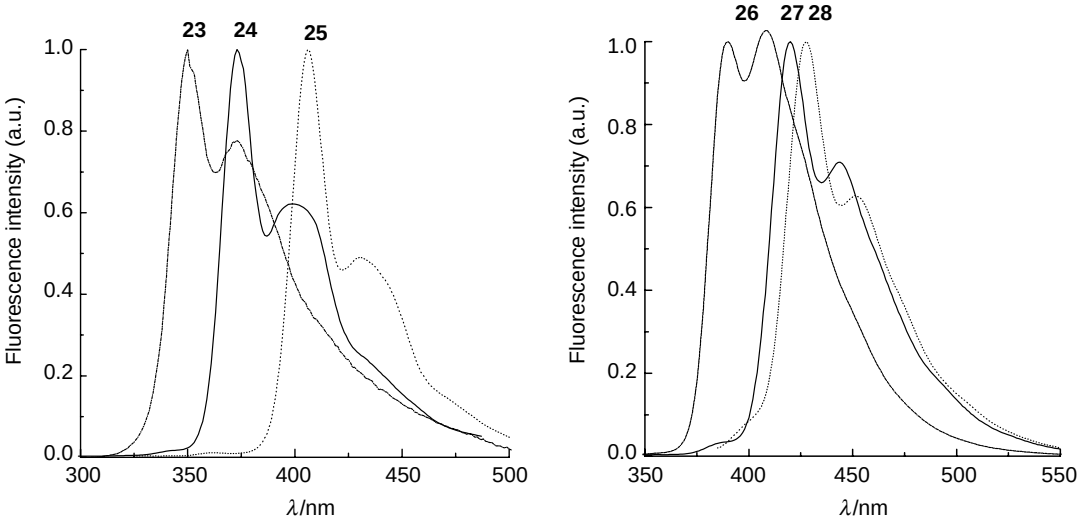


Figure 3. Normalized fluorescence emission spectra for compounds **23**–**25** and **26**–**28** in CH_2Cl_2 at room temperature.

the ethynylphenyl units in the chain, as it was observed in compounds **17** and **19**, Table 2.

However, an important increasing of the fluorescence emission quantum yield was observed in compound **22** triple bond linked to the thiophene ring versus compound **21** with the conjugated double bond connecting with the thiophene ring. Compounds **21** and **22** show two fluorescence wavelength emission bands, while the end-capped 1,4-(*N*,*N*-dimethylaminophenyl) chains show an unique emission band (compounds **17** and **19**), Figure 2.

Recently, we report the fluorescence emission of the terminal acetylenes **23**–**25** connected with different linear linkers such as benzene, 1,5-naphthalene and 1,3-diyne.[14d] In all the cases was observed a similar bathochromic shift close-up 20 nm by each ethynylphenyl unit increasing the conjugate chain. Nevertheless, the high-angle structure of the 2,5-tiophene in compounds **26**–**28** produces an irregular bathochromic shift for each ethynylphenyl unit in the conjugated chain, Figure 3. However, compounds **26**, **27** and **28** show a significant increasing in the fluorescence quantum yield with the number of the ethynylphenyl units in the conjugated chain, Table 3.

Table 3. UV–vis absorption and fluorescence emission radiation for compounds **23**–**28** in CH_2Cl_2 at room temperature

Compound	UV–vis λ_{max} (nm)	ε (M^{-1} cm^{-1})	Fluorescence λ_{max} (nm)	Φ_f[a]
23	344	55,100	350, 373	0.10
24	346	75,000	373, 395	0.28
25	345	99,100	406, 428	0.60
26	355	46,900	391, 410	0.20[a]
27	379	78,900	421, 447	0.42[a]
28	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.

3. Conclusions

New nano conjugated thienylethenyl and thienylethynyl derivatives can be synthesized through the Sonogashira

reaction between 2- or 2,5-dihalothiophene and 1,4-(thienylethynyl)phenylacetylene (or (thienylethenyl)phenylacetylene) in good yield. Conjugated 1,4-di(2-thienylethynylphenyl)- (or 2-thienylethenylphenyl)-1,3-butadiynes can be obtained by the homocoupling of the terminal acetylenes in excellent yield.

The conjugated 1,3-butadiyne derivatives can be efficiently prepared by the catalytic Eglinton–Glaser or Cadiot–Chodkiewicz reactions.

The end-capped (*N*,*N*-dimethylaminophenyl)- and [3,5-di(trimethylsilylethynyl)-1-ethynyl]-2,5-di(phenylethynyl)$_n$-thiophene were obtained in good yield by the heterocoupling between the appropriate terminal acetylene and 2,5-di(iodo)thiophene, catalyzed by the bis(triphenylphosphine)-palladium and cuprous iodide system in diethylamine.

All the new conjugated 2- or 2,5- thiophene derivatives show fluorescent radiation emission which, for the conjugation by triple bond linking ethynylphenyl module exhibit highest quantum yields than the double one (29–54%).

4. Experimental

4.1. General procedures

Melting points were determined in open capillaries and are uncorrected. FT-IR spectra were recorded using KBr pellets or NaCl plates and only partial data is reported. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 300 MHz. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 75 MHz. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform. Mass spectra were obtained at an ionizing potential of 70 eV and reported as *m*/*e* (relative intensity). Accurate masses are reported for the molecular ion (M+1) or a suitable fragment ion. Flash chromatography was performed on silica gel 60 (200–400 mesh) using the indicated solvents. The UV–vis spectra frequencies are given in nm and ε in L mol^{-1} cm^{-1}.

4.1.1. (*E*,*E*)-1,4-Di(2′-thienyl)-1,3-butadiene[16] (2) To a solution of dichlorobistriphenylphosphine nickel (915 mg, 1.4 mmol) in dry tetrahydrofuran (10 ml), under argon atmosphere was added tetrabutylammonium iodide (518 mg, 1.4 mmol) and zinc powder (136 mg, 2 mmol) and the mixture was stirred until the solution takes a dark red color. After 30 min with stirring was added a solution of 1-chloro-2-(2′-thienyl)ethene (**1**) (200 mg, 1.4 mmol) in dry tetrahydrofuran (10 ml) and the mixture was stirred overnight at room temperature. Finally, was added dichloromethane and filtered to remove the catalyst. The organic layer was dried on anhydrous magnesium sulphate, filtered off and the solvent removed. The residual solid was purified by silica gel column chromatography using hexane as the eluent. The (*E*,*E*)-1,4-di(2′-thienyl)-1,3-butadiene (**2**), 187 mg (62%), was isolated as a yellow solid, mp 140–143 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 381, 362, 268. Fluorescence (CH_2Cl_2), λ_{max} (nm): 431 (ϕ=0.021). FT-IR (KBr, cm^{-1}): 1653, 1541, 1457, 978. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (d, 2H, J=4.4 Hz); 7.02 (d, 2H, J=6.9 Hz); 6.99 (dd, 2H, J=6.9, 4.4 Hz); 6.72 (d, 2H, J=17.0 Hz); 6.73 (dd, 2H, J=17.0, 8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.0, 128.6, 127.6, 125.9, 125.5, 124.4. MS (70 eV): 218 (M$^+$, 100), 184 (36), 173 (9), 134 (17), 121 (8), 109 (7), 97 (16).

4.1.2. (*E*)-1-(*p*-Iodophenyl)-2-(2′-thienyl)ethene (*E*)-5. To a solution of *p*-(iodobenzyl)(triphenyl)phosphonium bromide (560 mg, 1.0 mmol) in toluene (25 ml), under dryness and argon atmosphere and at 0 °C, was added potassium *tert*-butoxide (112 mg, 1.0 mmol). The mixture was stirred for 30 min and then, was slowly added a solution of 2-thiophenecarboxaldehyde (112 mg, 0.1 ml, 1.0 mmol) in anhydrous toluene (5 ml). The mixture was stirred at room temperature overnight. After evaporation of solvent, the residual solid was extracted with dichloromethane and a little amount of water. The organic layer was dried on anhydrous magnesium sulphate, filtered off and solvent removed, to give a (*Z*/*E*) isomers mixture (50:50).

A solution of the (*Z*/*E*) mixture in ethanol was completely transformed to the *E*-isomer by sunlight exposure for 72 h, giving (*E*)-1-(*p*-iodophenyl)-2-(2′-thienyl)ethene (*E*)-**5**, as a yellow solid, mp 155–157 °C, 129 mg (41%). UV–vis (CH_2Cl_2), λ_{max} (nm): 335, 284. FT-IR (KBr, cm^{-1}): 3075, 1525, 1487, 1429, 960, 815. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (d, 1H, J=5.0 Hz); 7.60 (d, 2H, J=8.4 Hz); 7.23 (d, 1H, J=16.1 Hz); 7.19 (d, 2H, J=8.4 Hz); 7.06 (d, 1H, J=3.4 Hz); 7.00 (dd, 1H, J=5.0, 3.4 Hz); 6.83 (d, 1H, J=16.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.4, 137.7, 136.5, 127.7, 127.3, 127.0, 126.5, 124.8, 122.5, 92.6. $C_{12}H_9IS$ (311.95): Anal. Calcd C 46.17, H 2.91; found: C 45.96, H 3.12.

4.1.3. 1-(Bromo-*p*-iodophenyl)-2-(bromo-2′-thienyl)-ethane. To a solution of (*E*)-1-(*p*-iodophenyl)-2-(2′-thienyl)ethene (*E*)-**5** (850 mg, 2.72 mmol) in tetrachloromethane (30 ml), at 0 °C was added slowly bromine (435.2 mg, 2.72 mmol) in tetrachloromethane (60 ml), and the mixture was vigorously stirred for 6 h. The solvent was removed to give 1-(bromo-*p*-iodophenyl)-2-(bromo-2′-thienyl)ethane, as a white solid, 1.29 g (100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, 2H, J=8.1 Hz); 7.41 (d, 1H, J=4.8 Hz); 7.23 (d, 1H J=4.3 Hz); 7.22 (d, 2H, J=8.1 Hz); 7.00 (dd, 1H, J=4.8, 4.3 Hz); 5.75 (d, 1H, J=11.2 Hz); 5.30 (d, 1H, J=11.2 Hz).

4.1.4. 1-(*p*-Iodophenyl)-2-(2′-thienyl)ethylene (*E*)-8. To a solution of 1-(bromo-*p*-iodophenyl)-2-(bromo-2′-thienyl)ethane (1.29 g, 2.72 mmol) in anhydrous tetrahydrofuran (60 ml), and potassium *tert*-butoxide (919.4 mg, 8.20 mmol). The mixture was stirred at room temperature for 2 h and then, the solvent was removed to give 1-(*p*-iodophenyl)-2-(2′-thienyl)ethene (**8**) as a white solid, mp 89–91 °C, 828 mg (98%). UV–vis (CH_2Cl_2), λ_{max} (nm): 330, 310, 266. FT-IR (KBr, cm^{-1}): 3421, 1518, 1481, 819. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, 2H, J=8.4 Hz); 7.30 (d, 1H, J=5.2 Hz); 7.28 (d, 1H, J=3.4 Hz); 7.23 (d,

2H, J=8.4 Hz); 7.02 (dd, 1H, J=5.2, 3.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.5, 132.8, 132.2, 127.6, 127.2, 122.9, 122.5, 94.3, 92.1, 84.1. $C_{12}H_7IS$ (309.93): Anal. Calcd C 46.47, H 2.27; found: C 46.31, H 2.55.

4.1.5. (*E*)-1-[4-(3-Hydroxy-3-methyl-1-butyn)phenyl]-2-(2′-thienyl)ethene, (*E*)-6. *General procedure to the heterocoupling reaction*. To a solution of (*E*)-1-(*p*-iodophenyl)-2-(2′-thienyl)ethene (*E*)-**5**, 5 g (16.02 mmol) in freshly distilled and saturated in argon diethylamine (25 ml), and 2-methylbut-3-yn-2-ol (2.05 g, 24.3 mmol), was added in this order, dichlorobis[(triphenyl)phosphine]-palladium (113 mg, 0.16 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature and after 20 h, was concentrated at reduced pressure and then was added an aqueous solution of saturated ammonium chloride and potassium cyanide. The mixture was extracted with dichloromethane and the organic layer was dried on anhydrous magnesium sulphate. After filtration, solvent was removed to give (*E*)-1-(4-(3-hydroxy-3-methyl-1-butyn)-phenyl)-2-(2′-thienyl)ethene, 4.03 g (94%) as a brown solid, mp 144–147 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (br s, 4H); 7.25 (d, 1H, J= 5.0 Hz); 7.24 (d, 1H, J=16.1 Hz); 7.08 (d, 1H, J=3.4 Hz); 7.00 (dd, 1H, J=5.0, 3.4 Hz); 6.88 (d, 1H, J=16.1 Hz); 1.62 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.6, 136.8, 131.9, 127.4, 127.7, 126.5, 126.0, 124.7, 122.5, 121.6, 94.6, 84.0, 65.6, 31.0.

4.1.6. (*E*)-1-(2′-Thienyl)-2-(*p*-ethynylphenyl)ethene, (*E*)-7. To a solution of the propargylic derivate (*E*)-**6** (5.04 g, 18.8 mmol) in dry toluene (50 ml), under argon atmosphere, was added a little amount of powered sodium hydroxide. The mixture was warmed at reflux temperature during 12 h. After, the solution was filtered and the solvent was eliminated at reduced pressure. The residual oil was purified by silica gel column chromatography using hexane/dichloromethane 2:1 as the eluent to give (*E*)-**7**, 2.8 g (72%) as a yellow solid, mp 117–119 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 341, 240. Fluorescence (CH_2Cl_2), λ_{max} (nm): 450 and 420 (ϕ=0.129). FT-IR (KBr, cm^{-1}): 3271, 1590, 1514, 1411, 949, 829. ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, 3.4 Hz); 6.88 (d, 1H, J=16.1 Hz); 3.15 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.5, 137.5, 132.5, 127.7, 127.4, 126.6, 126.1, 124.8, 122.9, 118.9, 83.7, 77.9. $C_{14}H_{10}S$ (210.05): Anal. Calcd C 79.96, H 4.79; found: C 79.71, H 4.60.

4.1.7. 1-[4-(3-Hydroxy-3-methyl-1-butyn)phenyl]-2-(2′-thienyl)ethyne (9). Following the general method used for the synthesis of **6**, a mixture of 1-(*p*-iodophenyl)-2-(2′-thienyl)ethyne (550 mg, 1.77 mmol) (**8**), 2-methyl-but-3-yn-2-ol (149 mg, 1.77 mmol) in diethylamine (10 ml), dichlorobis[(triphenyl)phosphine]palladium (13.3 mg, 0.018 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature for 8 h. After purification gives 1-(4-(3-hydroxy-3-methyl-1-butyn)phenyl)-2-(2′-thienyl)ethylene (**9**), 400 mg (85%) as a white solid, mp 102–105 °C. FT-IR (KBr, cm^{-1}): 3240, 1523, 1428, 832. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (d, 2H, J= 8.6 Hz); 7.37 (d, 2H, J=8.6 Hz); 7.29 (d, 1H, J=5.2 Hz); 7.27 (d, 1H, J=3.4 Hz); 7.01 (dd, 1H, J=5.2, 3.4 Hz); 1.61 (s, 6H).

4.1.8. 1-(2′-Thienyl)-2-(*p*-ethynylphenyl)ethyne[25] (10) Following the general method used for the synthesis of **7**, propargylic derivate (**9**) (400 mg, 1.50 mmol) in dry toluene (15 ml) was warmed at the reflux temperature during 12 h to give 1-(2′-thienyl)-2-(4-ethynylphenyl)ethyne (**10**), 295 mg (94%) as a yellow solid, mp 90–92 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 337, 316, 281, 269. Fluorescence (CH_2Cl_2), λ_{max} (nm): 410 and 392 (ϕ=0.142). FT-IR (KBr, cm^{-1}): 3273, 2195, 1523, 1489, 1421, 832. ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, 3.2 Hz); 3.19 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.2, 132.1, 131.2, 127.7, 127.2, 123.4, 122.9, 122.0, 92.5, 83.2, 79.0, 77.4. $C_{14}H_8S$ (208.03): Anal. Calcd C 80.73, H 3.87; found: C 80.61, H 4.02.

4.1.9. 1-[*p*-(3-Hydroxy-3-methyl-1-butyn)phenyl]-2-(*p*-*N*,*N*-dimethylaminophenyl)ethyne. Following the general method used for the synthesis of **6**, a mixture of terminal acetylene **11** (221 mg, 0.64 mmol), 2-methyl-but-3-yn-2-ol (53 mg, 0.64 mmol) in diethylamine (3 ml), dichlorobis [(triphenyl)phosphine]palladium (6 mg, 0.0064 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature for 8 h. After purification gives 1-[*p*-(3-hydroxy-3-mehyl-1-butyn)phenyl]-2-(*p*-*N*,*N*-dimethylaminophenyl)ethyne 158 mg (82%) as a brown solid, mp 90–93 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (d, 2H, J= 8.6 Hz); 7.40 (d, 2H, J=9.0 Hz); 7.35 (d, 2H, J=8.6 Hz); 6.66 (d, 2H, J=9.0 Hz); 3.00 (s, 6H); 1.62 (s, 6H).

4.1.10. 1-(*p*-*N*,*N*-Dimethylaminophenyl)-2-(*p*-ethynylphenyl)ethyne (12). Following the general method used for the synthesis of **7**, propargylic derivate (158 mg, 0.52 mmol) in dry toluene (5 ml) was warmed at the reflux temperature during 12 h to give 1-(*p*-*N*,*N*-dimethylaminophenyl)-2-(*p*-ethynylphenyl)ethyne (**12**), 115.4 mg (90%) as a red solid, mp 138–140 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 354, 280, 269. Fluorescence (CH_2Cl_2), λ máx (nm): 443 (ϕ=0.238). FT-IR (KBr): 3240 (C≡CH); 2208 (C≡C); 1606 and 1523 (C=C); 1351 (C–N); 818 (*p*-disust. ArH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (s, 4H,); 7.40 (d, 2H, J=8.6 Hz); 6.66 (d, 2H, J=8.6 Hz); 3.15 (s, 1H); 3.00 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2, 132.7, 131.9, 131.0, 124.7, 120.8, 111.7, 109.5, 92.9, 87.0, 83.5, 78.4, 40.1. $C_{18}H_{15}N$ (245.12): Anal. Calcd C 88.13, H 6.16, N 5.71; found: C 87.92, H 6.14, N 5.58.

4.1.11. (*E*)-1-(2′-Thienyl)-2-(4-bromoethynylphenyl)-ethene (*E*)-13. Bromine (152 mg) was added to a solution of potassium hydroxide (142 mg, 2.54 mmol) in water (5 ml) and vigorously stirred at −5 °C for 15 min. A pale yellow solution of KOBr was formed and then, was slowly added (*E*)-1-(2′-thienyl)-2-(*p*-ethenylphenyl)ethene (*E*)-**7** (200 mg, 0.95 mmol) in 15 ml of tetrahydrofuran, maintained the solution between 10–20 °C. The mixture was stirred at room temperature overnight and then the solvent removed. The residual solid was extracted with dichloromethane and the organic layer was dried on anhydrous magnesium sulphate, filtered and solvent evaporated to give a brown solid that was purified by silica gel column

chromatography using hexane–dichloromethane (1/1) as the eluent, to give (*E*)-1-(2-thienyl)-2-(4-bromoethenylphenyl)-ethene (*E*)-**13**, 200 mg (70%) as a red-orange solid. This compound should be used without delay.

4.1.12. (*E*,*E*)-1,4-Di(4-(2-(2-thienyl)ethenyl)phenyl)-1,3-butadiyne, (*E*,*E*)-14. To a solution of hydroxylamine·HCl (200 mg) in water (10 ml), an aqueous solution of ethylamine (70%, 10 ml) methanol (50 ml) and a little amount of copper(I) chloride, under argon atmosphere, was added (*E*)-1-(2-thienyl)-2-(4-ethenylphenyl)ethene (*E*)-**7** (147 mg, 0.70 mmol) and (*E*)-1-(2′-thienyl)-2-(4-bromoethenylphenyl)ethene (*E*)-**13** (200 mg, 0.70 mmol) between 30–35 °C. After 1 h the mixture was hydrolyzed with a saturated aqueous ammonium chloride solution with vigorous stirring and extracted with dichloromethane. The organic layer was dried on anhydrous magnesium sulphate, filtered and the solvent evaporated to give (*E*,*E*)-1,4-di-(4-(2-(2-thienyl)ethenyl)phenyl)butadiyne (*E*,*E*)-**14**, 65 mg (45%), as a yellow solid, mp >300 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 347, 248. Fluorescence (CH_2Cl_2), λ_{max} (nm): 454 and 427 (ϕ=0.289). FT-IR (KBr, cm^{-1}): 2143, 1621, 1514, 1410, 831. ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, 3.4 Hz); 6.88 (d, 1H, J=16.1 Hz). MS (70 eV): 418 (M^+, 100), 209 (M^{2+}, 6). $C_{28}H_{18}S_2$ (418.08): Anal. Calcd C 80.34, H 4.33; found: C 80.17, H 4.49.

4.1.13. (1,4-Di(4-(2′-thienyl)ethynyl)phenyl)-1,3-butadiyne (15). To a solution of cuprous chloride (35.4 mg, 0.18 mmol) in dry pyridine (5 ml), under an oxygen atmosphere, at 40 °C was added a solution of 1-(2′-thienyl)-2-(*p*-ethynylphenyl)ethyne (**8**) (150 mg, 0.72 mmol) in dry pyridine (5 ml) and the mixture was stirred for 30 min. The solvent was removed and the residual solid was washed with ammonium hydroxide and extracted with dichloromethane. The organic layer was dried on anhydrous magnesium sulphate, filtered and solvent evaporated to give (1,4-di(4-(2′-thienyl)ethynyl)-phenyl)-1,3-butadiyne (**15**), 69 mg (61%) as a yellow solid, mp 239–240 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 359, 260, 244. Fluorescence (CH_2Cl_2), λ_{max} (nm): 421 (ϕ=0.364). FT-IR (KBr, cm^{-1}): 2198, 1594, 1521, 1487, 829. ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, 3.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.1, 132.8, 131.6, 129.3, 127.8, 123.8, 121.9, 120.9, 92.4, 85.8, 82.6, 75.6. MS (MALDI-TOF): 414.0. $C_{28}H_{14}S_2$ (414.05): Anal. Calcd C 81.13, H 3.40; found: C 80.98, H 3.63.

4.1.14. (Di-(*p*-(2′-thienyl)ethynyl)phenyl)ethyne (16). Following the general method used for the synthesis of **6**, a mixture of terminal acetylene **8** (100 mg, 0.32 mmol), 1-(2′-thienyl)-2-(*p*-ethynylphenyl)ethylene (**10**) (66 mg, 0.32 mmol) in diethylamine (10 ml), dichlorobis[triphenylphosphine]palladium (23 mg, 0.032 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature for 30 min. After purification gives (di(*p*-(2′-thienyl)ethynyl)phenyl)ethyne (**16**), 99 mg (38%), as a brown-red solid, p.f.> 230 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 352, 243. Fluorescence (CH_2Cl_2), λ_{max} (nm): 410 and 390 (ϕ=0.296). FT-IR (KBr, cm^{-1}): 2197, 1595, 1524, 1424, 831. ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, 3.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.4, 131.5, 131.3, 127.8, 127.2, 123.9, 123.0, 121.5, 92.5, 85.4, 82.1. MS (MALDI-TOF): 390.0. $C_{26}H_{14}S_2$ (390.05): Anal. Calcd C 79.96, H 3.61; found: C 79.75, H 3.97.

4.1.15. 2,5-[Di(*p*-*N*,*N*-dimethylamino)phenylethynyl]-thiophene (17). Following the general method used for the synthesis of **6**, a mixture of terminal acetylene **11** (100 mg, 0.68 mmol), 2,5-di(iodo)thiophene (231 mg, 0.68 mmol) in diethylamine (10 ml), dichlorobis[triphenylphosphine]palladium (48 mg, 0.068 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature for 3 h. After purification gives 2,5-[di(*p*-*N*,*N*-dimethylamino)phenylethynyl]thiophene (**17**) 246 mg (98%), as a yellow solid, p.f. 181–183 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 385. Fluorescence (CH_2Cl_2), λ_{max} (nm): 456 (ϕ=0.23). FT-IR (KBr, cm^{-1}): 2157, 1578, 1466, 1372. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, 4H, J=8.0 Hz); 7.05 (s, 2H); 6.64 (d, 4H, J=8.0 Hz); 2.99 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.1, 133.4, 131.5, 122.3, 113.8, 112.3, 92.7, 86.4, 41.0. MS (FAB+) *m*/*z* 370.1 (M^+, 100), 170.1 (31). $C_{24}H_{22}N_2S$ (370.15): Anal. Calcd C 77.80, H 5.98, N 7.56; found: C 78.63, H 5.78, N 7.43

4.1.16. 2,5-[Di(*p*-*N*,*N*-dimethylamino)(phenylethynyl)(phenylethynyl)]thiophene (19). Following the general method used for the synthesis of **6**, a mixture of terminal acetylene **12** (115.4 mg, 0.47 mmol), 2,5-di(iodo)thiophene (157 mg, 0.47 mmol) in diethylamine (10 ml), dichlorobis[triphenylphosphine]palladium (33 mg, 0.047 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature for 5 h. After purification gives 2,5-[di(*p*-*N*,*N*-dimethylamino)(phenylethynyl)(phenylethynyl)]-thiophene (**19**) 227 mg (85%), as a yellow solid, p.f. 227–230 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 393. Fluorescence (CH_2Cl_2), λ_{max} (nm): 512 (ϕ=0.30). FT-IR (KBr, cm^{-1}): 2153, 1552, 1428, 1381. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (m, 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). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.3, 133.2, 131.9, 131.5, 122.6, 122.3, 113.9, 112.2, 92.9, 92.8, 92.7, 86.5, 40.4. MS (FAB+): 570.2 (M^+, 100), 370.1 (43). $C_{24}H_{22}N_2S$ (570.20): Anal. Calcd C 84.18, H 5.30, N 4.91; found: C 84.93, H 5.29, N 4.73.

4.1.17. 2,5-Di-[2-(4-((*E*)-2-(thiophen-2-yl)vinyl)phenylethynyl)]thiophene (21). Following the general method used for the synthesis of **6**, a mixture of terminal acetylene **7** (60 mg, 0.29 mmol), 2,5-di(iodo)thiophene (50 mg, 0.15 mmol) in diethylamine (10 ml), dichlorobis[triphenylphosphine]palladium (21 mg, 0.03 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature for 7 h. After purification gives 2,5-di-[2-(4-((*E*)-2-(thiophen-2-yl)vinyl)phenylethynyl)]thiophene (**21**) 46 mg (65%), as a yellow solid, p.f. 261–262 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 367. Fluorescence (CH_2Cl_2), λ_{max} (nm): 462 and 440 (ϕ=0.10). FT-IR (KBr, cm^{-1}): 3295, 1579, 1505, 1437, 825. ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, 3.8 Hz); 6.90 (d, 2H, J=15.9 Hz). MS (MALDI-TOF):

500.0. $C_{32}H_{20}S_3$ (500.07): Anal. Calcd C 76.76, H 4.03; found: C 76.61, H 4.32.

4.1.18. 2,5-Di-[2-(thienylethynyl)(phenylethynyl)]thiophene (22). Following the general method used for the synthesis of **6**, a mixture of terminal acetylene **10** (47 mg, 0.23 mmol), 2,5-di(iodo)thiophene (41 mg, 0.12 mmol) in diethylamine (10 ml), dichlorobis[triphenylphosphine]palladium (16 mg, 0.023 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature for 7 h. After purification gives 2,5-di-[2-(thienylethynyl)(phenylethynyl)]thiophene (**22**) 48 mg (85%), as a yellow solid, p.f. 234–235 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 379. Fluorescence (CH_2Cl_2), λ_{max} (nm): 423 and 398 ($\phi=0.34$). FT-IR (KBr, cm^{-1}): 3311, 1592, 1519, 1448, 830. ^1H NMR (300 MHz, $CDCl_3$): δ 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, $J=4.8$, 4.3 Hz). MS (MALDI-TOF): 495.9. $C_{32}H_{16}S_3$ (496.04): Anal. Calcd C 77.38, H 3.25; found: C 77.72, H 3.06.

4.1.19. 2,5-Di-[(3,5-bis-trimethylsilylethynylphenyl)-ethynyl]thiophene (26). Following the general method used for the synthesis of **6**, a mixture of terminal acetylene **23** (175 mg, 0.60 mmol), 2,5-di(iodo)thiophene (100 mg, 0.30 mmol) in diethylamine (10 ml), dichlorobis[triphenylphosphine]palladium (42 mg, 0.06 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature for 12 h. After purification gives 2,5-di-[(3,5-bis-trimethylsilylethynylphenyl)ethynyl]thiophene (**26**) 191 mg (97%), as a green solid, p.f. 139–140 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 355. Fluorescence (CH_2Cl_2), λ_{max} (nm): 410 and 391 ($\phi=0.20$). FT-IR (KBr, cm^{-1}): 2156, 1579, 1410, 1250, 758. ^1H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, 4H, $J=1.6$ Hz); 7.53 (t, 2H, $J=1.6$ Hz); 7.14 (s, 2H); 0.24 (s, 36H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.1, 134.3, 132.2, 124.5, 123.8, 123.0, 103.0, 95.9, 92.6, 83.1, −0.2. MS (70 eV): 668 (M^+, 100), 320 (23), 73 (90). $C_{40}H_{44}SSi_4$ (669.19): Anal. Calcd C 71.79, H 6.63; found: C 71.83, H 6.60.

4.1.20. 2,5-Di-{[(3,5-bis-trimethylsilylethynylphenyl)-ethynylphenyl]ethynyl}thiophene (27). Following the general method used for the synthesis of **6**, a mixture of terminal acetylene **24** (233 mg, 0.60 mmol), 2,5-di (iodo)thiophene (100 mg, 0.30 mmol) in diethylamine (10 ml), dichlorobis[triphenylphosphine]palladium (42 mg, 0.06 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature for 12 h. After purification gives 2,5-di-{[(3,5-bis-trimethylsilylethynylphenyl)ethynylphenyl]ethynyl}thiophene (**27**) 249 mg (97%), as a green solid, p.f. 218–220 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 379. Fluorescence (CH_2Cl_2), λ_{max} (nm): 447 and 421 ($\phi=0.42$). FT-IR (KBr, cm^{-1}): 2159, 1577, 1409, 1249, 759. ^1H NMR (300 MHz, $CDCl_3$): δ 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). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.0, 134.5, 132.1, 131.6, 131.4, 124.7, 123.8, 123.4, 123.0, 122.7, 103.1, 95.8, 93.9, 89.9, 89.8, 84.9, −0.2. MS (70 eV): 868.3 (M^+, 100); 419.3 (30). $C_{56}H_{52}SSi_4$ (869.42): Anal. Calcd C 77.36, H 6.03; found: C 77.43, H 5.98.

4.1.21. 2,5-Di-{{{[3,5-bis(trimethylsilylethynyl)phenyl]-ethynylphenyl}ethynylphenyl}ethynyl}thiophene (28). Following the general method used for the synthesis of **6**, a mixture of terminal acetylene **25** (100 mg, 0.20 mmol), 2,5-di(iodo)thiophene (34 mg, 0.10 mmol) in diethylamine (10 ml), dichlorobis[triphenylphosphine]palladium (10 mg, 0.02 mmol) and a little amount of copper(I) iodide. The mixture was stirred at room temperature for 12 h. After purification gives 2,5-di-{{{[3,5-bis(trimethylsilylethynyl)-phenyl]ethynylphenyl}ethynylphenyl}ethynyl}thiophene (**28**) 88 mg (80%), as a green solid, p.f. 291–293 °C. UV–vis (CH_2Cl_2), λ_{max} (nm): 377. Fluorescence (CH_2Cl_2), λ_{max} (nm): 454 and 429 ($\phi=0.54$). FT-IR (KBr, cm^{-1}): 2159, 1577, 1409, 1249, 759. ^1H NMR (300 MHz, $CDCl_3$): δ 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), 0.24 (s, 36H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.0, 134.5, 132.2, 131.6, 131.4, 124.7, 123.8, 123.5, 123.2, 123.1, 122.9, 103.1, 95.8, 94.0, 91.2, 91.1, 90.1, 89.7, 84.27, −0.2. MS (70 eV): 1068 (M^+, 100), 520 (40). $C_{72}H_{66}SSi_4$ (1069.65): Anal. Calcd C 80.85, H 5.65; found: C 80.91, H 5.59.

Acknowledgements

We thank M. C. Rodriguez and S. I. Pereira for the computational analyses.

References and notes

1. (a) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (c) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817.
2. Gust, D.; Moore, T. A. *Science* **1989**, *244*, 35.
3. Ziessel, R. In *Photosensitization and Photocatalysis using Inorganic and Organometallic Compounds*; Kalyanasundaram, K., Grätzel, M., Eds.; Kluwer Academic: Dordecht, 1993; p 217.
4. O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
5. Reynolds, J. R. *J. Mol. Electron* **1986**, *2*, 1.
6. Grubbs, R. H.; Gorman, C. B.; Ginsburg, E. J.; Perry, J. W.; Marder, S. R. In *Materials with Nonlinear Optics, Chemical Perspectives*; Marder, S. R., Sohn, J. E., Stricky, G. D., Eds.; ACS Symposium Series: Washington, DC, 1991; p 455.
7. Barker, J. R. In *Molecular Electronics*; Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Edward Arnold: London, 1995; p 345.
8. Varanasi, P. R.; Jen, A. K. Y.; Chandrasekhar, J.; Namboothiri, I. N. N.; Rathna, A. *J. Am. Chem. Soc.* **1996**, *118*, 12443.
9. Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 6575.
10. (a) Zhu, Y.; Wolf, M. O. *J. Am. Chem. Soc.* **2000**, *122*, 10121. (b) Granström, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature* **1998**, *395*, 257. (c) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, 1998.
11. Torsi, L.; Dodabalapur, A.; Rothberg, L. J.; Fung, A. W. P.; Katz, H. E. *Science* **1996**, *272*, 1462.
12. (a) Lu, H. F.; Chan, H. S. O.; Ng, S. C. *Macromolecules* **2003**, *36*, 1543. (b) Lukes, V.; Breza, M.; Vegh, D.; Hrdlovic, P.; Krajcovic, J.; Laurinc, V. *Synth. Met.* **2002**, *129*, 85. (c) Raimundo, J. M.; Blanchard, P.; Gallego-Planas, N.; Mercier, N.; Ledoux-Rak, I.; Hierle, R.; Roncali, J. *J. Org.*

Chem. **2002**, *67*, 205. (d) Otsubo, T.; Aso, Y.; Takimiya, K. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1789. (e) Zhu, Y.; Wolf, M. O. *Chem. Mater.* **1999**, *11*, 2995. (f) Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123. (g) Ley, K. D.; Schanze, K. S. *Coord. Chem. Rev.* **1998**, *171*, 287. (h) Reddinger, J. L.; Reynolds, J. R. *Macromolecules* **1997**, *30*, 673. (i) Segawa, H.; Wu, F. P.; Nakayama, N.; Maruyama, H.; Sagisaka, S.; Higuchi, N.; Fujitsuka, M.; Shimidzu, T. *Synth. Met.* **1995**, *71*, 2151. (j) Zotti, G.; Zecchin, S.; Schiavon, G.; Berlin, A.; Pagani, G.; Canavesi, A. *Chem. Mater.* **1995**, *7*, 2309.

13. (a) Peng, Z. H.; Pan, Y. C.; Xu, B. B.; Zhang, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 6619. (b) Xu, Z. F.; Moore, J. S. *Acta Polym.* **1994**, *45*, 83.
14. (a) Xu, M. H.; Pu, L. *Tetrahedron Lett.* **2002**, *43*, 6541. (b) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376.
15. (a) Rodríguez, J. G.; Tejedor, J. L. *J. Org. Chem.* **2002**, *67*, 7631. (b) Rodríguez, J. G.; Esquivias, J. *Tetrahedron Lett.* **2003**, *26*, 4831. (c) Rodríguez, J. G.; Tejedor, J. L.; Esquivias, J.; Díaz, C. *Tetrahedron Lett.* **2003**, *26*, 6375. (d) Rodríguez, J. G.; Esquivias, J.; Lafuente, A.; Díaz, C. *J. Org. Chem.* **2003**, *68*, 8120. (e) Rodríguez, J. G.; Lafuente, A.; Rubio, L. *Tetrahedron Lett.* **2004**, *45*, 5685. (f) Rodríguez, J. G.; Lafuente, A.; Rubio, L.; Esquivias, J. *Tetrahedron Lett.* **2004**, *45*, 7061.
16. Birnbaum, D.; Kohler, B. E.; Spangler, C. W. *J. Chem. Phys.* **1991**, *94*, 1684.
17. Beny, J. P.; Dhawan, S. N.; Kagan, J.; Sundlass, S. *J. Org. Chem.* **1982**, *47*, 2201.
18. Baati, R.; Barma, D. K.; Murali Krishna, U.; Mioskowski, C.; Falck, J. R. *Tetrahedron Lett.* **2002**, *6*, 959.
19. (a) Vaitiekunas, A.; Nord, F. F. *J. Org. Chem.* **1954**, *19*, 902. (b) Keskin, H.; Miller, R. E.; Nord, F. F. *J. Org. Chem.* **1951**, *16*, 199.
20. Johansen, O.; Sasse, W. H. F.; Hoskinson, R. M.; Russell, I. M. *J. Text. Inst.* **1976**, *67*, 146.
21. (a) Glaser, G. *Chem. Ber.* **1869**, *2*, 422. (b) Glaser, G. *Liebigs Ann. Chem.* **1870**, 159.
22. Sarkar, A.; Okada, S.; Nakanishi, H.; Matsuda, H. *Helv. Chem. Acta* **1999**, *82*, 138.
23. All calculations have been performed at the B3LYP* level, using 6-31G basis set for hydrogen, carbon, nitrogen and sulfur, and the Hay–Wadt small-core effective core potential (ECP). (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200. (d) Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 76 and references therein.
24. Mayor, M.; Didschies, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 3176.
25. Han, X.; Yang, M.; Xu, G.; Liu, X.; Ye, P. *Macromol. Rapid Commun.* **2001**, *22*, 358.