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The synthesis and characterization of heterocyclic azo dyes derived from 5-*N*,*N*-dialkylamino-2,2′-bithiophene couplers

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ABSTRACT

Heterocyclic azo dyes were synthesized by diazotation of several substituted anilines and coupling with 5-*N*,*N*-dialkylamino-2,2′-bithiophenes to give 4-phenylazo-5-*N*,*N*-dialkylamino-2,2′-bithiophenes. This reaction contrasts with the behavior of 5-alkoxy-2,2′-bithiophenes towards aryldiazonium salts which provides 5-phenylazo-5-alkoxy-2,2′-bithiophenes. The thermal stability of the derivatives was evaluated using thermogravimetric analysis and their solvatochromic behaviour was investigated in several solvents of different polarity. The experimental results indicate that the heterocyclic azo dyes could be used as thermally stable, solvatochromic probes.

1. Introduction

N,*N*-Dialkylamino-2,2′-bithiophenes are among the most interesting building blocks for the synthesis of more complex heterocyclic conjugated systems with several interesting optical applications [1,2]. When these bithiophene derivatives are substituted with strong acceptor groups at 5′-position, they exhibit enhanced nonlinear optical (NLO) properties which significantly exceed those of the corresponding dialkylaniline derivatives. Moreover, 5-*N*,*N*-dialkylamino-2,2′-bithiophenes substituted with acceptor groups at the 5′- position are excellent indicators of the solvent polarity due to their positive solvatochromism [1c,d,g,i,2]. This type of compounds can therefore find applications in electro-optical devices [3] and sensors.

Arylazo heterocycles are a versatile class of colored organic compounds that have recently attracted, the interest of many research groups due to their diverse applications not only as classical synthetic dyes and pigments but also as solvatochromic probes and thermally stable organic second-order nonlinear optical (NLO) chromophores [4]. Other recent applications, include memory and recording devices, molecular switches, thermochromic, photovoltaic and fluorescent devices, supramolecular systems, holographic data storage materials, acid–base and metal sensors and active ligands in Pd-catalyzed cross-coupling reactions [4b,5].

We have recently reported the synthesis and the characterization of donor–acceptor substituted heterocyclic azo dyes containing either thienylpyrrole [6] or 5-alkoxy-2,2′-bithiophene moieties [7]. These new π-conjugated systems exhibit interesting electrochemical properties, high thermal stability, excellent solvatochromic behavior and NLO activity, and good photochromic properties [6,7].

These previous studies motivated us to explore the potential of conjugated 5-*N*,*N*-dialkylamino-2,2′-bithiophenes as π-conjugated heterocyclic bridges functionalized with phenylazo groups. This paper reports the synthesis, solvatochromic properties and the thermal stability of 4-arylazo-2,2′-bithiophenes **4**–**7** which have *meta* CO_2H or *para* CO_2Me, CN and NO_2 groups as electron-withdrawing groups substituted on the phenylazo moiety and the conjugated 5-*N*,*N*-dialkylamino-2,2′-bithiophenes, as strong π-electron donor moieties.

To the best of our knowledge, no similar dyes containing 5-*N*,*N*-dialkylamino-2,2′-bithiophene conjugated bridges linked to arylazo moieties, have been reported in the literature.

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2. Results and discussion

2.1. *Synthesis*

As heterocyclic analogues of the well-known *N*,*N*-dialkylanilines amino-thiophenes could be used as important precursors for the synthesis of organic dyes. Thus, *N*,*N*-disubstituted 2-amino-thiophenes and *N*,*N*-disubstituted 5-amino-2,2′-bithiophenes could be successfully transformed, especially if they are unsubstituted at their 5 position (2-aminothiophenes) for example into azo dyes [8], or into other derivatives which involved the functionalization of the unsubstituted 5′-position (*N*,*N*-disubstituted 5-amino-2,2′-bithiophenes), through electrophilic aromatic substitutions or other methods of synthesis [1b–f,i,j].

Recently we have developed an efficient method for the synthesis of 5-*N*,*N*-dialkylamino-2,2′-bithiophenes [1a]. These compounds have proved to be versatile substrates in formylation, dicyanovinylation and tricyanovinylation reactions [1b] and also in Stille cross-coupling reactions [1c,d] allowing the preparation of several new donor–acceptor substituted oligothiophenes. Therefore, it was decided to use 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2** as coupling components which will react with diazonium salts functionalized with acceptor groups in order to obtain new bithiophene azo dyes.

2.1.1. *Synthesis of 5-*N,N*-dialkylamino-2,2′-bithiophenes **2a–d***

The 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2a**–**d** were synthesized through a combination of the Friedel-Crafts and the Lawesson reaction [1a,9] from the *N*,*N*-dialkylamino-4-(2′-thienyl)-4-oxobutanamides **1a**–**d** (Scheme 1). Amides **1a**–**b**, **1d** and bithiophene derivatives **2a**–**b** and **2d** have been reported by us recently [1a]. In order to compare the effect of the electronic nature of the 5-*N*,*N*-dialkylamino groups on the optical properties of phenylazo-bithiophenes **4**–**7**, 5-pyrrolidino-2,2′-bithiophene **2c** was also synthesized from the new pyrrolidino-4-(2′-thienyl)-4-oxobutanamide **1c** using the same synthetic methodology [1a]. Direct amidation of 4-oxo-(2′-thienyl)butanoic acid [1a,9,10] with pyrrolidine was carried out through a DCC–BtOH mediated reaction. Amide **1c** was obtained as a colourless solid in good yield (80%). Treatment of amide **1c** with an equimolar amount of Lawesson's reagent (LR) in toluene gave bithiophene **2c** in 47% yield. The synthesis of 5-pyrrolidino-2,2′-bithiophene **2c** has been reported earlier by Effenberger et al. [2b] through two different methods of synthesis. Pd-catalyzed coupling reaction *via* an organotin intermediate gave a mixture of two compounds in 43% yield. These two compounds were obtained in a ratio **2c**: phenyl-5-pyrrolidinothiophene = 70:30 (determined by HPLC and ^{1}H NMR). Neither by chromatography nor by recrystallization could compound **2c** and phenyl-5-pyrrolidinothiophene be separated. Therefore, an alternative route for the synthesis of **2c** was performed by the same investigators through the lithiation of 2,2′-bithiophene followed by reaction with sulfur giving 5-mercapto-2,2′-bithiophene in 40% yield, subsequent reaction with pyrrolidine allowed the preparation of **2c** in 25–37% yield. In comparison to Effenberger's methods the 5-pyrrolidino-2,2′-bithiophene **2c** was obtained by us, through the combination of the Friedel-Crafts and Lawesson reactions, in higher yield from low cost commercially available reagents and using simple work-up procedures allowing the good yield preparation and easy isolation of this derivative.

2.1.2. *Synthesis of 5-*N,N*-dialkylamino-2,2′-bithiophene azo dyes **4–7***

In our recent work, 5-alkoxy- and 5-*N*,*N*-dialkylamino-2,2′-bithiophenes were demonstrated to be highly reactive towards electrophilic reagents. Moreover, the position of substitution on the bithiophene moiety, depends on the size of the electrophile. For example, with tetracyanoethylene (TCNE) 5-alkoxy-2,2′-bithiophenes and 5-*N*,*N*-dialkylamino-2,2′-bithiophenes yield deeply coloured 5′-tricyanovinyl-2,2′-bithiophenes [1b].

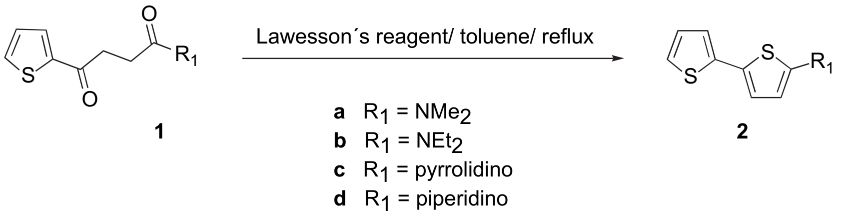
More recently the synthesis and characterization of 5′-phenyl-azo-5-alkoxy-2,2′-bithiophenes using as coupling components 5-alkoxy-2,2′-bithiophenes and aryldiazonium salts were described [7]. On the other hand the azo coupling reaction of 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2** with aryldiazonium salts **3**, using the same experimental conditions reported for the synthesis of 5′-phenylazo-5-alkoxy-2,2′-bithiophenes, gave selectively, 4-phenyl-azo-5-*N*,*N*-dialkylamino-2,2′-bithiophenes **4**–**7** in fair to good yields (10–62%), (Scheme 2, Table 1).

N,*N*-Disubstituted 2-aminothiophenes as heterocyclic analogues of the *N*,*N*-dialkylanilines exhibit a similar reactivity towards electrophilic reagents. Thus, with aryldiazonium salts they are transformed as long as their 5-position is unsubstituted, into *N*,*N*-disubstituted 2-amino-5-arylazothiophenes [11]. Otherwise, e.g. if *N*,*N*-disubstituted 2-aminothiophenes are substituted by a phenyl group in 5-position, they yield, *N*,*N*-disubstituted 2-amino-3-arylazothiophenes [12].

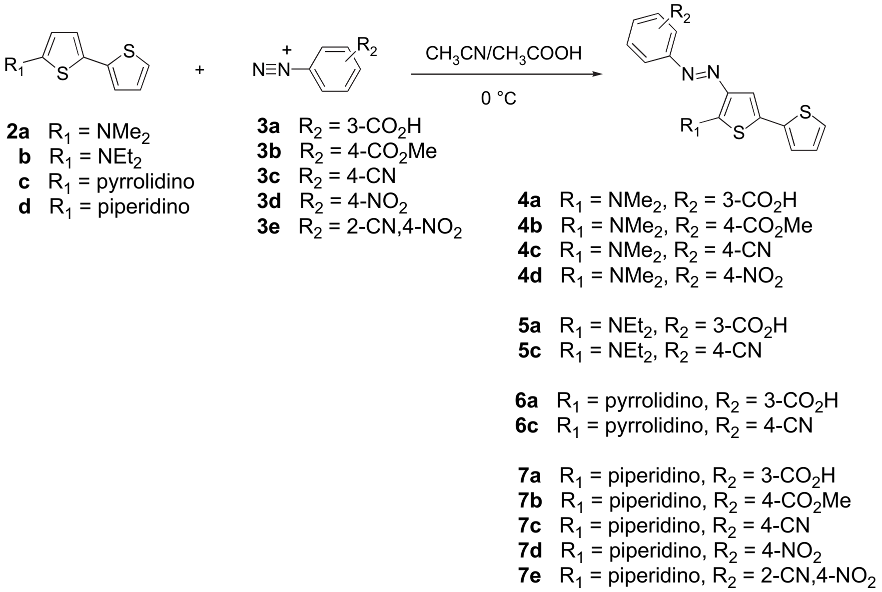
The reactivity of 5-*N*,*N*-dialkylamino-2,2′-bithiophenes contrasts to the behavior of 5-alkoxy-2,2′-bithiophenes towards aryldiazonium salts [7]. The results showed that, in the case of the coupling reaction of the 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2** with aryldiazonium salts **3**, the reaction occurs in the most activated 4-position. Monosubstitution at 5′ position and/or disubstitution on both 4- and the 5′-positions is never observed. Despite the steric hindrance, the 4 position is still favored for the electrophilic reaction, compared to the 5′-position.

In order to interpret these results we must consider several factors:

i) an increase of the electron density at the 4-position of the bithiophene moiety due to the 5-*N*,*N*-dialkylamino-substituents;
ii) the diazonium salts are not sterically bulky species;
iii) the steric hindrance of an *ortho*-dialkylamino substituent to the attack of an electrophilic aryldiazonium salt is significantly lower for the five-membered thiophene ring than for the six-membered benzene ring.



Scheme 1. Synthesis of 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2** through reaction of *N*,*N*-dialkylamino-4-(2′-thienyl)-4-oxobutanamide**s 1** with the Lawesson's reagent.



Scheme 2. Synthesis of azobithiophenes **4–7** through azo coupling of 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2** with aryldiazonium salts **3**.

Therefore, our reactivity studies on 5-alkoxy- and 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2** with electrophiles showed that the position for the electrophilic substitution depends not only on the size of the electrophile but also on the electronic nature of the group substituted on 5-position of the bithiophene moiety (alkoxy or dialkylamino) [1b,7].

The structures of bithiophene azo dyes **4–7** were unambiguously confirmed by their analytical and spectral data. For example, in the ^{1}H NMR spectrum of 5-*N*,*N*-dialkylamino-4′-cyanophenylazo-2,2′-bithiophene derivatives **4c**–**7c**, in acetone-d_6, one signal at about 7.52–7.59 ppm was detected as a singlet indicating the presence of only one proton in a trisubstituted thiophene ring. This signal was attributed to the 3-H proton. For the same bithiophene azo dyes, **4c**–**7c**, three signals at about 7.09–7.13 ppm (multiplet), 7.22–7.24 ppm (double doublet) and 7.45–7.48 ppm (double doublet) were detected. These signals were attributed respectively, to the 4′, 3′ and 5′-H protons in the second thiophene ring.

2.2. *UV–visible study of 5′-*N,N*-dialkylamino-2,2′bithiophene azo dyes* **4–7**

The electronic absorption spectra of all the push-pull compounds **4**–**7** show an intense lowest energy charge-transfer absorption band in the UV–visible region. The position of this band is strongly influenced by the structure of the compounds, for example by the type of substitution pattern in the donor and the acceptor moieties. Dramatic differences in energy occur upon arylazo substitution of bithiophenes **2**. For example, bithiophene **2d** (λ_{max} = 353.0 nm) has bathochromic shift of 232.5 nm upon arylazo substitution (bithiophene azo dye **7e**, λ_{max} = 585.5 nm) (Table 1, entries 9 and 13 respectively). The impact of the electronic nature of the *N*,*N*-dialkylamino substituent at the 5-position on the bithiophene moiety can be seen by comparing the absorption maxima of compounds **4a** and **7a** as the longest wavelength transition is shifted from 473.0 nm in azo dye **4a** to 483.0 nm for azo dye **7a** (Table 1, entries 1 and 9 and

Table 1
Yields, UV–visible, IR absorption spectra and T_d data of 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2** and 5-*N*,*N*-dialkylamino-2,2′-bithiophenes azo dyes **4–7**.

Entry	Bithiophene	λ_{max}[a] (nm) (ε) ($dm^3\ cm^{-1}\ mol^{-1}$)	R_1	R_2	Azo bithiophene	Yield (%)	λ_{max}[a] (nm) (ε) ($dm^3\ cm^{-1}\ mol^{-1}$)	IR ν (cm^{-1})[b]	T_d (°C)[d]
1	**2a**	355.5 (27,570)	NMe_2	3-CO_2H	**4a**	27	473.0 (19,496)	1689 (C=O), 2386–3429 (OH)	209
2			NMe_2	4-CO_2Me	**4b**	58	498.0 (27,200)	1709[c] (C=O)	248
3			NMe_2	4-CN	**4c**	49	502.0 (16,162)	2214 (CN)	222
4			NMe_2	4-NO_2	**4d**	36	537.0 (23,890)	–	227
5	**2b**	363.5 (8719)	NEt_2	3-CO_2H	**5a**	62	478.0 (15,733)	1683 (C=O), 2357–3429 (OH)	262
6			NEt_2	4-CN	**5c**	53	509.0 (26,386)	2214 (CN)	201
7	**2c**	364.5 (46,122)	Pyrrolidino	3-CO_2H	**6a**	40	474.5 (18,276)	1698 (C=O), 2500–3429 (OH)	212
8			Pyrrolidino	4-CN	**6c**	23	504.0 (22,381)	2214[c] (CN)	–
9	**2d**	353.0 (16,358)	Piperidino	3-CO_2H	**7a**	55	483.0 (14,738)	1683 (C=O), 2357–3257 (OH)	210
10			Piperidino	4-CO_2Me	**7b**	16	504.0 (22,460)	1719[c] (C=O)	239
11			Piperidino	4-CN	**7c**	55	510.5 (25,069)	2214 (CN)	203
12			Piperidino	4-NO_2	**7d**	32	544.0 (24,270)	–	216
13			Piperidino	2-CN-4-NO_2	**7e**	10	585.5 (16,309)	2220[c] (CN)	238

[a] All the UV–visible spectra were recorded in acetone.

[b] The IR spectra were recorded in KBr.

[c] The IR spectra were recorded in Nujol.

[d] Decomposition temperature (T_d) measured at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere, obtained by TGA.

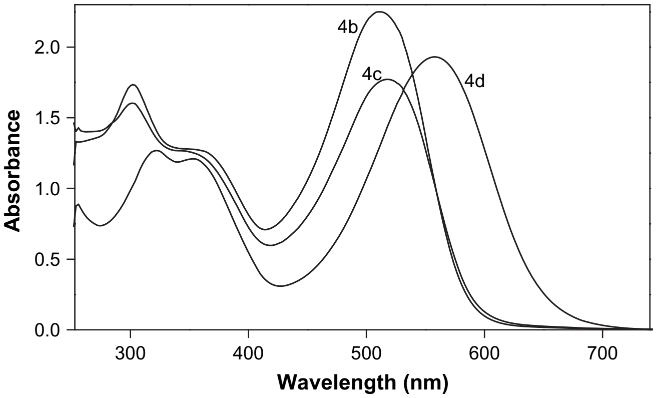


Fig. 1. UV–visible absorption spectra of compounds **4b**, **4c** and **4d** in DMSO.

respectively). The influence of the strength of the acceptor group substituted on the arylazo moiety is demonstrated by comparison of the absorption maxima of compounds **4b**, **4c** and **4d** in DMSO (Fig. 1) as the longest wavelength transition is shifted from 510.0 nm in 4-carboxymethylphenylazo-bithiophene **4b** to 558.0 nm for 4-cyano-phenylazo-bithiophene **4d**.

In general, the stronger the donor and/or acceptor group, the smaller the energy difference between ground and excited states, and the longer the wavelength of absorption [1g]. We suspect that this effect can be attributed to a stabilization of LUMO by the electron-withdrawing groups, but it would be interesting to confirm through a quantum computation, e.g. the semi-empirical Pariser–Parr–Pople method.

2.3. *Solvatochromic study of 5′-*N,N*-dialkylamino-2,2′bithiophene azo dyes* **4–7**

In agreement with other solvatochromic studies for heteroaryl–azo dyes, the increase of the electron-withdrawing strength of the substituent of the diazo component and/or the increase of the electron-donating strength of the coupling moiety was found to cause pronounced bathochromism [6a,b,7,13]. These red shifts in absorption were always accompanied by positive solvatochromic shifts. Especially noteworthy is the extremely large positive solvatochromism exhibited by acceptor-substituted 2-*N*,*N*-dialkylamino-(oligo)thiophenes making these compounds good indicators for measuring the polarity of solvent [1c–e,i,2].

In view of these facts and having in mind our recent results, we decide to study the solvatochromic properties of azo dyes **4–7**. Initially a preliminary study of the absorption spectra of bithiophene azo dyes **4–7** was performed in 4 selected solvents of different solvation character (diethyl ether, ethanol, chloroform and DMSO). For all azo dyes the highest energy transitions were found with less polar solvents such as diethyl ether. More polar solvents such as DMSO resulted in lower energy transitions. This behavior has been defined as a positive solvatochromic response that is related to a greater stabilization of the excited state relative to the ground state with increasing polarity of the solvent. Moreover, compounds **4c** ($\Delta\nu_{max} = 1020$ cm^{-1}), **4d** ($\Delta\nu_{max} = 1310$ cm^{-1}) and **7c** ($\Delta\nu_{max} = 981$ cm^{-1}) showed the longest shifts in wavenumber maxima. Therefore, compounds **4c** and **4d** were submitted to a full solvatochromic study involving 14 solvents (Table 2). Due to their pronounced solvatochromism, (**4c**, $\Delta\nu_{max} = +1271$ cm^{-1}; **4d** $\Delta\nu_{max} = +1115$ cm^{-1}), good correlation with π^* values by Kamlet et al. [14] for the solvents investigated and the long wavelength absorption in the visible range, **4c** and **4d** seemed to be very appropriate solvent polarity indicating dyes.

Table 2
Solvatochromic data [λ_{max} (nm) and υ_{max} (cm^{-1}) of the charge-transfer band] for azobithiophenes **4c** and **4d** in 14 solvents with π^* values by Kamlet et al. [14].

Solvents[a]	π^{*b}	Compound **4c** λ_{max} (nm) υ_{max} (cm^{-1})	Compound **4d** λ_{max} (nm) υ_{max} (cm^{-1})
n-Hexane	−0.08	448 22,321	504 19,841
Diethyl ether	0.27	492 20,325	520 19,231
Ethanol	0.54	502 19, 920	534 18,726
Toluene	0.54	500 20,000	530 18,867
1,4-Dioxane	0.55	498 20,080	528 18,939
Ethyl acetate	0.55	498 20,000	530 18,867
THF	0.58	500 19,920	534 18,726
Methanol	0.60	502 19,920	534 18,726
Acetone	0.71	502 19,920	536 18,656
Acetonitrile	0.75	502 19,920	538 18,587
Chloroform	0.76	506 19,763	542 18,450
Dichloromethane	0.82	506 19,763	542 18,450
DMF	0.88	512 19,531	550 18,181
DMSO	1.00	518 19,305	558 17,921

[a] Solvent used as received.
[b] The correlation coefficient *r* obtained for the linear solvation energy relationship with π^* values by Kamlet et al. for solvents was $r = 0.9069$ for **4c** and $r = 0.9812$ for **4d**.

The thermal properties of the chromophores **4–7** were investigated by thermogravimetric analysis under a nitrogen atmosphere, measured at a heating rate of 20 °C min^{-1} (Table 1). All the dyes are thermally stable with decomposition temperatures varying from 201 to 262 °C. For the piperidino and the *N*,*N*-dimethylamino-bithiophene azo dyes **4** and **7**, the acceptor groups substituted on the phenylazo moiety do seem to have some impact on the thermal stability of the compounds (e.g. **4a**, $R_2 = CO_2H$, $T_d = 209$ °C; **4b**, $R_2 = CO_2Me$, $T_d = 248$ °C) showing that, the carboxymethyl azo dyes are the most stable.

3. Conclusions

In summary, we have achieved the first synthesis of a series of 5-*N*,*N*-dialkylamino-2,2′-bithiophene azo dyes **4–7** from easily available 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2** and inexpensive commercially available anilines. Simple work-up procedures produce fair to good yields of these derivatives.

Compounds **4–7** exhibit dramatic changes in their optical properties in comparison to 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2**. By comparing the synthesized derivatives, it can be shown that the linear optical properties of these compounds is significantly influenced by the withdrawing group on the phenylazo moiety as well as the type of substituent on the 5′-position of the bithienyl π-conjugated bridge.

The solvatochromic behavior of compounds **4–7** was determined by regression analyses of absorption maxima in several solvents of different polarity. Due to their pronounced solvatochromic properties azo dyes **4–7** could be used as solvatochromic probes.

4. Experimental

4.1. *General*

Reaction progress was monitored by thin layer chromatography (0.25 mm thick precoated silica plates: Merck Fertigplatten Kieselgel 60 F254), while purification was effected by silica gel column chromatography (Merck Kieselgel 60; 230–400 mesh). NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR using the solvent peak as internal reference. The solvents are indicated in parenthesis before the chemical shift values (δ relative to TMS and given in ppm). Mps were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a BOMEM MB 104 spectrophotometer. UV–vis absorption spectra (200–800 nm) were obtained using a Shimadzu UV/2501 PC spectrophotometer. Elemental analyses were carried out on a Leco CHNS 932 instrument. Mass spectrometry analyses were performed at the "C.A.C.T.I.-Unidad de Espectrometria de Masas" at the University of Vigo, Spain.

Light petroleum refers to solvent boiling in the range 40–60 °C.

3-Carboxyaniline, 4-carboxymethylaniline, 4-cyanoaniline, 4-nitroaniline and 2-cyano-4-nitroaniline used as precursors for the synthesis of aryldiazonium salts **3a**–**d** were purchased from Aldrich and Fluka and used as received.

4.2. Synthesis of 5-N,N-dialkylamino-2,2′-bithiophenes **2**

The synthesis of *N*,*N*-dialkylamino-4-(2′-thienyl)-4-oxobutanamides **1a**–**b** and **1d** and 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **2a**–**b, d** has been described elsewhere [1a].

*4.2.1. Synthesis of pyrrolidino-4-(2′-thienyl)-4-oxobutanamide (**1c**)*

Amide **1c** was obtained using the experimental method described in Refs. [1a] and [9], by reacting 4-oxo-(2-thienyl)butanoic acid (5.4 mmol) in CH_2Cl_2 with 1,3-dicyclohexylcarbodiimide (DCC) (7.1 mmol) and 1-hydroxybenzotriazole (BtOH) (7.1 mmol) and adding pyrrolidine (5.4 mmol) at rt during 24 h.

4.2.1.1. Pyrrolidino-4-(2′-thienyl)-4-oxobutanamide. Beige solid (80%). Mp 95.6–97.0 °C (ethyl ether). IR (KBr) ν 1660 (C=O), 1629 (C=O), 1461, 1414, 768 cm^{-1}. ^1H NMR (Acetone-d_6) δ 1.90 (t, 2H, $J = 6.3$ Hz CH_2) 2.00 (t, 2H, $J = 6.3$ Hz, CH_2), 2.69 (t, 2H, $J = 6.3$ Hz CH_2), 3.28 (t, 2H, $J = 6.3$ Hz, CH_2), 3.36 (t, 2H, $J = 6.3$ Hz, NCH_2), 3.56 (t, 2H, $J = 6.3$ Hz, NCH_2), 7.24–7.27 (m, 1H, 4′-H), 7.89 (dd, 1H, $J = 5.1$ and 1.2 Hz, 5′-H), 7.96 (dd, 1H, $J = 3.9$, 1.2 Hz, 3′-H). ^{13}C NMR (Acetone-d_6) δ 24,11, 25.75, 28.24, 33.83, 45.49, 46.26, 127.84, 131.81, 133.17, 143.67, 169.72, 191.90. Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.70; H, 6.33; N, 5.90; S, 13.50. Found: C, 60.45; H, 6.32; N, 5.85; S, 13.50.

*4.2.2. Synthesis of 5-pyrrolidino-2,2′-bithiophene (**2c**)*

Bithiophene **2c** was obtained using the experimental method described in Refs. [1a] and [9], by heating the amide **1c** (2.3 mmol) in toluene (12 ml) with the Lawesson reagent (2.3 mmol) at reflux during 150 min.

*4.2.2.1. 5-Pyrrolidino-2,2′-bithiophene (**2c**).* Yellow solid (47%). Mp 88.0–88.5 °C (lit. [2b] 88.0 °C, *n*-hexane) UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 364.5 (46,122). IR (liquid film) ν 3102, 2964, 2932, 2874, 1508, 1470, 1430, 1383, 1345, 1299, 1234, 1201, 1108, 1070, 941, 896, 844, 783, 711, 613 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.90–2.00 (m, 4H, 2xCH_2), 3.15–3.25 (m, 4H, 2xNCH_2), 5.67 (d, 1H, $J = 4.2$ Hz, 4-H), 6.90–6.98 (3H, m, 3- 4′- and 3′-H), 7.24 (1H, dd, $J = 4.5$ and 1.5 Hz, 5′-H).

4.3. General procedure for azo coupling of bithiophenes **2** *with 3-carboxy-, 4-carboxymethyl-, 4-cyano-, 4-nitro-, and 2-cyano-4-nitro-substituted aryldiazonium salts (**3a–e**)*

4.3.1. Diazotisation of 3-carboxy-, 4-carboxymethyl-, 4-cyano-, 4-nitro- and 2-cyano-4-nitroaniline

Primary amine (4.0 mmol) was pasted with $NaNO_2$ (4.0 mmol) and water (10 ml) to a smooth slurry and it was added to a well-stirred mixture of HCl ($d = 1.18$; 3 ml) and ice (3 g) at 0–5 °C. The reaction mixture was stirred for 30 min.

*4.3.2. Coupling reaction with 5′-N,N-diakylamino-2,2′-bithiophenes (**2**)*

The diazonium salt solution previously prepared (4.0 mmol) was added dropwise to the solution of bithiophene **2** (4.0 mmol) in acetonitrile (50 ml) and a few drops of acetic acid. The ensuing mixture was stirred at 0 °C for 1 h and thereafter left overnight at room temperature. After this time the resulting mixture was diluted with petroleum ether (20 ml) and water (40 ml) and the ensuing product was isolated by filtration. The crude 5-*N*,*N*-dialquilamino-4-phenylazo-bithiophenes **4**–**7** were purified by column chromatography on silica with dichoromethane as eluent.

*4.3.2.1. 5-N,N-dimethylamino-4-(3″-carboxyphenylazo)-2,2′-bithiophene (**4a**).* Pink reddish solid (27%). Mp > 211 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 473.0 (19,496). IR (KBr) ν 542, 600, 615, 634, 662, 682, 701, 736, 758, 811, 834, 882, 910, 923, 997, 1014, 1062, 1147, 1165, 1200, 1241, 1267, 1282, 1305, 1355, 1384, 1407, 1420, 1446, 1477, 1542, 1567, 1604, 1622, 1689 (C=O), 2386–3429 (OH) cm^{-1}. ^1H NMR (DMSO-d_6) δ 3.47 (s, 6H, 2xCH_3), 7.07–7.10 (m, 1H, 4′-H), 7.23 (d, 1H, $J = 3.6$, 1.2 Hz, 3′-H), 7.46 (s, 1H, 3-H), 7.48 (dd, 1H, $J = 5.1$, 1.2 Hz, 5′-H), 7.57 (t, 1H, $J = 7.8$ Hz, 5″-H), 7.81–7.86 (m, 2H, 4″ and 6″-H), 8.14 (m, 1H, 2″-H). ^{13}C NMR (DMSO-d_6) δ 45.2, 112.7, 120.2, 122.1, 123.3, 124.9, 125.0, 128.2, 128.4, 129.5, 132.1, 135.8, 136.5, 153.5, 160.0, 167.3. MS (EI) m/z (%): 357 (M^+, 53), 221 (100), 193 (18), 149 (16), 129 (8), 78 (41), 63 (41). HRMS: m/z (EI) for $C_{17}H_{15}N_3O_2S_2$; calcd 357.0606; found: 357.0616. Anal. Calcd for $C_{17}H_{15}N_3O_2S_2$: C, 57.12; H, 4.23; N, 11.76. Found: C, 57.35; H, 4.12; N, 11.93.

*4.3.2.2. 5-N,N-dimethylamino-4-(4″-carboxymethylphenylazo)-2,2′-bithiophene (**4b**).* Red solid (58%). Mp 171.5–172.4 °C. UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 498.0 (27,200), 343.0 sh (15,320). IR (Nujol) ν 510, 525, 566, 645, 697, 722, 773, 826, 842, 857, 896, 920, 965, 1017, 1096, 1108, 1141, 1202, 1272, 1310, 1341, 1548, 1598, 1709 (C=O), 2672, 2728 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.52 (s, 6H, 2xNCH_3), 3.93 (s, 3H, OCH_3), 7.00 (m, 1H, 4′-H), 7.08 (dd, 1H, $J = 3.6$, 1.2 Hz, 3′-H), 7.20 (dd, 1H, $J = 5.1$, 1.2 Hz, 5′-H), 7.57 (s, 1H, 3-H), 7.69 (d, 2H, $J = 8.4$ Hz, 2″-H and 6″-H), 8.10 (d, 2H, $J = 8.7$ Hz, 3″-H and 5″-H). MS (EI) m/z (%): 371 (M^+, 44), 222 (14), 221 (100), 209 (9), 164 (6), 132 (6), 127 (7), 69 (8). HRMS: m/z (EI); for $C_{18}H_{17}N_3O_2S_2$; calcd: 371.0762; found: 371.0762. Anal. Calcd for $C_{18}H_{17}N_3O_2S_2$: C, 58.20; H, 4.61; N, 11.31; S, 17.26. Found: C, 58.41; H, 4.31; N, 11,501; S, 17.49.

*4.3.2.3. 5-N,N-dimethylamino-4-(4″-cyanophenylazo)-2,2′-bithiophene (**4c**).* Dark red solid with metallic luster (49%). Mp > 167 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 502.0 (16,162). IR (KBr) ν 687, 831, 1100, 1144, 1313, 1419, 1545, 1595, 2214 (CN), 2922 cm^{-1}. ^1H NMR (acetone-d_6) δ 3.61 (s, 6H, 2xCH_3), 7.10–7.13 (m, 1H, 4′-H), 7.24 (dd, 1H, $J = 3.5$, 1.2 Hz, 3′-H), 7.46 (dd, 1H, $J = 5.1$, 1.2 Hz, 5′-H), 7.59 (s, 1H, 3-H), 7.78–7.86 (m, 4H, 4xAr–H). ^{13}C NMR (acetone-d_6) δ 45.9, 110.3, 113.6, 119.7, 122.7, 124.2, 125.5, 126.5, 128.9, 133.9, 137.7, 138.2, 157.3, 162.6. MS (EI) m/z (%): 338 (M^+, 57), 310 (3), 208 (12), 221 (100), 193 (12), 180 (7), 127 (13), 102 (10). HRMS: m/z (EI); for $C_{17}H_{14}N_4S_2$; calcd: 338.0660; found: 338.0656 Anal. Calcd for $C_{17}H_{14}N_4S_2$: C, 60.33; H, 4.17; N, 16.55; S, 18.95. Found: C, 60.53; H, 4.47; N, 16.80; S, 18.55.

*4.3.2.4. 5-N,N-dimethylamino-4-(4″-nitrophenylazo)-2,2′-bithiophene (**4d**).* Dark red solid (36%). Mp 184.7–185.9 °C. UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 537.0 (23,890), 343 sh (15,700). IR (Nujol) ν 755, 809, 830, 850, 857, 896, 921, 995, 1017, 1097, 1146, 1164, 1202, 1252, 1281, 1294, 1337, 1401, 1415, 1505, 1553, 1584 cm^{-1}. ^1H NMR (Acetone-d_6) δ 3.61 (s, 6H, 2xCH_3), 7.10–7.13 (m, 1H, 4′-H), 7.27 (dd, 1H, $J = 3.6$, 1.2 Hz, 3′-H), 7.48 (dd, 1H, $J = 5.4$, 1.2 Hz, 5′-H), 7.61 (s, 1H, 3-H), 7.84 (d, 2H, $J = 9.0$ Hz, 2″-H and 6″-H), 8.34 (d, 2H,

$J = 9.0$ Hz, $3''$-H and $5''$-H). ^{13}C NMR (acetone-d_6) δ 46.1, 110.6, 113.5, 122.4, 122.5, 124.4, 125.5, 125.7, 129.0, 137.6, 138.8, 146.5, 159.0. MS (EI) m/z (%): 358 (M^+, 49), 236 (8), 222 (15), 221 (100), 208 (14), 193 (19), 180 (9), 170 (7), 137 (11), 127 (11), 111 (10), 97 (18), 83 (18), 81 (29), 69 (34). HRMS: m/z (EI); for $C_{16}H_{11}N_4O_2S_2$; calcd: 358.0558; found: 358.0566. Anal. Calcd for $C_{16}H_{11}N_4O_2S_2$: C, 53.61; H, 3.94; N, 15.63; O, 8.93; S, 17.89. Found: C, 53.41; H, 3.74; N, 15.33; S, 17.69.

*4.3.2.5. 5-*N,N*-diethylamino-4-($3''$-carboxyphenylazo)-2,2′-bithiophene (**5a**).* Dark red solid with metallic luster (62%). Mp > 207 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 478.0 (15,733). IR (KBr) ν 508, 569, 599, 610, 682, 692, 735, 756, 787, 813, 835, 906, 950, 998, 1010, 1079, 1143, 1162, 1185, 1208, 1229, 1260, 1295, 1339, 1399, 1430, 1443, 1484, 1528, 1566, 1583, 1683 (C=O), 2357–3429 (OH) cm^{-1}. ^{1}H NMR (acetone-d_6) δ 1.45 (t, 6H, $J = 7.0$ Hz, $2xCH_2CH_3$), 3.96–3.98 (q, 4H, $J = 7.0$ Hz, $2xCH_2CH_3$), 7.10–7.14 (m, 1H, $4'$-H), 7.21 (dd, 1H, $J = 3.8$, 1.2 Hz, $3'$-H), 7.43 (dd, 1H, $J = 5.1$, 1.2 Hz, $5'$-H), 7.59 (s, 1H, 3-H), 7.65 (t, 1H, $J = 7.8$ Hz, $5''$-H), 7.94–8.00 (m, 2H, $4''$ and $6''$-H), 8.38–8.40 (m, 1H, $2''$-H). ^{13}C NMR (acetone-d_6) δ 12.9, 50.7, 114.1, 120.8, 122.7, 123.7, 125.0, 126.9, 128.8, 129. 1,130.1, 132.5, 136.3, 138.0, 155.0, 159.3, 167.5. MS (EI) m/z (%): 385 (M^+, 18), 357 (8), 249 (100), 220 (16), 207 (32), 195 (9), 180 (8), 163 (22), 137 (21), 127 (16), 121 (12), 108 (11), 96 (8), 92 (7), 65 (24). HRMS: m/z (EI) for $C_{19}H_{19}N_3O_2S_2$; calcd: 385.0919; found: 385.0922. Anal. Calcd for $C_{19}H_{19}N_3O_2S_2$ C, 59.20; H, 4.97; N, 10.90; S, 16.64. Found C, 59.40; H, 5.10; N, 11.13; S, 16.83.

*4.3.2.6. 5-*N,N*-diethylamino-4-($4''$-cyanophenylazo)-2,2′-bithiophene (**5c**).* Dark red solid with metallic luster (53%). Mp > 177 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 509.0 (26,386); 360 sh (14,580). IR (KBR) ν 574, 680, 837, 1006, 1075, 1206, 1256, 1319, 1394, 1526, 2214 (CN), 2972 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 1.44 (t, 6H, $J = 7.2$ Hz, $2xCH_2CH_3$), 3.98–4.00 (q, 4H, $J = 7.2$ Hz, CH_2CH_3), 7.10–7.12 (m, 1H, $4'$-H), 7.23 (dd, 1H, $J = 3.6$, 1.2 Hz, $3'$-H), 7.45 (dd, 1H, $J = 5.1$, 1.2 Hz, $5'$-H), 7.57 (s, 1H, 3-H), 7.79–7.86 (m, 4H, 4xAr–*H*.). ^{13}C NMR (acetone-d_6) δ 12.7, 50.9, 110.3, 113.8, 119.7, 121.5, 122.6, 124.1, 125.4, 128.9, 133.9, 137.4, 137.7, 157.5, 160.8. MS (EI) m/z (%): 366 (M^+, 46), 308 (5), 249 (100), 220 (17), 209 (27), 102 (18). HRMS: m/z (EI); for $C_{19}H_{18}N_4S_2$; calcd: 366.0973; found: 366.0963. Anal. Calcd for $C_{19}H_{18}N_4S_2$ C, 62.27; H, 4.95; N, 15.29; S, 17.50. Found C, 62.60; H, 4.70; N, 15.10; S, 17.80.

*4.3.2.7. 5-Pyrrolidino-4-($3''$-carboxyphenylazo)-2,2′-bithiophene (**6a**).* Dark red solid (40%). Mp > 210 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 474.5 (18,276). IR (KBr) ν 506, 537, 618, 647, 661, 686, 717, 737, 756, 762, 817, 834, 880, 921, 966, 997, 1016, 1048, 1075, 1152, 1164, 1186, 1239, 1272, 1300, 1324, 1348, 1370, 1416, 1441, 1466, 1531, 1587, 1602, 1623, 1698 (C=O), 2500–3429 (OH) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 2.78–2.81 (m, 4H, 2x NCH_2CH_2), 3.77–3.81 (m, 4H, $2xNCH_2$), 7.07–7.10 (m, 1H, $4'$-H), 7.24 (dd, 1H, $J = 3.0$, 1.2 Hz, $3'$-H), 7.47–7.50 (m, 2H, 3-H and $5'$-H), 7.56 (t, 1H, $J = 7.8$ Hz, $5''$-H), 7.80–7.84 (m, 2H, $4''$-H and $6''$-H), 8.13 (m, 1H, $2''$-H). ^{13}C NMR (DMSO-d_6) δ 25.3, 53.7, 112.3, 120.6, 122.4, 123.2, 124.5, 124.8, 127.8, 128.3, 129.4, 131.8, 135.4, 136.6, 153.6, 157.0, 167.2. MS (EI) m/z (%): 383 (M^+, 16), 247 (100), 247 (72), 219 (16), 196 (13), 187 (9), 120 (13), 92 (15), 69 (13). HRMS: m/z (EI) for $C_{19}H_{17}N_3O_2S_2$; calcd: 383.0762; found: 383.0771. Anal. Calcd for C, 59.51; H, 4.47; N, 10.96; S, 16.72. Found C, 59.80; H, 4.66; N, 10.90; S, 16.89.

*4.3.2.8. 5-Pyrrolidino-4-($4''$-cyanophenylazo)-2,2′-bithiophene (**6c**).* Dark red solid (23%). Mp 198.1–199.0 °C. UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 504.0 (22,381). IR (Nujol) ν 543, 680, 831, 1125, 1175, 1282, 1307, 1375, 1538, 1595, 2214 (CN) cm^{-1}. ^{1}H NMR (acetone-d_6) δ 2.80–2.84 (m, 4H, 2x NCH_2CH_2), 3.88–3.92 (m, 4H, $2xNCH_2$), 7.10–7.12 (m, 1H, $4'$-H), 7.24 (dd, 1H, $J = 3.6$, 1.2 Hz, $3'$-H), 7.45 (dd, 1H, $J = 5.1$, 1.2 Hz, $5'$-H), 7.57 (s, 1H, 3-H), 7.81–7.85 (m, 4H, 4xAr–H). (EI) m/z (%): 364 (M^+, 33), 297 (4), 247 (100), 219 (15), 118 (88), 91 (22). HRMS: m/z (EI) for $C_{19}H_{16}N_4S_2$; calcd: 364.0819; found: 364.0816. Anal. Calcd for $C_{19}H_{16}N_4S_2$ C, 62.61; H, 4.42; N, 15.37; S, 17.59. Found C, 62.75; H, 4.30; N, 15.46; S, 17.80.

*4.3.2.9. 5-Piperidino-4-($3''$-carboxyphenylazo)-2,2′-bithiophene (**7a**).* Brown reddish solid (55%). Mp > 207 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 483.0 (14,738). IR (KBr) ν 506, 520, 541, 561, 582, 609, 646, 664, 680, 701, 739, 758, 810, 836, 852, 884, 911, 934, 955, 997, 1024, 1041, 1071, 1126, 1154, 1214, 1232, 1242, 1272, 1290, 1336, 1360, 1384, 1445, 1509, 1565, 1575, 1605, 1683 (C=O), 2357–3257 (OH) cm^{-1}. ^{1}H NMR (acetone-d_6) δ 1.85–1.88 (m, 6H, $3xNCH_2CH_2$), 3.99 (m, 4H, $2xNCH_2$), 7.01–7.04 (m, 1H, $4'$-H), 7.21 (dd, 1H, $J = 3.8$, 1.2 Hz, $3'$-H), 7.43 (dd, 1H, $J = 5.1$, 1.2 Hz, $5'$-H), 7.54 (s, 1H, 3-H), 7.63 (t, 1H, $J = 8.1$ Hz, $5''$-H), 7.92–8.04 (m, 2H, $4''$-H and $6''$-H), 8.37 (m, 1H, $2''$-H). ^{13}C NMR δ 24.7, 26.3, 54.7, 114.1, 121.7, 123.6, 123.8, 125.1, 125.9, 128.8, 129.8, 129.9, 133.8, 137.7, 138.0, 151.2, 154.7, 168.8. MS (EI) m/z (%): 397 (M^+, 21), 261 (100), 137 (4), 69 (4). HRMS: m/z (EI) for $C_{20}H_{19}N_3O_2S_2$; calcd: 397.0919; found: 397.0922. Anal. Calcd for $C_{20}H_{19}N_3O_2S_2$ C, 60.43; H, 4.82; N, 10.57; S, 16.13. Found C, 60.77; H, 5.21; N, 10.30; S, 16.40.

*4.3.2.10. 5-Piperidino-4-($4''$-carboxymethylphenylazo)-2,2′-bithiophene (**7b**).* Dark red solid (16%). Mp 132.7–134.6 °C. UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 504.0 (22,460), 360.0 sh (15,330). IR (Nujol) ν 697, 718, 772, 817, 853, 917, 967, 1002, 1019, 1095, 1115, 1143, 1165, 1216, 1245, 1275, 1311, 1337, 1352, 1395, 1419, 1451, 1512, 1566, 1599, 1698, 1709, 1719 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.78–1.82 (m, 6H, $3xNCH_2CH_2$), 3.91–3.93 (m, 4H, $2xNCH_2$), 3.94 (s, 3H, OCH_3), 7.0 (dd, 1H, $J = 5.1$, 1.2 Hz, $4'$-H), 7.06 (dd, 1H, $J = 3.9$ Hz, 1.5 Hz, $3'$-H), 7.19 (dd, 1H, $J = 5.1$, 1.2 Hz, $5'$-H), 7.50 (s, 1H, 3-H), 7.69 (d, 2H, $J = 8.4$ Hz, $2''$-H and $6''$-H), 8.10 (d, 2H, $J = 8.4$ Hz, $3''$-H and $5''$-H). ^{13}C NMR δ 24.1, 25.6, 52.1, 54.1, 113.5, 121.3, 121.4, 122.85, 124.0, 127.6, 128.6, 130.6, 137.5, 137.8, 156.8, 161.0, 167.0. MS (EI) m/z (%): 411 (M^+, 19), 263 (11), 262 (18), 261 (100). HRMS: m/z (EI) for $C_{21}H_{21}N_3O_2S_2$; calcd: 411.1075; found: 411.1079. Anal. Calcd for $C_{21}H_{21}N_3O_2S_2$ C, 61.29; H, 5.14; N, 10.21; S, 15.58. Found C, 61.47; H, 5.10; N, 10.35; S, 15.80.

*4.3.2.11. 5-Piperidino-4-($4''$-cyanophenylazo)-2,2′-bithiophene (**7c**).* Dark red solid (55%). Mp > 162.4–163.3 °C. UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 510.5 (25,069), 339.0 sh (17,679). IR (KBr) ν 543, 630, 699, 837, 1131, 1162, 1206, 1313, 1519, 1588, 2214 (CN), 2853, 2934 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 1.80–1.87 (m, 6H, $3xNCH_2CH_2$), 4.04–4.07 (m, 4H, $2xNCH_2$), 7.09–7.12 (m, 1H, $4'$-H), 7.22 (dd, 1H, $J = 3.6$, 1.2 Hz, $3'$-H), 7.45 (dd, 1H, $J = 5.1$, 1.2 Hz, $5'$-H), 7.52 (s, 1H, 3-H), 7.78–7.88 (m, 4H, 4xAr–*H*). ^{13}C NMR δ 24.0, 25.7, 54.2, 109.9, 113.3, 119.4, 121.9, 121.9, 123.1, 124.3, 125.6, 127.7, 132.8, 133.1, 137.2, 138.0. MS (EI) m/z (%): 378 (M^+, 23), 311 (9), 261 (100), 127 (7), 102 (7). HRMS: m/z (EI) for $C_{20}H_{19}N_4S_2$; calcd: 378.0973; found: 378.0966. Anal. Calcd for $C_{20}H_{19}N_4S_2$ C, 63.46; H, 4.79; N, 14.80; S, 16.94. Found C, 63.24; H, 4.90; N, 14.70; S, 16.65.

*4.3.2.12. 5-Piperidino-4-($4''$-nitrophenylazo)-2,2′-bithiophene (**7d**).* Dark red solid (32%). Mp 178.2–178.9 °C. UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 544.0 (24,270), 423.0 sh (6663). IR (Nujol) ν 695, 705, 723, 753, 811, 828, 850, 881, 910, 998, 1018, 1082, 1101, 1146, 1162, 1197, 1262, 1197, 1216, 1240, 1254, 1281, 1299, 1332, 1377, 1399, 1462, 1499, 1538, 1583, 1596 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.82–1.88 (m, 6H, $3xNCH_2CH_2$), 4.02–4.04 (m, 4H, $2xNCH_2$), 7.01–7.03 (m, 1H, $4'$-H), 7.08 (dd, 1H, $J = 3.6$, 1.2 Hz, $3'$-H), 7.22 (dd, 1H, $J = 5.1$, 1.2 Hz, $5'$-H), 7.49 (s, 1H, 3-H), 7.70 (d, 2H, $J = 9.0$ Hz, $2''$-H and $6''$-H), 8.28 (d, 2H, $J = 9.0$ Hz, $3''$-H and $5''$-H). ^{13}C NMR δ 24.0, 25.7, 54.3, 113.2, 121.5, 121.9, 123.3, 124.5, 124.9, 127.7, 137.1, 138.5, 145.9, 157.9, 162.4. MS (EI) *m*/*z* (%): 398 (M^+, 21), 263 (9), 262 (17), 261 (100), 219 (5), 84 (5). HRMS: *m*/*z* (EI) for $C_{19}H_{18}N_4O_2S_2$; calcd: 398.0871; found: 398.0866. Anal. Calcd for $C_{19}H_{18}N_4O_2S_2$ C, 57.27; H, 4.55; N, 14.06; S, 16.09. Found C, 57.30; H, 4.25; N, 14.36; S, 16.33.

*4.3.2.13. 5-Piperidino-4-(2″-cyano-4”-nitrophenylazo)-2,2′-bithiophene (**7e**).* Dark blue solid (10%). Mp > 194.5 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 585.5 (16,309), 344.0 sh (12,000). IR (Nujol) ν 693, 718, 831, 906, 1012, 1069, 1156, 1225, 1294, 1507, 1569, 2220 (CN) cm^{-1}. ^1H NMR (acetone-d_6) δ 1.86 (m, 6H, 3x C*H*$_2$), 4.10 (m, 4H, 2xNC*H*$_2$), 7.01–7.04 (m, 1H, 4′-H), 7.12 (dd, 1H, J = 3.6, 1.2 Hz, 3′-H), 7.28 (dd, 1H, J = 5.1 Hz, 1.2 Hz, 5′-H), 7.55 (s, 1H, 3-H), 7.58 (d, 1H, J = 9.0 Hz, 6″-H), 8.31 (dd, J = 9.3 Hz, 2.4 Hz, 5″-H), 8.55 (d, 1H, J = 2.4 Hz, 3″-H). ^{13}C NMR ($CDCl_3$) δ 23.8, 25.9, 54.7, 108.8, 113.3, 116.4, 117.1, 123.3, 124.3, 125.5, 127.9, 128.0, 129.7, 136.3, 140.9, 141.0, 143.9, 159.5. MS (EI) *m*/*z* (%): 423 (M^+, 26), 281 (5), 261 (100), 234 (7), 163 (8), 90 (5). HRMS: *m*/*z* (EI) for $C_{20}H_{17}N_5O_2S_2$; calcd: 423.0824; found: 423.0807. Anal. Calcd for $C_{20}H_{17}N_5O_2S_2$C, 56.72; H, 4.05; N, 16.54; S, 15.14. Found C, 56.90; H, 4.10; N, 16.30; S, 15.25.

*4.4. Thermogravimetric analysis of compounds (**4**–**7**)*

Thermogravimetric analysis of samples was carried out using a TGA instrument model Q500 from TA Instruments, under high purity nitrogen supplied at a constant 50 ml min^{-1} flow rate. All samples were subjected to a 20 °C min^{-1} heating rate and were characterized between 25 and 500 °C.

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