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Push–pull bithiophene azo-chromophores bearing thiazole and benzothiazole acceptor moieties: Synthesis and evaluation of their redox and nonlinear optical properties

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ABSTRACT

Three series of bithiophene azo dyes functionalized with thiazol-2-*yl* or benzothiazol-2-*yl*-diazene acceptor moieties were synthesized through azo coupling reaction using 2,2′-bithiophene, 5-alkoxy-2,2′-bithiophenes, 5-*N*,*N*-dialkylamino-2,2′-bithiophenes and thiazolyl- and benzothiazolyl diazonium salts as coupling components. The 5-alkoxy-2,2′-bithiophene precursors yielded the 5-thiazolylazo-5′-alkoxy-2,2′-bithiophenes, while the azo coupling reaction of 5-*N*,*N*-dialkylamino-2,2′-bithiophenes with the thiazolyl diazonium salt gave 4-thiazolyl-azo-5-*N*,*N*-dialkylamino-2,2′-bithiophenes. A different reactivity behavior was observed for 2,2-bithiophene with thiazolyl diazonium salts which gave rise to the expected azo dyes together with several arylation products. The redox behavior, thermal stability, and the first hyperpolarizability of the novel chromophores were evaluated through cyclic voltammetry, thermogravimetric analysis (TGA) and hyper-Rayleigh scattering (HRS) respectively. By varying the position of the thiazolyldiazene acceptor group on the bithiophene system, the electrochemical behavior as well as the optical (linear and nonlinear) properties of the donor–acceptor π-conjugated systems can readily be tuned. Push–pull 5-thiazolylazo-5′-alkoxy-2,2′-bithiophenes exhibit the most promising redox and the solvatochromic properties and second-order nonlinear optical response. The redox and the optical properties also show notable variations for the different heterocyclic spacers and were also sensitive to the electronic acceptor strength of the (benzo)thiazolyldiazene moieties.

1. Introduction

Heterocyclic azo dyes are a versatile class of colored compounds that have attracted the interest of many research groups, in part because of their multiple industrial applications in the fields of textiles, papers, leather, additives, foodstuffs, cosmetics, holographic data storage materials, laser materials, xerography, laser printing and as materials for organic solar cells and chemosensors [1]. In addition, other heterocyclic azo dyes have found uses as organic second-order nonlinear optical materials (NLO) suitable for applications such as harmonic generation and optical switching [2].

Previously the two lowest singlet excitation energies of 18 azo dyes have been studied by *ab* initio quantum-chemical methods within the second-order polarization propagator approximation (SOPPA) by Åstrand et al.. Various combinations of five-membered rings such as furan, thiophene, pyrrole, oxazole, thiazole, and imidazole have been investigated as diazo components for a potential use in optical data storage materials. Diazo compounds with two heterocyclic five-membered rings are found to have $\pi \rightarrow \pi^*$ excitation energies corresponding to laser wavelengths in the region 450–500 nm whereas one five-membered ring and a phenyl group as diazo components have excitation wavelengths in the 400–435 nm region. The results of these theoretical chemical calculations suggest that they could be used as suitable azo components in optical data storage materials. In particular, it was shown that azo dyes with two five-membered rings (*e.g.* thiophene, pyrrole and thiazole) as diazo components can, in principle, be obtained with excitation energies corresponding to laser wavelengths considerably longer than for azobenzenes, which would be desirable for some optical data storage devices.

Prior theoretical and experimental and studies [1,2a–c] have stimulated a strong interest in our research group to engage in the synthesis and characterization of novel heterocyclic azo dyes bearing thiophene, pyrrole and thiazole heterocycles. The optical and electronic characterization of several novel chromophores previously synthesized by us, confirmed that they possess the

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essential characteristics necessary for use as efficient solvatochromic probes, nonlinear optical and photochromic materials [3,4], supporting the main conclusions of Åstrand et al. theoretical studies described above.

Our compounds were obtained through an azo coupling reaction using bithiophene [5] or thienylpyrroles derivatives [6] and aryl or heteroaryldiazonium salts as coupling components. We have recently employed this synthetic methodology to obtain thienylpyrrole derivatives functionalized with phenyldiazene [3a,b] and thiazolyldiazene groups [3d], and bithiophene chromophores bearing phenyldiazene [4a–c] acceptor moieties. The electrochemical, thermal and optical properties of these compounds indicate that they have good potential to be used in applications as nonlinear optical [3d,4a,b] and photochromic materials [3c,d,4d].

In view of these facts and as a continuation of our recent studies on the synthesis and characterization of heterocyclic azo dyes for optical applications, we considered it worthwhile to synthesize bithiophene derivatives functionalized with thiazolyl- and benzothiazolyldiazene moieties and evaluate their electrochemical, thermal and optical (linear and nonlinear) properties.

2. Results and discussion

2.1. Synthesis

Usually thiophene azo dyes are synthesized through azo coupling reaction of 2-aminothiophenes with arylamines [2a,j,7], although the difficulties of synthesizing 2-aminothiophenes are well known. To overcome these difficulties, we have recently developed a novel methodology of synthesis for bithienylaryldiazenes using as coupling components 5-alkoxy- or 5-*N*,*N*-dialkylamino-2,2′-bithiophenes and aryldiazonium salts. In our recent work, 5-alkoxy- and 5-*N*,*N*-dialkylamino-2,2′-bithiophenes were shown to be highly reactive with aryldiazonium salts. Moreover, we also demonstrated that the position of the electrophilic substitution on the bithiophene moiety, depends on the electronic nature of the group substituted on 5-position of the bithiophene system (alkoxy or *N*,*N*-dialkylamino). For instance, azo coupling reaction of 5-alkoxy-2,2′-bithiophenes with aryldiazonium salts gave 5′-phenylazo-5-alkoxy-2,2′-bithiophenes **8** [4a,b]. On the other hand, the coupling reaction of the 5-*N*,*N*-dialkylamino-2,2′-bithiophenes under the same reaction conditions occurs in the activated 4-position to yield 4-phenylazo-5-*N*,*N*-dialkylamino-bithiophenes **9**–**10** [4c] (Fig. 1). Despite the steric hindrance, the 4-position is still favored for the electrophilic reaction, as compared to the 5′-position.

Having in mind these earlier results we were motivated to study the reactivity of the azo coupling reaction of 5-alkoxy-, 5-*N*,*N*-dialkyamino-bithiophenes and also the unsubstituted bithiophene with heterocyclic thiazolyl- and benzothiazolyl diazonium salts.

In previous studies, we have synthesized and studied the solvatochromic and the redox properties of 5-*N*,*N*-dialkyamino bithienyl-aryldiazenes. In this manuscript, we report on the use of the hyper-Rayleigh scattering technique to characterize the second-order optical nonlinearities of some of these azo dyes and compare them with the novel bithienyl-thiazolyldiazenes. The thienylpyrrole azo dye **12c** (Fig. 2) was also synthesized in order to compare the difference of the π-conjugated bridge/donor auxiliary effect of the bithiophene system with thienylpyrrole heterocyclic spacer [3d] on the electronic and optical properties of these push–pull compounds. Alternatively, thiazolyl- and benzothiazolyl diazonium salts were chosen as coupling components for the synthesis of heterocyclic azo dyes **4**–**7** having in mind that the substitution of a phenyl group by electron-deficient 2-thiazole or 2-benzothiazole heterocycle in a donor–acceptor organic chromophore significantly enhances the respective first hyperpolarizability values, β [8,9].

Therefore, 2,2′-bithiophene **1a**, 5-alkoxy-**1b**–**c** and 5-*N*,*N*-dialkylamino-2,2′-bithiophenes **1d**–**e** [5] have been used as coupling components together with thiazolyl **2a**–**c** and benzothiazolyl diazonium salts **3** in order to prepare heterocyclic azo dyes **4**–**7** (Scheme 1, Table 1). Diazotation of 2-aminothiazole derivatives and 2-aminobenzothiazole with $NaNO_2$ in HCl (6 N) at 0–5 °C in water gave rise to the corresponding diazonium salts **2**–**3**, which reacted immediately with bithiophenes **1a**–**e** in acetonitrile at 0 °C given thiazolyldiazenes **4**–**6** and benzothiazolyldiazene **7** in fair to good yields (9–80%). Generally, higher yields were obtained in the synthesis of thiazolyldiazenes **4**–**6**, probably due to the higher stability of diazonium salts **2** when compared to **3**.

The thienylpyrrole azo dye **12c** (Fig. 2) was also synthesized with yield of 61% under the same experimental conditions described above using 1-(4-methoxyphenyl)-2-thieno-2-*yl*-pyrrole **11** [6] and thiazol-2-*yl*-diazonium salt **2c** as coupling components. A higher yield was obtained for **12c** compared to **6a** probably due to the stronger donor electronic character of thienylpyrrole as coupling component compared to 2,2′-bithiophene, making it more activated to react through an electrophilic aromatic substitution such the azo coupling reaction. 1-(4-Methoxyphenyl)-2-thieno-2-*yl*-pyrrole exhibits an analogous reactivity with thiazol-2-*yl*-diazonium salt **2c** when compared to the reaction with aryldiazonium salts [3a,b]. As a result, the corresponding azo dye **12c** was obtained having the thiazolyldiazene moiety substituted at 5-position of the pyrrole ring.

The 5-alkoxy- and 5-*N*,*N*-dialkylamino-2,2′-bithiophenes also exhibit a similar reactivity in azo coupling reactions with thiazolyl- and benzothiazolyl diazonium salts when compared to aryldiazonium salts [4a,b]. In effect, azo coupling of 5-alkoxy-2,2′-bithiophenes **1b**–**c** with thiazolyl diazonium salts **2a**–**b** gave 5′-thiazolylazo-5-alkoxy-2,2′-bithiophenes **4b**–**c** and **5b**–**c** and azo coupling reaction of

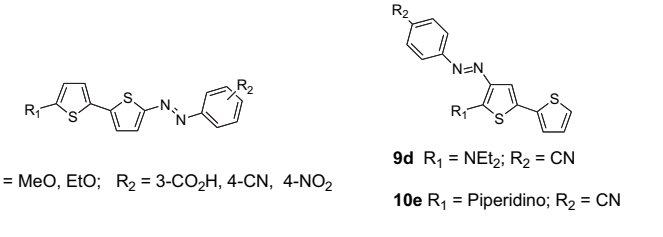


Fig. 1. Structure of 5′-phenylazo-5-alkoxy-2,2′-bithiophenes **8** [4a,b] and 4-phenylazo-5-*N*,*N*-dialkylamino-bithiophenes **9d** and **10e** [4c].

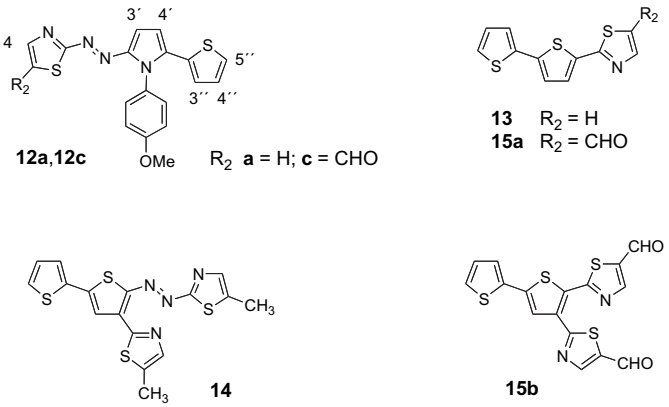
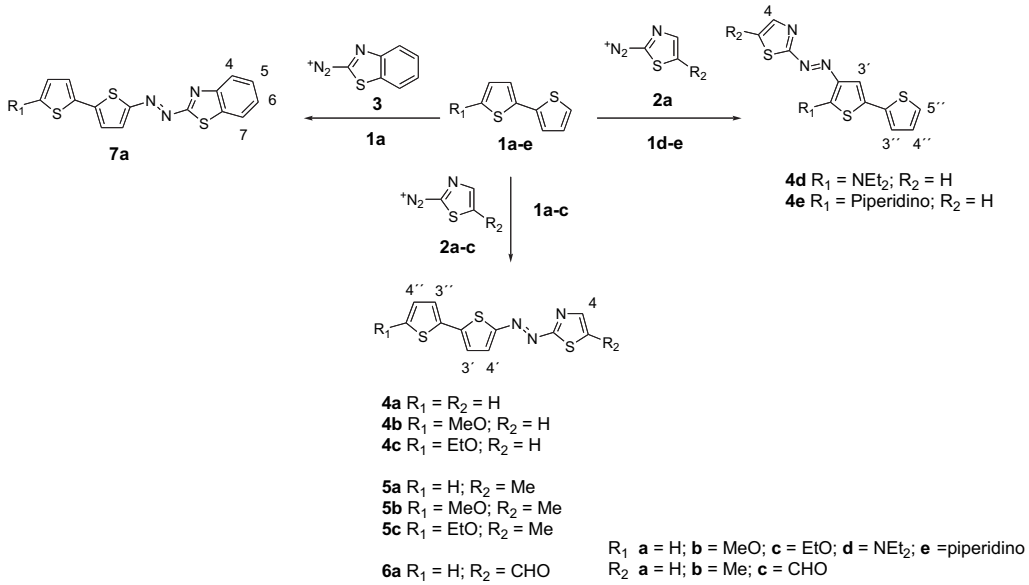


Fig. 2. Structure of azo dyes **12a** [3d] and **12c** and arylation products **13**–**15**.



Scheme 1. Synthesis of bithienyl diazenes **4**–**7** trough azo coupling reaction of 2,2′-bithiophene derivatives **1a**–**e** with thiazolyl **2a**–**c** and benzothiazolyl diazonium **3** salts.

5-*N*,*N*-dialkylamino-2,2′-bithiophenes **1d**–**e** with thiazolyl diazonium salt **2a**, gave selectively, 4-thiazolylazo-5-*N*,*N*-dialkylamino-2,2′-bithiophenes **4d**–**e** (Scheme 1). These results can be explained by taking in account several factors such as the increase of the electron density at the 4-position of the bithiophene moiety due to the 5-*N*,*N*-dialkylamino-substituents keeping in mind that the thiazolyl diazonium salt are not sterically a bulky species.

However an unexpected reactivity was observed for the azo coupling reaction of 2,2′-bithiophene **1a** with thiazolyl diazonium salts **2a**–**c**. This suggests that, under conditions in which thiazolyl diazonium salts **2a**–**c** couples with 5-alkoxy- and 5-*N*,*N*-dialkylamino-2,2′-bithiophenes to yield the corresponding azo dyes **4b**–**e** and **5b**–**c** the same ions interact with bithiophene giving complex reaction mixtures constituted by several deeply colored compounds (TLC). Therefore, using the same reaction conditions that were applied for the preparation of 5-alkoxy- and 5-*N*,*N*-dialkylamino-bithiophenes (0.5 equiv. of bithiophene **1a** and 1 equiv. of diazonium salts **2a**–**c**) all the coupling reactions gave the expected azo dyes **4a**, **5a** and **6a** in 23, 10 and 15% yields respectively, together with the arylation products **14** (17%) and traces (3%) of **15a** (Fig. 2). The arylation compounds **14** and **15a** were isolated and completely characterized by the usual spectroscopic techniques.

In order to study the reactivity of bithiophene with thiazolyl diazonium salts **2a**–**c** under different conditions, equimolar amounts of both coupling components were used. In these conditions more complex reaction mixtures were obtained and the yields of the expected azo dyes **4a** and **6a** decreased markedly from 23 to 10% (**4a**) or from 15 to 4% (**6a**). Concurrently we also observed an increase of the yields of the arylation products. The by-product **13** was obtained at a 5% yield in a mixture with the corresponding azo dye **4a** (10%). In the case of the azo coupling with diazonium salt **2c**, the pure azo dye **6a** was obtained at 4% yield together with a fraction which seems to be a mixture (^{1}H NMR and HPLC–MS) of the arylation products **15a** and **15b** in a 63% yield. An opposite behavior was observed for azo dye **5a**; in this case the yield increased from 10 to 21% together with the decrease of the arylation product **14** from 17 to 6% yield (Table 1). ^{1}H NMR and HPLC–MS were used in order to identify the components of the fractions that were not possible to separate by column chromatography. The arylation product **13** (5%) was identified in a mixture together with the corresponding azo dye **4a** (10%). On the other hand both arylation products **15a**–**b** were recognized in a mixture at a yield of 63%. These unexpected arylation products **13**–**15** probably arise because the same diazonium salts **2a**–**c** can interact also with the bithiophene with evolution of nitrogen to give the arylation products **13**–**15** [10a] (Fig. 2).

In fact, Tedder et al. reported earlier the arylation of thiophene under conditions in which 2,4-dinitrobenzenediazonium salts couple with anisole to yield the corresponding azo dye. Using thiophene as coupling component, these investigators obtained the arylation coupling product 5-(2,4-dinitrophenyl)thiophene [10a]. However when the thiophene ring was substituted by *t*-butyl, phenyl and dimethyl groups the azo coupling using the same diazonium salt gave the corresponding azo-thiophenes [10b].

Table 1
Yields and T_d data for bithiophene azo dyes **4**–**7**, thienylpyrrole azo dye **12c** and arylation products **13**–**15**.[a]

Bithiophene/ thienylpyrrole	Heterocyclic azo dye	R_1	R_2	Yield[a] (%)	T_d [c] (°C)
1a	**4a**	H	H	23, 10[b]	200
1b	**4b**	MeO	H	36	200
1c	**4c**	EtO	H	11	231
1d	**4d**	NEt_2	H	80	[d]
1e	**4e**	Piperidino	H	10	223
1a	**5a**	H	CH_3	10, 21[b]	241
1b	**5b**	MeO	CH_3	42	274
1c	**5c**	EtO	CH_3	9	214
1a	**6a**	H	CHO	15, 4[b]	231
1a	**7a**	H	–	9	283
11	**12c**	–	CHO	61	200
1a	**13**	H	H	5[b]	–
1a	**14**	H	CH_3	17, 6[b]	–
1a	**15a** and **15b**	H	CHO	3 (**15a**), 63[b] (**15a** + **15b**)	–

[a] Yield for azo dyes **4**–**7** and for arylation products **13**–**15** when 0.5 equiv. of bithiophene and 1.0 equiv. of thiazolyl diazonium salt **2a** were used.
[b] Yield for azo dyes **4a**–**6a** and for arylation products **13**–**15** when 1.0 equiv. of bithiophene and 1.0 equiv. of thiazolyl diazonium salt **2a** were used.
[c] Decomposition temperature (T_d) measured at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere, obtained by TGA.
[d] Compound **4d** was obtained as an oil.

The fact that arylation occurs with bithiophene derivatives suggests that there is a competition between arylation and azo coupling reactions; if the nucleus is sufficiently activated (*e.g.* by alkoxy or *N*,*N*-dialkylamino groups) azo coupling is preferred.

2.2. Electronic structure analysis

The electronic structures of the heterocyclic azo dyes were first analyzed by ^{1}H NMR spectroscopy (Table 2) and cyclic voltammetry (Table 3).

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″-alkoxy-5-thiazolylazo-2,2′-bithiophene derivatives **4b**–**c**, in $CDCl_3$, two signals at about 6.21–6.23 and 7.11–7.12 ppm, were detected. Both signals appear as doublets with coupling constants of 4.2 Hz indicating the presence of two adjacent protons in a di-substituted thiophene ring. These signals were attributed to the 4″-H and 3″-H protons respectively. On the other hand in the ^{1}H NMR spectrum of 5-*N*,*N*-dialkylamino-4-thiazolylazo-2,2′-bithiophene derivatives **4d**–**e**, in $CDCl_3$, one signal at about 7.57–7.59 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, **4d**–**e**, three signals at about 6.99–7.04 ppm (multiplet), 7.03–7.05 ppm (double doublet) and 7.20–7.22 ppm (double doublet) were detected. These signals were attributed respectively, to the 4″, 3″ and 5″-H protons at the second thiophene ring.

In the ^{1}H NMR spectra of benzothiazolyldiazene **7a** functionalized with a benzothiazol-2-*yl*-diazene moiety on the 5′-position of the thiophene ring four additional signals at about 7.42–7.47 (multiplet), 7.52 (double triplet), 7.87 (double doublet), and 8.13 (double doublet) were also detected and were attributed respectively, to the 5, 6, 4 and 7-H protons in the benzothiazole ring.

For thienylpyrrolyl-azo dye **12c** functionalized with a thiazolyldiazene moiety on the 2′-position of the pyrrole ring two doublets at 7.00 and 7.44 ppm were detected with coupling constants of 4.6 Hz indicating the presence of two adjacent protons (4′-H and 3′-H) at the corresponding pyrrole moiety.

The arylation products were also characterized by ^{1}H NMR spectra. For example, for compound **14** two doublets at 2.58 and 2.60 ppm were observed with coupling constants of 0.6 Hz which were attributed to the 5-Me groups and two doublets were also observed at 7.64 and 7.70 ppm with a coupling constant of 1.2 Hz due to the two 4-H in the thiazole rings. Three double doublets were also detected at 7.10, 7.41 and 7.44 and were attributed respectively, to the 4″, 5″ and 3″-H in the thiophene ring. A singlet at 7.96 ppm was also observed due to the 3′-H in the first thiophene ring. The ESI HRMS indicates that $[M+1]^+$ of 389 *m*/*z* can be attributed to the molecular formula $C_{16}H_{12}N_4S_4$ (389.0019).

The study of the NMR chemical shifts in push–pull derivatives bearing thiazole **4**–**6** and benzothiazole **7a** electron-deficient heterocycles can also confirm their push–pull character with a significant intramolecular charge transfer (ICT) from the donor bithiophene moiety to the acceptor (benzo)thiazole groups (Table 2). In particular, the effect of the substitution of a thiazolyl group for dye **4a** by a benzothiazole heterocycle (*e.g.* **7a**) is noteworthy. All the protons of the bithiophene system in **7a** (3′-H and 4′-H, and 3″, 4″and 5″-H) were shifted to higher chemical shifts (*e.g.* 4′-H and 3′-H $\delta = 7.37$ and 7.91 ppm respectively) as compared to the corresponding thiazolyldiazene azo dye **4a** (*e.g.* 4′-H and 3′-H

Table 2
Chemical shifts of protons of the heterocyclic azo dyes **4**–**7** and **12c**.[a]

Comp.	R_1	R_2	5-H	4-H	4′-H	3′-H	3″-H	4″-H	5″-H
4a	H	H	7.32	7.98	7.81	7.31	7.42	7.10	7.39
4b	MeO	H	7.34	7.95	7.75	7.14	7.12	6.23	–
4c	EtO	H	7.75	7.95	7.33	7.13	7.11	6.21	–
4d	NEt_2	H	7.03	7.75	–	7.59	7.03–7.04	7.00–7.04	7.20
4e	Piperidino	H	7.04–7.05	7.77	–	7.57	7.04–7.05	6.99	7.22
5a	H	CH_3	–	7.66	7.75	7.29	7.39	7.09	7.37
5b	MeO	CH_3	–	7.64	7.70	7.10	7.11	6.21	–
5c	EtO	CH_3	–	7.63	7.70	7.10	7.09	6.20	–
6a	H	CHO		8.52	7.94	7.40	7.50	7.13	7.47
7a	H	–	7.42–7.47	7.87	7.91	7.37	7.42–7.47	7.12	7.42–7.47
12c	–	CHO	–	8.35	7.00	7.44	7.14	7.01–7.02	7.38

[a] Proton NMR measurements carried out in deuterated chloroform at 400 MHz. The numbering scheme of protons is shown in Scheme 1 and Fig. 2.

Table 3
Electrochemical data for compounds **4**–**7** and **12c**.

Compound	Reduction[a]				Oxidation[a]			
	$-^1E_{pc}$ (V)	ΔE^b (mV)	$-^2E_{pc}$ (V)	ΔE^b (mV)	$^1E_{pa}$ (V)	$-E_{HOMO}{}^c$(eV)	$-E_{LUMO}{}^c$ (eV)	Band gap[d] (eV)
4a	1.23	63	2.04	90	0.80	5.19	3.16	2.03
4b	1.26	63	1.99	95	0.61	5.00	3.13	1.87
4c	1.26	62	2.07	93	0.59	4.98	3.13	1.85
4d	1.74	61	2.21	__	0.32	4.71	2.65	2.06
4e	1.67	60	2.36	__	0.31	4.70	2.72	1.98
5a	1.29	63	2.09	63	0.77	5.16	3.10	2.06
5b	1.31	54	2.05	100	0.70	5.09	3.08	2.01
5c	1.61	60	2.13	95	0.64	5.03	2.78	2.25
6a	0.86	63	1.61	60	0.98	5.37	3.53	1.84
7a	1.08	54	1.93	85	0.93	5.32	3.31	2.01
12c	0.98	65	1.69	__	0.76	5.15	3.41	1.74

[a] Measurements made in dry DMF containing 1.0 mM in each compounds and 0.10 M $[NBu_4][BF_4]$ as base electrolyte at a carbon working electrode with a scan rate of 0.1 V s^{-1}. All *E* Values are quoted in volts *vs* the ferrocinium/ferrocene-couple. E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.
[b] $\Delta E = |E_{red} - E_{ox}|$.
[c] $E_{HOMO} = -(4.39 + E_{ox})$ (eV) and $E_{LUMO} = -(E_{red} + 4.39)$ (eV).
[d] Calculated form the difference between the onset potentials for oxidation and reduction.

$\delta = 7.31$ and 7.81 ppm respectively) thus indicating a decrease of the electron density due to the stronger electron-withdrawing power. That is a higher charge-demand c_x, of the benzothiazole ring [11] provokes a more efficient charge transfer from the donor to the acceptor group.

A similar effect was observed in the chemical shifts for all protons of the bithiophene system **6a** (*e.g.* 4′-H and 3′-H $\delta = 7.40$ and 7.94 ppm respectively) bearing a thiazole ring functionalized with a formyl group when compared to thiazolyldiazene **4a**. On the other hand azo dyes **4b**–**c** bearing electron-donating alkoxy groups substituted on position 5′ of the bithiophene system exhibit high field signals for all protons of the bithienyl and thiazolyl moieties demonstrating the easy electron communication within the whole heterocyclic system.

A similar behavior was observed for 4-thiazolylazo-5-*N*,*N*-dialkylamino-2,2′-bithiophenes **4d**–**e** functionalized with the stronger electron-donating *N*,*N*-dialkylamino groups substituted on the *ortho* position to the thiazolyldiazene acceptor moieties which exhibit lower chemical shifts for all protons of the bithienyl and thiazolyl moieties. Noteworthy are the lower chemical shifts values for the thiazole protons (4-H and 5-H, $\delta = 7.75$–7.77 and 7.03–7.05 ppm respectively) for compounds **4d**–**e** compared to compound **4a** (4-H and 5-H $\delta = 7.98$ and 7.32 ppm respectively).

The ^{1}H NMR analysis for thienylpyrrole azo dye **12c** also confirms its push–pull character. Moreover, the thienylpyrrole derivative exhibit lower chemical shifts for all protons of the thienylpyrrole group and also for the thiazole ring (*e.g.* 3′-H, 4′-H and 4-H $\delta = 7.00$, 7.44 and 8.35 ppm respectively) compared to all bithiophene azo dye **6a** protons (*e.g.* 3′-H, 4′-H and 4-H, $\delta = 7.40$, 7.94 and 8.52 ppm respectively) demonstrating its stronger electron donor character and the easy electron communication through the entire conjugated system.

All bithienyl-thiazolyldiazenes **4**–**7** showed a donor–acceptor character with reversible reduction and irreversible oxidation processes. The irreversible oxidation process is associated with the oxidation of the thiophene moiety [3a,12] and the two reduction process are associated with the reduction of heterocyclic azo moiety. These values are comparable with those reported previously for other similar compounds [13,14].

Results show that the electronic nature of substituent group ($R_1 = H$, alkoxy, *N*,*N*-dialkylamino) in bithiophene moiety has a significant influence on the value of oxidation potential of this system. The substitution of the bithiophene system by stronger electron-donating groups such as *N*,*N*-dialkylamino leads to a significant shift of the cathodic potential values (*e.g.* azo dyes **4d** and **4e**). In contrast, the electronic donor or acceptor nature of the substituent ($R_2 = H$, CH_3, CHO) on the thiazole ring does not influence significantly the value of oxidation potential of compounds, **4a**, **5a** and **6a**.

All synthesized bithienyl azo dyes bearing a thiazole acceptor group exhibited two monoelectronic reductions. The one-electron stoichiometry for these reduction processes is ascertained by comparing the current heights with known one-electron redox processes under identical conditions [15]. The first process is reversible and the second process partially reversible, except for molecule **5a**, which underwent a second reversible process and molecules **4d**–**e** which exhibit irreversible processes. Compounds **4a**–**c** showed reversible reduction peaks, with similar onset potentials between −1.23 and −1.26 V, which were assigned to the reduction of the thiazolyldiazene moiety. This shows that for these compounds the substitution of the bithiophene system by groups with different electronic character has no influence on the reductions potentials. However, the reduction potentials values are significantly influenced by the substituent on 5′-position of the bithiophene moiety. The *N*,*N*-dialkylamino substituents shifts the value of the reduction potential of compounds **4d** and **4e** to more negative values compared to the unsubstituted **4a** and the alkoxy derivatives **4b**–**c** (*e.g.* **4a**, $^1E_{pc} = -1.23$ V; **4c**, $^1E_{pc} = -1.26$ V and **4e**; $^1E_{pc} = -1.67$ V). The substitution of the thiazole ring by the methyl group has little influence on the values of reduction potentials of compounds **5a**–**c**. In contrast, the potentials are strongly influenced by the electronic acceptor nature of the formyl group. As a consequence, the difference between the reduction potential values obtained for the first process of **4a** and **6a** is 370 mV showing a high anodic shift due to the substitution of the thiazole ring by a stronger acceptor group (Fig. 3). Moreover, the reduction potential of the second process of the reduction reflects also the effect of the electronic nature of the R_2 group substituted on the thiazole heterocycle.

The substitution of a thiazole heterocycle (**4a**) by a benzothiazole acceptor group (**7a**) on the diazene system results in a decrease of the reduction potential while increasing the oxidation potential suggesting a stronger electron-accepting ability of compound **7a** compared to **4a**. These results are in agreement with the ^{1}H NMR analysis that showed increased densities for azo dye **4a** and decreased density for compound **7a**.

On the other hand, comparison of compounds **6a** and **12c** bearing the same acceptor moiety (5-formyl-thiazol-2-*yl*-diazene) but different heterocyclic π-spacers, showed that the thienylpyrrole system (**12c**) has a greater donor ability compared to the bithienyl group which results in a decrease of the oxidation potential from 0.98 to 0.76 V. At the same time it was also observed a cathodic shift of the reduction potential (*e.g.* **6a** $^1E_{pc} = -1.23$ V and **12c** $^1E_{pc} = -0.98$ V) for compound **6a**. These results are also in agreement with the reactivity and the ^{1}H NMR analysis which showed increasing electronic densities for the thienylpyrrole protons compared to the bithienyl protons.

At this moment another comparison can also be made between bithienyl azo dye **6a** and thienylpyrrolyl-azo dye **12c**. Here, the substitution of the bithiophene system (**6a**) by the thienylpyrrole spacer (**12c**) maintaining the same acceptor 5-formyl-thiazol-2-*yl*-diazene group results in a cathodic shift of the reduction potential (*e.g.* **6a** $^1E_{pc} = -1.23$ V and **12c** $^1E_{pc} = -0.98$ V) for compound **6a**. Comparison of the reduction potentials between compound **12c** and thienylpyrrole-thiazolyldiazene **12a** [3d] reported earlier by us, showed that the increase of the acceptor electronic ability of the formyl group substituted on the thiazole heterocycle leads also to a reduction of the potential of compound **12c**.

For azo dyes **4d** and **4e** it was also observed that the functionalization of the 5-*N*,*N*-dialkylamino-bithiophenes at 4-position by the diazenethiazolyl group destabilizes the π-conjugated system,

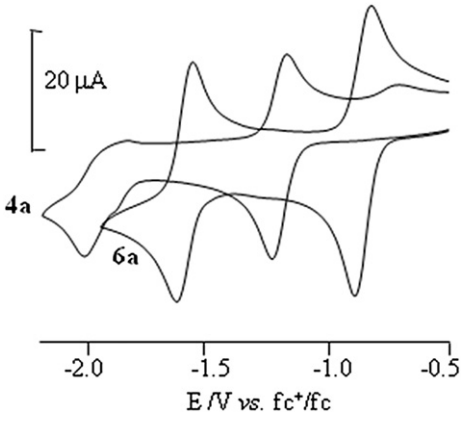


Fig. 3. Cyclic voltammograms of compound **4a** and **6a** in DMF − 0.1 mol dm^{-3} [NBu_4][BF_4] at a vitreous carbon electrode, scan rate 0.1 V s^{-1}.

probably due to a decrease in the planarity of the structures, leading to the irreversibility of the second reduction.

On the basis of these potentials values, we estimated the HOMO and LUMO energy levels from the potentials of the anodic and cathodic processes [16,17]. The resulting HOMO energy levels of compounds **4**–**7** were located within a reasonable range of 4.70–5.37 eV, with variations that reflect different amounts of intramolecular charge transfer (ICT) resulting from the presence of the electron donors with different electro-donating abilities [18,19]. The LUMO energy levels of compounds **4**–**7** were located within a reasonable range of 2.65–3.53 eV and were significantly greater than those of aryldiazene thienylpyrroles [3a,20]. In addition, the electrochemical band gaps of **4**–**7** were estimated from the difference between the potential values for oxidation and reduction [12,21,22]. The corresponding values were in the range of 1.85–2.06 eV slightly larger than their respective optical band gaps.

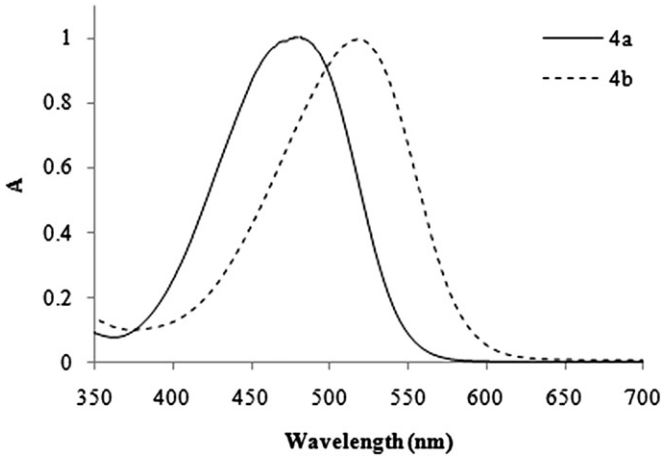


Fig. 4. UV–visible absorption normalized spectra of compounds **4a** and **4b** in dioxane at room temperature.

2.3. Optical properties

Bithiophene **4**–**7** and thienylpyrrole **12c** azo dyes showed good solubility in common polar and non-polar organic solvents such as dioxane, diethyl ether, ethanol and DMSO. The extinction coefficients (ε) in dioxane and wavelength maxima λ_{max} of compounds **4**–**7** and **12c** in four solvents, are summarized in Table 4 and were compared with the π^* values for each solvent, as determined by Kamlet and Taft [23].

All chromophores exhibit broad and intense CT absorptions in the region of 477–539 nm in dioxane. The 5-alkoxy-2,2′-bithiophene azo dyes **4b** and **5b** exhibited a red-shifted λ_{max} (36–41 nm) relative to unsubstituted derivatives **4a** and **5a** due to the stronger donor strength of alkoxy groups (Fig. 4).

The thienylpyrrole azo dye **12c** also exhibits a red-shift of λ_{max} by 24 nm compared to the bithiophene derivative **6a** due to the stronger auxiliary donor effect of the thienylpyrrole spacer (Fig. 5).

It was also observed that the donor ability of the methyl group on the thiazole ring has a smaller impact on the UV–vis spectra of compounds **5a**–**c**. On the other hand, the acceptor electronic strength of the formyl group substituted on the thiazole heterocycle has a significant effect on the electronic absorption property of thiazolyl azo dye **6a**. Thiazole being an electron-deficient five-membered heteroaromatic ring, will exhibit an auxiliary acceptor effect when linked to withdrawing groups [8,11a]. Therefore, azo dye **6a** exhibited a distinctively red-shifted λ_{max} (38 nm) with respect to the unsubstituted derivative **4a**. Due to the electron density deficiency on the ring C atoms, the benzothiazole heterocycle acts also as an electron-withdrawing group [11a]. Moreover, due to a larger electronic delocalization, benzothiazole azo dye **7a** exhibits a bathochromic shift of 16 nm compared to thiazole azo dye **4a** (Fig. 6).

On the other hand thiazole, due to its electronic nature, counteracts the electron-donating effect of the methyl group, resulting in a smaller bathochromic shift of λ_{max} (6–9 nm) for compounds **5a**–**c** compared to thiazolyl azo dyes **4a**–**c**. These results agree with the general trend of band gap estimations based on the redox properties (Table 3), displaying increased band gaps for azo dyes **4a** and **5a** and decreased band gaps for compounds **4b**–**c**, **5b** and **6a** functionalized with stronger donor and acceptor groups on the bithiophene and thiazole moieties respectively.

Heterocyclic azo dyes tend to display a larger solvatochromic effect than azobenzene dyes due to stronger polarization of their electronic system, especially in the excited state. Similar solvatochromic behavior was reported for other azo dyes containing thiophene, pyrrole and (benzo)thiazole fragments [2a,f,j,3a,b,d,4a–c].

All thiazole **4**–**6**, **12c** and benzothiazole **7a** azo dyes exhibited a large positive solvatochromism ($\Delta\upsilon_{max} = 814$–$1619\ cm^{-1}$) from diethyl ether to DMSO, an effect typically associated with good optical nonlinearities (Table 4, Fig. 7) [24]. In comparison, 5-*N*,*N*-dialkylamino-2,2′-bithienyl azo dyes **4d**–**e** substituted by the thiazolyldiazene moiety on the 4-position of the bithiophene spacer have a smaller $\Delta\upsilon_{max}$ (757–$814\ cm^{-1}$) than their bithiophene and 5-alkoxy-2,2′-bithiophene **4b** analogs $\Delta\lambda_{max}$ (1079–$1619\ cm^{-1}$) suggesting larger β values for the latter more planar chromophores.

The molecular first hyperpolarizabilities β of novel heterocyclic diazenes **5**–**7**, **12c** and the arylation products **14** and **15a** were

Table 4
Solvatochromic data [λ_{max} (nm) and $\Delta\upsilon_{max}$ (cm^{-1}) of the charge-transfer band] for bithiophene and thienylpyrrole azo dyes **4**–**7** and **12c** in 4 solvents with π^* values by Kamlet and Taft [23].

Azo dye	Diethyl ether (0.54) λ_{max} (nm)	Ethanol (0.54) λ_{max} (nm)	1,4-Dioxane (0.55) λ_{max} (nm)	DMSO (1.00) λ_{max} (nm)	$\Delta\upsilon_{max}$[a] (cm^{-1})	ϵ (Dioxane) ($M^{-1}\,cm^{-1}$)
4a	460	483	477	497	1619	(30,240)
4b	509	525	518	536	1079	(28,980)
4c	509	524	513	531	814	(33,690)
4d	504	520	514	524	754	(19,970)
4e	509	525	520	531	814	(23,120)
5a	468	490	483	501	1408	(33,060)
5b	509	526	519	540	1127	(36,130)
5c	510	526	522	535	916	(29,600)
6a	501	520	515	535	1268	(30,610)
7a	482	500	493	517	1315	(27,990)
12c	534	553	539	565	1028	(39,720)

[a] $\Delta\upsilon_{max} = \upsilon_{max\ (diethyl\ ether)} - \upsilon_{max\ (DMSO)}/cm^{-1}$.

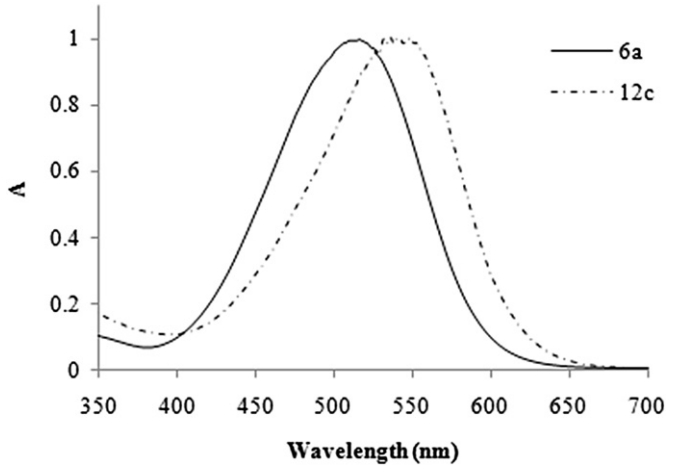


Fig. 5. UV–visible absorption normalized spectra of compounds **6a** and **12c** in dioxane at room temperature.

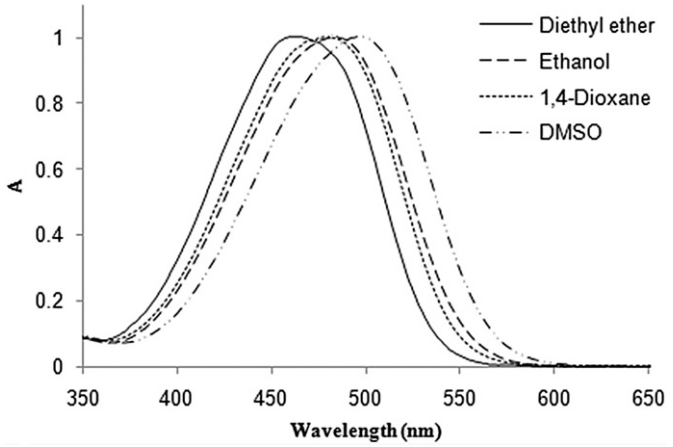


Fig. 7. UV–visible absorption normalized spectra of compound **4a** in four solvents of different polarity (diethylether, dioxane, ethanol and DMSO) at room temperature.

measured by hyper-Rayleigh scattering (HRS) method [25] using the 1064 nm fundamental wavelength of a q-switched Nd:YAG laser. Dioxane was used as the solvent, and the β values were measured against a reference solution of *p*-nitroaniline (*p*NA) [26] in order to obtain quantitative values, while care was taken to properly account for possible fluorescence of the dyes (see Experimental section for more details). The static hyperpolarisability β_0 values [27] were calculated using a very simple two-level model neglecting damping. They are therefore only indicative and should be treated with caution (Table 5).

From Table 5 it can be seen that the β values for azo dyes **4a**–**c** bearing the thiazolyldiazene group linked at the 5′-position of the bithiophene system exhibit higher first hyperpolarizabilities ($\beta = 172–307 \times 10^{-30}$ esu) as compared to their 5-*N*,*N*-dialkykamino-birhiophene counterparts **4d**–**e** ($\beta = 133–148 \times 10^{-30}$ esu). The results obtained showed that, the substitution of the diazophenyl group on the 4-position on the bithiophene moiety functionalized with *N*,*N*-dialkylamino groups on the 5-position (stronger donor groups compared to alkoxy) produced smaller values of the first molecular hyperpolarizability β than the 5-alkoxy-2,2′-bithiophene azo dyes having the same diazophenyl groups substituted in the 5′-position of the bithiophene moiety (*e.g.* **4c**, $R_1 = EtO$, $\beta = 307 \times 10^{-30}$ esu and **4d**, $R_1 = NEt_2$, $\beta = 148 \times 10^{-30}$). This might be indicative of a reduction in the effective conjugation due to steric effects, due perhaps to the *N*,*N*-dialkylamino-groups on the series **4d**–**e** molecules not being coplanar with the rest of the molecule, thereby limiting the conjugation that can be achieved [28].

At this stage, a comparison can also be made between the nonlinear optical data of the new 5′-*N*,*N*-dialkylamino-2,2′-bithiophene chromophores **4d**–**e** bearing a thiazolyldiazene moiety with similar azo dyes functionalized with an aryldiazene group at 4-position of the 5-*N*,*N*-dialkylamino-2,2′-bithiophene system (**9d**, **10e)** (Fig. 1). Earlier, we reported the synthesis, solvatochromic and electrochemical properties of these 5-*N*,*N*-dialkylamino-bithienyl-aryldiazenes [4c]. The first hyperpolarizabilities β, of these compounds were now also measured. The results obtained suggest that the electron-deficient thiazole heterocycle has a larger acceptor strength than the phenyl ring, even when it is substituted by

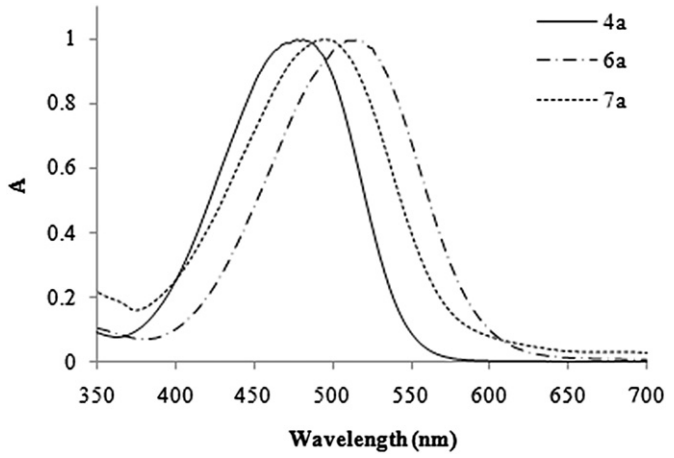


Fig. 6. UV–visible absorption normalized spectra of compounds **4a**, **6a** and **7a** in dioxane at room temperature.

Table 5
UV–vis absorptions, β and β_0 values for the novel azo dyes **4**–**7**, **12c**, the arylation products **14** and **15a** and 5-*N*,*N*-dialkylamino-bithienyl-aryldiazenes **9d** and **10e** [4c] and thienylpyrrole-thiazolyldiazene **12a** [3d].[a]

Azo dye	λ_{max} (nm)	β[b] (10^{-30} esu)	β_0[c] (10^{-30} esu)
4a	477	172	27 ± 3
4b	518	291	12 ± 1
4c	513	307	16 ± 1
4d	514	148	7.5 ± 0.8
4e	520	133	4.5 ± 0.5
5a	483	166	23 ± 2
5b	519	294	11 ± 1
5c	522	150	4.2 ± 0.4
6a	515	286	14 ± 1
7a	493	207	23 ± 2
9d [4c]	509	101	6.9 ± 0.6
10e [4c]	510	125	8.2 ± 0.8
12a [3d]	486	164	21 ± 15
12c	539	610[d]	12 ± 1
14	533	71	0.2 ± 0.02
15a	396	67	26 ± 10
*p*NA	352	16.9 [26]	8.5

[a] Experimental hyperpolarizabilities and spectroscopic data measured in dioxane solutions.
[b] All the compounds are transparent at the 1064 nm fundamental wavelength.
[c] Data corrected for resonance enhancement at 532 nm using the two-level model with $\beta_0 = \beta\ [1 - (\lambda_{max}/1064)^2][1 - (\lambda_{max}/532)^2]$; damping factors not included 1064 nm [27].
[d] Value obtained by making measurements at various concentrations and extrapolating to infinite dilution in order to correct for the absorption of the generated second harmonic light as it propagates through the solution to the detection system.

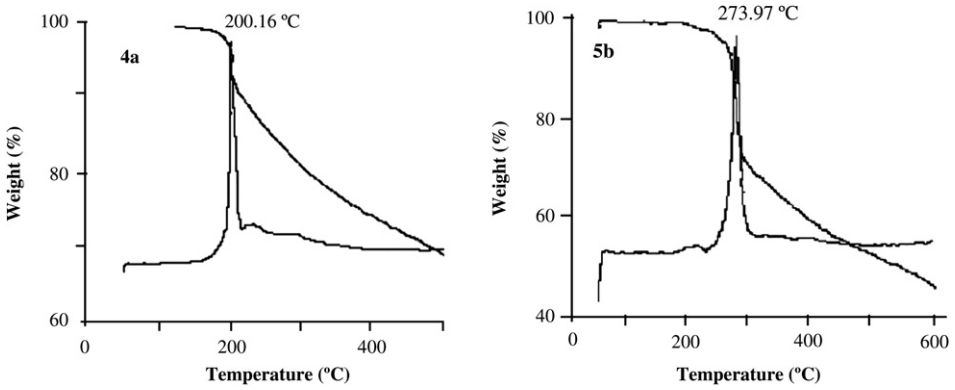


Fig. 8. Thermal analysis data for compounds **4c** (left) and **5b** (right) through TGA recorded under a nitrogen atmosphere, measured at a heating rate of 20 °C min^{-1}.

a strong acceptor group such as cyano, as the β value of the thiazolyldiazenes **4d**–**e** ($\beta = 133–148 \times 10^{-30}$ esu) are larger than the corresponding values for phenyldiazenes **9d** and **10e** ($\beta = 101–125 \times 10^{-30}$ esu). Most of this effect appears to be due to the red shift of the absorption maxima and a subsequent enhancement of the nonlinear response as the generated second harmonic light approaches the charge-transfer transition energy.

From Table 5 it is apparent as well that the increase of the donor strength of the of the substituent on 5′-position of the bithiophene system (dyes **4a**–**c**) also resulted in a significant resonant enhancement, with enhanced β values accompanied by a red-shifted absorption maxima (*e.g.* **4a**, R = H, λ_{max} 477 nm, $\beta = 172 \times 10^{-30}$ esu; **4c**, R = EtO, λ_{max} 513 nm, $\beta = 307 \times 10^{-30}$ esu).

Also noteworthy is the effect of the electronic nature of the group that substitutes the thiazole ring at 5-position. It was observed that, the increase of the acceptor strength of the CHO group (**6a**) compared to H (**4a**), results both in red-shifted absorption maxima and a resonance enhanced β value for bithiophene azo dye **6a** ($\beta = 286 \times 10^{-30}$ esu). A similar effect was observed for thienylpyrrole azo dyes **12a** and **12c**. Therefore compound **12c** having a stronger acceptor moiety exhibits a higher beta value (610×10^{-30} esu) for incident light at 1064 nm as compared to the unsubstituted derivative **12a** (164×10^{-30} esu) [3d]. Due to the deficiency of electron density on the ring C atoms, the thiazole heterocycle acts as electron-withdrawing group and also as an auxiliary acceptor leading to an increase in molecular hyperpolarizability [8,9a,11a]. Conversely, the methyl group linked to 5-position of the thiazole ring **5a** counters the withdrawing effect of the thiazole ring leading to lower beta value for **5a** ($\beta = 166 \times 10^{-30}$ esu).

Comparison of the β values for thienylpyrrole azo dye **12c** with bithiophene azo dye **6a** showed also that the substitution of a bithiophene spacer by a thienylpyrrole heterocyclic bridge enhances the first order hyperpolarizability from 286×10^{-30} to 610×10^{-30} esu at 1064 nm probably due to the stronger auxiliary donor effect of the pyrrole heterocycle compared to the thiophene ring [15,29]. These results are in agreement with the redox and the NMR studies described above.

Benzothiazole azo dye **7a** exhibits a larger β value (207×10^{-30}) compared to the corresponding thiazole chromophore **4a** probably due a greater electronic delocalization. In the probable resonance structures, the distance between the charges in **7a** being longer compared to **4a**, the electric moment of the first diazene must be greater, increasing the value of the molecular hyperpolarizability.

The study of the first order hyperpolarizability β for the arylation product **15a** without the N=N bridge exhibits a much lower λ_{max} (396 nm) and beta values (67×10^{-30} esu) when compared to the corresponding azo dye **6a** ($\lambda_{max} = 515$ nm, $\beta = 286 \times 10^{-30}$ esu).

For optoelectronic applications, the thermal stability of organic materials is critical for device stability. Therefore, the thermal properties of the chromophores **4**–**7** and **12c** were investigated by thermogravimetric analysis under a nitrogen atmosphere, measured at a heating rate of 20 °C min^{-1} (Table 1). All the chromophores are thermally stable with decomposition temperatures varying from 200 to 283 °C. For the thiazolyldiazenes **4**–**6** the electronic nature of the group substituted on the 5-position of the thiazole ring does seem to have some impact on the thermal stability of the compounds. The 5-methyl-thiazolyldiazenes **5a**–**c**, are the most stable showing higher decomposition temperatures (Fig. 8).

Benzothiazole azo dye **7a** exhibits also an improved stability by *ca* 83 °C compared to the corresponding thiazole derivative **4a**.

3. Conclusions

In conclusion we have synthesized and characterized several novel bithiophene and thienylpyrrole azo dyes bearing thiazole or benzothiazole acceptor groups linked to the diazene group through position 2 of the thiazole moiety.

By varying the heterocyclic spacer (bithiophene or thienylpyrrole), the electronic nature of the donor and acceptor groups linked to the bithiophene and thiazole moieties respectively, or the position of substitution of the thiazolyldiazene acceptor moiety on the bithiophene system, the thermal and the electrochemical properties as well as the optical (linear and nonlinear) properties of push–pull π-conjugated systems can be tuned. More interesting redox properties and the largest first hyperpolarizabilities were observed for thienylpyrrole azo dye **12c** and bithiophene azo dyes **4b**–**c**, **5b** and **6a** functionalized with donor alkoxy groups in 5′-position of the bithiophene spacer and formyl acceptor group substituted in the 5-position of the thiazole heterocycle. Due to their good first order hyperpolarizability and redox properties together with their good thermal stability these compounds are attractive novel heterocyclic NLO-chromophores.

4. Experimental

4.1. Materials

4.1.1. *2-Aminothiazole, 2-amino-5-methylthiazole, 2-amino-5-formylthiazole and 2-aminobenzothiazole were used as precursors for the synthesis of aryldiazonium salts **2**–**3** and 2,2-bithiophene **1a** were purchased from Aldrich and Fluka and used as received*

The synthesis of bithiophenes **1b**–**e** [5] and thienylpyrrole **11** [6] has been described elsewhere. TLC analyses were carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel

60F_{254}) and spots were visualized under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (230–240 mesh).

4.2. Synthesis

*4.2.1. General procedure for the azo coupling of bithiophenes **1a–e** and thienylpyrrole 11 with thiazolyl-**2a–c** and benzothiazolyl-**3** diazonium salts to afford azo dyes **4a–e**, **5a–c**, **6a**, **7a** and **12c***

4.2.1.1. Diazotation of 2-aminothiazole, 2-amino-5-methylthiazole, 2-amino-5-formylthiazole and 2-aminobenzothiazole. Heteroaromatic amines (1.0 mmol) were dissolved in HCl 6 N (1 mL) at 0–5 °C. A mixture of $NaNO_2$ (1.0 mmol) in water (2 mL) was slowly added to the well-stirred mixture of the thiazole solution at 0–5 °C. The reaction mixture was stirred for 10 min.

*4.2.1.2. Coupling reaction with bithiophenes **1** and thienylpyrrole **11**.* The diazonium salt solution previously prepared (1.0 mmol) was added dropwise to the solution of bithiophenes **1** or thienylpyrrole **11** (0.52 mmol) in acetonitrile (10 mL) and 2–3 drops of acetic acid. The combined solution was maintained at 0 °C for 1–2 h while stirred and then diluted with chloroform (20 mL), washed with water and dried with anhydrous $MgSO_4$. The dried solution was evaporated and the remaining azo dyes purified by column chromatography on silica with dichloromethane/*n*-hexane as eluent.

*4.2.1.3. 2-(Thiazol-2-yl)-1-(5-(thiophen-2-yl)thiophen-2-yl)diazene (**4a**).* Dark pink solid (23%). Mp 130–131 °C. ^{1}H NMR ($CDCl_3$) δ 7.10 (dd, 1H, $J = 5.0$ and $J = 3.8$ Hz, 4''-H), 7.31 (d, 1H, $J = 4.0$ Hz, 3'-H), 7.32 (d, 1H, $J = 3.6$ Hz, 5-H), 7.39 (dd, 1H, $J = 4.8$ and 1.0 Hz, 5''-H), 7.42 (dd, 1H, $J = 3.8$ and 1.0 Hz, 3''-H), 7.81 (d, 1H, $J = 4.0$ Hz, 4'-H), 7.98 (d, 1H, $J = 3.6$ Hz, 4-H), ^{13}C NMR ($CDCl_3$) δ 120.7, 124.5, 126.5, 127.6, 128.5, 136.4, 136.8, 143.7, 144.6, 156.5, 176.4. λ_{max}(Dioxane)/nm 477 (ε/dm^3 mol^{-1} cm^{-1} 30,240). IR (Liquid film): ν 3105, 1640, 1503, 1483, 1450, 1406, 1305, 1244, 1222, 1212, 1136, 1044, 878, 846, 801, 753 cm^{-1}. MS (ESI) m/z (%) = 278 ([M + H]$^+$, 20). HMRS: m/z (ESI) for $C_{11}H_7N_3S_3$; calcd 277.9875; found: 277.9876.

*4.2.1.4. 1-(5-(5-Methoxythiophen-2-yl)thiophen-2-yl)-2-(thiazol-2-yl)diazene (**4b**).* Dark pink solid (36%). Mp 147–149 °C. ^{1}H NMR ($CDCl_3$) δ 3.97 (s, 3H, OCH_3), 6.23 (d,1H, $J = 4.2$ Hz, 4''-H), 7.12 (d, 1H, $J = 4.2$ Hz, 3''-H), 7.14 (d, 1H, $J = 4$ Hz, 3'-H), 7.34 (d, 1H, $J = 3.6$ Hz, 5-H), 7.75 (d, 1H, $J = 4$ Hz, 4'-H), 7.95 (d, 1H, $J = 3.6$ Hz, 4-H). ^{13}C NMR ($CDCl_3$) δ 60.5, 105.6, 120.2, 122.8, 123.2, 125.5, 136.7, 143.7, 145.9, 155.2, 168.7, 176.7. λ_{max}(Dioxane)/nm 518 (ε/dm^3 mol^{-1} cm^{-1} 28,980). IR (Liquid film): ν 3163, 2033, 1552, 1514, 1377, 1350, 1305, 1268, 1226, 1169, 1152, 1066, 1049, 971, 892, 874, 772 cm^{-1}. MS (ESI) m/z (%) = 308 ([M + H]$^+$, 100). HMRS: m/z (ESI) for $C_{12}H_{10}N_3OS_3$; calcd; 307.9983 found: 307.9980.

*4.2.1.5. 1-(5-(5-Ethoxythiophen-2-yl)thiophen-2-yl)-2-(thiazol-2-yl)diazene (**4c**).* Dark pink solid (11%). Mp 128–130 °C. ^{1}H NMR ($CDCl_3$) δ 1.47 (t, 3H, $J = 7.2$ Hz, CH_3), 4.47 (q, 2H, $J = 7.2$ Hz, CH_2), 6.21 (d, 1H, $J = 4.2$ Hz, 4''-H), 7.11 (d, 1H, $J = 4.2$ Hz, 3''-H), 7.13 (d, 1H, $J = 3.8$ Hz, 3'-H), 7.33 (d, 1H, $J = 3.8$ Hz, 4'-H), 7.75 (d, 1H, $J = 3.6$ Hz, 5-H), 7.95 (d, 1H, $J = 3.6$ Hz, 4-H). ^{13}C NMR ($CDCl_3$) δ 14.6, 69.8, 106.4, 120.2, 122.7, 123.1, 125.5, 136.7, 143.7, 146.1, 155.1, 167.8, 176.7. λ_{max}(Dioxane)/nm 513 (ε/dm^3 mol^{-1} cm^{-1} 33,690). IR (Liquid film): ν 3243, 2980, 1721, 1547, 1506, 1485, 1465, 1445, 1414, 1389, 1344, 1311, 1275, 1228, 1209, 1139, 1108, 1060, 1027, 992, 876 cm^{-1}. MS (ESI) m/z (%) = 322 ([M + H]$^+$, 100), 295 (34), 224 (5). HMRS: m/z (ESI) for $C_{13}H_{12}N_3S_3$; calcd 322.0137; found: 322.0137.

*4.2.1.6. 5-N,N-Diethylamino-4-(thiazol-2-yl-azo)-2,2'-bithiophene (**4d**).* Pink oil (80%). ^{1}H NMR ($CDCl_3$) δ 1.39 (t, 6H, $J = 7.2$ Hz, 2 × CH_3), 3.82 (q, 4H, $J = 7.2$ Hz, 2 × CH_2), 7.00-7.04 (m, 1H, 4''-H), 7.03 (d, 1H, $J = 3.6$ Hz, 5-H), 7.03-7.04 (m, 1H, 3''-H), 7.20 (dd, 1H, $J = 5.2$ and 1.2 Hz, 5''-H), 7.59 (s, 1H, 3'-H), 7.75 (d, 1H, $J = 3.6$ Hz, 4-H). ^{13}C NMR ($CDCl_3$) δ 12.1, 50.6, 109.6, 113.7, 116.1, 121.9, 123.4, 124.7, 127.7, 136.4, 136.8, 141.9, 143.7, 161.2, 180.1. λ_{max}(Dioxane)/nm 514 (ε/dm^3 mol^{-1} cm^{-1} 19,970). IR (Liquid film): ν 3449, 3075, 2975, 2931, 1538, 1492, 1464, 1435, 1359, 1332, 1291, 1263, 1216, 1173, 1150, 1138, 1075, 1015, 878, 833, 818, 784, 749, 700, 622 cm^{-1}. MS (ESI) m/z (%) = 349 ([M + H]$^+$, 100), 295 (9), 249 (4), 223 (10). HMRS: m/z (ESI) for $C_{15}H_{17}N_4S_3$; calcd 349.0609; found: 349.0610.

*4.2.1.7. 5-Piperidino-4-(thiazol-2-yl-azo)-2,2'-bithiophene (**4e**).* Dark pink solid (10%). Mp 151–152 °C ^{1}H NMR ($CDCl_3$) δ 1.80–1.85 (m, 6H, 3 × CH_2), 3.95-3.98 (m, 4H, 2 × NCH_2), 6.99 (dd, 1H, $J = 5.2$ and 3.6 Hz, 4''-H), 7.04-7.05 (m, 2H, 5 and 3''-H), 7.22 (dd, 1H, $J = 5.2$ and 1.2 Hz, 5''-H), 7.57 (s, 1H, 3'-H), 7.77 (d, 1H, $J = 3.6$ Hz, 4-H). ^{13}C NMR ($CDCl_3$) δ 23.9, 25.7, 54.4, 113.8, 116.3, 122.3, 123.5, 124.8, 127.7, 136.9, 137.3, 142.0, 162.6, 179.9 λ_{max}(Dioxane)/nm 520 (ε/dm^3 mol^{-1} cm^{-1} 23,120). IR (Liquid film): ν 3082, 2917, 2849, 2362, 1535, 1507, 1491, 1462, 1438, 1388, 1336, 1292, 1245, 1221, 1174, 1145, 1017, 998, 910, 877, 857, 832, 819, 754, 718, 701, 663, 622 cm^{-1}. MS (ESI) m/z (%) = 361 ([M + H]$^+$, 100). HMRS: m/z (ESI) for $C_{16}H_{16}N_4S_3$; calcd 360.0537; found: 361.0610.

*4.2.1.8. 2-(5-Methylthiazol-2-yl)-1-(5-(thiophen-2-yl)thiophen-2-yl) diazene (**5a**).* The first compound eluted from the column chromatography was diazene **5a** as a pink solid (10%). Mp 166–167 °C. ^{1}H NMR ($CDCl_3$) δ 2.53 (d, 3H, $J = 1.2$ Hz, CH_3), 7.09 (dd, 1H, $J = 5.2$ and 3.6 Hz, 4''-H), 7.29 (d, 1H, $J = 4$ Hz, 3'-H), 7.37 (dd,1H, $J = 5.2$ and 1.2 Hz, 5''-H), 7.39 (dd, 1H, $J = 3.6$ and 1.2 Hz, 3''-H), 7.66 (d, 1H, $J = 1.2$ Hz, 4-H), 7.75 (d, 1H, $J = 4$ Hz, 4'-H). ^{13}C NMR ($CDCl_3$) δ 30.9, 124.3, 126.2, 127.2, 128.5, 135.4, 136.7, 136.9, 142.1, 143.7, 156.7, 174.4. λ_{max}(Dioxane)/nm 483 (ε/dm^3 mol^{-1} cm^{-1} 33,060). IR (Liquid film): 3062, 2358, 1500, 1447, 1427, 1335, 1213, 1129, 1041, 842, 791 cm^{-1}. Anal. calcd. for $C_{12}H_9N_3S_3$ (291,42): C, 48.60; H, 3.29; N, 14.16; S, 32.96%; found C, 48.88; H, 3.53; N, 14.41; S, 32.94%.

The second compound eluted was the diazene **14** as a dark pink solid (17%). Mp 211–213 °C. ^{1}H NMR ($CDCl_3$) δ 2.58 (d, 3H, $J = 1.2$ Hz, CH_3), 2.60 (d, 3H, $J = 1.2$ Hz, CH_3), 7.10 (dd, 1H, $J = 5.2$ and 3.6 Hz, 4''-H), 7.41 (dd, 1H, $J = 5.2$ and 1.2 Hz, 5''-H), 7.44 (dd, 1H, $J = 3.6$ and 1.2 Hz, 3''-H), 7.64 (d, 1H, $J = 1.2$ Hz, 4-H or 4'-H), 7.70 (d, 1H, $J = 1.2$ Hz, 4'-H or 4-H), 7.96 (br s, 1H, 3''-H). ^{13}C NMR ($CDCl_3$) δ 12.20, 13.14, 123.45, 126.78, 127.87, 128.48, 136.63, 137.81, 139.43, 140.55, 157.87, 174.95. λ_{max}(Dioxane)/nm 533 (ε/dm^3 mol^{-1} cm^{-1} 46,230). IR (Liquid film): 2921, 2851, 1501, 1456, 1416, 1320, 1284, 1221, 1158, 1132, 1063, 900 cm^{-1}. MS (ESI) m/z (%) = 389 ([M + 1]$^+$, 100), 381 (5), 295 (10). HMRS: m/z (ESI) for $C_{16}H_{12}N_4S_4$; calcd 389.0018; found: 389.0019.

*4.2.1.9. 1-(5-(5-Methoxythiophen-2-yl)thiophen-2-yl)-2-(5-methyl thiazol-2-yl)diazene (**5b**).* Dark pink solid (42%). Mp 265–266 °C. ^{1}H NMR ($CDCl_3$) δ 2.53 (d, 3H, $J = 1.2$ Hz, CH_3), 3.96 (s, 3H, OCH_3), 6.21 (d, 1H, $J = 4.4$ Hz, 4''-H), 7.10 (d, 1H, $J = 4.4$ Hz, 3'-H), 7.11 (d, 1H, $J = 4.4$ Hz, 3''-H), 7.64 (d, 1H, $J = 1.2$ Hz, 4-H), 7.70 (d, 1H, $J = 4.4$ Hz, 4'-H). ^{13}C NMR ($CDCl_3$) δ 12.9, 60.4, 105.6, 122.7, 123.3, 125.2, 135.9, 136.1, 141.7, 145.3, 155.5, 168.5, 174.6. λ_{max}(Dioxane)/nm 519 (ε/dm^3 mol^{-1} cm^{-1} 36,130). IR (Liquid film): 3579, 3085, 2933, 2897, 1513, 1480, 1451, 1432, 1317, 1226, 1135, 1065, 1049, 972, 859, 788, 764 cm^{-1}. MS (EI) m/z (%) = 321 ([M]$^+$, 10), 278 (25), 246 (27), 221 (41), 209 (17), 195 (100), 168 (29), 152 (16), 141 (15), 122 (13), 71 (14). HMRS: m/z (EI) for $C_{13}H_{11}N_3OS_3$; calcd 321.0064; found: 321.0068.

*4.2.1.10. 1-(5-(5-Ethoxythiophen-2-yl)thiophen-2-yl)-2-(5-methyl thiazol-2-yl)diazene (**5c**).* Dark pink solid (9%). Mp 146–147 °C. ^{1}H NMR ($CDCl_3$) δ 1.46 (d, 3H, $J = 0.8$ Hz, CH_3), 2.52 (t, 3H, $J = 7.2$ Hz, OCH_2CH_3), 4.16 (q, 2H, $J = 7.2$ Hz, OCH_2CH_3), 6.20 (d, 1H, $J = 4$ Hz, 4''-H), 7.09 (d, 1H, $J = 4$ Hz, 3''-H), 7.10 (d, 1H, $J = 4.2$ Hz, 3'-H), 7.63 (d, 1H, $J = 0.8$ Hz, 4-H), 7.70 (d, 1H, $J = 4.2$ Hz, 4'-H). ^{13}C NMR ($CDCl_3$) δ 12.9, 14.6, 69.8, 106.4, 122.6, 123.2, 125.3, 135.9, 136.1, 141.7, 145.4, 155.4, 167.6, 174.6. λ_{max}(Dioxane)/nm 522 (ε/dm^3 mol^{-1} cm^{-1} 29,600). IR (Liquid film): 3148, 2925, 1552, 1519, 1509, 1476, 1463, 1429, 1394, 1361, 1336, 1315, 1284, 1266, 1253, 1224, 1210, 1170, 1164, 1047, 1024, 887, 834, 799, 780, 768, 748 cm^{-1}. MS (EI) *m*/*z* (%) = 335 ([M]$^+$, 10), 278 (26), 250 (14), 246 (29), 225 (21), 223 (10), 196 (100), 168 (25), 140 (21), 71 (15) . HMRS: *m*/*z* (EI) for $C_{14}H_{13}N_3OS_3$; calcd 335.0022; found: 335.0022.

*4.2.1.11. 2-(5-Formylthiazol-2-yl)-1-(5-(thiophen-2-yl)thiophen-2-yl)diazene (**6a**).* The first compound eluted from the column chromatography was the 5-(thiazol-2-*yl*)-2,2′-bithiophene **15a** as an yellow solid (3%). Mp 183–184 °C. ^{1}H NMR ($CDCl_3$) δ 7.08 (dd, 1H, $J = 5.2$ and 3,8 Hz, 4''-H), 7.20 (d, 1H, $J = 3.9$ Hz, 3'-H), 7.32-7.35 (m, 2H, 3''-H and 5''-H), 7.60 (d, 1H, $J = 3.9$ Hz, 4'-H), 8.34 (s, 1H, 4-H), 10.02 (s, 1H, C*H*O). λ_{max}(Dioxane)/nm 396 (ε/dm^3 mol^{-1} cm^{-1} 11,190). IR (Liquid film): 2925, 2811, 1667, 1517, 1499, 1424, 1412, 1359, 1275, 1219, 1153, 1067, 1050, 914, 882, 867, 845, 792, 716 cm^{-1}. MS (ESI) *m*/*z* (%) = 300 ([M + Na]$^+$, 10).

The second compound eluted from the column chromatography was the diazene **6a** as a dark pink solid (15%). Mp 210–211 °C. ^{1}H NMR ($CDCl_3$) δ 7.13 (dd, 1H, $J = 5.2$ and 3,8 Hz, 4''-H), 7.41 (d, 1H, $J = 4.4$ Hz, 3'-H), 7.47 (dd, 1H, $J = 5.2$ and 0.8 Hz, 5''-H), 7.50 (dd, 1H, $J = 3.8$ and 0.8 Hz, 3''-H), 7.94 (d, 1H, $J = 4.4$ Hz, 4'-H), 8.52 (s, 1H, 4-H), 10.05 (s, 1H, C*H*O). ^{13}C NMR ($CDCl_3$) δ 125.4, 127.6, 128.9, 136.6, 138.3, 139.4, 147.9, 151.7, 156.3, 181.3, 182.8. λ_{max}(Dioxane)/nm 515 (ε/dm^3 mol^{-1} cm^{-1} 30,610). IR (Liquid film): 3058, 2842, 1658, 1504, 1449, 1417, 1316, 1279, 1262, 1141, 1058, 893, 873, 850, 814, 723, 643 cm^{-1}. MS (microTOF) *m*/*z* (%) = 305 ([M]$^+$, 14), 277 (33), 194 (18), 181 (82), 179 (28), 165 (16), 146 (21), 128 (58), 127 (100), 121 (68). HMRS: *m*/*z* (MicroTOF) for $C_{12}H_7N_3OS_3$; calcd 304.9751; found: 304.9760.

*4.2.1.12. 2-(Benzo[d]thiazol-2-yl)-1-(5-(thiophen-2-yl)thiophen-2-yl)diazene (**7a**).* Pink solid (9%). Mp 274–275 °C. ^{1}H NMR ($CDCl_3$) δ 7.12 (dd, 1H, $J = 4.8$ and 3.6 Hz, 4''-H), 7.37 (d, 1H, $J = 4.4$ Hz, 3'-H), 7.42-7.47 (m, 3H, 5-H, 3''-H and 5''-H), 7.52 (dt, 1H, $J = 7.2$ and 1.4 Hz, 6-H), 7.87 (dd, 1H, $J = 7.8$ and 1.4 Hz, 4-H), 7.91 (d, 1H, $J = 4.4$ Hz, 4'-H), 8.13 (dd, 1H, $J = 7.8$ and $J = 1.4$ Hz, 7-H). ^{13}C NMR ($CDCl_3$) δ 122.1, 124.6, 124.9, 126.6, 126.9, 127.1, 128.0, 128.7, 134.5, 136.7, 137.7, 146.1, 152.9, 156.5, 174.9. λ_{max}(Dioxane)/nm 493 (ε/dm^3 mol^{-1} cm^{-1} 27,990). IR (Liquid film): 3430, 3077, 1503, 1482, 1448, 1430, 1359, 1334, 1251, 1224, 1183, 1153, 1046, 848, 802, 722, 692 cm^{-1}. MS (ESI) *m*/*z* (%) = 328 ([M + H]$^+$, 100), 313 (5), 299 (9), 296 (7), 295 (42). HMRS: *m*/*z* (ESI) for $C_{15}H_{10}N_3S_3$; calcd 328.0032; found: 328.0031.

*4.2.1.13. 1-(1-(4-Methoxyphenyl)-5-(thiophen-2-yl)-1H-pyrrol-2-yl)-2-(5-formylthiazol-2-yl)diazene (**12c**).* Dark pink solid (98 mg, 61%). Mp 151–153 °C. ^{1}H NMR ($CDCl_3$) δ 3.96 (s, 3H, OCH_3), 7.00 (d, 1H, $J = 4.6$ Hz, 4'-H), 7.01-7.02 (m, 1H, 4''-H), 7.06 (d, 2H, $J = 8.8$ Hz, 3‴ and 5‴-H), 7.14 (dd, H, $J = 4.0$ and 0.8 Hz, 3''-H), 7.28 (d, 2H, $J = 8.8$ Hz, 2‴and 6‴-H), 7.38 (dd, 1H, $J = 5.2$ and 0.8 Hz, 5''-H), 7.44 (d, 1H, $J = 4.4$ Hz, 3'-H), 8.35 (s, 1H, 4-H), 9.89 (s, 1H, C*H*O). ^{13}C NMR ($CDCl_3$) δ 55.6, 109.2, 114.6, 115.9, 116.2, 116.4, 116.6, 128.0, 128.6, 129.0, 129.7, 131.1, 132.1, 135.6, 142.4, 151.3, 160.7, 182.6, 184.4 λ_{max}(Dioxane)/nm 539 (ε/dm^3 mol^{-1} cm^{-1} 30,610). IR (Liquid film): 3102, 3076, 3009, 2933, 2837, 2742, 1888, 1662, 1608, 1587, 1511, 1471, 1442, 1420, 1393, 1378, 1337, 1308, 1276, 1250, 1233, 1204, 1186, 1149, 1089, 1047, 1019, 998 cm^{-1}. MS (ESI) *m*/*z* (%) = 395 ([M + H]$^+$, 21),268 (5), 256 (11), 255 (19), 254 (100), 239 (4), 211 (4). HMRS: *m*/*z* (ESI) for $C_{19}H_{15}N_4O_2S_2$; calcd 395.0631; found: 395.0629.

4.3. Instruments

NMR spectra were obtained using a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR or a Bruker Avance III 400 at an operating frequency of 400 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C NMR using the solvent peak as internal reference at 25 °C. All chemical shifts are given in ppm using δ_H $Me_4Si = 0$ ppm as reference and *J* values are given in Hz. Assignments were made by comparison of chemical shifts, peak multiplicities and *J* values and were supported by spin decoupling-double resonance and bidimensional heteronuclear HMBC and HMQC correlation techniques. IR spectra were determined on a BOMEM MB 104 spectrophotometer using KBr discs. UV–visible absorption spectra (200–800 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. Mass spectrometry analyses were performed at the "C.A.C.T.I. – Unidad de Espectrometria de Masas" at the University of Vigo, Spain. Electrospray ionization mass spectra were recorded using a Thermo-Finnigan LCQ Deca XP Plus quadrupole ion trap instrument on samples diluted in ethanol/water (1:1 v/v). 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. All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Cyclic voltammetry (CV) was performed using a potentiostat/galvanostat (AUTOLAB/PSTAT 12) with the low current module ECD from ECO-CHEMIE and the data analysis processed by the General Purpose Electrochemical System software package also from ECO-CHEMIE. Three electrode-two compartment cells equipped with vitreous carbon-disc working electrodes, a platinum-wire secondary electrode and a silver-wire pseudo-reference electrode were employed for cyclic voltammetric measurements. The concentration of the compounds were 1 mmol dm^{-3} and 0.1 mol dm^{-3} [NBu_4][BF_4] was used as the supporting electrolyte in dry *N*,*N*-dimethylformamide solvent. The cyclic voltammetry was conducted usually at 0.1 V s^{-1}, or at different scan rates (0.02–0.50 V s^{-1}), for investigation of scan rate influence. The potential is measured with respect to ferrocinium/ferrocene as an internal standard.

4.4. Optical studies

4.4.1. Solvatochromic study

The solvatochromic study was performed using 10^{-4} M solutions of dyes **4**–**7** and **12c** in several solvents at room temperature.

4.4.2. Nonlinear optical measurements using the hyper-Rayleigh scattering (HRS) method [25]

Hyper-Rayleigh scattering (HRS) was used to measure the first hyperpolarizability β of response of the molecules studied. The experimental set-up for hyper-Rayleigh measurements has been previously described in reference [13] and is similar to the one presented by Clays et al. [25] The incident laser beam came from a Q-switched Nd:YAG laser operating at a 10 Hz repetition rate with approximately 10 mJ of energy per pulse and a pulse duration (FWHM) close to 12 ns at the fundamental wavelength of 1064 nm. The incident beam had a vertical polarization was weakly focused (beam diameter ~0.5 mm) into the solution contained in a 5 cm long cuvette. The hyper-Rayleigh signal at right angles to the

incident beam was collimated using a high numerical aperture lens passed through an interference filter centered at the second harmonic wavelength (532 nm) before being detected by a photomultiplier (Hamamatsu model H9305-04). The current pulse from the photomultiplier was integrated using a Stanford Research Systems gated box-car integrator (model SR250) with a 20 ns gate centered on the temporal position of the incident laser pulse.

The hyper-Rayleigh signal was normalized at each pulse using the second harmonic signal from a 1 mm quartz plate to compensate for fluctuations in the temporal profile of the laser pulses due to longitudinal mode beating. Dioxane was used as a solvent, and the β values were calibrated using a reference solution of *p*-nitroaniline (*p*NA) [26] also dissolved in dioxane at a concentration of 1×10^{-2} mol dm^{-3} (external reference method). The hyperpolarizability of *p*NA dissolved in dioxane is known from EFISH measurements [26] carried out at the same fundamental wavelength. The concentrations of the solutions under study were chosen so that the corresponding hyper-Rayleigh signals fell well within the dynamic range of both the photomultiplier and the box-car integrator. All solutions were filtered (0.2 μm porosity) to avoid spurious signals from suspended impurities. The small hyper-Rayleigh signal that arises from dioxane was taken into account and particular care to avoid reporting artificially high hyperpolarizabilities due to a possible contamination of the hyper-Rayleigh signal by molecular fluorescence near 532 nm using two different interference filters with different transmission pass bands centered near the second harmonic at 532 nm (for more details consult reference [13]). The polarization of the detected signal was not discriminated and the values reported in Table 5 assume that the first hyperpolarizability tensor is dominated by a single longitudinal element as is common for strong linear charge push–pull charge-transfer molecules.

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