5′-Alkoxy-2,2′-bithiophene azo dyes: a novel promising series of NLO-chromophores

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ABSTRACT

A series of bithienyl azo dyes have been prepared from their corresponding coupling components, 5-alkoxy-2,2′-bithiophenes. The solvatochromic behaviour of the compounds was investigated. The hyperpolarizabilities β of derivatives **3–5** were measured using hyper-Rayleigh scattering and thermogravimetric analysis (TGA) was used to evaluate their thermal stability. The experimental results indicate that good nonlinearity–thermal stability is well balanced for azo-bithiophene NLO-chromophores **3–5** making them good candidates for NLO applications.

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1. Introduction

During the past decade, the design and synthesis of donor–acceptor substituted hetero aromatic compounds have attracted widespread interest because it was experimentally and theoretically demonstrated that they increase the second-order molecular NLO properties of push–pull chromophores with respect to the corresponding aryl analogues.[1] For the practical application of second-order NLO materials, not only a high hyperpolarizability but also good thermal stability is required. In this respect, promising candidates are (oligo)thiophene derivatives,[2] as well as conjugated pyrrole,[3] (benzo)thiazole[1j,4] and (benz)imidazole[5] heterocycles. One of the most recent approaches to the design of highly NLO-active systems is based on the presence of a five-membered heterocyclic ring in a push–pull donor–acceptor chromophore.[2–5] These heterocyclic NLO-chromophores have great potential especially for use in optical communication, information processing, frequency doubling and integrated optics.[6]

Besides their classic applications in synthetic dyes and pigments, heteroaryl diazo chromophores could act also as organic second-order nonlinear optical (NLO) materials suitable for applications such as second harmonic generation. As an efficient segment of π-electron conjugating bridge, diazo (N=N) bond is widely used in the design of NLO-chromophores.[7] Recently, several investigators reported the synthesis and characterization of new diazo NLO-chromophores containing five-membered heterocycles (thiophene, pyrrole and thiazole) as spacers. These materials exhibit high thermal stability and excellent solvatochromic and nonlinear optical properties.[7a,8]

Other interesting applications recently proposed include memory and recording devices, molecular switches, thermochromic, photovoltaic and fluorescence devices, supramolecular systems, acid–base and metal sensors and active ligands in Pd-catalyzed cross-coupling reactions.[8n,o,9] Matharu et al. describe also, for the first time, the synthesis and the characterization of a novel azo-methoxythiophene polyester with has strong potential application as a new holographic data storage material.

We have recently reported the synthesis and characterization, including the solvatochromic and nonlinear optical properties and thermal stability, of donor–acceptor substituted (oligo)thiophene derivatives and azo dyes containing pyrrole and thiophene heterocycles. These new NLO-chromophores exhibit good photochromic properties,[8n] excellent NLO activity and high thermal stability.[2h,i,k,3e–g,4c,e,f,5f]

These previous studies motivated us to explore the potential of conjugated 5-alkoxy-2,2′-bithiophenes as π-conjugated heterocyclic

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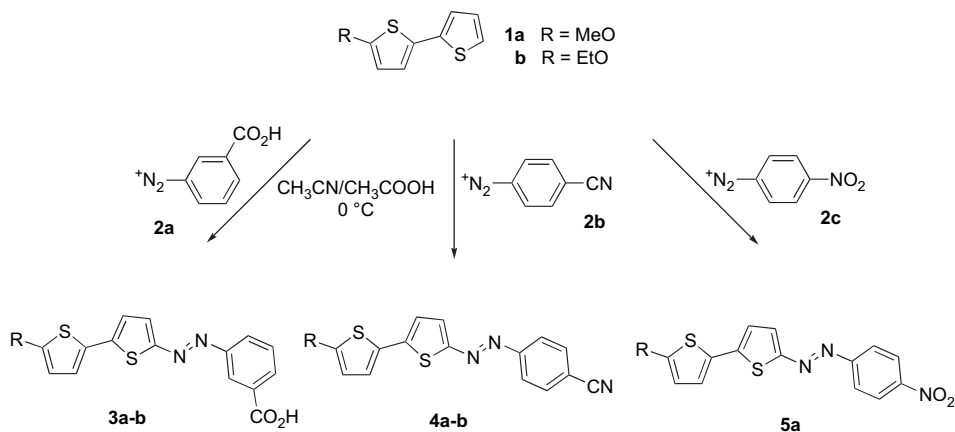
Scheme 1. Synthesis of azo-bithiophenes **3–5** through diazo coupling of 5′-alkoxy-2,2′-bithiophenes **1** with aryldiazonium salts **2**.

bridges functionalized with phenylazo groups. We report in this paper the synthesis, the solvatochromic, the nonlinear optical studies and the thermal stability of 5-arylazo-2,2′-bithiophenes **3–5**, which have the *meta* CO_2H or *para* CN and NO_2 groups as electron-withdrawing groups substituted on the phenylazo moiety and the conjugated 5-alkoxy-2,2′-bithiophene, as strong π-electron donor moieties.

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

2. Results and discussion

2.1. Synthesis

Usually, thiophene azo dye derivatives are prepared through azo coupling reactions of 2-aminothiophenes, with aryl-amines.[7a,8a–d,f,g,q,s] It is known that the synthesis of 2-amino-thiophene derivatives is troublesome although it is a rather simple heterocycle. Therefore, we decided to use a different methodology of synthesis in order to obtain new thiophene azo dyes using 5-alkoxy-2,2′-bithiophenes as coupling components, which will react with diazonium salts functionalized with acceptor groups.

Thiophene derivatives undergo electrophilic aromatic substitution much more readily than benzene, but till the work of Tedder et al.[10] there have been no reports of thiophene or any thiophene derivatives coupling with a diazonium salt. Even these authors report the synthesis of only four thiophene azo dyes obtained from the coupling of 2-*tert*-butylthiophene, 2-phenyl-thiophene, 2,4- and 2,5-dimethylthiophene with the very active 2,4-dinitrobenzenediazonium salt.[10]

Recently we have developed a method for the synthesis of 5-alkoxy-2,2′-bithiophenes **1** through a combination of the Friedel–Crafts and the Lawesson reactions.[2f] In our recent reactivity study with 5-alkoxy-2,2′-bithiophenes, we noticed that these compounds are highly reactive towards electrophilic reagents. Moreover, the position of substitution on the bithiophene moiety

depends on the size of the electrophile.[2h] In the case of diazo coupling reactions in 5-alkoxy-2,2′-bithiophenes **1**, the 5′-position of the thiophene ring was found to be much more reactive than the 4-position, *ortho* to the alkoxyl group. Therefore, diazo coupling was made selectively at the 5′-position of bithiophene moiety to give compounds **3–5** in moderate to good yields (27–48%), (Scheme 1, Table 1). These results are in accordance with the selectivity of the reaction of electrophiles with 5-alkoxy-2,2′-bithiophenes as has been shown earlier in the case of tricyanovi-nylation reactions.[2h]

Due to the poor stability of methoxythiophenes in acidic media there are only two recent articles describing the diazo coupling of alkoxythiophenes. Matharu et al.[8u,9f] obtained several methoxy-substituted azothiophenes using simple, commercially available 2-, 4- or 3,4-methoxythiophenes as coupling components. These investigators used two procedures: in the first an aqueous solution of diazonium chloride was added to the methoxythiophene dissolved in glacial acetic acid containing 4 M NaOH, which serve to form the necessary buffer. In the second procedure a diazonium tetrafluoroborate was added to solution of the methoxythiophene dissolved in glacial acetic acid containing anhydrous sodium acetate.

In our work, the synthesis of phenylazo-bithiophenes **3–5** was achieved through the usual way: an aqueous solution of diazonium chloride was added to the alkoxy-bithiophenes dissolved in acetonitrile containing some drops of glacial acetic acid. The azo compounds synthesized prove to be very stable (all the samples have an unchanged melting point after storage for 4 years).

The structures of bithiophene azo dyes **3–5** were unambiguously confirmed by their analytical and spectral data. In the ¹H NMR spectrum of 5-alkoxy-5′-phenylazo-2,2′-bithiophene derivatives **3–5**, in $CDCl_3$, two signals at about 7.13–7.15 ppm and 7.75–7.79 ppm, were detected. Both signals appear as doublets with coupling constants of 4.2 Hz indicating the presence of two adjacent protons in a disubstituted thiophene ring. These signals were attributed to the 3′-H and 4′-H protons, respectively.

Table 1
Yields, UV–visible and IR absorption spectra of 5-alkoxy-2,2′-bithiophenes **1** and 5-alkoxy-2,2′-bithiophene azo dyes **3–5**

Entry	Bithiophene	R	λ_{max}[a] (nm) (ε)	Diazonium salt	Azo-bithiophene	Yield (%)	λ_{max}[a] (nm) (ε)	IR[b] ν (cm⁻¹)
1	**1a**	MeO	319.0 (14,994)	**2a**	**3a**	47	467.0 (21,260)	1679 (C=O), 2360–3430 (OH)
2	**1b**	EtO	319.5 (14,517)	**2a**	**3b**	48	471.5 (24,020)	1693 (C=O), 2360–3420 (OH)
3	**1a**	MeO	—	**2b**	**4a**	37	496.0 (23,300)	2220 (CN)
4	**1b**	EtO	—	**2b**	**4b**	48	499.0 (22,960)	2220 (CN)
5	**1a**	MeO	—	**2c**	**5a**	27	509.0 (20,240)	—

[a] All the UV–visible spectra were recorded in ethanol.
[b] All the IR spectra were recorded in KBr.

2.2. UV–visible study of 5′-alkoxy-2,2′-bithiophene azo dyes 3–5

Electronic absorption spectra of all push–pull compounds **3–5** 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 **1**. For example, bithiophene **1a** (λ_{max}=319.0 nm) is shifted 190.0 nm upon arylazo substitution (bithiophene azo dye **5a**, λ_{max}=509.0 nm) (Table 1, entries 1 and 5, respectively). The effect produced by adding an azo bridge is seen by comparing the absorption maxima, in ethanol, of 5-methoxy-5′-(4″-nitrophenyl)-2,2′-bithiophene reported recently by us,[2i] to 5-methoxy-5′-(4″-nitrophenylazo)-2,2′-bithiophene **5a**; the longest wavelength transition is shifted from 413.0 nm to 508.0 nm for azo-bithiophene **5a**.

The influence of the strength of the acceptor group substituted on the arylazo moiety is demonstrated by comparison of the absorption maxima of compounds **4a** and **5a** as the longest wavelength transition is shifted from 496.0 nm in azo-bithiophene **4a** to 509.0 nm for azo-bithiophene **5a** (Table 1, entries 3 and 5, respectively; Fig. 1). This effect has been attributed to the stabilization of LUMO by the electron-withdrawing groups.[2k]
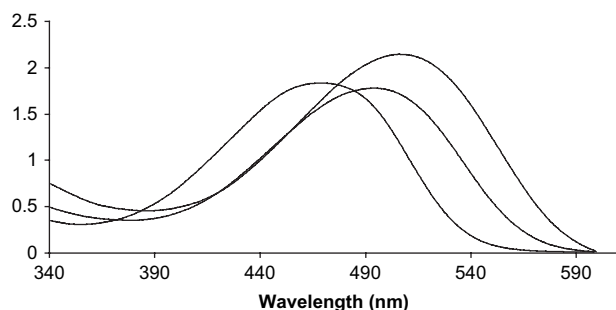

Figure 1. UV–visible absorption spectra of compounds **3a**, **4a** and **5a** in dioxane.

The impact of the electronic nature of the substituent at 5-position on the bithiophene moiety can be seen by comparing the absorption maxima of compounds **3a** and **3b** as the longest wavelength transition is shifted from 467.0 nm in azo dye **3a** to 471.5 nm for azo dye **3b** (Table 1, entries 1 and 2, respectively).

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. The increase of the β values characteristic of the NLO effects is accompanied by an increase of λ_{max} in the UV–visible spectra, i.e., by a decrease in the intramolecular charge-transfer (ICT) values.[2k]

2.3. Solvatochromic study of 5′-alkoxy-2,2′-bithiophene azo dyes 3–5

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.[3e,11] In general, red shifts in absorption were accompanied by positive solvatochromic shifts. Especially noteworthy is the extremely large positive solvatochromism exhibited by 5-acceptor-substituted 2-amino- or 2-alkoxy-(oligo)thiophenes making these compounds good indicators for measuring the polarity of solvent.[2i,12] This red shift, suggests an increase of molecular hyperpolarizability, according to theoretical and experimental NLO studies.[2k]

In order to investigate whether compounds **3–5** could act as suitable probes for the determination of solvent polarity, we made a preliminary study of the absorption spectra of azo dye compounds **3–5** in three selected solvents of different solvation character (ethanol, DMF and DMSO) (Table 2). For all azo dyes the highest energy transitions were found with less polar solvents such as ethyl ether. More polar solvents such as DMSO resulted in lower energy transitions. This behaviour 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 **3a** ($\Delta\nu_{max}$=922 cm^{-1}), **3b** ($\Delta\nu_{max}$=632 cm^{-1}) and **4a** ($\Delta\nu_{max}$=744 cm^{-1}) showed the longest shifts in wavenumber maxima. Therefore, **3a**, **3b** and **4a** were submitted to a full solvatochromic study involving 12 solvents. Because of the pronounced solvatochromism, (**3a**, $\Delta\nu_{max}$=+1271 cm^{-1}; **3b** $\Delta\nu_{max}$=+1115 cm^{-1}; **4a**, $\Delta\nu_{max}$=+1180 cm^{-1}), good correlation with π^* values by Kamlet et al.[13] for the solvents investigated and the long wavelength absorption in the visible range, **3a**, **3b** and **4a** seemed to be very appropriate solvent polarity indicating dyes (Table 3).

2.4. Nonlinear optical properties and thermal stability of 5′-alkoxy-2,2′-bithiophene azo dyes 3–5

We have used the hyper-Rayleigh scattering (HRS) method[14,15] to measure the first hyperpolarizability β of 5′-alkoxy-2,2′-bithiophene azo dyes **3–5** using the 1064 nm fundamental wavelength of a laser bean. Dioxane was used as solvent, and the β values were measured against a reference solution of *p*-nitroaniline (*p*-NA)[16,17] in order to obtain quantitative values, while care was taken to properly account for possible fluorescence of the dyes (see Section 4 for more details). The static hyperpolarisability β values were calculated using a very simple two-level model neglecting damping. They are therefore only indicative and should be treated with caution (Table 4).

The experimental results obtained for the nonlinearities β of chromophores **4a**, **5a** and **5b** show that compounds having strong acceptor groups at the *para* position of the aryl ring, CN and NO$_2$, exhibit the highest β values (Table 4, entries 3, 4 and 5, respectively). Compounds **3a** and **4a** having the acceptor carboxylic group at the *meta* position of the aryl ring exhibit the lowest β and β_0 values (Table 4, entries 1 and 2, respectively).

Comparison of the β values for the azo derivatives containing a methoxyl group substituted at the 5-position of the bithiophene donor moiety (**3a** and **4a**) leads to larger nonlinearities than the substitution by the ethoxyl group at the same position of the bithiophene units (**3b** and **4b**). Azo dyes **3–5** exhibit high molecular nonlinearities, as their values are 13–16 times higher than that of

Table 2
Solvatochromic data [λ_{max} (nm) and ν_{max} (cm^{-1}) of the charge-transfer band] for azo-bithiophene **3–5** in three solvents with π^* values by Kamlet et al.[13a]

Solvents[a]	π^*	3a		3b		4a		4b		5a	
		λ_{max} (nm)	ν_{max} (cm^{-1})	λ_{max} (nm)	ν_{max} (cm^{-1})	λ_{max} (nm)	ν_{max} (cm^{-1})	λ_{max} (nm)	ν_{max} (cm^{-1})	λ_{max} (nm)	ν_{max} (cm^{-1})
Ethanol	0.54	467.0	21,413	471.5	21,208	496.0	20,161	499.0	20,040	509.0	19,646
Dimethylformamide	0.88	476.0	21,008	481.5	20,768	505.0	19,801	509.0	19,646	521.0	19,193
Dimethylsulfoxide	1.00	488.0	20,491	486.0	20,576	515.0	19,417	515.0	19,417	528.0	18,939

[a] Solvent used as received.

Table 3
Solvatochromic data [λ_{max} (nm) and ν_{max} (cm^{-1}) of the charge-transfer band] for azo-bithiophenes **3a**, **3b** and **4a** in 12 solvents with π^* values by Kamlet et al.[13a]

Solvents[a]	π^*[b]	Compound **3a**		Compound **3b**		Compound **4a**	
		λ_{max} (nm)	ν_{max} (cm^{-1})	λ_{max} (nm)	ν_{max} (cm^{-1})	λ_{max} (nm)	ν_{max} (cm^{-1})
Diethyl ether	0.27	459.5	21,762	461.0	21,691	485.5	20,597
Toluene	0.54	468.5	21,344	474.5	21,074	495.5	20,181
Ethanol	0.54	467.0	21,413	471.5	21,208	496.0	20,161
Dioxane	0.55	468.5	21,344	471.0	21,231	494.5	20,222
Ethylacetate	0.55	462.5	21,621	469.0	21,321	489.0	20,449
Tetrahydrofuran	0.58	472.0	21,186	474.0	21,180	499.5	20,020
Acetone	0.71	471.5	21,208	478.0	20,920	494.0	20,242
Acetonitrile	0.75	465.5	21,482	473.5	21,119	489.5	20,429
Chloroform	0.76[13b]	471.5	21,208	475.0	21,052	496.0	20,161
Dichloromethane	0.82	475.5	21,030	480.5	20,811	501.0	19,960
Dimethylformamide	0.88	476.0	21,008	481.5	20,768	505.0	19,801
Dimethylsulfoxide	1.00	488.0	20,491	486.0	20,576	515.0	19,417

[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=0.9979 for **3b**, r=0.9005 for **3a** and r=0.8361 for **4a**. These values were obtained without toluene, acetonitrile and ethylacetate (**3a**) or without toluene and acetonitrile (**4a**), which deviate slightly from the regression line.[2i,12b]

Table 4
UV–visible absorptions, β and β_0 values and T_d data for compounds **3–5**[a]

Entry	Azo-bithiophene	λ_{max} (nm)	β[b] (10^{-30} esu)	β_0[c] (10^{-30} esu)	T_d (°C)[d]
1	**3a**	468.5	240	43	232
2	**3b**	472.5	220	37	230
3	**4a**	494.5	270	29	249
4	**4b**	497.0	260	26	263
5	**5a**	505.5	260	20	239
6	*p*-NA	352.0	16.9[16,17]	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.[18–20]
[d] Decomposition temperature (T_d) measured at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere, obtained by TGA.

the well known *p*-NA molecule for an incident laser wavelength of 1064 nm (the corresponding β_0 values are 2.5 to 4 times higher than that of *p*-NA).

The thermal stabilities of the chromophores **3–5** were investigated by thermogravimetric analysis under a nitrogen atmosphere, measured at a heating rate of 20 °C min^{-1} (Table 4). All the chromophores are thermally stable with decomposition temperatures varying from 230 to 263 °C. The results indicate that, the different alkoxyl groups substituted on the bithiophene moiety have little impact on the overall stabilities of the chromophores (e.g., **3a**, R=MeO, T_d=232 °C; **3b**, R=EtO, T_d=230 °C). On the contrary, the acceptor groups substituted on the phenylazo moiety do seem to have some impact on the thermal stability of the compounds (e.g., **3b**, R$_2$=CO$_2$H, T_d=230 °C; **4b**, R$_2$=CN, T_d=263 °C) showing that, the cyano azo dyes are the most stable.

3. Conclusions

In summary, we have achieved the first synthesis of a series of 5-alkoxy-2,2′-bithiophene azo dyes **3–5** from easily available 5-alkoxy-bithiophenes **1** and low cost, commercially available anilines. Simple work-up procedures produce moderate to good yields of these derivatives.

By comparing the several different synthesized derivatives, it can be shown that the withdrawing group on the phenylazo moiety and the type of substituent on the 5′-position of the bithienyl π-conjugated bridge have significant influence on the linear and nonlinear optical properties of these compounds. Compounds **3–5** exhibit dramatic changes in their optical properties in comparison to 5-alkoxy-2,2′-bithiophenes **1**.

The solvatochromic behaviour of compounds **3–5** was determined by regression analyses of absorption maxima in several solvents of different polarity. Due to their pronounced solvatochromic properties azo dyes **3–5** could be used as solvatochromic probes.

Hyper-Rayleigh scattering was used to determine the first hyperpolarisability, β, the data showing that β is dependent on the alkoxyl groups substituted on the bithiophene moiety and on the strength and position of substitution (*meta* or *para*) of the withdrawing group on the phenylazo moiety. The results also show that azo dyes **3–5** have significant molecular nonlinearities, their values being 13–16 times higher than that of the well known *p*-NA molecule for incident laser wavelength of 1064 nm.

Thermal stability of chromophores **3–5** was estimated by thermogravimetric analysis. Experimental results for compounds **3–5**, indicate that good nonlinearity–thermal stability is well balanced for these chromophores, which possess β values from 220×10^{-30} esu to 270×10^{-30} esu and higher decomposition temperatures, (230–263 °C), making them good candidates for NLO applications.

4. Experimental

4.1. General

Reaction progress was monitored by thin layer chromatography (0.25 mm thick precoated silica plates: Merck Fertigplatten Kieselgel 60 F$_{254}$), 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 parts per million). Mps were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a BOMEM MB 104 spectrophotometer. 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.

Light petroleum refers to solvent boiling in the range 40–60 °C. The synthesis of 5′-alkoxy-2,2′-bithiophenes **1** was described elsewhere.[2f]

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

4.2. General procedure for diazo coupling of bithiophenes 1 with 3-carboxy-, 4-cyano- and 4-nitro-substituted aryldiazonium salts 2a–c

(i) *Diazotisation of 3-carboxy-, 4-cyano- and 4-nitroaniline.* Aniline (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.

(ii) *Coupling reaction with 5′-alkoxy-2,2′-bithiophenes 1.* The diazonium salt solution previously prepared (4.0 mmol) was added drop wise to the solution of bithiophenes 1 (4.0 mmol) in acetonitrile (50 ml) and some drops of acetic acid. The combined solution was maintained at 0 °C for 1 h while stirring and afterwards was left over night at room temperature. After this time the resulting mixture was diluted with petrol ether (20 ml) and water (40 ml) and the formed product was isolated by filtration. The organic layer was diluted with chloroform, washed with water and dried with anhydrous $MgSO_4$. The dried solution was evaporated and the remaining 5-alkoxy-5′-phenylazo-bithiophenes 3–5 were purified by column chromatography on silica with dichloromethane as eluent.

4.2.1. 5-Methoxy-5′-(3″-carboxyphenylazo)-2,2′-bithiophene (3a)

Orange brownish solid (47%). Mp>200 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 471.5 (12,030). IR (KBr) ν 502, 527, 640, 658, 677, 695, 707, 722, 757, 786, 818, 876, 917, 936, 999, 1040, 1057, 1077, 1096, 1157, 1206, 1221, 1257, 1280, 1309, 1358, 1375, 1424, 1454, 1489, 1526, 1556, 1584, 1596, 1679 (C=O), 2360–3430 (OH) cm^{-1}. ^{1}H NMR (acetone-d_6) δ 4.03 (s, 3H, OCH_3), 6.41 (d, 1H, J=3.9 Hz, 4-H), 7.30 (d, 1H, J=3.9 Hz, 3-H), 7.35 (d, 1H, J=4.2 Hz, 3′-H), 7.74 (t, 1H, J=7.5 Hz, 5″-H), 7.91 (d, 1H, J=4.2 Hz, 4′-H), 8.09–8.19 (m, 2H, 4″ and 6″-H), 8.48 (m, 1H, 2″-H). ^{13}C NMR (DMSO-d_6) δ 60.6, 105.9, 121.7, 122.2, 122.9, 125.6, 127.3, 129.9, 131.0, 132.1, 135.4, 142.0, 151.6, 155.5, 166.7, 167.3. MS (EI) m/z (%): 344 (M$^+$, 100), 329 (40.6), 301 (8.13), 195 (11.9), 151 (11.9), 121 (11.3), 110 (6.88), 69 (8.13). HRMS: m/z (EI) for $C_{16}H_{12}N_2O_3S_2$: calcd 344.0289; found 344.0290.

4.2.2. 5-Ethoxy-5′-(3″-carboxyphenylazo)-2,2′-bithiophene (3b)

Orange brownish solid (48%). Mp>195 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 478.0 (46,600). IR (KBr) ν 525, 570, 624, 638, 658, 676, 694, 708, 732, 759, 778, 794, 815, 876, 907, 998, 1037, 1058, 1079, 1109, 1158, 1214, 1230, 1257, 1281, 1297, 1361, 1374, 1388, 1415, 1449, 1481, 1521, 1556, 1585, 1594, 1693 (C=O), 2357–3314 (OH) cm^{-1}. ^{1}H NMR (acetone-d_6) δ 1.46 (t, 3H, J=7.0 Hz, OCH$_2$CH_3), 4.27 (q, 2H, J=7.0 Hz, OCH_2CH$_3$), 6.39 (d, 1H, J=3.9 Hz, 4-H), 7.29 (d, 1H, J=3.9 Hz, 3-H), 7.34 (d, 1H, J=3.9 Hz, 3′-H), 7.74 (t, 1H, J=8.1 Hz, 5″-H), 7.90 (d, 1H, J=3.9 Hz, 4′-H), 8.09–8.18 (m, 2H, 4″-H and 6″-H), 8.48 (m, 1H, 2″-H). ^{13}C NMR (acetone-d_6) δ 14.8, 70.4, 107.0, 110.6, 123.3, 123.7, 125.7, 127.8, 130.5, 132.0, 132.8, 135.6, 143.4, 153.1, 157.2, 167.0, 167.7. MS (EI) m/z (%): 358 (M$^+$, 100), 329 (92), 301 (16), 281 (6.3), 231 (11), 207 (15), 181 (53), 153 (19), 137 (16), 121 (54), 69 (42). HRMS: m/z (EI) for $C_{17}H_{14}N_2O_3S_2$: calcd 358.0446; found 358.0441.

4.2.3. 5-Methoxy-5′-(4″-cyanophenylazo)-2,2′-bithiophene (4a)

Brown solid (37%). Mp>179.1 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 494.0 (15,280). IR (KBr) ν 562, 774, 837, 1031, 1144, 1263, 1344, 1476, 1513, 1595, 1732, 2220 (CN), 2922 cm^{-1}. ^{1}H NMR (CDCl3) δ 3.96 (s, 3H, OCH_3), 6.21 (d, 1H, J=4.2 Hz, 4-H), 7.10 (d, 1H, J=4.2 Hz, 3-H), 7.13 (d, 1H, J=4.2 Hz, 3′-H), 7.74–7.77 (m, 3H, 2″-H, 6″-H and 4′-H), 7.88–7.90 (d, 2H, J=8.7 Hz, 3″ and 5″-H). ^{13}C NMR (CDCl$_3$) δ 60.4, 105.4, 112.7, 118.7, 122.5, 123.0, 123.3, 124.8, 133.1, 135.8, 144.3, 154.5, 156.3, 168.2. MS (EI) m/z (%): 325 (M$^+$, 100), 310 (70), 282 (5), 251 (9), 205 (15), 195 (15), 149 (19), 102 (28), 71 (14). HMRS: m/z (EI) for $C_{16}H_{11}N_3OS_2$: calcd 325.0344; found 325.0341.

4.2.4. 5-Ethoxy-5′-(4″-cyanophenylazo)-2,2′-bithiophene (4b)

Brown reddish solid (48%). Mp>168.4 °C (with decomposition). UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 497.5 (12,240). IR (KBr) ν 762, 831, 1037, 1344, 1457, 1513, 2220 (CN), 2928, 2984 cm^{-1}. ^{1}H NMR (CDCl3) δ 1.46 (t, 3H, J=7.2 Hz, OCH$_2$CH_3), 4.75 (q, 2H, J=7.2 Hz, OCH_2CH$_3$), 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=4.2 Hz, 3′-H), 7.74–7.77 (m, 3H, 2″-H, 6″-H and 4′-H), 7.87–7.90 (d, 2H, J=8.0 Hz, 3″-H and 5″-H). ^{13}C NMR (CDCl$_3$) δ 14.6, 69.7, 106.2, 112.6, 118.7, 122.4, 123.0, 123.5, 124.9, 133.1, 135.8, 144.5, 154.5, 156.2, 167.3. MS (EI) m/z (%): 339 (M$^+$, 75), 310 (100), 282 (3), 254 (3), 181 (11), 153 (6), 137 (7), 102 (33). HRMS: m/z (EI): for $C_{17}H_{13}N_3OS_2$: calcd 339.0500; found 339.0497.

4.2.5. 5-Methoxy-5′-(4″-nitrophenylazo)-2,2′-bithiophene (5a)

Violet solid (27%). Mp 177.1–177.4 °C. UV (acetone): λ_{max} nm (ε/M^{-1} cm^{-1}) 508.5 (24,980). IR (Nujol) ν 568, 687, 775, 792, 846, 855, 981, 1017, 1056, 1107, 1148, 1207, 1238, 1263, 1326, 1365, 1419, 1518, 1544, 1586, 1602 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 3.97 (s, 3H, OCH_3), 6.22 (d, 1H, J=4.2 Hz, 4-H), 7.13 (d, 1H, J=4.2 Hz, 3-H), 7.15 (d, 1H, J=4.2 Hz, 3′-H), 7.79 (d, 1H, J=4.2 Hz, 4′-H), 7.93 (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 (CDCl$_3$) δ 60.4, 105.4, 122.6, 123.0, 123.2, 124.7, 125.0, 136.3, 144.8, 144.8, 155.9, 156.3, 168.4. MS (EI) m/z (%): 345 (M$^+$, 100), 331 (40), 330 (98), 315 (10), 284 (8), 256 (11), 205 (13), 195 (53), 181 (28), 151 (58), 149 (13), 136 (12), 122 (41), 111 (13), 84 (21). HMRS: m/z (EI) for $C_{15}H_{11}N_3O_3S_2$: calcd 345.0242; found 345.0231.

4.3. Nonlinear optical measurements for compounds 4 and 5 using the hyper-Rayleigh scattering (HRS) method[14]

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 is similar to the one presented by Clays and Persoons.[14] 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 power could be varied using a combination of a half wave-plate and Glan polarizer. The incident beam was weakly focused (beam diameter ∼0.5 mm) into the solution contained in a 5 cm long cuvette. The hyper-Rayleigh signal was collimated using a high numerical aperture lens passed through an interference filter centred 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 25 ns gate centred 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)[15] 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 carried out at the same fundamental wavelength.[16,17] 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 according to the expression:

$$I_{2\omega} = G\left(N_{solvent}\langle\beta^2_{solvent}\rangle + N_{solute}\langle\beta^2_{solute}\rangle\right)I^2_\omega$$

where the factor G is an instrumental factor that takes into account the detection efficiency (including geometrical factors and linear absorption or scattering of the second harmonic light on its way to the detector) and local field corrections. The brackets indicate an average over the spatial orientations of the molecules. The error associated with the HRS measured β values is estimated to be less than 20% of the quoted values except for compound **3a**, which has an estimated uncertainty of 30% due to the higher amount of fluorescence detected.

We took particular care to avoid reporting artificially high hyperpolarizibilities due to a possible contamination of the hyper-Rayleigh signal by molecular fluorescence near 532 nm. Measurements were carried out using two different interference filters with different transmission pass bands centred near the second harmonic at 532 nm. The transmission band of the narrower filter (CVI model F1.5-532-4) was 1.66 nm (full width at half maximum) with a transmission of 47.6% at the second harmonic, while the corresponding value for the wider filter (CVI model F03-532-4) was 3.31 nm, with a transmission of 63.5% at the second harmonic. The transmission of each filter at the second harmonic wavelength was carefully determined using a crystalline quartz sample. We assume that any possible fluorescence emitted from the solutions is essentially constant over the transmission of both interference filters. Then by comparing the signals obtained with the two different filters we can determine the relative contributions of the hyper-Rayleigh and possible fluorescence signals.

More concretely the overall detected signal can have contributions from both the second harmonic signal and any possible fluorescence that is emitted within the passband of the filter. Denoting S_{NB} as the actual signal measured (after correction for the solvent contribution) using the 'narrow' (CVI model F1.5-532-4), we have

$$S_{NB} = T_{NB}S^{2\omega} + A_{NB}S^F$$

while the corresponding signal obtained using the 'wide' (CVI model F03-532-4) band interference filter is

$$S_{WB} = T_{WB}S^{2\omega} + A_{WB}S^F.$$

Here $S^{2\omega}$ is the second harmonic signal incident on the filters while S^F is the average fluorescence signal over the passband of the filters. We assume that the fluorescence component is broad enough that the average fluorescence signal is essentially identical for both filters. The transmissions T_{NB} and T_{WB} are, respectively, the transmission of the 'narrow' and 'wide' band interference filters at the second harmonic wavelength (47.6% and 63.5%), while A_{NB} and A_{WB} represent the area under the respective filter's transmission curve. The transmission curves were obtained using a dual-beam spectrophotometer with slits adjusted to give 0.1 nm resolution. We obtained values of 1.29 nm and 2.18 nm for A_{NB} and A_{WB}, respectively. Solving the above equations for $S^{2\omega}$ and S^F we arrive at the following expression for the actual hyper-Rayleigh and fluorescence contribution to the signal obtained using the narrow band interference filter:

$$S^{2\omega}_{NB} = \left(\frac{S_{NB}A_{WB} - S_{WB}A_{NB}}{T_{NB}A_{WB} - T_{WB}A_{NB}}\right)T_{NB}$$

$$S^F_{NB} = \left(\frac{S_{WB}T_{NB} - S_{NB}T_{WB}}{T_{NB}A_{WB} - T_{WB}A_{NB}}\right)A_{NB}$$

This allows us to determine if fluorescence is present and to reliably correct for its presence provided that the integrated contribution is less than 80% of the total detected signal within the temporal gate of the box-car integrator (25 ns). When using the 'narrow' band filter the estimated fraction of the total detected signal due to fluorescence is listed in the following table:

Compound	S^F_{NB}/S_{NB}
3a	0.27
3b	0.42
4a	0.20
4b	0.15
5a	0.11

We estimate that the error associated with the above values is less than 25% of the value quoted.

4.4. Thermogravimetric analysis of compounds 3–5

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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