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Thiazole azo dyes with lateral donor branch: Synthesis, structure and second order NLO properties

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ABSTRACT

Three azo dyes with a thiazole based donor-π-acceptor structure containing a methoxyphenyl group as the lateral donor branch were synthesized and fully characterized. The formyl azo dye precursor was synthesized using 5-formylaminothiazole derivative as the diazo component and *N*,*N*-diethylaninline as the coupling component. Knoevenagel condensation of this precursor with different acceptors, namely, indandione, malononitrile and dicyanovinylindanone afforded the desired nonlinear optical chromophores **a**–**c**, respectively.

The optical property, thermal stability and second order nonlinear optical activity were evaluated and a single crystal structural characterization was performed for two of the dyes. All nonlinear optical dyes **a**–**c** have good nonlinearity and good thermal stability. Compared with dyes **a** and **b**, dye **c** shows more than triple second order nonlinear optical response, the result that makes this molecule an unusual example of asymmetrical 2D charge transfer chromophore.

1. Introduction

The rapid progress of hi-tech applications based on optoelectronics has inspired many scientists to develop novel designs for functional dyes [1]. Organic second-order nonlinear optical (NLO) materials typically take the form of dipolar D-π-A type organic chromophores, where D (A) is an electron donor (acceptor) group and π is a conjugated bridge [2]. This structural feature results in the requisite ground-state charge asymmetry and the redistribution conjugation of electric charges under the influence of electric fields by virtue of its π-conjugated system [3]. NLO chromophores with high first order molecular hyperpolarizability and good thermal and photochemical stabilities have been actively pursued.

Several reports indicated that ground state benzenoid D-π-A type chromophores are less polarizable than a simple polyene of comparable length indicating insufficient intramolecular charge transfer (CT), which is a direct consequence of the loss of aromatic stabilization upon polarization [4–7]. Therefore, ground state less aromatic D-π-A type chromophores have been designed by replacing the benzene ring of a chromophore with easily polarizable five-membered heteroaromatic rings, such as thiophene, pyrrole and thiazole, resulting in an enhanced molecular hyperpolarizability [8]. Also, recent theoretical calculations suggest that heterocyclic rings play a subtle role in the second-order NLO properties of donor-acceptor compounds and the increase or decrease of NLO properties of these heteroaromatic systems depends not only on the electronic nature of the aromatic rings, but also on the location of these heterocycles in the system [9].

Azo dyes are the most widely used class of colorants because of their versatile applications in various fields that range from textile to non-textile applications [10]. In this context, thiazole azo dyes similar to other heterocyclic analogs have the advantage of bright and strong shades that range from red to green and blue [11–14]. In addition, thiazole azo dyes are of great importance since they have pronounced bathochromic absorptions compared to corresponding benzenoid dyes as the heterocyclic ring can act as auxiliary electron acceptor due to the electronegativity of the nitrogen and sulfur atoms [9b,c,15,16]. In this interest, recent reports on heterocyclic azo dyes as NLO chromophores have been reported [13,17–20].

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Also, some promising results of NLO based thiazole azo dyes have recently been published by some of us [21].

Stemmed by this information and in continuation of our interest on the synthesis and characterization of thiazole azo dyes for optical applications, it was worthy to synthesize novel thiazole azo dyes with lateral donor branch and to study their structure and second order NLO properties.

2. Experimental

2.1. General

All solvents and reagents were of the highest purity available, purchased from Sigma–Aldrich Company and used as received. Basic Ethanol solution was made as a fresh stock solution (0.5 ml piperidine, 1.5 ml glacial acetic acid and 48 ml absolute ethanol) for the synthesis of dye **a**–**c**.

^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 solutions on a Bruker Avance 600 MHz spectrometer. Infrared spectra were performed on a PerkinElmer spectrum 100 FTIR spectrometer. Mass spectra were measured on a GCMS-QP1000 EX spectrometer at 70 eV. HRMS spectra of the chromophores were recorded with a MALDI TOF DE-PRO apparatus on a matrix of 2,5-dihydroxybenzoic acid. Elemental microanalyses were performed at the Taibah University Microanalytical Center. Melting points were determined in open capillary tubes in a Stuart Scientific melting point apparatus and are uncorrected. UV/Vis absorption spectra were recorded with a Jasco V560 spectrophotometer. The thermal stability of the compounds was studied by thermogravimetric analysis (TA SDT 2960, air, 10 K/min).

Single crystals of **b** and **c** suitable for X-ray analysis were obtained at room temperature by slow evaporation of CH_2Cl_2/heptane solutions. One crystal of **b** (dark green 0.55 × 0.50 × 0.01 mm) and one crystal of **c** (dark red 0.60 × 0.01 × 0.01 mm) were mounted at 173 K under N_2 flow on a Bruker-Nonius KappaCCD diffractometer equipped with a graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å, CCD rotation images, thick slices, φ and ω scans to fill asymmetric unit). Semiempirical absorption correction (SADABS) was applied. Both the structures were solved by direct methods (SIR97 package [22]) and refined by the full matrix least-squares method on F^2 against all independent measured reflections (SHELXL program of SHELX97 package [23]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined according to a riding model. The final refinement converged to $R_1 = 0.0547$ and $R_1 = 0.1265$ for **b** and **c,** respectively. Crystals of **c** were poor quality and weakly diffracting and disordered CH_2Cl_2 crystallization solvent molecules were found. Some restrains were introduced in the last stage of refinement to treat the disorder of CH_2Cl_2. This may account for the high R values obtained. Crystal data and refinement details are summarized in Table 2. CCDC 870850 (**b**) and 870851 for (**c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033.

The molecular quadratic optical nonlinearities of chromophores, in the form of $\mu_g\beta$ products (μ_g is the ground state permanent dipole moment and β the first hyperpolarizability of the molecules, according to convention B [24,25]), were measured on a standard Electric Field Induced Second Harmonic Generation (EFISHG) set-up [26] operating at 1907 nm fundamental wavelength, obtained by Raman-shifting the emission from a Nd:YAG laser, and which has the advantage of being far from the absorption bands of the molecules.

The data were also corrected for the dispersion effect on the basis of the two-level model [27] to obtain static $\mu\beta_0$ coefficients, according to the formula:

$$\mu\beta = \frac{\mu\beta_0}{\left(1-\dfrac{\omega^2}{\omega_{eg}^2}\right)\left(1-\dfrac{4\omega^2}{\omega_{eg}^2}\right)} = \frac{\mu\beta_0}{\left(1-\dfrac{\lambda_{eg}^2}{\lambda^2}\right)\left(1-\dfrac{4\lambda_{eg}^2}{\lambda^2}\right)}$$

where β_0 is the intrinsic molecular hyperpolarizability, ω (λ) is the excitation frequency (wavelength) of the fundamental beam, ω_{eg} (λ_{eg}) is the transition frequency (wavelength) associated with the charge transfer band.

2.2. 4-(4-methoxyphenyl)thiazol-2-amine *(**2**)*

A mixture of thiourea (0.53 g, 7 mmol) and **1** (1.6 g, 7 mmol) in 70 ml acetone was stirred overnight at room temperature and filtered to afford the corresponding hydrobromide salt quantitatively. Then, the salt was treated with 5% ammonia solution with stirring and filtered to give the desired thiazole product **2** as a white powder. Yield: 94%. Mp 205–206 °C [28]. ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.77 (s, 3H, OCH_3), 6.84 (s, 1H, 5-H), 6.93 (d, 2H, $J = 4.8$ Hz, Ar–H), 7.04 (s, 2H, NH_2), 7.3 (d, 2H, $J = 4.8$ Hz, Ar–H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 55.02, 99.28, 113.76, 126.78, 127.77, 149.59, 158.45, 168. MS m/z (%) 206 (M^+, 100), 191 (45.8), 149 (43.4), 121 (33.8), 77 (25). IR ν/cm^{-1} 3438, 3267, 3118, 2965, 1623, 1535, 1492, 1177, 1033, 834, 737, 698. Calcd for $C_{10}H_{10}N_2OS$: C, 58.23%; H, 4.89%; N, 13.58%; S, 15.54. Found: C, 58.45%; H, 4.93%; N, 13.74%; S, 15.04.

2.3. N-(4-(4-methoxyphenyl)thiazol-2-yl)acetamide *(**3**)*

A mixture of **2** (4.12 g, 20 mmol), acetic anhydride (20 ml) and glacial acetic acid (100 ml) with few drops of conc. H_2SO_4 was refluxed for 1 h. The reaction mixture was allowed to cool at room temperature and then recrystallized from ethanol to afford compound **3**. Yield: 85.7%. Mp 189–190 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.16 (S, 3H, $COCH_3$), 3.79 (S, 3H, OCH_3), 6.99 (d, 2H, $J = 7.14$ Hz, Ar–H), 7.42 (S, 1H, 5-H), 7.82 (d, 2H, $J = 7.08$ Hz, Ar–H), 12.2 (S, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ 22.63, 55.27, 105.96, 114.22, 127.12, 127.27, 148.72, 157.94, 159.08, 168.8.

2.4. N-(5-formyl-4-(4-methoxyphenyl)thiazol-2-yl)acetamide *(**4**)*

To an ice cooled flask containing *N,N*-dimethylformamide (86 ml) was added $POCl_3$ (53.5 ml) dropwise with stirring. After addition, the solution was stirred at room temperature for 90 min. Then the flask was cooled again in ice-bath and compound **3** (65 mmol) was added. The reaction mixture was warmed gradually to run at 75 °C for 2 h. Then cooled to room temperature and poured onto ice–water, basified (sat. aqueous K_2CO_3 solution) and extracted with $CHCl_3$ (4 × 30 ml) washed, dried ($MgSO_4$) and evaporated. Yield: 75.63%. Mp 124–126 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.16 (S, 3H, $COCH_3$), 3.87 (S, 3H, OCH_3), 6.99 (d, 2H, $J = 4.8$ Hz, Ar–H), 7.66 (d, 2H, $J = 4.8$ Hz, Ar–H), 8.41 (S, 1H, NH), 9.80 (S, 1H, CHO). ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.41, 55.42, 114.02, 126.32, 126.89, 131.21, 156.94, 160.90, 162.99, 179.29, 183.65.

2.5. 2-Amino-4-(4-methoxyphenyl)thiazole-5-carbaldehyde *(**5**)*

A mixture of compound **4** (2.256 g, 8 mmol) and 25% HCl in methanol was refluxed for 30 min, then cooled to room temperature and poured onto ice-water, basified with 25% ammonia solution, filtered off and recrystallized from ethanol. yield: 77.48%. Mp 227–229 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.8 (S, 3H, OCH_3), 7.03 (d, 2H, $J = 4.8$ Hz, Ar–H), 7.66 (d, 2H, $J = 4.8$ Hz, Ar–H), 8.35 (S, 2H, NH_2),9.56 (S, 1H, CHO). ^{13}C NMR (125 MHz, DMSO-d_6)

δ 55.35, 114.08, 121.63, 125.87, 131.05, 160.62, 163.31, 172.55, 181.41.

*2.6. 2-((4-(diethylamino)phenyl)diazenyl)-4-(4-methoxyphenyl) thiazole-5-carbaldehyde **(6)***

NaNO$_2$ (516 mg, 7.48 mmol) was added to 95–98% H$_2$SO$_4$ (5.6 ml) and the mixture was heated at 65 °C until complete dissolution. After being cooled in an ice-bath (0–5 °C), the nitrosylsulphuric acid solution was diluted with AcOH (3.2 ml) over 3 min and then left for 10 min. Following cooling to −5 °C, compound **5** (1.0 g, 6.15 mmol) was added portion wise and, once the addition was complete (15 min), the reaction mixture was stirred for 2 h at 5 °C. The so formed diazonium salt solution was added gradually (10 min) to a mixture of N,N-diethylaniline (1.0 ml, 6.29 mmol) in water (62 ml) and 95–98% H$_2$SO$_4$ (1.2 ml), at 0 °C under vigorous stirring, after which the reaction mixture was left at rt for 1 h. The resulting solid was then collected by filtration, washed with water and dried. Column chromatography on silica gel using CHCl$_3$ as the eluent afforded compound **6** as violet crystals. Yield: 43.3%. Mp 167–169 °C. ^{1}H NMR (600 MHz, CDCl$_3$) 1.28 (t, 6H, *J* = 7.2 Hz, N (CH$_2$C*H*$_3$)$_2$), 3.53 (q, 4H, *J* = 7.2 Hz, N(C*H*$_2$CH$_3$)$_2$), 3.91 (s, 3H, OCH$_3$), 6.76 (d, 2H, *J* = 9.6 Hz, Ar–H), 7.05 (d, 2H, *J* = 7.2 Hz, Ar–H), 7.8 (d, 2H, *J* = 7.2 Hz, Ar–H), 7.98 (d, 2H, *J* = 9 Hz, Ar–H), 10.01 (s, 1H, CHO). ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.73, 45.26, 55.44, 111.68, 114.17, 125.98, 130.70, 131.44, 134.87, 142.69, 153.09, 161.10, 162.94, 182.16, 184.90.

*2.7. General procedure for the synthesis of NLO chromophores **a**–**c***

A mixture of dye **6** (1.18 g, 3 mmol) and indandione (0.438 g, 3 mmol) or malononitrile (0.198 g, 3 mmol) or 3-dicyanovinylindan-1-one (0.582 g, 3 mmol) in basic ethanol solution (7 ml) was stirred at room temperature overnight, filtered off and purified by column chromatography on silica gel using CHCl$_3$ as the eluent, affording dyes **a** or **b** or **c**, respectively.

*2.7.1. Dye **a***

Yield: 75%. Mp 185–187 °C. ^{1}H NMR (600 MHz, CDCl$_3$) 1.3 (t, 6H, *J* = 7.2 Hz, N(CH$_2$C*H*$_3$)$_2$), 3.55 (q, 4H, *J* = 7.2 Hz, N(C*H*$_2$CH$_3$)), 3.92 (s, 3H, OCH$_3$), 6.78 (d, 2H, *J* = 9 Hz, Ar–H), 7.08 (d, 2H, *J* = 9 Hz, Ar–H), 7.6 (d, 2H, *J* = 9 Hz, Ar–H), 7.79 (m, 2H, Ar–H), 7.96 (m, 1H, Ar–H), 7.99 (m, 1H, Ar–H), 8.03 (d, 2H, *J* = 9.6 Hz, Ar–H), 8.09 (s, 1H, CH=C). ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.77, 45.28, 55.45, 114.20, 122.88, 122.96, 124.96, 125.36, 126.46, 132.17, 134.86, 135.02, 136.03, 140.45, 142.03, 143.50, 152.97, 161.16, 168.24, 181.88, 189.71, 190.26. IR ν/cm^{-1} 2924, 1678, 1600, 1564, 1514, 1351, 1292, 1245, 1213, 1140, 1014, 986. HRMS calcd for C$_{30}$H$_{26}$N$_4$O$_3$S: 522.63. Found: 522.91.

*2.7.2. Dye **b***

Yield: 59.7%. Mp 158–160 °C. ^{1}H NMR (600 MHz, CDCl$_3$) 1.31 (t, 6H, *J* = 7.2 Hz, N(CH$_2$C*H*$_3$)$_2$), 3.56 (q, 4H, *J* = 7.2 Hz, N(C*H*$_2$CH$_3$)), 3.9 (s, 3H, OCH$_3$), 6.78 (d, 2H, *J* = 9 Hz, Ar–H), 7.07 (d, 2H, *J* = 9 Hz, Ar–H), 7.64 (d, 2H, *J* = 7.2, Ar–H), 7.86 (s, 1H, CH=C), 8.00 (m, 2H, Ar–H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.80, 45.51, 55.53, 113.44, 114.49, 114.89, 123.42, 125.43, 131.73, 143.56, 150.61, 153.81, 161.57, 166.44, 182.41. IR ν/cm^{-1} 2917, 2211, 1598, 1538, 1412, 1335, 1224, 1195, 1099, 1063. HRMS calcd for C$_{24}$H$_{22}$N$_6$OS: 442.55. Found: 442.97.

*2.7.3. Dye **c***

Yield: 66.6%. Mp 208–210 °C. ^{1}H NMR (600 MHz, CDCl$_3$) 1.31 (t, 6H, *J* = 7.2 Hz, N(CH$_2$C*H*$_3$)$_2$), 3.56 (q, 4H, *J* = 7.2 Hz, N(C*H*$_2$CH$_3$)), 3.92 (s, 3H, OCH$_3$), 6.78 (d, 2H, *J* = 9.6 Hz, Ar–H), 7.08 (d, 2H, *J* = 7.2 Hz, Ar–H), 7.76 (m, 4H, Ar–H), 7.93 (d, 1H, *J* = 7.2 Hz, Ar–H), 8.03 (m, 2H, Ar–H), 8.66 (d, 1H, *J* = 7.8 Hz, Ar–H), 8.75 (s, 1H, CH=C). ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.80, 45.42, 55.49, 69.77, 113.90, 114.44, 114.78, 123.85, 125.11, 125.80, 126.01, 132.47, 134.36, 135.15, 136.96, 138.06, 139.94, 143.91, 153.39, 160.77, 161.68, 170.58, 183.00, 188.07. IR ν/cm^{-1} 2211, 1746, 1697, 1595, 1519, 1214, 1102, 1065. HRMS calcd for C$_{33}$H$_{26}$N$_6$O$_2$S: 570.68. Found: 570.95.

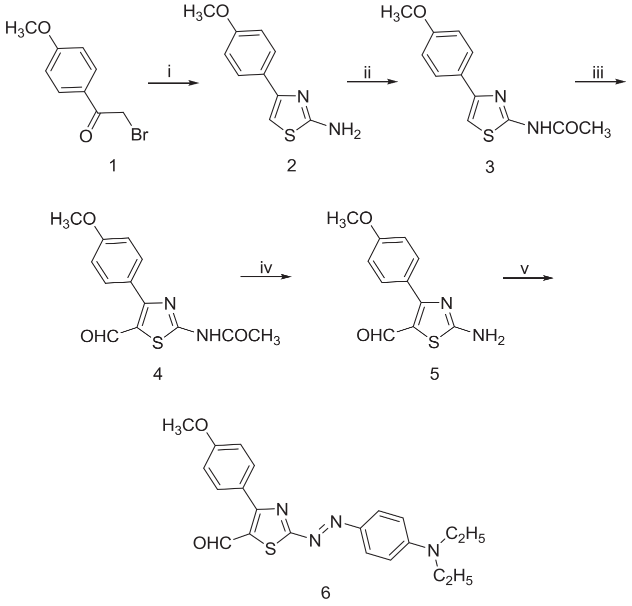
3. Results and discussion

3.1. Synthesis

Hantzsch thiazole synthesis in which the reaction proceeds between α-halocarbonyl compounds and thioureas or thioamides provides a useful method for the synthesis of thiazoles. Likewise the synthetic procedure reported earlier for the synthesis of other thiazole derivatives, compound **2** was obtained quantitatively by the treatment of **1** with thiourea in acetone at room temperature after being neutralized with dilute ammonia [29]. It is known that heteroaromatic compounds undergo Vilsmeier–Haack formylations at the electron rich positions [30]. Thus, it is expected that compound **2** can be easily formylated at the fifth position in the thiazole ring. For this propose, it was necessary to protect the amino group by the usual acetylation reaction as indicated in Scheme 1 to furnish compound **3**, which underwent formylation to produce the formyl product **4** in good yield. Acid catalyzed deacetylation of **4** affords the thiazole derivative **5** in good yield.

The common practice of diazotization and coupling was used to prepare azo dye **6** using thiazole derivative **5** as the diazo component and N,N-diethylaniline as the coupling component. Thus, thiazole derivative **5** was diazotized with nitrosyl sulfuric acid and then coupled with N,N-diethylaniline dissolved in 0.36 M H$_2$SO$_4$ in an ice bath to get the corresponding azo dye **6** (Scheme 1) as the aldehyde precursor for the NLO chromophores (**a**–**c**). The structures of compounds **2**–**6** were confirmed by their analytical and spectral data.

Knoevenagel condensation [31] of aldehyde **6** with 1H-indene-1,3(2H)-dione, malononitrile and 2-(3-oxo-2,3-dihydro-1H-inden-



Scheme 1. Synthesis of 2-((4-(diethylamino)phenyl)diazenyl)-4-(4-methoxyphenyl) thiazole-5-carbaldehyde. Reagents and conditions. (i) thiourea, acetone, rt, 5% ammonia solution; (ii) Ac$_2$O, reflux; (iii) DMF-POCl$_3$, 0–80 °C; (vi) 25% HCl/MeOH, reflux; (v) H$_2$SO$_4$, NaNO$_2$, AcOH, −5–5 °C, N,N-diethylaniline, H$_2$SO$_4$, H$_2$O, °C to rt.

1-ylidene)malononitrile in refluxing ethanol in the presence of piperidine/acetic acid catalyst affords good yields of the corresponding NLO chromophores **a**, **b**, and **c**, respectively (Scheme 2). All NLO dyes were fully characterized and their crystal structures have been solved.

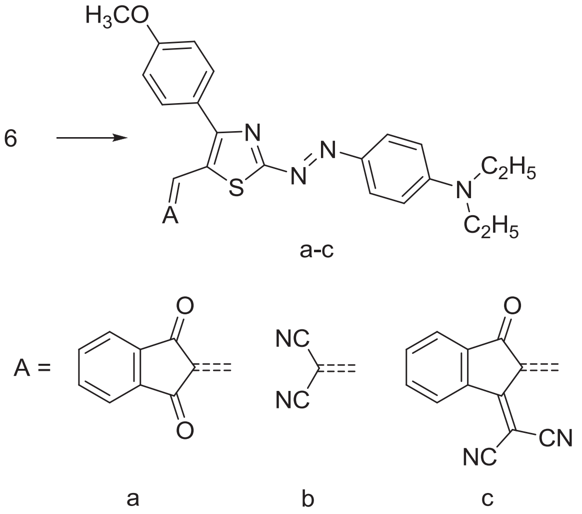
3.2. Optical properties

3.2.1. Linear optical properties

Electronic absorption spectra of NLO chromophores **a**–**c** in chloroform solution are shown in Fig. 1. Intense CT absorption bands are observed in the UV–visible region. The molar absorptivity as well as the position of these bands are affected by the strength of the acceptor group. This effect is demonstrated by comparison of the absorption maxima and the molar absorptivity of dyes **a** and **c** in which indandione is less electron acceptor than dicyanovinyl moieties, respectively. Dye **b** on the other hand exhibits a CT absorption band similar to dye **a**. Furthermore, the absorption characteristics of such type of dyes can be realized based on the fact that the electronic absorption of azobenzene derivative reveals two bands, one weak in the visible and the second strong in the UV-region, corresponding to n–π* and π–π*, respectively. The presence of strong electron donors and acceptors as in the case of dyes **a**–**c** reduce the charge transfer transitional energy of π–π* transition and consequently, the stronger the acceptor the higher the stabilization of LUMO energy and the longer the wavelength of absorption which overlaps the weak n–π* [32]. This structural feature is beneficial for obtaining high NLO properties as discussed below.

3.2.2. Nonlinear optical properties

Nonlinearities of the synthesized dyes were evaluated by measuring the $\mu\beta$ coefficients by means of the Electric Field Induced Second Harmonic Generation (EFISH) technique, at 1907 nm fundamental wavelength. The obtained values are reported in Table 1 and can be considered not affected by resonance effects, being the second harmonic signal generated from chloroform solutions of these dyes (953.5 nm) far beyond the range of linear absorption, as it can be evinced from UV–Visible spectra. Results show **a** and **b** to have similar nonlinear coefficients whose difference is lower than the experimental error of the measurement. However a more evident difference arises between the two molecules as far as the values of their figures of merit are concerned, calculated as the ratio $\mu\beta_0$/MW. This evidence suggests that the dicyanovinyl group has a stronger electron-withdrawing effect which is responsible for the higher nonlinear response of molecule **b**. As expected, the dye **c** shows the largest $\mu\beta$ value, which results sensibly higher as compared to the dyes **a** and **b**. This performance can be ascribed to the larger extension of the conjugated system as well as the increased electron withdrawing strength of the acceptor group resulting from the combination of dicyanovinyl and indandione moieties. This marked rise follows a pronounced batochromic shift of the absorption and therefore is partially reduced upon correction due to the dispersion effect, leading to a lower increase of static $\mu\beta_0$ coefficient for **c** with respect to **a** and **b**.



Scheme 2. Synthesis of nonlinear optical dyes **a**–**c**. Reagents and conditions. (dye **a**) 1H-Indene-1,3(2H)-dione, piperidine, glacial AcOH, absolute ethanol, rt; (dye **b**) Malononitrile and the same as for dye **a**; (dye **c**) 2-(3-Oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile and the same as for dye **a**.

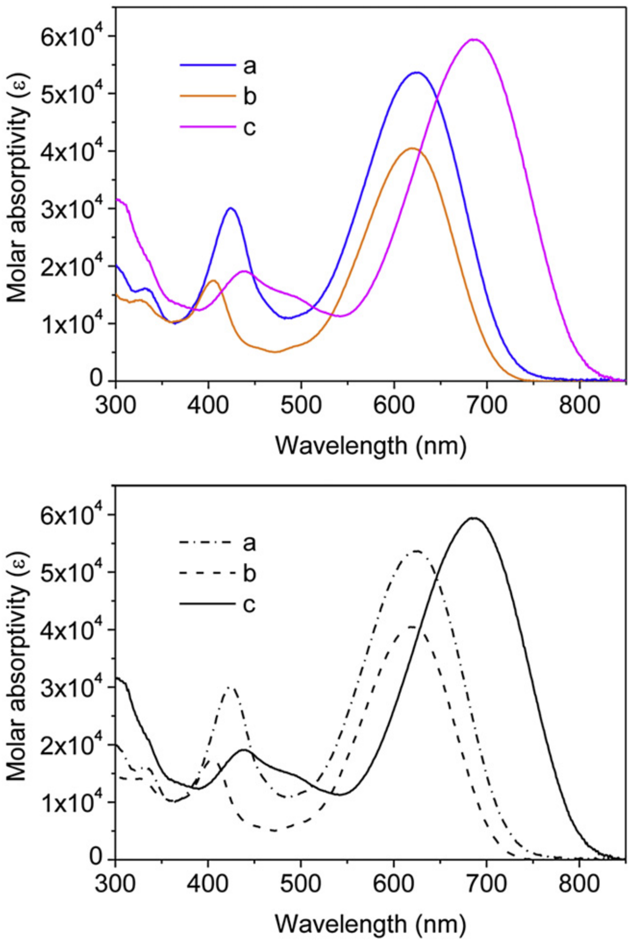


Fig. 1. UV–visible absorption spectra of dyes **a**–**c** in chloroform.

The dye **c** can be compared with dye *c* reported in a previous work [6] based on 4-chlorothiazole, where the only difference in the conjugated structure is therefore a chlorine atom linked on the

Table 1
Linear and nonlinear optical properties of dyes **a**–**c**.

Dye	λ_{max} (nm)[a]	$\mu\beta$ (10^{-48} esu)[b]	$\mu\beta_0$ (10^{-48} esu)[b]	$\mu\beta_0$/MW
a	623	1450	740	1.42
b	619	1550	800	1.81
c	686	4700	1970	3.45

[a] UV–Vis maximum absorption wavelength in chloroform.
[b] Error ±10%.

Table 2
Crystal data and structure refinement details for **b** and **c**.

	b	**c**
Empirical formula	$C_{24}H_{22}N_5OS$	$C_{33}H_{26}N_6O_2S \cdot CH_2Cl_2$
Formula weight	428.53	655.58
Temperature	173(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 21/c	P 21/c
Unit cell dimensions	$a = 15.855(2)$ Å	$a = 6.225(3)$ Å
	$b = 14.666(4)$ Å	$b = 21.279(4)$ Å
	$c = 9.442(2)$ Å	$c = 24.312(8)$ Å
	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 92.85(1)°$	$\beta = 99.51(3)°$
	$\gamma = 90°$	$\gamma = 90°$
Volume	2192(8) $Å^3$	3176(2) $Å^3$
Z	4	4
Calculated density	1.340 mg/m^3	1.371 mg/m^3
Absorption coefficient	0.174 mm^{-1}	0.312 mm^{-1}
θ range for data collection	3.06–27.51°	3.19–25.03°
$F(000)$	928	1360
Reflections collected/unique	12,906/4866 [R(int) = 0.0836]	18,840/5440 [R(int) = 0.1966]
Data/restraints/parameters	4866/0/292	5440/17/418
Goodness-of-fit on F^2	1.011	1.062
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0546$, $wR_2 = 0.0886$	$R_1 = 0.1269$, $wR_2 = 0.3043$
R indices (all data)	$R_1 = 0.1455$, $wR_2 = 0.1145$	$R_1 = 0.2708$, $wR_2 = 0.3985$
Largest diff. peak and hole	0.268 and −313 eA^{-3}	0.698 and −0.685 eA^{-3}

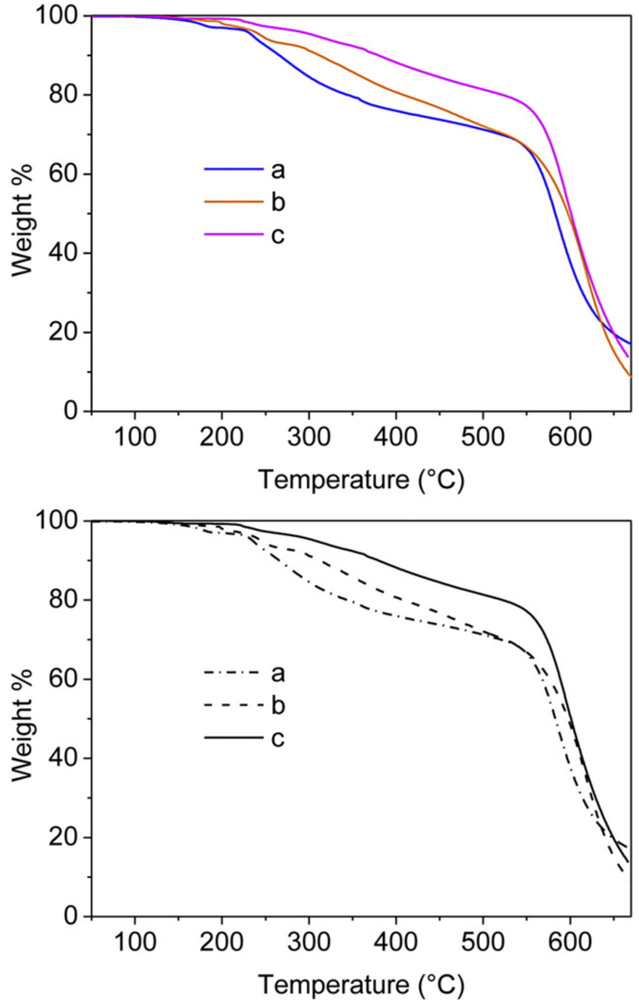


Fig. 2. Thermogravimetric analysis of the dyes **a**–**c**.

fourth position of thiazole instead of a 4-methoxyphenyl group. The higher activity shown by dye **c** suggests the methoxyphenyl ring to significantly affect molecular electronic properties, even if it results sterically hindered by the acceptor in the crystalline structure and partially rotated respect to the conjugated backbone, by effect of the auxiliary donor methoxy group inserted in the middle of the molecule and/or the relevant lateral extension of the π-conjugated structure, which makes this molecule an unusual example of asymmetrical 2D charge transfer chromophore.

3.3. Thermal stability

The thermal stability of NLO chromophores is a prerequisite for their uses in optoelectronics. Fig. 2 shows the thermogravimetric analysis of dyes **a**–**c**. All dyes are thermally stable with similar decomposition temperatures nearby 200 °C.

3.4. Crystal structure studies

Single crystals suitable for X-ray diffraction were obtained for **b** and **c** by evaporation of CH_2Cl_2/heptane solutions at ambient temperature. All attempts to obtain crystals of **a** failed. Compounds studied are not easy to crystallize. Owing to their bent and Y shape, voids may be formed during the crystallization, so the presence of a suitable crystallization solvent seem to be the necessary condition to form a stable crystalline phase. In particular, the structure resolution of **c** showed that, in the crystal, disordered molecules of CH_2Cl_2 crystallization solvent are located in channels parallel to **a** axis. The molecular structures of **b** and **c** are reported in Figs. 3 and 4.

Both compounds **b** and **c** have similar features. They crystallize in P 21/c space group, all bond lengths and angles are normal and in agreement with similar compounds [33,34]. The double bond character in the azo group is confirmed by N2–N3 bond length and a conjugated double-bond character is shown by the N1–C7 and N1–C9 bond lengths. As already found [21], the methyne H atom is

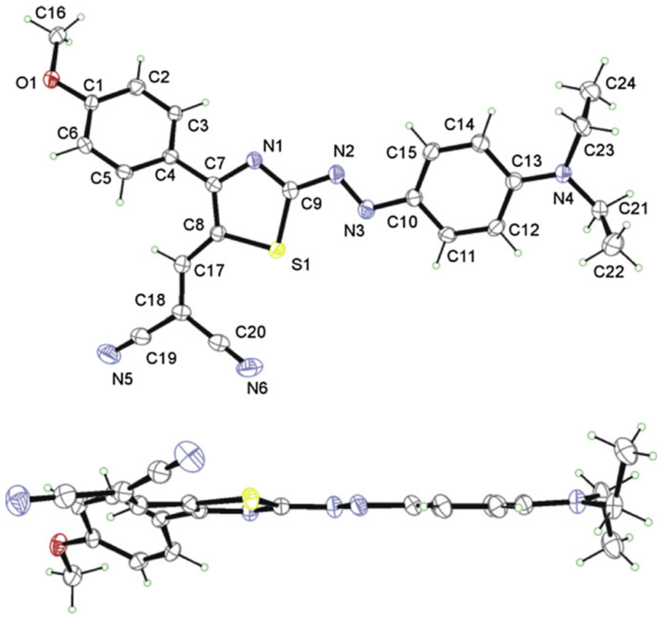


Fig. 3. Molecular structure of **b**. Up: view perpendicular to the mean plane of molecule. Down: view along the edge of mean plane. Thermal ellipsoids are drawn at 50% probability level. N2–N3 1.297(3), N1–C7 1.368(3), N1–C9 1.318(3), C7–C8 1.382(4), C17–C18 1.361(4), S1–C8 1.744(2), S1–C9 1.731(3) Å, C13–N4–C21–C22 −88.8(3), C13–N4–C23–C24 −88.5(3), C3–C4–C7–N1 34.6(4)°.

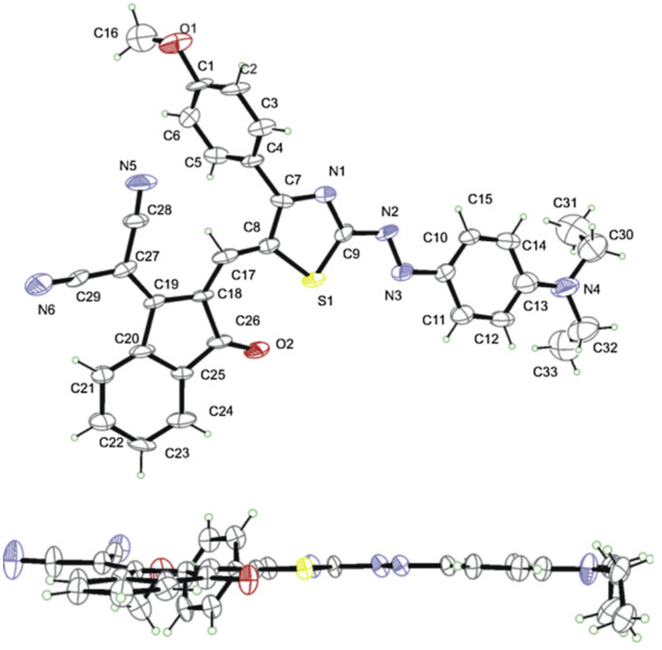


Fig. 4. Molecular structure of **c**. Up: perpendicular view to the mean plane of molecule. Down: view along the edge of mean plane. Thermal ellipsoids are drawn at 30% probability level.CH_2Cl_2 solvent molecule is not shown. N2–N3 1.30(1), N1–C7 1.35(1), N1–C9 1.31(1), C7–C8 1.42(1), C17–C18 1.36(1), S1–C8 1.738(82), S1–C9 1.726(9) Å, C13–N4–C30–C31 80(1), C13–N4–C32–C33 80(1), C3–C4–C7–N1 −63(1)°.

trans to S atom of thiazole group. The anti disposition of methyne and azo groups linked to thiazole and the methoxyphenyl group linked at C7 atom gives the observed bent [35] and Y-shape of molecules. Both in **b** and **c** the molecule is characterized by a quite overall planarity except for methoxyphenyl and ethyl groups. As already observed [36] the amino group is planar in both compounds, thus indicating a degree of conjugation of N atom with the bonded phenyl ring. The observed planarity of the molecule in both compounds suggests the possibility of conjugation extended to the entire molecule. In the crystal packing of **b** (see Fig. 5) the molecules are arranged in a parallel way forming sheets of molecules, but no π–π stacking is observed.

In the crystal packing of **c** coplanar molecules are piled up in a slipped way to form π–π stacked endless columns along (1 0 0) direction. In a π-stack (see Fig. 6) the interplanar distance between molecules is about 3.4 Å and a weak S····π interaction is observed ($S\cdots\cdots C_g^i = 3.472$ Å, C_g is the centroid of C10–C15 ring, $i = x - 1, y, z$).

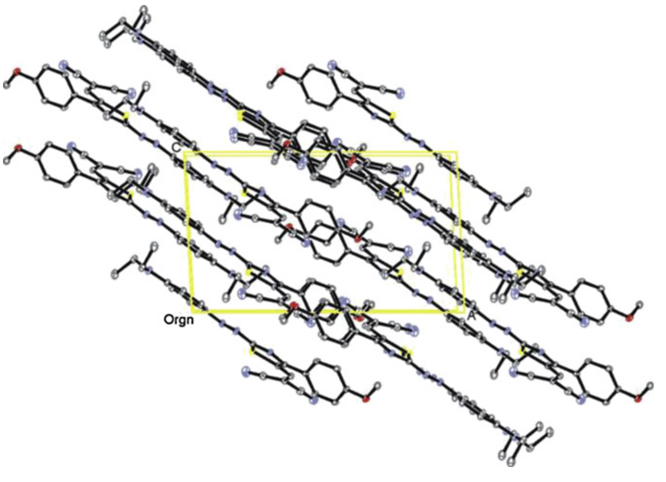


Fig. 5. Crystal packing of **b** viewed along (0 1 0) direction. H atoms are not shown for clarity.

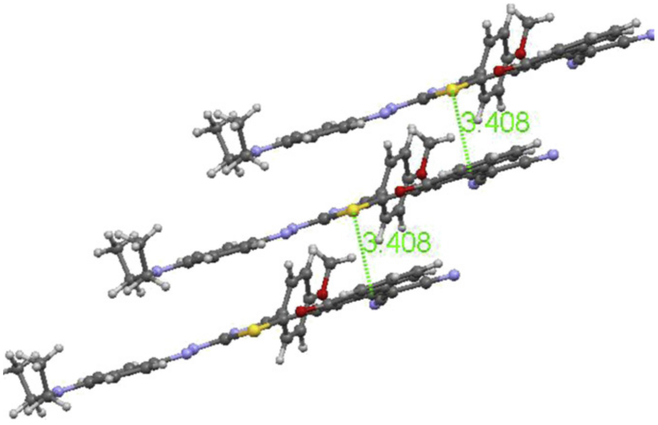


Fig. 6. Stacked molecules of **c** showing the interlayer distance.

4. Conclusions

New thiazole based azo dyes with a lateral donor branch have been synthesized for potential NLO applications. The chromophores **a**–**c** were obtained by functionalization of the same formyl azo dye with three different acceptor groups, indandione, malononitrile and 3-dicyanovinylindan-1-one. All the chromophores reveal good thermal stability and strong absorption bands, whose maxima are affected by the strength of the acceptor group. The chromophores also show large values of $\mu\beta$ in chloroform. In this regard 3-dicyanovinylindan-1-one acceptor gave the major contribution in the case of dye **c**, whose $\mu\beta$ value (4700×10^{-48} esu) resulted as high as three times that of chromophores **a** (1450×10^{-48} esu) and **b** (1550×10^{-48} esu). This NLO response together with the results of crystal study makes these molecules interesting examples of unusual asymmetrical 2D charge transfer chromophores. Future synthetic design for NLO chromophores based on thiazole azo dyes containing different size of lateral donating groups are in progress.

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