# High nonlinear optical response in 4-chlorothiazole-based azo dyes

Fabio Borbone [a,*], Antonio Carella [a], Laura Ricciotti [a], Angela Tuzi [a], Antonio Roviello [a], Alberto Barsella [b]

[a] Dipartimento di Chimica "Paolo Corradini", Università degli Studi di Napoli Federico II, Complesso Universitario Monte Sant'Angelo, Via Cintia 80126, Napoli, Italy
[b] IPCMS-CNRS, GONLO, 23 Rue du Loess, 67037 Strasbourg Cedex, France

## ARTICLE INFO

## ABSTRACT

Four azo dyes showing high nonlinear optical properties were prepared, based on a 4-chlorothiazole azo moiety functionalized with strong acceptor groups and/or further donor/acceptor groups along the conjugated backbone. The effects of the acceptors as well as the lateral donor/acceptor groups upon absorption properties, thermal stability and second order nonlinear optical activity were evaluated.

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## 1. Introduction

Organic materials for application in second order nonlinear optics (NLO) have drawn considerable interest in the last two decades both from academic and industrial world, with the results published in a wide number of reviews [1–5]. The origin of this interest stems from the potentially higher activity achievable with this class of materials as compared to the traditional inorganic ones, from the ease of processing and integration with the well established semiconductor technology and from the possibility of addressing materials features, specific for the field of application, by designing a proper synthetic strategy.

Second order NLO organic materials are typically based on NLO chromophores that can be incorporated in polymer [6–10] or hybrid organic–inorganic matrix [11,12] or in crosslinked system [13]. The dendritic approach, in which the chromophore is functionalized with branched bulky groups to hinder its tendency to crystallize, has also been largely employed in the recent years [14].

In all these approaches the choice of the proper chromophore plays a fundamental role: high NLO activity, expressed as the value of first order molecular hyperpolarizability β, along with a fair good photo- and thermal stability and a good solubility are required.

Typically, second order NLO chromophores are constituted by an electron acceptor moiety linked to an electron donor group through a conjugated bridge that allows a charge transfer of π-electrons. Both the strength of the electron donor and acceptor groups and the nature of the conjugated bridge are important parameters in defining the activity of the chromophore. In this context, the old established experience gained by the dyeing chemists represented a huge database from which taking inspiration for new molecular structures useful for NLO applications. For instance, derivatives of indandione (like bis-dicyanovinyl derivative or the Sandoz group) represent a class of very effective electron-withdrawing groups and have been widely employed in push–pull dyes to tune the absorption of the dyes toward the near IR zone of the spectrum [15,16]; more recently NLO chromophores containing as electron-acceptor group this class of indandione derivatives have proved to be extremely efficient [17,18].

For what concerns the conjugated bridge, it is well known that the use of heteroaromatic rings greatly enhances the molecular hyperpolarizability of the dye because the lower resonance energy of these rings, as compared with benzene, favours the charge transfer (process in which the bridge itself turns from aromatic to quinoid form) [19]. Particularly, very good results can be obtained by using five membered heterocycles as thiophene and thiazole, as proved both by theoretical [19–21] and experimental works [22,23]. Also the position of these heterocycles along the bridge plays an important role and being the just mentioned thiophene and thiazole electron poor rings, their direct linking to the electron acceptor group has a further beneficial effect on the NLO activity, because the hetero-aromatic rings behave as auxiliary acceptors [19–21].

* Corresponding author. Tel.: +39 081 674446; fax +39 081 674367.
E-mail address: fabio.borbone@unina.it (F. Borbone).

Driven by the above considerations, we report here on the synthesis and NLO characterization of four chromophores, whose molecular structure is reported in Fig. 1, containing as electron acceptor group an indandione derivative (1, 2 or 3, see Fig. 1).

Chromophores c, e and f are molecules already described in previous papers (at least for what concerns the conjugated core) and characterized only with regard to their linear optical properties while they have not been investigated yet for what concerns their NLO properties; chromophore d is instead a totally new structure. All the chromophores are diazo compounds and share the common feature of having a thiazole ring directly linked to the electron acceptor group; previous works have shown that the ability of the thiazole ring to act as an auxiliary acceptor is also related to the electron density on the carbon atom of the ring directly linked to the acceptor (the lower the electron density the higher the acceptor properties of the thiazole) [21]. We reckon therefore that the presence of an electronegative chlorine atom on 4-position of thiazole ring should enhance his ability to act as auxiliary acceptor by reducing electron density on carbon in position 5.

Chromophores have been characterized for what concerns their spectral and structural properties; their NLO activity have been measured by means of EFISH techniques and the results will be discussed in the next section.

## 2. Results and discussion

The precursors azo compounds a (R=R′=H) and b (R = NHCOCH₃ and R′ = OCH₃) were synthesized by diazotation of 2-amino-4-chloro-5-formylthiazole with nitrosylsulfuric acid and copulation on respectively N-phenyldiethanolamine and N-{3-[bis (2-hydroxyethyl)amino]-4-methoxyphenyl}acetamide (Fig. 2). Chromophores c, d and e were synthesized by condensation of precursor a with respectively acceptors 1, 2, 3 and subsequent acetylation; in the case of chromophore d the acetylation was simultaneous to the condensation. Chromophore f was obtained by condensation of compound b with electron-acceptor group 3 and following acetylation.

For chromophore e it was possible to obtain single crystals suitable for X-ray diffraction (by slow evaporation of CHCl₃/heptane solution) and its molecular structure has been solved and presented in Fig. 3. Compound crystallizes in P − 1 space group with two crystallographically independent molecules (denoted A and B)
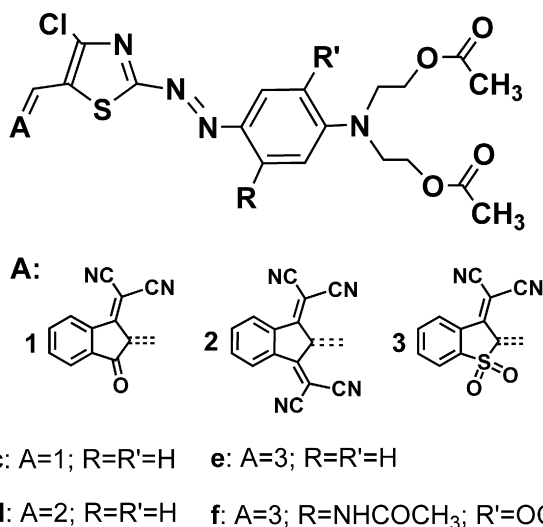


**Fig. 1.** Schematic representation of dyes structures.

and two CHCl₃ solvent molecules in the asymmetric unit. Each chloroform molecule is involved in weak hydrogen bonding interactions both with A and B molecule and a dimeric Ci symmetric adduct is formed. The two molecules A and B are geometrically similar, only one of them is reported in the figure and discussed. All bond lengths and angles were normal and in agreement with similar compounds [26—28]. In the molecule, the methine H atom is trans both to S atom of thiazole ring and to S atom of sulfone group. The dicyanomethylene group is slightly rotated (C19-C20-C27-C29 = 173.7(9)° and 176.6(9)° for molecule A and B respectively). The molecule is characterized by a quite overall planarity and by a bent shape. The overall planarity is in keep with the extension of conjugation along the whole molecule. The bent shape is a consequence of the anti disposition of methine and azo groups linked to thiazole. One of the ester tails linked to aminic N atom is roughly in plane with the molecule, being stabilized in this conformation by an intramolecular weak C−H···O interaction (C14−H···O1 3.48(1)Å, 170.5(7)° and 3.52(2)Å, 173.8(7)° for molecule A and B respectively). The other ester tail is pendant. In the crystal packing the molecules are arranged in a parallel way through weak C−H···N and C−H···O interactions (C11A−H···N6A(i) 3.32(1)Å, 123°; C7A−H···O3B(ii) 3.38(2)Å, 131°; C24B−H···N4A(iii) 3.30(1)Å, 133°; C23A−H···N4B(iv) 3.38(1)Å, 126°; C5B−H···O1B(v) 3.43(2) Å, 164°; C8B−H···O3A(vi) 3.41(1) Å, 157°; (i) −x, −y + 1, −z + 1; (ii) x + 1, y − 1, z − 1; (iii) −x + 1, −y + 1, −z + 1; (iv) −x, −y + 1, −z + 2; (v) −x, −y + 2, −z + 2; (vi) x − 1, y + 1, z + 1). Sheets of molecules spaced by the pendant tails are formed. A π−π stacking of aromatic groups is observed (Fig. 4) between the sheets with interlayer distance of about 3.4 Å. The chloroform molecules are involved in weak C−H···O interactions with sulfone oxygen atoms and are located in channels parallel to [1 0 0] crystallographic direction (C1−H···O6A 3.34(1) Å 139°; C1−H···O5B 3.21(1) Å 130°; C2−H···O5A 3.11(1) Å 130°; C2−H···O6B 3.47(1) Å 126°).

As also reported in the literature [16,29] and for similar chromophores these dyes show a strong bathochromic effect on the absorption depending on the strength of their electron acceptor groups. The dye d shows a 37 nm red shift of the absorption maximum in chloroform (Fig. 5, Table 1) with respect to the dye c due to the stronger electron withdrawing effect of two dicyanomethylene groups. A similar absorption spectrum is observed for the dye e bearing the moiety 3, known in the literature as Sandoz group and as one of the strongest electron acceptor groups. The dye f has the highest red shift compared with the dye c, 129 nm, revealing that the NHCOCH₃ and OCH₃ groups on the phenyl ring give a great contribution to the bathochromic shift of chromophore f, whose absorption maximum is notably higher than that of the same chromophore without these groups (e).

The thermal stability of the dyes was studied by means of thermogravimetric analysis (Fig. 6) and the decomposition temperatures are reported in Table 1. As shown the dyes stabilities are quite similar and no significant effects of acceptor groups can be observed.

The μβ coefficients were measured by Electric Field Induced Second Harmonic Generation (EFISH) technique. The measurements were performed in chloroform solution at a wavelength of 1905 nm where the second harmonic (952.5 nm) is out the absorption region of the chromophores. The results are listed in Table 1 and reveal that the dye c has the lowest NLO coefficient, as expected being the acceptor 1 an indandione functionalized with a single dicyanomethylene group.

Indeed the addition of a second dicyanomethylene group (dye d) favours a strong increase in the molecular second order NLO response, which is more than doubled in the value of μβ coefficient. The acceptor 3 turns out again to have the largest effect also on the nonlinear properties since the dye e has the highest μβ coefficient

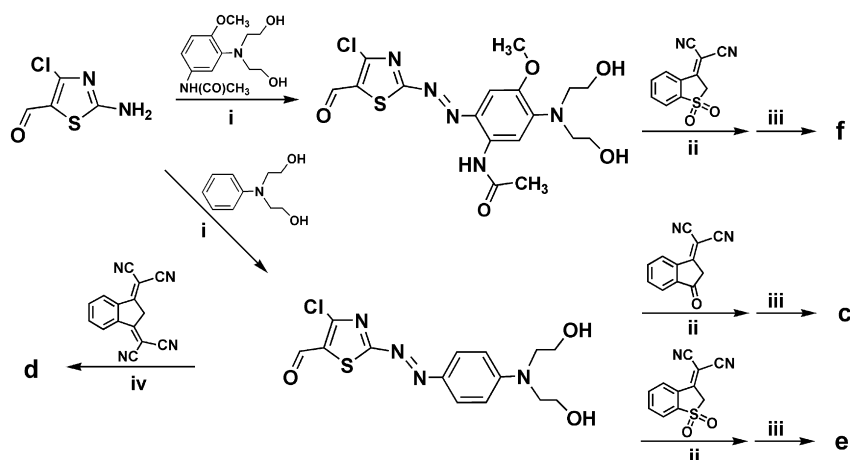**Fig. 2.** Scheme for the synthesis of dyes. i: 1) H₂SO₄/NOHSO₄, 2) H₂0/H₂SO₄; ii: EtOH, reflux, 4 h; iii: dioxane/Ac₂O, reflux, 4 h; iv: Ac₂O, 70 °C, 4 h.

(5400·10⁻⁴⁸ esu) of the series based on the azo compound **b**, revealing a strong contribution of the SO₂ moiety. Finally the dye **f** as well shows a large nonlinear coefficient but in this case the acetamido and methoxy groups have a detrimental effect on the NLO response causing a decrease of μβ compared to the dye **e**. These results confirm that these type of chlorothiazole-based azo dyes, already known for their linear absorption properties, also show a strong nonlinear optical response. This feature can be exploited for the synthesis of highly active NLO polymers, for example by using the easily achievable di-hydroxylated form of the dyes, aimed at the fabrication of efficient electro-optic devices.

## 3. Conclusions

Four NLO chromophores based on a 4-chlorothiazole azo moiety were synthesized. The chromophores were functionalized with indandione derivatives as strong terminal acceptor groups and with lateral methoxy and acetamido groups along the conjugated backbone. The chromophores show a strong bathochromic effect

on the absorption depending on the nature of their electron acceptor groups, being notably higher in the case of the chromophore functionalized with the 3-dicyanomethylene-2,3-dihydrobenzo[b]thiophene-1,1-dioxide and the methoxy and acetamido side groups. All the chromophores have a good thermal stability in air and show growing μβ coefficients when the acceptor moiety is varied from 3-(dicyanomethylene)-1-indanone to 1,3-bis(dicyanomethylidene)indane and 3-dicyanomethylene-2,3-dihydrobenzo[b]thiophene-1,1-dioxide. In this last case a decrease of the coefficient is observed if methoxy and acetamido side groups are present on the phenyl ring.

## 4. Experimental

All solvents and reagents were purchased by Aldrich and used without further purification. The thermal stability of the compounds was studied by thermogravimetric analysis (TA SDT 2960, air, 10 K/min). ¹H NMR and ¹³C NMR spectra were recorded with a Varian XL 200-MHz apparatus. UV/Vis absorption spectra



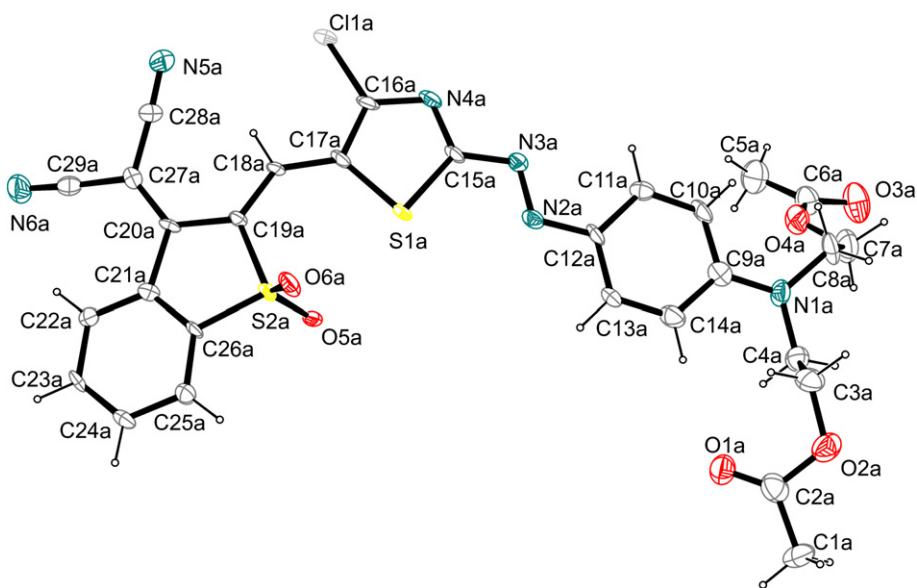**Fig. 3.** Ortep view of **e** with ellipsoids drawn at 30% probability level. Molecule B and CHCl₃ solvent molecules are not shown for clarity. N2–N3 1.28 (1), 1.28(1)Å; N2–C12 1.39(1), 1.39(1)Å; N3–C15 1.37(1), 1.36(1)Å; N4–C15 1.33(1), 1.31(1)Å; N4–C16 1.35(1), 1.36(1)Å; S1–C15 1.728(9), 1.745(9)Å; S1–C17 1.755(9), 1.730(9)Å; S2–C19 1.770(9), 1.756(9)Å; S2–C26 1.747(8), 1.747(9)Å; C18–C19 1.37(1), 1.34(1)Å; C19–C20 1.48(1), 1.47(1)Å; C21–C26 1.37(1), 1.36(1)Å; C20–C27 1.36(1), 1.37(1)Å.
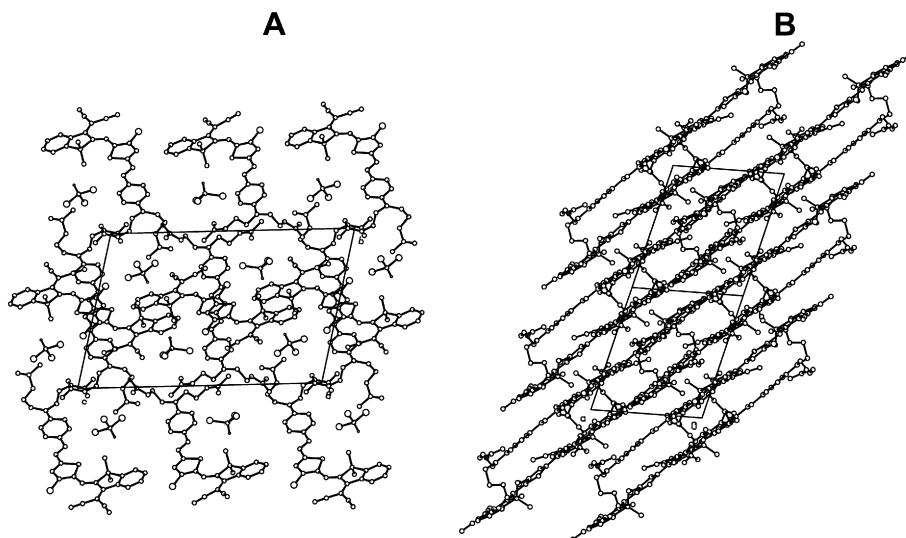
**A**

**B**

**Fig. 4.** A) Crystal packing of **e** viewed along (1 0 0) direction, only H atoms in $CHCl_3$ molecules are reported for clarity. B) Crystal packing viewed along (0 1 −1) direction, showing the sheets of co-planar molecules and the interlayer aromatic π–π stacking.

were recorded with a Jasco V560 spectrophotometer in chloroform solutions. FT-IR spectra were recorded with a Jasco FT/IR-430 spectrophotometer on KBr pellets. Single crystals of dye **e** suitable for X-ray diffraction were obtained by slow evaporation of $CHCl_3$/heptane solution. One crystal (dark green 0.55 × 0.50 × 0.15 mm) was mounted at 173 K under $N_2$ flow on a Bruker-Nonius KappaCCD diffractometer equipped with a graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å, CCD rotation images, thick slices, $\varphi$ and $\omega$ scans to fill asymmetric unit). Semi-empirical absorption correction (SADABS) was applied. The structure was solved by direct methods (SIR97 package [24]) and refined by the full matrix least-squares method on $F^2$ against all independent measured reflections (SHELXL program of SHELX97 package [25]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced in calculated positions and refined according to a riding model. The final refinement converged to $R_1 = 0.0959$, $wR_2 = 0.2047$. Crystals were poor quality and weakly diffracting. This may explain the high $R$ values obtained. Some constrains on C–C bond lengths in one ester tail were introduced in the last stage of refinement. Crystal data and refinement details are summarized in Table 2. CCDC 771330 contains 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.
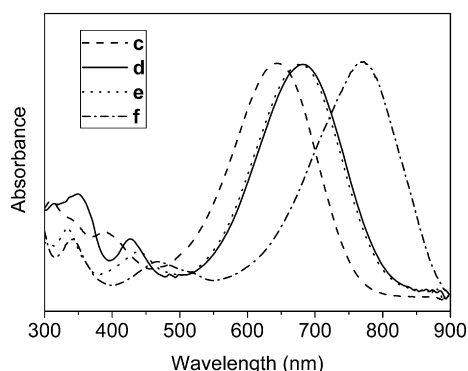


**Fig. 5.** UV–Vis spectra of the dyes in chloroform.

## 4.1. Syntheses

### 4.1.1. Synthesis of 2-((4-(bis(2-hydroxyethyl)amino)phenyl)diazenyl)-4-chlorothiazole-5-carbaldehyde (**a**)

2-amino-4-chloro-5-formylthiazole (2.00 g, 12.3 mmol) was dissolved in 5 mL $H_2SO_4$ and 2.5 mL nitrosylsulfuric acid 40% wt. solution were added at 0–5 °C under stirring. After 1 h the solution was added to 2.23 g (12.3 mmol) N,N-dihydroxyethylaniline in 120 mL of water containing 1 mL $H_2SO_4$. After 4 h the product was filtered and washed with water. Yield: 44%.

^{1}H NMR (DMSO; 300 MHz) $\delta$: 3.98 (m, 8H), 5.11 (s, 2H), 7.22 (d, 2H, $J = 9.0$ Hz), 7.98 (d, 2H, $J = 9.0$ Hz), 10.07 (s, 1H).

### 4.1.2. Synthesis of N-(5-(bis (2-hydroxyethyl) amino)-2-((4−chloro−5−formylthiazol−2-yl) diazenyl)-4-methoxyphenyl) acetamide (**b**)

2-amino-4-chloro-5-formylthiazole (2.00 g, 12.3 mmol) was dissolved in 3 mL $H_2SO_4$ and 2.5 mL nitrosylsulfuric acid 40% wt. solution were added at 0–5 °C under stirring. After 1 h the solution was added to 3.30 g (12.3 mmol) N-{3-[bis(2-hydroxyethyl)amino]-4-methoxyphenyl}acetamide in 100 mL of water containing 0.5 mL $H_2SO_4$. After 4 h the solution was neutralized with potassium hydroxide and saturated with sodium chloride. The product was filtered, washed with water and then with hot ethanol. Yield: 55%.

^{1}H NMR (DMSO; 300 MHz) $\delta$: 3.84 (m, 3H), 3.89 (m, 8H), 5.00 (s, 2H), 7.36 (s, 1H), 8.05 (s, 1H), 9.95 (s, 1H), 10.0 (s, 1H).

### 4.1.3. Synthesis of dyes **c**, **e**, **f**, **d**

Dye **c**: 3-(Dicyanomethylene)-1-indanone (0.761 g, 3.92 mmol) and compound **a** (1.39 g, 3.92 mmol) were dissolved in 80 mL ethanol at reflux for 4 h. The product was filtered and washed with ethanol. 0.500 g of the product were dissolved in 15 mL dioxane

**Table 1**
Linear and nonlinear optical properties and decomposition temperatures of dyes.

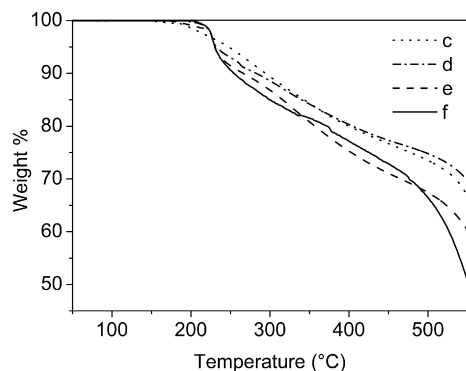| Dye | μβ ($10^{-48}$ esu) | $\lambda_{max}$ (nm) | $T_d$ (°C) |
|---|---|---|---|
| **c** | 2150 | 643 | 248 |
| **d** | 5200 | 680 | 232 |
| **e** | 5400 | 676 | 230 |
| **f** | 4600 | 772 | 230 |

**Fig. 6.** Thermogravimetric analysis of the dyes.

containing 4 mL acetic anhydride at reflux for 4 h. The acetylated chromophore was precipitated in 100 mL hexane and purified by chromatography. Yield: 72%.

$^1$H NMR (CDCl$_3$; 200 MHz) $\delta$: 2.07 (s, 6H); 3.82 (t, 4H, $J$ = 5.8 Hz); 4.35 (t, 4H, $J$ = 5.8 Hz); 6.90 (d, 2H, $J$ = 8.8 Hz); 7.78 (m, 2H); 7.95 (d, 1H, $J$ = 7.4 Hz); 8.00 (d, 2H, $J$ = 8.8 Hz); 8.70 (d, 1H, $J$ = 5.8 Hz); 8.97 (d, 1H, $J$ = 28.8 Hz). $^{13}$C NMR (CDCl$_3$; 200 MHz) $\delta$: 20.80, 30.55, 50.16, 61.07, 112.63, 112.79, 124.35, 125.08, 125.62, 125.73, 128.72, 128.82, 133.55, 134.89, 135.86, 137.28, 140.39, 140.79, 144.93, 153.95, 170.69, 182.27, 188.40. IR (KBr) $\nu_{max}$: 2929 (w), 2219 (w), 1735 (m), 1700 (w), 1599 (m), 1542 (m), 1466 (w), 1240 (m), 1216 (m), 1198 (m), 1115 (s), 1050 (m), 1020 (w), 990 (w), 875 (w), 833 (w), 723 (w). HRMS calcd for C$_{30}$H$_{23}$ClN$_6$O$_5$S: 614.11. Found: 614.71. Calcd for C$_{30}$H$_{23}$ClN$_6$O$_5$S: C, 58.58; H, 3.77; N, 13.66. Found: C, 58.63; H, 4.12; N, 13.42.

The same procedure was applied for the synthesis of chromophores **e** and **f** by using suitable amounts of compounds **a** and **b** respectively.

*Dye **e***: $^1$H NMR (CDCl$_3$; 200 MHz) $\delta$: 2.06 (s, 6H); 3.83 (t, 4H, $J$ = 5.8 Hz); 4.34 (t, 4H, $J$ = 5.8 Hz); 6.91 (d, 2H, $J$ = 9.0 Hz); 7.88 (m, 3H); 7.99 (m, 2H); 8.85 (d, 1H, $J$ = 7.6 Hz); 9.10 (s, 1H). $^{13}$C NMR (CDCl$_3$; 200 MHz) $\delta$: 20.97, 50.19, 61.07, 73.97, 113.00, 113.69, 114.29, 122.47, 122.95, 126.12, 128.82, 129.09, 131.18, 135.06, 135.73, 138.87, 144.76, 151.16, 154.12, 154.55, 170.88, 182.96.

IR (KBr) $\nu_{max}$: 2927 (w), 2215 (w), 1752 (m), 1733 (m), 1599 (m), 1582 (m), 1557 (m), 1520 (m), 1409 (w), 1312 (w), 1243 (m), 1210 (m), 1125 (s), 1098 (s), 873 (w), 831 (w), 765 (w), 728 (w), 643 (w). HRMS calcd for C$_{29}$H$_{23}$ClN$_6$O$_6$S$_2$: 650.08. Found: 650.60. Calcd for C$_{29}$H$_{23}$ClN$_6$O$_6$S$_2$: C, 53.49; H, 3.56; N, 12.91. Found: C, 53.55; H, 3.98; N, 12.66.

*Dye **f***: $^1$H NMR (CDCl$_3$; 200 MHz) $\delta$: 2.08 (s, 6H); 2.34 (s, 3H); 3.89 (s, 3H); 3.99 (t, 4H, $J$ = 5.4 Hz); 4.39 (t, 4H, $J$ = 5.4 Hz); 7.37 (s, 1H); 7.87 (m, 2H); 7.95 (m, 1H); 8.22 (s, 1H); 8.83 (d, 1H, $J$ = 7.7 Hz); 9.07 (s, 1H); 9.17 (s, 1H). $^{13}$C NMR (THF-$d8$; 200 MHz) $\delta$: 21.47, 22.33, 31.74, 36.05, 56.30, 57.32, 59.54, 61.86, 63.94, 105.75, 119.13, 123.59, 123.95, 126.86, 127.35, 127.60, 129.84, 131.10, 131.53, 133.67, 136.25, 136.91, 137.54, 139.13, 141.09, 153.64, 169.81, 171.48. IR (KBr) $\nu_{max}$: 2946 (w), 2210 (w), 1739 (m), 1698 (m), 1605 (m), 1582 (m), 1549 (m), 1505 (s), 1463 (m), 1438 (m), 1374 (m), 1238 (m), 1198 (m), 1172 (s), 1136 (s), 1096 (s), 1043 (s), 951 (w), 922 (w), 660 (w). HRMS calcd for C$_{32}$H$_{28}$ClN$_7$O$_8$S$_2$: 737.11. Found: 737.62. Calcd for C$_{32}$H$_{28}$ClN$_7$O$_8$S$_2$: C, 52.07; H, 3.82; N, 13.28. Found: C, 52.22; H, 4.03; N, 13.31.

*Dye **d***: 1,3-Bis(dicyanomethylidene)indane (0.683 g, 2.82 mmol) and compound **a** (1.00 g, 2.82 mmol) were stirred in 12 mL acetic anydride at 70 °C for 4 h. The product was precipitated in 200 mL hexane and purified by chromatography. Yield: 43%.

$^1$H NMR (CDCl$_3$; 300 MHz) $\delta$: 2.04 (s, 6H); 3.82 (t, 4H, $J$ = 6.0 Hz); 4.33 (t, 4H, $J$ = 6.0 Hz); 6.89 (d, 2H, $J$ = 9.0 Hz); 7.79 (d, 2H, $J$ = 4.2 Hz); 7.99 (d, 2H, $J$ = 9.0 Hz); 8.55 (m, 2H); 8.69 (s, 1H). $^{13}$C NMR (CDCl$_3$; 200 MHz) $\delta$: 20.84, 50.20, 61.02, 77.35, 112.93, 113.03, 125.15, 126.00, 126.08, 129.42, 129.56, 131.19, 131.83, 135.16, 144.84, 152.70, 154.59, 170.72, 179.81. IR (KBr) $\nu_{max}$: 2950 (w), 2220 (w), 1746 (m), 1595 (m), 1552 (m), 1463 (m), 1244 (m), 1225 (m), 1132 (s), 1051 (m), 872 (w), 835 (w), 718 (w). HRMS calcd for C$_{33}$H$_{23}$ClN$_8$O$_4$S: 662.13. Found: 662.64. Calcd for C$_{33}$H$_{23}$ClN$_8$O$_4$S: C, 59.77; H, 3.50; N, 16.90. Found: C, 59.64; H, 3.76; N, 16.62.

## Acknowledgement

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**Table 2**
Crystal data and structure refinement details for **e**.

| | |
|---|---|
| Empirical formula | C$_{29}$H$_{23}$ClN$_6$O$_6$S$_2$···CHCl$_3$ |
| Formula weight | 770.47 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | $P-1$ |
| Unit cell dimensions | $a$ = 10.028(2) Å |
| | $b$ = 15.513(2) Å |
| | $c$ = 23.183(7) Å |
| | $\alpha$ = 102.49(2)° |
| | $\beta$ = 91.62(2)° |
| | $\gamma$ = 104.84(1)° |
| Volume | 3390(1) Å$^3$ |
| Z | 4 |
| Calculated density | 1.510 Mg/m$^3$ |
| Absorption coefficient | 0.525 mm$^{-1}$ |
| $F(000)$ | 1576 |
| $\theta$ range for data collection | 3.04–25.00° |
| Reflections collected/unique | 55296/11803 [$R$(int) = 0.2854] |
| Data/restraints/parameters | 11803/21/863 |
| Goodness-of-fit on $F^2$ | 1.002 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0959, $wR_2$ = 0.2047 |
| $R$ indices (all data) | $R_1$ = 0.2651, $wR_2$ = 0.2788 |
| Largest diff. peak and hole | 0.733 and −0.476 eA$^{-3}$ |

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