Polarization, second-order nonlinear optical properties and electrochromism in 4*H*-pyranylidene chromophores with a quinoid/aromatic thiophene ring bridge.

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Abstract

Push-pull systems, in which the proaromatic 4*H*-pyranylidene electron donor is conjugated with a dicyanomethylene acceptor through a quinoid thiophene as (part of) the electron relay, have been prepared, and their properties have been compared to those of a parent compound featuring an aromatic thiophene moiety. Different experimental techniques (X-ray diffraction, ¹H NMR, IR, Raman, UV-vis, cyclic voltammetry, spectroelectrochemistry, and NLO measurements) combined with theoretical calculations have been used for the study of the chromophores. Quinoidal derivatives, although neutral, show strongly polarized structures, with positive $\mu\beta$ values and a progressive increase of the intramolecular charge transfer (ICT) on lengthening the π -spacer. Comparison between compounds that only differ in the character (quinoid or aromatic) of the thiophene unit shows a more efficient ICT for the quinoid thiophene-containing chromophore, which influences the second-order NLO response. Furthermore, the thienyl ring has been also found to play a significant role in the ICT process for the analogous aromatic derivative.

Introduction

Organic molecules with an electron donor (D) and an electron acceptor (A) linked by a π -conjugated spacer are intensely investigated compounds across many branches of actual chemistry, including nonlinear optics (NLO),¹ dye-sensitized solar cells (DSSC)² and fluorescent emitters in organic light-emitting diodes (OLEDs)³ among many others. In this type of systems, intramolecular charge transfer (ICT) from the donor to the acceptor takes place, thereby polarizing the ground electronic state of the chromophore. ICT may be affected by several factors, among which the nature of the conjugated spacer plays a critical role.⁴

In the field of second-order NLO, polyenic or aromatic bridges have been extensively used in spite of having serious drawbacks, as the former imparts poor thermal and chemical stabilities, and the latter leads to ineffective charge polarization. In this context, the use of moderately aromatic structures (with resonance energies below that of benzene), such as thiophene,⁵ and the introduction of pro-aromatic⁶ bridges^{7–8} are two widely-used strategies for tuning the molecular polarization and, in consequence, the second-order nonlinearities. Although several chromophores with a thiophene ring as a part of the π -relay⁵ have been studied, the use of the thienoquinoid moiety as spacer^{7d,8,9} in merocyanines for second harmonic generation remains much less explored, being their NLO properties very influenced by the solvent polarity.¹⁰ Further, as far as we know, there is only a pair of related chromophores differing only in the quinoid/aromatic character of the thiophene ring for which their polarization and photorefractive figures of merit have been reported.¹¹ Comparison of this couple shows a more polarized structure for the quinoidal system, displaying a bathochromic shift of the absorption band in the UV-vis and a higher photorefractive response. Also in the field of organic dyes for DSSC, a D-A structure connected through a quinoidal thiophene as the π -conjugated relay has been recently reported¹² pursuing to effectively extend the π -conjugation, resulting in a further bathochromic shift of the absorption maximum compared to related compounds with similar π -conjugation length.¹³

Taking all these data into account, in this paper we describe the synthesis, characterization, study of the ground-state polarization and the NLO response of a series of D- π -A compounds with dicyanomethylene as the acceptor group, the pro-aromatic ring

4*H*-pyranylidene ring as donor¹⁴ and a quinoid thiophene as (part of) the electron relay (**1a–c**), together with a comparable pair of quinoid/aromatic thiophene derivatives (**1b/2**) having the methine bridge in different positions. (Scheme 1) Given the strong dependence of the absorption properties of these compounds with the degree of electron charge transfer, we also conducted a study of their electro-chromic properties by spectroelectrochemical experiments.

Scheme 1. Structures of target compounds **1a–c**, **2**.

Results and Discussion

Synthesis

Compounds **1a–c** (with a quinoid thiophene unit) were prepared by acetic anhydride mediated reaction between 2-dicyanomethylthiophene **3**¹⁵ and the commercially available pyranone **4** or the 4*H*-pyranylidene aldehydes **5b–c**.^{16,14a} (Scheme 2)

Scheme 2. Synthesis of compounds **1a–c**.

Compound **2** (with an aromatic thiophene moiety) was obtained from the aldehyde **6**¹⁷ by reaction with malononitrile in absolute ethanol. (Scheme 3)

Scheme 3. Synthesis of compound **2**.

X-ray diffraction: crystal structures of **1c** and **2**

Single crystals of **1c** and **2** were obtained by slow diffusion of hexane into a solution of the corresponding chromophore in CH₂Cl₂ at room temperature. Although these compounds are not isomers (unlike **1b** and **2**), the analysis of their structures in the solid state can afford useful information concerning the different degree of ICT between quinoid and aromatic thiophene-containing chromophores. The X-ray molecular structure of **1c** is represented in Fig. 1. The π -system is completely planar, with the donor, the thiophene ring and the acceptor group in the same plane. The polyenic chain has an all-*trans* geometry, except for the C15=C16 formal double bond of *Z* configuration.

Fig. 1 Molecular structure of compound **1c**. Selected bond lengths (Å): C15–C16 1.369(4), C16–C17 1.412(4), C17–C18 1.360(4), C18–C19 1.417(4), C19–C20 1.390(4).

A detailed comparison between the bond lengths of the quinoid thiophene moiety and C19–C20 bond (see values in caption of Fig. 1) and the corresponding bond distances in compounds **7**¹⁸ and **8**^{9a} (Fig. 2) taken as references, indicates that: (i) the C19–C20 distance

in **1c** is considerably longer than the analogous bond in compound **7**, thus confirming a certain zwitterionic (dicyanomethanide) contribution to the ground state of **1c**. The same conclusion can be obtained if CC distances **b** and **c** in **7** are compared with C18–C19 and C17–C18 respectively in **1c**, pointing to a partial aromatic character for the thiophene moiety; (ii) the aforementioned bond lengths C19–C20, C18–C19 and C17–C18 in compound **1c** are similar to the corresponding bonds **a**, **b**, **c** in the 1,3-dithiole derivative **8**, for which a certain zwitterionic character of the ground state was established.^{7d,9a} Moreover, the fact that the C15–C16 bond in **1c** is shorter than the corresponding **e** in **8** is consistent with the decrease of polarization in the former.

Fig. 2 Structure and selected bond lengths (in Å) for compounds **7** and **8**.

Some structural parameters of the pyranilidene ring (Fig. 3) also reveal the ICT from the terminal donor of the molecule, showing intermediate values between the totally quinoid and the aromatic forms. The following features are highlighted: i) shortening of the C–O bonds; ii) lengthening of the pyran exocyclic bond; and iii) a decreased degree of C–C bond length alternation, which can be evaluated through the parameter δr ¹⁹ (Fig. 3) ($\delta r = (a - b + c - d)/2$, with $\delta r = 0$ for benzene and $\delta r \approx 0.10$ for fully quinoid rings), is found for our compounds, in agreement with those of other 4*H*-pyranilidene- π -A systems previously described.^{8,14a}

The Bird index (I_6)²⁰ of the donor, (Fig. 3) used as an estimation of the aromaticity of the ring, ($I_6 = 25.4$ for fully quinoid pyrans; $I_6 = 50$ for pyrylium cations^{14a}) also indicates the partial contribution of the zwitterionic forms to the ground state of the chromophores. Nevertheless, this contribution is smaller than those found for other 4*H*-pyranilidene-containing merocyanines.^{8,14a,21}

Compd	C–O ^a	C ₄ –C _{exo} ^a	δr	l_6
1c	1.377	1.381	0.09	32.7
2	1.378	1.357	0.11	23.0

^a Bond length in Å

Bond lengths involved in the calculation of δr

Fig. 3 Structural parameters for the pyranylidene donor in compounds **1c** and **2**.

As an additional confirmation of the ICT, the bond length alternation (BLA) value along the spacer (defined as the difference between the average carbon-carbon single and double bond lengths²²) is 0.029 Å. Unlike some other analogues with different acceptor moieties, (in particular 1,1,3-tricyano-2-phenylpropene^{14a} and 2-dicyanomethylenethiazole^{14b}) which show BLA values close to zero (from the X-ray structures), **1c** has been found to possess a moderately-polarized structure. This fact may have a positive effect on the NLO response (see NLO properties) as places the chromophore, at least in the solid state, far from the cyanine limit.

Compound **2** (Fig. 4) also shows a completely planar structure. The thiophene exocyclic bonds (C1–C9 and C4–C5) have an *s*-trans geometry, as found in a related chromophore with a 1,3-dithiole unit as donor.²³

Fig. 4 Molecular structure of compound **2**. Selected bond lengths (Å): C1–C2 1.389(10), C2–C3 1.388(10), C3–C4 1.404(11).

Comparison of the standard C=C and C–C bonds of 1.362 and 1.424 Å in unsubstituted aromatic thiophenes²⁴ with C1–C2 (C3–C4) and C2–C3 respectively reveals the π -electron delocalization along the thiophene ring in **2**. These distances are similar to those found for the thiophene unit in the related chromophore with a 1,3-dithiole unit as donor²³ above

mentioned. The structural parameters for **2** (Fig. 3) indicate a limited polarization of the donor fragment given that δr and Bird index parameters together with C₄–C_{exo} bond lengths (C9=C10 bond in derivative **2**) exhibit values corresponding to a fully quinoid 4*H*-pyranylidene ring. In fact, the C9=C10 bond is even shorter than the C₄–C_{exo} one in 2,2',6,6'-tetraphenylbipyranlydene (1.385 Å) taken as reference for a quinoidal derivative.²⁵ Thus, surprisingly, in the solid state, the thiophene moiety seems to be the main donor involved in the ICT process towards the acceptor unit.

¹H NMR Spectroscopy

The structures of the synthesized chromophores were also analyzed by ¹H NMR spectroscopy, in order to obtain information about their ground-state electronic structure. Charge transfer from the donor to the acceptor group is evidenced by the high ³J_{HH} values of the methine protons of the =CH–CH= spacer in CD₂Cl₂ (³J = 13.2 Hz for **1b**; ³J = 12.3 and 12.6 Hz for **1c**). Moreover, these values confirm a major polarization for the shorter compound (**1a**) and an *s-trans* conformation for these single bonds in solution, in the same way as it was found for **1c** in the solid state (X-ray diffraction section). The ΔJ value²⁶ for compound **1c** is 0.5 Hz in CD₂Cl₂ and in acetone-*d*₆, indicating that although the quinoid form mainly contributes to the ground state description, the compound shows an important ICT, and subsequently a strongly polarized structure. Accordingly, the chemical shifts of the polymethine protons of **1c** show an oscillatory behavior²⁷ (in acetone-*d*₆, starting from donor end group: 5.98, 7.66, 6.43, 7.44 ppm) that reflects the alternation in the electron density of the carbon atoms to which H are bonded.

The chemical shifts of the thiophenic protons can also be useful to study the polarization of compounds **1a–c**. Comparison of the NMR spectra of the quinoidal chromophores with that of the tautomer of 2-dicyanomethylthiophene **3**, named as **3'**¹⁵ (Fig. 5), shows that H_a (bonded to a carbon with partially positive electron density, more distant from the acceptor) is deshielded in the series **1a**>**1b**>**1c** with respect to **3'**, whereas H_b (bonded to a carbon with partially negative electron density, proximal to the acceptor) is shielded (**1a**<**1b**<**1c**). These data also support the important charge transfer from the donor to the acceptor, with a higher contribution of the zwitterionic form for the shortest merocyanine **1a**.

n	Compd	H _a	H _b
0	1a	7.50	6.92
1	1b	7.25	6.93
2	1c	7.20	6.97

Fig. 5 Chemical shifts (ppm, in CDCl₃) of the thiophene ring protons for compounds **1a–c**, together with those of **3'** (tautomer of **3**). Data for **3'** were taken from reference.¹⁵ D = donor unit.

On the other hand, given that the hydrogen atoms at the 3- and 5-positions of a pyranilydene unit undergo downfield shifts with the increased aromatization of the ring,^{14a,28} the decrease in chemical shifts (in ppm) for such protons in CD₂Cl₂ on passing from **1a** (6.57, 6.17) to **1b** (6.46, 6.14) and **1c** (6.36, 5.97) reveals a lower contribution of the zwitterionic form to the ground electronic state as the polyenic π -spacer lengthens, in agreement with other 4*H*-pyranilydene- π -A derivatives.^{5d,14a,29}

Calculated structures

The geometry of the reported compounds was optimized at the PCM-M06-2X/6-31G* level in dichloromethane, resulting in every case in a planar donor-spacer-acceptor arrangement. Analysis of Mulliken charges on the various molecular domains for compounds **1a–c**, and **2** (Fig. 6) allows us to gain a deeper understanding of their ground electronic state polarization. In general, strongly polarized structures have been found for all the studied systems, with the negative charge concentrated on the acceptor¹¹ and the positive charge spreading over the donor and the thiophene ring for the quinoidal derivatives **1a–c**. The high positive charge found for the thiophene unit supports its auxiliary donor character,^{5d,30} even when located next to the acceptor group.^{5a,31}

Fig. 6 Mulliken atomic charges on various molecular domains for compounds **1a–c**, **2** at the PCM-M06-2X/6-311+G(2d,p)/PCM-M06-2X/6-31G* level. (D = donor unit).

For the series **1a–c**, a decrease of the positive charge on the donor on lengthening the spacer was observed. This finding is in agreement with a lower contribution of the zwitterionic form to the ground state as the length of the π -spacer increases, as disclosed by the ^1H NMR data. Compound **1a** is the most polarized chromophore within this series.

Comparison of systems **1b** and **2** reveals the strong difference about the charge on the thiophene ring: it is negligible for compound **2**, whereas it becomes positive and even higher than the charge supported by the pyranilydene donor unit in **1b**. Theoretical description of the geometry obtained for system **2** differs from its experimental X-ray structure, since in the solid state the charge transfer seems to take place only from the thiophene moiety to the acceptor unit likely due to the counter-polarizing effect of the surrounding molecules in the crystal. Concerning the electron-withdrawing group, the higher dicyanomethanide character found for system **1b** regarding its aromatic isomer **2**, supports the more efficient charge transference towards the acceptor provided by the quinoidal thiophene ring. This conclusion is in agreement with the previously reported quinoid/aromatic thiophene-containing pair of chromophores,¹¹ as evaluated through the resonance parameter c^2 .¹¹

Infra-Red Spectroscopy

Vibrational spectroscopy is particularly useful to obtain valuable information regarding the ICT taking place in D–A chromophores.³² The C≡N stretching band, $\nu(\text{C}\equiv\text{N})$, of the nitrile groups is known to be very sensitive to the electron density on these groups, downshifting its associated frequency upon ICT in the case of push-pull compounds bearing a dicyanomethylene acceptor. Taking molecule **7** (Fig. 2) as reference, for which the $\nu(\text{C}\equiv\text{N})$ band is observed as a single peak at 2222 cm^{-1} ,³³ the corresponding $\nu(\text{C}\equiv\text{N})$ absorptions in compounds **1a–c** (Table 1) appear at significantly lower frequencies. In the studied compounds, the $\nu(\text{C}\equiv\text{N})$ behaves as **1b,1c**>**1a** revealing the variable ICT from the donor towards the electron-withdrawing C(CN₂) group. The shortest compound **1a** is the most polarized, in agreement with ¹H NMR data and calculated results.

Table 1 Infra-Red Data^a

Compd	$\nu(\text{C}\equiv\text{N})$
1a	2162, 2189
1b	2197
1c	2197
2	2210

^a All ν data are in cm^{-1} .

Measured on KBr pellets.

Comparison of system **1b** with its aromatic analogue **2** shows a lower value of the $\nu(\text{C}\equiv\text{N})$ frequency for the quinoidal derivative, pointing to a higher degree of charge transfer (as disclosed by Mulliken charges analysis).

Vibrational Raman Properties

Whereas infrared frequencies give information only of the partially charged nitrile groups, Raman frequencies of the bands of all chemical groups (not only CN) involved in the π -conjugated path can give us reliable information on their π -electronic shapes. The Raman spectra of the studied compounds display medium intensity bands around 2200 cm^{-1} that correspond to the equivalent infrared active stretching vibrations of the

dicyanomethylene groups, or $\nu(\text{C}\equiv\text{N})$. Such as in infrared spectroscopy, the frequency position of the $\nu(\text{C}\equiv\text{N})$ is very sensitive to the electron density on the $\text{C}\equiv\text{N}$ groups, showing a frequency decrease when the electron density on them is increased (this is further explained in the spectroelectrochemistry section in terms of the antibonding character of the LUMO on the CN group). In compound **2** the $\nu(\text{C}\equiv\text{N})$ is at 2209 cm^{-1} , (Fig. 7) while in the **1** series it shifts to 2188 , 2191 (undefined) and 2195 cm^{-1} in **1a**, **1b** and **1c** respectively, highlighting the accumulation of negative charge on these groups due to an extensive ground electronic state polarization. This is compatible with a slightly, or non-polarized, structure in **2** (the thiophene is aromatic and the cyano groups are almost uncharged) and zwitterionic structures for the **1a–c** molecules, with the negative charge centred in the CN groups and the positive charge shared among the thiophene and the *4H*-pyranylidene units, in agreement with the calculated Mulliken charges (See Fig. 6; calculated structures section). Interestingly, the bands due to the $\text{C}=\text{C}$ stretching mode of the thiophene ring appear at rather similar frequencies: 1399 cm^{-1} in **2**, 1416 cm^{-1} in **1a**, $1403/1394\text{ cm}^{-1}$ in **1b**, and 1389 cm^{-1} in **1c**. Taking into account that the Raman active band in aromatic thiophene is at 1406 cm^{-1} , it can be argued that the thiophene ring in **2** has an aromatic character, but this is also the case of compounds **1a–c**, due to the charge polarization promoted by the aromatization of the initially quinoidal thiophene. The $\text{C}=\text{C}$ stretching mode of the *4H*-pyranylidene moiety is at 1661 cm^{-1} in **2**, 1651 cm^{-1} in **1a**, 1649 cm^{-1} in **1b** and **1c**, indicating that this group is also affected by the charge reorganization as a result of the donor-acceptor interaction in the ground electronic state, and that these changes mostly take place on passing from **2** to **1a–c**, like it was observed in the case of the $\nu(\text{C}\equiv\text{N})$ and of the $\text{C}=\text{C}$ thiophene stretching frequencies.

Fig. 7 Solid-state FT-Raman ($\lambda = 1064$ nm) spectra of compounds **1a–c** and **2** (bottom to top).

The parallel variation of the frequencies corresponding to the main groups (cyano, thiophene, and 4*H*-pyranylidene) in the Raman spectra for all the systems is a further indication of the extension of charge polarization through the whole conjugated pathway from the donor to the acceptor. In general, experimental (crystal structures, ^1H NMR data, IR and Raman spectroscopies) and theoretical data all show a higher polarization, and hence a higher degree of charge transfer, for the quinoidal chromophores compared to the aromatic system **2**.

Electrochemistry

The redox properties of the target compounds were measured by cyclic voltammetry (CV) (Table 2) (See voltammograms in ESI). Chromophores **1a–c**, **2** show one oxidation and one reduction waves corresponding to the electron processes of oxidation of the donor unit and reduction of the acceptor fragment respectively. For quinoidal derivatives, oxidation process is reversible (**1a**) or quasi-reversible (**1b–c**) whereas for compound **2**, some low-current wave is observed.

The electrochemical band gaps and HOMO/LUMO energy levels were estimated from the electrochemical data. Thus, electrochemical band gaps were calculated from onset potentials of the anodic and cathodic waves, by the empirical relationship: $\text{HOMO} = -(E_{\text{ox, onset}} + 4.4) \text{ eV}$; $\text{LUMO} = -(E_{\text{red, onset}} + 4.4) \text{ eV}$.³⁴

Table 2 Electrochemical data^a and E_{HOMO} and E_{LUMO} values determined from electrochemical data and theoretically calculated

Compd	E_{ox}^a (V)	E_{red}^a (V)	E_{HOMO}^b (eV)	E_{LUMO}^b (eV)	E_{gEChem}^b (eV)	E_{HOMO}^c (eV)	E_{LUMO}^c (eV)	E_{gTheor}^c (eV)
1a	0.87 ^a	-1.23	-5.16	-3.48	1.68	-6.60	-2.24	4.36
1b	0.75	-0.96	-4.95	-3.60	1.35	-6.35	-2.41	3.94
1c	0.64	-0.93	-4.80	-3.71	1.09	-6.16	-2.55	3.61
2	0.82	-1.23	-5.04	-3.60	1.44	-6.42	-2.25	4.17

^a 10^{-3} M in CH_2Cl_2 versus Ag/AgCl (3 M KCl), glassy carbon working electrode, Pt counter electrode, 20 °C, 0.1 M NBu_4PF_6 , 100 mV s^{-1} scan rate. Ferrocene internal reference $E^{1/2} = +0.43$ V. ^b HOMO and LUMO energies and electrochemical HOMO–LUMO gaps determined from the onset of the oxidation and the reduction waves in cyclic voltammograms. ^c Calculated at the PCM-M06-2X/6-311+G(2d,p) level in CH_2Cl_2 . ^d Reversible oxidation wave ($E^{1/2}$)

Both oxidation and reduction processes become easier on chain lengthening (**1a**→**1b**→**1c**). The observed trends are also confirmed by computational calculations (Table 2) which show that the E_{HOMO} (E_{LUMO}) values increase (decrease) with the length of the spacer. Thus, a larger conjugation length gives rise to a decrease of the electrochemical band gap. The calculated HOMO–LUMO gaps are overestimated with respect to the electrochemical ones (more than 2.0 eV), but similar trends using any of these two methods were encountered. It is worth mentioning that direct comparison of electrochemical and calculated band gaps assumes a “frozen orbital approximation” and must be done with caution.³⁵

Comparison of compound **1b** with its aromatic analogue **2** shows lower oxidation/reduction potentials (absolute values) for the former, due, presumably, to the stabilizing effect imparted on the electrochemically generated radical ions by the gain of aromaticity from the quinoid thiophene ring. Besides, **1b** show lower electrochemical (and

calculated) band gap than **2**. The same behavior has been described in related systems with a thienothiophene moiety in the π -spacer.⁸

UV-Vis Spectroscopy

The UV-vis absorption data of compounds **1a–c**, **2** in solvents of different polarity, together with the calculated λ_{max} and oscillator strengths (f values) in CH_2Cl_2 (using a polarizable continuum model –PCM– and the M06-2X³⁶ meta-exchange functional) are gathered in Table 3 (see spectra in ESI). The choice of this functional has been based on the accurate results obtained in the calculation of charge-transfer transitions with high spatial orbital overlap, that are even better than those provided by the more widely used CAM-B3LYP.^{30c,37} The calculated lowest excitations are associated to a one electron HOMO to LUMO transitions.

The four molecules show very strong and broad electronic absorption bands in the visible region. For **1b–c** the two bands on the high-frequency side are associated and the second one can be attributed to vibronic transitions. This assignment is based on: i) the energy spacing between these sub-bands ($1100 \pm 100 \text{ cm}^{-1}$; e.g. for **1c**, 1093 cm^{-1} in CH_2Cl_2 and 1258 cm^{-1} in DMF) which correspond to totally symmetric C=C/C–C vibrational modes coupling the ground electronic state to the pertinent excited state (S_1) through the ICT vibrational coordinate along the π -spacer;³⁸ and ii) the variation of the spectral shape with solvent polarity, i.e., an increase in the lower energy band at the expense of the higher energy one on increasing the solvent polarity.³⁹

Table 3 UV-Vis data^a

Compd	λ_{max} (log ϵ)	λ_{max} (log ϵ)	λ_{max} (log ϵ)	λ_{max}^b	f^b
	1,4-dioxane	CH_2Cl_2	DMF		
1a	504 (4.53)	507 (4.42)	506 (4.29)	507	1.37
	539 (4.65)	542 (4.65)	540 (4.60)		
	581 (4.48)	585 (4.60)	582 (4.68)		
1b	573 (4.73)	587 (4.67)	584 (4.62)	588	1.85
	607 (4.74)	627 (4.82)	627 (4.88)		
	662 (sh)	684 (4.68)	685 (4.91)		

1c	619 (4.82)	658 (4.79) 709 (4.81) 788 (4.55)	656 (4.73) 715 (4.85) 790 (4.79)	664	2.32
2	536 (4.60)	568 (4.64)	557(4.61)	542	1.22

^a All λ_{max} data are in nm. ^b PCM-TD-M06-2X/6-311+G(2d,p) calculations in CH₂Cl₂.

For the series **1a–c**, the λ_{max} values increase on lengthening the spacer, showing an accentuated bathochromic shift with solvent polarity, and reaching a shift of ~ 100 nm in CH₂Cl₂ or even greater in DMF. On the energy scale, these shifts decrease on increasing conjugation length, being 0.31 and 0.24 eV in CH₂Cl₂ and 0.32 and 0.24 eV in DMF. This behavior points to weakly alternated structures, suggesting an important zwitterionic character for these systems, in agreement with calculated Mulliken charges and IR/Raman spectroscopies.

The character of the thiophene (quinoid or aromatic) moiety has a significant effect on the electronic absorption properties of the chromophores **1b** and **2**. Thus, the presence of the quinoid ring causes a significant red shift of the maximum absorption wavelength in **1b** when compared to **2**. This shift is greater than 110 nm (0.37 eV in CH₂Cl₂ and 0.42 eV in DMF), surpassing that encountered when a thienothiophene unit (aromatic or quinoid) is evaluated in related compounds.⁸ In general, larger molar extinction coefficients ϵ in all the solvents studied are found for compound **1b**. This trend parallels that of the calculated oscillator strengths f in CH₂Cl₂. These results, obtained from the comparison of D- π -A systems which only differ in the quinoid/aromatic character of the thiophene unit, are in agreement with the two examples reported in the literature.^{11–12}

Concerning the dependence of the band position on solvent polarity, compound **1a** presents an almost negligible solvatochromism. This point can be explained³³ regarding the HOMO and the LUMO of **1a**, (Fig. 8) whose topologies are not dominated by the polar end groups, being spread over the whole conjugated backbone.

For systems **1b–c**, **2** positive solvatochromism for low polarity solvents (cf. dioxane and CH₂Cl₂) that becomes negligible/slightly negative for **1b/2** respectively when increasing polarity (cf. CH₂Cl₂ and DMF) was observed. This variety of behavior has already been reported for other D- π -A systems,⁴⁰ including some 4*H*-pyranylidene derivatives.^{8,29}

Fig. 8 Illustration of the HOMO (bottom) and LUMO (top) of compound **1a**.

UV-Vis-NIR and Infrared spectroelectrochemistry

Fig. 9 shows the electronic absorption spectra of the three quinoidal **1a–c** systems together with that of the aromatic parent **2**, obtained in CH₂Cl₂ during the oxidative and reductive regimes according to the redox properties of the cyclic voltammetry experiments above. For **1c**, reduction gives rise to the net disappearance of the absorption band of the neutral compound, accompanied by the increase of a new broad band due to the formation of the radical anion which displays subpeaks at 340, 402 and 491 nm. The overall intensity of the bands corresponding to the reduced species is considerably smaller than those of the neutral. Both neutral/anionic bands interconvert through a well-defined isosbestic point. The decrease of intensity of the lowest energy electronic absorption band in the anion regarding that of the neutral, together with the displacement to higher energies (658/709/788 nm $\rightarrow$ 340/402/491 nm) upon reduction, are clear indications of the collapse of the neutral ICT band given the compensation of the electron-withdrawal effect of the dicyano-vinyl acceptor group in the radical anion. A similar behavior is observed for **1b**, with the appearance of a new band at 434 nm, considerably weaker than those of the neutral form at 587/627/684 nm, which also corresponds to the radical anion (conversion also

proceeds through a clear isosbestic point). In the case of **1a**, the conversion to radical anion does not proceed through an isosbestic point. Nonetheless, it can be seen that the new band of the negatively charged species of **1a** displays its maximal absorbance around 350–400 nm. This blue-shift of the absorption band might correspond to the formation of a radical anion, as in the cases of **1b** and **1c**.

Fig. 9 UV-Vis-NIR absorption spectra of compounds **1a–c** and **2** obtained in CH_2Cl_2 during their potentiostatic oxidation (top) or reduction (down) in intervals of 15 mV. Black lines: spectra of the neutral species. Red lines: radical cation spectra. Green lines: radical anion spectra. Dashed lines correspond to transition spectra.

The red-shift of the bands of the radical anions from 350–400 nm in **1a** to 434 nm in **1b** and 340/402/491 nm in **1c** is an indication of the increased conjugation of the injected charge along the whole path from the acceptor to the donor, promoted by the precursor quinoidal sequences in the neutral compounds. The comparison of the UV–Vis absorption data of **1b** and **1c** with those of the aromatic compound **2**, reveals the similitude of the radical anions of **2** and **1b**, both with absorption maxima at 435 nm and 434 nm respectively. This fact points to the complete delocalization of the negative charge in the two isomers since both have the same number of π electrons ($12 e^-$ without considering the common CN groups) placed in different positions. The situation changes completely in the neutral forms, where the nature and placement of the active π electrons defines the position of the lowest energy absorption band and therefore the relevant optical properties.

A similar behavior is found in the oxidative processes compared to reductions. The electron extraction leads to stable radical cations for **1b** and **1c** with clear isosbestic points. In **1c** the radical cation is characterized by a new broad band at 448 nm, whose wavelength is comparable to those of the bands of the radical anion (340/402/491nm) revealing that although the extraction of the electron takes place on the donor part of the molecule, it has an effect in the optical properties similar to the inclusion of one electron in the acceptor. Such a similar response points towards a scenario promoted by the coalescence of the donor-acceptor interaction in the neutral compound either with oxidation or reduction. The same pattern than for **1c** is found for the oxidation to the radical cation in **1b**. However, the case of the oxidation of **1a** is particular: the decrease of the neutral absorption band gives rise to a well-defined band with maxima at 554 and 593 nm, together with another one at 370 nm. These bands progressively evolve with the increment of the potential into one single feature at higher energies, with its maximum absorption value at 365 nm. The species with the highest potential is assigned to a radical cation, given its similitude with those of **1b–c**. The spectra that appear between the neutral form and the cation might arise from a transitory meta-stable species (self-assembled dimers are possible) generated in the vicinity of the electrode which is reversibly transformed into the stable cation.

In compound **2**, oxidation gives rise to a broad band with maximum at 356 nm, at rather different position than in **1b** besides their similar π electron nature (number of π electrons), likely indicating that the electron extraction takes place mostly in the aromatic thiophene for **2**, while in the **1** series oxidation comes from the thiophene-pyrane unit. In conclusion, both oxidation and reduction produce the disappearance of the strong visible absorptions of the neutral compounds and the formation of rather transparent solutions, highlighting a significant reversible electrochromic effect.

Fig. 10 displays the infrared spectra of **1b** and **2** obtained during the electrochemical oxidation and reduction processes in CH_2Cl_2 . In the significant region of the $\nu(\text{CN})$ absorption bands, reduction of **1b** gives rise to the disappearance of the neutral absorption associated to the $\nu(\text{CN})$ vibration at 2202 cm^{-1} , and to the growth of two well resolved peaks at 2163 cm^{-1} and 2108 cm^{-1} .³³ These two peaks display the characteristic two pattern bands of the tetracyano anionic species, such as those of TCNQ and TCNE derivatives.⁴¹ The emergence of the same two absorptions in a dicyano-substituted push-pull compound

might be justified by a strong vibrational coupling of the two CN stretches in the anionic species, which is translated into two infrared bands. The $2202\text{ cm}^{-1} \rightarrow 2163\text{ cm}^{-1}/2108\text{ cm}^{-1}$ downshift is a result of the antibonding character of the LUMO wavefunction between the C and N atoms in the cyano groups (an increase of the charge on the LUMO upon reduction produces an enlargement of the CN bond and a frequency downshift). A similar two-band profile is observed for the aromatic compound **2** after reduction and generation of the radical anion. Noticeably, the frequency change is greater in **2** (68 cm^{-1} ; $2216\text{ cm}^{-1} \rightarrow 2148\text{ cm}^{-1}$) than in **1b** (39 cm^{-1} ; $2202\text{ cm}^{-1} \rightarrow 2163\text{ cm}^{-1}$), which indicates a higher ability to accept additional electrons in **1b** than in **2** (smaller frequency changes indicate less structural reorganization and energy requirements to accommodate electrons). In both cases, however, the whole charge in the anion is placed in the dicyano group, leading to the complete disappearance of the characteristic charge-transfer band of the neutral molecules, in agreement with the electronic absorption UV–Vis data.

Fig. 10 IR absorption spectra of compounds **1b** and **2** obtained in CH_2Cl_2 during their potentiostatic oxidation (left) or reduction (right) in intervals of 15 mV. Black lines: spectra of the neutral species. Red lines: radical cation spectra. Green lines: radical anion spectra. Dashed lines correspond to transition spectra.

During oxidation, the neutral $\nu(\text{CN})$ vibration at 2202 cm^{-1} in **1b** gives rise to a single band at higher frequency, 2224 cm^{-1} , which is in line with the extraction taking place in the

donor group. The CN groups are then affected by the decreasing of the ground electronic state polarization, as the initial donor loses its electron releasing character upon the formation of a cation on it. The $2202\text{ cm}^{-1} \rightarrow 2224\text{ cm}^{-1}$ frequency upshift shows the removal of charge from the antibonding state of the CN group upon oxidation, causing the strengthening of the bond and an increased vibrational frequency. A similar situation is found during oxidation in compound **2**, with a $2216\text{ cm}^{-1} \rightarrow 2229\text{ cm}^{-1}$ frequency upshift in accordance with the generation of a radical cation within the thiophene donor group. The frequency upshift with oxidation and the frequency downshift upon reduction follow a different pattern in the two almost π -isoelectronic compounds: now the upshift is smaller in **2** (13 cm^{-1} ; $2216\text{ cm}^{-1} \rightarrow 2229\text{ cm}^{-1}$) than in **1b** (22 cm^{-1} ; $2202\text{ cm}^{-1} \rightarrow 2224\text{ cm}^{-1}$) in agreement with the greater ability to release electrons (less frequency changes indicate less structural reorganization and energy requirements to expulse electrons).

Nonlinear Optical properties

The second-order nonlinear optical properties of compounds **1a–c**, **2** were measured by electric field-induced second harmonic generation (EFISHG) in CH_2Cl_2 at 1907 nm. (Table 4) For the sake of comparison, Disperse Red 1, a common benchmark for organic NLO chromophores shows a $\mu\beta$ value of ca. 720×10^{-48} esu in CH_2Cl_2 , under the same experimental conditions.

Table 4. NLO Properties

Compd	$\mu\beta^a$ (10^{-48} esu)
1a	90
1b	1220
1c	5030
2	860
^a Experimental uncertainty less than $\pm 15\%$.	

Inspection of Table 4 reveals that $\mu\beta$ values in the series **1a–c** increase with the conjugation length. The low response for **1a** together with its solvatochromism, ^1H NMR data, IR frequencies and calculated data clearly supports the important polarization of the ground electronic state of this compound, which is near the cyanine limit. Lengthening the spacer gives rise to more alternated structures with higher second-order nonlinearities.

The influence of the character of the thiophene moiety (aromatic or quinoid) can be inferred from the analysis of $\mu\beta_0$ values of compounds **1b** and **2**. Thus, **1b** presents a higher response than **2**, in agreement with the more efficient ICT upon the quinoid ring introduction.

Finally, it could be also pertinent to compare the NLO properties of the herein reported compounds to those of related derivatives. Thus, comparison with the analogue of **1c** bearing 1,1,3-tricyano-2-phenylpropene as acceptor^{14a} ($\mu\beta = 1550 \times 10^{-48}$ esu measured in the same conditions) shows higher response for compound **1c** in consonance with their less polarized structure (as it has been seen in X-ray section) and closer, although surpassed, to the maximum of the Marder's plot.^{22b}

On the other hand, while compounds **1a–c** show positive $\mu\beta$ values in agreement with a predominantly quinoid form for their ground electronic state, their analogues in which the thiophene ring has been substituted by a thiazole^{14b} show negative figures of merit, due to their higher polarization, being essentially zwitterionic molecules. Nevertheless, absolute values are of the same order, or even slightly higher for the series herein studied (e.g. analogue of **1c** measured in the same conditions: $\mu\beta = -3900 \times 10^{-48}$ esu).

Conclusions

Merocyanines featuring a quinoid or an aromatic thiophene moiety have been prepared and studied by different experimental techniques, together with theoretical calculations. Compounds **1a–c** exist as a resonance hybrid of the quinoid and zwitterionic forms, showing strongly polarized structures, and can be considered as left-handed chromophores, in agreement with a predominantly quinoidal form for their ground state. This polarization decreases on lengthening the spacer, with chromophore **1a** having the highest contribution of the zwitterionic form among the series.

Derivative **1b**, with a quinoid thiophene ring in the π -spacer shows a more efficient ICT than its aromatic analogue **2**, as shown by X-ray studies, calculated Mulliken charges, absorption frequencies of the C $\equiv$ N groups in IR and Raman spectroscopy. As a consequence, a higher NLO response has been found for **1b** when compared to **2**. Moreover, CV and UV-vis spectra showed favored redox processes and bathochromically shifted λ_{max} values respectively for the quinoid system **1b**.

Concerning chromophore **2**, the UV-vis and IR spectroelectrochemistry studies, along with the crystalline structure, point to the important role of the thiophene ring in the ICT process towards the dicyanomethylene moiety, acting as the main electron-donating fragment.

Finally, a reversible electrochromic effect has been observed from the spectroelectrochemical study associated with the interconversion of neutral/anion/cationic species derived from systems **1a–c**, **2**. The changes in the optical properties upon redox processes are consistent with the coalescence of the ICT feature in the neutral species giving rise to colorless solutions which describes a potential use of these compounds as electrochromic materials combined with the parallel changes (switch on $\rightarrow$ off) of the NLO property associated with any of the redox process.

Experimental

For general experimental methods see ESI.

Starting materials: Compounds **3**,¹⁵ **5b–c**,^{16,14a} and **6**¹⁷ were prepared as previously described.

2-(5-(2,6-dimethyl-4H-pyran-4-ylidene)thiophen-2-ylidene)malononitrile (1a). Acetic anhydride (1.5 mL) was added to a mixture of 2-dicyanomethylthiophene (**3**) (0.100 g, 0.67 mmol) and 2,6-dimethyl-4H-pyran-4-one (**4**) (0.083 g, 0.67 mmol) under an argon atmosphere. The mixture was heated at reflux for 5 min, then slowly cooled to room temperature and stirred for 4 h. The reaction was cooled to 0°C and hexane was added. The resulting solid was filtered off and washed with hexane. The crude product was purified by flash column chromatography (silicagel) by using CH₂Cl₂ as the eluent to afford compound **1a** as a dark violet solid (0.053 g, 0.21 mmol, 33%). Mp 302–306 °C (dec.). Found: C, 66.37; H, 3.68; N, 10.81. Calc. for C₁₄H₁₀N₂OS: C 66.12, H 3.96, N 11.02 %. IR (KBr, cm^{−1}

¹): 2189 (C≡N), 2162 (C≡N), 1655 (C=C), 1577 (C=C). ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 5.2 Hz, 1H), 6.92 (d, *J* = 5.2 Hz, 1H), 6.50 (d, *J* = 0.7 Hz, 1H), 6.09 (d, *J* = 0.7 Hz, 1H), 2.28 (s, 3H), 2.27 (s, 3H). ¹³C NMR: not registered due to its low solubility. HRMS (ESI⁺): *m/z* calcd for C₁₄H₁₁N₂OS 255.0587, found 255.0573 [M+H]⁺; calcd for C₁₄H₁₀N₂NaOS 277.0406, found 277.0389 [M+Na]⁺; calcd for C₂₈H₂₀N₄NaO₂S₂ 531.0920, found 531.0900 [2M+Na]⁺.

(Z)-2-(5-(2-(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)ethylidene)thiophen-2-ylidene)malononitrile (1b). 2-dicyanomethylthiophene (**3**) (0.089 g, 0.6 mmol) was added to a solution of aldehyde **5b** (0.134 g, 0.57 mmol) in acetic anhydride (1.5 mL) at 40°C under an argon atmosphere. The mixture was heated at reflux for 90 min, then slowly cooled to room temperature and then to 0°C. Hexane was added and the resulting solid was filtered off and washed with cold EtOH, then with a mixture of hexane/CH₂Cl₂ (9.8:0.2) to afford compound **1b** as a dark green solid (0.139 g, 0.38 mmol, 68%). Mp 296–300 °C (dec.). Found: C, 72.72; H, 6.46; N, 7.95. Calc. for C₂₂H₂₄N₂OS: C 72.49, H 6.64, N 7.69 %. IR (KBr, cm⁻¹): 2197 (C≡N), 1650 (C=C), 1577 (C=C). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.47 (d, *J* = 13.2 Hz, 1H), 7.31 (d, *J* = 5.2 Hz, 1H), 6.90 (d, *J* = 5.2 Hz, 1H), 6.46 (d, *J* = 1.8 Hz, 1H), 6.14 (d, *J* = 1.8 Hz, 1H), 5.76 (d, *J* = 13.2 Hz, 1H), 1.30 (s, 9H), 1.27 (s, 9H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 172.8, 170.5, 170.3, 148.4, 144.8, 135.0, 133.3, 124.7, 117.0, 116.0, 110.6, 107.8, 101.1, 57.7, 36.5, 36.8, 28.0, 27.9. HRMS (ESI⁺): *m/z* calcd for C₂₂H₂₅N₂OS 365.1682, found 365.1695 [M+H]⁺; calcd. for C₂₂H₂₄N₂NaOS 387.1502, found 387.1507 [M+Na]⁺.

2-((Z)-5-((E)-4-(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)but-2-enylidene)thiophen-2-ylidene)malononitrile (1c). Acetic anhydride (1.5 mL) was added to a mixture of aldehyde **5c** (0.080 g, 0.31 mmol) and 2-dicyanomethylthiophene (**3**) (0.055 g, 0.37 mmol), under an argon atmosphere. The mixture was heated at reflux for 90 min, then slowly cooled to room temperature, and then to 0°C. Hexane was added and the resulting solid was filtered off and washed with hexane, then with a mixture of hexane/CH₂Cl₂ (9.8:0.2) to give compound **1c** as a dark green solid (0.097, 0.25 mmol, 84%). Mp 242–246 °C. Found: C, 74.03; H, 6.49; N, 7.03. Calc. for C₂₄H₂₆N₂OS: C 73.81, H 6.71, N 7.17 %. IR (KBr, cm⁻¹): 2197 (C≡N), 1650 (C=C), 1551 (C=C). ¹H NMR (400 MHz, CD₃COCD₃): δ 7.66 (t, *J* =

13.3 Hz, 1H), 7.56 (d, $J = 5.2$ Hz, 1H), 7.44 (d, $J = 12.5$ Hz, 1H), 6.97 (d, $J = 5.2$ Hz, 1H), 6.67 (d, $J = 1.7$ Hz, 1H), 6.43 (t, $J = 13.0$ Hz, 1H), 6.19 (d, $J = 1.7$ Hz, 1H), 5.98 (d, $J = 12.8$ Hz, 1H), 1.30 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 173.2, 168.8, 168.7, 144.8, 143.4, 143.2, 138.3, 137.0, 126.2, 122.9, 116.8, 115.8, 114.3, 107.3, 100.9, 59.7, 36.7, 36.4, 28.2, 28.1. HRMS (ESI^+): m/z calcd for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{OS}$ 391.1839, found 391.1842 $[\text{M}+\text{H}]^+$.

2-((5-((2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)methyl)thiophen-2-yl)methylene)malononitrile (2). Absolute ethanol (1.5 mL) was added to a mixture of aldehyde **6** (0.061 g, 0.19 mmol) and malononitrile (0.014 g, 0.21 mmol) under an argon atmosphere. The mixture was heated at reflux overnight. Reaction was cooled to room temperature and the solvent was evaporated. The crude product was dissolved in a small amount of dichloromethane and precipitated with hexane. The resulting solid was filtered off and washed with hexane affording compound **2** as a bright violet solid (0.047 g, 0.13 mmol, 66%). Mp 225–227 °C. Found: C, 72.28; H, 6.41; N, 7.86. Calc. for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{OS}$: C 72.49, H 6.64, N 7.69 %. IR (KBr, cm^{-1}): 2210 ($\text{C}\equiv\text{N}$). ^1H NMR (300 MHz, CDCl_3): δ 7.60 (s, 1H), 7.50 (d, $J = 4.2$ Hz, 1H), 6.85 (d, $J = 4.2$ Hz, 1H), 6.65 (d, $J = 1.9$ Hz, 1H), 5.98 (s, 1H), 5.88 (d, $J = 1.9$ Hz, 1H), 1.30 (s, 9H), 1.24 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ 168.9, 165.9, 156.6, 148.4, 137.1, 130.7, 125.7, 116.0, 115.1, 105.9, 104.6, 100.6, 36.2, 35.7, 27.8. HRMS (ESI^+): m/z calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{OS}$ 365.1682, found 365.1658 $[\text{M}+\text{H}]^+$; calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{NaOS}$ 387.1502, found 387.1463 $[\text{M}+\text{Na}]^+$.

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Electronic supplementary information (ESI) available

General experimental methods, NMR and UV–vis spectra, voltammograms and HRMS spectra of new compounds, X-ray crystallographic data and diagrams of the crystal structures of **1c** and **2** (CCDC-1007965 and 1007966 respectively), NLO measurements, computed energies and Cartesian coordinates of optimized geometries.

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