Dithienopyrrole as a rigid alternative to the bithiophene π -relay in chromophores with second-order nonlinear optical properties

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Abstract: 4*H*-pyranylidene- containing push-pull chromophores built around a bithiophene (BT) π -relay or a rigidified thiophene-based unit namely cyclopenta[1,2-*b*:3,4-*b'*]dithiophene (CPDT) or dithieno[3,2-*b*:2',3'-*d'*]pyrrole (DTP), have been synthesized and characterized. The effect of these different relays on the polarization and on the second-order nonlinear optical (NLO) properties has been studied. For the sake of comparison, the corresponding reported dithieno[3,2-*b*:2',3'-*d'*]thiophene (DTT) derivatives have also been included in the discussion. Replacement of the BT core by a rigidified unit (CPDT, DTP) leads to more polarized systems. Calculated NBO charges and electrochemical measurements show that dithienopyrrole has a remarkable donor character which allows an important charge transfer between the donor and the acceptor. The influence of the rigidification of the BT relay on the NLO responses depends on the acceptor strength. For the weakest acceptor employed (thiobarbituric acid) passing from BT relay to the rigidified units always involves an increase of the $\mu\beta_0$ figure of merit. Nevertheless, for the strongest acceptor (2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, TCF), a slight increase of $\mu\beta_0$ with respect to the BT chromophore is only observed for the DTP derivative. Thus, rigidification of the BT core it is not enough to improve the second-order nonlinearity, and the incorporation of a DTP moiety has proven to be the most efficient approach for this purpose.

Introduction

Push-pull molecules bearing electron donors (D) and acceptors (A) linked by a π -conjugated core have been extensively studied during the last decades due to their wide application in nonlinear optics (NLO),^[1] and other research fields like organic light emitting diodes (OLEDs)^[2] or dye-sensitized solar-cells (DSSCs).^[3]

The π -conjugated spacer plays a determining role in D- π -A systems,^[4] the most studied for second-order NLO materials, given that the intramolecular charge transfer (ICT) throughout this fragment defines to a large extent the final properties in this sort of compounds. Olefinic spacers represent, in principle, the most effective way to achieve charge redistribution between D and A groups, but they lead to poor thermal and chemical

stabilities. The reverse situation characterizes aryl-type π -relays. The replacement of polyene-like spacers by heteroaromatic conjugated bridges with aromatization energies lower than that of benzene offers a good balance between NLO activity and stability. In this sense, thiophene,^[5] thiazole^[6] or bithiophene (BT)^[7] have been widely used with successful results.

On the other hand, and focusing on the BT relay, its covalent bridging has already been investigated in the context of polymeric and low-molecular weight systems. Rigidification can be achieved by introducing different groups (i.e.: C=O, CR₂, SiR₂, NR, PR, P(O)R, S), thus giving rise to a variety of fused central cycles. This approach has often been used to favor more rigid structures with extended π -conjugation in order to modify the electronic and/or optical properties of the resulting materials, but the bridge can also provide a point of attachment for groups to increase solubility, to impart chirality or to allow anchoring to another structure.^[8]

Regarding second-order NLO activity, rigidification of the BT spacer by noncovalent intramolecular interactions between sulfur and oxygen atoms through a 2,2'-bi(3,4-ethylenedioxythiophene) (BEDOT) moiety has been studied:^[9] the replacement of BT by BEDOT reveals a marked red shift of the absorption maximum (~ 118 nm) and a large enhancement of the molecular hyperpolarizability β . Thus, the limitation of the rotational and vibrational disorder imposed by the noncovalent rigidification appears to play a determining role on the improvement of the second-order NLO response.

On the other hand, different push-pull chromophores based on a dithieno[3,2-*b*:2',3'-*d'*]thiophene (DTT) spacer (Scheme 1) have been described.^[10] Such systems can be viewed as a particular sulfur-bridged BT, and our group has recently studied D- π -A compounds^[11] bearing a DTT unit as π -spacer, which combine high second-order molecular nonlinearities with good thermal stabilities.

Other thiophene-containing fused heterocycles (Scheme 1) as cyclopenta[1,2-*b*:3,4-*b'*]dithiophene (CPDT)^[12] or dithieno[3,2-*b*:2',3'-*d'*]pyrrole (DTP)^[13] have been barely considered as π -conjugated relays for NLO: only one chromophore for second harmonic generation bearing a CPDT ring as π -electron relay has been reported,^[14] and, to the best of our knowledge, no merocyanines with a DTP moiety in their structure have been studied in relation to second-order NLO activity.

Scheme 1. Structure of BT relay together with the thiophene-fused heterocycles used in this work.

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Within this context, we present here the synthesis, characterization and study of two novel series of push-pull chromophores derived from the BT relay and its rigidified π -

conjugating counterparts CPDT and DTP. (Scheme 2) The corresponding reported DTT derivatives **1–2(d)**^[11] have been also included in this study for comparison. All chromophores include the proaromatic 4*H*-pyranylidene unit as donor.^[15]

Scheme 2. Structure of target compounds together with the previously reported^[11] **1–2(d)**.

Results and Discussion

Synthesis

For the synthesis of the chromophores herein studied **1–2(a–c)**, the previously unreported aldehydes **3(a–c)** were chosen as precursors. These compounds were obtained according to the synthetic strategy depicted in Scheme 3.

Scheme 3. Synthesis of the precursor aldehydes **3(a–c)**.

Concerning CPDT and DTP derivatives **3(b–c)**, they were prepared from the unsubstituted cores 4,4-dihexylcyclopenta[2,1-*b*:3,4-*b'*] dithiophene **5b**^[16] and *N*-hexyldithieno[3,2-*b*:2',3'-*d'*]pyrrole **5c**^[17] respectively in two steps. Thus, **4(b–c)** were synthesized by reaction of DMF on the dilithiated derivatives of **5(b–c)** respectively, formed in the presence of TMDEA (*N,N,N',N'*-tetramethylethylenediamine).^[18] Compound **4c** has been previously described in a patent of 2011,^[19] using another method (−78°C, *N*-formylpiperidine as reagent and without the addition of TMEDA), although its preparation has been reported to take place in lower yield (40%) than in conditions of Scheme 3 (75%). Moreover, in that reference^[19] it appears not fully characterized.

Then, the Horner reaction of 2,6-diphenyl-4*H*-pyran-4-yl)diphenylphosphine oxide (**6**)^[20] with **4b–c** afforded the corresponding aldehydes bearing a CPDT (**3b**) or a DTP (**3c**) moiety. It should be noted that reaction conditions were carefully tuned (temperature and order of slow addition of reagents) for the purpose of minimizing the formation of pyranylidene-disubstituted derivatives as by-products.^[11]

A three-step synthetic route was chosen for compound **3a** to avoid the substantial formation of this undesired derivative observed in the Horner reaction. New BT containing- aldehyde **4a** was prepared by lithiation of **5a**^[21] followed by reaction with DMF. Thus, the Horner reaction with **6** in the presence of BuLi, followed by the subsequent acid hydrolysis afforded the desired precursor aldehyde **3a**.

The Knoevenagel reaction between acceptors **7** (1,3-diethyl-2-thiobarbituric acid) and **8** (2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, TCF) and aldehydes **3a–c** afforded the new D- π -A compounds **1–2(a–c)** in yields ranging from 33 to 82%. (Scheme 4) The conditions used for the Knoevenagel condensation were in each case adapted to the nature of the acceptor moiety. According to the $^3J_{\text{HH}}$ coupling constants analysis, the $-\text{CH}=\text{CH}-$ bond in compounds **2** shows an *E* configuration.

Scheme 4. Synthesis of the chromophores **1–2(a–c)**.

Calculated structures

The molecular geometries of compounds **1–2(a–c)** and the previously reported systems **1–2(d)**^[11] were optimized at the PCM-M06-2X/6-31G* level in dichloromethane. The resulting structures were planar, including BT systems **1–2(a)**,^[22] even though no constraints were imposed during the geometry optimization.

The BLA value, defined as the difference between the average carbon–carbon single and double bond lengths,^[23] has been widely used as a parameter reflecting the ground-state polarization of merocyanines. The calculated BLA values of the thiophene rings attached to the donor (labeled as I) and to the acceptor (labeled as II) moieties are shown in Figure 1.

Compd	X	BLA ring I	BLA ring II
1a	no bridge	+0.024	0
1b	C(C ₆ H ₁₃) ₂	+0.016	−0.023
1c	NC ₆ H ₁₃	+0.017	−0.025
1d	S	+0.022	−0.008
2a	no bridge	+0.026	+0.021
2b	C(C ₆ H ₁₃) ₂	+0.017	−0.002
2c	NC ₆ H ₁₃	+0.019	−0.006
2d	S	+0.024	+0.013

Figure 1. Calculated BLA values (in Å) for ring I and II in systems **1–2(a–d)**. (PCM-M06-2X/6-31G* level in CH₂Cl₂) (D = donor unit; A = acceptor moiety).

Inspection of data reveals a strong quinoidization of the whole electron relay induced by the attachment to the donor and the acceptor moieties,^[24] which is particularly important for the

acceptor-substituted thienyl ring. Thus, as it has been previously evidenced in D- π -A chromophores bearing BT^[7c,22,25] or DTT^[10c] as relays, there is a coexistence of two different molecular domains within the π -conjugated spacer: there is a higher degree of quinoidization (some derivatives show negative BLA values) in the fused thienyl ring directly linked to the acceptor, caused by the stronger interaction of the relay with the electron-withdrawing group than with the donor moiety.

On the other hand, BLA is reduced in (**b–d**) chromophores (both rings I and II) compared to the corresponding **a** analogues, showing that the rigidification of the BT relay results in more polarized structures, following the order: **b>c>d>a**. A similar trend was reported when the unsubstituted fused cores (BT, DTT, CPDT) were compared^[26] (BLA values: 0.052, 0.045, 0.042 Å respectively). Moreover, these results are consistent with those obtained for compounds **9** and **10** in Figure 2, containing BT and DTT as relays, showing a higher degree of polarization for DTT when compared to its BT analogue.^[25,10c]

9	R = Me	X = no bridge	BLA ring I: 0.025	BLA ring II: 0.006
10	R = nBu	X = S	BLA ring I: 0.014	BLA ring II: −0.004

Figure 2. Calculated BLA values (in Å) for ring I and II in compounds **9**^[25] and **10**.^[10c] (Calculation level: DFT/B3LYP/6-31G**).

Finally, when thiobarbiturate and TCF derivatives are compared, higher BLA values were encountered for chromophores **2**, showing their lower polarization relative to their analogues **1**.

Analysis of natural bond orbital (NBO) atomic charges on various molecular domains for compounds **1–2(a–d)** (Figure 3) allows a deeper understanding of the polarization of the chromophores.

Compd	Donor	π -spacer	Acceptor
1a	+0.125	+0.098	−0.223
1b	+0.134	+0.166	−0.300
1c	+0.125	+0.173	−0.298
1d	+0.132	+0.092	−0.224
2a	+0.122	+0.042	−0.164
2b	+0.126	+0.115	−0.241
2c	+0.120	+0.120	−0.240
2d	+0.127	+0.036	−0.163

Figure 3. Calculated NBO charges on various molecular domains from the optimized PCM-M06-2X/6-31G* molecular geometries in dichloromethane.

The negative charge is concentrated on the acceptor moiety whereas the positive charge is spread over the donor and the π -bridge, in agreement with previously reported results for BT^[7c,22,25] and DTT derivatives.^[10c] Therefore, the π -conjugated electron relay is highly polarized, bearing the 50% (**2c**) or even more (**1b–c**) of the net positive charge of the whole NLO-phore.

Regarding the effect of the rigidification of the BT relay on the molecular polarization it can be observed that **b–c** chromophores are less alternated than their **a,d** analogues. Focusing exclusively on the π -spacer, the positive charge born by the π -system ring increases in the order **d** < **a** < **b** < **c**, for both series **1** and **2**. Thus, substitution of a BT relay by a DTP or CPDT ring gives rise to more polarized structures, revealing the role of auxiliary donors of these spacers.

Thiobarbiturate systems **1** are more polarized than their TCF analogues **2**, thus confirming the BLA results.

Electrochemistry

The redox properties of compounds **1–2(a–c)** were studied by cyclic voltammetry (CV) in CH₂Cl₂ and the results are presented in Table 1.

Table 1. Electrochemical data^[a] and E_{HOMO} and E_{LUMO} values theoretically calculated^[b] for **1–2(a–d)**.

Compd	E_{ox1} (V)	E_{ox2} (V)	E_{red} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
1a	+0.55	+1.44	−0.85	−6.17	−2.53
1b	+0.56	+1.43	−0.95	−6.07	−2.47
1c	+0.52	+1.37	−0.97	−6.08	−2.42
1d ^[c]	+0.55	+1.55	−0.84	−6.22	−2.53
2a	+0.57	+1.39	−0.66	−6.16	−2.79
2b	+0.50	+1.35	−0.73	−5.82	−2.52
2c	+0.48	+1.28	−0.72	−6.04	−2.71
2d ^[c]	+0.54	+1.56	−0.63	−6.20	−2.79

[a] 10^{−3} M in CH₂Cl₂ versus Ag/AgCl (3 M KCl), glassy carbon working electrode, Pt counter electrode, 20 °C, 0.1 M NBu₄PF₆, 100 mV s^{−1} scan rate. Ferrocene internal reference $E^{1/2}$ = +0.43 V. [b] Calculated at the PCM-M06-2X/6-311+G(2d,p)//M06-2X/6-31G* level in CH₂Cl₂. [c] Reference^[11].

All the voltammograms show three irreversible waves, corresponding to one reduction step (involving the acceptor unit) and two oxidation steps. The first oxidation is related to the 4*H*-pyranylidene moiety, while the second oxidation process is attributed to the bridge. This assignment can be made taking into account that E_{ox} for compounds dithieno[3,2-*b*:2',3'-*d'*]thiophene-2,6-dicarbaldehyde,^[10a] **4b** and **4c** are 1.65, 1.76 and 1.63 V respectively in the same conditions, and that the introduction of the relay in a π -conjugated system results in a decrease in the oxidation potentials due to a higher electronic delocalization. Moreover, values of E_{ox2} for compounds (**1–2a**)

are consistent with those of other D- π -A systems featuring BT as π -conjugated spacer.^[7e–f,27]

Electron densities related to frontier orbitals (see topologies for **1c** chosen as model compound in Figure 4) are mainly supported by the 4*H*-pyranylidene and its adjacent thienyl ring for the HOMO, and by the acceptor and its nearest thiophene unit in the case of LUMO, which agrees well with the above assignments of the redox processes. These results are in line with those found for other D-A compounds bearing BT,^[7c,22] CPDT and DTP^[28] relays.

Figure 4. Illustration of the HOMO (left) and LUMO (right) of compound **1c**.

The influence on E_{ox1} of passing from BT derivatives **a** to rigidified **b–d** ones depends on the acceptor moiety. Thus, for TCF chromophores **2**, the rigidification of BT relay implies a decrease on E_{ox1} following the order (BT)**2a** > (DTT)**2d** > (CPDT)**2b** > (DTP)**2c**. On the other hand, for thiobarbiturate derivatives **1**, only compound **1c** lowers the E_{ox1} value obtained for **1a**. Inspection of E_{HOMO} values indicates that for both series **1,2** higher values are found for **b** and **c** derivatives. Moreover, they show the lowest calculated gaps.

When the E_{ox2} data (related to the bridges) are compared, the results are similar for series **1** and **2**, with an increase on the ease of oxidation in the order (DTT)**d** < (BT) **a** < (CPDT)**b** < (DTP) **c**. Except for derivatives **d**, these results are consistent with those encountered for the isolated fused-ring systems^[17a,29] and for their alkylated analogues,^[8b] and reveal the strong donor character of dithienopyrrole as it was previously evidenced in conjugated donor-acceptor polymers,^[30] and in agreement with the calculated data.

Concerning the reduction process, the rigidification of bithiophene as DTT relay (compounds **d**) has no influence on E_{red} , whereas CPDT and DTP derivatives exhibit increased $|E_{\text{red}}|$ values, when compared with BT compounds (**1–2a**). E_{LUMO} data are in agreement with this observed trend.

A shift of the $|E_{\text{red}}|$ values towards less cathodic potentials is observed when changing the acceptor from the thiobarbiturate group (compounds **1**) to the TCF moiety (compounds **2**), confirming the superior electron-withdrawing ability of the TCF unit. On the other hand, there is a slight shift of the E_{ox} values (E_{ox1} and E_{ox2}) towards less anodic potentials when passing from **1** derivatives to their TCF counterparts. These trends are confirmed by computational calculations, which show that E_{HOMO} (E_{LUMO}) values for systems **2** are higher (lower) than those encountered for their **1** analogues.

UV-Vis Spectroscopy

The UV-vis absorption maxima and the extinction coefficients ($\log \epsilon$) of the studied compounds in different solvents are summarized in Table 2. For the sake of comparison, data for systems (1–2)d are also gathered. (See spectra in Supporting Information). All chromophores show intense and broad CT bands, extending into the near-infrared in some cases (2b–c).

Table 2. UV-Vis data.^[a]

Compound	$\lambda_{\max}$ (log ϵ) 1,4-dioxane	$\lambda_{\max}$ (log ϵ) CH ₂ Cl ₂	$\lambda_{\max}$ (log ϵ) DMF
1a	630 (4.68)	655 (4.70)	643 (4.56)
1b	603 (4.70) 671 (4.86)	614 (4.59) 697 (4.86)	612 (sh) 691 (4.85)
1c	615 (4.89) 659 (5.03)	632 (sh) 680 (5.01)	674 (4.99)
1d ^[b]	636 (4.76)	659 (4.75)	642 (4.61)
2a	658 (4.65)	703 (4.68)	666 (4.47)
2b	717 (4.40)	658 (4.33) 800 (4.50)	657 (4.36) 755 (4.43)
2c	686 (4.47) 740 (4.52)	718 (sh) 788 (4.87)	770 (4.37)
2d ^[b]	658 (4.46)	708 (4.64)	675 (4.52)

[a] All $\lambda_{\max}$ data are in nm; units for ϵ are M⁻¹ cm⁻¹. [b] Data from reference [11].

Whereas the spectra of BT derivatives (1–2)a show broad unresolved absorption bands,^[7c] those of CPDT and DTP systems (1–2)b–c exhibit structured bands in some of the solvents studied, typical of rigid conjugated systems.^[9] Similar trends were reported when the unsubstituted heterocyclic cores (BT, CPDT, DTP) were compared,^[9,29,31] in the same way as when they act as relays in symmetrically substituted derivatives.^[8b] Concerning the previously reported DTT chromophores,^[11] broad and structureless bands were observed, as for other D- π -A systems featuring this π -spacer.^[10a]

Comparison of compounds that only differ in the acceptor unit shows a bathochromic shift for TCF derivatives 2, in line with its higher electron-withdrawing character, and in agreement with their electrochemical properties.

Rigidification of the BT relay has a significant effect on the electronic absorption properties of the chromophores. Thus, CPDT and DTP derivatives (1–2)b–c present a significant red shift of $\lambda_{\max}$ when compared to (1–2)a, more pronounced in derivatives 2, with the more efficient acceptor TCF (e.g., 0.21 eV for 2a/2b and 0.11 eV for 1a/1b, both in CH₂Cl₂). This trend parallels that reported for other D- π -A compounds featuring these π -spacers.^[14,28a] Moreover, (1–2)b are bathochromically shifted with respect to (1–2)c (for compounds 2, this behavior is only observed in CH₂Cl₂), in agreement with the trend followed

by D- π -A compounds intended for DSSCs with CPDT and DTP as π -bridges.^[28,32]

Data in Table 2 indicate in all cases a positive solvatochromism on passing from 1,4-dioxane to CH₂Cl₂, which becomes negative when comparing CH₂Cl₂ and DMF. Although this change in behavior has already been reported for other D- π -A systems^[6c,10a,33] the transition energies for compounds 2a–c have been plotted as a function of the π^* polarity scale^[34] (Figure 5) in order to ascertain the dependence of the band position on solvent polarity for these compounds. The negative slope of the linear correlation for the transition energies indicates a positive solvatochromic response as a result of the higher stabilization of the excited state relative to the ground state on increasing solvent polarity. The same behavior can be assumed for compounds 1a–c.

Figure 5. Correlation between transition energy and solvent polarity (π^* scale) for compounds 2a–c. (Ethyl acetate: 0.45, 1,4-dioxane: 0.49, acetonitrile: 0.66, DMF: 0.88, DMSO:1.00).

TD-DFT calculations (see Table S1 in Supporting Information) are only in moderate agreement with experimental results yielding overestimated vertical excitation energies by 0.13–0.24 eV. The first excited state is mainly contributed by a one electron HOMO to LUMO transition. An increased dipole moment on excitation is predicted in every case in agreement with the observed positive solvatochromic effect and positive hyperpolarizabilities.

Calculations also predict the correct trends in excitation energies. There is a bathochromic shift on passing from compounds 1 to their analogues 2 with a decreased excitation energy of 0.14–0.22 eV due to the lower LUMO energy of compounds 2 having a stronger acceptor, and the predicted absorption band for rigidified compounds also follows the experimental trend $\lambda(b) > \lambda(c) > \lambda(d)$.

Nonlinear Optical properties

The second-order nonlinear optical properties of derivatives (1–2)a–c were measured by electric field-induced second harmonic generation (EFISHG) in dichloromethane at 1907 nm, and the zero-frequency $\mu\beta_0$ values were calculated by using the two-level model^[35] with the lowest energy absorption band for each compound. (Table 3) Data for the previously reported (1–2)d^[11]

are also gathered. As it has been mentioned before, broad bands have been found for all systems, extending into the near-infrared in some cases. Specifically, $\mu\beta$ values for compounds **2b–c** have been obtained taken into account their absorption ($\alpha_{2\omega}$) at the harmonic wavelength (954 nm). This correction is especially significant for **2b** and, thus, the estimation of their $\mu\beta_0$ values should be treated with caution. For the sake of comparison, Disperse Red 1, a common benchmark for organic NLO chromophores shows a $\mu\beta_0$ value of ca. 490×10^{-48} esu in CH_2Cl_2 , under the same experimental conditions.

Table 3. Experimental and calculated NLO properties.

Compound	$\mu\beta_{\text{exp}}^{[a]}$ (10^{-48} esu)	$\mu\beta_{\text{calc}}^{[b]}$ (10^{-48} esu)	$\mu\beta_{\text{calc}}^{[c]}$ (10^{-48} esu)
1a	3100	1440	2685
1b	4100	1650	2877
1c	5000	2100	2857
1d ^[d]	4000	1800	2403
2a	15600	6130	7946
2b	13000 ^[e]	3300	10344
2c	26000	6840	10997
2d ^[d]	9200	3500	6447

[a] $\mu\beta$ values determined in CH_2Cl_2 at 1907 nm (experimental uncertainty less than $\pm 15\%$, except for **2b** ($\sim 20\%$)). [b] Experimental $\mu\beta_0$ values in CH_2Cl_2 calculated using the two-level model. [c] Calculated at the HF/6-31G*/PCM-M06-2x/6-31G* level in CH_2Cl_2 . [d] Experimental data from reference ^[11]. [e] The $\mu\beta$ value was determined from a freshly prepared sample.

For all the π -relays studied, derivatives **2** have remarkably superior responses than their analogues **1**, revealing again the higher strength of the TCF acceptor.

The influence on the NLO properties of passing from BT chromophores **a** to the rigidified **b–d** ones depends on the acceptor moiety. Thus, for thiobarbiturate-containing compounds **1** rigidification of the BT core implies in all cases an increase of the NLO response, being remarkably important for the DTP system **1c** ($\mu\beta_0$ (**1c**)/ $\mu\beta_0$ (**1a**) = 1.46). Nevertheless, for TCF derivatives **2**, a slight increase of the $\mu\beta_0$ value is observed only by substituting the BT relay for the DTP core. ($\mu\beta_0$ (**2c**)/ $\mu\beta_0$ (**2a**) = 1.12) Chromophores **2b,d** present lower NLO responses (close to half in terms of $\mu\beta_0$ values) than **2a**.

In any case, for both series **1–2**, DTP derivative **c** show the highest $\mu\beta_0$ value, pointing again to the strong donor character for this fused-ring system, in agreement with calculated data and the electrochemical measurements. This auxiliary donor character favors the ICT throughout the whole chromophore.

The calculated $\mu\beta_0$ values (HF/6-31G*, Table 3) reproduce essentially the trends observed in the experimental results, in terms of the influence of the acceptor and the DTP as π -relay, e.g., better responses for **2** systems than for the analogues **1** and for **c** chromophore in series **2**. However, regarding the influence of the rigidification of the BT moiety, $\mu\beta_0$ calculations do not reproduce the influence on the acceptor unit, and CPDT and DTP heterocycles show always the highest values, with a greater difference in the **2** series than in the **1** one, contrary to the experimental data.

Taking all data into account, results show that the role played by the rigidification of the BT ring is less relevant than the character of the fused heterocycle formed, e.g., it is not enough to rigidify the BT moiety for improving the NLO response, it is extremely important how this rigidification is made. And for this purpose, the inclusion of a DTP ring (used for the first time as π -spacer in NLO-chromophores) has proven to be the most efficient approach.

Thermal stability

Thermal stabilities of compounds (**1–2**)**a–c** were studied by thermogravimetric analysis (TGA) (Table 4), estimating their decomposition temperatures (T_d) as the intercept of the leading edge of the weight loss with the baseline of the TGA scans.

Table 4. Thermal Stability.

Compd	T_d (°C)	Compd	T_d (°C)
1a	307	2a	303
1b	288	2b	293
1c	293	2c	304
1d ^[a]	343	2d ^[a]	342

[a] Data from reference ^[11].

All derivatives (**1–2**)**a–c** are thermally stable with decomposition temperatures above 288°C. For series **b–c**, derivatives of acceptor TCF **2** show higher decomposition temperatures than those of their thiobarbiturate analogues.

Concerning the effect of the rigidification of BT relay, the inspection of values reveals that only DTT systems (**1–2**)**d**^[11] show a significant enhancement of the thermal stability. The presence of hexyl chain,^[9] may be related to the lower T_d values found, in general, for CPDT and DTP chromophores **b–c** compared to BT derivatives **a** (apart from compounds **2c** and **2a**, which values are essentially identical).

Conclusions

The influence of the rigidification of the BT unit on the ground-state polarization and on the second-order NLO properties has been studied by synthesizing D- π -A systems containing BT (**a**), CDPT (**b**) and DTP (**c**) moieties as π -relays and comparing their

NLO responses. Their analogous and previously reported DTT derivatives^[11] **1–2(d)** have also been included in this comparison.

Substitution of the BT moiety by a rigidified fragment (either CPDT or DTP) in the chromophores herein studied leads to more polarized structures, as shown by the calculated BLA values and NBO charges. These data, together with the lower E_{ox2} value (related to the heterocyclic π -spacer) found for DTP systems **c** reveal the strong donor character of the dithienopyrrole moiety.

On the other hand, CV and UV–vis spectra show lower gaps for CPDT and DTP chromophores compared to their BT analogues, being **b < c**. Regarding the thermal stability, only DTT-containing compounds **d** have higher T_d values than those of the BT systems.

The second-order nonlinearities are influenced by the acceptor group and by the manner in which the rigidification of the BT moiety is made. For thiobarbiturate derivatives **1** rigidification leads in all cases to an enhancement of the NLO response, but for compounds **2**, with the more efficient TCF, only DTP derivative **2c** slightly improves the $\mu\beta_0$ value of its BT analogue.

Thus, the replacement of the BT core by a DTP unit provides the best approach to upgrade the second-order nonlinearities. Moreover, this heterocyclic unit, used for the first time in D- π -A compounds intended for NLO, has proven to allow a good charge transfer between the end groups of the chromophores and it is accessible by a relatively easy synthetic route. In addition, a wide range of substituents can be incorporated in the N atom, allowing tuning the properties of the resulting materials. Taking these data into account, dithienopyrrole becomes a suitable π -relay for the preparation of novel structures with high second-order NLO responses.

Experimental Section

General information: See Supporting Information.

Starting materials: 1,3-diethyl-2-thiobarbituric acid (**7**) is commercially available. Compounds **5a**,^[21] **6**^[20] and acceptor TCF (**8**)^[36] were prepared as previously described. 4,4-dihexylcyclopenta[2,1-*b*:3,4-*b'*]dithiophene **5b** was prepared following the same procedure reported for the corresponding diethylhexyl analogue.^[16b] *N*-hexyldithieno[3,2-*b*:2',3'-*d'*]pyrrole **5c** was prepared following the same procedure reported for the corresponding *N*-(2-hexyldecyl) analogue.^[17b]

5'-(1,3-dioxolan-2-yl)-2,2'-bithiophene-5-carbaldehyde (4a) To a solution of (**5a**) (0.602 g, 2.53 mmol) in dry THF (18 mL) at -78°C , *n*BuLi 1.6 M in hexanes (2 mL, 3.2 mmol), was added under argon atmosphere. The reaction mixture was stirred for 30 min, and dry DMF (0.5 mL, 6.44 mmol) was then added. After stirring for further 2.5 hours at -78°C , a solution of saturated NH_4Cl (50 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 $\times$ 50 mL), and the resulting organic layer was washed with a solution of saturated NH_4Cl (50 mL), dried over MgSO_4 and evaporated. The crude product was purified by flash column chromatography (silicagel) using hexane/AcOEt 8:2 as eluent, affording **4a** (0.571 g, 2.14 mmol, 84%) as a yellow solid. M.p. $158\text{--}160^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 9.86 (s, 1H, $-\text{CHO}$), 7.67 (d, J = 3.9 Hz, 1H,

BT-*H*), 7.24–7.23 (m, 2H, BT-*H*), 7.12 (d, J = 3.7 Hz, 1H, BT-*H*), 6.09 (s, 1H, $-\text{CH}-\text{OCH}_2\text{CH}_2\text{O}-$), 4.17–4.02 ppm (m, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$); ^{13}C NMR (100 MHz, CDCl_3): δ 182.5, 146.7, 143.6, 141.8, 137.3, 136.6, 127.2, 125.6, 124.4, 99.8, 65.2 ppm; IR (KBr): ν = 2885 (C-H), 2836 (C-H), 1653 (C=O), 1553 (C=C, Ar), 1517 cm^{-1} (C=C, Ar); HRMS (ESI⁺): m/z calcd for $\text{C}_{12}\text{H}_{10}\text{NaO}_3\text{S}_2$: 288.9964 [M+Na]⁺; found: 288.9952; elemental analysis calcd (%) for $\text{C}_{12}\text{H}_{10}\text{O}_3\text{S}_2$: C 54.12, H 3.78; found C 53.87, H 3.95.

5'-(2,6-diphenyl-4*H*-pyran-4-ylidene)methyl)-2,2'-bithiophene-5-carbaldehyde (3a) To a solution of **6** (0.704 g, 1.62 mmol) in dry THF (20 mL) at -78°C , *n*BuLi 1.6 M in hexanes (1.3 mL, 2.11 mmol) was added under argon atmosphere. The solution turns to dark green and was stirred at this temperature for 15 minutes. Then, a solution of **4a** (0.432 g, 1.62 mmol) in dry THF (5 mL) was slowly added via a syringe. The mixture was stirred and the reaction medium was slowly warmed to room temperature (TLC monitoring). When the reaction finished, an aqueous solution of HCl 1N (40 mL) was added and the mixture was stirred for 1 h at room temperature. The aqueous layer was extracted with CH_2Cl_2 (3 $\times$ 50 mL). The resulting organic layer was dried over MgSO_4 and evaporated. The crude product was purified by flash column chromatography (silicagel) using hexane/AcOEt 8.5:1.5 as eluent, affording **3a** (0.566 g, 1.29 mmol, 80%) as a dark red solid. M.p. $189\text{--}191^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 9.84 (s, 1H, $-\text{CHO}$), 7.87–7.82 (m, 2H, phenyl-*H*), 7.77–7.72 (m, 2H, phenyl-*H*), 7.66 (d, J = 4.0 Hz, 1H, BT-*H*), 7.55–7.38 (m, 6H, phenyl-*H*), 7.28 (d, J = 4.0 Hz, 1H, BT-*H*), 7.23 (d, J = 4.0 Hz, 1H, BT-*H*), 7.09 (dd, J_1 = 1.8 Hz, J_2 = 0.6 Hz, 1H, pyranilidene-*H*), 6.89 (d, J_1 = 4.0 Hz, J_2 = 0.6 Hz, 1H, BT-*H*), 6.43 (d, J = 1.8 Hz, 1H, pyranilidene-*H*), 6.07 ppm (s, 1H, pyranilidene=C-*H*); ^{13}C NMR (75 MHz, CDCl_3): δ 182.3, 153.9, 151.5, 147.8, 144.3, 140.6, 137.6, 133.0, 132.8, 132.2, 129.8, 129.5, 129.3, 128.8, 128.7, 126.6, 126.4, 125.1, 124.5, 123.1, 108.4, 107.1, 102.6 ppm; IR (KBr): ν = 1643 cm^{-1} (C=O); HRMS (ESI⁺): m/z calcd for $\text{C}_{27}\text{H}_{19}\text{O}_2\text{S}_2$: 439.0821 [M+H]⁺; found: 439.0799; elemental analysis calcd (%) for $\text{C}_{27}\text{H}_{18}\text{O}_2\text{S}_2$: C 73.94, H 4.14; found C 73.72, H 3.94.

4,4-dihexylcyclopenta[2,1-*b*:3,4-*b'*]dithiophene (5b) To a suspension of CPDT^[16b] (0.204 g, 1.34 mmol), hexyl bromide (0.26 mL, 2.8 mmol) and potassium iodide (4 mg, 0.024 mmol) in DMSO (5 mL), potassium hydroxide (0.234 g, 4.25 mmol) was added in several portions at 0°C under argon atmosphere. The mixture was stirred for 12 h at room temperature, then water (10 mL) was added and the aqueous layer was extracted with diethyl ether (4 $\times$ 50 mL). The combined organic layer was washed with water (2 $\times$ 50 mL), dried over MgSO_4 and evaporated. The crude product was purified by flash column chromatography (silicagel) using hexane as eluent, affording **5b** (0.408 g, 1.18 mmol, 88%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.14 (d, J = 4.9 Hz, 2H, CPDT-*H*), 6.93 (d, J = 4.9 Hz, 2H, CPDT-*H*), 1.85–1.77 (m, 4H, C- CH_2 -C₅H₁₁), 1.21–1.08 (m, 12H, C- CH_2 -(CH₂)₃-C₂H₅), 0.98–0.89 (m, 4H, C-(CH₂)₄-CH₂-CH₃), 0.80 ppm (t, J = 6.9 Hz, 6H, C-(CH₂)₅-CH₃); ^{13}C NMR (100 MHz, CDCl_3): δ 158.1, 136.4, 124.4, 121.6, 53.2, 37.7, 31.6, 29.7, 24.5, 22.6, 14.0 ppm; HRMS (ESI⁺): m/z calcd for $\text{C}_{21}\text{H}_{30}\text{S}_2$: 346.1783 [M⁺]; found: 346.1794.

4,4-dihexylcyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2,6-dicarbaldehyde (4b) To a solution of 4,4-dihexylcyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**5b**) (0.245 g, 0.7 mmol) and previously dried TMEDA (325 μL , 2.16 mmol) in dry hexane (5 mL) at room temperature, *n*BuLi 1.6 M in hexanes (1.35 mL, 2.16 mmol) was added under argon atmosphere. The mixture was refluxed for 1 hour, cooled to room temperature, and then, to -40°C . Dry

THF (4 mL), and dry DMF (180 μ L, 2.30 mmol) were added and the mixture was warmed up to room temperature for 3 hours. HCl 1N (50 mL) was then added, and the aqueous phase was extracted with AcOEt (3 $\times$ 50 mL). The organic layer was washed with water (3 $\times$ 50 mL), dried over MgSO₄ and evaporated. The crude product was purified by flash column chromatography (silicagel) using hexane/AcOEt 9.5:0.5 as eluent, affording **4b** (0.214 g, 0.53 mmol, 76%) as a yellow powder. M.p. 98 °C (dec.); ¹H NMR (400 MHz, CDCl₃): δ = 9.91 (s, 2H, -CHO), 7.62 (s, 2H, CPDT-H), 1.94–1.87 (m, 4H, C-CH₂-C₅H₁₁), 1.23–1.10 (m, 12H, C-CH₂-(CH₂)₃-C₂H₅), 1.00–0.88 (m, 4H, C-(CH₂)₄-CH₂-CH₃), 0.81 ppm (t, *J* = 7.0 Hz, 6H, C-(CH₂)₅-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 182.9, 161.3, 146.6, 145.1, 129.5, 54.3, 37.5, 31.5, 29.5, 24.6, 22.5, 14.0 ppm; IR (KBr): $\bar{\nu}$ = 1656 cm⁻¹ (C=O); HRMS (ESI⁺): *m/z* calcd for C₂₃H₃₁O₂S₂: 403.1760 [M+H]⁺; found: 403.1744; elemental analysis calcd (%) for C₂₃H₃₀O₂S₂: C 68.61, H 7.51; found C 68.33, H 7.30.

4,4-dihexyl-6-(2,6-diphenyl-4H-pyran-4-ylidenemethyl)cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (3b) To a solution of **6** (0.128 g, 0.298 mmol) in dry THF (4 mL) at -30°C, *n*BuLi 1.6 M in hexanes (0.85 mL, 1.36 mmol), was added under argon atmosphere. The solution turns to dark green and was stirred at this temperature for 15 minutes. Then, this solution was slowly added with a cannula to a solution of **4b** (0.120 g, 0.298 mmol) at -30°C in dry THF (3 mL) and the mixture was stirred for a further hour. A solution of saturated NH₄Cl (50 mL) was then added and the aqueous phase was extracted with AcOEt (3 $\times$ 50 mL). The resulting organic layer was dried over MgSO₄ and evaporated. The crude product was purified by flash column chromatography (silicagel) using hexane/AcOEt 9.5:0.5 as eluent, affording **3b** (0.117 g, 0.189 mmol, 63%) as a dark red solid. M.p. 29–31°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.80 (s, 1H, -CHO), 7.91–7.85 (m, 2H, phenyl-H), 7.81–7.75 (m, 2H, phenyl-H), 7.56–7.40 (m, 7H, phenyl-H + CPDT-H), 7.16 (dd, *J*₁ = 1.8 Hz, *J*₂ = 0.5 Hz, 1H, pyranylidene-H), 6.80 (d, *J* = 0.5 Hz, 1H, CPDT-H), 6.46 (d, *J* = 1.8 Hz, 1H, pyranylidene-H), 6.14 (s, 1H, pyranylidene=C-H), 1.92–1.80 (m, 4H, C-CH₂-C₅H₁₁), 1.21–1.11 (m, 12H, C-CH₂-(CH₂)₃-C₂H₅), 1.03–0.93 (m, 4H, C-(CH₂)₄-CH₂-CH₃), 0.82 ppm (t, *J* = 6.7 Hz, 6H, C-(CH₂)₅-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 182.1, 162.9, 157.3, 153.8, 151.4, 147.9, 142.2, 133.0, 132.9, 129.8, 129.3, 128.8, 128.7, 125.1, 124.5, 119.5, 108.6, 108.4, 102.9, 53.7, 37.8, 31.6, 29.6, 24.5, 22.6, 14.0 ppm; IR (KBr): $\bar{\nu}$ = 1652 (C=O), 1576 (C=C, Ar), 1558 cm⁻¹ (C=C, Ar); HRMS (ESI⁺): *m/z* calcd for C₄₀H₄₂O₂S₂: 618.2621 [M⁺]; found: 618.2619; calcd for C₄₀H₄₃O₂S₂: 619.2699 [M+H]⁺; found: 619.2679; elemental analysis calcd (%) for C₄₀H₄₂O₂S₂: C 77.63, H 6.84; found C 77.92, H 7.07.

N-hexyldithieno[3,2-b:2',3'-d]pyrrole (5c) A solution of 3,3'-dibromo-2,2'-bithiophene^[17b] (0.500 g, 1.54 mmol) in dry toluene (6 mL) was purged with argon for 20 min. Then ^tBuONa (0.392 g, 3.96 mmol), Pd₂(dba)₃ (36.4 g, 0.04 mmol) and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) (0.113 g, 0.175 mmol) were added. Finally, hexylamine (0.25 mL, 1.54 mmol) was added and the mixture was heated at 110°C for 7h. After the reaction was cooled to room temperature, water (50 mL) was added and the aqueous layer extracted with diethyl ether (3 $\times$ 50 mL). The combined organic layer was washed with water (3 $\times$ 50 mL) and a saturated solution of NaCl (3 $\times$ 50 mL), then dried over MgSO₄. Evaporation of the solvent and purification by flash column chromatography (silicagel) using hexane/AcOEt 9:1 as eluent, afforded **5c** (0.308 g, 1.17 mmol, 76%) as a colorless oil which solidified on standing (white solid). M.p. 42–44°C (Ref. ^[17a]: m.p. 41.7–42.5°C); ¹H NMR (300 MHz, CDCl₃): δ = 7.13 (d, *J* = 5.3 Hz, 2H, DTP-H), 7.00 (d, *J* = 5.3 Hz, 2H, DTP-H), 4.19 (t, *J* = 7.0 Hz, 2H, N-CH₂-C₅H₁₁), 1.91–1.82 (m, 2H, N-CH₂-CH₂-C₄H₉), 1.36–1.25 (m, 6H, N-(CH₂)₂-(CH₂)₃-CH₃), 0.88–0.84 ppm (m, 3H, N-(CH₂)₅-CH₃); ¹³C NMR (75 MHz, CDCl₃): δ =

144.9, 122.7, 114.6, 110.9, 47.4, 31.4, 30.3, 26.7, 22.5, 14.0 ppm; HRMS (ESI⁺): *m/z* calcd for C₁₄H₁₇NS₂: 263.0797 [M⁺]; found: 263.0811; elemental analysis calcd (%) for C₁₄H₁₇NS₂: C 63.83, H 6.50, N 5.32; found C 64.10, H 6.64, N 5.12.

N-hexyldithieno[3,2-b:2',3'-d]pyrrole-2,6-dicarbaldehyde (4c) This compound was prepared following the same procedure above explained for **4b**, starting from: *N*-hexyldithieno[3,2-b:2',3'-d]pyrrole (**5c**) (0.300 g, 1.14 mmol), previously dried TMEDA (520 μ L, 3.47 mmol), *n*BuLi 1.6 M in hexanes (2.2 mL, 3.52 mmol) and dry DMF (260 μ L, 3.36 mmol). The crude product was purified by flash column chromatography (silicagel) using hexane/AcOEt 8:2 as eluent, then 7:3, affording **4c** (0.275 g, 0.86 mmol, 75%) as a yellow powder. M.p. 158–160 °C; ¹H NMR (400 MHz, CDCl₃): δ = 9.95 (s, 2H, -CHO), 7.69 (s, 2H, DTP-H), 4.27 (t, *J* = 7.0 Hz, 2H, N-CH₂-C₅H₁₁), 1.96–1.87 (m, 2H, N-CH₂-CH₂-C₄H₉), 1.37–1.27 (m, 6H, N-(CH₂)₂-(CH₂)₃-CH₃), 0.87 ppm (t, *J* = 7.0 Hz, 3H, N-(CH₂)₅-CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 183.2, 147.3, 144.1, 122.0, 118.7, 47.7, 31.3, 30.2, 26.7, 22.4, 13.9 ppm; IR (KBr): $\bar{\nu}$ = 1659 cm⁻¹ (C=O); HRMS (ESI⁺): *m/z* calcd for C₁₆H₁₈NO₂S₂: 320.0773 [M+H]⁺; found: 320.0766; calcd for C₁₆H₁₇NNaO₂S₂: 342.0593 [M+Na]⁺; found: 342.0581; calcd for C₃₂H₃₄N₂NaO₂S₄: 661.1294 [2M+Na]⁺; found: 661.1310; elemental analysis calcd (%) for C₁₆H₁₇NO₂S₂: C 60.16, H 5.36, N 4.38; found C 60.45, H 5.66, N 4.21.

N-hexyl-6-(2,6-diphenyl-4H-pyran-4-ylidenemethyl)dithieno[3,2-b:2',3'-d]pyrrole-2-carbaldehyde (3c) This compound was prepared following the same procedure above explained for **3b**, starting from: **6** (0.408 g, 0.939 mmol), *n*BuLi 1.6 M in hexanes (0.65 mL, 1.04 mmol) and **4c** (0.300 g, 0.939 mmol). The crude product was purified by flash column chromatography (silicagel) using hexane/AcOEt 8:2 as eluent, then 7:3, affording **3c** (0.241 g, 0.449 mmol, 48%) as a dark red solid. M.p. 68–70°C; ¹H NMR (300 MHz, CDCl₃): δ = 9.82 (s, 1H, -CHO), 7.90–7.84 (m, 2H, phenyl-H), 7.79–7.72 (m, 2H, phenyl-H), 7.55 (s, 1H, DTP-H), 7.53–7.38 (m, 6H, phenyl-H), 7.21 (d, *J* = 1.6 Hz, 1H, pyranylidene-H), 6.76 (s, 1H, DTP-H), 6.42 (d, *J* = 1.6 Hz, 1H, pyranylidene-H), 6.12 (s, 1H, pyranylidene=C-H), 4.15 (t, *J* = 7.0 Hz, 2H, N-CH₂-C₅H₁₁), 1.93–1.82 (m, 2H, N-CH₂-CH₂-C₄H₉), 1.40–1.28 (m, 6H, N-(CH₂)₂-(CH₂)₃-CH₃), 0.93–0.82 ppm (m, 3H, N-(CH₂)₅-CH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 182.4, 153.7, 151.4, 149.4, 146.0, 144.0, 139.1, 133.1, 132.9, 129.7, 129.3, 129.2, 128.8, 128.7, 125.0, 124.5, 123.9, 118.7, 113.5, 108.7, 108.5, 107.6, 102.8, 47.4, 31.4, 30.2, 26.7, 22.5, 14.0 ppm; IR (KBr): $\bar{\nu}$ = 1642 (C=O), 1578 cm⁻¹ (C=C, Ar); HRMS (ESI⁺): *m/z* calcd for C₃₃H₃₀NO₂S₂: 536.1712 [M+H]⁺; found: 536.1713; elemental analysis calcd (%) for C₃₃H₂₉NO₂S₂: C 73.99, H 5.46, N 2.61; found C 74.11, H 5.28, N 2.83.

5-((5'-(2,6-diphenyl-4H-pyran-4-ylidene)methyl)-2,2'-bithiophen-5-yl)methylene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6-dione (1a) To a solution of **3a** (0.056 g, 0.128 mmol) in absolute ethanol (6 mL), 1,3-diethyl-2-thiobarbituric acid (**7**) (0.030 g, 0.152 mmol) was added in one portion under argon atmosphere, and the mixture was refluxed for 24 h. The reaction was cooled to room temperature and then to 0°C. The resulting solid was isolated by filtration and washed with cold hexane and a cold mixture of hexane/CH₂Cl₂ 8:2. Product **1a** was obtained as a dark blue solid (0.047 g, 0.076 mmol, 60%). M.p. 276–278°C; ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.59 (s, 1H, BT-CH=acceptor), 7.94–7.91 (m, 2H, phenyl-H), 7.86–7.81 (m, 2H, phenyl-H), 7.56–7.42 (m, 9H, phenyl-H + BT-H), 7.19 (d, *J* = 2.1 Hz, 1H, pyranylidene-H), 7.02 (d, *J* = 4.2 Hz, 1H, BT-H), 6.56 (d, *J* = 2.1 Hz, 1H, pyranylidene-H), 6.18 (s, 1H, pyranylidene=C-H), 4.63–4.52 (m, 4H, N-CH₂-CH₃), 1.36–1.26 ppm (m,

6H, N-CH₂-CH₃); ¹³C NMR: not registered due to its low solubility; IR (KBr): $\bar{\nu}$ = 1649 (C=O), 1547 (C=C, Ar), 1512 cm⁻¹ (C=C, Ar); HRMS (ESI⁺): *m/z* calcd for C₃₅H₂₈N₂O₃S₃: 620.1257 [M]⁺; found: 620.1239; calcd for C₃₅H₂₉N₂O₃S₃: 621.1335 [M+H]⁺; found: 621.1297; elemental analysis calcd (%) for C₃₅H₂₈N₂O₃S₃: C 67.71, H 4.55, N 4.51; found C 67.97, H 4.64, N 4.70.

4,4-dihexyl-5-[6-(2,6-diphenyl-4H-pyran-4-ylidenemethyl)cyclopenta[2,1-b:3,4-b']dithiophene-2-ylmethyl]-1,3-diethyl-2-thioxodihydropyrimidin-4,6-dione (1b) This compound was prepared following the same procedure above explained for **1a**, starting from **3b** (0.049 g, 0.078 mmol) and 1,3-diethyl-2-thiobarbituric acid (**7**) (0.017 g, 0.083 mmol) in absolute ethanol (5 mL). Reaction time: 5 hours. Solvents used for washing: a cold mixture of hexane/CH₂Cl₂ 9:1. Product **1b** was obtained as a dark green solid (0.021 g, 0.026 mmol, 33%). M.p. 240–242°C; ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.59 (s, 1H, CPDT-CH=acceptor), 7.96–7.90 (m, 2H, phenyl-H), 7.86–7.80 (m, 2H, phenyl-H), 7.64–7.44 (m, 7H, phenyl-H + CPDT-H), 7.28 (dd, *J*₁ = 1.6 Hz, *J*₂ = 0.4 Hz, 1H, pyranylidene-H), 6.88 (s, 1H, CPDT-H), 6.60 (d, *J* = 1.6 Hz, 1H, pyranylidene-H), 6.25 (s, 1H, pyranylidene=C-H), 4.65–4.51 (m, 4H, N-CH₂-CH₃), 2.01–1.82 (m, 4H, C-CH₂-C₅H₁₁), 1.37–1.24 (m, 6H, N-CH₂-CH₃), 1.22–1.11 (m, 12H, C-CH₂-(CH₂)₃-C₂H₅), 1.05–0.92 (m, 4H, C-(CH₂)₄-CH₂-CH₃), 0.86–0.76 ppm (m, 6H, C-(CH₂)₅-CH₃); ¹³C NMR: not registered due to its low solubility; IR (KBr): $\bar{\nu}$ = 1651 (C=O), 1545 (C=C, Ar), 1491 cm⁻¹ (C=C, Ar); HRMS (ESI⁺): *m/z* calcd for C₄₈H₅₂N₂O₃S₃: 800.3135 [M]⁺; found: 800.3116; calcd for C₄₈H₅₃N₂O₃S₃: 801.3213 [M+H]⁺; found: 801.3149; elemental analysis calcd (%) for C₄₈H₅₂N₂O₃S₃: C 71.96, H 6.54, N 3.50; found C 72.05, H 6.26, N 3.32.

N-hexyl-5-[6-(2,6-diphenyl-4H-pyran-4-ylidenemethyl)dithieno[3,2-b:2',3'-d]pyrrole-2-ylmethyl]-1,3-diethyl-2-thioxodihydropyrimidin-4,6-dione (1c) This compound was prepared following the same procedure above explained for **1a**, starting from **3c** (0.067 g, 0.126 mmol) and 1,3-diethyl-2-thiobarbituric acid (**7**) (0.027 g, 0.135 mmol) in absolute ethanol (4 mL). Reaction time: 5 hours. Solvents used for washing: cold hexane and a cold mixture of hexane/CH₂Cl₂ 8:2. Product **1c** was obtained as a dark blue solid (0.074 g, 0.103 mmol, 82%). M.p. 85°C (dec.); ¹H NMR (300 MHz, CD₂Cl₂): δ = 8.60 (s, 1H, DTP-CH=acceptor), 7.96–7.87 (m, 2H, phenyl-H), 7.86–7.77 (m, 2H, phenyl-H), 7.61–7.40 (m, 7H, phenyl-H + DTP-H), 7.28 (br s, 1H, pyranylidene-H), 6.80 (s, 1H, DTP-H), 6.57 (br s, 1H, pyranylidene-H), 6.22 (s, 1H, pyranylidene=C-H), 5.50–4.68 (m, 4H, N-CH₂-CH₃), 4.17 (t, *J* = 6.8 Hz, 2H, N-CH₂-C₅H₁₁), 1.97–1.81 (m, 2H, N-CH₂-CH₂-C₄H₉), 1.41–1.20 (m, 12H, N-(CH₂)₂-(CH₂)₃-CH₃ + N-CH₂-CH₃), 0.93–0.81 ppm (m, 3H, N-(CH₂)₅-CH₃); ¹³C NMR: not registered due to its low solubility; IR (KBr): $\bar{\nu}$ = 1647 (C=O), 1581 (C=C, Ar), 1497 cm⁻¹ (C=C, Ar); HRMS (ESI⁺): *m/z* calcd for C₄₁H₄₀N₃O₃S₃: 718.2226 [M+H]⁺; found: 718.2253; elemental analysis calcd (%) for C₄₁H₃₉N₃O₃S₃: C 68.59, H 5.48, N 5.85; found C 68.84, H 5.20, N 5.64.

(E)-2-(3-cyano-4-(2-(5'-((2,6-diphenyl-4H-pyran-4-ylidene)methyl)-2,2'-bithiophen-5-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (2a) To a solution of **3a** (0.100 g, 0.23 mmol) and acceptor TCF (**8**) (0.053 g, 0.26 mmol) in CHCl₃ (5 mL), triethylamine (33 μ L, 0.24 mmol) was added under argon atmosphere, and the mixture was refluxed for 28 h. The reaction was cooled to room temperature and then to 0°C. The resulting solid was isolated by filtration and washed with cold hexane. Product **2a** was obtained as a copper-coloured solid (0.087 g, 0.141 mmol, 61%). M.p. 293°C (dec.); ¹H NMR (400 MHz, [D₆]DMSO, 323K): δ = 8.09 (d, *J* = 15.8 Hz, 1H, -CH=CH-acceptor), 7.94–7.92 (m,

2H, phenyl-H), 7.88–7.86 (m, 2H, phenyl-H), 7.80 (d, *J* = 4.0 Hz, 1H, BT-H), 7.60–7.47 (m, 8H, phenyl-H + BT-H), 7.16 (d, *J* = 4.0 Hz, 1H, BT-H), 7.11 (d, *J* = 1.3 Hz, 1H, pyranylidene-H), 6.87 (d, *J* = 1.3 Hz, 1H, pyranylidene-H), 6.76 (d, *J* = 15.8 Hz, 1H, -CH=CH-acceptor), 6.29 (s, 1H, pyranylidene=C-H), 1.80 ppm (s, 6H, TCF-CH₃); ¹³C NMR (100 MHz, [D₆]DMSO, 323K): δ = 174.0, 153.4, 150.6, 143.8, 139.2, 137.7, 137.3, 132.0, 131.8, 131.7, 129.6, 129.1, 129.0, 128.6, 128.4, 127.3, 126.9, 125.1, 124.6, 124.0, 112.2, 112.0, 111.4, 110.5, 108.2, 107.1, 101.8, 98.0, 25.1 ppm; IR (KBr): $\bar{\nu}$ = 2229 (C≡N), 1648 (C=C), 1563 cm⁻¹ (C=C); HRMS (ESI⁺): *m/z* calcd for C₃₈H₂₅N₃O₂S₂: 619.1383 [M]⁺; found: 619.1366; elemental analysis calcd (%) for C₃₈H₂₅N₃O₂S₂: C 73.64, H 4.07, N 6.78; found C 73.43, H 3.93, N 6.95.

4,4-dihexyl-(E)-2-(3-cyano-4-(2-(6-(2,6-diphenyl-4H-pyran-4-ylidenemethyl)cyclopenta[2,1-b:3,4-b']dithiophene-2-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (2b) To a solution of **3b** (0.056 g, 0.09 mmol) and acceptor TCF (**8**) (0.020 g, 0.10 mmol) in absolute EtOH (3 mL), a mixture of pyridine (70 μ L) and acetic acid (35 μ L) was added under argon atmosphere, and the mixture was refluxed for 28 h. The reaction was cooled to room temperature and then to 0°C. The resulting solid was isolated by filtration and washed with cold EtOH and cold hexane. Product **2b** was obtained as a dark blue solid (0.037 g, 0.046 mmol, 51%). M.p. 213–215°C; ¹H NMR (400 MHz, CDCl₃): δ = 7.92–7.86 (m, 2H, phenyl-H), 7.82–7.76 (m, 2H, phenyl-H), 7.57–7.42 (m, 7H, phenyl-H + -CH=CH-acceptor), 7.29 (s, 1H, CPDT-H), 7.18 (d, *J* = 1.4 Hz, 1H, pyranylidene-H), 6.81 (s, 1H, CPDT-H), 6.52 (d, *J* = 1.4 Hz, 1H, pyranylidene-H), 6.47 (d, *J* = 14.9 Hz, 1H, -CH=CH-acceptor), 6.20 (s, 1H, pyranylidene=C-H), 1.92–1.82 (m, 4H, C-CH₂-C₅H₁₁), 1.73 (s, 6H, TCF-CH₃), 1.29–1.09 (m, 12H, C-CH₂-(CH₂)₃-C₂H₅), 1.00–0.92 (m, 4H, C-(CH₂)₄-CH₂-CH₃), 0.89–0.75 ppm (m, 6H, C-(CH₂)₅-CH₃); ¹³C NMR: not registered due to its low solubility; IR (KBr): $\bar{\nu}$ = 2221 cm⁻¹ (C≡N); HRMS (ESI⁺): *m/z* calcd for C₅₁H₄₉N₃O₂S₂: 799.3261 [M]⁺; found: 799.3208; elemental analysis calcd (%) for C₅₁H₄₉N₃O₂S₂: C 76.56, H 6.17, N 5.25; found C 76.73, H 5.96, N 5.36.

N-hexyl-(E)-2-(3-cyano-4-(2-(6-(2,6-diphenyl-4H-pyran-4-ylidenemethyl)dithieno[3,2-b:2',3'-d]pyrrole-2-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (2c) This compound was prepared following the same procedure above explained for **2b**, starting from **3c** (0.070 g, 0.13 mmol), acceptor TCF (**8**) (0.020 g, 0.10 mmol), absolute EtOH (5 mL) and a mixture of pyridine (100 μ L) and acetic acid (50 μ L). Reaction time: 48 hours. Solvents used for washing: cold hexane, then a cold mixture of hexane/CH₂Cl₂ 7:3. Product **2c** was obtained as a dark blue solid (0.074 g, 0.102 mmol, 79%). M.p. 202°C (dec.); ¹H NMR (300 MHz, [D₆]DMSO, 335K): δ = 8.16 (d, *J* = 15.4 Hz, 1H, -CH=CH-acceptor), 8.00–7.85 (m, 5H, phenyl-H + DTP-H), 7.63–7.47 (m, 6H, phenyl-H), 7.25 (s, 1H, DTP-H), 7.24 (d, *J* = 1.5 Hz, 1H, pyranylidene-H), 6.93 (d, *J* = 1.5 Hz, 1H, pyranylidene-H), 6.64 (d, *J* = 15.4 Hz, 1H, -CH=CH-acceptor), 6.36 (s, 1H, pyranylidene=C-H), 4.36–4.25 (m, 2H, N-CH₂-C₅H₁₁), 1.82–1.75 (s, 6H, TCF-CH₃), 1.37–1.22 (m, 8H, N-CH₂-(CH₂)₄-CH₃), 0.87–0.79 ppm (m, 3H, N-(CH₂)₅-CH₃); ¹³C NMR: not registered due to its low solubility; IR (KBr): $\bar{\nu}$ = 2220 cm⁻¹ (C≡N); HRMS (ESI⁺): *m/z* calcd for C₄₄H₃₆N₄O₂S₂: 716.2274 [M]⁺; found: 716.2234; elemental analysis calcd (%) for C₄₄H₃₆N₄O₂S₂: C 73.71, H 5.06, N 7.82; found C 73.93, H 4.84, N 7.68.

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Substitution of the bithiophene (BT) π -spacer by a rigidified fragment in the 4H-pyranylidene chromophores herein studied leads to more polarized structures. The strong donor character of the dithienopyrrole (revealed by electrochemistry and calculated charges) provides the best approach to improve the second-order NLO response.

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Dithienopyrrole as a rigid alternative to the bithiophene π -relay in chromophores with second-order nonlinear optical properties