Chromophores

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 the second-order non-linear 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

that 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 used (thiobarbituric acid), passing from the BT relay to the rigidified units always involves an increase in 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 in $\mu\beta_0$ with respect to the BT chromophore is only observed for the DTP derivative. Thus, rigidification of the BT core 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 that have electron donors (D) and acceptors (A) linked by a π -conjugated core have been extensively studied over the last decades due to their wide applications in nonlinear optics (NLO)^[1] and other research fields, such as organic light emitting diodes (OLEDs)^[2] and dye-sensitized solarcells (DSSCs).^[3]

The π -conjugated spacer plays a determining role in D- π -A systems,^[4] and is the most studied system 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 type of compound. 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 stability. The reverse situation characterizes aryl-type π -relays. The replacement of polyene-like spacers

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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.

However, Considering 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) to give rise to a variety of fused central cycles. This approach has often been used to favor more rigid structures with extended π -conjugation 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-ethylenedioxy-thiophene) (BEDOT) moiety has been studied.^[9] The replacement of BT by BEDOT reveals a marked redshift of the absorption maximum ($\Delta\lambda \approx 118$ 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 in the improvement of the second-order NLO response.

Different push-pull chromophores based on a dithieno[3,2b:2',3'-d]thiophene (DTT) spacer (Scheme 1) have been described.^[10] Such systems can be viewed as a particular sulfur-



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

bridged BT, and our group has recently studied D- π -A compounds^[11] with a DTT unit as π -spacer, which combine high second-order molecular nonlinearity with good thermal stability.

Other thiophene-containing fused heterocycles (Scheme 1), such 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 with 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.

Within this context, we present herein the synthesis, characterization, and study of two novel series of push-pull chromophores derived from the BT relay and its rigidified π -conjugated counterparts CPDT and DTP. (Scheme 2) The corre-



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Scheme 2. Structures of the target compounds together with previously reported 1d and 2d.^[11]



Scheme 3. Synthesis of precursor aldehydes 3a-c.

sponding previously reported DTT derivatives 1 d and $2 d^{[11]}$ have been also included in this study for comparison. All chromophores include the proaromatic 4*H*-pyranylidene unit as the donor.^[15]

Results and Discussion

Synthesis

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

CPDT and DTP derivatives **3b**-**c** were prepared from the unsubstituted cores of 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, compounds **4b**-**c** were synthesized by reaction of DMF with the dilithiated derivatives of **5b**-**c**, formed in the presence of TMEDA (*N*,*N*,*N'*,*N'*-tetramethylethylenediamine).^[18] The synthesis of compound **4c** has been previously described in a patent in 2011,^[19] by 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%) compared with the yield under the conditions in Scheme 3 (75%). Moreover, in that reference^[19] the compound does not appear fully characterized.

Next, a Horner reaction of 2,6-diphenyl-4*H*-pyran-4-yl)diphenylphosphine oxide (6)^[20] with 4b-c afforded the corresponding aldehydes with a CPDT (3b) or a DTP (3c) moiety. It should be noted that the reaction conditions were carefully tuned (temperature and order of slow addition of reagents) to minimize the formation of pyranylidene-disubstituted derivatives as byproducts.^[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 subsequent acid hydrolysis afforded 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 af-



Scheme 4. Synthesis of chromophores 1 a-c and 2 a-c.

forded new D- π -A compounds **1a**-**c** and **2a**-**c** in yields that ranged 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 analysis of the ${}^{3}J_{HH}$ coupling constants, the CH=CH bond in compounds 2 shows an E configuration.

Calculated Structures

The molecular geometries of compounds 1a-c and 2a-c and the previously reported systems 1d and 2d^[11] were optimized at the PCM-M06-2X/6-31G* level in dichloromethane. The resulting structures were planar, including BT systems 1 a and 2a,^[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 that reflects the ground-state polarization of merocyanines. The calculated BLA values of the thiophene rings attached to the donor (labeled I) and to the acceptor (labeled II) moieties are shown in Figure 1.

	Compou	X Ind	BLA ring l	BLA ring ll
	1a	no bridge	+0.024	0
	1b	$C(C_6H_{13})_2$	+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	$C(C_6H_{13})_2$	+0.017	-0.002
	2c	NC_6H_{13}	+0.019	-0.006
	2d	S	+0.024	+0.013

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

Inspection of the data reveals a strong quinoidization of the whole electron relay induced by the attachment to the donor and acceptor moieties,^[24] which is particularly important for the acceptor-substituted thienyl ring. Thus, as has been previously shown in ${}_{\mathsf{D}}\mathsf{D}\text{-}\pi\text{-}\mathsf{A}$ chromophores with $\mathsf{BT}^{[^{7c,\,22,\,25]}}$ or $\mathsf{DTT}^{[^{10c]}}$ as relays, there is a coexistence of two different molecular domains within the π -conjugated spacer; there is a higher degree of guinoidization (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.

Conversely, the BLA is reduced in the **b**-**d** chromophores (both rings I and II) compared with the corresponding a analogues, which shows that the rigidification of the BT relay results in more polarized structures and follows the order $\mathbf{b} > \mathbf{c} >$ d > a. A similar trend was reported when the unsubstituted fused cores (BT, DTT, CPDT) were compared^[26] (BLA values of 0.052, 0.045, 0.042 Å, respectively). Moreover, these results are consistent with those obtained for compounds 9 and 10 that contained BT and DTT as relays (see Figure 2), which showed a higher degree of polarization for DTT when compared with its BT analogue.^[25, 10c]



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Figure 2. Calculated BLA values [Å] for rings 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, which showed their lower polarization relative to their analogues 1.

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

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, with 50% (2c) or more (1bc) 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** chromo-

	Compound	Donor	π-spacer	Acceptor
Ph O Ph	1a	+0.125	+0.098	-0.223
	1b	+0.134	+0.166	-0.300
$\langle \langle \langle \rangle \rangle$	1c	+0.125	+0.173	-0.298
S S	A 1d	+0.132	+0.092	-0.224
L/Jo>	2a	+0.122	+0.042	-0.164
X	2b	+0.126	+0.115	-0.241
π spacer	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.

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phores are less alternated than their **a**,**d** analogues. Focusing exclusively on the π spacer, the positive charge borne 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, which reveals 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 a-c and 2 a-c were studied by using cyclic voltammetry (CV) in CH_2Cl_2 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 a–d and 2 a–d .						
	<i>E</i> _{ox} 1 [V]	<i>E</i> _{ox} 2 [V]	$E_{\rm red}$ [V]	E _{HOMO} [eV]	$E_{\rm LUMO}$ [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	
1 d ^[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	
2 c	+0.48	+1.28	-0.72	-6.04	-2.71	
2 d ^[c]	+0.54	+1.56	-0.63	-6.20	-2.79	
[a] Conditions: 10^{-3} M in CH ₂ Cl ₂ vs. Ag/AgCl (3 M KCl), glassy carbon working electrode, Pt counter electrode, 20 °C, 0.1 M NBu ₄ PF ₆ , 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 CH ₂ Cl ₂ . [c] Ref. [11].						

All the voltammograms show three irreversible waves that correspond to one reduction step (involving the acceptor unit) and two oxidation steps. The first oxidation is related to the 4*H*-pyranylidene moiety, whereas the second oxidation process is attributed to the bridge. This assignment can be made taking into account that the E_{ox} values for compounds dithie-no[3,2-*b*:2',3'-*d*]thiophene-2,6-dicarbaldehyde,^[10a] **4b**, and **4c** are 1.65, 1.76, and 1.63 V, respectively, under 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_{ox} 2 for compounds **1a** and **2a** are consistent with those of other D- π -A systems that feature BT as the π -conjugated spacer.^[7e-f,27]

Electron densities related to frontier orbitals (see topologies for **1 c** chosen as the 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.

The influence on $E_{ox}1$ on going from BT derivatives **a** to rigidified **b**-**d** derivatives depends on the acceptor moiety. Thus, for TCF chromophores **2**, the rigidification of BT relay implies a decrease in $E_{ox}1$ in the order (BT)**2 a** > (DTT)**2 d** > (CPDT)**2 b** >



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

(DTP)**2 c**. Conversely, for thiobarbiturate derivatives **1**, only compound **1 c** presents a E_{ox} **1** lower than the E_{ox} **1** value obtained for **1 a**. Inspection of E_{HOMO} values indicates that for both series **1** and **2**, higher values are found for **b** and **c** derivatives. Moreover, they show the lowest calculated gaps.

When the E_{ox}^2 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 was previously shown for conjugated donor–acceptor polymers,^[30] and in agreement with the calculated data.

Concerning the reduction process, the rigidification of bithiophene as a 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 **1a** and **2a**. E_{LUMO} data are in agreement with this observed trend.

A shift in the $|E_{red}|$ values towards less cathodic potentials is observed on changing the acceptor from the thiobarbiturate group (compounds 1) to the TCF moiety (compounds 2), which confirms the superior electron-withdrawing ability of the TCF unit. Moreover, there is a slight shift in the E_{ox} values ($E_{ox}1$ and $E_{ox}2$) towards less anodic potentials on going 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 ε) of the studied compounds in different solvents are summarized in Table 2. For the sake of comparison, data for systems **1d** and **2d** are also gathered (see spectra in the Supporting Information). All chromophores show intense and broad CT bands that extend into the near-infrared in some cases (**2b**-c).

Whereas the spectra of BT derivatives **1a** and **2a** show broad unresolved absorption bands,^[7c] those of CPDT and DTP systems **1b,c** and **2b,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 deriva-

Table 2. UV/Vis data.					
	λ_{\max} [nm] $(\log \varepsilon)^{[a]}$ 1,4-dioxane	λ_{\max} [nm] $(\log \varepsilon)^{[a]}$ CH ₂ Cl ₂	λ_{\max} [nm] $\left(\log arepsilon ight)^{[a]}$		
1a	630 (4.68)	655 (4.70)	643 (4.56)		
1b	603 (4.70)	614 (4.59)	612 (sh)		
	671 (4.86)	697 (4.86)	691 (4.85)		
1c	615 (4.89)	632 (sh)	674 (4.99)		
	659 (5.03)	680 (5.01)			
1 d ^[a]	636 (4.76)	659 (4.75)	642 (4.61)		
2 a	658 (4.65)	703 (4.68)	666 (4.47)		
2b	717 (4.40)	658 (4.33)	657 (4.36)		
		800 (4.50)	755 (4.43)		
2 c	686 (4.47)	718 (sh)	770 (4.37)		
	740 (4.52)	788 (4.87)			
2 d ^[b]	658 (4.46)	708 (4.64)	675 (4.52)		
[a] The unit for ε is M^{-1} cm ⁻¹ . [b] Data from Ref. [11].					

tives.^[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]

A comparison of compounds that only differ in the acceptor unit shows a bathochromic shift for TCF derivatives **2**, in line with the 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 **1b,c** and **2b,c** present a significant redshift in λ_{max} when compared with **1a** and **2a**, which is more pronounced in derivatives **2** that have 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, **1b** and **2b** are bathocromically shifted with respect to **1c** and **2c** (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 going from 1,4-dioxane to CH_2CI_2 , which becomes negative when comparing CH_2CI_2 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) 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**.

TD-DFT calculations (see Table S1 in the Supporting Information) are only in moderate agreement with experimental results, and give 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.



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

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

Nonlinear Optical Properties

The second-order nonlinear optical properties of derivatives **1 a-c** and **2a-c** were measured by using electric-field-induced second harmonic generation (EFISHG) in dichloromethane at $\lambda = 1907$ 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 d** and **2 d**^[11] are also given. As mentioned previously, broad bands, which extend into the near-infrared in some cases, have been found for all systems. Specifically, $\mu\beta$ values for compounds **2 b-c** have been obtained by taking into account their absorption ($\alpha_{2\omega}$) at the harmonic wavelength ($\lambda = 954$ nm). This correction is especially significant for **2 b** and thus the estimation of their $\mu\beta_0$ values should be treat-

Table 3. Experimental and calculated NLO properties.						
	$\mueta^{[a]}$ [10 $^{-48}$ esu]	$\mu eta_o^{[b]}$ [10 ^{–48} esu]	$\mu eta_0^{[c]}$ [10 ^{–48} esu]			
1a	3100	1440	2685			
1b	4100	1650	2877			
1c	5000	2100	2857			
1 d ^[d]	4000	1800	2403			
2a	15600	6130	7946			
2b	13 000 ^[e]	3300	10344			
2 c	26 000	6840	10997			
2 d ^[d]	9200	3500	6447			

[a] $\mu\beta$ values determined in CH₂Cl₂ at λ =1907 nm (experimental uncertainty less than ±15%, except for **2b** (\approx 20%)). [b] Experimental $\mu\beta_0$ values in CH₂Cl₂ calculated by using the two-level model. [c] Calculated at the HF/6-31G*//PCM-M06-2x/6-31G* level in CH₂Cl₂. [d] Experimental data from Ref. [11]. [e] The $\mu\beta$ value was determined from a freshly prepared sample.

ed with caution. For the sake of comparison, Disperse Red 1, a common benchmark for organic NLO chromophores, shows a $\mu\beta_0$ value of approximately 490×10^{-48} esu in CH₂Cl₂ under the same experimental conditions.

For all the π relays studied, derivatives **2** have remarkably superior responses compared with analogues **1**, which again reveals the higher strength of the TCF acceptor.

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

In any case, in both series **1** and **2**, DTP derivative **c** show the highest $\mu\beta_0$ value, which again points to the strong donor character of 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) essentially reproduce the trends observed in the experimental results, in terms of the influence of the acceptor and the DTP as the π relay; for example, better responses for **2** systems than for analogues **1** and for chromophore **c** 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 always show the highest values, with a greater difference in series **2** than in series **1**, contrary to the experimental data.

Taking all data into account, the results show that the role played by the rigidification of the BT ring is less relevant than the character of the fused heterocycle formed, that is, it is not enough to rigidify the BT moiety to improving the NLO response, it is extremely important how this rigidification is made. 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

The thermal stability of compounds 1a-c and 2a-c were studied by using thermogravimetric analysis (TGA; see Table 4) to estimate their decomposition temperatures (T_d), defined as the intercept of the leading edge of the weight loss with the baseline of the TGA scans.

All derivatives 1 a-c and 2a-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 d** and **2 d**^[11] show a significant enhancement in thermal stability. The presence of hexyl chains^[9] may be related to the lower T_d values ull Paper

Table 4. Thermal stability.						
	<i>T_d</i> [°C]		$T_d [^{\circ}C]$			
1a	307	2 a	303			
1b	288	2 b	293			
1c	293	2 c	304			
1 d ^[a]	343	2 d ^[a]	342			
[a] Data from Ref. [11].						

found, in general, for CPDT and DTP chromophores **b**–**c** compared with BT derivatives **a** (apart from compounds **2c** and **2a**, the values of which are essentially identical).

Conclusion

The influence of the rigidification of the BT unit on groundstate polarization and second-order NLO properties has been studied by synthesizing D- π -A systems that contain 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 **d** and 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 $E_{ox}2$ value (related to the heterocyclic π spacer) found for DTP systems **c** reveal the strong donor character of the dithienopyrrole moiety.

Additionally, CV and UV/Vis spectra show lower gaps for CPDT and DTP chromophores compared with their BT analogues ($\mathbf{b} < \mathbf{c}$). Regarding thermal stability, only DTT-containing compounds \mathbf{d} have higher $T_{\rm d}$ values than those of the BT systems.

The second-order nonlinearity is 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 nonlinearity. Moreover, this heterocyclic unit, used for the first time in D- π -A compounds intended for NLO, has proved to allow a good charge transfer between the end groups of the chromophores and is accessible by a relatively easy synthetic route. In addition, a wide range of substituents can be incorporated on the N atom, which allows 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

For general information, see the Supporting Information.

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Starting Materials

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

nBuLi (1.6 M) in hexanes (2 mL, 3.2 mmol), was added to a solution of 5a (0.602 g, 2.53 mmol) in dry THF (18 mL) at -78 °C under an argon atmosphere. The reaction mixture was stirred for 30 min, then dry DMF (0.5 mL, 6.44 mmol) was added. After stirring for a further 2.5 h at -78 °C, a solution of saturated NH₄Cl (50 mL) was added. The aqueous phase was extracted with CH₂Cl₂ (3×50 mL), and the resulting organic layer was washed with a solution of saturated NH₄Cl (50 mL), dried over MgSO₄, and evaporated. The crude product was purified by flash column chromatography (silica gel) with hexane/AcOEt (8:2) as the eluent, which gave 4a as a yellow solid (0.571 g, 2.14 mmol, 84%). M.p. 158-160°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 9.86$ (s, 1 H, -CHO), 7.67 (d, J = 3.9 Hz, 1 H, BT-H), 7.24-7.23 (m, 2H, BT-H), 7.12 (d, J=3.7 Hz, 1H, BT-H), 6.09 (s, 1H, -CH-OCH₂CH₂O-), 4.17-4.02 ppm (m, 4H, -OCH₂CH₂O-); ¹³C NMR (100 MHz, CDCl₃): 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): $\tilde{\nu} = 2885$ (C–H), 2836 (C–H), 1653 (C=O), 1553 (C=C, Ar), 1517 cm⁻¹ (C=C, Ar); HRMS (ESI⁺): *m/z* calcd for C₁₂H₁₀NaO₃S₂: 288.9964 [*M*+Na]⁺; found: 288.9952; elemental analysis calcd (%) for $C_{12}H_{10}O_3S_2$: C 54.12, H 3.78; found C 53.87, H 3.95.

5'-((2,6-Diphenyl-4H-pyran-4-ylidene)methyl)-2,2'-bithiophene-5-carbaldehyde (3 a)

nBuLi (1.6 м) in hexanes (1.3 mL, 2.11 mmol) was added to a solution of 6 (0.704 g, 1.62 mmol) in dry THF (20 mL) at -78 °C under an argon atmosphere. The solution turned dark green, and was stirred at this temperature for 15 min. Then, a solution of 4a (0.432 g, 1.62 mmol) in dry THF (5 mL) was slowly added by syringe. The mixture was stirred and the reaction medium was slowly warmed to RT (TLC monitoring). When the reaction finished, an aqueous solution of HCl (1 N, 40 mL) was added and the mixture was stirred for 1 h at RT. The aqueous layer was extracted with CH_2CI_2 (3×50 mL), and the resulting organic layer was dried over MgSO₄ and evaporated. The crude product was purified by using flash column chromatography (silica gel) with hexane/AcOEt (8.5:1.5) as the eluent to give **3a** as a dark red solid (0.566 g, 1.29 mmol, 80%). M.p. 189–191 °C; ¹H NMR (400 MHz, CDCl₃): $\delta =$ 9.84 (s, 1 H, -CHO), 7.87-7.82 (m, 2 H, phenyl-H), 7.77-7.72 (m, 2 H, phenyl-H), 7.66 (d, J=4.0 Hz, 1 H, BT-H), 7.55-7.38 (m, 6 H, phenyl-H), 7.28 (d, J=4.0 Hz, 1 H, BT-H), 7.23 (d, J=4.0 Hz, 1 H, BT-H), 7.09 (dd, $J_1 = 1.8$ Hz, $J_2 = 0.6$ Hz, 1 H, pyranylidene-H), 6.89 (dd, $J_1 =$ 4.0 Hz, J₂=0.6 Hz, 1 H, BT-H), 6.43 (d, J=1.8 Hz, 1 H, pyranylidene-H), 6.07 ppm (s, 1 H, pyranylidene = C-H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 182.3, 153.9, 151.5, 147.8, 144.3, 140.6, 137.6, 133.0, 132.8,$ 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): $\tilde{\nu} = 1643 \text{ cm}^{-1}$ (C=O); HRMS (ESI⁺): m/z calcd for C₂₇H₁₉O₂S₂: 439.0821 [*M*+H]⁺; found: 439.0799; elemental analysis calcd (%) for C₂₇H₁₈O₂S₂: C 73.94, H 4.14; found C 73.72, H 3.94.

4,4-Dihexylcyclopenta[2,1-b:3,4-b']dithiophene (5b)

Potassium hydroxide (0.234 g, 4.25 mmol) was added in several portions 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) at 0 °C under an argon atmosphere. The mixture was stirred for 12 h at RT, 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 MgSO₄, and evaporated. The crude product was purified by using flash column chromatography (silica gel) with hexane as the eluent to give 5b as a colorless oil (0.408 g, 1.18 mmol, 88%). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.14$ (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-CH₂-C₅H₁₁), 1.21–1.08 (m, 12H, C-CH₂-(CH₂)₃-C₂H₅), 0.98–0.89 (m, 4H, $C-(CH_2)_4-CH_2-CH_3$, 0.80 ppm (t, J=6.9 Hz, 6 H, C-(CH_2)_5-CH_3); ¹³C NMR (100 MHz, CDCl₃): 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 C₂₁H₃₀S₂: 346.1783 [*M*]^{+•}; found: 346.1794.

4,4-Dihexylcyclopenta[2,1-b:3,4-b']dithiophene-2,6-dicarbaldehyde (4b)

nBuLi (1.6 м) in hexanes (1.35 mL, 2.16 mmol) was added 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 RT under an argon atmosphere. The mixture was heated at reflux for 1 h, cooled to RT and then to -40 °C. Dry THF (4 mL) and dry DMF (180 $\mu\text{L},$ 2.30 mmol) were added and the mixture was warmed to RT for 3 h. HCl (1 N, 50 mL) was then added and the aqueous phase was extracted with AcOEt (3×50 mL). The organic layer was washed with water (3×50 mL), dried over MgSO₄, and evaporated. The crude product was purified by using flash column chromatography (silica gel) with hexane/AcOEt (9.5:0.5) as the eluent to give 4b as a yellow powder (0.214 g, 0.53 mmol, 76%). M.p. 98°C (decomp.); ¹H NMR (400 MHz, CDCl₃): $\delta \!=\!$ 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): $\delta = 182.9$, 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): $\tilde{v} = 1656 \text{ cm}^{-1}$ (C=O); HRMS (ESI⁺): *m/z* calcd for C₂₃H₃₁O₂S₂: 403.1760 [*M*+H]⁺; found: 403.1744; elemental analysis calcd (%) for $C_{23}H_{30}O_2S_2$: 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)

nBuLi (1.6 м) in hexanes (0.85 mL, 1.36 mmol) was added to a solution of 6 (0.128 g, 0.298 mmol) in dry THF (4 mL) at -30 °C under an argon atmosphere. The solution turned dark green and was stirred at this temperature for 15 min. Then, the solution was slowly added by using 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 1 h. 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 using flash column chromatography (silica gel) wit hexane/AcOEt (9.5:0.5) as the eluent to give **3b** as a dark red solid (0.117 g, 0.189 mmol, 63%). M.p. 29–31 °C; ¹H NMR (300 MHz, CDCl₃): $\delta = 9.80$ (s, 1 H, -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, 1 H, CPDT-H), 6.46 (d, J=1.8 Hz,

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1 H, pyranylidene-*H*), 6.14 (s, 1 H, pyranylidene = C-*H*), 1.92–1.80 (m, 4H, C- $CH_2-C_5H_{11}$), 1.21–1.11 (m, 12 H, C- $CH_2-(CH_2)_3-C_2H_5$), 1.03–0.93 (m, 4H, C- $(CH_2)_4-CH_2-CH_3$), 0.82 ppm (t, *J*=6.7 Hz, 6H, C- $(CH_2)_5-CH_3$); 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): $\tilde{\nu}$ = 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; *m/z* 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 (5 c)

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 *t*BuONa (0.392 g, 3.96 mmol), [Pd₂(dba)₃] (36.4 g, 0.04 mmol; dba = dibenzylideneacetone), 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 7 h. After the reaction was cooled to RT, water (50 mL) was added and the aqueous layer was extracted with diethyl ether $(3 \times 50 \text{ mL})$. The combined organic layer was washed with water $(3 \times 50 \text{ mL})$ and a saturated solution of NaCl $(3 \times 50 \text{ mL})$, then dried over MgSO₄. Evaporation of the solvent and purification by flash column chromatography (silica gel) by using hexane/AcOEt (9:1) as the eluent gave 5c as a colorless oil that solidified on standing to give a white solid (0.308 g, 1.17 mmol, 76%). 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-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 by following the same procedure as for **4b**, starting from *N*-hexyldithieno[3,2-*b*:2',3'-*d*]pyrrole (**5c**; 0.300 g, 1.14 mmol), previously dried TMEDA (520 µL, 3.47 mmol), nBuLi (1.6 м) in hexanes (2.2 mL, 3.52 mmol) and dry DMF (260 μL, 3.36 mmol). The crude product was purified by using flash column chromatography (silica gel) with hexane/AcOEt (8:2 \rightarrow 7:3) as the eluent to give 4c as a yellow powder (0.275 g, 0.86 mmol, 75%). M.p. 158–160 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 9.95$ (s, 2 H, -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, 3 H, N-(CH₂)₅-CH₃); ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 183.2$, 147.3, 144.1, 122.0, 118.7, 47.7, 31.3, 30.2, 26.7, 22.4, 13.9 ppm; IR (KBr): $\tilde{\nu} = 1659 \text{ cm}^{-1}$ (C=O); HRMS (ESI⁺): m/zcalcd for C₁₆H₁₈NO₂S₂: 320.0773 [*M*+H]⁺; found: 320.0766; calcd for C₁₆H₁₇NNaO₂S₂ 342.0593 [*M*+Na]⁺; found: 342.0581; calcd for C₃₂H₃₄N₂NaO₄S₄: 661.1294 [2*M*+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 (3 c)

This compound was prepared by following the same procedure as for 3b, starting from 6 (0.408 g, 0.939 mmol), *n*BuLi (1.6 M) in hex-

anes (0.65 mL, 1.04 mmol), and 4c (0.300 g, 0.939 mmol). The crude product was purified by using flash column chromatography (silica gel) with hexane/AcOEt (8:2 \rightarrow 7:3) as the eluent to give 3cas a dark red solid (0.241 g, 0.449 mmol, 48%). M.p. 68-70°C; ¹H NMR (300 MHz, CDCl₃): $\delta = 9.82$ (s, 1 H, -CHO), 7.90–7.84 (m, 2 H, 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, 1 H, DTP-H), 6.42 (d, J=1.6 Hz, 1 H, pyranylidene-H), 6.12 (s, 1 H, pyranylidene = C-H), 4.15 (t, J = 7.0 Hz, 2 H, 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, 3 H, N-(CH₂)₅-CH₃); ¹³C NMR (75 MHz, $CDCI_3$): $\delta = 182.4$, 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): $\tilde{\nu} = 1642$ (C=O), 1578 cm⁻¹ (C=C, Ar); HRMS (ESI⁺): m/z calcd for $C_{33}H_{30}NO_2S_2$: 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 (1 a)

1,3-Diethyl-2-thiobarbituric acid (7; 0.030 g, 0.152 mmol) was added in one portion to a solution of 3a (0.056 g, 0.128 mmol) in absolute ethanol (6 mL) under an argon atmosphere, and the mixture was heated at reflux for 24 h. The reaction was cooled to RT 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): $\delta =$ 8.59 (s, 1 H, BT-CH = acceptor), 7.94-7.91 (m, 2 H, 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, 1 H, pyranylidene-H), 6.18 (s, 1 H, 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 low solubility; IR (KBr): $\tilde{\nu}$ = 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 $C_{35}H_{28}N_2O_3S_3$: 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-ylmethylen]-1,3-diethyl-2-thioxodihydropyrimidin-4,6-dione (1 b)

This compound was prepared by following the same procedure as for 1a, starting from 3b (0.049 g, 0.078 mmol) and 1,3-diethyl-2thiobarbituric acid (7; 0.017 g, 0.083 mmol) in absolute ethanol (5 mL), with a reaction time of 5 h. The solvent used for washing was a cold mixture of hexane/CH $_2\text{Cl}_2$ (9:1). Product $\textbf{1}\,\textbf{b}$ was obtained as a dark green solid (0.021 g, 0.026 mmol, 33%). M.p. 240-242 °C; ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 8.59$ (s, 1 H, CPDT-CH = acceptor), 7.96-7.90 (m, 2H, phenyl-H), 7.86-7.80 (m, 2H, phenyl-H), 7.64–7.44 (m, 7 H, phenyl-H+CPDT-H), 7.28 (dd, $J_1 = 1.6$ Hz, $J_2 =$ 0.4 Hz, 1 H, pyranylidene-H), 6.88 (s, 1 H, 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); ^{13}C NMR: not registered due to low solubility; IR (KBr): $\tilde{\nu}\!=\!1651$ (C= O), 1545 (C=C, Ar), 1491 cm⁻¹ (C=C, Ar); HRMS (ESI⁺): *m/z* calcd for

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N-Hexyl-5-[6-(2,6-diphenyl-4H-pyran-4-ylidenemethyl)dithieno[3,2-b:2',3'-d]pyrrole-2-ylmethylen]-1,3-diethyl-2-thioxodihydropyrimidin-4,6-dione (1 c)

This compound was prepared by following the same procedure as 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), with a reaction time of 5 h. The solvents used for washing were 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 (decomp.); 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 (brs, 1H, pyranylidene-H), 6.80 (s, 1 H, DTP-H), 6.57 (brs, 1 H, pyranylidene-H), 6.22 (s, 1 H, pyranylidene = C-H), 5.50-4.68 (m, 4 H, 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, 12 H, 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 low solubility; IR (KBr): $\tilde{\nu} = 1647$ (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 (2 a)

Triethylamine (33 μ L, 0.24 mmol) was added 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) under an argon atmosphere, and the mixture was heated at reflux for 28 h. The reaction was cooled to RT and then to 0°C. The resulting solid was isolated by filtration and washed with cold hexane. Product 2a was obtained as a copper-colored solid (0.087 g, 0.141 mmol, 61%). M.p. 293 °C (decomp.); ¹H NMR (400 MHz, $[D_6]DMSO$, 323 K): $\delta = 8.09$ (d, J = 15.8 Hz, 1 H, -CH=CHacceptor), 7.94-7.92 (m, 2H, phenyl-H), 7.88-7.86 (m, 2H, phenyl-H), 7.80 (d, J=4.0 Hz, 1 H, BT-H), 7.60–7.47 (m, 8 H, phenyl-H+BT-H), 7.16 (d, J=4.0 Hz, 1 H, BT-H), 7.11 (d, J=1.3 Hz, 1 H, 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, 323 K): $\delta =$ 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): $\tilde{\nu} = 2229$ (C \equiv N), 1648 (C=C), 1563 cm⁻¹ (C=C); HRMS (ESI⁺): m/z calcd for $C_{38}H_{25}N_3O_2S_2$: 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)

A mixture of pyridine (70 μ L) and acetic acid (35 μ L) was added 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) under an argon atmosphere, and the mixture was heated at reflux for 28 h. The reaction was cooled to RT 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=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 low solubility; IR (KBr): $\vec{\nu}$ = 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 (2 c)

This compound was prepared by following the same procedure as 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), with a reaction time of 48 h. The solvents used for washing were 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 (decomp.); ¹H NMR (300 MHz, [D₆]DMSO, 335 K): $\delta = 8.16$ (d, J = 15.4 Hz, 1 H, -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, 1 H, pyranylidene-H), 6.64 (d, J =15.4 Hz, 1 H, -CH=CH-acceptor), 6.36 (s, 1 H, 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 low solubility; IR (KBr): $\tilde{\nu} =$ 2220 cm⁻¹ (C \equiv 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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