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Efficient second-order nonlinear optical chromophores based on dithienothiophene and thienothiophene bridges



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Dedicated to the memory of our colleague Christian Claessens

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1. Introduction

Over the last decades great efforts have been dedicated to obtain materials exhibiting good second-order nonlinear optical (NLO) properties due to their potential application in optical devices.¹ Following this trend, many high performing organic systems (specially donor- π -acceptor (D- π -A) type molecules) have been synthesized, but the combination of high molecular hyperpolarizabilities and good thermal stability in the same system is still a subject of interest in materials science. Polyene-type structures have often been included in the conjugated spacer between the donor and the acceptor moieties because they provide the best conjugation pathway for the charge transfer, but poor thermal stabilities are associated with the presence of these olefinic fragments.² The reverse situation is found for aryl-type spacers. Then, the replacement of aryl rings by heteroaromatic rings with lower resonance energies is the common way to obtain

ABSTRACT

Two series of push–pull systems bearing dithienothiophene or thienothiophene as (part of) π -conjugated spacer have been synthesized. These compounds combine high second-order molecular nonlinearities with good thermal stabilities, showing one of the thienothiophene (TT) derivative the highest $\mu\beta_0$ value found for a 4*H*-pyranylidene-containing merocyanine.

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a good balance between nonlinear optical response and thermal stability.³ In this context, thiophenes are among the most studied heterocyclic spacers for D- π -A systems, ^{3b,4} due to their relatively low resonance energies, and have allowed the preparation of chromophores with high stabilities and nonlinearities. On the other hand, conjugated spacers based on fused thiophene rings have been much less studied in this field, even though thieno[3,2b]thiophene $(TT)^5$ and dithieno[3,2-b:2',3'-d]thiophene $(DTT)^6$ show a lower resonance energy per electron when compared to thiophene⁷ and allow to increase conjugation, which typically results in increased NLO responses. Just a few chromophores bearing these fused heterocycles as (part of) the electron relay have been reported.^{3a,8,9} Moreover, just one of the papers^{8a} approaches these systems from the standpoint of the establishment of structure-activity relationships, and it is focused on the comparison between thiophene and thieno[3,2-b]thiophene moieties.

In this work we focus our attention on the synthesis, characterization, and study of six new fused thiophene derivatives **1**–**4**, which are expected to be efficient NLO chromophores and to show high thermal stability. New D- π -A molecules bear the proaromatic 4*H*pyran-**4**-ylidene unit as donor¹⁰ and two common strong organic acceptors. To the best of our knowledge, no such merocyanines



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with a 4*H*-pyran-4-ylidene moiety and dithienothiophene or thienothiophene relays in their structure have been previously reported. The influence of these fused heterocycles on the optical and thermal properties is discussed and compared with that exerted by a single thiophene unit in the π -spacer.



2. Results and discussion

2.1. Synthesis

For the synthesis of the target systems **1–4**, the previously unreported aldehydes **8a,b** and **9** were chosen as precursors. Compounds **8a**, **9** were prepared by a Horner reaction between pyranylphosphine oxide **7**¹¹ and dicarbaldehydes **5**¹² and **6**,^{9b} respectively (Scheme 1). Reaction conditions were carefully tuned (temperature, order of slow addition of reagents) in order to minimize the formation of pyranylidene-disubstituted derivatives as by-products. Thus, a yield of 61% could be achieved for **8a**, whereas lower yields were obtained for **9** due to the insolubility of dicarbaldehyde **6**. Aldehyde **8b** was obtained from reaction of **8a** and tributylphosphonium salt **10**¹³ in the presence of sodium ethoxide and a subsequent acid hydrolysis.



Scheme 1. Synthesis of aldehyde precursors 8 and 9.

The Knoevenagel reaction between acceptors **11** and **12** (2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, TCF)¹⁴ and aldehydes **8a,b**, **9** afforded the six new D- π -A compounds **1**–**4** (Scheme 2).



Scheme 2. Synthesis of chromophores 1–4.

It is worth noting that the reaction of aldehyde **8b** and acceptor **12** under the same conditions used for aldehydes **8a** and **9** afforded compound **2a** instead of the expected **2b**. This vinylene-shortening reaction has already been reported for other Knoevenagel-type reactions by us¹⁵ and other authors.¹⁶ Different reaction conditions reported¹⁷ for Knoevenagel reactions involving acceptor **12** were tried with the same result. To overcome this drawback, the reaction between aldehyde **8b** and acceptor **12** was tested under microwave conditions.¹⁸ In this approach the addition of a base is not necessary, and therefore the aforementioned side-reaction is less likely to happen. Using this procedure compound **2b** was eventually isolated in low yield.

2.2. ¹H NMR studies

Compounds **1b**, **2a**,**b**, and **4** have an *all-trans* geometry along the spacer according to ${}^{3}J_{HH}$ coupling constant analysis. Whereas the *s*-trans conformation for the bond linking the donor moiety to the thieno[3,2-*b*]thiophene spacer is confirmed by selective ge-1D NOESY experiments carried out on model compound **8a** (300 MHz, CDCl₃, rt), the same conformation can be assumed for NLO chromophores **1–4**.

¹H NMR data also provide valuable information about groundstate polarization of the studied D- π -A systems. The chemical shifts of the H atoms along the polyenic spacer show the typical oscillatory behavior¹⁹ of a merocyanine-like compound, and the high ³J_{HH} values for the =CH–CH= protons in the olefinic part of the spacer for compounds **1b** and **2b** (12.8 Hz for compound **1b** (CDCl₃); 11.4 Hz for **2b** (CD₂Cl₂)) show the contribution of their zwitterionic form to their electronic ground states.

A slight downfield shift for the protons of the pyranylidene ring of compound **2a** when compared to **2b** was observed (6.61 and 7.23 ppm for **2a** and 6.56 and 7.20 ppm for **2b** in CD₂Cl₂). This finding indicates a higher contribution of the aromatic pyrylium form for the shortest system, in agreement with other D- π -A systems with a 4*H*-pyran-4-ylidene unit previously described.^{10,15c,20}

¹H NMR spectra of DTT derivatives **3**, **4** were recorded in different conditions as a result of their low solubility, leaving them out of the comparison with 1-2.

2.3. Calculated structures

For a better understanding of the role of fused thiophene conjugated spacers in these chromophores, natural bond orbital (NBO) atomic charge calculations for the target compounds and for analogous systems bearing a single thiophene spacer **13**, **14**²⁰ (Fig. 1) were carried out. The resulting charges for comparable systems are shown in Fig. 2. It can be seen that part of the net positive charge of the push–pull system is supported by the thiophene relays, in agreement with previously reported results.^{9d}



Fig. 1. Structures of compounds 13 and 14.

Ph∖	Compd	Donor	π-spacer	Acceptor
Ph-	13	+0.196	+0.082	-0.276
π-spacer A	1a	+0.159	+0.086	-0.245
A:	3	+0.146	+0.094	-0.240
	14	+0.190	+0.069	-0.259
	2a	+0.177	+0.070	-0.247
O CN	4	+0.167	+0.080	-0.247

Fig. 2. Calculated NBO charges from the optimized $B3P86-6-31G^*$ molecular geometries.

However, the portion of the positive charge located on the spacer is highly dependent on the relative strength of the donor group. While DTT relays linked to a relatively weak dialkylaminophenyl donor bear a positive charge that can be even greater than that supported by the donor itself,^{9d} for the systems herein reported most of the net positive charge (61–72%) is located on the strong pyranylidene donor and the charge on the fused thiophene relay is always below 0.1e.

Moreover, the charge on both the donor and acceptor ends of the push—pull system decreases and the charge of the relay increases on increasing the number of fused thiophenes (DTT>TT>thiophene). In other words, larger spacers have a stronger donor character and decrease the ground state charge transfer from the pyranylidene to the acceptor.

2.4. Electrochemistry

Electrochemical properties of compounds 1-4 were studied by cyclic voltammetry (CV) in CH₂Cl₂. All compounds show irreversible waves corresponding to the oxidation of the pyranylidene fragment and to the reduction of the corresponding acceptor moieties (Table 1).

Table 1	
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Electrochemical data,^a E_{HOMO} , and E_{LUMO} values^b

Compd	$E_{\rm ox}\left({\sf V}\right)$	$E_{\rm red}\left(V\right)$	$E_{\rm HOMO}~({\rm eV})$	$E_{\rm LUMO}~({\rm eV})$
1a	+0.72	-0.89	-5.68	-3.42
1b	+0.59	-0.72	-5.62	-3.55
3	+0.55	-0.84	-5.61	-3.45
2a	+0.69	-0.71	-5.84	-3.85
2b	+0.55	-0.60	-5.75	-3.90
4	+0.54	-0.63	-5.75	-3.87
13	+0.67	-0.89	-5.80	-3.43
14	+0.67	-0.69	-5.91	-3.85

^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 B3P86-6-31-G* level in the gas phase.

For a given acceptor, lengthening the conjugated spacer with a vinylene unit leads to a decrease of E_{ox} and $|E_{red}|$ values in all cases, pointing to the weaker interaction between donor and acceptor groups.

For systems with the same conjugated spacer, there is a shift of the $|E_{red}|$ values toward less cathodic potentials when changing the acceptor from thiobarbiturate group to TCF, pointing to the superior electron-withdrawing ability of the latter acceptor when compared to the former. On the other hand, E_{ox} values are not dramatically influenced by the change of the electron-withdrawing group.

Concerning the number of fused thiophenes, comparison of TT systems **1a** and **2a** with their thiophene analogues **13** and **14**²⁰ (Fig. 1) shows slightly increased potentials for the thienothiophene derivatives. This increase is in contrast to the effect of the introduction of an additional fused thiophene ring in compounds **3**, **4** (DTT derivatives), for which both E_{ox} and $|E_{red}|$ are lower than those of **1a**, **2a**, respectively.

Finally, these observed trends in $E_{ox}(|E_{red}|)$ are confirmed by the calculated B3P86-6-31-G^{*} HOMO (LUMO) energies (Table 1) except for **13** and **14** when comparing with their TT analogues (**1a** and **2a**).

2.5. UV-vis spectroscopy

Absorption spectra for compounds **1–4** afforded λ_{max} data recorded in Table 2 (see spectra in Supplementary data). All systems show broad, low energy absorption bands corresponding to an intramolecular charge transfer (ICT).

Table 2	
UV-vis	data ^a

Compd	λ _{max} (log ε) 1,4-Dioxane	$\lambda_{\max} (\log \epsilon)$ CH ₂ Cl ₂	$\lambda_{\max} (\log \epsilon)$ DMF
1a	625 (4.88)	653 (4.88)	638 (4.76)
1b	642 (4.84)	677 (4.84)	669 (4.75)
3	636 (4.76)	659 (4.75)	642 (4.61)
2a	656 (4.80)	711 (4.84)	681 (4.72)
2b	660 (4.61)	708 (4.68)	668 (4.56)
4	658 (4.46)	708 (4.64)	675 (4.52)
13	611 (4.76)	644 (4.64)	_
14	665 (4.55)	708 (4.70)	—

^a All λ_{max} data are in nm.

Comparison of compounds that only differ in the acceptor group shows a bathochromic shift for TCF derivatives **2**, **4**, in agreement with its higher electron-withdrawing ability, and in line with their electrochemical properties.

For thieno[3,2-*b*]thiophene derivatives **1** and **2**, lengthening the spacer has a different effect on λ_{max} values depending on the acceptor moiety. Systems 1a,b, containing thiobarbiturate acceptor, show the expected bathochromic shift when conjugation is enlarged. The same behavior was observed for the aldehyde precursors 8a,b (471 (467) nm for 8a and 499 (495) nm for 8b, in CH₂Cl₂ (DMF)). For compounds **2a**,**b**, with the stronger TCF acceptor, enlarging conjugation hardly affects maximum absorption wavelength in solvents like dioxane and CH₂Cl₂, and results in a slightly hypsochromic shift when solvent polarity is increased (13 nm, 0.03 eV, DMF). This hypsochromic behavior with increasing conjugation has been reported for other push-pull systems with different donors, acceptors, and π -linkers, ^{21,22} in some of which^{21f,g} a similar reliance of the shifts with the acceptor strength has been established. Moreover, it has been found for a series of push-pull substituted oligothiophenes that the blue shift becomes more pronounced with increasing solvent polarity.²²

Meier explained this behavior^{21g,22} considering the ICT apart from the extension of conjugation. If the decrease of the ICT effect with increasing *n* prevails, the result is an overall hypsochromic shift.

Concerning the number of fused thiophenes, the replacement of thiophene by TT and subsequently by DTT also affects to the ICT band position in a different way depending on the acceptor moiety. Thus, for systems with thiobarbituric acid, there is a slight red shift of λ_{max} (in CH₂Cl₂ and dioxane) on going from **13** to **1a** and **3**, as a result of the extended conjugation, and in agreement with the behavior of the unsubstituted fused systems,²³ and a previous comparison between thiophene- and thieno[3,2-*b*]thiophene-D- π -A systems.^{8a} However, there is an almost negligible shift of λ_{max} for TCF derivatives (cf. **14/2a/4**) in CH₂Cl₂, and for the non-polar dioxane a slight blue shift is encountered on passing from thiophene to TT and DTT relay.

Concerning the dependence of the band position on solvent polarity, positive solvatochromism for low polarity solvents (from dioxane to CH_2Cl_2) that becomes negative when increasing solvent polarity (from CH_2Cl_2 to DMF) was observed for compounds **1–4**. Nevertheless, the extended and broad shape of the bands precludes an accurate identification of the longest wavelength absorption, particularly for TCF derivatives **2**, **4**.

This solvatochromic behavior resembles that of other reported dithienothiophene-^{9a-b} or dithienylethylene-²⁴containing systems.

Moreover, attempts to establish linear correlations of transition energy with typical solvent parameters, such as *Z*-scale, E_T^N , π^* or $E_T(30)^{25}$ failed.^{21f}

2.6. Nonlinear optical properties

Second-order nonlinear optical properties of compounds **1–4** were measured by electric field-induced second harmonic generation at 1907 nm and the zero-frequency $\mu\beta_0$ values were calculated by means of the two-level model²⁶ using the lowest energy absorption band for each compound (It should be noted that, for all systems broad bands have been found.). For the sake of comparison, Disperse Red 1, a common benchmark for organic NLO chromophores shows a $\mu\beta_0$ value of ca. 480×10^{-48} esu and 370×10^{-48} esu in CH₂Cl₂ and DMSO, respectively, under the same experimental conditions. Both the experimental and theoretical results (CPHF, coupled perturbed Hartree–Fock) are recorded in Table 3, where data for compounds **13** and **14**²⁰ are also gathered.

Moreover, for systems with thiobarbituric acid moiety, lengthening conjugation with an additional thiophene ring (cf. **1a/3**) leads to an increased $\mu\beta_0$ value. In contrast, as regards TCF acceptor derivatives, the dithienothiophene derivative 4 has a lower NLO response than the shortest one 2a. This experimental fact is also reproduced by calculated $\mu\beta_0$ values (HF 6-31G^{*}), that predict an almost negligible difference between β_0 values of compounds **2a** and **4**. a lower dipole moment for **4** when compared to **2a**, and a larger angle between μ and β vectors (θ) for **4** (θ $(2a)=24.2^{\circ}; \theta(4)=28.0^{\circ})$. One of the possible explanations to this fact could be the difference on the preferred conformation for both types of compounds. Calculations suggest that while TT derivatives show a 'rod-type' conformation, the presence of the DTT relay induces a more 'folded' shape, thereby decreasing the total polarity of the molecules. The longer resonance pathway is not able therefore to compensate the important loss of dipole moment with the strongest acceptor. Calculated values for $\mu\beta_0$ are in all cases overestimated but reproduce quite well the experimental trends.

Measurements in DMSO were also performed to ascertain the position of these chromophores on the Marder's plot.²⁷ For this purpose, acceptor TCF derivatives **2(a,b)**, **4** were chosen. Compound **3** was also measured to check the effect of the electronwithdrawing group. Results show a decline of $\mu\beta_0$ in all cases compared to those measured in dichloromethane, indicating that our systems are left-hand chromophores and that the maximum of the Marder's plot has been exceeded. None of the values approach zero or reach the negative zone, because the neutral form predominates in this solvent polarity range. This fact contrasts with other reported systems bearing dithienothiophene as electron relay, which show similar solvatochromic behavior, but undergo sign inversion in highly polar solvents.^{9b}

Finally, it seems pertinent to point out that the $\mu\beta_0$ values for derivative **2b** in CH₂Cl₂ is, to the best of our knowledge, the highest one shown by a pyranylidene donor-based chromophore.

Table 3

Experimental and CPHF-calculated NLO properties

Compd	$\mu\beta^{a} (10^{-48} \text{ esu}) (CH_{2}Cl_{2})$	$\mu {\beta_0}^{\rm b} (10^{-48} {\rm esu})$ (CH ₂ Cl ₂)	$\mu\beta^{c}$ (10 ⁻⁴⁸ esu) (DMSO)	$ \mu \beta_0^{d} (10^{-48} \text{ esu}) $ (DMSO)	$\mu {\beta_0}^{\rm e}$ (10 ⁻⁴⁸ esu)	eta_0 tot ^e (10 ⁻³⁰ esu)	μ_g^e (D)
1a	2800	1310	_	_	2779	213	13.6
1b	5400	2340	_	—	5876	417	14.6
3	4000	1800	2300	1120	3146	273	11.6
2a	14,900	5670	8000	3300	11,962	545	24.1
2b	21,900	8500	9300	4000	19,379	831	25.1
4	9200	3500	6200	2650	9987	572	19.8
13	1380	665	—	—	1162	94	13.0
14	6790	2630	1400	—	7165	328	23.4

^a μβ values determined in CH₂Cl₂ at 1907 nm (experimental uncertainty better than ±15% except for compounds **4** (~20%) and **3** (~30%) (see Section 4.2)).

^b Experimental $\mu\beta_0$ values in CH₂Cl₂ calculated using the two-level model.

^c $\mu\beta$ values determined in DMSO at 1907 nm (experimental uncertainty ±15%).

^d Experimental $\mu\beta_0$ values in DMSO calculated using the two-level model.

^e Calculated at the CPHF/6-31G*//B3P86/6-31G* level (gas phase).

 $\mu\beta$ values for TCF derivatives **2**, **4** are remarkably superior to those of their thiobarbituric acid analogues **1**, **3**, respectively, highlighting again the higher acceptor strength of the former.

For TT derivatives **1** and **2**, the incorporation of a double bond in the spacer leads to an important increase of the NLO response in dichloromethane, as expected when conjugation is increased.

Comparison of systems **1a** and **2a** with previously reported derivatives bearing a thiophene moiety **13** and **14**²⁰ could also be useful to illustrate the features conferred by these fused heterocycles. Measurements in dichloromethane show an increase of around 50% in nonlinear optical response when a simple thiophene is substituted by thieno[3,2-*b*]thiophene, (cf. **1a/13**; **2a/14**) as previously observed.^{8a}

2.7. Thermal stability

Thermal stabilities of compounds **1–4** were studied by thermogravimetric analysis (TGA) (Table 4), estimating their

Table 4	
Thermal	stability

j			
Compd	<i>T</i> _d (°C)	Compd	<i>T</i> _d (°C)
1a	289	2a	315
1b	280	2b	310
3	343	4	342
13	272	14	334

decomposition temperatures (T_d) as the intercept of the leading edge of the weight loss with the baseline of the TGA scans.

All derivatives **1–4** are thermally stable with decomposition temperatures above 280 °C, in particular derivatives of acceptor TCF, for which decomposition temperatures are higher than those of their thiobarbiturate analogues, apart from compounds **3** and **4**, with T_d values essentially identical. As expected, introduction of an additional double bond in the spacer leads to a slight decrease of thermal stability for both acceptors. With the exception of **2a**, thieno[3,2-*b*]thiophene derivatives are more stable than the thiophene systems (cf. **1a**/**13**) in agreement with previous results.^{8a} Derivatives **3** and **4** show very high decomposition temperatures, and are the most stable systems for a given acceptor.

3. Conclusions

Merocyanines 1–4, featuring fused thiophenes as electron relays have been synthesized and studied, and their properties compared to those of analogous systems bearing a thiophene spacer. The relay supports part of the net positive charge of the D- π -A systems, increasing with the number of fused thiophenes. EFISH measurements reveal that 1–4 are located in the left-hand side of the Marder's plot, in region B, not reaching the cyanine limit region.

For a given acceptor, the best NLO response has been obtained for compounds bearing a TT ring conjugated with a vinylene unit (**1,2**)**b**, showing **2b** the highest $\mu\beta_0$ value reported for a pyranylidene donorbased NLO chromophore, together with a decomposition temperature above 300 °C. Thus, D- π -A compounds containing dithienothiophene and thienothiophene as (part of) conjugated spacer provide a good balance between NLO properties and thermal stability.

4. Experimental

4.1. General experimental methods

Reactions under microwaves were carried out in a CEM Discover reactor using sealed reaction vessels. Temperature was monitored with an external surface sensor. Power was set to be 20 W and maximum temperature was set to be 120 °C. Infrared measurements were carried out in KBr using a Perkin-Elmer Fourier Transform Infrared 1600 spectrometer. Melting points were obtained on a Gallenkamp apparatus in open capillaries and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker ARX300 or a Bruker AV400 at 300 or 400 MHz and 75 or 100 MHz, respectively; δ values are given in parts per million (ppm) (relative to TMS) and J values in hertz (Hz). ¹H-¹H COSY experiments were recorded on a Bruker AV400 or a Bruker AV500 at 400 or 500 MHz in order to establish peaks assignment and spatial relationships. ¹H-¹³C-HSQC and ¹H-¹³C-HMBC experiments were recorded on a Bruker AV500 at 500 MHz in order to find some of the carbon signals for compounds 1a and 2a. Selective ge-1D NOESY experiments (mixing time: 0.95-3.17 s; selective 180 pulse: 40 ms) were recorded on a Bruker ARX300 at 300 MHz for compound 8a, in order to determine the conformation for the bond linking the donor moiety to the π -spacer. MALDI-ToF mass spectra were recorded on a Bruker MicroFlex spectrometer with a nitrogen laser (3.68 eV) using dithranol as matrix; accurate mass measurements were achieved using PEG as external reference and calibrating with [PEG+Na]⁺. Electrospray mass spectra were recorded on a Bruker Q-ToF spectrometer; accurate mass measurements were achieved using sodium formate as external reference. Electronic spectra were recorded with an UV-Vis UNICAM UV4 spectrophotometer. Cyclic voltammetry measurements were performed with a µ-Autolab ECO-Chemie potentiostat using a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode. The experiments were carried out under argon in CH₂Cl₂, with Bu₄NPF₆ as supporting electrolyte (0.1 mol L⁻¹). Scan rate was 100 mV s⁻¹. Thermogravimetric analysis (TGA) were carried out on a TA Instruments TGA Q5000 at 10 °C/min in nitrogen atmosphere from 40 °C to 600 °C; from 600 °C to 750 °C heating was continued in synthetic air atmosphere. Elemental analyses were carried out with a Perkin–Elmer CHN2400 microanalyzer.

4.2. NLO measurements

Electric field-induced second harmonic generation (EFISH) measurements have been performed using as the fundamental radiation the 1.9 µm output of a H₂ Raman shifter pumped by a Q-switched Nd:YAG laser. This laser operates at 1064 nm, with a repetition rate of 10 Hz and pulse width of 8 ns. A computer controlled NLO spectrometer completes the SHG experimental set-up. The 1.9 µm incident light is split in two beams. The less intense one is directed to a N-(4-nitrophenyl)-(L)-prolinol (NPP) powder sample whose SH signal is used as a reference in order to reduce the effects of laser fluctuations. The other beam is passed through a linear polarizer and focused into the EFISH wedge shaped liquid cell. Voltage pulses of 5 kV and 3 µs are applied across the cell (2 mm gap between the electrodes) synchronously with the laser pulses. The harmonic signals from both the EFISH cell and the NPP reference are measured with two photomultipliers. Interference filters are used to remove the residual excitation light beyond the sample and the reference.

The molecular $\mu\beta$ values have been determined in dichloromethane and DMSO for compounds **2–4** and in dichloromethane for compounds **1**. As a rule, several solutions of concentration in the range $(1-5)\times10^{-4}$ M were measured. However, due to the low solubility of compounds **3** and **4**, the use of solutions below 10^{-4} M (in dichloromethane) was required. The small difference between the EFISH signals from these solutions and the pure solvent limited the accuracy of $\mu\beta$ values of these chromophores, especially in the case of the thiobarbituric acid derivative **3**.

 $\mu\beta_0$ values were extrapolated using a two-level dispersion model.^{26a} Under the same experimental conditions $\mu\beta_0$ deduced for DR1 in dichloromethane was 480×10^{-48} esu, quite close to the value reported in the same solvent by Dirk et al.²⁸ $\mu\beta_0$ value of the same chromophore in DMSO was 370×10^{-48} esu.

4.3. Computational procedures

All theoretical calculations were performed by using the Gaussian 09²⁹ program. The molecular geometries were optimized using the B3P86³⁰ functional and the 6-31G^{*31} basis set. Molecular hyperpolarizabilities at zero-frequency were calculated by the coupled perturbed Hartree–Fock method (CPHF) using the HF/6-31G^{*} model.

4.4. Synthesis and characterization

Compounds **5**,¹² **6**,^{9b} **7**,¹¹ **10**,¹³ and **12**^{14a} were prepared as previously described.

4.4.1. 5-(2,6-Diphenyl-4H-pyran-4-ylidenemethyl)thieno[3,2-b]thiophen-2-carbaldehyde (**8a**). To a solution of **7** (0.55 g, 1.31 mmol) in dry THF (20 mL) at $-30 \degree$ C, *n*-BuLi (0.85 mL, 1.36 mmol) 1.6 M in hexanes was added under argon atmosphere. The solution turned to dark green and was stirred at this temperature for 45 min. Then, a suspension of **5** (0.28 g, 1.41 mmol) in dry THF (14 mL) was slowly added via a syringe and the mixture was stirred for one further hour. A solution of saturated NH₄Cl (60 mL) was then added and the aqueous phase was extracted with AcOEt (4×50 mL). The resulting organic layer was dried over MgSO₄ and evaporated. The crude product was purified by flash column chromatography (silicagel) using CH₂Cl₂ as eluent, affording **8a** (0.33 g, 0.8 mmol, 61%) as a dark red solid. Found: C 72.91, H 3.73. C₂₅H₁₆O₂S₂ requires C 72.79, H

3.91%. Mp 213–217 °C. IR (KBr, cm⁻¹): 1660 (C=O), 1581 (C=C, Ar), 1556 (C=C, Ar). ¹H NMR (300 MHz, CDCl₃): δ 9.91 (s, 1H, –*CHO*), 7.92–7.83 (m, 3H, phenyl–*H*+TT–*H*), 7.81–7.76 (m, 2H, phenyl–*H*), 7.56–7.42 (m, 6H, phenyl–*H*), 7.18 (d, *J*=1.9 Hz, 1H, pyranylidene–*H*), 7.13 (s, 1H, TT–*H*), 6.50 (d, *J*=1.9 Hz, 1H, pyranylidene–*H*), 6.15 (s, 1H, pyranylidene=C–*H*). ¹³C NMR (75 MHz, CDCl₃): δ 182.6, 154.4, 152.1, 151.3, 147.0, 143.2, 136.9, 132.8, 132.6, 131.3, 130.0, 129.5, 129.0, 128.8, 128.7, 125.2, 124.6, 116.6, 108.4, 107.4, 102.6. HRMS (MALDI⁺): found 412.0594 [M⁺•]. C₂₅H₁₆O₂S₂ requires 412.0586; found 413.0638 [M+H]⁺. C₂₅H₁₇O₂S₂ requires 413.0665.

4.4.2. (E)-3-(5-(2,6-Diphenyl-4H-pyran-4-ylidenemethyl)thieno[3,2-b]thiophen-2-yl)acrylaldehyde (8b). To a mixture of 8a (0.18 g, 1.44 mmol) and 1,3-dioxolan-2-ylmethyltributylphosphonium bromide (10) (0.28 g, 0.75 mmol) in dry DMF (3 mL) a 0.48 M solution of sodium ethoxide in ethanol (1.5 mL, 0.73 mmol) was added under argon atmosphere. The mixture was stirred at 90 °C for 22 h and then water (75 mL) was added. The aqueous phase was extracted with AcOEt (4×50 mL), and the resulting organic layer was washed with brine, dried over MgSO₄, and evaporated. To a solution of the crude residue in THF (10 mL), an aqueous solution of HCl 1 N (40 mL) was added and the mixture was stirred for 90 min at room temperature. Then, water (50 mL) was added and the aqueous phase was extracted with AcOEt (4×50 mL). The organic layer was dried over MgSO₄ and evaporated. The crude product was purified by flash column chromatography (silicagel) using CH₂Cl₂/hexane (9:1) as eluent, yielding **8b** (0.14 g, 0.34 mmol, 72%) as a dark red solid. Found: C 73.55, H 3.90. C₂₇H₁₈O₂S₂ requires C 73.94, H 4.14%. Mp 220-222 °C. IR (KBr, cm⁻¹): 1651 (C=O), 1600 (C=C), 1552 (C=C). ¹H NMR (300 MHz, CDCl₃): δ 9.63 (d, *I*=7.7 Hz, 1H, −CHO), 7.89−7.83 (m, 2H, phenyl−H), 7.81-7.75 (m, 2H, phenyl-H), 7.61 (d, J=15.3 Hz, 1H, -CH= CH–CHO), 7.54–7.40 (m, 7H, phenyl–*H*+TT–*H*), 7.16 (d, *J*=2.1 Hz, 1H, pyranylidene-H), 7.08 (br s, 1H, pyranylidene-H), 6.48 (s, 1H, TT-H), 6.47 (dd, J₁=15.3 Hz, J₂=7.7 Hz, 1H, -CH=CH-CHO), 6.14 (s, 1H, pyranylidene=C–H). ¹³C NMR (100 MHz, CDCl₃): δ 192.5, 185.9, 154.2, 151.9, 148.7, 145.0, 139.5, 133.0, 132.8, 130.5, 129.9, 129.4, 128.8, 128.7, 125.7, 125.1, 125.0, 124.8, 124.6, 116.5, 108.5, 107.6, 102.7. HRMS (ESI⁺): found 439.0804 [M+H]⁺. C₂₇H₁₉O₂S₂ requires 439.0821.

4.4.3. 6-(2,6-Diphenyl-4H-pyran-4-ylidenemethyl)dithieno[3,2b:2',3'-d]thiophen-2-carbaldehyde (9). To a solution of 7 (0.33 g, 0.75 mmol) in dry THF (8 mL) at -30 °C *n*-BuLi (0.55 mL, 0.88 mmol) 1.6 M in hexanes was added under argon atmosphere. The solution turned to dark green and was stirred at this temperature for 15 min. Then, this solution was slowly added with a cannula to a suspension of $\mathbf{6}$ (0.19 g, 0.75 mmol) at $-30 \,^{\circ}$ C in dry THF (12 mL) and the mixture was stirred for further 30 min. A solution of saturated NH₄Cl (50 mL) was then added and the aqueous phase was extracted with AcOEt $(4 \times 50 \text{ mL})$. The resulting organic layer was dried over MgSO₄ and evaporated. The crude product was purified by flash column chromatography (silicagel) using hexane/CH₂Cl₂ (1:1) as eluent, then (3:7), affording 9 (0.12 g, 0.25 mmol, 34%) as a dark red solid. Found: C 69.46, H 3.35. C₂₇H₁₆O₂S₃ requires C 69.20, H 3.44%. Mp >280 °C (dec). IR (KBr, cm⁻¹): 1650 (C=O), 1580 (C=C, Ar). ¹H NMR (400 MHz, CDCl₃): δ 9.93 (s, 1H, -CHO), 7.92 (s, 1H, DTT-H), 7.92–7.86 (m, 2H, phenyl–H), 7.82–7.78 (m, 2H, phenyl–H), 7.58–7.39 (m, 6H, phenyl-H), 7.16 (dd, $J_1=1.8$ Hz, $J_2=0.6$ Hz, 1H, pyranylidene-H), 7.14 (d, J=0.6 Hz, 1H, DTT-H), 6.48 (d, J=1.8 Hz, 1H, pyranylidene-H), 6.14 (s, 1H, pyranylidene=C-H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 183.1, 154.8, 148.0, 143.4, 133.4, 133.2, 130.9, 130.8, 130.5, 130.0, 129.4, 129.3, 125.7, 125.1, 118.1, 108.8, 107.8, 102.9. HRMS (ESI⁺): found 469.0388 [M+H]⁺. C₂₇H₁₇O₂S₃ requires 469.0385.

4.4.4. 5-[5-(2,6-Diphenyl-4H-pyran-4-ylidenemethyl)thieno[3,2-b]thiophen-2-ylmethylen]-1,3-diethyl-2-thioxodihydropyrimidin-4,6-dione (**1a**). To a solution of **8a** (0.096 g, 0.23 mmol) in absolute ethanol (8 mL), 1,3-diethyl-2-thiobarbituric acid (11) (0.048 g, 0.24 mmol) was added in one portion under argon atmosphere and the mixture was refluxed for 3 h. The reaction mixture was cooled to room temperature and then to 0 °C. The resulting solid was isolated by filtration and washed with cold ethanol, hexane, and pentane. Product 1a was obtained as a dark green solid (0.11 g, 0.18 mmol, 79%). Found: C 66.87, H 4.29, N 4.43. C₃₃H₂₆N₂O₃S₃ requires C 66.64, H 4.41, N 4.71%. Mp 278–282 °C. IR (KBr, cm⁻¹): 1644 (C=O), 1537 (C=C, Ar), 1101 (C=S). ¹H NMR (300 MHz, CDCl₃): δ 8.65 (s, 1H, -TT-CH=A), 7.95 (s, 1H, TT-*H*), 7.89–7.81 (m, 2H, phenyl-*H*), 7.80–7.73 (m, 2H, phenyl-*H*), 7.55–7.40 (m, 6H, phenyl-H), 7.18 (s, 1H), 7,09 (s, 1H), 6.55 (br s, 1H, pyranylidene—*H*), 6.21 (s, 1H, pyranylidene=*C*-*H*), 4.64–4.51(m, 4H, -NCH₂CH₃), 1.39–1.25 (m, 6H, -NCH₂CH₃). ¹³C NMR (125 MHz, CDCl₃): δ 128.9, 125.2, 124.7, 119.9, 116.7, 108.8, 108.0, 46.6, 29.6. HRMS (MALDI⁺): found 594.1105 [M⁺•]. C₃₃H₂₆N₂O₃S₃ requires 594.1100; found: 595.1201 [M+H]⁺. C₃₃H₂₇N₂O₃S₃ requires 595.1178.

4.4.5. (E)-5-[3-(5-(2,6-Diphenyl-4H-pyran-4-ylidenemethyl)thieno [3,2-b]thiophen-2-yl)alylidene]-1,3-diethyl-2-thioxodihydropyrimidin-4,6-dione (1b). To a solution of 8b (0.048 g, 0.23 mmol) in absolute ethanol (4 mL), 1,3-diethyl-2-thiobarbituric acid (11) (0.025 g, 0.13 mmol) was added in one portion under argon atmosphere and the mixture was refluxed for 2 h. The reaction mixture 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 (9:1). Product 1b was obtained as a dark blue solid (0.052 g, 0.083 mmol, 76%). Found: C 67.46, H 4.74, N 4.66. C35H28N2O3S3 requires C 67.71, H 4.55, N 4.51%. Mp 285-287 °C. IR (KBr, cm⁻¹): 1649 (C=O), 1542 (C=C, Ar). ¹H NMR (300 MHz, CDCl₃): δ 8.35 (dd, J₁=14.0 Hz, J₂=12.8 Hz, 1H, -TT-CH=CH-CH=A), 8.15 (d, *I*=12.8 Hz, 1H, -TT-CH=CH-CH=A), 7.95-7.84 (m, 2H, phenyl-H), 7.83-7.72 (m, 2H, phenyl-H), 7.63 (d, J=14.0 Hz, 1H, -TT-CH= CH–CH=A), 7.58–7.38 (m, 7H, phenyl–H+TT–H), 7.19 (s, 1H), 7.10 (s, 1H), 6.53 (s, 1H), 6.18 (s, 1H, pyranylidene=C-H), 4.65-4.50 (m, 4H, -NCH₂CH₃), 1.23-1.20 (m, 6H, -NCH₂CH₃). ¹³C NMR: not registered due to its low solubility. HRMS (MALDI⁺): found 620.1212 [M⁺•]. C₃₅H₂₈N₂O₃S₃ requires 620.1257; found 621.1328 [M+H]⁺. C₃₅H₂₉N₂O₃S₃ requires 621.1335.

4.4.6. (E)-5-[6-(2,6-Diphenyl-4H-pyran-4-ylidenemethyl)dithieno[3,2b:2',3'-d]thiophen-2-yl-alylidene]-1,3-diethyl-2-thioxodihydropyrimidin-4,6-dione (3). To a solution of 9 (0.050 g, 0.11 mmol) in absolute ethanol (4 mL), 1,3-diethyl-2-thiobarbituric acid (11) (0.023 g, 0.11 mmol) was added in one portion under argon atmosphere and the mixture was refluxed for 24 h. The reaction mixture 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 (9:1). Product **3** was obtained as a dark blue solid (0.044 g, 0.068 mmol, 62%). Found: C 64.41, H 4.17, N 4.11. C₃₅H₂₆N₂O₃S₄ requires C 64.59, H 4.03, N 4.30%. Mp 288–290 °C. IR (KBr, cm⁻¹): 1651 (C=O), 1542 (C=C, Ar). ¹H NMR (500 MHz, DMSO- d_6 , 90 °C): δ 8.70 (s, 1H, -DTT-CH=A), 8.58 (s, 1H, -DTT-H), 8.04-7.97 (m, 2H, phenyl-H), 7.93–7.86 (m, 2H, phenyl–H), 7.70–7.42 (m, 7H, phenyl–H+DTT–H), 7.24 (s, 1H, pyranylidene–H), 6.93 (s, 1H, pyranylidene–H), 6.39 (s, 1H, pyranylidene=C-H), 4.53 (q, J=7.7 Hz, 4H, -NCH₂CH₃), 1.37-1.20 (m, 6H, -NCH₂CH₃). ¹³C NMR: not registered due to its low solubility. HRMS (MALDI⁺): found 650.0843 [M⁺•]. C₃₅H₂₆N₂O₃S₄ requires 650.0821; found: 651.0866 [M+H]⁺. C₃₅H₂₇N₂O₃S₄ requires 651.0899.

4.4.7. (*E*)-2-(3-Cyano-4-(2-(5-(2,6-diphenyl-4H-pyran-4-ylidenemethyl)thieno[3,2-b]thiophen-2-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (**2a**). To a solution of **8a** (0.049 g, 0.12 mmol) and acceptor TCF (**12**) (0.027 g, 0.13 mmol) in CHCl₃ (2.5 mL), triethylamine (17 μ L, 0.12 mmol) was added via a syringe under argon atmosphere and the mixture was refluxed for 24 h. The reaction mixture 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 bright maroon solid (0.040 g, 0.067 mmol, 58%). Found: C 72.61, H 3.75, N 7.24. C₃₆H₂₃N₃O₂S₂ requires C 72.83, H 3.90, N 7.80%. Mp 274–278 °C. IR (KBr, cm⁻¹): 2223 (C≡N), 1649 (C=C), 1538 (C= C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.22 (d, *J*=15.9 Hz, 1H, -TT-CH= CH-A), 8.09 (s, 1H, -TT-H), 7.98 (d, J=7.1 Hz, 2H, phenyl-H), 7.91 (d, I=7.1 Hz, 2H, phenyl-H), 7.64–7.46 (m, 7H, phenyl-H+TT-H), 7.19 (s, 1H, pyranylidene–*H*), 7.06 (s, 1H, pyranylidene–*H*), 6.68 (d, *J*=15.9 Hz, 1H, -TT-CH=CH-A), 6.38 (s, 1H, pyranylidene=C-H), 1.81 (s, 6H, TCF–CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆, 60 °C): δ 173.8, 140.7, 131.8, 131.6, 130.1, 128.8, 128.6, 124.9, 124.3, 117.4, 111.0, 108.6, 108.0, 104.2, 98.0, 25.3. ¹³C NMR (125 MHz, CDCl₃) δ: 172.2, 155.1, 152.7, 152.6, 152.5, 147.0, 140.2, 138.9, 128.7, 128.6, 127.9, 125.1, 124.4, 116.6, 110.5, 108.5, 107.5, 102.7, 96.5, 26.4. HRMS (MALDI⁺): found 593.1210 [M⁺•]. $C_{36}H_{23}N_3O_2S_2$ requires 593.1226; found 594.1248 $[M+H]^+$. C₃₆H₂₄N₃O₂S₂ requires 594.1304.

4.4.8. 2-(3-Cyano-4-((1E,3E)-4-(5-((2,6-diphenyl-4H-pyran-4-ylidene) methyl)thieno[3,2-b]thiophen-2-yl)buta-1,3-dienyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (2b). A suspension of 8b (0.056 g, 0.13 mmol) and acceptor TCF (12) (0.033 g, 0.17 mmol) in absolute ethanol (5 mL) in a sealed tube under nitrogen atmosphere was irradiated with microwaves (20 W) for 8 min. Then the tube was cooled to 60 °C and underwent the same procedure for six times. The reaction mixture was cooled to room temperature and the solvent was evaporated. The crude residue was purified by flash column chromatography (neutral alumina) using CH₂Cl₂/hexane (7:3) as eluent, then CH₂Cl₂. Product **2b** was obtained as a dark blue solid (0.011 g, 0.018 mmol, 14%). Found: C 73.85, H 4.21, N 6.61. C₃₈H₂₅N₃O₂S₂ requires C 73.64, H 4.07, N 6.78%. Mp >250 °C (dec). IR (KBr, cm^{-1}): 2223 (C=N), 1650 (C=C), 1551 (C=C). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.95–6.87 (m, 2H, phenyl–*H*), 7.86–7.77 (m, 2H, phenyl–*H*), 7.64–7.34 (m, 9H, phenyl-H+TT-H+TT-CH=CH-CH=CH-A), 7.20 (d, J=1.4 Hz, 1H, pyranylidene-H), 7.13 (s, 1H, TT-H), 6.82 (dd, J₁=14.7 Hz, J₂=11.4 Hz, 1H, TT-CH=CH-CH=CH-A), 6.56 (d, J=1.4 Hz, 1H, pyranylidene–H), 6.49 (d, J=15.2 Hz, 1H, TT–CH= CH–CH=CH–A), 6.20 (s, 1H, pyranylidene=C–H), 1.72 (s, 6H, TCF- CH_3). ¹³C NMR: not registered due to its low solubility. HRMS (ESI⁺): found: 619.1377 [M⁺•]. C₃₈H₂₅N₃O₂S₂ requires 619.1383; found 642.1278 [M+Na]⁺. C₃₈H₂₅N₃O₂S₂Na requires 642.1280.

4.4.9. (E)-2-(3-Cyano-4-(2-(6-(2,6-diphenyl-4H-pyran-4-ylidenemethyl)dithieno[3,2-b:2',3'-d]thiophen-2-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (4). To a solution of 9 (0.050 g, 0.11 mmol) and acceptor TCF (12) (0.024 g, 0.12 mmol) in CHCl₃ (3.5 mL), triethylamine (15 µL, 0.11 mmol) was added under argon atmosphere and the mixture was refluxed for 24 h. The reaction mixture 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 (7:3). Product **4** was obtained as a dark solid (0.026 g, 0.040 mmol, 37%). Found: C 70.42, H 3.44, N 6.63. C₃₈H₂₃N₃O₂S₃ requires C 70.24, H 3.57, N 6.47%. Mp >300 °C (dec). IR (KBr, cm⁻¹): 2223 (C=N), 1652 (C=C), 1540 (C=C). ¹H NMR (500 MHz, DMSO- d_6 , 90 °C): δ 8.19 (d, J=15.8 Hz, 1H, DTT-CH=CH-A), 8.18 (s, 1H, DTT-H), 8.01-7.94 (m, 2H, phenyl-H), 7.92–7.85 (m, 2H, phenyl–*H*), 7.64–7.45 (m, 7H, phenyl–*H*+DTT–*H*), 7.20 (s, 1H, pyranylidene–*H*), 6.90 (s, 1H, pyranylidene–*H*), 6.80 (d, J=15.8 Hz, 1H, DTT-CH=CH-A), 6.35 (s, 1H, pyranylidene=C-H), 2.09 (s, 3H, TCF-CH₃), 1.83 (s, 3H, TCF-CH₃). ¹³C NMR: not registered due to its low solubility. HRMS (MALDI⁺): found: 649.0941 [M⁺•]. C₃₈H₂₃N₃O₂S₃ requires 649.0947.

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Supplementary data

NMR and UV—vis spectra of new compounds, computed energies, and Cartesian coordinates of optimized geometries can be found. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.03.027.

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