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Synthesis, Characterization, and Optical Properties of 4*H*-Pyran-4-ylidene Donor-Based Chromophores: The Relevance of the Location of a Thiophene Ring in the Spacer

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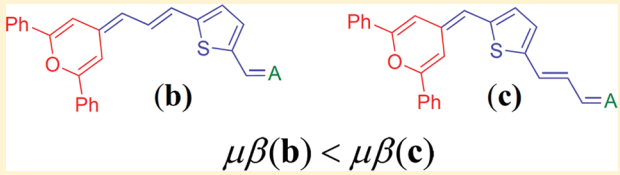
Supporting Information

ABSTRACT: A series of new 4*H*-pyran-4-ylidene donor-based chromophores with a thiophene ring in the spacer has been synthesized. The linear and nonlinear optical (NLO) properties of these compounds have been determined and compared with the results of computational calculations. The position of the thiophene ring proved essential to optimize the figure of merit $\mu\beta$, with the best results obtained when the heterocyclic system was closer to the donor moiety.



INTRODUCTION

In recent years, a large number of push−pull organic molecules have been synthesized and used for the preparation of materials with electronic and optical applications.[1,2] Generally, the main effort has been focused on the design of new chromophores with large first hyperpolarizability values (β). While enormous progress has been made in this field, interest in organic electro-optic materials has reemerged, and it is still desirable to develop highly efficient nonlinear optical (NLO) chromophores.[3] A typical strategy used in the design of new NLO chromophores involves the careful optimization of the ground-state polarization by choosing the appropriate pair of donor and acceptor moieties linked through a π-conjugated spacer.[4−8] In this sense, the proaromatic 4*H*-pyran-4-ylidene unit has been scarcely employed as a donor in NLO and constitutes an interesting option to prepare new push−pull systems.[9−12] The donor character of this moiety is comparable to and even higher than those of other common donors used in the field of NLO, including triarylamines,[13−16] *N*,*N*-dialkylaryl/heteroarylamines,[17−21] pyrid-4-ylidenes,[22,23] and 1,3-dithiol-2-ylidenes,[24−27] as demonstrated by the increased ground-state polarization shown by push−pull compounds bearing a pyranylidene moiety.[11,28]

Polyenes are often used as π-conjugated spacers, and they lead to large nonlinear responses. However, these systems have the drawback of lower chemical and thermal stability, an important aspect to consider in the manufacture of a device.[29−31] A typical way to optimize the stability is to include in the spacer an aromatic and, even better, a heteroaromatic ring with low resonance energy. The aromaticity of the ring lowers the HOMO energy, thus reducing the ease with which the material is oxidized or chemically modified. On the other hand, the nature of the heterocyclic system and its position in the spacer can determine the second-order NLO properties of the molecule because the heterocycle can act as an auxiliary donor or acceptor group.[32] For instance, significantly enhanced NLO responses have been obtained with a pyrrole attached to the donor[33−35] and a thiazole ring in the acceptor side.[36−38] The thiophene ring is certainly one of the most widely employed heteroaromatic spacers in push−pull systems, and as a π-excessive heterocycle,[39] it should behave as an auxiliary donor when it is closer to the donor.[34,40,41] However, several authors have found greater nonlinearities when thiophene is next to the acceptor group, and therefore, the general rule is not always followed.[36,42−45]

In this paper, we describe the synthesis and the second-order NLO properties of 12 efficient new chromophores. All of the molecules include a 4*H*-pyran-4-ylidene as the donor moiety, a thiophene ring as part of the conjugated π-system, and four common strong organic acceptors. Despite the fact that the thiophene ring is a very common heteroaromatic unit in push−pull systems, to our knowledge, there are only two papers in which the synthesis of a 4*H*-pyran-4-ylidene derivative linked to a thiophene ring[46,47] is described. Although one of these papers concerns a study of the third-order nonlinearities,[47] the second order NLO properties of such molecules remain unexplored. In order to investigate the role of the thiophene position within the spacer, we prepared two isomers for each acceptor, changing the location of the heterocycle toward the donor and the acceptor units (series **b** and **c**). The second-order NLO properties of the chromophores were evaluated and compared to the results of theoretical calculations.

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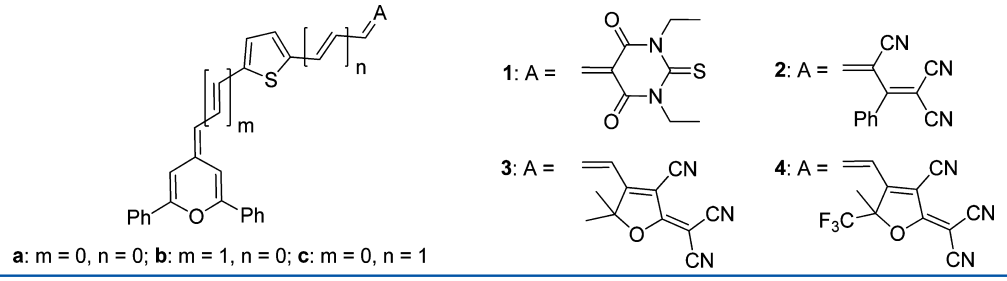
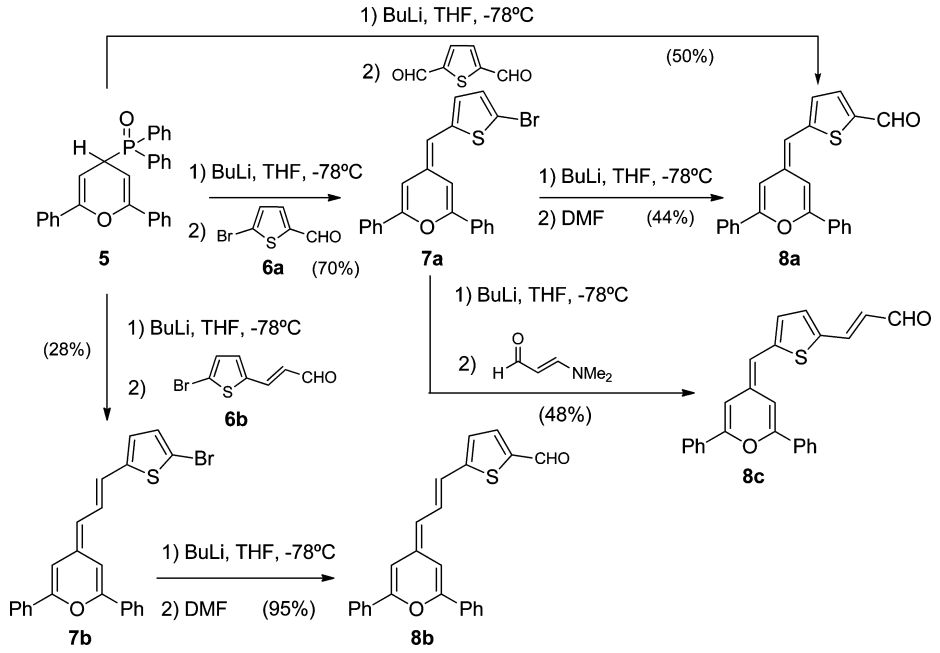
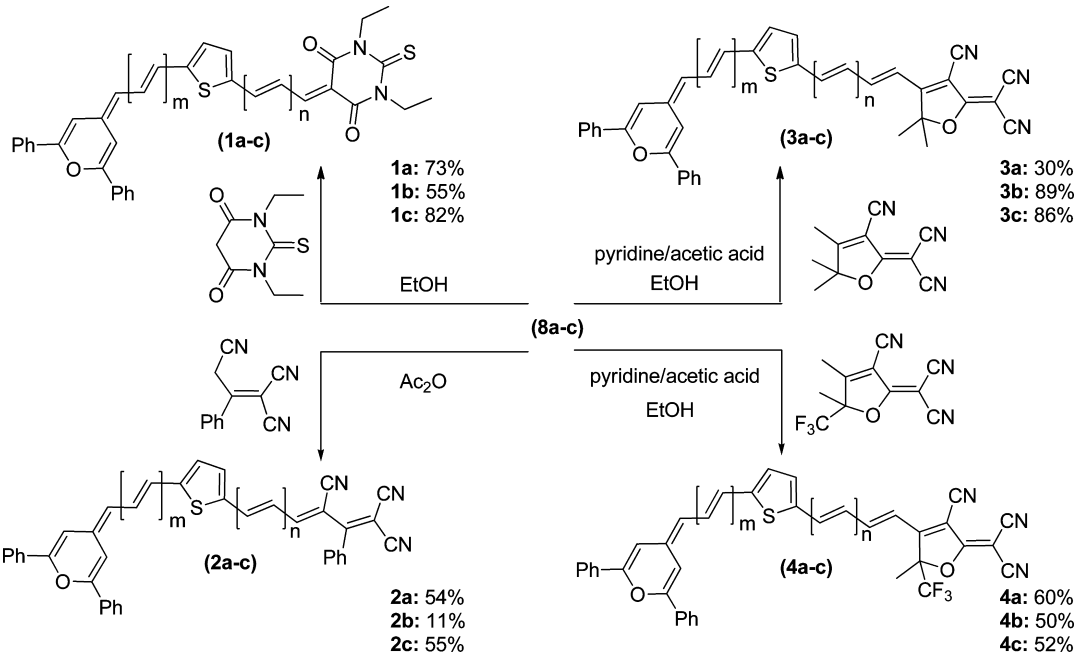


Scheme 1



Scheme 2



RESULTS AND DISCUSSION

Synthesis. The twelve new chromophores [**1**−**4**(**a**−**c**)] described in this paper were prepared from aldehydes **8**(**a**−**c**). These precursor aldehydes were obtained according to the synthetic strategy depicted in Scheme 1. Thus, the bromo derivatives **7a** and **7b** were prepared by a Horner reaction of pyranylphosphine oxide **5**[48] with commercially available 5-

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bromo-2-thiophenecarbaldehyde **6a** and with the bromoaldehyde **6b**,[49] respectively. Compound **7a** is unstable on exposure to light and chlorinated solvents, and it was necessary to use it immediately in the next step. Derivatives **7a** and **7b** were then treated with butyllithium and anhydrous *N*,*N*-dimethylformamide to obtain, after aqueous acidic workup, compounds **8a** and **8b**, respectively. Moreover, aldehyde **8a** can be prepared in one step and with a better yield by an alternative synthetic route, coupling pyranylphosphine oxide **5** with 2,5-thiophenedicarbaldehyde. In this case, only one 4*H*-pyran-4-ylidene ring was incorporated, probably because of the lower reactivity of the formyl group in aldehyde **8a** after introduction of the donor group. Aldehyde **8c** was obtained in moderate yield from bromothiophene **7a** followed by lithiation and reaction with *N*,*N*-dimethylaminoacrolein.

Finally, chromophores [**1**−**4**(**a**−**c**)] were obtained by Knoevenagel condensation of aldehydes **8**(**a**−**c**) and the corresponding acceptors[50−52] (**1**−**4**) in yields ranging from 11 to 89% (Scheme 2). Typically, it was necessary to purify the final products by flash chromatography (see the Experimental Section).

^{1}H NMR Studies. The study of the chemical shifts and coupling constants of some representative protons in the NMR spectra can afford valuable information about both the geometry and the distribution of the electronic density along the molecule. Concerning compounds **1**−**4**, $^3J_{HH}$ coupling constant analysis of the spacer shows that in all cases the CH═CH bonds have an (*E*)-configuration (15.4 Hz > $^3J_{HH}$ > 14.3 Hz), while for the CH−CH bonds, an *s-trans* conformation is proposed (a nuclear Overhauser effect was not observed between the ═CH—CH═ protons).

The chemical shifts of some representative hydrogen atoms (H_a, H_b, H_c and H_d) of the NLO chromophores are shown in Table 1. In particular, analysis of the protons in positions 3 and 5 of the 4*H*-pyran-4-ylidene ring may serve to evaluate the donor ability and the ground state polarization of the donor fragment. For the compounds reported here, we observed a decrease in the chemical shifts of the hydrogens H_a and H_b (Figure 1) on lengthening the spacer, a finding that suggests an increased contribution of the zwitterionic canonical form **ZW$_a$** for the shorter compounds, in agreement with previously described D−π−A systems with a 4*H*-pyran-4-ylidene moiety.[11,12]

Table 1. ^{1}H NMR Chemical Shifts of Some Representative Hydrogen Atoms[a]

compd	δ H_a (ppm)	δ H_b (ppm)	δ H_c (ppm)	δ H_d (ppm)
1a	6.74	7.70	7.16	
1b	6.49	6.99	7.11	7.72
1c	6.57	7.23	6.98	7.41
2a	6.67		7.00	
2b	6.51	6.92	7.00	7.48
2c	6.59	7.23	6.96	7.31
3a	6.62		7.01	7.43
3b	6.54	6.95	7.01	7.39
3c	6.52	7.19	6.95	7.22
4a	6.71	7.32	7.05	7.52
4b	6.60	7.01	7.07	7.48
4c	6.60	7.23	6.99	7.32

[a]In some cases, it was not possible to specify a chemical shift because of the overlap of the signals with those of other protons.

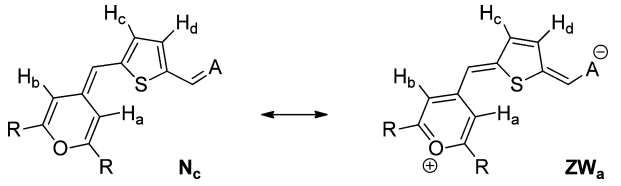

Figure 1. Representative canonical forms for compounds (**1**−**4**)**a**.

Furthermore, if we compare the largest isomers [**1**−**4**(**b**,**c**)] (Figure 2), in which the thiophene ring is closer to the donor, compounds (**1**−**4**)**c**, the pyranylidene ring protons (H_a, H_b) are shifted downfield in most cases, suggesting that the 4*H*-pyran-4-ylidene ring has a higher aromatic character (greater contribution of canonical form **ZW1$_c$**) than in the corresponding compounds (**1**−**4**)**b**. It can therefore be concluded that the pyranylidene ring increases its donor character when the thiophene is closer, with the latter acting as an auxiliary donor.

On the other hand, the arrangement in which the thiophene ring is closer to the acceptor unit [compounds (**1**−**4**)**b**] is better suited for transferring part of its own electron density (as in canonical form **ZW2$_b$**, Figure 2) to the acceptor, as evidenced by ^{1}H NMR spectroscopy because, in all cases, the hydrogens H_c and H_d are more deshielded in compounds (**1**−**4**)**b** than in (**1**−**4**)**c**.

Calculated Geometries and Charges. The optimization of the molecular geometries of the studied compounds by DFT methods (B3P86/6-31G* model chemistry) resulted, in every case, in a planar arrangement of the pyranylidene-thiophene-acceptor π system, with the two phenyl groups linked to the 4*H*-pyran-4-ylidene moiety twisted ca. 20−22° with respect to the molecular plane. The phenyl and dicyanovinyl groups, in the acceptor moiety of compounds **2** and **9**, arrange also out of the molecular plane because of steric hindrance in agreement with previously reported X-ray studies on related derivatives.[53]

The Bird Index, despite its limitations, is a simple way to estimate the aromaticity of a molecule.[54,55] This index can be obtained from experimentally determined or calculated bond lengths and it has proven to be of general applicability in the case of heterocycles. It has been established that a lower value signifies that the molecule is less aromatic. The Bird Index (I_6)[55] values for the 4*H*-pyran-4-ylidene moiety of all synthesized compounds are shown in Table 2, and as can be seen, these are in the range of 41 to 42, which is consistent with previously reported results[11] and confirms a significant contribution of the zwitterionic limiting forms (values of ca. 50 are described for pyrylium cations). It can also be seen from the results in Table 2 that the I_6 index (and thus the aromaticity) decreases on increasing the length of the polyenic chain. In all cases reported here, the 4*H*-pyran-4-ylidene ring in compounds (**1**−**4**)**c** is more aromatic (and therefore more strongly donating) than in compounds (**1**−**4**)**b**, thus confirming the auxiliary donor effect of thiophene in the former compounds. The aromaticity of the thiophene ring can also be estimated from its Bird Index (I_5) (66 for thiophene itself).[54] In this case, the differences are more important when comparing the longest isomers [**1**−**4**(**b**,**c**)], with higher values of I_5 obtained for compounds (**1**−**4**)**c**, in which the thiophene ring is closer to the 4*H*-pyran-4-ylidene unit. These results are in agreement with the ^{1}H NMR data described above.

The polarization degree of a molecule can also be estimated by the bond-length alternation (BLA).[7] In this paper, BLA is calculated as the difference between the average carbon−carbon

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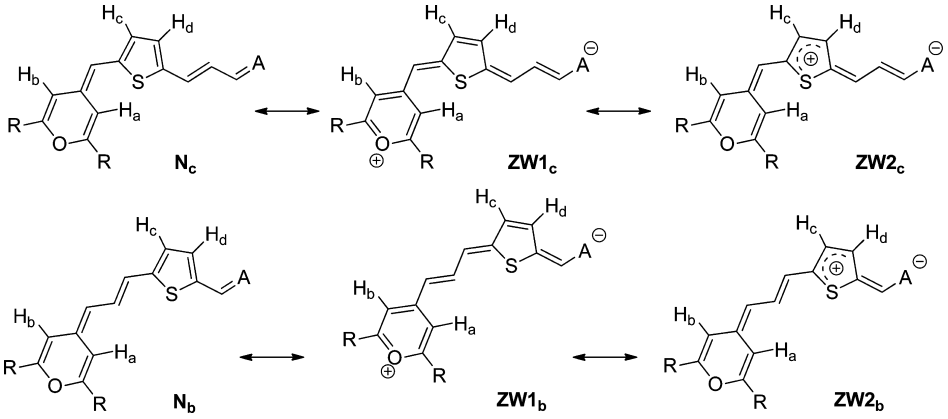

Figure 2. Representative canonical forms for compounds (**1**–**4**)**b** and (**1**–**4**)**c**.

Table 2. Calculated[a] Values of Bird Index, Mulliken Charge, and BLA for Compounds [1–4(a–c)]

compd	I_6[b]	I_5[c]	q(D)[d] [e]	BLA[e]
1a	42.0	56.8	+0.317	+0.012
1b	41.1	58.6	+0.279	+0.022
1c	41.4	62.0	+0.293	+0.024
2a	42.2	57.8	+0.325	+0.013
2b	41.4	57.8	+0.288	+0.022
2c	41.8	61.9	+0.307	+0.020
3a	42.2	58.2	+0.316	+0.022
3b	41.2	58.4	+0.285	+0.028
3c	41.6	61.8	+0.302	+0.027
4a	42.7	58.4	+0.336	+0.017
4b	42.0	58.5	+0.300	+0.024
4c	42.2	62.0	+0.318	+0.023

[a]B3P86/6-31G* level. [b]Bird Index for the 4*H*-pyran-4-ylidene moiety. [c]Bird Index for the thiophene ring. [d]Mulliken charge in the pyranylidene moiety. [e]Along the bonds shown in Figure 3.

single and double bond lengths in the conjugated bridge, including the thiophene ring (see Figure 3). BLA values are likely to be lower than expected because the formally double C=C bonds of the thiophene ring are slightly longer than the formally single C–C bond.

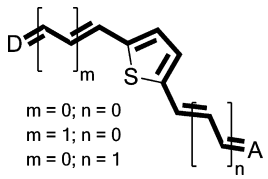

Figure 3. Bond lengths involved in calculated BLA values.

Mulliken charge analysis estimates partial atomic charges in a molecule from calculations carried out by computational chemistry, and because of its simplicity, it is a very useful method to estimate the polarization of a molecule.[56] The Mulliken charges q(D) supported by the 4*H*-pyran-4-ylidene moiety are shown in Table 2, and as expected, q(D) decreases on lengthening the chain of the spacer,[11] probably because of a weaker donor–acceptor interaction. Moreover, Mulliken charge analysis shows a good correlation between I_6 and q(D), even when comparing chromophores **b** and **c**, indicating that derivatives (**1**–**4**)**c** are more zwitterionic (and therefore more aromatic) in the ground state than compounds (**1**–**4**)**b**, a finding consistent with the ^{1}H NMR data (see above).

Electrochemistry. The redox properties of the push–pull systems were studied by cyclic voltammetry (CV) in CH_2Cl_2 (Table 3). All compounds show two irreversible waves, corresponding to the oxidation of the 4*H*-pyran-4-ylidene fragment and to the reduction of the acceptor moieties, respectively.

Table 3. Electrochemical Data[a] and E_{HOMO} and E_{LUMO} Values[b]

compd	E_{ox} (V)	E_{red} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
1a	+0.67	−0.89	−5.80	−3.43
1b	+0.55	−0.87	−5.61	−3.48
1c	+0.65	−0.78	−5.66	−3.53
2a	+0.82	−0.76	−5.93	−3.71
2b	+0.62	−0.71	−5.74	−3.74
2c	+0.72	−0.63	−5.79	−3.79
3a	+0.67	−0.69	−5.91	−3.85
3b	+0.50	−0.64	−5.75	−3.87
3c	+0.57	−-0.59	−5.80	−3.89
4a	+0.82	−0.59	−5.98	−3.99
4b	+0.63	−0.54	−5.81	−4.00
4c	+0.71	−0.49	−5.86	−4.02
9	+0.64	−0.71	−6.06	−3.82
10	+0.51	−0.69	−6.03	−3.92

[a]10^{-3} M in CH_2Cl_2 versus Ag/AgCl (3 M KCl), glassy carbon working electrode, Pt counter electrode, 20 °C, 0.1 M NBu_4PF_6, 100 mV s^{-1} scan rate. Ferrocene internal reference $E^{1/2}$ = +0.43 V. [b]Calculated at the B3P86/6-31G* level in the gas phase.

It must be remarked that, as expected, the introduction of a thiophene ring in the spacer renders the oxidation more difficult and, to a lesser extent, the reduction processes. For instance, when comparing the redox properties of **2a** (E_{ox} = +0.82 V; E_{red} = −0.76 V) and **3a** (E_{ox} = +0.67 V; E_{red} = −0.69 V) with those of the previously reported **9** (E_{ox} = +0.64 V; E_{red} = −0.71 V) and **10** (E_{ox} = +0.51 V; E_{red} = −0.69 V) (Figure 4),[11] we observe an increase in the electrochemical bandgap for the former compounds. This behavior can be explained by the loss of aromaticity of the thiophene ring in the intramolecular charge transfer (ICT), which is a disadvantageous process from an energetic point of view.

Otherwise, the lengthening of the polyenic chain of the NLO chromophores facilitates the oxidation and reduction processes

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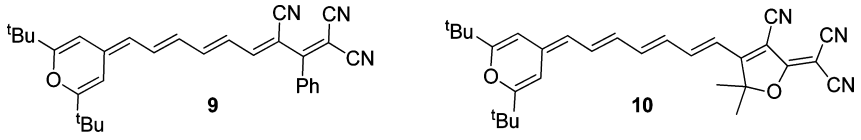

Figure 4. Structures of compounds **9** and **10**.

and gives rise to a decrease in the E_{ox} and E_{red} values, a change that indicates a weaker interaction between the donor and acceptor groups (Table 3). The observed trends are also confirmed by computational calculations, which show that the E_{HOMO} (E_{LUMO}) values increase (decrease) with the length of the spacer. Concerning the electrochemical bandgap, major differences were not found between isomers **b** and **c**, except for a slight increase for the latter systems. The E_{ox} data in Table 3 also allow a qualitative comparison of the electron-withdrawing ability of the corresponding acceptors. Thus, on comparing chromophores with the same spacer length, the results obtained show that the strongest acceptor is **4** (CF_3–TCF), while thiobarbiturate **1** is the weakest.

Linear Optical Properties. The UV–vis absorption maxima and the extinction coefficients (log ε) of the studied chromophores in 1,4-dioxane and CH_2Cl_2 are summarized in Table 4. All compounds show the typical strong and broad

Table 4. UV–Vis Data

Compd	λ_{max} [a] (log ε) 1,4-dioxane	λ_{max} [a] (log ε) CH_2Cl_2	λ_{max} [b] (gas phase)	λ_{max} [b,c] (CH_2Cl_2)	λ_{max} [b,c] (DMF)
1a	611 (4.76)	644 (4.64)	533	636	655
1b	643 (4.76)	668 (4.59)	584	730	760
1c	657 (4.62)	688 (4.70)	583	721	748
2a	647 (4.66)	676 (4.70)	563	687	710
2b	672 (4.66)	715 (4.61)	621	791	825
2c	677 (4.34)	731 (4.44)	610	768	797
3a	665 (4.55)	708 (4.70)	594	665	761
3b	697 (4.48)	739 (4.74)	654	836	873
3c	673 (4.65)	733 (4.71)	636	809	842
4a	724 (4.80)	825 (4.96)	607	756	782
4b	770 (4.69)	845 (4.74)	669	863	900
4c	751 (4.60)	827 (4.80) 903 (sh)	650	832	865
9		719 (4.92) 787			
10		753 (4.92) 841 (4.94)			

[a]All λ_{max} data are in nm. [b]TD-DFT calculations at the B3P86/6-31G* level. [c]PCM solvation model

band in the visible region of the spectrum, corresponding to an ICT, and in some cases, the UV–vis spectra show vibronic bands (**2a**, **3a**, **4a–c**). In all series, for a given acceptor, a bathochromic shift is observed on lengthening the spacer, and on increasing the acceptor strength, significant red-shifts in absorption occur in the order 4 ≫ 3 > 2 > 1. It is important to highlight that compounds with the strong acceptor TCF–CF_3 (**4a–c**) show pronounced bathochromic shifts (>100 nm as compared to TCF systems **3a–c**), and in some cases, the absorption bands are extended into the near-infrared.

As expected, when comparing compounds **2a** with **9** and **3a** with **10**, the replacement of a diene by a thiophene ring leads to a moderate hypsochromic shift of the absorption band.[21,57,58]

The data in Table 4 indicate in all cases a positive solvatochromism on passing from 1,4-dioxane to CH_2Cl_2. In order to confirm whether this solvatochromic behavior is general, we also determined absorption maxima (λ_{max}) in more polar solvents like acetone, DMF, and DMSO. As shown in Figure 5, the transition energy plot as a function of solvent polarity (E_T^N) based on an empirical relationship[59] declines with increasing solvent polarity, thus confirming the aforementioned positive solvatochromism.[60,61] This observation indicates an increase in the dipole moment upon excitation ($\mu_g < \mu_e$) (where μ_g and μ_e are the ground- and excited-state dipole moments, respectively) and can be interpreted in terms of the predominance of the neutral form in the ground-state structure, a situation in accordance with theoretical calculations (DFT). Likewise, as can be seen in the graph, for compounds with the strong acceptor CF_3–TFC **4**(**a–c**), the slope is higher, and therefore these compounds show a marked positive solvatochromism relative to the other molecules, a result that could indicate a higher second-order NLO response ($\mu\beta$). The λ_{max} TD-DFT calculated data (in gas phase, CH_2Cl_2, and DMF) are shown in Table 4, and it can be seen that the theoretical data in CH_2Cl_2 fit much better to the experimental data. In any case, TD-DFT calculations predict the positive solvatochromism observed in this series of compounds.

NLO Properties. The second-order NLO properties of derivatives **1–4** were measured by electric field-induced second harmonic generation (EFISH) in dichloromethane at 1907 nm, and the static $\mu\beta_0$ values were calculated by using the two-level model[62] (for the sake of comparison, disperse red 1 gives a $\mu\beta_0$ value of ca. 480 × 10^{-48} esu under the same experimental conditions). Both the experimental and theoretical results (CPHF, coupled perturbed Hartree–Fock) are collected in Table 5. As mentioned above, in some cases the UV–vis spectra show vibronic bands and/or relevant absorption at harmonic wavelength [especially for compounds **4**(**a–c**)]; thus, the estimation of their $\mu\beta_0$ values should be treated with caution. For the sake of comparison, the experimental $\mu\beta$ values of the previously reported derivatives **9** and **10**[11] are shown in Table 5, and these data allow some interesting conclusions to be drawn.

In all cases positive $\mu\beta$ values were obtained and the second-order NLO response increased on lengthening the spacer, with the best results obtained with the strongest acceptors **3** and **4**.

Comparison of the $\mu\beta$ values of derivatives **2a** and **3a** with those of **9** and **10**, respectively, reveals that the incorporation of a thiophene ring gives rise to a lower NLO response.[57,63,64] However, compounds **9** and **10** have the drawback of considerably lower thermal and photochemical stability (see below) and a narrower transparency range than **2a** and **3a**, respectively, which make them less suitable for practical purposes. Moreover, with the exception of derivatives **1b** and **1c** (which display the same response within the limits of the experimental error) a general behavior is observed for the molecules in this study: the second-order NLO response is, in all cases, higher for compounds in series **c**. Since for a given acceptor the length of conjugation in both cases is the same, it is reasonable to consider that the location of thiophene is the key factor. On considering the results, it can be stated that for

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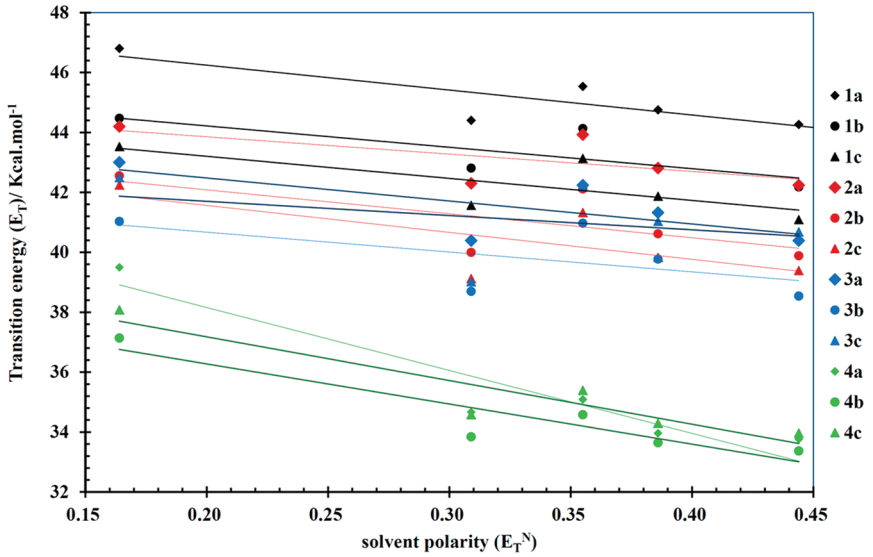

Figure 5. Solvatochromism study in 1,4-dioxane, CH_2Cl_2, acetone, DMF, and DMSO for compounds [**1**–**4**(**a**–**c**)].

Table 5. Experimental and CPHF-Calculated NLO Properties and TD-DFT-Calculated Parameters

compd	$\mu\beta^a$ (10^{-48} esu)	$\mu\beta_0{}^b$ (10^{-48} esu)	$\mu\beta_0{}^c$ (10^{-48} esu)	$\beta_0{}^c$ (10^{-30} esu)	$\mu_g{}^d$ (D)	$\Delta\mu_{ge}{}^d$ (D)	f^d	E^d (eV)
1a	1380	665	1162	90	12.1	0.9	1.66	2.33
1b	3130	1400	3218	239	13.1	3.6	1.98	2. 12
1c	3400[e]	1420	3626	260	13.9	1.6	1.99	2.13
2a	2900	1260	2753	142	18.8	3.1	1.59	2.20
2b	6900	2600	6443	320	20.1	5.3	1.77	2.00
2c	8500	2990	7187	347	20.7	4.1	2.03	2.03
3a	6790	2630	7165	306	22.8	2.4	2.00	2.09
3b	12000	4100	13404	561	24.2	5.0	2.10	1.90
3c	17000	5900	14326	584	24.8	4.2	2.38	1.95
4a	13600	2740	8970	381	23.1	2.3	2.04	2.04
4b	35000[f]	6000	17445	721	24.6	4.3	2.14	1.85
4c	40000[f]	8000	18493	742	25.3	3.7	2.42	1.91
9	7500	2000						
10	17400	3110						

[a] $\mu\beta$ values determined in CH_2Cl_2 at 1907 nm (experimental accuracy ±15%). [b] Experimental $\mu\beta_0$ values calculated using the two-level model. [c] Calculated at the CPHF/6- 31G* level. [d] TD-DFT calculations at the B3P86/6-31G* level. [e] The $\mu\beta$ value was determined from a freshly prepared sample because of its relative instability in CH_2Cl_2. [f] The proximity to harmonic resonance makes this extrapolated value questionable.

this type of molecule, the thiophene ring exerts an auxiliary donor effect when it is closer to the 4*H*-pyran-4-ylidene moiety. The $\mu\beta_0$ values calculated using the CPHF approach are gathered in Table 5. It can be seen that while calculated values are overestimated, they reproduce quite well the experimental trends because both μ_g and β_0 (and therefore $\mu\beta_0$) are larger for the NLO chromophores in series **c**.

We also calculated (see Table 5) the parameters involved in the two level model[62] ($\beta_0 \propto (\Delta\mu_{ge}f/E^3)$) using the time-dependent density functional theory (TD-DFT) method. In this approach, $\Delta\mu_{ge}$ represents the difference in dipole moment between the first excited state and the ground state, f is the oscillator strength, and E is the first excitation energy. However, a comparison of the second-order NLO properties of compounds **b** and **c** is not easy on the basis of this simple approach: while oscillator strengths (f) are larger for compounds **c**, the dipole moment changes upon excitation ($\Delta\mu_{ge}$) are larger for **b**. As a consequence of these opposing effects, the small differences in the NLO behavior of **b** and **c** are probably found in higher excited states that are not considered in the two level approach.

Positive BLA and hyperpolarizability β values suggest that molecules in this study are located in the A/B region of the Marder plot,[7] i.e., very close and on the left-hand side of the peak (higher values of β on increasing the polarity). In order to validate this hypothesis, EFISH measurements were carried out on compounds **3a**–**c** in DMSO [$\mu\beta$ (10^{-48} esu) **3a**, 1400; **3b**, 7900; **3c**, 9100]. In all three cases, a significant decrease in the $\mu\beta$ values was observed, but they still remain positive, indicating that the cyanine limit has not been exceeded.

Thermal Stability. The thermal stabilities of the chromophores were studied by thermogravimetric analysis (TGA) under nitrogen at a heating rate of 10 °C/min. The decomposition temperatures (T_d) were estimated as the temperature at the intercept of the leading edge of the weight loss with the baseline of the TGA scans.

The results show that all compounds (**1**–**4**) are thermally stable, with decomposition temperatures above 220 °C [T_d (°C): **1a**, 272; **1b**, 229; **1c**, 268; **2a**, 294; **2b**, 233; **2c**, 231; **3a**, 334; **3b**, 268; **3c**, 264; **4a**, 281; **4b**, 251; **4c**, 220; **9**, 184; **10**, 205]. The shortest derivatives (**1**–**4**)**a** have the highest T_d values, and the thermal stability decreases on lengthening the π-

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conjugated system. As expected, inclusion of a thiophene ring in the spacer leads to an increase in T_d by more than 100 °C compared to those of their polyene analogues (compounds **9** and **10** versus **2a** and **3a**). Systems with the TCF acceptors have the highest thermal stability (slightly lower for the fluorinated compounds **4** in agreement with previously reported data);[27] they are soluble in common solvents, and consequently, they are very promising candidates for use as active materials in electro-optic devices (their properties compare favorably, for instance, to those described for the benchmark chromophore CLD-1: $\mu\beta$ = 14065 × 10^{-48} esu; T_d = 275 °C).[65]

In summary, a new series of efficient 4*H*-pyran-4-ylidene NLO chromophores with a thiophene ring in the π-spacer and four strong acceptors have been synthesized and studied. The chromophores show high hyperpolarizability values and adequate thermal stability for potential EO applications, obtaining the best nonlinear responses with strong TCF-type acceptors. Both experimental and theoretical data show that higher $\mu\beta$ values are obtained when the thiophene ring is closer to the pyranylidene ring, and therefore, the thiophene acts as an auxiliary donor. In all cases, EFISH measurements reveal that the chromophores are located at the A/B region of the Marder plot, probably slightly to the left of the positive maximum on the BLA graph.

EXPERIMENTAL SECTION

Starting materials: 2,5-thiophenedicarbaldehyde, 5-bromo-2-thiophenecarbaldehyde **6a** and *N*,*N*-dimethylaminoacrolein are commercially available and were used without further purification. Compounds **5**[48] and **6b**[49] were prepared as previously reported.

(4*H*-Pyran-4-yl)diphenylphosphine Oxide, 5. A solution of 2,6-diphenylpyrylium fluoroborate[66] (0.81 g; 2.54 mmol) in anhydrous acetonitrile (5 mL) was prepared and purged with argon at room temperature. To the solution were added both sodium iodide (0.40 g; 2.67 mmol) and methyl diphenylphosphinite (0.6 mL; 2.99 mmol). The mixture was stirred for 1 h and then diluted five times with water. The resulting solid was filtered off, washed with water, and dried. Pure compound **5** was obtained by recrystallization from ethyl acetate.

Yield: white solid (6.97 g; 16 mmol; 94%); mp 185−189 °C; IR (Nujol/NaCl, cm^{-1}) 1175 (P═O), 1674 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92−7.81 (m, 4H), 7.59−7.42 (m, 10H), 7.41−7.28 (m, 6H), 5.40 (t, J = 4.2 Hz, 2H), 4.32 (dt, J = 21.0 Hz, J' = 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 151.2, 133.6 (× 2), 132.0 (× 2), 131.9, 130.9, 129.9, 128.8, 128.5, 128.4, 128.2, 124.6, 92.4, 38.5, 37.8; MS (ESI$^+$) $C_{29}H_{23}NaO_2P$ [M + Na] 457, $C_{29}H_{23}KO_2P$ [M + K] 473.

4-[(5-Bromothiophen-2-yl)methylene]-2,6-diphenyl-4*H*-pyran, 7a. A solution of 2,6-diphenyl(4*H*-pyran-4-yl)-diphenylphosphine oxide **5** (350 mg; 0.81 mmol) in anhydrous THF (8 mL) was prepared, purged with argon, and cooled to −78 °C. To the solution was added dropwise *n*-BuLi (0.55 mL; 0.88 mmol; 1.6 M in hexanes), and the resulting mixture was stirred for 15 min. 5-Bromo-2-thiophenecarbaldehyde **6a** (0.2 mL; 1.60 mmol) was added dropwise, and the mixture was stirred for 1.5 h and then quenched with saturated NH_4Cl solution. After removal of the THF, the organic layer was extracted with ethyl acetate (2 × 30 mL). The combined organic layers were washed with water (2 × 30 mL) and dried over anhydrous $MgSO_4$. Pure compound **7a** was obtained by silica gel column chromatography (20% ethyl acetate in hexanes).

Yield: orange solid (231 mg; 0.57 mmol; 70%) (observations: unstable product in the presence of chlorinated solvents and/or light); mp 213-217 °C; IR (Nujol/NaCl, cm^{-1}) 1580 (C═C); ^{1}H NMR (400 MHz, CD_3COCD_3) δ 7.98−7.86 (m, 4H), 7.59−7.42 (m, 6H), 7.08 (d, J = 3.9 Hz, 1H), 7.04 (d, J = 1.9 Hz, 1H), 6.88 (d, J = 3.9 Hz, 1H), 6.72 (d, J = 1.9 Hz, 1H), 6.15 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 153.9, 151.5, 144.2, 133.6, 133.5, 130.5, 130.2, 129.7, 129.2 (× 2), 129.1, 128.8, 125.5, 125.0, 108.9, 108.5, 107.4, 102.7; HRMS (ESI$^+$) Calcd for $C_{22}H_{16}BrOS$ [M + H]$^+$ 407.0100, found 407.0087.

5-[(2,6-Diphenyl-4*H*-pyran-4-ylidene)methyl]thiophene-2-carbaldehyde, 8a.

Method 1. A solution of 4-[(5-bromothiophen-2-yl)methylene]-2,6-diphenyl-4*H*-pyran **7a** (104 mg; 0.25 mmol) in anhydrous THF (3 mL) was prepared, purged with argon, and cooled to −78 °C. To the solution was added dropwise *n*-BuLi (0.17 mL; 0.27 mmol; 1.6 M in hexanes), and the resulting mixture was stirred for 3 min. Anhydrous *N*,*N*-dimethylformamide (0.13 mL; 1.61 mmol) was added, and the mixture was stirred for one additional hour. Saturated NH_4Cl solution was added to quench the reaction, and the mixture was then warmed to room temperature. After the solvent was evaporated, the organic layer was extracted with ethyl acetate (2 × 25 mL). The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After removal of the solvent, the aldehyde was purified by silica gel column chromatography (20% ethyl acetate in hexanes). Yield: red solid (45 mg; 0.13 mmol; 50%).

Method 2. A solution of 2,6-diphenyl(4*H*-pyran-4-yl)-diphenylphosphine oxide **5** (1.20 g; 2.76 mmol) in anhydrous THF (35 mL) was prepared, purged with argon, and cooled to −78 °C. *n*-BuLi (1.7 mL; 2.72 mmol; 1.6 M in hexanes) was added dropwise to the solution, and the resulting mixture was stirred for 15 min. 2,5-Thiophenedicarbaldehyde (0.39 g; 2.76 mmol) was added dropwise, and the mixture was stirred for an additional 20 min. Saturated NH_4Cl solution was added to quench the reaction, and the mixture was then warmed to room temperature. After the solvent was evaporated, the organic layer was extracted with ethyl acetate (2 × 50 mL). The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After removal of the solvent, the aldehyde was purified by silica gel column chromatography (10% ethyl acetate in hexanes).

Yield: red solid (429 mg; 1.20 mmol; 44%); mp 141−148 °C; IR (Nujol/NaCl, cm^{-1}) 1645 (C═O), 1578 (C═C); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.81 (s, 1H), 7.94−7.78 (m, 4H), 7.67 (d, J = 4.0 Hz, 1H), 7.56−7.42 (m, 6H), 7.24 (d, J = 2.0 Hz, 1H), 7.02 (d, J = 4.0 Hz, 1H), 6.57 (d, J = 2.0 Hz, 1H), 6.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 155.0, 152.5, 152.4, 139.0, 137.4, 132.7, 132.5, 132.4, 130.1, 129.6, 128.8, 128.7, 126.2, 125.3, 124.7, 108.6, 107.0, 102.7; HRMS (ESI$^+$) Calcd for $C_{23}H_{17}O_2S$ [M + H]$^+$ 357.0944, found 357.0946; Calcd for $C_{23}H_{16}NaO_2S$ [M + Na]$^+$ 379.0763, found 379.0758.

(*E*)-4-[3-(5-Bromothiophen-2-yl)allylidene]-2,6-diphenyl-4*H*-pyran, 7b. A solution of 2,6-diphenyl(4*H*-pyran-4-yl)-diphenylphosphine oxide **5** (515 mg; 1.19 mmol) in anhydrous THF (8 mL) was prepared, purged with argon, and cooled to −78 °C. *n*-BuLi (0.8 mL; 1.28 mmol; 1.6 M in hexanes) was added dropwise to the solution, and the resulting mixture was stirred for 15 min. A solution of (*E*)-3-(5-bromothiophen-2-yl)acrylaldehyde **6b** (302 mg; 1.31 mmol) in anhydrous THF (4 mL) was added dropwise. The mixture was stirred for an additional 5 h (TLC monitoring using 30% ethyl acetate in hexanes), and then saturated NH_4Cl solution was added to quench the reaction. After removing the THF, the crude product was extracted with ethyl ether (2 × 40 mL), washed with water (2 × 40 mL), and dried over anhydrous $MgSO_4$. Pure compound **7b** was obtained by silica gel column chromatography (30% ethyl acetate in hexanes).

Yield: orange solid (145 mg; 0.33 mmol; 28%); mp 116−120 °C; IR (KBr, cm^{-1}) 1581 (C═C); ^{1}H NMR (300 MHz, CD_3COCD_3) δ 8.03−7.82 (m, 4H), 7.57−7.40 (m, 6H), 7.24 (dd, J = 15.0 Hz, J' = 11.7 Hz, 1H), 7.17 (d, J = 1.8 Hz, 1H), 7.01 (d, J = 3.8 Hz, 1H), 6.83 (d, J = 3.8 Hz, 1H), 6.65 (d, J = 1.8 Hz, 1H), 6.56 (d, J = 15.0 Hz, 1H), 5.80 (d, J = 11.7 Hz, 1H); ^{13}C NMR not registered because of rapid decomposition in solution; HRMS (ESI$^+$) Calcd for $C_{24}H_{17}BrOS$ [M]$^+$ 432.0178, found 432.0173.

(*E*)-5-[3-(2,6-Diphenyl-4*H*-pyran-4-ylidene)prop-1-enyl]-thiophene-2-carbaldehyde, 8b. A solution of (*E*)-4-[3-(5-bromothiophen-2-yl)allylidene]-2,6-diphenyl-4*H*-pyran **7b** (462 mg; 1.07 mmol) in anhydrous THF (13 mL) was prepared, purged with argon, and cooled to −78 °C. *n*-BuLi (0.73 mL; 1.17 mmol; 1.6 M in

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hexanes) was added dropwise to the solution, and the resulting mixture was stirred for 1 h, and then anhydrous *N*,*N*-dimethylformamide (0.55 mL; 7.09 mmol) was added. The reaction was stirred for one additional hour, and then saturated NH_4Cl solution was added to quench the reaction. After removal of the THF, the organic layer was extracted with ethyl acetate (2 × 30 mL), and the combined organic layers were washed with water (2 × 40 mL) and dried over anhydrous $MgSO_4$. Pure compound **8b** was obtained by silica gel column chromatography (20% ethyl acetate in hexanes).

Yield: red solid (386 mg; 1.01 mmol; 95%); mp 150−154 °C; IR (Nujol/NaCl, cm^{-1}) 1655 (C═O), 1569 (C═C); ^1H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.88−7.71 (m, 4H), 7.59 (d, J = 3.9 Hz, 1H), 7.53−7.38 (m, 7H), 7.29 (dd, J = 14.9 Hz, J' = 11.9 Hz, 1H), 6.97 (d, J = 3.9 Hz, 1H), 6.80 (d, J = 1.6 Hz, 1H), 6.55 (d, J = 14.9 Hz, 1H), 6.41 (d, J = 1.6 Hz, 1H), 5.75 (d, J = 11.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.1, 154.6, 153.1, 139.8, 137.7, 133.4, 132.8, 132.7, 129.8, 129.5, 129.4, 128.8, 128.7, 124.9, 124.8, 124.6, 119.4, 113.8, 108.3, 102.1; HRMS (ESI$^+$) Calcd for $C_{25}H_{18}O_2S$ $[M]^{+\cdot}$ 382.1022, found 382.1019; Calcd for $C_{25}H_{18}NaO_2S$ $[M + Na]^+$ 405.0920, found 405.0909.

(*E*)-3-{5-[(2,6-Diphenyl-4*H*-pyran-4-ylidene)methyl]-thiophen-2-yl}acrylaldehyde, 8c. A solution of 4-[(5-bromothiophen-2-yl)methylene]-2,6-diphenyl-4*H*-pyran **7a** (724 mg; 1.78 mmol) in anhydrous THF (15 mL) was prepared, purged with argon, and cooled to −78 °C. To the solution was added *n*-BuLi (1.2 mL; 1.95 mmol; 1.6 M in hexanes), the resulting mixture was stirred for 30 min, and then *N*,*N*-dimethylaminoacrolein (1.0 mL; 9.0 mmol) was added. The reaction mixture was stirred for 2.5 h (TLC using 30% ethyl acetate in hexanes) and then allowed to cool to room temperature. The reaction was quenched by addition of HCl (1 N) (36 mL; 36 mmol). The solvent was evaporated, and the organic layer was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. After removal of the solvent, the aldehyde was purified by silica gel column chromatography (30% ethyl acetate in hexanes).

Yield: red solid (327 mg; 0.86 mmol; 48%); mp 140−143 °C; IR (KBr, cm^{-1}) 1667 (C═O), 1556 (C═C); ^1H NMR (300 MHz, $CDCl_3$) δ 9.60 (d, J = 8.0 Hz, 1H), 7.89−7.74 (m, 4H), 7.59−7.40 (m, 7H), 7.26 (d, J = 3.9 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 6.92 (d, J = 3.9 Hz, 1H), 6.49 (d, J = 2.0 Hz, 1H), 6.48 (dd, J = 15.4 Hz, J' = 8.0 Hz, 1H), 6.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 154.5, 152.1, 148.0, 144.4, 135.7, 133.5, 132.8, 132.7, 131.1, 130.0, 129.5, 128.9, 128.7, 126.7, 125.1, 125.1, 124.6, 108.6, 107.3, 102.8; HRMS (ESI$^+$) Calcd for $C_{25}H_{19}O_2S$ $[M + H]^+$ 383.1100, found 383.1117; Calcd for $C_{25}H_{18}NaO_2S$ $[M + Na]^+$ 405.0920, found 405.0926; Calcd for $C_{25}H_{18}KO_2S$ $[M + K]^+$ 421.0659, found 421.0673.

Compounds 1a−c: General Procedure. Equimolar quantities of 1,3-diethyl-2-thioxodihydropyrimidine-4,6-dione (100 mg; 0.5 mmol) and the corresponding aldehyde **8a** (178 mg; 0.5 mmol), **8b** (191 mg; 0.5 mmol), or **8c** (191 mg; 0.5 mmol) were dissolved into absolute ethanol under an argon atmosphere. The mixture was heated under reflux for 30 min (**8a**) and (**8b**) or 5 h (**8c**) (TLC monitoring) and then cooled to 0 °C. The resulting solid was filtered off, washed with ethanol/dichloromethane mixtures, and dried.

5-{[5-(2,6-Diphenyl-4*H*-pyran-4-ylidene)methyl]thiophen-2-yl}methylene-1,3-diethyl-2-thioxodihydropyrimidine-4,6-(1*H*,5*H*)-dione, 1a. Yield: green solid (197 mg; 0.37 mmol; 73%); mp 258−261 °C; IR (KBr, cm^{-1}) 1655 (C═O), 1377 (C−N), 1253 (C−O), 1144 (C═S); ^1H NMR (400 MHz, CD_2Cl_2) δ 8.53 (s, 1H), 8.03 (d, J = 3.9 Hz, 1H), 7.93−7.80 (m, 4H), 7.70 (s, 1H), 7.62−7.43 (m, 6H), 7.16 (d, J = 3.9 Hz, 1H), 6.74 (s, 1H), 6.31 (s, 1H), 4.64 (q, J = 6.9 Hz, 2H), 4.56 (q, J = 6.9 Hz, 2H), 1.39 (t, J = 6.9 Hz, 2H), 1.29 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.0, 161.7, 156.6, 150.7, 147.2, 146.5, 136.5, 135.2, 132.5, 130.7, 130.2, 129.0, 127.8, 125.6, 125.1, 109.5, 108.4, 104.6, 43.8, 43.1, 12.6, 12.5; HRMS (ESI$^+$) Calcd for $C_{31}H_{27}N_2O_3S_2$ $[M + H]^+$ 539.1457, found 539.1400.

(*E*)-5-({5-[3-(2,6-Diphenyl-4*H*-pyran-4-ylidene)prop-1-enyl]-thiophen-2-yl}methylene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione, 1b. Yield: green solid (155 mg; 0.28 mmol; 55%); mp 263−265 °C; IR (Nujol/NaCl, cm^{-1}) 1651 (C═O), 1562 (C═S), 1529 (C═C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.96−7.74 (m, 4H), 7.72 (d, J = 4.0 Hz, 1H), 7.63−7.42 (m, 7H), 7.11 (d, J = 4.0 Hz, 1H), 6.99 (s, 1H), 6.61 (d, J = 14.7 Hz, 1H), 6.49 (s, 1H), 5.83 (d, J = 11.9 Hz, 1H), 4.63 (q, J = 6.9 Hz, 2H), 4.59 (q, J = 6.9 Hz, 2H), 1.38 (t, J = 6.9 Hz, 3H), 1.32 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 163.2, 161.3, 160.2, 154.2, 153.4, 148.2, 148.0, 136.0, 135.6, 132.6, 132.3, 130.1, 129.8, 128.8, 126.7, 125.3, 124.8, 120.2, 119.4, 115.4, 108.9, 108.8, 107.5, 102.8, 100.0, 43.9, 43.0, 12.6, 12.4; HRMS (ESI$^+$) Calcd for $C_{33}H_{28}N_2O_3S_2$ $[M]^{+\cdot}$ 564.1536, found 564.1532.

(*E*)-5-(3-{5-[(2,6-Diphenyl-4*H*-pyran-4-ylidene)methyl]-thiophen-2-yl}allylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione, 1c. The crude product was purified by silica gel column chromatography (10% hexane in dichloromethane).

Yield: dark red solid (232 mg; 0.41 mmol; 82%); mp 292−292 °C; IR (KBr, cm^{-1}) 1655 (C═O), 1536 (C═C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, J = 14.3 Hz, J' = 12.5 Hz, 1H), 8.14 (d, J = 12.5 Hz, 1H), 7.95−7.76 (m, 4H), 7.60−7.44 (m, 7H), 7.42 (d, J = 4.2 Hz, 1H), 7.23 (d, J = 1.9 Hz, 1H), 6.99 (d, J = 4.2 Hz, 1H), 6.57 (d, J = 1.9 Hz, 1H), 6.20 (s, 1H), 4.59 (q, J = 7.0 Hz, 2H), 4.56 (q, J = 7.0 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H), 1.31 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 161.1, 160.2, 157.7, 155.9, 153.3, 152.3, 147.7, 138.3, 136.2, 133.7, 132.5, 132.3, 130.4, 129.9, 129.0, 128.9, 128.3, 125.6, 124.8, 123.1, 111.1, 109.2, 108.1, 103.4, 43.6, 43.0, 29.7, 12.6, 12.5; HRMS (ESI$^+$) Calcd for $C_{33}H_{29}N_2O_3S_2$ $[M + H]^+$ 565.1614, found 565.1596.

Compounds 2a−c: General Procedure. Equimolar quantities of 2-phenyl-1-propene-1,1,3-tricarbonitrile (97 mg; 0.5 mmol) and the corresponding aldehyde **8a** (178 mg; 0.5 mmol), **8b** (191 mg; 0.5 mmol), or **8c** (191 mg; 0.5 mmol) were dissolved in acetic anhydride under an argon atmosphere. The mixture was heated to 100 °C for 3 h (**8a**), 3.5 h (**8b**), or 1 h (**8c**). After cooling to room temperature, a saturated solution of $NaHCO_3$ was added and stirred for 15 min, and the organic phase was extracted with AcOEt. The combined organic layers were dried over anhydrous $MgSO_4$, and the crude product was purified by filtration or silica gel column chromatography.

(*Z*)-4-{5-[(2,6-Diphenyl-4*H*-pyran-4-ylidene)methyl]-thiophen-2-yl}-2-phenylbuta-1,3-diene-1,1,3-tricarbonitrile, 2a. The crude product was isolated by filtration, washed with cold hexane, and dried.

Yield: green solid (144 mg; 0.27 mmol; 54%); mp 285−288 °C; IR (KBr, cm^{-1}) 2202 (C≡N), 1519 (C═C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01−7.79 (m, 4H), 7.68−7.42 (m, 9H), 7.02 (d, J = 4.5 Hz, 1H), 6.69 (d, J = 1.8 Hz, 1H), 6.30 (s, 1H). The ^{13}C NMR spectrum was not registered because of the low solubility of **2a**; HRMS (ESI$^+$) Calcd for $C_{35}H_{21}N_3NaOS$ $[M + Na]^+$ 554.1298, found 554.1291; Calcd for $C_{35}H_{21}KN_3OS$ $[M + K]^+$ 570.1037, found 570.1029.

(*Z*)-4-{5-[(*E*)-3-(2,6-Diphenyl-4*H*-pyran-4-ylidene)prop-1-enyl]thiophen-2-yl}-2-phenylbuta-1,3-diene-1,1,3-tricarbonitrile, 2b. The crude product was purified by silica gel column chromatography (first 30% ethyl acetate in hexanes, and then the polarity was gradually increased to 50% ethyl acetate in hexanes).

Yield: red solid (31 mg; 0.06 mmol; 11%); mp 285−288 °C; IR (KBr, cm^{-1}) 2212 (C≡N), 1538 (C═C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92−7.73 (m, 5H), 7.65−7.37 (m, 13H), 7.00 (d, J = 4.2 Hz, 1H), 6.92 (br s, 1H), 6.59 (d, J = 14.6 Hz, 1H), 6.51 (br s, 1H), 5.83 (d, J = 12.1 Hz, 1H); ^{13}C NMR was not registered because of low solubility; HRMS (ESI$^+$) Calcd for $C_{37}H_{23}N_3OS$ $[M]^{+\cdot}$ 557.1556, found 557.1534; Calcd for $C_{37}H_{24}N_3OS$ $[M + H]^+$ 558.1635, found 558.1598; Calcd for $C_{37}H_{23}N_3NaOS$ $[M + Na]^+$ 580.1454, found 580.1450.

(3*Z*,5*E*)-6-{5-[(2,6-Diphenyl-4*H*-pyran-4-ylidene)methyl]-thiophen-2-yl}-2-phenylhexa-1,3,5-triene-1,1,3-tricarbonitrile, 2c. The crude product was purified by silica gel column chromatography (30% ethyl acetate in hexanes).

Yield: dark green solid (153 mg; 0.28 mmol; 55%); mp 245−249 °C; IR (KBr, cm^{-1}) 2213 (C≡N), 1574 (C═C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91−7.76 (m, 4H), 7.64−7.39 (m, 11H), 7.31 (d, J = 4.0 Hz, 1H), 7.29 (d, J = 14.4 Hz, 1H), 7.26 (d, J = 11.8 Hz, 1H), 7.23 (d, J = 1.9 Hz, 1H), 7.07 (dd, J = 14.4 Hz, J' = 11.8 Hz, 1H), 6.96 (d, J = 4.0 Hz, 1H), 6.59 (d, J = 1.9 Hz, 1H), 6.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 157.7, 156.7, 154.1, 153.1, 143.9, 138.2, 137.0,

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134.9, 134.8, 132.9, 132.8, 132.5, 131.2, 130.6, 130.3, 129.7, 129.6, 129.4, 129.1, 126.1, 125.4, 121.3, 115.1, 115.0, 113.6, 109.7, 108.6, 104.3, 104.2, 104.0; HRMS (ESI$^+$) Calcd for $C_{37}H_{23}N_3OS$ $[M]^+$ 557.1556, found 557.1552.

Compounds 3a–c: General Procedure. Equimolar quantities of 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (100 mg; 0.5 mmol) and the corresponding aldehyde **8a** (178 mg; 0.5 mmol), **8b** (191 mg; 0.5 mmol), or **8c** (191 mg; 0.5 mmol) were dissolved in absolute ethanol. To this mixture was added a pyridine/acetic acid (10 equiv/7 equiv) solution, and the resulting mixture was heated under reflux for 24 h (**8a** and **8c**) or 48 h (**8b**) (TLC monitoring) and then cooled. The solvent was evaporated, and the crude product was dissolved in dichloromethane. Finally, the solution was washed with saturated $NaHCO_3$ solution, water and dried over anhydrous $MgSO_4$, and the resulting solid was purified as described below.

(*E*)-2-[3-Cyano-4(2-{5-[(2,6-diphenyl-4*H*-pyran-4-yliedene)-methyl]thiophen-2-yl}vinyl)-5,5-dimethylfuran-2(5*H*)-ylidene]-malononitrile, 3a. The resulting solid was filtered off and purified by recrystallization from dichloromethane.

Yield: copper solid (110 mg; 0.21 mmol; 41%); mp 336–340 °C; IR (KBr, cm^{-1}) 2220 (C≡N), 1524 (C═C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.75 (m, 5H), 7.60–7.46 (m, 7H), 7.43 (d, J = 4.2 Hz, 1H), 7.01 (d, J = 4.2 Hz, 1H), 6.62 (d, J = 1.8 Hz, 1H), 6.56 (d, J = 15.4 Hz, 1H), 6.23 (s, 1H), 1.76 (s, 6H). The ^{13}C NMR spectrum was not registered because of the low solubility of **3a**; HRMS (ESI$^+$) Calcd for $C_{34}H_{23}N_3O_2S$ $[M]^{+\cdot}$ 537.1501, found 537.1505; Calcd for $C_{34}H_{23}N_3NaO_2S$ $[M + Na]^+$ 560.1403, found 560.1398; Calcd for $C_{34}H_{23}KN_3O_2S$ $[M + K]^+$ 576.1143, found 576.1125.

2-[3-Cyano-4-((*E*)-2-{5-[(*E*)-3-(2,6-diphenyl-4*H*-pyran-4-ylidene)prop-1-enyl]thiophen-2-yl}vinyl)-5,5-dimethylfuran-2(5*H*)-ylidene]malononitrile, 3b. The resulting solid was filtered off and sequentially washed with hexane, hexane/CH_2Cl_2 (9/1), hexane/CH_2Cl_2 (8/2), cold ethanol, and dried.

Yield: dark red solid (251 mg; 0.45 mmol; 89%); mp 305–308 °C; IR (Nujol/NaCl, cm^{-1}) 2219 (C≡N), 1541 (C═C); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.94–7.77 (m, 4H), 7.72 (d, J = 15.4 Hz, 1H), 7.60–7.29 (m, 8H), 7.01 (d, J = 4.1 Hz, 1H), 6.95 (br s, 1H), 6.63 (d, J = 14.5 Hz, 1H), 6.61 (d, J = 15.4 Hz, 1H), 6.54 (br s, 1H), 5.87 (d, J = 12.2 Hz, 1H), 1.76 (s, 6H). The ^{13}C NMR spectrum was not registered because of the low solubility of **3b**; HRMS (ESI$^+$) Calcd for $C_{36}H_{25}N_3O_2S$ $[M]^{+\cdot}$ 563.1662, found 563.1655; Calcd for $C_{36}H_{25}N_3NaO_2S$ $[M + Na]^+$ 586.1560, found 586.1546.

2-[3-Cyano-4-((1*E*,3*E*)-4-{5-[(2,6-diphenyl-4*H*-pyran-4-ylidene)methyl]thiophen-2-yl}buta-1,3-dienyl)-5,5-dimethylfuran-2(5*H*)-ylidene]malononitrile, 3c. The resulting solid was filtered off and washed with cold hexane.

Yield: dark green solid (242 mg; 0.43 mmol; 86%); mp 261–264 °C; IR (KBr, cm^{-1}) 2216 (C≡N), 1547 (C═C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.72 (m, 4H), 7.61 (dd, J = 15.2 Hz, J' = 11.4 Hz, 1H), 7.55–7.41 (m, 5H), 7.28 (d, J = 14.5 Hz, 1H), 7.22 (d, J = 4.0 Hz, 1H), 7.19 (d, J = 1.5 Hz, 1H), 6.95 (d, J = 4.0 Hz, 1H), 6.75 (dd, J = 14.5 Hz, J' = 11.4 Hz, 1H), 6.52 (d, J = 1.5 Hz, 1H), 6.42 (d, J = 15.2 Hz, 1H), 6.16 (s, 1H), 1.71 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 155.4, 153.0, 149.4, 148.1, 148.0 (× 2), 139.0, 138.1, 133.9, 132.8, 132.5, 130.3, 129.8, 129.0, 128.8, 127.8, 125.4, 124.8, 115.6, 112.3, 111.5, 111.3, 109.0, 107.9, 103.3, 96.7, 26.5; HRMS (ESI$^+$) Calcd for $C_{36}H_{25}N_3O_2S$ $[M]^{+\cdot}$ 563.1662, found 563.1665; Calcd for $C_{36}H_{25}N_3NaO_2S$ $[M + Na]^+$ 586.1560, found 586.1550; Calcd for $C_{36}H_{25}N_3KO_2S$ $[M + K]^+$ 602.1299, found 602.1299.

Compounds 4a–c: General Procedure. Equimolar quantities of 2-(3-cyano-5-methyl-5-(trifluoromethyl)furan-2(5*H*)-ylidene]-malononitrile (127 mg; 0.5 mmol) and the corresponding aldehyde **8a** (178 mg; 0.5 mmol), **8b** (191 mg; 0.5 mmol), or **8c** (191 mg; 0.5 mmmol) were dissolved in absolute ethanol. To this mixture was added a pyridine/acetic acid (10 equiv/7 equiv) solution, and the resulting mixture was heated under reflux for 4 h (**8a**), 24 h (**8b**), or 2 h 30 min (**8c**) (TLC monitoring) and then cooled. The solvent was evaporated, and the crude product was dissolved in dichloromethane. A saturated $NaHCO_3$ solution was added, and the mixture was stirred for 15 min. The phases were separated, and the aqueous layer was washed with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated. The resulting crude product was purified as described below.

(*E*)-2-[3-Cyano-4-(2-{5-[(2,6-diphenyl-4*H*-pyran-4-ylidene)-methyl]thiophen-2-yl}vinyl)-5-methyl-5-(trifluoromethyl)-furan-2(5*H*)-ylidene]malononitrile, 4a. The pure compound was obtained by silica gel column chromatography [first using 100% dichloromethane, and then the polarity was gradually increased to CH_2Cl_2/AcOEt (98/2)].

Yield: dark green solid (177 mg; 0.30 mmol; 60%); mp 259–264 °C; IR (KBr, cm^{-1}) 2220 (C≡N), 1527 (C═C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 15.0 Hz, 1H), 7.97–7.74 (m, 4H), 7.60–7.48 (m, 7H), 7.32 (d, J = 1.9 Hz, 1H), 7.05 (d, J = 4.4 Hz, 1H), 6.71 (d, J = 1.9 Hz, 1H), 6.47 (d, J = 15.0 Hz, 1H), 6.31 (s, 1H), 1.92 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 175.6, 160.9, 157.7, 156.2, 155.2, 152.4, 140.1, 137.7, 137.4, 134.4, 132.0, 131.8, 131.2, 130.6, 129.7, 129.2, 129.1, 104.1, 56.2, 29.7, 19.5, 10.0; HRMS (ESI$^+$) Calcd for $C_{34}H_{20}F_3N_3O_2S$ $[M]^+$ 591.1222, found 591.1200.

2-[3-Cyano-4-((*E*)-2-{5-[(*E*)-3-(2,6-diphenyl-4*H*-pyran-4-ylidene)prop-1-enyl]thiophen-2-yl}vinyl)-5-methyl-5-(trifluoromethyl)furan-2(5*H*)-ylidene] malononitrile, 4b. The resulting solid was purified by reverse C18 column chromatography (first using a mixture of 70% acetonitrile in water, and then the polarity was gradually changed to 100% acetonitrile).

Yield: dark red solid (154 mg; 0.25 mmol; 50%); mp 266–269 °C; IR (KBr, cm^{-1}) 2224 (C≡N), 1520 (C═C); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.09 (d, J = 15.1 Hz, 1H), 7.98–7.76 (m, 4H), 7.59–7.38 (m, 8H), 7.07 (d, J = 4.4 Hz, 1H), 7.01 (d, J = 1.8 Hz, 1H), 6.66 (d, J = 14.5 Hz, 1H), 6.60 (d, J = 1.8 Hz, 1H), 6.51 (d, J = 15.1 Hz, 1H), 5.93 (d, J = 12.2 Hz, 1H), 1.93 (s, 3H). ^{19}F NMR (282 MHz, CD_2Cl_2) δ −78.80; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.1, 161.9, 158.5, 155.3, 154.6, 141.0, 139.1, 137.6, 133.2, 133.0, 132.8, 130.9, 130.6, 129.5 (× 2), 129.4, 128.7, 125.9, 125.8, 125.4, 120.3, 115.9, 112.1 (× 2), 111.7, 110.8, 109.5, 103.3, 97.6, 96.2, 19.8; HRMS (ESI$^+$) Calcd for $C_{36}H_{22}F_3N_3O_2S$ $[M]^{+\cdot}$ 617.1379, found 617.1385; Calcd for $C_{36}H_{22}F_3N_3NaO_2S$ $[M + Na]^+$ 640.1277, found 640.1274.

2-[3-Cyano-4-((1*E*,3*E*)-4-{5-[(2,6-diphenyl-4*H*-pyran-4-ylidene)methyl]thiophen-2-yl}buta-1,3-dienyl)-5-methyl-5-(trifluoromethyl)furan-2(5*H*)-ylidene]malononitrile, 4c. The resulting solid was filtered off and washed with hexane/dichloromethane mixtures and dried.

Yield: red/copper solid (161 mg; 0.26 mmol; 52%); mp 227–232 °C; IR (KBr, cm^{-1}) 2222 (C≡N), 1558 (C═C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 14.3 Hz, J = 11.8 Hz, 1H), 7.94–7.75 (m, 4H), 7.62–7.45 (m, 6H), 7.41 (d, J = 14.3 Hz, 1H), 7.32 (d, J = 4.2 Hz, 1H), 7.23 (d, J = 1.6 Hz, 1H), 6.99 (d, J = 4.2 Hz, 1H), 6.77 (dd, J = 14.3 Hz, J' = 11.8 Hz, 1H), 6.35 (d, J = 14.3 Hz, 1H), 6.60 (d, J = 1.6 Hz, 1H), 6.23 (s, 1H), 1.87 (s, 3H), 6.23 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 161.2, 166.2, 153.8, 152.1, 150.3, 141.5, 138.5, 136.1, 134.4, 132.4, 132.1, 130.6, 130.1, 129.1, 128.9, 125.5, 125.3, 124.8, 114.3, 111.7, 111.5, 111.0, 109.4, 108.5, 103.6, 19.3; HRMS (ESI$^+$) Calcd for $C_{36}H_{22}F_3N_3O_2S$ $[M]^{+\cdot}$ 617.1379, found 617.1370; Calcd for $C_{36}H_{22}F_3N_3NaO_2S$ $[M + Na]^+$ 640.1277, found 640.1283.

■ ASSOCIATED CONTENT

Supporting Information

General experimental methods, NMR and UV–vis spectra of new compounds, NLO measurements, computed energies and Cartesian coordinates of optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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