

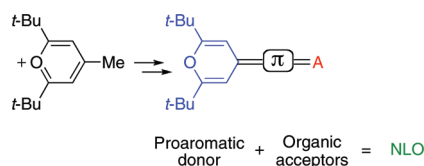
4H-Pyran-4-ylidenes: Strong Proaromatic Donors for Organic Nonlinear Optical Chromophores

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Merocyanines where a polyenic spacer separates a 4H-pyran-4-ylidene moiety and different strong organic acceptors have been synthesized. According to NMR studies and X-ray diffraction data, these compounds have weakly alternated structures and remarkably zwitterionic ground states, with a partial aromatic character that is compared to those of other pyran derivatives. The proaromaticity of the 4H-pyran-4-ylidene donor lies behind the cyanine-like behavior and low (positive or negative) second-order optical nonlinearities of the shorter derivatives. On the other hand, lengthening the π -spacer gives rise to rapidly increasing $\mu\beta_{1907}$ values up to $17,400 \times 10^{-48}$ esu.

Introduction

Conjugated donor–acceptor (D– π –A) compounds constitute the blueprint in the search for new materials endowed with nonlinear optical (NLO) properties and are being widely investigated because of their technological and fundamental interest.¹ These compounds display first molecular hyperpolarizabilities (β), related to intramolecular charge transfer (ICT) excitations, which are dependent on the nature of the donor, acceptor, and spacer moieties.² One of the successful strategies in the design of these NLO chromophores involves tuning the ground-state polarization of the chromophore, which in valence bond terminology depends on the relative contributions of the neutral and zwitterionic limiting forms.³

It was soon discovered that chromophores incorporating aromatic subunits displayed lower β values than the corresponding polyenes of the same conjugation length, since their ground states are usually dominated by neutral, aromatic forms that lose resonance energy on charge separation.⁴ To overcome this drawback, Marder proposed a strategy consisting in the use of fragments that, conversely, gain aromaticity on charge transfer. This strategy has since then been applied to proaromatic acceptors,⁵ spacers,⁶ and donors, the most widely used proaromatic electron donors being pyrid-4-ylidenes⁷ and 1,3-dithiol-2-ylidenes.⁸ On the other hand, the donor ability of the isoelectronic pyran-4-ylidene moiety has received much less attention in the search for new NLO chromophores. Thus, from a theoretical point of view, Marks suggested that heavily substituted 4-quinopyrans could display very high hyperpolarizabilities due to their twisted intramolecular charge transfer nature

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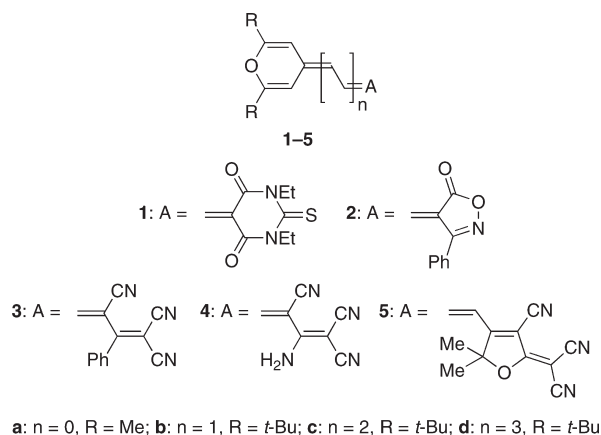
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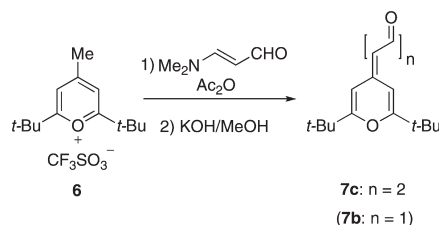
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and, therefore, zwitterionic character.⁹ On the experimental side, the only studies aimed at taking advantage of the potential proaromaticity of 4-pyranylidene in the field of compounds with second-order NLO responses were reported by Caro, who prepared and studied push–pull compounds in which such donors are conjugated to Fischer-type carbenes^{10a,b} and organoiron(II) fragments.^{10c}

In this paper we describe the synthesis and characterization of new D– π –A compounds (**1**–**5**) where a 4H-pyran-4-ylidene donor unit is linked to different strong organic acceptors and report the first study on the second-order NLO properties of these purely organic pyranilydene-based merocyanines. Experimental and theoretical evidence supporting the proaromaticity of the pyran-4-ylidene moiety are presented, and its partly aromatic character is compared to that of other pyran/pyrylium derivatives.



SCHEME 1



Results and Discussion

Synthesis. The shortest derivatives (**1a**,¹¹ **2a**,¹¹ **3a**,¹² **4a**,¹³ and **5a**¹²) with $n=0$ are known compounds and were prepared as previously reported. For the synthesis of the longer molecules, 4H-pyranilydene aldehydes **7b,c** were chosen as precursors. At this stage, the replacement of the methyl groups on the pyran ring by *tert*-butyl seemed convenient to avoid possible side-reactions in the (vinylogous) formylation step. Thus, aldehyde **7b** was prepared as previously described,¹⁴ and the previously unreported aldehyde **7c** was synthesized using a similar procedure, namely, the reaction of salt **6**¹⁵ with 3-dimethylaminoacrolein/ Ac_2O ,¹⁶ followed by hydrolysis (overall yield, 39% from **6**) (Scheme 1).

Knoevenagel reactions of **7b,c** with acceptors **8**–**12**, where **12** is the so-called “tricyanofuran” or TCF acceptor, afforded the vinylogous push–pull compounds **1b,c**–**5b,c**, respectively (Scheme 2). On passing, it should be noted that there are very few pyran-4-ylidene derivatives linked to an acceptor through a polyenic spacer, and most of them feature weak acceptors, such as carbonyl groups.^{17a–d} (Moreover, some cyanines having a formal pyrylium cation linked to a pyran-4-ylidene moiety through a conjugated spacer with an odd number of carbon atoms (the so-called pyrylocyanines) have also been described.)^{17e–h}

The synthesis of molecules with more extended π -systems required another approach because, under a variety of conditions, we were not able to prepare the higher vinylogue of aldehyde **7c**. Therefore, we decided to take advantage of the well-known electrophilicity of enamido substituents linked to strong acceptor groups and of the nucleophilic character of the exocyclic carbon atom of 4-methylpyrylium derivatives (as their corresponding anhydrobases). To that end, acceptor vinylogues **8'**–**12'** were prepared by the reaction of acceptors **8**–**12**, respectively, with glutacetaldehyde dianilide hydrochloride

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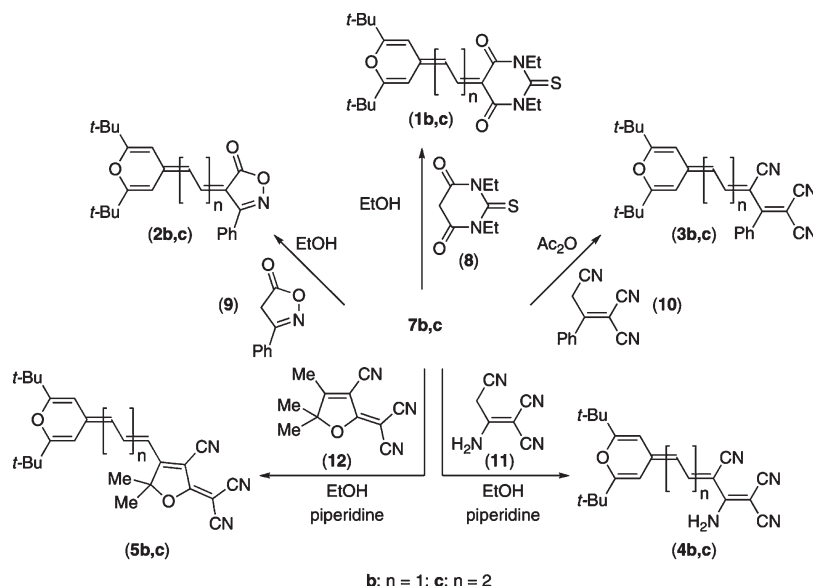
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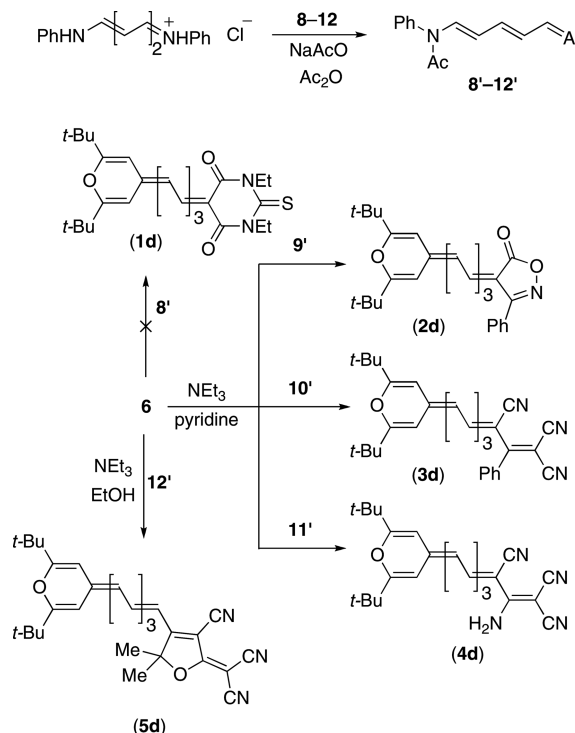
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SCHEME 2



SCHEME 3



(Scheme 3). Compounds **8'**,¹⁸ **9'**,^{18,19} and **12'**^{7c} have been described, but only the latter has been adequately characterized. New compounds **10'** and **11'** were also prepared by the same general method. The reaction of these extended acceptors with pyrylium salt **6** in the presence of triethylamine afforded the desired merocyanines **2d–5d** (unfortunately, the thiobarbituric

derivative **1d** turned out to be unstable and could not be isolated) (Scheme 3).

¹H NMR Studies. Concerning the new aldehyde **7c**, ³J_{HH} coupling constants reveal that it has an all-*trans* geometry, with an *s-trans* conformation for the formyl group (see Experimental Section). This contrasts to the *s-cis* conformation, which minimizes steric crowding in the corresponding doubly vinylogous ketones.^{17b}

Concerning compounds **1–5**, ³J_{HH} coupling constants analysis along the spacer shows that CH=CH and CH–CH bonds have (*E*)-configuration and *s-trans* conformation, respectively. On the other hand, the isoxazolone-exocyclic C=C bond in compounds **2** has a (*Z*)-geometry, as demonstrated by the downfield shift of the H atom located five bonds away from the carbonyl oxygen atom.^{8c,20} Similarly, the HC=C(CN) bond in compounds **3** (see below) shows the expected (*Z*)-geometry. Concerning compounds **4**, NOE and NOESY experiments at different temperatures on model compound **4b** did not allow to establish the configuration of the HC=C(CN) bond, but previous studies on related compounds show a (*Z*)-geometry for that fragment, configuration that is also assumed for **4**.²¹

¹H NMR spectra also afford valuable information concerning the contribution of the neutral (**N**) and zwitterionic (**ZW**) limiting forms to the description of the ground state of these compounds, that is, about the proaromatic character of the 4*H*-pyran-4-ylidene moiety (Figure 1).

In fact, previous NMR experiments²² (and dipole moment measurements)²³ on simple 4-methylene-4*H*-pyran derivatives

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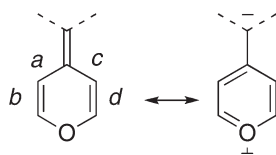
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FIGURE 3. Bond lengths involved in the δr parameter.TABLE 1. Structural Parameters (Å) of **2b**, **3c**, **13**, and **14**

compd	C–O	C ₄ –C _{exo}	δr
2b	1.360	1.393	0.087
3c	1.361	1.391	0.084
13 ^a	1.354	1.466	0.043
14 ^b	1.389	1.385	0.107

^a Reference 33. ^b Reference 34.

bipyranylidene (**14**),³⁴ which can be safely considered as a quinoid derivative (Figure 4). As expected, δr for **14** is much larger than for **13**, but the latter still shows a substantial δr value, in good agreement with the low aromaticity of pyrylium cations.³⁵

Moreover, the geometries of **2b** and **3c** are similar to those reported for other push–pull pyran-4-ylidene derivatives, such as 4-dicyanomethylene-2,6-dimethyl-4*H*-pyran,³⁶ **3a**,¹² and 4-methylenepyran Fischer-type carbene complexes,^{10b,31} where available structural data show that these compounds have intermediate features between those of cation **13** and compound **14** (with the following average values: C–O 1.36–1.37 Å; C₄–C_{exo} 1.39–1.40 Å; δr 0.08–0.09 Å).

These experimental geometries, together with those of pyrylium cations, allow a qualitative estimation of the proaromatic character of the herein reported compounds and of other 4-methylenepyran derivatives. It is known that geometry-based indices of aromaticity³⁷ suffer from some limitations, but their easy availability and reasonable success on treating the aromaticity of closely related compounds make them adequate enough for qualitative comparisons. Thus, we have calculated the Bird index (I_6)³⁸ for a wide variety of pyran derivatives using experimental (X-ray diffraction) geometries. Concerning the extreme models, pyrylium cations^{33,39} show I_6 values of ca. 50 (for benzene $I_6 = 100$), whereas that of compound **14**³⁴ is much lower ($I_6 = 25.4$). Compounds **2b** and **3c** show intermediate values (39.2 and 38.5, respectively), nearly identical to those calculated

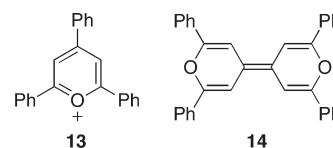


FIGURE 4. Aromatic and quinoid pyran derivatives.

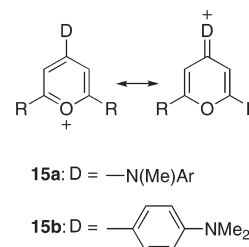


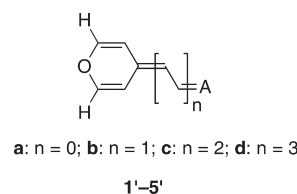
FIGURE 5. Pyrylium cations 4-substituted with donor groups.

for the previously mentioned push–pull pyran-4-ylidene derivatives ($I_6 = 38$ –40).

Thus, whereas the geometries of all these compounds are closer to the quinoid than to the aromatic type as judged from bond distance parameters (Table 1), their I_6 values indicate a noticeable contribution of the zwitterionic limiting form. This intermediate quinoid/aromatic character may be due to the fact that the energetic cost of the charge separation needed to adopt a more aromatic structure (**ZW**, Figure 1) is hardly compensated for by the low aromaticity of the pyrylium form. In fact, these compounds can be considered either as pyran-4-ylidene derivatives bearing acceptor groups (N, Figure 1) or as pyrylium salts substituted with strong (negatively charged) donor groups (**ZW**, Figure 1), a situation reminiscent of that found for cations **15** (Figure 5),⁴⁰ where the stabilization of the positive charge by the electron donor group (D) leads to an increase in the quinoid contribution and, therefore, to less aromatic structures (e.g., for **15b**^{40b} (R = Ph): C–O 1.363 Å; C₄–C_{exo} 1.438 Å; δr 0.068 Å; $I_6 = 42.7$).

These examples suggest that the relatively high alternation found in the pyran ring of push–pull pyran-4-ylidenes should not be taken as evidence against the proaromatic character of the pyran-4-ylidene moiety.

Calculated Structures. We have also carried out theoretical calculations at the B3P86/6-31G* level on the model compounds **1'–5'**, where the alkyl groups on the pyran ring of compounds **1–5** have been replaced by H atoms for the sake of simplicity (the validity of such replacement has been confirmed by comparison of the DFT calculated geometries of compound **3a** and its simplified model **3'a**, see Supporting Information).



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TABLE 2. B3P86/6-31G* Calculated Values for Compounds 1'a–d

compd	δr (Å)	C ₄ –C _{exo} (Å)	BLA ^a (Å)	<i>I</i> ₆	charge ^b (e)
1'a	0.090	1.404		47.1	+0.39
1'b	0.097	1.385	0.022	42.7	+0.34
1'c	0.100	1.380	0.034	41.1	+0.29
1'd	0.101	1.379	0.037	40.6	+0.27

^a Along the polyenic spacer. ^b In the pyranilidene moiety.

In the few cases where experimental geometries are available (**2b**, **3a**,¹² **3c**) we have found that calculations on the corresponding model compounds overestimate both BLA along the spacer (by ca. 0.03 Å) and δr values while underestimating C–O bond distances, giving rise to *I*₆ values higher (by ca. 3–5 units) than those of the experimentally determined structures. While this precludes a direct comparison between the calculated and solid-state structures, the DFT geometries should still give information about the main structural features of the model compounds. They are exemplified by the values shown in Table 2 for the series 1'a–d (the same trends are observed for the remaining series).

It can be seen that the pyran rings are calculated to display high δr values and relatively short C₄–C_{exo} bonds, but the charges in the donor moiety are also high, pointing to a noticeable zwitterionic (proaromatic) character that decreases on lengthening the polyenic spacer, reflecting the higher energy required to separate charges over longer distances. This trend is in good agreement with the decrease in *I*₆ values and the increase in BLA on passing from 1'a to 1'd. The progressive shortening of the C₄–C_{exo} bond also supports this reasoning and confirms the previously observed good correlation between that bond length and the aromatic character of pyrylium ions.^{39d}

Electrochemistry. The electrochemical properties of compounds 1–5 were studied by cyclic voltammetry (Table 3). Most of these merocyanines show two irreversible waves, corresponding to the oxidation of the donor and the reduction of the acceptor moieties, respectively. Lengthening the π spacer gives rise to a shift of *E*_{ox} values toward less anodic potentials and to a shift of *E*_{red} values toward less cathodic potentials. The easier oxidation and reduction processes on chain lengthening point to a decrease in the interaction between the donor and acceptor end groups and, therefore, to a smaller contribution of the zwitterionic form to the ground state of the longer derivatives, in line with the calculated Mulliken charges (Table 2). Moreover, the observed trends in *E*_{ox} (*E*_{red}) are also confirmed by theoretical calculations, which show that *E*_{HOMO} (*E*_{LUMO}) values increase (decrease) with the length of the spacer. For any given acceptor, the decrease in *E*_{ox} is much more noticeable than that in |*E*_{red}|, in agreement with the trends shown by the energy levels of the frontier orbitals (Table 3). *E*_{ox} values also allow a broad comparison of the electron-withdrawing abilities of the different acceptor groups. Thus, values in Table 3 show that thiobarbiturate is a stronger acceptor than isoxazolone, in line with the lower Mulliken charges supported by the donor moiety in compounds **2** (**2a**, +0.32; **2b**, +0.30; **2c**, +0.26; **2d**, +0.25; cf. Table 2), and that the acceptor strength slightly decreases on passing from compounds **3** to **4**. Broader comparisons between structurally disparate acceptors must take into account the length of the spacer separating the D and A moieties, since this parameter has a marked influence on *E*_{ox} values. For instance, when the

oxidation potentials of compounds **1c**, **3b**, and **5a** (all of them with the same number of carbon atoms in the conjugation path) are compared, it becomes clear that the electron-withdrawing ability of the corresponding acceptor groups decreases in the sequence **5** > **3** > **1**.

UV–vis Spectroscopy. The UV–vis absorption data of compounds 1–5 are collected in Table 3, inspection of which reveals some common trends. For a given acceptor, λ_{max} values increase with the conjugation length, showing large vinylene shifts of ca. 100 nm (on the energy scale these shifts decrease on lengthening the spacer; thus, for the series **5a**, **5b**, **5c**, **5d**, the observed shifts are of 0.48, 0.26, and 0.20 eV, respectively). This is indicative of a cyanine-like (rather than a polyene-like) behavior, thus suggesting an important zwitterionic character for these derivatives, in agreement with theoretical calculations (Table 2). The observed bathochromic shifts and the increased log ϵ values on lengthening the spacer are also well reproduced by TDDFT calculations (see below).

When different acceptors are compared, λ_{max} approximately decrease in the following order: **5** > **3** > **4** \approx **1** \approx **2**. This order, although based on a crude comparison obviating the very different structures of the acceptor groups, suggests a parallel decrease in the corresponding acceptor strengths, in agreement with the results of cyclic voltammetry. A more detailed comparison can be made between the structurally similar derivatives **3** and **4**. The replacement of the phenyl group in compounds **3** by an amino group in **4** gives rise to a strong hypsochromic shift. Those substituents are linked to an odd-numbered carbon atom of the polymethine chain and the lower λ_{max} values are therefore expected on the basis of Dewar's rules.⁴¹ In fact, the amino group not only causes a strong destabilization of the LUMOs of compounds **4**, when compared to **3** (Table 3), but also a slight and unexpected stabilization of the corresponding HOMOs. Both factors result in increased HOMO–LUMO gaps and higher excitation energies (Table 4) for compounds **4**.

The solvatochromism of compounds 1–5 is small. With a few exceptions, compounds **3** and **5** show small, positive solvatochromic effects, whereas the reverse holds for compounds **4**. For compounds **1** and **2**, the shorter derivatives show a small, negative solvatochromism, which becomes positive for the longer ones (**2c,d**). This behavior reinforces the previously mentioned cyanine-like character of 1–5, which decreases on lengthening the spacer, in good agreement with the calculated increase in BLA values on passing from the shorter to the longer derivatives (Table 2).

Nonlinear Optical Properties. The second-order NLO properties of compounds 1–5 were measured by electric field-induced second harmonic generation (EFISH) at 1907 nm in dichloromethane (except where noted), and the static (zero-frequency) $\mu\beta_0$ values were calculated by the two-level model,⁴² using the lowest energy absorption band of each compound (for the sake of comparison, a common benchmark of organic NLO chromophores, Disperse Red 1, shows a $\mu\beta_0$ value of ca. 400×10^{-48} esu).⁴³

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TABLE 3. Electrochemical Data,^a E_{HOMO} and E_{LUMO} Values^b (eV), and UV–vis Data

compd	E_{ox}	E_{red}	E_{HOMO}	E_{LUMO}	λ_{max} (CH ₂ Cl ₂) (log ϵ)	λ_{max} (DMSO)
1a	+1.56	−1.40	−6.73	−3.36	392 (sh), 409 (4.79)	407
1b	+1.19	−1.11 ^c	−6.55	−3.50	501 (4.81), 530 (5.18)	502, 530
1c	+0.83	−0.94 ^d	−6.25	−3.58	584 (4.93), 628 (5.25)	585, 627
1d^e			−6.03	−3.64		
2a	+1.50	−1.50	−6.58	−3.04	397 (4.35)	396
2b	+1.10	−1.15 ^f	−6.23	−3.26	498 (4.72), 530 (4.68)	502, 529
2c	+0.77	−1.04	−5.99	−3.36	579 (4.82), 623 (4.76)	583, 626
2d	+0.57	−0.93	−5.81	−3.44	610 (sh), 654 (4.86), 715 (4.68)	663, 725
3a	+1.64	−1.11, −1.70	−6.95	−3.62	455 (4.42)	460
3b	+1.20	−0.89 ^g	−6.52	−3.74	535 (4.72), 568 (4.89), 601 (sh)	536 (sh), 570, 600 (sh)
3c	+0.88	−0.76	−6.26	−3.79	629 (4.89), 678 (5.11)	629 (sh), 678
3d	+0.64	−0.71	−6.06	−3.82	719 (4.92), 787 (5.07)	718 (sh), 782
4a	+1.67	−1.35	−7.02	−3.32	382 (4.26)	358
4b	+1.14	−1.12	−6.60	−3.61	506 (4.62), 532 (4.64)	485
4c	+0.87	−1.04	−6.32	−3.69	584 (4.72), 625 (4.71)	552, 603 (sh)
4d	+0.59	−0.86	−6.10	−3.74	643 (4.71), 719 (4.56)	558, 713 (sh)
5a	+1.32	−1.10	−6.67	−3.81	513 (4.60)	517
5b	+1.00	−0.83 ^h	−6.43	−3.87	592 (4.74), 639 (4.97)	595, 637
5c	+0.68	−0.77	−6.21	−3.90	675 (4.86), 740 (5.03)	680, 739
5d	+0.51	−0.69	−6.03	−3.92	688 (sh), 753 (4.92), 841 (4.94)	763, 847

^a In volts, 10^{−3} M in CH₂Cl₂ vs Ag/AgCl (KCl 3 M), glassy carbon working electrode, Pt counter electrode, 20 °C, 0.1 M Bu₄NPF₆, 100 mV s^{−1} scan rate. Ferrocene internal reference $E^{1/2} = +0.43$ V. ^b Calculated for model compounds **1'**–**5'** in the gas phase for the geometries shown in Schemes 2 and 3, at the B3P86/6-31G*//B3P86/6-31G* level. ^c $E_{\text{red}}^{1/2}$ ($\Delta E_{\text{p}} = 0.12$ V). ^d $E_{\text{red}}^{1/2}$ ($\Delta E_{\text{p}} = 0.10$ V). ^e Not isolated. ^f $E_{\text{red}}^{1/2}$ ($\Delta E_{\text{p}} = 0.10$ V). ^g $E_{\text{red}}^{1/2}$ ($\Delta E_{\text{p}} = 0.11$ V). ^h $E_{\text{red}}^{1/2}$ ($\Delta E_{\text{p}} = 0.08$ V).

TABLE 4. Experimental^a and Calculated^{b,c} NLO Properties

compd	experimental		TD-DFT ^d						CPHF ^e
	$\mu\beta^f$	$\mu\beta_0^f$	μ_{g} (D)	μ_{c} (D)	$\Delta\mu_{\text{gc}}$ (D)	$\Delta\mu_{\text{gc}}(z)$ (D)	E (eV)	f	$\mu\beta_0^g$
1a	−50	−40	6.83	14.29	21.13	−21.13	3.43	0.3900	−131
1b	−90	−60	9.18	3.52	12.65	−12.63	3.13	0.9923	−157
1c	600	300	11.36	9.35	2.20	−2.04	2.85	1.6607	255
1d			13.31	18.39	5.16	+5.05	2.60	2.1456	1421
2a	0	0	7.99	2.89	9.46	−9.08	3.48	0.1204	−63
2b	100	64	9.31	6.27	9.52	−7.41	3.13	0.4950	−21
2c	740	380	10.80	8.51	2.39	−2.31	2.89	1.2031	312
2d	3500	1320	12.23	17.17	5.58	+4.67	2.64	1.8227	1096
3a	60	43	11.71	15.61	7.29	+2.27	3.15	0.3717	−82
3b	210	120	14.38	15.12	2.37	+0.56	2.96	1.1168	−54
3c	1550	670	16.42	20.95	5.59	+4.20	2.68	1.6086	787
3d	7500	2000	18.37	26.85	9.34	+8.06	2.44	2.0492	2820
4a	25	21	11.36	7.99	13.88	−11.35	3.45	0.2460	−109
4b	190	120	13.98	6.56	12.90	−11.40	3.03	0.7356	−103
4c	705	360	16.06	10.14	6.58	−6.17	2.79	1.4039	540
4d	2650	980	17.97	20.13	2.65	+2.09	2.56	2.0463	2198
5a^h	140	90	14.23	5.55	12.88	−11.86	2.90	0.5395	−119
5aⁱ			15.57	5.28	13.80	−13.01	2.92	0.7621	−355
5b^h	630	310	15.83	5.76	11.79	−11.26	2.60	0.8545	306
5bⁱ			18.01	8.54	10.37	−9.96	2.71	1.2921	336
5c^h	4500	1520	17.84	10.92	7.11	−6.99	2.44	1.4440	1824
5cⁱ			20.27	17.67	2.62	−2.60	2.51	1.9578	2404
5d^h	17400	3110	19.59	19.27	1.30	−0.36	2.28	2.0312	4745
5dⁱ			22.37	27.89	5.70	+5.47	2.31	2.4691	6341

^a In CH₂Cl₂ (in DMSO for **4a**), at 1907 nm. ^b On B3P86/6-31G* geometries. ^c On model compounds **1'**–**5'** for the geometries shown in Schemes 2 and 3. ^d B3P86/6-31G* level. ^e CPHF/6-31G* level. ^f In 10^{−48} esu. Experimental accuracy: $\pm 10\%$, except for **3a**, **5a** ($\pm 15\%$), and **1a**, **1b**, **2b**, **4a** ($\pm 20\%$). ^g In 10^{−48} esu. ^h Calculated value for the conformer with TCF-exocyclic *s-cis* C–C bond. ⁱ Calculated value for the conformer with TCF-exocyclic *s-trans* C–C bond.

Inspection of Table 4 reveals that $\mu\beta_0$ values increase with the conjugation length and that compounds **5** and **3**, bearing the strongest acceptors, display the highest second-order NLO responses. CPHF-calculated $\mu\beta_0$ values are in reasonably good agreement with the experimental ones. Thus, the small hyperpolarizabilities shown by the shorter derivatives (series **a** and **b**) are qualitatively predicted, although in most cases the calculated β values are negative, indicating an overestimation of the zwitterionic character of such compounds. On the other hand, positive $\mu\beta_0$ values are correctly

predicted for the longer derivatives (series **c** and **d**). Even though DFT calculated hyperpolarizabilities are usually overestimated,⁴⁴ we have carried out TDDFT calculations, which readily afford the parameters involved in the two-level model and provide a better understanding of the factors responsible for the NLO response. In this approach $\beta_0 \propto \Delta\mu_{\text{gc}} f / E^3$, where $\Delta\mu_{\text{gc}}$ stands for the difference between the

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excited- and ground-state dipole moments (μ_e and μ_g , respectively), f is the oscillator strength, and E is the first excitation energy. Within each series of compounds (**1–5**) f increases and E decreases on lengthening the spacer, thus explaining the increase in $\mu\beta_0$ values on passing from series **a** to **d**. On the other hand, the variation of $\Delta\mu_{ge}$ is more complex, and this is partly due to the widely different relative orientations of the μ_e and μ_g vectors for these compounds. To get a clearer picture of this factor, we have included in Table 4 the $\Delta\mu_{ge}(z)$ parameter, defined as the projection of $\Delta\mu_{ge}$ onto the ground state dipole moment direction, arbitrarily named z . Inspection of $\Delta\mu_{ge}(z)$ values reveals that, except for compounds **3**, they are predicted to pass from strongly negative to positive values on increasing the chain length. Since the experimentally determined $\mu\beta_0$ values of most compounds herein reported are positive, this parameter indicates that TDDFT also overestimates the zwitterionic character of these derivatives, although it correctly predicts the negative $\mu\beta_0$ values observed for **1a–b**.

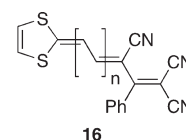
Comparison of the NLO properties of compounds **3** and **4** provides convincing evidence about an important aspect to which only a few experimental⁴⁵ and theoretical⁴⁶ efforts have been devoted, namely, the influence of the substituents of either the spacer or the acceptor on the NLO properties of merocyanines. Thus, and concerning a structure perturbation of the acceptor, it can be seen that $\mu\beta$ values of compounds **3** are higher than those of **4**, as a consequence of the replacement of a phenyl substituent by a strong electron-donating amino group at an odd-numbered carbon atom of the polymethine chain. Inspection of Table 4 reveals that this modification results both in higher excitation energies and lower oscillator strengths and, therefore, has a detrimental effect on the NLO response of compounds **4**.

Compounds **5** may be present as mixtures of conformers (*s-cis/s-trans* around the TCF-exocyclic C–C bond) under the conditions of the EFISH experiment, since calculations show that their energies are very close. The calculated parameters of each conformer are gathered in Table 4, but it can be seen that their $\mu\beta_0$ values are very similar, except for **5c,d**. This fact lends support to previous theoretical results suggesting that, in many cases, the conformational dependence of β is small, thus making it possible to consider only one conformation for computational studies.⁴⁷

The thermal stabilities of NLO chromophores **1–5** were studied by thermogravimetric analysis (TGA) (and differential scanning calorimetry (DSC) in some cases), their decomposition temperatures (T_d) being estimated as the temperature that is the intercept of the leading edge of the weight loss by the baseline of the TGA scans. TGA shows that the shortest derivatives studied (**b**) have high T_d values (T_d (°C): **1b**, 279; **2b**, 240; **3b**, 304; **4b**, 246; **5b**, 290) and that the thermal stability decreases on lengthening the spacer (T_d :

b > **c** > **d**) for every series of compounds (**1–5**). Comparison of the different series reveals that compounds **3** and **5** are the most thermally stable, with T_d values in the range 304–184 °C for **3b–d**, and 290–205 °C for **5b–d**. On the other hand, isoxazolone-containing compounds **2** have the lowest thermal stability (T_d range for **2b–d**: 240–152 °C), in agreement with previous observations on NLO chromophores containing such acceptor.⁴⁸

Finally, it seems pertinent to compare the NLO properties of the herein reported compounds to those of related derivatives. Concerning the acceptor moiety, the only directly comparable compounds are the pyranilidene-derived Fischer carbene complexes reported by Caro.^{10a,b} They show high, rapidly increasing $\mu\beta_{1907}$ values, which are similar to those of compounds **3**, but lower than those of compounds **5**. The shortest Fischer carbene derivative shows a negative β value, thus pointing to a strong zwitterionic character which decreases for the longer derivatives, a trend also shown by the present compounds. Therefore, series **1–5** and the previously reported organometallic derivatives show a qualitatively similar behavior, the electron-withdrawing ability of the C(OMe)W(CO)₅ fragment being surpassed by that of the TCF acceptor. Concerning the donor ability of the 4*H*-pyran-4-ylidene moiety, a straightforward comparison with another proaromatic donor (1,3-dithiol-2-ylidene) is possible thanks to the use of a common acceptor. To that end, compounds **3'** and **16**, featuring a common acceptor, have been chosen as models, since the linear and nonlinear optical properties of the dimethyl analogues of **16** have been studied both theoretically and experimentally.^{8d}



16
a: n = 0; b: n = 1; c: n = 2; d: n = 3

A comparison of the ground-state Mulliken charges on the donor fragment in compounds **3'** (**3'a**, +0.38; **3'b**, +0.33; **3'c**, +0.29; **3'd**, +0.27) and **16** (**16a**, +0.23; **16b**, +0.18; **16c**, +0.14; **16d**, +0.12) reveals that compounds **3'** are more polarized (have more zwitterionic ground states) than their dithiole counterparts, although their μ_g values are very similar, (cf. Table 4 and ref 8d) probably because of the strong negative charge supported by the oxygen atom of the pyran ring. This effect must also lie behind the lower μ_e (and hence, $\Delta\mu_{ge}$) values of compounds **3'**, compared to those of **16**. Even though oscillator strengths are larger for the pyran derivatives, the dithiole compounds have lower excitation energies and higher $\Delta\mu_{ge}$ values and therefore, it is unsurprising that they show higher $\mu\beta_0$ values^{8d} than their pyran analogues. These trends also hold when other dithiole/pyran families are compared, although the higher NLO-efficiency of the former tends to level-off for the longer derivatives.^{8c,21c} Besides, the lower $\Delta\mu_{ge}$ values, the higher oscillator strengths and the solvatochromism of pyranilidenes **1–5**, together

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with the small (positive or negative) $\mu\beta_0$ values of the shorter derivatives (**a,b**) clearly support the important zwitterionic character of these compounds, which are near the cyanine limit and, therefore, lie in region C of Marder's plot.³ On increasing the chain length, BLA (Table 2) and $\mu\beta_0$ values (Table 4) also increase, the longer derivatives (**c,d**) falling in region B of such plot.

Further comparisons between the donor ability of 4*H*-pyran-4-ylidenes and other proaromatic six-membered donors can also be established, although they are somewhat restricted by the lack of appropriate reference compounds or by the different experimental setups used in the measurement of the corresponding second-order NLO properties. Thus, *N*-substituted 4-pyridylidenes linked to the TCF acceptor (**12**) through a polyenic chain display zwitterionic ground states and strong negative solvatochromism,^{7c} pointing to a superior donor ability of the nitrogen heterocycle when compared to its oxygen analogue. Although a reliable comparison between the NLO properties of these pyridylidene derivatives and those of **5** is hampered by the fact that the former were measured by hyper-Rayleigh scattering (HRS), the high negative value ($\mu\beta_0 = -500 \times 10^{-48}$ esu)³ determined by EFISH in CH₂Cl₂ for a 4-pyridylidene analogue of **1b** reinforces the previous assumption. Concerning other closely related donors, such as chalcogenopyranylidenes, the very few reports to date show that replacement of the oxygen atom of the pyranylidene ring by sulfur generally leads to an enhancement of the second-order NLO responses, although the reversed trend is observed for chromene derivatives.^{10a,b}

In summary, polyenic merocyanines featuring a 4*H*-pyran-4-ylidene donor fragment have been prepared in one or two steps from 4-methylpyrylium salts. Experimental (X-ray diffraction, NMR, and UV-vis) data and theoretical calculations demonstrate the proaromaticity of the 4*H*-pyran-4-ylidene moiety in these push-pull compounds. Its partial aromatic character has been estimated and compared, for the first time, to that of pyrylium cations and simpler 4-methylenepyrans. The short merocyanines, with an important aromatic (zwitterionic) contribution are close to, or even surpass, the cyanine limit, whereas lengthening the spacer gives rise to more alternated structures with high second-order nonlinearities. The NLO properties of these all-organic, thermally stable compounds compare favorably to those of related organometallic pyranylidenes.

Experimental Section

Compounds **6**,¹⁵ **7b**,¹⁴ **10**,⁴⁹ **12**,⁵⁰ **8'**,¹⁸ **9'**,^{18,19} and **12**^{7c} were prepared as previously described.

(E)-4-(2,6-Di-*tert*-butyl-4*H*-pyran-4-ylidene)-but-2-enal (7c). To a solution of 2,6-di-*tert*-butyl-4-methylpyrylium triflate (**6**) (706 mg, 2 mmol) in acetic anhydride (10 mL) was added 3-dimethylaminoacrolein (90%) (0.6 mL, 6 mmol) under argon. The mixture was stirred at room temperature for 2 h. CH₂Cl₂ (100 mL) was added, and the resulting organic layer was washed with diluted H₃PO₄ (1/50 v/v; 2 × 100 mL), water (2 × 100 mL),

and finally saturated aqueous NaHCO₃ (5 × 75 mL). The organic layer was dried (MgSO₄) and evaporated. To the crude iminium salt was added methanolic KOH (5%, 37.5 mL), and the mixture was heated at 60 °C for 30 min. Then, a second portion of methanolic KOH (37.5 mL) was added to complete the hydrolysis, and the reaction was stirred for another 30 min. The mixture was cooled to room temperature, and CH₂Cl₂ (100 mL) and water (100 mL) were added. The organic layer was separated and washed with water (2 × 100 mL), dried (MgSO₄), and evaporated. The crude product was purified by flash chromatography (silica gel) using hexane/AcOEt (9:1) to afford a yellow to brown oil that precipitated (205 mg, 39%) on standing at 4 °C. Mp 101–103 °C. IR (Nujol, cm⁻¹): 1575 (C=C), 1643 (C=O). ¹H NMR (CDCl₃, 400 MHz): δ 9.50 (d, *J* = 8.2 Hz, 1H), 7.49 (dd, *J* = 14.4 Hz, *J'* = 12.3 Hz, 1H), 6.24 (d, *J* = 1.6 Hz, 1H), 6.00 (dd, *J* = 14.4 Hz, *J'* = 8.2 Hz, 1H), 5.80 (d, *J* = 1.6 Hz, 1H), 5.65 (d, *J* = 12.3 Hz, 1H), 1.25 (s, 9H), 1.21 (s, 9H). ¹³C NMR (CDCl₃, 75 MHz): δ 193.0, 166.7, 166.5, 148.2, 141.5, 124.6, 109.6, 105.4, 99.0, 36.0, 35.7, 27.8, 27.7. HRMS (ESI⁺): calcd for C₁₇H₂₅O₂ (M + H)⁺ 261.1849; found 261.1863; calcd for C₁₇H₂₄NaO₂ (M + Na)⁺ 283.1669; found 283.1682. Anal. Calcd for C₁₇H₂₄O₂: C 78.42, H 9.29. Found: C 78.77, H 9.06.

Compounds 1b,c: General Procedure. 1,3-Diethylthiobarbituric acid (**8**) (72 mg, 0.36 mmol) was added to a solution of 0.36 mmol of the corresponding aldehyde (**7b–c**) in absolute ethanol (2 mL). The solution was refluxed under argon atmosphere for 40–50 min (TLC monitoring), then cooled. The resulting solid was filtered off, washed with cold ethanol, and dried. For **1b** evaporation of the filtrate and chromatography (silica gel) using CH₂Cl₂ as eluent gave a second fraction.

5-(2-(2,6-Di-*tert*-butyl-4*H*-pyran-4-ylidene)ethylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6-dione (1b). Yield: maroon solid (66 mg; 44%). Mp 234–236 °C. IR (Nujol, cm⁻¹) 1643 (C=O), 1240 (C=S). ¹H NMR (CD₂Cl₂, 400 MHz): δ 8.56 (d, *J* = 14.2 Hz, 1H), 7.61 (d, *J* = 14.2 Hz, 1H), 7.04 (d, *J* = 1.7 Hz, 1H), 6.55 (d, *J* = 1.7 Hz, 1H), 4.53 (q, *J* = 6.9 Hz, 2H), 4.52 (q, *J* = 6.9 Hz, 2H), 1.35 (s, 9H), 1.31 (s, 9H), 1.25 (t, *J* = 6.9 Hz, 3H), 1.24 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 178.5, 173.5, 172.9, 162.3, 156.7, 150.2, 113.2, 110.0, 104.6, 102.8, 43.4, 42.9, 36.9, 36.6, 28.0, 27.9, 12.5. MS (EI⁺): *m/z* 416 (M⁺, 80), 383 (100), 328 (50). Anal. Calcd for C₂₃H₃₂N₂O₃S: C 66.31, H 7.74, N 6.72. Found: C 66.59, H 7.61, N 6.83.

(E)-5-(4-(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)but-2-enylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6-dione (1c). Yield: bright blue-violet solid (104 mg; 66%). Mp 215–217 °C. IR (Nujol, cm⁻¹) 1654 (C=O), 1193 (C=S). ¹H NMR (C₂D₆CO, 300 MHz): δ 8.15 (t, *J* = 13.0 Hz, 1H), 8.02 (d, *J* = 13.0 Hz, 1H), 7.83 (t, *J* = 13.0 Hz, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 6.51 (d, *J* = 1.8 Hz, 1H), 6.14 (d, *J* = 13.0 Hz, 1H), 4.50 (q, *J* = 6.9 Hz, 2H), 4.49 (q, *J* = 6.9 Hz, 2H), 1.36 (s, 9H), 1.32 (s, 9H), 1.22 (t, *J* = 6.9 Hz, 3H), 1.20 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (C₂D₆CO, 75 MHz): δ 173.1, 172.8, 162.8, 161.7, 158.8, 157.8, 152.1, 125.4, 117.2, 110.0, 104.3, 44.5, 43.9, 38.4, 38.1, 29.1, 29.0, 13.8, 13.7. MS (EI⁺): *m/z* 442 (M⁺, 100), 409 (30), 57 (55). Anal. Calcd for C₂₅H₃₄N₂O₃S: C 67.84, H 7.74, N 6.33. Found: C 68.10, H 7.65, N 6.52.

Compounds 2b,c: General Procedure. 3-Phenyl-5-isoxazolone (**9**) (77 mg, 0.48 mmol) was added to a solution of 0.48 mmol of the corresponding aldehyde (**7b–c**) in absolute ethanol (3 mL). The solution was refluxed under argon atmosphere for 40–50 min (TLC monitoring), then cooled. The resulting solid was filtered off, washed with cold ethanol and cold pentane, and dried. For **2c** evaporation of the filtrate and chromatography (silica gel) using hexane/AcOEt (7:3) as eluent gave a second fraction.

(Z)-4-(2-(2,6-Di-*tert*-butyl-4*H*-pyran-4-ylidene)ethylidene)-3-phenyl-5-isoxazolone (2b). Yield: dark blue microcrystalline solid (74 mg; 41%). Mp 222–224 °C. IR (Nujol, cm⁻¹) 1709 (C=O), 1654 (C=C), 1545 (C=N). ¹H NMR (CDCl₃, 400 MHz): δ 7.70

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(d, $J = 13.6$ Hz, 1H), 7.64–7.61 (m, 2H), 7.54–7.51 (m, 3H), 7.26 (d, $J = 13.6$ Hz, 1H), 6.51 (d, $J = 1.8$ Hz, 1H), 6.37 (d, $J = 1.8$ Hz, 1H), 1.29 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 172.4, 171.3, 162.8, 152.3, 142.7, 130.1, 129.4, 128.9, 128.6, 128.3, 110.0, 108.7, 104.3, 101.3, 101.0, 36.5, 36.4, 27.9, 27.6. MS (EI^+): m/z 377 (M^+ , 100), 221 (30). Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{NO}_3$: C 76.36, H 7.21, N 3.71. Found: C 76.51, H 7.00, N 3.98.

(Z)-4-[(E)-4-(2,6-Di-*tert*-butyl-4H-pyran-4-ylidene)but-2-enylidene]-3-phenyl-5-isoxazolone (2c). Yield: dark green solid (147 mg; 76%). Mp 123–125 °C. IR (Nujol, cm^{-1}) 1708 (C=O), 1654 (C=C), 1551 (C=N). ^1H NMR (CDCl_3 , 300 MHz): δ 7.70–7.40 (m, 7H), 7.33 (d, $J = 12.6$ Hz, 1H), 6.40 (d, $J = 1.8$ Hz, 1H), 6.02 (d, $J = 1.8$ Hz, 1H), 5.90 (d, $J = 12.8$ Hz, 1H), 1.27 (s, 9H), 1.26 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 169.5, 169.3, 162.7, 150.2, 149.7, 146.1, 130.1, 129.2, 128.9, 128.4, 121.5, 114.2, 107.3, 107.1, 100.8, 36.4, 36.2, 31.0, 27.9. MS (EI^+): m/z 403 (M^+ , 100), 57 (75). Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_3$: C 77.39, H 7.24, N 3.47. Found: C 77.61, H 7.04, N 3.69.

Compounds 3b,c: General Procedure. To a solution of the corresponding aldehyde (**7b–c**) (0.37 mmol) in 2 mL of Ac_2O , 1,1,3-tricyano-2-phenylpropene (**10**) (71 mg, 0.37 mmol) was added. The mixture was heated under argon at 75 °C for 1 h (TLC monitoring) and then allowed to cool to room temperature. The resulting solid was isolated by filtration, washed with cold pentane, and dried. In the case of **3b**, CH_2Cl_2 (50 mL) was added to the filtrate, and then, washed with NaOH 10% (3 \times 50 mL) and water (2 \times 50 mL). The organic layer was dried over MgSO_4 and evaporated, giving a second fraction, after purification by column chromatography (silica gel, eluent: hexane/AcOEt (7:3)).

(Z)-5-(2,6-Di-*tert*-butyl-4H-pyran-4-ylidene)-2-phenylpenta-1,3-diene-1,1,3-tricarbonitrile (3b). Yield: violet microcrystalline solid (64 mg; 42%). Mp 243–245 °C. IR (Nujol, cm^{-1}) 2204 (C \equiv N), 1643 (C=C), 1548 (C=C, Ar). ^1H NMR (CDCl_3 , 400 MHz): δ 8.25 (d, $J = 13.3$ Hz, 1H), 7.56–7.40 (m, 5H), 6.56 (d, $J = 1.5$ Hz, 1H), 6.36 (d, $J = 1.5$ Hz, 1H), 6.22 (d, $J = 13.3$ Hz, 1H), 1.31 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 173.7, 172.9, 167.2, 153.4, 149.4, 135.7, 131.4, 129.3, 128.9, 116.4, 115.7, 115.5, 111.2, 108.8, 102.7, 96.4, 70.8, 36.8, 36.7, 29.7, 28.1, 27.8. MS (EI^+): m/z 409 (M^+ , 100). Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}$: C 79.19, H 6.65, N 10.26. Found: C 79.28, H 6.47, N 10.08.

(3Z,5E)-7-(2,6-Di-*tert*-butyl-4H-pyran-4-ylidene)-2-phenylhepta-1,3,5-triene-1,1,3-tricarbonitrile (3c). Yield: dark blue solid (80 mg; 50%). Mp 234–236 °C. IR (Nujol, cm^{-1}) 2203 (C \equiv N), 1648 (C=C), 1552 (C=C, Ar). ^1H NMR (CDCl_3 , 400 MHz): δ 7.58–7.49 (m, 3H), 7.41–7.34 (m, 4H), 6.68 (t, $J = 12.7$ Hz, 1H), 6.49 (d, $J = 1.5$ Hz, 1H), 6.13 (d, $J = 1.5$ Hz, 1H), 5.88 (d, $J = 13.0$ Hz, 1H), 1.30 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 171.2, 170.9, 166.6, 155.9, 149.5, 148.5, 135.2, 131.5, 129.6, 129.0, 122.1, 115.9, 115.5, 114.9, 114.4, 108.1, 101.7, 98.7, 36.6, 36.4, 28.0, 27.8. MS (EI^+): m/z 435 (M^+ , 100), 57 (50). Anal. Calcd for $\text{C}_{29}\text{H}_{29}\text{N}_3\text{O}$: C 79.97, H 6.71, N 9.65. Found: C 80.22, H 6.56, N 9.90.

(Z)-2-Amino-5-(2,6-di-*tert*-butyl-4H-pyran-4-ylidene)penta-1,3-diene-1,1,3-tricarbonitrile (4b). To a stirred solution of the aldehyde **7b** (200 mg, 0.85 mmol) and 2-amino-1,1,3-tricyanopropene (**11**) (113 mg, 0.85 mmol) in absolute ethanol (3 mL) was added piperidine (two drops). The mixture was refluxed under argon for 1 h 15 min (TLC monitoring). After cooling, the resulting solid was isolated by filtration, washed with water and cold pentane, and dried. Yield: bright purple solid (127 mg; 43%). Mp 213–215 °C. IR (Nujol, cm^{-1}) 2209 (C \equiv N). ^1H NMR (CDCl_3 , 400 MHz): δ 8.78 (d, $J = 13.0$ Hz, 1H), 6.76 (d, $J = 1.8$ Hz, 1H), 6.28 (d, $J = 1.8$ Hz, 1H), 6.02 (d, $J = 13.0$ Hz, 1H), 5.70 (br s, 2H), 1.33 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 172.6, 172.1, 163.9, 152.5, 148.4, 117.6, 116.4, 108.9, 107.7, 102.3, 87.5, 58.4, 54.8, 46.9, 36.7, 36.5, 27.8. MS (EI^+): m/z 348

(M^+ , 100). Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_4\text{O}$: C 72.39, H 6.94, N 16.08. Found: C 72.14, H 7.11, N 16.33.

(3Z,5E)-2-Amino-7-(2,6-di-*tert*-butyl-4H-pyran-4-ylidene)hepta-1,3,5-triene-1,1,3-tricarbonitrile (4c). To a solution of aldehyde **7c** (54 mg, 0.21 mmol) and 2-amino-1,1,3-tricyanopropene (**11**) (27 mg, 0.21 mmol) in absolute ethanol (4 mL) were added pyridine (0.1 mL) and acetic acid (0.05 mL). The mixture was refluxed under argon for 2 h 20 min. (TLC monitoring). The solvent was evaporated and the crude product was purified by chromatography (silica gel) using hexane/AcOEt (8:2), then hexane/AcOEt (7:3), and finally hexane/AcOEt (6:4). Yield: dark purple solid (34 mg; 44%). Mp 158–162 °C. IR (Nujol, cm^{-1}) 2209 (C \equiv N). ^1H NMR (CDCl_3 , 400 MHz): δ 8.02 (d, $J = 12.2$ Hz, 1H), 7.49 (t, $J = 13.0$ Hz, 1H), 6.50 (t, $J = 12.6$ Hz, 1H), 6.49 (d, $J = 1.7$ Hz, 1H), 6.05 (d, $J = 1.7$ Hz, 1H), 5.80 (d, $J = 13.0$ Hz, 1H), 5.77 (br s, 2H), 1.31 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 169.9, 169.8, 164.2, 154.2, 148.9, 147.0, 120.4, 116.5, 116.1, 115.9, 113.3, 107.4, 101.1, 90.1, 48.3, 36.5, 36.1, 27.9, 27.8. HRMS (ESI^+): calcd for $\text{C}_{23}\text{H}_{27}\text{N}_4\text{O}$ ($\text{M} + \text{H}$) $^+$ 375.2179; found 375.2169; calcd for $\text{C}_{23}\text{H}_{26}\text{N}_4\text{NaO}$ ($\text{M} + \text{Na}$) $^+$ 397.1999; found 397.1986. Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{N}_4\text{O}$: C 73.77, H 7.00, N 14.96. Found: C 73.89, H 6.82, N 15.19.

Compounds 5b,c: General Procedure. To a solution of the corresponding aldehyde (**7b–c**) (1.46 mmol) and TCF (**12**) (290 mg, 1.46 mmol) in absolute ethanol (3 mL) was added piperidine (three drops). The mixture was refluxed under argon for 2–2.5 h (TLC monitoring) and then cooled to room temperature. The solvent was distilled, and the residue was purified by column chromatography (silica gel) using hexane/AcOEt (65:35) as eluent.

(E)-2-[3-Cyano-4-(3-(2,6-di-*tert*-butyl-4H-pyran-4-ylidene)prop-1-enyl)-5,5-dimethylfuran-2(5H)-ylidene]malononitrile (5b). Yield: dark blue-gray solid (89 mg; 15%). Mp 297–298 °C. IR (Nujol, cm^{-1}) 2217 (C \equiv N). ^1H NMR ($\text{C}_2\text{D}_6\text{CO}$, 300 MHz): δ 8.58 (t, $J = 13.2$ Hz, 1H), 6.86 (br s, 1H), 6.55 (d, $J = 1.5$ Hz, 1H), 6.18 (d, $J = 14.1$ Hz, 1H), 6.11 (d, $J = 12.9$ Hz, 1H), 1.66 (s, 6H), 1.34 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 177.4, 172.6, 172.0, 171.8, 150.5, 145.7, 114.0, 113.6, 113.1, 108.3, 107.8, 102.3, 95.7, 53.3, 36.7, 36.5, 27.8, 26.4. MS (MALDI $^+$): m/z 415 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_2$: C 75.15, H 7.03, N 10.11. Found: C 75.01, H 7.21, N 10.36.

2-[3-Cyano-4-((1E,3E)-5-(2,6-di-*tert*-butyl-4H-pyran-4-ylidene)penta-1,3-dienyl)-5,5-dimethylfuran-2(5H)-ylidene]malononitrile (5c). Yield: dark blue solid (129 mg; 20%). Mp 231–232 °C. IR (Nujol, cm^{-1}) 2216 (C \equiv N). ^1H NMR (CDCl_3 , 400 MHz): δ 7.38 (t, $J = 12.8$ Hz, 2H), 6.46 (d, $J = 1.4$ Hz, 1H), 6.29 (t, $J = 12.6$ Hz, 1H), 6.02–5.99 (m, 2H), 5.77 (d, $J = 12.8$ Hz, 1H), 2.17 (s, 6H), 1.31 (s, 9H), 1.26 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 177.0, 172.0, 170.0, 169.6, 150.2, 146.2, 145.5, 126.0, 114.5, 113.5, 113.1, 112.9, 111.8, 107.5, 101.1, 96.0, 36.5, 36.2, 29.7, 28.0, 27.9, 26.6. MS (MALDI $^+$): m/z 441 (M^+), 464 ($\text{M} + \text{Na}$) $^+$, 480 ($\text{M} + \text{K}$) $^+$. Anal. Calcd for $\text{C}_{28}\text{H}_{31}\text{N}_3\text{O}_2$: C 76.16, H 7.08, N 9.52. Found: C 75.93, H 7.37, N 9.71.

Compounds 10' and 11': General Procedure. A mixture of *N*-((2E,4E)-5-(phenylamino)penta-2,4-dienylidene)aniline hydrochloride (1 g, 3.52 mmol), the corresponding acceptor (**10**, **11**) (3.52 mmol), and anhydrous sodium acetate (289 mg, 3.52 mmol) in acetic anhydride (5 mL) was refluxed under argon for 5–10 min. After cooling, the resulting solid was isolated by filtration and washed with water, methanol, and finally ether.

***N*-Phenyl-*N*-((1E,3E,5Z)-6,8,8-tricyano-7-phenylocta-1,3,5,7-tetraenyl)acetamide (10')**. Yield: bright maroon solid (789 mg; 58%). Mp 217–220 °C. IR (Nujol, cm^{-1}) 2212 (C \equiv N). ^1H NMR (CDCl_3 , 400 MHz): δ 8.12 (d, $J = 13.7$ Hz, 1H), 7.62–7.50 (m, 6H), 7.40–7.37 (m, 2H), 7.20–7.14 (m, 3H), 6.98 (dd, $J = 14.1$ Hz, $J' = 11.6$ Hz, 1H), 6.58 (dd, $J = 14.1$ Hz, $J' = 12.0$ Hz, 1H), 5.28 (dd, $J = 13.7$ Hz, $J' = 11.6$ Hz, 1H), 1.96 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 169.3, 166.4, 157.6, 151.9, 141.6, 137.9, 133.5, 132.5, 130.7, 130.0, 129.6, 129.3, 128.1, 125.1, 114.0, 113.6, 112.8, 112.3, 105.2, 80.5, 23.3. MS (ESI^+): m/z 391 ($\text{M} + \text{H}$) $^+$, 413 ($\text{M} + \text{Na}$) $^+$, 429 ($\text{M} + \text{K}$) $^+$. Anal. Calcd for $\text{C}_{25}\text{H}_{18}\text{N}_4\text{O}$: C 76.91, H 4.65, N 14.35. Found: C 77.23, H 4.40, N 14.52.

***N*-((1*E*,3*E*,5*Z*)-7-Amino-6,8,8-tricyanoocta-1,3,5,7-tetraenyl)-*N*-phenylacetamide (**11'**)**. Yield: red-maroon solid (602 mg; 52%). Mp 224–226 °C. IR (Nujol, cm^{-1}) 3339, 3220 (NH), 2215, 2198 ($\text{C}\equiv\text{N}$). ^1H NMR ($\text{DMSO}-d_6$, 300 MHz): δ 8.75 (s, 2H), 8.12 (d, $J = 13.6$ Hz, 1H), 7.66–7.53 (m, 4H), 7.37–7.30 (m, 3H), 6.42 (dd, $J = 14.1$ Hz, $J' = 11.8$ Hz, 1H), 5.33 (dd, $J = 13.5$ Hz, $J' = 11.5$ Hz, 1H), 1.93 (s, 3H). ^{13}C NMR ($\text{DMSO}-d_6$, 75 MHz): δ 168.9, 164.7, 154.8, 150.3, 140.6, 138.1, 130.1, 129.1, 128.4, 123.0, 115.6, 115.1, 114.1, 111.7, 98.3, 48.5, 23.0. MS (EI^+): m/z 329 (M^+ , 15), 287 (100), 195 (50), 93 (100), 77 (70). Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}$: C 69.29, H 4.59, N 21.26. Found: C 69.50, H 4.45, N 21.55.

2-(3-Cyano-4-((1*E*,3*E*,5*E*)-7-(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)hepta-1,3,5-trienyl)-5,5-dimethylfuran-2(5*H*)-ylidene)malonitrile (5d**)**. A solution of 2,6-di-*tert*-butyl-4-methylpyrylium triflate (**6**) (270 mg, 0.76 mmol), acceptor **12'**, (150 mg, 0.38 mmol), triethylamine (0.21 mL), and catalytic pyridine in ethanol (12 mL) was refluxed under argon atmosphere for 30 min (TLC monitoring). After cooling, the resulting solid was isolated by filtration, washed with cold ethanol, and dried. A second fraction is recovered from the filtrate. Ether (50 mL) was added, the organic layer was washed with HCl 10% (2×50 mL) and water (2×50 mL) and dried (MgSO_4), and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (eluent, hexane/AcOEt (3:1)). Yield: green-brown solid (134 mg, 76%). Mp 211–213 °C.

IR (Nujol, cm^{-1}) 2211 ($\text{C}\equiv\text{N}$). ^1H NMR (CDCl_3 , 400 MHz): δ 7.65 (dd, $J = 13.7$ Hz, $J' = 11.8$ Hz, 1H), 7.17–7.04 (m, 2H), 6.35 (dd, $J = 13.2$ Hz, $J' = 12.1$ Hz, 1H), 6.29 (t, $J = 12.8$ Hz, 1H), 6.27 (d, $J = 1.5$ Hz, 1H), 6.13 (d, $J = 14.8$ Hz, 1H), 5.88 (d, $J = 1.5$ Hz, 1H), 5.69 (d, $J = 12.7$ Hz, 1H), 1.63 (s, 6H), 1.27 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 176.6, 172.0, 167.9, 167.7, 151.4, 149.4, 142.3, 141.8, 127.3, 126.2, 113.9, 113.4, 113.2, 112.5, 112.5, 112.2, 106.6, 100.3, 96.2, 36.2, 35.9, 27.9, 27.8, 26.6. MS (EI^+): m/z 467 (M^+ , 25), 78 (80), 63 (100). Anal. Calcd for $\text{C}_{30}\text{H}_{33}\text{N}_3\text{O}_2$: C 77.06, H 7.11, N 8.99. Found: C 77.23, H 7.01, N 9.22.

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Supporting Information Available: General experimental methods, analytical data for **8'** and **9'**, synthesis and analytical data for **2d–4d**, NMR and UV–vis spectra of new compounds, NLO measurements, DSC curves of **3b–d**, X-ray crystallographic data in CIF format and diagram of the crystal structures of **2b** and **3c**, computed energies and Cartesian coordinates of optimized geometries, and contour plots of frontier molecular orbitals of compounds **3'**. This material is available free of charge via the Internet at <http://pubs.acs.org>.