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PAPER

Cycloaddition reactions of polyenic donor–π-acceptor systems with an electron-rich alkyne: access to new chromophores with second-order optical nonlinearities†‡

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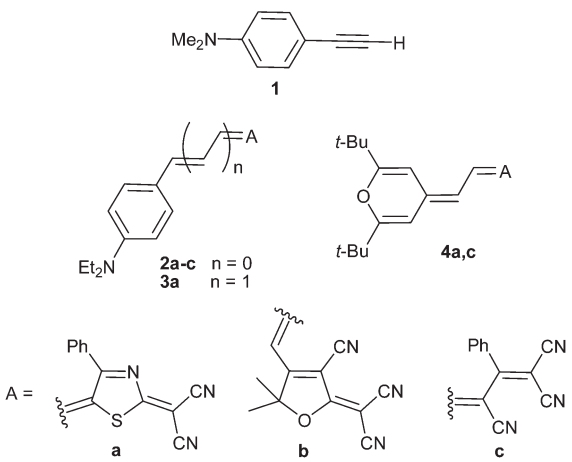
The formal [2 + 2] cycloaddition–cycloreversion (CA–CR) between 4-ethynyl-*N*,*N*-dimethylaniline and polyenic Donor–π-Acceptor (D–π-A) systems takes place to yield compounds bearing two donors and one acceptor. Structural, linear and second-order nonlinear optical (NLO) properties of the new molecules reveal the stronger polarization of these systems when compared to analogous merocyanines lacking the dimethylaminophenyl (DMA) ring.

Introduction

Recently, formal [2 + 2] cycloaddition of electron-poor alkenes to electron-rich alkynes, followed by electrocyclic ring opening of the initially formed cyclobutene has attracted substantial interest[1] and is considered to be a promising methodology to obtain new Donor–Acceptor (D–A) products with varied applications, including second-[2] and third-order nonlinear optical (NLO) properties.[3]

Concerning deficient alkenes, most of the examples have been centered on tetracyanoethene (TCNE)[2a,4] and 7,7,8,8-tetracyanoquinodimethane (TCNQ)[4c,5] moieties. Just recently, other olefins like dicyanoquinonediimides (DCNQIs)[3e] or dicyanovinyl/tricyanovinyl derivatives[6–8] are starting to be considered. On the other hand, simple push–pull alkenes (which can be considered as electronically confused olefins) have only seldom been studied in this reaction,[6,9] and the reactivity of their polyenic D–π-A analogues remains unexplored.

We report here several examples of [2 + 2] cycloaddition–cycloreversion (CA–CR) reactions between electron rich alkyne **1** and polyenic D–π-A systems **2–4**.[10–12] Although the starting push–pull chromophores possess more than one C=C bond that might be involved in the reaction, only one regioisomer is obtained.



Results and discussion

Synthesis and crystal structure analysis

Compounds containing acceptors **a** and **b** were prepared as shown in Scheme 1. New chromophores (**5–7**)**a** and **5b** have been obtained in low to moderate yields (15–29%). We tried to favor the reaction by increasing the temperature, prolonging reaction time, using more polar solvents, or by adding excess of either the D–A system or the alkyne, without reaching the complete consumption of any initial compound.[13] No other regioisomer was observed. The reduced reactivity of the starting D–π-A compounds compared to tetracyanoethene (TCNE)[4a] or 7,7,8,8-tetracyanoquinodimethane (TCNQ)[5a] arises from the

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† Dedicated to the memory of Professor Enrique Meléndez.

‡ Electronic supplementary information (ESI) available: General experimental methods, NMR and UV-vis spectra of new compounds, X-ray crystallographic data and diagrams of the crystal structures of **5a**, **7c** and **10**, computed energies, Cartesian coordinates of optimized geometries and molecular orbital contour plots for **5a** and **7a**, and NLO measurements. CCDC 894169 (**5a**), 894170 (**7c**) and 894171 (**10**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob26515j

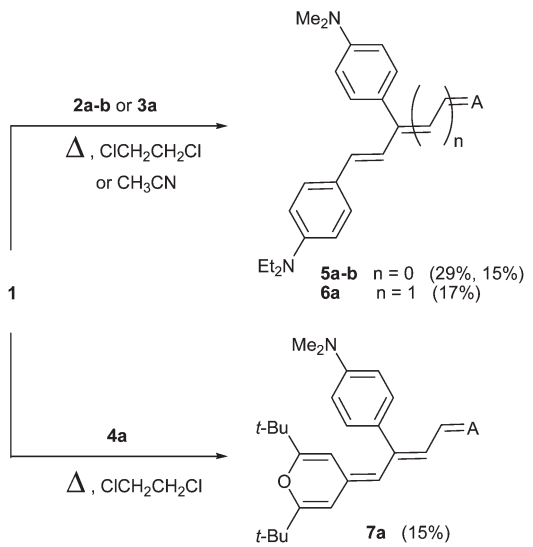
presence of an electron-donating group.[6] The same differences in reactivity have been encountered in the CA–CR reactions of electronically-confused alkynes.[5b,13]

The structure of **5a** was unambiguously established by X-ray diffraction (Fig. 1) and those of **5b**, **6a**, **7a** by spectral data. The D–π-A skeleton of **5a** is essentially planar, with a twisting angle between the mean planes of the diethylaminophenyl (DEAP) and thiazole rings of 6.5°, thus ensuring efficient intramolecular charge transfer (ICT), and in agreement with the X-ray structure of its precursor **2a**.[10] On the other hand, the dimethylaminophenyl (DMA) group is not coplanar with the π-spacer. Moreover, the polyenic chain has an all-*trans* geometry. Bond length alternation in anilino rings is a good indication of the efficiency of the charge transfer taking place from the donor to the acceptor moieties, and can be expressed through the δ*r* parameter of the ring.[14] Whereas the DEAP ring exhibits a very high δ*r* value of 0.063 revealing its partly quinoid character due to the ICT process, the δ*r* of the DMA ring averages to 0.004, which is very close to that of benzene as a result of its deviation from the essentially planar π-system. However, this additional anilino moiety shows a strong electron-donating σ-inductive effect (see UV-vis absorption section).

Previous studies on related [2 + 2] CA–CR reactions point to a stepwise zwitterionic mechanism.[6,15] The present reactions are also presumed to take place similarly, since the regioisomer obtained is the one in which the zwitterionic intermediate is most stabilized (Fig. 2). Moreover, in the synthesis of compounds **a** there is an aromatization of the thiazole ring that further stabilizes the considered intermediate.[3e,5a]

These reactions testified to the high torquoselectivity of the cyclobutene ring opening.[3e,7] Taking **5b** as a model compound, selective ge-1D NOESY experiments confirmed the outward rotation of the donor group in the conrotatory ring-opening of the two isomeric cyclobutene intermediates (ESI: Fig. S3–4‡).

When 1,1,3-tricyano-2-phenylpropene-containing chromophores **2c** and **4c** are used the expected final product, together with another compound (Scheme 2) resulting from a formal [4 + 2] cycloaddition,[9,16] were isolated. The identities and structures of the final products were established by X-ray diffraction (**7c**, **10**) (Fig. 3 and S36 in ESI‡), and spectral data (**5c**, **9**). Moreover, compound **5c** could not be isolated as a pure product, but as a mixture with its cyclobutene precursor **8**, (ratio **5c**/**8**: 10/7) (ESI: Fig. S16‡) and all attempts to purify it failed. Intermediate cyclobutenes have only seldom been isolated.[15,17] In the same way as for the synthesis of chromophores represented in Scheme 1, yields obtained were also low to moderate, recovering



Scheme 1 Synthesis of compounds **5a–b**, **6a**, **7a**.

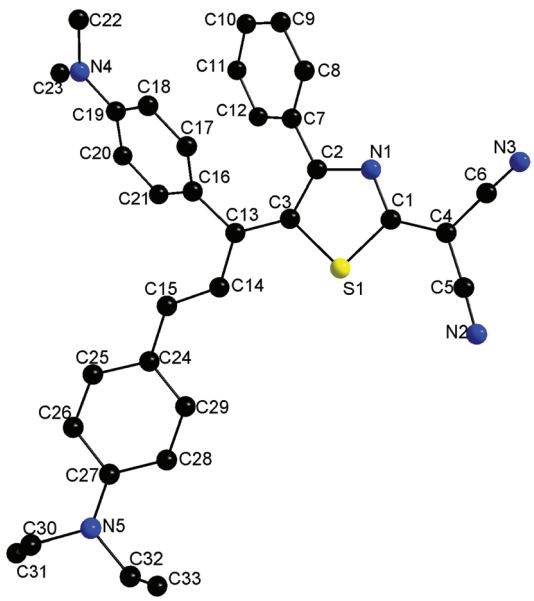


Fig. 1 Molecular structure of **5a**.

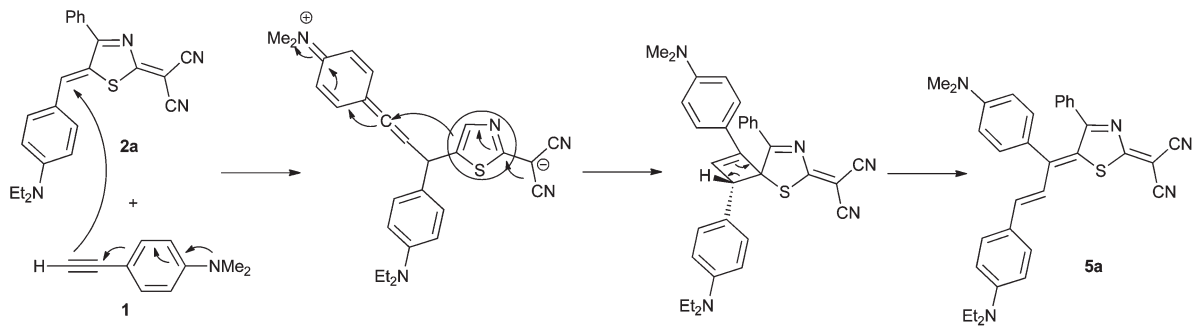
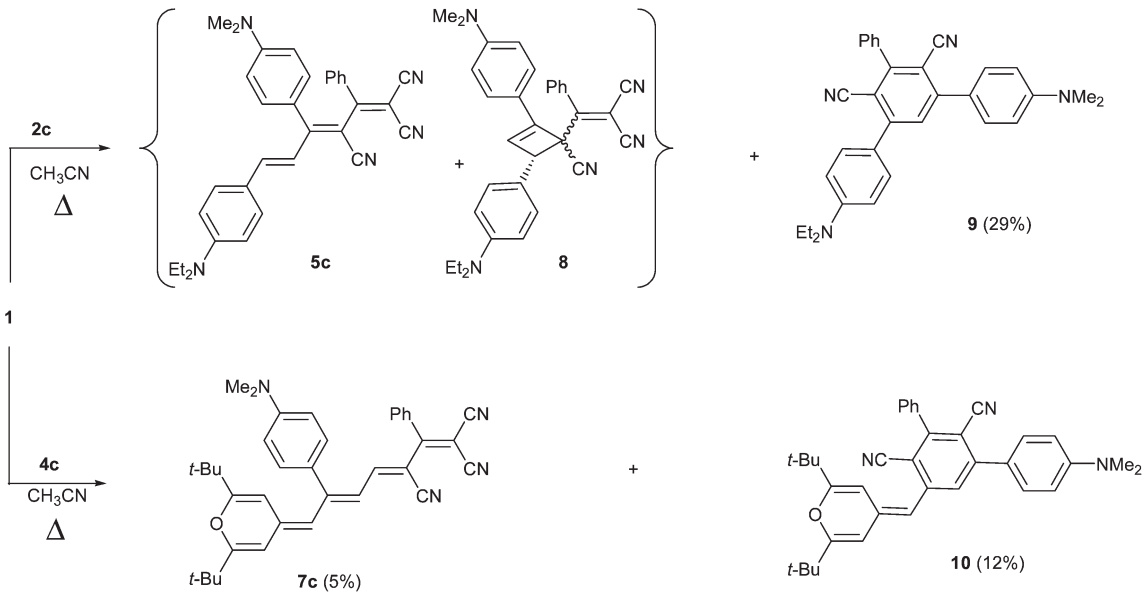


Fig. 2 Non-concerted dipolar mechanism for the [2 + 2] cycloaddition of **1** with **2a**.



Scheme 2 Reaction of compounds **2c**, **4c** with **1**.

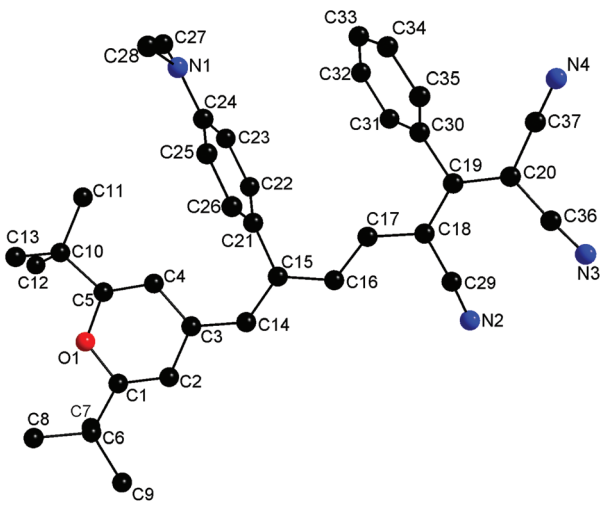


Fig. 3 Molecular structure of **7c**.

starting materials apart from cycloaddition products. Moreover, due to the structural similarity of the final and starting push–pull compounds, subsequent repeated chromatographic purifications on silica gel were needed. Both facts (the reduced reactivity and the difficulties in the purification) contribute to explain the low to moderate yields.

The [2 + 2] (**5c** + **8**) and the [4 + 2] (**9**) products are generated from the same zwitterionic intermediate (ESI: Fig. S25‡). On the other hand, **7c** and **10** arise from the reaction of two different double bonds of the initial D–A compound (Fig. 4). Whereas **7c** is generated from the most stabilized zwitterionic intermediate, compound **10** arises from a less stabilized intermediate, allowing a 1,4-elimination of HCN[9,18] leading to aromatisation.

The crystal structure of **7c** (Fig. 3) confirms the (*Z*)-configuration of the two double bonds and that the PhC–C(CN) bond has an s-*trans* conformation, typical of this moiety.[12,19] The geometry of **7c** is similar to that of compound **11c**,[12] bearing the same acceptor (Fig. 5). Both compounds, **7c** and **11c**, are strongly polarized derivatives with an important zwitterionic character.[12] In order to see how the additional DMA ring in **7c** influences the ICT, the Bird Index (I_6)[20] of the pyranylidene rings (**7c**/**11c**: 40.6/38.5) and the average bond lengths of the two C≡N groups of the dicyanomethylene fragment (**7c**/**11c**: 1.147 Å/1.139 Å) were compared. These results point to a slightly more polarized structure for **7c** as a consequence of the additional DMA ring, despite its deviation from the planar main π-system.

UV-vis spectroscopy

The UV-vis absorption data of compounds **5a–b**, **6a**, **7a,c** are collected in Table 1 (see spectra in ESI‡). For the sake of comparison, data for compounds **3a**,[10] **11a,c**[10,12] (Fig. 5) are also included.

Spectra have been registered in four solvents of different polarity (solvent polarity E_T^N:[21] DMF: 0.386, CH_2Cl_2: 0.309, $CHCl_3$: 0.259, dioxane: 0.164). Compounds **5a–b**, **6a**, **7a,c** show intense and broad CT bands in all solvents resulting from different D–A transitions.[4b] Concerning the dependence of the band position on solvent polarity, positive solvatochromism was observed for compounds **5a–b** and **6a** and negative for compound **7a**. The behavior of compound **7c** is different: taking into account data in DMF, CH_2Cl_2 and $CHCl_3$ this compound shows an almost negligible solvatochromism, but when comparing with dioxane, it exhibits positive solvatochromism. This variety of behavior has already been reported for other D–π-A systems,[22] including 4*H*-pyranylidene derivatives.[23]

The combination of DEAP as main donor and dicyanomethylene-thiazole as acceptor (**5a**, **6a**) gives rise to the higher solvatochromism, reaching $\Delta\lambda$ values of 87 and 127 nm respectively (0.21 and 0.26 eV respectively). When comparing **5a** and **6a**,

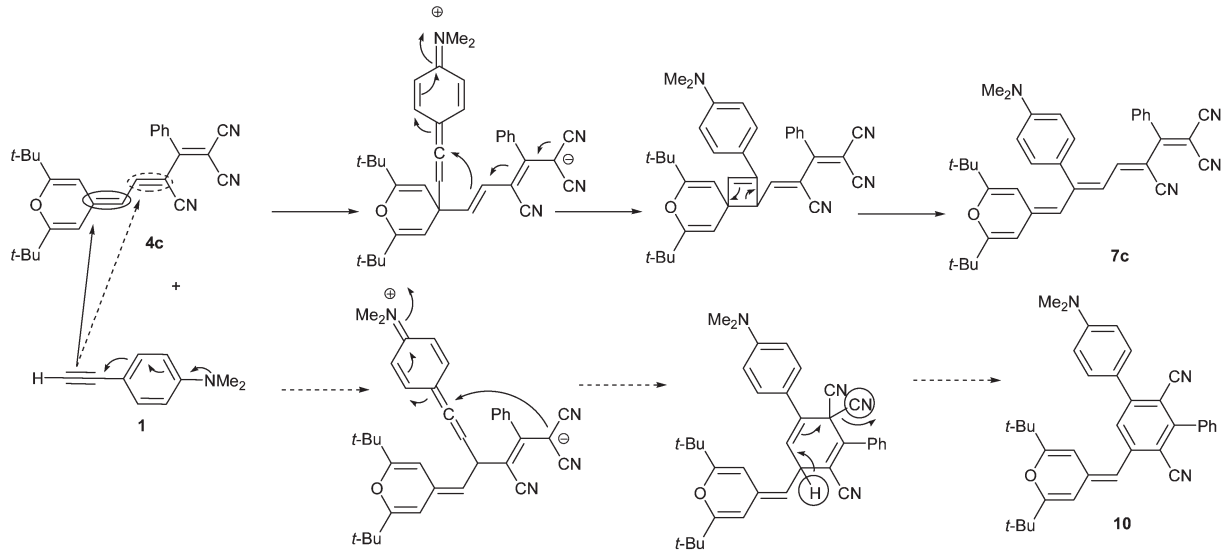


Fig. 4 Non-concerted dipolar mechanism for the [2 + 2] (continuous line) and [4 + 2] (dotted line) cycloaddition of **1** with **4c** in formation of **7c** and **10** respectively.

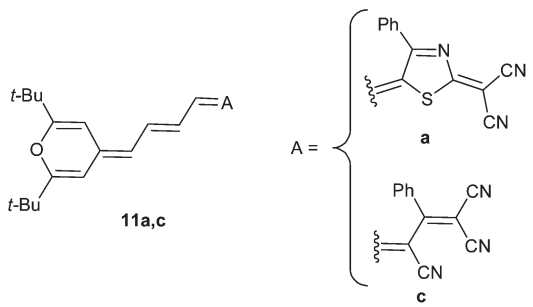


Fig. 5 Structures of compounds **11a,c**.

there is a vinylene shift of 79 nm in CH_2Cl_2, pointing to weakly alternated structures.[10]

As previously mentioned (crystal structure analysis of compound **5a**), the additional DMA moiety, even if nearly orthogonal to the extended π-system, also contributes to the donor potency, as ascertained by the bathochromic shifts shown (in CH_2Cl_2) by **5a**, **7a,c** when compared to **3a**, and **11a,c**, lacking the DMA ring. PCM-B3P86/6-31G* calculations in CH_2Cl_2 (Table 2) on compounds **5a**, **7a**, **3a**, **11a** provide a rationale for the observed trend in λ. In fact, the additional DMA moiety causes an increase in energy of the HOMO and the LUMO, the destabilization of the former being slightly higher than that of the latter. In other words, the HOMO–LUMO gap and the excitation energy (**5a**: 1.81 eV, **3a**: 1.88 eV, **7a**: 1.76 eV, **11a**: 1.83 eV) are lowered as a consequence of the modification introduced (see Fig. S48–49 in ESI‡ for molecular orbital contour plots for **5a** and **7a**).

Electrochemistry

The redox properties were investigated by cyclic voltammetry (CV) in CH_2Cl_2 (Table 1). New chromophores **5a–b**, **6a**, **7a,c** display three waves corresponding to one reduction step and two oxidation steps, the first oxidation involving the conjugated donor (either DEAP or 4*H*-pyranylidene moieties) and the second one corresponding to the additional DMA donor group, taking into account that E_{ox} for **1** in the same conditions is 1.04 V.

Remarkably, E_{ox} value to which the additional DMA ring is oxidized is strongly modulated by the main donor, being approximately 150 mV higher for pyranylidene-containing chromophores than for DEAP derivatives. This trend might be due to the fact that the additional DMA ring is located at a greater distance from the main donor in DEAP derivatives, and thus is more easily oxidized.

As expected, on passing from **5a** to **6a**, lengthening the spacer gives rise to a decrease of both first E_{ox} and $|E_{red}|$ values pointing to a decrease in the interaction between the donor and acceptor end groups. Finally, when comparing compounds **5a**, **7a,c** with their respective analogues without the DMA ring, (**3a**, **11a,c**) no substantial changes are observed in either E_{ox} of the conjugated donor or $|E_{red}|$.

Nonlinear optical properties

The second-order NLO properties of **5a**, **6a**, **7a,c** have been measured by electric field-induced second harmonic generation (EFISH) in CH_2Cl_2 at 1907 nm (Table 3). The corresponding static (zero-frequency) $\mu\beta_0$ values determined using the two-level model[24] are also gathered in Table 3. (For the sake of comparison, Disperse Red 1, a common benchmark for organic NLO-chromophores, gives a $\mu\beta_0$ value of ~480 × 10^{-48} esu under the same experimental conditions.) Reported data for compounds **3a**,[10] **11a,c**[10,12] are also included. In order to get further insight into the NLO behavior of these compounds, the β_{vec0} values have been estimated using the theoretically calculated ground state dipole moments μ_g.

New chromophores show positive $\mu\beta_0$ values (in 10^{-48} esu) ranging from +300 to +1710 except for **7a** which presents a

Table 1 UV-vis data[a] and electrochemical properties[b]

Compd	λ_{max} (DMF) (log ε)	λ_{max} (CH_2Cl_2) (log ε)	λ_{max} ($CHCl_3$) (log ε)	λ_{max} (dioxane) (log ε)	E_{ox}	E_{red}
5a	681 (sh) 759 (4.86)	631 (sh) 694 (4.64) 747 (4.75)	623 (sh) 684 (4.64) 742 (4.71)	593 (sh) 672 (4.29)	+0.84 +1.08[c]	−0.60
3a[10]	—	679 (4.76) 732 (4.83)	—	—	+0.85[c]	−0.61
6a	677 (sh) 755 (sh) 844 (4.97)	609 (sh) 672 (sh) 759 (4.76) 826 (4.82)	605 (sh) 750 (4.68) 810 (4.65)	558 (sh) 717 (4.46)	+0.79 +1.05[c]	−0.46
7a	779 (4.87)	734 (sh) 799 (4.89)	745 (4.67) 810 (4.85)	677 (sh) 736 (4.59) 806 (4.47)	+0.71 +1.23	−0.59[c]
11a[10]	—	726 (4.80) 790 (5.00)	—	—	+0.71	−0.65
5b	598 (4.48)[d]	572 (4.47) 665 (4.45)	562 (4.40) 661 (4.37)	535 (4.39) 608 (4.34)	+0.82[c] +1.01[c]	−0.81
7c	584 (sh) 635 (sh) 688 (5.07)	582 (sh) 641 (sh) 691 (5.00)	559 (sh) 642 (sh) 694 (4.91)	531 (sh) 635 (4.54) 672 (sh)	+0.86 +1.18	−0.79[c]
11c[12]	—	629 (4.89) 678 (5.11)	—	—	+0.88	−0.76

[a] In nm. [b] In volts, 10^{-3} M in CH_2Cl_2 *vs.* Ag/AgCl (KCl 3 M), glassy carbon working electrode, Pt counter electrode, 20 °C, 0.1 M Bu_4NPF_6, 100 mV s^{-1} scan rate. Ferrocene internal reference $E^{1/2}$ = +0.46 V. [c] Reversible wave ($E^{1/2}$). [d] Extremely broad band.

Table 2 E_{HOMO} and E_{LUMO} values[a] (eV) for compounds **5a**, **3a**, **7a**, **11a**

Compd	E_{HOMO}	E_{LUMO}
5a	−5.79	−3.67
3a[10]	−5.92	−3.78
7a	−5.68	−3.64
11a[10]	−5.77	−3.71

[a] Calculated at the PCM-B3P86/6-31G* level in CH_2Cl_2.

Table 3 Second-order NLO properties

Compd	$\mu\beta$ [a,b]	$\mu\beta_0$ [b,c]	μ_g [d]	β_{vec0} [e]
5a	+2050	+670	30.9	+22
3a[10]	+5940	+2080	28.2	+74
6a	+8400	+1710	34.7	+49
7a	−6600	−1630	36.9	−44
11a[10]	−3900	−1010	34.9	−29
7c	+730	+300	32.2	+9
11c[12]	+1550	+670	30.3	+22

[a] Determined in CH_2Cl_2 at 1907 nm; experimental accuracy: ±15%. [b] In 10^{-48} esu. [c] Experimental $\mu\beta_0$ values calculated using the two-level model. [d] In Debye, calculated in CH_2Cl_2 using the PCM-B3P86/6-31G* model. [e] In 10^{-30} esu, estimated using the experimental $\mu\beta_0$ and the calculated μ_g values.

negative $\mu\beta_0$ value of −1630, in agreement with its solvatochromic behaviour.

Lengthening the polyenic chain from **5a** to **6a**, gives rise, as expected, to an important increase in $\mu\beta_0$, as a result of increased μ_g and β_{vec0} values.

The new synthesized systems bear two donors and one acceptor and the addition of a DMA group leads to more polarized chromophores, with a large μ_g. As a consequence, for left-hand side[25] chromophores (region B) (**3a**, **11c**), introduction of the DMA ring (**5a**, **7c**) results in a decreased NLO response, whereas for **11a**, located in region C–D of Marder's plot, this modification results in **7a** having an increased negative NLO response. The more polarized structure for **5a**, **7a,c** when compared to **3a**, **11a,c** respectively, is in agreement with X-ray diffraction data for **7c**/**11c**.

Conclusions

The reactivity of a series of polyenic D–π-A systems (electronically confused alkenes) towards the electron-rich alkyne **1** has been studied, the formal [2 + 2] cycloaddition taking place on the C=C bond located closer to the donor end of the molecule. The final obtained compounds, with two donors and one acceptor, present more polarized structures than their analogues without the DMA ring. As a consequence of the presence of the DMA moiety an increased negative second-order NLO response for the new right-hand side[25] chromophore **7a** was found. Moreover, for molecules containing acceptor **c**, the resulting product from a [4 + 2] CA was also isolated.

Experimental

For general experimental methods see ESI.‡

Compounds **2a–c**,[10,11] **3a**[10] and **4a,c**[10,12] were prepared as previously described.

Compounds 5a, 6a, 7a. General procedure

To a solution of 4-ethynyl-*N*,*N*-dimethylaniline (**1**) (73 mg, 0.50 mmol) in 1,2-dichloroethane (6 mL), the corresponding

thiazole-containing D–π-A compound (**2a**, **3a**, **4a**) (0.50 mmol) was added under argon atmosphere. The reaction was refluxed overnight, then the solvent was evaporated and the residue was purified by flash chromatography on silica gel.

2-{(*E*)-5-[(*E*)-3-{4-(Diethylamino)phenyl}-1-{4-(dimethylamino)-phenyl}allylidene]-4-phenylthiazol-2-ylidene}malononitrile (5a)

Eluent: CH_2Cl_2. Yield: green solid (78 mg, 29%). Mp 205–207 °C. Found: C, 74.62; H, 5.76; N, 13.39. Calc. for $C_{33}H_{31}N_5S$: C, 74.83; H, 5.90; N, 13.22%. IR (Nujol, cm^{-1}): 2195 (C≡N), 1601 (C═C, Ar), 1560 (C═C, Ar), 1518 (C═C, Ar). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.56–7.51 (2H, m), 7.36–7.26 (5H, m), 7.13–7.07 (2H, m), 7.02 (1H, d, J = 14.9 Hz), 6.90 (1H, d, J = 14.9 Hz), 6.63–6.59 (2H, m), 6.59–6.56 (2H, m), 3.43 (4H, q, J = 7.0 Hz), 3.04 (6H, s), 1.20 (6H, t, J = 7.0 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 174.2, 159.1, 153.5, 151.5, 150.1, 136.0, 134.1, 132.4, 130.2, 130.1, 129.0, 125.7, 123.8, 123.5, 112.2, 111.9, 45.4, 40.5, 12.9. HRMS (ESI^+): calcd for $C_{33}H_{32}N_5S$ 530.2373, found 530.2404 $[M + H]^+$.

2-{(*Z*)-5-[(2*Z*,4*E*)-5-{4-(Diethylamino)phenyl}-3-{4-(dimethyl-amino)phenyl}penta-2,4-dienylidene]-4-phenylthiazol-2-ylidene}-malononitrile (6a)

Eluent: CH_2Cl_2. Yield: dark green solid (45 mg, 17%). Mp 246–248 °C. Found: C, 75.81; H, 5.80; N, 12.71. Calc. for $C_{35}H_{33}N_5S$: C, 75.64; H, 5.99; N, 12.60%. IR (Nujol, cm^{-1}): 2197 (C≡N), 1606 (C═C, Ar), 1521 (C═C, Ar). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.71–7.67 (2H, m), 7.63 (1H, d, J = 12.8 Hz), 7.52–7.44 (3H, m), 7.44–7.39 (2H, m), 7.34–7.28 (2H, m), 7.13 (1H, d, J = 15.3 Hz), 6.99 (1H, d, J = 15.3 Hz), 6.79–6.74 (2H, m), 6.70–6.65 (2H, m), 6.62 (1H, d, J = 12.8 Hz), 3.44 (4H, q, J = 7.1 Hz), 3.06 (6H, s), 1.20 (6H, t, J = 7.1 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 150.6, 145.9, 141.8, 141.1, 140.9, 135.6, 133.6, 133.0, 132.4, 131.8, 131.4, 130.6, 129.2, 125.9, 124.7, 124.5, 124.0, 117.3, 115.3, 112.2, 112.1, 45.2, 40.6, 40.6, 12.9. HRMS (ESI^+): calcd for $C_{35}H_{34}N_5S$ 556.2529, found 556.2525 $[M + H]^+$.

2-{(*Z*)-5-[(*E*)-4-{2,6-Di-*tert*-butyl-4*H*-pyran-4-ylidene}-3-{4-(dimethylamino)phenyl}but-2-enylidene]-4-phenylthiazol-2-ylidene}malononitrile (7a)

Eluent: CH_2Cl_2–AcOEt (10 : 0.2). Yield: dark green solid (44 mg, 15%). Mp 286–290 °C. Found: C, 75.83; H, 6.32; N, 9.32. Calc. for $C_{37}H_{38}N_4OS$: C, 75.73; H, 6.53; N, 9.55%. IR (Nujol, cm^{-1}): 2191 (C≡N), 1634 (C═N), 1602 (C═C, Ar), 1551 (C═C, Ar), 1511 (C═C, Ar). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.63–7.59 (2H, m), 7.46 (1H, d, J = 13.3 Hz), 7.44–7.36 (3H, m), 7.24–7.18 (2H, m), 6.79–6.73 (2H, m), 6.58 (1H, d, J = 13.3 Hz), 6.32 (1H, br s), 6.10 (1H, s), 5.97 (1H, br s), 3.04 (6H, s), 1.40–1.00 (18H, m). The ^{13}C NMR spectrum was not registered because of the low solubility of **7a**. HRMS (ESI^+): calcd for $C_{37}H_{39}N_4OS$ 587.2839, found 587.2810 $[M + H]^+$.

2-[3-Cyano-4-{(3*E*)-4-{4-(diethylamino)phenyl}-2-{4-(dimethylamino)phenyl}buta-1,3-dienyl}-5,5-dimethylfuran-2-ylidene]malononitrile (5b)

To a solution of 4-ethynyl-*N*,*N*-dimethylaniline (**1**) (29 mg, 0.20 mmol) in acetonitrile (6 mL), **2b** (70 mg, 0.20 mmol) was added under argon atmosphere. The reaction was refluxed for three days (TLC monitoring), then it was cooled down to room temperature. The solvent was evaporated and the residue was purified by flash chromatography (silica gel) using CH_2Cl_2 as eluent. A further purification through TLC preparative using diethyl ether as eluent was needed to afford a blue solid (15 mg, 15%). Mp 128–132 °C. Found: C, 76.49; H, 6.39; N, 14.03. Calc. for $C_{32}H_{33}N_5O$: C, 76.31; H, 6.60; N, 13.91%. IR (Nujol, cm^{-1}): 2220 (C≡N), 1608 (C═C, Ar), 1576 (C═C, Ar), 1522 (C═C, Ar). ^1H NMR (400 MHz, CD_2Cl_2): δ 7.54–7.50 (2H, m), 7.39–7.35 (2H, m), 7.14 (1H, d, J = 15.3 Hz), 7.01 (1H, d, J = 15.3 Hz), 6.77–6.73 (2H, m), 6.71–6.67 (2H, m), 5.81 (1H, s), 3.44 (4H, q, J = 7.1 Hz), 3.07 (6H, s), 1.64 (6H, s), 1.20 (6H, t, J = 7.1 Hz). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 178.9, 174.4, 164.0, 153.0, 150.7, 146.8, 132.5, 131.2, 127.3, 123.7, 123.6, 114.0, 113.2, 112.1, 112.0, 110.1, 98.2, 45.1, 40.5, 26.6, 12.9. HRMS (ESI^+): calcd for $C_{32}H_{34}N_5O$ 504.2758, found 504.2734 $[M + H]^+$; calcd for $C_{32}H_{33}N_5NaO$ 526.2577, found 526.2544 $[M + Na]^+$.

Compounds (5c + 8, 9) and (7c, 10). General procedure

To a solution of 4-ethynyl-*N*,*N*-dimethylaniline (**1**) (363 mg, 2.50 mmol) in acetonitrile (20 mL), the corresponding 1,1,3-tricyano-2-phenylpropene-containing chromophore (**2c**, **4c**) (2.50 mmol) was added under argon atmosphere. The reaction was refluxed for four days (TLC monitoring), then it was cooled down to room temperature. The solvent was evaporated and the residue was purified by flash chromatography (silica gel).

Compounds 5c + 8, 9

Eluent: CH_2Cl_2–diethyl ether (100 : 0.3).

(3*E*,5*E*)-6-(4-(Diethylamino)phenyl)-4-(4-(dimethylamino)-phenyl)-2-phenylhexa-1,3,5-triene-1,1,3-tricarbonitrile (5c) + 2-((1-cyano-4-(4-(diethylamino)phenyl)-2-(4-(dimethylamino)-phenyl)cyclobut-2-enyl)(phenyl)methylene)malononitrile (8)

A mixture of **5c** and **8** (ratio **5c**/**8** 10 : 7) was isolated after a further purification through several TLC preparative using diethyl ether as eluent. Blue solid. Yield: (416 mg, 28%). IR (Nujol, cm^{-1}): 2216 (C≡N), 2197 (C≡N), 1605 (C═C, Ar), 1574 (C═C, Ar), 1522 (C═C, Ar). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.59–7.53 (6H, m), 7.48–7.23 (11H, m), 7.08–7.00 (2H, m, (**5c**)), 6.87 (1H, d, J = 15.2 Hz, (**5c**)), 6.78–6.73 (2H, m, (**8**)), 6.72–6.67 (2H, m, (**8**)), 6.66–6.61 (2H, m, (**5c**)), 6.59–6.53 (2H, m, (**5c**)), 6.28 (1H, d, J = 4.2 Hz, (**8**)), 4.36 (1H, d, J = 4.2 Hz, (**8**)), 3.47–3.32 (8H, m), 3.01–2.99 (12H, m), 1.22–1.13 (12H, m). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 169.1, 152.8, 151.5, 150.8, 149.4, 149.1, 143.2, 137.0, 136.0, 134.5, 132.8, 132.5, 131.6, 131.5, 131.0, 130.1, 129.5, 129.1, 129.0, 128.5, 126.6,

123.8, 123.5, 123.0, 121.8, 118.5, 118.2, 116.4, 115.9, 114.9, 114.1, 114.0, 112.7, 112.1, 111.9, 111.8, 111.8, 48.8, 45.1, 44.7, 40.5, 40.4, 12.8, 12.8. HRMS (ESI$^+$): calcd for $C_{33}H_{32}N_5$ 498.2652, found 498.2623 $[M + H]^+$.

4-Diethylamino-4″-dimethylamino-2′,4′-dicarbonitrile-3′-phenyl-[1,1′:5′,1″-terphenyl] (9)

To obtain **9** as a pure sample, it was further dissolved in the minimum amount of CH_2Cl_2 and then hexane was added. The precipitate was filtered, washed with hexane and dried to afford a yellow solid (402 mg, 29%). Mp 240–241 °C. Found: C, 81.94; H, 6.52; N, 11.57. Calc. for $C_{32}H_{30}N_4$: C, 81.67; H, 6.43; N, 11.91%. λ_{max} (CH_2Cl_2)/nm 392 (log ε: 4.36). IR (Nujol, cm^{-1}): 2221 (C≡N), 1606 (C═C, Ar), 1580 (C═C, Ar), 1569 (C═C, Ar), 1523 (C═C, Ar). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.51 (10H, m), 6.83–6.78 (2H, m), 6.77–6.73 (2H, m), 3.42 (4H, q, J = 7.1 Hz), 3.04 (6H, s), 1.21 (6H, t, J = 7.1 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 152.5, 151.8, 149.9, 149.8, 149.3, 137.2, 130.7, 130.4, 130.1, 129.8, 129.7, 129.1, 124.8, 123.7, 118.0, 117.9, 112.3, 111.6, 109.5, 109.5, 44.9, 40.5, 12.8. HRMS (ESI$^+$): calcd for $C_{32}H_{31}N_4$ 471.2543, found 471.2517 $[M + H]^+$; calcd for $C_{32}H_{30}N_4Na$ 493.2363, found 493.2337 $[M + Na]^+$.

Compounds 7c, 10

Eluent: CH_2Cl_2–AcOEt (100 : 1).

(3*E*,5*Z*)-7-(2,6-Di-*tert*-butyl-4*H*-pyran-4-ylidene)-6-(4-(dimethylamino)phenyl)2-phenylhepta-1,3,5-triene-1,1,3-tricarbonitrile (7c)

A further purification through flash chromatography using CH_2Cl_2–AcOEt (100 : 0.5) was needed. Then, the residue was dissolved in the minimum amount of CH_2Cl_2, hexane was added and the precipitate was filtered, washed with hexane and dried to afford a blue solid (14 mg, 5%). Mp 272–276 °C. Found: C, 80.32; H, 6.75; N, 10.34. Calc. for $C_{37}H_{38}N_4O$: C, 80.11; H, 6.90; N, 10.10%. IR (Nujol, cm^{-1}): 2212 (C≡N), 2202 (C≡N), 1644 (C═C, Ar), 1610 (C═C, Ar). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.45–7.38 (3H, m), 7.30–7.25 (2H, m), 7.11 (1H, d, J = 13.2 Hz), 7.06–7.00 (2H, m), 6.79 (1H, d, J = 13.2 Hz), 6.65–6.60 (2H, m), 6.19 (1H, s), 5.98 (1H, s), 5.87 (1H, br s), 2.99 (6H, s), 1.26 (9H, s), 1.04 (9H, s). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 166.9, 166.8, 154.9, 152.5, 149.7, 136.4, 131.3, 131.1, 129.9, 129.1, 125.7, 122.1, 116.9, 116.9, 116.1, 115.4, 112.6, 110.0, 105.0, 97.0, 40.6, 36.7, 28.1, 28.0. HRMS (ESI$^+$): calcd for $C_{37}H_{39}N_4O$ 555.3118, found 555.3090 $[M + H]^+$; calcd for $C_{37}H_{38}N_4ONa$ 577.2938, found 577.2890 $[M + Na]^+$.

4-Dimethylamino-5′-(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidenemethyl)[1,1′:3′,1″-terphenyl]-2′,4′-dicarbonitrile (10)

A further purification through flash chromatography on silica gel using CH_2Cl_2–AcOEt (100 : 0.5) was needed first, and then a TLC preparative using hexane–AcOEt (7 : 3) as eluent to afford a yellow solid (30 mg, 12%). Mp 239–242 °C. λ_{max} (CH_2Cl_2)/nm 411 (log ε: 4.42). IR (Nujol, cm^{-1}): 2218 (C≡N), 1666, 1610 (C═C, Ar), 1554 (C═C, Ar), 1553 (C═C, Ar), 1521 (C═C, Ar). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.69 (1H, s), 7.59–7.49 (7H, m), 6.85–6.78 (2H, m), 6.52 (1H, d, J = 1.6 Hz), 5.93–5.91 (2H, m), 3.04 (6H, s), 1.27 (9H, m), 1.24 (9H, s). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 167.7, 165.7, 152.2, 151.8, 149.4, 147.0, 138.4, 137.4, 130.4, 130.1, 129.8, 129.1, 126.6, 125.5, 118.3, 117.3, 112.4, 109.5, 107.1, 106.2, 106.0, 99.0, 40.6, 36.6, 36.2, 28.2, 28.1. HRMS (ESI$^+$): calcd for $C_{36}H_{38}N_3O$ 528.3009, found 555.3025 $[M + H]^+$.

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Notes and references

1 See for example: (*a*) S.-i. Kato and F. Diederich, *Chem. Commun.*, 2010, **46**, 1994–2006 and references cited therein; (*b*) T. Michinobu, *Pure Appl. Chem.*, 2010, **82**, 1001–1009 and references cited therein.
2 (*a*) C. Cai, I. Liakatas, M.-S. Wong, M. Bösch, C. Bosshard, P. Günter, S. Concilio, N. Tirelli and U. W. Suter, *Org. Lett.*, 1999, **1**, 1847–1849; (*b*) H. Ma, B. Chen, T. Sassa, L. R. Dalton and A. K.-Y. Jen, *J. Am. Chem. Soc.*, 2001, **123**, 986–987; (*c*) J. Luo, H. Ma, M. Haller, A. K.-Y. Jen and R. R. Barto, *Chem. Commun.*, 2002, 888–889; (*d*) Y. Li, K. Tsuboi and T. Michinobu, *Macromolecules*, 2010, **43**, 5277–5286.
3 See for example: (*a*) B. Esembeson, M. L. Scimeca, T. Michinobu, F. Diederich and I. Biaggio, *Adv. Mater.*, 2008, **20**, 4584–4587; (*b*) B. B. Frank, M. Kivala, B. Camafort Blanco, B. Breiten, W. B. Schweizer, P. R. Laporta, I. Biaggio, E. Jahnke, R. R. Tykwinski, C. Boudon, J.-P. Gisselbrecht and F. Diederich, *Eur. J. Org. Chem.*, 2010, 2487–2503; (*c*) B. Breiten, I. Biaggio and F. Diederich, *Chimia*, 2010, **64**, 409–413; (*d*) M. T. Beels, M. S. Fleischman, I. Biaggio, B. Breiten, M. Jordan and F. Diederich, *Opt. Mater. Express*, 2012, **2**, 294–303; (*e*) M. Chiu, B. Jaun, M. T. R. Beels, I. Biaggio, J.-P. Gisselbrecht, C. Boudon, W. B. Schweizer, M. Kivala and F. Diederich, *Org. Lett.*, 2012, **14**, 54–57.
4 See for example: (*a*) T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio and F. Diederich, *Chem. Commun.*, 2005, 737–739; (*b*) T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross and F. Diederich, *Chem.–Eur. J.*, 2006, **12**, 1889–1905; (*c*) M. Jordan, M. Kivala, C. Boudon, J.-P. Gisselbrecht, W. B. Schweizer, P. Seiler and F. Diederich, *Chem.–Asian J.*, 2011, **6**, 396–401.
5 (*a*) M. Kivala, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross and F. Diederich, *Chem. Commun.*, 2007, 4731–4733; (*b*) P. Reutenauer, M. Kivala, P. D. Jarowski, C. Boudon, J.-P. Gisselbrecht, M. Gross and F. Diederich, *Chem. Commun.*, 2007, 4898–4900.
6 P. D. Jarowski, Y.-L. Wu, C. Boudon, J.-P. Gisselbrecht, M. Gross, W. B. Schweizer and F. Diederich, *Org. Biomol. Chem.*, 2009, **7**, 1312–1322.
7 F. Silvestri, M. Jordan, K. Howes, M. Kivala, P. Rivera-Fuentes, C. Boudon, J.-P. Gisselbrecht, W. B. Schweizer, P. Seiler, M. Chiu and F. Diederich, *Chem.–Eur. J.*, 2011, **17**, 6088–6097.
8 D. T. S. Rijkers, F. de Prada López, R. M. J. Liskamp and F. Diederich, *Tetrahedron Lett.*, 2011, **52**, 6963–6967.
9 G. Jayamurugan, J.-P. Gisselbrecht, C. Boudon, F. Schoenebeck, W. B. Schweizer, B. Bernet and F. Diederich, *Chem. Commun.*, 2011, **47**, 4520–4522.
10 R. Andreu, E. Galán, J. Orduna, B. Villacampa, R. Alicante, J. T. López Navarrete, J. Casado and J. Garín, *Chem.–Eur. J.*, 2011, **17**, 826–838.
11 (*a*) L. Han, Y. Jiang, W. Li, Y. Li and P. Hao, *Spectrochim. Acta, Part A*, 2008, **71**, 86–89; (*b*) S. Tada and Y. Ito, *Jp. Pat.*, 61103862 A, 1986 (Chem. Abstr., 1987, **106**, 76075).

12 R. Andreu, L. Carrasquer, S. Franco, J. Garín, J. Orduna, N. Martínez de Baroja, R. Alicante, B. Villacampa and M. Allain, *J. Org. Chem.*, 2009, **74**, 6647–6657.
13 M. Kivala, C. Boudon, J.-P. Gisselbrecht, B. Enko, P. Seiler, I. B. Müller, N. Langer, P. D. Jarowski, G. Gescheidt and F. Diederich, *Chem.–Eur. J.*, 2009, **15**, 4111–4123.
14 C. Dehu, F. Meyers and J.-L. Brédas, *J. Am. Chem. Soc.*, 1993, **115**, 6198–6206.
15 Y.-L. Wu, P. D. Jarowski, W. B. Schweizer and F. Diederich, *Chem.–Eur. J.*, 2010, **16**, 202–211.
16 R. Gompper and H.-U. Wagner, *Angew. Chem., Int. Ed.*, 1988, **27**, 1437–1455.
17 S.-i. Kato, M. T. R. Beels, P. La Porta, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, I. Biaggio and F. Diederich, *Angew. Chem., Int. Ed.*, 2010, **49**, 6207–6211.
18 R. M. Acheson and J. Woollard, *J. Chem. Soc., Perkin Trans. 1*, 1975, 744–748.
19 (*a*) S. Alías, R. Andreu, M. J. Blesa, S. Franco, J. Garín, A. Gragera, J. Orduna, P. Romero, B. Villacampa and M. Allain, *J. Org. Chem.*, 2007, **72**, 6440–6446; (*b*) R. Andreu, L. Carrasquer, J. Garín, M. J. Modrego, J. Orduna, R. Alicante, B. Villacampa and M. Allain, *Tetrahedron Lett.*, 2009, **50**, 2920–2924.
20 C. W. Bird, *Tetrahedron*, 1986, **42**, 89–92.
21 C. Reichardt and T. Welton, *Solvents and Solvents Effects in Organic Chemistry*, Wiley-VCH Verlag GmbH & Co., Weinheim, 4th edn, 2010.
22 See for example: (*a*) J. A. Davies, A. Elangovan, P. A. Sullivan, B. C. Olbricht, D. H. Bale, T. R. Ewy, C. M. Isborn, B. E. Eichinger, B. H. Robinson, P. J. Reid, X. Li and L. R. Dalton, *J. Am. Chem. Soc.*, 2008, **130**, 10565–10575; (*b*) M. C. Ruiz Delgado, J. Casado, V. Hernández, J. T. López Navarrete, J. Orduna, B. Villacampa, R. Alicante, J.-M. Raimundo, P. Blanchard and J. Roncali, *J. Phys. Chem. C*, 2008, **112**, 3109–3120.
23 E. Galán, R. Andreu, J. Garín, L. Mosteo, J. Orduna, B. Villacampa and B. E. Diosdado, *Tetrahedron*, 2012, **68**, 6427–6437.
24 (*a*) J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664–2668; (*b*) D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195–242.
25 (*a*) G. Bourhill, J.-L. Brédas, L.-T. Cheng, S. R. Marder, F. Meyers, J. W. Perry and B. G. Tiemann, *J. Am. Chem. Soc.*, 1994, **116**, 2619–2620; (*b*) For D–A polyenes, β can be maximized when there is an optimal degree of mixing between neutral and charge-separated canonical forms. As a function of increasing polarization, and starting from chromophores with weak D and A groups, β is positive, first increases, peaks in a positive sense, decreases, crosses through zero at the cyanine limit, and then becomes negative when the ground state of the molecule becomes zwitterionic. The rationalization of this behavior has allowed the establishment of very useful guidelines for the design of NLO chromophores. Molecules showing high positive (negative) β values with ground-states lying halfway between the neutral (zwitterionic) and the cyanine limit forms have been named left (right)-hand side chromophores.