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Synthesis and nonlinear optical properties of chromophores for photorefractive polymer materials

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ABSTRACT

The synthesis and nonlinear optical (NLO) properties of a series of nitrostilbene-, dinitrostilbene-, and dicyanomethylenedihydrofuran-based chromophores potentially useful in photorefractive multifunctional polymers are reported. Electronic absorption spectra have been measured in different solvents. Electric field induced second harmonic (EFISH) generation results show that the 2-dicyanomethylen-3cyano-5,5-dimethyl-2,5-dihydrofuran moieties lead to the best NLO performances. Dinitrophenyl-based chromophores have shown a reduced nonlinear response as compared with the mononitro analogues. Nonlinear optical properties of a selected nitro-dinitro couple have been also determined theoretically. © 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Under the name of photorefractive (PR) effect lies the synergistic collaboration of four physical processes, namely charge photogeneration, charge transport, charge trapping and electrooptic response, which altogether lead to a spatial modulation of the refraction index after irradiation of the material with a laser light intensity pattern.¹ Once these conditions are achieved, an internal redistribution of charges takes place, which induces the variation on the refraction index. This effect was first observed in inorganic materials like LiNbO₃, BaTiO₃ and GaAs.² However, the application of these materials has been limited by technical problems like sample preparation. On the other hand, organic PR materials exhibit some PR performances, which are better than the corresponding of inorganic materials, with the exception of speed of grating formation. Moreover, organic materials are produced and processed easier and at lower cost than the inorganic ones. This is why they are candidates for applications in optical holographic data storage, real-time image processing and phase conjugation.³

There are three main strategies to achieve photorefractivity in organic materials. The first one consists in the mixing as a blend of an inert polymer with different molecules, each of them responsible for one, or even two, of the required physical processes. The second one is the preparation of a functional homopolymer

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showing one or two of the functional properties needed to originate PR effect, and doped with molecules responsible for the rest of the functional properties. The last possibility is the synthesis of a multifunctional copolymer by using all the required physically active molecules as comonomers.⁴ All these strategies have their own advantages, disadvantages and limitations.

In recent times, we have devoted some effort to the preparation of improved photosensitizers, i.e., molecules for charge photogeneration, in a successful attempt to increase the photorefractive speed. Thus, we have designed and synthesized some trinitrofluorenone- C_{60} dyads that generated PR compositions showing faster photorefractive responses than the corresponding compositions containing either trinitrofluorenone or C_{60} .⁵ Now, we have focused our research in the study of the effect of material preparation (blend, multifunctional polymer, sol–gel hybrid organic–inorganic material) on the PR performances. Hence, we have designed and studied some series of nonlinear optical (NLO) compounds, bearing a hydroxy group to allow for further anchoring to a polymer chain.

Among other properties, chromophores for PR applications should posses large dipole moment (μ) and first hyperpolarizability (β) values, besides a high linear polarizability anisotropy.^{3,4,6} It is well known that the use of π -conjugated bridges endcapped with strong electron donor and acceptor groups (D– π –A systems) leads to molecules with high $\mu\beta$ values, but usually with red shifted electronic spectra, detrimental for many applications.⁷ In the 1990s, a systematic relation between the ground state polarization, which depends on both the strength of the terminal groups and the length and nature of the π -bridge, and β values was proposed.⁸ Among the





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different approaches followed to increase the NLO efficiency, molecules having novel electron deficient heterocyclic acceptors have been studied. In particular, 2,5-dihydrofuran-substituted chromophores have shown very high $\mu\beta$ values⁹ and good thermal stability and some of them have been successfully incorporated into PR polymer composites.¹⁰ On the other hand, in order to eliminate some of the problems (as phase separation or sublimation) arising when using blends, the chemical incorporation of NLO moieties into a polymeric structure has attracted much attention.^{3,4a} Given the better thermal and temporal stabilities of these systems, the possibility of easy covalent insertion in polymeric chains is an interesting molecular characteristic.

Here, we present the synthesis, characterization and nonlinear optical study of new push–pull chromophores **1–8**, which can be used in a PR composition, as a blend, or can be attached to form a multifunctional PR polymer. To the best of our knowledge, this is the first time that the NLO properties of 2-dicyanomethylen-3-cyano-5,5-dimethyl-2,5-dihydrofuran-based chromophores bearing oxygen atoms as donors are described. The preparation of the polymers and the study of the PR properties of the blends and polymers are out of the scope of this paper and will be presented elsewhere.

2. Results and discussions

2.1. Synthesis of NLO chromophores

The preparation of the different NLO chromophores (Chart 1) was accomplished by two different strategies. Thus, the nitrostilbene derivatives **1** and **2** were obtained via Heck reaction,¹¹ while the dinitrostilbene derivatives **3–5** and the tricyano derivatives **6–8** were synthesized using Knoevenagel condensations.¹²

The synthesis of compound **1** is depicted in Scheme 1. Thus, bromination of 2-hexyloxyphenol¹³ followed by alkylation afforded compound **10** in good yield. However, this compound failed to couple with 4-nitrostyrene.¹⁴ Treatment of compound **10** with butyllithium and subsequent quenching with *N*-formylpiperidine generated aldehyde **11**, which also failed to yield **1** by either Knoevenagel condensation or Wittig reaction. Lithium-mediated exchange of bromine by iodine in compound **10** led to **12** in low yield. This compound happened to be very unstable, and was characterized only by ¹H NMR. However, quick handling of **12** allowed for coupling with 4-nitrostyrene to afford **1**.



Scheme 1. (i) Br₂, CH₂Cl₂ (ii) 2-chloroethanol, KI, K₂CO₃, 120 °C, DMF; (iii) *n*-BuLi, –78 °C then I₂; (iv) *p*-nitrostyrene, Pd(OAc)₂, triethylamine, DMF; (v) *n*-BuLi, –78 °C, THF then *N*-formylpiperidine; (vi) dinitrotoluene, AcOH, NH₄OAc, pyridine, molecular sieves, 80 °C; (vii) 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, AcOH, NH₄OAc, pyridine, molecular sieves, 80 °C.



Scheme 2. (i) 2-Chloroethanol, KI, K₂CO₃, 120 °C, DMF; (ii) *p*-nitrostyrene, Pd(OAc)₂, triethylamine, DMF.

Scheme 2 shows the synthesis of compound **2**. Thus, alkylation of 4-iodo-2,5-dimethylphenol¹⁵ afforded compound **13**, which underwent Heck reaction with *p*-nitrostyrene to yield the nitrostilbene in moderate yield. Interestingly, Heck reaction using the bromo analogue **14** yielded only starting materials.

The dinitrostilbene **3** was prepared by Knoevenagel condensation between **11** and 2,4-dinitrotoluene (Scheme 1). Alkylation of 4-bromo-2,5-dimethylphenol,¹⁶ followed by lithium–bromine exchange and quenching with *N*-formylpiperidine generated aldehyde **16** (Scheme 3), which afforded **4** after condensation with 2,4-dinitrotoluene. Compound **5** was prepared in a similar way starting from 2-ethylhexyl 4-bromo-2,5-dimethylphenyl ether.¹⁷

Knoevenagel condensation of aldehydes **11**, **16** and **17** with 2dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran¹⁸ afforded compounds **6** (Scheme 1), **7** and **8** (Scheme 3), respectively.

The *E* configuration for alkenes 1-8 was assigned as a result of the coupling constants (ca. 16 Hz) showed by the olefinic protons in the corresponding ¹H NMR spectra.

2.2. Optical characterization

UV–vis spectra of compounds **1–8**, showing a visible wavelength band, have been measured in methanol, CH_2Cl_2 and DMSO. The wavelength of maximal charge transfer absorption (λ_{max}) is shown in Table 1.

For a given donor group, a progressive bathochromic shift of λ_{max} in the sequence: nitrophenyl<dinitrophenyl<dihydrofuran derivative acceptors is observed, as expected according to the increasing withdrawing character of the groups. As an example, the optical absorption spectra of compounds **2**, **4**, **7** (bearing the hydroxyethyl dimethylphenyl ether donor) are shown in Figure 1. The same behaviour is observed regardless of the donor group. On

 Table 1

 UV-vis data and experimental nonlinearities of compounds 1-8

Compound	λ_{max} (nm) MeOH//DCM//DMSO	$\mu\beta^{\mathrm{a}}$ (10 ⁻⁴⁸ esu)	$\mu\beta(0)^{a} (10^{-48} \text{ esu})$
1	377//381//397	90±10	73
2	380//386//398	$150{\pm}20$	120
		130±20 ^b	103 ^b
3	400//406//414	54 ± 6	42
4	405//414//417	90±20	70
		$80{\pm}20^{b}$	62 ^b
5	405//423//419	$190{\pm}20$	145
6	458//462//469	$360{\pm}30$	259
7	461//465//469	$460{\pm}40$	330
8	468//476//471	$460{\pm}60$	324

 $\mu\beta(0)$ values have been deduced using the two-level dispersion model.¹⁹

 a In CH₂Cl₂ at 1.907 μ m.

^b In DMSO at 1.907 μm.



Figure 1. UV-vis absorption spectra of compounds 2, 4 and 7 in CH₂Cl₂.

the other hand, the absorption bands slightly shift to lower energy in the following sequence of donor groups: hydroxyethyl hexyloxyphenyl ether<hydroxyethyl dimethylphenyl ether<ethylhexyl dimethylphenyl ether.

Second order nonlinearities of these compounds have been investigated by using the EFISH technique at 1.907 μ m. The experimental $\mu\beta$ and $\mu\beta(0)$ values are also summarized in Table 1.

It can be seen that the higher $\mu\beta$ values measured in this work correspond to compounds **6–8**, having the 2-dicyanomethylen-3-cyano-5,5-dimethyl-2,5-dihydrofuran moiety as acceptor. As we mentioned above, dihydrofuran-based groups are very efficient



Scheme 3. (i) For compound 14: 2-chloroethanol, NaOH, H₂O, reflux; (ii) *n*-BuLi, –78 °C, 12-crown-4, THF, then *N*-formylpiperidine; (iii) benzene, AcOH, Et₂NH, dinitrotoluene, reflux; (iv) NaH, DMF, 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, reflux.

acceptors,⁹ so it was thus expected that these molecules gave rise to higher NLO responses than those of the (di)nitrophenyl-substituted counterparts (compounds 1–5), as confirmed by the experiment. However, those values are far from the extremely high molecular nonlinearities found for other chromophores ended with the same acceptor group and much stronger donor moieties.⁹ Regarding nitrocompounds, the obtained $\mu\beta$ values are in good agreement with the results reported for related nitrostilbene chromophores bearing oxygen as donor.²⁰ The $\mu\beta(0)$ values obtained for the dinitro derivative **5** and dihydrofuran derivatives **6–8** (in the range 150– 330×10^{-48} esu) are comparable to those of other classical NLO chromophores utilized in high performance PR composites, ^{3,21,22} as 2,5-dimethyl-4-(2-hydroxyethoxy)-4'-nitroazobenzene (DMHNAB) or 2,5-dimethyl-4-(4'-nitrophenylazo)anisole (DMNPAA)²³ ($\mu\beta(0) \approx$ 200×10^{-48} esu).

2.3. Theoretical calculations

Regarding the experimental values of compounds 1/3 and 2/4, it should be noted that dinitro compounds did not represent an improvement over their mononitro analogues. Concerning spectroscopic properties, the predictable bathochromic shift of the absorption band of 3 and 4 relative to 1 and 2, respectively, is observed in the UV-vis spectra taken in CH₂Cl₂ as well as in DMSO and MeOH. Although the dinitro substitution usually gives rise to an enhancement of the NLO response, a decrease of the measured $\mu\beta$ values in a series of dinitrostilbenes when compared to nitrostilbenes had been previously reported.^{20,24} The authors concluded that there was an important change in the orientation of the dipole moment and hence the projection of β on the dipole moment direction and so the measured $\mu\beta$ values were reduced. An analogous change in the orientation of μ was confirmed theoretically for chromophores having 1,3-dithiol-2-ylidene donor and azine spacer.²⁵ However, in these compounds the change was not as large and both experimental and calculated $\mu\beta$ values increased on passing from nitro to dinitro substitution. Trying to take some insight into this fact, $\mu\beta(0)$ values for model compounds 2 and 4 were calculated (CPHF/6-31G*//B3P86/6-31G* model). While calculations predict again a change in the orientation of μ on passing from **2** to **4**, it is not large enough to cause a decrease in $\mu\beta$; as shown in Table 2, CPHF results show a pronounced increase of the NLO response going from nitro to dinitro chromophores. Although CPHFcalculated values are usually closer to the experimental ones than those calculated by TD-DFT, we have also used the latter method in order to obtain a more intuitive description of the NLO behaviour of the studied compounds.

Therefore, we have calculated the parameters needed to evaluate β_0 in the two-level model¹⁹ ($\beta_0 \propto \Delta \mu_{ge} \ \mu^2_{ge}/E^2$, where $\Delta \mu_{ge}$ is the difference between the excited and ground state dipole moments, μ_{e} and μ_{g} , respectively, μ_{ge} is the transition dipole moment, related to the oscillator strength, and *E* is the excitation energy). A summary of these parameters is gathered in Table 2. As opposed to CPHF results, a higher $\beta(0)$ value is obtained using TD-DFT parameters and the two-level approach. The decrease of the transition

Table 2	2
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Calculated NLO properties of compounds 2 and 4

Compound	TD-DFT ^a					CPHF ^b
	<i>E</i> (eV)	$\mu_{g}(D)$	$\mu_{\rm ge}({\rm D})$	$\Delta \mu_{ge}(D)$	β(0) ^c	$\mu\beta(0)^{c}$
2	3.00	8.66	8.29	24.27	216	115
4	2.68	9.10	7.04	19.33	156	470

^a B3P86/6-31G* level.

b CPHF/6-31G* level.

^c In 10^{-30} esu. ^d In 10^{-48} esu.

energy from 2 to 4 obtained by TD-DFT calculations agrees with the bathochromic shift observed in UV-vis spectra, although theoretical λ_{max} values are overestimated (λ_{max} =413 nm and 463 nm for **2** and 4, respectively). This decrease should favour the NLO response of compound **4**, but the calculated μ_{ge} and $\Delta \mu_{ge}$ values point into the opposite sense and then the $\beta(0)$ value calculated using the two-level model expression (see above) is higher for 2. The higher difference between excited and ground state dipole moments obtained for **2** seems to agree with the stronger solvatochromism observed when absorption spectra are taken in CH₂Cl₂ and DMSO (12 nm vs 3 nm for 2 and 4, respectively). Moreover, the lower transition dipole moment μ_{ge} calculated for compound **4** is also in qualitative accordance with the lower oscillator strength (f) estimated from the area under the measured absorption band of **4** as compared to 2 (Fig. 1). A ratio of f values close to 0.8 has been obtained from this comparison.

Finally, and concerning the donor end of the molecules, it is worth mentioning the general trend that 1-alkoxy-2,5-dimethyl substitution leads to better NLO responses than the 1,2-dialkoxy pattern, as shown when comparing the 1/2, 3/4 and 6/7 couples.

3. Conclusion

The synthesis and NLO characterization of some push-pull alkenes have been accomplished. Results show that the 2-dicyanomethylen-3-cyano-5,5-dimethyl-2,5-dihydrofuran moiety acting as acceptor leads to the best NLO performances. Somewhat surprisingly, the use of a 2.4-dinitrophenyl group as electron-accepting subunit results in lower NLO responses when compared to 4nitrophenyl-substituted compounds. CPHF calculations, which usually provide $\beta(0)$ values closer to the experimental ones than those calculated by TD-DFT, fail to predict the experimental trend. Bearing in mind that TD-DFT method is used only to take an intuitive description of NLO behaviour, it provides us with the decrease of the transition dipole moment, μ_{ge} , as well as with the difference $\Delta \mu_{ge}$ between the excited and ground state dipole moments, when passing from nitro to dinitro substitution. These results lead to $\mu\beta(0)$ values lower for the compound with double nitro substitution as observed in the experiment.

4. Experimental

4.1. Synthesis of NLO chromophores

All chemicals were reagent-grade, purchased from commercial sources, and used as received, unless otherwise specified. Column Chromatography: SiO_2 (40–63 µm). TLC plates coated with SiO_2 60F₂₅₄ were visualized by UV light. NMR spectra were measured with a Bruker AC 300 and with a Bruker AVANCE DRX-500. UV-vis spectra were recorded with a Helios Gamma spectrophotometer and IR spectra with a Nicolet Impact 400D spectrophotometer. Mass spectra were obtained from an Agilent 5973 Network Mass spectrometer. Elemental analyses were performed on a Thermo Finnigan Flash 1112 CHN elemental analyzer.

4.1.1. Synthesis of 4-bromo-2-hexyloxyphenol (9)

To a cooled solution (0 $^{\circ}$ C) of 2-hexyloxyphenol¹³ (4.5 g, 23.20 mmol) in 100 mL of dichloromethane was added dropwise a solution of bromine (3.7 g, 23.15 mmol) in 50 mL of dichloromethane. After addition, the reaction was stirred at room temperature for 1 h, then was washed with 10% sodium hydroxide and dried with magnesium sulfate; the solvent was distilled off by an evaporator. The crude product was purified by chromatography on silica gel (hexane/ethyl acetate, 9:1) to give an oil (4.94 g, 78%). ¹H NMR (CDCl₃): δ 6.97 (d, 1H, J=8.8 Hz), 6.96 (s, 1H), 6.80 (d, 1H, J=8.8 Hz), 3.99 (t, 2H, J=6.6 Hz), 1.72-1.80 (m, 2H), 1.26-1.46 (m, 6H), 0.91 (t, 3H, *J*=6.9 Hz); ¹³C NMR (CDCl₃): δ 146.6, 144.9, 123.8, 115.6, 114.8, 111.4, 69.1, 31.4, 28.9, 25.5, 22.5, 13.9; MS (EI) *m/z*: 272 (M⁺, 38), 274 (37), 190 (99), 188 (100); IR (KBr): 3541 cm⁻¹. Anal. Calcd for C₁₂H₁₇BrO: C, 52.76; H, 6.27. Found: C, 52.75; H, 6.42%.

4.1.2. Synthesis of 2-(4'-bromo-2'-hexyloxyphenoxy)ethan-1-ol (**10**)

A mixture of 4-bromo-2-hexvloxyphenol 9 (6 g. 22 mmol), potassium carbonate (6 g, 43.5 mmol), potassium iodide (1.8 g, 10.8 mmol), 2-chloroethanol (3 mL), and DMF (30 mL) was heated at 120 °C for 24 h. The reaction mixture was cooled in an ice bath. Hydrochloric acid (10%, 40 mL) and diethyl ether (20 mL) were added and the two phases were separated. The water phase was extracted twice with diethyl ether. The resulting organic phases were combined and washed with water. The organic extracts were dried over sodium sulfate an evaporated. The residue was purified by chromatography on silica gel (hexane/ethyl acetate, 2:1) to gave an oil (4.80 g, 69%). ¹H NMR (CDCl₃): δ 6.97 (m, 2H), 6.77 (d, 1H, J=9.0 Hz), 4.05 (t, 2H, J=4.8 Hz), 3.94 (t, 2H, J=6.8 Hz), 3.87 (t, 2H, J=4.8 Hz), 1.76-1.85 (m, 2H), 1.30-1.48 (m, 6H), 0.89 (t, 3H, J=6.9 Hz); ¹³C NMR (CDCl₃): δ 150.4, 147.5, 123.6, 117.1, 116.5, 114.2, 72.1, 69.2, 61.2, 31.4, 28.9, 25.6, 22.5, 13.9; MS (EI) *m/z*: 316 (M⁺, 35), 318 (34), 234 (39), 232 (41), 190 (99), 188 (100); IR (KBr): 3368 cm⁻¹. Anal. Calcd for C₁₄H₂₁BrO₃: C, 53.01; H, 6.67. Found: C, 52.95; H, 6.68%.

4.1.3. Synthesis of 3-hexyloxy-4-(2'-hydroxyethoxy)benzaldehyde (**11**)

To a solution of 2-(4'-bromo-2'-hexvloxvphenoxv)ethan-1-ol 10 (3.85 g, 12.10 mmol) in tetrahydrofuran (50 mL) at $-78 \degree \text{C}$ under nitrogen atmosphere was added butyllithium (12 mL of a 2.5 M solution in hexanes) and the reaction mixture was stirred 1 h. Then, 3.4 g of *N*-formylpiperidine were added, and the reaction was kept at room temperature for 24 h. After cooling in an ice bath, hydrochloric acid (10%, 40 mL) was added. The crude was extracted with diethyl ether and the organic extracts were washed and dried with anhydrous sodium sulfate. Solvent was removed, and the residue was purified by chromatography on silica gel (hexane/ethyl acetate, 2:1) to yield an oil (1.19 g, 37%). ¹H NMR (acetone- d_6): δ 9.85 (s, 1H), 7.50 (dd, 1H, J=8.2, 1.9 Hz), 7.42 (d, 1H, J=1.9 Hz), 7.17 (d, 1H, J=8.2 Hz), 4.20 (t, 2H, J=4.8 Hz), 4.10 (t, 2H, J=6.8 Hz), 3.9 (t, 2H, J=4.8 Hz), 1.77-1.85 (m, 2H), 1.35-1.53 (m, 6H), 0.90 (t, 3H, J=6.9 Hz); ¹³C NMR (acetone- d_6): δ 192.3, 156.4, 151.4, 132.4, 127.5, 114.7, 113.4, 72.7, 70.7, 62.2, 33.3, 31.0, 27.4, 24.3, 15.3; MS (EI) m/z: 266 (M⁺, 44), 182 (48), 138 (100); IR (KBr): 3437, 1689 cm⁻¹. Anal. Calcd for C₁₅H₂₂O₄: C, 67.65; H, 8.33. Found: C, 67.64; H, 8.24%.

4.1.4. Synthesis of 2-(2'-hexyloxy-4'-iodophenoxy)ethan-1-ol (12)

To a solution of 2-(4'-bromo-2'-hexyloxyphenoxy)ethan-1-ol **10** (7.87 g, 21.61 mmol) in tetrahydrofuran (40 mL) at -78 °C under nitrogen atmosphere was added butyllithium (17.3 mL of a 2.5 M solution in hexanes) and the mixture was stirred 1 h. Then, a solution of iodine (5.58 g) in tetrahydrofuran (10 mL) was added over 15 min. The reaction was kept at room temperature for 45 min and water (30 mL) was added. The crude was extracted with diethyl ether and the organic extracts were washed and dried with anhydrous sodium sulfate. Solvent was removed, and the residue was purified by chromatography on silica gel (hexane/ethyl acetate, 2:1) to yield an oil (1.76 g, 22%). ¹H NMR (CDCl₃): δ 7.19 (dd, 1H, *J*=8.4, 2.0 Hz), 7.13 (d, 1H, *J*=2.0 Hz), 6.65 (d, 1H, *J*=8.4 Hz), 4.03 (t, 2H, *J*=4.8 Hz), 3.92 (t, 2H, *J*=6.8 Hz), 3.85 (t, 2H, *J*=4.8 Hz), 1.76–1.85 (m, 2H), 1.28–1.50 (m, 6H), 0.90 (t, 3H, *J*=6.9 Hz).

4.1.5. Synthesis of (E)-1-[3'-hexyloxy-4'-(2"-hydroxyethoxy)-phenyl]-2-(4'-nitrophenyl)-ethene (1)

A mixture of 2-(2'-hexyloxy-4'-iodophenoxy)ethan-1-ol **12** (1 g, 2.75 mmol), 4-nitrostyrene¹⁴ (0.51 g, 3.44 mmol), $Pd(OAc)_2$

(67.9 mg, 0.3 mmol), and triethylamine (0.5 mL) in 10 mL of dry DMF was stirred under argon at 130 °C for 24 h. After the mixture was washed with water, extracted with ether and evaporated, the residue was purified by flash column chromatography (hexane/ethyl acetate, 2:1) to afford the corresponding coupled product (0.42 g, 39%). ¹H NMR (CDCl₃): δ 8.19 (d, 2H, *J*=8.8 Hz), 7.59 (d, 2H, *J*=8.8 Hz), 7.20 (d, 1H, *J*=16.3 Hz), 7.10 (s, 1H), 7.08 (d, 1H, *J*=8.8 Hz), 6.99 (d, 1H, *J*=16.3 Hz), 6.94 (d, 1H, *J*=8.8 Hz), 4.15 (t, 2H, *J*=4.6 Hz), 4.06 (t, 2H, *J*=6.7 Hz), 3.93 (t, 2H, *J*=4.6 Hz), 1.78–1.90 (m, 2H), 1.33–1.52 (m, 6H), 0.91 (t, 3H, *J*=7.0 Hz); ¹³C NMR (acetone-*d*₆): δ 152.0, 151.5, 148.3, 146.6, 135.2, 132.0, 128.6, 126.1, 125.8, 123.0, 116.4, 114.0, 73.0, 70.8, 62.4, 33.3, 31.0, 27.5, 24.3, 15.3; MS (EI) *m/z*: 385 (M⁺, 94), 355 (18), 301 (22), 257 (100); IR (KBr): 3425, 1512, 1346 cm⁻¹; mp: 92–93 °C. Anal. Calcd for C₂₂H₂₇NO₅: C, 68.55; H, 7.06; N, 3.63. Found: C, 68.61; H, 7.08; N, 3.75%.

4.1.6. Synthesis of 2-(4'-iodo-2',5'-dimethylphenoxy)ethan-1-ol (**13**)

A mixture of 4-iodo-2,5-dimethylphenol¹⁵ (3.8 g, 15.32 mmol), potassium carbonate (4.3 g, 31.2 mmol), potassium iodide (1.3 g, 7.8 mmol), 2-chloroethanol (2.1 mL) and DMF (30 mL) was heated at 120 °C overnight. The reaction mixture was cooled in an ice bath. Hydrochloric acid (10%, 40 mL) and diethyl ether (20 mL) were added and the two phases were separated. The water phase was extracted twice with diethyl ether. The resulting organic phases were combined and washed with water. The organic extracts were dried over sodium sulfate an evaporated. The residue was purified by chromatography on silica gel (hexane/ethyl acetate, 2:1) to afford a white solid (2.9 g, 65%). ¹H NMR (CDCl₃): δ 7.53 (s, 1H), 6.72 (s, 1H), 4.04 (t, 2H, *J*=4.8 Hz), 3.96 (t, 2H, I=4.8 Hz), 2.37 (s, 3H), 2.15 (s, 3H); ¹³C NMR (CDCl₃): δ 156.9, 140.1, 139.5, 126.5, 113.1, 89.8, 69.4, 61.5, 27.9, 15.2; MS(EI) m/z: 292 (M⁺, 98), 248 (100), 121 (62), 91 (40); IR (KBr): 3294 cm⁻¹; mp: 110–112 °C. Anal. Calcd for C₁₀H₁₃IO₂: C, 41.12; H, 4.49. Found: C, 41.49; H, 4.48%.

4.1.7. Synthesis of (E)-1-[2',5'-dimethyl-4'-(2"-hydroxyethoxy)-phenyl]-2-(4'-nitrophenyl)-ethene (**2**)

A mixture of 2-(4'-iodo-2',5'-dimethylphenoxy)ethan-1-ol 13 (2.34 g, 8.01 mmol), 4-nitrostyrene (1.56 g, 10.45 mmol), Pd(OAc)₂ (43 mg, 0.19 mmol), and triethylamine (1.7 mL) in 30 mL of dry DMF was refluxed under argon for 17 h. After the mixture was washed with water, extracted with ethyl acetate and evaporated, the residue was purified by flash column chromatography (hexane/ethyl acetate, 2:1) to generate an orange solid (1.2 g, 48%). ¹H NMR (CDCl₃): δ 8.18 (d, 2H, J=8.8 Hz), 7.58 (d, 2H, J=8.8 Hz), 7.42 (s, 1H), 7.43 (d, 1H, J=16.1 Hz), 6.93 (d, 1H, J=16.1 Hz), 6.66 (s, 1H), 4.11 (t, 2H, *I*=5.0 Hz), 4.0 (t, 2H, *I*=5.0 Hz), 2.42 (s, 3H), 2.25 (s, 3H): ¹³C NMR (acetone- d_6): δ 159.5, 148.1, 146.9, 137.6, 132.5, 129.5, 129.1, 128.6, 126.6, 126.3, 125.7, 115.0, 71.7, 62.4, 20.8, 17.0; MS (EI) *m*/*z*: 313 (M⁺, 100), 283 (17), 269 (55), 208 (28), 179 (20); IR (KBr): 3291, 1589, 1338 cm⁻¹; mp: 112–114 °C. Anal. Calcd for C₁₈H₁₉NO₄: C, 68.99; H, 6.16; N, 4.47. Found: C, 69.00; H, 6.16; N, 4.63%.

4.1.8. Synthesis of 2-(4'-bromo-2',5'-dimethylphenoxy)ethan-1-ol (14)

A mixture of 4-bromo-2,5-dimethylphenol¹⁶ (20.1 g, 0.1 mol), 2chloroethanol (16.1 g, 0.2 mol), sodium hydroxide (0.10 mol) and water (40 mL) was refluxed for 24 h. The reaction mixture was cooled in an ice bath followed by suction filtration to afford the crude product. Purification by chromatography on silica gel (hexane/ethyl acetate, 2:1) gave a white solid (18.87 g, 77%). ¹H NMR (CDCl₃): δ 7.20 (s, 1H), 6.62 (s, 1H), 3.98 (t, 2H, *J*=4.8 Hz), 3.88 (t, 2H, *J*=4.8 Hz), 2.27 (s, 3H), 2.10 (s, 3H); ¹³C NMR (CDCl₃): δ 155.8, 135.8, 133.8, 126.2, 115.2, 113.9, 69.6, 61.5, 22.8, 15.5; MS (EI) *m/z*: 244 (M⁺, 55), 246 (54), 200 (100), 198 (98), 121 (99), 91 (44); IR (KBr): 3291 cm⁻¹; mp: 108–110 °C. Anal. Calcd for $C_{10}H_{13}BrO_2$: C, 49.00; H, 5.35. Found: C, 49.45; H, 5.33%.

4.1.9. Synthesis of 4-(2'-hydroxyethoxy)-2,5-dimethylbenzaldehyde (**16**)

To a solution of 2-(4'-bromo-2',5'-dimethylphenoxy)ethan-1-ol 14 (5 g. 20.41 mmol) and 12-crown-4 (3.52 g. 20 mmol) in tetrahydrofuran (40 mL) at -78 °C under nitrogen atmosphere was added slowly butyllithium (18 mL of 2.5 M solution in hexanes) and the mixture reaction was stirred 1 h. Then, 3 g of N-formylpiperidine were added, and the reaction was kept at room temperature for 24 h. After cooling in an ice bath, dilute hydrochloric acid (40 mL) was added. The crude was extracted with diethyl ether and the organic extracts were washed and dried with anhydrous sodium sulfate. Solvent was removed, and the residue was purified by chromatography on silica gel (hexane/ethyl acetate, 2:1) to give a yellow solid (2.06 g, 52%). ¹H NMR (CDCl₃): δ 10.05 (s, 1H), 7.53 (s, 1H), 6.62 (s, 1H), 4.14 (t, 2H, J=4.8 Hz), 4.00 (t, 2H, J=4.8 Hz), 2.59 (s, 3H), 2.21 (s, 3H); ¹³C NMR (CDCl₃): δ 191.2, 160.9, 141.0, 133.9, 126.8, 124.5, 113.2, 69.3, 60.8, 19.1, 15.3; MS (EI) m/z: 194 (M⁺, 69), 149 (100), 121 (20), 91 (18), 77 (26); IR (KBr): 3313, 1687 cm⁻¹; mp: 72–74 °C. Anal. Calcd for C₁₁H₁₄O₃: C, 68.02; H, 7.27. Found: C, 67.58; H, 7.25%.

4.1.10. Synthesis of 4-(2'-ethylhexyloxy)-2,5-dimethylbenzaldehyde (**17**)

To a solution of 1-bromo-4-(2'-ethylhexyloxy)-2.5-dimethylbenzene¹⁷ **15** (4.6 g, 14.68 mmol) in tetrahydrofuran (50 mL) at -78 °C under nitrogen atmosphere was added butyllithium (10 mL of a 1.6 M solution in hexanes) and the mixture reaction was stirred 1 h. Then, 3.4 g of *N*-formylpiperidine were added, and the reaction was kept at room temperature for 12 h. After cooling in an ice bath, hydrochloric acid (10%, 40 mL) was added. The crude was extracted with diethyl ether and the organic extracts were washed and dried with anhydrous sodium sulfate. Solvent was removed, and the residue was purified by chromatography on silica gel (hexane/ethyl acetate, 9:1) to yield an oil (3.35 g, 87%). ¹H NMR (CDCl₃): δ 10.09 (s, 1H), 7.56 (s, 1H), 6.63 (s, 1H), 3.91 (d, 2H, J=5.5 Hz), 2.63 (s, 3H), 2.21 (s, 3H), 1.72–1.80 (m, 1H), 1.29–1.55 (m, 8H), 0.88–0.96 (m, 6H); ¹³C NMR (CDCl₃): δ 191.2, 161.7, 141.1, 134.0, 126.8, 124.8, 113.2, 70.4, 39.4, 30.6, 29.0, 23.9, 22.9, 19.5, 15.6, 14.0, 11.2; MS (EI) m/z: 262 (M⁺, 26), 150 (100); IR (KBr): 1697 cm⁻¹. Anal. Calcd for C₁₇H₂₆O₂: C, 77.82; H, 9.99. Found: C, 77.34; H, 10.04%.

4.1.11. Synthesis of (E)-1-(2',4'-dinitrophenyl)-2-[3'-hexyloxy-4'-(2"-hydroxyethoxy)phenyl]-ethene (**3**)

To a solution of dry pyridine (10 mL), glacial acetic acid (0.12 mL), ammonium acetate (32 mg) and molecular sieves (3 Å pellets, 2 g) was added 3-hexyloxy-4-(2'-hydroxyethoxy)benzaldehyde (0.6 g, 2.3 mmol) and 2,4-dinitrotoluene (0.5 g, 2.7 mmol). After the solution was stirred for 48 h at 80 °C, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and filtered. After removal of solvent under reduced pressure, the residue was purified by chromatography on silica gel (hexane/ethyl acetate, 1:2) to yield a orange solid (0.41 g, 41%). ¹H NMR (CDCl₃): δ 8.80 (d, 1H, *J*=2.4 Hz), 8.39 (dd, 1H, *J*=8.8, 2.4 Hz), 7.95 (d, 1H, J=8.8 Hz), 7.49 (d, 1H, J=16.0 Hz), 7.23 (d, 1H, J=16.0 Hz), 7.1-7.2 (m, 2H), 6.94 (d, 1H, J=8.0 Hz), 4.16 (t, 2H, J=4.8 Hz), 4.06 (t, 2H, J=6.8 Hz), 3.96 (t, 2H, J=4.8 Hz), 1.83-1.89 (m, 2H), 1.33-1.52 (m, 6H), 0.91 (t, 3H, *J*=7.1 Hz); ¹³C NMR (CDCl₃): δ 150.1, 149.6, 147.1, 145.8, 138.8, 138.0, 129.5, 128.5, 127.0, 121.8, 120.7, 119.2, 114.8, 111.5, 71.3, 69.2, 61.1, 31.5, 29.1, 25.6, 22.5, 14.0; MS (EI) *m*/*z*: 430 (M⁺, 10), 266 (15), 251 (20), 138 (32), 44 (100); IR (KBr): 3430, 1591, 1348 cm⁻¹; mp: 59–60 °C. Anal. Calcd for C₂₂H₂₆N₂O₇: C, 61.39; H, 6.09; N, 6.51. Found: C, 61.28; H, 6.17; N, 6.21%.

4.1.12. Synthesis of (E)-1-[2',5'-dimethyl-4'-(2"-hydroxyethoxy)-phenyl]-2-(2',4'-dinitrophenyl)-ethene (**4**)

A solution of 4-(2'-hydroxyethoxy)-2,5-dimethylbenzaldehyde 16 (1.94 g, 10.00 mmol), 2,4-dinitrotoluene (2 g, 10.98 mmol), diethylamine (4 mL) and glacial acetic acid (2 mL) in benzene was refluxed for 24 h using a Dean-Stark trap. The reaction solution was cooled to room temperature and the solvent removed. Afterwards, the residue was purified by chromatography on silica gel (hexane/ethyl acetate, 1:2) to give a yellow solid (1.47 g, 41%). ¹H NMR (CDCl₃): δ 8.71 (d, 1H, *I*=2.3 Hz), 8.43 (dd, 1H, *I*=8.8, 2.3 Hz), 8.29 (d, 1H, J=8.8 Hz), 7.64 (d, 1H, J=15.9 Hz), 7.49 (s, 1H), 7.26 (d, 1H, J=15.9 Hz), 6.83 (s, 1H), 4.01 (t, 2H, J=4.8 Hz), 3.74 (t, 2H, I=4.8 Hz), 2.43 (s, 3H), 2.17 (s, 3H); ¹³C NMR (DMSO- d_6): δ 157.8, 146.9, 145.2, 138.2, 136.5, 134.8, 129.0, 127.8, 126.9, 126.2, 124.0, 120.2, 119.1, 113.3, 69.6, 59.5, 19.3, 15.5; MS (EI) m/z: 358 (M⁺, 58), 314 (15), 193 (29), 165 (20), 149 (100), 91 (16); IR (KBr): 3426, 1508, 1346 cm⁻¹; mp: 177–178 °C. Anal. Calcd for C₁₈H₁₈N₂O₆·¹/₄ H₂O: C, 59.58; H, 5.14; N, 7.72. Found: C, 59.54; H, 5.02; N, 7.86%.

4.1.13. Synthesis of (E)-1-(2',4'-dinitrophenyl)-2-[4'-(2"ethylhexyloxy)-2',5'-dimethylphenyl]-ethene (**5**)

A flask was equipped with a Dean-Stark trap and a reflux condenser. The flask was charged with 4-(2'-ethylhexyloxy)-2,5dimethylbenzaldehyde 17 (1.5 g, 5.7 mmol), 2,4-dinitrotoluene (1.09 g, 6 mmol), diethylamine (2 mL) and glacial acetic acid (1 mL) in 100 mL of benzene. The mixture was heated under reflux for 24 h and was allowed to cool to ambient temperature and rotary evaporated. The residue was recrystallized from diethyl ether/hexane to give the product as an orange solid (1.1 g, 45%). ¹H NMR (CDCl₃): δ 8.78 (d, 1H, *I*=2.3 Hz), 8.38 (dd, 1H, *I*=8.8, 2.3 Hz), 7.95 (d, 1H, J=8.8 Hz), 7.50 (d, 1H, J=15.8 Hz), 7.43 (s, 1H), 7.40 (d, 1H, J=15.8 Hz), 6.65 (s, 1H), 3.88 (d, 2H, J=5.5 Hz), 2.44 (s, 3H), 2.22 (s, 3H), 1.72-1.78 (m, 1H), 1.32-1.52 (m, 8H), 0.95 (t, 3H, J=7.0 Hz), 0.92 (t, 3H, J=7.0 Hz); ¹³C NMR (acetone- d_6): δ 157.9, 146.9, 145.2, 138.2, 136.6, 134.9, 129.0, 127.8, 127.0, 126.2, 123.8, 120.2, 119.0, 113.1, 69.8, 30.6, 30.0, 28.4, 23.5, 22.4, 19.3, 15.4, 13.8, 11.0; MS (EI) m/z: 426 (M⁺, 46), 314 (14), 282 (23), 150 (100); IR (KBr): 1585, 1346 cm⁻¹; mp: 123–125 °C. Anal. Calcd for C₂₄H₃₀N₂O₅: C, 67.59; H, 7.09; N, 6.57. Found: C, 67.67; H, 7.21; N, 6.43%.

4.1.14. Synthesis of 3-cyano-4-{(E)-2'-[3"-hexyloxy-4"-(2"'hydroxyethoxy)phenyl]-1'-ethenyl}-5,5-dimethyl-2propanylidendinitrile-2,5-dihydrofuran (**6**)

To a solution of dry pyridine (20 mL), glacial acetic acid (0.12 mL), ammonium acetate (32 mg) and molecular sieves (3 Å pellets, 2 g) was added 3-hexyloxy-4-(2'-hydroxyethoxy)benzaldehyde 11 (0.6 g, 2.3 mmol) and 3-cyano-4,5,5-trimethyl-2-propanylidendinitrile-2,5-dihydrofuran¹⁸ (0.5 g, 2.5 mmol). After the solution was stirred for 48 h at 80 °C, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (20 mL) and filtered. After removal of solvent under reduced pressure, the residue was purified by chromatography on silica gel (hexane/ethyl acetate, 1:3) to yield a red solid (0.31 g, 30%). ¹H NMR (CDCl₃): δ 7.57 (d, 1H, J=16.3 Hz), 7.23 (dd, 1H, J=8.4, 2.0 Hz), 7.10 (d, 1H, J=2.0 Hz), 6.96 (d, 1H, J=8.4 Hz), 6.87 (d, 1H, J=16.3 Hz), 4.20 (t, 2H, J=4.9 Hz), 4.06 (t, 2H, J=6.6 Hz), 4.00 (t, 2H, J=4.9 Hz), 1.76-1.84 (m, 2H), 1.34-1.53 (m, 6H), 0.91 (t, 3H, J=7.0 Hz); ¹³C NMR (acetone- d_6): δ 178.6, 177.2, 155.5, 151.5, 149.9, 129.7, 126.9, 115.5, 115.3, 114.8, 114.1, 113.4, 112.6, 100.5, 100.0, 72.7, 71.0, 62.2, 56.8, 33.3, 31.0, 27.4, 27.1, 24.3, 15.3; MS (EI) *m*/*z*: 447 (M⁺, 18), 324 (24), 319 (48), 240 (10), 44 (100); IR (KBr): 3472, 2226 cm⁻¹; mp: 178–180 °C. Anal. Calcd for $C_{26}H_{29}N_3O_4 \cdot 1H_2O$: C, 67.08; H, 6.71; N, 9.03. Found: C, 67.35; H, 6.45; N, 9.47%.

4.1.15. Synthesis of 3-cyano-4-{(E)-2'-[4"-(2"'-hydroxyethoxy)-2",5"-dimethylphenyl]-1'-ethenyl}-5,5-dimethyl-2propanylidendinitrile-2,5-dihydrofuran (**7**)

A mixture of 4-(2'-hydroxyethoxy)-2,5-dimethylbenzaldehyde 16 (1.98 g, 10.24 mmol), 3-cyano-4,5,5-trimethyl-2-propanylidendinitrile-2,5-dihydrofuran (2.80 g, 14.05 mmol), sodium hydride (0.01 g. 0.42 mmol) and anhydrous *N.N*-dimethylformamide (20 mL) was refluxed for 24 h. The mixture was poured into water (50 mL) followed by extraction with dichloromethane. The organic extract was washed with water and dried. After removal of solvent under reduced pressure, the residue was purified by chromatography on silica gel (hexane/ethyl acetate, 1:3) to afford a red solid (1.96 g, 51%). ¹H NMR (acetone- d_6): δ 8.38 (d, 1H, J=16.1 Hz), 7.87 (s, 1H), 7.12 (d, 1H, J=16.1 Hz), 6.95 (s, 1H), 4.19 (t, 1H, J=4.8 Hz), 3.93 (t, 1H, J=4.8 Hz), 2.50 (s, 3H), 2.21 (s, 3H), 1.85 (s, 6H); ¹³C NMR (DMSO-d₆): δ 177.5, 176.1, 160.7, 144.8, 140.6, 129.2, 125.0, 127.4, 113.5, 112.9, 112.3, 112.1, 112.0, 99.0, 94.6, 70.0, 59.7, 59.4, 53.1, 24.8, 19.0, 15.4; MS (EI) m/z: 375 (M⁺, 100), 331 (58), 316 (18), 149 (20), 115 (8), 91 (16); IR (KBr): 3436, 2229 cm⁻¹; mp: 235–237 °C. Anal. Calcd for C₂₂H₂₁N₃O₃·1H₂O: C, 67.16; H, 5.89; N, 11.68. Found: C, 67.27; H, 5.79; N, 11.95%.

4.1.16. Synthesis of 3-cyano-4-{(*E*)-2'-[4"-(2"' -ethylhexyloxy)-2",5"-dimethylphenyl]-1'-ethenyl}-5,5-dimethyl-2propanylidendinitrile-2,5-dihydrofuran (**8**)

A mixture of 4-(2'-ethylhexyloxy)-2,5-dimethylbenzaldehyde 17 (1.34 g, 5.12 mmol), 3-cyano-4,5,5-trimethyl-2-propanylidendinitrile-2,5-dihydrofuran (1.4 g, 7.03 mmol), sodium hydride (5 mg, 0.21 mmol) and dry DMF (25 mL) was refluxed for 24 h under inert atmosphere. The mixture was poured into water (25 mL) followed by extraction with dichloromethane. The organic extract was washed with water and dried. After removal of solvent under reduced pressure, the residue was purified by chromatography on silica gel (hexane/ethyl acetate, 1:3) to afford a red solid (1.25 g, 55%). ¹H NMR (CDCl₃): δ 8.12 (d, 1H, J=16.1 Hz), 7.56 (s, 1H), 6.77 (d, 1H, J=16.1 Hz), 6.69 (s, 1H), 3.92 (d, 1H, J=5.5 Hz), 2.47 (s, 3H), 2.22 (s, 3H), 1.77 (s, 6H), 1.30–1.53 (m, 8H), 0.94 (t, 3H, *J*=7.0 Hz), 0.90 (t, 3H, *I*=7.0 Hz); ¹³C NMR (acetone- d_6): δ 178.9, 177.7, 163.3, 146.9, 142.8, 130.8, 127.4, 127.0, 115.3, 114.2, 114.1, 113.5, 100.4, 97.8, 72.3, 56.4, 41.2, 32.3, 30.7, 26.9, 25.7, 24.7, 20.7, 16.9, 15.3, 12.4; MS (EI) *m*/*z*: 443 (M⁺, 23), 331 (100); IR (KBr): 2226 cm⁻¹; mp: 174–175 °C. Anal. Calcd for C₂₈H₃₃N₃O₂·¹/₂ H₂O: C, 74.31; H, 7.57; N, 9.28. Found: C, 74.14; H, 7.57; N, 9.28%.

4.2. Optical measurements

UV–vis absorption spectra of the reported compounds were measured in MeOH, CH₂Cl₂ and DMSO solutions.

The quadratic nonlinear response of compounds **1–8** was measured by the Electric Field Induced Second Harmonic generation (EFISH) technique. The fundamental wavelength at 1.907 μ m was generated in a hydrogen Raman cell pumped by the 1.064 μ m light from a Q-switched Nd:YAG laser (10 pps, 8 ns/pulse). The vertically polarized fundamental beam was split in two. One of them was focused into a wedge shaped EFISH cell. The other one, acting as a reference beam, excited a NPP [*N*-(4-nitrophenyl)-L-prolinol] powder sample whose second harmonic signal is used to correct for laser fluctuations. The voltage applied through the 2 mm separated electrodes of the liquid sample cell was 4.5 kV. The output light from the sample was detected with a photomultiplier, with suitable interference filters to block the fundamental beam out.

The values of $\mu\beta$ have been determined in CH₂Cl₂. Static $\mu\beta(0)$ values were deduced from the experimental results using a two-level dispersion model.¹⁹ Two different solutions were measured, at least. One of them was ca. 7×10^{-3} M, and the other ones were more

diluted. In the case of compound **4**, it was necessary to use even lower concentrations. Its quite low NLO response made it difficult to obtain accurate $\mu\beta$ values in CH₂Cl₂. Therefore, the molecular non linearity of compound **4** was measured in a highly polar solvent as DMSO. For sake of comparison, compound **2** was measured in DMSO as well. Under the same experimental conditions, the $\mu\beta$ value of the azo dye Disperse Red 1 (DR1) was determined to be 670×10^{-48} esu in CH₂Cl₂ and 600×10^{-48} esu in DMSO.

4.3. Computational procedures

Theoretical calculations were performed by means of the Gaussian 03 program. TD-DFT calculations used the B3P864 functional and the 6-31G(d) basis set. Molecular hyperpolarizabilities at zero frequency were calculated by the Coupled Perturbed Hartree Fock Method (CPHF) using the HF/6-31G* model chemistry and the default parameters provided by the 'polar' keyword.

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