Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 64 (2008) 3772–3781
Tetrahedron
www.elsevier.com/locate/tet

Synthesis and nonlinear optical properties of linear and Λ-shaped pyranone-based chromophores

Guy Koeckelberghs [a,b], Leen De Groof [a], Javier Pérez-Moreno [b], Inge Asselberghs [b], Koen Clays [b], Thierry Verbiest [b], Celest Samyn [a,*]

[a] *Laboratory of Macromolecular and Physical Organic Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium*
[b] *Laboratory of Molecular Electronics and Photonics, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Heverlee, Belgium*

Received 10 January 2008; received in revised form 4 February 2008; accepted 5 February 2008
Available online 7 February 2008

Abstract

New, pyranone-based chromophores were synthesized and their (nonlinear) optical properties were measured. The chromophores were prepared by first condensing an electron withdrawing group with pyranone, followed by reaction with an aldehyde-functionalized π-conjugated bridged donor molecule. This approach enables one to easily incorporate the pyranone moiety and to prepare both linear and Λ-shaped chromophores. The (nonlinear) optical properties were measured using femtosecond hyper-Rayleigh scattering. These measurements demonstrated the advantages of this approach.

Keywords: Nonlinear optics; Chromophores; Pyranone; Λ-Shaped chromophores

1. Introduction

The continuous interest in poled polymers for nonlinear optical (NLO) applications has resulted in the development of numerous chromophores and a profound understanding of their structure–property relationship.[1,2] Most chromophores are linear, rigid, π-conjugated molecules, end-capped with an electron donating and electron withdrawing group. The DπA-structure, present in these molecules, triggers their large second-order hyperpolarizabilities. Apart from linear DπA chromophores, also Λ-shaped chromophores have been developed.[3–11] Their assets are double. First, depending on the angle between the constituting linear DπA parts, the hyperpolarizability of Λ-shaped chromophores can be higher than the hyperpolarizability of the individual, linear chromophores they consist of. Second, unlike linear chromophores, which are usually incorporated as side-chains in polymer systems, Λ-shaped chromophores can be built-in into accordion-type polymers.[6,9,11,12] After poling—to obtain the necessary macromolecular noncentrosymmetry—accordion polymers tend to relax slower, resulting in a more stable NLO response.

Some 2,6-dimethyl-4*H*-pyran-4-on (pyranone)-based chromophores, both linear and Λ-shaped, have already been prepared and studied. The advantage of the incorporation of the pyranone unit is that it not only extends the π-conjugation in comparison with analogous chromophores, which lack this group, but also that it gives the possibility to prepare both linear and Λ-shaped chromophores.[3,10,11] The Λ-shaped pyranone-based chromophores, which have been prepared and studied before, were typically equipped with rather moderate electron withdrawing groups (usually a dicyanomethylene group) and/or a poor variety of rather simple π-conjugated systems.

In this manuscript, the synthesis and (nonlinear) optical properties of some new linear and Λ-shaped chromophores are described. They all consist of a pyranone unit, which is functionalized with different electron withdrawing groups and one (linear) or two (Λ-shaped) amino-substituted

* Corresponding author. Tel.: +32 (0) 16 32 74 38; fax: +32 (0) 16 32 79 90.
E-mail address: celest.samyn@chem.kuleuven.be (C. Samyn).

0040-4020/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.02.009

π-conjugated system(s). A variety of moderate to excellent electron withdrawing groups are used, together with an extended π-conjugated bridge. The (nonlinear) optical properties of both types of chromophores are compared and evaluated in detail.

2. Results and discussion

2.1. Chromophore design

Several parameters in the design of the chromophores were taken into account. A general structure of the chromophores is presented in Figure 1. All chromophores contain an amino functionality as donor, while four different acceptor groups were incorporated. Special attention has been given to the π-conjugated bridge, in which a central thiophene moiety was incorporated. The choice of the thiophene moiety can be motivated as follows: on one hand, Marder et al. have shown that very easily polarizable spacers, such as polyenic spacers, when substituted with strong electron donating and electron withdrawing groups, show minor NLO properties.[13] Moreover, polyenic chromophores tend to have low thermal and photochemical stabilities. Aromatic spacers based on benzene, on the other hand, show superior stability, but are much less polarizable. Thiophene-based chromophores, however, have shown to combine the necessary stability with large second-order nonlinear hyperpolarizabilities.[14–21] As mentioned earlier, a pyranone unit was incorporated to further extent the conjugation length.

Next, also the shape of the (linear) chromophores was taken into account. When incorporated to further extend the polymer system, the highly dipolar chromophores interact with each other above a critical chromophore concentration, resulting in a centrosymmetric, NLO inactive, ensemble. These unwanted interactions can be diminished by carefully substituting the linear chromophore with alkyl groups, resulting in an ellipsoidal shape.[22] Moreover, these alkyl groups increase the solubility of the chromophore.

Finally, the chromophores are substituted with one (linear chromophores) or two (Λ-shaped chromophores) alcohol functionalities, allowing them to be covalently attached to a polymer backbone (linear chromophores) or to be built-in in accordion polymers (Λ-shaped chromophores). The synthesis and nonlinear optical properties of those polymers, including the influence of the molecular structure of the polymer (linear vs accordion) on their properties, are now under investigation.

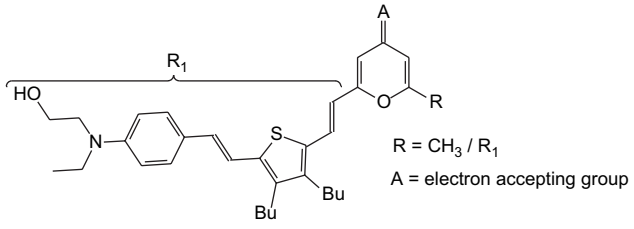


Figure 1. General structure of the chromophores.

2.2. Chromophore synthesis

The synthesis of the chromophores is displayed in Scheme 1. First, aldehyde **1** is reduced with $NaBH_4$ to the corresponding alcohol **2**, which is converted into the phosphonium salt **3** in a one-step reaction with triphenyl phosphonium bromide. Next, **3** was reacted with **4** using a Wittig reaction, rendering **5** as a cis/trans mixture. Although a Horner reaction would result in pure trans-alkene, a Wittig reaction was preferred to introduce a double bond. The reason for this approach is the fact that we encountered great difficulties in converting the alcohol **2** into its corresponding chloride. Presumably, polymerization of the benzylic halide occurs. Compound **5** was protected as an acetate ester, after which the aldehyde functionality was introduced by a Vilsmeyer reaction. After deprotection of **7**, the building block **8** was obtained, still as a mixture of cis and trans isomers.

The key step in the chromophore synthesis is the Knoevenagel condensation of **9a–d** with aldehyde **8**. This renders all-trans chromophores. Compounds **9a–d** were prepared by a Knoevenagel condensation of **10** with the appropriate acceptor molecules (Scheme 2).

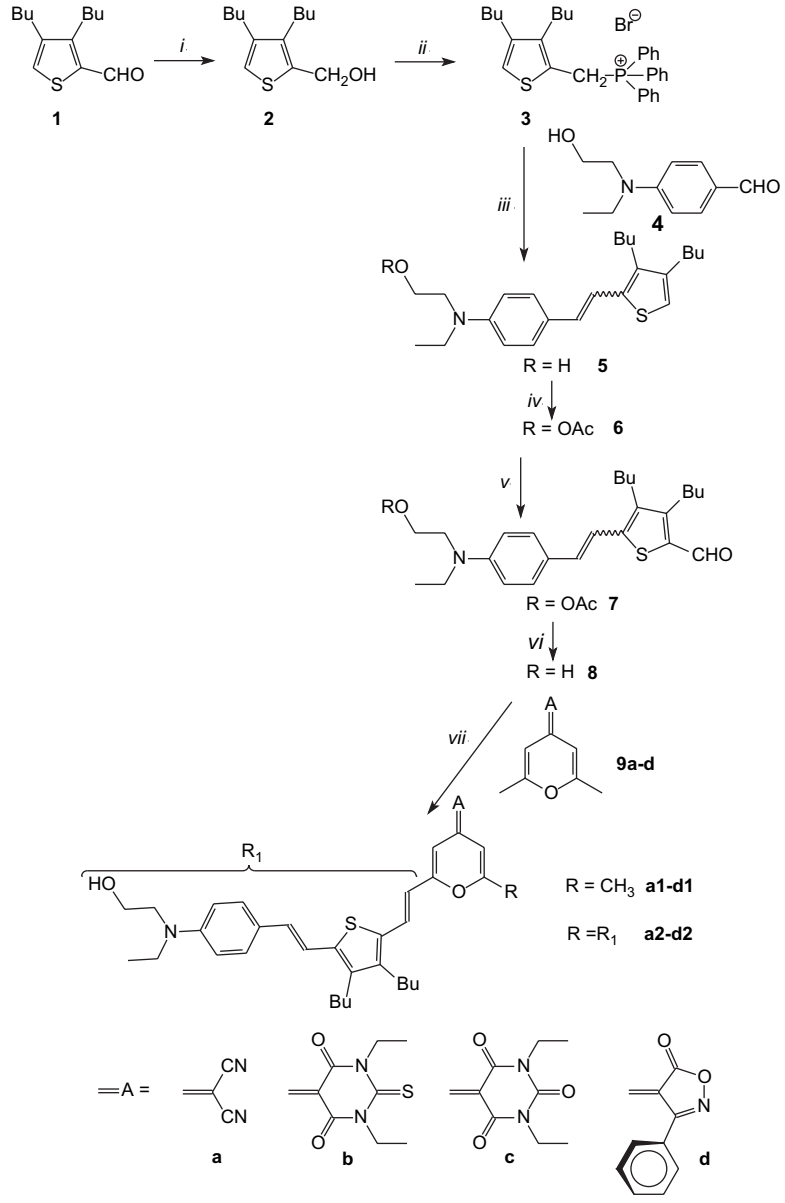
Although it would be advantageous for the synthesis of these particular chromophores to first condense **10** with **8** and then react the acceptor molecules **11–14** with **15** (since that approach would reduce the total number of reaction steps, Scheme 3), the former pathway was preferred, since it allows to condense a large number of different aldehydes with **9a–d**. Consequently, this is an easy, fast and general way to prolong the conjugation length of already existing chromophores—which are typically synthesized by condensing their corresponding aldehydes with the appropriate acceptor molecules—by two double bonds. It is worthwhile to mention that it was also tried to condense **10** first with **8** and then react the acceptor molecules with **15**. Unfortunately, this synthesis failed at the first stage.

In the condensation reaction of the pyranone derivatives **9a–d** with aldehyde **8**, both mono and di-reaction takes places, resulting in the linear (**a1–d1**) and Λ-shaped (**a2–d2**) chromophores, respectively. In all cases, they could easily be separated by column chromatography.

During the synthesis of **d1**, **9d**, which is asymmetric, can react with the aldehyde at each of both methyl groups, resulting in two different mono-reacted chromophores. Unfortunately, both isomers could not be separated and purified; therefore, that chromophore was not further investigated.

2.3. Linear optical properties

The optical properties of the chromophores are listed in Table 1. In order to avoid the influence of the intramolecular H-bridge between the terminal OH and the amino functionality, which weakens the electron donating capacity of the dialkylamino functionality, the alcohol groups of the chromophores **a–d** were converted into acetate groups for this study. The acylation was performed with acetic anhydride (Scheme 4). No base was added to prevent nucleophilic attack on the

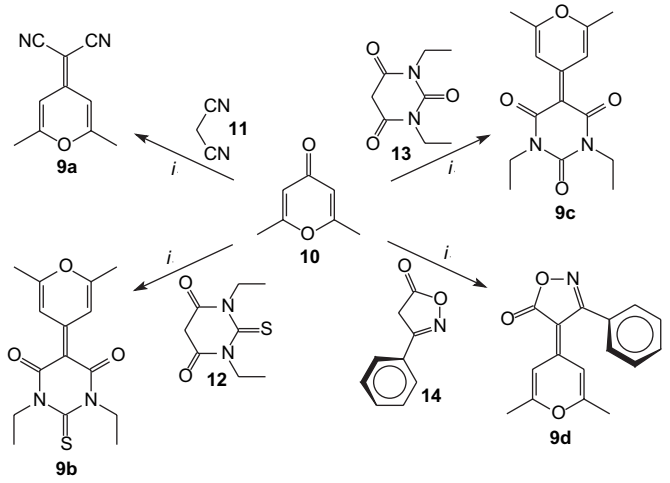


Scheme 1. Synthesis of the chromophores. Reagents and conditions: (i) (1) $NaBH_4$, (2) H_2O; (ii) $P(C_6H_5)_3 \cdot HBr$; (iii) NaOEt; (iv) Ac_2O; (v) $OPCl_3$/DMF; (vi) NaOH (aq); (vii) piperidine, H_2O.

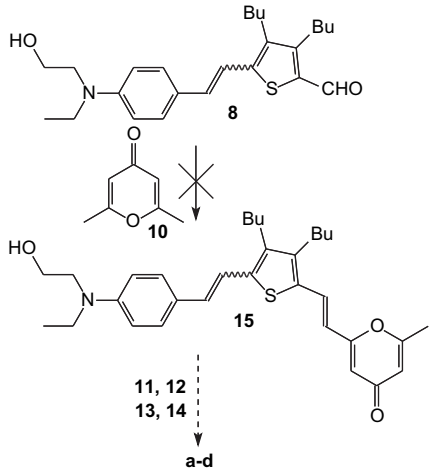
π-conjugated bridge.[23] It must be noted that it was also tried to convert the hydroxyl group to a *tert*-butyldimethylether, but that the reaction resulted in very low yields and highly impure reaction compounds. Probably, nucleophilic attack of the base present (DMAP) is the most common side-reaction.

Although the general belief is that intramolecular H-bridges on the amino functionality would weaken its electron donating capability, this effect is not observed upon comparing the alcohol-terminated chromophores **xi** (**x**=**a**, **b**, **c** or **d**; **i**=1 or 2) with the acetate-terminated ones **xi**−**OAc**. Quite on the contrary, all **xi**−**OAc** show a wavelength of maximal absorption that is 10 nm blue-shifted with respect to the maximum for the **xi** variants. This points at a minor negative electronic effect on the donor, rather than the expected positive effect through preventing H-bridging. This spectral shift (10 nm) is minor with respect to the shifts that are induced by the structural modifications for this study (linear or Λ-shape, and variation of electron acceptor strength). Because (intermolecular) H-bridges can also have a concentration−dependant effect, especially on even-order nonlinear properties because of the importance of noncentrosymmetry, the second-order nonlinear optical properties have therefore only been determined of the acetate-terminated **xi**−**OAc** variants.

The effect of the use of our pyranone conjugated moiety is already clearly observed in the red-shift for the wavelength of maximal absorption for our new pyranone-based chromophores when comparing with the analogous chromophores without this moiety.[16] This clearly demonstrates already in the linear optical properties one of the assets of our protocol, e.g., the increase of the conjugation length, resulting in a higher λ_{max} by simply condensing aldehyde **8** with the pyranone-based electron-accepting groups **9a**−**d** instead of the electron-accepting groups **11**−**14**.



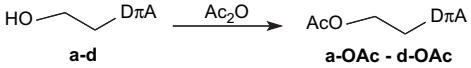
Scheme 2. Synthesis of the pyranone derivatives **9a–d**. Reagents and conditions: (i) Ac_2O.



Scheme 3. Alternative pathway to chromophores **a–d**.

Table 1
Linear optical properties of the chromophores in THF

Chromophore	λ_{max} (nm)	ε (10^3 l mol^{-1} cm^{-1})	FWHM (nm)	S (M^{-1} cm^{-1} nm)	Ratio
a1	534	43.0			
a1–OAc	523	34.0	140	4760	1
a2	564	65.8			
a2–OAc	553	69.0	158	10,900	2.3
b1	577	43.7			
b1–OAc	567	43.5	140	6090	1
b2	601	54.3			
b2–OAc	591	68.5	177	12,154	2
c1	549	45.0			
c1–OAc	539	42.0	130	5460	1
c2	579	64.4			
c2–OAc	566	62.5	160	10,000	1.8
d2	590	68.3			
d2–OAc	580	80.0			



Scheme 4. Acylation of the chromophores **a–d**.

When comparing the effect of the different electron acceptors on the linear optical properties, it is clear that the dicyanomethylene benchmark acceptor group is the weakest in our series. The wavelengths of maximal observation progressively shift to larger values upon replacing this benchmark by barbituric acid, thiobarbituric acid and isoxazolone. This will have its influence on the second-order nonlinear optical properties (vide infra).

The effect of the molecular structural motif (linear vs Λ-shaped) is already visible in their different linear optical properties. Careful inspection of the absorption spectra not only reveals a substantial red-shift of the wavelength of maximal absorption for the Λ-shaped motives with respect to the linear molecules. The former molecules, incorporating two chromophoric subunits sharing the pyranone-acceptor moiety, also exhibit a larger oscillator strength and a larger full-width-half-max (FWHM) spectral breath (a consequence of a second transition, showing up as a shoulder to the right of the maximum). A similar behaviour has also been observed by Moylan et al.[3] They assumed that two transitions are present in Λ-shaped chromophores, closely situated to the single transition of the parent linear chromophore. The absorption of the Λ-shaped chromophores is a superposition of two transitions, which can explain the red-shift and significant increase in extinction coefficient.

We have analyzed the spectra in terms of their maximum extinction coefficient (in M^{-1} cm^{-1}) and FWHM (in nm), resulting in an approximated area S (in M^{-1} cm^{-1} nm). This integrated linear property relates very nicely to the number of chromophoric subunits in the molecules: around 5000 M^{-1} cm^{-1} nm for the **x1–OAc** molecules versus around 10,000 M^{-1} cm^{-1} nm for the **x2–OAc** variants (Table 1).

2.4. Second-order nonlinear optical properties

The second-order nonlinear optical properties of the acetate-terminated chromophores have been determined in THF. We have used femtosecond hyper-Rayleigh scattering (HRS) at 800 nm to determine the depolarization ratio and the first hyperpolarizability (molecular second-order nonlinear polarizability) of the molecules in solution. The femtosecond pulses at high repetition rate provide the means to check for multiphoton fluorescence contribution to the HRS signal. We have clearly observed that the apparent first hyperpolarizability as a function of amplitude modulation frequency is constant. This is a clear experimental proof of the absence of this potential source of systematic overestimation of the first hyperpolarizability.

Concerning the molecular motive (linear or Λ-shaped), the first observation relates the HRS depolarization ratio ρ. For the linear molecules **x1–OAc**, this ρ-value should be relatively high (in the limit of strictly only one hyperpolarizability tensor

element β_{zzz} contributing along the unique molecular z-axis, in combination with a limiting experimental numerical aperture of zero, this ρ-value should be 5). For Λ-shaped molecules **x2–OAc** with more off-diagonal tensor elements contributing, this depolarization ratio ρ should be lower, with a lower limit of 1.5.[8] A larger ρ-value for all **x1–OAc** and the lower ρ-value for all **x2–OAc** is consistently observed (Table 2).

Next, from the intensity HRS measurements, the overall, symmetry-independent β_{HRS} can be determined. A slightly larger one can be observed for the β_{HRS} of the Λ-shaped chromophores. For a more detailed analysis of this overall response towards specific hyperpolarizability tensor elements, an assumption about the (approximate, effective for nonlinear optics) molecular symmetry should be made. This effective symmetry is largely determined by the relative orientation of the electron donating and accepting groups and the conjugation path, rather than by saturated substitutions. The symmetry for the **x1–OAc** molecular motives can be $C_{\infty,v}$ with a single β_{zzz} hyperpolarizability tensor element. For the **x2–OAc** Λ-shaped molecules, C_{2v} symmetry with two hyperpolarizability tensor elements β_{zzz} and β_{zxx} can be assumed. It is also assumed that the Λ-shaped molecules are built up from two monomeric **x1–OAc** subunits with a monomeric hyperpolarizability $\beta_{mono}=\beta_{zzz}$. The relations between these parameters as a function of the angle between the two subunits in the Λ-shaped chromophore based on pyranone (120°) have been enumerated in earlier publications about correlated chromophores.[8,24] The fact that the retrieved β_{mono} for the Λ-shaped molecules are within experimental error identical to the β_{zzz} for the monomeric **x1–OAc** molecules, validates our assumption that the Λ-shaped chromophores can indeed be considered as consisting of two correlated monomeric subunits with an angle of 120° between the two arms.

Continuing the analysis of our use of the pyranone as a conjugated building block, we observe that also concerning their second-order nonlinear optical properties, our chromophores outperform their non-pyranone-based analogues.[16] This observation further justifies our chromophore design strategy based on the pyranone moiety.

The trend in hyperpolarizability value upon increasing the electron-accepting capacity in the **x1–OAc** series clearly follows the expectations from the linear optical properties: the dicyanomethylene benchmark shows the lowest hyperpolarizability and this value steadily increases for the barbituric acid and thiobarbituric acid and reaches its maximum for isoxazolone as acceptor moiety.

When comparing the hyperpolarizability values between monomeric **x1–OAc** and Λ-shaped dimeric chromophores **x2–OAc**, only the overall HRS response in terms of β_{HRS} can be analyzed without taking the symmetry into consideration. A slight improvement in overall nonlinear response is observed for the Λ-shaped molecules. The detailed analysis in terms of contributing tensor elements (see above) clearly reveals the correlated nature of the two.

Due to the correlated nature of the two chromophoric subunits at 120° with respect to each other, it can be expected that the Λ-shaped chromophores will perform better in nonlinear optical devices such as an electro-optic modulator, than their linear counterparts. The reason is double. First, they will more effectively be aligned, due to their larger dipole moment, which increases the macroscopic nonlinear optical response. Second, the polarization sensitivity of any nonlinear device made of these Λ-shaped molecules will be less. There will be more nonlinear response irrespective of the incoming polarization, because of the off-diagonal tensor elements present in these Λ-shaped molecules.

Table 2
Second-order nonlinear optical properties of the chromophores in THF

Chromophore	ρ	β_{HRS} (10^{-30} esu)	β_{zzz} (10^{-30} esu)	β_{zxx} (10^{-30} esu)	β_{mono} (10^{-30} esu)
a1–OAc	2.4±0.3	260±20	630±50	—	630±50
a2–OAc	1.7±0.2	300±20	150±10	450±30	600±40
b1–OAc	2.0±0.2	340±20	830±50	—	830±50
b2–OAc	1.4±0.2	490±20	250±10	750±30	990±40
c1–OAc	2.2±0.2	350±20	850±50	—	850±50
c2–OAc	1.5±0.2	380±20	190±10	580±30	770±40
d2–OAc	1.6±0.2	400±40	200±20	620±60	800±80

3. Conclusion

New, pyranone-based chromophores were synthesized and their linear and second-order nonlinear optical properties were measured. The chromophores were prepared by first condensing an electron withdrawing group to pyranone, followed by reaction with an aldehyde-functionalized π-conjugated bridge donor molecule. This approach enables one to easily incorporate the pyranone moiety in new chromophores and to prepare both linear and Λ-shaped chromophores. The nonlinear optical properties were measured using femtosecond hyper-Rayleigh scattering and analyzed assuming a simple symmetry. The measurements of the (nonlinear) optical properties demonstrate the advantages of this synthetic approach for chromophores with enhanced properties.

4. Experimental

4.1. General

^{1}H and ^{13}C nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz. All starting materials were purchased from Acros Organics, Fluka, Merck or Aldrich and were used as received. *N*,*N*-dimethylformamide (DMF) was distilled over CaH_2 and further dried over molecular sieve (4 Å). Compounds **1**[25] and **9a**[26] were synthesized according to literature procedures. The experimental details for hyper-Rayleigh scattering experiments at 800 nm were as previously described.[27]

4.2. Synthesis of 3,4-dibutyl-5-(hydroxymethyl)thiophene **2**

A solution of **1** (236 mmol, 53.2 g) in ethanol (360 mL) was added dropwise at 0 °C to a suspension of $NaBH_4$

(236 mmol, 8.68 g) in ethanol (90 mL). The reaction mixture was stirred overnight at room temperature in a flask, equipped with a $CaCl_2$-tube. The solvent was removed and the reaction mixture was redissolved in dichloromethane and washed with a saturated NH_4Cl-solution. The organic layer was separated and dried over $MgSO_4$. The crude reaction product was purified with column chromatography (silica gel; eluents: dichloromethane/hexane 4/6) and isolated as an oil.

Yield: 46.4 g (88%).

^{1}H NMR ($CDCl_3$, ppm): δ=6.87 (s, 1H), 4.75 (s, 2H), 2.51 (m, 4H), 1.65 (m, 4H), 1.44 (m, 4H), 0.97 (t, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=142.5, 140.4, 134.2, 119.2, 64.5, 33.1, 31.9, 27.3, 26.7, 22.9, 22.5, 14.0, 13.9.

MS: *m*/*z*=225 (M^+).

$C_{13}H_{22}OS$ calcd: C 68.97%, H 9.80%; found: C 68.86%, H 9.68%.

4.3. Synthesis of (3,4-dibutyl-5-thienylmethyl)triphenylphosphonium bromide ***3***

Triphenylphosphonium bromide (110 mmol, 39.0 g) and **2** (110 mmol, 24.9 g) were dissolved in acetonitrile (280 mL). After refluxing for 4 h, the solution was concentrated to 100 mL and the product was precipitated in diethylether. The precipitate was filtered off, washed with diethylether and dried.

Yield: 48.0 g (89%).

Mp: 174 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=7.66 (dd, 15H), 6.77 (s, 1H), 5.38 (d, *J*=12.4 Hz, 2H), 2.36 (t, 2H), 1.90 (t, 2H), 1.48 (m, 2H), 1.35 (m, 2H), 1.21 (m, 2H), 1.00 (m, 2H), 0.94 (t, 3H), 0.77 (t, 3H).

^{13}C NMR ($CDCl_3$, ppm): δ=143.7, 142.4, 135.2, 134.2, 130.2, 121.0, 118.3, 117.2, 32.0, 28.6, 26.3, 25.7, 22.8, 22.4, 13.9, 13.8.

MS: *m*/*z*=552 (M^+), 470 (M^+-Br).

4.4. Synthesis of 2-[N-ethyl-N-[4-[2-[2-(3,4-dibutyl)-thienyl]ethenyl]phenyl]amino]ethanol ***5***

A solution of NaOEt (150 mmol, 500 mL, 0.3 M) in ethanol was added dropwise to a solution of **4** (100 mmol, 19.3 g) and **3** (100 mmol, 55.3 g) in ethanol (1 L). After the reaction mixture was refluxed for 5 h, it was cooled and the solvent was removed in vacuo. The residue was dissolved in dichloromethane, washed with water and dried over $MgSO_4$. The crude reaction product was purified with column chromatography (silica gel; eluents: ethylacetate) and isolated as an oil in a mixture of cis/trans isomers (30/70).

Yield: 26.7 g (69%).

^{1}H NMR ($CDCl_3$, ppm): trans: δ=7.35 (d, 2H), 7.05 (d, *J*=16.8 Hz, 1H), 6.81 (d, *J*=16.8 Hz, 1H), 6.73 (d, 2H), 6.71 (s, 1H), 3.82 (m, 2H), 3.47 (m, 4H), 2.62 (t, 1H), 2.50 (t, 4H), 1.60 (m, 4H), 1.44 (m, 4H), 1.19 (t, 3H), 0.99 (t, 6H).

cis: δ=7.18 (d, 2H), 6.65 (d, 2H), 6.48 (d, *J*=8.8 Hz, 1H), 6.46 (d, *J*=8.8 Hz, 1H), 6.71 (s, 1H), 3.82 (m, 2H), 3.47 (m, 4H), 2.62 (t, 1H), 2.50 (t, 4H), 1.60 (m, 4H), 1.44 (m, 4H), 1.19 (t, 3H), 0.99 (t, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=148.0, 143.5, 139.2, 138.0, 130.8, 127.8, 127.7, 126.6, 117.5, 113.2, 60.6, 52.9, 46.1, 33.6, 32.3, 29.2, 27.5, 23.2, 23.1, 14.4, 12.4.

MS: *m*/*z*=385 (M^+), 354 ($M^+-C_8H_3O$).

$C_{24}H_{35}NOS$ calcd: C 74.76%, H 9.15%, N 3.63%; found: C 74.58%, H 8.95%, N 3.54%.

4.5. Synthesis of 2-[N-ethyl-N-[4-[2-[2-(3,4-dibutyl)-thienyl]ethenyl]phenyl]amino]ethylethanoate ***6***

A mixture of **5** (10.0 mmol, 3.86 g) and acetic anhydride (5 mL) was stirred at 60 °C for 12 h in a flask, equipped with a $CaCl_2$-tube. Acetic acid and the excess acetic anhydride was evaporated and the crude mixture was purified with column chromatography (silica gel; eluents: dichloromethane) and isolated as an oil in a mixture of cis/trans isomers (10/90).

Yield: 3.90 g (90%).

^{1}H NMR ($CDCl_3$, ppm): trans: δ=7.34 (d, 2H), 7.03 (d, *J*=16.1 Hz, 1H), 6.79 (d, *J*=16.1 Hz, 1H), 6.69 (d, 2H), 6.68 (s, 1H), 4.23 (t, 2H), 3.56 (t, 2H), 3.42 (q, 2H), 2.61 (t, 2H), 2.48 (t, 2H), 2.04 (s, 3H), 1.60 (m, 4H), 1.42 (m, 4H), 1.18 (t, 3H), 0.95 (t, 6H).

cis: δ=7.15 (d, 2H), 6.59 (d, 2H), 6.45 (d, *J*=8.8 Hz, 1H), 6.42 (d, *J*=8.8 Hz, 1H), 6.68 (s, 1H), 4.23 (t, 2H), 3.56 (t, 2H), 3.42 (q, 2H), 2.61 (t, 2H), 2.48 (t, 2H), 2.04 (s, 3H), 1.60 (m, 4H), 1.42 (m, 4H), 1.18 (t, 3H), 0.95 (t, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=171.0, 147.0, 143.1, 138.7, 137.6, 127.5, 127.4, 125.9, 116.9, 112.0, 61.7, 48.8, 45.3, 33.2, 31.9, 28.8, 26.7, 22.8, 22.7, 20.9, 14.0, 12.3.

MS: *m*/*z*=427 (M^+), 354 ($M^+-C_3H_5O_2$).

$C_{26}H_{37}NO_2S$ calcd: C 73.02%, H 8.72%, N 3.28%; found: C 72.89%, H 8.65%, N 3.17%.

4.6. Synthesis of 2-[N-ethyl-N-[4-[2-[2-(3,4-dibutyl)thien-5-al]ethenyl]phenyl]amino]ethylethanoate ***7***

$OPCl_3$ (10.7 mmol, 1.0 mL) was dropwise added to a solution of **6** (8.90 mmol, 3.80 g) and DMF (23.2 mmol, 1.8 mL) in dry dichloroethane (200 mL). The mixture was refluxed for 18 h, cooled and poured into a NaOAc-solution (800 mL, 1 M). After the mixture was stirred vigorously for 2 h, the layers were separated and the organic phase was dried over $MgSO_4$. The crude reaction product was purified with column chromatography (silica gel; eluents: dichloromethane) and isolated as a solid in a mixture of cis/trans isomers (10/90).

Yield: 2.50 g (62%).

^{1}H NMR ($CDCl_3$, ppm): trans: δ=9.97 (s, 1H), 7.40 (d, 2H), 7.08 (d, *J*=16.1 Hz, 1H), 6.99 (d, *J*=16.1 Hz, 1H), 6.72 (d, 2H), 4.25 (t, 2H), 3.60 (t, 2H), 3.45 (q, 2H), 2.86 (t, 2H), 2.63 (t, 2H), 2.10 (s, 3H), 1.4 (m, 8H), 1.23 (t, 3H), 0.96 (t, 6H).

cis: δ=9.97 (s, 1H), 7.15 (d, 2H), 6.59 (d, 2H), 6.39 (d, *J*=8.8 Hz, 1H), 6.34 (d, *J*=8.8 Hz, 1H), 4.25 (t, 2H), 3.60 (t, 2H), 3.45 (q, 2H), 2.86 (t, 2H), 2.63 (t, 2H), 2.10 (s, 3H), 1.4 (m, 8H), 1.23 (t, 3H), 0.96 (t, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=181.7, 171.0, 153.0, 148.3, 148.0, 140.3, 134.0, 132.6, 128.4, 124.5, 115.2, 111.9, 61.5, 48.7, 45.4, 34.4, 33.3, 26.7, 26.1, 22.8, 20.9, 13.9, 12.3.

MS: *m*/*z*=455 (M^+), 427 (M^+-CO), 382 ($M^+-C_3H_5O_2$).

$C_{27}H_{37}NO_3S$ calcd: C 71.17%, H 8.18%, N 3.07%; found: C 70.78%, H 8.05%, N 2.99%.

4.7. Synthesis of 2-[2-[4-[N-ethyl-N-(2-hydroxyethyl)amino]-phenyl]ethenyl]-3,4-dibutyl-thien-5-al ***8***

A NaOH-solution (16.5 mmol, 3.3 mL, 5 M in water) was added to a solution of **7** (5.50 mmol, 2.50 g) in ethanol (5 mL) and the mixture was stirred overnight at 40 °C. The reaction mixture was neutralized with an HCl-solution (5 M) and extracted with dichloromethane. The combined organic layers were washed with a saturated $NaHCO_3$-solution and dried over $MgSO_4$. The crude reaction product was purified with column chromatography (silica gel; eluents: dichloromethane) and isolated as an oil in a mixture of cis/trans isomers (10/90).

Yield: 2.10 g (97%).

^{1}H NMR ($CDCl_3$, ppm): trans: δ=9.97 (s, 1H), 7.39 (d, 2H), 7.08 (d, *J*=16.1 Hz, 1H), 7.00 (d, *J*=16.1 Hz, 1H), 6.75 (d, 2H), 3.83 (m, 2H), 3.51 (m, 4H), 2.86 (t, 2H), 2.63 (t, 2H), 1.66 (t, 1H), 1.4 (m, 8H), 1.21 (t, 3H), 0.97 (t, 6H).

cis: δ=9.97 (s, 1H), 7.13 (d, 2H), 6.64 (d, 2H), 6.43 (d, *J*=8.8 Hz, 1H), 6.38 (d, *J*=8.8 Hz, 1H), 3.83 (m, 2H), 3.51 (m, 4H), 2.86 (t, 2H), 2.63 (t, 2H), 1.66 (t, 1H), 1.4 (m, 8H), 1.21 (t, 3H), 0.97 (t, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=182.1, 153.5, 148.8, 140.7, 134.2, 133.0, 128.8, 124.9, 115.6, 112.7, 60.6, 52.8, 46.0, 34.8, 33.7, 27.3, 26.5, 23.2, 14.4, 14.3, 12.4.

MS: *m*/*z*=413 (M^+), 382 (M^+-CH_3O).

$C_{25}H_{35}NO_2S$ calcd: C 72.60%, H 8.53%, N 3.39%; found: C 72.49%, H 8.42%, N 3.27%.

4.8. Synthesis of the pyranone derivatives ***9b–d***

The general procedure is as follows: a solution of **10** (15.0 mmol, 1.86 g) and **12–14** (15.0 mmol) in acetic acid anhydride (100 mL) was refluxed overnight under argon atmosphere. The reaction mixture was allowed to reach room temperature and then poured into ice water. The precipitate was filtered off and washed with a $NaHCO_3$-solution. Finally, the crude reaction product was recrystallized from ethanol.

Compound **9b**: Yield: 3.10 g (67%).

Mp: 196 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.84 (s, 2H), 4.58 (q, 4H), 2.48 (s, 6H), 1.32 (t, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=178.2, 166.1, 162.2, 158.7, 112.1, 97.0, 43.7, 21.1, 12.9.

MS: *m*/*z*=306 (M^+).

$C_{15}H_{18}N_2O_3S$ calcd: C 58.80%, H 5.92%, N 9.14%; found: C 58.71%, H 5.81%, N 9.08%.

Compound **9c**: Yield: 2.74 g (64%).

Mp: 202 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.80 (s, 2H), 3.98 (q, 4H), 2.43 (s, 6H), 1.24 (t, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=165.1, 164.1, 157.7, 151.0, 111.1, 95.7, 36.8, 21.0, 13.8.

MS: *m*/*z*=290 (M^+).

$C_{15}H_{18}N_2O_4$ calcd: C 62.06%, H 6.25%, N 9.65%; found: C 61.98%, H 6.18%, N 9.59%.

Compound **9d**: Yield: 2.66 g (67%).

Mp: 196 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.24 (s, 1H), 6.10 (s, 1H), 7.48 (m, 5H), 2.38 (s, 3H), 2.09 (s, 3H).

^{13}C NMR ($CDCl_3$, ppm): δ=173.5, 165.7, 164.6, 162.7, 150.6, 131.6, 130.3, 129.3, 129.0, 108.0, 94.6, 20.8, 20.7.

MS: *m*/*z*=268 (M^+).

$C_{16}H_{13}NO_3$ calcd: C 71.91%, H 4.90%, N 5.24%; found: C 71.81%, H 4.85%, N 5.19%.

4.9. Synthesis of the alcohol-functionalized chromophores

The general procedure is as follows: piperidine (0.3 mL) was added to a solution of the pyranone derivative **9a–d** (3.00 mmol) and aldehyde **8** (2.5 mmol) in toluene (15 mL). The mixture was refluxed in a Dean Stark apparatus until the calculated amount of water was azeotropically distilled off. The reaction mixture was allowed to reach room temperature and the solvents were evaporated in vacuo. The crude reaction product was purified with column chromatography (silica gel; the eluents is indicated for each chromophore individually) and recrystallized from ethanol.

Compounds **a1–2**: Eluents: dichloromethane/acetonitrile 90/10.

Compound **a1**: Yield: 200 mg (14%).

Mp: 193 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=7.53 (d, *J*=15.4 Hz, 1H), 7.36 (d, 2H), 7.00 (d, *J*=16.1 Hz, 1H), 6.89 (d, *J*=16.1 Hz, 1H), 6.75 (d, 2H), 6.56 (s, 1H), 6.47 (s, 1H), 6.32 (d, *J*=15.4 Hz, 1H), 3.82 (q, 2H), 3.5 (m, 4H), 2.6 (m, 4H), 2.37 (s, 3H), 1.70 (t, 1H), 1.46 (m, 8H), 1.19 (t, 3H), 0.98 (m, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=161.5, 159.6, 156.1, 148.3, 147.6, 141.8, 140.5, 131.3, 130.9, 129.1, 128.1, 125.1, 115.5, 115.4, 115.3, 114.5, 112.5, 106.1, 60.3, 58.1, 52.4, 45.6, 33.7, 33.3, 26.8, 26.7, 22.8, 22.6, 19.9, 14.0, 13.8, 12.0.

MS: *m*/*z*=576 (M^+).

$C_{35}H_{41}N_3O_2S$ calcd: C 74.04%, H 7.28%, N 7.40%; found: C 73.81%, H 7.14%, N 7.31%.

Compound **a2**: Yield: 349 mg (15%).

Mp: 264 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=7.60 (d, *J*=15.4 Hz, 2H), 7.39 (d, 4H), 7.03 (d, *J*=15.4 Hz, 2H), 6.92 (d, *J*=15.4 Hz, 2H), 6.76 (d, 4H), 6.57 (s, 2H), 6.42 (d, *J*=15.4 Hz, 2H), 3.84 (q, 2H), 3.5 (m, 8H), 2.7 (m, 8H), 1.64 (t, 2H), 1.48 (m, 16H), 1.18 (t, 6H), 0.97 (m, 12H).

^{13}C NMR ($CDCl_3$, ppm): δ=160.3, 158.4, 155.0, 146.2, 140.7, 139.4, 130.1, 129.3, 128.0, 127.5, 123.3, 114.4, 114.3, 113.2, 110.4, 105.3, 105.0, 60.1, 57.0, 47.8, 44.3, 32.1, 32.2, 30.8, 28.6, 25.7, 25.6, 21.7, 21.6, 19.8, 18.9, 12.3, 12.8, 11.3.

MS: *m*/*z*=964 (M^+).

$C_{60}H_{74}N_4O_3S_2$ calcd: C 74.80%, H 7.74%, N 5.82%; found: C 74.69%, H 7.71%, N 5.75%.

Compound **b1**: Eluents: dichloromethane/ethylacetate 90/10.

Yield: 119 mg (11%).

Mp: 204 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.89 (s, 1H), 8.70 (s, 1H), 7.63 (d, J=15.4 Hz, 1H), 7.37 (d, 2H), 7.00 (d, J=16.1 Hz, 1H), 6.88 (d, J=16.1 Hz, 1H), 6.75 (d, 2H), 6.54 (d, 15.4 Hz, 1H), 4.61 (q, 4H), 3.83 (t, 2H), 3.49 (m, 4H), 2.62 (m, 4H), 2.50 (s, 3H), 1.79 (s, 1H), 1.48 (m, 8H), 1.33 (t, 6H), 1.19 (t, 3H), 1.00 (m, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=176.6, 162.7, 161.6, 160.8, 156.3, 147.3, 146.7, 141.0, 139.6, 130.8, 130.0, 128.1, 127.1, 124.1, 115.1, 114.5, 111.6, 111.4, 110.2, 95.7, 59.3, 51.4, 44.6, 42.3, 32.7, 32.3, 25.8, 25.7, 21.8, 21.7, 19.7, 12.9, 12.8, 11.5, 11.0.

MS: m/z=701 (M^+).

$C_{40}H_{51}N_3O_4S_2$ calcd: C 68.47%, H 7.28%, N 5.99%; found: C 68.36%, H 7.19%, N 5.91%.

Compound **b2**: Yield: 552 mg (22%).

Mp: 266 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.84 (s, 2H), 7.66 (d, J=15.4 Hz, 2H), 7.38 (d, 4H), 7.02 (d, J=15.7 Hz, 2H), 6.90 (d, 15.7 Hz, 2H), 6.75 (d, 4H), 6.60 (d, J=15.4 Hz, 2H), 4.60 (q, 4H), 3.82 (t, 4H), 3.48 (m, 8H), 2.67 (m, 8H), 1.75 (s, 2H), 1.50 (m, 16H), 1.35 (t, 6H), 1.19 (t, 6H), 0.99 (m, 12H).

^{13}C NMR ($CDCl_3$, ppm): δ=177.5, 161.8, 160.9, 156.3, 148.3, 147.1, 141.7, 140.6, 132.2, 130.9, 128.3, 128.2, 125.2, 117.0, 115.5, 112.9, 112.5, 96.6, 60.3, 52.4, 45.6, 43.4, 33.7, 33.4, 27.2, 26.7, 22.8, 22.7, 14.1, 14.0, 12.6, 12.0.

MS: m/z=1096 (M^+).

$C_{65}H_{84}N_4O_5S_3$ calcd: C 71.13%, H 7.71%, N 5.10%; found: C 71.08%, H 7.62%, N 5.07%.

Compounds **c1**–**2**: Eluents: dichloromethane/ethylacetate 60/40.

Compound **c1**: Yield: 418 mg (25%).

Mp: 207 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.88 (d, J=1.47 Hz, 1H), 8.69 (d, J=1.47 Hz, 1H), 7.58 (d, J=15.4 Hz, 1H), 7.37 (d, 2H), 7.00 (d, J=15.7 Hz, 1H), 6.87 (d, J=15.7 Hz, 1H), 6.75 (d, 2H), 6.53 (d, J=15.4 Hz, 1H), 4.02 (m, 4H), 3.82 (m, 2H), 3.47 (m, 4H), 2.60 (m, 4H), 2.49 (s, 3H), 1.88 (s, 1H), 1.47 (m, 8H), 1.25 (t, 6H), 1.19 (t, 3H), 0.99 (m, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=163.7, 163.1, 161.7, 156.5, 150.7, 148.2, 147.1, 141.3, 140.5, 131.8, 130.7, 128.3, 128.0, 125.2, 116.6, 115.6, 112.5, 111.8, 110.4, 95.4, 60.3, 52.4, 45.6, 36.4, 33.7, 33.3, 26.8, 26.7, 22.8, 22.7, 20.6, 14.0, 13.8, 13.5, 12.0.

MS: m/z=685 (M^+).

$C_{40}H_{51}N_3O_5S$ calcd: C 70.07%, H 7.45%, N 6.13%; found: C 70.02%, H 7.38%, N 6.05%.

Compound **c2**: Yield: 352 mg (14%).

Mp: 269 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.84 (s, 2H), 7.62 (d, J=15.4 Hz, 2H), 7.38 (d, 4H), 7.01 (d, J=15.8 Hz, 2H), 6.89 (d, J=15.8 Hz, 2H), 6.74 (d, 4H), 6.58 (d, J=15.4 Hz, 2H), 4.05 (m, 4H), 3.83 (m, 4H), 3.49 (m, 8H), 2.65 (m, 8H), 1.84 (s, 2H), 1.50 (m, 16H), 1.27 (t, 6H), 1.19 (t, 6H), 0.99 (m, 12H).

^{13}C NMR ($CDCl_3$, ppm): δ=163.7, 160.2, 155.6, 150.8, 148.2, 146.5, 141.2, 140.5, 132.2, 130.6, 128.1, 127.7, 125.2, 117.4, 115.6, 112.5, 112.2, 95.3, 60.3, 52.4, 45.6, 36.4, 33.7, 33.4, 27.2, 26.7, 22.8, 22.7, 14.1, 14.0, 13.6, 12.0.

MS: m/z=1080 (M^+).

$C_{65}H_{84}N_4O_6S_2$ calcd: C 72.22%, H 7.78%, N 5.19%; found: C 72.15%, H 7.71%, N 5.09%.

Compound **d2**: Eluents: dichloromethane/ethylacetate 80/20.

Compound **d2**: Yield: 515 mg (15%).

Mp: 226 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.26 (d, J=1.47 Hz, 1H), 7.60 (d, J=16.0 Hz, 1H), 7.55 (m, 4H), 7.35 (m, 5H), 7.02 (d, J=15.4 Hz, 1H), 6.98 (d, J=15.4 Hz, 1H), 6.96 (d, J=16.0 Hz, 1H), 6.86 (d, J=15.4 Hz, 1H), 6.85 (d, J=15.4 Hz, 1H), 6.75 (d, 2H), 6.74 (d, 2H), 6.55 (d, J=15.4 Hz, 1H), 6.20 (d, J=1.44 Hz, 1H), 6.02 (d, 15.4 Hz, 1H), 3.83 (t, 4H), 3.48 (m, 8H), 2.64 (m, 8H), 1.94 (s, 2H), 1.48 (m, 16H), 1.19 (t, 6H), 0.97 (t, 12H).

^{13}C NMR ($CDCl_3$, ppm): δ=173.6, 162.3, 160.5, 159.6, 148.7, 148.3, 148.2, 147.0, 141.8, 141.6, 140.6, 140.5, 132.0, 131.8, 131.5, 131.0, 129.9, 128.9, 128.1, 128.0, 125.1, 124.9, 116.4, 115.8, 115.5, 115.4, 112.5, 112.4, 108.2, 107.0, 94.2, 60.3, 52.4, 45.6, 33.7, 33.6, 33.4, 27.1, 26.7, 22.9, 22.8, 22.7, 14.1, 14.0, 12.0.

MS: m/z=1057 (M^+).

$C_{66}H_{79}N_3O_5S_2$ calcd: C 74.93%, H 7.47%, N 3.97%; found: C 74.82%, H 7.40%, N 3.94%.

4.10. Synthesis of the acetate-functionalized chromophores

The general procedure is as follows: a solution of the alcohol-functionalized chromophore **xi** (90.0 μmol) in acetic anhydride (10 mL) was stirred for 14 h at room temperature. Then, the solvent was evaporated in vacuo and the crude reaction product was redissolved in dichloromethane and washed with a saturated $NaHCO_3$-solution, a saturated NaCl-solution and dried over $MgSO_4$. Finally, the product was purified with column chromatography (silica gel; eluents: dichloromethane/ethylacetate (9/1)) and isolated as a solid.

Compounds **a1**–**OAc**: Yield: 34.6 mg (63%).

Mp: 116 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=7.54 (d, J=15.4 Hz, 1H), 7.37 (d, 2H), 7.01 (d, J=16.1 Hz, 1H), 6.89 (d, J=16.1 Hz, 1H), 6.72 (d, 2H), 6.55 (d, J=2.2 Hz, 1H), 6.48 (d, J=2.2 Hz, 1H), 6.33 (d, J=15.4 Hz, 1H), 4.22 (t, 2H), 3.59 (t, 2H), 3.45 (q, 2H), 2.61 (m, 4H), 2.37 (s, 3H), 2.06 (s, 3H), 1.45 (m, 8H), 1.20 (t, 3H), 0.97 (t, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=169.9, 160.5, 158.6, 155.1, 146.6, 140.8, 139.5, 130.3, 129.9, 128.1, 127.1, 123.9, 114.5, 114.4, 113.5, 110.9, 105.1, 105.0, 60.5, 57.1, 47.7, 44.4, 32.7, 32.3, 30.9, 28.7, 25.8, 25.7, 21.8, 21.6, 19.9, 18.9, 12.9, 12.8, 11.3.

MS: m/z=609 (M^+).

$C_{37}H_{43}N_3O_3S$ calcd: C 72.87%, H 7.11%, N 6.89%; found: C 72.75%, H 7.05%, N 6.76%.

Compounds **a2**–**OAc**: Yield: 23.3 mg (37%).

Mp: 214 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=7.59 (d, J=15.4 Hz, 2H), 7.38 (d, 4H), 7.03 (d, J=16.1 Hz, 2H), 6.90 (d, J=16.1 Hz, 2H),

6.72 (d, 4H,), 6.54 (s, 2H), 6.40 (d, J=15.4 Hz, 2H), 4.25 (t, 4H), 3.59 (t, 4H), 3.45 (q, 4H), 2.66 (m, 8H), 2.06 (s, 6H), 1.49 (m, 16H), 1.23 (t, 6H), 0.99 (q, 12H).

^{13}C NMR ($CDCl_3$, ppm): δ=169.9, 157.4, 154.4, 146.6, 145.9, 140.6, 139.5, 130.1, 129.9, 127.4, 127.1, 123.9, 114.9, 114.4, 110.9, 105.2, 60.5, 56.5, 47.7, 44.4, 32.6, 32.4, 28.7, 26.1, 25.7, 21.9, 21.7, 19.9, 13.1, 12.9, 11.3.

MS: m/z=1046 (M^+).

$C_{64}H_{78}N_4O_5S_2$ calcd: C 73.39%, H 7.51%, N 5.35%; found: C 73.28%, H 7.46%, N 5.25%.

Compounds **b1−OAc**: Yield: 41.9 mg (70%).

Mp: 176 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.89 (d, J=1.8 Hz, 1H), 8.70 (d, J=1.8 Hz, 1H), 7.60 (d, 1H), 7.36 (d, 2H), 7.00 (d, J=15.4 Hz, 1H), 6.88 (d, J=15.4 Hz, 1H), 6.71 (d, 2H), 6.53 (d, J=15.4 Hz, 1H), 4.57 (q, 4H), 4.24 (t, 2H), 3.58 (t, 2H), 3.43 (q, 2H), 2.61 (m, 4H), 2.49 (s, 3H), 2.05 (s, 3H), 1.44 (m, 8H), 1.32 (t, 6H), 0.98 (m, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=169.9, 157.4, 154.4, 146.6, 145.9, 140.6, 139.5, 130.1, 129.9, 127.4, 127.1, 123.9, 114.9, 114.4, 110.9, 105.2, 60.5, 56.5, 47.7, 44.4, 32.6, 32.4, 28.7, 26.1, 25.7, 21.9, 21.7, 19.9, 13.1, 12.9, 11.3.

MS: m/z=1046 (M^+).

$C_{42}H_{53}N_3O_5S_2$ calcd: C 67.80%, H 7.18%, N 5.65%; found: C 67.71%, H 7.11%, N 5.54%.

Compounds **b2−OAc**: Yield: 26.0 mg (44%).

Mp: 188 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.84 (s, 2H), 7.68 (d, J=15.4 Hz, 2H), 7.39 (d, 4H), 7.03 (d, J=15.7 Hz, 2H), 6.96 (d, J=15.7 Hz, 2H), 6.72 (d, 4H), 6.60 (d, J=15.4 Hz, 2H), 4.60 (q, 4H), 4.25 (t, 4H), 3.59 (t, 4H), 3.44 (q, 4H), 2.65 (m, 8H), 2.06 (s, 6H), 1.44 (m, 16H), 1.36 (t, 6H), 1.20 (t, 6H), 0.96 (t, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=176.5, 169.9, 160.8, 159.9, 155.3, 146.6, 146.0, 140.7, 139.6, 131.1, 129.9, 127.3, 127.2, 124.0, 116.0, 114.4, 112.0, 110.9, 95.6, 60.5, 47.7, 44.4, 42.3, 32.7, 32.3, 30.9, 28.7, 28.6, 28.3, 26.2, 25.7, 21.8, 21.7, 19.9, 13.0, 12.9, 11.6, 11.3.

MS: m/z=1180 (M^+).

$C_{69}H_{88}N_4O_7S_3$ calcd: C 70.14%, H 7.51%, N 4.74%; found: C 69.98%, H 7.37%, N 4.66%.

Compounds **c1−OAc**: Yield: 32.0 mg (54%).

Mp: 119 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.89 (d, J=2.2 Hz, 1H), 8.70 (d, J=2.2 Hz, 1H), 7.58 (d, J=15.4 Hz, 1H), 7.38 (d, 2H), 7.01 (d, J=15.4 Hz, 1H), 6.88 (d, J=15.4 Hz, 1H), 6.72 (d, 2H), 6.53 (d, J=15.4 Hz, 1H), 4.25 (t, 2H), 4.02 (m, 2H), 3.59 (t, 2H), 3.44 (q, 2H), 2.60 (m, 4H), 2.47 (s, 3H), 2.06 (s, 3H), 1.45 (m, 8H), 1.25 (t, 6H), 1.20 (t, 3H), 0.99 (m, 6H).

^{13}C NMR ($CDCl_3$, ppm): δ=169.9, 162.7, 162.1, 160.7, 155.5, 149.7, 146.6, 146.1, 140.3, 139.4, 130.8, 129.6, 127.3, 127.1, 124.0, 115.6, 114.5, 110.9, 110.8, 109.3, 94.4, 60.5, 47.8, 44.3, 35.4, 32.7, 32.3, 28.7, 25.8, 25.7, 21.8, 21.7, 19.9, 19.6, 12.9, 12.8, 12.5, 11.3.

MS: m/z=727 (M^+).

$C_{42}H_{53}N_3O_6S$ calcd: C 69.30%, H 7.34%, N 5.77%; found: C 69.18%, H 7.28%, N 5.62%.

Compounds **c2−OAc**: Yield: 32.0 mg (59%).

Mp: 218 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.85 (s, 2H), 7.62 (d, J=15.4 Hz, 2H), 7.39 (d, 4 Hz), 7.03 (d, J=16.1 Hz, 2H), 6.90 (d, J=16.1 Hz, 2H), 6.72 (d, 4H), 6.60 (d, J=15.4 Hz, 2H), 4.25 (t, 4H), 4.04 (q, 4H), 3.59 (t, 4H), 3.44 (q, 4H), 2.65 (m, 8H), 2.06 (s, 6H), 1.45 (m, 16H), 1.27 (t, 6H), 1.20 (t, 6H), 0.96 (m, 12H).

^{13}C NMR ($CDCl_3$, ppm): δ=169.9, 162.7, 159.2, 154.6, 149.8, 146.6, 145.5, 140.2, 139.5, 131.2, 129.6, 127.1, 126.6, 124.1, 123.6, 116.4, 114.5, 111.1, 110.9, 94.3, 60.5, 47.8, 44.3, 35.4, 32.6, 32.3, 28.2, 26.2, 25.7, 21.8, 19.9, 13.1, 13.0, 12.6, 11.3.

MS: m/z=1164 (M^+).

$C_{69}H_{88}N_4O_8S_2$ calcd: C 71.10%, H 7.61%, N 4.81%; found: C 70.99%, H 7.50%, N 4.69%.

Compounds **d2−OAc**: Yield: 22.0 mg (38%).

Mp: 168 °C.

^{1}H NMR ($CDCl_3$, ppm): δ=8.30 (d, J=2.2 Hz, 1H), 7.59 (d, J=15.4 Hz, 1H), 7.54 (m, 4H), 7.37 (m, 5H), 7.03 (d, J=16.1 Hz, 1H), 7.00 (d, J=16.1 Hz, 1H), 6.99 (d, J=15.4 Hz, 1H), 6.93 (d, J=16.1 Hz, 1H), 6.88 (d, J=16.1 Hz, 1H), 6.72 (d, 4H), 6.57 (d, J=15.4 Hz, 1H), 6.20 (d, J=2.2 Hz, 1H), 6.03 (d, J=15.4 Hz, 1H), 4.25 (t, 4H), 3.59 (t, 4H), 3.45 (q, 4H), 2.65 (m, 8H), 2.06 (s, 6H), 1.47 (m, 16H), 1.20 (t, 6H), 0.96 (m, 12H).

^{13}C NMR ($CDCl_3$, ppm): δ=173.5, 171.0, 162.3, 160.4, 159.5, 148.6, 147.7, 146.9, 141.7, 141.5, 140.6, 140.5, 132.0, 131.5, 130.9, 130.8, 129.8, 128.9, 128.8, 128.2, 128.1, 125.0, 124.9, 116.4, 115.9, 115.4, 111.9, 108.2, 107.0, 94.4, 61.5, 61.4, 48.8, 45.4, 33.6, 33.4, 29.7, 29.4, 27.1, 26.7, 22.8, 22.7, 20.9, 14.0, 12.3.

MS: m/z=1142 (M^+).

$C_{70}H_{83}N_3O_7S_2$ calcd: C 73.59%, H 7.32%, N 3.68%; found: C 73.45%, H 7.25%, N 3.58%.

Acknowledgements

This work was supported by the Fund for Scientific Research-Flanders (FWO-Vlaanderen), the Katholieke Universiteit Leuven (GOA) and the Belgian Government (IUAP). G.K. and I.A. are postdoctoral fellows of the Fund for Scientific Research (FWO-Vlaanderen).

References and notes

1. Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, NY, 1991.
2. Zyss, D. S. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic: Orlando, FL, 1987.
3. Moylan, C. R.; Ermer, S.; Lovejoy, S. M.; McComb, I.-H.; Leung, D. S.; Wortmann, R.; Krdmer, P.; Twieg, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 12950.
4. Yang, M. L.; Champagne, B. *J. Phys. Chem. A* **2003**, *107*, 3942.
5. Acebal, P.; Blaya, S.; Carretero, L. *J. Chem. Phys.* **2004**, *121*, 8602.
6. Kuo, W. J.; Hsiue, G. H.; Jeng, R. J. *Macromol. Rapid Commun.* **2001**, *22*, 601.
7. Ostroverkhov, V.; Ostroverkhova, O.; Petschek, R. G.; Singer, K. D.; Sukhomlinova, L.; Twieg, R. J.; Wang, S.-X.; Chien, L. C. *Chem. Phys.* **2000**, *257*, 263.

8. Boutton, C.; Clays, K.; Persoons, A.; Wada, T.; Sasabe, H. *Chem. Phys. Lett.* **1998**, *286*, 101.
9. Tsai, H. C.; Kuo, W. J.; Hsiue, G. H. *Macromol. Rapid Commun.* **2005**, *26*, 986.
10. Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. *J. Mater. Chem.* **1997**, *7*, 2175.
11. Gubbelmans, E.; Verbiest, T.; Picard, I.; Persoons, A.; Samyn, C. *Polymer* **2005**, *46*, 1784.
12. Lindsay, G. A.; Stenger-Smith, J. D.; Henry, R. A.; Hoover, J. M.; Nissan, R. A. *Macromolecules* **1992**, *25*, 6075.
13. Marder, S. R.; Perry, J. W. *Adv. Mater.* **1993**, *5*, 804.
14. Effenberger, F.; Würthner, F.; Steybe, F. *J. Org. Chem.* **1995**, *60*, 2082.
15. Bedworth, P. V.; Cai, Y.; Jen, A.; Marder, S. R. *J. Org. Chem.* **1996**, *61*, 2242.
16. Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90.
17. Cai, C.; Liakatas, I.; Wong, M.-S.; Bösch, M.; Bosshard, C.; Günter, P.; Concilio, S.; Tirelli, N.; Suter, U. W. *Org. Lett.* **1999**, *1*, 1847.
18. Raimundo, J.-M.; Blanchard, P.; Gallego-Planas, N.; Mercier, N.; Ledoux-Rak, I.; Hierle, R.; Rancoli, J. *J. Org. Chem.* **2002**, *67*, 205.
19. Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H. *Science* **2000**, *288*, 119.
20. Raposo, M. M. M.; Fonseca, A. M. C.; Kirsch, G. *Tetrahedron* **2004**, *60*, 4071.
21. Pérez-Moreno, J.; Zhao, Y.; Clays, K.; Kuzyk, M. *Opt. Lett.* **2007**, *32*, 59.
22. Dalton, L.; Harper, A.; Ren, A.; Wang, F.; Todorova, G.; Chen, J.; Zhang, C.; Lee, M. *Ind. Eng. Chem. Res.* **1999**, *38*, 8.
23. Luo, J.; Cheng, Y.-J.; Kim, T.-D.; Hau, S.; Jang, S.-H.; Shi, Z.; Zhou, X.-H.; Jen, A. K.-Y. *Org. Lett.* **2006**, *8*, 1387.
24. Hendrickx, E.; Boutton, C.; Clays, K.; Persoons, A.; van Es, S.; Biemans, T.; Meijer, B. *Chem. Phys. Lett.* **1997**, *270*, 241.
25. Spangler, C. W.; He, M. *J. Chem. Soc., Perkin Trans. 1* **1995**, *6*, 715.
26. Woods, L. L. *J. Am. Chem. Soc.* **1958**, *80*, 1440.
27. Olbrechts, G.; Strobbe, R.; Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1998**, *69*, 2233.