Synthesis and Properties of Chiral Helical Chromophore-Functionalised Polybinaphthalenes for Second-order Nonlinear Optical Applications

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Abstract

Chiral, helical, nonlinear optical polybinaphthalenes were prepared by covalent bonding of chromophores to the backbone of polybinaphthalenes via a Mitsunobu reaction. This was achieved in a two-step reaction, with the formation of a precursor polymer by a Suzuki coupling reaction, which was afterwards functionalised with chromophores. It was tried to achieve a chiral ordering of the chromophores by attaching them to a chiral, helical polymer backbone. Poled films of the polymers were measured for their second-harmonic generation effect and showed nonresonant nonlinear susceptibilities ($\chi^{(2)}_{zzz}(0)$) up to 10.6 pm/V.

Keywords: Polybinaphthalenes; Nonlinear optics; Chirality
1. Introduction

In the past decade, chomophore-functionalised polymer systems have been intensively studied for their nonlinear optical (NLO) properties [1], because of their potential applications as high speed frequency doublers and mixers, amongst others. This interest has led to the development of a large number of new chromophores with moderate to superb hyperpolarizabilities. Since polymer materials show additional advantages compared to their inorganic analogues, s.a. a good processability, a low dielectric constant, a large architectural diversification, … nearly all organic NLO materials are polymeric. Most of these polymers adapt a random coil conformation. Only a few [2] chiral, helical, rod-like polymer systems have been investigated as NLO materials. Polybinaphthalenes, with chromophores attached as side-chain, are to the best of our knowledge even novel polymer materials, although they may be interesting NLO candidates. When incorporated as side-chains, the chromophores can easily be poled (as in random coil-like systems). But, since the chromophores are attached to a rigid, non bendable backbone, the undesired dipolar interactions between the chromophores will be largely reduced in these systems. Moreover, if chiral, helical polymers are used, these systems can benefit from the chirality of the sample. The use of chirality in second-order nonlinear optics has been theoretically thoroughly investigated [3]. These studies have demonstrated that chirality can relax the requirement for a polar ordering. Moreover, chiral contributions can increase the NLO response.

In this paper polybinaphthalenes were chosen as polymer system, since these polymers are helical (if appropriately designed) and show excellent thermal, chemical and photochemical stability. Chirality was obtained by polymerisation of chiral (S) dibromo-binaphthalene monomers and a bis(boronic acid) derivative. To enhance solubility, film forming properties and possibilities to synthetical diversification, the chromophores were linked as side chains.
Therefore, these polymers meet with all requirements, necessary to be useful as nonlinear optical materials.

2. Experimental

2.1. Materials and instrumentation

All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka and Avocado. Reagent grade solvents were dried when necessary and purified by distillation. The glass transition temperatures were measured with a DSC-7 apparatus from Perkin-Elmer at a heating rate of 50 °C/min (polymers) or 30 °C/min (chromophores). Gel permeation chromatography (GPC) measurements were done with a Waters apparatus with a tuneable absorbance detector and a differential refractometer in tetrahydrofuran (THF) as eluent towards polystyrene standards. \(^1\)H nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz. UV-VIS spectra were recorded with a Varian Cary 400. The optical rotations were measured with an Analis Optical Activity Polaar 20.

2.2. Second-harmonic generation measurements

Thin films were obtained by spincoating a solution of the polymer in chloroform onto ITO substrates. After drying, poly(acrylic acid) was spincoated above the chromophore-functionalised polymer film to prevent bleaching during poling. The films were carefully dried. Subsequently, they were corona-poled at approximately \(T_g\). The corona-poling set-up consisted of a thin wire, positioned 1 cm above the polymer film, that was charged to 4 kV. The nonlinear optical properties were measured by second harmonic generation (SHG). All susceptibility components were determined by analysing the polarisation of the second-harmonic signal emanating from the samples, for different input polarisations of the fundamental beam [4].
2.3. Synthesis of S(-)-6,6′-dibromo-2-hexyloxy-2′-methoxymethoxy-[1,1′-binaphthalene] 3b:

Fig.1

2.3.1. Synthesis of S(-)-6,6′-dibromo-2-hexyloxy-[1,1′-binaphthalene]-2-ol 2

A solution of 14.4 g (32.4 mmol) of 1 [5], dissolved in 70 ml of dry N,N-dimethylformamide (DMF), was slowly added to a suspension of 0.78 g (32.4 mmol) of NaH in 30 ml of dry DMF under argon atmosphere. After 15 min, 4.6 ml (32.4 mmol) of hexylbromide and 100 mg of anhydrous NaI were added and the mixture was stirred overnight at 50 °C. After cooling, the reaction mixture was poured into 200 ml of water and extracted with dichloromethane. The organic layer was washed with a saturated NaHCO₃-solution and brine and dried over MgSO₄. After removal of the solvents, the crude compound was purified by column chromatography (silicagel; eluent: hexane / dichloromethane (60:40 v/v)) and isolated as an oil.

Yield : 8.2g (48%)

\[ \alpha_d^{25} = +32.4 \text{ deg dm}^{-1} \text{mol}^{-1} \text{L} \] (c = 0.06 in CHCl₃)

\(^1\)H NMR (CDCl₃, ppm): \( \delta = 8.05 \) (d; J = 1.5 Hz; 1H), 8.00 (d; J = 1.5 Hz; 1H), 7.93 (d; 1H), 7.80 (d; 1H), 7.46 (d; 1H), 7.34 (d; 1H), 7.34 (dd; 1H), 7.28 (dd; 1H), 7.02 (d; 1H), 6.86 (d; 1H), 4.89 (d; 1H), 3.99 (m; 2H), 1.43 (qu; 2H), 1.01 (m; 6H), 0.75 (t; 3H).

\(^{13}\)C NMR (CDCl₃, ppm): \( \delta = 155.7, 151.6, 132.5, 132.2, 130.6, 130.4, 130.2, 130.1, 130.0, 129.6, 128.9, 126.6, 126.5, 118.7, 118.1, 117.0, 116.2, 115.7, 114.9, 69.6, 31.2, 29.0, 26.9, 25.2, 22.4, 13.9.

MS: \( m/z = 528 (M^+), 444 (M^+ - C₆H₁₂), 364 (M^+ - C₆H₁₂, -Br), 284 (M^+ - C₆H₁₂, -Br₂) \).

2.3.2. Synthesis of S(-)-6,6′-dibromo-2-hexyloxy-2′-methoxymethoxy-[1,1′-binaphthalene] 3b
A solution of 5.28 g (10.0 mmol) of 2, dissolved in 30 ml of dry tetrahydrofuran (THF), was slowly added to a suspension of 573 mg (12.0 mmol) of NaH in 20 ml of dry THF under argon atmosphere. After 15 min, 0.90 ml (12.0 mmol) of chloromethylmethylether was added very slowly and the mixture was stirred overnight at room temperature. The reaction mixture was poured into 100 ml of water and extracted with dichloromethane. The organic layer was washed with a saturated NaHCO₃-solution, with brine and dried over MgSO₄. After removal of the solvents, the crude compound was purified by column chromatography (silicagel; eluent: hexane / dichloromethane (60:40 v/v)) and isolated as an oil.

Yield: 4.70 g (82%)

\[ \alpha_{\text{D}}^{25} = -156 \text{ deg dm}^{-1} \text{ mol}^{-1} \text{ l} \quad (c = 3.30 \text{ in CHCl}_3) \]

\(^1\)H NMR (CDCl₃, ppm): δ = 8.01 (d (br); 2H), 7.85 (d; 1H), 7.82 (d; 1H), 7.56 (d; 1H), 7.42 (d; 1H), 7.34 (dd; 1H), 7.28 (dd; 1H), 7.00 (d; 1H), 6.94 (d; 1H), 5.30 (s; 1H), 5.07 (d; 1H), 4.96 (d; 1H), 3.95 (m; 2H), 3.17 (s; 3H), 1.37 (m; 2H), 1.0 (m; 6H), 0.73 (t; 3H).

\(^{13}\)C NMR (CDCl₃, ppm): δ = 154.7, 152.8, 150.5, 134.0, 133.7, 133.2, 130.6, 129.9, 129.4, 129.2, 128.4, 128.2, 121.5, 120.4, 95.4, 69.9, 55.9, 31.3, 29.3, 25.3, 22.4, 14.0.

MS: \( m/z = 572 (M^+) \), 444 (\( M^+ - C_6H_{12} \)), 364 (\( M^+ - C_6H_{12}, -Br \)), 284 (\( M^+ - C_6H_{12}, -Br_2 \)).

2.4. Synthesis of the precursor polymers: Fig. 2

ppol I was synthesized according to literature procedure [6], by reaction of 3a [7] and 4 [6]. The synthesis of ppol II was as follows: 2.65 g (5.00 mmol) of 3b, 1.82 g (5.00 mmol) of 4 and 290 mg (250 μmol) of Pd(0)[PPh₃]₄ were dissolved in 25 ml of THF. The solution was purged with argon and 15 ml of a K₂CO₃-solution (1 M in water) was added. The reaction mixture was refluxed for two days under argon atmosphere while vigorously stirred. After cooling, water was added and the polymer was extracted with dichloromethane. The polymer solution was washed with brine, dried over anhydrous Na₂SO₄ and concentrated. The
polymer was isolated by precipitation in methanol and collected by filtration. Finally, the
disposable in THF, reprecipitated in methanol and dried under reduced
pressure.
The obtained MOM-protected polymer was dissolved in 25 ml of THF. The solution was
purged with argon, treated with 25 ml of HCl (6 M) and the mixture was refluxed overnight
under argon atmosphere. After cooling, water was added and the polymer was extracted with
dichloromethane. The organic layer was washed with a saturated NaHCO$_3$-solution, with
brine and dried over anhydrous Na$_2$SO$_4$. The polymer solution was then concentrated and the
polymer was precipitated in methanol. After filtration and drying, the polymer was
redissolved in THF and reprecipitated in methanol. This procedure was repeated twice.
Yield : 2.8 g (86%)

$^1$H NMR (CDCl$_3$, ppm): $\delta = 8.13$ (s; 1H), 8.09 (s; 1H), 8.04 (d; 1H), 7.90 (d; 1H), 7.57 (d;
1H), 7.52 (d; 1H), 7.46 (d; 1H), 7.34 (d; 1H), 7.28 (d; 1H), 7.13 (d; 1H), 7.07 (d; 2H), 4.98 (s;
1H), 3.9 (m; 6H), 1.6 (m; 4H), 0.9-1.6 (m; 20H), 0.75 (m; 9H).

$^{13}$C NMR (CDCl$_3$, ppm): $\delta = 155.6, 151.4, 150.5, 134.4, 134.3, 133.3, 133.2, 133.1, 132.9,
131.0, 130.9, 130.5, 130.4, 130.0, 129.9, 129.5, 129.3, 129.1, 128.4, 127.9, 124.5, 117.5,

2.5. Synthesis of chromophore 8a: Fig. 3

2.5.1. Synthesis of 4-(N,N-diethylamino)-2-(2-hydroxyethoxy)benzaldehyde 6a

Under argon atmosphere a solution of 19.3 g (100 mmol) of 4-(N,N-diethylamino)-6-
hydroxybenzaldehyde 5 in 100 ml of dry DMF was added dropwise at 0 °C to a solution of
2.88 g (120 mmol) of NaH in 50 ml of dry DMF. After 15 minutes of stirring, 8.52 ml (120
mmol) of 2-bromoethanol and 750 mg (5.0 mmol) of anhydrous NaI were added and the
reaction mixture was stirred overnight at 60 °C under argon atmosphere. The mixture was
cooled and poured into 250 ml of water. The product was extracted with dichloromethane and the combined organic layers were washed with a saturated NaHCO₃-solution, with brine and dried over MgSO₄. After evaporation of the solvent, the crude compound was purified by column chromatography (silicagel; eluent: dichloromethane / ethylacetate (90:10 v/v)).

Yield : 19.5 g (82 %)

m.p. : 80.5 °C

¹H NMR (CDCl₃, ppm): δ = 10.0 (s; 1H), 7.64 (d; J = 9.1 Hz; 1H), 6.31 (dd; J = 9.1 Hz, J = 2.2 Hz; 1H), 6.07 (d; J = 2.2Hz; 1H), 4.18 (t; 2H), 4.00 (q; 2H), 3.42 (q; 4H), 2.83 (t; 1H), 1.22 (t; 6H).

¹³C NMR (CDCl₃, ppm): δ = 187.6, 163.3, 153.9, 132.2, 114.4, 104.6, 94.2, 70.2, 61.0, 44.8, 12.6.

MS: m/z = 237 (M⁺), 222 (M⁺ - CH₃O).

2.5.2. Synthesis of chromophore 8a

In a round-bottomed flask, equipped with a CaCl₂-tube, 5.93 g (25.0 mmol) of 6a and 5.10 g (27.5 mmol) of 7 [8] were dissolved in 50 ml of dry DMF. 4.8 ml of acetic acid, 4.8 ml of acetic acid anhydride and 9.6 ml of piperidine were added and the mixture was stirred overnight at 40 °C. After cooling, 200 ml of water was added and the product was extracted with dichloromethane. The combined organic layers were washed with a saturated NaHCO₃-solution, with brine and dried over MgSO₄. After evaporation of the solvent, the compound was purified by column chromatography (silicagel; eluent: dichloromethane / ethylacetate (90:10 v/v)).

Yield : 7.40 g (73 %)

m.p. : 163 °C

λₘₐₓ = 526 nm (ε = 4.0·10⁴ l·mol⁻¹·cm⁻¹)
$^1$H NMR (CDCl$_3$, ppm): $\delta = 7.44$ (d; $J = 9.1$ Hz; 1H), 7.00 (d; $J = 16.1$ Hz; 1H), 6.85 (d; $J = 16.1$ Hz; 1H), 6.72 (s; 1H), 6.34 (dd; $J = 9.1$ Hz, $J = 2.2$ Hz; 1H), 6.14 (d; $J = 2.2$ Hz; 1H), 4.17 (t; 2H), 4.04 (q; 2H), 3.41 (q; 4H), 2.56 (s; 2H), 2.45 (s; 2H), 1.93 (t; 1H), 1.21 (t; 6H), 1.07 (s; 6H).

$^{13}$C NMR (CDCl$_3$, ppm): $\delta = 169.2, 159.0, 156.3, 150.6, 132.9, 129.1, 124.1, 120.9, 114.6, 113.8, 112.9, 105.6, 95.4, 74.5, 69.9, 61.5, 44.7, 43.1, 39.2, 32.0, 28.1, 12.7.$

MS: m/z = 405 (M$^+$), 390 (M$^+$ - CH$_3$O).

IR (cm$^{-1}$): 3524, 2959, 2926, 2869, 2208.

2.6. Synthesis of chromophore 8b: Fig. 3

2.6.1. Synthesis of 4-(N,N-diethylamino)-2-(6-hydroxyhexyloxy)benzaldehyde 6b

The procedure, described for 6a, was followed, starting from 9.66 g (50.0 mmol) of 5 and 7.96 ml (60.0 mmol) of 6-chlorohexanol. The compound was purified by column chromatography (silicagel; eluent: dichloromethane / ethylacetate (90:10 v/v)) and isolated as an oil.

Yield: 13.1 g (91 %)

$^1$H NMR (CDCl$_3$, ppm): $\delta = 10.2$ (s; 1H), 7.70 (d; $J = 9.1$ Hz; 1H), 6.26 (dd; $J = 9.1$ Hz, $J = 2.2$ Hz; 1H), 6.01 (d; $J = 2.2$ Hz; 1H), 4.03 (t; 2H), 3.66 (t; 2H), 3.41 (q; 4H), 1.85 (qu; 2H), 1.5 (m; 6H), 1.21 (t; 6H).

$^{13}$C NMR (CDCl$_3$, ppm): $\delta = 187.2, 163.9, 153.9, 130.2, 114.3, 104.3, 93.2, 67.9, 62.8, 44.9, 32.6, 29.1, 26.0, 25.4, 12.6.$

MS: m/z = 293 (M$^+$), 278 (M$^+$ - CH$_3$O).

2.6.2. Synthesis of chromophore 8b
The procedure, described for chromophore 8a, was followed, starting from 7.19 g (25.0 mmol) of 6b and 5.10 g (27.5 mmol) of 7. The compound was purified by column chromatography (silica; eluent: dichloromethane / acetonitrile (90:10 v/v)).

Yield : 13.1 g (91 %)
m.p. : 109 °C

$\lambda_{\text{max}} = 530 \text{ nm (} \epsilon = 4.2 \cdot 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \text{)}$

$^1\text{H NMR (CDCl}_3, \text{ ppm): } \delta = 7.35 (d; J = 9.1 \text{ Hz; 1H}), 7.33 (d; J = 16.1 \text{ Hz; 1H}), 6.97 (d; J = 16.1 \text{ Hz; 1H}), 6.68 (s; 1H), 6.29 (dd; J = 9.1 \text{ Hz; J = 2.2 Hz; 1H}), 6.10 (d; J = 2.2Hz; 1H), 4.04 (t; 2H), 3.66 (q; 2H), 3.41 (q; 4H), 2.56 (s; 2H), 2.46 (s; 2H), 1.91 (qu; 2H), 1.55 (m; 7H), 1.21 (t; 6H), 1.06 (s; 6H).

$^{13}\text{C NMR (CDCl}_3, \text{ ppm): } \delta = 169.2, 159.8, 156.8, 150.7, 134.5, 130.5, 124.3, 120.5, 114.7, 113.8, 112.7, 104.8, 94.7, 74.0, 68.2, 62.8, 44.7, 43.1, 39.2, 32.8, 32.0, 29.3, 28.1, 26.3, 25.7, 12.8.$

MS: $m/z = 461 (M^+) , 446 (M^+ - \text{CH}_3\text{O}).$

IR (cm$^{-1}$): 3531, 2931, 2870, 2210.

2.7. Synthesis of chromophore 15a: Fig. 4

2.7.1. Synthesis of 2-thienylmethylenetriphenylphosphonium bromide 10

68.5 ml (600 mmol) of 2-thiophenemethanol was added to a solution of 206 g (600 mmol) of triphenylphosphine hydrobromide in 600 ml of acetonitrile. The reaction mixture was refluxed for 4 h and cooled down. The precipitate was filtered off, dried and used without further purification in the next step.

Yield : 250 g (95%)
m.p. : 153.3 °C
$^1$H NMR (CDCl$_3$, ppm): $\delta = 7.92$ (t; 3H), 7.74 (m; 12H), 7.48 (m; 1H), 6.97 (dd; J = 5.0 Hz, J = 3.1 Hz; 1H), 6.78 (d; J = 3.1 Hz; 1H), 5.52 (d; J = 14.6 Hz; 2H).

$^{13}$C NMR (CDCl$_3$, ppm): $\delta = 135.6$ (d; J = 2.9 Hz), 134.3 (d; J = 10.3 Hz), 130.9 (d; J = 8.0 Hz), 130.5 (d; J = 12.6 Hz), 128.8 (d; J = 9.8 Hz), 128.3 (d, J = 4.0 Hz), 127.7 (d; J = 2.9 Hz), 118.1 (d; J = 85.6 Hz).

MS: $m/z = 358$ (M$^+$ - HBr).


48.3 g (250 mmol) of 9a and 110 g (250 mmol) of 10 were dissolved in 500 ml of absolute ethanol. To this solution, 250 ml (375 mmol) of a NaOEt-solution (1.5 M in ethanol) was added dropwise and the reaction mixture was refluxed for 5 h under argon atmosphere. The cooled reaction mixture was poured into 500 ml of iced water and extracted with dichloromethane. The combined organic layers were washed with a saturated NaHCO$_3$-solution, with brine and dried over MgSO$_4$. After evaporation of the solvents, the compound was purified by column chromatography (silicagel; eluent: dichloromethane / ethylacetate (90:10 v/v)). The product was isolated as a mixture of cis and trans (cis/trans: 4/6).

Yield : 51.7 g (76%)

m.p. : 101.2 °C

$^1$H NMR (CDCl$_3$, ppm): trans : $\delta = 7.34$ (d; 2H), 7.10 (m; 1H), 7.03 (d; J = 15.7 Hz; 1H), 6.95 (m; 2H), 6.85 (d; J = 15.7 Hz; 1H), 6.74 (d; 2H), 3.81 (q; 2H), 3.45 (m; 4H), 1.64 (t; 1H), 1.17 (t; 3H).

cis : $\delta = 7.26$ (d; 2H), 7.10 (m; 1H), 6.95 (m; 2H), 6.72 (d; 2H), 6.54 (d; J = 12.1 Hz; 1H), 6.48 (d; J = 12.1 Hz; 1H), 3.81 (q; 2H), 3.45 (m; 4H), 1.64 (t; 1H), 1.17 (t; 3H).
13C NMR (CDCl₃, ppm): δ = 146.4, 146.3, 143.0, 139.7, 129.2, 128.8, 127.7, 126.6, 126.3, 126.1, 125.4, 123.5, 123.4, 123.3, 123.0, 121.8, 119.0, 116.1, 110.7, 110.1, 59.7, 51.4, 44.4, 11.2.

MS: m/z = 273 (M⁺), 242 (M⁺ - CH₃O).

2.7.3. Synthesis of 2-[2-{4-[N-ethyl-N-[2-{(t-
butyldimethyl)silyloxy]ethyl}amino]phenyl}ethenyl]thiophene 12a

In a 250 ml-flask, equipped with a CaCl₂-tube, 51.7 g (189 mmol) of 11a and 34.2 g (227 mmol) of t-butyldimethylsilylchloride were dissolved in 100 ml of dry DMF. The solution was cooled in an ice bath and 30.9 g (454 mmol) of imidazole was added in several portions. The reaction mixture was stirred overnight at 40 °C. After cooling, water was added and the mixture was extracted with pentane. The combined organic layers were washed with a saturated NaHCO₃-solution, with brine and dried over MgSO₄. After evaporation of the solvent, the product was isolated as an oil and used without further purification (cis/trans: 3.7/6.3).

Yield: 74.7 g (100 %)

1H NMR (CDCl₃, ppm): trans: δ = 7.29 (d; 2H), 7.05 (m; 1H), 7.03 (d; J = 16.4 Hz; 1H), 6.87 (m; 2H), 6.80 (d; J = 16.4 Hz; 1H), 6.74 (d; 2H), 3.72 (t; 2H), 3.39 (m; 4H), 1.12 (t; 3H), 0.83 (t; 9H), 0.06 (s; 6H).

cis: δ = 7.26 (d; 2H), 7.05 (m; 1H), 6.87 (m; 2H), 6.72 (d; 2H), 6.54 (d; J = 12.1 Hz; 1H), 6.53 (d; J = 12.1 Hz; 1H), 3.72 (t; 2H), 3.39 (m; 4H), 1.12 (t; 3H), 0.83 (t; 9H), 0.06 (s; 6H).

13C NMR (CDCl₃, ppm): δ = 146.5, 146.3, 143.1, 139.7, 129.0, 128.8, 127.7, 126.6, 126.4, 126.1, 125.5, 123.5, 123.4, 123.3, 123.0, 121.8, 119.1, 116.1, 110.6, 110.2, 59.6, 51.4, 44.4, 24.7, 17.2, 11.2, -6.4.

MS: m/z = 387 (M⁺), 242 (M⁺ - C7H17OSi).

41.8 g (108 mmol) of 12a was dissolved in 300 ml of dry THF. The solution was purged with argon, cooled to -78 °C and 94 ml (220 mmol) of n-butyllithium (2.34 M in hexane) was added. The solution turned dark blue. The temperature was slowly raised to -30 °C and 35 ml of dry DMF was added. Upon addition, the solution became yellow. After 2 h of stirring at -30 °C, 500 ml of HCl (2 M) was added (the solution turns deep red) and the mixture was vigorously stirred at 40 °C for 4 h. After cooling, the reaction mixture was neutralised with NH₃-solution (5 M) and extracted with dichloromethane. The combined organic layers were washed with a saturated NaHCO₃-solution, with brine and dried over MgSO₄. After evaporation of the solvents, the compound was purified by column chromatography (silicagel; eluent: dichloromethane / ethylacetate (90:10 v/v)), followed by recrystallisation from chloroform / hexane. No cis-isomer was detected.

Yield : 24.2 g (74%)

m.p. : 106.2 °C

¹H NMR (CDCl₃, ppm): δ = 9.81 (s; 1H), 7.62 (d; J = 4.0 Hz; 1H), 7.37 (d; 2H), 7.08 (d; J = 16.1 Hz; 1H), 7.05 (d; J = 4.0 Hz; 1H), 6.98 (d; J = 16.1 Hz; 1H), 6.73 (d; 2H), 3.82 (q; 2H), 3.52 (t; 2H), 3.46 (q; 2H), 1.71 (t; 1H), 1.19 (t; 3H).

¹³C NMR (CDCl₃, ppm): δ = 182.4, 154.3, 148.6, 140.0, 137.7, 133.4, 128.5, 125.0, 123.8, 116.1, 112.1, 60.1, 52.2, 45.5, 11.9.

MS: m/z = 301 (M⁺), 270 (M⁺ - CH₃O), 242 (M⁺ - CH₃O, -CO).

2.7.5. Synthesis of 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-(2H,5H)-furan 14 [9]

10.0 g (100 mmol) of 3-hydroxy-3-methyl-2-butanone and 13.2 g (200 mmol) of malononitrile were dissolved in 250 ml of absolute ethanol. The solution was purged with
argon and 1.0 ml of LiOEt (1.0 M in ethanol) was added. The flask was equipped with a Soxhlet extraction apparatus, containing a thimble, filled with molecular sieve, and the mixture was refluxed for 8 h under argon atmosphere. The solution was concentrated and cooled down (-20 °C). The precipitate was filtered off, washed with cold ethanol and recrystallised from ethanol.

Yield : 16.0 g (81%)
m.p. : 197.5 °C

$^1$H NMR (CDCl$_3$, ppm): δ = 2.36 (s; 3H), 1.63 (s; 6H).

$^{13}$C NMR (CDCl$_3$, ppm): δ = 182.5, 175.2, 111.0, 110.4, 109.0, 104.8, 99.8, 58.5, 24.4, 14.2.

MS: $m/z = 199$ (M$^+$), 174 (M$^+$ -CH$_3$).

2.7.6. Synthesis of chromophore 15a

2.3 g (7.50 mmol) of 13a and 1.8 g (9.00 mmol) of 14 were dissolved in 25 ml of chloroform. The solution was purged with argon and 0.2 ml of triethylamine was added. The mixture was refluxed under argon atmosphere, until 13a had completely disappeared (takes about 12 h). Then, the reaction mixture was cooled and 25 ml of hexane was added. The chromophore was filtered off and recrystallised twice from ethylacetate / hexane.

Yield : 1.0 g (30%)
m.p. : 239 °C

$\lambda_{\text{max}} = 635$ nm ($\epsilon = 4.7 \times 10^4$ 1·mol$^{-1}$·cm$^{-1}$)

$^1$H NMR (acetone-d6, ppm): δ = 8.13 (d; J = 15.7 Hz; 1H), 7.75 (d; J = 4.0 Hz; 1H), 7.48 (d; 2H), 7.20 (s; 2H), 7.19 (d; J = 4.0 Hz; 1H), 6.80 (d; J = 15.7 Hz; 1H), 6.76 (d; 2H), 3.86 (t; 1H), 3.73 (q; 2H), 3.51 (m; 4H), 1.87 (s; 6H), 1.17 (t; 3H).

$^{13}$C NMR (DMSO-d6, ppm): δ = 177.0, 174.6, 153.8, 148.8, 140.6, 139.2, 137.7, 134.6, 129.2, 127.7, 123.0, 115.8, 113.2, 112.5, 111.6, 111.4, 99.4, 96.4, 58.5, 52.8, 25.7, 12.2.
MS: \( m/z = 482 (M^+) \), 451 (\( M^+ - CH_3 \)), 184 (C\textsubscript{10}H\textsubscript{6}N\textsubscript{3}O).

IR (cm\(^{-1}\)): 3522, 2929, 2869, 2224.

2.8. Synthesis of chromophore 15b: Fig. 4


The procedure, described for 11a, was followed, starting from 57.2 g (229 mmol) of 9b. The product was isolated as an oil (cis/trans: 3.5/6.5).

Yield: 65.1 g (86%)

\(^1\)H NMR (CDCl\(_3\), ppm): trans : \( \delta = 7.34 \) (d; 2H), 7.19 (m; 1H), 7.08 (d; \( J = 16.1 \) Hz; 1H), 6.97 (m; 2H), 6.86 (d; \( J = 16.1 \) Hz; 1H), 6.64 (d; 2H), 3.67 (t; 2H), 3.40 (q; 2H), 3.28 (t; 2H), 1.61 (m; 4H), 1.42 (m; 4H), 1.22 (t; 3H).

cis : \( \delta = 7.27 \) (d; 2H), 7.19 (m; 1H), 6.97 (m; 2H), 6.62 (d; 2H), 6.51 (d; \( J = 12.1 \) Hz; 1H), 6.46 (d; \( J = 12.1 \) Hz; 1H), 3.67 (t; 2H), 3.40 (q; 2H), 3.28 (t; 2H), 1.61 (m; 4H), 1.42 (m; 4H), 1.22 (t; 3H).

\(^{13}\)C NMR (CDCl\(_3\), ppm): \( \delta = 147.7, 147.4, 144.1, 140.9, 130.1, 130.1, 128.8, 127.6, 127.5, 127.0, 126.6, 124.5, 124.3, 124.1, 123.6, 122.8, 119.9, 117.0, 111.5, 111.5, 63.1, 50.4, 44.9, 32.9, 27.6, 27.0, 12.4.

MS: \( m/z = 329 (M^+) \), 314 (\( M^+ - CH_3 \)).


The procedure, described for 12a, was followed, starting from 65.1 g (198 mmol) of 11b. The product was isolated as an oil (cis/trans: 3.2/6.8).

Yield = 77.9 g (89%)
\[ ^1\text{H NMR (CDCl}_3, \text{ppm): trans: } \delta = 7.34 \text{ (d; 2H), 7.11 \text{ (m; 1H), 7.03 \text{ (d; J = 15.7 Hz; 1H), 6.92 \text{ (m; 2H), 6.86 \text{ (d; J = 15.7 Hz; 1H), 6.63 \text{ (d; 2H), 3.63 \text{ (t; 2H), 3.40 \text{ (q; 2H), 3.28 \text{ (t; 2H), 1.60 \text{ (m; 4H), 1.38 \text{ (m; 4H), 1.18 \text{ (t; 3H), 0.91 \text{ (s; 9H), 0.06 \text{ (s; 6H).}}}}}}}}\]

\[ \text{cis : } \delta = 7.26 \text{ (d; 2H), 7.11 \text{ (m; 1H), 6.92 \text{ (m; 2H), 6.61 \text{ (d; 2H), 6.51 \text{ (d; J = 12.1 Hz; 1H), 6.46 \text{ (d; J = 12.1 Hz; 1H), 3.63 \text{ (t; 2H), 3.40 \text{ (q; 2H), 3.28 \text{ (t; 2H), 1.6 \text{ (m; 4H), 1.38 \text{ (m; 4H), 1.18 \text{ (t; 3H), 0.91 \text{ (s; 9H), 0.06 \text{ (s; 6H).}}}}}}}}\]

\[ ^{13}\text{C NMR (CDCl}_3, \text{ppm): } \delta = 147.6, 147.4, 144.1, 140.8, 130.1, 130.0, 128.8, 127.6, 127.4, 127.0, 126.5, 124.5, 124.3, 124.2, 123.6, 122.8, 119.8, 117.0, 111.6, 111.2, 63.0, 50.4, 44.9, 32.9, 27.6, 27.0, 25.8, 18.1, 12.4, -4.8. \]

MS: \( m/z = 443 \text{ (M}^+\text{), 428 \text{ (M}^+\text{ - CH}_3\text{), 242 \text{ (M}^+\text{ - C}_{11}H_{25}OSi).} \]

2.8.3. Synthesis of 2-2-\{4-\{N-ethyl-N-(6-hydroxyhexyl)amino\}phenyl\}ethenyl\}thien-5-al 13b

The procedure, described for 12a, was followed, starting from 44.4 g (100 mmol) of 12b. The product was isolated as an oil.

Yield : 28.4 g (79%)

\[ ^1\text{H NMR (CDCl}_3, \text{ppm): } \delta = 9.81 \text{ (s; 1H), 7.62 \text{ (d; J = 4.0 Hz; 1H), 7.36 \text{ (d; 2H), 7.08 \text{ (d; J = 16.1 Hz; 1H), 7.04 \text{ (d; J = 4.0 Hz; 1H), 6.96 \text{ (d; J = 16.1 Hz; 1H), 6.62 \text{ (d; 2H), 3.66 \text{ (q; 2H), 3.40 \text{ (q; 2H), 3.30 \text{ (t; 2H), 1.58 \text{ (m; 4H), 1.39 \text{ (m; 4H), 1.23 \text{ (t; 1H), 1.18 \text{ (t; 3H).}}}}}}}}\]

\[ ^{13}\text{C NMR (CDCl}_3, \text{ppm): } \delta = 182.3, 154.5, 148.5, 140.0, 137.7, 133.7, 128.4, 124.8, 122.9, 115.6, 111.5, 62.8, 50.3, 45.0, 32.7, 27.6, 27.0, 25.7, 12.4. \]

MS: \( m/z = 357 \text{ (M}^+\text{), 270 \text{ (M}^+\text{ - C}_5H_{11}O), 242 \text{ (M}^+\text{ - C}_5H_{11}O, -CO).} \]

2.8.4. Synthesis of chromophore 15b
The procedure, described for chromophore $15a$, was followed, starting from 4.00 g (11.2 mmol) of $13b$. The product was purified by column chromatography (silicagel; eluent: dichloromethane / ethylacetate (90:10 v/v)).

Yield: 2.56 g (42%)

m.p.: 177 °C

$\lambda_{\text{max}} = 640 \text{ nm } (\varepsilon = 5.0 \cdot 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$

$^1H$ NMR (CDCl$_3$, ppm): δ = 7.78 (d; J = 15.7 Hz; 1H), 7.39 (d; 2H), 7.38 (d; J = 3.7 Hz; 1H), 7.03 (d; J = 3.7 Hz; 1H), 6.99 (d; J = 16.1 Hz; 1H), 6.66 (d; 2H), 6.56 (d; J = 15.7 Hz; 1H), 3.68 (q; 2H), 3.43 (q; 2H), 3.33 (t; 2H), 1.76 (s; 6H), 1.65 (m; 4H), 1.45 (m; 4H), 1.23 (t; 1H), 1.21 (t; 3H).

$^{13}C$ NMR (CDCl$_3$, ppm): δ = 175.8, 172.9, 154.7, 148.9, 146.4, 137.7, 137.3, 129.1, 122.8, 112.3, 111.6, 111.5, 111.1, 96.9, 95.8, 62.9, 50.4, 45.1, 32.7, 27.6, 26.9, 26.6, 25.7, 12.4.

MS: $m/z = 538$ (M$^+$), 523 (M$^+ - $CH$_3$), 184 (C$_{10}$H$_6$N$_3$O).

IR (cm$^{-1}$): 3499, 2930, 2869, 2225.

2.9. Functionalisation of precursor polymers: Fig. 5

General procedure: Prior to reaction, the chromophores were recrystallised ($16a$-$b$ and $17a$-$b$ from ethanol, $8a$-$b$ and $15a$-$b$ from ethylacetate) and all reagents and solvents were thoroughly dried. 0.333 mmol of naphthol groups ($\textit{ppol I-II}$), 0.400 mmol of chromophore and 0.666 mmol of PPh$_3$ were dissolved in 15 ml of dry THF. The solution was purged with argon and 0.666 mmol of diethylazodicarboxylate (DEAD) was injected. The reaction vessel was sealed and the mixture was stirred for two days at room temperature. The polymer was isolated by precipitation in methanol, collected by filtration and dried. Finally, the polymer was redissolved in THF, reprecipitated in methanol and dried. This procedure was repeated until the filtrate was only slightly coloured.
3. Results and discussion

In this paper, the synthesis and properties of chromophore-functionalised polybinaphthalenes are reported. Several parameters in the molecular structure, including the spacer length, the nature of the chromophore and the number of chromophores per binaphthalene unit, were varied, in order to investigate the influence of these parameters on the (NLO) properties of these materials.

The polymer backbone consists of chiral binaphthalene unit, connected with rigid groups, to ensure the chiral, helical conformation [6-7, 10]. Hexyl groups were incorporated for solubility reasons and the chromophores were linked to the polymer backbone through the naphthol functions. The precursor polymers were prepared by means of a Suzuki reaction, because this pathway yields the highest molecular weights [7]. Direct polymerisation of chromophore-functionalised monomers to obtain chromophore-functionalised polymers, is not possible under this conditions, since this would lead to chromophore degradation. Therefore, the synthesis of chromophore-functionalised polybinaphthalenes was a two-step process, in which chromophores were introduced into precursor polymers in a second, separate step.

Two precursor polymers, with different number (1 or 2) of naphthol groups per binaphthalene unit, were synthesized. The number of naphthol groups per binaphthalene unit, available for functionalisation, was varied, since the two naphthol groups in a binaphthalene unit point in the opposite direction. It is therefore very likely that, when both are substituted with chromophores, the two chromophores will point in an opposite direction as well. This would result in a quasi centrosymmetrical ordering, which makes large second-order NLO responses impossible. As a consequence, systematically blocking one of the two naphthol groups with an alkyl group, can – in principal - increase the NLO response.
These precursor polymers were functionalised with 8 chromophores. The molecular structure of chromophores 16a-b and 17a-b is presented in Fig. 6. 16a is a commercial product (disperse red 1) and 16b, 17a [11] and 17b [11] were synthesized according to literature procedures. The synthesis of chromophores 8a and 8b is schematically shown in Fig. 3 and corresponds to a Knoevenagel condensation between the aldehyde 6a-b and 7. For the synthesis of 15a-b, the pathway, described in the literature [12] for analogous chromophores, was modified. In general, the key aldehyde 13a-b is prepared form the acetyl protected derivative of 9a-b, which is reacted with diethylthiophenephosphonate in a Horner reaction. Subsequently, the aldehyde functionality is introduced using a classical Vilsmeier reaction and finally, the alcohol group is deprotected. This pathway is characterised by its low yield (<10%). In our alternative procedure, 9a-b was reacted with the phosphonium salt 10, which can be readily obtained from 2-thiophenemethanol and triphenylphosphonium hydrobromide, in a classical Wittig reaction. In the next step the alcohol is converted into a silyl ether. The aldehyde group is then introduced by treatment with n-butyllithium, followed by addition of DMF and hydrolysis. Under proper reaction conditions, the conversion of the intermediary amino alcohol to the aldehydes 13a-b could be performed together with the deprotection of the silyl ether to the alcohol. The overall yield in this procedure exceeds 60%, which is about 8 times higher than in the classical route. Moreover, the intermediary compounds are more easily purified. The chromophores 15a-b were finally obtained by a condensation of 13a-b with the tricyano acceptor 14.

With these chromophores, the influence of the chromophore on the (NLO) properties was investigated. The chromophores differ from each other in their spacer length and the DπA-structure. While the DπA-structure of the chromophore clearly determines the NLO properties (amongst others), one can expect that the spacer length influences the ordering of the chromophores in these systems. In case of shorter, more rigid spacers, the backbone tends
to impose its chiral ordering more efficiently to the chromophores, which may benefit the NLO response. However, we must notice that if an additional ordering is performed, *s.a.* an electrical poling, the chiral ordering can be overruled and the advantages, proper to chirality, can in that case decrease or even disappear.

The chromophores were attached to the polymer backbone under Mitsunobu conditions. This reaction is known for its very mild reaction conditions. In this work, this is reflected in the fact that no decomposition of the chromophores, neither of the polymers, was observed during the functionalisation.

The physical properties of the polymers are listed in Tab. 1. The degree of functionalisation (DF) is defined as the percentage of naphthol groups that were successfully substituted by chromophores and was determined by UV-VIS and $^1$H NMR spectroscopy. These data show that the applied method, the functionalisation of precursor polymers by means of a Mitsunobu reaction, is very suitable to prepare these molecules.

The molecular weights and polydispersities were measured with GPC towards polystyrene standards. Although they seem quite low, we may assume that they are underestimated [12] and should be estimated about 2 times higher. In any way, they are sufficiently high to ensure good film forming properties and chiral ordering of the chromophores – as was experimentally proven.

$^1$H NMR experiments confirm the structure of both precursor polymers and chromophore-functionalised polymers. No end groups were detected, which indicates that the materials are of (relative) high molecular weight. Finally, no evidence for structure inhomogeneity was found.

Concerning the glass transition temperatures ($T_g$), it is remarkable that the chromophore-functionalised polymers show a clear $T_g$, while no $T_g$ could be observed from the precursor polymers (without chromophores). We assume that the observed phenomenon is the
weakening of the chromophores in the polymer system and not of the whole material. It is clear that this cannot be explained by the classical model of chromophore-functionalised polymers. In this model, the two components (polymer matrix and chromophores) mix perfectly well with each other. In that case, Fox’s law counts, which means that the inverse of the $T_g$ of the mixture is a weight average of the inverses of the $T_g$ of the components. The $T_g$’s of the chromophores are given in Tab. 2. Since the $T_g$ of the chromophores is lower than the $T_g$ of the polymer matrix, the chromophore acts as a plasticizer. Clearly, the chromophore-functionalised polybinaphthalenes do not fit in this model. The polymer backbone is helical, which is an ordered structure and the polymers without chromophores do not show a glass transition. What is observed, is not the weakening of a mixture of polymer backbone-chromophore, but the weakening of the *chromophores in the polymer system*. In that case, the $T_g$ of the system should increase when the $T_g$ of the chromophore increases, which is experimentally confirmed. Moreover, we will show in a following paper that the $T_g$ of the system is also increased when *both*, and not just one, naphthol groups per binaphthalene unit are functionalised with chromophore and when the chromophore concentration (i.e. the degree of functionalisation) is increased, which is in contrast with Fox’s law. (Unfortunately, it is not possible to investigate the influence of these parameters with this polymer systems, because the chromophore concentration cannot be varied under controlled condition.) Indeed, attaching the chromophore to a rigid, rod-like backbone reduces the mobility of the chromophores, which increases the $T_g$. Therefore, the $T_g$ of polybinaphthalenes, functionalised with chromophores with a long, flexible spacer, is lower than the $T_g$ of analogous systems with a short, more rigid spacer.

The optical rotations are quite high. It is important to notice that they increase dramatically when chromophores, of which $\lambda_{\text{max}}$ is close to the applied wavelength (589 nm), are
introduced. This seems to suggest that the chiral helical polymer backbone imposes its chiral ordering to the chromophores [2d]. Analogous results are obtained from CD experiments. Thin films were spincoated from polymers with the highest optical rotations (pol I-8a, pol I-8b, pol I-15a, pol I-15b, pol II-15a and pol II-15b). Although nonlinear optical processes can, in principal, be observed in isotropic chiral media, it remains in practice necessary to perform a polar ordering. Therefore, the chromophores were aligned by corona poling. The nonlinear optical properties were analysed by second-harmonic generation. The results are presented in Tab. 3. The symmetry of the poled samples was investigated by polarised UV-Vis and second-harmonic generation. These experiments showed that all samples had a $C_{\infty}$-symmetry with 4 nonvanishing susceptibility components, i.e. $\chi^{(2)}_{zzz}$, $\chi^{(2)}_{zzx}$, $\chi^{(2)}_{zxx}$ and $\chi^{(2)}_{xyz}$. The xyz-type component can only be present in chiral samples, while the other components can be observed in any sample, chiral or achiral. Our experiments showed that the chiral component is very weak and in most cases even negligible. Probably, the chiral ordering of the chromophores is lost during poling, resulting in a vanishing xyz-component. This hypothesis was partially confirmed by CD-experiments, in which the chromophore peak largely and in most cases completely disappeared (Fig. 7). On the other hand, the magnitude of the other susceptibility components was much larger. The reason is that these components are not linked to the chirality of the system, but instead originate from the polar order, introduced by the poling procedure. Susceptibility values of over 100 pm/V were observed, which illustrates the potential of these materials for nonlinear optical applications.

4. Conclusions

In this work chiral, helical chromophore-functionalised polybinaphtalalenes were synthesized. These polymers were obtained in a two-step process. First, precursor polymers were prepared via a Suzuki-coupling. In a second step, chromophores could be incorporated under Mitsunobu conditions. With this pathway, several parameters in the molecular structure of
the materials could be varied, which has made this class of polymers accessible to the field of (chiral) nonlinear optics. The nonlinear optical properties of these materials were measured and show reasonable high (achiral) responses.
Acknowledgements

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References


Table 1: Physical properties of the precursor polymers and chromophore-functionalised polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>DF&lt;sup&gt;a&lt;/sup&gt; / mole %</th>
<th>$\overline{M}_n$ / $10^3$ g mol&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>D&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$T_g$ / °C</th>
<th>$[\alpha]_D$&lt;sup&gt;0&lt;/sup&gt; / $10^2$ deg·dm&lt;sup&gt;-1&lt;/sup&gt;·g&lt;sup&gt;-1&lt;/sup&gt;·ml&lt;sup&gt;(c / 10&lt;sup&gt;-2&lt;/sup&gt; g·ml&lt;sup&gt;-1&lt;/sup&gt;)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppol I</td>
<td>7.8</td>
<td>2.4</td>
<td>c</td>
<td></td>
<td>3.3 (0.021)</td>
</tr>
<tr>
<td>ppol II</td>
<td>7.1</td>
<td>2.4</td>
<td>c</td>
<td></td>
<td>1.5 (0.034)</td>
</tr>
<tr>
<td>pol I-16a</td>
<td>30</td>
<td>12</td>
<td>2.0</td>
<td>151</td>
<td>2.9 (0.010)</td>
</tr>
<tr>
<td>pol I-16b</td>
<td>45</td>
<td>10</td>
<td>20</td>
<td>141</td>
<td>3.6 (0.008)</td>
</tr>
<tr>
<td>pol I-17a</td>
<td>70</td>
<td>13</td>
<td>2.3</td>
<td>160</td>
<td>125 (0.009)</td>
</tr>
<tr>
<td>pol I-17b</td>
<td>40</td>
<td>15</td>
<td>2.0</td>
<td>123</td>
<td>145 (0.010)</td>
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<tr>
<td>pol I-8a</td>
<td>50</td>
<td>14</td>
<td>2.0</td>
<td>153</td>
<td>174 (0.010)</td>
</tr>
<tr>
<td>pol I-8b</td>
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<td>14</td>
<td>2.0</td>
<td>126</td>
<td>185 (0.008)</td>
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<tr>
<td>pol I-15a</td>
<td>10</td>
<td>7.5</td>
<td>2.3</td>
<td>143</td>
<td>671 (0.002)</td>
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<tr>
<td>pol I-15b</td>
<td>10</td>
<td>7.7</td>
<td>2.0</td>
<td>118</td>
<td>681 (0.002)</td>
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<tr>
<td>pol II-16a</td>
<td>60</td>
<td>8.7</td>
<td>2.2</td>
<td>85</td>
<td>4.0 (0.010)</td>
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<tr>
<td>pol II-16b</td>
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<td>8.5</td>
<td>2.1</td>
<td>93</td>
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<td>10</td>
<td>2.0</td>
<td>128</td>
<td>149 (0.010)</td>
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<tr>
<td>pol II-17b</td>
<td>50</td>
<td>7.5</td>
<td>2.1</td>
<td>100</td>
<td>129 (0.012)</td>
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<td>pol II-8a</td>
<td>25</td>
<td>7.0</td>
<td>2.3</td>
<td>116</td>
<td>178 (0.008)</td>
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<tr>
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<td>15</td>
<td>8.5</td>
<td>2.1</td>
<td>114</td>
<td>148 (0.018)</td>
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<tr>
<td>pol II-15a</td>
<td>35</td>
<td>7.9</td>
<td>2.2</td>
<td>162</td>
<td>1.28·10&lt;sup&gt;4&lt;/sup&gt; (0.003)</td>
</tr>
<tr>
<td>pol II-15b</td>
<td>35</td>
<td>7.6</td>
<td>2.1</td>
<td>138</td>
<td>1.20·10&lt;sup&gt;4&lt;/sup&gt; (0.004)</td>
</tr>
</tbody>
</table>

<sup>a</sup> degree of functionalisation

<sup>b</sup> polydispersity: $D = \overline{M}_w / \overline{M}_n$

<sup>c</sup> couldn’t be detected
Table 2: Glass transition temperatures of the chromophores

<table>
<thead>
<tr>
<th></th>
<th>16a</th>
<th>16b</th>
<th>17a</th>
<th>17b</th>
<th>8a</th>
<th>8b</th>
<th>15a</th>
<th>15b</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g/°C$</td>
<td>a</td>
<td>a</td>
<td>46</td>
<td>16</td>
<td>52</td>
<td>23</td>
<td>108</td>
<td>66</td>
</tr>
</tbody>
</table>

\(^{a}\) couldn’t be made amorphous
Table 3: Nonlinear properties of the chromophore-functionalised polymers **pol I-8a** – **pol I-15b** and **pol II-15a** - **pol II-15b**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\chi^{(2)}_{zzz}$ / pm·V⁻¹</th>
<th>$\chi^{(2)}_{zzz}(0)$ / pm·V⁻¹</th>
<th>$\chi^{(2)}_{xxc}$ / pm·V⁻¹</th>
<th>$\chi^{(2)}_{xxx}$ / pm·V⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pol I-8a</strong></td>
<td>103</td>
<td>6.6</td>
<td>36.5</td>
<td>46.6</td>
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<tr>
<td><strong>pol I-8b</strong></td>
<td>112</td>
<td>7.8</td>
<td>35.8</td>
<td>40.7</td>
</tr>
<tr>
<td><strong>pol I-15a</strong></td>
<td>32.2</td>
<td>10.6</td>
<td>9.0</td>
<td>14.9</td>
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<tr>
<td><strong>pol I-15b</strong></td>
<td>23.8</td>
<td>8.6</td>
<td>7.3</td>
<td>12.3</td>
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<tr>
<td><strong>pol II-15a</strong></td>
<td>19.9</td>
<td>5.8</td>
<td>4.8</td>
<td>9.0</td>
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<tr>
<td><strong>pol II-15b</strong></td>
<td>18.7</td>
<td>6.3</td>
<td>5.6</td>
<td>8.8</td>
</tr>
</tbody>
</table>
Figure captions:

Figure 1: Synthesis of 3b.

Figure 2: Polymerisation of the binaphthalene monomers via a Suzuki reaction.

Figure 3: Synthesis of chromophores 8a-b.

Figure 4: Synthesis of chromophores 15a-b.

Figure 5: Functionalisation of the precursor polymers (ppol II) with chromophores.

Figure 6: Structure of chromophores 16a-b, 17a-b.

Figure 7: CD-spectrum of pol I-8b before and after poling.
Figure 1

1. 1 eq. NaH
2. 1 eq. hexbr

1.) NaH
2.) ClCH₂-OCH₃
1.) Pd[PPh₃]₄, PPh₃
   THF / 1 M K₂CO₃ (aq)
2.) THF / 6 M HCl (aq)

R = MOM 3a
R = hex 3b

R = H  ppol I
R = hex ppol II
Figure 3

5

1.) NaH
2.) HO-Br or HO-Cl

6a
n = 1
6b
n = 3

7

AcOH, Ac₂O, piperidine

8a
n = 1
8b
n = 3
Figure 6

\[
\begin{align*}
\text{n = 1 } & \quad 16a \\
\text{n = 3 } & \quad 16b
\end{align*}
\]

\[
\begin{align*}
\text{n = 1 } & \quad 17a \\
\text{n = 3 } & \quad 17b
\end{align*}
\]
Figure 7

\[ \theta / \text{millidegrees} \]

- before poling
- after poling

\[ \lambda / \text{nm} \]