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Poly(phenylquinoxalines) for second-order nonlinear optical applications

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Abstract

Second-order non-linear optical (NLO) poly(phenylquinoxalines) with high glass transition temperatures were prepared by reaction of bis(1,2-diketone)chromophore monomer and a tetramine at room temperature. Glass transition temperatures in the range of 187–260 °C were obtained. Thin spincoated films of the polymers were corona-poled and analysed by second-harmonic generation (SHG). Second-order susceptibility values $d_{33}(\omega)$ up to 114 pm/V were obtained. Poled order stability measurements over a period of 750 h resulted in up to 91% of remaining NLO-response at 125 °C.

Keywords: Poly(phenylquinoxalines); Non-linear optics; Second harmonic generation

1. Introduction

Second-order non-linear optical (NLO) polymers are of considerable interest for the development of high speed modulators and switches. Several important properties are required to be useful in applications for devices, e.g. large optical non-linearities, low optical loss and stability of the NLO-response in function of time at prolonged elevated temperatures [1–4]. Cross-linking during poling is one of the approaches to obtain a high poled-order stability [5,6]. Another approach is the synthesis of high glass transition polymers, such as polyimides [7–15] or maleimide-based polymers [16–21].

In a previous paper [22] we investigated the synthesis of chromophore functionalised second-order NLO poly(phenylquinoxalines) with high glass transition temperatures, obtained by reaction of a bis(1,2-diketone)chromophore monomer and a tetramine in *m*-cresol at room temperature. Due to the restricted solubility of these polymers in organic solvents the spincoated films were of low optical quality and gave relatively low SHG values.

This paper reports the synthesis of a new series of soluble poly(phenylquinoxalines). To improve the solubility tetraaminodiphenylether or fluorinated moieties were incorporated in the polymer chain. The heterocyclic polymers, with high glass transition temperatures (>187 °C), are expected to be excellent polymer materials with high poling stabilities of the NLO response of electric poled spincoated thin films.

2. Experimental part

2.1. Materials and instrumentation

All starting reagents were purchased from Aldrich Chemical Co. or Acros Organics and used without purification unless stated otherwise. Tetrahydrofuran was dried over sodium potassium alloy and distilled prior to use. *N*-Methylpyrrolidinone (NMP) and *m*-cresol were purified by distillation over CaH_2.

Differential scanning calorimetry (DSC) measurements were done with a DCS-7 apparatus from Perkin–Elmer with a heating range of 20 °C/min. The second run was taken for measuring the glass transition temperature (T_g). The

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decomposition temperature (T_d) was estimated as the intercept of the leading edge of the thermal decomposition peak by the base line of each DSC scan.

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 and ^{13}C nuclear magnetic resonance (NMR) measurements were done with a Bruker 250 MHz apparatus with tetramethylsilane (TMS) as internal standard and chloroform or dimethyl sulfoxide as solvent.

2.2. Second harmonic generation measurements

Thin films were obtained by spincoating a solution of the poly(phenylquinoxalines) in cyclohexanone onto ITO substrates. The spincoated films were carefully dried under vacuum for at least 48 h at a temperature about 10 °C below the boiling point of the spincoating solvent. Subsequently they were corona-poled with a needle electrode at 1 cm above the film surface, 10 °C below T_g and an applied voltage of 7–8 kV during 20 min. The second-order susceptibility was measured using the Maker-fringe method [23]. A quartz crystal was used as a reference ($d_{11}=0.3$ pm/V) [24] and the measurements were done at a fundamental wavelength of 1064 nm. The thermal stability of the NLO-response was investigated by heating the corona-poled polymer films at 125 °C and following the normalised second-harmonic coefficient $d_{33}(t)/d_{33}(t=0)$ as a function of time, where $d_{33}(t)$ and $d_{33}(t=0)$ represent the second-harmonic coefficient at time t and time 0, respectively.

2.3. Synthesis of chromophores a–j

2.3.1. Synthesis of chromophore a: Fig. 1

Chromophore a: 13 g (0.10 mol) of tetracyanoethylene (TCNE) was added slowly to a solution of 18 g (0.10 mol) of *N*-phenyldiethanolamine (**1**) in 25 ml of *N*,*N*-dimethylformamide (DMF), maintaining the temperature below 40 °C. The reaction mixture was stirred at 60 °C for 10 min and then cooled in an ice bath. The precipitate was filtered off, washed with cold acetic acid and with methanol and purified by column chromatography (SiO_2; ethylacetate), followed by recrystallisation from ethanol. Yield: 18 g (63%), mp 180.0–184.5 °C, λ_{max} (THF) = 520 nm, ^{1}H NMR (DMSO-d_6, ppm): $\delta=3.64$ (t; 4H; $^3J=5.1$ Hz), 3.67 (q; 4H; $^3J=5.1$ Hz), 4.91 (t; 2H; $^3J=5.1$ Hz), 7.06 (d; 2H; $^3J=9.5$ Hz), 7.90 (d; 2H; $^3J=9.5$ Hz), ^{13}C NMR (DMSO-d_6, ppm): $\delta=53.8$, 58.7, 74.8, 113.7, 115.0, 115.2, 115.3, 117.1, 132.7, 136.0, 155.1.

2.3.2. Synthesis of chromophore b [15]: Fig. 2

Chromophore b was synthesised according to the procedure of Yu et al. [25]: 4-[bis(2-hydroxyethyl)amino]-benzaldehyde was reacted with 4-nitrophenylacetic acid in the presence of piperidine at 110 °C. Yield: 56%, mp 182.3–183.0 °C, λ_{max} (THF) = 428 nm, ^{1}H NMR (DMSO-d_6, ppm): $\delta=3.48$ (t; 4H; $^3J=5.1$ Hz), 3.56 (q; 4H; $^3J=5.1$ Hz), 4.79 (t; 2H; $^3J=5.1$ Hz), 6.73 (d; 2H; $^3J=8.8$ Hz), 7.07 (d; 1H; $^3J=17$ Hz), 7.40 (d; 1H; $^3J=17$ Hz), 7.47 (d; 2H; $^3J=8.8$ Hz), 7.74 (d; 2H; $^3J=8.8$ Hz), 8.17 (d; 2H; $^3J=8.8$ Hz), ^{13}C NMR (DMSO-d_6, ppm): $\delta=53.5$, 58.5, 111.7, 121.0, 123.6, 124.4, 126.6, 129.0, 134.3, 145.4, 145.6, 149.0.

2.3.3. Synthesis of chromophore c: Fig. 3

2,4-[Bis((2-hydroxyethyl)oxy)]benzaldehyde (**3**). A solution of 9.7 g (0.070 mol) of 2,4-dihydroxybenzaldehyde (**2**) in 70 ml of dry DMF, was slowly added to a suspension of 4.1 g (0.17 mol) of sodium hydride (NaH) in 70 ml of dry DMF at 0 °C under argon atmosphere. After 1 h, 21 g (0.17 mol) of 2-bromo-ethanol and a catalytic amount of anhydrous sodium iodide was added very slowly under stirring at 0 °C. The reaction mixture was stirred at 70 °C under argon atmosphere. After two days the mixture was poured into 100 ml of water and extracted with dichloromethane. The organic layer was dried over $MgSO_4$. After removal of the solvents, the crude compound was purified by column chromatography (SiO_2; ethylacetate), followed by recrystallisation from ethanol. Yield: 9.0 g (57%), mp 103.2–105.8 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta=4.03$ (m; 4H), 4.18 (m; 4H), 4.95 (m; 2H), 6.53 (s; 1H; H_f), 6.61 (d; 1H; $^3J=8.4$ Hz), 7.81 (d; 1H; $^3J=8.4$ Hz), 10.29 (s; 1H).

Chromophore c was synthesised using the same procedure as for chromophore b, starting from 3.6 g (16 mmol) of 2,4-[bis((2-hydroxyethyl)oxy)]benzaldehyde (**3**), 4.3 g (24 mmol) of 4-nitrophenylacetic acid and 1.1 ml of piperidine. The compound was finally purified by recrystallisation from ethanol. Yield: 1.9 g (34%), mp 176.5–179.3 °C, λ_{max} (THF) = 329 nm, ^{1}H NMR (DMSO-d_6, ppm): $\delta=3.73$ (q; 2H; $^3J=5.1$ Hz), 3.80 (q; 2H; $^3J=5.1$ Hz), 4.04 (t; 2H; $^3J=5.1$ Hz), 4.08 (t; 2H; $^3J=5.1$ Hz), 4.88 (t; 1H; $^3J=5.1$ Hz), 5.01 (t; 1H; $^3J=5.1$ Hz), 6.58 (d; 1H; $^3J=9.1$ Hz), 6.62 (s; 1H), 7.32 (d; 1H; $^3J=16$ Hz), 7.63 (d; 1H; $^3J=9.1$ Hz), 7.65 (d; 1H; $^3J=16$ Hz), 7.78 (d; 2H; $^3J=8.8$ Hz), 8.21 (d; 2H; $^3J=8.8$ Hz), ^{13}C NMR (DMSO-d_6, ppm): $\delta=59.8$, 60.0, 70.3, 71.1, 102.7, 107.0, 118.4, 124.2, 124.8, 127.4, 128.7, 128.8, 145.5, 146.0, 158.7, 161.2.

2.3.4. Synthesis of chromophore d: Fig. 4

2-[3-Oxo-indane-1-ylidene]-1,3-propanedinitrile (**5**). To a solution of 2.2 g (15 mmol) of 1,3-indanedione and 2.0 g (30 mmol) of 1,3-propanedinitrile in 30 ml of ethanol was added 1.6 g (20 mmol) of sodium acetate. After stirring 1 h at room temperature, 50 ml of water was added and then hydrochloric acid (1 N) till a pH of 2 was reached. The precipitate was collected by filtration, washed with water and dried. The product was purified by recrystallisation from acetic acid. Yield: 2.4 g (82%), mp 237.9–239.9 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta=3.75$ (s; 2H), 7.87 (m; 1H), 7.92

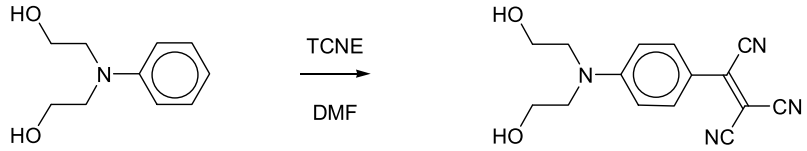

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Fig. 1. Synthesis of chromophore a.

(m; 1H), 8.01 (dd; 1H; $^3J=7.3$ Hz; $^4J=1.5$ Hz), 8.68 (d; 1H; $^3J=7.7$ Hz).

Chromophore d was synthesised by the procedure of Bello et al. [26]: 1.9 g (10 mmol) of 2-[3-oxo-indane-1-ylidene]-1,3-propanedinitrile (**5**) and 2.5 g (12 mmol) of 2,2′-(*N*-(4-nitrosophenyl)aminodiethanol (**4**) were dissolved in ethanol and stirred at room temperature for 12 h. The precipitate was filtered off, washed with cold ethanol and dried. The compound was finally purified by recrystallisation from ethanol. Yield: 2.8 g (74%), mp 222.1–224.7 °C, λ_{max} (THF) = 608 nm, ^{1}H NMR (DMSO-d$_6$, ppm): $\delta=3.79$ (m; 8H), 4.94 (t; 2H; $^3J=5.1$ Hz), 6.84 (d; 2H; $^3J=9.1$ Hz), 7.70 (m; 2H), 7.80 (d; 1H; $^3J=7.0$ Hz), 7.98 (d; 2H; $^3J=9.1$ Hz), 8.24 (d; 1H; $^3J=7.7$ Hz), ^{13}C NMR (DMSO-d$_6$, ppm): $\delta=54.5$, 59.8, 70.1, 113.4, 115.0, 116.0, 124.9, 134.0, 135.2, 135.6, 136.0, 136.4, 137.1, 138.5, 141.0, 154.4, 160.5, 182.0.

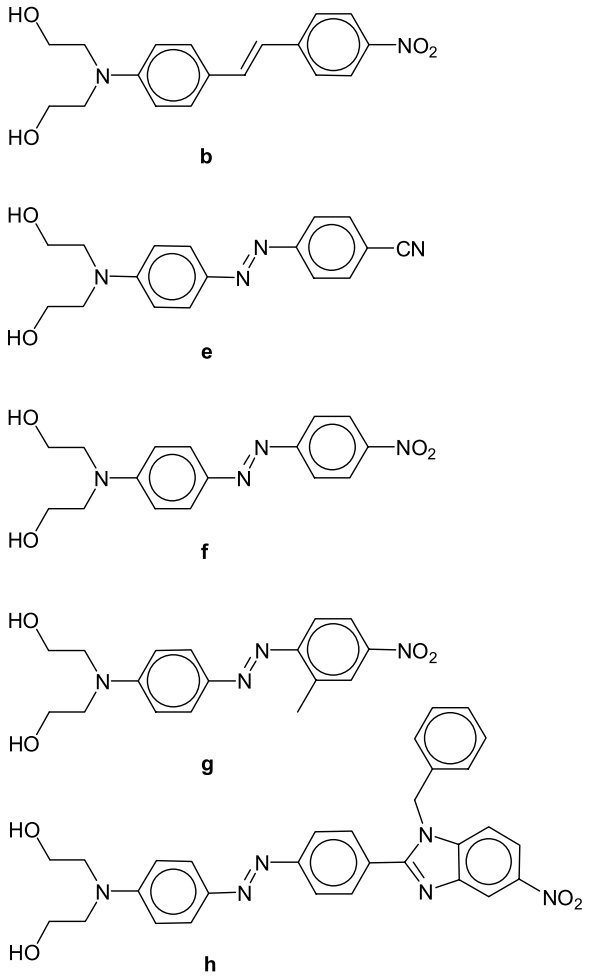

Fig. 2. Structure of chromophore b, e, f, g and h.

2.3.5. Synthesis of chromophore e, f and g: Fig. 2

The procedure of Dalton and co-workers [27] was followed by reaction of *N*-phenyldiethanolamine (**1**) and the diazonium salt prepared of the respective amines and yielded 54% of e, mp 173.2–174.5 °C, λ_{max} (THF) = 458 nm, 57% of f, mp 207.8–209.3 °C, λ_{max} (THF) = 487 nm and 65% of g, mp 199.7–201.9 °C, λ_{max} (THF) = 485 nm, respectively.

^{1}H NMR of e (DMSO-d$_6$, ppm): $\delta=3.62$ (m; 8H), 4.88 (t; 2H; $^3J=5.1$ Hz), 6.89 (d; 2H; $^3J=8.8$ Hz), 7.81 (d; 2H; $^3J=8.8$ Hz), 7.86 (d; 2H; $^3J=8.0$ Hz), 7.96 (d; 2H; $^3J=8.0$ Hz), ^{13}C NMR of e (DMSO-d$_6$, ppm): $\delta=53.7$, 58.5, 111.2, 111.9, 119.2, 122.7, 126.1, 133.9, 142.7, 152.3, 155.2.

^{1}H NMR of f (DMSO-d$_6$, ppm): $\delta=3.64$ (m; 8H), 4.88 (t; 2H; $^3J=4.7$ Hz), 6.91 (d; 2H; $^3J=9.5$ Hz), 7.82 (d; 2H; $^3J=9.5$ Hz), 7.92 (d; 2H; $^3J=8.8$ Hz), 8.35 (d; 2H; $^3J=8.8$ Hz), ^{13}C NMR of f (DMSO-d$_6$, ppm): $\delta=53.7$, 58.5, 112.0, 122.8, 125.3, 126.4, 142.9, 147.1, 152.7, 156.6.

^{1}H NMR of g (DMSO-d$_6$, ppm): $\delta=2.69$ (s; 3H), 3.60 (m; 8H), 4.87 (t; 2H; $^3J=4.8$ Hz), 6.89 (d; 2H; $^3J=9.5$ Hz), 7.65 (d; 2H; $^3J=9.5$ Hz), 7.82 (d; 1H; $^3J=8.8$ Hz), 8.12 (dd; 1H; $^3J=8.8$ Hz, $^4J=2.2$ Hz), 8.24 (d; 1H; $^4J=2.2$ Hz), ^{13}C NMR of g (DMSO-d$_6$, ppm): $\delta=17.5$, 53.7, 58.5, 112.0, 116.4, 122.5, 126.3, 126.5, 137.4, 143.6, 146.9, 152.5, 154.7.

2.3.6. Synthesis of chromophore h: Fig. 2

Chromophore h was prepared using the procedure described in a previous paper [22]: 2-(4-aminophenyl)-1-benzyl-5-nitro-benzimidazole was reacted with sodium nitrite in hydrochloric acid and transformed into its tetraflouroborate salt. 2.8 g (6.3 mmol) of the salt and 1.2 g (6.6 mmol) of *N*-phenyldiethanolamine were dissolved in 10 ml DMF under cooling. The reaction was then continued by stirring at room temperature for another 12 h. The reaction mixture was poured in 500 ml of iced water, the precipitate was filtered and dried. The crude compound was finally purified by column chromatography (SiO_2; ethylacetate). Yield: 1.4 g (41%), mp 176.4–180.8 °C, λ_{max} (THF) = 432 nm, ^{1}H NMR (DMSO-d$_6$, ppm): $\delta=3.57$ (t; 4H; $^3J=5.0$ Hz), 3.61 (t; 4H; $^3J=5.0$ Hz), 4.86 (broad s; 2H), 5.73 (s; 2H), 6.87 (d; 2H;

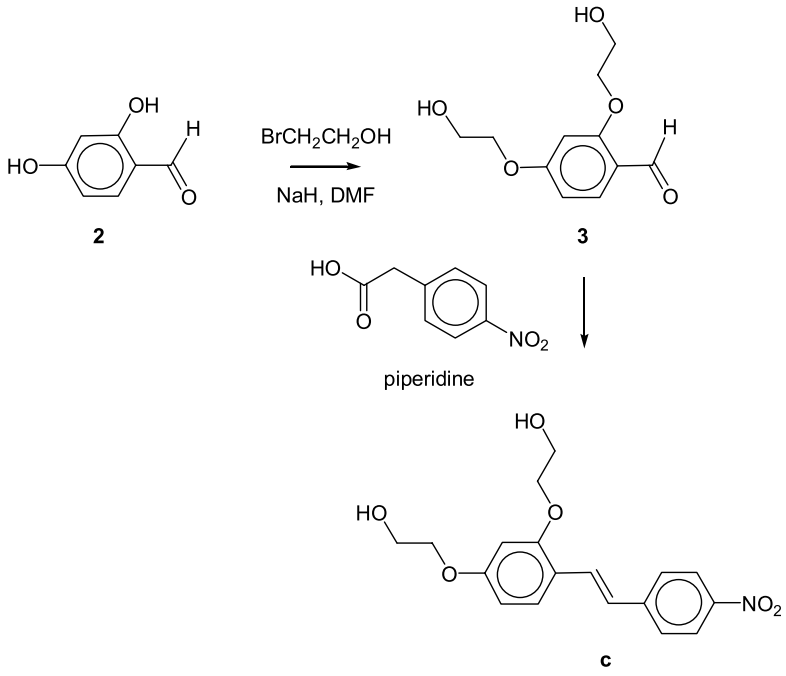

Fig. 3. Synthesis of chromophore c.

^{3}J=9.2 Hz), 7.03 (d; 2H; ^{3}J=7.0 Hz), 7.28 (m; 3H), 7.76 (d; 1H; ^{3}J=8.8 Hz), 7.78 (d; 2H; ^{3}J=9.2 Hz), 7.87 (d; 2H; ^{3}J=8.8 Hz), 7.90 (d; 2H; ^{3}J=8.8 Hz), 8.18 (dd; 1H; ^{3}J= 8.8 Hz, ^{4}J=2.2 Hz), 8.62 (d; 1H; ^{4}J=2.2 Hz), ^{13}C NMR (DMSO-d_6, ppm): δ=49.0, 54.2, 59.1, 112.2, 112.5, 116.6, 119.5, 122.7, 126.2, 127.0, 128.5, 129.1, 129.3, 131.7, 137.3, 141.5, 143.2, 143.4, 144.4, 152.4, 155.2, 157.4.

2.3.7. Synthesis of chromophore i: Fig. 5

2-[2-(2,6-Dimethyl-4H-pyrane-4-ylidene)-3-oxo-indane-1-ylidene]-1,3-propanedinitrile (**6**). 2.5 g (20 mmol) of 2,6-dimethyl-4*H*-pyran-4-on and 3.9 g (20 mmol) 2-[3-oxo-indane-1-ylidene]-1,3-propanedinitrile (**5**) were refluxed for 12 h in 150 ml of acetic anhydride. After evaporation of the solvent, the residue was dissolved in boiled water. After cooling the precipitate was filtered, washed with cold water and dried. The crude compound was finally purified by column chromatography (SiO_2; dichloromethane/ethylacetate 9/1). Yield: 5.7 g (95%), mp 214.2–216.0 °C, ^{1}H NMR (DMSO-d_6, ppm): δ=2.55 (s; 6H), 7.60 (m; 1H), 7.68 (s; 2H), 7.73–7.76 (m; 2H), 8.29 (d; 1H; ^{3}J=8.0 Hz), ^{13}C NMR (DMSO-d_6, ppm): δ=20.4, 64.2, 109.3, 112.4, 115.8, 116.7, 122.7, 123.1, 133.3, 134.0, 136.3, 140.0, 149.8, 153.5, 167.3, 187.4.

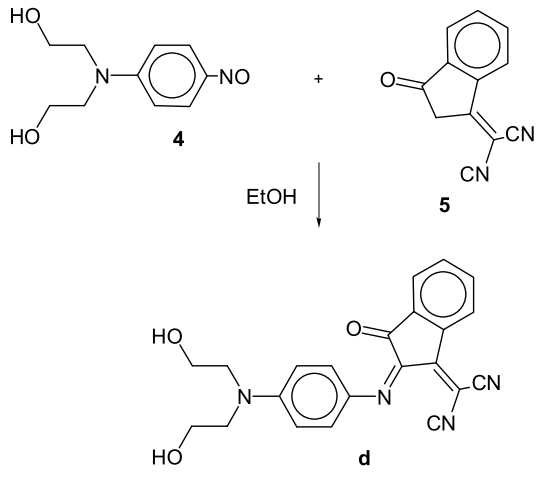

Fig. 4. Synthesis of chromophore d.

Chromophore i was synthesised by the procedure of Moylan et al. [28]. 1.5 g (5.0 mmol) of 2-[2-(2,6-dimethyl-4*H*-pyrane-4-ylidene)-3-oxo-indane-1-ylidene]-1,3-propanedinitrile (**6**) and 2.7 g (15 mmol) of 4-[*N*-(2-hydroxyethyl)-*N*-methylamino]benzaldehyde (**7**) were dissolved in toluene whereto a few drops of piperidine were added. Water was removed by azeotropic distillation using a Dean–Stark trap. After three days, the reaction mixture was cooled, the precipitate was filtered and purified by column chromatography (SiO_2; dichloromethane), followed by recrystallisation from ethanol. Yield: 1.0 g (33%), mp 267.5–269.7 °C, λ_{max} (NMP)=608 nm, ^{1}H NMR (DMSO-d_6, ppm): δ=3.05 (s; 6H), 3.51 (t; 4H; ^{3}J=5.1 Hz), 3.58 (q; 4H; ^{3}J=5.1 Hz), 4.78 (t; 2H; ^{3}J=5.1 Hz), 6.79 (d; 4H; ^{3}J= 8.8 Hz), 7.10 (d; 2H, ^{3}J=16 Hz), 7.50 (s; 2H), 7.63 (m; 3H), 7.68 (d; 4H; ^{3}J=8.8 Hz), 7.79 (d; 2H; ^{3}J=16 Hz), 8.29 (d; 1H; ^{3}J=8.0 Hz), ^{13}C NMR (DMSO-d_6, ppm): δ=45.2, 58.8, 61.2, 73.1, 109.5, 112.2, 112.8, 114.3, 118.0, 125.9, 126.7, 127.1, 128.2, 128.8, 129.6, 131.3, 131.4, 133.9, 136.1, 149.2, 150.2, 151.4, 162.4, 187.8.

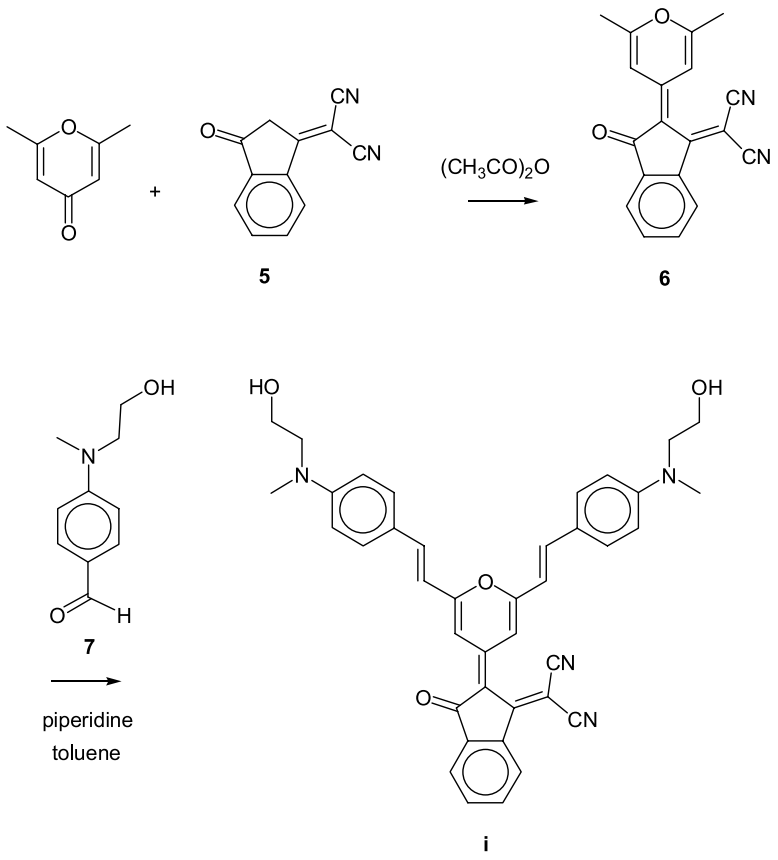

Fig. 5. Synthesis of chromophore i.

2.3.8. Synthesis of chromophore j: Fig. 6

2-[1,1-Dioxide-2,3-dihydrobenzothiophene-3-ylidene]-1,3-propanedinitrile (**9**) [29]. 1.8 g (10 mmol) of 1,1-dioxide-2,3-dihydrobenzothiophene-3-on (**8**) was reacted with 0.66 g (10 mmol) of 1,3-propanedinitrile in the presence of 25 ml of ethanol at 60 °C. After cooling, the precipitate was filtered, washed with cold ethanol and dried. Yield: 2.2 g (96%), mp 209.4–211.7 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 4.56$ (s; 2H), 7.90 (m; 2H), 7.98 (d; 1H; $^3J = 7.3$ Hz), 8.67 (d; 1H; $^3J = 8.0$ Hz).

2-[2-(2,6-Dimethyl-4H-pyrane-4-ylidene)-1,1-dioxide-2,3-dihydrobenzothiophene-3-ylidene]-1,3-propanedinitrile (**10**) was prepared using the same procedure as for **6**, starting from 2,6-dimethyl-4*H*-pyran-4-on and 2-[1,1-dioxide-2,3-dihydrobenzothiophene-3-ylidene]-1,3-propanedinitrile (**9**) and yielded 80%, mp 261.0–262.4 °C, ^{1}H NMR (DMSO-d_6, ppm): $\delta = 2.57$ (s; 6H), 7.06 (s; 2H), 7.90 (m; 2H), 8.09 (d; 1H; $^3J = 7.3$ Hz), 8.55 (d; 1H; $^3J = 8.0$ Hz), ^{13}C NMR (DMSO-d_6, ppm): $\delta = 20.4$, 64.8, 110.5, 115.7, 116.6, 121.9, 124.3, 130.7, 134.4, 134.7, 138.6, 146.5, 146.6, 151.7, 167.3.

Chromophore j was synthesised using the same procedure as for chromophore **i**, starting from 4-[*N*-(2-hydroxyethyl)-*N*-methylamino]benzaldehyde (**7**) and 2-[2-(2,6-dimethyl-4*H*-pyrane-4-ylidene)-1,1-dioxide-2,3-dihydrobenzothiophene-3-ylidene]-1,3-propanedinitrile (**10**) and yielded 49%, mp 299.7–301.3 °C, λ_{max} (NMP) = 530 nm, ^{1}H NMR (DMSO-d_6, ppm): $\delta = 3.07$ (s; 6H), 3.53 (t; 4H; $^3J = 5.1$ Hz), 3.60 (q; 4H; $^3J = 5.1$ Hz), 4.80 (t; 2H; $^3J = 5.1$ Hz), 6.80 (d; 4H; $^3J = 8.8$ Hz), 7.01 (s; 2H), 7.16 (d; 2H; $^3J = 16$ Hz), 7.71 (d; 4H; $^3J = 8.8$ Hz), 7.85 (d; 2H; $^3J = 16$ Hz), 7.87 (m; 2H), 8.06 (d; 1H; $^3J = 7.3$ Hz), 8.59 (d; 1H; $^3J = 8.1$ Hz), ^{13}C NMR (DMSO-d_6, ppm): $\delta = 45.3$, 56.8, 58.6, 71.1, 111.0, 112.1, 113.0, 113.7, 117.2, 118.3, 122.6, 121.6, 124.1, 130.9, 131.2, 133.6, 134.6, 138.3, 140.9, 148.9, 150.8, 151.7, 162.5.

2.4. Synthesis of chromophore monomers Ma–Mj: Fig. 7

2.4.1. Synthesis of 1-(4-hydroxyphenyl)-2-phenyl-1,2-ethanedione (*11*) [22]

The synthesis has been described in a previous paper [22]. Oxidation of benzyl-4-hydroxyphenyl ketone with selenium dioxide, yielded 93% of 11, mp 128.1–129.8 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.93$ (d; 2H; $^3J = 8.8$ Hz), 7.52 (t; 2H; $^3J = 7.8$ Hz), 7.67 (t; 1H; $^3J = 7.8$ Hz), 7.92 (d; 2H; $^3J = 8.8$ Hz), 7.99 (d; 2H; $^3J = 7.8$ Hz).

2.4.2. Synthesis of chromophore monomers Ma–Mj

General procedure [30]: 2.50 mmol of chromophore, 6.25 mmol of 1-(4-hydroxyphenyl)-2-phenyl-1,2-ethanedione (**11**) and 6.88 mmol of triphenylphosphine was

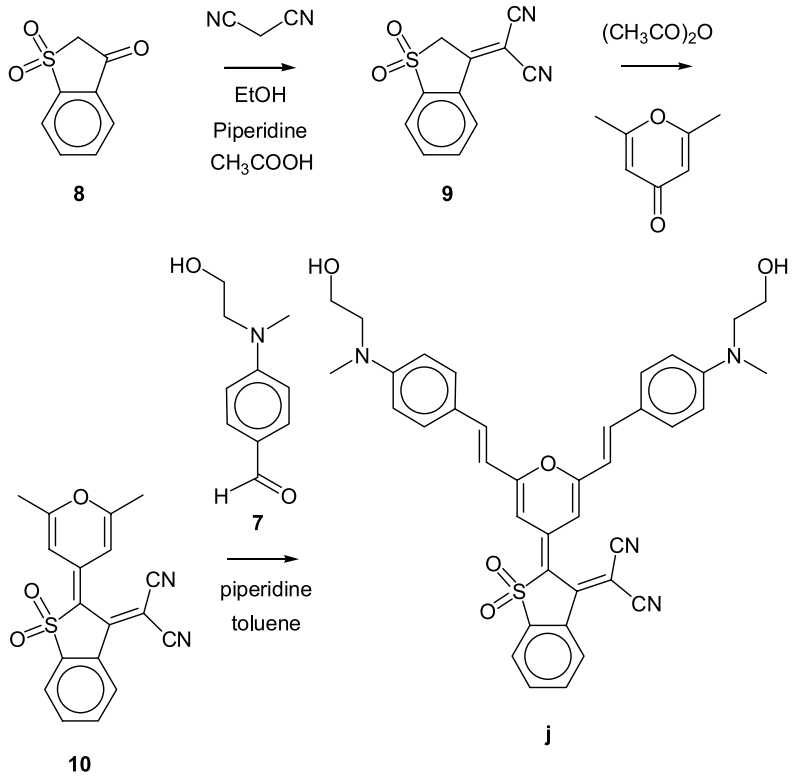

Fig. 6. Synthesis of chromophore j.

dissolved in 25 ml of dry THF. The solution was cooled in an ice bath and 6.88 mmol of diisopropyl azodicarboxylate (DIAD) was added dropwise. The mixture was stirred under inert atmosphere for 24 h at room temperature. After evaporation of THF, the crude reaction product was purified by column chromatography (SiO_2; dichloromethane/ethylacetate 9/1).

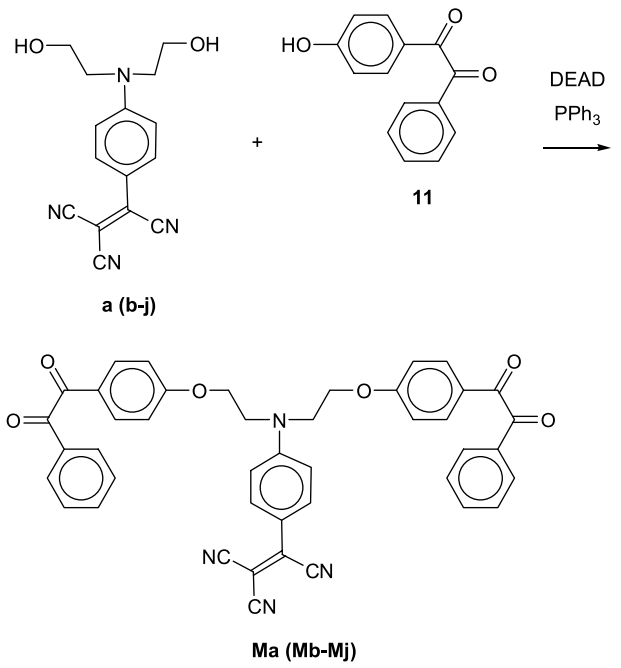

Fig. 7. Synthesis of chromophore monomers Ma–j.

Monomer Ma. Yield: 39%, mp 97.0–98.2 °C, ^{1}H NMR (DMSO-d_6, ppm): $\delta = 4.12$ (t; 4H; $^3J = 5.1$ Hz), 4.32 (t; 4H; $^3J = 5.1$ Hz), 7.12 (d; 4H; $^3J = 8.9$ Hz), 7.23 (d; 2H; $^3J = 9.5$ Hz), 7.61 (t; 4H; $^3J = 7.5$ Hz), 7.86 (t; 2H; $^3J = 7.5$ Hz), 7.87 (m; 8H), 7.95 (d; 2H; $^3J = 9.5$ Hz). Elemental analysis $C_{43}H_{30}N_4O_6$ (M_w 698) calcd: C 73.92%, H 4.33%, N 8.02%; Found: C 73.23%, H 4.18%, N 7.86%.

Monomer Mb [22]. Yield: 45%, mp 90.6–96.9 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 3.98$ (t; 4H; $^3J = 5.0$ Hz), 4.29 (t; 4H; $^3J = 5.0$ Hz), 6.79 (d; 2H; $^3J = 8.8$ Hz), 6.95 (d; 4H; $^3J = 8.4$ Hz), 6.97 (d; 1H; $^3J = 16$ Hz), 7.20 (d; 1H; $^3J = 16$ Hz), 7.47 (d; 2H; $^3J = 8.8$ Hz), 7.52 (t; 4H; $^3J = 7.8$ Hz), 7.58 (d; 2H; $^3J = 8.4$ Hz), 7.67 (t; 2H; $^3J = 7.8$ Hz), 7.94 (d; 4H; $^3J = 8.4$ Hz), 7.98 (d; 4H; $^3J = 7.8$ Hz), 8.20 (d; 2H; $^3J = 8.4$ Hz).

Monomer Mc. Yield: 36%, mp 85.0–87.3 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 4.46$ (m; 8H), 6.60 (s; 1H), 6.63 (d; 1H; $^3J = 16$ Hz), 6.79 (d; 4H; $^3J = 8.8$ Hz), 7.06 (d; 1H; $^3J = 9.1$ Hz), 7.11 (d; 1H; $^3J = 16$ Hz), 7.49 (d; 2H; $^3J = 8.6$ Hz), 7.52 (d; 1H; $^3J = 9.1$ Hz), 7.55 (t; 4H; $^3J = 7.4$ Hz), 7.68 (t; 2H; $^3J = 7.4$ Hz), 7.99 (m; 8H), 8.15 (d; 2H; $^3J = 8.6$ Hz; H_t).

Elemental analysis $C_{46}H_{35}NO_{10}$ (M_w 761) calcd: C 72.53%, H 4.63%, N 1.84%; Found: C 72.24%, H 4.52%, N 1.79%.

Monomer Md. Yield: 40%, mp 160.8–161.7 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 4.12$ (t; 4H; $^3J = 5.1$ Hz), 4.38 (t; 4H; $^3J = 5.1$ Hz), 6.88 (d; 2H; $^3J = 8.9$ Hz), 6.97 (d; 4H; $^3J = 9.0$ Hz), 7.52 (t; 4H; $^3J = 7.5$ Hz), 7.66 (t; 2H; $^3J = 7.5$ Hz), 7.82 (m; 2H), 7.97 (m; 10H), 8.31 (d; 1H; $^3J = 7.3$ Hz), 8.68 (d; 1H; $^3J = 7.7$ Hz).

Elemental analysis $C_{50}H_{34}N_4O_7$ (M_w 802) calcd: C 74.80%, H 4.27%, N 6.98%; Found: C 74.17%, H 4.19%, N 6.63%.

Monomer Me [22]. Yield: 33%, mp 172.0–173.9 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 4.04$ (t; 4H; $^3J = 5.1$ Hz), 4.32 (t; 4H; $^3J = 5.1$ Hz), 6.87 (d; 2H; $^3J = 9.0$ Hz), 6.95 (d; 4H; $^3J = 9.1$ Hz), 7.50 (t; 4H; $^3J = 7.2$ Hz), 7.65 (t; 2H; $^3J = 7.2$ Hz), 7.76 (d; 2H; $^3J = 9.0$ Hz), 7.88–7.97 (m; 12H).

Monomer Mf [22]. Yield: 42%, mp 137.9–139.2 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 4.05$ (t; 4H; $^3J = 5.1$ Hz), 4.33 (t; 4H; $^3J = 5.1$ Hz), 6.88 (d; 2H; $^3J = 9.5$ Hz), 6.95 (d; 4H; $^3J = 9.0$ Hz), 7.50 (t; 4H; $^3J = 7.6$ Hz), 7.65 (t; 2H; $^3J = 7.6$ Hz), 7.92–7.80 (m; 12H), 8.34 (d; 2H; $^3J = 8.8$ Hz).

Monomer Mg [22]. Yield: 55%, mp 171.6–172.2 °C, ^{1}H NMR (DMSO-d_6, ppm): $\delta = 2.70$ (s; 3H), 4.05 (t; 4H; $^3J = 5.0$ Hz), 4.38 (t; 4H; $^3J = 5.0$ Hz), 7.07 (d; 2H; $^3J = 9.2$ Hz), 7.13 (d; 4H; $^3J = 8.9$ Hz), 7.61 (t; 4H; $^3J = 7.7$ Hz), 7.64 (d; 2H; $^3J = 9.2$ Hz), 7.82 (t; 2H; $^3J = 7.7$ Hz), 7.81–7.99 (m; 9H), 8.13 (dd; 1H; $^3J = 8.8$ Hz, $^4J = 2.2$ Hz), 8.28 (d; 1H; $^4J = 2.2$ Hz).

Monomer Mh [22]. Yield: 57%, mp 109.5–110.3 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 4.05$ (t; 4H; $^3J = 5.1$ Hz), 4.36 (t; 4H; $^3J = 5.1$ Hz), 5.57 (s; 2H), 6.89 (d; 2H; $^3J = 9.1$ Hz), 6.97 (d; 4H; $^3J = 8.8$ Hz), 7.12 (d; 2H; $^3J = 7.0$ Hz), 7.38 (m; 3H), 7.52 (t; 4H; $^3J = 7.5$ Hz), 7.67 (t; 2H; $^3J = 7.5$ Hz), 7.82 (d; 1H; $^3J = 9.1$ Hz), 7.86 (d; 2H; $^3J = 9.1$ Hz), 7.96 (m; 12H), 8.21 (dd; 1H; $^3J = 9.1$ Hz, $^4J = 2.2$ Hz), 8.80 (d; 1H; $^4J = 2.2$ Hz).

Monomer Mi. Yield: 11%, mp 136.4–137.7 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 3.17$ (s; 6H), 3.90 (t; 4H; $^3J = 5.1$ Hz), 4.28 (t; 4H; $^3J = 5.1$ Hz), 6.74 (d; 4H; $^3J = 8.8$ Hz), 6.77 (d; 4H; $^3J = 9.2$ Hz), 7.04 (s; 2H), 7.15 (d; 2H; $^3J = 16$ Hz), 7.51–7.55 (m; 8H), 7.65 (t; 4H; $^3J = 8.0$ Hz), 7.72 (t; 2H; $^3J = 8.0$ Hz), 7.75 (d; 1H; $^3J = 7.5$ Hz), 7.95 (d; 4H; $^3J = 9.2$ Hz), 7.98 (d; 4H; $^3J = 8.0$ Hz), 8.46 (d; 1H; $^3J = 8.0$ Hz).

Elemental analysis $C_{67}H_{50}N_4O_8$ (M_w 1038) calcd: C 77.44%, H 4.85%, N 5.39%; Found: C 76.86%, H 4.51%, N 5.19%.

Monomer Mj. Yield: 19%, mp 145.6–146.9 °C, ^{1}H NMR (DMSO-d_6, ppm): $\delta = 3.18$ (s; 6H), 3.91 (t; 4H; $^3J = 5.1$ Hz), 4.29 (t; $^3J = 5.1$ Hz; 4H), 6.79 (d; 4H; $^3J = 8.8$ Hz), 6.72 (d; 4H; $^3J = 9.2$ Hz), 7.00 (s; 2H), 7.15 (d; 2H; $^3J = 16$ Hz), 7.55 (t; 4H; $^3J = 7.5$ Hz), 7.66 (t; 2H; $^3J = 7.5$ Hz), 7.70 (d; 4H; $^3J = 8.8$ Hz), 7.72 (m; 4H), 7.90 (d; 1H; $^3J = 7.3$ Hz), 7.95 (d; 4H; $^3J = 9.2$ Hz), 7.99 (d; 4H; $^3J = 7.5$ Hz), 8.75 (d; 1H; $^3J = 8.1$ Hz).

Elemental analysis $C_{66}H_{50}N_4O_9S$ (M_w 1074) calcd: C 73.73%, H 4.69%, N 5.21%; Found: C 73.48%, H 4.52%, N 5.07%.

2.5. Synthesis of monomers M1 and M2

2.5.1. Synthesis of monomer M1: Fig. 8

The same general procedure was followed as for the previous chromophore monomers from 1-(4-hydroxyphenyl)-2-phenyl-1,2-ethanedione (**11**) and 2,2-hexafluoroisopropylidene-di(1,4-phenylene-oxy-ethanol). Yield: 30%, mp 62.6–64.4 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 4.39$ (t; 4H; $^3J = 5.1$ Hz), 4.43 (t; 4H; $^3J = 5.1$ Hz), 6.94 (d; 4H; $^3J = 9.1$ Hz), 7.04 (d; 4H; $^3J = 8.8$ Hz), 7.33 (d; 4H; $^3J = 8.8$ Hz), 7.53 (t; 4H; $^3J = 7.7$ Hz), 7.67 (t; 2H; $^3J = 7.7$ Hz), 7.96–8.00 (m; 8H).

2.5.2. Synthesis of monomer M2 [31]: Fig. 9

4,4′-Diacetamidodiphenyl ether (**12**). To a solution of 20 g (0.10 mol) of 4,4′-oxydianiline in 75 ml of glacial acetic acid was added dropwise 23 g (0.23 mol) of acetic anhydride at such a rate as to maintain a temperature of 50 °C. The precipitate was collected, washed with cold water and dried. The filtrate of the reaction was poured into 150 ml of iced water, the precipitate was filtered, washed and dried. Yield: 27 g (96%), mp 217.8–220.2 °C, ^{1}H NMR (DMSO-d_6, ppm): $\delta = 2.00$ (s; 6H), 6.89 (d; 4H; $^3J = 8.5$ Hz), 7.52 (d; 4H; $^3J = 8.5$ Hz), 10.21 (s; 2H).

3,3′-Dinitro-4,4′-diacetamidodiphenyl ether (**13**). To 180 ml of acetic acid was slowly added 25 ml of nitric acid (14 N) at such rate to keep the temperature below 10 °C. 20 g (0.075 mol) of 4,4′-diacetamidodiphenyl ether (**12**) was added in small portions under cooling. The mixture was then stirred for 30 min at room temperature and poured into 500 ml of iced water. The precipitate was filtered, washed with cold water, dried and purified by column chromatography (SiO_2; dichloromethane/acetonitrile 9/1). Yield: 22 g (80%), mp 211.6–212.4 °C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 2.03$ (s; 6H), 7.44 (dd; 2H; $^3J = 8.8$ Hz, $^4J = 2.5$ Hz), 7.57 (d; 2H; $^3J = 8.8$ Hz), 7.62 (d; 2H; $^4J = 2.5$ Hz), 10.22 (s; 2H).

3,3′-Dinitro-4,4′-diaminodiphenyl ether (**14**). To a solution of 15 g (0.040 mol) of 3,3′-dinitro-4,4′-diacetamidodiphenylether (**13**) in 100 ml of methanol, a solution of 6.7 g (0.12 mol) of potassium hydroxide in 70 ml of methanol, was added dropwise and under cooling. After 2 h of stirring at room temperature, an additional amount of 4.5 g (0.080 mol) of potassium hydroxide in methanol was added and the mixture was stirred for 3 h more. The reaction mixture was then poured into 500 ml of water, the precipitate was collected, washed with water and dried. The product was finally purified by recrystallisation from ethanol. Yield: 11 g (97%), mp 177.9–178.7 °C, ^{1}H NMR (DMSO-d_6, ppm): $\delta = 7.06$ (d; 2H; $^3J = 8.8$ Hz; H_c), 7.27 (dd; 2H; $^3J = 8.8$ Hz, $^4J = 2.6$ Hz), 7.39 (broad s; 4H), 7.44 (d; 2H; $^4J = 2.6$ Hz).

3,3′,4,4′-Tetraminodiphenyl ether (M2). To a warm solution of 61 g (0.27 mol) of stannous chloride dihydrate in 175 ml of concentrated hydrochloric acid is added 8.7 g (0.030 mol) of 3,3′-dinitro-4,4′-diaminodiphenyl ether (**14**)

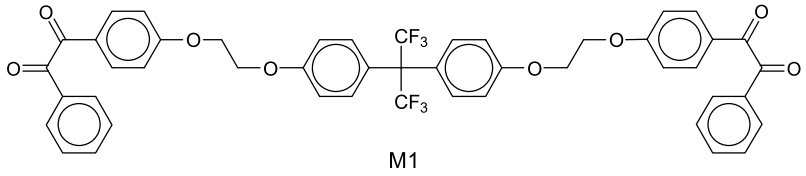

Fig. 8. Structure of monomer M1.

at such a rate as to maintain the temperature at 50 °C. The mixture is heated to 65 °C for 3 h and then cooled to −10 °C to yield a white solid. This tetrahydrochloric salt is collected by filtration and dissolved in 300 ml of hot water. To the solution was added 300 ml of concentrated hydrochloric acid. Cooling produces white needles of the salt which are collected and pressed dry under a stream of nitrogen. The salt is then dissolved in water and added dropwise to a solution of 18 g (0.45 mol) of sodium hydroxide in deoxygenated water which is cooled in an ice bath. The precipitate is collected by filtration under an inert atmosphere, washed with water and dried under reduced pressure. Yield: 6.1 g (89%), mp 185.6–187.9 °C, ^{1}H NMR (DMSO-d_6, ppm): $\delta = 4.18$ (s; 4H), 4.58 (s; 4H), 6.03 (dd; 2H; $^{3}J = 8.0$ Hz, $^{4}J = 2.5$ Hz), 6.19 (d; 2H; $^{4}J = 2.5$ Hz); 6.47 (d; 2H; $^{3}J = 8.0$ Hz), ^{13}C NMR (DMSO-d_6, ppm): $\delta = 105.4$, 106.9, 115.3, 130.3, 136.7, 150.4.

2.6. Synthesis of poly(phenylquinoxalines) P1 and P2

2.6.1. Synthesis of poly(phenylquinoxalines) P1: Fig. 10

General procedure [32]. A solution of 1.0 equiv of 3,3′-diaminobenzidine, 0.9 equiv of the chromophore monomer Ma (Md, Me, Mf, Mg, Mh, and Mi) and 0.1 equiv of monomer M1 in *m*-cresol was stirred under inert atmosphere at room temperature. After 24 h the polymer was precipitated in methanol, filtered, washed and dried. The polymer was purified by a second precipitation in methanol. Finally the polymer was dried under reduced pressure.

2.6.2. Synthesis of poly(phenylquinoxalines) P2: Fig. 11

General procedure [32]. An equimolar solution of the chromophore monomer Mb (Mc, Mf, Mg, Mi and Mj) and 3,3′,4,4′-tetraminodiphenyl ether (M2) in *m*-cresol was stirred at room temperature for 24 h. The polymer was collected using the same procedure as for polymer P1.

3. Results and discussion

Chromophore a was obtained by reaction of *N*-phenyldiethanolamine and tetracyanoethylene. The preparation of chromophore b was achieved by reaction of 4-[bis(2-hydroxyethyl)amino]benzaldehyde and 4-nitrophenylacetic acid in the presence of piperidine as base. The starting material for the preparation of chromophore c is 2,4-dihydroxybenzaldehyde which was transformed into 2,4-[bis(2-hydroxyethyl)oxy]benzaldehyde after reaction with bromoethanol in the presence of NaH. Finally reaction with 4-nitrophenylacetic acid resulted in the formation of c.

To obtain chromophore d, 2-[3-oxo-indane-1-ylidene]-1,3-propanedinitrile and 2,2′-(N-(4-nitrosophenyl)amino-diethanol were reacted in ethanol.

Through reaction of *N*-phenyldiethanolamine with the diazonium salt of 4-aminobenzonitrile, of 4-nitrophenyl aniline, of 3-methyl-4-nitrophenyl aniline and of (4-aminophenyl)-1-benzyl-5-nitrobenzimidazole, chromophores e,f,g and h were obtained.

Condensation of 4-[*N*-(2-hydroxyethyl)-*N*-methylamino] benzaldehyde with 2-[2-(2,6-dimethyl-4*H*-pyrane-4-

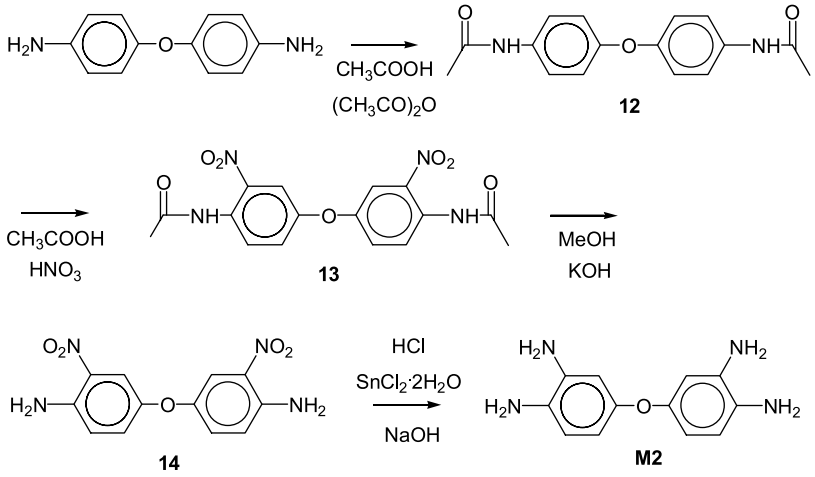

Fig. 9. Synthesis of monomer M2.

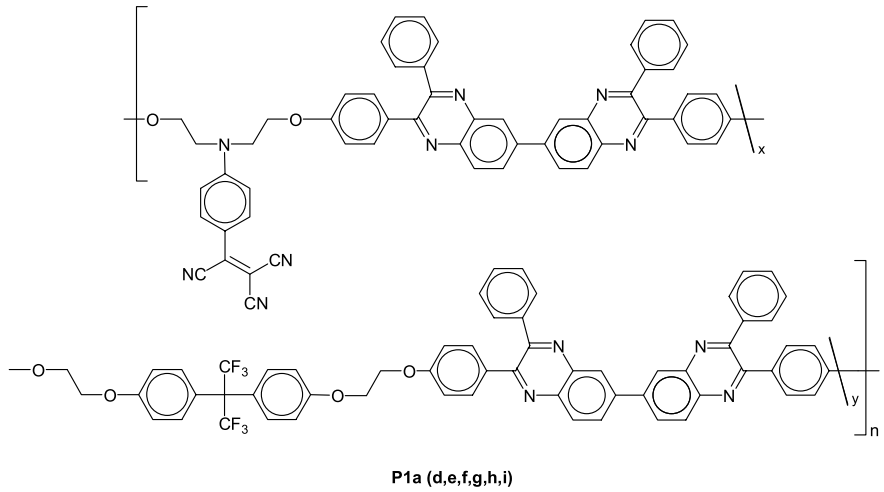

Fig. 10. Structure of polymer P1a,d–i (codes a, d–i refer to the respective chromophore monomers Ma, Md–i).

ylidene)-3-oxo-indane-1-ylidene]-1,3-propanedinitrile or 2-[2-(2,6-dimethyl-4*H*-pyrane-4-ylidene]-1,1-dioxide-2,3-dihydrobenzothiophene-3-ylidene]-1,3-propanedinitrile, resulted in chromophores i and j.

The choice of these chromophores was done to get a better insight how azo chromophores (e–h) incorporated in a poly(phenylquinoxaline) structure, behave for their second-order NLO effect depending on the kind of acceptor and of incorporated substituent (g), compared to the results with stilbene chromophores (b and c) and from those with strong acceptor molecules a,d,i and j).

Chromophore monomers Ma–j were obtained by reaction of bis(hydroxyalkyl)chromophores a–j with 1-(4-hydroxyphenyl)-2-phenyl-1,2-ethanedione under Mitsunobu conditions. Monomer M1 was obtained from the diol obtained from hexafluoroisopropylidene diphenol under the same reaction circumstances.

Tetraamine M2 was prepared by reduction of 3,3′-dinitro-4,4′-aminodiphenyl ether, obtained itself from 4,4′-diacetamidodiphenyl ether, which by nitration was transformed into his 3,3′dinitro derivative. After hydrolysis and reduction M2 was formed. 3,3′,4,4′-biphenyl tetraamine is a commercial product.

The synthesis of the chromophore-functionalised poly-(phenylquinoxalines) P1 and P2 is a one-step process, this by reaction of bis(1,2-diketone)chromophore monomer with a tetramine under very mild circumstances. The respective chromophore functionalized monomers could be synthesised by the Mitsunobu reaction with 1-(4-hydroxyphenyl)-2-phenyl-1,2-ethanedione and chromophore in the presence of DIAD and PPh_3.

Polymers P1a, P1d, P1e, P1f, P1g, P1h, and P1i were obtained by cyclopolycondensation of monomer M1 and the chromophore monomers Ma, Md, Me, Mf, Mg, Mh, Mi with 3,3′-diaminobenzidine, respectively. The structure of the chromophore-functionalised poly(phenylquinoxalines) P1 are presented in Fig. 10.

Polymers P2b, P2c, P2f, P2g, P2i and P2j were synthesised by reaction of 3,3′,4,4′-tetraminodiphenyl ether (M2) and the chromophore monomers Mb, Mc, Mf,

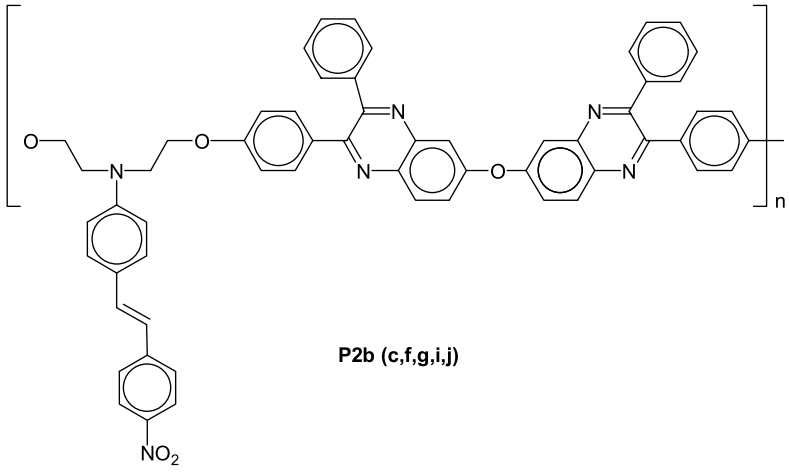

Fig. 11. Structure of polymer P2b,c,f,g,i,j (codes b, c, f, g, i and j refer to the respective chromophore monomers Mb, Mc, Mf, Mg, Mi, Mj).

Mg, Mi and Mj, respectively. The structure of the synthesised polyphenylquinoxalines P2 is given in Fig. 11.

The weight percentages of NLO-dye in the polymers (wt%), molecular weights ($\bar{M}_w$), polydispersities (D), glass transition temperatures (T_g) and decomposition temperatures (T_d) are given in Table 1.

The molecular weights of polymers P1 are between 5500 and 27,000 g/mol and for P2 between 8400 and 31,000 g/mol. The rigidity of the main chain leads to high glass transition temperatures; the T_g's of P1 are between 199 and 255 °C and for P2 values up to 260 °C were obtained. These T_g's are comparable with those from other poly (phenylquinoxalines) [22] and polyimides [15] studied by us, as well as from polyquinolines synthesised by Jen and coworkers [34–37]. Poly(phenylquinoxalines) studied by Hergenrother [32,33] with aromatic groups incorporated in the main chain, but not chromophore functionalised, show much higher T_g's, even above 300 °C, because of the higher rigidity of the polymer backbone. Furthermore the decomposition temperatures of the polymers P1 and P2 are between 42 and 123 °C higher than the respective T_g's. Since poling is done below T_g, significant thermal decomposition is not expected to occur during the poling process. The polymers P1 were loaded with 22–39 wt% of chromophore and the polymers P2 with 33–51 wt% of chromophore.

The poly(phenylquinoxalines) studied in a previous paper [22] were only soluble in *m*-cresol and chloroform. The incorporation of a fluoro component M1 into the polymer chain reveals in polymers P1 with a better solubility than the polymers from Ma–j and 3,3′-diamino benzidine, which have a higher rigidity. A same effect is expected for polymers P2 where a more flexible ether bridge is incorporated. Better solubility reveals in better quality films after spincoating.

All polymer systems of P1 and P2 could be spincoated from cyclohexanone onto ITO glass substrates, yielding good quality films. The samples were heated under vacuum (10 °C below the boiling temperature of cyclohexanone) during several days to remove any residual solvent. The film thickness was measured with a DEKTAK 2 profilometer. Non-centrosymmetry in the polymers was induced by corona-poling at a temperature just below the T_g. The SHG results are summarised in Table 2. The polymers have d_{33} values between 1.6 and 114 pm/V, measured at 1064 nm. Most of the values are higher than those obtained for previous studied poly(phenylquinoxalines) [22]. However, since the second harmonic wavelength was 532 nm, which is rather close to the absorption region of all chromophores, these values are resonantly enhanced and should be corrected for absorption. Using the two-level model, we obtained non-resonant $d_{33}(0)$ values of 0.45–33 pm/V, most of them can be compared to the results obtained for polyimides [7–9,15] and maleimide-based polymers [17,19].

From the results we see higher non-linearities for polymers P2 f,g,i compared to those obtained for P1 f,g,i. This can be explained by a better alignment of the chromophores during poling in P2 polymers and also because of less interactions between the chromophores. We also must note that a difference in effective poling field (a parameter unknown in a corona-poling experiment) can lead to differences in d_{33}. Although a nitro group is a stronger

Table 2
Wavelength of maximum absorption (λ_{max}) and second-harmonic coefficients ($d_{33}(\omega)$ and $d_{33}(0)$) of chromophore-functionalised poly(phenylquinoxalines) P1a,d,e,f,g,h,i and P2b,c,f,g,i,j

Polymer	λ_{max} (nm)	$d_{33}(\omega)$ (pm/V)	$d_{33}(0)$ (pm/V)
P1a	506	7.5	0.55
P1d	593	5.3	0.89
P1e	439	114	33
P1f	474	2.7	0.45
P1g	464	6.0	1.2
P1h	432	1.6	0.45
P1i	596	5.8	1.2
P2b	443	7.1	1.8
P2c	390	3.0	1.7
P2f	486	67	10
P2g	470	42	7.5
P2i	609	10	2.1
P2j	639	5.0	1.4

Table 1
Synthesis and properties of chromophore-functionalised poly(phenylquinoxalines) P1a,d,e,f,g,h,i and P2b,c,f,g,i,j

Polymer	wt%	$\bar{M}_w$ (10^4 g/mol)	D	T_g (°C)	T_d (°C)
P1a	28	5.5	2.0	208	292
P1d	22	18	1.9	230	310
P1e	23	27	1.8	211	295
P1f	30	24	2.1	199	306
P1g	30	16	2.0	204	305
P1h	38	13	2.0	204	316
P1i	39	7.8	1.9	255	310
P2b	33	31	2.2	201	318
P2c	34	15	2.3	187	287
P2f	33	30	1.9	199	322
P2g	34	19	1.9	188	298
P2i	49	8.4	1.9	260	340
P2j	51	9.2	2.0	256	298

acceptor than a cyano group, better quality of the film as well as better alignment and less interactions can be the reason for the higher value of the non-linearity obtained for the dialkylamino cyanobenzene functionalised polymer P1e. Polymer P2f has a higher SHG effect than P2g, in the latter the additional methyl group can be a reason for more interactions between the chromophores, which results in a lower SHG value.

The poling order parameters for P2f and P2g are 0.21 and 0.14, respectively, for P1e: 0.22 and for P1i and P2i they are, respectively, 0.54 and 0.42.

Polymers P2b and P2c with stilbenoid chromophores incorporated, which have smaller hyperpolarisabilities than azo chromophores show indeed smaller SHG values at the macroscopic level.

Chromophores a and d have a shorter conjugation length than the other chromophores which is revealed in the SHG effect of the polymers.

Although we should have expected high values for the polymers with chromophores i and j incorporated, surprisingly the SHG values are low. The accordion structure of the polymers may be a reason for the more difficult alignment of the chromophores.

The thermal stability of three polymer systems of P1 and four polymer systems of P2 was studied by plotting $d_{33}(t)/d_{33}(t=0)$ as function of time, where $d_{33}(t)$ and $d_{33}(t=0)$ represent the SHG effect at time t and 0, respectively, versus time at 125 °C. The results of these measurements are given in Figs. 12 and 13. It can be seen that for polymers P1a, P1f and P1i, after an initial decrease, the non-linearity does not significantly change over 750 h. P1a and P1f stabilise at, respectively, 43 and 58% of remaining NLO efficiency, while P1i results in 63% of the initial value, after 750 h. P2f shows very high stability of the NLO effect, after 750 h of heating at 125 °C, 91% of the second harmonic signal remained. The systems P2b, P2g and P2j show a larger decrease in the NLO-response and stabilise, respectively, at 68, 48 and 44%.

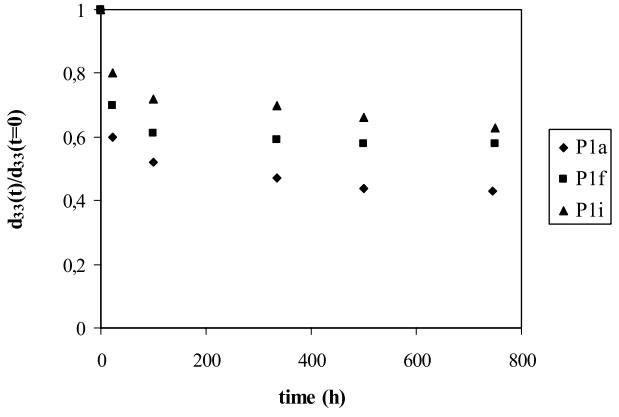

Fig. 12. Plot of the normalised second-harmonic coefficients as a function of time at 125 °C of polymers P1a, P1f and P1i.

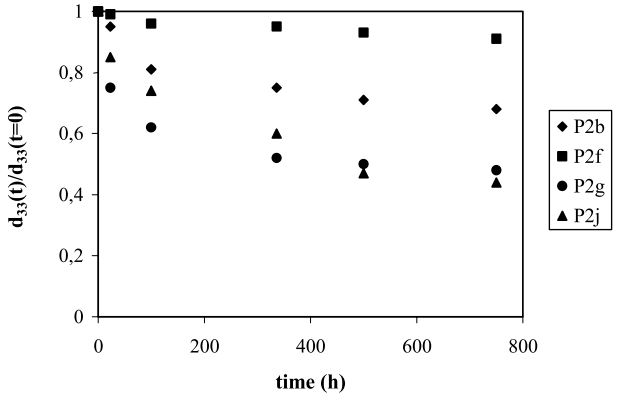

Fig. 13. Plot of the normalised second-harmonic coefficients as a function of time at 125 °C of polymers P2b, P2f, P2g and P2j.

4. Conclusion

We synthesised 13 new and soluble chromophore-functionalised poly(phenylquinoxalines) by cyclopolycondensation of the respective bis(1,2-diketone)chromophore monomers with a tetramine. The polymers exhibit high glass transition temperatures (187–260 °C), which results in a stable NLO-response at elevated temperatures. One of the polymer systems lost only 9% of its non-linearity after 750 h of heating at 125 °C. Some of these polymers are therefore very promising candidates for the construction of devices in the field of electro-optics and photonics.

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