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# Synthesis and characterization of polyene chromophores with hydroxyl functionalization

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**Abstract**

Eight hydroxyl functionalized donor–acceptor polyene chromophores **3–10** were synthesized and characterized. Knoevenagel condensation reaction of aromatic polyenals with 2-cyanoacetamide derivatives was utilized to synthesize chromophores with *all-E* configuration. Chromophores of this kind can be attached covalently to polymers or functionalized with dendrons in order to tune the properties. The structures of the molecules were verified by $^{1}$H NMR, $^{13}$C NMR, ESI-TOF mass spectrometry and UV–vis measurements. Reduced bond-length alternation of the molecules in DMSO-$d_6$ solution were observed by calculating the average difference of the vicinal coupling constants between adjacent CH=CH and CH–CH bonds of the conjugated bridge. Thermal stability of the molecules was determined by thermogravimetric analysis (TG). The decomposition temperatures varied between 190 and 256 °C. All measured compounds displayed absorption maximum in visible region, and found to exhibit positive solvatochromic behavior.


*Keywords:* Polyenes; Chromophores; Conjugated aldehydes; Cyanoacetamide; Knoevenagel condensation

## 1. Introduction

Conjugated organic materials possessing nonlinear optical (NLO) and electro-optical (EO) properties have shown great potential for various applications such as high-speed telecommunication and optical data processing [1–3]. Generally, organic NLO chromophores are ‘‘push–pull’’ compounds, usually represented as D–π–A chromophores, based on electron-donating (D) and electron-withdrawing (A) groups interacting through π-conjugated bridge (π). Parameter that describes the NLO effect of such molecules is hyperpolarizability ($\beta$). This phenomenon is due to the occurrence of intermolecular charge transfer in the dipolar molecules determined by the strength of donor and acceptor moieties and the connectivity of π-electron bridge [4,5].

Polyene chromophores are widely known for their nonlinear optical properties. A lot of effort has been put into synthesizing highly efficient NLO chromophores with sufficient thermal and chemical stabilities to be of practical use, and to prevent chromophore aggregation. Careful design of D–π–A chromophores involves the choosing of the appropriate donor and acceptor moieties as well as controlling the length and environment of the conjugated bridge. Several studies concerning the synthesis of such molecules to fill these criteria have been published [5–10]. In recent studies dendrons attached to NLO chromophores have shown improved thermal stability and electro-optic properties as well as solubility [11,12].

A poled-polymer procedure [13] is the most commonly used method to create non-centrosymmetry, which is necessary for non-crystallized organic chromophores to be applicable in NLO applications. In this process a large electric field at or above glass transition temperature ($T_g$) of a polymer interacts with a dipole molecule causing orientation of the molecules align in the direction of applied electric field.

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Non-centrosymmetry of a material is maintained when polymer is cooled below $T_g$ in the presence of applied field [8,13]. Comparing with dominate inorganic material in current applications, $LiNbO_3$, some very large $r_{33}$ values, which describe the materials' electro-optic activity, have been demonstrated with organic poled-polymer systems [14].

Herein we report the synthesis of D–π–A polyene chromophores containing either dimethylamino or diethanolamino group as an electron donor and cyano group as an electron acceptor. These chromophores possess hydroxyl groups at either acceptor end or both donor and acceptor ends, affording reactive sites to further process the compound, for example by incorporation into polymers or dendritic molecules.

## 2. Experimental

### 2.1. General

All starting materials were purchased from major suppliers and used without any further purification. Tetrahydrofuran was distilled from benzophenone/sodium prior to use. Dichloromethane and ethanol were dried over 4 Å sieves. Column chromatography was performed with Merck 60 $F_{254}$ silica gel, particle size 0.040–0.063 mm. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance DRX 500 NMR (500.13 and 125.76 MHz) or on a Bruker Avance DPX 250 NMR (250.13 and 62.90 MHz) spectrometers in DMSO-$d_6$ or $CDCl_3$ solutions. The solvent signal was used as an internal standard. Mass spectral data was obtained with micromass LCT electronspray ionization time-of-flight (ESI-TOF) instrument with positive-ion mode. Absorption spectra were scanned on Perkin Elmer Lambda 25 UV–vis spectrometer using ethanol or 1:1 ethanol/chloroform as solvents. A solvatochromic behavior was studied with Varian Cary100 UV–vis spectrometer. All solvents were of analytical grade. Decomposition temperatures were determined utilizing Perkin Elmer TGA7 thermogravimetric analyser under the following conditions: heating rate 10 °C/min; atmosphere, air at 60 mL/min; sample size of 1 mg. Melting points were measured on Mettler Toledo FP62 apparatus at a heating rate 2 °C/min, and are uncorrected.

### 2.2. Synthesis

Intermediates **1a** and **1b** [15], and **2a–2d** [16] were synthesized according to procedures described in the literature.

#### 2.2.1. 2-Cyano-N-(2-hydroxy-1,1-bis-hydroxymethyl-ethyl)-acetamide (**2a**)

Yield: 11.1 g (80%). $^1$H NMR (DMSO-$d_6$, 250 MHz): $\delta_{ppm} = 3.55$ (d, 6H, C$H_2$OH, $J = 5.0$ Hz), 3.61 (s, 2H, NCC$H_2$CO), 4.54 (t, 3H, O$H$, $J = 5.4$ Hz), 7.38 (s, 1H, N$H$). $^{13}$C NMR (DMSO-$d_6$, 63 MHz): $\delta_{ppm} = 26.15$ (NC$C$H$_2$CO), 59.74 ($C$H$_2$OH), 62.79 (NH$C$(CH$_2$OH)$_3$), 116.39 ($C$N), 162.63 ($C$O).

#### 2.2.2. 2-Cyano-N-(2-hydroxy-1-hydroxymethyl-ethyl)-acetamide (**2b**)

Yield: 1.3 g (38%). $^1$H NMR (DMSO-$d_6$, 250 MHz): $\delta_{ppm} = 3.40$ (d, 4H, C$H_2$OH, $J = 5.5$ Hz), 3.60 (s, 2H, NCC$H_2$CO), 3.63–3.75 (m, 1H, NHC$H$), 4.67 (s, 2H, O$H$), 7.97 (d, 1H, N$H$, $J = 8.0$ Hz). $^{13}$C NMR (DMSO-$d_6$, 63 MHz): $\delta_{ppm} = 25.39$ (NC$C$H$_2$CO), 53.58 ($C$H(CH$_2$OH)$_2$), 59.90 ($C$H$_2$OH), 116.36 ($C$N), 162.03 ($C$O).

#### 2.2.3. 2-Cyano-N-[2-(2-hydroxy-ethoxy)-ethyl]-acetamide (**2c**)

Yield: 15.3 g (92%). $^1$H NMR (DMSO-$d_6$, 250 MHz): $\delta_{ppm} = 3.24$ (m, 2H, NHC$H_2$), 3.40–3.52 (m, 6H, C$H_2$O), 3.61 (s, 2H, NCC$H_2$CO), 4.55 (br s, 1H, O$H$), 8.26 (br s, 1H, N$H$). $^{13}$C NMR (DMSO-$d_6$, 63 MHz): $\delta_{ppm} = 25.29$ (NC$C$H$_2$CO), 39.32 (NH$C$H$_2$), 60.27 ($C$H$_2$OH), 68.73 ($C$H$_2$O), 72.17 ($C$H$_2$O), 116.23 ($C$N), 167.14 ($C$O).

#### 2.2.4. 2-Cyano-N-(2-hydroxy-ethyl)-acetamide (**2d**)

Yield: 27.5 g (56%). $^1$H NMR (DMSO-$d_6$, 250 MHz): $\delta_{ppm} = 3.13$ (q, 2H, NHC$H_2$, $J = 5.7$ Hz), 3.42 (t, 2H, C$H_2$OH, $J = 5.8$ Hz), 3.59 (s, 2H, NCC$H_2$CO), 4.75 (br s, 1H, O$H$), 8.23 (br s, 1H, N$H$). $^{13}$C NMR (DMSO-$d_6$, 63 MHz): $\delta_{ppm} = 25.21$ (NC$C$H$_2$CO), 41.99 (NH$C$H$_2$), 59.42 ($C$H$_2$OH), 116.21 ($C$N), 162.15 ($C$O).

### 2.3. General procedure for the synthesis of polyene chromophores **3–8**

Aldehyde **1a** or **1b** (1 equiv.) was dissolved in warm ethanol. Cyanoacetamido derivative **2a–2d** (1.1 equiv.) in minimum ethanol, and one drop of piperidine were added. The mixture was refluxed for 1–3 h under nitrogen atmosphere. The reaction mixture was cooled and precipitated product was filtered.

#### 2.3.1. (2E,4E,6E )-2-Cyano-7-(4-dimethylamino-phenyl)-hepta-2,4,6-trienoic acid (2-hydroxy-1,1-bis-hydroxy methyl-ethyl)-amide (**3**)

Purified by crystallization from ethyl acetate and hexane to give a red solid. Yield: 49 mg (27%). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta_{ppm} = 2.98$ (s, 6H, NC$H_3$), 3.63 (d, 6H, C$H_2$OH, $J = 5.6$ Hz), 4.73 (t, 3H, O$H$, $J = 5.7$ Hz), 6.63 (dd, 1H, C$H$-4, $J = 12.2$, 14.0 Hz), 6.72 (d, 2H, Ar $H$-2, $J = 8.8$ Hz), 6.86 (s, 1H, N$H$), 6.95 (d, 1H, C$H$-7, $J = 15.1$ Hz), 7.05 (dd, 1H, C$H$-6, $J = 10.9$, 15.2 Hz), 7.25 (dd, C$H$-5, $J = 10.9$, 14.2 Hz), 7.45 (d, 2H, Ar $H$-3, $J = 8.8$ Hz), 7.85 (d, 1H, C$H$-3, $J = 12.0$ Hz). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta_{ppm} = 39.67$ ($C$H$_3$), 59.85 (NH$C$), 62.36 ($C$H$_2$OH), 103.45 ($C$-2), 111.94 (Ar $C$H-3), 116.22 ($C$N), 123.14 ($C$H-6), 123.61 (Ar $C$-1), 123.76 ($C$H-4), 129.10 (Ar $C$H-2), 142.29 ($C$H-7), 149.48 ($C$H-5), 151.06 (Ar $C$-4), 151.65 ($C$H-3), 160.81 ($C$O). ESI-TOF MS: $m/z$ calcd. for $C_{20}H_{25}N_3O_4$ 394.17 $[M + Na]^+$, found 394.09 $[M + Na]^+$.

*2.3.2. (2E,4E,6E )-2-Cyano-7-(4-dimethylamino-phenyl)-hepta-2,4,6-trienoic acid (2-hydroxy-1-hydroxymethyl-ethyl)-amide (**4**)*

Red solid, yield:129 mg (66%). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta_{ppm} = 2.98$ (s, 6H, NC$H_3$), 3.47 (t, 4H, C$H_2$OH, $J = 5.7$ Hz), 3.85 (m, 1H, C$H$), 4.68 (t, 2H, O$H$, $J = 5.7$ Hz), 6.64 (dd, 1H, C$H$-4, $J = 11.9$, 14.2 Hz), 6.72 (d, 2H, Ar $H$-2, $J = 9.0$ Hz), 6.95 (d, 1H, C$H$-7, $J = 15.3$ Hz), 7.04 (dd, 1H, C$H$-6, $J = 10.9$, 15.2 Hz), 7.21 (dd, 1H, C$H$-5, $J = 10.9$, 14.2 Hz), 7.45 (d, 2H, Ar $H$-3, $J = 8.9$ Hz), 7.54 (d, 1H, N$H$, $J = 8.1$ Hz), 7.89 (d, 1H, C$H$-3, $J = 11.8$ Hz). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta_{ppm} = 39.66$ (C$H_3$), 53.83 (NHC$H$), 59.97 (C$H_2$OH), 103.71 (C-2), 111.95 (Ar C$H$-3), 116.08 (C$N$), 123.15 (C$H$-6), 123.64 (Ar C-1), 123.92 (C$H$-4), 129.08 (Ar C$H$-2), 142.10 (C$H$-7), 149.07 (C$H$-5), 151.03 (Ar C-4), 151.29 (C$H$-3), 161.03 (C$O$). ESI-TOF MS: *m/z* calcd. for $C_{19}H_{23}N_3O_3$ 364.16 $[M + Na]^+$, found 364.10 $[M + Na]^+$.

*2.3.3. (2E,4E,6E )-2-Cyano-7-(4-dimethylamino-phenyl)-hepta-2,4,6-trienoic acid [2-(2-hydroxy-ethoxy)-ethyl]-amide (**5**)*

Purified by column chromatography in silica ($SiO_2$) eluting with ethyl acetate to give a red solid. Yield: 67 mg (39%). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta_{ppm} = 2.98$ (s, 6H, NC$H_3$), 3.34 (q, 2H, NHC$H_2$, $J = 5.8$ Hz), 3.42–3.52 (m, 6H, C$H_2$), 4.56 (t, 1H, O$H$, $J = 5.4$ Hz), 6.64 (dd, 1H, C$H$-4, $J = 12.0$, 14.1 Hz), 6.72 (d, 2H, Ar $H$-2, $J = 8.9$ Hz), 6.95 (d, 1H, C$H$-7, $J = 15.2$ Hz), 7.04 (dd, 1H, C$H$-6, $J = 10.9$, 15.2 Hz), 7.21 (dd, 1H, C$H$-5, $J = 10.9$, 14.2 Hz), 7.45 (d, 2H, Ar $H$-3, $J = 8.8$ Hz), 7.86 (d, 1H, C$H$-3, $J = 11.9$ Hz), 8.13 (t, 1H, N$H$, $J = 5.4$ Hz). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta_{ppm} = 39.34$ (NHC$H_2$), 39.67 (C$H_3$), 60.14 (C$H_2$OH), 68.54 (C$H_2$O), 72.02 (C$H_2$O), 103.37 (C-2), 111.95 (Ar C$H$-3), 115.92 (C$N$), 123.12 (C$H$-6), 123.63 (Ar C-1), 123.85 (C$H$-4), 129.10 (Ar C$H$-2), 142.21 (C$H$-7), 149.24 (C$H$-5), 151.05 (Ar C-4), 151.43 (C$H$-3), 161.27 (C$O$). ESI-TOF MS: *m/z* calcd. for $C_{20}H_{25}N_3O_3$ 376.18 $[M + Na]^+$, found 378.20 $[M + Na]^+$.

*2.3.4. (2E,4E,6E )-2-Cyano-7-(4-dimethylamino-phenyl)-hepta-2,4,6-trienoic acid (2-hydroxy-ethyl)-amide (**6**)*

Red solid, yield: 108 mg (49%). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta_{ppm} = 2.98$ (s, 6H, NC$H_3$), 3.24 (q, 2H, NHC$H_2$, $J = 6.0$ Hz), 3.46 (q, 2H, C$H_2$OH, $J = 6.0$ Hz), 4.70 (t, 1H, O$H$, $J = 5.6$ Hz), 6.64 (dd, 1H, C$H$-4, $J = 11.9$, 14.2 Hz), 6.72 (d, 2H, Ar $H$-2, $J = 9.0$ Hz), 6.95 (d, 1H, C$H$-7, $J = 15.3$ Hz), 7.04 (dd, 1H, C$H$-6, $J = 10.9$, 15.2 Hz), 7.21 (dd, 1H, C$H$-5, $J = 10.8$, 14.2 Hz), 7.45 (d, 2H, Ar $H$-3, $J = 8.9$ Hz), 7.87 (d, 1H, C$H$-3, $J = 11.9$ Hz), 8.05 (t, 1H, N$H$, $J = 5.5$ Hz). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta_{ppm} = 39.67$ (C$H_3$), 42.22 (NHC$H_2$), 59.39 (C$H_2$OH), 103.52 (C-2), 111.94 (Ar C$H$-3), 115.96 (C$N$), 123.13 (C$H$-6), 123.64 (Ar C-1), 123.88 (C$H$-4), 129.07 (Ar C$H$-2), 142.11 (C$H$-7), 149.10 (C$H$-58), 151.03 (Ar C-4), 151.33 (C$H$-3), 161.22 (C$O$). ESI-TOF MS: *m/z* calcd. for $C_{18}H_{21}N_3O_2$ 334.15 $[M + Na]^+$, found 334.18 $[M + Na]^+$.

*2.3.5. (2E,4E,6E )-7-{4-[Bis-(2-hydroxy-ethyl)-amino]-phenyl}-2-cyano-hepta-2,4,6-trienoic acid (2-hydroxy-1,1-bis-hydroxymethyl-ethyl)-amide (**7**)*

Purified by crystallization from ethyl acetate and hexane to give a red solid. Yield: 62 mg (34%). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta_{ppm} = 3.48$ (m, 4H, NC$H_2$), 3.56 (m, 4H, C$H_2$OH), 3.63 (d, 6H, C$H_2$OH, $J = 5.6$ Hz), 4.73–4.77 (m, 5H, O$H$), 6.62 (dd, 1H, C$H$-4, $J = 12.3$, 13.9 Hz), 6.72 (d, 2H, Ar $H$-2, $J = 8.8$ Hz), 6.85 (s, 1H, N$H$), 6.92 (d, 1H, C$H$-7, $J = 15.3$ Hz), 7.02 (dd, 1H, C$H$-6, $J = 11.0$, 15.3 Hz), 7.25 (dd, C$H$-5, $J = 11.0$, 14.1 Hz), 7.41 (d, 2H, Ar $H$-3, $J = 8.8$ Hz), 7.85 (d, 1H, C$H$-3, $J = 12.0$ Hz). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta_{ppm} = 53.06$ (C$H_2$N), 58.10 (C$H_2$OH), 59.87 (NHC), 62.37 (C$H_2$OH), 103.17 (C-2), 111.50 (Ar C$H$-3), 116.28 (C$N$), 122.75 (C$H$-6), 123.07 (Ar C-1), 123.51 (C$H$-4), 129.30 (Ar C$H$-2), 142.37 (C$H$-7), 149.29 (Ar C-4), 149.63 (C$H$-5), 151.69 (C$H$-3), 160.87 (C$O$). ESI-TOF MS: *m/z* calcd. for $C_{22}H_{29}N_3O_6$ 454.20 $[M + Na]^+$, found 454.21 $[M + Na]^+$.

*2.3.6. (2E,4E,6E )-7-{4-[Bis-(2-hydroxy-ethyl)-amino]-phenyl}-2-cyano-hepta-2,4,6-trienoic acid (2-hydroxy-1-hydroxymethyl-ethyl)-amide (**8**)*

Red solid, yield: 147 mg (82%). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta_{ppm} = 3.47$ (t, 8H, overlapping (C$H_2$)$_2$N and C$H_2$OH), 3.56 (q, 4H, CH$_2$C$H_2$OH), 3.83–3.87 (m, 1H, C$H$), 4.68 (t, 2H, O$H$, $J = 5.7$ Hz), 4.76 (t, 2H, O$H$, $J = 5.4$ Hz), 6.62 (dd, 1H, C$H$-4, $J = 11.9$, 14.2 Hz), 6.72 (d, 2H, Ar $H$-2, $J = 9.0$ Hz), 6.93 (d, 1H, C$H$-7, $J = 15.2$ Hz), 7.02 (dd, 1H, C$H$-6, $J = 10.8$, 15.2 Hz), 7.20 (dd, 1H, C$H$-5, $J = 10.8$, 14.2 Hz), 7.41 (d, 2H, Ar $H$-3, $J = 9.0$ Hz), 7,52 (d, 1H, N$H$, $J = 8.1$ Hz), 7.89 (d, 1H, C$H$-3, $J = 11.8$ Hz). $^{13}$C NMR (DMSO-$d_6$, 63 MHz): $\delta_{ppm} = 53.08$ (NC$H_2$), 53.82 (NHC$H$), 58.10 (C$H_2$OH), 59.98 (C$H_2$OH), 103.44 (C-2), 111.50 (Ar C$H$-3), 116.15 (C$N$), 122.76 (C$H$-6), 123.09 (Ar C-1), 123.68 (C$H$-4), 129.27 (Ar C$H$-2), 142.19 (C$H$-7), 149.23 (C$H$-5), 149.25 (Ar C-4), 151.34 (C$H$-3), 161.07 (C$O$). ESI-TOF MS: *m/z* calcd. for $C_{21}H_{27}N_3O_5$ 424.18 $[M + Na]^+$, found 424.19 $[M + Na]^+$.

*2.3.7. (2E,4E,6E )-7-{4-[Bis-(2-hydroxy-ethyl)-amino]-phenyl}-2-cyano-hepta-2,4,6-trienoic acid [2-(2-hydroxy-ethoxy)-ethyl]-amide (**9**)*

Red solid, yield: 138 mg (67%). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta_{ppm} = 3.34$ (q, 2H, C$H_2$NH, $J = 5.8$ Hz), 3.42–3.51 (m, 10H, C$H_2$), 3.54–3.57 (m, 4H, C$H_2$OH), 4.57 (t, 1H, O$H$, $J = 5.4$ Hz), 4.76 (t, 2H, O$H$, $J = 5.4$ Hz), 6.62 (dd, 1H, C$H$-4, $J = 11.9$, 14.2 Hz), 6.71 (d, 2H, Ar $H$-2, $J = 9.0$ Hz), 6.93 (d, 1H, C$H$-7, $J = 15.2$ Hz), 7.02 (dd, 1H, C$H$-6, $J = 10.8$, 15.2 Hz), 7.21 (dd, 1H, C$H$-5, $J = 10.8$, 14.2 Hz), 7.41 (d, 2H, Ar $H$-3, $J = 8.9$ Hz), 7.86 (d, 1H, C$H$-3, $J = 11.9$ Hz), 8.12 (t, 1H, N$H$, $J = 5.6$ Hz). $^{13}$C NMR (DMSO-$d_6$, 126 MHz): $\delta_{ppm} = 39.31$ (NHC$H_2$), 53.07 (NC$H_2$), 58.09 (C$H_2$OH), 60.14 (C$H_2$OH), 68.55 (C$H_2$O), 72.02 (C$H_2$O), 103.09 (C-2), 111.49 (Ar C$H$-3), 115.98 (C$N$), 122.72 (C$H$-6), 123.08 (Ar C-1), 123.60 (C$H$-4), 129.28 (Ar C$H$-2), 142.28 (C$H$-7), 149.26 (Ar C-4), 149.39

(*C*H-5), 151.47 (*C*H-3), 161.31 (*C*O). ESI-TOF MS: *m/z* calcd. for $C_{22}H_{29}N_3O_5$ 438.20 $[M + Na]^+$, found 438.25 $[M + Na]^+$.

*2.3.8. (2E,4E,6E )-7-{4-[Bis-(2-hydroxy-ethyl)-amino]-phenyl}-2-cyano-hepta-2,4,6-trienoic acid (2-hydroxy-ethyl)-amide (**10**)*

Red solid, yield: 72 mg (43%). $^1$H NMR (DMSO-$d_6$, 500 MHz): $\delta_{ppm} = 3.25$ (q, 2H, NHC$H_2$, $J = 5.9$ Hz), 3.43–3.49 (m, 6H, C$H_2$), 3.54–3.58 (m, 4H, C$H_2$OH), 4.70 (t, 1H, O*H*, $J = 5.6$ Hz), 4.76 (t, 2H, O*H*, $J = 5.4$ Hz), 6.62 (dd, 1H, C*H*-4, $J = 11.9$, 14.2 Hz), 6.71 (d, 2H, Ar *H*-2, $J = 9.0$ Hz), 6.91 (d, 1H, C*H*-7, $J = 15.2$ Hz), 7.01 (dd, 1H, C*H*-6, $J = 10.8$, 15.2 Hz), 7.20 (dd, 1H, C*H*-5, $J = 10.8$, 14.2 Hz), 7.41 (d, 2H, Ar *H*-3, $J = 8.9$ Hz), 7.87 (d, 1H, C*H*-3, $J = 11.9$ Hz), 8.03 (t, 1H, N*H*, $J = 5.6$ Hz). $^{13}$C NMR (DMSO-$d_6$, 63 MHz): $\delta_{ppm} = 42.24$ (NH*C*$H_2$), 53.08 (N*C*$H_2$), 58.11 (*C*$H_2$OH), 59.42 (*C*$H_2$OH), 103.25 (*C*-2), 111.50 (Ar *C*H-3), 116.04 (*C*N), 122.74 (*C*H-6), 123.10 (Ar *C*-1), 123.65 (*C*H-4), 129.28 (Ar *C*H-2), 142.21 (*C*H-7), 149.25 (Ar *C*-4), 149.27 (*C*H-5), 151.40 (*C*H-3), 161.28 (*C*O). ESI-TOF MS: *m/z* calcd. for $C_{20}H_{25}N_3O_4$ 394.17 $[M + Na]^+$, found 394.16 $[M + Na]^+$.

## 3. Results and discussion

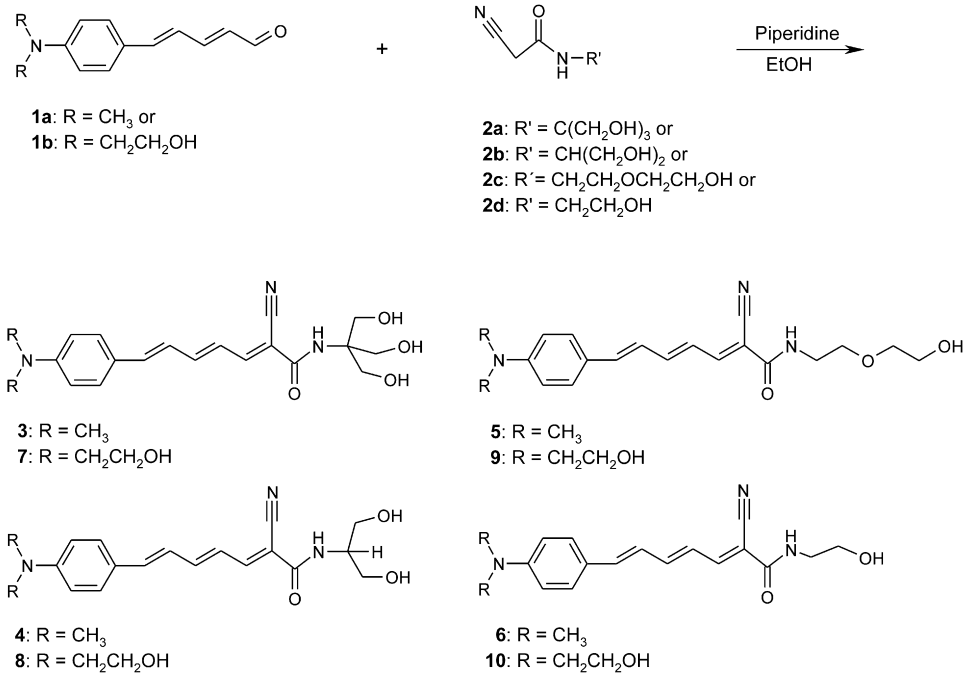
### 3.1. Synthesis

The synthetic route to donor–acceptor polyenes is shown in Scheme 1. Aryl polyenals **1a** and **1b** were obtained from the reaction of 5-(*N*,*N*-diethylamino)-2,4-pentadien-1-al [17] with aryl bromides according to procedure described by Friedli et al. [15]. *N*,*N*-(Dimethylamino)phenyl and *N*,*N*-(dihydroxyethylamino)phenyl donors were chosen since they both are known to act as donors. *N*,*N*-(Dihydroxyethylamino)phenyl functionalized chromophores are widely used in polymer systems [13], and addition of this group to the system increased the hydroxyl functionality to both ends. Cyanoacetamido derivatives **2a–2d** with one to three OH-groups were chosen in order to add reactive sites to the acceptor end of the molecules. 2-Cyanoacetamide derivatives were obtained according to a simple procedure [16], where ethyl cyanoacetate was refluxed with 1 equiv. of primary amines in ethanol or acetonitrile. Polyenes **3–10** were synthesized by the Knoevenagel condensation reaction of aryl polyenal **1a** or **1b** with 2-cyanoacetamide derivatives **2a–2d** following the published procedure [15]. In general, aldehyde and 2-cyanoacetamide derivative were refluxed in ethanol in the presence of a catalytic amount of piperidine, and crystallized product was then filtered. If the product did not crystallize at this stage, ethanol was evaporated and the product was crystallized from a solution of ethyl acetate and hexane. Dye **5** was purified by column chromatography on silica gel eluting with ethyl acetate. Yields of the products ranged from 27% up to 82%.

The structures were fully characterized by $^1$H and $^{13}$C NMR spectroscopy and ESI-TOF mass spectrometry. NMR methods such as HMQC (heteronuclear multiple quantum coherence), HMBC (heteronuclear multiple bond correlation), DEPT (distortionless enhancement by polarization transfer) and COSY (correlation spectroscopy) experiments were performed to facilitate characterizing the structures.

### 3.2. NMR studies

$^1$H NMR measurements were carried out to verify stereochemistry of the compounds **3–10**. Vicinal coupling constants




Scheme 1. Synthesis of polyene chromophores **3–10**.

across double bonds were determined in DMSO-$d_6$ and the range of 13.9–15.3 Hz indicated *all-E* configuration [18].

Bond-length alternation (BLA) is a structural parameter that is defined as the average difference between adjacent carbon–carbon bonds in a polymethine chain. It has been demonstrated that there is strong correlation between BLA and hyperpolarizability [4,6,19,20]. Since we could not obtain decent single crystals for the X-ray diffraction studies, the bond-length alternation was estimated by NMR methods in solution described by Marder et al. [4]. The difference between the vicinal coupling constants, $\Delta[^3J_{HH}]$, of double and single bond protons for alternated polyene (BLA ≈ 0.1 Å) is approximately 6.5 Hz, and for cyanine (BLA = 0 Å) the difference vanishes. It is established that for optimal NLO response the BLA lies between the polyene and the cyanine-like structures [4]. Therefore the vicinal coupling constants and corresponding average differences, $\Delta J$, between the adjacent CH=CH and CH–CH bonds were calculated (see Section 2). The difference between coupling constants decreased from donor end to the acceptor end from 4.2–4.4 Hz to 1.6–2.4 Hz. The average vicinal coupling constants of the CH=CH bonds differed from those of the adjacent CH–CH bonds by 3.0–3.4 Hz, clearly indicating the change in geometry from polyene-like to cyanine-like structure, and thus reduced bond-length alternation.

### 3.3. Absorption spectra

UV–vis absorption spectra of the conjugated polyenes **3**–**10** were measured in either 1:1 ethanol/chloroform or ethanol solutions, and the results are shown in Table 1. The compounds appeared to display an intense absorption maximum in the visible region. Molar absorption coefficients ranged from 31,100 to nearly 40,000 $cm^{-1}\,M^{-1}$.

Solvatochromic behavior of the compounds **3**–**9** was also studied with use of aprotic solvents. The wavelengths of the absorption maxima ($\lambda_{max}$) measured at solvents of different polarity are collected in Table 2.

All the measured polyenes displayed positive solvatochromism: maximum absorption band shifted to larger wavelengths (bathochromic shift) and broadening of the absorption peak was observed with increasing solvent polarity. As an example, the absorption spectra of compound **7** are shown in Fig. 1. A solvatochromism is induced by a change in the dipole moment of the molecule upon excitation. In positive solvatochromism the dipole moment of the first excited state increases with respect to the dipole moment of the ground state ($\mu_g < \mu_e$) [21]. Due to the similar donor–acceptor strength and the same length of the conjugated bridge, the molecules exhibited analogous solvatochromic behavior. The changes of $\lambda_{max}$ between the least polar dioxane and the most polar DMSO were 10–21 nm. The molecules **7**–**9** with *N*,*N*-(dihydroxyethylamino)phenyl group in the donor end had to some extent larger bathochromic shift compared to the corresponding molecules **3**–**5** with *N*,*N*-(dimethylamino)phenyl donor. The data obtained here were comparable with previously published results demonstrating the characteristic positive solvatochromic behavior of conjugated push–pull polyenes [4,22].

Table 1
Absorption data of the compounds **3**–**10**

| Compound | $\lambda_{max}$ [a] (nm) | $\varepsilon_{max}$ ($cm^{-1}\,M^{-1}$) |
|---|---|---|
| **3** | 486 | 36,400 |
| **4** | 481 | 35,200 |
| **5** | 478 | 35,900 |
| **6** | 478 | 31,600 |
| **7** | 481[b] | 31,100 |
| **8** | 477[b] | 39,900 |
| **9** | 479 | 37,600 |
| **10** | 480 | 31,500 |

[a] $\lambda_{max}$ measured in 1:1 chloroform/ethanol.
[b] $\lambda_{max}$ measured in ethanol.

Table 2
Absorption solvatochromism data of polyenes **3**–**9** ($\lambda_{max}$ (nm))

| | Dioxane | Ethyl acetate | Acetone | DMF | DMSO |
|---|---|---|---|---|---|
| **3** | 467 | 467 | 471 | 475 | 477 |
| **4** | 460 | 458 | 463 | 468 | 471 |
| **5** | 457 | 456 | 460 | 467 | 472 |
| **6** | 459 | 457 | 461 | 466 | 472 |
| **7** | 475 | 480 | 482 | 489 | 492 |
| **8** | 467 | 468 | 471 | 482 | 484 |
| **9** | 465 | 465 | 469 | 478 | 486 |

### 3.4. Thermal stability

To be of practical use the thermal stability of chromophores is a crucial issue particularly in poled-polymer systems. The onset decomposition temperature ($T_d$) of the chromophores was determined by a thermogravimetric analysis (TG) in an air atmosphere at a heating rate of 10 °C/min. The results are listed in Table 3 and the TG curves are shown in Fig. 2.

The $T_d$ of the chromophores varied from 190 to 256 °C with respect to the end groups of the acceptor. Molecules with the

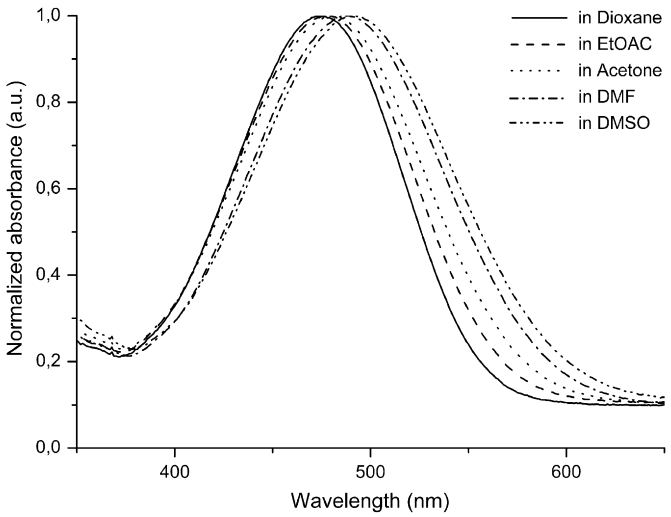



Fig. 1. Absorption spectra of compound **7** in solvents of different polarity.

Table 3
Thermal data of compounds **3**–**10**

| Compound | $T_m$[a] (°C) | $T_d$[b] (°C) |
|---|---|---|
| **3** | 171 | 190 |
| **4** | 172 | 231 |
| **5** | 106 | 256 |
| **6** | 199 | 237 |
| **7** | 193 | 191 |
| **8** | 199 | 232 |
| **9** | 191 | 253 |
| **10** | 183 | 224 |

[a] Melting point ($T_m$) is measured at a heating rate of 2 °C/min.
[b] Decomposition temperature ($T_d$) is an onset temperature of TG in air at a heating rate of 10 °C/min.

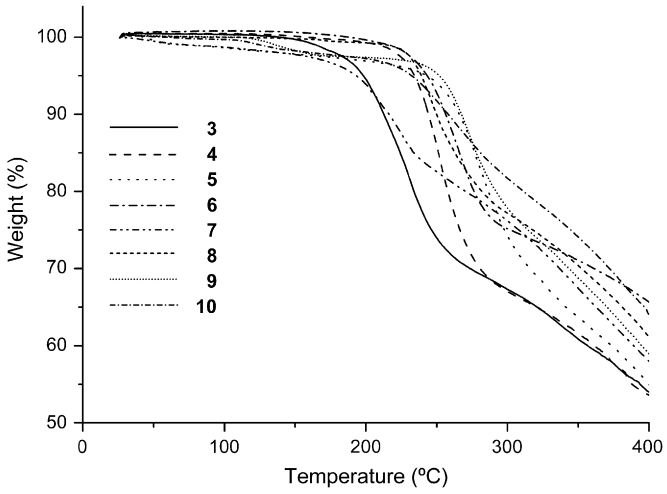



Fig. 2. The TG curves of the molecules **3**–**10**.

same acceptor end had very similar decomposition temperatures. The donor end hydroxyl groups did not have significant effect on the decomposition temperatures. The chromophores **3** and **7** with three hydroxyl groups in the acceptor end exhibited the lowest decomposition temperatures, and the only temperatures below 200 °C. The $T_d$ values increased with the decreasing number of the hydroxyl groups in the acceptor end. Molecules **5** and **9** with the ethoxyethanol end group exhibited the highest $T_d$ values 256 and 253, respectively.

## 4. Conclusions

Eight new polyene chromophores with hydroxyl functionality were synthesized and characterized by convenient methods. The chromophores were readily obtained from Knoevenagel condensation reaction between aromatic polyenals and 2-cyanoacetamide derivatives. Bond-length alternation of the *all-E* chromophores were estimated by the NMR method utilizing vicinal coupling constants of the adjacent CH═CH and CH–CH bonds. The geometric structure of the molecules was found to resemble that of a cyanine-like structure, indicating reduced bond-length alternation. All the measured compounds appeared to display positive solvatochromic behavior. Thermal stability was evaluated and decomposition temperature of the molecules ranged from 190 to 256 °C.

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