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# Influence of the Conjugation Pattern on the Photophysical Properties of Alkoxy-Substituted PE/PV Hybrid Polymers

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**ABSTRACT:** Alkoxy-substituted phenylene–ethynylene (PE)/phenylene–vinylene (PV) hybrid polymers of general constitutional structure  $(-\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}-\text{CH}=\text{CH}-)_n$  (**2**),  $(-\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}-\text{CH}=\text{CH}-\text{Ar}-\text{C}\equiv\text{C}-)_n$  (**3**), and  $(-\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}-\text{CH}=\text{CH}-\text{Ar}-\text{CH}=\text{CH}-)_n$  (**4**) have been synthesized and characterized. Comparisons of their photophysical properties in solution as well as in solid state (photoconductivity, absorption, emission, and electroluminescence) with those of their corresponding alkoxy-substituted poly(phenylene–ethynylene) (**1**) and poly(phenylene–vinylene) (**5**) have been carried out. Large octadecyloxy groups were selected as side chains in order to reduce the effect of  $\pi$ – $\pi$  stacking interaction on the properties of the polymers in the solid state. This resulted in easy detection of photoconductivity and higher fluorescence quantum yields in solid state. The hybrid conjugation pattern in **4** is more favorable for photoconductivity than that in **2**. A red shift of the absorption and emission spectra in solution is observed from **1** over **2b**, **3**, and **4** to **5**. LED devices of ITO/PEDOT/polymer/Ca configuration have been fabricated with all compounds, except **2a**. The phenylvinylene side groups in **3** not only give rise to a red shift of the solid-state photoluminescence spectrum and electroluminescence spectrum (relative to **2b**) but also bring about a decrease of the turn-on voltage and improve the electroluminescence efficiency for more than 100 times.

## Introduction

The discovery of electroluminescence in poly(phenylene–vinylene)s (PPV) by Burroughes et al.<sup>1</sup> paved the way to intensified studies of the properties of the derivatives of PPV, making them the most thoroughly investigated type of semiconducting polymers.<sup>2–5</sup> PPVs have mostly been used as active layer in the design of light-emitting diodes. Their poor electron-accepting nature resulted in low electroluminescence efficiencies in the early monolayered LED devices.<sup>1,4</sup> To circumvent this problem, many approaches to enhance the electron affinity of PPVs have been proposed in the literature,<sup>6–14</sup> the most recent one of which has been the incorporation of triple bonds ( $-\text{C}\equiv\text{C}-$ ) into the polymer backbone, leading to phenylene–vinylene/phenylene–ethynylene hybrid polymers.<sup>15–21</sup>

Alkyl-substituted hybrid polymers of the general chemical structure  $(-\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}-\text{CH}=\text{CH}-)_n$  were synthesized through Mo(CO)<sub>6</sub>-catalyzed acyclic diyne metathesis by Bunz et al.<sup>15</sup> The absorption bands of alkyl-substituted conjugated polymers are blue-shifted compared to their corresponding alkoxy-substituted congeners due to less electron-donating nature of alkyl groups and strong steric hindrance.<sup>22</sup> In this article we report the synthesis and characterization of alkoxy-substituted hybrid polymers **2** (having the same general structure as those of Bunz) and **3** (bearing styryl side groups). For the purpose of comparison, the correspond-

ing alkoxy-substituted poly(phenylene–ethynylene) (PPE, **1**) and poly(phenylene–vinylene) (PPV, **5**) have also been synthesized and characterized. The above-mentioned comparison takes into account the hybrid polymer **4**, whose synthesis has been described elsewhere (Chart 1).<sup>20</sup>

## Experimental Section

**Instrumentation.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained in deuterated chloroform using a Bruker DRX 400 and a Bruker AC 250. Chemical shifts ( $\delta$  values) are given in parts per million with tetramethylsilane as an internal standard. Elemental analysis was measured on a CHNS-932 Automat Leco. Infrared spectroscopy was recorded on a Nicolet Impact 400. A homemade apparatus served for the thermogravimetric measurements. Differential scanning calorimetry (DSC) was obtained with a Perkin-Elmer DSC 2C while heating at a rate of 10 °C/min. Gel permeation chromatography (GPC) was performed on a set of Knauer using THF as eluent and polystyrene as a standard. The absorption spectra were recorded in dilute chloroform solution ( $10^{-5}$ – $10^{-6}$  M) on a Perkin-Elmer UV/vis–NIR spectrometer Lambda 19. Quantum-corrected emission spectra were measured in dilute chloroform solution ( $10^{-6}$  M) with a LS 50 luminescence spectrometer (Perkin-Elmer). Photoluminescence quantum yields were calculated according to Demas and Crosby<sup>23</sup> against quinine sulfate in 0.1 N sulfuric acid as a standard ( $\phi_n = 55\%$ ). The solid-state absorption and emission were measured with a Hitachi F-4500 spectrometer. The films were spin-casted from chlorobenzene solutions (concentration  $10^{-2}$ – $10^{-3}$  M). The quantum yield in the solid state was determined against a CF<sub>3</sub>P–PPV (poly{1,4-phenylene–[1-(4-trifluoromethylphenyl)ethynylene]-2,5-dimethoxy-1,4-phenylene–[2-(4-trifluoromethylphenyl)ethynylene]}) copolymer reference that has been measured by integrating sphere as 0.43.<sup>24</sup>

**LED Fabrication and Measurement.** PEDOT/PSS (Bayer Co.) was spin-cast onto ITO glass (OFC Co.) to be used as an anode. The polymer solutions (20 mg/mL in chloroform)

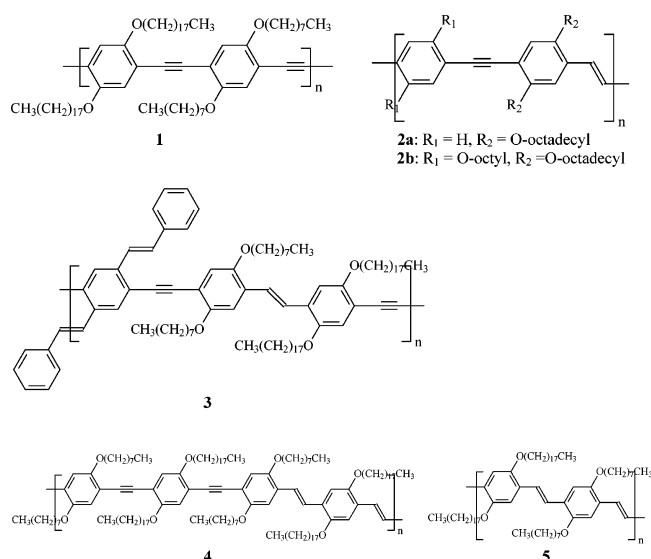
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Chart 1



were filtered through 0.2  $\mu\text{m}$  Millex-FGS Filters (Millipore Co.) and were spin-cast onto dried PEDOT/ITO substrates under a nitrogen atmosphere. The polymer films were typically 75 nm thick. Calcium electrodes of 400 nm thickness were evaporated onto the polymer films at about  $10^{-7}$  Torr, followed by a protective coating of aluminum. The devices were characterized using a homemade system, which has been described elsewhere.<sup>25</sup>

**Materials.** All starting materials were purchased from commercial suppliers (Fluka, Merck, and Aldrich). Toluene, tetrahydrofuran, and diethyl ether were dried and distilled over sodium and benzophenone. Diisopropylamine was dried over KOH and distilled. If not otherwise specified, the solvents were degassed by bubbling with argon or nitrogen 1 h prior to use.

**Bromohydroquinone (7).** A solution of bromine (47 mL, 0.45 mol) in 200 mL of acetic acid was added slowly and dropwise within 2–3 h in a cooled (ice bath) suspension of hydroquinone (6) (100 g, 0.9 mol) in 1 L of acetic acid. The mixture was further stirred for 2 h while keeping the temperature between 2 and 8 °C. Acetic acid was removed under reduced pressure, and the residue was recrystallized twice from a 20 to 1 mixture of chloroform and ethanol. 100 g (58%) of white solid was obtained. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 6.75$  (m), 6.94 (d,  $3J = 8.76$  Hz), 7.01 (d,  $4J = 2.87$  Hz), 7.28 (s). <sup>13</sup>C NMR (62.89 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 110.18$ , 110.29, 116.59, 116.72, 116.76, 118.90, 119.96, 146.97, 147.06, 149.88 (C<sub>aryl</sub>'s). Anal. Calcd for C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>Br (189.00): C, 38.13; H, 2.67. Found: C, 38.44; H, 2.66.

**1-Bromo-2,5-diocadecyloxybenzene (8).** A suspension of KOH powder (56.1 g, 1 mol) in dried DMSO (300 mL) was stirred and degassed in a 500 mL three-neck flask for 1 h. 2-Bromohydroquinone (7) (14.8 g, 0.078 mol) and octadecyl bromide (104.0 g, 0.312 mol) were then added, whereby the temperature rose to 30 °C. The reaction mixture was stirred for 8 h at room temperature and finally poured into ice water. The precipitated product was filtered and washed with water and ethanol. The recrystallization from 500 mL of toluene/ethanol (4/1) gave 50 g (92%) of colorless crystals. Mp: 68–70 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 0.88\text{--}1.91$  (70H, m,  $-(\text{CH}_2)_{16}\text{CH}_3$ ), 3.88–4.00 (4H, m,  $-\text{CH}_2\text{O}-$ ), 6.77–6.87 (2H, m, C<sub>aryl</sub>-H), 7.13 (1H, d,  $4J = 2.40$  Hz, C<sub>aryl</sub>-H). <sup>13</sup>C NMR (62 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 12.30$ , 20.89, 24.20, 24.42, 26.39, 26.98, 27.49, 27.56, 27.77, 27.79, 27.90, 30.13, 31.06, 32.18 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>-), 67.07, 68.49, 69.17 ( $-\text{CH}_2\text{O}-$ ), 111.05, 112.26, 112.62, 112.99, 113.63, 117.74, 148.01, 151.83 (C<sub>aryl</sub>'s). Anal. Calcd for C<sub>42</sub>H<sub>77</sub>O<sub>2</sub>Br (693.976): C, 72.69; H, 11.18; Br, 11.51. Found: C, 73.02; H, 10.90; Br, 11.87.

**1-Bromo-4-bromomethyl-2,5-diocadecyloxybenzene (9).** A suspension of 8 (10 g, 14.4 mmol), paraformaldehyde (2.8 g,

96 mmol), and NaBr (3.7 g, 36 mmol) in glacial acetic acid (160 mL) was heated at 100–110 °C. A mixture of concentrated sulfuric acid (10 g) and glacial acetic acid (10 g) was added dropwise, and the reaction mixture was stirred for 2 days at 100–110 °C. After the reaction mixture was cooled at 0 °C, the precipitate was filtered off, washed with water, and recrystallized from hexane (100 mL). 7.9 g (70%) of white solid was obtained. Mp: 82–84 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 0.88\text{--}1.86$  (70H, m,  $-(\text{CH}_2)_{16}\text{CH}_3$ ), 3.88–4.03 (4H, m,  $-\text{CH}_2\text{O}-$ ), 4.52 and 4.55 (2H, 2s,  $-\text{CH}_2\text{P}-$ ), 6.80–7.13 (2H, m, C<sub>aryl</sub>-H). <sup>13</sup>C NMR (62 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 14.49$ , 23.07, 26.39, 29.68, 29.75, 29.96, 29.98, 30.05, 30.09, 32.32 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>-), 29.11 ( $-\text{CH}_2\text{Br}$ ), 69.43, 69.60, 70.64 ( $-\text{CH}_2\text{O}-$ ), 113.62, 115.06, 116.46, 117.81, 126.48, 127.93, 149.89, 151.07, 151.61, 152.35 (C<sub>aryl</sub>'s). Anal. Calcd for C<sub>43</sub>H<sub>78</sub>O<sub>2</sub>Br<sub>2</sub> (786.92): C, 65.65; H, 9.99; Br, 20.30. Found: C, 65.29; H, 9.58; Br, 20.30.

**4-Bromo-2,5-diocadecyloxybenzyl diethylphosphonate (10).** A mixture of 9 (2.6 g, 3.3 mmol) and an excess of triethyl phosphite (1 g, 6 mmol) was heated slowly to 160 °C, and the evolving ethyl bromide was distilled off simultaneously. After heating 3 h at 160 °C, vacuum was applied for 1 h at 180 °C. The resulting oil solidified after cooling at room temperature. It was recrystallized from hexane (10 mL). 1.8 g (75%) of white solid was obtained. Mp: 61–62 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 0.87\text{--}1.84$  (76H, m,  $-(\text{CH}_2)_{16}\text{CH}_3$  and CH<sub>3</sub>-ethyl), 3.20 (2H, d,  $3J = 21.71$  Hz,  $-\text{CH}_2\text{P}-$ ), 3.89–4.11 (8H, m,  $-\text{CH}_2\text{O}-$ ), 6.98 and 7.05 (2H, s, C<sub>aryl</sub>-H). <sup>13</sup>C NMR (62 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 14.50$  (CH<sub>3</sub>-octadecyl), 16.72 and 16.81 (CH<sub>3</sub>-ethyl), 23.08, 25.63, 26.38, 26.47, 27.85, 29.75, 29.99, 30.09, 32.31 ( $-(\text{CH}_2)_{16}-$ ), 62.29 and 62.39 ( $-\text{CH}_2\text{O}-$ ethyl), 69.68 and 70.50 ( $-\text{CH}_2\text{O}-$  octadecyl), 111.06, 111.13, 117.09, 117.17, 117.31, 117.36, 120.72, 120.86, 149.71, 149.77, 151.43, 151.55 (C<sub>aryl</sub>'s). Anal. Calcd for C<sub>47</sub>H<sub>88</sub>BrO<sub>5</sub>P (844.0905): C, 66.88; H, 10.51; Br, 9.47. Found: C, 67.80; H, 10.17; Br, 9.62.

**1-(4-Bromophenyl)-2-(4-bromo-2,5-diocadecyloxyphenyl)ethylene (12a).** A solution of 4-bromobenzaldehyde (11a) (1.0 g, 5.40 mmol) and 10 (4.5 g, 5.4 mmol) in toluene (100 mL) was heated at reflux under argon. Potassium *tert*-butoxide (1.21 g, 10.8 mmol) was added portionwise to it, and the mixture was heated for 3 h under reflux. The reaction was quenched with 5% aqueous HCl (20 mL). It was then extracted with water until neutrality. After drying the toluene solution, the solvent was removed under vacuum, and the resulting solid was chromatographed on a silica gel column using toluene as eluent. The obtained yellow substance was washed with little amount of methanol and dried. Yield: 3.6 g (76%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 0.78\text{--}2.28$  (70H, m, CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>-), 3.31 (t,  $3J = 6.66$  Hz,  $-\text{CH}_2\text{O}-$ ), 3.51 (t,  $3J = 6.62$  Hz,  $-\text{CH}_2\text{O}-$ ), 3.81–3.99 (4H,  $-\text{CH}_2\text{O}-$ ), 6.55–7.41 (phenyl and vinylene H's). <sup>13</sup>C NMR (62 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 14.10$ , 22.69, 26.02, 26.19, 26.30, 29.29, 29.36, 29.61, 29.70, 31.93 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>-), 69.61, 70.36 ( $-\text{CH}_2\text{O}-$ ), 111.81, 112.28, 117.89, 121.27, 123.87, 124.24, 125.59, 126.16, 126.78, 127.97, 128.09, 130.47, 131.34, 131.77, 136.68, 136.91, 149.86, 151.17 (phenyl and vinylene C's). UV-vis (THF):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$ ): 297.6 (24 700), 346.4 (22 900). Anal. Calcd for C<sub>50</sub>H<sub>82</sub>Br<sub>2</sub>O<sub>2</sub> (875.01): C, 68.63; H, 9.45. Found: C, 70.04; H, 9.72.

**1-(4-Trimethylsilylphenyl)-2-(4-trimethylsilylphenyl)-2,5-diocadecyloxyphenyl ethylene (13a).** A solution of 12a (3.6 g, 4.1 mmol) in diisopropylamine (60 mL) was degassed for 1 h. Pd(PPh<sub>3</sub>)<sub>4</sub> (140 mg, 0.2 mmol) and CuI (0.2 mg, 0.2 mmol) were given to it. Trimethylsilylacetylene (0.88 g, 9 mmol) was added dropwise to it. The reaction mixture was then stirred for 4 h at 80 °C. After cooling, the ammonium bromide precipitate was filtered off. The solvent was removed on a rotary evaporator; the remaining solid was dissolved in toluene and purified through silica gel column chromatography with toluene as eluent. 3.3 g (80%) of a brown-yellowish substance were thus obtained. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = 0.00\text{--}0.07$  ((CH<sub>3</sub>)<sub>3</sub>Si-), 0.66–1.98 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>-), 3.20–3.85 ( $-\text{CH}_2\text{O}-$ ), 6.45–7.32 (phenylene and vinylene H's). <sup>13</sup>C NMR (62 MHz, CDCl<sub>3</sub>):  $\delta/\text{ppm} = -0.12$ , 0.38, 0.42 ((CH<sub>3</sub>)<sub>3</sub>Si-), 14.51, 23.08, 26.47, 26.60, 29.75, 29.89, 30.09,



32.32 ( $\text{CH}_3(\text{CH}_2)_{16}-$ ), 69.76, 70.13 ( $-\text{CH}_2\text{O}-$ ), 95.46, 99.73 ( $-\text{C}\equiv\text{C}-$ ), 105.64, 111.20, 113.31, 117.71, 122.43, 124.62, 126.72, 128.22, 129.45, 132.67, 138.26, 150.89, 155.04 (phenylene and vinylene C's). Anal. Calcd for  $\text{C}_{60}\text{H}_{100}\text{O}_2\text{Si}_2$  (909.62): C, 79.23; H, 11.08. Found: C, 78.66; H, 10.90.

**1-(4-Ethynylphenyl)-2-(4-ethynyl-2,5-diocetyldecyloxyphenyl)ethylene (14a).** A solution of 2.3 mL of aqueous KOH (20%) in 26 mL of methanol was added dropwise to a stirred solution of the trimethylsilyl derivative **13a** (3.3 g, 3.62 mmol) in 50 mL of THF. The reaction was stirred for 1 day at room temperature. A black greaselike precipitate was obtained, which was subsequently extracted twice with ethanol to provide 1.2 g (43%) of a yellow substance.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 0.78 \rightarrow 1.78$  (70H, m,  $\text{CH}_3(\text{CH}_2)_{16}-$ ), 3.06 (1H, s,  $\equiv\text{C}-\text{H}$ ), 3.19 (1H, s,  $\equiv\text{C}-\text{H}$ ), 3.31 (t,  $^3J = 6.68$  Hz,  $-\text{CH}_2\text{O}-$ ), 3.89 (2H, t,  $^3J = 6.50$  Hz,  $-\text{CH}_2\text{O}-$ ), 3.98 (2H, t,  $^3J = 6.60$  Hz,  $-\text{CH}_2\text{O}-$ ), 6.84  $\rightarrow$  7.45 (8H, phenylene and vinylene H's).  $^{13}\text{C}$  NMR (62 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 14.52, 23.09, 26.36, 26.60, 29.71, 29.76, 30.01, 30.10, 32.32$  ( $\text{CH}_3(\text{CH}_2)_{16}-$ ), 69.78, 70.23, 71.37 ( $-\text{CH}_2\text{O}-$ ), 80.74, 82.11, 84.15 ( $-\text{C}\equiv\text{C}-$ ), 111.14, 112.20, 118.16, 121.45, 124.78, 126.83, 128.45, 129.52, 132.84, 138.54 (phenylene and vinylene C's), 150.86, 155.00 ( $\text{C}_{\text{phenyl}}-\text{OR}$ ). Anal. Calcd for  $\text{C}_{54}\text{H}_{84}\text{O}_2$  (765.26): C, 84.75; H, 11.06. Found: C, 66.09; H, 9.35.

**1-(4-Bromo-2,5-diocetyldecyloxyphenyl)-2-(4-bromo-2,5-diocetyldecyloxyphenyl)ethylene (12b).** A solution of 4-bromo-2,5-diocetyldecyloxybenzaldehyde (**11b**) (1.0 g, 2.26 mmol) and **10** (1.90 g, 2.26 mmol) in toluene (50 mL) was heated at reflux under argon. Potassium *tert*-butoxide (1.21 g, 10.8 mmol) was added in two portions to it, and the mixture was heated for 3 h under reflux. The reaction was quenched with 5% aqueous HCl (20 mL). It was then extracted with water until neutrality. After drying the toluene solution, the solvent was removed under vacuum, and the resulting solid was chromatographed on a silica gel column using toluene as eluent. The obtained yellow substance was washed with a little amount of methanol and dried. Yield: 1.92 g (75%).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 0.79 \rightarrow 2.28$  (100H, m,  $\text{CH}_3(\text{CH}_2)_{16}-$  and  $\text{CH}_3(\text{CH}_2)_6-$ ), 3.30  $\rightarrow$  3.97 (8H, m,  $-\text{CH}_2\text{O}-$ ), 6.61  $\rightarrow$  7.33 (phenyl and vinylene H's).  $^{13}\text{C}$  NMR (62 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 14.48, 23.07, 26.39, 26.45, 26.53, 29.44, 29.65, 29.75, 30.09, 32.23, 32.32$  ( $\text{CH}_3(\text{CH}_2)_{16}-$  and  $\text{CH}_3(\text{CH}_2)_6-$ ), 69.26, 69.99, 70.68 ( $-\text{CH}_2\text{O}-$ ), 112.26, 115.21, 118.28, 124.18, 125.77, 127.42, 150.26, 151.49 (phenyl and vinylene C's). UV-vis (THF):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/(\text{L mol}^{-1} \text{cm}^{-1})$ ): 292.8 (19 420), 362.4 (25 270). Anal. Calcd for  $\text{C}_{66}\text{H}_{114}\text{Br}_2\text{O}_4$  (1131.45): C, 70.06; H, 10.15; Br, 14.12. Found: C, 70.55; H, 10.10; Br, 13.69.

**1-(4-Trimethylsilylethynylene-2,5-diocetyldecyloxyphenyl)-2-(4-trimethylsilylethynylene-2,5-diocetyldecyloxyphenyl)ethylene (13b).** A solution of **12b** (5.7 g, 5 mmol) in diisopropylamine (70 mL) was degassed for 1 h.  $\text{Pd}(\text{PPh}_3)_4$  (175 mg, 0.25 mmol) and CuI (47.6 mg, 0.25 mmol) were added to it. Trimethylsilylacetylene (1.08 g, 11 mmol) was added dropwise to it. The reaction mixture was then stirred at reflux for 4 h. After cooling, the ammonium bromide precipitate was filtered off. The solvent was removed on a rotary evaporator; the remaining solid was dissolved in toluene and purified through silica gel column chromatography with toluene as eluent. 4.6 g (80%) of a yellow substance was thus obtained.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 0.05 \rightarrow 0.09$  ( $(\text{CH}_3)_3\text{Si}-$ ), 0.68  $\rightarrow$  1.98 ( $\text{CH}_3(\text{CH}_2)_{16}-$  and  $\text{CH}_3(\text{CH}_2)_6-$ ), 3.20  $\rightarrow$  3.85 ( $-\text{CH}_2\text{O}-$ ), 6.45  $\rightarrow$  7.27 (phenylene and vinylene H's).  $^{13}\text{C}$  NMR (62 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = -0.55, 0.00$  ( $(\text{CH}_3)_3\text{Si}-$ ), 14.04, 14.06, 22.64, 26.08, 26.14, 29.32, 29.44, 29.50, 29.67, 31.84, 31.89 ( $\text{CH}_3(\text{CH}_2)_{16}-$  and  $\text{CH}_3(\text{CH}_2)_6-$ ), 69.32, 69.60 ( $-\text{CH}_2\text{O}-$ ), 99.10, 101.69 ( $-\text{C}\equiv\text{C}-$ ), 110.77, 112.55, 117.31, 124.31, 125.81, 128.62, 150.27, 150.39, 154.65 (phenylene and vinylene C's). Anal. Calcd for  $\text{C}_{76}\text{H}_{132}\text{O}_4\text{Si}_2$  (1166.05): C, 78.28; H, 11.41. Found: C, 77.25; H, 10.87.

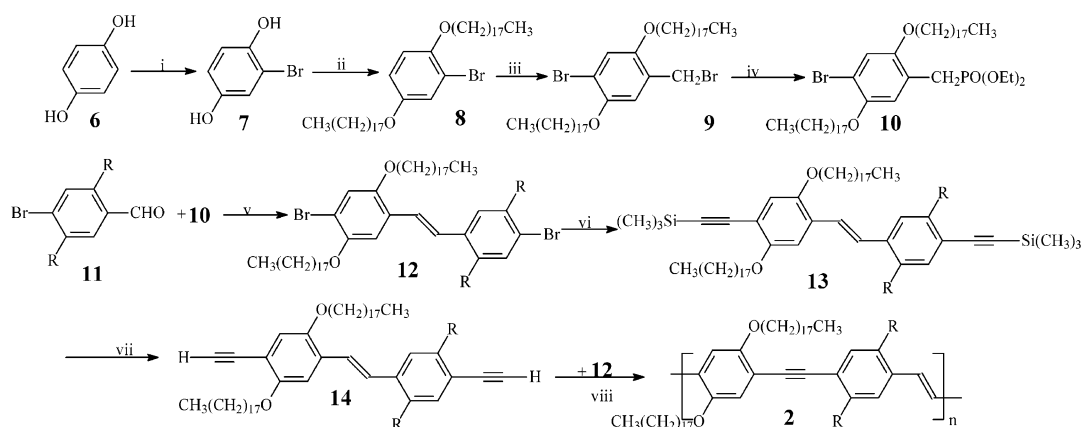
**1-(4-Ethynyl-2,5-diocetyldecyloxyphenyl)-2-(4-ethynyl-2,5-diocetyldecyloxyphenyl)ethylene (14b).** A solution of 2.3 mL of aqueous KOH (20%) in 26 mL of methanol was added dropwise to a stirred solution of **7b** in 52 mL of THF. The reaction was stirred 3 h at room temperature. The diethynyl compound precipitated after standing for long time. The brown-yellow

solid was filtered, dissolved in toluene, and purified over a silica gel column with toluene as eluent. 3 g (79%) of brown-orange solid were obtained.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 0.88 \rightarrow 1.88$  ( $\text{CH}_3(\text{CH}_2)_{16}-$  and  $\text{CH}_3(\text{CH}_2)_6-$ ), 3.34 ( $-\text{C}\equiv\text{C}-\text{H}$ ), 3.64  $\rightarrow$  4.10 ( $-\text{CH}_2\text{O}-$ ), 6.71  $\rightarrow$  7.47 (phenylene and vinylene H's).  $^{13}\text{C}$  NMR (62 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 14.50, 23.08, 26.00, 26.56, 29.71, 29.75, 30.10, 32.24, 32.32$  ( $\text{CH}_3(\text{CH}_2)_{16}-$  and  $\text{CH}_3(\text{CH}_2)_6-$ ), 69.76, 70.16 ( $-\text{CH}_2\text{O}-$ ), 80.85, 81.95 ( $-\text{C}\equiv\text{C}-$ ), 111.18, 111.89, 118.18, 124.87, 129.27, 150.78, 155.04 (phenylene and vinylene C's). Anal. Calcd for  $\text{C}_{70}\text{H}_{116}\text{O}_4$  (1021.69): C, 82.29; H, 11.44. Found: C, 81.39; H, 11.20.

**Poly[1,4-(2,5-diocetyldecyloxyphenylene)ethynylene-1,4-(2,5-diocetyldecyloxyphenylene)ethene-1,2-diyl] (2b).** Dibromo derivative **12b** (2.00 g, 1.76 mmol), diethynyl derivative **14b** (1.806 g, 1.76 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (82 mg,  $7.07 \times 10^{-2}$  mmol, 4 mol %), and CuI (13.4 mg,  $7.07 \times 10^{-2}$  mmol, 4 mol %) were added to a degassed solution of diisopropylamine (15 mL) and toluene (40 mL). After degassing for a further 30 min, the reaction was then stirred for 3 days at 80 °C. The precipitated diisopropylammonium bromide was filtered off. Aqueous HCl was given to the filtrate, and the organic phase was extracted with water until neutrality (pH = 6–7). The organic phase was dried in a Dean-Stark apparatus, filtered and evaporated to 50 mL, and precipitated in 300 mL of methanol. The polymer was extracted for 1 day with methanol and dried under vacuum at 50 °C. 2.9 g (85%) of a magenta substance were obtained. GPC (THF):  $\bar{M}_n = 8600$  g/mol,  $\bar{M}_w = 34\,000$  g/mol,  $\bar{M}_z = 91\,000$  g/mol,  $\bar{M}_p = 18\,000$  g/mol; polydispersity index = 3.94.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 0.85 \rightarrow 1.84$  (100H,  $\text{CH}_3(\text{CH}_2)_{16}-$  and  $\text{CH}_3(\text{CH}_2)_6-$ ), 3.62  $\rightarrow$  4.09 (8H,  $-\text{CH}_2\text{O}-$ ), 6.6  $\rightarrow$  7.13 (4H, arylene H's), 7.40  $\rightarrow$  7.47 (2H, vinylene H's).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 14.47, 23.07, 26.52, 26.64, 29.76, 29.91, 30.12, 32.32$  ( $\text{CH}_3(\text{CH}_2)_{16}-$  and  $\text{CH}_3(\text{CH}_2)_6-$ ), 69.79, 70.42, 71.37 ( $-\text{CH}_2\text{O}-$ ), 91.76 ( $-\text{C}\equiv\text{C}-$ ), 111.68, 117.58, 118.34 ( $\text{C}_{\text{phenyl}}-\text{H}$ ), 124.60 (vinylene C's), 113.98, 128.80 ( $\text{C}_{\text{phenyl}}-\text{C}$ ), 151.10, 154.44 ( $\text{C}_{\text{phenyl}}-\text{OR}$ ). UV-vis ( $\text{CHCl}_3$ ,  $1.28 \times 10^{-5}$  M):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/(\text{L mol}^{-1} \text{cm}^{-1})$ ): 323 (19 420), 454 (29 600). Anal. Calcd for  $(\text{C}_{68}\text{H}_{114}\text{O}_4)_n$  (995.65) $_n$ : C, 82.03; H, 11.54. Found: C, 80.27; H, 11.05; Br, 2.47.

**Poly[1,4-phenyleneethynylene-1,4-(2,5-diocetyldecyloxyphenylene)ethene-1,2-diyl] (2a).** Dibromo derivative **12a** (800 mg, 0.914 mmol), diethynyl derivative **14a** (1.806 g, 1.76 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (42.2 mg,  $3.62 \times 10^{-2}$  mmol, 4 mol %) and CuI (7 mg,  $3.62 \times 10^{-2}$  mmol, 4 mol %) were added to a degassed solution of diisopropylamine (7.5 mL) and toluene (20 mL). After degassing for further 30 min, the reaction was then stirred 50 h at 80 °C. The precipitated diisopropylammonium bromide was filtered off. Aqueous HCl was given to the filtrate, and the organic phase was extracted with water until neutrality (pH = 6–7). The organic phase was dried in a Dean-Stark apparatus, filtered, and precipitated in 200 mL of methanol. The polymer was extracted for 1 day with methanol and dried under vacuum at 50 °C. 1 g (74%) of an orange-brown substance was obtained. GPC (THF):  $\bar{M}_n = 6000$  g/mol,  $\bar{M}_w = 26\,500$  g/mol,  $\bar{M}_z = 70\,090$  g/mol,  $\bar{M}_p = 12\,900$  g/mol; polydispersity index = 4.46.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 0.80 \rightarrow 1.79$  (70H,  $\text{CH}_3(\text{CH}_2)_{16}-$ ), 3.32 and 3.95 (4H,  $-\text{CH}_2\text{O}-$ ), 6.96  $\rightarrow$  7.45 (8H, phenylene and vinylene H's).  $^{13}\text{C}$  NMR (62 MHz,  $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 14.13, 22.71, 26.13, 29.73, 31.94$  ( $\text{CH}_3(\text{CH}_2)_{16}-$ ), 69.37 ( $-\text{CH}_2\text{O}-$ ), 126.49, 128.01, 131.86 (phenylene and vinylene C-H). IR (KBr): 3066 (w,  $\text{C}_{\text{phenyl}}-\text{H}$ ), 2920 and 2850 (vs,  $-\text{CH}_2-$ ,  $\text{CH}_3-$ ), 1600 (w,  $-\text{C}=\text{C}_{\text{phenyl}}$ ), 1207 (s,  $\text{C}_{\text{phenyl}}-\text{OR}$ ), 968  $\text{cm}^{-1}$  (m, trans  $-\text{CH}=\text{CH}-$ ). UV-vis ( $\text{CHCl}_3$ ,  $1.8 \times 10^{-5}$  M):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/(\text{L mol}^{-1} \text{cm}^{-1})$ ): 432.4 (29 370). Anal. Calcd for  $(\text{C}_{52}\text{H}_{82}\text{O}_2)_n$  (739.22) $_n$ : C, 84.49; H, 11.18. Found: C, 81.49; H, 10.68; Br, 2.58.

**Poly[1,4-(2,5-bis(trans-styryl)phenylene)ethynylene-1,4-(2,5-diocetyldecyloxyphenylene)ethene-1,2-diyl] (3).** *trans,trans*-2,5-Distyryl-1,4-dibromobenzene (**15**) (438 mg, 1 mmol), **14b** (1021 mg, 1 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (46 mg,  $4 \times 10^{-2}$  mmol, 4 mol %), and CuI (7 mg,  $4 \times 10^{-2}$  mmol, 4 mol %) were added to a degassed solution of diisopropylamine (20 mL), toluene (80 mL), and THF (20 mL). After stirring for 24 h at 65–70 °C, 2 mL of phenylacetylene and 2 mL of bromobenzene were added to the reacting mixture,

Scheme 1<sup>a</sup>

11a, 12a, 13a, 14a, 2a: R = H

11b, 12b, 13b, 14b, 2b: R = *n*-octyl

<sup>a</sup> (i) Br<sub>2</sub>, CH<sub>3</sub>COOH, 5 °C. (ii) C<sub>18</sub>H<sub>37</sub>Br, KOH, DMSO, Ar. (iii) (CH<sub>2</sub>O)<sub>*n*</sub>, NaBr/H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH. (iv) P(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, 180 °C. (v) *t*-BuOK, toluene, 3–4 h, 110 °C. (vi) (CH<sub>3</sub>)<sub>3</sub>SiC≡CH, diisopropylamine, (PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>/CuI, 3–4 h, Ar. (vii) KOH/MeOH, THF, 3 h. (viii) Pd(PPh<sub>3</sub>)<sub>4</sub>/CuI, diisopropylamine, toluene, 3 days, 80 °C.

and the reaction was allowed to continue for further 24 h. After cooling to room temperature, the mixture was poured on a 2 cm plug of silica gel 60 to remove the diisopropylammonium bromide salt and the catalysts. The plug was washed with toluene. The combined filtrate was reduced to 100 mL under vacuum and was added dropwise into 500 mL of stirred methanol. The precipitate was extracted 9 h with methanol, dissolved in 80 mL of toluene, and reprecipitated in a methanol/ethanol (9/1) mixture. 1058 mg (81.4%) of a brown-red substance was obtained after drying in a vacuum. GPC (THF):  $\bar{M}_n$  = 18 000 g/mol,  $\bar{M}_w$  = 85 000 g/mol,  $\bar{M}_z$  = 315 000 g/mol,  $\bar{M}_p$  = 36 800 g/mol; polydispersity index = 4.7. VPO (CHCl<sub>3</sub>):  $\bar{M}_n$  = 35 000 g/mol. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm = 0.79→1.85 (100H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>– and CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>–), 4.03→4.11 (8H, –CH<sub>2</sub>O–), 6.99→7.99 (22H, vinylenes and phenylene H's). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm = 14.5→32.33 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>– and CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>–), 69.81, 70.40 (–CH<sub>2</sub>O–), 111.42, 117.36, 127.35, 128.27, 129.05, 137.74 (phenylene and vinylenes C's). IR (FTIR): 3030 (w, C<sub>phenyl</sub>–H), 2921 and 2852 (vs, –CH<sub>2</sub>–, CH<sub>3</sub>–), 2202 (w, disubst –C≡C–), 1598 (w, –C=C<sub>phenyl</sub>–), 1205 (s, C<sub>phenyl</sub>–OR), 960 cm<sup>–1</sup> (m, trans –CH=CH–). UV–vis (CHCl<sub>3</sub>, 9 × 10<sup>–6</sup> M):  $\lambda_{\max}$ /nm ( $\epsilon$ /L mol<sup>–1</sup> cm<sup>–1</sup>): 336.8 (43 700), 368 (44 800), 460.8 (56 200). Anal. Calcd for (C<sub>92</sub>H<sub>130</sub>O<sub>4</sub>)<sub>*n*</sub> (1300.04)<sub>*n*</sub>: C, 85.00; H, 10.08. Found: C, 83.61; H, 10.39; Br, 0.15.

**Poly[2,5-diiodoctadecyloxyphenyleneethene-1,2-diyl-2,5-diiodoctyloxyphenyleneethene-1,2-diyl] (5).** 2,5-Diiodoterephthalaldehyde (**18**) (1.00 g, 2.56 mmol) and 2,5-diiodoctadecyloxy-*p*-xylylenebis(diethylphosphonate) (**19**) (2.343 g, 2.56 mmol) were dissolved in dried toluene (50 mL) while stirring vigorously under argon and heating under reflux. Potassium *tert*-butoxide (1.14 g, 10.24 mmol) was added to this solution. After 2 h heating at reflux, the reaction was quenched with aqueous HCl. The organic phase was separated and extracted several times with distilled water until the water phase became neutral (pH = 6–7). The organic layer was dried in a Dean-Stark apparatus. The resulting toluene solution was filtered, evaporated to the minimum (50 mL), and precipitated in methanol (300 mL). The resulting precipitate was extracted for 8 h with methanol and dried under vacuum. 1.7 g (68%) of bright red polymer was obtained. GPC (THF):  $\bar{M}_n$  = 6600 g/mol,  $\bar{M}_w$  = 10 300 g/mol,  $\bar{M}_z$  = 15 300 g/mol,  $\bar{M}_p$  = 7400 g/mol; polydispersity index = 1.55. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm = 0.77→1.78 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>– and CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>–), 3.53 and 3.97 (–CH<sub>2</sub>O–), 6.66→7.41 (phenylene and vinylenes H's). <sup>13</sup>C NMR (62 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm = 14.12, 22.70, 26.33, 29.40, 29.75, 31.93 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>– and CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>–), 69.51 (–CH<sub>2</sub>O–), 110.54, 123.34, 127.47, 151.10 (phenylene and vinylenes C's). IR (FTIR): 3058 (w, C<sub>phenyl</sub>–H), 2920 and 2850 (vs, –CH<sub>2</sub>– and CH<sub>3</sub>–), 1600 (w, –C=C<sub>phenyl</sub>–), 1204 (vs, C<sub>phenyl</sub>–OR), 966 cm<sup>–1</sup>

(s,trans-CH=CH–). UV–vis (CHCl<sub>3</sub>):  $\lambda_{\max}$ /nm ( $\epsilon$ /L mol<sup>–1</sup> cm<sup>–1</sup>) 328 (15 962), 488.4 (43 211). Anal. Calcd for (C<sub>68</sub>H<sub>116</sub>O<sub>4</sub>)<sub>*n*</sub> (997.67)<sub>*n*</sub>: C, 81.87; H, 11.72. Found: C, 81.38; H, 11.51.

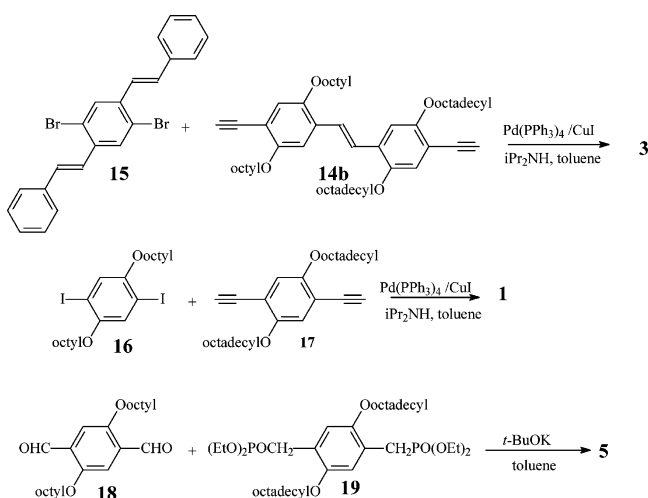
**Poly(2,5-diiodoctadecyloxyphenyleneethynylene-2,5-diiodoctyloxyphenyleneethynylene) (1).** 1,4-Diiodo-2,5-diiodoctyloxybenzene (**16**) (1 g, 1.7 mmol), 1,4-diethynyl-2,5-diiodoctadecyloxybenzene (**17**) (1.127 g, 1.7 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (70 mg, 0.0605 mmol), and CuI (13 mg, 0.0605 mmol) were added to a degassed solution of diisopropylamine (20 mL) and toluene (40 mL). The mixture was heated at 85–90 °C. After a reaction time of 12 h, 0.5 mL of phenylacetylene was added; 14 h later 0.5 mL of bromobenzene was also added. The reaction mixture was heated at 85–90 °C for further 8 h and was allowed to cool to room temperature. The ammonium iodide salt was filtered off and washed with toluene; the combined filtrate was evaporated to ca. 70 mL and precipitated in 300 mL of methanol. The resulting substance was extracted in hot methanol, dissolved in toluene, and reprecipitated in acetone. After drying in a vacuum at 50 °C, 1.5 g (90%) of dark yellow polymer was obtained. GPC (THF):  $\bar{M}_n$  = 28 000 g/mol,  $\bar{M}_w$  = 71 000 g/mol,  $\bar{M}_z$  = 158 000 g/mol,  $\bar{M}_p$  = 41 000 g/mol; polydispersity index = 2.53. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm = 0.80→1.84 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>– and CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>–), 3.62 and 4.01 (–CH<sub>2</sub>O–), 6.99, 7.31, and 7.51 (phenylene H's). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm = 14.40, 21.89, 23.03, 26.43, 27.83, 29.70, 29.81, 30.08, 32.29 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>– and CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>–), 70.29 (–CH<sub>2</sub>O–), 92.00 (–C≡C–), 114.99 (C<sub>phenyl</sub>–C≡), 118.04 (C<sub>phenyl</sub>–H), 154.066 (C<sub>phenyl</sub>–OR). IR (FTIR): 2920 and 2852 (vs, –CH<sub>2</sub>–, CH<sub>3</sub>–), 2205 (w, disubst –C≡C–), 1598 (w, –C=C<sub>phenyl</sub>–), 1211 cm<sup>–1</sup> (s, C<sub>phenyl</sub>–OR). UV–vis (CHCl<sub>3</sub>):  $\lambda_{\max}$ /nm ( $\epsilon$ /L mol<sup>–1</sup> cm<sup>–1</sup>) 313 (13 130), 435.2 (23 230). Anal. Calcd for (C<sub>68</sub>H<sub>112</sub>O<sub>4</sub>)<sub>*n*</sub> (993.64)<sub>*n*</sub>: C, 82.20; H, 11.36. Found: C, 81.53; H, 11.05; I, 1.14.

## Results and Discussion

**Synthesis and Characterization.** Polymers **2** were obtained in an eight step synthetic route starting from hydroquinone (**6**), as illustrated in Scheme 1. The monobromination of **6** in cooled acetic acid gave 2-bromohydroquinone (**7**) in 58% yield. 2-Bromo-1,4-diiodoctadecyloxybenzene (**8**) was obtained in 92% yield after reacting **7** with octadecyl bromide in the presence of KOH in anhydrous dimethyl sulfoxide. The subsequent bromomethylation of **8** using paraformaldehyde and NaBr/H<sub>2</sub>SO<sub>4</sub> in acetic acid led to 1-bromo-4-bromomethyl-2,5-diiodoctadecyloxybenzene (**9**) in 70% yield. The latter was converted to the corresponding phosphonate ester **10** by the Michealis–Arbusov reaction<sup>26</sup> in 75% yield. The



Scheme 2

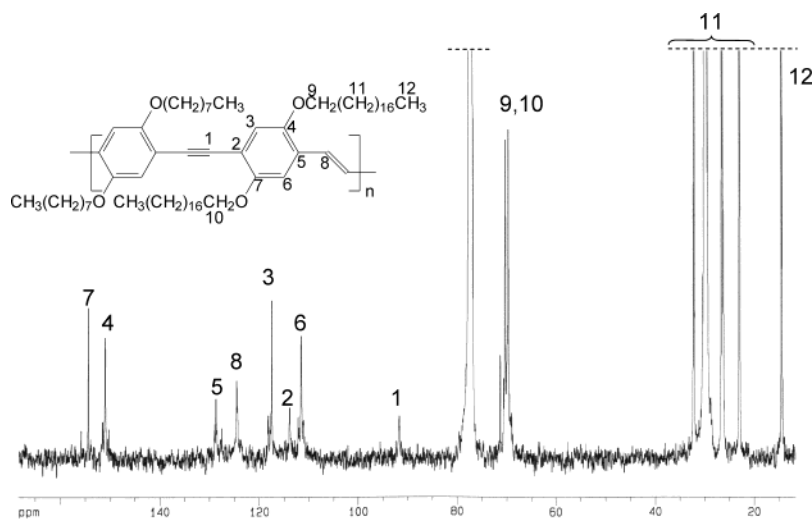


Horner–Wadsworth–Emmons (HWE) olefination reaction of **10** with commercially available 4-bromobenzaldehyde (**11a**) and with 4-bromo-2,5-dioctylbenzene<sup>20</sup> provided both dibromo derivatives **12a** and **12b** in 76 and 75% yield, respectively. The ethynylation of **12** using trimethylsilylacetylene according to Sonogashira reaction conditions<sup>27</sup> provided **13a,b** (80%), whose hydrolysis resulted in the diethynyl derivatives **14a** (43%) and **14b** (79%). The Sonogashira reactions of **12a** with **14a** and of **12b** with **14b** led to polymers **2a** (74%) and **2b** (85%), respectively, after work-up.

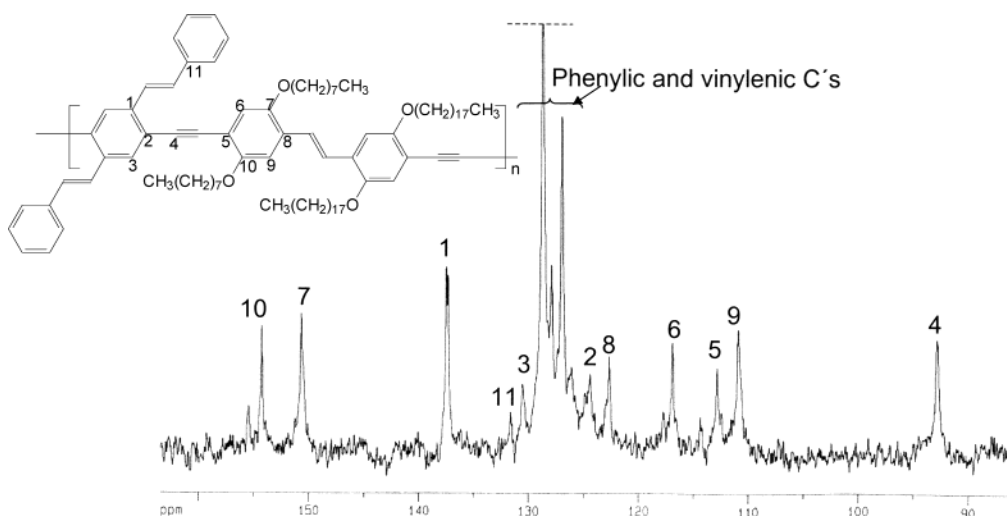
The diethynyl derivative **14b** was further used as a starting material for the synthesis of polymer **3** (Scheme 2). The styryl-substituted hybrid polymer **3** was obtained as a red material in 81% yield after reacting **14b** with *trans,trans*-2,5-distyryl-1,4-dibromobenzene (**15**).<sup>28</sup> Polymers **2** and **3** are nonregioregular as a result of different side chains (octadecyloxy and octyloxy) attached to the backbone. Scheme 2 also depicts the synthesis of PPE **1** and PPV **5** having the same alkoxy side groups as **2b** and **3**. PPE **1** was obtained as an orange material in a yield of 90% after allowing 1,4-diodo-2,5-dioctyloxybenzene (**16**)<sup>29</sup> and 1,4-diethynyl-2,5-dioctadecylbenzene (**17**)<sup>30</sup> to react under the same conditions as for the synthesis of **2** and **3**. End-capping with phenylacetylene and bromobenzene was done in the cases of **1** and **3**. The HWE polycondensation reaction of 2,5-dioctyloxyterephthalaldehyde (**18**)<sup>31</sup> and 2,5-dioctadecyloxy-*p*-xylylenebis(diethylphosphonate) (**19**)<sup>19</sup> provided PPE **5** as a bright red material in 68% yield. The chemical structures of the monomers and of the polymers were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analysis, and infrared spectroscopy. Figures 1 and 2 depict the <sup>13</sup>C NMR (100 MHz) spectra of **2b** and **3**, respectively, in CDCl<sub>3</sub>. The peaks could be readily assigned to the side chains (14–72 ppm) and the backbone carbons (91–155 ppm). The NMR spectra of PPE **1** and PPV **5** are similar to those obtained from the literature.<sup>31,32</sup> The average molecular weights were obtained by GPC with polystyrene as standards. THF was used as the eluting solvent. Number-average molecular weights,  $\bar{M}_n$ , of 28 000 g/mol (PDI = 2.5), 6000 g/mol (PDI = 4.4), 8600 g/mol (PDI = 3.9) 18 000 g/mol (PDI = 4.7), and 6600 g/mol (PDI = 1.5) were measured for **1**, **2a**, **2b**, **3**, and **5**, respectively. End groups bromine content of 2.58% for **2a** and 2.47% for **2b** were obtained from the elemental analysis. Assuming bromine at both ends of the polymers, estimated  $\bar{M}_n$  values of 6200 g/mol

for **2a** and 6500 g/mol for **2b** are obtained.<sup>33</sup> These values approximately correlate with those obtained from GPC. This assumption, however, cannot be made for **1** and **3**, where end-capping was carried out. Residual iodine of 1.14% for **1** and bromine of 0.15% for **3** were measured.  $\bar{M}_n$  values of  $2.2 \times 10^5$  g/mol for **1** and  $1.06 \times 10^6$  g/mol for **3** would be estimated from the halogen contents, which are very far from the reality. The extremely high solubility of compound **3** enabled us to furthermore determine its  $\bar{M}_n$  value through vapor pressure osmometry (VPO). A value of 35 000 g/mol was obtained, which is approximately the same as the GPC peak value,  $\bar{M}_p$  = 37 000 g/mol. All the polymers are thermostable up to 300–320 °C under ambient conditions, where around 5% weight loss was recorded by thermogravimetric analysis. The DSC analysis shows side chains dependent transition phases in the region between 40 and 80 °C for all polymers except **3** (Figure 3),<sup>34,35</sup> but no glass transition temperature,  $T_g$ , was observed after heating to 200 °C.

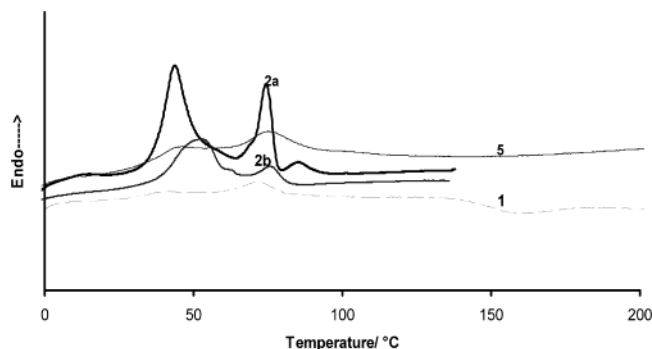
**Photoconductivity Studies.** Photoconductivity measurements were carried out on thin film samples (thickness  $\approx$  100 nm) casted from a chlorobenzene solution on thin glass substrates. Three samples of each compound were measured for the purpose of reproducibility. No sensitizer was required for the detection of photoconductivity in all cases. Data from the photoconductivity measurements are presented in Table 1. Figure 4 illustrates the photoconductivity spectra of polymers **1**, **2b**, **3**, **4**, and **5**. It can be ascertained from the results obtained that three parameters have an influence on the photoconductive behavior of the polymers: (1) size and (2) numbers of the grafted alkoxy side chains and (3) the backbone conjugation pattern. The comparison of compounds **2a** and **2b**, having the same backbone conjugation pattern ( $-\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}-\text{CH}=\text{CH}-$ )<sub>n</sub> but different numbers of side chains per repeating units, clearly shows that photoconductivity is easily detected with **2b** (20 V) possessing a higher number of side groups than with **2a** (400 V) with less side chains. The maximal photocurrents,  $I_{ph}$ , of **2a** and **2b** are  $3.2 \times 10^{-11}$  A (at 20 600 cm<sup>-1</sup>) and  $6.4 \times 10^{-11}$  A (at 19 600 cm<sup>-1</sup>), respectively. The higher number of side chains in **1**, **2b**, **3**, **4**, and **5** and the presence of octadecyloxy groups, in particular, help to reduce the influence of  $\pi-\pi$  intermolecular interaction on the photoconductivity. This explains the low threshold voltages of 20 and 10 V needed for these compounds.<sup>20</sup> However, to understand the differences in the photoconductive behavior of polymers **1**, **2b**, **3**, **4**, and **5**, having different conjugation patterns, one should recall the fact that  $\pi$ -electrons in the surroundings of triple bonds ( $-\text{C}\equiv\text{C}-$ ) find themselves in a deeper *potential well* than, for example,  $\pi$ -electrons of double bonds ( $-\text{CH}=\text{CH}-$ ), so that their migration along the molecule requires the overcoming of a higher energy threshold.<sup>36</sup> The phenylene ethynylene “homopolymer” **1** has the lowest  $I_{ph}$  of  $3.8 \times 10^{-12}$  A (at 20 000 cm<sup>-1</sup>), which is at least 1 order of magnitude less than that of its hybrid counterpart **2b**. The hybrid conjugation pattern in **4** ( $-\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}-\text{CH}=\text{CH}-\text{Ph}-\text{CH}=\text{CH}-$ )<sub>n</sub>, which can be considered as a quasi-phenylene–ethynylene/phenylene–vinylene “block copolymer”, is more favorable for photoconductivity than that in **2b** and **3**. This is evident through the lower threshold voltage of 10 V for the detection of its photoconductivity. The fact that its maximal photocurrent,  $I_{ph} = 1.1 \times 10^{-9}$  A (at 20 000



**Figure 1.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of polymer **2b**.



**Figure 2.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of polymer **3**.



**Figure 3.** DSC heating curves of polymers **1**, **2a**, **2b**, and **5**.

$\text{cm}^{-1}$ ), is 4 times higher than that of the phenylene–vinylene “homopolymer” **5**,  $I_{\text{ph}} = 3.0 \times 10^{-10}$  A (at 20 000  $\text{cm}^{-1}$ ), obtained at the same voltage, shows the influence of additional effects.

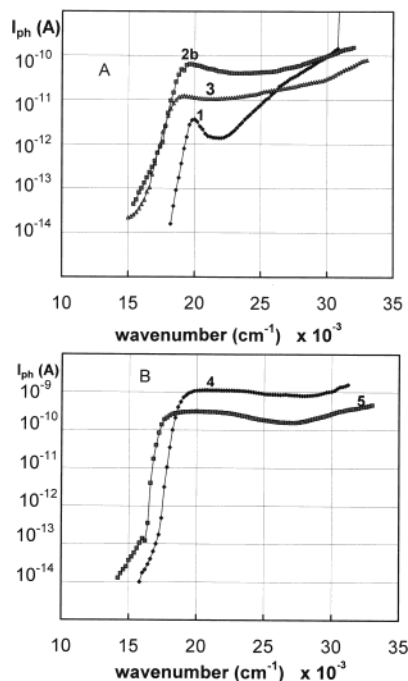
**Absorption and Photoluminescence Studies.** The absorption and photoluminescence characteristics of the polymers have been investigated in dilute chloroform solution as well as in thin films. The positions of the absorption maxima,  $\lambda_a$ , the extinction coefficients at the maximum wavelength,  $\epsilon_{\text{max}}$ , the full width at half-maximum of the absorption spectra,  $\text{fwhm}_a$ , and the

**Table 1.** Data from Photoconductivity Studies (Surface Cell, Slit Width, 0.2 mm; Irradiation, 20  $\mu\text{W}/\text{cm}^2$ )

code	voltage [V]	$I_{\text{ph}}$ [A] <sup>a</sup>	$\nu_{\text{max}}$ [ $\text{cm}^{-1}$ ] <sup>b</sup>
<b>1</b>	20	$3.8 \times 10^{-12}$	20 000
<b>2a</b>	400	$3.2 \times 10^{-11}$	20 600
<b>2b</b>	20	$6.4 \times 10^{-11}$	19 600
<b>3</b>	20	$1.2 \times 10^{-11}$	19 200
<b>4</b>	10	$1.1 \times 10^{-9}$	20 000
<b>5</b>	10	$3.0 \times 10^{-10}$	20 000

<sup>a</sup> Maximal photocurrent. <sup>b</sup> Wavenumber of irradiating light at  $I_{\text{ph}}$ .

optical energy gaps,  $E_g^{\text{opt}}$ , are presented in Table 2. The  $E_g^{\text{opt}}$  values are calculated from  $\lambda_T$ , the intersection of the tangent through the turning point of the lower energy band edge of the spectrum and the lengthened baseline.<sup>37</sup> Data from the photoluminescence studies are summarized in Table 3, namely the emission maxima,  $\lambda_e$ , the Stokes shifts, the  $\text{fwhm}_e$ , and the fluorescence quantum yields,  $\phi_{\text{fl}}$ . The maxima of the excitation spectra are mostly identical with those of the absorption maxima. In solution the absorption spectra are characterized by an unstructured broad ( $\text{fwhm}_a$ : 4000–6000  $\text{cm}^{-1}$ ) long wavelength absorption band indicating different geometries of the absorbing chromophore units. The absorption maxima are determined by the conjuga-



**Figure 4.** Photoconductivity spectra of **1**, **2b**, **3**, **4**, and **5** (surface type cell, slit width 0.2 mm, irradiation 20  $\mu\text{W}/\text{cm}^2$ , threshold voltage 20 V (A) and 10 V (B)).

**Table 2.** UV-Vis Data in Dilute  $\text{CHCl}_3$  Solution and in Solid State (Thin Films of 100–150 nm Thickness Spin-Casted from Chlorobenzene Solution)

code	$\lambda_a$ [nm]	$\epsilon_{\text{max}}$ [ $\text{M}^{-1} \text{cm}^{-1}$ ] <sup>b</sup>	fwhm <sub>a</sub> [ $\text{cm}^{-1}$ ]	$\lambda_T$ [nm]	$E_g^{\text{opt}}$ [eV] <sup>c</sup>
<b>1</b>	435	23 230	5680	486	2.55
<b>1<sup>a</sup></b>	462 (sh: 500)		4530	514	2.41
<b>2a</b>	432	29 370	5490	487	2.54
<b>2a<sup>a</sup></b>	448		5460	510	2.43
<b>2b</b>	454	29 600	5330	516	2.40
<b>2b<sup>a</sup></b>	472		5740	550	2.25
<b>3</b>	461	56 200		516	2.40
<b>3<sup>a</sup></b>	487, 510			565	2.19
<b>4</b>	472	86 300	4770	520	2.38
<b>4<sup>a</sup></b>	496		4280	560	2.21
<b>5</b>	488	43 200	4730	554	2.23
<b>5<sup>a</sup></b>	487		5760	590	2.10

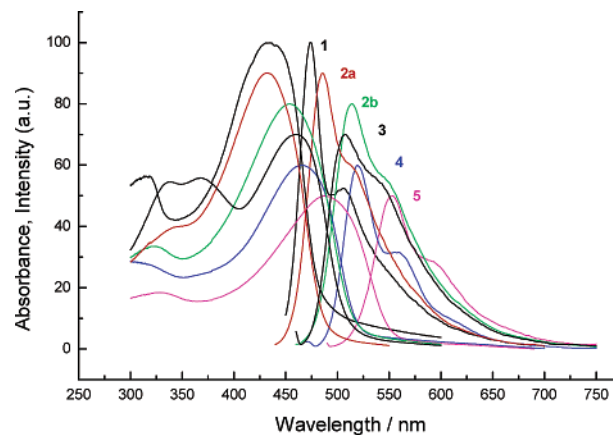
<sup>a</sup> Solid state. <sup>b</sup> Per mole of the constitutional unit. <sup>c</sup>  $E_g^{\text{opt}} = hc/\lambda_T$ .

**Table 3.** Photoluminescence Data in Dilute Chloroform Solution ( $\sim 10^{-8}$  M) and in Solid State<sup>a</sup>

code	$\lambda_e$ [nm]	Stokes shift [ $\text{cm}^{-1}$ ]	fwhm <sub>e</sub> [ $\text{cm}^{-1}$ ]	$\phi_f$ [%]
<b>1</b>	474, 506	1890	2070	(52) 43
<b>1<sup>a</sup></b>	552	3530	2910	21
<b>2a</b>	486	2570	2600	54
<b>2a<sup>a</sup></b>	547	4040	3080	19
<b>2b</b>	513	2530	2700	47
<b>2b<sup>a</sup></b>	578	3890	3000	16
<b>3</b>	507	1970	2820	76
<b>3<sup>a</sup></b>	596	3760	2830	14
<b>4</b>	519 (sh: 560)	1920	2180	77
<b>4<sup>a</sup></b>	552, 592	2050	2080	54
<b>5</b>	551 (sh: 591)	2340	2230	42
<b>5<sup>a</sup></b>	582, 628	3350	1250	27

<sup>a</sup> Solid state.

tion length which increases as well with the number of double bonds as with the number of alkoxy side groups per repeating unit from the pure PPE (**1**) to the pure PPV (**5**) as depicted in Figure 5.



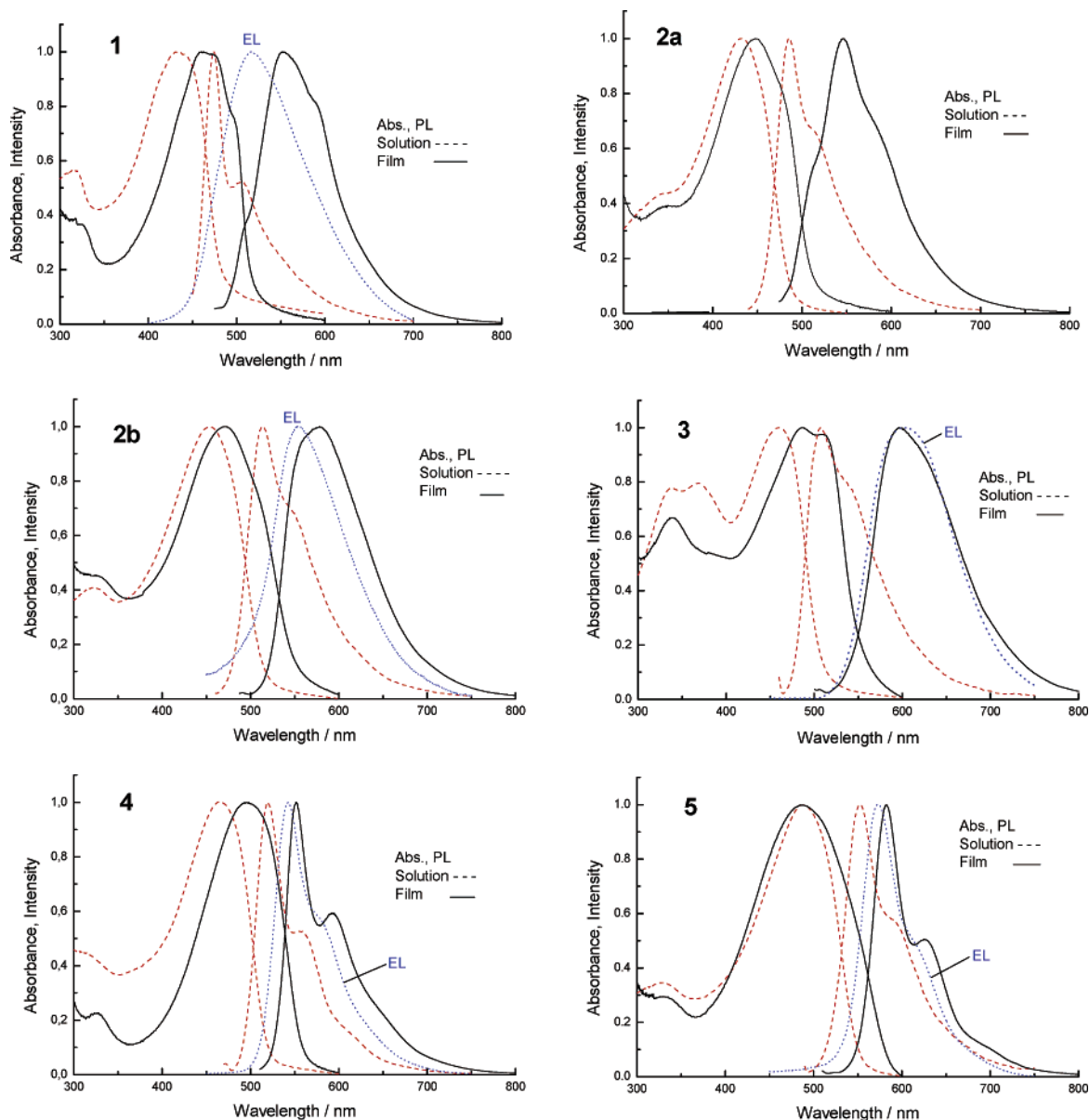
**Figure 5.** Normalized absorption and fluorescence spectra of the polymers in dilute chloroform solution. Normalization: **1** to 100, **2a** to 90, **2b** to 80, **3** to 70, **4** to 60, and **5** to 50.

The fluorescence spectra are moderately red-shifted with a Stokes shift of 2000–2500  $\text{cm}^{-1}$ . The better resolvable vibrational structure and the smaller bandwidths (fwhm<sub>e</sub>: 2000–3000  $\text{cm}^{-1}$ ) in comparison with the absorption spectra are caused by the reduced flexibility of the emitting chromophore due to stronger conjugation in the excited  $S_1$  state.

There is a bathochromic shift of the absorption and emission spectra from the solution to the solid state, as shown in Figure 6, which can be attributed to an enhanced planarization of the conjugated backbone forced by the formation of aggregates in the solid film. A vibrational structure of the absorption spectra is indicated with **1** and **3** in the solid film. An asymmetric broadening in the low-energy band edge with the other compounds (except **4**) can be interpreted as vestiges of a vibrational structure.

The fwhm values of the absorption spectra are nearly the same in the solution and the solid state. This is also valid for the fluorescence spectra. An increase of the Stokes shifts between 1000 and 2000  $\text{cm}^{-1}$  from solution to the solid state is observed. The fluorescent band shapes vary in a less uniform manner. Compounds **4** and **5** show the closest similarity between film and solution. The vibrational structure is better resolvable in the solid film. Particularly with **3** and **2b** in the film, an additional unstructured largely Stokes-shifted emission occurs, which can be interpreted as an excimer-like fluorescence.<sup>38</sup> Compounds **2a** and **1** represent intermediate cases. The interpretation of the long-wavelength emission as an excimer luminescence is based on the systematic dependence of its intensity on the size and number of the chain substituents. Thus, for instance, the formation of excimers is reduced to some extent through the grafting of long octadecyloxy side groups, which may also explain the relatively high fluorescence quantum yields in the films. The higher number of alkoxy side chains in **2b** give rise to a red shift of its absorption [ $\Delta\lambda_a = 22$  nm (solution) and 24 nm (film)] and emission maxima [ $\Delta\lambda_e = 27$  nm (solution) and 31 nm (film)] relative to those of **2a**. The differences of their other absorption and emission characteristics are minimal, however. Two-dimensional and extended  $\pi$ -conjugation is obtained in **3** comparatively to **2b** through the attachment of styryl units as side groups. The observed absorption maxima in solution ( $\lambda_a = 461$  nm) and in the film ( $\lambda_a = 487$  and 510 nm), as we assume, are emanating from a largely nonplanar con-





**Figure 6.** Normalized absorption and photoluminescence spectra in dilute chloroform solution and in film and normalized electroluminescence spectra.

jugated system in the ground state. The large Stokes shift of 109 nm ( $3750\text{ cm}^{-1}$ ) in the film leading to an emission maximum,  $\lambda_e = 596\text{ nm}$ , gives evidence of large contribution of an excimer emission. This is furthermore confirmed by the large fwhm value of 106 nm ( $2820\text{ cm}^{-1}$ ) and the relatively low fluorescence quantum yield of 14%. Similar explanations can be applied to **2b** and to a lesser extent to **2a**. Taking the conjugation pattern into consideration, there is a gradual bathochromic shift of the absorption from phenylene-ethynylene polymer **1** [ $E_g^{\text{opt}} = 2.55\text{ eV}$  (solution) and  $2.41\text{ eV}$  (film)] through the hybrid compounds **2b** [ $E_g^{\text{opt}} = 2.40\text{ eV}$  (solution) and  $2.25\text{ eV}$  (film)] and **4** [ $E_g^{\text{opt}} = 2.38\text{ eV}$  (solution) and  $2.21\text{ eV}$  (film)] to the phenylene-vinylene polymer **5** [ $E_g^{\text{opt}} = 2.23\text{ eV}$  (solution) and  $2.10\text{ eV}$  (film)]. This is also valid with the emission in solution but not in the solid state, where other factors play an important role. Compound **4** exhibits a higher  $\epsilon_{\text{max}}$  and a higher fluorescence quantum yield in solution as well as in the film than **2b**, which are related to its sharp and well-structured emission curves in solution as well as in the solid state. This situation is similar to that of polymer **5**.

**Electroluminescence Studies.** Polymer LEDs were made by using **1**, **2b**, **3**, **4**, and **5** as an emissive layer and PEDOT as a hole transporting layer. The devices emit green, green-yellow, yellow-orange, green-yellow, and yellow-orange light with EL peak wavelengths at 516, 554, 602, 543, and 574 nm, respectively (Figure 6). The maxima of the electroluminescence spectra are located between the emission maxima in solution and those in solid film, except in the case of **3**, where a clear overlap of the electroluminescence and the solid-state fluorescence is observed. This might be ascribed to the different preparation methods for the solid film (e.g., for PL, from chlorobenzene solution; for EL, from chloroform solution), which might lead to different film morphologies, as demonstrated, for instance, by Heeger et al.<sup>39</sup> Data from the electroluminescence investigations are summarized in Table 4. Comparing polymer **1** with polymer **5**, one observes a  $\sim 60\text{ nm}$  red shift, when triple bonds are substituted by double bonds. When one of the two triple bonds in the green-emitting polymer **1** was replaced with one double bond, the band gap decreased; a green-yellow polymer **2b** was obtained with the

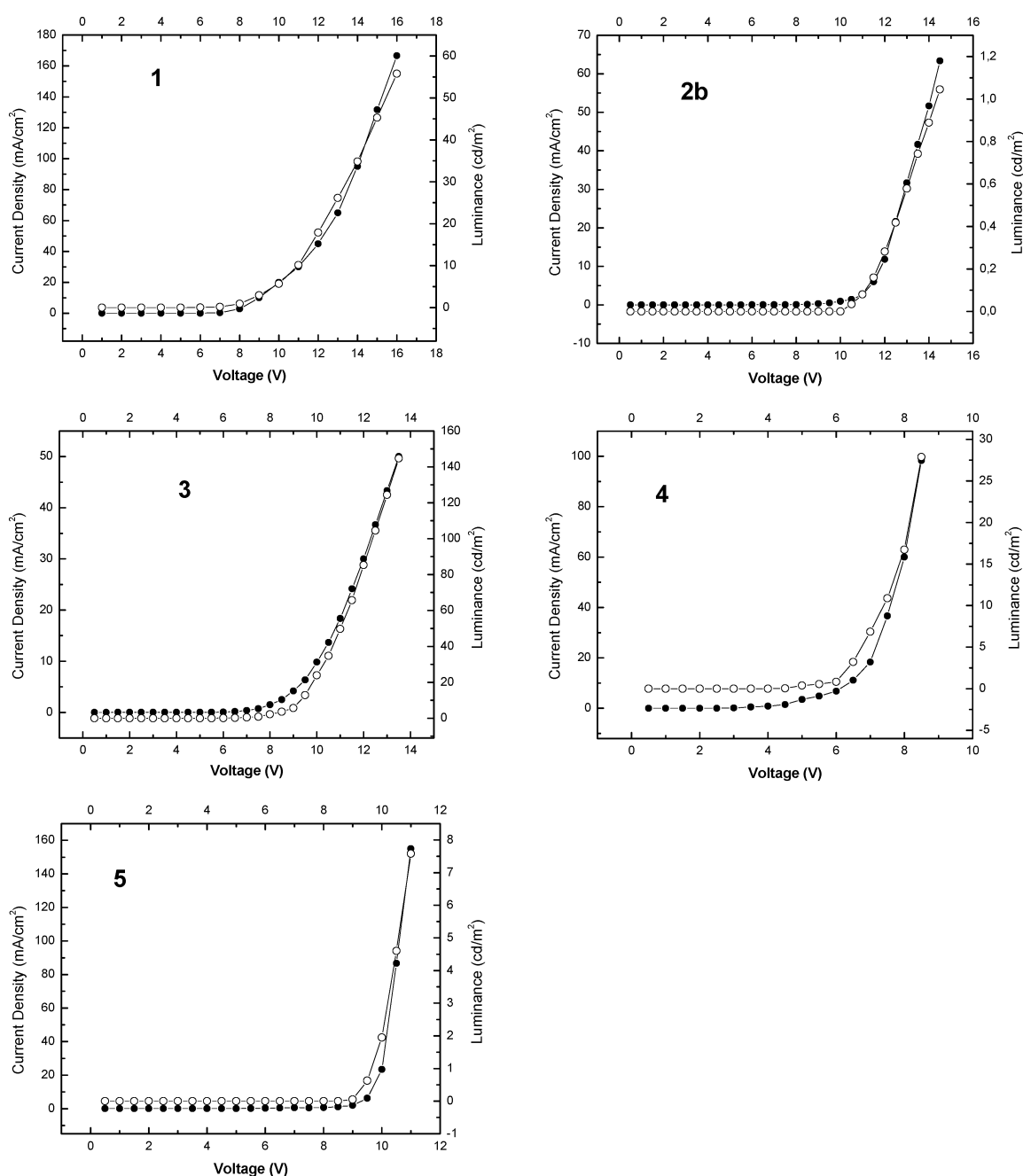
**Table 4. Data from Electroluminescence Investigation (Film Casted from CHCl<sub>3</sub> Solution)<sup>a</sup>**

code	$\lambda_{el}$ [nm]	fwhm <sub>el</sub> [cm <sup>-1</sup> ]	$\eta$ [%]	luminance [cd/m <sup>2</sup> ]
<b>1</b>	516	4060	$4.6 \times 10^{-2}$	55.7
<b>2b</b>	554	3023	$1.4 \times 10^{-3}$	1.0
<b>3</b>	602	2928	0.15	144.7
<b>4</b>	543, 581 (sh)	2069	$1.7 \times 10^{-2}$	27.9
<b>5</b>	574, 619 (sh)	1803	$4.9 \times 10^{-3}$	7.6

<sup>a</sup>The following setup was used: ITO/PEDOT/polymer/Ca.

emission energy between that of **1** and **5**. When using the repetition units (ru) of polymer **1** and polymer **5** to form a conjugated -ru1-ru5-ru1-ru5- alternating copolymer, we get polymer **4**, which has an almost average emission energy. The emission peak of **4** stands in the middle of **1** and **5**, suggesting that if there is intramolecular energy transfer from the triple bond units to double bond units, the transfer would be incomplete. Or

we may tentatively conclude that most of the triple bond units and double bond units act as independent chromophores in the LED and contribute simultaneously to the total emission. The use of styryl side groups in **3** leads to a yellow-orange emission. The phenylvinylene units in polymer **3** could facilitate the intramolecular energy transfer significantly and also intermolecular energy transfer. From polymer **2b** to **3**, there is 48 nm red shift in EL, demonstrating a successful chemical color-tuning method for LED. The turn-on voltages of the five devices were 7, 10, 7, 6, and 9 V (Figure 7). These data are related to the band gap of the polymers, the work function of electrode, and the thickness of device. The external quantum efficiency,  $\eta$ , of the devices reaches  $4.6 \times 10^{-2}\%$ ,  $1.4 \times 10^{-3}\%$ , 0.15%,  $1.7 \times 10^{-2}\%$ , and  $4.9 \times 10^{-3}\%$ . Comparing polymer **3** with **2b**, the styryl units do not only red shift the EL spectrum and decrease the device turn-on voltage but also im-



**Figure 7.** Current density (●)–voltage–luminance (○) relationship for devices ITO/PEDOT/polymer/Ca.

prove the LED efficiency more than 100 times. The higher efficiency may be due to excellent intramolecular energy transfer and lower electron/hole injection barrier.

## Conclusions

Hybrid phenylene–vinylene/phenylene–ethynylene polymers **2a**, **2b**, **3**, and **4** have been synthesized and characterized. A comparison of their photophysical properties taking into account the phenylene–ethynylene “homopolymer” **1** and the phenylene–vinylene “homopolymer” **5** has been carried out. It can be ascertained from the obtained results that three parameters have an influence on the photophysical properties of the polymers: (1) size and (2) numbers of the grafted alkoxy side chains and (3) the backbone conjugation pattern. The conjugation pattern in **4** is more favorable to photoconductivity than that in **2b**. The long octadecyloxy side groups not only contribute to the red shift of the absorption and emission spectra of the above-mentioned compounds with respect to their alkyl-substituted congeners, but they do also limit to a greater extent the intermolecular  $\pi$ – $\pi$  stacking, thus enabling an easy detection of photoconductivity and higher fluorescence quantum yields in solid films. The maxima of the electroluminescence spectra lie between those of the emission spectra in solution and the emission spectra in solid state, except in the case of polymer **3** where a clear overlap of the solid film photoluminescence and electroluminescence can be observed. The styryl side groups in **3** not only contribute to the red shift of the electroluminescence but also bring about a decrease of the turn-on voltage (relative to **2b**) and an enhancement of the EL efficiency to more than 100 times.

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