Synthesis and Photophysical and Electroluminescent Properties of Poly(1,4-phenylene–ethynylene)-alt-poly(1,4-phenylene–vinylene)s with Various Dissymmetric Substitution of Alkoxy Side Chains

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Supporting Information

ABSTRACT: The synthesis and characterization of a set of conjugated polymers, poly(1,4-phenylene–ethynylene)-alt-poly(1,4-phenylene–vinylene)s (PPE–PPVs), with a dissymmetrical configuration (partial or total) of alkoxy side chains is reported. Five new polymers bearing octyloxy and/or octadecyloxy side chains at the phenylene–ethynylene and phenylene–vinylene segments, respectively, were obtained. Two symmetrical substituted polymers were used for comparison. Polymers with weight-average molecular weight, $M_w$, up to 430 000 g/mol and degree of polymerization between 17 and 322 were obtained by a Horner-Wadsworth-Emmons olefination polycondensation reaction of the respective luminophoric dialdehydes and bisphosphonates. As expected, identical conjugated backbones in all polymers result in very similar photophysical response in dilute solution, with high fluorescence quantum yields between 50% and 80%. In contrast, the thin film properties are dependent on the combinatorial effects of side chain configuration, molecular weight, and film thickness parameters, which are the basis of the resulting comparison and discussion.

INTRODUCTION

In recent years, intense research efforts have been dedicated to the synthesis and the study of soluble semiconducting π-conjugated polymers.1−5 Because of their tunable photophysical and electronic properties6−10 in combination with good processability, flexibility11,12 and stability,12,13 they hold high promise for advanced electronics and photonics.14 A broad variety of applications have been proposed, including nonlinear optics,15−16 optical information storage, organic light-emitting-diodes (OLEDs),16−21 and electrochromic devices.22,23 Particular attention is also given to organic field-effect transistors (OFETs)24,25 and organic photovoltaics (OPVs).26−27 Poly(1,4-phenylene–ethynylene)-alt-poly(1,4-phenylene–vinylene)s (PPE–PPVs) are an interesting class of materials.28,29 They combine the intrinsic properties of poly(p-phenylene–ethylene) (PPE) and poly(p-phenylene–vinylene) (PPV) in a single polymeric backbone with additional structure-specific features.30−33 The number, position, and nature (linear, branched, chain length, etc.) of the grafted alkyl and/or alkoxy side chains can significantly influence the properties of the polymers.33 Thus, the side chains not only facilitate the solubility,33 but can also remarkably affect optical, electronic and charge carrier transport, in particular in the solid state.34,35

Over the years an extensive number of PPE–PPVs functionalized symmetrically with alkoxy side chains at the phenylene–ethynylene (PE) and the phenylene–vinylene (PV) segments have been described. These polymers can be labeled with $P_{n'/n}$, where $n$ and $n'$ represent the number of carbons in the alkoxy side chains attached to the PE ($R_1 = R_2$) and PV ($R_3 = R_4$) segments, respectively. Distinctive effects on the photophysical properties have been observed, in particular in solid state, namely the color appearance of the polymers, the absorption and emission characteristics, as well as the quantum yields of optical transitions.36−37 For instance, while the vast majority of the $P_{n'/n}$ polymers (e.g., $P_{18/18'}$, $n' = 4−7$, 9, 10, 12, 14, 16, 18; $P_{17/7}$, $P_{19/9}$; $P_{n/8}$, $n = 12−15$) exhibit a yellow color in the solid state, specific side chain combinations...
Scheme 1. Synthesis of Bisphosphonate (3ab) and Luminophoric Dialdehydes (7ab and 8ab)

Scheme 2. Synthesis of PPE−PPVs (P) using the Horner−Wadsworth−Emmons Polycondensation Reaction of Bisphosphonates (3) and Dialdehydes (7)
(P16/6, P16/8, P17/8, P18/8, and P19/8) cause the precipitated polymers to take on an orange appearance.\(^3\)\(^{112}\)\(^{37}\)

To further explore the impact of variations in the side chain configuration, we report on PPE−PPVs with disymmetric substituted PE (\(R_1 \neq R_2\)) and/or PV building blocks (\(R_1 \neq R_3\)).

In this paper, we describe the synthesis and detailed characterization of five new conjugated polymers with different combinations of octadecyloxy (OC\(_{18}\)H\(_{37}\)) and octyloxy (OC\(_8\)H\(_7\)) substituents, including syntheses of two new polycondensation monomers 3ab and 7ab (Scheme 1 and 2).

The electrochemical, photophysical and electroluminescent properties of these new materials are investigated and compared to newly synthesized batches of known reference polymers with symmetrical substitution—P18/8 (\(R_1 = R_2 =\) octadecl; \(R_3 = R_4 =\) octyl) and P8/18 (\(R_1 = R_2 =\) octyl; \(R_3 = R_4 =\) octadecl; Scheme 2).

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The synthesis of the polymers P via the Horner–Wadsworth–Emmons (HWE) olefination reactions requires the preparation of the respective bisphosphonates 3 and luminophoric dichaldehydes 7. The polycondensation monomers 3 and 7 were synthesized in multistep reaction sequences starting either from hydroquinone, for symmetric substituted compounds 3aa, 3bb, 7aa, and 7bb (aa, \(R_1 = R_2 =\) octyl; bb, \(R_1 = R_2 =\) octadecl) as described elsewhere,\(^{10}\) or from 4-octyloxyphenol, for the new disymmetric substituted compounds as depicted in Scheme 1.

The synthesis of the bisphosphonate 3ab involved a sequence of Williamson etherification, bromomethylation and Michaelis–Arbuzov reaction. Dialdehyde 7ab was also synthesized in several steps in analogy to the literature for the symmetric substituted compounds.\(^{38}\) The diiodination of 1-octadecyloxy-4-octyloxybenzene 1ab was followed by a Pdcatalyzed Sonogashira cross-coupling reaction with trimethylsilylelacetylene, the deprotection of the acetylene units, and finally another Sonogashira reaction leading to the desired product 7ab, which was obtained as bright yellow substance alongside a small amount of dicyne dialdehyde 8ab. For the purification of the materials, column chromatography and/or recrystallization were performed. The desired polymers P were obtained by reacting 2,5-dialkoxy-p-xylene-bis(diethylphosphonates) (3) and 1,4-bis(4-formylphenylethynyl)-2,5-dialkoxybenzenes (7) in various combinations (Scheme 2).

Olefination reactions via HWE are commonly characterized by high reaction rate, high yields, high selectivity (high preference of trans (E) double bonds), and very low structural defects.\(^5\) In contrast to cross-coupling reactions such as Heck, Sonogashira, Suzuki and Stille, a metal catalyst, which might be problematic during purification, is not required. All polycondensation reactions except one were performed within a 1 h reaction time. The synthesis of the polymer with the fully disymmetric side chain distribution (P18−8/18−8) was repeated with an extended reaction time (by 25 min) in order to obtain a high molecular mass batch of this material (P18−8/18−8a).

The structure and purity of the synthesized materials were verified by NMR spectroscopy (\(^1\)H and \(^13\)C NMR). The spectra of the synthesized intermediates and polycondensation monomers are characterized by well resolved and defined signals. Despite the combination of substituents with different alkyl chain lengths in the new compounds, the recorded peak patterns show a high resemblance to the spectra of the uniformly substituted materials. Figure 1 displays the \(^1\)H NMR spectrum of the new dialdehyde 7ab and of the polymer it was used to synthesize, P18−8/18−8.

The methyl and the methylene proton signals of the alkyl chains appear in the high-field region between 0.86 and 1.89 ppm. The signals of the methylene protons at the carbon adjacent to oxygen are found at approximately 4 ppm. Further downfield, between 7 and 7.8 ppm, the aromatic proton signals arise. In the spectrum of the polymer, characteristic signals of the polycondensation monomers (dialdehyde, ~10 ppm (−CHO); bisphosphonate, ~3.3 ppm (−H\(_2\)CP)) are absent. In addition, the loss of signal resolution and the strong broadening of the signals are clear indications of the formation of polymer material. The spectrum suggests an all trans (E) configuration of the polymer. Peaks indicating the presence of vinylenic double bonds with a cis (Z) configuration are not observed.\(^{38}\) For the comprehensive investigation of the five new polymers, infrared (IR) and Raman spectroscopic measurements were performed. Figure 2(top) depicts the IR spectra of all polymers bearing disymmetric side chains. The spectra show a very weak band in the range of 3070 to 3000 cm\(^{-1}\) that is assigned to arylene and vinylenic vibrations (vω, ω, vω).
-C≡C-H and vinylene -C≡C-H), and very strong -C-H vibration peaks between 2950 and 2800 cm⁻¹ (vs, -C-H). The weak ethynyl band appears at approximately 2205 cm⁻¹ (w, -C≡C-). Two weak peaks located at 1689 and 1599 cm⁻¹ originate from vinylenic vibration (w, vinylenic-C=C-), and the peaks in the range between 1530 and 1360 cm⁻¹ are attributed to aromatic elements (vs, aromatic-C=C-). Signals at 1213 cm⁻¹ (strong) and 1043 cm⁻¹ (medium) are attributed to the alkoxy functionalities (s, m C≡C-OR). The band at 965 cm⁻¹ is assigned to the vinylenic double bonds with trans (E) configuration. Signals indicating the presence of cis (Z) configuration were not identified.  

In the Raman spectra (Figure 2, bottom) a very weak signal in the range of 2950 to 2830 cm⁻¹ is observed and assigned to C-H vibrations of the aliphatic chains (vw, -C-H). The strong peak at 2205 cm⁻¹ originates from ethynyl units (s, -C≡C-), while the signals at 1626 cm⁻¹ and in the range from 1600 to 1530 cm⁻¹ are assigned to vinylenic (m, vinylenic-C=C-) and aromatic features (vs, aromatic-C=C-), respectively. The alkoxy functionalities appear in the peaks at 1240 and 1091 cm⁻¹ (w, C≡C-OR). A strong peak at 1178 cm⁻¹ is attributed to the alky chains (s, -C-C-).

The weight-average molecular weight (Mₜₗ), polydispersity index (PDI) and degree of polymerization (Pₙ) of the new polymers were determined by size exclusion chromatography (SEC) measurements. The SEC results are summarized in Table 1, and the SEC curves of the polymers under study are shown in Supporting Information (Figure S3). The synthesized polymers exhibit Mₜₗ values between 20 100 and 89 700 g/mol with Pₙ between 17 and 85, and polydispersity indexes between 2.1 and 4.9, except P18/8–18–8a which has the highest weight M_w = 431 000 g/mol with PDI of 4.1 and a corresponding Pₙ of 322.

**Photophysical Properties.** The photophysical properties of the new polymers bearing disymmetric alkoxy side chains together with two polymers P18/8 and P8/18 bearing symmetric alkoxy side chains were studied in solutions and thin films. Absorption and photoluminescence (PL) emission spectra measured in tetrahydrofuran (THF) solution are displayed in Figure 3, and their characteristic data summarized in Table 2.

Absorption spectra exhibited a broad absorption band with maxima in the range 440–455 nm corresponding to the absorption of the π-π* transition of the conjugated backbone. The maximum positions correlate well with the M_w of the polymers (see Tables 1 and 2), except for the blue-shifted maximum of the P18–8/8–18–8 absorption compared with P18/8 with a lower M_w. One can assume the influence of the dissymmetrical alkyl chains on the backbone conjugation. P18–8/8–18–8a with the highest M_w exhibits an approximately 15 nm red-shift of the absorption maximum compared to P18–8/18–8–8 of the same chemical structure but has a lower M_w. When comparing the absorption spectra of the polymers P18/8–18, P8/18–8 and P18–8/18–8 with similar M_w, a blue shift of P18–8/18–8 compared to the other ones is observed, which indicates that the dissymmetry of the side chains slightly influences the backbone conjugation as already mentioned above. PL emission spectra in THF solution are of similar shapes, with maxima located at 488–490 nm and a shoulder at approximately 520 nm reflecting the vibronic structure. The PL emission maxima differ only slightly between polymers in a similar manner to the absorption maxima. There are similarities between PL excitation and absorption spectra. PL quantum yields, η_PL of the new polymers are in the range 0.50–0.80. There is no straightforward dependence of the absorption and PL in dilute solution on the combination of side chains.

To discuss the results in detail one should take into account differences in M_w of the polymers under study and discuss the possible influence of the various side chain combinations of polymers with similar M_w. Comparison of the polymers necessitates a division into groups with similar M_w. The photophysical properties of the polymers under study are shown in Figure 3, and their characteristic data summarized in Table 2.

Fig. 3. UV–vis absorption and PL emission spectra of the polymers under study measured in dilute THF solution.

Table 2. Photophysical Properties of the Polymers Measured in Dilute THF Solutions (λ_abmax Absorption Maximum, λ_plmax Emission Maximum, λ_plmax Maximum of Excitation Spectra, and η_pl Photoluminescence Quantum Yield)

<table>
<thead>
<tr>
<th>polymer</th>
<th>λ_abmax (nm)</th>
<th>λ_plmax (nm)</th>
<th>λ_plmax (nm)</th>
<th>η_pl (%)</th>
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<tr>
<td>P18/8</td>
<td>443</td>
<td>487, 520</td>
<td>444</td>
<td>0.70</td>
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<tr>
<td>P8/18</td>
<td>447</td>
<td>489, 521</td>
<td>448.5</td>
<td>0.64</td>
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<tr>
<td>P18/18–8</td>
<td>445</td>
<td>488, 517</td>
<td>443.5</td>
<td>0.66</td>
</tr>
<tr>
<td>P8/18–8</td>
<td>444</td>
<td>487, 521</td>
<td>443.5</td>
<td>0.71</td>
</tr>
<tr>
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<td>489, 520</td>
<td>443.5</td>
<td>0.63</td>
</tr>
<tr>
<td>P8–8/8</td>
<td>451</td>
<td>490, 520</td>
<td>446</td>
<td>0.74</td>
</tr>
<tr>
<td>P18–8/18–8</td>
<td>440</td>
<td>488, 516</td>
<td>444</td>
<td>0.53</td>
</tr>
<tr>
<td>P18–8/8–18–8a</td>
<td>455</td>
<td>490, 522</td>
<td>451</td>
<td>0.64</td>
</tr>
</tbody>
</table>

*aExcitation wavelength at λ_abmax *bEmission wavelength at λ_plmax
compared. In both cases the P18–8/8 and P8/18–8 polymers with shorter alkyls on vinlyene and ethynylene segments, respectively, exhibit a slightly higher $\eta_{PL}$ values than those of polymers P18–8/18 and P18/18–8 with longer alkyls. The absorption and PL results for P18/8 solution correlate well with the results obtained by previous studies of chloroform solutions of P18/8 with a higher $M_w$ ($M_w = 115$ 600 g/mol, PDI = 3.77, $P_n \sim 26$)\textsuperscript{45} and of P18/8 with a similar $M_w$.\textsuperscript{35}

Absorption and photoluminescence spectra measured in thin films are displayed in Figure 4 and 5, respectively, and characteristic data summarized in Table 3. The thin film absorption is red-shifted compared with the polymer absorption in solution, which indicates influence of intermolecular interactions in solid state. Contrary to the photophysical properties of the solution, a clear influence of the side chain combination on photophysical behavior is observed in solid state.

Figure 4a shows the absorption spectra of thin films of all polymers under study, and Figure 4b demonstrates the influence of film thickness on the absorption for selected polymers. The main absorption maxima in thin films are located in the range 453–455 nm for thicker films and slightly red-shifted for thinner films. A second maximum or shoulder at approximately 480–484 nm is well resolved in the absorption spectra of all polymers except P18/8. This fact demonstrates the influence of various combinations of side chains on the intermolecular interactions of conjugated segments. The contribution of the absorption of the first and second peak for the same polymer depends on the film thickness. In the measured range of the thicknesses, the absorbance of the second peak increases with decreasing film thickness for all polymers under study except P18/8, for which the absorption spectrum lacks a second peak as already mentioned above. Absorption coefficient values are higher for the thinner films. An example is shown in Figure 4b and its inset for P18–8/18–8 and P18–8/18–8a. It should be noted that the value of absorption coefficient evaluated from transmission measurements could be also influenced by reflection losses. This effect is particularly noticeable in the spectral region corresponding to the long wavelength tail.\textsuperscript{39} The changes observed in the absorption spectra for different film thicknesses cannot be fully accounted for by reflection losses therefore morphology differences between films are taken into account and discussed. One can assume that the spin-coating process induces an orientation of main chains in-plane more pronounced in thinner films which could explain the higher absorption. An influence of alkyl chain length on the absorption is also detected. The absorption coefficients of thin films made of P18/8–8 or P18–8/8 with longer symmetrical alkyl chains are lower than those of thin films made of P8/18–8 or P18–8/8 with shorter symmetrical alkyl chains. It correlates well with the higher volume of the alkyl chains in P18/18–8 or P18–8/18 than in P8/18–8 or P18–8/8.

The PL emission spectra of thin films shown in Figure 5 differ in the shape and exhibit red-shifts compared with the PL emission in solutions, for which similar PL emission spectrum shapes were observed for all polymers. PL excitation spectra of thin films follow roughly the absorption ones, but possess a better resolution of the vibration structure. The most pronounced PL emission maximum red-shift was observed in the P18/8 PL spectrum, which exhibits a broad, featureless emission band and a very large Stokes shift (152 nm), characteristics of excimers or aggregates in the solid state.\textsuperscript{40} The PL emission maxima of the other polymers are blue-shifted compared to those in the P18/8 PL spectrum. Relative PL efficiency of thin films, $\phi_{PL,rel}$, is introduced for a PL efficiency comparison of the polymers under study relatively to each other. New polymers possessing dissymmetric side chains, and also P8/18 with symmetrical side chains with the longer ones on PV building blocks, exhibit higher $\phi_{PL,rel}$ in thin films than that of P18/8 thin films. Further, we compare the data from several points of view with respect to various side chain combinations, taking into account polymer $M_w$ variation.
In both cases, the data comparison reveals the same for the ethynylene segment.

The shapes of the PL spectra are symmetric alkyls on ethynylene or vinylene segments are polymers of P18 in alkyl chains. Comparison of these polymers demonstrates an emission maximum of P18/18 and P8/18 polymers differ as shown in Figure 6a. PL emission maxima of P8/18 with the longer side chains located on PV units and of P18–8/18–8 with dissymmetric side chains on the both units. The shape of both the absorption and emission spectra of the P18/8, P8/18 and P18–8/18–8 polymers differ as shown in Figure 6a. PL emission maxima of P8/18 with the longer side chains located on PV units and of P18–8/18–8 with dissymmetric side chains are blue-shifted compared with that of P18/8. The thin film made of P18–8/18–8a with higher M\textsubscript{w} exhibited a slightly higher PL\textsubscript{rel} and red-shifted PL maximum compared P18–8/18–8 thin film (see Figure 6b). PL emission spectra of P18–8/18–8, P8/18–8, P8/18–8/8, P8–8/8 with longer or shorter symmetric alkyls on ethynylene or vinylene segments are shown in Figure 6c and d. The shapes of the PL spectra are similar for thin films of P18–8/18–8 and P8–8/8 (same molar mass of repeat unit), but differ from those of thin films made of P8/18–8 and P18–8/8 with the same molar mass of the repeat unit but lower than that of the P18–8/8 and P8/18–8.

More clearly resolved vibration structure was observed in PL spectra of P18–8/8 or P18–8/8 with 3 longer (C\textsubscript{18}) alkyl chains. Comparison of these polymers demonstrates an influence of the alkyl chain length on their photophysical properties in thin films. Similarly, as in solution, the comparison of P18–8/18 and P18–8/8 PL\textsubscript{rel} values reveals a slight influence of the length of the symmetrical side chains on the vinylene segment, and similarly the P18/18–8 and P18–8/8 data comparison reveals the same for the ethynylene segment. In both cases, the P18–8/8 and P18–8/8 polymers with shorter (C\textsubscript{6}) alkyls on vinylene and ethynylene segments, respectively, exhibit a slightly higher PL\textsubscript{rel} than those for polymers P18–8/8/8 and P18–8/8 with longer alkyls. The introduction of dissymmetric side chains leads to the changes in both absorption and PL spectra of the polymers, reflecting differences in backbone interactions between main chain segments.

### Electrochemical Properties.

Cyclic voltammetry (CV) measurements were performed to obtain information on the electronic structure of the new polymers. An example of a representative CV curve of P18–8/18–8 thin films coated on a Pt wire is displayed in Figure 7.

Quasi-reversibility in both oxidation and reduction were observed for all new polymers. The ionization potential (HOMO level), E\textsubscript{IP} and electron affinity (LUMO level), E\textsubscript{A} were estimated from the onset potentials, E\textsubscript{onset} of the oxidation and reduction peaks on the basis of the reference energy level of ferrocene (4.8 eV below the vacuum level) using the equation E\textsubscript{IP} = 1–(E\textsubscript{onset} – E\textsubscript{fer} – 4.8 eV), where E\textsubscript{fer} is the value for ferrocene vs the Ag/Ag\textsuperscript{+} electrode. The E\textsubscript{IP} and E\textsubscript{A} values were evaluated as averages from CV curves measured at a scan rate of 50 mV s\textsuperscript{−1} and are given in Table 4.

Similar values of the ionization potential, in the range 5.23–5.27 eV, and electron affinity, in the range 2.75–2.79 eV, were measured for all polymers. The electrochemical bandgap values, E\textsubscript{elect} = 2.47–2.5 eV, were evaluated. These results are in good agreement with the optical band gap values of 2.39–2.46 eV determined from thin film absorption spectra.

### Electroluminescence.

The new polymers were used to create an active layer in samples of light-emitting devices (LEDs). LEDs with a hole-injecting electrode formed by ITO covered with a PEDOT:PSS layer and an electron-injecting electrode of calcium covered with aluminum (Ca/Al) were prepared and studied. The electroluminescent (EL) spectra of the LEDs are shown in Figure 8. The EL maxima are summarized together with the PL maxima in Table 5.

The electroluminescence of P18/8 and P8/18 bearing symmetric alkyl side chains has already been studied with different luminance efficiencies (0.11\textsuperscript{11} or 0.22\textsuperscript{11} to 1.79\textsuperscript{1}). Our LEDs made of P18/8 exhibited luminance efficiency values, \(\eta_{\text{EL}}\), in the range of 0.22–0.46 as measured on several LED samples even with the similar active layer thickness. The lower value is consistent with the luminance efficiency of 0.22 reported for LEDs made with similar device configuration using the polymer with similar molar weight.\textsuperscript{31} The \(\eta_{\text{EL}}\) values for LEDs made of P8/18 approach the published data of luminance efficiency of 0.12.\textsuperscript{31}
weights. The devices made using copolymers exhibited higher $\eta$ changes in $\eta$ is evident from a comparison of the length of the symmetrical side chains on the vinylene segment comparable to those for LEDs made of $P_{18}\text{-}copolymers$.

Figure 6. UV–vis absorption (dashed), PL excitation and emission spectra of the polymers under study measured in thin films: (a) $P_{18}/8$, $P_{8}/18$, $P_{18}/8/18$–8 (polymers with the same molar mass of repeat unit), (b) $P_{18}/8/8/8/18$–8, $P_{18}/8/18$–8a (same polymer with different $M_w$), and (c, d) $P_{18}/8/8$, $P_{8}/18/8$, $P_{18}/8/8/8/18$, $P_{18}/8/8$–8 comparison of symmetrical alkyl chains increasing or decreasing repeat unit), (b) $P_{18}/8/8/8/18$–8, $P_{8}/18/8$, $P_{18}/8/8/8/18$, $P_{18}/8/8$–8 with two di-

LEDs made using the new polymers $P_{8}/18/8–8$, $P_{18}/8/8/8/18$, $P_{18}/8/8/8/18$, and $P_{18}/8/8/8/18$–8a exhibited $\eta_{EL}$ values comparable to those for LEDs made of $P_{18}/8$, whereas the $\eta_{EL}$ values of $P_{8}/18$, $P_{18}/8/8$, and $P_{18}/8/8/8/18$–8 with two different molar weights shows that the changes in $\eta_{EL}$ with $M_w$ are not significant. An influence of the length of the symmetrical side chains on the vinylene segment is evident from a comparison of the $\eta_{EL}$ values of the copolymers $P_{18}/8/8/8/18$–8 and $P_{18}/8/8/8/18$ with very similar molar weights. The devices made using copolymer $P_{18}/8/8/8/18$ exhibited higher $\eta_{EL}$ values than those made using $P_{18}/8/8/8/18$ with the shorter side chains on the vinylene segment. $\eta_{EL}$ values of $P_{8}/18/8/8/18$ LEDs are higher than those of $P_{18}/8/8/8/18$ LEDs, which correlates with the measured $\phi_{P_{LED}}$ values of corresponding thin films.

The maximum luminance values of approximately 900 cd m$^{-2}$ were observed from the best devices made with $P_{18}/8/8/8/18$. An example of the luminance dependency on the applied voltage is displayed in Figure 9. The higher onset voltages of more than 5 V are caused by an interface barrier, probably higher for electrons, and also can be influenced by a higher active layer thickness. Maxima of the EL spectra are red-shifted compared with those of PL thin film spectra, which indicates that charge trapping takes place in the EL process. On the basis of our various comparison, one can conclude that introducing dissymmetric side chains in both segments influence the EL efficiency, but not in a way that correlates straightforwardly with the PL results. Further optimization of LEDs is needed. The performance can be improved using an active blend layer, such as those reported in our previous papers.42–45

**CONCLUSION**

Five new poly(p-phenylene–ethylenylene)-alt-poly(p-phenylene–vinylene)s with a disymmetrical configuration (partial or total) of octyloxy and/or octadecyloxy chains at the phenylene–ethylenylene and/or phenylene–vinylene segments, respectively, and two corresponding polymers with symmetrical configuration were synthesized using polycondensation reactions of the respective dialdehydes and bisphosphonates. The polymers have average molecular weights $M_w$ up to 430 000 g/mol. For all polymers, similar values of the ionization potential (5.23–5.27 eV) and electron affinity (2.75–2.79 eV) were obtained by means of cyclic voltammetry. The values of electrochemical bandgap are similar (2.47–2.5 eV) and in good agreement with the optical bandgap values (2.39–2.46 eV) determined from thin film absorption spectra. Differences in absorption and photoluminescence were found both in solution and in thin films. The influence of various combinations of side chains on absorption and PL emission is more pronounced in
thin films compared to solutions. The PL thin film emission spectra of all new polymers are blue-shifted compared to that of P18/8 with symmetrical side chains. In thin films, new polymers possessing dissymmetric side chains and P8/18 with symmetrical side chains with the longer ones on phenylene segment exhibit higher PL efficiency values by a factor of 2−5. Polymer LEDs were prepared and characterized using the new polymers. The introduction of dissymmetric side chains in both segments influences the EL efficiency as shown by various comparisons, but a comparison with the PL results is not straightforward. Charge trapping takes place in the EL process as indicated by the red-shift of EL compared to thin film PL.

### EXPERIMENTAL SECTION

1. Materials and Methods. The starting materials were purchased from commercial suppliers such as Sigma-Aldrich and were used without further purification unless specified. Solvents and reaction mixtures were deaerated by bubbling with nitrogen for 1 h prior to use. The polymers with symmetric side chain configuration (P8/18, P18/8) were synthesized as described in the literature. 1H NMR and 13C NMR spectra were measured in CDCl3 with a Gemini 300 MHz spectrometer at 298 K using trimethylsilane as an internal standard. IR experiments were performed on a Bruker Fourier transform infrared (FTIR) spectrophotometer IFS 66/S with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector in the attenuated total reflection (ATR) mode. All polymers were dissolved in chlorobenzene (VWR chemicals) and then spin-coated onto the ZnSe crystal, which is used as a reflection element for the ATR-FTIR measurements. The crystal was precleaned with diamond paste and then rinsed with acetone in a reflux system before further treatments. For the Raman measurements, all the

<table>
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<tr>
<th>polymer</th>
<th>d (nm)</th>
<th>λ_{ELmax} (nm)</th>
<th>η_{EL} (%) at 15 V (Cd/A)</th>
<th>η_{ELmax} (Cd/A)</th>
<th>λ_{PLmax} (nm)</th>
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<tr>
<td>P18/8</td>
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<td>0.22−0.46</td>
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<td>606</td>
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<td>P18/18−8</td>
<td>115</td>
<td>556</td>
<td>0.10</td>
<td>0.11</td>
<td>545</td>
</tr>
<tr>
<td>P8/18−8</td>
<td>117</td>
<td>509, 543, 579</td>
<td>0.29−0.32</td>
<td>0.36</td>
<td>544</td>
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<tr>
<td>P18−8/18</td>
<td>98</td>
<td>543</td>
<td>0.18−0.24</td>
<td>0.24</td>
<td>512, 543</td>
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<tr>
<td>P18−8/8</td>
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<td>512, 550, 586</td>
<td>0.08</td>
<td>0.12</td>
<td>544</td>
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<tr>
<td>P8−8/18−8</td>
<td>124</td>
<td>581</td>
<td>0.14−0.28</td>
<td>0.40</td>
<td>546</td>
</tr>
<tr>
<td>P18−8/18−8a</td>
<td>131</td>
<td>578, 610</td>
<td>0.21−0.31</td>
<td>0.33</td>
<td>555</td>
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</table>

*Excitation wavelength at λ_{absmax}
polymers were measured in powder form on a FT-Raman Bruker MultiRam spectrometer with a liquid nitrogen cooled Ge detector and a Nd:YAG laser at 1064 nm. Size exclusion chromatography (SEC) measurements were performed using a Pump Deltachrom (Watrex Comp.) with a Midsas autosampler and two columns of MIXED-B LS PL gel, particle size 10 µm. An evaporative light scattering detector (PL-ELS-1000 from Polymer Laboratories) was used; THF was the mobile phase. Polystyrene standards were used for calibration. Mass spectra (MALDI-TOF MS) were acquired with an UltraflaxeXtonic (Bruker Daltonics, Bremen, Germany) in the positive ion reflector mode. The spectra were the sum of 1000 shots with a DPSS, Nd: YAG laser (355 nm, 1000 Hz). Delayed extraction and external calibration was used.

1. Sample Preparation. Thin films were prepared by spin-coating from 1,2-dichlorobenzene solutions. Thin films were spin-coated onto fused silica substrates for optical studies or coated on a Pt wire electrode by dipping for electrochemical measurements. For polymer light-emitting devices (LED), polymer layers were prepared on indium—tin oxide (ITO) substrates covered with a thin layer of poly[3,4-(ethylenedioxy)thiophene]/poly(styrenesulfonate) (PEDOT:PSS). All polymer films were dried in a vacuum (10⁻³ Pa) at 373 K for 2 h. The ITO glass substrates were purchased from Merck (Germany) and PEDOT:PSS (CLEVIOS P VP Al 4083) from Heraeus Clevios GmbH (Germany). The 50 nm thick PEDOT:PSS layers were prepared by spin-coating and dried in air at 396 K for 15 min. The calcium (20 nm) and, subsequently, 60–80 nm thick aluminum electrodes were vacuum-evaporated on top of the polymer films to form LEDs. Typical active areas of the LEDs were 4–8 mm², precise values used for EL efficiency evaluation were determined by optical microscopy. Layer thicknesses were measured using a KLA-Tencor P-10 profilometer.

1.2. Cyclovoltammetric Measurements. Cyclic voltammetry (CV) was performed with a PA4 polarographic analyzer (Laboratory Instruments, Prague, CZ) with a three-electrode cell. Platinum (Pt) wire electrodes were used as both working and counter electrodes. A nonaqueous Ag/Ag⁺ electrode (Ag in 0.1 M AgNO₃ solution) was used as the reference electrode. CV measurements were made in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in anhydrous acetonitrile under nitrogen atmosphere. Typical scan rates were 20, 50, and 100 mV s⁻¹.

1.3. Photophysical Measurements. UV–vis spectra were measured on a PerkinElmer Lambda 35 UV/vis spectrometer. Solvents of spectroscopic grade were used. The absorption spectra of thin films were measured in the glovebox using fiber optics connected to the spectrophotometer. Steady-state PL spectra were recorded using a PerkinElmer LSS5 Fluorescence spectrophotometer. The PL quantum yield of the polymer in solution was calculated relative to the quinine sulfate in 0.1 M H₂SO₄, which was used as a standard (PL quantum yield 0.577).³⁶

1.4. Electroluminescence Measurements. EL spectra were recorded using an Acton Research Spectrograph with single photon-counting detection (SPEX, RCA C31034 photomultiplier). LEDs were supplied from a Keithley 237 source measure unit, which served to simultaneously record the current flowing through the sample. Current–voltage and luminance–voltage characteristics were recorded simultaneously using the Keithley 237 source measure unit and a Minolta LS110 Luminance Meter or a silicon photodiode with integrated amplifier (EG&G HUV-4000B) for the detection of total light output. A voltage signal from the photodiode was recorded with a Hewlett-Packard 34401A multimeter. All thin film preparations and the device fabrication were carried out in a glovebox under a nitrogen atmosphere.

2. Polymer Synthesis. The synthesis of the monomers, the bisphosphonate 3ab and the dialedhyde 7ab, and the polymers was performed in analogy to literature³⁷ and is well described in Supporting Information. All polymers were prepared under similar conditions (monomer concentration, stirring rate, reaction temperature and time). The synthesis of P18–8/18–8 was repeated, extending the reaction time by 25 min, in order to obtain a batch (P18–8/18–8a) with high molecular mass, the synthesis of which is described below as an example. The details of other polymer syntheses are described in Supporting Information.

2.1. Poly[1,4-phenyleneethynylene-1,4-(2-octadecyloxy-5-octyloxy)phenoxy]-1,4-phenylethane-1,2-diy] (P18–8/18–8a) The dialedhyde 7ab (450 mg, 0.62 mmol) and the bisphosphonate 3ab (477 mg, 0.62 mmol) were dissolved in dry toluene (25 mL) while stirring vigorously under argon and heating under reflux (110 °C) and reacted upon the addition of an excess of potassium tert-butoxide (425 mg, 3.78 mmol) for 1 h and 25 min. Benzaldehyde (5 mL) and, 10 min later, toluene (30 mL) and aqueous HCl (10 wt %, 10 mL) were added to quench the reaction. 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. After filtration the toluene solution was concentrated under vacuum and precipitated in methanol. The polymer was extracted for 24 h with methanol (Solvlett), dissolved once more in toluene, and precipitated again in methanol. Filtration and drying yielded a bright yellow fibrous polymer (630 mg, 86%).

SEC (THF): Mₚ = 431 000 g/mol, PDI = 4.1.³⁷

¹H NMR (300 MHz, CDCl₃, 298 K), δ/ppm: 0.87 (broad s, 12H, 4 × CH₃), 1.23–1.89 (m, 88H, 44 × CH₂), 4.07 (broad s, 8H, 4 × O–CH₂), 7.03–7.54 (m, 16H, 12 × aromatic H and 4 × vinylene H).

¹³C NMR (75 MHz, CDCl₃, 298 K), δ/ppm: 14.1 (CH₃), 22.73, 26.13, 26.32, 29.36, 29.41, 29.45, 29.50, 29.71, 29.76, 31.87, 31.97 (all H), 110.63, 114.04, 116.88, 124.38 (all H–Caryl), 126.41 (C=C), 126.91 (C=C), 128.40 (Caryl–Caryl), 131.91 (Caryl–C–C), 136.79 (Caryl–C–C), 147.17 (Caryl–O), 153.66 (Caryl–O).

IR: 3070–3000 cm⁻¹ (vw, C=C), 2930–2800 cm⁻¹ (vs, C=C), 2205 cm⁻¹ (w, vinylene –C≡C–), 1689 and 1599 cm⁻¹ (w, vinylene –C≡C–), 1530–1360 cm⁻¹ (w, aromatic C=C=C), 1213 and 1043 cm⁻¹ (s, m, Caryl–OR), 965 cm⁻¹ (m, trans=C=C=).³⁷

Raman: 2950–2830 cm⁻¹ (vw, C=C), 2205 cm⁻¹ (s, C=C), 1626 cm⁻¹ (m, vinylene –C=C–), 1600–1530 cm⁻¹ (vs, aromatic –C≡C–), 1240 and 1091 cm⁻¹ (w, Caryl–OR), 1178 cm⁻¹ (s, –C=C–).

UV–vis (CHCl₃): λₘₐₓ/nm = 442.

Anal. Calcd for [C₉₆H₆₂O₃]ₙ (%): C, 84.22; H, 10.43. Found: C, 84.29; H, 10.60.
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REFERENCES


