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Efficient Solid-State Photoluminescence in New Poly(2,5-dialkoxy-*p*-phenyleneethynylene)s

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ABSTRACT: A series of novel poly(2,5-dialkoxy-*p*-phenyleneethynylene)s (PPEs) has been prepared by the palladium-catalyzed cross-coupling polycondensaton of aryl acetylenes and aryl iodides. Different alkoxy side chains including *n*-hexadecyloxy, *n*-octyloxy, (2-ethylhexyl)oxy, (2-methylpropyl)oxy, (3-(dimethylamino)propyl)oxy, and (7-carboxyheptyl)oxy groups were attached to the rigid-rod polymer main chain. With this structural concept, polymers having an identical conjugated backbone but different supramolecular structures in the solid state could be achieved. X-ray diffraction measurements on thin films show that the polymers which have sterically hindered side chains are essentially disordered, while those with only linear side chains can form lamellar structures with significant degrees of long-range order. High photoluminescence (PL) quantum yields, up to 0.86 in solution and 0.36 in the solid state, have been measured for the new materials. While the solution quantum yields are independent of the functionalization, solid-state quantum efficiencies were found to be related to the degree of long-range order in the samples, decreasing with increasing order. The coplanar orientation of the conjugated polymer backbones is assumed to lead to the formation of excimer complexes which provide nonemissive decay channels for the excited states. These nonemissive orientations are more significant in the materials having a greater degree of long-range order.

I. Introduction

In recent years there has been a considerable interest in the photoluminescent and electroluminescent (EL) properties of conjugated polymers.[1] Since these materials combine the processability and outstanding mechanical properties of polymers with exceptional electronic and photophysical properties of organic semiconductors, they are attractive candidates for active layers in EL devices.[2,3] The EL properties of a number of different conjugated polymers have been investigated, including poly(*p*-phenylenevinylene) and its ring-substituted derivatives,[2−9] poly(alkylthiophene)s,[10,11] poly(phenylene)s,[12,13] and others.[14] Current research interests on EL polymers include tailoring of the spectral characteristics and the improvement of their processability and long-term stability, but one of the most challenging problems is to optimize the radiative recombination efficiency and the carrier transport characteristics of the EL material in order to achieve high quantum yields in photoluminescence and high-efficiency EL devices.

Recently, the photophysical properties of different poly(2,5-dialkoxy-*p*-phenyleneethynylene)s have been studied in this laboratory[15,16] and elsewhere.[17−20] PL quantum yields of up to 0.40 measured on solutions of PPEs derivatized with linear alkyloxy side groups[15] and the reported emission from EL devices based on poly(2,5-bis(hexyloxy)-*p*-phenyleneethynylene) and poly(2,5-bis(butyloxy)-*p*-phenyleneethynylene)[17] make these materials another class of prospective materials for EL applications.

While unsubstituted poly(*p*-phenyleneethynylene) is completely insoluble,[21] the materials investigated in the studies cited above were made soluble by attaching linear alkoxy side chains to the rigid-rod polymer backbone and by controlling their molecular weight.[22] Many reports on rigid-rod polymers show that a derivatization with long alkyl side chains not only enhances the solubility but also can lead to highly ordered supramolecular architectures in the solid state.[23−25] In these supramolecular structures, the polymers were found to form highly ordered layers, where the stiff polymer main chains are oriented coplanar, and the linear alkyl side chains, sometimes interdigitated or tilted, extend laterally within the planes of their respective main chains. Only recently, similar structures have been found for PPEs derivatized with *n*-hexadecyloxy and *n*-octyloxy groups in this laboratory.[16]

Based on these findings, we surmise that the solid-state structure of derivatized PPEs can be controlled by the choice of the side chains, and polymers having an identical conjugated backbone but different supramolecular structures can be obtained. Because many electronic properties of conjugated polymers depend on the degree of order,[26] this structural concept can be an important tool to tailor the electronic properties of rigid-rod conjugated polymers. In this paper, we report the preparation of a series of new poly(2,5-dialkoxy-*p*-phenyleneethynylene)s bearing different side chains and the investigation of their solid-state structures. Focusing on their photoluminescence properties, we discuss the electronic properties of these new polymers and relate them to their supramolecular structures.

II. Results and Discussion

Synthesis and Characterization of Polymers. A series of six new poly(2,5-dialkoxy-*p*-phenyleneethynylene)s was prepared by the palladium-catalyzed cross-coupling condensation, known as the Heck reaction,[27] of an aryl acetylene and different aryl iodides as shown in Scheme 1 and Table 1.

The aryl acetylene used in this work was 1,4-diethynyl-2,5-bis(octyloxy)benzene (**II**). For the derivatization of the aryl iodides (**I**) (see Experimental Section for details), three different classes of substituents were chosen, which are linear alkoxy groups (*n*-hexadecyloxy, *n*-octyloxy; abbreviated HDO, O), sterically hindered

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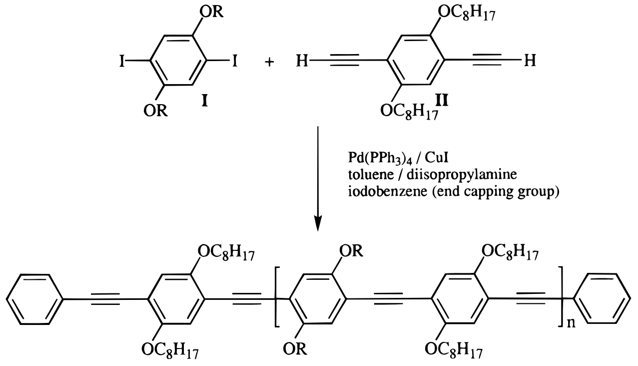
Scheme 1. Synthesis and Molecular Structures of the Poly(2,5-dialkoxy-*p*-phenyleneethylene)s Investigated in This Work[a]



[a] **HDO-OPPE**, **R** = *n*-hexadecyl; **O-OPPE**, **R** = *n*-octyl; **EHO-OPPE**, **R** = 2-ethylhexyl; **MPO-OPPE**, **R** = 2-methylpropyl; **DPO-OPPE**, **R** = 3-(dimethylamino)propyl; **CHO-OPPE**, **R** = 7-carboxyheptyl.

Table 1. General Properties of the Poly(2,5-dialkoxy-*p*-phenyleneethynylene)s

polymer	R	M_r[a]	$\bar{x}_n$[b]
HDO-OPPE	*n*-hexadecyl	937.54	24
O-OPPE	*n*-octyl	713.11	23
EHO-OPPE	2-ethylhexyl	713.11	28
MPO-OPPE	2-methylpropyl	600.89	22
DPO-OPPE	3-(dimethylamino)propyl	658.97	28
CHO-OPPE	7-carboxyheptyl	743.09	na

[a] Molecular weight of the polymer's repeat unit. [b] Number-average degree of polymerization determined by ^{1}H-NMR spectroscopy.

alkoxy groups ((2-ethylhexyl)oxy, (2-methylpropyl)oxy; EHO, MPO), and ionizable alkoxy groups ((3-(dimethylamino)propyl)oxy, (7-carboxyheptyl)oxy; DPO, CHO). In order to obtain completely soluble materials, the number-average degree of polymerization $\bar{x}_n$ was carefully controlled by the ratio of the two bifunctional monomers.[28] Because energy transfer processes from the polymer main chain to the end groups were found to have an important impact on the PL properties of some of the PPEs reported before,[15] it might be important to terminate the polymer chains with well-defined, highly emissive end groups. The polymers prepared in this work were therefore endcapped with phenyl groups, which also enable a straightforward determination of $\bar{x}_n$ by ^{1}H NMR spectroscopy.

According to Yamamoto et al.,[29] the polycondensations were performed using $Pd(PPh_3)_4$/CuI as catalysts in a mixture of toluene and diisopropylamine. The reaction time was typically 22 h at a temperature of 70 °C. The polymers remained soluble during the reaction (except **CHO-OPPE**) and were isolated by precipitation into acetone or ethanol and purified by extensive washing. The chemical structures of the polymers were confirmed by ^{1}H NMR spectroscopy and elemental analysis. The slightly higher than theoretically expected number-average degrees of polymerization may mainly result from the loss of low molecular weight material during the workup, which is evident from the color of the filtrates.

All polymers (except **CHO-OPPE**) could be redissolved and were completely soluble in concentrations of 4% (w/v) or more in $CHCl_3$ and 1% (w/v) or more in toluene or CH_2Cl_2. Pyridine was found to be the best solvent for **CHO-OPPE**, which precipitated during the polycondensation. However, this polymer lacks high solubility, probably due to the too different nature of the substituents requiring polar solvents on the one hand (carboxy group) and apolar solvents on the other hand (alkyl chains). The insufficient solubility prevented the ^{1}H NMR spectroscopic characterization of this polymer. The elemental analysis shows a significant content of N and a slight offset in C and H and hence points to the presence of ammonium salts instead of the free carboxylic acid side chains. The soluble PPEs could be processed into thin, uniform films of high optical quality by spin-coating from $CHCl_3$ or toluene.

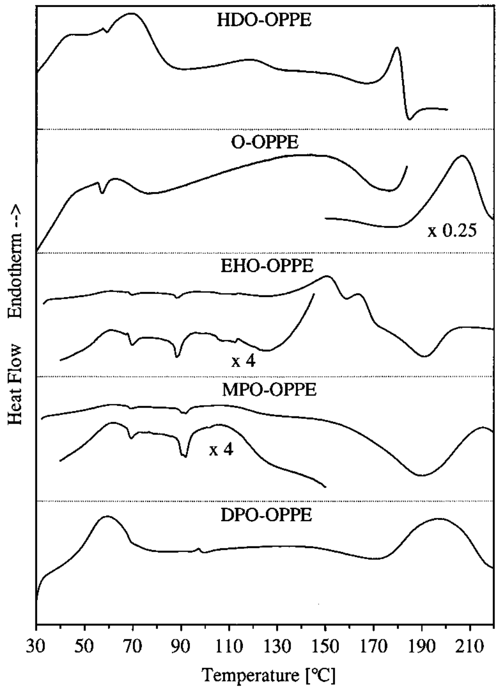


Figure 1. DSC heating scans of the PPEs obtained under N_2 at a heating rate of 20 °C/min.

Thermal Properties. The thermal properties of the polymers have been investigated using differential scanning calorimetry (DSC) and polarized microscopy. Figure 1 shows the thermograms for the processable PPEs prepared in this work. The trace of **HDO-OPPE** is similar to the one of a higher molecular weight analogue reported previously.[16] It shows a number of solid-state transitions with maxima around 70, 125 (both endothermic), and 58 °C (exothermic). The strong endotherm observed at 179 °C corresponds to the formation of the isotropic melt as can be seen by polarized microscopy. The solid-state transitions were found reversible only when the sample was kept under its melting point, indicating a subsequent decomposition of the polymer upon melting. This finding is in agreement with the previously reported decomposition temperatures of substituted PPEs.[19,22] The DSC of **O-OPPE** shows similar features, with transitions at 58 (exothermic), 64, 150 (broad), and 207 °C (all endothermic). For **EHO-OPPE**, distinctive exothermic solid-state transitions were observed at 70 and 88 °C (maybe also 107 °C), and they might overlay a broad endotherm. An endothermic transition at 150 °C corresponds to the formation of the isotropic melt. A broad exothermic peak with a maximum at 191 °C could be attributed to the decomposition of the polymer. The DSC of **MPO-OPPE** is similar to that of **EHO-OPPE** with exothermic solid-state transitions at 69 and 90 °C. However, this polymer did not melt, and consequently, only a broad decomposition exotherm was observed at 192 °C. The trace of **DPO-OPPE** shows endotherm solid-state transitions at 60, 98, and 143 (broad) °C. Another endothermic transition at 197 °C corresponds to the melting of the polymer. However, the material was found to change its color and to turn dark at temperatures above 130 °C, indicating the decomposition of the polymer.

Polarized microscopy showed that pristine spin-cast films of all polymers are isotropic. Upon heating, no formation of a thermotropic phase could be observed for any of the polymers. This finding is attributed to the low degree of polymerization and the resulting small axial ratio of the polymers described here and is in agreement with the lack of the formation of a mesophase in other PPEs with comparable substituents and degrees of polymerization.[22]

Solid-State Structure. The supramolecular structure of the polymers discussed here was investigated on thin spin-cast films, identical to those used for the characterization of their photophysical properties. Experiments were made on both, pristine and annealed samples, assuming that tempering above the solid-state transition temperatures would help to equilibrate the supramolecular structure. Samples referred to as *annealed* were tempered under a N_2 atmosphere for 30–120 min at 125 °C. To ensure the chemical integrity of the polymers, annealed films were redissolved in $CHCl_3$ and their UV spectra were taken. The UV spectra perfectly matched the ones of the pristine polymers. However, a small fraction of each annealed film remained insoluble, indicating that a small degree of cross-linking might take place during the thermal treatment.

The wide-angle X-ray diffraction (WAXD) patterns of the new PPEs are shown in Figure 2a–e. The width of the peaks and the lack of higher order reflections at low angles indicate that the pristine films adopt only a small extent of long-range order and the broad, halo typical reflections from the wide-angle region point to a low degree of crystallinity. In the case of the polymers bearing only linear side chains (**HDO-OPPE** and **O-OPPE**), the annealing process was found to significantly enhance the long-range order. The diffraction pattern for annealed **HDO-OPPE** shows an intense and sharp first-order reflection at a *d* spacing of 25.5 Å and clearly resolved higher order reflections at 12.7, 6.4, and 4.4 Å. These spacings are similar to the ones of the higher molecular weight analogue reported before and are characteristic for the formation of a layered structure in which the stiff polymer main chains are oriented coplanar and the linear alkyl side chains extend laterally within the planes of their respective main chains (Scheme 2).[16,25] The presence and intensity of the even reflections (12.7 and 4.4 Å) are indicative for an interdigitated orientation of the side chains. The *d* spacing of 25.5 Å for the first-order reflection, which represents the thickness of the layers, suggests that the side chains are tilted with respect to the conjugated polymer main chains.[16,25] The width of the wide-angle reflections points to a low degree of crystallinity of the alkyl side chains. Annealed **O-OPPE** shows an intense and sharp first-order reflection at a *d* spacing of 18.2 Å, a clearly resolved higher order reflection at 6.2 Å, and a sharp, intense wide-angle reflection at 4.1 Å. The even, higher order reflections are completely suppressed, and in analogy to structural comparable polymers,[16,25] we suggest a layered structure in which the alkyl side chains of coplanar adjacent polymer main chains are not interdigitated. The *d* spacing of 18.2 Å for the first-order reflection indicates that the side chains are tilted with respect to the conjugated polymer main chains. The sharpness and intensity of the wide-angle peak also suggest an appreciable degree of side chain crystallinity for this sample.

The diffraction pattern of annealed **DPO-OPPE**, bearing ((dimethylamino)propyl)oxy side chains, shows a sharp first-order reflection at a *d* spacing of 15.8 Å and a sharp, intense wide-angle reflection at 4.2 Å. The comparable low intensity of the first-order reflection and the lack of higher order reflections suggests that this polymer only adopts a comparable small degree of long-range order, but the sharpness and intensity of the wide-angle peak point to an appreciable degree of side chain crystallinity. The diffraction patterns for polymers with sterically hindered side groups (**EHO-OPPE** and **MPO-OPPE**) show essentially no changes upon annealing (apart from an apparent relaxation in the case of **EHO-OPPE**), and these materials exhibit virtually no long-range order and crystallinity.

Photoluminescence. The photophysical characteristics of the polymers were investigated in solution and the solid state. The absorption and emission spectra obtained for diluted and deoxygenated $CHCl_3$ solutions are shown in Figure 3. All spectral data for measurements in solution are summarized in Table 2. **HDO-OPPE**, **O-OPPE**, **EHO-OPPE**, and **MPO-OPPE** show almost identical electronic properties in solution. The absorption spectra exhibit an absorption band at 318 nm and a broad main transition centered around 449 nm. The PL spectra, which are attributed to fluorescence because of the short lifetime of the excited states,[15] are insensitive to the excitation wavelength in a range from 320 to 480 nm. All data given here were obtained exciting at the wavelength of the main absorption band. The splitting of the emission spectra into two well-resolved bands around 474 and 506 nm and the lack of mirror image similarity between absorption and emission spectra are related to vibronic coupling. The fact that the emission bands are much narrower than the absorption bands and show well-resolved vibronic bands is consistent with emission from localized excited states, most likely after a migration of the excitions along the polymer main chains to segments that represent low-energy states. The PL quantum yields were determined relative to a quinine sulfate standard. The new PPEs were found to be highly emissive, having quantum efficiencies between 0.83 and 0.86.

The striking similarity of the electronic properties of these polymers in solution indicates that these molecular properties are predominantly governed by the rigid-rod and highly conjugated polymer backbone and are not influenced by the nature of the attached side chains. The polymer bearing 3-(dimethylamino)propoxy side groups, **DPO-OPPE**, however shows slightly blue-shifted absorption and emission spectra. Its PL quantum yield of 0.62 is significantly lower than the ones of the other materials of the series. This behavior can be attributed to either inter- or intramolecular electronic interactions of the alkylamino groups with the conjugated π-system. It is consistent with bimolecular quenching studies performed on a polymer with a repeat unit similar to **HDO-OPPE** and different alakylamines, which show Stern–Volmer type diffusion-controlled quenching of the fluorescence.[30]

The solid-state photophysics of the new PPEs were investigated under ambient conditions on pristine and annealed films. The results are summarized in Figure 4a–e and Table 3. (Note that the heights of the spectra in Figure 4 are arbitrarily adjusted in order to optimally fit the graphs.) Pristine films of the new materials show similar absorption spectra with well-resolved features which may represent vibratiional modes as well as different intermolecular interactions. Compared with solution, the spectra show little broadening but are

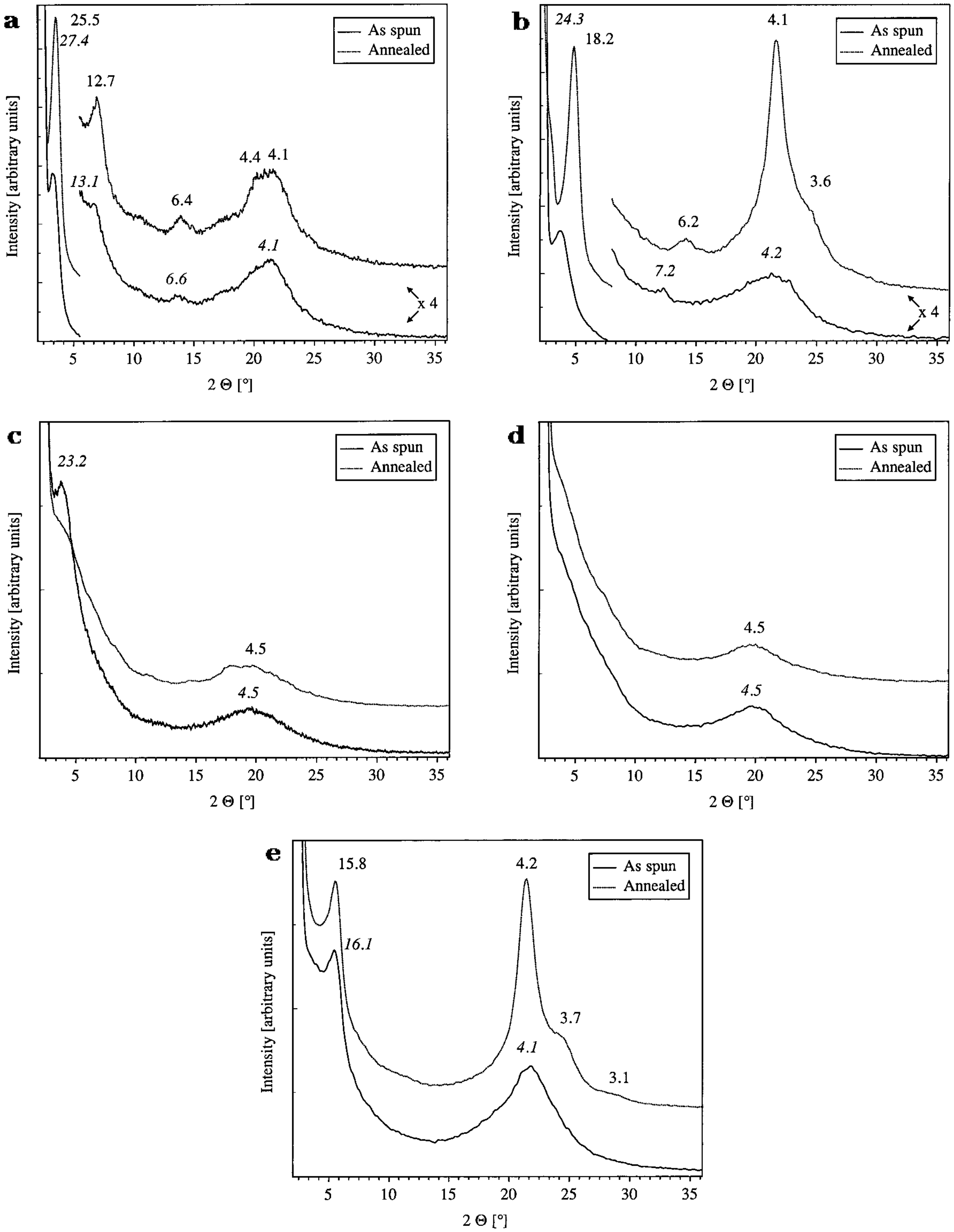
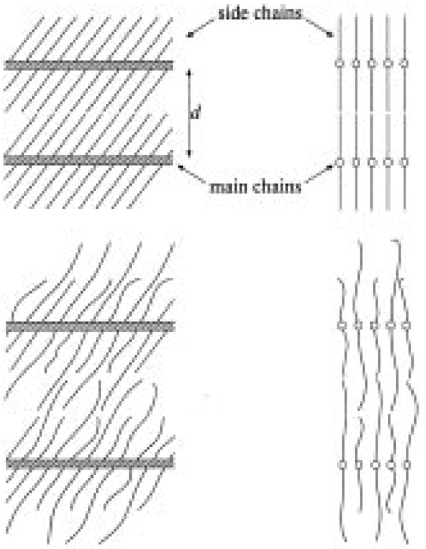


Figure 2. X-ray diffractograms of pristine and annealed thin films of **HDO-OPPE** (a), **O-OPPE** (b), **EHO-OPPE** (c), **MPO-OPPE** (d), and **DPO-OPPE** (e). Peaks are labeled with *d* spacings in angstroms, using italic numbers forpristine samples.

significantly red-shifted, showing a trend of larger red shift with longer side chains. The PL spectra of pristine films show emission bands with characteristic features, which we attribute to vibronic coupling. The two polymers having only linear side chains (**HDO-OPPE** and **O-OPPE**) have significantly narrower spectra with better resolved bands than the polymers derivatized with sterically hindered substituents. Since the measurement of absolute quantum yields is very difficult in the solid state, the thin-film PL quantum yields were approximated, using an optical dense configuration (see ref 31 and Experimental Section for details) and a quinine sulfate solution as a reference. Pristine samples of **HDO-OPPE**, **O-OPPE**, **EHO-OPPE**, and **MPO-OPPE** were found to be highly emissive, with PL quantum yields between 0.28 and 0.36, in contrast to the significantly lower value of 0.07 for **DPO-OPPE**.

The absorption spectra of the annealed films are slightly red-shifted and compared to the pristine samples, exhibit a redistribution between the different bands. The annealing process was found to have a significant impact on the photoluminescence of **HDO-OPPE** and **O-OPPE**. Most remarkable is the change in quantum yield down to 0.09 and 0.11, respectively. While the emission spectrum of annealed **HDO-OPPE** remained essentially unchanged, the emission band of **O-OPPE** experienced a slight red shift and a redistribution between different vibrational modes. In contrast to

Scheme 2. Possible Structures (Strongly Idealized) for the Solid-State Ordering of O-OPPE (Top) and HDO-OPPE (Bottom) (Adapted from Refs 16 and 25)



these polymers, the PL quantum yield for the polymers bearing sterically hindered side chains, **EHO-OPPE** and **MPO-OPPE**, did not change significantly. Both spectra, especially that of **EHO-OPPE**, exhibit a much better resolution of the vibrational modes. Besides a slight red shift and a redistribution between different modes, the PL characteristics of **DPO-OPPE** remained unchanged upon annealing.

The different PL quantum yields obtained for different samples of the new PPEs can be related to the degree of long-range order in the samples. The effect can be explained based on classical concentration quenching considerations, which are well documented for planar conjugated systems and discussed elsewhere.[32] Pristine films of **HDO-OPPE**, **O-OPPE**, **EHO-OPPE**, and MPO-**OPPE** as well as annealed samples of **EHO-OPPE** and **MPO-OPPE** show comparable, high PL quantum yields, consistent with the finding that these samples adopt no significant extent of long-range order. The disorder, the large content of aliphatic side chains, and the lack of specific intermolecular interactions in these samples make the rigid-rod conjugated polymer backbones behave as if they were “dissolved” in a hydrocarbon solvent. In contrast, the substantially reduced PL quantum yields of annealed films of **HDO-OPPE** and **O-OPPE** can be explained when taking the significant degree of long-range order of these samples into account. The close proximity of the coplanar-oriented polymer main chains seems to enable the formation of new excimer complexes which provide nonemissive decay channels for the excited states. A similar effect has been reported for poly(3-hexylthiophene)s.[33] Films of **DPO-OPPE** show a significantly lower PL quantum yield than the other materials of the series since electronic interactions of the alkylamino groups with the conjugated π-system and the resulting fluorescence quenching seem to be the dominant mechanism.

III. Conclusion

In an effort to optimize the photoluminescence (and ultimately electroluminescence) quantum yield, we have designed and synthesized a series of novel poly(2,5-dialkoxy-*p*-phenyleneethynylene)s. We have shown that the supramolecular structure of these polymers can be easily and significantly influenced by the nature of substituents covalently linked to the rigid-rod polymer main chains. In samples with a high degree of long-range order, the coplanar orientation of the conjugated polymer backbones leads to the formation of excimer complexes which provide nonemissive decay channels for the excited states and hence result in comparably low PL quantum yields. In samples that adopt only a small extent of long-range order, the rigid-rod conjugated polymer backbones behave as if they were “dissolved” in a hydrocarbon solvent and consequently high solid-state PL quantum yields have been determined for such samples. The high and stable PL quantum yield combined with a good processability makes the poly(2,5-dialkoxy-*p*-phenyleneethynylene)s derivatized with sterically hindered side chains promising materials for electroluminescent devices. Studies of the nonlinear optical properties of the polymers and the fabrication of light-emitting diodes based on the new polymers discussed here are currently in progress.

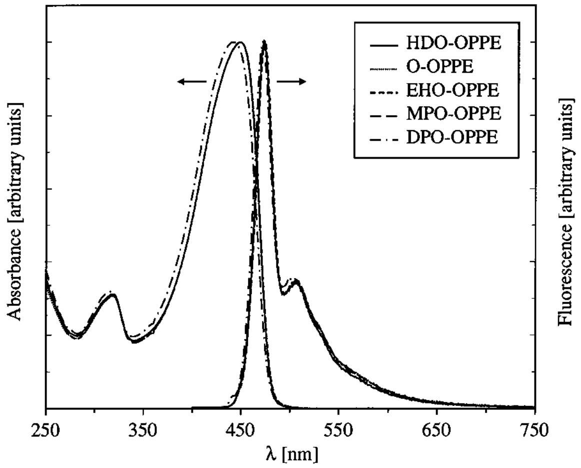


Figure 3. Absorption and emission spectra of the PPEs in $CHCl_3$ at 295 K. Note that intensities were arbitrarily chosen in order to optimally fit the graphs.

Table 2. Spectral Properties of the Poly(2,5-dialkoxy-*p*-phenyleneethynylene)s in Solution[a]

polymer	absorption λ_{max}, nm	extinction coefficient,[b] L/mol·cm	emission λ_{max}, nm	ϕ_{fl}[c]
HDO-OPPE	448	5.26×10^4	473, 506	0.86
O-OPPE	449	5.01×10^4	474, 505	0.83
EHO-OPPE	449	5.17×10^4	474, 506	0.86
MPO-OPPE	449	5.03×10^4	473, 505	0.82
DPO-OPPE	442	5.32×10^4	472, 505	0.62

[a] All experiments were performed in $CHCl_3$. [b] Per mole of the polymer's repeat unit. [c] Fluorescence quantum yield. The wavelength of the absorption maximum was chosen for the excitation.

IV. Experimental Section

Materials. All reagents and solvents were purchased from Aldrich Chemical Co. and Fluka. Only analytical grade quality chemicals were used. Quinine sulfate 7-hydrate was obtained from Kodak Eastman. Spectroscopic grade $CHCl_3$ (Aldrich) was used for all absorption and emission experiments. ACS reagent grade $CHCl_3$ (Aldrich, 99.8%) was used for the preparation of polymer films. Diisopropylamine was dried over KOH, and toluene was dried over CaH_2. Both solvents were distilled under an Ar atmosphere and deoxygenated by sparging with Ar for at least 1 h prior to use. All other compounds were used as received.

Methods. All alkylations and cross-coupling reactions were carried out under a dry Ar atmosphere using standard vacuum-line and glovebox techniques. Melting points were determined on a Hoover capillary melting point apparatus. ^1H NMR and ^{13}C NMR spectral data are expressed in ppm relative

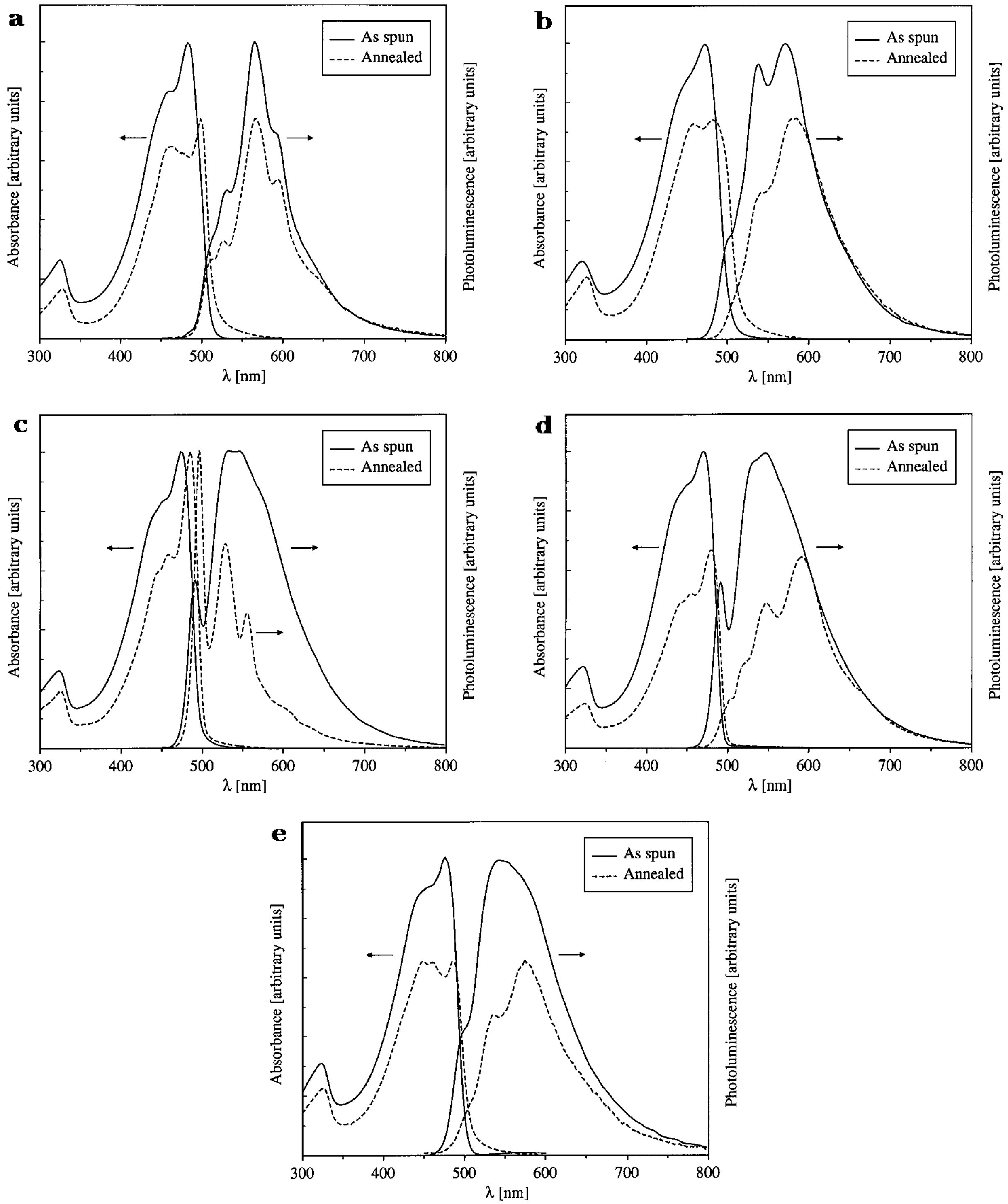


Figure 4. Absorption and emission spectra of pristine and annealed thin films of **HDO-OPPE** (a), **O-OPPE** (b), **EHO-OPPE** (c), **MPO-OPPE** (d), and **DPO-OPPE** (e) at 295 K. Note that intensities were arbitrarily chosen in order to optimally fit the graphs.

to internal standard and were obtained in $CHCl_3$ or dimethyl sulfoxide (DMSO) on a Bruker 250 and a Varian XL 300 NMR spectrometer. Elemental analyses were obtained from Oneida Research Services. DSC measurements were performed on a Perkin-Elmer Series 7 analysis system under N_2 at a heating rate of 20 °C/min. UV−vis spectra and optical density measurements were obtained on a HP 8452A diode array spectrophotometer. Polarization microscopy was performed on a Zeiss Axioscop MC 80, equipped with a Mettler FP 28 hot stage which was controlled by a Mettler FP 90 processor. Wide-angle X-ray diffraction data were obtained on a Rigaku RU 200 diffractometer with a thin-film attachment using Cu Kα radiation. All measurements were done in the reflection mode at an incident angle of 1° with an incident slit of 0.2 mm and a width-limiting slit of 5 mm. Data were collected in a range of $2° \leq 2\theta \leq 36°$ at intervals of 0.02° and at a scanning rate of 2°/min. The measurements were performed on rotating polymer films of about 1 μm thickness on silicon substrates. Refractive indices were determined from the interference fringes in the UV−vis transmission spectra of thin polymeric films on fused-silica substrates as previously reported.[34,35]

Monomer Synthesis. Synthesis of the 1,4-Dialkoxybenzenes. All 2,5-dialkoxybenzenes were prepared by the alkylation of hydroquinone with primary alkyl bromides according to a previously published procedure.[36]

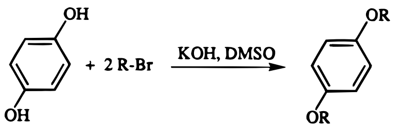


Table 3. Spectral Properties of Thin Films of the Poly(2,5-dialkoxy-*p*-phenyleneethynylene)s

	absorption λ_{max}, nm		emission λ_{max}, nm			ϕ_{fl}[b]	
polymer	pristine[c]	annealed	pristine	annealed	n[a]	pristine	annealed
HDO-OPPE	464, 482	462, 498	534, 564, 585[d]	526, 566, 593	1.76	0.33	0.09
O-OPPE	456, 475	458, 483	503,[d] 538, 572	535,[d] 581	1.78	0.36	0.11
EHO-OPPE	454, 473	457, *84*	491, 532, 549	496, 528, 555	1.76	0.31	0.28
MPO-OPPE	450, 470	455, 479	491, 532,[d] 549	503,[d] 547, 592	1.77	0.28	0.27
DPO-OPPE	454, 476	449, 461, 485	500,[d] 543	535, 574	1.84	0.07	0.07

[a] Refractive index of pristine films at 550 nm. [b] Fluorescence quantum yield. The wavelength of the characteristic shoulder in the absorption spevtrum of pristine films was chosen for the excitation. [c] The first value corresponds to the characteristic shoulder, the second to the sharp maximum of the absorption spectrum. [c] The first value corresponds to the characteristic shoulder, the second to the sharp maximum of the absorption spectrum. [d] Shoulder.

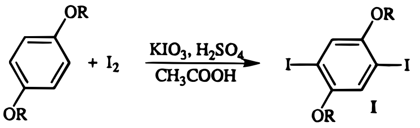
1,4-Bis((2-ethylhexyl)oxy)benzene. A suspension of powdered KOH (24.0 g, 0.428 mol) and dry DMSO (120 mL) was stirred and degassed at room temperature for 60 min, and hydroquinone (5.51 g, 0.050 mol) and 2-ethylhexyl bromide (38.0 g, 0.197 mol) were added. The reaction mixture was then stirred for 2 h at room temperature and finally poured into ice water (500 mL). The organic layer was collected and the aqueous layer was extracted with hexane (3 × 100 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated to give a yellow to brown oil. Distillation under reduced pressure yielded a colorless liquid (15.1 g, 90%): bp 165 °C (0.05 Torr). ^1H NMR (250 MHz, $CHCl_3$) δ 6.80 (s, 4 H, ar), 3.76 (d, $^3J(H,H) = 5.7$ Hz, 4 H, OCH_2), 1.67 (m, 2 H, CH), 1.43, 1.30 (2 × m, 16 H, CH_2), 0.86 (m, 12 H, CH_3). Anal. Calcd for $C_{22}H_{38}O_2$: C, 78.99; H, 11.45. Found: C, 79.03; H, 11.53.

1,4-Bis((2-methylpropyl)oxy)benzene. This compound was prepared by a procedure identical to the above, using 2-methylpropyl bromide instead of 2-ethylhexyl bromide. When the reaction mixture was poured into ice water, an off-white solid precipitated. The residue was collected, dried, and recrystallized from methanol/acetone to yield a white, fluffy material (74%): mp 56 °C. ^1H NMR (250 MHz, $CHCl_3$) δ 6.80 (s, 4 H, ar), 3.64 (d, $^3J_{(H,H)} = 6.5$ Hz, 4 H, OCH_2), 2.00 (m, 2 H, CH), 0.89 (d, $^3J(H,H) = 6.5$ Hz, 12 H, CH_3). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.50; H, 10.19.

1,4-Bis(octyloxy)benzene and **1,4-bis(hexadecyloxy)benzene**, the synthesis of which have been previously described,[15] were also obtained by this method.

Synthesis of the 1,4-Dialkoxy-2,5-diiodobenzenes (I). The 1,4-dialkoxy-2,5-diiodobenzenes (**I**) were prepared either by the iodination of 1,4-dialkoxybenzenes or by the alkylation of 2,5-diiodohydroquinone in analogy to reactions described before.[19,37]

Iodination of 1,4-dialkoxybenzenes:

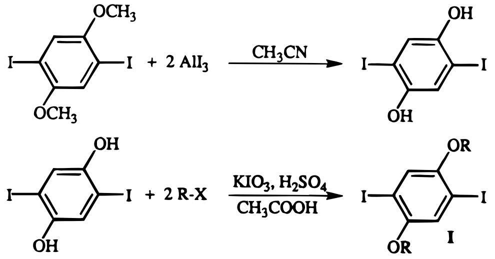


1,4-Bis((2-ethylhexyl)oxy)-2,5-diiodobenzene. 1,4-Bis((2-ethylhexyl)oxy)benzene (14.9 g, 0.0445 mol), KIO_3 (3.83 g, 0.0179 mol), and I_2 (12.6 g, 0.0496 mol) were added to a stirred solution of acetic acid (270 mL), 96% H_2SO_4 (4.8 mL), and H_2O (20 mL). The reaction mixture was stirred at reflux for 16 h and then cooled to room temperature. Aqueous Na_2SO_4 (20%) was added until the brown color of iodine had disappeared, and the reaction mixture was poured into ice water (500 mL). The organic layer was collected and the aqueous layer was extracted with hexane (3 × 200 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated to give a yellow to brown oil. After chromatography (silica gel, hexane) the pure product was obtained as a slightly yellow liquid (24.1 g, 90%): ^1H NMR (250 MHz, $CHCl_3$) δ 7.14 (s, 2 H, ar), 3.79 (d, $^3J_{(H,H)} = 5.3$ Hz, 4 H, OCH_2), 1.70 (m, 2 H, CH), 1.50 (m, 8 H, CH_2), 1.30 (m, 8 H, CH_2), 0.91 (m, 12 H, CH_3). ^{13}C NMR (100 MHz, $CHCl_3$) δ 153.09 (ar-O), 122.57 (ar-H), 86.27 (ar-I), 72.56 (OCH_2), 39.67 (CH), 30.73, 29.27, 24.16, 23.25 (all CH_2), 14.33 (CH_3), 11.43 (CH_3). Anal. Calcd for $C_{22}H_{36}I_2O_2$: C, 45.07; H, 6.19; I, 43.29. Found: 45.44; H, 6.33; I, 43.01.

1,4-Bis(2-methylpropyl)oxy)-2,5-diiodobenzene. This compound was prepared by a procedure identical to the above, using 1,4-bis((2-methylpropyl)oxy)benzene instead of 1,4-bis((2-ethylhexyl)oxy)benzene. When the reaction mixture was poured into ice water after refluxing for 7 h, an off-white solid precipitated. The residue was collected, washed with water, dried, and recrystallized from ethanol to yield white crystals (71%): mp 79 °C. ^1H NMR (250 MHz, $CHCl_3$) δ 7.13 (s, 2 H, ar), 3.67 (d, $^3J_{(H,H)} = 6.4$ Hz, 4 H, OCH_2), 2.10 (m, 2 H, CH), 1.04 (d, $^3J_{(H,H)} = 6.6$ Hz, 12 H, CH_3). ^{13}C NMR (100 MHz, $CHCl_3$) δ 152.99 (ar-O), 122.71 (ar-H), 86.31 (ar-I), 76.69 (OCH_2), 28.61 (CH), 19.51 (CH_3). Anal. Calcd for $C_{14}H_{20}I_2O_2$: C, 35.47; H, 4.25; I, 53.53. Found: C, 35.74; H, 4.25; I, 53.66.

1,4-Dimethoxy-2,5-diiodobenzene, 1,4-bis(octyloxy)-2,5-diiodobenzene, and **1,4-bis(hexadecyloxy)-2,5-diiodobenzene,** the synthesis of which have been previously described,[15,38] were also obtained by this method.

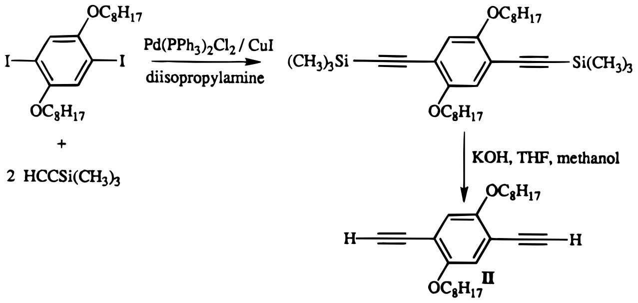
Alkylation of 2,5-diiodohydroquinone:



1,4-Bis((3-(dimethylamino)propyl)oxy)-2,5-diiodobenzene. Al powder (2.70 g, 0.100 mol) and I_2 (19.03 g, 0.0750 mol) were added under an Ar atmosphere to ice-cooled, dry acetonitrile (80 mL). The mixture was then stirred and slowly warmed to reflux, and the reaction was pursued until the violet color of the iodide disappeared after 20 min. The mixture was allowed to cool and a suspension of 1,4-dimethoxy-2,5-diiodobenzene (15.6 g, 0.040 mol) in dry acetonitrile (70 mL) was added. The reaction mixture was then stirred for 17 h at reflux and finally poured into aqueous HCl (200 mL, 0.5 M). The mixture was extracted with diethyl ether (3 × 200 mL), and the combined organic layers were extracted with an aqueous solution of NaOH (250 mL, 5%). The aqueous solution was immediately acidified with HCl and extracted with diethyl ether (3 × 200 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated to give the crude 2,5-diiodohydroquinone as a brown solid (12.8 g, 88%). The crude compound (1.64 g, 4.54 mmol) was added to a degassed suspension of powdered KOH (2.54 g, 45.4 mmol) and dry DMSO (20 mL). 3-(Dimethylamino)propyl chloride hydrochloride (2.87 g, 18.2 mmol) was added, and the reaction mixture was stirred for 17 h at room temperature. When the reaction mixture was finally poured into ice water (100 mL), a white solid precipitated. The residue was collected, washed with water, dried, and recrystallized from heptane to yield white crystals (1.47 g, 70%): mp 99 °C. ^1H NMR (250 MHz, $CHCl_3$) δ 7.17 (s, 2 H, ar), 3.97 (t, $^3J_{(H,H)} = 6.3$ Hz, 4 H, OCH_2), 2.47 (t, $^3J_{(H,H)} = 7.2$ Hz, 4 H, NCH_2), 2.23 (s, 12H, NCH_3), 1.94 (m, 4 H, CH_2). ^{13}C NMR (100 MHz, $CHCl_3$) δ 152.96 (ar-O), 122.94 (ar-H), 86.43 (ar-I), 68.59 (OCH_2), 56.43 (NCH_2), 45.72 (NCH_3), 27.56 (CH_2). Anal. Calcd for $C_{16}H_{26}I_2N_2O_2$: C, 36.11; H, 4.92; I, 47.69; N, 5.26. Found: C, 36.22; H, 4.94; I, 47.94; N, 5.15.

1,4-Bis((7-carboxyheptyl)oxy)-2,5-diiodobenzene. This compound was prepared by a procedure identical to the above using 8-bromooctanoic acid instead of 3-(dimethylamino)propyl chloride hydrochloride. When the reaction mixture was poured into acidified ice water, an off-white solid precipitated. The residue was collected, washed with diluted aqueous HCl, dried, and recrystallized from ethanol to yield a white powder (2.39 g, 82%): mp 152−155 °C. ^{1}H NMR (250 MHz, DMSO) δ 11.93 (s, COOH), 7.31 (s, 2 H, ar), 3.95 (t, $^3J_{(H,H)} = 6.1$ Hz, 4 H, OCH_2), 2.20 (t, $^3J_{(H,H)} = 7.3$ Hz, 4 H, $HOOCCH_2$), 1.65, 1.45, 1.32 (all m, 20 H, CH_2). ^{13}C NMR (100 MHz, DMSO) δ 174.48 (COOH), 152.34 (ar-O), 122.38 (ar-H), 86.88 (ar-I), 69.56 (OCH_2), 33.67 (CH_2COOH), 28.61, 28.55, 28.41, 25.43, 24.46 (all CH_2). Anal. Calcd for $C_{22}H_{32}I_2O_6$: C, 40.89; H, 4.99. Found: C, 41.41; H, 5.05.

Synthesis of 1,4-Diethynyl-2,5-bis(octyloxy)benzene (II). Monomer **II** was prepared from 1,4-bis(octyloxy)-2,5-diiodobenzene and (trimethylsilyl)acetylene by a palladium(II)-catalyzed cross-coupling reaction and subsequent cleavage of the trimethylsilyl protecting group:[27]



1,4-Bis((trimethylsilyl)ethynyl)-2,5-bis(octyloxy)benzene. 1,4-Bis(octyloxy)-2,5-diiodobenzene (15.5 g, 26.4 mmol), $(PPh_3)PdCl_2$ (0.925 g, 1.32 mmol), and CuI (0.252 g, 1.32 mmol) were dissolved in diisopropylamine. (Trimethylsilyl)acetylene (5.5 g, 56.0 mmol) was added at room temperature over the course of 10 min to the vigorously stirred solution; during the addition of a white precipitate formed. After the addition was completed, the reaction mixture was stirred at reflux for 1 h. After cooling, toluene (100 mL) was added and the white ammonium iodide precipitate was filtered off. The solution was passed through a 4 cm plug of silica gel using toluene as eluent. The evaporation of the solvent led to a yellow oil which crystallized upon standing. Recrystallization from ethanol (twice) yielded white needles (12.3 g, 88%): mp 66 °C. ^{1}H NMR (250 MHz, $CHCl_3$) δ 6.86 (s, 2 H, ar), 3.92 (t, 4 H, OCH_2), 1.76 (m, 4 H, CH_2), 1.48 (m, 4 H, CH_2), 1.26 (m, 16 H, CH_2), 0.86 (t, 6 H, CCH_3), 0.22 (s, 18 H, $SiCH_3$). ^{13}C NMR (100 MHz, $CHCl_3$) δ 154.25 (ar-O), 117.43 (ar-H), 114.18 (ar-C), 101.30, 100.29 (both acetylene), 69.67 (OCH_2), 32.07, 29.62, 29.57, 29.52, 26.25, 22.89 (all CH_2), 14.31 (CH_3), 0.17 ($SiCH_3$). Anal. Calcd for $C_{32}H_{54}O_2Si_2$: C, 72.94; H, 10.33. Found: C, 72.51; H, 10.36.

1,4-Diethynyl-2,5-bis(octyloxy)benzene (II). Methanol (220 mL) and aqueous KOH (15 mL, 20%) were added at room temperature to a stirred solution of 1,4-bis((trimethylsilyl)ethynyl)-2,5-bis(octyloxy)benzene (13.1 g, 24.9 mmol) in tetrahydrofuran (440 mL), and the reaction mixture was stirred for 2 h. The mixture was filtered and after evaporation of the solvent, a yellow solid was obtained. Recrystallization from hexane with charcoal yielded pale yellow crystals (7.47 g, 79%): mp 65 °C. ^{1}H NMR (250 MHz, $CHCl_3$) δ 6.93 (s, 2 H, ar), 3.95 (t, $^3J_{(H,H)} = 6.6$ Hz, 4 H, OCH_2), 3.32 (s, 2 H, CH), 1.78 (m, 4 H, CH_2), 1.40, 1.26 (both m, 20 H, CH_2), 0.86 (t, 6 H, CH_3). ^{13}C NMR (100 MHz, $CHCl_3$) δ 154.18 (ar-O), 117.92 (ar-H), 113.45 (ar-C), 82.60, 79.98 (both acetylene), 69.84 (OCH_2), 31.99, 29.48, 29.42, 29.31, 26.09, 22.85 (all CH_2), 14.29 (CH_3). Anal. Calcd for $C_{26}H_{38}O_2$: C, 81.63; H, 10.01. Found: C, 81.52; H, 10.04.

Polymer Synthesis. HDO-OPPE. 1,4-Diethynyl-2,5-bis(octyloxy)benzene (**II**) (0.6027 g, 1.575 mmol), 1,4-bis(hexadecyloxy)-2,5-diiodobenzene (1.1530 g, 1.422 mmol), iodobenzene (0.0637 g, 0.312 mmol), $Pd(PPh_3)_4$ (0.0680 g, 0.0588 mmol), and CuI (0.0112 g, 0.0588 mmol) were combined in toluene (35 mL) and diisopropylamine (15 mL). The reaction mixture was then stirred at 70 °C. Ammonium iodide salts were formed immediately after the start of the reaction and the mixture became highly fluorescent. Two hours before the end of the reaction, an additional amount of iodobenzene (0.0273 g, 0.134 mmol) was added. After a total reaction time of 22 h, the reaction mixture was cooled to room temperature and added dropwise to rapidly stirred acetone (900 mL). After stirring for 2 h, the precipitate was collected and washed with acetone, hot ethanol, and hot acetonitrile. After drying overnight at room temperature, **HDO-OPPE** was obtained as an orange solid (1.316 g, 93%): $\bar{x}_n = 24$ by ^{1}H NMR. ^{1}H NMR (250 MHz, $CHCl_3$) δ 7.52 (m, 2 H/end group, end group), 7.32 (m, 3 H/end group, end group), 7.00, 6.99 (2 × s, 4 H, ar), 4.01 (m, 8 H, OCH_2), 1.84 (m, 8 H, CH_2), 1.50 (m, 8 H, CH_2), 1.23 (m, 64 H, CH_2), 0.85 (m, 12 H, CH_3). Anal. Calcd for $C_{866}H_{1292}O_{50}$ ($\bar{x}_n = 24$): C, 82.16; H, 11.05. Found: C, 81.65; H, 11.10.

O-OPPE. This polymer was prepared by a procedure identical to **HDO-OPPE** using 1,4-bis(octyloxy)-2,5-diiodobenzene instead of 1,4-bis(hexadecyloxy)-2,5-diiodobenzene. **O-OPPE** was obtained as an orange solid (91%): $\bar{x}_n = 23$ by ^{1}H NMR. ^{1}H NMR (250 MHz, $CHCl_3$) δ 7.51 (m, 2 H/end group, end group), 7.31 (m, 3 H/end group, end group), 7.00 (s, 4 H, ar), 4.01 (t, $^3J_{(H,H)} = 6.4$ Hz, 8 H, OCH_2), 1.84 (m, 8 H, CH_2), 1.50 (m, 8 H, CH_2), 1.25 (m, 32 H, CH_2), 0.85 (m, 12 H, CH_3). Anal. Calcd for $C_{590}H_{872}O_{48}$ ($\bar{x}_n = 23$): C, 81.14; H, 10.06. Found: C, 79.84; H, 10.10.

EHO-OPPE. This polymer was prepared by a procedure identical to **HDO-OPPE** using 1,4-bis((2-ethylhexyl)oxy)-2,5-diiodobenzene instead of 1,4-bis(hexadecyloxy)-2,5-diiodobenzene. The reaction mixture was precipitated into ethanol instead of acetone, and the obtained polymer was washed only with hot ethanol and hot acetonitrile. **EHO-OPPE** was obtained as a yellow solid (83%): $\bar{x}_n = 28$ by ^{1}H NMR. ^{1}H NMR (250 MHz, $CHCl_3$) δ 7.51 (m, 2 H/end group, end group), 7.33 (m, 3 H/end group, end group), 7.00, 6.99 (2 × s, 4 H, ar), 4.00 (t, $^3J_{(H,H)} = 6.3$ Hz, 4 H, OCH_2), 3.91 (m, 4 H, OCH_2), 1.85 (m, 6 H, 2 × CH_2 + 2 × CH), 1.50 (m, 16 H, CH_2), 1.28 (m, 20 H, CH_2), 0.87 (t, $^3J_{(H,H)} = 7.4$ Hz, 6 H, CH_3), 0.86 (m, 12 H, CH_3). Anal. Calcd for $C_{710}H_{1052}O_{58}$ ($\bar{x}_n = 28$): C, 81.09; H, 10.08. Found: C, 80.63; H, 10.11.

MPO-OPPE. This polymer was prepared by a procedure identical to **HDO-OPPE** using 1,4-bis((2-methylpropyl)oxy)-2,5-diiodobenzene instead of 1,4-bis(hexadecyloxy)-2,5-diiodobenzene. The reaction mixture was precipitated into ethanol instead of acetone, and the polymer was washed only with hot ethanol and hot acetonitrile. **MPO-OPPE** was obtained as a yellow solid (92%): $\bar{x}_n = 22$ by ^{1}H NMR. ^{1}H NMR (250 MHz, $CHCl_3$) δ 7.51 (m, 2 H/end group, end group), 7.31 (m, 3 H/end group, end group), 7.00, 6.98 (2 × s, 4 H, ar), 4.01 (t, 4 H, OCH_2), 3.91 (d, 4 H, OCH_2), 2.15 (m, 2 H, CH), 1.82 (m, 4 H, CH_2), 1.49 (m, 4 H, CH_2), 1.25 (m, 16 H, CH_2), 1.07 (d, 12 H, CH_3), 0.85 (m, 6 H, CH_3). Anal. Calcd for $C_{478}H_{660}O_{46}$ ($\bar{x}_n = 22$): C, 80.38, H, 9.31. Found: C, 79.24; H, 9.33.

DPO-OPPE. This polymer was prepared by a procedure identical to **HDO-OPPE** using 1,4-bis((3-(dimethylamino)propyl)oxy)-2,5-diiodobenzene instead of 1,4-bis(hexadecyloxy)-2,5-diiodobenzene. **DPO-OPPE** was obtained as an orange solid (87%): $\bar{x}_n = 28$ by ^{1}H NMR. ^{1}H NMR (250 MHz, $CHCl_3$) δ 7.51 (m, 2 H/end group, end group), 7.32 (m, 3 H/end group, end group), 7.03, 7.00 (2 × s, 4 H, ar), 4.08 (t, $^3J_{(H,H)} = 6.2$ Hz, 4 H, OCH_2), 4.02 (t, $^3J_{(H,H)} = 6.4$ Hz, 4 H, OCH_2), 2.49 (t, $^3J_{(H,H)} = 7.0$ Hz, 4 H, NCH_2) 2.22 (s, 12 H, NCH_3), 2.00 (m, 4 H, CH_2), 1.84 (m, 4 H, CH_2), 1.50 (m, 4 H, CH_2), 1.25 (m, 16 H, CH_2), 0.84 (m, 6 H, CH_3). Anal. Calcd for $C_{626}H_{912}N_{28}O_{58}$ ($\bar{x}_n = 28$): C, 77.05; H, 9.42; N, 4.02. Found: C, 74.50; H, 9.16; N, 3.82.

CHO-OPPE. This polymer was prepared by a procedure identical to **HDO-OPPE** using 1,4-bis((7-carboxyheptyl)oxy)-2,5-diiodobenzene instead of 1,4-bis(hexadecyloxy)-2,5-diiodobenzene. At the end of the reaction a red, rubberlike solid had formed. The reaction mixture was cooled to room temperature and poured into rapidly stirred ethanol. After stirring for 2 h, the product was collected and washed with ethanol. After drying overnight at room temperature, **CHO-OPPE** was obtained as a red solid (90%). Anal. Calcd for

$C_{662}H_{928}O_{106}$ (hypothetical $\bar{x}_n = 26$): C, 75.14; H, 8.84; N, 0.00. Found: C, 70.98; H, 9.21; N, 1.63.

Film Preparation. The polymers were dissolved in $CHCl_3$ at concentrations of 1−4% (w/v) polymer. The solutions were filtered through a 0.2 μm filter (Gelman Acro-disc PTFE) and were spin-cast on glass (for absorption and fluorescence measurements), fused silica (for refractive index measurements), or silicon (for WAXD experiments) substrates. The polymer films were dried under vacuum at room temperature and in the dark. The thickness of the films as measured with a Detak 3 profilometer was typically 0.2 μm for absorption measurements and 1.1 μm for fluorescence and WAXD measurements. Samples referred to as *annealed* were tempered under an N_2 atmosphere for 30−120 min at 125 °C and then slowly cooled to room temperature.

Photoluminescence Measurements. All photoluminescence spectra were recorded on a SPEX Fluorolog 2 (Model F212 I) which was controlled by a Spex DM 3000f computer. All slits were kept at 2 mm, corresponding to a band-pass of 3.4 nm for excitation and emission. All spectra were corrected for the spectral dipersion of the Xe lamp, the instrument throughput, and the detector response. A reference detector accounted for fluctuation in lamp intensity; in addition, measurements of a quinine sulfate reference were taken before and after the experiments. All experiments were performed at 22 ± 2 °C. The photoluminescence quantum yields given here are averaged over at least three measureents, with a standard deviation of typically below 0.02.

All emission studies in solution were performed in deoxygenated $CHCl_3$ at absorptions between 0.05 and 0.1. Four-sided quartz cells with a length of 1 cm were used, and the detector was arranged perpendicular to the incident beam. Photoluminescence quantum yields were determined relative to quinine sulfate in 1 N H_2SO_4 assuming a quantum yield of 0.546 at an excitation wavelength of 365 nm ($c < 10^{-4}$ M).[31,39] Quantum yields were calculated using the expression[31]

$$\phi_x = \phi_r \left(\frac{\int A_r(\nu)\,d\nu}{\int A_x(\nu)\,d\nu}\right)\left(\frac{{n_x}^2}{{n_r}^2}\right)\left(\frac{D_x}{D_r}\right)$$

where ϕ is the quantum yield, $\int A_r(\nu)\,d\nu$ is the integral over the absorption in the bandwidth of excitation, n is the refractive index, and D is the integral over the emission spectrum. The subscripts x and r refer to the sample and the reference solution. Refractive indices of pure 1 N H_2SO_4 and $CHCl_3$ were used.[40]

Emission studies on polymer films were performed in air. The samples were positioned normal to the incident beam. The emission was detected at an angle of 22.5° from the incident beam. Quantum yields were determined relative to quinine sulfate in 1 N H_2SO_4 in a 2 mm quartz cell. A quantum yield of 0.51 at an excitation wavelength of 365 nm and a concentration of 5×10^{-3} M was assumed.[31,39] Quantum yields were calculated using the approximation for an optical dense configuration:[31]

$$\phi_x \approx \phi_r \left(\frac{{n_x}^2}{{n_r}^2}\right)\left(\frac{D_x}{D_r}\right)$$

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