Synthesis and Characterization of a New Efficient Blue-Light-Emitting Copolymer

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ABSTRACT: In this paper we present the synthesis, the characterization, and the use in light-emitting diodes of a new blue-light-emitting copolymer, poly[2,5,2″,5″-tetraoctyl-*p*-terphenyl-4,4″-ylenevinylene-*p*-phenylenevinylene]. This copolymer, obtained by a poly-Heck reaction, has a fully unsaturated backbone consisting of regularly alternating terphenylene and phenylenebisvinylene blocks. The presence of well-defined chromophores, resulting from steric interactions in the polymer chain, gives rise to bright blue fluorescence, both in solution and in thin solid films. Blue-light-emitting diodes were fabricated by using this copolymer as an emitter layer.

Introduction

In the past 20 years there has been a dramatically growing interest in the development of organic materials for use in optoelectronic devices (for recent reviews see refs 1 and 2). When compared to classical inorganic semiconductors, organic materials and especially polymers present many potential advantages, such as very good mechanical and optical properties, ease of processability, and almost an unlimited number of accessible chemical structures.

The high photoluminescence observed in many organic semiconductors raised the possibility of solid-state light emission under an applied electric field (electroluminescence). Light-emitting devices (LED) were first fabricated from small organic molecules.[3,4] These systems present the main disadvantage that active molecules can recrystallize during device operation, leading to poor device stability. The use of conjugated polymers, potentially more stable, in such devices was first realized in the early 1990s.[5,6] Since then, a great number of polymer materials suitable for LED's have been developed.[7,8] Color tuning[9,10] and high efficiencies[11] have already been achieved, so that flat panel displays fabrication may soon be possible.

The most efficient polymeric systems are actually based on poly(*p*-phenylenevinylene) (PPV) films, which emit basically green light.[11] There is still a big challenge in obtaining highly efficient blue-light-emitting devices, which also cannot be made easily out of inorganic materials. Several organic conjugated systems, presenting higher band gaps, suitable for blue light emission have already been studied. They include small conjugated molecules,[4,12] poly(*p*-phenylene) (PP) polymers,[13] and PPV oligomers dispersed in a polymer matrix[14] or built into a flexible polymer chain.[15]

In this article we describe the synthesis, the characterization, and the application in light-emitting diodes of a new blue-light-emitting, rigid copolymer, poly[2,5,2″,5″-tetraoctyl-*p*-terphenyl-4,4″-ylenevinylene-*p*-phenylenevinylene], hereafter abbreviated as TOP–PPV. The fully unsatured backbone of this polymer (Figure 1a) consists of regularly alternating tetraoctylterphenylene (TOP) and *p*-phenylenebisvinylene blocks. In this type of π-aromatic structure, the blue PPV-like chromophores are linked through another conjugated unit presenting a higher bandgap. Solubility of the conjugated form is obtained through the presence of long octyl side chains on the terphenylene units.

Polymer Synthesis and Characterization

The synthetic approach to this polymer is sketched in Figure 1a. The key intermediate in the synthesis is the dihalogenated, alkyl-substituted terphenylene monomer. This compound was obtained through a nickel-catalyzed Grignard coupling[16] between 2-bromo-1,4-dioctylbenzene and *p*-diiodobenzene. The monobrominated dioctylbenzene could be obtained by monobromination of the dioctylbenzene liquid. The latter was also synthesized from a nickel-catalyzed Grignard coupling[16] between dibromobenzene and octyl bromide. The block copolymer was synthesized via a Heck coupling reaction[17] between the terphenylene monomer and *p*-divinylbenzene. The Heck coupling (reaction of an organic halide with a vinylbenzene, giving a carbon–carbon double bond) was previously shown to have a great potential in polymerization reactions[18–20] and leads to the formation of pure trans double bonds with very few side reactions. By using the same Heck coupling with two of the intermediate compounds from the copolymer synthesis, namely, 2-bromo-1,4-dioctylbenzene and *p*-divinylbenzene, we could also obtain a model compound, 1,4-bis(2,5-dioctylstyryl)benzene (Figure 1b). This oligomer, hereafter abbreviated as BDOSB, corresponds to the PPV part from the TOP–PPV copolymer.

The TOP–PPV copolymer could be obtained in good yields via Heck coupling when using the dibrominated terphenylene monomer. Attempts to polymerize the diiodinated terphenylene monomer (not described here) were less successful. They led to low monomer conversion and only small oligomers (dimers, trimers, etc.) formation. This result is surprising since it is known that the Heck reaction is generally more effective with aryl iodides than with aryl bromides. In our case, it turns out that the presence of long aliphatic side chains in the ortho position of the halide induces an important steric hindrance. Presumably the combination of the long side chain with the bulky iodine atom results in difficult formation of the organopalladium intermediate.[17]

GPC measurements with THF as eluent indicated M_w = 4500 (M_w/M_n = 1.7). This molecular weight appears to be relatively low, identically to what has been

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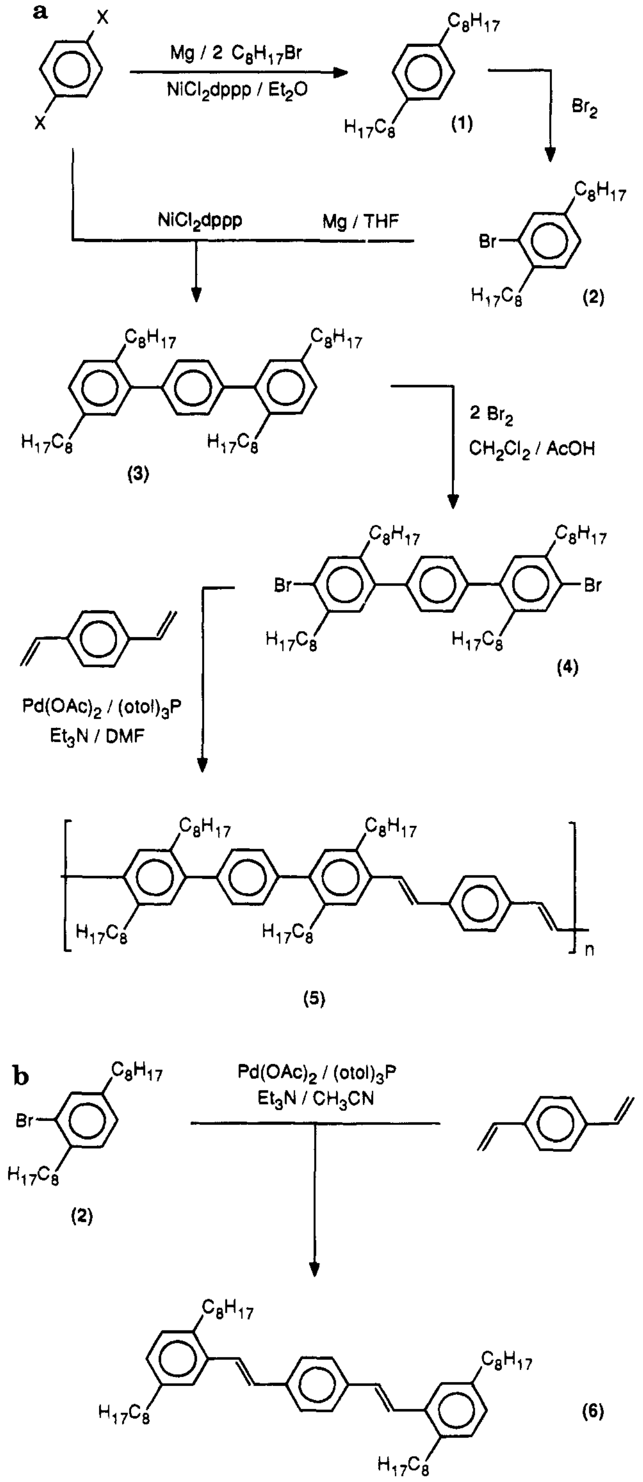

Figure 1. Schematic representation of syntheses: (a) monomers and TOP–PPV copolymer; (b) BDOSB model compound.

observed in other polymerizations of this type.[18,19] It shows that the reaction is rather slow and that the oligomers formed probably become less and less reactive during their growth until they eventually precipitate. Optimization of the reaction conditions and alternative synthetic routes are under investigation.

The solubility of TOP–PPV is very good in common organic solvents such as tetrahydrofuran, chloroform, or toluene. Casting or spin coating from solution produces homogeneous, pinhole-free thin films, as evidenced by the realization of operational LED's (see further on).

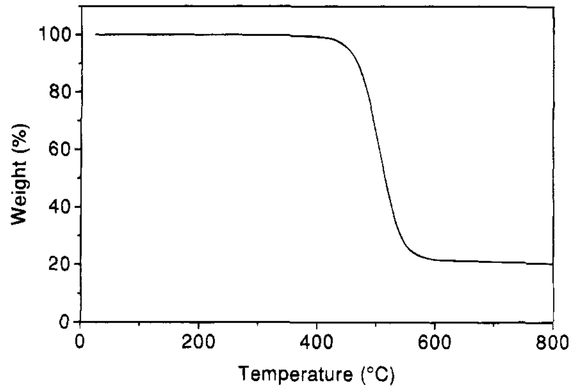

Figure 2. TGA plot of TOP–PPV copolymer under nitrogen.

NMR spectra of the copolymer are globally consistent with the expected repeating unit (see Experimental Section). In the ^{1}H NMR spectrum all the aromatic peaks are between 7 and 8 ppm. The absence of peaks at about 6.5 ppm indicates that no *cis*-vinylene bonds are present. Since the molecular weight is low, small peaks corresponding to vinyl end groups can be seen at 5.3 and 5.9 ppm. In the ^{13}C NMR spectrum a few small extra peaks are also observed in the aromatic region, which render exact assignment difficult. Elemental analysis indicates the presence of some bromine (0.89%) corresponding to terphenylene end groups.

Infrared spectroscopy spectra of the TOP–PPV copolymer show a peak at 960 cm^{-1} that corresponds to the stretching of *trans*-vinylene bonds,[21] whereas no peak corresponding to the stretching of *cis*-vinylene bonds[21] can be seen in the 890–900 cm^{-1} region. This clearly confirms that only trans double bonds are formed by the Heck reaction.

Thermogravimetric analysis (TGA) revealed a very good thermal stability up to 420 °C under nitrogen (Figure 2). This is similar to the stability observed in substituted PPV's.[20] Differential scanning calorimetry (DSC) thermograms show a glass transition at −20 °C and melting of the side chains at 50 °C. Those results are consistent with the structure of the copolymer, i.e., the presence of octyl side chains and a relatively low molecular weight. Increase of the T_g can be achieved by decreasing the length of the side chains (but with a drop in the solubility) and/or by obtaining higher molecular weight.

Optical Properties in Solution

The optical properties of this new copolymer are of primary importance for our purpose. A first step is the study of the absorption and emission features in solution.

The UV–visible absorption spectrum of TOP–PPV in THF solution has a maximum at 365 nm (Figure 3a). The solutions show very intense blue fluorescence with maxima at 422 and 446 nm (Figure 3a). The fluorescence quantum yield was measured as $\Phi = 0.8$ (excitation at 360 nm). In a nonpolar solvent like hexane, absorption and emission are 6 nm blue shifted, and the quantum yield goes even up to $\Phi = 0.9$.

The absorption, emission, and quantum yield of TOP–PPV are comparable to those generally observed for substituted PPV oligomers.[22] We measured those features for the model compound BDOSB. In THF solution the absorption maximum is at 355 nm, and two emission bands are visible at 400 and 420 nm (Figure 3b). The fluorescence quantum yield is $\Phi = 0.8$. There is a

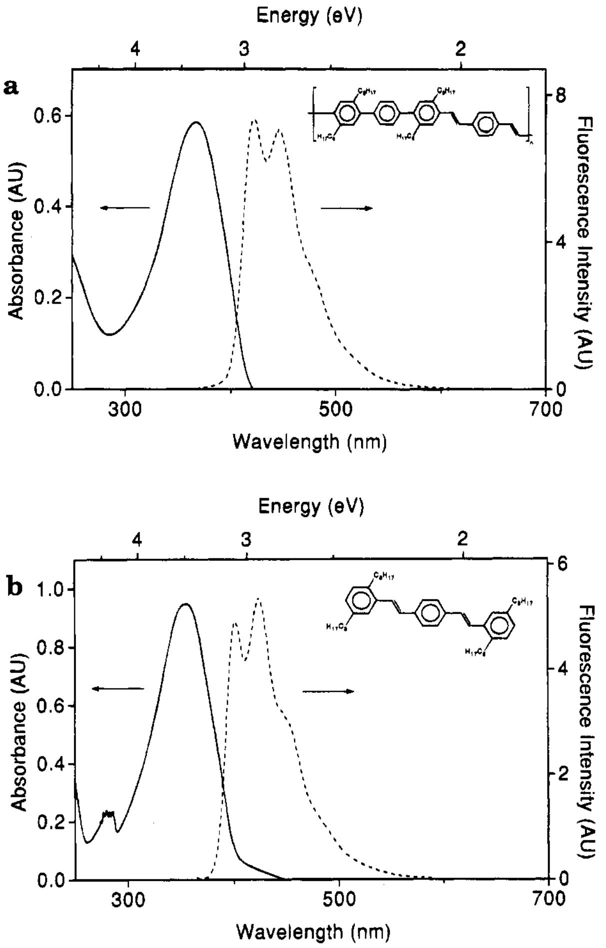

Figure 3. Absorption (—) and emission (- - -) spectra in THF solutions of (a) TOP–PPV copolymer and (b) BDOSB model compound.

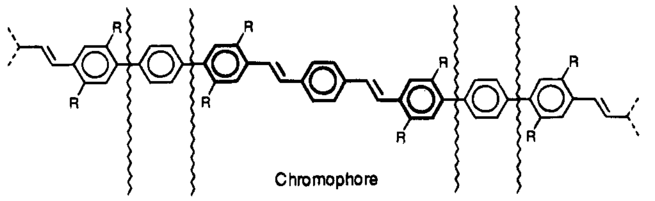

Figure 4. Schematic representation of TOP–PPV copolymer backbone with well-defined chromophores; twisted lines indicate conjugation interruption.

striking similarity between the optical properties of the TOP–PPV copolymer and the BDOSB model compound. The fluorescence quantum yields appear to be exactly the same, and the absorption and emission peaks of the copolymer are simply 10–20 nm red shifted when compared to the oligomer.

Those results confirm that the active chromophores in the copolymer are the PPV blocks (Figure 4). The interruption of the conjugation can be understood by considering the steric interactions on the copolymer backbone. It is shown that even in nonsubstituted polyphenylenes, two adjacent phenyl rings are not coplanar.[23] Steric hindrance between the protons of the phenyls induces a twist of about 23°, which still enables a reasonable overlap of the π orbitals. The presence of bulky side chains, like the octyl chains here, is responsible for a much larger twist angle between the phenyl rings, disabling the possibility of conjugation through the three consecutive phenyl rings from the terphenylene in our copolymer. So the conjugation of the fully unsaturated backbone is regularly interrupted, resulting in well-defined PPV chromophores connected to each other by noncoplanar phenylene groups. A very interesting point is that in this copolymer structure the photoluminescence efficiency in solution does not drop when compared to that of the chromophore molecules.

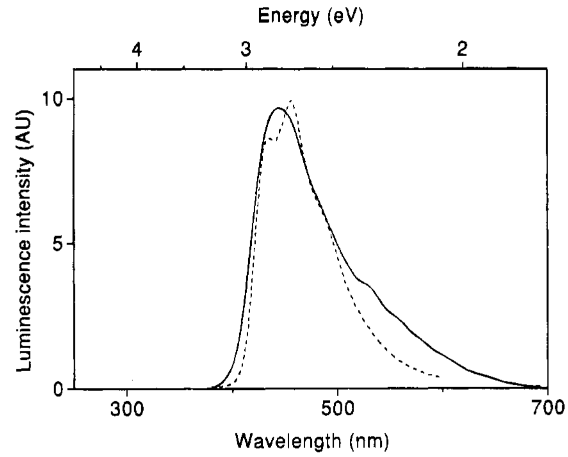

Figure 5. Photoluminescence spectrum (- - -) of TOP–PPV thin film (excitation at 360 nm) and electroluminescence spectrum (—) of an ITO/TOP–PPV/Al device.

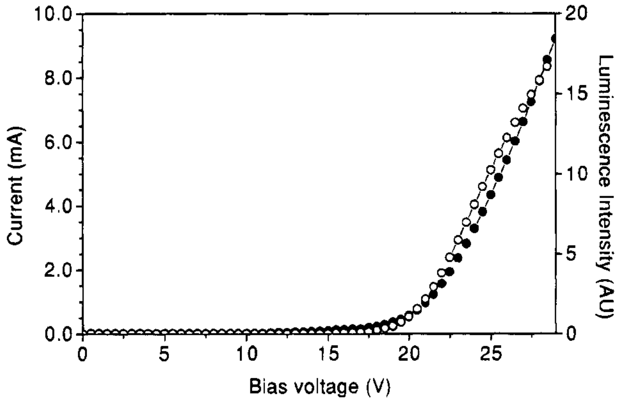

Figure 6. Current–voltage (●) and luminescence–voltage (○) characteristics of an ITO/TOP–PPV/Al device.

The TOP–PPV copolymer also appears to be a very efficient blue laser dye in solution. Those results are reported elsewhere.[24]

Light-Emitting Diodes

Light-emitting devices were fabricated in the following way.[25] A thin polymer film was used as an active layer and was sandwiched between two electrodes. Indium tin oxide was used as a transparent hole-injecting anode, and aluminum as an electron-injecting cathode. By applying a positive voltage to the ITO, current flows through the device and the emitted blue light can be seen through the transparent ITO and its glass substrate.

Figure 5 shows the photoluminescence spectrum of a thin film of TOP–PPV and the electroluminescence spectrum of an ITO/TOP–PPV/Al device. The two spectra are almost identical, indicating that the same excited states are involved in the two processes. The emission is centered at about 440 nm, which is slightly red shifted when compared to the photoluminescence from solutions.

Figure 6 represents typical current–voltage and luminescence–voltage measurements in a device. Current and light arise at almost the same voltage, which increases with the film thickness.[26] The device measured in Figure 6 shows a turn-on voltage of 17.5 V obtained in a 70 nm thick film, corresponding to a field of 2.5×10^8 V/m. This turn-on voltage is relatively high but is consistent with the fact that we are dealing with a high-band-gap polymer in which it is difficult to inject charges. Furthermore, we use here a nonoptimized device configuration.

The external efficiency of the devices was measured in an integrating sphere and found to be in the range of $10^{-2}\%$ photons/electrons. The highest value obtained was 0.03% photons/electrons. Those efficiencies appear to be low but the result has to be tempered since we talk here about *external* quantum efficiencies measured, as said before, on nonoptimized devices. To optimize the devices we can consider the use of a metal with a lower work function (calcium or magnesium, for example) known to facilitate the injection of electrons[27-29] and/or realize devices with multilayer structures including additional charge injection and transport layers.[4,11,12,30]

Conclusion

We synthesized and characterized a new soluble blue-light-emitting copolymer composed of regularly alternating *p*-phenylene and *p*-phenylenevinylene blocks. Steric hindrance introduced by the side chains results in a controlled regular interruption of the conjugation in the unsaturated polymer backbone. This is the first example of a rigid, fully unsaturated copolymer with a well-defined conjugation length. The well-defined conjugated PPV segments give to this copolymer optical properties similar to those observed in small dye molecules, in particular exceptionally efficient blue fluorescence. Light-emitting diodes could be fabricated and show blue electroluminescence. The optimization of the devices will confirm the great potential of this new copolymer.

Experimental Section

Measurements. NMR spectra were collected on a Varian (VXR 300) spectrometer with chloroform-*d* as solvent and internal standard. IR spectra were recorded on a Mattson Instruments FT-IR spectrometer. UV spectra were recorded on an SLM Aminco 3000 Array spectrophotometer. Fluorescence was measured on an SLM Aminco SPF-500 spectrofluorometer. The GPC measurements were performed on a Spectra-Physics 1000 system equipped with a Viscotek H502 viscometer and a Shodex RI-71 refractive index detector coupled to a Dawn light scattering apparatus; polystyrene standards were used for calibration. Thermogravimetric analysis was performed on a Perkin-Elmer Thermal Analysis System 7. Differential scanning calorimetry thermograms were recorded on a Perkin-Elmer DSC 7.

Materials. Diethyl ether was distilled successively over phosphorus pentoxide (P_2O_5) and lithium aluminum hydride ($LiAlH_4$), tetrahydrofuran (THF) was distilled over $LiAlH_4$, and triethylamine was dried over potassium hydroxide (KOH). Other solvents were used as received (P.A. grade). 1-Bromooctane, 1,4-dibromobenzene, 1,4-diiodobenzene, palladium acetate ($Pd(OAc)_2$), and tri-*o*-tolylphosphine were used as received (Janssen Chimica or Aldrich Chemicals). Dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) ($NiCl_2$[dppp]) was synthesized according to the literature.[31] Pure *p*-divinylbenzene was isolated from a commercial mixture of isomers following the literature procedure.[32] All reactions were carried out under a dry argon atmosphere.

Monomer Synthesis. 1,4-Dioctylbenzene (1). A solution of 1-bromooctane (385.8 g, 2.0 mol) in diethyl ether (300 mL) was added slowly to magnesium turnings (72.9 g, 3.0 mol) in diethyl ether (450 mL). The reaction mixture was refluxed for 1 h. The obtained Grignard reagent was added slowly at room temperature to a solution of 1,4-dibromobenzene (189.0 g, 0.8 mol) and $NiCl_2$[dppp] (0.5 g) in dry diethyl ether (600 mL) at such a rate as to maintain gentle boiling of the ether. After addition of another portion of $NiCl_2$[dppp] (100 mg), stirring was continued for 2 days at 30 °C. The reaction mixture was poured into a cold 5% aqueous HCl solution (1 L). After the layers were separated, the water layer was extracted with diethyl ether, the combined ether layers were dried over $MgSO_4$ and filtered, and the solvent was removed by evaporation. Vacuum distillation (168 °C/0.4 mbar) of the crude product provided the pure title product (162.5 g/67%). ^{1}H NMR 0.93 (t, CH_3, 6H), 1.33 (m, CH_2, 20H), 1.65 (m, β-CH_2, 4H), 2.61 (t, CH_2, 4H), 7.14 (s, arom C*H*, 4H); ^{13}C NMR 14.2 (CH_3), 22.8, 29.4, 29.5, 29.6, 31.7, 32.0, 35.7 (CH_2), 128.3 (arom *C*H), 140.1 (arom *C*).

2-Bromo-1,4-dioctylbenzene (2). Bromine (86.4 g, 0.54 mol) was added dropwise to a mixture of 1,4-dioctylbenzene (162.5 g, 0.54 mol) and iodine (0.23 g, 1.84 mmol) under exclusion of light at room temperature. After stirring overnight, the reaction mixture was poured into an aqueous solution (500 mL) of 20% KOH and 10% sodium thiosulfate. Stirring was continued until the color disappeared (ca. 5 min). The aqueous solution was extracted with diethyl ether (2300 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed by evaporation. Kugelrohr distillation (185 °C/0.1 mbar) of the residue provided the title product (175.2 g/85%). ^{1}H NMR 0.91 (t, CH_3, 6H), 1.30 (m, CH_2, 20H), 1.59 (m, β-CH_2, 4H), 2.56/2.70 (m, CH_2, 4H), 7.04 (dd, arom C*H*, 1H), 7.13 (dd, C*H*, 1H), 7.37 (s, C*H*, 1H); ^{13}C NMR 14.0 (CH_3), 22.6, 29.1, 29.2, 29.3, 29.9, 31.2, 31.8 (CH_2), 127.3, 130.0, 132.3 (arom *C*H), 124.1, 139.0, 142.2 (arom *C*).

2,5,2″,5″-Tetraoctyl-*p*-terphenyl (3). 2-Bromo-1,4-dioctylbenzene (175.2 g, 0.46 mol) was added dropwise to magnesium turnings (16.77 g, 0.69 mol) in boiling THF (50 mL). The reaction mixture was refluxed for 0.5 h. The Grignard reagent was then added dropwise to a solution of *p*-diiodobenzene (60.7 g, 0.18 mol) and $NiCl_2$[dppp] (0.5 g) in THF (1 L). When addition was complete, stirring was continued for 2 days at 40 °C. The reaction mixture was poured into a cold 5% aqueous HCl solution (500 mL). After the layers were separated, the water layer was extracted with diethyl ether (2200 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed by evaporation. The crude product was recrystallized twice from a methanol/diethyl ether (1/3) mixture, giving the title product (59.7 g/48%). ^{1}H NMR 0.86 (t, CH_3, 12H), 1.21/1.29 (m, CH_2, 40H), 1.56 (m, β-CH_2, 8H), 2.61 (t, CH_2, 8H), 7.13 (s, arom C*H*, 2H), 7.20 (s, arom C*H*, 4H), 7.36 (s, arom C*H*, 2H); ^{13}C NMR 14.1 (CH_3), 22.6, 29.2, 29.3, 29.5, 31.6, 32.7, 35.6 (CH_2), 127.2, 128.8, 129.1, 130.1 (arom *C*H), 137.6, 140.1, 140.5, 141.4 (arom *C*). Exact mass calcd for $C_{50}H_{78}$, 677.91, measd 677.91. Anal. Calcd for $C_{50}H_{78}$: C, 88.42; H, 11.58. Found: C, 87.99; H, 11.68. Mp 56–58 °C.

4,4″-Dibromo-2,5,2″,5″-tetraoctyl-*p*-terphenyl (4). Bromine (6.6 g, 41.2 mmol) was added carefully to a mixture of 2,5,2″,5″-tetraoctyl-*p*-terphenyl (12.7 g, 18.7 mmol) and a few crystals of iodine in dichloromethane (50 mL) and glacial acetic acid (15 mL) under exclusion of light. After one night of stirring, the reaction mixture was poured into an aqueous solution (20 mL) of 20% KOH and 10% sodium thiosulfate. Stirring was continued until the color disappeared. Layers were separated and the aqueous solution was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed by evaporation. Recrystallization from diethyl ether afforded the pure monomer (8.0 g/51%). ^{1}H NMR 0.87 (t, CH_3, 12H), 1.21/1.29 (m, CH_2, 40H), 1.61 (m, β-CH_2, 8H), 2.56 (t, CH_2, 4H), 2.73 (t, CH_2, 4H), 7.11 (s, arom C*H*, 2H), 7.31 (s, arom C*H*, 4H), 7.47 (s, arom C*H*, 2H); ^{13}C NMR 14.0 (CH_3), 22.6, 29.2, 29.4, 29.5, 31.6, 32.7, 35.6 (CH_2), 123.2 (arom *C*Br), 128.7, 131.5, 133.0 (arom *C*H), 139.1, 139.6, 139.7, 140.6 (arom *C*). Exact mass too high to be measured. Anal. Calcd for $C_{50}H_{76}Br_2$: C, 71.75; H, 9.15; B, 19.09. Found: C, 70.60; H, 8.90; Br, 19.94. Mp 79–80 °C.

Polymer Synthesis. Poly[2,5,2″,5″-tetraoctyl-*p*-terphenyl-4,4″-ylenevinylene-*p*-phenylenevinylene] (5). A mixture of monomer **4** (1.0 g 1.2 mmol), *p*-divinylbenzene (0.155 g, 1.2 mmol), $Pd(OAc)_2$ (0.011 g, 0.05 mmol), tri-*o*-tolylphosphine (0.071 g, 0.23 mmol), triethylamine (2 mL), and DMF (5 mL) was placed in a heavy-wall pressure tube. The tube was degassed, closed (Teflon bushing), and heated to 100 °C. After 40 h of reaction, thin-layer chromatography showed that the monomers were consumed. The reaction mixture was then poured into methanol (75 mL). The precipitated material was filtered off and dried under vacuum, giving a brown-yellow polymer (0.88 g, conversion = 91%). The crude polymer was dissolved in chloroform and then filtered through a small column of Kieselgel to remove traces of catalyst. The resulting solution was concentrated and precipitated in methanol (75 mL). The yellow polymer was collected by filtration and thoroughly dried under vacuum. ^{1}H NMR (broad signals) 0.89 (t, CH_3, 12H), 1.25/1.29/1.5 (m, CH_2, 48H), 2.64 (m, CH_2, 8H), 7.1–7.6 (3 main peaks, arom C*H* and vinyl C*H*, 16H); ^{13}C NMR 14.1 (*C*H_3), 22.6, 29.2, 29.3, 29.5, 31.8, 32.7, 35.6 (*C*H_2), 126.4, 126.8, 128.8, 129.2, 130.1, 131.5 (arom *C*H), 134.7, 137.2, 137.6, 138.1, 138.2, 140.1 (arom *C*). Anal. Calcd for $C_{60}H_{84}$ (repeating unit): C, 89.49; H, 10.51. Found: C, 88.02; H, 10.51; Br, 0.89.

Model Compound Synthesis. 1,4-Bis(2,5-dioctylstyryl)benzene (6). A mixture of 2-bromo-1,4-dioctylbenzene (**2**) (1.7 g, 4.5 mmol), *p*-divinylbenzene (0.25 g, 1.9 mmol), $Pd(OAc)_2$ (0.020 g, 0.09 mmol), tri-*o*-tolylphosphine (0.060 g, 0.20 mmol), triethylamine (2 mL), and acetonitrile (5 mL) was placed in a heavy-wall pressure tube. The tube was degased, closed (Teflon bushing), and heated to 100 °C. After 40 h, the reaction mixture was poured into 5% aqueous HCl (100 mL). The solution was extracted with chloroform (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed by evaporation. Recrystallization from hexane afforded the pure compound (0.616 g/44%). ^{1}H NMR 0.91 (t, CH_3, 12H), 1.30 (m, CH_2, 40H), 1.63 (m, β-CH_2, 8H), 2.64 (t, CH_2, 4H), 2.75 (t, CH_2, 4H), 6.99/7.14 (m, 6H; comprises 1d, olef C*H*, 2H, and 2d, arom C*H*, 4H), 7.37/7.45 (m, 4H; comprises 1d, olef C*H*, 2H, and 1d, arom C*H*, 2H), 7.55 (s, arom C*H*, 4H); ^{13}C NMR 14.1 (*C*H_3), 22.6, 29.3, 29.5, 29.6, 31.3, 31.6, 31.9, 33.1, 35.7 (*C*H_2), 125.5, 126.4, 126.8, 127.8, 129.1, 129.6 (arom *C*H), 135.5, 137.1, 138.0, 140.6 (arom *C*). Anal. Calcd for $C_{54}H_{82}$: C, 88.70; H, 11.30. Found: C, 87.60; H, 11.16. Mp 46–47 °C.

Light-Emitting Devices. A thin polymer film (50–175 nm) was spin coated (1000–5000 rpm) from a filtered (10 μm filter) toluene solution (3%) on an indium tin oxide coated glass substrate. An aluminum electrode was evaporated (vacuum below 10^{-6} mbar) on top of the polymer film with a mask. All fabrication steps were performed in clean room conditions. For photoluminescence studies of thin films, the polymer was spin coated from the same solutions on glass slides.

Film thicknesses were measured with a Sloan Dektak 2030 ST surface texture analysis system. Electroluminescence measurements (I–V–L and quantum efficiencies) were performed on a system comprising a Keithley 236 source–measure unit coupled to a sample holder and a Labsphere integrating sphere with a calibrated silicon photodiode coupled to a SR400 photon counter. Measurements were done at room temperature in air.

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