Conjugated Polymers with Main Chain Chirality. 2. Synthesis of Optically Active Polyarylenes

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ABSTRACT: An optically active polyarylene, (*R*)-**3**, has been prepared from the palladium-catalyzed Suzuki cross-coupling of an optically active binaphthyl molecule, (*R*)-2,2′-bis(hexyloxy)-1,1′-binaphthyl-6,6′-diboronic acid, (*R*)-**2**, with 1,4-dibromobenzene. GPC analysis of (*R*)-**3** shows $M_w = 41\,000$ and $M_n = 20\,000$ (PDI = 2.0). The specific optical rotation of (*R*)-**3** is $[\alpha]_D = -289.4°$ ($c = 0.5$, THF). The UV spectrum of the polymer displays a strong absorption at $\lambda_{max} = 328$ nm. Maximum emissions at 388 and 407 nm are observed in the fluorescence spectrum of (*R*)-**3**. The polymer emits strong blue light under a UV lamp. Another optically active polyarylene, (*R*)-**4**, was also obtained by the polymerization of (*R*)-**2** with 4,4′-dibromobiphenyl. GPC analysis shows its molecular weight is $M_w = 47\,000$ and $M_n = 14\,000$ (PDI = 3.4). The specific optical rotation is $[\alpha]_D = -275°$ ($c = 0.22$, CH_2Cl_2). Polymers *rac*-**3** and *rac*-**4** were synthesized by the polymerization of the racemic monomer *rac*-**2** with either 1,4-dibromobenzene or 4,4′-dibromobiphenyl. Atomic force microscopic study on the polymer films spin-coated on mica shows interesting surface morphology. Pits and pinholes are observed; however, none of the polymers has long-range order.

Introduction

Since the discovery of the high conductivity of doped polyacetylenes, the study of organic conducting polymers has attracted very broad attention.[2] Conjugated materials of different structures including polyacetylenes, poly(*p*-phenylenes), poly(*p*-phenylenevinylenes), polypyrroles, and polythiophenes have been synthesized.[2] However, remarkably few studies on optically active conjugated polymers have been reported.[3] Recently, we prepared (*R*)-**1** as one of the first conjugated polymers that contains an inherently chiral configuration in the main chain.[4] This polymer is synthesized by the Suzuki coupling of an optically active binaphthyldiboronic acid monomer with a conjugated aryl dibromide linker molecule, and it shows high fluorescence quantum efficiency and emits blue light.

Among conjugated polymers, poly(*p*-phenylene) (PPP) represents an especially interesting class of materials.[2,5] Like other conjugated polymers, PPP shows greatly enhanced conductivity upon doping. It also exhibits excellent resistance to oxidation, radiation, and thermal degradation. The use of PPP as electrode materials in electrochemical cells and in high energy density rechargeable batteries is among many potential applications of this polymer.[5] In this paper, we report the synthesis of optically active PPP analogs by carrying out the Suzuki cross-coupling of optically active binaphthylboronic acids with aryl bromides.

Results and Discussion

Based on the procedure developed recently in our laboratory, optically active 1,1′-bi-2-naphthol can be conveniently prepared from 2-naphthol in large scale with high yield and high optical purity.[8] Using (*R*)-1,1′-bi-2-naphthol as the starting material, (*R*)-2,2′-bis-(hexyloxy)-1,1′-binaphthyl-6,6′-diboronic acid, (*R*)-**2**, the monomer for the synthesis of main chain chiral conjugated polymers, has been readily synthesized.[4] When (*R*)-**2** is treated with 1,4-dibromobenzene in the presence of tetrakis(triphenylphosphine)palladium(0) catalyst, the Suzuki coupling occurs to generate a chiral polymer (*R*)-**3** (Scheme 1).[9] This polymer has a conjugated aromatic backbone and is an optically active analog of PPP. GPC analysis (THF, polystyrene standard) indicates that the molecular weight of (*R*)-**3** is $M_w = 41\,000$ and $M_n = 20\,000$ (PDI = 2.0). This polymer is soluble in common organic solvents such as THF, chloroform, methylene chloride, and benzene. The specific optical rotation of (*R*)-**3** is $[\alpha]_D = -289.4°$ ($c = 0.5$, CH_2Cl_2). The chiral configuration of the polymer is quite stable. When the toluene solution of the polymer is heated at reflux for 40 h, there is only 5% decrease in the absolute value of its optical rotation.

Figure 1 is the ^1H NMR spectrum of (*R*)-**3** in chloroform-*d*. The aromatic region in this spectrum is remarkably well-resolved and each signal has been assigned. In the infrared spectrum of the polymer, a strong C−H out-of-plane bending absorption is observed at 814 cm^{-1}, a characteristic of the *p*-phenylene moiety. The UV spectrum of the methylene chloride solution of the polymer shows a maximum absorption at $\lambda_{max} = 328$ nm. When the polymer is spin-coated on glass slides, the UV absorption of the polymer films is shifted slightly to a shorter wavelength, $\lambda_{max} = 324$ nm. When excited at 328 nm, the fluorescence spectrum of the methylene chloride solution of the polymer shows strong emissions at $\lambda_{emi} = 388$ and 407 nm.

Thermogravimetric analysis (TGA) shows that the onset decomposition temperature of (*R*)-**3** is 394 °C. At 476 °C, the polymer loses ∼32% of its mass, corresponding to the loss of the hexyl groups in (*R*)-**3**. The thermal stability of this polymer at high temperature is strongly influenced by its purity. As shown in Figure 2a, ca. 90% of the polymer mass has been lost at 800 °C when (*R*)-**3** is purified by precipitation out of methylene chloride solution with methanol twice. When (*R*)-**3** is purified further by the same precipitation procedure, it becomes much more stable from 480 to 800 °C (Figure 2b). This result demonstrates that trace amounts of impurities, probably some residual palladium species, can cause

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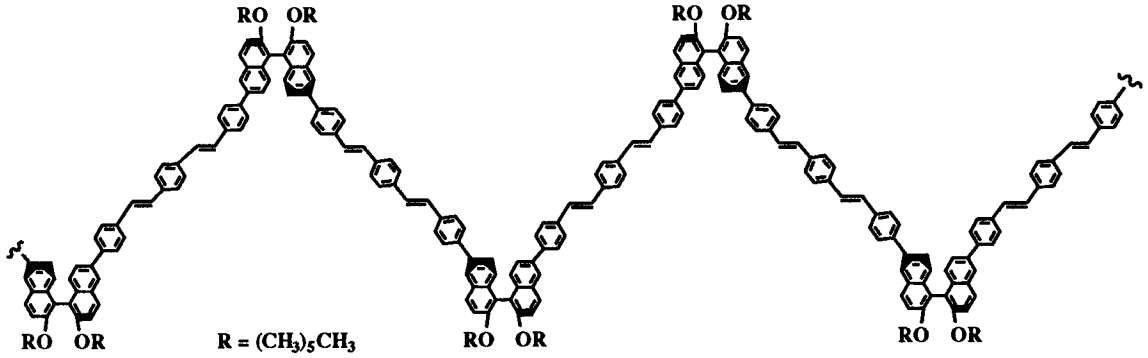


(*R*)-**1**

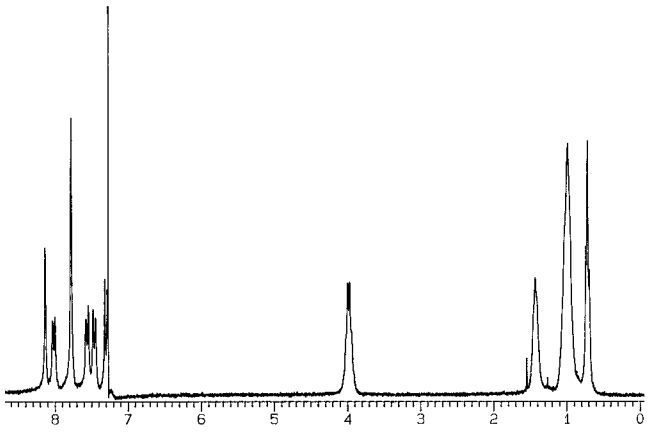


Figure 1. ^{1}H NMR spectrum of (*R*)-**3**.

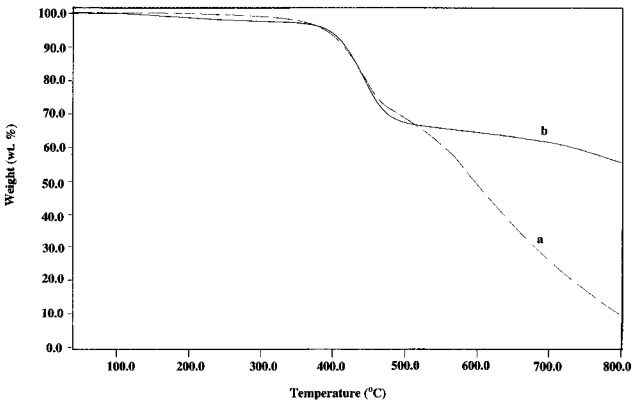
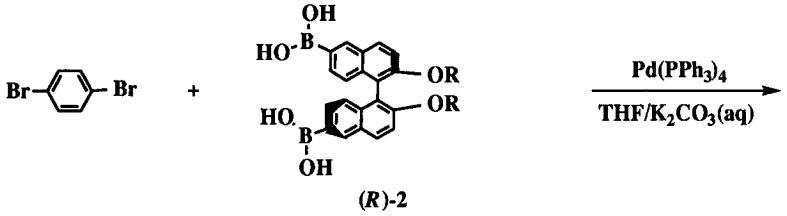


Figure 2. (a) TGA plot of (*R*)-**3** (heating rate 40 °C/min). (b) TGA plot of (*R*)-**3** after rigorous purification (heating rate 40 °C/min).

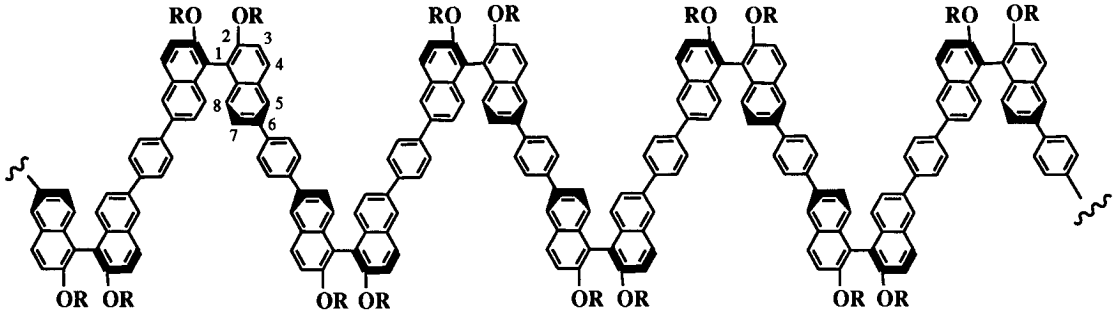
large differences in the thermal stability of this material at high temperature. The specific optical rotation of the rigorously purified (*R*)-**3** is $[\alpha]_D = -286.7°$ ($c = 0.45$, CH_2Cl_2). Differential scanning calorimetry (DSC) indicates a high glass transition temperature (T_g) of 202 °C for the polymer.

The Suzuki cross-coupling polymerization of 1,4-dibromobenzene with *rac*-**2** has produced polymer *rac*-**3**. GPC analysis of *rac*-**3** gives $M_w = 37\,000$ and $M_n = 22\,000$ (PDI = 1.7). The ^{1}H and ^{13}C NMR spectra of *rac*-**3** are also very well resolved and identical to those of (*R*)-**3**. This may indicate that either the stereoregularity of the polymer does not affect the NMR signals in this polymer system or *rac*-**3** is actually a highly stereoregular polymer made of a pair of racemic polymers (*R*)-**3** and (*S*)-**3**. Whether this polymerization process is highly stereoselective awaits further investigation. TGA shows that from 386 to 469 °C, *rac*-**3** loses its hexyl groups, as (*R*)-**3** does, to give a highly stable material. DSC shows its T_g at 193 °C. The UV spectrum of the polymer in methylene chloride solution shows $\lambda_{max} = 328$ nm. *rac*-**3** shows emission maxima at 387 and 405 nm when excited at 328 nm.

Scheme 1. Synthesis of the Optically Active Polyarylene (*R*)-3

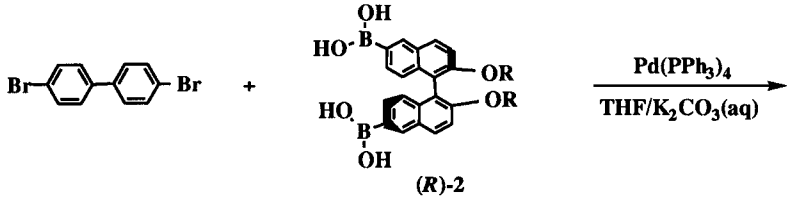


(*R*)-**2**

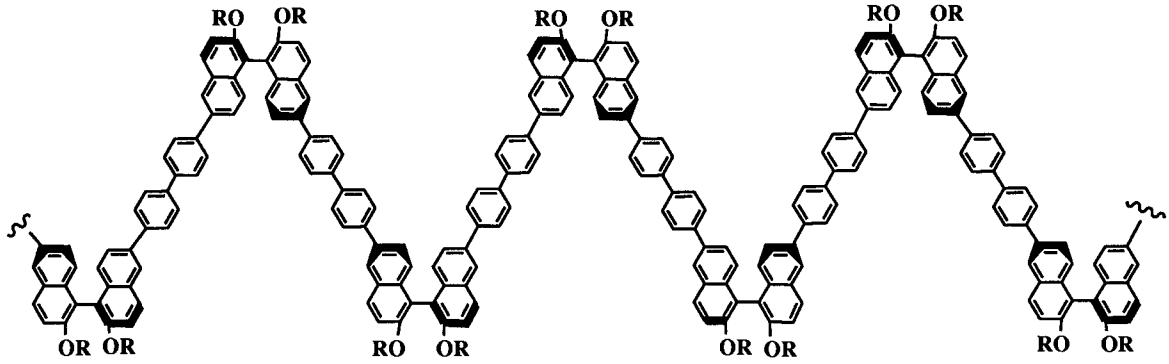


(*R*)-**3** R = $-CH_2(CH_2)_4CH_3$

Scheme 2. Synthesis of the Optically Active Polyarylene (*R*)-4

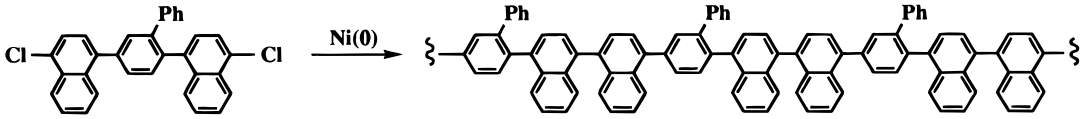


(*R*)-2



(*R*)-4

Scheme 3. Polymerization of 2,5-Bis(4-chloro-1-naphthyl)biphenyl



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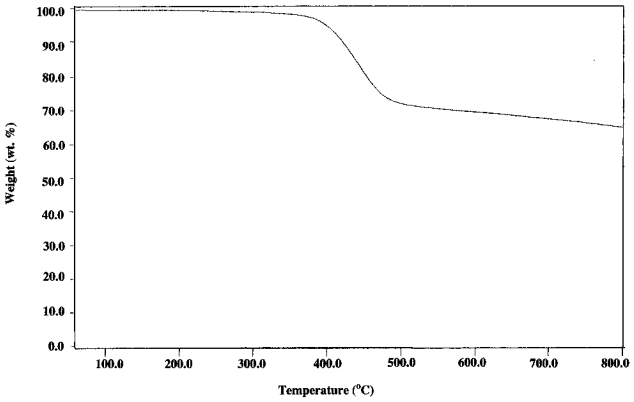


Figure 3. TGA plot of (*R*)-**4** (heating rate 40 °C/min).

Another optically active conjugated polymer, (*R*)-**4**, that contains a longer conjugated repeat unit has also been prepared by the Suzuki coupling of (*R*)-**2** with 4,4′-dibromobiphenyl (Scheme 2). GPC analysis of (*R*)-**4** shows $M_w = 47\,000$ and $M_n = 14\,000$ (PDI = 3.4). The specific optical rotation of the polymer is $[\alpha]_D = -275°$ ($c = 0.22$, CH_2Cl_2). This polymer is soluble in common organic solvents. Both the ^1H and ^{13}C NMR spectra of (*R*)-**4** are very well resolved and are similar to those of (*R*)-**3**. A strong infrared absorption for the *p*-phenylene moiety is observed at 814 cm^{-1}. TGA shows that (*R*)-**4** loses ~28% of its mass (the hexyl groups of the polymer) from 396 to 478 °C. The polymer is very stable after the loss of its hexyl groups, and no significant mass change is observed from 480 °C up to 800 °C (Figure 3). DSC shows the T_g of (*R*)-**4** at 229 °C. The UV spectrum of the polymer in methylene chloride solution displays $\lambda_{max} = 334$ nm. When the polymer is spin-coated on glass slides, the polymer film gives the same UV absorption maximum as that of the polymer solution. The fluorescence spectrum of the polymer solution exhibits emission maxima at 415 and 396 nm when excited at 334 nm.

rac-**4** is also prepared from the reaction of *rac*-**2** with 4,4′-dibromobiphenyl. Its NMR spectra are identical to those of (*R*)-**4**. GPC of *rac*-**4** shows $M_w = 92\,000$ and $M_n = 23\,000$ (PDI = 4.0). The thermal stability of *rac*-**4** is similar to that of (*R*)-**4** as shown by TGA. *rac*-**4** loses its hexyl groups from 389 to 467 °C, generating a very stable material. DSC indicates that the polymer has a T_g at 241 °C. The UV spectrum of the polymer solution shows $\lambda_{max} = 332$ nm. In the fluorescence spectrum of *rac*-**4** in methylene chloride solution, emission maxima are observed at 415 and 396 nm when the polymer is excited at 332 nm.

Percec *et al.* have studied the Ni(0)-mediated polymerization of 2,5-bis(4-chloro-1-naphthyl)biphenyl (Scheme 3).[9] This process produces an optically inactive oligomer **5** ($M_n \approx 2000$). **5** is composed of a mixture of *R* and *S* binaphthyl units. An optically active analog of **5** has recently been obtained by Tour *et al.* In their work, an optically active multifunctional 1,1′-binaphthyl monomer **6** was treated with (1,5-cyclooctadiene)nickel-(0) to generate an oligomer **7** (Scheme 4).[10] The specific optical rotation of **7** is $[\alpha]_D = -56°$. This value is similar to that of its monomer ($[\alpha]_D = -86°$). However, in the polymer system we report here, the optical rotations of the polymers (*R*)-**3** and (*R*)-**4** are about −300°. Thus, these polymers rotate the plane of polarized light to the opposite direction of their monomer {(*R*)-**2**, $[\alpha]_D = +35.6°$ ($c = 0.22$, DMSO)}[4] and have greatly enhanced optical rotations. The circular dichroism spectra of (*R*)-**3** and (*R*)-**4** have been obtained (Figures 4 and 5). The main chain chirality of the conjugated polymer systems leadsto the observed strong CD effects (Table 1). The

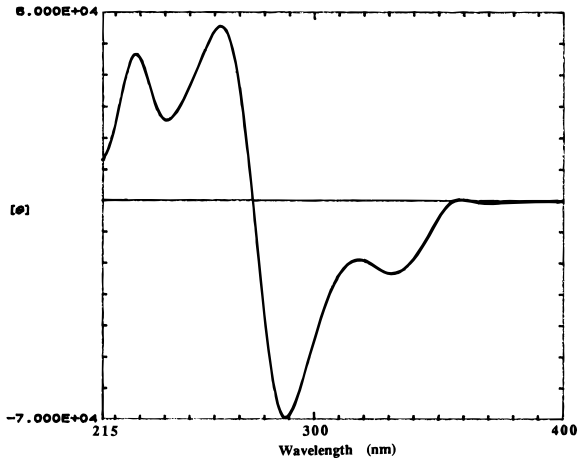


Figure 4. Circular dichroism spectrum of (*R*)-**3**.

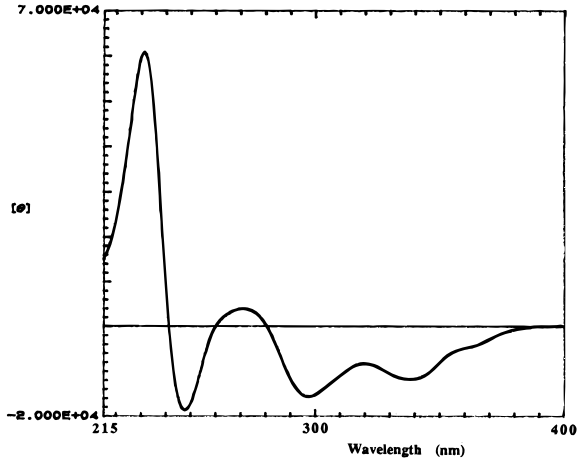
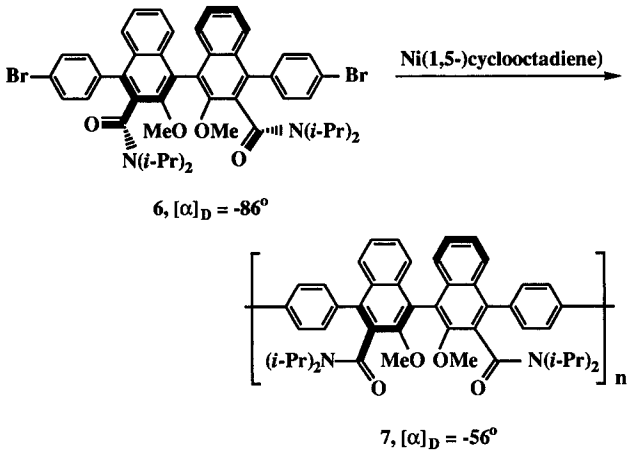


Figure 5. Circular dichroism spectrum of (*R*)-**4**.

Scheme 4. Synthesis of an Oligomer 7



calculation of molar ellipticity is based on the molecular weights of the polymer repeat units.

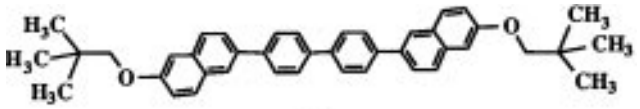
In solution, the mean dihedral angle of a binaphthyl molecule is approximately 90°. Thus conjugation between the two naphthalene rings is minimal and the absorption spectrum of 1,1′-binaphthyl in solution is approximately additive over the two constituent units.[11] To study the conjugation in the binaphthyl-based polymers, compound **8**, the repeat unit of polymer (*R*)-**3**, was synthesized (Scheme 5). During the preparation of **8**, we were initially frustrated by the insolubility of this molecule. The repeat unit prepared from either 6-methoxy-2-naphthylboronic acid or 6-(hexyloxy)-2-naphthylboronic acid is not soluble in any organic solvent, which is a surprise since both of the polymers (*R*)-**3** and *rac*-**3** are soluble in a number of organic solvents. This unexpected behavior of the repeat unit might be due to the intermolecular $\pi-\pi$ stacking of this planar molecule. In contrast, because of the chiral configuration of the binaphthyl units in the polymers, the main chains of (*R*)-**3** and *rac*-**3** are not planar and interchain $\pi-\pi$ stacking of these polymers is probably very small, which makes them soluble in organic solvent. In order to make a soluble repeat unit, neopentyl groups are introduced. In DMF solution, neopentyl iodide reacts with 6-bromo-2-naphthol to give **9** (Scheme 5). **9** is then converted to the boronic acid **10** by reaction with magnesium and trimethyl borate. The Suzuki coupling of **10** with 1,4-dibromobenzene produces the repeat unit **8**, which is found to be soluble in a number of organic solvents including chloroform and methylene chloride. This enhanced solubility may be the result of the reduced intermolecular $\pi-\pi$ stacking when bulky neopentyl groups are attached to the repeat unit.

Table 1. Molar Ellipticity from the CD Spectra of (*R*)-3 and (*R*)-4

polymer	$\lambda_{CD\ (nm)}$	$[\theta]_\lambda \times 10^{-5}$ (deg·L/mol·cm)
(*R*)-**3**	228	2.46
	262	2.54
	285	−3.14
	331	−1.04
(*R*)-**4**	232	4.2
	247	−1.23
	273	0.30
	297	−0.98
	340	−0.69
	364	−0.25

The UV spectrum of **8** in methylene chloride solution displays a major absorption at λ_{max} = 322 nm. The fluorescence spectrum of **8** shows emission maxima at λ_{emi} = 378, 396, and 417 nm when excited at 322 nm. Comparing the UV spectrum of **8** with those of (*R*)-**3** and *rac*-**3**, only a very small red shift (∼6 nm) from the repeat unit to the polymers is observed. This indicates that the conjugation in the polymers is almost the same as that of its repeat units and there is essentially no conjugation between the adjacent repeat units in these polymers. Thus the degree of conjugation in the polymer is determined by the repeat unit.

From the Suzuki coupling of **10** with 4,4′-dibromobiphenyl, compound **11** is also synthesized as the repeat unit of polymers (*R*)-**4** and *rac*-**4**. The one extra phenyl ring in **11** makes this molecule much less soluble than



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8. The UV spectrum of **11** in methylene chloride solution shows λ_{max} = 324 nm. The fluorescence spectrum of **11** displays λ_{emi} = 387, 408, and 418 nm when excited at 324 nm. The UV spectroscopic study shows only a small red shift (∼10 nm) in the absorption maxima from the repeat unit **11** to polymers (*R*)-**4** and *rac*-**4**, indicating almost no extended conjugation between the repeat units in these polymers. The bandgaps of polymers **3** and **4** are similar to that of an alkylated soluble poly(*p*-phenylene), **12** (λ_{max} = 330

Scheme 5. Synthesis of the Repeat Unit 8

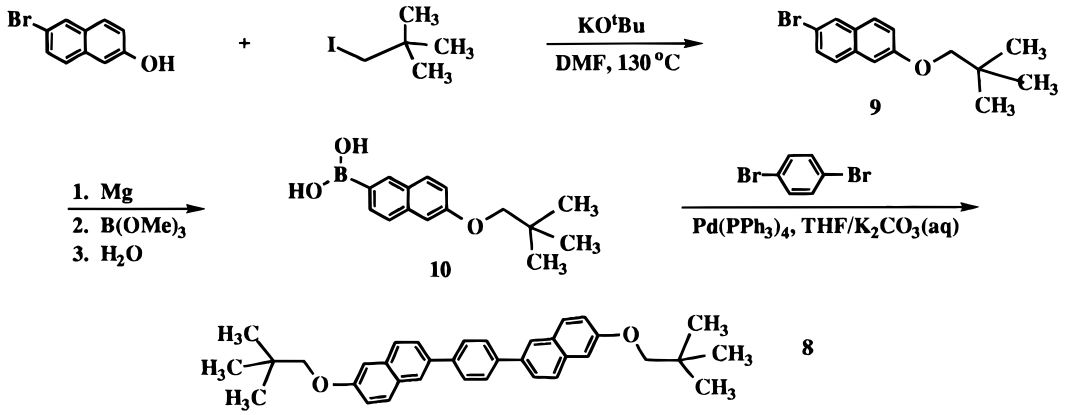
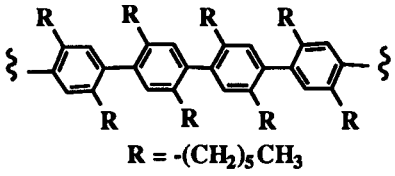


Table 2. UV Absorption and Fluorescence Spectroscopic Data of the Polymers and the Repeat Units

	UV absorption (CH_2Cl_2), λ_{max} (nm)	fluorescence (CH_2Cl_2), λ_{emi} (nm)
(*R*)-**3**	234, 282, 328	388, 407
rac-**3**	232, 282, 328	387, 405
(*R*)-**4**	238, 293, 334	396, 415
rac-**4**	240, 293, 332	396, 415
8	234, 272, 322	378, 396, 417
11	240, 280, 324	408, 389

nm).[12] Table 2 summarizes the UV absorption and fluorescence spectroscopic data of **3**, **4**, **8**, and **11**.



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To investigate if the optically active polymers and the polymers made from racemic monomers could have morphological differences at the submicron level, the surface morphology of these polymers was studied using atomic force microscopy (AFM).[13,14] No long-range order (periodicity) on the surfaces was observed, which is typical for most polymer films.[15] These materials were spin coated on freshly cleaved muscovite mica before imaging. As shown in Figure 6, both *rac*-**4** and (*R*)-**4** are rough and porous. *rac*-**4** has pits which range from 500 to 1000 Å in depth and 1000 to 2000 Å in diameter. There are lots of pinholes which range from 100 to 300 Å in depth and 2000 to 3500 Å in diameter. In contrast, (*R*)-**4** shows a considerably rougher surface with only a few large shallow pits. These shallow pits range from 0.5 to 2.0 μm in diameter and 100 to 250 Å in depth.

The surface morphology of *rac*-**3** is similar to that of (*R*)-**4**. The image of *rac*-**3** shown in Figure 7 reveals pits ranging from 400 to 600 Å in depth and 0.5 to 2 μm in diameter. Differing from (*R*)-**4**, many pinholes are present at the boundaries between the pits. These pinholes are similar in geometry and size, ranging from 1000 to 2000 Å in diameter and 400 to 600 Å in depth. (*R*)-**3** exhibits large pits whose size ranges from 0.5 to 1.5 μm in diameter and 1000 to 1500 Å in depth. Very interestingly, pinholes are present both at the boundaries of the pits and at the bottom of the pits. The size of the pinholes varies. The smallest one is 2000−3000 Å in diameter and 200−400 Å in depth. Larger pinholes are in the range of 0.5−1 μm in diameter and 500−1500 Å in depth.

In summary, main chain chiral polyarylenes have been synthesized and characterized. These materials are soluble in common organic solvents and thus easy to process. The chiral configuration of the polymers has shown very good thermal stability. Study of the repeat units of these polymers demonstrates that the conjugation of these main chain chiral conjugated polymers is determined by the conjugation in the repeat unit. It is therefore possible to chemically tune the electrical and optical properties of these materials by varying the conjugated linker molecules. We are currently studying the application of these chiral conjugated polymers in asymmetric electrosynthesis by using electrodes coated with these materials.

Experimental Section

General Data. NMR spectra were recorded on JEOL 270 MHz and JEOL 400 MHz spectrometers. Infrared spectra were recorded on a 2020/Galaxy Series FT-IR spectrometer by preparing KBr pellets of the materials. Elemental analyses were carried out using a Perkin-Elmer 2400 Series II CHN S/O analyzer. Mass spectra were obtained using aHewlett-Packard 5890 Series II GC/DIP MS. High-resolution fast atom bombardment (FAB) mass spectroscopic analyses were done by the University of California Riverside mass spectroscopy facility. Thermogravimetric analyses were carried out using a Perkin-Elmer TGA 7 analyzer. Gel permeation chromatography (GPC) utilized a Waters 510 HPLC pump, a Waters 410 differential refractometer, and Ultrastyragel Linear GPC columns. THF was used as the eluting solvent in the GPC analysis, and polystyrene standards were used. UV−vis spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Emission spectra were taken using a Spex Fluorolog spectrofluorometer. Circular dichroism spectra were recorded using a JASCO J-710 spectropolarimeter. Optical rotations were measured on a JASCO polarimeter at 589 nm. Differential scanning calorimetry studies were carried out using a Perkin-Elmer DSC 7. The atomic force microscopy images were taken using a homemade instrument.

THF and ether were dried with sodium benzophenone. 1,4-Dibromobenzene, 4,4′-dibromobiphenyl, 6-bromo-2-naphthol, neopentyl iodide, magnesium, trimethyl borate, and potassium *tert*-butoxide were purchased from Aldrich and used directly. Tetrakis(triphenylphosphine)palladium(0) was purchased from Strem Chemicals and used directly.

Synthesis of the Optically Active Polymer (*R*)-3. Under nitrogen, to a mixture of (*R*)-**2** (271 mg, 0.5 mmol) and 1,4-dibromobenzene (116 mg, 0.5 mmol) in THF (5.0 mL) and K_2CO_3 (7.5 mL, 1 M aqueous solution) was added a THF solution (2.5 mL) of $Pd(PPh_3)_4$ (25 mg, 0.022 mmol). The resulting mixture was refluxed for 48 h. The organic layer was separated and then diluted with CH_2Cl_2 (50 mL). The solution was washed with 1 N HCl (20 mL) and brine (10 mL). After separation, the solvent of the organic layer was removed to give a yellowish solid. The solid was redissolved in CH_2Cl_2

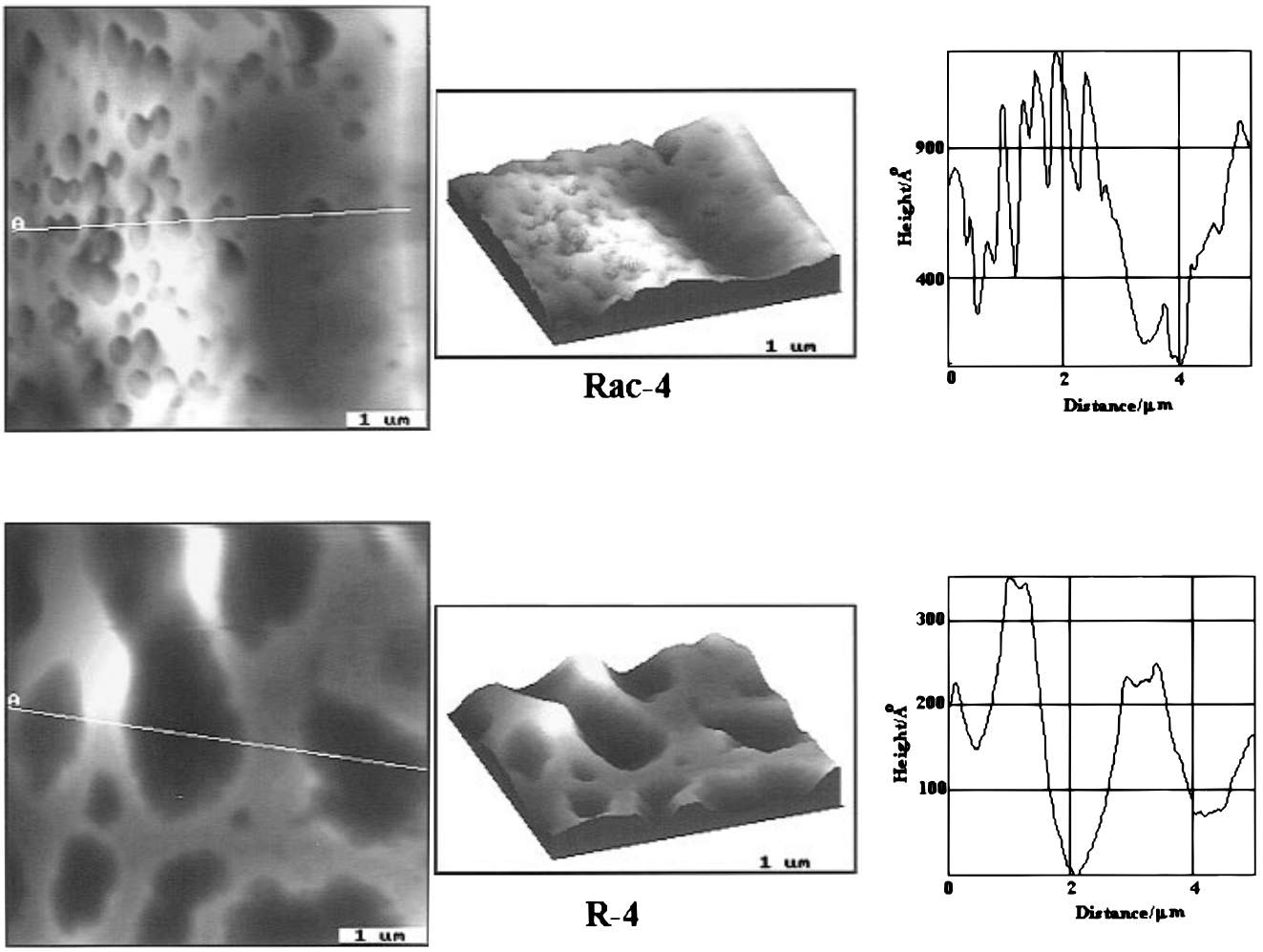

Figure 6. AFM images of *rac*-**4** (top) and (*R*)-**4** (bottom).

and precipitated out twice with MeOH. The solid, (*R*)-**3**, was isolated by centrifugation and was dried under vacuum at room temperature for 24 h. The yield was 90% (238 mg). $[\alpha]_D = -289.4°$ ($c = 0.5$, CH_2Cl_2). $[\alpha]_D = -274.0°$ ($c = 0.5$, CH_2Cl_2, after refluxing in toluene for 40 h). $[\alpha]_D = -266.0°$ ($c = 0.5$, CH_2Cl_2, after refluxing in toluene for another 24 h). GPC (THF, polystyrene standard): $M_w = 41\,000$ and $M_n = 20\,000$ (PDI = 2.0). DSC: $T_g = 202$ °C. TGA: $T_{onset} = 394$ °C. UV−vis λ_{max} (CH_2Cl_2, nm) 234, 282, 328. UV−vis λ_{max} (thin films spin-coated on glass slides, nm) 286, 324. Fluorescence λ_{emi} (CH_2Cl_2, nm) 388, 407 ($\lambda_{exc} = 328$ nm). FT-IR (KBr, cm^{-1}) 2924 (s), 2861 (s), 1591 (s), 1522 (w), 1491 (s), 1462 (s), 1400 (s), 1341 (s), 1271 (s), 1244 (s), 1092 (s), 1057 (s), 943 (w), 885 (w), 814 (s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 2H, H-5), 8.02 (d, $J = 7.5$ Hz, 2H, H-4), 7.78 (s, 4H), 7.56 (d, $J = 9.1$ Hz, 2H, H-7), 7.46 (d, $J = 7.5$ Hz, 2H, H-3), 7.30 (d, $J = 9.1$ Hz, 2H, H-8), 3.98 (br, 4H), 1.43 (br, 4H), 0.98 (br, 12H), 0.72 (br, t, $J = 6$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.73, 139.81, 135.57, 133.46, 129.48 (including a shoulder), 127.46, 126.08, 125.62, 125.57, 120.47, 116.19, 69.76, 31.34, 29.35, 25.34, 22.46, 13.91. Anal. Calcd for $C_{38}H_{40}O_2$: C, 86.32; H 7.62. Found: C, 85.59; H, 7.45.

Synthesis of the Polymer *rac*-3. *rac*-**3** was prepared similarly to (*R*)-**3** in 91% yield by polymerization of *rac*-**2** with 1,4-dibromobenzene. GPC (THF, polystyrene standard): $M_w = 37\,000$ and $M_n = 22\,000$ (PDI = 1.7). DSC: $T_g = 193$ °C. TGA: $T_{onset} = 386$ °C. UV−vis λ_{max} (CH_2Cl_2, nm) 232, 282, 328. Fluorescence λ_{emi} (CH_2Cl_2, nm) 387, 405 ($\lambda_{exc} = 328$ nm). FT-IR (KBr, cm^{-1}) 2928 (s), 2866 (s), 1624 (w), 1593 (s), 1522 (s), 1491 (s), 1462 (s), 1400 (s), 1341 (s), 1271 (s), 1244 (s), 1094 (s), 1057 (s), 945 (w), 887 (w), 814 (s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 2H, H-5), 8.02 (d, $J = 8.6$ Hz, 2H, H-4), 7.78 (s, 4H), 7.56 (d, $J = 8.6$ Hz, 2H, H-7), 7.47 (d, $J = 8.1$ Hz, 2H, H-3), 7.30 (d, $J = 8.6$ Hz, 2H, H-8), 3.99 (br, m, 4H), 1.44 (br, 4H), 0.99 (br, 12H), 0.73 (br, t, $J = 7$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.73, 139.83, 135.57, 133.46, 129.48, 127.49, 126.11, 125.65, 125.57, 120.47, 116.19, 69.76, 31.34, 29.35, 25.34, 22.48, 13.94. Anal. Calcd for $C_{38}H_{40}O_2$: C, 86.32; H, 7.62. Found: C, 85.18; H, 7.63.

Synthesis of the Optically Active Polymer (*R*)-4. To a mixture of (*R*)-**2** (136 mg, 0.25 mmol) and 4,4′-dibromobiphenyl (78 mg, 0.25 mmol) in THF (5.0 mL) and K_2CO_3 (7.5 mL, 1 M aqueous solution) was added a THF solution (2.5 mL) of Pd(PPh_3)$_4$ (15 mg, 0.013 mmol). The resulting mixture was refluxed for 24 h. The organic layer was separated and then diluted with CH_2Cl_2 (30 mL). This solution was washed with 1 N HCl (10 mL) and brine (10 mL). After separation, the solvent of the organic layer was removed to give a grayish solid which was redissolved in CH_2Cl_2 and precipitated out twice with MeOH. The solid, (*R*)-**4**, was isolated by centrifugation and was dried under vacuum at room temperature for 24 h. The yield was 93% (142 mg). $[\alpha]_D = 275°$ ($c = 0.22$, CH_2Cl_2). GPC (THF, polystyrene standard): $M_w = 47\,000$ and $M_n = 14\,000$ (PDI = 3.4). DSC: $T_g = 229$ °C. TGA: $T_{onset} = 396$ °C. UV−vis λ_{max} (CH_2Cl_2, nm) 238, 293, 334. UV−vis λ_{max} (thin films spin-coated on glass slides, nm) 294, 334. Fluorescence λ_{emi} (CH_2Cl_2, nm) 396, 415. FT-IR (KBr, cm^{-1}) 2951 (s), 2934 (s), 2861 (s), 1624 (w), 1593 (s), 1493 (s), 1466 (s), 1400 (m), 1343 (s), 1277 (s), 1246 (s), 1094 (s), 1059 (s), 1003 (m), 945 (w), 889 (w), 814 (s). ^{1}H NMR (400 MHz, $CDCl_3$, broad peaks) δ 8.14 (s, 2H), 8.03 (d, $J = 8.5$ Hz, 2H), 7.78−7.76 (two broad peaks, 8H), 7.57 (d, $J = 8.1$ Hz, 2H), 7.47 (d, $J = 9.1$ Hz, 2H), 7.31 (d, $J = 9.1$ Hz, 2H), 3.99 (m, 4H), 1.44 (br, 4H), 0.98 (br, 12H), 0.73 (t, $J = 6.5$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.78, 140.19, 139.25, 135.51, 133.51, 129.48, 127.54, 127.31, 126.13, 125.62, 120.45, 116.19, 69.76, 31.34, 29.35, 25.34, 22.48, 13.94. Anal. Calcd for $C_{44}H_{44}O_2$: C, 87.38; H, 7.33. Found: C, 86.49; H, 7.35.

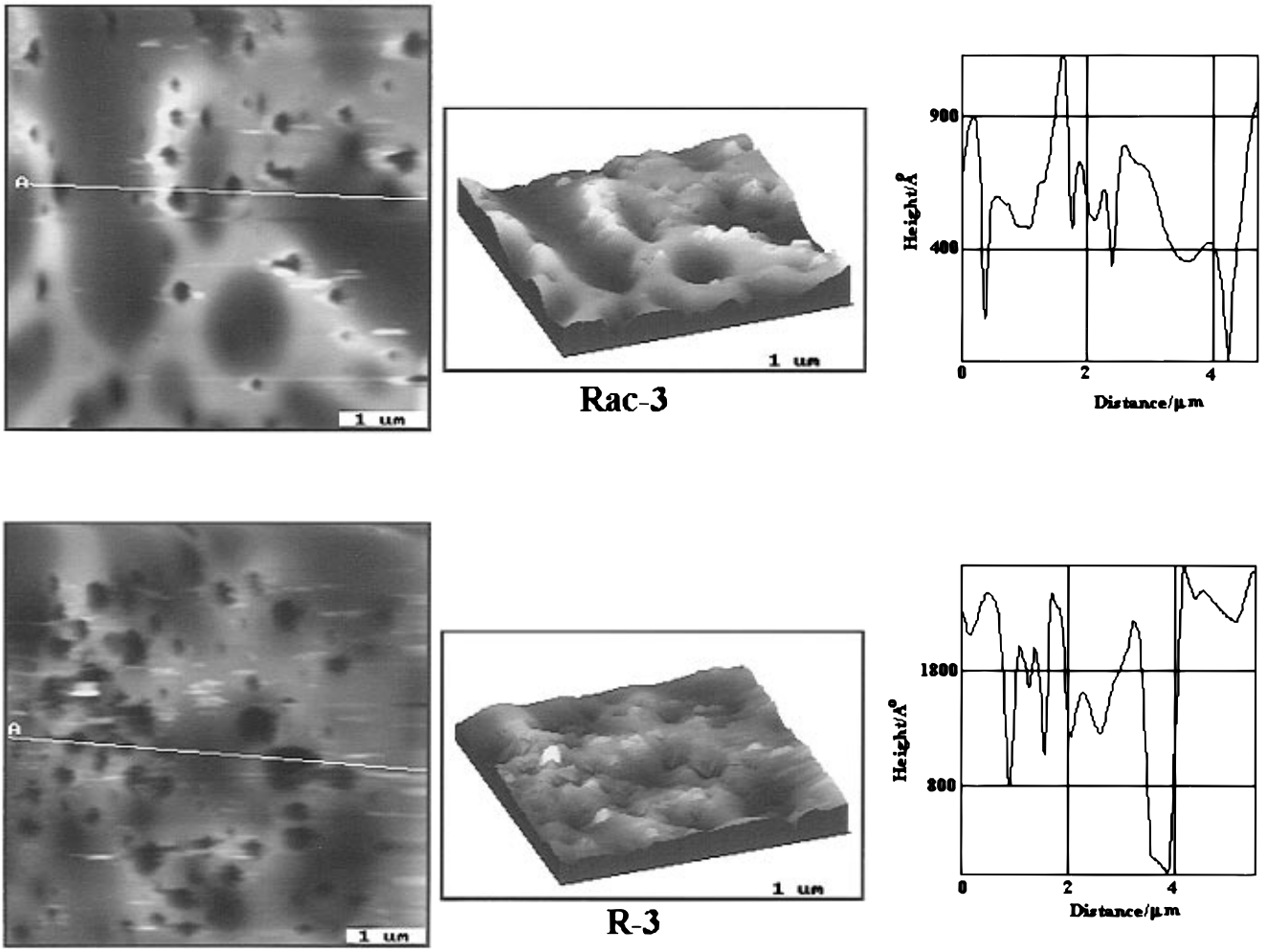

Figure 7. AFM images of *rac*-**3** (top) and (*R*)-**3** (bottom).

Synthesis of the Polymer *rac*-4. *rac*-**4** was prepared similarly to (*R*)-**4** in 94% yield by polymerization of *rac*-**2** with 4,4′-biphenyl. GPC (THF, polystyrene standard): $M_w = 92\,000$ and $M_n = 23\,000$ (PDI = 3.9). DSC: $T_g = 241$ °C. TGA: $T_{onset} = 389$ °C. UV−vis λ_{max} (CH_2Cl_2, nm) 240, 293, 332. Fluorescence λ_{emi} (CH_2Cl_2, nm) 396, 415. FT-IR (KBr, cm^{-1}) 2951 (s), 2928 (s), 2868 (s), 1624 (m), 1593 (s), 1493 (s), 1466 (s), 1400 (m), 1343 (s), 1275 (s), 1246 (s), 1092 (s), 1055 (s), 1003 (s), 945 (w), 887 (w), 812 (s). ^{1}H NMR (400 MHz, $CDCl_3$, broad peaks) δ 8.14 (s, 2H), 8.03 (d, $J = 8.6$ Hz, 2H), 7.78−7.76 (two broad peaks, 8H), 7.57 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 9.1$ Hz, 2H), 7.31 (d, $J = 8.6$ Hz, 2H), 3.99 (br, 4H), 1.45 (br, 4H), 0.99 (br, 12H), 0.73 (br, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.78, 140.19, 139.25, 135.50, 133.51, 129.48, 127.54, 127.31, 127.18, 126.13, 125.62, 120.45, 116.19, 69.78, 31.34, 29.35, 25.34, 22.48, 13.94. Anal. Calcd for $C_{44}H_{44}O_2$: C, 87.38; H, 7.33. Found: C, 85.69; H, 7.27.

Synthesis of the Repeat Unit, 1,4-Bis(6′-(neopentyloxy)naphthyl-2′-yl)benzene (8). (a) Alkylation of 6-Bromo-2-naphthol To Prepare 6-Bromo-2-(neopentyloxy)naphthalene (9). To a solution of 6-bromo-2-naphthol (2.23 g, 10 mmol) and neopentyl iodide (2.30 g, 11.6 mmol) in DMF (20 mL) was added *t*-BuOK (2.0 g). The reaction mixture was heated at 130 °C under nitrogen for 4 h and monitored by TLC. After the reaction was completed, the mixture was poured into water (30 mL) and extracted with EtOAc (2 × 50 mL). The combined organic layer was washed with brine (2 × 10 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (hexane:EtOAc = 1:9) to give 2-(neopentyloxy)-6-bromonaphthalene (**9**) (2.50 g, 85%) as a white solid. Mp 98−100 °C. FT-IR (cm^{-1}) 2957 (s), 2911 (s), 2868 (s), 1626 (s), 1586 (s), 1501 (s), 1480 (s), 1454 (s), 1397 (s), 1362 (s), 1329 (m), 1260 (s), 1211 (s), 1167 (s), 1125 (m), 1049 (s), 1019 (s), 912 (s), 897 (s), 851 (s), 820 (s), 804 (s), 750 (w), 648 (m). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.93 (m, 1H, H-5), 7.65 (d, $J = 8.8$ Hz, 1H, H-8), 7.60 (d, $J = 8.8$ Hz, 1H, H-4), 7.53 (dd, $J = 2.9$, 8.8 Hz, 1H, H-3), 7.23 (dd, $J = 2.9$, 8.8 Hz), 1H, H-7), 7.11 (d, $J = 2.2$ Hz, 1H, H-1), 3.76 (s, 2H, OCH_2), 1.14 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 270 MHz) δ 157.69, 133.02, 129.78, 129.53, 129.40, 128.25 (br), 120.11, 116.72, 106.29, 77.74, 31.80, 26.62. Anal. Calcd for $C_{15}H_{17}OBr$: C, 61.45; H, 5.84. Found: C, 61.28; H, 5.98.

(b) Conversion of 9 to 6-(Neopentyloxy)-2-naphthylboronic Acid, (10). Under nitrogen, to a mixture of Mg (192 mg, 8 mmol) and THF (5 mL) was slowly added a THF solution (30 mL) of **9** (1.465 g, 5 mmol) and 1,2-dichloroethane (0.297 g, 3 mmol) over 30 min. The mixture was then refluxed for 6 h. The resulting Grignard reagent was slowly added to a THF solution (20 mL) of trimethyl borate (1.56 g) at −78 °C. After the addition, the mixture was warmed to room temperature and stirred for 24 h. A 2 N HCl (20 mL) solution was then added and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic layer was washed with brine (2 × 10 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (hexane:EtOAc = 9:1 to 7:3) to give **10** as a white solid (780 mg, 60%). Mp 287−292 °C. FT-IR (cm^{-1}) 3364 (br m), 2957 (m), 2913 (w), 2870 (w), 1630 (s), 1576 (w), 1483 (s), 1348 (s), 1325 (s), 1275 (s), 1256 (s), 1202 (s), 1169 (s), 1125 (m), 1049 (m), 1019 (s), 932 (w), 853 (m), 812 (m), 723 (m). ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.70 (br s, 1H), 8.23 (d, $J = 7.7$ Hz, 1H), 7.95 (d, $J = 8.8$ Hz, 1H), 7.83 (d, $J = 7.2$ Hz, 1H), 7.24 (d, $J = 8.8$ Hz, 1H), 7.16 (s, 1H, H-1), 3.76 (s, 2H, OCH_2), 1.14 (s, 9H, CH_3). ^{13}C NMR (270 MHz, $CDCl_3$) δ 158.86, 137.41, 137.33, 131.39, 130.52, 128.25, 126.03, 125.19, 119.25, 106.31, 77.76, 31.87, 26.69.

(c) Preparation of the Repeat Unit 8. Under nitrogen, to a mixture of 1,4-dibromobenzene (58 mg, 0.25 mmol) and

10 (140 mg, 0.54 mmol) in THF (5.0 mL) and K_2CO_3 (6 mL, 1 M aqueous solution) was added a THF solution (2 mL) of Pd(PPh_3)$_4$ (10 mg, 0.0087 mmol). The resulting mixture was refluxed for 24 h. The organic layer was separated and diluted with CH_2Cl_2 (100 mL). The solution was then washed with 1 N HCl (20 mL) and brine (10 mL). After separation, the solvent in the organic layer was removed and the residue was purified by flash chromatography to give a white solid. Recrystallization from CH_2Cl_2 gave pure **8** as a white crystalline solid (78 mg, 62.5%). Mp > 300 °C. UV−vis λ_{max} (CH_2Cl_2, nm) 322, 272, 234. Fluorescence λ_{emi} (CH_2Cl_2, nm) 417, 396, 378. FT-IR (KBr, cm^{-1}) 2955 (s), 2905 (s), 2866 (m), 1632 (s), 1601 (s), 1524 (m), 1503(s), 1470 (s), 1391 (s), 1364 (s), 1277 (s), 1254 (s), 1206 (vs), 1168−1126 (several peaks), 1051 (s), 1020 (s), 938 (m), 893 (m), 841 (s), 802 (s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (br, 2H), 7.83 (br, 4H), 7.81 (br, 4H), 7.78 (dd, J = 8.6, 1.6 Hz, 2H), 7.22 (dd, J = 9.1, 2.1 Hz, 2H), 7.17 (d, J = 2.1 Hz, 2H), 3.76 (s, 4H), 1.11 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.74, 139.83, 135.60, 133.89, 129.53, 129.07, 127.82, 127.54, 127.21, 125.75, 125.42, 119.60, 106.26, 77.89, 31.90, 26.69. MS (DIP) m/e 502 (M^+), 432 ($M^+ - OC_5H_{10}$), 362 ($M^+ - 2OC_5H_{10}$, 100). Anal. Calcd for $C_{36}H_{38}O_2$: C, 86.03; H, 7.62. Found: C, 85.65; H, 7.61.

Synthesis of the Repeat Unit 4,4′-Bis(6″-(neopentyloxy)naphthyl-2″-yl)biphenyl (11). Compound **11** was obtained in 70% yield from the reaction of **10** with 4,4′-biphenyl similarly to the preparation of **8**. FT-IR (KBr, cm^{-1}) 2957 (s), 2919 (s), 2868 (m), 1630 (s), 1603 (s), 1499 (s), 1364 (m), 1277 (s), 1250 (vs) 1204 (vs), 1155−1125 (several peaks), 1051 (s), 1020 (s), 924 (m), 891 (m), 892 (s), 802 (s). UV−vis λ_{max} (CH_2Cl_2, nm) 324, 280, 240. Fluorescence λ_{emi} (CH_2Cl_2, nm) 408, 389. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.05 (m, 2H), 7.81 (m, 14H), 7.23 (dd, J = 2.9, 8.8 Hz, 2H), 7.17 (d, J = 2.2 Hz, 2H), 3.76 (s, 4H, OCH_2), 1.11 (s, 18H, CH_3). MS (DIP) m/e 578 (M^+), 508 ($M^+ - OC_5H_{10}$), 438 ($M^+ - 2OC_5H_{10}$, 100). Anal. Calcd for $C_{42}H_{42}O_2$: C, 87.16; H, 7.31. Found: C, 86.56; H, 7.10.

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