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A New Class of Chiral Conjugated Polymers with a Propeller-Like Structure

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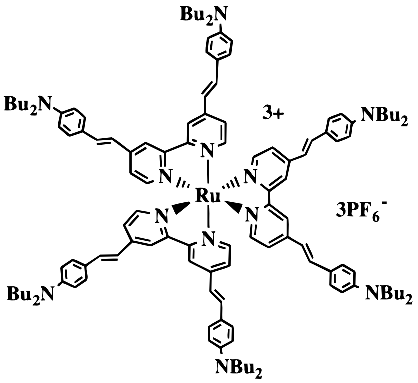
ABSTRACT: A new class of chiral conjugated materials, “propeller” polymers, have been designed and synthesized. By using the transition metal catalyzed cross-coupling reactions including the coupling of terminal alkynes with aryl halides and the Suzuki reaction, chiral binaphthyl monomers are reacted with *o*-phenylene and *m*-phenylene halides to construct the “propeller” polymers. Due to the chirality of the binaphthyl units and the rigidity of the conjugated system, the dipole units in these novel materials are expected to form a novel propeller-like three-dimensional configuration. Molecular weights of these polymers are analyzed by gel permeation chromatography and laser light scattering. The structures of these polymers are studied by using NMR, UV, IR, CD, and fluorescence spectroscopic methods. The repeat units of these materials are synthesized which provide further evidence for the structure of the polymers. The thermal properties of these polymers are studied by using thermal gravimetric analysis as well as differential scanning calorimetry.

Introduction

Chiral conjugated polymers represent a class of potentially useful materials and have received growing attention recently.[1−6] There are two fundamental classes of chiral conjugated polymers: one has its chirality derived from the side-chain chiral substituents[2,3] and the other one contains inherently chiral configuration in the main chain.[4−6] Based on optically active 1,1′-binaphthyl compounds, we have constructed a family of main chain chiral conjugated polymers.[4] For example, an optically active poly(aryleneethynylene), (*R*)-**1**, has been prepared from the palladium-catalyzed cross-coupling reaction of a chiral binaphthyl monomer, (*R*)-**2**, with 4,4′-diethynylbiphenyl, **3** (Scheme 1).[4c] (*S*)-**4**[4d] and (*R*)-**5**[4b] are two other examples of the chiral conjugated polymers prepared in our laboratory. These chiral conjugated polymers have potential applications in areas such as asymmetric electrosynthesis, polarized photo- and electroluminescence, enantioselective sensing, and asymmetric catalysis. The chirality of these materials may also lead to enhanced nonlinear optical (NLO) properties.[7]

Organic NLO materials are potentially very useful in optical information storage and processing and in telecommunication.[8−10] Recently, the study of three-dimensional octopolar molecules as a new class of second-order NLO materials has been proposed by Zyss *et al.*[11−14] They have synthesized a ruthenium complex **6** that has an octopolar geometry.[14] This propeller molecule has a threefold rotation axis with zero net dipole. However, it is found that the β value of this molecule is in excess of 10^{-27} esu comparable to the best dipolar NLO molecules. NLO materials based on such propeller molecules will be less sensitive to materials orientation and avoid the drawbacks associated with dipole moments. Organic polymers with their chromophores arranged in a three-dimensional configuration similar to that of **6** were unknown. Since polymeric materials have the advantages of good processibility and mechanical flexibility, we have carried out a program to prepare multipolar organic polymers.



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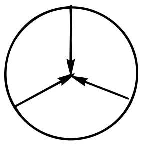
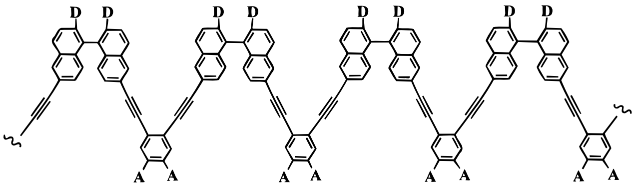


the dipole arrangement of 6

Applying the strategy we have developed in the preparation of the polymers such as (*R*)-**1**, we have designed a class of multipolar polymers with the structure of **7**. In **7**, the *o*-phenylene units rather than the *p*-phenylene units in (*R*)-**1** are incorporated with the chiral binaphthyls. Electron donor (D) and acceptor (A) substituents are introduced to construct the dipole units of this polymer. When an (*R*)-binaphthyl is used to



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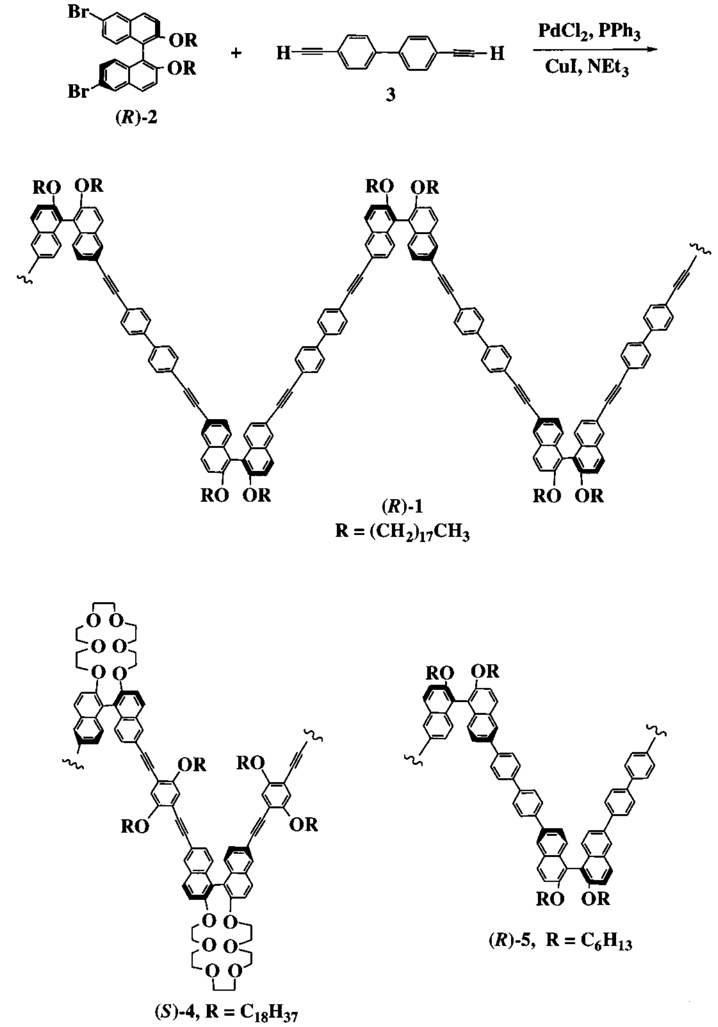
Scheme 1. Synthesis of Main Chain Chiral Conjugated Polymers



prepare this polymer, in the resulting optically active (*R*)-**7**, all of its binaphthyl units will have the same *R* configuration (Figure 1). The dihedral angle between the two naphthalene rings of a binaphthyl molecule is

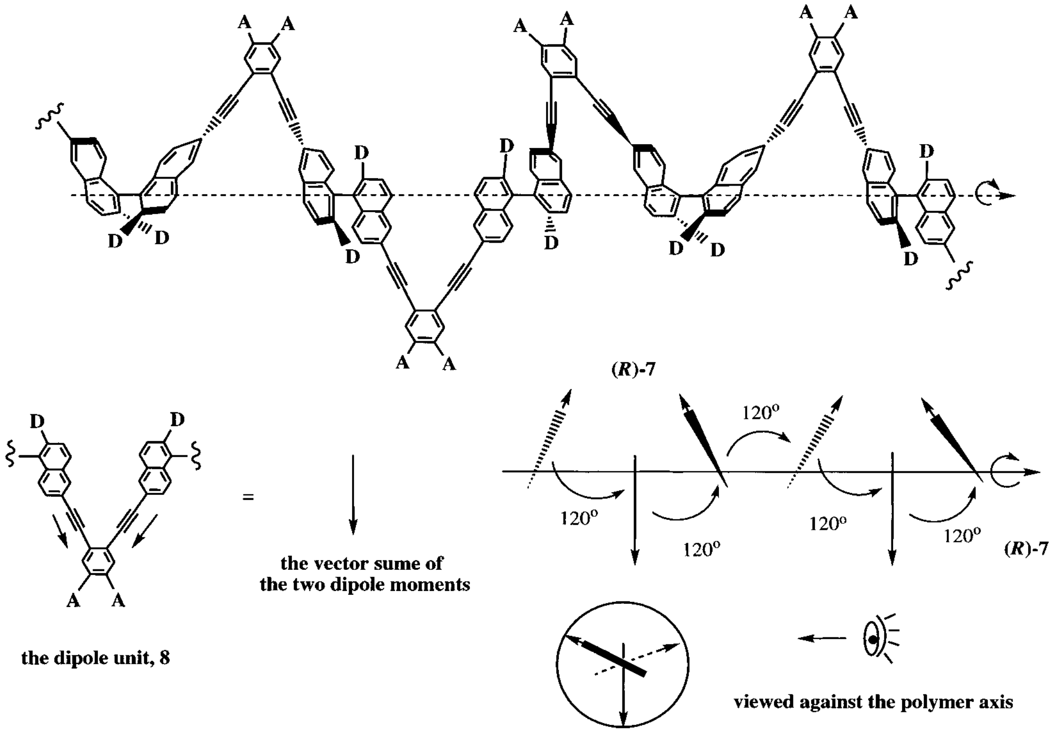


Figure 1. Structure of the "propeller" polymer.

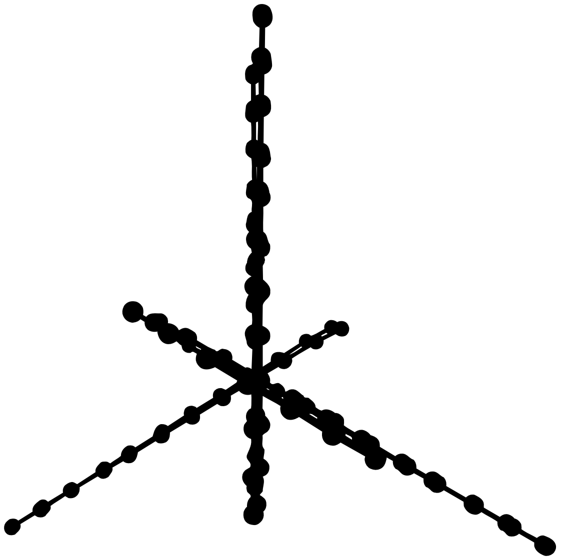


Figure 2. Computer-generated picture of the main frame of (*R*)-**7**.

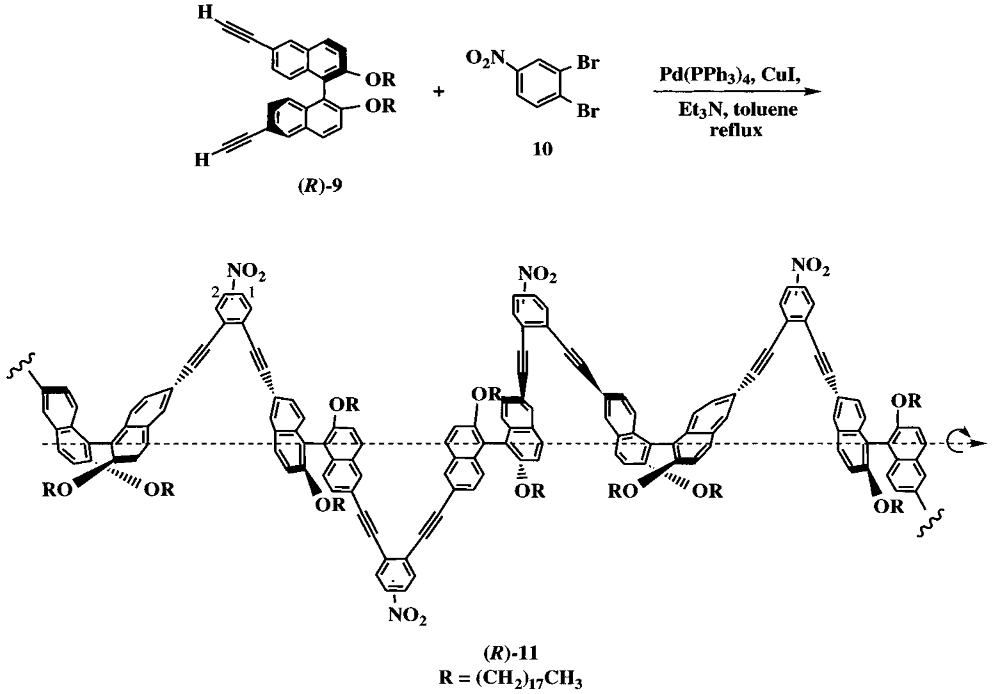
about 60−120°.[15] The dipole unit of (*R*)-**7** is **8**. If all of the aromatic rings in **8** are coplanar and the anglebetween each adjacent repeat unit in (*R*)-**7** is assumed to be 120°, this polymer would have a propeller-like structure with a threefold screw axis where the dipole unit **8** is progressively rotating around the polymer axis. The structure of this multipolar polymer is in some way similar to that of the propeller molecule **6**. In organic chemistry, a propeller structure is a center with blades that forms a chiral configuration. Herein, the term "propeller" polymer is used to differentiate the structure of (*R*)-**7** from that of other ordinary helical polymers. In (*R*)-**7**, the revolving blades is the main chain of the polymer itself. However, in normal helical polymers such as polyisocyanides, it is the substituents that progressively revolve along the polymer main chain. Figure 2 shows one of the possible conformations of (*R*)-**7** viewed along the polymer axis drawn with Spartan SGI Version 4.0.2 (the substituents are omitted). The unique three-dimensional structure and the chirality of such "propeller" polymers may lead to interesting electrical and optical properties. Herein, our detailed synthesis and characterization of this exciting class of new materials is described.

Results and Discussion

1. "Propeller" Polymer from the Reaction of 6,6′-Diethynyl-2,2′-dioctodecyloxy-1,1′-binaphthyl (*R*)-9 with 3,4-Dibromonitrobenzene, 10. Using the procedure developed in our laboratory, 6,6′-Diethynyl-2,2′-dioctodecyloxy-1,1′-binaphthyl, (*R*)-**9** (R = $C_{18}H_{37}$),[4c] is prepared as the monomer to synthesize the "propeller" polymers. When a 1:1 mixture of (*R*)-**9** and 3,4-dibromonitrobenzene, **10**,[16] is heated at reflux in a triethylamine−toluene solution under nitrogen in the presence of $Pd(PPh_3)_4$ and CuI catalysts,[17] a cross-coupling reaction takes place to give a chiral polymer (*R*)-**11** in 92% yield (Scheme 2). In the dipole unit of this polymer, the electron donors, the octodecyloxy groups, and the electron acceptors, the nitro groups, are connected through a conjugated aryleneethynylene system. The nitro groups of (*R*)-**11** are randomly bonded to the 1- or 2-position of the *o*-phenylene unit. (*R*)-**11** is purified by repetitive precipitation out of its methylene chloride solution with methanol. Gel permeation chromatography (GPC) analysis of (*R*)-**11** shows M_w = 7200 and M_n = 5100 (PDI = 1.4).[18] This polymer is soluble in a number of organic solvents including chloroform, methylene chloride, THF, and benzene. Its specific optical rotation is $[\alpha]_D = -160.0°$ (c = 0.15, CH_2Cl_2). The aromatic region of the ^1H NMR spectrum of (*R*)-**11** is very broad and complicated with signals in the range δ 7.1−8.4. In the IR spectrum of (*R*)-**11**, a medium absorption at 2199 cm^{-1} corresponding to the alkyne triple bond stretch of (*R*)-**11** is observed.

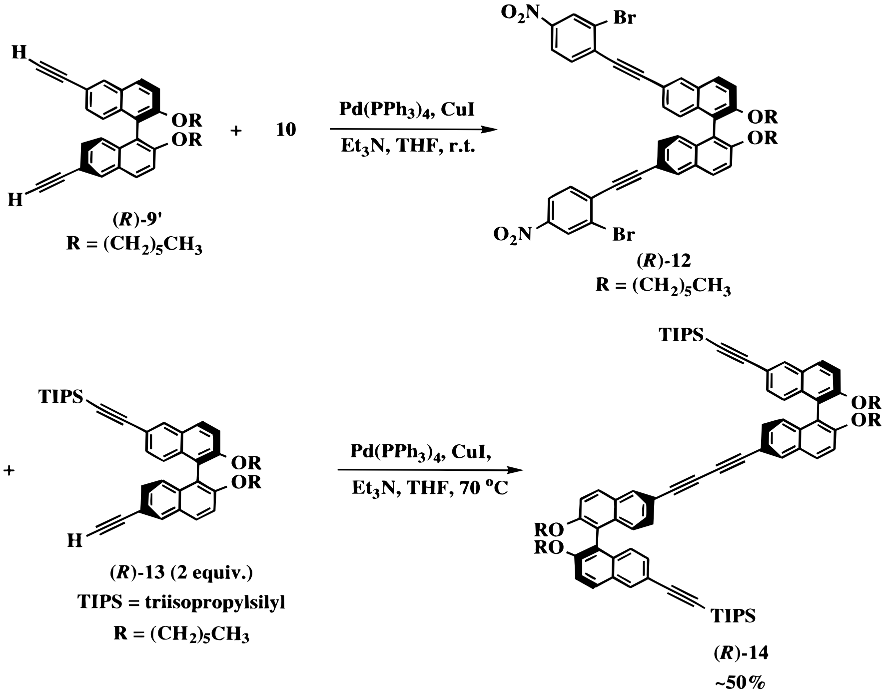
Polymerization of **10** with the racemic monomer *rac*-**9** leads to the formation of polymer *rac*-**11**. GPC analysis shows that *rac*-**11** has M_w = 7400 and M_n = 5200 (PDI = 1.4). The molecular weight and the polydispersity of

Scheme 2. Synthesis of the "Propeller" Polymer (*R*)-11



(*R*)-**11**
R = $(CH_2)_{17}CH_3$

Scheme 3. Stepwise Coupling of (*R*)-9′ with 10



rac-**11** are almost the same as those of (*R*)-**11**, suggesting that the chirality of the binaphthyl monomer has little effect on the polymerization. A weak triple bond stretch absorption of *rac*-**11** is observed at 2203 cm^{-1} in its IR spectrum. The NMR spectra of *rac*-**11** are similar to those of (*R*)-**11**.

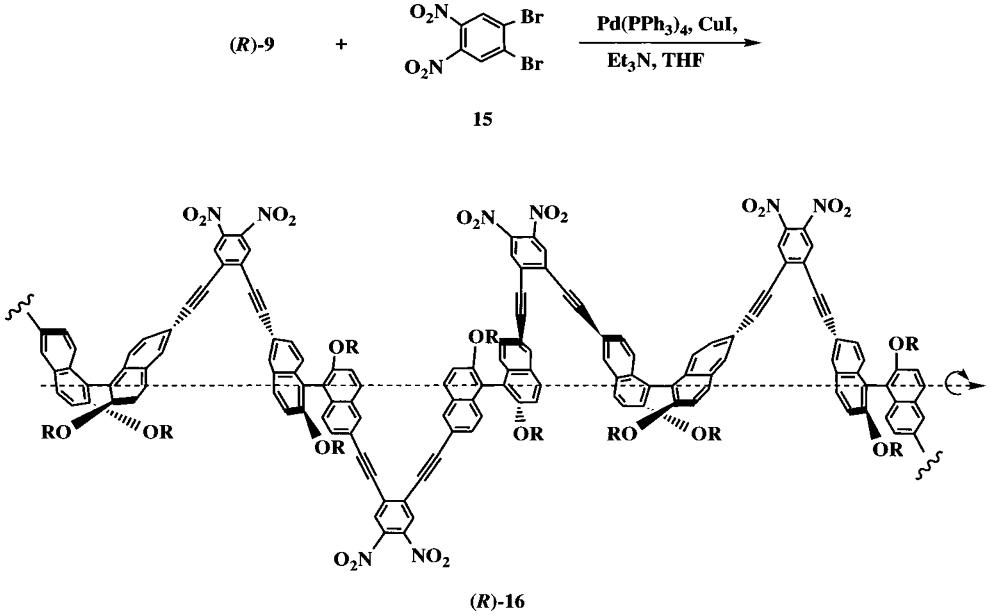
To gain more understanding of the coupling process between (*R*)-**9** with **10**, we have studied this reaction in a stepwise fashion (Scheme 3). We find that the reaction of (*R*)-**9′** [R = $(CH_2)_5CH_3$] with **10** gives (*R*)-**12** at room temperature in high yield. When (*R*)-**12** is reacted with 2 equiv of (*R*)-**13**, a monoprotected diethynylbinaphthyl compound, besides the aryl bromide and terminal alkyne coupling products, ca. 50% of (*R*)-**14**, a self-coupling product of (*R*)-**13**, is obtained.[19] This suggests that in the polymerization of (*R*)-**9** with **10**, there should be significant competition between the self-coupling of (*R*)-**9** and the cross-coupling polymerization between (*R*)-**9** and **10**. Because the bromine atom trans to the nitro group in **10** is highly activated, its coupling with (*R*)-**9** proceeds very fast to generate (*R*)-**12**. However, the bromine atoms in (*R*)-**12** are meta to the nitro groups and thus much less reactive. The self-coupling of (*R*)-**9** becomes competitive in the polymerization process. Therefore, (*R*)-**11** probably contains both the desired aryl bromide−alkyne coupling fragments and the undesired alkyne−alkyne coupling fragments in the polymer chain. This explains why the ^1H and ^{13}C NMR spectra of this polymer are very broad and complicated.

2. “Propeller” Polymer from the Reaction of (*R*)-9 with 1,2-Dibromo-4,5-dinitrobenzene, 15. In order to avoid the competition from the self-coupling of the binaphthyl alkyne monomer and to obtain a structurally well-defined “propeller” polymer, 1,2-dibromo-4,5-dinitrobenzene, **15**,[20] is prepared. Unlike **10**, **15** is symmetric and both of its bromine atoms are trans to the nitro groups. This molecule is therefore highly activated toward the cross-coupling reaction. In fact, the polymerization of **15** with (*R*)-**9** in the presence of $Pd(PPh_3)_4$ and CuI can proceed at room temperature in a triethylamine−THF solution to generate (*R*)-**16** (Scheme 4). After purification, GPC analysis of (*R*)-**16** shows $M_w = 18\,000$ and $M_n = 12\,000$ (PDI = 1.5). This molecular weight of (*R*)-**16** is much higher than that of (*R*)-**11**. The reaction between (*R*)-**9** and **15** can even take place at 0 °C. (*R*)-**16** is soluble in chloroform, methylene chloride, and THF. Its specific optical rotation is $[\alpha]_D = -163.9°$ ($c = 0.16$, CH_2Cl_2).

(*R*)-**16** has a much better defined structure, as shown by its well-resolved ^{13}C NMR spectrum in which all of the resonances can be attributed. The two alkyne carbons are observed at δ 101.9 and 85.8. Although the ^1H NMR spectrum of (*R*)-**16** is still relatively broad, it is much less complicated than that of (*R*)-**11**. In the IR spectrum of (*R*)-**16**, a strong absorption at 2201 cm^{-1} corresponding to the alkyne triple bond stretch of the polymer is observed. Polymerization of **15** with the racemic monomer *rac*-**9** leads to the formation of polymer *rac*-**16**. GPC analysis shows that the molecular weight of *rac*-**16** is $M_w = 14\,200$ and $M_n = 10\,000$ (PDI = 1.4). Powder X-ray diffraction study of (*R*)-**16** indicates that this polymer is not crystalline.

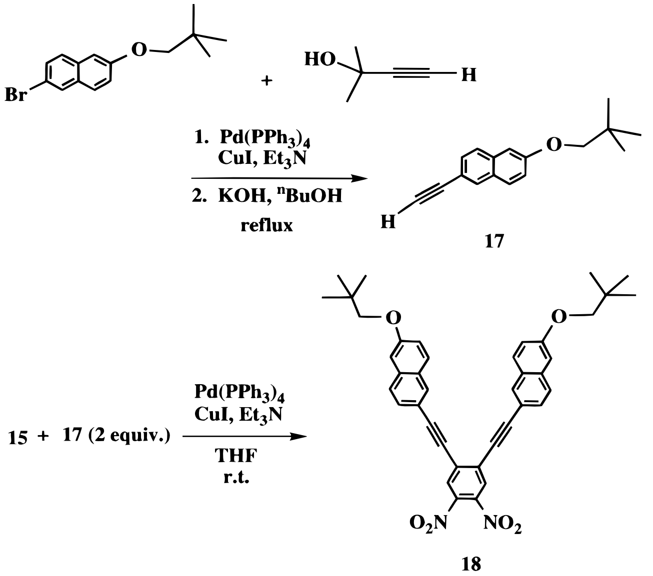
The repeat unit of (*R*)-**16** is synthesized to further characterize the structure of this polymer (Scheme 5). 6-Ethynyl-2-neopentoxynaphthalene, **17**, is made from the reaction of 6-bromo-2-neopentoxynaphthalene with 2-methyl-3-butyn-2-ol followed by base-promoted deprotection. The reaction of **15** with 2 equiv of **17** in the presence of $Pd(PPh_3)_4$/CuI catalysts generates **18** as the repeat unit of the polymer (*R*)-**16** in over 95% yield. No side products are observed in this reaction. The high yield production of **18** indicates that the cross-coupling polymerization between **15** and (*R*)-**9** should lead to the expected polymer structure. In the IR spectrum of **18**, a strong alkyne absorption is observed at 2205 cm^{-1} almost identical to that of (*R*)-**16**. The NMR signal distribution of **18** and (*R*)-**16** is similar though the ^1H NMR spectrum of (*R*)-**16** is significantly broader. Two alkyne resonance peaks at δ 102.0 and 85.6 are observed in the ^{13}C NMR spectrum of **18**, which are essentially the same as those observed in the ^{13}C NMR spectrum of (*R*)-**16**. The synthesis and characterization of **18** strongly supports the structure of (*R*)-**16**.

Scheme 4. Synthesis of the "Propeller" Polymer (*R*)-16



(*R*)-16
R = $(CH_2)_{17}CH_3$

Scheme 5. Synthesis of the Polymer Repeat Unit 18



3. "Propeller" Polymer with Fluorine Electron Acceptors.[22] From the polymerization of (*R*)-**9** with 3,4,5,6-tetrafluoro-1,2-diiodobenzene, **19**, polymer (*R*)-**20** that contains fluorine atoms as the electron acceptors is synthesized (Scheme 6). The polymerization of (*R*)-**9** with **19** is carried out in a refluxing triethylamine/toluene (1:4) solution in the presence of $Pd(PPh_3)_4$/CuI catalysts. After stirring under nitrogen for 2 days, (*R*)-**20** is obtained in 93% yield. GPC analysis of (*R*)-**20** shows its molecular weight is $M_w = 7200$ and $M_n = 5100$ (PDI = 1.4). The specific optical rotation of (*R*)-**20** is $[\alpha]_D = -103°$ (c = 0.29, CH_2Cl_2). Two major alkyne peaks can be observed at δ 101.9 and 79.17 in the ^{13}C NMR spectrum of (*R*)-**20**. The ^{19}F NMR of this polymer displays two dominating signals at δ 121.2 and 141.2 (reference to trifluoroacetic acid) with two very small peaks. The IR spectrum of (*R*)-**20** gives a medium absorption at 2211 cm^{-1} corresponding to the stretch of the carbon−carbon triple bonds in the polymer. The polymerization of *rac*-**9** with **19** leads to the formation of *rac*-**20**. The molecular weight of *rac*-**20** is $M_w = 7600$ and $M_n = 5300$ (PDI = 1.4). The triple bond of the polymer exhibits an IR absorption identical to that of (*R*)-**20**. Both (*R*)-**20** and *rac*-**20** are soluble in common organic solvents.

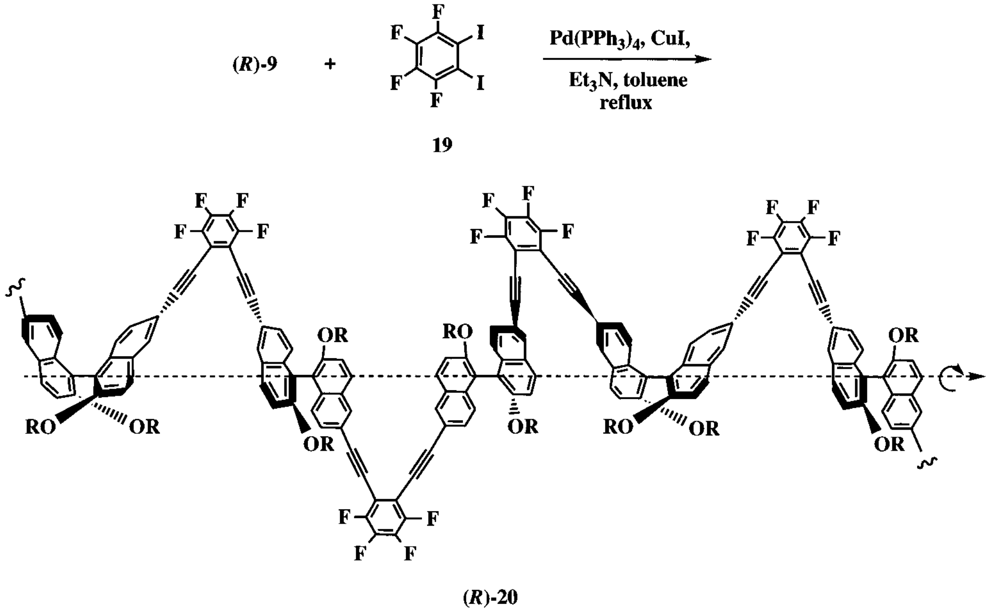
Polymerization of 1,2-diiodobenzene with *rac*-**9** has also been carried out similarly. The resulting polymer *rac*-**21** has a molecular weight of $M_w = 8100$ and $M_n = 5400$ (PDI = 1.5) as measured by GPC analysis. The IR spectrum of *rac*-**21** shows a medium absorption at 2204 cm^{-1} for the triple bonds in the polymer chain. The ^{13}C NMR spectrum of *rac*-**21** displays four alkyne signals indicating a mixed structure probably arising from the competitive self-coupling of *rac*-**9**, as we have shown in the reaction of (*R*)-**12** with (*R*)-**13**.

4. "Propeller" Polymer of a Longer π System in the Repeat Unit. The coupling of (*R*)-**2** with mono-protected 1,4-diethynylbenzene **22** gives (*R*)-**23** which is converted to (*R*)-**24**, a binaphthyl monomer that contains two extended alkyne substituents, by base-promoted deprotection.[21] Polymerization of (*R*)-**24** with **15** generates polymer (*R*)-**25** that has a more extended conjugation in its repeat unit than those described above (Scheme 7). GPC shows its molecular weight is M_w = 10 700 and M_n = 6000 (PDI = 1.80). The specific optical rotation of (*R*)-**25** is $[\alpha]_D = -228°$ (c = 0.13, CH_2Cl_2). A strong absorption at 2200 cm^{-1} is observed for the triple bond stretch of this polymer in the IR spectrum.

(*R*)-**24** is also polymerized with **10** to generate polymer (*R*)-**26**. Its molecular weight is M_w = 14 200 and M_n = 6900 (PDI = 2.1) as measured by GPC. The specific optical rotation of (*R*)-**26** is $[\alpha]_D = -284°$ (c = 0.14, CH_2Cl_2). A triple bond stretch absorption with medium intensity is observed at 2202 cm^{-1} in the IR spectrum of (*R*)-**26**. Polymerization of *rac*-**24** with **10** gives *rac*-**26**. GPC shows its molecular weight is M_w = 10 500 and M_n = 6000 (PDI = 1.8). Polymerization of *rac*-**24** with *o*-diiodobenzene gives *rac*-**27**. Its molecular weight is M_w = 11 600 and M_n = 6400 (PDI = 1.8) as measured by GPC. Without the nitro group, *rac*-**27** only gives a weak absorption at 2202 cm^{-1} for its triple bonds in the IR spectrum.

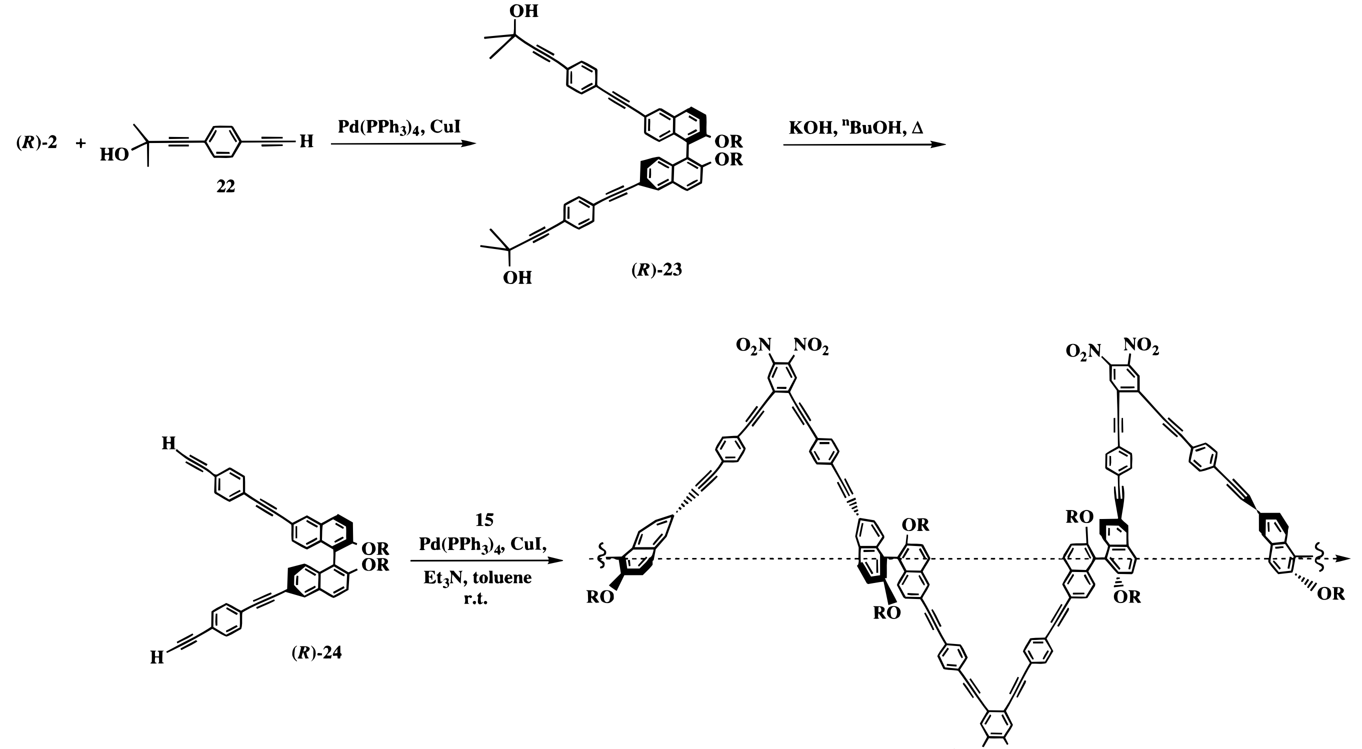
5. "Propeller Polymer" Prepared from the Suzuki Coupling Reaction. The Suzuki coupling[23] of a

Scheme 6. Synthesis of Polymer (*R*)-20 That Contains Fluorine Acceptors



(*R*)-20
R = $(CH_2)_{17}CH_3$

Scheme 7. Synthesis of Polymer (*R*)-25



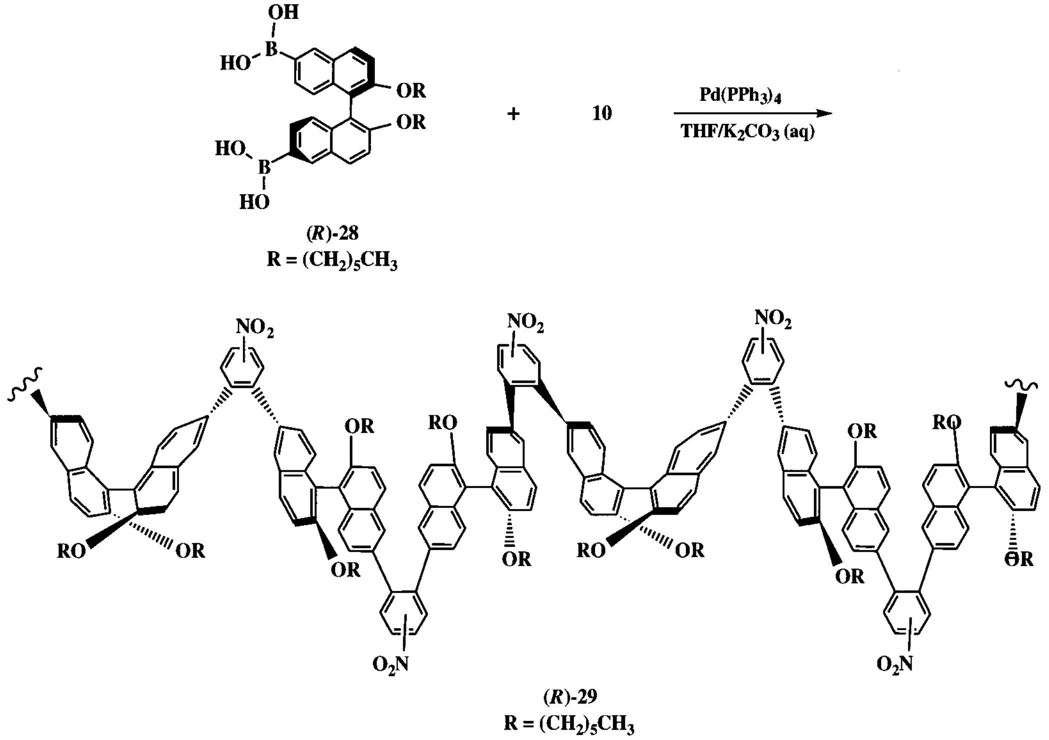
R = $(CH_2)_{17}CH_3$

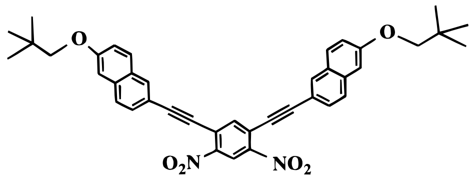
(*R*) 25

chiral binaphthyl diboronic acid molecule (*R*)-**28** with *p*-dibromoaryls has been used to prepare the optically active polyarylenes and poly(arylenevinylene)s in our laboratory.[4a,b] The same polymerization process can be also used to synthesize the "propeller" polymers. From the coupling of (*R*)-**28** with **10**, polymer (*R*)-**29** is obtained (Scheme 8). GPC analysis shows that (*R*)-**29** has M_w = 10 100 and M_n = 4900 (PDI = 2.1). The specific optical rotation of the polymer is $[\alpha]_D = -70.9°$ (c = 0.5, CH_2Cl_2). When the racemic monomer *rac*-**28** is reacted with **10**, *rac*-**29** is obtained. GPC analysis of *rac*-**29** shows its molecular weight is M_w = 6300 and M_n = 3700 (PDI = 1.7). Comparing to (*R*)-**29**, *rac*-**29** has much more complicated aromatic signals at δ 6.8–8.4 in its ^1H NMR spectrum, suggesting that *rac*-**29** might not be a racemic mixture of *R* and *S* polymers.

6. *m*-Dibromophenylene-Based Chiral Conjugated Polymer.[22] The "propeller" polymers described above are all constructed from the coupling of binaphthyls with *o*-phenylenes. *m*-Phenylene units can be also used to build the similar multipolar chiral materials. We have polymerized 4,6-dinitro-1,3-dibromobenzene, **30**,[24] with (*R*)-**9** to generate (*R*)-**31** (Scheme 9). The reaction is carried out at room temperature for 57 h in a triethylamine–THF (1:4) solution in the presence of $Pd(PPh_3)_4$ (5 mol %) and CuI (5 mol %) catalysts.

Scheme 8. Synthesis of Polymer (*R*)-29





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Polymer (*R*)-**31** is obtained in 92% yield. GPC analysis of (*R*)-**31** shows that its molecular weight is $M_w = 30\ 500$ and $M_n = 16\ 300$ (PDI = 1.9). The molecular weight of (*R*)-**31** is much higher than those polymers made of *o*-phenylene units. Polymer (*R*)-**31** is soluble in common organic solvents such as chloroform, methylene chloride, and THF. The ^{1}H NMR spectrum of (*R*)-**31** shows seven major peaks well resolved in the aromatic region corresponding to the seven different aromatic protons: δ 8.92 (s), 8.21 (s), 8.03 (s), 7.97 (d, $J = 9$ Hz), 7.45 (d, $J = 9$ Hz), 7.37 (d, $J = 9$ Hz), 7.14 (d, $J = 9$ Hz). In the ^{13}C NMR spectrum of (*R*)-**31**, two singlets at δ 83.9 and 77.2 are observed for the two alkyne carbons of the polymer. The IR spectrum of (*R*)-**31** displays a very strong absorption at 2199 cm^{-1} for the triple bond stretch in the polymer. Polymerization of *rac*-**9** with **30** produces *rac*-**31**. GPC analysis of *rac*-**31** shows its molecular weight is $M_w = 20\ 000$ and $M_n = 12\ 000$ (PDI = 1.61). A strong IR absorption at 2198 cm^{-1} is observed for the triple bonds of the polymer.

The repeat unit of (*R*)-**31** has been obtained. The coupling of **30** with 2 equiv of **17** in the presence of Pd(PPh$_3$)$_4$ and CuI generates **32** in high yield. The IR spectrum of **32** shows a very strong absorption at 2202 cm^{-1} for the triple bond stretch. The alkyne carbons of **32** also show two ^{13}C NMR signals at δ 83.9 and 78.0. All of the spectroscopic signals of **32** are very similar to those of polymer (*R*)-**31** which supports the structure for the polymer.

7. UV and CD Spectra of the "Propeller" Polymers. Table 1 summarizes the UV absorptions of the "propeller" polymers and the repeat units. As shown in the table, the UV absorptions of (*R*)-**16** are very similar to those of its repeat unit **18**, and the absorptions of (*R*)-**31** are also close to those of **32**. Therefore, these polymers have very little extended conjugation along the polymer chain. This observation is consistent with what we have established earlier for the binaphthyl-based conjugated polymers such as (*R*)-**1**,[4b,c] i.e. the conjugation of these polymers is mostly determined by the conjugation in their repeat units. Although, (*R*)-**25** has a more extended π system than (*R*)-**16**, the absorption wavelength of (*R*)-**25** is significantly blue-shifted. This shows that increasing the length of the *p*-phenylene–ethynylene fragments in the repeat unit actually significantly reduces the push–pull conjugation between the alkoxy donors and the nitro acceptors because of the increased distance between these two functional groups.

The UV study also reveals that although both of the repeat units of (*R*)-**16** and (*R*)-**31** have the same conjugation length in their alkoxy and nitro push–pull system, (*R*)-**31** and **32** show much longer absorption wavelengths. In the repeat unit of (*R*)-**16**, the nitro groups are para and meta to the alkyne substituents, which are different from the relative positions of the

Table 1. UV–Vis Absorption Wavelengths of the "Propeller" Polymers and the Repeat Units

	(*R*)-**11**	(*R*)-**16**	**18**	(*R*)-**20**	*rac*-**21**	(*R*)-**25**	(*R*)-**26**	*rac*-**27**	(*R*)-**29**	(*R*)-**31**	**32**
$\lambda_{\max\,(\mathrm{nm})}$	234	238	236	262	236	234	232	234	246	256	244
	295 (sh)	277 (sh)	300	278	276	296	296	302	350	284 (sh)	282
	346	309 (sh)	354	344	340 (sh)	346	362	342		359 (sh)	354
	380	358	406							442	430
		418									

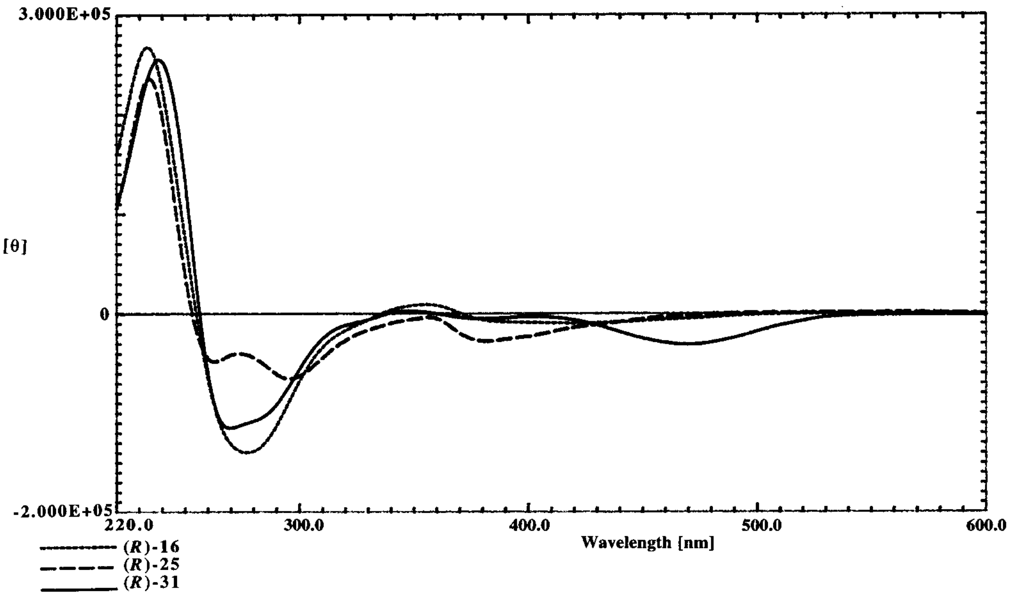
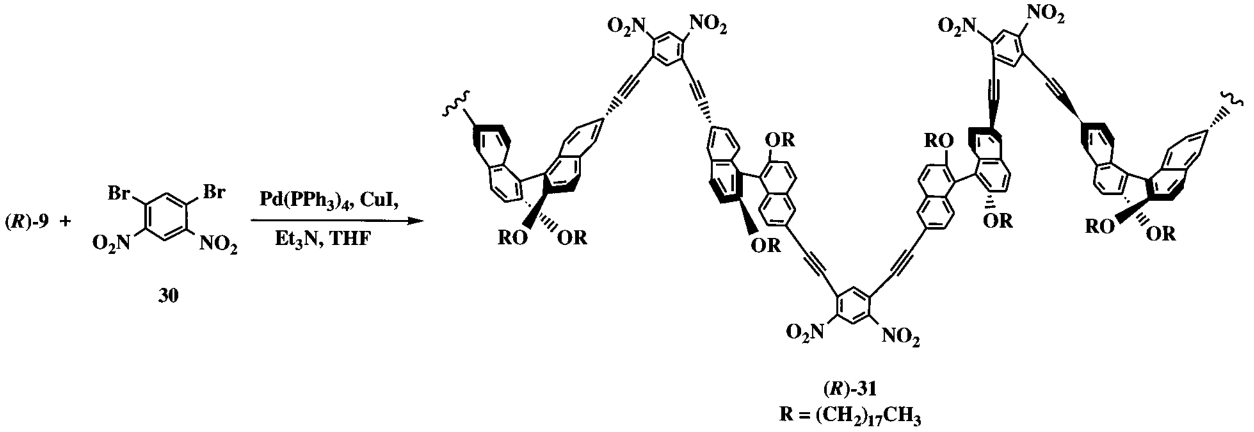


Figure 3. CD spectra of (*R*)-**16**, (*R*)-**25**, and (*R*)-**31**.

Scheme 9. Synthesis of a *m*-Phenylene-Based Polymer



nitro groups in **32** where the nitro groups are para and ortho to the two alkyne substituents. The nitro groups of **18** are not conjugated with their meta substituents whereas the nitro groups in **32** are conjugated with both of its ortho and para alkyne substituents. This leads to more effective conjugation in (*R*)-**31** and **32** than in (*R*)-**16** and **18**. All of the optically active polymers give the same UV spectra as their corresponding optically inactive polymers. This is more evidence that the conjugation of these materials is mostly determined by the conjugation within their repeat units not by the stereostructure of the polymers.

The fluorescence spectra of these polymers have been studied. All of the polymers containing nitro groups show either very weak fluorescence signals or no fluorescence at all. But *rac*-**21** and the fluorine-containing polymers **20** give very strong fluorescence signals at 420–460 nm. Thus the fluorescence of the polymers **11**, **16**, **29**, and **31** are mostly quenched by their nitro groups.

Figures 3 and 4 are the circular dichroism (CD) spectra of these polymers in methylene chloride solution. As shown in the figures, all of these polymers have two similar strong positive and negative Cotton effects at ca. 235 and 270 nm. These two peaks are caused by the chiral binaphthyl units. The major differences between these polymers are at the longer wavelength because of their different conjugation in the repeat units. Due to the more extended π electron in the repeat unit, (*R*)-**25** shows significantly increased CD effects at 383 nm with the decrease of the CD effects in the shorter wavelength when comparing to (*R*)-**16**. As we have discussed earlier, the *m*-phenylene-based polymer (*R*)-**31** has better effective conjugation than the *o*-phenylene-based polymers and thus gives much stronger CD signals at higher wavelengths. Table 2 summarizes the CD spectral data of these polymers.

8. Laser Light Scattering Study of the "Propeller" Polymers. The molecular weights of the polymers described above are all measured by GPC relative to polystyrene standards. In order to obtain the absolute value of the molecular weights of these polymers, a laser light scattering (LLS) study of some of these polymers has been carried out.[25,26] The values of d*n*/d*C*, M_w, the second virial coefficient A_2, and the hydrodynamic radius R_h are summarized in Table 3. The GPC molecular weights of these polymers are also included for comparison. For all the samples, the radius of gyration (R_g) of the polymer chain is too small to be accurately determined. Except for the sample of (*R*)-**11**, the values of M_w from LLS are ~20% larger than those from GPC. This is understandable because in LLS the scattered light intensity is proportional to the square of the molar mass and the polymer chains with

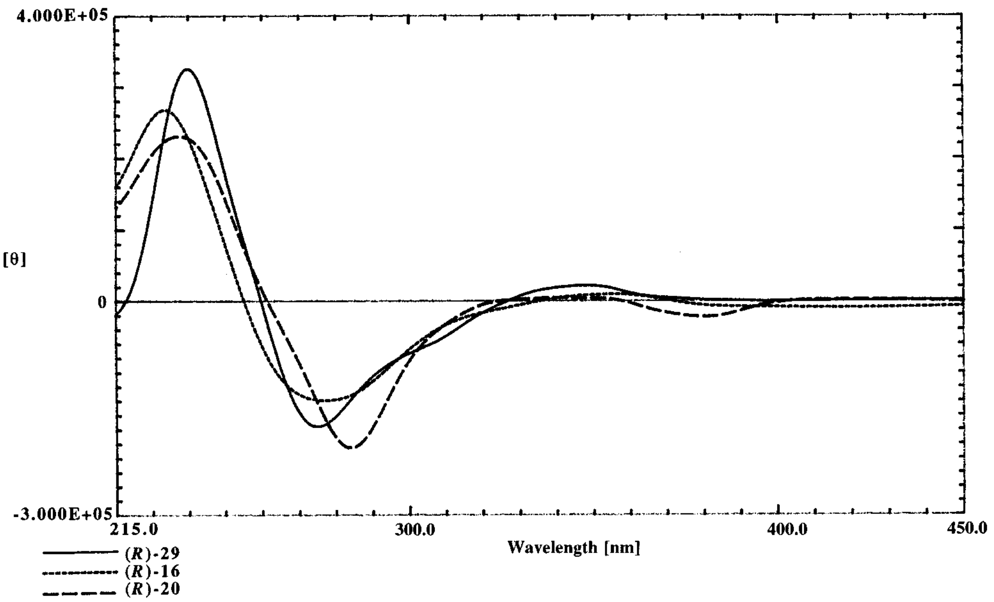


Figure 4. CD spectra of (*R*)-**16**, (*R*)-**20**, and (*R*)-**29**.

Table 2. CD Spectral Data of the "Propeller" Polymers

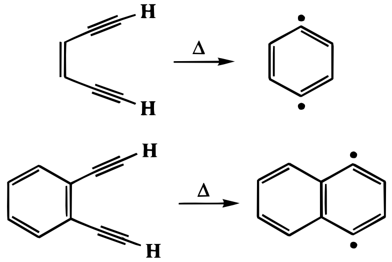
	λ_{max} (nm)	[θ]
(*R*)-**11**	235	2.19×10^5
	264	-5.42×10^4
	351	4.82×10^3
	396	-5.05×10^3
(*R*)-**16**	234	2.68×10^5
	277	-1.40×10^5
	356	9.14×10^3
	419	-9.71×10^3
(*R*)-**20**	237	2.38×10^5
	284	-2.14×10^5
	381	-2.38×10^4
(*R*)-**25**	234	2.29×10^5
	264	-4.63×10^4
	296	-6.56×10^4
	383	-2.78×10^4
(*R*)-**29**	240	3.34×10^5
	275	-1.80×10^5
	306 (sh)	-6.18×10^4
	348	2.12×10^4
(*R*)-**31**	238	2.53×10^5
	270	-1.16×10^5
	470	-3.11×10^4

Table 3. Static and Dynamic LLS Results for the "Propeller" Polymers in THF at 25 °C

sample	M_w (GPC)	(d*n*/d*C*)/ (mL/g)	M_w	A_2/ (mol·mL)/g^2	R_h/nm
(*R*)-**11**	7 200	0.215	2.20×10^4	5.15×10^{-3}	
rac-**26**	10 500	0.267	1.24×10^4	2.66×10^{-3}	
rac-**27**	11 600	0.255	1.38×10^4	-6.24×10^{-3}	
(*R*)-**29**	10 100	0.250	1.22×10^4		2.59
rac-**29**	6 300	0.250	7.78×10^3		2.59

a higher molar mass is weighted more than those with a lower molar mass, which leads to a higher weight-average molar mass. The difference between GPC and LLS for the sample of (*R*)-**11** is significantly large (ca. 3 times) and may be attributed to the difference between its three-dimensional structure and that of polystyrene used in the GPC analysis. It seems that the sample of (*R*)-**11** is different from other samples because its d*n*/d*C* is clearly smaller. Table 3 shows that for the pair of (*R*)-**29** and *rac*-**29**, it is expected that A_2 decreases as M_w increases. As for the pair of *rac*-**26** and *rac*-**27**, we find that introducing the group of $-NO_2$ has changed A_2 from negative to positive, namely it increases the solubility in THF.

Scheme 10. Bergman Cyclization



9. Thermal Analysis of the "Propeller" Polymers. "Propeller" Polymers Containing Triple Bonds. Differential scanning calorimetry (DSC) analysis of the "propeller" polymers containing alkyne triple bonds shows large irreversible exothermic peaks at ca. 200 °C (Table 4). This indicates that chemical decompositions of these polymers occur at these temperatures. Polymers containing nitro groups give much larger exothermic peaks than the polymers that do not contain nitro groups, and the *m*-dinitrophenylene-based polymers **31** and the repeat unit **32** give a much larger exothermic peak than the *o*-phenylene-based polymers. In the *o*-phenylene-based polymers, their repeat units contain ene−diyne fragments that are known to undergo the Bergman cyclization (Scheme 10) at ca. 200 °C.[27,28] Thus, the ene−diyne cyclization might have occurred for the *o*-phenylene-based polymers. Polymers **20**, **21**, and **27** do not contain nitro groups and they either show no decomposition or release much less heat at the decomposition temperature. This is probably

Table 4. DSC Data of the "Propeller" Polymers and the Repeat Units

	(*R*)-**11**	*rac*-**11**	(*R*)-**16**	*rac*-**16**	**18**	(*R*)-**20**	*rac*-**20**	*rac*-**21**	(*R*)-**25**	(*R*)-**26**	*rac*-**26**	*rac*-**27**	(*R*)-**31**	*rac*-**31**	**32**
temp (°C)	200	193	202	202	196	231	231	a	190	176	180	183	154	154	226
Δ*H* (J/g)	−79.5	−107.3	−94.2	−113.3	−142	−34.7	−35.7		−57.9	−61.0	−68.6	−15.8	−359.6	−447.9	−466.4

[a] No decomposition up to 300 °C.

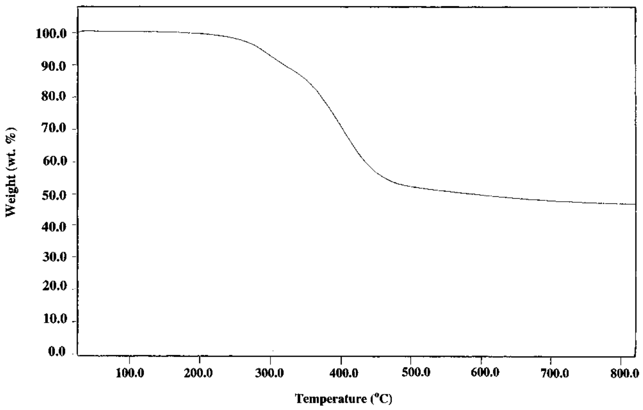


Figure 5. TGA plot of (*R*)-**16** (N_2, heat rate 10.0 °C/min).

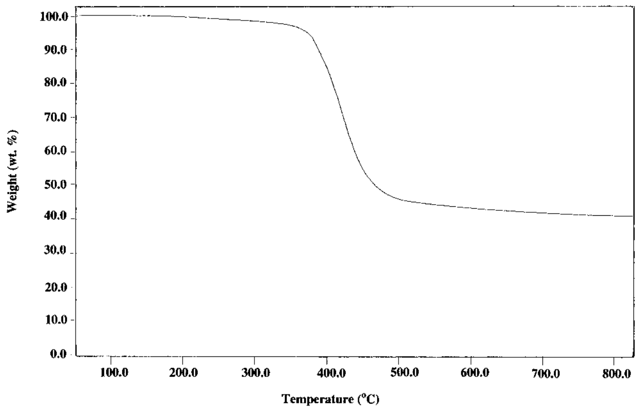


Figure 6. TGA plot of (*R*)-**21** (N_2, heat rate 10.0 °C/min).

because there is a smaller number of ene−diyne fragments in the polymers. Due to the competitive self-coupling of the binaphthylalkyne monomers, these polymers are expected to contain a significant amount of the structure shown for (*R*)-**14**.

The *m*-phenylene-based polymers cannot undergo the Bergman cyclization. The extremely large exothermic peaks of the *m*-phenylene polymers suggest that the decomposition of these polymers should take a very different reaction pathway. Scheme 11 gives one of the speculated thermal reactions for the *m*-phenylene-based polymers **31** and the repeat unit **32**. The driving force for the formation of the free radicals **33** and **34** from the nitro alkyne cyclization could be the aromaticity of the resulting heterocycles and the electron delocalization.[29] Unlike other polymers we have described, these *m*-phenylene-based polymers are also light sensitive under ambient conditions. Further study of the thermal and photoconversion of these polymers is in progress.

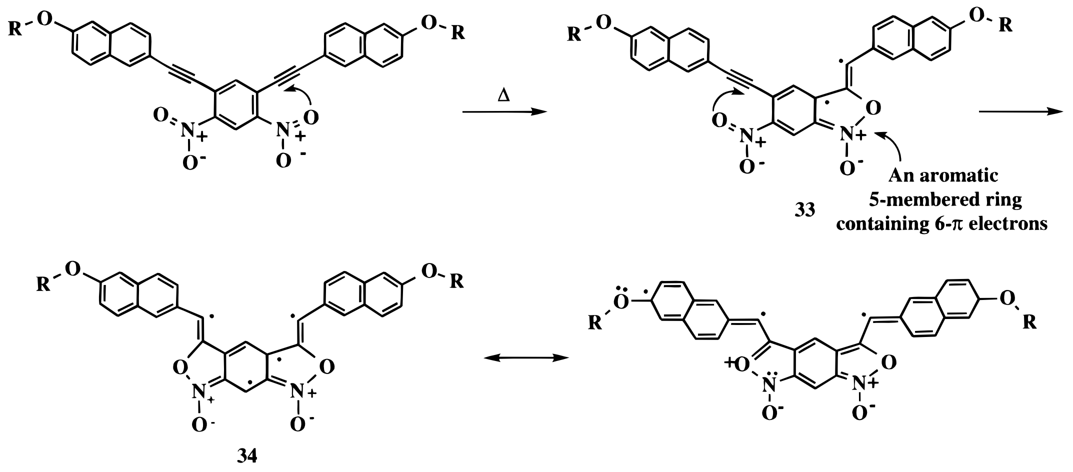
All of these polymers give similar thermal gravimetric analysis (TGA) results. At temperatures around 310−380 °C they start to show 5% mass loss. The polymers that do not contain nitro groups start to decompose at the higher end of this temperature range whereas the polymers containing nitro groups begin to lose mass at the lower temperature. After the loss of their alkyl groups (ca. 42−56% of the polymer weight), these materials are stable up to more than 800 °C without significant mass change. The nitro group containing polymers probably slowly lose their nitro groups after 400 °C. The thermal stability of these polymers is similar to other binaphthyl-based polymers prepared in our laboratory such as (*R*)-**1**.[4] Figures 5 and 6 are the TGA plots of (*R*)-**16** and *rac*-**21**, respectively, which are typical for these polymers.

"Propeller" Polymers without Triple Bonds. Polymers (*R*)-**29** and *rac*-**29** do not contain triple bonds and show somewhat different thermal properties. DSC study shows that (*R*)-**29** has a glass transition temperature (T_g) at 148 °C and *rac*-**29** has a T_g at 142 °C. A small irreversible exothermic peak at ca. 270 °C ($\Delta H = -7$ to -9 J/g) is observed for both of the polymers, indicating probably a phase transition rather than a chemical reaction. The TGA analysis of these two polymers gives results similar to those of the propeller polymers containing triple bonds. (*R*)-**29** loses its alkyl groups from 236 to 470 °C, after which the polymer becomes significantly more stable. It probably slowly loses its nitro groups from 500 °C up to more than 800 °C. *rac*-**29** shows a similar decomposition pattern.

Summary

A new class of chiral binaphthyl-based polymers that have an exciting propeller-like three-dimensional multipolar structure have been designed and synthesized. The dipolar units of these materials contain alkoxyl groups as the electron donors and nitro groups as the electron acceptors across a conjugated linker to form a push−pull system. The Suzuki coupling reaction and the cross-coupling of alkynes and aryl bromides are used to construct these novel chiral materials. These materials have been studied by various spectroscopic methods including NMR, IR, UV, CD, and fluorescence. The repeat units of these polymers have been obtained which provides evidence for the structure of these materials.

Scheme 11. Proposed Thermal Decomposition Pathway for the Polymers 31 and the Repeat Unit 32



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TGA and DSC studies of these polymers show interesting thermal properties. The synthesis and characterization of these polymers makes it possible to carry out further investigation of their potentially interesting optical and electrical properties.

Experimental Section

The general data about the analytical instruments and the LLS experiment were published.[4c] THF and ether were dried with sodium benzophenone. Triethylamine was dried with calcium hydride. 1,2-Dinitrobenzene, 1,2-dibromobenzene, 1,2-diiodobenzene, 3,4,5,6-tetrafluoro-1,2-diiodobenzene, 1,3-dibromobenzene, and 2-methyl-3-butyn-2-ol were purchased from Aldrich and used directly. Tetrakis(triphenylphosphine)palladium(0), palladium chloride, and cuprous iodide were purchased from Strem and used directly.

Preparation and Characterization of Polymer (*R*)-11. Under nitrogen, to a 50 mL flame-dried Schlenk flask were loaded (*R*)-**9** (210 mg, 0.25 mmol), **10** (70 mg, 0.25 mmol), triethylamine (2 mL), and toluene (8 mL). The resulting solution was degassed for 30 min and then was combined with tetrakis(triphenylphosphine)palladium(0) (14.4 mg, 0.013 mmol) and cuprous iodide (2.4 mg, 0.013 mmol) in the drybox. After this reaction mixture was refluxed under nitrogen for 33 h, it was cooled to room temperature and filtered to remove the insoluble triethylamine hydrobromide salt. The salt was rinsed with diethyl ether until the filtrate was clear. The combined filtrate was evaporated to dryness to give a brown residue which was dissolved in a minimum amount of CH_2Cl_2 and precipitated with methanol (75 mL) twice. After centrifugation and drying under vacuum, (*R*)-**11** was obtained as a brown solid in 92% yield (220 mg). GPC: $M_w = 7200$ and $M_n = 5100$ (PDI = 1.4). $[\alpha]_D = -160.0°$ ($c = 0.15$, CH_2Cl_2). FT-IR (KBr), cm^{-1}: 2918 (s), 2852 (s), 2199 (m), 1618 (m), 1588 (s), 1518 (s), 1482 (s), 1342 (s), 1273 (s), 1246 (s), 1091 (m), 1051 (m), 887 (m). UV−vis (CH_2Cl_2), nm: 234, 295 (sh), 346, 380. Fluorescence (CH_2Cl_2, very weak), nm: 405 (sh), 419, 454 (sh) ($\lambda_{exc} = 357$ nm). ^1H NMR (270 MHz, $CDCl_3$): δ 8.41−7.41 (br, 13H), 3.98−3.94 (br, $-OCH_2$, 4H), 1.47−1.01 (br, $-CH_2-$, 64H), 0.94−0.85 (br, $-CH_3$, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 155.8, 155.6, 146.6, 146.4, 134.6−115.7 (multiple peaks), 105.0, 96.9, 88.9 (three peaks), 69.3, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 25.6, 22.6, 14.1. Anal. Calcd for $C_{66}H_{87}NO_4$: C, 82.76; H, 9.09; N, 1.46. Found: C, 81.19; H, 8.96; N, 1.48.

Preparation and Characterization of Polymer *rac*-11. In a procedure similar to that for (*R*)-**11**, *rac*-**11** was prepared from the reaction of *rac*-**9** with **10** as a brown solid in 100% yield. GPC: $M_w = 7400$ and $M_n = 5200$ (PDI = 1.4). FT-IR (KBr), cm^{-1}: 2922 (s), 2854 (s), 2202 (w), 1618 (m), 1588 (m), 1520 (s), 1487 (s), 1342 (s), 1273 (s), 1244 (s), 1091 (m), 1051 (m). ^1H NMR (270 MHz, $CDCl_3$): δ 8.41−7.41 (br, 13H), 3.98−3.94 (br, $-OCH_2$, 4H), 1.47−1.01 (br, $-CH_2-$, 64H), 0.94−0.85 (br, $-CH_3$, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 155.7, 146.4, 134.7−115.8 (multiple peaks), 105.0, 97.0, 87.6 (three peaks), 69.3, 31.9, 29.7, 29.3, 29.2, 25.6, 22.7, 14.1. Anal. Calcd for $C_{66}H_{87}NO_4$: C, 82.76; H, 9.09; N, 1.46. Found: C, 80.96; H, 8.81; N, 1.44.

Preparation and Characterization of (*R*)-12. Under nitrogen, to a 100 mL flame-dried Schlenk flask were loaded (*R*)-**9′** (1.31 g, 2.61 mmol), **10** (1.61 g, 5.74 mmol), triethylamine (30 mL), and THF (30 mL). The resulting solution was degassed for 30 min and then was combined with tetrakis(triphenylphosphine)palladium(0) (30 mg, 0.026 mmol) and cuprous iodide (15 mg, 0.078 mmol) in the drybox. This reaction mixture was then stirred at 0 °C in an ice bath for 19 h during which the temperature increased to 16 °C. The produced insoluble triethylamine hydrobromide salt was removed by filtration and the salt was rinsed with diethyl ether until the filtrate was clear. The combined filtrate was evaporated to dryness to give a dark residue. After crystallization from ethyl acetate and hexane, (*R*)-**12** was obtained as an orange solid in 90% yield (2.12 g). FT-IR (KBr), cm^{-1}: 2928 (m), 2868 (m), 2206 (s), 1618 (m), 1589 (s), 1518 (s), 1489 (m), 1462 (s), 1340 (s), 1273 (s), 1242 (s), 1145 (m), 1089 (m), 1037 (m), 889 (m), 827 (m). UV−vis (CH_2Cl_2), nm: 234, 252, 298, 362, 390. ^1H NMR (270 MHz, $CDCl_3$): δ 8.50 (d, $J = 2.2$ Hz, 2H), 8.16 (s, 2H), 8.15 (dd, $J = 8.6$, 2.2 Hz, 2H), 7.96 (d, $J = 8.8$ Hz, 2H), 7.69 (d, $J = 8.6$ Hz, 2H), 7.45 (d, $J = 9.1$ Hz, 2H), 7.35 (dd, $J = 8.6$, 1.6 Hz, 2H), 7.13 (d, $J = 8.6$ Hz, 2H), 3.98 (m, 4H), 1.43 (m, 4H), 1.01 (m, 12H), 0.74 (t, $J = 7$ Hz, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 156.0, 146.8, 134.3, 133.2, 132.8, 132.5, 129.7 128.5, 128.4, 127.7, 125.8, 125.7, 122.2, 119.8, 116.5, 116.0, 100.7, 86.9, 69.4, 31.4, 29.3, 25.4, 22.6, 14.0. HRMS (FAB) Calcd for $C_{48}H_{42}N_2O_6Br_2$: m/z 900.1410. Obsd: m/z 900.1431.

Preparation and Characterization of (R)-14. Under nitrogen, to a 50 mL flame-dried Schlenk flask was loaded (*R*)-**12** (470 mg, 0.52 mmol), (*R*)-**13** (690 mg, 1.05 mmol), triethylamine (10 mL), and THF (10 mL). The resulting solution was degassed for 30 min and then was combined with tetrakis(triphenylphosphine)palladium(0) (30 mg, 0.026 mmol) and cuprous iodide (5 mg, 0.026 mmol) in the drybox. After this reaction mixture was stirred at 70 °C for 24 h, it was filtered to remove the insoluble triethylamine hydrobromide salt. The salt was rinsed with diethyl ether until the filtrate was clear. The combined filtrate was evaporated to dryness to give a dark residue. After flash column chromatography (silica gel, 3% ethyl acetate in petroleum ether) purification, (*R*)-**14** was obtained as a yellow solid in 51% yield (0.35 g). FT-IR (KBr), cm^{-1}: 2941 (s), 2862 (s), 2146 (s), 1616 (s), 1589 (s), 1485 (s), 1464 (s), 1336 (s), 1275 (s), 1246 (s), 1091 (s), 1045 (s), 885 (s), 825 (s), 796 (m). UV−vis (CH_2Cl_2), nm: 256, 264, 294, 352, 376. ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, $J = 1.32$ Hz, 2H), 8.00 (d, $J = 1.6$ Hz, 2H), 7.87 (q, $J = 4.6$ Hz, 4H), 7.39 (m, 4H), 7.25 (m, 4H), 7.04 (t, $J = 8.9$ Hz, 4H), 3.93 (m, 8H), 1.38 (m, 8H), 1.13 (s, 42H), 0.98 (m, 24H), 0.74 (t, $J = 6.72$ Hz, 12H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 155.8, 155.3, 134.1, 133.6, 133.2, 132.0, 129.4, 129.3, 129.2, 128.9, 128.7, 128.6, 125.6, 125.3, 120.3, 119.9, 118.4, 116.6, 116.1, 115.9, 107.9, 90.0, 82.5, 74.0, 69.5, 69.4, 31.4, 31.3, 29.3, 25.4, 22.6, 19.1, 18.9, 14.0, 11.8, 11.5. HRMS (FAB) Calcd for $C_{90}H_{114}O_4Si_2$: m/z 1314.8256. Obsd: m/z 1314.8239.

Preparation and Characterization of 1,2-Dibromo-4,5-dinitrobenzene, 15. A mixture of 1,2-dinitrobenzene (2.0 g, 11.9 mmol), bromine (5.71 g, 35.7 mmol), silver sulfate (7.43 g, 23.8 mmol), and sulfuric acid (98%, 20 mL) was heated to 155 °C during 30 min and then maintained at that temperature for 10 min. The mixture was then cooled to room temperature and was poured slowly into an excess of crushed ice. The crude product was collected by filtration. The product **15** was purified by flash column chromatography (silica gel, 10% ethyl acetate in hexane) to give a white solid in 53% yield (2.06 g). ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 (s). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 141.5, 130.9, 129.7. IR (KBr), cm^{-1}: 3097 (m), 1531 (s), 1452 (m), 1354 (s), 1330 (s), 1240 (m), 1153 (m), 1111 (m), 900 (s), 850 (m).

Preparation and Characterization of Polymer (*R*)-16. Under nitrogen, to a 50 mL flame-dried Schlenk flask was loaded (*R*)-**9** (210 mg, 0.25 mmol), **15** (82 mg, 0.25 mmol), triethylamine (1 mL), and THF (4 mL). The resulting solution was degassed for 30 min and then was combined with tetrakis(triphenylphosphine)palladium(0) (14.4 mg, 0.013 mmol) and cuprous iodide (2.4 mg, 0.013 mmol) in the drybox. After this reaction mixture was stirred at room temperature for 2 days, it was filtered to remove the insoluble triethylamine hydrobromide salt. The salt was rinsed with diethyl ether until the filtrate was clear. The combined filtrate was evaporated to dryness to give a brown residue which was dissolved in a minimum amount of CH_2Cl_2 and precipitated with methanol (75 mL) twice. After filtration and drying under vacuum, (*R*)-**16** was obtained as an orange solid in 83% yield (208 mg). GPC: $M_w = 18\,000$ and $M_n = 12\,000$ (PDI = 1.5). $[\alpha]_D = -163.9°$ ($c = 0.16$, CH_2Cl_2). FT-IR (KBr), cm^{-1}: 2922 (s), 2852 (s), 2201 (s), 1618 (m), 1593 (s), 1543 (s), 1464 (s), 1342 (s), 1273 (s), 1244 (s), 1153 (m), 1091 (m), 1049 (m), 904 (w), 889 (w), 823 (w). UV−vis (CH_2Cl_2), nm: 238, 277 (sh), 309 (sh), 358, 418. ^1H NMR (400 MHz, $CDCl_3$): δ 8.18−8.11 (br, m), 8.0−7.94 (br, m), 7.79 (br), 7.67 (br), 7.35−7.33 (br m), 7.19−7.13 (br m), 3.94 (br m, $-OCH_2$, 4H), 1.37−0.96 (br, $-CH_2-$, 64H), 0.86 (br, $-CH_3$, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ

156.1, 140.9, 134.7, 134.5, 133.3, 130.9, 129.8, 128.3, 127.7, 125.8, 119.7, 116.0, 115.9, 101.9, 85.8, 69.3, 32.0, 29.9, 29.8, 29.7, 29.5, 29.3, 29.2, 25.8, 22.8, 14.2.

Preparation and Characterization of Polymer *rac*-16. In a procedure similar to (*R*)-**16**, *rac*-**16** was prepared from the reaction of *rac*-**9** with **15** as a brown solid in 94% yield. GPC: $M_w = 14\,000$ and $M_n = 10\,000$ (PDI = 1.5). FT-IR (KBr), cm^{-1}: 2924 (s), 2851 (s), 2198 (s), 1618 (m), 1593 (s), 1543 (s), 1462 (s), 1340 (s), 1271 (s), 1244 (s), 1153 (s), 1091 (m), 1051 (m), 887 (m), 823 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16−8.14 (br, m), 8.03−7.94 (br, m), 7.78 (br), 7.69−7.64 (br, m), 7.33−7.32 (br, m), 7.1−7.13 (br, m), 3.93 (br, $-OCH_2$, 4H), 1.46−0.94 (br, $-CH_2-$, 64H), 0.85 (br, $-CH_3$, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 156.1, 141.0, 140.9, 134.5, 133.3, 131.0, 129.9, 129.8, 128.6, 128.4, 127.7, 125.8, 119.7, 116.1, 115.9, 101.9, 85.8, 69.3, 32.0, 29.9, 29.8, 29.7, 29.5, 29.3, 29.2, 25.8, 22.8, 14.2.

Preparation and Characterization of 6-Ethynyl-2-neopentoxynaphthalene, 17. (1) Preparation of 6-(2-Hydroxy-2-methyl-3-butyn-4-yl)-2-neopentoxynaphthalene. Under nitrogen, to a 50 mL flame-dried Schlenk flask was loaded 6-bromo-2-neopentoxynaphthalene (0.77 g, 2.63 mmol), 2-methyl-3-butyn-2-ol (0.29 g, 3.42 mmol), and triethylamine (20 mL). After the resulting solution was degassed for 30 min, tetrakis(triphenylphosphine)palladium(0) (32 mg, 0.055 mmol) and cuprous iodide (15 mg, 0.079 mmol) were added in the drybox. The mixture was refluxed under nitrogen for 30 h. It was then cooled to room temperature and filtered to remove the insoluble triethylamine hydrobromide salt. The salt was washed with ethyl ether until the ether washings were clear. The combined filtrate was evaporated to dryness. Purification by flash chromatography (silica gel, 20% ethyl acetate in hexane) afforded 6-(2-hydroxy-2-methyl-3-butyn-4-yl)-2-neopentoxynaphthalene (0.55 g, 71%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.66 (d, J = 8.9 Hz, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.41 (dd, J = 8.6, 2.4 Hz, 1H) , 7.16 (dd, J = 8.9, 2.4 Hz, 1H) , 7.07 (d, J = 2.4 Hz, 1H), 3.70 (s, 2H), 1.62 (s, 6H), 1.07 (s, 9H).

(2) Preparation of 17. To a vigorously stirred solution of 6-(2-hydroxy-2-methyl-3-butyn-4-yl)-2-neopentoxynaphthalene (0.5 g, 1.69 mmol) in 1-butanol (10 mL) at reflux under nitrogen was added at once pulverized potassium hydroxide (94 mg, 1.69 mmol). The solution was refluxed for 2 h. The solvent was removed by roto-evaporation, and the residue was washed with water (3 × 50 mL). After drying under vacuum, the product **17** was purified by flash column chromatography (silica gel, 10% ethyl acetate in hexane) to give a white solid in 82% yield (0.33 g). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.68 (d, J = 9.1 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.46 (dd, J = 8.5, 1.6 Hz, 1H), 7.17 (dd, J = 8.9, 2.3 Hz, 1H), 7.06 (d, J = 2.3 Hz, 1H), 3.70 (s, 2H), 3.09 (s, 1H), 1.03 (s, 9H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 158.7, 134.7, 132.3, 129.4, 129.3, 128.4, 126.9, 120.1, 116.9, 106.6, 84.3, 76.6, 76.5, 31.7, 26.4. FT-IR (KBr), cm^{-1}: 3313 (s), 2974 (s), 2918 (s), 2870 (s), 2106 (m), 1624 (s), 1599 (s), 1496 (m), 1473 (s), 1394 (s), 1363 (s), 1261 (s), 1236 (s), 1170 (s), 1049 (s), 1016 (s), 900 (s), 858 (s), 819 (s). MS, m/z (M + 1): 269.

Preparation and Characterization of the Repeat Unit 18. Under nitrogen, to a 50 mL flame-dried Schlenk flask was loaded **17** (220 mg, 0.92 mmol), **15** (150 mg, 0.46 mmol), triethylamine (10 mL), and THF (10 mL). The resulting solution was degassed for 30 min and then was combined with tetrakis(triphenylphosphine)palladium(0) (26 mg, 0.022 mmol) and cuprous iodide (4 mg, 0.022 mmol) in the drybox. After this reaction mixture was stirred at room temperature under nitrogen for 2 days, it was filtered to remove the insoluble triethylamine hydrobromide salt. The salt was rinsed with diethyl ether until the filtrate was clear. The combined filtrate was evaporated to dryness to give a brown residue which was dissolved in a minimum amount of CH_2Cl_2 and precipitated with methanol (75 mL) three times. After filtration and drying under vacuum, **18** was obtained as an orange solid in 95% yield (279 mg). FT-IR (KBr), cm^{-1}: 2955 (s), 2908 (s), 2868 (s), 2205 (s), 1626 (s), 1601 (s), 1543 (s), 1467 (s), 1394 (s), 1363 (s), 1338 (s), 1253 (s), 1213 (s), 1170 (s), 1132 (s), 1047 (m), 1016 (s), 852 (m), 806 (m). UV−vis (CH_2Cl_2), nm: 236, 300, 354, 406. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 2H), 8.05 (s, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.9 Hz, 2H), 7.59 (dd, J = 8.3, 1.6 Hz, 2H), 7.21 (dd, J = 8.8, 2.4 Hz, 2H), 7.12 (d, J = 2.2 Hz, 2H), 3.74 (s, $-OCH_2$, 4H), 1.04 (s, $-CH_3$, 18H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 159.2, 141.1, 135.3, 132.8, 131.3, 129.6, 128.6, 128.3, 127.6, 127.3, 120.4, 116.1, 106.7, 102.0, 85.6, 78.1, 32.0, 26.7. MS (FAB) Calcd for $C_{40}H_{36}N_2O_6$: m/z 640.2573. Obsd: m/z 640.2611.

Preparation and Characterization of Polymer (*R*)-20. Under nitrogen, to a 50 mL flame-dried Schlenk flask was loaded (*R*)-**9** (210 mg, 0.25 mmol), **19** (100 mg, 0.25 mmol), triethylamine (2 mL), and toluene (8 mL). The resulting solution was degassed for 30 min and then was combined with tetrakis(triphenylphosphine)palladium(0) (14.4 mg, 0.013 mmol) and cuprous iodide (2.4 mg, 0.013 mmol) in the drybox. After this reaction mixture was refluxed under nitrogen for 2 days, it was cooled to room temperature and filtered to remove the insoluble triethylamine hydrobromide salt. The salt was rinsed with diethyl ether until the filtrate was clear. The combined filtrate was evaporated to dryness to give a brown residue which was dissolved in a minimum amount of CH_2Cl_2 and precipitated with methanol (75 mL) twice. The polymer, (*R*)-**20**, was isolated as a yellow solid in 93% yield (230 mg) after drying under vacuum. GPC: $M_w = 7200$ and $M_n = 5100$ (PDI = 1.4). $[\alpha]_D = -103°$ (c = 0.287, CH_2Cl_2). FT-IR (KBr), cm^{-1}: 2924 (s), 2852 (s), 2210 (m), 1618 (m), 1591 (s), 1502 (s), 1465 (s), 1338 (m), 1273 (s), 1249 (s), 1087 (m), 1053 (m), 981 (s), 889 (m), 825 (m), 789 (w), 721 (w). UV−vis (CH_2Cl_2), nm: 262, 278, 344. Fluorescence (CH_2Cl_2), nm: 432 (sh), 459 (λ_{exc} = 394 nm). ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.17−8.08 (br, m), 7.87 (d, J = 8.7 Hz), 7.67 (br m), 7.40−7.37 (br m), 7.12 (br m), 3.97−3.93 (br, $-OCH_2$, 4H), 1.43−0.92 (br, $-CH_2-$, 64H), 0.86−0.85 (br, $-CH_3$, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 141.2, 121.2 with a few very low intensity peaks between 150 and 100. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 156.1, 149.8, 146.3, 142.9, 139.1, 135.0, 134.4, 132.8, 130.0, 129.1, 128.7, 128.6, 128.5, 128.0, 125.8, 125.6, 120.2, 120.0, 116.9, 116.0, 111.96, 101.9, 79.2, 78.6, 77.2, 69.3, 31.8, 29.6, 29.5, 29.4, 29.2, 29.1, 29.0, 28.9, 25.5, 22.5, 13.8. Anal. Calcd for $C_{66}H_{84}F_4O_2$: C, 80.65; H, 8.35. Found: C, 77.80; H, 8.29.

Preparation and Characterization of Polymer *rac*-20. In a procedure similar to the preparation of (*R*)-**20**, *rac*-**20** was obtained from the reaction of *rac*-**9** with **19** as a brown solid in 89% yield. GPC: $M_w = 7600$ and $M_n = 5300$ (PDI = 1.44). FT-IR (KBr), cm^{-1}: 2924 (s), 2852 (s), 2210 (m), 1618 (m), 1591 (s), 1502 (s), 1467 (s), 1338 (m), 1273 (s), 1249 (s), 1087 (m), 1049 (m), 981 (s), 889 (m), 825 (m), 798 (w), 742 (w). UV−vis (CH_2Cl_2), nm: 282, 348. Fluorescence (CH_2Cl_2), nm: 429, 455 (λ_{exc} = 395 nm). ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.17−8.09 (br m), 7.87 (d, J = 8.7 Hz), 7.67−7.63 (br m), 7.40−7.37 (br m), 7.12 (br m), 3.97−3.91 (br, $-OCH_2$, 4H), 1.42−0.94 (br, $-CH_2-$, 64H), 0.86 (br, $-CH_3$, 6H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 145.2, 141.1, 123.9, 121.2. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 156.1, 150.1, 146.3, 142.9, 134.4, 132.8, 130.0, 129.1, 128.7, 128.6, 128.5,128.0, 125.8, 125.6, 120.2, 120.0, 116.9, 116.0, 111.96, 102.1, 79.2, 77.2, 69.4, 31.8, 29.6, 29.5, 29.4, 29.2, 29.1, 29.0, 28.9, 25.5, 22.5, 13.9. Anal. Calcd for $C_{66}H_{84}F_4O_2$: C, 80.65; H, 8.35. Found: C, 77.51; H, 8.23.

Preparation and Characterization of Polymer *rac*-21. In a procedure similar to the preparation of (*R*)-**20**, *rac*-**21** was obtained from the reaction of *rac*-**9** with 1,2-diiodobenzene in 69% yield as a dark solid. GPC: $M_w = 8100$ and $M_n = 5400$ (PDI = 1.5). UV−vis (CH_2Cl_2), nm: 236, 276, 340 (sh). Fluorescence (CH_2Cl_2), nm: 419, 452 (sh). FT-IR (KBr), cm^{-1}: 3063 (m), 2922 (s), 2852 (s), 2204 (m), 1616 (m), 1591 (s), 1464 (s), 1342 (s), 1271 (s), 1244 (s), 1143 (m), 1093 (s), 1051 (s), 885 (m), 825 (s), 798 (m), 754 (s). ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.05 (s), 7.86 (t, J = 8.6 Hz), 7.54 (m), 7.37 (dd, J = 2.0, 8.9 Hz), 7.28 (m), 7.19 (m), 6.98 (d, J = 8.9 Hz), 6.86 (d, J = 8.9 Hz), 3.89 (m), 1.23−1.01 (br m), 0.85 (br s). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 155.4, 134.2, 133.7, 132.2, 132.1, 132.0, 131.6, 131.3, 129.8, 129.4, 129.3, 128.9, 128.8, 128.7, 128.5, 127.8, 127.7, 126.4, 126.1, 125.6, 125.2, 120.4, 120.1, 118.1, 116.1, 116.0, 94.8, 94.7, 94.3, 94.0, 88.5, 88.4, 88.0, 87.5, 69.7, 32.1, 29.9, 29.7, 29.5, 29.4, 29.3, 25.8, 22.8, 14.3.

Preparation and Characterization of 1-Ethynyl-4-(2-hydroxy-2-methyl-3-butyn-4-yl)benzene, 22. (1) Preparation of 1,4-Bis(2-hydroxy-2-methyl-3-butyn-4-yl)benzene, A. Under nitrogen, to a 250 mL flame-dried Schlenk flask was loaded 1,4-dibromobenzene (20 g, 84.7 mmol) and 2-methyl-3-butyn-2-ol (21.4 g, 254 mmol). The flask was then taken into the drybox and was combined with $PdCl_2$ (150 mg, 0.85 mmol), triphenylphosphine (2.3 g, 8.8 mmol), and cuprous iodide (0.60 g, 3.1 mmol). After the addition of triethylamine (150 mL), the solution was refluxed for 36 h. It was then cooled to room temperature and filtered to remove the insoluble triethylamine hydrobromide salt. The salt was washed with diethyl ether until the ether solution was clear. The combined filtrate was evaporated to dryness. The dark residue was washed with water (80 mL), 3% HCl (3 × 60 mL), and water (3 × 80 mL). After drying under vacuum at 90 °C for 4 h, it was recrystallized from toluene to give **A** as a white solid in 98% yield (20.04 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 4H), 2.05 (s, 2H), 1.62 (s, 12H).

(2) Preparation of 1-ethynyl-4-(2-hydroxy-2-methyl-3-butyn-4-yl)benzene, 22. To a solution of **A** (2.0 g, 8.3 mmol) in isopropyl alcohol (40 mL) under nitrogen was added pulverized potassium hydroxide (2.3 g, 41.5 mmol). The solution was kept at 60 °C overnight. The solvent was roto-evaporated, and the residue was washed with water (3 × 40 mL). After drying under vacuum, the product was purified by flash column chromatography (silica gel, 20% ethyl acetate in hexane) to give **22** as a white solid in 65% yield (1.0 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.06 Hz, 2H), 7.37 (d, J = 8.06 Hz, 2H), 3.16 (s, 1H), 2.02 (s, 1H), 1.63 (s, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 131.9, 131.5, 95.6, 82.7, 81.6, 78.8, 64.8, 31.4.

Preparation and Characterization of the Binaphthyl Monomer (*R*)-24. (1) Preparation of 23. Under nitrogen, to a 50 mL flame-dried Schlenk flask was loaded (*R*)-**2** (2.53 g, 2.67 mmol), **22** (1.13 g, 6.14 mmol), and triethylamine (30 mL). The resulting solution was degassed for 30 min and then was combined with $PdCl_2$ (24 mg, 0.13 mmol), triphenylphosphine (0.35 g, 1.3 mmol), and cuprous iodide (89 mg, 0.47 mmol) in the drybox. After this reaction mixture was refluxed for 23 h, it was filtered to remove the insoluble triethylamine hydrobromide salt. The salt was rinsed with diethyl ether until the filtrate was clear. The combined filtrates were evaporated to dryness. The product was purified by flash column (silica gel, 30% ethyl acetate in hexane) to give **23** as a light yellow solid in 83% yield (2.55 g). ^1H NMR (270 MHz, $CDCl_3$): δ 8.05 (s, 2H), 7.90 (d, J = 9.5 Hz, 2H), 7.48−7.36 (m, 10H), 7.28 (dd, J = 1.5, 8.8 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 3.96−3.92 (m, $-OCH_2$, 4H), 2.02 (s, 2H), 1.62 (s, 12H), 1.41−0.99 (m, $-CH_2-$, 64H), 0.85 (t, $-CH_3$, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 155.3, 133.6, 131.6, 131.5, 131.4, 129.2, 128.6, 128.5, 125.5, 123.4, 122.2, 120.0, 117.6, 115.9, 95.3, 91.9, 88.6, 81.9, 69.4, 65.6, 31.9, 31.4, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 25.6, 22.7, 14.1.

(2) Preparation of (*R*)-24. To a vigorously stirred solution of **23** (2.24 g, 1.94 mmol) in 1-butanol (25 mL) at reflux under nitrogen was added at once pulverized potassium hydroxide (0.54 g, 9.7 mmol). The solution was refluxed for 30 min. The solvent was roto-evaporated, and the residue was washed with water (3 × 50 mL). After drying under vacuum, the product was purified by flash column chromatography (silica gel, 10% ethyl acetate in hexane) to give a light yellow solid (*R*)-**24** (1.34 g, 67%). $[\alpha]_D = -176°$ (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 2H), 7.92 (d, J = 9.1 Hz, 2H), 7.51−7.42 (m, 10H), 7.30 (dd, J = 1.6, 9.1 Hz, 2H), 7.12 (d, J = 9.1 Hz, 2H), 4.05−3.93 (m, $-OCH_2$, 4H), 3.18 (s, 2H), 1.44−1.01 (m, $-CH_2-$, 64H), 0.88 (t, $-CH_3$, 6H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 155.4, 133.7, 132.0, 131.7, 131.3, 129.2, 128.6, 128.5, 125.5, 124.1, 121.6, 120.0, 117.6, 115.9, 92.2, 88.5, 83.3, 78.7, 69.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 25.6, 22.7, 14.1. UV−vis (CH_2Cl_2), nm: 240, 298, 334. IR (KBr), cm^{-1}: 3302 (m), 2922 (s), 2850 (s), 2204 (w), 2108 (w), 1618 (m), 1589 (s), 1465 (s), 1344 (s), 1271 (s), 1244 (s), 1141 (m), 1091 (s), 1049 (s), 887 (m), 837 (s), 800 (m). HRMS (FAB) Calcd for $C_{76}H_{94}O_2$: m/z 1038.7254. Obsd: m/z 1038.7302.

Preparation and Characterization of *rac*-24. By using a procedure similar to the preparation of (*R*)-**24**, *rac*-**24** was obtained from *rac*-**2** as a light yellow solid. ^1H NMR (270 MHz, $CDCl_3$): δ 8.08 (s, 2H), 7.92 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 2.2 Hz, 8H), 7.43 (d, J = 9.5 Hz, 2H), 7.31 (dd, J = 1.5, 8.8 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 3.98−3.94 (m, $-OCH_2$, 4H), 3.18 (s, 2H), 1.44−1.01 (m, $-CH_2-$, 64H), 0.88 (t, $-CH_3$, 6H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 155.4, 133.7, 132.0, 131.7, 131.5, 131.4, 129.2, 128.6, 125.5, 124.1, 121.6, 120.0, 117.6, 115.9, 92.2, 88.5, 83.3, 78.7, 69.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.6, 22.7, 14.1. IR (KBr), cm^{-1}: 3319 (s), 2922 (s), 2850 (s), 2197 (m), 2108 (w), 1620 (s), 1601 (s), 1465 (s), 1344 (s), 1265 (s), 1248 (s), 1089 (s), 1055 (s), 889 (m), 835 (s), 794 (m). HRMS (FAB) Calcd for $C_{76}H_{94}O_2$: m/z 1038.7254. Obsd: m/z 1038.7285.

Polymers (*R*)-25, *rac*-25, (*R*)-26, *rac*-26, and *rac*-27 Were Prepared in a Similar Way. Preparation and Characterization of Polymer *rac*-27. *The procedure for the preparation of rac-**27** from rac-**24** and 1,2-diiodobenzene is typical for these polymers.* Under nitrogen, to a 50 mL flame-dried Schlenk flask was loaded *rac*-**24** (260 mg, 0.25 mmol), 1,2-diiodobenzene (83 mg, 0.25 mmol), triethylamine (2 mL), and toluene (8 mL). The resulting solution was degassed for 30 min and then was combined with tetrakis(triphenylphosphine)palladium(0) (14.4 mg, 0.013 mmol) and cuprous iodide (2.4 mg, 0.013 mmol) in the drybox. After this reaction mixture was refluxed for 33 h, it was filtered to remove the insoluble triethylamine hydrobromide salt. The salt was rinsed with diethyl ether until the filtrate was clear. The combined filtrate was evaporated to dryness to give a dark residue which was dissolved in a minimum amount of CH_2Cl_2 and precipitated with methanol (2 × 75 mL). After drying under vacuum, *rac*-**27** was obtained as a brown solid in 97% yield (269 mg). GPC: M_w = 11 600 and M_n = 6400 (PDI = 1.80). UV−vis (CH_2Cl_2), nm: 234, 302, 342. FT-IR (KBr), cm^{-1}: 2924 (s), 2850 (s), 2202 (w), 1618 (m), 1587 (s), 1510 (s), 1464 (s), 1342 (s), 1267 (s), 1242 (s), 1069 (s), 1043 (s), 885 (m), 835 (s), 798 (m). ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (s), 7.90 (br s), 7.53 (s), 7.41 (br s), 7.30 (d, J = 7.2 Hz), 7.11 (d, J = 7.8 Hz), 3.97 (br m, $-OCH_2$, 4H), 1.38−0.86 (br m, $-CH_2-$, 64H), 0.84 (br, $-CH_3$, 6H). ^{13}C NMR (100.9 MHz, $CDCl_3$): δ 155.5, 138.9, 135.3, 133.8, 132.5, 131.8, 129.3, 128.7, 128.2, 127.7, 125.6, 123.8, 122.8, 120.1, 117.8, 116.0, 93.6, 92.4, 90.1, 88.9, 69.5, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 22.8, 14.2.

Characterization of Polymer (*R*)-25. (*R*)-**25** was obtained as a red solid in 77% yield from the reaction of (*R*)-**24** with **15**. GPC: M_w = 10 700 and M_n = 6000 (PDI = 1.80). $[\alpha]_D = -228°$ (c = 0.13, CH_2Cl_2). UV−vis (CH_2Cl_2) nm 234, 296, 346. FT-IR (KBr), cm^{-1}: 2922 (s), 2850 (s), 2200 (s), 1618 (s), 1543 (s), 1464 (s), 1340 (s), 1269 (s), 1242 (s), 1089 (m), 1047 (m), 885 (m), 835 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (s), 8.07 (br m), 8.02 (m), 7.89 (br m), 7.56 (m), 7.49 (s), 7.41 (br m), 7.30 (d, J = 7.5 Hz), 7.12 (d, J = 8.8 Hz), 3.94 (br m), 1.39 (br s), 1.23 (br s), 1.09 (br s), 1.00 (br s), 0.85 (t). ^{13}C NMR (100.9 MHz, $CDCl_3$): δ 155.6, 141.8, 141.3, 140.8, 133.9, 132.2, 132.0, 131.9, 131.8, 131.6, 129.4, 129.1, 128.7, 128.6, 128.4, 125.6, 120.7, 120.3, 120.0, 117.4, 116.0, 101.4 (m), 100.5, 93.7 (m), 88.6, 86.9, 86.8, 69.5, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 22.8, 14.2.

Characterization of Polymer (*R*)-26. (*R*)-**26** was obtained as a brown solid in 90% yield from the reaction of (*R*)-**24** with **10**. GPC: M_w = 14 200 and M_n = 6900 (PDI = 2.1). $[\alpha]_D = -284°$ (c = 0.14, CH_2Cl_2). UV−vis (CH_2Cl_2), nm: 232, 296, 362. FT-IR (KBr), cm^{-1}: 2920 (s), 2850 (s), 2202 (m), 1618 (m), 1585 (s), 1520 (s), 1464 (s), 1340 (s), 1269 (s), 1242 (s), 1089 (m), 1039 (m), 885 (m), 835 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, J = 2.1 Hz), 8.17 (dd, J = 2.6, 8.9 Hz), 8.07 (br m), 7.90 (br m), 7.68 (d, J = 8.6 Hz), 7.56 (m), 7.49 (s), 7.43 (br m), 7.30 (d, J = 8.8 Hz), 7.12 (d, J = 8.8 Hz), 3.97 (br m), 1.39 (br s), 1.24 (br s), 1.09 (br s), 0.88 (br s), 0.85 (t). ^{13}C NMR (100.9 MHz, $CDCl_3$): δ 155.6, 147.0, 133.8, 133.4, 132.5, 132.0, 131.7, 131.6, 129.4, 128.7, 128.6, 127.7, 126.0, 125.6, 125.1, 122.2, 121.2, 120.1, 117.5, 116.0, 99.3, 93.2, 88.7, 88.5, 69.5, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 22.8, 14.2.

Characterization of Polymer *rac*-26. *rac*-**26** was obtained as a yellow solid in 78% yield from the reaction of *rac*-

24 with **10**. GPC: $M_w = 10\,500$ and $M_n = 6000$ (PDI = 1.79). UV−vis (CH_2Cl_2), nm: 234, 318, 358. FT-IR (KBr), cm^{-1}: 2922 (s), 2850 (s), 2202 (s), 1616 (m), 1587 (s), 1520 (s), 1464 (s), 1342 (s), 1269 (s), 1242 (s), 1092 (s), 1039 (m), 865 (m), 835 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (s), 8.41 (s), 8.15 (s), 8.07 (s), 7.90 (s), 7.68 (d, $J = 8.3$ Hz), 7.56 (s), 7.48 (s), 7.41 (s), 7.30 (d, $J = 8.1$ Hz), 7.12 (d, $J = 8.6$ Hz), 3.97 (br m), 1.40 (s), 1.22 (s), 1.09 (s), 1.00 (s), 0.85 (t). ^{13}C NMR (100.9 MHz, $CDCl_3$): δ 155.6, 147.0, 146.8, 133.9, 133.4, 132.5, 132.0, 131.9, 131.8, 129.4, 128.7, 127.7, 126.0, 125.6, 124.9, 124.7, 122.8, 122.2, 121.8, 120.1, 117.5, 116.0, 99.3, 98.8, 95.9, 93.2, 92.9, 88.7, 88.5, 88.1, 69.5, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 22.8, 14.2.

Preparation and Characterization of Polymer (*R*)-29. To a mixture of (*R*)-**28** (271 mg, 0.5 mmol) and **10** (141 mg, 0.5 mmol) in THF (5 mL) and 1 M aqueous solution of K_2CO_3 (7.5 mL) was added a THF (2.5 mL) solution of $Pd(PPh_3)_4$ (30 mg) under nitrogen. The reaction mixture was heated at reflux for 43 h. The organic layer was separated and diluted with CH_2Cl_2 (50 mL). The solution was then washed with 1 N HCl (15 mL) and brine (15 mL). After removal of the solvent, a solid was obtained which was repetitively dissolved in CH_2Cl_2 and precipitated with MeOH. Centrifugation of the mixture gave a yellow solid, (*R*)-**29** (260 mg, 91%). GPC: $M_w = 10\,100$ and $M_n = 4900$ (PDI = 2.05). $[\alpha]_D = -70.92°$ (c = 0.5, CH_2Cl_2). FT-IR (KBr), cm^{-1}: 2932 (s), 2859 (s), 1622 (s), 1591 (s), 1580 (s), 1524 (s), 1485 (s), 1468 (s), 1337 (s), 1273 (s), 1246 (s), 1182 (m), 1140 (w), 1094 (s), 1059 (s), 949 (w), 889 (m), 824 (m), 801 (m), 739 (w). UV−vis (CH_2Cl_2), nm: 246, 350. Fluorescence (CH_2Cl_2, very weak), nm: 410 ($\lambda_{exc} = 329$ nm). ^1H NMR (270 MHz, $CDCl_3$): δ 0.64 (t, $J = 6.6$ Hz, 6H), 0.89 (m, 12H), 1.20 (m, 4H), 3.76 (m, 4H, OCH_2), 6.781 (m, 4H), 7.28 (m, 2H), 7.76 (m, 5H), 8.19, 8.36 (m, 2H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.79, 22.33, 25.08, 29.12, 31.06, 69.60, 116.06, 120.05, 121.98, 125.21, 125.87, 127.60, 128.77, 128.95, 129.24, 131.86, 133.10, 134.33, 141.53, 146.82, 155.057. Anal. Calcd for $C_{38}H_{39}NO_4$: C, 79.56; H, 6.85; N, 2.44. Found: C, 77.22; H, 7.31; N, 2.58.

Preparation and Characterization of Polymer *rac*-29. In a procedure similar to that of (*R*)-**29**, *rac*-**29** was prepared from the reaction of *rac*-**24** with **10** as a yellow solid in 92% yield. FT-IR (KBr), cm^{-1}: 2930 (s), 2869 (s), 1622 (m), 1591 (s), 1580 (s), 1524 (s), 1485 (s), 1468 (s), 1343 (s), 1273 (s), 1248 (s), 1184 (m), 1140 (w), 1094 (s), 1061 (s), 949 (w), 889 (m), 824 (m), 801 (m), 739 (w). GPC: $M_w = 6300$ and $M_n = 3700$ (PDI = 1.7). UV−vis (CH_2Cl_2), nm: 246, 350. Fluorescence (CH_2Cl_2, very weak), nm: 433, 463 ($\lambda_{exc} = 350$ nm). ^1H NMR (270 MHz, $CDCl_3$): δ 0.64 (m, 6H), 0.73−0.91 (m, 16H), 3.74 (m, 4H, OCH_2), 6.88 (m, 4H), 7.22 (m, 2H), 7.73 (m, 5H), 8.25, 8.41 (m, 2H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 13.84, 22.33, 25.13, 29.13, 31.21, 69.50, 115.98, 120.05, 122.03, 125.22, 125.91, 127.60, 128.64, 128.90, 129.28, 131.94, 133.12, 133.71, 134.45, 141.56, 146.84, 154.98. Anal. Calcd for $C_{38}H_{39}NO_4$: C, 79.55; H, 6.85; N, 2.44. Found: C, 76.81; H, 6.79; N, 2.54.

Preparation and Characterization of Polymer (*R*)-31. Under nitrogen, to a 50 mL flame-dried Schlenk flask was loaded (*R*)-**9** (420 mg, 0.50 mmol), **30** (164 mg, 0.50 mmol), triethylamine (2 mL), and THF (8 mL). After the resulting solution was degassed for 30 min, it was taken into the drybox and tetrakis(triphenylphosphine)palladium(0) (28.8 mg, 0.026 mmol) and cuprous iodide (4.8 mg, 0.026 mmol) were added. This reaction mixture was stirred at room temperature for 2 days, and was filtered to remove the insoluble triethylamine hydrobromide salt. The salt was rinsed with diethyl ether until the filtrate was clear. The combined filtrate was evaporated to dryness to give a dark residue which was dissolved in a minimum amount of CH_2Cl_2 and precipitated with methanol (75 mL) twice. After drying under vacuum, (*R*)-**31** was obtained as an orange solid in 92% yield (460 mg). GPC: $M_w = 30\,500$ and $M_n = 16\,300$ (PDI = 1.87). FT-IR (KBr), cm^{-1}: 2926 (s), 2850 (s), 2198 (s), 1618 (m), 1595 (s), 1535 (m), 1487 (m), 1460 (s), 1334 (s), 1269 (s), 1238 (s), 1145 (m), 1091 (m), 1047 (m), 1014 (m), 829 (m), 800 (w). UV−vis (CH_2Cl_2), nm: 256, 284 (sh), 359 (sh), 442. ^1H NMR (270 MHz, $CDCl_3$): δ 8.92 (s), 8.21 (s), 8.03 (s), 7.97 (d, $J = 9.4$ Hz), 7.44 (d, $J = 9.2$ Hz), 7.36 (d, $J = 8.1$ Hz), 7.13 (d, $J = 8.1$ Hz), 3.97 (br m, $-OCH_2$, 4H), 1.40−0.86 (br, $-CH_2-$, 64H), 0.81 (br, $-CH_3$, 6H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 156.6, 146.6, 140.3, 134.8, 134.1, 130.7, 130.2, 128.6, 125.9, 123.9, 122.6, 119.8, 116.2, 115.9, 104.7, 83.9, 77.2, 69.2, 31.7, 29.5, 29.4, 29.3, 29.1, 28.9, 25.4, 22.4, 13.8. Anal. Calcd for $C_{66}H_{86}N_2O_6$: C, 79.04; H, 8.58; N, 2.79. Found: C, 78.38; H, 8.54; N, 2.80.

Preparation and Characterization of Polymer *rac*-31. By using a similar procedure, *rac*-**31** was prepared as a brown solid in 95% yield from the reaction of *rac*-**9** with **30**. GPC: $M_w = 20\,000$ and $M_n = 12\,000$ (PDI = 1.61). FT-IR (KBr), cm^{-1}: 2922 (s), 2852 (s), 2198 (s), 1616 (m), 1595 (s), 1535 (m), 1487 (m), 1460 (s), 1334 (s), 1271 (s), 1238 (s), 1145 (m), 1091 (m), 1051 (m), 1014 (m), 889 (m), 829 (m), 800 (w). UV−vis (CH_2Cl_2), nm: 260, 284 (sh), 359 (sh), 440. ^1H NMR (270 MHz, $CDCl_3$): δ 8.92 (s), 8.21 (s), 8.03 (s), 7.97 (d, $J = 9.1$ Hz), 7.43 (d, $J = 8.5$ Hz), 7.37 (d, $J = 8.3$ Hz), 7.13 (d, $J = 8.6$ Hz), 3.97 (br m, $-OCH_2$, 4H), 1.40−0.86 (br, $-CH_2-$, 64H), 0.81 (br, $-CH_3$, 6H). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 156.5, 146.5, 140.3, 134.8, 134.1, 130.2, 128.7, 128.6, 125.9, 124.0, 122.6, 119.8, 116.2, 116.0, 104.7, 84.0, 77.2, 69.2, 31.7, 29.5, 29.4, 29.3, 29.1, 29.0, 28.9, 25.4, 22.4, 13.8. Anal. Calcd for $C_{66}H_{86}N_2O_6$: C, 79.04; H, 8.58; N, 2.79. Found: C, 78.73; H, 8.79; N, 2.82.

Preparation and Characterization of the Repeating Unit 32. Under nitrogen, to a 50 mL flame-dried Schlenk flask was loaded **17** (0.15 g, 0.63 mmol), **30** (0.10 g, 0.315 mmol), triethylamine (10 mL), and THF (5 mL). After the resulting solution was degassed for 30 min, it was taken into the drybox and tetrakis(triphenylphosphine)palladium(0) (36 mg, 0.032 mmol) and cuprous iodide (6.0 mg, 0.032 mmol) were added. This reaction mixture was stirred at room temperature for 2 days and was filtered. The resulting orange solid was washed with 3 M HCl (3 × 15 mL) and H_2O (3 × 20 mL). After being dried, **30** was crystallized from CH_2Cl_2 to give 170 mg of orange solid in 84% yield. FT-IR (KBr), cm^{-1}: 2957 (m), 2868 (m), 2202 (s), 1622 (s), 1604 (s), 1581 (s), 1498 (m), 1464 (s), 1396 (s), 1363 (s), 1255 (s), 1201 (s), 1170 (m), 1130 (m), 1012 (s), 871 (m), 815 (m). UV−vis (CH_2Cl_2), nm: 244, 282, 354, 430. ^1H NMR (270 MHz, $CDCl_3$): δ 8.94 (s, 1H), 8.11 (s, 2H), 8.08 (s, 1H), 7.75 (m, 4H), 7.62 (d, $J = 1.4$ Hz, 1H), 7.59 (d, $J = 1.6$ Hz, 1H), 7.21 (d, $J = 2.4$ Hz, 2H), 7.12 (d, $J = 2.0$ Hz, 2H), 3.73 (s, 4H), 1.08 (s, 18H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 159.1, 146.2, 146.0, 135.6, 130.0, 129.8, 128.8, 128.4, 127.0, 124.1, 120.5, 116.0, 106.7, 104.6, 83.9, 78.0, 77.2, 32.0, 26.4. HRMS (FAB) Calcd for $C_{40}H_{36}N_2O_6 + H^+$: m/z 641.2652. Obsd: m/z 641.2614. Anal. Calcd for $C_{40}H_{36}N_2O_6$: C, 75.00; H, 5.62; N, 4.37. Found: C, 73.91; H, 5.51; N, 3.71.

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