Asymmetric Synthesis of Helical Poly(quinoxaline-2,3-diyl)s by Palladium-Mediated Polymerization of 1,2-Diisocyanobenzenes: Effective Control of the Screw-Sense by a Binaphthyl Group at the Chain-End

Yoshihiko Ito,* Toshiyuki Miyake, Seiji Hatano, Ryoto Shima, Takafumi Ohara, and Michinori Suginome

Contribution from the Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Received July 15, 1998

Abstract: Aromatizing polymerization of 1,2-diisocyanobenzene derivatives was mediated by optically active organopalladium(II) complexes bearing 1,1′-binaphth-2-yl groups to give optically active poly(quinoxaline-2,3-diyl)s with varying screw-sense selectivities, which crucially depended upon the substituents on the binaphthyl groups. The most effective catalyst, which has 7′-methoxy-1,1′-binaphthyl group, induced the formation of a single screw-sense. Isolation and structural analyses (single-crystal X-ray diffraction and ^{1}H NMR spectroscopy) of intermediary [oligo(quinoxalinyl)]palladium complexes revealed that the screw-sense selection in the polymerization may be decisively governed by the diastereomeric ratios of the (terquinoxalinyl)-palladium(II) complex intermediate.

Introduction

Much interest has been focused on the synthesis of optically active polymers directing toward development of new functional materials.[1] In addition to the asymmetric polymerization of prochiral olefinic monomers,[2,3] isocyanates and isocyanide, which are devoid of prochirality, can also produce optically active polymers with helical chirality of their backbones.[1,4−6] Unlike the stereochemical control for the asymmetric polymerization of the prochiral monomers, the screw-sense generated at the early stage of the polymerization was transmitted to the propagating polymer main chains throughout the polymerization. Thus, generation of helically well-ordered polymers with stable screw-sense, which is able to be transmitted to newly formed polymer main-chains effectively, are highly desired for development of new methodology for the synthesis of optically active helical polymers.

We reported an aromatizing polymerization of 1,2-diisocyanobenzenes promoted by methylpalladium(II) complexes, producing poly(quinoxaline-2,3-diyl)s.[7] The polymerization proceeds with successive insertion of the two isocyano groups of the diisocyanobenzene to the carbon−palladium bond of organopalladium complex to give 2-quinoxalinylpalladium complexes, whose carbon−palladium bond undergoes further successive insertion of the diisocyanobenzenes to provide the quinoxaline polymers. The poly(quinoxaline)s thus produced feature their rigid helical structures, which arise from a sequence of quinoxaline rings with regular dihedral angles between the two adjacent rings.

The first attempt for the synthesis of optically active, helical poly(quinoxaline)s started with separation and isolation of two diastereomerically pure bromo[oligo(quinoxalinyl)]palladium-(II)-L^*_2 (L^* = di((*S*)-2-methylbutyl)phenylphosphine) complexes, which were produced by the oligomerization of 3,6-di-*p*-tolyl-1,2-diisocyanobenzene with optically active *trans*-(bromo)methylpalladium(II)-L^*_2.[8] Right- and left-handed bromo(quinquequinoxalinyl)palladium(II)-L^*_2 thus prepared were subjected to ligand exchange reaction with a large excess of

(1) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349−372. Pu, L. *Acta Polym.* **1997**, *48*, 116−141.

(2) For asymmetric cyclopolymerization of 1,5-hexadiene mediated by optically active Zr complexes, see: Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270−6271. Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91−98.

(3) For asymmetric synthesis of poly(olefin-*alt*-CO) mediated by optically active palladium complexes, see: Brookhart, M.; Wagner, M. L. *J. Am. Chem. Soc.* **1994**, *116*, 3641. Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. Nozaki, K.; Sato, N.; Takaya, H. *J. Am. Chem. Soc.* **1995**, *117*, 9911. Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 4455.

(4) For screw-sense selective polymerization of isonitriles mediated by optically active transition-metal catalysts, see: Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 6818−6825. Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 7926−7927. Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9101−9111. Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1554−1556.

(5) For optically active poly(isonitrile)s, see also: Nolte, R. J. M.; van Beijnen, A. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1974**, *96*, 5932−5933. Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 4400−4402.

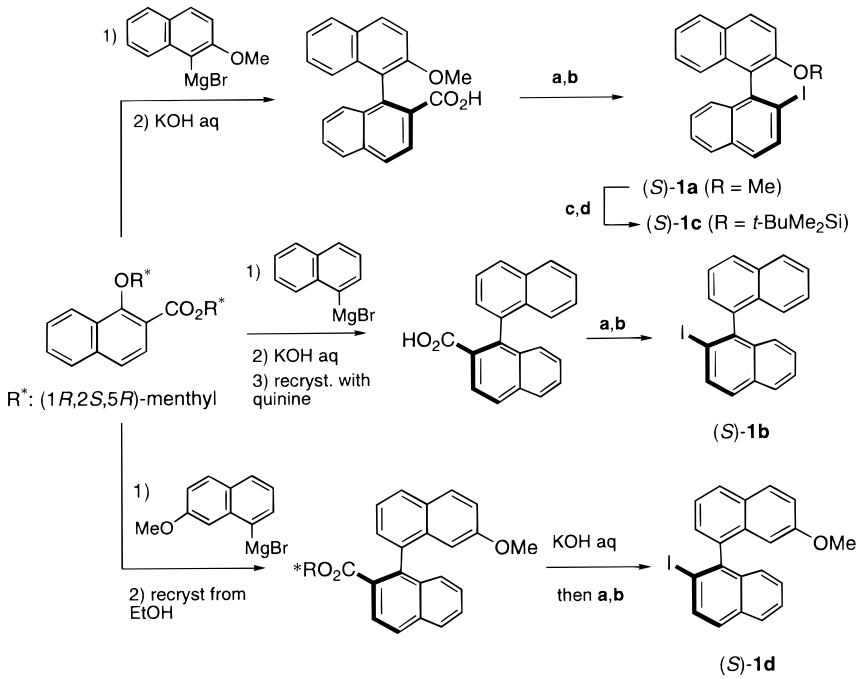
(6) For optically active poly(isocyanate)s, see: Goodman, M.; Chen, S.-C. *Macromolecules* **1970**, *3*, 398−402. Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860−1866. Okamoto, Y.; Matsuda, M.; Nakano, T.; Yashima, E. *Polym. J.* **1993**, *25*, 391−396.

(7) (a) Ito, Y.; Ihara, E.; Murakami, M.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 6446−6447. (b) Ito, Y.; Ihara, E.; Uesaka, T.; Murakami, M. *Macromolecules* **1992**, *25*, 6711−6713. (c) Ito, Y.; Ihara, E.; Murakami, M. *Polym. J.* **1992**, *24*, 297.

(8) (a) Ito, Y.; Ihara, E.; Murakami, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1509−1510. (b) Ito, Y.; Ihara, E.; Murakami, M.; Sisido, M. *Macromolecules* **1992**, *25*, 6810−6813. (c) Ito, Y.; Kojima, Y.; Murakami, M. *Tetrahedron Lett.* **1993**, *51*, 8279−8282. (d) Ito, Y.; Kojima, Y.; Murakami, M.; Suginome, M. *Heterocycles* **1996**, *42*, 597−615. (e) Ito, Y.; Kojima, Y.; Murakami, M.; Suginome, M. *Bull. Chem. Soc. Jpn.* **1997,** *70*, 2801−2806.

10.1021/ja982500m CCC: $15.00
Published on Web 11/05/1998

Scheme 1[a]



[a] Reagents and conditions: (a) (i) $ClCO_2Me$, Et_3N, acetone, −15 °C; (ii) aq, NaN_3 −15 °C; (iii) benzene 80 °C; (iv) aq KOH, 80 °C; (b) (i) $NaNO_2$, H_2SO_4, 0 °C; (ii) KI, H_2SO_4, 0 °C; (c) BBr_3, CH_2Cl_2, −78 °C; (d) *t*-$BuMe_2SiCl$, imidazole, DMF, rt.

achiral dimethylphenylphosphine. The enantiomerically pure right- and left-handed bromo(quinquequinoxalinyl)palladium-(II) bis(dimethylphenylphosphine) complexes isolated were used as a catalyst for polymerization of 1,2-diisocyanobenzenes, providing right- and left-handed helical poly(quinoxaline-2,3-diyl)s after removal of the palladium moiety with methylmagnesium bromide, which exhibited symmetrical CD spectra and the same optical rotations with opposite sign.[8a]

The screw-sense selective polymerization, however, involves a tedious operation for the optical resolution, which is not applicable for gram-scale synthesis of optically active poly-(quinoxaline)s. Besides, the optically active, helical poly-(quinoxaline)s derived from the (bromo)methylpalladium complexes underwent slow racemization in solution. In this paper, we describe the asymmetric polymerization of 1,2-diisocyanobenzenes promoted by optically active iodo(1,1′-binaphth-2-yl)palladium(II) complexes as initiators.[9,10] The axial chirality of the binaphthyl group, which becomes far from the living palladium terminus with propagation of the polymerization, successfully induced high screw-sense selectivity to provide optically pure, helical poly(quinoxaline-2,3-diyl)s. Moreover, isolation and structural characterization of intermediary [oligo-(quinoxalinyl)]palladium complexes shed light on mechanism for induction of helical chirality of the poly(quinoxaline)s.

Result and Discussion

Synthesis of Optically Active Palladium(II) Initiators Bearing 1,1′-Binaphth-2-yl Groups. General preparation of alkyl- or arylpalladium(II) complexes involves transmetalation of organometallic species with palladium(II) complexes, or oxidative addition of organic halides with palladium(0) complexes. The optically active binaphthylpalladium(II) complexes were conveniently prepared by the latter method, i.e., reaction of binaphthyl halides with palladium(0)−phosphine complexes, since the oxidative addition of the carbon−halogen bond onto palladium was expected to proceed with retention of configuration of the starting optically active binaphthyl halides.

Optically pure 2-iodo-1,1′-binaphthyls **1a**−**d** were synthesized according to the Miyano's procedure, which involves stereoselective nucleophilic aromatic substitution reaction of (1*R*)-menthyl 1-((1*R*)-menthoxy)naphthalene-2-carboxylate with the corresponding 1-naphthyl Grignard reagents, giving binaphthalenecarboxylic esters (Scheme 1).[11] In contrast to the highly diastereoselective coupling with 2-methoxy-1-naphthylmagnesium bromide, giving the corresponding binaphthylcarboxylic acid with (*S*)-axial configuration, those with 1-naphthyl and 7-methoxy-1-naphthyl Grignard reagents gave 88:12 and 94:6 mixtures of the corresponding diastereomers, respectively, with the (*S*)-axial chirality predominating. For the synthesis of **1b**, binaphthalenecarboxylic acid obtained by hydrolysis of the diastereomeric mixture was purified by recrystallization of its quinine salt to give the corresponding enantiomerically pure acid. For the 7′-methoxy-1,1′-binaphthalene-2-carboxylate derivative, recrystallization of the diastereomeric mixture of the menthyl ester from ether−methanol gave diastereomerically pure ester, which was used for the synthesis of (*S*)-**1d**. The corresponding (*R*)-**1d** was similarly synthesized from the enantioisomeric (*1S*)-menthyl 1-((*1S*)-menthoxy)naphthalene-2-carboxylate. The TBDMS derivative (*S*)-**1c** was synthesized from (*S*)-**1a** by demethylation with BBr_3 followed by treatment with TBDMSCl in the presence of base. Though it was difficult to separate iodides **1a**−**d** from the accompanying protiodeiodinated compounds, which were formed as byproducts in the Sandmeyer reaction, the crude iodides were used for the

(9) Ito, Y.; Ohara, T.; Shima, R.; Suginome, M. *J. Am. Chem. Soc.* **1996**, *118*, 9188−9189.

(10) Ito, Y.; Miyake, T.; Ohara, T.; Suginome, M. *Macromolecules* **1998**, *31*, 1697−1699.

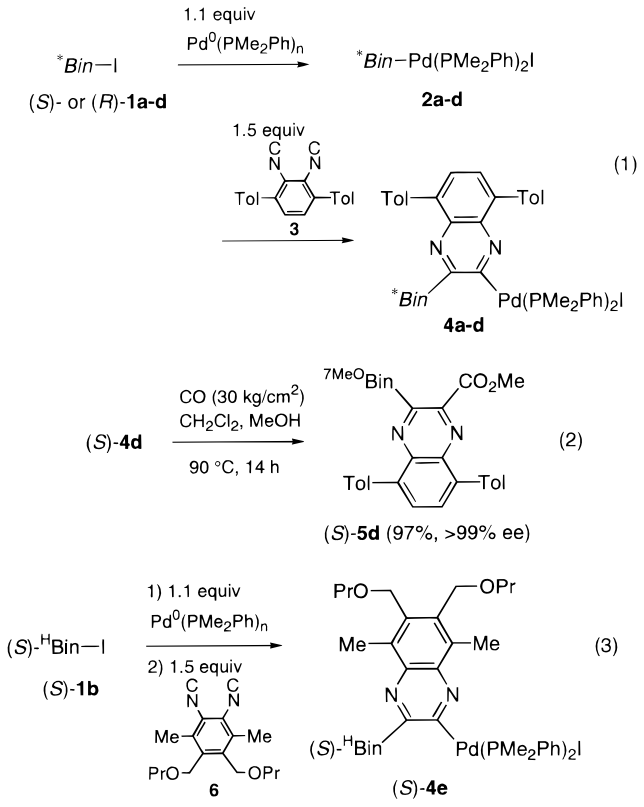
(11) Hattori, T.; Hotta, H.; Suzuki, T.; Miyano, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 613−622. They introduced *p* (plus) and *m* (minus) notation, which indicates the direction of the twist of the two naphthalene rings, for designation of the axial chirality of 1,1′-binaphthyl skeletons without considering their substituents.

synthesis of binaphthylpalladium initiators without further purification.

The substituted binaphthyl iodides (*S*)-**1a**, (*S*)-**1c**, and (*R*)-**1d** all have *p*-chirality, while (*S*)-**1b** and (*S*)-**1d** have *m*-chirality (Chart 1).[11]

The binaphthyl iodides **1a**−**d** were reacted with $(PhMe_2P)_n$-Pd(0), generated in situ from (η^5-cyclopentadienyl)(η^3-allyl)-palladium(II) and 3 equiv of $PhMe_2P$ at −78 °C,[12] to give bis(dimethylphenylphosphine)(1,1′-binaphth-2-yl)palladium-(II) iodide derivatives **2a**−**d** (eq 1). The complexes **2a**−**d** were then reacted with 3,6-di-*p*-tolyl-1,2-diisocyanobenzene (**3**) to afford the corresponding [3-(binaphth-2-yl)quinoxalin-2-yl]-palladium(II) complexes **4a**−**d**, which are stable and easily handled as initiators for the polymerization of 1,2-diisocyanobenzenes.

The complete retention of the enantiopurity of (*S*)-**1d** in the transformation to (*S*)-**4d** was confirmed by a chiral HPLC analysis of binaphthalenecarboxylic ester (*S*)-**5d**, which was prepared by reaction of (*S*)-**4d** with carbon monoxide in the presence of methanol (eq 2).[13] In addition to **4a**−**d**, a



[(binaphthyl)quinoxalinyl]palladium(II) complex **4e** was also prepared from (*S*)-**1b** and the corresponding diisocyanide **6** according to the similar procedure (eq 3).

Synthesis of Enantiomerically Pure Right-Handed Helical Polymers via Isolation of (Quinquequinoxalinyl)palladium-(II) Complex. We were pleased to find that, in the attempted oligomerization of 5 molar equiv of **3** with (*S*)-**4a**, diastereomerically pure (quinquequinoxalinyl)palladium(II) complex

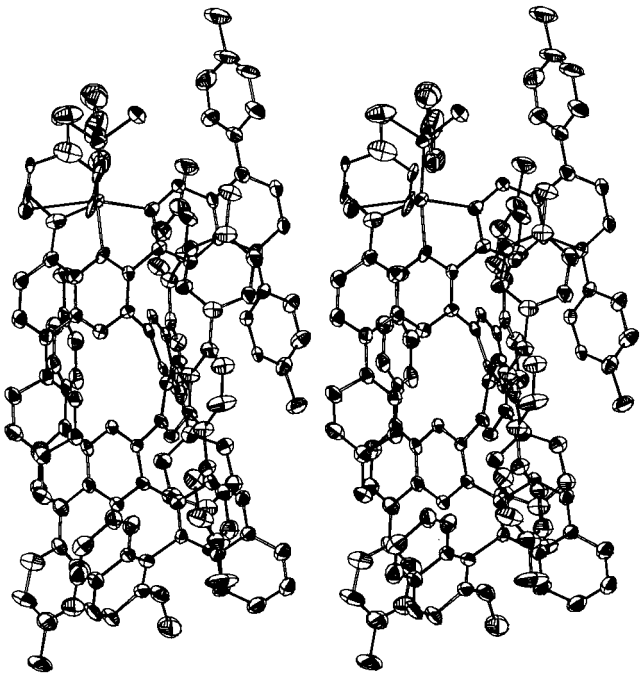
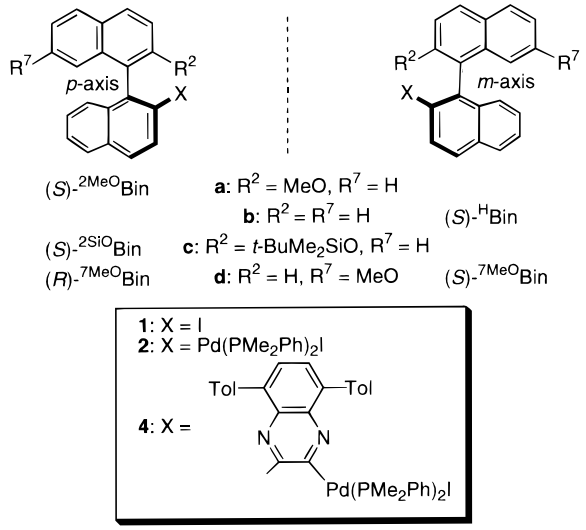
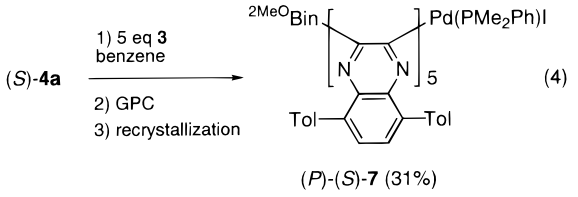


Figure 1. ORTEP drawing of (*P*)-(*S*)-**7** (30% probability, stereoview).

Chart 1. Binaphthyl Derivatives **1**, **2**, and **4**



(*S*)-**7** was separated and isolated in 31% yield as reddish crystals by recrystallization from hexane−CH_2Cl_2 (eq 4). A 400 MHz



^{1}H NMR spectrum of the palladium complex exhibited the distinct 10 methyl singlets of the tolyl groups and one methyl singlet of the 2-methoxynaphthyl group. A single-crystal X-ray analysis of (*S*)-**7** revealed a right-handed helical structure (i.e., helical chirality of *P*), in which the two adjacent quinoxaline rings Q(1)−Q(2), Q(2)−Q(3), and Q(3)−Q(4) are arranged at the dihedral angles of approximately +150°, except for those near the palladium terminus, Q(4)−Q(5), which is deviated to nearly +170°, probably due to the intramolecular coordination

(12) Bennett, M. A.; Chiraratvatana, C.; Robertson, G. B.; Tooptakong, U. *Organometallics* **1988**, *7*, 1403−1409 and references therein.

(13) The ^{1}H NMR spectrum of (*S*)-**5d** at room temperature exhibited two signals for each two methoxy groups, indicating slow rotation around the C−C bond between quinoxaline and naphthalene rings. The measurement at 100 °C in toluene-d_8 allowed to observe coalesced signals for the methoxy groups.

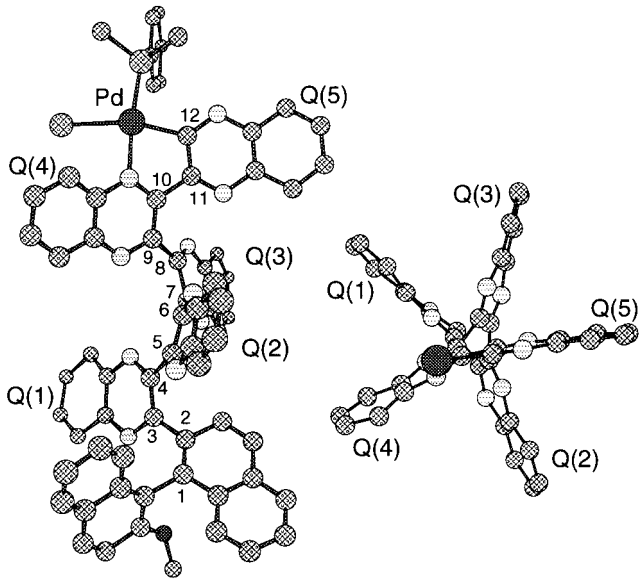
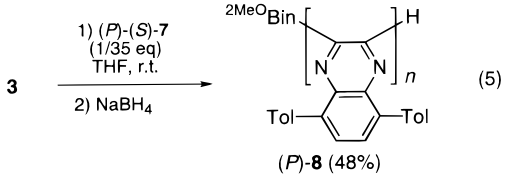


Figure 2. Skeletal structure of (*P*)-(*S*)-**7** determined by the X-ray analysis. A side view (left; tolyl groups were omitted) and a top view (right; binaphthyl, tolyl, phosphine, and iodo groups are omitted). Selected bond distances (Å) and torsion angles (deg) are follows: Pd−Cl = 2.002(16), Pd−I = 2.733(2), Pd−P = 2.2214(5), Pd−N = 2.144(11); Cl−C2−C3−C4 = 147.3(21), C3−C4−C5−C6 = 151.8(19), C5−C6−C7−C8 = 146.1(19), C7−C8−C9−C10 = 145.2(19), C9−C10−C11−C12 = 168.5(21).

of the nitrogen atom of Q(4) to the iodo(dimethylphenylphosphine)palladium terminus (Figures 1 and 2). The helical structure once formed was stable with no change of CD spectrum even on heating in benzene at 80 °C for 24 h.

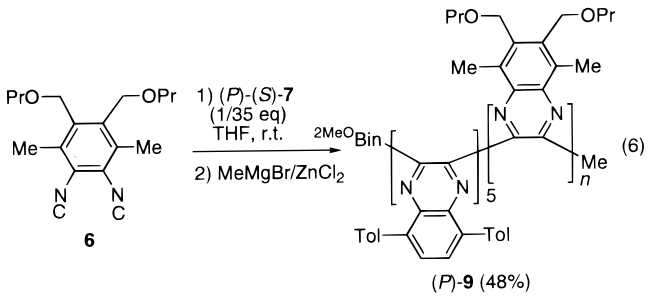
The stable palladium(II) complex (*P*)-(*S*)-**7** was still active and induced the polymerization of **3** (35 equiv) at room temperature, producing poly(quinoxaline) **8** after quenching the living palladium terminus by $NaBH_4$ (eq 5). The polymers showed a remarkably strong CD spectrum between 250 and 370 nm (Figure 3). As previously demonstrated with optically active



(5)

quinque- as well as sexi-quinoxalinylpalladium(II) complexes isolated by optical resolution, the polymerization of **3** with (*P*)-(*S*)-**7** may proceed with retention of its preorganized screw-sense to give highly pure, right-handed (*P*) helical poly(quinoxaline)s **8** after quenching, which can be regarded as a standard for determination of the screw-sense selectivity.

Another standard polymer (*P*)-**9**, which was synthesized by the reaction of 35 molar equiv of **6** with (*P*)-(*S*)-**7** (eq 6), showed



(6)

a similar CD spectrum characteristic of optically active (*P*)-helical poly(quinoxaline)s but significantly different from that of (*P*)-**8**, presumably due to the lack of phenyl chromophore on each quinoxaline (Figure 4).

Screw-Sense Selective Polymerization of 1,2-Diisocyano-3,6-di-*p*-tolylbenzene (3). With the standard CD spectra in hand, [(substituted binaphthyl)quinoxalinyl]palladium(II) complexes **4a**−**d** were tested as the initiators for screw-sense selective polymerization of **3** (40 equiv) in THF at room temperature (Table 1). A catalyst (*S*)-**4a**, having a 2′-methoxy substituent on the binaphthalene, promoted a polymerization of

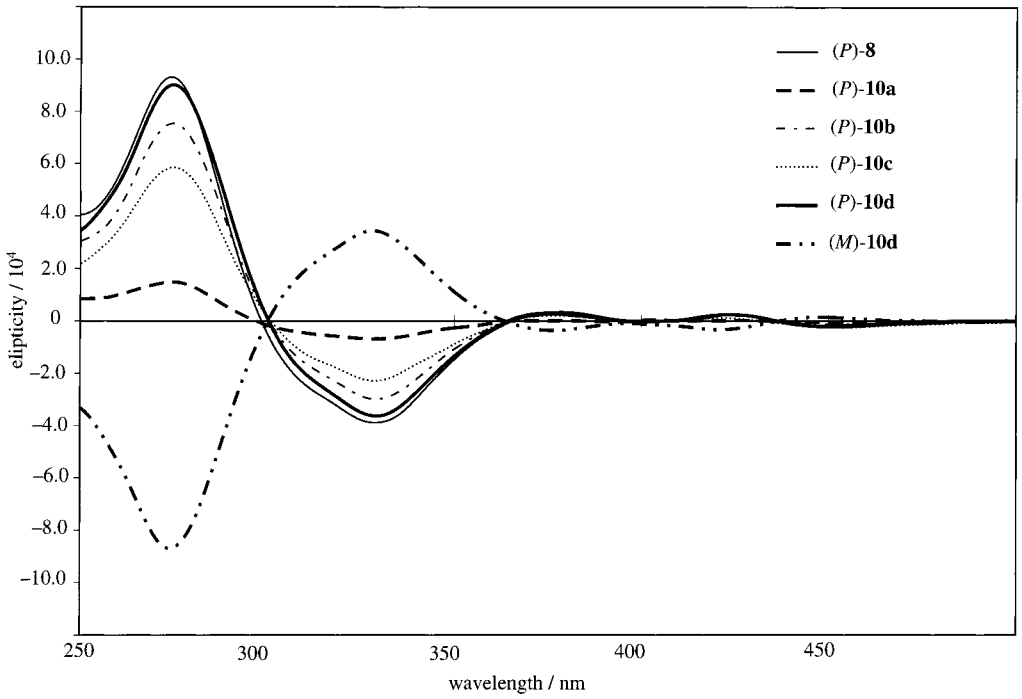


Figure 3. CD spectra of (*P*)-**8**, (*P*)-**10a-d**, and (*M*)-**10d**.

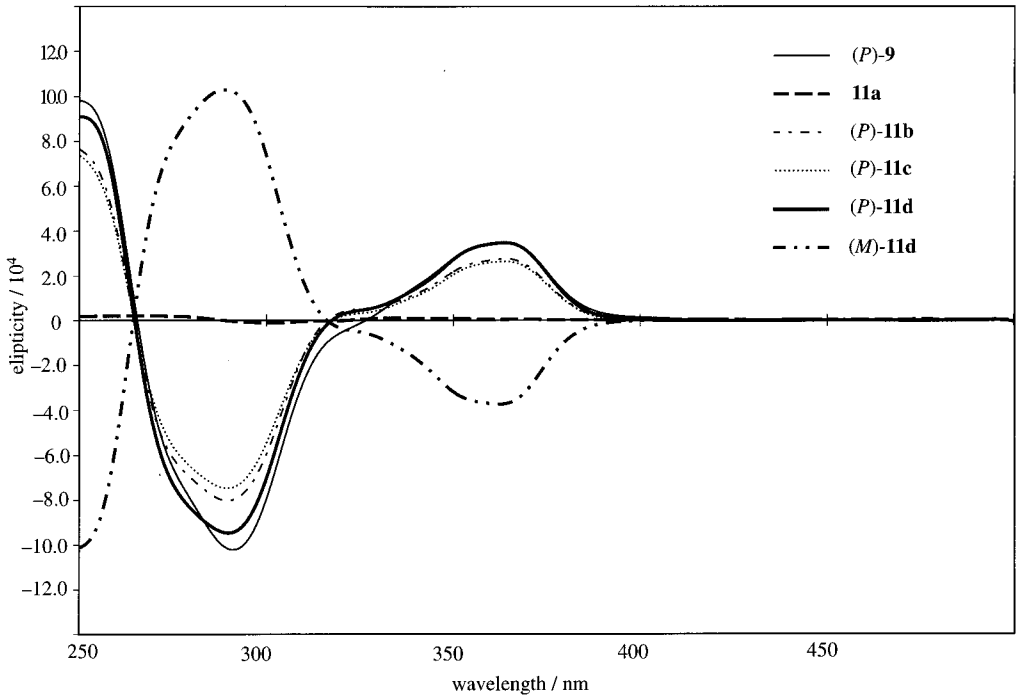
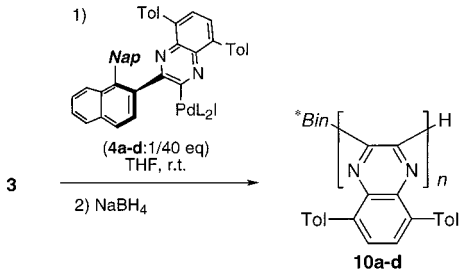
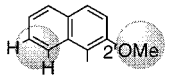
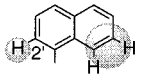
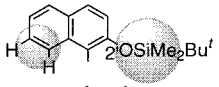
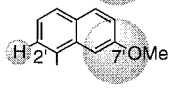
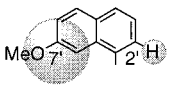


Figure 4. CD spectra of (*P*)-**9**, (*P*)-**11a-d**, and (*M*)-**11d**.

Table 1. Asymmetric Polymerization of **3** in the Presence of Optically Active **4a**−**d**



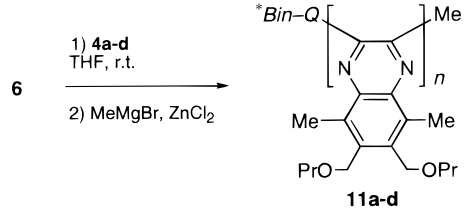
10a-d

entry	catalyst	***Nap*** of **4**[a]	polymer (yield/%)[b]	ee/% (config)[c]	$M_n/10^3$	M_w/M_n
1	(*S*)-**4a**		**10a** (69)	20 (*P*)	5.81	1.29
2	(*S*)-**4b**		**10b** (78)	84 (*P*)	4.23	1.30
3	(*S*)-**4c**		**10c** (35)	63 (*P*)	10.2	1.90
4	(*S*)-**4d**		**10d** (64)	>95 (*P*)	8.92	1.47
5	(*R*)-**4d**		**10d** (70)	>95 (*M*)	6.39	1.28

[a]The shadowed circles in the Table indicate approximate bulkiness in respect of chiral axes of the binaphthyl groups. [b]Isolated by preparative GPC (no recycling). [c]Determined by CD spectra in comparison with (*P*)-**8** (cf. Figure 4).

3, giving poly(quinoxaline) **10a** in 69% yield after quenching with $NaBH_4$. Though the polymer **10a** exhibited a CD spectrum characteristic of the right-handed optically active helical structure, the intensity of the CD spectrum indicated that the catalyst (*S*)-**4a** induced screw-sense selectivity of only 20% based on that of the standard polymer (*P*)-**8** (entry 1; Figure 4). Of note is that right-handed helical polymer **10b** with 84% ee was obtained in the polymerization of **3** catalyzed by (*S*)-**4b** at room temperature (entry 2). Furthermore, catalyst (*S*)-**4c**, which has a bulky (*tert*-butyldimethylsilyl)oxy group at the 2′-position, induced right-handed screw-sense in 63% ee (entry 3). The highest screw-sense selectivity was attained by using catalyst

Table 2. Polymerization of **6** in the Presence of Optically Active **4a**−**d**[a]



11a-d

entry	catalyst (**Bin*)	**6**/**4**	polymer (yield/%)	$M_n/10^3$	M_w/M_n	ee/% (config)
1	(*S*)-**4a** (^{2MeO}Bin)	40	**11a** (77)	7.3	1.48	<1
2	(*S*)-**4b** (^{H}Bin)	40	**11b** (74)	8.3	1.30	79 (*P*)
3	(*S*)-**4e** (^{H}Bin)	40	**11b′** (72)	10.0	1.25	79 (*P*)
4	(*S*)-**4c** (^{2SiO}Bin)	40	**11c** (76)	20.0	2.43	75 (*P*)
5	(*S*)-**4d** (^{7MeO}Bin)	40	**11d** (79)	11.1	1.39	>95 (*P*)
6	(*R*)-**4d** (^{7MeO}Bin)	40	**11d** (78)	8.8	1.15	>95 (*M*)
7	(*S*)-**4d**	60	**11d**^{60} (87)	15.1	1.33	>95 (*P*)
8	(*S*)-**4d**	100	**11d**^{100} (70)	23.8	1.21	>95 (*P*)

[a] The group Q in the equation stands for the 5,8-di-*p*-tolylquinoxaline-2,3-diyl unit derived from **4**. [b] Isolated by preparative GPC (no recycling). [c] Determined by CD spectra in comparison with (*P*)-**9** (cf. Figure 5.

(*S*)- and (*R*)-**4d**, which have a 7′-methoxy substituent on the binaphthyl group (entry 4 and 5). Based on the CD spectrum, nearly complete screw-sense selectivity for the right-handed helical (*P*)-**10d** as well as for left-handed helical (*M*)-**10d** was observed in the polymerization using (*S*)-**4d** and (*R*)-**4d**, respectively (Figure 4). The coincidence of the shape of the CD spectra for the polymers **10a**−**d** with varying ee may indicate that each polymer chain adopts pure *P*- or *M*-helix without any other conformation, which may cause the significant change of the CD shape. Optically active polymers thus obtained were configurationally stable in solutions, resulting in no CD spectral change even at 80 °C for at least several days.

It is remarkable that the (*S*)-catalysts always produce the right-handed helical polymers (*P*)-**10** regardless of the opposite axial chirality of the binaphthyl skeletons between 2′-substituted ones ((*S*)-**4a** and **4c**) and 2′-unsubstituted ones ((*S*)-**4b** and **4d**). As may be seen by shadowed circles of different size in Table 1 (small, medium, and large ones), the difference in steric bulkiness at the both side of the chiral axes through the binaphthyl groups may determine the screw-sense selectivity of the polymerization. Thus, 7′-methoxy derivative **4d** (entries 4 and 5), which has much different bulkiness in respect to the axis, i.e., H (small) vs methoxyaryl moiety (large), gave nearly complete selectivity, while the 2′-methoxy derivative **4a**, in which the bulkiness in respect to the axis is comparable, i.e., methoxy (medium) vs aryl moiety (medium), may result in low selectivity (entry 1). According to this assumption, the moderate selectivities with catalysts **4b** and **4c** may be attributed to the moderate differences in the bulkiness in respect of the chiral axes, i.e., H (small) vs aryl (medium) in **4b** and aryl (medium) vs *tert*-butyldimethylsiloxy (large) in **4c**.[14]

Screw-Sense Selective Polymerization of 1,2-Diisocyano-3,6-dimethylbenzenes Having Alkoxyalkyl Side-Chains at 4,5-Positions. Though the 3,6-di-*p*-tolyl groups of **3** effectively stabilize the optically active helical structure of the polymers, the bulky aromatic groups caused slow polymerization (5 days for polymerization of **3** with **4d**) and low solubility of the polymers produced. The polymerization of 1,2-diisocyanobenzene **6**, which has less sterically demanding methyl groups at the 3,6-positions as well as two propoxymethyl groups at the 4,5-positions, was carried out.

Polymerization of **6** proceeded smoothly (18−36 h) at room temperature in the presence of the optically active catalysts **4a**−**d**, providing poly(quinoxaline-2,3-diyl)s **11a**−**d**, after quenching with $CH_3MgBr/ZnCl_2$ (Table 2). As was observed in the polymerization of **3**, catalyst (*S*)-**4b** produced **11b** of *P*-helix with high selectivity (79% ee), while (*S*)-**4a** resulted in the formation of racemate **11a** (Table 2, entries 1 and 2). Catalyst (*S*)-**4c** also produced **11c** with *P*-helix of 75% ee in 76% yield (entry 4).[14] Furthermore, nearly complete screw-sense selection was achieved by use of (*S*)- and (*R*)-**4d** having the 7′-methoxy group to afford *P*- and *M*-helical polymers **11d**, respectively (entries 5 and 6). The tolyl groups of the catalysts **4a**−**d** were not essential to attain high screw-sense selectivity; catalyst (*S*)-**4e** (eq 3) having two methyl groups instead of the two tolyl groups on the quinoxaline ring promoted the polymerization of **6** with the selectivity identical to that using the corresponding (*S*)-**4b** (entry 3).

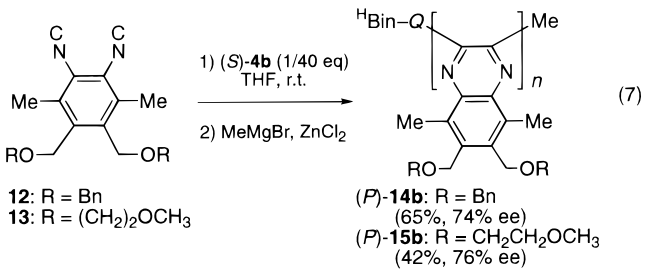
Applicability of the present asymmetric polymerization for the synthesis of higher molecular weight poly(quinoxaline)s was successfully demonstrated by polymerization with 60 and 100 molar equiv of **6** in the presence of a catalyst (*S*)-**4d** at room temperature (Table 2, entries 7 and 8). Notably, complete screw-sense selectivity was attained even for the synthesis of as high poly(quinoxaline)s as the quinoxaline 100mer, whose CD spectrum is comparable with that of the standard poly(quinoxaline) (*P*)-**9**.

Optically active poly(quinoxaline-2,3-diyl)s **11** having a binaphthyl group at the polymer end showed remarkable stabilities of the helical structure in solutions, while the corresponding polymers having methyl groups, which were derived from methylpalladium(II) complex catalyst, underwent racemization at room temperature.[8e] Helical polymers **11** were not racemized even at 80 °C in benzene for 60 h. Presumably, the binaphthyl group may serve as a "wedge" to prevent rotation of the bond between the quinoxaline rings near the polymer end.

With the chiral binaphthylpalladium(II) catalyst (*S*)-**4b**, screw-sense selective polymerization of 1,2-diisocyanobenzenes **12** and **13**, which have benzyloxymethyl and methoxyethoxymethyl side-chains at the 4,5-positions, respectively, was carried out (eq 7). The poly(quinoxaline-2,3-diyl)s **14b** and **15b** thus obtained showed CD spectra identical to that for (*P*)-**11b**, suggesting that the screw-sense selectivity as well as the helical

(14) The relatively large M_n as well as M_w/M_n value for the polymerization with **4c** may be due to the sterically bulky 2-*tert*-butyldimethylsilyloxy group on the binaphthyl initiator, which will probably cause slow initiation in comparison with the following propagation steps.

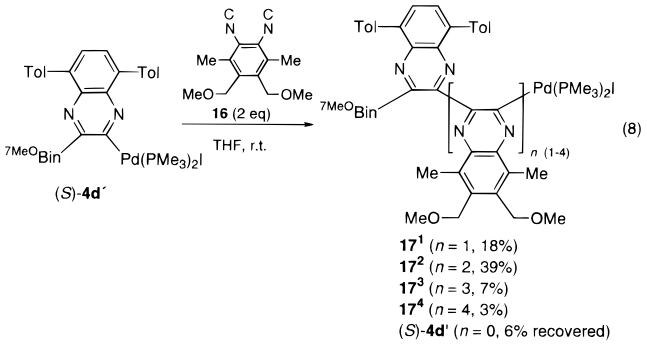
conformation of the polymers was not affected by the alkoxyside chains of the quinoxaline rings.



(7)

The Origin of the Screw-Sense Selection. Isolation and Characterization of Intermediary [Oligo(quinoxalinyl)]palladium(II) Complexes. The present asymmetric polymerization of 1,2-diisocyanobenzenes is particularly unique in that only one chiral group at the polymer end, which departs from the living palladium terminus on propagation of the polymerization, is capable of controlling the whole helical structure of the polymers. As already mentioned above, the preorganized right-handed helix of the (quinquequinoxalinyl)palladium(II) (*P*)-(*S*)-**7** having 2′-methoxybinaphthyl group at the initiating terminal can induce helical structure with the same screw-sense in the subsequent polymerization of 1,2-diisocyanobenzene, although the corresponding [mono(quinoxalinyl)]palladium complex (*S*)-**4a** having a 2′-methoxybinaphthyl group failed to give high selectivity. The findings indicate that in the present screw-sense selective polymerization, the screw-sense of the helix has been already fixed at the pentamer stage but not yet determined at the formation of [mono(quinoxalinyl)]palladium complex. How and when was the screw-sense selectivity originated in the asymmetric polymerization? To get insight into the asymmetric induction, we carried out oligomerization of **16**, which have methoxy groups at the 4- and 5-positions instead of the propoxy groups in **6**, in the presence of catalysts **4a′** and **4d′**, which have trimethylphosphine ligands instead of dimethylphenylphosphine ligands in **4a** and **4d** for clarity in ^{1}H NMR analysis.[15]

Reaction of 2 equiv of **16** with **4d′** (^{7MeO}Bin) at room temperature for 17 h afforded an oligomer mixture **17^1**∼**17^4** along with the recovered **4d′**, which were isolated with preparative GPC (eq 8). Noteworthy is that oligomers **17^2**, **17^3**,



(8)

and **17^4** thus isolated existed as a single species in solutions as observed by ^{1}H NMR spectroscopy (Table 3, entries 1−3). Though (biquinoxalinyl)palladium complex **17^1** isolated by GPC did not give the assignable ^{1}H NMR spectrum, presumably due to partial loss of the phosphine ligands, addition of Me_3P to the solution allowed observation of a single set of signals in ^{1}H NMR.[16] Not only the (terquinoxalinyl)palladium complexes **17^2**, but also **17^1,** catalyzed the polymerization of **6** to give optically active, right-handed helical polymers corresponding to (*P*)-**11d** as judged by CD spectra.

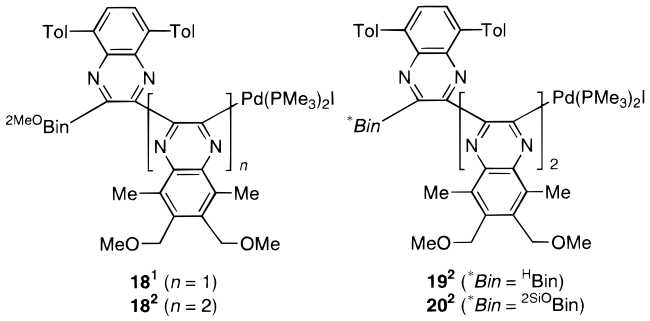
(15) The difference in the phosphine ligands of **4**, i.e., PMe_2Ph or PMe_3, had essentially no effect on the polymerization reactions with respect to the reaction rate, polymer yields, and the screw-sense selectivity.

Table 3. Diastereomeric Ratios of [Oligo(quinoxalinyl(palladium(II) Complexes **17**−**20**

entry	oligomer	*Bin	no. of quinoxaline unit/n + 1	diastereomeric ratio[a] (de)
1	**17^2**	^{7MeO}Bin	3	>99:1 (>98%)
2	**17^3**	^{7MeO}Bin	4	>99:1 (>98%)
3	**17^4**	^{7MeO}Bin	5	>99:1 (>98%)
4	**18^2**	^{2MeO}Bin	3	52:48 (4%)
5	**19^2**	^{H}Bin	3	89:11 (79%)
6	**20^2**	^{2SiO}Bin	3	84:16 (69%)

[a] Determined by ^{1}H NMR spectroscopy.

Chart 2



Unlike the 7′-methoxybinaphthylquinoxaline oligomers **17^n**, oligo(quinoxaline)s **18^n** ($n \geq 2$), which were produced with (2′-methoxybinaphthyl)palladium complex **4a′**, were all existing as mixtures of diastereomers (Chart 2). For example, (terquinoxalinyl)palladium **18^2** obtained by preparative GPC in 31% yield in the oligomerization of **16** catalyzed by **4a′** exhibited two sets of signals corresponding to the two diastereomers (1:1) by ^{1}H NMR (Table 3, entry 4). The fact that (biquinoxalinyl)palladium **18^1** showed a ^{1}H NMR spectrum assignable to a single species on addition of PMe_3 indicates that the diastereoisomerism may occur with the formation of **18^2**, suggesting that the ratios of the diastereomers at the stage of **17^2** and **18^2** might govern the screw-sense selectivities of the present asymmetric polymerization of **6**.

Indeed, ^{1}H NMR spectra revealed that (terquinoxalinyl)-palladium complexes **19^2** (^{H}Bin) and **20^2** (^{2SiO}Bin), which were derived by palladium initiators **4b′** and **4c′**, respectively, were existing as mixtures of two diastereomers in ratios of 89:11 and 84:16 (Chart 2; Table 3, entries 5 and 6). The diastereomeric ratios were nearly consistent with the screw-sense selectivities of the poly(quinoxaline)s derived from the polymerization of **6** with **4b** and **4c** (Table 2).

Conformational Analysis of the (Terquinoxalinyl)palladium(II) Complexes in Solution by ^{1}H NMR. The diastereoisomerism in the (terquinoxalinyl)palladium complexes, which may arise from helical conformations of the three consecutive quinoxalines and axial chirality of the binaphthyl groups, was examined by conformational analysis of (terquinoxalinyl)-palladium complexes **17^2** in solution by means of ^{1}H NMR spectroscopy.

Prior to the analysis, ^{1}H NMR of **17^2** was assigned with help of deuterated diisocyanobenzenes **16′** and **16″** (Chart 3), each of which has two CD_3 groups either on the aromatic ring or on the ether oxygen atoms instead of the respective CH_3 groups in

(16) In contrast to this observation, addition of PMe_3 to the solutions of **17$^{2-4}$** resulted in no change in their ^{1}H NMR spectra.

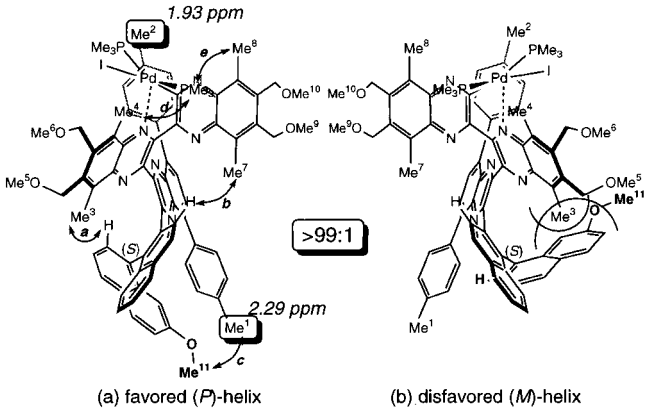
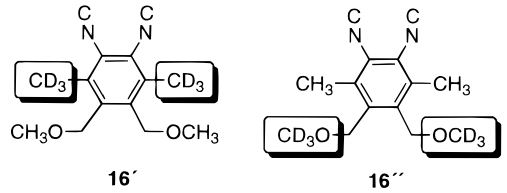


Figure 5. Possible helical conformation of **17²**. (a) Right-handed helical conformation. (b) Left-handed helical conformation (not existing). The curved arrows indicate observed NOEs. The assignment of the Me signals in ^{1}H NMR was based on the synthesis of deuterated derivatives **17²-i** ($Me^{3,4,7,8} = CD_3$) **17²-ii** ($Me^{5,6,9,10} = CD_3$), **17²-iii** ($Me^{7,8} = CD_3$), and **17²-iv** ($Me^{9,10} = CD_3$).

Chart 3



16 (Figure 5). Thus, **17²-i**, whose four aromatic methyl groups ($Me^{3,4,7,8}$) of the quinoxaline rings were labeled by deuterium, was prepared and isolated by the reaction of two equiv of **16′** with **4d′**. A similar reaction of **16″** with **4d′** provided **17²-ii**, in which the four methoxy groups ($OMe^{5,6,9,10}$) of the quinoxaline rings were deuterated. Furthermore, **17²-iii**, deuterated at the only two aromatic methyl groups ($Me^{7,8}$) of the third quinoxaline from the starting binaphthyl group, and **17²-iv**, deuterated at the only two methoxy groups ($OMe^{9,10}$) of the third quinoxaline, were prepared by the reaction of 1 equiv of **16′** and **16″** with **17¹**, respectively.

The 400 MHz ^{1}H NMR of **17²** showed eleven singlets corresponding to the methyl groups between 1.9 and 3.6 ppm, in addition to the aromatic signals between 6.6 and 8.7 ppm, benzylic methylene protons between 4.2 and 4.7 ppm, and two doublets assignable to the methyl groups of PMe_3. The aromatic proton signals were completely assigned by a COSY experiment. Furthermore, comparison of the ^{1}H NMR spectra of the deuterated **17²-i**−**iv** led to assignment of the eleven methyl singlets, though each pair of methyl groups on the same quinoxaline ring were not distinguished at this stage.

On the basis of the assignment, ROESY measurement of **17²** permitted us to assume favorable conformation in solution. Remarkable NOE between the binaphthyl aromatic protons and the aromatic methyl groups (**a**−**c** in Figure 5) as well as between PMe_3 and the aromatic methyl groups (**d** and **e** in Figure 5) strongly suggests that the three consecutive quinoxalines in **17²** adopt a right-handed helical structure in solution. In Figure 5a, a plausible helical conformation of **17²** is depicted, being in accordance with the NOEs as well as the X-ray structure of (*P*)-(*S*)-**7**.[17] The NMR experiments also enabled assignment of the two methyl singlets of the tolyl group; the two signals at 1.93 and 2.29 ppm were assignable to Me^2 and Me^1, respectively. For comparison, a possible left-handed helical conformation is also given in Figure 5b. Obviously, if the two structures are compared, the left-handed helix is disfavored by steric repulsion between the 7′-methoxybinaphthyl moiety and the methyl group of the second quinoxaline ring (Me^3).

Helical conformations of other (terquinoxalinyl)palladium(II) complexes **18²**, **19²**, and **20²** were also elucidated by ^{1}H NMR analyses of the corresponding labeled derivatives prepared by the reactions of **4a′**, **4b′**, and **4c′** with **16″**, respectively. The deuterium-labeled (terquinoxalinyl)palladium(II) complexes **18²**, **19²**, and **20²** ($CD_3^{5,6,9,10}$) exhibited diastereomeric pairs of signals at 1.93 ± 0.01 ppm and 1.88 ± 0.01 ppm in varying ratios (Table 3, entries 4−6), which were assignable to the Me^2 groups. It is reasonably assumed that one of each diastereomeric pair exhibiting a signal at 1.93 ± 0.01 ppm has a helical conformation with the relative spatial arrangement of the terminal naphthyl group as illustrated with **17²-i** (Figure 5a). Possible helical conformations of **18²**, **19²**, and **20²** are presented in Figure 6. It is now understood that both the (*S*)-^{H}Bin (Figure 6b) and (*S*)-^{2SiO}Bin (Figure 6c) groups induce (*P*)-helices regardless of the opposite axial chirality of the two binaphthyl groups. These findings are in good agreement with the observed screw-sense selectivities of the polymerization of **6** using palladium initiator (*S*)-**4b** and (*S*)-**4c**, both of which provided the (*P*)- and (*M*)-poly(quinoxaline)s in 90:10 and 88:12 ratios, respectively (Table 2).

Thus, the screw-sense in the present polymerization of 1,2-diisocyanobenzenes may be induced by sterically favorable initiation with differentiation of the relative steric bulkiness on the substituted naphthalene in respect to the axes of the binaphthyl groups; i.e., the sterically bulkier group may preferentially occupy the less congested space through the propagation.

Temperature-dependent ^{1}H NMR measurements revealed that the right-handed (*P*) and left-handed (*M*) helical **18²-i** were in equilibrium; the signals at 1.88 and 1.93 ppm ($\Delta\nu = 14.7$ Hz) coalesced at 312 K and those at 2.30 and 2.24 ppm ($\Delta\nu = 17.4$ Hz) coalesced at 318 K in C_6D_6. Thus, the activation energy for the *P*−*M* interconversion is calculated to be 16.1−16.3 kcal/mol (67.4−68.2 kJ/mol).

On the basis of the NMR structural analysis of oligo(quinoxaline)s, the screw-sense selective polymerization of 1,2-diisocyanobenzene initiated by (*S*)-**4d** is schematically presented in Scheme 2. The palladium initiator (*S*)-**4d** undergoes insertion of the diisocyanobenzene to give (biquinoxalinyl)palladium(II) species, which may be in rapid equilibrium between the two conformers, each of which may lead either to right- or left-handed helical poly(quinoxaline)s. However, subsequent insertion of the diisocyanide may take place exclusively with the formation of right-handed helical (*P*)-(terquinoxalinyl)palladium species corresponding to **17²**. Even if the corresponding left-handed (*M*)-(terquinoxalinyl)palladium(II) species might be formed, the *P*−*M* equilibrium to the right-handed (*P*)-species maintains the right-handed screw-sense for further polymerization. The equilibrium between (*M*)- and (*P*)-helical conformations may be negligible for the higher [oligo(quinoxalinyl)]-palladium, since no equilibrium was spectroscopically detected for the pentameric (*P*)-(*S*)-**7** having the terminal ^{2MeO}Bin group.

Conclusion

Highly screw-sense selective polymerization of diisocyanobenzenes was promoted by optically active 1,1′-binaphth-2-ylpalladium(II) complexes to give optically active poly-

(17) The dotted line between the palladium and the nitrogen of the second quinoxaline shown in Figures 5 and 6 represents a weak coordinative bond, the exsistence of which is presumed from the related X-ray structures of ter- and quaterquinoxalinylpalladium complexes reported by us. See ref 7a.

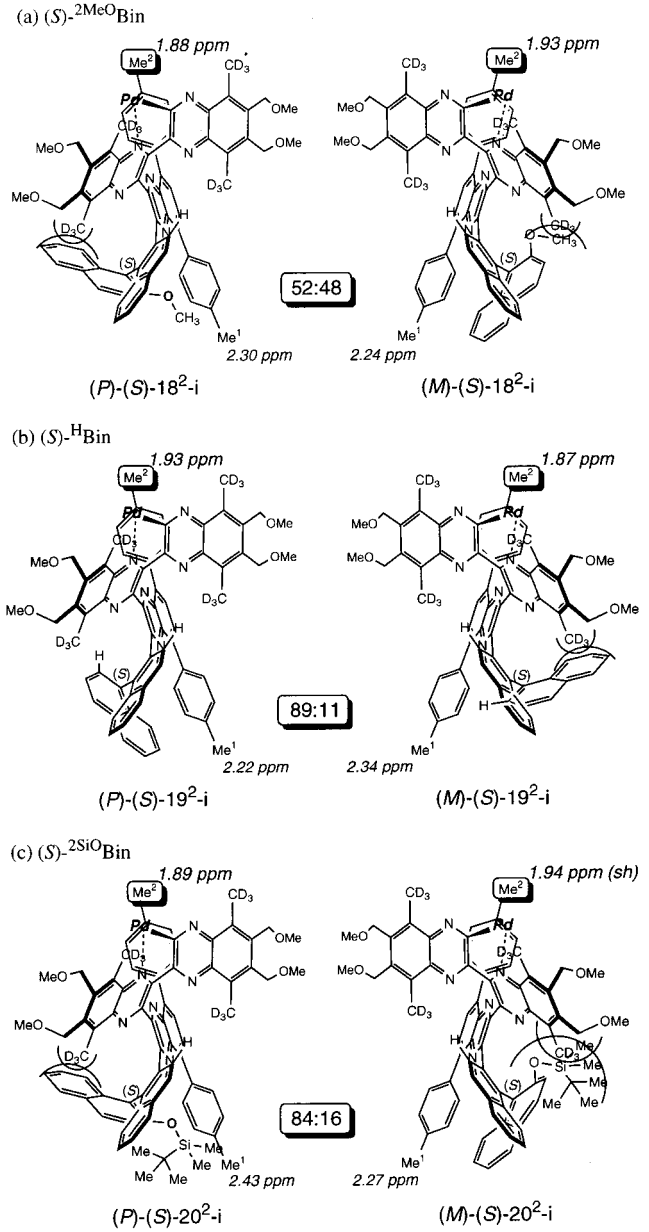


Figure 6. Plausible right- and left-handed helical conformations of (terquinoxalinyl)palladium complexes **18²**−**20²** having various (*S*)-binaphthyl groups. (Assumed from the chemical shift of the Me^2 groups.)

(quinoxaline-2,3-diyl)s of stable helical structures. The choice of substituents on the binaphthyl groups was crucially important to attain the high screw-sense selectivity; 7′-methoxybinaphth-2-ylpalladium(II) complex produced helical poly(quinoxaline)s of a single screw-sense. The highly effective control of the helical sense by the 7′-methoxy-1,1′-binaphthyl group at the initiation terminal of the polymer may arise from highly diastereoselective formation of the (terquinoxalinyl)palladium-(II) intermediate, whose screw-sense was completely maintained for further propagation. The complete retention of the helical structure in the polymerization was demonstrated by the synthesis of optically pure polymers with varying molecular weights up to 100mer.

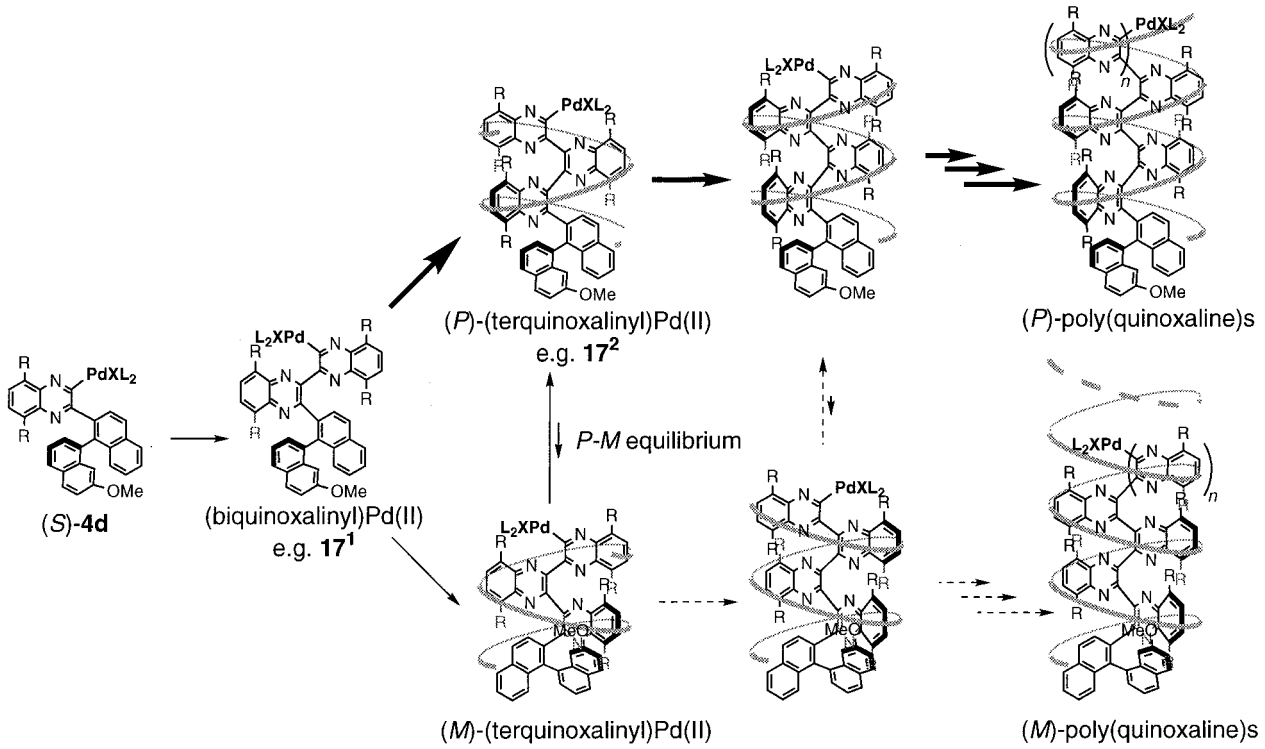
The asymmetric polymerization has successfully been applied for the screw-sense selective synthesis of poly(quinoxaline-2,3-diyl)s having hydrophobic and/or hydrophilic side chains, by which the surface of the polymer is modifiable for new functional materials.

Experimental Section

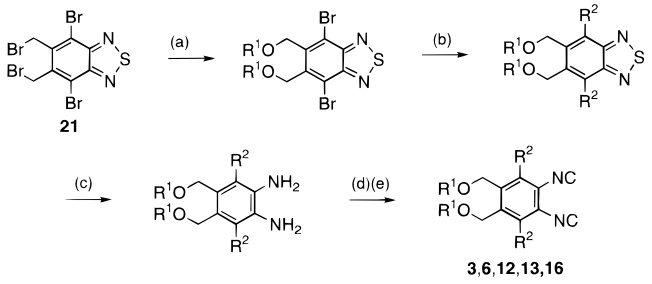
General. All reactions using palladium complexes were carried out under a dry nitrogen or argon atmosphere. Solvents were purified by distillation in the presence of appropriate drying agents under argon. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Gemini 2000 equipped with a 7.0 T magnet (300 MHz for ^1H NMR), unless otherwise noted. The GPC analysis was carried out with TSK-GEL G3000HHR column ($CHCl_3$, polystyrene standard). Recycling preparative GPC was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns in a series ($CHCl_3$). For the FABMS measurements (positive), 3-nitrobenzyl alcohol was used for the matrix. The CD spectra were recorded on JASCO J-720. *Mean residue ellipticity*, θ, per quinoxaline unit, was used for expression of intensity of the CD spectrum of the polymer. On the estimation of the enantiomeric excesses of the poly(quinoxaline)s by examination of the CD spectra, the concentration of the polymers subjected to the CD measurements were also confirmed by UV measurements.

1,2-Diisocyanobenzene Derivatives. The synthesis of 1,2-diisocyanobenzenes is outlined in Scheme 3. All compounds are prepared from 4,7-dibromo-5,6-di(bromomethyl)-2,1,3-benzothiadiazole (**21**). The compounds **3**, **6**, **12**, **13**, and **16** were prepared according to the reported procedure.[7b] The following is a representative procedure for the synthesis of **16** ($R^1 = R^2 =$ Me). **Step a:** To a solution of methanol (5.1 mL, 120 mmol) in THF (125 mL) was added ethylmagnesium bromide (1.7 M in THF, 38 mL, 62 mmol) dropwise at room temperature over 0.5 h with external cooling by a water bath under a nitrogen atmosphere; the mixture was stirred for additional 1 h at room temperature. To the mixture were added hexamethylphosphoramide (HMPA, 22 mL, 120 mmol) and **21** (6 g, 12 mmol) at room temperature; then the mixture was stirred at 70 °C for 1 d. To the mixture cooled to room temperature was added water (100 mL). Extraction with Et_2O (100 mL × 3) followed by column chromatography on silica gel (eluent: hexane/ether = 10:1, CH_2Cl_2 was used for dissolving the compound) gave 4,7-dibromo-5,6-bis(methoxymethyl)-2,1,3-benzothiadiazole (3.5 g, 73%). ^1H NMR ($CDCl_3$) δ 3.49 (s, 6H), 4.98 (s, 4H). **Step b:** To a suspension of $ZnCl_2$ (3.3 g, 24 mmol) in THF (18 mL) was added methylmagnesium bromide (2.4 M in THF, 5.0 mL, 12 mmol) at 0 °C under a nitrogen atmosphere; the mixture was stirred for additional 0.5 h at room temperature. To the mixture were added 4,7-dibromo-5,6-bis(methoxymethyl)-2,1,3-benzothiadiazole (1.2 g, 3.0 mmol) and $PdCl_2$(dppf) (0.22 g, 0.30 mmol) at room temperature; the mixture was stirred at 70 °C for 24 h. To the mixture cooled to room temperature was slowly added water (*evolution of methane*). Extraction with ether followed by column chromatography on silica gel (hexane/ether = 3:1) afforded 5,6-bis(methoxymethyl)-4,7-dimethyl-2,1,3-benzothiadiazole (0.57 g, 74%). ^1H NMR ($CDCl_3$) δ 2.78 (s, 6H), 3.47 (s, 6H), 4.69 (s, 4H). **Step c:** To a solution of sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al, 3.4 M in toluene, 24 mL, 89 mmol) in THF (56 mL) was added water (1.6 mL, 89 mmol) dropwise over 20 min at 0 °C under a nitrogen atmosphere (*evolution of hydrogen gas*); the mixture was stirred for additional 0.5 h at 0 °C. To the mixture was added 5,6-bis(methoxymethyl)-4,7-dimethyl-2,1,3-benzothiadiazole (2.2 g, 8.9 mmol) in THF (28 mL) at 0 °C; the mixture was stirred at 0 °C for 1 h and at room temperature for 10 h. To the mixture were added water and ether (evolution of hydrogen gas); the resultant suspension was filtered through a pad of Celite. Extraction with ether followed by column chromatography on silica gel (eluent: AcOEt/Et_3N = 50:1, CH_2Cl_2 was used for dissolving the compound) afforded 4,5-bis(methoxymethyl)-3,6-dimethyl-1,2-phenylenediamine (1.2 g, 60%). ^1H NMR ($CDCl_3$) δ 2.21 (s, 6H), 3.41 (s, 10H), 4.48 (s, 4H). **Steps d and e:** To a solution of 4,5-bis(methoxymethyl)-3,6-dimethyl-1,2-phenylenediamine (1.2 g, 5.4 mmol) in CH_2Cl_2 was added CH_3CO_2CHO (1.9 g, 21 mmol) dropwise at 0 °C under a nitrogen atmosphere; the mixture was stirred at 0 °C−room temperature for 10 h. Precipitates formed were collected by filtration to afford the corresponding diformamide (1.3 g, 88%). To a solution of the diformamide (1.3 g, 4.7 mmol) in THF (45 mL) were added triethylamine (6.7 mL, 47 mmol) and $POCl_3$ (1.2 mL, 14 mmol) at 0 °C under a nitrogen atmosphere; the mixture was stirred at 0 °C for 1 h. To the

Scheme 2. The Chain-End Control Mechanism of the Screw=Sense Selective Polymerization of 1,2-Diisocyanobenzenes in the Presence of (*S*)-**4d** (^{7MeO}Bin)



Scheme 3[a]



[a] Reagents and conditions: (a) R^1OH (10 equiv), EtMgBr (5 equiv), THF, HMPA (10 equiv), 80 °C, 24 h; (b) R^2MgBr (4 equiv), $ZnCl_2$ (8 equiv), $PdCl_2$(dppf) (0.1 equiv), THF, reflux, 24 h; (c) Red-Al (10 equiv), H_2O (10 equiv), THF, room temperature, 10 h; (d) CH_3CO_2CHO (4 equiv), CH_2Cl_2 0 °C−room temperature, 10 h; (e) $POCl_3$ (3 equiv), Et_3N (10 equiv), THF, 0 °C, 1 h.

mixture was added saturated aq $NaHCO_3$ at 0 °C. Extraction with Et_2O followed by column chromatography on silica gel (hexane/ether = 3:1 to 1:1) afforded **16** (0.49 g, 42%).

1,2-Diisocyano-4,5-bis(methoxymethyl)-3,6-dimethylbenzene (16): ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 6H), 3.44 (s, 6H), 4.48 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 15.5, 58.8, 67.9, 124.1, 134.3, 138.0, 173.2; IR (KBr) 2124, 1102 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.68; H, 6.57; N, 11.34.

The following diisocyanides were prepared by the procedures similar to that used for **16**. **1,2-Diisocyano-3,6-dimethyl-4,5-bis[(phenylmethoxy)methyl]benzene (12)**: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 6H), 4.44 (s, 4H), 4.47 (s, 4H), 7.30−7.42 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 15.4, 65.2, 73.3, 124.0, 128.26, 128.32, 128.6, 134.3, 137.3, 138.1, 173.1; IR (KBr) 2120, 1100 cm^{-1}. Anal. Calcd for $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.10; N, 7.07. Found: C, 78.67; H, 6.03; N, 7.07. **1,2-Diisocyano-4,5-bis[(2-methoxyethoxy)methyl]-3,6-dimethylbenzene** (**13**): ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 6H), 3.36 (s, 6H), 3.50−3.58 (m, 4H), 3.64−3.70 (m, 4H), 4.62 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 15.5, 59.0, 66.6, 70.1, 71.9, 124.0, 134.3, 138.1, 172.9; IR (KBr) 2124, 1100 cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O_4$: C, 65.04; H, 7.28; N, 8.43. Found: C, 65.03; H, 7.33; N, 8.28.

Deuterated Diisocyanobenzenes 16′ and 16″. The CD_3 groups of **16′** and **16″** were introduced with CD_3MgI (1 M in ether, Aldrich) at step (b) and CD_3OD (Aldrich) at step a (Scheme 3), respectively, according to the procedure for the synthesis of **16**.

1,2-Diisocyano-4,5-bis(methoxymethyl)-3,6-bis(trideuteriomethyl)benzene (16′): ^{1}H NMR ($CDCl_3$) δ 3.44 (s, 6H), 4.48 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 14.7 (pseudo septet (1:3:6:7:6:3:1), J = 19.7 Hz), 58.7, 67.8, 123.9, 134.1, 138.0, 173.0; IR (KBr) 2125, 1098 cm^{-1}; FABHRMS (pos) calcd for $[C_{14}H_{10}D_6N_2O_2 + H]^+$: *m*/*z* 251.1660. Found: *m*/*z* 251.1665.

1,2-Diisocyano-4,5-bis[(trideuteriomethoxy)methyl]-3,6-dimethylbenzene (16″): ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 6H), 4.48 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 15.4, 57.8 (pseudo septet, J = 22.0 Hz), 67.7, 123.9, 134.2, 138.0, 173.1; IR (KBr) 2126, 1122 cm^{-1}; FABHRMS (pos) calcd for $[C_{14}H_{10}D_6N_2O_2 + H]^+$: *m*/*z* 251.1660. Found: *m*/*z* 251.1673.

Optically Pure Binaphthyl Iodides 1. The iodides were prepared according to the procedure reported by Miyano et al. The following is a representative procedure (four steps) for preparation of (*S*)-**1d**. **(1*R*)-Menthyl (*S*)-7′-Methoxy-1,1′-binaphthalene-2-carboxylate.** To a solution of 7-methoxy-1-naphthylmagnesium bromide (12 mmol) in THF−benzene (1:1, 140 mL) was added (1*R*)-menthyl 1-((1*R*)-menthoxy)naphthalene-2-carboxylate (4.9 g, 10.5 mmol) in benzene (60 mL) at 0 °C; the mixture was stirred at 0 °C for 2 h and at room temperature for 12 h. To the mixture was added saturated aq NH_4Cl (200 mL). The organic layer was washed with saturated aq NH_4Cl, water, and brine successively, and dried over magnesium sulfate. Evaporation followed by column chromatography on silica gel (hexane:ether = 20:1) afforded (1*R*)-menthyl 7′-methoxy-1,1′-binaphthalene-2-carboxylate (3.3 g, 68%) as a 94:6 mixture of the diastereomers. Recrystallization from ether−methanol gave the diastereomerically pure ester with (*S*)-axial chirality (2.2 g, 45%). ^{1}H NMR ($CDCl_3$) δ −0.2−1.6 (m, 18H), 3.44 (s, 3H), 4.43 (dt, J = 4.3, 10.9 Hz, 1H), 6.47 (d, J = 2.5 Hz, 1H), 7.08 (dd, J = 2.5, 9.0 Hz, 1H), 7.10−7.52 (m, 5H), 7.75−8.03 (m, 5H) (the corresponding ester with (*R*)-axial chirality exhibited its methoxy signal at 3.46 ppm), ^{13}C NMR ($CDCl_3$) δ 15.7, 20.5, 21.8, 22.6, 25.6, 31.0, 33.9, 39.6, 46.1, 54.9, 74.5, 98.6, 105.1, 118.2, 123.0, 125.9, 126.6, 127.4, 127.5, 127.7, 127.9, 128.0, 128.8, 129.6, 129.9, 133.0, 134.6, 134.7, 136.3, 139.6, 157.6, 168.1, IR (KBr) 2964, 1704, 1274, 1134, 828, 772 cm^{-1}. Anal. Calcd for $C_{32}H_{34}O_3$:

C, 82.37; H, 7.34. Found: C, 82.33; H, 7.30. **(*S*)-7′-Methoxy-1,1′-binaphthalene-2-carboxylic Acid.** A mixture of the ester (1.8 g, 3.9 mmol) and KOH (8.8 g, 156 mmol) in ethanol (80 mL) was heated under reflux for 24 h. After evaporation of the solvent, water and ether were added to the residue. The aqueous phase was washed with ether several times and then acidified with hydrochloric acid. Extraction with ether followed by evaporation afforded (*S*)-7′-methoxy-1,1′-binaphthalene-2-carboxylic acid (1.3 g, 98%). ^{1}H NMR ($CDCl_3$) δ 3.47 (s, 3H), 6.43 (d, J = 2.5 Hz, 1H), 7.13 (dd, J = 2.5, 9.0 Hz, 1H), 7.25−7.30 (m, 2H), 7.42 (dd, J = 7.3, 7.9 Hz, 1H), 7.50−7.59 (m, 1H), 7.80−8.10 (m, 6H). **(*S*)-2-Amino-7′-methoxy-1,1′-binaphthalene.** To a solution of the acid (1.20 g, 3.7 mmol) in acetone (19 mL) were added triethylamine (0.57 mL, 4.0 mmol) and then ethyl chloroformate (0.66 mL, 4.4 mmol) in acetone (1.9 mL) at −15 °C. The mixture was stirred at −15 °C for 30 min; then, sodium azide (0.71 g, 11 mmol) in water (3.8 mL) was added to the solution at −15 °C. After 1 h at −15 °C, organic material was extracted with cold benzene several times. The organic layer was washed with cold brine and dried over sodium sulfate. After filtration, the benzene solution was heated under reflux in the presence of MS4A for 2 h. To the mixture was added KOH (10 g, 178 mmol) and water (20 mL) at room temperature; the mixture was stirred for 12 h at room temperature. Extraction with benzene followed by column chromatography on silica gel (hexane:ether = 4:1) afforded (*S*)-2-amino-7′-methoxy-1,1′-binaphthalene (0.87 g, 80%). ^{1}H NMR ($CDCl_3$) δ 3.16 (br s, 2H), 3.57 (s, 3H), 6.72 (d, J = 2.6 Hz, 1H), 7.10−7.27 (m, 4H), 7.38−7.55 (m, 3H), 7.76−7.93 (m, 4H), ^{13}C NMR ($CDCl_3$) δ 56.9, 106.0, 120.0, 120.5, 124.0, 125.8, 126.4, 128.2, 129.7, 129.8, 129.9, 130.9, 131.5, 131.8, 135.2, 135.5, 136.1, 143.6, 160.0, IR (KBr) 3464, 3372, 1624, 838 cm^{-1}. Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.62. Found: C, 84.23; H, 5.80; N, 4.68. The enantiomeric excess (>99.5% ee) of the amine was confirmed by chiral HPLC analysis (Chiralcel-AD; hexane: *i*-PrOH = 98:2). **(*S*)-2-Iodo-7′-methoxy-1,1′-binaphthalene (1d).** To a mixture of the amine (0.15 g, 0.5 mmol) and sulfuric acid (2.5 M, 12 mL) was added sodium nitrite (0.15 g, 2.2 mmol) in water (1.5 mL) at −15 °C; the mixture was stirred for 30 min at −5 °C. To the mixture was added urea (0.38 g, 6.3 mmol) in sulfuric acid (2.5 M, 2 mL). To the mixture was slowly added potassium iodide (0.42 g, 2.5 mmol) in sulfuric acid (2.5 M, 3.6 mL) at −5 °C. CH_2Cl_2 was added to the solution, and the organic layer was separated. The layer was washed with saturated aq Na_2SO_3, 1 N aq NaOH, 1 N HCl, and water. Column chromatography on silica gel (hexane only to hexane:ether = 50:1) afforded (*S*)-**1d** (57 mg). The material contained 7′-methoxy-1,1′-binaphthalene (ca. 25 mol %), and the calculated yield of (*S*)-**1d** was 22%. The iodide was used for the next step without further purification. ^{1}H NMR ($CDCl_3$) δ 3.55 (s, 3H), 6.47 (d, J = 2.6 Hz, 1H), 7.11−7.18 (m, 1H), 7.19 (d, J = 2.6 Hz, 1H), 7.23 (d, J = 1.3 Hz, 1H), 7.29−7.34 (m, 1H), 7.40−7.53 (m, 2H), 7.67 (d, J = 8.8 Hz, 1H), 7.82−8.00 (m, 3H), 8.05 (d, J = 8.8 Hz, 1H).

(*S*)-Bis(dimethylphenylphosphine)iodo[3-(2′-methoxy[1,1′-binaphthalen]-2-yl)-5,8-bis(4-methylphenyl)-2-quinoxalinyl]palladium ((*S*)-4a). To a THF (5 mL) solution of (cyclopentadienyl)(π-allyl)palladium-(II) (26 mg, 0.122 mmol) was added dimethylphenylphosphine (52 μL, 0.366 mmol) at −78 °C; the mixture was stirred at −78 °C for 15 min. Then, (*S*)-**1a** (50 mg, 0.122 mmol) was added to the mixture at −78 °C. The mixture was allowed to warm to room temperature and then heated to 50 °C. After 2 h at 50 °C, the mixture was cooled to room temperature, and **3** (56 mg, 0.182 mmol) was added. The mixture was stirred for 3 h at room temperature and then subjected to preparative TLC to give (*S*)-**4a** (113 mg, 84%). (*S*)-**4a**: $[\alpha]^{20}_D$ = −173 (*c* 0.164, benzene); mp 208.0−208.5 °C. ^{1}H NMR (C_6D_6) δ 1.18 (t, J = 3.4 Hz, 3H), 1.19 (t, J = 3.3 Hz, 3H), 1.45 (t, J = 3.4 Hz, 3H), 1.55 (t, J = 3.5 Hz, 3H), 2.27 (s, 3H), 2.36 (s, 3H), 2.71 (s, 3H), 6.53 (d, J = 9.1 Hz, 1H), 6.60−7.00 (m, 12H), 7.10−7.50 (m, 14H), 7.60−7.80 (m, 3H), 8.08 (d, J = 8.7 Hz, 1H), 10.21 (d, J = 8.8 Hz, 1H); ^{31}P NMR (C_6D_6) δ −12.55 (s). Anal. Calcd for $C_{59}H_{53}N_2OP_2PdI\bullet^1/_2C_6H_6$: C, 65.30; H, 4.94; N, 2.45. Found: C, 65.50; H, 4.88; N, 2.46.

(*S*)-[3-(1,1′-Binaphthalen-2-yl)-5,8-bis(4-methylphenyl)-2-quinoxalinyl]bis(dimethylphenylphosphine)iodopalladium ((*S*)-4b). By a procedure similar to that used for the synthesis of (*S*)-**4a**, (*S*)-**4b** was prepared in 77% yield from (*S*)-**1b** (56 mg, 0.182 mmol). (*S*)-**4b**: $[\alpha]^{20}_D$ = +87.9 (*c* 0.132, benzene); mp 158.0−158.5 °C. ^{1}H NMR (C_6D_6) δ 1.07 (m, 6H), 1.38 (d, J = 6.3 Hz, 3H), 1.57 (d, J = 6.7 Hz, 3H), 2.26 (s, 3H), 2.35 (s, 3H), 6.50−7.90 (m, 31H), 8.08 (d, J = 8.4 Hz, 1H), 9.20 (d, J = 8.8 Hz, 1H); ^{31}P NMR (C_6D_6) δ −8.81 (d, J = 410 Hz), −14.41 (d, J = 410 Hz). Anal. Calcd for $C_{58}H_{51}N_2P_2PdI$: C, 65.03; H, 4.80; N, 2.61. Found: C, 65.02; H, 4.50; N, 2.47.

(*S*)-[3-[2′-(*tert*-Butyldimethylsilyl)oxy[1,1′-binaphthalene]-2-yl]-5,8-bis(4-methylphenyl)-2-quinoxalinyl]bis(dimethylphenylphosphine)-iodopalladium ((*S*)-4c). By a procedure similar to that used for the synthesis of (*S*)-**4a**, (*S*)-**4c** was prepared in 15% yield from (*S*)-**1c** (87 mg, 0.17 mmol). (*S*)-**4c** was isolated by a column chromatography on silica gel (hexane:ether = 3/1, then hexane:CH_2Cl_2 = 1/2). (*S*)-**4c**: $[\alpha]^{20}_D$ = +153.7 (*c* 0.89, benzene); mp 112.5−116.0 °C. ^{1}H NMR (C_6D_6) δ −0.50 (s, 3H), 0.20 (s, 3H), 0.57 (s, 9H), 1.10 (d, J = 7.5 Hz, 3H), 1.42 (d, J = 7.8 Hz, 6H), 1.58 (d, J = 7.5 Hz, 3H), 2.32 (s, 3H), 2.46 (s, 3H), 6.3−6.6 (m, 3H), 6.67 (t, J = 6.8 Hz, 2H), 6.77−6.92 (m, 7H), 7.02−7.40 (m, 14H), 7.43 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 7.5 Hz, 1H), 8.19 (d, J = 9.0 Hz, 1H), 10.17 (d, J = 9.9 Hz, 1H); ^{31}P NMR (C_6D_6) δ −13.2 (d, J = 401 Hz), −12.0 (d, J = 401 Hz). Anal. Calcd for $C_{64}H_{65}IN_2OP_2PdSi$: C, 63.97; H, 5.45; N, 2.33. Found: C, 64.20; H, 5.57; N, 1.96.

(*S*)-Bis(dimethylphenylphosphine)iodo[3-(7′-methoxy[1,1′-binaphthalen]-2-yl)-5,8-bis(4-methylphenyl)-2-quinoxalinyl]palladium ((*S*)-4d). By a procedure similar to that used for the synthesis of (*S*)-**4a**, (*S*)-**4d** was prepared in 82% yield from (*S*)-**1d** (70 mg, 0.17 mmol). (*S*)-**4d** was isolated by a column chromatography on silica gel (hexane: ether = 3/1, then hexane:CH_2Cl_2 = 1/2). (*S*)-**4d**: $[\alpha]^{20}_D$ = +189 (*c* 0.31, benzene); mp 129.8−132.5 °C. ^{1}H NMR (C_6D_6) δ 0.89 (t, J = 2.7 Hz, 3H), 1.39 (t, J = 3.5 Hz, 3H), 1.47 (t, J = 3.6 Hz, 3H), 1.53 (t, J = 3.3 Hz, 3H), 2.27 (s, 3H), 2.35 (s, 3H), 2.96 (s, 3H), 6.5−7.0 (m, 14H), 7.15−7.3 (m, 12H), 7.47 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 6.0 Hz, 2H), 7.76 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 8.7 Hz, 1H), 9.13 (d, J = 8.4 Hz, 1H); ^{31}P NMR (C_6D_6) δ −12.28 (s), −12.19 (s). HRFABMS (pos) calcd for $[C_{59}H_{53}IN_2OP_2Pd + H]^+$ *m*/*z* 1101.1791; found *m*/*z* 1101.1709; calculated signals (intensity/% based on MH^+): *m*/*z* 1099 (25), 1100 (67), 1101 (100), 1102 (53), 1103 (75), 1104 (43). Found: *m*/*z* 1100 (68), 1101 (100), 1102 (59). (*R*)-**4d**: $[\alpha]^{20}_D$ = −179 (*c* 0.28, benzene).

(*S*)-Iodo[3-(7′-methoxy[1,1′-binaphthalen]-2-yl)-5,8-bis(4-methylphenyl)-2-quinoxalinyl]bis(trimethylphosphine)palladium ((*S*)-4d′). To a THF (16 mL) solution of (cyclopentadienyl)(π-allyl)-palladium(II) (114 mg, 0.54 mmol) was added trimethylphosphine (1 M in THF, 1.6 mL, 1.6 mmol); the mixture was stirred for 15 min at −78 °C. Then, (*S*)-**1d** (198 mg, 0.48 mmol) in THF (1 mL) was added to the mixture at −78 °C. The mixture was allowed to warm to room temperature and then heated to 50 °C. After stirring for 2 h at 50 °C, **3** (223 mg, 0.72 mmol) was added to the mixture cooled to room temperature. The mixture was stirred for 2 h at room temperature and then subjected to column chromatography on silica gel (hexane:ether = 3/1) to give (*S*)-**4d′** (379 mg, 81%). (*S*)-**4d′**: ^{1}H NMR (C_6D_6) δ 0.74 (dd, J = 2.2, 4.2 Hz, 9H), 0.89 (dd, J = 2.4, 3.3 Hz, 9H), 2.22 (s, 3H), 2.23 (s, 3H), 3.01 (s, 3H), 6.74 (d, J = 2.1 Hz, 1H), 6.87 (t, J = 8.5 Hz, 1H), 6.90−7.10 (m, 4H), 7.10−7.25 (m, 3H), 7.33 (d, J = 8.7 Hz, 1H), 7.36 (d, J = 9.0 Hz, 1H), 7.40−7.60 (m, 6H), 7.65−7.73 (m, 3H), 7.95 (d, J = 8.7 Hz, 1H), 9.00 (d, J = 8.7 Hz, 1H); ^{31}P NMR (C_6D_6) δ −20.0 (s), −20.1 (s). Anal. Calcd for $C_{49}H_{49}IN_2OP_2Pd$: C, 60.23; H, 5.05; N, 2.87. Found: C,5.25; H, 60.05; N, 2.75.

(*S*)-[3-(1,1′-Binaphthalen-2-yl)-6,7-bis(1-propyloxymethyl)-5,8-dimethyl-2-quinoxalinyl]bis(dimethylphenylphosphine)iodopalladium ((*S*)-4e). By a procedure similar to that used for the synthesis of (*S*)-**4a**, (*S*)-**4e** was prepared in 77% yield from (*S*)-**1b** (56 mg, 0.182 mmol). (*S*)-**4e**: mp 87−94 °C. ^{1}H NMR (C_6D_6) δ 0.80−0.95 (m, 9H), 1.32 (d, J = 7.2 Hz, 3H), 1.40−1.60 (m, 10H), 1.65 (d, J = 7.5 Hz, 3H), 3.05 (s, 3H), 3.23 (t, J = 6.6 Hz, 2H), 3.39 (t, J = 6.6 Hz, 2H), 4.50 (d, J = 10.5 Hz, 1H), 4.54 (d, J = 11.1 Hz, 1H), 4.70 (d, J = 11.1 Hz, 1H), 4.75 (d, J = 10.5 Hz, 1H), 6.06 (d, J = 7.5 Hz, 1H), 6.40 (t, J = 7.5 Hz, 2H), 6.62 (t, J = 7.5 Hz, 1H), 6.80−7.30 (m, 11H), 7.52 (d, J = 8.7 Hz, 1H), 7.60−7.70 (m, 5H), 8.07 (d, J = 8.4 Hz, 1H), 9.37 (d, J = 8.7 Hz, 1H); ^{31}P NMR (C_6D_6) δ −12.08 (d, J = 410 Hz), −14.24 (d, J = 410 Hz). FABMS (pos) calcd signals (intensity/% based on MH^+) for $[C_{54}H_{59}IN_2OP_2Pd + H]^+$: *m*/*z* 1061

(26), 1062 (68), 1063 (100), 1064 (50), 1065 (75), 1066 (41), 1067 (39), 1068 (19). Found: *m*/*z* 1061 (48), 1062 (82), 1063 (100), 1064 (61), 1065 (79), 1066 (44), 1067 (37), 1068 (17).

(*S*)-Methyl 3-(7′-methoxy[1,1′-binaphthalen]-2-yl)-5,8-bis(4-methylphenyl)-2-quinoxalinecarboxylate (5d). A mixture of (*S*)-**4d** (10 mg, 9.1 μmol), MeOH (5 mL), and CH_2Cl_2 (1 mL) was heated under CO pressure of 30 atm at 90 °C for 14 h. Preparative TLC on silica gel (hexane: ether = 2:1) gave (*S*)-**5d** (5.7 mg, 97%). HPLC analysis (Chiralcel AD, hexane:*i*-PrOH = 96:4) showed no signal corresponding to the (*R*)-isomer. ^{1}H NMR (at 90 °C, $CD_3C_6D_5$) δ 2.16 (s, 3H), 2.36 (s, 3H), 3.06 (br s, 3H), 3.22 (br s, 3H), 6.77 (br s, 1H), 6.85−7.05 (m, 8H), 7.19 (t, J = 7.2 Hz, 1H), 7.25−7.55 (m, 9H), 7.65−7.75 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 21.0, 51.6, 54.3, 105.0, 106.2, 119.5, 122.9, 126.6, 128.9, 129.0, 129.3, 129.8, 130.4, 131.3, 131.7, 133.3, 134.5, 135.6, 137.3, 137.5, 138.0, 158.2; IR (neat) 1734, 1140, 814 cm^{-1}. HRFABMS (pos) calcd for $[C_{45}H_{34}N_2O_3 + H]^+$: *m*/*z* 651.2647. Found: *m*/*z* 651.2645.

(Dimethylphenylphosphine)iodo[3‴′-(2′-methoxy[1,1′-binaphthalen]-2-yl-5,5′,5″,5‴,5⁗,8,8′,8″,8‴,8⁗-decakis(4-methylphenyl)[2,2′:3′,2″:3″<bold>′,2‴:3‴,2⁗:3⁗,2⁗′-quinquequinoxalin]-3-yl]palladium ((*P*)-(*S*)-7). To a benzene (30 mL) solution of (*S*)-**4a** (107 mg, 0.097 mmol) was added **3** (30 mg, 0.097 mmol) in benzene (30 mL) at room temperature. The mixture was heated at 50 °C for 2 h and then cooled to room temperature. The operation, i.e., addition of **3** (30 mg, 0.097 mmol) followed by heating at 50 °C, was repeated four times more. Volatile material was evaporated in vacuo, and residual solids were subjected to preparative GPC ($CHCl_3$) to give crude pentamer. The crude material was recrystallized in CH_2Cl_2/hexane to give pure (*P*)-(*S*)-**7** (65 mg, 31%). (*P*)-(*S*)-**7**: mp 255−260 °C (dec). ^{1}H NMR (400 MHz, C_6D_6) δ 0.89 (s, 3H), 1.66 (s, 3H), 1.70 (d, J = 11.4 Hz, 3H), 1.83 (s, 3H), 1.88 (s, 3H), 1.92 (d, J = 11.4 Hz, 3H), 1.96 (s, 3H), 2.00 (s, 3H), 2.04 (s, 3H), 2.16 (s, 3H), 2.34 (s, 3H), 2.41 (s, 3H), 3.52 (s, 3H), 5.91 (d, J = 7.9 Hz, 2H), 6.24 (d, J = 7.4 Hz, 2H), 6.31 (d, J = 7.6 Hz, 2H), 6.45−7.86 (m, 57H), 7.88 (d, J = 8.7 Hz, 2H), 8.23 (d, J = 8.0 Hz, 2H). Anal. Calcd for $C_{139}H_{106}IN_{10}$OPPd: C, 76.00; H, 4.86; N, 6.38. Found: C, 75.92; H, 4.91; N, 6.31.

X-ray Diffraction Study of (*P*)-(*S*)-7. A single crystal of (*P*)-(*S*)-**7** mounted on a glass fiber was subjected to the data collection. Crystal data for **7** ($C_{139}H_{106}IN_{10}$OPPd): crystal size 0.30 × 0.20 × 0.50 mm; monoclinic, space group $P2_1$ (no. 4), Z = 2; a = 12.853(4), b = 40.251(9), c = 12.486(3) Å; β = 117.36(2)°; V = 5737(2) Å^3, ρ_{calcd} = 1.27 g/cm^3; μ = 40.22 cm^{-1}; max 2θ = 125° ($Cu_{K\alpha}$, λ = 1.54178 Å, graphite monochromator, ω/2θ-scan, T = 293 K); 10431 reflections measured, 9746 independent, 8803 included in the refinement, Lorentzian polarization; direct method, anisotropical refinement for non-hydrogen atoms by full-matrix least-squares against $|F|$ with program package CrystanG (Mac Science), 1376 parameters; R = 0.070, R_w = 0.091. Hydrogen atoms were not included in the refinement.

Synthesis of Poly[5,8-di(4-methylphenyl)quinoxaline-2,3-diyl] (*P*)-8. To a THF (0.5 mL) solution of (*P*)-(*S*)-**7** (2.4 mg, 1.1 μmol) was added **3** (12 mg, 0.038 mmol) at room temperature. The mixture was stirred for 6 days, and then THF (1 mL) and $NaBH_4$ (1.4 mg, 0.036 mmol) were added. Extraction with CH_2Cl_2 followed by purification by preparative GPC (no recycling) gave poly(2,3-quinoxaline)s (*P*)-**8** (7 mg, 48%). M_n = 7.18 × 10^3, M_w/M_n = 1.37. UV ($CHCl_3$) λ_{max} = 271 nm (ϵ 2.89 × 10^4). ^{1}H NMR ($CDCl_3$) δ 1.0−2.6 (br m, 6*n*H), 5.0−8.0 (br m, 10*n*H).

Synthesis of Poly[5,8-dimethyl-6,7-bis(propoxymethyl)quinoxaline-2,3-diyl] (*P*)-9. To a THF (2 mL) solution of (*P*)-(*S*)-**7** (1.7 mg, 0.77 μmol) was added **3** (8.1 mg, 27 μmol) at room temperature. The mixture was stirred for 12 h, and then a solution of $ZnCl_2$ (375 mg, 2.7 mmol) and MeMgBr (1.35 mmol) in THF (1 mL) was added at room temperature. After 0.5 h, water (0.5 mL) was added, and organic materials were extracted with $CHCl_3$, dried over sodium sulfate, and evaporated in vacuo. The residue was subjected to preparative GPC ($CHCl_3$) to give polymers (*P*)-**9** (8.1 mg, 85%). M_n = 6.18 × 10^3, M_w/M_n = 1.65. UV ($CHCl_3$) λ_{max} = 290 nm (ϵ 8.0 × 10^5). ^{1}H NMR ($CDCl_3$) δ 0.90 (br s, 6*n*H), 1.58 (br s, 4*n*H), 2.33 (br s, 6*n*H), 3.45 (br s, 4*n*H), 4.57 (br s, 4*n*H); ^{13}C NMR ($CDCl_3$) δ 10.7, 12.0, 22.9, 67.1, 72.7, 135.6, 136.2, 138.9, 152.2.

General Procedure for the Synthesis of Poly[5,8-bis(4-methylphenyl)quinoxaline-2,3-diyl]s 10a−d. To a THF (1.4 mL) solution of **4** (3−4 mg, 3.0 μmol) was added **3** (37.1 mg, 0.120 mmol) at room temperature. The mixture was stirred for 5 days, and then THF (3 mL) and $NaBH_4$ (4.1 mg, 0.108 mmol) were added. Extraction with CH_2Cl_2 followed by purification by preparative GPC (no recycling) gave poly(2,3-quinoxaline)s **10a−d** in the yields shown in Table 1. **10**: ^{1}H NMR ($CDCl_3$) δ 1.0−2.6 (br m, 6*n*H), 5.0−8.0 (br m, 10*n*H); ^{13}C NMR ($CDCl_3$) δ 20.1 (br s), 127−133 (br m), 134−140 (br m).

General Procedure for the Synthesis of Poly[5,8-dimethyl-6,7-bis(propoxymethyl)quinoxaline-2,3-diyl]s 11a−d. To a solution of **4a−d** (1.0 × 10^{-3} mmol) in THF (3 mL) was added **6** (12 mg, 4.0 × 10^{-2} mmol) at room temperature. The mixture was stirred for 18−24 h, and then a solution of $ZnCl_2$ (13.6 mg, 0.10 mmol) and MeMgBr (5.0 × 10^{-2} mmol) in THF (1 mL) was added at room temperature. After 0.5 h, water (0.5 mL) was added, and organic materials were extracted with $CHCl_3$, dried over sodium sulfate, and evaporated in vacuo. The residue was subjected to preparative GPC ($CHCl_3$) to give polymers **11a−d** in the yields indicated in Table 1. The binaphthyl endo-groups were not detectable by the NMR measurements. **11**: ^{1}H NMR ($CDCl_3$) δ 0.90 (br t, J = 6.9 Hz, 6*n*H), 1.4−1.7 (br m, 4*n*H), 2.34 (br s, 6*n*H), 3.47 (br s, 4*n*H), 4.58 (br s, 4*n*H); ^{13}C NMR ($CDCl_3$) δ 10.7, 12.0, 22.9, 67.2, 72.7, 135.5, 136.4, 138.9, 152.2. Anal. Calcd for **11d** (n = 39, $C_{21}H_{15}O + C_{22}H_{16}N_2 + (C_{18}H_{24}O_2N_2)_{39} + CH_3$): C, 72.71; H, 7.93; N, 9.09. Found: C, 72.23; H, 7.81; N, 8.33.

Synthesis of (*P*)-Poly[5,8-dimethyl-6,7-bis(benzyloxymethyl)quinoxaline-2,3-diyl] (14b). To a solution of (*S*)-**4b** (5.1 mg, 4.7 × 10^{-3} mmol) in THF (14 mL) was added **12** (70 mg, 0.19 mmol) at room temperature; the mixture was stirred for 16 h at room temperature. To the mixture was added a solution of $ZnCl_2$ (64 mg, 0.47 mmol) and MeMgBr (0.24 mmol) in THF (1 mL) at room temperature. After 0.5 h, water (0.5 mL) was added, and organic materials were extracted with $CHCl_3$, dried over sodium sulfate, and evaporated in vacuo. The residue was subjected to preparative GPC ($CHCl_3$) to give polymer **14b** (52 mg, 70%). **14b**: M_n = 9.04 × 10^3, M_w/M_n = 1.15. The CD spectrum was identical to that of (*P*)-**11b**. **14b**: ^{1}H NMR ($CDCl_3$) δ 2.34 (br s, 6*n*H), 4.10−4.60 (br m, 8*n*H), 7.22 (br s, 10*n*H); ^{13}C NMR ($CDCl_3$) δ 12.1, 66.6, 73.0, 127.7, 128.35, 128.41, 135.7, 136.3, 138.3, 139.0, 152.2.

Synthesis of (*P*)-Poly[5,8-dimethyl-6,7-di[(2-methoxyethoxy)methyl]quinoxaline-2,3-diyl] (15b). By a procedure similar to that for **14b**, **15b** (11 mg, 42%) was synthesized from (*S*)-**4b** (1.9 mg, 1.8 × 10^{-3} mmol) and **13** (23.5 mg, 7.0 × 10^{-2} mmol). **15b**: M_n = 6.81 × 10^3, M_w/M_n = 2.32. The CD spectrum was identical to that of (*P*)-**11b**. **15b**: ^{1}H NMR ($CDCl_3$) δ 2.34 (br s, 6*n*H), 3.32 (br s, 6*n*H), 3.53 (br s, 4*n*H), 3.66 (br s, 4*n*H), 4.65 (br s, 2*n*H), 4.74 (br s, 2*n*H); ^{13}C NMR ($CDCl_3$) δ 12.1, 58.9, 67.6, 69.7, 71.9, 135.6, 136.3, 138.9, 152.2.

Synthesis of Iodobis(trimethylphosphine)[oligo(quinoxalinyl)]-palladium(II) Complexes 17^1−17^4. To a solution of **4d′** (99 mg, 0.1 mmol) in THF (10 mL) was added **16** (50 mg, 0.2 mmol) at room temperature. The mixture was stirred at room temperature for 20 h. Evaporation of the solvent gave a crude mixture of [oligo(quinoxalinyl)]-palladium(II) complexes, which was subjected to preparative GPC to afford **17^1** (27 mg, 18%), **17^2** (72 mg, 39%), **17^3** (16 mg, 7%), and **17^4** (7 mg, 3%) together with recovered starting complex **4d′** (7 mg, 6%).

Iodo[3′-(7′-methoxy[1,1′-binaphthalene]-2-yl)-6,7-bis(methoxymethyl)-5,8-dimethyl-5′,8′-bis(4-methylphenyl)[2,2′-biquinoxalin]-3-yl]bis(trimethylphosphine)palladium (17^1): ^{1}H NMR (400 MHz, C_6D_6) δ 0.57 (br s, 9H), 0.81 (s, br, 9H), 2.13 (s, 3H), 2.21 (s, 3H), 2.61 (br s, 3H), 2.90 (br s, 3H), 2.99 (s, 3H), 3.20 (s, 3H), 3.24 (s, 3H), 4.58−4.72 (m, 4H), 6.40−6.82 (br s, 1H), 6.82−7.10 (m, 5H), 7.10−7.34 (m, 6H), 7.37 (d, J = 9.0 Hz, 1H), 7.45−7.55 (m, 7H), 7.58 (d, J = 8.6 Hz, 1H), 8.0−8.4 (br s, 1H); ^{31}P NMR (C_6D_6) δ −21.05 (br s). FABMS (pos) calcd signals (intensity/% based on MH$^+$) for $[C_{63}H_{65}IN_4O_3P_2Pd + H]^+$: *m*/*z* 1219 (25), 1220 (66), 1221 (100), 1222 (57), 1223 (76), 1224 (46), 1225 (41), 1226 (22), 1227 (7). Found: *m*/*z* 1219 (55), 1220 (73), 1221 (100), 1222 (69), 1223 (87), 1224 (50), 1225 (49), 1226 (24), 1227 (4).

Iodo[3″-(7′-methoxy[1,1′-binaphthalene]-2-yl)-6,6′,7,7′-tetrakis(methoxymethyl)-5,5′,8,8′-tetramethyl-5″,8″-bis(4-methylphenyl)-[2,2′:3′,2″-terquinoxalin]-3-yl]bis(trimethylphosphine)palladium (17²): ^{1}H NMR (500 MHz, C_6D_6) δ 0.72 (d, J = 7.1 Hz, 9H), 1.12 (d, J = 7.1 Hz, 9H), 1.93 (s, 3H), 2.02 (s, 3H), 2.29 (s, 3H), 2.34 (s, 3H), 2.91 (s, 3H), 2.95 (s, 3H), 2.98 (s, 3H), 3.13 (s, 3H), 3.14 (s, 3H), 3.15 (s, 3H), 3.54 (s, 3H), 4.25 (d, J = 11.2 Hz, 2H), 4.34 (d, J = 11.2 Hz, 1H), 4.38 (d, J = 11.2 Hz, 1H), 4.49 (d, J = 10.8 Hz, 1H), 4.54 (d, J = 10.8 Hz, 1H), 4.56−4.62 (m, 2H), 6.61 (d, J = 7.9 Hz, 2H), 6.70 (d, J = 7.9 Hz, 2H), 6.87 (d, J = 7.9 Hz, 2H), 6.93 (t, J = 8.3 Hz, 1H), 7.00 (d, J = 7.7 Hz, 1H), 7.01 (d, J = 7.9 Hz, 2H), 7.03 (t, J = 8.3 Hz, 1H), 7.05 (d, J = 2.2 Hz, 1H), 7.09 (t, J = 7.1 Hz, 1H), 7.23 (d, J = 7.7 Hz, 1H), 7.25 (d, J = 8.8 Hz, 1H), 7.28 (dd, J = 9.0, 2.2 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 7.48 (d, J = 7.1 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 8.3 Hz, 1H), 8.46 (d, J = 8.6 Hz, 1H), 8.67 (d, J = 7.1 Hz, 1H); ^{31}P NMR (C_6D_6) δ −23.65 (d, J = 392 Hz), −22.66 (d, J = 392 Hz). Anal. Calcd for $C_{77}H_{81}IN_6O_5P_2Pd$: C, 63.09; H, 5.57; N, 5.73. Found: C, 63.12; H, 5.53; N, 5.67. FABMS (pos) calcd signals (intensity/% based on MH^+) for $[C_{77}H_{81}IN_6O_5P_2Pd + H]^+$: *m*/*z* 1463 (22), 1464 (63), 1465 (100), 1466 (67), 1467 (78), 1468 (53), 1469 (45), 1470 (27), 1471 (11). Found: *m*/*z* 1463 (45), 1464 (75), 1465 (100), 1466 (75), 1467 (79), 1468 (53), 1469 (41), 1470 (18), 1471 (9). Deuterated derivatives **17²-i-iv** were prepared similarly by reactions of **16′** or **16″** and identified by ^{1}H NMR and MS. **Compound 17²-i**: ^{1}H NMR (C_6D_6) showed signals identical to that for **17²** except for disappearance of singlets at 2.02, 2.34, 3.15, and 3.54 ppm. FABMS (pos) *m*/*z* 1477 (MH^+). **Compound 17²-ii**: ^{1}H NMR (C_6D_6) showed signals identical to that for **17²** except for disappearance of singlets at 2.95, 2.98, 3.13, and 3.14 ppm. FABMS (pos) *m*/*z* 1477 (MH^+). **Compound 17²-iii**: ^{1}H NMR (C_6D_6) showed signals identical to that for **17²** except for disappearance of singlets at 2.02 and 3.15 ppm. FABMS (pos) *m*/*z* 1471 (MH^+). **Compound 17²-iv**: ^{1}H NMR (C_6D_6) showed signals identical to that for **17²** except for disappearance of singlets at 2.98 and 3.13 ppm. FABMS (pos) *m*/*z* 1471 (MH^+).

Iodo[3‴-(7′-methoxy[1,1′-binaphthalene]-2-yl)-6,6′,6″,7,7′,7″-hexakis(methoxymethyl)-5,5′,5″,8,8′,8″-hexamethyl-5‴,8‴-bis(4-methylphenyl)[2,2′:3′,2″:3′<bold>′,2‴-quaterquinoxalin]-3-yl]bis(trimethylphosphine)palladium (17³): ^{1}H NMR (400 MHz, C_6D_6) δ 1.03 (d, J = 7.3 Hz, 9H), 1.23 (d, J = 7.3 Hz, 9H), 1.74 (s, 6H), 1.77 (s, 3H), 2.26 (s, 6H), 2.30 (s, 3H), 2.87 (s, 3H), 2.95 (s, 3H), 2.96 (s, 3H), 3.02 (s, 3H), 3.08 (s, 3H), 3.12 (s, 3H), 3.20 (s, 3H), 3.22 (s, 3H), 3.43 (s, 3H), 4.18 (d, J = 11.2 Hz, 1H), 4.27−4.47 (m, 8H), 4.57 (d, J = 11.2 Hz, 1H), 4.65 (d, J = 10.6 Hz, 1H), 4.69 (d, J = 10.6 Hz, 1H), 6.65 (d, J = 8.1 Hz, 2H), 6.79 (t, J = 9.2 Hz, 1H), 6.9−7.0 (m, 4H), 7.1−7.2 (m, 6H), 7.24 (dd, J = 2.4, 9.2 Hz, 1H), 7.31−7.36 (m, 3H), 7.41 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 9.2 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 8.48−8.50 (m, 2H); ^{31}P NMR (C_6D_6) δ −23.03, −23.76. FABMS (pos) calcd signals (intensity/% based on MH^+) for $[C_{91}H_{97}IN_8O_7P_2Pd + H]^+$: *m*/*z* 1707 (20), 1708 (60), 1709 (100), 1710 (76), 1711 (82), 1712 (61), 1713 (50), 1714 (32). Found: *m*/*z* 1707 (60), 1708 (76), 1709 (100), 1710 (71), 1711 (60), 1712 (53), 1713 (42), 1714 (37).

Iodo[3⁗-(7′-methoxy[1,1′-binaphthalene]-2-yl)-6,6′,6″,6‴,7,7′,7″,7‴-octakis(methoxymethyl)-5,5′,5″,5‴,8,8′,8″,8‴-octamethyl-5⁗,8⁗-bis(4-methylphenyl)[2,2′:3′,2″:3′<bold>′,2‴:3‴,2⁗-quinquequinoxalin]-3-yl]bis(trimethylphosphine)palladium (17⁴): ^{1}H NMR (400 MHz, C_6D_6) δ 1.20 (dd, J = 5.4, 1.6 Hz, 9H), 1.30 (dd, J = 5.4, 1.6 Hz, 9H), 1.62 (s, 3H), 1.92 (s, 3H), 2.09 (s, 3H), 2.10 (s, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 2.23 (s, 3H), 2.29 (s, 3H), 2.78 (s, 3H), 2.80 (s, 3H), 2.84 (s, 3H), 2.93 (s, 3H), 2.94 (s, 3H), 2.98 (s, 3H), 3.14 (s, 3H), 3.17 (s, 3H), 3.20 (s, 3H), 3.70 (s, 3H), 4.0−4.4 (m, 12H), 4.5−4.7 (m, 4H), 6.61 (d, J = 8.1 Hz, 2H), 6.65 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 7.7 Hz, 2H), 6.90−7.03 (m, 4H), 7.1−7.2 (m, 3H), 7.25−7.35 (m, 2H), 7.4−7.5 (m, 2H), 7.55 (d, J = 8.1 Hz, 1H), 7.65−7.70 (m, 2H), 8.69 (d, J = 8.6 Hz, 1H), 8.76 (d, J = 6.2 Hz, 1H); ^{31}P NMR (C_6D_6) δ −23.57, −23.68. FABMS (pos) calcd signals (intensity/% based on MH^+) for $[C_{105}H_{113}IN_{10}O_9P_2Pd + H]^+$: *m*/*z* 1951 (19), 1952 (57), 1953 (100), 1954 (85), 1955 (88), 1956 (69), 1957 (56), 1958 (37), 1959 (18). Found: *m*/*z* 1951 (56), 1952 (74), 1953 (100), 1954 (92), 1955 (80), 1956 (60), 1957 (43), 1958 (24), 1959 (17).

Synthesis of 18¹ and 18². To a solution of **4a′** (99 mg, 0.1 mmol) in THF (mL) was added **16** (50 mg, 0.2 mmol) at room temperature. The mixture was stirred at room temperature for 10 h. Evaporation of the solvent gave a crude mixture of [oligo(quinoxalinyl)]palladium(II) complexes, which was subjected to preparative GPC to afford **18¹** (30 mg, 22%) and **18²** (48 mg, 31%) together with higher oligomers (39 mg) and recovered starting complex **4d′** (8 mg, 8%).

Iodo[3′-(2′-methoxy[1,1′-binaphthalene]-2-yl)-6,7-bis(methoxymethyl)-5,8-dimethyl-5′,8′-bis(4-methylphenyl)[2,2′-biquinoxalin]-3-yl]bis(trimethylphosphine)palladium (18¹): **18¹:** ^{1}H NMR (C_6D_6) δ 0.55 (br s, 9H), 0.81 (br s, 9H), 2.20 (s, 3H), 2.23 (s, 3H), 2.30−2.90 (br, 6H), 2.97 (br s, 3H), 3.24 (s, 3H), 3.26 (br s, 3H), 4.68 (br s, 3H), 4.72 (s, 3H), 6.50−7.68 (m, 20H), 7.96 (br s, 2H); ^{31}P NMR (C_6D_6) δ 22.5 (br). FABMS (pos) calcd signals (intensity/% based on MH^+) for $[C_{63}H_{65}IN_4O_3P_2Pd + H]^+$: *m*/*z* 1219 (25), 1220 (65), 1221 (100), 1222 (57), 1223 (76), 1224 (46), 1225 (41). Found: *m*/*z* 1219 (29), 1220 (80), 1221 (100), 1222 (79), 1223 (65), 1224 (43), 1225 (32).

Iodo[3″-(2′-methoxy[1,1′-binaphthalene]-2-yl)-6,6′,7,7′-tetrakis(methoxymethyl)-5,5′,8,8′-tetramethyl-5″,8″-bis(4-methylphenyl)-[2,2′:3′,2″-terquinoxalin]-3-yl]bis(trimethylphosphine)palladium (18²). This compound was obtained as a mixture of two diastereomers ((*P*)-(*S*)-isomer: (*M*)-(*S*)-isomer = 52:48). **18²:** ^{1}H NMR (500 MHz, C_6D_6: (*P*)-(*S*)- and (*M*)-(*S*)-isomers are denoted by isomer A and B, respectively, in the following description) δ 0.71 (d, J = 6.1 Hz, 9H for isomer A), 0.75 (s, 9H for isomer B), 1.10 (s, 9H for isomers A and B), 1.89 (s, 3H for isomer A), 1.93 (s, 3H for isomer B), 2.20 (s, 3H for isomer B), 2.22 (s, 3H for isomer B), 2.24 (s, 3H for isomer B), 2.30 (s, 3H for isomer A), 2.38 (s, 3H for isomer A), 2.53 (s, 3H for isomer A), 2.92−3.22 (m, 18 H for isomers A and B), 3.64 (s, 3H for isomers A and B), 4.20−4.58 (m, 6H for isomers A and B), 4.58−4.72 (m, 2H for isomers A and B), 6.40−7.70 (m, 19 H for isomers A and B), 7.78−8.00 (m, 1H for isomer A and 2H for isomer B), 8.34 (br s, 1H for isomer B), 8.44 (d, J = 8.6 Hz, 1H for isomer A), 8.90 (d, J = 7.7 Hz, 1H for isomer A); ^{31}P NMR (C_6D_6) δ −23.8, −23.64, −23.59, −23.4. FABMS (pos) calcd signals (intensity/% based on MH^+) for $[C_{77}H_{81}IN_6O_5P_2Pd + H]^+$: *m*/*z* 1463 (22), 1464 (63), 1465 (100), 1466 (67), 1467 (78), 1468 (53), 1469 (45), 1470 (27), 1471 (11). Found: *m*/*z* 1463 (58), 1464 (74), 1465 (100), 1466 (77), 1467 (74), 1468 (54), 1469 (47), 1470 (29), 1471 (25). **18²-i:** ^{1}H NMR (500 MHz, C_6D_6: (*P*)-(*S*)- and (*M*)-(*S*)-isomers are denoted by isomer A and B, respectively, in the following description) δ 0.71 (d, J = 6.1 Hz, 9H for isomer A), 0.75 (s, 9H for isomer B), 1.10 (s, 9H for isomers A and B), 1.89 (s, 3H for isomer A), 1.93 (s, 3H for isomer B), 2.24 (s, 3H for isomer B), 2.30 (s, 3H for isomer A), 2.95−3.22 (m, 15 H for isomers A and B), 4.20−4.58 (m, 6H for isomers A and B), 4.58−4.72 (m, 2H for isomers A and B), 6.40−7.70 (m, 19 H for isomers A and B), 7.78−8.00 (m, 1H for isomer A and 2H for isomer B), 8.34 (br s, 1H for isomer B), 8.44 (d, J = 8.6 Hz, 1H for isomer A), 8.90 (d, J = 7.7 Hz, 1H for isomer A). FABMS (pos) *m*/*z* 1477 $[C_{77}H_{69}D_{12}IN_6O_5P_2Pd + H]^+$.

Synthesis of 19²-i. To a solution of **4b′** (67 mg, 0.071 mmol) in THF (mL) was added **16′** (36 mg, 0.142 mmol) at room temperature. The mixture was stirred at room temperature for 10 h. Evaporation of the solvent gave a crude mixture of [oligo(quinoxalinyl)]palladium(II) complexes, which was subjected to preparative GPC to afford **19²-i** (49 mg, 48%). **19²-i:** ^{1}H NMR (500 MHz, C_6D_6) δ 0.71 (d, J = 7.2 Hz, 9H), 1.13 (d, J = 7.2 Hz, 9H), 1.93 (s, 3H), 2.22 (s, 3H), 2.93 (s, 3H), 2.95 (s, 3H), 3.14 (s, 3H), 3.15 (s, 3H), 4.25−4.40 (m, 4H), 4.49−4.62 (m, 4H), 6.56 (d, J = 7.4 Hz, 2H), 6.69 (d, J = 7.9 Hz, 2H), 6.72 (d, J = 7.5 Hz, 2H), 6.88 (t, J = 7.9 Hz, 1H), 6.95−7.31 (m, 10H), 7.49−7.54 (m, 2H), 7.67−7.72 (m, 2H), 8.47 (d, J = 8.6 Hz, 1H), 8.57 (d, J = 6.6 Hz, 1H); ^{31}P NMR (C_6D_6) δ −22.9, −23.3. FABMS (pos) calcd signals (intensity/% based on MH^+) for $[C_{76}H_{67}D_{12}IN_6O_4P_2Pd + H]^+$: *m*/*z* 1445 (22), 1446 (63), 1447 (100), 1448 (66), 1449 (78), 1450 (53), 1451 (44), 1452 (26), 1453 (10). Found: *m*/*z* 1445 (47), 1446 (83), 1447 (100), 1448 (78), 1449 (76), 1450 (58), 1451 (42), 1452 (29), 1453 (12).

Synthesis of 20²-i. To a solution of **4c′** (44 mg, 0.041 mmol) in THF (1.5 mL) was added **16′** (21 mg, 0.082 mmol) at room temperature.

The mixture was stirred at room temperature for 10 h. Evaporation of the solvent gave a crude mixture of [oligo(quinoxalinyl)]palladium(II) complexes, which was subjected to preparative GPC to afford **20^2-i** (26 mg, 40%). **20^2-i:** ^{1}H NMR (500 MHz, C_6D_6) δ −0.06 (s, 6H), 0.46 (s, 9H), 0.69 (s, 9H), 1.12 (s, 9H), 1.89 (s, 3H), 2.43 (s, 3H), 3.02 (s, 3H), 3.11 (s, 3H), 3.13 (s, 3H), 3.21 (s, 3H), 4.35−4.51 (m, 4H), 4.56−4.67 (m, 4H), 6.66−7.31 (m, 17H), 7.39 (br s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.72 (br s, 1H), 8.60 (br s, 1H), 8.75 (br s, 1H); ^{31}P NMR (C_6D_6) δ −23.7, −23.6. FABMS (pos) m/z 1578 [$C_{82}H_{81}D_{12}IN_6O_5P_2PdSi$ + H]$^+$.

Acknowledgment. This work was supported by Grant-in-Aids from Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: Tables of positional and thermal parameters, and interatomic distances and angles for **7** (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA982500M