Communication

Chirality-Amplifying, Dynamic Induction of Single-Handed Helix by Chiral Guests to Macromolecular Chiral Catalysts Bearing Boronyl Pendants as Receptor Sites

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Chirality-Amplifying, Dynamic Induction of Single-Handed Helix by Chiral Guests to Macromolecular Chiral Catalysts Bearing Boronyl Pendants as Receptor Sites

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Supporting Information Placeholder

ABSTRACT: Helical chirality of poly(quinoxaline-2,3-diyl)s bearing a boronyl pendant at the 5-position of the quinoxaline ring was induced by condensation with chiral guests such as a diol, diamine, and amino alcohol. Reversible induction of a single-handed helical structure was achieved by using less than an equimolar amount of chiral amino alcohols to the boronyl pendants. Majority-rule-effect-based chiral amplification on the polyquinoxaline main chain was demonstrated with chiral amino alcohols with low enantiomeric excess (ee). The helical macromolecular scaffold whose helicity was thus induced was utilized in palladium-catalyzed asymmetric silaboration of *meso*-methylenecyclopropane (up to 92% ee) by introducing (diarylphosphino)phenyl pendants at their side chains.

Because of their unique chiral structures, helical synthetic macromolecules that contain either *P*- or *M*-helical conformation in excess are finding various applications, including chiral separation, chirality sensing, circularly polarized light (CPL) emission, and CPL reflection.[1] Particular interest is being focused on the use of purely single-handed helical macromolecules as chiral catalysts in asymmetric catalysis,[2] although the requirement for the induction of the "pure" helical sense still hampers this development. In all these applications, the dynamic nature of helical structures along with their rod-like molecular shape makes them highly characteristic, in comparison with chiral small molecules, thus enabling switchable chiral functions, where the change of external conditions alters the enantiodiscrimination or CPL handedness.[3] One major strategy for induction of the nonracemic helical sense involves introduction of chiral side chains through inconvertible, strong covalent bonds into all planar or quasiplanar repeating units.[4] Such inconvertible chiral groups in the macromolecular scaffolds make the whole structure robust, but it does make their synthesis laborious.

In contrast, there is another class of induction where chiral guests serve as a source of helical chirality.[5] This strategy allows the use of macromolecules devoid of chiral groups on their backbones, to which chirality is induced by the addition of chiral guests. Most typically, Yashima and coworkers reported that achiral polyacetylenes bearing carboxyl or boronyl groups at the pendant groups adopt nonracemic helical structures upon addition of chiral guests to their solutions.[5b–d] This type of helix induction by a chiral guest has the advantages of less-laborious synthesis and wider variation of the choice of chiral sources. However, despite these advantages, helix induction by chiral guests has never yet been combined with application to asymmetric catalysis.

In this paper, we demonstrate the induction of a single-handed helical structure to helical poly(quinoxaline-2,3-diyl)s[4q,r] (PQX hereafter) bearing boronyl pendants (PQXboh) using several chiral guest molecules.[6,7] The single-handed PQX was used as a chiral catalyst in asymmetric catalytic reactions with high enantioselectivity. We also demonstrate the use of a chiral guest with low enantiopurity to obtain high enantioselectivities through chiral amplification.

A binary, "achiral" random copolymer PQXboh bearing boronyl pendants along with propoxymethyl side chains was chosen as a scaffold and synthesized by living polymerization. PQXboh is reported to be a versatile synthetic intermediate, to which various pyridine-based pendants such as 4-aminopyrid-3-yl and 2,2′-bipyrid-6-yl are easily introduced by postpolymerization cross-coupling.[2p,q] **PQXboh(190/10*)** containing 10 boronyl pendants (on average) was dissolved in toluene in the presence of molecular sieves 4A with various chiral diol, diamine, and amino alcohols (0.01 M, 200 equiv to boronyl group), separately (Figure 1a). After stirring for 15–24 h at room temperature, circular dichroism (CD) spectra were measured to determine the degree of helix induction without removing the chiral guest. The screw-sense excess (se) of each sample was determined by comparison of the g value (Kuhn dissymmetry factors, $\Delta\varepsilon/\varepsilon$) at 371.5 nm with the expected g value (g_{max}) for purely single-handed PQX (*vide infra*) (Figure 1b).[8] The chiral diol (*S*,*S*)-**1** induced *M*-helical structure ($g = -1.87 \times 10^{-3}$), which was assumed to be ca. 90% se, while the diamine derivative (*S*,*S*)-**2** induced *M*-helical structure with moderate se. We found that the corresponding amino alcohol (*S*,*S*)-**3** induced almost pure *M*-helical conformation efficiently ($g = -2.10 \times 10^{-3}$). Similarly, its diastereomer, (*S*,*R*)-**4**, afforded single-handed *P*-helical conformation efficiently ($g = +2.03 \times 10^{-3}$). The two diastereomers (*S*,*S*)-**3** and (*S*,*R*)-**4** gave a pair of mirror-image CD spectra of *P*- and *M*-helices (Figure 1c). Aminoindanol (*S*,*R*)-**5** also induced the *M*-helix efficiently. We further tested amino alcohols derived from amino acids. Phenylglycinol (*R*)-**6** showed efficient induction of the *P*-helical structure ($g = +2.16 \times 10^{-3}$), while valinol (*R*)-**7** showed moderate but clear induction of the *P*-helix. Use of alaninol (*S*)-**8** with opposite absolute configuration resulted in formation of the *M*-helical structure with much less screw-sense induction. These results clearly indicate that the stereochemistry of a *N*-bound stereogenic carbon center serves as a determinant of the helical chirality of PQXboh. Amino alcohol (*R*)-**9**, which lacks a *N*-bound

stereogenic carbon center, resulted in the formation of a *M*-helix with moderate se. *N*-Methylated amino alcohol (*S*,*S*)-**10** exhibited the induction of screw-sense opposite to that of nonmethylated (*S*,*S*)-**3** with much lower se.

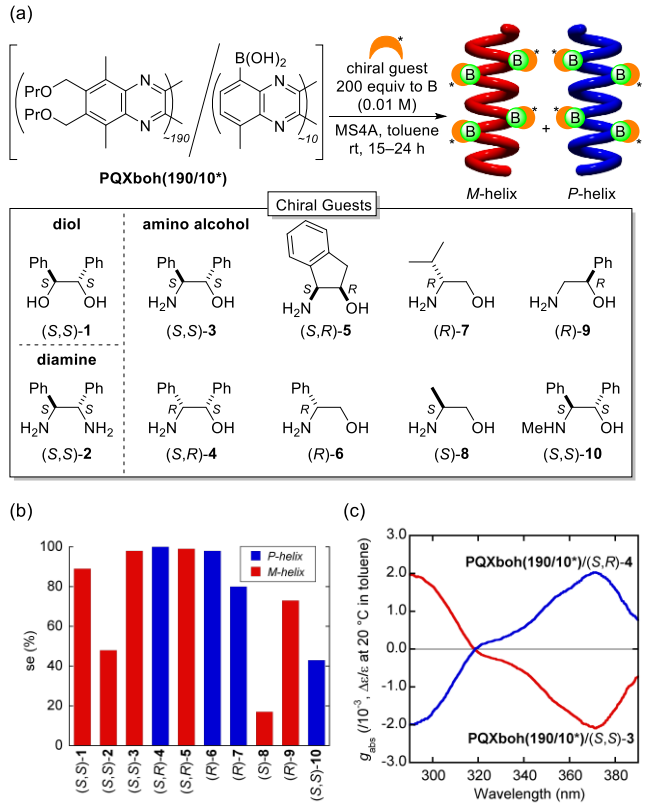


Figure 1. (a) Helical chirality induction of **PQXboh(190/10*)** with chiral guests. (b) Induced se of **PQXboh(190/10*)** with chiral guests in toluene at 20 °C. (c) CD spectra of **PQXboh(190/10*)** with chiral guests (*S*,*S*)-**3** and (*S*,*R*)-**4** in toluene at 20 °C.

To determine the effect of chiral guests in detail, the helix stabilization energy (ΔG_h) per chiral guest was estimated by changing the degree of polymerization (DP) of **PQXboh(n/m*)** ([*n* + *m*] = 60–400), while the ratio of boronyl units (*n*/*m* = 19/1) was maintained. The *g* values were plotted against the DP of **PQXboh(n/m*)** (Figure 2a). Hyperbolic tangent curves fit into the obtained positive nonlinear plots.[4e] The ΔG_h of (*S*,*S*)-**3** in toluene was found to be highest; it was estimated to be −1.54 kJ mol^{-1}. It should be remarked here that this value is 1.5 times higher than the highest ΔG_h for PQX bearing covalently attached 2-alkoxymethyl groups at the 6- and 7-positions of the quinoxaline rings (−1.01 kJ/mol for 2-octyloxymethyl).[4r] We found that the amount of chiral guest could be reduced to 1.0 equiv to boronyl groups for the induction of pure helical sense of **PQXboh(380/20*)** (Figure 2b). Remarkably, even the use of 0.5 equiv of chiral guest (*S*,*S*)-**3** afforded 92% se.

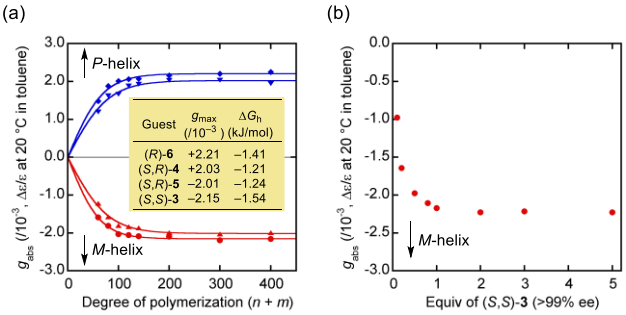
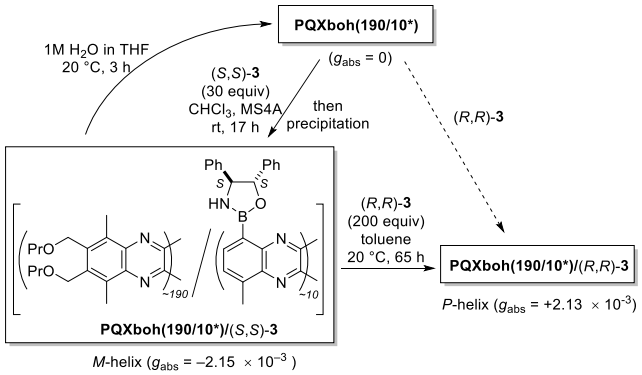


Figure 2. (a) Relationships between DP (*n* + *m*) and dissymmetry factor *g* of **PQXboh(n/m*)** (*n*/*m* = 19/1) at 371.5 nm in toluene at 20 °C: (*S*,*S*)-**3** (●), (*S*,*R*)-**4** (▼), (*S*,*R*)-**5** (▲), and (*R*)-**6** (♦). In the table insert, g_{max} (*g* values for pure helix) and ΔG_h (helix stabilization energy per unit) calculated from curve fittings are shown. (b) Helical chirality induction of **PQXboh(380/20*)** with different equivalents (equiv) of (*S*,*S*)-**3**.

By reprecipitation from acetonitrile, **PQXboh(190/10*)**/(*S*,*S*)-**3**, in which the boronyl group was converted to an oxazaborolidine group, was isolated (Scheme 1). The isolated PQX showed pure left-handed helical structure on measurement of its CD spectrum in the absence of the excess chiral guest (toluene, 20 °C). **PQXboh(190/10*)**/(*S*,*S*)-**3** was made CD silent within 3 h upon hydrolysis (1 M H_2O in tetrahydrofuran at 20 °C). Direct replacement of the chiral amino alcohol on **PQXboh** was achieved by mixing **PQXboh(190/10*)**/(*S*,*S*)-**3** with 200 equiv of (*R*,*R*)-**3**, resulting in complete reversal of the screw-sense (Scheme 1).

Scheme 1. Reversible Helical Chirality Induction of PQXboh with Chiral Amino Alcohol

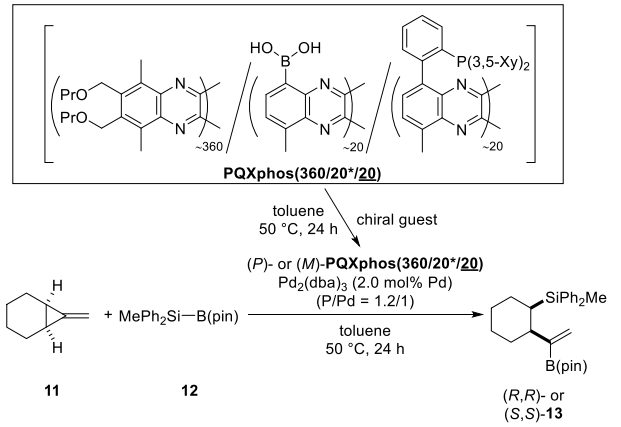


Based on these results, a chiral-guest-responsive helical polymer ligand was synthesized by incorporating coordinating groups as the third component.[2i–m,o] The ternary **PQXphos(360/20*/20)** bearing both boronyl and 2-[bis(3,5-dimethylphenyl)phosphino]phenyl pendants was employed in the palladium-catalyzed asymmetric silaborative C–C bond cleavage of *meso*-methylenecyclopropane **11** (Table 1).[2l,9] A control experiment without **PQXphos(360/20*/20)** but with (*S*,*S*)-**3** gave only a trace amount of product **13** (<1%, entry 1). In the absence of chiral guest, **PQXphos(360/20*/20)** afforded racemic **13** (entry 2). However, upon pretreatment of achiral **PQXphos(360/20*/20)** (2.4 mol% P and 2.4 mol% B) with (*S*,*S*)-**3** (1.2 mol%, 0.5 equiv to the boronyl pendants) at 50 °C for 24 h in toluene, the silaboration afforded (*R*,*R*)-**13** in 85% yield with 87% ee (entry 3). Use of larger amounts of chiral guest in the pretreatment afforded the product with slightly higher enantioselectivity (92% ee with 2.0 equiv chiral guest, entries 4 and 5). Use of the enantiomeric chiral guest (*R*,*R*)-**3**

resulted in the formation of an enantiomeric product with the same ee (entry 6).

These results suggest that the chirality of the chiral guest was successfully transferred to the helical main chain of PQX and in turn to the reaction center, as found in PQXphos bearing covalently bonded chiral side chains. Note that ligand exchange on the silylboron reagents was not observed during the reaction. It may also be interesting to note that **PQXphos(380/20)** bearing no boronyl pendant unexpectedly resulted in the formation of (*S*,*S*)-**13** in 5% ee in the presence of (*S*,*S*)-**3**, which, however had preference to form the opposite enantiomer (entry 7). As suggested by the mechanism of chirality transfer, some other chiral guests (*S*,*R*)-**4**, (*S*,*R*)-**5**, and (*R*)-**6** (1.0 equiv) shown in Figure 2 can also be used as the source of chirality in the silaboration reactions (entries 8–10).

Table 1. Palladium-Catalyzed Asymmetric Silaborative C–C Bond Cleavage of *meso*-Methylenecyclopropane[a]



entry	PQXphos	chiral guest (equiv to B atom)	% yield[b]	% ee[c]
1	–	(*S*,*S*)-**3**[d]	<1	N.D.[e]
2	(360/20*/20)	no addition	88	0
3	(360/20*/20)	(*S*,*S*)-**3** (0.5 eq)	85	87 (*R*,*R*)
4	(360/20*/20)	(*S*,*S*)-**3** (1.0 eq)	86	91 (*R*,*R*)
5	(360/20*/20)	(*S*,*S*)-**3** (2.0 eq)	86	92 (*R*,*R*)
6	(360/20*/20)	(*R*,*R*)-**3** (1.0 eq)	81	92 (*S*,*S*)
7	(380/20)	(*S*,*S*)-**3** (1.0 eq)	84	5 (*S*,*S*)
8	(360/20*/20)	(*S*,*R*)-**4** (1.0 eq)	88	72 (*S*,*S*)
9	(360/20*/20)	(*S*,*R*)-**5** (1.0 eq)	93	86 (*R*,*R*)
10	(360/20*/20)	(*R*)-**6** (1.0 eq)	94	82 (*S*,*S*)

[a]**11** (0.15 mmol), **12** (0.10 mmol), $Pd_2(dba)_3$ (1.0 μmol), and ligand (2.4 μmol) were heated with toluene (0.20 mL) at 50 °C. [b]Isolated yield. [c]Determined by chiral SFC analysis after oxidation to the corresponding β-silyl ketones. [d]2.4 mol% to **12**. [e]Not determined.

We then looked at the possibility and the degree of chiral amplification[10,11] using binary **PQXboh(380/20*)** (Figure 3a). In the presence of 200 equiv of (*S*,*S*)-**3** with varying optical purity, helical chirality induction was carried out at 80 °C. A positive nonlinear relationship between the enantiopurity of the chiral guest and screw-sense induction was observed in a CD spectrum, measured in toluene at 20 °C. The plot indicated that even a chiral guest with 20% ee can induce >90% se. A similar chiral amplification was observed for phosphorous-containing, ternary **PQXphos(360/20*/20)** (Figure 3b).

Chirality-amplifying catalytic asymmetric synthesis was demonstrated with the use of **PQXphos(360/20*/20)** and (*S*,*S*)-**3** (Scheme 2). **PQXphos(360/20*/20)** was treated with 10 equiv of (*S*,*S*)-**3** with 33% ee at 80 °C for 96 h, and then excess (*S*,*S*)-**3** was removed by precipitation with acetonitrile. The recovered (*M*)-**PQXphos(360/20*/20)**/(*S*,*S*)-**3** afforded (*R*,*R*)-**13** with 87% ee. This result demonstrates that PQX serves as an efficient chiral amplifier in catalytic asymmetric synthesis.[2o]

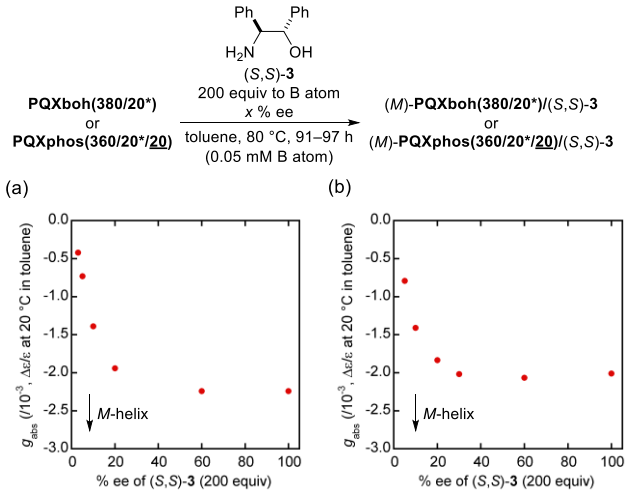
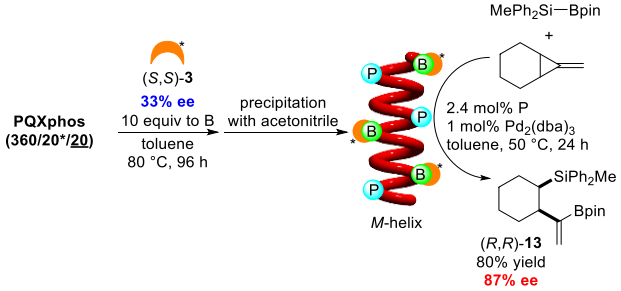


Figure 3. Helical chirality induction of (a) **PQXboh(380/20*)** and (b) **PQXphos(360/20*/20)** with 200 equiv of (*S*,*S*)-**3** with varying optical purity.

Scheme 2. Chiral Amplification on Polyquinoxaline Scaffold toward Pd-Catalyzed Asymmetric Silaboration.



In conclusion, we demonstrated the efficient helical chirality induction of PQXs by introducing boronyl pendants as chiral guest receptor sites. Taking advantage of the long persistence length of the helical PQX scaffold, a pure single-handed structure was induced by condensation with a small amount of chiral amino alcohol. Chiral amplification on the PQX scaffold was achieved by using a chiral guest with low ee, forming a pure single-handed helical structure. The induced helically chiral macromolecular scaffold provided an efficient asymmetric reaction environment in a palladium-catalyzed reaction. Separation of chirality induction sites and catalytically active sites in the macromolecular scaffold enables the rational design of chiral amplification systems.

ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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(8) The screw-sense excess (se) of each sample (**1**, **2**, and **7**–**10**) was estimated using an averaged g_{max} value (± 2.10) calculated from the values for (*S*,*S*)-**3**, (*S*,*R*)-**4**, (*S*,*R*)-**5**, and (*R*)-**6** (Figure 2a).

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