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Chirality induction of π-conjugated chains through chiral complexation

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Abstract—Chirality induction of π-conjugated polyanilines through chiral complexation with the chiral palladium(II) complexes was demonstrated to afford the chiral conjugated polymer complexes. Complexation of the emeraldine base of poly(*o*-toluidine) (POT) with the chiral palladium(II) complex bearing one labile coordination site led to the formation of the chiral conjugated polymer complex, which exhibited an induced circular dichroism (ICD) based on the chirality induction into a π-conjugated backbone. The mirror image of the CD signal was observed with the chiral conjugated polymer complex, which was obtained from the chiral palladium(II) complex possessing the opposite configuration. The chirality of the podand ligand moieties of the palladium complex is considered to induce a propeller twist of the π-conjugated molecular backbone. The crystal structure of the chiral conjugated complex of *N*-bis(4′-dimethylaminophenyl)-1,4-benzoquinonediimine (L^3) as a model compound of the polyaniline revealed a chiral propeller twist conformation of the π-conjugated backbone. Furthermore, chiral complexation with the cationic palladium(II) complexes provided the ionic chiral conjugated complexes.

1. Introduction

π-Conjugated polymers have received extensive interest because of the potential application to electronic materials depending on their electrical properties.[1] Much progress has been made in understanding the chemistry and physics of the π-conjugated polymers. One of the most important π-conjugated polymers, polyaniline, is redox-active and exists in various redox states from leucoemeraldine in a high reduction state to pernigraniline in a high oxidation state. The redox properties have been demonstrated to be controlled by the introduction of an acceptor unit.[2] The structural and chiral control is to be investigated for further functionalization. Chiral polyaniline has been focused on due to their potential applications in molecular recognition and chiral separation.[3] Chiral polyaniline and its derivatives were synthesized only by doping with a chiral acid,[4] polymerization of aniline in the presence of a chiral acid dopant,[5] or template polymerization of aniline in the presence of a chiral molecular template.[6] Another interesting function of polyanilines is coordination properties of two nitrogen atoms of the quinonediimine moiety. In a previous paper, the emeraldine base form of polyanilines, which contains the quinonediimine unit, has been revealed to coordinate to transition metals, affording the conjugated polymer complex systems.[7] The polymer complex can effectively serve as an oxidation catalyst.[7a,b,d] Furthermore, we have already demonstrated that the controlled complexation of polyanilines with palladium(II) compounds by changing the coordination mode is achieved to afford the single-strand or cross-linked network conjugated complexes, in which the quinonediimine moieties serve as bridging coordination sites.[7f] Also, controlled complexation with the redox-active quinonediimine derivative has been achieved to afford the conjugated polymeric complex, the conjugated trimetallic macrocycle, or the conjugated bimetallic complex, depending on the coordination mode.[7g,h,8] The introduction of chiral complexes is considered to be a strategy to induce chirality into a π-conjugated backbone of polyanilines, giving the chiral conjugated complexes.[7h] We herein describe a full scope of chirality induction of polyaniline derivatives through complexation with chiral palladium(II) compounds.

2. Results and discussion

Chiral palladium(II) complexes, ((*S*,*S*)-L^1)Pd(MeCN) ((*S*,*S*)-**1**) and ((*R*,*R*)-L^1)Pd(MeCN) ((*R*,*R*)-**1**), were designed and prepared by the treatment of the *N*-heterocyclic tridentate podand ligands, *N*,*N*′-bis[(*S*)-1-methoxycarbonyl-2-phenylethyl]-2,6-pyridinedicarboxamide ((*S*,*S*)-L^1H_2) and *N*,*N*′-bis[(*R*)-1-methoxycarbonyl-2-phenylethyl]-2,6-pyridinedicarboxamide ((*R*,*R*)-L^1H_2), respectively, with $Pd(OAc)_2$ in acetonitrile as shown in Scheme 1. This similar synthetic method was also used for the synthesis of chiral

Keywords: Polyaniline; Quinonediimine; Palladium complex; Chiral conjugated complex; Chirality induction.
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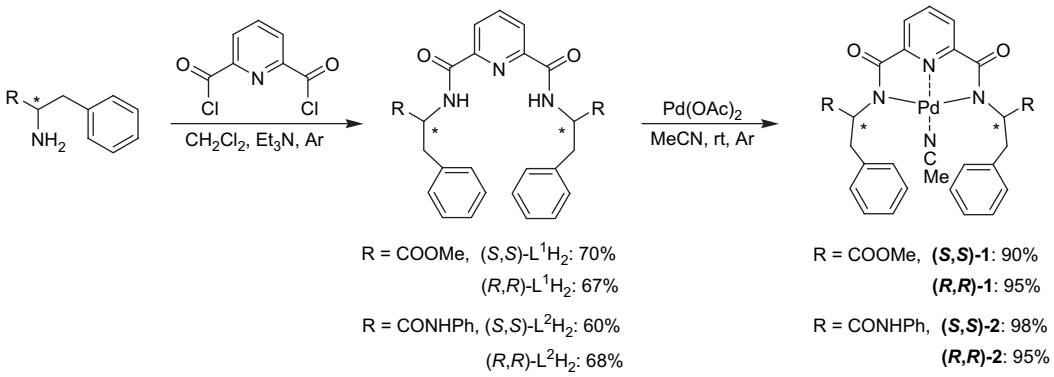


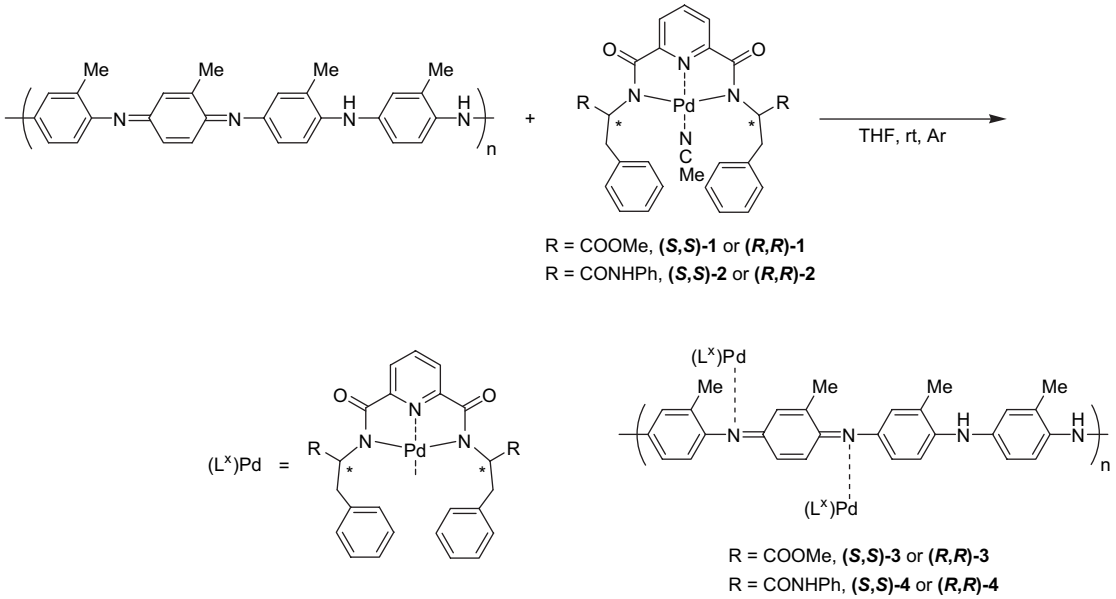
Scheme 1.

palladium complexes, ((*S*,*S*)-L^2)Pd(MeCN) ((*S*,*S*)-**2**) and ((*R*,*R*)-L^2)Pd(MeCN) ((*R*,*R*)-**2**), bearing the amide moieties instead of the ester ones. These palladium(II) complexes have one interchangeable coordination site through exchange of acetonitrile. π-Conjugated polymers with potential metal-coordination sites are expected to coordinate to the palladium center by displacement of this labile ligand.

Treatment of the emeraldine base form of poly(*o*-toluidine) (POT)[7g] with the chiral palladium(II) complex (*S*,*S*)-**1** or (*S*,*S*)-**2** in THF led to the formation of the conjugated polymer complex, POT–((*S*,*S*)-L^1Pd) ((*S*,*S*)-**3**) or POT–((*S*,*S*)-L^2Pd) (*S*,*S*)-**4**, respectively, as shown in Scheme 2. The electronic spectrum of (*S*,*S*)-**3** in THF exhibited broad absorption at around 500–800 nm, which is probably due to a low-energy charge-transfer transition with significant contribution from palladium (Fig. 1). This result indicates the coordination of the quinonediimine nitrogen atoms to the palladium centers. It should be noted that the complex (*S*,*S*)-**3** exhibits an induced circular dichroism (ICD) at around 500–800 nm. Furthermore, the mirror image of the CD signal was observed with (*R*,*R*)-**3**, which was obtained from the complexation of POT with (*R*,*R*)-**1** (Fig. 1). These findings suggest that the chirality induction of a π-conjugated backbone of POT is achieved by the chiral complexation. A similar absorption spectrum was observed in the case of the amide (*S*,*S*)-**4** as shown in Figure 1.

To gain further insight into chirality induction, the chiral complexation with a model unit of polyaniline, *N*,*N*′-bis(4′-dimethylaminophenyl)-1,4-benzoquinonediimine (L^3),[9] was investigated. The complexation of L^3 with 2 molar equiv of (*S*,*S*)-**1** or (*R*,*R*)-**1** afforded the chiral conjugated 1:2 complex, ((*S*,*S*)-L^1)Pd(L^3)Pd((*S*,*S*)-L^1) ((*S*,*S*)-**5**) or ((*R*,*R*)-L^1)Pd(L^3)Pd((*R*,*R*)-L^1) ((*R*,*R*)-**5**), respectively (Scheme 3). The chiral conjugated complexes, ((*S*,*S*)-L^2)Pd(L^3)Pd((*S*,*S*)-L^2) ((*S*,*S*)-**6**) and ((*R*,*R*)-L^2)Pd(L^3)Pd((*R*,*R*)-L^2) ((*R*,*R*)-**6**), were also prepared from (*S*,*S*)-**2** or (*R*,*R*)-**2**, respectively, by the same complexation route. The electronic spectra of (*S*,*S*)-**5** and (*S*,*S*)-**6** in dichloromethane exhibited a broad absorption at around 600–900 nm based on the similar chiral complexation as mentioned above (Fig. 2).

Variable temperature ^{1}H NMR studies of the conjugated complex (*S*,*S*)-**5** indicated interesting molecular dynamics in solution (Fig. 3). The protons of the quinonediimine moiety of the *syn*-isomer at 233 K were observed at 9.14 and 7.14 ppm as singlet peaks, whereas the *anti* isomer



Scheme 2.

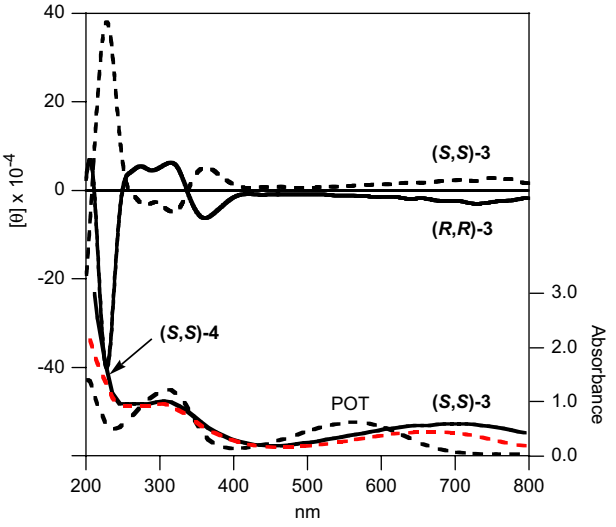


Figure 1. CD spectra (top) of (*S*,*S*)-**3** and (*R*,*R*)-**3** in THF (1.3×10^{-3} M of the monomer unit), and UV–vis spectra (bottom) of (*S*,*S*)-**3**, (*S*,*S*)-**4**, and POT in THF (1.3×10^{-3} M of the monomer unit).

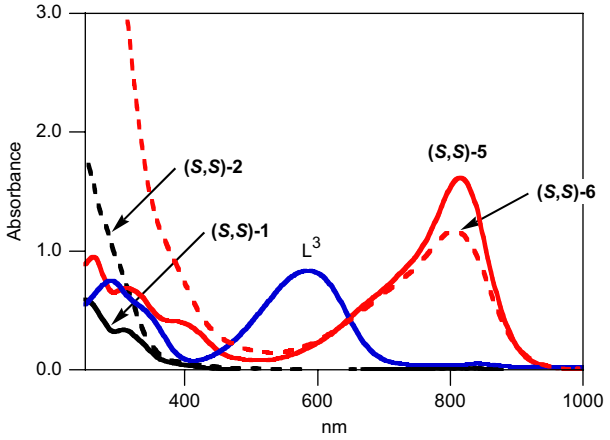
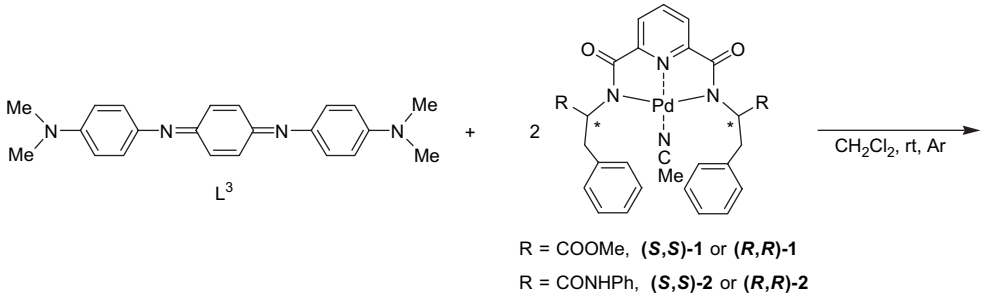


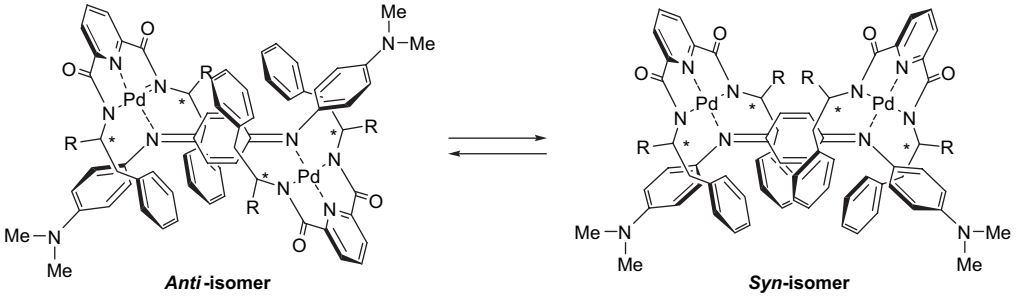
Figure 2. UV–vis spectra of L^3, (*S*,*S*)-**1**, (*S*,*S*)-**2**, (*S*,*S*)-**5**, and (*S*,*S*)-**6** in dichloromethane (5.0×10^{-5} M).

exhibited doublet peaks of those protons at 7.84 and 6.92 ppm. As the temperature was lowered, the peaks of (*S*,*S*)-**5***syn* increased gradually. The equilibrium constant K_{eq} between (*S*,*S*)-**5***syn* and (*S*,*S*)-**5***anti* was calculated from variable temperature ^{1}H NMR spectra shown in Figure 3. The temperature dependence of K_{eq} is used to construct the van't Hoff plot of ln K_{eq} versus T^{-1} (Fig. 4). The *syn* configuration is enthalpically more favorable than the *anti* one in CD_2Cl_2 by 2.3 kcal mol^{-1}, but entropically less favorable by 11.0 cal mol^{-1} K^{-1}.

The mirror image relationship of the CD signals around the CT band of the quinonediimine moiety in dichloromethane was observed between (*S*,*S*)-**5** and (*R*,*R*)-**5** as shown in Figure 5. The ICD at around 600–800 nm appears to be reflected by the chirality of the palladium(II) complexes. Such ICD was not observed in the case of **1**. Similar chiral complexation was also observed in the case of the chiral complexes **6** (Fig. 6). These results indicate the chirality induction into the quinonediimine moiety through the chiral complexation.

Further structural information was obtained by the single-crystal X-ray structure determination. The crystal structure of (*R*,*R*)-**5** indicates that the two (L^1)Pd units are bridged by the quinonediimine moiety of L^3 to form the C_2-symmetrical 2:1 complex (*R*,*R*)-**5***syn* with the Pd–Pd separation 7.59 Å, as depicted in Figure 7. Each phenylene ring of L^3 has an opposite dihedral angle of 47.3° with respect to the quinonediimine plane, resulting in a propeller twist of 75.6° between the planes of the two phenylene rings. Schematic





Scheme 3.

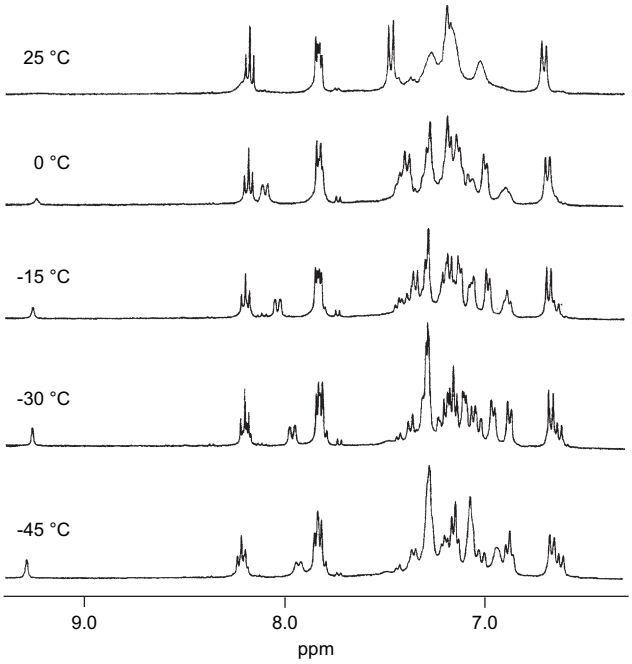


Figure 3. Variable temperature ^{1}H NMR spectrum of (*S*,*S*)-**5** in CD_2Cl_2.

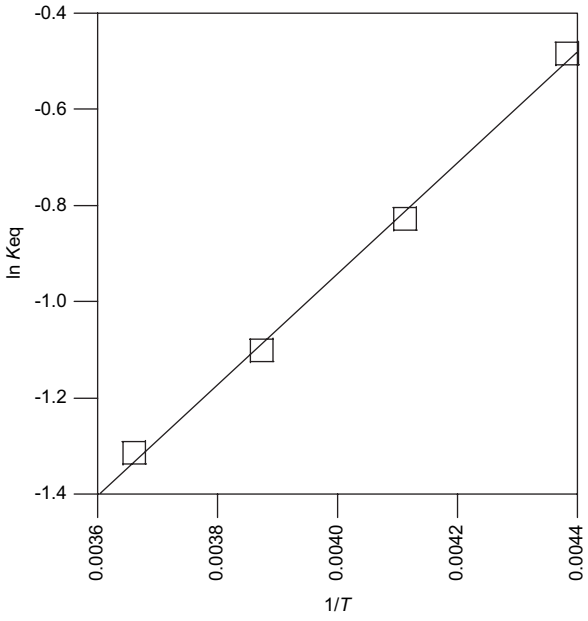


Figure 4. Plot of ln K_{eq} versus T^{-1} for (*S*,*S*)-**5** in CD_2Cl_2.

representation of the crystal structure of (*R*,*R*)-**5***syn* is shown in Figure 8. The chirality of the podand moieties of (L^1)Pd is considered to induce a propeller twist in the π-conjugated chain. Similar complexation behavior is considered to be the case with the polymer complexation. Therefore, the random twist conformation of POT might be transformed into the helical conformation with a predominant screw sense through the chiral complexation. Furthermore, these findings strongly indicate that the chiral structure of quinonediimines is controlled by chiral complexation.

Chirality induction was realized by the complexation of polyanilines and oligoanilines with the chiral palladium

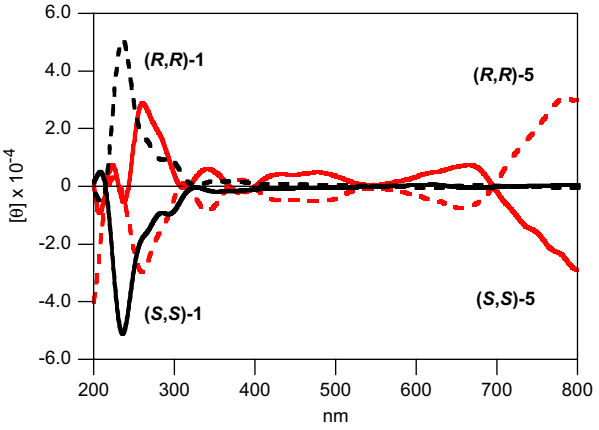


Figure 5. CD spectra of **1** (1.0×10^{-4} M) and **5** (5.0×10^{-5} M) in dichloromethane.

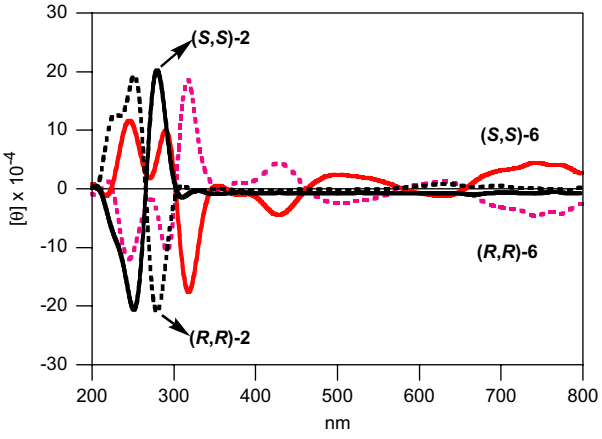


Figure 6. CD spectra of **2** (4.0×10^{-5} M) and **6** (2.0×10^{-5} M) in dichloromethane.

complexes. In order to obtain further insight, the complexation with the cationic palladium complexes **7**[10] possessing weak Pd–N coordination bonds instead of Pd–N covalent bonds in the complexes **1** and **2** was investigated (Fig. 9). The cationic palladium complexes, ((*S*,*S*)-L^4)Pd(MeCN) ((*S*,*S*)-**7**) and ((*R*,*R*)-L^4)Pd(MeCN) ((*R*,*R*)-**7**), were prepared, respectively, by the treatment of the *N*-heterocyclic tridentate podand ligand, 2,6-bis[(*S*)-4′-isopropyloxazolin-2′-yl]-pyridine ((*S*,*S*)-L^4H_2) and 2,6-bis[(*R*)-4′-isopropyloxazolin-2′yl]pyridine ((*R*,*R*)-L^4H_2), with $Pd(MeCN)_4(BF_4)_2$ in acetonitrile (Scheme 4).

The complexation of L^3 with 2 molar equiv of (*S*,*S*)-**7** or (*R*,*R*)-**7** led to the formation of the chiral conjugated 1:2 complex, ((*S*,*S*)-L^4)Pd(L^3)Pd((*S*,*S*)-L^4) ((*S*,*S*)-**8**) or ((*R*,*R*)-L^4)Pd(L^3)Pd((*R*,*R*)-L^4) ((*R*,*R*)-**8**), respectively, as shown in Scheme 5. The complexes **8** are more stable in the coordination solvent, acetonitrile. In the ^{1}H NMR spectrum of the conjugated complex (*S*,*S*)-**8**, two sets of peaks based on *syn* and *anti* isomers were observed at 298 K in CD_3CN. The electronic spectra of **8** in acetonitrile exhibited a broad absorption at around 600–900 nm (Fig. 10), probably due to the chiral complexation of the quinonediimine moiety as observed in the conjugated complexes **5** and **6**.

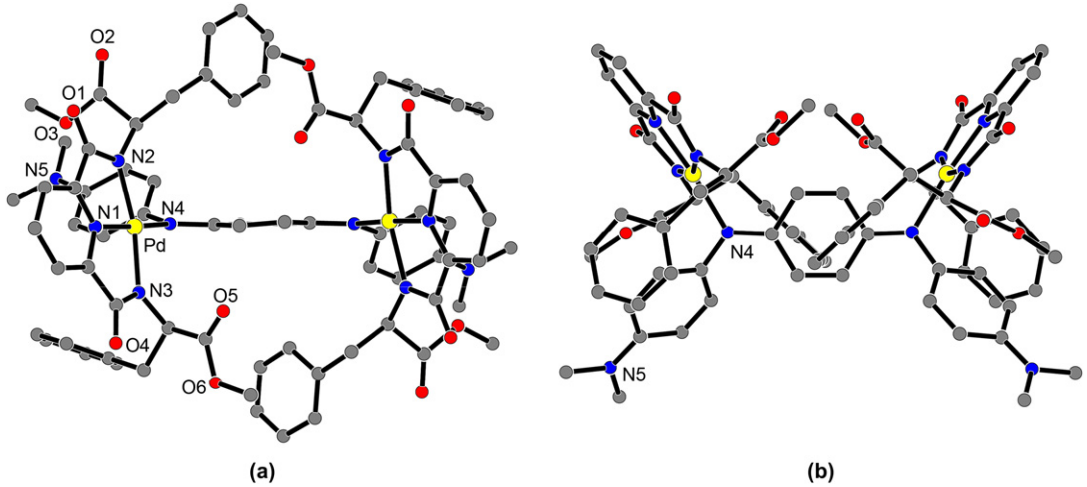


Figure 7. (a) Top view and (b) side view of the X-ray crystal structure of (*R*,*R*)-**5***syn* (hydrogen atoms are omitted for clarity).

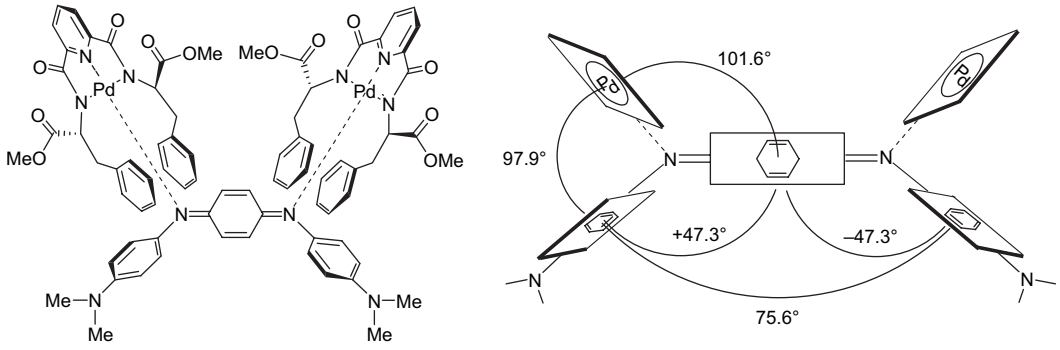


Figure 8. Schematic representation of (*R*,*R*)-**5***syn*.

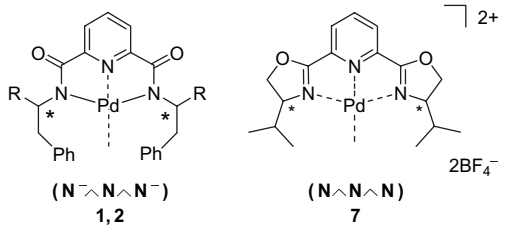
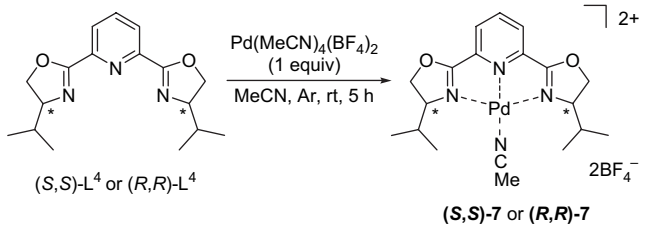


Figure 9. Structure of palladium(II) complexes **1**, **2**, and cationic palladium(II) complex **7**.

The CD spectra of (*S*,*S*)-**8** and (*R*,*R*)-**8** exhibited ICD at around 600–800 nm based on the CT band of the quinonediimine moiety, and these are in a good mirror image relationship (Fig. 11). Such ICD was not observed in the case of **7**. These findings indicate the similar complexation behavior as observed with the chiral conjugated complexes **5** and **6**.



Scheme 4.

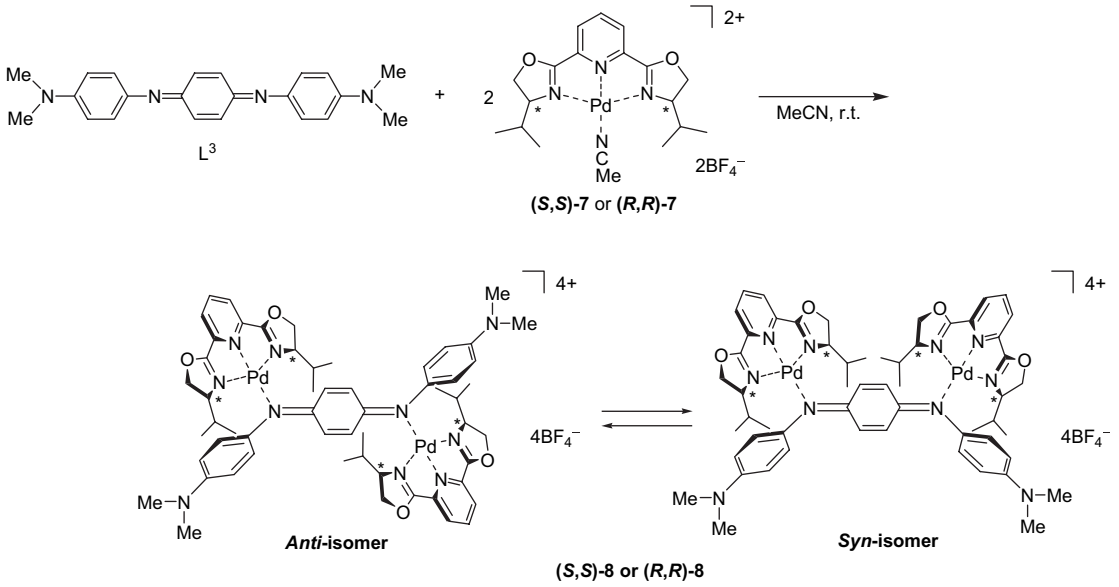
3. Conclusion

Chirality induction of a π-conjugated backbone of the emeraldine base of poly(*o*-toluidine) and the quinonediimine derivative through chiral complexation with the chiral palladium(II) complexes bearing one interchangeable coordination site was achieved to afford the chiral conjugated complexes. The crystal structure of the chiral conjugated complex **5** with the quinonediimine derivative revealed a chiral propeller twist conformation of the π-conjugated moiety. The chirality of the podand ligand is considered to regulate a propeller twist of the π-conjugated backbone. Our strategy for chirality induction through chiral complexation provides an efficient and feasible route to chiral d,π-conjugated complexes, in which the introduced metals are envisioned to play an important role as a metallic dopant and interact with each other through π-conjugation. These chiral conjugated complexes are considered to be potent as promising functionalized materials and asymmetric redox catalysts.

4. Experimental

4.1. General comments

All reagents and solvents were purchased from commercial sources and were further purified with the standard methods,



Scheme 5.

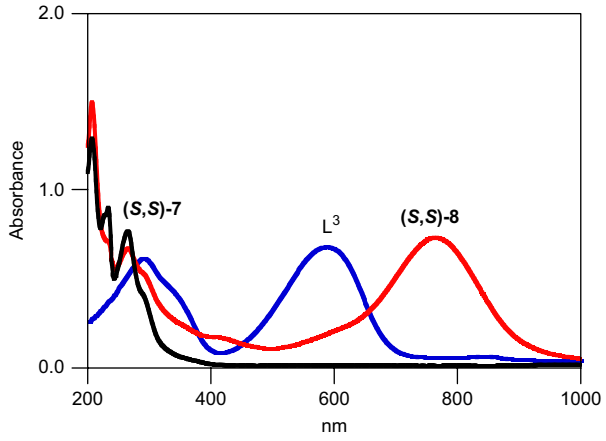


Figure 10. UV–vis spectra of L^3 (4.0×10^{-5} M), (*S*,*S*)-**7** (4.0×10^{-5} M), and (*S*,*S*)-**8** (4.0×10^{-5} M) in MeCN.

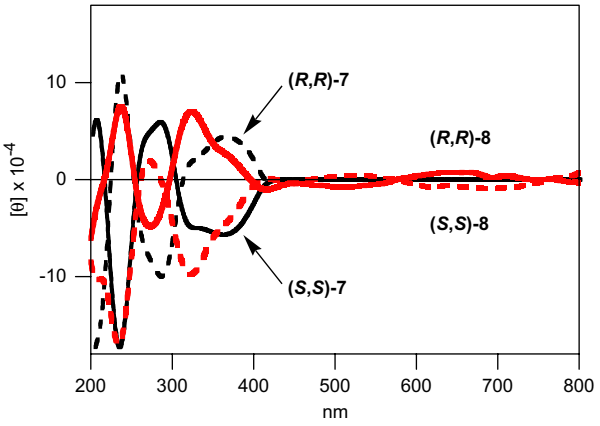


Figure 11. CD spectra of **7** (8.0×10^{-5} M) and **8** (4.0×10^{-5} M) in MeCN.

if necessary. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were obtained with a JASCO FT/IR-480plus. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-400 spectrometer (400 and 100 MHz, respectively). Mass spectra were run on a JEOL JMS-700 mass spectrometer. Electronic spectra were obtained by using a Hitachi U-3500 spectrophotometer. CD spectra were recorded using JASCO J-720 and J-725 spectropolarimeters.

4.2. Synthesis of poly(*o*-toluidine)

Poly(*o*-toluidine) was prepared according to our previous procedure.[7g] The molecular weight of poly(*o*-toluidine) was estimated to be 4191 as determined by gel permeation chromatography (GPC) (polystyrene standard with THF as an eluent). Elemental analysis ($C_{7.00}H_{6.75}N_{1.00}$) indicated the emeraldine base structure consisting of the amine and imine moieties at ca. 1:1 ratio.

4.3. Synthesis of 1

To a stirred mixture of phenylalanine methyl ester hydrochloride (129.4 mg, 0.6 mmol) and triethylamine (0.21 mL, 1.5 mmol) was added drop-wise 2,6-pyridyldicarbonyl dichloride (61.2 mg, 0.3 mmol) in dichloromethane (8 mL) under argon at 0 °C for 7 h and then at room temperature for 18 h. The resulting mixture was diluted with dichloromethane, washed with saturated $NaHCO_3$ aqueous solution and brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo. The chiral ligands, *N*,*N*′-bis[(*S*)-1-methoxycarbonyl-2-phenylethyl]-2,6-pyridinedicarboxamide ((*S*,*S*)-L^1H_2) and *N*,*N*′-bis[(*R*)-1-methoxycarbonyl-2-phenylethyl]-2,6-pyridinedicarboxamide ((*R*,*R*)-L^1H_2), were isolated by recrystallization from acetonitrile.

4.3.1. (*S*,*S*)-L^1H_2. Yield 70%; mp 124–126 °C (uncorrected); IR (KBr, cm^{-1}): 3335, 1754, 1679, 1656, 1548, 1516; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.36 (d, 2H, J=8.4 Hz, H_{NH}), 8.19 (d, 2H, J=7.6 Hz, H_{py}), 8.03 (t, 1H, J=7.6 Hz, H_{py}), 7.29–7.18 (m, 10H, H_{ph}), 4.95–4.89 (m,

2H, H_{ethyl}), 3.72 (s, 6H, H_{OMe}), 3.34 (dd, 2H, J=14.0, 5.6 Hz, H_{ethyl}), 3.19 (dd, 2H, J=14.0, 8.8 Hz, H_{ethyl}); MS (EI): m/z=489 (M^+). Anal. Calcd for $C_{27}H_{27}N_3O_6$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.37; H, 5.41; N, 8.55.

4.3.2. (*R*,*R*)-L^{1}H$_2$. Yield 67%; mp 124–126 °C (uncorrected); IR (KBr, cm^{-1}): 3335, 1754, 1679, 1656, 1548, 1516; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.36 (d, 2H, J=8.4 Hz, H_{NH}), 8.19 (d, 2H, J=7.6 Hz, H_{py}), 8.03 (t, 1H, J=7.6 Hz, H_{py}), 7.29–7.18 (m, 10H, H_{ph}), 4.95–4.89 (m, 2H, H_{ethyl}), 3.72 (s, 6H, H_{OMe}), 3.34 (dd, 2H, J=14.0, 5.6 Hz, H_{ethyl}), 3.19 (dd, 2H, J=14.0, 8.8 Hz, H_{ethyl}); MS (EI): m/z=489 (M^+). Anal. Calcd for $C_{27}H_{27}N_3O_6$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.42; H, 5.29; N, 8.43.

A mixture of (*S*,*S*)-L^{1}H$_2$ or (*R*,*R*)-L^{1}H$_2$ (24.5 mg, 0.05 mmol) and $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) in acetonitrile (5.0 mL) was stirred under argon at room temperature for 2 h. After evaporation of the solvent, the palladium complex (*S*,*S*)-**1** or (*R*,*R*)-**1** was isolated as yellow crystal by recrystallization from benzene and hexane.

4.3.3. (*S*,*S*)-1. Yield 90%; mp 200–201 °C (decomp.); IR (KBr, cm^{-1}): 1730, 1594; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.07 (t, 1H, J=8.0 Hz, H_{py}), 7.53 (d, 2H, J=8.0 Hz, H_{py}), 7.34 (d, 4H, J=8.1 Hz, H_{ph}), 7.26 (dd, 4H, J=8.1, 7.5 Hz, H_{ph}), 7.16 (t, 2H, J=7.5 Hz, H_{ph}), 4.70 (dd, 2H, J=10.0, 4.2 Hz, H_{ethyl}), 3.69 (s, 6H, H_{OMe}), 3.27 (dd, 2H, J=13.6, 4.2 Hz, H_{ethyl}), 2.85 (dd, 2H, J=13.6, 10.0 Hz, H_{ethyl}); MS (FAB): m/z=594 ((M−MeCN)$^+$+1). Anal. Calcd for $C_{29}H_{28}N_4O_6Pd$: C, 54.85; H, 4.44; N, 8.82. Found: C, 54.85; H, 4.21; N, 8.60.

4.3.4. (*R*,*R*)-1. Yield 95%; mp 200–201 °C (decomp.); IR (KBr, cm^{-1}): 1730, 1594; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.07 (t, 1H, J=8.0 Hz, H_{py}), 7.53 (d, 2H, J=8.0 Hz, H_{py}), 7.34 (d, 4H, J=8.1 Hz, H_{ph}), 7.26 (dd, 4H, J=8.1, 7.5 Hz, H_{ph}), 7.16 (t, 2H, J=7.5 Hz, H_{ph}), 4.70 (dd, 2H, J=10.0, 4.2 Hz, H_{ethyl}), 3.69 (s, 6H, H_{OMe}), 3.27 (dd, 2H, J=13.6, 4.2 Hz, H_{ethyl}), 2.85 (dd, 2H, J=13.6, 10.0 Hz, H_{ethyl}); MS (FAB): m/z=594 ((M−MeCN)$^+$+1). Anal. Calcd for $C_{29}H_{28}N_4O_6Pd$: C, 54.85; H, 4.44; N, 8.82. Found: C, 54.79; H, 4.11; N, 8.56.

4.4. Synthesis of 2

To a stirred mixture of phenylalanine–phenylamide hydrochloride (144.2 mg, 0.6 mmol) and triethylamine (0.42 mL, 1.5 mmol) was added drop-wise 2,6-pyridyldicarbonyl dichloride (61.2 mg, 0.3 mmol) in dichloromethane (8 mL) under argon at 0 °C for 7 h and then at room temperature for 18 h. The resulting mixture was diluted with dichloromethane, washed with saturated $NaHCO_3$ aqueous solution and brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo. The chiral ligands, *N*,*N*′bis[(*S*)-1-phenylcarbamoyl-2-phenylethyl]-2,6-pyridinedicarboxamide ((*S*,*S*)-L^{2}H$_2$) and *N*,*N*′-bis[(*R*)-1-phenylcarbamoyl-2-phenylethyl]-2,6-pyridinedicarboxamide ((*R*,*R*)-L^{2}H$_2$), were isolated by recrystallization from acetonitrile.

4.4.1. (*S*,*S*)-L^{2}H$_2$. Yield 60%; mp 250–252 °C (uncorrected); IR (KBr, cm^{-1}): 3292, 1695, 1675, 1646, 1599, 1559, 1539; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.55 (d, 2H, J=7.7 Hz, H_{NH}), 8.32 (d, 2H, J=7.7 Hz, H_{py}), 8.01 (t, 1H, J=7.7 Hz, H_{py}), 7.89 (br s, 2H, H_{NH}), 7.42 (d, 4H, J=8.0 Hz, H_{ph}), 7.35–7.26 (m, 12H, ph), 7.23 (t, 2H, J=7.3 Hz, H_{ph}), 7.10 (t, 2H, J=7.7 Hz, H_{ph}), 4.96 (dd, 2H, J=7.7, 7.5 Hz, H_{ethyl}), 3.40–3.31 (m, 4H, H_{ethyl}); MS (EI): m/z=611 (M^+). Anal. Calcd for $C_{37}H_{33}N_5O_4$: C, 72.65; H, 5.44; N, 11.45. Found: C, 72.37; H, 5.41; N, 11.35.

4.4.2. (*R*,*R*)-L^{2}H$_2$. Yield 68%; mp 250–252 °C (uncorrected); IR (KBr, cm^{-1}): 3292, 1695, 1675, 1646, 1599, 1559, 1539; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.55 (d, 2H, J=7.7 Hz, H_{NH}), 8.32 (d, 2H, J=7.7 Hz, H_{py}), 8.01 (t, 1H, J=7.7 Hz, H_{py}), 7.89 (br s, 2H, H_{NH}), 7.42 (d, 4H, J=8.0 Hz, H_{ph}), 7.35–7.26 (m, 12H, ph), 7.23 (t, 2H, J=7.3 Hz, H_{ph}), 7.10 (t, 2H, J=7.7 Hz, H_{ph}), 4.96 (dd, 2H, J=7.7, 7.5 Hz, H_{ethyl}), 3.40–3.31 (m, 4H, H_{ethyl}); MS (EI): m/z=611 (M^+). Anal. Calcd for $C_{37}H_{33}N_5O_4$: C, 72.65; H, 5.44; N, 11.45. Found: C, 72.26; H, 5.51; N, 11.34.

A mixture of (*S*,*S*)-L^{2}H$_2$ or (*R*,*R*)-L^{2}H$_2$ (30.6 mg, 0.05 mmol) and $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) in acetonitrile (5.0 mL) was stirred under argon at room temperature for 2 h. After evaporation of the solvent, the palladium complex (*S*,*S*)-**2** or (*R*,*R*)-**2** was isolated as yellow crystal by recrystallization from benzene and hexane.

4.4.3. (*S*,*S*)-2. Yield 98%; mp 202–203 °C (decomp.); IR (KBr, cm^{-1}): 3280, 1596, 1495; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 9.07 (s, 2H, H_{NH}), 7.73 (dd, 4H, J=7.7, 1.0 Hz, H_{ph}), 7.53 (t, 1H, J=7.7 Hz, H_{py}), 7.36–7.30 (m, 8H, H_{ph} and H_{ph}), 7.23 (d, 2H, J=7.7 Hz, H_{py}), 7.10 (t, 6H, J=7.3 Hz, H_{ph} and H_{ph}), 7.02 (t, 2H, J=7.3 Hz, H_{ph}), 5.18 (dd, 2H, J=9.9, 4.4 Hz, H_{ethyl}), 3.42 (dd, 2H, J=14.1, 4.4 Hz, H_{ethyl}), 2.68 (dd, 2H, J=14.1, 9.9 Hz, H_{ethyl}); MS (FAB): m/z=716 ((M−MeCN)$^+$+1). Anal. Calcd for $C_{39}H_{34}N_6O_4Pd$: C, 61.87; H, 4.53; N, 11.10. Found: C, 61.77; H, 4.52; N, 11.09.

4.4.4. (*R*,*R*)-2. Yield 95%; mp 202–203 °C (decomp.); IR (KBr, cm^{-1}): 3280, 1596, 1495; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 9.07 (s, 2H, H_{NH}), 7.73 (dd, 4H, J=7.7, 1.0 Hz, H_{ph}), 7.53 (t, 1H, J=7.7 Hz, H_{py}), 7.36–7.30 (m, 8H, H_{ph} and H_{ph}), 7.23 (d, 2H, J=7.7 Hz, H_{py}), 7.10 (t, 6H, J=7.3 Hz, H_{ph} and H_{ph}), 7.02 (t, 2H, J=7.3 Hz, H_{ph}), 5.18 (dd, 2H, J=9.9, 4.4 Hz, H_{ethyl}), 3.42 (dd, 2H, J=14.1, 4.4 Hz, H_{ethyl}), 2.68 (dd, 2H, J=14.1, 9.9 Hz, H_{ethyl}); MS (FAB): m/z=716 ((M−MeCN)$^+$+1). Anal. Calcd for $C_{39}H_{34}N_6O_4Pd$: C, 61.87; H, 4.53; N, 11.10. Found: C, 61.80; H, 4.50; N, 10.88.

4.5. Synthesis of 3

To POT (2.73 mg, 26 mmol) in THF solution (20 mL) was added **1** (0.5 molar equiv to the monomer unit of POT, 8.25 mg, 13 mmol) in THF solution. The mixture was stirred at room temperature for 30 min and filtered through a membrane under argon. The electronic and CD spectra of the filtrate **3** in THF were measured. The electronic and CD spectra were measured in a 0.10 cm quartz cell at room temperature with 1.3×10^{-3} M concentration of the monomer unit of POT under argon.

4.6. Synthesis of 4

To POT (2.73 mg, 26 mmol) in THF solution (20 mL) was added **2** (0.5 molar equiv to the monomer unit of POT, 9.84 mg, 13 mmol) in THF solution. The mixture was stirred at room temperature for 30 min and filtered through a membrane under argon. The electronic spectrum of the filtrate **4** in THF was measured. The electronic spectrum was measured in a 0.10 cm quartz cell at room temperature with 1.3×10^{-3} M concentration of the monomer unit of POT under argon.

4.7. Synthesis of 5

N,*N*′-Bis(4′-dimethylaminophenyl)-1,4-benzoquinonediimine (L^3) was prepared according to the literature procedure.[9] A mixture of L^3 (13.8 mg, 0.04 mmol) and (*S*,*S*)-**1** or (*R*,*R*)-**1** (50.8 mg, 0.08 mmol) was stirred in dichloromethane (10 mL) under argon at room temperature for 4 h. After evaporation of the solution, the chiral complex (*S*,*S*)-**5** or (*R*,*R*)-**5** was isolated by recrystallization from chloroform and ethyl ether.

4.7.1. (*S*,*S*)-5. Yield 90%; mp 180–181 °C (decomp.); IR (KBr, cm^{-1}): 1731, 1591, 1362, 1162; ^1H NMR (600 MHz, CD_2Cl_2, 233 K, *syn*:*anti*=1:2): δ 9.14 (s, 2H, phenylene$_{syn}$), 8.09 (t, 2H, J=7.2 Hz, py$_{anti}$), 8.08 (t, 2H, J=7.2 Hz), 7.84 (d, 2H, J=9.6 Hz, phenylene$_{anti}$), 7.73–7.69 (m, 8H, py$_{syn}$ and py$_{anti}$), 7.26 (d, 4H, J=9.3 Hz, ph$_{syn}$), 7.18 (d, 4H, J=9.3 Hz, ph$_{anti}$), 7.14 (s, 2H, phenylene$_{syn}$), 7.11–6.95 (m, 24H, ph$_{syn}$ and ph$_{anti}$), 6.92 (d, 2H, J=9.6 Hz, phenylene$_{anti}$), 6.86–6.83 (m, 8H, ph$_{syn}$), 6.78–6.76 (m, 8H, ph$_{anti}$), 6.56 (d, 4H, J=9.3 Hz, ph$_{anti}$), 6.52 (d, 4H, J=9.3 Hz, ph$_{syn}$), 3.52–3.48 (m, 2H, ethylene$_{syn}$), 3.40 (s, 6H, OMe), 3.38 (s, 6H, OMe), 3.33 (s, 6H, OMe), 3.32 (s, 6H, OMe), 3.24–3.20 (m, 4H, ethylene$_{anti}$), 3.15–3.13 (m, 2H, ethylene$_{syn}$), 3.12 (br s, 24H, CH$_{3(amine)}$), 3.05–3.00 (m, 4H, ethylene$_{anti}$), 2.94–2.87 (m, 8H, ethylene$_{syn}$, ethylene$_{syn}$ and ethylene$_{anti}$), 2.71–2.69 (m, 2H, ethylene$_{syn}$), 2.38–2.36 (m, 2H, ethylene$_{syn}$); MS (FAB): m/z=1532 (M^+). Anal. Calcd for $C_{76}H_{74}N_{10}O_{12}Pd_2\cdot0.5CHCl_3$: C, 57.72; H, 4.72; N, 8.80. Found: C, 57.86; H, 4.67; N, 9.11.

4.7.2. (*R*,*R*)-5. Yield 95%; mp 180–181 °C (decomp.); IR (KBr, cm^{-1}): 1731, 1591, 1362, 1162; ^1H NMR (600 MHz, CD_2Cl_2, 233 K, *syn*:*anti*=1:2): δ 9.14 (s, 2H, phenylene$_{syn}$), 8.09 (t, 2H, J=7.2 Hz, py$_{anti}$), 8.08 (t, 2H, J=7.2 Hz), 7.84 (d, 2H, J=9.6 Hz, phenylene$_{anti}$), 7.73–7.69 (m, 8H, py$_{syn}$ and py$_{anti}$), 7.26 (d, 4H, J=9.3 Hz, ph$_{syn}$), 7.18 (d, 4H, J=9.3 Hz, ph$_{anti}$), 7.14 (s, 2H, phenylene$_{syn}$), 7.11–6.95 (m, 24H, ph$_{syn}$ and ph$_{anti}$), 6.92 (d, 2H, J=9.6 Hz, phenylene$_{anti}$), 6.86–6.83 (m, 8H, ph$_{syn}$), 6.78–6.76 (m, 8H, ph$_{anti}$), 6.56 (d, 4H, J=9.3 Hz, ph$_{anti}$), 6.52 (d, 4H, J=9.3 Hz, ph$_{syn}$), 3.52–3.48 (m, 2H, ethylene$_{syn}$), 3.40 (s, 6H, OMe), 3.38 (s, 6H, OMe), 3.33 (s, 6H, OMe), 3.32 (s, 6H, OMe), 3.24–3.20 (m, 4H, ethylene$_{anti}$), 3.15–3.13 (m, 2H, ethylene$_{syn}$), 3.12 (br s, 24H, CH$_{3(amine)}$), 3.05–3.00 (m, 4H, ethylene$_{anti}$), 2.94–2.87 (m, 8H, ethylene$_{syn}$, ethylene$_{syn}$, and ethylene$_{anti}$), 2.71–2.69 (m, 2H ethylene$_{syn}$), 2.38–2.36 (m, 2H, ethylene$_{syn}$); MS (FAB): m/z=1532 (M^+). Anal. Calcd for $C_{76}H_{74}N_{10}O_{12}Pd_2\cdot0.5CHCl_3$: C, 57.72; H, 4.72; N, 8.80. Found: C, 57.62; H, 4.75; N, 8.95.

4.8. Equilibrium measurement of 5

Measurement of the equilibrium constants at various temperatures was carried out by the integration of the appropriate peaks during ^1H NMR spectroscopy. Spectra were taken in CD_2Cl_2 from 228 to 298 K. The thermodynamic parameters were determined from the van't Hoff plot of $\ln K_{eq}$ versus T^{-1}.

4.9. X-ray structure analysis of (*R*,*R*)-5*syn*

All measurements for (*R*,*R*)-**5** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The structure of (*R*,*R*)-**5** was solved by heavy-atom Patterson Methods and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 6478 observed reflections ($I>2\sigma(I)$) and 451 variable parameters.

4.9.1. Crystal data for (*R*,*R*)-5*syn*. $C_{76}H_{74}O_{12}N_{10}Pd_2$, Fw=1532.28, monoclinic, space group $C2$ (#5), a=33.1760(1), b=15.3324(4), c=18.1523 Å, β=155.9623(8)°, V=3761.1(1) Å^3, Z=2, T=4.0 °C, D_{calcd}=1.353 g cm^{-3}, μ (Mo Kα)=5.44 cm^{-1}, Mo Kα radiation (λ=0.71069 Å), $R1$=0.066, $wR2$=0.177. Crystallographic data (excluding structure factors) for the structure reported in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 223573. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk].

4.10. Synthesis of 6

A mixture of L^3 (13.8 mg, 0.04 mmol) and (*S*,*S*)-**2** or (*R*,*R*)-**2** (60.4 mg, 0.08 mmol) was stirred in acetonitrile (10 mL) under argon at room temperature for 4 h. After evaporation of the solution, the chiral complex (*S*,*S*)-**6** or (*R*,*R*)-**6** was isolated by recrystallization from chloroform and ethyl ether.

4.10.1. (*S*,*S*)-6. Yield 85%; mp 207–208 °C (decomp.); IR (KBr, cm^{-1}): 3387, 1677, 1594, 1518; ^1H NMR (400 MHz, CD_2Cl_2, 273 K, *syn*:*anti*=1.6:1): δ 10.01 (s, 4H, NH$_{anti}$), 9.77 (s, 4H, NH$_{syn}$), 8.32 (s, 2H, phenylene$_{syn}$), 8.14 (t, 4H, J=7.7 Hz, py$_{syn}$ and py$_{anti}$), 8.00 (d, 1H, J=9.5 Hz, phenylene$_{anti}$), 7.87 (d, 4H, J=7.7 Hz, py$_{anti}$), 7.79 (d, 4H, J=7.7 Hz, py$_{syn}$), 7.71 (d, 1H, J=9.5 Hz, phenylene$_{anti}$), 7.45 (d, 4H, J=7.9 Hz, NHph$_{anti}$), 7.39 (d, 4H, J=7.9 Hz, NHph$_{syn}$), 7.29–7.15 (m, 26H, NHph$_{anti}$, NHph$_{syn}$ and ph$_{anti}$), 7.08–6.95 (m, 44H, ethylene-ph$_{anti}$, ethylene-ph$_{syn}$, and ph$_{syn}$), 6.84 (d, 1H, J=9.5 Hz, phenylene$_{anti}$), 6.79 (d, 1H, J=9.5 Hz, phenylene$_{anti}$), 6.72 (s, 2H, phenylene$_{syn}$), 6.57 (d, 4H, J=8.4 Hz, ph$_{anti}$), 6.44 (d, 4H, J=8.4 Hz, ph$_{syn}$), 3.76–3.20 (m, 24H, ethylene), 3.09 (s, 6H, Me$_{anti}$), 3.05 (s, 6H, Me$_{anti}$), 2.80 (s, 6H, Me$_{syn}$), 2.76 (s, 6H, Me$_{syn}$); MS (FAB): m/z=1777 (M^++1). Anal. Calcd for $C_{96}H_{86}N_{14}O_8Pd_2\cdot0.5CHCl_3$: C, 64.32; H, 4.89; N, 10.88. Found: C, 64.12; H, 4.67; N, 10.92.

4.10.2. (*R*,*R*)-6. Yield 87%; mp 207–208 °C (decomp.); IR (KBr, cm^{-1}): 3387, 1677, 1594, 1518; ^1H NMR

(400 MHz, CD_2Cl_2, 273 K, *syn*:*anti*=1.6:1): δ 10.01 (s, 4H, NH_{anti}), 9.77 (s, 4H, NH_{syn}), 8.32 (s, 2H, $phenylene_{syn}$), 8.14 (t, 4H, J=7.7 Hz, py_{syn} and py_{anti}), 8.00 (d, 1H, J=9.5 Hz, $phenylene_{anti}$), 7.87 (d, 4H, J=7.7 Hz, py_{anti}), 7.79 (d, 4H, J=7.7 Hz, py_{syn}), 7.71 (d, 1H, J=9.5 Hz, $phenylene_{anti}$), 7.45 (d, 4H, J=7.9 Hz, $NHph_{anti}$), 7.39 (d, 4H, J=7.9 Hz, $NHph_{syn}$), 7.29–7.15 (m, 26H, $NHph_{anti}$, $NHph_{syn}$, and ph_{anti}), 7.08–6.95 (m, 44H, ethylene-ph_{anti}, ethylene-ph_{syn}, and ph_{syn}), 6.84 (d, 1H, J=9.5 Hz, $phenylene_{anti}$), 6.79 (d, 1H, J=9.5 Hz, $phenylene_{anti}$), 6.72 (s, 2H, $phenylene_{syn}$), 6.57 (d, 4H, J=8.4 Hz, ph_{anti}), 6.44 (d, 4H, J=8.4 Hz, ph_{syn}), 3.76–3.20 (m, 24H, ethylene), 3.09 (s, 6H, Me_{anti}), 3.05 (s, 6H, Me_{anti}), 2.80 (s, 6H, Me_{syn}), 2.76 (s, 6H, Me_{syn}); MS (FAB): m/z=1777 (M^++1). Anal. Calcd for $C_{96}H_{86}N_{14}O_8Pd_2\cdot 0.5CHCl_3$: C, 64.32; H, 4.89; N, 10.88. Found: C, 64.03; H, 4.75; N, 10.95.

4.11. Synthesis of 7

A mixture of 2,6-bis[(*S*)-4′-isopropyloxazolin-2′-yl]pyridine ((*S*,*S*)-L^4H_2) or 2,6-bis[(*R*)-4′-isopropyloxazolin-2′-yl]pyridine ((*R*,*R*)-L^4H_2) (45.2 mg, 0.15 mmol) and $Pd(MeCN)_4(BF_4)_2$ (66.6 mg, 0.15 mmol) in acetonitrile (5.0 mL) was stirred under argon at room temperature for 5 h. After evaporation of the solution, the palladium complex ((*S*,*S*)-L^4)$Pd(MeCN)(BF_4)_2$ ((*S*,*S*)-**7**) or ((*R*,*R*)-L^4)$Pd(MeCN)(BF_4)_2$ ((*R*,*R*)-**7**) was isolated as pale-yellow crystal by recrystallization from acetonitrile and ethyl ether.

4.11.1. (*S*,*S*)-7. Yield 98%; mp 204–206 °C (decomp.); IR (KBr, cm^{-1}): 2964, 1641, 1608, 1578; ^1H NMR (400 MHz, CD_3CN): δ 8.56 (t, 1H, J=8.04 Hz, H_{py}), 8.08 (d, 2H, J=8.04 Hz, H_{py}), 5.05–4.94 (m, 4H, H_{ox}), 4.44–4.39 (m, 2H, H_{ox}), 2.12–2.07 (m, 2H, H_{ox}), 1.95 (s, 3H, H_{NH}), 0.98 (d, 6H, J=6.6 Hz, H_{Me}), 0.97 (d, 6H, J=6.6 Hz, H_{Me}). Anal. Calcd for $C_{19}H_{26}N_4O_2Pd(BF_4)_2$: C, 36.66; H, 4.21; N, 9.00. Found: C, 36.49; H, 4.19; N, 9.01.

4.11.2. (*R*,*R*)-7. Yield 95%; mp 204–206 °C (decomp.); IR (KBr, cm^{-1}): 2964, 1641, 1608, 1578; ^1H NMR (400 MHz, CD_3CN): δ 8.56 (t, 1H, J=8.04 Hz, H_{py}), 8.08 (d, 2H, J=8.04 Hz, H_{py}), 5.05–4.94 (m, 4H, H_{ox}), 4.44–4.39 (m, 2H, H_{ox}), 2.12–2.07 (m, 2H, H_{ox}), 1.95 (s, 3H, H_{NH}), 0.98 (d, 6H, J=6.6 Hz, H_{Me}), 0.97 (d, 6H, J=6.6 Hz, H_{Me}). Anal. Calcd for $C_{19}H_{26}N_4O_2Pd(BF_4)_2$: C, 36.66; H, 4.21; N, 9.00. Found: C, 36.77; H, 4.28; N, 8.82.

4.12. Synthesis of 8

A mixture of L^3 (17.2 mg, 0.05 mmol) and (*S*,*S*)-**7** or (*R*,*R*)-**7** (62.3 mg, 0.10 mmol) was stirred in acetonitrile (5 mL) under argon at room temperature for 5 h. After evaporation of the solution, the chiral complex (*S*,*S*)-**8** or (*R*,*R*)-**8** was isolated by recrystallization from acetonitrile and diethyl ether.

4.12.1. (*S*,*S*)-8. Yield 80%; mp 198–199 °C (decomp.); IR (KBr, cm^{-1}): 2961, 1591, 1502; ^1H NMR (400 MHz, CD_3CN, 233 K, *syn*:*anti*=1:2.2): δ 8.63 (s, 2H, $phenylene_{syn}$), 8.542 (t, 2H, J=8.0 Hz, py_{anti}), 8.538 (t, 2H, J=8.0 Hz, py_{syn}), 8.46 (d, 2H, J=8.7 Hz, $phenylene_{anti}$), 8.12 (d, 4H, J=8.0 Hz, py_{anti}), 8.11 (d, 4H, J=8.0 Hz, py_{syn}), 7.90 (d, 8H, J=8.6 Hz, ph_{syn} and ph_{anti}), 7.43 (d, 2H, J=8.7 Hz, $phenylene_{anti}$), 7.24 (s, 2H, $phenylene_{syn}$), 6.94 (d, 8H, J=8.6 Hz, ph_{syn} and ph_{anti}), 4.87–4.79 (m, 16H, Ox_{syn} and Ox_{anti}), 3.95–3.88 (m, 2H, Ox_{syn}), 3.80–3.73 (m, 2H, Ox_{anti}), 3.58–3.50 (m, 2H, Ox_{syn}), 3.32–3.24 (m, 2H, Ox_{anti}), 3.18 (br s, 24H, NCH_3), 1.49–1.42 (m, 8H, CH), 0.84–0.75 (m, 24H, CH_3), 0.67–0.58 (m, 24H, CH_3); MS (FAB): m/z=1420 (($M-BF_4$)$^+$). Anal. Calcd for $C_{56}H_{70}N_{10}O_4Pd_2(BF_4)_4$: C, 44.62; H, 4.68; N, 9.29. Found: C, 44.64; H, 4.41; N, 9.18.

4.12.2. (*R*,*R*)-8. Yield 71%; mp 198–199 °C (decomp.); IR (KBr, cm^{-1}): 2961, 1591, 1502; ^1H NMR (400 MHz, CD_3CN, 233 K, *syn*:*anti*=1:2.2): δ 8.63 (s, 2H, $phenylene_{syn}$), 8.542 (t, 2H, J=8.0 Hz, py_{anti}), 8.538 (t, 2H, J=8.0 Hz, py_{syn}), 8.46 (d, 2H, J=8.7 Hz, $phenylene_{anti}$), 8.12 (d, 4H, J=8.0 Hz, py_{anti}), 8.11 (d, 4H, J=8.0 Hz, py_{syn}), 7.90 (d, 8H, J=8.6 Hz, ph_{syn} and ph_{anti}), 7.43 (d, 2H, J=8.7 Hz, $phenylene_{anti}$), 7.24 (s, 2H, $phenylene_{syn}$), 6.94 (d, 8H, J=8.6 Hz, ph_{syn} and ph_{anti}), 4.87–4.79 (m, 16H, Ox_{syn} and Ox_{anti}), 3.95–3.88 (m, 2H, Ox_{syn}), 3.80–3.73 (m, 2H, Ox_{anti}), 3.58–3.50 (m, 2H, Ox_{syn}), 3.32–3.24 (m, 2H, Ox_{anti}), 3.18 (br s, 24H, NCH_3), 1.49–1.42 (m, 8H, CH), 0.84–0.75 (m, 24H, CH_3), 0.67–0.58 (m, 24H, CH_3); MS (FAB): m/z=1420 (($M-BF_4$)$^+$). Anal. Calcd for $C_{56}H_{70}N_{10}O_4Pd_2(BF_4)_4$: C, 44.62; H, 4.68; N, 9.29. Found: C, 44.44; H, 4.74; N, 9.61.

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References and notes

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