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Chirality induction of polyaniline derivatives through chiral complexation

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Abstract—Chirality induction of π-conjugated polyaniline derivatives was achieved by chiral complexation with chiral palladium(II) complexes. The crystal structure of the chiral conjugated complex with a model compound of the polyaniline, *N*,*N*-bis(4′-dimethylaminophenyl)-1,4-benzoquinonediimine, revealed a chiral propeller twist conformation of the π-conjugated moiety.

Polyanilines are one of the promising electrically conducting polymers with chemical stability.[1] In recent year, there has been increased interest in chiral induction of polyanilines because of their potential use in diverse areas such as surface modified electrodes, molecular recognition, and chiral separation.[2] Chiral polyaniline has been reported to be formed only by chiral acid dopant.[3] In previous papers, complexation of polyanilines with transition metals modulates the redox properties of the emeraldine base, which is related to the catalytic function in the oxidation reaction.[4] Furthermore, the controlled complexation with palladium(II) compounds has been achieved to afford the cross-linked network or single-strand conjugated complex,[5a] in which the quinonediimine moieties serve as bridging coordination sites.[5] Use of chiral complexes is envisioned to induce chirality to a π-conjugated backbone, giving the chiral d,π-conjugated complexes. In this context, we herein report a new method for chirality induction of polyaniline derivatives through complexation with chiral palladium(II) complexes.

Chiral palladium(II) complexes, [((*S*,*S*)-L^1)Pd(MeCN)] ((***S***,***S***)-**1**) and [((*R*,*R*)-L^1)Pd(MeCN)] ((***R***,***R***)-**1**),[6] were designed and prepared by treatment of $Pd(OAc)_2$, respectively, with the *N*-heterocyclic tridentate podand ligand, *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] in acetonitrile. Treatment of the emeraldine base of poly(*o*-toluidine) (POT)[7] in THF with (***S***,***S***)-**1** led to the formation of the chiral conjugated polymer complex, [POT–((*S*,*S*)-L^1Pd)] ((***S***,***S***)-**2**),[8] as shown in Scheme 1. The electronic spectrum of (***S***,***S***)-**2** in THF exhibited a broad absorption around 500–900 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***)-**2** exhibited an induced CD (ICD) around 500–850 nm. Furthermore, the mirror image of the CD signal was observed with (***R***,***R***)-**2**, which was obtained from (***R***,***R***)-**1** (Fig. 1). These findings support that the chirality induction is achieved by the chiral complexation.

To gain further insight into chirality induction, the chiral complexation with a model compound of polyaniline, *N*,*N*′-bis(4-dimethylaminophenyl)-1,4-benzoquinonediimine (L^2),[9] was investigated. The complexation of L^2 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^2)Pd((*S*,*S*)-L^1)] ((***S***,***S***)-**3**) or [((*R*,*R*)-L^1)Pd(L^2)Pd((*R*,*R*)-L^1)] ((***R***,***R***)-**3**), respectively.[10] The electronic spectrum of (***S***,***S***)-**3** in CH_2Cl_2 exhibited a broad absorption around 600–900 nm in Figure 2, probably due to the similar complexation as mentioned above.

Keywords: Polyaniline; Quinonediimine; Chirality induction; Chiral complexation.

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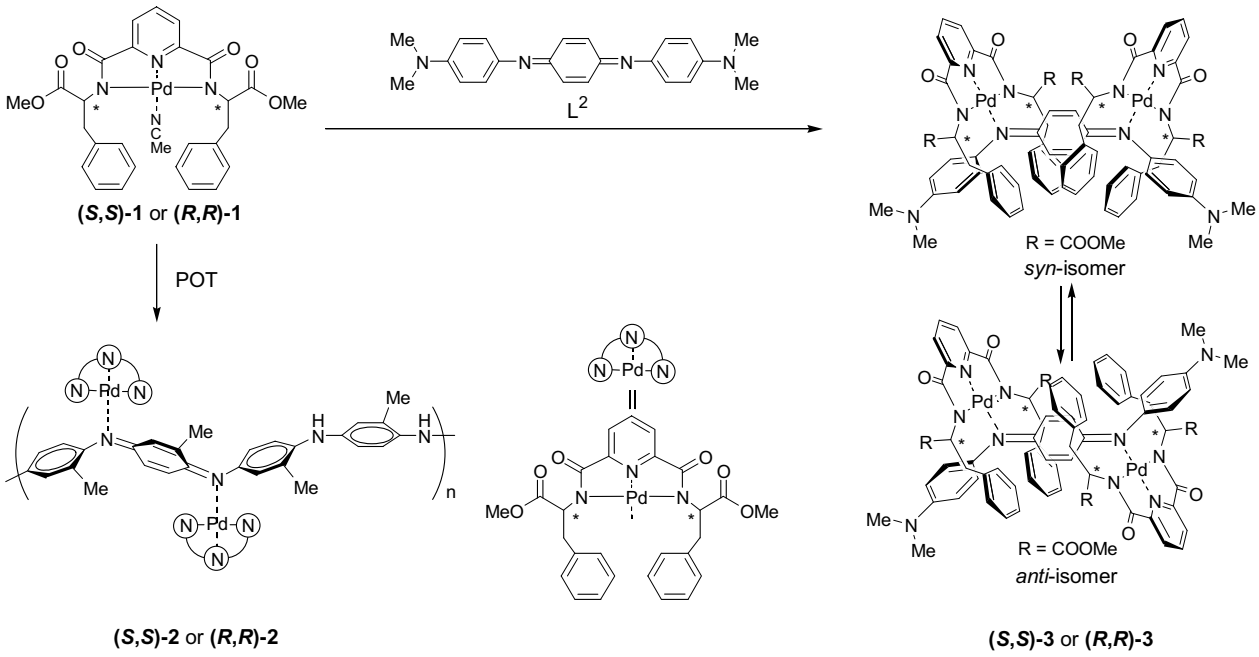

Scheme 1.

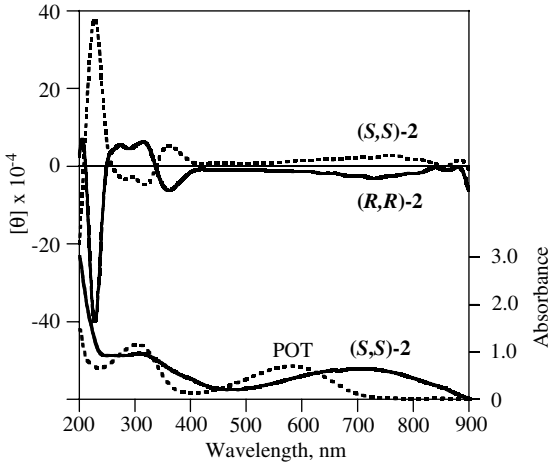

Figure 1. CD spectra (top) of (***S***,***S***)-**2** and (***R***,***R***)-**2**, and electronic spectra (bottom) of (***S***,***S***)-**2** and POT in THF (1.3×10^{-3} M).

Variable temperature ^{1}H NMR studies of the conjugated complex (***S***,***S***)-**3** indicated interesting molecular dynamics in solution. The phenylene protons of the quinonediimine moiety of the *syn*-isomer were observed at 9.14 and 7.14 ppm as singlet peaks, whereas the *anti*-isomer exhibited doublet peaks of those protons at 7.84 and 6.92 ppm. As the temperature was lowered, the peaks of the conformer (***S***,***S***)-**3*syn*** increased gradually. The equilibrium constant K_{eq} between (***S***,***S***)-**3*syn*** and (***S***,***S***)-**3*anti*** was calculated from variable temperature ^{1}H NMR spectra. The temperature dependence of K_{eq} was used to construct the van't Hoff plot of ln K_{eq} versus K^{-1}.[11] The complex (***S***,***S***)-**3*syn*** is enthalpically more favorable than (***S***,***S***)-**3*anti*** 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 CT band of the quinonediimine moiety was observed between (***S***,***S***)-**3** and (***R***,***R***)-**3** in CH_2Cl_2 as shown in Figure 3. The ICD around 600–900 nm appears to be

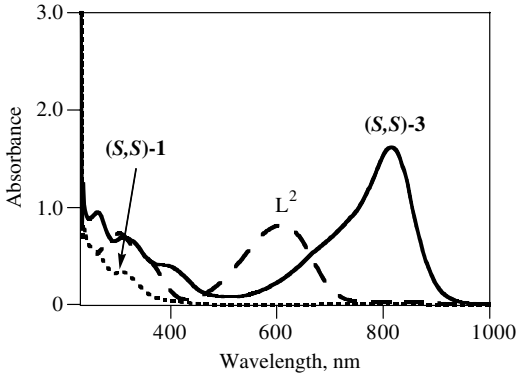

Figure 2. Electronic spectra of **1**, **3** and L^2 in CH_2Cl_2 (5.0×10^{-5} M).

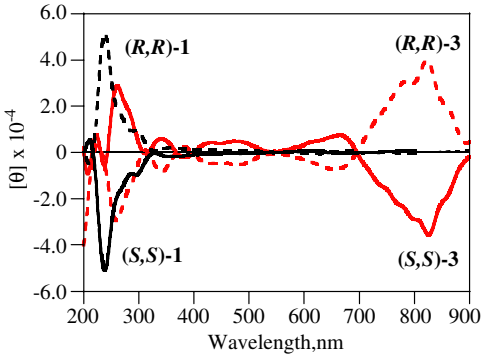

Figure 3. CD spectra of **1** (1.0×10^{-4} M) and **3** (5.0×10^{-5} M) in CH_2Cl_2.

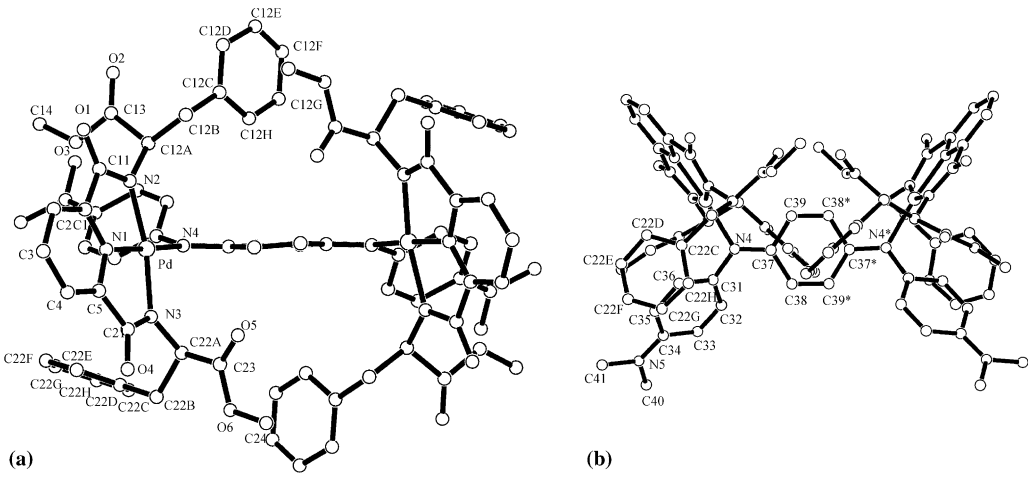

Figure 4. (a) Top view and (b) side view of the X-ray crystal structure of (***R***,***R***)-3***syn*** (hydrogen atoms are omitted for clarity).

reflected by the chirality of the palladium(II) complexes. Such ICD was not observed in the case of **1**. These results suggest that chirality of the quinonediimine moiety is also induced through chiral complexation.

Further structural information was obtained by the single-crystal X-ray structure determination.[12] The crystal structure of (***R***,***R***)-**3** indicates that the two [(L^1)Pd] units are bridged by the quinonediimine moiety of L^2 to form the C_2-symmetrical 2:1 complex (***R***,***R***)-**3*syn*** with the Pd–Pd separation 7.59 Å, as depicted in Figure 4. Each phenylene ring of L^2 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 (Fig. 5). The chirality of the podand moieties of [(L^1)Pd] is considered to induce a propeller twist of the π-conjugated molecular chain. The similar complexation behavior is assumed to be the case with the polymer complexation. The random twist conformation of POT might be transformed into the helical conformation with a predominant screw sense through the complexation.

In conclusion, chirality induction of emeraldine and quinonediimine derivatives was demonstrated by chiral complexation with the quinonediimine moiety. The stereoselective controlled formation of the conjugated complexes is achieved through the complexation. The chiral d,π-conjugated complexes might be of potential as functionalized materials and asymmetric catalysts.

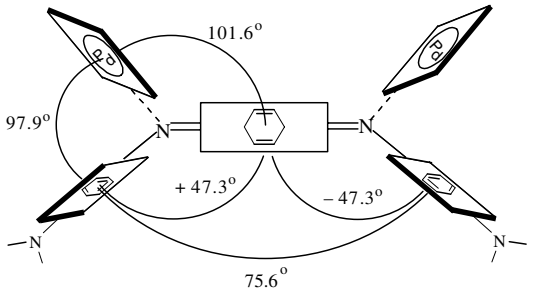

Figure 5. Schematic representation of (***R***,***R***)-3***syn***.

Acknowledgements

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6. 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 dropwise 2,6-pyridyldicarbonyl dichloride (61.2 mg, 0.3 mmol) in CH_2Cl_2 (8 mL) under argon at 0 °C for 7 h and then at room temperature for 18 h. The resulting mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$ aqueous solution and brine, and then dried over Na_2SO_4. The chiral ligands, *N*,*N*′-bis(*S*-1-methoxycarbonyl-2-phenylethyl)-2,6-pyridinedicarboxamide [(*S*,*S*)-L^1H_2] (102.8 mg, 70%) and *N*,*N*′-bis(*R*-1-methoxycarbonyl-2-phenylethyl)-2,6-pyridinedicarboxamide [(*R*,*R*)-L^1H_2] (98.3 mg, 67%), were respectively obtained by evaporation of the residue solution. L^1H_2: ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.36 (d, 2H, $J = 8.4$ Hz, NH), 8.19 (d, 2H, $J = 7.6$ Hz, py), 8.03 (t, 1H, $J = 7.6$ Hz, py), 7.29–7.18 (m, 10H, ph), 4.95–4.89 (m, 2H, CH), 3.72 (s, 6H, CH_3), 3.34 (dd, 2H, $J = 14.0$, 5.6 Hz, CH_2), 3.19 (dd, 2H, $J = 14.0$, 8.8 Hz, CH_2). A mixture of (*S*,*S*)-L^1H_2 or (*R*,*R*)-L^1H_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*)-1** or (***R*,*R*)-1** was isolated in good yield ((***S*,*S*)-1**: 95%, (***R*,*R*)-1**: 98%) as yellow powder by reprecipitation from benzene and hexane. **1**: Mp 200–201 °C (decomp.). IR (KBr): 1730, 1594 cm^{-1}; UV/vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 308 (3.83) nm. ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.07 (t, 1H, $J = 8.0$ Hz, py), 7.53 (t, 2H, $J = 8.0$ Hz, py), 7.34 (d, 4H, $J = 8.1$ Hz, ph), 7.26 (dd, 4H, $J = 8.1$, 7.5 Hz, ph), 7.16 (t, 2H, $J = 7.5$ Hz, ph), 4.70 (dd, 2H, $J = 10.0$, 4.2 Hz, CH), 3.69 (s, 6H, Me), 3.27 (dd, 2H, $J = 13.6$, 4.2 Hz, CH_2), 2.85 (dd, 2H, $J = 13.6$, 10.0 Hz, CH_2), 1.97 (s, 3H, CH_3CN). MS (FAB): $m/z = 594$ ([M−CH_3CN]$^+$). Anal. Calcd for $C_{29}H_{28}O_6N_4$ Pd: C, 54.85; H, 4.44; N, 8.82. Found: C, 54.79; H, 4.11; N, 8.56.
7. Preparation of POT is based on our previous procedure: Hirao, T.; Fukuhara, S.; Otomaru, Y.; Moriuchi, T. *Synth. Met.* **2001**, *123*, 373, The molecular weight of POT was estimated to be 4.2×10^3 as determined by gel permeation chromatography (GPC) (polystyrene standards with THF as the eluent). Elemental analysis ($C_{7.00}H_{6.75}N_{1.00}$) indicates the emeraldine base structure consisting of the amine and imine moieties at ca. 1:1 ratio.
8. To POT in THF solution was added 0.5 equiv molar of **1** in THF solution as compared with the monomer unit of POT and the mixture was stirred at room temperature for 30 min. The mixture was filtered through membrane under argon. The electronic and CD spectra of the filtrate were measured, respectively. The electronic and CD spectra were measured in a 0.10 cm quartz cell at room temperature with concentration of 1.3×10^{-3} M of the monomer unit under argon.
9. *N*,*N*′-Bis(4′-dimethylaminophenyl)-1,4-benzoquinonediimine (L^2) was prepared by using the literature method Wei, Y.; Yang, C.; Ding, T. *Tetrahedron Lett.* **1996**, *37*, 731.
10. A mixture of L^2 (13.8 mg, 0.04 mmol) and (***S*,*S*)-1** or (***R*,*R*)-1** (50.8 mg, 0.08 mmol) was stirred in CH_2Cl_2 (10 mL) under argon at room temperature for 4 h. After evaporation of the solution, the chiral complex (***S*,*S*)-3** or (***R*,*R*)-3** was isolated in good yield ((***S*,*S*)-3**: 90%, (***R*,*R*)-3**: 95%) by reprecipitation from chloroform and diethyl ether. **3**: Mp 180–181 °C (decomp.). IR (KBr): 1731, 1591, 1362, 1162 cm^{-1}; UV/vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 816 (4.51) nm. ^{1}H 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, $ethylene_{syn}$, $ethylene_{syn}$, $ethylene_{anti}$), 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 $C_{76}H_{74}O_{12}N_{10}Pd_2\cdot0.5CHCl_3$: C, 57.72; H, 4.72; N, 8.80. Found: (***S*,*S*)-3**) C, 57.86; H, 4.67; N, 9.11. (***R*,*R*)-3**) C, 57.62; H, 4.75; N, 8.95.
11. Measurement of the equilibrium constants at various temperatures was carried out by integration of the appropriate peaks during ^{1}H NMR spectroscopy. Spectra were taken in CD_2Cl_2 from 243 to 298 K. The thermodynamic parameters were determined from the van't Hoff plot of $\ln K_{eq}$ versus K^{-1}.
12. Crystal data for (***R*,*R*)-3*syn***: $C_{76}H_{74}O_{12}N_{10}Pd_2$, $M_r = 1532.28$, monoclinic, space group $C2$ (#5), $a = 33.1760(1)$, $b = 15.3324(4)$, $c = 18.1523$ Å, $\beta = 155.9623(8)°$, $V = 3761.1(1)$ Å^3, $Z = 2$, $T = 4.0$ °C, $D_{calc} = 1.353$ g cm^{-3}, μ (MoKα) = 5.44 cm^{-1}, MoKα radiation ($\lambda = 0.71069$ Å), $R = 0.066$, $R_w = 0.177$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been 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 CB21EZ, UK (fax: (+44)1223-336-033; e-mail: linstead@ccdc.cam.ac.uk; deposit@ccdc.cam.ac.uk).