Synthesis of a Stimuli-Responsive P-Chiral Polymer with Chiral Phosphorus Atoms and Azobenzene Moieties in the Main Chain

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Abstract: A reaction of the P-chiral compound (*S*,*S*)-1,2-bis(boranato(*tert*-butyl)methylphosphino)ethane with an azobenzene derivative gave stimuli-responsive polymers with P-chiral phosphines in the main chain. This is the first example of a stimuli-responsive P-chiral polymer. The polymer isomerized from the *trans* to the *cis* form upon UV irradiation and reverted to the *trans* form reversibly. The polymer was able to coordinate to platinum, and the resulting polymer complex ex- hibited the Cotton effect owing to the chirality of the phosphorus atoms. The structure of the P-chiral polymer ob- tained could be changed reversibly by light and thermal stimuli, and the poly- mer chain was induced to rotate heli- cally when complexed with transition metals through the chiral phosphorus atoms.

Keywords: azobenzene · chiral phosphorus atoms · isomerization · polymerization · stimuli response

Introduction

Chiral polymers, for example, DNA, polypeptides, and artifi- cial helical polymers, have received much attention due to their chiral structure and characteristic properties such as molecular recognition and catalytic activity.[1–5] A number of chiral polymers, such as those with chiral atoms[6–19] and chiral axes,[20,21] or helically induced polymers[22–29] have been synthesized by asymmetric reactions by the construc- tion of chiral building blocks or by introduction of helical structures with chiral additives. However, most naturally oc- curing and synthetic chiral polymers contain carbon atoms as the chiral center or axis. Polymers with heteroatoms as chiral centers in the main chain are limited so far.[30–33] This is because of the difficulty of not only producing highly enantiomerically enriched heteroatom-containing com- pounds but also their racemization. In the case of phospho- rus, in particular, configurational instability and gradual rac- emization at high temperature are often observed in diaryl- and triarylphosphines.[34] However, it is known that trialkyl- phosphines hardly racemize even at high temperature be- cause of high inversion energy.[35] Recently, we focused on the chiral phosphorus atom as a chiral component of poly- mers and oligomers.[36] These were synthesized by the use of the key monomer (*S*,*S*)-1,2-bis(boranato(*tert*-butyl)methyl- phosphino)ethane, (*S*,*S*)-**1**,[37] which has two chiral phospho- rus atoms. The optically active oligophosphine[38] containing eight chiral phosphorus atoms, which was prepared by a stepwise oxidative coupling reaction of (*S*,*S*)-**1**, exhibited the features of a polymer, whereas the corresponding chiral tet- raoligophosphine containing four chiral phosphorus atoms behaved as a low-molecular-weight compound.[36] We also synthesized P-chiral copolymers with chiral phosphorus atoms and benzene moieties in the main chain and revealed that they show a chiral higher-order structure (helical con- formation) induced by the chirality of the optically active phosphorus atom.[39] We introduce herein a novel stimuli-re- sponsive P-chiral polymer and investigate changes in its structure on exposure to external stimulus. Such stimuli enable a polymer to alter its physical and chemical proper- ties, for example, viscosity, refractive index, conductivity, pH, solubility, wettability, mechanical properties, polymer morphology, and so on. The modulation of their properties is thus expected to provide application for these polymers in tunable functional materials, especially in the case of chiral polymers, to which much attention has been paid in recent years.[13,22–25,40–47] In some cases, drastic conformational changes such as helical reversal or helix–coil transition can be caused by external stimuli.[41,44–46]

Herein we report the synthesis of a P-chiral stimuli-re- sponsive polymer that contains the optically active phos- phine unit (*S*,*S*)-**1** and azobenzene units in the main chain.

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FULL PAPERS

We employed the azobenzene group as the stimuli-responsive functional group. Azobenzene is a well-known photoresponsive chromophore, and its light- and heat-stimulated geometric isomerizations have been extensively studied over four decades.[53] Reversible *trans* to *cis* isomerization of azobenzene is induced by UV irradiation, and *cis* to *trans* by visible light or heat. Azobenzene systems undergo efficient and fully reversible photo- and thermoisomerization reactions to provide versatile photoswitchable systems.[44–52] Furthermore, in this study, the P-chiral stimuli-responsive polymer has a chiral phosphine group. Therefore, the polymers obtained are expected to coordinate to transition metals as well as show response to light and thermal stimuli, which can lead to drastic changes in conformation and higher-order structure. To the best of our knowledge, this is the first example of the synthesis of stimuli-responsive P-chiral polymers.
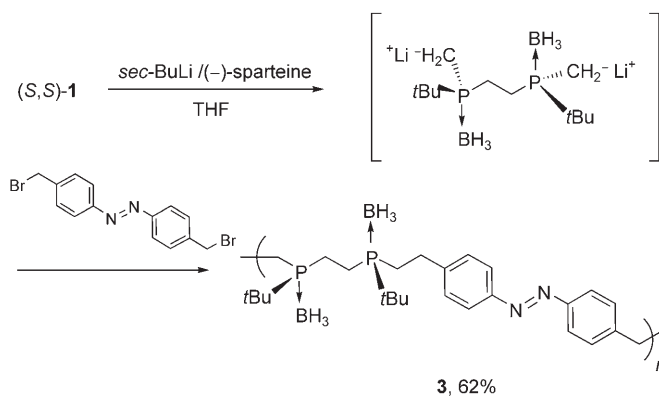
Results and Discussion

Synthesis of Polymer 3

Our strategy for the synthesis of a stimuli-responsive P-chiral polymer involves the use of (*S*,*S*)-**1** as a P-chiral unit and an azobenzene derivative as a photo- and thermoresponsive moiety. (*S*,*S*)-**1** was chosen as the P-chiral moiety because of its easy preparation with high enantiomeric excess (>99%);[37] it was synthesized according to the procedure of Imamoto et al. (Scheme 1).[37] The azobenzene derivative 4,4′-bis(bromomethyl)azobenzene (**2**) was prepared according to the procedure of Guo and Zhong.[54]
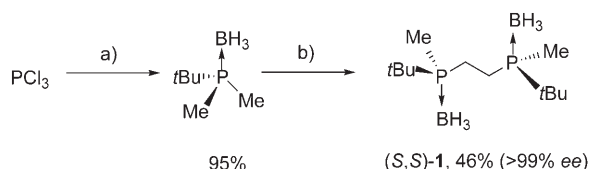
Scheme 1. Synthesis of (*S*,*S*)-**1**. Reagents: a) 1) *t*BuMgCl, 2) MeMgBr, 3) BH$_3$/THF; b) 1) 1 equiv each of *sec*-BuLi and (−)-sparteine, 2) CuCl$_2$, 3) aq. NH$_3$.

The polymerization procedure is shown in Scheme 2. The dianion of (*S*,*S*)-**1**, which was derived from the lithiation of (*S*,*S*)-**1** by *sec*-BuLi, attacked the benzylic position of azobenzene derivative **2** to yield polymer **3** as an orange powder (62% yield). In this reaction, (−)-sparteine was

Abstract in Japanese:

キラルリン原子とアゾベンゼンを組み合わせることで、光、熱、さらには金属配位によってその高次構造が変化する光学活性高分子の合成に成功した。得られた高分子は、キラルリン原子由来のキラルな高次構造をとっていることが示唆された。ヘテロ原子を光学活性中心として有する高分子の報告例は少なく、キラルリン原子を有する刺激応答性高分子の初めての例である。

Scheme 2. The polymerization process.

used as an activator of the alkyllithium, although this polymerization is not an asymmetric reaction. As shown in the ^{1}H NMR spectrum of **3** (Figure 1), the peaks for the BH$_3$
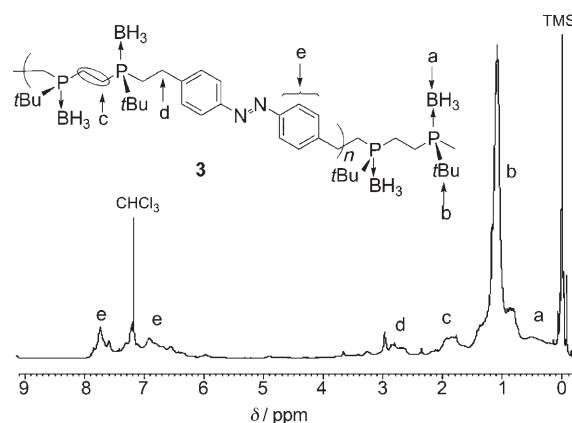
Figure 1. ^{1}H NMR spectrum of polymer **3** (CDCl$_3$).

group were observed at around 0.5 ppm, the peaks for the *tert*-butyl group appeared at 1.1–1.3 ppm, and the methylene proton peaks (PC*H*$_2$) were observed at 1.7–2.3 ppm. The aromatic proton peaks were observed at 6.6–7.1 and 7.6–8.0 ppm. The new benzylic methylene proton peaks (C*H*$_2$C$_6$H$_4$) appeared at 2.6–3.1 ppm, and no benzylic proton peak of monomer **2** was observed at 4.5 ppm. The ^{31}P NMR spectrum of polymer **3** exhibited three broad peaks at 29, 33, and 35 ppm. In view of the chemical shift of monomer (*S*,*S*)-**1** (29 ppm), the phosphorus peak of polymer **3** at 29 ppm was attributed to the terminal phosphine of **3**, and other two peaks were assigned to the internal phosphines. These results indicate that most of the end groups are (*S*,*S*)-**1** moieties. According to GPC analysis using a calibration curve with a polystyrene standard, the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the molecular-weight distribution (M_w/M_n) were found to be 3000, 5000, and 1.6, respectively.

Synthesis of (*S,S*)-1–Pt

To verify the coordination ability of polymer **3** to platinum, (*S,S*)-**1**–Pt complex was synthesized as a model compound. The coordination reaction of (*S,S*)-**1** to platinum is shown in Scheme 3. First, the BH₃ groups of (*S,S*)-**1** were removed by
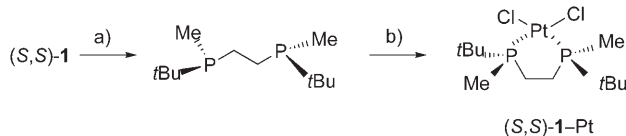
Scheme 3. Synthesis of model complex (*S,S*)-**1**–Pt. Reagents: a) 1) excess CF₃SO₃H, 2) KOH; b) [PtCl₂(COD)] in CH₂Cl₂. COD = 1,5-cyclooctadiene.

CF₃SO₃H and KOH according to the procedure in the literature,[37] and then [PtCl₂(COD)] was added to this solution in CH₂Cl₂ in situ. After purification by column chromatography on silica gel, (*S,S*)-**1**–Pt complex was obtained in 67% yield as a colorless solid. The product was characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy and elemental analysis. The ³¹P NMR spectrum of (*S,S*)-**1**–Pt exhibited a peak at 55 ppm, which was shifted downfield relative to that of (*S,S*)-**1** (29 ppm). The (*S,S*)-**1**–Pt complex also exhibited Pt–P coupling ($J_{P,Pt} = 3528$ Hz).

Coordination of Polymer 3 to Platinum

The same reaction described above (Scheme 3) was applied to the complexation of polymer **3** to platinum (Scheme 4). After purification by HPLC to remove the residual [PtCl₂
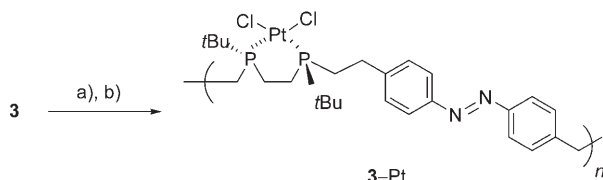
Scheme 4. Coordination reaction of polymer **3** to platinum. Reagents: a) 1) excess CF₃SO₃H, 2) KOH; b) [PtCl₂(COD)] in CH₂Cl₂.

(COD)], the platinum polymer complex **3**–Pt was obtained quantitatively. According to its ³¹P NMR spectrum, the phosphorus peaks of **3**–Pt were shifted downfield with respect to **3** (35 ppm) to around 55 ppm owing to coordination to platinum. The molecular weights were found to be $M_n = 1900$ and $M_w = 2400$, respectively. These were smaller than those of **3** owing to the folded structure caused by complexation. All compounds and polymers were air- and moisture-stable because of coordination of phosphine to the BH₃ group or platinum.

Photochemical and Thermal *trans* and *cis* Isomerization of Polymer 3

To examine the isomerization behavior of the azobenzene units of polymer **3**, photochemical *trans→cis* and thermal *cis→trans* isomerization were investigated by UV/Vis spectroscopy. At first, a solution of polymer **3** in chloroform was irradiated for 2 min with a Xe lamp (300–420 nm) to induce photoisomerization of the azobenzene chromophores from the *trans* to the *cis* form (Scheme 5). The photostationary
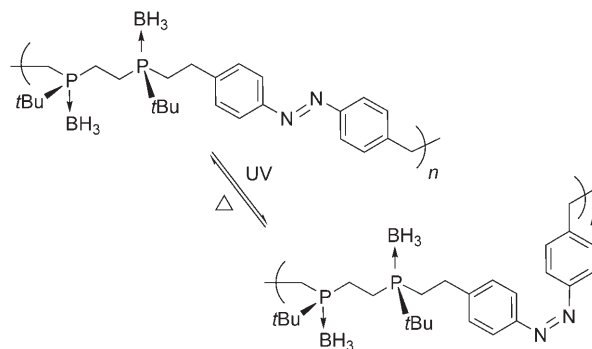
Scheme 5. Isomerization of polymer **3**.

state was achieved immediately after UV irradiation. The inset of Figure 2 shows the UV spectral changes of the solution of polymer **3** during the photoisomerization process. In
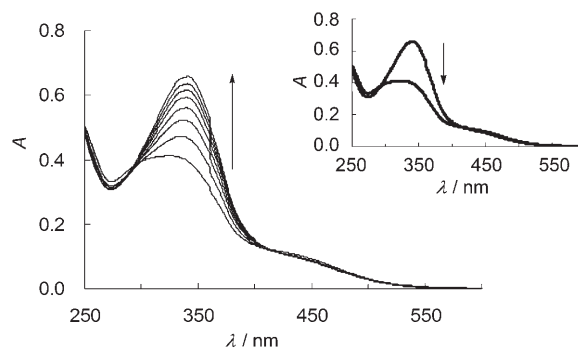
Figure 2. UV/Vis absorption spectra of polymer **3** showing thermal recovery of absorption at 40°C (every 30 s). Inset: Photoisomerization by UV irradiation.

the photostationary state, the absorption at around 340 nm resulting from the π–π* transition of the *trans*-azobenzene component decreased and the absorption at 450 nm derived from the *cis*-azobenzene units increased relative to that before UV irradiation (thermal equilibrium). These results indicate that the azobenzene moieties of polymer **3** changed from *trans* to *cis* upon UV irradiation. On the basis of the assumption that all the azobenzene units existed in the stable *trans* form in the initial state, 58% and 42% of the

azobenzene units in the photostationary polymer **3** were *trans* and *cis*, respectively.

In the reverse process, *cis*→*trans* isomerization occurred by heating at 40°C. Thermal recovery of the absorption spectra during heating at 40°C is shown in Figure 2 (every 30 s). The absorbance of the π–π* band of the *trans* isomer at around 340 nm increased progressively; the initial absorption was recovered within 210 s. This implies that thermodynamically unstable *cis*-azobenzene isomerizes thermally to the more-stable *trans* form completely. These *trans*→*cis* and *cis*→*trans* isomerizations were reversible.[55]

Photochemical and Thermal *trans* and *cis* Isomerization of Polymer Complex 3–Pt

The isomerization behavior of polymer complex **3**–Pt was also examined, and the UV/Vis spectra are shown in Figure 3. Similarly to polymer **3**, the absorption band of the
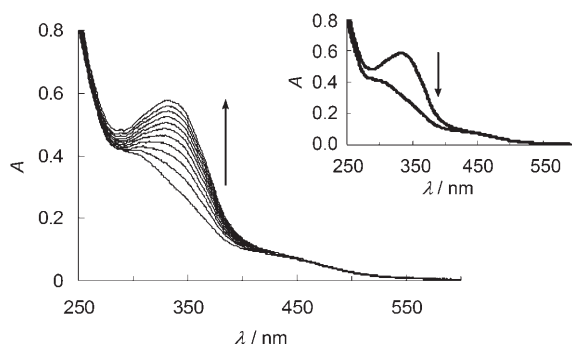
Figure 3. UV/Vis absorption spectra of polymer complex **3**–Pt showing thermal recovery of absorption at 40°C (every 60 s). Inset: Photoisomerization by UV irradiation.

π–π* transition of the *trans*-azobenzene moieties (340 nm) decreased immediately after UV irradiation (Figure 3, inset), indicating that the azobenzene units of **3**–Pt isomerized from the *trans* form to the *cis*. On the basis of the assumption that all the azobenzene units were in the stable *trans* form in the initial state, 49% of the azobenzene moieties of **3**–Pt were in the *cis* form and the other 51% were *trans* in the photostationary state. As with polymer **3**, polymer complex **3**–Pt also reverted from the *cis* to the *trans* form reversibly by heating. Figure 3 shows the thermal *cis*→*trans* isomerization behavior during heating at 40°C (every 60 s). The absorbance of the π–π* band of the *trans* isomer at around 340 nm increased during heating, and thermal recovery was attained after 600 s.[55] It took three times longer time for **3**–Pt to recover from the *cis* form to the *trans* than **3**. This is because the mobility of **3**–Pt was reduced by the complexation of the phosphine units with platinum.

CD Analysis of Polymer Complex 3–Pt

According to CD measurements, polymer complex **3**–Pt exhibited the Cotton effect at around 300 nm (Figure 4 A), whereas polymer **3** without platinum showed no Cotton
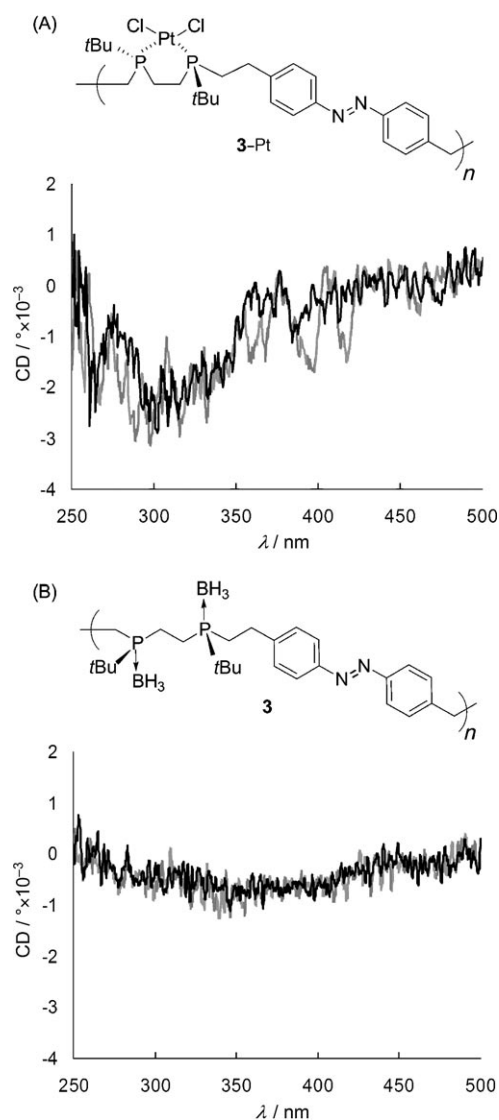
Figure 4. CD spectra of A) polymer complex **3**–Pt and B) polymer **3** before (gray) and after (black) UV irradiation in CHCl₃.

effect (Figure 4 B). This result indicates that the chirality of the phosphorus atom in **3**–Pt affected the structure of the polymer more than in **3**, because the chiral phosphine units in the former were fixed by complexation with platinum. In both cases, there was no change in the CD spectra during photochemical and thermal isomerization. The *trans*→*cis* isomerization seems hardly to affect the CD spectra in the azobenzene region, indicating that *trans*→*cis* isomerization is not a good trigger of change in the chiral structure in this system. However, the CD spectrum changed after complexation. This result implies that complexaion could be a trigger for generating chiral structures, because the complexation occurred directly at the chiral phosphorus center. The azobenzene-containing P-chiral polymer obtained can change its structure by light and thermal stimuli and its higher-order structure by coordination of the chiral center to a transition metal. The polymer can be expected to coordinate to other

transition metals; thus, multistimuli-responsive P-chiral polymers have potential uses as tunable materials.

Conclusions

The reaction of the optically active phosphine compound (*S*,*S*)-**1** with the azobenzene derivative **2** gave stimuli-responsive polymers that contain P-chiral phosphorus atoms in the main chain. The resulting polymer photochemically isomerized from the *trans* form to the *cis* and thermally isomerized from *cis* to *trans* upon heating reversibly. Polymer **3** was able to rotate helically after complexation with transition metals such as platinum. The resulting polymer complex **3**–Pt exhibited the Cotton effect because of its chiral higher-order structure derived from the chirality of the phosphorus atoms.

Experimental Section

General

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL EX-400 spectrometer, and samples were analyzed in CDCl$_3$ with Me$_4$Si (TMS) as an internal standard. ^{31}P NMR (161.9 MHz) spectra were also recorded on the JEOL EX-400 spectrometer, and samples were analyzed in CDCl$_3$ with H$_3$PO$_4$ as an external standard. The following abbreviations are used: s: singlet, d: doublet, m: multiplet, br: broad. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8020 and an RI-8020 (TSK-GEL α-3000) chromatograph with *N*,*N*-dimethylformamide (DMF) containing 10 mM LiBr as an eluent after calibration with standard polystyrene. UV/Vis absorption spectra were obtained on a JASCO V-530 spectrometer. CD spectra were recorded on a JASCO J-600 spectropolarimeter with CHCl$_3$ as a solvent. The removal of the monomer and the remaining [PtCl$_2$(COD)] from polymers was carried out on a recycling preparative HPLC chromatograph (Japan Analytical Industry Co. Ltd., Model 918R) equipped with JAJGEL-1H and 2H columns (GPC) using CHCl$_3$ as an eluent. Column chromatography was performed with Wakogel C-300 silica gel. Elemental analysis was performed at the Microanalytical Center of Kyoto University. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102 A spectrometer.

Materials

THF and Et$_2$O were distilled from sodium benzophenone ketyl under nitrogen. (−)-Sparteine was distilled from KOH under nitrogen. (*S*,*S*)-**1**[37] and **2**[54] were prepared as described in the literature. Unless otherwise noted, the materials were obtained from commercial sources. All reactions were performed under a nitrogen atmosphere with standard Schlenk techniques.

Syntheses

3: A solution of (−)-sparteine (0.31 mL, 1.33 mmol) in THF (10 mL) was cooled to −78 °C under a nitrogen atmosphere. *sec*-BuLi (1.01 M in cyclohexane/*n*-hexane, 1.32 mL, 1.33 mmol) was added to this stirred solution by a syringe. After 15 min, a solution of (*S*,*S*)-**1** (0.15 g, 0.56 mmol) in THF (2 mL) was added dropwise, and the mixture was stirred at −78 °C over 3 h. A solution of **2** (0.20 g, 0.56 mmol) in THF (8 mL) was added, and the reaction mixture was allowed to warm slowly to room temperature. After 15 h, the reaction was quenched by addition of HCl (2 M), and the mixture was extracted with CH$_2$Cl$_2$ (3×20 mL). The combined extracts were washed with aqueous Na$_2$SO$_4$ and brine. The organic layer was dried over MgSO$_4$. After the solvent was removed, the residue was purified by HPLC to remove the monomer. The polymer was obtained as

orange solids (0.16 g, 62 %). ^{1}H NMR (CDCl$_3$): $\delta = 0.12$–0.90 (br, B*H*$_3$), 1.05–1.26 (br, Bu and PC*H*$_3$), 1.70–2.29 (br, PC*H*$_2$), 2.62–3.14 (br, C*H*$_2$C$_6$H$_4$), 6.55–7.08 (br, C$_6$*H*$_4$), 7.55–7.98 ppm (br, C$_6$*H*$_4$); ^{13}C NMR (CDCl$_3$): $\delta = 5.6$ (P*C*H$_3$), 15.7 (P*C*H$_2$), 25.3 (C(*C*H$_3$)$_3$), 29.5 (-*C*(CH$_3$)$_3$), 36.5 (-*C*H$_2$C$_6$H$_4$-), 122.6 (*C*$_6$H$_4$), 129.0 (*C*$_6$H$_4$), 151.0 ppm (*C*$_6$H$_4$); ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = 29.7$, 32.9, 34.6 ppm.

(*S*,*S*)-**1**–Pt: The removal of borane was carried out by the treatment of (*S*,*S*)-**1** with CF$_3$SO$_3$H and KOH according to the procedure in the literature.[37] After that, (*S*,*S*)-**1** (0.13 g, 0.54 mmol) without borane was dissolved in CH$_2$Cl$_2$ (15 mL). An equimolar amount of [PtCl$_2$(COD)] (0.20 g, 0.54 mmol) was added to this solution, which was then refluxed for 15 h. After the solvent was removed, the residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$/EtOAc (100:0–0:100 *v*/*v*) to obtain (*S*,*S*)-**1**–Pt (0.17 g, 0.36 mmol, 67 %) as a colorless powder. ^{1}H NMR (CDCl$_3$): $\delta = 1.33$ (d, $^3J = 15.6$ Hz, 18H, Bu), 1.48–1.63 (br, 2H, PC*H*$_2$), 1.78 (d, $^2J = 11.2$ Hz, 6H, PC*H*$_3$), 2.05–2.31 ppm (br, 2H, PC*H*$_2$); ^{13}C NMR (CDCl$_3$): $\delta = 8.8$ (d, $J_{\text{C,P}} = 35.6$ Hz, PCH$_3$), 26.1 (d, $J_{\text{C,P}} = 31.0$ Hz, PCH$_2$), 27.5 (s, C(CH$_3$)$_3$), 32.7 ppm (d, $J_{\text{C,P}} = 36.0$ Hz, *C*(CH$_3$)$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = 55.4$ ppm ($J_{\text{Pt,P}} = 3530$ Hz); HRMS (FAB): calcd for C$_{12}$H$_{28}$Cl$_2$P$_2$Pt: 499.0691 [*M*]$^+$; found: 499.0686; elemental analysis: calcd (%) for C$_{12}$H$_{28}$Cl$_2$P$_2$Pt: C 28.80, H 5.64; found: C 28.51, H 5.76.

3–Pt: Polymer complex **3**–Pt was prepared according to the procedure described for the preparation of (*S*,*S*)-**1**–Pt, but with **3** instead of (*S*,*S*)-**1**. Polymer **3**–Pt was obtained as an orange powder after purification with HPLC to remove the remaining [PtCl$_2$(COD)]. ^{1}H NMR (CDCl$_3$): $\delta = 1.00$–1.75 (br, Bu and PC*H*$_3$), 1.80–2.43 (br, PC*H*$_2$), 2.52–3.34 (br, C*H*$_2$C$_6$H$_4$), 6.30–7.21 (br, C$_6$*H*$_4$), 7.50–7.97 ppm (br, C$_6$*H*$_4$); ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = 46$ (m), 56 (m), 69 ppm (m).

Measurements of Photoisomerization and Thermal Isomerization Process

For the UV/Vis measurements, a solution of **3** (5.8×10^{-5} M) or **3**–Pt (4.4×10^{-5} M) in chloroform was placed in a quartz cell (cell length = 1 cm). The solution was irradiated at 300–420 nm with a 175-W Xe lamp filtered through a Toshiba UV-D33S glass filter. Thermal recovery was performed by immersing a sample solution into a water bath (40 °C), and the process was monitored by UV/Vis spectroscopy every 30 or 60 s.

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