Thermoresponsive On−Off Switching of Chiroptical Property Induced in Poly(4′-ethynylbenzo-15-crown-5)/α-Amino Acid System

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ABSTRACT: Cis-transoidal poly(4′-ethynylbenzo-15-crown-5) (**2**) prepared by the polymerization of 4′-ethynylbenzo-15-crown-5 with $Rh(nbd)BPh_4$ has been used as a thermoresponsive material with a chiral on−off switching property. In the circular dichroism (CD) spectrum of **2** in the presence of the perchloric acid salt of L-phenylglycine (L-Pgly·$HClO_4$) at −30 °C, a large Cotton effect with an intensity of $+2.96 \times 10^4$ deg cm^2 dmol^{-1} was observed in the range from 300 to 550 nm corresponding to the absorption of the conjugated polymer backbone, indicating that **2** formed the one-handed helical structure triggered by the host−guest complexation with L-Pgly·$HClO_4$. However, the induced CD (ICD) intensity significantly decreased with the increasing temperature and almost completely disappeared at 30 °C or over. Furthermore, an alternate temperature modulation between −30 and 30 °C brought about the reversible on−off switching of the ICD of **2**.

Introduction

The stimuli-responsive property in macromolecular and supramolecular systems has a potential for use in a wide variety of applications, such as switches,[1] sensors,[2] and molecular machines including tweezers,[3] shuttles,[4] rotary motors,[5] and elevators.[6] Hence, expanding the limit and scope of the stimuli-responsive molecular system is always required. In addition, much attention has focused on the design and construction of the dual-stimuli-responsive molecular system in recent years. For example, de Silva et al. synthesized a compound consisting of 10-cyanoanthracene as a fluorophore, a tertiary amine as a receptor targeting H^+, and a benzo-15-crown-5 as a receptor for Na^+, for which switching "on" of the fluorescence was only achieved by the simultaneous provision of these two cations.[7] Thus, this system operates as a molecular photonic AND logic gate based on fluorescent signaling, which has never been achieved for molecules capable of responding to just one kind of external stimulus. Moreover, the molecular system with the stimuli-responsive property that is precisely tunable by another kind of stimuli should be also categorized as a dual-stimuli-responsive one.

Dynamic helical polymers are composed of alternating sequences of right- and left-handed helices separated by helix reversal points that move along the polymer main chain, and the population of the predominant one-handed helical sequence generally changes in response to external stimuli.[8] This dynamic feature in the main chain conformation has been applied to the facile synthetic strategy of a one-handed helical polymer. Yashima et al. developed a helicity induction, for which the one-handed helical conformation was induced into the main chain of an optically inactive polymer triggered by a complex formation with chiral small molecules.[9] This complex exhibited a characteristic induced circular dichroism (ICD) in the absorption region corresponding to the polymer backbone. Therefore, the helicity induction provides us with not only an easy method for the synthetic technique of the helical polymers but also a stimuli-responsive property of the ICD. Since this discovery, the helicity inductions of a number of polymers with various types of binding sites have already been investigated.[10−15] However, there are a few studies regarding the design and construction of a dual-stimuli-responsive helicity system; i.e., the chiroptical property of the macromolecular helicity preorganized by the first external stimulus is tuned by the second external stimulus.[16] As an example, for poly(phenylacetylene) having a bulky phenyl phosphonate group at the pendant, the helix inversion was accomplished by changing the temperature after the formation of the induced helical structure by the helicity induction technique, resulting in the inversion of the sign of the ICD, whose inversion system is reversibly controlled by temperature as the second external stimulus.[16b] In addition, the on−off switching system for the induced helical chirality is also one of the precise control of the ICD with the second external stimulus. Thus, of great importance is the development of an on−off switching system as well as the inversion system. Among the second external stimuli for controlling the ICD, a temperature change has a great advantage in the modulation process because the temperature control essentially does not affect the components in the system, promising the possible reversibility for the on−off switching. Therefore, we are now focusing on the development of the ICD thermoresponsive on−off switching system for the induced helical polymer, which should also be a dual-stimuli-responsive system.

For the helicity induction, the size, shape, and position of the binding site significantly affects the sensitivity and applicability of the helicity induction, so that the precise design of the binding site is the key to accomplish our purpose. Among the various types of binding sites, the crown ether has a significant advantage in molecular design and synthesis,[17] and thus a number of polymers with a specially designed crown ether as the binding site have been employed for the helicity induction.[18] For instance, the helicity induction of poly(phenylacetylene) bearing aza-18-crown-6 pendants has been known as a pioneering study for the helicity induction based

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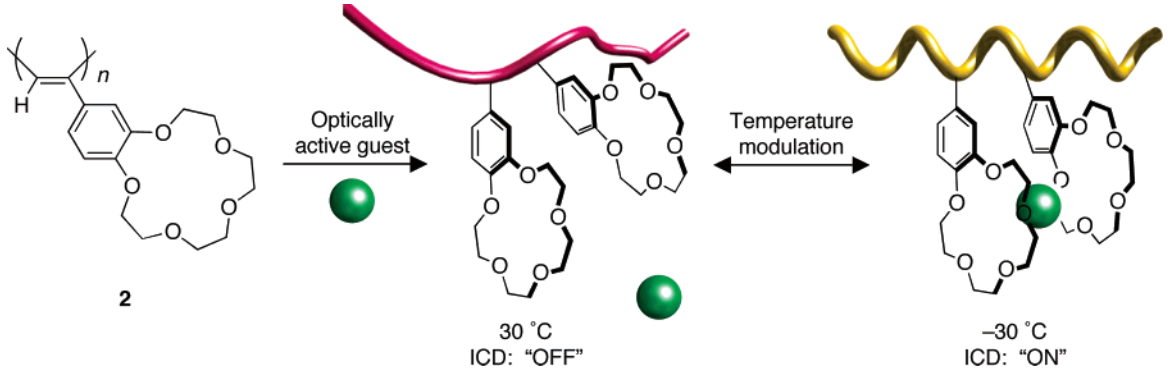


Figure 1. Schematic illustration of the macromolecular helicity induction of **2** driven by the host−guest complexation with an optically active guest and the thermoresponsive on−off switching of an ICD based on the construction and collapse of the one-handed helical structure.

on the complex formation between the crown ether and chiral guest molecules, in which the polymer could respond to an extremely small amount of chiral guest molecules and formed a one-handed helical structure.[18a] Additionally, we previously reported that a poly(phenyl isocyanate) bearing crown cavities on the backbone, which was prepared by the cyclopolymerization of the corresponding α,ω-diisocyanate monomer, also formed the induced one-handed helical structure through the host−guest complexation with a chiral guest.[18e] For these polymers, their induced one-handed helical structures are stably organized over a wide temperature range, so that it should be difficult to realize the thermoresponsive on−off switching of the ICD. In contrast, the ICD intensity of poly(phenylacetylene) bearing the aza-15-crown-5 pendants highly depended on the temperature probably because of the low complexation ability of aza-15-crown-5-ether toward guest cations.[18d] We considered the relationships between the kind of binding site and the temperature dependence of the helical chirality that have been reported so far and now found a helicity induction system capable of completely controlling the construction and collapse of the induced helical structure by temperature. Hence, we now report the present system as a novel on−off switching system of induced helical chirality (Figure 1).

Experimental Section

Materials. 4′-Ethynylbenzo-15-crown-5 (**1**)[19] and Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)B^-(C_6H_5)$_3$] (Rh(nbd)BPh_4)[20] were synthesized by previously reported methods. L-Phenylalanine (L-Phe), D-phenylalanine (D-Phe), and L-leucine (L-Leu) (>99.9% ee) were purchased from the Peptide Institute, Inc. (Osaka, Japan). L-Phenylglycine (L-Pgly, >99%), L-valine (L-Val, >99%), and L-methionine (L-Met, >99%) were obtained from the Kanto Chemical Co., Ltd. (Tokyo, Japan). D-4-Hydroxyphenylglycine (D-Hpgly, >98%) was purchased from the Acros Organics (Geel, Belgium). The perchloric acid ($HClO_4$) salts of these amino acids were prepared in accordance with a previous report.[21] THF was dried over sodium benzophenone ketyl and then vacuum transferred from CaH_2. Dry acetonitrile (purity >99.5%, water content <0.005 vol %) and chloroform for the spectroscopy (>99.0%) were obtained from the Kanto Chemical and used without further purification. Triphenylphosphine was available from Kanto Chemical and used after recrystallization from dichloromethane/diethyl ether. 18-Crown-6 (>98.0%) was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI, Tokyo, Japan).

Instruments. The ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-A400II instrument. The laser Raman spectra were recorded using a JASCO NRS-1000. Size exclusion chromatography (SEC) was performed at 40 °C using a Jasco high-performance liquid chromatography (HPLC) system (PU-980 Intelligent HPLC pump, CO-965 Column oven, RI-930 Intelligent RI detector, and Shodex DEGAS KT-16) equipped with a Shodex Asahipak GF-310 HQ column (linear, 7.6 mm × 300 mm) and a Shodex Asahipak GF-7M HQ column (linear, 7.6 mm × 300 mm) in DMF containing lithium chloride (0.01 M) at a flow rate of 0.4 mL min^{-1}. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymer were calculated on the basis of a polystyrene calibration. Circular dichroism (CD) spectra were measured in a 1 mm path length using a Jasco J-720 spectropolarimeter. Preparation of the polymerization solution was carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) under a dry argon atmosphere (H_2O, O_2 <1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively.

Polymerization. The polymerization of **1** was carried out in a dry Schlenk flask under an argon atmosphere. In a glovebox (under moisture- and oxygen-free argon atmosphere, H_2O, O_2 < 1 ppm), Rh(nbd)BPh_4 (5.3 mg, 10 μmol) was weighed into a dry Schlenk flask and dissolved in dry THF (2.1 mL). To the solution was added a solution of **1** in dry THF (0.33 mol L^{-1}, 3.0 mL, 1.0 mmol). The concentrations of the monomer and the rhodium catalyst were 0.2 and 0.002 mol L^{-1}, respectively. After stirring at 25 °C for 24 h, the reaction was terminated by adding triphenylphosphine (16 mg, 62 μmol) and then poured into a large amount of diethyl ether. The precipitate was purified by reprecipitation with chloroform/diethyl ether and then dried in vacuo to give polymer **2** as a yellow powder. Yield, 0.25 g (83%). $M_n = 2.5 \times 10^4$, $M_w/M_n = 2.1$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (m, 3H, aromatic), 5.76 (s, 1H, =CH), 3.69 (m, 16H, $-CH_2-$).

CD Measurements. The concentration of **2**, which was calculated on the basis of the monomeric units, was 3.4 mmol L^{-1} for all measurements. The molar ratio of the chiral guests to the monomeric units in **2** was 1.0, except for the titration experiment. A typical procedure is described as follows: A stock solution of **2** (6.8 mmol L^{-1}) in chloroform/acetonitrile (1/1, v/v) was prepared in a 5 mL flask, and a 1 mL aliquot of the solution was transferred to a 2 mL flask. l-Pgly·$HClO_4$ (1.7 mg, 6.8 μmol) was added to the 2 mL flask. The solution was diluted with chloroform/acetonitrile (1/1, v/v) to 2 mL and then vigorously shaken. After 10 min, the CD and UV spectra were measured in a 1 mm quartz cell using a spectropolarimeter with a thermostat.

Results and Discussion

Poly(4′-ethynylbenzo-15-crown-5) (**2**) was synthesized by the polymerization of 4′-ethynylbenzo-15-crown-5 using Rh(nbd)-BPh_4. The molecular weight and polydispersity of **2** were estimated to be 2.5×10^4 and 2.1, respectively. In the ^{1}H NMR spectrum of **2**, the signal at 5.76 ppm due to the main-chain protons appeared along with those at 6.30 ppm due to aromatic protons and at 3.69 ppm due to the methylene protons in the crown ether moiety (see Supporting Information). On the basis of the sharpness and the region of the signal due to the main chain proton, it was found that **2** possessed a highly cis-

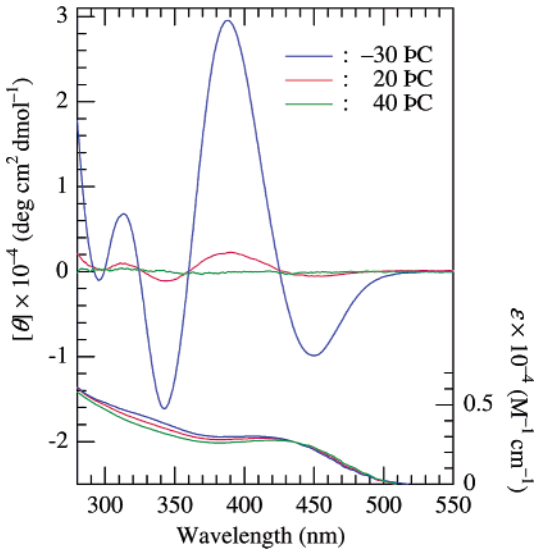
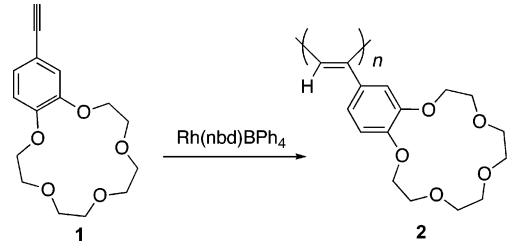


Figure 2. CD and absorption spectra of **2** with L-Pgly·$HClO_4$ in chloroform/acetonitrile (1/1, v/v) at −30, 20, and 40 °C ([monomeric units in **2**] = 3.4 mmol L^{-1} and [L-Pgly·$HClO_4$]/[monomeric units in **2**] = 1.0).

Scheme 1. Synthesis of Poly(4′-ethynylbenzo-15-crown-5) (2)



transoidal structure as the main-chain configuration.[19] This belief was also strongly supported by the characteristic peaks at 1554 and 1336 cm^{-1} due to the cis structure in the laser Raman spectrum of **2** (see Supporting Information).

We examined the potential of the macromolecular helicity induction in **2** driven by the host−guest interaction with chiral guests. Figure 2 shows the circular dichroism (CD) and absorption spectra of **2** at −30, 20, and 40 °C in the presence of the L-Pgly·$HClO_4$ as the chiral guest. The CD spectrum of the **2**/L-Pgly·$HClO_4$ system at 20 °C showed a characteristic induced CD (ICD), i.e., a split-type Cotton effect, in the range from 300 to 550 nm corresponding to the absorption of the conjugated polymer backbone. Therefore, this result clearly indicated that **2** formed a helical structure with an excess single screw sense triggered by the host−guest complexation with L-Pgly·$HClO_4$. However, the ICD magnitude was relatively low in comparison with that for other helicity induction systems.[9−15] Hence, it is suggested that the induced helical structure of **2** in this condition does not consist of the completely one-handed helical sense. In contrast, in the CD spectrum of **2** at −30 °C, an incomparably intense ICD was observed without changing the spectrum pattern, indicating that the main chain of **2** at −30 °C formed more stably organized one-handed helical structure than that at 20 °C.

Hence, the helicity induction of **2** at various temperatures was examined in order to clarify the temperature effect on the helicity induction of **2**. Figure 3 shows the temperature dependence of the molar ellipticity value for the second Cotton effect ($[\theta]_{2nd}$) in the CD spectra of **2** with L-Pgly·$HClO_4$ in chloroform/acetonitrile (1/1, v/v). The ICD intensity of **2** significantly increased with the decreasing temperature, and this

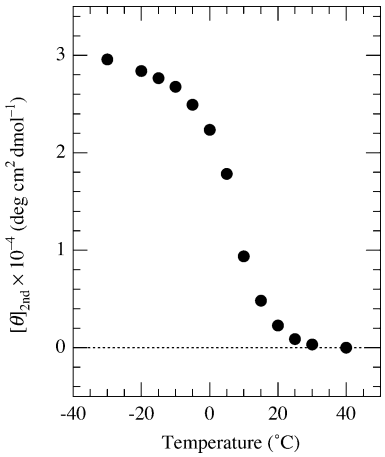


Figure 3. Temperature dependence of the $[\theta]_{2nd}$ values for the **2**/L-Pgly·$HClO_4$ system in chloroform/acetonitrile (1/1, v/v) in the temperature range from −30 to 40 °C ([monomeric units in **2**] = 3.4 mmol L^{-1} and [L-Pgly·$HClO_4$]/[monomeric units in **2**] = 1.0).

change was also reversible. In particular, the change in the ICD intensity in the temperature range from −5 to 15 °C was quite drastic. Additionally, it should be noted that the characteristic CD spectrum completely disappeared at 30 °C or above, indicating that equal amounts of right- and left-handed helical sequences existed in the main chain of **2** in this temperature range. Although a number of polymers with specially designed binding sites have been employed for the helicity induction, such a drastic temperature dependence and an ICD on−off switching are hardly observed for the polymers with the induced helical structure.[22] Hereafter, we would like to focus on the elucidation of the ICD temperature dependence for **2**.

First, the helicity induction of **2** in the presence of various $HClO_4$ salts of amino acids was examined in order to confirm the importance of the chirality of the guest molecules (Table 1). Polymer **2** exhibited an ICD through the complex formation with the $HClO_4$ salts of every amino acid. As we expected, the sign of the Cotton effect was reflected in the absolute configuration of the amino acid, suggesting that the chirality of the guest molecules was the driving force for controlling the helical sense of **2**. In addition, the ICD intensity of the **2**/L-Phe·$HClO_4$ system decreased with the increasing temperature in a manner similar to that of the **2**/L-Pgly·$HClO_4$ system and reached zero at 30 °C (see Supporting Information). Hence, the structure of the chiral guest was not the most important factor for bringing about the ICD on−off switching property of **2**.

Previously, Green et al. reported that the optical activity of the helical polyisocyanate drastically changed by changing the temperature, and this change was caused by aggregation of the polymer chains.[23] Hence, we performed the CD measurements of **2** over a wide range of concentrations from 0.01 to 0.44% in order to confirm the aggregation behavior of **2**. However, for any concentration, the temperature effect was similar to that shown in Figure 3, indicating that the ICD temperature dependence of **2** was not ascribed to the aggregation. Therefore, we concluded that the drastic temperature dependence and the on−off switching of ICD of **2** was caused by the significant change in the population of the predominant one-handed helical sequences by changing the temperature through a reversible helix−helix transition that was characteristic of dynamic helical polymers.

With respect to the reason arising from the drastic temperature dependence of the ICD intensity, the complexation ability of **2** should be considered. Thus, we carried out the titration experiment of the $[\theta]_{2nd}$ values for the **2**/L-Pgly·$HClO_4$ system

Table 1. Cotton Effect Intensities for the ICD of 2 in the Presence of Perchloric Acid Salts of Amino Acids[a]

	first Cotton		second Cotton		third Cotton	
amino acid	$[\theta] \times 10^{-4}$ (deg cm^2 dmol^{-1})	λ (nm)	$[\theta] \times 10^{-4}$ (deg cm^2 dmol^{-1})	λ (nm)	$[\theta] \times 10^{-4}$ (deg cm^2 dmol^{-1})	λ (nm)
L-Pgly	−0.99	450	+2.96	388	−1.61	343
L-Phe	−0.80	448	+2.79	388	−1.50	342
D-Phe	+0.79	448	−2.73	387	+1.47	343
L-Leu	−0.83	447	+2.93	387	−1.66	343
L-Val	−0.68	449	+2.65	387	−1.62	343
L-Met	−0.93	449	+2.99	388	−1.61	343
D-Hpgly	+1.06	450	−3.02	388	+1.55	342

[a] CD measurements of **2** in the presence of perchloric acid salts of amino acids were performed in chloroform/acetonitrile (1/1, v/v) at −30 °C ([monomeric units in **2**] = 3.4 mmol L^{-1} and [guest]/[monomeric units in **2**] = 1.0).

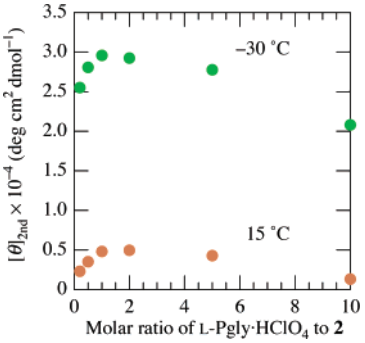


Figure 4. Titration curve of the $[\theta]_{2nd}$ values. CD measurements of **2** with L-Pgly·$HClO_4$ were performed in chloroform/acetonitrile (1/1, v/v) at −30 and 15 °C ([monomeric units in **2**] = 3.4 mmol L^{-1} and [L-Pgly·$HClO_4$]/[monomeric units in **2**] = 0.2−10).

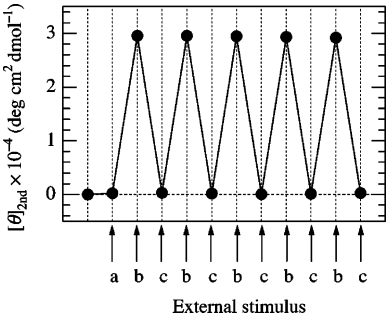


Figure 5. Plots of the $[\theta]_{2nd}$ values of **2** upon continuous external stimuli. The first plot is the $[\theta]_{2nd}$ value for the solution of **2** in chloroform/acetonitrile (1/1, v/v) at 30 °C ([monomeric units in **2**] = 3.4 mmol L^{-1}). The stimuli (a−c) represent the addition of 1.0 equiv of L-Pgly·$HClO_4$ relative to **2** at 30 °C (a), changing temperature to −30 °C (b), and changing temperature to 30 °C (c).

at 15 and −30 °C in order to evaluate the influence of temperature upon the host−guest complexation of **2**, as shown in Figure 4. The intensity of the ICD at −30 °C linearly increased with the increasing amount of L-Pgly·$HClO_4$ and reached a maximum value, i.e., $+2.96 \times 10^4$ deg cm^2 dmol^{-1}, when the molar ratio of L-Pgly·$HClO_4$ to the monomeric units in **2** was 1.0. However, further addition of L-Pgly·$HClO_4$ brought about a decrease in the ICD magnitude. The reason for this result is not clear at present, while a similar behavior has been observed in the helicity induction system of poly(phenylacetylene) bearing aza-15-crown-5 ether pendants.[18d]

For the titration curve at 15 °C, the maximum ICD value of $+0.50 \times 10^4$ deg cm^2 dmol^{-1} was observed at 2.0 equiv of L-Pgly·$HClO_4$ relative to the monomeric units in **2**. In addition, the ICD intensity decreased with the further addition of L-Pgly·$HClO_4$ in a manner similar to that at −30 °C and could never reach the high intensity that was observed in the titration experiment at −30 °C. This suggested that the host−guest complexation ability of **2** should significantly depend on the temperature. In previous papers regarding the guest binding ability of **2**, we have clarified that two crown ether rings in **2** cooperatively combine with a single guest cation, and thus the complexation ability of **2** is attributed to the 2:1 crown−cation complex rather than the 1:1 complex.[19] For the 2:1 crown−cation complex formation, the conformational change in the main chain significantly affects the binding ability because the distance, direction, and position of the two crown ether rings, which are the most important factor for forming the 2:1 crown−cation complex, entirely depend on the main-chain conformation. Therefore, the change in the mobility of the main chain on the basis of the temperature change significantly influences the binding ability, in sharp contrast to the 1:1 complex, leading to the drastic temperature dependence of the ICD of **2**.

To estimate whether the on−off switching of ICD is repeatable or not, we carried out the CD measurements of **2** with continuously applied external stimuli, as shown in Figure 5. The characteristic ICD of **2** did not appear by only adding 1.0 equiv of L-Pgly·$HClO_4$ at 30 °C (a in Figure 5). Subsequently, the temperature change from 30 to −30 °C (b in Figure 5) caused the full ICD to occur, which disappeared by changing temperature to 30 °C once more (c in Figure 5). Additionally, a further alternate temperature modulation between −30 and 30 °C brought about the appearance and disappearance, respectively, of the ICD without a significant decrease in the magnitude of the full ICD. Therefore, the on−off switching of the ICD of **2** should be repeatable many times by the temperature modulation.

The addition of L-Pgly·$HClO_4$ as the chiral guest is the essential driving force for forming the one-handed helical structure, as described earlier. Thus, we also examined the on−off switching of the ICD on the basis of the doping/undoping process of the chiral guest. The characteristic ICD of the **2**/L-Pgly·$HClO_4$ system at −30 °C almost completely disappeared by the addition of 2.0 equiv of 18-crown-6, which is a host capable of binding L-Pgly·$HClO_4$ more strongly than **2** (Figure 6A). Moreover, the ICD was recovered by the further addition of 2.0 equiv of L-Pgly·$HClO_4$ relative to **2**, though the complete recovery of the ICD intensity was not accomplished (Figure 6B). It should be noted that both the temperature modulation and the doping/undoping process of the chiral guest could control the on−off switching of the ICD of **2**. Therefore, polymer **2** could also possibly to be applied as a dual-stimuli-responsive material.

Conclusions

We have demonstrated the on−off switching of induced circular dichroism (ICD) for a cis-transoidal poly(phenylacetylene) bearing crown ether pendant, **2**. To the best of our knowledge, this is the first report describing the thermoresponsive on−off switching of an ICD. For this reversible switching system, a precise temperature modulation is not required because

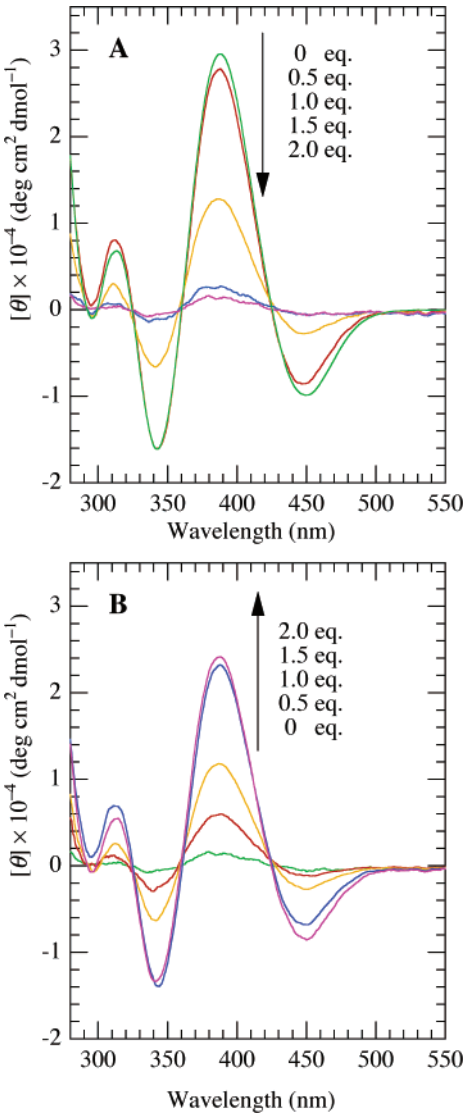


Figure 6. CD spectral changes of **2** upon the addition of 18-crown-6 (0.5−2.0 equiv to monomeric units in **2**) to the **2**/L-Pgly·$HClO_4$ system (A) and a further addition of L-Pgly·$HClO_4$ (0.5−2.0 equiv to monomeric units in **2**) to the **2**/L-Pgly·$HClO_4$/18-crown-6 system (B). CD measurements were performed in chloroform/acetonitrile (1/1, v/v) at −30 °C. Concentrations of monomeric units in **2** and L-Pgly·$HClO_4$ in the initial condition are 3.4 and 3.4 mmol L^{-1}, respectively.

the on−off switching of the ICD depends on only whether the temperature is lower than 30 °C. In addition, the on−off switching is realized around room temperature. Thus, these features of **2** have a great advantage for use as a thermoresponsive on−off switching system. For the construction of such an induced one-handed helical structure of **2**, it was essential that both the presence of a suitable guest molecule and temperature control were simultaneously satisfied. Therefore, the helicity induction system of **2** should be a novel type, and we expected that this system should be utilized for not only thermoresponsive on−off switching systems but also more complicated or rather advanced molecular devices capable of responding to two kinds of external stimuli.

Supporting Information Available: Figures showing ^1H NMR spectrum of **2** in $CDCl_3$, laser Raman spectrum of **2** in the solid state, temperature dependence of the $[\theta]_{2nd}$ values for the **2**/L-Phe·$HClO_4$ system in chloroform/acetonitrile (1/1, v/v) in the temperature range from −30 to 40 °C. This material is available free of charge via the Internet at https://pubs.acs.org.

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