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Thermo- and Solvent-Responsive Polymer Complex Created from Supramolecular Complexation between a Helix-Forming Polysaccharide and a Cationic Polythiophene

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Abstract: The helical structure is one of key structural components for both biological systems and artificial chiral systems. So far, we have succeeded in fabricating "tight" insulated molecular wires consisting of a triple-stranded cohelical structure formed through supramolecular wrapping of synthetic polymers by a helix-forming polysaccharide (schizophyllan). Herein, we have designed a new modified polysaccharide (Cur-oeg) to form a "loose" macromolecular complex with a conjugated polymer (CP) that allows structural changes in response to external stimuli. Cur-oeg forms a helical complex with an achiral cationic polythiophene (PT1), and the effective conjugation length is changed by temperature, showing a large absorption peak shift from 403 to 482 nm between 85 and 5 °C. According to the change in the conjugation system, the fluorescence and the induced circular dichroism show the continuous spectral shifts under temperature control. The color changes in the absorption and the fluorescence are detectable with observation by the naked eye and are reversibly controlled under thermal cycles, indicating that this system has the function of a "molecular thermometer". It is shown that the induced thermoresponsiveness is associated with structural rearrangement of the helical conformation of PT1 in the complex. Moreover, another unique responsiveness is discovered for the film state: that is, the film color is varied when it is exposed to the vapor of water or methanol (vaporchromism), resulting from the structural change of PT1 occurring even in the film state. These flexible molecular motions in both the solution state and the film state can be applicable to the design of CP-based smart sensors, polarized materials, switching devices, etc.

Introduction

The helical motif that is found in natural polymers including DNAs, polypeptides, and polysaccharides plays important roles in the biological activities. Beyond the biological systems, the helical structure is also applied to artificial key technologies such as chiral sensing, separation of natural compounds, and design of polarized materials.[1] Until now, a lot of chiral complexes have been developed through templating methods utilizing chiral self-assemblies and helical biopolymers.[2] Recently, we have succeeded in fabricating unique helical polymer complexes through a supramolecular wrapping method using helix-forming polysaccharides such as Schizophyllan (SPG) and Curdlan (Cur) that are classified into a β-1,3-glucan family.[3] First, we found that SPG forms cohelical complexes with certain DNAs or RNAs that are constructed from two SPG chains and one DNA or RNA chain.[4] Subsequently, we noticed that a modified polythiophene with a *syn*-type conformation has a similar helical pitch length with SPG as well as DNA.[4a−c] We

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(1) (a) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102–6211. (b) Palmans, A. R. A.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 8948–8968. (c) Tang, K.; Green, M. M.; Cheon, K. S.; Selinger, J. V.; Garetz, B. A. *J. Am. Chem. Soc.* **2003**, *125*, 7313–7323. (d) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039–4070. (e) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893–4011. (f) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013–4038. (g) Goto, H.; Akagi, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 4322–4328.

(2) (a) Janssen, P. G. A.; Ruiz-Carretero, A.; González-Rodríguez, D.; Meijer, E. W.; Schenning, A. P. H. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 8103–8106. (b) Ho, H.-A.; Najari, A.; Leclerc, M. *Acc. Chem. Res.* **2008**, *41*, 168–178. (c) Hannah, K. C.; Armitage, B. A. *Acc. Chem. Res.* **2004**, *37*, 845–853. (d) Woolfson, D. N.; Ryadnov, M. G. *Curr. Opin. Chem. Biol.* **2006**, *10*, 559–567. (e) Kim, O.-K.; Je, J.; Jernigan, G.; Buckley, L.; Whitten, D. *J. Am. Chem. Soc.* **2006**, *128*, 510–516.

(3) (a) Numata, M.; Shinkai, S. *Adv. Polym. Sci.* **2008**, *220*, 65–121. (b) Sakurai, K.; Uezu, K.; Numata, M.; Hasegawa, T.; Li, C.; Kaneko, K.; Shinkai, S. *Chem. Commun.* **2005**, 4383–4398.

(4) (a) Sakurai, K.; Shinkai, S. *J. Am. Chem. Soc.* **2000**, *122*, 4520–4521. (b) Okobira, T.; Miyoshi, K.; Uezu, K.; Sakurai, K.; Shinkai, S. *Biomacromolecules* **2008**, *9*, 783–788. (c) Miyoshi, K.; Uezu, K.; Sakurai, K.; Shinkai, S. *Biomacromolecules* **2005**, *6*, 1540–1546. (d) Sakurai, K.; Mizu, M.; Shinkai, S. *Biomacromolecules* **2001**, *2*, 641–650. (e) Mizu, M.; Koumoto, K.; Anada, T.; Matsumoto, T.; Numata, M.; Shinkai, S.; Nagasaki, T.; Sakurai, K. *J. Am. Chem. Soc.* **2004**, *126*, 8372–8373. (f) Kimura, T.; Beppu, A.; Sakurai, K.; Shinkai, S. *Biomacromolecules* **2005**, *6*, 174–179.

 10.1021/ja1067349

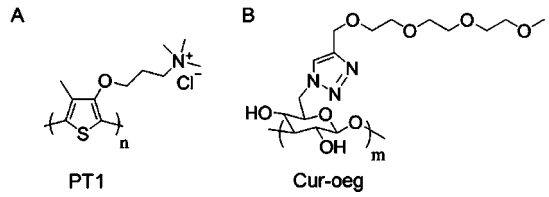

Figure 1. Chemical structures of a cationic polythiophene (PT1) and a PEGylated Curdlan (Cur-oeg).

thus found that a cationic polythiophene (PT1, Figure 1A) and amino acid-modified polythiophenes form stoichiometric cohelical complexes with SPG, in which the composition of polythiophene to SPG is also 1:2.[5] In these SPG-wrapped complexes, each polythiophene chain is insulated from any other chains, and aggregation of PT1 is suppressed even in the solid state.

By using this supramolecular wrapping technique, we have succeeded in constructing insulated molecular wires of various conjugated polymers (CPs) with SPG.[6] It is known that the solution properties of CPs are affected by both intermolecular aggregation and single-chain conformational change. To distinguish these two factors therefore becomes essential for well-defined applications of controlled CP structures.[7] Since our supramolecular wrapping method has achieved the insulation of each CP chain, chemical and physical changes observed are simply attributable to events occurring in the single chain. The immobilization of the helical PT1 structure by the SPG wrapping brought forth an advantage to create new functions arising from the single chain; for example, PT1/SPG complex emits a circular polarized light arising from the chirality of the helical complex.[8] Moreover, the redox potential of modified polythiophenes can be changed by the SPG wrapping because of the immobilization in the helical structure; that is, the complexed polythiophenes can acquire oxidation resistance.[9] Through these studies, it has firmly been established that SPG can form the "tight" triple-stranded helical complexes with modified polythiophenes, the helical structure of which features high stability and high robustness.[8,9]

On the other hand, it is known that the biological systems employ more dynamic higher-order structures to realize the required functionalities. From this viewpoint, the "tight" SPG complexes are not suitable to design "dynamic" functional materials. It occurred to us that fabrication of a "loose" complex would be important to realize stimuli-responsive functions leading to sensors and devices. Herein, we report a new PEGylated β-1,3-glucan polysaccharide, Cur (Cur-oeg, Figure 1B) through "Click Chemistry". We have found that the Cur-oeg wrapping is able not only to insulate each PT1 chain but also to tune the induced helical structure of the isolated PT1 single chain in response to the environmental conditions because of the decreased "tightness", resulting in color changes in the absorption and the fluorescence detectable by naked eye observation. Moreover, a film made of PT1/Cur-oeg complex shows a unique color change against the exposed vapors such as water and methanol. In this paper, we thoroughly investigated the mechanistic background of these color changes in solution and tried to explain why some color changes are reversible while some color changes are irreversible in the film state.

Results and Discussion

Synthesis and Characterization of Cur-oeg. We have established site-selective and quantitative modification of the 6-OH group in native Curdlan using "Click Chemistry".[10] Cur-oeg was synthesized according to the similar procedure (for the detail see Supporting Information). In dimethyl sulfoxide (DMSO), 6-azido-6-deoxy Curdlan (Cur-N_3) was treated with alkyne-terminated triethylene glycol monomethyl ether in the presence of propylamine as a base and $CuBr_2$-ascorbic acid as a catalyst. The reaction was monitored by FT-IR measurements until a peak ascribable to the N_3 group disappeared. The product was purified by dialysis against distilled water and collected by lyophilization. The molecular weight of the obtained Cur-oeg was estimated by SEC to be weight-average molecular weight $M_w = 7.1 \times 10^4$ ($M_w/M_n = 1.9$, degree of polymerization (DP) $= \sim 182$).

SPG and Cur form triple-stranded helices that can be confirmed by a measurement of optical rotatory dispersion (ORD). Optical rotation occurs when refractive index shows a difference between right-handed and left-handed circularly polarized lights. ORD measurements have been employed to characterize helical conformation of polymers including polysaccharides, polypeptides, and synthetic polymers.[11,12] For the β-1,3-glucan of SPG and Cur, a helix-forming triple-stranded structure shows a positive signal,[11] whereas a single-stranded random coil structure shows a negative signal[12] in the ultraviolet to visible region. Figure 2A shows ORD spectra of Cur-oeg in DMSO and aqueous solutions. An ORD signal of Cur-oeg was characterized by a negative sign in DMSO, which acts as a denaturing-solvent to give a single-stranded SPG and Cur. This result is consistent with the signal of SPG itself in DMSO (Figure 2B). Cur-oeg also showed a negative sign even in aqueous solution in contrast to a positive sign of triple-stranded aqueous SPG. Consequently, one may consider that Cur-oeg adopts a single-stranded random coil in aqueous media. Previously, we reported that modified Curdlan tethering a quaternized amino group also shows a negative sign in water, taking a single-stranded form.[10c] Therein, electrostatic repulsion is a major factor to destabilize the triple-stranded form. The present results

(5) (a) Haraguchi, S.; Tsuchiya, Y.; Shiraki, T.; Sugikawa, K.; Sada, K.; Shinkai, S. *Chem.—Eur. J.* **2009**, *15*, 11221–11228. (b) Li, C.; Numata, M.; Bae, A.-H.; Sakurai, K.; Shinkai, S. *J. Am. Chem. Soc.* **2005**, *127*, 4548–4549.
(6) (a) Shiraki, T.; Haraguchi, S.; Tsuchiya, Y.; Shinkai, S. *Chem. Asian J.* **2009**, *4*, 1434–1441. (b) Numata, M.; Fujisawa, T.; Li, C.; Haraguchi, S.; Ikeda, M.; Sakurai, K.; Shinkai, S. *Supramol. Chem.* **2007**, *19*, 107–113. (c) Numata, M.; Hasegawa, T.; Fujisawa, T.; Sakurai, K.; Shinkai, S. *Org. Lett.* **2004**, *6*, 4447–4450.
(7) (a) Matthews, J. R.; Goldoni, F.; Schenning, A. P. H. J.; Meijer, E. W. *Chem. Commun.* **2005**, 5503–5505. (b) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schening, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491–1546.
(8) Haraguchi, S.; Numata, M.; Li, C.; Nakano, Y.; Fujiki, M.; Shinkai, S. *Chem. Lett.* **2009**, *38*, 254–255.
(9) Haraguchi, S.; Tsuchiya, Y.; Shiraki, T.; Sada, K.; Shinkai, S. *Chem. Commun.* **2009**, 6086–6088.
(10) (a) Hasegawa, T.; Umeda, M.; Numata, M.; Li, C.; Bae, A. H.; Fujisawa, T.; Haraguchi, S.; Sakurai, K.; Shinkai, S. *Carbohydr. Res.* **2006**, *341*, 35–40. (b) Hasegawa, T.; Umeda, M.; Numata, M.; Fujisawa, T.; Haraguchi, S.; Sakurai, K.; Shinkai, S. *Chem. Lett.* **2006**, *35*, 82–83. (c) Ikeda, M.; Hasegawa, T.; Numata, M.; Sugikawa, K.; Sakurai, K.; Fujiki, M.; Shinkai, S. *J. Am. Chem. Soc.* **2007**, *129*, 3979–3988. (d) Ikeda, M.; Haraguchi, S.; Numata, M.; Shinkai, S. *Chem. Asian J.* **2007**, *2*, 1290–1298.
(11) (a) Itou, T.; Teramoto, A.; Matsuo, T.; Suga, H. *Macromolecules* **1986**, *19*, 1234–1240. (b) Sakurai, K.; Shinkai, S. *Carbohydr. Res.* **2000**, *324*, 136–140. (c) Ogawa, K.; Watanabe, T.; Tsurugi, J.; Ono, S. *Carbohydr. Res.* **1972**, *23*, 399–405.
(12) (a) Janssen, H. M.; Peeters, E.; van Zundert, M. F.; Genderen, M. H. P.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 122–125. (b) Duda, C. A.; Stevens, E. S. *Biopolymer* **1991**, *31*, 1379–1385.

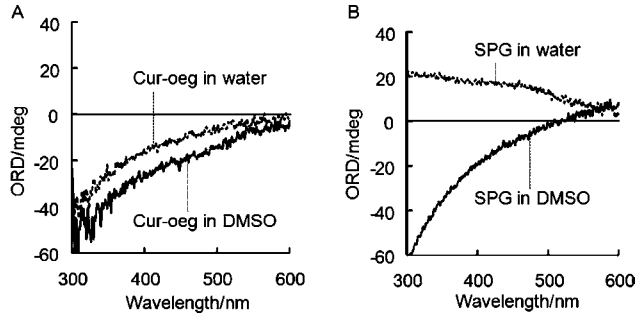

Figure 2. ORD curves of (A) Cur-oeg and (B) SPG in DMSO or in water containing 5 vol % DMSO. Concentrations of polysaccharides were 5 mg/mL in a 1-cm optical cell at 25 °C.

indicate that the increase in the hydrophilicity due to the "neutral" side chains can be another factor to destabilize the triple-stranded form.

Supramolecular Complexation between Cur-oeg and PT1. PT1 was synthesized according to a published paper,[5b] and the ^{13}C NMR measurement (Figure S1, Supporting Information) revealed that the head-to-tail regioregularity was over 95%.[13] M_w of the PT1 was estimated by SEC to be 4.1×10^4 ($M_w/M_n = 3.4$, DP = ∼165), which was comparable with the reported values for other water-soluble poly(alkoxythiophene)s.[14]

Complexation between PT1 and SPG can occur only through a denaturation−renaturation process of SPG, because complexation can take place only when SPG is denatured.[5b,8,9] On the other hand, Cur-oeg already exists as a single-stranded form in DMSO and water. When PT1 was mixed with Cur-oeg in aqueous media, the mixed solution displayed the red-orange color, whereas aqueous PT1 itself gave a yellow solution. In UV/vis spectroscopy, an absorption peak of PT1 ascribable to the $\pi-\pi^*$ transition was largely red-shifted from 414 to 458 nm by the interaction with Cur-oeg (Figure 3A). This result clearly indicates that an interaction between PT1 and Cur-oeg causes elongation of the effective conjugation length, followed by a conformational change of PT1 to a more planar structure.[13,15] Although PT1 itself is an achiral polymer, the mixture of PT1 and Cur-oeg showed a splitting type of induced circular dichroism (ICD) with a first positive and a second negative Cotton effect at 500 and 420 nm, respectively, in the $\pi-\pi^*$ transition region (Figure 3B). A similar ICD pattern has been observed for the PT1/SPG complex that possesses a right-handed helical conformation derived from a nature of right-handed helix-forming β-1,3-glucans.[5b] In addition, this type of CD pattern can be observed for higher-order structures with a right-handed helical motif of polymers and molecular assemblies.[14c,16,17] One can conclude, therefore, that PT1 entrapped in the helix is also twisted into the right-handed helical structure.

According to a change in the effective conjugation length, an emission peak of PT1 was also shifted from 529 to 571 nm in the presence of Cur-oeg (Figure 3C). As shown in Figure 3D, TEM observation revealed that a fibrous structure was formed from a mixture of PT1 and Cur-oeg. On the other hand, PT1 itself or Cur-oeg itself gave random or spherical aggregates with various sizes under the TEM observation (Figure S2, Supporting Information). From these results, it is clear that the supramolecular complexation between PT1 and Cur-oeg creates the one dimensional (1D)-shaped fibrous structure. We previously reported that the characteristic nanowire form is created from the complexes of SPG with various conjugated polymers.[3,6] Therefore, the inherent helix-forming nature of β-1,3-glucans is also present in Cur-oeg and does configurate the helical nanofibrous structure through the wrapping action on PT1. As shown in an inset in Figure 3D, the 1D-shaped fibrous structure was also confirmed by AFM. The height of the fibers was estimated to be 0.82−1.2 nm (the average value of 33 fibers was 1.1 nm), which is comparable with that of conjugated polymer/SPG complexes where each conjugated polymer chain is wrapped separately.[5,6a,b] One can conclude, therefore, that Cur-oeg can insulate each PT1 chain by the wrapping action. From the above-described results, it is undoubted that a chiral macromolecular complex (PT1/Cur-oeg complex) including single PT1 chain is formed by simply mixing PT1 and Cur-oeg in aqueous media.

A stoichiometric proportion between PT1 and Cur-oeg in the complex was investigated through a continuous variation method (Job's plot) in CD spectroscopy. The plot for the ICD intensity at 500 nm gave a maximum at $[PT1]_{unit}/([PT1]_{unit} + [Cur\text{-}oeg]_{unit}) = 0.5$ (Figure 4). This value corresponds to the 1:1 stoichiometric interaction between PT1 and Cur-oeg with respect to each monomer unit. In addition, a CD titration of PT1 varying the Cur-oeg concentration was performed. From the titration curve in Figure 5A, the composition was also determined to be 1:1.

Assuming the 1:1 complexation between PT1 and Cur-oeg, an apparent binding constant (K) was estimated to be $K_{25\ °C} = 3.7 \times 10^4\ M^{-1}$ through an analysis of the plot according to the least-squares method. Figure 5B compares UV/vis absorption spectra of PT1 with increasing Cur-oeg concentration, in which an isosbestic point is confirmed at 435 nm. It is clear, therefore, that one energetically stable species is yielded in the complex. Previously, we reported that a stoichiometry of PT1/SPG complex is 1:2 and the complex consists of a triple-stranded cohelical structure because of the coincidence of the helix pitch length between the *syn*-type helical polythiophene chain and the helical SPG chain.[4a−c,18] Since the ICD pattern of PT1/Cur-oeg complex also showed a right-handed helical conformation, the helical pitch of PT1 should be also close to that of the *syn*-type polythiophene. However, the stoichiometry is 1:1, but not 1:2. We consider, therefore, that the difference in the stoichiometry would be associated with some essential difference in their solution properties: for example, PT1 and Cur-oeg may form a more dynamic, "loose" double-stranded helical structure,

(13) (a) Faïd, K.; Fréchette, M.; Ranger, M.; Mazerolle, L.; Lévesque, I.; Leclerc, M. *Chem. Mater.* **1995**, *7*, 1390–1396. (b) Lévesque, I.; Leclerc, M. *Chem. Mater.* **1996**, *8*, 2843–2849.
(14) (a) Le Floch, F.; Ho, H.-A.; Harding-Lepage, P.; Bédard, M.; Neagu-Plesu, R.; Leclerc, M. *Adv. Mater.* **2005**, *17*, 1251–1254. (b) Ho, H.-A.; Boissinot, M.; Bergeron, M. G.; Corbeil, G.; Doré, K.; Boudreau, D.; Leclerc, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1548–1551. (c) Lukkari, J.; Salomäki, M.; Viinikanoja, A.; Ääritalo, T.; Paukkunen, J.; Kocharova, N.; Kankare, J. *J. Am. Chem. Soc.* **2001**, *123*, 6083–6091. (d) Chayer, M.; Fäid, K.; Leclerc, M. *Chem. Mater.* **1997**, *9*, 2902–2905.
(15) Leclerc, M. *Adv. Mater.* **1999**, *11*, 1491–1498.
(16) Nilsson, K. P. R.; Olsson, J. D. M.; Konradsson, P.; Inganäs, O. *Macromolecules* **2004**, *37*, 6316–6321.
(17) (a) den Bergh, K. V.; Cosemans, I.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2010**, *43*, 3794–3800. (b) Messmore, B. W.; Sukerkar, P. A.; Stupp, S. I. *J. Am. Chem. Soc.* **2005**, *127*, 7992–7993. (c) Hannah, K. C.; Armitage, B. A. *Acc. Chem. Res.* **2004**, *37*, 845–853.
(18) (a) Chuah, C. T.; Sarko, A.; Deslandes, Y.; Marchessault, R. H. *Macromolecules* **1983**, *16*, 1375–1382. (b) Deslandes, Y.; Marchessault, R. H.; Sarko, A. *Macromolecules* **1980**, *13*, 1466–1471. (c) Atkins, E. D. T.; Parker, K. D. *J. Polym. Sci.* **1969**, *28*, 69–81. (d) McIntire, T. M.; Brant, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 6909–6919.

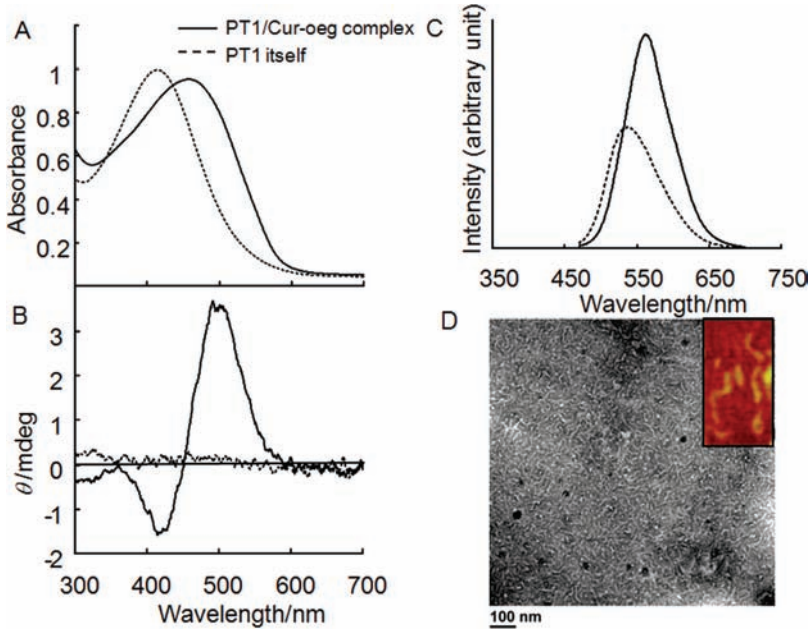

Figure 3. (A) UV/vis absorption, (B) CD, and (C) fluorescence spectra of PT1/Cur-oeg complex (solid line) and PT1 itself (dashed line) in water containing 5 vol % DMSO at 25 °C; $[PT1]_{unit} = 0.2$ mM, $[Cur\text{-}oeg]_{unit} = 0.6$ mM, $\lambda_{ex} = 458$ nm. These data were collected after once heating to 85 °C. (D) TEM image of PT1/Cur-oeg complex; negative stain with 1 wt % phosphotungstic acid aqueous solution adjusted to pH 7 with NaOH. An inset image is an AFM image of the complex.

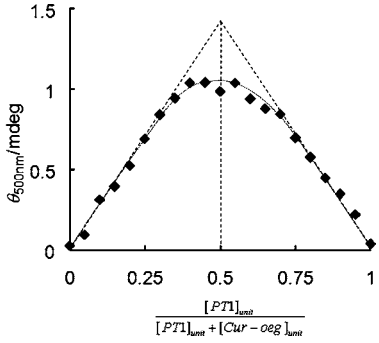

Figure 4. Job's plot using the peak intensity of the first positive Cotton effect at 500 nm ($\theta_{500\ nm}$) of the ICD signal in PT1/Cur-oeg complex; $[PT1]_{unit} + [Cur\text{-}oeg]_{unit} = 0.2$ mM, 25 °C, in water containing 5 vol % DMSO.

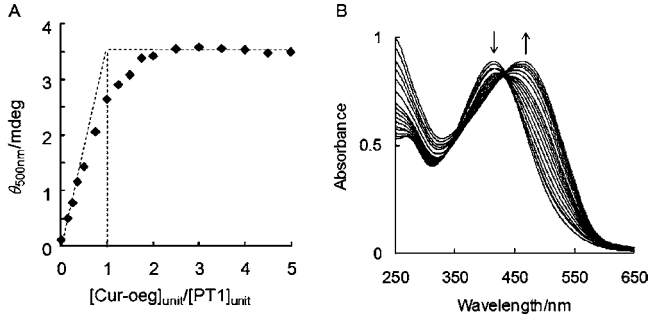

Figure 5. (A) Peak intensity change at 500 nm ($\theta_{500\ nm}$) for ICD of PT1/Cur-oeg complex as a function of the molar ratio of $[Cur\text{-}oeg]_{unit}$ to $[PT1]_{unit}$. (B) Spectral changes of UV/vis absorption of PT1 upon adding Cur-oeg; $[PT1]_{unit} = 0.2$ mM, $[Cur\text{-}oeg]_{unit} = 0-1$ mM, 25 °C, in water containing 5 vol % DMSO.

which is different in the stoichiometry from the "tight" triple-stranded helical structure of PT1/SPG complex.

PT1/Cur-oeg complex showed the splitting-type ICD that displayed a similar pattern with that of PT1/SPG complex (Figure 3), suggesting the formation of right-handed helix with PT1. The stoichiometry of PT1/Cur-oeg complex was 1:1, which is different from the 1:2 stoichiometry of PT1/SPG complex. It is difficult to explain why the stoichiometry is different between these two complexes. Two possible explanations come to our mind; first, Cur-oeg bearing one oligoethylene glycol chain on every glucose unit is more sterically crowded than SPG bearing one glucose side group on every three glucose units. Second, the PT1/SPG complex is a fully packed triple-stranded helix and shows a "rigid" nature, whereas the PT1/Cur-oeg complex is a double-stranded helix having "grooves" as in the case of double-stranded DNAs and can show a "dynamic" nature (vide infra).

Thermoresponsive Properties of the PT1/Cur-oeg Complex. Interestingly, we have found that the PT1/Cur-oeg complex shows novel thermoresponsiveness in the optical properties. As shown in Figure 6, the solution color of the PT1/Cur-oeg complex continuously changed from reddish orange to yellow by changing the temperature from 5 to 85 °C. In addition, the fluorescence also displayed a color change from orange to green with the increase in the temperature.

Parts A−C of Figure 7 show temperature dependencies of the UV/vis absorption, CD, and fluorescence spectra, respectively. The absorption spectrum at 25 °C gave a peak at 458 nm. Upon increasing temperature, the peak was blue-shifted to 403 nm at 85 °C. On the other hand, when the temperature was decreased to 5 °C, the peak was red-shifted to 482 nm: that is, the absorption peak of the PT1/Cur-oeg complex arising from the $\pi-\pi^*$ transition of PT1 was reversibly shifted in response to the temperature change with an 80 nm wide range. As we have confirmed that the spectral change should be induced by the conformational change of the PT1 single chain (but not by the aggregation of PT1), this remarkable spectral shift is ascribable to a change in the effective conjugation length of PT1 in the complex. A fluorescence peak of the PT1/Cur-oeg complex was varied from 533 to 569 nm by a change in the

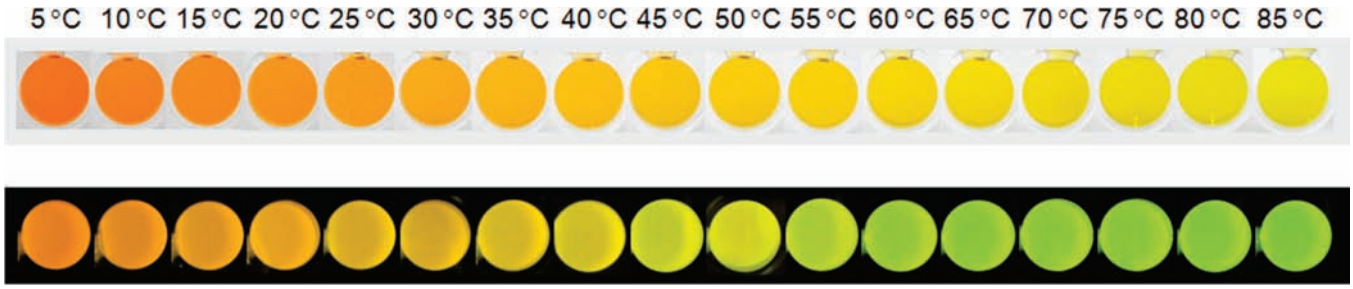

Figure 6. Photographs of the PT1/Cur-oeg complex solution under the temperature control from 5 to 85 °C; upper line: bright images, lower line: fluorescence images (λ_{ex} = 365 nm), $[PT1]_{unit}$ = 0.2 mM, $[Cur\text{-}oeg]_{unit}$ = 0.6 mM, in water containing 5 vol % DMSO.

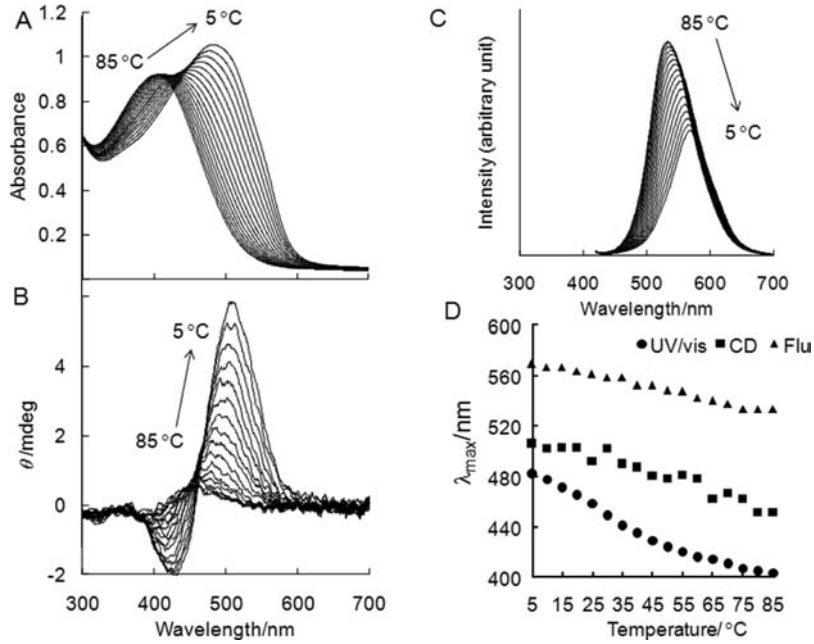

Figure 7. (A) UV/vis absorption, (B) CD, and (C) fluorescence spectra of the PT1/Cur-oeg complex for the temperature change from 85 to 5 °C; in water containing 5 vol % DMSO, $[PT1]_{unit}$ = 0.2 mM, $[Cur\text{-}oeg]_{unit}$ = 0.6 mM, λ_{ex} = 409 nm. (D) Temperature dependence of peak wavelengths of the UV/vis absorption (dot), the first Cotton effect of CD (square), and the fluorescence (triangle).

temperature from 85 to 5 °C. Moreover, the ICD peak of the first positive Cotton effect in the PT1/Cur-oeg complex was also shifted from 511 to 451 nm according to the temperature change from 85 to 5 °C. The decreased ICD intensity at higher temperature can be explained as such that the structural fluctuation occurring at higher temperature causes the uniformity decrease in the helical motif of the PT1/Cur-oeg complex. The peak shifts induced by the temperature change are summarized in Figure 7D. These novel results clearly reveal that thermal stimulus can induce the rearrangement of the PT1/Cur-oeg complex helical structure, changing the effective conjugation length of PT1; that is, the mechanism of the present thermoresponsive system is essentially different from that of conventional thermoresponsive supramolecular assemblies utilizing thermally controlled association−dissociation systems.[19]

As references, "tight" PT1/SPG complex and PT1 itself were compared with "loose" PT1/Cur-oeg complexes under the same temperature conditions (Figure S3A−D and Figure S4A−C, respectively (Supporting Information)). A peak of the PT1/SPG complex in the UV/vis absorption spectrum appeared within a range from 445 to 455 nm between 85 and 5 °C (Figure S3A (Supporting Information)). In fluorescence spectroscopy, it is difficult to find a distinct emission peak shift from 564 nm upon heating or cooling (Figure S3B (Supporting Information)). In the ICD signal of the PT1/SPG complex, the peak wavelength was scarcely changed (Figure S3C (Supporting Information)). These findings consistently support the view that the PT1/SPG complex is classified as a very stable "tight" complex. In the case of PT1 itself, on the other hand, the peak shift of UV/vis absorption spectra induced by the temperature change was only 22 nm at most (Figure S4A (Supporting Information)): this shift value is not so large as that of the PT1/Cur-oeg complex. A fluorescence peak wavelength of PT1 itself was not affected by temperature, whereas the emission intensity was increased at higher temperature (Figure S4B (Supporting Information)). This phenomenon has also been observed for other modified PTs and can be explained as follows: the higher temperature decreases the effective conjugated length, which suppresses the migration efficiency of excited electron through the extended conjugation leading to thermal deactivation of the excited

(19) (a) Tsuda, A.; Sakamoto, S.; Yamaguchi, K.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 15722–15723. (b) Wang, H.; Kaiser, T. E.; Uemura, S.; Würthner, F. *Chem. Commun.* **2008**, 1181–1183. (c) Enozawa, H.; Hasegawa, M.; Takamatsu, D.; Fukui, K.; Iyoda, M. *Org. Lett.* **2006**, *8*, 1917–1920. (d) Morikawa, M.-a.; Yoshihara, M.; Endo, T.; Kimizuka, N. *J. Am. Chem. Soc.* **2005**, *127*, 1358–1359. (e) Kawano, S.; Fujita, N.; Shinkai, S. *Chem.—Eur. J.* **2005**, *11*, 4735–4742. (f) Schenning, A. P. H. J.; Jonkheijm, P.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2001**, *123*, 409–416.

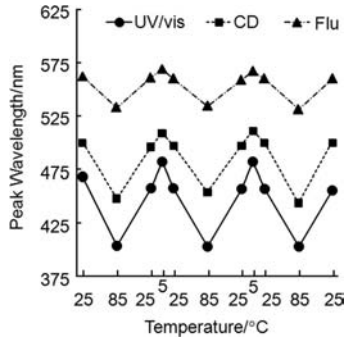

Figure 8. Response against thermal cycles of peak wavelengths for the UV/vis absorption (dot), the first Cotton effect of CD (square), and the fluorescence (triangle).

state.[12b,20] From these findings as summarized in Figures 7D, S3D, and S4C (Supporting Information), one can propose that only the PT1/Cur-oeg complex can express an attractive nature that the spectral properties sensitively response to the temperature change.

Important is the finding that the spectral changes in UV/vis, CD, and fluorescence of the PT1/Cur-oeg complex all show the reversibility under the thermal cycles (Figure 8). Thus, the dynamic behavior can be applied to a "molecular thermometer system".[21] Several similar ideas utilizing phase transition points were reported, as exemplified by a hydration and dehydration system in poly(*N*-isopropylacrylamide) derivatives.[22] However, our system is totally different; it features multireading outputs based on continuous spectral shifts that can be detected even by naked eye observation (in UV/vis absorption and fluorescence) and CD measurements, as shown in Figures 6, 7, and 8.

The behaviors of the PT1/Cur-oeg complex were further characterized at higher temperature by the CD titration and the TEM observation. The titration at 55 °C was conducted in the same manner as the above-described measurements (Figure S5A (Supporting Information)). The titration curve showed that the stoichiometry of the PT1/Cur-oeg complex is also 1:1 at 55 °C. The apparent binding constant between PT1 and Cur-oeg at 55 °C still maintained the sufficiently high value of 10^4 order ($K_{55\ °C} = 1.4 \times 10^4\ M^{-1}$). In UV/vis absorption spectroscopy at 55 °C, an isosbestic point was observed at 420 nm (Figure S5B (Supporting Information)). One can consider from these results that the stability of the PT1/Cur-oeg complex is much less affected by the temperature elevation. A TEM sample of the PT1/Cur-oeg complex was prepared from a hot solution on the heated TEM grid, which was dried at 55 °C (Figure S6A (Supporting Information)). In the TEM image, one-dimensional structure was recognized, which seems to be created by the shrinkage of the extended fibers observed for the 25 °C sample

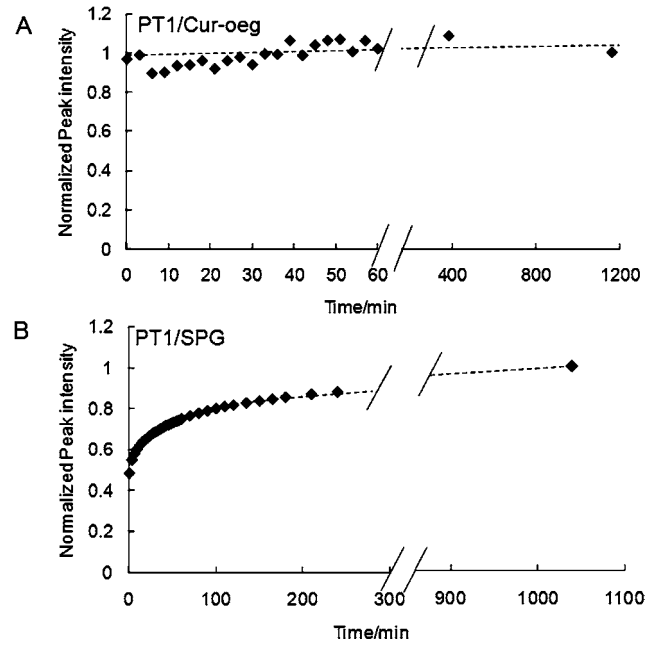

Figure 9. Relative ICD intensity changes of (A) PT1/Cur-oeg complex and (B) PT1/SPG complex as a function of time after mixing of each component. The intensities were normalized by the final intensity as a standard point. $[PT1]_{unit} = 0.2$ mM, $[Cur\text{-}oeg]_{unit} = 0.6$ mM, $[SPG]_{unit} = 0.4$ mM, in water containing 5 vol % DMSO.

(Figures 3D and S6B (Supporting Information)). The shrunk fiber morphology is consistent with the optical measurement results of heated PT1/Cur-oeg complex, where complexed PT1 takes a less planar conformation due to the thermal fluctuation.

The unique thermoresponsiveness of the PT1/Cur-oeg complex is significantly related to the high mobility of the molecular main-chain characteristic of this complex. It is most likely that this flexible motion would arise from the "loose" structure of the PT1/Cur-oeg complex that is different from the "tight" triple-stranded helix of the PT1/SPG complex without thermoresponsiveness. To confirm this hypothesis, we monitored the dynamic complexation processes by kinetic CD measurements. Figure 9 shows the time dependence of the CD intensity for formation of the PT1/Cur-oeg complex and the PT1/SPG complex. In formation of the PT1/Cur-oeg complex, the CD intensity reached an equilibrium maximum soon after mixing. On the other hand, the PT1/SPG complex took a long time (half-life $\approx$ 40 min) to reach the saturated value. One can consider, therefore, that the PT1/Cur-oeg complex keeps the motional freedom to rapidly reach the energy-minimum conformation, whereas the stable PT1/SPG complex features the "tight" polymeric structure and can be formed only through the slow reorganization process.

Color Changes of a Film Prepared from the PT1/Cur-oeg Complex. Parts A and B of Figure 10 show photographs and UV/vis absorption spectra of PT1/Cur-oeg films that were prepared by a wet cast process from the aqueous solution followed by vacuum drying. The as-prepared film showed the orange color with a peak at 469 nm, which was red-shifted by 11 nm from that of the solution sample. This change suggests that solidification of the PT1/Cur-oeg complex as the film induces a partial conformational change in the complex structure. The film color immediately turned into violet upon exposure to moist air, and new peaks appeared at 542 and 580 nm with a shoulder at 511 nm, which are ascribable to the $\pi-\pi^*$ transition of PT1 with the vibronic bands. It is known that this spectral pattern is attributed to formation of a planar PT1 conformer

(20) (a) Murray, K. A.; Holmes, A. B.; Moratti, S. C.; Rumbles, G. *J. Mater. Chem.* **1999**, *9*, 2109–2115. (b) Jung, S.-D.; Hwang, D.-H.; Zyung, T.; Kim., W. H.; Chittibabu, K. G.; Tripathy, S. K. *Synth. Met.* **1998**, *98*, 107–111. (c) Xu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 4457–4460.

(21) (a) Uchiyama, S.; Kawai, N.; de Silva, A. P.; Iwai, K. *J. Am. Chem. Soc.* **2004**, *126*, 3032–3033. (b) Uchiyama, S.; de Silva, A. P.; Iwai, K. *J. Chem. Educ.* **2006**, *83*, 720–727, and references cited therein. (c) Tang, L.; Jin, J. K.; Qin, A.; Yuan, W. Z.; Mao, Y.; Mei, J.; Sun, J. Z.; Tang, B. Z. *Chem. Commun* **2009**, 4974–4976. (d) Engeser, M.; Fabbrizzi, L.; Licchelli, M.; Sacchi, D. *Chem. Commun.* **1999**, 1194–1192. (e) Lupton, J. M. *Appl. Phys. Lett.* **2002**, *81*, 2478–2480.

(22) (a) Balamurugan, S. S.; Bantchev, G. B.; Yang, Y.; McCarley, R. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4872–4876. (b) Choi, J.; Ruiz, C. R.; Nesterov, E. E. *Macromolecules* **2010**, *43*, 1964–1974.

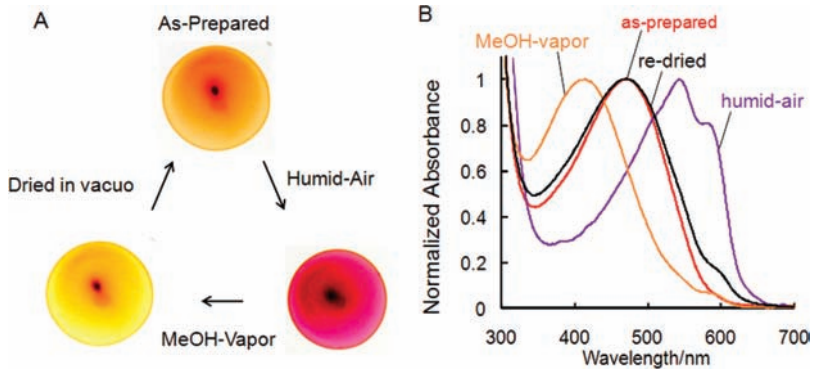

Figure 10. (A) Photographs and (B) normalized UV/vis absorption spectra of a PT1/Cur-oeg film. The as-prepared film was subjected to humid air and methanol vapor and then dried in vacuo again.

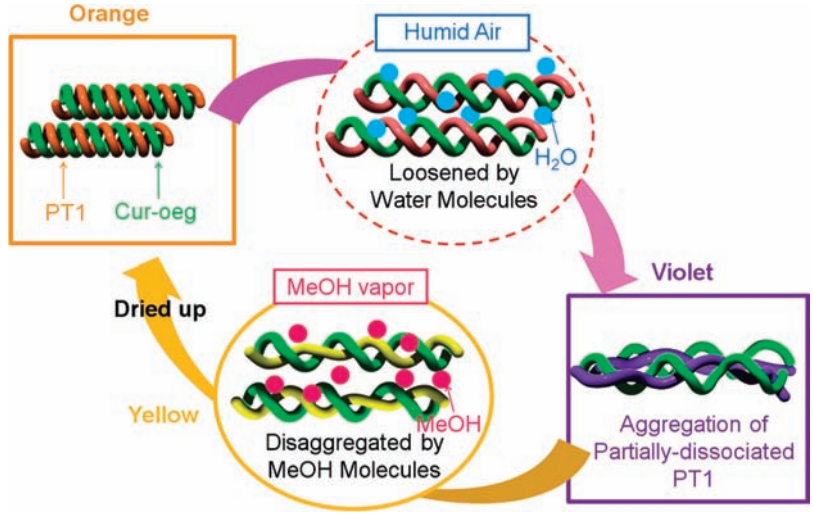

Figure 11. Schematic representation of the vapor-induced color change in PT1/Cur-oeg complex film.

induced by aggregation in an ordered packing manner.[12b,23] The violet color did not come back to the original orange color even after redrying in vacuo. In addition, when a film of the PT1/Cur-oeg complex was prepared by slowly drying under the ambient atmosphere (but not in vacuo), the resultant film directly gave the violet color.

To obtain further insights into the violet color change, aqueous PT1/Cur-oeg complex was mixed with acetone or 1,4-dioxane, which acts as an aggregation-inducing poor solvent for PT1. In 90 vol % organic solvents, the solution color turned into violet, and absorption peaks appeared at 511 nm, 542 nm, and 587 nm (Figure S7A(Supporting Information)). These peaks are consistent with those of the violet film sample. In CD spectroscopy, an ICD signal was observed for the violet-colored solutions (Figure S7B (Supporting Information)). The similar color change and ICD signal were also observed for the aggregated complexes of PT1 with chiral biomolecules.[24] Thus, one can reconfirm that the violet color arises from PT1 aggregation partially dissociated from the PT1/Cur-oeg complex.

From these results, one can propose that in the rapid drying process Cur-oeg wrapping can immobilize the complex structure kinetically, whereas in the slow drying process the PT1 aggregation can occur through partial dissociation of the PT1/Cur-oeg complex. When a 5-fold amount of Cur-oeg was used for preparation of the PT1/Cur-oeg film, formation of such PT1 aggregates was suppressed even under the humid air conditions, and the orange color without PT1 aggregation was maintained. Thus, these results consistently support a view that the intermolecular aggregation of PT1 chains is the origin of the violet color in the PT1/Cur-oeg film.

For the methanol vapor, on the other hand, the film color changed to yellow, and a peak blue-shifted to 412 nm was observed. This change indicates that methanol, which acts as a good solvent for PT1, dissociated the PT1 aggregate, and the PT1 chain possesses a much less planar conformation. Vacuum drying of the methanol-vapor-exposed film provided the orange color film whose absorption peak appeared at 469 nm again.

These results are interpreted as follows (Figure 11): the humid air destabilizes the complex structure and induces aggregation of PT1 chains partially dissociated from the PT1/Cur-oeg complexes in the condensed film state. The PT1 aggregate formed is stable in the film state, but exposure to the good solvent such as methanol can make it swollen and dissociated. After drying from the methanol atmosphere, therefore, the original structure of PT1 can be reconstructed in the PT1/Cur-

(23) (a) Almeida, S.; Rivera, E.; Reyna-González, J. M.; Huerta, G.; Tapia, F.; Aguilar-Martínez, M. *Synth. Met.* **2009**, *159*, 1215–1223. (b) Gonçalves, V. C.; Ferreira, M.; Olivati, C. A.; Cardoso, M. R.; Mendonça, C. R.; Balogh, D. T. *Colloid Polym. Sci.* **2008**, *286*, 1395–1401. (c) Le Bouch, N.; Auger, M.; Leclerc, M. *Macromol. Chem. Phys.* **2008**, *209*, 2455–2462. (d) Garreau, S.; Leclerc, M.; Errien, N.; Louarn, G. *Macromolecules* **2003**, *36*, 692–697. (e) Roux, C.; Leclerc, M. *Macromolecules* **1992**, *25*, 2141–2144.

(24) (a) Li, C.; Numata, M.; Takeuchi, M.; Shinkai, S. *Chem. Asian J.* **2006**, *1*−*2*, 95–101. (b) Li, C.; Numata, M.; Takeuchi, M.; Shinkai, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 6371–6374. (c) Yao, Z.; Li, C.; Shi, G. *Langmuir* **2008**, *24*, 12829–12835.

oeg film. Survey of the literature reveals that there are several examples for chromic changes of polythiophenes against temperature, solvent, chemicals, and so on.[13b,14e,15,20b,23c,25] To the best of our knowledge, however, the reports about "vaporchromism" of the film have still been very limted.[23d,26]

From aqueous PT1 itself, the violet-colored film was obtained through the vacuum-drying process. The absorption peak appeared at 542 nm with shoulders at 585 and 511 nm (Figure S8A (Supporting Information)), indicating that the PT1 chains are enjoying intermolecular aggregation therein. Humid air gave no color change in the PT1 film. In contrast, methanol vapor induced a blue-shift of the absorption peak to 406 nm, indicating that the aggregated PT1 chains were dissociated, owing to the good solubilization ability of methanol. Drying in vacuo from the methanol vapor conditions provided a violet film again. Hence, Cur-oeg wrapping is effective for preventing PT1 chains from aggregation and immobilizing the metastable complex structure in the film state. On the other hand, the robust PT1/SPG complex afforded an orange colored film with an absorption peak at 463 nm (Figure S8B (Supporting Information)). This absorption peak, however, always appeared at the same wavelength even after exposing to the humid air or methanol vapor. Therefore, one can consider that only PT1/Cur-oeg complex, less stable and more flexible than PT1/SPG complex, can reveal multicolor changes sensitive to vapors of water and organics, leading to the unique reversible or irreversible processes. This vaporchromism is useful to develop a new class of vapor sensors for humidity and organics or remote-controllable devices based on the structural changes of CPs.

Conclusion

Chiral conformation of PT1 has successfully been manipulated through the supramolecular wrapping with Cur-oeg. Several novel behaviors reported herein cannot be realized with a stable, "tight" PT1/SPG complex. First, rapid complex formation, without the troublesome denaturation process, has become possible. This is because Cur-oeg exists as a single strand in aqueous solution and the main chain is flexible. Second, the "loose" structure characteristic of PT1/Cur-oeg complex has allowed the precise tuning of the effective conjugation length of PT1 by a temperature change. Thermochromism of polythiophenes is well-known, but most of the responsive functions are based on switching of two-phase structures between aggregation-induced planar and nonplanar conformations.[13b,15,23a,27] On the other hand, our system is a unipolymeric event that features the continuous and wide-range variation of UV/vis absorption and fluorescence wavelengths. Third, the complex structure of PT1 was kept in the film state of PT1/Cur-oeg complex, allowing the partial dissociation in response to the vapor. This property has led to novel "vaporchromism". It is clear, therefore, that the complex structure with a "loose" cohelical motif is important to realize tunable conformational changes even in the film state.

Examples for helix induction in conjugated systems through the interaction with optically active molecules have been reported[1a,e,28] and applied to sensing and switching employing conformational conversion of CPs between two phases including helix inversion,[29] coil transition,[30] and effective conjugation length changes.[31] To the best of our knowledge, however, there are few reports about successive control of the helical conformation of CPs by external stimuli, except for this research. In addition, the PT1/Cur-oeg complex film shows a directional reversibility among three different color structures of PT1. We believe, therefore, that our system not only provides a new concept for the design of stimuli-responsive systems in insulated molecular wires[32] but also presents further extension methods toward finely tunable applications of smart sensors, polarized materials, and switching devices.

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Supporting Information Available: Detailed procedures of sample preparation, ^{13}C NMR spectrum of PT1 itself, additional TEM images and UV/vis absorption, fluorescence, and CD spectra of PT1/Cur-oeg complex, PT1 itself, and Cur-oeg itself in the solution states and the film states. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) (a) Zhang, B.; Zhao, X. *J. Mater. Sci.* **2009**, *44*, 2765–2773. (b) Ewbank, P. C.; Loewe, R. S.; Zhai, L.; Reddinger, J.; Sauvé, G.; McCullough, R. D. *Tetrahedron* **2004**, *60*, 11269–11275. (c) McCullough, R. D.; Ewbank, P. C.; Loewe, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 633–634. (d) Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B.-L.; Suganuma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. *J. Am. Chem. Soc.* **1998**, *120*, 2047–2058. (e) Tachibana, H.; Hosaka, N.; Tokura, Y. *Macromolecules* **2001**, *34*, 1823–1827. (f) Toba, M.; Takeoka, Y.; Rikukawa, M. *Synth. Met.* **2003**, *135*−*136*, 339–340.

(26) Lanzi, M.; Costa-Bizzarri, C.; Della-Casa, C.; Paganin, L.; Fraleoni, A. *Polymer* **2003**, *44*, 535–545.

(27) (a) Faïd, K.; Leclerc, M. *J. Am. Chem. Soc.* **1998**, *120*, 5274–5278. (b) Brustolin, F.; Goldoni, F.; Meijer, E. W.; Sommerdijk, N. A. J. M. *Macromolecules* **2002**, *35*, 1054–1059. (c) Goto, H.; Okamoto, Y.; Yashima, E. *Macromolecules* **2002**, *35*, 4590–4601. (d) Langeveld-Voss, B. M. W.; Peeters, E.; Janssen, R. A. J.; Meijer, E. W. *Synth. Met.* **1997**, *84*, 611–614. (e) Mucci, A.; Parenti, F.; Schenetti, L. *Macromol. Rapid Commun.* **2003**, *24*, 547–550. (f) Gonçalves, V. C.; Balogh, D. *Eur. Polym. J.* **2006**, *42*, 3303–3310. (g) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W. *J. Mol. Struct.* **2000**, *521*, 285–301.

(28) (a) Ho, H.-A.; Béra-Abérem, M.; Leclerc, M. *Chem.*—*Eur. J.* **2005**, *11*, 1718–1724. (b) Majidi, M. R.; Kane-Maguire, L. A. P.; Wallace, G. G. *Polymer* **1995**, *36*, 3597–3599.

(29) (a) Fujiki, M. *J. Am. Chem. Soc.* **2000**, *122*, 3336–3343. (b) Yashima, E.; Maeda, K.; Sato, O. *J. Am. Chem. Soc.* **2001**, *123*, 8159–8160. (c) Sakurai, S.; Okoshi, K.; Kumaki, H.; Yahisma, E. *J. Am. Chem. Soc.* **2006**, *128*, 5650–5651. (d) Sanda, F.; Terada, K.; Masuda, T. *Macromolecules* **2005**, *38*, 8149–8154. (e) Zhao, H.; Sanda, F.; Masuda, T. *Polymer* **2005**, *46*, 2841–2846. (f) Meudtner, R. M.; Hecht, S. *Angew. Chem., Int. Ed.* **2008**, 4926–4930. (g) Maxein, G.; Zentel, R. *Macromolecules* **1995**, *28*, 8438–8440.

(30) Amaya, T.; Saio, D.; Koga, S.; Hirao, T. *Macromolecules* **2010**, *43*, 1175–1177.

(31) Yoon, B.; Lee, S.; Kim, J.-M. *Chem. Soc. Rev.* **2009**, *38*, 1958–1968.

(32) Frampton, M. J.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 1028–1064.