J|A|C|S
ARTICLES

Supramolecular Helical Assembly of an Achiral Cyanine Dye in an Induced Helical Amphiphilic Poly(phenylacetylene) Interior in Water

Toyoharu Miyagawa,[†] Miho Yamamoto,[‡] Reiko Muraki,[‡] Hisanari Onouchi,[†,§] and Eiji Yashima*,[†,‡]

Contribution from the Yashima Super-structured Helix Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), 101 Creation Core Nagoya, 2266-22 Anagahora, Shimoshidami, Moriyama-ku, Nagoya 463-0003, Japan, Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan, and Venture Business Laboratory (VBL), Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

Received December 14, 2006; E-mail: yashima@apchem.nagoya-u.ac.jp

Abstract: A water-soluble amphiphilic poly(phenylacetylene) bearing the bulky aza-18-crown-6-ether pendants forms a one-handed helix induced by L- or D-amino acids and chiral amino alcohols through specific host−guest interactions in water. We now report that such an induced helical poly(phenylacetylene) with a controlled helix sense can selectively trap an achiral benzoxazole cyanine dye among various structurally similar cyanine dyes within its hydrophobic helical cavity inside the polymer in acidic water, resulting in the formation of supramolecular helical aggregates, which exhibit an induced circular dichroism (ICD) in the cyanine dye chromophore region. The supramolecular chirality induced in the cyanine aggregates could be further memorized when the template helical polymer lost its optical activity and further inverted into the opposite helicity. Thereafter, thermal racemization of the helical aggregates slowly took place.

Introduction

The supramolecular assembly of achiral molecules into helical architectures with a controlled helical sense has recently attracted significant attention.[1] Among them, helical J-aggregates of achiral cyanine dyes[2] and porphyrins[3] are particularly interesting because of their potential application to optoelectronic materials[4] as well as models for antennae systems in photosynthesis,[5] together with the relation to the origin of biomolecular homochirality.[6] Water-soluble charged biopolymers, such as DNA,[2a,c,f,3a,d] polypeptides,[2h,3a,c,e] and polysaccharides,[2i,3f] have often been used as templates for the supramolecular chirality induction. The spontaneous generation of optically active J-aggregates without chiral auxiliaries is also possible by chance or through stirring or spinning in one direction.[6]

Recently, we reported that a positively charged poly(phenylacetylene) could trap a hydrophobic chiral guest within its hydrophobic cavity in water, and the resulting helical poly(phenylacetylene) with a predominantly one-handed screw sense

---

[†] ERATO, JST.

[‡] Graduate School of Engineering, Nagoya University.

[§] VBL, Nagoya University.

(1) For recent reviews, see: (a) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097. (b) Elemans, J. A. A. W.; Rowan, A. E.; Nolte, R. J. M. *J. Mater. Chem.* **2003**, *13*, 2661−2670. (c) Spector, M. S.; Selinger, J. V.; Schnur, J. M. *Top. Stereochem.* **2003**, *24*, 281−372. (d) van Bommel, K. J. C.; Friggeri, A.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980−999. (e) Shimizu, T.; Masuda, M.; Minamikawa, H. *Chem. Rev.* **2005**, *105*, 1401−1443. (f) Keizer, H. M.; Sijbesma, R. P. *Chem. Soc. Rev.* **2005**, *34*, 226−234. (g) Ajayaghosh, A.; George, S. J.; Schenning, A. P. H. J. *Top. Curr. Chem.* **2005**, *258*, 83−118. (h) Maeda, K.; Yashima, E. *Top. Curr. Chem.* **2006**, *265*, 47−88. (i) Amabilino, D. B.; Veciana, J. *Top. Curr. Chem.* **2006**, *265*, 253−302.

(2) For recent examples, see: (a) Wang, M.; Silva, G. L.; Armitage, B. A. *J. Am. Chem. Soc.* **2000**, *122*, 9977−9986. (b) Prins, L. J.; Thalacker, C.; Würthner, F.; Timmerman, P.; Reinhoudt, D. N. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 10042−10045. (c) Garoff, R. A.; Litzinger, E. A.; Connor, R. E.; Fishman, I.; Armitage, B. A. *Langmuir* **2002**, *18*, 6330−6337. (d) Würthner, F.; Yao, S.; Beginn, U. *Angew. Chem., Int. Ed.* **2003**, *42*, 3247−3250. (e) von Berlepsch, H.; Kirstein, S.; Böttcher, C. *J. Phys. Chem. B* **2003**, *107*, 9646−9654. (f) Hannah, K. C.; Armitage, B. A. *Acc. Chem. Res.* **2004**, *37*, 845−853. (g) Morikawa, M.; Yoshihara, M.; Endo, T.; Kimizuka, N. *J. Am. Chem. Soc.* **2005**, *127*, 1358−1359. (h) Renikuntla, B. R.; Armitage, B. A. *Langmuir* **2005**, *21*, 5362−5366. (i) Kim, O.-K.; Je, J.; Jernigan, G.; Buckley, L.; Whitten, D. *J. Am. Chem. Soc.* **2006**, *128*, 510−516. (j) Zhao, X.; Schanze, K. S. *Langmuir* **2006**, *22*, 4856−4862.

(3) For recent examples, see: (a) Pasternack, R. F.; Giannetto, A.; Pagano, P.; Gibbs, E. J. *J. Am. Chem. Soc.* **1991**, *113*, 7799−7800. (b) Lauceri, R.; Raudino, A.; Scolaro, L. M.; Micali, N.; Purrello, R. *J. Am. Chem. Soc.* **2002**, *124*, 894−895. (c) Koti, A. S. R.; Periasamy, N. *Chem. Mater.* **2003**, *15*, 369−371. (d) Chen, X.; Liu, M. *J. Inorg. Biochem.* **2003**, *94*, 106−113. (e) Lauceri, R.; De Napoli, M.; Mammana, A.; Nardis, S.; Romeo, A.; Purrello, R. *Synth. Met.* **2004**, *147*, 49−55. (f) Hasegawa, T.; Fujisawa, T.; Numata, M.; Li, C.; Bae, A.-H.; Haraguchi, S.; Sakurai, K.; Shinkai, S. *Chem. Lett.* **2005**, *34*, 1118−1119.

(4) Kobayashi, T. *J-Aggregates*; World Scientific: Singapore, 1996.

(5) (a) Chiefari, J.; Griebenow, K.; Griebenow, N.; Balaban, T. S.; Holzwarth, A. R.; Schaffner, K. *J. Phys. Chem.* **1995**, *99*, 1357−1365. (b) Balaban, T. S.; Tamiaki, H.; Holzwarth, A. R.; Schaffner, K. *J. Phys. Chem. B* **1997**, *101*, 3424−3431. (c) Balaban, T. S.; Bhise, A. D.; Fischer, M.; Linke-Schaetzel, M.; Roussel, C.; Vanthuyne, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2140−2144.

(6) (a) Ohno, O.; Kaizu, Y.; Kobayashi, H. *J. Chem. Phys.* **1993**, *99*, 4128−4139. (b) De Rossi, U.; Dähne, S.; Meskers, S. C. J.; Dekkers, H. P. J. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 760−763. (c) Kirstein, S.; von Berlepsch, H.; Böttcher, C.; Burger, C.; Ouart, A.; Reck, G.; Dähne, S. *ChemPhysChem* **2000**, 146−150. (d) Rubires, R.; Farrera, J.-A.; Ribó, J. M. *Chem.*−*Eur. J.* **2001**, *7*, 436−446. (e) Ribó, J. M.; Crusats, J.; Sagués, F.; Claret, J.; Rubires, R. *Science* **2001**, *292*, 2063−2066. (f) Yamaguchi, T.; Kimura, T.; Matsuda, H.; Aida, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 6350−6355. For chiral J-aggregates formation at the air/water interface, see: (g) Zhang, L.; Lu, Q.; Liu, M. *J. Phys. Chem. B* **2003**, *107*, 2565−2569.

10.1021/ja068951l CCC: $37.00 © 2007 American Chemical Society

induced by the chiral guest could serve as a template for further supramolecular helical arrays of an achiral porphyrin with opposite charges along the helical backbone, resulting in the formation of optically active J-homoaggregates.[7] This unique property of the helical poly(phenylacetylene) as a specific host and template to entrap hydrophobic guests and to arrange achiral dyes in a helical array in water, respectively, promoted us to explore other helical poly(phenylacetylene)s as novel hosts in water.

We now find that a water-soluble neutral poly(phenylacetylene) bearing the bulky amphiphilic aza-18-crown-6 ether pendants (poly-**1**)[8,9] can encapsulate an achiral cyanine dye, 3,3-diethyloxadicarbocyanine iodide (**O-5**), within its hydrophobic cavity in acidic water, resulting in the formation of supramolecular J-aggregates. In the presence of chiral amino acids, such as L- or D-tryptophan (Trp), capable of interacting with the exterior crown ether pendants through specific host−guest complexations, the host polymer forms a predominantly one-handed helical conformation,[8] which further generates optical activity in the cyanine aggregates included in the helical cavity after annealing, thus showing an induced circular dichroism (ICD) in the achiral cyanine chromophore region. Moreover, the supramolecular chirality induced in the cyanine aggregates can be “memorized” even after inversion of the template poly-**1** helicity in the presence of excess Trp with the opposite configuration (Figure 1). Although a number of cyanine aggregates with optical activity based on supramolecular chirality have been synthesized, they are mostly formed on the exterior surfaces of charged biopolymers as a template, except for DNA.[10] To the best of our knowledge, helical cyanine dye aggregates formed within a helical cavity of artificial helical polymers have not yet been reported.[11]

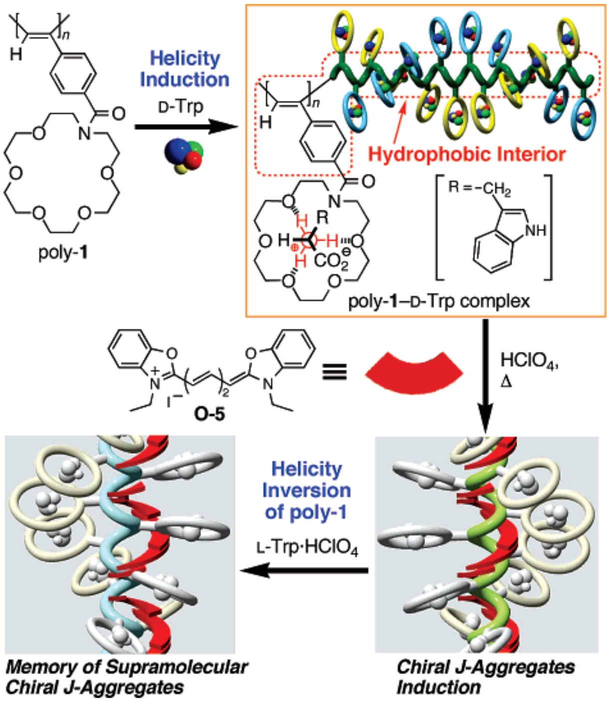


Figure 1. Schematic illustration of one-handed helicity induction in poly-**1** upon complexation with D-Trp, subsequent supramolecular helical aggregate formation of achiral **O-5** within the helical cavity of poly-**1** in acidic water, and memory of the supramolecular chirality after helicity inversion of the poly-**1** by excess L-Trp. The helix senses of poly-**1** are assigned on the basis of the Cotton effect signs of the ICDs of analogous helical polyacetylenes and their helical senses determined by atomic force microscopy (AFM) observations.[12]

Results and Discussion

Inclusion Complexation of Poly-1 with Achiral Cyanine Dyes in Water. As previously reported, poly-**1**, bearing the bulky crown ether as the pendant for the amino acid binding site, formed an induced one-handed helix upon host−guest complexation with L- or D-amino acids in acidic water,[8b] and the complex exhibited an intense ICD in the polymer backbone region. We anticipated that the induced helix could serve as a novel template for further inclusion of an achiral cyanine dye in the hydrophobic helical cavity inside the poly-**1**, resulting in the formation of helically arranged cyanine aggregates. To this end, we first investigated the guest-inclusion ability of optically inactive, but dynamically racemic, helical poly-**1** for a series of well-investigated cationic cyanine dyes (Chart 1) in water, which differ in their heterocyclic groups, and included benzoxazole (**O-5**), benzothiazole (**S-5**), dimethylindole (**I-5**), and quinoline (**Q-5**). Carbocyanines with different conjugation lengths as the linker (**O-3** and **O-7**) were also used. These cyanine dyes are soluble in neutral water but aggregated in acidic water (pH 2.1) and then precipitated, except for **O-7**. However, interestingly, among the structurally similar cyanine dyes, only the **O-5** composed of the less-hindered carbocyanine was entrapped in the hydrophobic cavity of poly-**1** in acidic water, resulting in the formation of J-aggregates (Figure 2), while the other bulky cyanine dyes (**S-5**, **I-5**, and **Q-5**) precipitated even in the presence of poly-**1**, and **O-7** showed no aggregation with

---

(7) Onouchi, H.; Miyagawa, T.; Morino, K.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 2381−2384.

(8) (a) Nonokawa, R.; Yashima, E. *J. Am. Chem. Soc.* **2003**, *125*, 1278−1283. (b) Nonokawa, R.; Yashima, E. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1004−1013. For reviews, see ref 1h and: (c) Yashima, E. *Anal. Sci.* **2002**, *18*, 3−6. (d) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.*−*Eur. J.* **2004**, *10*, 43−51.

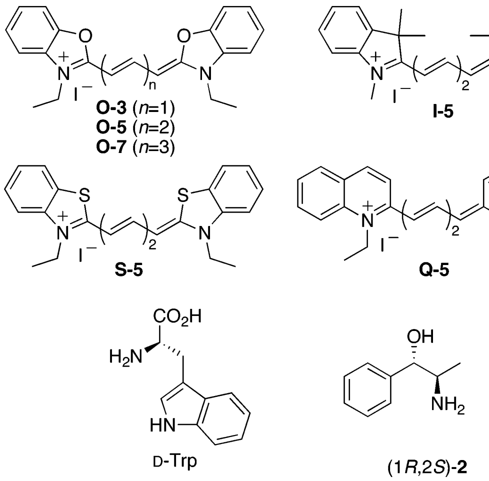
(9) *Cis-transoidal* poly-**1** was prepared by the polymerization of (4-ethynylbenzoyl)monoaza-18-crown-6 with a rhodium catalyst according to the previously reported method.[8a] The stereoregularity of poly-**1** was examined by ^{1}H NMR spectroscopy and found to be almost *cis-transoidal*. The number average molecular weight (M_n) and the distribution (M_w/M_n) were estimated to be 2.1 × 10^4 and 4.1, respectively, as determined by size exclusion chromatography (SEC) with polystyrene standards using tetrahydrofuran (THF) containing 0.1 wt % tetra-*n*-butyl ammonium bromide as the eluent.

(10) Armitage and co-workers reported a DNA-templated assembly of helical cyanine dye aggregates within the minor groove of the DNA by a cooperative chain-growth mechanism; see refs 2c and 2f.

(11) Encapsulation of organic molecules within helical capsules or hollows created by polysaccharides and foldamers is known. See refs 2i, 2j, 3f, and: (a) Hui, Y.; Zou, W. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Eds.; VCH: Weinheim, Germany, 1988; pp 203−221. (b) Prince, R. B.; Barnes, S. A.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 2758−2762. (c) Tanatani, A.; Mio, M. J.; Moore, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 1792−1793. (d) Petitjean, A.; Cuccia, L. A.; Lehn, J.-M.; Nierengarten, H.; Schmutz, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1195−1198. (e) Star, A.; Steuerman, D. W.; Heath, J. R.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2508−2511. (f) Numata, M.; Hasegawa, T.; Fujisawa, T.; Sakurai, K.; Shinkai, S. *Org. Lett.* **2004**, *6*, 4447−4450. (g) Inouye, M.; Waki, M.; Abe, H. *J. Am. Chem. Soc.* **2004**, *126*, 2022−2027. (h) Garric, J.; Léger, J.-M.; Huc, I. *Angew. Chem., Int. Ed.* **2005**, *44*, 1954−1958. (i) Li, C.; Numata, M.; Bae, A.-H.; Sakurai, K.; Shinkai, S. *J. Am. Chem. Soc.* **2005**, *127*, 4548−4549. (j) Kim, O.-K.; Je, J.; Melinger, J. S. *J. Am. Chem. Soc.* **2006**, *128*, 4532−4533. (k) Sanji, T.; Kato, N.; Kato, M.; Tanaka, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 7301−7304. (l) Waki, M.; Abe, H.; Inouye, M. *Chem.*−*Eur. J.* **2006**, *12*, 7839−7847. (m) Ikeda, M.; Furusho, Y.; Okoshi, K.; Tanahara, S.; Maeda, K.; Nishino, S.; Mori, T.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 6491−6495.

(12) (a) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1245−1248. (b) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 5650−5651.

Chart 1. Structures of Achiral Cyanine Dyes, D-Trp, and (1*R*,2*S*)-**2**



poly-**1** (Figure S1). This remarkable guest-selective inclusion of cyanines in the poly-**1** interior is noteworthy.

O-5 exists as a mixture of a monomer and face-to-face π-stacked dimer (H-aggregates)[13] (λ = ca. 575 and 535 nm, respectively) in the presence and absence of poly-**1** in neutral water (a and c in Figure 2). However, upon the addition of aqueous $HClO_4$, the solution color gradually changed from pink to turquoise blue within 3 min, accompanied by a large red shift in the absorption up to ca. 90 nm (λ = ca. 670 nm, d in Figure 2). The large red-shifted absorption is characteristic for the J-aggregate formation, although the peak was quite broad, in contrast to the narrow absorption peaks observed in typical cyanine J-aggregates.[2,4,14] This indicates that the **O-5** may be rather loosely self-assembled into the J-aggregates, which are isolated and stabilized within the hydrophobic cavity of poly-**1** under the acidic condition that free the **O-5** precipitates in the absence of poly-**1**. The changes in the ^{1}H NMR spectra of **O-5** in D_2O in the presence of poly-**1** before and after the addition of $HClO_4$ support such an inclusion of the **O-5** aggregates within the hydrophobic cavity of the poly-**1** interior in acidic water; the aromatic proton resonances derived from **O-5** with poly-**1** completely disappeared when the pD was adjusted to 2.4 by adding an aqueous $HClO_4$ solution, but sharp resonances corresponding to the free **O-5** were again observed when the solution was diluted with CD_3OD (D_2O/CD_3OD = 1/1 (v/v)) because the included **O-5** aggregates in the poly-**1** interior were released into the solvent as a monomer and dimers in the mixed solvent (Figure S2). A possible structure of the **O-5** aggregates will be discussed later. However, the absorption spectra of the **O-5** aggregates were highly time dependent, and the red-shifted band at 670 nm gradually decreased with time after the addition of $HClO_4$ at room temperature (ca. 22−25 °C), and the solution color changed from turquoise blue to yellow (Figure S3), probably due to the decomposition or isomerization of **O-5** in acidic water.[15] We note that the **O-5** aggregates prepared in the presence of poly-**1** under the acidic condition became stable once the solution pH was further adjusted to weakly alkaline (see below).

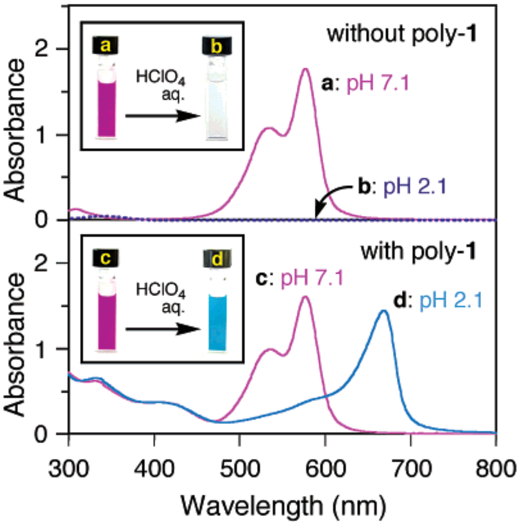


Figure 2. Absorption spectral changes of **O-5** in the absence (a and b) and presence (c and d) of poly-**1** in neutral (a and c, pink lines, pH 7.1) and acidic waters (b, purple dotted line and d, blue line, pH 2.1). **O-5** immediately precipitated at pH 2.1 in the absence of poly-**1**, and the precipitate was removed by filtration before the absorption measurement (b). All spectra were measured in a 0.5 mm quartz cell at room temperature (ca. 22−25 °C). Inset photographs show the visible difference of **O-5** in the absence (a and b) and presence of poly-**1** (c and d) at different pH. [poly-**1**] = 1.0 mg/mL (2.6 mM monomer unit), [**O-5**] = 0.26 mM, and [$HClO_4$] = 0.020 M (b and d).

Chiral J-Aggregates Formation within an Induced Helical Poly-1 Cavity. As previously reported, poly-**1** exhibited a characteristic, split-type intense ICD with L- or D-Trp and an amino alcohol, (1*R*,2*S*)- or (1*S*,2*R*)-**2** (Chart 1), in the polymer backbone region (300−480 nm) in acidic water.[8b] However, the ICD intensity of poly-**1** significantly decreased with increasing pH for Trp, while the poly-**1**−**2** complex maintained an intense ICD even in the neutral and alkaline pH ranges (Figure S4).[8b] This indicates that the crown ether−ammonium ion complexation plays a dominant role for Trp, whereas the hydrophobic interaction between the poly-**1** and **2**, probably inclusion complexation of **2** into the hydrophobic poly-**1** interior, as that for the cyanine dye aggregation, also functions as a chiral bias for the helicity induction in poly-**1** in water.

Taking these differences in the helicity induction mechanism of poly-**1** with Trp and **2** into consideration, we then investigated if a predominantly one-handed helical poly-**1** induced by the optically active Trp and **2** could act as a template for the supramolecular helical assembly of achiral cyanine dyes with a controlled helix sense. This was done by following the changes in the CD spectra of **O-5** in the presence of the induced helical poly-**1** in acidic water.

Ternary mixtures consisting of poly-**1**, **O-5**, and optically active Trp or **2** were prepared in neutral water. Under these

---

(13) (a) Kasatani, K.; Ohashi, M.; Kawasaki, M.; Sato, H. *Chem. Lett.* **1987**, 1633−1636. (b) Buss, V. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 869−870. (c) Oliveira, A. S.; Ferreira, L. F. V.; Worrall, D. R.; Wilkinson, F. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4809−4814. (d) Sidorowicz, A.; Pola, A.; Dobryszycki, P. *J. Photochem. Photobiol., B* **1997**, *38*, 94−97.

(14) The spectroscopic behavior of the cyanine J-aggregates has been extensively studied, but aggregates of **O-5** reported to date are mostly the H-aggregates, and the **O-5**-based J-aggregates showing a characteristic large red-shifted absorption with a narrow band have scarcely been reported. See: Mishra, A.; Behera, R. K.; Behera, P. K.; Mishra, B. K.; Behera, G. B. *Chem. Rev.* **2000**, *100*, 1973−2011. For the H-aggregates of **O-5**, see also refs 2c and 13.

(15) Cyanine dyes are not stable in strong acidic and alkaline solutions. For examples, see: (a) Maruszewski, K.; Sidorowicz, A.; Ulatowska, A.; Podbielska, H.; Srek, W. *J. Mol. Struct.* **1998**, *450*, 193−200. (b) Ye, Y.; Bloch, S.; Kao, J.; Achilefu, S. *Bioconjugate Chem.* **2005**, *16*, 51−61. The fact that neutralization of the acidic solution of the ternary mixture or addition of methanol after 24 h gave absorption spectra being completely different from that of the original **O-5** in neutral water supports the decomposition or isomerization of the **O-5** to other compounds.

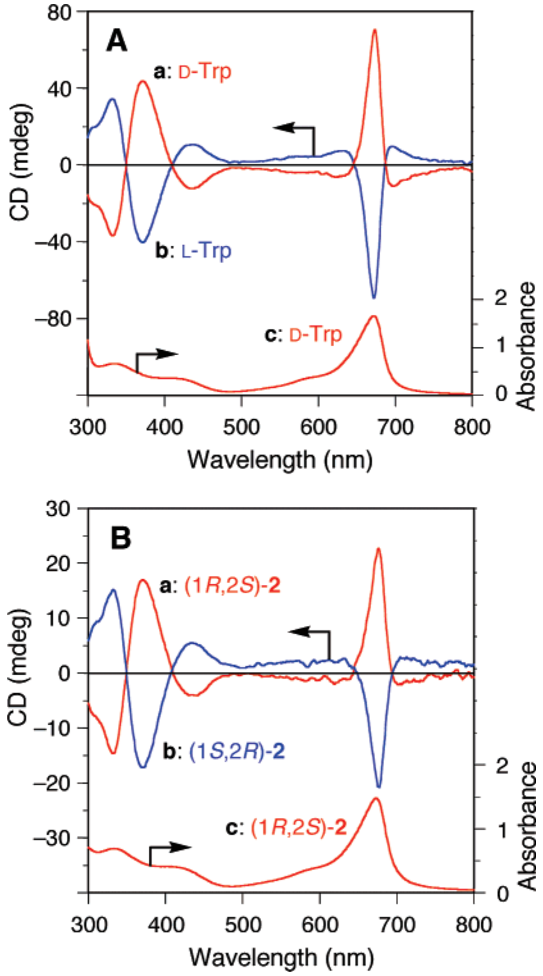


Figure 3. Helical J-aggregates formation of **O-5** in a helical poly-**1** interior. CD (a and b) and absorption spectra (c) of poly-**1** with D- and L-Trp ([Trp]/[poly-**1**] = 10) (A) and (1*R*,2*S*)- and (1*S*,2*R*)-**2** ([**2**]/[poly-**1**] = 50) (B) in the presence of **O-5** in acidic water (pH 2.1 (A) and 1.4 (B)) after heating the solution at 55 °C for 90 (A) and 60 s (B), followed by cooling in an ice bath for 60 s. All spectra were measured in a 0.5 mm quartz cell at room temperature (ca. 24−28 °C). [poly-**1**] = 1.0 mg/mL, [**O-5**]/[poly-**1**] = 0.1, and [$HClO_4$] = 0.036 (A) and 0.20 M (B).

conditions, the poly-**1** showed a very weak or strong ICD with optically active Trp or **2**, respectively, as mentioned above (Figure S4). Upon the addition of aqueous $HClO_4$, the solution colors immediately changed from pink to turquoise blue without any precipitation, accompanied by a large red shift in the absorption up to ca. 90 nm (c in Figure 3), as observed in the binary system of poly-**1** and **O-5** together with the appearance of an intense ICD in the polymer backbone region in the presence of Trp, indicating the J-aggregate formation of **O-5** and the induction of an excess of one helical sense of poly-**1** in acidic water. Although the cyanine aggregates showed almost no ICD in the chromophore regions at this stage, to our surprise, we observed extraordinarily intense ICDs in the **O-5** chromophore regions after annealing the samples at 55 °C for 90 (Trp) and 60 s (**2**), followed by cooling in an ice bath for 60 s (Figure 3).[16] Each pair of enantiomers of Trp and **2** clearly exhibited mirror-image ICDs from each other in both the poly-**1** and **O-5** chromophore regions. We note that the ICD intensity in the **O-5** aggregate region was found to be very sensitive to the heating temperature, time, and the $HClO_4$ concentration. The CD spectra in Figure 3 were measured under the optimized conditions (see Figures S5−S8).[17,18] These observations indicate that the as-prepared **O-5** aggregates before annealing may be racemic and composed of equal amounts of right- and left-handed helices, which reassemble into helical aggregates with a predominant screw sense after annealing under the control of the induced helical poly-**1** in acidic water.[19]

The helical **O-5** aggregates were stable at temperatures below 10 °C, but the ICD intensity gradually decreased with the increasing temperature (15−25 °C) and almost disappeared at ca. 25 °C within 8 h in acidic water, accompanied by changes in the absorption spectra. Similar time-dependent absorption spectral changes were observed for the racemic **O-5** J-aggregates in the presence of the poly-**1** template with no chiral additives due to decomposition or isomerization of **O-5** in acidic water, as already described (see Figure S3).[15]

The pH effect on the stability of the helical **O-5** J-aggregates induced by the helical poly-**1** complexed with D-Trp and (1*R*,2*S*)-**2** was then investigated (Figure 4). **O-5** exists in monomeric and dimeric forms in neutral and alkaline waters.[13] However, interestingly, the absorption peak due to the **O-5** J-aggregates trapped within the hydrophobic cavity of the (1*R*,2*S*)-**2**−poly-**1** almost remained in alkaline water even at pH 12.3 (Figure 4B). Moreover, the ICD intensity of the helical J-aggregates significantly increased with the increasing solution pH, although the ICD intensity of the polymer backbone region slightly decreased. These results suggest that the helical **O-5** J-aggregates are stabilized within the helical cavity of the poly-**1** template and hardly dissociate into alkaline solution under the conditions at which **O-5** favorably exists in monomeric and dimeric forms. In addition, the helical **O-5** aggregates induced by the (1*R*,2*S*)-**2**−poly-**1** complex were markedly stable in weak alkaline water, and their ICDs hardly changed with time at 30 °C for 8 h (Figure S9). On the contrary, the optical activity of the helical **O-5** J-aggregates induced by the D-Trp−poly-**1** complex significantly decreased with the increasing solution pH accompanied by a decrease in the ICD intensity of the polymer backbone region (Figure 4A) because, in alkaline water, Trp cannot efficiently interact with the pendant crown ether residues, as mentioned above, so that the chirality of the **O-5** J-aggregates almost disappeared at pH 12.2.

Memory of Supramolecular Helical J-Aggregates. A more interesting phenomenon related to the chiral memory effect[3b,e,7,20] was observed in the supramolecular helical J-aggregates of **O-5** trapped inside the helical poly-**1** induced by D-Trp and (1*R*,2*S*)-**2** and loosely isolated from the surroundings during the addition

---

[16] When the one-handed helicity was first induced in poly-**1** with D-Trp or (1*R*,2*S*)-**2** in acidic water, then **O-5** was added, but the J-aggregates showed no ICD before annealing the mixture at high temperature.

[17] The optically active **O-5** aggregates showed no linear dichroism. The **O-5** aggregates on double, triple, and quadruple helices of DNA as templates, but the aggregate structures are clearly different from the present J-aggregates because of differences in their absorption and CD spectra. See refs 2c, 2f, and: (a) Chen, Q.; Kuntz, I. D.; Shafer, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 2635−2639. (b) Ren, J.; Chaires, J. B. *J. Am. Chem. Soc.* **2000**, *122*, 424−425.

[18] In the presence of a higher amount of **O-5** ([**O-5**]/[poly-**1**] > 0.1 (mol/mol)), the polymer complexed with **O-5** precipitated under acidic conditions. Therefore, the molar ratio ([**O-5**]/[poly-**1**]) was fixed at 0.1. A molecular modeling study suggests that the helical cavity of poly-**1** composed of 20 monomer units may be occupied by five **O-5** molecules (see Figure 7). This means that approximately 40% of the poly-**1** cavity is likely occupied by 0.1 equiv of **O-5**.

[19] For kinetically controlled self-assembly of a chiral cyanine dye, see: Lohr, A.; Lysetska, M.; Würthner, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 5071−5074.

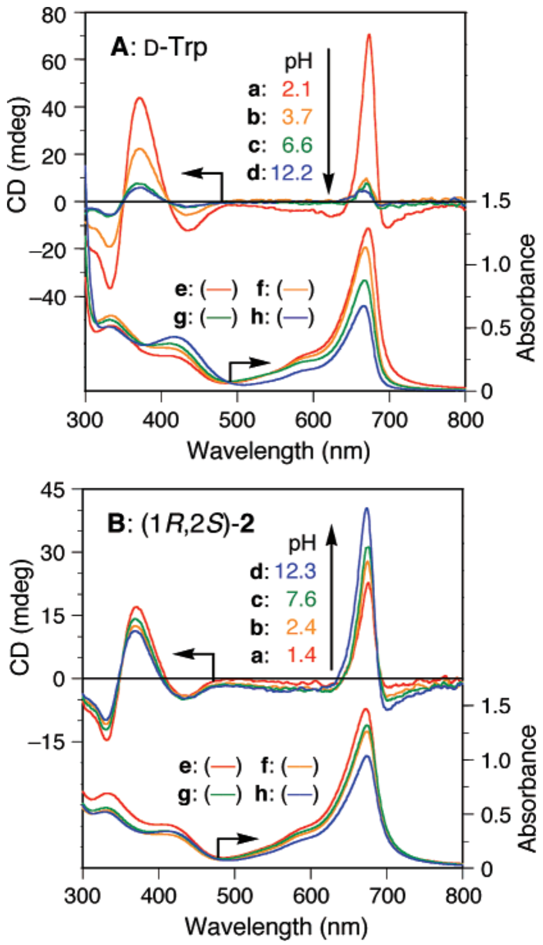


Figure 4. CD (a−d) and absorption spectral changes (e−h) in chiral J-aggregates of **O-5** induced by the helical poly-**1** assisted by D-Trp ([D-Trp]/[poly-**1**] = 10) (A) and (1*R*,2*S*)-**2** ([(1*R*,2*S*)-**2**]/[poly-**1**] = 50) at different pHs. The pH was adjusted by adding NaOH(aq) to the original acidic polymer solution at pH 2.1. All spectra were measured at room temperature (ca. 25−26 °C) in a 0.5 mm quartz cell. [poly-**1**] = 1.0 mg/mL; [**O-5**]/[poly-**1**] = 0.1.

experiments of the opposite enantiomers to the helical **O-5** aggregates in acidic water (Figure 5). Apparently, the optical activity due to the one-handed helicity of poly-**1** was completely lost after the addition of equivalent amounts of L-Trp and (1*S*,2*R*)-**2** to the helical **O-5** J-aggregate acidic solutions containing the D-Trp− and (1*R*,2*S*)-**2**−poly-**1** complexes, respectively, because Trp and **2** exist as a racemic mixture in the solutions (b in Figure 5). The further addition of L-Trp and (1*S*,2*R*)-**2** produced an inversion of the Cotton effects, indicating inversion of the helicity of poly-**1**, as evidenced by the mirror-image ICDs in the poly-**1** chromophore regions (300−480 nm) (c in Figure 5). However, rather surprisingly, the helical J-aggregates of **O-5** maintained their optical activity, and their ICDs hardly changed, accompanied by negligible changes in their absorption spectra (see also Figure S10). These results suggest that the supramolecular chirality of the **O-5** J-aggregates induced within the template poly-**1** helical cavity is maintained even after the template helical polymer is inverted into the opposite helicity (Figure 1). In acidic water, the ICD intensities gradually decreased with time, accompanied by significant changes in their absorption spectra, and the **O-5** J-aggregates lost their chiral memory at 30 °C within several hours because of decomposition or isomerization of the cyanine dye under the acidic conditions, as observed for a similar decrease in the ICD intensity of the chiral J-aggregated **O-5** induced by a preferred helical poly-**1** assisted by (1*R*,2*S*)-**2** (see Figure S9).

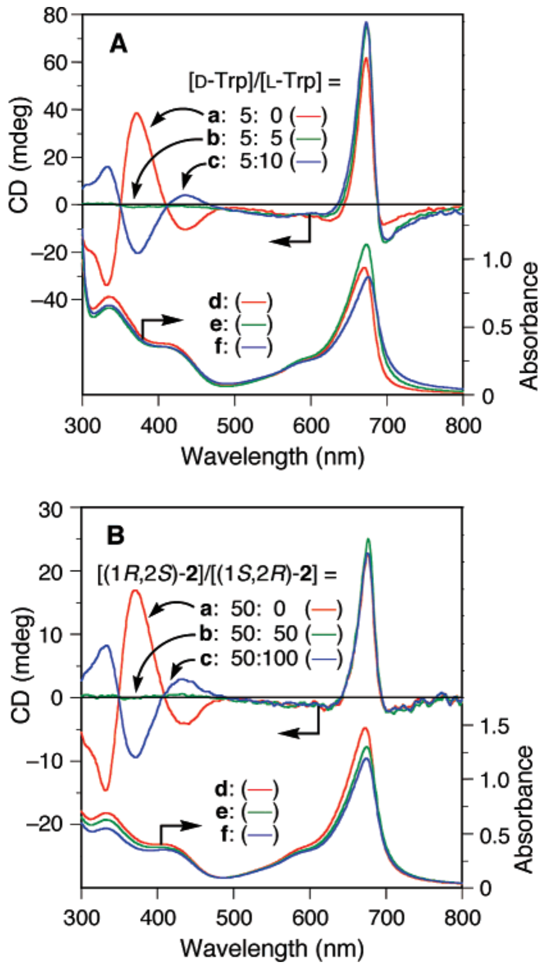


Figure 5. CD (a−c) and absorption spectral changes (d−f) in chiral J-aggregates of **O-5** induced by the helical poly-**1** assisted by D-Trp ([D-Trp]/[poly-**1**] = 5) (A) and (1*R*,2*S*)-**2** ([(1*R*,2*S*)-**2**]/[poly-**1**] = 50) in acidic water (pH 2.1 (A) and 1.4 (B)) upon the addition of L-Trp ([L-Trp]/[D-Trp] = 0 (a and d, red lines), 1/1 (b and e, green lines), and 2/1 (c and f, blue lines)) (A) and (1*S*,2*R*)-**2** ([(1*S*,2*R*)-**2**]/[1*R*,2*S*]-**2**) = 0 (a and d, red lines), 1/1 (b and e, green lines), and 2/1 (c and f, blue lines)) (B), respectively, at room temperature (ca. 24−25 °C). All spectra were measured in a 0.5 mm quartz cell. [poly-**1**] = 1.0 mg/mL, [**O-5**]/[poly-**1**] = 0.1, and [$HClO_4$] = 0.036 (A) and 0.20 M (B).

Under neutral and weakly alkaline conditions, **O-5** is stable in solution, and the same memory experiments were performed at pH 8.9 for the supramolecular helical J-aggregates of **O-5** trapped inside the helical poly-**1** induced by (1*R*,2*S*)-**2** or (1*S*,2*R*)-**2**. As expected, the helical J-aggregated **O-5** induced by the helical poly-**1**−(1*R*,2*S*)-**2** complex maintained its optical activity in the presence of (1*S*,2*R*)-**2** ([(1*R*,2*S*)-**2**]/[(1*S*,2*R*)-**2**] = 1/1 and 1/2). However, the ICD intensities of the **O-5**

---

(20) (a) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449−451. (b) Maeda, K.; Morino, K.; Okamoto, Y.; Sato, T.; Yashima, E. *J. Am. Chem. Soc.* **2004**, *126*, 4329−4342. (c) Morino, K.; Watase, N.; Maeda, K.; Yashima, E. *Chem.*−*Eur. J.* **2004**, *10*, 4703−4707. (d) Hasegawa, T.; Morino, K.; Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E. *Macromolecules* **2006**, *39*, 482−488. For supramolecular chiral memory effect, see refs 3b, 3e, and: (e) Furusho, Y.; Kimura, T.; Mizuno, Y.; Aida, T. *J. Am. Chem. Soc.* **1997**, *119*, 5267−5268. (f) Sugasaki, A.; Ikeda, M.; Takeuchi, M.; Robertson, A.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3259−3264. (g) Prins, L. J.; de Jong, F.; Timmerman, P.; Reinhoudt, D. N. *Nature* **2000**, *408*, 181−184. (h) Kubo, Y.; Ohno, T.; Yamanaka, J.; Tokita, T.; Iida, T.; Ishimaru, Y. *J. Am. Chem. Soc.* **2001**, *123*, 12700−12701.

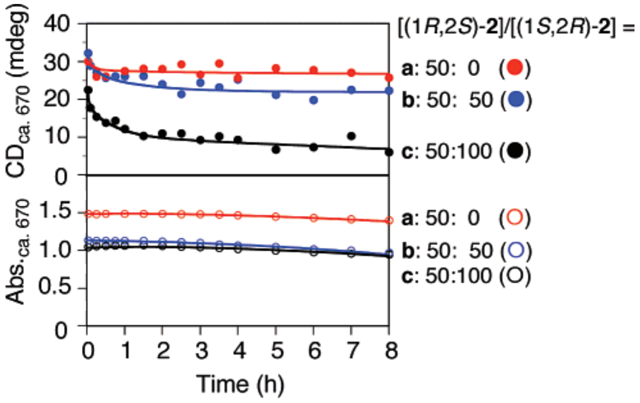


Figure 6. Time-dependent CD and absorbance intensity changes for the chiral J-aggregates of **O-5** induced by the helical poly-**1** assisted by (1*R*,2*S*)-**2** ([(1*R*,2*S*)-**2**]/[poly-**1**] = 50) (a) and after the further addition of (1*S*,2*R*)-**2** ([(1*R*,2*S*)-**2**]/[(1*S*,2*R*)-**2**] = 1/1 (b) and 1/2 (c)) in water at pH 8.9. Changes in the CD intensity (top) and absorbance (bottom) at ca. 670 nm were followed in a 0.5 mm cell at 25 °C. [poly-**1**] = 1.0 mg/mL; [**O-5**]/[poly-**1**] = 0.1.

aggregates gradually decreased with time at 25 °C (Figure 6), accompanied by negligible changes in the absorption spectra. These results suggest that the helical J-aggregates of **O-5** may slowly racemize once the template helical polymer loses its optical activity (b in Figure 6), and the decrease in the optical activity of **O-5** becomes much faster when the poly-**1** is inverted into the opposite helix (c in Figure 6). The racemization rate of the helical **O-5** aggregates at [(1*R*,2*S*)-**2**]/[(1*S*,2*R*)-**2**] = 1/1 depended on the concentration of **O-5** and tended to be faster when the solution was diluted with water at the constant pH of 8.9. We then followed the changes in the ICD intensities of the helical **O-5** aggregates in a slightly diluted solution ([poly-**1**] = 0.6 mg/mL, [**O-5**]/[poly-**1**] = 0.1, [(1*R*,2*S*)-**2**]/[(1*S*,2*R*)-**2**] = 1/1) at different temperatures. On the basis of the first-order decrease in the ICD intensities followed by the Arrhenius plot (Figure S11 and Table S1), the activation energy E_a for the thermal racemization of the helical **O-5** aggregates and the half-life period at 25 °C were estimated to be 28.9 kcal/mol and 5.5 h, respectively.[21]

The chiral memory of the self-assembled supramolecular J-aggregates has also been achieved, in particular for charged achiral porphyrins assisted by chiral, small molecules or biopolymers as the template in water,[3b,e,7] but the chiral J-aggregates were likely formed on the chiral template exterior surfaces, resulting in rather large aggregates. The present chiral J-aggregates were formed within the helical cavity in a helical polymer induced by a small chiral molecule. This process is considered to be a typical example of the hierarchical amplification of chirality, whereby the chiral information of small molecules first transfers to the macromolecular helicity of a dynamic helical polymer with an excess single-handed helix. Subsequently, achiral cyanine dyes assemble into helical aggregates with a controlled helix sense within the helical cavity of the induced helical polymer as the template.

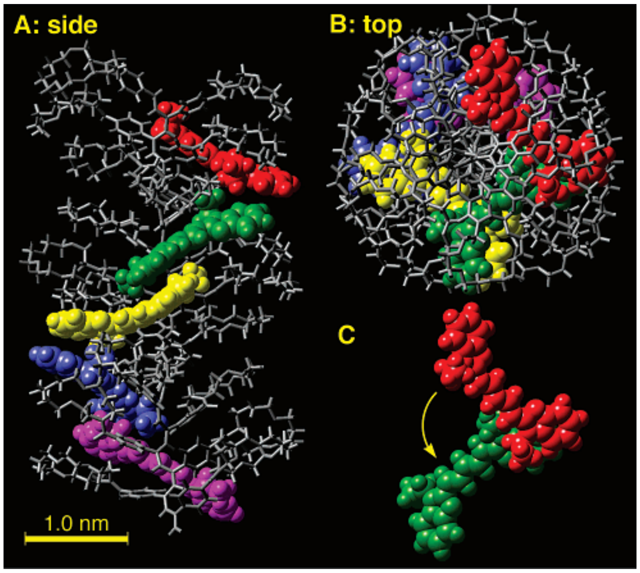


Figure 7. A possible structure of a helically twisted **O-5** aggregate within the hydrophobic cavity of a helical poly-**1** (20 mer). Shown are space-filling (**O-5**) and cylinder (poly-**1**) models in the side (A) and top views (B). Trp or **2** is omitted for clarity. The main chain has a left-handed helix with a right-handed helical array of the pendants; the self-assembled **O-5** is encapsulated with a right-handed helical array within the helical cavity of poly-**1**, and the adjacent **O-5** molecules adopt a counterclockwise orientation (C).

Although we have no direct evidence for the structure of the chiral J-aggregates of **O-5** encapsulated in a helical cavity of poly-**1** due to the difficulty in determining their structures by NMR (Figure S2), a possible model can be proposed on the basis of the calculated helical structure of a poly(phenylacetylene)[22] together with the present results (Figure 7). The helical poly-**1** induced by the optically active Trp or **2** has either a right- or left-handed helical structure due to the appearance of an ICD in the polymer backbone region. A helical groove or ditch, with regularly arranged amphiphilic crown ether residues, exists along the helical axis. On the basis of the Cotton effect signs of the ICDs of analogous helical polyacetylenes, and their helical senses determined by AFM observations,[12] the poly-**1**, showing a positive second Cotton effect at ca. 370 nm, can be assigned to be a left-handed helix with a right-handed helical array of the pendants (Figure 7). The polar crown ether groups are located outside, and hydrophobic aromatic groups are placed inside the π-conjugated polymer main chain so that hydrophobic cyanine dyes that fit in the cavity size, such as **O-5**, can move into the hydrophobic right-handed helical groove. Because the helix sense of the J-aggregates may be determined by the twist sense of the groove in the template helical polymer, the self-assembled **O-5** may be encapsulated with a right-handed helical array within the helical cavity of poly-**1** induced by D-Trp and (1*R*,2*S*)-**2** in a head-to-tail fashion like a circular staircase. This speculation was supported by the red-shifted absorption band and the ICD induction of the self-assembled **O-5**. The J-aggregated **O-5** entrapped in the helical cavity of poly-**1** induced by D-Trp and (1*R*,2*S*)-**2** exhibited an intense positive peak at ca. 670 nm as well as a weak, but apparent, negative peak at ca. 700 nm (Figures 3−5). This split-type ICD may be indicative of a helical J-aggregate formation of **O-5** with a right-handed helical array because the adjacent **O-5** molecules adopt a counterclockwise orientation (Figure 7C).

---

(21) When the helical **O-5** aggregates were diluted with 0.20 M NaClO$_4$ (pH was adjusted to 9.0) instead of water, the racemization took place much slower than when diluted with water. The reason is not clear at the present time, but electrostatic interactions between **O-5** and salts, which may prevent the effective stacking of **O-5**, may be taken into consideration.

(22) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6345−6359.

In addition, the supramolecular helical chirality of the **O-5** J-aggregates, once formed by assistance of the helical polymer template, can be maintained even after inversion of the helicity of the template, as described above. We emphasize that, in sharp contrast to the electrostatic basis, charged DNA−dye helical aggregate systems,[2a,c,f] the helical poly-**1** is neutral and specifically encapsulates the hydrophobic **O-5** J-aggregates, which may be bound loosely within the helical cavity through rather weak hydrophobic interactions. Therefore, the J-aggregates of **O-5** entrapped in the helical cavity of poly-**1** may be memorized after the helicity inversion of poly-**1** since the favorable van der Waals interaction between each dye may be strong enough to maintain the helicity of the J-aggregates after the helicity inversion of the template polymer for a short while. In other words, if the template polymer is a charged polymer like DNA, the helical J-aggregated structure will not be memorized after inversion of the template helicity because the helical J-aggregates bind strongly with the charged template polymer through electrostatic interactions so that the helicity of the J-aggregates will invert immediately. Apparently, a further study is necessary to elucidate the structure of the helical aggregates and the mechanism of helicity induction and its memory.

Conclusions

In summary, we have demonstrated that a water-soluble neutral poly(phenylacetylene) can specifically trap an achiral cyanine dye in its cavity inside the polymer in water, and the helical poly(phenylacetylene) induced by chiral molecules can serve as a novel template for the supramolecular chirality induction in the achiral cyanine dye, resulting in the formation of helical J-aggregates. The supramolecular chirality of the J-aggregates, once formed, can be maintained without the assistance of the template helical polymer. The results described here indicate a new and promising approach for producing supramolecular helical structures from achiral molecules based on the self-assembly of organic dyes assisted by a one-handed helicity induction in a dynamically racemic helical poly(phenylacetylene). We previously reported that an induced helical poly(phenylacetylene) by small chiral molecules could be memorized when the chiral molecules are replaced by achiral ones.[20a−d] Therefore, this memory effect combined with the present results implies that the supramolecular chirality of helical aggregates composed of achiral chromophores may be memorized by a template polymer with the macromolecular helicity memory even in the absence of chiral molecules used as a helicity inducer. In addition, we believe that the already-prepared water-soluble, optically active helical polyacetylenes[1h,8d,23] and polyisocyanides[24] may be used as novel hosts for the enantioselective encapsulation of chiral dyes in their hydrophobic helical cavities. The work is now in progress in our laboratory.

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA068951L

---

(23) For examples, see: (a) Li, B. S.; Cheuk, K. K. L.; Salhi, F.; Lam, J. W. Y.; Cha, J. A. K.; Xiao, X.; Bai, C.; Tang, B. Z. *Nano Lett.* **2001**, *1*, 323−328. (b) Yashima, E.; Maeda, K.; Sato, O. *J. Am. Chem. Soc.* **2001**, *123*, 8159−8160. (c) Maeda, K.; Kamiya, N.; Yashima, E. *Chem.−Eur. J.* **2004**, *10*, 4000−4010. (d) Lam, J. W. Y.; Tang, B. Z. *Acc. Chem. Res.* **2005**, *38*, 745−754. (e) Maeda, K.; Mochizuki, H.; Watanabe, M.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 7639−7650.

(24) For examples, see: (a) Cornelissen, J. J. L. M.; Donners, J. J. J. M.; de Gelder, R.; Graswinckel, W. S.; Metselaar, G. A.; Rowan, A. E.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *Science* **2001**, *293*, 676−680. (b) Ishikawa, M.; Maeda, K.; Mitsutsuji, Y.; Yashima, E. *J. Am. Chem. Soc.* **2004**, *126*, 732−733. (c) Ishikawa, M.; Taura, D.; Maeda, K.; Yashima, E. *Chem. Lett.* **2004**, *33*, 550−551. (d) Hase, Y.; Ishikawa, M.; Muraki, R.; Maeda, K.; Yashima, E. *Macromolecules* **2006**, *39*, 6003−6008.