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Molecular-Level Helical Stack of a Nucleotide-Appended Oligo(*p*-phenylenevinylene) Directed by Supramolecular Self-Assembly with a Complementary Oligonucleotide as a Template

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Abstract: The nucleotide-appended oligo(*p*-phenylenevinylene), {bis[2,5-bis(2-methoxyethoxy)-1,4-phenylene]bis(2,1-ethenediyl-1,4-phenylenemethylene)}bis(2′-deoxy-3′-thymidylic acid) (**8**), has been synthesized, and self-assembly of the single-component **8** and binary self-assembly of **8** with a complementary single-stranded 20-meric oligodeoxyadenylic acid (**9**) have been examined in aqueous solutions. Atomic force microscopy (AFM), UV−visible (UV−vis), and circular dichroism (CD) measurements revealed that right-handed helical stacks with 6.4- and 5.1-nm diameters self-assemble from the binary components of **8** and **9** as a template depending on the residual stoichiometry of the two components (thymine (T):adenine (A) = 1:1 and T:A = 2:1, respectively). The concentration of **9** was found to strongly influence the CD spectra of **8** in aqueous solutions. Consequently, we concluded that the one side of the thymine moieties in the stacked assemblies of **8** complexes with a single chain of **9**. Complementary T−A base pairs thus formed and induced helical stack of the oligo(*p*-phenylenevinylene)s in the binary self-assembly. In contrast, self-assembly of the single-component **8** and binary self-assembly of **8** with the noncomplementary 20-meric oligothymidylic acid (**10**) produced no remarkable formation of fibrous structures like helical stacks.

Introduction

Molecular recognition-driven self-assembly, established by J.-M. Lehn,[1] has been widely developed for two decades. For example, complementary hydrogen bonding has been implemented to direct molecular self-assembly into supramolecular fibers,[2] liquid crystals,[3] helical columnar structures,[4] dendrimers,[5] and supramolecular membranes.[6] DNA has also attracted much attention as a building block to fabricate versatile nanostructures since molecular recognition ability is already incorporated in the DNA molecules.[7] Homoditopic 1,ω-amphiphiles (bolaamphiphiles) possess a hydrophobic skeleton and two water-soluble groups on both ends. If the hydrophilic moieties with hydrogen-bonding functionalities are connected to both ends of a hydrophobic spacer, such bolaamphiphiles generally form stable one-dimensional supramolecular fibers in water.[8] We reported spontaneous formation of a fibrous network from nucleotide-appended bolaamphiphiles in which 3′-phosphorylated thymidine moieties are connected to both ends of an oligomethylene spacer.[9] When the thymidylic acid-appended bolaamphiphiles are allowed to interact with strands of oligad-

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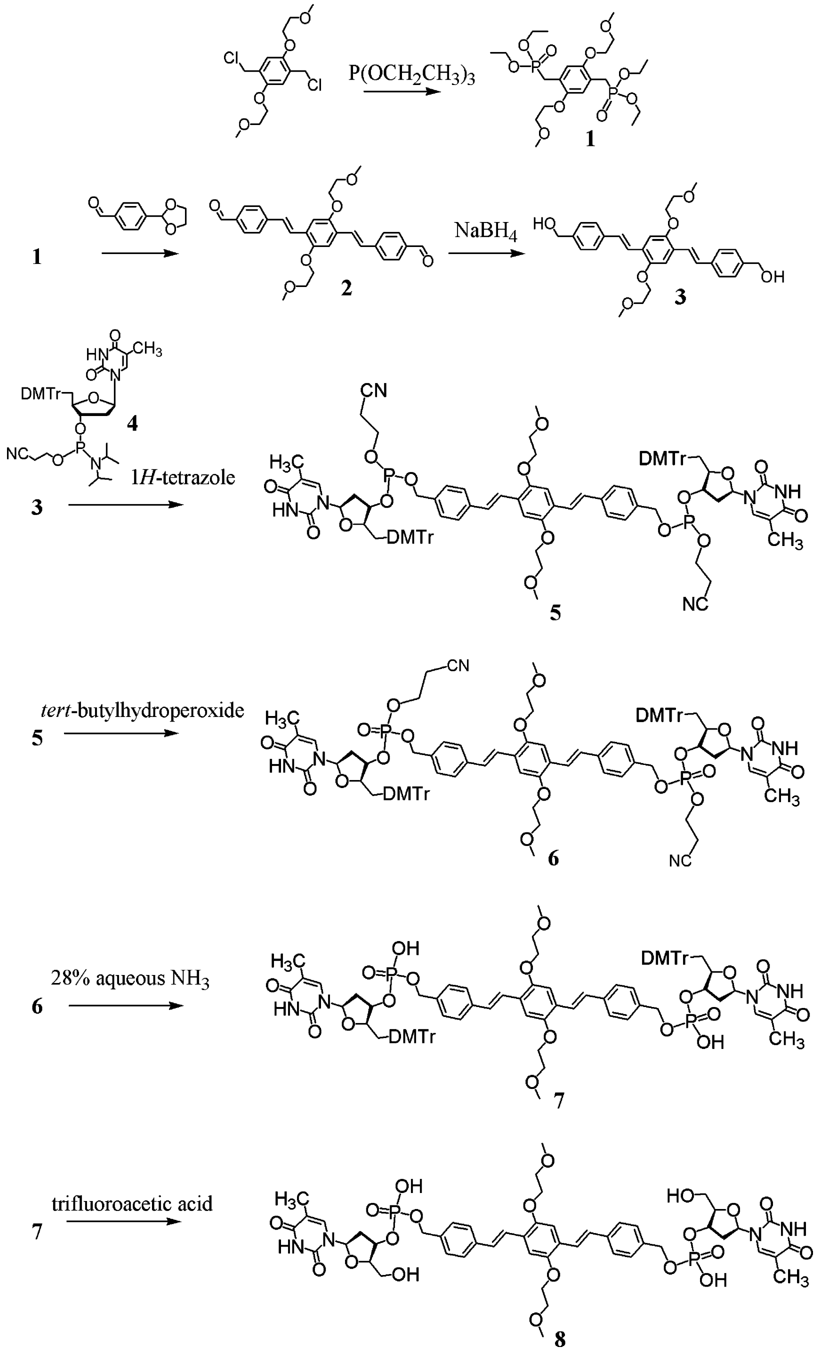
Scheme 1



enylic acid, complementary A−T hydrogen bonding results in the formation of helical stacks with a DNA-like double helix.[10]

On the other hand, it is nowadays a challenging theme to synthesize well-defined structures of π-conjugated oligo(*p*-phenylenevinylene) (OPV) assemblies as an application toward molecular electronic devices.[11] We also reported self-assembled multicomponent systems of OPVs with other dyes and observed efficient energy- and electron-transfer properties.[12] Inspiration from these works has allowed us to design a new bola-shape molecule **8** (Scheme 1) that possesses an oligo(*p*-phenylenevinylene) (OPV) core instead of an oligomethylene spacer chain and a thymidylic acid at both ends of the molecule. The thymidylic acid moieties impart strong hydrophilicity and chirality as well as molecular recognition ability to the molecular building block. Moreover, π-conjugated OPV moieties generally self-assemble into π-stacked structures, which have also been observed in aqueous systems.[13] Combining all knowledge allows us to yield the concept of a supramolecular donor/acceptor system in which the sequence of complementary single-stranded

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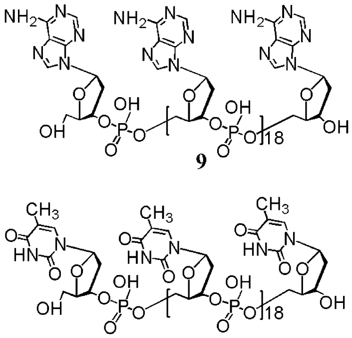
Chart 1



9

10

oligodeoxy nucleotides (ssODNs) may regulate the exact positioning of cytidylic acid-functionalized acceptor molecules inside donor OPV assemblies. To date, only DNA−perylene conjugates[14] or oligonucleotide−perylenediimide conjugates[15] in which DNA is covalently connected to the dye molecules have induced stacking of π-conjugated molecules. In this paper we describe the synthetic approach toward molecular-level helical stacks by supramolecular self-assembly of the thymidylic acid-appended OPV molecules with the complementary 20-meric adenylic acid **9** (Chart 1) as a template in aqueous solutions.

Results and Discussion

Synthesis of the Nucleotide-Appended Oligo(*p*-phenylenevinylene) 8. The synthetic route of the nucleotide-appended oligo(*p*-phenylenevinylene) molecule **8** is shown in Scheme 1. Toluene-4-sulfonic acid 2-methoxy-ethyl ester and hydroquinone were coupled via Williamson ether formation, and subsequent chloromethylation of the aromatic ether with formaldehyde and HCl gave 1,4-bis-chloromethyl-2,5-bis-(2-methoxy-ethoxy)-benzene.[16] The chlorinated precursor was then reacted with phosphorus acid triethyl ester by Michaelis−Arbuzow reaction to give tetraethoxy{[2,5-bis(2-methoxyethoxy)-1,4-phenylene]-bis(methylene)}bisphosphonate (**1**). Acid-catalyzed reaction of benzene-1,4-dicarbaldehyde with ethylene glycol[17] was carried out, and the subsequent Wittig−Horner reaction of the product with **1** gave (*E*,*E*)-1,4-bis(4-formylstyryl)-2,5-bis(2-methoxy-ethoxy)benzene (**2**). The obtained dialdehyde molecule of **2** was reduced using $NaBH_4$ to give (*E*,*E*)-1,4-bis(4-hydroxymethyl-styryl)-2,5-bis(2-methoxyethoxy)benzene (**3**). Compound **5** was obtained by the coupling of the OPV derivative **3** with 5′-dimethoxytrityl-2′-deoxythymidine-3′-[(2-cyanoethyl)-*N*,*N*-diisopropyl]phosphoramidite (**4**) using the phosphoramidite method[18] in the presence of 1*H*-tetrazole. Subsequently, oxidization of **5** and deprotection of **6** were performed by *tert*-butylhydroperoxide and 28% NH_3 aqueous solution, respectively. Final compound **8** was obtained from **7** by removal of the protecting dimethoxytrityl group (DMTr) with trifluoroacetic acid.

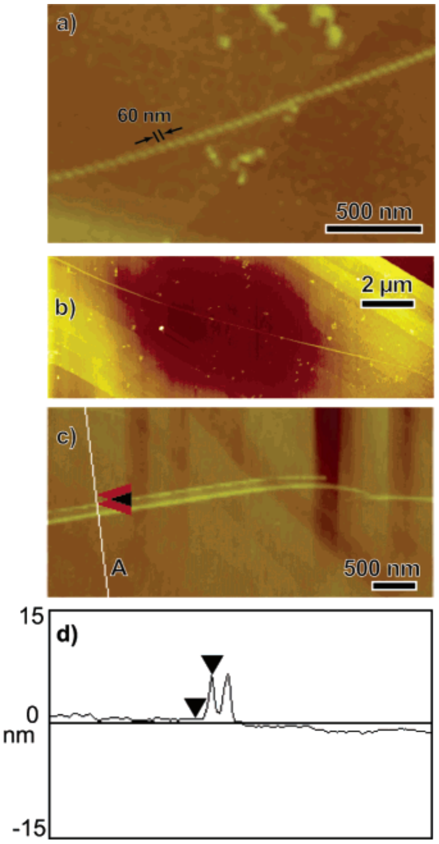


Figure 1. (a−c) AFM images for the binary self-assembly of **8**/**9** (T:A = 1:1, 1.8×10^{-2} M/1.8×10^{-3} M). (d) Section profiles along the *A* axis in Figure 1c.

Observation by Atomic Force Microscopy (AFM). To investigate the self-assembly behavior of the binary components of **8** and **9** (abbreviated as **8/9** hereafter), we carried out microscopic observations using atomic force microscopy. The AFM image clearly showed the exclusive formation of elongated helical stacks with a helically coiled morphology for the residual stoichiometry of thymine (T):adenine (A) = 1:1 (Figure 1a). The helical pitch and length of the helical stack were estimated to be 60 nm (Figure 1a) and more than 15 μm (Figure 1b), respectively. The observed right-handed helicity is very compatible with the observed positive Cotton effect for the circular dichroism (CD) measurements of the **8/9** systems shown later (Figures 3b and 6b). On the basis of the section profile along the *A* axis (Figure 1c) we were able to determine 6.4-nm height as a fiber width (Figure 1d), which is a bit longer than the extended molecular length of **8** (l = 3.9 nm) calculated by molecular modeling. The binary self-assembly with the stoichiometry of T:A = 2:1 gave relatively shorter fibrous structures with lengths of 2−3 μm shorter than those with T:A = 1:1 (Figure 2a). We also found unauthorized objects as a minor component in the binary self-assembly with the stoichiometry of T:A = 2:1. Right-handed helicity was not clearly observable, probably owing to tightly twisted features of the helical stacks

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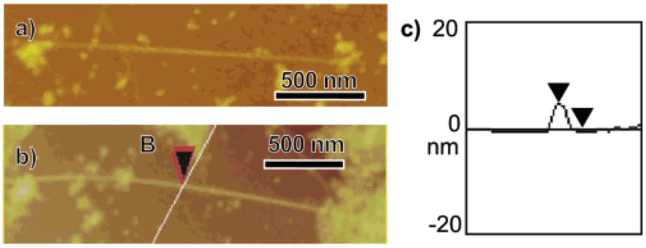

Figure 2. (a, b) AFM images for the binary self-assembly from **8**/**9** (T:A = 2:1, 1.8 × 10^{-2} M/9 × 10^{-4} M). (c) Section profiles along the *B* axis in Figure 2b.

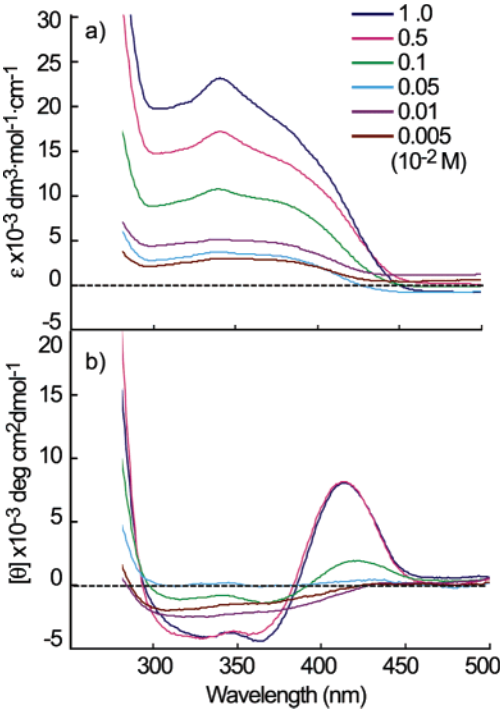

Figure 3. Concentration dependence of the (a) UV−vis and (b) CD spectra of the binary self-assembly of **8**/**9** (T:A = 1:1) in 0.1 × TE buffer solutions.

or experimental scan conditions for AFM. The CD spectrum of this system, discussed later, supports that the helical stacks should form a right-handed-helical structure. Interestingly, we were able to obtain the length of 5.1 nm as a fiber height (Figure 2c) from the section profile of the *B* axis in Figure 2b. Thus, the aspect ratios of the binary self-assemblies with two different stoichiometries were estimated to be approximately 2000 and 500 for the longer and shorter helical stacks, respectively. It should be noted that the lateral dimensions, generally the width of the samples, are inaccurate because of the geometry of the cantilever tip.[19] Therefore, the aspect ratios were calculated by the heights and lengths of the helical stack. In contrast, we were unable to observe any helical stacks for self-assembly of the single-component **8** using AFM. Moreover, a binary mixture of **8** and noncomplementary **10** (T:T = 1:1) (Chart 1) gave amorphous aggregates 10−30 nm wide. These findings support the view that the complementary A−T base pairing is crucial to form the helical stacks.

Table 1. Concentration Dependence of the Optical Data for the Binary Self-Assembly of **8**/**9**

concentration of **8**/**9** (M) (T:A = 1:1)	$\epsilon_{338} \times 10^{-4}$ ($dm^3\ mol^{-1}\ cm^{-1}$)	$\epsilon_{380} \times 10^{-4}$ ($dm^3\ mol^{-1}\ cm^{-1}$)	*g* value × 10^4
$1.0 \times 10^{-2}/1.0 \times 10^{-3}$	1.7	1.8	3.5
$5.0 \times 10^{-3}/5.0 \times 10^{-4}$	1.1	1.4	2.3
$1.0 \times 10^{-3}/1.0 \times 10^{-4}$	1.0	0.9	0.4
$5.0 \times 10^{-4}/5.0 \times 10^{-5}$	0.35	0.3	
$1.0 \times 10^{-4}/1.0 \times 10^{-5}$	0.48	0.4	
$5.0 \times 10^{-5}/5.0 \times 10^{-6}$	0.27	0.2	

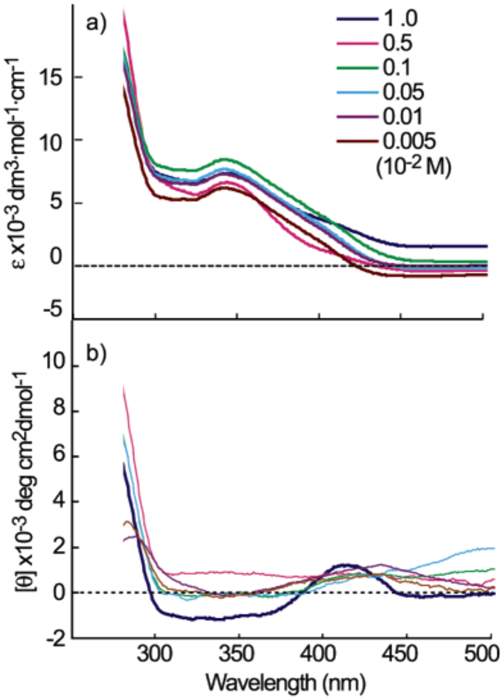

Figure 4. Concentration dependence of the (a) UV−vis and (b) CD spectra of the single-component **8** in 0.1 × TE buffer solutions.

Concentration Dependence of the Binary Mixtures and Single Component. The self-assembly behavior of the binary mixture of **8**/**9** (T:A = 1:1) proved to strongly depend on the concentration of **8** used (5 × 10^{-5} to 1 × 10^{-2} M). The UV−vis absorption band of the binary mixture of **8**/**9** gave an absorption maximum at λ = 338 nm with a broad shoulder around 380 nm for the OPV moiety and at λ = 270 nm for thymine and adenine moiety (Figure 3a). The UV−vis absorption region of the OPV moiety showed a strong dependence on the concentration of each component. The CD spectral changes of the binary mixture in the concentration range between 5 × 10^{-5} and 1 × 10^{-2} M in 0.1 × Tris/EDTA (TE) buffers are also shown in Figure 3b. At concentrations above 1 × 10^{-3} M we were able to observe strong positive and negative Cotton bands at λ = 415 and 360 nm, respectively, with a zero crossing at λ = 380 nm. These CD spectra strongly suggest the right-handed helical arrangement of the transition dipoles of the OPV moiety in the binary self-assembly.[20] On the other hand, no bisignated CD signals appeared at concentrations below 5 × 10^{-4} M. Therefore, the helical stack in the binary self-assembly occurs only at concentrations between 5 × 10^{-4} and 1 × 10^{-3} M. The molar absorption coefficient (ϵ) at λ = 338 and 380 nm and the anisotropy factor *g* values[21] at = 415 nm (g_{415}) of the binary self-assembly are summarized in Table 1.

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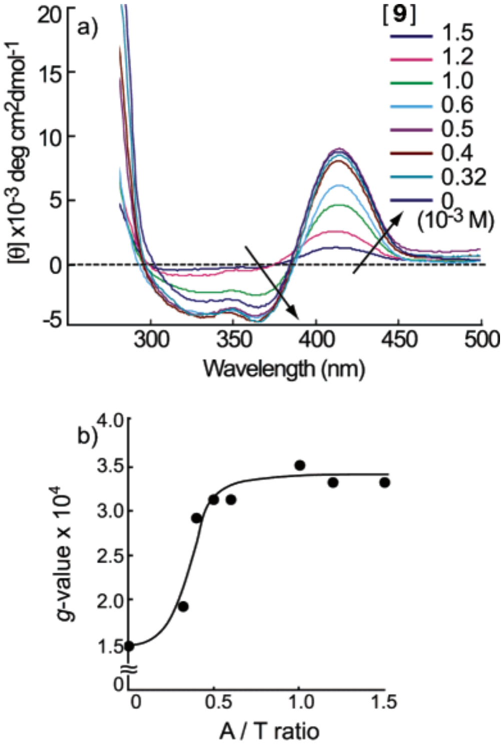

Figure 5. (a) CD spectra of the binary self-assembly of **8**/**9** at 0 °C when changing the concentrations of **9**. (b) Plot of the anisotropy factor *g* value against the A:T ratio at $\lambda = 415$ nm.

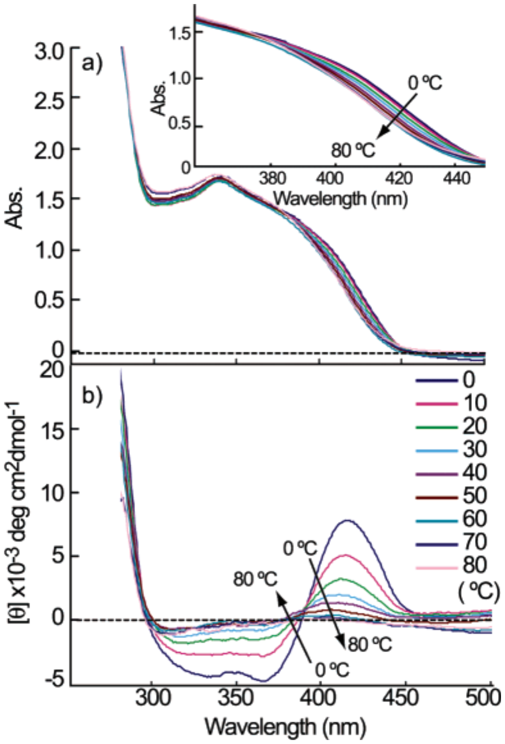

Figure 6. Temperature dependence of the (a) UV−vis and (b) CD spectra of the binary self-assembly of **8**/**9** (T:A = 1:1, $1.0 \times 10^{-2}/1.0 \times 10^{-3}$ M) in 0.1 × TE buffer solutions.

The observed relatively stronger $\pi-\pi^*$ absorption at $\lambda =$ 380 nm for the binary self-assembly of **8**/**9** indicated that the molecular conformation of the OPV moiety is sensitive to whether **9** is present or absent in aqueous solutions. UV−vis spectra of the single-component **8** (1×10^{-2} M), having a broad absorption band originating from the OPV moiety with a maximum at $\lambda = 338$ nm (Figure 4a), showed a different pattern from that of molecularly dissolved OPV derivatives.[13b] The molar absorption coefficient (ϵ) of **8** hardly changed upon decreasing the concentration from 1×10^{-2} to 5×10^{-4} M. On the other hand, addition of THF to aqueous solutions of **8** increased the intensity of the $\pi-\pi^*$ transition of the OPV moiety (at $\lambda = 380$ nm, data not shown). One possible explanation for the increase in the absorption intensity is that the changed solvent polarity affects the delicate conformation of the OPV moiety in the assembly. Similar spectral changes influenced by the change in solvent polarity were observed for other π-conjugated systems such as polythiophenes in THF/water mix-

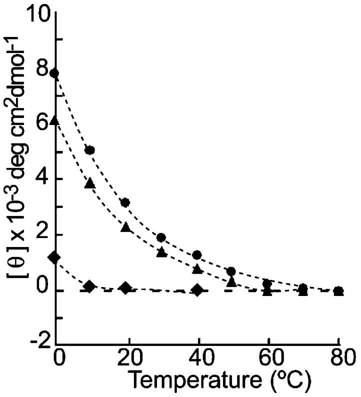

Figure 7. Temperature dependence of the CD intensity at $\lambda = 415$ nm for the binary self-assembly of **8**/**9** ((●) T:A = 1:1, 1.0×10^{-2} M/1.0×10^{-3} M, (▲) T:A = 2:1, 1.0×10^{-2} M/0.5×10^{-3} M) and the self-assembly of **8** ((♦) 1.0×10^{-2} M) in 0.1 × TE buffer solutions.

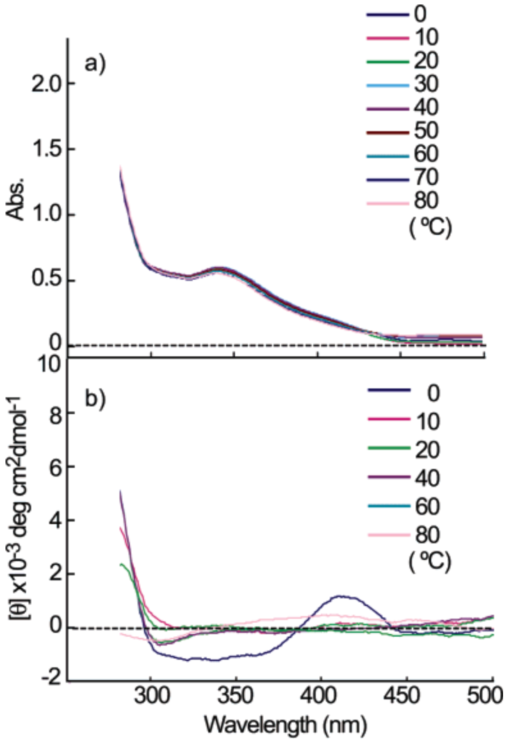

Figure 8. Temperature dependence of the (a) UV−vis and (b) CD spectra of the single-component **8** (1.0×10^{-2} M) in 0.1 × TE buffer solutions.

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(21) The *g* value is calculated as follows: $g = \mathrm{CD}/(\mathrm{OD} \times 32980)$, where CD is in mdeg and OD is the optical density for the same sample, see: Langeveld-Voss, B. M. W.; Waterval, R. J. M.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1999**, *32*, 227−230.

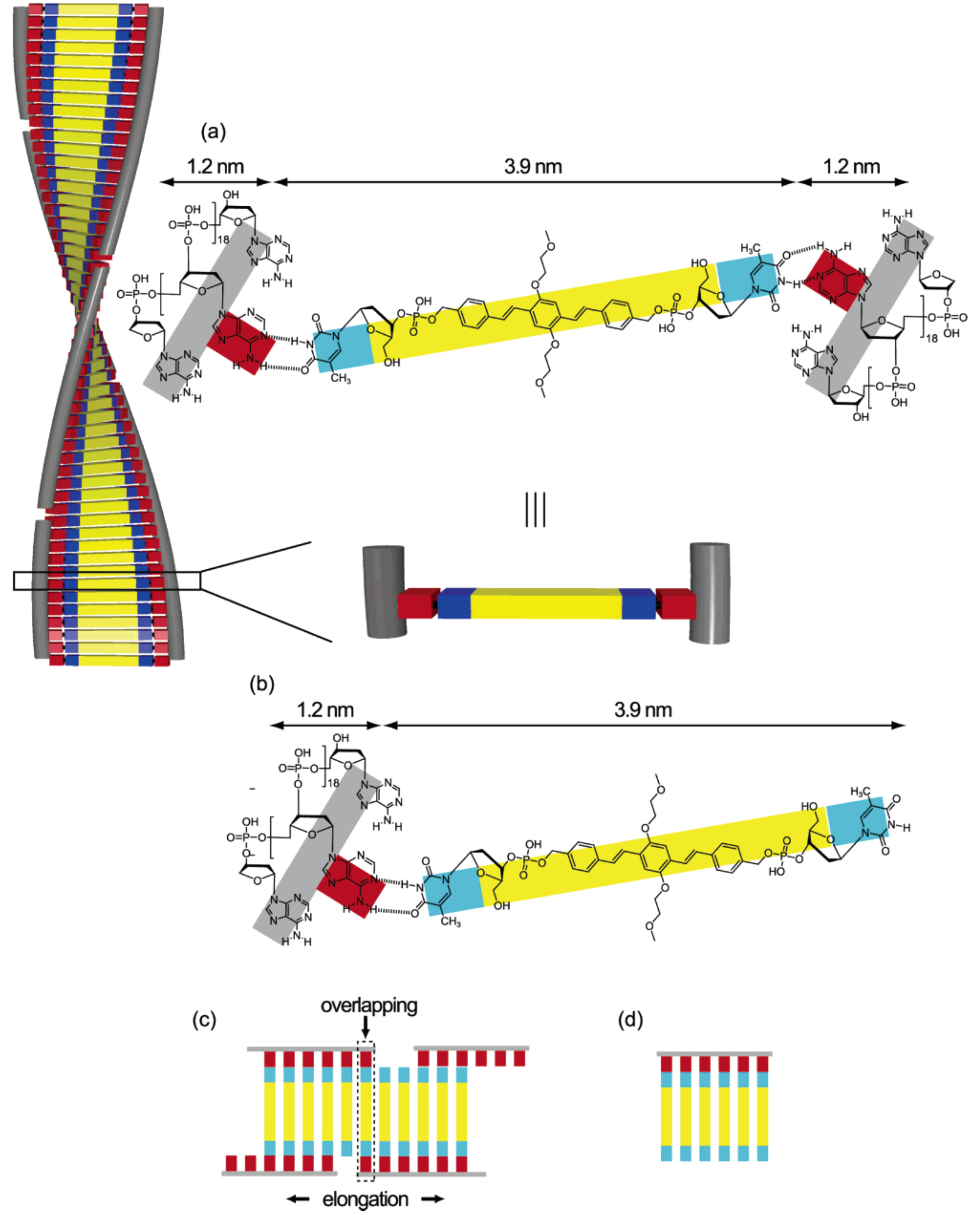

Figure 9. Proposed structure for the binary self-assembly of (a) **8**/**9** (T:A = 1:1) and (b) **8**/**9** (T:A = 2:1). Possible elongation mechanism for the helical stacks self-assembled from (c) **8**/**9** (T:A = 1:1) and (d) **8**/**9** (T:A = 2:1).

tures,[22] cationic poly(*p*-phenylene) derivatives,[23] and poly[bis(*p*-alkoxyphenyl)silylene]s.[24] The increasing extinction coefficient in THF could also be due to less tight packing of **8** than in aqueous solutions, as observed for polythiophenes.[22] The CD spectrum of the single-component **8** gave a weak positive Cotton effect with a zero crossing in the $\pi-\pi^*$ absorption region (1×10^{-2} M, anisotropy factor $g_{415} = 1.5 \times 10^{-4}$), which disappears at concentrations below 5×10^{-3} M (Figure 4b). Thus, UV−vis and CD spectra revealed that the single-component **8** aggregates in aqueous solutions in a nonhelical fashion.

Concentration Effect of the Complementary Component 9. We carried out CD measurements for the binary self-assemblies of **8** (the fixed concentration = 1.0×10^{-2} M) with changing concentrations of **9** from 0 to 1.5×10^{-3} M (T:A = 1:0 to 1:1.5) at 0 °C. As a result we were able to confirm the templating process of the complementary oligonucleotide **9**, which strongly depends on its concentrations. Figure 5a shows that the intensity of the positive Cotton effect from the OPV moiety becomes stronger upon increasing concentration of **9**, supporting induction of helicity in the binary self-assembly. To determine the optical activity of the OPV moiety as a function of the concentration of **9**, we plotted the anisotropy factor *g* values at 415 nm against the concentration of **9** (Figure 5b). Consequently, we found that the *g* value reaches a plateau at a T:A ratio between 2:1 and 1.7:1 (Figure 5b). This fact directly suggests that one side of the thymine moieties in stacked assemblies of **8** forms the binary complex with a single chain of **9**. Thus, the complementary A−T base pairs form to induce the helical stack of the OPV moiety in the binary self-assembly.

Temperature Dependence on the Stability of the Binary Self-Assembly. Variable-temperature UV−vis spectra of **8**/**9** showed a temperature dependence involving a blue shift of the $\pi-\pi^*$ absorption region upon heating (Figure 6a), suggesting transition from a helical to nonhelical aggregate of the OPV moiety in the binary self-assembly. No disassembly of the molecule **8** itself takes place since the UV−vis spectra are different from that of molecularly dissolved OPV derivatives,[13b] even at 80 °C. Moreover, as compared to the CD spectra at temperatures above 50 °C, relatively stronger exciton coupling with a zero crossing around 380 nm is observable in the variable-temperature CD measurements for the **8**/**9** system (T:A = 1:1) at temperatures ranging from 0 to 50 °C (Figure 6b). Actually, the CD intensities at 415 nm plotted against temperature gradually decrease upon heating from 0 to 50 °C, meaning that the transformation from a helical to nonhelical molecular assembly occurs noncooperatively (Figure 7, filled circles). The helical formation process of the binary self-assembly, therefore, differs from that of DNA molecules, where formation of double-stranded helical structures takes place cooperatively.[25] The CD intensity for the binary self-assembly of **8**/**9** with a molar stoichiometry of T:A = 2:1 (Figure 7, filled triangles) gave a similar temperature-dependence curve to that in the case with a stoichiometry of T:A = 1:1 (Figure 7, filled circles).

On the other hand, variable-temperature UV−vis spectra of **8** demonstrated no remarkable changes upon increasing temperature (Figure 8a). A weak positive Cotton effect in the $\pi-\pi^*$ absorption region appeared at 0 °C in the CD spectrum of **8** and disappeared at temperatures above 10 °C (Figures 8b and 7, diamonds). Therefore, a single strand of **9** drives the helical structure and contributes to the stability of the binary self-assembly.

Plausible Helical Structure for the Binary Self-Assembly of 8/9. All these results support the view that right-handed helical stack structures formed from the binary self-assembly of **8/9** (T:A = 1:1 and 2:1), similar to the DNA-like nanofibers with an oligomethylene chain as a spacer instead of the OPV moiety. Since oligodeoxyadenylic acids are known to form right-handed single helices in neutral aqueous solutions,[26] templating of **8** with **9** induces the right-handed helical stack with formation of A−T base pairs like DNA double strands. It is reasonable to depict that the obtained 6.4-nm thickness for the binary self-assembly of **8/9** (T:A = 1:1) (Figure 1) corresponds to the total width of **8** (3.9 nm) and two adenylic acid monomers in the strand of **9** (two times 1.2 nm) (Figure 9a and 9c), while the thinner 5.1-nm fiber width of the binary self-assembly **8/9** (T:A = 2:1) (Figure 2) is compatible with the sum of the lengths of **8** (3.9 nm) and a single strand of **9** (1.2 nm) (Figure 9b and 9d). Therefore, we can produce two types of helical stacks with different widths by changing the concentrations of **9**. Moreover, the observed relatively longer helical stack from the binary self-assembly of **8/9** (T:A = 1:1) allows us to consider that the partial overlapping of **9** at the end of the stacked **8**/**9** system makes the helical stack easily elongate (Figure 9c). Considering the typical $\pi-\pi$ stacking distance of 0.35 nm, we assume that approximately 170 molecules of **8** form a single helical pitch (60 nm) in the helical stack.

In conclusion, we synthesized the thymidylic acid-appended OPV derivative **8** and examined its homo and binary self-assembling properties with complementary oligoadenylic acid 20-mer **9** in aqueous solutions. UV−vis and CD spectroscopic measurements and AFM microscopic observations revealed formation of helical stack structures with widths corresponding to the sum of those of one molecule of **8** and two adenylic acid moieties or the sum of those of one molecule of **8** and a single adenylic acid. Sequence-dependent binary self-assembly by combining a variety of OPV derivatives having a nucleotide at both ends with the complementary single-stranded oligodeoxy nucleotide as templates is now in progress.

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

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