# Synthesis and Molecular Recognition of Conjugated Polymer with DNA-Mimetic Properties

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ABSTRACT: The synthesis of a new DNA-mimetic π-conjugated poly(*p*-phenylenebutadiynylene) (polymer **9**), which is functionalized with thymine nucleobases, as well as polyethylene glycol chains at every repeat unit is reported. This polymer was characterized by UV−vis, fluorescence, nuclear magnetic resonance, infrared, and Raman spectroscopy as well as gel permeation chromatography. These show its water-induced aggregation and a sharp transition from the aggregated phase to a more molecularly dissolved species when the temperature is increased. Molecular recognition properties of **9** with a number of guest molecules, including (i) 2,6-diacetamidopyrimidine and thymine derivatives in chloroform, (ii) adenosine and thymidine in water, and (iii) DNA d[$A_{20}$] and DNA d[$T_{20}$] in water, were investigated by UV−vis, fluorescence, thermal denaturation, circular dichroism (CD), nuclear magnetic resonance, and some control experiments. These results demonstrate that polymer **9** selectively binds complementary small molecules, both in organic solvents and in water, with concomitant enhancement in its fluorescence intensity and effectively discriminates between complementary and noncomplementary molecules. Importantly as well, this polymer forms a complex with complementary DNA, which shows enhanced fluorescence, a sharp thermal transition reminiscent of a natural DNA duplex, and a dramatic change in the secondary structure of the DNA guest. This is the first example of the hydrogen-bonding association of a conjugated polymer selectively to complementary DNA, with excellent discrimination between complementary and noncomplementary strands. Thus, the incorporation of nucleobases into conjugated polymers presents a useful tool to control chain−chain interactions and phototophysical properties through selective binding to DNA and its derivatives, to evolve sensor platforms for these biomolecules, and to possibly probe and modify the structure of the guest DNA.

## Introduction

Over the past two decades, π-conjugated polymers have drawn considerable attention because of their unique optical and electronic properties and applications in a number of areas, such as field-effect transistors,[1] solar cells,[2] light-emitting diodes,[3] nonlinear optical materials,[4] and sensors.[5,6] In most of these applications, the performance of these organic semiconducting materials is highly dependent on their supramolecular organization and packing at the molecular level. Thus, a current challenge is the fine control of chain−chain interactions in conjugated polymers. A number of approaches to induce organization in π-conjugated polymers have been used, including incorporation of liquid crystalline,[7] chiral,[8] ion- and pH-sensitive chains,[9] self-assembly of block copolymers containing conjugated blocks,[10] templated formation of conjugated polymers within self-assembled surfactant structures,[11] and Langmuir−Blodgett techniques.[12] Conjugated polymers have also been functionalized with receptor moieties, such as sugars,[13] crown ethers,[14] calixarenes,[15] metal-binding units,[16] iptycenes,[17] biotin,[18] amino acids,[19] and oligopeptide moieties,[20] to control their conformation and chain−chain association.[21]

Among these molecular recognition groups, we have been interested in the incorporation of DNA bases and analogues into polymeric materials, as an especially attractive method to control supramolecular organization.[22] In nonconjugated polymers, this approach can organize polymeric chains into unusual morphologies[22] and allows noncovalent binding of the polymer to a number of other moieties (e.g., nanoparticles,[23a] dendritic molecules,[23b] and other polymers[23c]). More recently, we reported the use of this approach to construct the first small molecule-responsive block copolymer micelles, which can selectively deaggregate and open when a specific guest is added.[22] The incorporation of nucleobases into π-conjugated polymers would allow the application of the above strategies to (i) finely control chain−chain interaction in these materials using simple hydrogen-bonding molecules or DNA, (ii) create molecule-responsive organic semiconducting materials, (iii) evolve sensors for DNA bases and for DNA itself, and (iv) readily construct multicomponent devices using hydrogen-bonding interactions. So far, this approach has been examined in a limited number of contributions. The electrochemical response of uracil, adenine,[24] or flavin-substituted[25] polythiophenes to their complementary small molecule partners has been studied, polythiophenes and polyphenylenevinylenes have been attached to CdSe nanocrystals[26] and to fullerenes[27] by complementary H-bond interactions, and end-termination with a molecular recognition group[28] has been shown to enhance alignment in conjugated polymers. However, no previous study has examined the effect of hydrogen-bonded molecular recognition on the photophysical properties and the degree of aggregation of conjugated polymers[29] and the possibility to bind and "sense" DNA itself, in addition to small molecules, using these conjugated materials.

We here present the synthesis of a new water-soluble π-conjugated poly(*p*-phenylenebutadiynylene) (polymer **9**) with thymine groups as well as poly(ethylene glycol) chains as substituents on each repeat unit. We have investigated the phototophysical and molecular recognition properties of this DNA-mimetic conjugated polymer with a number of guests. Polymer **9** aggregates in aqueous media and shows a sharp transition from the aggregated phase to more molecularly dissolved species when the temperature is increased. In addition, this polymer can selectively recognize complementary small molecules in both organic solvents and water, with concomitant increase in its fluorescence intensity, and shows the ability to effectively discriminate between complementary and non-

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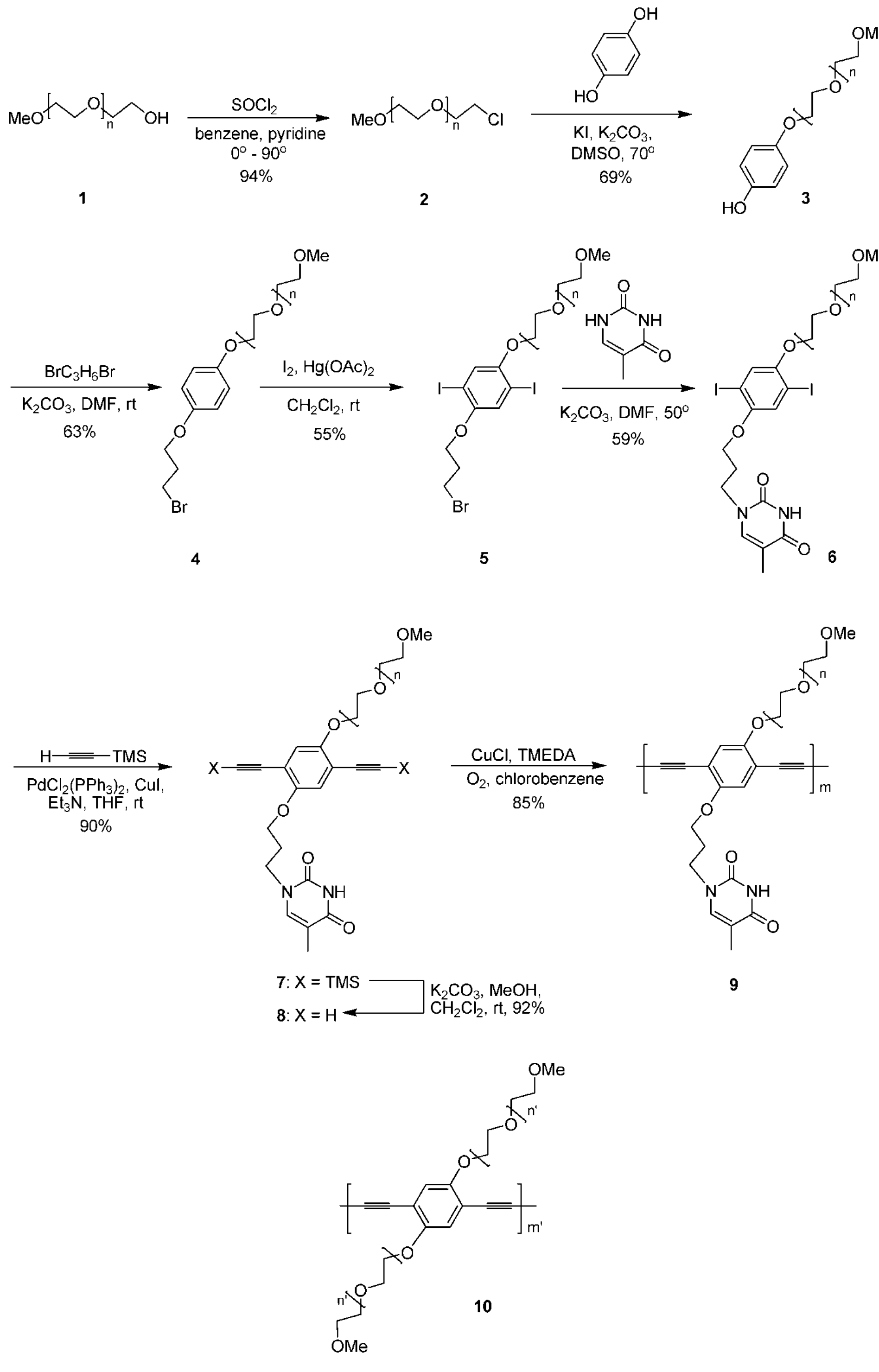
**Scheme 1. Synthetic Route for Polymer 9 and Structure of Control Polymer 10**



complementary molecules. Finally, this polymer is able to selectively bind, with enhanced fluorescence, to complementary DNA strands in water, to form a hydrogen-bonded complex that shows a sharp thermal transition reminiscent of a natural DNA duplex. At a higher concentration, the polymer associates with complementary DNA to form a complex with high stability, and a dramatic change in the secondary structure of the DNA guest, as evidenced by CD spectroscopy. Thus, the incorporation of nucleobases into conjugated polymers presents a useful tool to control chain–chain interactions and phototophysical properties through selective binding to DNA and its derivatives, to probe and alter the structure of the guest DNA molecule, and to develop new sensors for nucleic acids.

## Results and Discussion

**Synthesis and Characterization.** The newly developed polymer was synthesized using copper-catalyzed alkyne coupling.[30] The general synthetic route and structures of the polymer are shown in Scheme 1. To enhance the solubility of the polymer in water and disfavor micelle formation, poly(ethylene glycol) chains **1** were employed as solubilizing polar groups and were appended to the monomer molecule (average $M_w = 500$). Alkylation of hydroquinone with 1-[2-(2-chloroethoxy)polyethoxy]methane (**2**) in the presence of $K_2CO_3$ in DMSO afforded its mono-PEGylated derivative **3** in 69% yield. Alkylation of **3** with 1,3-dibromopropane in DMF afforded its bromopropyl

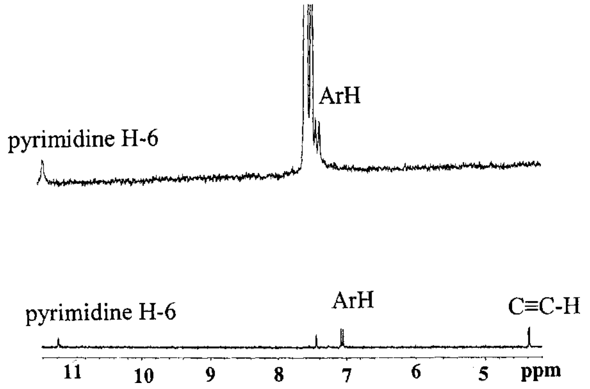


**Figure 1.** $^1$H NMR spectra of polymer **9** (top) and monomer **8** (bottom) in $d_6$-DMSO (showing the disappearance of the terminal alkyne protons at 4.39 ppm in polymer **9**).

derivative **4** in 63% yield. Then **4** was treated with $I_2$ and $Hg(OAc)_2$ to provide 2-[2-(2-methoxyethoxy)polyethoxy]-5-bromopropoxy-1,4-diiodobenzene (**5**)[31] in 55% yield. The synthesis of thymine-containing monomer **6** was performed using **5** as alkylating agent in the presence of $K_2CO_3$ in DMF. Palladium-catalyzed Sonogashira coupling of **6** with TMS−acetylene followed by deprotection of the TMS group in basic medium afforded the bis-alkynyl derivative **8** in excellent (90%) yield. Treatment of the monomer **8** in the presence of a catalytic amount of CuCl and TMEDA for 3 days under an oxygen atmosphere gave the polymer **9** in 85% yield after purification. Polymer **9** showed good solubility in most chlorinated organic solvents, DMF or DMSO, as well as in water. The number-average molecular weight ($M_n$) of the synthesized polymers **9**, as determined by gel permeation chromatography (GPC) using poly(ethylene oxide) as standard, was 32 100 (PDI, $M_w/M_n$ = 1.96). For control experiments, we also synthesized polymer **10**, which has similar structural features to **9** but does not possess thymine units.

Polymer **9** was characterized by $^1$H NMR, Raman, IR, UV−vis, and fluorescence studies. In the $^1$H NMR spectrum of **9** in DMSO, the peak corresponding to the terminal alkyne protons at 4.39 ppm of monomer **8** disappeared, consistent with high coupling yields (Figure 1).

IR and Raman signals also aided the identification of the chemical structure of the poly(*p*-phenylenebutadiynylene) (PPB) backbone. The Raman spectrum of polymer **9** shows the presence of butadiynylene (−C≡C−C≡C−) segments. Typical spectra are shown in Figure 2a. Monomer **8** shows a characteristic Raman peak at about 2110 cm$^{-1}$ due to $\nu_{C\equiv C}$, and polymer **9** shows peaks at 2200 cm$^{-1}$, which are distinct from the monomer **8** and identical with the reported values of poly(*p*-phenylenebutadiynylene).[32] The characteristic IR absorption peaks of the monomer **8** at 3220 cm$^{-1}$ due to stretching vibration

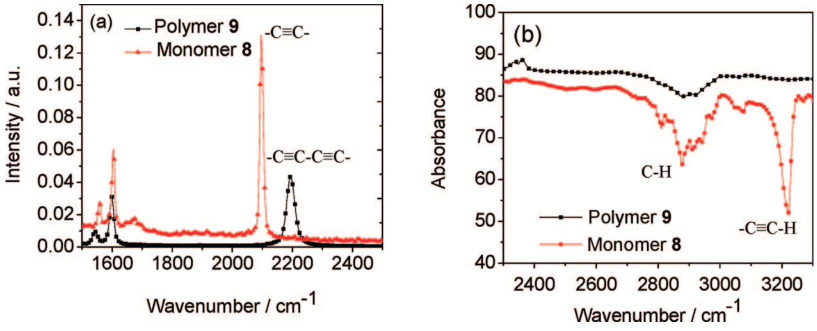


**Figure 2.** (a) Raman spectra excited at 1064 nm and (b) FT-IR spectra of polymer **9** and monomer **8**.

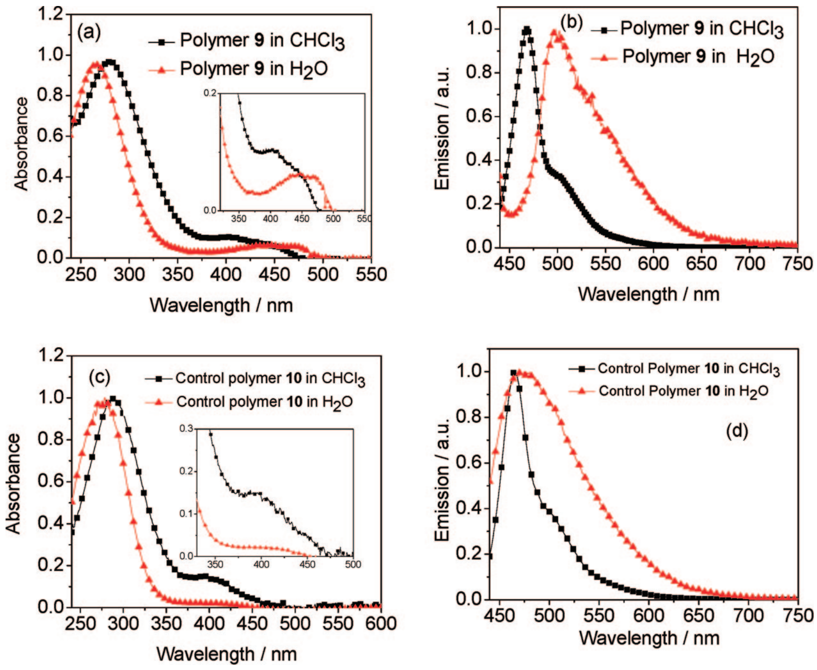


**Figure 3.** (a) UV−vis spectra at $10^{-3}$ M and (b) fluorescence emission spectra at $10^{-4}$ M of polymer **9**, (c) UV−vis spectra at $10^{-3}$ M, and (d) fluorescence emission spectra at $10^{-4}$ M of control polymer **10** in chloroform and water. Emission spectra were obtained from excitation at 436 nm.

**Table 1. Physical Data of Polymer 9 and Control Polymer 10 in $CHCl_3$ and $H_2O$**

| compound | $\lambda_{\max}^{\text{abs}}$[a]/nm | $\lambda_{\max}^{\text{em}}$[b,c]/nm | $\Phi_{\text{FL}}$[b,c,d] | $\zeta_1$[e]/ns | $\zeta_2$[e]/ns | $\zeta_1$[f]/ns | $\zeta_2$[f]/ns |
|---|---|---|---|---|---|---|---|
| polymer **9** in $CHCl_3$ | 279, 403 | 468 | 0.04 | 0.5 (82%) | 0.4 (18%) | 0.6 (92%) | 0.5 (8%) |
| polymer **9** in $H_2O$ | 266, 451 | 502 | 0.01 | 2.3 (82%) | 0.6 (18%) | 3.8 (100%) | na |
| control polymer **10** in $CHCl_3$ | 287, 400[g] | 464 | 0.78 | 0.6 (90%) | 0.4 (10%) | 0.6 (89%) | 0.4 (11%) |
| control polymer **10** in $H_2O$ | 278, 400[g] | 485 | 0.32 | 2.4 (77%) | 0.6 (23%) | 2.4 (84%) | 0.6 (16%) |

[a] Absorption recorded at $10^{-3}$ M. [b] Excitation at 436 nm. [c] Emission recorded at $10^{-4}$ M. [d] Using fluorescein in 0.1 M NaOH ($\Phi_{436} = 0.92$) as standard. [e] Lifetime recorded at $10^{-4}$ M. [f] Lifetime recorded at $10^{-6}$ M. [g] UV−vis max peak at higher wavelength is very broad.

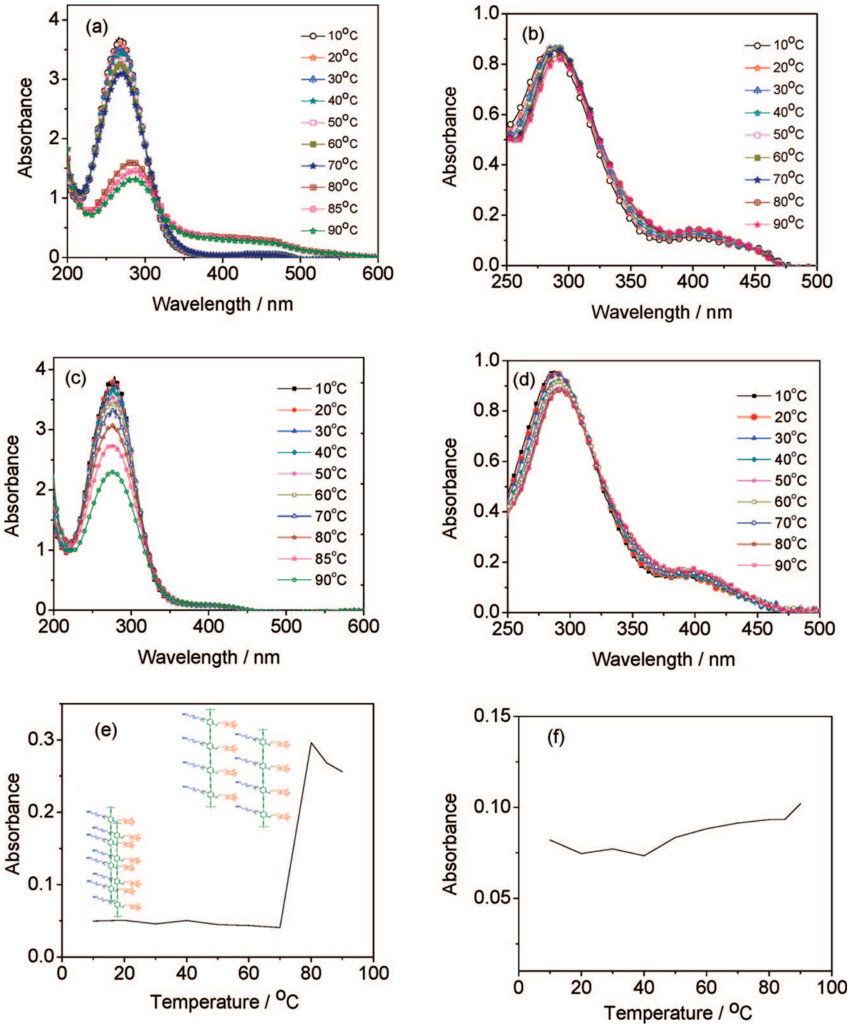


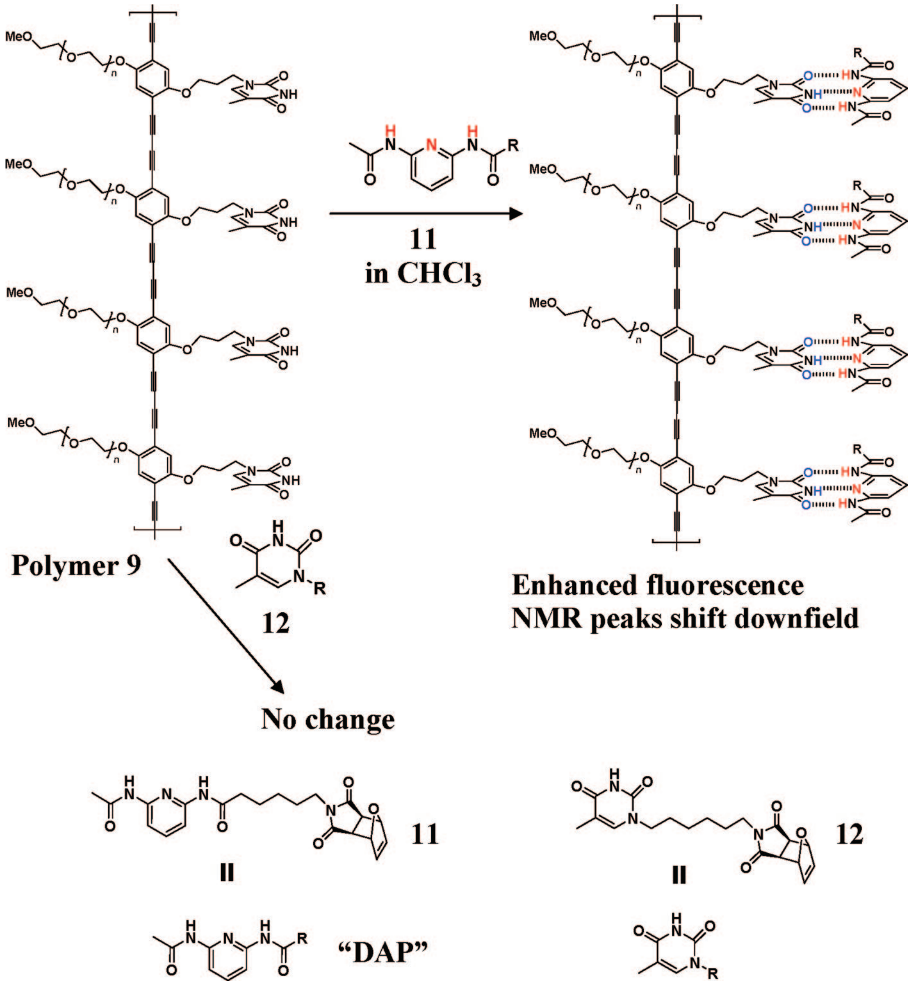
**Figure 4.** Temperature-dependent UV−vis spectra at $10^{-4}$ M of (a) polymer **9** in water, (b) polymer **9** in chloroform, (c) control polymer **10** in water, (d) control polymer **10** in chloroform, (e) thermal denaturation of polymer **9** in water measured at 451 nm, and (f) thermal denaturation of polymer **10** in water measured at 400 nm.

of acetylenic C−H ($\nu_{\text{C-H}}$) disappeared in polymer **9**, also consistent with efficient polymerization (Figure 2b).

**Photophysical Properties.** The spectroscopic properties of polymer **9** were measured at room temperature in $CHCl_3$ and water solutions and are significantly different in these two solvents. UV−vis absorption and fluorescence spectra of the polymer in both solvents are shown in Figure 3, and the optical data are summarized in Table 1. The absorption spectrum of **9** in $CHCl_3$ shows two major transitions, the lowest energy peak corresponding to $\pi-\pi^*$ electronic transitions along the conjugated polymer main chain ($\lambda_{\max}^{\text{abs}} = 403$ nm) and the second corresponding to both thymine units as well as $\pi-\pi^*$ transitions in the polymer ($\lambda_{\max}^{\text{abs}} = 279$ nm). These assignments are consistent with previous literature reports[33] but were also confirmed by comparison to control polymer **10**, which has similar structural features to **9** but does not possess thymine units (Table 1). The emission spectrum in $CHCl_3$ shows a band at 468 nm, with a shoulder at 502 nm upon excitation at 436 nm, consistent with $\pi-\pi^*$ transitions in the poly(*p*-phenylenebutadiynylene) (PPB) backbone.[34] Interestingly, the fluorescence quantum yield of polymer **9** in $CHCl_3$ ($\Phi = 0.04$) is much lower than control polymer **10**, which contains no thymine units ($\Phi = 0.78$). This is consistent with significant quenching of the polymer fluorescence by the thymine units in polymer **9**.

When **9** is dissolved in water, its UV−vis transition at $\lambda_{\max}^{\text{abs}} = 403$ nm is significantly red-shifted to $\lambda_{\max}^{\text{abs}} = 451$ nm. As well, the emission bands of **9** undergo a red shift and broadening in water (main peak at 502 nm with shoulder at 550 nm), and the fluorescence quantum yield decreases in water ($\Phi = 0.01$) when compared to $CHCl_3$. The absorption and emission data are consistent with a significant increase in $\pi-\pi$ stacking interactions of the conjugated polymer chains in water. These data suggest that while polymer **9** is solvated in $CHCl_3$, it most likely undergoes water-induced aggregation into a morphology where the hydrophobic backbone chains are relatively tightly packed, with $\pi-\pi$ interactions, and the pendant PEG chains

**Scheme 2. Binding of Complementary and Noncomplementary Molecules to Polymer 9 in $CHCl_3$**



are pointed into the aqueous medium. This aggregation in aqueous medium has been observed with other $\pi$-conjugated polymers containing hydrophilic pendant chains.[35]

Fluorescence lifetime measurements confirmed the water-induced aggregation of polymer **9**. In $CHCl_3$, the fluorescence decay of polymer **9** is wavelength independent and can be described by a short lifetime component with 0.5 ns at 510 nm. In water, the fluorescence decay of **9** is wavelength dependent. The decay near the emission maximum ($\lambda = 510$ nm) is increased to 2.3 ns (Table 1). The broad, red-shifted, less efficient, and longer-lived fluorescence observed from polymer **9** in $H_2O$ is characteristic of conjugated polymer aggregates.[35,36] It is of note that this longer lived component is still observed at lower polymer concentrations ($10^{-6}$ M) in water (Table 1), indicating that polymer aggregation occurs even at these low concentrations. Similar behavior is observed in control polymer **10**, which contains no thymine units: the emission wavelength is red-shifted in water relative to $CHCl_3$, and the emission lifetimes become wavelength dependent with a significantly longer-lived component.

We also examined the temperature dependence of aggregate formation from polymer **9** in water. UV−vis spectra were taken at temperatures increasing from 10 to 90 °C (heating rate: 0.5 °C/min). Interestingly, a sharp increase was observed for the UV−vis band of **9** at 451 nm, at a "thermal denaturation" temperature of 80 °C (Figure 4a,e).[37] No such sharp transitions are observed for polymer **9** in chloroform (Figure 4b). These observations are consistent with thermally induced dissociation

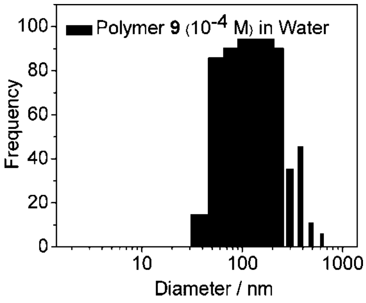


**Figure 5.** Dynamic light scattering spectra of polymer solution in water at $2.05 \times 10^{-4}$ M concentration.

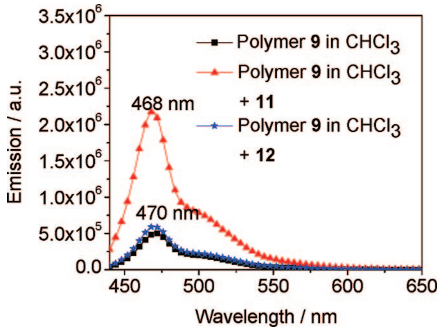


**Figure 6.** Fluorescence spectra of polymer ($10^{-4}$ M) (black), polymer ($10^{-4}$ M) with DAP monomer **11** (red), and polymer ($10^{-4}$ M) with THY monomer **12** (blue) excited at 436 nm.

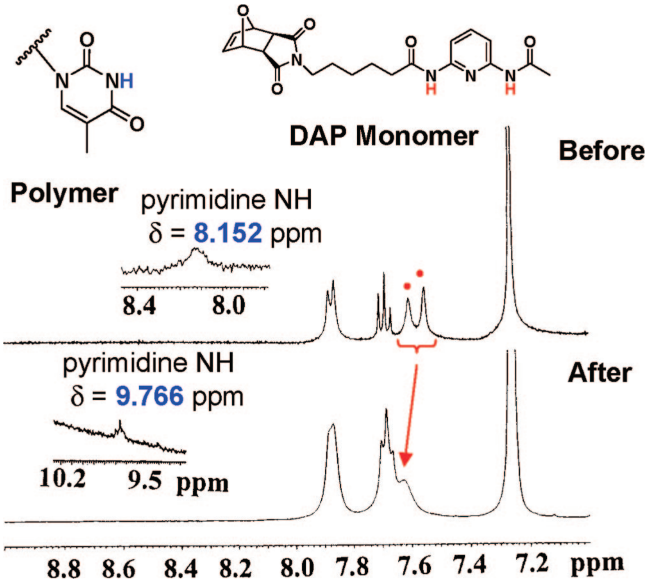


**Figure 7.** Proton NMR spectra of DAP monomers in $CDCl_3$ solution (top) and DAP monomers with an addition of polymer **9** ($10^{-4}$ M) (bottom).

of the polymer **9** aggregates in water, reducing the $\pi$-stacking interactions between the conjugated polymer chains. Interestingly as well, no such sharp transitions are observed in control polymer **10** in either aqueous (Figure 4c,f) or $CHCl_3$ solutions (Figure 4d), pointing to the possible role of the thymine units in the apparent cooperativity of this transition.

We have confirmed aggregation of the polymer in water by dynamic light scattering (DLS) measurements, which show aggregates of 144 nm approximate diameter (Figure 5). Previous studies have shown that some PPB polymers exhibit liquid crystalline properties;[32,34a–c] however, no thermotropic liquid crystalline behavior was observed when the aggregated state of **9** was examined using polarized optical microscopy and differential scanning calorimetry. This is likely due to the presence of PEG, as well as thymine side groups on polymer **9**, which reduces the ability of the polymer chains to associate into a well-defined liquid crystalline phase.

**Molecular Recognition Properties.** *With Complementary Small Molecule in $CHCl_3$.* The molecular recognition behavior of polymer **9** with small molecules in chloroform was examined. For this, a derivative of 2,6-diacetamidopyrimidine (DAP, **11**),[23] which is complementary to the thymine units, was used (Scheme 2).

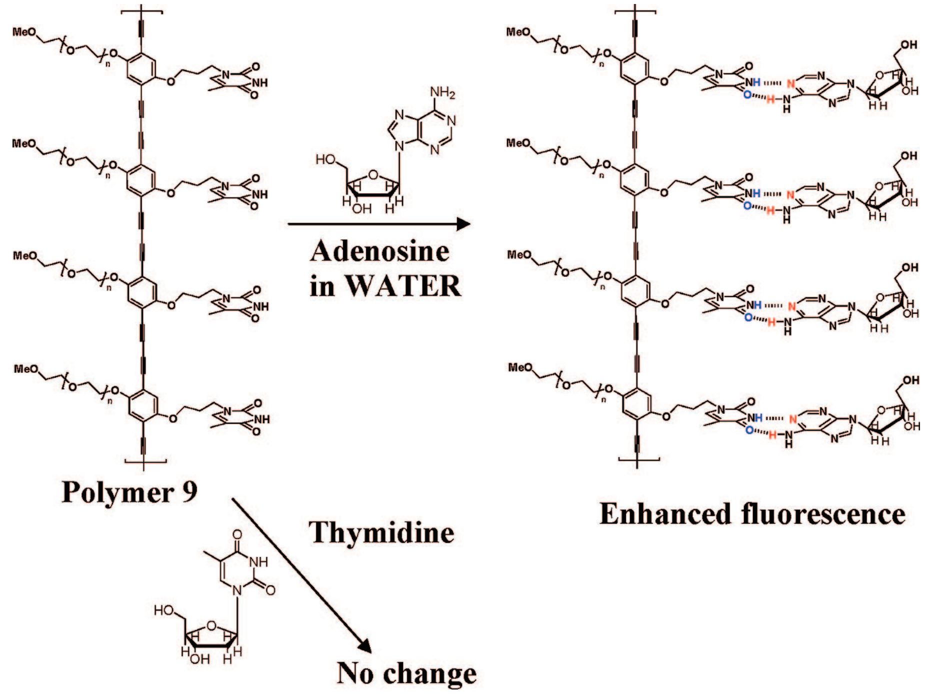
Addition of the DAP molecule **11** in an equimolar ratio to the thymine units of polymer **9** in chloroform ($2.48 \times 10^{-4}$ M) resulted in a large (3.7-fold) increase in the fluorescence intensity of the polymer as well as a slight blue shift. On the other hand, addition of a noncomplementary thymine derivative **12** to polymer **9** caused no change to its fluorescence spectrum (Figure 6). As well, addition of DAP to polymer **10**, which has the same conjugated backbone but no thymine units, caused no change in fluorescence. This is consistent with specific molecular recognition of the thymine units in the polymer with the added DAP molecules **11**, which possibly reorients the thymine units and reduces their quenching effect on the polymer backbone.

Hydrogen-bond molecular recognition was confirmed using $^1$H NMR spectroscopy (Figure 7). Upon addition of polymer **9** to the DAP guest molecules **11** in a $CDCl_3$ solution, the NH resonances of the DAP units experience a downfield shift and broadening, and the thymine NH proton peak is even more dramatically shifted downfield (8.15−9.77 ppm) consistent with H-bonded interactions for these protons.

Thus, polymer **9** can recognize and “sense” a complementary small molecule by specific molecular recognition in chloroform, with significant increase in fluorescence intensity, and can effectively discriminate between complementary and noncomplementary small molecules.

*With Complementary Small Molecule in Water.* The molecular recognition behavior of polymer **9** in water was also examined. For this, adenosine, which is complementary to the thymine units of polymer **9**, was used. Addition of this molecule (equimolar ratio to the thymine units of **9**) to polymer **9** ($4.97 \times 10^{-6}$ M) in water results causes an increase (1.5-fold) in fluorescence intensity (Figure 8). In a control experiment, addition of noncomplementary

**Scheme 3. Binding of Complementary and Noncomplementary Molecules to Polymer 9 in Water**



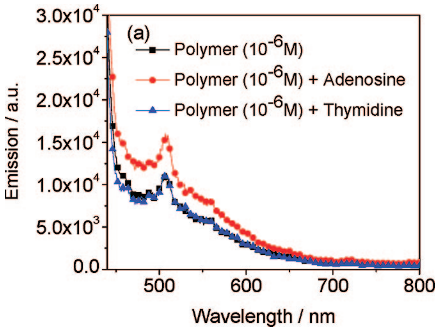


**Figure 8.** Fluorescence spectra of polymer **9** ($10^{-6}$ M) (black), adenosine with polymer **9** ($10^{-6}$ M) (red), and thymidine with polymer **9** ($10^{-6}$ M) (blue) (1:1 mole ratio per repeat unit) excited at 436 nm.

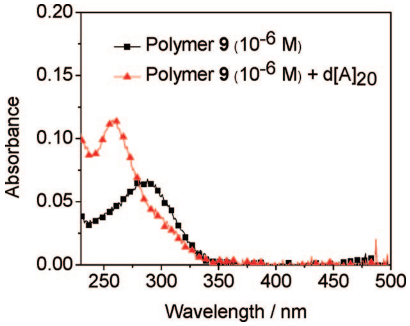


**Figure 9.** UV−vis spectrum of polymer **9** ($10^{-6}$ M) with d[A]$_{20}$ in water.

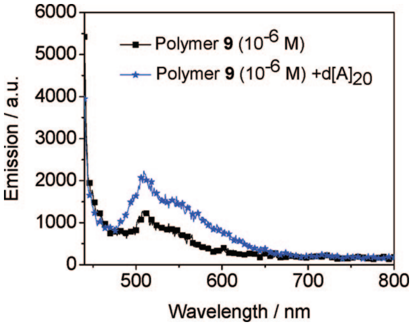


**Figure 10.** Fluorescence spectra of polymer **9** ($10^{-6}$ M) (black) and polymer **9** ($10^{-6}$ M) and d[A]$_{20}$ (blue) excited at 436 nm.

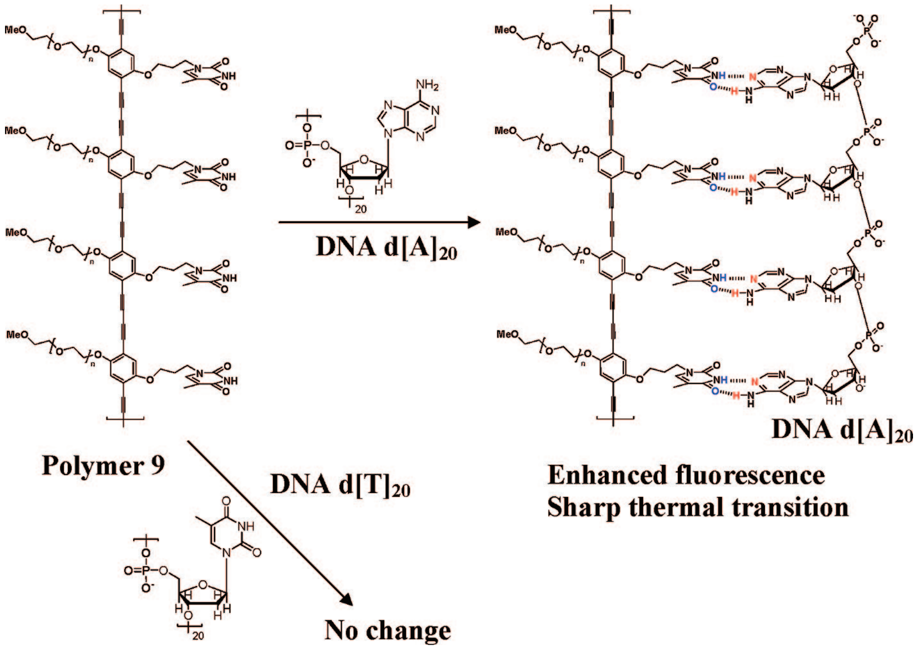
thymidine molecules to **9** causes no change in fluorescence (Figure 8). These results suggest that polymer **9** can undergo selective hydrogen-bonded molecular recognition to complementary guest molecules in water as well. This association likely causes a reduction in the quenching effect of the free thymine units due to possible reorientation upon hydrogen bonding as well as a decrease in the degree of $\pi$-stacking between different polymer chains as adenosine binds. Both effects can lead to an increase in fluorescence intensity (Scheme 3).

However, the emission intensity increase in water is much smaller than that of the polymer with DAP molecules in CHCl$_3$. This is a reflection of the reduced binding constants between the thymine units of polymer **9** and complementary molecules in water, which is a competitive solvent to hydrogen bonding. Thus, polymer **9** can sense and selectively recognize complementary small hydrophilic molecules in water as well, albeit with lower binding affinities than in CHCl$_3$.

*With Single-Stranded Complementary DNA (d[A]$_{20}$).* The association of polymer **9** with complementary single-stranded DNA d[A]$_{20}$ was examined with UV−vis, fluorescence, thermal denaturation experiments, circular dichroism (CD), and control experiments. The first set of experiments used a lower concentration of **9** in water ($1.24 \times 10^{-6}$ M). After addition of an equimolar amount of single-stranded DNA (d[A]$_{20}$), the absorption spectrum shows peaks at 260 nm (predominantly corresponding to the adenines in the DNA strand) and 288 nm (corresponding to the thymine units and the conjugated backbone of **9**) (Figure 9; the peak at ~450 nm corresponding to the conjugated chains could not be observed at this concentration).

As well, addition of this complementary DNA (d[A]$_{20}$) causes a ~2-fold enhancement in fluorescence intensity of **9** (excitation at 436 nm) (Figure 10). In a control experiment, a noncomplementary d[T$_{20}$] DNA strand was added to polymer **9**, and no observable changes in the fluorescence spectra of this conjugated polymer were detected. This result is consistent with specific, hydrogen-bonded association of the thymine units of polymer **9** with complementary DNA A$_{20}$. This is likely reducing their quenching effect on the conjugated polymer backbone and

**Scheme 4. Binding of Complementary and Noncomplementary DNA to Polymer 9 at Low Concentration in Water**



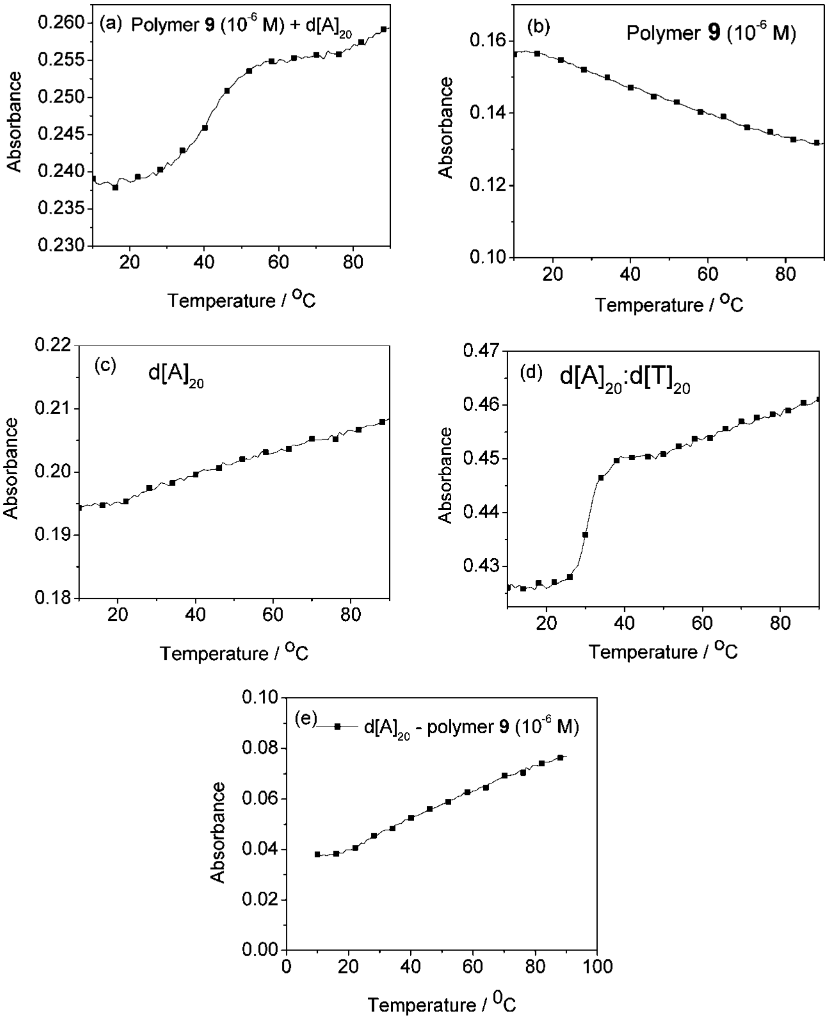


**Figure 11.** Temperature-dependent UV−vis spectra of (a) the polymer **9** ($10^{-6}$ M) and d[A]$_{20}$ complex and control thermal denaturation experiments of (b) polymer **9** ($10^{-6}$ M), (c) d[A]$_{20}$ and (d) dsDNA(AT$_{20}$) pairs, and (e) adding the two profiles for polymer **9** ($10^{-6}$ M) and A$_{20}$ measured at 260 nm.

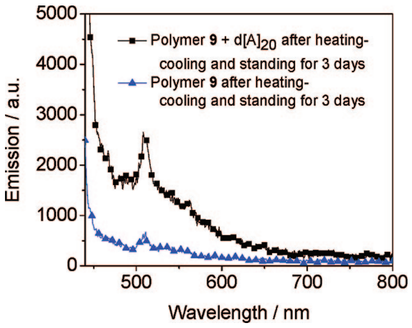


**Figure 12.** Fluorescence spectra of polymer with d[A]$_{20}$.

possibly separates the conjugated polymer strands and reduces their $\pi-\pi$ stacking.

The temperature dependence of the UV−vis spectra of polymer **9**:DNA was examined. Interestingly, the peak at 260 nm corresponding to the adenine units on DNA shows a sharp increase in absorbance at 43 °C, suggesting a transition from an associated state, where the adenine units are $\pi$-stacked, to a more dissociated state, where these units are separated (Figure 11a). The shape of this curve suggests cooperativity in this transition, similar to the interaction of two complementary DNA strands (a thermal denaturation experiment on natural d[A$_{20}$]:d[T$_{20}$] duplex in water is shown in Figure 11d). Heating the components separately, i.e. polymer **9** (Figure 11b) or single-

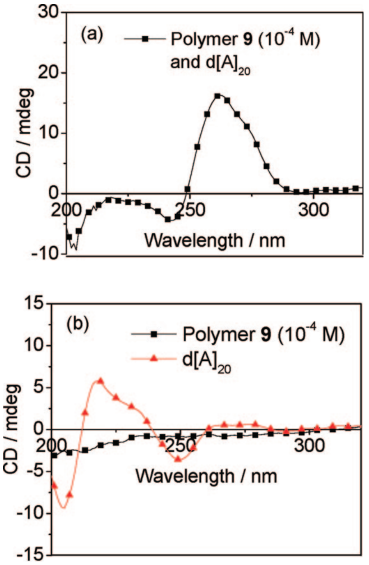


**Figure 13.** (a) CD spectra of the polymer **9** and d[A]$_{20}$ complex after heating−cooling and standing for 3 days. (b) CD spectra of polymer **9** (black) and d[A]$_{20}$ (red) after heating−cooling and standing for 3 days.

stranded DNA d[A$_{20}$] (Figure 11c), did not give rise to this sharp transition, nor is this thermal denaturation profile a result of

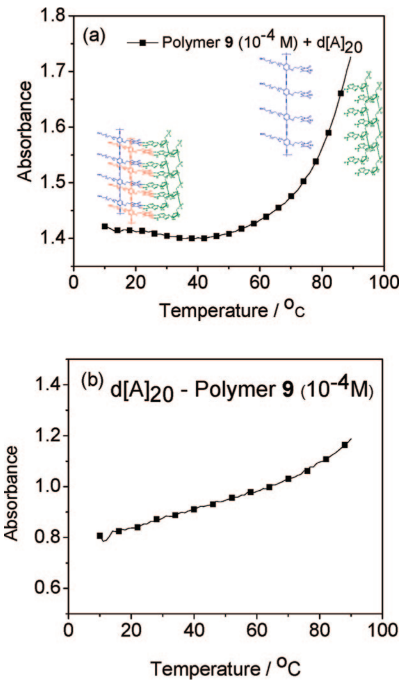


**Figure 14.** Temperature-dependent UV−vis spectrum of (a) polymer **9** ($10^{-4}$ M) and d[A]$_{20}$ complex after heating and cooling and standing for 3 days and (b) addition of the two separate profiles for each of polymer **9** ($10^{-4}$ M) and A$_{20}$ alone, measured at 260 nm.

simply adding the two profiles for polymer **9** and A$_{20}$ (Figure 11d). As well, no sharp increase in absorbance with increased temperature was observed for the noncomplementary mixture **9**:d[T$_{20}$]. These results are consistent with a specific hydrogen-bonding interaction of polymer **9** with complementary single-stranded DNA to give a complex with enhanced fluorescence. The results also indicate the ability of polymer **9** to recognize and discriminate between complementary and noncomplementary DNA (Scheme 4). The shape of the UV/vis thermal denaturation curve of polymer **9**:DNA A$_{20}$ suggests cooperative dissociation of the hydrogen-bonded network between polymer **9** and DNA upon heating and shows similarity to a natural DNA duplex thermal denaturation curve. We are currently further investigating the apparent cooperativity of this transition.

The association of polymer **9** with complementary DNA at higher concentrations ($2.05 \times 10^{-4}$ M) was also examined. When **9** is initially mixed with an equimolar amount of complementary DNA d[A$_{20}$], very few changes are detected in the emission and circular dichroism spectra. This is likely due to increased aggregation in this more concentrated sample, leading to decreased initial access to the thymine units. However, when the mixture is slowly heated and cooled (heat to 90 °C, cool to 10 at 0.5 °C/min) and then left standing for 3 days, dramatic spectroscopic changes were observed (Figures 12 and 13).

The fluorescence intensity of the polymer **9**:DNA complex is now increased (3-fold) after this heat−cool cycle (Figure 12) as compared to polymer **9** alone. This is consistent with binding of this polymer to the DNA A$_{20}$ and reduction of the degree of quenching of free thymine units and of the $\pi$-stacking of the conjugated polymer chains.[38]

Remarkably, this complex exhibits dramatic changes in its circular dichroism (CD) spectra (Figure 13a). While no CD spectrum could be recorded for polymer **9** alone, consistent with its lack of chirality, and only a weak CD trace was obtained for DNA A$_{20}$ alone in water (Figure 13b), a large, intense CD signal was observed for the associated complex polymer **9**:DNA (A$_{20}$) (Figure 13a). A large positive Cotton peak at 262 nm, a

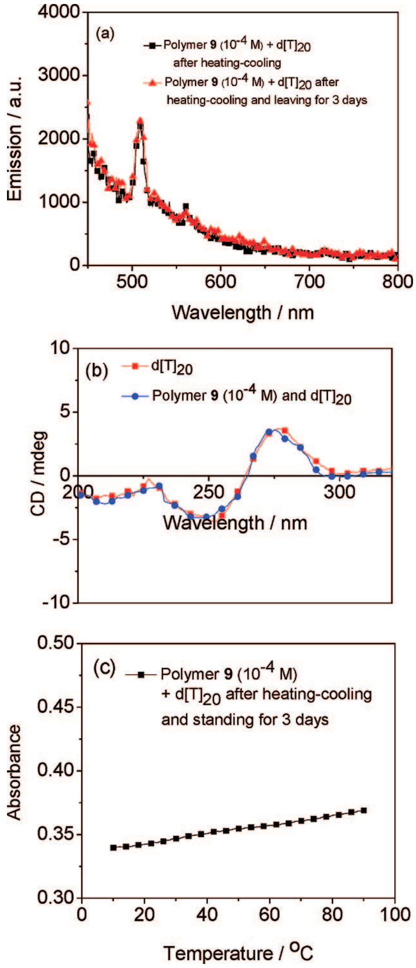


**Figure 15.** (a) Fluorescence, (b) CD, and (c) temperature-dependent UV−vis spectra measured at 260 nm of polymer **9** ($10^{-4}$ M) + d[T]$_{20}$ after heating−cooling cycle and standing for 3 days.

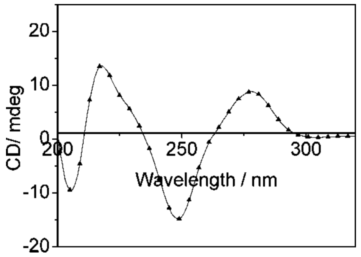


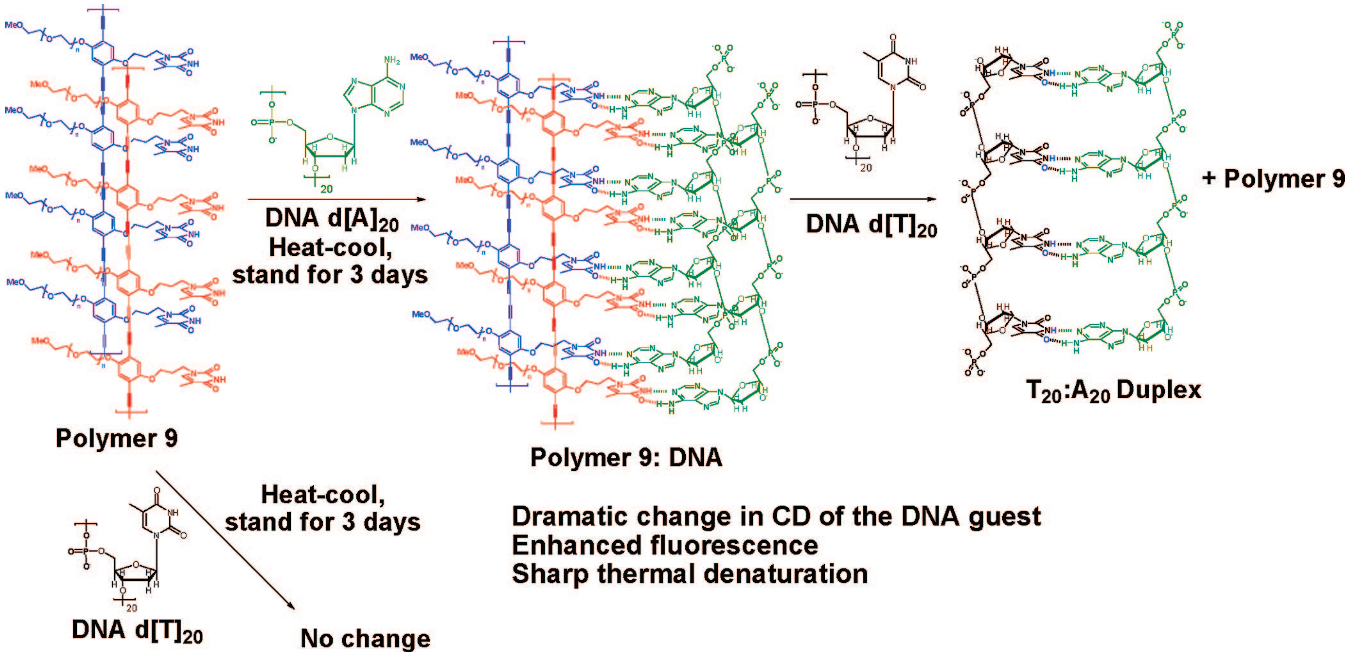
**Figure 16.** CD spectra of the addition of d[T]$_{20}$ to polymer **9** and d[A]$_{20}$ complex in an exchange experiment.

negative maximum at 243 nm, and zero crossing at 249 nm were recorded and are nearly identical to the typical signature of an A-form duplex DNA.

When a UV−vis thermal denaturation experiment was performed on this polymer **9**:DNA complex, a sharp and dramatic increase in the 260 nm absorbance was detected at a melting temperature of 80 °C (Figure 14).

On the other hand, when noncomplementary single-stranded DNA (T$_{20}$) is added to the same concentration of polymer solution and a similar heat−cool cycle is performed, there are no changes in the fluorescence or CD spectra of the polymer (Figure 15). Thermal denaturation experiments of this polymer **9**: DNA T$_{20}$ mixture show no additional transitions beyond that of the polymer alone. This demonstrates that polymer **9** binds specifically to DNA A$_{20}$ using hydrogen-bonding interactions.

**Scheme 5. Binding of Complementary and Noncomplementary DNA to Polymer 9 at High Concentration in Water**



In an exchange experiment, an equimolar amount of DNA T$_{20}$ is added to the polymer **9**:DNA A$_{20}$ complex. In this case, the CD features of this complex disappear, and the CD signature of double-stranded DNA A$_{20}$:T$_{20}$ arises, consistent with displacement of polymer **9** from the DNA A$_{20}$ strand and its replacement with DNA T$_{20}$. This suggests that the complex of polymer **9** with DNA is less stable than natural T$_{20}$:A$_{20}$ (Scheme 5 and Figure 16).

Overall, these data are consistent with binding of the conjugated polymer **9** at higher concentration to DNA A$_{20}$ by molecular recognition to form a complex with enhanced fluorescence, high melting temperature, and significant changes in the secondary structure of the bound DNA strand, possibly to A-form DNA (Scheme 5). Even at this higher concentration, polymer **9** can efficiently discriminate between complementary and noncomplementary DNA strands and displays distinct photophysical properties in the presence of these two molecules. To our knowledge, this is the first example of selective hydrogen-bonding association of a conjugated polymer with DNA[39] and points to a new approach to use molecular recognition with complementary biomolecules to finely control the degree of chain−chain association of a conjugated polymer and its photophysical properties.

## Conclusions

In summary, we have synthesized a new water-soluble $\pi$-conjugated poly($p$-phenylenebutadiynylene) polymer, which is functionalized with thymine nucleobases as well as poly(ethylene glycol) chains at every repeat unit. The polymer was characterized by UV−vis, fluorescence, $^1$H NMR, IR, Raman spectroscopy, and GPC experiments. These show the water-induced aggregation of this polymer into a morphology with increased $\pi$-stacking of the conjugated main chain, and its thermal denaturation, in a sharp transition, into a more molecularly dissolved phase, with decreased conjugated chain interactions. Importantly, we have demonstrated that this conjugated polymer selectively binds complementary small molecules, both in organic solvents and in water, as well as DNA strands and effectively discriminates between complementary and noncomplementary molecules. This binding is accompanied by an enhancement in its fluorescence intensity. Thus, polymers such as **9** can serve as a new platform to develop fluorescence sensors of DNA, DNA bases, and analogues. At higher concentration, polymer **9** forms a complex with complementary DNA, with high thermal stability, enhanced fluorescence, and a dramatic change in the secondary structure of the DNA guest (possibly to A-form DNA). The association of the conjugated polymer with DNA occurs with excellent discrimination between complementary and noncomplementary strands. Ongoing work is focused on expanding the use of these conjugated polymers as fluorescence sensors of biomolecules and as chemical biology tools to probe and influence changes in DNA structure.

## Experimental Section

**General Considerations.** All polymerization reactions were carried out under a dry oxygen atmosphere, using standard Schlenk techniques. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian M400 spectrometer operated at 400.140 and 100.035 MHz, representively. Chemical shifts are reported in ppm relative to the deuterated solvent resonances. UV/vis spectra were recorded on a Varian Cary 300 spectrophotometer. GPC spectra were recorded using a PL-GP 50 Plus Integrated GPC system equipped with two PL aquagel-OH column (7.5 × 300 mm) in series and in-line with a Varian RI-4 detector. Water was used as eluent at a flow rate of 0.6 mL/min, and the instrument was calibrated with poly(ethylene oxide) standards from Aldrich. Fluorescence experiments were carried out on a PTI (Photon Technology International) TimeMaster model C-720F spectrofluorimeter. Fluorescence quantum yields were measured by the relative method using fluorescein in 0.1 M NaOH ($\varphi_{436} = 0.92$) as a reference. In these measurements, the slit widths were adjusted so that the spectral bandwidth of the absorption and emission instruments were identical at 2.0 nm, and the absorbance of the sample and the reference were chosen so they were in the 0.1−0.2 range and nearly identical at the same excitation wavelength. Emission quantum yields were then calculated according to the method described by Crosby and Demas, taking into account the differences between the refractive indices of the sample and reference solutions. High-resolution mass spectral data (HRMS) were obtained on a Bruker APEX II FT-MS mass spectrometer. Raman spectra were measured with a FT-Raman system using 1064 nm laser. FT-IR spectra were measured with MIRacle ATR spectrometers. Lifetime studies were carried out on a Fluo Time 200 PICOQUANT time-resolved spectrometer using

PDL 800-B pulsed diode laser at 475 nm. In these measurements, the slit widths were adjacted to 2 nm with IRF as a reference.

**Materials.** Hydroquinone, poly(ethylene glycol) ether (average $M_w = 500$), and other reagents were purchased from Aldrich and used as received. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification.

**1-(2-(2-Chloroethoxy)polyethoxy)methane (2).** To a 250 mL round-bottomed flask containing 50 mL of benzene and 1 mL of pyridine, 2-(2-methoxypolyethoxy)ethanol (20 g, 0.04 mol) was added to the mixture, followed by dropwise addition of thionyl chloride (4 mL) with stirring under an ice bath. The solution was then refluxed for 12 h. After cooling to room temperature, the reaction mixture was poured into a large amount of ice water and extracted with $CH_2Cl_2$ (3 × 50 mL). The organic layer was dried with anhydrous $MgSO_4$ and evaporated to dryness. The crude product was distilled under reduced pressure (80 C/1mmHg) to yield the desired product (58−60 °C) which was colorless liquid 19.4 g. (94%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 3.97 (t, $J = 4.4$ Hz, 2H, $OCH_2$), 3.79 (t, $J = 4.4$ Hz, 2H, $OCH_2$), 3.71 (t, $J = 4.8$ Hz, 2H, $OCH_2$), 3.60 (t, $J = 4.8$ Hz, 2H, $ClCH_2$), 3.38 (s, 3H, $OCH_3$). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ (ppm) 71.8, 71.1, 70.3, 58.9, 42.6. HRMS (ESI) Calcd for $C_{23}H_{48}O_{11}Cl$ $[M]^+$ $n = 10$, 535.278 770; found: 535.28797 or $C_{25}H_{52}O_{12}Cl$ $[M]^+$ $n = 11$, 579.313 74, found: 579.31418 or $C_{27}H_{56}O_{13}Cl$ $[M]^+$ $n = 12$, 623.339 82, found: 623.340 40.

**1-[2-(2-Methoxyethoxy)polyethoxy]-4-hydroxybenzene (3).** To a stirred solution of hydroquinone (4.2 g, 38.5 mmol), potassium carbonate (5.3 g, 38.6 mmol), and potassium iodide (4.8 g, 28.8 mmol) in DMSO under $N_2$ was added 1-[2-(2-chloroethoxy)polyethoxy]methane (10 g, 19.2 mmol). The reaction mixture was heated to 70 °C overnight under $N_2$. After cooling to room temperature, the reaction mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layer was washed with water six times, dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was filtered through silica gel column chromatography using $CH_2Cl_2$:EtOAc (v:v 100:5) as eluent affording a viscous liquid of 7.8 g (69% yield). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 6.77 (s, 4H, ArH), 4.05 (t, $J = 5.2$ Hz, 2H, $OCH_2$), 3.80 (t, $J = 5.2$ Hz, 2H, $OCH_2$), 3.69−3.71 (m, 2H, $OCH_2$), 3.60−3.65 (m, 50H, $OCH_2$), 3.52−3.55 (m, 2H, $OCH_2$), 3.37 (s, 3H, $OCH_3$). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ (ppm) 151.9, 150.8, 115.9, 115.4, 71.7, 70.5, 70.3, 70.1, 69.7, 67.9, 58.8. HRMS (ESI) Calcd for $C_{29}H_{52}O_{13}Na$ $[M + Na]^+$ $n = 10$, 631.329 63; found: 631.330 02 or $C_{31}H_{56}O_{14}Na$ $[M + Na]^+$ $n = 11$, 675.354 94, found: 675.35623 or $C_{33}H_{60}O_{15}Na$ $[M + Na]^+$ $n = 12$, 719.380 86, found: 719.382 45.

**1-[2-(2-Methoxyethoxy)polyethoxy]-4-bromopropoxybenzene (4).** $K_2CO_3$ (7.2 g, 7.9 mmol), 1,3-dibromopropane (8.4 g, 41.4 mmol), and DMF (40 mL) were placed in a flame-dried round-bottomed flask, and the setup was purged with $N_2$. **3** (6.1 g, 10.4 mmol) was dissolved in DMF (30 mL), purged with $N_2$, and transferred dropwise to the reaction flask. The resulting mixture was then stirred at room temperature for 4 h. The reaction mixture was extracted with $CH_2Cl_2$ (3 × 30 mL).The combined organic layer was washed with water three times, dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was filtered through silica gel column chromatography using $CH_2Cl_2$/MeOH (v:v 100:5) as eluent affording a viscous yellow liquid of 4.6 g (63% yield). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 6.81 (s, 4H, ArH), 4.00−4.06 (m, 4H, $OCH_2$), 3.80 (t, $J = 4.4$ Hz, 2H, $OCH_2$), 3.73 (t, $J = 5.6$ Hz, 2H, $OCH_2$), 3.56−3.72 (m, 44H, $OCH_2$, $BrCH_2$), 3.51−3.53 (m, 2H, $OCH_2$), 3.35 (s, 3H, $OCH_3$), 2.25−2.28 (m, 2H, $CH_2$). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ (ppm) 152.9, 133.5, 115.4, 115.2, 71.7, 71.2, 70.6, 70.4, 69.8, 69.6, 67.9, 65.7, 58.9, 32.3, 30.0. HRMS (ESI) Calcd for $C_{30}H_{57}O_{12}BrN$ $[M + NH_4]^+$ $n = 9$, 702.305 42; found: 702.305 87 or $C_{32}H_{61}O_{13}BrN$ $[M + NH_4]^+$ $n = 10$, 746.331 42, found: 746.332 08 or $C_{34}H_{65}O_{14}BrN$ $[M + NH_4]^+$ $n = 11$, 790.357 66, found: 790.358 30.

**2-[2-(2-Methoxyethoxy)polyethoxy]-5-bromopropoxy-1,4-diiodobenzene (5).** To a round-bottom flask equipped with a magnetic stirrer was added **4** (4.6 g, 6.5 mmol), $Hg(OAc)_2$ (6.2 g, 19.5 mmol), $I_2$ (4.9 g, 19.5 mmol), and $CH_2Cl_2$ (70 mL). The reaction mixture was stirred for 4 h at room temperature, and the formed slurry was filtered through Celite 521. The Celite was washed with $CH_2Cl_2$. The filtrate was washed with $Na_2S_2O_3$, $NaHCO_3$, water, and brine and dried over $MgSO_4$. The crude product was isolated through silica gel column chromatography using $CH_2Cl_2$/MeOH(v:v 100:5) as eluent affording a viscous brown liquid of 3.4 g (55% yield). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.22 (s, 1H, ArH), 7.18 (s, 1H, ArH), 4.04−4.09 (m, 4H, $OCH_2$), 3.84−3.87 (m, 2H, $OCH_2$), 3.77−3.86 (m, 2H, $OCH_2$), 3.62−3.72 (m, 62H, $OCH_2$, $BrCH_2$), 3.51−3.56 (m, 2H, $OCH_2$), 3.36 (s, 3H, $OCH_3$), 2.27−2.34 (m, 2H, $CH_2$). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ (ppm) 152.7, 152.2, 123.0, 122.4, 86.3, 86.0, 71.6, 71.0, 70.8, 70.4, 70.2, 70.1, 70.0, 69.3, 67.2, 58.6, 32.0, 30.1. HRMS (ESI) Calcd for $C_{32}H_{56}O_{13}BrI_2$ $n = 10$, $[M + H]^+$ 981.101 56; found: 981.098 82 or $C_{34}H_{60}O_{14}BrI_2$ $n = 11$, $[M + H]^+$ 1025.127 26, found: 1025.12504 or $C_{36}H_{64}O_{15}BrI_2$ $n = 12$, $[M + H]^+$ 1069.153 96, found: 1069.151 25.

**2-[2-(2-Methoxyethoxy)polyethoxy]-5-thyminepropoxy-1,4-diiodobenzene (6).** To a stirred solution of thymine (1.2 g, 9.5 mmol), potassium carbonate (1.3 g, 9.4 mmol) in DMF under $N_2$ was added **5** (3.6 g, 3.8 mmol). The reaction mixture was heated to 60 °C overnight under $N_2$. After cooling to room temperature, the reaction mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layer was washed with water six times, dried over anhydrous $Mg_2SO_4$, and evaporated to dryness. The crude product was isolated through a silica gel column chromatography using $CH_2Cl_2$:MeOH (v:v 100:5) as eluent, affording a viscous dark brown liquid of 2.2 g (59% yield). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.16 (br s, 1H, pyrimidine NH), 7.23 (s, 1H, pyrimidine H-6), 7.16 (s, 1H, ArH), 7.12 (s, 1H, ArH), 4.11 (m 4H, $OCH_2$), 3.97−4.01 (m, 2H, $NCH_2$), 3.86−3.89 (m, 2H, $OCH_2$), 3.76−3.78 (m, 2H, $OCH_2$), 3.63−3.69 (m, 34H, $OCH_2$, $BrCH_2$), 3.53−3.55 (m, 2H, $OCH_2$), 3.37 (s, 3H, $OCH_3$), 2.19−2.21 (m, 2H, $CH_2$), 1.85 (s, 3H, $CH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 164.5, 153.1, 152.0, 151.0, 141.0, 123.3, 122.4, 110.0, 86.6, 85.7, 71.8, 71.0, 70.6, 70.4, 70.2, 69.9, 69.4, 66.2, 58.9, 45.9, 28.0, 12.2. HRMS (ESI) Calcd for $C_{33}H_{56}O_{13}N_3I_2$ $[M + NH_4]^+$ $n = 8$, 956.190 59; found: 956.189 70 or $C_{35}H_{60}O_{14}N_3I_2$ $[M + NH_4]^+$ $n = 9$, 1000.216 77, found: 1000.215 92 or $C_{37}H_{64}O_{15}N_3I_2$ $[M + NH_4]^+$ $n = 10$, 1044.242 13, found: 1044.243 24.

**2-[2-(2-Methoxyethoxy)polyethoxy]-5-thyminepropoxy-1,4-bis(trimethylsilylethynylbenzene (7).** To a stirred solution of **6** (1.1 g, 1.0 mmol), $PdCl_2(PPh_3)_2$ (72 mg, 0.10 mmol), and CuI (9.8 mg, 0.05 mmol) and triethylamine (10 mL) under $N_2$ was added (trimethylsilyl)acetylene (0.3 g, 2.5 mmol). After stirring at room temperature for 6 h, the reaction mixture was extracted with $CH_2Cl_2$. The combined organic layer was washed with water three times, dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was purified by silica gel column chromatography using $CH_2Cl_2$/MeOH (v:v 100:5) as eluent to afford a viscous dark brown liquid **7** of 0.88 g (90% yield). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.06 (s, 1H, pyrimidine NH), 7.22 (s, 1H, pyrimidine H-6), 6.94 (s, 1H, ArH), 6.89 (s, 1H, ArH), 4.11−4.15 (m, 4H, $OCH_2$), 3.95−4.01 (m, 2H, $NCH_2$), 3.87 (t, $J = 5.2$ Hz, 2H, $OCH_2$), 3.76−3.78 (m, 2H, $OCH_2$), 3.64−3.65 (m, 40H, $OCH_2$), 3.53−3.55 (m, 2H, $OCH_2$), 3.37 (s, 3H, $OCH_3$), 2.17−2.20 (m, 2H, $CH_2$), 1.78 (s, 3H, $CH_3$), 0.23−0.26 (m, 18H, $Si(CH_3)_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 164.5, 153.8, 152.9, 150.9, 141.3, 117.5, 114.3, 113.4, 109.9, 100.9, 100.6, 100.5, 100.3, 71.7, 70.9, 70.5, 70.3, 70.2, 69.4, 64.8, 58.7, 45.4, 27.5, 11.9, −0.14, −0.18. HRMS (ESI) Calcd for $C_{45}H_{78}O_{14}N_3Si_2$ $[M + NH_4]^+$ $n = 9$, 940.502 93; found: 940.501 69 or $C_{47}H_{82}O_{15}N_3Si_2$ $[M + NH_4]^+$ $n = 10$, 984.529 28, found: 984.527 90 or $C_{49}H_{86}O_{16}N_3Si_2$ $[M + NH_4]^+$ $n = 11$, 1028.556 15, found: 1028.554 12.

**2-[2-(2-Methoxyethoxy)polyethoxy]-5-thyminepropoxy-1,4-bis(ethynyl)benzene (8).** To a stirred solution of **7** (0.32 g, 0.33 mmol) in $CH_2Cl_2$ (20 mL) and methanol (20 mL) was added potassium carbonate (0.23 g, 1.07 mmol). After stirring at room temperature for 2 h, the reaction mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layer was washed with water three times, dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was purified by silica gel column chromatography using $CH_2Cl_2$/MeOH (v:v 100:2) as eluent to afford a colorless viscous liquid of 250 mg (92% yield). $^1H$ NMR (400 MHz, $CDCl_3$: $\delta$ (ppm) 8.05 (s, 1H, pyrimidine NH), 7.13 (s,1H, pyrimidine H-6), 7.02 (s,1H, ArH), 6.93 (s,1H, ArH), 4.15 (t, $J = 5.2$ Hz, 4H, $OCH_2$), 4.01 (t, $J = 6.0$ Hz, 2H, $NCH_2$), 3.96 (t, $J = 6.4$ Hz, 2H, $OCH_2$), 3.87 (t, $J = 4.4$ Hz, 2H, $OCH_2$), 3.74−3.77(m, 2H, $OCH_2$), 3.60−3.79 (m, 40H, $OCH_2$), 3.53−3.55 (m, 2H, $OCH_2$), 3.37 (s, 4H, $OCH_3$, CH), 2.14−2.21 (m, 2H, $CH_2$), 1.82 (s, 3H, $CH_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 164.4, 154.1, 153.1, 150.9, 141.2, 118.2, 117.5, 113.8, 112.9, 110.2, 83.3, 83.0, 79.5, 79.2, 71.8, 71.0, 70.6, 70.4, 69.5, 69.4, 58.9, 45.8, 27.8, 12.1. HRMS (ESI) Calcd for $C_{43}H_{70}O_{16}N_3$ $[M + NH_4]^+$ $n = 11$, 884.475 06; found: 884.475 06 or $C_{45}H_{74}O_{17}N_3$ $[M + NH_4]^+$ $n = 12$, 928.500 61, found: 928.501 28 or $C_{47}H_{78}O_{18}N_3$ $[M + NH_4]^+$ $n = 13$, 972.527 22, found: 972.527 49.

**Polymer 9.** A flask was charged with **8** (40 mg, 0.05 mmol), CuCl (0.6 mg, 0.006 mmol), TMEDA (0.8 mg, 0.006 mmol), chlorobenzene (1.0 mL), and a stir bar under a flow of nitrogen. A stream of oxygen was bubbled through the reaction mixture for 5 h at room temperature, and the reaction mixture was left stirring for an additional 67 h under an oxygen atmosphere. The residue was washed with $CHCl_3$ and poured into a large amount of methanol to give polymer **9** in 85% yield (34 mg). $^1H$ NMR (500 MHz, $D_2O$): $\delta$ (ppm) 7.94 (s, pyrimidine H-6), 7.41 (s, ArH), 7.33 (s, ArH), 4.01 (s, $OCH_2$), 3.86 (s, $NCH_2$), 3.76 (s, $OCH_2$), 3.52 (bs, $OCH_2$), 3.13 (s, $OCH_3$), 2.58 (bs, $CH_2$), 1.64 (s, $CH_3$).

**1,4-Di[2-(2-Methoxyethoxy)polyethoxy]benzene (1′).** To a stirred solution of hydroquinone (1.5 g, 13.6 mmol), sodium hydride (1.3 g, 54.4 mmol), and potassium iodide (1 g, 6.0 mmol) in DMF under $N_2$ was added 1-[2-(2-chloroethoxy)polyethoxy]methane (15 g, 29 mmol). The reaction mixture was heated to 60 °C overnight under $N_2$. After cooling to room temperature, the reaction mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layer was washed with water six times, dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was filtered through silica gel column chromatography using $CH_2Cl_2$: MeOH (v:v 10:1) as eluent affording a viscous yellow liquid of 9.9 g (71% yield). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ (ppm) 6.81 (s, 2H, ArH), 4.05 (t, $J = 5.4$ Hz, 2H, $OCH_2$), 3.81 (t, $J = 4.5$ Hz, 2H, $OCH_2$), 3.67−3.72 (m, 2H, $OCH_2$), 3.63−3.64 (m, 40H, $OCH_2$), 3.52−3.56 (m, 2H, $OCH_2$), 3.36 (s, 3H, $OCH_3$). $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ (ppm) 153.0, 115.4, 71.9, 70.7, 70.6, 70.5, 69.8, 68.0, 59.0.

**2,5-Di[2-(2-Methoxyethoxy)polyethoxy]-1,4-diiodobenzene (2′).** To a round-bottom flask equipped with a magnetic stirrer was added **1′** (6.1 g, 5.7 mmol), $Hg(OAc)_2$ (5.4 g, 16.9 mmol), $I_2$ (4.3 g, 16.9 mmol), and $CH_2Cl_2$ (80 mL). The reaction mixture was stirred for 4 h at room temperature, and the formed slurry was filtered through Celite 521. The Celite was washed with $CH_2Cl_2$. The filtrate was washed with $Na_2S_2O_3$, $NaHCO_3$, water, and brine and dried over $MgSO_4$. The crude product was isolated through silica gel column chromatography using $CH_2Cl_2$/MeOH(v:v 10:1) as eluent affording a viscous brown liquid of 5 g (66% yield). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ (ppm) 7.22 (s, 1H, ArH), 4.09 (t, $J = 4.8$ Hz, 2H, $OCH_2$), 3.87 (t, $J = 4.8$ Hz, 2H, $OCH_2$), 3.77 (t, $J = 5.2$ Hz, 2H, $OCH_2$), 3.64−3.69 (m, 44H, $OCH_2$), 3.53−3.55 (m, 2H, $OCH_2$), 3.37 (s, 3H, $OCH_3$). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ (ppm) 152.9, 123.2, 86.2, 71.7, 70.9, 70.5, 70.4, 70.1, 69.4, 67.2, 58.8.

**2,5-Di[2-(2-Methoxyethoxy)polyethoxy-1,4-bis(trimethylsilylethynylbenzene (3′).** To a stirred solution of **2′** (2.9 g, 2.2 mmol), $PdCl_2(PPh_3)_2$ (0.3 g, 0.42 mmol), CuI (40 mg, 0.21 mmol), and triethylamine (10 mL) under $N_2$ was added (trimethylsilyl)acetylene (0.7 g, 7.1 mmol). After stirring at room temperature for 6 h, the reaction mixture was extracted with $CH_2Cl_2$. The combined organic layer was washed with water three times, dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was purified by silica gel column chromatography using $CH_2Cl_2$/MeOH (v:v 10:1) as eluent to afford a viscous dark brown liquid **7′** of 2.7 g (96% yield). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 6.89 (s, 1H, ArH), 4.10 (t, $J = 5.4$ Hz, 2H, $OCH_2$), 3.85−4.87 (m, 2H, $OCH_2$), 3.75−3.77 (m, 2H, $OCH_2$), 3.63−3.64 (m, 42H, $OCH_2$), 3.52−3.55 (m, 2H, $OCH_2$), 3.37 (s, 3H, $OCH_3$), 0.23 (m, 18H, $Si(CH_3)_3$). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 153.9, 117.5, 114.3, 100.9, 100.6, 71.9, 71.2, 70.8, 70.6, 69.7, 69.6, 59.0, 0.08.

**2,5-Di[2-(2-Methoxyethoxy)polyethoxy]-1,4-bis(ethynyl)benzene (4′).** To a stirred solution of **3′** (2.7 g, 2.1 mmol) in $CH_2Cl_2$ (50 mL) and methanol (50 mL) was added potassium carbonate (1.2 g, 8.6 mmol). After stirring at room temperature for 2 h, the reaction mixture was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic layer was washed with water three times, dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was purified by silica gel column chromatography using $CH_2Cl_2$/MeOH (v:v 100:2) as eluent to afford a colorless viscous liquid of 2 g (83% yield). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 6.98 (s,1H, ArH), 4.13 (t, $J = 5.1$ Hz, 4H, $OCH_2$), 3.85 (t, $J = 4.8$ Hz, 2H, $OCH_2$), 3.74−3.77 (m, 2H, $OCH_2$), 3.63−3.67(m, 50H, $OCH_2$), 3.52−3.57 (m, 2H, $OCH_2$), 3.37 (s, 3H, $OCH_3$), 3.35 (s, 1H, CH). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ (ppm): 154.1, 118.3, 113.6, 83.3, 79.6, 72.0, 71.1, 70.7, 70.6, 69.6, 69.5, 59.1.

**Control Polymer 10.** A flask was charged with **4′** (150 mg, 0.13 mmol), CuCl (1.2 mg, 0.012 mmol), TMEDA (0.3 mL, 0.012 mmol), chlorobenzene (2.0 mL), and a stir bar under a flow of nitrogen. A stream of oxygen was bubbled through the reaction mixture for 5 h at room temperature, and the reaction mixture was left stirring for an additional 67 h under an oxygen atmosphere. The residue was washed with $CHCl_3$ and poured into a large amount of methanol to give polymer **10** in 95% yield (148 mg). $^1H$ NMR (500 MHz, $D_2O$): $\delta$ (ppm) 7.02 (s, ArH), 4.20 (s, $OCH_2$), 3.88 (s, $OCH_2$), 3.76 (s, $OCH_2$), 3.65 (s, $OCH_2$), 3.50 (s $OCH_2$), 3.34 (s, $OCH_3$),

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$\pi$-stacking interactions of the polymer chains upon aggregation in water or (ii) forced coplanarization of the aromatic units upon aggregation, thus reducing the polymer band gap. However, the latter phenomenon is usually accompanied by band sharpening, while we observe broadening of the UV−vis band in water. In addition, the structure of **9** includes two acetylenes in the repeat unit, whose facile rotation should allow communication between twisted aromatic rings. Thus, we interpret the red shift and broadening as arising from increased $\pi-\pi$ stacking between polymer chains in water. Bunz, U. H. F *Chem. Rev.* **2000**, *100*, 1605–1644.

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