Construction and Molecular Understanding of an Unprecedented, Reversibly Thermochromic Bis-Polydiacetylene

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A new type of bis-PDA, in which two PDAs are linked via an intervening p-phenylene group, is developed. The Bis-PDA-Ph displays exceptional thermochromic reversibility owing to the presence of unique hydrophobic interactions between alkyl chains as well as aryl moieties. The Bis-PDA-Ph has a well-packed structure that causes it to display a clear blue to red colorimetric transition at elevated temperatures. To elucidate the molecular origin of the thermochromic response, a theoretical simulation of the new PDA, the results of which successfully explain the thermochromic reversibility phenomenon, is conducted. Furthermore, Bis-PDA-Ph-embedded polymer fibers are used as a thermochromic sensor material. It displays excellent reversibility between 20–120 °C, which is the largest temperature range reported thus far for PDA based sensors. Finally, transient absorption spectroscopy is employed for the first time to analyze the temperature-dependent fluorescence change of the new PDA.

1. Introduction

Since the time of the first report by Wegner in 1969,^[1] polydiacetylenes have become an extensively studied family of conjugated polymers.^[2–5] PDAs are generated by UV light irradiation of self-assembled diacetylene monomers, which promotes rapid polymerization to form ene-yne conjugated, blue colored polymers. The blue PDAs, which typically have absorption maxima at ≈640 nm, undergo a dramatic, naked-eye observable colorimetric change to red corresponding to absorption maxima at

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≈550 nm, when they are subjected to various types of environmental stimulation. The results of independent studies by Kim^[6] and Jelinek^[7] and their respective coworkers in 2005, which demonstrated that PDAs can serve as novel sensor systems, have stimulated the large effort that has been recently given to the development of new chemosensors based on PDAs.^[8–27]

Temperature is one of the common environmental stimulations that cause colorimetric transitions of PDAs. A number of studies have focused on thermochromic transitions of these materials, which in some cases are reversible.^[28–35] However, in most of the cases reported earlier, the temperature ranges for the reversible thermochromic PDA transitions were rather narrow and the production of clear blue to red transitions was rare and in some cases

not fully reversible (i.e., initial blue color cannot be fully recovered). For example, interesting bis-PDAs were recently found to be temperature sensors, but the temperatures over which they operate are in the 25–55 °C range.^[33] Moreover, even though the sensory properties of PDA systems have been actively studied, no theoretical studies or simulations of the transitions taking place in these materials have been described.

In the investigation described below, we prepared a new type of PDA, (Bis-PDA-Ph), in which two PDA moieties are connected via p-phenylene group. Bis-PDA-Ph displays reversible, blue to red and red to blue, temperature induced color changes even though it does not possess the typical types of groups (hydrogen bonding), which promote this phenomenon. Furthermore, thermochromic changes displayed by Bis-PDA-Ph-embedded electrospun fibers are highly reversible and occur over the rather wide temperature range of 20 to 120 °C, the largest recorded thus far. In addition, we carried out the first theoretical simulation of a PDA system and used the results to explain the thermochromic reversibility of the new PDA. We believe simulations, like those performed in this effort, will provide detailed information about the molecular basis for the reversible thermochromic behavior of PDAs. Finally, the results of transient absorption studies provided important information about the nature of fluorescence changes associated with the thermochromic transitions of the new PDA.

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Scheme 1. Synthesis of Bis-PCDA-Ph.

2. Results and Discussion

2.1. DA monomer and PDA preparation, Dynamic Light Scattering (DLS)

The DA monomer, Bis-PCDA-Ph (1), used in this study was prepared using the route shown in **Scheme 1**. 10, 12-Pentacosadiynoic acid (PCDA) was first activated by reaction with oxalyl chloride. The formed acid chloride was then reacted with *p*-hydroquinone to generate 1 in 90% yield. This substance was fully characterized by using ¹H NMR and ¹³C NMR spectroscopy, and FAB high resolution mass spectrometry. UV irradiation of selfassembled 1 in water for 30 s induced formation of the bluecolored Bis-PDA-Ph (**Scheme 2**). Furthermore, the particle size of Bis-PDA-Ph has been characterized with dynamic light scattering (DLS). This experiment was repeated 3 times in order to acquire an average data in Table S1 (Supporting Information).

2.2. Thermochromism of Bis-PDA-Ph in solution

Figure 1a shows images of a vial containing an aqueous solution of Bis-PDA-Ph at various temperatures. The blue color of the Bis-PDA-Ph polymer at room temperature changes to red as the temperature is increased to 100 °C. As explained in the introduction, previously reported PDAs display thermochromic behavior over relatively narrow temperature ranges or initially they undergo color changes that deteriorate to violet (or purple) to red rather than blue to red after the first cycle. The observations demonstrate that, unlike previously reported PDAs, Bis-PDA-Ph displays a highly distinct blue color at 20 °C and red color at 100 °C. In addition, the temperature induced color change is highly reversible, surviving more than 20 heating-cooling cycles without significant color bleaching (Figure 1b). The UV absorption spectrum of an aqueous solution of Bis-PDA-Ph at 20 °C and 100 °C, displayed in Figure 1c, shows that the blue color at room temperature is associated with an absorption maximum at ~630 nm and that of the red form of this PDA at 100 °C absorbs at 540 nm.

2.3. Theoretical Simulations of PDAs Systems

We carried out what we believe to be the first theoretical simulation of PDA systems. The setup of the Bis-PDA-Ph system



Scheme 2. Self-assembly and polymerization of Bis-PCDA-Ph.

used in the simulation is described fully in the Experimental Section and summarized in Figure 2 The model involves the use of the monomer stage to construct an ene-yne conjugated Bis-PDA-Ph polymer composed of 8 monomeric units, all connected in the same manner so that they represent infinitely long polymer chains. Sheets composed of polymeric PDA are stacked side by side with a separation of 0.5 nm to form a membrane. Finally, the PDA membrane is encased in water with water molecules within 0.28 nm of the membrane being absent. The resulting initial configuration, consisting of 14939 atoms and dimensions of 4.0 $\text{nm}\times3.9$ $\text{nm}\times10.4$ nm, is then subjected to molecular dynamics (MD) simulations using the CHARMM package (v. 38a1)^[35] with the help of the CHARMM-GUI website.^[36] The force fields for the model PDA system were obtained from CHARMM general force fields^[37] and the TIP3P water model was used.

The results of calculations show that the initial Bis-PDA-Ph membrane system maintains its general structure upon heating from 300 K to 400 K, presumably the consequence of

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Figure 1. a) Photographs of as aqueous solution of Bis-PDA-Ph at 20 °C, 70 °C, and 100 °C. b) Colorimetric response value (see Experimental Section) of the Bis-PDA-Ph solutions to cycles of temperature changes in the \approx 20–100 °C range. c) UV-Vis spectra of an aqueous solution of Bis-PDA-Ph at 20 °C and 100 °C.

the presence of the rigid π -conjugation that exists along the backbone of the polymer.

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Representative snapshots of the equilibrated Bis-PDA-Ph systems at these two temperatures are shown in **Figure 3** and the



Figure 2. Simulation model step: a) Bis-PCDA-Ph (1) monomer, b) Bis-PDA-Ph sheet, and c) side (upper) and top (lower) views of Bis-PDA-Ph membrane system in the presence of water.

equilibrium structural properties are summarized in Table S2 (Supporting Information). The first noticeable structural feature of the membrane is that the Bis-PCDA-Ph monomer tails are significantly tilted from the membrane normal direction

 $(\theta = 23.2^{\circ} \text{ at } T = 300 \text{ K})$. Because of this arrangement, the membrane thickness decreases significantly from its initial value of 6.23 nm to 5.76 nm and at the same time the area per monomer decrease slightly from 0.24 nm² to 0.22 nm². Interestingly, the area per monomer values arising from these calculations are consistent with those coming from previous studies,^[38] which are 0.24, 0.24, and 0.19 nm² for monomeric, blue, and red phases of mono-PDA Langmuir films, respectively.

As temperature increases to 400 K, the hydrocarbon tails of Bis-PCDA-Ph monomeric units move back in the membrane normal direction with the tilt angle $\theta = 14.9^{\circ}$ but, interestingly, the membrane thickness does not change. On the other hand, the area per monomer increases slightly from 0.22 nm² to 0.23 nm², a change that is mostly caused by the increased distance between the PDA polymer sheets from 0.449 nm at *T* = 300 K to 0.464 nm at *T* = 400 K.

The structural response of the Bis-PDA-Ph membrane system to changes in temperature was examined by measuring the orientation correlation function, C_1 , which is defined

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Figure 3. Representative simulation snapshots at a) T = 300 K and b) T = 400 K for the Bis-PDA-Ph membrane system. Upper figures are views from the direction normal to the Bis-PDA-Ph polymer sheets and lower figures from the top with the omission of water molecules. Snapshots and animations were generated by using VMD.^[34]

as the inner product between two unit normal vectors of the neighboring conjugated ene-vne planes along the Bis-PDA-Ph polymer backbone. The correlation function is a measure of the conjugation length along the Bis-PDA-Ph polymer backbone. In **Figure 4** are shown C_1 as well as tilt angle θ responses to linear temperature changes between 300 K and 400 K at a rate of 1.0 K ps⁻¹ (an animation of changes in the Bis-PDA-Ph system upon changing temperatures is provided in Supporting Information). Because the ene-yne conjugated backbone of the Bis-PDA-Ph is rigid, C1 changes only slightly. However, the finite skeletal changes reflected in changes in C_1 are clearly discernable and, except at the initial stage, they are well correlated with the temperature change even if it takes place rapidly. This observation indicates that π - π interactions between the benzene rings along with the rigid ene-yne network are mainly responsible for promoting the reversibility of the thermochromic transition of Bis-PDA-Ph.

2.4. Transient Absorption (TA) Spectroscopy Studies

PCDA-PDA, derived by polymerization of the PCDA monomer, was prepared as a control material for the TA studies. Transient



Figure 4. Responses of a) the orientation correlation function, C₁, and b) the monomer tilt angle, θ , to temperature changes for the Bis-PDA-Ph membrane system. The rate of the linear temperature change is 1.0 K/ps and the system temperature is also shown in (c).

absorption (TA) experiments were carried out to assess the electronic relaxation dynamics of Bis-PDA-Ph and PCDA-PDA. Bis-PDA-Ph and PCDA-PDA were electronically excited by irradiation with 630 nm light pulses at 22 °C and 525 nm light pulses at 80 °C, and the rates of relaxation of the corresponding electronic excited states were measured by using time-delayed probe pulses at different wavelengths (**Figure 5**, see Supporting Information). Decay profiles for Bis-PDA-Ph and PCDA-PDA at 22 °C are characterized by an initial fast relaxation process with a large amplitude at short times followed by a slow decay component with a very small amplitude at long times. Approximately 70% of TA signals decay within the first few ps. The slow relaxation behaviors of excited Bis-PDA-Ph and PCDA-PDA



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Figure 5. Transient absorption (TA) signals of Bis-PDA-Ph and PCDA-PDA at 22 and 80 °C. The inset shows the TA signals at long relaxation times (t > 90 ps). TA signals of Bis-PDA-Ph at 22 and 80 °C and PCDA-PDA at 22 °C decay almost completely at 1000 ps. In contrast, TA signal of PCDA-PDA at 80 °C decays on a much longer timescale.

at long times are shown in the inset of Figure 5. In addition, intermediate electronic relaxation processes connect the initial fast and slow decay components. The multi-timescale relaxation processes reflect the complicated electronic structures of chromophores present in Bis-PDA-Ph and PCDA-PDA.

3. Conclusion

In the study described above, we prepared the new bis-PDAs, Bis-PDA-Ph, in which two PDA moieties are linked via a *p*-phenylene group. Bis-PDA-Ph displayed excellent thermochromic reversibility as a consequence of the existence of unique hydrophobic interactions between alkyl chains as well as π - π interactions between aryl groups. The tightly packed structure of this PDA is responsible for the deep blue to red colorimetric transitions that take place in response to temperature changes over a range that is larger than those displayed by other types of PDAs developed to date. For the first time, a theoretical simulation of the PDA system was carried out. The results of this effort provide information about the molecular nature of reversible thermochromic process. In addition, Bis-PDA-Ph-embedded polymer fibers were prepared and utilized as a thermochromic sensor material. The fibers were observed to undergo a reversible color transition between 20 and 120 °C, which is the largest temperature range reported thus far for PDAs. Finally, transient absorption spectroscopy studies were conducted to gain information about the origin of fluorescence changes that some PDAs undergo in response to temperature.

4. Experimental Section

Methods: Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel (230–400 mesh).

¹H NMR and ¹³C NMR spectra were recorded using a 300 MHz NMR spectrometer. Chemical shifts were expressed in ppm and coupling constants (/) in Hz.

Synthesis of Bis-PCDA-Ph: Oxalyl chloride (0.63 mL, 4.96 mmol) was added dropwise to a methylene chloride solution containing 0.502 g (1.34 mmol) of 10, 12-pentacosadiynoic acid. After 1 h of stirring, one drop of dimethylformamide (DMF) was added to the solution and the resulting mixture was stirred for 4 h. To the residue obtained by concentration of the solution was added a solution containing 0.07 g (0.67 mmol) of hydroquinone and 0.4 mL (4 mmol) of triethylamine in 20 mL of THF. The resulting solution was stirred overnight at room temperature under N_2 . The residue obtained by concentration was subjected to silica gel column chromatography (CH₂Cl₂ 100%) to give Bis-PCDA-Ph (0.50 g, 90%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ (ppm): 0.83–0.87 (t, J = 6.9 Hz, 6H), 1.23–1.53 (m, 52H), 1.68–1.73 (m, 9H), 1.69–1.76 (m, 4H), 2.20–2.24 (m, 8H), 2.50–2.55 (t, / = 7.5 Hz, 4H), 7.06 (s, 4H). ¹³C NMR (300 MHz, CDCl₃) δ (ppm) 172.15, 148.05, 122.38, 77.44, 77.01, 76.59, 65.31, 34.31, 31.92, 29.65, 29.63, 29.61, 29.48, 29.35, 29.10, 29.08, 29.03, 28.90, 28.86, 28.75, 28.35, 28.29, 24.86, 22.63, 19.21, 19.19. FAB HRMS m/z = 823.6606 [M]+, calc. for C₅₆H₈₇O₄ = 823.6610

Preparation and Polymerization of Polymers: Preparation of PDA vesicles in aqueous solution was achieved by using the following method. A solution of Bis-PCDA-Ph monomer (16.5 mg, 0.02 mmol) in THF (2 mL) was injected into 18 mL of deionized water while shaking to yield a solution containing a total monomer concentration of 1 mM. The sample was then sonicated at 80 °C for 30 min. The resulting solution was filtered through a 0.8 μ m filter, giving a filtrate that was cooled to 4 °C for 12 h. Polymerization was carried out at room temperature by irradiating the solution with a 254 nm UV light (1 mW cm⁻²) for 30 s.

Determination of CR Values: To determine the thermochromic properties of the PDA, UV spectroscopy measurements were carried out using a 1 cm optical path length cell. The blue polymer was first transformed to its red phase by using a heating-cooling cycle. UV-Vis spectra were recorded during the first cycle. To quantify the extent of the blue-to-red color transitions, the CR value (%) was calculated using the following equation,

$$CR = [(PB_0 - PB_1) / PB_0] \times 100$$
(1)

where PB = $A_{blue}/(A_{blue} + A_{red})$, A_{blue} and A_{red} are the respective absorbances at 630 nm and 540 nm in the UV-Vis spectrum. PB₀ and PB₁ are the respective pre- and post-thermal perturbations values. The temperature of the aqueous PDA solution was controlled by using a water-bath system.

Molecular Model and Simulation Methods: A schematic for the set up of the model system is given in Figure 3. The Bis-PDA-Ph monomers, consisting of two PDA molecules linked by an aryl group, were transformed to the ene-yne conjugated polymer in the form of a sheet. The first and last monomers were connected by the same conjugation, a configuration which when combined with the periodic boundary condition imposed by the computer simulation represents an infinitely long polymer. The number of monomers per polymer was set a 8 in this model system. Eight polymeric PDA sheets were then stacked side by side to form a membrane. The initial distance between the neighboring sheets was set to 0.5 nm. Finally, the PDA membrane was soaked in water solution and water molecules within 0.28 nm from the membrane were removed. The resulting initial configuration consists of 14 939 atoms with 4.0 nm \times 3.9 nm \times 10.4 nm in dimension.

The molecular dynamics (MD) simulations were performed using the CHARMM package (v. 38a1)^[31] with the help of the CHARMM-GUI website.^[32] The force fields for the model PDA system were obtained from CHARMM general force fields^[33] and the TIP3P water model was used in this study. The long-range electrostatic interaction between charged atoms was treated by the PME method with the real space cutoff of 1.6 nm and the cutoff distance for the Lennard-Jones potential between non-bonded atom pairs was also set to 1.6 nm.

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www.MaterialsViews.com $20 \circ C$ $40 \circ C$ $60 \circ C$ $80 \circ C$ $100 \circ C$ $120 \circ C$ $120 \circ C$

Figure 6. Temperature promoted color transitions of the Bis-PDA-Ph based electrospun fibers.

The initial PDA membrane system was first energy-minimized by the steepest descent and the Newton-Raphson methods with 500 steps before being heated gradually up to 300 K with the rate of 10 K ps⁻¹ at constant volume. The heated PDA membrane system was then equilibrated with equilibrium NPT MD simulations until both the system energy and structural properties such as area per monomer and membrane thickness converged to a plateau. The pressure of 1.0 atm was applied in all directions independently: that is, the surface tension was set to zero.

Transient Absorption (TA) Experiments: In TA experiments, visible light pulses are used to excite electronically the PDAs and then relaxation of the electronic excited states of the PDAs is monitored by using timedelayed probe pulses at different wavelengths. The TA experimental setup is shown in Figure S1 (Supporting Information). Pulses at 800 nm with an *ca*. per pulse energy of 0.5 mJ and a \approx 35 fs pulse duration, generated using a femtosecond Ti:Sapphire oscillator and amplifer system (SpectraPhysics) operating at 1 kHz, were used to pump an optical parametric amplifier (OPA, SpectraPhysics) which then generates the signal (1.2–1.6 μ m) and idler (1.6–2.4 μ m) in the near-IR range. The pump pulses at 630 nm or 520 nm in the visible range were generated by using second harmonic generation of the signal or fourth harmonic generation of the idler from the OPA, respectively. White light used as the probe pulse was generated by focusing 800 nm pulses onto a 2 mm thick sapphire disk. The instrumental response function of the TA experimental setup was ≈200 fs. The probe beam was focused onto the sample by using a parabolic mirror (focal length = 100 mm) and its diameter was approximately 100 µm at the sample position. The pump beam was focused by using a lens with a 20 cm focal length and the diameter of the pump beam was almost 3 times larger than that of the probe beam at the sample position. The power of the pump beams was ca. 200 μW . After passing through the sample, the probe beam was collimated with a parabolic mirror (focal length = 100 mm), dispersed through a monochromator, and detected by using a Si photodiode. TA signals were measured with a lock-in amplifier by chopping the pump beam at 500 Hz. The sample solutions were housed in a 1 mm thick glass cell for TA experiments at room temperature (22 °C). For TA experiments at 80 °C, a home made temperature controlled cell with a 750 μm Teflon spacer was used and its temperature was controlled by using a temperature controller and measured with a K-type thermocouple. The temperature of the cell was maintained within at 80 \pm 0.2 $^{\circ}\text{C}$ during the elevated temperature TA experiments. The normalized TA signals associated with Bis-PDA-Ph and PCDA-PDA are shown in Figure S2 (Supporting Information). For quantitative analyses, the normalized TA signals of Bis-PDA-Ph and PCDA-PDA, fitted by using the multi-exponential function,

$$S(t) = \sum_{i=1}^{k} A_i \exp\left(-t / \tau_i\right)$$
⁽²⁾

are summarized in Table S2 (Supporting Information). The fitted curves are presented in $\ensuremath{\textit{Figure 6}}$

Preparation of Bis-PCDA-Ph Electrospun Fibers: To prepare the electrospun fibers, 0.015 g of Bis-PCDA-Ph and 0.15 g of Polyethylene oxide (PEO, $M_w = 600\ 000$) as a matrix polymer were added to a mixture of 4 mL CHCl₃ and 4 mL THF. The solution was vigorously stirred for 1 h and then placed in a syringe with the needle tip at a flow rate of $30\ \mu$ L h⁻¹ via an electrospinning system (NanoNC ESR200R2). Through the needle (gauge 27), which was connected to a high voltage (8.0 kV) power supply, the precursor solution was ejected to form fine fibers on a silicon (Si) wafer or filter paper on the surface of a grounded aluminum plate located 15 cm below the tip of the needle. After being dried in air for ~10 h, the as spun fibers were subjected to UV light irradiation at 254 nm (4 W) for 1 min in order to induce polymerization. The structure and morphology of the fibers were assessed using electron microscopy (FE-SEM, JEOL JSM-6700F).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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