Single Crystal to Single Crystal Polymerization of a Self-Assembled Diacetylene Macrocycle Affords Columnar Polydiacetylenes

Weiwei L. Xu, † Mark D. Smith, ‡ Jeanette A. Krause, § Andrew B. Greytak, † Shuguo Ma, † Cory M. Read, † and Linda S. Shimizu*†

†Department of Chemistry and Biochemistry and ‡College of Engineering and Computing, University of South Carolina, Columbia, South Carolina 29208, United States
§The Richard C. Elder X-ray Crystallographic Facility, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, United States

ABSTRACT: This manuscript describes a single-crystal-to-single-crystal polymerization of the dihydrate of diacetylene 1 (1·2H2O) to give an unusual polydiacetylene (PDA) structure that consists of aligned nanotubes, with each covalently bonded nanotube having two parallel PDA chains that run parallel down opposite sides of a channel defined by the macrocycle. Each PDA nanotube is connected with four other columns via amide hydrogen bonds with an N-(H)···O distance of 2.888(4) Å. Such well-ordered polymers should display quasi-one-dimensional electronic structures and may be of interest for the formation of highly conductive organic materials. We obtained the 1·2H2O form in bulk, which was polymerized by heating. Powder X-ray diffraction suggests that bulk PDA powder is single crystal and displays a similar structure as the PDA single crystals. Furthermore, we showed that PDA crystals absorbed I2 vapor. We believe that this unique PDA structure, which is amenable to property control via adsorbed guests, will be an attractive one for investigating charge-transfer doping in PDA-based organic electronic materials. We also observed two additional crystal forms, including 1·MeOH, which also shows a columnar assembly, and a tetrahydrate 1·4H2O that shows water tetramers that link four cycles into a 2D sheet structure.

INTRODUCTION

Carbon nanotubes1–3 and carbon nanofibers are widely studied because of their attractive electrical,4−7 mechanical,8,9 and thermal properties.10 Carbon rich tubular and fibrous structures have also been made via self-assembly or by polymerization of a variety of synthetic monomers.11−13 Polyacetylene14,15 and polydiacetylene (PDA) are of particular interest given their conductivity and optical properties. PDAs have potential applications in organic solar cells and as sensors.16−18 Diacetylene monomers are readily synthesized with a wide variety of functional groups. They can be assembled into columns or fibers and polymerized to give PDAs. Our group previously reported the synthesis of a diacetylene macrocycle that crystallizes as a dihydrate (1·2H2O) and undergoes polymerization upon heating to likely afford oligo- or polydiacetylenes as indicated by Raman spectroscopy and solid-state nuclear magnetic resonance (NMR).19 In this manuscript, we report that the dihydrate can be polymerized to a PDA through a single crystal to single crystal (SCSC) process. This process proceeds readily in smaller crystals and shows that significant atomic movement occurred within the crystal during the polymerization process. The resulting coaxial column contains two PDA chains that are aligned and run parallel down the sides of the nanotube column (Figure 1b). The two polymers of a single tube are rigid and separated by a fixed distance. The crystal consists of bundles of many highly oriented PDA nanotubes, which are connected through amide N-(H)···O hydrogen bonds to four neighboring nanotubes (Figure 1d). Such well-ordered polymers with quasi-one-dimensional electronic structures may be of interest for the formation of highly conductive materials due to the high density of states at the band edge and minimal disorder, as has been seen in the case of doped semiconducting carbon nanotubes.20,21 PDAs are of interest due to their robust nature and potentially tunable structures. They consist of a chain of alternating ene−ynes that show sensitivity to environmental conditions including temperature, pH, host−guest interactions, and solvent. PDAs display a relatively low band gap (~ 2.0 eV).22−24 Bulk PDA films display fast photoconduction properties and large nonlinear responses and are amenable to doping, which dramatically increases their conductivity.22−32 Because of their remarkable environmental sensitivity, PDAs have been incorporated into peptide nanostructures,33−45 helical polymers,46−48 liquid crystals,49−50 and sensors.51−57

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PDAs are typically synthesized from diacetylenes by UV irradiation or thermal polymerization, which can occur in either solution or in the solid state. However, following polymerization, the PDA polymers are often insoluble, making full structural characterization challenging. Wegner first reported that precise preorganization of diacetylene units within crystals facilitated a topochemical polymerization. When neighboring diacetylene units are prealigned with a repeat distance ($d1$) of 4.9 Å, a C1–C4 contact distance ($d2$) of 3.5 Å, and a tilt angle of 45°, the polymerization may be initiated by thermal or photochemical treatment. Supramolecular interactions have been used to assemble diacetylene monomers into structures that are prone to subsequent topochemical polymerization. For example, Goroff and Lauher utilized halogen bonding to preorganize diacetylenes within a cocrystal. Subsequent polymerization gave poly(diiododiacetylene). A recent report by Fowler and Lauher utilized a polyether bonding to preorganize diacetylenes within crystals. One polymorph stacked into columnar structures with a repeat distance of 4.84 Å. Slow annealing over 35 days gave a SCSC transformation to the PDA. Our group has been investigating the use of diacetylene-containing macrocycles that self-assemble to give tubular supramolecular polymers and can subsequently be polymerized to give covalent tubular polymers. Herein, we report three crystal forms of macrocycle 1. We observed the SCSC polymerization of 1·2H$_2$O to afford the PDA, when annealed at 190 °C under inert atmosphere (N$_2$ gas) for 12 h. We also observed a methanol solvate 1·MeOH with a distinctive blue color and a tetrahydrate (1·4H$_2$O). Neither of these crystalline forms underwent the SCSC polymerization.

This manuscript also investigates the properties of the crystalline PDA and examines the absorption of iodine by the PDA crystals and powder. We readily obtained the bulk crystals of 1·2H$_2$O and polymerized them by heating. Powder X-ray diffraction of the PDA samples prepared in bulk suggests that bulk PDA powder is single phase and displays a similar structure as the PDA single crystals. PDA crystals were doped with I$_2$ vapor to afford a ratio of 1:14 iodine (calculated as I$_2$) to PDA monomer. Comparison of X-ray photoelectron spectroscopy (XPS) survey scans of the PDA and PDA·I$_2$ complexes showed new peaks after iodine exposure, which were attributed to triiodide I$_3^−$ and pentaiodide I$_5^−$.

Finally, we report the formation of microcrystals by spin-coating a solution of 1 (1.0 mg/mL) on silicon wafers, glass, and quartz slides, and then thermally treating the assemblies at 190 °C for 3 h to facilitate polymerization. In general, the SEM imaging of the microcrystals on silicon substrates after polymerization gave good contrast (Figure 1c). The initial concentration of the spin-coated solution appears to influence the average length of the needles. Such microcrystalline PDAs may have advantages over larger crystals and could show faster equilibration with guests, be amenable for transport measurements, and may be more suitable for integration into thin film organic electronic devices.

### EXPERIMENTAL METHODS

All chemicals were purchased from Sigma-Aldrich or VWR and used without further purification. $^1$H and $^{13}$C NMR were recorded on Varian Mercury/VX 300 and 400 NMR spectrometers. Both the solid-state $^{13}$C CP-MAS and FSLG-HETCOR experiments were run on a Bruker AVANCE III-HD 500 MHz spectrometer equipped with a Doty Scientific 4 mm MAS probe. The CP-MAS was run with a 2 ms contact time with linear ramping on the $^1$H channel. The FSLG-HETCOR experiment had the contact time set at 200 μs. Sample rotation was 8.2 kHz, and data acquisition was performed with $^1$H decoupling using 100 kHz field and SPINAL64 modulation. Raman spectra were recorded with a J Y Horiba LabRam system using a 652 nm excitation laser. The solid-state UV–visible spectroscopic data were collected by using a Perkin-Elmer Lambda 35 UV–visible scanning spectrophotometer equipped with an integrating sphere. The DSC data of 1·2H$_2$O was collected on a TA Q2000 differential scanning calorimeter.

**Synthesis.** Macrocycle 1 was synthesized as reported. Characterization data: $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 9.14 (t, $J = 4.8$ Hz, 4
Table 1. Crystal and Refinement Data for Macrocycle 1 (1·2H₂O, 1·MeOH, and 1·4H₂O) and for the PDA Crystals

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<th></th>
<th>C₂₉H₂₄N₄O₄·2H₂O</th>
<th>C₂₉H₂₄N₄O₄·CH₂OH</th>
<th>C₂₉H₂₄N₄O₄·4H₂O</th>
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<td>7730, 2841</td>
<td>7430, 2200</td>
<td>12582, 1821</td>
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<td>0.1021</td>
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<td>0.893</td>
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<td>R₁ [ I &gt; 2σ (I) ]</td>
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<td>wR₂ (all data)</td>
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<td>0.2975</td>
<td>0.0920</td>
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<td>0.87/−0.56</td>
<td>0.17/−0.16</td>
<td>0.35/−0.22</td>
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Crystallographic Conditions. The X-ray quality crystals of 1·2H₂O were obtained readily by a slow evaporation of solvents. The diacetylene macrocycle (10 mg) was first dissolved in 5 mL MeOH/CH₂Cl₂/H₂O 45:55:10 (v:v:v), then the macrocycle solution was filtered through a syringe filter. Slow evaporation in the dark afforded colorless needlelike crystals; however, the crystals turned reddish in color over several days when exposed to light. Rare bluish crystals of the methanol solvate were collected at 150 K on a Bruker SMART APEX II CCD detector at Beamline 11.3.1 at the Advanced Light Source, which is equipped with a Bruker SMART APEX II CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to 2 Å. For the data for all crystals are summarized in Table 1.

Polymerization. Polymerizations were carried out by heating monomer crystals under an inert atmosphere (N₂ gas) at 190 °C for 12 h. The crystals of 1·2H₂O showed a SCSC transformation. The SCSC nature of the transformation was verified by performing the X-ray intensity data collections before and after the thermal polymerization process using the same crystal. The bulk PDA crystals displayed a dark purple/brown color. By examining the bulk PDA crystals with high-resolution NMR (75 MHz, DMSO-d₆), H NMR: δ 165.8, 134.0, 130.3, 128.7, 126.3, 76.2, 66.2, 29.4 ppm.

Preparation of Microcrystals. Micropores were prepared by spin-coating 1.0 and 1.5 mg/mL macrocycle solutions at a rate of 1000 rpm for 90 s on Si wafers, glass, and quartz slides using a SCS 6800 Spin Coater. Further thermal treatment of the microcrystals at 190 °C induced the polymerization process and afforded PDA microcrystals.

Scanning Electron Microscopy. PDA microcrystals prepared by spin-coating 1.0 and 1.5 mg/mL macrocycle 1 solution on Si wafers, glass, and quartz slides followed by thermal treatment were next examined by SEM. SEM images of PDA microcrystals were taken by using a TESCAN Vega-3 SBU pressure scanning electron microscope.

PXRD Studies. The powder X-ray diffraction experiments were performed on a Rigaku D/Max 2100 Powder X-Ray Diffractometer (Cu Kα radiation), and the experiments were run using a zero background slide on which the sample was gently pressed. The data were collected at increments of 0.04 degrees, and an exposure time of 5 s/step in the angular range of 5–60 degree 2θ at ambient temperature.

Iodine Doping. An iodine loading chamber (Figure S15 of the Supporting Information) was used to expose the sample to iodine vapor while deterring 1·2H₂O crystallization. In the chamber, the iodine partial pressure P₁ was controlled to be half of P₁, which represents the vapor pressure of iodine at ambient temperature. The sample of PDA crystals (5 mg) was exposed to iodine vapor in the chamber at 27 °C for 0–96 h to afford a doped sample PDA-I₂. The iodine doping reached saturation at ~48 h. The degree of doping was measured using a TA SDT Q600 thermogravimetric analysis (TGA).

X-ray Photoelectron Spectroscopy (XPS). XPS was conducted using a Kratos AXIS Ultra DLD XPS system, which was equipped with a monochromatic Al Kα source. The monochromatic Al Kα source was operated at 15 keV and 120 W, and the pass energy was fixed at 40 eV for the detailed scans. The binding energy was calibrated using an Ag foil with Ag3d₅/₂ set at 368.21 ± 0.025 eV for the monochromatic Al Kα X-ray source.

**RESULTS AND DISCUSSION**

Previous work demonstrated that macrocycle 1 assembled into columnar structures and underwent a thermal reaction to give oligo- or polydiacetylenes. Although the crystals examined cracked lengthwise during this process, both the assembled macrocycle 1 and its subsequent polymerization PDA significantly crystalline. Both assembled 1 and the polymerized PDA showed 1·2H₂O gas adsorption isotherms indicative of microporous systems. We set out to investigate if the...
polymerization could be carried out in a SCSC process. Our first objective was to scale both the synthesis and crystallization of macrocycle I. The key step was an Eglinton acetylene—acetylene coupling reaction that could be carried out on a 0.5–1 g scale; however, optimal purification of the product required column chromatography, which proved to be the limiting step. With gram quantities of the material in hand, we studied crystallization conditions for I. The 1·2H2O crystal form was readily and reproducibly obtained by slow evaporation of I (2 mg/mL in 45:55:5 MeOH/CH2Cl2/H2O) and exhibited a structure identical to that previously reported.19 Crystals of 1·2H2O were initially colorless but gradually turned reddish after prolonged exposure to ambient light. A minor crystalline form 1-MeOH was occasionally observed in small quantities (<1%) under the same crystallization conditions and was blue in color. The tetrahydrate crystals 1·4H2O were from a solution of I (1 mg/mL) in MeOH/CH2Cl2/H2O 50:50:15 (v:v:v). We will examine each of these structures in more detail below.

The X-ray analysis of the abundant dihydrate crystal (1·2H2O) was described in our previous report.19 We present the structure again as this manuscript reports its subsequent SCSC polymerization. The 1·2H2O crystal is monoclinic with a P21/c space group with unit cell dimensions of a = 4.99 Å, b = 14.69 Å, c = 16.87 Å, β = 96.90°, and a unit cell volume of 1226.89 Å³ (Table 1). Macrocycle 1 lies on a crystallographic inversion center. It is relatively planar and stacks into columns with a repeat distance (d1) of 4.99 Å and a tilt angle of 41.6°; the orientation angle of two adjacent cycles is 63.9° (Figure 2a).

Figure 2. Dihydrate 1·2H2O crystals obtained by slow evaporation of 1 from 45:55:5 MeOH/CH2Cl2/H2O. (A) Columnar assembly of 1 displays neighboring macrocycles that self-assemble into a columnar structure through amide—amide hydrogen bonding with an N–(H)···O distance of 2.81 Å. (B) Solid-state UV–vis absorption spectrum of crystal 1 shows two bands with λmax = 288 and 571 nm.

The macrocycle self-assembles into a columnar structure through amide—amide hydrogen bonding with an N–(H)···O distance of 2.81 Å. Two sets of diacetylene units are aligned along each side of the column. The diacetylene moieties in adjacent macrocycles have a contact distance (d2) of 3.58 Å and display a supramolecular organization that is close to the ideal topochemical polymerization requirements for polymerization.38,39 Although both colorless and reddish crystals were examined, no differences were detected by X-ray diffraction. However, the reddish 1·2H2O crystals do show a new broad UV–vis absorption band with λmax = 571 nm (Figure 2b), which may indicate the presence of a small percentage of oligo or polydiacetylene on the surface of the crystal. This is further supported by the Raman spectrum of the crystals, which shows two characteristic resonance bands at ~1506 and ~2107 cm⁻¹ for polydiacetylene (Figure S5 of the Supporting Information).38,69 The observation of these Raman PDA bands, while the majority of the crystal is monomer by X-ray diffraction, illustrates that Raman is not necessarily a good method for assessing conversion.

A small needlelike single crystal (0.52 × 0.05 × 0.04 mm³) was subjected to X-ray analysis, and its structure was confirmed as the dihydrate 1·2H2O. The crystal was then heated at 190 °C under an inert atmosphere (N2) for 12 h, which induces a loss of interstitial water molecules and facilitates the polymerization to afford the PDA. Aside from a slight darkening in color, the small crystal appeared identical to the unheated crystal (Figure 3, inset). A second X-ray data collection was performed on the heated crystal, and the polymeric structure C29H30N4O4 (repeat unit) was confirmed (Figure 3b). Although significant atomic movement occurred within the crystal, the single-crystal-to-single-crystal transformation took place without a change in space group (P21/c for both forms). The unit cell dimensions changed slightly to a = 4.90 Å, b = 14.59 Å, c = 16.29 Å, β = 104.12° (Table 1). The unit cell volume correspondingly decreased from 1226.89 to 1127.70 Å³, which is primarily due to loss of the interstitial water molecule guests and the creation of hydrogen bonds between polymeric columns. The asymmetric unit consists of half of one polymeric formula unit, which is situated about a crystallographic inversion center. Comparison of the two structures shows that upon reaction, the relatively planar macrocycle 1 becomes a more folded repeat unit in the PDA and displays a smaller interior cavity. Figure 4a highlights the reacted monomer unit within the columnar PDA.

Figure 3. Single-crystal-to-single-crystal (SCSC) transformation of dihydrate 1·2H2O to a PDA. (A) The initial dihydrate 1·2H2O structure highlights the observed repeat distance d1 = 4.99 Å, the contact distance d2 = 3.58 Å, the tilt angle θ = 41.6° and the orientation angle Φ = 63.9°. (B) Upon heating at 190 °C for 12 h, the diacetylene macrocycles undergo a SCSC polymerization process to afford a PDA.
phenyl hydrogens that point into the center of the cycle and the distance between double bonds on either side. Each column consists of two polydiacetylene chains. These individual columnar polymers are organized in three dimensions by hydrogen bonds. Each polymeric column is surrounded by six columns and interacts with four other columns via N(1)–H(1)···O(2) intermolecular hydrogen bonds of 2.888(4) Å (Figure 4d).

To highlight the movement that occurs over the course of the polymerization, we juxtaposed the two crystal structures in Figure 5a. The PDA is depicted on top and the dihydrate column highlights one monomeric unit. The major conformation of the cycle is caused by the presence of two opposite solvent regions, which was modeled as methanol. The disorder may expand like clay to absorb guests in between the strong hydrogen bonds.70–74 For example, self-assembled materials may modulate weak noncovalent interactions in order to absorb guests.75–82 Prior work on our pyridyl bis-urea columns with unsatisfied exterior acceptors demonstrated that the columns may expand like clay to absorb guests in between the strong columnar assembly.83,84 Thus, we are currently investigating the uptake of guests by these PDA materials to determine if the guests are indeed absorbed in the channels or are alternatively taken up in between neighboring PDA columns.

**New Crystal Forms of 1.** While most of our work was carried out on the dihydrate 1·2H₂O crystal form of 1, we observed two additional forms: a methanol solvate 1·MeOH and a tetrahydrate 1·4H₂O. Distinctive, pale blue block crystals of 1·MeOH were obtained under the same crystallization conditions from a solution of 1 (2 mg/mL) in 45:55:5 MeOH/CH₂Cl₂/H₂O; however, these crystals were unusual and only observed in small quantities (<1%). This crystal form displays a smaller, triclinic unit cell with a volume of 578.7 Å³, which is approximately half the volume observed for monoclinic 1·2H₂O. The asymmetric unit consists of half of one disordered C₂₈H₂₀N₄O₄ crystal form of 1·2H₂O, which was modeled as methanol. The disorder of the cycle is caused by the presence of two opposite conformations of the –C(O)NH– group (C8, O2, and N2) and also affects the phenyl ring atoms C2–C7 and atoms C12–C14 of the attached –CH₂CC– grouping. The macrocycles are not planar but bent, with the two aryl units pointing on opposite sides of a plane formed from the diacetylenes (Figure 6b).

The starting material was measured as 177.1° and 173.6°, respectively. Upon polymerization, the corresponding bond angles of polymer were shifted to 118.1° and 116.4°.

Our previous work on the heat-treated 1·2H₂O crystals demonstrated that the oligo or polydiacetylene show gas adsorption isotherms indicative of a microporous material;19 analysis of the X-ray structure of the PDA suggests that the interior channel of the columns has a very small diameter. The column size of PDA was estimated to be 4.9 × 2.3 Å (accounting for van der Waals radii). Figure 5b displays a space-filling model of PDA crystals, which indicates that individual columns are tightly packed with no obvious room left for guest molecules; however, close-packed systems may expand to absorb guests.70–74 For example, self-assembled materials may modulate weak noncovalent interactions in order to absorb guests.75–82 Prior work on our pyridyl bis-urea columns with unsatisfied exterior acceptors demonstrated that the columns may expand like clay to absorb guests in between the strong columnar assembly.83,84 Thus, we are currently investigating the uptake of guests by these PDA materials to determine if the guests are indeed absorbed in the channels or are alternatively taken up in between neighboring PDA columns.

**Figure 4.** Views from the PDA single crystal: (A) A side view of the PDA column highlights one monomeric unit. (B) Top view of the monomer unit. (C) Intrapolymeric N(2)–H(2)···O(1) hydrogen bonds shown as red dashed lines. Bonds connected to not shown neighboring monomeric units in the polymeric column were labeled as yellow dots. (D) Packing diagram of polymeric columns looking down from the a axis. The columns are joined via N(1)–H(1)···O(2) hydrogen bonds.

**Figure 5.** (A) The background drawing shows the crystal structure of the diacetylene monomer in the dihydrate 1·2H₂O crystals. The foreground drawing shows the structure of the PDA. All the molecules were cut in half for clarity. The macrocycle rotates by a pivot of methylene carbons. The C9–C10–C11 bond angle changed from 177.1° to 118.1°, and the C12–C13–C14 bond angle changed from 173.6° to 116.4°. The repeat distance d1 of the adjacent cycle is essentially unchanged (4.986 Å in 1·2H₂O to 4.985 Å in the PDA). (B) Packing diagram of the polymeric columns of the PDA looking down the a axis. The center column is shown as a space-filling model to emphasize the small channel, which is approximately 2.3 × 4.9 Å in diameter.
The individual macrocycles stack into columns through the formation of hydrogen bonds \([\text{N(H)}\cdots\text{O}; \text{D}\cdots\text{A} = 2.71(3) \text{ Å}], \text{DHA angle } = 138.4^\circ\) between the nondisordered amides (Figure 6c) of neighboring macrocycles. The repeat distance \(d1\) is 4.53 Å in 1·MeOH, and the contact distance \(d2\) of the reacting carbon atoms is \(\sim 3.70 \text{ Å}﻿\).

Given that the diacetylene units in the 1·MeOH crystals are organized close to ideal topochemical polymerization requirements,58,59 we subjected the crystal to the same annealing conditions. The crystal was heated at 190 °C under an inert atmosphere \(\text{(N}_2\text{)}\) for 12 h and turned dark purple/brown. We observed a Raman spectrum typical for an oligo- or polydiacetylene,58,69 with characteristic resonance bands at \(\sim 1500\) and \(\sim 2100 \text{ cm}^{-1}\) for polydiacetylene (Figure S8 of the Supporting Information); however, as observed earlier, these bands are not indicative of the yield. However, the sample also showed a broad absorption band between 200 and 700 nm, which also suggests the formation of some oligodiacylenes or PDA (Figure S9 of the Supporting Information).

Slow evaporation of 1 from a different solvent mixture \((1 \text{ mg/mL in } 50:50:15 \text{ MeOH/CH}_2\text{Cl}_2/\text{H}_2\text{O})\) afforded colorless short rodlike crystals of the tetrahydrate 1·4H₂O with the formula \(\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_4\cdot4\text{H}_2\text{O}\). The data crystal was a two-component nonmerohedral twin. The compound crystallizes in the triclinic system. The space group \(\text{P1}\) is situated about a crystallographic inversion center and two asymmetric unit consists of half of one \(\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_4\) cycle that is not disordered. The crystallographic inversion center and two independent water molecules (Figure 7a). The molecular structure showed that there are four water molecules incorporated within each cycle, two trapped in the cavity of the macrocycle and another two positioned above and below the macrocycle plane.

The macrocycles do not form direct hydrogen bonds between neighboring macrocycles. Instead, macrocycles assemble through hydrogen bonds to intervening water molecules (Figure 7b). The water tetrabromides link the cycles into a 2D sheet in which the cycles pack parallel to each other. Macrocycle 1 further stacks to form columns. However, the columns in the tetrahydrate crystals have a large offset with a steep tilt angle \(\theta = 69.0^\circ\) with respect to the column axis (Figure 7c). The shortest distance of acetylene carbons on adjacent cycles is \(6.34 \text{ Å}﻿\), a distance large and unfavorable for diacetylene polymerization. The shortest intercolumnar distance between acetylene units is \(\sim 3.78 \text{ Å}﻿\) (Figure 7d).

We used differential scanning calorimetry (DSC) to investigate the thermal transitions of the 1·4H₂O crystals. (Figure S11 of the Supporting Information). The tetrahydrate crystals showed two irreversible endothermic transitions at \(\sim 100 \text{ °C}\) and \(\sim 118 \text{ °C}\), respectively. The first transition likely corresponds to the loss of water as observed by TGA (Figure S12 of the Supporting Information). A single exothermic peak was seen at 270 °C. The integration of the peak gave an enthalpy of 275 kJ/mol. We are currently investigating the crystal transition that occurs at 118 °C and the possible polymerization. In comparison, the dihydrate 1·2H₂O bulk crystals displayed an endothermic transition at 90 °C, which corresponded to a loss of water and multiple irreversible exothermic reactions between 180—260 °C.19 Integration of these peaks gave a polymerization enthalpy of 250 kJ/mol, approximately twice the value measured for polymerizations of crystalline diacetylenes (150—165 kJ/mol).55

**Properties of the PDAs.** We observed the SCSC polymerization of the dihydrate 1·2H₂O form to give the PDA crystal. To investigate the purity and homogeneity of the PDAs formed by heating of bulk crystals, we used powder X-ray diffraction (PXRD). After annealing, the bulk crystals turned a dark purple/brown color. The PDA crystals were ground into powder form and examined by PXRD. The observed PXRD
Assuming this weight loss corresponded to I₂, we calculated a sample of PDA crystals (5 mg) was exposed to iodine vapor in Figure 8b shows the UV–vis absorption spectrum of PDA single crystal (blue). (B) UV–vis absorption spectrum of PDA suspension in MeCN.

Figure 8. (A) Observed powder X-ray diffraction (PXRD) pattern of bulk PDA crystals (red) and simulated PXRD pattern calculated from coordinates of the PDA single crystal (Figure 8a, red line) with no discernible additional peaks, suggesting that the polymerization proceeds cleanly in the bulk material. We note that several peaks from the simulated pattern were observed with decreased intensity in the experimental pattern. These intensity differences are due to severe preferred orientation of the sample and are not uncommon for polycrystalline polymer samples. The observations suggest that the bulk PDA powder is a single phase and displays a similar structure as the PDA single crystals.

UV–vis absorption and Raman spectra provided further evidence that the bulk crystals also form the PDA upon heating. Figure 8b shows the UV–vis absorption spectrum of heated bulk 1·2H₂O measured as a suspension in MeCN. Two broad absorption bands overlapped in the visible light range, \( \lambda_{\text{max}} \approx 571 \) and 620 nm, were attributed to the presence of different lengths of PDA in our sample. The Raman spectrum of the bulk PDAs (Figure S14 of the Supporting Information) showed two intense resonance bands belonging to the ene in the poly(ene–yne) of the polymer at \( \sim 1506 \) and \( \sim 2107 \) cm⁻¹.

**Iodine Doping.** Iodine doping has been used to modulate the properties of PDAs and increase conductivity. We investigated the doping of our PDAs with iodine using an apparatus to control the partial pressure of iodine to discourage the growth of iodine crystals. The iodine partial pressure \( P_{I_2} \) in the loading chamber was controlled to 0.5 \( P_{I_2} \text{ atm} \), where \( P_{I_2} \text{ atm} \) was the vapor pressure of iodine at room temperature (27 °C). A sample of PDA crystals (5 mg) was exposed to iodine vapor in the chamber for 0–96 h to afford a doped sample PDA–I₂. The degree of doping was measured by TGA (Figure S16 of the Supporting Information) and showed saturation after \( \sim 48 \) h.

Figure 9. Comparison of XPS survey scans: (A) PDA crystals; expansion \( \sim 400 \) eV area is shown in the inset. (B) Iodine-treated PDA crystals; expansion between 600 and 650 eV is shown in inset.

A one step desorption with a \( \sim 3.5\% \) weight loss was observed. Assuming this weight loss corresponded to I₂, we calculated a 1:14 iodine to PDA monomer unit ratio.

X-ray photoelectron spectroscopy (XPS) was used to investigate the nature of the iodine species absorbed by PDA crystals. The XPS survey scan spectrum of the PDA crystal (Figure 9a) composed of three peaks were assigned to C1s (\( \sim 285 \) eV), N1s (\( \sim 400 \) eV), and O1s (\( \sim 532 \) eV). In comparison, two new peaks were observed in the spectrum of iodine-saturated PDA crystals, which were located at \( \sim 620 \) eV and assigned to iodine 3d₅/₂ and 3d₇/₂ photoemissions (Figure 9b). Deconvolution results of C1s, N1s, O1s, and 13d₅/₂ XPS spectra of both PDA crystal and PDA–I₂ complex are reported in Table S2 of the Supporting Information. After doping with iodine, 13d₅/₂ and 13d₇/₂ peaks appeared in the XPS spectra. The 13d₅/₂ peak was chosen to do further analysis and could be deconvoluted into two peaks at 618.3 and 620.4 eV. This indicated the existence of two structures of iodine in the PDA–I₂ complex, and these two peaks are attributed to triiodide \( I_3^- \) and pentaiodide \( I_5^- \), respectively. In addition, amide carboxyl and methylene C1s peaks shifted to 287.6 and 285.5 eV after iodine incorporated into PDA, and a new O1s peak was also found at 531.1 eV. The chemical shift of C=O C1s and O1s photoemission to the lower binding energy area suggests that the carbonyl in PDA might associate with the polyiodide anions.

In order to investigate the interaction of the polyiodide anions with the PDA, we compared the FT-IR, solid-state C¹³, and Raman spectra of the PDA and PDA–I₂ complexes (see Figures S17 and S18 of the Supporting Information). Only Raman spectroscopy displayed differences between the PDA and the PDA–I₂ complex (Figure 10). The Raman spectrum of PDA consists of four main peaks. Peaks located at \( \sim 1506 \) and \( \sim 2107 \) cm⁻¹ corresponded to the typical stretch of PDAs. The peak at \( \sim 941 \) cm⁻¹ is likely due to the –CH deformation of the aromatic ring, while the origin of the peak at \( \sim 1200 \) cm⁻¹ may be due to the C=N stretch of the amide groups. After treatment with iodine, both the –CH deformation and C=N stretch peaks shifted to high energy; the detail of the shift is shown in the inset diagram of Figure 10, which indicates that there may be interactions between the polyiodide anions and the amide carbonyl.

**Formation of Microcrystals.** We have established that the dihydrate 1·2H₂O can be obtained in bulk and polymerized to give PDAs. Next, we investigated if this process could be carried out in smaller microcrystals deposited on different surfaces. Microcrystalline PDAs may show faster equilibration with...
guests, be amenable for transport measurements, and more suitable for integration into thin film organic electronic devices. First, a solution of I in 50:50 MeOH/CH2Cl2 (1.0 mg/mL and 1.5 mg/mL) was deposited on different substrates (Si wafers, glass, or quartz slides) by spin-coating at a rate of 1000 rpm. The substrates were examined before and after thermal treatment, which was used to induce polymerization to afford PDAs. In general, the SEM imaging of the microcrystals on silicon substrates before heating were subject to poor contrast and focus. A relatively brighter secondary electron signal versus background is observed in the polymerized samples (Figures 1c and 11). This could be indicative of reduced charging under the electron beam due to higher conductivity, as would be expected in the polymerized fibers. Such conductivity changes must ultimately be confirmed by transport measurements. Therefore, we focused on these samples. We investigated different spin-coating factors, such as concentration of macrocycle solution, spin rate, and time to find the optimal condition to obtain well-distributed microcrystals. We generated PDA microcrystals by spin-coating a solution of I (1.0 mg/mL) at a rate of 1000 rpm for 90 s on silicon wafers, and then heating the spin-coated samples at 190 °C for 3 h. Figure 11a shows the SEM image of these microcrystals, which have a 1-D needlelike structure that were randomly distributed over the surface. A normal distribution fit gave an average microcrystal length of ~3 µm (Figure 11b). Microcrystals generated at higher solution concentration (1.5 mg/mL) are shown in Figure 11c and have a similar 1-D structure but display a larger average length of ~5 µm (Figure 11d). These experiments suggest that the size of microcrystals can be controlled by the concentration of I in the initial solution. SEM images of microcrystals generated on silicon, glass, and quartz (see Figure S19 of the Supporting Information) revealed no obvious differences in morphology.

Raman spectroscopy was again used to monitor the transformation of monomer to polydiacetylene in the microcrystals. Microcrystals generated by spin-coating a 1.0 mg/mL macrocycle solution at a spin rate of 1000 rpm for 90 s on a silica wafer were subjected to Raman spectroscopy before and after thermal treatment (Figure S20 of the Supporting Information). After heating, the alkyne absorption of macrocycle I, microcrystals at ~2266 cm⁻¹ disappeared. Two new bands were observed at ~1506 and ~2107 cm⁻¹, which correspond to the characteristic carbon double and triple bond absorption of polydiacetylene. This suggests that the diacetylene monomer was converted into polydiacetylene during the heating process; however, we are currently investigating methods to probe the efficiency and yield of this process.

**CONCLUSION**

In summary, we observed that the dihydrate 1·2H2O form of the diacetylene macrocycle underwent a SCSC transformation upon heating in an inert atmosphere to give a polydiacetylene. Significant atomic movement occurred within the crystal during the polymerization process. The resulting PDA is a columnar covalent nanotube containing two PDA chains that are parallel and aligned along the nanotube. The two polymers within a single tube are rigid and separated by a fixed distance. These individual columnar polymer PDAs are organized in three dimensions by a series of hydrogen bonds that link each nanotube with four neighboring nanotubes. We showed that this unique PDA structure was able to absorb iodine and is likely amenable to property control via adsorbed guests. Comparison of X-ray photoelectron spectroscopy (XPS) survey scans of the PDA and PDA-I3 complexes showed new peaks after iodine exposure, which were attributed to triiodide, I3⁻, and penta-iodide, I5⁻, respectively. We found that these materials can also be assembled by spin-coating onto different substrates and polymerized by heating. While it is known that PDA crystallinity, morphology, and alignment affect its optical and electronic properties, it is challenging to design model systems with controlled structures that can test the structure–property relationship. Our future work is focused on examining the effects of crystal size and doping levels on their electronic and optical properties.

**ASSOCIATED CONTENT**

* Supporting Information

CIF files of crystallographic data, 1H NMR, 13C NMR, PXRD, DSC, TGA, IR, XPS, Raman, and absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

*Corresponding Author

E-mail: shimizls@mailbox.sc.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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ABBREVIATIONS

PDA, polydiacetylene; SCSC, single-crystal-to-single-crystal; PXRD, powder X-ray diffraction experiments; SEM, scanning electron microscope; XPS, X-ray photoelectron spectroscopy; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis; TLC, thin layer chromatography

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