

Thermal Reaction of a Columnar Assembled Diacetylene Macrocycle

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Conjugated polymers have demonstrated utility in organic solar cells,¹ chemical sensors,² and optoelectronics.³ Microporous materials such as metal organic frameworks (MOFs) and zeolites show practical applications in gas storage,⁴ separation,⁵ catalysis,⁶ and as confined environments for reactions.⁷ MOFs and covalently linked organic frameworks⁸ utilize transition metal ions or organic monomeric units to afford porous materials with high surface areas and excellent thermal stabilities. An alternate strategy for forming porous materials relies on the columnar assembly of molecular building blocks directed by noncovalent interactions. We sought to combine the attributes of a conjugated polymer with porous materials. Herein, we report a diacetylene macrocycle that was readily synthesized and self-assembled into columns to afford porous crystals (Figure 1). Heating initiated a topochemical polymerization of the preorganized diacetylene units to give covalent conjugated polydiacetylenes (PDAs). These stable conjugated materials maintained permanent porosity as evidenced by their type I gas adsorption isotherms with CO₂ (g). Conjugated porous PDAs could have applications for sensing and in electronics.

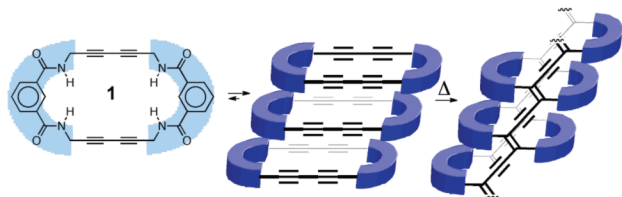


Figure 1. Diacetylene macrocycle **1** self-assembled into columns via amide hydrogen bonds. Upon heating the diacetylene units may undergo a topochemical polymerization to yield polydiacetylenes.

Supramolecular interactions have been employed to construct networks of diacetylenes. Relatively few diacetylenes whose structures have been elucidated by X-ray undergo polymerization to afford PDAs. Topochemical polymerization of diacetylene requires a precise prealignment of reacting units in the crystalline phase with a monomer repeat distance (d_m) of ~ 4.9 Å, a neighboring C1–C4 distance ($R_{1,4}$) of 3.5 Å, and an orientation angle of 45°. Although acyclic diacetylenes have been polymerized, few systems with supramolecularly assembled macrocyclic diacetylenes have been investigated.¹¹

Diacetylene **1** was synthesized in two steps from isophthaloyl chloride and propargylamine (Supporting Information, SI). The key step was an Eglinton acetylene–acetylene coupling reaction.¹² Recrystallization yielded white needle crystals, and X-ray analysis revealed the desired macrocycle. Macrocycle **1** stacked in columns with each individual cycle tilted at an angle of 41.6° with respect to the column axis (Figure 2a). The macrocycles assembled by amide–amide hydrogen bonds into tubular structures with N–H...O distances of 2.81 Å. Water molecules in the channel were also involved in hydrogen bonding with carbonyl oxygen atoms, which

served to stabilize the column. However, the exact pattern could not be determined due to disorder of the water molecules. Two sets of diacetylenes were aligned along the column on each side. This columnar assembly adopted a monomer repeat distance d_m at 4.98(6) Å and positioned neighboring C1–C4 distance $R_{1,4}$ at 3.58(1) Å, close to the structural parameters preferred for diacetylene polymerizations.¹⁰ The shortest intercolumnar distance between diacetylene units is ~ 6.2 Å (Figure 2b).

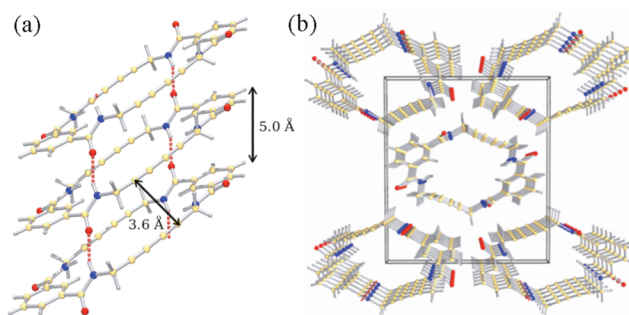


Figure 2. X-ray crystal structure of macrocycle: (a) A single tubular array oriented by N–H...O hydrogen bonds; H₂O molecules were omitted for clarity. (b) Packing diagram of the porous structure looking down the tube axis.

Thermally induced transitions of **1** were studied by differential scanning calorimetry (DSC) (Figure 3a). Assembled **1** showed an irreversible endothermic transition at ~ 90 °C, which corresponded to a loss of water as observed by TGA (SI). Irreversible exothermic reactions commenced at ~ 180 °C within a reasonable range for the reaction of diacetylenes. These multiple exotherms suggested that the two sets of diacetylene units did not react simultaneously. The integration of the peaks gave a polymerization enthalpy of 250 kJ/mol, nearly twice the value measured for polymerizations of crystalline diacetylenes (~ 150 – 165 kJ/mol),¹¹ which was likely due to the presence of two diacetylene units within each macrocycle. The heated crystals turned dark purple/brown and were insoluble, suggesting the formation of PDAs.¹¹ Cooling and reheating showed no phase transitions in this range (inset). Batches of crystals (30 mg) were heated at 180 °C for 12 h and afforded similar dark insoluble crystals. UV-irradiation also initiated the reaction but to a less extent ($\sim 15\%$) based on recovery of the soluble monomer. The UV–vis absorption spectra after heating showed that the sharp monomer absorbance $\lambda_{\text{max}} = 256$ nm had disappeared, replaced by a broad absorbance in the visible range, consistent with an increased conjugation length in PDAs (SI). The presence of different length oligomers, the aggregation of PDAs in the solid state, or cross-links could account for the broad UV–vis spectrum.¹² Cross-links are less likely due to the large separation of diacetylene units in neighboring columns of assembled **1**.

Powder X-ray diffraction (PXRD) was used to probe the structure of **1** after heating because the crystals were no longer of quality

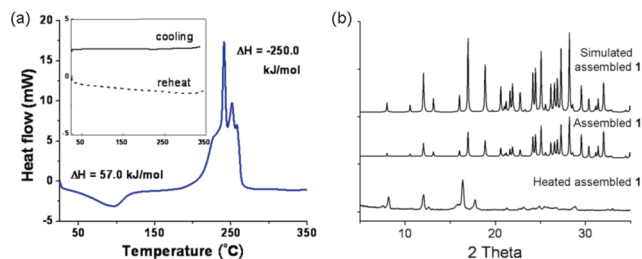


Figure 3. Effects of heating on host **1**: (a) DSC plots of **1** (heating rate 10 °C/min). Inset shows cooling (20 °C/min) and reheating. (b) PXRD patterns of assembled **1** and heat-treated **1**.

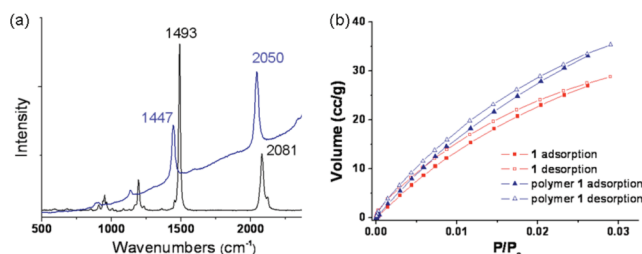


Figure 4. (a) Raman spectra (excitation at 632 nm) of single crystal samples of assembled **1** (bottom) and heat-treated **1** (top). (b) CO₂ gas adsorption isotherms at 0 °C of assembled **1** and heat-treated **1**.

for single crystal X-ray studies. The crystals of assembled **1** were gently pressed to powder form and examined by PXRD (Figure 3b). The observed PXRD pattern closely matched the patterns simulated from the crystal structure, indicating that the gently pressed powder has a similar structure. Vigorous grinding induced larger changes in the PXRD pattern, similar to the pattern observed upon removal of water at 150 °C (SI). Next, the crystals were heated (180 °C, 12 h), pressed to a powder, and examined by PXRD. They displayed a sharp pattern by PXRD consistent with a well-ordered crystalline structure (Figure 3b, bottom). Low angle peaks at 8.2° and 12.0° (2θ) were observed before and after heating, suggesting some similarities in the long-range order before and after heat treatment.

Further evidence for reaction of **1** to a PDA was provided by Raman spectroscopy (Figure 4a). After heating the diacetylene absorption of **1** at ~2081 cm⁻¹ disappeared. Two new bands were observed at 2050 and 1447 cm⁻¹. The resonance enhanced absorption of the double bonds at 1447 cm⁻¹ is characteristic of the ene in the poly(ene-yne) of similar PDAs.¹³ Solid-state magic angle spinning ¹³C NMR spectroscopy also suggested efficient conversion of the monomer to PDAs (SI).

Assuming the structure is not changed by removal of water, the size of the channels in assembled **1** was estimated as ~5.0 × 4.1 Å. Gas adsorption measurements with CO₂ (g) at 0 °C (Figure 4b) were used to test whether the channels of assembled **1** were accessible and showed a type I isotherm, consistent with a microporous material.¹⁴ The Brunauer–Emmett–Teller (BET) method was applied to the isotherm at P/P_0 between 0.012 and 0.029 to give a calculated surface area of ~350 m²/g. The pore volume was calculated as 0.10 cm³/g. A similar type I gas

adsorption isotherm with CO₂ (g) at 0 °C was observed for the heated material, which displayed a slightly larger surface area (480 m²/g). These results indicated that the polymer retained accessible channels and suggested that the reaction occurs down individual columns.

In summary, we synthesized a diacetylene macrocycle that assembled into columnar structures and underwent a thermal reaction to give oligo- or polydiacetylenes. Both the assembled monomer and the covalent polymer are crystalline materials that displayed permanent porosity. The covalent polymer is a robust, insoluble crystalline material. We are currently investigating if assembled **1** and heat-treated **1** exhibit changes in their optoelectronic properties or conductivity upon guest absorption or environmental perturbations, as PDAs have great potential as sensing materials.

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Supporting Information Available: Synthesis and characterization of host **1** including crystal data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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