

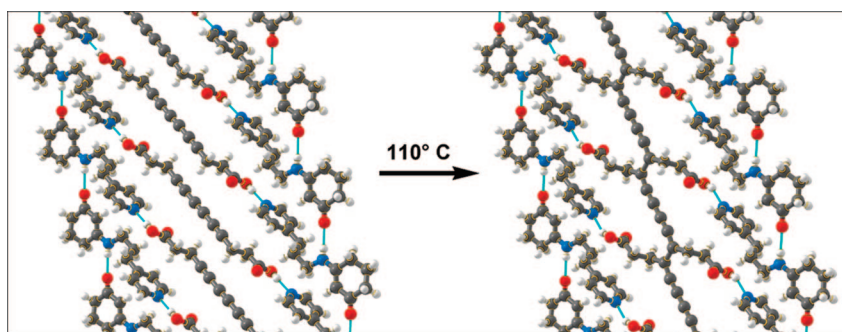
Single-Crystal-to-Single-Crystal Topochemical Polymerizations by Design

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CON SPECTUS



The polymerization of simple conjugated dienes has long been of interest: polydienes occur throughout Nature, and polyisoprene and its analogues form the basis of entire industries. In contrast, the polymers of similar small conjugated compounds, diacetylenes, trienes, and triacetylenes, are either unknown or laboratory curiosities. For 40 years, the only viable synthetic method for the 1,4-polymerization of a diacetylene was a topochemical polymerization in a condensed phase. But such an approach is hit or miss: if the diacetylene monomers have a solid-state structure preorganized at distances matching the repeat distance in the final polymer, then thermal or photochemical energy can bring about the polymerization. However, most monomers lack the proper structural parameters and simply do not react.

As discussed in this Account, we have developed a supramolecular host–guest strategy that imposes the necessary structural parameters upon a diacetylene monomer that otherwise does not polymerize. We apply this strategy in the synthesis of new types of conjugated polymers made from diacetylenes, triacetylenes, and trienes. To implement the host–guest strategy, we chose a host that would self-assemble into a supramolecular structure with the requisite intermolecular spacing. For diacetylenes, the ideal spacing is 4.9 Å, and the oxalamides, which routinely crystallize with a spacing of 5 Å, make ideal host molecules. We chose specific oxalamide host substituents that bind to the diacetylene guest molecule, typically through hydrogen bonding. We have focused upon the single-crystal-to-single-crystal polymerizations, allowing us to obtain and characterize the polymers in perfect crystalline form and to define and better understand the reaction trajectories.

We have prepared several new classes of polydiacetylenes using this strategy, including the first terminal polydiacetylenes and an aryl-substituted diacetylene. Interestingly, to prepare poly(diiododiacetylene), we used halogen bonds to bind the host and guest. The simplest polydiacetylene known, poly(diiododiacetylene), lacks the side chains that complicate the structures of similar previous polymers. Future studies should provide insights into the role of such side chains in conjugated materials.

We further demonstrated the strength of the host–guest strategy by moving from the polydiacetylenes to the polytriacetylenes. Although the structural requirements for a triacetylene polymerization had been stated decades ago, no one had ever found a triacetylene with the requisite spacing of 7.4 Å. We designed a series of pyridine-substituted vinylogous amide hosts to achieve this spacing. Cocrystallization of these host molecules with a triacetylene dicarboxylic acid gave us the desired structure. Using thermal annealing, we completed the synthesis of the triacetylene polymer.

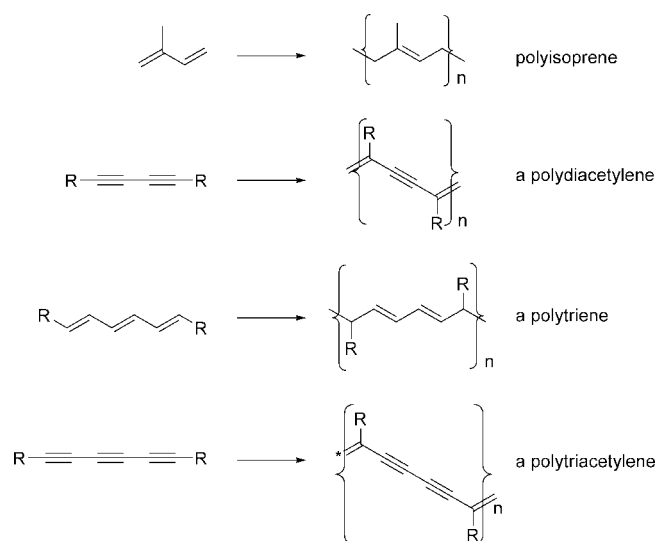


FIGURE 1. Polymers of four simple conjugated monomers. Dienes like isoprene can be polymerized 1,4 in solution. In contrast, the 1,4-polymerization of a diacetylene, the 1,6-polymerization of a triene, and the 1,6-polymerization of a triacetylene are unknown in solution.

Introduction

The polymerization of simple conjugated dienes has long been of interest. Nature discovered the polydienes, and the chemistry of polyisoprene and its analogues are the basis of entire industries. In contrast the polymers of similar small conjugated compounds, diacetylenes, trienes, and triacetylenes, are either unknown or laboratory curiosities, Figure 1. The big problem is the synthesis. With a suitable catalyst, dienes will undergo 1,4-polymerization in solution, but such selective catalysts for diacetylenes are not known. Similarly the solution 1,6-polymerization of a triacetylene is an unknown reaction.

About 40 years ago, Wegner¹ discovered that the 1,4-diacetylene polymerization could take place in the solid state via a topochemical reaction. If the reactive monomers are preorganized at a distance commensurate with the repeat distance in the final polymer,² then the application of thermal or photochemical energy can bring about the polymerization, Figure 2. This preorganization occurs fortuitously for some crystalline diacetylenes, but it is neither a reliable nor a general means of synthesis. The vast majority of diacetylene monomers crystallize in some other manner incommensurate with their corresponding polymer, so no polymerization occurs, and the corresponding polymer remains unknown.

Polydiacetylenes are conjugated polymers that show optoelectronic behavior. They have potential applications as optical limiters and waveguides, and sensitivity to environmental changes that make them ideal candidates for the synthesis of chemical or biological sensors. They have similarities to other

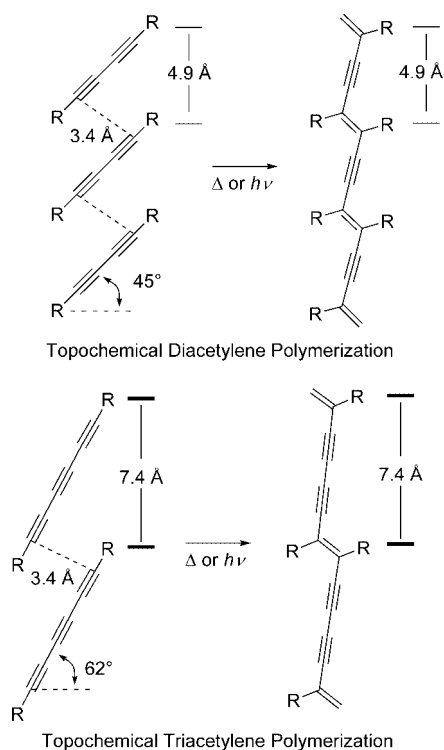


FIGURE 2. A diacetylene or a triacetylene will polymerize if the monomer units are preorganized at a distance commensurate with the repeat distance in the prospective polymer. A close approach of the reacting carbon atoms is also necessary.

important conjugated polymers such as the polyacetylenes, the polythiophenes, polyanilines, and polyphenylenes. All of this makes them important materials for further study but only if reliable synthetic methods can be developed.

In this Account, we describe our efforts to develop rational strategies for the preparation of polydiacetylenes. We have not found an alternative to topochemical polymerization, but we have developed a supramolecular host–guest strategy that allows us to impose the necessary structural parameters upon a diacetylene monomer that otherwise does not polymerize. This has allowed us to expand the scope of the reaction and to prepare new types of diacetylene polymers. The supramolecular host–guest strategy allows one to target a specific diacetylene that does not polymerize on its own. It is a general and rational strategy that can be extended to a great variety of diacetylenes and other reactive monomers as well.

We have extended the strategy to the triene and triacetylene systems and have discovered the first crystal-to-crystal 1,6-triene polymerization and the first 1,6-triacetylene polymerizations. In all of our work, our goal has been to achieve single-crystal-to-single-crystal topochemical polymerizations. Such precise polymerizations allow one not only to obtain and characterize the final product in perfect crystalline form but also to define and understand reaction trajectories more fully.

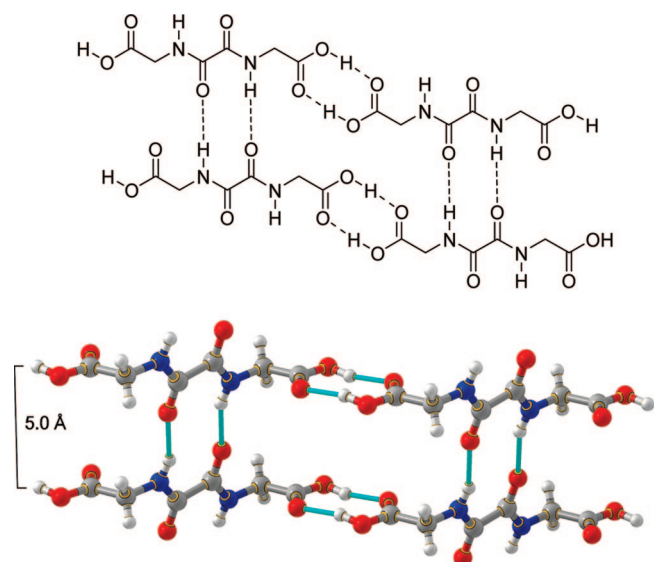


FIGURE 3. The crystal structure of the oxalamide of glycine, **H1**. The molecules are self-complementary in two directions. In the vertical direction, an α -network of amide hydrogen bonds forms with a characteristic repeat distance of 5.0 Å. In the horizontal direction, a second α -network is formed by the dicarboxylic acid structure. If longer chain ω -amino acids are used, the structure lengthens in the horizontal direction, but the 5.0 Å repeat distance characteristic of the amide hydrogen bonds remains.

Crystal Design for Structure and Function: Polydiacetylenes

The precise supramolecular design or “crystal engineering” of a solid-state structure is not an easy task. The intramolecular forces that hold molecules together in a crystal are weak but numerous, and predictions of supramolecular structure are difficult at best and often impossible. Great strides in the field have been made over the last 15 years or so, and the future of crystal engineering is bright, but supramolecular synthesis is still far from routine.

We began our studies by designing families of compounds whose molecules would self-assemble into predictable layer structures based upon self-complementary hydrogen bonds.^{3–5} One prototypical system consisted of the oxalamide prepared from glycine, **H1**, Figure 3. The molecules of **H1** form self-complementary hydrogen bonds in two dimensions. A dicarboxylic acid α -network forms in one direction; a second α -network of paired amide hydrogen bonds forms in a second direction. Longer chain ω -amino acids can be substituted for the glycine with no change in the basic lattice. The key point is that the short 5.0 Å amide to amide distance is reproducible within the entire series of compounds studied.

The 5.0 Å amide to amide repeat distance is significant because this is the spacing required for a successful diacetylene polymerization. We considered the design of a diacety-

lene directly attached to an oxalamide. The single molecule would contain the necessary structural elements that would force it to self-assemble at 5.0 Å, as well as the diacetylene functionality required for polymerization. Upon reflection, it became evident that such a “single-molecule” approach might have significant problems. Incorporating the diacetylene and the functionality necessary for self-assembly into the necessary supramolecular structure requires a reasonable amount of organic synthesis and leaves little room for error. Either the molecule will crystallize in a manner suitable for polymerization, or it will not. And if it does not, then there is little one can do to change the crystal structure of a single molecule. The one-molecule approach also limits the range of monomers we can utilize. We desired a more general method that could be applied to a great variety of substrates.

Another strategy is a host–guest “two-molecule” approach to the problem.^{6,7} We already had a library of previously prepared oxalamide host molecules. New ones can be prepared if needed. A diacetylene monomer can be synthesized and cocrystallized as a guest with one of the host molecules. This two-molecule approach is synthetically convergent and flexible. The structure and function are divided, with the structure established by the host and imposed upon the functional guest. The convergence of this strategy is important. If one host does not work, then another can be tried.

Our first successful crystal-to-crystal diacetylene polymerization followed this two-molecule host–guest approach. The host oxalamide **H1** was cocrystallized with the guest diacetylene **G1**. The two components form an **H1/G1** cocrystal with the structure shown in Figure 4. The oxalamide host molecules form an α -network with a repeat distance of 4.97 Å, only slightly longer than the ideal value of 4.9 Å. The neighboring C(1)–C(4) atoms were 3.38 Å apart, very close for non-bonded atoms. Heating the single crystals brought about a clean polymerization. The central atoms of the diacetylene moiety pivot around an inversion center bringing the reacting C(1)–C(4) carbon atoms of neighboring molecules together, Figure 5. The result of this polymerization reaction is a single crystal with polymer chains embedded in a lattice of the host molecules.

The crystalline product, with all the diacetylene chains in perfect alignment, has highly anisotropic spectroscopic properties. The crystals have a deep red color by transmitted light, with a beautiful gold luster in reflected light, Figure 6. The polydiacetylene polymer with its pyridyl side chains can be extracted into acid solution giving colored solutions.

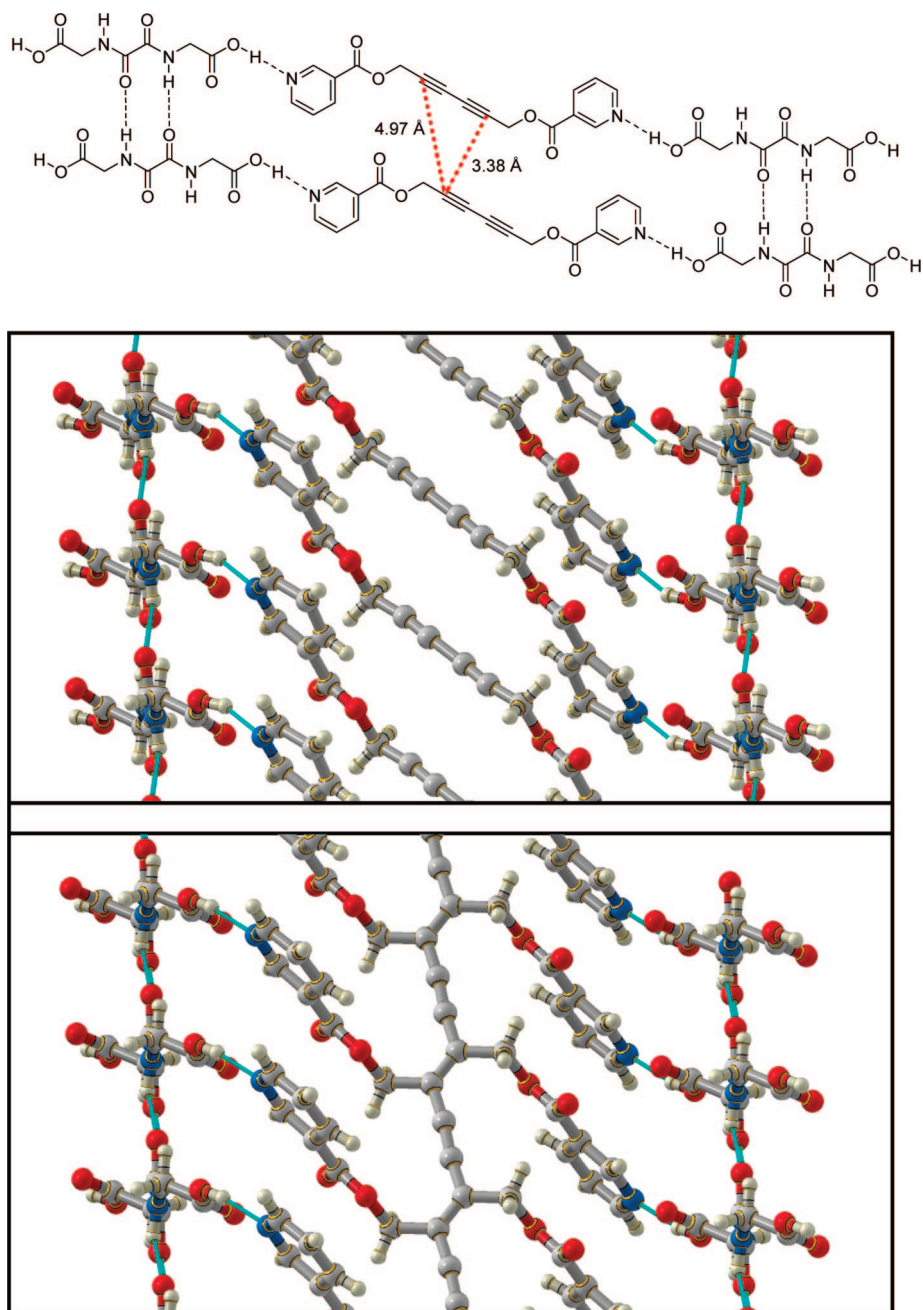


FIGURE 4. A designed single-crystal-to-single-crystal diacetylene polymerization. The oxalamide host molecule **H1** was chosen because it is known to form a hydrogen-bonded α -network with a repeat distance of about 5.0 Å. The nicotinyl ester groups of the diacetylene guest monomers, **G1**, form strong pyridine carboxylic acid hydrogen bonds to the host molecules. The monomer crystal structure is shown in the middle figure and the polymer crystal structure in the bottom figure.

The two-molecule host–guest strategy is a general one.⁸ Figure 7 shows a dicarboxylic acid derived polydiacetylene prepared by “reversing” the substituents. The pyridyl groups were moved to the host, **H2**, and the carboxylic acid groups to the guest, **G2**. In this case, the crystals of the monomer polymerize so easily that we have never been able to determine the crystal structure of the unpolymerized **H2/G2** cocrystal. The polymer of **G2** has been prepared and studied in solution before,^{9,10} but this new synthesis is more straightfor-

ward, and the crystal structure of the polymer has been determined for the first time.

New Types of Polydiacetylenes

The host–guest supramolecular strategy can be extended in many directions, and has allowed us to prepare a variety of new types of crystalline polydiacetylenes. We will briefly discuss the polymerization of the three distinct types of diacety-

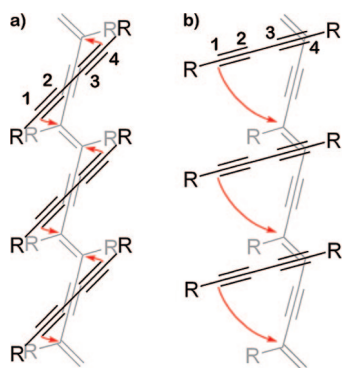


FIGURE 5. Two extreme mechanisms for a topochemical diacetylene polymerization. Structure (a) shows the “turnstile” mechanism commonly found for symmetric diacetylenes. The monomers pivot in a conrotary manner about the molecular centers. Each C(1) and C(4) atom moves about 1 Å as the new bond joining the monomers is formed. The R group must pivot about 30°. Structure (b) shows the “swinging gate” mechanism. In this mechanism, the molecules pivot at a stationary C(4) atom. The C(1) atom along with its R group does most of the movement and must travel about 3 Å. The R group on C(4) can remain stationary. lenes: aryl-substituted diacetylenes, terminal diacetylenes, and the unique diiododiacetylene.

Aryl-Substituted Polydiacetylenes. Aryl-substituted polydiacetylenes have been of considerable interest^{11–13} because they offer a way to extend the conjugation of the polymer onto the side chains. Such conjugation would be expected to influence the optical and transport properties of the polymers. Despite the high interest no one has prepared a crystalline aryl polydiacetylene.

An obvious extension of our initial study of a pyridyl ester, **G1**, was to attempt the polymerization of guest **G3**, a compound with the pyridyl rings directly attached to the diacetylene.¹⁴ Cocrystals of the **G3** with our standard glycol oxalamide host, **H1**, have the structure shown in Figure 8. The **H1/G3** structural parameters look very good, with a repeat distance of 4.93 Å and a close C(1)–C(4) contact of 3.62 Å. Thermal annealing all the way up to the 235 °C melting point of the crystals changed their color, but no substantial polymerization took place. Somewhat surprisingly, UV irradiation did cause the polymerization to take place, but the crystals crumbled into a purple powder as the reaction proceeded. No single-crystal structural study of the polymer was possible.

So what is the problem with aryl diacetylenes? We believe it has to do with the large required movement of the pyridyl side groups. The C(1) and C(4) carbons change their hybridization from sp to sp^2 as the reaction proceeds. The required bond angle change, from 180° to 120°, requires a considerable movement of the attached pyridine ring. This movement likely causes the destruction of the crystal lattice. The energy barrier seems to be too high for a thermal polymerization. The

UV polymerization occurs, but it is inherently a surface phenomenon, and it gives a high yield only because the crystal disintegrates revealing more surface as the reaction proceeds.

Terminal Polydiacetylenes. Terminal polydiacetylenes were not known until our work a few years ago. The synthesis of terminal diacetylenes is more difficult than symmetrical disubstituted diacetylene. Their lack of symmetry decreases the probability of simple translational packing, a common supramolecular structural feature for many topochemical polymerizations.

We set out to prepare a terminal polydiacetylene using our standard two-molecule host–guest approach. A modification of the strategy was needed because by definition a terminal diacetylene lacks one of the hydrogen bond “handles” we normally employed to form a layer of aligned diacetylene monomers. Our way around the problem was to use a resorcinol derivative of a diacetylene, **G4**.¹⁵ With two phenol hydroxyl groups, we could mimic our earlier structures. The cocrystals formed with guest **G4** and the host **H2** gave us one of our most surprising results. Instead of forming a planar layer structure, the layers curved in on themselves, forming a helix, with the diacetylenes on the inside of the helix (Figure 9). All the expected hydrogen bonds formed, and the repeat distance of 5.09 Å was within the acceptable range, but the overall supramolecular structure was unexpected. The polymerization proceeded thermally as designed, yielding a unique structure with a tubular helix of host molecules wrapped around a pair of polydiacetylene chains. The helical tube has a diameter of 15 Å and represents a possible pathway to nanotube synthesis.

In carrying out these experiments, we discovered an unanticipated structure that demonstrated to us that our understanding of the polymerization process was far from complete. Diacetylene **G4** forms a hydrate, **G4**·H₂O, that polymerizes in a clean crystal-to-crystal manner. Surprisingly, the intramolecular distances are not all that close to the ideal. The repeat distance is only 4.72 Å, the neighboring C(1)–C(4) contact is somewhat long at 3.96 Å, and the ideal 45° declination angle is large at 54.3°. Despite these unfavorable parameters, the polymerization occurs readily at a low temperature of 50 °C. An examination of atom movement, Figure 10, shows that the C(1) atom moves about 2.45 Å while the C(4) atom moves less than 0.5 Å. This unsymmetrical atom movement is rather different from what we see in the symmetrical diacetylenes. It suggests a second possible mechanism, a “swinging gate mechanism”, Figure 5, in which the diacetylene pivots at the C(4) carbon atom. The resorcinol hydrate structure shown in Figure 10 is formed by a mechanism intermediate between

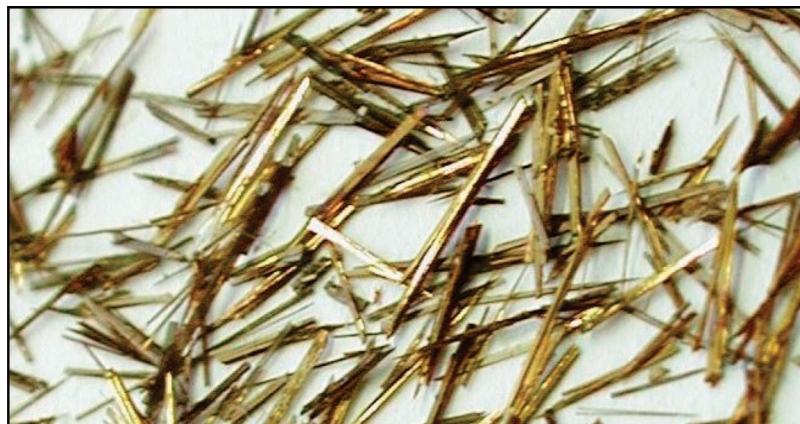


FIGURE 6. Crystals of the polydiacetylene formed upon heating the **H1/G1** cocrystals. The longest crystals are about 3–4 mm in length.

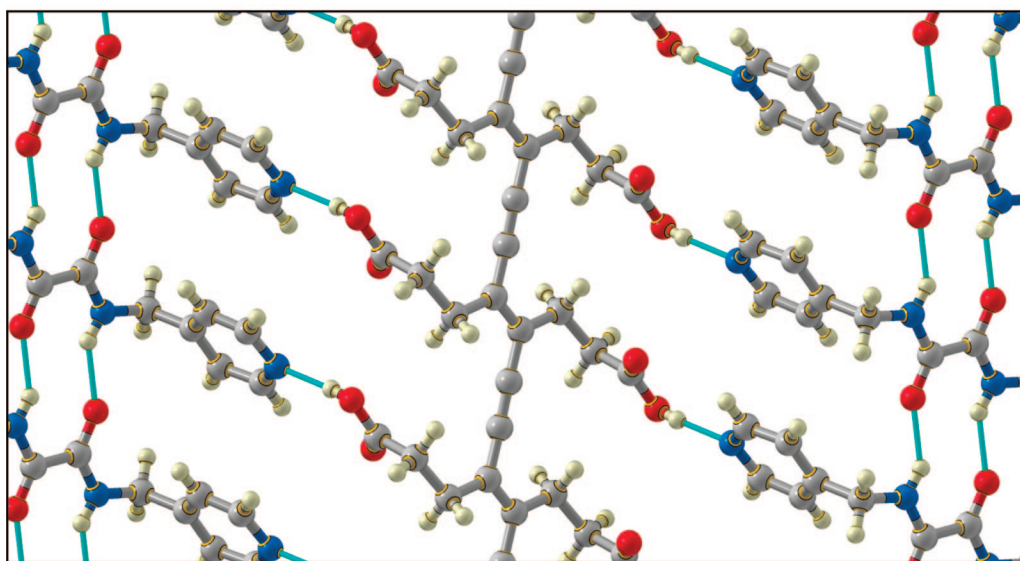
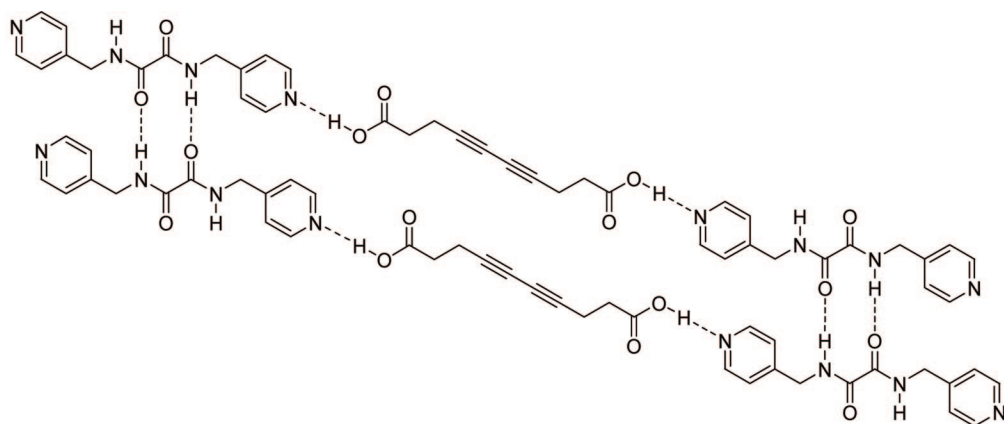
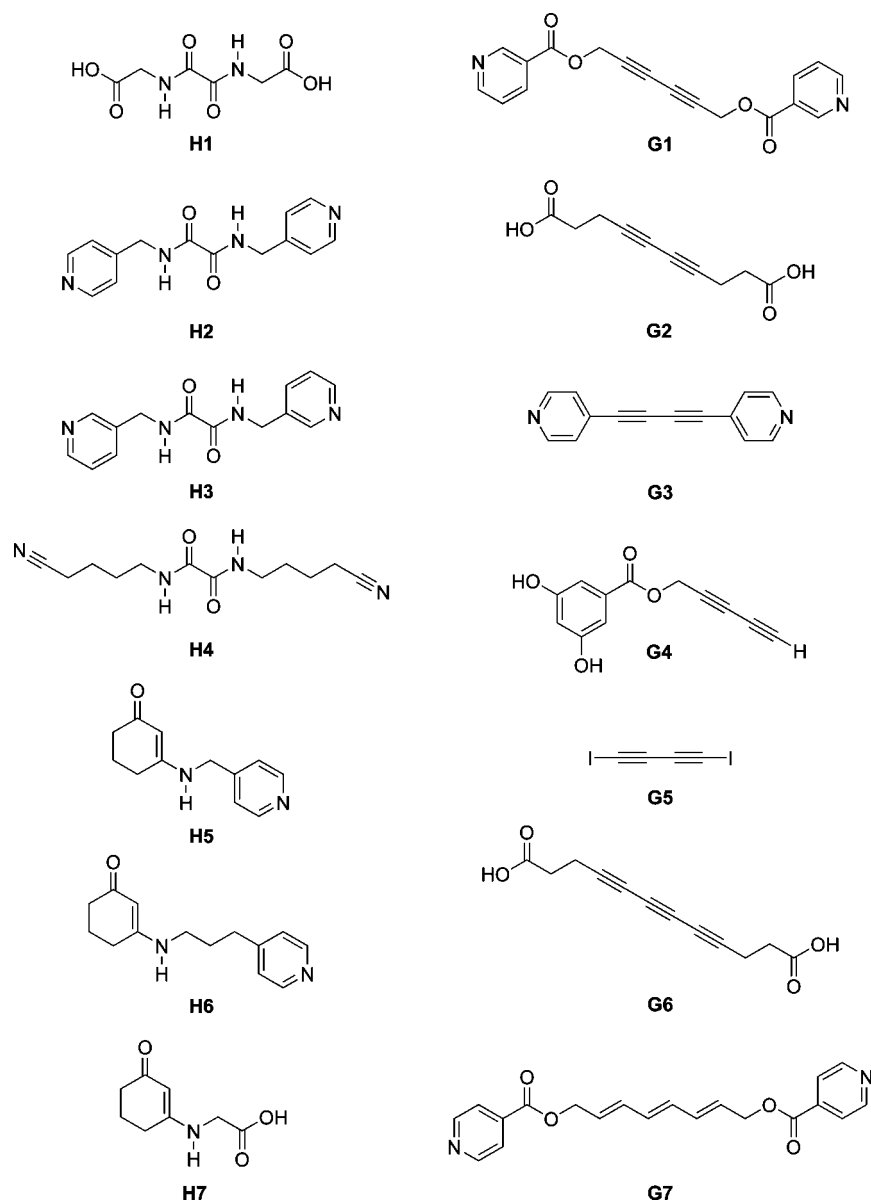


FIGURE 7. This polymer is formed by a reversal of the chemistry shown in Scheme 1. An oxalamide host, **H2**, aligns the monomers of a dicarboxylic acid diacetylene guest, **G2**.

these two extremes. The extreme “swinging gate” mechanism may be found in other terminal diacetylenes and may be relevant to diacetylenes in noncrystalline environments, such as surface-anchored diacetylenes.

Diiododiacetylene. Hydrogen bonds may be the most familiar strong intramolecular interaction, but they are certainly not the only possibility. We have also investigated the use of halogen bonds to organize molecules in the solid state.

SCHEME 1. A Selection of Oxalamide (**H1–H4**) and Vinylogous Amide (**H5–H7**) Host Molecules along with a Series of Polymerizable Guest Molecules (**G1–G7**)

Halogen bonds are formed when a Lewis acidic halogen atom, often bonded to an sp or sp^2 carbon atom, encounters a strong Lewis base, typically a nitrogen or oxygen atom with a lone pair of electrons.¹⁶ Iodoacetylenes are particularly good at forming these halogen bonds due to the high effective electronegativity of sp -hybridized acetylene carbon atoms and the high polarizability of the iodine atoms.

Our first experiments utilized the bispyridyl host compounds, **H2** and **H3**, that we originally designed for organizing carboxylic acid and phenol guests.¹⁷ The pyridine halogen bond to an iodoacetylene seems quite reliable, and cocrystals were formed with little difficulty. The most favorable structure, **H3/G5**, is shown in Figure 11. The repeat distance of

5.11 Å and the neighboring C(1)–C(4) contact distance of 3.90 Å were both within the range suitable for a polymerization reaction. The crystals turn dark under heat, UV, or γ -ray irradiation, but no crystallographic evidence for polymerization was observed. Temporarily we abandoned further studies of this system as we sought an alternate family of host compounds.

Our alternate hosts were a series of oxalamides with alkyl nitrile substituents.^{18,19} The pendant nitrile nitrogen atoms, although less basic than pyridine, are still capable of forming halogen bonds to the diiododiacetylene. Cocrystallization of host compound **H4** with diiododiacetylene **G5** gave a 1:2 **H4/G5**₂ cocrystal with the structure shown in Figure 12. These

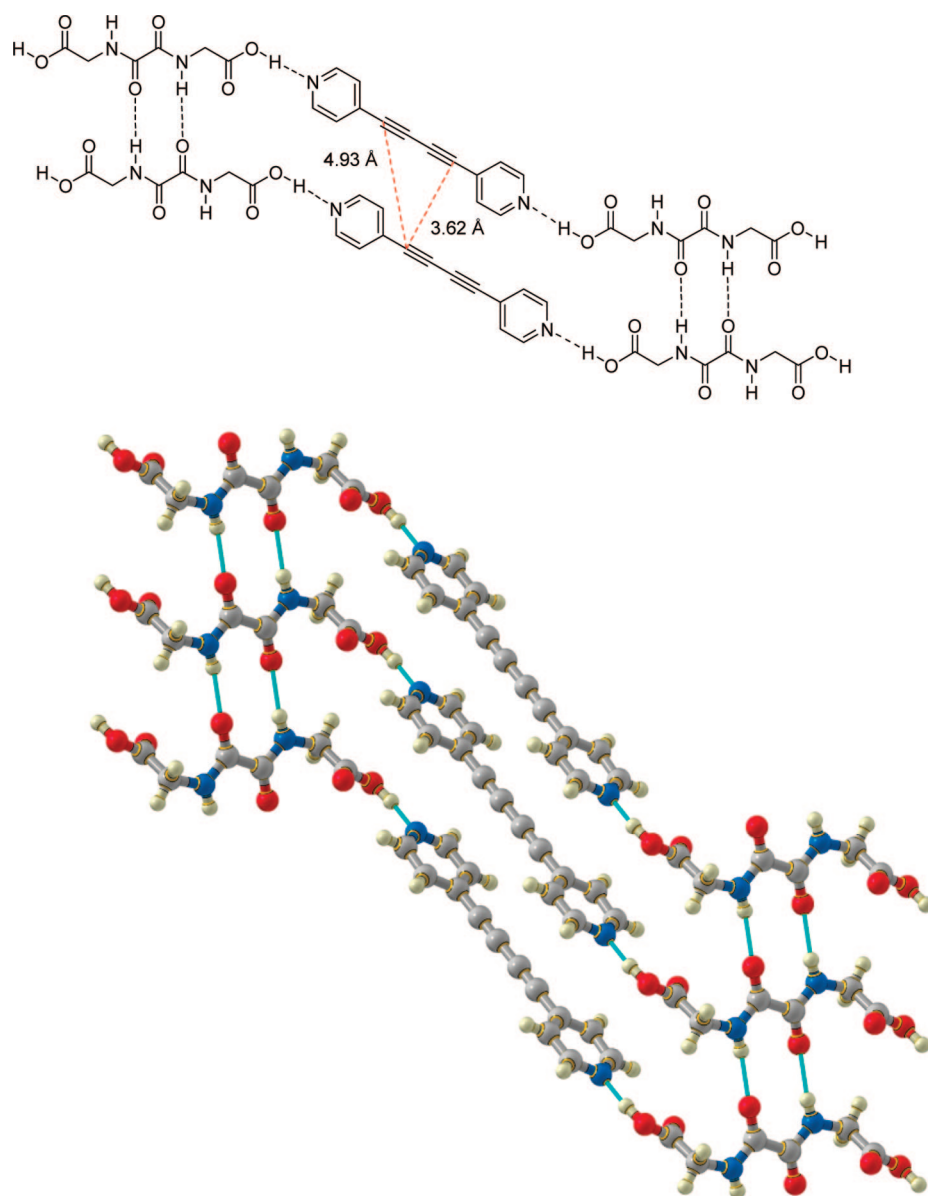


FIGURE 8. The crystal structure of diacetylene **G3** cocrystallized with host molecule **H1**. The crystals readily polymerized under UV irradiation but crumbled into a purple powder as the irradiation continued. The crystal structure of the polymer was thus unobtainable.

crystals polymerized spontaneously at room temperature. Indeed, initially we had difficulty preparing a suitable crystallographic sample of the unpolymerized cocrystal.

Poly(diiododiacetylene) is certainly the simplest polydiacetylene known. It lacks the side chains that complicate the structures of all previous such polymers. Future studies of its optical, electronic, and chemical properties will be of high interest and will shed light on the role of intermolecular interactions in conjugated materials. We are also intrigued with the prospect of using the polymer a precursor to the carbyne as a starting material for the synthesis of other polydiacetylenes via post-polymerization substitution reactions.

After successfully preparing poly(diiododiacetylene) using the **H4** nitrile host, we returned to a study of the initial cocrystals made with the pyridine host **H3**.²⁰ Our crystallographic studies, Figure 11, revealed that the **H3/G5** structural parameters were compatible with a polymerization reaction, but standard polymerization attempts had failed. Since we now knew that the targeted polymer was a viable compound, we turned to high external pressure as a means of inducing the polymerization. The crystals responded to pressures starting at 0.3 GPa in a diamond anvil cell. The initial crystals were colorless and transparent; as the pressure was increased, they changed to blue

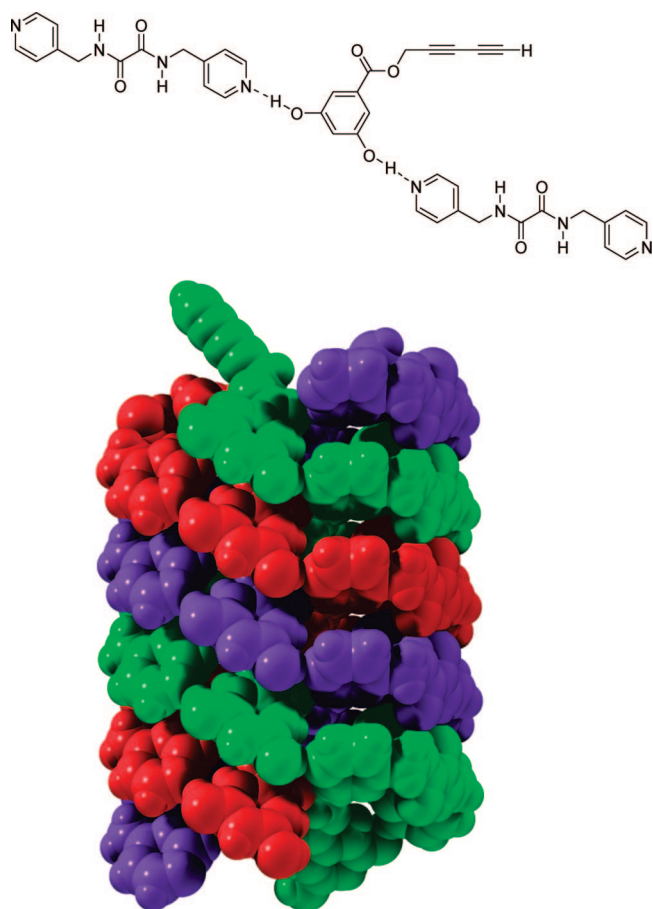


FIGURE 9. To extend our standard strategy to a terminal diacetylene, resorcinol derivative **G4** with a headgroup with two hydrogen bond “handles” was chosen. Surprisingly, the **H2/G4** structure formed a helix with the host molecules on the outside and the diacetylenes on the inside. The polymerization proceeds smoothly with two parallel polydiacetylene chains forming within the helical structure.

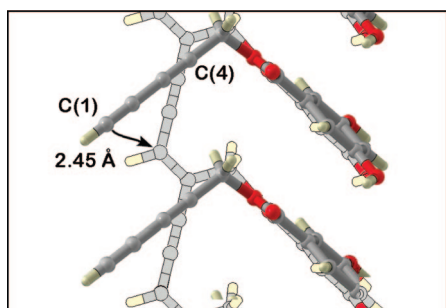


FIGURE 10. The diacetylene **G4** also forms a crystalline hydrate that readily polymerizes. The reaction proceeds with a large 2.5 Å movement of the end C(1) carbon atom. In contrast, C(4) only moves about 0.5 Å. This is the best example of the “swinging gate” mechanism shown in Figure 5.

and opaque and then on to black as the pressure was raised to 6 GPa. Solid-state Raman and magic angle spinning NMR revealed that a high percentage of the **H3/G5** sample had polymerized under pressure to give a polymer

with spectroscopic signatures similar to the more fully characterized **H4/G5₂** sample.

Characterization of Diacetylene Polymers. Although the emphasis of this Account is upon the design and realization of single-crystal-to-single-crystal topochemical polymerizations, it is appropriate to briefly mention methods of characterization of the resultant polymers. Single crystals of the diacetylene polymers are highly colored in various reddish or blue hues. A high degree of polymerization often leads to crystals that exhibit a metallic sheen. In the solid state, the polymers are routinely characterized by their Raman spectra. The high polarizability of the delocalized polymer greatly enhances the Raman peak intensities. Generally a very strong peak corresponding to the triple-bond stretch is seen in the 2050–2150 cm^{-1} range, while an even stronger double bond stretch appears in the 1350–1450 cm^{-1} range. Solid-state ^{13}C MAS NMR spectra have been useful for following the polymerization process, particularly so for compounds that have not given us diffraction-quality crystals. Single-crystal electron absorption spectroscopy has sometimes given us spectacular results, as shown in Figure 13.

Polydiacetylenes with pyridine or carboxylic acid substituents are generally soluble in acid or base, respectively. For example, the pyridyl ester shown in Figure 4 dissolves in aqueous HCl, although subsequent acid hydrolysis of the ester linkage leads to deposits of what is likely the polymer of the corresponding diol. In contrast, the polymer of 4,6-decadienedioic acid, shown in Figure 7, dissolves in sodium hydroxide and is perfectly stable. Gel permeation chromatography measurements of one preparation showed a molecular weight of about 160 000 g/mol with a relatively narrow polydispersity index ($\text{PDI} = 1.5$).²¹ Poly(diiododiacetylene) is not generally soluble, but the polymer can be separated from its host and forms blue suspensions in various solvents.

Polytriacetylenes

Soon after the discovery of the topochemically polymerized diacetylenes, Wegner recognized that the same principle should be applicable to triacetylenes.²² If triacetylene monomers could be preorganized in a manner commensurate with a triacetylene polymer, then a topochemical polymerization would be expected. Attempts were made to discover topochemically active triacetylene monomers, but none were found. It was a curious synthetic problem. The target was of considerable interest, the requirements were well defined, but for many years no one was able to prepare a triacetylene with the necessary supramolecular

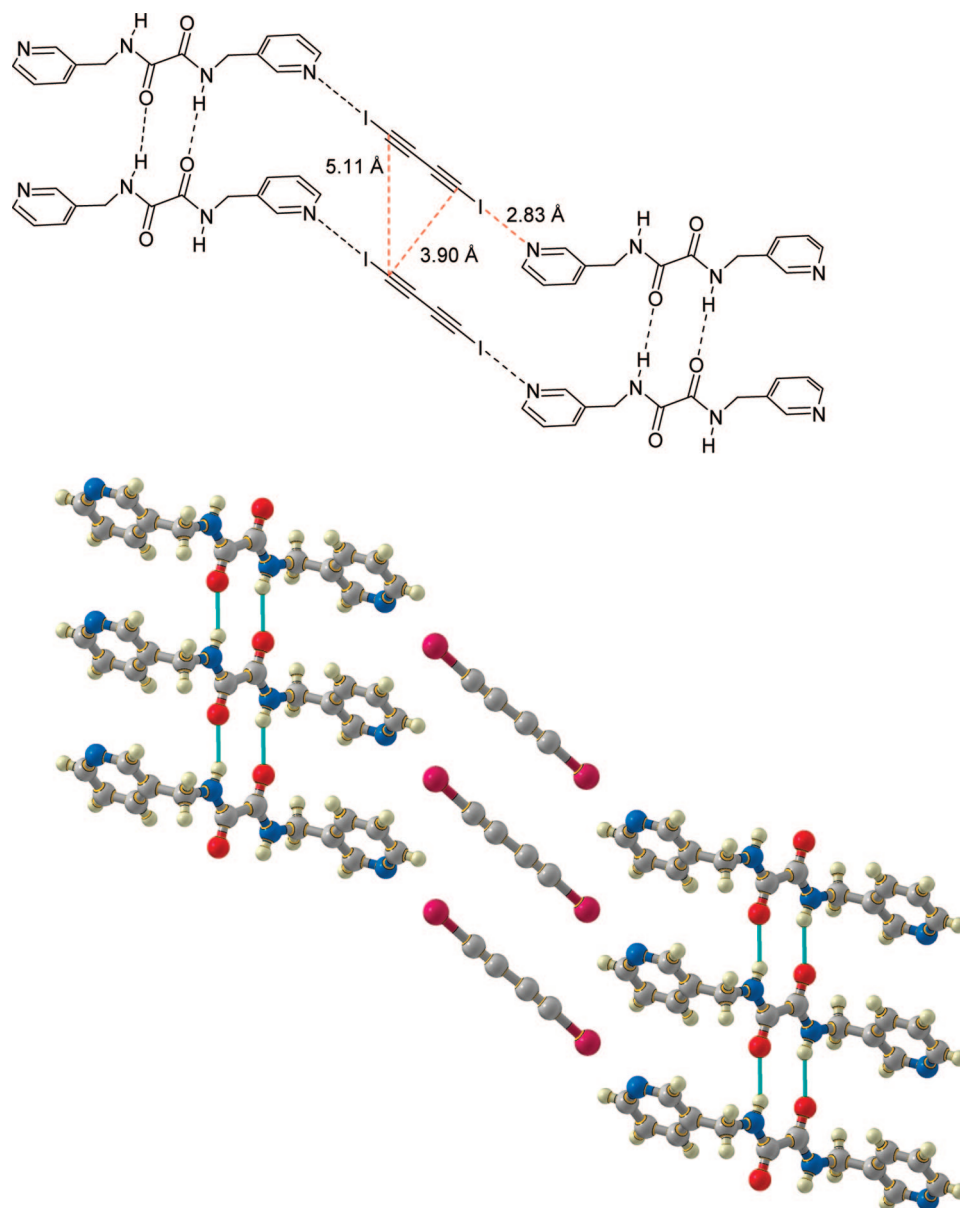


FIGURE 11. The crystal structure of host **H3** and diiododiacetylene **G5**. The repeat distance of 5.11 Å is a bit longer than the ideal. Little polymerization occurs under normal conditions, but solid-state MAS-NMR studies indicate nearly complete polymerization after pressing the sample to pressures >6 GPa.

structural features required for topochemical polymerization. A polytriacetylene was an ideal synthetic target to test the generality of our supramolecular host-guest strategy.

More recently, Diederich²³ investigated the polytriacetylenes and related oligomers, not by the 1,6-polymerization of a triacetylene, but by an alternate route involving the direct organometallic coupling of diethynyl alkenes in solution, Scheme 2. Crystallographic studies of his oligomers revealed a repeat distance of 7.4 Å, which was consistent with the value that we predicted from molecular modeling of the parent polymer. This became our targeted

distance for a topochemical polymerization, Figure 2. Our specific targeted triacetylene was **G6**, a simple dicarboxylic acid analogous to the diacetylene **G2**.²⁴

The first step was to identify a suitable host that could be used to organize triacetylene guest molecules at a 7.4 Å spacing. After discarding numerous alternatives and searching the crystallographic literature, we settled upon the vinylogous amide host **H5** with a pendant pyridine ring. Using succinic and adipic acids as models, we found that host **H5** readily formed 2:1 cocrystals of the form **H5**₂/**dicarboxylic acid**. The repeat distances in these two cases were 7.20 and 7.18 Å, respectively.

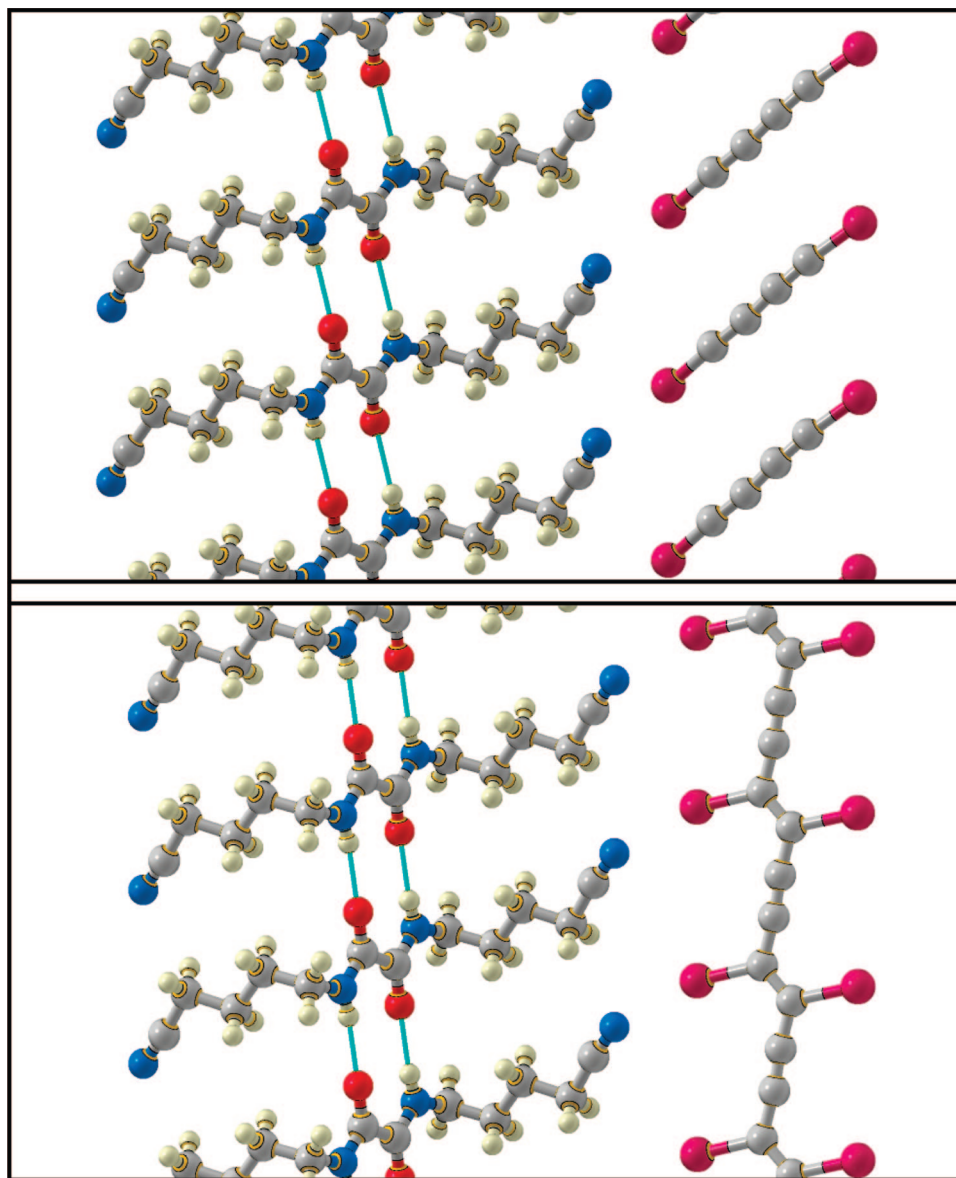


FIGURE 12. A designed single-crystal-to-single-crystal diiododiacetylene polymerization. The oxalamide dinitrile host molecule **H4** was chosen because it is known to form a hydrogen-bonded α -network with a repeat distance of about 5.0 Å. The nitriles form halogen bonds to the diiododiacetylene **G5** guest monomers. The **H4/G5₂** monomer structure is shown in the top figure with an intramolecular spacing of 4.94 Å; the monomer polymerizes spontaneously to give the polymer shown in the bottom figure.

The **H5₂/G6** structure is shown in Figure 14. The repeat distance is 7.14 Å, the crucial tilt angle is 60.8°, and the neighboring C(1)–C(6) contact distance is 3.5 Å. These distances were close to the values we wanted, except that the repeat distance was shorter than the ideal 7.4 Å. Although the crystals developed a pale pink color, we were very disappointed that neither thermal annealing nor UV irradiation gave any further sign of polymerization. Upping the energy, we turned to ⁶⁰Co γ -radiation and found that the crystals turned dark red. Crystallographic investigation of irradiated single crystals showed that a topochemical polymerization was taking place. The same crystals were cycled through repeated

8–10 Mrad γ -radiation exposures, each followed by a crystallographic structure determination, until the conversion reached 70%. At that point, with an accumulated γ -radiation exposure of about 30 Mrad, the crystals underwent a phase change to a glassy state that precluded further crystallographic studies. Although this system gave us the first example of a topochemical 1,6-polymerization, we were not completely satisfied. The γ -radiation method is far from ideal: it leads to decomposition and is not very convenient. We needed something better; we needed a thermal triacetylene polymerization.

The polymer crystals at the 70% conversion level had a repeat distance of 7.20 Å. This value was short of the 7.4 Å

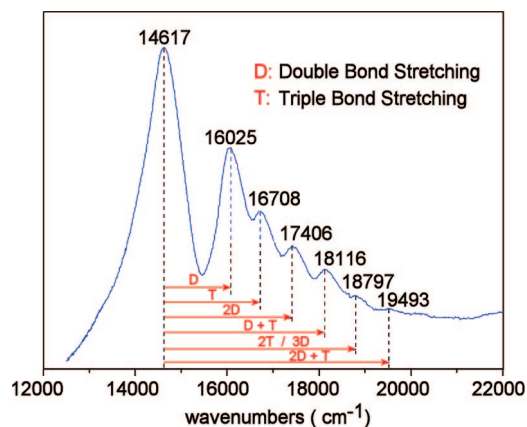
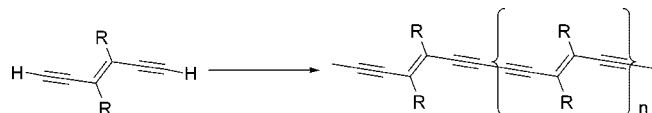


FIGURE 13. The UV/visible spectrum of the poly(diiiododiacetylene) cocrystal shown in Figure 12. The major peak at 14617 cm^{-1} (684 nm) corresponds to the $\pi\text{-}\pi^*$ transition of the polymer chain. The detailed vibrational progression at higher frequencies corresponds to an excitatory coupling with the double bond (1400 cm^{-1}) and triple bond (2100 cm^{-1}) stretching modes.¹⁹

SCHEME 2. Diederich Route to Polytriacetylenes and Oligomers



value we were expecting and perhaps explains the seeming reluctance of the monomers to polymerize under thermal conditions. To test this hypothesis, we sought an alternate host that would lengthen the repeat distance.²⁵ Molecular modeling suggested **H6**, a host molecule very similar to **H5**, but because of more favorable intermolecular interactions, the two extra methylene groups were predicted to give a longer repeat distance.

The **H6**₂/**G6** cocrystals were also easily formed, and a crystallographic study gave us just what we were looking for, a longer repeat distance of 7.28 \AA . Thermal annealing brought about a clean polymerization, which was complete after 72 h at $115\text{ }^\circ\text{C}$. The final polymer structure has a repeat distance of 7.35 \AA , much closer to the ideal 7.4 \AA distance. The **H6** pyridine host could be extracted with acid; the **G6** carboxylic acid laden polymer could be dissolved in aqueous NaOH to give colored solutions very similar to those of the polymer of diacetylene **G2**. The Raman spectrum of the **G6** polymer showed two intense peaks, a 2153 cm^{-1} triple-bond stretch and a 1543 cm^{-1} double-bond stretch.

Polytrienes

Once we completed our initial polytriacetylene synthesis, we realized that our same vinylogous host system could potentially be used to carry out a triene polymerization.²⁶ Modeling of a polytriene suggested that the ideal repeat distance

should be around 7.2 \AA , a close match to the observed vinylogous amide repeat distance. We chose triene **G7** as our target and attempted to prepare cocrystals with the vinylogous amide host **H7**. In this case, we failed in our initial efforts to isolate the targeted cocrystals, but we soon noticed that good fortune was with us and that triene **G7** had crystallized on its own in a manner suitable for a topochemical polymerization.²⁷

Figure 15 shows the triene monomer lined up with a repeat spacing of 7.25 \AA and with a C(1)–C(6) distance of 4.09 \AA . Heating the crystals to $110\text{ }^\circ\text{C}$ for 8 h smoothly brought about single-crystal-to-single-crystal polymerization to give the polytriene structure. This was not a designed structure, but *ex post facto* analysis does reveal a supramolecular feature that may be used for future designs.

The pyridine rings in the monomer structure are interleaved. This alternating $\pi\text{-}\pi$ stacking is quite common in pyridinyl and other aromatic systems. A database analysis of pyridine structures revealed that the average spacing between π -stacked pyridine rings is 3.57 \AA . The observed 7.25 \AA spacing in the **G7** crystal is twice this distance due to the interleaving of the pyridine rings. Future designs based upon this interleaving principle may bring about additional candidates for both triene and triacetylene polymerizations.

Conclusions and Future Directions

We have developed a supramolecular host–guest strategy that allows us to synthesize polymers via designed topochemical reactions. We have focused upon polymers that are not accessible by conventional means of synthesis. In doing so, we have significantly extended the number of known single-crystal-to-single-crystal polymerizations. A number of significant new classes of conjugated polymers have been discovered, and we are eager to more fully elucidate their chemical and physical applications.

The versatility and reliability of our host molecules is worth noting. For example, in this Account, we have shown how the same pyridine-substituted host molecules **H2** and **H3** can be used to organize carboxylic acid, phenol, and iodoacetylene guest molecules. In other work, we have used the same host to organize various metal ions. In each case, the guests are spaced at 5 \AA .²⁸ Other hosts of various shapes and sizes have been developed to impose different distances. These host molecules can be considered as standard “reagents” for supramolecular syntheses that can be used in other applications where the control of structure and distance is important.

Most of our work has been with diacetylenes, but the same synthetic strategy has been extended to triacetylenes and

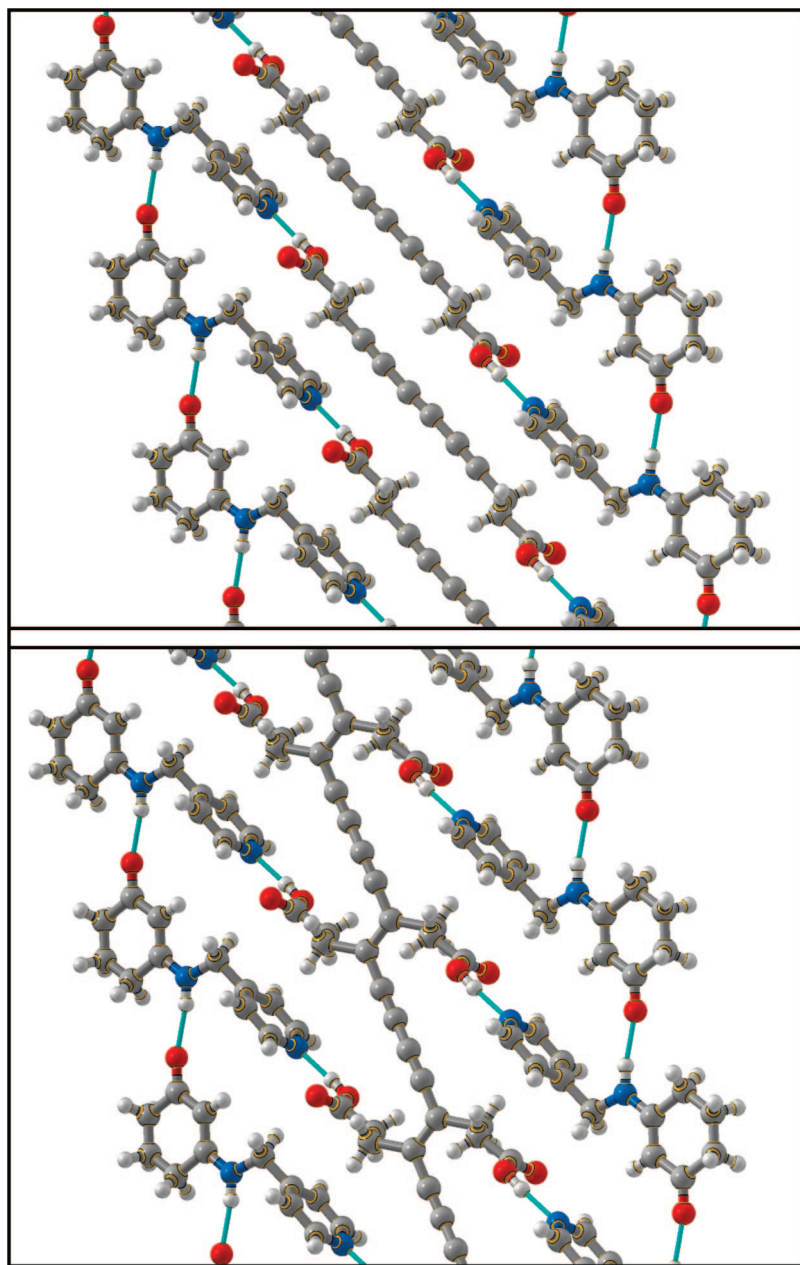


FIGURE 14. A designed single-crystal-to-single-crystal triacetylene polymerization. Vinyllogous amide host **H5** cocrystallized with triacetylene guest **G6**.

trienes. There is no reason that designed topochemical polymerizations via host–guest chemistry cannot be further extended to other sorts of addition polymers. The general strategy would be the same: Estimate or determine the structure and repeat distances of the chosen polymer. Choose a family of host compounds that will impose a similar repeat distance. Build into the host molecules the functionality needed to bond and orient the monomer guests in accordance with the targeted polymer. Use heat, radiation, or chemical means to initiate the polymerization. And as in any synthetic strategy, utilize intuition and perseverance to optimize and refine the system.

We are grateful for contributions of our many students and co-workers whose names appear as coauthors on the papers we cite in this Account. None of this work would have been possible without their efforts. We also wish to acknowledge financial support from the National Science Foundation for this research (Grants CHE-0453334 and CHE-0446749).

BIOGRAPHICAL INFORMATION

Joseph Wallace Lauher was born in the State of Illinois and obtained in a B.A. in chemistry in 1970 from Illinois Wesleyan University. He attended graduate school at Northwestern University and received his Ph.D. in 1974 working with Professor James Ibers. He

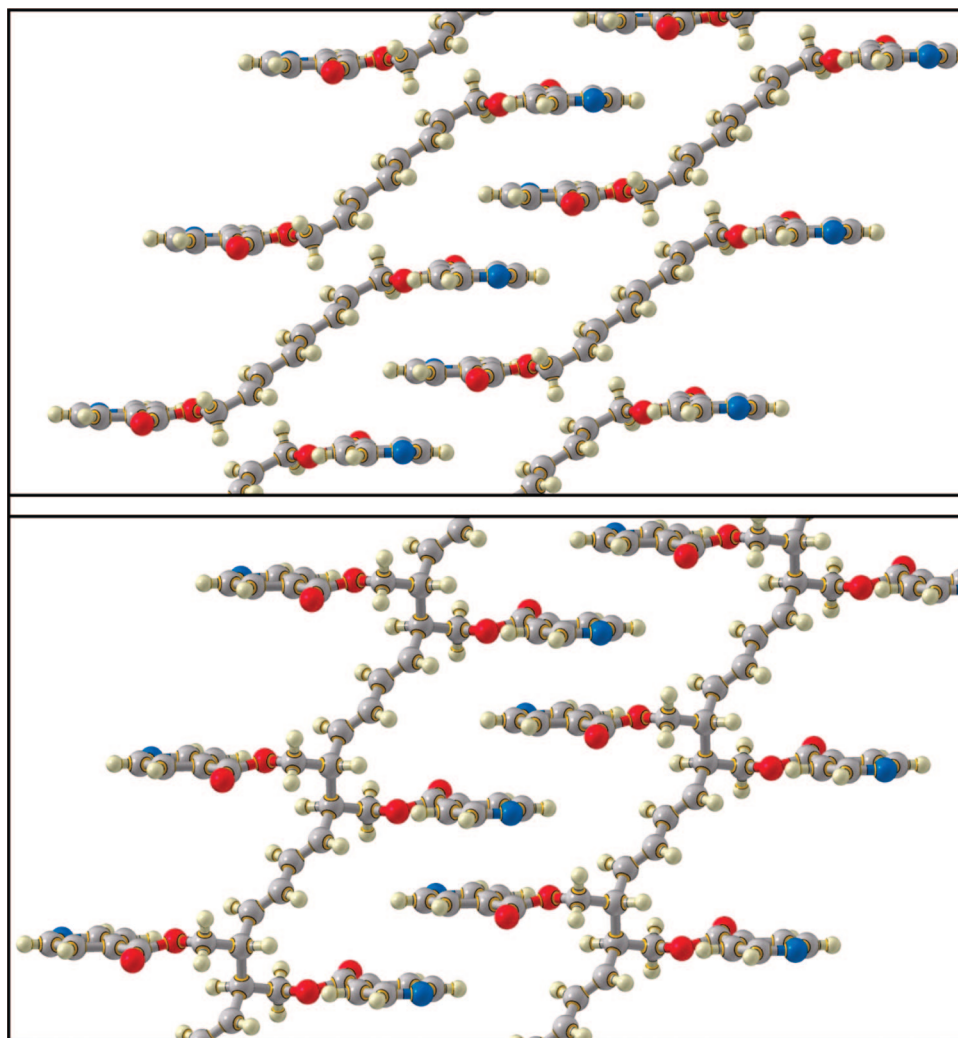


FIGURE 15. A single-crystal-to-single-crystal triene polymerization. Compound **G7** packs with interleaved pyridine rings. This establishes a repeat distance 7.2 Å, which is twice the expected π - π stacking distance of 3.57 Å.

spent the following year at Cornell as a postdoctoral student with Professor Roald Hoffmann. In 1975, he moved to the State University of New York at Stony Brook, where he now holds the position of Professor of Chemistry. In 2005, he was a Visiting Fellow at Sidney Sussex College, Cambridge. His research interests have varied widely over the years, ranging from synthetic, structural, and theoretical organometallic chemistry to his current interest in synthetic and structural solid-state organic chemistry. He has also developed the molecular graphics program Chem-Ray, which was used to produce the molecular images in this Account.

Frank Wilson Fowler was born in the State of Maine and obtained a B.A. in chemistry in 1964 from the University of South Florida. He attended graduate school at the University of Colorado and received his Ph.D. in 1967 working with Professor Fred Hassner. In the same year, he went to the University of East Anglia in Norwich, England, as a Leverhulme Fellow working with Professor Allan Katritzky. In 1968, he moved to the State University of New York at Stony Brook, where he now holds the position of Professor of Chemistry. His research interests have varied from the development of methods for preparation of nitrogen heterocycles and their application to prob-

lems in synthetic chemistry to the development of strategies for the preparation of designed supramolecular structures.

Nancy Sarah Goroff was born in Chicago in 1968. In 1990, she earned her A.B. from Harvard University, where she worked with Joseph J. Grabowski. She conducted her graduate research at UCLA under the joint guidance of François Diederich and Orville L. Chapman. After obtaining her Ph.D. in organic chemistry in 1994, she held postdoctoral fellowships at Michigan State University, with James E. Jackson, and at the University of Michigan, with Seyhan Ege and Brian Coppola. In 1997, she joined the faculty at Stony Brook, where she is now Associate Professor in Chemistry. Her research focuses on unusual carbon-rich molecules and materials, including conjugated polymers, nonplanar aromatic compounds, and three-dimensional chromophores.

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