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A rational design of molecular materials

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ABSTRACT: Supramolecular chemistry was used to solve two practical problems, the preparation of layered polydiacetylenes and the first ever 1,6-polymerization of a triacetylene to give a polytriacetylene Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: supramolecular chemistry; topochemical polymerization; hydrogen bonding

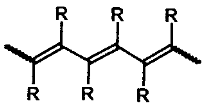
INTRODUCTION

Supramolecular chemistry has been one of the most rapidly developing fields of science. This development is due to the now recognized importance of intermolecular interactions, structure and cooperativity in almost all aspects of molecular science and many technological endeavors. From biology to pharmacology to materials science the challenges are to understand existing supramolecular constructs and to design and build new functional supramolecular entities for function and application. This is an exciting era in supramolecular chemistry because we are now at the stage where the goal of preparing designed supramolecular structures is becoming a reality. It is time to take our ideas and to demonstrate that they can be used to solve practical problems.

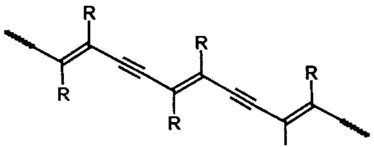
In this paper we present a synopsis of our work and a solution to two practical problems, the preparation of layered polydiacetylenes and the first ever 1,6-polymerization of a triacetylene. These are problems that can only be solved by using supramolecular chemistry.

TWO PROBLEMS

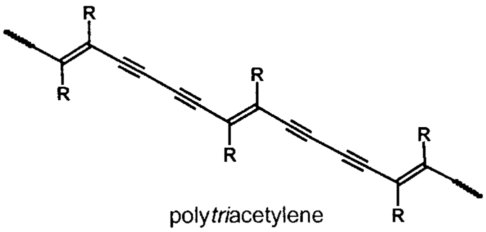
The family of polymers derived from acetylene and its oligomers[1–3] have been widely explored as candidates for advanced materials. The availability of these polymers varies because of the different synthetic methods used for each class of compound. The polyacetylenes are the most accessible, they can be made by direct solution polymerization of the monomers. The polydiacetylenes cannot be made in solution, instead they come from topochemical polymerizations, that is, organization of the diynes is required for a successful 1,4-polymerization. Unfortunately, most diacetylene monomers do not naturally self-assemble into precursor structures compatible with the requirements for a topochemical polymerization. This means that only selected polydiacetylenes, those that have monomers that assemble in a fortuitous manner, are readily available. There is no general method for organizing diacetylenes that do not self-assemble naturally. Since optical and electrical properties of polydiacetylenes are highly anisotropic it would be very desirable to develop methods that would align monomers not just to give polydiacetylene polymers, but to give polymers that are aligned in a crystal. This alignment would transfer the inherent anisotropic properties of the molecule to the crystal. This defines problem one: can one devise ways to align diacetylene monomers into



polyacetylene



poly*di*acetylene



poly*tri*acetylene

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layers with each monomer aligned in accordance with the requirements needed for a topochemical polymerization? If the monomers are organized into layers there will be an increased probability that the resulting polymers will be parallel with coplanar backbones, transferring the anisotropic properties of the polymers to the crystal.

Problem two goes beyond the well-studied diacetylenes to triacetylenes. The polymerization of triacetylenes to produce polytriacetylenes is unknown and presents a most difficult problem to solve. Solution polymerization does not work, no fortuitous topochemical polymerization has ever been observed and no 1,6-polymerization of a triacetylene has ever been reported. However, Diederich and co-workers have synthesized triacetylene polymers and oligomers, not by the direct polymerization of a triacetylene, but by clever indirect means.[4–14] Significantly, they report that the polytriacetylene oligomers appear to be more stable than either the polyacetylenes or polydiacetylenes. This is an important property since the instability of polyacetylenes is one of the primary reasons why this fascinating class of conjugated polymers has resisted commercial development. Clearly a general route to the 1,6-polymerization of a triacetylene is desirable.

PREORGANIZATION REQUIREMENTS FOR A TOPOCHEMICAL POLYMERIZATION

The structural parameters required for the 1,4-topochemical polymerization of a diacetylene are well known [Fig 1(a)]. The monomers must be aligned with an intermolecular repeat spacing of about 5.0 Å, a distance that corresponds to the repeat distance in the resulting polymer. In addition, the monomers must be tilted at an angle of 45° with respect to the translation axis. This angle brings the C-4 carbon of one diacetylene into close van der Waals contact with the C-1 carbon of the neighboring diacetylene monomer. The reaction can then take place with a minimum amount of atom motion, merely an in-place rotation of the diacetylene core unit. The reaction has been studied extensively and has been observed with many different diacetylenes. The reaction is dependent upon the C-1 to C-4 non-bonded distances. If the distance is fortuitously close, significantly less than about 3.8 Å, then a reaction is expected. However, most diacetylenes do not crystallize in accordance with these structural requirements and polymerization is not possible.

A rational approach to the topochemically controlled polymerization of diacetylenes is desirable. The problem to solve is how to impose the required preorganization on to molecule that does not normally self-assemble in accordance with the strict requirements for a topochemically controlled polymerization.

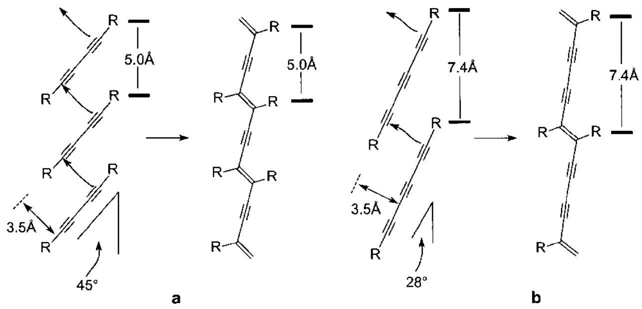


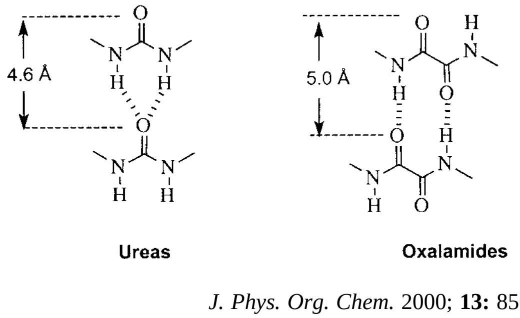
Figure 1. The preorganization requirements for the topochemical polymerization of (a) a diacetylene and (b) a triacetylene

Similarly, the structural parameters required for the topochemical polymerization of a triacetylene can be derived[15,16] [Fig. 1(b)]. Again, the monomeric units must match the repeat distance, 7.4 Å, expected for the polymer. For a van der Waals contact between the C-1 and C-6 carbons of neighboring molecules an acute angle of 28° can be calculated. No example of a fortuitously aligned triacetylene is known. Various triacetylenes have been examined over the years, but none has been found with the proper preorganization and none undergoes the desired 1,6-polymerization reaction. Interestingly, some triacetylenes do crystallize in the accordance with the requirements for a 1,4-polymerization. They appear to polymerize via a 1,4-mechanism to give a polydiacetylene with ethynyl substituents.[17]

HOST–GUEST STRATEGY

So can one achieve such preorganization by design? Our approach is based upon a library of functional groups that reliably assemble into one-dimensional hydrogen-bonded α-networks, each is characterized by a specific intermolecular repeat distance.[18–20] Our prototypical group is the disubstituted urea functionality. Such ureas form a pair of hydrogen bonds in a very reliable and reproducible manner. The crystal structures of most disubstituted ureas show a characteristic spacing of about 4.55–4.70 Å. We have shown that the one-dimensional urea α-networks can be linked together to form a two-dimensional β-network using functional groups such as dicarboxylic acids (Fig. 2).

Similarly to the ureas, oxalamides also self-assemble



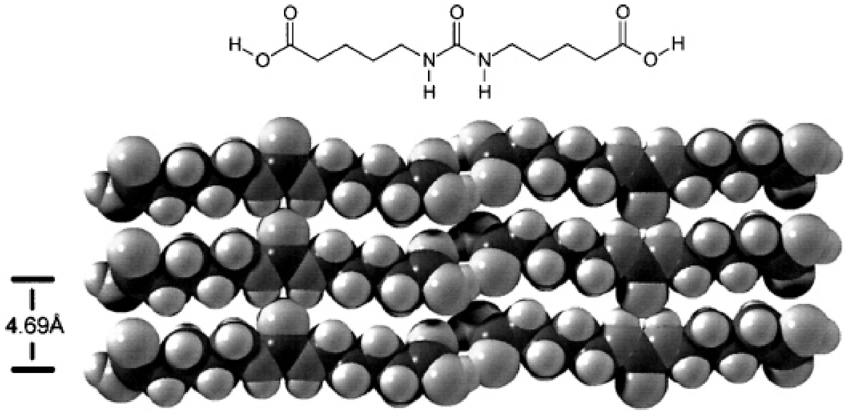


Figure 2. A disubstituted urea with carboxylic acid side-chains forms a two-dimensional hydrogen-bonded β-network with a characteristic intermolecular distance of 4.69 Å

in a reliable manner forming pairs of complementary hydrogen bonds. The $C{=}O\cdots H{-}N$ hydrogen bonds formed by the oxalamides are linear instead of bent as they are in the ureas. This makes the molecular repeat slightly longer. This fact will become important as we move on to applications.

Molecules such as that shown in Fig. 2 self-assemble into layers yielding interesting networks, but their real value come about when they are used as host molecules to impose structural parameters upon a guest. Since the molecules are carboxylic acids, they have a natural affinity for bases such as pyridines. A co-crystal formed from the urea of glycine and bipyridine is shown in Fig. 3. The urea host forms an α-network with the characteristic urea spacing. This distance is in turn imposed upon the bipyridine guest. The host and guest together form a layered β-network.

TOPOCHEMICAL POLYMERIZATION OF LAYERED DIACETYLENES BY DESIGN

After studying a number of model compounds using various ureas as hosts, we turned our attention to the layered diacetylene problem. The pyridine-substituted diacetylene shown in Fig. 4 was prepared and co-crystallized with the urea of glycine.[21] The resulting host–guest structure formed layers in accordance with our design, but the detailed structural parameters were somewhat outside the ideal margins for a diacetylene polymerization. The repeat distance of 4.70 Å was slightly short and the critical C-1—C-4 distance, 4.12 Å, slightly long. Nevertheless, polymerization did occur when the crystals were heated, to produce a purple powder, a color characteristic of many diacetylene polymers.

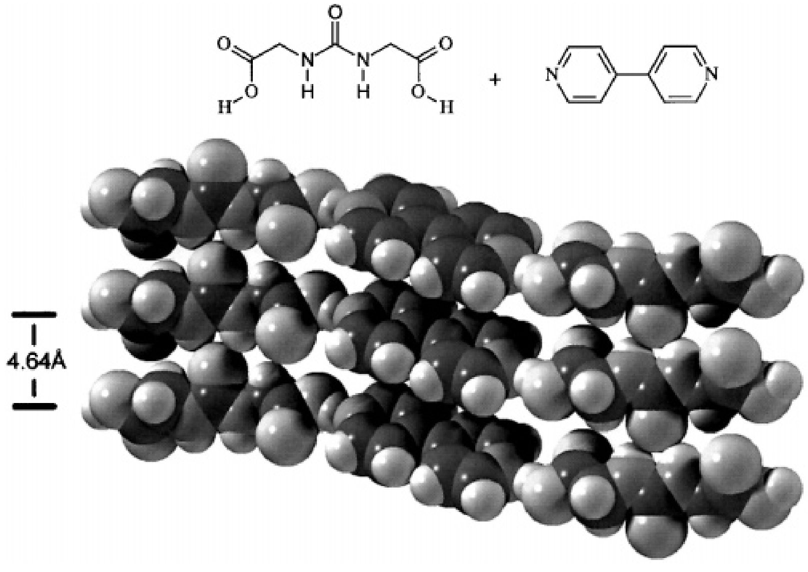


Figure 3. The crystal structure of the co-crystal formed from the urea of glycine and bipyridine. The urea host forms an α-network with an intermolecular spacing of 4.64 Å. This distance is imposed upon the bipyridine guest by the urea host

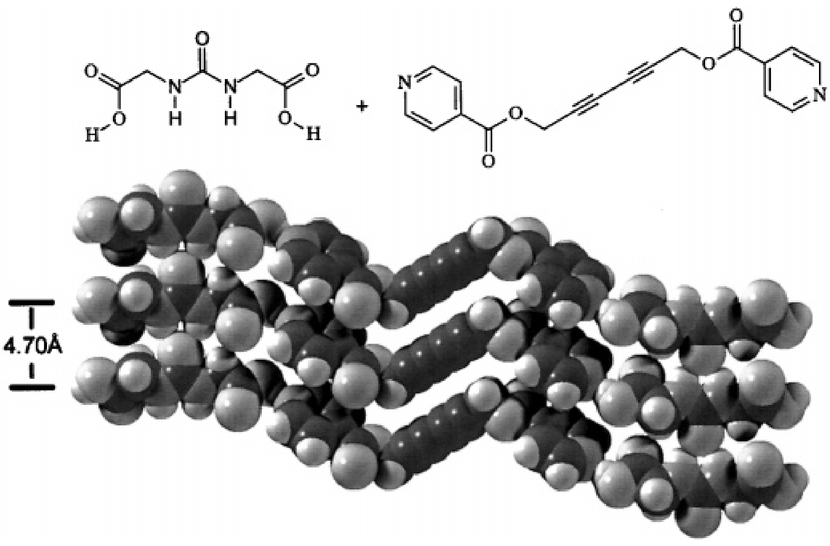


Figure 4. The crystal structure of the co-crystal of the urea of glycine and a pyridine substituted diacetylene. The urea forms a hydrogen-bonded α-network with the repeat distance of 4.70 Å. This distance is imposed upon the diacetylene guest by the urea guest. The critical C-1— C-4 intermolecular distance is 4.12 Å, longer than the ideal distance for a topochemical reaction

A demonstration of the versatility of this method is shown in Fig. 5. A pyridine-substituted urea can be co-crystallized with a diacetylenedicarboxylic acid. The desired layered structure is formed, but again the structural parameters are slightly outside the ideal range. The compound polymerizes, but only with difficulty.

The problem with the ureas is that the repeat distance of 4.55–4.70 Å is slightly too short. As mentioned above, the oxalamides form α-networks which are slightly longer. They have a repeat distance close to 5.0 Å, equal to the ideal distance needed for a diacetylene polymerization [Fig. 1(a)]. Co-crystallization of the oxalamide of glycine with a bispyridyl-substituted diacetylene (Fig. 6) gives a crystal with the diacetylene monomers preorganized in layers with almost perfect agreement with the ideal values shown in Fig. 1. The intermolecular repeat is 4.97 Å, with the diacetylene molecules inclined at an angle of 43°. The critical distance between the C-4 carbon of one diacetylene and the C-1 carbon of its neighbor is close at 3.38 Å, a value well within the region where reactivity can be expected.

At room temperature these oxalamide crystals slowly polymerize crystal-to-crystal to give the desired diacetylene polymer in the form of a single crystal. Thermal

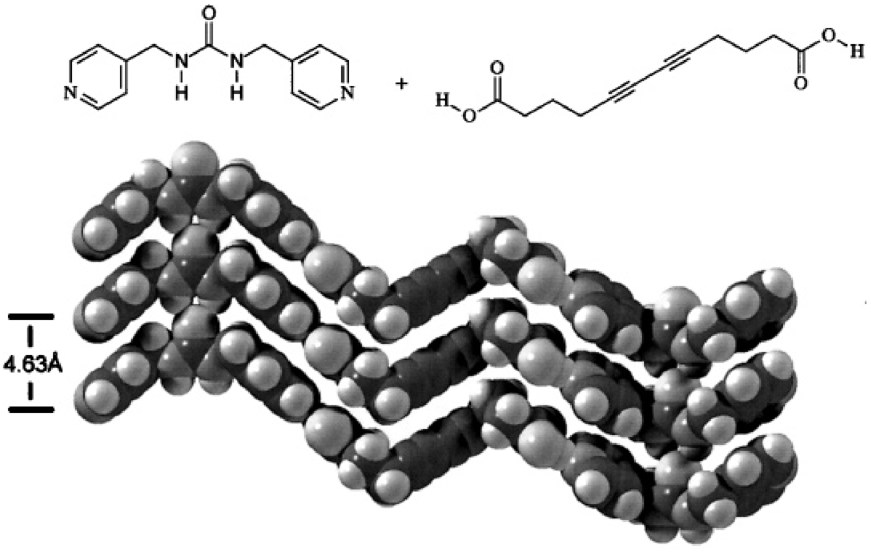


Figure 5. In this crystal structure of the host, guest substituents of the molecules in Fig.4 have been reversed. The pyridine-substituted urea forms an α-network with repeat distance of 4.63 Å. The critical C-1— C-4 distance is 4.33 Å, longer than desirable for polymerization

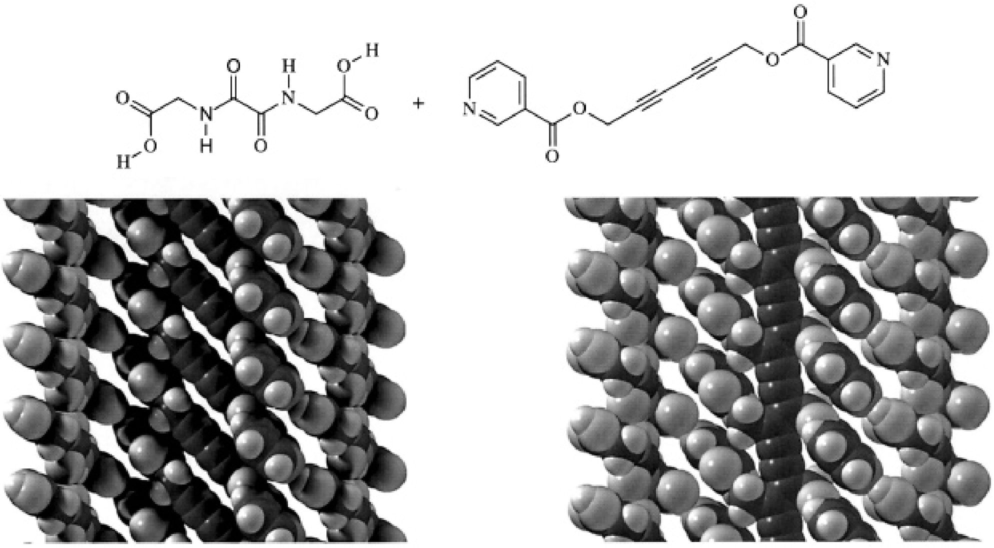


Figure 6. On the left, the crystal structure of the co-crystal formed from the oxalamide of glycine with a bis-pyridyl substituted diacetylene shows a repeat distance of 4.97 Å. The critical distance between the C-4 of one diacetylene and the C-1 carbon of the next molecule is only 3.38 Å. Under mild thermal annealing conditions the crystals undergo a clean crystal-to-crystal polymerization to give the diacetylene polymer as shown in the crystal structure on the right

annealing at only slightly elevated temperatures increases the rate of conversion. The polymer crystals occur as needles with highly anisotropic optical properties perpendicular to the long axis of the crystal. In one direction they have a very deep red color with a metallic golden sheen; in the perpendicular direction they are colorless. This anisotropy is due to the fact that all the polydiacetylene chains are not just parallel but are also coplanar, a natural consequence of our layer design.

The significance of this diacetylene polymerization is that it demonstrates a way to bring about a topochemical polymerization by design. We used our accumulated knowledge of supramolecular chemistry to design and synthesize a host–guest system in which the diacetylene monomers were brought into layers, preorganized in a precisely defined manner. Previous studies of diacetylene polymerization relied upon studies of single molecules. A given diacetylene will either crystallize with the proper preorganization or it will not. There is little that the chemist can do to change the crystallization preference of a *single* molecule. However, with a host–guest strategy one can engineer the host to fine-tune the environment of the guest.

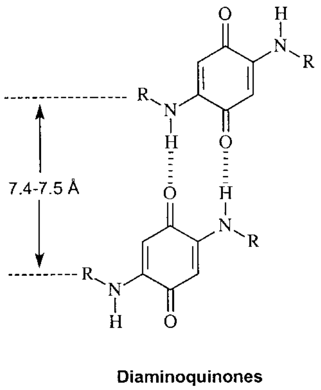
TOPOCHEMICAL TRIACETYLENE POLYMERIZATION BY DESIGN

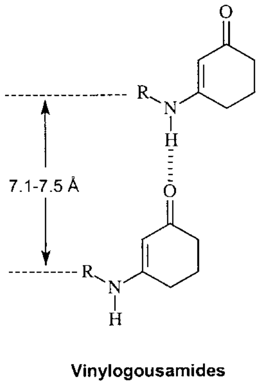
The conjugated polymers have attracted the interest of materials science because of their useful optical and electrical properties. Polyacetylene, polydiacetylene and polytriacetylene are the simplest known linearly conjugated polymers. However, in contrast to polyacetylene and polydiacetylene, polytriacetylene has never been prepared by the direct polymerization of triacetylene monomers. Because a successful 1,6-polymerization of a triacetylene requires significant organization of the triacetylene molecules, we considered this reaction a significant test of our supramolecular synthetic strategies.[22]

Unsuccessful attempts to accomplish this polymerization were reported by Wegner and co-workers as early as 1973, soon after the remarkable discovery of the topochemically controlled 1,4-polymerization of diacetylenes.[23] At this time the supramolecular requirements for polymerization were recognized. In 1994, Enkelmann summarized other unsuccessful attempts at 1,6-polymerization of triacetylenes and provided a more complete analysis of the criteria necessary for a successful polymerization.[16] As shown in Fig. 1(b), the preorganization requirements are a intermolecular monomer spacing of about 7.4 Å with a 28° tilt of the linear triacetylene relative to the translation axis. These requirements seem rather extreme and it is perhaps not surprising that no triacetylene has been found that crystallizes in such a manner fortuitously.

The design and synthesis of a system that would meet these preorganization criteria would serve a significant test of our supramolecular synthetic abilities. As we approached the problem, we recognized that the focus of our design should be on not the triacetylene, but the host molecule. The most critical structural parameter to control is the required simple translation distance of about 7.4 Å since close packing of the triacetylenes will produce the required 28° tilt angle.

Model building (Macromodel version 6.2 using the MM2 force field was used in modeling calculations[24]) suggested that the 2,5-diaminoquinones would self-





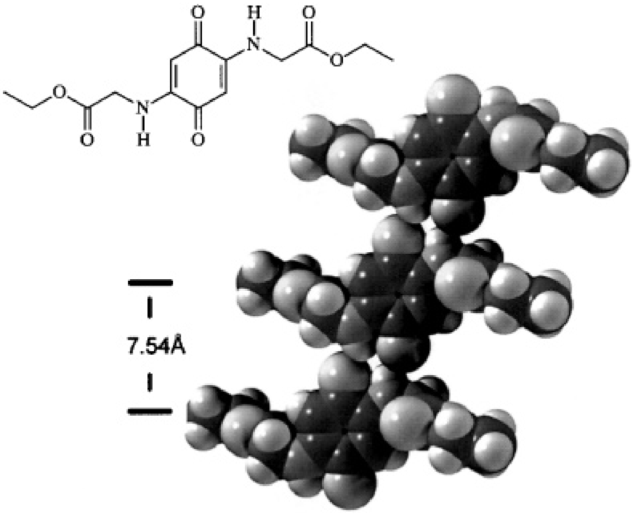
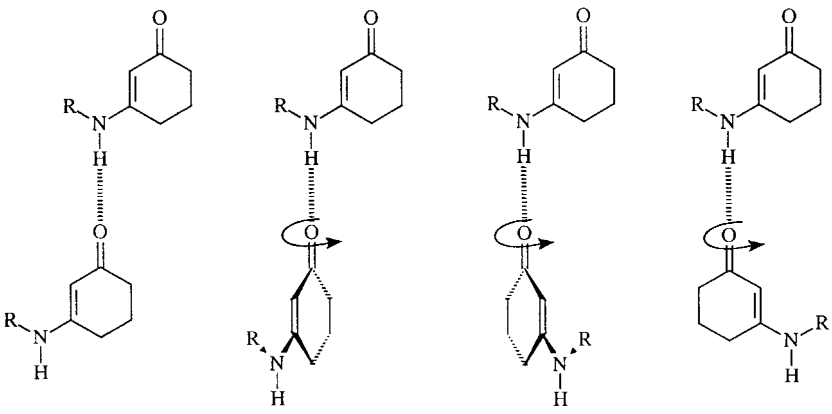


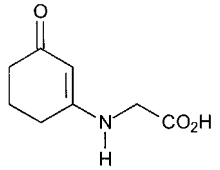
Figure 7. The crystal structure of the glycine ethyl ester derivative of benzoquinone shows that the molecules have self-assembled to give an intermolecular repeat distance of 7.54 Å

assemble via simple translation to give the desired molecular repeat (7.4 Å). This was confirmed by experiment. The glycine ethyl ester derivative of benzoquinone, R = $CH_2CO_2C_2H_5$, was prepared and a single-crystal x-ray structure confirmed that it self-assembled with a molecular repeat of 7.54 Å (Fig. 7). Unfortunately, as a class, the diaminoquinones are extremely insoluble and are therefore not ideal host molecules. It is very difficult to prepare a co-crystal of two different molecules if one has a very low solubility.

After having problems with the 2,5-diaminoquinones, we turned to a simpler system, the cyclic vinylogous amides. These molecules are relatively easy to synthesize and they have good solubilities in common solvents. The problem is that the projected hydrogen-bonded α-network is based on an unsymmetric molecule with only one hydrogen bond and not two as is the case in all of our previously used host molecules. Host networks based on symmetrical molecules with two hydrogen bonds, like the ureas, the oxalamides and the 2,5-diaminoquinones, naturally are coplanar and generally form simple translationally related one-dimensional α-networks. With only one hydrogen bond, there is no expectation for neighboring molecules in a network to self-assemble using simple translational symmetry, nor is there an expectation that they will form coplanar networks. Inspection of the Cambridge Structural Database (CSD) confirmed our fears. Among the six simple vinylogous amide derivatives reported in the CSD, only one assembled via simple translation (the derivative, with a *m*-nitrophenyl substituent on nitrogen, displayed a simple translational distance of 7.313 Å,[25]). The other formed hydrogen-bonded networks using the anticipated hydrogen-bonded motif, but neighboring molecules were related by a glide plane or screw axis. These types of symmetry double the crystallographic repeat distance to an undesirable 14–15 Å. Despite these discouraging data, we proceeded with our plan based on the assumption that a good host–guest design would still lead us to our desired structure. In particular, we realized that although a single vinylogous host molecule can form only one amide hydrogen bond, the designed 2:1 host–guest assemblies of molecules would have two host molecules and thus could form two amide hydrogen bonds, making it more likely that the molecules would assemble via simple translation.

Having settled on the vinylogous amides as a host family, we still needed to identify a specific host





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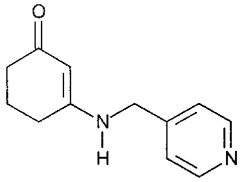

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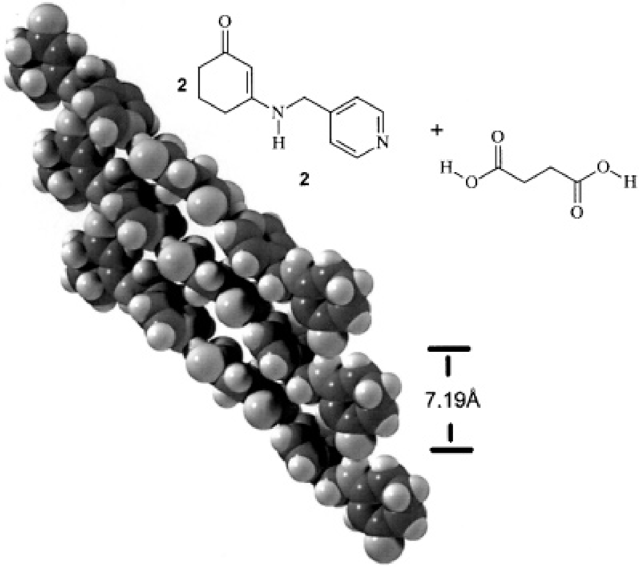

Figure 8. The crystal structure of the 2:1 co-crystal of vinylogous amide **2** with succinic acid. The intermolecular spacing is 7.19 Å

molecule. We synthesized a number of candidate molecules, **1** and **2** being representative examples.

Attempts to grow test co-crystals of molecule **1** with bipyridine proved to be difficult because of the relative solubilities of the two molecules, so we turned to pyridine derivative **2**. The 2:1 co-crystals of **2** with succinic acid (Fig. 8) and adipic acid were successful with the molecules assembling in accordance with our design. Encouraged by these results, we turned to the actual triacetylene experiment.

The symmetrical triacetylene diacid **3** was synthesized. A 2:1 methanol solution of the host pyridine **2** and the triacetylene **3** was allowed to evaporate slowly, yielding pale red crystals. X-ray diffraction revealed that the molecules had indeed co-crystallized in a 2:1 ratio and had assembled in accordance with our design (Fig. 9). Equivalent molecules in the α-network were related simple translation at a distance of 7.143(2) Å. The triacetylene core was tilted an angle of 29.2° with respect to the translational direction. This brings the triacetylene functionalities into van der Waals contact with the crucial non-bonded C-1 to C-6 at 3.487(2) Å. Overall these values are in remarkably good agreement with the ideal values outlined in Fig. 1.

Since the crystals showed a close van der Waals contact between the anticipated reaction centers, it seemed that we should be able to induce a polymerization

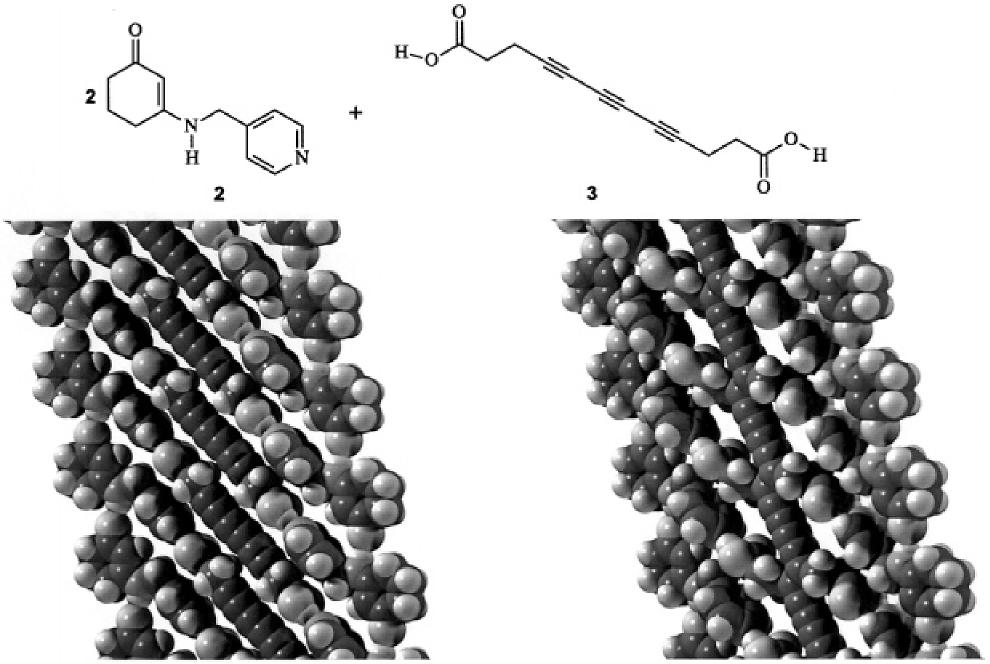

Figure 9. The pyridine host **2** and the triacetylenedicarboxylic acid guest **3** were co-crystallized to yield the crystal structure shown on the left. The intermolecular repeat distance is 7.143 Å with a 29.2° tilt of the triacetylene core with respect to the translation axis. This brings the key C-6 of one triacetylene molecule in to close (3.487 Å) contact with the C-1 carbon of its neighbor. Upon γ irradiation the molecules polymerize to give the polymer structure shown on the right

reaction. However, no significant polymerization was observed when the crystals were heated at 109 °C for 72 h or irradiated for 72 h with a Hanovia 550 W medium-pressure mercury lamp. Following these negative experiments, we turned to a higher energy source, ^{60}Co γ-radiation (the γ-ray source used had an output of 0.8 Mrad h^{-1} and was located at Brookhaven National Laboratories, Upton, NY, USA). Exposure of the host–guest crystals to about 8 Mrad of γ-rays resulted in a dramatic change to a deep red color. X-ray crystallography revealed that the polymerization was taking place and that the irradiated crystals consisted of a solid solution of the original triacetylene monomers and the resultant polytriacetylene polymer (Fig. 9). The γ-irradiation of a single crystal was continued in stages with a complete x-ray diffraction data set collected at each stage. The polymerization was found to continue to occur approximately linearly with irradiation time. After 40 Mrad of radiation, with the crystals polymerized to about 70%, a phase change occurs in the crystals to an amorphous ‘glassy’ state that no longer gives useful diffraction data.

The structure of the resulting polymer is shown in Fig. 9. The molecule networks are aligned with the *a* axis of the triclinic unit cell. In a fresh monomer crystal this distance is 7.143(2) Å. As the polymerization proceeds the axis lengthens in proportion, but only slightly. The highest observed value of 7.210(6) Å was for a crystal polymerized to an extent of 70%. Since this value is still considerable shorter than the 7.4 Å repeat distance predicted for the polymer, it is likely that strain may build up in the crystals as the polymerization proceeds. One can hypothesize that this strain is responsible for the phase change to an amorphous state that takes place as the polymerization proceeds beyond 70%. Perhaps a host that would give a slightly longer spacing would give crystals that would polymerize more readily.

The resulting triacetylene polymer is a polycarboxylic acid and is soluble in sodium hydroxide. Its physical and chemical properties have been discussed elsewhere and are under further investigation. Most significantly, in agreement with earlier observations by Deiderich and co-workers, the triacetylene polymer seems to be fairly stable. Further studies of this and other polytriacetylenes as candidates for advanced materials may prove to be rewarding.

CONCLUSION

We have demonstrated the successful application of supramolecular chemistry to two significant problems in synthetic chemistry. We have shown that we now know enough about intermolecular interactions to design supramolecular structures with a reasonable expectation that we will be able successfully to carry out the required syntheses. The work is a part of the natural evolution of synthetic chemistry from the molecular to the supramolecular level.

Acknowledgements

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REFERENCES

1. Diederich F. In *Modern Acetylene Chemistry*, Stang PJ, Diederich F (eds). VCH: Weinheim, 1995; 443–471.
2. Bunz HF. *Angew. Chem., Intl. Ed. Engl.* 1994; **33**: 1073–1076.
3. Diederich F, Gobbi L. *Topics Curr. Chem.* 1999; **201**: 43–79.
4. Schenning APHJ, Martin RE, Ito M, Diederich F, Boudon C, Gisselbrecht J-P, Gross M. *J. Chem. Soc., Chem. Commum.* 1998; 1013–1014.
5. Martin RE, Gubler U, Boudon C, Gramlich V, Bosshard C, Gisselbrecht J-P, Gunter P, Gross M, Diederich F. *Chem. Eur. J.* 1997; **3**: 1505–1512.
6. Schreiber M, Tykwinski RR, Diederich F, Spreiter R, Gubler U, Bosshard C, Poberaj I, Gunther P, Boudon C. *Adv. Mater.* 1997; **9**: 339–343.
7. Nierengarten JF, Herrmann A, Tykwinski RR, Ruettimann M, Diederich F. *Helv. Chim. Acta* 1997; **80**: 293–316.
8. Schreiber M, Anthony J, Diederich F, Spahr ME, Nesper R, Hubrich M, Bommeli F, Degiorgi L, Wachter P. *Adv. Mater.* 1994; **6**: 786–790.
9. Boldi AM, Anthony J, Gramlich V, Knobler CB, Boudon C, Gisselbrecht J-P, Bross M, Diederich F. *Helv. Chim. Acta* 1995; **78**: 779–796.
10. Anthony J, Boldi AM, Rubin Y, Hobi M, Gramlich V, Knobler CB, Seiler P, Diederich F. *Helv. Chim. Acta* 1995; **78**: 13–45.
11. Anthony J, Boudon C, Diederich F, Gisselbrecht J-P, Gramlich V, Gross M, Hobi M, Seiler P. *Angew. Chem., Int. Ed. Engl.* 1994; **106**: 794–798.
12. Niergarten J-F, Guillon D, Heinrich B, Nicoud J-F. *J. Chem. Soc., Chem. Commun.* 1997; 1233–1234.
13. Anthony J, Boudon C, Diederich F, Gisselbrecht J-P, Gramlich V, Gross M, Hobi M, Seiler P. *Angew. Chem., Int. Ed. Engl.* 1994; **33**: 763–766.
14. Martin RE, Mäder T, Diederich F. *Angew. Chem. Int. Ed. Engl.* 1999; **38**: 817–820.
15. Baughman RH, Yee KC. *J. Polym. Sci.: Macromol. Rev.* 1978; **13**: 219–239.
16. Enkelmann V. *Chem. Mater.* 1994; **6**: 1337–1340.
17. Sarkar A, Okada S, Matsuzawa H, Matsuda H, Nakanishi H, *J. Mater. Chem.* 2000; **10**: 819–828.
18. Zhao XQ, Chang YL, Fowler FW, Lauher JW. *J. Am. Chem. Soc.* 1990; **112**: 6627–6634.
19. Chang YL, West, MA, Fowler FW, Lauher JW. *J. Am. Chem. Soc.* 1993; **115**: 5991–6000.
20. Coe S, Kane J, Nguyen T, Toledo L, Wininger E, Fowler FW, Lauher JW. *J. Am. Chem. Soc.* 1997; **119**: 86–93.
21. Kane JJ, Liao R-F, Lauher JW, Fowler FW. *J. Am. Chem. Soc.* 1995; **117**: 12003–12004.
22. Xiao J, Yang M. Lauher JW, Fowler FW. *Angew. Chem., Int. Ed. Engl.* 2000; **39**: 2132–2135.
23. Kiji J, Kaiser J, Wegner G, Schulz RC. *Polymer* 1973; **14**: 433–439.
24. Mohamadi F, Richards NBG, Guida WC, Liskamp R, Lipton M, Caufield C, Chang G, Hendrickson T, Still WC. *J. Comput. Chem.* 1990; **11**: 440–467.
25. Huang K-S, Britton D, Etter MC. *Acta Crystallogr., Sect. C.* 1995; **51**: 1661–1664.