encapsulation complexes are rare.[16–18] Imprinting[19, 20] in hydrogen-bonded assemblies provides another route to such systems, and recent work promises that behaviors similar to those observed here will also be found in metal–ligand assemblies.[8] The result augurs well for the application of these capsules in dynamic combinatorial libraries and other enantioselective processes, such as the catalysis of reactions with rates comparable to that of guest exchange.[21]

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A Supramolecular Solution to a Long-Standing Problem: The 1,6-Polymerization of a Triacetylene[**]

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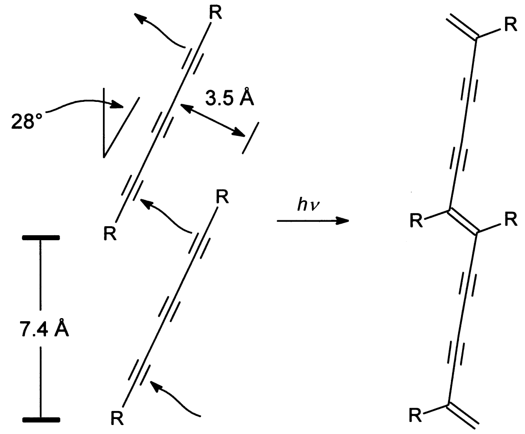
The 1,6-polymerization of a triacetylene is an unknown transformation.[1, 2] Unsuccessful attempts to accomplish this polymerization were reported as early as 1972, soon after the remarkable discovery of the topochemically controlled 1,4-polymerization of diacetylenes.[3] It was recognized that a successful 1,6-polymerization would require preorganization of the reactants. In 1994 Enkelmann gave a more up-to-date report of other unsuccessful attempts of the 1,6-polymerization of triacetylenes and provided a more complete analysis of the criteria necessary for a successful polymerization.[4] The structural parameters needed for a topochemical triacetylene polymerization can be derived if one assumes that the monomeric units must be preorganized with a defined simple translational distance of 7.4 Å, matching the geometric parameters of the expected polymer (Scheme 1). If the monomers are spaced at this distance and tilted at an angle just under 30° then the neighboring triacetylene functionalities will be in 3.5 Å van der Waals contact, a condition that should maximize the chances of polymerization. These exacting structural requirements are unlikely to be met by any randomly chosen triacetylene.



Scheme 1. A triacetylene should polymerize if it is preorganized with a defined geometry that matches the geometrical parameters of the expected polymer product.

The 1,6-polymerization of a triacetylene is thus a curious chemical problem. It is a long-standing synthetic problem of

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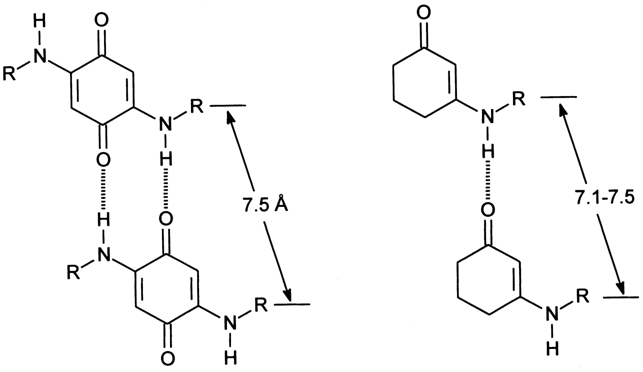
considerable interest and the requirements are very well defined, yet no one has been able to devise a successful synthesis. We believed that the solution to the problem could be found in the fledgling field of supramolecular chemistry. The successful synthesis of a polytriacetylene through a designed 1,6-polymerization would serve as a significant test for supramolecular synthesis in the same manner that complex natural products have often served as a test for conventional molecular syntheses.

The most critical structural parameter to control is the required simple translation distance of about 7.4 Å. If a chemical functionality could be discovered that would self-assemble at such a repeat distance, then one could use this functionality to achieve the necessary preorganization of the triacetylene chains. Inspection of models[5] suggested the 2,5-diaminoquinone functionality (**1**) would use complementary hydrogen bonds to self-assemble by simple translation with a molecular repeat distance (7.46 Å) close to that believed to be required for polymerization (7.4 Å). Molecular modeling predictions were confirmed by experiment. The glycine ethyl ester derivative of benzoquinone (**1**, $R = CH_2CO_2C_2H_5$; Scheme 2) was prepared and a single-crystal X-ray structure confirmed that it self-assembled with a molecular repeat of 7.54 Å. Unfortunately, as a class, the diaminoquinones proved to be extremely insoluble, limiting their application to the organization of polytriacetylenes for a topochemical polymerization.



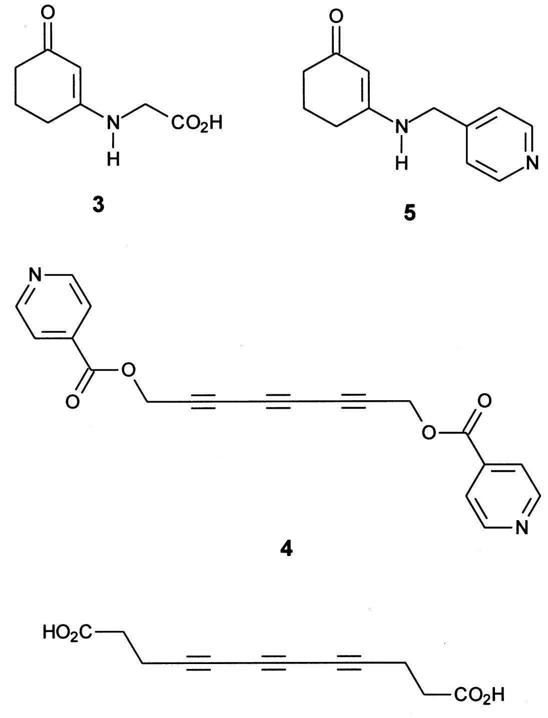
1 **2**

Scheme 2. The diaminoquinones (**1**) and the aminoquinones (**2**) are functional groups capable of self-assembling with a translational distance of approximately 7.4 Å.

Molecular modeling studies also suggested that derivatives of vinylogous amide **2**[6] could self assemble to give a molecular repeat close to that required for polymerization. They should also have better solubility properties. However, the presence of only one complementary hydrogen bond suggested that the self-assembly of vinylogous amides by simple translation (Scheme 2) might not be dependable. Inspection of the Cambridge Structural Database (CSD) confirms this analysis. Among the six simple derivatives of **2** reported in the CSD only one assembled by simple translation (7.31 Å).[7] The other five reported vinylogous amides all assembled using the anticipated hydrogen-bonding 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. However, we were encouraged by this data and believed the desired spacing could be accomplished by good design.

The next step in the organization of the triacetylene for a topochemical polymerization was to address the problem of associating the triacetylene monomer with the vinylogous amide. The most straightforward approach would be to create a covalent bond between the vinylogous amide and the triacetylene functional groups. Although this approach would probably succeed, one of its disadvantages is the complexity of the organic synthesis and of the ultimate polymer.

An alternative approach is to use host–guest chemistry, that is, to prepare two molecules, the vinylogous amide (the host) and the triacetylene (the guest). The host provides the required supramolecular structural elements and the guest provides the function. The association of these two molecules can be accomplished using a noncovalent link, such as a hydrogen bond. Suitable hydrogen-bonding functionalities that we have previously used[8] are carboxylic acids and pyridines.[9] Possible compounds to explore this strategy are the pyridines and carboxylic acids shown in Scheme 3. The major advantages of this approach are the simplification of the molecular synthesis and flexibility. One good host can be used to organize a number of different guests or a number of different hosts can be applied to a specific guest of interest. The disadvantage of this approach is that it requires predictable assemblies using weak noncovalent bonds.



3 **5** **4** **6**

Scheme 3. Vinylogous amide hosts and triacetylene hosts suitable for the topochemical preparation of a polytriacetylene.

Because of solubility differences between the carboxylic acid host **3** and the dipyridine **4**, preliminary attempts to grow co-crystals were not promising. Therefore, we turned our attention to the pyridine host **5**. We were pleased to observe that **5** readily co-crystallizes (2:1) with simple dicarboxylic acids such as succinic and adipic acid. Single-crystal X-ray structure determinations demonstrate that the host molecules assemble as illustrated in Scheme 2 with simple translational distances of 7.20 and 7.18 Å, respectively. Curiously, glutaric acid, with an odd number of methylene groups, forms a 1:1 co-crystal with **5**, but with a completely different pattern of hydrogen bonds.

Encouraged by the above results, the triacetylene diacid **6** was prepared. Evaporation of a 2:1 solution of pyridine host **5** and the triacetylene diacid **6** in methanol produced a host–guest compound as pale red crystals. A single-crystal X-ray structure of the host–guest complex (Figure 1 a) clearly shows that the molecules have self-assembled in accordance with our design. Equivalent atoms are spaced at 7.143(2) Å, with the triacetylene core at an angle of 29.2° with respect to the translational direction. The triacetylene chains are in van der Waals contact with the crucial nonbonded C1 to C6 distance of adjacent triacetylene molecules of 3.487(2) Å. Although the repeat distance of 7.143(2) Å is slightly shorter than the targeted value of 7.4 Å, overall these parameters are in good agreement with the numbers illustrated in Scheme 1.

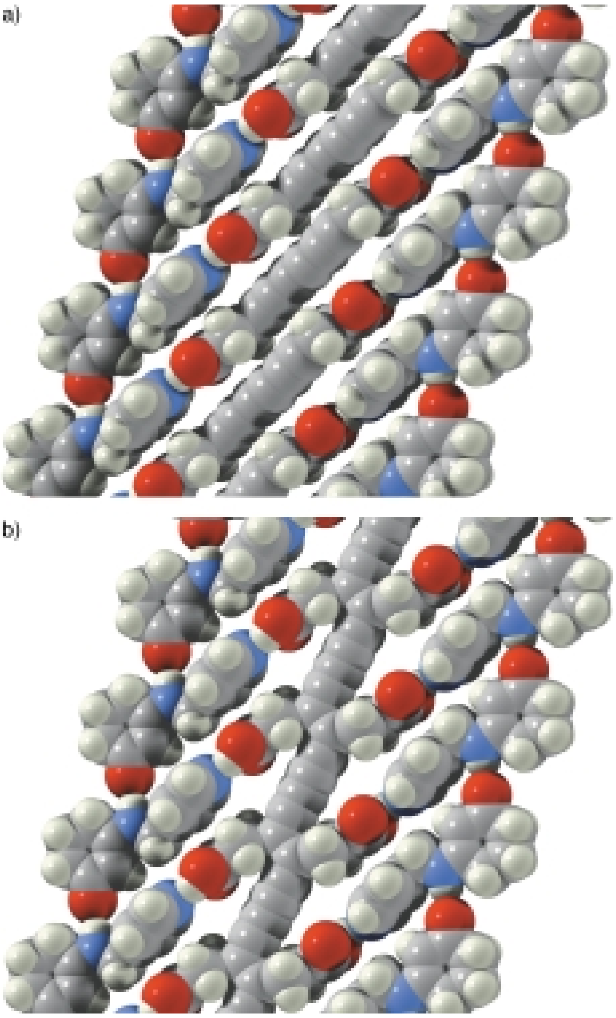


Figure 1. X-ray crystallographic structures of a) the host–guest triacetylene monomer structure and b) the resulting triacetylene polymer.

Preliminary experiments to effect polymerization with both heat and light were disappointing: No significant polymerization was observed when the crystals were heated to 109 °C for 72 h or irradiated for 72 h with a Hanovia 550 W medium-pressure mercury lamp. However, exposure of the host–guest crystals to ^{60}Co γ-radiation[10] resulted in the crystals becoming dark red, a color transformation consistent with polymerization. The topochemical polymerization was followed by X-ray crystallography. Individual single crystals were mounted and the structure of each individual crystal was determined repeatedly after radiation doses of about 8–10 Mrads of γ radiation. The analysis of the diffraction data showed that the irradiated crystals consist of a solid solution of the monomer and its polymer. The polymerization was about 70 % complete after 40 Mrads of radiation (Figure 1 b). Further irradiation and polymerization brings about a sudden phase change in the crystals to an amorphous “glassy” state that no longer gives useful diffraction data.

The polytriacetylene was isolated by first extracting the irradiated crystals with concentrated HCl to remove the pyridine host and then by extracting the residue with methanol to remove any unreacted triacetylene. A red, amorphous solid was isolated in about 70 % yield that does not melt up to 300 °C. It is insoluble in common organic solvents such as methanol, acetone, ethyl acetate, and dichloromethane. The carboxylic acid polymer slowly dissolved in sodium hydroxide to form a red solution in concentrated 1M NaOH or alternatively a yellow solution in dilute 0.1M NaOH.[11] The UV/Vis spectrum (0.011 g L^{-1} in 0.1M NaOH) of the polymer shows a $\lambda_{max} = 446$ nm.

Raman spectroscopy has proven to be an excellent method for characterizing conjugated polymers.[12] The nonpolar multiple bonds usually display intense Raman bands. The polytriacetylene described here is no exception. The Raman spectrum of the polytriacetylene (0.011 g L^{-1}) shows only two intense bands in the 2500–500 cm^{-1} region at 2148 and 1552 cm^{-1}. These can be assigned to the C≡C and C=C bonds, respectively.

The poly(triacetylenes) are conjugated polymers with a delocalized π system along the polymer backbone. This structural feature imparts special properties to these compounds making them attractive candidates for the development into advanced materials.[13] The host–guest strategy described above allows for the preparation of other derivatives of this new conjugated polymer and provides a dramatic illustration of the natural evolution of synthetic chemistry from the molecular to the supramolecular level.

Experimental Section

X-ray structure analysis: The host–guest complex (Figure 1) crystallizes in space group $P\bar{1}$ with $a = 7.143(2)$, $b = 10.695(3)$; $c = 11.2825(3)$ Å, $\alpha = 77.28(2)$, $\beta = 90.421(2)$, $\gamma = 80.15(2)°$. $R_w = 4.8$, $R = 6.5$ for 221 variables and 1064 unique observations with $I > 3\sigma$. Freshly prepared crystals consisting of the host and the triacetylene monomer are of high quality. Upon γ irradiation (^{60}Co, 0.8 Mrad h^{-1}), the polymerization begins and the cell constants of the single crystals begin to change. After irradiation the single crystals consist of solid solutions of the monomer and the polymer (Figure 1b). A typical crystal after 30 Mrads of γ radiation maintained its $P\bar{1}$ space group symmetry with $a = 7.201(2)$, $b = 10.751(3)$, $c = 11.1421(3)$ Å, $\alpha = 76.94(2)$, $\beta = 87.67(2)$, $\gamma = 80.18(2)^\circ$. $R_w = 5.7$, $R = 6.3$ for 208 variables and 1211 unique observations with $I > 3\sigma$. The occupancy of the three independent central atoms of the triacetylene polymer refined to 0.58 for this particular crystal. The experiment was repeated for many different crystals all of which gave similar, but not identical parameters. The *a* axis of the triclinic unit cell corresponds to the critical polymerization direction. In a fresh crystal this axis has length of 7.143(2) Å. As the polymerization proceeds, the *a* 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 considerably 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. As the degree of polymerization exceeds 70%, this accumulated strain in the crystals may be the driving force of the change to an amorphous state. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-138504–135509. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The host compounds **3** and **5** were prepared by refluxing 1,3-cyclohexanedione with one equivalent of the appropriate amine in benzene, and the water produced during the reaction was removed with a Dean–Stark trap. Glycine and 4-aminomethylpyridine gave 71% and 91% yields of the vinylogous amides **3** (m.p. 215 °C) and **5** (m.p. 138 °C), respectively.

The triacetylenes were prepared by two successive Cadiot–Chodkiewicz reactions (CuCl (0.1 equiv), NH_2OH-HCl (0.3 equiv), and propylamine (3 equiv) in methanol). Triacetylene **6** was prepared by treating 4-pentynoic acid with 1-bromo-2-triethylsilylacetylene under the above Cadiot–Chodkiewicz reaction conditions to give the triethylsilyl-protected diacetylene (59%). The protecting group was removed (95%) using 1 M tetrabutylammonium fluoride (TBAF) in THF and the diacetylene was coupled with 5-bromo-4-pentynoic acid under the above Cadiot–Chodkiewicz reaction conditions[14] to give the triacetylene **6** (95%).

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Mixed Ferrocene–Cobaltocenium Dendrimers: The Most Stable Organometallic Redox Systems Combined in a Dendritic Molecule[**]

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José Losada[*]

Exciting advances continue to be made in dendrimer chemistry.[1] The incorporation of metals in dendritic structures has attracted growing interest as it generates new metallodendrimers[2] with interesting redox, magnetic, catalytic, and photo-optical properties. At the same time, new synthetic methods have been used for the introduction of functionally diverse terminal groups in the same molecule,[3] which give access to dendritic macromolecules having special properties and a variety of functions.

In the last few years, we reported the synthesis of several families of silicon- and nitrogen-based dendritic molecules containing organometallic moieties as surface functional groups.[4] In particular, poly(propylene imine) dendrimers functionalized with ferrocene or cobaltocenium moieties were shown to act as multisite redox-active guests for inclusion complexation by β-cyclodextrins, which yielded soluble supramolecular assemblies of high molecular weight.[5] Here we report on the synthesis and redox properties of novel metallodendrimers containing both ferrocene and cobaltocenium units. To our knowledge, this is the first time that multiple neutral and cationic redox-active organometallic moieties are present in a dendritic structure.[6, 7] These peripherally heterogeneous dendrimers combine the advantages of both metallocenes, in particular, their stability and redox reversibility on oxidation and reduction, respectively. Electrode surfaces modified with these metallodendrimers were successfully used as a novel type of glucose sensor.

The new mixed-metal dendrimers **1**–**4** were obtained by treatment of the first four generations of poly(propylene imine) dendrimers DAB-dendr-$(NH_2)_x$ ($x =$ 4, 8, 16, 32) with an equimolar mixture of freshly prepared chlorocarbonylferrocene and the PF_6^- salt of chlorocarbonylcobaltocenium in CH_2Cl_2/CH_3CN (1/1) (Scheme 1). They were isolated as air-stable orange-brown shiny solids. Ideally, each metallodendritic molecule should have the same number of ferrocene and cobaltocenium units on the surface (see the schematic representation of **4**). However, the experimental results

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