Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Strategies for the Preparation of Layered Polydiacetylenes

Tam Luong Nguyen [a], Frank W. Fowler [a] & Joseph W. Lauher [a]

[a] Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY, 11794, USA

Version of record first published: 04 Oct 2006

To cite this article: Tam Luong Nguyen, Frank W. Fowler & Joseph W. Lauher (1998): Strategies for the Preparation of Layered Polydiacetylenes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 313:1, 253-258

To link to this article: http://dx.doi.org/10.1080/10587259808044284

Mol. Cryst. Liq. Cryst., 1998, Vol. 313, pp. 253–258
Reprints available directly from the publisher
Photocopying permitted by license only

Strategies for the Preparation of Layered Polydiacetylenes

TAM LUONG NGUYEN, FRANK W. FOWLER and JOSEPH W. LAUHER
Department of Chemistry, State University of New York at Stony Brook,
Stony Brook, NY 11794, USA

We previously reported that ureylene and oxalamide dicarboxylic acids self-assemble to form layered supramolecular structures. Since the intermolecular repeat distances within these ureylene and oxalamide layers were similar to that distance necessary for the topochemical polymerization of diacetylenes, we envisioned using both the ureylene and oxalamide functionality to orient diacetylene for topochemical polymerization. Our approach uses host-guest chemistry to layer the diacetylene functionality. This strategy proved successful when the urea functionality was used to orient diacetylenes. We now report on the successful use of the oxalamide functionality to orient diacetylenes for topochemical polymerization.

Keywords: polydiacetylenes, topochemical polymerization, hydrogen bond

Introduction

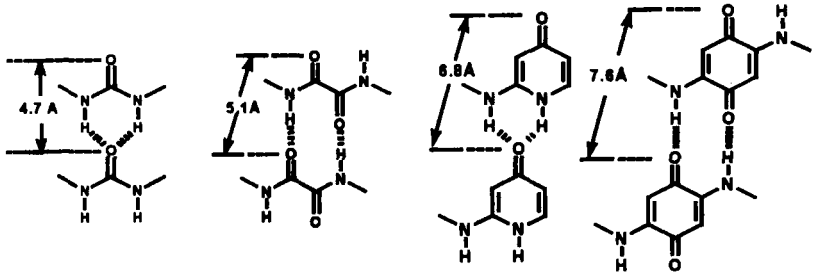
Since the properties of all materials depend upon the relative orientation of the constituent molecules, a rational approach to the preparation of advanced materials will require the development of strategies for the preparation of supramolecular structures.

An important supramolecular goal is the preparation of layered networks. A successful supramolecular synthesis of these networks does not require complete control over the solid state. Rather the fundamental requirement is a molecular constituent capable of controlling the structure. In this instance, the molecular constituent must be capable of two independent, nonparallel intermolecular associations. The self-assembly of these molecular components would lead to a layered solid.

An important intermolecular interaction is the hydrogen bond. Because of its strength, directionality and predictability, the hydrogen bond is a powerful tool for preparing designed supramolecular structures. Because numerous organic functional groups are capable of hydrogen bonding, the different two-dimensional networks that can be developed are unlimited[1].

Functional Layers

For the development of functional layered materials, it is important to control the spacing of the molecules within the layer. Control over the molecular repeat distance can be established by varying the hydrogen bonding functionality in one of the directions of the layer. We have utilized functional groups that establish repeat distances ranging from 4.7 Å to 7.6 Å[2,3,4].



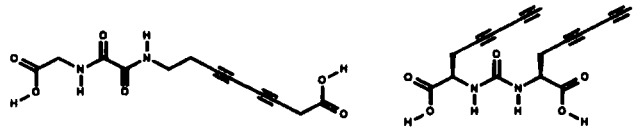
An Application

Intermolecular spacing is critical in topochemical reactions. One well-documented topochemical reaction is the C1 – C4 polymerization of diacetylenes. For polymerization to occur, the diacetylene monomers must be properly aligned with a molecular repeat distance of ≈ 5.0 Å[5]. Since this distance is similar to the molecular repeat distance of the ureylene and

oxalamide functional groups, they could be used to orient diacetylenes for topochemical polymerization. A second hydrogen bonding functional group would lead to a layered diacetylene network.

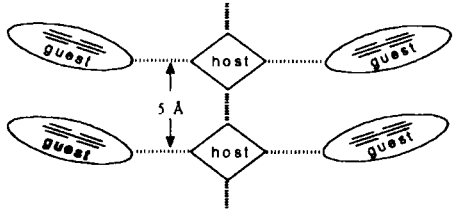
Supramolecular Synthetic Approaches

There are two fundamentally different approaches towards the preparation of layered diacetylenes. The more traditional approach is to prepare either a ureylene or oxalamide molecule with the diacetylene functionality and additional substituents leading to a two-dimensional network.



Although this strategy is predicted to be successful in layering diacetylenes, its major difficulty is the complexity of the molecular synthesis.

An alternative approach uses host-guest chemistry to layer the diacetylene functionality. An advantage of this approach over the first method is the simplicity of the molecular synthesis since the diacetylene and the functionality necessary for the formation of the two-dimensional network are distributed between two molecules.



The success of this approach relies on the host-guest chemistry. The strong intermolecular interaction that we employ is the pyridine-carboxylic acid hydrogen bond[6].

Ureylene Host

To explore the feasibility of our host-guest strategy for layering diacetylenes, we prepared a crystal of the ureylene dicarboxylic acid **1** and the dipyridine **2**[7]. The determination of its crystal structure confirmed the formation of two-dimensional network. The diacetylene functionalities were spaced at 4.71 Å with their main chains oriented at an angle of 56.3° relative to the axis of translation (fig. 1). This spacing and orientation is in accordance with the values needed for a successful polymerization.

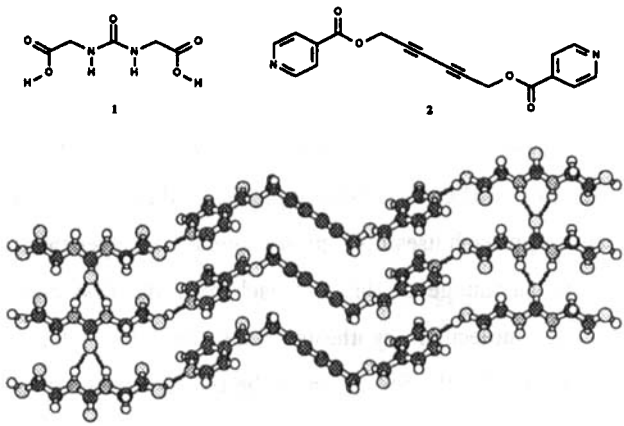
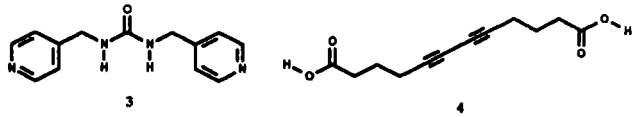


FIGURE 1 The structure of the **1** – **2** co-crystal.

We were also able to prepare a crystal of the urea **3** and diyne **4**. Similar to the first co-crystal, this crystal structure featured a layered network in which the diacetylenes were spaced at 4.63 Å with an orientation angle of



61.0°. Initial experiments indicate that polymerization in these two systems can occur under thermal conditions.

Oxalamide Host

Though the ureylene host layered the diacetylenes, the intermolecular repeat distance along the diacetylene stack was ≈ 4.7 Å which is 0.3 Å shorter than the optimal polymerization distance of 5.0 Å. A functional group better suited to match this critical 5.0 Å repeat distance is the oxalamide functionality which typically has a repeat distance of 4.9 – 5.1 Å.

A simple substitution of the ureylene host **3** with the oxalamide host **5**[8] yielded a co-crystal[9] similar to the **3** – **4** crystal (fig. 2).

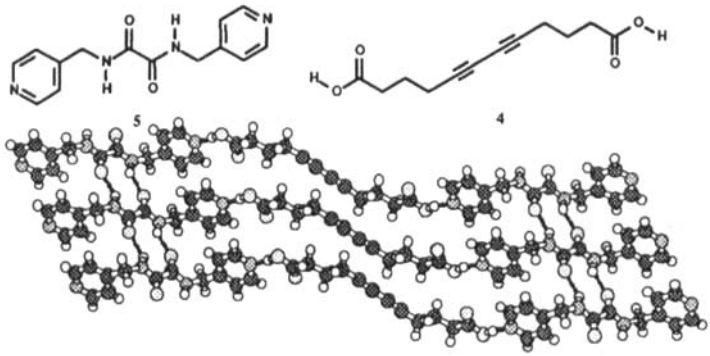


FIGURE 2 The structure of the **4** - **5** co-crystal.

The crystal structure was determined[10]. A key feature of this crystal structure was the spacing of the diacetylenes at 5.1 Å with an orientation angle of 45 °. This spacing and orientation matches the conditions necessary for the topochemical polymerization of the diacetylenes. We are currently investigating the polymerization process of this and other host-guest systems and the nature of these interesting diacetylene polymers.

Conclusions

A strength of the host-guest strategy is the ability to "fine tune" the crystal environment of the guest molecule by making subtle changes in either the host

or guest molecule. The flexibility of the host molecule allowed us to increase the molecular repeat distance along the stacked diacetylenes by 0.4 Å through the simple exchange of a ureylene host for an oxalamide one.

A strategy for the preparation of layered supramolecular structures has been developed and applied to the organization of diacetylenes for topochemically controlled polymerization.

Acknowledgements

This research is supported by the National Science Foundation under Grant No. CHE-9630042.

References

1. For some recent examples of two-dimensional networks, see: (a) M. D. Hollingsworth, M. E. Brown, B. D. Santarsiero, J. C. Huffman, *Chem. Mater.*, **6**, 1127 (1994). (b) V. A. Russell, M. C. Etter, *Chem. Mater.*, 6, 1206, (1994). (c) D. B. Aakeröy, M. Nieuwenhyzen, *J. Am. Chem. Soc.*, **116**, 10983 (1994).
2. X. Zhou, Y. –L. Chang, F. W. Fowler, J. W. Lauher, *J. Am. Chem. Soc.*, **112**, 6627 (1990).
3. S. Coe, J. J. Kane, T. L. Nguyen, L. M. Toledo, E. Wininger, F. W. Fowler, J. W. Lauher, *J. Am. Chem. Soc.*, **119**, 86 (1997).
4. L. M. Toledo, J. W. Lauher, F. W. Fowler, *Chem. Mater.*, **6**, 1222 (1994).
5. V. Enkelmann, *J. Am. Chem. Soc.*, **63**, 91 (1984).
6. C. M. Paleos, D. Tsiourvas, *Angew. Chem. Intl. Ed. Engl.*, 34, 1696 (1995).
7. J. J. Kane, R.-F. Liao, J. W. Lauher, F. W. Fowler, *J. Am. Chem. Soc.*, **117**, 12003 (1995).
8. The oxalamide **5**, mp 213 –214 °C, was prepared in 77% yield from the neat addition of diethyl oxalate to 4-(aminomethyl)pyridine at rt. Purification was achieved by recrystallization from methanol.
9. The co-crystal was obtained by recrystallization of equimolar of the diyne **4** and the oxalamide **5** in a 1:15 mixture of water and acetone.
10. Crystal data. **4-5** co-crystal, a = 5.136(11) Å, b = 9.146(6) Å, c = 13.710(8) Å, α = 103.364(5)°, β = 95.656(11)°, γ = 97.177(12)°, triclinic P $\bar{1}$, Z=1, R = 0.044, R_w = 0.047 for 1015 independent reflections.