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

Porphyrin Sponges: Programmable Lattice Clathrates

M. P. Byrn [a], C. J. Curtis [a], I. Goldberg [a], T. Huang [a], Y. Hsiou [a], S. I. Khan [a], P. A. Sawin [a], S. K. Tendick [a], A. Terzis [a] & C. E. Strouse [a]

[a] Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA, 90024-1569, U.S.A.

Version of record first published: 27 Oct 2006.

To cite this article: M. P. Byrn , C. J. Curtis , I. Goldberg , T. Huang , Y. Hsiou , S. I. Khan , P. A. Sawin , S. K. Tendick , A. Terzis & C. E. Strouse (1992): Porphyrin Sponges: Programmable Lattice Clathrates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 211:1, 135-140

To link to this article: http://dx.doi.org/10.1080/10587259208025812

Mol. Cryst. Liq. Cryst. 1992, Vol. 211, pp. 135–140
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

PORPHYRIN SPONGES: PROGRAMMABLE LATTICE CLATHRATES

M. P. BYRN, C. J. CURTIS, I. GOLDBERG, T. HUANG, Y. HSIOU,
S. I. KHAN, P. A. SAWIN, S. K. TENDICK, A. TERZIS, C. E. STROUSE
Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA, 90024-1569, U.S.A.

(Received July 12, 1991)

Abstract Structural systematics, programmability, and guest transport are discussed for a large class of lattice clathrates based on tetraarylporphyrins.

Keywords: lattice clathrate, porphyrin, intercalate, molecular packing

INTRODUCTION

Tetraarylporphyrins have recently been shown[1-3] to exhibit remarkable versatility as lattice clathrate hosts. This versatility is reflected in the fact that complete structural data are now available for nearly 400 porphyrin-based clathrates. The availability of this large base of structural data and the ease with which high-quality crystals containing new guest species can be produced allow an unusually detailed examination of the structural systematics of these materials. They also make possible a wide range of scientific and technological applications. This report provides an overview of the structural data available for "porphyrin sponges", and discusses some unique features of these materials that might be utilized in the designed construction of new lattice clathrates.

THE TETRAPHENYLPORPHYRIN MOLECULE

There are several features of the metallotetraphenylporphyrin molecule that are clearly related to its unusual utility as a clathrate host. This molecule (Fig. 1) is relatively large, quite rigid, and highly symmetric. It is non-polar and has no potential for hydrogen bonding. It is also thermally robust. The porphinato ligand binds a metal atom tightly, but allows access from two directions. Just as nature uses porphyrin molecules to harness the rich chemistry of transition metals, many applications of the porphyrin-based clathrates exploit the reactivity of the metal center.

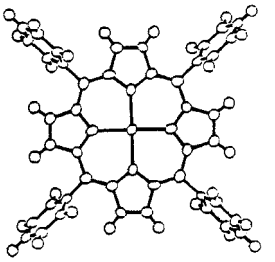

FIGURE 1 A tetraphenylporphyrin molecule.

CLATHRATE FORMATION

The driving force for clathrate formation is the fact that tetraphenylporphyrin (TPP) molecules cannot pack efficiently in three dimensions. The four phenyl groups are restricted to be nearly orthogonal to the porphyrin plane, and they prevent efficient stacking. On the other hand, TPP molecules can pack quite efficiently in one or two dimensions. As a result, similar sheet structures are observed in a wide range of materials. These clathrates are not unlike the graphite intercalates in that the guest molecules are incorporated between sheets of host molecules. Indeed, a recent survey of structural data reveals the existence of porphyrin based clathrates analogous to both "stage 1" and "stage 2" intercalates.

TYPICAL PORPHYRIN-BASED CLATHRATES.

"Stage 1" Clathrates

Previous reports from this laboratory[1-3] have described the structural systematics of over 100 "isostructural" triclinic porphyrin-based clathrates. These materials consist of alternating sheets of host and guest molecules. Figure 2 shows two views of one such "stage 1" clathrate. The 1-dimensional chains and the corrugated sheets of porphyrin molecules seen here are features that are observed in most porphyrin-based clathrates. The absence of covalent or hydrogen-bonding interactions between host molecules results in a very flexible host that is able to accommodate guests of widely varying size and shape. The same gross structure is often maintained, even in cases where the guest volume is comparable to that of the host.

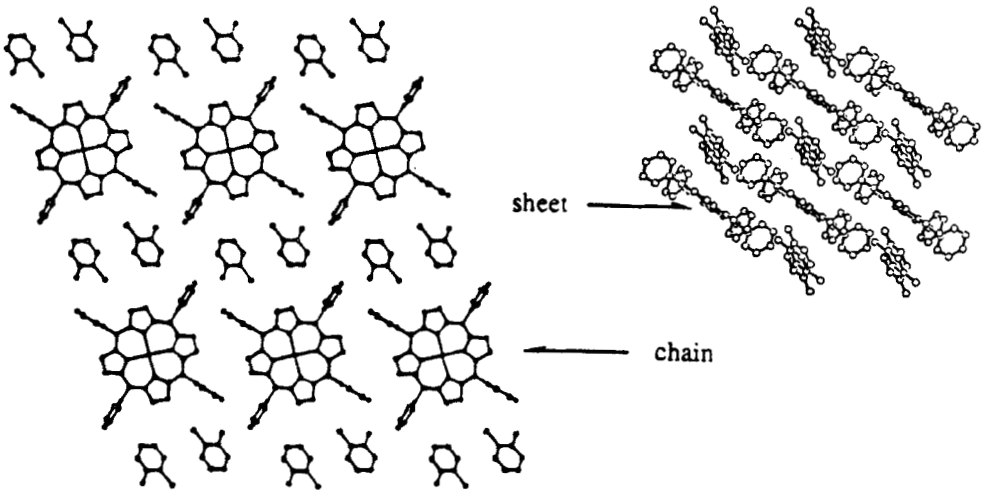

FIGURE 2 Two views of a typical "stage 1" porphyrin sponge.

"Stage 2" Clathrates

A second class of triclinic porphyrin-based clathrates exhibits double sheets of porphyrin molecules separated by sheets of guest molecules. The host stacking within the double sheets is similar to that found in the "stage 1" materials. Over a dozen "stage 2" intercalates have been identified to date. A typical example is shown in Figure 3.

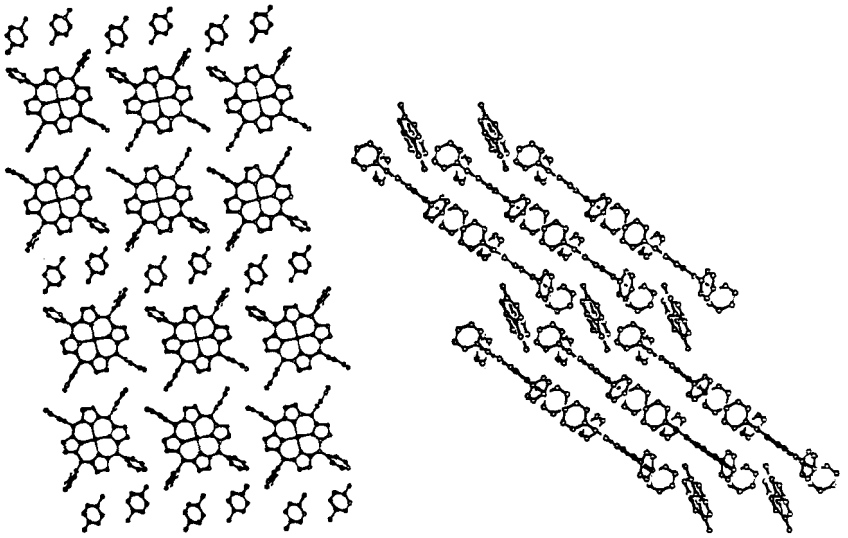

FIGURE 3 Two views of a typical "stage 2" porphyrin sponge.

Monoclinic Clathrates

Two commonly occurring monoclinic packing arrangements have also been identified. In the first structure shown in Figure 4, sheets are observed that are similar to those found for the "stage 1" clathrates. The second structure shown in Figure 4 exhibits some of the structural features found in the materials described above, but the sheet structure is not preserved.

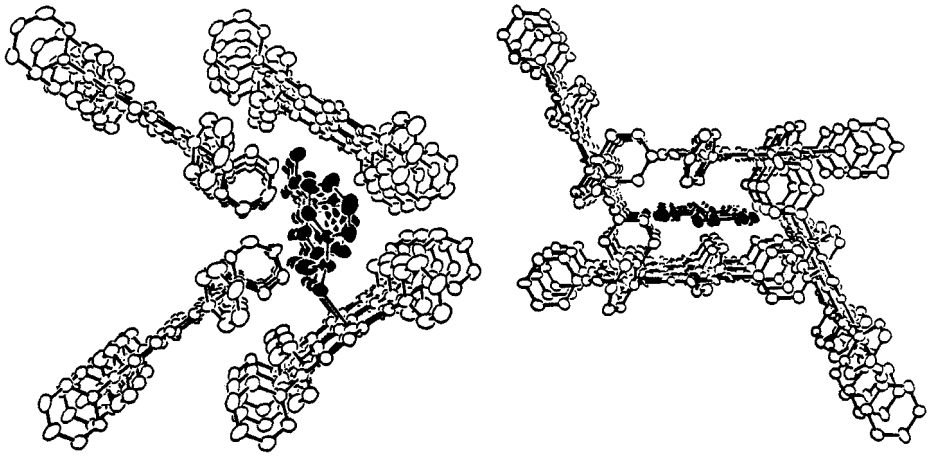

FIGURE 4 Monoclinic porphyrin sponges.

PROGRAMMABILITY

A particular advantage of porphyrin based hosts is that there are many ways in which they can be "programmed" for specific applications. Because the axial coordination sites of the porphyrin metal atom coincide with the guest sites, interaction between the guest and the metal atom has a significant influence on lattice energetics. For guests that function as ligands, the strength of the metal-guest interaction can be controlled by the choice of metal atom. Alternatively, the metal atom can be replaced by two hydrogen atoms.

Since the porphinato ligand has a -2 charge, a metal atom oxidation state of +2 will result in the incorporation of neutral guests. On the other hand, a higher metal atom oxidation state will result in the incorporation of anionic guests, while a lower oxidation state will result in the incorporation of cations. Metal atom oxidation states ranging from 0 to +5 have been observed in these materials.

A more subtle type of programming takes advantage of the fact that the crystal packing is dominated by the large, rigid porphyrin molecules. This packing is centrosymmetric, and most often two inversion related guests are incorporated per TPP molecule. In clathrates based on five-coordinate metalloporphyrin hosts, the axial ligand occupies one of the guest sites. In these materials the other guest site will preferentially accommodate molecules similar in size and shape to the axial ligand. This provides a rational basis for the use of these hosts in chemical separations.

Another type of programming involves modification of the TPP molecule itself. Tetraarylporphyrins with substituents on the phenyl groups are easily prepared from the corresponding benzaldehydes. One example of this kind of modification is an effort to prepare a more rigid "porphyrin sponge" in which the host molecules are linked by hydrogen bonding or coordination. A number of such materials have been prepared. Two "polymeric sponges" based on the p-hydroxy substituted TPP are shown in Figure 5.

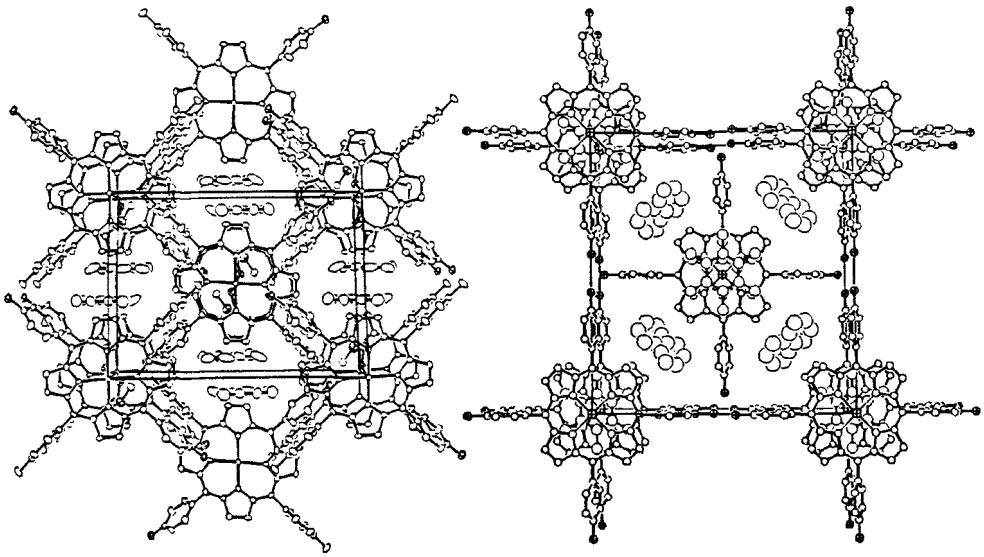

FIGURE 5 Polymeric porphyrin sponges.

GUEST LOSS AND UPTAKE

Many applications of these clathrate materials involve the transfer of guests to or from the vapor phase. For this reason, examinations of the structural and kinetic aspects of these processes have been undertaken. A number of significant and unexpected observations have been made.

Powder x-ray diffraction measurements have been used to follow the structural changes that take place upon loss of the guest species. In general it has been found that a mixture of two phases, one tetragonal and one triclinic, is formed. The detailed structures of these phases have been deduced from the powder patterns by comparison with known structures (see Figure 6). Desolvation at low temperature favors formation of the tetragonal phase, while desolvation at high temperature favors formation of the triclinic phase. Both of these phases incorporate guest molecules from the vapor phase to produce crystalline materials whose powder patterns match those of the clathrates grown from solution.

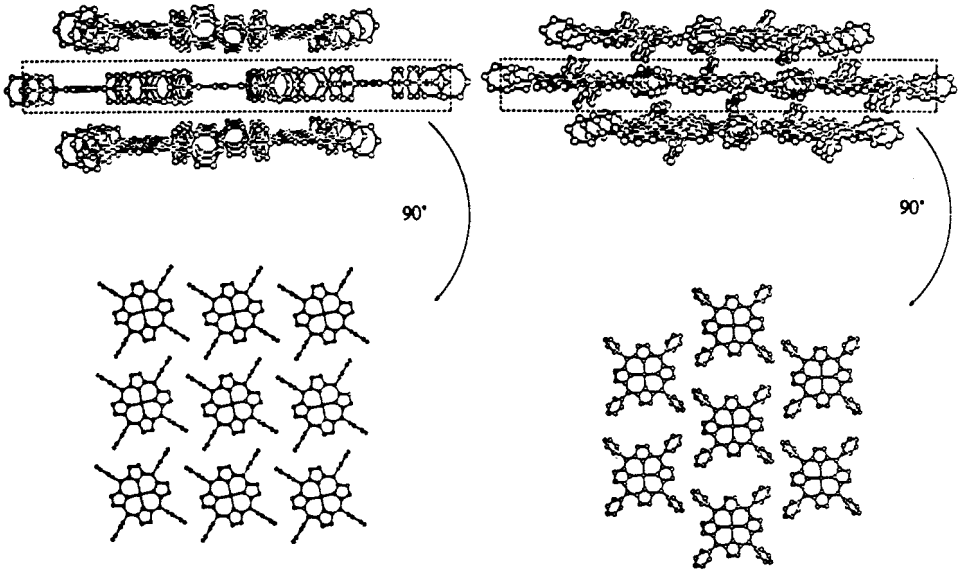

FIGURE 6 Tetragonal and triclinic forms of unsolvated ZnTPP.

APPLICATIONS

Many applications of these materials are currently being developed. Some applications simply involve transformation of liquids to solids. For example, formation of a clathrate greatly simplifies crystal structure determination of a material that is a liquid at room temperature. Incorporation into a clathrate isolates and immobilizes the guest molecule, generally enhancing its stability. As mentioned above, these materials can also be programmed to carry out chemical separations. A large number of potential applications take advantage of the rich and well-studied chemistry of metalloporphyrins. In some of these applications the host lattice serves the same function as the protein molecule in heme enzymes. It controls access of potential substrates to the reactive metal center. It is expected that some of the polymeric "sponges" might be particularly useful in mimicking the chemistry of these enzymes.

CONCLUSIONS

The common structures observed for many TPP-based clathrates demonstrate that van der Waals interactions between rigid molecules with self-complementary shapes are sufficient to govern the solid state structure. In this regard, the TPP molecule can be viewed as a prototype building block for the designed construction of molecular solids in general, and lattice clathrates in particular.

ACKNOWLEDGEMENT

This material is based upon work supported by the National Science Foundation (CHE 9003933) and the National Institutes of Health (GM 35329). Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the funding agencies. Some of the structural data used in the investigations described herein were obtained from the Cambridge Structural Database.

REFERENCES

1. M. P. Byrn, C. J. Curtis, S. I. Khan, P. A. Sawin, R. Tsurumi and C. E. Strouse, J. Am. Chem. Soc., 112, 1865 (1990).

2. M. P. Byrn and C. E. Strouse, J. Am. Chem. Soc., 113, 2501 (1991).

3. M. P. Byrn, C. J. Curtis, I. Goldberg, Y. Hsiou, S. I. Khan, P. A. Sawin, S. K. Tendick and C. E. Strouse, accepted for publication, J. Am. Chem. Soc..