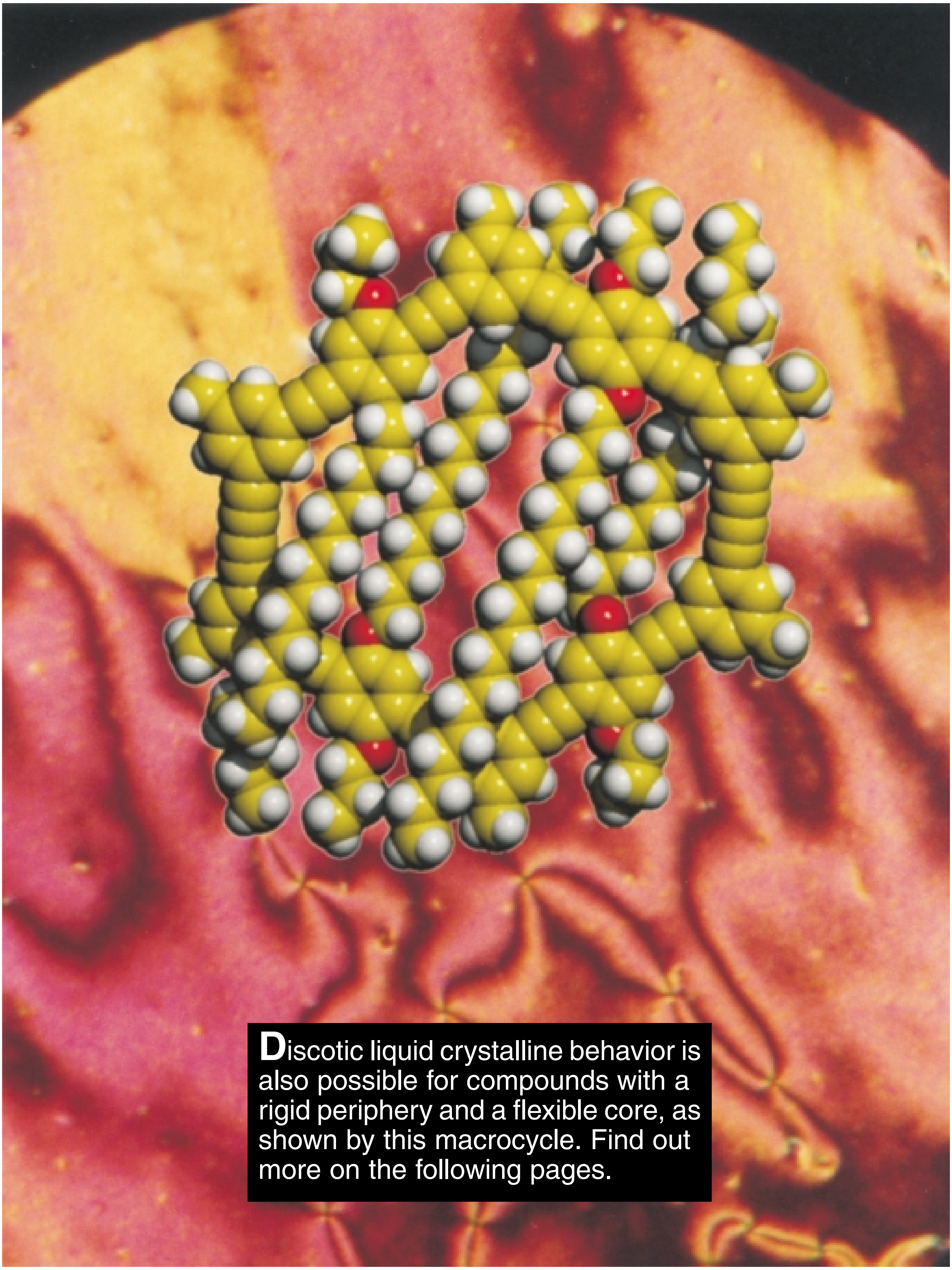


Discotic liquid crystalline behavior is also possible for compounds with a rigid periphery and a flexible core, as shown by this macrocycle. Find out more on the following pages.

Alkyl-Substituted Shape-Persistent Macrocycles: The First Discotic Liquid Crystal Composed of a Rigid Periphery and a Flexible Core**

Sigurd Höger,* Volker Enkelmann, Klaus Bonrad, and Carsten Tschierske

Dedicated to Professor Gerhard Wegner
on occasion of his 60th birthday

More than twenty years ago, Chandrasekhar et al. found that disklike molecules composed of a rigid core and flexible side chains pointing outward (discotics) could form columnar thermotropic mesophases (Figure 1 a).[1] Later columnar mesomorphism was also found for molecular architectures, which differ from those of classical discotics.[2] Macrocyclic compounds are of special interest in this context because the formation of channel structures should be possible if the backbone of the rings remains intact and is not collapsed.[3] This can be accomplished in flexible rings by the formation of host–guest complexes,[4, 5] whereas, shape-persistent rings are, per se, noncollapsed (Figure 1 b).

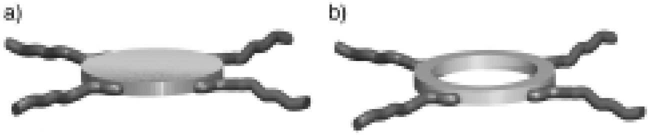
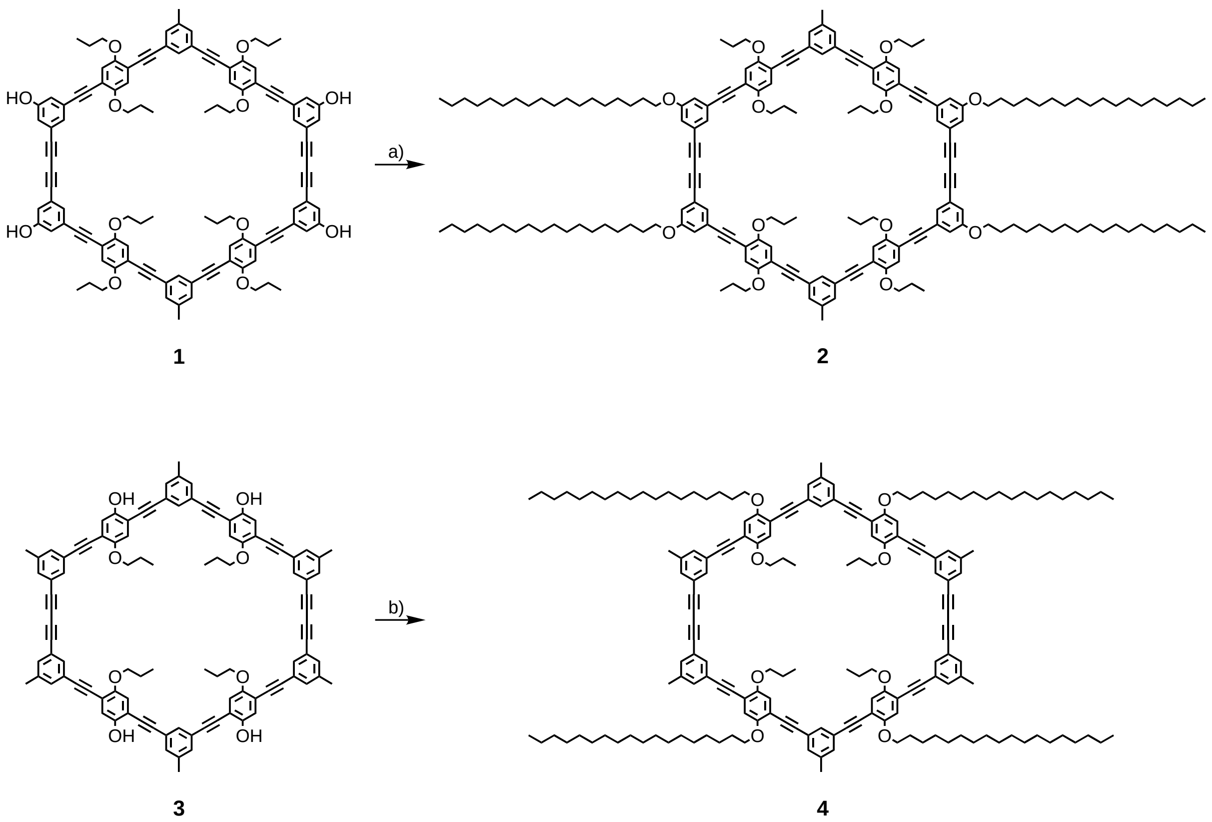


Figure 1. Design principle of disklike (a) and cyclic molecules (b) capable of forming thermotropic mesophases.

During our work on the synthesis and properties of shape-persistent macrocyclic amphiphiles, we also investigated their nonpolar derivatives **2** and **4** (Scheme 1).[6] Compound **2** was prepared by base-catalyzed alkylation of the phenol **1** with 1-bromooctadecane. Efforts to prepare **4** under the same conditions starting from **3** were unsuccessful, we only obtained an intractable mixture of different products. However, alkylation of **3** with 1-octadecanol under Mitsunobu conditions gave **4** in good yields (Scheme 1).



1 **2** **3** **4**

Scheme 1. Synthesis of nonpolar amphiphile derivatives **2** and **4**. a) 1-bromooctadecane, K_2CO_3, DMF, 70 °C, 4 d (14 %); b) 1-octadecanol, diethylazodicarboxylate (DEAD), PPh_3, THF, room temperature, 4 h (63 %).

At first glance, both compounds contain the same macrocyclic backbone and differ only in the positions where the octadecyl chains are attached to the ring. Both **2** as well as **4** correlate with the principle design of thermotropic liquid crystals described above.[7] Contrary to our expectations, crossed-polarized microscopic investigations revealed that **2**

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melts isotropically at about 220 °C, and even with quenching we were not able to observe the appearance of a texture typical for a mesophase.[8] In sharp contrast, compound **4** exhibits liquid crystalline properties. The compound melts at 185 °C to form a mesophase ($\Delta H = 152.7\ \mathrm{kJ\,mol^{-1}}$) that becomes isotropic at 207 °C ($\Delta H = 0.73\ \mathrm{kJ\,mol^{-1}}$). The observed Schlieren texture suggests the formation of a nematic phase (Figure 2). This is consistent with observed reflections of the crystalline **4** that disappear above the transition temperature. Also we observe only a broad reflection at approximately 4.5 Å, typical for the scattering behavior of liquid or liquid crystalline paraffin chains.[9]

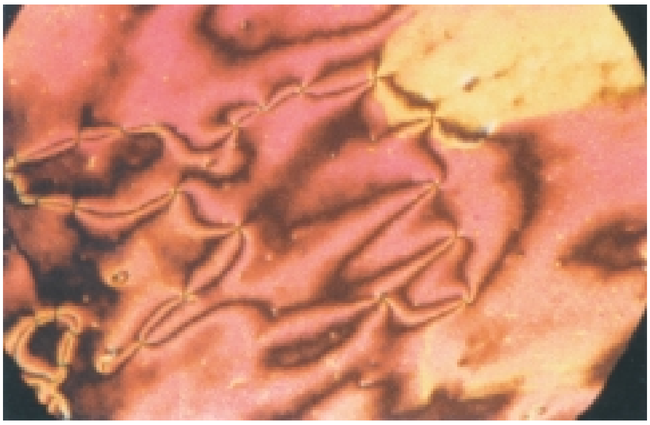

Figure 2. Texture of **4** at 200 °C viewed between crossed polarizers.

The significant difference in the thermic behavior of **2** and **4** can be explained by their different molecular architectures. It can be expected that in the solid state the interiors of the (nonsolvated) macrocycles are filled with alkyl chains. Since these point outward in **2** and backfolding is improbable for enthalpic and entropic reasons, it is expected that the interior of one ring is filled by the alkyl chains of neighboring rings. The interiors of the rings induce an interlocking of the molecules ("physical crosslinks"). According to the structural formulas in Scheme 1, one should expect a similar behavior for **4**. However, single-crystal X-ray analysis shows that in **4** there is an intramolecular interaction between the rings and the alkyl chains, by which each molecule fills its cavity with its *own* side chains (Figure 3 a).[10] In this case the molecules become mobile when the alkyl chains melt and can form the liquid crystalline phase by parallel arrangement. Owing to network formation, the mechanical coupling of the rings of **2** does not breakdown before it is completely molten.[11]

It should be pointed out that **4** is not completely planar in the solid state. Therefore the alkyl chains are not arranged in one plane but are located alternately above and below the plane of view. Together with the chains of neighboring rings, they form a dense packing (Figure 3 b). The lattice parameters of the alkyl chain subcell are $a = 4.22$, $b = 4.66$, $c = 2.56$ Å, $\alpha = 87.5$, $\beta = 108.4$, $\gamma = 105.2°$.[12] These correlate well with those of the triclinic structure of polyethylene ($a = 4.26$, $b = 4.46$, $c = 2.55$ Å, $\alpha = 90$, $\beta = 107$, $\gamma = 101°$) and show that the side chains can adopt a low-energy packing independent of the cyclic backbone.[13] This side chain packing also separates adjacent rings and prevents intermolecular interactions of the atoms in the aromatic framework.

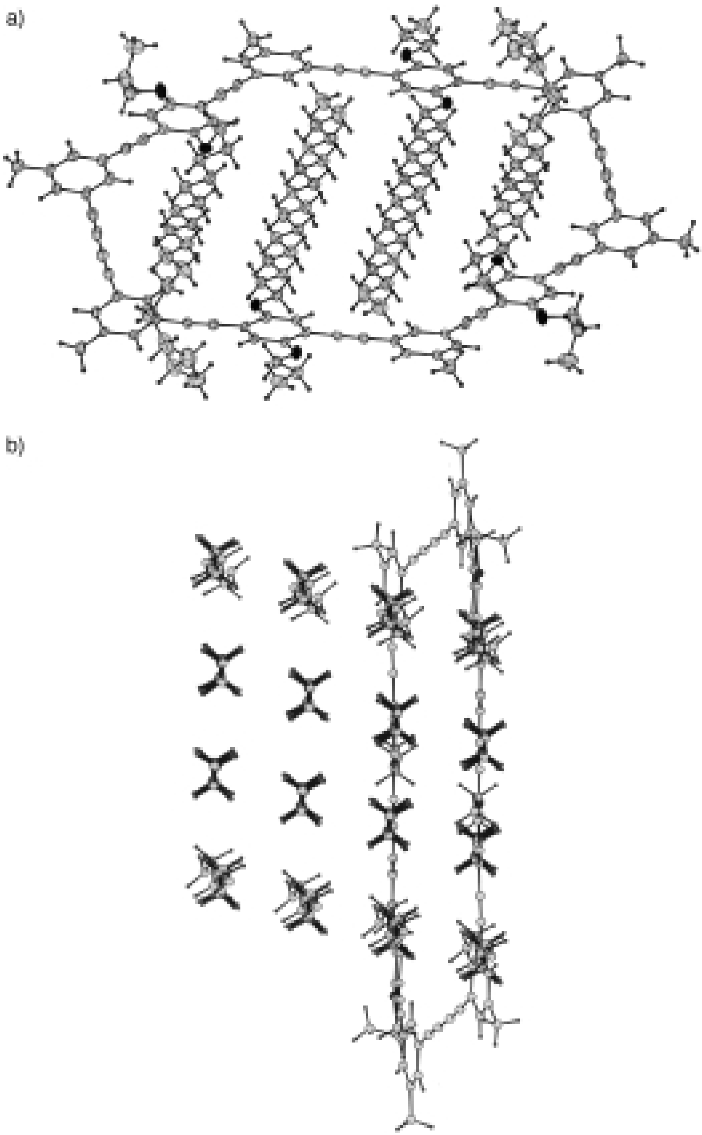

Figure 3. Top: Structure of **4** in the crystal. Projection along *a*. Bottom: View of the alkyl chain packing. For clarity, only one macrocycle is shown.

Unlike **2**, the interior of **4** is filled intramolecularly with its own alkyl chains, and does not act as a crosslinker. It should be pointed out that this has its origin in the ability of the central arene units of the rings to rotate freely, as we have shown earlier.[14] Notable is the fact that the liquid crystalline macrocycle **4** has a topology that is opposite to all discotics described so far: a rigid ring acts as a framework for flexible side groups pointing to the *inside* (Figure 4).[15]

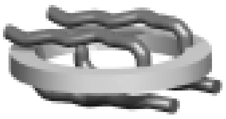

Figure 4. Schematic representation of the arrangement of the alkyl chains in **4**.

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[7] One of the basic conditions for the formation of columnar liquid crystalline phases is an optimal coverage of the periphery of the central core by lateral chains (B. Kohnke, K. Praefke, *Chem. Z.* **1985**, *109*, 121). Owing to the size of our rigid structure and the attachment of only four octadecyloxy groups, the appearance of such a mesophase is improbable.

[8] When **2** is heated for a longer period above 220 °C, a temperature well above the clearing point of **4**, we cannot eliminate the possibility of partial decomposition.

[9] The exact type of the nematic phase (e.g., nematic discotic, nematic-columnar, etc.) could not be determined yet.

[10] Crystals of **4** were grown from a CH_2Cl_2 solution by slow evaporation. Crystal structure data for **4**: $C_{174}H_{220}O_8$, triclinic, space group $P\bar{1}$, $a = 9.729(4)$ $b = 16.124(4)$ $c = 24.746(7)$ Å, $\alpha = 106.248(21)$, $\beta = 98.083(29)$, $\gamma = 89.741(20)$ °, $V = 3687.6$ Å^3, $\rho_{calcd} = 1.069$ g cm^{-3}, $\mu = 4.633$ cm^{-1}, $T = 165$ K. Nonius CAD4 diffractometer, graphite-monochromated $Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å, $\theta/2\theta$ scans, 5958 independent reflections, of which 3028 were observed ($I > 3\sigma(I)$), empirical absorption correction. The structure was solved by direct methods (Shelxs) and refined by full-matrix least-squares analyses on F with anisotropic temperature factors for C an O. The hydrogen atoms were refined with fixed isotropic temperature factors in the riding mode. The refinement converged at $R = 0.0569$ and $R_w = 0.0571$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139443. 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).

[11] Nematic and smectic phases can be also observed for some other alkylated shape-persistent macrocycles, for example, a) C. C. Ling, R. Darcy, W. Risse, *J. Chem. Soc. Chem. Commun.* **1993**, 438; b) N. Usol'tseva, K. Praefcke, D. Singer, B. Gündogan, *Liq. Cryst.* **1994**, *16*, 601. However, in all those cases, the interior of the rings is much smaller, such that a complete intraannular arrangement of the side chains can be excluded.

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[15] The investigation of the conformation of **4** in the melt as well as the extension of this concept to macrocycles with a fixed intraannular arrangement of the flexible side groups is part of our current studies.

De Novo Prediction of Inorganic Structures Developed through Automated Assembly of Secondary Building Units (AASBU Method)**

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Alan M. Gorman, Clive M. Freeman, and
Gérard Férey*

Simulations of the crystal structures and of the properties of solids are topical and were recognized early in materials science as a challenging task. Several computational approaches to predicting crystal structures have been described, such as:

1) Local optimization of approximate, preconstructed models by potential or first principles methods.[1, 2]
2) Monte Carlo or genetic algorithm based sampling of packing arrangements of molecular crystals.[3]
3) Assembly of atoms or ions assuming unit cell and symmetry by, for example, simulated annealing[4–9] or a genetic algorithm.[10]
4) Operations for combining two-dimensional periodic sheets.[11]
5) Enumeration of framework structures[12–14] given defined symmetry and connectivity constraints.[15]

The motivation for these efforts is to aid the often difficult process of crystal structure determination, to help rationalize different but related structure types, or to help limit the domain of structures that are possible to a given system.[5] In certain cases, combination with other desired structural attributes, for example microporosity, can allow these structure prediction methods to be applied in a genuine design sense.

In general, we lack an ability to develop viable synthesis routes based solely on a knowledge of the crystal structure. Inspired by molecular chemistry, for which rational synthesis routes are almost invariably developed, it is interesting to consider how rational approaches might be developed for the synthesis of inorganic structures, for example, zeolites[16, 17] or larger pore materials.[18–21] The desire to develop virtual libraries that might be accessible by rational synthesis is made more pressing by the recent emergence of combinatorial and high-throughput experimentation approaches to inorganic chemistry (see [22, 23] and references therein).

The prediction of periodic inorganic structures is a difficult task involving many degrees of freedom, which are related to the chemical and structural diversity of inorganic structures.

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