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STRUCTURE-DEPENDENT AND MORPHOLOGY-DEPENDENT EXCHANGE OF GUESTS IN PERMEABLE MOLECULAR CRYSTALS

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ABSTRACT: Our understanding of the properties of porous crystalline materials is largely based on studies of zeolites and other inorganic substances. The advent of new analogues, including purely molecular networks, has created opportunities to base knowledge of porous materials on a broader foundation. We have used permeable molecular crystals of tetrakis(3,5-dihydroxyphenyl)silane **(1)** to show how the exchange of guests depends on both structure and morphology. Specifically, exchange is faster in polymorphs with wider channels and in crystalline morphologies with well-developed faces that cut the channels.

Key words: Crystal engineering**,** porous molecular networks, guests exchange, polymorphism, hydrogen bond.

RESUME: Notre compréhension des propriétés des matériaux cristallins poreux est en grande partie basée sur des études des zéolites et d'autres substances inorganiques. L'arrivée de nouveaux analogues, y compris les réseaux purement moléculaires, a permis une meilleure connaissance des matériaux poreux. Nous avons employé les cristaux moléculaires perméables du tétrakis(3,5-dihydroxyphenyl)silane **(1)** pour montrer comment l'échange des molécules invitées dépend de la structure et de la morphologie. Spécifiquement, l'échange est plus rapide dans les polymorphes avec des canaux plus larges et dans des morphologies cristallines avec des faces bien développées qui coupent les canaux.

Mots clés: Ingénuerie des cristaux, réseaux moléculaires poreux, échange de molécules invitées, polymorphisme, pont hydrogène.

INTRODUCTION:

Porous crystalline materials are widely used in science and technology for separation, catalysis, and storage [1]. In these applications, potential guests enter the porous host selectively and then diffuse along well-defined channels. The flux of guests entering a single crystal of a porous host is expected to be proportional to its surface area [2]. More particularly, the flux should depend on the area of crystal faces that cut across channels. For example, in a hypothetical square prism of length a and sides b that incorporates parallel channels perpendicular to the basal faces (Figure 1), the flux of guests will be proportional to $2b^2$. In contrast, the flux will be proportional to $2ab$ if a crystal of the same dimensions now has similar channels perpendicular to a pair of prism faces. In the second crystal, the flux will be increased by a factor equal to the aspect ratio a/b. When permeable crystals can adopt two widely different prismatic morphologies, with the openings of channels exposed on basal faces that are either exceedingly small (as in needles) or highly prominent (as in plates), then the flux can differ by several orders of magnitude in crystals of similar size.

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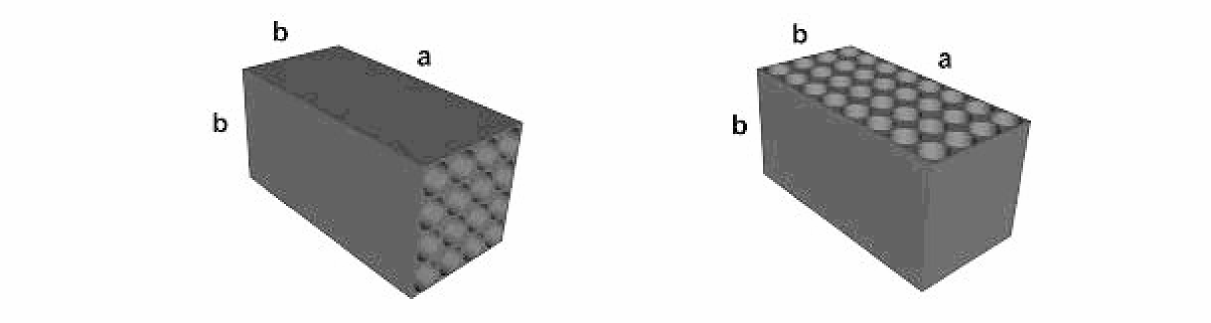
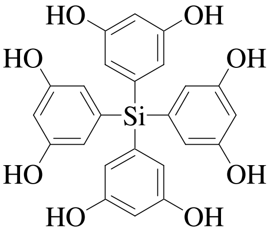


Figure 1: Hypothetical square prismatic morphologies of a permeable molecular crystal with length *a* and sides *b*, showing channels aligned with the long axis (left) or perpendicular to it (right).

Surprisingly, such correlations of structure, morphology, and exchange do not appear to have been studied systematically [3]. In part, this reflects the difficulty of obtaining single crystals of classical porous materials, such as zeolites, in multiple forms suitable for comparing diffusivities [4]. In contrast, polymorphism is ubiquitous among molecular crystals [5], single crystals can often be grown routinely, and additives have been used extensively to control morphology [6]. Moreover, new strategies make it possible to engineer molecular crystals with permeabilities that rival those of zeolites and related inorganic materials [7, 8]. Prolific sources of such crystals are specially designed molecules that associate with multiple neighbors by forming strong directional interactions. These molecules, which have been called tectons from the Greek word for builder [9], tend to crystallize according to directional preferences to form porous networks rather than normal close-packed structures [10]. In favorable cases, large fractions of the volumes of the resulting crystals (up to 75%) can be used to include guests, and the guests can be exchanged selectively in single crystals without loss of crystallinity [7]. Molecular tectonics, when combined with a broad survey of conditions of crystallization, is therefore a powerful tool for producing permeable crystals in diverse forms.

RESULTS AND DISCUSSION:

We have used the strategy of molecular tectonics to establish that exchange depends on structure and morphology. Crystals of tetrakis(3,5-dihydroxyphenyl)silane **(1)** are known to consist of diamondoid hydrogen-bonded networks [11], and two pseudopolymorphic forms with submaximal three-fold interpenetration have been observed.



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The structure of Form I can be represented by a repeating TTTSS pattern of interpenetrated diamondoid topologies (Figure 2), three composed of tetraresorcinol **(1)** (T) and two in which missing tectons are replaced by included solvent (S). In Form II, a TTSTS pattern of interpenetration is observed.

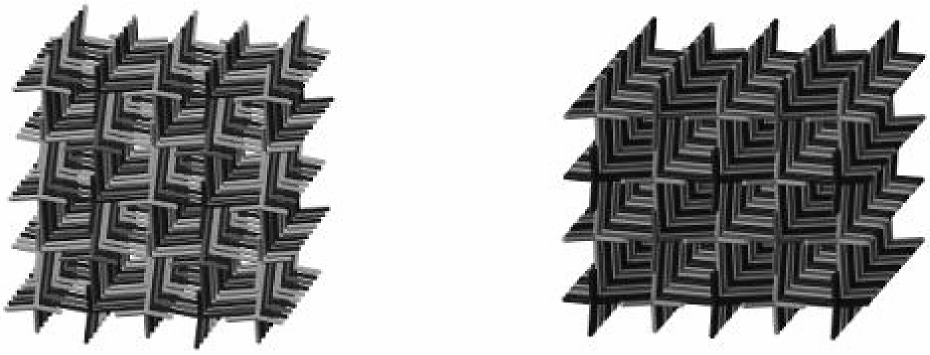


Figure 2: Representations of the structures of crystals of tetraresorcinol **(1)** in Form I (left) and Form II (right). Diamondoid networks built from compound **(1)** are shown in gray and black (symmetry-independent or symmetry-equivalent), and volumes of diamondoid topology occupied by solvent are shown in light-gray.

Figure 3 shows optical micrographs of typical crystals of Form II, which can be obtained as needles (Form IIa) and as lozenges (Form IIb) by crystallization from hexane/THF and hexane/THF/ethyl acetate, respectively.

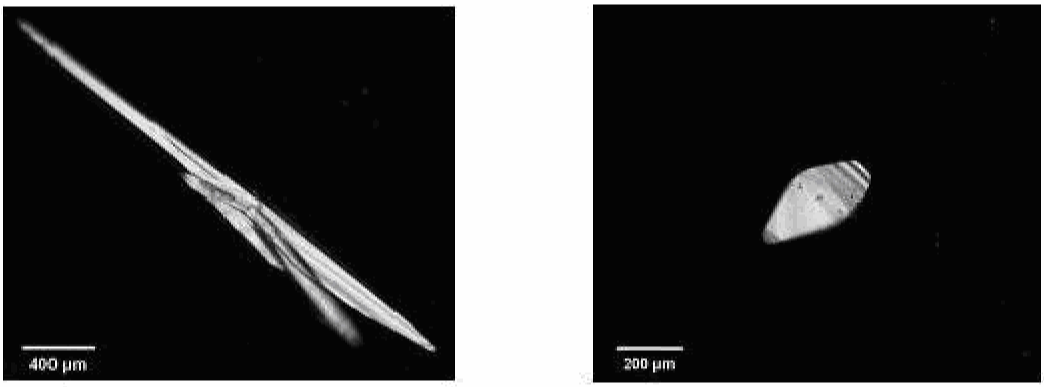
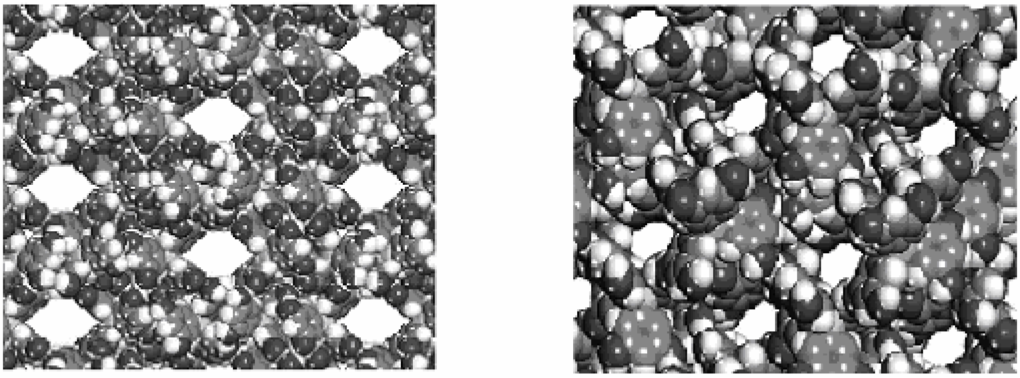


Figure 3: Optical micrographs of crystals of tetraresorcinol **(1)** in Forms IIa (left) and IIb (right). In both, the long axis is aligned with *c*.

In Form I, the volumes occupied by solvent merge to create a single three-dimensional system of interconnected channels with a diamondoid topology. Approximately 45% of the volume of the crystals is accessible to guests, and the cross sections of the channels are approximately 9 x 6 Å^2 in the *a* and *b* directions and negligible in the *c* direction. In contrast, Form II has non-adjacent volumes occupied by solvent, thereby creating two independent interpenetrated systems



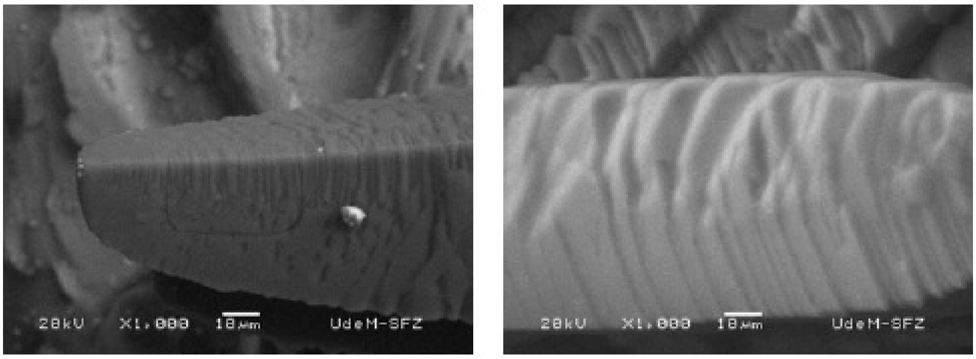
a **b**

Figure 4: Channels in permeable crystals of tetraresorcinol **(1)** in Form I, viewed along the a or b axes (Figure 4a), and in Form II, viewed along the abc diagonal (Figure 4b). In both views, guests are omitted. Atoms of hydrogen appear in white, carbon in gray, oxygen in dark-gray, and silicon in light-gray.

of channels, each with diamondoid topology. Approximately 52% of the volume of the crystals is accessible to guests, and the cross sections of channels are largest 4 x 3 $Å^2$ along the *abc* diagonal. As a result, channels in Form II cut by a given surface are more numerous but smaller than those in Form I (Figures 4a and 4b).

Diffusion of typical guests in either Form II should therefore be significantly slower than in Form I, and the mechanism may change from single-file diffusion in Form II to more efficient counter-current processes in Form I. Qualitative confirmation was obtained by taking single crystals of Form I (S = ethyl acetate) and Form IIa (S = THF) of similar volume and exposing them to mixtures of hexane/THF and hexane/ethyl acetate, respectively, at 25 °C for 12 h. Under these conditions, exchange was complete in Form I but negligible in Form IIa. Further evidence of different rates was obtained by removing crystals from their mother liquors and exposing them to air, which led to more rapid loss of guests and crystallinity in the case of Form I than in the case of crystals of Form II.

The widely different rates suggest that exchange or loss of guests in such molecular crystals occurs by diffusion within well-defined channels, much as it is considered to take place in porous inorganic analogues. Scrutiny of crystals by electron microscopy showed no gross fractures or highly irregular surfaces that might offer alternative explanations of the different rates of exchange or loss of guests (Figure 5).



a **b**

Figure 5: Low-vacuum scanning electron micrographs of crystals of tetraresorcinol **(1)** in Form IIa (Figure 5a) and Form IIb (Figure 5b).

This is noteworthy because molecular crystals are inherently less robust. Forms I and II would not show different rates if exchange depended primarily on defects, recrystallization, or other processes involving extensive molecular movement. These conclusions are reinforced by the following independent evidence of the structural integrity of porous molecular networks: 1) Diffusion is not isotropic but occurs preferentially in directions aligned with channels [12]; and 2) exchange can produce metastable phases that retain the architecture of the original crystals [13].

Unexpectedly, exchange in Form II is morphology-dependent. Needles containing THF (Form IIa, Figure 3) underwent negligible exchange under the standard conditions (exposure to hexane/ethyl acetate at 25 °C for 24 h), whereas lozenges (Form IIb, Figure 3) exchanged slowly but completely. Indexation of the crystals established that the long axis of the needles and lozenges is aligned with *c*, so the most porous faces are extremely small in Form IIa but well-developed in Form IIb (Figure 6).

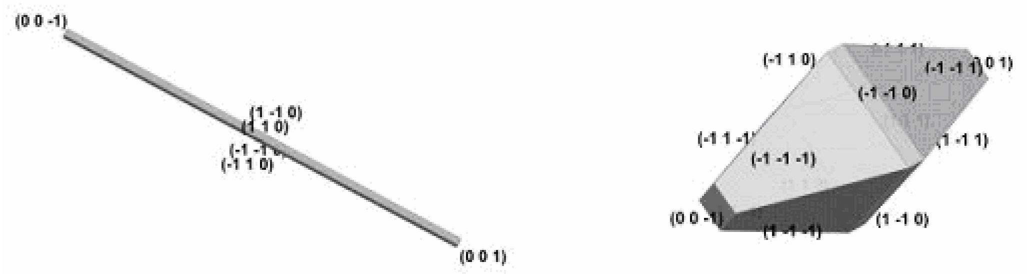


Figure 6: Drawings of idealized crystals of tetraresorcinol **(1)** in Forms IIa (left) and IIb (right).

The distinctly different rates of exchange observed in crystals of similar size (Form I > Form IIb > Form IIa) show that the permeability depends not only on the internal structure and the diameter of channels, but also on the relative size of faces that cut the channels. This phenomenon has not been taken into account in previous studies of exchange in porous crystalline materials of any type, and it may help account for wide discrepancies in quantitative analyses of diffusivity [2].

CONCLUSION:

Zeolites and related porous inorganic materials have been studied for many decades, whereas the systematic exploration of molecular analogues has just begun. Initial studies of these analogues have tended to follow paths established by pioneers in the study of zeolites, and the potential of permeable molecular crystals to provide the field of porous materials with leading insights has not been obvious. By establishing how structure, morphology, and exchange are related in permeable molecular crystals, the present work offers deeper understanding of all types of porous materials.

EXPERIMENTAL SECTION:

Crystals were grown by allowing hexane to diffuse slowly at 25 °C into solutions of tetraresorcinol **(1)** in ethyl acetate, THF, or in an equal mixture of ethyl acetate and THF containing approximately 10 mg/mL. Exchange of guests was shown to be complete (≥95%) or negligible (≤5%) by ^{1}H NMR spectroscopy of dissolved samples. Retention of crystallinity in exchanged samples was confirmed by X-ray powder diffraction. The percentage of volume in crystals that is accessible to guests was estimated by the PLATON program [14, 15]. The shapes of crystals were drawn using the program WinXMorph [16]. Scanning electron micrographs were recorded using a low-vacuum JSM-6460LV instrument equipped with a backscattered electron detector. Crystals were taken directly from their mother liquors and deposited on conductive stubs with carbon adhesive tape, and images were recorded at 20 kV under a pressure of approximately 25 Pa.

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