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Microporous and mesoporous electronic materials: flexible open-framework nanomaterials for molecular recognition, towards the electronic nose

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A novel class of flexible open-framework microporous tin(IV) chalcogenide electronic materials is described, whose structure-property relationships are sensitive to the identity and loading of the imbibed molecular guests. The discovery of these materials could represent an important step towards the practical realization of an abiological electronic nose. The inorganic character of their open-framework structures and the compositional tunability of their electronic band structures, makes these molecular recognition host-guest inclusion electronic materials, potentially integratable into transistor and diode array-type chemoselective devices. The research briefly described in this paper, demonstrates that certain key elements, considered to be central to the development of molecule discriminating sensors, have now been brought to practice with the nanoporous tin(IV) chalcogenide class of materials. A natural extension of this work has led to the discovery of novel mesoporous forms of these materials.

INTRODUCTION

Although the biochemical, molecular biological, neurophysiological and perceptual details of smell are not fully understood, the simplest picture of this remarkable olfactory sensory system is one of molecular recognition, in which one or more kinds of protein-based receptor sites, respond selectively to the binding of specific molecules and subsequently transmit a diagnostic electrical signal to particular locations in the brain.[1] This sensory system is extraordinarily sensitive and versatile. It is able to reproducibly distinguish mixtures of both complex and simple molecules, it can regenerate and it can have a working lifetime of up to a hundred years. Not surprisingly, many ingenious chemical and biochemical sensors have been devised over the past 20 years or so, designed to mimic the sensory action of the human nose. In this context it is interesting that no device currently exists that even begins to approach the full performance characteristics and specifications of the human nose. With this accumulated knowledge, how would one now go about the challenge of discovering and building the perfect abiological electronic nose?

Towards Molecule Discriminating Devices

By taking lessons from zeolite synthesis methodology, it has recently proven feasible to employ organic templates to organize and interconnect simple molecular "Lego-type" metal chalcogenide building-blocks, into architecturally exquisite, crystalline microporous metal chalcogenides.[2] Thus, familiar kinds of metal chalcogenide bulk semiconductors can now be chemically synthesized, from the "atom-up", in new forms that are decorated with periodic arrays of molecular dimensionality pores. These novel kinds of nanoporous electronic materials are expected to display properties that are unique compared to those of the bulk and nanocluster forms of the material. By analogy with zeolite and molecular sieve materials, renown for their use in shape-selective catalysis and molecule separation applications,[3] it is expected that crystalline nanoporous electronic materials could find potential device oriented applications, for example, as molecule discriminating transistors and light emitting diodes,[4] of the type illustrated in **Figure 1**. These thin

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Dedicated to Dr. Edith Flanigen in celebration of her 65th birthday and in recognition of her pioneering efforts with this new class of nanomaterials, as well as the continued encouragement and support of this research.

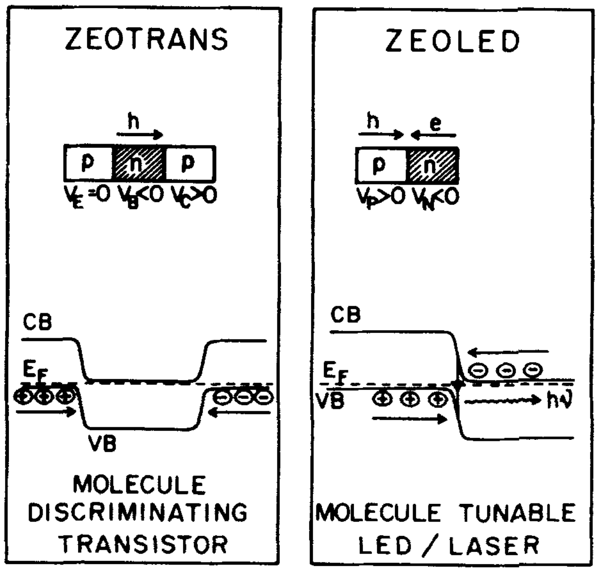


Figure 1 Proposed designs for a molecule discriminating **pnp**-transistor and a **pn**-light emitting diode.[4]

film **pnp**- and **pn**-junction geometries, incorporate a doped microporous semiconductor as the chemoselective sensing element. Only molecules of the correct size, shape and polarity can be adsorbed into the nanoporous semiconductor region of the device and perturb the electronic band structure, to cause for instance, switching action of the transistor, or shifting of the frequency of the emitted light for the diode. Other exploitable types of transducer action for these microporous electronic materials include adsorbate induced capacitance and mass changes. A neural network array of such devices, each with a different composition and/or pore size/shape sensing element, would produce a characteristic pattern of electrical or optical responses, that could be used to recognise the component molecules of a gaseous mixture. This represents a novel approach to the practical realization of an electronic nose. In what follows, I will describe some of our recent research aimed towards achieving this challenging goal involving novel micro- and mesoporous forms of tin sulfide.

Synthesis and Structure Characterization of Microporous Tin(IV) Chalcogenides

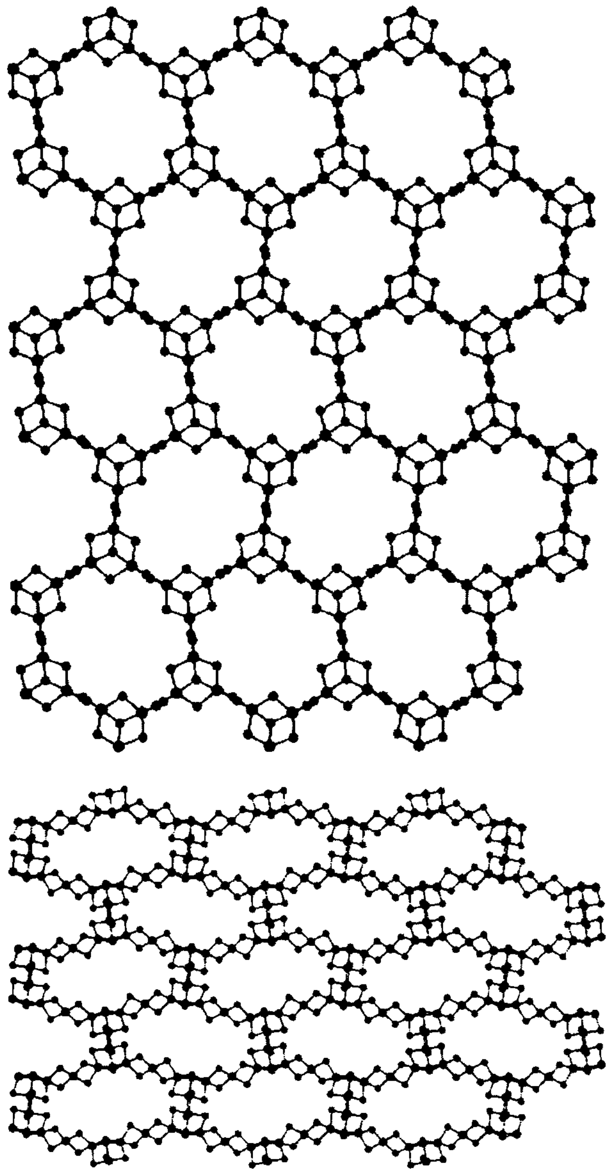


Figure 2 Single crystal XRD structural projections, viewed orthogonally to a single microporous layer, of (A) TEA-SnS-1 and (B) TPA-SnS-3.[6] (See Color Plate XVII.)

A new class of crystalline microporous tin(IV) chalcogenides has been synthesized by organic template mediated hydrothermal synthesis using both SnX_2 and Sn/X source materials, where X=S, Se.[5] These materials are denoted R-SnX-n, where R refers to the occluded template (usually, but not necessarily an amine, or a quaternary alkylammonium cation) and n refers to the particular structure type. In this presentation, I will briefly focus attention on structure types R-SnX-1 and R-SnX-3. In **Figure 2**, pertinent single crystal XRD structural information is shown for TEA-SnS-1 and TPA-SnS-3,[6] where TEA = Et_4N^+ and TPA = $^nPr_4N^+$. Both materials are composed of parallel stacked microporous layers, which are planar in the case of TEA-SnS-1 and corrugated (undulating) for TPA-SnS-3. Recall, that the bulk tin(IV) chalcogenides are built of parallel stacked planar dense layers based on octahedrally coordinated tin(IV) and trigonally coordinated S(-II).[7] The pore sizes and shapes in TEA-SnS-1 and TPA-SnS-3 are quite distinct, **Figure 2**. Note the ubiquitous presence of Sn_3S_4 broken-cube cluster building-blocks, that comprise the porous layers of these materials. When viewed orthogonally to the microporous layers of TEA-SnS-1 and TPA-SnS-3, a beautiful image of the hexagonal and elliptical-shaped, 24-atom ring tunnels and 36-atom ring tunnels respectively, can be observed, **Figure 3**. The organic cations lie between the layers and within the pores and their size, shape and location bears a resemblance to the overall structure and dimensions of the material, suggesting a templating function (space-filling, charge-balancing, structure-directing) for the Et_4N^+ and ${}^nPr_4N^+$ species, employed for the synthesis of these materials.[5,6]

Flexible Open-Frameworks

A remarkable property of these R-SnX-1 and R-SnX-3 materials, is the ability of their open-frameworks to undergo elastic deformations in response to the inclusion of different templates, and as we have very recently discovered, adsorbed molecular guests.[8] This interesting phenomenon was first unveiled in our single crystal XRD studies of TMA-SnS-1/TEA-SnS-1 and TPA-SnS-3/TBA-SnS-3 structure types, where TMA=Me_4N^+ and TBA=${}^nBu_4N^+$, **Figure 4**. Inspection of the porous layers in these R-SnS-1 and R-SnS-3 pairs, reveals that the layers can undergo what appear to be shear-type structural deformations that transforms the regular hexagonal and elliptical-shaped pores, respectively into distorted versions thereof. One finds intralayer and interlayer restructuring, involving alterations in pore size and shape, changes in interlayer distances and variations in layer stacking sequences. This presents some fascinating crystallographic challenges and some stimulating opportunities.[8]

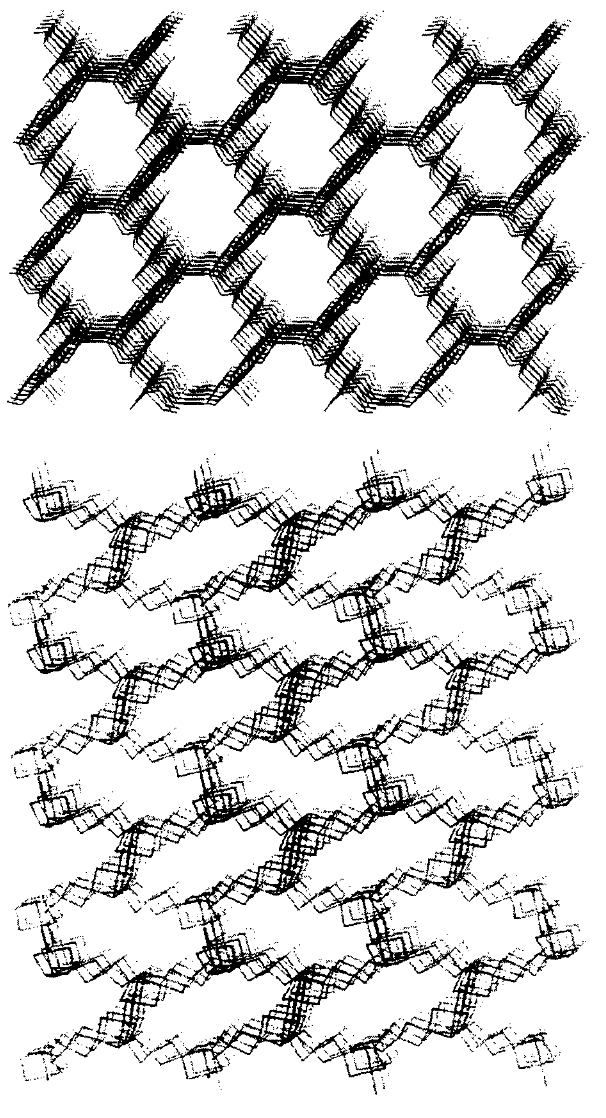


Figure 3 Single crystal XRD structural projections viewed down the (A) 24-atom ring hexagonal-shaped tunnels of TEA-SnS-1 and down the (B) 36-atom ring elliptical-shaped tunnels of TPA-SnS-3.[6] (See Color Plate XVIII.)

Small Molecule Adsorption

Elemental and thermogravimeric analyses of as-synthesized TEA-SnS-1 consistently show the presence of about $2H_2O$ molecules per formula unit of TEA-SnS-1.[9] Only one of these imbibed H_2O guests (denoted physisorbed) can be removed by evacuation of the material at room temperature. The desorption/adsorption process is reversible and shows a Type 1 isotherm,[2a] **Figure 5**. Similar adsorption isotherms are observed for CO_2 but Ar is excluded, showing that these types of materials have characteristics of layered molecular sieves, being able to discriminate between adsorbates differing by as little as 0.1Å in kinetic diameter.[2a] A key property discovered for TEA-SnS-1 is the extraordinary sensitivity of its structure to the adsorption of small molecule guests, such as, H_2O, H_2S, H_2Se.[9] For example, the monoclinic angle of its $P2_1/n$ unit cell can be continuously tuned anywhere between about 96° and 90°, on varying the loading of physisorbed water from zero to one per formula unit of TEA-SnS-1. This material functions as a humidity sensor, showing a structure that flexes differently for different seasons of the year! This "cameleon type behaviour" is conveniently monitored by *in situ* PXRD, paying particular attention to the $(101)/(\bar{1}01)$ monoclinic unit cell reflections, which are degenerate for $\beta=90°$ and non-degenerate for $\beta \neq 90°$, **Figure 6**. The interlayer d-spacing can be continuously tuned from about 9.289Å to 8.722Å, for $\beta=90°$ and $\beta=96°$, respectively. Concommitantly, the electrical conductivity changes by six orders of magnitude[9] and the optical absorption edge shifts by 25nm.[8] These kinds of reversible structural, electrical and optical transducer effects that accompany the adsorption of small polar molecules into TEA-SnS-1, in which the interlamellar space expands and the unit cell monoclinicity decreases upon adsorption, bodes well for the potential of these kinds of microporous electronic materials in molecule discriminating device applications.

Cooperative Reconstruction, Metamorphic Materials

A valuable insight into the details of the above types of structural metamorphoses, induced by the adsorption of molecular guests into microporous R-SnX-n materials,

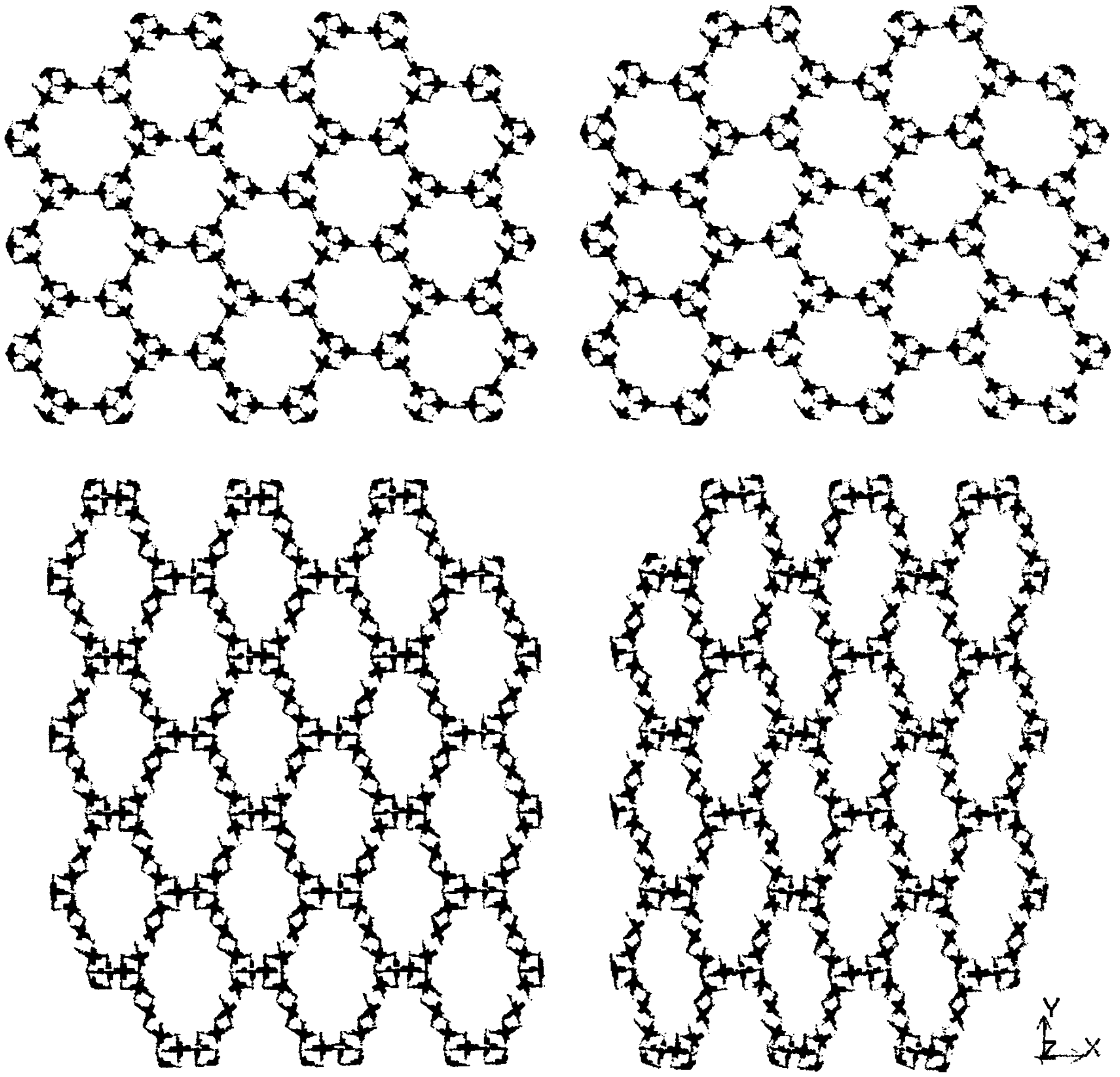


Figure 4 Single-crystal XRD structural representations of the shear-type elastic deformations observed for the microporous layers of tin(IV) sulfides (A) TMA-SnS-1 (B) TEA-SnS-1 (C) TPA-SnS-3, (D) TBA-SnS-3.[8] (See Color Plate XIX.)

has recently emerged from two single crystal XRD studies of TMA-SnSe-1 which have been synthesized containing either $3H_2O$ or $2H_2O$ molecules in a hexagonal pore, **Figure 1**.[8] The former material is orthorhombic **$P2_12_12_1$** with unit cell dimensions **a**=13.675Å, **b**=16.062Å, c=24.067Å. The latter material is monoclinic, **C2/m** with unit cell dimensions **a**=21.175Å, **b**=13.640Å, c=9.500Å, β=106.30Å. In the orthorhombic form the $3H_2O$ molecules appear to form a hydrogen-bonded cluster, whereas in the monoclinic structure, the $2H_2O$ molecules are separate and discrete. The TMA^+ cations within the pores and between the layers, occupy quite distinct locations in the orthorhombic and monoclinic unit cells of TMA-SnSe-1. The most spectacular structural feature of this system concerns the cooperative reconstruction of the nanoporous layers, the TMA^+ cations and the imbibed H_2O molecules, following the removal of just a **single** H_2O molecule from the pores of the orthorhombic TMA-SnSe-1 material to form monoclinic TMA-SnSe-1, **Figure 7**. Clearly the open-framework and its occluded guests are intimately, precisely and delicately interlocked through what appears to be hydrogen-bonding and van der Waals types of interactions. A small change in the loading or identity of the guest, can cause what amounts to a massive change in the internal structure of the entire host-guest inclusion system (that is, characteristics of an inorganic enzyme mimic), with concomitant alterations in the electronic

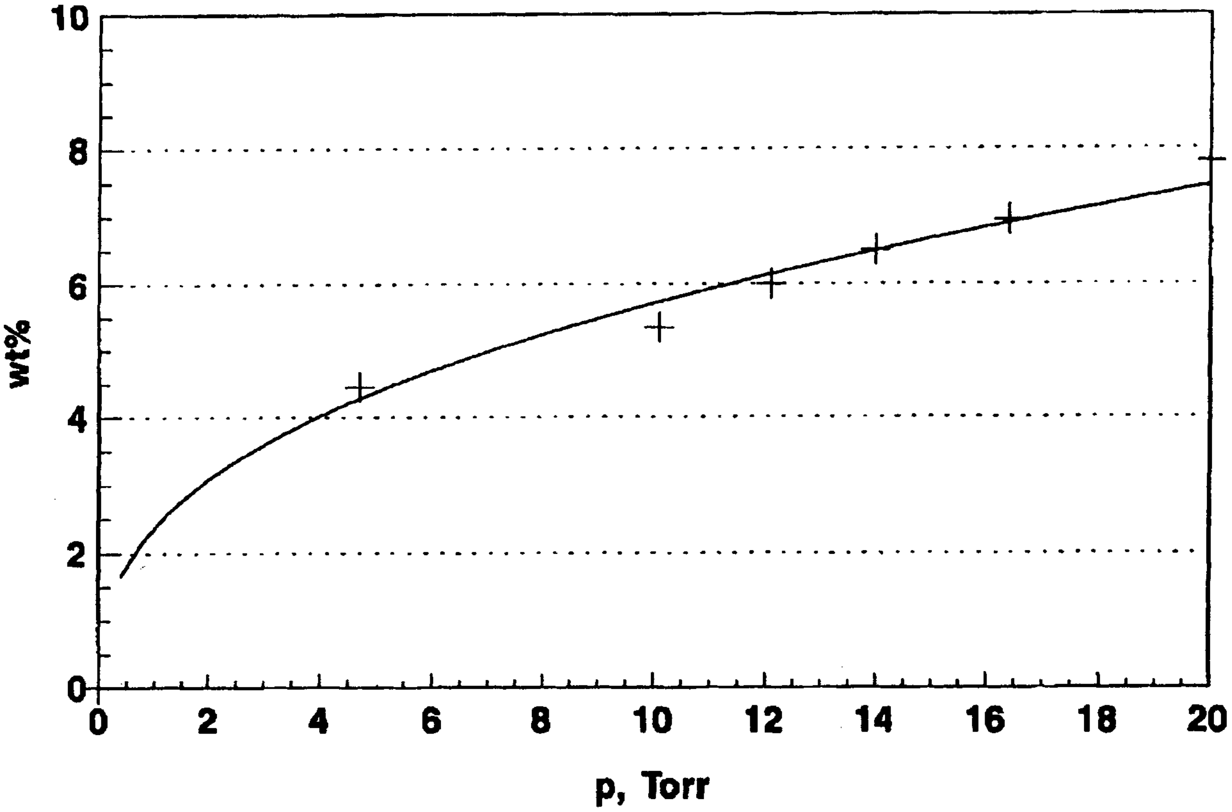


Figure 5 Type 1 adsorption isotherm observed for H_2O in R-SnS-1 type materials.[2a]

band structure of the material. For instance, the orthorhombic to monoclinic transition of TMA-SnSe-1 is accompanied by a roughly 25 nm red-shift of the absorption edge of the material.[8] Analogous sensitivities of the absorption edges of the R-SnX-n materials have been observed on changing the identity of the template R, the chalcogenide (for example, the ternary microporous tin(IV) thioselenides, TMA-SnS_xSe_{1-x}-1, where $0 \leq x \leq 1$), the structure type n, and the loading of an adsorbed molecular guest.[8,10]

Probing the Adsorption Process

The adsorption of molecular guests into TEA-SnS-1 can also be conveniently monitored by *in situ* Mid-IR spectroscopy of self-supporting wafers of the material.[9] Beginning with TEA-SnS-1$(H_2O)_c(H_2O)_p$ one observes the νOH stretching modes of physisorbed water $(H_2O)_p$ at about 3564, 3484 cm^{-1} with those of what is believed to be best described as chemisorbed water $(H_2O)_c$ between 2900-2300 cm^{-1}, **Figure 8**. The respective δOH deformation modes are clearly apparent at 1619, 1564 cm^{-1}. Evacuation of this sample at room temperature preferentially removes $(H_2O)_p$ as seen by inspection of **Figure 8**. The process is reversible and can be recycled indefinitely, **Figure 8**. The Et_4N^+ νCH, νCN, δCH, δCN diagnostic modes, remain essentially invariant to the $(H_2O)_p$ adsorption/desorption process, **Figure 8**. The ability to control and monitor the adsorption of other molecular guests, like H_2S and H_2Se, in TEA-SnS-1, is demonstrated in **Figure 8**. Again these adsorption events of H_2S and H_2Se are reversible and reproducible, **Figure 8**. Incidently, the identification of $(H_2O)_c$ in the TEA-SnS-1 structure is effectively established through D_2O exchange experiments, **Figure 9**. For a sample containing mainly $(D_2O)_c$ one finds that the manifold of $(H_2O)_c$ IR νOH bands at 2900-2300 cm^{-1} all show the expected deuterium isotope shift to about 2300-1800 cm^{-1} for the νOD bands of $(D_2O)_c$. The bathochromic shift of the νOH bands on passing from $(H_2O)_p$ to $(H_2O)_c$ is expected for a hydrogen-bonded chemisorbed form of $(H_2O)_c$ compared to that of the essentially molecular physisorbed form $(H_2O)_p$. Consistent with this proposed difference in the strength of adsorption of $(H_2O)_p$ and $(H_2O)_c$ is the observation that the former can be removed from TEA-SnS-1 by evacuation at RT, whereas the latter requires about 210–350°C.[9] A structural model for the $(H_2O)_c$ guests, involves strong hydrogen-bonding to the sulfur framework. These interactions play a key role in the thermal properties of the materials in the temperature range of 200–600°C, the details of which have been recently reported.[9]

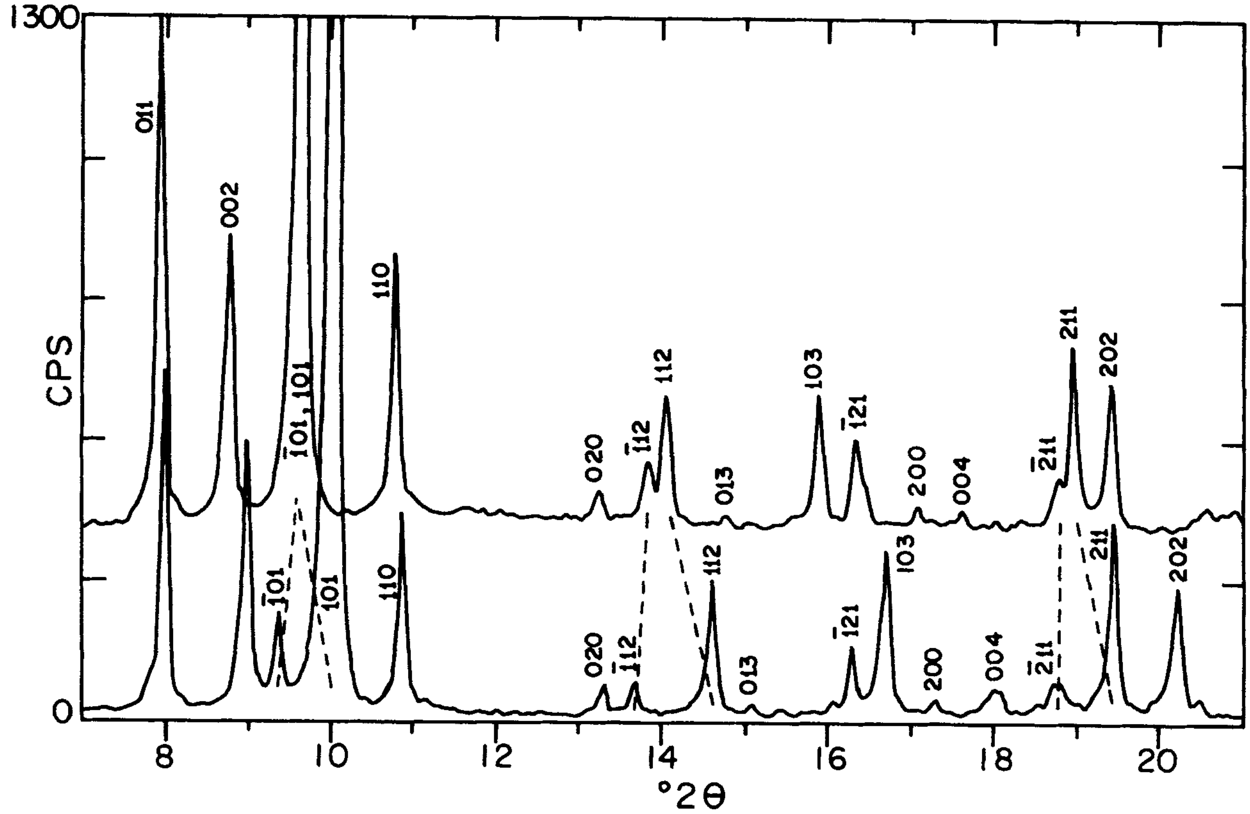


Figure 6 *In situ* PXRD patterns showing the sensitivity of the TEA-SnS-1 structure to the adsorption-desorption of H_2O molecular guests.[9]

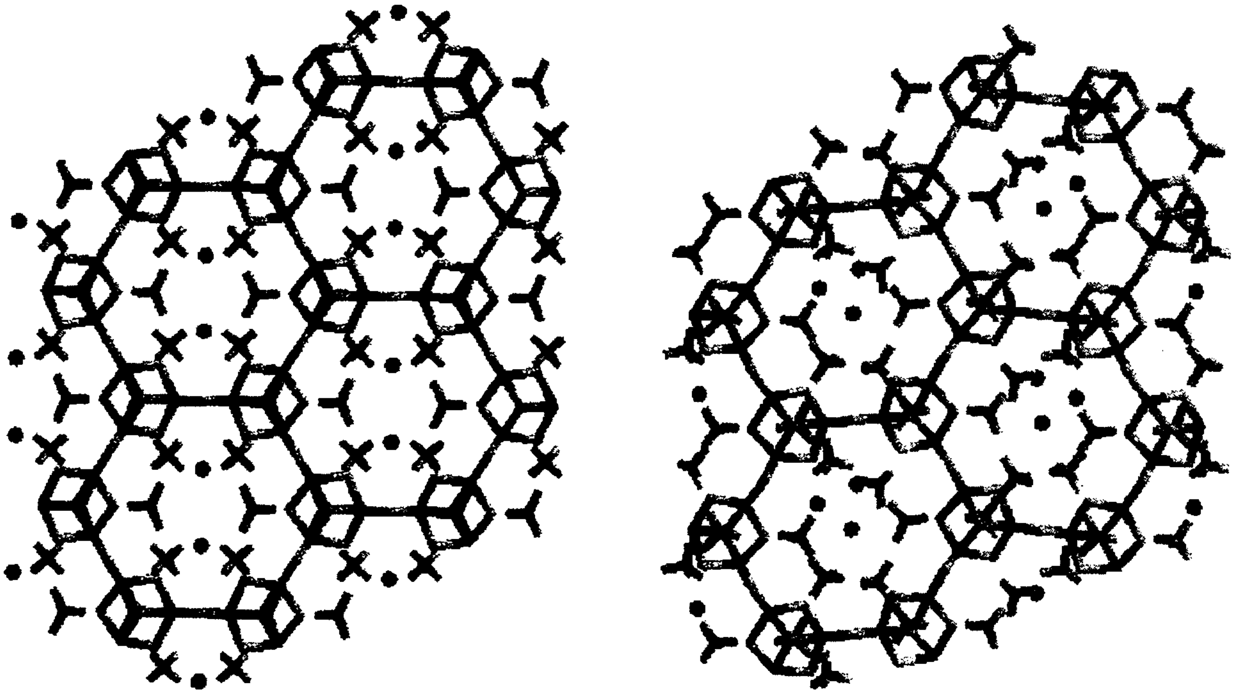


Figure 7 Single crystal XRD study of the cooperative reconstruction observed for the TMA-SnSe-1 metamorphic structure, on changing the number of H_2O molecular guests in a pore from three to two, (A) orthorhombic form (B) monoclinic form.[8] (See Color Plate XX.)

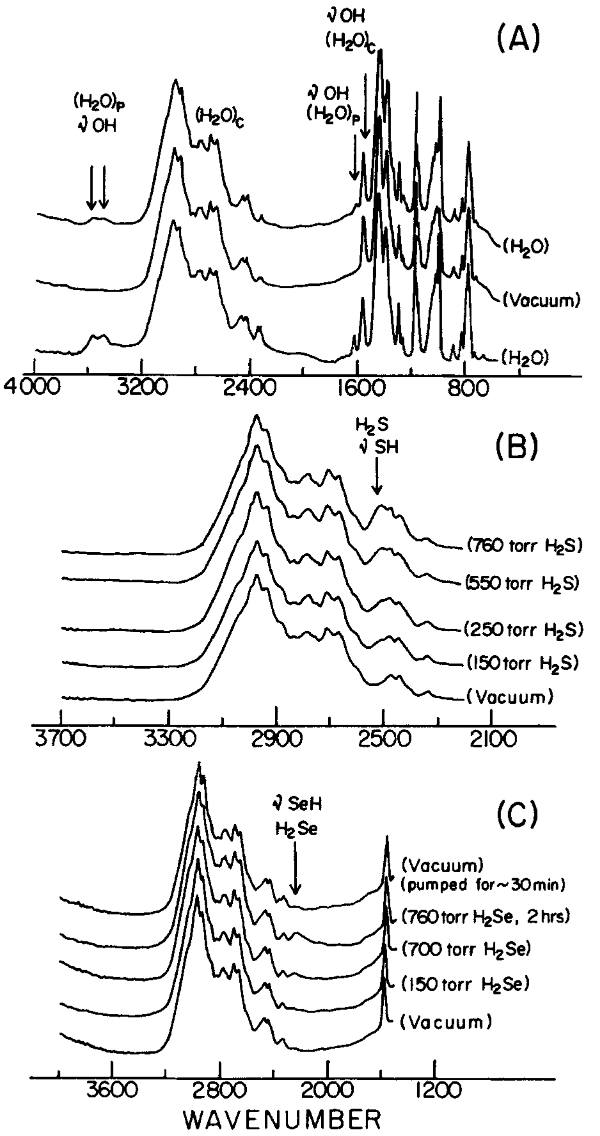


Figure 8 *In situ* Mid-IR spectroscopic study of the adsorption-desorption of (A) H_2O (B) H_2S (C) H_2Se molecular guests in TEA-SnS-1.[9]

Flexible Open Frameworks and Molecular Recognition; Towards the Abiological Electronic Nose

R-SnX-n structure-types, represent a novel class of flexible open-framework microporous electronic materials, whose structure-property relationships are sensitive to the identity and loading of imbibed molecular guests.[2,8] Their discovery could represent an important step towards the practical realization of an abiological electronic nose. The inorganic character of their open-framework structures and the compositional tunability of their electronic band structures, makes these molecular recognition host-guest inclusion electronic materials, potentially integratable into transistor, diode, capacitance and mass-sensitive neural network array-type chemoselective devices.[4] The work briefly described in this paper, demonstrates that certain key elements, considered to be central to the development of molecule discriminating inorganic-materials-based sensors, have now been brought to practice. The most noteworthy of these include (a) the ability to synthesize and structurally characterize phase pure, microcrystalline and single crystal forms (up to 5 mm in size) of a broad range of microporous electronic materials containing tunable size, molecule dimension pores (3 to 15Å), (b) the demonstration of Type 1 reversible adsorption/desorption isotherms for certain molecular guests, (c) the structural elucidation of adsorbed molecule induced, cooperative-reconstruction processes of the host-guest inclusion system, (d) the observation of perturbations of the electronic band structure resulting from the adsorption/desorption of molecular guests.

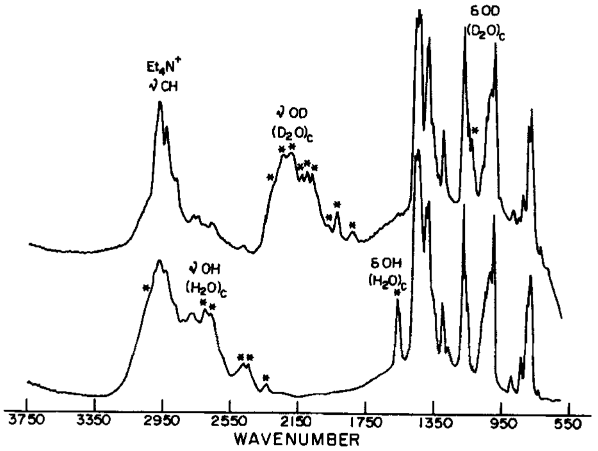


Figure 9 *In situ* Mid-IR spectroscopic D_2O labelling study of TEA-SnS-1, which serves to distinguish the νOH/δOH vibrational modes of physisorbed $(H_2O)_p$ from those of chemisorbed $(H_2O)_c$ molecular guests.[9]

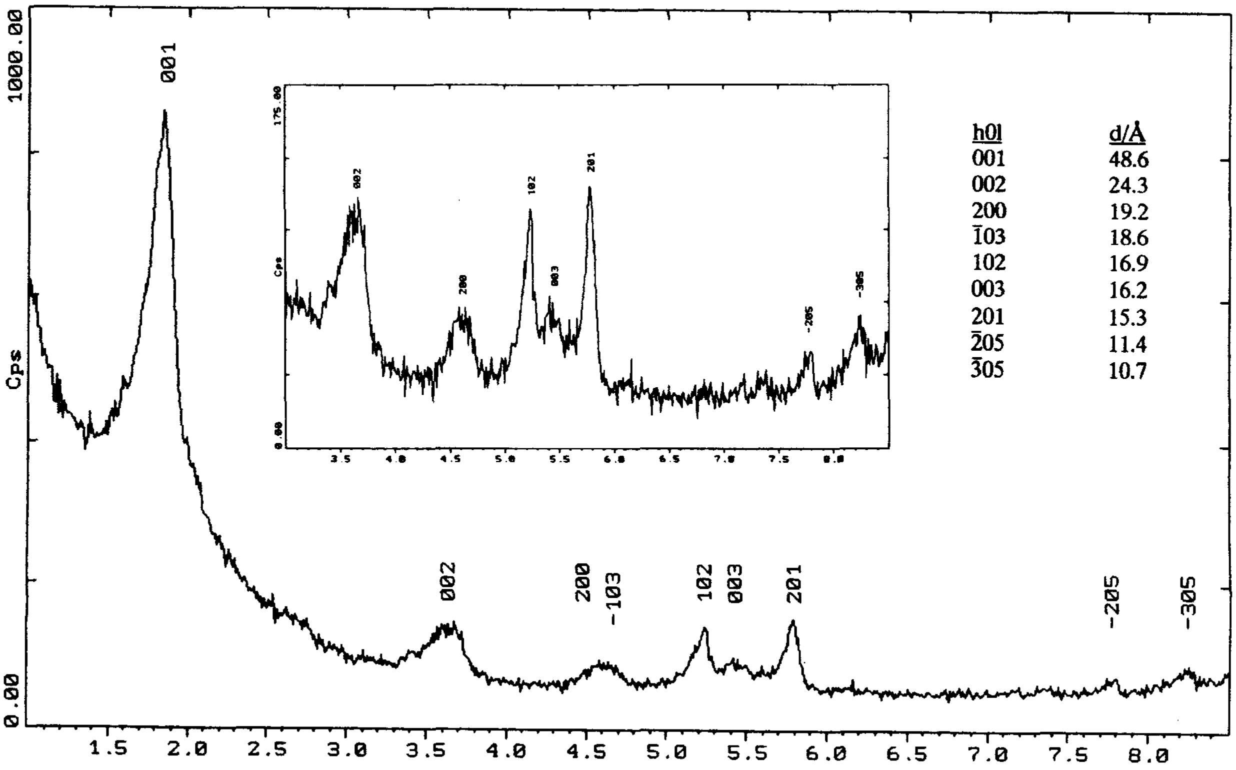
What is required now, aside from extensive on-going investigations of the details of the aforementioned discoveries, is the practical demonstration of doping and band-filling effects, the search for insulator-semiconductor-metal-superconductor transitions, and the quantification of electronic transport, optical, capacitance and mass transducer effects for powder, single crystal and thin film samples of R-SnX-n materials. Hopefully these efforts will bring us closer to the realization of a new generation of molecule discriminations devices.

Entering the Frontier: Mesoporous Tin(IV) Chalcogenides

A natural extension to the work described above on microporous tin(IV) chalcogenides is to move into the mesoscopic size domain and attempt to synthesize mesoporous forms of these materials.[11] By taking lessons from the recent pioneering work of Mobil researchers on the surfactant-based synthesis of mesoporous silica materials,[12] we have successfully synthesized tin(IV) sulfide mesoporous materials. To the best of our knowledge this is the first time that the synthesis of a non-oxide mesoporous material, whose composition is that of a well known bulk semiconductor, namely SnS_2, has been brought to practice. Recently, Ciesla and coworkers have demonstrated that this synthetic approach works well as a new route to mesoporous transition metal oxides, exemplified by tungsten(VI) oxide.[13] Using a surfactant template and soluble tin and sulfur source materials, reaction profiling covering a broad range of compositions, temperatures, pH's and times has been successfully employed to optimize the synthesis of mesoporous tin(IV) sulfides and obtain materials that are approaching phase purity. In **Figure 10** a representative example of a PXRD pattern of a tin sulfide surfactant-based material is shown. Noteworthy is the observation of at least 9 reflections below 10° 2θ which can be well indexed on the assumption of a pseudo-hexagonal unit cell with a=44Å, c=56Å. The first most intense reflection of this novel phase yields a d-spacing of 48.6Å which is in the same range as that observed for the mesoporous silica phase that we have synthesized using the same surfactant template. The SEM determined morphology of this tin sulfide surfactant-based material is needle-like, **Figure 11** and the EDX established a Sn/S ratio of approximately 2. Together these results strongly suggest that this novel product phase has a pseudo-hexagonal symmetry mesoporous channel structure with inorganic walls that have a composition close to that of SnS_2 with a wall thickness comparable to that found in the corresponding mesoporous silica-based material around 10Å.

Transmission electron microscopy (TEM) lattice images of this novel mesoscopic form of tin sulfide clearly revealed the presence of regularly repeating patterns of mesopores with fairly uniform channels, **Figure 11.** Regions of the micrographs can be found in which the mesopores are found to be organized with pseudo-hexagonal symmetry and pore centre-to-centre unit cell dimensions in the range of 40Å ≤ 50Å. The wall thickness of the tin sulfide inorganic channel regions is estimated from these TEM images to be in the range of 10Å. These microscopy results are in excellent accord with the conclusions drawn from the aforementioned PXRD analysis and together provide convincing evidence that this novel tin sulfide product phase is indeed the first recorded example of a mesoporous metal sulfide material.

There seems little doubt that our synthetic method has led to a new class of mesoporous materials with a composition based on tin sulfide and with a structure



h0l	d/Å
001	48.6
002	24.3
200	19.2
$\bar{1}03$	18.6
102	16.9
003	16.2
201	15.3
$\bar{2}05$	11.4
$\bar{3}05$	10.7

Figure 10 PXRD pattern of a novel mesoporous tin sulfide surfactant-based material indexed in a pseudo-hexagonal unit cell with **a** = 44Å, **c** = 56Å.[11]

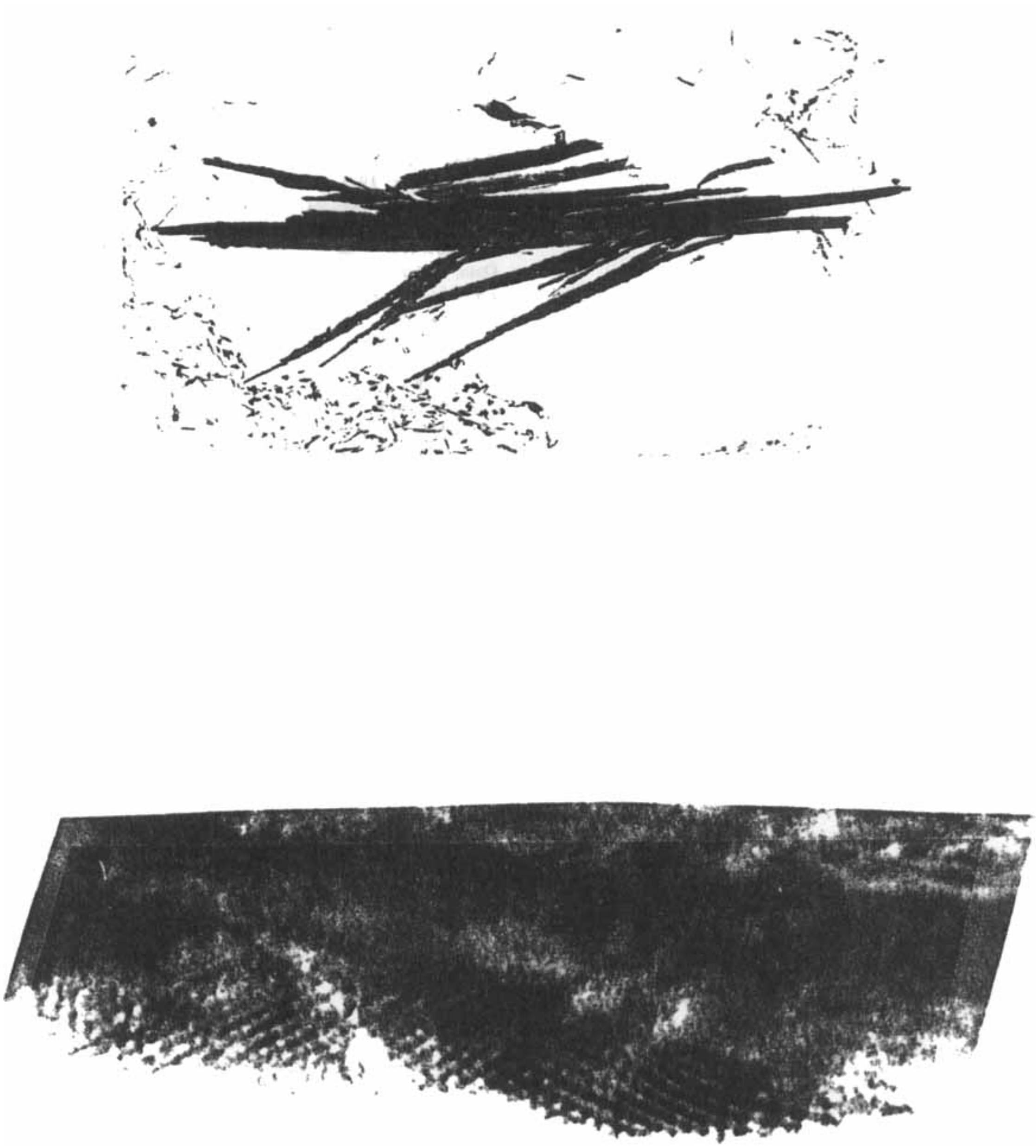


Figure 11 SEM micrograph and transmission electron microscope lattice image of the novel tin sulfide-based material presented in **Figure 10**, respectively showing its needle-like crystal morphology and periodic patterns of mesopores, the latter having pseudo-hexagonal symmetry with pore centre-to-centre unit cell dimensions estimated to be 40Å ≤ 50Å and a wall thickness in the range of 10Å.[11]

based on a regular pseudo-hexagonal array of uniform channels. The channel centre-to-centre distance of the surfactant-based tin sulfide material is 44Å × 56Å with a wall thickness of about 10Å. Detailed studies of the range of compositions, structural characterization, electrical and optical properties, template removal, thermal stability and mode of formation for this new generation of mesoporous metal chalcogenides forms the subject of intensive ongoing investigations in our laboratory.

ACKNOWLEDGEMENTS

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lent efforts, critical support and unrelenting enthusiasm, given at all of the high and low points of the project, involved in unravelling the aesthetics and mysteries of this fascinating and challenging new class of microporous and mesoporous electronic materials.

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