

Open-Pore Organic Material for Retaining Radioactive I₂ and CH₃I**

By Tino Hertzsch, Claire Gervais, Jürg Hulliger,* Bernd Jaeckel, Salih Guentay, Horst Bruchertseifer, and Antonia Neels

Application of ultrasound and ball milling produces micrometer-sized crystallites of tris-(*o*-phenylenedioxy)-cyclotriphosphazene (TPP) that show zeolite-like reversible sorption of I₂ and CH₃I (methyl iodide). The thermal stability of open-pore TPP is improved by partial loading with pyrazine. The sorption properties of open-pore TPP are investigated by the ¹³¹I radioactive tracer method. Comparison with activated charcoal (ACC) shows that TPP has a higher sorption efficiency for I₂ dissolved in water than ACC. In the case of a humid gaseous source of CH₃I also, TPP exhibits better sorption properties than ACC. Partial loading of open-pore TPP by pyrazine increases its thermal stability by 50 °C and the binding properties for retaining CH₃I are also improved. Force-field calculations show a difference of $\Delta E \approx 20 \text{ kJ mol}^{-1}$, making the open-pore system less stable than the apohost.

1. Introduction

Technical filter materials for the processing of gases and water contaminated by I₂ and CH₃I (methyl iodide) contain activated charcoal, inorganic zeolites loaded with silver, or clay materials.^[1–4] A major drawback of these materials used in the nuclear industry is their low sorption capacity for filtering humid gases or water.

Here, we present a first example of an organic open-pore material, tris-(*o*-phenylenedioxy)-cyclotriphosphazene (TPP), showing significantly better sorption properties for I₂ and CH₃I under *wet* conditions. In particular, cleaning of water contaminated by I₂ and CH₃I has been achieved. The ¹³¹I-tracer method was used to quantify the sorption properties. Open-pore molecular crystals featuring channels that allow a reversible uptake and release of guest atoms or molecules are of great interest.^[5,6] However, organic networks tend to be flexible, being unstable in many cases, and are thus not able to maintain empty cavities after removal of the solvent. In some cases a polymorphic modification, referred to as an *apohost*, is obtained, which is left

after desorption of guests.^[7] In the case of TPP we have found that crystallites smaller than about 20–30 μm can be used for reversible sorption of guest molecules, because at this size of the material the zeolitic form is preferentially preserved. Recently, we have shown that, for a similar material—the 2,4,6-tris-(4-bromophenoxy)-1,3,5-triazine (BrPOT) channel inclusion compound with CS₂—the open-pore modification could be obtained only on the basis of micrometer-sized crystals.^[8] The open-pore system of BrPOT provides empty channels with a van der Waals diameter as large as 12 Å.^[8] Reducing the crystal size to the micrometer range or even smaller is favorable for an application such as the sorption of gases.

In the next section (Sec. 2) we describe the preparation of the open-pore microcrystals, followed by a characterization, including thermal stability. In Section 3 we report on the sorption properties explored by the radioactive tracer method.

2. Synthesis and Characterization of the Zeolite State

Among the growing family of organic zeolite-like materials, TPP shows remarkable properties.^[9,10] It was claimed earlier that after removal of solvents the hexagonal inclusion lattice (*P6/m*) converts into a distorted open-pore form (*P2/n*).^[11] However, it was also observed that crystals of a size larger than about 100 μm converted into the monoclinic form during desolvation. Our crystallization attempts with common solvent molecules have confirmed this. Just recently, Sozzani et al. have solved the crystal structure of the empty-channel modification upon a single crystal of size 80 μm × 80 μm × 100 μm.^[12]

Here we report that, by reducing the crystal size to the micrometer range, removal of a template becomes possible without the collapse of the hexagonal channel structure of most crystallites in a powder sample up to a critical temperature.

[*] Prof. J. Hulliger, Dr. T. Hertzsch, Dr. C. Gervais, Dr. B. Jaeckel, S. Guentay
Department of Chemistry and Biochemistry, University of Berne
Freiestrasse 3, CH-3012 Berne (Switzerland)
E-mail: publication.hulliger@iac.unibe.ch

Prof. H. Bruchertseifer
Paul Scherrer Institute
CH-5232 Villigen PSI (Switzerland)

Dr. A. Neels
Institut de Chimie, Université de Neuchâtel
Avenue de Belleveaux 51, CH-2007 Neuchâtel (Switzerland)

[**] We thank the Swiss National Science Foundation, project NFP 47 II (4047-057476/2), for financial support, N.-R. Behrnd for his assistance, and T. Wüst for technical advice. We also thank Accelrys for providing computational tools.

Microcrystalline TPP was obtained in two ways: i) by crystallization from tetrahydrofuran (THF) initiated by a fast drop of temperature and the action of ultrasound, and ii) by ball milling the monoclinic phase, followed by a solid-to-solid transformation during the uptake of THF from the gas phase. In the first method, the effect of the ultrasonic bath is essentially to enhance the nucleation rate and to promote secondary nucleation. Solution nuclear magnetic resonance (NMR) and thermogravimetric analysis (TGA) showed that, under these conditions, crystals yielded a composition of TPP(THF)_{0.6}. An average particle size in the range of 10–30 μm was found. Guest-free crystals were transparent and did not feature cracks on prismatic faces (Fig. 1). Even smaller crystallites with an average particle size of 5 μm were obtained by the second method.

After exposure of the samples to vacuum at room temperature for several days, the same morphology for the loaded and for the open-pore form of TPP (i,ii) was found by scanning electron microscopy (SEM) (Fig. 1). For both procedures of preparation (i,ii), powder X-ray diffraction (PXRD) confirmed a hexagonal channel-type structure (Fig. 2), providing evidence of a slight change of the cell constants. No electron density was found in channels of guest-free TPP. The crystal structures were solved from PXRD data and Rietveld refined (Fig. 2 and Table 1; see also the Experimental section). The powder analysis agrees well with the recent single-crystal structure solution by Sozzani et al.^[12] Two weak signals—marked by asterisks (Fig. 3)—show the presence of a small quantity of the monoclinic phase in some of the prepared samples.

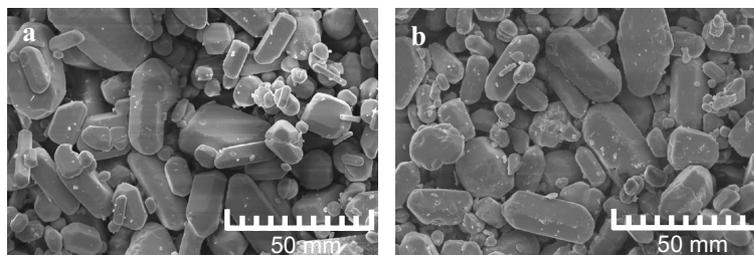


Figure 1. Sorption/desorption behavior of microcrystalline TPP investigated by SEM: a) Inclusion crystals of TPP(THF)_{0.6}. b) Guest-free TPP crystals obtained by fast cooling in an ultrasonic bath and vacuum treatment (average crystal size smaller than ~30 μm) showing hexagonal morphology.

What are possible stabilizing forces supporting guest-free channels of TPP? The rigid trigonal arrangement of the TPP molecular frame seems to be responsible for structural stability because van der Waals forces provide small energies for stabilizing empty channels. Force-field calculations applied to estimate the lattice energy difference ΔE of the empty channel structure (E_h) and the monoclinic structure (E_m) of TPP gave $\Delta E = E_h - E_m \approx 20 \text{ kJ mol}^{-1}$. This confirms that the monoclinic form is more stable. As ΔE is of the order of a hydrogen bond or of typical energies for donor–acceptor complexes, it appears reasonable that guest molecules such as I₂ can stabilize the channel structure of TPP.

Thermal treatment and investigations by PXRD showed that open pores can exist in the long term up to about 50 °C. At higher temperatures, gradually mixtures of the monoclinic and hexagonal crystal forms were observed (Fig. 3). If the TPP is to

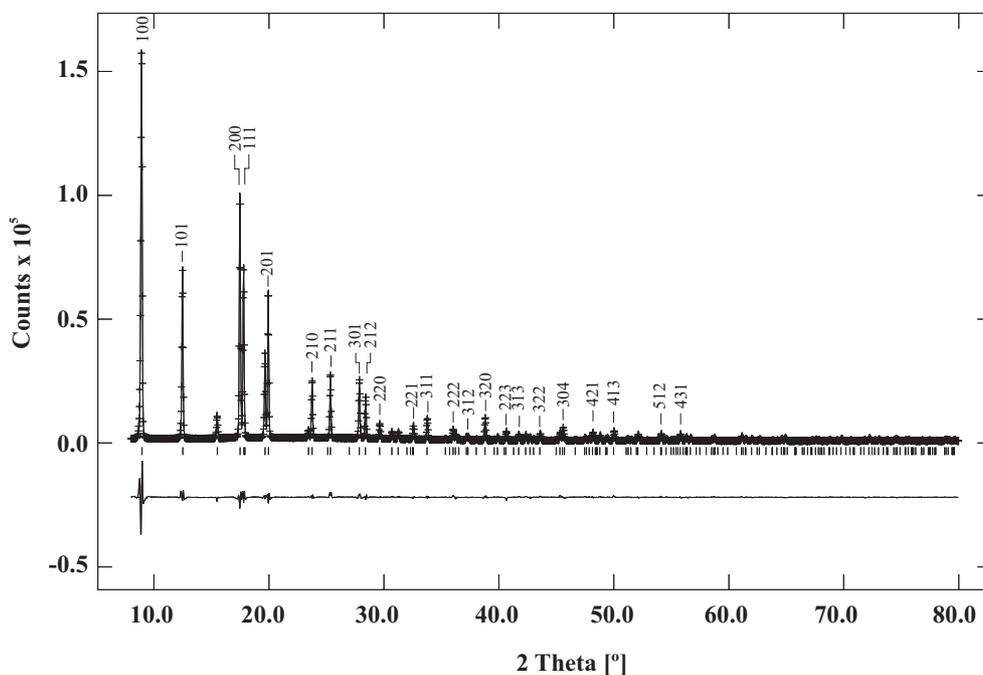


Figure 2. Rietveld plot of the guest-free channel structure of TPP. The bottom curve shows the difference plot using the same scale. Further crystallographic information on TPP was deposited [13]. No monoclinic phase is present in this sample.

Table 1. Crystallographic data of TPP(THF)_{0.6} and guest-free TPP from PXRD and single-crystal analysis using a crystal 80 μm × 80 μm × 100 μm [12].

	TPP(THF) _{0.6}	Guest-free TPP	Guest-free TPP, single-crystal data
Crystal system	hexagonal	hexagonal	hexagonal
Space group	<i>P6₃/m</i>	<i>P6₃/m</i>	<i>P6₃/m</i>
<i>a</i> = <i>b</i> [Å]	11.657(6)	11.4665(1)	11.454(4)
<i>c</i> [Å]	10.064(7)	10.1689(1)	10.160(4)
<i>V</i> [Å ³]	1184.4(13)	1157.89(1)	1154(1)
<i>Z</i>	2	2	2
ρ_{calc} [g cm ⁻³]	1.423	1.317	1.321

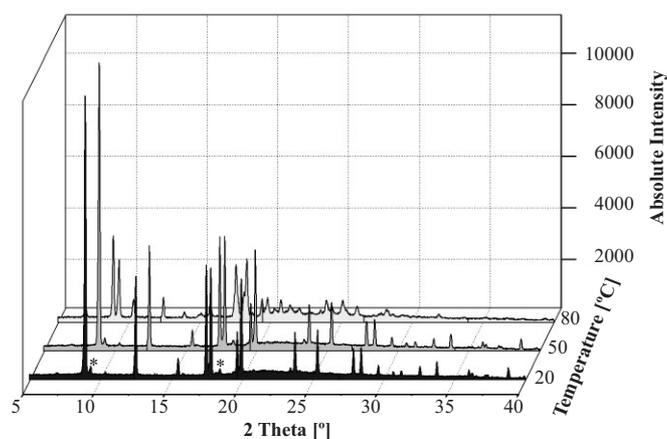


Figure 3. Temperature-dependent PXRD for open-pore, microcrystalline TPP. The guest-free channel structure is observed up to about 50 °C. A mixture of the monoclinic and hexagonal phases is seen above 80 °C. Peaks marked by asterisks stem from a small amount of the monoclinic phase in the sample used for the thermal analysis.

be used for filtering, an appropriate amount of preloading of TPP does not degrade its sensitivity, so the thermal stability can be increased by admitting guest molecules such as pyrazine (pz). The TPP(pz)_{0.35} inclusion kept its channel structure up to about 100 °C (Fig. 4). In particular, inclusion of some pyrazine provides additional binding for guest molecules such as I₂ or CH₃I.

3. Retention of Radioactive Iodine Compounds

Empty or partially loaded inclusion crystals of TPP show a high affinity for the uptake of molecular iodine, made available from gas or in solution. As previously demonstrated, in-diffusion of I₂ into TPP(THF)_{0.35} leads to a reduction of the content of THF.^[14] Consequently, no empty channels would be needed for an uptake, i.e., filtering, of I₂. The effectiveness of TPP acting in a filter setup was tested by passing a flow of 25 mL min⁻¹ argon saturated with I₂ (25 °C) through a column (diameter 3 mm, length 50 mm) filled with TPP(THF)_{0.35} crystallites of an average size of 200 μm (Fig. 5).

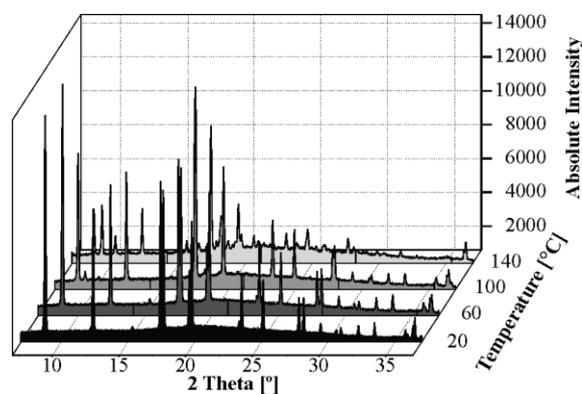


Figure 4. PXRD investigations of TPP preloaded with pyrazine (pz), showing a higher thermal stability. The hexagonal crystal structure of TPP(pz)_{0.35} is maintained up to about 100 °C.

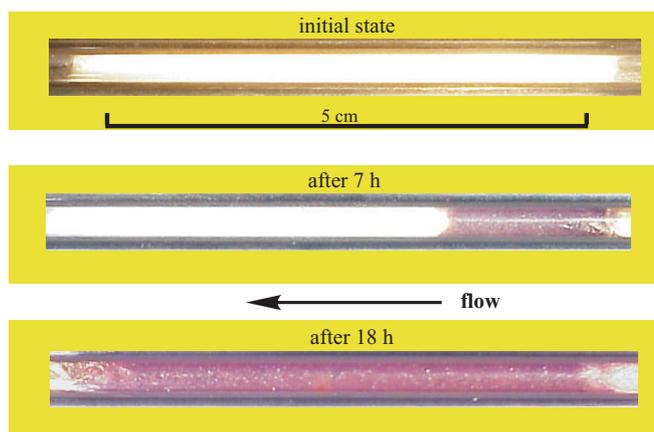


Figure 5. Filter column filled with TPP(THF)_{0.35}: After 7 h the interface between I₂-loaded crystals and TPP(THF)_{0.35} was still very sharp. The maximum capacity for sorption of iodine was exceeded after 18 h.

Because of the sharp interface between loaded and fresh material, we demonstrate here an effective sorption showing high capacity as well. No I₂ could be detected at the outlet of the filter. This shows that even loaded and large TPP crystals can act as an effective filter material. Similar experiments using microcrystalline and empty TPP material have confirmed the observation given in Figure 5. Therefore, the *sensitivity* to traces of I₂ must be very high.

For a quantitative analysis of the filtering performance of TPP, microcrystalline material was tested. Activated charcoal (ACC) treated with amine was used for comparison of the sorption properties. To carry out the analysis, tagged iodine components (I₂ and CH₃I) were provided from a water solution by passing an argon stream through small filters filled with either TPP or ACC (60 mg placed in a syringe of 1 mL). A trash filter with ACC prevented the release of radioactive gases into the atmosphere. The amount of iodine retained in the filters was determined by a radioactive tracer method (¹³¹I (half-life *t*_{1/2} = 8.07 days) using marked I₂ and CH₃I).

Data on the sorption behavior of filter materials (TPP and ACC) treated by a gaseous phase under dry (I) or wet (II) conditions, and by an aqueous solution (III) are summarized in Table 2.

Table 2. Methyl iodide (1–7) and iodine (8,9) retained by TPP and ACC filters in a dry (I) or wet (II) atmosphere and from water (III). Percentage of initial content is given.

Filter material	Amount [μmol]	Solution [%]	Filter 1 [%]	Filter 2 [%]	Outlet [%]
I (1) TPP	0.68	3.7	96.3	–	0
(2) TPP	9.40	2.2	97.8	–	0
(3) ACC	9.00	1.7	97.0	–	1.3
II (4) TPP	9.4	15.5	52.1	32.3	0.1
(5) ACC	9.4	2.0	29.9	22.9	45.2
III (6) TPP	0.056	–	97.8	–	2.2
(7) ACC	0.056	–	39.6	–	60.4
(8) TPP	0.1	–	98.1	–	1.9
(9) ACC	0.1	–	66.0	–	34.0

A quantitative sorption of CH₃I in a dry atmosphere (I) at low (1) and high concentrations (2) was observed by TPP and ACC (3). However, the sorption properties of TPP and ACC changed significantly under *wet* conditions (II); whereas just 0.1 % of CH₃I passed the filters for TPP (4), for ACC (5) 45.2 % of CH₃I was not retained.

For filtering of radioactive compounds from solution (III) the filter was flushed with water. Subsequently, 2 mL of the sample solution was pressed through the filter within 1 min. Despite a relatively small contact time of the filter with an aqueous solution containing CH₃I, 97.8 % was retained by TPP (6), whereas only 39.6 % could be kept by ACC (7).

No evident difference in retention by TPP and ACC was found for filtering of I₂ in dry or wet gaseous atmosphere. Both filter materials showed a complete sorption of I₂ under these conditions. However, in the case of I₂ sorption from water, 98.1 % of I₂ was retained in the probe filter for TPP (8), whereas ACC (9) showed only 66 % efficiency. Because, in real world applications, filtering may take place under intense radiation, guest-free TPP was exposed to γ -rays (⁶⁰Co source, 14 and 86 kGy). Surprisingly, irradiation showed no significant effect on the sorption measured thereafter. Chemically, TPP seemed to be stable under these conditions because ¹H NMR and PXRD revealed no indication of decomposition or a structural change, respectively.

A disadvantage of open-pore TPP may be the volatility of CH₃I: The interactions between CH₃I and the TPP channels are much weaker than those between I₂ and the TPP channels (8–15 kJ mol⁻¹).^[15] Because of a similar behavior found for ACC, charcoal is treated by *N,N,N',N'*-tetraethylenediamine in order to enhance interactions to CH₃I. In our case, it was possible to introduce pyrazine (pz) into channels of TPP by sorption from the gas phase. Subsequently, the TPP(pz)_{0.35} material could retain most of the included CH₃I. The resulting inclusion TPP(pz)_{0.35}(CH₃I)_{0.35} showed a higher stability at room temperature than open-pore TPP, which lost most of its CH₃I during a few hours in vacuum.

4. Summary

We present a first example of an organic micrometer-sized zeolite-like material that may be used to remove radioactive I₂ and CH₃I from a humid environment or water. In the case of CH₃I, the filtering effectiveness of TPP was significantly better than for ACC. Further improvement of sorption with respect to CH₃I was achieved by introducing pyrazine into the channels. Aspects of real world applications have been covered by a patent application.^[16]

As a principle of general interest, we have found that crystallization of micrometer-sized particles can provide conditions to obtain open pores of purely organic channel-type inclusion compounds.^[17] In view of the fact that many other inclusion compounds lose their channel structure when the solvent is removed, crystallization of particles in the micrometer range might be a promising route for gaining access to open-pore materials.

Further work on the sorption isotherms and the active volume of the TPP will be published elsewhere.^[18]

5. Experimental

5.1. Preparation of Tris-(*o*-phenylenedioxy)-cyclophosphazene (TPP)

Hexachlorocyclophosphazene (recrystallized in heptane and sublimed at 100 °C and 1 mbar (1 mbar = 100 Pa)), pyrocatechol, and anhydrous sodium carbonate were refluxed in dry THF for 3 h. The resulting precipitate was filtered, washed with 2 M HCl and dried. The white solid was purified by Soxhlet recrystallization from benzene and repeated sublimation (10⁻² mbar, 210 °C) [19].

5.2. Preparation of Guest-Free TPP Crystals

TPP was dissolved in THF at 60 °C. Crystals smaller than 30 μm were obtained by fast cooling in an ice-cooled ultrasonic bath. The content of THF was determined by ¹H NMR ($x \sim 0.60$). Solvent-free crystals were obtained by exposing them to vacuum at room temperature for at least 2 days. TPP(pz)_{0.35} crystals were obtained by in-diffusion of pyrazine into empty channels of TPP for one week (30 °C). The content of pyrazine was determined by ¹H NMR.

5.3. Determination of the Guest-Free Channel Structure of TPP [13]

A powder sample was inserted into glass capillaries (Lindemann) of 0.5 mm diameter. The PXRD data were collected on a computer-controlled STOE-STADIP focusing powder diffractometer equipped with a curved Ge(111) monochromator, where the Cu K α_1 line could be well separated ($\lambda = 1.54059 \text{ \AA}$) [20]. The compound was measured in the range $8^\circ \leq 2\theta \leq 100^\circ$ using a step width of 0.01°. The indexing procedure was performed using TREOR in the program EXPO2004 [21,22]. The structure solution was carried out using the program DASH, introducing a structural model of a known structure of TPP [23,24]. The obtained position of the molecule in the given symmetry and unit cell was used for Rietveld refinement in GSAS/EXPGUI [25,26]. After an initial refinement of the scale and unit-cell constants, the atomic positions

were refined using soft constraints defining the geometry of the molecule within some allowable errors [27]. Subsequent Rietveld refinement was carried out using gradually relaxing bond restraints. The phosphor atom position was refined anisotropically, while the rest of the non-hydrogen atoms were refined isotropically, applying an overall temperature factor for the C, N, and O atoms. The temperature factor of the H atoms was fixed. In the final cycles of refinement, the shifts in all parameters were less than their estimated standard deviations. Neutral atom scattering factors were used for all atoms. No corrections were made for anomalous dispersion, absorption effects, or preferred orientation (texture).

5.4. Determination of the Structure of TPP(THF)_{0.6}

The TPP(THF)_{0.6} powder was measured under the same conditions as the guest-free TPP. The indexing procedure revealed an isomorphism with known published structures [24]. The refinement of the unit cell parameters was performed using single indexed reflections of the PXRD pattern using the program WinXPow [28].

5.5. Force-Field Calculation

Optimizations of the crystal structures were performed using the module Discover of the software package Materials Studio [29]. The following set of parameters was used: compass force-field [30], Ewald summation for coulombic and van der Waals interactions, Newton-Raphson method for energy minimization. The unit-cell parameters as well as intramolecular and intermolecular interactions were minimized.

Received: April 21, 2005

Final version: August 16, 2005

Published online: November 7, 2005

- [1] S. B. Hingorani, K. S. Venkateswarlu, *Chem. Eng. World* **1977**, 12, 59.
- [2] N. Ikeda, *Radioisotopes* **1961**, 10, 245.
- [3] R. R. Bellamy, *Nucl. Safety* **1974**, 15, 711.
- [4] B.-S. Choi, G.-I. Park, J.-W. Lee, H.-Y. Yang, S.-K. Ryu, *J. Radioanal. Nucl. Chem.* **2003**, 19, 256.
- [5] Y. Aoyama, *Top. Curr. Chem.* **1998**, 198, 1321.
- [6] T. Hertzsch, J. Hulliger, E. Weber, P. Sozzani, in *Encyclopedia of Supramolecular Chemistry*, Marcel Dekker, New York **2004**, pp.996–1005.
- [7] K. Endo, T. Sawaki, M. Koyanagi, K. Kobayashi, H. Masuda, Y. Aoyama, *J. Am. Chem. Soc.* **1995**, 117, 8341.
- [8] R. K. R. Jetti, F. Xue, T. C. W. Mak, A. Nangia, *Cryst. Eng.* **1999**, 2, 215.
- [9] B. T. Ibragimov, S. A. Talipov, *J. Incl. Phenom. Mol. Recognit. Chem.* **1994**, 17, 317.
- [10] R. D. Chapman, R. D. Gilardi, M. F. Welker, C. B. Kreutzberger, *J. Org. Chem.* **1999**, 64, 960.
- [11] P. Sozzani, A. Comotti, R. Simonutti, T. Meersmann, J. W. Logan, A. Pines, *Angew. Chem. Int. Ed.* **2000**, 39, 2695.
- [12] P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angew. Chem. Int. Ed.* **2005**, 44, 1816.
- [13] CCDC 268818 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
- [14] T. Hertzsch, F. Budde, E. Weber, J. Hulliger, *Angew. Chem. Int. Ed.* **2002**, 41, 2281.
- [15] J. A. Joens, *J. Org. Chem.* **1989**, 54, 1126.
- [16] J. Hulliger, T. Hertzsch, *US Patent WO 03/041836*, **2003**.
- [17] H. I. Süß, J. Hulliger, *Microporous Mesoporous Mater.* **2005**, 78, 23.
- [18] C. Couderc, T. Hertzsch, N.-R. Behrnd, K. Krämer, J. Hulliger, *Microporous Mesoporous Mater.*, in press.
- [19] M. R. Allock, E. J. Walsh, *Inorg. Chem.* **1971**, 10, 1643.
- [20] E. R. Wölfel, *J. Appl. Crystallogr.* **1981**, 14, 291.
- [21] P.-E. Werner, L. Eriksson, M. Westdahl, *J. Appl. Crystallogr.* **1985**, 18, 367.
- [22] A. Altomare, R. Caliandro, M. Camalli, C. Cuocci, C. Giacovazzo, A. G. G. Moliterni, R. Rizzi, *J. Appl. Crystallogr.* **2004**, 37, 1025.
- [23] DASH, CCDC Software, 12 Union Road, Cambridge CB2 1EZ, UK.
- [24] H. R. Allock, M. L. Levin, R. R. Whittle, *Inorg. Chem.* **1986**, 25, 41.
- [25] A. Larson, R. Dreele, *General Structure Analysis System (GSAS)*, Los Alamos National Laboratory Report LAUR, **2000**.
- [26] B. H. Toby, *J. Appl. Crystallogr.* **2001**, 34, 210.
- [27] A. J. C. Wilson, E. Prince, *International Tables for X-Ray Crystallography*, Vol. C, Kluwer Academic, Dordrecht, The Netherlands **1999**.
- [28] *WinXPow: STO E Powder Diffraction Software*. Stoe & Cie GmbH, Darmstadt, Germany **1997**.
- [29] *Materials Studio*, Release 3.0, Accelrys Inc., San Diego, CA **2003**.
- [30] H. Sun, *J. Phys. Chem. B* **1998**, 102, 7338.