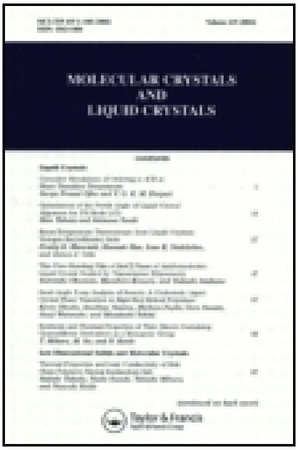

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Structural and Physical Properties of Hydrogen and Fluoro Decorated Triazine Channel Inclusions

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Structural and Physical Properties of Hydrogen and Fluoro Decorated Triazine Channel Inclusions

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With the advantage of a channel diameter of about 12 Å for phenoxy-substituted triazines, fullerenes were included into the channels of 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine (BrPOT). Preliminary investigations on photoconductivity of the inclusion crystals showed results probably related to the predominance of host-guest interplay rather than guest-guest interactions. To reverse this balance, a modification of the channel wall was attempted by perfluorination of the phenoxy substituted triazine. However, the fluoro derivative of BrPOT formed no inclusion compounds with typical solvents, whereas 2,4,6-tris(pentafluorophenoxy)-1,3,5-triazine (F5POT) showed channel inclusion formation with p-xylene and p-chlorotoluene (host-guest ratio 2:1). Reversibility of solvent uptake for the F5POT/p-xylene system is demonstrated.

Keywords: channel inclusion; fullerene; perfluoro compounds; triazine

FULLERENE INCLUSION INTO CHANNELS OF BrPOT

Substituted triazines are of particular interest in crystal engineering [1]. For instance, 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine (BrPOT) [2] forms trigonal networks and 1D channels with a van der Waals diameter of about 12 Å. Due to its nanometer scale, channels of BrPOT allow inclusion of not only a variety of solvent molecules but also bigger molecules, for instance fullerenes [3]. Single crystals

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with C_{60} and C_{70} inclusion were grown by lowering the temperature from saturated solutions of toluene or carbon disulfide. Analysis by X-ray diffraction of the crystals obtained reveals that both systems, $BrPOT(C_{60})_{0.2}$ $(C_7H_8)_{0.6}$ and $BrPOT(C_{60})_{0.15}(CS_2)_{0.7}$, belong to the centrosymmetric space group ($P6_3/m$). Even though the percentage of the fullerene molecules in the channels is quite low, the spherical structure, polarizability and the weak acceptor properties of C_{60} may give rise to a number of solid state properties. Here, BrPOT $(C_{60})_{0.6}(C_7H_8)_{0.6}$ crystals showed photoconductivity upon irradiation at 532 nm. As shown in Figure 1, the intensity of the photocurrent for crystals of $BrPOT(C_{60})_{0.2}(C_7H_8)_{0.6}$ and $BrPOT(C_{60})_{0.15}(CS_2)_{0.7}$ depends on the polarization of the applied laser light. Surprisingly,

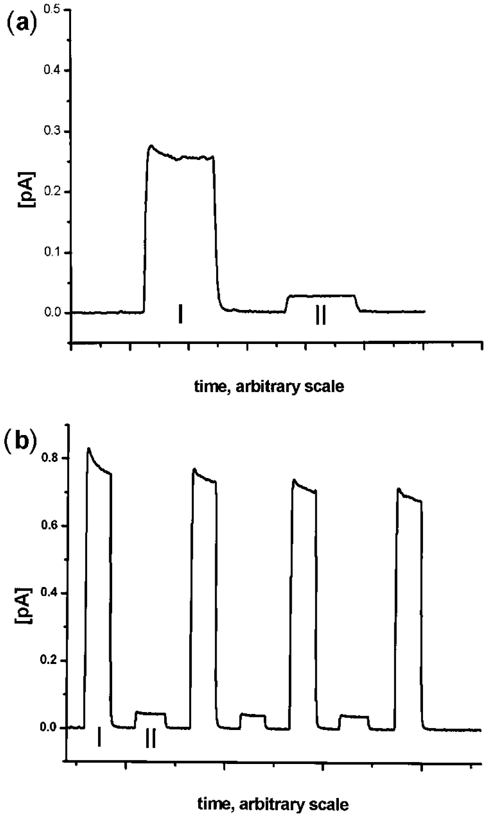

FIGURE 1 Photocurrent of a) $BrPOT(C_{60})_{0.2}(toluene)_{0.6}$ and b) BrPOT $(C_{60})_{0.15}(CS_2)_{0.7}$ measured at 1000 V and illumination at 532 nm. Polarization of the laser light perpendicular (I) and parallel (II) to the channel axis.

for a polarization perpendicular to the axis of the channels, the conductivity was higher than for a polarization parallel to the channel axis. This effect may be explained by two main factors. (i) Interactions between guest molecules and the channel wall may increase the photoconductivity in the perpendicular direction. (ii) A lack of 1D close packing of guests may lead to a reduction of the conductivity along the channel axis.

MODIFICATION OF THE CHANNEL WALL BY PERFLUORINATION

In order to achieve close packing of guests, attempts have been made to decorate the channel walls with fluorine atoms. The effect of perfluorination of the host compound might introduce specific new host–guest interactions or result in a channel that is more steric in nature, favouring close packing of interacting guest molecules. A number of perfluoro derivatives of potential host compounds have been synthesized. In order to keep the trigonal characteristics, the tetrafluorinated analogue of BrPOT, 2,4,6-tris(4-bromo-tetrafluorophenoxy)-1,3,5-triazine (BrF4POT), was investigated. The resulting crystals belong to the monoclinic space group $P2_1$ and, surprisingly, showed no inclusion properties. Instead of Br_3 sythons which stabilized the cavity in BrPOT, a three dimensional network with strong bromo-bromo interactions was present. Typical Piedfort units (PU's) [4], as known for BrPOT [1], also were not observed, instead the dominating interactions here are perfluorophenyl stacking interactions. Contrary to BrF4POT, the perfluorinated 2,4,6-tris(pentafluorophenoxy)-1,3,5-triazine (F5POT) showed inclusion formation with *p*-xylene (Figure 2) and *p*-chlorotoluene [5]. The 2:1 (host:guest) composition found for both inclusion systems was determined by thermal gravimetry. X-ray analysis revealed packing in the triclinic space group $P1$. As shown in Figure 2, the triazine rings are stacked along the *a* axis at a distance of 6 Å, generating channels with dimensions of about 10.5×6 Å. No close packing of solvent molecules was observed. This could be explained by the presence of F···H contacts between the guest molecules and the channel wall, which is constituted of perfluorophenyl rings. This result is in agreement with previous analyses of other channel forming inclusion compounds, which show that only hosts with topologically homogeneous and electronically inactive channel walls prefer to build up one-dimensional close packing for a variety of guest molecules [6].

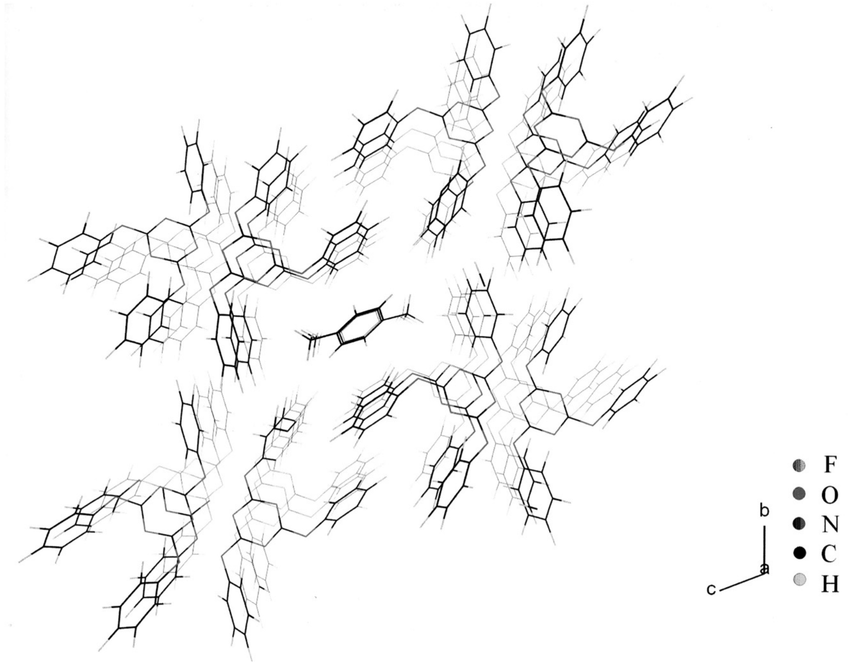

FIGURE 2 Crystal structure of F5POT(p-xylene)$_{0.5}$, viewed along the a axis.

SORPTION/DESORPTION PROPERTIES OF PERFLUORINATED COMPOUNDS

In order to investigate the sorption/desorption properties, crystals of F5POT(p-xylene)$_{0.5}$ were grown from saturated p-xylene solutions by lowering the temperature. These mm sized crystals were exposed to vacuum at 60°C for 3 days resulting in complete desorption of the solvent molecules and collapse of the channel structure. The powder diffraction data of the sample agrees with the pattern of the guest-free phase of F5POT (Fig. 3a and c). Evidence for reversible sorption/desorption properties of F5POT by solid state transformation through the gas phase was obtained by the following procedure: Fine crystals of F5POT(p-xylene)$_{0.5}$ were sealed in ampoules and kept at 100°C for 3 days. After this period, one tube was opened at 100°C and found to contain a mixture of F5POT(p-xylene)$_{0.5}$ and the guest-free phase. In another tube, the sample was brought down to room temperature at a rate of 1°C/h, leading to F5POT (p-xylene)$_{0.5}$ crystals only. In Figure 3, the X-ray powder diffraction

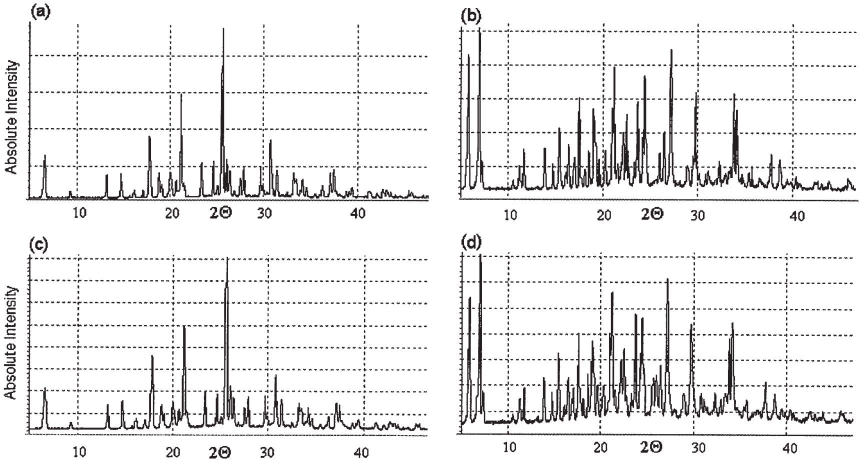

FIGURE 3 X-ray powder diffraction data of a) solvent-free phase of F5POT; b) crystals of F5POT(p-xylene)$_{0.5}$ grown from solution; c) crystals of F5POT(p-xylene)$_{0.5}$ after 3 days at vacuum and 60°C; d) crystals of F5POT(p-xylene)$_{0.5}$ after resorption of gaseous p-xylene.

patterns show the reversible sorption/desorption process from the gas phase.

SUMMARY AND PERSPECTIVES

Inclusion crystals of BrPOT$(C_{60})_{0.2}(C_7H_8)_{0.6}$ and BrPOT$(C_{60})_{0.15}(CS_2)_{0.7}$ show photoconductivity of different intensity depending on the included solvent as well as on the direction of polarization with respect to the channel axis. First results show a clear change of the inclusion properties due to fluorination of the host compound. Specific host–guest interactions allow no close packing of guest molecules. Inclusion of p-chlorotoluene and p-xylene was accomplished for the perfluorinated triazine F5POT. Reversible sorption of p-xylene was demonstrated. Further work will focus on a broad investigation of inclusion properties of perfluorinated triazines and other host compounds.

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