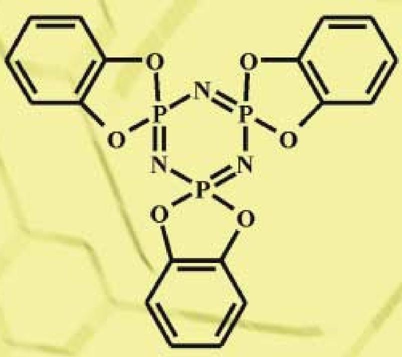
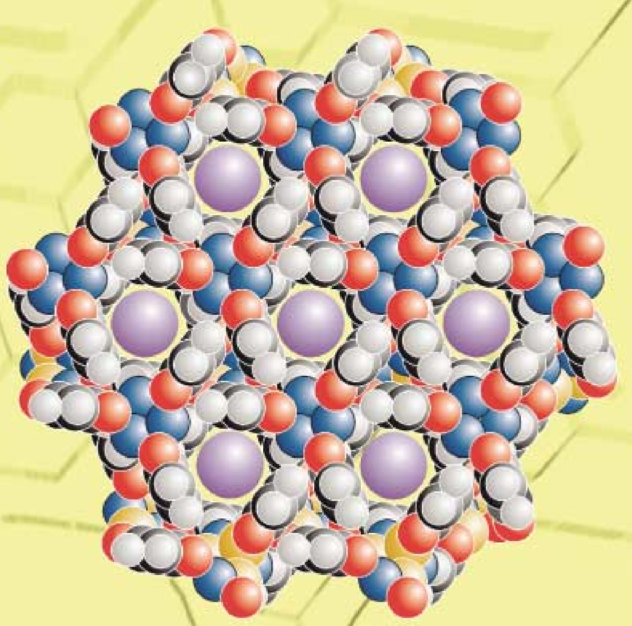
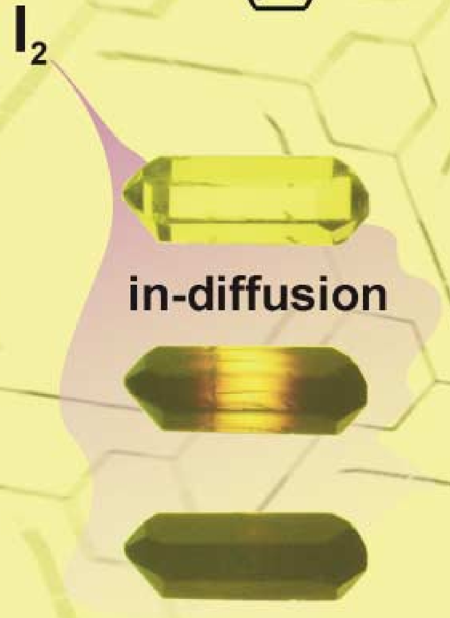
phosphazene molecule



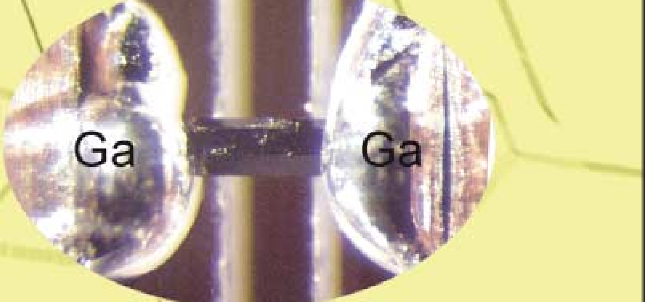
channel architecture





The trigonal arrangement of phosphazene molecules provides a hexagonal channel structure, wherein iodine forms molecular chains by inward diffusion and crystallization. The iodine chains show electrical conductivity. For more information see the following pages.

chains of iodine



conductivity: 10^{-6}–10^{-8} $\Omega^{-1}m^{-1}$

1433-7851/02/4113-2281 $ 20.00+.50/0

Supramolecular-Wire Confinement of I_2 Molecules in Channels of the Organic Zeolite Tris(*o*-phenylenedioxy)cyclotriphosphazene**

Tino Hertzsch, Felix Budde, Edwin Weber, and Jürg Hulliger*

1D arrays of atoms or molecules with the property of conducting charge or photonic energy are considered major components for setting up future devices based on molecular-sized functional units.[1] Molecular wires typically include conjugated chain-type molecules in solution[2] and carbon nanotubes.[3] By use of scanning-probe microscopy techniques, it is possible to prepare atomic arrays in chains or other structures on a substrate.[4] Recently, potassium-doped fullerene chains were found in channels of an inorganic material.[5] In crystals of inorganic zeolites, dyes can transport photonic energy.[6] Dielectric crystalline host structures that provide an ordered array of aligned functional molecules are therefore of general interest to investigate transport properties along or perpendicular to chains of guest molecules.

Here, we report on the synthesis of inclusion crystals of tris(*o*-phenylenedioxy)cyclotriphosphazene (TPP, Figure 1)[7] and I_2, as well as on the conductivity properties of single $\mathrm{TPP} \cdot y(I_2)$ crystals, measured parallel $(\parallel)$ and perpendicular $(\perp)$ to the channel axis of this organic zeolite.

TPP belongs to a growing family of cyclophosphazenes, some of which form channel-type inclusion compounds.[8] A quasicylindrical channel topology was reported for an inclusion complex with benzene as the guest molecule. Unit cell parameters of $a = 1.804$, $c = 10.054$ Å ($P6_3$ for benzene guest) suggest a channel diameter of ≈ 5 Å[9] and an interchannel distance of about 12 Å. After the release of benzene, the channel structure was found to be metastable up to a temperature of about 150 °C.[10] Because of a reversible uptake of guest molecules, hexagonal TPP was recognized as one of the first organic zeolites.

Iodine is a 2D semiconductor[11] and one of the best characterized n-type molecular donors for the formation of $n \rightarrow \sigma^*$ charge-transfer complexes.[12] The electrical conductivity in the (b,c) plane, where I_2 molecules form a 2D network, is about 3400 times larger than the conductivity perpendicular to this plane. In supramolecular solid-state structures, chain formation, intercalation, and inclusion in cavities are known.[13] Sorption and mass-transport properties of a 1D inclusion complex of I_2 in the zeolite MFI were investigated.[14], and inclusion of a number of solvents in TPP is known.[8] Diffusive guest exchange and cocrystallization with nonlinear-optical molecules has recently produced new materials, whose polarity can be explained by a Markov model.[15] Previous and present results support promising inclusion and zeolite-type properties of TPP, even for atoms (Xe[10]) and other small species (H_2O, Br_2, CH_3I).

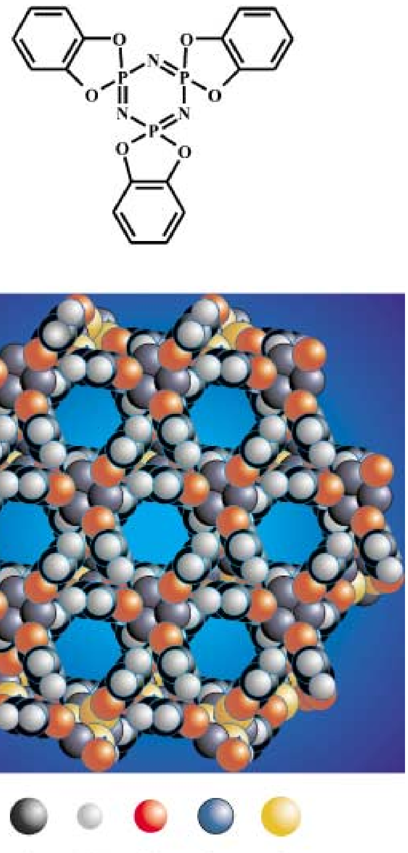


Figure 1. Molecular structure of TPP and the channel topology viewed along the c axis (channels with a diameter of about 5 Å). From data in ref. [8].

The investigations herein were based upon a single observation: Colorless, transparent, needle-shaped (1–2 mm long) single crystals of $\mathrm{TPP} \cdot 0.6(\mathrm{THF})$ (Figure 2a) and some crystals of iodine were brought together in a closed system at room temperature ($p(I_2) \approx 0.3$ Torr). A few seconds after I_2 was brought into the system (Figure 2b), staining started from the capping faces and extended continuously into the volume of the crystals. After 1–2 days, most crystals were entirely colored (Figure 2c). I_2 inclusion in the crystal with TPP was also obtained by cocrystallization from the vapor phase and from a mesitylene solution. All reactions (I, II, III, see Figure 3) produced hexagonal, dichroitic, purple to black single crystals. The optical density of the crystals varied, depending on the conditions of preparation; hence, the degree of loading could be varied.

With regard to the above-mentioned electronic properties of iodine, it would be desirable to form a closed chain of interacting I_2 molecules along the channels in the TPP. Assuming a van der Waals contact between the I_2 molecules

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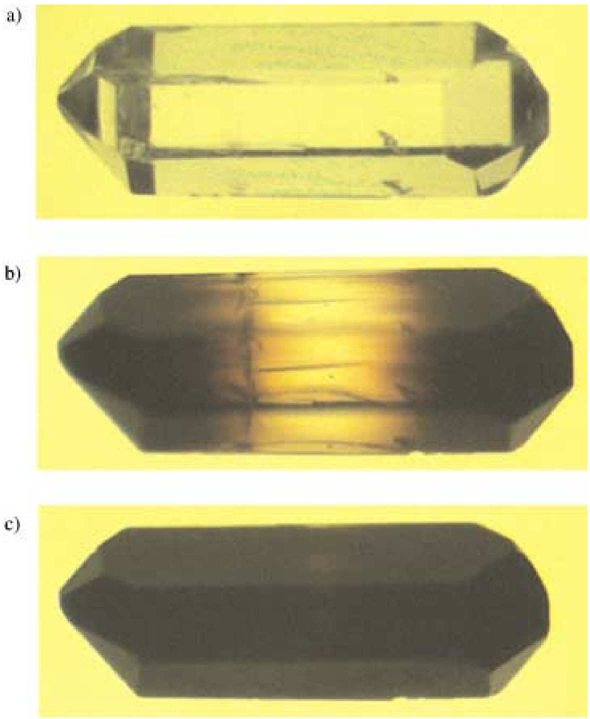

Figure 2. Crystals of TPP $\cdot x'$(THF)$\cdot y$(I_2) (typical size: 2 mm) featuring three states of the process of diffusion in and diffusion out of iodine and THF, respectively. a) Initial state; b) early state, in which only capping faces were colored; c) final state, in which iodine has stained crystals up to the center. The figure supports the concept of the counterdiffusion of THF and iodine.

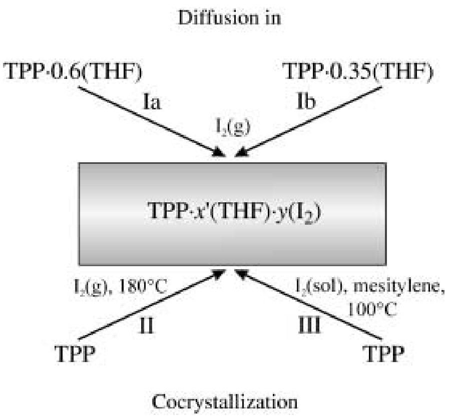

Figure 3. Different routes to the inclusion of I_2 molecules into channels of the TPP zeolite. sol = solvated.

aligned along the channels, the maximum I_2 content would yield TPP $\cdot y$(I_2) crystals, with a value of $y \approx 0.75$.

Table 1 summarizes the chemical composition of all the TPP $\cdot x'$(THF)$\cdot y$(I_2) and TPP $\cdot y$(I_2) inclusion crystals we obtained. When diffusion experiments were performed using of TPP $\cdot$ 0.6(THF) single crystals (I a), most THF ($x \approx 0.4$) remained in the channels. It was also possible to increase the I_2 content by a partial desorption of the template solvent prior to the diffusion of iodine into the crystal: TPP $\cdot$ 0.35(THF) crystals (route I b) contained more iodine than the TPP $\cdot$ 0.6(THF) material which was exposed to I_2 at the same temperature.

Table 1. Synthetic routes to and chemical compositions of TPP $\cdot x'$(THF)$\cdot$ y(I_2) and TPP $\cdot y$(I_2) crystals.

Synthetic route	Reaction conditions	Composition of TPP $\cdot x$(THF)$\cdot y$(I_2)	Decomposition temperature [°C]
I a	TPP $\cdot$ 0.6(THF), I_2, 25 °C, 24 h	$x' = 0.4$, $y = 0.16$	230–248
I b	TPP $\cdot$ 0.35(THF), I_2, 25 °C, 24 h	$x' = 0.25$, $y = 0.45$	238–249
II	TPP, I_2, 180 °C evacuated	$x' = 0$, $y = 0.40$	244–249
III	TPP, I_2, mesitylene, 100 °C, slow cooling	$x' = 0$, $y = 0.65–0.75$	247–250

Given that 1 mm-long single crystals of TPP $\cdot x$(THF) did not disintegrate or crack after diffusion of I_2 into the crystals, we wondered by what type of mechanism the staining and the release of THF might occur simultaneously. Counterdiffusion of THF and I_2 is likely, because it was observed that staining started and progressed from the capping faces only. A mechanism of counterdiffusion was recently proposed[15] to explain the staining of the volume of TPP $\cdot x$(THF) crystals by much larger guest molecules than I_2 (phenyls, biphenyls, stilbenes). However, such a mechanism would involve the channel wall showing some flexibility. A mechanism for solid-state reactions in molecular crystals was recently proposed, which assumed considerable flexibility of molecular lattices.[16]

Cocrystallization from the vapor phase (route II; Figure 3) needed temperatures of 180 °C to provide a sufficiently high vapor pressure of TPP. These crystals obtained by this method were very small and showed a considerably lower I_2 content than those from route I b. Exploration of reactions I, II, and III showed that cocrystallization from mesitylene (route III) gave rise to the maximum loading. The TPP $\cdot y$(I_2) crystals formed at a starting T of 80–100 °C had an I_2 content in the range of $x \approx 0.65–0.75$. Here, it is important to note that mesitylene was not co-included with I_2.

All TPP $\cdot y$(I_2) crystals obtained showed a remarkable thermal stability; according to thermogravimetric (TG) and differential-scanning calorimetry (DSC) measurements, an efficient I_2(g) loss started above 150 °C and decomposition (melting) was observed near $T \approx 250$ °C. No significant weight loss caused by I_2 desorption was observed at 25 °C, under vacuum, over 12 h of treatment.

Structurally, I_2 molecules are aligned in a parallel fashion (confirmed by the dichroism), and are surrounded by two sets of three phenyl rings, which form a π-electron wall around the I_2 molecule (Figure 1). As reported for complexes with aromatic molecules,[17] a stabilizing interaction of $\Delta H^\circ_f = 8–15\,\mathrm{kJ\,mol^{-1}}$ is expected to support inclusion-crystal formation. A van der Waals length of 6.8 Å (I_2) and stacking along a period of TPP molecules of $c \approx 10$ Å will most likely result in an incommensurate structural relationship between the guest and the host sublattices. Partial loading ($y < 0.75$) can be a source of translational disorder of I_2 along individual channels. X-ray single-crystal and powder data confirmed the structure of the TPP host lattice.[18]

Electrical measurements on single crystals were performed by contacting them with liquid Ga. A special cell for mounting small crystals between copper electrodes was constructed, which allowed the crystals to be monitored during measurements. An atmosphere of 1–2 bar $\mathrm{SF_6(g)}$ was used, and conductivity measurements (Keithley electrometer 6517A) were performed on six single crystals of $\mathrm{TPP}\cdot y(\mathrm{I_2})$ ($y \approx 0.65$–0.75, $T = 25\,^{\circ}\mathrm{C}$), which were obtained from two different crystallization attempts (route III, Figure 3). $\sigma_{\parallel}$ values in the order of 10^{-6}–$10^{-8}\ \Omega^{-1}\,\mathrm{m}^{-1}$ were found for a potential of 50 V. However, three of these crystals were exposed to a voltage of 50 V, an increase in the current I (up to a factor of two) was observed with time. In cases where the voltage was 500–1000 V, the conductivity could be enhanced by a factor of 30–300, depending on the individual crystals. For crystals in which a stable current was established after several hours, an anisotropy factor ($\sigma_{\parallel}$, $\sigma_{\perp}$) of about 30 was measured. This factor provides evidence for a preferred conductivity along $\mathrm{I_2}$ chains in the TPP channels. Further investigation of the nonlinearity and the time dependence of the $I(U)$ function is in progress.

In summary, we present the first example of $\mathrm{I_2}$ molecules being brought into a chainlike configuration, surrounded by a π-donor-type environment, which separates chains laterally. Observed values of the conductivity of $\mathrm{TPP}\cdot y(\mathrm{I_2})$ are of the same order as those in the (b,c) plane[11] of iodine ($1.7 \times 10^{-6}\ \Omega^{-1}\,\mathrm{m}^{-1}$, 25 °C). Efficient sorption of $\mathrm{I_2}$ by the $\mathrm{TPP}\cdot x(\mathrm{THF})$ zeolite crystals may find application in the sensing and removal of radioactive $^{129}\mathrm{I_2}$.[19]

Experimental Section

^{1}H NMR spectra were recorded on a Bruker-Spectroscopin AC 300 spectrometer. The UV/Vis spectra were measured on a Cary spectrometer.

Preparation of TPP: Hexachlorocyclophosphazene (recrystallized in heptane), sublimed pyrocatechol, and anhydrous sodium carbonate were mixed in dry THF. The resulting precipitate was filtered off and dried. The product was purified by recrystallization (toluene) and a double sublimation ($p = 10^{-2}$ mbar, $T = 210\,^{\circ}\mathrm{C}$).

Preparation of the $\mathrm{TPP}\cdot x(\mathrm{THF})$ clathrate: TPP was dissolved in THF at 60 °C. Single crystals up to several millimeters long were obtained by slow cooling ($1\,^{\circ}\mathrm{C\,h^{-1}}$). The ratio of TPP/THF was determined by ^{1}H NMR spectroscopy ($x \approx 0.60$, Ia). Partially desolvated clathrate crystals were obtained when exposed to vacuum at room temperature for 24 h ($x \approx 0.35$, Ib).

Preparation of inclusion compounds $\mathrm{TPP}\cdot x'(\mathrm{THF})\cdot y(\mathrm{I_2})$ (route I): $\mathrm{TPP}\cdot x(\mathrm{THF})$ crystals were sealed in ampoules ($V \approx 3\ \mathrm{cm^3}$) with an excess of iodine and placed into the homogeneous hot zone of a glass oven at a temperature of 25–100 °C.

Preparation of inclusion compounds $\mathrm{TPP}\cdot y(\mathrm{I_2})$, route II: Cocrystallization was performed in the gas phase in ampoules ($V \approx 3\ \mathrm{cm^3}$), up to 180 °C, with a small temperature gradient between iodine(l) and TPP(s).

Route III: Sublimated TPP and an excess of iodine were dissolved in mesitylene at 80–100 °C. Black single crystals (III), were obtained by slow cooling ($1\,^{\circ}\mathrm{C\,h^{-1}}$). The ratio of TPP/iodine was measured by UV/Vis spectroscopy, by using three independent series of crystals and standard solutions for iodine. The average content (y) of $\mathrm{I_2}$ varied between 0.65–0.75 for different batches. A value of $y = 0.75$ demonstrates that batches with a maximum concentration of iodine could be prepared.

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Trapping Energy from and Injecting Energy into Dye–Zeolite Nanoantennae**

Huub Maas and Gion Calzaferri*

The light-harvesting system in green plants is a supramolecular machine that collects light energy for photosynthesis. The beauty of this photonic antenna has inspired many researchers to examine and even try to mimic it. Different approaches have been used to build artificial photonic antennae.[1–5] Exciting results based on a host–guest system have been obtained in our group[6–10] with the host material zeolite L, a hexagonal crystal with one-dimensional channels

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