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PAPER

Synthesis and crystal structure of tris(2,3-triphenylenedioxy) cyclotriphosphazene: a new clathration system†

Mathias Reynes,[a] Olivier J. Dautel,*[a] David Virieux,[a] David Flot[b] and Joël J. E. Moreau*[a]

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A new host compound **TTPP** (tris(2,3-triphenylenedioxy)cyclotriphosphazene), which is able to form a porous network, has been synthesized in five steps. When it crystallizes as a single component, **TTPP** exhibits a crystal structure with a monoclinic unit cell, the space group $P2_1/c$ (no. 14) and unit cell dimensions of $a = 14.909(2)$ Å, $b = 31.013(4)$ Å, $c = 9.074(1)$ Å, $\beta = 102.12(1)°$. Co-crystallization of **TTPP** with 1,2,4-trichlorobenzene forms an inclusion crystal having a triclinic unit cell with a $P\bar{1}$ space group (no. 2) and unit cell dimensions of $a = 8.769(2)$ Å, $b = 15.024(2)$ Å, $c = 21.216(2)$ Å, $\alpha = 94.82(0)°$, $\beta = 99.98(0)°$, $\gamma = 98.23(1)$. The guest lies in two kinds of channel-like cavities with dimensions of 6.1 × 8.4 Å^2 and 10.7 × 12.4 Å^2 respectively. This represents the biggest porous network built up by spirocyclotriphosphazene derivatives to date.

Introduction

Spirocyclic triphosphazene derivatives are known to form host–guest inclusion compounds with a wide variety of organic or inorganic molecules.[1] In their unique paddle-wheel shapes, aromatic units are perpendicularly oriented to the central cyclotriphosphazene hub. This feature permits the formation of channel walls, which are set up by planar aromatic entities. The bulky shape associated with molecular rigidity can be connected to the formation of inclusion compounds featuring properties often associated with inorganic zeolites. The oldest member of this family, and probably also the most widely studied, is the tris(*o*-phenylenedioxy)cyclotriphosphazene (**TPP**).[2] The formation of inclusion compounds with this host leads to hexagonal structures in which guest molecules occupy crystalline channels of 5 Å width.[3,4] The **TPP** host can also selectively discriminate small molecules or polymers based on their size, shape, aromaticity or even acidity.[5–9] **TPP** has also been used as a template for inclusion polymerization of various vinyl, diene or acrylate monomers.[10–12] Porosity has been studied for gas storage[13] and inclusion of iodine shows that semi-conducting properties can be brought to such materials.[14]

So far, Allcock *et al.* have reported the synthesis and inclusion behavior of several host molecules including tris(*o*-phenylenedioxy)cyclotriphosphazenes (**TPP**),[2,5] tris(2,3-naphthalenedioxy)cyclotriphosphazene (**TNP**)[15,16] and tris(9,10-phenanthrenedioxy)cyclotriphosphazene (**TPhenP**).[17]

Typical syntheses involve the reaction of aryldioxy reagents with the reactive hexachlorocyclotriphosphazene. Interestingly the host can be tailored by using the appropriate aromatic diol paddles. **TNP** hosts form inclusion compounds with the same hexagonal structure but with larger channel sizes. Thus, tunnel diameter can be easily tuned by enhancing aryldioxy paddle length from catechol to naphthalenediol: channel diameters are respectively 5 Å and 10 Å for **TPP** and **TNP**. The latter, having larger pores, allows inclusion and polymerization of bigger guests such as octyl acrylate that cannot be included in **TPP** for polymerization or separation.[18] Moreover, enlarged pores favor guest–guest interactions which could be an important feature for monomer polymerizations and conductance properties of guest species.[6,18]

With the aim of increasing pore sizes, Allcock *et al.* synthesized **TPhenP** and obtained different inclusion structures depending on the nature of the molecular guest.[17] Two of those structures are reported but none of them correspond to **TPP** nor **TNP** structures.[17] **TPhenP** host also gives networks presenting tunnel-like cavities. When *o*-dichlorobenzene is included, channel dimensions are approximately 5.8 Å large and 6.4 Å in width. When *p*-xylene is included, two kinds of channel are formed with sizes of approximately 5.91 Å and 7.3 Å.

The present work reports the synthesis of a new host compound, tris(2,3-triphenylenedioxy)cyclotriphosphazene (**TTPP**), and the elaboration of the related porous network. The design of such a host is motivated by three main objectives: firstly, to elaborate new porous networks with cavity sizes bigger than those previously reported for spirocyclic triphosphazenes; secondly, to investigate if networks based on the same topology as **TPhenP** can be obtained while enhancing cavity size; and

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[a] *Architectures Moléculaires et Matériaux Nanostructurés, Institut Charles Gerhardt Montpellier, UMR CNRS 5253, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale F-34296, Montpellier Cedex 05, France. E-mail: olivier.dautel@enscm.fr; Fax: +33 4 6714 7217; Tel: +33 4 6714 7212*
[b] *ESRF, 6, rue Jules Horowitz, BP181, 38042 Grenoble Cedex 9, France*

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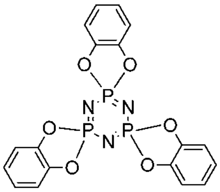
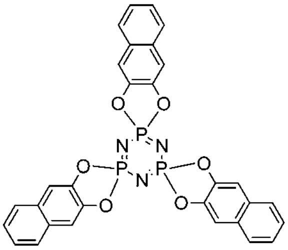
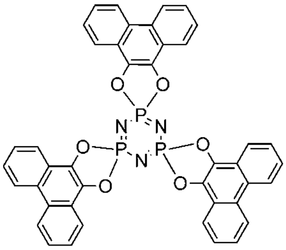
thirdly, to increase the stability of the porous network by enhancing π-stacking interactions between host walls. According to these objectives, **TTPP** appears to be a valuable target.



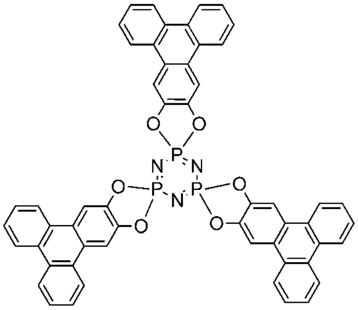
TPP



TNP



TPhenP



TTPP

Experimental section

Synthesis of 1,2-dibromo-4,5-dimethoxybenzene, 1

A solution of Br_2 (33.56 g, 210 mmol) in CCl_4 (100 mL) was added dropwise to a solution of 1,2-dimethoxybenzene (9.67 g, 70 mmol, 8.9 mL) in CCl_4 (200 mL) and the mixture was stirred for 3 days at room temperature. The excess of bromine was then neutralized by adding a solution of sodium metabisulfite in water (0.5 mol L^{-1}). The solution was extracted three times with CH_2Cl_2. The organic layers were combined, washed with water, dried over $NaSO_4$ and concentrated under reduced pressure to yield 1,2-dibromo-4,5-dimethoxybenzene **1** (20.50 g, 69 mmol) as a white powder (99% yield). NMR ^1H ($CDCl_3$, 400 MHz): δ (ppm) = 7.04 (s, 2H); 3.84 (s, 6H); NMR ^{13}C ($CDCl_3$, 100 MHz): δ (ppm) = 148.88 (2C); 115.93 (2CH); 114.76 (2C); 56.27 ($2CH_3$).

Synthesis of 4′,5′-dimethoxy-1,1′:2′,1′′-terphenyl, 2

Into a round bottom flask were introduced successively 1,2-dibromo-4,5-dimethoxybenzene **1** (5.92 g, 20 mmol), phenylboronic acid (7.32 g, 60 mmol), toluene (50 mL) and sodium carbonate (6.36 g, 60 mmol) in water (30 mL). Nitrogen was bubbled into the mixture for 2 h at 60 °C. The catalyst ($Pd(PPh_3)_4$, 924 mg, 0.8 mmol) was then added and the reaction mixture was stirred for 23 h at reflux. Toluene was evaporated and the crude residue was extracted three times with CH_2Cl_2. The organic layers were combined and evaporated. Subsequent elution from silica gel with a dichloromethane–pentane mixture as eluent (50 : 50 then 60 : 40) gave the desired product. After concentration, the product was recrystallized in cyclohexane giving colorless crystals (5.65 g, 97% yield). NMR ^1H ($CDCl_3$, 400 MHz): δ (ppm) = 7.18 (m, 10H); 6.95 (s, 2H); 3.95 (s, 6H); NMR ^{13}C ($CDCl_3$, 100 MHz): δ (ppm) = 148.12 (2C); 141.40 (2C); 132.97 (2C); 129.94 (4CH); 127.86 (4CH); 126.26 (2CH);113.58 (2CH); 56.04 ($2CH_3$); HRMS (TOF ES+) $[M + H]^+$ ($C_{20}H_{18}O_2$): calculated: 291.1385; found: 291.1370.

Synthesis of 2,3-dimethoxytriphenylene, 3

Into a Schlenk tube were introduced 4′,5′-dimethoxy-1,1′:2′,1′′-terphenyl **2** (2.32 g, 8 mmol) and anhydrous $FeCl_3$ (3.24 g, 20 mmol). The Schlenk tube was purged three times with nitrogen and anhydrous CH_2Cl_2 (130 mL) and nitromethane (5 mL) were added. The reaction mixture was stirred for 5 h at room temperature. Methanol (80 mL) and water (80 mL) were added and stirred for five minutes. Organic solvents were evaporated and the resulting mixture was extracted three times with CH_2Cl_2. Organic layers were combined, washed with water, dried over $NaSO_4$ and evaporated under reduced pressure. The resulting solid was solubilized in a minimum amount of CH_2Cl_2 and filtered through a silica plug. After concentration, the product was recrystallized from toluene giving white crystals (1.93 g, 83% yield). NMR ^1H ($CDCl_3$, 400 MHz): δ (ppm) = 8.66 (m, 2H); 8.50 (m, 2H); 7.99 (s, 2H); 8.38 (m, 4H); 4.13 (s, 6H); NMR ^{13}C ($CDCl_3$, 100 MHz): δ (ppm) = 149.41 (2C); 129.46 (2C); 129.14 (2C); 127.03 (2CH); 126.27 (2CH); 124.15 (2C); 123.39 (2CH); 122.74 (2CH); 104.47 (2CH); 55.97 ($2CH_3$); HRMS (TOF ES+) (M + 1) ($C_{20}H_{16}O_2$): calculated: 289.1229; found: 289.1233.

Synthesis of triphenylene-2,3-diol, 4

Into a Schlenk tube was introduced 2,3-dimethoxytriphenylene **3** (577 mg, 2 mmol). The Schlenk tube was purged three times with nitrogen and anhydrous CH_2Cl_2 (60 mL) was added. The mixture was cooled at −78 °C under a nitrogen atmosphere. A solution of 1M BBr_3 in CH_2Cl_2 (8 mL, 8 mmol) was added dropwise. The reaction mixture was stirred while the temperature rose slowly from −78 °C to room temperature. The excess of BBr_3 was destroyed by reaction with water. The reaction mixture was extracted three times with CH_2Cl_2 and with ether. Organic layers were combined, washed with water, dried over $NaSO_4$ and evaporated under reduced pressure. The resulting solid was solubilized in hot toluene and filtered. Recrystallisation from toluene gave the desired white product (470 mg, 90% yield). NMR ^1H (DMSO-*d6*, 400 MHz): δ (ppm) = 9.65 (s, 2H); 8.72 (m, 2H); 8.43 (m, 2H); 8.01 (s, 2H); 7.61 (m, 4H); NMR ^{13}C (DMSO-*d6*, 100 MHz): δ (ppm) = 146.76 (2C); 129.12 (2C); 128.07 (2C); 127.27 (2CH); 125.97 (2CH); 123.42 (2CH); 122.75 (2C); 122.57 (2CH); 108.48 (2CH).

Synthesis of tris(2,3-triphenylenedioxy)cyclotriphosphazene, 5

Into a Schlenk tube were introduced triphenylene-2,3-diol **4** (729 mg, 2.8 mmol), hexachlorocyclotriphosphazene (325 mg, 0.93 mmol) and potassium carbonate (774 mg, 5.6 mmol). The Schlenk tube was purged three times with nitrogen and anhydrous THF was added (125 mL). The reaction mixture was stirred for 4.5 days at 40 °C. Solvent was evaporated and the resulting solid was washed twice with water and then with methanol. After recrystallisation in *o*-dichlorobenzene, the desired product was obtained as a white solid (641 mg, 76%). NMR ^{31}P (*o*-dichlorobenzene-*d6*, 400 MHz): δ (ppm) = 35 (3P); HRMS (TOF ES+) ($C_{54}H_{30}N_3O_6P_3$): calculated: 909.135; found: 909.026.

Crystal preparation

a) Guest free crystals of TTPP 5. Compound **5** was dissolved in hot tetrahydronaphthalene until the solubility limit was reached. The hot solution was filtered and the filtrate was introduced into a sealed tube. Crystals were grown by slow cooling from 200 °C to room temperature at a rate of 1 °C h^{-1}.

b) 1,2,4-trichlorobenzene–TTPP 5 inclusion adduct. The same procedure as for the guest free crystals was followed using 1,2,4-trichlorobenzene instead of tetrahydronaphthalene.

X-ray diffraction

Data collection. Because of the small crystal volume and small scattering power, synchrotron radiation was required for structure determination. Microdiffraction patterns were recorded at the ID23-2 structural biology microfocus beamline (European Synchrotron Radiation Facility - ESRF, Grenoble) where the beam is focussed down to approximately 8 μm in diameter.[19] Each sample was mounted on a nylon loop embedded with Paratone oil from Hampton Research (Fig. 1). Several crystals were tested to select a single crystal of suitable quality for data collection. The best **TTPP 5** crystal was approximately 100 × 5 × 4 μm^3 and the best 1,2,4-trichlorobenzene-**TTPP 5** inclusion adduct crystal was approximately 250 × 10 × 10 μm^3. Data were collected by the oscillation technique using a two-dimensional CCD detector (marMOSAIC; ~225 × 225 mm^2, 2048 × 2048 pixels and a pixel size of 0.073254 × 0.073254 mm^2). The measurements were carried out at a fixed temperature of 100(2) K using an Oxford 700 Cryostream device.

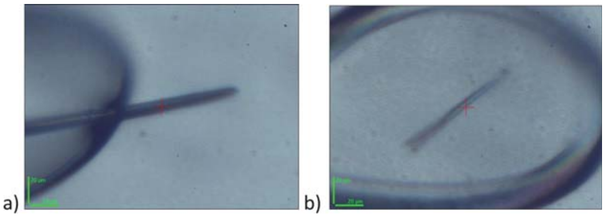


Fig. 1 Photographs of a) **TTPP 5** crystal and b) 1,2,4-trichlorobenzene-**TTPP 5** inclusion adduct crystal on a nylon loop embedded with Paratone oil. The red cross indicates the beam position.

X-ray diffraction

Structure solution and refinement. The frames were indexed and the reflections integrated using the XDS software suite.[20] Each reflection intensity was corrected from the action of intensity loss due to air absorption. XDS (in the CORRECT step) applies Lorentz and polarization factors as well as factors which partially compensate from damage and absorption effects to intensities and standard deviations of all reflections. These factors were determined from many symmetry-equivalent reflections usually found in the data images such that their integrated intensities become as similar as possible. Therefore, due to the small scattering volume of the crystal, absorption effects due to the crystal itself are expected to be very weak.

The crystal structure of the non-hydrogen atoms was determined by direct methods using SHELXS97.[21] Refinement was carried out with SHELXL97. After a few least-squares cycles, anisotropic displacement parameters were employed on all N, P, O and C atoms. The hydrogen atoms were placed in idealized positions with C–H = 0.95 Å during the refinement. Rings were refined without any constraints. SHELXS97 and SHELXL97 were used through the WinGX Graphical User Interface.[22]

Crystal data for TTPP 5

$C_{54}H_{30}N_3O_6P_3$, monoclinic, $P2_1/c$ (no.14), a = 14.909(2) Å, b = 31.013(4) Å, c = 9.0740(1) Å, β = 102.120(7)°, V = 4102.05(9) Å^3, T = 100(2) K, R_1 = 0.0401 for 6340 independent observed reflections [$F > 4\sigma(\mathrm{Fo})$], S = 1.027. Data collection: φ scans, 2° oscillation range, 1 pass of 2.5 s exposure time per image, 120 images, λ = 0.8726 Å, 16 bunch mode.

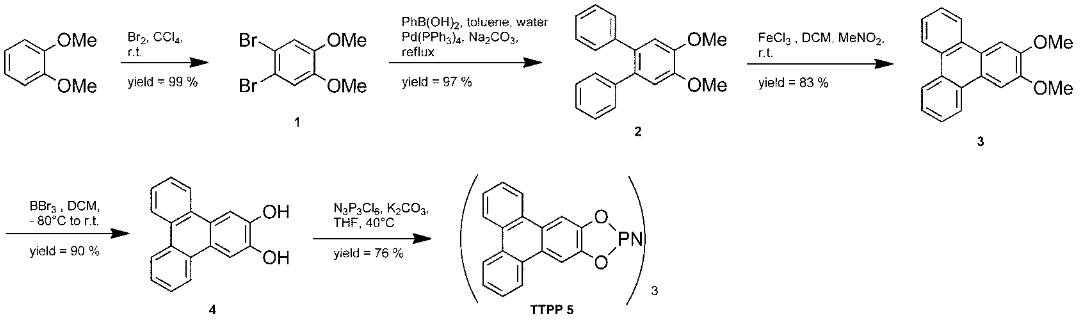
Crystal data for 1,2,4-trichlorobenzene-TTPP 5 inclusion adduct

$C_{54}H_{29}N_2O_6P_3$, 2 $C_6H_3Cl_3$ triclinic, $P\bar{1}$ (no.2), a = 8.769(2) Å, b = 15.024(2) Å, c = 21.216(2) Å, α = 94.818(3)°, β = 99.983(5)°, γ = 98.226(6)°, V = 2707.4(8) Å^3, T = 100(2)K, R_1 = 0.0669 for 6770 independent observed reflections [$F > 4\sigma(\mathrm{Fo})$], S = 1.043. Data collection: φ scans, 3° oscillation range, 1 pass of 0.8 s exposure time per image, 120 images, λ = 0.8726 Å, 7/8 multi-bunch mode.

Results and discussion

TTPP 5 synthesis

Compound **5** was prepared in five steps starting from veratrol (Scheme 1). Bromination of veratrol by bromine afforded the 1,2-dibromo-4,5-dimethoxybenzene (**1**) in 99% yield. Then, **1** underwent a double Suzuki coupling reaction with phenylboronic acid in the presence of $Pd(PPh_3)_4$ and Na_2CO_3 to obtain the 4′,5′-dimethoxy-1,1′:2′,1″-terphenyl (**2**) in 97% yield. The key step consisted of a cyclodehydrogenation of **2** mediated by $FeCl_3$ to give 2,3-dimethoxytriphenylene (**3**) in 83% yield. Deprotection of **3** by BBr_3 gave triphenylene-2,3-diol **4** in 90% yield. The final step consisted of the trisubstitution reaction of



Scheme 1 Five step synthesis of **TTPP 5.**

hexachlorocyclotriphosphazene by **4** to afford tris(2,3-triphenylenedioxy)cyclotriphosphazene **5** in 76% yield.

Crystal structure

a) Guest free crystal structure. Guest free **5** crystallized alone in a monoclinic unit cell with a space group of $P2_1/c$ (Fig. 2a). Each unit cell has four **TTPP** molecules. This structure does not contain any porosity in which guest molecules might accommodate. The packing arrangement is described by a columnar arrangement along the *c* axis of interdigitated **TTPP** molecules (Fig. 2b). Very short C–C distances could be observed between **TTPP** molecules constituting the stacks (C(17)–C(52) = 3.303 Å and C(17)–C(53) = 3.418 Å) suggesting a stabilization of the columns by π–π stacking interactions along the *c* axis. However, no short contacts could be observed between the columns. Only van der Waals interactions take place in the *ab* plane. The **TPhenP** guest free structure has not been reported yet and interestingly guest free-**TNP** crystallizes in a very different manner. In the latter, paddles are not wide enough to interact by π-stacking interactions and the structure is only stabilized by van der Waals interactions, showing the benefits of the larger paddles of the **TPhenP**.

b) Crystal structure of 1,2,4-trichlorobenzene host–5 inclusion adduct. When co-crystallized with an appropriate guest such as 1,2,4-trichlorobenzene, **TTPP 5** forms an organic clathrate. Two molecules of **TTPP 5** and four of 1,2,4-trichlorobenzene are disclosed in a triclinic unit cell with a $P\bar{1}$ space group (Fig. 3).

Host molecules interact by π–π stacking interactions and show very short C–C distances between the overlapping aromatic fragments (C(1)–C(11) = 3.293 Å and C(9)–C(17) = 3.359 Å). Guest molecules lie in two kinds of tunnel-like cavities. The dimensions of the smallest channel (Fig. 4, guest in red) are

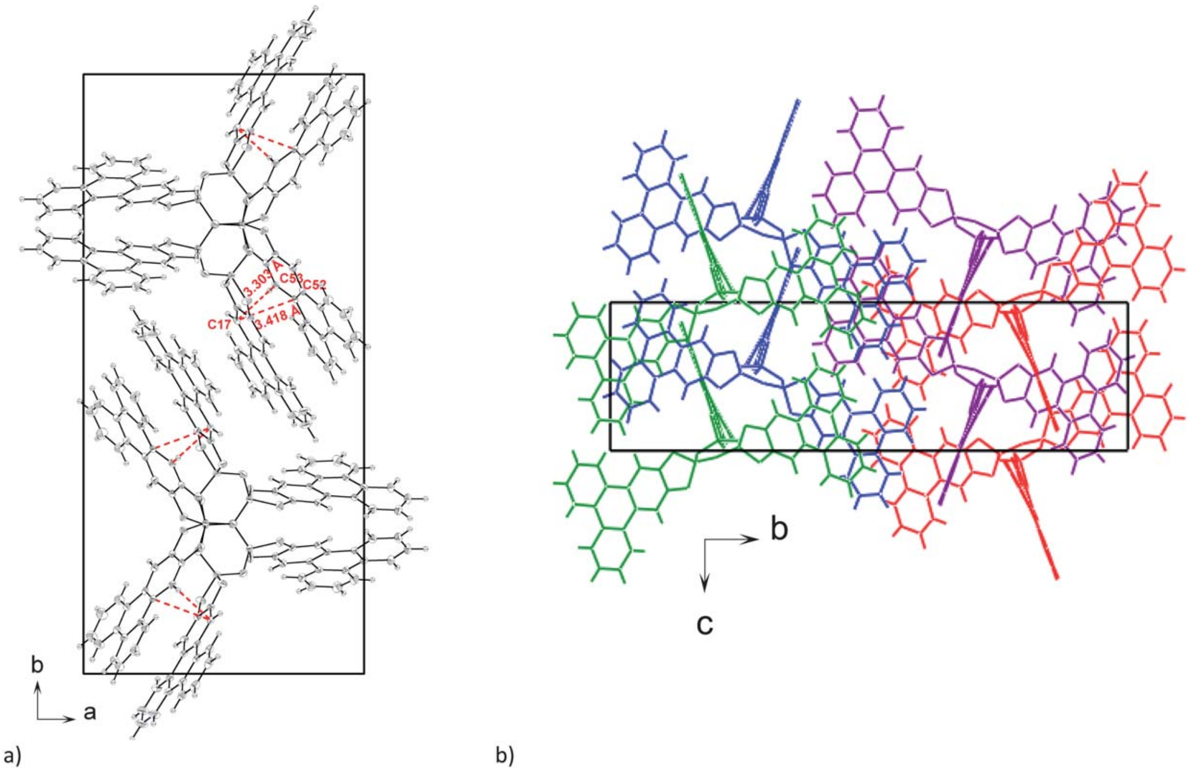


Fig. 2 **TTPP** in guest free crystal structure unit cell: a) View down *c*-axis (π–π interactions between triphenylene units appear in red), b) View down *a*-axis. Molecules present a columnar arrangement along *c*-axis. Molecules are colored for clarity.

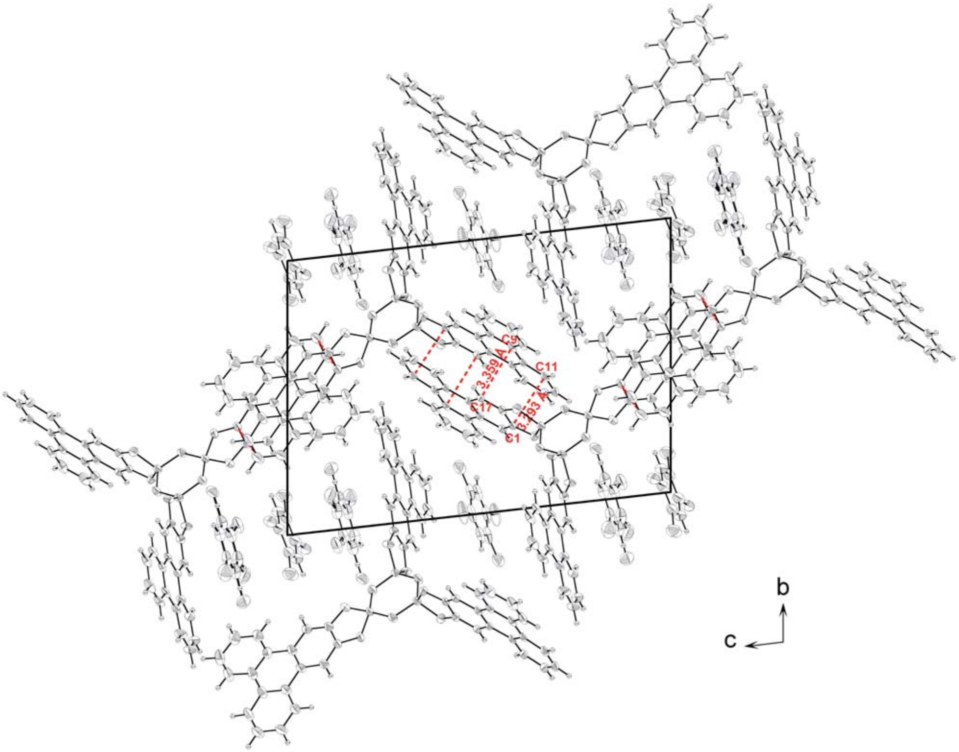


Fig. 3 Unit cell of 1,2,4-trichlorobenzene–**5** adduct (π–π interactions between triphenylene units appear in red).

approximately 6.1 × 8.4 Å^2 at the widest point. Along this channel, 1,2,4-trichlorobenzene molecules are stacked between two adjacent triphenylene units in one type of environment. However, four different orientations are possible. As a result, disorder at the positions of the chlorine atoms is observed. Each chlorine (Cl_8 and Cl_9) atom has an occupation rate of 0.75. The dimensions of the biggest channel (Fig. 4, guest in blue) are approximately 10.7 × 12.4 Å^2 at the widest point. Three guest molecules in the same plane have two different environments: two molecules in the closest positions from the cavity walls are stacked with their adjacent triphenylene unit, and one molecule in the center of the tunnel-like cavities lies between the other two guest molecules.

Molecules located at the channel periphery have two different possible orientations, with one preferred over the other with a ratio of 80/20. Disorder at chlorine positions is modeled with different occupancies: $Cl_3 = 1$, $Cl_2 = 0.8$, $Cl_4 = 0.2$, $Cl_5 = 0.2$ and $Cl_1 = 0.8$. Molecules located at the center of the channel have two possible orientations. Disorder at chlorine positions is modeled by occupancy factors of 1 for Cl_6 and 0.5 for Cl_7.

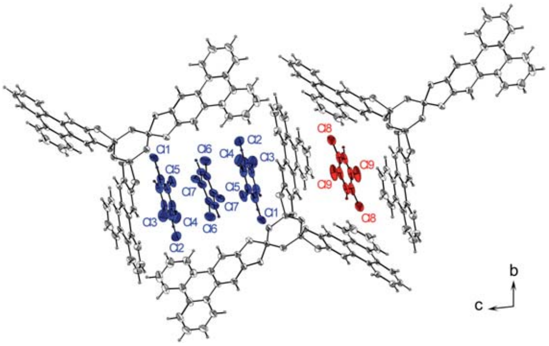


Fig. 4 Tunnel-like cavities containing guest molecules.

This structure is comparable to the one reported for the **TPhenP** inclusion compound of *p*-xylene which presents two different kinds of channel. However, longer paddles offer larger pore sizes, which permit the inclusion of three molecules of solvent instead of the two reported in literature.

Molecular structures

Aromatic side groups lie perpendicular to the plane of the phosphazene ring according to the tetrahedral geometry of the phosphorus atoms (Fig. 5 and Fig. 6). **TTPP** molecules have a radial distribution of triphenylene units with an almost 3-fold arrangement for both guest free and guest containing structures.

This orientation is known to be a consequence of the spirocyclic 5-membered ring strain and was already reported for **TPP**, **TNP** and **TPhenP** molecules.[4,16,17] However, this particular behavior is generally not observed for guest free structures.

For example, **TNP** adopts a very different geometry when crystallized alone.[23] Interactions and C_3 geometry do not match each other. In order to stabilize the network structure, **TNP** molecules lose their 3-fold arrangement. Side groups are bent away at the oxygen atom and a compact packing is obtained. However, when **TNP** molecules are co-crystallized with guest compounds such as benzene, a hexagonal lattice is formed in which the C_3-symmetry is retained by stabilizing host–guest interactions and by guest “cushioning”.

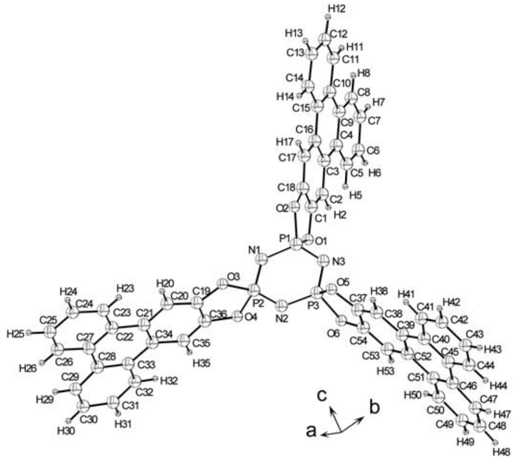


Fig. 5 Molecular structure of **TTPP** in 1,2,4-trichlorobenzene–**TTPP 5** inclusion adduct.

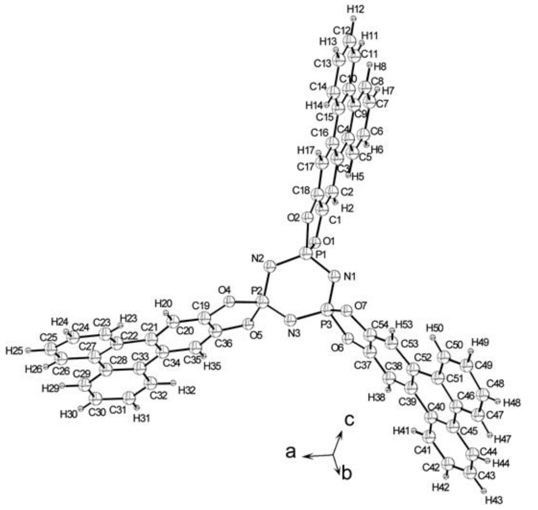


Fig. 6 Molecular structure of **TTPP 5** in guest free crystal structure.

Interatomic distances and angle values are comparable for **TTPP** molecules in both crystal structures and are close to those reported for the **TNP** host in guest containing hexagonal structures. Mean values for triphosphazene and five-membered spirocyclic rings are reported in Table 1 and Table 2.

There is however a noteworthy difference in the **TTPP** molecular structure between the two crystal structures. In the guest free crystal, triphenylene side groups are oriented above and below the cyclotriphosphazene mean plane. Consequently, the cyclotriphosphazene ring is slightly distorted in a boat like conformation. This distortion comes from a π-interaction between each **TTPP** within the columnar arrangement. For 1,2,4-trichlorobenzene inclusions, the phosphazene ring is planar indicating that in this lattice, hosts are less constrained.

Table 1 Bond lengths (Å) and bond angles (deg) in **TTPP** in guest free crystal structure (mean values)

P–N	1.582	O–C	1.395
P–O	1.619	C–C	1.392
N–P–N	117.3	N–P–O	110.2
P–N–P	121.8	P–O–C	109.8
O–P–O	96.9	O–C–C	111.7

Table 2 Bond lengths (Å) and bond angles (deg) in **TTPP** in 1,2,4-trichlorobenzene-**TTPP** structure (mean values)

P–N	1.583	O–C	1.398
P–O	1.620	C–C	1.388
N–P–N	117.3	N–P–O	110.1
P–N–P	122.4	P–O–C	109.4
O–P–O	97.3	O–C–C	111.9

Conclusions

A porous network based on a cyclotriphosphazene core has been elaborated from tris(2,3-triphenylenedioxy)cyclotriphosphazene (**TTPP**) as the host. **TTPP** exhibits larger channel sizes than those previously reported. The porosity of the 1,2,4-trichlorobenzene–**TTPP** inclusion adduct has been modulated compared to the *p*-xylene–**TPhenP** adduct while maintaining the same topology. Since the inclusion compound is stabilized by π–π stacking interactions, a better stability is expected. Studies of the structural stability are currently in progress. In parallel, the influence of guest molecules on the **TTPP** crystal structure, optical and conductive properties are also under investigation.

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