Cyclotriphosphazene \([N_3P_3(2,2’-dioxynaphthalene)_2-(4-pyridinoxy)_2]\) and its halogen bonded complex with 1,4-diiodotetrafluorobenzene

Roberta Bertani, Elena Ghedini, Mario Gleria, Pierangelo Metrangolo*, Hannes Neukirch, Tullio Pilati and Giuseppe Resnati*

* Department of Chemical Engineering Processes; University of Padua; 35125 Padua, Italy.
† C.N.R.-Institute of Molecular Sciences and Technologies c/o Department of Chemical Sciences; University of Padua; 35131 Padua, Italy.
‡ NFMLab - Department of Chemistry, Materials, and Chemical Engineering “G. Natta”; Polytechnic of Milan; 20131 Milan, Italy. Fax: +39 02 2399 3080; Tel: +39 02 2399 3032 (G. R.), 3041(P. M.); E-mails: giuseppe.resnati@polimi.it; pierangelo.metrangolo@polimi.it; Web-site: http://nfmlab.chem.polimi.it

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Electronic Supplementary Information
Experimental Methods

General:

Commercially available chemicals were used without further purification, unless otherwise stated. Chemicals were purchased from Apollo Scientific, Fluka and Sigma-Aldrich. All reactions were carried out under nitrogen atmosphere. K$_2$CO$_3$ was dried at 413 K prior to use. Acetone used as solvent was predistilled from KMnO$_4$ and distilled twice from anhydrous CaSO$_4$. Methanol was distilled from CaH$_2$. Hexachlorocyclotriphosphazene (N$_3$P$_3$Cl$_2$) (Fluka) was recrystallized from hot petroleum ether and dried in vacuum.

Single crystal X-ray diffraction measurements were performed on a Bruker APEX-CCD diffractometer, graphite monochromator Mo-Kα radiation (λ = 0.71073 Å), equipped with an OXFORD low temperature device.

IR spectra were taken on a FT-IR Nexus (4000-400 cm$^{-1}$) of the Nicolet Instrument Corporation equipped with the Smart Endurance UATR system; the wavenumbers (ν) are given in cm$^{-1}$. The temperature-dependent IR spectra in the gas phase were recorded with a Nicolet Nexus FT-IR spectrophotometer equipped with the Specac Eurotherm 2216E controller and a Hellma gas cell.

$^1$H- and $^{31}$P-NMR solution spectra were obtained at 298 K on Bruker Avance DRX-400 and Bruker AC-200 spectrometers.

The melting point of the crystals of pure 1 was established with a Reichert- Instrument by observing the melting processes through an optical microscope.

The thermal analysis of 3 was recorded with a Linkam DSC600 Stage (temperature range: 77 K to 873 K, heating rate 10°/min) coupled with the LN94 cooling system.

Synthesis:

Compound 1 was prepared starting from [N$_3$P$_3$Cl$_2$(O$_2$C$_{12}$H$_8$)$_2$] (see: G. A. Carriedo, L. Fernandez-Catuxo, F. J. Garcia-Alonso, P. Gomez-Elipe, P. A. Gonzalez, Macromolecules 1996, 20, 5320)

**IR** (KBr; cm\(^{-1}\), selected bands): \( \nu_{\text{CH}} 3067, 3032; \ \nu_{\text{C=C}} \) and \( \nu_{\text{C=N}} 1576; \ \delta_{\text{pyridine ring}} 994, \ \nu_{\text{POAr}} 975; \ \nu_{\text{PN}} 1230 \) and 1173.

\(^{31}\text{P NMR (CDCl}_3\): \( \delta \) 25.30 (d, \(^2\text{J}_{\text{PP}} 96.7 \text{ Hz})\); 9.70 (dd, \(^2\text{J}_{\text{PP}} 99.5 \text{ Hz})\); 8.55 (dd, \(^2\text{J}_{\text{PP}} 99.3 \text{ Hz})\)

\(^1\text{H NMR (CDCl}_3\): \( \delta \) 7.07-8.66

**Crystallization of 1**: Cyclotriphosphazene 1 was dissolved in a vial of clear borosilicate glass at room temperature. Chloroform was used as solvent. The open vial was placed in a closed cylindrical wide-mouth bottle containing CCl\(_4\). CHCl\(_3\) was allowed to diffuse at room temperature and after 3 days white crystals of 1 were obtained.

**Mp** (CHCl\(_3\)): 519-523 K.

**Formation of the molecular complex 3**: Equimolar amounts of cyclotriphosphazene 1 and 1,4-diiodotetrafluorobenzene 2 were dissolved in a vial of clear borosilicate glass at room temperature. Chloroform was used as solvent. The open vial was placed in a closed cylindrical wide-mouth bottle containing CCl\(_4\). CHCl\(_3\) was allowed to diffuse at room temperature and after 3 days white crystals of 3 were obtained.

**Mp** (CHCl\(_3\), onset temperature): 512 K (with decomposition).

**IR** (cm\(^{-1}\), selected bands): \( \nu_{\text{CH}} 3069, 3034; \ \nu_{\text{C=C}} \) and \( \nu_{\text{C=N}} 1580 (3); \ \nu_{\text{C=C}} 1462 (2); \ \delta_{\text{pyridine ring}} 999, \ \nu_{\text{POAr}} 971; \ \nu_{\text{PN}} 1221 \) and 1166.

**Temperature-dependent IR spectra of 3**: The spectra were recorded at the following temperatures (K): 313, 323, 333, 338, 343, 348, 353, 363, 373, 378, 383, 388, 393, 398, 403, 408, 413, 423, 433.
Figure S1. Thermal Analysis of 3.