Cyclotriphosphazene [N₃P₃(2,2'-dioxybiphenyl)₂-(4-pyridinoxy)₂] and its halogen bonded complex with 1,4-diiodotetrafluorobenzene

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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. K₂CO₃ was dried at 413 K prior to use. Acetone used as solvent was predistilled from KMnO₄ and distilled twice from anhydrous CaSO₄. Methanol was distilled from CaH₂. Hexachlorocyclotriphosphazene (N₃P₃Cl₂) (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-*K* α radiation ($\lambda = 0.71073$ 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.

¹H-, and ³¹P-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 [N₃P₃Cl₂(O₂C₁₂H₈)₂] (see: G. A. Carriedo, L. Fernandez-Catuxo, F. J. Garcia-Alonso, P. Gomez-Elipe, P. A. Gonzalez, *Macromolecules* 1996, **20**, 5320) according to the procedure described in the ref. G. A. Carriedo, F. J. Garcia Alonso, J. L. Garcia, R.

J. Carbajo, F. Lopez Ortiz, Eur. J. Inorg. Chem. 1999, 1015.

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

³¹P NMR (CDCl₃): δ 25.30 (d, ²J_{PP} 96.7 Hz); 9.70 (dd, ²J_{PP} 99.5 Hz); 8.55 (dd, ²J_{PP} 99.3 Hz)

¹H NMR (CDCl₃): δ 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 CCl₄. CHCl₃ was allowed to diffuse at room temperature and after 3 days white crystals of **1** were obtained.

Mp (CHCl₃): 519-523 K.

Formation of the molecular complex 3: Equimolar amounts of cyclotriphosphazene **1** and 1,4diiodotetrafluorobenzene **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 CCl₄. CHCl₃ was allowed to diffuse at room temperature and after 3 days white crystals of **3** were obtained.

Mp (CHCl₃, onset temperature): 512 K (with decomposition).

IR (cm⁻¹, selected bands): v_{CH} 3069, 3034; $v_{C=C}$ and $v_{C=N}$ 1580 (3); $v_{C=C}$ 1462 (2); $\delta_{pyridine ring}$ 999, v_{POAr} 971; v_{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.

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Figure S1. Thermal Analysis of 3.

