The reactions of non-gem-hexanedioxytetrachlorocyclotriphosphazene with 2-(2-hydroxyethyl)thiophene, benzyl alcohol and 1,1,3,3-tetramethylguanidine. Spectroscopic studies of the derived products.

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**Supplemental Materials**

**Synthesis of 2,4,6,6-tetrachloro-2,4-(hexane-1,6-dioxy)cyclotriphosphazatriene, N3P3Cl4[O(CH2)6O] (1):**

Compound **1** was synthesized and evaluated using conventional methods according to the literature [32, 43]. Cyclochlorotriphosphazene, N3P3Cl6, (8 g, 22.99 mmol) was dissolved in THF (150 mL) and placed in a 500 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and to the stirred solution, pyridine (7.27 g, 91.95 mmol) in dry THF (20 mL) was quickly added under an argon atmosphere. Solid 1,6-hexane-diol (5.42 g., 45.98 mmol) in dry THF (25 mL) was then added dropwise to the reaction mixture whiles stirring at room temperature (1 h). Then the reaction mixture was left stirring for a further 36 h and the reaction was followed on TLC silica gel plates using benzene/diethyl ether (3:1). After attaining room temperature, the pyridine hydrochloride and the other insoluble materials were filtered off and the filtrate was concentrated (25 mL). TLC revealed the formation of the two major and two minor compounds. Separation of these compounds was achieved by using column chromatography (240 g, silica gel, and a solvent system of benzene: diethyl ether (4:1) as the eluent. Fractions containing the major compounds were collected, taken to dryness, and then the residue recrystallized from light petroleum (b.p. 40-60 0C) containing a few drops of benzene. (**i**) The first cyclophosphazene derivative was identified as the isomeric mono spiro derivative, N3P3Cl4[O(CH2)6O] (3.2%). (**ii**) The second compound was identified as single-bridged derivative, N3P3Cl5[O(CH2)6O]2N3P3Cl5 (6.4%). (**iii**) The third compound was identified as the mono-ansa compound, N3P3Cl4[O(CH2)6O], 2,4,6,6-tetrachloro-2,4-(hexane-1,6-dioxy)cyclotriphosphazatriene (**1**), an oil, yield 1.16 g (25.3%). Anal. Cal. for C6H12O2N3P3Cl4 (M, 392.9); C, 18.34: H, 3.08; N, 10.69%. Found: C, 18.37; H, 3.13; N, 10.68%; [M+H]+, 393.7. 1H NMR, 298 K (CDCl3); δPOCH2: 4.32/4.15, δPOCCH2: 1.70, δPOCCCH2:1.57/1.38 *3J*(PH): 21.0/22.70 Hz. 31P NMR, (CDCl3), δPCl2: 26.90, δP(OR)Cl: 19.92, *2J*[PCl2–P(OR)Cl]: 67.3 Hz.

(**iv**) The fourth compound was identified as the double-bridged derivative, N3P3Cl4[O(CH2)6O]2N3P3Cl4 derivatives (48%). (**v**) The fifth compound was identified as tri-bridged, N3P3Cl3[O(CH2)6O]3N3P3Cl3 derivative (17.1%).



**Figure S 1**.{31P-1H} decoupled NMR spectrum of compound **6**, in CDCl3 at 162.00 MHz, (room temperature), referenced to external 85% H3PO4.

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**Figure S 2**. {31P-1H} decoupled NMR spectrum of compound **8**, in CDCl3 at 162.00 MHz, (room temperature), referenced to external 85% H3PO4.



**Figure S 3**: TLC-MS spectrum of compound **6**.



**Figure S 4**: TLC-MS spectra of compounds (a) **1** and (b) **9**.