
Phosphazene-Based Ionic Liquids

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Abstract

This chapter presents the definition, synthesis, and possible application of cyclo and polyphosphazene-based ionic liquids (PzILs). PzILs constitute an alternative class of phosphorus nitrogen compounds and their derivatives have been widely used in biologically-active materials, electrolytes, lubricants, catalysts or nanomaterials. Considerable information is available on substitution reactions taking place at the phosphorus atoms of poly and cyclophosphazenes, thus, a wide variety of phosphazene derivatives have been obtained. However, quaternization of ring nitrogen atoms has received less attention. In addition, phosphazenes containing aliphatic and aromatic substituents with terminal tertiary amino groups are synthesized and subsequently quaternized with methyl iodide. The successive metathesis with salts such as $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ or NaBF_4 gives the respective PzILs. In the compounds identified as protonic ionic liquids (PILs) or protic molten salts (PMOSs), the positively charged position is determined by X-ray diffraction study. PzILs are also soluble in water and in many polar organic solvents.

Keywords: phosphazene-based ionic liquid, biologically-active material, electrolyte, lubricant, catalyst

1. Introduction

Phosphazenes, which are cyclic or linear chain inorganic compounds formed by the bonding and repetition of phosphorus and nitrogen atoms with $(\text{P}=\text{N})_n$ bonds, comprise an important class of inorganic compounds (**Figure 1**). There are many phosphazene compounds ranging from oligomers to polymers. Among the phosphazene compounds, the hexachlorocyclotriphosphazene ($\text{N}_3\text{P}_3\text{Cl}_6$, trimer) and octachlorocyclotetraphosphazene ($\text{N}_4\text{P}_4\text{Cl}_8$, tetramer) derivatives have attracted considerable attention (**Figure 1a,b**) [1]. The reaction of PCl_5 with NH_4Cl in a chlorinated solvent gives a mixture of colorless solids of the formula $(\text{NPCl}_2)_n$. As the most popular compounds $\text{N}_3\text{P}_3\text{Cl}_6$ and $\text{N}_4\text{P}_4\text{Cl}_8$ are readily separated by

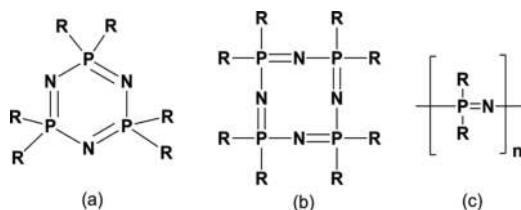


Figure 1. Phosphazene structures.

distillation under reduced pressure. Cyclic phosphazene compounds containing five, six, seven and higher $-P=N$ units are also known, but these compounds are not very common [2]. Polyphosphazenes are inorganic-organic polymers containing alternate phosphorus and nitrogen atoms, each skeletal phosphorus atom having bonds with one or more organic or inorganic substituent (**Figure 1c**) [3].

Phosphazenes exhibit highly customizable physical and chemical characteristics which depend on the substituents bonded to the phosphorus atom. Thus, they have found wide application in a variety of fields involving their use in rechargeable batteries [4], membranes [5] and lubricants [6], liquid crystals [7], anticancer agents [8], antibacterial reagents [9], flame-retardants [10], biological materials [11], and synthetic bones [12].

This chapter deals with the structures and applications of PzILs which are formed by quaternization of the ring nitrogen or phosphorus in the phosphazene, or the nitrogen atom in the substituent bonded to the phosphorus atom.

2. Phosphazene-based ionic liquids

The PzIL consists of repeating phosphorus-nitrogen units having a pendant group bonded to the phosphorus atoms of the phosphazene. PzILs may have cyclic or linear structure (**Figure 2**). The positive charge is positioned in a substituent attached to the phosphorus atom, or in the skeleton nitrogen or phosphorus atom. The positive charge's position is reported to be effective on the stability, viscosity and other properties of PzIL [13].

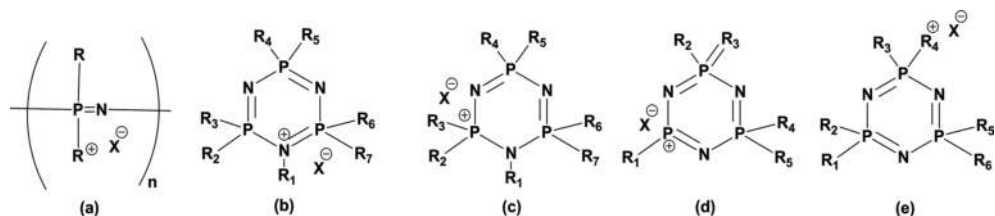


Figure 2. General chemical structure of PzILs.

2.1. Phosphazene-based ionic liquids in which quaternization occurs on the nitrogen atom or phosphorus atom of phosphazene

Ring and the exocyclic nitrogens are two possible basic sites of cyclophosphazenes. The formation of the protonation and the pK_a ' values of cyclophosphazene derivatives were investigated in the literature [14–16]. The ring-nitrogen protonation of cyclophosphazene bases with HCl, HBr, HF, $HClO_4$, and CH_3COOH were supported by infrared and NMR data [17, 18]. The protonation of the ring was determined by the crystal structure of $N_3P_3Cl_2(NHPr^i)_4 \cdot HCl$ and $[N_3P_3HCl_4(NH_2)_2]^+ [N(POCl_2)_2]^-$ (Figure 3) [19, 20].

Reportedly, the reactions of $N_3P_3Cl_6$ with $AlCl_3$, $AlBr_3$, $GaCl_3$ under anaerobic conditions or in the presence of water or HX yielded protonated phosphazenes $P_3N_3Cl_6 \cdot HMX_4$. The protonated species distorted the P_3N_3 ring and weakened the two P–N bonds that flank the protonated nitrogen. The crystal structures of $N_3P_3Cl_6 \cdot HAlCl_4$, $N_3P_3Cl_6 \cdot HGaCl_4$, $N_3P_3Cl_6 \cdot HAlBr_4$ are shown in Figure 4 [21, 22].

Despite the low basicity and nucleophilicity, various phosphazenium compounds have been obtained using potent electrophilic reagents based on carborane anions. (Figure 5) [18].

N-alkyl phosphazenium cations are obtained by alkylation of the ring nitrogen atom of cyclotriphosphazenes containing organoamino substituents with alkyl halides (Figure 6). As

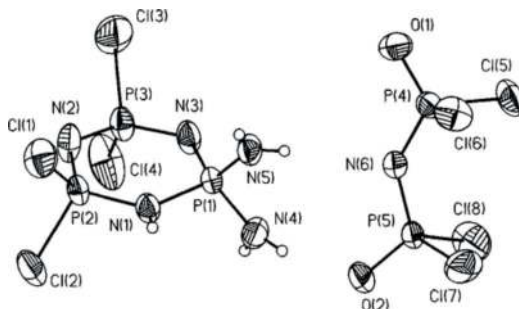


Figure 3. The crystal structure of $[N_3P_3HCl_4(NH_2)_2]^+ [N(POCl_2)_2]^-$.

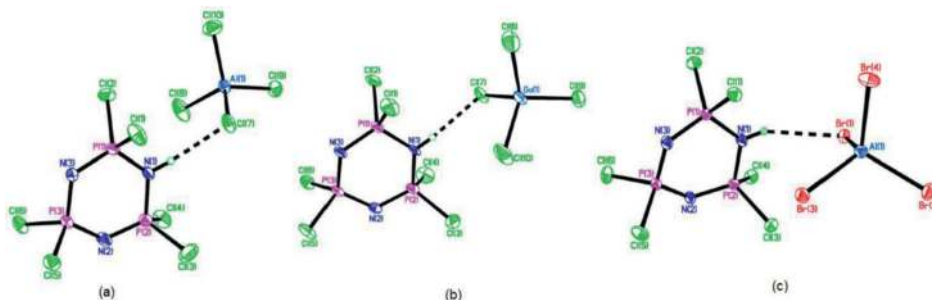


Figure 4. The crystal structures of $N_3P_3Cl_6 \cdot HMX_4$, (a) $N_3P_3Cl_6 \cdot HAlCl_4$; (b) $N_3P_3Cl_6 \cdot HGaCl_4$; (c) $N_3P_3Cl_6 \cdot HAlBr_4$.

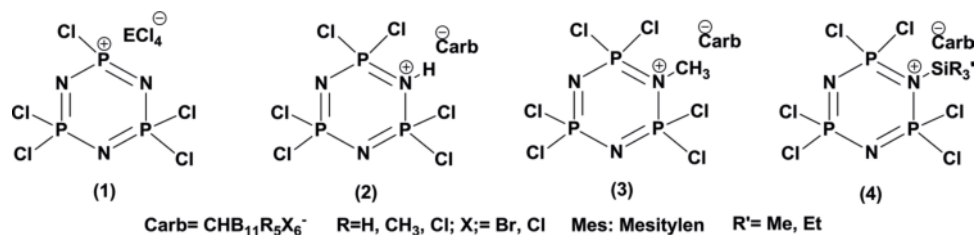


Figure 5. N-protonated, N-methylated, and N-silylated adducts of $\text{N}_3\text{P}_3\text{Cl}_6$.

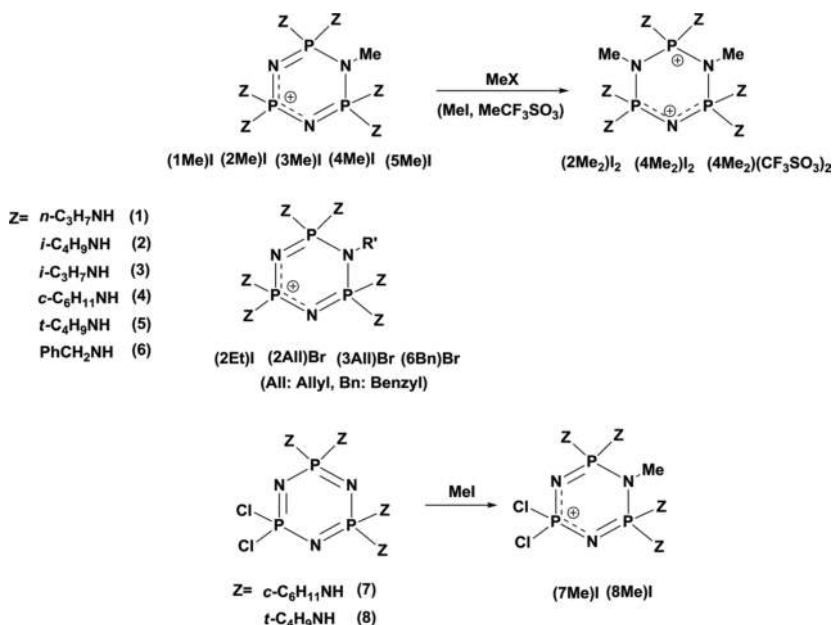


Figure 6. N-alkyl phosphazhenium salts.

observed in the X-ray crystal structures, the associated P-N bonds of the alkylation of the ring N sites are significantly longer. Highly stable phosphazhenium salts generate complex supra-molecular networks with $\text{NH}\dots\text{X}$ interactions in the solid state (Figure 7). N-Alkyl phosphazhenium salts react with silver nitrate to form complexes with silver ions. Depending on the steric requirement of the RNH substituents, one or both of the free ring nitrogen sites are coordinated with silver ions (Figure 8) [23].

Industrial application of High performance nonmetallic molecular phosphazene catalysts involves the synthesis of polypropylene glycols (PPGs). Phosphazhenium salts (PZN) have giant cations that are 10–12 Å in diameter and they exhibit unique catalytic behavior in various anionic organic reactions that are highly demanded in chemical industry (Figure 9). Reportedly, a phosphazhenium ion (a macrocationic species), should considerably activate anionic active species [24, 25].

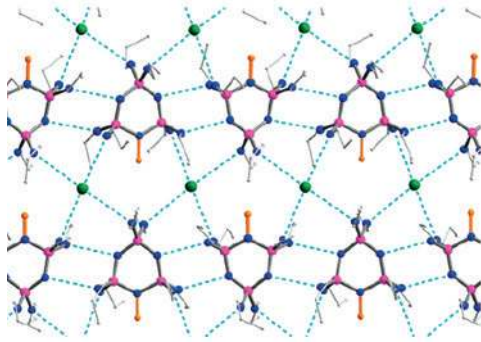


Figure 7. Supramolecular structure of (1Me)I. The dashed lines show hydrogen bonds.

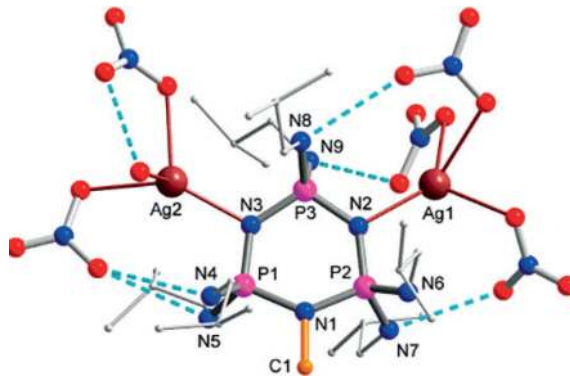


Figure 8. The crystal structure of $\text{Ag}_2[2\text{Me}](\text{NO}_3)_3 \cdot \text{H}_2\text{O}$.

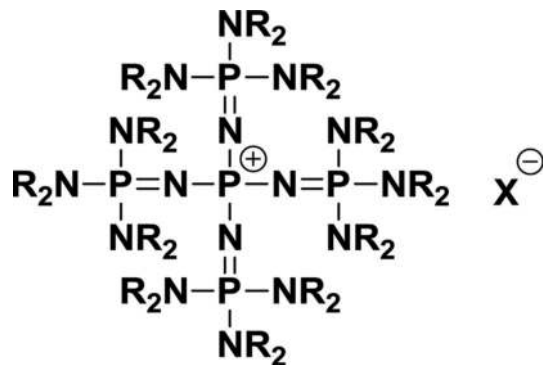


Figure 9. Chemical structure of phosphazanium salt (PZN).

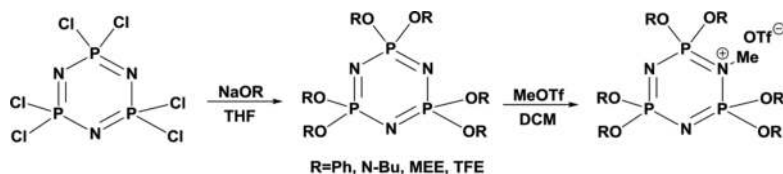


Figure 10. Quaternization of the cyclotriphosphazenes.

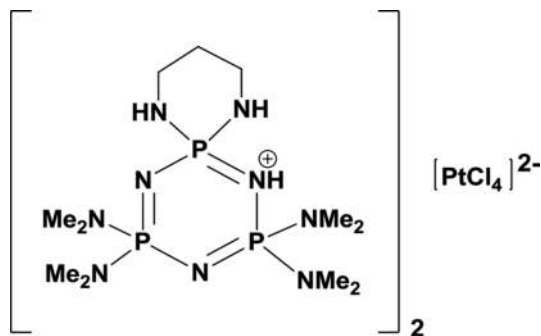


Figure 11. Mono protonated cyclotriphosphazene, $[\text{HN}_3\text{P}_3(\text{NMe}_2)_4(\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NH})]_2[\text{PtCl}_4]$.

Organophosphazenes bearing -OR substituted groups are readily quaternized at the ring nitrogen atoms to form phosphazene cations with alkyl halides, methyl trifluoromethanesulfonate ($\text{CF}_3\text{SO}_3\text{CH}_3$) or trimethylxonium tetrafluoroborate $[(\text{CH}_3)_3\text{O}(\text{BF}_4)]$ (Figure 10). Lower electron densities at the ring nitrogen atoms render alkoxy or aryloxy-substituted cyclotriphosphazenes inert to iodomethane at room temperature or lead to the rearrangement of the alkoxyphosphazene to the N-alkyloxophosphazene at higher temperatures [26].

The transition metal chemistry of cyclophosphazenes has also attracted great interest. The nature of cyclophosphazene-adducted compounds usually depends both on the phosphazene base and the corresponding Lewis acid. For example, for the $\text{N}_6\text{P}_6(\text{NMe}_2)_{12}\cdot\text{CuCl}_2$, Lewis acid is not bonded to a particular ring atom. However, it is located on the ring and is attached to more than one nitrogen atom [27]. A mono protonated (amino) *spiro* cyclic cyclotriphosphazene salt was synthesized and its crystal structure was clarified. The protonation occurs at one of the nitrogen atoms adjacent to the spiro phosphorus atom of the P_3N_3 ring (Figure 11). The protonation caused elongation of the P-N bonds in the ring and puckering of the phosphazene ring. In the crystal lattice, 2n cyclophosphazanium cations are connected by $n[\text{PtCl}_4]^{2-}$ anions with N-H...Cl hydrogen bonds to generate a linear polymeric structure [28]. A great number of cyclophosphazanium cations with metal anions, such as $[\text{HN}_3\text{P}_3(\text{NMe}_2)_6][\text{Mo}_6\text{O}_{19}]$, $[\text{HN}_3\text{P}_3(\text{NMe}_2)_6][\text{CoCl}_4]$, $[\text{MeN}_4\text{P}_4\text{Me}_8][\text{Cr}(\text{CO})_5\text{I}]$, $[\text{HN}_4\text{P}_4\text{Me}_8][\text{CoCl}_4]$, $[\text{H}_2\text{N}_4\text{P}_4\text{Me}_8][\text{PtCl}_4]$ and $[\text{H}_2\text{N}_5\text{P}_5\text{Me}_{10}][\text{CuCl}_4]$, have been obtained.

2.2. Phosphazene-based ionic liquids in which quaternization occurs on a pendant group of phosphazene bonded to a phosphorus atom

Due to the more sterically suitable positions of the nitrogen atoms of the phosphazene ring, the alkylation occurred at the exocyclic nitrogen atoms Rapko and Feistel presented the parameters in their study on the dialkyl cation of hexakisdimethylamino cyclotriphosphazene ($[\text{N}_3\text{P}_3(\text{NMe}_2)_6(\text{Me})_2]^{2+}[(\text{BF}_4^-)_2]$), (**Figure 12**). The position of the alkylation was investigated by hydrolytic degradation of the obtained cyclotriphosphazene salts [29].

Allcock et al. synthesized phosphazanium iodide salts by quaternization of several cyclic phosphazenes either at side-group sites or at the skeletal nitrogen atom (**Figure 13**). With the exception of piperidino derivatives, in which case the reactive sites were the skeletal nitrogen atoms, quaternization occurred at the side-group sites. The compound $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{N}(\text{CH}_3)_2$ was not quaternized, since the side-group nitrogen atoms are directly attached to the phosphazene ring due to their protected or inactivated nature [30].

2.3. Applications of phosphazene-based ionic liquids

PzILs are prepared by quaternization of a wide variety of phosphazenes either at the side-group or at the skeletal nitrogen atoms. These ILs have been used as anticancer, antibacterial reagents [31–34], adsorbents and surface modifiers of fluorescent nanoparticles [35], lubricants [36, 37], chemosensors for metal ions [38], electrolyte solutions for energy storage devices [39–41], as gate dielectric layer for OFETs [42], or as polyelectrolytes [26, 43, 44].

2.3.1. Anticancer, antibacterial reagents

Several studies have been performed on cyclotriphosphazene-based protic molten salts (PMOSs) synthesized with cyclotriphosphazenes and bulky organic acids. Recently, aminocyclotriphosphazenes have received greater attention due to their anti-cancer agent properties [45, 46]. In contrast to cyclotriphosphazene derivatives, there are not many studies related to cyclotriphosphazene salts as antimicrobial and anticancer agents [31–34]. Phosphazanium salts are very soluble in common apolar and polar organic solvents and some are quite soluble in water. Solubility in biological liquid is very important in pharmacological studies.

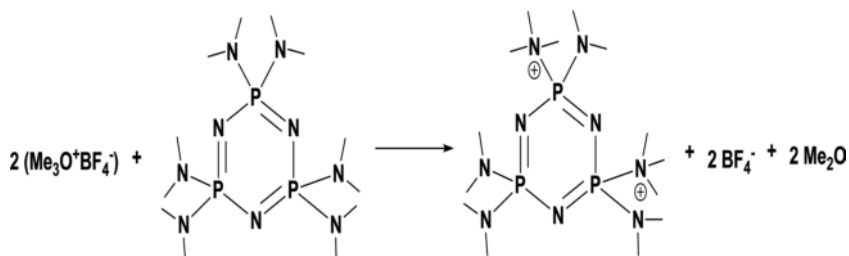


Figure 12. The synthesis of dimethyl hexakisdimethylamino cyclotriphosphonium difluoroborate.

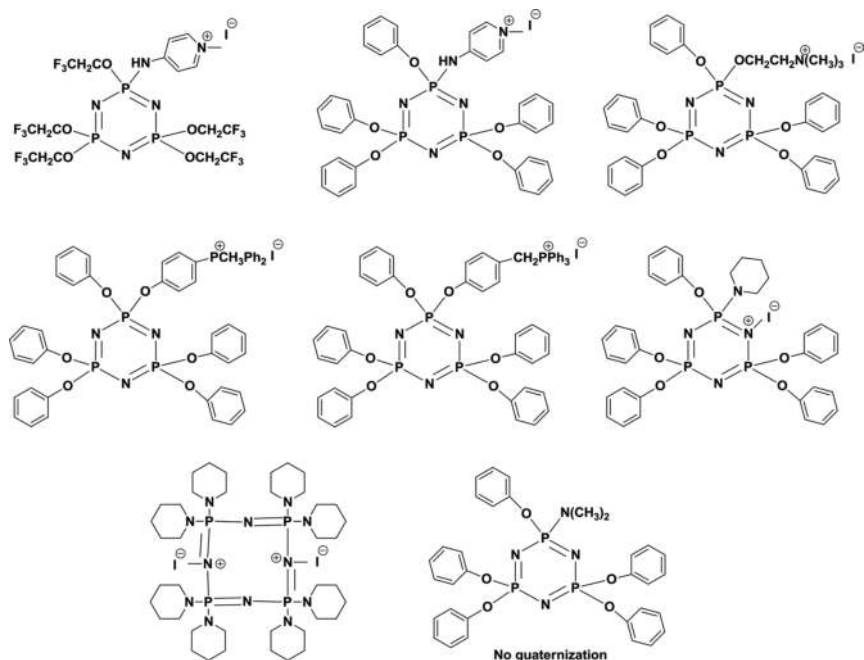


Figure 13. Various cyclotriphosphazene iodide salts.

Therefore, studies on the biological and anti-cancer activities of the salts of cyclotriphosphazenes are likely to attract great interest because of their organic solvent/water solubility and various PMOS diversity with different properties.

Akbaş et al. prepared the salicylic acid salts (1–6) of pyrrolidine and piperidine substituted cyclotriphosphazenes (Figure 14). The crystallographic data of 5 clearly indicate that the nitrogen of the phosphazene ring was protonated (Figure 15). The antimicrobial and cytotoxic activities of the phosphazene salts (1–6) were also investigated. Compounds 5 and 6 appear to be good candidates for anti-cancer agents because they have significant cytotoxic activity against DLD-1 cancer cells. All of the compounds have an antimicrobial effect on bacterial and yeast strains between 312 and 625 μM (bacterial strains) and 19.5–312 μM (yeast strains) and compounds 4–6 are found to be most effective against yeast strains [31].

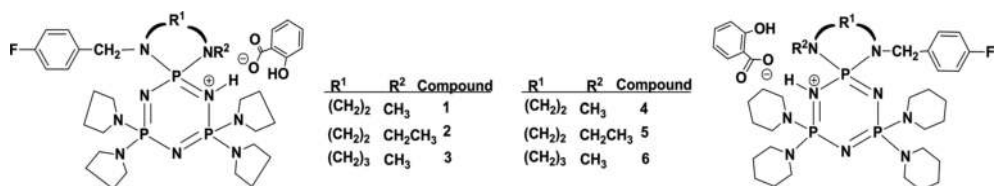


Figure 14. Salicylic acid salts of the mono(4-fluorobenzyl)spirocyclotriphosphazenes.

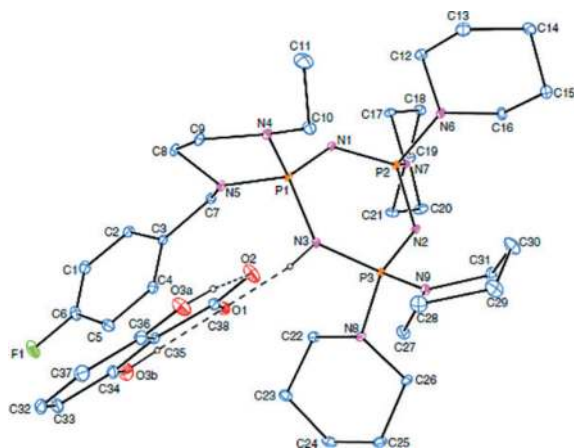


Figure 15. The crystal structure of compound 5.

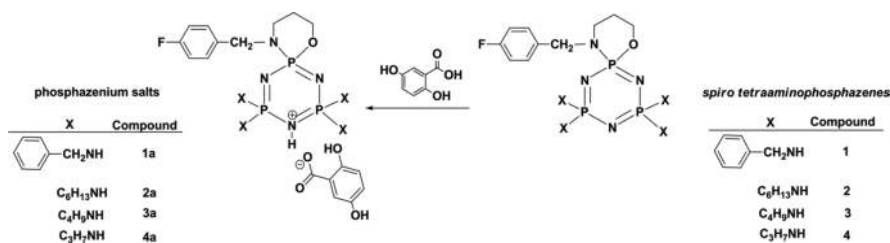


Figure 16. The synthesis of 4-fluorobenzylspiro(N/O)cyclotriphosphazene salts.

Elmas et al. synthesized phosphazene salts (**1a-4a**) from the reactions of the phosphazene bases (**1-4**) with gentisic acid (**Figure 16**). The crystallographic data of **4a** unambiguously indicate that the nitrogen of the phosphazene ring is monoprotonated (**Figure 17**). Also, In vitro antimicrobial activities of compounds were investigated and the PILs (**1a**, **3a** and **4a**) were found to be significantly active against *C. albicans* [32].

Akbaş et al. obtained the PILs or PMOSs (**1-3**) from the reactions of $[N_3P_3(NC_4H_8)_6]$ with the gentisic, decanoic and boric acids (**Figure 18**). Their biological activity in cultured cell lines was investigated. The binding of **1,2** or **3** to calf thymus (CT-DNA) and bovine serum albumin (BSA) led to remarkable changes in spectral characteristics. The potent low cytotoxic, strong apoptotic, and effective DNA topoisomerase inhibitory characteristics of these PILs revealed that they can be a good candidate for anticancer drugs [33].

Okumuş et al. obtained the PMOSs from the reactions of tetrapyrrolidino- and tetrapiperidino-substituted cyclotriphosphazenes with the gentisic and γ -resorcylic acids (**Figure 19**). The crystallographic result of **1b** and **2b** exhibited that the N atom of the phosphazene ring adjacent to the spiro precursor was mono protonated (**Figure 20**). In addition, their

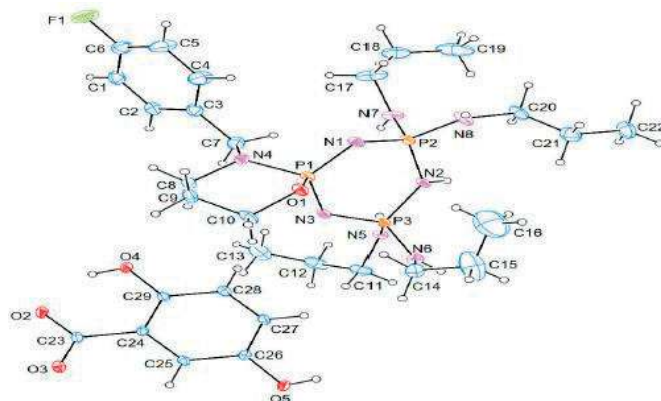


Figure 17. The crystal structure of compound 4a.

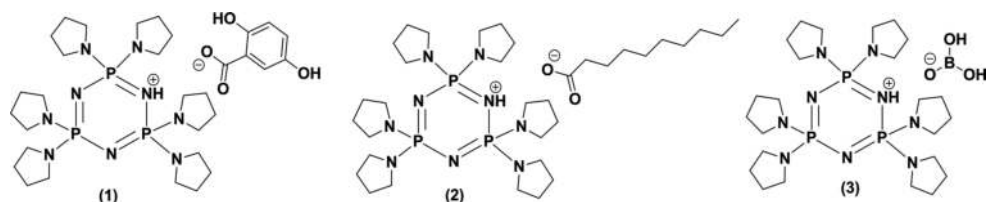


Figure 18. The syntheses of the PILs (1–3) with $[N_3P_3(NC_4H_9)_6]$ and gentisic, decanoic and boric acids, respectively.

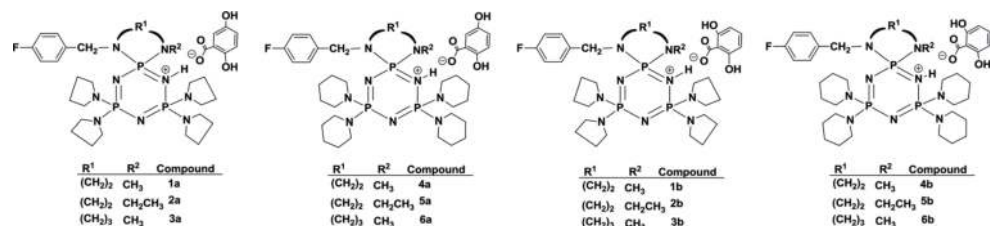


Figure 19. The gentisic and γ -resorcylic acid salts of the tetrapyrrolidino and tetrapiperidino mono(4-fluorobenzyl) spirocyclotriphosphazenes.

cytotoxic and antiproliferative activities against A549, Hep3B and normal FL cell lines were investigated. The findings also displayed that the PMOS (**1b-6b**) were strong antiproliferatives and they had excusable cytotoxic activities against the cells [34].

2.3.2. Adsorbents and surface modifiers of fluorescent nanoparticles

Veldboer et al., quaternized the cyclotriphosphazenes having terminal tertiary amino functions with methyl iodide (**Figure 21**) and the resulting salts were studied as surface modifiers for lanthanide phosphate nanoparticles. It was observed that the quaternized cyclic

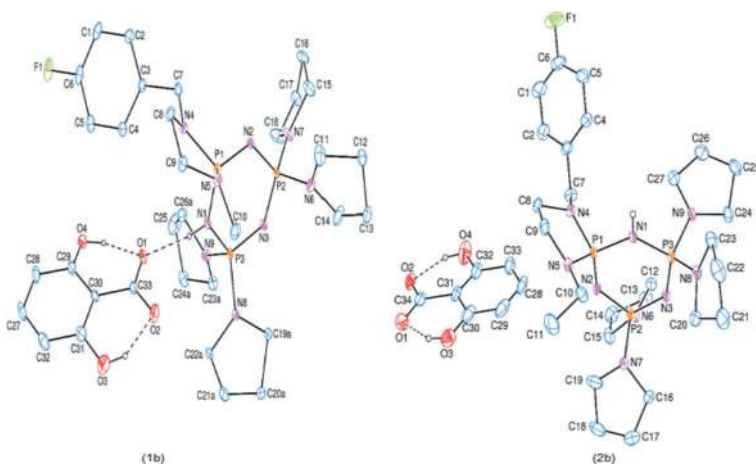


Figure 20. The crystal structure of 1b and 2b.

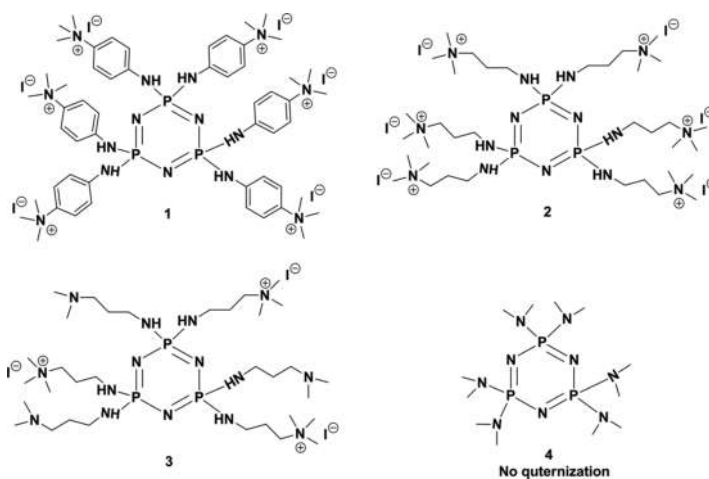


Figure 21. The synthesis of cyclotriphosphazene iodide salts.

phosphazenes were well suited for coupling to the nanocrystalline surface and a strategy for surface modification of cyclotriphosphazenes containing cationic substituents was developed. A good solubility of nanoparticles in an aqueous medium is a significant precondition for the prediction of bioanalytical applications such as fluorescent immunoassays. This is the main purpose of specially designed molecule surface modifiers. The stable nanocrystal-linker complexes in methanol were formed with compounds 3 and 4, while the fully quaternized cyclic phosphazenes 1 and 2 interact strongly with nanoparticles, resulting in an agglomeration. It was found that aromatic groups may interfere with the UV absorption in nanocrystals, but no significant effect of aliphatic side chains was observed [35].

2.3.3. Lubricants

Omotowa et al. investigated the tribological properties of PzILs containing trimethylammonium and N-methylpyridinium chains (**Figure 22**). (Dimethylamino)ethoxy, pyridylmethoxy, or (dimethylamino)propoxy side groups linked to the phosphorus in the phosphazene ring were quaternized at the side group nitrogen with iodomethane to obtain polyiodo salts. Subsequently, polyquaternary PZILs were formed with salts such as $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ or NaBF_4 by the anions exchange reaction. These PzILs were investigated for use as lubricants for aircraft gas turbine engines and as additives in water lubrication of silicon nitride ceramics. Friction and wear properties of water with 5–8 (0.25 weight %) as boundary lubricant additives were tested on silicon nitride ceramic interfaces. It was observed that these PzILs lead to a decrease in the running-in period. The PzILs, 5–8, are more viscous than the free cyclophosphazene bases and are highly viscous for use as oils. For a faster transition to low friction, ionic liquids with higher solubility must be used [36].

Recently, additives obtained from phosphazene having polar functions which can interact with tribological surfaces, have been developed. Singh et al. obtained The $\text{PzP}(-\text{NHP})_6$ salt with $\text{N}_3\text{P}_3\text{Cl}_6$ and 2,6-di-*tert*-butyl-4-(dimethylaminomethyl) phenol (**Figure 23**). This compound contains a phosphazene ring containing polar nitrogen and phosphorus atoms surrounded by hindered phenolic substituents with *tert*-butyl groups. Due to these properties, it can show an affinity for a metal surface to form a surface film which leads to anticorrosion, antiwear, and antifriction properties together with antioxidant characteristics. Reportedly, the $\text{PzP}(-\text{NHP})_6$ additive exhibits excellent antioxidant properties, and moderate anticorrosion, antiwear and antifriction properties. A doping concentration of 3000 ppm $\text{PzP}(-\text{NHP})_6$ decreased the average wear scar diameter (AWS) and average friction coefficient by 15.81% and ~27.27%, respectively, in comparison to those for the blank polyol base oil [37].

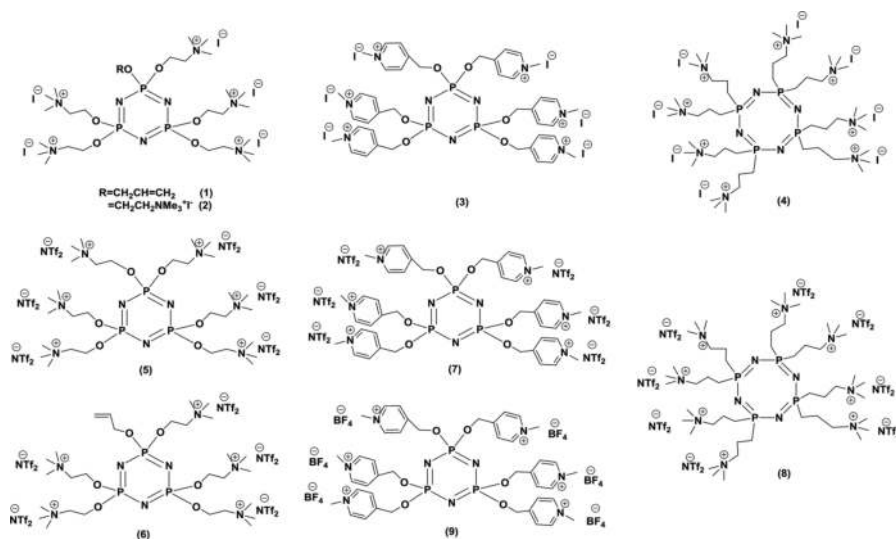


Figure 22. PzILs containing trimethylammonium and N-methylpyridinium chains.

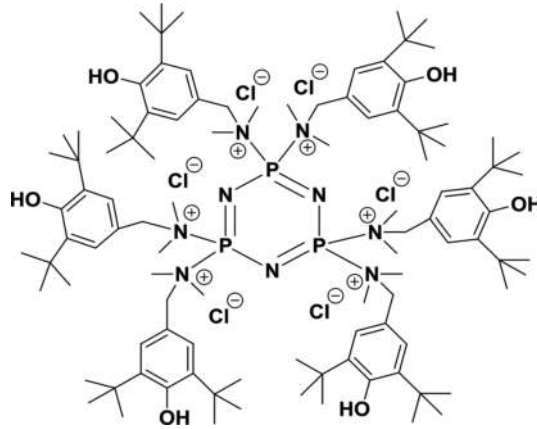


Figure 23. The structure of the PzP(-NHP)₆ salt.

2.3.4. Chemosensors for metal ions

Çiftçi et al. obtained the quaternized cationic and zwitterionic derivatives of 3-[2-(diethylamino)ethyl]-7-oxy-4-methylcoumarin substituted trimeric and tetrameric derivatives with dimethyl sulfate and 1,3-propanesultone, respectively (Figure 24). Quaternized ionic and zwitterionic compounds display excellent solubility in water and the effects of metal ions on the fluorescent behavior of the cytophosphazene salts were investigated using these compounds

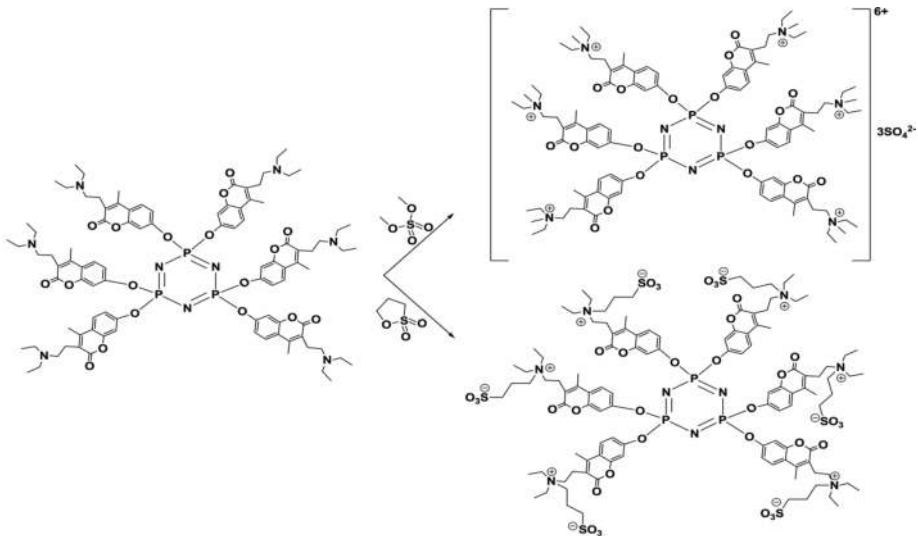


Figure 24. The quaternization of coumarin-substituted cyclophosphazene derivatives.

as chemosensors for metal ions. The results showed that cyclophosphazene salts exhibit highly selective fluorescence chemosensor behavior for Fe^{3+} ions in aqueous solution [38].

2.3.5. Electrolyte solutions for energy storage devices

The ionic liquid also serves as an ion source for the formation of an electric double layer when electrolytes are used for the electrical double layer capacitor. Thus, an additional supporting electrolyte is not required. The PzIL is decomposed during combustion to produce a nitrogen gas, a phosphate ester, and the like. Because of this nitrogen gas, phosphate ester and the like, the ionic compound overcomes the risk of low combustion. Further, when the ionic compound contains a halogen, the halogen acts as an active radical during the accidental combustion to reduce the risk of burning. Moreover, when the ionic compound contains an organic substituent, the oxygen has a protective effect, as it forms a carbide during combustion. When the ionic compound is in a liquid state at room temperature, it can be used as an electrolyte for an electric double layer capacitor, a lithium-ion battery or a dye-sensitized solar cell, a reaction solvent for an organic synthesis, an extracting solvent for an organic compound and a magnetic fluid. If the ionic compound is in a solid state at room temperature, it can be used as a salt. It exhibits high non-combustibility in both of the liquid and solid states and can significantly suppress the risk of combustion in the application. For this purpose, various PzILs have been synthesized (**Figure 25**) [39–41].

2.3.6. A gate dielectric layer for OFETs

Organic field effect transistors (OFETs) are very attractive with their potential applications in a wide area, as flexible and low cost electronic devices. Conventional electrolytes are not stable with their solvents and it is difficult to stabilize the electrolyte concentration. However, ionic liquids are attractive as a gate dielectric layer for OFETs with superior properties such as high thermal and chemical stability, non-volatility, non-toxicity and high polarizability. For this purpose, PzILs have been synthesized. The chain nitrogen atoms of free cyclotriphosphazene bases were quaternized by treatment with methyl iodide to give phosphazanium salts, PzIL1-PzIL4. Subsequently, polyquaternary PZILs have been formed with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (**Figure 26**). These PzILs have been used as the dielectric layer in OFETs. Due to the high dielectric effect of PzILs, the fabricated OFETs have operated in the low voltage ranges. On/

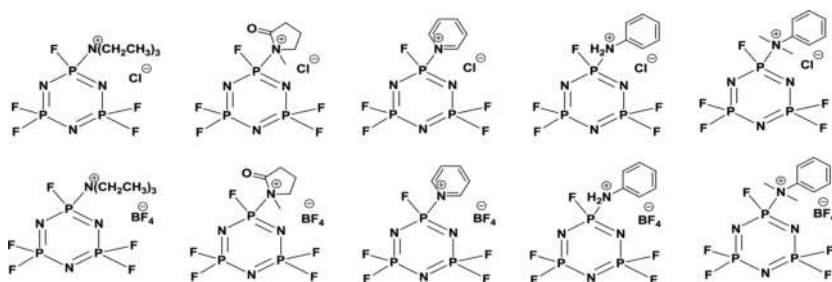


Figure 25. The conversion of chloropentafluorocyclophosphazenes to PzILs.

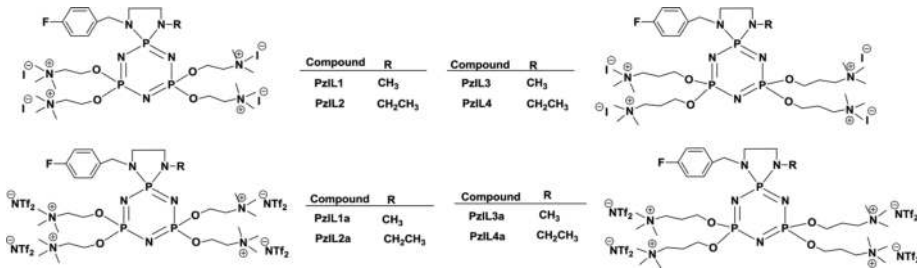


Figure 26. The chemical structure of mono(4-fluorobenzyl)cyclotriphosphazene ionic liquids.

off ratios of these OFETs are about 10^2 . The low value of on-off ratio could be caused by the increasing thickness and doping level of active organic layer [42].

2.3.7. Polyelectrolytes

Linear polyphosphazenes containing quaternary ammonium side groups have the potential for application as a polycation component in the formation of ordering polyelectrolyte multilayers. Polyelectrolyte multilayers comprise of ionically modified polyphosphazenes by layer-by-layer assembly of a cationic (PAZ⁺) and an anionic (PAZ⁻) polyphosphazene (Figure 27). The dc conductivity values of the PAZ⁻/PAZ⁺ films were found to be ten times greater than those of the PAH/PSS multilayers when these multilayers were compared to those of poly(sodium-4-styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) [43].

Polyelectrolytes were obtained by quaternization of the poly-alkoxy- and aryloxy- phosphazenes with strong alkylating reagents (Figure 28). Because of the lower electron donating abilities of the alkoxy and aryloxy side groups compared to the alkylamino side groups, quaternization is only carried out with methyl trifluoromethanesulfonate (MeOTf). Quaternary poly(alkoxyphosphazenes) have a high ionic conductivity without the need for plasticizers or additional salts [26].

Because of the atomic polarization of the iodide anion, it has been found that the iodide salts (ionomer) of poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP) (Figure 29) have a high

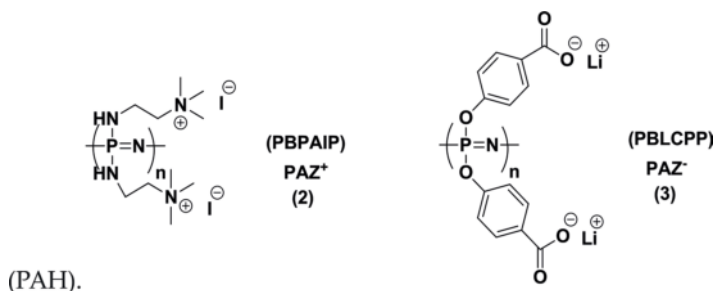


Figure 27. Structures of the (PAZ⁺) (2) and (PAZ⁻) (3) polyphosphazenes.

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