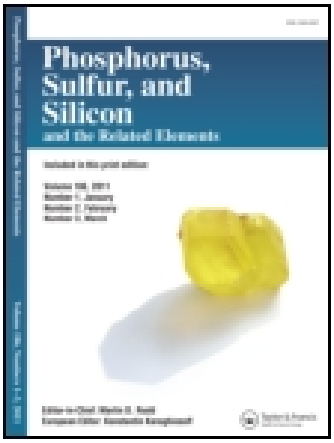

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis, Characterization, and Spectroscopic Properties of Hexa(4-Bromo-2-Formyl-Phenoxy)Cyclotriphosphazene and Hexa(4-Chloro-2-Formyl-Phenoxy)Cyclotriphosphazene and Fully Substituted Cyclotriphosphazene Derivatives Bearing a Schiff Base at Room Temperature

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SYNTHESIS, CHARACTERIZATION, AND SPECTROSCOPIC PROPERTIES OF HEXA(4-BROMO-2-FORMYL-PHENOXY)CYCLOTRIPHOSPHAZENE AND HEXA(4-CHLORO-2-FORMYL-PHENOXY)CYCLOTRIPHOSPHAZENE AND FULLY SUBSTITUTED CYCLOTRIPHOSPHAZENE DERIVATIVES BEARING A SCHIFF BASE AT ROOM TEMPERATURE

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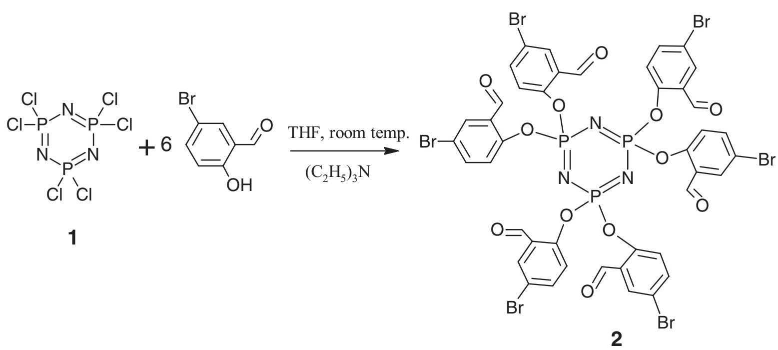
GRAPHICAL ABSTRACT



Abstract *Hexa(4-bromo-2-formyl-phenoxy)cyclotriphosphazene (**2**) and hexa(4-chloro-2-formyl-phenoxy)cyclotriphosphazene (**3**) were obtained from the reactions of hexachlorocyclotriphosphazene (**1**) with 5-bromosalicylaldehyde and 5-chlorosalicylaldehyde in the presence of $(C_2H_5)_3N$ and K_2CO_3 at room temperature, respectively. The new two organocyclotriphosphazenes bearing formyl groups were reacted with 4-cyano aniline, 2-phenyl aniline, 4-aceto aniline, 5-chloro-2-hydroxy aniline, 2-hydroxy aniline, 4-hydroxy aniline,*

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*2-(4-morpholino)ethyl amine, 4-carboxy aniline, 4-carbomoyl aniline, 2-mercapto aniline, and 5-amino isoquonoline to prepare cyclotriphosphazene derivatives containing a Schiff base at room temperature. However, fully phenoxy-substituted cyclotriphosphazenes containing a Schiff base were isolated from the reactions of the compound **2** and **3** with 5-chloro-2-hydroxy aniline, 2-hydroxy aniline, 4-hydroxy aniline, and 2-(4-morpholino)ethyl amine. The structures of the synthesized compounds were characterized by elemental analysis, IR, and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy. According to the results of the analysis, all synthesized compounds were found to be fully substituted organocyclotriphosphazenes, such as hexa[4-bromo-2-(5-chloro-2-hydroxy-pheyliminomethyl)phenoxy]cyclotriphosphaze (2a). All cyclotriphosphazene derivatives synthesized gave fluorescence emission peaks in range between 300 nm and 410 nm.*

Keywords Phosphazene; cyclotriphosphazene; organophosphazene; hexacholorocyclotriphosphazene; salicylaldehyde; Schiff base

INTRODUCTION

A large number of organocyclotriphosphazenes have been synthesized by the nucleophilic substitution reactions of halophosphazenes with organic reagents such as alcohol, phenol, amines, Grignard reagents, and thiols.[1–8] It has been estimated that more than 5,000 different cyclic and linear phosphazene derivatives have been isolated and characterized.[9] Organophosphazenes have been shown to possess a wide range of applications including inorganic hydraulic fluids and lubricants, biologically important substrates such as anticancer agents, insect chemosterilants, pesticides and fertilizers, and photosensitive materials.[10–13] Furthermore, it was reported that the antiproliferative activity of cyclotriphosphazenes containing Schiff bases was observed to be much higher against cancer cells than the normal cells.[14,15] Schiff bases also have a wide range of applications in several fields such as antibacterial, antifungal, antitumor activities, catalysis, and coordination chemistry.[16]

Although a large number of fully phenoxy-substituted cyclotriphosphazenes have been generated from the reactions of halophosphazenes with phenol and its derivatives, fully aryloxy-substituted cyclotriphosphazenes containing functional groups such as formyl, Schiff bases, and oximes are limited in the literature.[17–19] Fully phenoxy-substituted cyclotriphosphazenes bearing formyl groups were only obtained from the reactions of hexachlorocyclotriphosphazene with 4-hydroxybezaldehyde, salicylaldehyde (2-hydroxybenzaldehyde), 4-hydroxy-2-methoxy-benzaldehyde, and 4-hydroxy-3-metoxy-benzaldehyde(vanillin).[17,20–24] Organocyclotriphosphazenes containing Schiff bases were also derived from the reactions of hexa(4-formyl-phenoxy)cyclotriphosphazene and hexa(2-formyl-phenoxy)cyclotriphosphazene with some primary amines.[22,24–26] The organophosphazenes were reported to possess fluorescence properties.[22,27–31]

In this study, we report the synthesis of novel fully substituted hexa(4-bromo-2-formyl-phenoxy)cyclotriphosphazene (**2**) and hexa(4-chloro-2-formyl-phenoxy)cyclotriphosphazene (**3**) from the reactions of hexachlorocyclotriphosphazene with 5-bromosalicylaldehyde(5-bromo-2-hydroxy-benzaldehyde) and 5-chlorosalicylaldehyde (5-chloro-2-hydroxy-benzaldehyde) at room temperature. In addition, fully phenoxy-substituted cyclotriphosphazenes carrying Schiff base groups were derived from the reactions of the compounds **2** and **3** with 5-chloro-2-hydroxy aniline, 2-hydroxy aniline, 4-hydroxy aniline, 2-(4-morpholino)ethyl amine, and 2-phenyl aniline. The fluorescence spectra of all synthesized cyclotriphosphazene derivatives showed fluorescence emission peaks in range 300–410 nm in tetrahydrofuran (THF) solution.

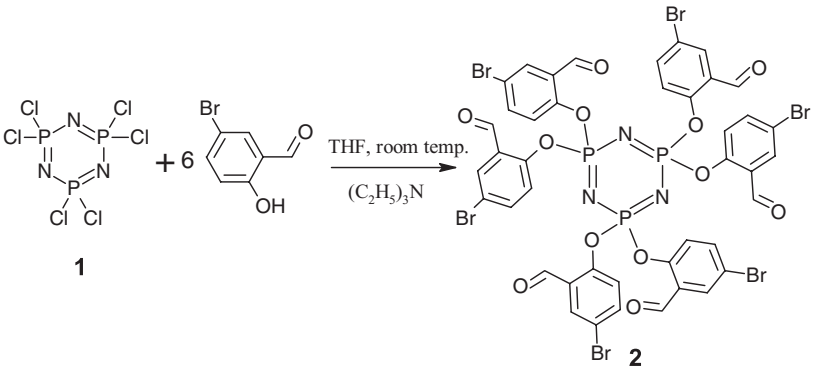

Figure 1 The reaction equation of $N_3P_3Cl_6$ with 5-bromosalicylaldehyde.

RESULTS AND DISCUSSION

5-bromosalicylaldehyde and 5-chlorosalicylaldehyde (10 equivalent of $N_3P_3Cl_6$) were used more than the amount of the reactions equation for the synthesis of fully phenoxy-substituted cyclotriphosphazene (Figs. 1 and 2).[15] Compounds (**2** and **3)** were easily isolated in good yield as white solids by precipitation from diethyl ether.

Fully substituted cyclotriphosphazene derivatives containing Schiff base were not isolated from all primary amines. Fully substituted cyclotriphosphazenes containing Schiff base (**2a–e** and **3a–d**) were only formed from the reactions of 5-chloro-2-hydroxy aniline, 2-hydroxy aniline, 4-hydroxy aniline, and 2-(4-morpholino)ethyl amine. Note that, **2a–e** and **3a–d** were obtained with the yields in a range 40%–84% (Figs. 3 and 4). The structures of the cyclotriphosphazenes derived from other primary amines were not characterized by spectroscopic methods. These compounds were determined to be partially substituted from the Fourier transform infrared (FT-IR) spectra which showed peaks of aldehyde group. Therefore, these compounds were not evaluated.

The results of elemental analysis, FT-IR and NMR(^{1}H, ^{13}C, ^{31}P) are appropriate to the chemical structure for all compounds as shown in the figures. All spectroscopic results were given in the experimental section. The synthesized organophosphazenes are solids and

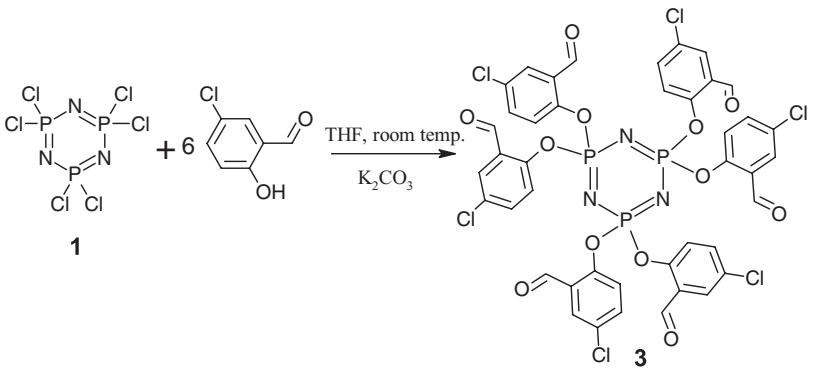

Figure 2 The reaction equation of $N_3P_3Cl_6$ with 5-chlorosalicylaldehyde.

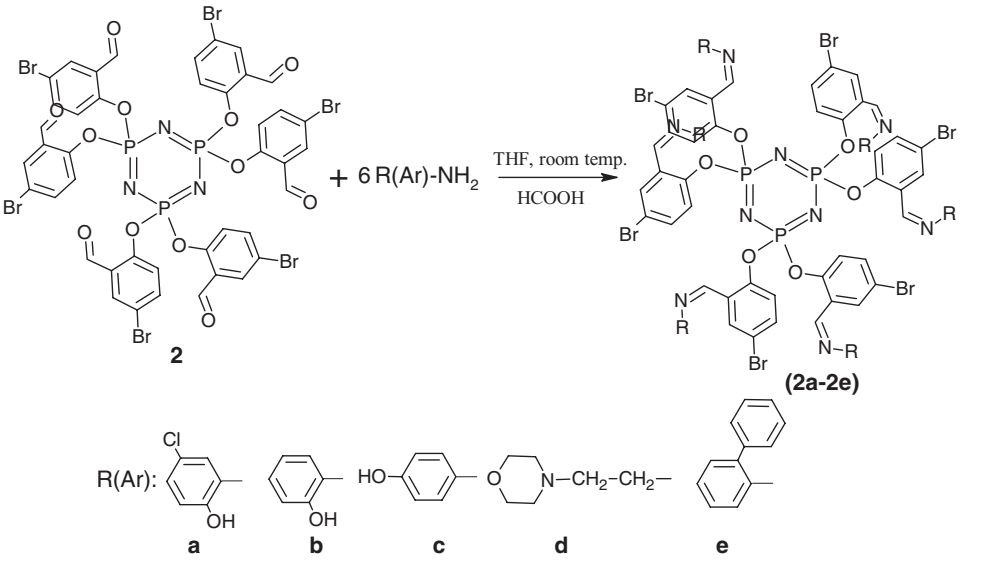

Figure 3 The reaction equation of the compound **2** with primary amines.

soluble in common organic solvents such as CH_2Cl_2, acetone, and THF. Unlike the majority of other similar studies, all of the reactions were carried out at room temperature.[17,20,21]

The FT-IR spectra of the compounds (**2** and **3**) exhibited strong two stretching bands at 1203 cm^{-1} and 1160 cm^{-1} attributed to P=N bonds of the cyclophosphazene ring, while two PCl_2 absorption peaks are not in spectra. Aldehyde carbonyl stretching bands for compounds **2** and **3** are observed at 1693 cm^{-1} and 1698 cm^{-1}, respectively. In the IR spectra of the compounds (**2a–e**) and (**3a–d**) derived from compounds **2** and **3**, the characteristic HC=N stretching bands are observed in the range 1619–1640 cm^{-1}.

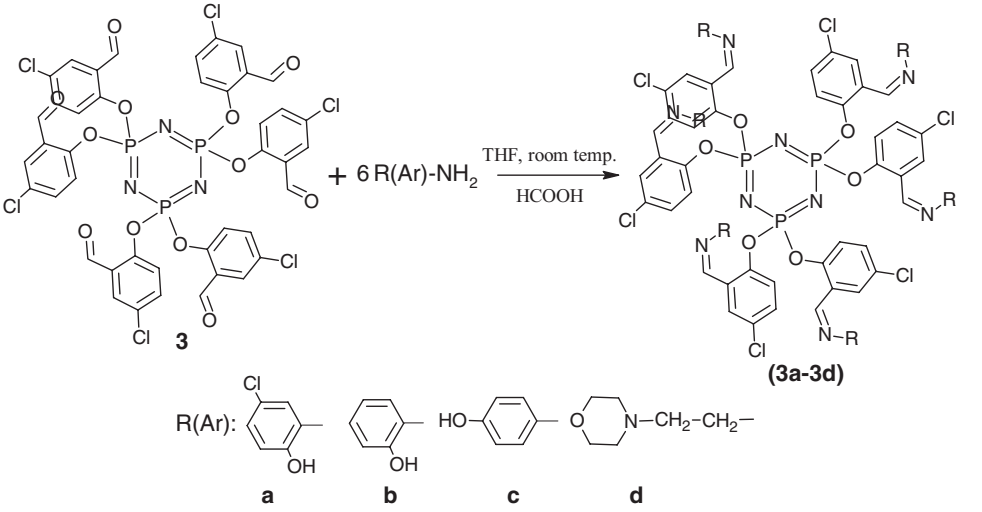

Figure 4 The reaction equation of the compound **3** with primary amines.

Table 1 Characteristic IR peaks data of all derived compounds

Compound	νHC=O	νHC=N	νP=N	νP−O−C(Aryl)
1	—	—	1213	—
2	1693	—	1203, 1192, 1177	959
3	1698	—	1196, 1170	956
2a	—	1619	1201, 1164	960
2b	—	1619	1207, 1164	960
2c	—	1619	1188, 1163	959
2d	—	1640	1204, 1163	956
2e	—	1619	1187, 1162	957
3a	—	1621	1203, 1163	960
3b	—	1619	1206, 1163	961
3c	—	1619	1189, 1162	950
3d	—	1640	1204, 1163	956

Most significantly, the IR spectra of the compounds (**2a–2e**) and (**3a–3d**) did not show stretching bands at 1693 and 1698 cm^{-1} belonging to aldehyde carbonyl (CH=O). The characteristic HC=O, HC=N, P=N, and P−O−C(Aryl) stretching bands for all of the compounds were given in Table 1.

The ^{31}P NMR spectra of the compounds **2** and **3** show singlet peaks at 7.7 and 7.9 ppm. The (^{1}H-decoupled) ^{31}P NMR spectra for compounds (**2a–e**, **3a–d**) exhibited a peak in the range 7.5–8.5 ppm as a singlet. The results indicate that the same organic groups are bond to phosphorus atoms. The spin systems for all compounds are interpreted as A_3. ^{31}P NMR spectra data of all derived cyclotriphosphazenes are given in Table 2.

The ^{1}H and ^{13}C NMR spectra of all synthesized cylotriphosphazenes derivates indicate all peaks corresponding to the protons and carbons of organic groups. In the ^{1}H and ^{13}C NMR spectra for **2a–e** and **3a–d**, imine (CH=N) proton and carbon chemical shift were observed at 8.0–8.3 ppm and 155–150 ppm, respectively. The formyl proton and carbon peak for the compounds **2** and **3** were assigned at 9.9 ppm and 185 ppm. These results show that all of the formyl groups were transformed into imines.

The absorption and fluorescence spectra results for all compounds were given in Table 3.

Whereas the absorption spectra for **2d** and **3d** from aliphatic amines display two strong bands between 230 nm and 300 nm, the other compounds derived from aromatic amines display three strong bands between 220 nm and 360 nm. The absorptions might be attributed to the π-π^* transition of the cyclotiphosphazene bonded organic groups.[22] The absorption spectra for the compounds **2** and **3** derived from 5-bromosalicylaldehyde and

Table 2 The ^{1}H-decoupled ^{31}P NMR spectral data of all derived cyclotriphosphazenes

Compound	δ ($P(OR)_2$) ppm	Compound	δ ($P(OR)_2$) ppm
2	7.7	**3**	7.9
2a	7.7	**3a**	7.3
2b	8.1	**3b**	7.7
2c	8.1	**3c**	8.0
2d	8.0	**3d**	8.2
2e	8.4	—	—

Table 3 The wavelength data of electronic absorption and fluorescence peaks for all compounds

Compound	Absorption $\lambda_{max.}$, nm (logε)	Excitation, $\lambda_{Ex.}$, nm (logε)	Emission $\lambda_{Em.}$, nm (logε)	Stoke's shift $\Delta\lambda_{ST}$
1	175 (4.0)[a]	—		
2	228 (4.8), 304 (4.1)	292 (7.3)	322 (7.3)	30
3	241 (4.8), 303 (4.2)	292 (7.2)	320 (7.2)	28
2a	228 (5.0), 270 (4.8), 375 (4.7)	284 (7.0)	317 (7.0)	33
2b	226 (5.0), 269 (4.8), 365 (4.8)	294 (7.5)	328 (7.5)	34
2c	244 (4.9), 283 (4.6), 354 (4.7)	265 (6.7)	316 (6.7)	51
2d	227 (5.1), 296 (4.3)	293 (7.5)	314 (7.5)	21
2e	—	335 (7.5)	410 (7.5)	75
3a	230 (5.2), 270 (5.1), 374 (4.9)	284 (7.2)	318 (7.3)	34
3b	239 (5.0), 272 (4.9), 365 (4.9)	301 (7.4)	329 (7.4)	28
3c	244 (5.1), 283 (4.8), 354 (5.0)	309 (6.8)	408 (6.9)	99
3d	231 (5.0), 293 (4.5)	293 (7.5)	311 (7.4)	18

[a]Reference [8].

5-chlorosalicylaldehyde display two strong bands between 220 nm and 305 nm caused by the π-π^* transition.

Fluorescence emission peaks for all of synthesized phosphazene derivatives were observed in fluorescence spectra which were measured in dilute THF solutions (5×10^{-5}) at room temperature. Fluorescence emission peaks appeared in the range 310–410 nm, in the ultraviolet range. The compound **2e** has the largest fluorescence emission peak wavelength (410 nm). Fluorescence emission peaks for organophosphazenes carrying Schiff bases derived from hexa(2-formyl-phenoxy)cyclotriphosphazene were detected in the range 300–550 nm.[22] In another study, fluorescence emission peaks for hydroxyl substituted hexa(phenoxy)cyclotriphosphazene derivatives were observed at around 298 nm.[29] There are also organophosphazene derivatives to given fluorescence emission peaks in the visible region.[31] Fluorescence emission peaks give organophosphazenes in the ultraviolet or visible region. The Stoke's shift values were also calculated. The values were found to have shifted to 18–99 nm.

CONCLUSIONS

Fully phenoxy-substituted cyclotriphosphazenes bearing a formyl group were easily synthesized from the reactions of hexachlorocylotriphosphazene with phenol-bearing formyl groups in the presence of K_2CO_3 or $(C_2H_5)_3N$ at room temperature. Then, fully phenoxy-substituted cyclotriphosphazenes containing a Schiff base were also easily isolated from the reaction of these compounds with some primary amines at room temperature.

Fully phenoxy substituted cyclotriphosphazenes containing Schiff bases were only obtained from aliphatic primary amines or primary amines bearing electron donor groups in the structure. All of the compounds were soluble in organic solvents such as chloroform, dichloromethane, THF, and acetone.

EXPERIMENTAL

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$), 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde, 4-cyanoaniline, 4-acetoaniline, 2-phenylaniline, 5-chloro-2-hydroxyaniline,

2-hydroxyaniline, 4-hydroxyaniline, 4-(2-aminoethyl)morpholine, 4-aminobenzoic acid, 4-aminobezamide, 2-aminothiophenol, 5-aminoisoquinoline, 5-aminoindazole, 2-aminofluorene, and 2-aminobezothiazole were purchased form Aldrich and used without further purification. The syntheses of hexa(4-bromo-2-formyl-phenoxy)cyclotriphosphazene and hexa(4-chloro-2-formyl-phenoxy)cyclotriphosphazene were carried out under an argon atmosphere. Syntheses of the other phosphazene derivates were carried out under room atmosphere. THF was distilled over metallic sodium in the presence of benzophenone under an argon atmosphere.

The NMR (^{1}H, ^{13}C, ^{31}P) spectra were recorded on a Bruker DPX FT-NMR (300 MHz) spectrometer ($SiMe_4$ as internal and 85% H_3PO_4 as external standards). IR spectra were recorded on a Perkin-Elmer 1000 FTIR spectrometer in KBr disks. The elemental compositions were determined on a LECO CHNS-O analyzer. The melting points were measured on a Electrothermal IA 9200 apparatus in capillary. The data of fluorescence emission spectra were obtained from Shimadzu RF-1504 spectrofluorometer using 1 cm cuvettes at room temperature in 5×10^{-5} M THF solution. UV-vis. spectra were recorded on a Shimadzu mini 1240 UV spectrophotometer.

Synthesis of Hexa(4-bromo-2-formyl-phenoxy)cyclotriphosphazene (2)

A solution of 5-bromosalicylaldehyde (28.9 g, 143.8 mmol) in THF (50 mL) was added to a stirred mixture of $N_3P_3Cl_6$ (**1**) (5 g, 14.38 mmol) and triethylamine (20 mL, 143.8 mmol) in THF (200 mL) at room temperature. The mixture was stirred for 48 h and then the precipitated triethylamine hydrochloride was filtered off. The solvent was evaporated on a rotary evaporator under reduced pressure. The product mixture was dissolved in dichloromethane (CH_2Cl_2) and compound **2** was obtained as white solid by precipitation with diethyl ether. Yield: 15.42 g (80%). M.p.: 175 °C. Anal. Calc. for $N_3P_3C_{42}H_{24}Br_6O_6$: C: 37.79, H: 1.81, N: 3.15. Found: C: 38,60, H: 2,03, N: 3,23. FTIR (KBr, cm^{-1}): 3083 (C—H aromatic), 2867 (H—CO aldehyde), 1693 (HC=O aldehyde), 1203, 1192, 1177 (P=N), 959 (P—OAr aryl). ^{1}H NMR δ (ppm): 9.9 (s, **H**C=O), 7.9 (d, 1H, $J = 2.46$ Hz.), 7.5 (dd, $J = 2.54$ Hz.), 6.9 (d, 1H). ^{13}C NMR δ (ppm): 186.1 (s, **C**=O), 149.8 (m, $J = 2.65$ Hz.), 138.2, 132.5, 128.8 ($J = 2.1$ Hz.), 122.8, 120.1. ^{31}P NMR δ (ppm): 7.7.

Synthesis of Hexa(4-chloro-2-formyl-phenoxy)cyclotriphosphazene (3)

A solution of 5-chlorosalicylaldehyde (22.52 g, 143.8 mmol) in THF (50 mL) was added to a stirred mixture solution of $N_3P_3Cl_6$ (**1**) (5 g, 14.38 mmol) and K_2CO_3 (24 g, 143.8 mmol) in THF (200 mL) at room temperature. The mixture was stirred for 48 h, and the precipitate was filtered off. The solvent was evaporated on a rotary evaporator under reduced pressure. The product mixture was dissolved in dichloromethane (CH_2Cl_2) and compound **3** was obtained as white solid by the precipitation in diethyl ether solvent. Yield: 9 g (59%). M.p.: 127 °C. Anal. Calc. % for $N_3P_3C_{42}H_{24}Cl_6O_6$: C: 47.22, H: 2.26, N: 3.93. Found, %: C: 47.32, H: 2.39, N: 3.62. FTIR (KBr, cm^{-1}): 3088 (C—H aromatic), 2874 (H—CO aldehyde), 1698 (HC=O aldehyde), 1196, 1170 (P=N), 956 (P—OAr aryl). ^{1}H NMR δ (ppm): 9.9 (s, **H**C=O), 7.7 (d, 1H, $J = 2.50$ Hz.), 7.4 (dd, $J = 2.70$ Hz.), 7.0 (d, 1H). ^{13}C NMR δ (ppm): 186.2 (s, H**C**=O), 145.3(m, $J = 2.65$ Hz.), 135.2, 132.7, 129.3, 128.6, 122.5. ^{31}P NMR δ (ppm): 7.9.

General Method for the Synthesis of Fully Substituted Cyclotriphosphazene Derivates Containing Schiff Base from the Compound 2

Fully substituted cylotriphosphazene derivatives containing a Schiff base were obtained from the reaction of the compound **2** (0.5 g, 0.38 mmol) with an excess of primary amine (3.8 mmol) in THF (25 mL) at room temperature. The mixture of compound **2** and primary amine was stirred for 2 days at room temperature. After the reaction was complete, the solvent was evaporated under reduced pressure. The crude product was washed several times with diethyl ether. The precipitate was filtered off and finally dried.

Synthesis of Hexa[4-bromo-2-(5-chloro-2-hydroxy-pheyliminomethyl)phenoxy]cyclotriphosphaze (2a)

5-chloro-2-hydroxy-aniline (0.55 g, 3.8 mmol). Note that, **2a** is a goldenrod solid (0.63 g, 80%). M.p.: 148 °C. Anal. Calc. % for $N_9P_3C_{78}H_{48}O_{12}Br_6Cl_6$: C: 44.86, H: 2.32, N: 6.04. Found, %: C: 44.98, H: 2.47, N: 6.11. FTIR (KBr, cm^{-1}): 3428 (—OH), 3070 (C—H aromatic), 2854 (H—CN imine), 1619 (HC=N imine), 1201, 1164 (P=N), 960 (P—OAr aryl). ^{1}H NMR δ (ppm): 8.70 (s, **H**—CN), 8.41–6.81 (the peaks of aromatic protons). ^{13}C NMR δ (ppm): 151.7 (s, H**C**=N), 151.3, 149.7 (P—O—**C**(Aryl)) 136.7, 135.34, 131.9, 129.6, 128.5, 124.1, 123.0, 119.4, 117.0, 117.0. ^{31}P NMR δ (ppm): 7.7.

Synthesis of Hexa[4-bromo-2-(2-hydroxy-pheyliminomethyl) phenoxy]cyclotriphosphaze(2b)

2-hydroxy-aniline (0.42 g, 3.8 mmol). Note that, **2b** is an olive solid (0.48 g, 67%). M.p.: 131 °C. Anal. Calc. % for $N_9P_3C_{78}H_{54}Br_6O_{12}$: C: 49.79, H: 2.89, N: 6.70. Found, %: C: 49.50, H: 2.96, N: 6.34. FTIR (KBr, cm^{-1}): 3427 (—OH), 3070 (C—H aromatic), 2849 (H—CN imine), 1619 (HC=N imine), 1207, 1164 (P=N), 960 (P—OAr aryl). ^{1}H NMR δ (ppm): 8.72 (s, **H**—CN), 8.50–6.62 (the peaks of aromatic protons). ^{13}C NMR δ (ppm): 153.0 (s, H**C**=N), 149.5, 148.6 (P—O—**C**(Aryl)) 135.5, 134.9, 131.3, 130.1, 129.3, 123.1, 119.8, 119.4, 116.6, 115.8. ^{31}P NMR δ (ppm): 8.1.

Synthesis of Hexa[4-bromo-2-(4-hydroxy-pheyliminomethyl)phenoxy]cyclotriphosphaze(2c)

4-hydroxy-aniline (0.42 g, 3.8 mmol). Note that, **2c** is a dark, olive-green solid (0.45 g, 59%). M.p.: 144 °C. Anal. Calc. % for $N_9P_3C_{78}H_{54}Br_6O_{12}$: C: 49.79, H: 2.89, N: 6.70. Found, %: C: 50.93, H: 3.38, N: 7.02. FTIR (KBr, cm^{-1}): 3383 (—OH), 3020 (C—H aromatic), 2813 (H—CN imine), 1619 (HC=N imine), 1188, 1163 (P=N), 959 (P—OAr aryl). ^{1}H NMR δ (ppm): 8.40 (s, **H**—CN), 8.22–6.53 (the peaks of aromatic protons). ^{13}C NMR δ (ppm): 157.0 (s, H**C**=N), 150.6, 148.5 (P—O—**C**(Aryl)) 148.2, 142.3, 134.1, 130.4, 130.1, 122.7, 120.6, 115.7. ^{31}P NMR δ (ppm): 8.1.

Synthesis of Hexa[4-bromo-2-(2-(4-morpholine)-ethyliminomethyl) phenoxy]cyclotriphosphaze (2d)

2-(4-morpholine)-ethylamine (0.50 mL, 3.8 mmol). Note that, **2d** is a maroon solid (0.56 g, 74%). M.p.: 82 °C. Anal. Calc. % for $N_{15}P_3C_{78}H_{96}Br_6O_{12}$: C: 46.65, H: 4.82, N: 10.46. Found, %: C: 47.62, H: 5.8, N: 11.06. FTIR (KBr, cm^{-1}): 3070 (C—H aromatic), 2954–2900 (C—H alkyl), 2852 (H—CN imine), 1640 (HC=N imine), 1204, 1163 (P=N), 956 (P—OAr aryl). ^{1}H NMR δ (ppm): 8.1 (s, **H**—CN), 7.9(d), 7.47(dd), 6.9(d), 3.51–2.35 CH_2 protons. ^{13}C NMR δ (ppm): 154.2 (s, H**C**=N), 148.1 (P—O—**C**(Aryl)) 134.8, 130.3, 129.9, 123.4, 119.3, 66.6, 58.8, 58.5, 53.8. ^{31}P NMR δ (ppm): 8.0.

Synthesis of Hexa[4-bromo-2-(2-phenyl-pheyliminomethyl) phenoxy]cyclotriphosphaze (2e)

2-phenylaniline (0.65 g, 3.8 mmol). Note that, **2e** is a yellow green solid (0.34 g, 40%). M.p.: 108 °C. Anal. Calc. % for $N_9P_3C_{114}H_{78}O_6Br_6$: C: 61.06, H: 3.51, N: 5.62. Found, %: C: 60.42, H: 3.495, N: 5.76. FTIR (KBr, cm^{-1}): 3060 (C—H aromatic), 2919 (H—CN imine), 1619 (HC=N imine), 1187, 1162 (P=N), 957 (P—OAr aryl). ^{1}H NMR δ (ppm): 8.4 (s, H—CN), 8.0–6.7 aromatic proton peaks. ^{13}C NMR δ (ppm): 153.2 (s, H**C**=N), 149.1 (P—O—**C**(Aryl)) 149.1 140.1, 136.77, 136.7, 135.7, 131.6, 130.9, 130.8, 129.4, 128.4, 127.7, 127.6, 124.2, 120.2, 118.8. ^{31}P NMR δ (ppm): 8.4.

General Method for the Synthesis of Fully Substituted Cylotriphosphazene Derivates Containing Schiff Base from the Compound 3

Fully substituted cylotriphosphazene derivates containing a Schiff base were obtained from the reaction of the compound **3** (0.5 g, 0.47 mmol) with the excess of primary amine (4.7 mmol) in THF (25 mL) at room temperature. The mixture of the compound **3** and primary amine was stirred for 2 days under room atmosphere. After the reaction was completed, the solvent was evaporated under reduced pressure. The crude product was washed several times with diethyl ether. The precipitate was filtered off and finally dried.

Synthesis of Hexa[4-chloro-2-(5-chloro-2-hydroxy-pheyliminomethyl) phenoxy]cyclotriphosphaze (3a)

5-chloro-2-hydroxy-aniline (0.68 g, 4.7 mmol). Note that, **3a** is a goldenrod solid (0.63 g, 80%). M.p.: 190 °C. Anal. Calc. % for $N_9P_3C_{78}H_{48}O_{12}Cl_{12}$: C: 51.43, H: 2.66, N: 6.92. Found, %: C: 52.93, H: 3.31, N: 6.45. FTIR (KBr, cm^{-1}): 3422 (—OH), 3071 (C—H aromatic), 2868 (H—CN imine), 1621 (HC=N imine), 1203, 1163 (P=N), 960 (P—OAr aryl). ^{1}H NMR δ (ppm): 8.5 (s, **H**—CN), 7.9–6.7 (the peaks of aromatic protons). ^{13}C NMR δ (ppm): 151.2 (s, H**C**=N), 150.7, 147.8 (P—O—**C**(Aryl)) 135.2, 132.3, 129.6, 129.1, 128.6, 125.0, 120.4, 116.7, 115.8. ^{31}P NMR δ (ppm): 7.3.

Synthesis of Hexa[4-chloro-2-(2-hydroxy-pheyliminomethyl) phenoxy]cyclotriphosphaze (3b)

2-hydroxy-aniline (0.52 g, 4.7 mmol). Note that, **3b** is a olive solid (0.48 g, 67%). M.p.: 145 °C. Anal. Calc. % for $N_9P_3C_{78}H_{54}Cl_6O_{12}$: C: 58.01, H: 3.37, N: 7.81. Found,

%: C: 58.85, H: 3.80, N: 7.95. FTIR (KBr, cm^{-1}): 3422 (−OH), 3050 (C−H aromatic), 2844 (H−CN imine), 1619 (HC=N imine), 1206, 1163 (P=N), 961 (P−OAr aryl). ^{1}H NMR δ (ppm): 8.5 (s, **H**−CN), 8.0–6.6 (the peaks of aromatic protons). ^{13}C NMR δ (ppm): 152.7 (s, H**C**=N), 149.1, 147.7 (P−O−**C**(Aryl)) 134.5, 132.08, 131.8, 130.1, 129.1, 128.6, 122.3, 121.5, 115.6, 115.6. ^{31}P NMR δ (ppm): 7.7.

Synthesis of Hexa[4-chloro-2-(4-hydroxy-pheyliminomethyl) phenoxy]cyclotriphosphaze (3c)

4-hydroxy-aniline (0.52 g, 4.7 mmol). Note that, **3c** is a dark olive solid (0.45 g, 59%). M.p.: 185 °C. Anal. Calc. % for $N_9P_3C_{78}H_{54}Cl_6O_{12}$: C: 58.01, H: 3.37, N: 7.81. Found, %: C: 57.03, H: 3.64, N: 7.49. FTIR (KBr, cm^{-1}): 3309 (−OH), 3020 (C−H aromatic), 2803 (H−CN imine), 1619 (HC=N imine), 1189, 1162 (P=N), 950 (P−OAr aryl). ^{1}H NMR δ (ppm): 9.5 (**H**−O−8.1 (s, **H**−CN), 8.0–6.6 (the peaks of aromatic protons). ^{13}C NMR δ (ppm): 157.5 (s, H**C**=N), 148.1, 147.8 (P−O−**C**(Aryl)) 141.5, 131.5, 131.2, 130.0, 127.0, 123.1, 122.9, 116.0. ^{31}P NMR δ (ppm): 8.0.

Synthesis of Hexa[4-chloro-2-(2-(4-morpholine)-ethyliminomethyl) phenoxy]cyclotriphosphaze (3d)

2-(4-morpholine)-ethylamine (0.62 mL, 4.7 mmol). Note that, **3d** is a maroon solid (0.56 g, 74%). M.p.: 85 °C. Anal. Calc. % for $N_{15}P_3C_{78}H_{96}Cl_6O_{12}$: C: 53.80, H: 5.56, N: 12.07. Found, %: C: 54.34, H: 6.24, N: 12.09. FTIR (KBr, cm^{-1}): 3070 (C−H aromatic), 2954–2900 (C−H alkyl), 2852 (H−CN imine), 1640 (HC=N imine), 1204, 1163 (P=N), 956 (P−OAr aryl). ^{1}H NMR δ (ppm): 8.1 (s, **H**−CN), 7.8(d), 7.36(dd), 7.0(d), 3.6–2.3 (the peaks of CH_2 protons). ^{13}C NMR δ (ppm): 154.3 (s, H**C**=N), 147.6 (P−O−**C**(Aryl)) 131.8, 131.2, 129.6, 127.3, 123.1, 66.6, 66.5, 53.9, 53.6. ^{31}P NMR δ (ppm): 8.2.

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