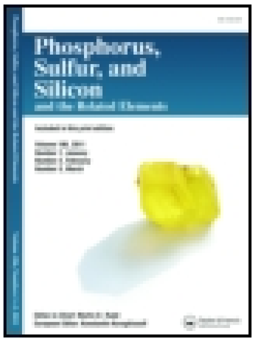

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Optimized synthesis of selected 4-oxybenzaldehyde and 2,2-dioxybiphenyl cyclotriphosphazene derivatives

Jipeng Chen, Le Wang, Yunxia Yang, Mengsheng Xu, Jinhua Xie, and Pan Liu

College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, China

ABSTRACT

Selected 4-oxybenzaldehyde and 2,2-dioxybiphenyl cyclotriphosphazene derivatives were synthesized via substitution reactions through tailored control. The reactions of cyclotriphosphazene with 4-oxybenzaldehyde and 2,2-dioxybiphenyl gave the following synthesized derivatives: one mono-substituted open-chain compound, $N_3P_3Cl_5(O_2C_7H_5)$ (**1**, 69%); mono spiro, $N_3P_3Cl_4(O_2C_{12}H_8)$ (**2**, 91.1%); non-gem tri-substituted, $N_3P_3Cl_3$ $(O_6C_{21}H_{15})$ (**3**, 17%); dispiro, $N_3P_3Cl_2(O_4C_{24}H_{16})$ (**4**, 92.3%); penta-substituted, $N_3P_3Cl(O_{10}C_{35}H_{25})$ (5, 92%)； hexa-substituted, $N_3P_3(O_{12}C_{42}H_{30})$. Most of these derivatives (**1–6**) are obtained with good yield (up to 97%), This work provides a simple and available approach to obtain versatile cyclotriphosphazene derivatives, which is expected to further promote the use of HCCP as phosphorus platform for the construction of multi-functional materials.

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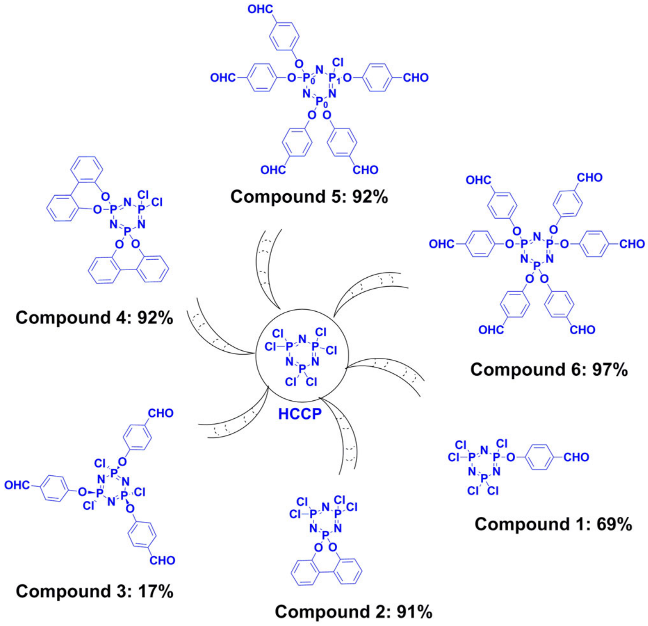
KEYWORDS
Hexachlorocyclotriphosphazene (HCCP); tailored control; ^{31}P NMR

GRAPHICAL ABSTRACT



Introduction

As an important branch of phosphorus chemistry, the hexachlorocyclotriphosphazene ring ($N_3P_3Cl_6$, HCCP) is a versatile symmetric heterocycle with six active chlorines[1–3] (Figure 1) which can be easily functionalized via selective substitutions of the six chlorines to produce many derivatives to showcase a wide range and unique chemical and biological properties, and has received extensive attention.[4–7] Phosphorus chemists have paid attention to coordination chemistry of the cyclotriphosphazene derivatives and focused on its symmetrical structural and terminal functional groups.[8–12] Many cyclotriphosphazene derivatives were reported and used in the fields of catalysts,[13,14] flame retardants,[15] biological materials,[16,17] and chemosensor.[18] Recently, the cyclotriphosphazene ring has been further developed as a versatile 'phosphorus' platform for the preparation of multi-functional materials with specific properties useful in diverse research areas. For example, Majoral's group have prepared dendrons bearing bi-

CONTACT Le Wang wangle316@sues.edu.cn College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, 201620, China.

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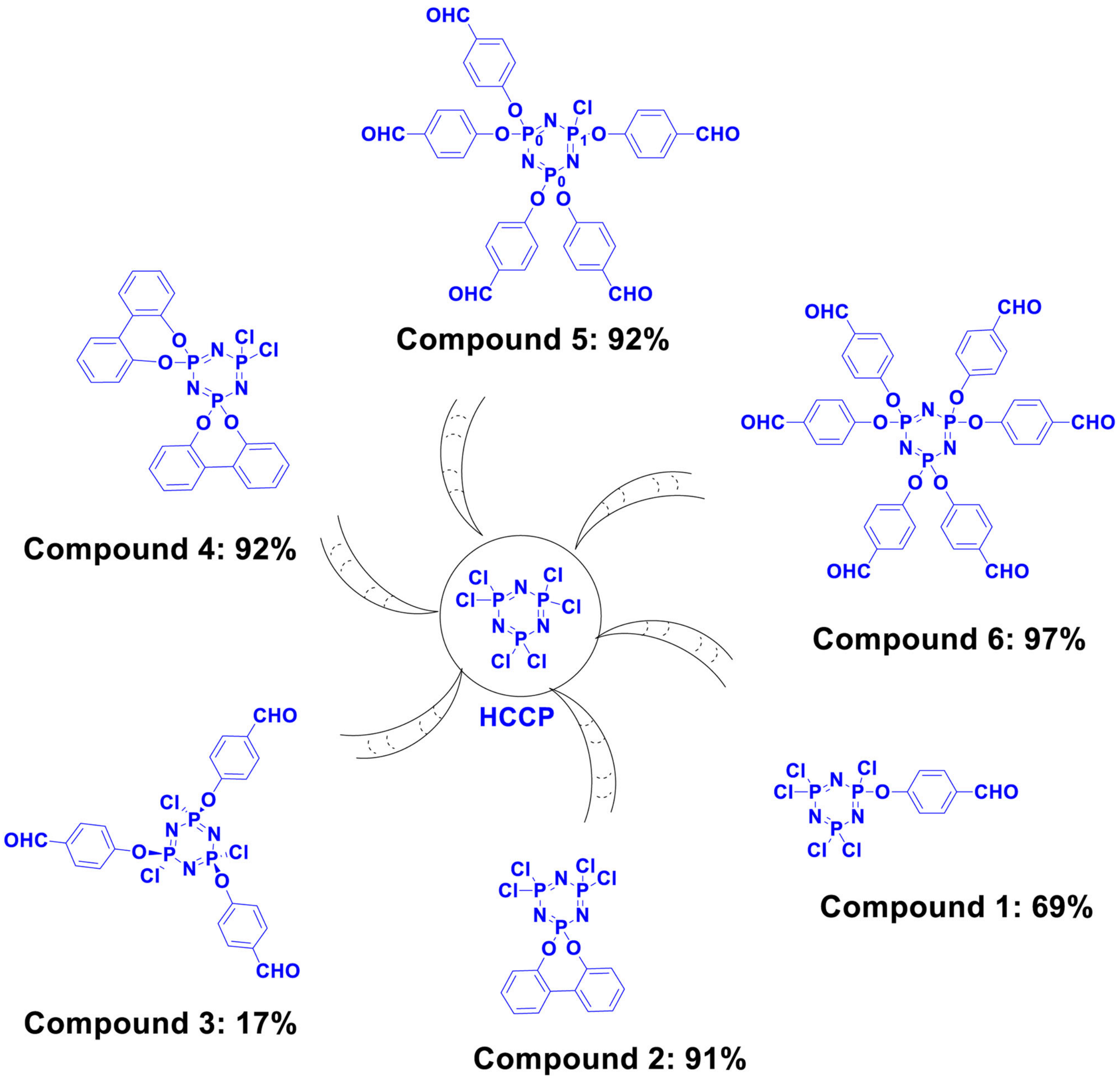


Figure 1. Optimized Synthesis of Selected 4-oxybenzaldehyde and 2,2-dioxybiphenyl cyclotriphosphazene derivatives (compounds **1–6**).

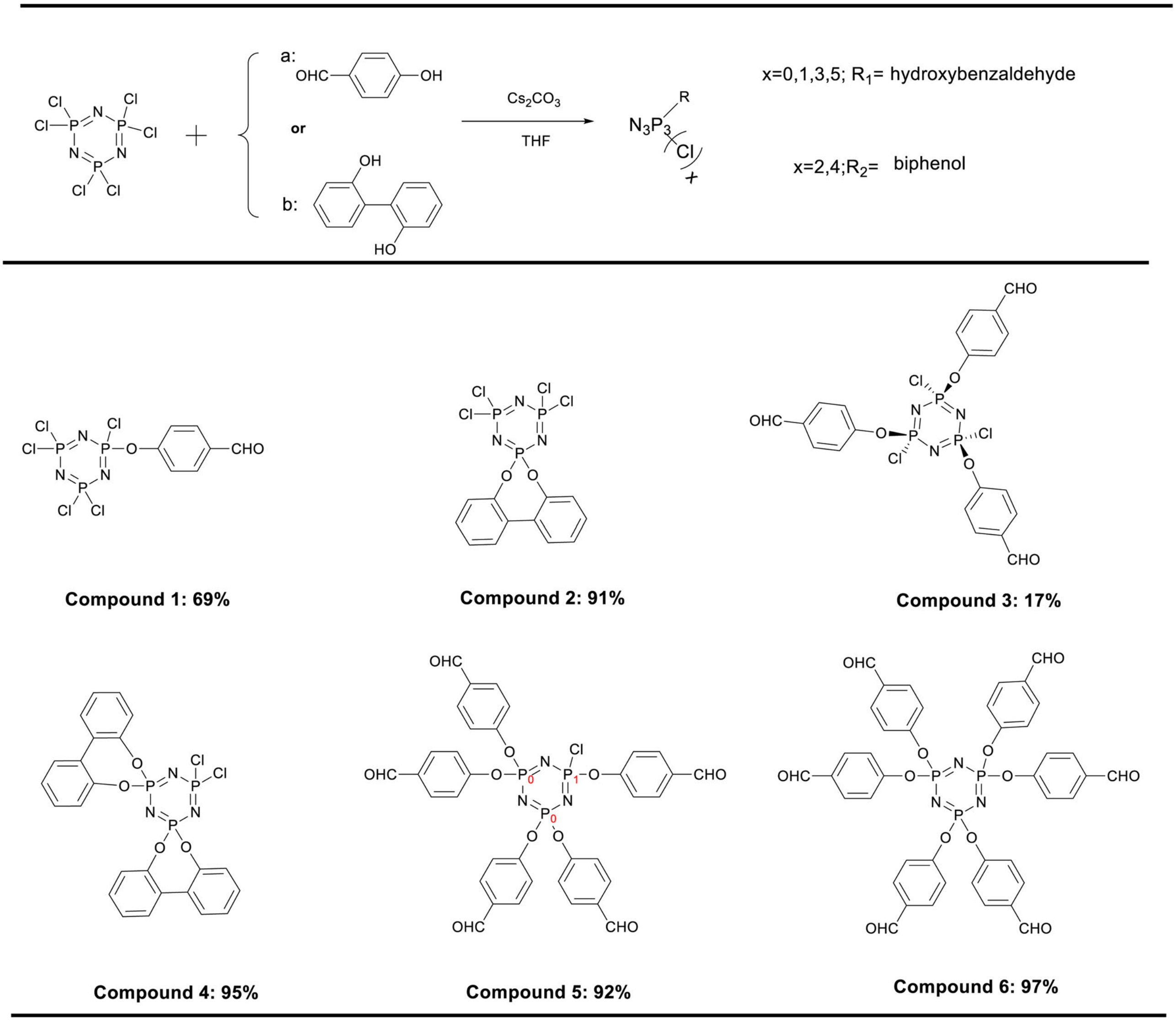
functional group based on cyclotriphosphazenes;[19] Turkey's groups have systematically looked at substitution reactions and the distribution of products;[20–23] We have also shown that different cyclen/imidazole moieties attached to a cyclotriphosphazene core have shown significant cooperativity.[24,25]

Therefore, these observations suggest the possibility of constructing multifunctional phosphorus materials according to selected synthesis of cyclotriphosphazene derivatives.[26,27] In this paper, different substituted cyclotriphosphazene derivatives from one to six were prepared with 4-oxybenzaldehyde and 2,2-dioxybiphenylphenol (Figure 1). The optimized synthesis reaction conditions of of selected 4-oxybenzaldehyde and 2,2-dioxybiphenyl cyclotriphosphazene derivatives, especially reaction conditions were followed by ^{31}P NMR will be described and analyzed.

Results and discussion

In this paper, the selected substitution reaction of cyclotriphosphazene has been systematically studied, and six well-defined organic phosphorus derivatives based on cyclotriphosphazene ring have been optimized synthesized with 4-oxybenzaldehyde moieties and 2,2-dioxybiphenyl groups. As shown in Scheme 1, most of compounds were obtained with good yield (up to 97%) under mild conditions (Cs_2CO_3 as base, room temperature) by employing optimized design system.

With six actives chlorines, cyclotriphosphazene derivatives are well known easily to produce multiple substituted products. Therefore, the selected substitution reaction of cyclotriphosphazene were systematically studied, and six well-defined organic phosphorus derivatives based on



Compound 1: 69%

Compound 2: 91%

Compound 3: 17%

Compound 4: 95%

Compound 5: 92%

Compound 6: 97%

Scheme 1. Synthetic route of cyclotriphosphazene derivatives (compounds **1–6**) (the yield of this compound was isolated yield).

cyclotriphosphazene ring have been synthesized with 4-oxybenzaldehyde moieties and 2,2-dioxybiphenyl groups. In this paper, two template compounds were firstly selected to investigate reaction conditions, and then six HCCP-based derivatives with different modification compounds (**1–6**) were obtained under the optimum condition.

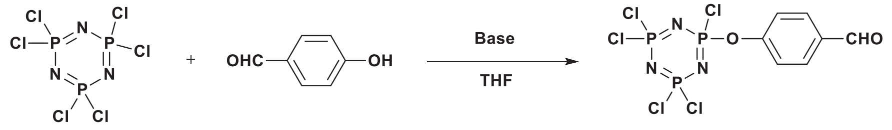
As shown in Table 1, different parameters such as types of base, were firstly investigated in order to optimize the reaction conditions of compound **1**. It is evident that Cs_2CO_3 and K_2CO_3 produced higher yield of 1 than other bases (e.g., NaH and Et_3N) (entries 1–4). Therefore, the influence on yield of compound **1** by bases (K_2CO_3 and Cs_2CO_3) were further invested by ^{31}P NMR spectra and was shown in Figure S1 (Supplementary material). According to ^{31}P NMR spectra, it was found that the yield of 1 was higher with K_2CO_3 as the base than that of Cs_2CO_3 with the time increased. It was speculative that high activity of Cs_2CO_3 induce multiple substituted products form, and that reduce the yield of compound **1** (Supplementary material Figure S2).

General procedure. To a stirred solution of base (1 equiv.) and substrate HCCP (1 mmol) dissolved in dry THF (10 mL), was added 2,2-dioxybiphenyl, then keep 0 °C (30 min) then r.t. (10 h). The crude yield of compound **2** was determined by ^{31}P NMR (Table 2).

In order to obtain a better yield, the proportion of the reaction was also examined. The research show that compounds **2** and **4** can be gained with high yield by using the molar ratio of 1:0.9 and 1:4.0 ($P_3N_3Cl_6$/2,2-dioxybiphenyl). While that was 1:5.0 for compound **5**. However, the yield of compound **3** was still as low as 17% with K_2CO_3 as base with regardless of the regulatory response ratio. That should be related to various geometrical and positional isomers results in the difficulty in separation of the isomeric mixtures.[28,29] More details were provided in the Experimental section.

All the pure products were separated and shown in Figure 2 and the yield were shown in Figure 1. Due to the symmetric structure, compounds **3** and **6** showed a singlet at 17.39 ppm and 7.08 ppm in ^{31}P NMR spectrum,

Table 1. The optimization of reaction conditions of compound **1** which containing with 4-hydroxybenzaldehyde.[a]

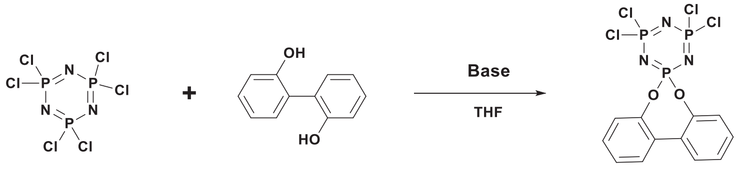


Compound 1

Entry	Base	Solvents	Temp. (°C)	Time (h)	Yield of 1[a] (%)
1	$(Et)_3N$	THF	r.t.	10	<10
2	NaH	THF	r.t.	10	22
3	K_2CO_3	THF	r.t.	10	67
4	Cs_2CO_3	THF	r.t.	10	63

[a]General procedure: To a stirred solution of base (1 equiv.) and substrate HCCP (1 mmol) dissolved in dry THF (10 mL), was added 4-hydroxybenzaldehyde, then keep 0 °C (30 min) then r.t. (10 h); The crude yield of compound **1** was determined by ^{31}P NMR.

Table 2. The optimization of reaction conditions of compound **2** which containing with 2,2-dioxybiphenyl.



Compound 2

Time/h	2	4	6	8	10
Yield[a]/%	94	94	96	94	96
Yield[b]/%	75	87	88	96	97

separately. Differently, compounds **1**, **2**, **4**, and **5** showed two typical coupling signals in ^{31}P NMR spectrum. For example, compound **1** showed a triplet at 11.74 ppm that was attributed to the two PCl_2 phosphine, and doublets at 22.50 ppm were ascribed to the 4-hydroxybenzaldehyde-substituted phosphine, while compound **5** displays two different signal at 20.50 ppm and 5.04 ppm. It is clear that these compounds exhibit significant difference in ^{31}P NMR chemical shift, and thus the progress of the reaction can be monitored by ^{31}P NMR.

Experimental

Method and apparatus

All chemical reagents and solvents were obtained commercially and used as received without further purification unless otherwise stated. Ultrapure water was purified from Millipore. Silica gel (100–200 mesh) was used for flash column chromatography. NMR spectra were recorded on a Bruker AV II 400 MHz; chemical shifts are quoted relative to SiMe4 (TMS, ^{1}H and ^{13}C, external) and H_3PO_4 (85%) (^{31}P, external). Coupling constants (*J*) were given in Hertz (Hz). The term m, q, t, d, s referred to multiple, quartet, triplet, doublet, singlet. Mass spectra were carried out on a Finnigan LCQDECA spectrometer and Agilent 1100 LC/MSD with ESI mode. The Supplemental Materials contains sample ^{1}H, ^{13}C and ^{31}P NMR spectra for the products 1–6 (Supplementary material Figures S3–S24)

Typical procedure for synthesis of compounds 1–6

Synthesis of [$N_3P_3Cl_5(O_2C_7H_5)$] (compound 1)

A mixture of K_2CO_3 (1.69 g, 5.18 mmol) and 4-oxybenzaldehyde (316.16 mg, 2.59 mmol) in anhydrous tetrahydrofuran (10 mL) was stirred at 0 °C for 30 min. Then HCCP (1.00 g, 2.88 mmol) in anhydrous tetrahydrofuran (20 mL) was added dropwise in ice bath, and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by ^{31}P NMR until the phosphorus spectrum signal ($\delta = 20.43$ ppm) of the raw material HCCP disappeared. Twenty-four hours later, the reaction was completed, and the salt was removed by centrifugation and the supernatant was collected. The solvent was removed in vacuo and the crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate (V:V = 20:1)). The procedure gave the compound **1** (0.86 g, 69.1%) as a colorless, crystalline solid. The NMR spectra was confirmed by literature.[30] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm10.01(s, 1H), 7.95 (d, 2H, $J = 8.2$ Hz), 7.44 (d, 2H, $J = 8.2$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ/ppm 20.81(d, 2 P, PCl_2, AB_2 System, $J = 63.2$ Hz); 11.74 (t, 1 P, $P(O_2C_{12}H_8$, $J = 63.2$ Hz)); ^{13}C NMR(100 MHz, $CDCl_3$) δ/ppm 190.34, 153.60, 134.51, 131.60, 122.06.

Synthesis of [$N_3P_3Cl_4(O_2C_{12}H_8)$](compound 2) and [$N_3P_3Cl_2(O_4C_{24}H_{16})$] (compound 4)

These two molecules were synthesized according to our previous report with some modification. To a cooled suspension (0 °C) of HCCP (1.00 g, 2.88 mmol) and Cs_2CO_3

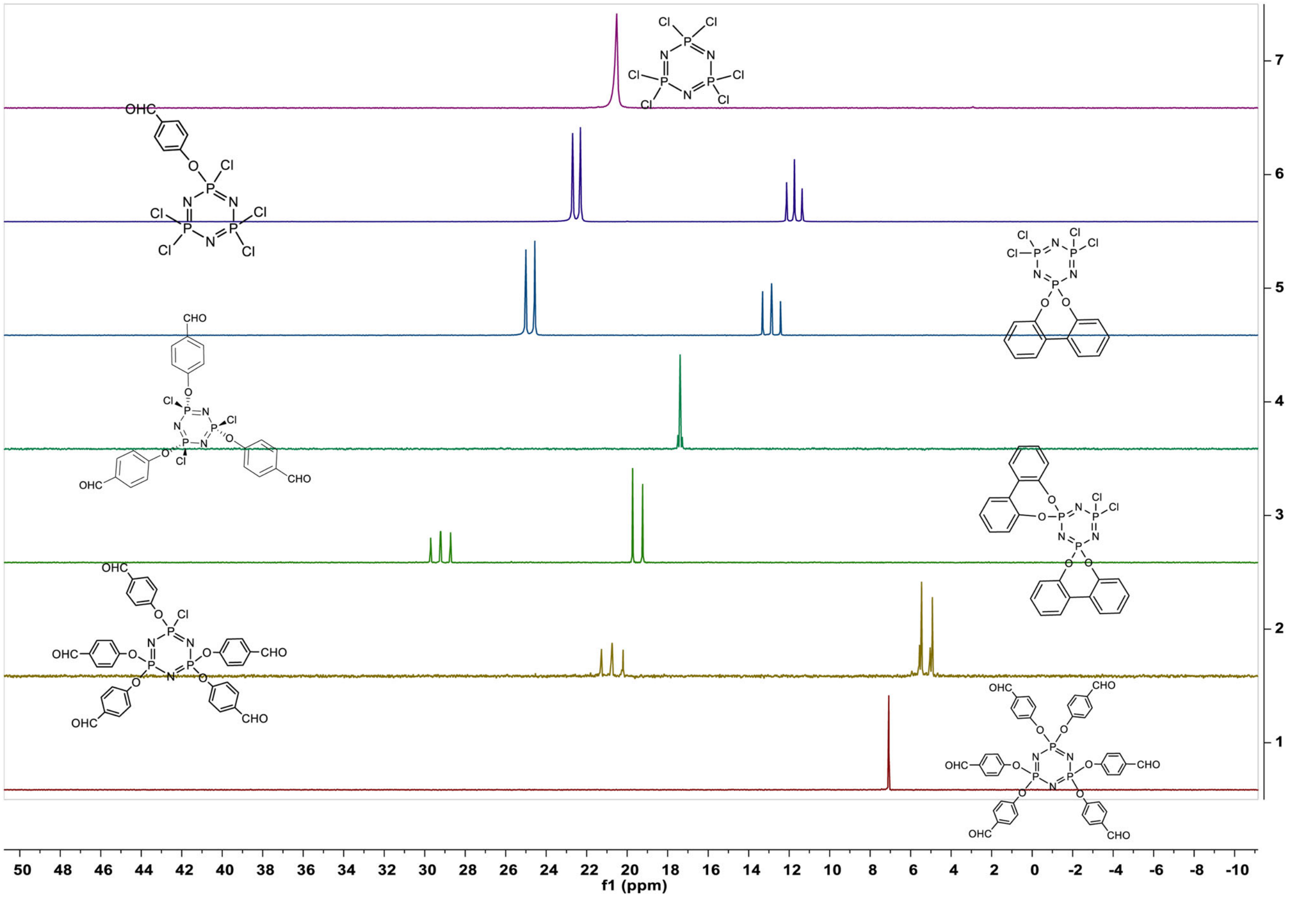


Figure 2. ^{31}P NMR spectrum of compounds **1–6** and HCCP.

(2.06 g, 6.33 mmol) in anhydrous THF (50 mL), 2,2-dihydroxybiphenyl (0.59 g, 3.16 mmol) was added drop by drop. The mixture was stirred at room temperature until the raw material HCCP disappeared, then the mixture was filtered and the organic phase was evaporated under vacuum. The product was recrystallized with petroleum ether and dichloromethane. White crystal. (1.21 g, 91.1%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.59 (m, 8 H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.78(d, 2 P, PCl_2, AB_2 System, $J = 71.3$ Hz), 12.87 (t, 1 P, P ($O_2C_{12}H_8$, $J = 71.3$ Hz)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.76, 129.84, 128.59, 126.48, 121.83.

Compound **4** were prepared by following a procedure similar to that used for 2. The quantities involved are as follows: HCCP (1.00 g, 2.88 mmol), Cs_2CO_3 (4.69 g, 14.38 mmol), 2,2-dihydroxybiphenyl (1.18 g, 6.33 mmol). White crystal. (1.52 g, 92.3%), ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 7.37–7.58 (m, 16H). ^{31}P NMR (162 MHz, $CDCl_3$)) δ 29.22 (dd, ^1P, PCl_2), 19.44 [d, 2 P, P (O_2C12H8)]; ^{13}C NMR (100 MHz, CDCl3) δ 147.80, 129.85, 128.59, 126.48, 121.83.

White crystal. (1.21 g, 91.1%). ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 7.33–7.59 (m, 8 H). ^{31}P NMR (162 MHz, $CDCl_3$) δ/ppm, 24.78(d, 2 P, PCl_2, AB_2 System, $J = 79.4$ Hz), 12.87 (t, 1 P, P ($O_2C_{12}H_8$, $J = 79.4$ Hz)); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm 147.76, 129.84, 128.59, 126.48, 121.83. MALDI-TOF-MS (m/z): $[M+H]^+$, 578.9803 (calcd. 578.9856).

Synthesis of [$N_3P_3Cl_3(O_6C_{21}H_{15})$] (compound 3)

A solution of 4-oxybenzaldehyde (1.05 g, 8.63 mmol) in THF (10 mL) was added to a suspension of K_2CO_3 (1.79 g, 12.94 mmol) in anhydrous tetrahydrofuran (10 mL) at 0 °C, then HCCP (1.00 g, 2.88 mmol, in 20 mL of THF) was added dropwise and the mixture was stirred at room temperature. The progress of the reaction was monitored by ^{31}P NMR, until the phosphorus spectrum signal ($\delta = 20.43$ ppm) of the raw material HCCP disappeared. After removal of salts by centrifugation, the clear solution was concentrated under reduced pressure and subjected to flash chromatography (silica gel, petroleum ether/ethyl acetate (V:V = 15:1) to afford compound **3** as a colorless, crystalline solid. The NMR spectra was confirmed by literature.[31]

White solid (0.30 g, 17.4%). ^1H NMR (400 MHz, $CDCl_3$) δ 10.03 (d, 3H, $J = 8.8$ Hz), 7.95 (d, 6H, $J = 8.5$ Hz), 7.49 (d, 2H, $J = 8.2$ Hz), 7.40 (d, 4H, $J = 8.4$ Hz). ^{31}P NMR (162 MHz, $CDCl_3$)) δ 18.14. ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.46, 153.82, 134.44, 131.56, 122.01. MALDI-TOF-MS (m/z): $[M+H]^+$, 603.9312 (calcd. 603.9098).

Synthesis of [$N_3P_3Cl(O_{10}C_{35}H_{25})$] (compound 5)

To a vigorously stirred solution of 4-oxybenzaldehyde (1.76 g, 14.38 mmol) in anhydrous THF (30 mL) was added K_2CO_3 (2.98 g, 21.57 mmol) and the mixture was stirred at 0 °C under nitrogen atmosphere for 30 min, then HCCP

(1.00 g, 2.88 mmol) in anhydrous THF (20 mL) was slowly added with stirring, allowed to warm to room temperature, and stirred for about 24 h. The progress of the reaction was monitored by ^{31}P NMR. The reaction mixture was centrifuged, filtered and evaporated. The solvent was removed in vacuo then the resultant crude product was purified by column chromatography (silica gel, petroleum ether /ethyl acetate (V:V = 10:1)). The procedure gave the compound **5** as a white solid. The spectra was in agreement with that reported in the literature.[32] White solid (2.05 g, 92.1%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.99 (t, 5H, $J = 8.0$ Hz), 7.82 (t, 10H, $J = 8.0$ Hz), 7.25 (s, 10H). ^{31}P NMR (162 MHz, CDCl$_3$) δ/ppm 20.74 (t, 1 P, P$_1$, AB$_2$ System, $J = 85.8$ Hz), 5.25 (d, 2 P, P$_0$, $J = 85.8$ Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ/ppm 190.22, 154.16, 134.06, 121.27. MALDI-TOF-MS (m/z): [M + H]$^+$, 776.0514 (calcd. 776.0332).

Synthesis of [$N_3P_3(O_{12}C_{42}H_{30})$] (compound 6)

A mixture of N$_3$P$_3$Cl$_6$ (1.00 g, 2.88 mmol), K$_2$CO$_3$ (3.94 g, 28.48 mmol) and 4-oxybenzaldehyde (2.32 g, 18.99 mmol) was stirred in anhydrous THF (100 mL) under nitrogen atmosphere at room temperature for 24 h. The reaction was monitored by ^{31}P NMR until a new single appeared. The reaction mixture was centrifuged and the solvent was removed under reduced pressure, the crude product was purified by recrystallized with petroleum ether and dichloromethane. The spectra is consistent with that in the literature.[33] White solid (1.63 g, 96.9%). ^{1}H NMR (400 MHz, CDCl$_3$) δ/ppm 9.96 (s, 6H), 7.76 (d, 12H, $J = 8.4$ Hz), 7.17 (d, 12H, $J = 8.4$ Hz). ^{31}P NMR (162 MHz, CDCl$_3$): δ 7.08. ^{13}C NMR (100 MHz, CDCl$_3$) δ 190.29, 154.51, 133.82, 131.95, 131.35, 121.22.

Conclusion

In summary, the substitution reaction of cyclotriphosphazene was studied and its 4-oxybenzaldehyde and 2,2-dioxybiphenyl cyclotriphosphazene derivatives also were selected prepared under mild conditions. All of these compounds were separated and obtained in good yield. We believe that the strategy presented in this work will be useful in the field of cyclotriphosphazene even phosphorus chemistry, which providing possibilities of multi-functionalization of cyclotriphosphazene materials in the future.

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