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Synthesis, thermal and photophysical properties of phenoxy-substituted dendrimeric cyclic phosphazenes

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ABSTRACT

In the present study, we describe the synthesis of a hydroxyl substituted bridged phenoxycyclotriphosphazene (**5**), [$N_3P_3(OPh)_5OPhO(OPh)_5N_3P_3OPhOH$], as a side group and its use for preparation of dendrimeric cyclic phosphazenes. For this purposes, compound **5** is synthesised in five steps from the reactions of cyclotriphosphazene with phenol derivatives. The dendrimeric compounds **6** and **7** have been prepared by the reactions of compound **5** with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, or octachlorocyclotetraphosphazene, $N_4P_4Cl_8$, respectively. Newly synthesized compounds have been fully characterized by elemental analysis, MALDI-TOF mass spectrometry, FT-IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The thermal stability and fluorescence spectral properties of dendrimeric compounds **6** and **7** are investigated and compared with that of the previously reported cyclic compounds **(I–II)**. Fluorescence quantum yields and lifetimes of dendrimeric compounds and their quenching behaviour by 1,4-benzoquinone are studied in dichloromethane.

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1. Introduction

The cyclic and polymeric phosphazenes are an important class of inorganic heterocyclic ring systems in basic and applied science [1,2]. They are usually prepared by nucleophilic substitution reactions of alkoxides, aryloxides or amines on halocyclophosphazenes or high polymers [3–5] and their physical and chemical properties can be tailored via appropriate substituted groups on phosphorus atoms [6]. The design of materials containing cyclotriphosphazenyl groups have attracted attention because of their special properties such as thermal stability, catalytic properties, electrical conductivity, liquid crystal and biomedical activity [7–9]. The thermal stability and flame resistance of polyphosphazenes that bear aryloxy side groups are especially well documented, and aryloxyphosphazene polymers have been developed commercially as foams for electrical, heat and sound insulation [10–12]. Cyclotriphosphazenes have also been investigated as flame retardant additives to organic polymers [13]. Compositions that contain cyclotriphosphazenes or polyphosphazenes with commercial polymers are relatively easy to prepare, and flame retardant poly(urethane) [14], poly(methylmethacrylate) [15], polystyrene [16] and various other polymers [17] have been produced in this way.

Luminescent compounds are attracting much current research interest because of their many applications including emitting materials for organic light emitting diodes, light harvesting materials for photocatalysis and fluorescent sensors for organic or inorganic analyzers [18]. Cyclophosphazenes have many advantages as useful luminescent materials for electroluminescent devices. For example, substituted cyclic phosphazenes are very stable and do not breakdown under very aggressive chemical conditions. Also the functional groups are projected above and below the cyclophosphazene plane thus producing a rigid spherical core from which to grow the dendrons of interest. Hence there has recently been considerable interest in fluorescent compounds based on cyclic phosphazene cores [19] or cyclolinear polymers with the cyclotriphosphazene units [20] for the development of electroluminescent devices. In phosphazene chemistry, there are many examples of organic or inorganic side group bearing cyclophosphazenes or polyphosphazenes [3–5]. However, there are limited examples of cyclophosphazenes and polyphosphazenes [21,22] or organic polymers [23,24] that bear organic group substituted cyclophosphazene ring as side group. We have recently reported [25] that comparison of the thermal stability and fluorescence spectral properties of cyclic and polymeric compounds bearing hexaphenoxycyclotriphosphazenenyl groups is shown in Scheme 1. The thermal stability and fluorescence spectral properties of cyclic structures (**I** or **II**) have been found to be superior to those of polymeric structure (**III**) when substituted with the same inorganic group (**R**). It was found that the dendrimeric arrangement of side groups was more effective than numbers of attached side groups for the thermal stability and fluorescence spectral properties which was reported in the previous study [25]. Hence, we have

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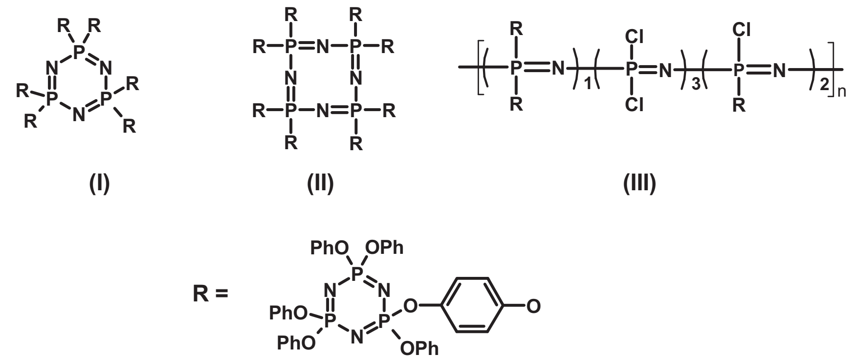
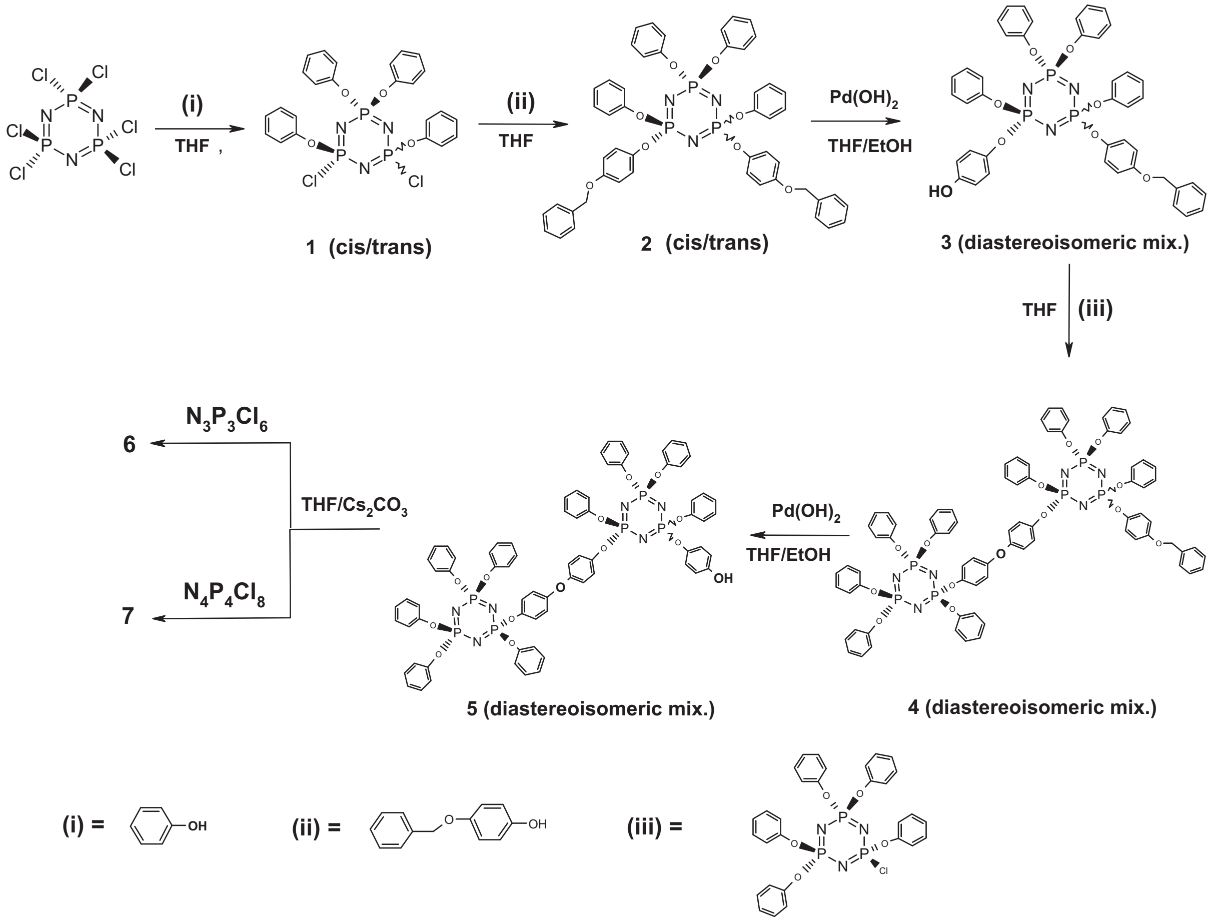


Scheme 1. Structures of previously reported cyclic and polymeric compounds.



Scheme 2. Chemical structure and synthetic pathway of compounds **1–7**.

undertaken a study to extend the side group length that contains the phenoxy substituted cyclophosphazenes.

In this report, we describe the molecular design, synthesis and characterization of compound **5** $[N_3P_3(OPh)_5OPhO(OPh)_5N_3P_3OPhOH]$, as a side group (Scheme 2). The nucleophilic substitution reaction of compound **5** with $N_3P_3Cl_6$ or $N_4P_4Cl_8$ provided yields of dendrimeric compounds **6** and **7** 62% and 68%, respectively (Fig. 1). The thermal stability and fluorescence spectral properties of compounds **7** and **8** are compared with that of previous compounds (**I–II**). Fluorescence quantum yields and lifetimes of dendrimeric compounds and their quenching behaviour by benzoquinone are investigated in dichloromethane.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (trimer) and octachlorocyclotetraphosphazene (tetramer) (Otsuka Chemical Co., Ltd.) were purified by fractional crystallization from *n*-hexane. The deuterated solvents ($CDCl_3$ and toluene-d_8) for NMR spectroscopy and the following chemicals were obtained from Merck; 4-(benzyloxy) phenol, cyclohexene, ethanol, phenol, $Pd(OH)_2$, Cs_2CO_3, NaH, acetone, triethylamine, silica gel 60 and tetrahydrofuran. 1,8,9-Anthracenetriol for MALDI matrix was obtained from Fluka. All other

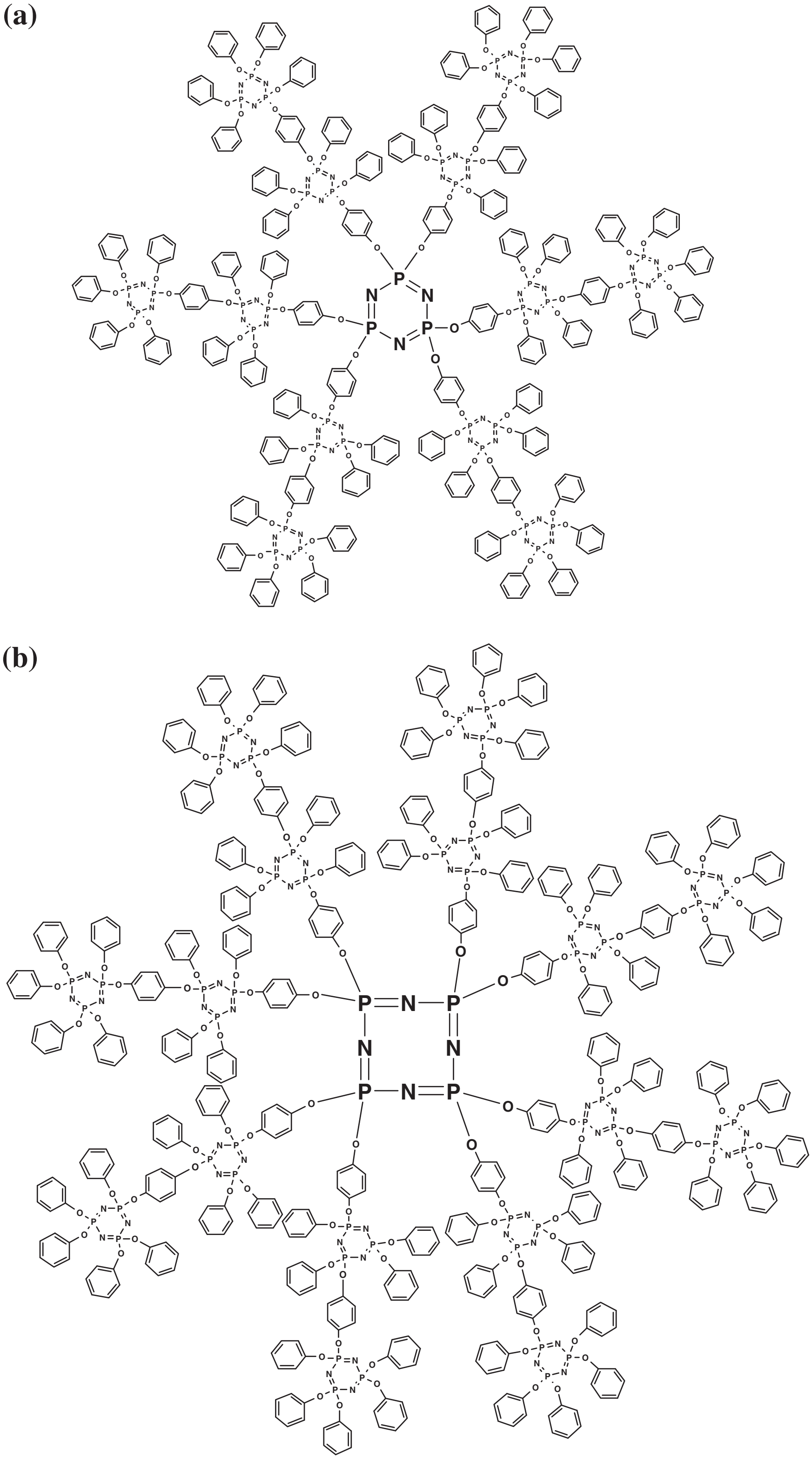


Fig. 1. Structures of (a) compound **6** and (b) compound **7**.

reagents and solvents were reagent grade quality and obtained from commercial suppliers.

2.2. Equipment

Elemental analyses were carried out using a Thermo Finnigan Flash 1112 Instrument. UV–Vis spectra were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Infrared spectra were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer using KBr pellets. Mass spectra were acquired in linear modes with average of 50 shots on a Bruker Daltonics Microflex mass spectrometer equipped with a nitrogen UV-Laser operating at 337 nm. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g crude mixture, 100 g silica gel was used in a column of 3 cm in diameter and 60 cm in length) and preparative thin layer chromatography was performed on silica gel 60 P F_{254}. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ or toluene-d_8 solutions on a Varian 500 MHz spectrometer. Thermal properties of compounds were investigated on Mettler Toledo TGA/SDTA 851 thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) DSC 821^{e} equipped with Mettler Toledo Star^{e} software at a heating rate of 10 °C min^{-1} under nitrogen flow (50 ml min^{-1}).

2.2.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [26]

$$\Phi_F = \Phi_F(\mathrm{Std})\frac{F \cdot A_{\mathrm{Std}} \cdot n^2}{F_{\mathrm{Std}} \cdot A \cdot n_{\mathrm{Std}}^2} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**6** and **7**) and the standard, respectively. A and A_{Std} are the respective absorbance of the samples and standard at the excitation wavelengths, respectively. The refractive indices (n) of the solvents were employed in calculating fluorescence quantum yields in different solvents. 2-Aminopyridine (in 0.1 M H_2SO_4) ($\Phi_F = 0.60$) [27] was employed as the standard. Both the samples and standard were excited at the same wavelength. The concentration of the solutions at the excitation wavelength fixed at 1×10^{-5} mol dm^{-3}. Natural radiative (τ_0) life times were determined using PhotochemCAD program which uses the Strickler–Berg equation [28]. The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \tag{2}$$

The rate constant for florescence (k_F) values were calculated using Eq. (3).

$$k_F = \Phi_F/\tau_F \tag{3}$$

2.2.2. Fluorescence quenching by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on the phenoxy substituted dendrimeric phosphazene derivatives (**6** and **7**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the compounds, and the concentrations of BQ in the resulting mixtures were 0, 2.4×10^{-6}, 4.8×10^{-6}, 7.2×10^{-6}, 9.6×10^{-6} and 12×10^{-6} mol dm^{-3}. The fluorescence spectra of phenoxy substituted dendrimeric phosphazene derivatives (**6** and **7**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern-Volmer (S-V) equation [29] (Eq. (4)):

$$\frac{I_0}{I} = 1 + \mathrm{K_{SV}}[\mathrm{BQ}] \tag{4}$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. [BQ] is the concentration of the quencher and K_{SV} is the Stern-Volmer constant which is the product of the bimolecular quenching constant (k_q) and the τ_F and is expressed in Eq. (5).

$$K_{SV} = k_q \cdot \tau_F \tag{5}$$

The ratios of I_0/I were calculated and plotted against [BQ] according to Eq. (4), and K_{SV} is determined from the slope.

2.3. Synthesis

1,1,3,5-Tetraphenoxy-3,5-dichlorocyclotriphosphazatriene (**1**), 1,1,3,3,5-pentaphenoxy-5-chlorocyclotriphosphazatriene (**iii**) and hexaphenoxycyclotriphosphazene were prepared and purified according to the literature procedures [30].

2.3.1. Synthesis of compound **2**

4-(Benzyloxy) phenol (1.38 g, 6.93 mmol), dry and finely powdered cesium carbonate (3.38 g, 10.4 mmol) were dissolved in dry THF (10 ml) under argon atmosphere. The solution was transferred to a 50 ml dropping funnel and slowly dropped to the solution of 1,1,3,5-tetraphenoxy-3,5-dichlorocyclotriphosphazatriene (2.0 g, 3.46 mmol) (**1**) in 10 ml dry THF under argon atmosphere. The reaction mixture was refluxed under argon for 24 h and followed by TLC indicating no starting material remaining. The precipitated salt (CsCl) was filtered off and the solvent was removed under reduced pressure. The crude product was purified by column chromatography [silica gel 60 (70–230 mesh) as adsorbent and dichloromethane:n-hexane (1:2) as the eluent]. 1,1,3,5-tetraphenoxy-3,5-[(4-benzyoxy)phenoxy]-cyclotriphosphazatriene (**2**) was obtained as viscous oil; Yield: 1.86 g (84%). *Anal.* Calc. for $C_{50}H_{42}N_3O_8P_3$ (905): C, 66.59; H, 5.37; N, 4.48. Found: C, 66.70; H, 5.28; N, 4.20%. ^{1}H NMR ($CDCl_3$) $\delta = 6.73–7.35$ (m, 38H, ArCH), 4.91 (br s, 4H, CH_2); $\{^{1}H\}^{13}C$ NMR ($CDCl_3$) $\delta = 156.04$ (ArC), 144.61 (ArC), 137.16 (ArC), 129.62 (ArCH), 128.87 (ArCH), 127.68 (ArCH), 125.02 (ArCH), 122.17(ArCH), 121.28 (ArCH), 77.27 (CH_2). MS (ESI) m/z (%): 906 (100) $[M+H]^+$.

2.3.2. Synthesis of compound **3**

Compound **2** (1.6 g, 1.7 mmol) was dissolved in 8 ml dry THF under argon atmosphere and 6 ml cyclohexene, palladium hydroxide (20 wt% on carbon, 0.4 g) and 6 ml ethanol were added to this solution. The mixture was refluxed for 24 h under argon atmosphere. Then the reaction mixture was filtered off and solvents were removed under reduced pressure. The crude product was purified by preparative TLC on silica gel using hexane:THF (1:1) as the eluent. Compound **3** was obtained as viscous oil; Yield: 1.2 g (84%). *Anal.* Calc. for $C_{43}H_{36}N_3O_8P_3$ (815): C, 63.54; H, 4.85; N, 5.05. Found: C, 63.60; H, 4.80; N, 5.20%. ^{1}H NMR ($CDCl_3$) $\delta = 6.57–7.47$ (m, 33H, ArCH), 5.16 (s, 1H, OH), 5.02 (br s, 2H, CH_2); $\{^{1}H\}^{13}C$ NMR($CDCl_3$) $\delta = 155.98$ (ArC-OH), 152.95 (ArC), 144.32 (ArC), 137.19 (ArC), 129.64 (ArCH), 128.91 (ArCH), 127.75 (ArCH), 125.06 (ArCH), 121.05(ArCH), 116.06 (ArCH), 77.27 (CH_2). MS (ESI) m/z (%): 816 (100) $[M+H]^+$.

2.3.3. Synthesis of compound **4**

1,1,3,3,5-Pentaphenoxy-5-chlorocyclotriphosphazatriene (**iii**) (0.87 g, 1.4 mmol) and compound **3** (1.12, 1.4 mmol) were dissolved in dry THF (10 ml) under argon atmosphere. After stirring for 15 min at 40 °C, dry and finely powdered cesium carbonate (0.66 g, 2.1 mmol) was added portion wise over 15 min with efficient stirring. The mixture was stirred at 80 °C for 24 h under argon atmosphere. Then the reaction mixture was filtered off and solvent was removed under reduced pressure. The crude product was purified by preparative TLC on silica gel using hexane:THF (1:1) as the eluent. Compound **4** was obtained as viscous oil; Yield: 1.5 g (77%). *Anal.* Calc. for $C_{73}H_{60}N_6O_{13}P_6$ (1414): C, 62.10; H, 4.51; N, 5.87. Found: C, 62.15; H, 4.58; N, 5.61%. ^{1}H NMR ($CDCl_3$) $\delta = 6.70–7.30$ (m, 58H, ArCH), 5.33 (br s, 2H, CH_2); $\{^{1}H\}$ ^{13}C NMR ($CDCl_3$) $\delta = 150.83$ (ArC), 136.03 (ArC), 129.67 (ArCH), 128.85 (ArC), 127.70 (ArCH), 125.77 (ArCH), 125.16 (ArCH), 122.06 (ArCH), 121.22(ArCH), 115.61 (ArCH), 77.27 (CH_2). MS (ESI) m/z (%): 1415 (100) $[M+H]^+$.

2.3.4. Synthesis of compound **5**

Compound **4** (1.4 g, 1 mmol) was dissolved in 5 ml dry THF under argon atmosphere and 3 ml cyclohexene, palladium hydroxide (20 wt% on carbon, 0.5 g) and 3 ml ethanol were added to this solution. The mixture was refluxed for 24 h under argon atmosphere and then filtered off. The solvents were removed under reduced pressure. Two isomeric compounds were purified by preparative TLC on silica gel using hexane: THF (1:1) as the eluent. The *racemic*-compounds **5a** and **5b** were obtained as viscous oil.

5a: Yield: 1.10 g (78%). *Anal.* Calc. for $C_{66}H_{54}N_6O_{13}P_6$ (1324): C, 59.83; H, 4.11; N, 6.34. Found: C, 59.90; H, 4.18; N, 6.31%. ^1H NMR ($CDCl_3$) δ = 6.68–7.27 (m, 53H, ArCH), 5.02 (s, 1H, OH); $\{^1H\}^{13}C$ NMR($CDCl_3$) δ = 151.74 (ArC-OH), 129.68 (ArC), 128.48 (ArC), 125.75 (ArCH), 125.11 (ArCH), 122.02 (ArCH), 121.22 (ArCH), 116.04 (ArCH). MS (ESI) *m/z* (%): 1325 (100) $[M+H]^+$:

5b: Yield: 1.10 g (78%). *Anal.* Calc. for $C_{66}H_{54}N_6O_{13}P_6$ (1324): C, 59.83; H, 4.11; N, 6.34. Found: C, 59.90; H, 4.18; N, 6.31%. ^1H NMR ($CDCl_3$) δ = 6.65–7.23 (m, 53H, ArCH), 5.03 (s, 1H, OH); $\{^1H\}^{13}C$

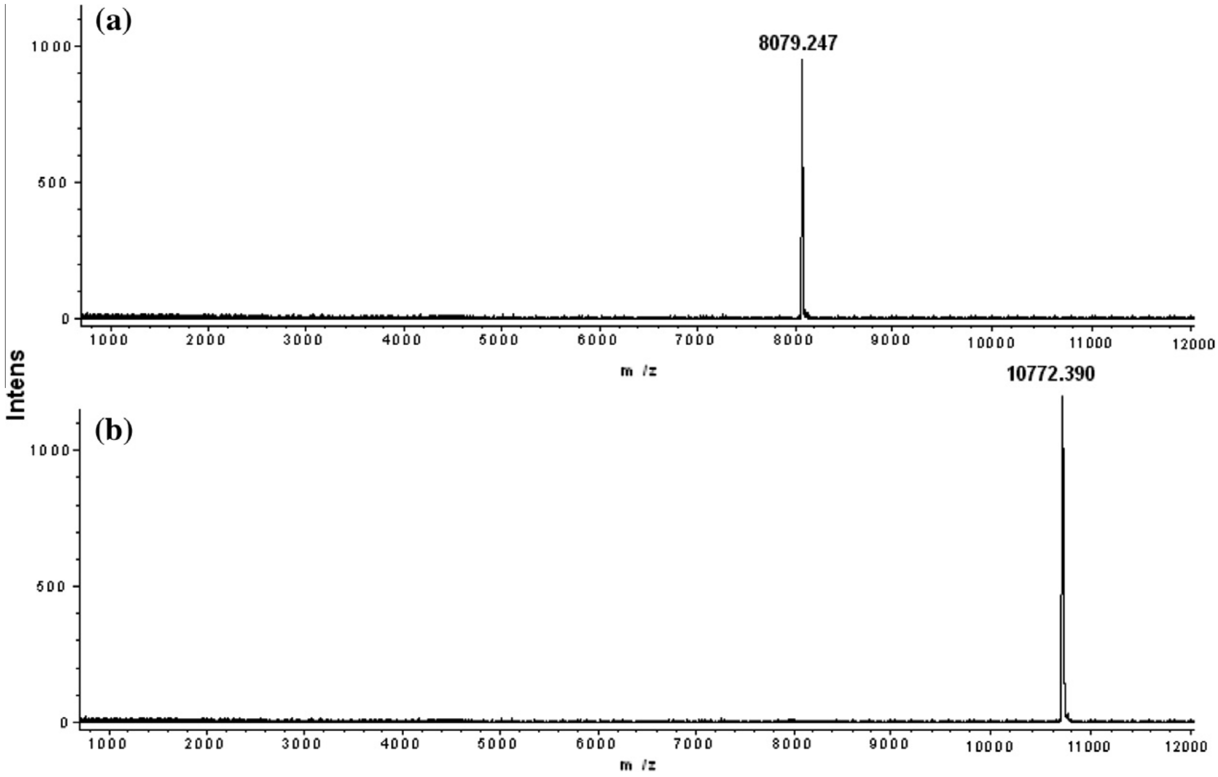


Fig. 2. Positive ion and linear mode MALDI-MS spectra of (a) **6** and (b) **7** were obtained in 1,8,9-anthracenetriol (20 mg/mL THF) MALDI matrix using nitrogen laser accumulating 50 laser shots.

Table 1
^{31}P NMR parameters of compounds **2–7**.[a]

Compounds	Chemical shifts/ppm					$^2J_{(PP)}$
	>P(phenoxy)$_2$	>P(phenoxy)(X)(Y)	X	Y	Cores $(N{=}P)_{3,4}$	(Hz)
2a	9.89	10.40	$OPhOCH_2Ph$	$OPhOCH_2Ph$	–	89.1
2b	9.88	10.39	$OPhOCH_2Ph$	$OPhOCH_2Ph$	–	89.1
$\Delta\delta$[b]	0.01	0.01			–	
3a	9.90	10.43	$OPhOCH_2Ph$	OPhOH	–	88.61
3b	9.89	10.42	$OPhOCH_2Ph$	OPhOH	–	88.87
$\Delta\delta$[b]	0.01	0.01			–	
4a	10.77	9.76	$OPhOCH_2Ph$	$OPhO[N_3P_3(OPh)_5]$[c]	–	86.6
4b	10.58	9.70	$OPhOCH_2Ph$	$OPhO[N_3P_3(OPh)_5]$[c]	–	86.5
$\Delta\delta$[b]	0.19	0.06			–	
5a	10.83	9.78	OPhOH	$OPhO[N_3P_3(OPh)_5]$[c]	–	86.8
5b	10.37	9.81	OPhOH	$OPhO[N_3P_3(OPh)_5]$[c]	–	86.2
$\Delta\delta$[b]	0.36	−0.03			–	
6	[d]	[d]	OPhO	$OPhO[N_3P_3(OPh)_5]$	9.45	–
7	[e]	[e]	OPhO	$OPhO[N_3P_3(OPh)_5]$	−11.16	–

[a] 202.38 MHz ^{31}P NMR measurements in $CDCl_3$ solutions at 298 K and spectra analyzed as A_2B or AB_2 spin systems.

[b] $\Delta\delta$ is the difference in chemical shift (ppm) of diastereoisomers.

[c] Signals observed more complicated and coupling constants not calculated.

[d] Signals displayed between 9.5 and 10.5 ppm and coupling constants not calculated.

[e] The broad signal displayed between 9 and 11 ppm and coupling constants not calculated.

NMR($CDCl_3$) δ = 152.14 (ArC-OH), 129.18 (ArC); 127.08 (ArC); 123.55 (ArCH); 123.56 (ArCH); 121.62 (ArCH); 121.90 (ArCH); 116.11 (ArCH). MS (ESI) *m*/*z* (%): 1325 (100) $[M+H]^+$.

*2.3.5. Synthesis of compound **6***

Trimer, $N_3P_3Cl_6$, (0.013 g, 0.04 mmol) and compound **5** (0.40 g, 0.3 mmol) were dissolved in dry THF (10 ml) under argon atmosphere. After stirring for 15 min at 40 °C, dry and finely powdered cesium carbonate (0.162 g, 0.5 mmol) was added portion wise over 15 min with efficient stirring. The reaction mixture was stirred at 80 °C for 24 h under argon atmosphere. The reaction mixture filtered off and solvent was removed under reduced pressure. The crude product was purified by preparative TLC on silica gel using *n*-hexane:THF (1:1) as the eluent. Compound **6** was obtained as highly viscous oil; Yield: 0.2 g (62%). *Anal.* Calc. for $C_{396}H_{318}N_{39}O_{78}P_{39}$ (8078): C, 58.87; H, 3.97; N, 6.76. Found: C, 58.76; H, 3.90; N, 6.80%. ^1H NMR ($CDCl_3$) δ = 6.69–7.31 (m, 318H, ArCH); $\{^1H\}^{13}C$ NMR ($CDCl_3$) δ = 150.86 (ArC), 136.03 (ArCH), 129.67 (ArC), 125.24 (ArCH), 121.28 (ArCH), MS (MALDI) *m*/*z* (%)*:* 8079 (100) $[M+H]^+$.

*2.3.6. Synthesis of compound **7***

Tetramer, $N_4P_4Cl_8$ (0.007 g, 0.015 mmol) and compound **5** (0.2 g, 0.15 mmol) were dissolved in dry THF (10 ml) under argon atmosphere. After stirring for 15 min at 40 °C, dry and finely powdered cesium carbonate (0.16 g, 0.5 mmol) was added portion wise over 30 min with efficient stirring. The reaction mixture was stirred at 80 °C for 48 h under argon atmosphere. The reaction mixture filtered off and solvent was removed under reduced pressure. The crude product was purified by preparative TLC on silica gel using hexane:THF (1:1) as the eluent. Compound **7** was obtained as highly viscous oil; Yield: 0.11 g (68%). *Anal.* Calc. for $C_{528}H_{424}N_{52}O_{104}P_{52}$ (10771): C, 58.87; H, 3.97; N, 6.76. Found: C, 58.80; H, 3.93; N, 6.70%. ^1H NMR ($CDCl_3$) δ = 6.71–7.35 (m, 424H, ArCH); $\{^1H\}^{13}C$ NMR ($CDCl_3$) δ = 150.87 (ArC), 136.07 (ArCH), 129.74 (ArC), 125.38 (ArCH), 121.32 (ArCH). MS (MALDI) *m*/*z* (%)*:* 10772 (100) $[M+H]^+$.

3. Results and discussion

The synthetic route of the studied compounds is shown in Scheme 2. Compound (*cis*/*trans*) **1** is synthesized [30] by the reaction of phenol with trimer in the presence of NaH as base in THF. Compound **1** is reacted with 4-benzyloxyphenol in the presence of Cs_2CO_3 in THF to obtain compound **2**. Compounds **1** and **2** possess two chiral centres and exist as a mixture of *cis* and *trans* isomers as expected, but no attempt is made to separate these isomers. One of the 4-benzyloxyphenoxy units of compound (*cis*/*trans*) **2** is converted to 4-hydroxyphenoxy group with cyclohexene in a mixture of THF/ethanol in the presence of $Pd(OH)_2$ as a catalyst to give compound **3** in good yields (84%). Compound **3** is reacted with 1,1,3,3,5-pentaphenoxy-5-chlorocyclotriphosphazatriene **(iii)** in the presence of Cs_2CO_3 in THF to obtain compound **4**. The 4-benzyloxyphenoxy unit of compound **4** is converted to 4-hydroxyphenoxy group with cyclohexene in a mixture of THF/ethanol in the presence of $Pd(OH)_2$ as a catalyst to give compound **5** in good yields (78%). Compounds **3**, **4** and **5** are obtained in the forms of diastereoisomeric mixtures and exist as two racemic mixtures as expected. However, only the two racemic forms (**5a** and **5b**) of compound **5** are separated by preparative TLC on silica gel using hexane:THF (1:1) as the eluent for comparison of fluorescence behaviours. Compounds **6** and **7** are obtained from nucleophilic displacement reactions of **5** with $N_3P_3Cl_6$ or $N_4P_4Cl_8$ in the presence of Cs_2CO_3 as the base under argon atmosphere.

The new compounds **2–7** are characterized by FT-IR, ^1H, ^{13}C and ^{31}P NMR, mass spectrometry and elemental analysis. All the results are consistent with the predicted structures as shown in the Section 2. In the FT-IR spectra, the new compounds show characteristic vibrations due to the P=N and P–O groups at around 1200 cm^{-1} (br) and 960 cm^{-1}, respectively. The aromatic C–H stretching bands are observed at around 3200–3400 cm^{-1} as expected [31]. The mass spectra of compounds **6** and **7** are obtained by MALDI-TOF spectrometry. Many different MALDI matrices are investigated to find an intense molecular ion peaks and low fragmentation. The 1,8,9-anthracenetriol MALDI matrix yielded the best MALDI-MS

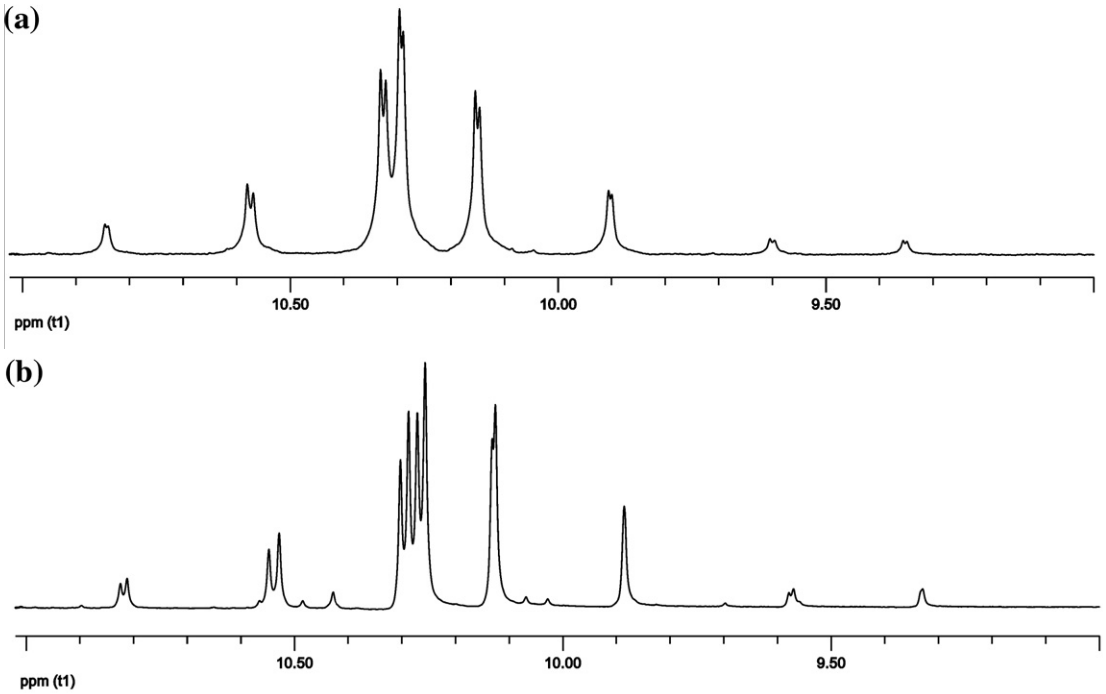


Fig. 3. Proton-decoupled ^{31}P NMR spectra of (a) compound **2** and (b) compound **3** in $CDCl_3$ solution.

spectra. The MS spectra of **6** and **7** provided definitive characterization. The protonated molecular ion peaks are observed at 8079 and 10772 Da for compounds **6** and **7**, respectively (Fig. 2).

In particular, ^{31}P NMR spectra are analyzed and the ^{31}P NMR chemical shifts and phosphorus–phosphorus coupling constants ($^2J_{PNP}$) of compounds **2–7** are summarised in Table 1. Since compounds **2–7** all show non-first order ^{31}P NMR spectra, it is necessary to carry out a simulation analysis to get the appropriate spectral parameters. Thus all coupling constants are obtained by simulation of the NMR spectra. The proton-decoupled ^{31}P NMR spectrum of compound **2** shows two A_2B spin systems (Fig. 3a), which was characterised by a small shift in the phosphorus–phosphorus coupling constant ($^2J_{PNP}$) in Table 1. By the analogy with compound **1** [30], compound **2** can have the two non-geminal phenoxy or the 4-benzyloxyphenoxy units in either *cis* or *trans* relationships to each other, both structures contain two equivalent chiral centres which lead to the diastereoisomers observed in the ^{31}P NMR spectrum (Fig. 3a). The diastereoisomers in compound **2**

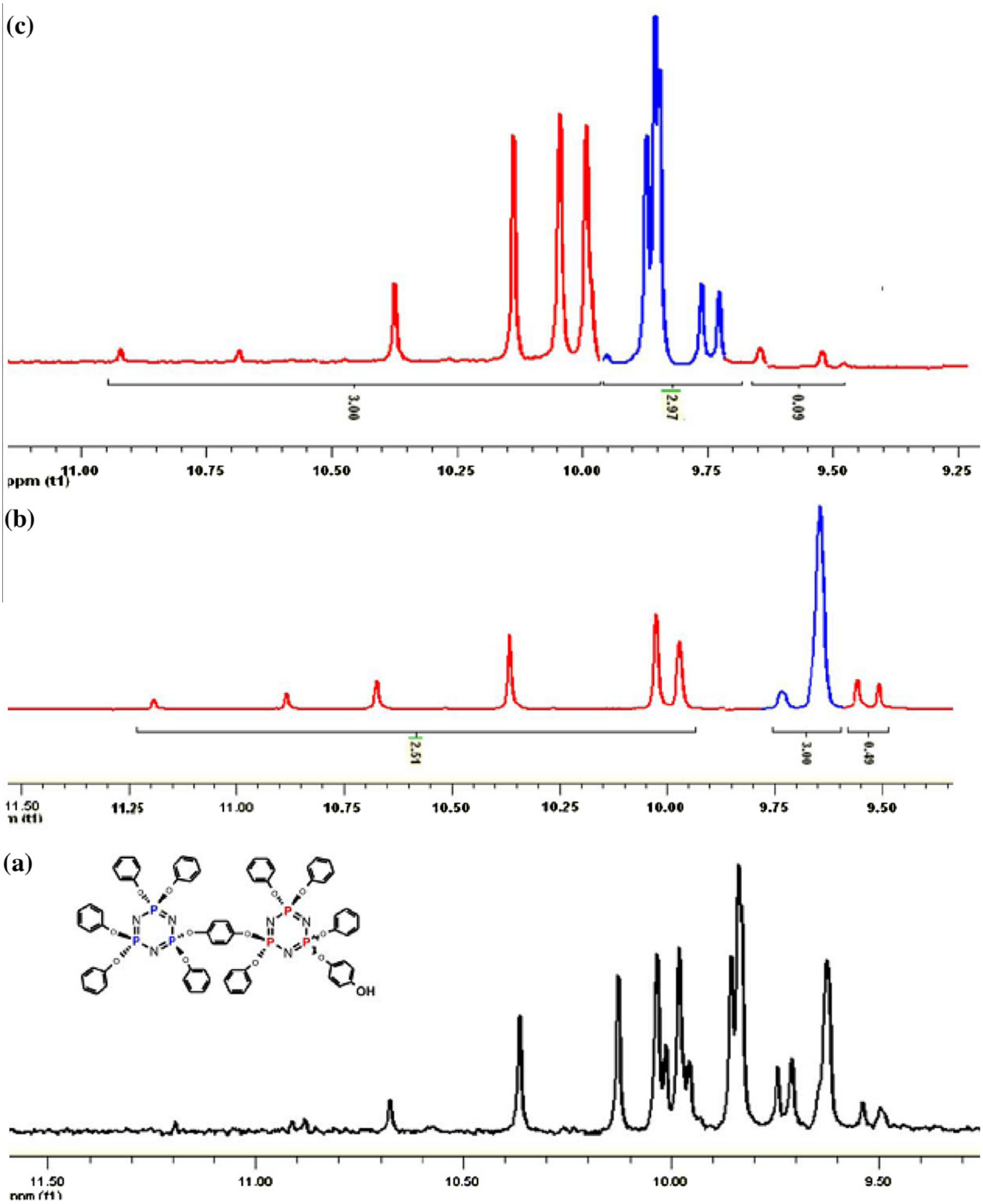


Fig. 4. Proton-decoupled ^{31}P NMR spectrum of compound **5** (a) diastereoisomer mixture, (b) and (c) compounds **5a** and **5b** in $CDCl_3$ solution.

can only be meso or racemate, in which the two non-geminal phenoxy or the 4-benzyloxyphenoxy units are *cis* or *trans* relationships, respectively. Furthermore, integration of phosphorus resonances of meso and racemic forms in the ^{31}P NMR gives 1:1 ratio which means that they are exist in approximately the same ratio. Although compound **3** can have the two phenoxy units in either *cis* or *trans* relationships to each other similar to compound **2**, it does not contain two equivalent chiral centres and the diastereoisomers in compound **3** can be two different racemates due to having two different chiral centres. The ^{31}P NMR spectrum of compound **3** is shown and the expected 2x A_2B spin system is observed in an approximate 1:1 ratio for the two different racemates in Fig. 3b. The compounds **4** and **5** show similar ^{31}P NMR spectra which consist of three AB_2 and/or two AB_2 and A_3 spin systems but they are more complicated to analyze (Fig 4a for compound **5**). After separating the two racemic forms of compound **5**, the proton-decoupled ^{31}P NMR spectra of compounds **5a** and **5b** exhibited a typical AB_2 spin system (a set of eight singlets) which can be separated from other peaks (Fig. 4b and c). The set of eight peaks in Fig. 4b and c may be assigned to a hydroxyl substituted trimer part [–N_3P_3–PhOH] because their ^{31}P NMR parameters and spectral profiles are very similar to a hydroxyl substituted phenoxycyclotriphosphazene, $N_3P_3(OPh)_5PhOH$, which was published our previously work [25]. The integration of the AB_2 part to the other remaining peaks of proton decoupled ^{31}P NMR spectra of compounds **5a** and **5b** give approximately 1:1 phosphorus ratio that confirmed each racemic form. In general, the *cis* and *trans*-isomers of cyclotriphosphazene derivatives can be distinguished by using ^{1}H NMR spectroscopy [20,32,33]. However, the two racemic forms (**5a** and **5b)** exhibit a complicated ^{1}H NMR spectra (not shown) so that all protons are observed in very similar spectral profiles which are indistinguishable from those of the racemic forms in spite of the two phenoxy units in either *cis* or *trans* relationships to each other. The ^{31}P NMR spectrum of compound **6** is displayed as a single broad line at *ca.* 9.45 ppm for the trimer core as expected [25] and the other lines in the range 10.5–9.5 ppm are observed as a more complicated AB_2-type spectrum and coupling constants were

Table 2
Thermal properties and molecular weights of **I**, **II**, **6** and **7**.

Compound	T_g (°C)	T_d (°C)	$[M+H]^+$	% Char yield
I[*]	26.2	422	4387	33.3
II[*]	24.5	445	5849	64.6
6	29.4	507	8079	47.7
7	28.8	512	10,772	62.7

[*] Data taken from Ref. [25].

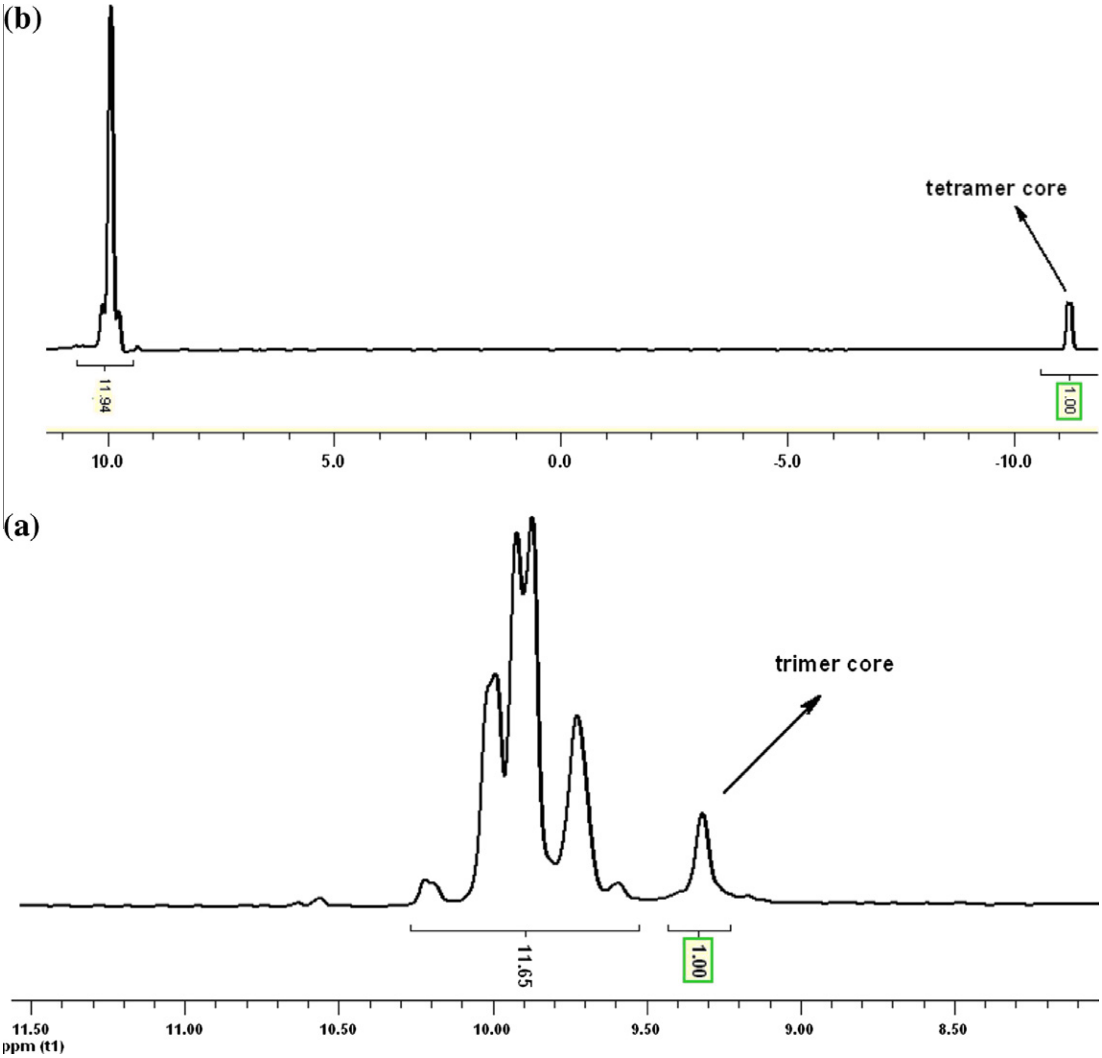


Fig. 5. Proton-decoupled ^{31}P NMR spectra of (a) compound **6** (b) compound **7** in toluene-d_8 solution.

not calculated in Fig. 5a. The ^{31}P NMR spectrum of compound **7** shows two sets of signals consisting of a broad line at between 11 and 9 ppm for side groups (compound **5**) and a single line at *ca.* -11.6 ppm for tetramer core as expected [34] (Fig. 5b). The integration of the broad signals part to the remaining singlet of the proton-decoupled ^{31}P NMR spectra of dendrimeric compounds **6** and **7** gives nearly a 12:1 phosphorus ratio that confirms the suggested structures.

Phosphazenes are attractive compounds due to their higher thermal stability and flame retardancy properties when compared

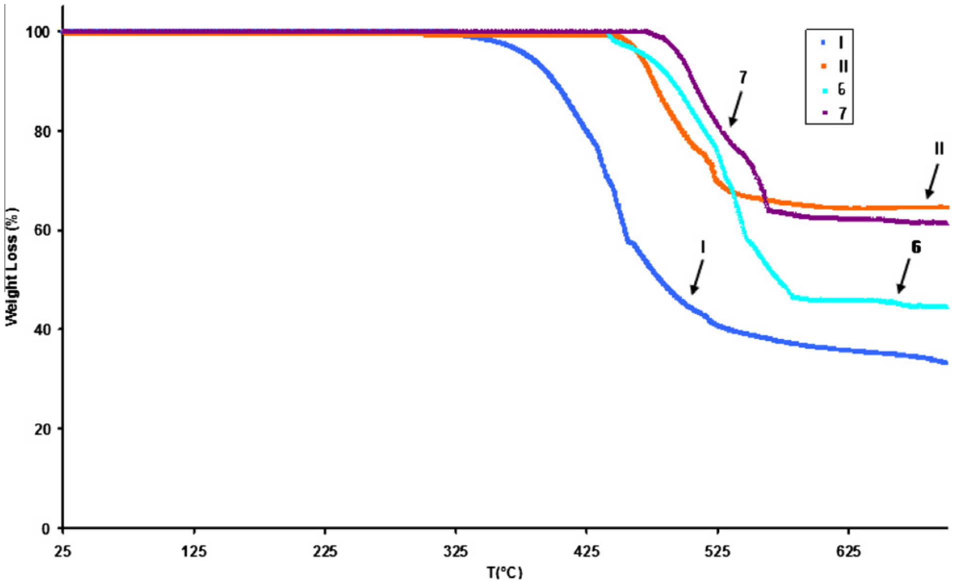


Fig. 6. TGA curves of **I**, **II**, **6** and **7** from 25 to 700 °C at a heating rate of 10 °C/min under N_2 flow of 50 mL/min.

Table 3
Photophysical parameters of compounds **I**, **II**, **6** and **7** in CH_2Cl_2.

Comp.	λ_{abs}	λ_{Em}	Φ_F	τ_F (ns)	τ_0 (ns)	$^{a}k_F$ (s^{-1}) ($\times 10^8$)	K_{SV} 10^4 (M^{-1})	k_q 10^{14} (M^{-1} s^{-1})
I	260,270[b]	298[b]	0.16[b]	0.14[b]	0.89[b]	11.42[b]	6.49	4.63
II	260,270[b]	298[b]	0.18[b]	0.32[b]	1.76[b]	5.62[b]	5.68	1.77
6	260,270	298	0.27	0.61	2.24	4.42	3.25	0.53
7	260,270	298	0.38	2.65	6.99	1.43	4.47	0.17

[a] k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.
[b] Data taken from Ref. [25].

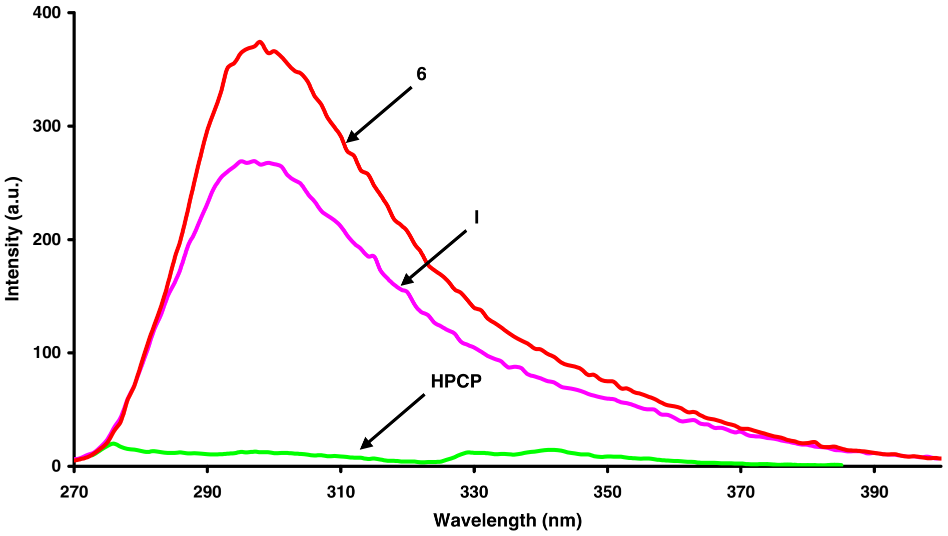


Fig. 7. Fluorescence emission spectra of compounds **HPCP** (hexaphenoxycyclotriphosphazene), **I** and **6** in CH_2Cl_2. Concentration: 1.0×10^{-5} mol dm^{-3}. Excitation wavelength: 260 nm.

as the organic homologues. Owing to the excellent thermal stability and char yield performance, aryloxy substituted polyphosphazene has attracted interest for its potential application as a flame retardant [35]. Differential scanning calorimetry (DSC) studies were carried out between −40 and 100 °C with heating rate of 10 °C/min under nitrogen flow to determine the transition temperatures of the dendrimers. The T_g of all phosphazene compounds (**I**, **II** and **6, 7**) are shown in Table 2. Thermogravimetric analysis (TGA) is utilized to evaluate the thermal stability of the dendrimeric compounds. The onset decomposition temperatures (T_d) are recorded at a heating rate of 10 °C/min. The curves of the TGA measurements are shown in Fig. 6 and T_d values are collected in Table 2. According to TGA thermograms of compounds (**I, II, 6** and **7**), they exhibit very good thermal stability with decomposition temperatures (T_d) in the range of 422–512 °C (Table 2). The increase of T_d from compound **I** to **7** can be explained with the increasing substitution degree of phenoxy groups. Therefore aryloxycyclophosphazenes could be useful candidates for flame retardant additives to organic polymers [35]. As a result, the high char yields and T_d's of dendrimeric phosphazene compounds (**I, II, 6** and **7**) make them a good flame retardant in theory [36], and it could suggest that the dendrimeric derivatives have excellent thermal properties.

The absorption and the fluorescence spectra of dendrimeric compounds were measured with dilute solutions (1×10^{-5} mol dm^{-3}) in CH_2Cl_2. All compounds were excited at 260 nm for fluorescence emission studies. All spectroscopic data, fluorescence quantum yields (Φ_F) and fluorescence lifetimes are summarised in Table 3. It is well known [6] that chlorophosphazenes ($N_3P_3Cl_6$, or $N_4P_4Cl_8$) are photochemically inert and do not interfere with the photophysical properties associated with the attached chromophores. Single crystal X-ray analysis of hexakis(aryloxy)cyclotriphosphazenes shows that the six aryloxy groups lie almost perpendicularly above and below the nearly planar cyclotriphosphazene core and these structural features make it possible for

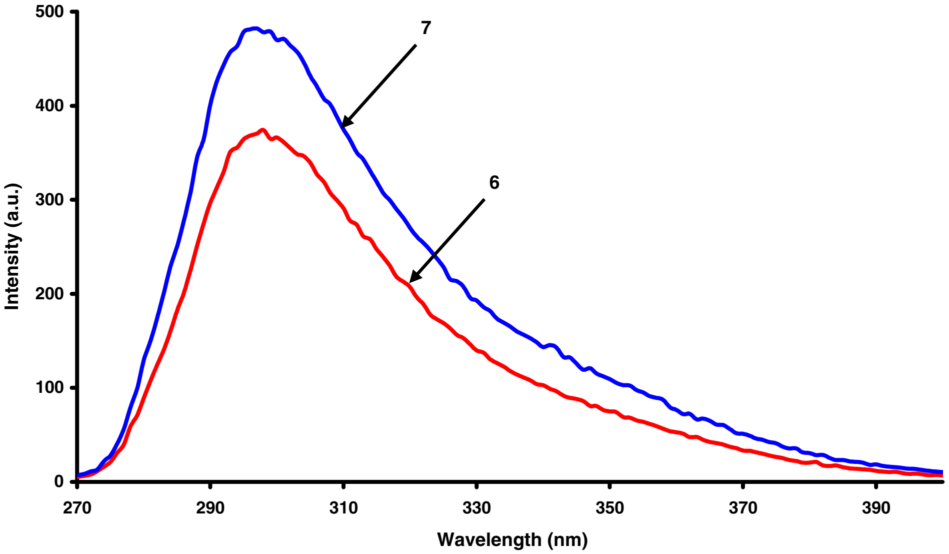


Fig. 8. Fluorescence emission spectra of compounds **6** and **7** in CH_2Cl_2. Concentration: 1.0×10^{-5} mol dm^{-3}. Excitation wavelength: 260 nm.

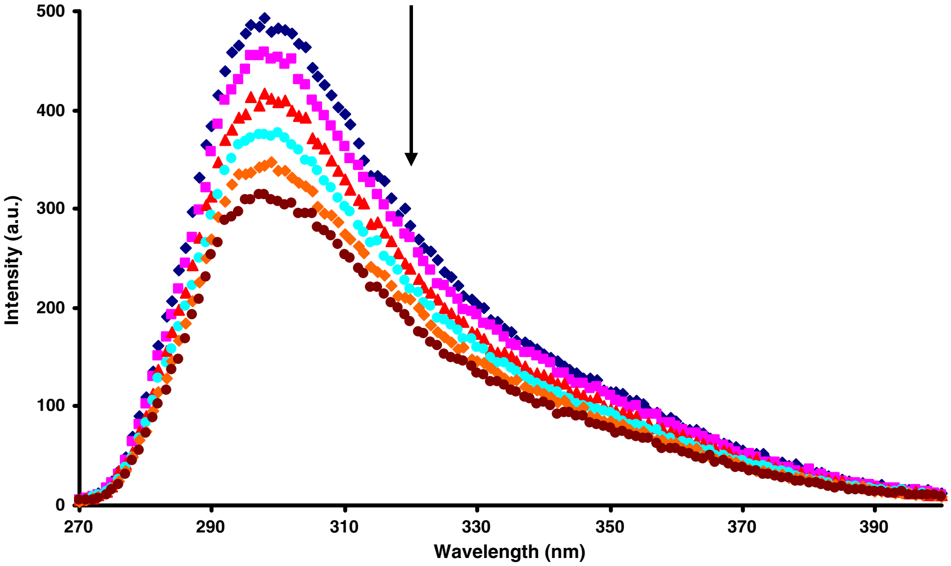


Fig. 9. Fluorescence emission spectral changes of **7** (1.00×10^{-5} mol dm^{-3}) on addition of different concentrations of BQ in CH_2Cl_2. [BQ] = 0, 2.4×10^{-6}, 4.8×10^{-6}, 7.2×10^{-6}, 9.6×10^{-6} and 12×10^{-6} mol dm^{-3}.

the three aryloxy groups to be located on the same side of the $(PN)_3$ plane, able to align through intramolecular non-covalent π–π interactions [20]. However, the absorption and emission spectra of hexaphenoxycyclotriphosphazene (**HPCP**) are similar to those of the individual phenols indicating that there are no interactions between the phenol units either in the ground state or in the emission state. Fig. 7 shows the comparison among the fluorescence emission spectra of **HPCP**, dendrimeric compounds **I** and **6** based on cyclotriphosphazene cores. Although **HPCP** does not exhibit fluorescence emission, the dendrimeric compounds have significantly more emission signals. With increasing side group length, dendrimeric compound **6** exhibits higher fluorescence emission than dendrimeric compound **I** (Fig. 7). This situation can be explained as the increasing of the non-covalent π–π interactions between the aryloxy groups on the cyclotriphosphazene core compounds. As expected [25], increasing the numbers of the side groups for compounds **7** (eight side groups) caused the higher fluorescence emission than compound **6** (six side groups) (Fig 8). Additionally, in order to observe the presence of isomers, and their influence on the photophysical properties, the emission spectra were studied under the same conditions (1×10^{-5} mol dm^{-3}) in CH_2Cl_2. The diastereoisomeric mixture of compound **5** and isolated racemic compounds of **5a** and **5b** show very weak fluorescence emissions and they are strictly identical. Hence, it can be said that the photophysical properties of the dendrimers (**6** and **7**) built with these small molecules (**5, 5a** and **5b**) do not depend on the presence of isomers. The fluorescence quantum yields (Φ_F) of the phosphazene derivatives are measured in CH_2Cl_2 and 2-aminopyridine in 0.1 M H_2SO_4 solution is used as a standard. Although there are many parameters that affect the fluorescence quantum yields [37], the fluorescence quantum yields (Φ_F) of dendrimeric compounds are increased with respect to the increment of the side groups and their values are: 0.16 for **I**, 0.18 for **II**, 0.27 for **6** and 0.38 for **7**, respectively (Table 3). Fluorescence lifetime refers to the average time a molecule stays in its excited state before fluorescing, and its value is directly related to that of Φ_F; i.e. the longer the lifetime, the higher the quantum yield of fluorescence. Any factor that shortens the fluorescence lifetime of a fluorophore indirectly reduces the value of Φ_F. Such factors include internal conversion and intersystem crossing. As a result, the nature and the environment of a fluorophore determine its fluorescence lifetime. Fluorescence lifetimes (τ_F) of dendrimeric compounds are calculated using the Strickler–Berg equation. Using this equation, a good correlation has been found between experimentally and theoretically determined lifetimes for the unaggregated molecules [38] as is the case in this work. Thus we suggest that the values obtained using this equation are an appropriate measure of fluorescence lifetimes. In addition the rate constants for fluorescence (k_F) and radiative lifetime (τ_0) are also measured for all dendrimeric compounds in this study (Table 3). It is found that the changes in data of the fluorescence lifetimes (τ_F), the rate constants for fluorescence (k_F) and radiative lifetime (τ_0) for dendrimeric compounds are consistent with the increase in their fluorescence quantum yields (Table 3).

The fluorescence quenching behaviour by 1,4-benzoquinone (BQ) of dendrimeric phosphazene compounds (**I**, **II**, **6** and **7**) are investigated in CH_2Cl_2. As an example, the quenching of compound **7** by BQ in CH_2Cl_2 is depicted in Fig. 9. It can be said that the presence of BQ quencher, an energy transfer occurs between the excited dendrimeric phosphazene derivatives (**I**, **II**, **6** and **7**) and the BQ. However, at this stage, we cannot comment on the possibility of interfacial energy transfer between dendrimeric compounds and BQ. The fluorescence quenching of dendrimeric phosphazene derivatives (**I**, **II**, **6** and **7**) by BQ in CH_2Cl_2 was found to obey Stern-Volmer kinetics. The slope of the plots shown in Fig. 10 gives the Stern-Volmer constant (K_{SV}) values. The K_{SV} and the bimolecular quenching constant (k_q) values are summarised in Table 3. The k_q values are of the order of 10^{14} M^{-1} s^{-1}, which exceed the proposed value of 10^{10} M^{-1} s^{-1} for diffusion-controlled (dynamic) quenching (according to the Einstein–Smoluchowski approximation at room temperature [39]. This is also an indication that the mechanism of BQ quenching by dendrimeric phosphazene compounds is not diffusion-controlled (i.e. not dynamic quenching, but static quenching). Increasing the length of the side groups leads to decreasing of the k_q values of the dendrimeric phosphazene compounds.

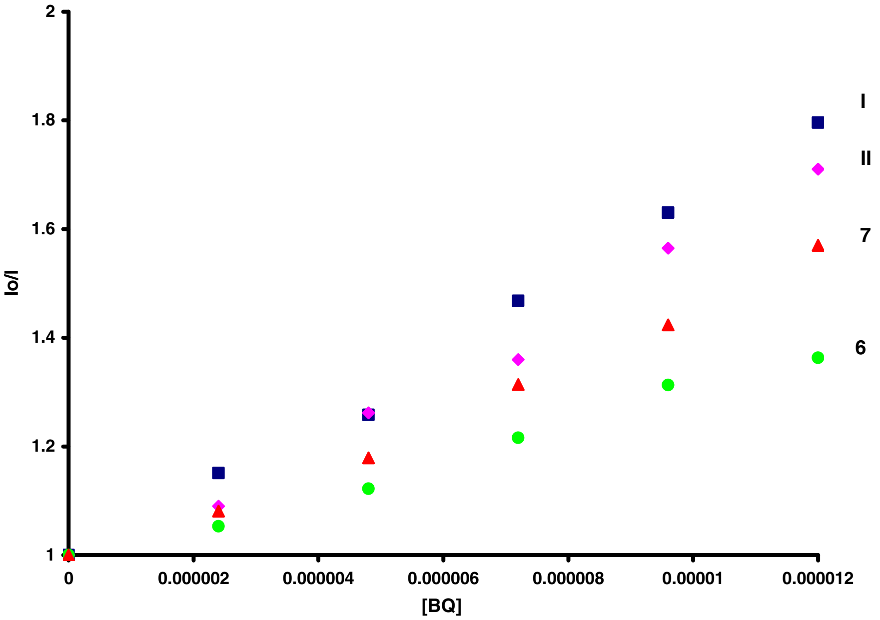


Fig. 10. Stern-Volmer plots for BQ quenching of **I**, **II**, **6** and **7** in CH_2Cl_2 (1.00×10^{-5} mol dm^{-3}). [BQ] = 0, 2.4×10^{-6}, 4.8×10^{-6}, 7.2×10^{-6}, 9.6×10^{-6} and 12×10^{-6} mol dm^{-3}.

4. Conclusions

In conclusion, we have reported the synthesis of a hydroxyl substituted dimeric phenoxycyclotriphosphazene (**5**) and its dendrimeric derivatives (**6** and **7**) based on cyclic phosphazenes. All compounds have been characterized by standard spectroscopic techniques. The thermal stability and fluorescence spectral properties of dendrimeric compounds (**6** and **7**) have been investigated and also compared with previously reported dendrimeric compounds (**I** and **II**). It is found that the dendrimeric compounds possess high thermal stability and char yields. It is also found that dendrimeric compounds show significantly more fluorescence emission with the increasing length of side groups. In this way, it can be said that these compounds appear to be promising candidates for some industrial applications such as flame retardant additives to polymers or light emitting electroluminescent devices.

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