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Fluorescence properties of fluorenylidene bridged cyclotriphosphazenes bearing aryloxy groups

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ABSTRACT

The synthesis and characterization of the first series of aryloxy full-substituted fluorenylidene open chain and bridged cyclotriphosphazene derivatives (**13**–**18**) are reported in this study. The synthetic route utilized includes the reaction of penta-substituted cyclotriphosphazenes (**5**, **7**, **9**) with 4,4′-(9-fluorenylidene)diphenol (**FDP**) (**11**) and 4,4′-(9-fluorenylidene)dianiline (**FDA**) (**12**) to give bridged compounds (**13**, **15**–**17**) and open chain compounds (**14** and **18**). The structural investigations of the compounds were verified by elemental analyses, mass spectrometry, UV–Vis, FT-IR, ^{1}H and ^{31}P NMR techniques, and X-ray crystallography (for **13** and **18**). The fluorescence behavior of the studied cyclotriphosphazene derivatives were also examined in THF solution. Compound **16** showed a high emission among the studied compounds to investigate its metal sensing properties. This compound showed high selectivity for copper (Cu^{2+}) and iron (Fe^{2+}/Fe^{3+}) ions in solution.

1. Introduction

Organic compounds like fluorene and pyrene are remarkable for their fluorescence properties, thus these compounds are suitable for many applications, such as fluorescent probes for applications in sensors, liquid crystals, organic light-emitting diodes and electrochromic materials [1–6]. 4,4′-(9-Fluorenylidene)diphenol, (**FDP**) or 4,4′-(9-fluorenylidene)dianiline, (**FDA**), which are conjugated fluorenes, have been used for many applications and they have the potential to detect metal ions in biological and environmental media. The binding of certain metal ions to the fluorene molecule may influence the fluorescent properties of the molecule and hence indicate its presence in a solution [7–11].

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), as one member of the phosphazane group, has a six-membered ring and offers a rigid platform for multifunctional molecular arrangements. The chemical and physical properties of cyclotriphosphazenes change with the nature of the substituted side groups. Therefore, by means of these side groups, it is possible to enhance different properties of the molecules, such as flame retardant properties [12–14], liquid crystals [15–17], biological activity [18–22] and fluorescence properties [23–28]. There has recently been considerable interest in fluorescent compounds based on cyclic phosphazene cores or cyclo-linear polymers with cyclotriphosphazene units for the development of electroluminescent devices [27–34]. Ozay and colleagues have been synthesized a 1,2,3-triazole ring functionalized hexapodal rhodamine derivative on a cyclotriphosphazene core which showed high selectivity towards Fe^{3+} ions [23]. In our recent work, the metal sensing studies of **FDP** and **FDA** bridged cyclotriphosphazenes and their derivatives showed high selectivity towards Cu^{2+} and Fe^{2+} ions [24,25]. The results of these studies have encouraged us to investigate new phenol, naphthol and pyrene modified cyclotriphosphazene compounds containing **FDP** and **FDA** on the cyclotriphosphazene core.

In this study, we report the first derivatives of fluorenylidene bridged cyclotriphosphazenes (**13**, **15**–**17**) and their open chain derivatives (**14** and **18**). First, we prepared some pentasubstituted cyclotriphosphazene compounds (**5**, **7**, **9**). For the synthesis of the target compounds, hexachlorocyclotriphosphazene (**1**) was reacted with the cesium salts of phenol (**2**), 2-naphthol (**3**) and 1-hydroxypyrene (**4**) to give the penta- and hexasubstituted cyclotriphosphazene compounds (Scheme 1). Then, the pentasubstituted cyclotriphosphazene compounds (**5**, **7**, **9**) were reacted with **FDP** (**11**) and **FDA** (**12**), and the aryloxy full-substituted fluorenylidene-bridged cyclotriphosphazene derivatives (**13**–**18**) were obtained (Scheme 2). All the compounds were characterized by elemental analysis, mass spectrometry, UV–Vis, FT-IR, ^{1}H, ^{31}P NMR and X-ray crystallography (for **13** and **18**), together with fluorescence spectroscopy techniques. The metal binding properties of the synthesized **FDP**-bridged cyclotriphosphazene compounds (**13-16**) were investigated by fluorescence spectroscopy.

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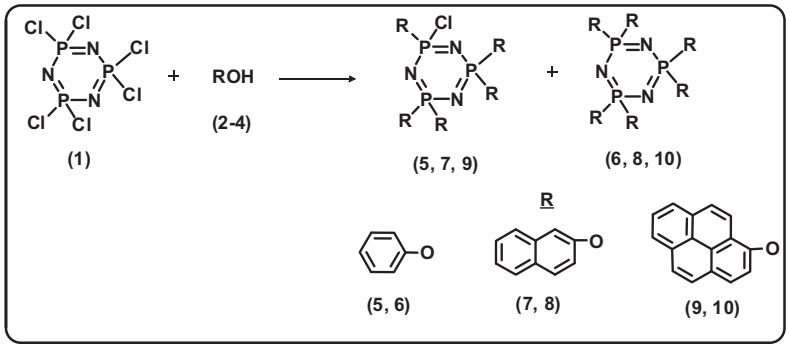
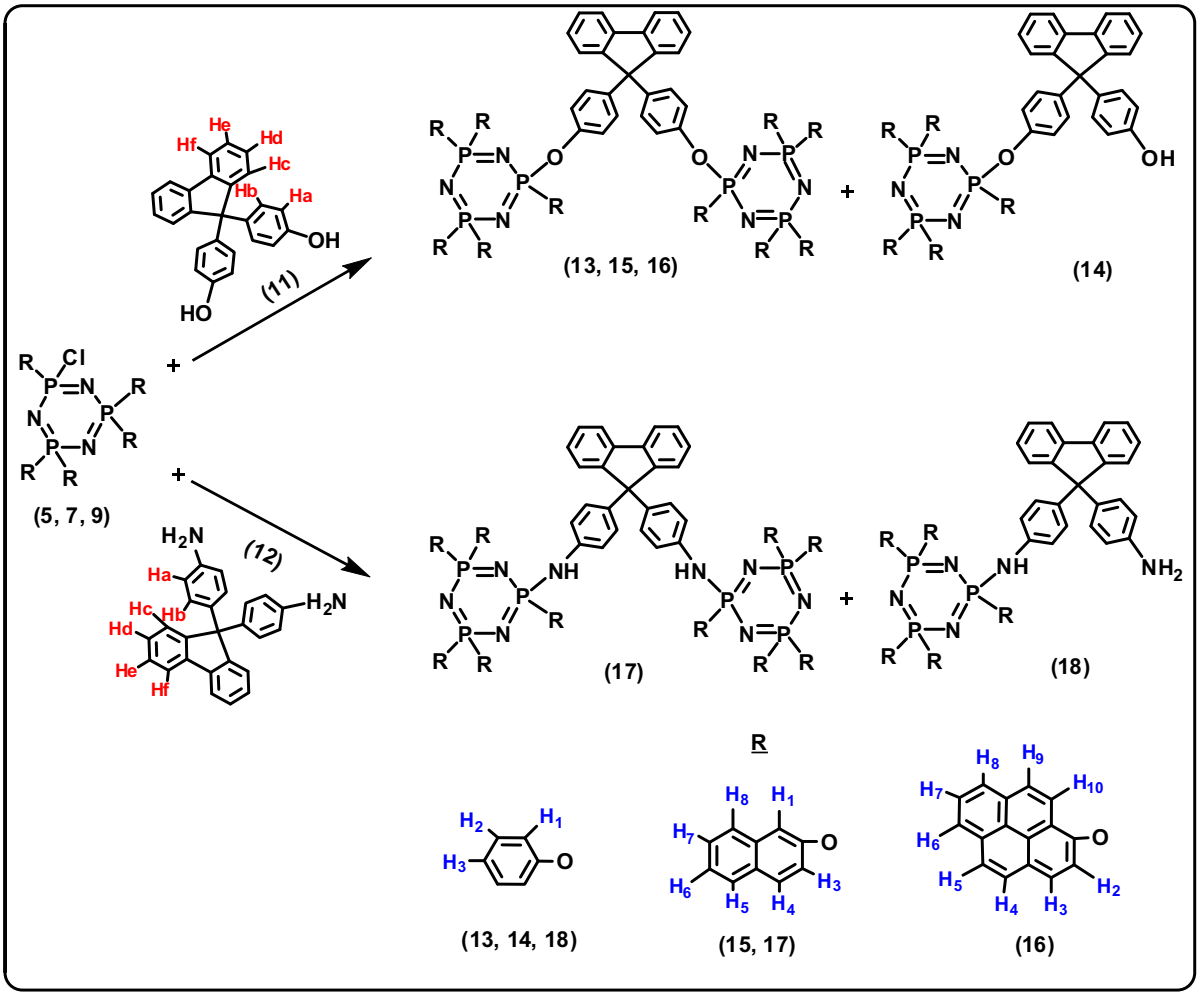


Scheme 1. The synthesis of penta- and hexasubstituted cyclotriphosphazene derivatives.



Scheme 2. The synthesis of FDP and FDA bridged and open chain cyclotriphosphazenes.

2. Experimental

2.1. General methods

Hexachlorocyclotriphosphazene (Otsuka Chemical Co., Ltd) was purified by fractional crystallization from *n*-hexane. Sodium hydride, (60% dispersion in mineral oil) was obtained from Merck; prior to use the oil was removed by washing with dry heptane followed by decantation. 4,4′-(9-Fluorenylidene)diphenol (99%) and (4,4′-(9-fluorenylidene)dianiline (99%) were obtained from Aldrich. Tetrahydrofuran (⩾99.0%), dichloromethane (⩾99.0%), benzene (⩾99.0%), ethyl acetate (⩾99.0%) *n*-hexane (⩾95.0%), 4-(Dimethylamino)pyridine (DMAP) (⩾99%) and Cesium carbonate (⩾99%) were obtained from Merck. THF was distilled over a sodium-potassium alloy under an atmosphere of dry argon. Silica gel 60 (230–400 mesh) for column chromatography was obtained from Merck. $CDCl_3$ for NMR spectroscopy was obtained from Goss Scientific. Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument. Positive ion and linear mode MALDI-MS of the compounds were obtained in dihydroxybenzoic

acid as a MALDI matrix using a nitrogen laser, accumulating 50 laser shots using a Bruker Microflex LT MALDI-TOF mass spectrometer. The mass spectra of some compounds were recorded on a Bruker MicroTOF LC–MS spectrometer using the electrospray ionisation (ESI) method; ^{35}Cl values were used for the calculated mass values. All reactions were monitored using thin-layer chromatography (TLC) on Merck 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 3 cm in diameter and 60 cm in length). All reactions were carried out under an argon atmosphere. Melting points were measured on a Gallenkamp apparatus using a capillary tube. ^1H and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^1H NMR and 85% H_3PO_4 as an external reference for ^{31}P NMR. FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Absorption spectra in the UV–Vis region were recorded with a Shimadzu 2101 UV–Vis spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature.

2.2. X-ray crystallography

Intensity data were recorded on a Bruker APEX II QUAZAR diffractometer. Absorption corrections by multi-scan were applied [35] and space groups were determined using XPREP implemented in APEX2 [36]. The structures were determined using the direct methods procedure in SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97 [37]. All non-hydrogen atoms were refined with anisotropic displacement factors and C-H hydrogen atoms were placed in calculated positions and allowed to ride on the parent atom. The final geometrical calculations and the molecular drawings were carried out with PLATON [38], MERCURY [39], and DIAMOND [40] programs.

2.3. Synthesis

Compounds **5**, **6**, **7** and **8** were prepared and purified according to the literature procedures [41–43].

2.3.1. Reaction of the trimer (*1*) with 1-hydroxypyrene (*4*) in a 1:5 ratio to form compounds *9* and *10*

Compound **1** (1 g, 2.8 mmol) was dissolved in 100 mL of dry THF in a 500 mL three-necked round-bottomed flask. The mixture was cooled in an ice-bath and Cs_2CO_3 (4.7 g, 14.4 mmol) in 10 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. Compound **4** (3.14 g, 14.4 mmol) in 50 mL dry THF was added dropwise over 1 h to the stirred mixture. The resulting reaction mixture was stirred for 3 days at room temperature and followed by ^{31}P NMR and TLC with silica gel plates using dichloromethane:*n*-hexane (1:2) as the mobile phase. The reaction mixture was filtered to remove the formed cesium chloride, THF was removed at reduced pressure and the resulting white solid was subjected to column chromatography using dichloromethane:*n*-hexane as the mobile phase. The first eluate was compound **9** (2.5 g, mp > 250 °C, powder), Rf = 0.35. *Anal.* Calc. for $C_{80}H_{45}ClN_3O_5P_3$: C, 76.46; H, 3.61; N, 3.34. Found: C, 76.42; H, 3.59; N, 3.32%. MALDI-TOF (*m*/*z*) calc.: 1255, found: 1256 $[M+H]^+$. ^1H NMR ($CDCl_3$, δ, ppm): 6.90–8.10 (m, ArCH). FTIR (ν, cm^{-1}): 3040 m((C–H)arom.), 1500 s(C=C), 1210 s(P=N), 1183 s (P=O). The second eluate was compound **10** [44].

2.3.2. Reaction of 2,2,4,4,6-pentaphenoxy-6-chlorocyclotriphosphazene (*5*) with 4,4′-(9-fluorenylidene)diphenol (*11*) in a 1:5 ratio to form compounds *13* and *14*

Compound **5** (1.2 g, 1.9 mmol) and compound **11** (0.8 g, 2.28 mmol) were dissolved in 100 mL of dry THF in a 250 mL three-necked round-bottomed flask. The mixture was cooled in an ice-bath and Cs_2CO_3 (0.62 g, 1.9 mmol) in 20 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The reaction mixture was stirred for 4 days under reflux and was followed by ^{31}P NMR and TLC with silica gel plates using *n*-hexane:THF (2:1) as the mobile phase. The reaction mixture was filtered to remove the formed cesium chloride, THF was removed at reduced pressure and the resulting white solid was subjected to column chromatography using *n*-hexane:THF (2:1) as the mobile phase. The first product was compound **13** (1.5 g, mp > 250 °C), Rf = 0.70. Compound **13** was re-crystallized from ethanol–CH_2Cl_2 (3:1) and obtained as white crystals, which were suitable for single crystal X-ray crystallography. *Anal.* Calc. for $C_{85}H_{66}N_6O_{12}P_6$: C, 65.89; H, 4.29; N, 5.42. Found: C, 65.86; H, 4.25; N, 5.40%. MALDI-TOF (*m*/*z*) calc.: 1548, found: 1549.8 $[M+H]^+$. ^1H NMR ($CDCl_3$, δ, ppm): 6.65 (H_a, 4H, d, $^3J_{H-H}$ = 7.5 Hz), 6.79 (H_1, 20H, d, $^3J_{H-H}$ = 8.3 Hz), 6.85 (H_b, 4H, d, $^3J_{H-H}$ = 7.6 Hz), 6.90 (H_3, 10H, t, $^3J_{H-H}$ = 6.8 Hz), 7.03 (H_c, H_d, 4H, m, $^3J_{H-H}$ = 7.3 Hz), 7.05 (H_2, 20H, m, $^3J_{H-H}$ = 7.6 Hz), 7.29 (H_e, 2H, t, $^3J_{H-H}$ = 7.5 Hz), 7.71 (H_f, 2H, d, $^3J_{H-H}$ = 7.6 Hz). FTIR (ν, cm^{-1}): 3060 m((C–H)arom.), 1485 s(C=C), 1259-1153 s(P=N), 1272 s(P=O). The second product was compound **14** (0.8 g, oily), Rf = 0.54. *Anal.* Calc. for $C_{55}H_{42}N_3O_7P_3$: C, 65.55; H, 4.46; N, 4.42. Found: C, 65.52; H, 4.45; N, 4.40%. MALDI-TOF (*m*/*z*) calc.: 949, found 950: $[M+H]^+$. ^1H NMR ($CDCl_3$, δ, ppm): 6.64 (H_a, 4H, d, $^3J_{H-H}$ = 8.8 Hz), 6.78 (H_b, 4H, d, $^3J_{H-H}$ = 8.7 Hz), 6.87–6.92 (H_1, 10H, m, $^3J_{H-H}$ = 8.3 Hz), 6.95–7.05 (H_3, 5H, t, $^3J_{H-H}$ = 8.7 Hz), 7.10–7.18 (H_2, 10H, m, $^3J_{H-H}$ = 7.9 Hz), 7.25 (H_d, 2H, d, $^3J_{H-H}$ = 7.5 Hz), 7.31 (H_c, 2H, d, $^3J_{H-H}$ = 7.8 Hz), 7.37 (H_e, 2H, t, $^3J_{H-H}$ = 7.5 Hz), 7.78 (H_f, 2H, d, $^3J_{H-H}$ = 7.6 Hz), 4.35 (1H, s, OH). FTIR (ν, cm^{-1}): 3400–3450 s(OH), 3065 m((C–H)arom.), 1487 s(C=C), 1200–1155 s(P=N), 1262 s(P=O).

2.3.3. Reaction of 2,2,4,4,6-pentanaphthoxy-6-chlorocyclotriphosphazene (*7*) with 4,4′-(9-fluorenylidene)diphenol (*11*) in a 1:5 ratio to form compound *15*

Compound **7** (1.2 g, 1.9 mmol) was dissolved in 100 mL of dry THF in a 250 mL three-necked round-bottomed flask. The mixture was cooled in an ice-bath and Cs_2CO_3 (0.62 g, 1.9 mmol) in 10 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. Compound **11** (0.8 g, 2.28 mmol) in 20 mL dry THF was added dropwise over 1 h to the stirred mixture. The resulting reaction mixture was stirred for 4 days under reflux and followed by ^{31}P NMR and TLC with silica gel plates using *n*-hexane:THF (2:1) as the mobile phase. The reaction mixture was filtered to remove the formed cesium chloride, THF was removed at reduced pressure and the resulting white solid was subjected to column chromatography using *n*-hexane: THF (2:1) as the mobile phase. The eluate was compound **15** (0.27 g, oily), Rf = 0.57. *Anal.* Calc. for $C_{125}H_{86}N_6O_{12}P_6$: C, 73.24; H, 4.23; N, 4.10. Found: C, 73.22; H, 4.20; N, 4.6%. MALDI-TOF (*m*/*z*) calc.: 2049, found: 2050.3 $[M+H]^+$. ^1H NMR ($CDCl_3$, δ, ppm): 6.43 (H_a, 4H, d, $^3J_{H-H}$ = 8.8 Hz), 6.48 (H_b, 4H, d, $^3J_{H-H}$ = 8.8 Hz), 6.82 (H_c, 2H, d, $^3J_{H-H}$ = 8.5 Hz), 7.30 (H_d, 2H, d, $^3J_{H-H}$ = 7.0 Hz), 7.50 (H_e, 2H, d, $^3J_{H-H}$ = 8.0 Hz), 7.67 (H_f, 2H, d, $^3J_{H-H}$ = 7.7 Hz), 6.96 (H_1, 10H, d, $^3J_{H-H}$ = 7.5 Hz), 7.08 (H_3, 10H, d, $^3J_{H-H}$ = 7.5 Hz), 7.08-7.23 ($H_{4,5,8}$, 30H, m, $^3J_{H-H}$ = 8.3–8.9 Hz), 7.30 (H_6, 10H, d, $^3J_{H-H}$ = 7.0 Hz), 7.55 (H_7, 10H, d, $^3J_{H-H}$ = 7.8 Hz). FTIR (ν, cm^{-1}): 3058 m((C–H)arom.), 1460 s(C=C), 1231 s(P=N), 1194 s(P=O).

*2.3.4. Reaction of 2,2,4,4,6-penta-oxypyrene-6-chlorocyclotriphosphazene (**9**) with 4,4′-(9-fluorenylidene)diphenol (**11**) in a 1:5 ratio to form compound **16***

Compound **9** (1.2 g, 1.95 mmol) was dissolved in 100 mL of dry THF in a 250 mL three-necked round-bottomed flask. The mixture was cooled in an ice-bath and Cs_2CO_3 (0.63 g, 1.95 mmol) in 10 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. Compound **11** (0.8 g, 2.28 mmol) in 10 mL dry THF was added dropwise over 0.5 h to the above stirred mixture. The reaction mixture was stirred for 4 days at room temperature and followed by ^{31}P NMR and TLC with silica gel plates using *n*-hexane:CH_2Cl_2 (2:3) as the mobile phase. The reaction mixture was filtered to remove the formed cesium chloride, THF was removed at reduced pressure and the resulting white solid was subjected to column chromatography using *n*-hexane:CH_2Cl_2 (2:3) as the mobile phase. The eluate was compound **16** (3 g, mp 195 °C) isolated as a white powder (0.27 g, white powder), Rf = 0.64. *Anal.* Calc. for $C_{185}H_{106}N_6O_{12}P_6$: C, 79.62; H, 3.83; N, 3.01. Found: C, 79.60; H, 2.98; N, 2.97%. MALDI-TOF (*m*/*z*) calc.: 2790, found: 2791.2 $[M+H]^+$. ^{1}H NMR($CDCl_3$, δ, ppm): 6.63 (H_a, 4H, d, $^3J_{H-H}$ = 8.2 Hz), 6.84 (H_b, 4H, d, $^3J_{H-H}$ = 8.4 Hz), 7.05 (H_c, 2H, d, $^3J_{H-H}$ = 8.4 Hz), 7.41 (H_d, 2H, d, $^3J_{H-H}$ = 8.6 Hz), 7.52 (H_e, 2H, d, $^3J_{H-H}$ = 8.6 Hz), 7.61 (H_f, 2H, d, $^3J_{H-H}$ = 9.2 Hz), 7.65 (H_2, 10H, d, $^3J_{H-H}$ = 8.9 Hz), 7.70–7.88 (H_{3-8}, 60H, m, $^3J_{H-H}$ = 8.9–9.6 Hz), 7.95 (H_9, 10H, d, $^3J_{H-H}$ = 7.7 Hz), 8.19 (H_{10}, 10H, d, $^3J_{H-H}$ = 9.2 Hz). FTIR (ν, cm^{-1}): 3042 m((C–H)arom.), 1502 s(C=C), 1200 s(P=N), 1180 s(P=O).

*2.3.5. Reaction of 2,2,4,4,6-pentanaphthoxy-6-chlorocyclotriphosphazene (**7**) with 4,4′-(9-fluorenylidene)dianiline (**12**) in a 1:5 ratio to form compound **17***

Compound **7** (1.2 g, 1.9 mmol) was dissolved in 150 mL of dry acetonitrile in a 500 mL three-necked round-bottomed flask. DMAP (0.23 g, 1.9 mmol) in 10 mL of dry acetonitrile was quickly added to the stirred solution under an argon atmosphere. Compound **12** (0.8 g, 2.28 mmol) in 20 mL dry acetonitrile was added dropwise over 0.5 h to the stirred mixture. The reaction mixture was stirred for 5 days at room temperature and followed by ^{31}P NMR and TLC with silica gel plates using hexane:DCM (1:1) as the mobile phase. The reaction mixture was filtered to remove the formed dimethylaminopiridinyum hydrochloride, the acetonitrile was removed at reduced pressure and the resulting white solid was subjected to column chromatography using *n*-hexane:CH_2Cl_2 (1:1) as the mobile phase. The compound **17** was the eluate (2.8 g, mp 166 °C), Rf = 0.57. *Anal.* Calc. for $C_{125}H_{88}N_8O_{10}P_6$: C, 73.31; H, 4.33; N, 5.47. Found: C, 73.29; H, 4.29; N, 5.45%. MALDI-TOF (*m*/*z*) calc.: 2047, found: 2048 $[M+H]^+$. ^{1}H NMR ($CDCl_{33}$, δ, ppm): 6.77 (H_a, 4H, d, $^3J_{H-H}$ = 79 Hz), 7.0 (H_b, 4H, d, $^3J_{H-H}$ = 8.9 Hz), 6.97 (H_c, 2H, d, $^3J_{H-H}$ = 8.2 Hz), 7.43 (H_e, 2H, d, $^3J_{H-H}$ = 8.2 Hz), 7.51 (H_f, 2H, d, $^3J_{H-H}$ = 8.2 Hz), 7.12–7.40 (H_{1-8}, H_d, 72H), 5.30 (NH, 2H, s). FTIR (ν, cm^{-1}): 3050 m((C–H)arom.), 1507 s(C=C), 1264–1197 s(P=N), 1146 s(P=O).

*2.3.6. Reaction of 2,2,4,4,6-pentaphenoxy-6-chlorocyclotriphosphazene (**5**) with 4,4′-(9-fluorenylidene)dianiline (**12**) in a 1:5 ratio to form compound **18***

Compound **5** (1.2 g, 1.9 mmol) was dissolved in 50 mL of dry THF in a 250 mL three-necked round-bottomed flask. The mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.05 g, 1.9 mmol) in 10 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. Compound **12** (0.8 g, 2.28 mmol) in 20 mL dry THF was added dropwise over 1 h to the above stirred mixture. The reaction mixture was stirred for 5 days at reflux temperature and followed by ^{31}P NMR and TLC with silica gel plates using *n*-hexane:THF (1:1) as the mobile phase. The reaction mixture was filtered to remove the formed sodium chloride, THF was removed at reduced pressure and the resulting white solid was subjected to column chromatography using *n*-hexane:THF (1:1) as the mobile phase. The eluate was compound **18** (1.8 g, mp 174 °C), isolated as a white powder and crystallized from *n*-hexane:DCM (5:1), Rf = 0.30. *Anal.* Calc. for $C_{55}H_{44}N_5O_5P_3$: C, 69.69; H, 4.68; N, 7.39. Found: C, 69.71; H, 4.67; N, 7.37%. MALDI-TOF (*m*/*z*) calc.: 2047, found: 2048 $[M+H]^+$. ^{1}H NMR ($CDCl_3$, δ, ppm): 5.30 (2H, NH_2, d, $^2J_{H-H}$ = 1.8 Hz), 6.66 (H_a, 4H, d, $^3J_{H-H}$ = 7.2 Hz), 6.92 (H_b, 4H, d, $^3J_{H-H}$ = 7.3 Hz), 6.98–7.35 (H_{1-3}, H_c, H_d, H_e, 32H), 7.77 (H_f, d, 2H, $^3J_{H-H}$ = 7.9 Hz). FTIR (ν, cm^{-1}): 3350–3394 d(NH_2), 3007 (N-H), 3050 m((C–H)arom.), 1507 s (C=C), 1260–1172 s(P=N), 1157 s(P=O).

3. Results and discussion

3.1. Synthesis and characterization of compounds **13**–**18**

In this study, firstly the reaction of hexachlorocyclotriphosphazene with phenol, 2-naphthol, and 1-hydroxypyrene gave the penta- (**5**, **7** and **9**) and hexa-substituted (**6**, **8** and **10**) cyclotriphosphazene compounds (Scheme 1). The target compounds (**13**–**18**) were then synthesized by the reaction of the pentasubstituted cyclotriphosphazene compounds (**5**, **7** and **9**) with di-functional 4,4′-(9-fluorenylidene)diphenol (**FDP**) (**11**) or 4,4′-(9-fluorenylidene)dianiline (**FDA**) (**12**) groups. The structures of the compounds **5**–**10** and **13**–**18** were verified by elemental analyses, mass spectrometry, UV–Vis, ^{1}H and ^{31}P NMR techniques, X-ray crystallography (for **13** and **18**) and fluorescence spectroscopy. The ^{31}P NMR chemical shifts and phosphorus-phosphorus coupling constants of the isolated compounds (**5**–**10**, **13**–**18**) are summarized in Table 1. Compounds **5**, **7** and **9** were reacted with **FDP** (**11**) in

Table 1
^{31}P NMR parameters for compounds **5**–**10** and **13**–**18** in $CDCl_3$ solution.

Comp.	δ(^{31}P NMR)[ppm]			R	R'	Spin system	^2J(PP) [Hz]	
	P(OCl)	P(OR_2)	P(ORR')				$^2J_{1,2}$	$^2J_{1,3}$
5	22.00	7.00	–	C_6H_4O	–	AX_2	82.85	82.85
6	–	9.10	–	C_6H_4O	–	A_3	–	–
7	23.00	7.70	–	$C_{10}H_6O$	–	A_2X	81.60	81.60
8	–	8.50	–	$C_{10}H_6O$	–	A_3	–	–
9	5.90	20.80	–	$C_{16}H_9O$	–	A_2X	78,69	78,69
10	–	9.40	–	$C_{16}H_9O$	–	A_3	–	–
13	–	8.60	–	C_6H_4O	$C_{25}H_{16}O_2$	A_2B	–	–
14	–	14.17	14.17	C_6H_4O	$C_{25}H_{17}O_2$	A_2B	–	–
15	–	9.74	8.85	$C_{10}H_6O$	$C_{25}H_{16}O_2$	A_2B	88.43	–
16	–	8.61	9.73	$C_{16}H_9O$	$C_{25}H_{16}O_2$	A_2B	89.81	–
17	–	6.70	23.0	C_6H_4O	$C_{25}H_{19}N_2$	AX_2	82.23	–
18	–	8.60	1.70	$C_{10}H_6O$	$C_{25}H_{18}N_2$	A_2X	96.26	96.26

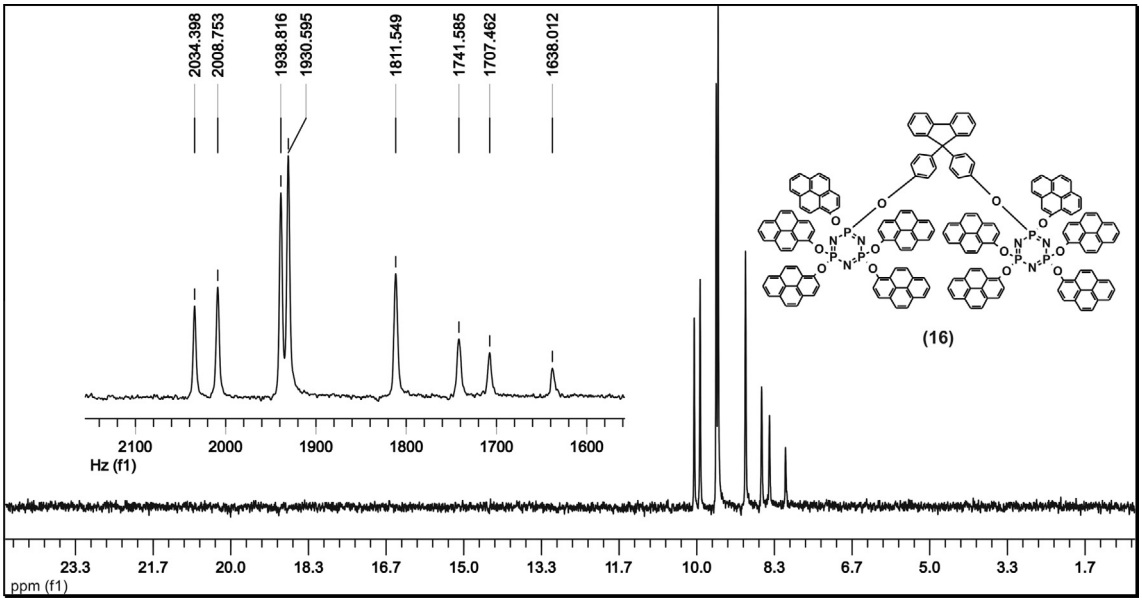


Fig. 1. ^{31}P NMR spectrum of the 1-hydroxypyrene substituted FDP-bridged compound (**16**) in $CDCl_3$ solution.

the presence of Cs_2CO_3 in THF and bridged (**13**, **15** and **16**) and open chain compounds (**14**) were isolated. The mass and elemental analyses of compounds **13**, **15** and **16** indicated that one chlorine atom in the pentasubstituted cyclotriphosphazene compounds (**5**, **7** and **9**) was replaced with **FDP** (**11**). The mass spectra of compounds **13**, **15** and **16** gave molecular ion peaks at *m*/*z* 1549.8, 2050.3 and 2791.2, respectively, confirming the exact composition, and no chlorine patterns for compounds **13**, **15** and **16** were observed (Figs. S1a, b and c, respectively). The proton decoupled ^{31}P NMR spectra of compounds **13**, **14**, **15** and **16** were observed as A_2B spin systems (Figs. S2 and S3 for compounds **13** and **15**) due to the different environments for the two different phosphorus nuclei on the cyclophosphazene ring (see Fig. 1 as an example for compound **16**). The reaction of compound **5** with **FDA** (**12**) gives only the open chain compound (**18**). The reaction of compound **7** with **FDA (12)** in the presence of Cs_2CO_3 in THF did not result in any product. Alternative reaction conditions were selected and compound **7** was reacted with **FDA** (**12**) in the presence of 4-dimethylaminopyridine (DMAP) in acetonitrile and in this case a bridged compound (**17**) was obtained. In addition, no product was obtained from the reaction of compound **9** with **FDA** (**12**), although different reaction conditions were tested. AX_2 and A_2X spin systems were observed in the proton decoupled ^{31}P NMR spectra of compounds **17** and **18** due to the different environments for the two different phosphorus nuclei on the cyclotriphosphazene ring.

3.2. X-ray structural analysis

The molecular structures of compounds **13** and **18** are presented in Figs. 2 and 3 and selected data collection and refinement parameters are reported in Table S1. Compound **13** is a mono-bridged cyclotriphosphazene compound, in that two penta-phenoxy-cyclophosphazene (P_3N_3) rings are linked by a 4,4′-(9-fluorenylidene)diphenol (FDP) bridge (Fig. 2). The crystal structure of compound **13** was investigated by comparing it to a previous derivative reported by our group in which two penta-chloro-cyclophosphazenes were linked by the same FDP bridge [24], hereinafter it will be referred to as the previous chloro derivative. In compound **13**, the two cyclotriphosphazene rings have slightly twisted planar conformations and the bond lengths and bond angles of the cyclotriphosphazene rings are found in similar ranges as were reported for its previous chloro derivative [24] (Table S2). The conformational arrangement of the FDP bridge of compound **13** is also similar to that of its previous chloro derivative: in compound **13**, the C4–C7–C20 bond angle belonging to the centre of the bridge is 109.62(2)° (Table S2 and Fig. S4) and the angles between the planes of the two benzyl rings of the bridge are 76.04 (Fig. S5) 112.84(12) and 69.68°, respectively. However, the conformational arrangements of the cyclotriphosphazene rings are significantly different in compound **13**; the two P_3N_3 rings of compound **13** have a similar orientation, with 123.06(16) and 117.57(17)° P1–O1–C1 and P4–O2–C23 bond angles, and the angles between the planes of the benzyl rings of the FDP bridge and the P_3N_3 rings are 69.07 and 84.98° (Table S2 and Fig. S6), hence the angle between the planes of the two P_3N_3 rings is 68.47° in compound **13** (Fig. S7). In the previous chloro derivative, the two P_3N_3 rings had different orientations; while one P_3N_3 ring had a similar arrangement to that of the P_3N_3 rings of compound **13**, the other P_3N_3 ring was oriented in the opposite direction, the P1–O1–C1 and P4–O2–C23 bond angles were 126.62(10) and 114.87(9)°, respectively, and the angle between the planes of the benzyl rings of the FDP bridge and the P_3N_3 rings were 18.03° and 69.68° [24]. This difference in the arrangements of the P_3N_3 rings may arise from the presence of the phenoxy substituents in compound **13**. There are many weak intermolecular π–π interactions with distances between the phenoxy ring centroids in the range 3.8485(18)–5.9686(16) Å, and these interactions may affect the orientations of the P_3N_3 rings. However, it should also be considered that the P–O–C moiety is sufficiently flexible to form a range orientations of the phosphazene rings.

Compound **18** is an open chain compound in which the cyclophosphazene (P_3N_3) ring is substituted with five phenoxy- and one 4,4′-(9-fluorenylidene)dianilino (**FDA**) moieties, one amino group of FDA is not substituted. The cyclotriphosphazene ring has a slightly twisted planar conformation, the maximum deviation from the main plane of the ring is −0.1227(7) Å for the P2 phosphorous atom. The bond lengths and bond angles are very similar to those observed for compound **13**. The conformational arrangement of the FDA bridged compound **18** is also similar to that observed for compound **13**; the C4–C7–C20 bond angle belonging to the centre of the bridge is 111.02(15)° (Table S2 and

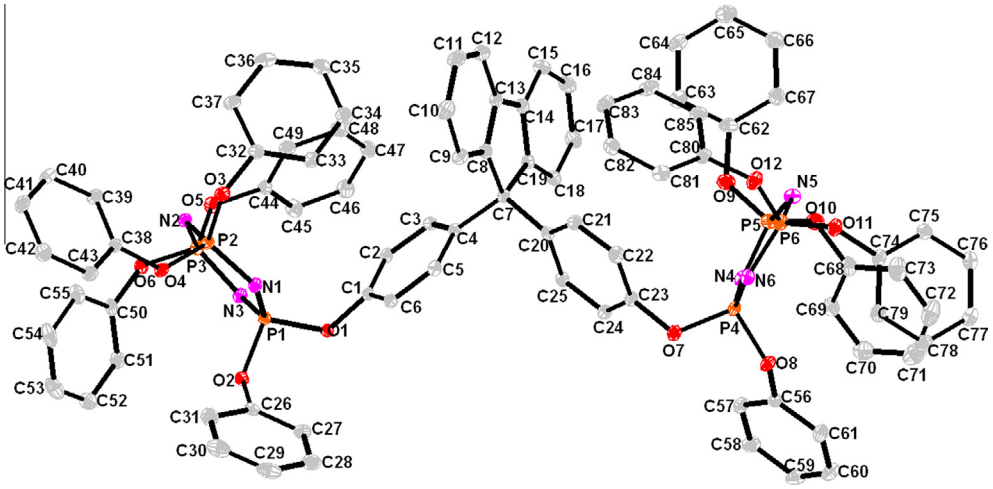


Fig. 2. Crystal structure of compound **13** with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The hydrogen atoms have been omitted for clarity.

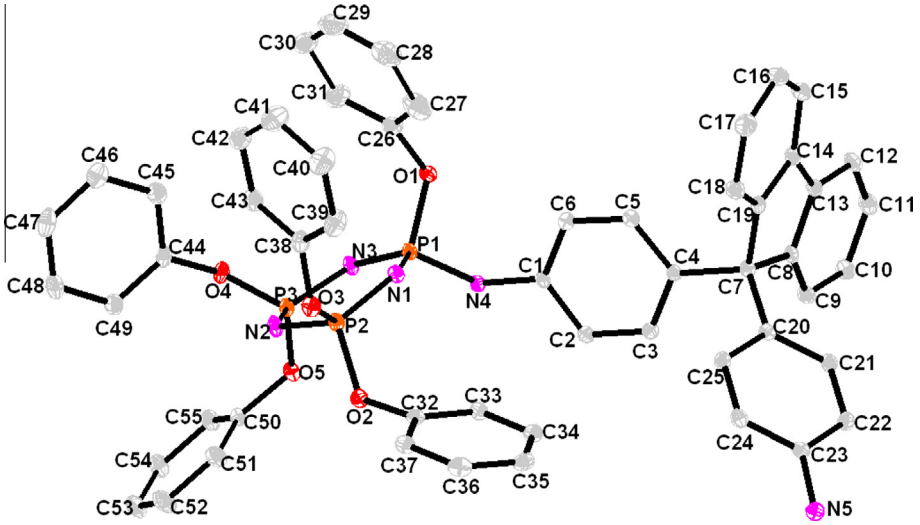


Fig. 3. Crystal structure of compound **18** with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The hydrogen atoms and ethyl acetate have been omitted for clarity.

Fig. S8) and the angles between the planes of the two phenol rings of the bridge is 70.46° (Fig. S9). The P1–N4–C1 bond angle is 125.72 (14)°. The angle between the planes of the aryl rings of FDA and the P_3N_3 rings is 84.52° (Table S2 and Fig. S10). In addition to the many weak intermolecular π–π interactions between the phenoxy rings, there are intermolecular N–H···N and N–H···O hydrogen bonds in the crystal packing of compound **18**; the distances between the donor and acceptor atoms are in the range 2.994(3)–3.163(2) Å, with the presence of free amine.

3.3. Chemosensor properties

The electronic absorption and fluorescence behavior of the newly synthesized cyclotriphosphazene derivatives were studied in THF. Absorption bands were observed at approximately 240, 275 and 310 nm for compounds **13** and **15**, and 240, 265, 275, 330 and 345 nm for compound **16** in the UV region of the electronic spectra (see Fig. S11 as an example for compound **16**). Compounds **13**, **14**, **15**, **17** and **18** were excited at 270 nm and compound **16** was excited at 345 nm for fluorescence emission studies. Fig. 4 shows the fluorescence emission spectra of all the studied compounds. While the phenol (**13**), 2-naphthol (**15**)

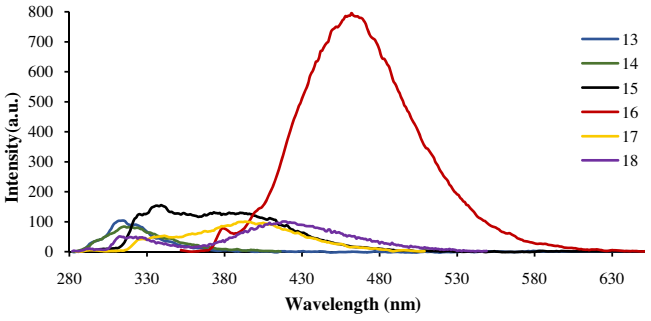


Fig. 4. The fluorescence emission spectra of **13**–**18** in THF. Concentration: 1.0×10^{-6} mol dm^{-3}. Excitation wavelength: 270 (**13**, **14**, **15**, **17**, **18**) and 345 (**16**) nm.

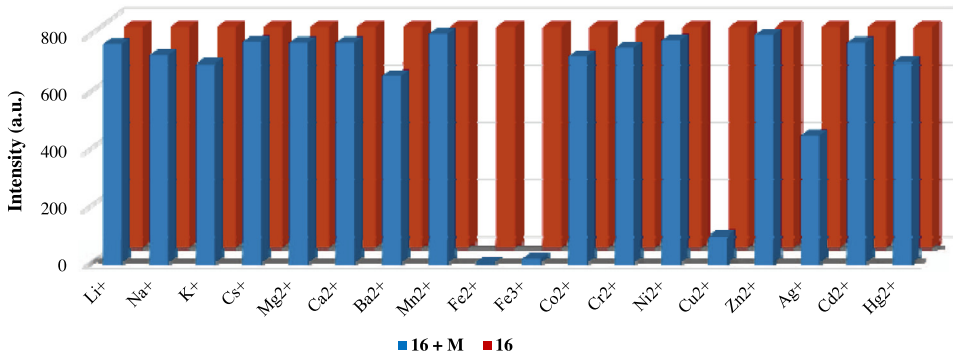


Fig. 5. The fluorescence intensities of compound **16** with and without metal ions. Addition of copper (Cu^{2+}) and iron (Fe^{2+}/Fe^{3+}) ions to the solution prevented fluorescence emission, hence provide a selective detection (5 μL of 5×10^{-3} M).

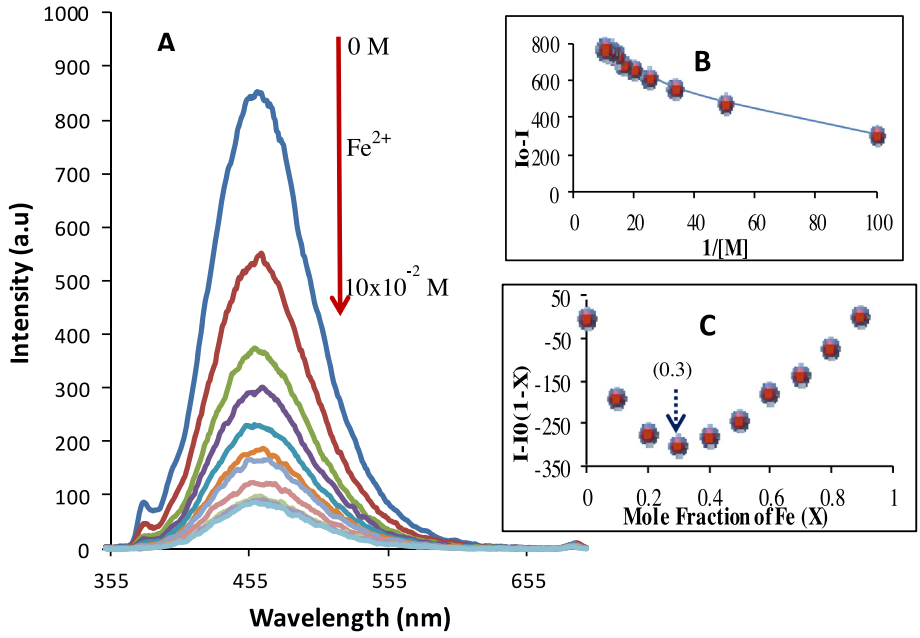


Fig. 6. (A) Fluorescence response of chemosensor **16** to various equivalents of Fe^{2+}. (B) The Benesi-Hildebrand graph and (C) Job's plot of the 16-Fe^{2+} complex in THF solution. The total concentration of **16** and Fe^{2+} was 1×10^{-2} M. The excitation wavelength was 345 nm. The monitored wavelength was 460 nm.

and 1-hydroxypyrene (**16**) substituted cyclotriphosphazene compounds showed emissions, the other synthesized cyclotriphosphazene derivatives showed very low fluorescence in THF at 1.0×10^{-6} mol dm^{-3}. The trend of the emission maximum for these aryloxy substituted (**FDP**) bridged cyclotriphosphazene derivatives are phenol substituted (**13**) < 2-naphthol substituted (**15**) < 1-hydroxypyrene substituted (**FDP**) bridged cyclotriphosphazene (**16**), according to the increasing number of conjugated π-electrons in the aromatic ring systems of the substituted groups (Fig. 4). Compound **16** shows the most intense fluorescence emission in the visible region of the spectrum. These measurements show that compound **16** exhibits highly fluorescence behavior in THF solution, however, the other bridged cyclotriphosphazene derivatives showed very weak fluorescence in this solvent. For this reason, only the 1-hydroxypyrene substituted **FDP** bridged compound was tested with metal ions for the determination of the possibility of this compound being used as a chemosensor.

As mentioned earlier, the metal binding properties of the fluoren molecules may allow the use of these molecules as metal sensors. The effects of a variety of metal ions (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+} Co^{2+}, Cr^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+} and Hg^{2+}) on the fluorescence properties of the newly synthesized compound **16** were investigated using fluorescence spectroscopy. All the fluorescence emission spectral studies were performed in THF solutions of the 1-hydroxypyrene substituted (**FDP**) bridged cyclotriphosphazene compound, while water solutions of the corresponding metal chlorides (nitrate derivative for the Ag ion) were used as the source of metal ions at room temperature. The fluorescence spectra of compound **16** exhibited little enhancement by the addition of 5 μL of 5×10^{-3} M metal ion solutions, except for copper (Cu^{2+}) and iron (Fe^{2+}/Fe^{3+}). A significant decrease in the fluorescence intensities were observed by the addition of the copper (Cu^{2+}) and iron (Fe^{2+}/Fe^{3+}) cations, while no or a minimal change was observed with the other metal ions (Fig. 5).

The titration of the probe compound **16** with copper (Cu^{2+}) and iron (Fe^{2+}/Fe^{3+}) cations showed a decrease in the fluorescence intensities with increasing concentrations of these cations (Fig. 6A for Fe^{2+} titration, Fig. S12A for Cu^{2+} titration and Fig. S13A for Fe^{3+} titration). The graphs from a Benesi–Hildebrand analysis showed non-linear behavior for the studied cyclotriphosphazene

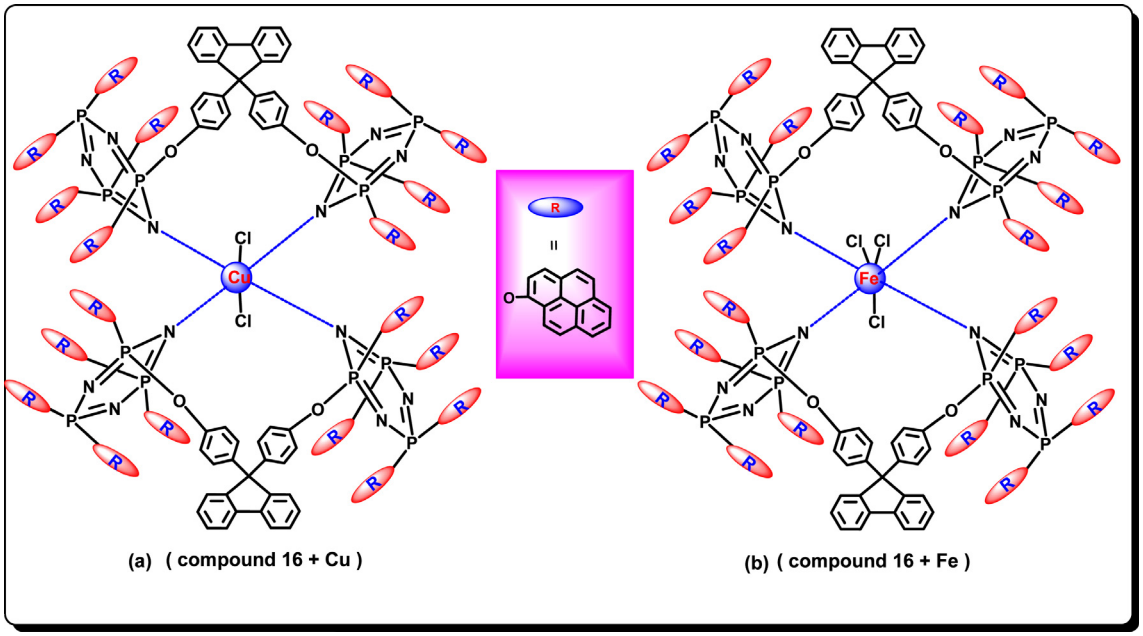


Fig. 7. The proposed structures between compound **16** and (a) Cu^{2+} and (b) Fe^{3+} ions as 2:1 complexes in aqueous solution (a similar structure is proposed for compound **16** and Fe^{2+} ions).

chemosensor compound **16** interactions with Cu^{2+} ions (Fig. S12B), indicating that the stoichiometry of the complexes between the cyclotriphosphazene chemosensor and Cu^{2+} cations is different from 1:1, as mentioned by Garcia-Beltran et al [45]. On the other hand, the Benesi–Hildebrand graphs showed a non-linear variation (Fig. 6B and Fig. S13B) as a result of the interactions this chemosensor with Fe^{2+} or Fe^{3+}, indicating that the stoichiometry of between this chemosensor and Fe^{2+} or Fe^{3+} cations is also different from 1:1. The continuous variation method was also used for the determination of the stoichiometry between the novel cyclotriphosphazene chemosensor and detected the metal cations. Consistent with the Benesi–Hildebrand graphs, the application of the method of continuous variation resulted in a Job's plot with a maximum at a mole fraction of Cu^{2+} close to 0.30, (Fig. S12C), indicating a preferred 2:1 stoichiometry for the formation of interactions between the fluorenylidene groups on the molecules and the Cu^{2+} cations. The proposed complex structure between compound **16** and the Cu^{2+} cations is given in Figs. 7(a). A maximum mole fraction for Fe^{2+} or Fe^{3+} cations was observed as 0.30 (Fig. 6C and Fig. S13C), indicating that the fluorenylidene groups on the cyclotriphosphazene molecules and the Fe^{2+} or Fe^{3+} ions preferred a 2:1 stoichiometry for the formation of a complex between the chemosensor compound (**16**) and the Fe^{2+} or Fe^{3+} cations. The proposed complex structure between the cyclotriphosphazene compound and the Fe^{3+} cations is given in Figs. 7(b).

4. Conclusions

In summary, aryloxy full-substituted fluorenylidene open chain and bridged cyclotriphosphazene derivatives were synthesized by nucleophilic reactions. All the newly synthesized compounds (**13–18**) were characterized by elemental analysis, mass spectrometry, UV–Vis, FT-IR, ^{1}H, ^{31}P NMR and fluorescence spectroscopies. Compound **16** showed high fluorescence behavior among the studied cyclotriphosphazene derivatives, indicating its possible use as a chemosensor. In particular, this compound showed "turn-off" fluorescence chemosensor behavior to copper (Cu^{2+}) and iron (Fe^{2+}/Fe^{3+}) ions in solution. This compound formed a 2:1 (L:M) complex structure with each of the copper (Cu^{2+}) and iron (Fe^{2+}/Fe^{3+}) ions as shown by a Job's plot. The newly synthesized FDP-bridged cyclotriphosphazene compound **16** has the potential for use as a chemosensor for these metal ions in solution.

Acknowledgment

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Appendix A. Supplementary data

^{31}P NMR and MS spectra, graphs of titrations of FDP-bridged compound **16** with Cu^{2+} and Fe^{3+} ions, the Benesi–Hildebrand graphs and Job's plots are given as Supporting information. CCDC 1015511 and 1015512 contain the supplementary crystallographic data for **13** and **18**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2015.10.047.

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