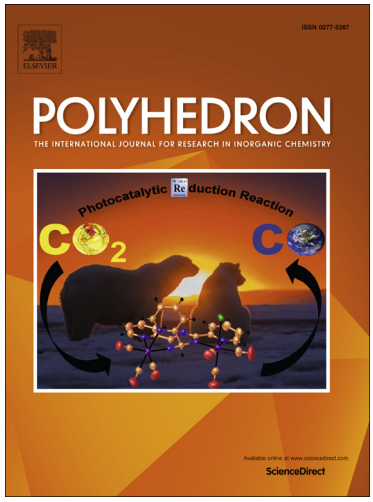


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# Structural and chemosensor properties of FDA and FDP derivatives of fluorenylidene bridged cyclotetraphosphazenes

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**ABSTRACT**

The first series of 4,4'-(9-fluorenylidene)diphenol (FDP) (**5**) and 4,4'-(9-fluorenylidene)dianiline (FDA) (**6**) bridged and open chained cyclotetraphosphazene derivatives (**15-23**) have been synthesized. Their florescence and chemosensor properties are reported. Nucleophilic substitution reactions of octachlorocylotetraphosphazene (**1**) with mono-functional reagents [phenol (**2**), 2-naphthol (**3**) and 1-hydroxypyrene (**4**)] were carried out and the heptasubstituted derivatives (**8**, **11** and **14**) were obtained. Then the reactions of **8**, **11** and **14** with 4,4′-(9-fluorenylidene)diphenol (**FDP**) (**5**) and 4,4′-(9-fluorenylidene)dianiline (**FDA**) (**6**), respectively gave bridged and open chained compounds. The structures of the synthesized compounds (**7**-**23**) were verified by elemental analyses, mass spectrometry, UV Vis, $^{1}H$ and $^{31}P$ NMR techniques and fluorescence spectroscopy. The metal sensing properties of the novel bridged open chain cyclotetraphosphazene derivatives were also examined by fluorescence spectroscopy. These complexes showed high selectivity for $Cu^{2+}$ and $Fe^{3+}$ ions in solution.

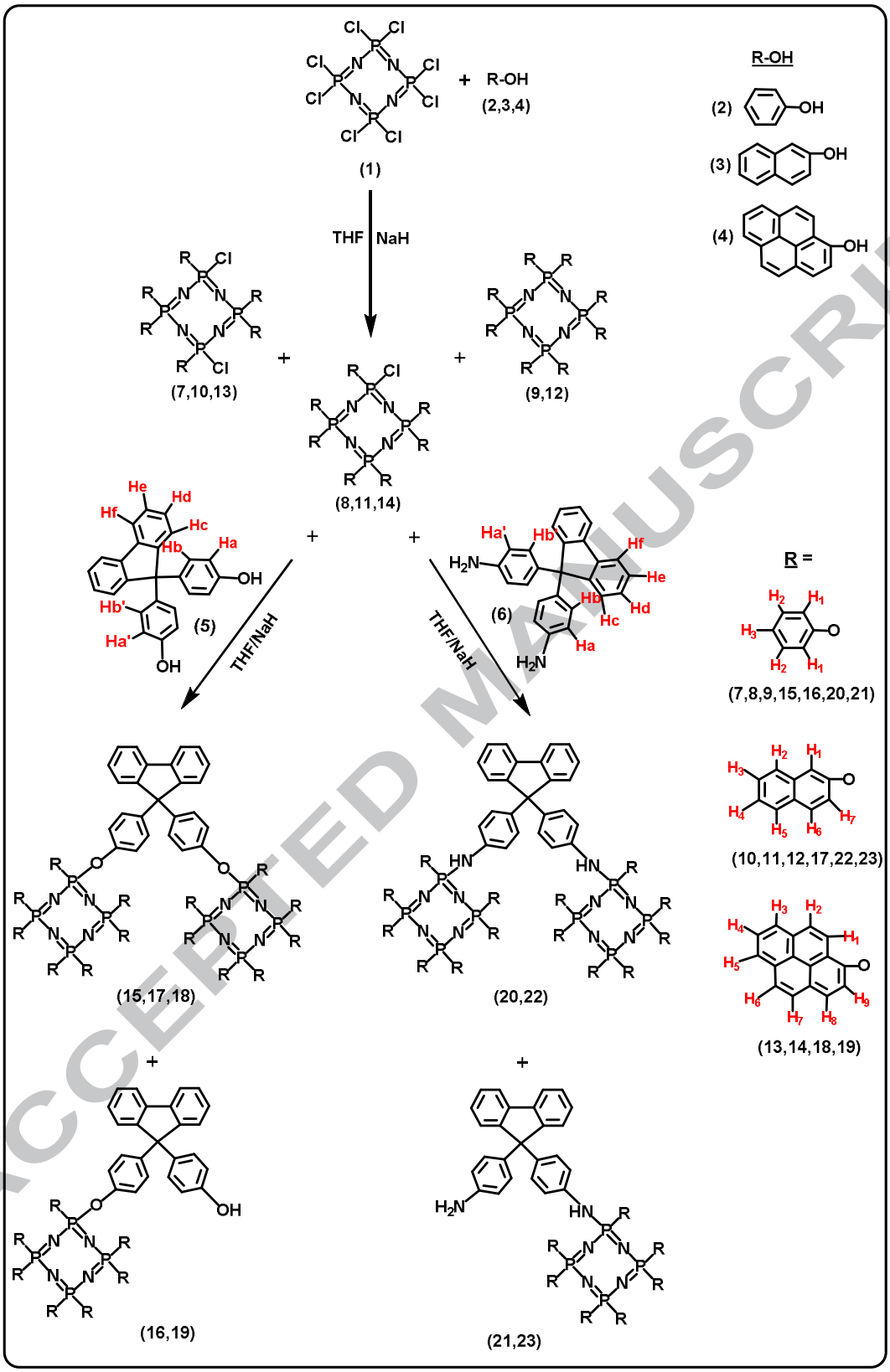
**KEYWORDS:** Cyclotetraphosphazenes, Fluorenylidene, Fluorescence Properties, Bridged structure, Chemosensors, $Cu^{2+}$ and $Fe^{3+}$ ions.

## 1. INTRODUCTION

The design of fluorescent chemosensors for ions is very important for the study of ions in biological processes since they may be linked to states of human disease. Examining the fluorescence properties of compounds to be synthesized as new sensors, determining their locations in the body and their usability for metal ion sensing as a fluorescence sensor are important [1,2]. For example, the development of chemosensors for sensing $Fe^{3+}$ ions has attracted interest because they play important roles in biology, chemistry and the environment. Iron is an important trace element and the most abundant in the cells of all organisms [3,4]. Deficiency of $Fe^{3+}$ ions causes anemia, diabetes, liver damage, Parkinson's disease and cancer [5,6], but an overdose of iron in humans is equally detrimental and can cause dis-function of certain organs, such as the heart, pancreas and liver [7]. On the other hand, copper is the third most abundant ion in the human body and plays an important role in many physiological systems [8,9]. If the blood concentration of copper ions falls outside the normal range [3,10], it can cause Alzheimer's, Wisons and Manke's diseases [11-14]. Therefore, the detection of trace amounts of $Cu^{2+}$ [15,16] and $Fe^{3+}$ [17,18] ions is critical. Some organic compounds, like fluorene and pyrene, are remarkable for their fluorescence properties, thus they and their derivatives are suitable for many applications, such as metal-organic frameworks, fluorescent probes and applications in sensors, liquid crystals, organic light-emitting diodes, as electrochromic applications [19-26]. Conjugated fluorenes, such as 4,4′-(9-fluorenylidene)diphenol (**5**) or 4,4′-(9-fluorenylidene)dianiline, (FDA) (**6**), have been used for many applications and they have the potential to detect metal ions in biological and environmental media as well. The binding of certain metal ions to the fluorene molecule may influence the fluorescent properties of the molecule and hence indicate its presence in solution [27-30]. Phosphazenes, particularly cyclic phosphazenes, are an important class of inorganic heterocyclic ring containing an [N = $PX_2$] repeat unit [31]. Some of the substituted cyclic

phosphazenes have high thermal stability and do not break down even under very aggressive chemical conditions. Among this family of compounds, the chlorocyclophosphazenes $N_3P_3Cl_6$ and $N_4P_4Cl_8$ (**1**), have received maximum attention [32,33], and of these, the cyclotriphosphazenes are the most prevalent. 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 [34-39]. The reactions of octachlorocyclotetraphosphazene, $N_4P_4Cl_8$, with mono-, di-, tri- and tetra-functional reagents have been studied [31,40-47] and there are reports of cyclotetraphosphazene compounds containing fluorescent groups [48-50]. However, discussion on substitution with a cyclotetraphosphazene bridged structure is relatively limited in the literature [46]. In our recent works, FDP and FDA bridged cyclotriphosphazenes, $N_3P_3Cl_6$, and their derivatives showed selectivity towards $Cu^{2+}$ and $Fe^{2}/Fe^{3+}$ ions [29,51,52]. The results of these studies have encouraged us to investigate new phenol, naphthol and pyrene modified cyclotetraphosphazene compounds containing FDP and FDA on the cyclotetraphosphazene core.

In the current study, new fully substituted fluorenylidene bridged (**15**, **17**, **18**, **20** and **22**) and open chain (**16**, **19**, **21** and **23**) cyclotetraphosphazene compounds have been synthesized, and their florescence and chemosensor properties are reported for the first time. All the compounds were characterized by elemental analysis, mass spectrometry, UV Vis, $^{1}H$, $^{31}P$ NMR and fluorescence spectroscopy (**15-23**). In addition, the metal binding properties of the synthesized FDP/FDA bridged and open chain cyclotetraphosphazene compounds (**15**, **16**, **18**, **19**, **20**) were investigated and compared by fluorescence spectroscopy.




**Scheme 1.** FDA and FDP containing cyclotetraphosphazene derivatives.

## 2. Experimental Section

### 2.1. General Materials and Methods.

Octachlorocyclotetraphosphazene (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. Phenol (99%), 2-naphthol (99%), 1-hydroxypyrene (99%), 4,4′-(9-fluorenylidene)diphenol (99%) and (4,4′-(9-fluorenylidene)dianiline (99%) were obtained from Aldrich. Tetrahydrofuran (≥ 99.0%), dichloromethane (≥ 99.0%) and *n*-hexane (≥ 95.0%) 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. $CDCl_3$ and $d_8$-THF for NMR spectroscopy were 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 the MALDI matrix using a nitrogen laser, accumulating 50 laser shots using a Bruker Microflex LT MALDI-TOF mass spectrometer. 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 3g crude mixture, 100g 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 $CDCl_3$ and $d_8$-THF 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. 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. The NMR simulation program, available free of charge, used was gNMR [53].

**2.2. Synthesis**

***2.2.1.*** *Reaction of octachlorocyclotetraphosphazene $N_4P_4Cl_8$ (**1**) with phenol (**2**) in a 1:7 ratio to form compounds **7**, **8** and **9**.*

Phenol (**2**) (4.26 g, 45.30 mmol) was dissolved in 50 mL of dry THF under an argon atmosphere in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 1.81 g, 45.30 mmol) in 20 mL of dry THF was quickly added to the above stirred solution under an argon atmosphere. Octachlorocyclotetraphosphazene $N_4P_4Cl_8$ (**1**), (3.00 g, 6.47 mmol) in 20 mL of dry THF was added to the stirred solution under an argon atmosphere. The reaction mixture was stirred for 2 days at room temperature and the reaction was followed on TLC silica gel plates using *n*-hexane-$CH_2Cl_2$ (3:2) as the eluent. Three products were observed on TLC. The reaction mixture was filtered to remove the formed sodium chloride and then the solvent was removed under reduced pressure. The resulting colorless solid was subjected to column chromatography, using *n*-hexane-$CH_2Cl_2$ (3:2) as the eluent. The first product was compound **7**, 1,1,3,5,5,7-hexaphenoxy-3,7-dichlorocyclotetraphosphazene, (0.31 g, 0.36 mmol, 6%, oily), Rf = 0.57. *Anal.* Calc. for $C_{36}H_{30}Cl_2N_4O_6P_4$: C, 53.42; H, 3.74; N, 6.92; M, 809. Found: C, 53.40; H, 3.72; N, 6.90%. MS (MALDI-TOF) m/z: 809 $[M]^+$. $^1H$ NMR, $CDCl_3$, 298 K, δ ppm: 7.29-7.24 m, 12H, $H_1$; 7.23-7.19 m, 6H, $H_3$; 7.13-7.11 m, 12H, $H_2$. The second product was compound **8**, 1,1,3,3,5,5,7-heptaphenoxy-7-dichlorocyclotetraphosphazene, (1.17 g, 1.35 mmol, 21%, oily), Rf = 0.47. *Anal.* Calc. for $C_{42}H_{35}ClN_4O_7P_4$: C, 58.18; H, 4.07; N, 6.46; M, 867. Found: C, 58.16; H, 4.05; N, 6.44%. MS (MALDI-TOF) m/z: 867 $[M]^+$. $^1H$ NMR, $CDCl_3$, 298 K, δ ppm: 7.11-7.06 m, 14H, $H_1$; 7.03-6.99 m, 7H, $H_3$; 6.95-6.91 m, 14H, $H_2$. The third product was compound **9**, 1,1,3,3,5,5,7,7-octaphenoxycyclotetraphosphazene, (0.65 g,

0.70 mmol, 11%, oily), Rf = 0.37. *Anal.* Calc. for $C_{48}H_{40}N_4O_8P_4$: C, 62.34; H, 4.36; N, 6.06; M, 924. Found: C, 62.31; H, 4.34; N, 6.06%. MS (MALDI-TOF) m/z: 924 $[M]^+$. $^1$H NMR, $CDCl_3$, 298 K, δ ppm; 7.08-7.04 m, 16H, $H_1$; 7.02-6.97 m, 8H, $H_3$; 6.88-6.84 m, 16H, $H_2$.

***2.2.2.*** *Reaction of octachlorocyclotetraphosphazene $N_4P_4Cl_8$ (**1**) with 2-naphthol (**3**) in a 1:7 ratio to form compounds **10**, **11** and **12**.*

2-Naphthol (**3**) (5.43 g, 37.73 mmol) was dissolved in 50 mL of dry THF under an argon atmosphere in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 1.50 g, 37.73 mmol) in 20 mL of dry THF was quickly added to the above stirred solution under an argon atmosphere. Octachlorocyclotetraphosphazene $N_4P_4Cl_8$ (**1**), (2.50 g, 5.39 mmol) in 20 mL of dry THF was added to the stirred solution under an argon atmosphere. The reaction mixture was stirred for 5 hours at room temperature and the reaction was followed on TLC silica gel plates using *n*-hexane-$CH_2Cl_2$ (3:2) as the eluent. Three products were observed on TLC. The reaction mixture was filtered to remove the formed sodium chloride and then the solvent was removed under reduced pressure. The resulting colorless solid was subjected to column chromatography, using *n*-hexane-$CH_2Cl_2$ (3:2) as the eluent. The first product was compound **10**, 1,1,3,5,5,7-hexa(2-naphthloxy)-3,7-dichlorocyclotetraphosphazene, (0.30 g, 0.27 mmol, 6%, oily), Rf = 0.51. *Anal.* Calc. for $C_{60}H_{42}Cl_2N_4O_6P_4$: C, 64.94; H, 3.81; N, 3.69; M, 1109. Found: C, 64.92; H, 3.78; N, 3.65%. MS (MALDI-TOF) m/z: 1110 $[M+H]^+$. $^1$H NMR, $CDCl_3$, 298 K, δ ppm: 7.65 d, 6H, $H_2$ ($^3J_{H2\text{-}H3}$ = 8.28 Hz); 7.50, s, 6H, $H_1$; 7.45-7.38, m, 12H, ($H_3$, $H_4$); 7.35-7.30, m, 12H, ($H_6$, $H_5$); 7.22, d, 6H, $H_7$ ($^3J_{H7\text{-}H6}$ = 8.90 Hz). The second product was compound **11**, 1,1,3,3,5,5,7-hepta(2-naphthloxy)-7-dichlorocyclotetraphosphazene, (1.62 g, 1.33 mmol, 25%, oily), Rf = 0.46. *Anal.* Calc. for $C_{70}H_{49}ClN_4O_7P_4$: C, 69.06; H, 4.06; N, 4.60; M, 1217. Found: C, 69.04; H, 4.03; N, 4.56%. MS (MALDI-TOF) m/z: 1217 $[M]^+$. $^1$H NMR, THF-$d_8$, 298 K, δ ppm: 7.68 d, 7H, $H_2$ ($^3J_{H2\text{-}H3}$ = 8.30 Hz); 7.46, s, 7H, $H_1$; 7.43-7.34,

m, 14H, ($H_3$, $H_4$); 7.31-7.28, m, 14H, ($H_6$, $H_5$); 7.17, d, 7H, $H_7$ ($^3J_{H7-H6}$ = 8.90 Hz). The third product was compound **12**, 1,1,3,3,5,5,7,7-octa(2-naphthloxy)cyclotetraphosphazene, (0.66 g, 0.50 mmol, 9%, oily), Rf = 0.41. *Anal.* Calc. for $C_{80}H_{56}N_4O_8P_4$: C, 72.51; H, 4.26; N, 4.23; M, 1325. Found: C, 72.49; H, 4.23; N, 4.2%. MS (MALDI-TOF) m/z: 1325 $[M]^+$. $^1$H NMR, $CDCl_3$, 298 K, δ ppm: 7.57 d, 8H, $H_2$ ($^3J_{H2-H3}$ = 8.18 Hz); 7.30, td, 8H, $H_3$ ($^3J_{H2-H3}$ = 8.18 Hz, $^3J_{H3-H4}$ = 7.30 Hz); 7.26, s, 8H, $H_1$; 7.21, td, 8H, $H_4$ ($^3J_{H4-H3}$ = 7.30 Hz, $^3J_{H4-H5}$ = 8.20 Hz); 7.19, d, 8H, $H_6$ ($^3J_{H6-H7}$ = 8.90 Hz); 7.14, d, 8H, $H_5$ ($^3J_{H5-H4}$ = 8.20 Hz); 6.92, d, 8H, $H_7$ ($^3J_{H7-H6}$ = 8.90 Hz).

***2.2.3.*** *Reaction of octachlorocyclotetraphosphazene $N_4P_4Cl_8$ (**1**) with 1-hydroxypyrene (**4**) in a 1:7 ratio to form compounds **13** and **14**.*

1-Hydroxypyrene (**4**) (2.00 g, 9.16 mmol) was dissolved in 50 mL of dry THF under an argon atmosphere in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.36 g, 9.16 mmol) in 40 mL of dry THF was quickly added to the above stirred solution under an argon atmosphere. Octachlorocyclotetraphosphazene $N_4P_4Cl_8$ (**1**), (0.60 g, 1.29 mmol) in 20 mL of dry THF was added to the stirred solution under an argon atmosphere. The reaction mixture was stirred for 7 hours at room temperature and the reaction was followed on TLC silica gel plates using *n*-hexane-$CH_2Cl_2$ (2:1) as the eluent. Two products were observed on TLC. The reaction mixture was filtered to remove the formed sodium chloride and then solvent was removed under reduced pressure. The resulting colorless solid was subjected to column chromatography, using *n*-hexane-$CH_2Cl_2$ (2:1) as the eluent. The first product was compound **13**, 1,1,3,5,5,7-hepta(1-oxypyrene)-3,7-dichlorocyclotetraphosphazene, (0.10 g, $6.43x10^{-2}$ mmol, 5%, oily), Rf = 0.21. *Anal.* Calc. for $C_{96}H_{54}Cl_2N_4O_6P_4$: C, 74.18; H, 3.50; N, 3.60; M, 1554. Found: C, 74.15; H, 3.46; N, 3.57; %. MS (MALDI-TOF) m/z: 1554 $[M+H]^+$. $^1$H

NMR, $CDCl_3$, 298 K, δ ppm: 8.40-7.10 m, 54H, ($H_1$-$H_9$). The second product was compound **14**, 1,1,3,3,5,5,7-hepta(1-oxypyrene)-7-chlorocyclotetraphosphazene, (0.30 g, 0.17 mmol, 15%, oily), Rf = 0.17. *Anal.* Calc. for $C_{112}H_{63}ClN_4O_7P_4$: C, 77.49; H, 3.66; N, 3.23; M, 1736. Found: C, 77.46; H, 3.64; N, 3.21; %. MS (MALDI-TOF) m/z: 1736 $[M]^+$. $^1H$ NMR, $CDCl_3$, 298 K, δ ppm: 8.40-7.10 m, 63H, ($H_1$-$H_9$).

***2.2.4.*** *Reaction of 1,1,3,3,5,5,7-heptaphenol-7-chlorocyclotetraphosphazene (**8**) with 4,4'-(9-fluorenylidene)diphenol (FDP) (**5**) in a 1:2 ratio to form compound **15** and **16**.*

1,1,3,3,5,5,7-Heptaphenoxy-7-chlorocyclotetraphosphazene (**8**), (0.70 g, 0.81 mmol) and 4,4′-(9-fluorenylidene)diphenol (FDP) (**5**) (0.14 g, 0.41 mmol) were dissolved in 100 mL of dry THF under an argon atmosphere in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.03 g, 0.81 mmol) in 40 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The reaction mixture was refluxed for 4 days and the reaction followed on TLC silica gel plates using *n*-hexane-$CH_2Cl_2$ (2:3) as the eluent. Two products were observed on TLC. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The resulting colorless solid was subjected to column chromatography, using *n*-hexane-THF (2:3) as the eluent. The first product was compound **15**, the phenol substituted FDP-bridged cyclotetraphosphazene derivative, (0.51 g, 0.25 mmol, 61% oily), Rf = 0.58. *Anal.* Calc. for $C_{109}H_{86}N_8O_{16}P_8$: C, 65.09; H, 4.33; N, 5.59; M, 2011. Found: C, 65.08; H, 4.31; N, 5.57 %, MS (MALDI-TOF) m/z: 2011 $[M+H]^+$ (Fig. S1a). $^1H$ NMR, $CDCl_3$, 298 K, δ ppm: 7.70, d, 2H, $H_f$, ($^3J_{Hf\text{-}He}$ = 7.23 Hz); 7.27, td, 2H, $H_e$, ($^3J_{He\text{-}Hf}$ = 7.23 Hz, $^3J_{He\text{-}Hd}$ = 7.49 Hz); 7.18-7.16, q, 4H, ($H_d$, $H_c$); 7.05-6.76, q, 74H, ($H_1$, $H_2$, $H_3$, $H_b$); 6.66, d, 4H, $H_a$, ($^3J_{Ha\text{-}Hb}$ = 8.65 Hz). The second product was compound **16**, the phenol substituted open chain FDP cyclotetraphosphazene derivative, (0.15 g, 0.12 mmol, 30%, oily), Rf = 0.40. *Anal.*

Calc. for $C_{67}H_{52}N_4O_9P_4$: C, 68.16; H, 4.47; N, 4.76; M, 1181. Found: C, 68.14; H, 4.44; N, 4.74 %, MS (MALDI-TOF) m/z: 1181 $[M]^+$. $^1$H NMR, $CDCl_3$, 298 K, δ ppm: 7.66, d, 2H, $H_f$, ($^3J_{Hf\text{-}He}$ = 7.56 Hz); 7.25, td, 2H, $H_e$, ($^3J_{He\text{-}Hf}$ = 7.56, $^3J_{He\text{-}Hd}$ = 7.44 Hz); 7.20, d, 2H, $H_c$, ($^3J_{Hc\text{-}Hd}$ = 7.66 Hz); 7.13, td, 2H, $H_d$, ($^3J_{Hd\text{-}He}$ = 7.44, $^3J_{Hd\text{-}Hc}$ = 7.66 Hz); 7.05-6.75, q, 39H, ($H_1$, $H_2$, $H_3$, $H_{a'}$, $H_{b'}$); 6.66, d, 2H, $H_b$, ($^3J_{Hb\text{-}Ha}$ = 8.80 Hz); 6.51, d, 2H, $H_a$, ($^3J_{Ha\text{-}Hb}$ = 8.80 Hz); 5.15, s, 1H, (OH).

***2.2.5.*** *Reaction of 1,1,3,3,5,5,7-hepta(2-naphthloxy)-7-chlorocyclotetraphosphazene (**11**) with 4,4'-(9-fluorenylidene)diphenol (FDP) (**5**) in a 1:2 ratio to form compound **17**.*

1,1,3,3,5,5,7-Hepta(2-naphthloxy)-7-chlorocyclotetraphosphazene (**11**), (1.5 g, 1.23 mmol) and 4,4′-(9-fluorenylidene)diphenol (FDP) (**5**) (0.21 g, 0.63 mmol) were dissolved in 100 mL of dry THF under an argon atmosphere in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.05 g, 1.23 mmol) in 40 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The reaction mixture was refluxed for 3 days and the reaction followed on TLC silica gel plates using *n*-hexane–$CH_2Cl_2$ (1:1) as the eluent. One product was observed on TLC. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The resulting colorless solid was subjected to column chromatography, using *n*-hexane–$CH_2Cl_2$ (1:1) as the eluent. The product was compound **17**, the 2-napthole substituted FDP-bridged cyclotetraphosphazene derivative, (1.01 g, 0.37 mmol, 60%, oily), Rf = 0.47. *Anal.* Calc. for $C_{165}H_{114}N_8O_{16}P_8$: C, 73.10; H, 4.21; N, 4.13; M, 2711. Found: C, 73.08; H, 4.20; N, 4.11 %, MS (MALDI-TOF) m/z: 2734 $[M+Na]^+$ (Fig. S1b). $^1$H NMR, THF-$d_8$, 298 K, δ ppm: 7.79, d, 2H, $H_f$, ($^3J_{Hf\text{-}He}$ = 7.55 Hz); 7.66-7.55, q, 14H, $H_2$; 7.40-7.08, q, 70H, ($H_1$, $H_3$, $H_4$, $H_5$, $H_6$); 7.35-7.27, q, 6H, ($H_c$, $H_d$, $H_e$); 7.00-6.85, q, 14H, $H_7$; 6.67, d, 4H, $H_b$, ($^3J_{Hb\text{-}Ha}$ = 8.86 Hz); 6.60, d, 4H, $H_a$, ($^3J_{Ha\text{-}Hb}$ = 8.86 Hz).

***2.2.6.*** *Reaction of 1,1,3,3,5,5,7-hepta(1-oxypyrene)-7-chlorocyclotetraphosphazene (**14**) with 4,4′-(9-fluorenylidene)diphenol (FDP) (**5**) in a 1:2 ratio to form compounds **18**-**19**.*

1,1,3,3,5,5,7-Hepta(1-oxypyrene)-7-chlorocyclotetraphosphazene (**14**) (0.05 g, 0.03 mmol) and 4,4′-(9-fluorenylidene)diphenol (FDP) (**5**) (0.005 g, 0.015 mmol) were dissolved in 100 mL of dry THF under an argon atmosphere in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.002 g, 0.04 mmol) in 40 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The reaction mixture was refluxed for 5 days and the reaction followed on TLC silica gel plates using *n*-hexane–$CH_2Cl_2$ (2:3) as the eluent. Two products were observed on TLC. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The resulting colorless solid was subjected to column chromatography, using *n*-hexane–$CH_2Cl_2$ (2:3) as the eluent. The first product was compound **18**, the 1-oxypyrene substituted FDP-bridged cyclotetraphosphazene derivative, (0.01 g, 2.66 x $10^{-3}$ mmol, 9%, oily), Rf = 0.76. *Anal.* Calc. for $C_{249}H_{142}N_8O_{16}P_8$: C, 79.76; H, 3.82; N, 2.99; M, 3746. Found: C, 79.74; H, 3.80; N, 2.96; %, MS (MALDI-TOF) m/z: 3746 $[M]^+$ (Fig. S1c). $^1$H NMR, $CDCl_3$, 298 K, δ ppm: 8.10-6.40, m, 142H, ($H_1$-$H_9$, $H_a$-$H_f$). The second product was compound **19**, the 1-oxypyrene substituted open chain FDP cyclotetraphosphazene derivative, (0.03 g, 1.45 x $10^{-2}$ mmol, 51%, oily), Rf = 0.58. *Anal.* Calc. for $C_{137}H_{80}N_4O_9P_4$: C, 80.27; H, 3.93; N, 2.73; M, 2048. Found: C, 80.25; H, 3.91; N, 2.71; %, MS (MALDI-TOF) m/z: 2049 $[M]^+$. $^1$H NMR, $CDCl_3$, 298 K, δ ppm: 8.15-6.45, m, 80H, ($H_1$-$H_9$, $H_a$-$H_f$).

***2.2.7.*** *Reaction of 1,1,3,3,5,5,7-heptaphenol-7-chlorocyclotetraphosphazene (**8**) with 4,4′-(9-fluorenylidene)dianiline (FDA) (**6**) in a 1:2 ratio to form compounds **20** and **21**.*

1,1,3,3,5,5,7-Heptaphenoxy-7-chlorocyclotetraphosphazene (**8**), (0.7 g, 0.81 mmol) and 4,4′-(9-fluorenylidene)dianiline (FDA) (**6**) (0.14 g, 0.41 mmol) were dissolved in 100 mL of dry THF under an argon atmosphere in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.03 g, 0.81 mmol) in 40 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The reaction mixture was refluxed for 2 days and the reaction followed on TLC silica gel plates using *n*-hexane-$CH_2Cl_2$ (1:3) as the eluent. Two products were observed on TLC. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The resulting colorless solid was subjected to column chromatography, using *n*-hexane-$CH_2Cl_2$ (1:3) as the eluent. The first product was compound **20**, the phenol substituted FDA-bridged cyclotetraphosphazene derivative, (0.42 g, 0.20 mmol, 51%, oily), Rf = 0.66. *Anal.* Calc. for $C_{109}H_{88}N_{10}O_{14}P_8$: C, 65.14; H, 4.41; N, 6.97; M, 2010. Found: C, 65.13; H, 4.40; N, 6.93 %, MS (MALDI-TOF) m/z: 2011 $[M+H]^+$. $^1$H NMR, $CDCl_3$, 298 K, δ ppm: 7.72, d, 2H, $H_f$, ($^3J_{Hf-He}$ = 7.51 Hz); 7.30, td, 2H, $H_e$, ($^3J_{He-Hf}$ = 7.51 Hz, $^3J_{He-Hd}$ = 7.35 Hz); 7.26, d, 2H, $H_c$, ($^3J_{Hc-Hd}$ = 7.45 Hz); 7.20, td, 2H, $H_d$, ($^3J_{Hd-He}$ = 7.35, $^3J_{Hd-Hc}$ = 7.45 Hz); 6.87-7.10, q, 56H, ($H_1$, $H_2$); 6.78, td, 14H, $H_3$; 6.45, d, 4H, $H_b$, ($^3J_{Hb-Ha}$ = 8.35 Hz); 6.45, d, 4H, $H_a$, ($^3J_{Ha-Hb}$ = 8.35 Hz); 4.27, d, 2H, NH, ($^3J_{PH-NH}$ = 9.72 Hz). The second product was compound **21**, the phenol substituted open chain FDA cyclotetraphosphazene derivative (0.16 g, 0.13 mmol, 34%, oily), Rf = 0.25. *Anal.* Calc. for $C_{67}H_{54}N_6O_7P_4$: C, 68.25; H, 4.62; N, 7.13; M, 1179. Found: C, 68.23; H, 4.60; N, 7.11 %, MS (MALDI-TOF) m/z: 1179 $[M]^+$. $^1$H NMR, THF-$d_8$, 298 K, δ ppm: 7.67, d, 2H, $H_f$, ($^3J_{Hf-He}$ = 7.31 Hz); 7.28-7.24, q, 4H, ($H_e$, $H_c$); 7.17, td, 2H, $H_d$, ($^3J_{Hd-Hc}$ = 7.34 Hz, $^3J_{Hd-He}$ = 7.42 Hz); 7.01-6.75, q, 35H, ($H_1$, $H_2$, $H_3$); 6.87 d, 2H, $H_{b'}$ ($^3J_{Hb'-Ha'}$ = 8.02 Hz); 6.72, d, 2H, $H_{a'}$ ($^3J_{Ha'-Hb'}$ = 8.02 Hz); 6.59, d, 2H, $H_b$, ($^3J_{Hb-Ha}$ = 8.35 Hz); 6.43, d, 2H, $H_a$, ($^3J_{Ha-Hb}$ = 8.35 Hz); 4.27, d, H, NH, ($^3J_{PH-NH}$ = 10.08 Hz); 3.72, s, 2H, NH.

***2.2.8.*** *Reaction of 1,1,3,3,5,5,7-hepta(2-naphthloxy)-7-chlorocyclotetraphosphazene (**11**) with 4,4′-(9-fluorenylidene)dianiline (FDA) (**6**) in a 1:2 ratio to form compounds **22** and **23**.*

1,1,3,3,5,5,7-Hepta(2-naphthloxy)-7-chlorocyclotetraphosphazene (**11**), (1.5 g, 1.23 mmol) and 4,4′-(9-fluorenylidene)dianiline (FDA) (**6**) (0.21 g, 0.63 mmol) were dissolved in 100 mL of dry THF under an argon atmosphere in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.05 g, 1.23 mmol) in 40 mL of dry THF was quickly added to the stirred solution under an argon atmosphere. The reaction mixture was refluxed for 2 days and the reaction followed on TLC silica gel plates using *n*-hexane-$CH_2Cl_2$ (1:1) as the eluent. Two products were observed on TLC. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The resulting colorless solid was subjected to column chromatography, using *n*-hexane-$CH_2Cl_2$ (1:1) as the eluent. The first product was compound **22**, the 2-napthole substituted FDA-bridged cyclotetraphosphazene derivative, (0.91 g, 0.33 mmol, 54%, oily), Rf = 0.63. *Anal.* Calc. for $C_{165}H_{116}N_{10}O_{14}P_8$: C, 73.10; H, 4.32; N, 5.22; M, 2710. Found: C, 73.08; H, 4.30; N, 5.20 %, MS (MALDI-TOF) m/z: 2774 $[M+2H+Na+K]^+$. $^1$H NMR, $CDCl_3$, 298 K, δ ppm: 7.82, d, 2H, $H_f$, ($^3J_{Hf\text{-}He}$ = 7.58 Hz); 7.68-7.54, q, 14H, $H_2$; 7.40-7.13, q, 76H, ($H_1$, $H_3$, $H_4$, $H_5$, $H_6$, $H_c$, $H_d$, $H_e$); 7.13-6.86, q, 14H, $H_7$; 6.59, d, 4H, $H_b$, ($^3J_{Hb\text{-}Ha}$ = 8.54 Hz); 6.38, d, 4H, $H_a$, ($^3J_{Ha\text{-}Hb}$ = 8.54 Hz); 4.47, d, 2H, NH, ($^3J_{PH\text{-}NH}$ = 9.71 Hz) (Fig. S3). The second product was compound **23**, the 2-napthole substituted open chain FDA cyclotetraphosphazene derivative, (0.28 g, 0.18 mmol, 29%, oily), Rf = 0.30. *Anal.* Calc. for $C_{95}H_{68}N_6O_7P_4$: C, 74.60; H, 4.48; N, 5.49; M, 1529. Found: C, 74.58; H, 4.46; N, 5.47 %, MS (MALDI-TOF) m/z: 1745 $[M+K+Na+Matrix(dihydroxybenzoic\ acid)]^+$. $^1$H NMR, $CDCl_3$, 298 K, δ ppm: 7.67, d, 2H, $H_f$, ($^3J_{Hf\text{-}He}$ = 7.56 Hz); 7.59-7.51, q, 7H, $H_2$; 7.35-7.08, q, 41H, ($H_1$, $H_3$, $H_4$, $H_5$, $H_6$, $H_c$, $H_d$, $H_e$); 7.01-6.76, q, 7H, $H_7$; 6.81 d, 2H, $H_{b'}$ ($^3J_{Hb'\text{-}Ha'}$ = 8.54 Hz); 6.66, d,

2H, $H_{a'}$, ($^3J_{Ha'-Hb'}$ = 8.54 Hz); 6.41, d, 2H, $H_b$, ($^3J_{Hb-Ha}$ = 8.51 Hz); 6.29, d, 2H, $H_a$, ($^3J_{Ha-Hb}$ = 8.51 Hz); 4.38, d, H, NH, ($^3J_{PH-NH}$ = 9.79 Hz); 3.85, s, 2H, NH.

## 3. RESULTS AND DISCUSSION

In this study, new fully substituted fluorenylidene bridged (**15**, **17**, **18**, **20** and **22**) and open chain (**16**, **19**, **21** and **23**) cyclotetraphosphazene compounds have been synthesized and their florescence and chemosensors properties are reported. For this purpose, octachlorocyclotetraphosphazene (**1**) was allowed to react with phenol (**2**), 2-naphthol (**3**) and 1-hydroxypyrene (**4**) to give hexa- (**7**, **10** and **13**), hepta- (**8**, **11** and **14**) and octasubstituted cyclotetraphosphazene compounds (**9** and **12**). The heptasubstituted cyclotetraphosphazene compounds (**8**, **11**, and **14**) were then reacted with FDP (**5**) and FDA (**6**) to give the fully substituted (**15**, **17**, **18**, **20** and **22**) and open chain (**16**, **19**, **21** and **23**) fluorenylidene bridged cyclotetraphosphazene derivatives (Scheme 1). All the products were purified by column chromatography and/or preparative TLC techniques. The structures of the compounds (**7**-**23**) were verified by elemental analyses, mass spectrometry, UV Vis, $^1H$ and $^{31}P$ NMR techniques and fluorescence spectroscopy. The elemental analyses, mass spectrometric and $^1H$ NMR results for each new compound are provided as part of the analytical data in the experimental section. The $^{31}P$ NMR chemical shifts and phosphorus-phosphorus coupling constants of the isolated compounds (**7**-**23**) are summarized in Table 1. Compounds **8**, **11** and **14** were reacted with FDP (**5**) and FDA (**6**) in the presence of NaH in THF, and bridged (**15**, **17**, **18**, **20** and **22**) and open chain compounds (**16**, **19**, **21** and **23**) were isolated. The mass spectrometry and elemental analyses of compounds **15**, **17**, **18**, **20** and **22** indicated that one chlorine atom in the heptasubstituted cyclotetraphosphazene compounds (**8**, **11** and **14**) was replaced with FDP (**5**)/FDA (**6**). The mass spectra of compounds **15**, **17** and **18** gave molecular ion peaks at m/z 2011.3$[M]^+$, 2734.7$[M+Na]^+$ and 3746.2$[M]^+$ respectively, confirming the exact composition,

and no chlorine patterns for compounds **15**, **17** and **18** were observed (Figs. S1a, S1b and S1c, respectively) in the supplementary information.

### *3.1. NMR characterization of compounds 7-23.*

The proton decoupled $^{31}$P NMR spectra of compounds **7**, **10** and **13** were observed as $A_2B_2$ spin systems due to the different environments for the two different phosphorus nuclei on the cyclotetraphosphazene ring. The >P(OCl) group in cyclotetraphosphazene ring of **7**, **10** and **13** are stereogenic, and thus it is anticipated that the hexasubstituted cyclotetraphosphazene compounds should be chiral and exist in *cis* and *trans* forms (as isomer mixtures, see Fig.S2 as an example for compound **7**). The proton decoupled $^{31}$P NMR spectra of compounds **15-17** were observed as $AB_2B'$ spin systems due to the different environments for the three different phosphorus nuclei on the cyclotetraphosphazene ring. The proton decoupled $^{31}$P NMR spectra of compounds **8**, **11**, **14**, **18-23** were observed as $AB_2C$ spin systems due to the different environments for the three different phosphorus nuclei on the cyclotetraphosphazene ring. The proton decoupled $^{31}$P NMR spectra of compounds **9** and **12** were observed as a single resonance ($A_4$ type) at δ -12.46 and -11.96 ppm, respectively because of the chemical environment equivalence of all the phosphorus nuclei. The proton-decoupled $^{31}$P NMR spectra of the new fully substituted fluorenylidene bridged (**15**, **17**, **18**, **20** and **22**) and open chain (**16**, **19**, **21** and **23**) cyclotetraphosphazene compounds showed second order effects (Figure 1), so it was necessary to carry out simulation analysis to get the appropriate spectral parameters. For example, the simulated and normal $^{31}$P NMR spectra of 2-naphthol substituted FDA-bridged cyclotetraphosphazene (**22**) are shown Figures 1a and 1b. The $^{31}$P NMR spectra of **15**, **17**, **18** and **20** are shown as examples in Figures S3-S6, respectively in the supplementary information.

The $^{1}$H NMR data also confirmed the structures of the newly synthesized compounds **7**–**23**. The $^{1}$H NMR chemical shifts and coupling constants of all the protons are given in the experimental section. The aromatic protons for all the compounds were observed between δ 8.00-6.50 ppm and some of them were distinguishable from each other. The $^{1}$H NMR spectrum of compound **22** is shown as an example in Figure S7. In addition, the NH protons for compound **22** were observed at δ 4.48 ppm, which have a two bond-coupling to phosphorous with an average $^{2}J_{P\text{-}H}$ of *ca* 9.71.Hz.

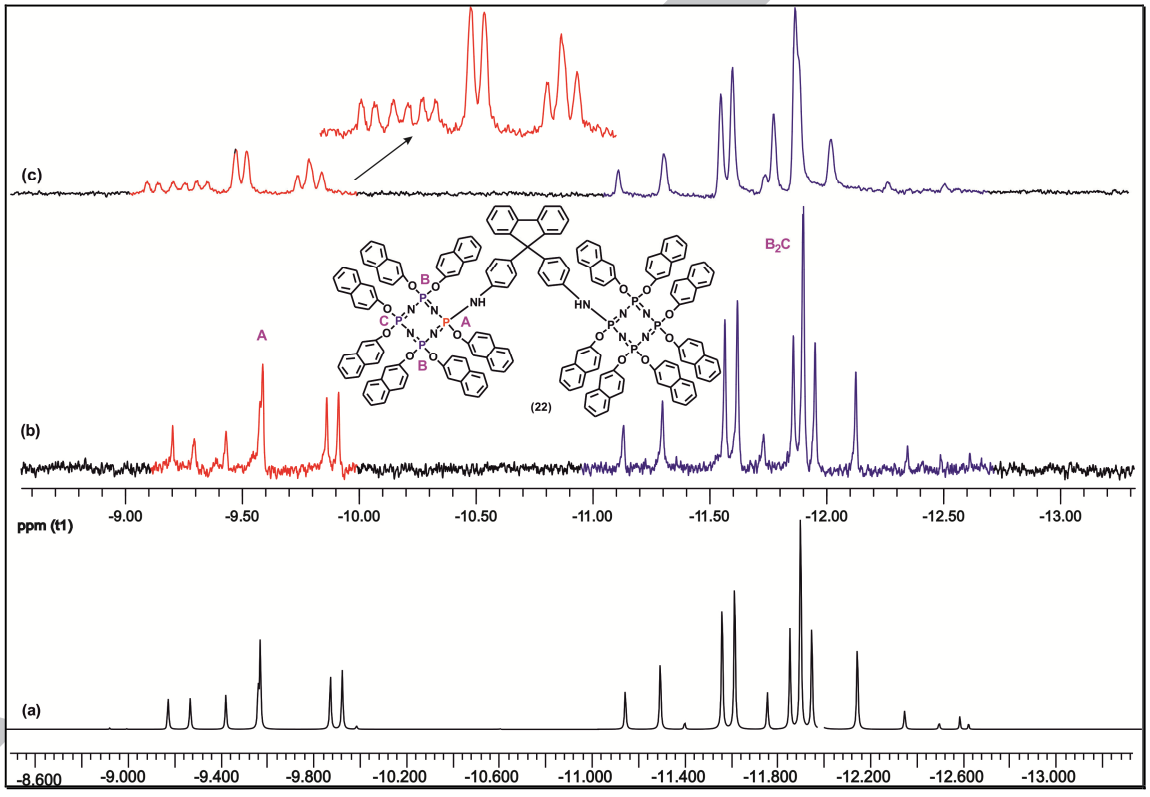



**Figure 1.** 2-Naphthol substituted FDA- bridged cyclotetraphosphazene (**22**) (a) The simulated $^{31}$P NMR spectrum of **22**; (b) the proton decoupled $^{31}$P NMR spectrum of compound **22**; (c) the proton coupled $^{31}$P NMR spectrum of compound **22** in $CDCl_3$ solution.

**Table 1.** $^{31}$P NMR parameters for compounds **7-23**.

| Comp. | δ ($^{31}$P NMR) [ppm] | | | | Spin System | $^{2}$J(PP) [Hz] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | B' | C | | $^{2}J_{AB}$ | $^{2}J_{AB'}$ | $^{2}J_{BB'}$ | $^{2}J_{BC}$ |
| ***(7)** [(a)] | -6.49, -6.58 | -14.80, -14.90 | - | - | $A_2B_2$ | 79.90, 80.10 | - | - | - |
| **(8)** [(a)] | -5.25 | -13.78 | - | -13.57 | $AB_2C$ | 78 | - | - | 75 |
| **(9)** [(a)] | -12.46 | - | - | - | $A_4$ | - | - | - | - |
| ***(10)** [(a)] | -6.04, -6.11 | -14.48, -14.51 | - | - | $A_2B_2$ | 80.56, 81.30 | - | - | - |
| **(11)** [(b)] | -4.74 | -13.21 | - | -13.06 | $AB_2C$ | 70 | - | - | 55 |
| **(12)** [(a)] | -11.96 | - | - | - | $A_4$ | - | - | - | - |
| ***(13)** [(a)] | -5.33, -5.42 | -13.31, -13.44 | - | - | $A_2B_2$ | 79.85, 79.54 | - | - | - |
| **(14)** [(a)] | -4.27 | -13.20 | - | -12.85 | $AB_2C$ | 70 | - | - | 58 |
| **(15)** [(a)] | -12.50 | -12.46 | -12.52 | - | $AB_2B'$ | 75 | 15 | 78 | - |
| **(16)** [(a)] | -12.41 | -12.39 | -12.40 | - | $AB_2B'$ | 75 | 15 | 77 | - |
| **(17)** [(b)] | -12.30 | -12.13 | -11.91 | - | $AB_2B'$ | 67 | - | 70 | - |
| **(18)** [(a)] | -14.95 | -13.34 | - | -13.14 | $AB_2C$ | 74 | - | - | 67 |
| **(19)** [(a)] | -14.97 | -13.41 | - | -13.14 | $AB_2C$ | 75 | - | - | 68 |
| **(20)** [(a)] | -10.03 | -12.33 | | -12.72 | $AB_2C$ | 80 | | | 78 |
| **(21)** [(b)] | -10.11 | -12.43 | | -12.78 | $AB_2C$ | 81 | | | 78 |
| **(22)** [(a)] | -9.54 | -12.18 | | -11.72 | $AB_2C$ | 71 | | | 69 |
| **(23)** [(a)] | -9.50 | -12.21 | | -11.70 | $AB_2C$ | 71 | | | 70 |

[(a)]202.38 MHz $^{31}$P NMR chemical shifts (ppm) in $CDCl_3$.
[(b)]202.38 MHz $^{31}$P NMR chemical shifts (ppm) in THF-$d_8$.
[(*)]*cis* and *trans* isomer mixture

### *3.2. Ground state electronic absorption and fluorescence properties*

The electronic absorption and fluorescence behavior of the newly synthesized fluorenylidene bridged cyclotetraphosphazene derivatives were studied in THF. Absorption bands were observed at approximately 240, 270, 300 and 310 nm for compounds **15-17** and **20-23**, and 240, 265, 275, 330 and 345 nm for compounds **18** and **19** in the UV region of the electronic spectra (see Figure 2a as an example for compound **18**). Compounds **15-17** and **20-23** were excited at 270 nm and compounds **18** and **19** were excited at 345 nm for the fluorescence emission studies. The fluorescence wavelengths were observed to be red shifted from those of phenol, naphthol and pyrene, respectively. The emission wavelength ranking

increases for these aryloxy substituted (FDP) bridged cyclotetraphosphazene derivatives as phenol substituted (**15**) < 2-naphthol substituted (**17**) < 1-hydroxypyrene substituted FDP bridged cyclotetraphosphazene (**18**), reflecting the increasing number of conjugated π-electrons in the aromatic ring systems of the substituted groups (Figure 2b). In addition to this, Figure S8 shows the fluorescence emission spectra of the FDP/FDA cyclotetraphosphazene compounds **15**-**23**. While the phenol (**15**, **16**, **20** and **21**) and 1-hydroxypyrene (**18** and **19**) substituted FDP/FDA bridged and open chain cyclotetraphosphazenes showed strong emissions, the 2-naphthol substituted FDP/FDA bridged and open chain cyclotetraphosphazene derivatives (**17**, **22** and **23**) showed low fluorescence behaviour in THF solution. Furthermore, while these measurements showed that the substituted bridged cyclotetraphosphazene compounds exhibited highly fluorescence behaviour in THF solutions, the substituted open chain cyclotetraphosphazene derivatives showed very weak fluorescence in this solvent. For this reason, only the phenol and 1-hydroxypyrene substituted FDP/FDA bridged open chain compounds were tested for metal ions sensing.

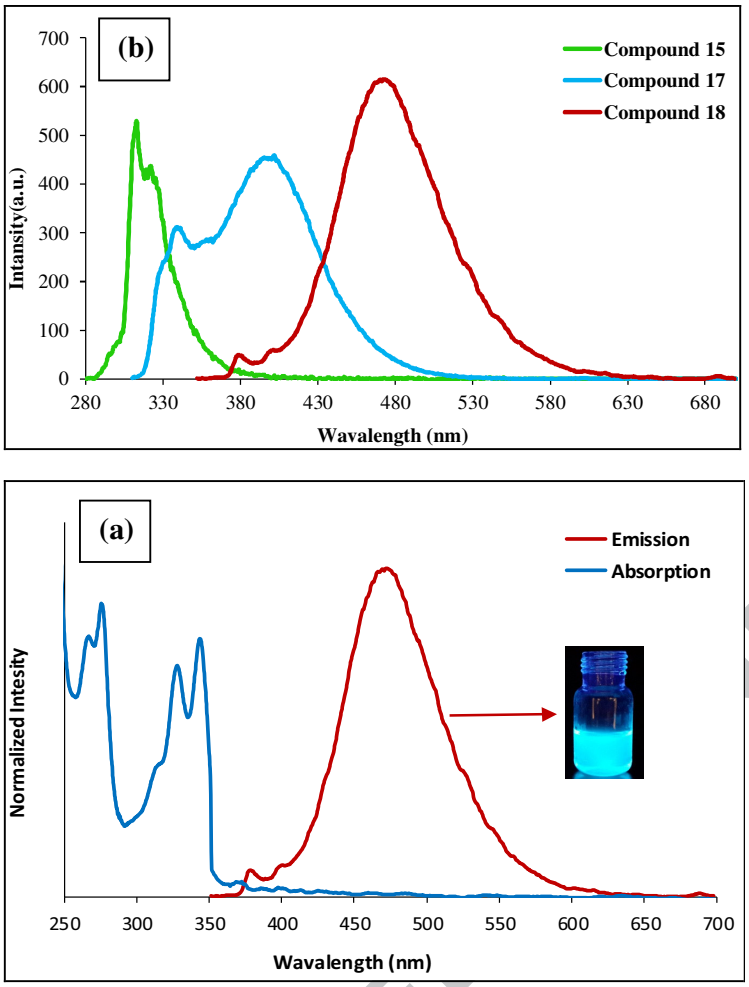



**Figure 2.** (a) Electronic absorption and fluorescence emission spectra of compound **18** in THF (excitation wavelength = 345 nm). (b) fluorescence emission spectra of compounds **15**, **17** and **18** in THF.

### *3.3. Chemosensor properties to metal ions*

The metal binding properties of fluorenylidene molecules may allow the use of these molecules as metal sensors. The effects of a variety of metal ions ($Li^{+}$, $Na^{+}$, $K^{+}$, $Cs^{+}$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Mn^{2+}$, $Fe^{3+}$ $Co^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Ag^{+}$, $Cd^{2+}$ and $Al^{3+}$) on the fluorescence properties of the newly synthesized compounds have been investigated using fluorescence spectroscopy. All fluorescence emission spectral studies were performed in THF solutions of the cyclotetraphosphazene compounds, while water solutions of the corresponding metal chlorides (the nitrate derivative for the Ag ion) were used as the source of metal ions at room

temperature. The fluorescence spectra of the novel cyclotetraphosphazene compounds exhibited little enhancement by the addition of the 5 µL of 5 x $10^{-3}$ M metal solutions, except for copper ($Cu^{2+}$) and iron ($Fe^{3+}$). A significant decrease in the fluorescence intensities were observed by the addition of the copper ($Cu^{2+}$) and iron ($Fe^{3+}$) cations, while no or minimal change was observed with the other metal ions (see Figure 3 as an example for compound **18**, Figs. S9, S12, S15 and S18 in the Supporting Information for the other compounds).

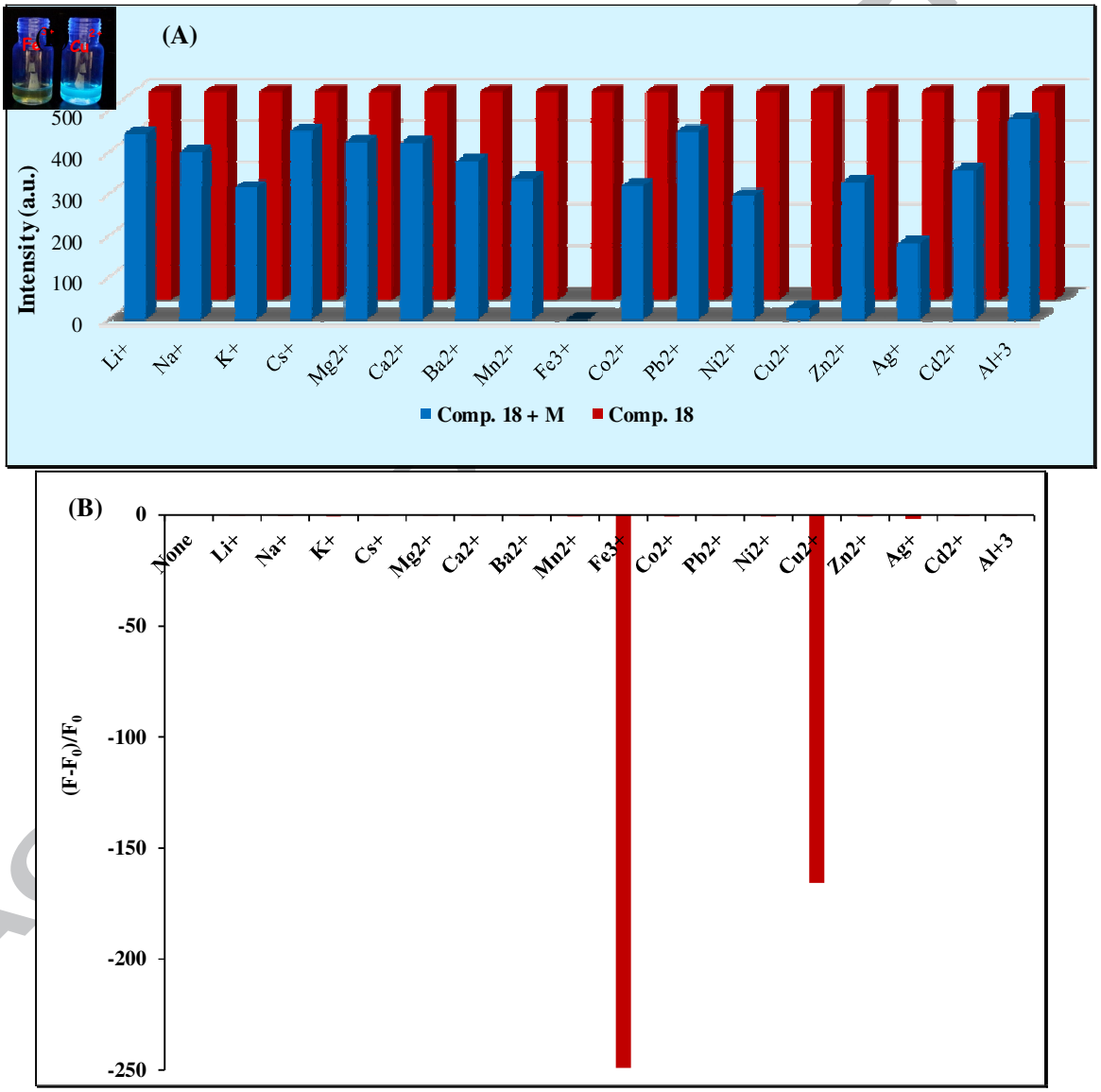



**Figure 3.** (A) The fluorescence intensities of compound **18** with and without metal ions. Addition of $Fe^{+3}$ or $Cu^{+2}$ ions to the solution prevent fluorescent emission, hence provide a selective detection (5 µL of 5 x $10^{-3}$ M). (B) Fluorescence intensity changes.

The titration of the probe compounds(**15**, **16**, **18**, **19** and **20** with $Cu^{2+}$ or $Fe^{3+}$ cations showed a decrease in the fluorescence intensities with increasing concentrations of these cations (see Figure 4A for the $Cu^{2+}$ titration and Figure 5A for the $Fe^{3+}$ titration, Figs. S10A, S11A, S13A, S14A, S16A, S17A, S19A and S20A in the Supporting Information for the other compounds). The graphs from a Benesi-Hildebrand analysis showed non-linear behavior for all the studied cyclotetraphosphazene chemosensor compound interactions with $Cu^{2+}$ ions, indicating that the stoichiometry of the complexes between cyclotetraphosphazene chemosensors and $Cu^{2+}$ or $Fe^{3+}$ cations are different from 1:1 (see Figure 4B for the $Cu^{2+}$ titration and Figure 5B for the $Fe^{3+}$ titration as an example for compound **18**, Figs. S10B, S11B, S13B, S14B, S16B, S17B, S19B and S20B in the Supporting Information for the other compounds), as mentioned by Garcia-Beltran et al. [54]. The continuous variation method was also used for the determination of the stoichiometry between the aryloxy substituted fluorenylidene bridged cyclotetraphosphazene chemosensors and detected metal cations. The resulting Job plot, showing a maximum mole fraction for the $Cu^{2+}$ or $Fe^{3+}$ cations of 0.33 (see Figure 4C for the $Cu^{2+}$ titration and Figure 5C for the $Fe^{3+}$ titration as an example for compound **18**, Figs. S10C, S11C, S13C, S14C, S16C, S17C, S19C and S20C in the Supporting Information for the other compounds), indicated that the cyclotetaphosphazene molecules and $Cu^{2+}$ or $Fe^{3+}$ ions prefer a 2:1 stoichiometry for the formation of complexes between the chemosensor compounds **15**, **16**, **18**, **19** and **20** and the $Fe^{3+}$ or $Cu^{2+}$ cations in THF solutions. The proposed complex structure between cyclotetraphosphazene compound **18** and $Fe^{3+}$/$Cu^{2+}$ cations is given in Figs. 6(a) and 6(b).

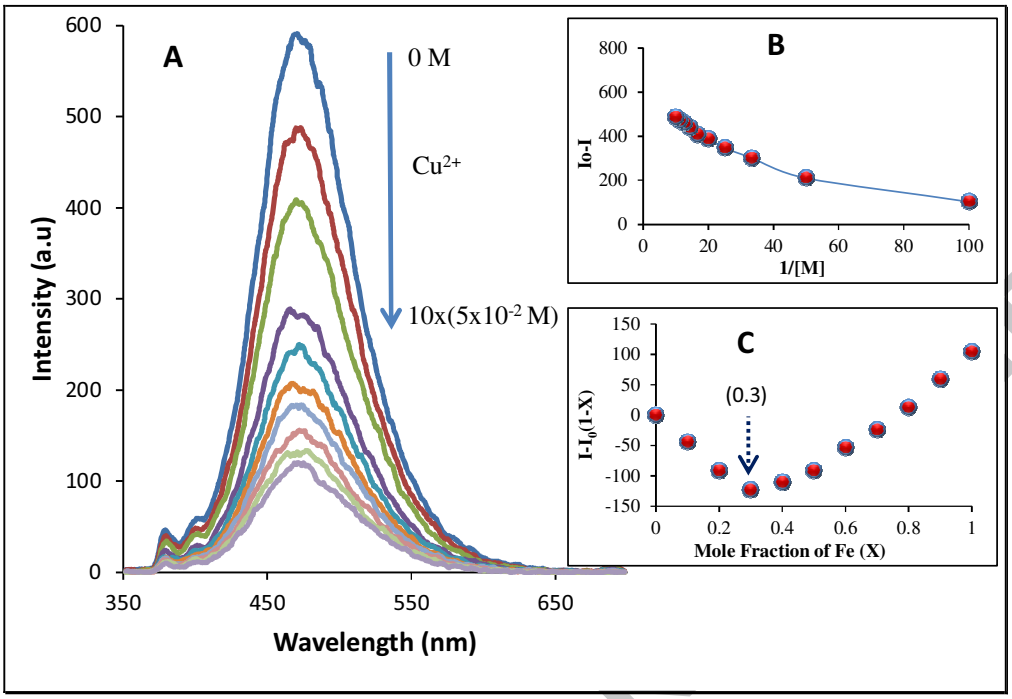



**Figure 4.** (A) Fluorescence response of chemosensor **18** to various equivalents of $Cu^{2+}$. (B) The Benesi-Hildebrand graph and (C) Job's plot of **18**-$Cu^{2+}$ complexes in THF solution. The total concentration of **18** and $Cu^{2+}$ was $5 \times 10^{-1}$ M. The excitation wavelength was 345 nm. The monitored wavelength was 470 nm.

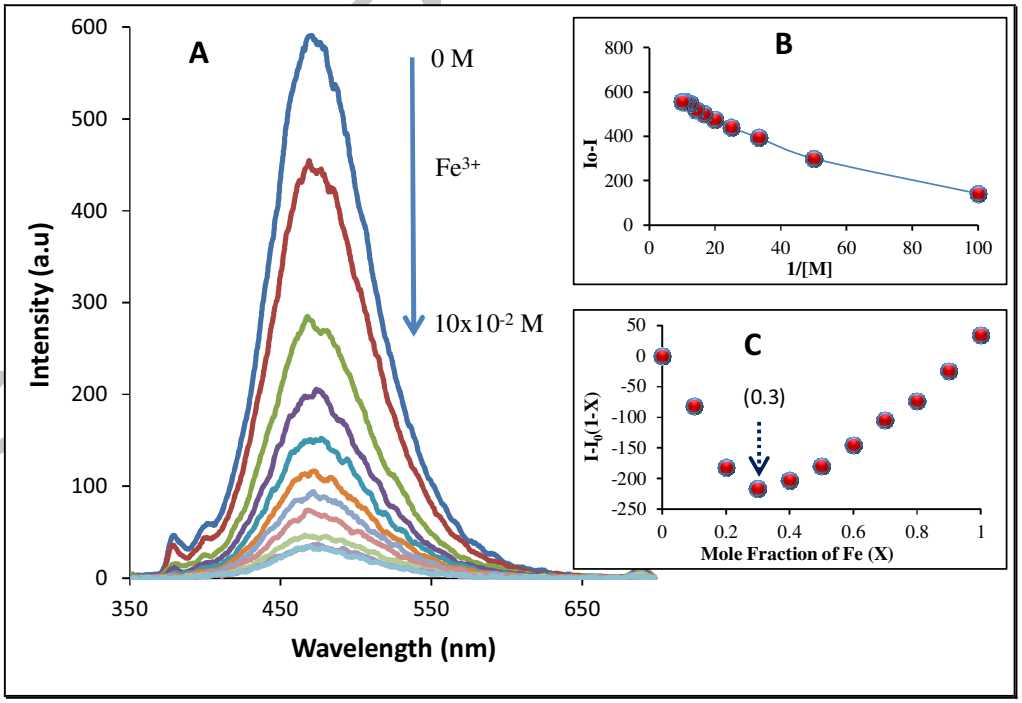



**Figure 5.** (A) Fluorescence response of chemosensor **18** to various equivalents of $Fe^{+3}$. (B) The Benesi-Hildebrand graph and (C) Job's plot of **18**-$Fe^{+3}$ complexes in THF solution. The

total concentration of **18** and $Fe^{+3}$ was 1 x $10^{-1}$ M. The excitation wavelength was 345 nm. The monitored wavelength was 470 nm.

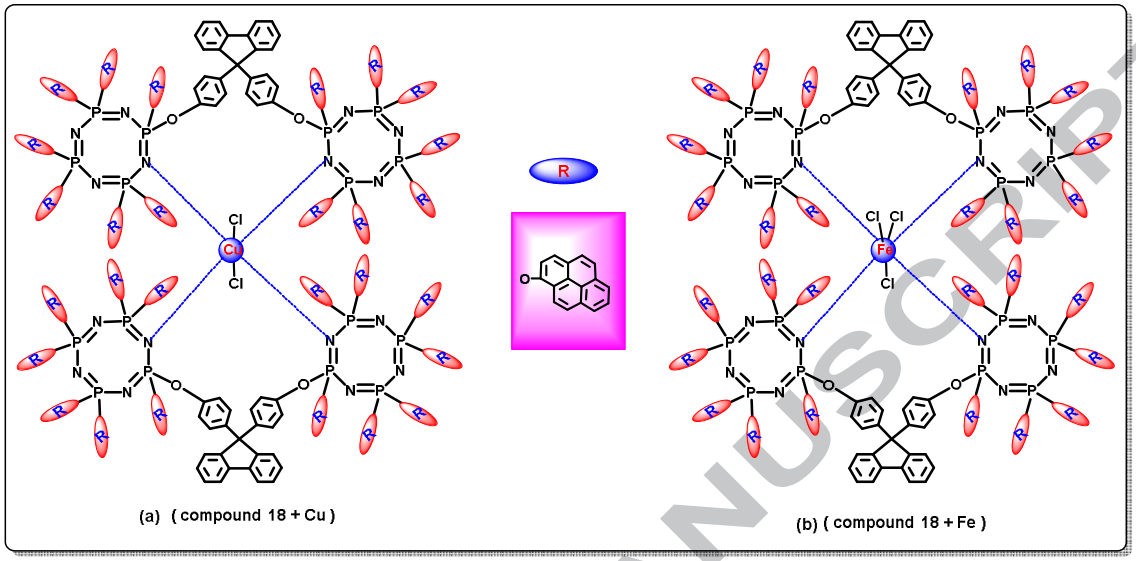



**Figure 6.** The proposed structures between (a) compound **18** and $Cu^{2+}$ and (b) $Fe^{3+}$ ions as a 2:1 complex in aqueous solution (a similar structure is proposed for the other compounds and $Cu^{2+}$/$Fe^{3+}$ ions).

## 4. CONCLUSIONS

In summary, phenol, 2-naphthol and 1-hydroxypyrene fully substituted fluorenylidene (FDA/FDP) bridged and open chain cyclotretraphosphazene derivatives were synthesized and characterized. All the synthesized compounds (**7-23**) were characterized by elemental analysis, mass spectrometry, UV Vis, $^{1}H$ and $^{31}P$ NMR and fluorescence spectroscopies. The fluorescence behavior of compounds **15**-**23** was investigated by florescence spectroscopy in THF solution. In addition, the effects of metal ions on the fluorescence behavior of the compounds were studied in order to determine the potential for using of these compounds as chemosensors for metal ions. A significant decrease in the fluorescence signals were observed by the addition of $Cu^{2+}$ and $Fe^{3+}$ cations, from the seventeen different metal ions tested. The newly synthesized FDP/FDA bridged and open chain phenol and 1-hydroxypyrene substituted

cyclotetraphosphazene derivatives (**15**, **16**, **18**, **19**, **20** and **21**) preferred the formation of 2:1 (ligand: metal) complexes with both $Fe^{3+}$ and $Cu^{2+}$ ions. The FDP/FDA bridged and open chain substituted cyclotetraphosphazene derivatives showed high selectivity towards $Cu^{2+}$ and $Fe^{3+}$ ions and these newly synthesized compounds showed potential for use as chemosensors for these metal ions in THF solution. The increase in the number of aromatic groups caused the increasing florescent nature. The fluorescence properties of fluorenylidene bridged cyclotriphosphazenes bearing phenol are quite low [55], but in this study the phenol substituted FDP and the FDA bridged cyclotriphosphazenes show quite good fluorescence behaviour and Fe and Cu sensor abilities. In addition to this, in the current study, the pyrene substituted fluorenylidene bridged and open chain cyclotetraphosphazene compounds (**18** and **19**) showed high fluorescence results, although they had lower concentrations. Thus, the FDP and FDA bridged and open chained cyclotetraphosphazene compounds show superior florescence behaviour relative to the corresponding cyclotriphosphazenes.

## ASSOCIATED CONTENT

**Supporting Information Available:** The $^{1}H$ NMR spectra of compound **22**, $^{31}P$ NMR spectra/J NMR spectra of compounds **7**, **15**, **17**, **18** and **20**, and the MS spectra for compounds **15**, **17** and **18**, the graphs of titrations of FDP/FDA-bridged compounds with $Cu^{2+}$ and $Fe^{3+}$ ions and the Benesi-Hildebrand graphs and Job's plots are given as Supporting Information. This material is available free of charge via the Internet at http://pubs.rsc.org.

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# Structural and chemosensor properties of FDA and FDP derivatives of fluorenylidene bridged cyclotetraphosphazenes

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The first series of 4,4'-(9-fluorenylidene)diphenol (FDP) (**5**) and 4,4'-(9-fluorenylidene)dianiline (FDA) (**6**) bridged and open chained cyclotetraphosphazene derivatives (**15-23**) were synthesized. Their florescence and chemosensors properties are reported. Nucleophilic substitution reactions of octachlorocylotetraphosphazene (**1**) with mono-functional reagents [phenol (**2**), 2-naphthol (**3**) and 1-hydroxypyrene (**4**)] were carried out and the heptasubstituted derivatives (**8**, **11** and **14**) were obtained. The reactions of **8**, **11** and **14** with 4,4′-(9-fluorenylidene)diphenol (**FDP**) (**5**) and 4,4′-(9-fluorenylidene)dianiline (**FDA**) (**6**) respectively gave bridged and open chained compounds. The structures of compounds (**7**-**23**) were verified by elemental analyses, mass spectrometry, UV Vis, $^{1}H$ and $^{31}P$ NMR techniques and fluorescence spectroscopy. The metal sensing properties of the novel bridged and open chain cyclotetraphosphazene derivatives were also examined by fluorescence spectroscopy. These complexes showed high selectivity for $Cu^{2+}$ and $Fe^{3+}$ ions in solution.

# Structural and chemosensor properties of FDA and FDP derivatives of a Fluorenylidene bridged cyclotetraphosphazenes