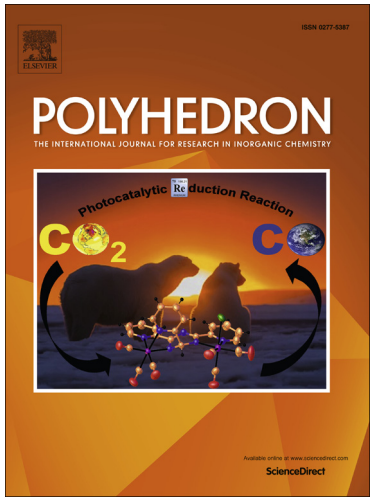

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PII: S0277-5387(15)00515-X
DOI: http://dx.doi.org/10.1016/j.poly.2015.09.013
Reference: POLY 11527

To appear in: *Polyhedron*

Received Date: 23 July 2015
Accepted Date: 6 September 2015

Please cite this article as: E. Şenkuytu, E.T. Eçik, M. Durmuş, G.Y. Çiftçi, Monofunctional amines substituted Fluorenylidene Bridged Cyclotriphosphazenes: 'Turn-Off' Fluorescence Chemosensors for Cu^{2+} and Fe^{3+} ions, *Polyhedron* (2015), doi: http://dx.doi.org/10.1016/j.poly.2015.09.013

Monofunctional amines substituted Fluorenylidene Bridged Cyclotriphosphazenes: 'Turn-Off' Fluorescence Chemosensors for Cu^{2+} and Fe^{3+} ions

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KEYWORDS: Cyclotriphosphazenes, Fluorenylidene, Fluorescence, Chemosensor, Fe^{3+} and Cu^{2+} ions.

ABSTRACT

In the present work, the reaction of 2,2,4,4-tetra(anilino)-6,6-dichlorocyclotriphosphazene (**4**) and 2,2,4,4-tetra(2-naphthylamino)-6,6-dichlorocyclotriphosphazene (**5**) with 4,4′-(9-fluorenylidene)diphenol, FDP, (**6**) and 4,4′-(9-fluorenylidene)dianiline FDA (**7**) were studied in THF and new aniline (**8** and **9**) and 2-naphthylamine (**10** and **11**) substituted FDP- bridged cyclotriphosphazenes and aniline (**12**) and 2-naphthylamine (**13**) substituted FDA- bridged cyclotriphosphazene derivatives were obtained. All newly synthesized monofunctional amines substituted fluorenylidene bridged cyclotriphosphazenes (**8-13**) were fully characterized by elemental analysis, ^{1}H and ^{31}P NMR spectroscopies, MALDI-TOF mass spectrometry and UV-Vis electronic absorption spectra. The florescence properties of the synthesized new compounds were studied. The chemosensory behavior of the compounds against to metal ions was also investigated. The obtained fluorenylidene bridged 2-naphthylamine substituted cyclotriphosphazenes (**10**, **11** and **13**) showed fluorescence chemosensor behavior with high selectivity for Fe^{3+} and Cu^{2+} ions in the solution.

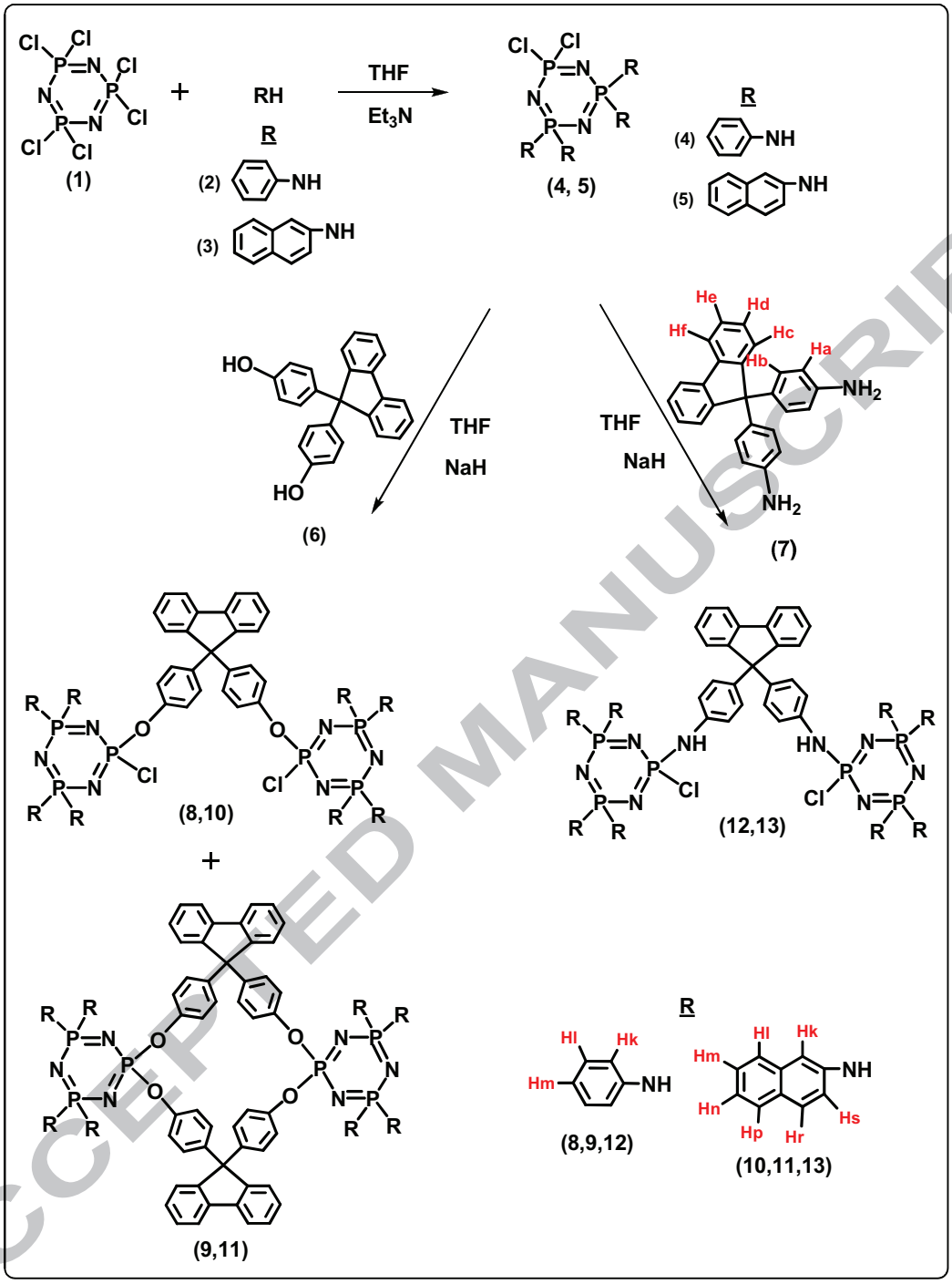
1. Introduction

Development of new fluorescent chemosensor is a challenging field in supramolecular chemistry and nowadays, many examples of fluorescent chemosensors or reagents are reported [1-3]. Ion sensing in cellular media is especially important for understanding of biochemical processes [4]. Among the essential transition metals in biological systems, the most abundant are Fe, Zn and Cu atoms [5, 6]. Especially, the fluorescent sensor for Cu^{2+} ion is used to clarify the physiological role of metal ion in tissues [7, 8]. The disturbed homeostasis of iron and zinc ions is suspected to play causative roles in many diseases such as hepatitis and cancer disease [9-12]. Also, the relative concentration of Fe^{2+}/Fe^{3+} is important for the biological sensing and imaging. Several scientists have focused on construction of selective and sensitive transition metal ion sensors for understanding essential recognition events in chemistry and biology [13].

Cyclotriphosphazene, six-membered ring, offers a rigid platform for multifunctional molecular arrangements and ring is resistant to the various reaction conditions. Over the past century nucleophilic substitution reactions of cyclotriphosphazene have been extensively investigated [14-16]. Generally, reactions of this ring with difunctional reagents may lead to different types of products such as open chain bridged, spiro, ansa, oligomer, polymer or their mixtures. The formation of these products depends on many factors such as the chain length of the difunctional reagents, used solvent, base, temperature and the nature of the reacting functional groups [17-20]. Thus cyclotriphosphazenes are a very interesting class of inorganic–organic hybrid compounds because it is possible to decorate cyclotriphosphazene core depending on the substituted side groups. They have wide applications such as organic light emitting diodes [21], biomedical materials such as anticancer and antimicrobial agents [22-26], liquid crystals [27, 28], and electrical conductivity [29]. Cyclotriphosphazenes have a potential application to detect metal ions in biological and environmental media as well but studies in this field are very limited. Only, on/off fluorescent rhodamine-based hexapodal Fe^{3+}

probe and fluorenylidene bridged cyclotriphosphazenes fluorescence probe for Cu^{2+} and Fe^{3+} are reported so far [30, 31]. The results of this study have encouraged us to developing new chemosensor containing cyclotriphosphazene core.

In the present study, firstly the reactions of $N_3P_3Cl_6$ (**1**) with aniline (**2**) and 2-naphthylamine (**3**) were studied and 2,2',4,4'-tetrakis(anilino)-6,6'-dichlorocyclotriphosphazene (**4**) and 2,2',4,4'-tetrakis(2-naphthylamino)-6,6'-dichlorocyclotriphosphazene (**5**) were obtained. Then the reactions of these compounds (**4**) and (**5**) with 4,4′-(9-fluorenylidene)diphenol, (FDP), (**6**) in THF gave target FDP-bridged cyclotriphosphazene compounds (**8-11**). The same approach was used for the synthesis of FDA-bridged cyclotriphosphazene compounds (**12** and **13**) by the reaction of compounds **4** and **5** with 4,4′-(9-fluorenylidene)dianiline, (FDA), (**7**). The new substituted mono (**8, 10, 12** and **13**) and double (**9** and **11**) fluorenylidene bridged cyclotriphosphazene derivatives were fully characterized by means of elemental analysis, UV-Vis, ^{1}H, and ^{31}P NMR spectroscopies and MALDI-TOF mass spectrometry. We also investigated fluorescence behavior of these compounds by UV-Vis electronic, florescence spectroscopy. The chemosensor properties of the newly synthesized cyclotriphosphazene compounds against to metal ions (Fe^{3+} and Cu^{2+}) were determine in solution.



Scheme 1. The synthesis route of aniline and 2-naphthylamine substituted FDA and FDP bridged cyclotriphosphazenes.

2. Experimental Section

2.1. Materials and Methods. Hexachlorocyclotriphosphazene (Otsuka Chemical Co., Ltd) was purified by fractional crystallization from *n*-hexane. Aniline (99%), 2-naphthylamine (99%), 4,4′-(9-fluorenylidene)diphenol (99%) and (4,4′-(9-fluorenylidene)dianiline (99%) were obtained from Aldrich. Tetrahydrofuran (≥99.0%), dichloromethane (≥99.0%), *n*-hexane (≥95.0%) and triethylamine (99.0%) 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 THF-d_6 for NMR spectroscopy is obtained from Goss Scientific. 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 of 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. Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument. Positive ion and linear mode MALDI-MS of compounds were obtained in dihydroxybenzoic acid as MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex LT MALDI-TOF mass spectrometer. ^{1}H and ^{31}P NMR spectra were recorded in $CDCl_3$ and THF-d_6 solutions on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^{1}H NMR and 85% H_3PO_4 as an external reference for ^{31}P NMR. Electronic 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. Synthesis

Aniline (**4**), and 2-naphthylamine (**5**) substituted cyclotriphosphazene compounds were prepared and purified according to the literature procedures [32, 33].

2.2.1. Reaction of 2,2,4,4-tetra(anilino)-6,6-dichlorocyclotriphosphazene (4) with 4,4′-(9-fluorenylidene)diphenol (FDP) (6) in a 1:2 ratio to form compounds 8 and 9.

2,2,4,4-tetra(anilino)-6,6-dichlorocyclotriphosphazene (**4**), (2.00 g, 3.48 mmol) and 4,4′-(9-fluorenylidene)diphenol(FDP) (**6**) (0.611 g, 1.74 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, 3.06 g, 76.58 mmol) in 40 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction mixture was refluxed for 6 days and the reaction followed on TLC silica gel plates using *n*-hexane:THF (2:1) as the eluent. Two products were observed on TLC plate. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The resulting colorless oily crude product was subjected to column chromatography, using *n*-hexane:THF (2:1) as the eluent. The aniline substituted FDP-mono bridged cyclotriphosphazene derivative (**8**) was obtained as first product from the column, (0.60 g, 0.42 mmol, % 24, m.p. 120 ^{o}C), Rf=0.41. *Anal.*Calc. For $C_{73}H_{64}Cl_2N_{14}O_2P_6$: C, 61.39; H, 4.66; N, 13.73, M, 1426.13. Found: C, 61.44; H, 4.50; N, 13.73 %, MS (MALDI-TOF) m/z: 1449.82 $[M+Na]^+$. ^{1}H NMR, $CDCl_3$, 298^{o}K: δ ppm, 7.74, d, 2H, (Hf); 7.42, td, 2H, (He); 7.25-7.14, m, 4H, (Hc, Hd); 7.04-6.95, m, 32H, (Hk, Hl); 6.96-6.83, m, 8H, (Hb, Ha); 6.85-6.77, m, 8H, (Hm); 5.45, t, 4H, NH ; 4.85, t, 4H, NH. The aniline substituted FDP-double bridged cyclotriphosphazene derivative (**9**) was obtained as second product from the column, (0.12 g, 0.05 mmol, % 4, m.p. 95 ^{o}C), Rf=0.30. *Anal.*Calc. For $C_{98}H_{80}N_{14}O_4P_6$: C,

69.09; H, 4.73; N, 11.51, M, 1703.62. Found: C, 69.07; H, 4.70; N, 11.49 %, MS (MALDI-TOF) m/z: 1704.45 [M+H]. ^{1}H NMR, $CDCl_3$, 298^{o}K: δ ppm, 7.72, d, 4H, (Hf); 7.30, td, 4H, (He); 7.15-7.02, m, 8H, (Hc, Hd); 6.94-6.86, m, 32H, (Hk, Hl); 6.84-6.73, m, 16H, (Hb, Ha); 6.71-6.66, m, 8H, (Hm); 5.75, t, 4H, NH ; 4.75, t, 4H, NH.

2.2.2. Reaction of 2,2,4,4-tetra(2-naphthylamino)-6,6-dichlorocyclotriphosphazene (5) with 4,4'-(9-fluorenylidene)diphenol (FDP) (6) in a 1:2 ratio to form compounds 10 and 11.

2,2,4,4-tetra(2-naphthylamino)-6,6-dichlorocyclotriphosphazene (**5**), (1.00 g, 1.29 mmol) and 4,4′-(9-fluorenylidene)diphenol (FDP) (**6**) (0.226 g, 0.65 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, 1.29 mmol ol) in 40 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction mixture was refluxed for 6 days and the reaction followed on TLC silica gel plates using *n*-hexane:THF (5:4) as the eluent. Two products were observed on TLC plate. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The resulting colorless oily crude product was subjected to column chromatography, using *n*-hexane:THF (5:4) as the eluent. The 2-napthilamine substituted FDP-mono bridged cyclotriphosphazene derivative (**10**) was obtained as first product from the column, (0.41 g, 0.21 mmol, % 18, m.p. 125 ^{o}C), Rf=0.41. *Anal.*Calc. For $C_{105}H_{80}Cl_2N_{14}O_2P_6$: C, 69.04; H, 4.41; N, 10.73, M, 1826.60. Found: C, 69.02; H, 4.39; N, 10.71 %, MS (MALDI-TOF) m/z: 1827.23 $[M+H]^{+}$. ^{1}H NMR, $CDCl_3$, 298^{o}K: δ ppm, 7.80, d, 2H, (Hf); 7.72-7.64, d, 8H, (Hl); 7.60-7.10, m, 6H, (He, Hc, Hd); 7.50-7.20, m, 40H, (Hm, Hk, Hn, Hr, Hp); 7.00-6.85, m, 8H, (Hs); 6.70, m, 4H, (Hb); 6.62, m, 4H, (Ha); 5.75-5.65, m, 8H, NH. The 2-napthilamino substituted FDP-double bridged cyclotriphosphazene derivative

(**11**) was obtained as second product from the column, (0.12 g, 0.05 mmol, % 4, m.p. >250 ^{o}C), Rf=0.33. *Anal.*Calc. For $C_{130}H_{96}N_{14}O_4P_6$: C, 74.21; H, 4.60; N, 9.32, M, 2104.09. Found: C, 74.20; H, 4.58; N, 9.30 %, MS (MALDI-TOF) m/z: 2104.33 $[M]^+$. ^{1}H NMR, THF-d_6, 298^{o}K: δ ppm, 7.75, d, 4H, (Hf); 7.67-7.61, d, 8H, (Hl); 7.53-7.18, m, 12H, (He, Hc, Hd); 7.54-7.17, m, 40H, (Hm, Hk, Hn, Hr, Hp); 7.08-6.99, m, 8H, (Hs); 7.02, d, 8H, (Hb); 6.80, d, 8H, (Ha); 5.70-5.40, m, 8H, NH.

2.2.3. Reaction of 2,2,4,4-tetra(anilino)-6,6-dichlorocyclotriphosphazene (4) with 4,4'-(9-fluorenylidene) dianiline (FDA) (7) in a 1:2 ratio to form compound 12.

2,2,4,4-tetra(anilino)-6,6-dichlorocyclotriphosphazene (**4**), (1.00 g, 1.74 mmol) and 4,4′-(9-fluorenylidene)dianiline (FDA) (**7**) (0.31 g, 0.87 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, 0.06 g, 1.74 mmol) in 40 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction mixture was stirred for 4 days at room temperature and the reaction followed on TLC silica gel plates using *n*-hexane–THF (2:1) as the eluent. Only one product was observed on TLC plate. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The resulting colorless oily crude product was subjected to column chromatography, using *n*-hexane-THF (2:1) as the eluent. The aniline substituted FDA-bridged cyclotriphosphazene derivative (**15**) was obtained, (0.15 g, 0.08 mmol, %5, m.p. 195 ^{o}C), Rf=0.64. *Anal.*Calc. For $C_{73}H_{66}Cl_2N_{16}P_6$: C, 61.56; H, 4.67; N, 15.74, M, 1424.16. Found: C, 61.54; H, 4.65; N, 15.72 %, MS (MALDI-TOF) m/z: 1425.28 [M+H].^{1}H NMR, $CDCl_3$, 298^{o}K: δ ppm, 7.74, d, 4H, (Hf); 7.42, td, 2H, (He); 7.25-7.14, m,

4H, (Hc, Hd); 7.12-6.95, m, 32H, (Hk, Hl); 6.96-6.83, m, 8H, (Hb, Ha); 6.85-6.77, m, 8H, (Hm); 5.45, t, 4H, NH; 4.85, t, 4H, NH.

2.2.4. Reaction of 2,2,4,4-tetra(2-naphthylamino)-6,6-dichlorocyclotriphosphazene (5) with 4,4'-(9-fluorenylidene)dianiline (FDA) (7) in a 1:2 ratio to form compound 13.

2,2,4,4-tetra(2-naphthylamino)-6,6-dichlorocyclotriphosphazene (**5**), (0.60 g, 0.77 mmol) and 4,4′-(9-fluorenylidene)dianiline (FDA) (**7**) (0.13 g, 0.38 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, 0.77 mmol) in 40 mL of dry THF was quickly added to a 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–THF (8:5) as the eluent. Only one product was observed on TLC plate. The reaction mixture was filtered to remove the formed sodium chloride and the solvent was removed under reduced pressure. The resulting colorless oily crude product was subjected to column chromatography, using *n*-hexane–THF (8:5) as the eluent. The 2-napthilamine substituted FDA-bridged cyclotriphosphazene derivative (**13**) was obtained, (0.11 g, 0.05 mmol, % 40, m.p. 146 ^{o}C), Rf=0.48. *Anal.*Calc. For $C_{105}H_{82}Cl_2N_{16}P_6$: C, 69.12; H, 4.53; N, 4.12.28, M, 1824.47. Found: C, 69.10; H, 4.51; N, 12.26 %, MS (MALDI-TOF) m/z: 1825.33 $[M+H]^+$. ^{1}H NMR, $CDCl_3$, 298^{o}K: δ ppm, 7.65, d, 2H, (Hf); 7.55-7.45, d, 8H, (Hl); 7.50-7.15, m, 10H, (He, Hc, Hd, Hb); 7.55-7.26, m, 40H, (Hm, Hk, Hn, Hr, Hp); 7.15-7.00, m, 8H, (Hs); 6.91, d, 4H, (Ha); 5.85-5.60, m, 10H, NH.

3. Results and Discussion

3.1. Synthesis and characterization

In this study, the reaction of 2,2',4,4'-tetrakis(aniline)-6,6'-dichlorocyclotriphosphazene (**4**) and 2,2',4,4'-tetrakis(2-naphthylamino)-6,6'-dichlorocyclotriphosphazene (**5**) with di-functional alcohol such as 4,4′-(9-fluorenylidene)diphenol, (**FDP**), (**6**) and di-functional amine such as 4,4′-(9-fluorenylidene)dianiline (**FDA**), (**7**) groups were investigated. The monofunctional amines substituted fluorenylidene bridged cyclotriphosphazenes (**8-13**) were synthesized (Scheme 1) and fully characterized by means of elemental analysis, MALDI-TOF mass spectrometry, ^{1}H and ^{31}P NMR spectroscopies. The mass, elemental analysis and ^{1}H-NMR data for each new isolated 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 newly synthesized compounds (**8-13**) are summarized in Table 1. The mass spectra of compounds (**8**-**13**) were obtained by MALDI-TOF-MS. Mass spectra results of all compounds clearly show the major molecular ion peaks, which confirmed the exact composition for the proposed structures. The molecular ion peak of compound **11** is shown as m/z (M^{+}) at 2104.3 (Fig. S1).

The proton decoupled ^{31}P NMR spectra of aniline substituted *mono* **FDP**-bridged cyclotriphosphazene (**8**) and aniline substituted *double* **FDP**-bridged cyclotriphosphazene (**9**) are depicted as Figures S2a and S2b, respectively as examples. The proton decoupled ^{31}P NMR spectra of compounds (**8** and **9)** showed as AX_2 spin systems due to the environments for the two different phosphorus nuclei of the cyclotriphosphazene ring. The proton decoupled ^{31}P NMR spectrum of the compound **8** has shown two signal. The signals consisted of one triplet for the –P(OCl) groups (δ=23.3 ppm) and a doublet for the -$P(R)_2$ (R=NHPh) groups (δ= 4.9 ppm), in which those have two bond–coupling constants phosphorous and

phosphorous, average of *ca* $^{2}J_{PP}$=52.9 Hz. Spectrum of compound **9** showed one doublet of doublets for the -PO_2 group (δ= 11.8 ppm) and one doublet for the -$P(R)_2$ (R=NHPh) group (δ= 5.2 ppm). Compound **12** (aniline substituted *mono* **FDA**-bridged cyclotriphosphazene) has shown an AX_2 spin system in the proton decoupled ^{31}P NMR. The resonance for the –P(NHCl) group was observed at δ=23.3 ppm as a triplet and the -$P(R)_2$ (R=NH Naphthyl) group was observed at δ=4.8 in this spectrum.

The proton decoupled ^{31}P NMR spectra of 2-naphthylamine substituted *mono* **FDP**-bridged cyclotriphosphazene (**10**), 2-naphthylamine substituted *double* **FDP**-bridged cyclotriphosphazene (**11**) compounds are depicted as Figs. 1a and 1b, respectively as examples. While the proton decoupled ^{31}P NMR spectra of compounds **10** and **12** showed as AX_2 spin systems, compound **11** showed as AB_2 spin systems, due to the close chemical shifts for the two different phosphorus nuclei of the cyclotriphosphazene ring. The proton decoupled ^{31}P NMR spectrum of the compound **10** has shown two signal. The signals consisted of one triplet for the –P(OCl) groups (δ=20.3 ppm) and a doublet for the -$P(R)_2$ (R=NH Naphthyl) groups (δ= 3.6 ppm). Spectrum of compound **11** showed one doublet of doublets for the -PO_2 group (δ= 6.3 ppm) and one doublet for the -$P(R)_2$ (R=NH Naphthyl) group (δ= 3.6 ppm). For the 2-naphthylamine substituted *mono* **FDA**-bridged cyclotriphosphazene compound (**13**), the resonance for the –P(NHCl) group was observed at δ=23.4 ppm as a triplet and the -$P(R)_2$ (R=NH Naphthyl) group was observed at δ=5.2 in this spectrum.

The ^{1}H NMR data also confirmed the structures of newly synthesized compounds **8-13.** The aromatic protons for all compounds were observed at between 7.8 and 6.6 ppm and some of them were distinguishable from each other, ^{1}H NMR spectrum of compound **9** is shown as an example in Figure S3. In addition, NH protons for all compounds were observed at between 5.8 - 4.7 ppm

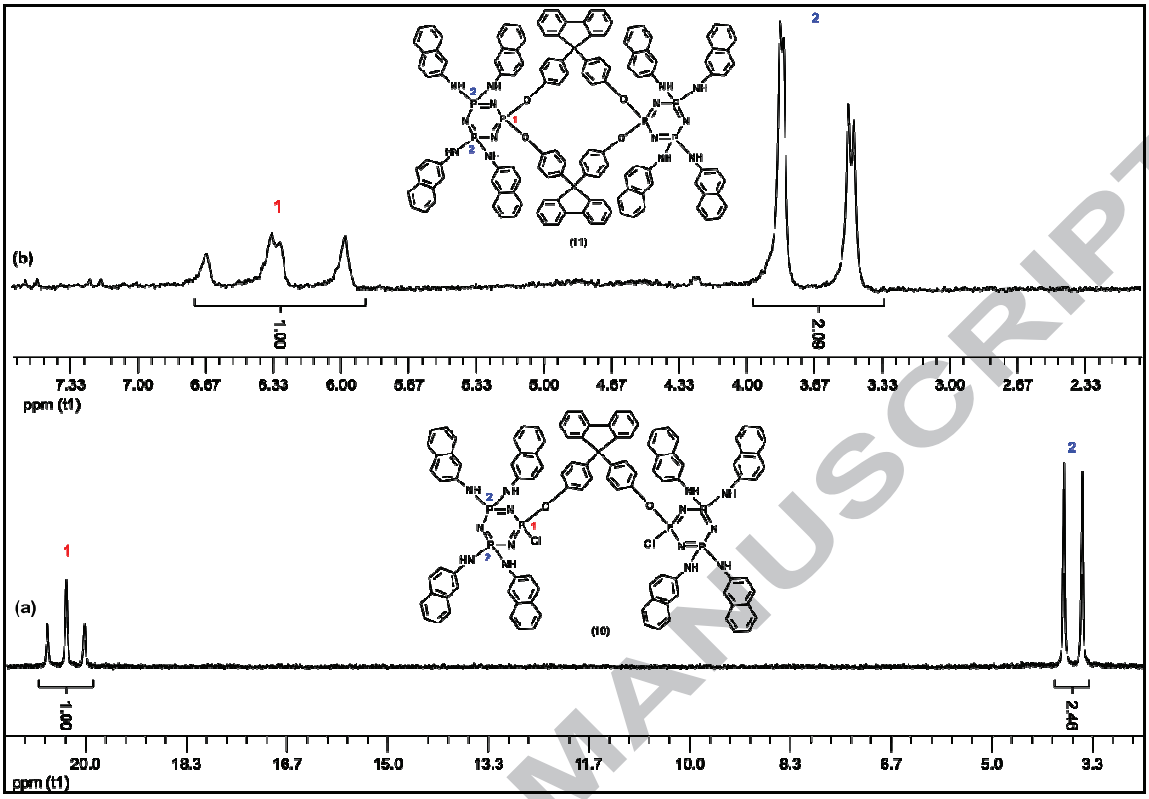


Figure 1. The proton decoupled ^{31}P NMR spectra of (a) 2-naphthylamine substituted mono FDP- bridged cyclotriphosphazene derivatives in $CDCl_3$ solution (**10**); (b) 2-naphthylamine substituted gem-bis FDP- bridged cyclotriphosphazene (**11**) derivatives in d_6-THF solution.

Table 1. $^{31}P\{^{1}H\}$ NMR parameters for synthesized cyclotriphosphazene compounds.

Compounds	δ (^{31}P NMR)[ppm]						Spin System	^{2}J(PP) [Hz]
	PCl_2	PClO	PO_2	PClNH	PR_2 R:(NHNaptl)	PR_2 R:(NHNaptl)		$^{2}J_{AX}$,$^{2}J_{AB}$
(4) [a,b]	25.77	-	-	-	1.91		AX_2	53.21
(5) [a,c]	24.69	-	-	-	-	1.01	AX_2	53.31
(8) [a]	-	23.30	-	-	4.92	-	AX_2	52.91
(9) [a]	-	-	11.84	-	5.29	-	AX_2	64.43
(10) [a]	-	20.32	-	-	-	3.66	AX_2	61.40
(11) [d]	-	-	6.31	-	-	3.67	AB_2	70.1
(12) [a]	-	-	-	23.32	4.89	-	AX_2	52.88
(13) [a]	-	-	-	23.41	-	5.23	AX_2	52.68

[a] 202.38 MHz ^{31}P NMR chemical shifts (ppm) in $CDCl_3$.
[b] [32]
[c] [33]
[d] 202.38 MHz ^{31}P NMR chemical shifts (ppm) in d_6-THF

3.2. Ground state electronic absorption and fluorescence properties

The ground state electronic absorption spectra of newly synthesized aniline and 2-naphthylamine substituted fluorenylidene bridged cyclotriphosphazene derivatives (**8-13**) were measured in tetrahydrofuran (THF) solution. Different absorption bands were observed in the UV region of electronic spectra (Fig. S4 as examples for compounds **8** and **10**). Two absorption bands were observed at approximately 275 and 310 nm in the UV region of electronic spectra for aniline substituted fluorenylidene bridged cyclotriphosphazene compounds (**8**, **9** and **12**). Six absorption bands were observed at approximately 270, 280, 290, 310, 330 and 340 nm in the UV region of electronic spectra for 2-naphthylamine substituted fluorenylidene bridged cyclotriphosphazene compounds (**10**, **11** and **13**). The compounds **8**, **9** and **12** gave different emission bands at 312 and 323 nm in THF (Fig. S5). The fluorescence emission spectra of the 2-naphthylamine substituted fluorenylidene bridged

cyclotriphosphazene derivatives (**10**, **11** and **13**) are shown in Figure S6. These compounds gave intense emission peaks at 370 nm. The 2-naphthylamine substituted fluorenylidene bridged cyclotriphosphazenes (**10**, **11** and **13**) showed higher fluorescence emission than that of other cyclophosphazene compounds **8**, **9** and **12** in THF (Fig. S5 and Fig. S6). These compounds (**10**, **11**, and **13**) also showed higher fluorescence behavior than chlorine substituted counterparts which were studied our previously work [30, 33]. This can be explained by non-covalent π – π interactions increasing number of conjugated π-electrons in the aromatic ring systems of the substituted groups. These measurements show that the compounds **10, 11** and **13** exhibited highly fluorescence behavior in THF solutions. However, the other bridged cyclotriphosphazene derivatives showed very weak fluorescence in this solvent. For this reason, only 2-naphthylamine substituted fluorenylidene bridged compounds were tested for metal ion sensing.

3.3. Chemosensor properties to metal ions

The metal binding capability of fluoren molecules may allow the use of the newly synthesized fluorenylidene bridged cyclotriphosphazene derivatives as metal sensors. In this study, 2-naphthylamine substituted fluorenylidene bridged cyclotriphosphazene compounds (**10, 11** and **13**) were tested to a variety of metal ions (Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Li^{+}, Na^{+}, K^{+} and Cs^{+}) using by fluorescence spectrometry. All fluorescence emission spectral studies were performed in THF solutions at room temperature. The aqueous solutions of the corresponding metal chlorides (nitrate derivative for Ag ion) were used as the source of metal ions. The fluorescence spectra of the new 2-naphthylamine substituted fluorenylidene bridged cyclotriphosphazene derivatives (**10, 11** and **13**) exhibited little enhancement by the addition of the 5 μL of $1.00x10^{-2}$ M metal solutions except for Fe^{3+} and

Cu^{2+}. A significant decrease in the fluorescence intensities were observed by the addition of the Fe^{3+} and Cu^{2+} cations to the THF solutions of substituted cyclophosphazene compounds (**10, 11** and **13**), while no or minimal change was observed with the other metal ions (Fig. 2 as an example for compound **10**, Figs. S7 and S11 in Supporting Information for other compounds).

The titration of the probe compounds (**10**, **11** and **13**) with Fe^{3+} or Cu^{2+} cations showed a decrease in the fluorescence intensities with increasing concentrations of these cations (Figure 3A for Cu^{2+} titration and Figure S8A for Fe^{3+} titration as an example for compound **10,** Figs. S9A, S10A, S12A and S13A in Supporting Information for other compounds). The graphs from a Benesi-Hildebrand analysis showed a non-linear behavior for all studied cyclotriphosphazene chemosensor compounds interactions with Fe^{3+} ions indicating the stoichiometry of between these chemosensors and Fe^{3+} or Cu^{2+} cations are different from 1:1 (Figure 3B for Cu^{2+} titration and Figure S8B for Fe^{3+} titration as an example for compound **10,** Figs. S9B, S10B, S12B and S13B in Supporting Information for other compounds). The continuous variation method was also used for the determination of the stoichiometry between the new 2-naphthylamine substituted fluorenylidene bridged cyclotriphosphazene chemosensors and detected metal cations. The resulting Job's with a maximum mole fraction for Cu^{2+} or Fe^{3+} cations was observed as 0.33 (Figure 3C for Cu^{2+} titration and Figure S8C for Fe^{3+} titration as an example for compound **10,** Figs. S9C, S10C, S12C and S13C in Supporting Information for other compounds), indicating that cyclotriphosphazene molecules and Cu^{2+} or Fe^{3+} ions preferred 2:1 stoichiometry for the formation of complexes between the chemosensor compounds (**10, 11** and **13**) and Fe^{3+} or Cu^{2+} cations in THF solutions.

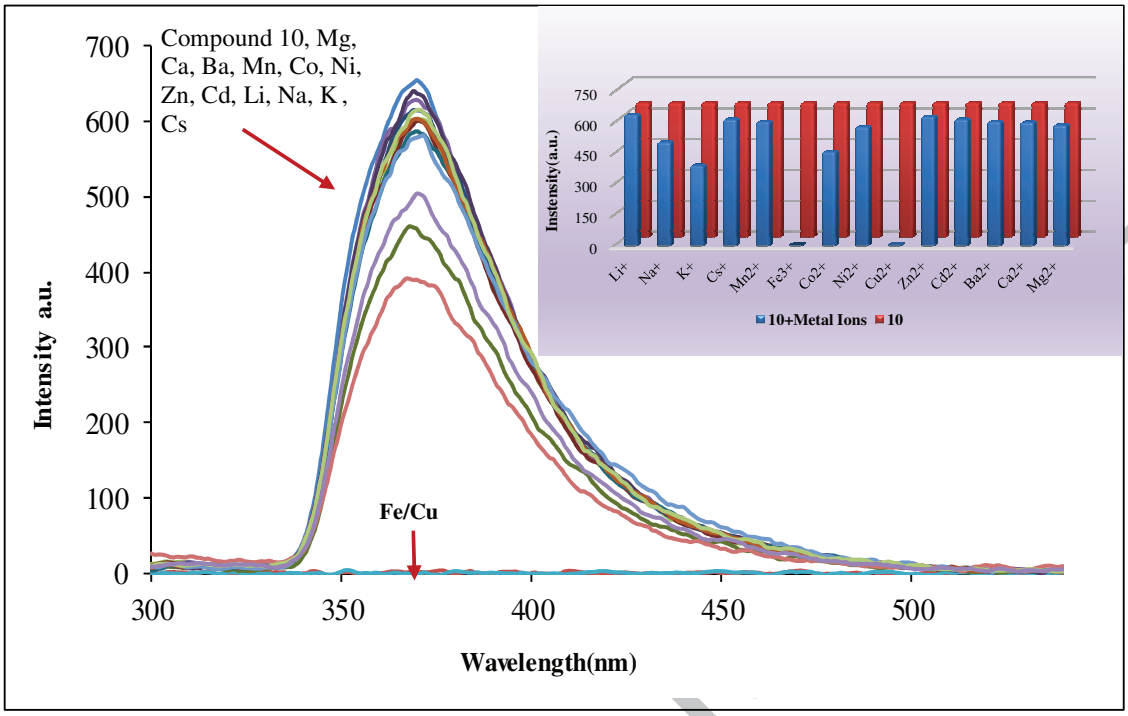


Figure 2. The fluorescence intensity of the compound **10** with and without metal ions in THF solution. Addition of Fe^{+3} and Cu^{2+} ions to the solution prevent fluorescent emission hence provide a selective detection.

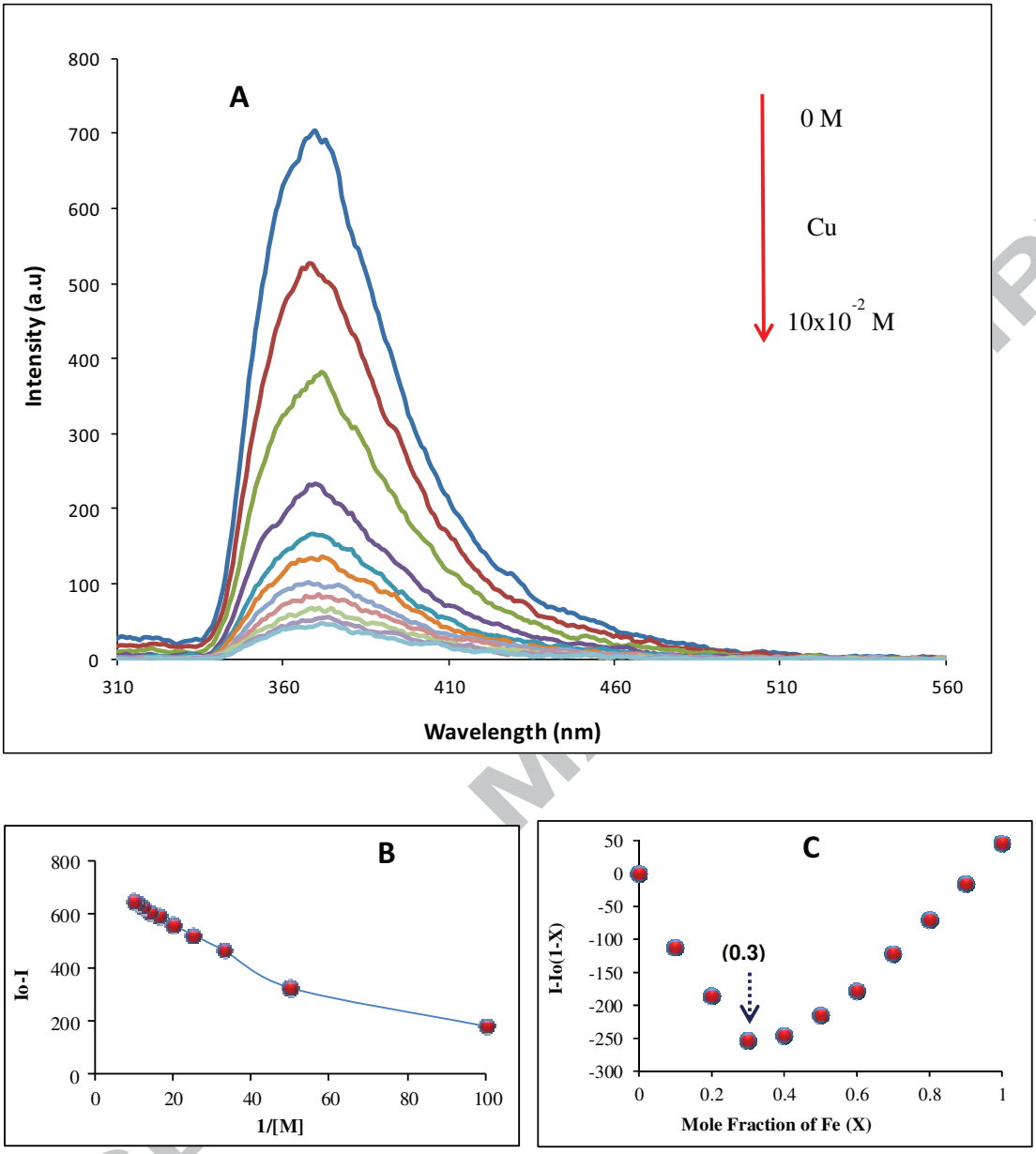


Figure 3. (A) Fluorescence response of chemosensor **10** to various equivalents of Cu^{+2}. (B) The Benesi-Hildebrand graph and (C) Job's plot of **10**-Cu^{+2} complexes in THF solutions. The total concentration of **10** and Cu^{+2} was $1x10^{-2}$ M. The excitation wavelength was 295 nm. The monitored wavelength was 370 nm (compound **10** C: $5x10^{-6}$ M).

4. Conclusion

In summary, we have been synthesized 4,4′-(9-fluorenylidene)diphenol (FDP) and 4,4′-(9-fluorenylidene)dianiline (FDA) bridged aniline and 2-naphthylamine substituted cyclotriphosphazenes for the first time. All newly synthesized compounds (**8-13**) were characterized by elemental analysis, MALDI-TOF mass spectrometry, UV-Vis, ^{1}H NMR and ^{31}P NMR spectroscopies. The fluorescence behavior of compounds **8-13** was investigated by florescence spectroscopy in THF solutions. In addition, the effects of metal ions on the fluorescence behavior of the compounds were studied in order to determine potential using of these compounds as chemosensors for metal ions. A significant decrease in the fluorescence signals were observed by the addition of the Cu^{2+} and Fe^{3+} cations among the fifteen different metal ions. The newly synthesized FDP and FDA bridged 2-naphthylamine substituted cyclotriphosphazene derivatives (**10, 11, 13**) preferred formation of 2:1 (ligand: metal) complexes with both Fe^{3+} and Cu^{2+} ions. FDP and FDA bridged substituted cyclotriphosphazene derivatives showed highly selectivity towards Cu^{2+} and Fe^{3+} ions and these newly synthesized compounds showed potential using as chemosensors for these metal ions in THF solution.

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ASSOCIATED CONTENT

Supporting Information Available: Example ^{1}H NMR, the graphs of titrations of FDP-bridged compounds with Cu^{2+} and Fe^{3+} ions and the Benesi-Hildebrand graphs and Job's plots were given as Supporting Information.

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ACKNOWLEDGMENTS

The authors thank the Scientific and Technical Research Council of Turkey for financial support TUBITAK (Grant **111T085**).

Monofunctional amines substituted Fluorenylidene Bridged Cyclotriphosphazenes: 'Turn-Off' Fluorescence Chemosensors for Cu^{2+} and Fe^{3+} ions

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The synthesis and characterization of the first series of amine substituted fluorenylidene-bridged cyclotriphosphazene derivatives were reported in this study. The florescence properties and chemosensor behaviors of the synthesized new compounds against to metal ions were studied. The fluorenylidene bridged 2-naphthylamino substituted cyclotriphosphazenes showed fluorescence chemosensor behavior with high selectivity for Fe^{3+} and Cu^{2+} ions in the solution.

Monofunctional amines substituted Fluorenylidene Bridged Cyclotriphosphazenes: 'Turn-Off' Fluorescence Chemosensors for Cu^{2+} and Fe^{3+} ions