

Novel Coumarin Substituted Water Soluble Cyclophosphazenes as “Turn-Off” Type Fluorescence Chemosensors for Detection of Fe³⁺ ions in Aqueous Media

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Abstract In the present work, 3-[2-(diethylamino)ethyl]-7-oxy-4-methylcoumarin substituted cyclotriphosphazene (**4**) and cyclotetraphosphazene (**5**) derivatives were synthesized by the reactions of hexachlorocyclotriphosphazene (**1**) or octachlorocyclotetraphosphazene (**2**) with 3-[2-(diethylamino)ethyl]-7-hydroxy-4-methylcoumarin (**3**) for the first time. The quaternized cationic (**6** and **7**) and zwitterionic (**8** and **9**) derivatives of these compounds (**4** and **5**) were obtained by the reactions of dimethyl sulfate and 1,3-propanesultone, respectively. All newly synthesized cyclophosphazene compounds (**4–9**) were fully characterized by elemental analysis and general spectroscopic techniques such as FT-IR, ³¹P-NMR, ¹H-NMR and MALDI-TOF mass. All these coumarin substituted cyclophosphazene compounds (**4–9**) were soluble in most of organic solvents and quaternized ionic and zwitterionic compounds (**6–9**) also showed excellent solubility in water. The fluorescence behaviors of novel cyclophosphazene compounds were investigated in methanol and water solutions. The chemosensor properties of newly synthesized water soluble quaternized ionic and zwitterionic cyclotriphosphazene and cyclotetraphosphazene derivatives (**6–9**) were investigated in aqueous media. These cyclophosphazene derivatives showed fluorescence chemosensor behavior with high selectivity for Fe³⁺ ions in aqueous solution.

Keywords Cyclophosphazene · Coumarin · Water soluble · Chemosensor · Fe³⁺ ions

Introduction

Phosphazenes, in the form of linear short-chain, cyclic, or high-molecular-weight polymers, consist of the repeating units of -[N = PR₂]- with trivalent nitrogen and pentavalent phosphorus atoms and constitute one of the most important compound groups in inorganic chemistry. When “R” is the halogen, it can be replaced with ease by alkoxy, aryloxy or amino groups via nucleophilic substitution reactions [1–6]. Hexachlorocyclotriphosphazene, trimer, N₃P₃Cl₆, (**1**) or octachlorocyclotetraphosphazene, tetramer, N₄P₄Cl₈ (**2**) namely cyclophosphazenes are a kind of phosphazene compounds that they show many special characteristics. Cyclotriphosphazenes can be easily functionalized on the phosphorus atoms, thus giving rise to a wide variety of substituted molecules [7–12]. Cyclophosphazenes exhibit useful properties for many applications such as liquid crystals [13, 14], hydraulic fluids and lubricants [15], electrical conductivity [16], rechargeable batteries [17], flame retardant materials [18], anticancer agents [19–21], antibacterial reagents [22] and biomedical materials [23] depends on the substituted side groups.

Coumarins have been widely used in the fields of biology, medicine, cosmetics and fluorescent dyes [24, 25]. The structure of benzopyrone group in the coumarin derivatives has many advantages including high fluorescence quantum yield, large Stokes shift, excellent light stability and low toxicity [26–28]. Moreover, coumarins play important roles as food constituents, antioxidants, stabilizers, immunomodulatory substances, lasers and anticancer agents [29–34]. Coumarin derivatives have also been used as fluorescent probes of pH,

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for detection of nitric oxide, nitroxide and hydrogen peroxide [35–37]. The development of fluorescent probes for detecting transition metal ions has attracted great interests of researchers because of the advantages of high selectivity and sensitivity, non-destructive analysis and simple instrumentation [29].

Fe^{3+} ions play an important role in many biological processes at the cellular level ranging from oxygen metabolism to DNA and RNA synthesis. Iron is indispensable for most organisms, and both its deficiency and excess cause various pathological disorders [38]. The detection of various metal ions such as iron (III) has developed quickly because of their importance in many biological and environmental processes [39, 40].

Although there were a few reports on coumarin-containing polyphosphazenes [41–43] and coumarin-containing cyclotriphosphazenes [44, 45], there is no study about the reaction of coumarin derivatives with cyclotetraphosphazenes. To our knowledge, there are several examples of the water soluble cyclophosphazenes [46–49] but there is no coumarin bearing water soluble derivative of the cyclophosphazenes has been reported until now. On the other hand, coumarin-base fluorescent chemosensors have received increasing interest in recent years [50] due to their low toxicity and easily modification of coumarin ring by different groups. Moreover, the carbonyl group of coumarin can take part in coordination with metal ions such as Fe^{3+} in this study. In fact, coumarin ring is an ideal model for the design of chemosensors because the response will be fast and efficient when guests, such as protons and metal ions, are bound to the host coumarin probes [39]. Therefore, we motivated to the design and synthesize coumarin substituted cyclophosphazenes chemosensors in this study.

The aim of this study is the synthesis of coumarin substituted cyclophosphazene compounds (**4** and **5**) from the reactions of $\text{N}_3\text{P}_3\text{Cl}_6$ or $\text{N}_4\text{P}_4\text{Cl}_8$ with 3-[2-(diethylamino)ethyl]-7-hydroxy-4-methylcoumarin (**3**). The obtained compounds **4** and **5** are the first examples of full coumarin substituted cyclotriphosphazene and cyclotetraphosphazene derivatives, respectively (Scheme 1). The newly synthesized compounds **4** and **5** were reacted with excess dimethylsulphate or 1,3-propanesultone in DMF to obtain water soluble coumarin derivatives of cyclophosphazenes and the quaternized ionic (**6** and **7**) and zwitterionic (**8** and **9**) compounds were obtained (Scheme 1). All newly synthesized cyclophosphazene compounds (**4**–**9**) were fully characterized by elemental analysis and general spectroscopic techniques such as FT-IR, ^{31}P -NMR, ^1H -NMR and MALDI-TOF mass. The fluorescence behaviors of these compounds were investigated in methanol and water solutions. The chemosensor properties of the newly synthesized water soluble cyclophosphazene compounds (**6**–**9**) were investigated against to different metal ions and these compounds were found highly selective to Fe^{3+} ions in aqueous solution.

Experimental

Materials

Hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene (Otsuka Chemical Co., Ltd) were purified by fractional crystallization from *n*-hexane. Cesium carbonate (99 %) and 1,3-propanesultone (99 %) were obtained from Alfa Aesar. 3-[2-(Diethylamino)ethyl]-7-hydroxy-4-methylcoumarin hydrochloride (≥ 99.0 %), *N,N*-dimethylformamide (≥ 99.0 %) were obtained from Sigma Aldrich. Dimethyl sulphate (99 %), tetrahydrofuran (≥ 99.0 %), dichloromethane (≥ 99.0 %), *n*-hexane (≥ 95.0 %), ethyl acetate (≥ 99.0 %) were obtained from Merck. All used solvents were purified by conventional methods. THF was distilled over a sodium–potassium alloy under an atmosphere of dry argon. All reactions were performed under a dry argon atmosphere. CDCl_3 and D_2O used for NMR spectroscopy are obtained from Goss Scientific.

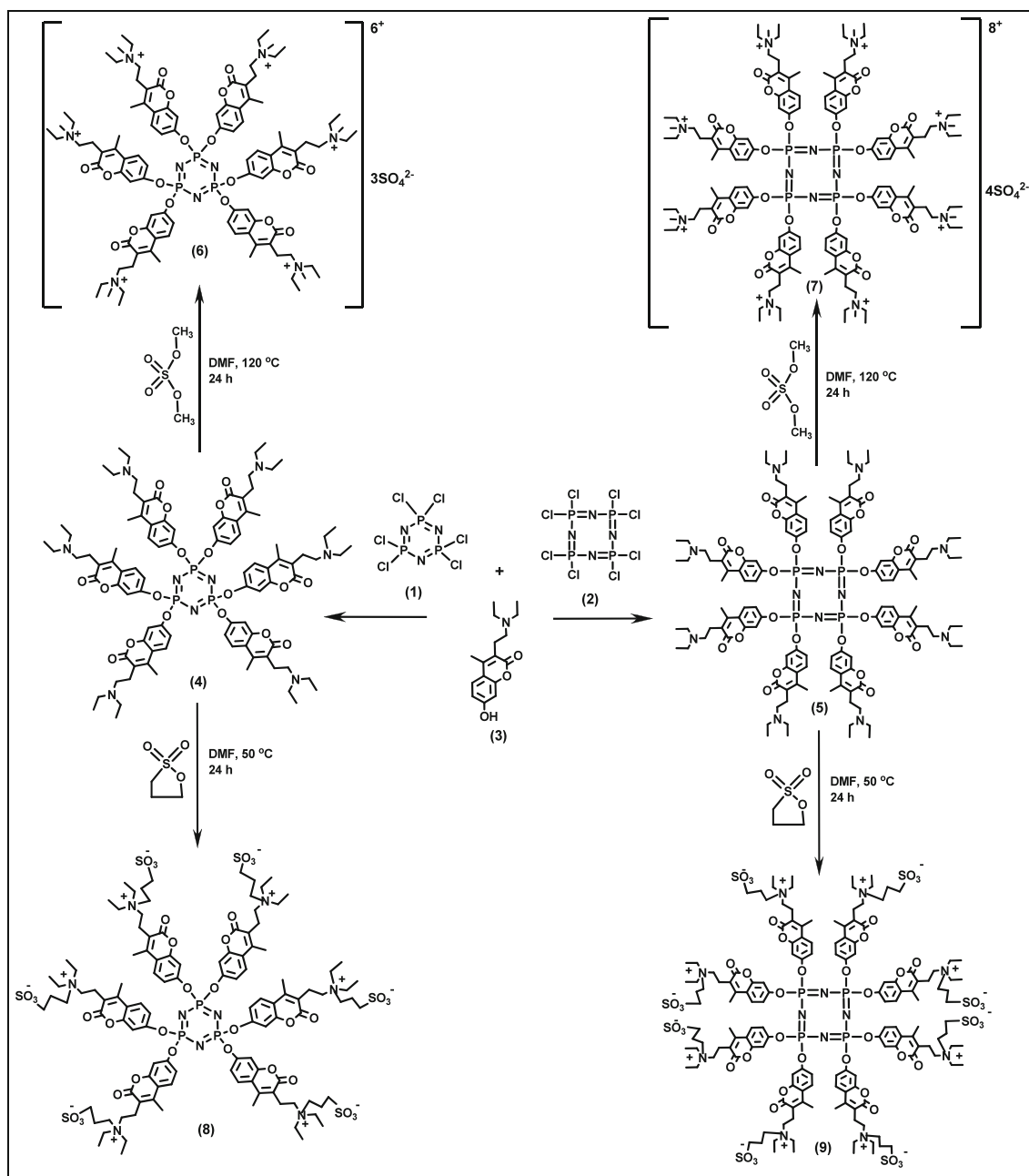
Equipments

Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument. Positive ion and linear mode MALDI-MS of complexes were obtained in dihydroxybenzoic acid as MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex LT MALDI-TOF mass spectrometer. Analytical Thin Layer Chromatography (TLC) was performed on silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. ^1H and ^{31}P NMR spectra were recorded in CDCl_3 or D_2O 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. UV/Vis spectra were recorded with a Shimadzu 2101 UV spectrophotometer. Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature.

Synthesis

Reaction of **1** with **3** to form compound **4**

3-[2-(Diethylamino)ethyl]-7-hydroxy-4-methylcoumarin hydrochloride (**3**) (0.2 g, 0.72 mmol) and Cs_2CO_3 (0.47 g, 1.44 mmol) were dissolved in 20 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 hexachlorocyclotriphosphazene (**1**), (0.042 g, 0.12 mmol 10 mL of dry THF) was quickly added to a stirred solution under an argon atmosphere. The reaction mixture was stirred for 3 days at room temperature and the reaction followed on



Scheme 1 Synthesis route of coumarin substituted cyclophosphazene derivatives

TLC silica gel plates using methanol as eluent. The reaction mixture was filtered to remove the formed cesium chloride and the solvent was evaporated under reduced pressure. The resulting colorless oil was dissolved in 5 mL of CH_2Cl_2 and this solution was dropped in *n*-hexane. The solid product was precipitated and collected by filtration. This process was repeated twice. The white solid product was obtained. Yield 0.13 g (60 %). M.p. 105 °C. Anal Calc. for $[(\text{N}_3\text{P}_3)(\text{C}_{16}\text{H}_{20}\text{NO}_3)_6]$, requires: C, 64.74; H, 6.79; N, 7.08 %, Found: C, 64.70; H, 6.76 N; 7.03 %. FT-IR: $\nu_{\text{max}}/\text{cm}^{-1}$: 3063 (Ar-CH), 2934–2890 (Aliphatic CH), 1708 (C = O), 1608 (C = C), 1209 (P = N), 1131 (C–O). ^{31}P NMR,

(202 MHz, CDCl_3 , 298 K) δ , ppm: 7.59. ^1H NMR (500 MHz, CDCl_3 , 298 K) δ , ppm: 7.49 (d, $J^3 = 8.79$ Hz, 6H, Ar-CH), 7.01 (dd, $J^3 = 8.77$ and $J^4 = 2.15$ Hz, 6H, Ar-CH), 6.88 (sd, $J^4 = 2.21$ Hz, 6H, Ar-CH), 2.79–2.70 (m, 12H, C- CH_2), 2.55–2.67 (m, 36H, N- CH_2), 2.38 (s, 18H, Ar- CH_3) 1.07 (t, $J^3 = 7.12$ Hz, 36H, C- CH_3). MALDI-TOF (m/z) calc. 1780.95, found: 1782.58 $[\text{M}+\text{H}]^+$.

Reaction of 2 with 3 to form compound 5

3-[2-(Diethylamino)ethyl]-7-hydroxy-4-methylcoumarin hydrochloride (3) (0.2 g, 0.72 mmol) and Cs_2CO_3 (0.47 g,

1.44 mmol) were dissolved in 20 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 octachlorocyclotetraphosphazene (**2**), (0.042 g, 0.09 mmol) in 10 mL of dry THF was quickly added to this stirred solution under an argon atmosphere. The reaction mixture was stirred for 3 days at room temperature and the reaction followed on TLC silica gel plates using methanol as eluent. The reaction mixture was filtered to remove the formed cesium chloride and the solvent was removed under reduced pressure. The resulting colourless oil was dissolved in 5 mL of CH_2Cl_2 and this solution was dropped in *n*-hexane. The solid product was precipitated and collected by filtration. This process was repeated twice. The white solid product **5** was obtained. Yield 0.12 g (57 %). M.p. 202 °C. Anal Calc. for $[(\text{N}_4\text{P}_4)(\text{C}_{16}\text{H}_{20}\text{NO}_3)_8]$, requires: C, 64.74; H, 6.79; N, 7.08 %, Found: C, 64.59; H, 6.77; N, 7.03 %. FT-IR: $\nu_{\text{max}}/\text{cm}^{-1}$: 3065 (Ar-CH), 2965–2876 (Aliphatic-CH), 1710 (C = O), 1609 (C = C), 1265 (P = N), 1135 (C–O). ^{31}P NMR, (202 MHz, CDCl_3 , 298 K) δ , ppm: –14.37. ^1H NMR (500 MHz, CDCl_3 , 298 K) δ , ppm: 7.45 (d, $J^3 = 8.83$ Hz, 8H, Ar-CH), 6.95 (dd, $J^3 = 8.81$ and $J^4 = 2.32$ Hz, 8H, Ar-CH), 6.82 (sd, 8H, $J^4 = 2.30$ Hz, Ar-CH), 2.74–2.81 (broad, 16H, C- CH_2), 2.61–2.70 (broad, 48H, N- CH_2), 2.36 (s, 24H, Ar- CH_3), 1.12 (t, $J^3 = 6.82$ Hz, 48H, C- CH_3). MALDI-TOF (m/z) calc. 2374.59, found: 2375.26 $[\text{M}+\text{H}]^+$.

Reaction of **4** with dimethylsulphate to form compound **6**

Compound **4** (0.05 g, 0.028 mmol) was heated to 120 °C in freshly distilled DMF (3 mL) and excess dimethylsulphate (0.1 mL) was added dropwise to this solution. The mixture was stirred at 120 °C for 24 h. After this time, the mixture was cooled to room temperature and the product was precipitated with ethyl acetate. The obtained product (**6**) showed excellent solubility in water. Yield 0.045 g (74 %). Anal Calc. for $[(\text{N}_3\text{P}_3)(\text{C}_{17}\text{H}_{23}\text{NO}_3)_6(\text{SO}_4)_3]$, requires: C, 56.74; H, 6.44; N, 5.84 %, Found: C, 56.69; H, 6.40; N, 5.79 %. FT-IR: $\nu_{\text{max}}/\text{cm}^{-1}$: 3066 (Ar-CH), 2958–2855 (Aliphatic-CH), 1704 (C = O), 1637 (C = C), 1204 (P = N), 1058 (C–O), 999 (S = O), 756 (S–O). ^{31}P NMR, (202 MHz, CDCl_3 , 298 K) δ , ppm: 7.78. ^1H NMR (500 MHz, D_2O , 298 K) δ , ppm: 7.50 (d, $J^3 = 8.63$ Hz, 6H, Ar-CH), 6.76 (dd, $J^3 = 8.65$ and $J^4 = 2.09$ Hz, 6H, Ar-CH), 6.65 (sd, $J^4 = 2.11$ Hz, 6H, Ar-CH), 3.45–3.70 (m, 36H, N- CH_2), 3.11 (s, 18H, N- CH_3), 2.81–2.84 (m, 12H, C- CH_2), 2.21 (s, 18H, Ar- CH_3), 1.33 (t, $J^3 = 7.10$, 36H, C- CH_3). MALDI-TOF (m/z) calc. 2159.39, found 2048.4 $[\text{M}-\text{SO}_4-\text{CH}_3]^+$, 1922.8 $[\text{M}-2\text{SO}_4-3\text{CH}_3]^+$, 1796.7 $[\text{M}-3\text{SO}_4-5\text{CH}_3]^+$.

Reaction of **4** with 1,3-propanesultone to form compound **8**

Compound **4** (0.05 g, 0.028 mmol) and excess 1,3-propanesultone (0.068 g, 0.56 mmol) were dissolved in DMF

(5 mL) and kept at 50 °C for 24 h under nitrogen atmosphere while stirring. After this time, the product was precipitated with ethyl acetate, filtered and washed with copious amounts of CH_2Cl_2 and acetone to remove excess 1,3-propanesultone. The obtained product (**8**) showed excellent solubility in water. Yield 0.056 g (85 %). Anal Calc. for $[(\text{N}_3\text{P}_3)(\text{C}_{19}\text{H}_{26}\text{NSO}_6)_6]$, requires: C, 54.47; H, 6.25; N, 5.01 %, Found: C, 54.30; H, 6.45; N, 4.79 %. FT-IR: $\nu_{\text{max}}/\text{cm}^{-1}$: 3066 (Ar-CH), 2937–2807 (Aliphatic-CH), 1704 (C = O), 1637 (C = C), 1169 (P = N), 1102(C–O), 1035 (S = O), 662 (S–O). ^{31}P NMR, (202 MHz, CDCl_3 , 298 K) δ , ppm: 7.83. ^1H NMR (500 MHz, D_2O , 298 K) δ , ppm: 7.53 (d, $J^3 = 8.54$ Hz, 6H, Ar-CH), 6.81 (dd, $J^3 = 8.55$ and $J^4 = 2.18$ Hz, 6H, Ar-CH), 6.66 (sd, $J^4 = 2.16$ Hz, 6H, Ar-CH), 4.43 (m, 12H, S- CH_2), 3.54–3.62 (m, 12H, N- CH_2), 3.32–3.45 (m, 36H, N- CH_2), 2.82–2.85 (m, 12H, C- CH_2), 2.57–2.63 (broad, 12H, C- CH_2), 2.27 (s, 18H, Ar- CH_3), 1.23 (t, $J^3 = 7.01$ Hz, 36H, C- CH_3). MALDI-TOF-MS: m/z: calcd. 2513.91, found 2144.9 $[\text{M}-3(\text{C}_3\text{H}_6\text{SO}_3)]^+$, 2021.8 $[\text{M}-4(\text{C}_3\text{H}_6\text{SO}_3)]^+$, 1898.9 $[\text{M}-5(\text{C}_3\text{H}_6\text{SO}_3)]^+$.

Reaction of **5** with dimethylsulphate to form compound **7**

Compound **5** (0.05 g, 0.021 mmol) was heated to 120 °C in freshly distilled DMF (4 mL) and excess dimethylsulphate (0.1 mL) was added dropwise to this solution. The mixture was stirred at 120 °C for 24 h. After this time, the mixture was cooled to room temperature and the product was precipitated with ethyl acetate. The obtained product (**7**) showed excellent solubility in water. Yield 0.04 g (76 %). Anal Calc. for $[(\text{N}_4\text{P}_4)(\text{C}_{17}\text{H}_{23}\text{NO}_3)_8(\text{SO}_4)_4]$, requires: C, 56.74; H, 6.44; N, 5.84 %, Found: C, 56.71; H, 6.41; N, 5.79 %. FT-IR: $\nu_{\text{max}}/\text{cm}^{-1}$: 3060 (Ar-CH), 2806–2930 (Aliphatic-CH), 1705 (C = O), 1641 (C = C), 1201 (P = N), 1047 (C–O), 1000 (S = O), 758 (S–O). ^{31}P NMR, (202 MHz, CDCl_3 , 298 K) δ , ppm: –15.85. ^1H NMR (500 MHz, D_2O , 298 K) δ , ppm: 7.56 (d, $J^3 = 8.76$ Hz, 8H, Ar-CH), 6.84 (dd, $J^3 = 8.73$ and $J^4 = 2.28$ Hz, 8H, Ar-CH), 6.68 (sd, $J^4 = 2.25$ Hz, 8H, Ar-CH), 3.32–3.45 (broad, 48H, N- CH_2), 3.02 (s, 24H, N- CH_3), 2.80–2.72 (broad, 16H, C- CH_2), 2.28 (s, 24H, Ar- CH_3), 1.28 (t, $J^3 = 6.94$ Hz, 48H, C- CH_3). MALDI-TOF-MS: m/z: calcd. 2879.12, found 2770 $[\text{M}-\text{SO}_4-\text{CH}_3]^+$, 2644.1 $[\text{M}-2\text{SO}_4-3\text{CH}_3]^+$, 2516.7 $[\text{M}-3\text{SO}_4-5\text{CH}_3]^+$, 2390.6 $[\text{M}-4\text{SO}_4-7\text{CH}_3]^+$.

Reaction of **5** with 1,3-propanesultone to form compound **9**

Compound **5** (0.05 g, 0.021 mmol) and excess 1,3-propanesultone (0.05 g, 0.42 mmol) were dissolved in DMF (3 mL) and kept at 50 °C for 24 h under nitrogen atmosphere while stirring. After this time, the product was precipitated with ethyl acetate, filtered and washed with copious amounts of CH_2Cl_2 and acetone to remove excess 1,3-propanesultone. The product (**9**) showed excellent solubility in water. Yield 0.064 g (91 %). Anal Calc. for $[(\text{N}_4\text{P}_4)(\text{C}_{19}\text{H}_{26}\text{NSO}_6)_8]$,

requires: C, 54.47; H, 6.25; N, 5.01 %, Found: C, 54.28; H, 6.45 N; 4.68 %. FT-IR: $\nu_{\max}/\text{cm}^{-1}$: 3066 (Ar-CH), 2810–2954 (Aliphatic-CH), 1705 (C = O), 1641 (C = C), 1166 (P = N), 1047 (C–O), 1032 (S = O), 732 (S–O). ^{31}P NMR, (202 MHz, CDCl_3 , 298 K) δ , ppm: -14.56 . ^1H NMR (500 MHz, D_2O , 298 K) δ , ppm: 7.68 (d, $J^3 = 8.57$ Hz, 8H, Ar-CH), 6.88 (dd, $J^3 = 8.59$ and $J^4 = 2.23$ Hz, 8H, Ar-CH), 6.54 (sd, $J^4 = 2.21$ Hz, 8H, Ar-CH); 4.36 (m, 16H, S- CH_2), 3.48–3.54 (m, 16H, N- CH_2), 3.25–3.34 (m, 48H, N- CH_2), 2.78–2.82 (broad, 16H, C- CH_2), 2.42–2.53 (broad, 16H, C- CH_2), 2.12 (s, 24H, Ar- CH_3), 1.18 (t, $J^3 = 7.22$ Hz, 48H, C- CH_3). MALDI-TOF-MS: m/z : calcd. 3351.74, found 2744.9 $[\text{M}-5(\text{C}_3\text{H}_6\text{SO}_3)]^+$, 2621.9 $[\text{M}-6(\text{C}_3\text{H}_6\text{SO}_3)]^+$, 2499.9 $[\text{M}-7(\text{C}_3\text{H}_6\text{SO}_3)]^+$, 2377.6 $[\text{M}-8(\text{C}_3\text{H}_6\text{SO}_3)]^+$.

Results and discussion

Synthesis and structural characterization of compounds 4–9

The synthesis route of new 3-[2-(diethylamino)ethyl]-7-oxy-4-methylcoumarin substituted cyclophosphazene derivatives (4–9) was given in Scheme 1. All newly synthesized cyclophosphazene compounds (4–9) were fully characterized by general spectroscopic techniques such as FT-IR, ^{31}P -NMR,

^1H -NMR and MALDI-TOF mass. The elemental analysis data of these compounds were also supplied. All results were confirmed the expected structures of the compounds.

The formed products in each reaction mixture were checked by TLC and proton-decoupled ^{31}P NMR spectroscopy. After purification of pure compounds from the reaction mixture, the proton decoupled ^{31}P NMR spectra of coumarin substituted cyclophosphazene (4, 6 and 8) and cyclotetraphosphazene (5, 7, and 9) compounds showed a sharp single peak because the chemical environment of all the phosphorus nuclei (A_3 and A_4 spin systems for cyclophosphazene and cyclotetraphosphazene compounds, respectively) are equivalence (Fig. 1 for compounds 4, 6, 8 and Fig. 2 for compounds 5, 7, 9). In addition to the elemental analysis results, the mass spectral data of the newly synthesized hexa- and octa-coumarin substituted cyclophosphazenes (4–9) were consistent with the assigned formulations. Mass spectra results of compounds 4 and 5 clearly show the major molecular ion peaks, which confirmed the exact composition and no chlorine pattern, could be recognized for the structures (Fig. 3a and b). The molecular ion peaks of compound 4 and 5 were observed at m/z 1782.5 and 2375.2 as $[\text{M}+\text{H}]^+$, respectively.

FT-IR spectra of the newly synthesized 3-[2-(diethylamino)ethyl]-7-oxy-4-methylcoumarin substituted cyclophosphazene compounds 4–9 showed characteristic

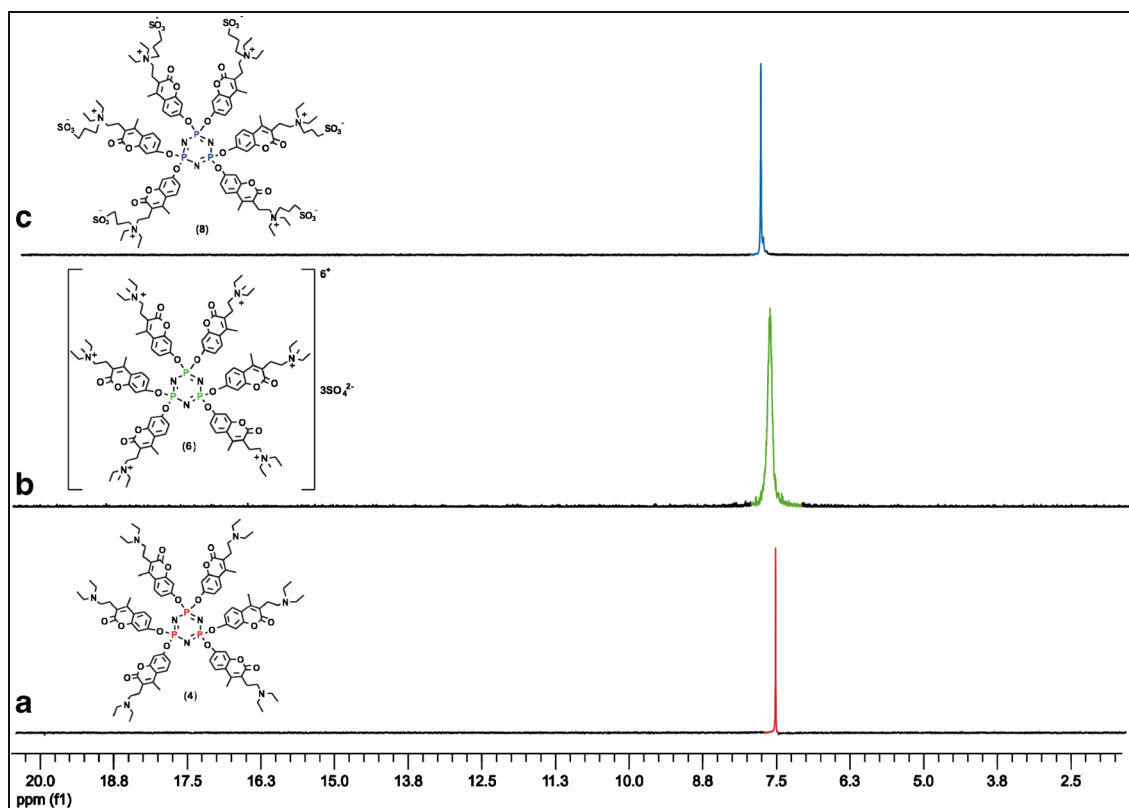


Fig. 1 ^{31}P NMR spectra of (a) compound 4 in CDCl_3 solution (b) compound 6 in D_2O solution and (c) compound 8 in D_2O solution

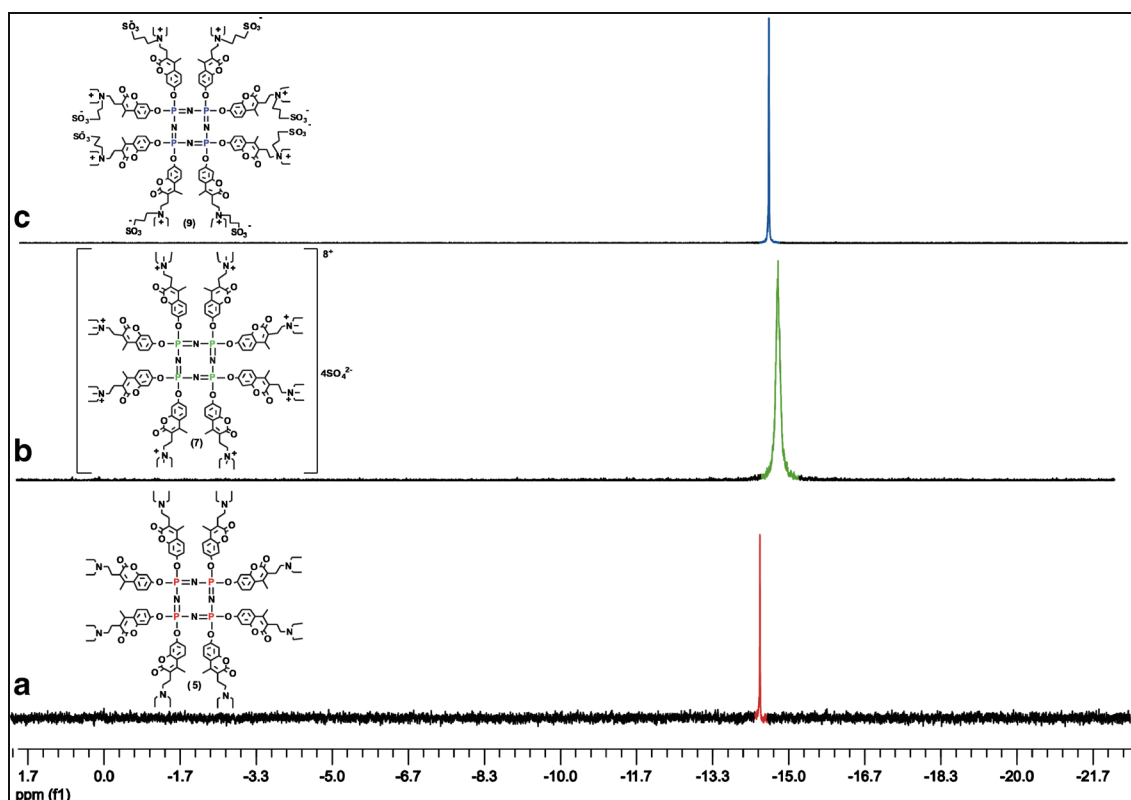


Fig. 2 ^{31}P NMR spectra of (a) compound 5 in CDCl_3 solution (b) compound 7 in D_2O solution and (c) compound 9 in D_2O solution

stretching bands of $\nu_{(\text{C-H})\text{arom}}$ at around 3000 cm^{-1} . The sharp peak in the IR spectra for the $\text{C}=\text{O}$ vibrations for the lactone ring were observed at around $1640\text{--}1715\text{ cm}^{-1}$. The vibration

bands assignable to the stretching of the $-\text{P}=\text{N}-$ bands for compounds 4–9 were observed at frequency in the range of $1165\text{--}1260\text{ cm}^{-1}$. The characteristic vibrations corresponding to ether groups ($\text{C}-\text{O}-\text{C}$) were observed at around $1135\text{--}1050\text{ cm}^{-1}$. The other main peaks were observed for aliphatic CH stretching at around $2806\text{--}2930\text{ cm}^{-1}$, $\text{S}=\text{O}$ stretching at around $1000\text{--}1035\text{ cm}^{-1}$ and $\text{S}-\text{O}$ stretching at around $750\text{--}660\text{ cm}^{-1}$. The observed peaks related to $\text{S}=\text{O}$ and $\text{S}-\text{O}$ groups were indicative for the formation of quaternized and zwitterionic complexes.

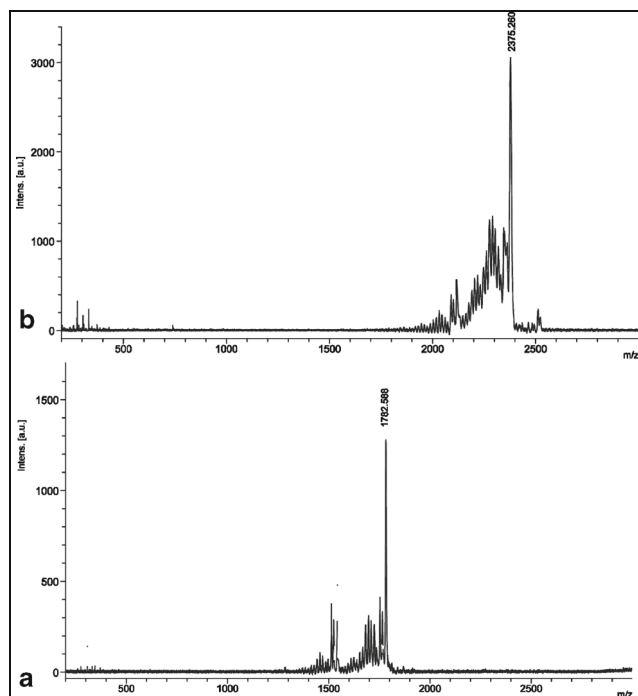


Fig. 3 The mass spectra of (a) compound 4 and (b) compound 5

Ground state electronic absorption and fluorescence properties

The ground state electronic absorption spectra of newly synthesized coumarin substituted cyclophosphazene derivatives (4–9) were measured in methanol. Mainly two absorption bands were observed at approximately 280 and 310 nm in the UV region of electronic spectra (Fig. 4 as examples for compounds 4, 6 and 8). The fluorescence behaviors were examined in methanol for all studied compounds (4–9) and in both methanol and aqueous solutions for quaternized ionic or zwitterionic compounds (6–9). All these compounds gave an emission band at 395 nm in methanol (Fig. 5 as examples for compounds 4, 6 and 8). These measurements show that the intensity of the

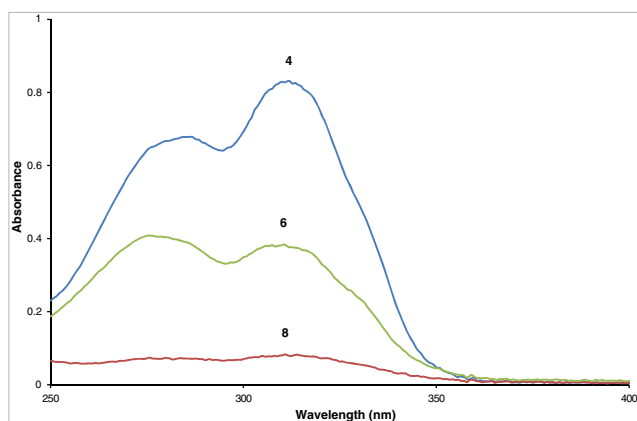


Fig. 4 Electronic absorption spectra of compounds **4**, **6** and **8** in methanol ($C = 2.5 \times 10^{-6}$ M)

emission peak was increased by the quaternization of the nitrogen atom on the coumarin group suggesting that the positive charge on the nitrogen atom changed the electron density on the coumarin ring. The zwitterionic compounds (**8** and **9**) showed more intense emission peaks than quaternized counterparts (**6** and **7**). Surprisingly, the emission peaks of water soluble coumarin substituted cyclophosphazene derivatives (**6–9**) were observed at 460 nm with approximately 60 nm red-shift in aqueous solution (Fig. 6 as an example for compound **6**). It could be due to the changing of electron density of coumarin ring in aqueous solution suggesting that the formation of hydrogen bonds between oxygen atoms on the coumarin ring and hydrogen atoms on the water molecules.

Chemosensor properties to metal ions

The metal binding capability of coumarin molecules may allow the use of the newly synthesized cyclophosphazene

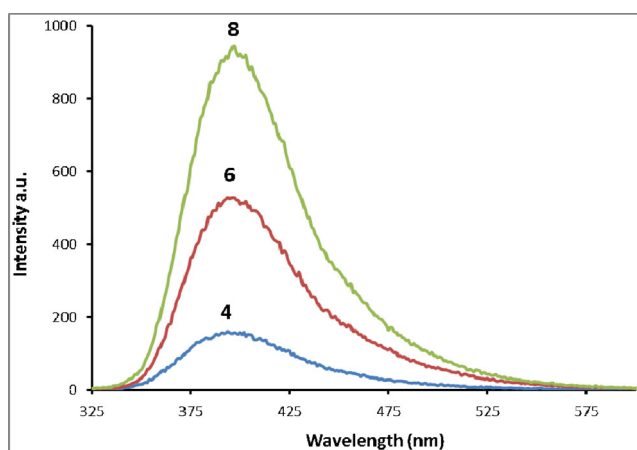


Fig. 5 Fluorescence emission spectra of compounds **4**, **6** and **8** in methanol ($C = 2.5 \times 10^{-6}$ M, $\lambda_{\text{ex}} = 315$ nm)

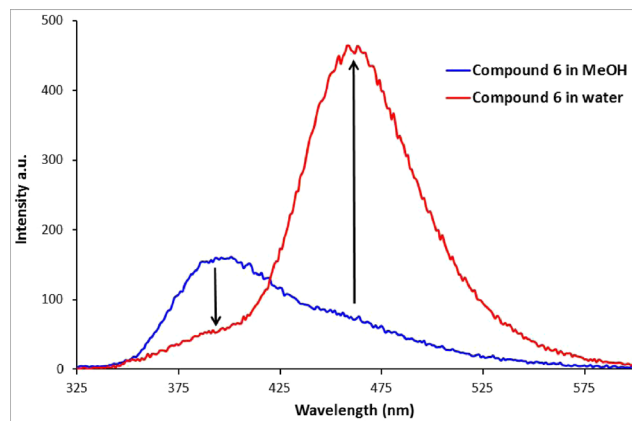
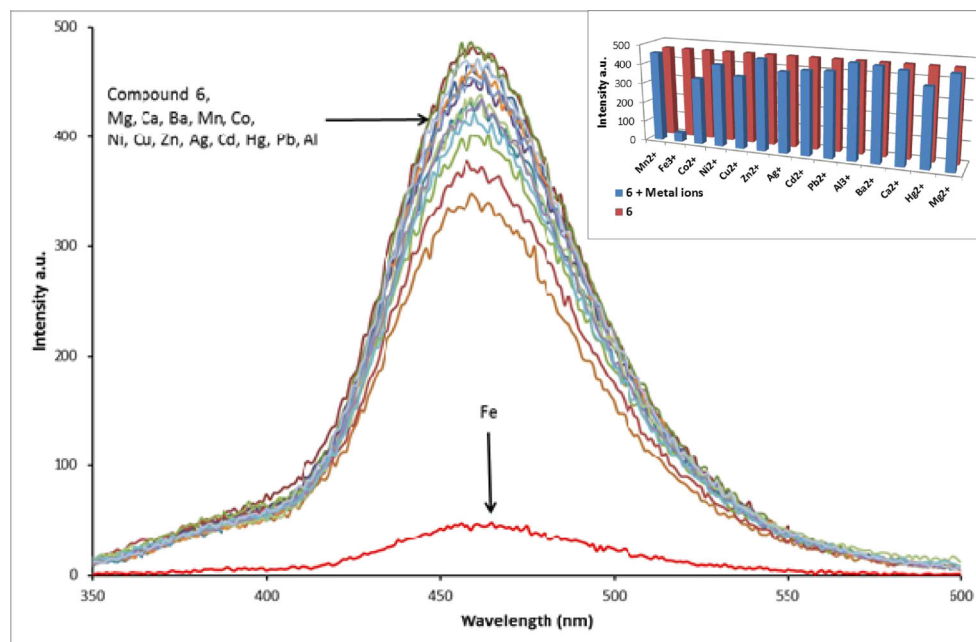


Fig. 6 Fluorescence emission spectra of compound **6** in methanol and water solutions ($C = 1.00 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 315$ nm)

derivatives as metal sensors. This study was especially focused investigation of chemosensor behavior of synthesized compounds in aqueous solution. For this purpose, the water soluble quaternized (**6** and **7**) and zwitterionic (**8** and **9**) coumarin substituted cyclophosphazene compounds 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+} , Ag^+ , Cd^{2+} , Hg^{2+} , Pb^{2+} and Al^{3+}) using fluorescence spectrophotometer. All fluorescence emission spectral studies were performed in aqueous 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 novel coumarin substituted cyclophosphazene compounds (**6–9**) exhibited little enhancement by the addition of the 5 μL of 1.00×10^{-2} M metal solutions except for Fe^{3+} . A significant decrease in the fluorescence intensities were observed by the addition of the Fe^{3+} cations to the aqueous solutions of quaternized (**6** and **7**) and zwitterionic (**8** and **9**) coumarin substituted cyclophosphazene compounds, while no or minimal change was observed with the other metal ions (Fig. 7 as an example for compound **6**).

The titration of the probe compounds (**6–9**) with Fe^{3+} cations showed a decrease in the fluorescence intensities by the increasing concentrations of Fe^{3+} cations (Fig. 8a as an example for compound **6**). The graphs from a Benesi-Hildebrand analysis showed a linear behavior for all studied water soluble cyclophosphazene chemosensor compounds interactions with Fe^{3+} ions indicated the stoichiometry of between these chemosensors and Fe^{3+} cations is 1:1 (Fig. 8b as an example for compound **6**). The Continuous Variation method was also used for the determination of the stoichiometry between the novel water soluble cyclophosphazene chemosensors and detected metal cations. Consistent with the Benesi-Hildebrand graphs, application of the Method of Continuous Variation resulted in a Job's with a maximum mole

Fig. 7 The fluorescence intensity of the compound **6** with and without metal ions in aqueous solution. Addition of Fe^{3+} ions to the solution prevent fluorescent emission hence provide a selective detection



fraction for Fe^{3+} cations was observed as 0.50 (Fig. 8c as an example for compound **6**), indicating that cyclophosphazene molecules and Fe^{3+} ions preferred 1:1 stoichiometry for the formation of complexes between the chemosensor compounds (**6–9**) and Fe^{3+} cations in aqueous solutions.

Fluorescence titration experiment can be used for determine limit of detection (LOD) and association constant (K_a). The detection limit values of cyclophosphazene chemosensors as fluorescent sensors for the analysis of Fe^{3+} were determined from the plot of fluorescence intensity as a function of the concentration of Fe^{3+} and Eq. 1 was used for calculation of LOD values. According to the fluorescence titration curve limits of detection of sensors for Fe^{3+} were determined by Stern-Volmer plot [51] and this value was found as 0.37 mg/L (6.76 μM) which is allowed for the detection of micromolar concentration range of Fe^{3+} .

$$\text{LOD} = 3\sigma/K \quad (1)$$

in this equation; σ is standard deviation of ten repetitive measurements of blank sample, K , slope of calibration curve. The Benesi-Hildebrand equation (Eq. 2) was used for determine the association constant (K_a) of cyclophosphazene- Fe^{3+} complexes [52, 53].

$$\frac{1}{F-F_0} = \frac{1}{K_a x (F_{\max} - F_0) x [\text{Fe}^{3+}]} + \frac{1}{F_{\max} - F_0} \quad (2)$$

fluorescence intensity of sensor at 460 nm at a given Fe^{3+} concentration is F , fluorescence intensity of free chemosensor is F_0 , maximum fluorescence intensity of chemosensor at 460 nm with Fe^{3+} is F_{\max} . In this equation, plotting $1/(F-F_0)$ versus $1/[\text{Fe}^{3+}]$. The data were linearly fitted to the Benesi-Hildebrand equation and the K_a value was obtained from the slope and intercept of the line. The association constant (K_a) for Fe^{3+} binding in coumarin substituted cyclophosphazene chemosensors were determined to be $4.91274 \times 10^5 \text{ M}^{-1}$.

The interference from competitive metal ions

Selectivity is significant and essential phenomenon for chemosensors. To further evaluate the selectivity of coumarin substituted cyclophosphazene chemosensors toward various metal ions, competitive experiments were conducted to study the influence of other metal ions on Fe^{3+} binding with these chemosensors. For this purpose, one equivalent of Mg^{2+} , Ca^{2+} , Ba^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ag^+ , Na^+ , Cd^{2+} , Hg^{2+} , Pb^{2+} , Cr^{3+} , K^+ , Li^+ and Al^{3+} as competitive metal ions was used and mixture of competitive metal ions absence and presence of Fe^{3+} were added to solution of coumarin substituted cyclophosphazene chemosensors. Figure 9 shows that competitive metal ions had no interference for detection of Fe^{3+} . According to these results, newly synthesized cyclophosphazene compounds can be clearly used for Fe^{3+} detection with high selectivity over other competitive metal ions in aqueous solution.

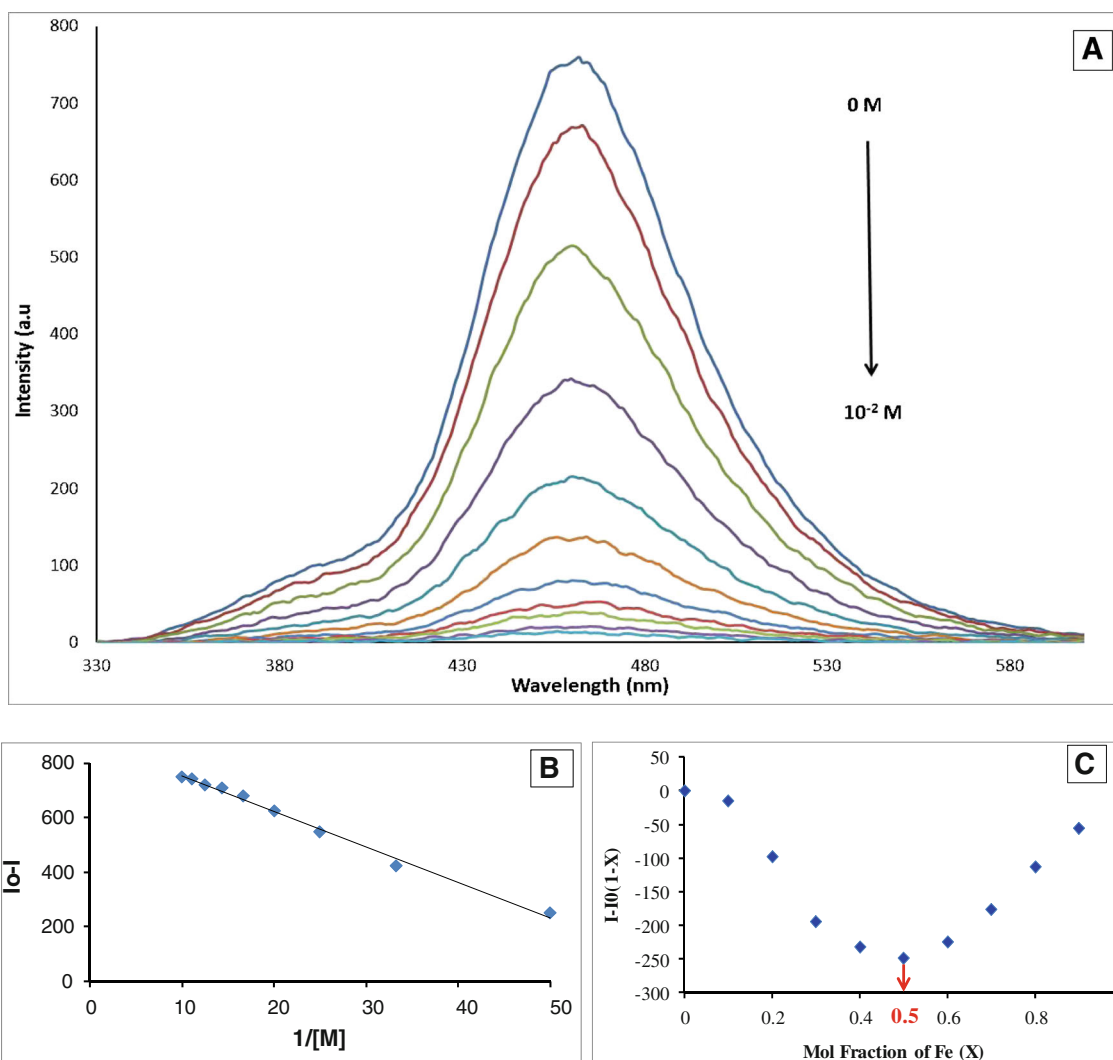
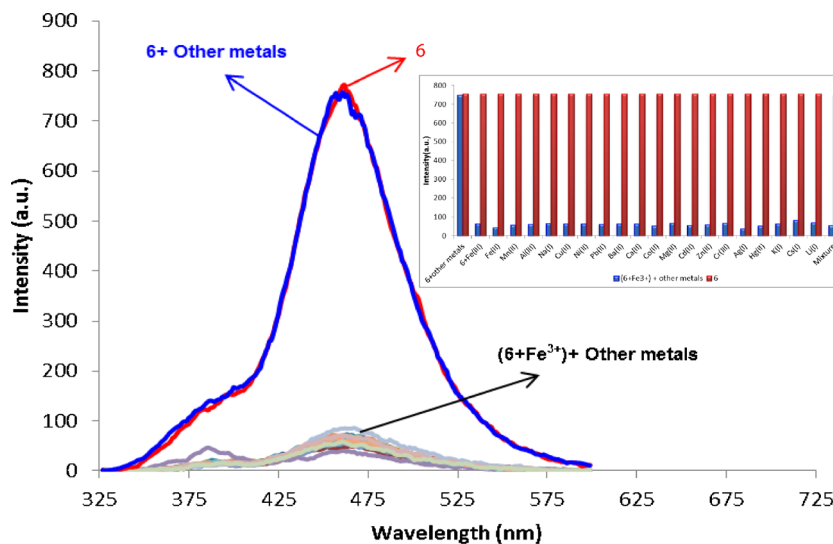


Fig. 8 (a) Fluorescence response of chemosensor **6** to various equivalents of Fe³⁺. (b) The Benesi-Hildebrand graph and (c) Job's plot of **6**-Fe³⁺ complexes in aqueous solutions. The total concentration of **6** and Fe³⁺ was 1 × 10⁻² M. The excitation wavelength was 320 nm. The monitored wavelength was 460 nm

Fig. 9 Fluorescence response of chemosensor **6** ($C = 1.00 \times 10^{-5}$ M) to various cations in aqueous solution (Excitation wavelength = 315 nm). The red bars represent the fluorescent intensity of chemosensor **6**. The blue bars represent the fluorescence changes that occur upon the addition of competing ions to the solution containing chemosensor **6** and Fe³⁺ (The concentration of the metal ions is 1 × 10⁻² M)



Conclusion

The synthesis and characterization of six or eight 3-[2-(diethylamino)ethyl]-7-oxy-4-methylcoumarin substituted trimeric and tetrameric phosphazene compounds (**4** and **5**) and their quaternized (**6** and **7**) and zwitterionic derivatives (**8** and **9**) were reported for the first time in this study. The newly synthesized coumarin substituted cyclophosphazene derivatives showed good solubility in most of organic solvents. In addition to this, the quaternized ionic (**6** and **7**) and zwitterionic derivatives (**8** and **9**) showed excellent solubility in water. The newly synthesized compounds **5**, **7** and **9** are the first examples of coumarin substituted cyclotetraphosphazene compounds. On the other hand, the synthesized quaternized (**6** and **7**) and zwitterionic (**8** and **9**) cyclophosphazene compounds are the first examples of water soluble derivatives of coumarin substituted cyclophosphazene compounds. The fluorescence behaviors of the synthesized compounds were investigated in methanol for all compounds and in both methanol and aqueous solutions for quaternized ionic and zwitterionic compounds. The studied quaternized ionic and zwitterionic compounds showed approximately 60 nm red-shifted emission peak in water compared to in methanol. This could be attributed to the formation of hydrogen bonds between coumarin groups and water molecules. In addition, the effects of metal ions to the fluorescence behavior of the studied compounds were studied in order to use the compounds as chemosensors for metal ions. For this purpose the water soluble quaternized ionic (**6** and **7**) and zwitterionic (**8** and **9**) compounds were tested because the determination of the metal ions in aqueous solution is very important for biological and environmental applications. A significant decrease in the fluorescence signal of quaternized ionic and zwitterionic compounds by the addition of the Fe^{3+} cation were observed in aqueous media. All coumarin substituted quaternized ionic and zwitterionic cyclophosphazene compounds (**6–9**) showed highly selectivity towards Fe^{3+} ions and these newly synthesized compounds have the potential to use as chemosensors for this metal ion in aqueous media.

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