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A new cyclotriphosphazene appended phenanthroline derivative as a highly selective and sensitive OFF–ON fluorescent chemosensor for Al^{3+} ions

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ABSTRACT

A new type of fluorescent chemosensor based on a novel cyclotriphosphazene appended phenanthroline derivative was synthesized and its sensing behavior toward metal ions was investigated by UV/vis and fluorescence spectroscopies. Addition of an Al^{3+} ion to an acetonitrile solution of the phenanthroline derivative exhibited a significant increase of fluorescence emission intensities, while 18 other metal ions induced no spectral changes. This phenanthroline derivative, as a candidate for an OFF-ON fluorescent chemosensor for Al^{3+}, was found to be highly selective and sensitive with a low limit of detection (1.825 μg L^{-1}).

1. Introduction

The design and construction of fluorescent chemosensors with high selectivity and sensitivity to metal ions such as aluminium, iron and copper have been the subject of intense study because of their potential application in supramolecular chemistry, organic chemistry, drug delivery, biological chemistry and environmental research [1–3]. Among these various metal cations, aluminium is the most plentiful metal ion and the third most plentiful of all elements in the earth [4]. Also, aluminium is extensively use in industrial process, pharmaceuticals and food additives [5,6]. However, over-exposure to aluminium can affect calcium absorption in bone and cause disturbances of bone development also disturbs iron absorption in blood and cause anemia. In addition, long-term exposure to aluminium can damage specific cells and causes several neurological diseases such as Alzheimer's [7] and Parkinson's disease [8]. Maximum acceptable daily aluminium intake to body was determined as a 3–10 mg in a day. World Health Organization was reported allowable aluminium intake into body as a 7 mg kg^{-1} [9–11]. In contrast to other metal cations, the detection of Al^{3+} is always problematic due to strong hydration ability, poor coordination capacity and lack of spectroscopic characteristics of Al^{3+} [12–14]. Consequently, there have been studied various methods on designing new, selective and sensitive Al^{3+} detection [15–17]. While many instrumental methods can be used for metal detection [18–21] including inductively coupled plasma atomic emission (ICP-AES), inductively coupled plasma mass spectroscopy (ICP-MS) and atomic absorption spectroscopy (AAS), chemosensors gains great attention due to their selectivity, sensitivity and simplicity for the determination of the different metal cations in aqueous or organic media [22–25]. Although various chemosensors have been described for the detection and determination other metal ions, the design of selective and sensitive fluorescence sensors for Al^{3+} ion is still important research area [26–28].

Phosphazene compounds are inorganic heterocyclic compounds which included phosphorus and nitrogen atoms and characterized by the double bond between them [29–31]. These compounds have halogen atoms bound to phosphorus atoms in their structure which may easily undergo a substitution reaction with nucleophilic compounds such as amines, alcohols, and phenols [32–34].

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Additionally, the cyclotriphosphazenes are interesting compounds as a core for the synthesis of new fluorescence sensors due to substituted groups on phosphorus atoms can be used as fluorophore and ionophore for metal detection [35,36]. There are many examples the simple protected aminophenanthroline derivatives and their transition metal complexes in literature (some examples: [37–40]). To the best of our knowledge, there is no selective phenanthroline example towards Al^{3+} ions in literature. It is well-known that cyclophosphazene or (pentaphenoxycyclophosphazene as starting material for compound **2**) is optically inert with no effect on chromophore emission therefore there is no part in to change the emission behavior of compound **2** which is a fluorescent probe for the selective determination of Al^{3+} with almost non-interference by Fe^{3+} although Cu^{2+} did interfere. However, the contribution of having the cyclophosphazene unit present is most probably that the steric routing of aminophenanthroline as pendant group attached to cyclophosphazene core behind its main advantages such as to produce a rigid spherical core from which to grow the fluorophore of interest and better thermal stability.

In this current study, we report a phenanthroline group has been appended with cyclotriphosphazene ring bearing five phenoxy substituents. We also demonstrated the sensor behavior of phenanthroline substituted phosphazene derivate **2** for selective fluorometric detection of Al^{3+} ion and determined the detection limit of compound **2** as 1.825 μg L^{-1} for Al^{3+}. Compound **2** was synthesized in a simple reaction and characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ESI-mass spectrometry. Compound **2** (1 μM) exhibits a characteristic weak monomer emission band from the phenanthroline moiety at 425 nm, which after addition of Al^{3+} ions the emission of compound **2** - Al complex shifts to 493 nm with a Stokes shift of 68 nm when excited at 300 nm. The stoichiometry between the phenanthroline sensor and Al^{3+} was determined by Job's plot as a 3:1 (ligand: metal ion) and limit of detection of compound **2** was calculated to be 6.764×10^{-8} M (1.825 μg L^{-1}) for Al^{3+} ions. To the best of our knowledge, only a few fluorescent sensors for Al^{3+} with moderate success have been reported [14,41–43]. The results indicated that the detection limit is lower than many other fluorescence sensors in the literature [44–47].

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (Otsuka Chemical Co. Ltd) was purified by fractional crystallization from n-hexane. The deuterated solvent ($CDCl_3$) for NMR spectroscopy and the following chemicals were obtained from Merck: tetrahydrofuran (THF), silica gel 60; Aldrich: phenol, 1,10-phenanthroline-5-amine, sodium hydride (NaH). All other reagents and solvents were reagent grade quality and were obtained from commercial suppliers.

2.2. Equipment

Electronic absorption spectra were recorded with a Shimadzu 2101 UV spectrophotometer in the UV–visible region. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. The fluorescence lifetimes were obtained using Horiba- Jobin-Yvon-SPEX Fluorolog 3-2iHR instrument with Fluoro Hub-B Single Photon Counting Controller at an excitation wavelength of 470 nm. Signal acquisition was performed using a TCSPC module. The mass analyzer was a Bruker Daltonics (Bremen, Germany) MicrOTOF mass spectrometer equipped with an orthogonal electrospray ionization (ESI) source. The instrument was operated in positive ion mode using a *m*/*z* range of 50–3000. The capillary voltage of the ion source was set at 4500 V and the capillary exit at 210 V. The nebulizer gas flow was 0.6 bar and drying gas flow 4 L/min. The drying temperature was set at 200 °C.The transfer time of the source was 88 ms and the hexapole radiofrequency (RF) was 800.0 Vpp. Elemental analysis was carried out using Thermo Finnigan Flash. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions on a Varian 500 MHz spectrometer. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck, Kieselgel 60A, 0.25 mm thickness) with F254 indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60A, 230–400 mesh). Suction column chromatography was performed on silica gel (Merck, Kieselgel 60A, 70–230 mesh).

2.3. Synthesis

The 1,1,3,3,5-pentaphenoxy-5-chlorocyclotriphosphazatriene (**1**) was prepared and purified according to the literature procedure [48].

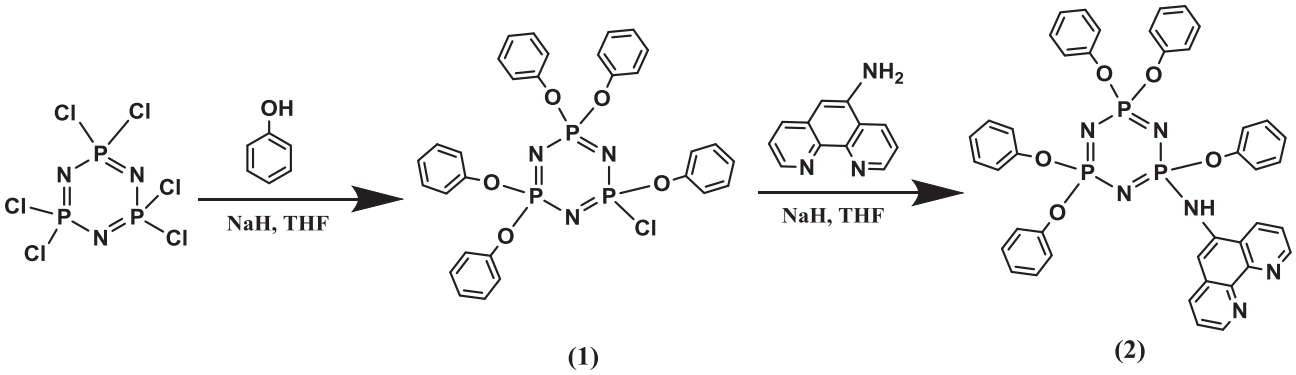
2.3.1. Synthesis of 1,1,3,3,5-pentanaphtoxy-5-(1,10-phenanthroline-5-amino) cyclotriphosphazatriene (*2*)

Sodium hydride (NaH) (0.044 g, 60%, 1.1 mmol) was added to a stirred solution of 1,10-phenanthroline-5-amine (0.18 g, 0.94 mmol) dissolved in THF (20 mL) under an argon atmosphere. Compound (**1**) (0.5 g, 0.78 mmol) in THF (20 mL) was added dropwise to a stirred solution under an argon atmosphere for 30 min. The reaction mixture was stirred for 3 h at room temperature and the reaction was followed by TLC. The precipitated salt was then filtered off and the solvent was removed under reduced pressure and compound **2** was isolated by column chromatography silicagel 60 (230–400 mesh) as adsorbent and THF/n-hexane (1:1) as the eluent. Yield 0.3 g (60%). Anal. Calc. for $[C_{42}H_{33}N_6O_5P_3]$ Found: C,63.40; H, 4.08; N, 10.51%; requires: C, 63.48; H, 4.19; N, 10.58%. MS (ESI) *m*/*z* (%) Calc.: 795.1798; found: 795.3481 (100) $[M+H]^+$.^{1}H NMR ($CDCl_3$, ppm) δ: 9.19 (s, 1H), 9.09 (s, 1H), 8.06 (d, $J = 7.16$ Hz, 1H), 7.82 (d, $J = 14.22$ Hz, 2H), 7.54 (d, $J = 17.22$ Hz, 2H), 7.18–7.14 (m, 5H), 7.07–6.98 (m, 20H), 5.43 (s, 1H, NH); {1H}^{13}C NMR ($CDCl_3$, ppm) δ:151.85, 151.00, 150.86, 150.30, 149.15, 146.78, 143.82, 136.12, 135.63, 132.93, 129.71, 129.64, 129.02, 128.51, 125.84, 125.26, 125.15, 123.63, 122.71, 121.57, 121.40, 121.24, 114.84; {1H}^{31}P NMR ($CDCl_3$, ppm), assigned as an AB_2 spin system δ: 13.05 [dd, 1P, P(OPh)(phenanthroline),A], 9.6 [dd, 2P, $P(OPh)_2$, B_2], $^{2}J_{P,P} = 83.4$ Hz and $^{2}J_{P,P} = 5.7$ Hz.

3. Results and discussion

3.1. Synthesis and structural characterization

The synthetic routes for the preparation of compounds **1** and **2** are shown in Scheme 1. Compound **1** was prepared according to a lit. procedure [48]. Compound **2** was obtained from nucleophilic displacement reaction of **1** with the commercially available 1,10-phenantroline-5-amine under an argon atmosphere, with NaH as a base. The compound **2** was purified by column chromatography on silica gel using n-hexane:THF (1:1) as the eluent. The new compound **2** was characterized by elemental analysis, mass spectrometry, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. All the results are consistent with the predicted structure as shown in the experimental section. Molecular weight of **2** has been determined by ESI mass spectrometry. Mass spectral identification is based on matching measured accurate mass and isotopic pattern of a sample. Theoretical and measured isotopic patterns as an additional



Scheme 1. Chemical structure and synthetic pathway of compound **2**.

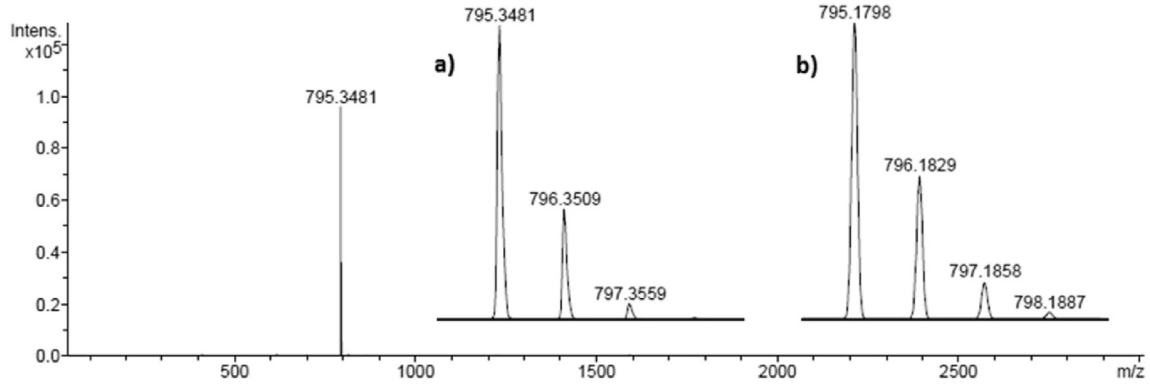


Fig. 1. Positive-ion mode electrospray ionization (ESI) mass spectrum of **2**. See inset: (a) experimental isotopic pattern and (b) theoretical isotopic pattern.

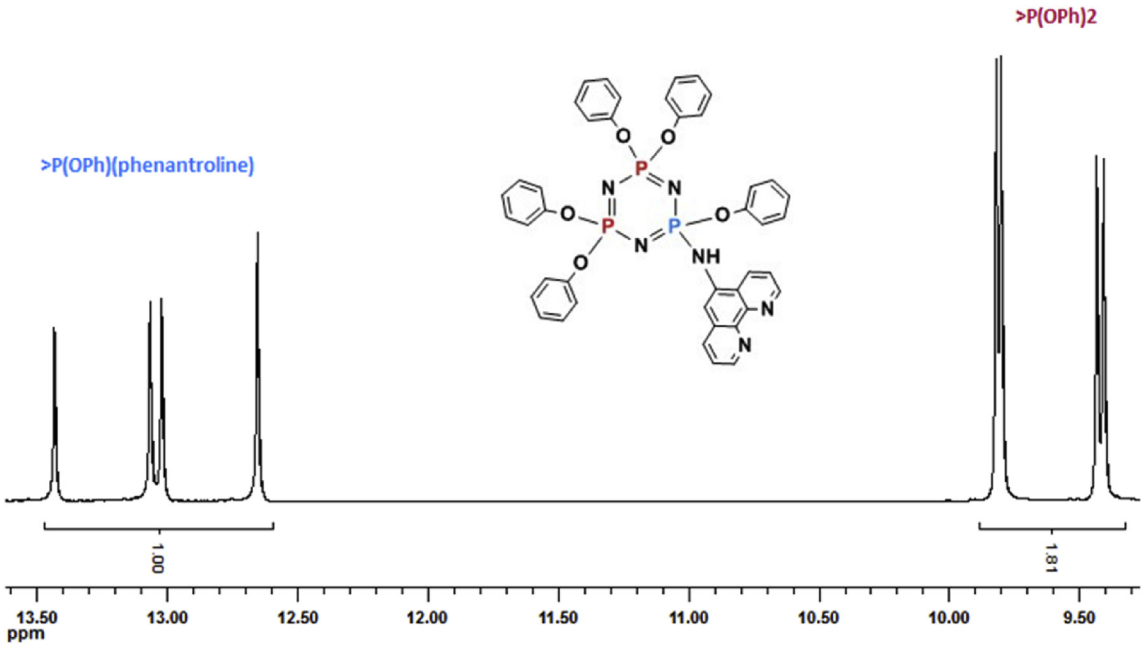


Fig. 2. The ^{31}P NMR spectra of compound **2** in $CDCl_3$.

identification tool to accurate mass determination of **2** and the positive ion ESI mass spectrum is given in Fig. 1. The peak group representing the protonated molecular ion of **2** was observed at 795.1798 Da mass (Fig. 1). The aromatic protons are shown in the region δ: 6.98–9.19 ppm. The proton signal of NH group is observed at 5.43 ppm as broad signal. The integration of the aromatic proton signals to the NH proton signal in the ^{1}H NMR spectrum of compound **2** gave approximately a 32:1 proton ratio that confirmed the suggested structure (Fig. S1). ^{13}C NMR spectrum of **2** shows all signals for aromatic carbons between 151.85 and 114.84 ppm (Fig. S2). The proton-decoupled ^{31}P NMR spectrum of compound **2** signals is observed AB_2 spin system and the resonances belonging to phosphorous atoms are observed at ca. 13.05 ppm for > P(OPh)(phenantroline) and at ca. 9.6 ppm for > $P(OPh)_2$, also the magnitude of the $^{2}J(P,P)$ at ca. 83.4 Hz and $^{2}J_{P,P}$ at ca. 5.7 Hz. (Fig. 2).

3.2. Chemosensor properties of compound 2

The UV–Vis spectroscopic experiment of compound **2** was measured in acetonitrile with dilute solutions of 1×10^{-5} M. Compound **2** exhibits an absorption band has a maximum at 272 nm, which remains unchanged upon the addition of 2 equiv. of various metal ions (Li^{+}, Na^{+}, K^{+}, Cs^{+},Mg^{2+}, Ca^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Ag^{+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Cr^{3+} and Fe^{3+}) are shown in Fig. 3. In the case of Al^{3+}, the absorption band has a maximum as red-shifted to 293 nm. A clear isosbestic point was observed at 279 nm when spectra were recorded with varying concentrations of Al^{3+}. As shown in Fig. 3a, addition of 2 equivalent Al^{3+} resulted in an obvious change indicating compound **2** had higher binding affinity towards Al^{3+} than other surveyed metal ions. In order to receive more information about binding mechanism of compound **2** towards Al^{3+} spectrometric titration experiments were performed in the presence of Al^{3+}. As depicted in Fig. 3b, while the sequential addition of Al^{3+} ions from 5 μM to 45 μM to the solution of compound **2** showed a gradual increase in absorbance at 293 nm. Consequently, compound **2** could provide as a sensitive fluorescent chemosensor for Al^{3+} cations. The changes in the absorption curve of compound **2** could be assigned to a charge transfer transition occurring between the ligand and metal ion.

Compound **2** alone did not show any significant emission upon

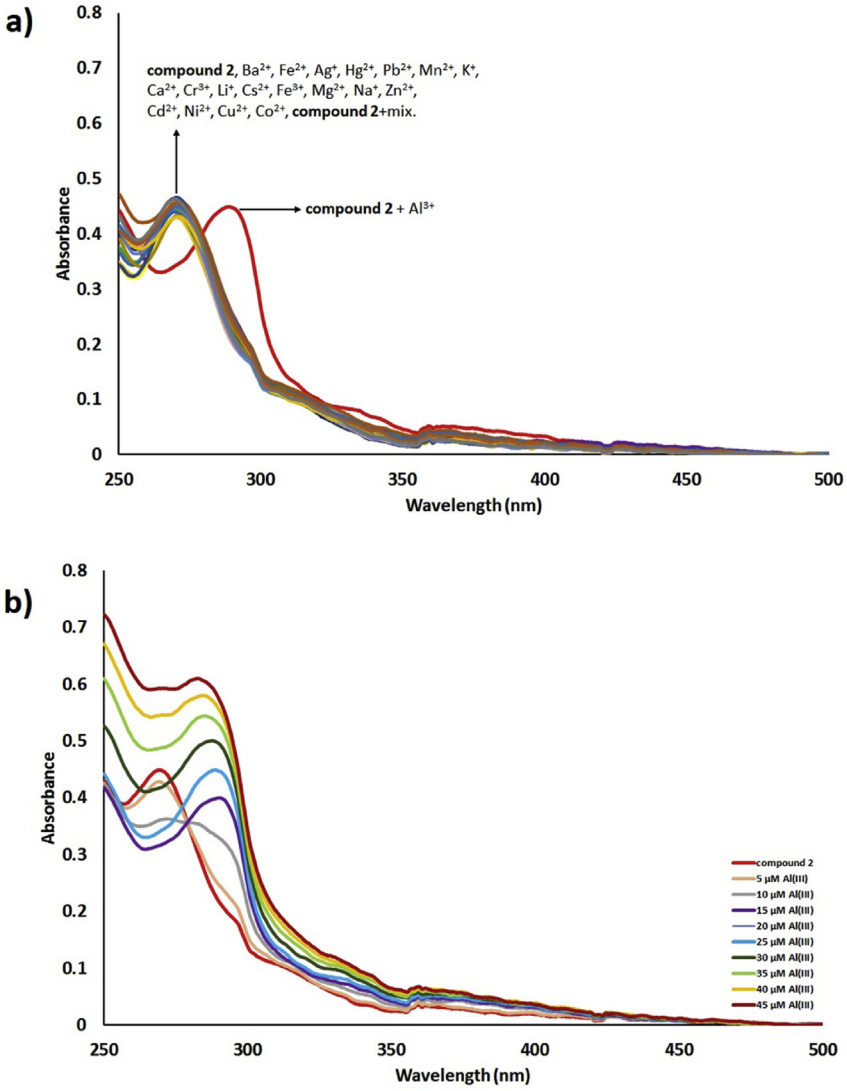


Fig. 3. UV–Vis absorption change profiles of compound **2** (10.0 μM) in CH_3CN with **a**) various metal ions (20.0 μM), **b**) gradual addition of Al^{3+}.

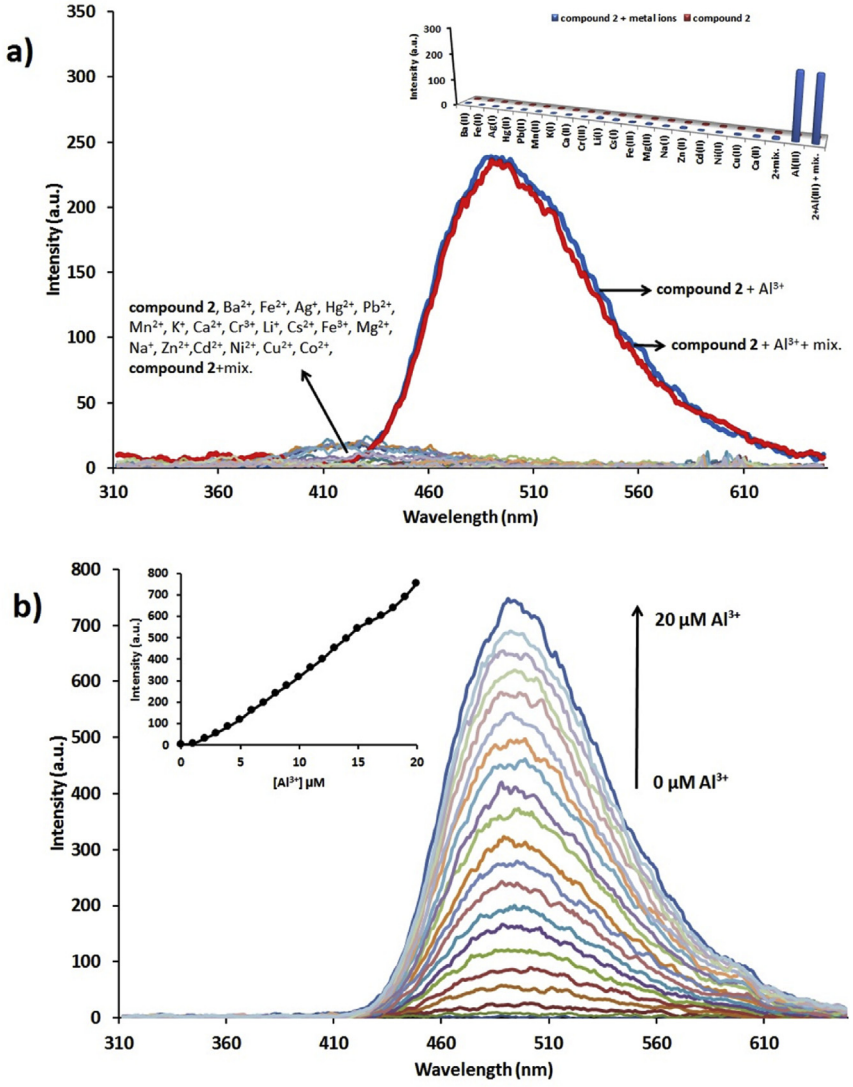


Fig. 4. Fluorescence responses of compound **2** (1.0 μM) in CH_3CN solution upon the addition of **a**) 8 equiv. various metal ions (Excitation wavelength = 300 nm). Inset: Metal ions selectivity of compound **2**. **b**) various concentration of Al^{3+} in CH_3CN solution (Excitation wavelength = 300 nm).

excitation at 300 nm. However, Al^{3+} treatment resulted in a large increase in intensity at a wavelength of 490 nm. In contrast, no fluorescence enhancement was observed after adding other mono-, di-, and tri-valent metal ions including Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Ag^+, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Cr^{3+} and Fe^{3+} (Fig. 4a). The selectivity of compound **2** for Al^{3+} was studied in the presence of various competing metal ions. For this purpose, competition ion studies were also performed for compound **2** in the presence of Al^{3+} at 1 μM mixed with 8 μM of the tested metal cations such as (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Ag^+, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Al^{3+}, Cr^{3+} and Fe^{3+}) (Fig. 4a inset). It was clearly found from this study that the interference of other ions was insignificant during the detection of Al^{3+}. Fluorescence titration experiments were carried out in order to understand the binding mode of compound **2** with Al^{3+} (Fig. 4b). The fluorescence titration profile of compound **2** with Al^{3+} in the range of 0–20 equivalents showed the Al^{3+} sensitivity of sensor. The detection limit of compound **2** for Al^{3+} ion by fluorescence changes was calculated on the basis of 3σ/k [49–51] where σ is deviation of the blank signal and k is slope of calibration curve was found to be 6.764×10^{-8} M ($1.825\ \mu g\ L^{-1}$) pointing to the high detection sensitivity (Fig. 5a). These results suggested that compound **2** can be used for the selective detection of Al^{3+} in acetonitrile solution. Job's plot analyses were used for investigate the stoichiometry between compound **2** and Al^{3+} (Fig. 5b). A Job plot obtained from emission data showed 3:1 stoichiometric complexation between compound **2** and Al^{3+}. As shown in Fig. 5c, the association constant K of the target complex was then calculated to be $1.51 \times 10^8\ M^{-1}$ via the Benesi–Hildebrand equation. Time resolved fluorescence studies (using a 390 nm laser source and monitoring 490 nm as λ_{ems}) revealed a single exponential decay for compound **2** emission and the lifetime was found to be 5.859 (±0.085) ns for compound **2** and 18.407 (±0.023) ns for compound **2** + Al^{3+}. Changes in the lifetime from τ = 5.859 ns to τ = 18.407 ns clearly showed binding of Al^{3+} to compound **2** (Fig. 6).

Precision of the sensor is an important analytical parameter for sensor application. Therefore, ten measurements were performed for 1×10^{-6} M of Al^{3+} under the same conditions. The relative standard deviation (% RSD) was calculated as %2.70.

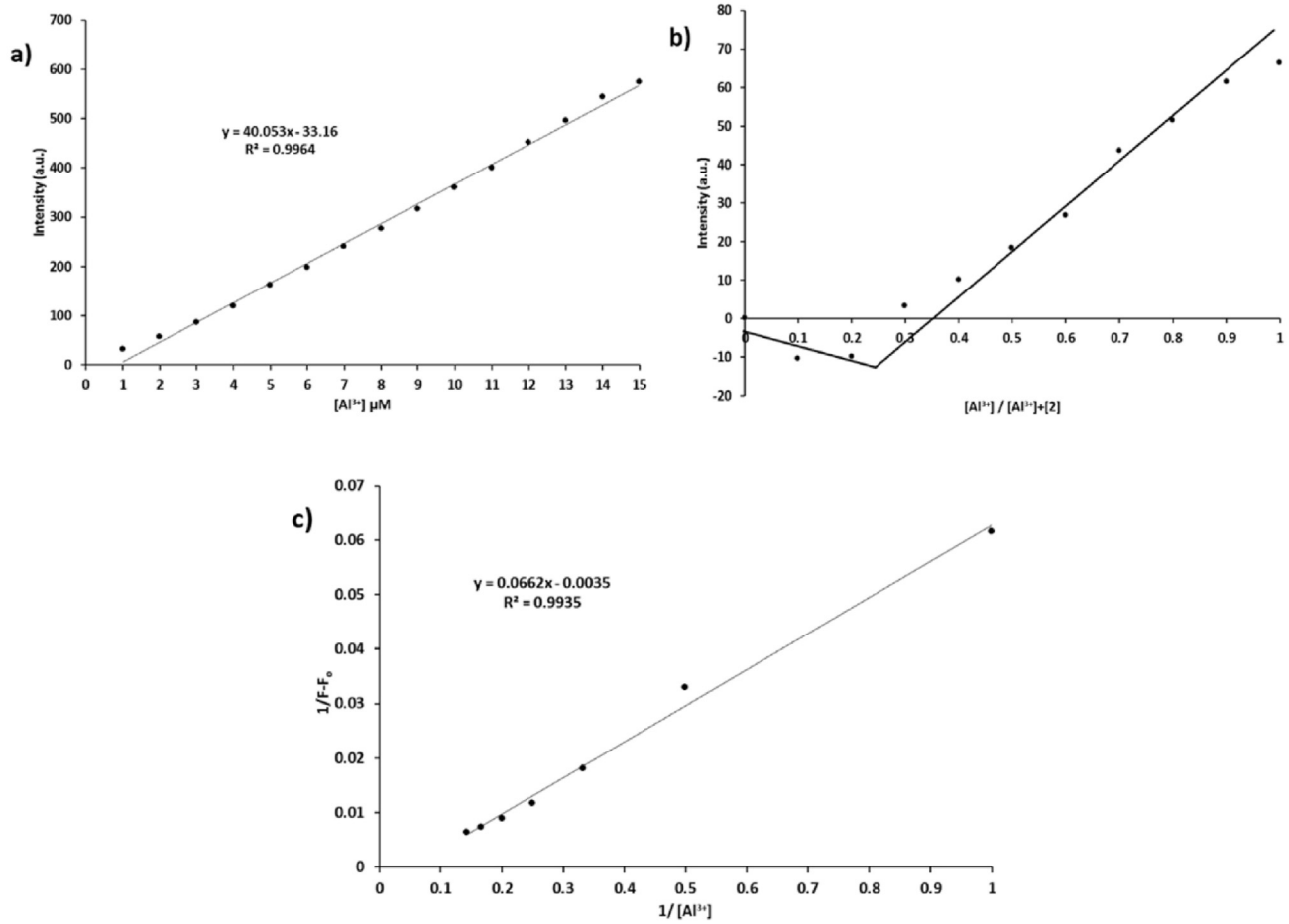


Fig. 5. **a**) Fluorescence intensity of compound **2** (1 μM) versus Al^{3+} ions. **b**) The Job's plot for compound **2** and Al^{3+}. **c**) Plot of $1/F-F_0$ against $1/[Al^{3+}]$ for compound **2** in CH_3CN solution.

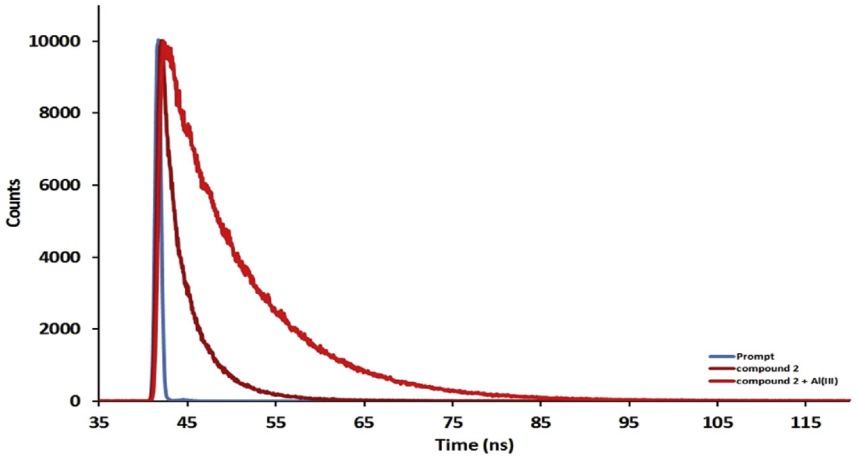


Fig. 6. Fluorescence decay profile of compound **2** in the presence and absence of Al^{+3} using laser excitation source of 390 nm.

According to these results, high reproducibility can provided for selected sensor.

4. Conclusion

In conclusion, a new type cyclotriphosphazene appended phenanthroline derivative (compound **2**) was synthesized and characterized for recognition of Al^{3+}. It was found that compound **2** showed a remarkable selectivity and sensitivity response towards Al^{3+} by using UV–vis and fluorescence methods. According to Job's plot, binding stoichiometry was found by fluorescence method as 3:1 2 + Al^{3+}. The detection limit of compound **2** was found to be 6.764×10^{-8} M (1.825 μg L^{-1}) for Al^{3+}.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.05.006.

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