



# A new cyclotriphosphazene appended phenanthroline derivative as a highly selective and sensitive OFF–ON fluorescent chemosensor for Al<sup>3+</sup> 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<sup>3+</sup> 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<sup>3+</sup>, was found to be highly selective and sensitive with a low limit of detection (1.825 µg L<sup>-1</sup>).

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## 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 used 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.

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World Health Organization was reported allowable aluminium intake into body as a 7 mg kg<sup>-1</sup> [9–11]. In contrast to other metal cations, the detection of Al<sup>3+</sup> is always problematic due to strong hydration ability, poor coordination capacity and lack of spectroscopic characteristics of Al<sup>3+</sup> [12–14]. Consequently, there have been studied various methods on designing new, selective and sensitive Al<sup>3+</sup> 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 gain 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 of other metal ions, the design of selective and sensitive fluorescence sensors for Al<sup>3+</sup> ion is still an important research area [26–28].

Phosphazene compounds are inorganic heterocyclic compounds which include phosphorus and nitrogen atoms and are 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].

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  $\text{Al}^{3+}$  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  $\text{Al}^{3+}$  with almost non-interference by  $\text{Fe}^{3+}$  although  $\text{Cu}^{2+}$  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  $\text{Al}^{3+}$  ion and determined the detection limit of compound **2** as  $1.825 \mu\text{g L}^{-1}$  for  $\text{Al}^{3+}$ . Compound **2** was synthesized in a simple reaction and characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{31}\text{P}$  NMR and ESI-mass spectrometry. Compound **2** ( $1 \mu\text{M}$ ) exhibits a characteristic weak monomer emission band from the phenanthroline moiety at 425 nm, which after addition of  $\text{Al}^{3+}$  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  $\text{Al}^{3+}$  was determined by Job's plot as a 3:1 (ligand: metal ion) and limit of detection of compound **2** was calculated to be  $6.764 \times 10^{-8} \text{ M}$  ( $1.825 \mu\text{g L}^{-1}$ ) for  $\text{Al}^{3+}$  ions. To the best of our knowledge, only a few fluorescent sensors for  $\text{Al}^{3+}$  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 ( $\text{CDCl}_3$ ) 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.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded in  $\text{CDCl}_3$  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-pentanaphoxy-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  $[\text{C}_{42}\text{H}_{33}\text{N}_6\text{O}_5\text{P}_3]$  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)  $[\text{M} + \text{H}]^+$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$ : 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);  $\{^1\text{H}\}^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$ : 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;  $\{^1\text{H}\}^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , ppm), assigned as an  $\text{AB}_2$  spin system  $\delta$ : 13.05 [dd, 1P, P(OPh)(phenanthroline),A], 9.6 [dd, 2P, P(OPh) $_2$ , B $_2$ ],  $^2J_{\text{P,P}} = 83.4$  Hz and  $^2J_{\text{P,P}} = 5.7$  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-phenanthroline-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,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  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

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