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Novel iron(III) selective fluorescent probe based on synergistic effect of pyrene-triazole units on a cyclotriphosphazene scaffold and its utility in real samples

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ABSTRACT

A novel Fe^{3+} fluorescent probe based on cyclotriphosphazene platform with three pyrene-triazole units at the upper rim as fluoroionophores and three triethylene glycol monomethyl ether units at the lower rim as solubility agents was designed and synthesized for Fe^{3+} ions in mixed aqueous media. The probe exhibited metal-binding ability due to the synergistic effect of among three pyrene-triazole moieties on a cyclotriphosphazene scaffold. The fluorescence emission was significantly quenched by the addition of Fe^{3+} while other added other metal ions and anions induced no spectral changes. The probe sensing conditions such as solvent effects, concentration, competitive metal/anion ions, pH, measurement time and ion binding capability were comprehensively investigated and optimized. The probe was also used for applications in direct determination of Fe^{3+} in real samples including sea water, tap water, industrial waste water and some medicine tablets. Obtained the results were validated with corresponding data from the spike/recovery test and ICP-OES as the standard analysis method. The synthesized probe was found to be highly selective and sensitive for Fe^{3+} with both a limit of detection (0.32 μM) and a limit of quantification (2.88 μM) as being satisfactory when compared with other existing system for the determination of iron ions.

1. Introduction

In past two decades, the significance of detection and determination of metal ions for living organisms and environmental media has been recognized [1,2]. Iron is important for oxygen transport in hemoglobin and myoglobin in human body [3,4]. Additionally, iron is an important element for production of energy and biological synthesis such as in DNA and RNA. However, both deficiency and excessive intake of iron in human body is associated with heart and liver diseases, cancer and neurobehavioral disorders such as Perkinson and Alzheimer's diseases [5–9]. Therefore, there is a great need for reliable, selective, and sensitive analytical methods for detection, determination and monitoring iron levels in not only biological but also industrial and environmental samples [10]. Many analytical methods have been used for determination of iron in environmental and biological samples including ion pair chromagraphy, electrothermal atomization atomic absorption spectrometry (ETAAS), voltammetry, inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy [11–15]. However, these analytical methods are not accessible in-field and they cannot achieve continuous monitoring. Also, they require pre-concentrating processes with expert analysts for advanced equipment's before analysis and also reagents such as adsorbents and eluents may be required [16]. Therefore, the design and development of simple, sensitive, selective and quick determination methods for iron ions in environmental samples still challenging and an important research area for various disciplines. Fluorescence sensor technology has been widely used for detection of metal ions in organic or aqueous media due to the simplicity and rapidity of the method [17]. Also fluorescence sensors provide more sensitive and selective detection which leads to low detection limits without any pre-treatment processes. Basically, fluorescence sensor systems contain fluorophore and ionophore groups and this system called as “fluoroionophore”. In fluoroionophore systems the ionophore moiety provides interaction with metal ions when fluorophore part converts these recognition event to analytical signals via photophysical characteristic of fluorophore [18]. The design and synthesis of iron selective fluorescence sensors is crucial because they can be used for analytic applications for iron determination in environmental and biological sample such as sea water, tap water, industrial waste water and medicine tablets owning to changes in signal of fluorophore [19]. Although there are many reports published in the

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scientific literature about the fluorescence sensors for iron(III) detection based on both ionophore and fluorophore systems [20–24], there are rarely studies of the applied to real samples [25,26]. The major challenge in applying the sensor to real samples might be the complex background matrices along with the low concentrations of analytes which cause lack of selectivity and high detection limits. Therefore, there is still need for development of chemical sensors that can be applied to real systems as much as the design and synthesize of selective chemosensor for Fe ions.

In fluorescence sensor technology, “click” chemistry has been widely used by researchers because of the simplicity of synthesis with Cu(I)-catalysed azide–alkyne cycloaddition reaction and various advantages of 1,2,3 triazoles such as binding with analyte and serving as a linker between ionophore and fluorophore [27–29]. On the other hand, pyrene as a fluorophore is one of the most useful fluorogenic units due to its excellent fluorescent properties. The pyrenyl sensing systems involving two or more pyrene groups showed monomer or/and excimer emission as to pyrene groups interactions which can be operated via coordination with metal ions and chancing signals can be used for quantitative analysis in environmental and biological samples [30–32].

On the basis of such precedents, a flouroinonophore pyrene-triazole which can be easily synthesized with a modified-cyclotriphosphazene platform. The inorganic ring, hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, can provide a suitable platform for the design and construction of different kinds of excellent receptors in molecular recognition by easy chemical modifications. It is advantageous that optical properties of cyclotriphosphazene derivatives can be adjusted by substituents on phosphorus atoms because the cyclotriphosphazene scaffold is optically inert in UV–vis region [33]. There has been considerable interest in preparation of fluorescent probes containing cyclophosphazene cores for a few years [23,34–37]. Another advantage is also that $N_3P_3Cl_6$ has a planar structure which can be upper- and lower-rim functionalized with the different groups.

By taking these advantages, we have designed and synthesized a novel fluorescent probe based on cyclotriphosphazene platform with three pyrene-triazole units at the upper rim as fluoroionophores and three triethylene glycol monomethyl ether units at the lower rim as solubility agents. Moreover, due to the synergistic effect of among three pyrene-triazole moieties at the upper rim on the ring, the probe has been gained improved metal-binding ability.

After fully characterized by the standard spectroscopic techniques and optimization studies, the probe has been applied to real samples and the validation of proposed method has been carried out with spike/recovery test and ICP-OES analysis.

2. Experimental section

2.1. Materials and reagents

The chemicals were obtained commercially as follows; sodium azide (≥ 99.0%) (Merck), chloroform-d_1 (Merck), dimethyl sulfoxide-d_6 (Merck) and THF-d_8 (Merck) (for NMR spectroscopy), n-hexane (99%) (Merck), dichloromethane (99.0%) (Merck), cyclohexane (99%) (Merck), ethanol (99%) (Merck), acetonitrile (99%) (Merck), triethylene glycol monomethyl ether (≥ 97%) (Merck), sodium hydride (> 60%) (Sigma-Aldrich), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDTA) (≥ 98.0%) (Sigma-Aldrich), diethyl ether (≥ 99%) (Sigma-Aldrich), copper(I) bromide (98%) (Sigma-Aldrich), 2-bromoethanol (95%) (Sigma-Aldrich), tetrahydrofuran (> 99%) (Sigma-Aldrich), Hexachlorocyclotriphosphazene (Sigma-Aldrich), 1-ethynyl pyrene (%96) (Alfa aesar), and 1,8,9-Anthracenetriol (Fluka) for MALDI matrix. Before to use, tetrahydrofuran (THF), (Aldrich) was distilled over sodium/potassium alloy under an atmosphere of dry argon and sodium hydride which 60% dispersion in mineral oil, was washed with n-hexane to remove mineral oil. Hexachlorocyclotriphosphazene (trimer), was purified by fractional crystallization from n-hexane. Dry argon atmosphere was used for all reactions. Thin layer chromatography (TLC) and column chromatography were carried out on Merck silica gel plates (Kieselgel 60, F_{254} indicator, 0.25 mm) and silica gel (Kieselgel 60, 70–230 mesh) respectively.

2.2. Apparatus

Shimadzu 2101 UV spectrophotometer was used for absorption spectra in the UV–visible region. Fluorescence spectra were investigated with a Varian Eclipse spectrofluorometer with using 1 cm pathlength cuvettes at room temperature and slit widths were all set to 5 nm. The fluorescence lifetimes were measured with using Horiba-Jobin-Yvon-SPEX Fluorolog 3-2iHR instrument with Fluoro Hub-B Single Photon Counting Controller at an excitation wavelength of 390 nm. Signal acquisition was performed using a TCSPC module. Bruker Daltonics Microflex MALDI-TOF mass spectrometer were used to obtain mass spectra. NMR (^{31}P, ^{1}H, ^{13}C) spectra were recorded on a Varian INOVA 500 MHz spectrometer in $CDCl_3$-d_1, THF-d_8 and DMSO-d_6 (for ^{1}H NMR) and $CDCl_3$ and THF-d_8 (for ^{31}P and ^{13}C NMR) solutions using 85% H_3PO_4 as external reference for ^{31}P and TMS as internal reference for ^{1}H and ^{13}C NMR.

2.3. Synthesis

The required 2-azido-1-ethanol and triethylene glycol monomethyl ether (TEGME) bearing hexachlorocyclotriphosphazene compound (**1**) were synthesized according to the literature [38,39]. The ^{1}H, ^{31}P, ^{13}C NMR and MALDI-MS spectra of newly synthesized compounds (**2**, **3** and **4**) were given in supplementary material (Figs. S1-S4).

2.3.1. ((4-Pyrenyl) – 1,2,3-triazol-1-yl)-ethanol (2)

1-Ethynyl pyrene (0.200 g, 0.883 mmol), PMDETA (0.255 g, 1.47 mmol) and Cu(I)Br (0.212 g, 1.47 mmol) were added successively to a solution of 2-azido-1-ethanol (0.0641 g, 0.736 mmol) in DCM under argon atmosphere. The reaction mixture was stirred for 8 h at room temperature and followed by TLC. After the reaction was completed, the reaction mixture was extracted with DCM/H_2O. The organic phase was dried over Na_2SO_4. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, THF-n-hexane, 2:1, v/v) to afford a yellow solid. Yield: 0.212 mg, % 92.1. ^{1}H NMR (THF-d_8), 298 K, δ (ppm); 9.08 (d, J = 9.2 Hz, 1 H), 8.44 (s, 1 H), 8.36 (d, J = 7.8 Hz, 1 H), 8.27-8.22 (m, 3 H), 8.18-8.12 (m, 3 H), 8.03 (t, J = 7.4 Hz, 1 H), 6.94 (s, 1 H), 4.62 (t, J = 4.5 Hz, 2 H), 4.04 (t, J = 4.9 Hz, 2 H), ^{13}C NMR (THF-d_8), 298 K, δ (s, ppm); 146.71, 131.71, 131.54, 130.94, 128.15, 127.25, 127.16, 126.79, 126.63, 126.38, 125.79, 125.55, 125.33, 125.13, 124.76, 124.37, 124.15, 123.90, 60.79, 52.68, $[M]^+$: 313.1232 *m/z* (calc. $[M]^+$: 313.1215).

2.3.2. cis-2,4,6-tris(2-azidoethoxy)-tris(methyltriglycol) cyclotriphosphazene (3)

Compound **1**, (3.21 g, 4.39 mmol) and 2-azido-1-ethanol (1.91 g, 21.95 mmol) were dissolved in dry THF (30 mL) under argon atmosphere. After stirring for 15 min at room temperature, sodium hydride (0.88 g, 21.95 mmol) was added. The reaction mixture was stirred for 6 h at room temperature and followed by TLC. Upon the completion of the reaction, the reaction mixture was filtered from G4 sintered filter and the solvent was removed under reduced pressure. Compound **3** was isolated by column chromatography (silica gel, THF-DCM-*n*-hexane, 1:1:1, v/v/v) as an oil. Yield: 2.54 g, 65.5%, ^{1}H NMR ($CDCl_3$), 298 K, δ (ppm); 4.06 – 4.02 (m, 12 H), 3.64 (t, J = 4.8 Hz, 6 H), 3.60 – 3.56 (m, 18 H), 3.48 (t, J = 4.6 Hz, 6 H), 3.41 (t, J = 4.5 Hz, 6 H), 3.31 (s, 9 H), ^{13}C NMR ($CDCl_3$), 298 K, δ (s, ppm); 71.84, 70.52, 69.87, 65.28, 64.74, 58.93, 53.51, 50.71, ^{31}P NMR ($CDCl_3$) δ = 17.63 (s, 3 P), $[M+H]^+$: 883.3284 *m/z* (calc. $[M+H]^+$: 883.3357).