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Fluorescence properties of fluorenylidene bridged cyclotriphosphazenes bearing aryloxy groups

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ABSTRACT

The synthesis and characterization of the first series of aryloxy full-substituted fluorenylidene open chain and bridged cyclotriphosphazene derivatives (**13–18**) are reported in this study. The synthetic route utilized includes the reaction of penta-substituted cyclotriphosphazenes (**5**, **7**, **9**) with 4,4′-(9-fluorenylidene)diphenol (**FDP**) (**11**) and 4,4′-(9-fluorenylidene)dianiline (**FDA**) (**12**) to give bridged compounds (**13**, **15–17**) and open chain compounds (**14** and **18**). The structural investigations of the compounds were verified by elemental analyses, mass spectrometry, UV–Vis, FT-IR, ^{1}H and ^{31}P NMR techniques, and X-ray crystallography (for **13** and **18**). The fluorescence behavior of the studied cyclotriphosphazene derivatives were also examined in THF solution. Compound **16** showed a high emission among the studied compounds to investigate its metal sensing properties. This compound showed high selectivity for copper (Cu^{2+}) and iron (Fe^{2+}/Fe^{3+}) ions in solution.

1. Introduction

Organic compounds like fluorene and pyrene are remarkable for their fluorescence properties, thus these compounds are suitable for many applications, such as fluorescent probes for applications in sensors, liquid crystals, organic light-emitting diodes and electrochromic materials [1–6]. 4,4′-(9-Fluorenylidene)diphenol, (**FDP**) or 4,4′-(9-fluorenylidene)dianiline, (**FDA**), which are conjugated fluorenes, have been used for many applications and they have the potential to detect metal ions in biological and environmental media. The binding of certain metal ions to the fluorene molecule may influence the fluorescent properties of the molecule and hence indicate its presence in a solution [7–11].

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), as one member of the phosphazane group, has a six-membered ring and offers a rigid platform for multifunctional molecular arrangements. The chemical and physical properties of cyclotriphosphazenes change with the nature of the substituted side groups. Therefore, by means of these side groups, it is possible to enhance different properties of the molecules, such as flame retardant properties [12–14], liquid crystals [15–17], biological activity [18–22] and fluorescence properties [23–28]. There has recently been considerable interest in fluorescent compounds based on cyclic phosphazene cores or cyclo-linear polymers with cyclotriphosphazene units for the development of electroluminescent devices [27–34]. Ozay and colleagues have been synthesized a 1,2,3-triazole ring functionalized hexapodal rhodamine derivative on a cyclotriphosphazene core which showed high selectivity towards Fe^{3+} ions [23]. In our recent work, the metal sensing studies of **FDP** and **FDA** bridged cyclotriphosphazenes and their derivatives showed high selectivity towards Cu^{2+} and Fe^{2+} ions [24,25]. The results of these studies have encouraged us to investigate new phenol, naphthol and pyrene modified cyclotriphosphazene compounds containing **FDP** and **FDA** on the cyclotriphosphazene core.

In this study, we report the first derivatives of fluorenylidene bridged cyclotriphosphazenes (**13**, **15–17**) and their open chain derivatives (**14** and **18**). First, we prepared some pentasubstituted cyclotriphosphazene compounds (**5**, **7**, **9**). For the synthesis of the target compounds, hexachlorocyclotriphosphazene (**1**) was reacted with the cesium salts of phenol (**2**), 2-naphthol (**3**) and 1-hydroxypyrene (**4**) to give the penta- and hexasubstituted cyclotriphosphazene compounds (Scheme 1). Then, the pentasubstituted cyclotriphosphazene compounds (**5**, **7**, **9**) were reacted with **FDP** (**11**) and **FDA** (**12**), and the aryloxy full-substituted fluorenylidene-bridged cyclotriphosphazene derivatives (**13–18**) were obtained (Scheme 2). All the compounds were characterized by elemental analysis, mass spectrometry, UV–Vis, FT-IR, ^{1}H, ^{31}P NMR and X-ray crystallography (for **13** and **18**), together with fluorescence spectroscopy techniques. The metal binding properties of the synthesized **FDP**-bridged cyclotriphosphazene compounds (**13-16**) were investigated by fluorescence spectroscopy.

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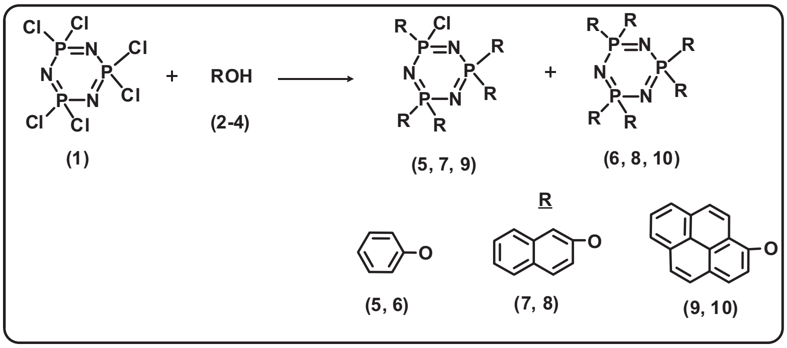
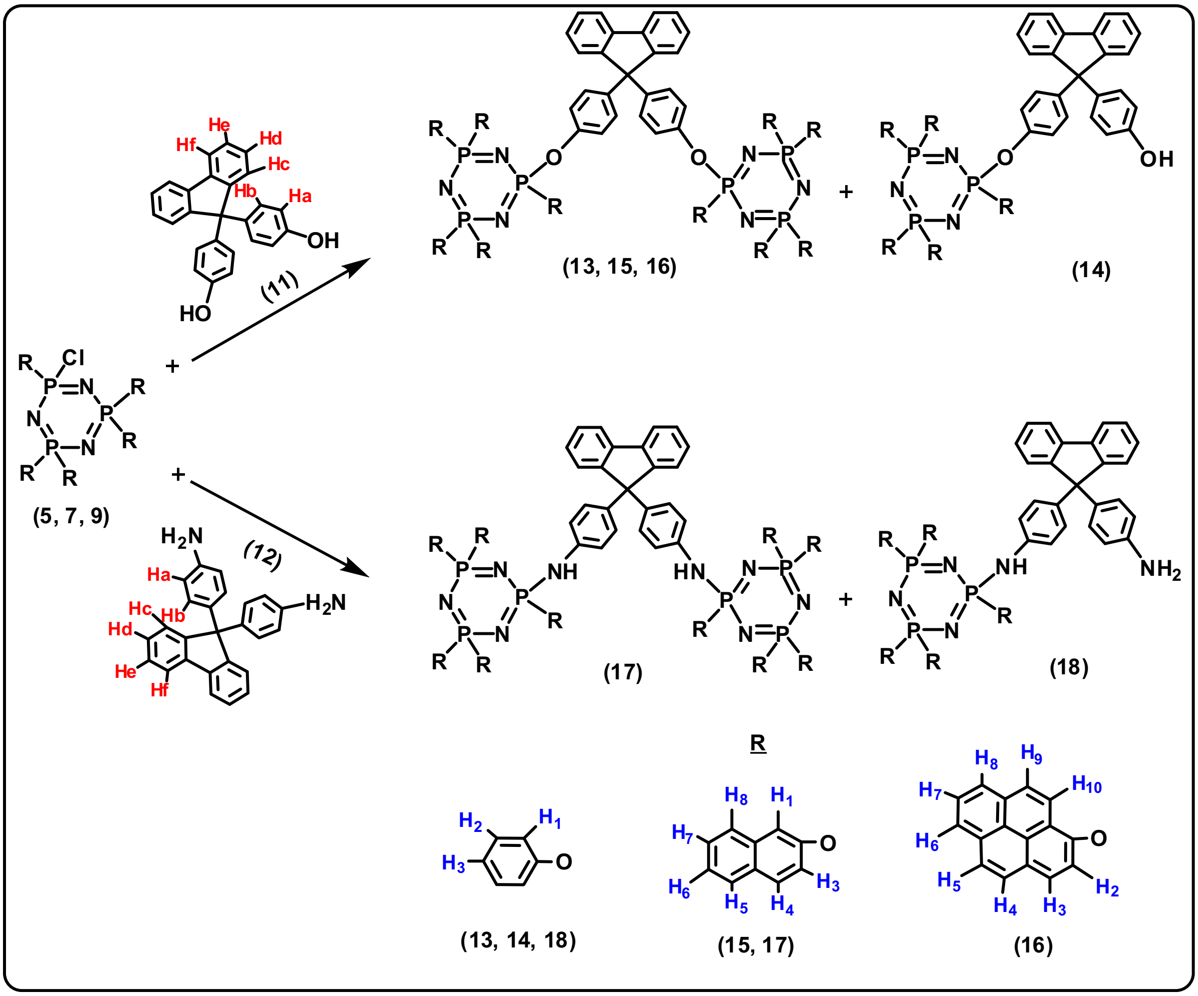


Scheme 1. The synthesis of penta- and hexasubstituted cyclotriphosphazene derivatives.



Scheme 2. The synthesis of FDP and FDA bridged and open chain cyclotriphosphazenes.

2. Experimental

2.1. General methods

Hexachlorocyclotriphosphazene (Otsuka Chemical Co., Ltd) was purified by fractional crystallization from *n*-hexane. Sodium hydride, (60% dispersion in mineral oil) was obtained from Merck; prior to use the oil was removed by washing with dry heptane followed by decantation. 4,4′-(9-Fluorenylidene)diphenol (99%) and (4,4′-(9-fluorenylidene)dianiline (99%) were obtained from Aldrich. Tetrahydrofuran (⩾99.0%), dichloromethane (⩾99.0%), benzene (⩾99.0%), ethyl acetate (⩾99.0%) *n*-hexane (⩾95.0%), 4-(Dimethylamino)pyridine (DMAP) (⩾99%) and Cesium carbonate (⩾99%) 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. $CDCl_3$ for NMR spectroscopy was obtained from Goss Scientific. Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument. Positive ion and linear mode MALDI-MS of the compounds were obtained in dihydroxybenzoic