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Fluorescent aminoarylcyclotetraphosphazenes

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ABSTRACT

In the present work, octachlorocyclotetraphosphazatetraene (**1**), $N_4P_4Cl_8$, is reacted with aniline (**2**), 1-napthylamine (**4**) and 2-aminoanthracene (**6**) to give octakis(arylamino)cyclotetraphosphazenes (**3**, **5** and **7**). These cyclotetraphosphazene compounds (**3**, **5** and **7**) have been fully characterized by elemental analysis, mass (MS), FT-IR, ^{1}H and ^{31}P NMR spectroscopies. The molecular and crystal structures of **5** have been characterized by X-ray crystallography. The structure of **5** is monoclinic with the space group *P*21/*c*. The octakis(1-napthylamino)-(**5**) and octakis(2-aminoanthracene)-(**7**) cyclotetraphosphazene compounds have been synthesised for the first time in this study. The fluorescence properties of **3**, **5** and **7** have been investigated in tetrahydrofuran (THF) and have been shown to have highly fluorescence behavior. This work also presents the quenching of arylamino substituted cyclotetraphosphazene derivatives (**3**, **5** and **7**) by *p*-benzoquinone (BQ) or hydroquinone (HQ).

1. Introduction

Cyclic and polymeric phosphazenes, having a variety of applications in science and technology, are an important class of inorganic heterocyclic ring systems [1]. In addition, phosphazenes exhibit very different physical and chemical characteristics depending on the type and properties of the attached substituents [2]. For example, it is possible to design materials with special properties such as ionic liquids [3], dendrimers having chiral ligands for asymmetric catalysis [4], liquid crystals [5], flame retardants [6–8], antitumor agents [9–11], antimicrobial agents [12], etc.

Luminescent compounds are attracting much current research interest because of their many applications, including emitting materials for organic light emitting diodes (OLEDs), light harvesting materials for photocatalysis and fluorescent sensors for organic or inorganic analyzers [2]. Cyclophosphazenes have many advantageous purposes for useful luminescent materials for electroluminescent devices [1]. For example, substituted cyclic phosphazenes are very stable and do not breakdown under very aggressive chemical conditions [1,13]. Some works on the photophysical properties of phosphazenes have been reported in the literature, especially for their use in OLEDs [14–25].

The eight membered tetramer (**1**), $N_4P_4Cl_8$, ring is significantly more reactive than the planar six-membered trimer, $N_3P_3Cl_6$, ring due to the structural flexibility [26,27]. However, studies on cyclotetraphosphazenes are limited [26–28]. According to our best knowledge, the reactions of $N_4P_4Cl_8$ with aniline have been studied [29,30], but there is no report so far on the fluorescence behavior of octakis(anilino)cyclotetraphosphazene (**3**). The nature of the substituents can strongly influence the photophysical properties of phosphazenes [1,17,25,31].

In the present study, we report on the synthesis and characterization of aminocyclotetraphophazenes (**3**, **5** and **7**), shown in Scheme 1, to investigate the fluorescence spectral properties of these compounds. For this purpose, the fluorescence quantum yields and lifetimes of these compounds have been investigated in THF. This work also shows the fluorescence quenching behavior of arylamino substituted cyclotetraphosphazene derivatives (**3**, **5** and **7**) by BQ or HQ.

2. Experimental

2.1. Materials

Octachlorocyclotetraphosphazatetraene (a gift from the Otsuka Chemical Co., Ltd.) was purified by fractional crystallization from *n*-hexane. THF (⩾99.0%), dichloromethane (⩾99.0%), *n*-hexane (⩾95.0%), triethylamine (>99%), aniline (>99%), 1-napthylamine (>99%), H_2SO_4 (98%) and 2-aminopyridine (⩾98%) were obtained from Merck. 2-Aminoanthracene (96%) was obtained from Aldrich and was used as received. THF was distilled over a sodium–potassium alloy under a dry argon atmosphere. HQ (>99.5) was obtained from Riedel-deHaen. BQ (⩾99.5%) was obtained from Fluka. All solvents used in this work were purified by conventional methods. THF-d_8 and $CDCl_3$ were used for NMR spectroscopy and were obtained from Merck.

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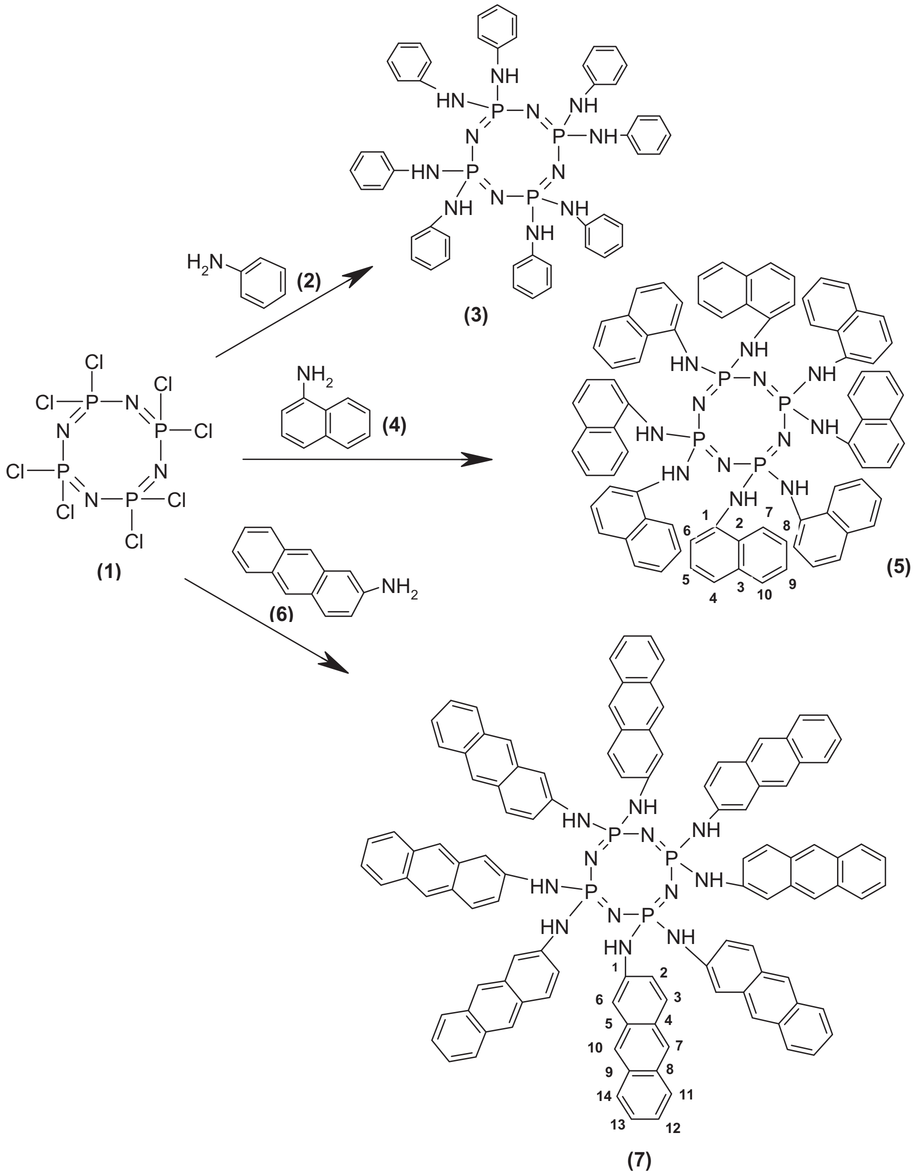

Scheme 1. The synthetic pathway for **3**, **5** and **7**.

2.2. Measurements

Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument. Mass spectra were obtained on a Bruker MicrOTOF LC/MS spectrometer using the electrospray ionization (ESI) method, ^{35}Cl values were used for the calculated masses. Infrared spectra were recorded on a Bio-Rad FTS 175C FTIR spectrophotometer using KBr pellets. Analytical thin layer chromatography (TLC) was performed on silica gel (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 70–230 mesh; for 3 g crude mixture, 100 g silica gel was used in a column of 3 cm diameter and 60 cm length). ^{1}H, ^{13}C and ^{31}P NMR in $CDCl_3$ for **3** and **5**, and THF-d_8 solution for **7** spectra were recorded on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^{1}H and ^{13}C NMR and 85% H_3PO_4 as an external reference for ^{31}P NMR measurements. Melting point analyses were collected on a Mettler Toledo DSC822^{e} instrument between 25 and 350 °C for DSC (differential scanning calorimeter) using a constant 10 °C/min heating rate with the Star^{e} Software. Calibration of the instrument was made using the standard In/Zn calibration method and spectra grade argon was used as a protective and purge gas for all thermal experiments. UV–Vis spectra were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature.

2.3. Fluorescence quantum yields and lifetime parameters

Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [32],

$$\Phi_F = \Phi_F(\mathrm{Std})\frac{F \cdot A_{\mathrm{Std}} \cdot n^2}{F_{\mathrm{Std}} \cdot A \cdot n^2_{\mathrm{Std}}}, \tag{1}$$

where, F and F_{Std} are the areas under the fluorescence emission curves of **3**, **5** and **7** and the standard, respectively. A and A_{Std} are the respective absorbance of the samples and standard at the excitation wavelengths. The refractive indices of the solvents were employed in calculating fluorescence quantum yields in different