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Synthesis, thermal and photophysical properties of naphthoxycyclotriphosphazenyl-substituted dendrimeric cyclic phosphazenes

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ABSTRACT

The synthesis and properties of naphthoxycyclotriphosphazenyl-substituted dendrimeric cyclic phosphazenes are reported. Compound **3**, $[N_3P_3(ONp)_5OPhOH]$, is prepared by the sequential reactions of hexachlorocyclotriphosphazene with 2-naphthol and 4-benzyloxyphenol derivatives, as side groups. The dendrimeric compounds **5**, **6** and **7** have been obtained by the reactions of compound **3** with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, octachlorocyclotetraphosphazene, $N_4P_4Cl_8$, and bisphenol bridged cyclophosphazene, $N_6P_6Cl_{10}$ (**4**), respectively. The newly synthesized compounds have been fully characterized by elemental analysis, ESI, MALDI-TOF mass spectrometry, FT-IR, ¹H, ¹³C and ³¹P NMR spectroscopy. The thermal stability and fluorescence spectral properties of all these novel compounds are investigated.

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1. Introduction

Cyclic and polymeric phosphazenes are an important class of inorganic heterocyclic ring systems [1,2], not only because they have wide applications due to their thermal stability, catalytic properties, electrical conductivity, liquid crystal and biomedical activity [3-5], but also because the reactions of various nucleophiles with the halogen atoms make it possible to modify the properties and applications of the phosphazenes to a great extent. They are usually prepared by nucleophilic substitution reactions of alkoxides, aryloxides or amines on halocyclophosphazenes or high polymers [6-8], and their physical and chemical properties can be tailored via the appropriate substituted groups on the phosphorus atoms [9]. Luminescent dendrimeric compounds are attracting much current research interest because of their many applications, including emitting materials for organic light emitting diodes, light harvesting materials for photocatalysis and fluorescent sensors for organic or inorganic analyzers [10].

Cyclophosphazenes have many advantages as useful luminescent materials for electroluminescent devices. For example, substituted cyclic phosphazenes are very stable and do not breakdown under very aggressive chemical conditions. Also the functional groups are projected above and below the cyclophosphazene plane

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thus producing a rigid spherical core from which to grow the dendrons of interest. Hence there has recently been considerable interest in fluorescent compounds based on cyclic phosphazene cores [11,12] or cyclo-linear polymers with cyclotriphosphazene units [13] for the development of electroluminescent devices. In phosphazene chemistry, there are many examples of organic or inorganic side groups bearing cyclophosphazenes or polyphosphazenes [3-5]. However, there are limited examples of cyclophosphazenes and polyphosphazenes [14,15] or organic polymers [16,17] that bear an organic group substituted cyclophosphazene ring as a side group. We have recently reported [18,19] that some dendrimeric cyclic phosphazenes were prepared with phenoxy substituted cyclic phosphazene as side groups, which possess a single reactive group at the core to avoid side reactions. It was found that the dendrimeric arrangement of the side groups was more effective than the number of attached side groups for the thermal stability and fluorescence spectral properties, as was reported in the previous study [18]. We thought that it would be interesting to carry out a similar synthetic strategy for the preparation of dendrimeric cyclic phosphazenes bearing naphthoxycyclotriphosphazenyl groups. We have chosen the naphthoxy substituent for the synthesis of dendrimeric structures because molecules functionalized with the naphthalene moiety, in addition to normal fluorescence, exhibits excimer fluorescence as well.

Here we describe the synthesis and characterization of naphthoxycyclotriphosphazenyl-substituted dendrimeric cyclic phosphazenes (Fig. 1) and an investigation of their thermal and photophysical properties.





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Fig. 1. Structures of the dendrimeric cyclic phosphazenes (5-7).

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene(trimer) and octachlorocyclotetraphosphazene (Otsuka Chemical Co. Ltd.) were purified by fractional crystallization from *n*-hexane. The deuterated solvents (CDCl₃ and toluene) for NMR spectroscopy and the following chemicals were obtained from Merck: cyclohexene, ethanol, 2naphthol, 4-benzyloxyphenoxy, Pd(OH)₂, Cs₂CO₃, NaH, acetone, triethylamine, silica gel 60, tetrahydrofuran. 1,8,9-Anthracenetriol for the MALDI matrix was obtained from Fluka. All other reagents and solvents were reagent grade quality and obtained from commercial suppliers.

2.2. Equipment

Elemental analyses were carried out using a Thermo Finnigan Flash 1112 Instrument. UV–Vis spectra were recorded with a Shimadzu 2001 UV Pc spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature. Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [20].

$$\Phi_{\rm F} = \Phi_{\rm F(Std)} \frac{F \cdot A_{\rm Std} \cdot n^2}{F_{\rm Std} \cdot A \cdot n_{\rm Std}^2} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (5, 6 and 7) and the standard, respectively. A and A_{Std} are the respective absorbance of the samples and standard at the excitation wavelengths, respectively. The refractive indices (n) of the solvents were employed in calculating fluorescence quantum yields in different solvents. 2-Aminopyridine (in 0.1 M H₂SO₄) (Φ_F = 0.60) [21] was employed as the standard. Both the samples and standard were excited at the same wavelength. Infrared spectra were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer using KBr dyes. Mass spectra were acquired in the linear mode with an average of 50 shots on a Bruker Daltonics Microflex mass spectrometer (Bremen, Germany) equipped with a nitrogen UV-Laser operating at 337 nm. 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 the 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. Analytical thin layer chromatography (TLC) was performed on Silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g; crude mixture, 100 g; silica gel was used in a column 3 cm in diameter and 60 cm in length) and preparative thin layer chromatography was performed on silica gel 60 P F_{254} . ¹H, 13 C and 31 P NMR spectra were recorded in CDCl₃ and toluene-d₇ solutions on a Varian 500 MHz spectrometer.

2.3. Synthesis

The bisphenol bridged cyclophosphazene compound $N_6P_6Cl_{10}$ (bisphenol) (**4**) was prepared and purified according to the literature procedure [22].

2.3.1. Synthesis of compound 1

A solution of sodium naphthoxide was prepared by the dropwise addition of 2.26 g of 2-naphthol (15.78 mmol) in dry THF (20 ml) to a solution of 0.80 g of 60% sodium hydride (20 mmol) dispersion in dry THF (10 ml) at 0 °C. Hexachlorocyclotriphosphazene (1.00 g, 2.87 mmol) in 20 ml dry THF was added dropwise over 0.5 h to a stirred reaction mixture of sodium naphthoxide. The reaction mixture was stirred for 1 day under an atmosphere of argon and the reaction was followed by TLC. Sodium hydrochloride was removed by filtration, the solvent removed under reduced pressure, and the resulting product was subjected to column chromatography using dichloromethane:n-hexane (1:1) as the eluant. 1,1,3,3,5-Pentanaphthoxy-5-chlorocyclotriphosphazatriene (1) was isolated and crystallization in dichloromethane:*n*-hexane (3:1). Yield: 1.6 g (60%), m.p. 137 °C. Anal. Calc. for C₅₀H₃₅ClN₃O₅P₃ (885): C, 67.70; H, 3.98; N, 4.74. Found: C, 67.60; H, 3.95; N, 4.78%. FT-IR v_{max}/cm⁻¹ (KBr pellet): 3036 (ArCH), 2868 (CH), 1625–1600 (ArC=C), 1270-1210 (P=N), 1105 (C-O), 965 (P-O); ¹H NMR $(CDCl_3)$ δ : 6.90–7.85 (m, 35H, ArH); $\{^{1}H\}^{13}C$ NMR $(CDCl_3)$ δ : 148.31 (ArC), 134.09 (ArCH), 131.49 (ArC), 129.96 (ArC), 128.81 (ArCH), 127.93 (ArCH), 126.89 (ArCH), 121.27 (ArCH), 118.48 (ArCH); MS (ESI) m/z (%): 886 (100) [M+H]+.

2.3.2. Synthesis of compound 2

4-(Benzyloxy) phenol (0.5 g, 2.48 mmol), dry and finely powdered cesium carbonate (1.47 g, 4.51 mmol) were dissolved in dry THF (10 ml) under an argon atmosphere. The solution was transferred to a 50 ml dropping funnel and slowly dropped onto a solution of 1,1,3,3,5-pentanaphthoxy-5-chlorocyclotriphosphazatriene (2 g, 2.26 mmol) (1) in 10 ml of dry THF under an argon atmosphere in a 50 ml three-necked round bottomed flask. The reaction mixture was refluxed under argon for 24 h, followed by TLC which indicated that no starting material remained. The precipitated salt (CsCl) was filtered off and the solvent was removed under reduced pressure. The crude product was purified by column chromatography [silica gel 60 (70-230 mesh) as adsorbent and dichloromethane:n-hexane 1:1 as the eluent]. 1,1,3,3,5-Pentanaphthoxy-5-[(4-benzyoxy)phenoxy]-cyclotriphosphazatriene (2) was obtained as a viscous oil. Yield: 1.52 g (61%). Anal. Calc. for C₆₃H₄₆N₃O₇P₃ (1065): C, 72.11; H, 4.73; N, 3.94. Found: C, 72.05; H, 4.78; N, 3.90%. FT-IR *v*_{max}/cm⁻¹ (KBr pellet): 3035 (ArCH), 2866 (CH), 1625-1605 (ArC=C), 1260-1211 (P=N), 1105 (C-O), 955 (P–O); ¹H NMR (CDCl₃) δ: 6.21–7.50 (m, 50H, ArH), 5.12 (br, s, 2H, CH₂); {¹H}¹³C NMR (CDCl₃) δ: 155.97 (ArC), 153.10 (ArC), 150.30 (ArC), 148.42 (ArCH), 144.46 (ArC), 137.14 (ArC), 131.26 (ArC), 129.71 (ArCH), 128.87 (ArCH), 127.94 (ArCH), 126.61 (ArCH), 125.56 (ArCH), 122.01(ArCH), 121.32 (ArCH), 70.39 (CH₂). MS (ESI) *m*/*z* (%): 1050 (100) [M+H]⁺.

2.3.3. Synthesis of compound 3

1,1,3,3,5-Pentanaphthoxy-5-[(4-benzyoxy)phenoxy]-cyclotriphosphazatriene (2) (1 g, 0.95 mmol) was dissolved in 10 ml of dry THF under an argon atmosphere and 6 ml of cyclohexene, palladium hydroxide (20 wt.% on carbon, 0.4 g) and 6 ml of ethanol were added to this solution. The mixture was refluxed for 24 h under an argon atmosphere and filtered. All of the solvents were removed under reduced pressure. 1,1,3,3,5-Pentanaphthoxy-5-[(4-hydroxy)phenoxy]-cyclotriphosphazatriene (3) was obtained by crystallization in dichloromethane: *n*-hexane (3:1). Yield: 0.59 g (62%), m.p. 129 °C. Anal. Calc. for C₅₆H₄₀N₃O₇P₃ (959): C, 70.07; H, 4.20; N, 4.38. Found: C, 70.10; H, 4.24; N, 4.36%. FT-IR *v*_{max}/cm⁻¹ (KBr pellet); 3610 (OH), 3045 (ArCH), 1590 (ArC), 1275-1184 (P=N), 960 (P-O); ¹H NMR (CDCl₃) δ: 6.15-7.80 (m, 40H, ArCH), 5.20 (s, 1H, OH); {¹H}¹³C NMR (CDCl₃) δ: 152.76 (ArC-OH), 148.50 (ArC), 144.22 (ArC), 134.07 (ArC), 129.57 (ArCH), 126.66 (ArCH), 122.11 (ArCH), 121.07 (ArCH), 117.96 (ArCH). 157.94 (ArCH). MS (ESI) m/z (%): 960 (100) [M+H]+.

2.3.4. Synthesis of compound 5

Trimer, N₃P₃Cl₆, (0.009 g, 0.025 mmol) and compound **3** (0.17 g, 0.181 mmol) were dissolved in dry THF (10 ml) under an argon atmosphere. After stirring for 15 min at 40 °C, dry and finely powdered cesium carbonate (0.08 g, 0.26 mmol) was added portionwise over 15 min with efficient stirring. The reaction mixture was stirred under an argon atmosphere at 80 °C for 24 h. and then filtered. The volatile materials were evaporated under vacuum and the product was purified by preparative TLC on silica gel using hexane:THF (1:1) as the eluent. Compound **5** is a highly viscous oil. Yield: 0.056 g (37%). *Anal.* Calc. for C₃₃₆H₂₃₄N₂₁O₄₂P₂₁ (5888): C, 68.5; H, 4.01; N, 5.00. Found: C, 68.75; H, 4.08; N, 5.06%. ¹H NMR (toluene-d₈) δ : 11.68–12.61 (m, 234H, ArCH); {¹H}¹³C NMR (toluene-d₈) δ : 142.35 (ArC), 133.74 (ArCH), 132.83 (ArC), 130.19 (ArCH), 129.80 (ArCH), MS (MALDI-TOF) *m/z* (%): 5889 (100) [M+H]⁺.

2.3.5. Synthesis of compound 6

Octachlorocyclotetraphosphazene(tetramer), N₄P₄Cl₈, (0.009 g, 0.019 mmol) and compound **3** (0.12 g, 0.13 mmol) were dissolved in dry THF (10 ml) under an argon atmosphere. After stirring for 15 min at 40 °C, dry and finely powdered cesium carbonate (0.06 g, 0.19 mmol) was added portionwise over 30 min with efficient stirring. The reaction mixture was stirred under an argon atmosphere at 80 °C for 48 h. And then filtered. The volatile materials were evaporated under vacuum and the product was purified by preparative TLC on silica gel using hexane:THF (1:1) as the eluent. Compound **6** is highly viscous oil. Yield: 0.064 g (42%). *Anal.* Calc. for C₄₄₈H₃₁₂N₂₈O₅₆P₂₈ (7850): C, 68.54; H, 4.01; N, 5.00. Found: C, 68.55; H, 4.05; N, 5.01%. ¹H NMR (toluene-d₈) δ : 11.76–12.60 (m, 312H, ArCH); {¹H}¹³C NMR (toluene-d₈) δ : 142.35 (ArC), 133.93 (ArCH), 132.83 (ArC), 130.19 (ArCH), 129.99 (ArCH); MS (MALDI-TOF) *m*/*z* (%): 7851 (100) [M+H]⁺.

2.3.6. Synthesis of compound 7

 $N_6P_6Cl_{10}$ (bisphenol) (**4**) (0.03 g, 0.035 mmol) and compound **3** (0.34 g, 0.35 mmol) were dissolved in dry THF (10 ml) under an argon atmosphere. After stirring for 15 min at 40 °C, dry and finely powdered cesium carbonate (0.13 g, 0.38 mmol) was added portionwise over 15 min with efficient stirring. The reaction mixture was stirred under an argon atmosphere at 80 °C for 24 h. and then filtered. The volatile materials were evaporated under vacuum and the product was purified by preparative TLC on silica gel using hexane:THF (1:1) as the eluent. Compound **7** is a highly viscous oil. Yield: 0.056 g (37%). *Anal.* Calc. for C₅₇₅H₄₀₄N₃₆O₇₂P₃₆ (10083): C, 68.48; H, 4.04; N, 5.00. Found: C, 68.45; H, 4.08; N, 5.02%. ¹H NMR (CDCl₃) δ : 11.68–12.61 (m, 398H, ArCH), 6.41 (br, 6H, CH₃);

{¹H}¹³C NMR (CDCl₃) δ : 138.51 (ArC), 129.24 (ArCH), 125.75 (ArC), 123.01 (ArCH), 73.2 (ArCH), 68.2 (CH₃); {¹H}³¹P NMR (toluene-d₈) δ : 10.41 [m, 4P, >*P*(OPh)₂, B₂], 10.77 [m, 2P, >*P*(OPh)(OPhO), A], 10.1 (s, 1P, >*P*R₂, C₃); ²*J*_{P,P} = 90.88 Hz; MS (MALDI-TOF) *m*/*z* (%): 10084 (100) [M+H]⁺.

3. Results and discussion

The synthetic routes to compounds **1–7** are shown in Scheme 1. Compound **1** was synthesized by the reaction of 2-naphthol with hexachlorocyclotriphosphazene. Compound 1 was reacted with 4-benzyloxyphenol in the presence of Cs₂CO₃ in THF to obtain compound 2. The 4-benzyloxyphenoxy unit of compound 2 was converted to a 4-hydroxyphenoxy group with cyclohexene in a mixture of THF/ethanol, in the presence of Pd(OH)₂ as a catalyst to give compound 3. Compounds 5, 6 and 7 were obtained from nucleophilic displacement reactions of **3** with N₃P₃Cl₆, N₄P₄Cl₈ and $N_6P_6Cl_{10}$ (bisphenol) (4) with cesium carbonate as the base under an argon atmosphere, respectively. The products were purified by preparative TLC on silica gel using hexane:THF (1:1) as the eluent. The newly synthesized compounds were characterized by IR. ¹H. ¹³C and ³¹P NMR. mass spectrometry and elemental analysis. All the results were consistent with the predicted structures, as shown in Section 2. The IR spectra of all these compounds feature peaks at around 1200 cm⁻¹ (br) (P=N) and 960 cm⁻¹ (P–O) for a phosphazene ring, as expected [23]. The mass spectra of compounds 5, 6 and 7 were obtained by MALDI-TOF spectrometry. Many different MALDI matrices were investigated to find an intense molecular ion peak and low fragmentation. 1,8,9-Anthracenetriol MALDI matrix yielded the best MALDI-MS spectra. The MS spectra of **5**, **6** and **7** provided definitive characterization. The peak group representing the protonated molecular ions of 5, 6 and 7 was observed at 5889, 7851 and 10084 Da mass, respectively.

In particular, the ³¹P NMR spectra were carefully analyzed and the ³¹P NMR chemical shifts and phosphorus-phosphorus coupling constants (²*I*_{PNP}) of compounds **1–3**, **5–7** are summarized in Table 1. The proton-decoupled 31 P NMR spectrum of compound **1** is observed as the expected A_2X spin system. The signal assignment is straightforward, with the triplet (1P) at ca. 23.86 ppm belonging to >P(naphthoxy)(Cl) and the doublet (2P) at ca. 8.76 ppm to >P(naphthoxy)₂. Since compounds **2** and **3** show non-first order ³¹P NMR spectra, it is necessary to carry out simulation analysis to get the appropriate spectral parameters. Following this analysis, the ³¹P NMR spectra were analyzed as AB₂ spin systems and the ³¹P NMR chemical shifts and ${}^{2}J_{(PP)}$ of compounds **2** and **3** are summarized in Table 1. As an example, the simulated and observed the proton-decoupled ³¹P NMR spectra of compound **3** are depicted as the AB₂ pattern in Fig. 2. Although similar AB₂ patterns in the ³¹P NMR spectra for the side groups of compounds **5**. **6** and **7** are expected, they are observed as broad signals rather than AB₂ patterns. The integration of the broad signals part to the remaining singlet of the proton-decoupled ³¹P NMR spectra of compounds 5, 6 and 7 gave approximately a 6:1, 6:1 and 5:1 phosphorus ratio, respectively, that confirmed the suggested structures.

Phosphazenes are attractive compounds due to their higher thermal stability and flame retardancy properties when compared with their organic homologs. Owing to the excellent thermal stability and char yield performance, the aryloxy substituted polyphosphazene has attracted interest for its potential application in flame retardants [24]. Differential scanning calorimetry (DSC) studies were carried out between -40 and $100 \,^{\circ}C$ with a heating rate of $10 \,^{\circ}C/min$ under a nitrogen flow to determine the transition temperatures of the dendrimeric compounds. The T_g values of all the new phosphazene compounds (**5**–**7**) are presented in Table 2. Thermogravimetric analysis (TGA) was utilized to evaluate the thermal stability of the dendrimeric compounds. The onset decomposition temperatures (T_d) are recorded at a heating rate of $10 \,^{\circ}C/$



Scheme 1. Chemical structure and synthetic pathway for 1-7.

Table 1	
³¹ P NMR	parameters of compounds 1–3 and 5–7 . ^a

Compounds	Chemical shifts (ppm)					$^{2}J_{(\mathrm{PP})}(\mathrm{Hz})$
	>P(naphthoxy) ₂	>P(naphthoxy)(X)	Х	$N_3P_3R_6$	$N_4P_4R_8$	
1 ^b	8.76	23.86	Cl	-	-	81.6
2 ^c	10.78	10.64	OPhOCH ₂ Ph	-	-	80.2
3 ^c	10.74	10.58	OPhOH	-	-	80.2
5	16.05 ^d	16.05 ^d	$OPhO(N_3P_3)$	14.81	-	-
6	16.13 ^d	16.13 ^d	$OPhO(N_4P_4)$	-	-5.97	-
7	15.03 ^d	15.03 ^d	N ₆ P ₆ (bisphenol)	13.76	-	-

 $^{\rm a}\,$ 202.38 MHz ^{31}P NMR measurements in toluene-d7 solutions at 298 K.

^b Compound **1** was analyzed as an A₂X spin system.

^c The parameters were obtained from simulation analysis.

^d Broad signals were observed for compounds 5, 6 and 7 and not calculated coupling constants.



Fig. 2. The proton decoupled ³¹P NMR spectrum of compound **3** (a) observed, (b) simulated.

Table 2Thermal properties and molecular weights of 5, 6 and 7.

Compound	$T_{\rm g}$ (°C)	$T_{\rm d}$ (°C)	$M_{\rm w}$	% Char yield
5 6	27.4 23.8	434 477	5884 7851	45.4 48.8
7	33.6	490	10084	60.5

min. The curves of the TGA measurements are shown in Fig. 3 and T_d values are collected in Table 2. According to the TGA thermograms of compounds **5**, **6** and **7**, they exhibit very good thermal stability with decomposition temperatures (T_d) in the range 434– 490 °C (Table 2). The increase of T_d from compounds **5–7** can be explained with the increasing substitution degree of napththoxy groups. These results correlate with the previously reported results on the thermal behavior of phenoxy based cyclophosphazenes dendrimers [18,19]. Therefore aryloxycyclophosphazenes could be useful candidates for flame retardant additives to organic polymers [24]. The high char yields and T_d values of the dendrimeric phosphazene compounds **5**, **6** and **7** make them a good flame retardants in theory [25], and it could suggest that the dendrimeric derivatives have excellent thermal properties.

The photophysical behaviors of the monomeric and polymeric naphthoxy phosphazene derivatives have been extensively studied



Fig. 3. TGA curves of 5, 6 and 7 from 25 to 700 $^\circ C$ at a heating rate of 10 $^\circ C/min$ under a N_2 flow of 50 mL/min.

[26,27]. Although the hexakis(2-naphthyloxy)cyclotriphosphazene showed intramolecular excimer behavior [26], the poly[bis(β -naphthoxy)phosphazene] did not [27]. The absorption and the



Fig. 4. The fluorescence emission spectra of 5, 6 and 7 in dichloromethane. Concentration: 1×10^{-6} mol dm⁻³. Excitation wavelength: 270 nm.

fluorescence spectra of the dendrimeric phosphazenes 5, 6 and 7 were measured in dichloromethane as dilute solutions $(1\times 10^{-6}\,mol\,dm^{-3})$ upon being excited at 270 nm. All the compounds display very similar absorption (276-277 nm) and emission (389-391 nm) wavelength maxima, that are well separated ($\Delta\lambda$ ca. 115 nm). The emission spectra of compound **5**, **6** and 7 are shown in Fig. 4. The trend in the emission maxima amongst the cyclic compounds was bisphenol bridged compound (7) > tetrameric core phosphazene derivative (6) > trimeric core phosphazene derivative (5), according to the number of the naphthol groups, as expected [18,19]. The fluorescence quantum yields $(\Phi_{\rm F})$ of the phosphazene derivatives were measured in CH₂Cl₂, and 2-aminopyridine in 0.1 M H₂SO₄ solution was used as a standard. Although there are many parameters that affect the fluorescence quantum yields [28], the fluorescence quantum yields ($\Phi_{\rm F}$) of dendrimeric compounds are increased with respect to the increment of the side groups, and their values are: 0.34 for 5, 0.36 for 6 and 0.39 for 7. Apart from the emission (389-391 nm) wavelength maxima, the emission spectra of the cyclic compounds showed two additional emission bands consisting of a maximum at 339 nm with a shoulder at 325 nm (Fig. 4). In order to get more information on the observed additional bands, the emission spectra of compound 3 and 2-naphthol were measured under the same conditions (1 \times 10⁻⁶ mol dm⁻³ in CH₂Cl₂, λ_{exc} 270 nm), as shown in Fig. 5. Although three emission bands were observed at 325, 340 and 390 nm for compound 3, the emission spectrum of 2naphthol showed only two bands at 326 and 339 nm. When the emission spectrum of 2-naphthol was taken in dichloromethane as a concentrated solution of $1 \times 10^{-1} \text{ mol dm}^{-3}$, three bands was observed at 328, 340 and 380 nm (not shown). The appearance of a 380 nm band in 2-naphthol originates from the formation of an intermolecular excimer. Intramolecular monomer/excimer observation is well known [29], and excimer formation with naphthalene derivatives or polyaromatic hydrocarbons occurs only in very concentrated solutions. Therefore, we can clearly say that the appearance of the 390 nm band in compound 3 arises from the formation of an excimer between the naphthol units. It is well known [9] that chlorophosphazenes $(N_3P_3Cl_6, \text{ or } N_4P_4Cl_8)$ are pho-



Fig. 5. The fluorescence emission spectra of 3 and 2-naphthol in dichloromethane. Concentration: 1×10^{-6} mol dm $^{-3}$. Excitation wavelength: 270 nm.

tochemically inert and do not interfere with the photophysical properties associated with the attached chromophores. Single crystal X-ray analysis of hexakis(2-naphthyloxy)cyclotriphosphazene showed [29] that the six naphthyloxy groups lie almost perpendicularly above and below the nearly planar cyclotriphosphazene core. This structural features make it possible for the three naphthyloxy groups to be located on the same side of the (PN)₃ plane, and they are able to align through intramolecular non-covalent π - π interactions. Therefore it can be suggested that the excimer interactions in compound **3** (dilute solutions of 1×10^{-5} mol dm⁻³ in CH₂Cl₂) is intramolecular rather than intermolecular. Hence, the two additional emission bands for the dendrimeric compounds **5**, **6** and **7** can be derived from the intramolecular excimer formation.

4. Conclusion

In conclusion, we have described the synthesis of a hydroxyl substituted penta(naphthoxy)cyclotriphosphazene (**3**) and its dendrimeric derivatives (**5**, **6** and **7**) based on cyclic phosphazenes. All the compounds have been characterized by standard spectroscopic techniques. The thermal stability and fluorescence spectral properties of the dendrimeric compounds (**5**, **6** and **7**) have been investigated. These compounds possess both high thermal stability and char yields and significantly more fluorescence emission on increasing the length of the side groups, making it potentially suitable for some industrial applications, such as flame retardant additives to polymers or light emitting electroluminescent devices.

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References

- J.E. Mark, H.R. Allcock, R. West, Inorganic Polymers, Prentice Hall, Englewood Cliffs, NJ, 1992.
- [2] I. Manners, Angew. Chem., Int. Ed. Engl. 35 (1996) 1602.
- [3] H.R. Allcock, Chemistry and Applications of Polyphosphazenes, Wiley-Interscience, New York, 2003.
- [4] H.R. Allcock, E.H. Klingenberg, Macromolecules 28 (1995) 4351.
- [5] R.E. Singler, R. Willingham, C. Noel, C. Friedrich, L. Bosio, E. Atkins, Macromolecules 24 (1991) 510.

- [6] H.R. Allcock, Phosphorus–Nitrogen Compounds, Academic Press, New York, 1972 (Chapters 6 and 7).
- [7] C.W. Allen, Chem. Rev. 91 (1991) 119.
- [8] R. de Jaeger, M. Gleria, Prog. Polym. Sci. 23 (1998) 179.
- [9] M. Gleria, R. De Jaeger (Eds.), Phosphazenes: A World Wide Insight, Nova Science Publishers, New York, 2004.
- [10] D. Astruc, E. Boisselier, C. Ornelas, Chem. Rev. 110 (2010) 1857.
- [11] S. Sundarraj, A. Sellinger, Macromol. Rapid Commun. 27 (2006) 247.
- [12] H.J. Bolink, S.G. Santamaria, S. Sudhakar, C. Zhen, A. Sellinger, Chem. Commun. 67 (2008) 618.
- [13] J. Xu, C.L. Toh, K.L. Ke, J.J. Li, C.M. Cho, X. Lu, E.W. Ta, C. He, Macromolecules 41 (24) (2008) 9624.
- [14] H.R. Allcock, D.C. Ngo, Macromolecules 25 (1992) 2802.
- [15] V. Maraval, A.M. Caminade, J.P. Majoral, J.C. Blais, Angew. Chem., Int. Ed. 42 (2003) 1822.
- [16] H.R. Allcock, W.R. Laredo, E.C. Kellam, R.V. Morford, Macromolecules 34 (2001) 787.
- [17] S.T. Fei, R.M. Wood, D.K. Lee, D.A. Stone, H.L. Chang, H.R. Allcock, J. Membr. Sci. 320 (2008) 206.
- [18] B. Çoşut, F. Hacıvelioğlu, M. Durmuş, A. Kılıç, S. Yeşilot, Polyhedron 28 (2009) 2510.
- [19] B. Çoşut, M. Durmuş, A. Kılıç, S. Yeşilot, Inorg. Chim. Acta 366 (2011) 161.
- [20] S. Fery-Forgues, D. Lavabre, J. Chem. Ed. 76 (1999) 1260.
- [21] R. Rusakowicz, A.C. Testa, J. Phys. Chem. 72 (1968) 2680.
- [22] M. Touaibia, R. Roy, J. Org. Chem. 73 (23) (2008) 9292.
- [23] H.R. Allcock, J. Am. Chem. Soc. 86 (1964) 2591.
- [24] P. Potin, R.D. Jaeger, Eur. Polym. J. 27 (1991) 341
- [25] A.F. Van, K.D.W. Van, J. Polym. Sci. Polym. Phys. Ed. 10 (1972) 2423.
- [26] N. Chattopadhyay, B. Haldar, A. Mallick, S. Sengupta, Tetrahedron Lett. 46 (2005) 3089.
- [27] L. Flamigni, N. Camaioni, P. Bortolus, F. Minto, M. Gleria, J. Phys. Chem. 95 (1991) 971.
- [28] D.F. Eaton, Pure Appl. Chem. 60 (1988) 1107.
- [29] G. Bandoli, U. Casellato, M. Gleria, A. Grassi, E. Montoneri, G.C. Pappalardo, Z. Naturforsch., B Chem. Sci. 44 (1989) 575.