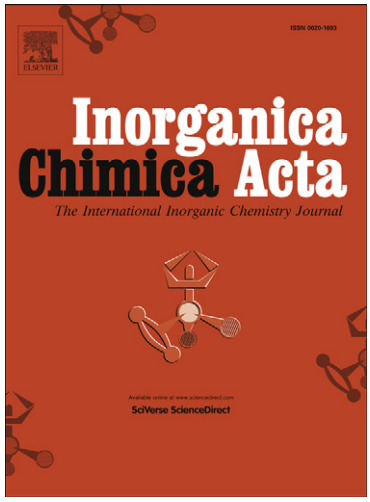

Syntheses, characterizations, thermal and photophysical properties of cyclophosphazenes containing adamantane units

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Syntheses, characterizations, thermal and photophysical properties of cyclophosphazenes containing adamantane units

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Abstract

In this study, phenoxy-adamantane substituted cyclophosphazene compounds (**5-8**) were synthesized in three steps. Firstly; adamantane derivatives (**1** and **2**) containing alkyne groups were prepared. Secondly; 2,2,4,4,6,6-hexzakis-(2'-azido-1'-ethoxy)-cyclotriphosphazatriene (**3**) and 2,2,4,4,6,6,8,8-octakis-(2'-azido-1'-ethoxy)-cyclotetraphosphazatetraene (**4**) were synthesized from the nucleophilic substitutions of 2-azido-1-ethanol with trimer ($N_3P_3Cl_6$) and tetramer ($N_4P_4Cl_8$) in THF respectively. Thirdly; cyclophosphazenes containing adamantane units (**5**-**8**) were obtained by the Cu (I) catalyzed *click* reactions of cyclophosphazenes (**3** and **4**) with compounds **1** and **2**. The structural investigations of newly synthesized compounds **1**-**8** were evaluated by elemental analysis and FT-IR (ATR), mass spectrometry, ^{1}H, ^{13}C, ^{1}H-^{13}C HSQC (for **6**) and ^{31}P NMR (for **3-8**) spectroscopies. Compound **1**–**8** were also reported for the first time. The thermal and photophysical properties of **5**-**8** were investigated.

Keywords: Cyclophosphazene, Adamantane, Thermal stability, Fluorescence, NMR.

Introduction

Cyclic phosphazenes are an important class of inorganic heterocyclic rings containing an [N=PX_2] repeat unit [1, 2]. The inorganic phosphazenes have been well studied in both the cyclic and linear form by several groups due to their diverse properties including catalytic properties [3], electrical conductivity [4], liquid crystal [5] and biomedical activity [6]. Phosphazenes are attractive due to their higher thermal stability and flame retardancy properties when compared with the organic homologues [7]. So, the physical and chemical properties of cyclic phosphazenes can be tailored via the appropriate substituted groups on the phosphorus atoms [8]. Owing to the excellent thermal stability and char yield performance, the adamantyl substituted polymers have attracted interest for its potential application in flame retardant [9-12]. However, there are limited examples of adamantyl substituted cyclophosphazenes or polyphosphazenes [9, 13].

The field of luminescent materials is attracting 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 [14]. Cyclic phosphazene based materials are suitable platform as luminescent materials because they provide high thermal stability and the functional groups are projecting in 3 dimensions thus producing a rigid spherical core from attach the dendrons interest. These rigid spheres have been shown to promote amorphous properties that are known to be important for electroluminescent devices [15, 16]. Recently there has been considerable interest in fluorescent compounds based on cyclic phosphazene cores for use in OLEDs [16-19].

In phosphazene chemistry, there are some examples of adamantyl side group bearing polyphosphazenes [9, 13a]. However, to the best of our knowledge, the synthesis of phenoxy-adamantyl containing cyclic phosphazenes has not yet been reported. Hence, we report the synthesis (Fig.1) and characterization of cyclic phophazenes bearing adamantyl groups (**5-8)**

shown in Fig. 2 to investigate the thermal stability and fluorescence spectral properties of these compounds. For this purpose, the fluorescence quantum yields and lifetimes of these compounds have been investigated in dichloromethane.

Experimental

Materials

Hexachlorocyclotriphosphazene (trimer,) and octachlorocyclotetraphosphazane (tetramer), which were obtained from Otsuka Chemical Co. Ltd., were purified by fractional crystallization from *n*-hexane. The following chemicals were obtained from Merck; H_2SO_4 (98%), 2-aminopyridine (≥98%), *n*-hexane (>96%), tetrahydrofuran (THF) (≥99%), dichloromethane (DCM) (≥99%), Na_2SO_4 (≥99.0%), K_2CO_3 (≥99%), N,N-dimethylformamide (DMF) (≥99%), dimethyl sulfoxide (DMSO) (≥99%), phenol (≥99%), ethanol (≥99.5%), NaOH (≥99%), diethylether (≥98%), Pd/C (%10). The following chemicals were obtained from Aldrich; sodium azide (≥99.5%), 1-bromoadamantane (99%), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDTA) (99%). 2-bromoethanol (97%), copper(I) bromide (98%), propargyl bromide (80% in toluene, stab. with MgO) were obtained from Alfa-aesar and used as received. All solvents used in this work were purified by conventional methods. THF was distilled over a sodium–potassium alloy under an argon atmosphere. NaH (Merck, 60% dispersion in mineral oil) was removed by washing with dry *n*-heptane followed by decantation. $CDCl_3$ used for NMR spectroscopy was obtained from Merck. 1, 8, 9-Anthracenetriol for the MALDI matrix was obtained from Fluka.

Measurements

UV/Vis spectra were recorded with a Shimadzu 2001 UV Pc spectrophotometer. Fluorescence emission spectra were recorded on a Varian Eclipse spectrofluoremeter using 1 cm pathlength cuvettes at room temperature. Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. 1) [20].

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**5**-**8**) 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 solvents. 2-aminopyridine (in 0.1 M H_2SO_4) (Φ_F = 0.60) [21] was employed as the standard. Both the samples and standard were excited at the same wavelength. The concentrations of the solutions at the excitation wavelengths were fixed at $1x10^{-5}$ mol.dm^{-3}. Natural radiative (τ_0) life times were determined using PhotochemCAD program which uses the Strickler-Berg equation [22]. Thin layer chromatography (TLC) was performed on Merck Silica gel plates (Merck 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck 60,0.063–0.200 mm; for 3 g crude mixture, 150 g silica gel was used in a column of 2 cm in diameter and 120 cm in length). Elemental analyses were obtained using a Carlo Erba 1106 Instrument. IR spectra were recorded between 4000 and 650 cm^{-1} using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal. The mass analyzer was a Bruker Daltonics MicrOTOF mass spectrometer equipped with orthogonal electrospray ionization (ESI) source. The instrument was operated in positive or negative ion mode using a range of m/z 50–3000. 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 337nm.

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^{1}H and ^{13}C and 85% H_3PO_4 as an

external reference for ^{31}P. Thermal properties of compounds were investigated on a Mettler Toledo TGA/SDTA 851. Thermogravimetric analysis (TGA) was carried out at temperature range from room temperature to 700°C at a heating rate of 10°C/min under a nitrogen gas atmosphere, and the differential scanning calorimeter (DSC 821^e) equipped with METTLER TOLEDOSTAR ^{e} software at a heating rate of 10 °C min^{-1} under nitrogen flow (50 mL min^{-1}).

Synthesis [23] and spectroscopic data for compounds **1** and **2** were given in supplementary information.

2-azido-1-ethanol was prepared according to the literature [24]. Care was taken to minimize the effect of possible explosions at all stages in the preparation and handling of the azide samples [24], but no untoward occurrences were experienced during this work.

Synthesis of compound 3.

Hexachlorocyclotriphosphazene (1 g, 2.87 mmol) and 2-azido-1-ethanol (2 g, 23 mmol) were dissolved in 40 mL of dry THF in a 100 mL three-necked round-bottomed flask under an argon atmosphere. The reaction mixture was cooled in an ice-bath and NaH (1.15 g, 28.70 mmol) in 15 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction mixture was stirred for 24 h at room temperature and the reaction followed on TLC silica gel plates using *n*-hexane:THF (3:2) as the mobile phase. The reaction mixture was filtered to remove the sodium chloride formed and any other insoluble material. The solvent was removed under reduced pressure and the resulting colorless oil was subjected to column chromatography, using *n*-hexane:THF (3:2) as the mobile phase. 2,2,4,4,6,6-hexzakis-(2'azido-1'-ethoxy)-cyclotriphosphazatriene (**3**) was obtained as a colorless oil (1.4 g, 2.15 mmol) in 75% yield. Anal. Calc. for $C_{12}H_{24}N_{21}O_6P_3$; requires: C, 22.13; H, 3.71; N, 45.16%; M, 651.38 m/z. Found: C, 22.10; H, 3.70; N, 45.15%. MS (ESI) m/z (%):652.31 (100) $[M+H]^+$. FT-IR (ATR, cm^{-1}) 2949 (-CH str), 2093 ($-N_3$), 1440, 1301, 1215 (P=N str), 1039, 963 (P-O-C str), 898, 749. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ, ppm) 4.05 (m, 2H, -O-

153 CH_2-) 3.40 (m, 2H, -CH_2-N_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, δ, ppm) 65.13 (s, -O-CH_2-
154), 50.69 (s, -CH_2-N_3).

155 ***Synthesis of compound 4.***

156 The work-up procedure was similar to that of compound **3**, using
157 octachlorocyclotetraphosphazene (1 g, 2.15 mmol), 2-azido-1-ethanol (1.69 g, 19.35 mmol)
158 NaH (0.78 g, 19.35 mmol). Compound **4,** 2,2,4,4,6,6,8,8-octakis-(2'-azido-1'-ethoxy)-
159 cyclotetraphosphazatetraene, (colorless oil,1.3 g, 1.50 mmol) was obtained in 70% yield.
160 Anal. Calc. for $C_{16}H_{32}N_{28}O_8P_4$; requires: C, 22.13; H, 3.71; N, 45.16%; M, 868.50 m/z.
161 Found: C, 22.12; H, 3.70; N, 45.15%. MS (ESI) m/z (%): 869.50 (100) $[M+H]^+$. FT-IR
162 (ATR, cm^{-1}) 2915 (-CH str), 2120 (-N_3), 1220 (P=N str), 962 (P-O-C str). ^{1}H NMR (500
163 MHz, $CDCl_3$, 25 °C, δ, ppm) 4.14 (m, 2H, -O-CH_2-), 3.49 (m, 2H, -CH_2-N_3). ^{13}C NMR (125
164 MHz, $CDCl_3$, 25 °C, δ, ppm) 65.22 (s, -O-CH_2-), 50.91 (s, -CH_2-N_3).

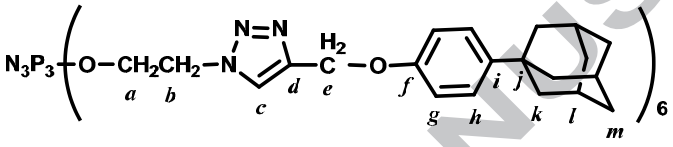
165 ***General method for synthesis of compounds 5–8***

166 Azido cyclophosphazenes (**3** or **4**) and alkyne derivatives (**1** or **2**), copper (I) bromide and
167 PMDTA in dry DCM (20 mL) in a sealed tube was stirred for 48 h at room temperature under
168 an argon atmosphere. The reaction mixture was poured into water and then extracted with
169 DCM. The extract was washed with water and brine and dried over anhydrous Na_2SO_4. The
170 solvent was evaporated and the crude product was purified by column chromatography with
171 *n*-hexane:THF (3:2)

172 ***Synthesis of* compound *5.***

173 Compound **3** (0.20 g, 0.31 mmol), **1** (0.58 g, 2.17 mmol), copper (I) bromide (0.44 g, 3.10
174 mmol) and PMDTA (0.53 g, 3.10 mmol) were used. White powder, mp: 112.0 °C. Yield: 0.6 g,
175 0.26 mmol, 86%. Anal. Calc. for $C_{126}H_{156}N_{21}O_{12}P_3$; requires: C, 67.27; H, 6.99; N, 13.08%;
176 M, 2249.64 m/z. Found: C, 67.25; H, 6.98; N, 13.06%. MS (MALDI) m/z (%): 2250.37
177 (100) $[M+H]^+$. FT-IR (ATR, cm^{-1}) 3139 (Ar C-H), 2901, 2847 (-CH str), 1609 and

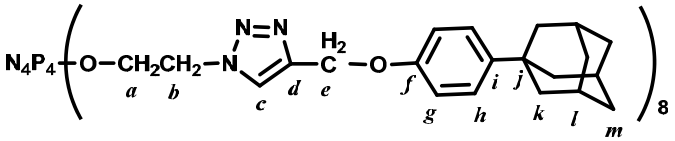
178 1511(C=C str), 1450, 1229 (P=N str), 1040 (C-O-C str), 963 (P-O-C str), 805. ^{1}H NMR (500
179 MHz, $CDCl_3$, 25 °C, δ, ppm) 7.71 (s, 1H, H_c), 7.26 (d, J = 8.8 Hz, 2H, H_h), 6.91 (d, J = 8.8 Hz,
180 2H, H_g), 5.10 (s, 2H, H_e), 4.44 (t, J = 4.8 Hz, 2H, H_a), 4.01 (br, s, 2H, H_b), 2.07 (br, s, 3H, H_l),
181 1.85 (d, J = 2.3 Hz, 6H, H_k), 1.74 (dd, J = 28.0, 12.1 Hz, 6H, H_m). ^{13}C NMR (125 MHz,
182 $CDCl_3$, 25 °C, δ, ppm) 156.20 (s, C^f), 144.68 (s, C^d), 144.30 (s, C^i), 126.19 (s, C^h), 124.50 (s,
183 C^c), 114.39 (s, C^g), 64.45 (s, C^b), 61.95 (s, C^e), 50.15 (s, C^a), 43.54 (s, C^k), 36.94 (s, C^m),
184 35.79 (s, C^j), 29.14 (s, C^l).
185



186

187 ***Synthesis of compound 6.***

188 Compound **4** (0.20 g, 0.23 mmol, **1** (0.55 g, 2.07 mmol), copper (I) bromide (0.40 g, 2.76 mmol)
189 and PMDTA (0.48 g, 2.76 mmol) were used. White powder, mp: 114.5 °C. Yield: 0.57 g, 0.19
190 mmol, 81.7%. Anal. Calc. for $C_{168}H_{208}N_{28}O_{16}P_4$; requires C, 67.27; H, 6.99; N, 13.08%; M,
191 2999.52 m/z. Found: C, 67.24; H, 6.96; N, 13.05%. MS (MALDI) m/z (%):3000.80
192 m/z$[M+H]^+$. FT-IR (ATR, cm $^{-1}$) 3139 (Ar C-H str), 2901, 2847 (-CH str), 1609 and 1511
193 (C=C str), 1450, 1317, 1241 (P=N str), 1041(C-O-C str), 954 (P-O-C str), 805. ^{1}H NMR (500
194 MHz, $CDCl_3$, 25 °C, , ppm) 7.70 (s, 1H, H_c), 7.24 (d, J = 8.7 Hz, 2H, H_h), 6.89 (d, J = 8.7
195 Hz, 2H, H_g), 5.07 (s, 2H, H_e), 4.39 (t, J = 4.8 Hz, 2H, H_a), 3.97 (br, s, 2H, H_b), 2.06 (br, s, 3H,
196 H_l), 1.84 (d, J = 2.1 Hz, 6H, H_k), 1.74 (dd, J = 29.0, 12.0 Hz, 6H, H_m). ^{13}C NMR (125 MHz,
197 $CDCl_3$, 25 °C, , ppm) 156.20 (s, C^f), 144.68 (s, C^d), 144.23 (s, C^i), 126.19 (s, C^h), 124.46 (s,
198 C^c), 114.39 (s, C^g), 64.63 (s, C^b), 61.93 (s, C^e), 50.29 (s, C^a), 43.54 (s, C^k), 36.94 (s, C^m), 35.78
199 (s, C^j), 29.14 (s, C^l).



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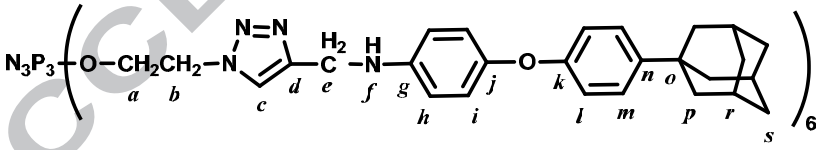
201

202 ***Synthesis of compound 7.***

203 Compound **3** (0.2 g, 0.31 mmol), **2** (0.78 g, 2.17 mmol), copper (I) bromide (0.44 g, 3.10
204 mmol mmol) and PMDTA (0.53 g, 3.10 mmol) were used. White powder, mp: 123.3 °C.
205 Yield: 0.53 g, 0.2 mmol, 61.13%. Anal. Calc. for $C_{162}H_{186}N_{27}O_{12}P_3$; requires: C, 67.27; H,
206 6.99; N, 13.08%; M, 2796.30 m/z. Found: C, 67.25; H, 6.98; N, 13.06%. MS (MALDI) m/z
207 (%):2797.40 (100) $[M+H]^+$. FT-IR (ATR, cm $^{-1}$) 3132 (N-H str), 3038 (Ar C-H str), 2901,
208 2847 (-CH str), 1501 and 1449 (C=C str), 1229 (P=N str), 1084, 1039 (C-O-C str), 958 (P-O-
209 C str), 874, 750. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, δ, ppm) 7.61 (s, 1H, H_c), 7.23 (d, J = 7.9
210 Hz, 2H, H_m), 6.85 (m, 4H, H_l, H_i), 6.74 (m, 2H, H_h), 4.59 (br, s, 2H, H_e), 4.38 (br, s, 2H, H_a),
211 4.09 (br, s, 1H, H_f), 3.94 (s, 2H, H_b), 2.06 (br, s, 3H, H_r), 1.86 (br, s, 6H, H_p), 1.74 (dd, J =
212 26.2, 11.8 Hz, 6H, H_s). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, δ, ppm) 156.01 (s, C^k), 149.75 (s,
213 C^d), 148.54 (s, C^j), 145.93 (s, C^n), 144.33 (s, C^g), 126.20 (s, C^c), 121.22 (s, C^m), 120.62 (s, C^i),
214 117.41 (s, C^l), 114.32 (s, C^h), 64.57 (s, C^b), 50.20 (s, C^a), 47.35 (s, C^e), 43.53 (s, C^p), 36.95 (s,
215 C^s), 35.91 (s, C^o), 29.15 (s, C^r).



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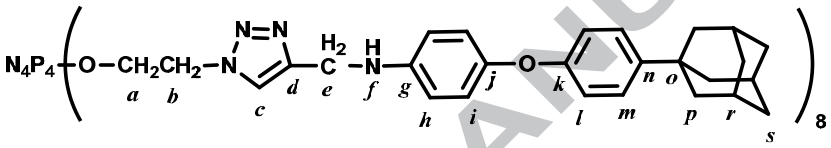
217 ***Synthesis of compound 8.***

218 Compound **4** (0.2 g, 0.23 mmol), **2** (0.74 g, 2.07 mmol), copper (I) bromide 0.40 g, 2.76
219 mmol) and PMDTA (0.48 g, 2.76) were used. White powder, mp: 130.8 °C.Yield: 0.46 g, 0.13
220 mmol, 53.68%. Anal. Calc. for $C_{216}H_{248}N_{36}O_{16}P_4$; requires: C, 69.58; H, 6.70; N, 13.52%; M,
221 3728.40 m/z. Found: C, 69.56; H, 6.70; N, 13.50%. MS (MALDI) m/z (%):3729.30 (100)

222 $[M+H]^+$. FT-IR (ATR, cm^{-1}) 3132 (N-H str), 3041 (Ar C-H str), 2901 and 2847 (-CH str),
223 1501 and 1450(C=C str), 1231(P=N str), 1084, 1042 (C-O-C str), 954 (P-O-C str), 874, 750.
224 ^1H NMR (500 MHz, $CDCl_3$, 25 °C, δ, ppm) δ 7.58 (s, 1H, H_c), 7.23 (d, J = 7.7 Hz, 2H, H_m),
225 6.82 (m, 4H, H_l, H_i), 6.61 (m, 2H, H_h), 4.57 (br, s, 2H, H_e), 4.35 (br, s, 2H, H_a), 4.11 (br, s,
226 1H, H_f), 3.88 (s, 2H, H_b), 2.05 (br, s, 3H, H_r), 1.84 (br, s, 6H, H_p), 1.73 (dd, J = 27.0, 11.9 Hz,
227 6H, H_s). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, δ, ppm) 156.54 (s, C^k), 149.77 (s, C^d), 148.52 (s,
228 C^j), 145.95 (s, C^n), 144.34 (s, C^g), 126.21 (s, C^c), 121.21 (s, C^m), 120.60 (s, C^i), 117.44 (s, C^l),
229 114.29 (s, C^h), 64.72 (s, C^b), 50.36 (s, C^a), 43.53 (s, C^e), 40.33 (s, C^p), 36.95 (s, C^s), 35.91 (s,
230 C^o), 29.15 (s, C^r).



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232

233 ## Results and discussion

234 ***Syntheses and characterizations of compounds***

235 First of all, adamantane derivatives containing alkyne groups (**1** and **2**) were synthesized for
236 using in the *click* reactions. Then, 2-azido-1-ethanol was prepared from the reaction of 2-
237 bromoethanol with sodium azide according to the literature [24]. Cyclophospazene derivatives
238 with azido groups (**3** and **4**) were synthesized from the reactions of 2-azido-1-ethanol with
239 trimer and tetramer, respectively. Further, end-group modifications of azide functional cyclic
240 phosphazenes (**3** and **4**) were achieved quantitatively via the Cu(I) catalyzed *click* reaction
241 between azide functional groups and compound **1**- **2** in the final step (Fig.1).

242 The structures of the compound **1**-**8** (Figs.1-2) were fully characterized by
243 spectroscopic techniques. The elemental analysis and FT-IR (ATR), ^1H and ^{13}C NMR results
244 for each new compound were provided as part of the analytical data in the synthesis section.

^{31}P NMR data for compound **3**-**8** were summarized in Table 1. General presentation of the reactions was shown in Fig.1 and structures of the compound **5-8** were shown in Fig. 2.

The FT-IR spectra of **5**-**8** showed characteristic stretching bands at around 3040–3060 cm^{-1} ($\nu_{C-H,\ aryl}$), 1215 -1241 cm^{-1} ($\nu_{P=N}$) and 3132 cm^{-1} (ν_{N-H}) and 954-963 cm^{-1} (ν_{P-O}) as expected [19,25]. As an example, steps of formation of compound **6** were investigated by FT-IR (ATR) spectra (Figs.3a-d). It was observed that the O-H stretching of 4-(1-adamantyl)phenol at 3206 cm^{-1} (Fig. 3a) disappeared after converted to alkyne derivative (**1**) [(-C≡CH) stretching at 3305 cm^{-1} (Fig.3b)]. N_3 streching of **4** was seen at 2093 cm^{-1} (Fig. 3c). The (-C≡CH) and N_3 stretching bands were disappeared after formation of compound **6** (Fig. 3d).

The MS spectrum of **1-8** provided definitive characterization and the results were given in the experimental section. The mass spectrum of compound **6** as an example was given in Fig. 4. The peak at 3000.803 Da representing the protonated molecular ion provided for definitive characterization. In addition mass spectra of other compounds also compatible with the calculated data.

The proton decoupled ^{31}P NMR spectra of all derivatives were observed as A_3 (for trimeric compounds) and A_4 (for tetrameric compounds) spin systems due to equivalent phosphorus nucleus of the cyclic phosphazene rings. The cyclotriphosphazenes (**3**, **5**, and **7**) showed singlet peak between at δ=16.85-17.39 ppm in high field compare with trimer, whereas cyclotetraphosphazenes (**4**, **6** and **8**) showed a signal between at δ= (-0.93)-(-1.45) ppm in low field compare with tetramer (Table 1).

The expected–carbon signals were assigned from the ^{13}C NMR spectra of all the phosphazenes. The average δ- shift values of OCH_2-, adamantyl and aromatic carbons were observed at around ≅ 50.20 ppm, ≈ 29.15-43.50 ppm and ≈ 111.39-156.54 ppm, respectively. As an example, the ^{1}H-^{13}C HSQC spectrum of **6** was illustrated in Fig. 5. This spectrum

correlated chemical shifts of protons directly bound to carbon atoms. Therefore, all carbon signals of **6** were verified and also confirmed the structure of compound **6**.

Afterwards, the ^{1}H NMR spectra of the compounds were evaluated. In general, ^{1}H NMR spectra of the compounds **5-8** were similar. As expected, the average δ- shift values of OCH_2-, adamantyl, aromatic and -CH-(triazole group) hydrogens were observed at around ≅ 4.05, ≈ 1.7-2.1, ≈ 6.9-7.3, ≈7.7 ppm, respectively. NH- proton was also seen as broad about = 4.09-4.11 ppm for compounds **7** and **8**.

Thermal Properties

The glass transition temperatures (T_g) of all compounds were clearly detected by DSC from 25 to 150°C with a heating rate of 10°C/min under nitrogen flow. The T_g of all new phosphazene compounds (**5**-**8**) represented in Table 1 and the DSC thermograms are given in supplementary information in Figure S1.

Phosphazenes are attractive compounds because they not only have a wide range of thermal stability, but also can provide improved flame retardant properties when compared with the organic homologues [19, 25, 26]. Owing to the excellent thermal stability and char yield, the adamantane substituted polyphosphazene have attracted interest for their potential application in flame retardants [9, 13]. TGA was utilized to evaluate the thermal stability of the cyclophosphazenes containing adamantane units in terms of onset decomposition temperatures (T_d). The decomposition temperatures were recorded at a heating rate of 10 °C/min and T_d-values were collected (Table 1). According to the TGA thermograms of compound **5**-**8** (Fig.6), the T_d-values of adamantane derivatives ranged from 282 to 293 °C indicated fairly high thermal stabilities. The T_d-values of adamantane based cyclophosphazenes increased with increasing rigid phenyl groups. Therefore, adamantane based cyclophosphazenes could be useful candidates for flame retardant additives to organic polymers [9, 13]. As a result, the high char yields and T_d's of phosphazene compounds (**5**-**8**)

make them a good flame retardant in theory [27] and the adamantane based cyclophosphazene derivatives exhibit excellent thermal properties. In order to see what happened after heating (up to 200°C), the emission spectra of compound **5-8** was measured under the same conditions. The spectrum of compound **5** as an example was exhibited in Fig. S2. However, no changes were observed. According to this result of compounds **5-8**, they remain stable until the decomposition temperatures.

Absorption and Fluorescence Properties

The absorption and the fluorescence spectra of compound **5-8** were measured in dichloromethane with dilute solutions of $1x10^{-5}$ mol.dm^{-3} upon excited 260 nm. Absorption bands were observed at 275 and 280 nm for compounds **5** and **6**, 250 and 310 nm for compounds **7** and **8** (Fig. 7). Fluorescence spectra in dichloromethane were depicted in Fig. 8. The increase of maximum fluorescence emissions for compounds **6** vs. **5** and **8** vs. **7** could be explained with the increasing substitution degree of cyclophosphazene core as expected [19, 25, 28]. Fluorescence emission peaks were observed at around 300 nm for compounds **5** and **6** in DCM. The most interesting observations from emission studies of compounds **7** and **8** are two bands at 287 and 357 nm (Fig. 8). In order to get more information on the observed additional band, the emission spectrum of compound **2** was measured under the same conditions ($1x10^{-1}$ mol.dm^{-3}, $1x10^{-3}$ mol.dm^{-3} and $1x10^{-5}$ mol.dm^{-3} in CH_2Cl_2, λ_{exc}:260 nm) (Fig. 9). The emission spectrum of **2** in dichloromethane ($1x10^{-5}$ mol.dm$^{-3)}$ showed only one band at 287 nm. As can be seen in Fig. 9, an obvious enhancement of the excimer emission occurred when the concentration of **2** increased up to $1x10^{-1}$ mol.dm^{-3}, whilst the accompanying monomer emission decreased. It was notable that the formation of the excimer emission in **2** was caused by an intermolecular excimer. Therefore, we could clearly say that the appearance of the 357 nm band in compounds **7** and **8** was originated from the formation of intramolecular interactions as reported in the earlier study [29]. These studies suggested

that intramolecular π-π interactions were stronger in compounds **7** and **8** than those in compounds **5** and **6**. Meanwhile, these results indicated strong hydrogen bonds (N-H…N) between (triazole)-aminodiphenyl ether moieties in compounds **7** and **8**. The fluorescence quantum yields (Φ_F) were determined by the standard method using $1x10^{-5}$ M 2-aminopyridine in a 0.1 M H_2SO_4 solution as the standard for compound **5**-**8**. The refractive indexes of the solvents were taken into account in the measurements. The fluorescence quantum yields (Φ_F) of phosphazene derivatives increased with respect to the increment of the side groups and their values were 0.11 for **5**, 0.14 for **6**, 0.18 for **7** and 0.20 for **8**. The tetrameric phosphazene compounds **6** and **8** showed higher fluorescence quantum yields than the trimeric core phosphazene compounds **5** and **7**. Fluorescence lifetimes (τ_F) of compound **5**-**8** were calculated using the Strickler-Berg equation [22]. The τ_F values were 0.27 ns for **5**, 0.28 ns for **6**, 0.52 ns for **7** and 0.45 ns for **8** in DCM. The comparison between the cyclophosphazenes (**5**-**8**), the compounds **7** and **8** showed longer τ_F values than the compounds **5** and **6** in DCM. The rate constants for fluorescence (k_F) and radiative lifetime (τ_0) were also measured for synthesized phosphazene compounds in this study. The k_F values were $4.21x10^8$ for **5**, $5.09x10^8$ for **6**, $3.42x10^8$ for **7** and $4.45x10^8$ for **8** and τ_0 values were 1.74 ns for **5**, 1.96 ns for **6**, 2.91 ns for **7** and 2.24 ns for **8** in DCM.

Conclusion

In this study, the cyclophosphazenes containing phenoxy-adamantane derivatives (**5-8**) were synthesized successfully in good yields through three-steps. The structures of all the starting compounds (**1**-**4**) and final products (**5**-**8**) were characterized by standard spectroscopic techniques and were reported for the first time. The thermal stability and fluorescence spectral properties of cyclic phosphazene compounds (**5**-**8**) were investigated. According to thermal analyses of adamantane substituted cyclophosphazene derivatives (**5**-**8**), it was found that compounds **7** and **8** had high thermal stabilities and char yields when compared to **5** and **6**.

The absorption and the fluorescence spectra of **5**-**8** were measured in DCM. It could be suggested that both intramolecular non-covalent π-π interactions and strong hydrogen bonds (N-H…N) between (triazole)-aminodiphenyl ether moieties resulted the higher fluorescence behavior of **7** and **8** when compared to **5** and **6.** Thus, it could be concluded that compound **5**-**8** might be suitable candidates for flame retardant additives to polymers or light emitting electroluminescent devices in some industrial applications.

Acknowledgment

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Table 1. ^{31}P NMR parameters and thermal properties of cyclophosphazenes

Compound	DSC(°C)	T_d (°C)[a]	Y[b](%)	^{31}P{H} NMR shifts (ppm)[c]
Trimer	-	-	-	19.9
Tetramer	-	-	-	-5.4
3	-	-	-	17.39
4	-	-	-	-1.45
5	112.0	282	24.95	16.85
6	114.5	288	22.02	-0.93
7	123.3	286	27.52	16.94
8	130.8	293	28.83	-1.10

[a] The temperature for which the weight loss is 5%.

[b] Char yields at 700°C.

[c] 202.38 MHz ^{31}P NMR chemical shifts (ppm) in $CDCl_3$

Captions for figures

Fig. 1. The reaction pathway for the phosphazene derivatives.

Fig.2. Structures of **5-8**.

Fig.3. FT –IR (ATR) spectra of **(a)** 4-(1-adamantyl) phenol, **(b) 1**, **(c) 4**, **(d) 6**

Fig.4. Positive ion and linear mode MALDI TOF-MS spectrum of **6** was obtained in 1,8,9-anthracenetriol (20 mg/mL THF) MALDI matrix using nitrogen laser accumulating 50 laser shots.

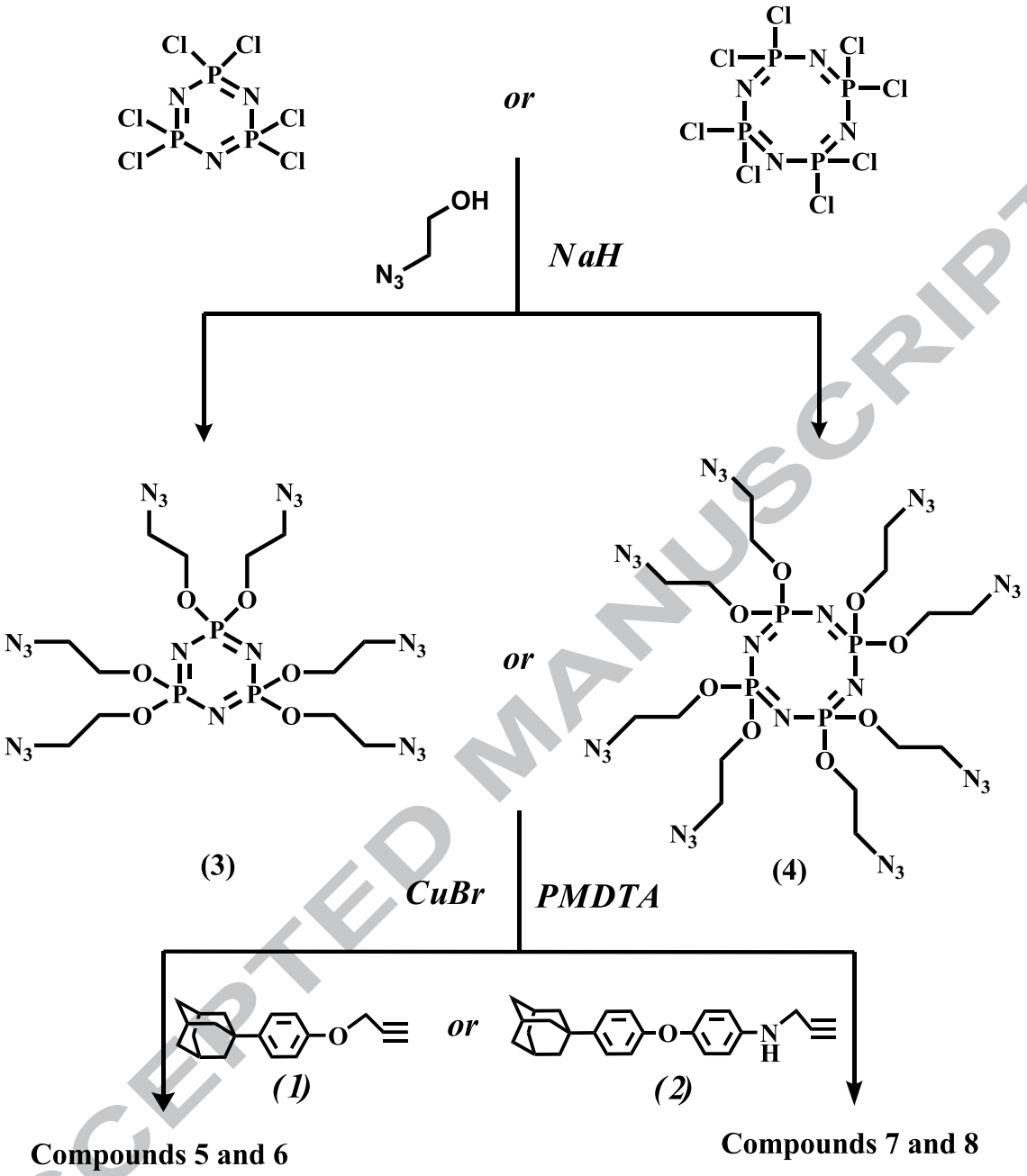
Fig.5. The ^{1}H-^{13}C HSQC spectrum of compound **6**.

Fig.6. TGA curves of compounds **5-8** from 25 to 700 ºC at a heating rate of 10°C/min under N_2 flow of 50 mL/min.

Fig. 7. The absorption spectra of **5**- **8** in dichloromethane. Concentration: $1x10^{-5}$ $mol.dm^{-3}$.

Fig.8. The fluorescence emission spectra of **5-8** in dichloromethane. Concentration: $1x10^{-5}$ $mol.dm^{-3}$. Excitation wavelength: 260 nm.

Fig. 9. The fluorescence emission spectra of **2** in dichloromethane. λ_{exc}: 260 nm.



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456 **Fig.1**. The reaction pathway for the phosphazene derivatives

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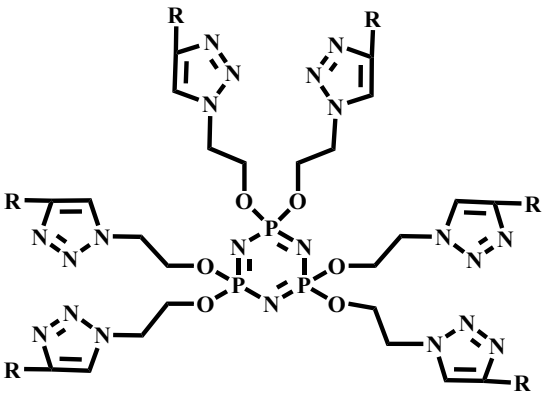
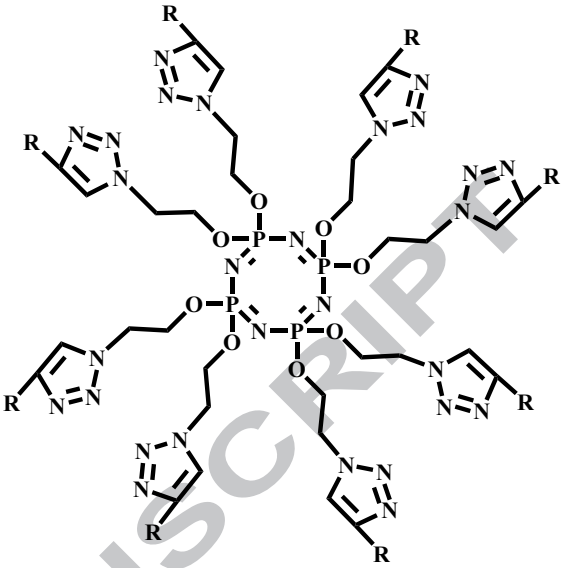
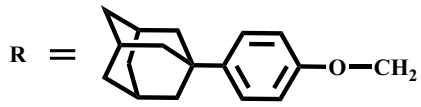


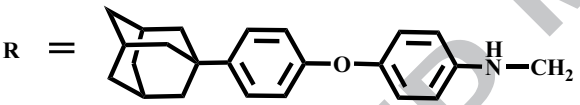
(5, 7)



(6, 8)



Compounds (5, 6)



Compounds (7, 8)

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461 **Fig.2**. Structures of **5-8**.

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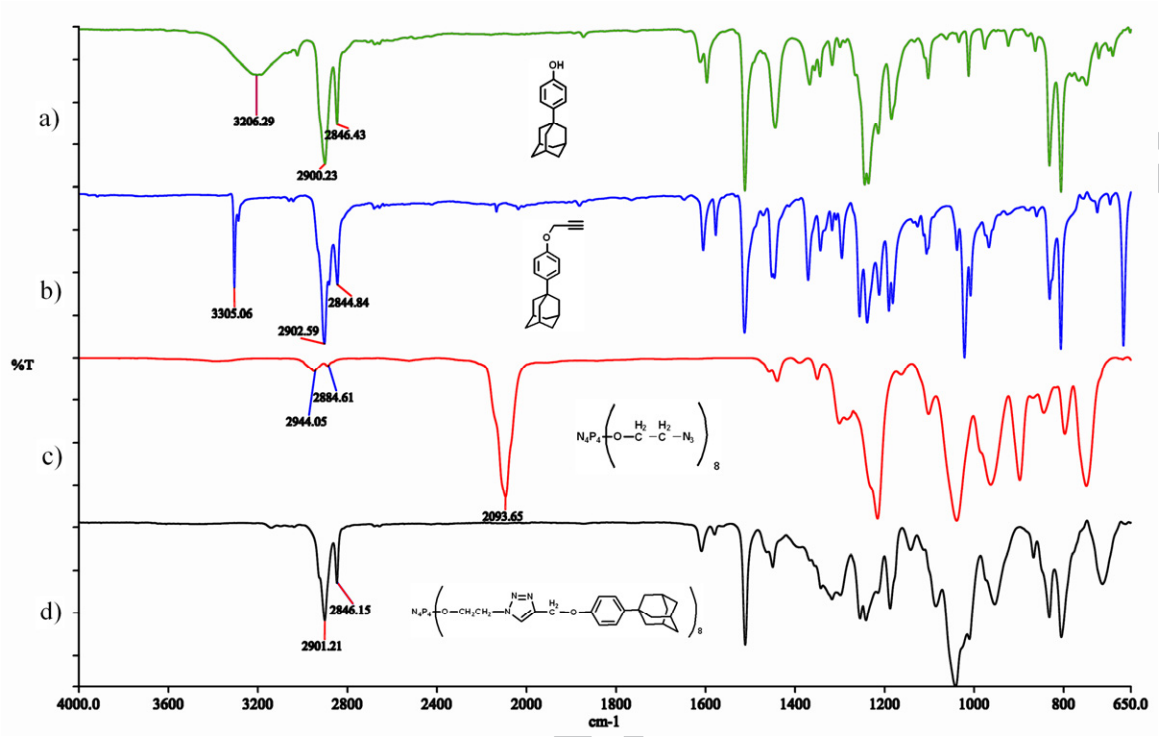

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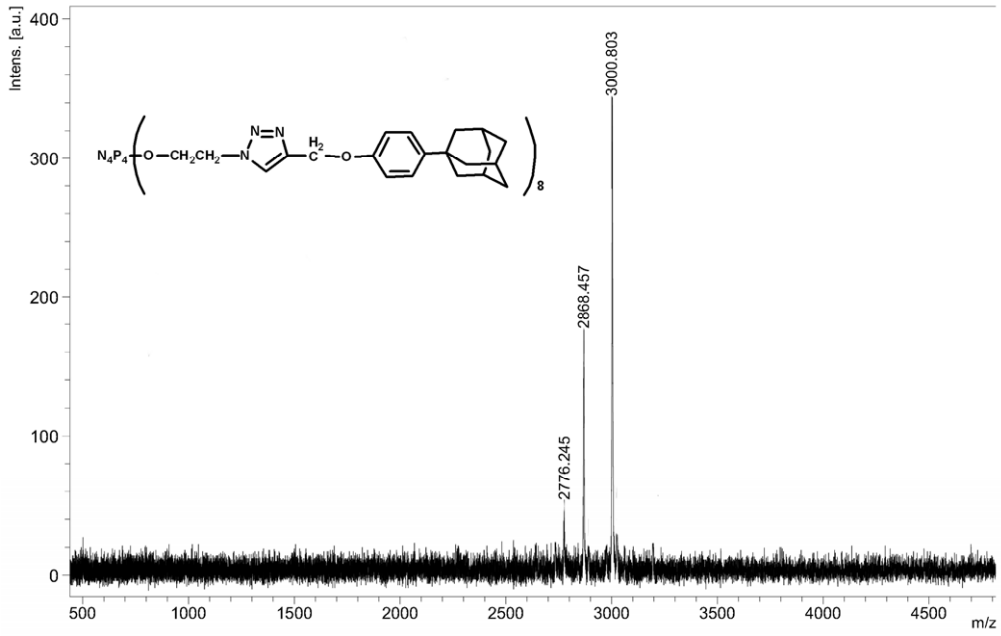

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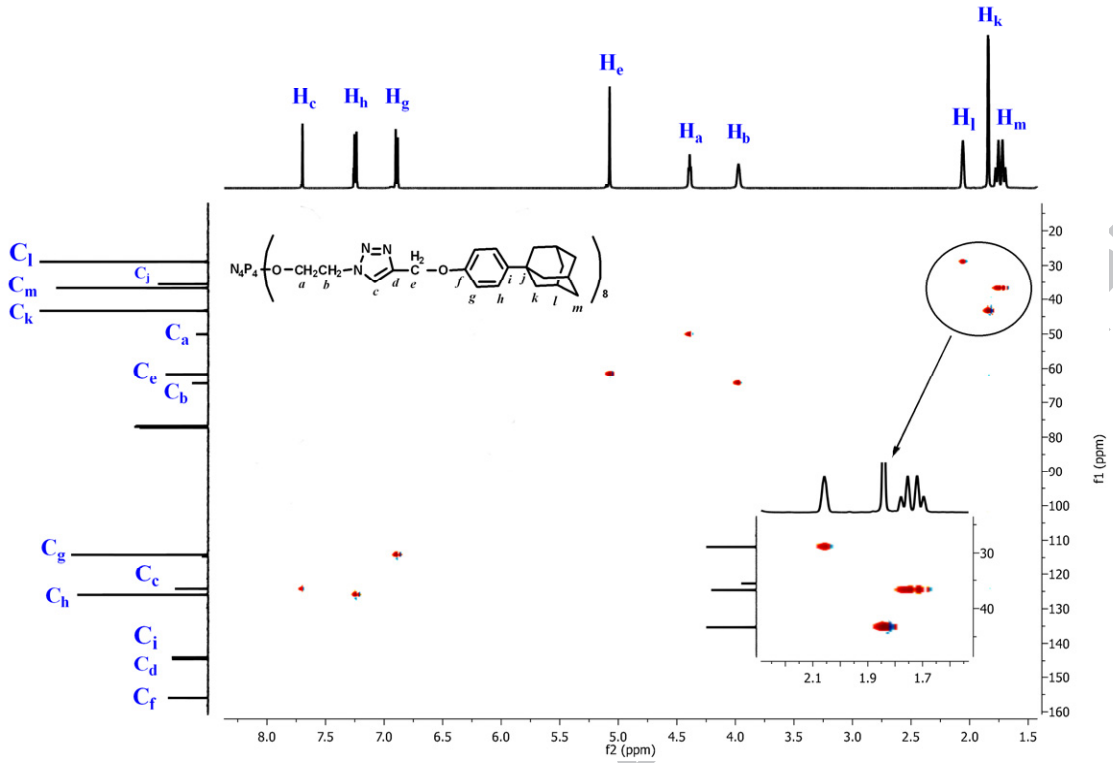

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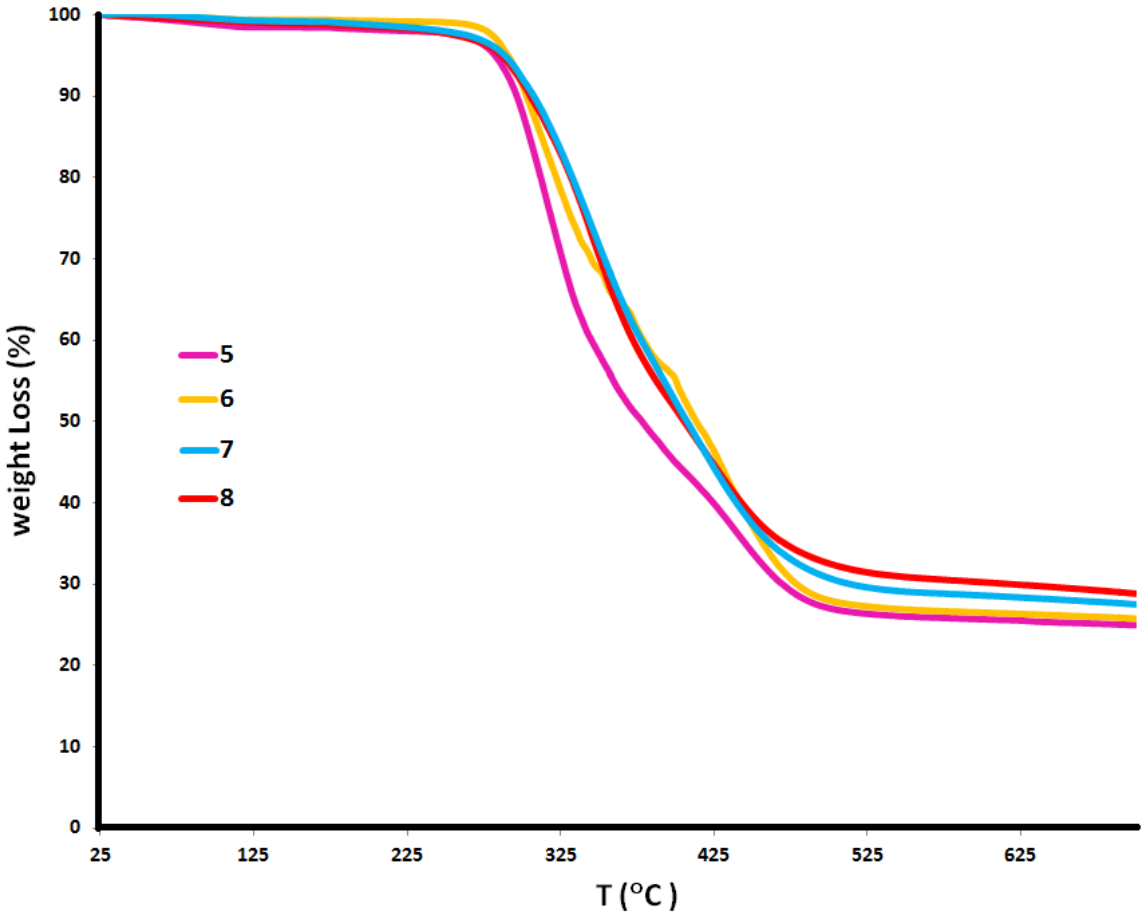


Fig. 6. TGA curves of compounds **5-8** from 25 to 700 ºC at a heating rate of 10°C/min under N_2 flow of 50 mL/min.

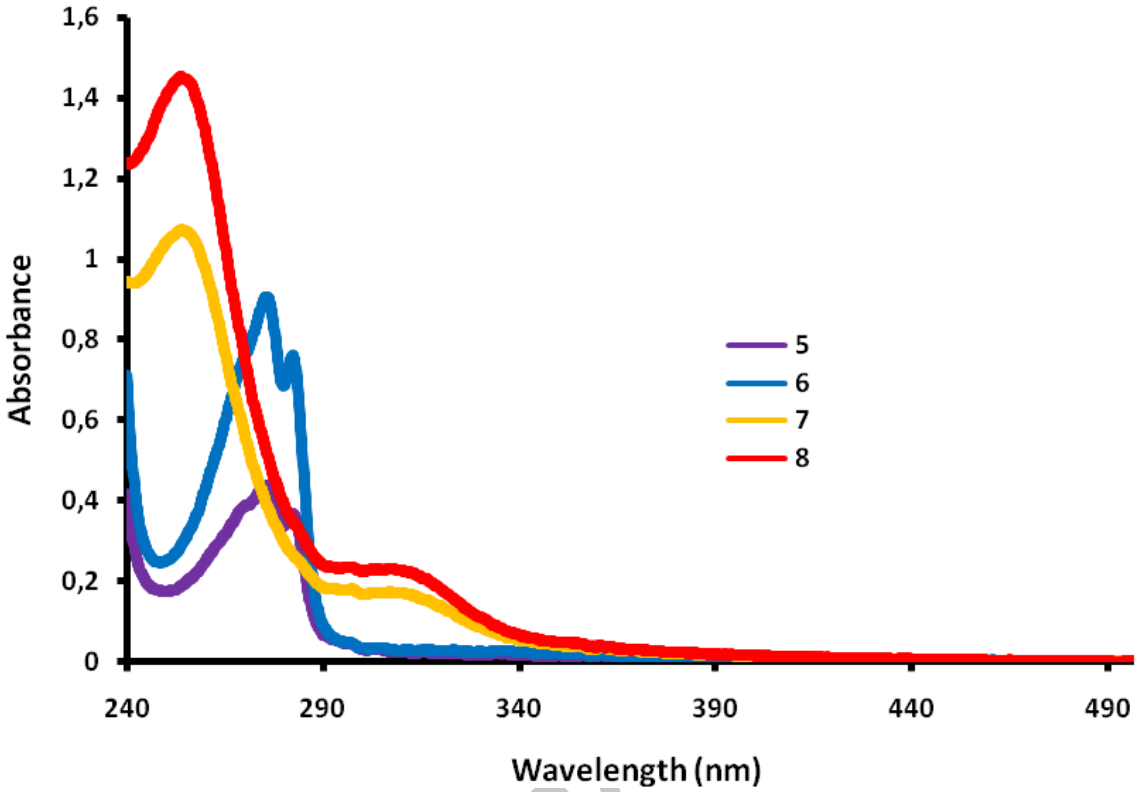
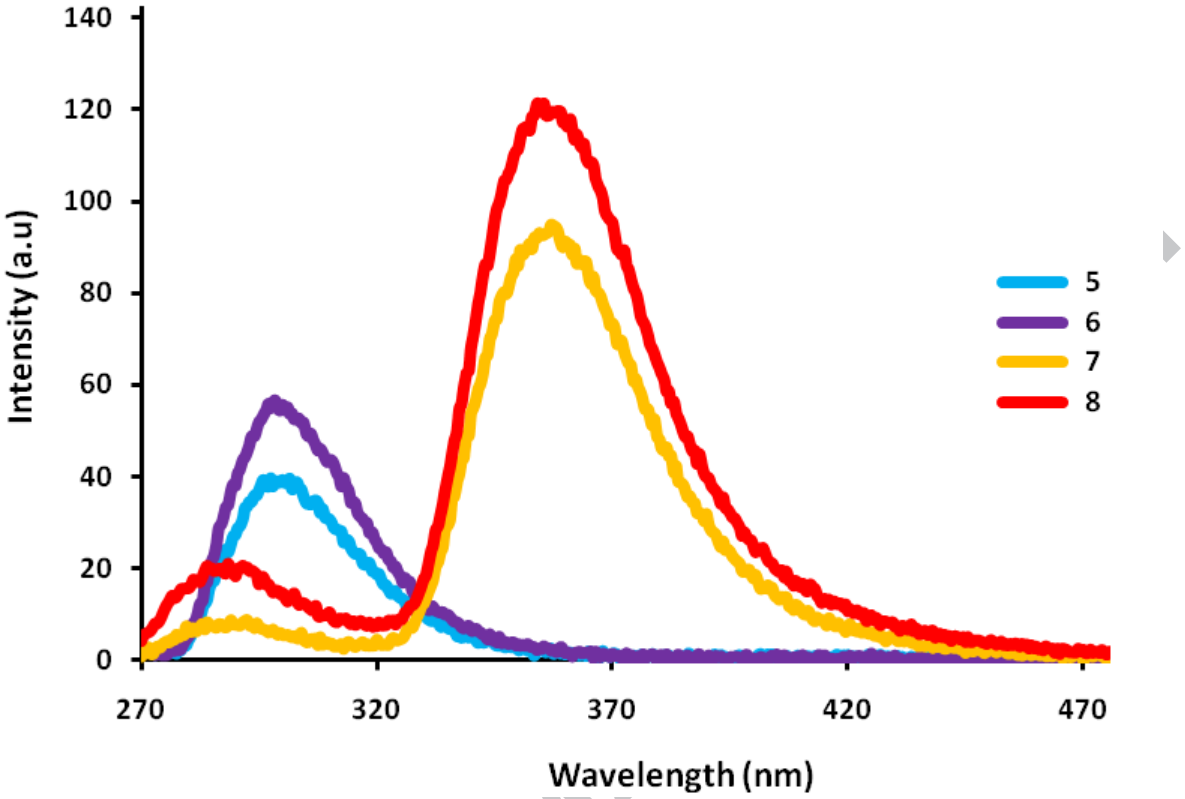


Fig. 7. The absorption spectra of **5**- **8** in dichloromethane. Concentration: $1x10^{-5}$ mol.dm^{-3}.



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528 **Fig. 8.** The fluorescence emission spectra of **5-8** in dichloromethane. Concentration: $1x10^{-5}$

529 $mol.dm^{-3}$. Excitation wavelength: 260 nm.

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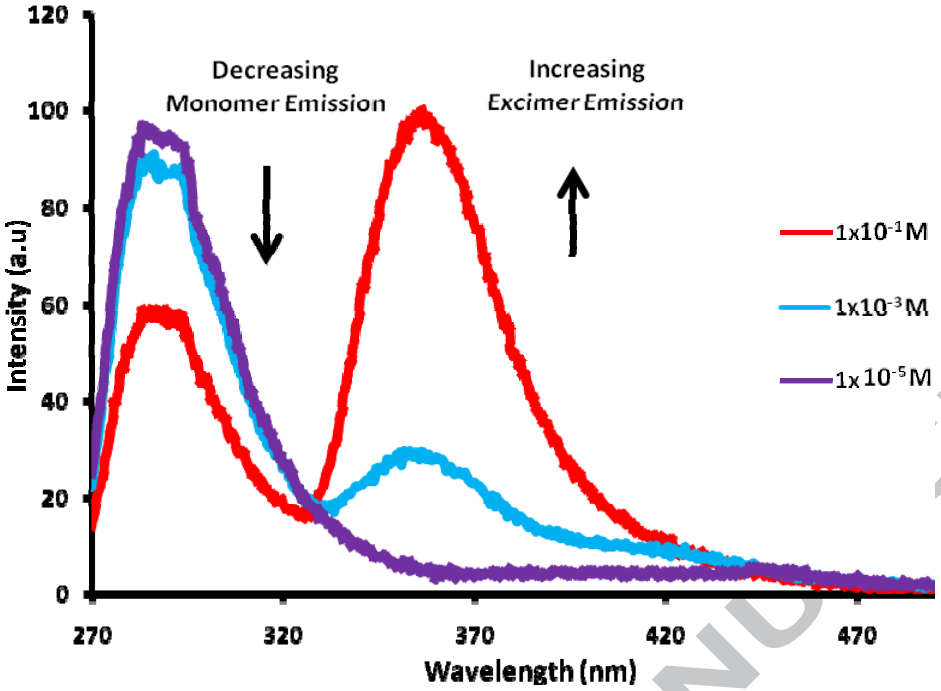

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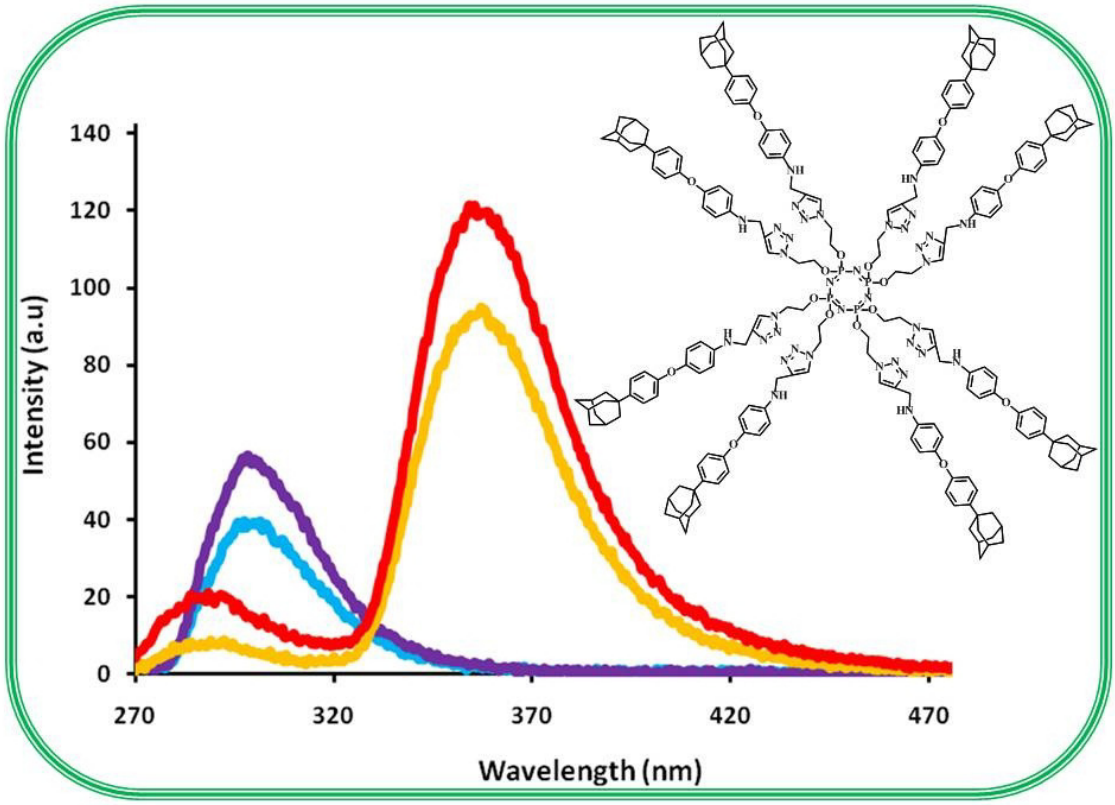
540 **Fig. 9.** The fluorescence emission spectra of **2** in dichloromethane. λ_{exc}: 260 nm.



Syntheses, characterizations, thermal and photophysical properties of cyclophosphazenes containing adamantane units

İlker Ün, Hanife İbişoğlu, Şule Şahin Ün , Bünyemin Çoşut, Adem Kılıç

In this work was shown that synthesis and characterization of cyclophosphazenes containing adamantane derivatives. The thermal stabilities and fluorescence spectral properties of these compounds have been investigated in CH_2Cl_2 solution.

Highlights:

- New cyclophosphazene compounds containing adamantane derivatives were synthesized.
- All compounds were fully characterized by spectroscopic techniques.
- The thermal and photophysical properties of these compounds were investigated.