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Synthesis, Characterization, and Liquid Crystalline Properties of Phosphazenes Incorporated *(E)*-3-(4-alkyloxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one

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Abstract : A series of new substituted cyclotriphosphazenes were prepared by reaction of hexachlorocyclotriphosphazenes, $(NPCl_2)_3$ separately with one and six equivalent of (E)-3-(4-alkyloxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one **(2a-c)** in the presence of base to afford mono[(E)-3-(4-alkyloxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1one **(3a-c)** in 18-27% yields and hexakis[(E)-3-(4-alkyloxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1one **(4a-c)** in 71-88% yields, respectively. All the synthesized compounds were characterized via elemental analysis (CHN), FTIR, and ^{1}H, ^{13}C and ^{31}P NMR. Their molecular structures were further ascertained through ^{1}H-^{1}H Correlation Spectroscopy (COSY) and Heteronuclear Multiple Quantum Coherence (HMQC). The texture observation was performed under polarizing optical microscopy (POM) over heating and cooling cycles.

Keywords : hexachlorocyclotriphosphazenes, chalcones, alkyloxy

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Introduction

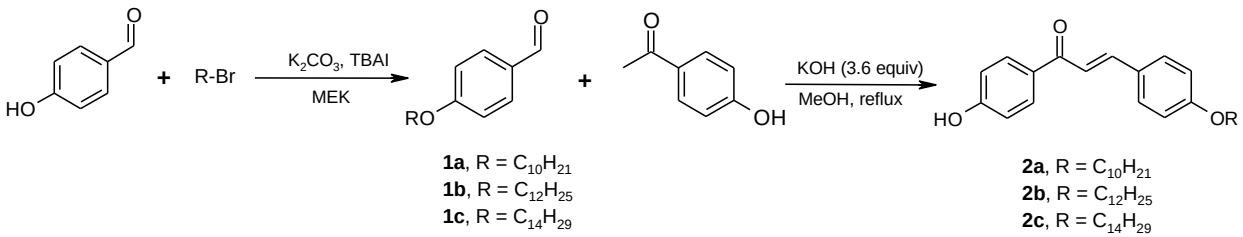
Phosphazenes are cyclic or linear molecules that contain a framework of alternating phosphorus and nitrogen atoms [1]. Studies on linear, cyclo- and polyphosphazenes have been widely investigated. These compounds were reported to possess interesting biomedical properties [2] and promising application such as effective flame retardants for fiber materials [3]. Nucleophilic substitution reactions of cyclotriphosphazenes have been widely reported. Nucleophilic substitution reactions normally involved the replacement of chlorine atom from P-Cl bonds by various nucleophiles such as phenols [4,5], amine [6] and azo [7] groups.

Phosphazenes skeletal system has been used in the field of photo reactive materials. Synthesis of cyclotriphosphazenes bearing cinnamates [8] and hydroxychalcones [9] as side groups had been studied for photosensitive phosphazenes that could undergo photocross-linking reaction under UV irradiation. In photochemistry, chalcones was reported to possess non-linear optical (NLO) property [10] for optical communications and optical electronics, liquid crystals for liquid crystal displays (LCD's) [11,12] and alignment film [13]. It was also reported to promote excellent blue light transmittance and good crystallizability [14,15], high photosensitivity and thermal stability for various crystalline electro-optical devices.

In this paper, we aim to synthesis mono- and hexa-substituted cyclotriphosphazenes bearing chalcones derivatives possessing long alkyl chains ranging from C10 to C14 which could be used as a potential liquid crystal compounds.

Results and Discussion

The series of chalcone derivatives (*E)*-3-[4-(alkyloxy)phenyl]-1-[4-hydroxyphenyl] prop-2-en-1-one **(2a-c)** were first prepared *via* Claisen-Schmidt condensation of **1a-c** with4-hydroxybenzaldehyde by the route depicted in Scheme 1.



1a, R = $C_{10}H_{21}$
1b, R = $C_{12}H_{25}$
1c, R = $C_{14}H_{29}$

2a, R = $C_{10}H_{21}$
2b, R = $C_{12}H_{25}$
2c, R = $C_{14}H_{29}$

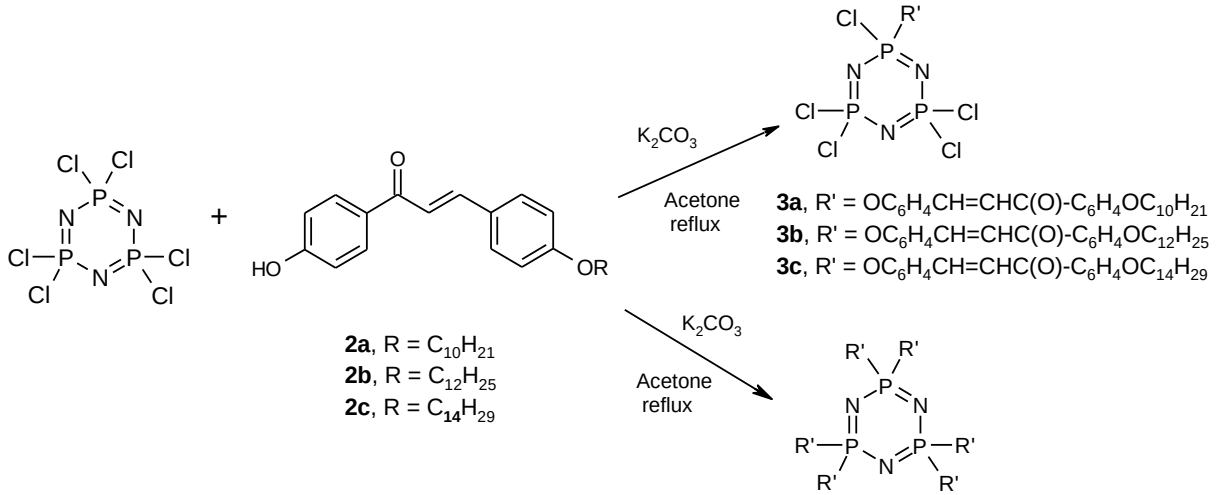
Scheme 1 : Synthesis of chalcone derivatives **2a-c**

The IR spectra of chalcone derivatives **2a-c** showed the presence of bands in the range of 2849-2922 cm^{-1} which were attributed to the introduction of the long alkyl chain via etherification of 4-hydroxybenzaldehyde. The presence of a shifted C=O stretching band to lower wavenumber in the region of 1636-1648 cm^{-1} can also substantiate the formation of the title compounds **2a-c**.

The structures of compounds **2a-c** were further confirmed by ^{1}H and ^{13}C NMR spectral analyses. The ^{1}H NMR spectra of **2a-c** showed the presence of O-alkoxy chain as indicated by proton resonances in the range of δ 1.25-1.79 where the $-OCH_2-$ protons gave a triplet at δ 3.90. A broad peak in the region of δ 6.09-6.49 was attributed to the hydroxyl group. In comparison with the ^{1}H NMR spectra of **1a-c**, the ^{1}H NMR of **2a-c** also showed new peaks attributed to *trans* vinylic proton H_a and H_b at δ 7.67 and δ 7.39, respectively with a coupling constant, J_{ab} = 15 Hz.

The ^{13}C NMR spectra of **2a-c** confirmed the presence of alkoxy group by showing resonances in the range of δ 14.1-68.2. The olefinic carbons C-a and C-b gave two signals in the regions of δ 136.1-144.4 and δ 127.5-130.2, respectively. The oxygenated aromatic carbons gave resonances in the range of δ 162-163 while the chemical shift of carbonyl gave a signal at δ 189.3 in the downfield region. The elemental analysis of **2a-c** was found to be comparable to the theoretical value.

The synthetic route for the preparation of monosubstituted cyclotriphosphazenes **3a-c** and hexasubstituted cyclotriphosphazenes **4a-c** is illustrated in Scheme **2**.



2a, R = $C_{10}H_{21}$
2b, R = $C_{12}H_{25}$
2c, R = $C_{14}H_{29}$

3a, R' = $OC_6H_4CH{=}CHC(O)\text{-}C_6H_4OC_{10}H_{21}$
3b, R' = $OC_6H_4CH{=}CHC(O)\text{-}C_6H_4OC_{12}H_{25}$
3c, R' = $OC_6H_4CH{=}CHC(O)\text{-}C_6H_4OC_{14}H_{29}$

4a, R' = $OC_6H_4CH{=}CHC(O)\text{-}C_6H_4OC_{10}H_{21}$
4b, R' = $OC_6H_4CH{=}CHC(O)\text{-}C_6H_4OC_{12}H_{25}$
4c, R' = $OC_6H_4CH{=}CHC(O)\text{-}C_6H_4OC_{14}H_{29}$

Scheme 2 : Synthesis of **3a-c** and **4a-c**

Monosubsubstituted cyclotriphosphazenes **3a-c** were obtained from the reaction of hexachlorocyclotriphosphazenes with one equivalent of chalcone derivatives **2a-c** in the presence of K_2CO_3 in acetone. The higher polarity of the acetone was believed to increase the rate of reaction compared to THF and dioxane [9,18,19]. The structures of the compounds **3a-c** were characterized by elemental analysis, IR, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies. The IR spectra of **3a-c** showed P=N stretching vibrations at 1162 cm^{-1}, which is the characteristic of cyclotriphosphazenes [20,21]. The absorption band observed at 954 cm^{-1} was attributed to the presence of the P-O-C bond [22].

The ^{31}P NMR spectra showed two resonances appeared as a triplet and a doublet at δ 12.5 and δ 23.0 respectively with a coupling constant, *J*=60 Hz, which implied the replacement of one chlorine from the cyclotriphosphazenes ring to form the monosubstituted phosphazenes [23]. The ^{1}H and ^{13}C NMR data supported the proposed structures of compound **3a-c** which were synthesized from the reaction of mono substituted*(E)*-1-(4-hydroxy-phenyl)-3-(4-alkoxy-phenyl)-propenone **2a-c** with cyclotriphosphazenes.

The reaction of hexachlorocyclotriphosphazenes separately with six equivalents of **2a-c** under the same reaction conditions afforded **4a-c** in high yield. The IR spectra showed the characteristic absorption bands at 1162 cm^{-1} which were attributed to P=N stretching vibrations. The absorption bands observed at 951 cm^{-1} in **4a-c** were attributed to the presence of P-O-C bond. ^{31}P NMR showed a single resonance at δ 9.0, which implied complete chlorine replacement [23]. The data obtained from elemental analysis, ^{1}H and ^{13}C NMR showed good agreement to the corresponded structures.

2D COSY was used to further substantiate the molecular structure of the target compounds. From the COSY spectrum of **3a**, it can be observed that the methyl proton signal (H-10") correlates with ethyl proton signal (H-9").The peaks which appeared in the range of δ 6.8 to δ 7.9 in the ^{1}H NMR spectrum of **2a** indicate the presence of aryl group. The proton H-3 was coupled with proton H-2, both gave a coupling constant of *J* = 8.60 Hz. The doublet of doublets (dd) shown by H-2' in the ^{1}H NMR of **2a** was ascribed to the coupling with aromatic proton H-3' and the olefinic proton H-b. The *trans* conformation of the vinylic proton of H-a at δ 6.4 was found to correlate to H-b.

The HMQC spectrum was further used to assign the attachment of hydrogen to carbon in chalcones moiety and phosphazenes ring. From the HMQC spectrum of **3a**, the carbon atoms occurred at different chemical shift can be assigned. The carbon peak at δ 14.1 and the proton triplet at δ 0.84 were assigned to the methyl group (10"-H_3). The carbon peaks from δ 22.7 to δ 1.9 and the proton multiplets from δ 1.3 to δ 1.8 were assigned to the methylene groups (2"-H_2 to 9"-H_2). The remaining methylene group, -OCH_2- (H-1") is deshielded by the adjacent oxygen atom to give the carbon peak at δ 68.2 and the proton triplet at δ 3.98. The signals owing to the C-3' and C-2' atoms were observed at δ 114.9 and δ 121.4, correlate to the doublet protons at δ 6.90 and δ 7.37, respectively. Meanwhile the signals correspond to the C-3 and C-2 atoms were observed at δ 130.5 and δ 136.4 showing correlation to the proton's doublet at δ 7.57 and δ 8.04, respectively. The carbon peaks at δ 118.9 and δ 145.5 and the two proton's doublets at δ 7.34 and δ 7.76 indicated the presence of the *trans* vinyl group(-CH_a=CH_b-). Meanwhile the carbon signals corresponded to the C-1', C-4', C-4, C-1 and C=O were observed at δ 127.1, δ 136.9, δ 152.2, δ 161.6, and δ 188.9 respectively.

Phase transition and liquid crystallinity of mono-substituted cyclotriphosphazenes and hexa-substituted cyclotriphosphazenes (3a-c and **4a-c)**

The phase transitions of the compounds **(3a-c** and **4a-c)** were studied by using polarizing optical microscope (POM). The phase transition temperatures are summarized in Table 1. No mesomorphic phase was observed for **3a-c** and **4a-c** by polarizing microscope observation. The field in the eyepiece turned black above the crystal phase. It is suggested that a direct transition from the crystalline to isotropic (Cr—I) liquid phase occurred at that temperature.

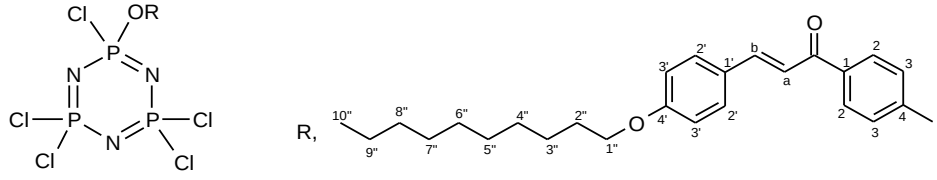


Figure 1 : mono-{*(E)*-3-[4-(alkyloxy)phenyl]-1-[4-hydroxyphenyl]prop-2-en-1-one}cyclotriphosphazenes **3a**

Table 1 : Transition temperature of compounds **(3a-c** and **4a-c)**

Compounds	Transitions	Temperature (˚C)	Melting Points (˚C)
3a	Cr—I	89.0	86.0
	I—Cr	66.5	
3b	Cr—I	71.0	77.0
	I—Cr	30.0	
3c	Cr—I	73.9	75.0
	I—Cr	69.0	
4a	Cr—I	126.0	126.9
	I—Cr	116.0	
4b	Cr—I	122.6	121.7
	I—Cr	113.0	
4c	Cr—I	128.0	127.9
	I—Cr	130.0	

Cr = Crystal, I = Isotropic

The non-mesomorphic phase of **(3a-c** and **4a-c)** might be due to the packing and the hindrance of the bond between the substituent (side chain) and the cyclotriphosphazenes ring which the side chains of the cyclotriphosphazenes ring not regularly aligned [24].

Structure-Mesomorphic Property Relationship Studies

The establishment of chemical structure–property relationships has become a common practice in the studies of compounds which exhibit liquid crystal properties. Terminal groups and intermolecular interactions play a major role in generating the parallel molecular arrangement which gives rise to the liquid crystalline phase [25, 26]. With this regards, the non-mesomorphic phase of **(3a-c** and **4a-c)** might be due to the absence of the electron donor–acceptor interactions which is required to enhance the orientational cohesive forces between molecules, thus producing sufficient order in the molecular arrangement of compounds to exhibit liquid crystal properties.

Experimental

Materials: 4-hydroxybenzaldehyde, 4-hydroxyacetophenone, and 1-bromoalkanes were obtained from Merck Company and used without any further purification. Hexachlorocyclotriphosphazenes was provided by Aldrich and was used as received. Acetone was distilled from calcium hydride under nitrogen before use. All other reagents and solvent were used as received. The reactions were performed under dry nitrogen.

Measurements: The melting points of the synthetic products were determined on a melting point measurement device and uncorrected. Infrared spectra were recorded on (FT-IR) 1605 Shimadzu Spectrophotometer by preparing samples in thin films on a sodium chloride plate or in potassium bromide pellet (KBr). ^{1}H NMR spectra were recorded at 500 MHz on a Jeol Delta 2-NMR spectrometer. ^{13}C NMR spectra were recorded at 125 MHz on the same spectrometer. The chemical shifts for ^{31}P NMR are relative to the external standard of 85% phosphoric acid.

4-Decyloxybenzaldehyde (1a)

A mixture of 1 bromodecane (4.17 mL, 24 mmol), 4-hydroxybenzaldehyde (2.44 g, 20 mmol), K_2CO_3 (3.32 g, 24 mmol), TBAI (0.89 g, 2.4 mmol) in MEK (80 mL) were refluxed for 11 h. The mixture was filtered and cooled at room temperature. Water (30 mL) was added to the filtrate and the layers were separated. The aqueous layer was extracted with dichloromethane (2 x 30 mL). The combined layers were washed with water (2 x 20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give **1a** (4.51 g, 86%) as yellowish oil. The FTIR and NMR data were consistent with the reported literature values [16]. The same general procedure gave compounds **1b-c**, with the scale (mL, mmol, [bromoalkane]) and yields given below.

4-Dodecyloxybenzaldehyde (1b)

Bromododecane (5.75 mL, 24 mmol). Yield 4.03 g, 90%. The FTIR and NMR data were consistent with the reported literature [16].

4-Tetradecyloxybenzaldehyde (1c)

Bromotetradecane (5.46 mL, 24 mmol). Yield 4.73 g, 74%. The FTIR and NMR data were consistent with the reported literature [16].

***(E)*-3-[4-(Decyloxy)phenyl]-1-[4-hydroxyphenyl]prop-2-en-1-one (2a)**

A mixture of 4-hydroxyacetophenone (2.72 g, 20 mmol) and **1a** (5.25 mL, 20 mmol) in 60 mL of methanol was added under stirring to a solution of KOH (4.04 g, 72 mmol) in methanol (10 mL). The mixture was refluxed for 10 h. The reaction was cooled to room temperature and acidified with cold acid (2N). The resulting precipitate was filtered, washed and dried. The crude was recrystallized from hexane: ethanol to give **2a** (6.83 g, 54%) as yellow crystals. The FTIR and NMR data were consistent with the reported literature [16]. The same general procedure gave compounds **2b-c** with the scale (mmol, mL [**1b-c**]) and yields given below.

***(E)*-3-[4-(Dodecyloxy)phenyl]-1-[4-hydroxyphenyl]prop-2-en-1-one (2b)**

1b (5.81 mL, 20 mmol). Yield: 8.32 g, 52%. The FTIR and NMR data were consistent with the reported literature [16].

***(E)*-3-[4-(Decyloxy)phenyl]-1-[4-hydroxyphenyl]prop-2-en-1-one (2c)**

1c (6.37 g, 20 mmol). Yield: 5.51 g, 54%. The FTIR and NMR data were consistent with the reports literature [16].

Mono-{*(E)*-3-[4-(decyloxy)phenyl]-1-[4-hydroxyphenyl]prop-2-en-1-one}cyclotri phosphazenes (3a)

A mixture of hexachlorocyclotriphosphazenes (0.5 g, 1.44 mmol), **2a** (0.55 g, 1.44 mmol), and K_2CO_3 (2.87 g) in acetone (40 mL) was refluxed temperature for 1 h. The mixture was allowed to cool to room temperature, filtered and concentrated in *vacuo*. The crude solid was recrystallized from acetone to afford **3a** (0.18 g, 18%) as yellow solid. m.p. 86-87 ˚C; (Found: C, 43.25; H, 4.42; N, 6.17. $C_{25}H_{31}Cl_5N_3O_3P_3$ Requires C, 43.41; H, 4.52; N, 6.07%); R_f 0.5 (1:16 THF/ hexane); υ_{max} (thin films/cm^{-1}) 1185 (P=N), 871 (P-O-C); δ_H (500 MHz, $CDCl_3$) 0.86 (3H, t, 10”-H_3), 1.26-1.78 (16H, m, 2”-H_2 to 9”-H_2), 3.98 (2H, t, 1”-H_2), 6.90 (2H, d, *J*= 8.1, 3’ x 2-H), 7.34 (1H, d, *J*= 15.5, H_b-H), 7.37 (2H, d, *J* = 8.6, 2’ x 2-H), 7.57 (2H, d, *J* = 8.1, 3 x 2-H), 7.76 (1H, d, *J*= 15.5, H_a-H), 8.04 (2H, d, *J*= 8.1, 2 x 2-H); δ_C (125.77 MHz, $CDCl_3$) 14.1, 22.6, 26.0, 29.1, 29.3, 29.4, 29.5, 29.5, 31.9, 68.2, 114.9, 118.8, 121.5, 127.1, 130.4, 130.4, 136.9, 145.5, 152.2, 161.5, 188.9; δ_P (200 MHz, $CDCl_3$) 12.5 (t, *J*= 60.0, P_a-P), 23.0 (d, *J*= 60.0, P_b-P). The same general procedure gave compounds **(3b-c)** and **(4a-c),** with the scale (gram, mmol [**2b-c**]), reaction times, yields and spectroscopy data given below.

Mono-{*(E)*-3-[4-(dodecyloxy)phenyl]-1-[4-hydroxyphenyl]prop-2-en-1-one}cyclotri phosphazenes (3b)

2b (0.59 g, 1.44 mmol), 1 h. Yield: 0.28 g, 27%. m.p. 77-78 ˚C; (Found: C, 45.24; H, 4.21; N, 5.44. $C_{27}H_{35}Cl_5N_3O_3P_3$ Requires C, 45.06; H, 4.90; N, 5.84%); R_f 0.52 (1:16 THF/ hexane); υ_{max} (thin films/cm^{-1}) 1185 (P=N), 872 (P-O-C); δ_H (500 MHz, $CDCl_3$) 0.86 (3H, t, 12”-H_3), 1.25-1.79 (20H, m, 2”-H_2 to 11”-H_2), 3.99 (2H, t, 1”-H_2), 6.90 (2H, d, *J*= 8.6, 3’ x 2-H), 7.05 (2H, d, *J*= 8.6, 2’ x 2-H), 7.34 (1H, d, *J*= 15.5, H_b-H), 7.37 (2H, d, *J* =8.6, 3 x 2-H), 7.56 (2H, d, *J*= 8.6, 2 x 2-H), 7.77 (1H, d, *J*= 15.5, H_a-H); δ_C (125.77 MHz, $CDCl_3$) 13.9, 14.1, 22.7, 26.0, 29.1, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 68.2, 114.8, 118.8, 121.5, 127.1, 130.4, 136.9, 145.5, 152.2, 152.4, 161.5, 188.9; δ_P (200 MHz, $CDCl_3$) 12.5 (t, *J*= 60.0, P_a-P), 23.3 (d, *J*= 60.0, P_b-P)

Mono-{*(E)*-3-[4-(tetradecyloxy)phenyl]-1-[4-hydroxyphenyl]prop-2-en-1-one}cyclo triphosphazenes (3c)

2c (0.59 g, 1.44 mmol), 1 h. Yield: 0.28 g, 26%**.** m.p. 75-76 ˚C; (Found: C, 45.96; H, 5.22; N, 5.55. $C_{29}H_{39}Cl_5N_3O_3P_3$ Requires C, 46.58; H, 5.26; N, 5.62%); R_f 0.44 (1:16 THF/ hexane); υ_{max} (thin films/cm^{-1}) 1186 (P=N), 871 (P-O-C); δ_H (500 MHz, $CDCl_3$) 0.80 (3H, t, 14”-H_3), 1.18-1.72 (24H, m, 2”-H_2 to 13”-H_2), 3.92 (2H, t, 1”-H_2), 6.82 (2H, d, *J* = 8.6, 3’ x 2-H), 7.27 (1H, d, *J*= 15.5, H_b-H), 7.29 (2H, d, *J* = 8.6, 2’ x 2-H), 7.49 (2H, d, *J* = 8.6, 3 x 2-H), 7.70 (1H, d, *J*= 15.5, H_a-H), 8.00 (2H, d, *J*= 8.1, 2 x 2-H); δ_C (125.77 MHz, $CDCl_3$) 14.1, 22.6, 26.1, 29.1, 29.1, 29.3, 29.5, 29.5, 29.6, 29.6, 29.6, 31.0, 31.9, 68.2, 114.9, 118.8, 121.4, 121.5, 127.1, 130.4, 130.4, 136.9, 145.5, 152.1, 152.2, 161.5, 188.9; δ_P (200 MHz, $CDCl_3$) 12.5 (t, *J*= 60.0, P_a-P), 23.3 (d, *J*= 60.0, P_b-P).

Hexakis-{*(E)*-3-[4-(decyloxy)phenyl]-1-[4-hydroxyphenyl]prop-2-en-1-one}cyclotriphosphazenes (4a)

2a (0.25 g, 0.72 mmol), 2 h. Yield: 53 g, 88%. m.p. 126-127 ˚C; (Found: C, 74.98; H, 8.27; N, 1.59. $C_{150}H_{186}N_3O_{18}P_3$ Requires C, 74.69; H, 7.76; N, 1.74%) R_f 0.38 (1:3 THF/ hexane); υ_{max} (thin films/cm^{-1}) 3062 (C-H in aromatic), 1179 (P=N), 893 (P-O-C); δ_H (500 MHz, $CDCl_3$) 0.89 (3H, t, 10”-H_3), 1.28-1.79 (16H, m, 2”-H_2 to 9”-H_2), 3.98 (2H, t, 1”-H_2), 6.87 (2H, d, *J* = 8.0, 3’ x 2-H), 7.05 (2H, d, *J*= 8.0, 2’ x 2-H), 7.30 (1H, d, *J* = 15.3, H_b-H), 7.49 (2H, d, *J*= 8.6, 3 x 2-H), 7.64 (1H, d, *J*= 15.5, H_a-H), 7.86 (2H, d, *J*= 8.6, 2 x 2-H); δ_C (125.77 MHz, $CDCl_3$) 14.1, 22.6, 26.0, 29.1, 29.3, 29.5, 29.5, 29.6, 31.9, 68.2, 114.9, 118.8, 121.5, 127.1, 130.4, 130.4, 136.9, 145.5, 152.2, 152.2, 188.9; δ_P (200 MHz, $CDCl_3$) 9.0 (s, 3P, N_3P_3 ring)

Hexakis{*(E)*-3-[4-(dodecyloxy)phenyl]-1-[4-hydroxyphenyl]prop-2-en-1-one}cyclotriphosphazenes (4b)

2b (0.25 g, 0.72 mmol), 2 h. Yield: 1.31 g, 71%. m.p. 121-124 ̊C; (Found: C, 75.18; H, 8.23; N, 1.68. $C_{162}H_{210}N_3O_{18}P_3$ Requires C, 75.41; H, 8.20; N, 1.63%); R_f 0.47 (1:3 THF/ hexane); υ_{max} (thin films/cm^{-1}) 3068 (C-H in aromatic), 1175 (P=N), 893 (P-O-C); δ_H (500 MHz, $CDCl_3$) 0.86 (3H, t, 12''-H_3), 1.25-1.78 (20H, m, 2''-H_2 to 11''-H_2), 3.95 (2H, t, 1''-H_2), 6.85 (2H, d, *J* = 8.6, 3' x 2-H), 7.03 (2H, d, *J*= 8.0, 3 x 2-H), 7.29 (1H, d, *J*= 15.5, H_b-H), 7.47 (2H, d, *J*= 8.5, 2' x 2-H), 7.62 (1H, d, *J*= 15.5, H_a-H), 7.85 (2H, d, *J*= 8.0, 2 x 2-H); δ_C (125.77 MHz, $CDCl_3$) 14.1, 22.6, 26.0, 29.1, 29.3, 29.6, 29.6, 29.6, 30.8, 31.9, 67.9, 68.1, 114.7, 118.4, 121.0, 127.1, 130.2, 130.5, 135.8, 145.3, 153.2, 161.4, 188.7; δ_P (200 MHz, $CDCl_3$) 9.0 (s, 3P, N_3P_3 ring)

Hexakis-{*(E)*-3-[4-(tetradecyloxy)phenyl]-1-[4-hydroxyphenyl]prop-2-en-1-one}cyclotriphosphazenes (4c)

2c (0.25 g, 0.72 mmol), 2 h. Yield: 1.48 g, 75%. m.p. 127-131 ̊C; (Found: C, 76.79; H, 8.56; N, 1.81. $C_{174}H_{234}N_3O_{18}P_3$ Requires C, 76.03; H, 8.58; N, 1.53%); R_f 0.49 (1:3 THF/ hexane); υ_{max} (thin films/cm^{-1}) 3068 (C-H in aromatic), 1175 (P=N), 887 (P-O-C); δ_H (500 MHz, $CDCl_3$) 0.80 (3H, t, 14''-H_3), 1.19-1.72 (24H, m, 2''-H_2 to 13''-H_2), 3.90 (2H, t, 1''-H), 6.79 (2H, d, *J*= 7.4, 3'x 2-H), 6.98 (2H, d, *J* = 8.1, 2' x 2-H), 7.22 (1H, d, *J* = 15.5, H_b-H), 7.41 (2H, d, *J*= 7.4, 3 x 2-H), 7.56 (1H, d, *J*= 15.5, H_a-H), 7.79 (2H, d, *J* = 7.5, 2 x 2-H); δ_C (125.77 MHz, $CDCl_3$) 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 29.6, 29.6, 29.7, 29.7, 29.7, 31.9, 68.2, 114.8, 118.5,121.0, 127.2, 130.2, 130.5, 135.8, 145.3, 153.2, 161.4, 188.7; δ_P (200 MHz, $CDCl_3$) 9.0 (s, 3P, N_3P_3 ring)

Conclusion

Monosubstituted cyclotriphosphazenes **3a-c** were obtained from the reaction of hexachlorocyclotriphosphazenes with one equivalent of chalcone derivatives **2a-c**. Hexasubstituted cyclotriphosphazenes **(4a-c)** were obtained from the reaction of hexachlorocyclotriphosphazenes with six equivalents of chalcone derivatives **2a-c** *via* replacement of all the chlorine atoms. The two dimensional COSY and ^1H-^{13}C HMQC further confirmed the molecular structure of the synthesized compounds. The phase transitions of the compounds (**3a-c** and **4a-c**) were studied using POM. However, all the final products (**3a-c** and **4a-c**) did not show mesomorphism characteristics as the POM observation gave direct transition from crystalline to isotropic (Cr—I) liquid phase.

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