Synthesis and characterization of chalcone-substituted phosphazenes

Zainab Ngaini and Norashikin I. Abdul Rahman

Abstract: A series of mono[(*E*)-1-(4-alkyloxyphenyl)-3-(4-hydroxy-phenyl)prop-2-en-1-one]cyclotriphosphazenes and hexakis[(*E*)-1-(4-alkyloxy-phenyl)-3-(4-hydroxy-phenyl) prop-2-en-1-one]cylotriphosphazenes have been synthesized. A convenient synthetic method was performed from the reaction of hexachlorocyclotriphosphazenes with 1 and 6 equiv. of (*E*)-1-(4-alkyloxyphenyl)-3-(4-hydroxy-phenyl)prop-2-en-1-one (**2a**–**2c**) to afford (**3a**–**3c**) in 17%–19% and (**4a**–**4c**) in 70%–82%, respectively. The compounds differ in the length of alkyl groups, C_nH_{2n+1}, where n = 10, 12, and 14.

Key words: hexachlorocyclotriphosphazenes, chalcones, alkyloxy, condensation.

Résumé : On a réalisé la synthèse d'une série de mono[(*E*)-1-(4-alkyloxyphényl)-3-(4-hydroxyphényl)prop-2-én-1-one]cyclotriphosphazènes et de hexakis[(*E*)-1-(4-alkyloxyphényl)-3-(4-hydroxyphényl)prop-2-én-1-one]cyclotriphosphazènes. On a exécuté une méthode de synthèse appropriée par réaction d'hexachlorocyclotriphosphazènes avec 1 et 6 equiv. de (*E*)-1-(4-alkyloxyphényl)-3-(4-hydroxyphényl)prop-2-én-1-one (**2a**–**2c**) qui ont conduit respectivement aux produits (**3a**–**3c**) avec des rendements allant de 17 à 19 % et aux produits (**4a**–**4c**) avec des rendements allant de 70 à 82 . Les composés diffèrent par la longueur des groupes alkyles, C_nH_{2n+1}, dans lesquels n = 10, 12 et 14.

Mots-clés : hexachlorocyclotriphosphazènes, chalcones, alkyloxy, condensation.

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Introduction

Phosphazenes are compounds containing a framework of alternating phosphorus and nitrogen atoms, either in cyclic or linear form.[1] Linear, cyclic, and poly phosphazenes have been widely investigated. These compounds are reported to possess interesting biomedical properties[2] and promising application as effective flame retardants for fiber materials.[3] Nucleophilic substitution reactions on hexachlorocyclotriphosphazenes have been widely reported.[4–6] The synthesis of cyclotriphosphazenes, bearing 4-oxychalcones[6] as side groups, has been studied for photosensitive phosphazenes that could undergo photo-cross-linking reaction under UV irradiation.

In photochemistry, chalcone derivatives were reported to possess outstanding nonlinear optic property for optical communications and optical electronics,[7] liquid crystal displays,[8,9] and alignment film.[10] Chalcones were also reported to promote excellent blue-light transmittance and good crystallability,[11,12] high photosensitivity, and thermal stability for various crystalline electro-optical devices.

Recently, we reported a very convenient method for the preparation of trimeric aryloxyphosphazenes directly from $[N_3P_3Cl_6]$ and (*E*)-3-(4-(alkyloxy)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one using K_2CO_3 in acetone.[13] This prompted us to try the reaction of cyclotriphosphazenes with other para-substituted hydroxy chalcones. We herein describe the synthesis of cyclotriphosphazenes incorporated with hydroxylated chalcones (*E*)-1-[4-(alkyloxy)phenyl]-3-[4-hydroxyphenyl] prop-2-en-1-one (**2a**–**2c**), which could be used as model reactions for various crystalline electro-optical devices.

Results and discussion

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

The structural assignments of compounds **2a**–**2c** were based on the analytical and spectral data. The IR spectra of the hydroxylated chalcones **2a**–**2c** showed the presence of bands at 2921–2852 cm^{-1}, which were attributed to the introduction of the long alkyl chain via etherification of 4-hydroxyacetophenone. The presence of a new C=O stretching frequency at 1651 cm^{-1} substantiated the formation of the title compound. The chemical structures of **2a**–**2c** were found to be consistent with ^1H NMR and ^{13}C NMR spectroscopic data and showed the peaks corresponding to the structures. In ^1H NMR spectra, the coupling constant, J_{ab} = 15.0–16.0 Hz, indicated all chalcones obtained were in trans-configuration.

The synthetic route for the preparation of mono-($N_3P_3Cl_5[OC_6H_4CH{=}CHC(O)C_6H_4OC_nH_{2n+1}]$) (**3a**–**3c**) and hexa-substituted cyclotriphosphazenes ($N_3P_3[OC_6H_4CH{=}CH$-$C(O)$–$C_6H_4OC_nH_{2n+1}]_6$) (**4a**–**4c**) is illustrated in Scheme 2.

Mono-subsubstituted cyclotriphosphazenes **3a**–**3c** were obtained from the reaction of hexachlorocyclotriphosphazenes with 1 equiv. of chalcone derivatives **2a**–**2c** in the presence of K_2CO_3 in acetone. The higher polarity of the

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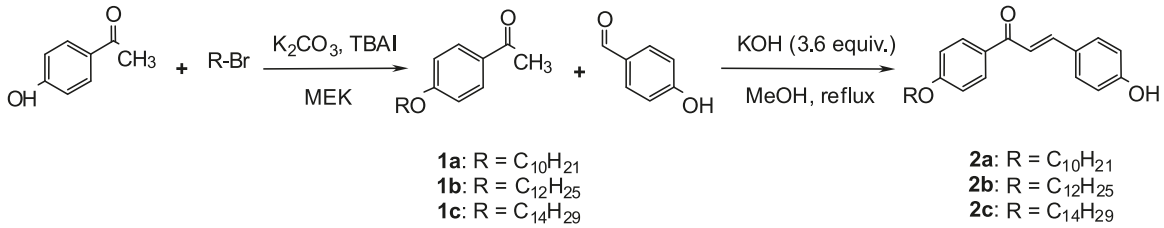
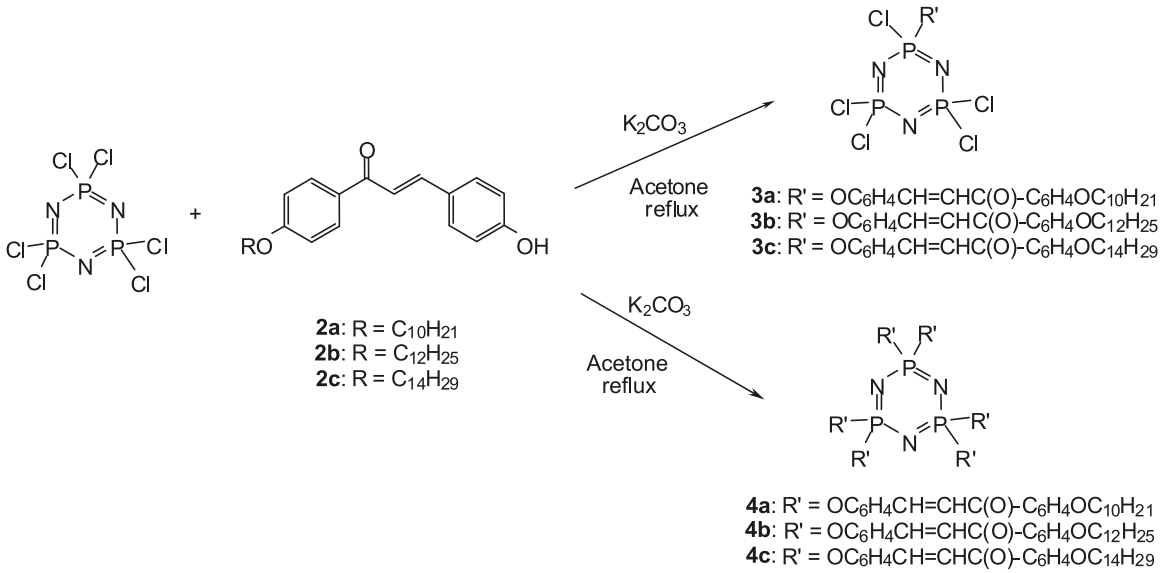
Scheme 1.



Scheme 2.



acetone[14] was believed to increase the rate of reaction compared with THF[6] and dioxane.[15] The IR spectra showed P=N stretching vibrations at 1183 cm^{-1}, which are characteristic of cyclotriphosphazenes.[16,17] The absorption bands observed at 871 cm^{-1} were attributed to the presence of the P–O–C bond.[18] ^{31}P NMR spectra showed two resonances as a triplet and a doublet at 12.74 ppm and 23.27 ppm, respectively, with a coupling constant, J = 60 Hz, which implied the replacement of one chlorine from the cyclotriphosphazenes ring for the mono-substituted phosphazenes.[19] ^{1}H and ^{13}C NMR data also confirmed the substitution of **2a**–**2c**, with the chemical shifts moving slightly downfield.

The reaction of hexachlorocyclotriphosphazenes with 6 equiv. of **2a**–**2c** under the same conditions afforded **4a**–**4c** in high yields. The IR spectra showed the characteristic absorption bands at 1180 cm^{-1}, which were attributed to P=N stretching vibrations. The absorption bands observed at 881 cm^{-1} in **4a**–**4c** were attributed to the presence of P–O–C bond. ^{31}P NMR showed a single resonance at δ 8.84 ppm, which implied complete chlorine replacement.[19] The data obtained from elemental analysis, ^{1}H, and ^{13}C NMR showed good agreement to the corresponding structures.

Conclusion

In summary, this research has demonstrated the nucleophilic substitution of (*E*)-1-[4-(alkyloxy)phenyl]-3-[4-hydroxyphenyl] prop-2-en-1-one (**2a**–**2c**) onto cyclotriphosphazenes, which afforded new mono{(*E*)-1-[4-(alkylyloxy)phenyl]-3-[4-hydroxyphenyl]prop-2-en-1-one}cyclotriphosphazenes (**3a**–**3c**) and hexakis{(*E*)-1-[4-(alkyloxy)phenyl]-3-[4-hydroxyphenyl]-prop-2-en-1-one}cyclotriphosphazenes (**4a**–**4c**). Compounds **3a**–**3c** gave lower melting points, whereas compounds **4a**–**4c** possessed higher melting points than the hydroxylated chalcones (**2a**–**2c**). These findings could potentially be used as model reactions for various crystalline electrooptical devices.

Experimental

General

4-Hydroxybenzaldehyde, 4-hydroxyacetophenone, and 1-bromoalkanes were obtained from Merck Company and used as received. Hexachlorocyclotriphosphazenes was provided by Aldrich and were recrystallized from hexane. Acetone was distilled from calcium hydride under nitrogen before use. All other reagents and solvents were used as received. The reactions were performed under dry nitrogen. Melting points were determined in open capillaries and are uncorrected. Infrared spectra were recorded on (FTIR) 1605 Shimadzu Spectrometer using KBr pellets. ^{1}H NMR spectra were recorded on a 500 MHz Jeol Delta 2-NMR, and ^{13}C NMR was recorded on a 125.77 MHz using TMS as the internal standard.

Synthesis of alkyloxyphenyl-ethanone (1a–1c)

General procedure

Bromoalkane (72 mmol), 4-hydroxyacetophenone (72 mmol), K_2CO_3 (72 mmol), and TBAI (6 mmol) in MEK (200 mL)

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were heated at reflux for 5 h. The mixture was filtered and cooled to room temperature. Water (30 mL) was added to the filtrate, and the layers separated. The aqueous layer was extracted with dichloromethane (2 × 30 mL). The combined layers were washed with water (2 × 20 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude was recrystallized from ethanol to give **1a**–**1c**.

1-(4-Decyloxyphenyl)-ethanone (1a)

Compound **1a** was obtained as colorless crystals. Yield: 89. FTIR and NMR data were consistent with the reported literature.[20]

1-(4-Dodecyloxyphenyl)-ethanone (1b)

Compound **1b** was obtained as colorless crystal. Yield: 78%; mp 52–53 °C. FTIR (thin films, cm^{-1}) υ_{max}: 2954, 2918, 2849 (C–H), 1676 (C=O), 1606 (aromatic), 1253 (alkyl aryl ethers). ^1H NMR (500 MHz, $CDCl_3$) δ_H: 0.85 (3H, t, 1 × CH_3), 1.24–1.77 (20H, m, 8 × CH_2), 2.52 (3H, s, 1 × CH_3), 3.98 (2H, t, OCH_2), 6.87 (2H, d, J = 9.2 Hz, Ar–H), 7.88 (2H, d, J = 9.2 Hz, Ar–H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C: 14.06, 22.63, 25.91, 26.24, 29.03, 29.29, 29.50, 29.53, 39.58, 29.60, 29.60, 31.86, 68.19, 114.06, 130.01, 130.50, 163.06, 196.71. Anal. calcd. (%) $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found (%): C, 78.73; H, 10.45.

1-(4-Tetradecyloxyphenyl)-ethanone (1c)

Compound **1c** was obtained as colorless crystals. Yield: 94%; mp 58–59 °C. FTIR (thin films, cm^{-1}) υ_{max}: 2954, 2917, 2849 (C–H), 1676 (C=O), 1605 (aromatic), 1253 (alkyl aryl ether). ^1H NMR (500 MHz, $CDCl_3$) δ_H: 0.84 (3H, t, 1 × CH_3), 1.23–1.76 (24H, m, 10 × CH_2), 2.50 (3H, s, 1 × CH_3), 3.96 (2H, t, OCH_2), 6.86 (2H, d, J = 8.0 Hz, Ar–H), 7.87 (2H, d, J = 8.0 Hz, Ar–H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C: 14.02, 22.60, 25.88, 26.16, 29.01, 29.28, 29.28, 29.47, 29.51, 29.57, 29.57, 29.59, 31.83, 68.13, 114.00, 129.97, 130.44, 163.02, 196.55. Anal. calcd. $C_{22}H_{36}O_2$: C, 79.46; H, 10.91. Found (%): C, 79.23; H, 10.51.

Synthesis of (alkyloxy)phenyl-hydroxyphenyl]prop-2-en-1-one (2a–2c)

General procedure

A mixture of 4-hydroxybenzaldehyde (12.5 mmol) and **1a** (12.5 mmol) in 35 mL of methanol was added under stirring to a solution of KOH (2.52 g) in methanol (10 mL). The mixture was heated at reflux for 10 h. The reaction was cooled to room temperature and acidified with cold diluted HCl (2 N). The resulting precipitate was filtered, washed, and dried. The crude was recrystallized from hexane:ethanol (7:1) to give **2a**–**2c**.

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

Compound **2a** was obtained as yellow crystals. Yield: 34. FTIR and NMR data were consistent with the reported literature.[20]

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

Compound **2b** was obtained as yellow crystals. Yield: 44%; mp 110.6–111.2 °C. FTIR (thin films, cm^{-1}) υ_{max}: 3195 (OH), 2921, 2852 (C–H), 1651 (C=O), 1581 (aromatic), 1223 (alkyl aryl ether), 990 (C=C). ^1H NMR (500 MHz, $CDCl_3$) δ_H: 0.81 (3H, t, 1 × CH_3), 1.21–1.87 (20H, m, 10 × CH_2), 3.95 (2H, t, OCH_2), 6.83 (2H, d, J = 8.6 Hz, Ar–H), 6.86 (2H, d, J = 8.6 Hz, Ar–H), 7.32 (1H, d, J = 15.45 Hz, 1 × olefinic H), 7.45 (2H, d, J = 8.0 Hz, Ar–H), 7.67 (1H, d, J = 15.45 Hz, 1 × olefinic H), 7.94 (2H, d, J = 8.0 Hz, Ar–H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C: 14.10, 22.67, 25.96, 29.08, 29.33, 29.55, 29.58, 29.61, 30.96, 31.89, 68.29, 114.30, 116.09, 119.03, 127.24, 130.45, 130.84, 144.66, 158.75, 163.12, 189.62. Anal. calcd. $C_{27}H_{36}O_3$: C, 79.37: H, 8.88. Found (%): C, 79.52; H, 8.90.

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

Compound **2c** was obtained as yellow crystals. Yield: 39%; mp 107–108 °C. FTIR (thin films, cm^{-1}) υ_{max}: 3208 (OH), 2918, 2850 (C–H), 1646 (C=O), 1585 (aromatic), 1223 (alkyl aryl ether), 990 (C=C). ^1H NMR (500 MHz, DMSO-d_6) δ_H: 0.82 (3H, t, 1 × CH_3), 1.24–1.71 (24H, m, 12 × CH_2), 4.04 (2H, t, OCH_2), 6.81 (2H, d, J = 8.6 Hz, Ar–H), 7.02 (2H, d, J = 9.15 Hz, Ar–H), 7.61 (1H, d, J = 15.45 Hz, 1 × olefinic H), 7.69 (1H, d, J = 15.45 Hz, 1 × olefinic H), 7.70 (2H, d, J = 9.15 Hz, Ar–H), 8.09 (2H, d, J = 8.60 Hz, Ar–H), 10.04 (1H, s, OH). ^{13}C NMR (125.77 MHz, DMSO-d_6) δ_C: 13.93, 22.09, 25.42, 28.54, 28.72, 28.97, 28.97, 29.02, 29.02, 29.05, 30.67, 31.29, 67.81, 114.28, 115.76, 118.36, 125.90, 130.60, 130.65, 130.81, 143.52, 159.92, 162.44, 187.12. Anal. calcd. (%) $C_{29}H_{40}O_3$: C, 79.77; H, 9.23. Found (%): C, 78.83; H, 9.04.

Synthesis of mono-substituted cyclotriphosphazene (3a–3c)

General procedure

A mixture of hexachlorocyclotriphosphazenes (2.01 mmol), **2a** (2.01 mmol), and K_2CO_3 (4.02 g) in acetone (60 mL) was heated at reflux for 1 h. The mixture was allowed to cool to room temperature and filtered. The filtrate was dried, filtered, and concentrated in vacuo. The crude solid was recrystallized from acetone to afford **3a**–**3c**.

Preparation of $N_3P_3Cl_5[OC_6H_4CH{=}CHC(O)C_6H_4OC_{10}H_{21}]$ (3a)

Compound **3a** was obtained as pale yellow solid. Yield: 17%; mp 74–75 °C. FTIR (thin films, cm^{-1}) υ_{max}: 1183 (P=N), 871 (P–O–C). ^1H NMR (500 MHz, $CDCl_3$) δ_H: 0.81 (3H, t, 1 × CH_3), 1.21–1.75 (16H, m, 8 × CH_2), 3.97 (2H, t, OCH_2), 6.89 (2H, d, J = 9.15 Hz, Ar–H), 7.24 (2H, d, J = 8.0 Hz, Ar–H), 7.44 (1H, d, J = 16.05, 1 × olefinic H), 7.60 (2H, d, J = 8.55 Hz, Ar–H), 7.68 (1H, d, J = 15.50 Hz, 1 × olefinic H), 7.95 (2H, d, J = 8.60 Hz, Ar–H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C: 14.09, 22.65, 25.96, 29.08, 29.29, 29.33, 29.52, 31.86, 31.91, 68.30, 114.34, 121.86, 122.71, 129.85, 130.55, 130.82, 133.78, 141.98, 150.31, 163.23, 188.25. ^{31}P NMR (200 MHz, $CDCl_3$) δ_P: 12.74 (t, J = 60.0 Hz, P_a–P), 23.27 (d, J = 60.0 Hz, P_b–P). Anal. calcd. (%) $N_3P_3Cl_5C_{25}H_{31}O_3$: C, 43.41; H, 4.52; N, 6.07. Found (%): C, 43.06; H, 4.44; N, 6.03.

Preparation of $N_3P_3Cl_5[OC_6H_4CH{=}CHC(O)C_6H_4OC_{12}H_{25}]$ (3b)

Compound **3b** was obtained as pale yellow solid. Yield:

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19%; mp 60–62 °C. FTIR (thin films, cm^{-1}) υ_{max}: 1183 (P=N), 871 (P–O–C). ^1H NMR (500 MHz, $CDCl_3$) δ_H: 0.86 (3H, t, 1 × CH_3), 1.26–1.80 (20H, m, 10 × CH_2), 4.02 (2H, t, OCH_2), 6.94 (2H, d, J = 8.60 Hz, Ar–H), 7.29 (2H, d, J = 8.60 Hz, Ar–H), 7.48 (1H, d, J = 15.45 Hz, 1 × olefinic H), 7.65 (2H, d, J = 8.0 Hz, Ar–H), 7.74 (1H, d, J = 15.45 Hz, 1 × olefinic H), 8.01 (2H, d, J = 8.0 Hz, Ar–H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C: 14.12, 22.68, 25.97, 29.00, 29.09, 29.25, 29.34, 29.42, 29.49, 29.58, 31.90, 68.32, 114.36, 121.87, 122.70, 129.86, 130.58, 130.83, 133.80, 141.95, 151.24, 163.25, 188.27. ^{31}P NMR (200 MHz, $CDCl_3$) δ_P: 12.74 (t, J = 60.0 Hz, P_a–P), 23.27 (d, J = 60.0 Hz, P_b–P). Anal. calcd. (%) $N_3P_3Cl_5C_{27}H_{35}O_3$: C, 45.06; H, 4.90; N, 5.84. Found (%): C, 45.03; H, 4.83; N, 5.76.

Preparation of $N_3P_3Cl_5[OC_6H_4CH=CHC(O)C_6H_4OC_{14}H_{29}]$ (3c)

Compound **3c** was obtained as pale yellow solid. Yield: 18%; mp 68–71 °C. FTIR (thin films, cm^{-1}) υ_{max}: 1184 (P=N), 871 (P–O–C). ^1H NMR (500 MHz, $CDCl_3$) δ_H: 0.87 (3H, t, 1 × CH_3), 1.25–1.80 (24H, m, 12 × CH_2), 4.03 (2H, t, OCH_2), 6.95 (2H, d, J = 8.60 Hz, Ar–H), 7.29 (2H, d, J = 8.60 Hz, Ar–H), 7.49 (1H, d, J = 16.00 Hz, 1 × olefinic H), 7.66 (2H, d, J = 8.60 Hz, Ar–H), 7.73 (1H, d, J = 15.45 Hz, 1 × olefinic H), 8.00 (2H, d, J = 8.05 Hz, Ar–H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C: 14.09, 22.66, 25.95, 29.08, 29.33, 29.33, 29.53, 29.50, 29.62, 29.62, 29.63, 29.66, 31.89, 68.31, 114.34, 121.89, 122.71, 129.85, 130.56. 130.81, 133.78, 141.97, 150.32, 163.23, 188.26. ^{31}P NMR (200 MHz, $CDCl_3$) δ_P: 12.74 (t, J = 60.0 Hz, P_a–P), 23.27 (d, J = 60.0 Hz, P_b–P). Anal. calcd. (%) $N_3P_3Cl_5C_{29}H_{39}O_3$: C, 46.58; H, 5.26; N, 5.62. Found (%): C, 46.43; H, 5.14; N, 5.59.

Synthesis of hexasubstituted cyclotriphosphazene (4a–4c)

General procedure

A mixture of hexachlorocyclotriphosphazenes (2.01 mmol), **2a** (12.06 mmol), and K_2CO_3 (24.12 g) in acetone (60 mL) was heated at reflux for 1 h. The mixture was allowed to cool to room temperature and filtered. The filtrate was dried, filtered, and concentrated in vacuo. The crude solid was recrystallized from acetone to afford **4a**–**4c**.

Preparation of $N_3P_3[OC_6H_4CH=CHC(O)–C_6H_4OC_{10}H_{21}]_6$ (4a)

Compound **4a** was obtained as pale yellow solid. Yield: 82%; mp 143–145 °C. FTIR (thin films, cm^{-1}) υ_{max}: 3067 (CH in aromatic), 1180 (P=N), 881 (P–O–C). ^1H NMR (500 MHz, $CDCl_3$) δ_H: 0.81 (3H, t, 1 × CH_3), 1.22–1.71 (16H, m, 8 × CH_2), 3.97 (2H, t, OCH_2), 6.89 (2H, d, J = 9.15 Hz, Ar–H), 7.20 (2H, d, J = 8.60 Hz, Ar–H), 7.25 (1H, d, J = 15.45 Hz, 1 × olefinic H), 7.41 (2H, d, J = 8.60 Hz, Ar–H), 7.62 (1H, d, J = 15.45 Hz, 1 × olefinic H), 7.95 (2H, d, J = 9.15 Hz, Ar–H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C: 14.09, 22.66, 25.99, 29.12, 29.31, 29.38, 29.55, 30.92, 31.87, 68.25, 114.29, 121.37, 121.88, 129.58, 130.47, 130.73, 132.35, 142.18, 151.65, 163.12, 188.01. ^{31}P NMR (200 MHz, $CDCl_3$) δ_P: 8.86 (s, 3P, N_3P_3 ring). Anal. calcd. (%) $N_3P_3C_{150}H_{186}O_{18}$: C, 74.69; H, 7.77; N, 1.74. Found (%): C, 73.86; H, 7.60; N, 1.83.

Preparation of $N_3P_3[OC_6H_4CH=CHC(O)–C_6H_4OC_{12}H_{25}]_6$ (4b)

Compound **4b** was obtained as pale yellow solid. Yield: 72%; mp 141–143 °C. FTIR (thin films, cm^{-1}) υ_{max}: 3064 (C–H in aromatic), 1180 (P=N), 883 (P–O–C). ^1H NMR (500 MHz, $CDCl_3$) δ_H: 0.86 (3H, t, 1 × CH_3), 1.25–1.78 (20H, m, 10 × CH_2), 3.97 (2H, t, OCH_2), 6.87 (2H, d, J = 7.45 Hz, Ar–H), 7.00 (2H, d, J = 8.00 Hz, Ar–H), 7.41 (1H, d, J = 16.00 Hz, 1 × olefinic H), 7.46 (2H, d, J = 8.00 Hz, Ar–H), 7.71 (1H, d, J = 16.00 Hz, 1 × olefinic H), 7.91 (2H, d, J = 7.45 Hz, Ar–H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C: 14.09, 22.66, 25.99, 29.12, 29.33, 29.38, 29.56, 29.59, 29.61, 29.64, 31.89, 68.25, 114.29, 121.36, 121.88, 129.58, 130.47, 130.73, 132.34, 142.19, 120.64, 163.13, 188.03. ^{31}P NMR (200 MHz, $CDCl_3$) δ_P: 8.84 (s, 3P, N_3P_3 ring). Anal. calcd. (%) $N_3P_3C_{162}H_{210}O_{18}$: C, 75.41; H, 8.20; N, 1.63. Found (%): C, 74.87; H, 8.17; N, 2.16.

Preparation of $N_3P_3[OC_6H_4CH=CHC(O)–C_6H_4OC_{14}H_{29}]_6$ (4c)

Compound **4c** was obtained as pale yellow solid. Yield: 70%; mp 137–138 °C. FTIR (thin films, cm^{-1}) υ_{max}: 3068 (C–H in aromatic), 1177 (P=N), 880 (P–O–C). ^1H NMR (500 MHz, $CDCl_3$) δ_H: 0.87 (3H, t, 1 × CH_3), 1.25–1.80 (24H, m, 12 × CH_2), 4.03 (2H, t, OCH_2), 6.95 (2H, d, J = 8.60 Hz, Ar–H), 7.29 (2H, d, J = 8.60 Hz, Ar–H), 7.49 (1H, d, J = 16.00 Hz, 1 × olefinic H), 7.66 (2H, d, J = 8.60 Hz, Ar–H), 7.73 (1H, d, J = 15.45 Hz, 1 × olefinic H), 8.00 (2H, d, J = 8.05 Hz, Ar–H). ^{13}C NMR (125.77 MHz, $CDCl_3$) δ_C: 14.09, 22.66, 25.95, 29.08, 29.33, 29.33, 29.53, 29.50, 29.62, 29.62, 29.63, 29.66, 31.89, 68.31, 114.34, 121.89, 122.71, 129.85, 130.56. 130.81, 133.78, 141.97, 150.32, 163.23, 188.26. ^{31}P NMR (200 MHz, $CDCl_3$) δ_P: 8.86 (s, 3P, N_3P_3 ring). Anal. calcd. (%) $N_3P_3C_{174}H_{234}O_{18}$: C, 76.03; H, 8.58; N, 1.53. Found (%): C, 75.90; H, 8.31; N, 1.70.

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