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Thermally Stable Blue-Light-Emitting Hybrid Organic−Inorganic Polymers Derived from Cyclotriphosphazene

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ABSTRACT: The synthesis and characterization of thermally stable cyclotriphosphazene-based hybrid organic−inorganic blue-light-emitting polymers were reported. Monomers 2,4-di(4-bromoaryl)-2,4,6,6-tetra(phenoxy)-cyclotriphosphazene (**3** and **4**) and 2,4-di(4-bromoaryl)-2,4,6,6-tetra(ethoxy)-cyclotriphosphazene (**7** and **9**) were prepared beginning from hexachlorocyclotriphosphazene through a two-step reaction with the corresponding sodium 4-bromo-aryloxides. Next, **3**, **4**, **7**, or **9** readily underwent a Suzuki cross-coupling reaction with suitable 9,9-dialkylflourene-2,7-bis(trimethyleneborate)s to afford the corresponding polymers. The structures and properties of the polymers were investigated by thermogravimetric analysis, differential scanning calorimetry, X-ray diffraction, and UV−vis and fluorescence spectroscopy. All polymers emitted blue light with high quantum yields. Subsequently, the thermal effect on the optical properties of the polymers was studied, revealing that the introduction of particular hybrid organic−inorganic three-dimensional cyclotriphosphazene in the polymer system prevented from aggregation of the polymer chain, enhanced thermal stability, and thus suppressed the undesirable green emission. On the basis of these studies, light-emitting polymer-based diode devices were fabricated.

Introduction

Poly(9,9-dialkylfluorene)s and conjugated fluorene alternating copolymers have been the subject of intense research efforts due to their blue light-emitting characteristics, high emission efficiencies, and structurally facile functionalization at the 9-position of fluorene monomers. There are increasing applications of these polymers in electronics and optoelectronics, particularly in the areas of polymer light-emitting diodes (PLED)[1,2] and organic thin-film transistors (OTFT).[3,4] However, poly(9,9-dialkylfluorene)s and fluorene alternating copolymers suffer from the undesirable appearance of a new broadband at long-wavelength around 530 nm during either device operation or thermal annealing, generally originating from the rearrangement of the polymer chain, and subsequent aggregate or excimer formation.[5−10] It has also been hypothesized that this band is due to the formation of keto defects[11−15] induced by the oxidative degradation of C-9 at the fluorene unit. The resulting long-wavelength emission can lead to the substantial loss of color integrity accompanied with a reduction of the overall quantum efficiency, subsequently deteriorating the device performance. Therefore, significant efforts have been made toward structural modification of fluorene-based monomers to reduce or even eliminate the green emission at wavelengths around 530 nm. The synthetic strategies employed to reduce the green emission focus primarily on structural modification of the 9-position of the fluorene unit. These methods include the introduction of bulky groups such as sterically hindered side chains,[16] dendritic moieties,[17] spiro-linked groups,[18,19] and the replacement of the susceptible C-9 of fluorene by a silicon atom.[20] Other effective methods to decrease the long-wavelength emission include the attachment of oligofluorene units into hyperbranched, star-like, or dendritic architectures[21−23] and the formation of fluorene alternating copolymers by incorporation of a comonomer with a variety of bulky side groups[24−30] These modified poly(fluorene)s and fluorene alternating copolymers have displayed improved optical stabilities,[19,22,31] and, in some cases, they have remarkably suppressed green emission.[20,23]

Alternatively, introduction of three-dimensional structure with an inorganic component in a luminescent polymer system provides a novel mechanism by which to control the unfavorable green emission of these polymers. The polymers with three-dimensional structures tend to form amorphous phases, which inhibit the formation of detrimental π-aggregates that are, in part, responsible for the green emission. Furthermore, the presence of molecularly linked inorganic components in a polymer backbone can enhance thermal stability, decrease flammability, and increase oxidation resistance, thus minimizing the green emission of polymers. Cyclotriphosphazene, composed of alternating nitrogen and phosphorus atoms, is a commonly used building block with an inorganic $(P{=}N)_3$ core, and it is extensively used as an interior core or pendent group to develop dendrimers or polymers, respectively. In most cases, cyclotriphosphazene-based materials are prepared form commercially available hexachlorocyclotriphosphazene ($(PN)_3Cl_6$), which can be readily modified with a variety of substituents *via* nucleophilic substitution.[32,33] The good reactivity of the P−Cl bond toward nucleophiles offers synthetic adaptability to introduce a large number of substituents with appropriate functionality, which can subsequently be transformed into desired synthetic precursors. Thus, it allows for the preparation of various types of molecules and polymers for varied applications, including flame retardants,[34,35] biodegradable materials,[36] liquid crystals,[37−41] and luminescent materials.[42]

Herein, we report the synthesis of cyclolinear polymers with cyclotriphosphazene units and blue light-emitting fluorene groups in the polymer backbone. The introduction of cyclotriphosphazene moieties improves the oxidative stability and, most importantly, the thermal stability of optical properties of the resulting luminescent materials.

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Experimental Section

Materials. Hexachlorocyclotriphosphazene was purified by recrystallization in ethyl acetate. Other commercially available reagents and solvents were used without further purification.

Instrumentation. ^{1}H, ^{13}C Nuclear Magnetic Resonance (NMR) and ^{31}P NMR spectra were recorded on a Bruker DRX 400-MHz NMR spectrometer in $CDCl_3$ at room temperature. Spectrometer operating frequencies were 400.13 MHz (^{1}H), 100.61 MHz (^{13}C), and 161.98 MHz (^{31}P). Tetramethyl silane (TMS) was used an internal standard for ^{1}H and ^{13}C NMR spectra, and 85% phosphoric acid was used an external standard for ^{31}P NMR spectra. Fourier transform infrared (FT-IR) spectra were acquired on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. Electron ionization mass spectra (EIMS) and electrospray ionization (ESI) mass spectra were recorded using a Micromass 7034E and Finnigan TSQ 7000 triple stage quadrupole mass spectrometer, respectively. Elemental analysis was conducted on a Perkin-Elmer 240C elemental analyzer for C, H, and N determination. Thermal analysis was performed in a Perkin-Elmer thermogravimetirc analyzer (TGA 7) in nitrogen or in air at a heating rate of 20 °C min^{-1} and a TA Instruments Differential Scanning Calorimetry (DSC) 2920 at a heating rate and a cooling rate of 10 °C min^{-1} in nitrogen. Gel permeation chromatography (GPC) analyses were carried out on a Waters 2690 system using polystyrene as standards and THF as eluent. Wide angle X-ray diffraction experiments were conducted in a Bruker GADDS X-ray diffractometer using Cu Kα 1.5418 Å radiation. UV−vis and fluorescence spectra were obtained using a Shimadzu UV3101PC UV−vis-NIR spectrophotometer and a Perkin-Elmer LS 50B luminescence spectrometer with a Xenon lamp as light source, respectively. The photoluminescence efficiency (ϕ_{PL}) of the polymers in THF solutions was measured by using quinine sulfate (1×10^{-5} M solution in 0.1 M H_2SO_4, assuming ϕ_{PL} of 0.55) as a standard.

***trans-/cis*-2,4-Dichloro-2,4,6,6-tetra(phenoxy)cyclotriphosphazene (*trans-/cis*-2).** Sodium phenoxide was prepared by directly adding phenol (22.71 g, 0.24 mol) in tetrahydrofuran to sodium hydride (9.70 g, 0.24 mol, 60% dispersion in mineral oil) (100 mL). Then the above solution was added dropwise to hexachlorocyclotriphosphazene (20.00 g, 0.057 mol) in tetrahydrofuran (75 mL) at room temperature. The resulting reaction mixture was allowed to reflux and stir for 12 h under nitrogen. After the reaction was complete, the solvent was then removed under reduced pressure. An appropriate amount of chloroform followed by water was added to dissolve the residue. The organic layer was washed with dilute hydrochloric acid and water. Finally the organic layer was dried with anhydrous magnesium sulfate and was removed under reduced pressure. The residue was chromatographed using chloroform/hexane as eluent to afford the corresponding mixture of *cis*-**2** and *trans*-**2** as a viscous liquid. Yield: 55%; the ratio of *cis*-**2** and *trans*-**2** estimated from the integration of phosphorus in their ^{31}P NMR spectra is 53%:47%. ^{31}P NMR: δ 20.80 (d, $^2J_{P-P} = 80.1$ Hz, *cis*- and *trans*-), 5.55 (t, $^2J_{P-P} = 80.7$ Hz, *cis*-); 5.43 (t, $^2J_{P-P} = 79.4$ Hz, *trans*-). ^{13}C NMR: δ 150.61, 130.32, 126.61, 126.55, 126.28, 126.15, 122.26, 121.85, 121.75, 121.56. IR (neat): 3064, 1589, 1486, 1258, 1237, 1173, 1069, 960, 945, 878, 801, 767, 688, 638, 571, 530 cm^{-1}.

***trans-/cis*-2,4-Di(4-bromophenoxyl)-2,4,6,6-tetra(phenoxy)-cyclotriphosphazene (*trans-/cis*-3).** Sodium 4-bromophenoxide was prepared by reacting 4-bromophenol (2.851 g, 0.016 mol) in tetrahydrofuran (60 mL) and sodium hydride (0.69 g, 0.029 mol, 60% dispersion in mineral oil) at room temperature. Then *trans-/cis*-**2** (4.06 g, 0.0070 mol) dissolved in tetrahydrofuran (75 mL) was added dropwise to the solution of sodium 4-bromophenoxide. After the addition was complete, the reaction mixture was allowed to reflux and stir for 12 h under nitrogen. Then the THF was removed under reduced pressure and the residue was redissolved in chloroform. The organic layer was washed with water and dried with anhydrous magnesium sulfate. The drying agent was filtered off and the chloroform was removed. The crude product was chromatographed using chloroform/hexane as eluent to afford a mixture of *trans*-**3** and *cis*-**3** as a white solid with a yield of 80%. Melting point: 112−115 °C. ^{1}H NMR: δ 6.71−6.76 (t, 4H), 6.91−6.93 (m, 8H), 7.12−7.30 (m, 16H). ^{13}C NMR: δ 150.68, 149.74, 132.44, 129.52, 125.03, 122.89, 120.98, 118.01. ^{31}P NMR: δ 9.12−9.53 (t). IR (KBr): 3090, 3062, 3043, 3014, 1590, 1483, 1456, 1399, 1289, 1262, 1237, 1177, 1095, 1068, 1024, 1008, 951, 905, 890, 877, 834, 818, 811, 775, 729, 689, 637, 631, 617, 611, 587, 575, 539, 514 504 cm^{-1}. EIMS (*m/z*): 850.3 (M^+). Anal. Calcd for $C_{36}H_{28}Br_2N_3O_6P_3$: C, 50.79; H, 3.31; N, 4.94. Found: C, 50.42; H, 3.55; N, 5.12.

***trans-/cis*-2,4-Di(4-(4-bromophenyl)phenoxy)-2,4,6,6-tetra-(phenoxy)cyclotriphosphazene (*trans-/cis*-4).** Yield: 78%. *Trans/cis*-**4** were prepared using a similar method to *trans/cis*-**3.** 4-(4-bromophenoxyl)phenol (3.51 g, 0.014mol) reacted with *trans/cis*-**2** (3.53 g, 0.0061mol) to give *trans/cis*-**4** as a white solid with a yield of 78%. Melting point: 111−114 °C. ^{1}H NMR: δ6.93−6.97 (t, 12H), 7.07−7.21 (m, 12H), 7.25−7.27 (d, 8H, $J = 8.2$ Hz), 7.49−7.51 (d, 4H, $J = 8.2$ Hz). ^{13}C NMR: δ150.78, 150.49, 139.15, 136.64, 132.02, 129.47, 128.43, 127.80, 124.95, 124.84, 121.66, 121.52, 121.10. ^{31}P NMR: δ9.26−9.58 (t). IR (KBr) 3061, 1590, 1513, 1486, 1455, 1387, 1270, 1207, 1175, 1161, 1074, 1024, 1004, 951, 945, 907, 887, 879, 854, 826, 816, 777, 770, 761, 709, 691, 573, 539, 501 cm^{-1}. MS (ESI) (*m/z*): 1004.2 (M^+). Anal. Calcd for $C_{48}H_{36}Br_2N_3O_6P_3$: C, 57.45; H, 3.62; N, 4.19. Found: C, 57.45; H, 3.37; N, 4.52.

***trans-/cis*-2,4-Di(4-bromophenoxy)-2,4,6,6-tetrachlorocyclotriphosphazene (*trans-/cis*-6) and *gem*-2,2-di(4-bromophenoxy)-4,4,6,6-tetrachlorocyclotriphosphazene (geminal-6).** *trans-/cis*-**6**, and *gem*-**6** were prepared according to the similar method of compound *trans-/cis*-**2**. Yield: 57%. The ratio of *cis*-**6**, *trans*-**6**, and *gem*-**6** estimated from the integration of phosphorus in ^{31}P NMR spectrum is 93.1%: 6.9% (^{31}P NMR spectra of *trans*-**6** and *cis*-**6** are exactly same and nondistinguishable). ^{1}H NMR: δ 7.52 (d, $J = 8.8$ Hz), 7.47 (d, $J = 8.8$ Hz), 7.16 (d, $J = 8.6$ Hz), 7.06 (d, $J = 8.6$ Hz). ^{13}C NMR: δ 148.89, 133.37, 123.58, 123.32, 120.32, 120.23. ^{31}P NMR: δ 25.43 (t, $^2J_{P-P} = 65.2$ Hz, *cis*- and *trans*-), δ24.62 (d, $^2J_{P-P} = 64.6$ Hz, *gem*-), 15.94 (d, $^2J_{P-P} = 65.2$ Hz, *cis*- and *trans*-), −0.22 (t, $^2J_{P-P} = 64.6$ Hz, *gem*-). IR (KBr): 3093, 3072, 1582, 1482, 1399, 1292, 1175, 1068, 1012, 966, 871, 827, 871, 827, 760, 741, 665, 609, 538, 514 cm^{-1}. EIMS (*m/z*): 620.8 (M^+). Anal. Calcd for $C_{12}H_8Br_2Cl_4N_3O_2P_3$: C, 23.22; H, 1.30. Found: C, 23.01; H, 1.51.

***trans*-2,4-di(4-bromophenoxy)-2,4,6,6-tetra(ethoxy)cyclotriphosphazene (*trans*-7).** *trans*-**7** and *cis*-**7** were prepared according to the similar method of compound *trans/cis*-**2**. Yield: 30%. Mp: 47−50 °C. ^{1}H NMR: δ 7.41 (d, 4H, $J = 8.6$ Hz), 7.14 (d, 4H, $J = 8.6$ Hz), 3.93 (m, 4H), 3.73 (m, 4H), 1.24 (t, 6H, $J = 7.0$ Hz), 1.19 (t, 6H, $J = 7.0$ Hz). ^{13}C NMR: δ 150.61, 132.60, 123.58, 118.00, 63.11, 62.31 (d, $^2J_{C-P} = 5.3$ Hz), 16.31, 16.25. ^{31}P NMR: δ $P(OC_2H_5)_2$, 17.17 (t), 16.66 (m), 16.20 (t); $P(OC_2H_5)(OC_6H_4Br)$, 14.56 (s), 14.06 (s). IR (KBr): 3092, 2979, 2932, 2903, 1583, 1483, 1394, 1249, 1185, 1044, 944, 891, 836, 792, 752, 701, 610, 557 cm^{-1}. EIMS (*m/z*): 659.1 (M^+). Anal. Calcd for $C_{20}H_{28}Br_2Cl_4N_3O_6P_3$: C, 36.44; H, 4.28. Found: C, 36.71; H, 4.34.

***cis*-2,4-di(4-bromophenoxy)-2,4,6,6-tetra(ethoxy)cyclotriphosphazene (*cis*-7).** Yield: 35%. Mp: 30−32 °C. ^{1}H NMR: δ 7.33 (d, 4H, $J = 8.7$ Hz), 6.96 (d, 4H, $J = 8.7$ Hz), 4.13 (m, 4H), 3.52 (m, 4H), 1.35 (t, 6H, $J = 6.0$ Hz), 1.32 (t, 3H, $J = 5.8$ Hz), 1.08 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR: δ 150.51, 132.58, 123.24, 117.84, 63.14, 62.39 (d, $^2J_{C-P} = 5.3$ Hz), 62.24 (d, $^2J_{C-P} = 5.3$ Hz), 16.36, 16.32, 16.22, 16.14. ^{31}P NMR: δ $P(OC_2H_5)_2$, 17.23 (t), 16.73 (m), 16.22 (t); $P(OC_2H_5)(OC_6H_4Br)$, 14.52 (s), 14.02 (s). IR (KBr): 3088, 3064, 2977, 2934, 2905, 1587, 1484, 1250, 1217, 1187, 1161, 1037, 966, 948, 933, 902, 885, 834, 791, 755, 743, 612, 520 cm^{-1}. EIMS (*m/z*): 659.0 (M^+). Anal. Calcd for $C_{20}H_{28}Br_2Cl_4N_3O_6P_3$: C, 36.44; H, 4.28. Found: C, 36.53; H, 4.47.

***trans-/cis*-2,4-Di(4-(4-bromophenyl)phenoxy)-2,4,6,6-tetrachlorocyclotriphosphazene (*trans-/cis*-8), and *gem*-2,2-Di(4-(4-bromophenyl)phenoxy)-4,4,6,6-tetrachlorocyclotriphosphazene (*gem*-8).** *trans*-**8**, *cis*-**8**, and *gem*-**8** were prepared according to the similar method of compound *trans/cis*-**2**. Yield: 61%. The ratio of *cis*-**8**, *trans*-**8** and *gem*-**8** estimated from the integration of phosphorus in ^{31}P NMR spectrum is 56.6%:43.0%:0.4%. Mp: 120−124 °C. ^{1}H NMR: δ 7.57 (d, $J = 8.4$ Hz), 7.53 (d, $J = 8.4$ Hz), 7.48 (d, $J = 8.6$ Hz), 7.42 (d, $J = 8.4$ Hz), 7.35 (d, $J = 8.4$ Hz), 7.34 (d, $J = 8.3$ Hz), 7.24 (d, $J = 8.4$ Hz). ^{13}C NMR: δ149.63, 139.19, 138.98, 138.89, 138.70, 132.45, 129.08, 128.95, 128.79, 128.68, 122.46, 122.41, 122.25, 122.04. ^{31}P NMR: δ 25.50 (t, $^2J_{P-P} = 65.5$ Hz, *cis*-), 25.30 (t, $^2J_{P-P} = 64.4$ Hz, *trans*-), 24.48 (d, $^2J_{P-P} = 63.8$ Hz, *gem*-), 16.06 (d, $^2J_{P-P} = 65.5$ Hz, *cis*-), 15.89 (d, $^2J_{P-P} = 64.4$ Hz, *trans*-), −0.14 (t, $^2J_{P-P} = 63.8$ Hz, *gem*-). IR (KBr): 3061, 3047, 1602, 1587, 1510, 1479, 1245, 1224, 1180, 1159, 985, 964, 872, 817, 755, 661, 605, 588, 543, 509 cm^{-1}. EIMS (*m*/*z*): 772.9 (M$^+$). Anal. Calcd for $C_{24}H_{16}Br_2Cl_4N_3O_2P_3$: C, 37.29; H, 2.09. Found: C, 37.12; H, 2.23.

***trans*-2,4-di(4-(4-bromophenyl)phenoxy)-2,4,6,6-tetra(ethoxy)cyclotriphosphazene (*trans*-9).** *trans*-**9** and *cis*-**9** were prepared according to the similar method of compound *trans/cis*-**2**. Yield: 35%. Mp: 130−132 °C. ^{1}H NMR: δ 7.55 (d, 4H, $J = 8.5$ Hz), 7.48 (d, 4H, $J = 8.6$ Hz), 7.39 (d, 4H, $J = 8.5$ Hz), 7.33 (d, 4H, $J = 8.6$ Hz), 3.98 (m, 4H), 3.75 (m, 4H), 1.25 (t, 6H, $J = 7.1$ Hz), 1.17 (t, 6H, $J = 7.1$ Hz). ^{13}C NMR: δ 151.36, 139.74, 136.99, 132.33, 128.90, 128.14, 122.22, 121.90, 63.02, 62.23 (d, $^2J_{C-P} = 5.2$ Hz), 16.40, 16.32.^{31}P NMR: δ $P(OC_2H_5)_2$, 17.36 (t), 16.86 (m), 16.35 (t); $P(OC_2H_5)(OC_6H_4C_6H_4Br)$, 14.62 (s), 14.11 (s). IR (KBr): 2982, 2903, 1603, 1513, 1480, 1390, 1254, 1214, 1195, 1164, 1074, 1038, 951, 935, 891, 817, 795, 764, 710, 554 cm^{-1}. EIMS (*m*/*z*): 811.1 (M$^+$). Anal. Calcd for $C_{32}H_{36}Br_2N_3O_6P_3$: C, 47.37; H, 4.47. Found: C, 47.56; H, 4.56.

***cis*-2,4-di(4-(4-bromophenyl)phenoxy)-2,4,6,6-tetra(ethoxy)-cyclotriphosphazene (cis-9).** Yield: 40%. Mp: 139−141 °C. ^{1}H NMR: δ 7.48 (d, 4H, $J = 8.4$ Hz), 7.34 (d, 4H, $J = 8.6$ Hz), 7.27 (d, 4H, $J = 8.5$ Hz), 7.15 (d, 4H, $J = 8.5$ Hz), 4.18 (m, 4H), 4.02 (m, 2H), 3.49 (m, 2H), 1.38 (t, 6H, $J = 7.1$ Hz), 1.33 (t, 3H, $J = 7.1$ Hz), 1.01 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR: δ 150.86, 139.14, 136.23, 131.93, 128.37, 127.63, 121.61, 121.48, 62.73, 61.98 (d, $^2J_{C-P} = 5.2$ Hz), 61.74 (d, $^2J_{C-P} = 5.0$ Hz), 16.07, 15.93, 15.85. ^{31}P NMR: δ $P(OC_2H_5)_2$, 17.49 (t), 16.99 (m), 16.48 (t); $P(OC_2H_5)(OC_6H_4C_6H_4Br)$, 14.70 (s), 14.19 (s). IR (KBr): 2931, 1604, 1514, 1481, 1390, 1252, 1215, 1187, 1075, 1039, 947, 896, 817, 761, 546 cm^{-1}. EIMS (*m*/*z*): 811.2 (M$^+$). Anal. Calcd for $C_{32}H_{36}Br_2N_3O_6P_3$: C, 47.37; H, 4.47. Found: C, 47.44; H, 4.67.

General Synthetic Procedures for Polymers P1−12. A mixture containing monomer **3**, (or **4**, or **7**, or **9**), $Pd(PPh_3)_4$, 9,9-dialkylflourene-2,7-bis(trimethyleneborate) (**5**) in degassed toluene and 2 M aqueous K_2CO_3 solution and a catalytic amount of Aliquat 336 was vigorously stirred at 120 °C for 3 days under nitrogen. The mixture was then cooled to room temperature and poured into a mixture of water and hydrazine. The mixture suspension was filtered and residue was extracted with $CHCl_3$. The combined organic extract was washed with dilute HCl and water. The organic layer was dried and was evaporated to dryness. The residue was then redissolved in a small amount of toluene. The toluene solution prepared above was slowly poured into cold methanol again. This reprecipitation process was repeated for three times, followed by extraction in a Soxhelt apparatus to afford the desired polymers.

P1. Yield: 73%. ^{1}H NMR: δ 7.41−7.82 (m, 10H), 6.85−7.21 (m, 24H), 2.04 (br, s, 4H), 1.07 (br, s, 12H), 0.72 (m, 10H). ^{31}P NMR: δ 8.9−9.9 (m). IR (KBr): 3065, 3042, 2927, 2856, 1592, 1509, 1489, 1465, 1270, 1202, 1160, 1070, 1024, 1007, 949, 903, 880, 817, 766, 729, 687 cm^{-1}. Anal. Calcd for $(C_{61}H_{60}N_3O_6P_3)_n$: 71.54; H, 5.91; N, 4.10. Found: C, 71.45; H, 6.26; N, 4.10.

P2. Yield: 62%. ^{1}H NMR: δ 7.38−7.59 (m, 10H), 6.90−7.24 (m, 24H), 2.08 (br, s, 4H), 0.85 (br, s, 12H), 0.53−0.63 (br d, 10H). ^{31}P NMR δ 8.9−9.9 (m). IR (KBr): 3065, 3042, 2955, 2922, 2855, 1592, 1510, 1490, 1465, 1269, 1202, 1179, 1069, 1024, 1007, 950, 903, 880, 848, 817, 767, 730, 687 cm^{-1}. Anal. Calcd for $(C_{65}H_{68}N_3O_6P_3)_n$: C, 72.28; H, 6.35; N, 3.89. Found: C, 71.98; H, 6.39; N, 3.94.

P3. Yield: 69%. ^{1}H NMR: δ 7.40−7.82 (m, 10H), 6.84−7.21 (m, 24H), 2.04 (br, s, 4H), 1.08 (br, s, 20H), 0.76 (m, 10H). ^{31}P NMR: δ 9.1−10.0 (m). IR (KBr): 3065, 3042, 2926, 2853, 1592, 1509, 1490, 1465, 1269, 1203, 1178, 1160, 1069, 1007, 1016, 1025, 950, 903, 880, 848, 817, 766, 729, 687 cm^{-1}. Anal. Calcd for $(C_{65}H_{68}N_3O_6P_3)_n$: C, 72.28; H, 6.35; N, 3.89. Found: C, 71.10; H, 6.82; N, 3.84.

P4. Yield: 67%. ^{1}H NMR: δ 7.40−7.82 (m, 10H), 6.84−7.21 (m, 24H), 2.06 (br, s, 4H), 1.00−1.29 (br, s, 36H), 0.70−0.89 (m, 10H). ^{31}P NMR: δ9.1−9.8 (m). IR (KBr): 3060, 3029, 2923, 2851, 1592, 1489, 1465, 1411, 1397, 1377, 1268, 1238, 1202, 1160, 1069, 1024, 1007, 950, 903, 881, 856, 767, 721, 688 cm^{-1}. Anal. Calcd for $(C_{73}H_{84}N_3O_6P_3)_n$: C, 73.53; H, 7.10; N, 3.52. Found: C, 73.06; H, 7.25; N, 3.46.

P5. Yield: 77%. ^{1}H NMR: δ 7.41−7.82 (m, 20H), 6.93−7.22 (m, 22H), 2.06 (br, s, 4H), 1.06 (br, s, 12H), 0.74 (m, 10H). ^{31}P NMR: δ 9.3−9.8 (t). IR (KBr): 3029, 2927, 2855, 1592, 1489, 1464, 1268, 1200, 1178, 1159, 1070, 1024, 1007, 949, 903, 880, 813, 766, 688 cm^{-1}. Anal. Calcd for $(C_{73}H_{68}N_3O_6P_3)_n$: C, 73.54; H, 5.83; N, 3.57. Found: C, 74.46; H, 6.13; N, 3.72.

P6. Yield: 72%. ^{1}H NMR: δ 7.30−7.83 (m, 20H), 6.75−7.27 (m, 22H), 2.10 (br, s, 4H), 0.86 (br, s, 12H), 0.55−0.62 (br d, 10H). ^{31}P NMR: δ 9.1−9.7 (m). IR (KBr): 3030, 2954, 2922, 2855, 1592, 1489, 1464, 1268, 1178, 1160, 1069, 1007, 1024, 950, 903, 880, 813, 766, 687 cm^{-1}. Anal. Calcd for $(C_{77}H_{77}N_3O_6P_3)_n$: C, 75.04; H, 6.22; N, 3.41. Found: C, 74.42; H, 6.16; N, 3.40.

P7. Yield: 71%. ^{1}H NMR: δ 7.41−7.84 (t, 20H), 6.92−7.24 (m, 22H), 2.06 (br, s, 4H), 1.07 (br, s, 20H), 0.77 (m, 10H). ^{31}P NMR: δ 9.2−9.8 (m). IR (KBr): 3031, 2928, 2850, 1592, 1496, 1464, 1270, 1159, 1069, 1024, 1007, 950, 881, 814, 766, 688 cm^{-1}. Anal. Calcd for $(C_{77}H_{76}N_3O_6P_3)_n$: C, 75.04; H, 6.22; N, 3.41. Found: C, 74.74; H, 6.54; N, 3.35.

P8. Yield: 70%. ^{1}H NMR: δ 7.40−7.82 (m, 20H), 6.93−7.22 (m, 22H), 2.04 (br, s, 4H), 1.00−1.35 (br, m, 36H), 0.75−0.90 (br, m, 10H). ^{31}P δ NMR: 9.2−9.8 (m). IR (KBr): 3066, 3042, 2924, 2852, 1593, 1509, 1490, 1466,, 1268, 1203, 1178, 1161, 1069, 1025, 1007, 950, 880, 818, 767, 688 cm^{-1}. Anal. Calcd for $(C_{85}H_{92}N_3O_6P_3)_n$: C, 75.93; H, 6.90; N, 3.13. Found: C, 76.35; H, 6.87; N, 2.90.

P9. Yield: 67%. ^{1}H NMR: δ 7.37−7.77 (m, 14H), 4.01 (m, 4H), 3.79 (m, 4H), 2.04 (m, 4H)1.19−1.31 (m, 12H), 1.06 (m, 12H), 0.75 (m, 10H). ^{31}PNMR: δ 16.44−17.45 (m, 1P, $P(OC_2H_5)_2$), 14.38−14.88 (br. d, 2P, $P(OC_2H_5)(Ar)$). IR (KBr): 3028, 2926, 2856, 1602, 1511, 1463, 1392, 1253, 1191, 1166, 1040, 937, 889, 818, 746, 635, 548 cm^{-1}. Anal. Calcd for $C_{45}H_{60}N_3O_6P_3$: C 64.97; H 7.27. Found: C,65.49; H,7.10.

P10. Yield: 69%. ^{1}H NMR: δ 7.21−7.67 (m, 14H), 4.19 (m, 4H), 4.03 (m, 2H), 3.05(m, 2H), 2.00(br. S, 4H), 1.32−1.39 (m, 12H), 1.02 (m, 12H), 0.70 (m, 10H). ^{31}P NMR: δ 16.23−17.49 (m, 1P, $P(OC_2H_5)_2$), 14.16−14.66 (br. d, 2P, $P(OC_2H_5)(Ar)$). IR (KBr): 2927; 2855, 1604, 1509, 1466, 1251, 1214, 1190, 1164, 1036, 945, 934, 887, 816, 744, 539 cm^{-1}. Anal. Calcd for $C_{45}H_{60}N_3O_6P_3$: C 64.97; H 7.27. Found: C,65.50; H,7.42.

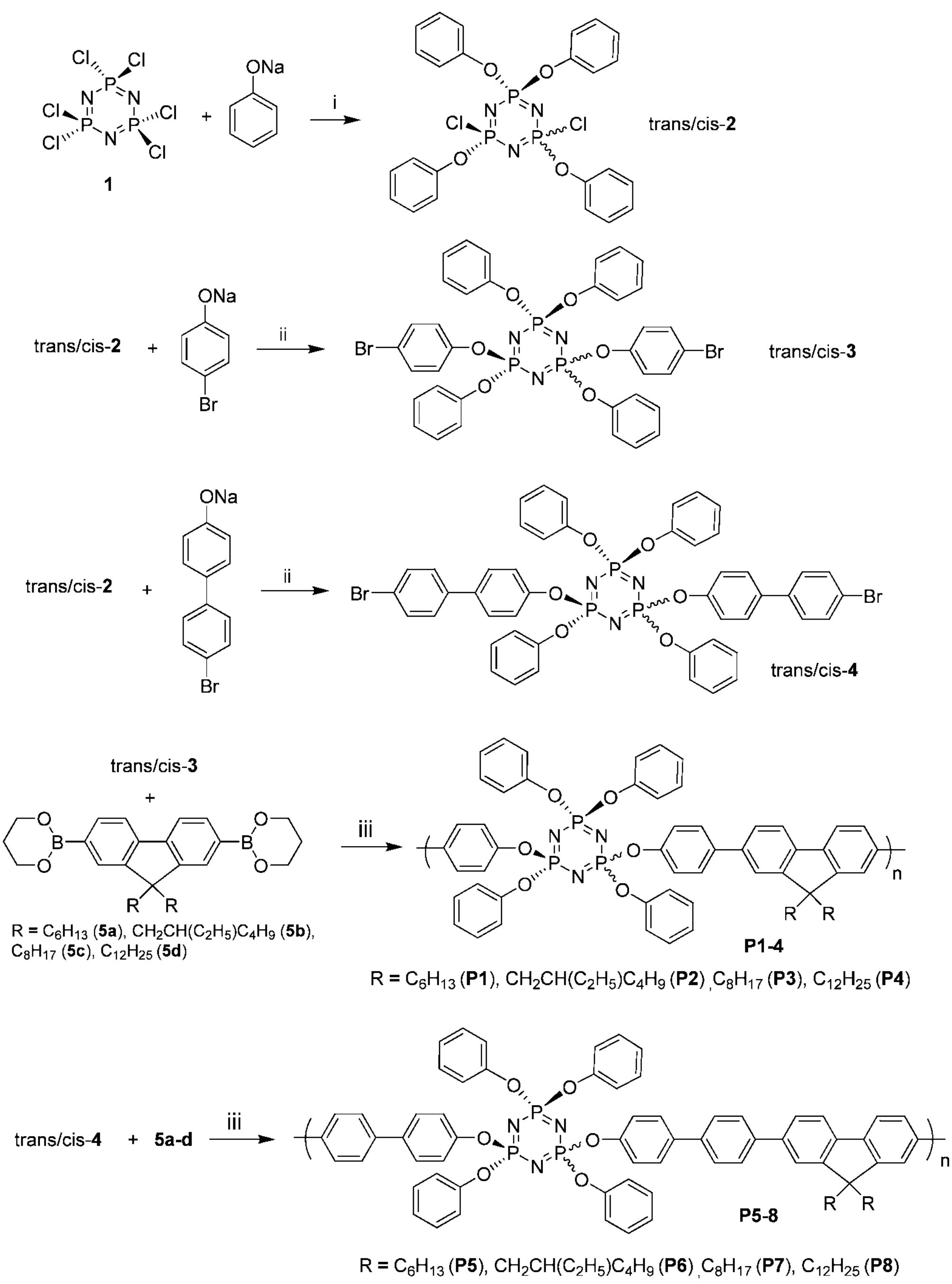
P11. Yield: 72%. ^{1}H NMR: δ 7.48−7.81 (m, 18H), 7.38−7.40 (m, 4H), 4.01 (m, 4H), 3.79 (m, 4H), 2.05 (br s 4H), 1.07−1.31 (m, 24H), 0.76 (t, 10H). ^{31}P NMR: δ 17.60−16.50 (m, 1P, $P(OC_2H_5)_2$), 14.36−14.87 (br. d, 2P, $P(OC_2H_5)(Ar)$). IR (KBr): 3028, 2926, 2855, 1603, 1498, 1463, 1391, 1253, 1189, 1163, 1038, 935, 888, 814, 757, 545 cm^{-1}. Anal. Calcd for $C_{57}H_{68}N_3O_6P_3$: C 69.57; H 6.96. Found: C 69.98; H, 7.25.

P12. Yield: 75%. ^{1}H NMR: δ 7.51−7.71 (m, 18H), 7.22−7.27 (m, 4H), 4.22 (m, 4H), 4.04 (m, 2H), 3.50 (m, 2H), 2.04 (br s 4H), 1.08−1.41 (m, 24H), 0.69 (t, 10H). ^{31}P NMR: δ 17.55−16.55 (m, 1P, $P(OC_2H_5)_2$), 14.25−14.75 (br. d, 2P, $P(OC_2H_5)(Ar)$). IR (KBr): 3030, 2926, 2855, 1604, 1499, 1463, 1391, 1252, 1209, 1188, 1163, 1087, 944, 889, 814, 756, 540 cm^{-1}. Anal. Calcd for $C_{57}H_{68}N_3O_6P_3$: C 69.57; H 6.96. Found: C 70.10; H, 6.85.

Results and Discussion

Synthesis of Cyclotriphosphazene-Based Monomers and Polymers. The synthetic routes leading to polymers **P1−8**, **P9−10**, and **P11−12** are outlined in Schemes 1, 2, and 3, respectively. Compound 2,4-dichloro-2,4,6,6-tetra(phenoxy)-

Scheme 1. Synthetic Route Leading to the Polymer P1−8[a]

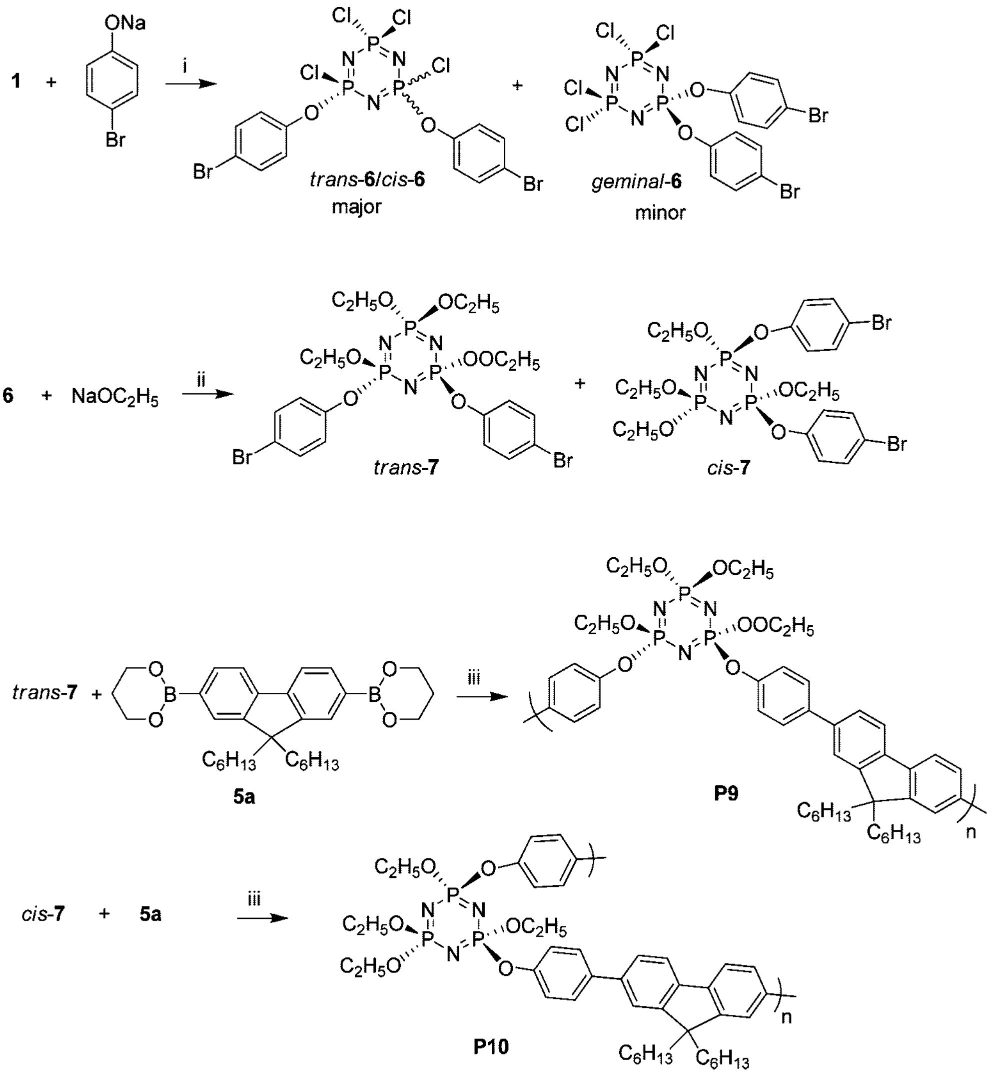


[a] Reaction conditions: (i) THF, room temperature; (ii) THF, reflux; (iii) $Pd(PPh_3)_4$, 2 M K_2CO_3, Aliquat 336, toluene, reflux at 105 °C, 3 days.

cyclotriphosphazene[43] (*trans*/*cis*-**2**) was readily prepared from hexachlorocyclotriphosphazene (**1**) and sodium phenoxide in 60% yield. Reaction of compound *trans-*/*cis*-**2** with sodium 4-bromophenoxide and sodium 4-(4-bromophenoxy)phenoxide afforded geometrical isomers *trans-*/*cis*-**3** and *trans-*/*cis*-**4** in 80% and 78% yields, respectively. Compound **6** (a mixture of *cis*-**6**, *trans*-**6**, and *gem*-**6**) was synthesized by reacting sodium 4-bromophenoxide with compound **1** in THF.[44] Further reaction between a mixture of *cis*-**6**, *trans*-**6**, and *gem*-**6,** and excess sodium ethoxide in THF was carried out to afford pure compounds *cis*-**7** and *trans*-**7** in yields of 30 and 35%, respectively (Scheme 2). According to the similar synthetic strategy, pure compounds *cis*-**9** and *trans*-**9** was prepared in 40% and 35% yields, respectively (Scheme 3). The chemical structures of all intermediates **2**−**9** were unambiguously characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectroscopy, mass spectrometry, and elemental analysis.

In general, the *cis* and *trans*-isomers of cyclotriphosphazene derivatives could be distinguished by using ^{31}P and ^{1}H NMR spectroscopy. In theory, ^{31}P NMR spectra of **3** and **4** should exhibit an AB_2 spin system, but the ^{31}P chemical shift difference ($\Delta\delta_{AB}$) between two phosphorus atom A and phosphorus atom B was very small, and thus only a triplet at δ 9−10, instead of a set of eight singlets, was observed. The chemical structures of compounds **2**,[43] **6**,[44] and **8**, including their geometrical isomers, were readily identified by ^{31}P NMR spectroscopy on the basis of their chemical shifts and splitting patterns (AX_2 spin system). However, the ^{31}P NMR spectra were indistinguishable for the geometrical isomers of compounds **7** and **9**. The ^{31}P NMR and ^{1}H NMR spectra of compounds *cis*-**9** and

Scheme 2. Synthetic Route Leading to the Polymer P9−10[a]



[a] Reaction conditions: (i) THF, room temperature; (ii) THF, reflux; (iii) Pd(PPh$_3$)$_4$, 2 M K$_2$CO$_3$, Aliquat 336, toluene, reflux at 105 °C, 3 days.

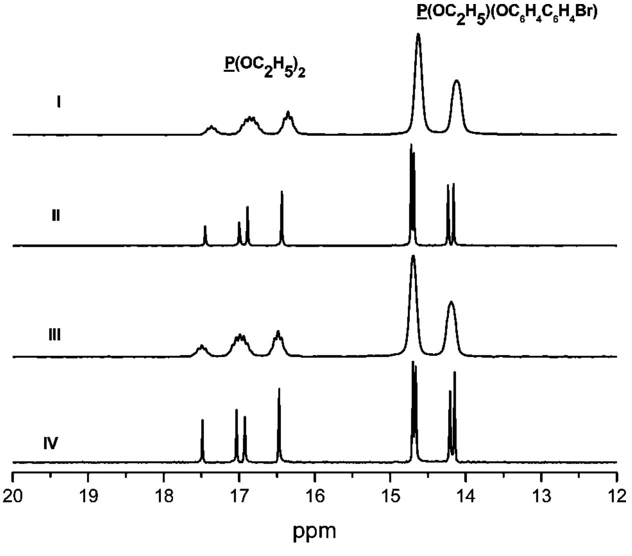
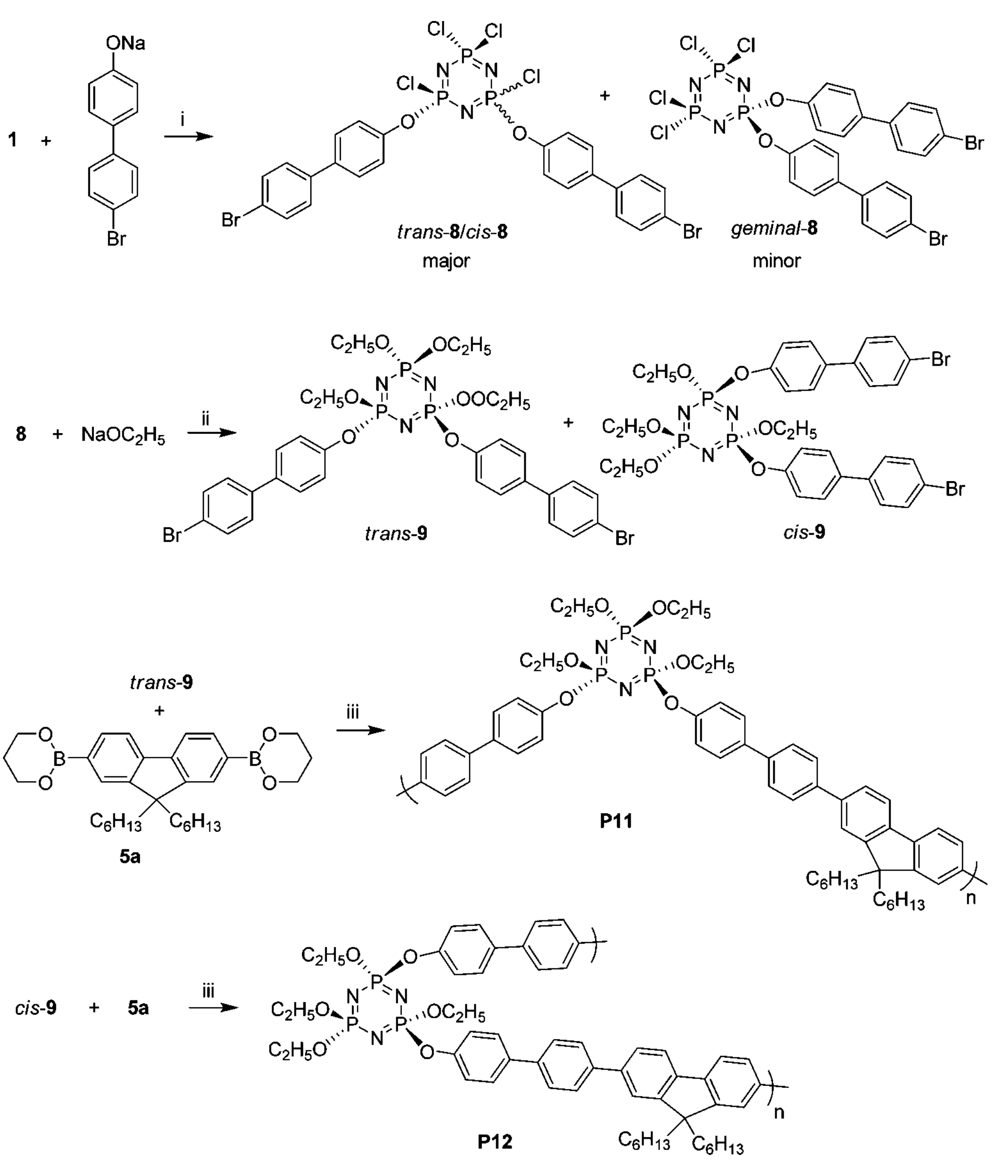


Figure 1. ^{31}P NMR spectra of *trans*-**9** (I and II) and *cis*-**9** (III and IV) in CDCl$_3$ at room temperature. Spectra I and III, ^{1}H nuclei coupled; spectra II and IV, ^{1}H nuclei decoupled.

trans-**9** are shown in Figures 1 and 2, respectively. Compounds *cis*-**9** and *trans*-**9** exhibited a complicated ^{1}H nuclei coupled ^{31}P NMR spectra due to coupling between phosphorus and methylene protons (OC$\underline{H_2}$CH$_3$), and they provided the same spectral profiles in which two sets of signals were attributed to two different environmental phosphorus atoms ($\underline{P}$(OCH$_2$CH$_3$)$_2$ and $\underline{P}$(OCH$_2$CH$_3$)(OC$_6$H$_4$C$_6$H$_4$Br)) at δ 16.2−17.6 and 13.9−14.9, respectively, with an integration ratio of 1:2 (Figure 1 (I, III)). However, the complicated splitting patterns could be simplified to appear eight characteristic singlets, corresponding to a typical AB$_2$ spin system, in their respective ^{1}H nuclei decoupled ^{31}P NMR spectra (Figure 1 (II, IV)). In the ^{1}H NMR spectrum of *cis*-**9** (Figure 2), only one OCH$_2$CH$_3$ group (*c*) is located in the shielding zone of the two biphenyl groups, resulting in upfield shifts of 0.53 and 0.32 ppm, for CH$_2$ and CH$_3$, respectively, relative to another *geminal* OCH$_2$CH$_3$ group (*b*) that is aligned below the cyclotriphosphazene ring. In contrast, for *trans*-**9**, two types of OCH$_2$CH$_3$ groups are located in the shielding zone of one biphenyl groups, and they show two sets of signals at δ 3.98 and 1.25, and δ 3.75 and 1.17, corresponding to $\underline{P}$(OCH$_2$CH$_3$)(OC$_6$H$_4$C$_6$H$_4$Br) and $\underline{P}$(OCH$_2$CH$_3$)$_2$, respectively (Figure 2).

Copolymers **P1−12** were synthesized from cyclotriphosphazene-based monomers (**3**, **4**, **7**, or **9**) and 9,9-dialkylflourene-2,7-bis(trimethyleneborate) (**5a−d**) *via* Pd(PPh$_3$)$_4$-catalyzed Suzuki cross-coupling reactions. All polymers were structurally characterized by spectroscopic methods and elemental analyses.

Scheme 3. Synthetic Route Leading to the Polymer P11−12[a]



[a] Reaction conditions: (i) THF, reflux; (ii) THF, reflux; (iii) Pd(PPh$_3$)$_4$, 2 M K_2CO_3, Aliquat 336, toluene, reflux at 105 °C, 3days.

The ^{31}P NMR spectra of the copolymers **P1−8** and **P9−12** clearly displayed signals in the range between δ 9−10 and 14.1−17.5, respectively, corresponding to characteristic phosphorus signals of cyclotriphosphazenes. This suggested that the cyclotriphosphazene rings were integrated into the polymer backbone, and they remained intact during the polymerization process. As an example, ^{31}P and ^{1}H NMR spectra of polymer **5** are illustrated in Figure 3. Molecular weights were determined by gel permeation chromatography (GPC) against a polystyrene standard, and thermal stabilities in air and inert atmosphere are summarized in Table 1. Polymers **P5−8** and **P11−12** have higher molecular weights (M_n) than the corresponding polymers **P1−4** and **P9−10**. All polymers were found to be completely soluble in common organic solvents such as chloroform, THF, toluene, and xylenes at ambient temperature.

Thermal and X-ray Diffraction Analysis of Polymers. Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of the polymers **P1−12**. For example, the TGA thermograms for polymers **P1−4** and **P5−8** in nitrogen are shown in Figure 4. Polymers **P1−8** exhibit very good thermal stability with decomposition temperatures (T_d) in the range of 419−446 °C in nitrogen (Table 1). The high T_d's for these polymers are primarily due to the presence of inorganic cyclotriphosphazene cores, which enhance the thermal stability of the polymers. The glass transition temperatures (T_g) of all polymers were also clearly detected by differential scanning calorimetry (DSC). For these two series, **P1−4** and **P5−8**, T_g's progressively decreased with an increase in the length of dialkyl chains at 9-position of the fluorene moiety (Figure 5). T_g's dropped from 90 to 39 °C when the alkyl chain was changed from hexyl to dodecyl in the **P5−8** polymer series. **P5−8** exhibited relatively higher T_g values than the corresponding **P1−4** polymers with the same alkyl groups. This is because the **P5−8** have longer rigid repeating units than those of the **P1−4** polymer series. However, polymers **P9−12** displayed inferior thermal stabilities when compared with **P1−8** by nearly 100 °C. It is also worthy noting that polymers **P10** and **P12**, derived from *trans*-monomers, have better thermal stabilities and higher T_g's than the corresponding polymers **P9** and **P11** derived from *cis*-monomers.

The packing of polymers **P1−12** in the solid state was found to be amorphous by wide-angle X-ray diffraction experiments, with two broad halos observed at $2\theta = 9−12°$ (~7.7−9.6 Å) and 19−22° (~4.1−4.5 Å) in the diffraction diagrams, as shown

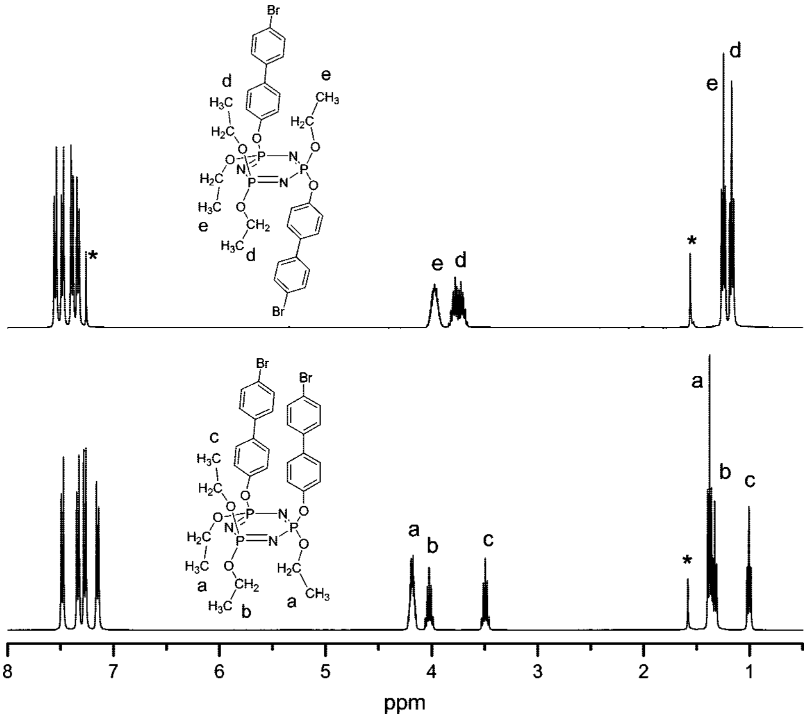


Figure 2. ^{1}H NMR spectra of *cis*-**9** (bottom) and *trans*-**9** (top) with ^{31}P nuclei coupled in $CDCl_3$ at room temperature. (∗) Residual water and undeuterated $CHCl_3$ in solvent.

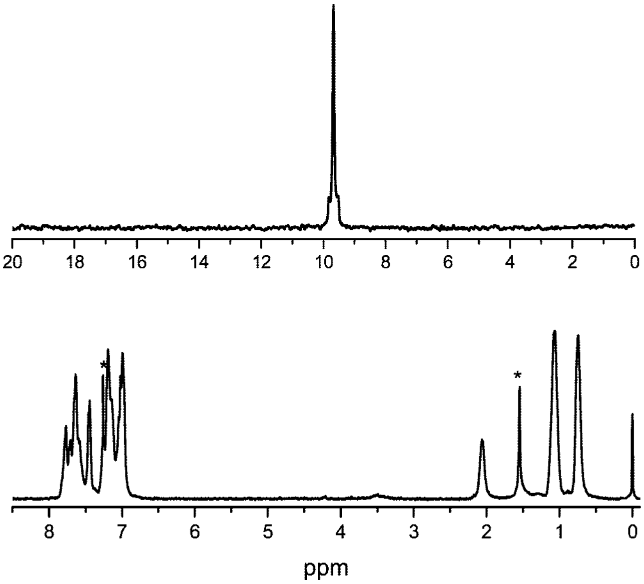


Figure 3. ^{31}P NMR (*top*) and ^{1}H NMR (*bottom*) spectra of **P5**. (∗) Residual water and undeuterated $CHCl_3$.

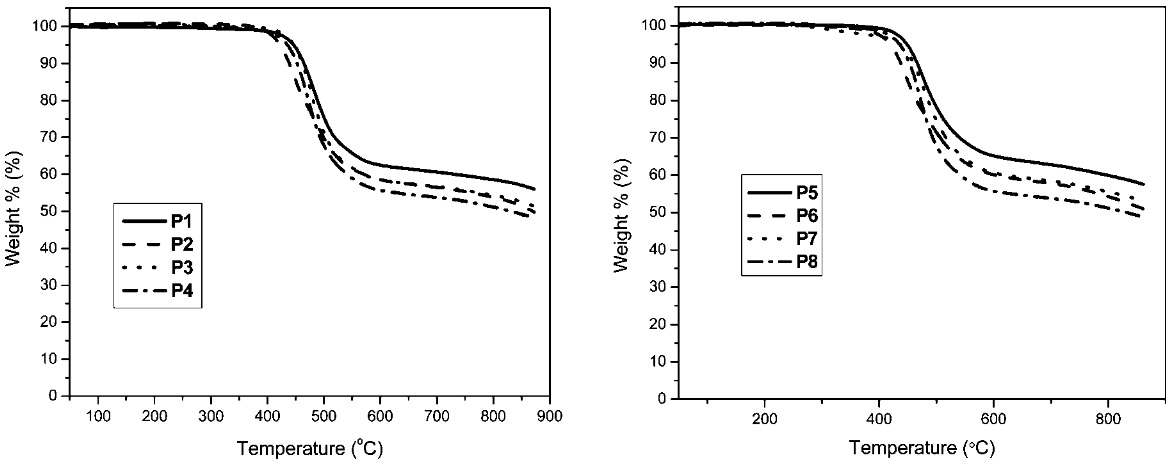
in Figure 6. The broad diffraction peaks with a *d*-spacing of 4.1−4.5 Å are ascribed to intermolecular alkyl−alkyl and intramolecular aryl−aryl interactions. The diffraction peaks centered at $2\theta = 9-12°$, with a *d*-spacing of 7.7−9.6 Å, are assigned to the average polymer interchain distance. The relative longer interchain distances indicate that the introduction of cyclotriphosphazene units suppress the aggregation of polymer chains. From Table 2, it is clear that the length of alkyl chains at the 9-postiton of the fluorene groups in **P1−8** has little effect on the magnitude of the interchain distances, suggesting the presence of interdigitated structures. Polymers **P5−8** and **P11−12**, with a longer and more rigid backbone than **P1−4** and **P9−10,** have slightly longer interchain distances by ~0.5 Å. Furthermore, the stereochemistry of the monomers was found to have a negligible effect on the average interchain distances. In comparison with polymers **P9−12** with ethoxy substituents in the cyclotriphosphazene ring, polymers **P1−8** have the longer average interchain distances by 1 Å because the relatively larger phenoxy groups in **P1−8** repel the interchain contacts such that they display slightly longer interchain distances.

Table 1. Synthetic Yields, Molecular Weights, M_w/M_n and Thermal Data of Polymers P1-P8.[a]

polymers	yield (%)	M_w	M_n	M_w/M_n	T_g	T_d (in N_2)	T_d (in air)
P1	73	17 300	9900	1.76	53	446	435
P2	62	18 600	9600	1.94	49	423	403
P3	69	11 900	7300	1.63	43	447	412
P4	67	32 600	14 500	2.15	16	436	382
P5	77	24 100	14 600	1.65	90	449	435
P6	72	26 500	13 500	1.96	71	419	403
P7	71	38 000	16 400	2.31	63	436	412
P8	70	25 100	11 700	2.24	39	436	419
P9	67	17 900	9300	1.92	45	292	289
P10	69	15 700	8500	1.85	59	329	326
P11	72	16 000	10 400	1.54	62	337	337
P12	75	33 200	14 100	2.35	83	355	349

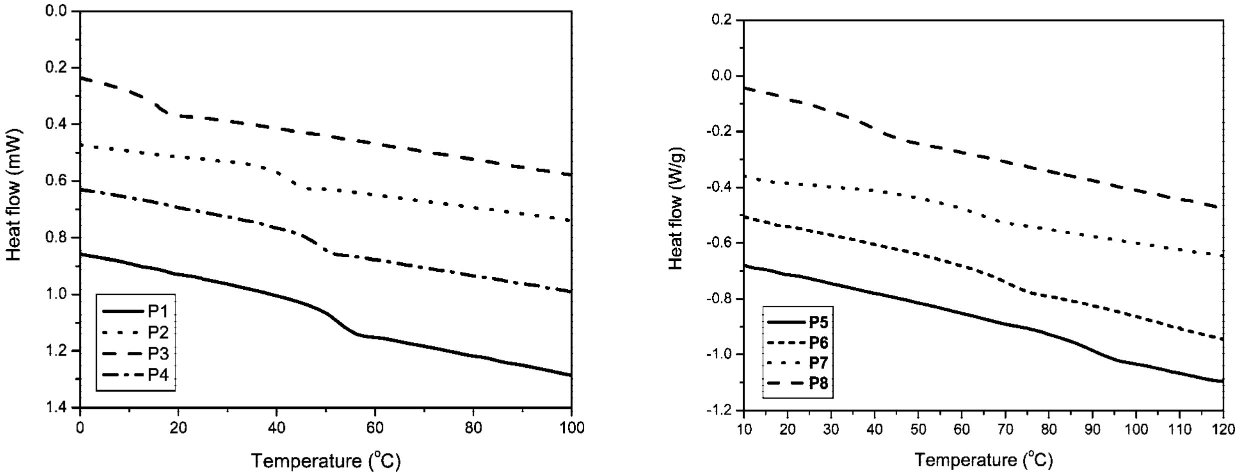
[a] M_w: the weight-average molecular weight. M_n: the number-average molecular weight. T_g: glass transition temperature. T_d: the decomposition temperature at which 5% weight loss occurs.

Optical Properties of Polymers. The UV−vis and fluorescence spectra of polymers **P1−12** were determined and are summarized in Table 3. Transparent and uniform films of polymers were prepared readily on quartz plates by spin-casting their THF solutions at room temperature. The UV−vis and photoluminescence spectra in both the solution and the film state are shown in Figures 7, 8, and 9. Polymers **P1−12** displayed a small red-shift of the 0−0 absorption bands in film compared to that in solution ($\Delta\lambda_{max} = 1-4$ nm; Table 2), suggesting that there is little change in molecular conformation from the solution to the film state. For polymers **P1−4** and **P9−10**, the absorption maxima were around 330 nm, while the absorption maxima for polymers **P5−8** and **P11−12** were red-shifted by 10 nm (341−345 nm), because **P5−8** and **P11−12** have longer conjugation lengths than **P1−4** and **P9−10**. However, all polymers in film state experienced some emission red-shifts



(a) (b)

Figure 4. TGA curves of **P1−4** (a) and **P5−8** (b) in N$_2$.



(a) (b)

Figure 5. DSC curves of **P1−P4** (a) and **P5−P8** (b) in N$_2$.

Table 2. X-ray Diffraction Data

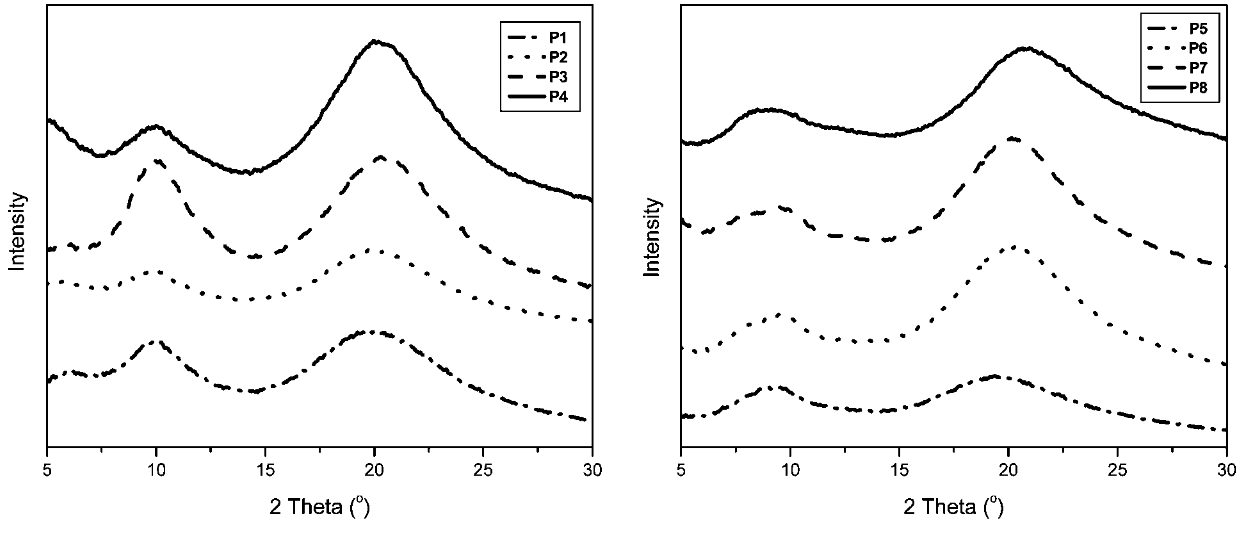
polymers	diffraction angle 2θ (deg)	*d*-spacing (Å)
P1	9.95, 19.93	8.89, 4.45
P2	9.88, 20.12	8.95, 4.41
P3	9.92, 20.41	8.92, 4.35
P4	9.94, 20.24	8.90, 4.39
P5	9.35, 19.55	9.46, 4.54
P6	9.56, 20.18	9.25, 4.40
P7	9.40, 20.21	9.41, 4.39
P8	9.25, 20.83	9.56, 4.26
P9	11.40, 22.07	7.76, 4.03
P10	11.34, 21.60	7.80, 4.11
P11	10.61, 21.50	8.34, 4.13
P12	10.35, 21.55	8.55, 4.12

relative to those in solution. Polymers **P1−4** and **P9−10**, with short conjugation lengths, underwent more significant emission red-shifts (29−35nm) from the solution to the film state as compared to polymers **P5−8** (17−21nm). Unlike polymers **P9−10**, polymers **P11−12** experienced significantly less-pronounced emission red-shifts from solution to the film state (3−10 nm).

The types of substituents in the cyclotriphosphazene ring have diverse effects on the absorption and emission maxima. For example, polymers **P9−10** with four ethoxy substituents exhibited similar absorption and emission characteristics to **P1−4** with four phenoxy substituents. **P9−10** displayed two emission maxima at 363−365 and 382−384 nm, which is very close to those of **P1−4**, with $\lambda_{\max}$ = 363−364 nm, 382−385 nm. In contrast, **P11−12** ($\lambda_{\max}$ = 397−399, 410−414 nm) showed less emission maxima than **P5−P8** ($\lambda_{\max}$ = 406−408, 426−428 nm) in the film state (Table 3).

The stereochemistry of the polymers plays an additional role in affecting the optical properties. For instance, **P10** and **P12**, derived from *cis*-monomers, displayed slightly lower absorption maxima but larger emission maxima both in solution and in the film state relative to **P9** and **P11**, which were prepared from *trans*-monomers.

All polymers displayed narrow full width at half-maximum (fwhm) of the emission spectra in the range of 45−54 nm, suggesting that these polymers have good color purities. The photoluminescence efficiencies (ϕ_{PL}) of the polymers in THF were measured by using quinine sulfate as a standard. The ϕ_{PL} of polymers **P1−8** is between 0.55 and 0.69, and it is less than the ϕ_{PL} values of polymers **P9−12** (0.73−0.88). The change in ϕ_{PL} values is likely related to the special alignment of substituents in the cyclotriphosphazene ring. Single crystal X-ray analysis of hexa(aryloxy)cyclotriphosphazene shows that the six aryloxy groups lie almost perpendicularly above and below the nearly planar cyclotriphosphazene core,[45−47] and this structural



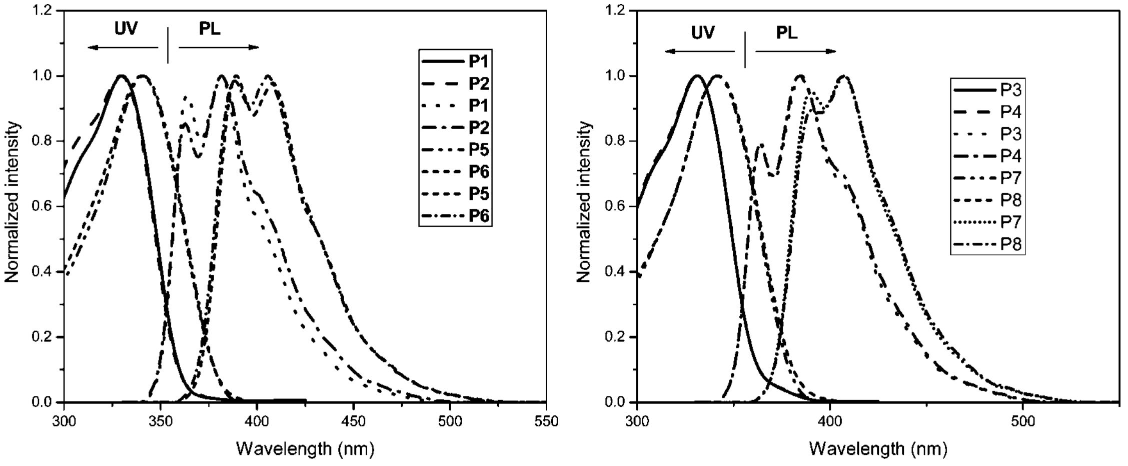
(a) (b)

Figure 6. Wide angle X-ray diffraction profiles of the polymers (a) **P1−4** and (b) **P5−8**. Intensity is offset for clarity.

Table 3. Optical Properties of Polymers P1−P8

polymers	UV (nm) λ_{max} (in THF)	UV (nm) λ_{max} (in film)	$\Delta\lambda_{max}$[b]	fluorescence (nm) λ_{max} (in THF)	fluorescence (nm) λ_{max} (in film)	fwhm (in film)	ϕ_{PL}[a] (in THF)	$\Delta\lambda_{max}$[b]
P1	330	332	2	364, 382, 402 (sh)[c]	394, 411	52	0.61	30, 29
P2	330	332	2	363, 382, 402 (sh)[c]	394, 410	52	0.60	31, 28
P3	331	333	2	364, 385, 407 (sh)[c]	399, 414	52	0.69	35, 29
P4	331	333	2	364, 384, 407 (sh)[c]	404	50	0.57	n. a.[d]
P5	341	343	2	389, 408	412	54	0.55	n. a.[d]
P6	341	342	1	389, 406	406, 426 (sh)	48	0.63	17, 20
P7	342	345	3	390, 408	410, 428 (sh)	48	0.59	20, 20
P8	341	345	4	380, 407	408, 428 (sh)	45	0.65	20, 21
P9	330	333	3	363, 382	392, 411	48	0.81	29, 29
P10	329	330	1	365, 384	392, 412	45	0.81	27, 28
P11	343	344	1	387, 407	397, 410	52	0.88	10, 3
P12	340	341	1	390, 410	399, 414	58	0.73	9, 4

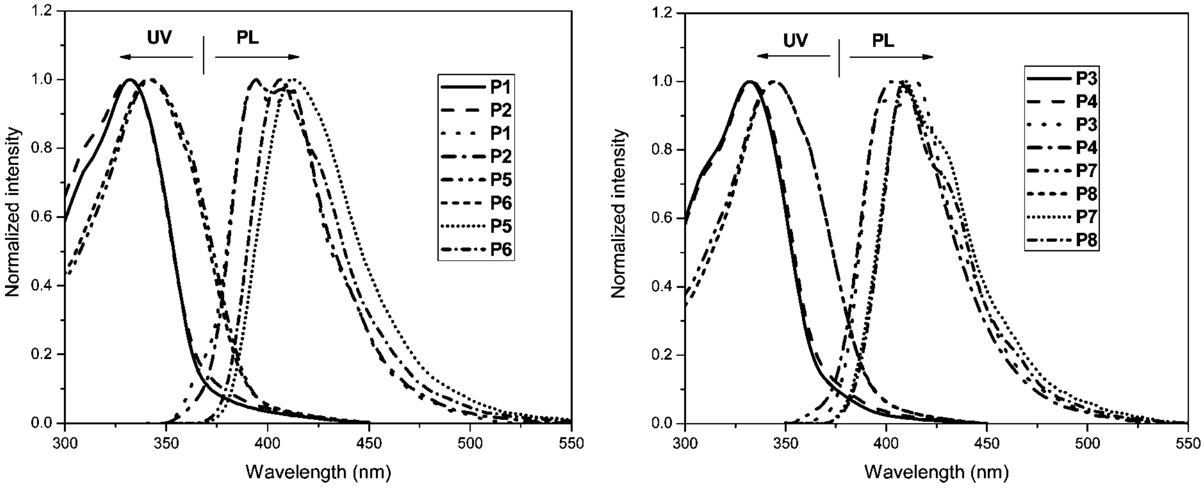
[a] The PL efficiency (ϕ_{PL}) of the polymers in THF solutions was measured by using quinine sulfate (ca. 1×10^{-5} M solution in 0.1 M H_2SO_4, assuming ϕ_{PL} of 0.55) as a standard. Absorption maxima of **P1−12** were taken as λ_{ex} (excitation wavelength) for **P1−P8**. [b] $\Delta\lambda_{max} = \lambda_{max}$ (in film)− λ_{max}(in solution). [c] sh = shoulder peak. [d] n.a. = not applicable.



(a) (b)

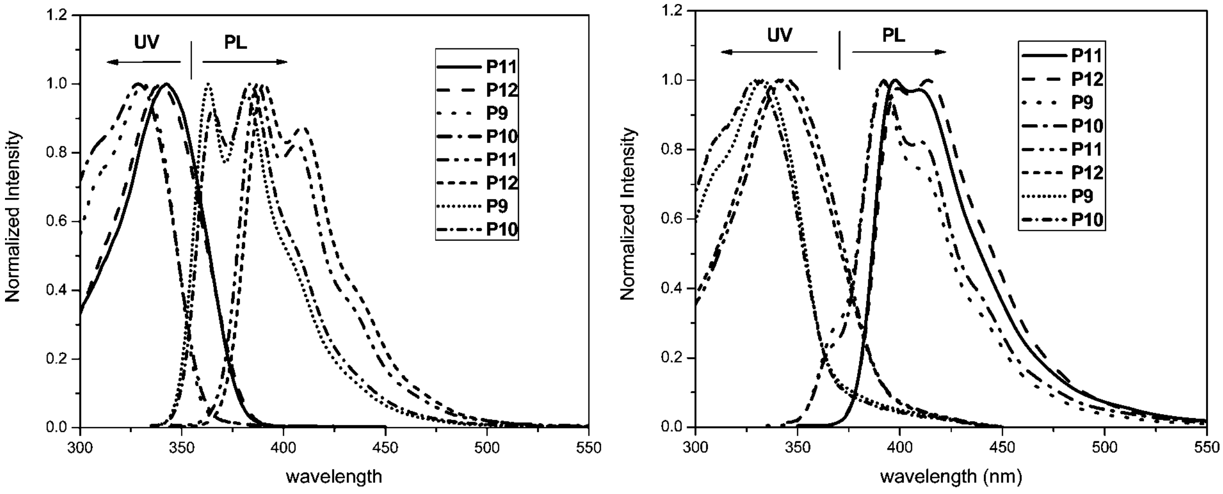
Figure 7. Photoluminescence spectra of **P1−2** and **P5−6** (a) and **P3−4** and **P7−8** (b) in THF.

feature makes it possible for the three aryloxy groups to be located on the same side of the $(PN)_3$ plane, able to align through intramolecular $\pi-\pi$ interactions. In fact, the downfield chemical shift of the aromatic protons in *cis*-**9** relative to corresponding aromatic protons in *trans*-**9** suggests the presence of such an aryl−aryl interaction. Molecular modeling of compound *trans*-**3** by Chem3D 8.0 shows that the biphenyl group cofacially interacts with one adjacent phenoxy group linked to the neighboring phosphorus atom. The centroid distance of the two aromatic groups is 3.48 Å, very close to the normal $\pi-\pi$



(a) (b)

Figure 8. Photoluminescence spectra of **P1−2** and **P5−6** (a) and **P3−4** and **P7−8** (b) in film state.



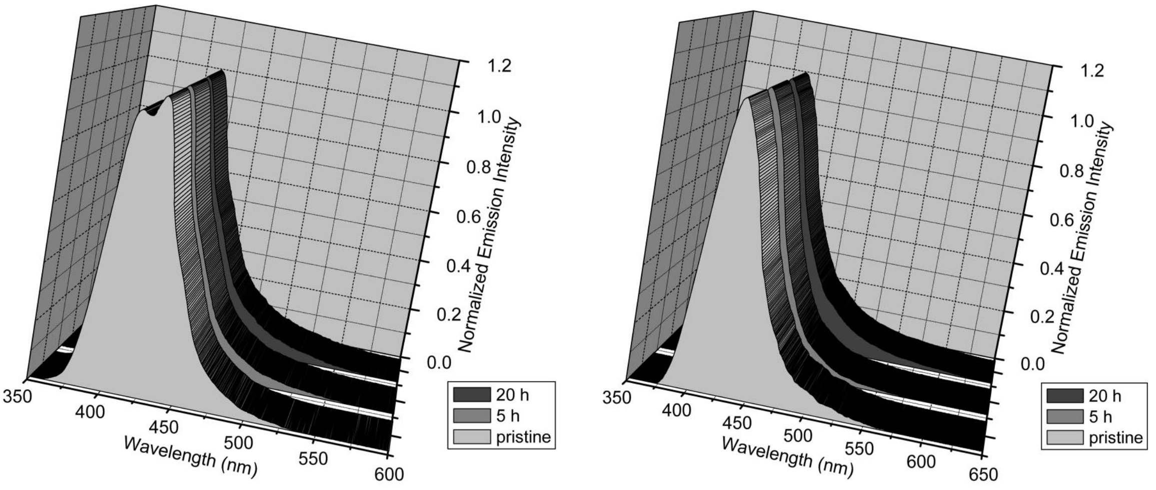
(a) (b)

Figure 9. Photoluminescence spectra of **P9−12** (a) in THF and (b) in the film state.

stacking contact. This type of noncovalent $\pi-\pi$ interaction has been demonstrated to be able to result in the emission spectral shifts accompanied by changes in ϕ_{PL}.[48,49] Therefore, the above-mentioned emission change $\Delta\lambda_{max}$ (17−35 nm) from the solution state to the film state for polymers **P5−8** is also likely to be due to these intramolecular $\pi-\pi$ interactions.

The spectral shifts and the variations in ϕ_{PL} values can be also explained by an electron transfer mechanism. The possibility of intramolecular electron transfer can be roughly estimated by the Rehm−Weller equation, which approximates the free energy change ($\Delta G^{\#}$) between a donor and an acceptor.[50,51] However, in our studied polymers system, the four phenoxy groups serve as acceptors and interact with one rigid backbone repeat unit (donor), making it impracticable to reliably estimate the value of $\Delta G^{\#}$ using this equation.

Thermal Effect on Optical Stability. In order to avoid the possible oxidation of C-9 in the fluorene unit, the emission spectra of polymers **P1−8**, using **P3** and **P5** as examples, were investigated at 200 °C under vacuum and ambient light. As evident by TGA experiments, polymers **P1−8** are stable and do not experience any degradation at this temperature. Therefore, any green emission observed under vacuum conditions should be attributed to a reordering of the polymer chain, and the subsequent aggregate formation, as the absence of oxygen rules out the oxidation of the potentially vulnerable C-9 of the fluorene unit to produce fluorenone moieties and, therefore, eliminates the possibility of keto defect-induced green emission. The emission spectra of **P3** and **P5** film after thermal annealing for 5 and 20 h are illustrated in Figure 10. Upon heating for 5 h at 200 °C, polymer **P3** produced nearly the exact same spectral profiles as its pristine film, and no excimer green emission was observed. Prolonging the thermal annealing did not result in additional green emission. Similar optical behaviors of polymer **P5** were observed under the same thermal treatment conditions, suggesting that the three-dimensional structure of the polymers prevented aggregation of the polymer chains and, hence, that it nearly completely suppressed formation of aggregation-induced excimer emission. In contrast, poly(9,9-dihexylfluorene) showed a strong green emission band centered at 520 nm in its emission spectrum upon annealing in nitrogen for 3.5 h.[19] Theses observed results are consistent with the fact that amorphous structure of our polymers, which is unfavorable toward aggregate formation, as evidenced by XRD experiments. The phenoxy substituents in the cyclotriphosphazene cores push away the



(a) (b)

Figure 10. Effect of thermal aging on PL spectra of (a) **P3** and (b) **P5** under ambient light and vacuum at 200 °C.

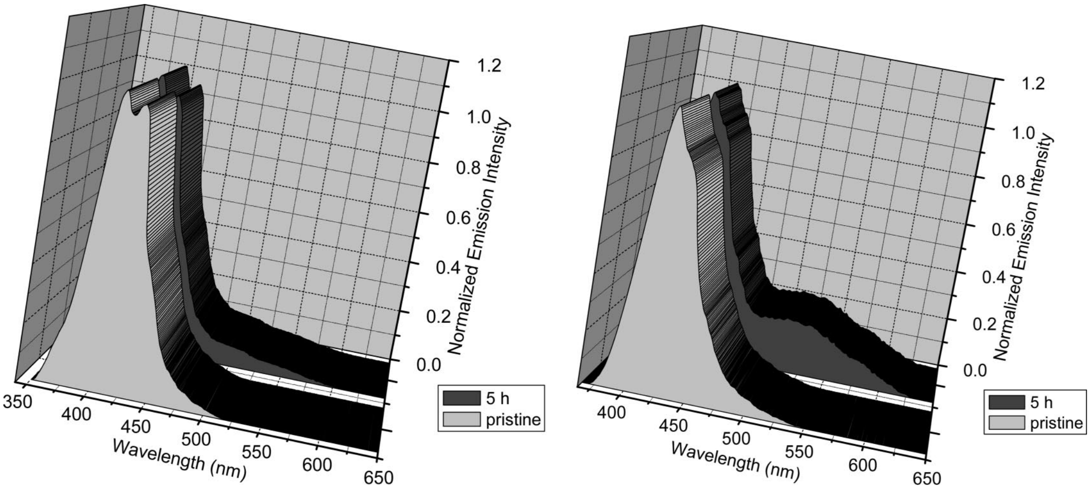


Figure 11. Effect of thermal aging on PL spectra of (a) **P1** and (b) **P7** under ambient light and in air at 200 °C.

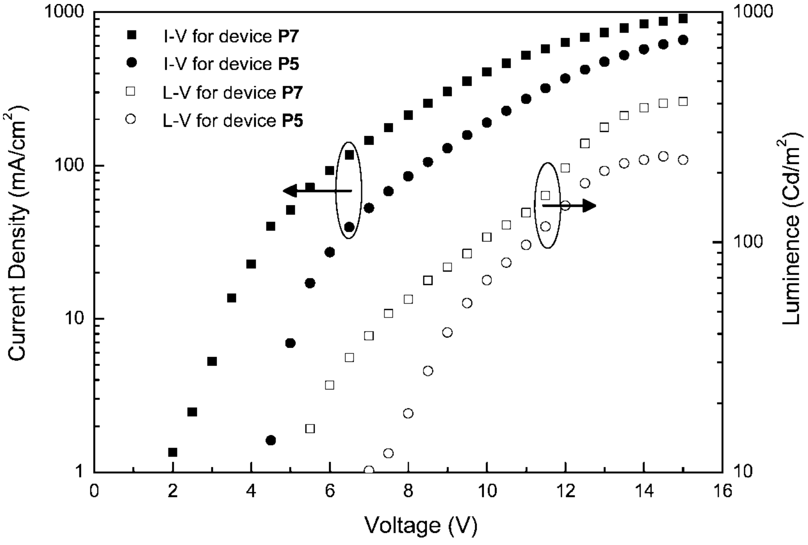


Figure 12. *I*−*V*−*L* characteristics of the PLED device.

backbone chains and subsequently make the interchain distance larger, preventing the formation of excimers.

The emission spectra of **P1−8** in air at 200 °C for 5 h were also examined to provide insight into how the thermal stability

Table 4. Electroluminescence Data of PLED Devices[a]

polymers	V_{on} (V)[b]	maximum brightness (cd/m^2) at 15 V	maximum current density (mA/cm^2)	maximum current efficiency (Cd/A)	luminance efficiency (lm/W)
P5	7	240	656	0.04	0.08
P7	5	410	870	0.05	0.12

[a] Devices structure: ITO/PDOT/polymer/Ca/Ag. [b] V_{on} is the turn-on voltage of current.

and oxidation-resistant ability of polymers influence the formation of green emission induced by keto defects. The emission spectra of **P1** and **P7** film after thermal annealing together with their individual pristine films are shown in Figure 11. **P1** exhibited a very weak featureless broadband the 500−600 nm region. In contrast, **P7** displayed a relatively stronger green emission band at 525 nm in air than **P1**, possibly resulting from monomeric fluorenone charge-transfer $\pi-\pi^*$ transitions and energy transfer from the fluorene to the fluorenone moiety. This is significantly different than the optical behavior of poly(9,9-dihexylfluorene) in air at the same temperature for 3−4 h, in which a strong green emission was observed.[19,20,22] Nonetheless, the original emission bands at 394 and 411 nm for **P1** and 410 and 428 nm for **P7** are still dominant in both emission spectra of **P1** and **P7**. Other polymers derived from monomers **3** and **4** also exhibited similar behaviors under annealing at the same temperatures. These results suggested that introduction of inorganic cyclotriphosphazene cores effectively retarded the oxidation of C-9 in the fluorene unit, thereby reducing keto defect-induced green emission.

Electroluminescence Properties of Polymers. Polymers **P5** and **P7** were fabricated into four-layer PLED devices, with a configuration of ITO/PDOT:PSS/**P5** or **P7**/Ca/Ag, using standard procedures of spin-coating. Under a biased voltage, the two PLED devices showed blue emissions with EL λ_{max} of 416 nm. The current−voltage and luminescence-voltage curves of **P5** and **P7** PLED devices are shown in Figure 12, and the electroluminescence data of the PLED devices are summarized in Table 4. The turn-on voltages of these PLED devices were 5 and 7 V, and their maximum current efficiencies and maximum luminance were 0.04 and 0.05 cd A^{-1} and 240 and 410 cd m^{-2} (at 15 V), respectively. The current density increased with increasing forward bias voltage, indicating typical rectifying characteristics. The relatively higher brightness in **P7** than **P5** may be due to the relatively higher quantum efficiency of **P7** than **P5**. The PLED brightness and efficiency are not high for these two materials, but we believe that they could be improved by optimizing the device architecture. These preliminary results seem to suggest that these polymers have the potential for application as PLED materials.

Conclusions

Cyclotriphosphazene-based polymers were synthesized from suitable cyclotriphosphazene precursors through Suzuki cross coupling reactions. All polymers provided blue light emission in high quantum yields. Incorporation of hybrid organic−inorganic cyclotriphosphazene cores in those polymers significantly enhanced the overall thermal stability of the polymers. The polymers are amorphous solids, as evidenced by two broad diffraction peaks at 7.7−9.6 Å and 4.1−4.5 Å. The introduction of the three-dimensional organic−inorganic hybrid architectures of the cyclotriphosphazene units prevented polymer aggregation and consequently diminished the formation of green excimer emission. The presence of the inorganic component ($(PN)_3$) also significantly reduced the green emission induced by polymer oxidation. In addition, the particular arrangement of substituents in the cyclotriphosphazene ring allowed the aryl groups to stack through intramolecular aromatic $\pi-\pi$ interactions, leading to a spectral red-shift.

The suppression of polymer aggregation and enhancement of thermal stability by introducing three-dimensional organic−inorganic hybrid architecture in the present polymer system allow for the prediction of a substantial reduction in both aggregation-induced excimer emission and keto-defect-induced emission. In turn, it offers an alternative way in which to design and synthesize nonaggregating thermally stable luminescent polymers with good color purity. Studies of the other types of thermally stable luminescent polymers and oligomers prepared starting from cyclotriphosphazene are under investigation in our laboratory.

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