Photoluminescent, Liquid-Crystalline, and Electrochemical Properties of *Para*-Phenylene-Based Alternating Conjugated Copolymers

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ABSTRACT: Novel liquid-crystalline alternating conjugated copolymers [P(P(6)CN-*alt*-Cz) and P(P(6)CN-*alt*-MeP)] with phenylene and carbazolylene or phenylene with methyl substitution onto the main chain have been synthesized through palladium-catalyzed Suzuki coupling reactions. The influence of the incorporation of carbazolylene and the substituted phenylene into the main chain on the thermal, mesomorphic, and luminescent properties has been investigated by Fourier transform infrared spectroscopy, thermogravimetry, differential scanning calorimetry, polarized optical microscopy, ultraviolet–visible spectroscopy, photoluminescence (PL), and cyclic voltammetry. These polymers show highly thermal stability, losing little of their weights when heated to 360 °C. The conju-

gated copolymers exhibit liquid crystallinity at elevated temperature. The existence of the chromophoric terphenyl core endows the copolymers with high PL and the polymer **P(P(6)CN-alt-Cz** containing carbazolylene unit can emit more pure blue light. All the copolymer films with low band gaps about 2.3–2.4 eV undergo reversible oxidation and reduction processes, significantly lower than the band gap of poly(*p*-phenylene). © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 434–442, 2010

KEYWORDS: conjugated polymers; liquid-crystalline polymers (LCP); liquid crystallinity; luminescence; photoluminescence; poly(*p*-phenylene)

INTRODUCTION π -Conjugated aromatic polymers represented by poly(p-phenylene) (PPP), poly(p-phenylene-vinylene), and polythiophene and their copolymers are promising candidates for advanced functional materials and devices, such as light-emitting diodes (LEDs),¹ electrochemical cells,² and optoelectronic devices.³ Liquid crystals (LCs) find largescale applications in LC displays and are promising materials for the induction of mesoor macroscale dynamics under molecular control, because they are spontaneously oriented and furthermore macroscopically aligned by an external force, such as shear stress, electric field, and magnetic force field, giving rise to electrical and optical anisotropies and even a linearly polarized luminescence.^{4,5} Side-chain liquid-crystalline polymers (LCPs), which prepared by introducing mesogenic moieties into backbones of main chains, are of both theoretical and practical interest because the side-chain substitution is essential to obtain solubility, at the same time, to control the molecular orientation.⁶

PPPs constitute a particularly important class of polymers in that they emit in the blue and can act as hosts for downhill energy transfer to generate green and red emitters in polymer LEDs.⁷ Besides, compared with the instability and intractability of PPP, PPP containing mesomorphic substitu-

ent derivatives offers the prospect of controlling polymer properties, such as solubility, emission wavelengths, processability, and molecular orientation.^{8,9} Thus, the LC conjugated PPPs have been extensively investigated by attaching different mesogenic units as the side chain.^{10,11} However, the study on the LC conjugated copolymer based on PPPs and other different aromatic moieties on the main chain is still lacking.

The terphenyl, which is not only a strong light-emitting chromophore but also a mesogenic core,^{12,13} has been introducing to the conjugated main chains as the mesogen pendants.^{14,15} In our previous work, the PPP homopolymer containing terphenyl mesogenic pendant, { $-[C_6H_3-COO-(CH_2)_6-O$ -terphenyl $-CN]_{n-}$, **PP(6)CN**}, has been synthesized.¹⁶ The terphenyl mesogen pendant endows the conjugated copolymers with good LC and the energy could transfer from the mesogen pendants to the main chain to favor the photoluminescence (PL). To realize more about this type of PPP bearing terphenyl mesogen, we move forward to prepare a series of LC alternating copolymer with other aryl moieties. In this article, we attempt to synthesis a novel alternating conjugated copolymer **P(P(6)CN-alt-MeP)**, where the phenylene with methyl substitution units is inserted into

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the repeated unit of PPPs containing terphenyl mesogenic pendants. The steric crowding between the bulky terphenyl mesogen pendants could be weakened by introducing phenylene ring with methyl substituents, which probably lead the copolymer with interesting properties. Besides, carbazole, an aromatic heterocycle, which is a well-known hole-transporting unit due to the electron-donating capabilities associated with its nitrogen atom, enables higher current densities and consequently higher luminance levels at lower voltages.^{17,18} Moreover, the carbazoles maintain a sufficiently high triplet energy level due to the limited electronic conjugation of biphenyl upon polymerization.¹⁹ For this reason, we also incorporated carbazolylene onto PPP main chain, and the properties of polymer **P(P(6)CN-alt-Cz)** containing terphenyl mesogenic pendant are systemically studied.

EXPERIMENTAL

Materials

The monomer 2,5-bromo-1-[(6-(4-(4'-cyano)terphenyloxy)hexyloxy)carbonyl]-benzene **[P(6)CN]** was synthesized according to the literature,¹⁶ and the obtained product was thoroughly purified before polymerization. Trimethyl borate, *n*-butyllithium, thiophene-3-acetic acid, 2,5-dibromotoulene, 6-bromo-1-hexanol, 4-(4-bromophenyl)phenol, 4-bromobenzonitrile, *N*-ethyl-carbazole, 1,3-dicyclohexylcarbodiimine, 4-(dimethylamino)pyridine, and tetrakis(triphenylphosphine)palladium were purchased from Alfa Aesar and used as received without any further purification. Tetrahydrofuran (THF) and CH₂Cl₂ were dried over sodium. Other chemicals were obtained from Shanghai Reagent and used as received.

Techniques

The infrared (IR) spectra were measured on a Shimadzu IR Prestige-21 Fourier transform infrared spectrophotometer with the KBr method. The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 400 NMR and Bruker AV 600 NMR spectrometer with deuterated chloroform or THF or DMSO as the solvent and tetramethylsilane($\delta = 0$) as the internal reference. The ultraviolet-visible (UV) spectra of the samples were obtained with a Hitachi UV-2300 spectrophotometer. Fluorescence measurement for PL of the polymers in THF was carried out on a Shimadzu RF-5301 PC, and fluorescence of solid state was recorded on a Hitachi F-4500 spectrofluorophotometer with a xenon lamp as the light source. The quantum yields were obtained on a FLS-920 (Edinburgh Instruments) with an integral sphere. The gel-permeation chromatography, so-called size-exclusion chromatography analysis, was conducted with a Breeze Waters system equipped with a Rheodyne injector, a 1515 Isocratic pump, and a Waters 2414 differential refractometer using polystyrene as the standard and THF/ N,N-dimethylformamide (DMF) as the eluent at a flow rate of 1.0 mL/min and 40 °C through a Styragel column set, Styragel HT3 and HT4 (19 mm \times 300 mm, $10^3 + 10^4$ Å) to separate molecular weight (MW) ranging from 10^2 to 10^6 . Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 7 for thermogravimetry at a heating rate of 20 °C/min under nitrogen with a sample size of 8-10 mg.

Differential scanning calorimetry (DSC) was used to determine phase-transition temperatures on a Perkin-Elmer DSC 7 differential scanning calorimeter with a constant heating/ cooling rate of 10 °C/min. Texture observations by polarizing optical microscopy (POM) were made with a Nikon E600POL POM equipped with an Instec HS 400 heating and cooling stage. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target ($\lambda = 1.54$ Å) and at a scanning rate of 1°/min. Cyclic voltammetry (CV) was carried out on a CHI660C electrochemical workstation with platinum working electrode at a scan rate of 20 mV/s against a Ag/AgNO₃ (0.1 M) reference electrode with nitrogen-saturated solution of tetra-n-butylammonium tetrafluoroborate (0.1 M, TBAPF₄) in acetonitrile (CH₃CN) and platinum wire as counter electrodes in a standard three-electrode cell. Elemental analyses (EA) were characterized by means of EA with Vario Elementar III.

Synthesis of 1,4-Toluenediboronic Acid (1)

To a solution of 5 g 3,6-dibromo toluene (0.02 mol) in THF (50 mL) at -100 °C, 15 mL of *n*-butyllithium (2.87 M in hexane, 0.043 mol) was added by syringe. The mixture was stirred at below -78 °C for 2 h. A solution of trimethyl borate 10.4 mL in THF was added rapidly to the solution and was stirred at -78 °C for another 2 h. The resulting mixture was warmed to room temperature and stirred for 24 h. The product was extracted into ether after the dilute hydrochloric acid was added. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum and the crude dissolved in a small amount of THF and reprecipitated with hexane to give a white solid with yield of 70%. IR (cm⁻¹): 3290, 2938, 1596, 1497, 792. ¹H NMR (ppm, THF-d): 7.73 (m, aromatic, 3H) 2.25(m, CH₃-Ar, 3H).

Synthesis of Conjugated Copolymer P(P(6)CN-alt-MeP)

Monomer **P(6)CN** (0.63 g, 1 mmol) and **1** (0.185 g, 1.03 mmol) were dissolved in 15 mL of dry toluene under N₂. To the solution were added K_2CO_3 (aq) (2.0 M, 5 mL; N₂ bubbled before use), $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol), and 5 mL ethanol. After the mixture was stirred for 3 days at 80 °C under an N₂ atmosphere, the solvent was evaporated. The resulting solid was dissolved in a small amount of THF and reprecipitated in methanol for 24 h. After filtration, the polymer was further washed with acetone and dried under vacuum to afford dark brown powder.

Polymer P(P(6)CN-alt-MeP)

Dark brown solid, Yield = 65%. IR (KBr, cm⁻¹): 2933, 2854, 2218, 1723, 1592, 1481, 806. ¹H NMR (ppm, THF-d): 8.10–8.00 (m, aromatic, 1H), 7.99–7.57 (m, aromatic, 15H), 6.98–6.90 (d, aromatic, 2H ortho to -O-), 4.30–4.25 (t, 2H, $-CH_2-O-Ar$), 4.01–3.98 (t, 2H, $-CH_2-OOC-$), 1.99–1.92 (m, 3H, CH₃-Ar), 1.60–1.51 (m, 4H, $-CH_2$ $CH_2(CH_2)_2CH_2CH_2-$), 1.51–1.37 (m, 4H, $-CH_2$ $CH_2(CH_2)_2CH_2CH_2-$). Anal. Calcd. for $[C_{39}H_{33}O_3N]_n$: C: 83.13; H: 5.86; N: 2.48. Found: C: 83.75; H: 5.69; N: 2.39. $M_n = 17,860; M_w/M_n = 2.13$.



SCHEME 1 Illustration of procedures for the synthesis of P(P(6)CN-*alt*-MeP) and P(P(6)CN-*alt*-Cz).

Synthesis of 3,6-Dibromo-N-ethyl-carbazole (2)

N-Ethyl-carbazole (10 g, 70.3 mmol) was slowly added to a solution of *N*-bromosuccinimide, NBS (30.2 g, 172 mmol), in 50 mL of DMF by a dropping funnel. After the addition, 10 mL of DMF was further added to the reaction mixture and refluxed at 0 °C for 20 h under an N₂ atmosphere. The reaction vessel was wrapped by aluminum foil to shield the reaction from light. When the reaction completed, the reaction mixture was allowed to warm to room temperature. The solution was poured into a large amount of saturated sodium sulfate cooled by ice water. The yellow precipitate was filtered off and recrystallized from an ethanol/water mixture to yield the product as white needle-like crystal. Yield: 63.0%. IR (cm⁻¹): 2943, 2864, 1280, 831, 743, 652, 482.

¹H NMR (ppm, THF-d): 8.10 (d, 2H); 7.59 (m, 2H); 7.27 (t, 2H); 3.91 (m, CH₂—N, 2H); 1.53 (t, CH₃—CH₂—N, 3H).

Synthesis of N-Ethyl-carbazole-3,6-diboronic Acid (3)

To a solution of 5 g 3,6-dibromo-*N*-ethyl-carbazole (14.1 mmol) in THF (50 mL) at -78 °C, 12 mL of *n*-butyllithium (2.87 M in hexane, 0.034 mol) was added by syringe. The mixture was stirred at -78 °C for 2 h. Trimethyl borate (8.2 mL) was added rapidly to the solution, and the mixture was stirred for 2 h at -78 °C. The resulting mixture was warmed to room temperature and stirred for 24 h. Dilute hydrochloric acid was added and the mixture was extracted with ether.

The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum, and the residue was washed by large amount of nhexane to provide 3.0 g of the title product as a pale-white solid in 65% yield.

IR (cm⁻¹): 3290, 2938, 1596, 1497, 1272, 792. ¹H NMR (ppm, THF-d): 8.02 (m, aromatic, 2H); 7.64 (m, aromatic, 2H); 7.13 (t, aromatic, 2H); 3.89 (m, CH₂—N, 2H); 1.51 (t, CH₃—CH₂—N, 3H).

Synthesis of Conjugated Copolymer P(P(6)CN-alt-Cz)

Monomer **P(6)CN** (0.63 g, 1 mmol) and **3** (0.36 g, 1.02 mmol) were dissolved in 15 mL of dry toluene under N₂. Tetrakis(triphenylphosphine)-palladium $[Pd(PPh_3)_4]$ (0.12 g, 0.1 mmol) was added into a mixture of toluene and 2 M potassium carbonate aqueous solution. The mixture was stirred at 85–90 °C for 72 h under the protection of N₂. After the mixture was cooled to the room temperature, it was poured into the stirred methanol. A solid was obtained by filtration. The copolymer was further purified by stirring in acetone for 24 h to remove oligomers and catalyst residues. The resulting product was dried under reduced pressure at room temperature.

Polymer P(P(6)CN-alt-Cz)

Orange solid, Yield = 69%. IR (KBr, cm^{-1}): 2933, 2854, 2218, 1723, 1592, 1480, 1268, 806. ¹H NMR (ppm, DMSO-

d): 8.10–8.00 (m, aromatic, 1H), 7.99–7.57 (m, aromatic, 17H), 6.98–6.90 (d, aromatic, 2H ortho to -0-), 4.38–4.29 (t, 2H, $-CH_2-0-Ar$), 4.09–4.01 (t, 2H, $-CH_2-00C-$), 3.49–3.42 (m, 2H, $-CH_2-N$), 1.73–1.58 (m, 4H, $-CH_2 \ CH_2(CH_2)_2 \ CH_2CH_2-$), 1.51–1.24 (m, 7H, $-CH_2 \ CH_2(CH_2)_2CH_2CH_2-$ and CH_3-CH_2-N). Anal. Calcd. for $[C_{46}H_{38}O_3N_2]_n$: C: 82.88; H: 5.71; N: 4.20. Found: C: 83.43; H: 5.51; N: 4.33. $M_n = 13,590$; $M_w/M_n = 2.43$.

RESULTS AND DISCUSSION

Synthesis of the Conjugated Copolymer

The synthetic routes and structures of the copolymers are shown in Scheme 1. Using tetrakis(triphenylphosphine) palladium(0) [Pd(PPh₃)₄] as catalyst, polymers **P(P(6)CN-alt-MeP)** and **P(P(6)CN-alt-Cz)** were synthesized by Suzuki coupling reaction of **P(6)CN** with 1,4-toluenediboronic acid and *N*-ethyl-carbazole-3,6-diboronic acid, respectively. These conjugated copolymers are readily dissolved in common organic solvents, such as DMF and DMSO, and polymer **P(P(6)CN-alt-MeP)** even can dissolved in THF. Number-average (M_n) and weight-average (M_w) MWs of the polymers are summarized in the Experimental section. All the intermediate and final products have been thoroughly purified and fully characterized, and the chemical structures of the copolymers are confirmed by FTIR, ¹H NMR, and EA.

Structural Characterization

All the purified monomers and polymerization products give satisfactory spectroscopic data corresponding to their expected molecular structures (see Experimental section for details). P(P(6)CN-alt-MeP) and P(P(6)CN-alt-Cz) exhibit the similar IR distinct peak at 2933-2863, 2218, 1733, and 1250 cm⁻¹, which are due to stretching vibrations of $-(CH_2)_6$, C \equiv N, C=O, and Ar-O, respectively. There is no obvious difference except the assigned peak to C-N at 1480 cm^{-1} showed in the spectrum of **P(P(6)CN-alt-Cz)**. The -OH bending vibration at \sim 3290 cm⁻¹ can be observed in the monomers 1 and 3, whereas the bending vibration disappears in the corresponding spectra of polymers P(P(6)CNalt-MeP) and P(P(6)CN-alt-Cz), indicating that the polymerizations were performed successfully by Pd-complex-catalyzed polycondensation (for details, see Supporting Information). The ¹H NMR spectra of copolymers correspond well to the proposed structure. Signals of aliphatic and aromatic protons are observed in the ranges of δ 1.2–4.4 and δ 6.9-8.1, respectively. Except the peaks of solvent and water remain in the spectra, no unexpected signals are observed in the spectra of the copolymers, and all the resonance peaks can be assigned to appropriate protons, as can be clearly seen from Figure 1. The ¹H NMR results are quite consistent with the EA results.

Thermal Stability

As the formation of mesophases of a thermotropic LCP is realized by the application of heat, the thermal stability of the polymer is thus of primary importance. The thermal stability of the copolymers is evaluated by TGA under a nitrogen atmosphere. All the copolymers exhibit excellent thermal stabilities with little decomposition at high temperatures $(\geq 360 \, ^\circ C)$, and the incorporation of terphenyl rings into the main-chain structure has clearly enhanced the resistance of the copolymer to thermolysis (see Supporting Information). The "jacket effect" of the bulky terphenyl mesogenic appendages well wraps the conjugated backbones and thus limits their perturbations by heat and/or attack by the degradative species. The DSC analysis further substantiates the thermal stability of the copolymers: no irreversible peaks suspiciously associated with copolymer degradation are observed at the high temperatures during the cycles of repeated heating–cooling scans.

Liquid Crystallinity

After checking the thermal stabilities of the copolymers, we proceed to study their mesomorphic behaviors. Figure 2 shows the POM microphotographs of the textures of **P(P(6)CN-alt-MeP)** and **P(P(6)CN-alt-Cz)**. When copolymers are cooled from its isotropic stage, bright colorful mesogenic textures emerged from the homotropic dark



FIGURE 1 ¹H NMR spectra of polymers **P(P(6)CN-***alt***-MeP)** and **P(P(6)CN-***alt***-Cz)**.





(b)

FIGURE 2 Mesomorphic textures observed on cooling (a) P(P(6)CN-*alt*-MeP) to 190 °C and (b) P(P(6)CN-*alt*-Cz) to 220 °C from their isotropic melts.

background, forming an anisotropic texture, suggesting that the terphenyl pendants with long flexible spacer $-(CH_2)_6$ favors the mesogens to undergo thermal transitions in a relatively independent fashion. The textures grow into bigger dimension upon further cooling, but the exact nature of the mesophases is difficult to identify. We repeatedly try to grow the LCs with care but failed to obtain any readily identifiable characteristic textures. With the aid of XRD measurements, the textures of **P(P(6)CN-alt-MeP)** and **P(P(6)CN-alt-Cz)** are identified to be associated with SmA and SmA_d phases, respectively (*vide post*). Reheating the copolymers, both of them exhibit enantiotropic optical anisotropy with colorful textures, suggesting that the mesomorphism is enantiotropic.

Figure 3 shows the DSC thermograms of **P(P(6)CN-alt-MeP)** and **P(P(6)CN-alt-Cz)** recorded under nitrogen. In the first

cooling and the second heating cycle, the DSC thermograms recorded of the copolymers scan exhibit two peaks. Polymer P(P(6)CN-alt-MeP) enters the SmA phase from its isotropic state at 256.6 °C. The mesophase is stable in a long temperature range over 82 °C before P(P(6)CN-alt-MeP) finally solidifies at 174.6 °C. The associated g-SmA and SmA-i transitions are observed at 179.2 and 283.9 °C, respectively. The mesomorphism is thus enantiotropic. The transition profiles of P(P(6)CN-alt-Cz) are similar to those of P(P(6)CN-alt-MeP), and the i-SmA_d and SmA_d-g transitions are found at 280.7 and 160.3 °C, respectively. In the second heating scan, its corresponding g-SmA_d and SmA_d-i transitions are observed at 181.1 and 287.5 °C, respectively. Compared with homopolymer **PP(6)CN** with the temperature transition range (\sim 45 °C), both of the copolymers possess a much broader temperature range (\sim 80 °C) and higher transition temperature, thanks for introducing the rigid aromatic rings onto the main chain. The thermal transitions and their



FIGURE 3 DSC thermograms of the copolymers recorded under nitrogen during (a) the second heating and (b) first cooling scans at a scan rate of 10 $^{\circ}$ C/min.

TABLE 1 Thermal Transitions and Corresponding Thermodynamic Parameters of P(P(6)CN-alt-MeP) and P(P(6)CN-alt-Cz)

	T, °C [ΔH, kJ/mru; ΔS, J/(mru K)]ª	
Copolymers	Cooling	Heating
P(P(6)CN- <i>alt</i> -MeP)	i 256.6 (-0.46; -0.86) SmA 174.6 (-4.81; -10.74) g	g 179.2 (5.35; 11.82) SmA 283.9 (0.50; 0.89) i
P(P(6)CN- <i>alt</i> -Cz)	i 280.7 (–11.01, –19.87) SmA _d 160.3 (–0.20; –0.46) g	g 181.1 (0.34; 0.74) SmA _d 287.5 (10.53; 18.79) i

Sm, smectic phase; g, glassy state; i, isotropic liquid; mru, monomer repeat unit.

^a Data taken from the DSC thermograms recorded under dry nitrogen in the first cooling and second heating scans.

corresponding enthalpy and entropy changes of **P(P(6)CN***alt*-**MeP)** and **P(P(6)CN**-*alt*-**Cz)** are summarized in Table 1. The large ΔH and ΔS changes involved in the mesomorphic transitions of **P(P(6)CN**-*alt*-**MeP)** and **P(P(6)CN**-*alt*-**Cz)** rule out the possibility of nematic phase and further support the assignment of smecticity to the mesophases of the polyphenylene derivates.²⁰

XRD analysis can provide useful information concerning molecular arrangement, mode of packing, and type of order in a mesophase of a polymeric LC. XRD patterns are obtained from the mesogenic PPPs quenched with liquid nitrogen from LC states, whereas the mesophases in the LC states are frozen by the rapid quenching with liquid nitrogen. The XRD diffractogram of a powdery sample can be generally divided into the low-angle Bragg reflections at $2\theta \sim 3^{\circ}$ corresponding to the layer spacing of molecular orientational order and the high-angle peaks at $2 heta \sim 20^\circ$ associated with the twodimensional liquid-like intermesogenic organization within the layers.^{21,22} The XRD diffractogram of the polymer P(P(6)CN-alt-MeP) consists of several low-angle and highangle peaks (Fig. 4). The diffuse peak located at $2\theta = 20^{\circ}$ gives the average distance of the shorter preferred spacing $(d_3 = 4.41 \text{ Å})$ occurring in the lateral packing arrangement of the mesogenic pendants (Table 2). The layer spacing derived from the Bragg reflection at $2\theta = 2.86^{\circ}$ ($d_1 = 30.86$ Å) is associated with molecular length at its most extended conformation (l = 28.40 Å). The existence of long-range



FIGURE 4 X-Ray diffraction patterns of the copolymers quenched from their liquid-crystalline states.

positional order in the polymer again rules out the possibility of nematic classification.²³ This confirms the SmA mesophase nature of **P(P(6)CN-alt-MeP)** and suggests that the mesogens are packed in a monolayer structure. Similarly, **P(P(6)CN-alt-Cz)** displays a sharp reflection at the low angle of $2\theta = 2.15^{\circ}$ corresponds to a layer spacing of 40.04 Å, which is longer than the molecular length (28.40 Å). Because the *d/l* ratio is ~1.40, the bilayer structure is thus an SmA_d type, in which the cyanoterphenyl mesogen is interdigitated in an antiparallel fashion. The mesogens of the copolymers are packing so well that the high-order secondary reflection at a middle angle ($2\theta = 5.45^{\circ}$ and $2\theta = 5.87^{\circ}$, respectively) was readily detected by the diffractometer.²⁴

Photophysical Properties

Figure 5 shows UV spectra of the polymers **P(P(6)CN-alt-MeP)** and **P(P(6)CN-alt-Cz)** in DMF solution. **P(P(6)CN-alt-Cz)** shows a band at 306 nm and a shoulder at 368 nm, which are assigned to π - π * transition of the terphenyl mesogenic core of the side chain and π - π * transition of the conjugated main chain, respectively. The low absorption of the main chain may be due to the carbazole ring twisting the backbone, which results in a weak conjugation of the main chain. When the carbazolylene is replaced by the *para*-linkage phenylene with methyl substitution units, from the UV spectrum of **P(P(6)CN-alt-MeP)**, we can see that the intensity of the absorption band of the main chain is dramatically enhanced, which means that increase of *para*-linkage phenylene with methyl substitution seems to improve the effective conjugate chain length.

A polymer with both LC and light-emitting properties may find unique technological applications. As P(P(6)CN-alt-MeP) and P(P(6)CN-alt-Cz) are PPPs derivatives bearing chromophoric pendant groups and have different photoactive materials such as phenylene and carbazolylene in the main chain, it is of interest to check the effects of the structural variables on their luminescence behaviors.²⁵ Fluorescence spectra of the copolymers in DMF solutions are depicted in Figure 6. The copolymers solution (0.05 mM) is excited at the two wavelengths of 320 nm (corresponding to the absorption of the conjugated side chains) and 375 nm (corresponding to the absorption of the polymer main chain), respectively. When the copolymers are excited at 320 nm, polymer **P(P(6)CN-alt-MeP)** displays an emission λ_{max} at 425 nm, even well extending to 600 nm, whereas the copolymer shows an emission λ_{\max} at 470 nm with very low intensity when excited at 375 nm. In comparison, monomer

Copolymers	<i>T</i> (°C)	<i>d</i> ₁ (—)	d ₂ (—)	d ₃ (—)	Molecular Length (<i>I</i> , —) ^b	Ratio d ₁ /I	Phase
P(P(6)CN- <i>alt</i> -MeP)	200	30.86	16.06	4.41	28.40	1.09	SmA
P(P(6)CN- <i>alt</i> -Cz)	220	40.04	15.07	4.41	28.40	1.40	SmA_{d}

conformation.

TABLE 2 X-Ray Diffraction Analysis Data of P(P(6)CN-alt-MeP) and P(P(6)CN-alt-Cz)^a

^a The mesophases in the liquid-crystal states at the given temperatures were frozen by the rapid quenching with liquid nitrogen.

P(6)CN exhibits a PL maximum at 399 nm under the excitation at 320 nm. Obviously, the emitting center is both the mesogenic terphenyl pendant and the backbone, and the PL peak at the long wavelength should come from the main chain of the copolymer. The relative intensity of the two PL peaks emitted from conjugated side chain (399 nm) and main chain (470 nm) is quit different. The PL peak of polymer P(P(6)CN-alt-MeP) at 399 nm is much weaker than that of monomer P(6)CN, whereas its PL peak at 470 nm is much stronger than that excited at 375 nm. It suggests that the energy transfer from the terphenyl pendant to the backbone favors the stronger light emitting of backbone.14,16 Therefore, although the 320 nm excitation pumps its terphenyl chromophore to the excited state, the UV light emitted from the pendant is reabsorbed by the PPP main chain, hence the emission of its backbone.²⁴ The same energy transfer can be observed in the case of polymer P(P(6)CNalt-Cz). Different from P(P(6)CN-alt-MeP), the emission λ_{max} of **P(P(6)CN-alt-Cz)** is blue-shifted to 412 nm after the introduction of carbazole unit into the main chain. The blueshift of the absorption maxima may be ascribed to two reasons. One is that the backbone of the P(P(6)CN-alt-Cz) has the less coplanarity than PPP and induces the distortion of the backbone, due to the linkage manner via the 3,6-position for the carbazole.²⁶ Another reason is that the carbazole can act as electron-withdrawing group on the copolymer backbone, which decrease the electron density of the copolymer backbone and thus shift the absorption maximum.²⁷ Besides,



FIGURE 5 UV spectra of the polymers P(P(6)CN-*alt*-MeP) and P(P(6)CN-*alt*-Cz) (0.05 mM) in DMF solutions.

another interesting result is that, compared with P(P(6)CN-alt-MeP), the introduction of the carbazole obviously depresses the full width (from 85 to 68 nm) at half-maximum. It indicates that introducing the carbazole onto the backbone can get more pure blue light emitting. The quantum yields (Φ_F) of the copolymers are also evaluated, and Φ_F of P(P(6)CN-alt-MeP) and P(P(6)CN-alt-Cz) is 43 and 37%, respectively.

^b Calculated from mesogenic pendants in their fully extended



FIGURE 6 Fluorescence spectral of the monomer **P(6)CN** (λ_{ex} = 320 nm) and of (a) **P(P(6)CN-***alt***-MeP)** and (b) **P(P(6)CN-***alt***-Cz)** at two excitation wavelengths 320 and 375 nm in DMF (0.05 mM).



FIGURE 7 Concentration dependence of fluorescence spectra in DMF of (a) **P(P(6)CN-***alt*-**MeP**) and (b) **P(P(6)CN-***alt*-**Cz**). Excitation wavelength: 320 nm.

Most conjugated copolymers emit intensely in diluted solution become weak emitters when concentrated or fabricated into films,^{28,29} because of the strong interchain interaction. The polymer strands aggregate together to form less luminescent species such as excimers, leading to red-shifted emissions with low efficiencies. Thus, the effect of the concentration of the copolymers on the PL is investigated (Fig. 7). The fluorescence spectral shapes of all copolymers are observed in the similar spectral profiles, even increasing the concentration from 0.05 to 0.2 and 0.5 mM, indicating that the copolymers do not form interchain aggregates in solutions.³⁰ We further fabricated the copolymers into films. Casting films give rise to a broadening of band, as shown in Figure 7, spreading from 350 to 600 nm with an intense blue luminescence when excited at 320 nm. The film of **P(P(6)CN-alt-MeP)** has a decreased maximum band at 455 nm, which is red-shift by 25 nm from the case of DMF solution, and the red-shift of **P(P(6)CN-alt-Cz)** is also about 25 nm. This slight shift is due to an increase of the interchain interaction of the stacked main chain and is suggestive of small amount of excimer absorption and emission of the backbone.

Electrochemical Properties

CV in CH₃CN solutions of 0.1 M TBAPF₄ was used to evaluate the ionization potentials and the redox stability of the copolymers synthesized. Using a Pt wire as the counter electrode and a $Ag/AgNO_3$ (0.1 M) electrode as the reference electrode, which was calibrated using the ferrocene/ferrocenium redox couple.³¹ The oxidation and reduction potentials can be used as a surrogate for HOMO energy levels and LUMO energy levels, which were calculated using the internal standard ferrocene value of -4.8 eV with respect to the vacuum level. Hence, the HOMO and LUMO energy levels of the copolymers can be estimated using the equations of $E_{\rm HOMO} = -(E_{\rm ox} + 4.8)$ eV and $E_{\rm LUMO} = -(E_{\rm red} + 4.8)$ eV, respectively, where E_{ox} and E_{red} are the onset potentials for oxidation and reduction, respectively, ³² The band gap of the copolymers derives from the difference between the HOMO and the LUMO energy levels. Cyclic voltammograms of the copolymer thin films and the obtained electrochemical results are summarized in Table 3 (for details, see Supporting Information). The band gap of polymers P(P(6)CN-alt-Cz) and P(P(6)CN-alt-MeP) is 2.33 and 2.37, respectively, significantly lower than the band gap of PPP without substitution, 3.5 eV, in the undoped state.

CONCLUSIONS

In this work, we succeeded in polymerizing novel LC polyphenylene derivates containing terphenylene mesogenic pendants, based on phenylene and carbazolylene (**P(P(6)CN**-*alt*-**CZ**) or phenylene with methyl substitution **P(P(6)CN**-*alt*-**MeP)**, by using Suzuki coupling reaction. The copolymers possess high heat stabilities and exhibit enantiotropic smecticity mesogenic phase. Thanks for introducing the rigid aromatic rings onto the main chain, both of the copolymers show a much broader mesophase temperature range (\sim 80 °C) and higher transition temperature than homopolymer **PP(6)CN**. The copolymers are of strong electronic absorption and high PL and they can emit strong blue light.

TABLE 3 Electrochemical Properties and Calculated Energy Differences of the Alternating Conjugated Copolymers

Copolymers	$E_{ m onset/ox}^{a}$ (V)	${\sf E_{f/ox}}^{\sf b}$ (V)	$E_{\rm onset/red}^{a}$ (V)	E _{f/red} ^b (V)	HOMO (eV)	LUMO (eV)	Band Gap ^c (eV)
P(P(6)CN- <i>alt</i> -MeP)	0.65	0.77	-1.72	-1.51	-5.45	-3.08	2.37
P(P(6)CN- <i>alt</i> -Cz)	0.64	0.76	-1.69	-1.47	-5.44	-3.11	2.33

^a Onset voltage for oxidation versus SCE.

^b Formal oxidation potential.

 $^{\rm c}$ Cyclic voltammetric band gap derived from the difference between HOMO and LUMO energy level.

The energy transfer from the terphenyl pendant to the backbone favors the stronger light emitting of backbone. The carbazolylene lead the light emission band of the copolymer to be blue-shifted with more pure blue light emitting. The mixed aromatic rings onto the polyphenylene main chain exert great influence on the electrochemical properties of the copolymers. The band gaps of copolymers are much lower than the band gap of PPP without substitution.

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