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Novel Fluorescent Carbazolyl−Pyridinyl Alternating Copoloymers: Synthesis, Characterization, and Properties

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ABSTRACT: A novel series of AB-type polymers comprised of alternating carbazolyl and pyridinyl units were synthesized using palladium(0)-catalyzed Suzuki cross-coupling reaction in good to high yields. In this series of alternating copolymers, the electron-rich 2,7-(*N*-(2-ethylhexyl)carbazolyl) unit was used as a light-emitting unit, and the electron-deficient unit of pyridinyl was introduced to tune the wavelength of the emitting light and improve their electron transportation. These polymers were characterized by ^{1}H NMR and ^{13}C NMR, gel permeation chromatography (GPC), thermal analysis, UV−vis, fluorescence spectroscopy, and cyclic voltammetry (CV). The glass transition temperature of these polymers ranged from 120 to 150 °C, and the polymers showed high thermal stability with decomposition temperatures in the range 370−400 °C in nitrogen. The different linkage pattern of pyridinyl units in the copolymer backbone has a significant effect on the electronic and optical properties in solution and in film phases. For pure blue emission and prevention of aggregation of polymer chain, the meta-linkage pattern (3,5- and 2,6-linkage) of pyridinyl units in the polymer backbone is more favorable than the para-linkage pattern (2,5-linkage) of the pyridinyl units. The cyclic voltammetry (CV) results indicate that these polymers with pyridinyl units possess lower LUMO energy levels for an easy electron injection from a cathode than poly[3,6-(*N*-octyl)carbazolyl] and its derivatives do.[7a]

Introduction

Ever since the first report of the polymeric light-emitting diodes (PLED) device fabricated from poly(*p*-phenylenevinylene)(PPV) in 1990,[1] PLEDs have attracted significant research attention from both academic community and industry, particularly on account of their potential applications in large-area, flat-panel displays which can be operated at relatively low driving voltages.[1,2] For full-color display applications, the development of red, green, and blue emitting materials (either polymers or oligomers or small organic molecules) with high efficiency and stability is required.[3−5] Among the three primary colors, only red and green PLEDs have sufficient efficiencies and lifetimes to be of commercial value. The pursuit of efficient and stable blue PLEDs based on conjugated polymers remains a challenge. This arises because it is hard to achieve a balanced charge injection due to the large band gap between the LUMO and HOMO energy levels.[6]

Recently, increasing interest has been paid to carbazole-based polymers because of their optical properties and good hole-transporting ability in light-emitting devices.[7] Among the carbazole-derivatived polymers, poly(*N*-alkyl-2,7-carbazolyl)s (PCs) have emerged as a promising class of conjugated polymers, which can be utilized as the blue light-emitting active layers in PLEDs.[8] However, poly(*N*-alkyl-2,7-carbazolyl) exhibits additional emission bands in the long wavelength region of the spectrum (453, 492 nm) in solid states, possibly because of their tendency to form π-aggregates/excimers in the solid state.[8a]

Poly(2,5-pyridinediyl) (PPy) and its derivatives,[9] such as poly(pyridine vinylene) (PPyV),[9a,b] with electron-accepting nature is a family of promising conjugated polymers because of their high luminescence,[9f] excellent electron transporting behavior, and their general resistance to oxidation.[9d] The application of pyridinyl as the π-deficient moiety in this novel series of polymer is driven by the consideration that polypyridinyl (PPy) was used in blue-emitting devices[10,11] and that polymers based on pyridine have been demonstrated to be highly luminescent.[12] Therefore, the incorporation of a pyridinyl unit into polymer backbone increases the electron affinity of the polymers, which not only makes the copolymers to be n-dopable and capable of better electron transportation[13] but also makes the polymers more resistant to oxidation. These polymers with pyridine units are expected to possess low LUMO energy levels for an easy electron injection from a cathode. Therefore, these copolymers of a carbazolyl unit and pyridinyl units are expected to possess low HOMO and LUMO energy levels and will achieve a relatively balanced charge injection.

As an extension of our research work concerning polymeric blue light-emitting diodes,[14] in the present work, we first present the synthesis and characterization of a novel series of blue-emissive alternating copolymers of *N*-(2-ethylhexyl)carbazolyl unit with three different pyridinyl units using the Suzuki cross-coupling approach (Scheme 1). A 1:1 alternating copolymer design was adopted because such arrangement would generally give more consistent physical properties as compared to random copolymers.

Experimental Part

Materials. The reagents 2-ethylhexyl bromide, 4,4′-dinitro-2-azidobiphenyl, *n*-BuLi, tetrakis(triphenylphosphine)palladium(0) [$(PPh_3)_4Pd(0)$], 3,5-dibromopyridine, 2-isopropoxy-4,4,5,5-

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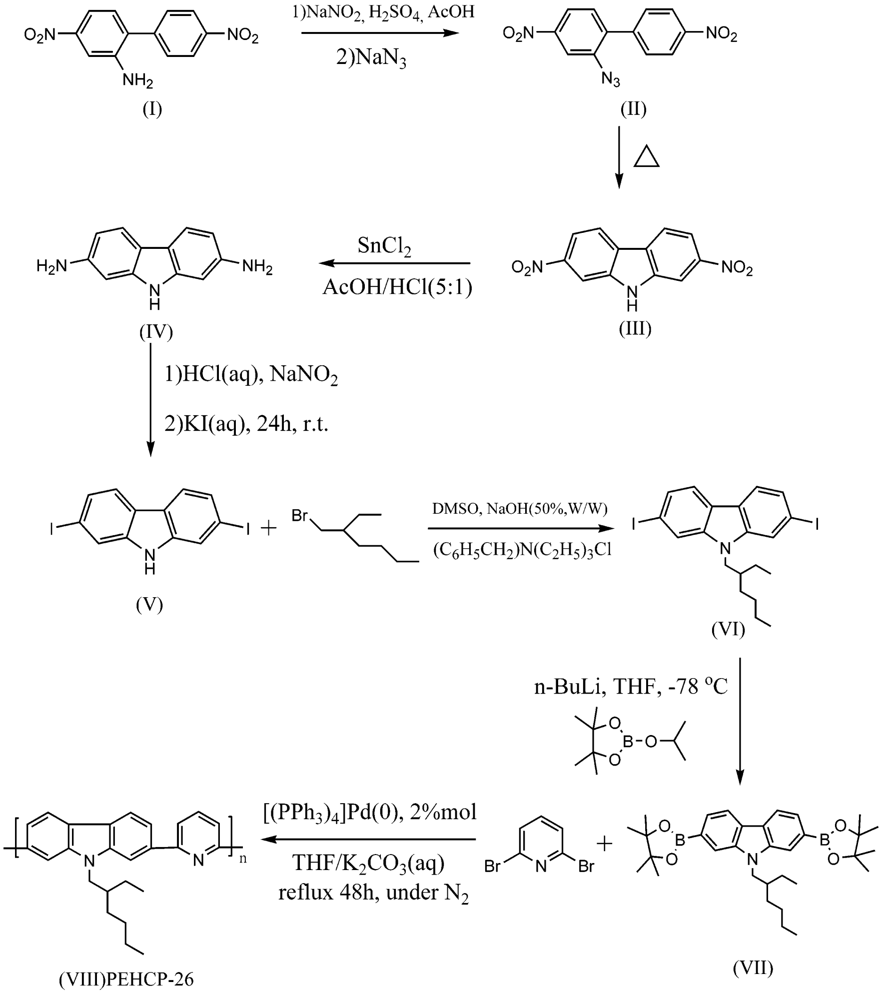
Scheme 1. Synthetic Approach to the Polymer PEHCP-26



tetramethyl-1,3,2-dioxaborolane, and tetrabutylammonium percholate (Bu_4NClO_4) (AR) were obtained from Aldrich; benzyltriethylammonium chloride, 2,5-dibromopyridine, and 2,6-dibromopyridine were obtained from Avocado Research Chemicals Ltd. NaOH (AR), $NaNO_2$ (AR), NaN_3, $SnCl_2$ (AR), KI (AR), DMSO (AR), toluene (AR), acetonitrile, and all other reagents were purchased from commercial sources and used without further purification. The solvents diethyl ether, chloroform, and THF were AR and were dried and distillated prior to use.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ACF 300 FT-NMR spectrometer operating at 300 MHz. Deuterated chloroform was used as the solvent, and tetramethylsilane (TMS) was used as the internal standard. Weight-average molecular mass (M_w) and number-average molecular mass (M_n) were determined by gel permeation chromatography (GPC) using a Perkin-Elmer mode 200 HPLC system equipped with Phenogel MXL and MXM columns using polystyrene as the standard and THF as the eluant. The thermal properties of the polymers were investigated by DSC and TGA under flowing nitrogen. Thermogravimetric analysis (TGA) was performed on a TA Instruments with a TGA 2960 thermogravimetric analyzer module at a heating rate of 20 °C min^{-1} with a nitrogen flow of 100 mL min^{-1}. The temperature regime was from room temperature to 800 °C. Differential scanning calorimetry (DSC) of the polymer powers was carried out using TA 2920 module at a heating rate of 20 °C min^{-1} with a nitrogen flow of 70 mL min^{-1}. Dilute polymer solution (1×10^{-5} M) was prepared in anhydrous spectrum-grade chloroform, and quinine sulfate (1×10^{-5} M in 0.1 M H_2SO_4) was used as the reference. The thin polymer films were deposited onto quartz glass plates by spin-coating. The absorption and fluorescence spectrum measurements of polymer solution and film were conducted on a Shimadzu UV-1601 PC UV−vis spectrophotometer and a Perkin-Elmer Instrument LS 55 luminescence spectrometer, respectively. Cyclic voltammetry of polymer films was conducted using a single-compartment, three-electrode cell comprising a platinum working electrode with the polymer spin-coated on it, a platinum counter electrode, and a reference electrode Ag/$AgNO_3$ using a HB-105 Hokuto Denko Ltd. arbitrary function generator and a HA-501 Hokuto Denko Ltd. potentiostat. 0.1 M tetrabutylammonium percholate in acetonitrile was used as the electrolyte solution.

Synthesis of Intermediate Compounds and Monomer. The intermediate compounds of 4,4′-dinitro-2-azidobiphenyl (**II**), 2,7-dinitrocarbazole (**III**), 2,7-diaminocarbazole (**IV**), 2,7-diiodocarbazole (**V**), *N*-(2-ethylhexyl)-2,7-diiodocarbazole (**VI**), and monomer 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(2-ethylhexyl)carbazole (**VII**) were synthesized following the procedure developed by Smith and Brown.[15] All these compounds have been characterized by NMR spectroscopy.

General Procedure for Polymerization by Suzuki Cross-Coupling Reaction. Representative procedure for polymerization by Suzuki cross-coupling reaction: 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(2-ethylhexyl)-carbazole (**VII**) (0.2 g, 0.36 mmol), 2,6-dibromopyridine (0.084 g, 0.36 mmol), and $(PPh_3)_4Pd(0)$ (8 mg, 0.007 mmol) (1 mol % based on total monomers) were dissolved in a mixture of THF and aqueous 2 M K_2CO_3(5 mL) (3/2 volume ratio) in a 25 mL three-necked round-bottomed flask. The solution was stirred under N_2 and was heated at 95 °C with vigorous stirring for 48 h. The resulting mixture was then poured into 100 mL of methanol. The precipitate was recovered by filtration and washed with 2 M dilute HCl and methanol. The solid product was extracted with acetone for 24 h in a Soxhlet apparatus to

Table 1. Properties of the Polymers

polymer	yield(%)	color	M_w[a] (kDa)	PDI	DP[b]	T_d[c]	T_g[d]
PEHCP-26	94	bellow-green	4.9	1.56	14	400	145
PEHCP-35	80	brown-yellow	4.3	1.35	12	392	128
PEHCP-25	47	yellow	1.4	1.22	4	372	122

[a] Weight-average molecular weights determined by GPC using polystyrene standards in THF. [b] Degree of polymerization. [c] Decomposition temperature, determined by TGA in nitrogen, based on 5% weight loss. [d] Determined by DSC in nitrogen at a scan rate of 20 °C/min.

remove oligomers and catalyst residues; 0.125 g of yellow-green poly[(2,7-(*N*-(2-ethylhexyl)carbazolyl)-*alt*-(2,6-pyridinyl)] (**VIII**) was obtained; yield 94%. This polymer was designated as PDEHCP-26, where the number 26 stands for the linkage pattern of pyridinyl unit in the polymer backbone. The other polymers were synthesized following a similar procedure.

Poly[(2,7-(*N*-(2-ethylhexyl)carbazolyl)-*alt*-(2,6-pyridinyl)] (PEHCP-26) (VIII). Yield 94%; yellow-green solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.86−8.32 (m, 9H, proton of pyridinyl unit and carbazolyl unit), 4.42 (m, 2H), 2.28 (m, 1H), 0.83−1.50 (m, 14H).

Poly[(2,7-(*N*-(2-ethylhexyl)carbazolyl)-*alt*-(3,5-pyridinyl)] (PEHCP-35). Yield 80%; brown-yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.0 (s,1H), 8.28 (dd, 2H), 7.57−7.70 (m, 6H), 4.33 (m, 2H), 2.20 (m, 1H), 0.82−1.46 (m, 14H).

Poly[(2,7-(*N*-(2-ethylhexyl)carbazolyl)-*alt*-(2,5-pyridinyl)] (PEHCP-25) Yield 47%; yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.57−9.12 (m, 9H, proton of pyridinyl unit and carbazolyl unit), 4.34 (m, 2H), 2.21 (m, 1H), 0.90−1.44 (m, 14H).

Result and Discussion

Synthesis. The synthetic route for monomer **VII** and this series of alternating copolymers is outlined in Scheme 1. The compound *N*-(2-ethylhexyl)-2,7-diiodocarbazole (**VI**) was prepared from 4,4′-dinitro-2-azidobiphenyl (**I**) with a total yield of 18% in five steps according to refs 8a and 15. The monomer compound **VII** was synthesized with a yield of 42.4% using *N*-(2-ethylhexyl)-2,7-diiodocarbazole (**VI**) as the starting material following a similar procedure reported in the literature.[14f,g,16] The polymerization is based on the Suzuki cross-coupling reaction. Poly[(2,7-(*N*-(2-ethylhexyl)carbazolyl)-*alt*-(2,5-pyridinyl)] (PEHCP-25) (**VIII**) was obtained in a moderate yield of 47%; poly[(2,7-(*N*-(2-ethylhexyl)carbazolyl)-*alt*-(3,5-pyridinyl)] (PEHCP-35) and poly[(2,7-(*N*-(2-ethylhexyl)carbazolyl)-*alt*-(2,6-pyridinyl)] (PEHCP-26) were obtained in high yields of 80 and 94%, respectively. All three polymers were easily soluble in chloroform and THF. The polymerization results are summarized in Table 1.

All the polymers were characterized by ^{1}H NMR and GPC. From the ^{1}H NMR spectrum and hydrogen assignment analysis (the latter mentioned above), the singals of carbazolyl, 2-ethylhexyl, and pyridinyl can be clearly seen. For example, PEHCP-25: δ (ppm) 7.57−9.12 (m, 9H, proton of pyridinyl unit and carbazolyl unit), 4.34 (m, 2H), 2.21 (m, 1H), 0.90−1.44 (m, 14H). The intergration indicates that the ratio of carbazolyl unit and pyridinyl unit in the polymer backbone is 1:1; therefore, ^{1}H NMR confirmed the proposed structures of polymer. The molecular weights of polymers were determined by GPC using THF as the eluent and polystyrene as the standard. The results of GPC are also shown in Table 1. PEHCP-26 and PEHCP-35 were found to be polymers with relatively low weight-average molecular weight (M_w) of ca. 4900 and 4300, corresponding to a polymerization degree of approximately 14 and 12, and a polydispersity index of 1.56 and 1.35, respectively. PEHCP-25 was actually an oligomer with a polymerization degree of 4; its M_n (1.1 kDa) is lower than that (5 kDa) of one very similar derivative, poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-4-heptyl-2,5-pyridine) (PCPy).[8b] The main reason for the relatively lower molecular weight of this series of carbazloyl−pyridinyl-based alterning copolymers might due to the lower activity of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(2-ethylhexyl)carbazole (**VII**) in Suzuki coupling in comparison with other monomer system, such as 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene.[14f] For example, M_w (66.3 kDa) of poly[2,7-(9,9-dihexylfluorenyl)-*alt*-(2,5-pyridinyl)] (PDHFP-25) with a DP of 162[14f] is much higher than that (1.4 kDa) of PEHCP-25 (**VIII**) with a DP of 4. The partial reason for the low value of DP of might be the unstable reaction condition (e.g., concentration) for Suzuki coupling because of the evaporation loss of solvent under nitrogen.

The thermal stabilities of polymers were evaluated by thermogravimetric analyses (TGA) in nitrogen, and the results are also summarized in Table 1. It is apparent that all the polymers exhibited excellent thermal stability with an onset of decomposition in the range 370−400 °C. Thermally induced phase transition behavior of the polymers was investigated with differential scanning calorimetry (DSC) under a nitrogen atmosphere. The glass transition temperatures (T_g) of polymers are also summarized in Table 1. T_g of the polymers was in the range 120−150 °C. T_g (122 °C) of PEHCP-25 is much higher than that (66 °C) of its very similar derivative, poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-4-heptyl-2,5-pyridine) (PCPy).[8b] The reason for large difference between T_g of PEHCP-25 and PCPy was mainly due to incorporation of long side chain heptyl into pyridinyl units leading to an obvious decrease of T_g of PCPy. T_g (122 °C) of PEHCP-25 oligomer is very close to that (128 °C) of PEHCP-35; the reason for this is due to the balance contribution of relatively low M_w of PEHCO-25 (low M_w, leading to increase of T_g) and more free movement of PEHCP-25 main chain (the less steric hindrance with *p*-pyridinyl linkage, leading to decrease of T_g). The relatively high glass transition temperature of fluorescent polymer is essential for its potential application, such as in PLEDs as emissive materials.[17] In all, the PEHCP series of polymers have excellent thermal stability and high T_g.

Optical Property. The UV−vis absorption and fluorescence emission spectra of the polymer solution in $CHCl_3$ and the polymers films, which were spin-cast from $CHCl_3$ solutions, were recorded at room temperature. The optical data are summarized in Table 2.

The UV−vis absorption and photoluminescence (PL) spectra of the PDEHCP series of polymers solutions are depicted in Figure 1. It is evident that the linkage pattern of the pyridinyl moiety in the polymer backbone has a major influence on the absorption maximum of polymer. The absorption maximum of PEHCP-25 with para-linkage of pyridinyl unit at 365 nm is blue-shifted in comparison with that of homopolymers poly(*N*-octyl-2,7-carbazole),[8a] poly(*N*-(2-ethylhexyl)-2,7-carbazole)

Table 2. Spectra Properties and Quantum Yield

	solution[a]			film[b]		
polymer	$\lambda_{max}{}^{c}$ (nm)	$\lambda_{pl}{}^{c}$ (nm)	Φ^{d}	$\lambda_{max}{}^{c}$ (nm)	$\lambda_{pl}{}^{c}$ (nm)	optical band gap (eV)
PEHCP-26	355	411, 428	0.395	361	436	2.97
PEHCP-35	337	403 (418)	0.458	344	431	3.02
PEHCP-25	365	420 (438)	0.376	376	463 (488)	2.77

[a] 1×10^{-5} M in anhydrous chloroform. [b] Spin-coating on quartz glass from anhydrous chloroform solution. [c] Wavelength of maximum absorbance or emission, wavelength of the shoulder peak is in parentheses. [d] Relative to 1×10^{-5} M quinine sulfate in 0.1 M H_2SO_4.

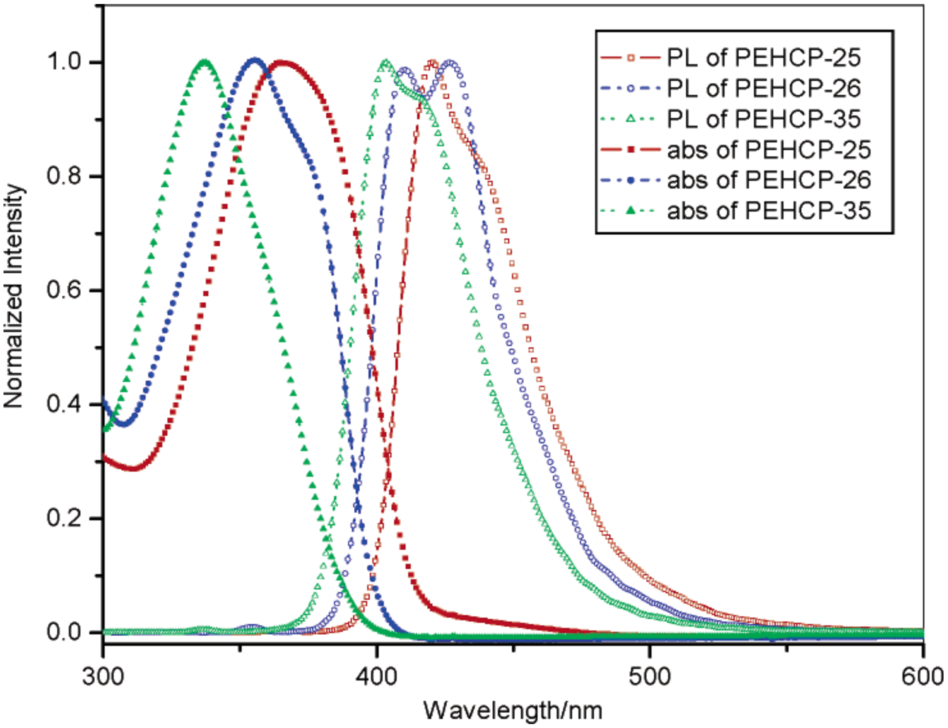


Figure 1. UV−vis absorption (abs) and photoluminescence (PL) spectra of PEHCP series polymers in $CHCl_3$ solution.

(PEHC),[8b] and poly(pyridine-2,5-diyl) (PPy),[13] being at 380, 380, and 373 nm, respectively, but slightly red-shifted in comparison with that of its very similar derivative, poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-4-heptyl-2,5-pyridine) (PCPy)[8b] at 354 nm because of the effect of incorporation of incorporation of long side chain heptyl into pyridinyl units. The absorption maximum of PEHCP-26 and PEHCP-35 with the para-linkage of the pyridinyl unit, being at 355 and 337 nm, respectively, is much blue-shifted in comparison with that of poly(*N*-octyl-2,7-carbazole),[8a] poly(*N*-(2-ethylhexyl)-2,7-carbazole) (PEHC),[8b] and poly(pyridine-2,5-diyl) (absorption maxima of poly(pyridine-2,6-diyl) and poly(pyridine-3,5-diyl) were unavailable). The difference among the absorption maximum of the PEHCP series of copolymers is attributed to the lesser extent of π-electron delocalization in the polymer backbone arising from meta-linkages, causing a reduction in the π-conjugation lengths. The effect of different linkage position of pyridinyl units on the absorption maximum of polymer in this series of polymers is similar to that one in our previous report.[14a,f,g]

The photoluminescence (PL) spectra, which were attributed to fluorescence on account of the short lifetime of the excited state,[18] were obtained by irradiative excitation at the wavelength of the absorption maximum. The blue emission maximum of PEHCP-25 with para-linkage of pyridinyl unit in the polymer backbone at 420 nm is almost equivalent with that of poly(*N*-octyl-2,7-carbazole)[8a] and poly(*N*-(2-ethylhexyl)-2,7-carbazole) (PEHC)[8b] at 417 and 420 nm, respectively, but also slightly red-shifted in comparison with that of PCPy)[8b] at 407 nm because of the same reason interpreted above, for PEHCP-26 and PEHCP-35, while the emission maximum of copolymers with the meta-linkage of the pyridinyl unit in the polymer backbone at 411 and 428 nm and 403 and 418 nm, respectively, is slightly violet-shifted as compared to that of poly(*N*-octyl-2,7-carbazole)[8a] and poly(*N*-(2-ethylhexyl)-2,7-carbazole) (PEHC).[8b]

The photoluminescence quantum yields in chloroform solution were measured according to the method described by Davey et al.[19] relative to 10^{-5} M quinine sulfate in 0.1 M H_2SO_4. The results are summarized in Table 2. High quantum yields of all the polymers are obtained, being in the range 35−50%.

Figure 2 shows the UV−vis absorption and photoluminescence (PL) spectra of the PEHCP series of polymers in thin films. As compared to absorption maxima of poly(*N*-octyl-2,7-carbazole)[8a] and poly(*N*-(2-ethylhexyl)-2,7-carbazole) (PEHC)[8b] at 382 and 383 nm, respectively, this series of pyridinyl-containing copolymers show blue-shifted absorption maxima in the range 344−476 nm. The absorption maximum of PEHCP-25 at 376 nm is also slightly red-shifted in comparison with that of poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-4-heptyl-2,5-pyridine) (PCPy)[8b] at 362 nm, which is as the same as in the solution discussed above. For PEHCP-25, in which the pyridinyl unit is para-linked in the polymer main chain, its absorption maximum in film at 376 nm

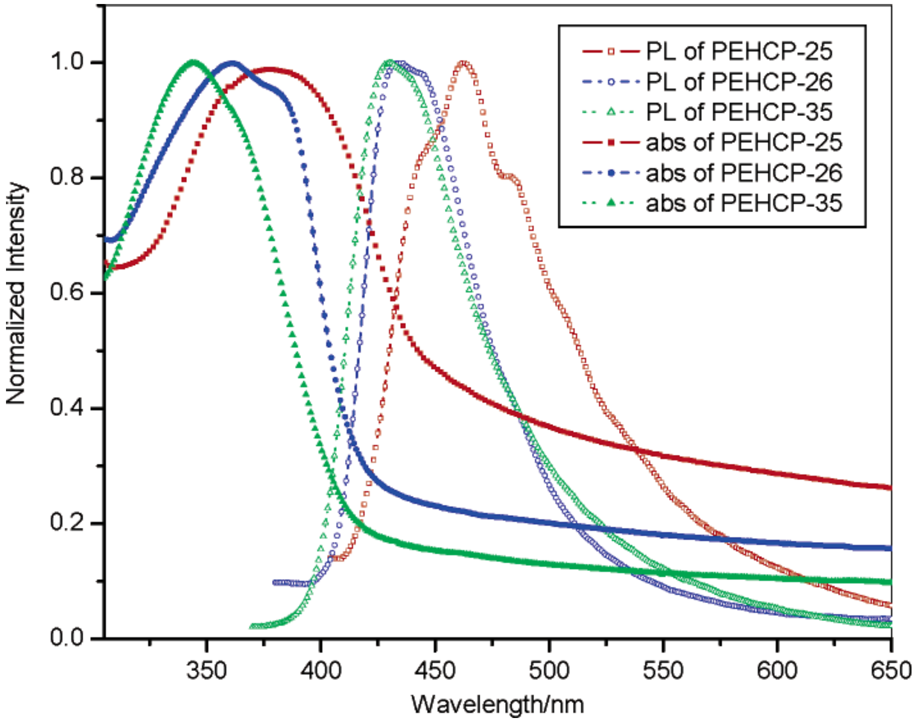


Figure 2. UV−vis absorption (abs) and photoluminescence (PL) spectra of PEHCP series polymers in thin films.

is red-shifted in comparison with the absorption maxima (at 361 and 344 nm, respectively) of PEHCP-26 and PEHCP-35 with meta-linkages of the pyridinyl units. This is attributed to the lower extent of π-electron delocalization of the polymer main chain arising from meta-linkages of the pyridinyl moiety, resulting in a reduction in the π-conjugation length.

In the film state, the blue emission peaks appear at 436, 431, and 463 nm (488 nm, shoulder peak) for PEHCP-26, PEHCP-35, and PEHCP-25, respectively. The PL emission of polymer in the solid state is red-shifted in comparison with that of polymer in solution, as PL emission was obtained by irradiative excitation at longer wavelength of the absorption maximum in the solid sate. From photoluminescence (PL) spectra of PEHCP-35 and PEHCP-26 (Figure 2), it can be seen that the two polymers can emit purer blue light without tailing phenomena and an additional red-shifted peak in the long wavelength region of the spectrum as compared with poly(*N*-octyl-2,7-carbazole),[8a] poly(*N*-octyl-3,6-carbazole),[7a] and PEHCP-25. The tailing phenomena and additional red-shifted peak in the long wavelength region of the spectrum often exist in carbazole-based conjugated polymers, such as peaks at 453 and 492 nm for poly(*N*-octyl-2,7-carbazole),[8a] a peak at 500−520 nm for poly(*N*-octyl-3,6-carbazole),[7a] and a peak at 488 nm for PEHCP-25. Therefore, PEHCP-35 and PEHCP-26 can emit purer blue light without any evidence of π-aggregates/excimers in the solid state as compared to the PL of poly(*N*-octyl-2,7-carbazole)[8a] and poly(*N*-octyl-3,6-carbazole).[7a] The emission of PEHCP-25 at 463 nm is obviously red-shifted in comparison with that of poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-4-heptyl-2,5-pyridine) (PCPy)[8b] at 430 nm; the reason may be due to the effect of long side chain heptyl into pyridinyl units. The results of PL in film states also show that optical properties of carbazole polymers can be well tuned by properly rational design of polymer architectures, such as the incorporation of different pyridinyl moieties into a polymer backbone.

Electrochemical Property. The electrochemical behavior of the polymers was investigated by cyclic voltammetry (CV). CV was performed in a solution of Bu_4NClO_4(0.10 M) in acetonitrile at a scan rate of 50 mV/s at room temperature under the protection of nitrogen. A platinum electrode coated with a thin polymer film was used as the working electrode. A Pt wire was used as the counter electrode, and an Ag/$AgNO_3$(0.01 M) electrode was used as the reference electrode. The resulting cyclic voltammograms are outlined in Figure 3.

The onset potentials for oxidation were observed to be 2.09, 2.01, and 1.86 V for PEHCP-26, PEHCP-35, and PEHCP-25, respectively. On the other hand, the onset potentials for reduction were −0.72, −0.55, and −1.26, respectively. From the onset potentials of the oxidation and reduction processes, the band gaps of the polymers were estimated to be 2.81, 2.56, and 3.12 eV for PEHCP-26, PEHCP-35, and PEHCP-25, respectively. According to the equations[20,21] $\mathrm{IP} = -([E_{\mathrm{onset}}]^{\mathrm{ox}} + 4.4)$ eV and $\mathrm{EA} = -([E_{\mathrm{onset}}]^{\mathrm{red}} + 4.4)$ eV, where $[E_{\mathrm{onset}}]^{\mathrm{ox}}$ and $[E_{\mathrm{onset}}]^{\mathrm{red}}$ are the onset potentials for the oxidation and reduction of the polymers, the HOMO and LUMO of the polymers were estimated to be −6.49, −6.41, and −6.26 eV and −3.68, −3.85, and −3.14 eV for PEHCP-26, PEHCP-35, and PEHCP-25, respectively. The corresponding electrochemical data of the polymers are summarized in Table 3. The HOMO (−6.26 to −6.49) and LUMO (−3.14 to −3.85) of this series of polymers are much lower than those of polymers derived from carbozole and benzothiadiazole; the HOMO and LUMO of the latter were in the range of −5.25 to −5.40 and −2.00 to −3.12, respectively.[7a]

From Table 3, we can see that these polymers with pyridinyl units possess very low LUMO energy levels for an easy electron injection from a cathode, which is consistent with our expectation. We can also find that the HOMO and LUMO energy levels of PEHCP-26 and PEHCP-35 are quite similar. As for PEHCP-25, its HOMO is close to those of the other two polymers while

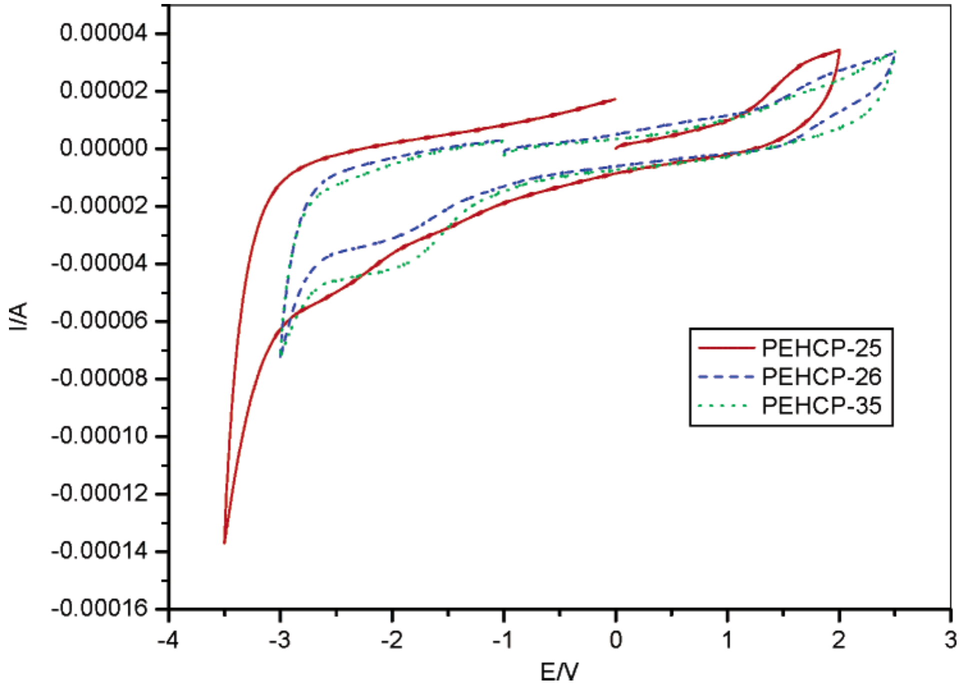


Figure 3. Cyclic voltammograms of PEHCP series polymer films coated on platinum plate electrodes in acetonitrile containing 0.1 M Bu_4NClO_4.

Table 3. Electrochemical Properties of the Polymers

			energy levels (eV)		
polymer	E_{onset}(V) (p-doping)	E_{onset}(V) (n-doping)	HOMO	LUMO	band gap
PEHCP-26	2.09	−0.72	−6.49	−3.68	2.81
PEHCP-35	2.01	−0.55	−6.41	−3.85	2.56
PEHCP-25	1.86	−1.26	−6.26	−3.14	3.12

its LUMO is much higher. Therefore, the different linkage position of pyridinyl units in the copolymer backbone will affect the energy levels of the polymers.

Conclusion

In summary, a novel series of well-defined carbazolyl−pyridinyl-based alternating copolymers have been synthesized by the Suzuki cross-coupling reaction in good to high yields. These polymers have relatively low molecular weight and have good solubility in common solvents, such as chloroform and THF. All the polymers show good thermal stability and have high T_g. The different linkage position of the pyridinyl unit in the polymer backbone has significant effects on the electronic and optical properties of polymers in solution and in film phases. The meta-linkage (3,5- and 2,6-linkage) of pyridinyl units in the polymer backbone is more favorable to polymer for pure blue emission and prevention of aggregation of polymer chain than the para-linkage (2,5-linkage) of the pyridinyl units. These polymers with pyridinyl units possess very low LUMO energy levels for an easy electron injection from a cathode. It also shows that the electronic and optical properties of fluorescent polymers can be well tuned by properly rationalized design of polymer architectures such as the incorporation of different pyridinyl moieties into the polycarbazole backbone.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.

(2) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.

(3) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.

(4) Segura, J. L. *Acta Polym.* **1998**, *49*, 319.

(5) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. A.; Santos, D.; Bre'das, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121.

(6) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34,* 5854.

(7) (a) Huang, J.; Niu, Y.; Yang, W.; Mo, Y.; Yuan, M.; Cao, Y. *Macromolecules* **2002**, *35*, 6080. (b) Lee, J. H.; Park, J. W.; Ko, J. M.; Chang, Y. H. *Polym. Bull. (Berlin)* **1993**, *31*, 339. (c) Justin Thomas, K. R.; Lin Jiann, T. *J. Am. Chem. Soc.* **2001**, *123*, 9404. (d) Lee, J. H.; Park, J. W.; Choi, S. K. *Synth. Met.* **1997**, *88*, 31. (e) Meng, H.; Chen, Z. K. *J. Phys. Chem. B* **1999**, *103*, 6429. (f) Chao, C. S.; Whang, W. T. *Macromol. Chem. Phys.* **2001**, *202*, 2864.

(8) (a) Morin, J.-F.; Leclerc, M. *Macromolecules* **2001**, *34,* 4680. (b) Morin, J.-F.; Leclerc, M. *Macromolecules* **2002**, *35*, 8413.

(9) (a) Dailey, S.; Halim, M.; Rebourt, E.; Horsburgh, L. E.; Samuel, I. D. W.; Monkman, A. P. *J. Phys.: Condens. Matter* **1998**, *10*, 5171. (b) Gebler, D. D.; Zhang, Y. Z.; Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Gustafston, T. L.; Wang, H. L.; Swager, T. M.; Macdiarmid, A. G.; Epstein, A. J. *J. Appl. Phys.* **1995**, *78*, 4264. (c) Feller, A. P.; Monkman, *Synth. Met.* **2001**, *116*, 149−152. (d) Yamamoto, T.; Maruyama, T.; Zhuo, Z.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc*. **1994**, *116*, 4832. (e) Yamamoto, T.; Zhuo, Z.; Kanbara, T.; Shimura, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B.-L.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem.* Soc. **1996**, *118*, 10389. (f) Horsburgh, L. E.; Monkman, A. P.; Samuel, I. D. W. *Synth. Met.* **1999**, *101*, 113.

(10) Yamamoto, T.; Suganuma, H.; Saitoh, Y.; Maruyama, T.; Inoue, T. *Jpn. J. Appl. Phys.* **1996**, *35*, L1142.

(11) Kanbara, T.; Kushida, T.; Saito, N.; Kuwajima, I.; Kubota, K.; Yamamoto, T. *Chem. Lett.* **1999**, 583.

(12) Wang, Y. Z.; Gebler, D. D.; Fu, D. K.; Swager, T. M.; Macdiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1997**, *85*, 1179.

(13) (a) Marsella, M. J.; Fu, D. K.; Swager, T. M. *Adv. Mater.* **1995**, *7*, 145. (b) Kim, J. K.; Yu, J. W.; Hong, J. M.; Cho, H. N.; Kim, D. Y.; Kim, C. Y. *J. Mater. Chem.* **1999**, *9*, 2171.

(14) (a) Ng, S. C.; Lu, H. F.; Chan, H. S. O.; Fujii, A.; Yoshino, K. *Adv. Mater.* **2000**, *12*, 1122. (b) Fujii, A.; Ootake, R.; Fujisawa, T.; Ozaki, M.; Ohmori, Y.; Laga, T.; Yoshino, K.; Lu, H. F.; Chan, H. S. O.; Ng, S. C. *Appl. Phys. Lett.* **2000**, *77*, 660. (c) Ng, S. C.; Lu, H. F.; Chan, H. S. O.; Fujii, A.; Tong, L. G.; Yoshino, K. *Macromoleclues* **2001**, *34*, 6895. (d) Ootake, R.; Fujisawa, T.; Sonoda, T.; Fujii, A.; Laga, T.; Lu, H. F.; Chan, H. S. O.; Ng, S. C.; Yoshino, K. *Synth. Met.* **2001**, *119*, 593. (e) Lu, H. F.; Chan, H. S. O.; Ng, S. C. *Macromolecules* **2003**, *36*, 1543. (f) Liu, S.; Ng, S. C.; Chan, H. S. O. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4792−4801. (g) Liu, S.; Ng, S. C.; Chan, H. S. O. *Synth. Met.* **2005**, *149*, 1.

(15) Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, *73*, 2438.

(16) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686.

(17) Tokito, S.; Tanaka, H.; Noda, K.; Okada, A.; Taga, Y. *Appl. Phys. Lett.* **1997**, *70*, 1929.

(18) Swager, T. M.; Gil, C. G.; Wrightton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886.

(19) Davey, A. P.; Elliott, S.; O'Connor, O.; Blau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433.

(20) de Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, *87*, 53.

(21) Cervini, R.; Li, X. C.; Spencer, G. W. C.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Synth. Met.* **1997**, *84*, 359.

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