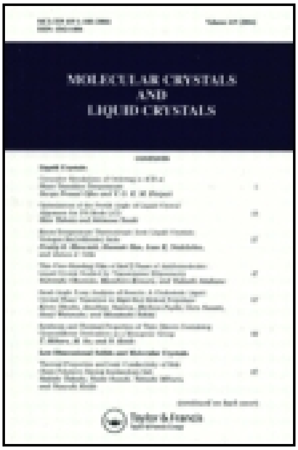

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Synthesis and Optical Properties of Copolymers Containing Carbazole and 1,3,4-Oxadiazole Groups as Blue Host Matrix and Charge Transport Materials for Polymer Light Emitting Devices

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Synthesis and Optical Properties of Copolymers Containing Carbazole and 1,3,4-Oxadiazole Groups as Blue Host Matrix and Charge Transport Materials for Polymer Light Emitting Devices

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Alternating copolymers with N-*arylcarbazole as hole injection and transport moieties with blue emission and 1,3,4-oxadiazole as electron transporting and hole blocking moieties were synthesized by Pd-catalyzed polycondensation reaction, and named as poly[*N-*(4-aminophenyl)-carbazole*-alt-N-*(2-ethylhexyl)-3,6-carbazole] (***P1***), poly [*N-*(4-aminophenyl)-carbazole*-alt-*2,5*-bis*(4-phenyl)-1,3,4-oxadiazole] (***P2***) and poly [*N-*(4-aminophenyl)-carbazole*-alt-*2,5*-bis*(4-methylenephenyl)-1,3,4-oxadiazole] (***P3***). It was observed that UV-Vis absorption spectra showed two main peaks at 290 ∼ 295 and 310 ∼ 380 nm and maximum photoluminescence peaks of the polymers were all in the range of blue light emission from 418 to 453 nm. It appeared that optical and electrochemical properties of polymers such as HOMO, LUMO levels and band gap energy could be fine tuned by chemical modification of polymer structures.*

Keywords: 1,3,4-oxadiazole; blue emission; charge transport; *N*-arylcarbazole; palladium-catalyzed polycondensation

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INTRODUCTION

Polymer light emitting diodes (PLEDs), based on conjugated polymers or polymers with conjugated segments with different chemical structures, emitting different colors across entire visible spectrum have been widely investigated [1]. In the field of research and industry, there is still a great demand to expand blue light emitting polymers for full color displays, because they can act as both active layer and host materials in PLEDs. However, stable blue PLEDs with balanced charge injection from two diodes have been still a challenge, because of wide band gap between highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO) energy levels [2]. Many blue PLEDs reported in literature have mainly used poly(1,4-phenylene)s [3], derivatives of poly(1,4-phenylenevinylene) [4], poly(thiophene)s [5], and especially carbazole- and fluorene-containing polymers [6].

Recently, increasing interest has been paid to carbazole-based polymers because electron donating carbazole groups are known as blue emission and hole transporting groups [7]. It was reported [8] that polycarbazole had a wide band gap of 3.2 eV, and an entirely new class of polycarbazole-based main chain copolymers with varieties of aromatic rings and heterocycles as a comonomer were synthesized by Suzuki coupling reaction. Leclerc's research group first reported a series of homopolymers and copolymers derived from *N*-alkyl-2,7-carbazoles [9]. Wong *et al.* prepared 9,9-dihehexylfluorene/9-aryl-carbazole hybrid copolymers. They pointed out that incorporating the electron-rich *N*-arylcarbazole hole-transporting groups into polyfluorene main chain could increase the HOMO levels as well as retain their blue emission. They also noted that advantage of the robust *N*-aryl groups increased the thermal stability and glass transition temperature of the resulting polymers, relative to *N*-alkyl-substituted congeners [10]. Some reports showed that soluble poly(1,4-phenylene-1,3,4-oxadiazole) were useful as a new type of blue electroluminescent materials [3(c), (d)]. Another prominent electron transporting property of oxadiazole-containing polymers has also been paid much attention [11].

In this study, we present new series of thermally stable alternating copolymers with well-defined chemical structure. The purpose of this study was to synthesize the alternating copolymers containing electron-rich *N*-arylycarbazole with either carbazole or 1,3,4-oxadiazole group. Structural effect of the polymers on the optical and electrochemical properties was also presented.

EXPERIMENTAL

Materials

2-Ethylhexylbromide (97%), 3,6-dibromocarbazole (97%), *p*-toluic hydrazide (99%), *p*-toluoly chloride (99%), phosphorus oxychloride (99%), polyphosphoric acid, copper (I) iodide (98%), trans-1,2-cyclohexane-diamine (99%), tin (II) chloride (98%), sodium *tert*-butoxide (97%), tris(dibenzylideneacetone)dipalladium(0) (Pd2(dba)$_3$), and tri-*tert*-butylphosphine (P(*t*-Bu)$_3$, 90%) were purchased from Aldrich Chemical Co. Reagent grades of carbazole, 4-bromobenzoylhydrazine, 4-bromobenzoylchloride, 4-iodonitrobenzene, potassium carbonate anhydrous and potassium phosphate were obtained from Tokyo Kasei Co. and used as received. Solvents were reagent grades and purified prior to use.

Synthesis

N-*(4-aminophenyl)-carbazole (1)*

In the first step, a mixture of 4-iodonitrobenzene (20 mmole), carbazole (15.24 mmol) and K_3PO_4 (42 mmol) were added to 100 ml of 1,4-dioxane at room temperature. After stirring for 30 min., CuI (0.4 mmol) and trans-1,2-cyclohexanediamine (2.4 mmol) were added to the mixture. The reaction mixture was refluxed for 24 h. After cooling down to room temperature, the resulting mixture was filtered. 1, 4-Dioxane was evaporated and ethyl acetate was added. The mixture was washed with distilled water and dried with MgSO4. *N*-(4-Nitrophenyl)-carbazole intermediate was obtained through column chromatography (hexane: ethylacetate = 9:1) with 98% of yield. ^{1}H-NMR (300 MHz in $CDCl_3$): δ 8.58 (1H, Ar–***H***), 8.55 (1H, Ar–***H***), 8.26 (1H, Ar–***H***), 8.23 (1H, Ar–***H***), 8.01(1H, Ar–***H***), 7.98 (1H, Ar–***H***), 7.60(1H, Ar–***H***), 7.58 (1H, Ar–***H***), 7.51 ~ 7.45 (2H, Ar–***H***), 7.39 ~ 7.33 (2H, Ar–***H***); ^{13}C-NMR (300 MHz in $CDCl_3$): δ 144.35, 140.70, 131.85, 127.94, 127.34, 126.36, 124.82, 121.91, 121.33, 110.65; GC-MS : $m/z = 288$ (m+).

In the second step, a mixture of *N*-(4-Nitrophenyl)-carbazole (5 mmol), SnC_{12} (30.4 mmol) and EtOH (15 ml) was heated at 70°C for 4 h. After the mixture was cooled to room temperature, 1 M NaOH solution was added until the mixture became basic. After extraction with ethyl acetate, the combined organic layers was washed with brine, dried with $MgSO_4$ and evaporated. The residue was recrystallized from ethanol and the final compound (***1***) was obtained with 98% yield. ^{1}H-NMR (300 MHz in $CDCl_3$): δ 8.15 (1H, Ar–***H***), 8.12 (1H, Ar–***H***), 7.42 ~ 7.22 (8H, Ar–***H***) 6.87 (1H, Ar–***H***), 7.84 (1H, Ar–***H***), 3.81

(2H, Ar$-$N$\boldsymbol{H}_2$); ^{13}C-NMR (300 MHz in $CDCl_3$): δ 145.89, 141.45, 128.48, 125.70, 122.92, 120.16, 119.39, 115.89, 109.75; GC-MS : $m/z = 258$ (m+).

2,5-(4-Bromophenyl)-1,3,4-oxadiazole (3)

In the first step, 4-bromobenzoyl chloride (0.1 mol) was added dropwise to a solution of 4-bromobenzoyl hydrazide (0.1 mol), triethylamine (0.1 mol) and DMF (150 ml) at room temperature. The resulting mixture was stirred for 2 h and then filtered. The solid collected was washed with water and methanol to give 2,5-bis(4-bromophenyl)-dihydrazide with 98% yield. ^{1}H-NMR (300 MHz in $CDCl_3$): δ 10.66 (2H, $-$NHN$\boldsymbol{H}-$), 7.87(2H, Ar$-\boldsymbol{H}$), 7.84(2H, Ar$-\boldsymbol{H}$), 7.77(2H, Ar$-\boldsymbol{H}$), 7.74(2H, Ar$-\boldsymbol{H}$); ^{13}C-NMR (300 MHz in $CDCl_3$): δ 164.96, 131.69, 131.60, 129.58, 125.79.

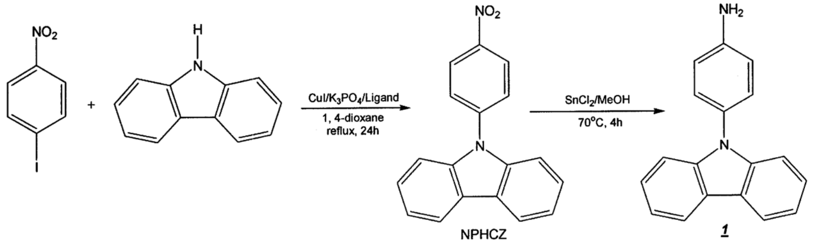
In the second step, a mixture of 2,5-*bis*(4-bromophenyl)-dihydrazide (5 mmol) and polyphosphoric acid (0.2 mol) was heated for the cyclization at 200°C for 2 h. After completion of reaction, the mixture was precipitated into 75 ml of deionized water. The precipitate was recrystallized from ethanol, and dried to give the product (***3***) with 89% yield. ^{1}H-NMR (300 MHz in $CDCl_3$): δ 8.02 (2H, Ar$-\boldsymbol{H}$), 7.99 (2H, Ar$-\boldsymbol{H}$), 7.70 (2H, Ar$-\boldsymbol{H}$), 7.68(2H, Ar$-\boldsymbol{H}$); ^{13}C-NMR (300 MHz in $CDCl_3$): δ 164.05, 132.50, 128.34, 126.64, 122.59.

Polymerization

All the polymers were prepared using Pd-catalyzed polycondensation. A mixture of monomer ***1*** (1.30 mmol) and monomer ***2*** (monomer ***3*** or ***4***) (1.30 mmol) was dissolved in toluene/DMF solvent (15 ml). NaO-*t*-Bu (3.9 mmol), $Pd_2(dba)_3$ (0.033 mmol) and $P(t\text{-}Bu)_3$ (0.2 mmol) were added to the solution at room temperature. The reaction mixture was stirred at 100°C for 48 h. After cooling to room temperature, the mixture was quenched by adding aqueous ammonia (25 ml) and the product was extracted with $CHCl_3$. The organic fraction was concentrated and reprecipitated from $CHCl_3$/methonal several times. Then, the products were filtered and dried in vacuum.

Characterization

NMR spectra were recorded on a Varian Unity Plus 300 with solvent of $CDCl_3$. GC-Mass spectra were recorded on a QP 5050 mass spectrometer. Number and weight average molecular weights were measured by using Waters gel permeation chromatography (GPC) equipped with Styragel HR 5E column using THF as an eluent against polystyrene standards at room temperature. Thermal analysis was



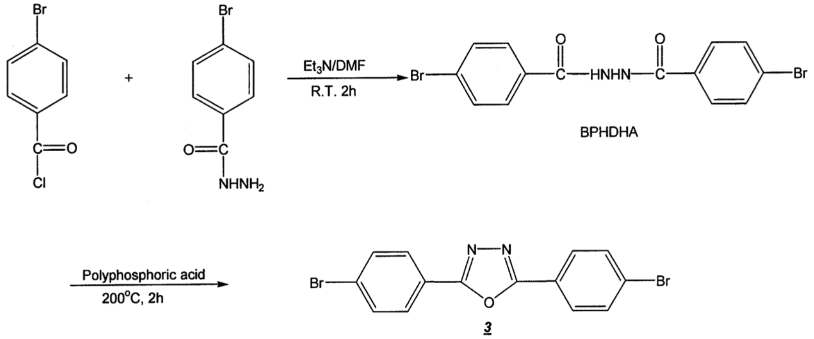
SCHEME 1 Synthetic route to monomer *1*.

performed on a Seiko EXSTAR 6000 TG/DTA 6300 at a heating of 20°C/min for thermogravimetric analyzer (TGA) and at a heating of 10°C/min for differential scanning calorimetry (DSC). UV-Visible absorption spectra were obtained by Shimadzu UV-2100. The photoluminescence (PL) spectra excited by He-Cd laser at 325 nm were monitored by Optical Multichannel Analyzer (Laser Photonics, OMA system). The ionization potential (IP) was measured by a photoelectron spectroscopy (Riken Keiki AC-2).

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers

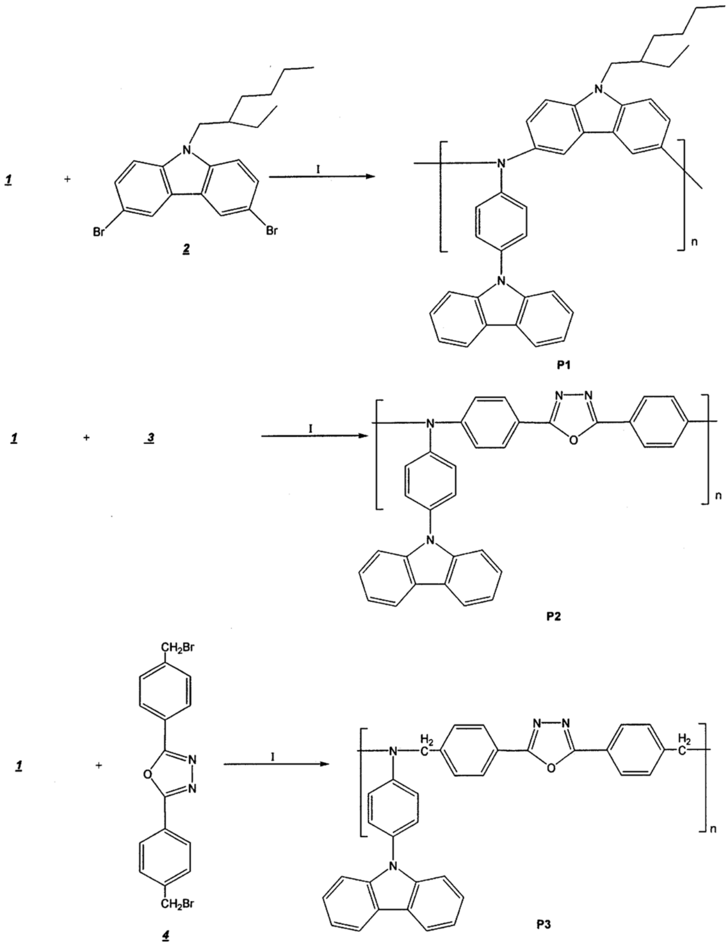
The synthetic procedures used to prepare the monomers *1* and *3* are outlined in Schemes 1 and 2, respectively. In Scheme 1, *N*-(4-nitrophenyl)-carbazole was first synthesized via Ullmann coupling of 4-iodonitrobenzene and carbazole with a high yield. The combination of air stable CuI and racemic trans-1,2-cyclohexanediamine in the presence of K_3PO_4 was employed as an efficient catalyst for the



SCHEME 2 Synthetic route to monomer *3*.

N-arylation of a number of heterocycles [12]. Then, the reduction of *N*-(4-nitrophenyl)-carbazole with a $SnCl_2$ catalyst in methanol gave the momoner ***1***. As can be seen in Scheme 2, the monomer ***3*** was prepared by oxadiazole ring cyclization reaction with polyphosphoric acid at 200°C. Two monomers *N*-(2-ethyhexyl)-3,6-dibromocarbazole (***2***) [13] and 2,5-*bis*(4-bromomethylenephenyl)-1,3,4-oxadiazole) (***4***) [11(a)] were synthesized according to the reference, respectively.

The synthesis of alternating copolymers such as poly[*N*-(4-aminophenyl)-carbazole-*alt*-*N*-(2-ethylhexyl)-3,6-carbazole] (**P1**), poly[*N*-(4-aminophenyl)-carbazole-*alt*-2,5-*bis*(4-phenyl)-1,3,4-oxadiazole] (**P2**)



SCHEME 3 Synthesis of conjugated copolymers.

TABLE 1 Physical Properties of Polymers

Polymers	Mn (g/mole)	PDI	T_g (°C)	$T_d{}^a$ (°C)
P1	5700	1.54	—	465
P2	2800	1.12	121	461
P3	2400	1.41	—	372

[a] Temperature resulting in 5 wt% loss of the initial weight.

and poly[*N*-(4-aminophenyl)-carbazole-*alt*-2,5-*bis*(4-methylenephenyl)-1,3,4-oxadiazole] (**P3**) is based on Pd-catalyzed polycondensation, as depicted in Scheme 3. All synthesized copolymers are designed to have a triarylamine and carbazole moieties (hole transporting ability with blue emission) as well as 1,3,4-oxadiazole group (electron transporting and hole blocking properties) in order to study how the chemical structure affects on optical and electrochemical properties of the polymers.

The molecular weights of the copolymers were measured by using GPC, and summarized in Table 1. During the polymerization, premature precipitation of the polymers were observed, which might be explained as the low solubility of the polymers in toluene or toluene/DMF mixture, resulting in relatively low molecular weights of the synthesized **P1**-**P3**. The thermal stability of the polymers measured by TGA was compared in Figure 1. Based on the decomposition temperature (T_d) at 5 wt% loss of the initial weight, **P1** and **P2** exhibited higher T_d around 460°C. **P3** exhibited lower T_d around 370°C, due to the C-N linkages in the main chain. However, these data revealed that

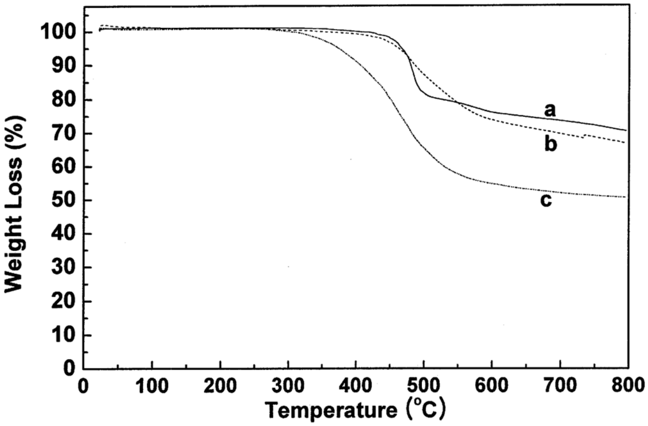


FIGURE 1 TGA curves of the polymers; (a) P1, (b) P2, and (c) P3.

the copolymers had excellent thermal stability under nitrogen atmosphere. While DSC curves of **P1**-**P3** showed neither crystallization nor melting peaks, only **P2** showed relatively high T_g at 121°C. No obvious glass transition temperatures of **P1** and **P3** were observed below 300°C.

Optical and Electrochemical Properties

UV-Vis absorption and PL emission spectral data for the polymers in THF solution are shown in Figures 2 and 3, respectively. In Figure 2, maximum UV absorption ($\lambda_{max,UV}$) of **P1** was observed at 292 nm with a small shoulder at 312 nm. However, **P2** showed $\lambda_{max,UV}$ at 292 nm with a new broad peak at 379 nm, attributed to the π-π^* electronic transitions of *N*-arylcarbazole and oxadiazole moieties [14]. This was also supported from the fact that absorption peaks of **P3** was mainly observed at 293 nm, however, greatly decreased at 343 nm, implying the interruption of the electronic transitions by the methylene groups between *N*-arylcarbazole and oxadiazole groups.

When exited at their UV-Vis absorption maximum peaks, the polymers exhibited blue emission in the range of 418 nm–453 nm. Compared with $\lambda_{max,PL}$ of **P1**, $\lambda_{max,PL}$ of **P2** were blue-shifted to shorter wavelength, possibly due to the presence of an electron withdrawing oxadiazole group in the polymer main chain. Moreover, $\lambda_{max,PL}$ of **P3** appeared at 418 nm, demonstrating 12 nm more blue shift than that of **P2**. This can be correlated with the fact that the interruption by

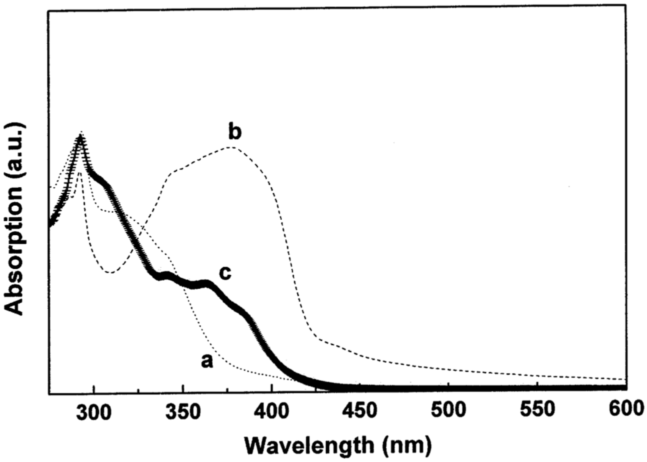


FIGURE 2 UV-Vis absorption spectra of the polymers; (a) P1, (b) P2 and (c) P3.

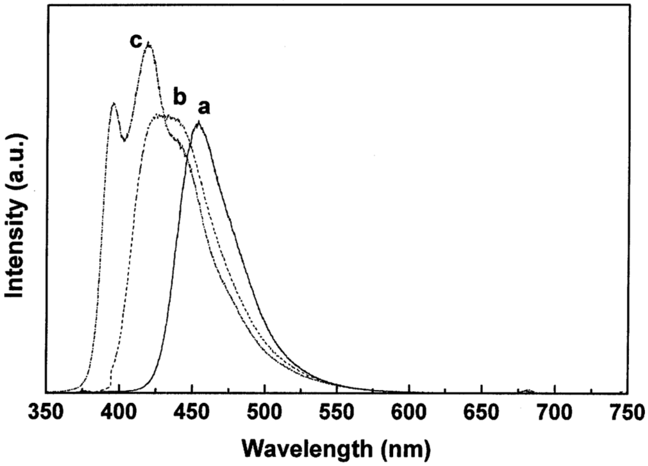


FIGURE 3 Photoluminescence spectra of the polymers; (a) P1, (b) P2 and (c) P3.

methylene groups in the polymer main chain decreases the conjugation length of **P3**.

The electrochemical properties of the polymers are listed in Table 2. The polymers showed HOMO energy levels of −5.01 eV for **P1**, −5.46 eV for **P2** and −5.54 eV for **P3**. LUMO energy levels of the polymers were also calculated to be −2.04 eV for **P1**, −2.45 eV for **P2** and −2.31 eV for **P3**. These data revealed that **P1** with two electron-donating carbazole units increased HOMO energy level as well as **P2** and **P3** with electron-withdrawing oxadiazole groups increased LUMO energy level in our polymers. This implied not only better hole injection ability of **P1** due to a closer match to the work function of ITO (work function = −4.8 eV), but also good electron transporting and hole blocking properties of **P2** and **P3**. The band gap energy of the polymers was

TABLE 2 Electrochemical Properties of Polymers

Polymers	$\lambda_{\max,\mathrm{UV}}$ (nm)	$\lambda_{\max,\mathrm{PL}}$ (nm)	Band gap (eV)[a]	HOMO (eV)[b]	LUMO (eV)[c]
P1	292, 312	453	2.97	−5.01	−2.04
P2	293, 379	430	3.01	−5.46	−2.45
P3	293, 342	418	3.23	−5.54	−2.31

[a] Calculated from the crosspoint of UV-Vis absorption and PL emission spectra.
[b] Measured by a RIKENKeiki AC-2.
[c] Estimated from the HOMO and band gap.

estimated from the wavelength at the junction of UV-Vis aborption and PL spectra. It appeared that band gap energy of **P3** was larger than those of **P1** and **P2**. This might be originated from short conjugation length of **P3** by introducing methylene groups in polymer chain.

CONCLUSIONS

This study reports the synthesis and characterization of *N*-arylcarbazole-based alternating copolymers that exhibit blue emissions in PL spectra. The polymers exhibit good thermal stability and stable optical properties. Moreover, possibility of tuning of charge transport properties and band gap energy levels apparently indicate that *N*-arylcarbazole-based polymers are promising materials as hole transporting and blue emitting layers or as host matrix materials for phosphorescent dopants in light-emitting devices.

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