Syntheses of light emitting poly(N-aryl-2,7-carbazole)s

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Abstract. Recent remarkable development of poly(2,7-carbazole)s and copolymers including a carbazolyl unit have demonstrated that they are one of key conjugated polymer materials for optoelectronic applications. This short review reports recent progress made in synthesis and characterization of poly(N-aryl-2,7-carbazole)s for application of light emitting diode. Main strategy and remaining challenges in the development of reliable emitting materials for devices of organic light emitting diodes are discussed.

1. Introduction

For many years, pyrrole-based materials have been investigated for the purpose of their electrical and optoelectronic applications, but there were few researches on light emissive applications except polycarbazoles. However, poly(3,6-carbazole)s have not been drawn much attention as emissive materials for organic light emitting diode (OLED), because they did not have excellent properties, \textit{i.e.}, low processability to make uniform thin films due to not so-high average molecular weights, low fluorescence quantum efficiency, and wide emission spectra in the blue light region. Initially, several polyindoles were synthesized and investigated to develop novel pyrrole-based blue emitting materials for availability of monomers and easy modification at N-position [1]. They were superior to poly(3,6-carbazole)s in terms of fluorescence (PL) quantum efficiency, color purity of blue PL in the solid state, and processability for thin films. However, OLED devices using poly(1-dodecyl-2,6-indolylene-1,4-phenylene) and poly(1-(4-dodecyloxyphenyl)-3-methyl-2,6-indolylene) as an emitting layer material only showed weak bluish emissions less than 100 cd/m\textsuperscript{2} with broad emission spectra ($\lambda_{\text{max}} = 470$~$480$ nm), when they energized at about 20 V. Around the same time, Morin and Leclerc have successfully synthesized poly(N-alkyl-2,7-carbazole)s [2], which were certainly not only a potential candidate for blue light emitting materials for OLED but also capable materials for other semiconducting applications such as organic solar cells [3].

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{structures.png}
\caption{Structures of pyrrole-based conjugated polymers.}
\end{figure}
2. Poly(N-aryl-2,7-carbazole)s

2.1. Synthesis

Several poly(N-aryl-2,7-carbazole)s, whose N-substituent is an aryl group instead of alkyl, have been synthesized by our group [4-9] and others [10-12] according to Scheme 1. N-Arylation of 2,7-dichlorocarbazole (X= Cl) [2] with halogenobenzene derivatives (Ar-Y) was carried out by CuI-trans-1,2-cyclohexanediamine catalyzed method [13]. In the case of arylation of 2,7-dibromocarbazole (X= Br) [14] using this method, reaction conditions to suppress formation of by-products such as carbazolylcarbazoles must be chosen. Reactions of 9H-carbazoles with fluoronitrobenzene (Y= F) under basic conditions are a good selective method for introducing an aniline moiety at N-position [7, 10, 15]. Usually poly(N-aryl-2,7-carbazole)s can be obtained by Yamamoto dehalogenative condensations of 2,7-dihalogenocarbazoles using a zerovalent Ni complex or by Suzuki coupling reaction of 2,7-dihalogenocarbazole with 2,7-diboronated carbazole using a Pd catalyst. Chemical and photophysical properties of typical polymers, P1, P2, and P3, synthesized from corresponding dihalogenomonomers (1, 2 and 3) by the Yamamoto method, are discussed in the following sections.

Scheme 1. Reaction pathway for synthesis of monomers and polymers.

2.2. General properties

Poly(N-aryl-2,7-carbazole)s having alkyl chains such as 2-ethylhexyloxy group (EHO) at N-aryl moiety shown in Scheme 1 were sufficiently soluble in organic solvents such as THF and CHCl3. GPC analysis showed number average molecular weights of these polymers were more than 5 kDa and generally around 10~30 kDa. They also showed a good thermal stability with a high glass transition temperature (Tg > 150°C), a high softening temperature (Ts > 210°C), and high degradation temperatures above Td = 350°C, at which temperature 5% of mass is reduced from the starting material in the thermal gravimetric analysis. They absorbed light around 380—390 nm (λmax) and fluoresced around 410—420 nm (λmax) in CHCl3 with high quantum efficiency about 0.8 in CHCl3.

2.3. OLED characteristics

A typical sample is poly(N-(2-ethylhexyloxy-4-phenyl)-2,7-carbazole) P1 [4, 5], which showed the photoabsorption λmax = 381 nm in film state, PL emission λmax = 432 nm in film state, almost quantitative PL quantum yield in CHCl3, wide band gap (Eg) between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) about 2.90 eV, and an energy level of HOMO about -5.45 eV (Figure 2). The deeper energy level of HOMO and higher quantum efficiency of P1 than corresponding N-alkyl substituted ones are advantageous to be applied poly(N-aryl-2,7-carbazole)s in OLED. These energy levels and Eg can be tuned by changing the N-aryl group of the polymers [7]; i.e., the HOMO level of P2 having an electron donating triphenylamino group at m-position was shallower (~5.27 eV) than that of P1, while that of P3 having an alkoxy group at m-position was deeper (~5.62 eV).
The OLED device having a configuration of ITO/poly(3,4-ethylenedioxythiophene doped)-poly(styrenesulfonic acid) (PEDOT-PSS) (100 nm)/Polymer P1 (100 nm)/Ca+Al (300 nm) showed blue emission started from a low turn on voltage (3 V), a maximum luminance ($L_{\text{max}}$) (about 1500 cd/m²), and a current efficiency $\eta_c$ higher than 0.1 cd/A at 10 V [4]. Other polymers (P2 and P3) having similar configuration of the device; ITO (150 nm)/PEDOT:PSS (60 nm)/polymer/Ba (5 nm)/Al (80 nm), showed EL spectra similar to PL with brightness over 1000 cd/m² at 10 V, which suggested that poly(N-aryl-2,7-carbazole)s were a potential material for blue OLED [8].

![Chemical structure and energy diagram of poly(N-(2-ethylhexyloxy-4-phenyl)-2,7-carbazole) 1 with reference data of work functions of typical materials.](image)

Figure 2. Chemical structure and energy diagram of poly(N-(2-ethylhexyloxy-4-phenyl)-2,7-carbazole) 1 with reference data of work functions of typical materials.

Figure 3 summarizes OLED characteristics of a device, ITO (150 nm)/PEDOT-PSS (90 nm)/P1 (70 nm)/CsF (2 nm)/Al (120 nm) [5]. It began to emit at 4 V, and brightness seemed to increase monotonically as increasing applied voltages to reach a $L_{\text{max}}$ of 34600 cd/m² at 10 V with a high current efficiency ($\eta_c$) (1.5 cd/A), and after that, luminance sharply decreased above 11 V but current continued to flow as shown in Figure 3a. These results suggest that the device damages during operations. A turning point can be recognized at 7 V as shown in Figure 3b in the changes of power and current efficiencies ($\eta_p$, $\eta_c$) and international commission on illumination (CIE) chromaticity coordinates ($x$, $y$) vs. operating voltages. The emitting color of the device was changed from blue (0.18, 0.15) at 7 V to blue green (0.22, 0.32) at 9 V before and after the turning point, then it changed green (0.24, 0.42) above 10 V in the last result. These color changes corresponding to spectra change of electroluminescence (EL) are summarized in Figure 4. The EL spectra under operating voltages below 7 V were similar to the PL spectrum, but EL spectra observed above 9 V were substantially different. This implies that different exciton might be predominantly formed under higher voltages than the turning voltage. In addition, each blue EL emission spectrum and luminance vs. operating voltages between 4-7 V were reversible and reproducible for several scans, but applying voltages over 9 V annihilated the reversibility within a few scans.

The low turn on voltages (about 4 V) but the low current efficiency observed in this device suggests that the energy barrier between the electrodes, interlayer, and the polymer emitting layer might not be serious but balanced exciton formation which could be controlled by carriers’ injection and transport must be inappropriate. In general, unbalanced operations affect stability of electroluminescence (EL) color and luminance of the OLED devices.
Figure 3. Current density and luminance (a) and efficiencies and CIE chromaticity coordinates (b) vs. operating voltages in the OLED device using P1 as the emitting layer material.

Figure 4. Electroluminescence spectra of the OLED device using P1 as emitter at various operating voltages and the reference PL spectrum in film state.
2.4 Modifications of poly(2,7-carbazole)s for OLED.
Stability of emission color during operation of OLED devices is intimately related to whether an exciton dominantly generated by balanced carriers' injection and transport. Since polycarbazoles are good hole injecting and transport materials, the higher operating voltages are applied in the device, the more holes are accumulated in the emitting layer. The supersaturated state of holes in the polymer must cause irreversible reactions at reactive 3,6-CH of carbazole [16] to form another π-extended low energy states or formation of electroplexes [17]. In order to suppress these unfavorable emissions, three attempts have been done by i) introduction of a buffering group for hole injection/transport, ii) copolymerization with electron accepting unit for carriers’ balance injection/transport, and iii) protection of 3,5-positions of poly(2,7-carbazole)s to stabilize them against electrooxidation.

Figure 5. Chemical structures of typical functionalized poly(N-aryl-2,7-carbazole)s.

2.4.1. Buffering effect. Since polymers with triphenylamine units have been known as useful materials for hole injection and transport [18], triphenylamine moieties in poly(N-aryl-2,7-carbazole)s could function to buffer holes, which might suppress color change due to unfavorable oxidation of the conjugated main chain during device operations. P2 having a triphenylamine moiety at the N-position (Figure 5) was also good blue emitting polymer, which showed absorption $\lambda_{\text{max}} = 391$ nm in CHCl$_3$, absorption $\lambda_{\text{max}} = 397$ nm in film state ($E_g = 2.9$ eV), PL $\lambda_{\text{max}} = 418$ nm in CHCl$_3$ ($\phi_{\text{PL}} = 0.32$) PL $\lambda_{\text{max}} = 450$ nm in the thin film state, and the HOMO level $= -5.27$ eV. Comparing the performance between P2 and P3 in the OLED device consisting of ITO/PEDOT:PSS/polymer/Ba/Al, color purity of blue and other performances for the P2-device (EL $\lambda_{\text{max}} = 450$ nm, $L = 1250$ cd/m$^2$, CIE($x = 0.16$, $y = 0.17$) at 10 V, $\eta = 0.52$ cd/A) were superior to those for the P3-device (EL $\lambda_{\text{max}} = 484$ nm, $L = 1090$ cd/m$^2$, CIE($x = 0.20$, $y = 0.24$) at 10 V, $\eta = 0.18$ cd/A) [8]. A different OLED (ITO/PEDOT:PSS/polymer/CsF/Al) device embedded a polymer similar to P2 showed similar performances; EL $\lambda_{\text{max}} = 426$ nm, CIE ($x = 0.18$, $y = 0.14$), and 710 cd/m$^2$ at 9 V ($\eta = 0.20$ cd/A) [9]. This polymer also showed a turning point at 9 V as well as P1, but color change was moderate from purplish blue (0.18, 0.12) at 6 V to blue green (0.21, 3.0) at 15 V via blue (0.19, 0.20) at 10 V ($L_{\text{max}} = 1170$ cd/m$^2$). These results suggest that the triphenylamine structure at N-position of poly(N-aryl-2,7-carbazole)s is effective to realize and sustain blue emission under driving voltages lower than 10 V.

2.4.2. Copolymerization effect. If electron injection ability of the polycarbazoles is improved by lowering the level of LUMO, the EL luminance and efficiency will increase and the EL color change could be suppressed. Copolymerization of the carbazolyl unit with other ones might be a good strategy to change the HOMO and LUMO energy levels, which should attain balanced carriers' injection/transport in poly(N-aryl-2,7-carbazole) based polymers. It has been already attempted that N-alkylcarbazole-2,7-diyl and fluorene-2,7-diyl based copolycondensates were synthesized to decrease barrier height for hole injection for the purpose of heightening the OLED performances of polyfluorenes [19,20]. From another perspective, a random copolycondensate, P4 (Figure 5), was
prepared by the Ni-mediated polycondensation of 2,7-dibromo-N-(octyloxyphenyl)carbazole and 2,7-dibromo-9,9-diiodofluorene in molar ratio of 1:1 [6] to lower the LUMO energy level of polycarbazole. The copolycondensate P4 absorbed light energy at about $\lambda_{\text{max}} = 390$ nm in CHCl$_3$ and 400 nm in thin film state ($E_g = 2.9$ eV), and fluoresced at about $\lambda_{\text{max}} = 417$ nm in CHCl$_3$ ($\phi_{\text{FL}} = 0.90$) and 430 nm in the thin film state, which were almost same to those of P1. The energy level of HOMO and LUMO situated lower than those of P1 and higher than those of poly(octyloxyfluorene). The OLED device having the configuration of ITO/PEDOT:PSS/P4/CsF/Al showed bluish EL (CIE: $x=0.21, y=0.22$) at operating voltages lower than 7 V, and notably higher performance, $L_{\text{max}}$ of 31200 cd/m$^2$ at 11.0 V. The current efficiencies (e.g., $\eta = 1.34$ cd/A [at 4 V]) observed under operating voltages lower than 7 V were higher than those of the other devices using polycarbazole reported so far. The color purity of blue emissions observed under operating voltages lower than 7 V was inferior to that of P1, but gradual color change from light blue (around the turn on voltage) to bluish green ($x=0.23, y=0.37$ at 12 V) during the operation was observed, which was comparable to polyfluorene. From these results, it is concluded that stability of the copolymer P4 in the device is situated between P1 and polyfluorene, but current efficiency of the P4-device is superior to the devices embedded homopolymers under operating voltages below the turning point (7 V), which is considered to be due to improved balance of carriers’ injection and transport.

2.4.3. Protection effect. Since presence of reactive C-H at 3,6-positions of carbazole is also considered as one of the factors of the color change during device operations, various 3,6-substituted poly(2,7-carbazole)s were designed, synthesized, and characterized in order to enhance EL efficiency and stability of the emission color. Poly(3,6-dimethyl-9-alkyl-9H-carbazole-2,7-diyl) and related alternating copolymer have been synthesized and characterized [21]. The 3,6-dimethyl substituted homopolymer showed an $E_g$ about 3.2 eV, HOMO level $= -5.5$ eV, fluorescence $\lambda_{\text{max}} = 397$ nm in the film state, and rather low $\phi_{\text{FL}} = 0.16$ in CH$_2$Cl$_2$. These results suggest that steric hindrance of the 3,6-dimethyl substituents reduces $\pi$-conjugation along the main chain of poly(2,7-carbazole). Similarly, poly(3,6-difluoro-9-(4-(butyloctyloxy)phenyl)-9H-carbazole-2,7-diyl) showed blue fluorescence ($\lambda_{\text{max}} = 436$ nm) in the film state, $\phi_{\text{FL}} = 0.27$ in solution, $E_g = 3.07$ eV, and a deeper HOMO level $= -5.83$ eV [11], which showed better photophysical properties than the methyl derivative to examine OLED behavior. Thus, P5 shown in Figure 5 was used as a typical example to examine the effect of 3,6-substituents in poly(2,7-carbazole)s. P5 showed blue fluorescence ($\lambda_{\text{max}} = 431$ nm) in the film state, $\phi_{\text{FL}} = 0.31$ in CHCl$_3$, $E_g = 3.08$ eV, and HOMO level $= -5.77$ eV [22], which were almost same to the above data of poly(3,6-difluoro-N-arylcabazole) [11]. The OLED device having the configuration of ITO/PEDOT:PSS/P5/CsF/Al showed blue EL at operating voltages lower than 10 V (CIE: $x=0.17, y=0.09$), $\eta_{\text{max}} = 0.33$ cd/A [at 5.5 V], and $L_{\text{max}}$ of 490 cd/m$^2$ at 8.0 V. The luminance was not so high but an ideal deep blue color near the primary blue of the national television system committee (NTSC) in 1953 was attained. The deep blue emission was stable under operating voltages below 10 V, and the color change from blue to greenish blue gradually occurred over 10 V. The good color purity and stability is ascribed to the 3,6-difluoro protection, whose steric and electronic effects enhance the chemical stability, slightly widen the $E_g$, deepen the HOMO level, and suppress $\pi$-stacking.

3. Conclusions

Several poly(N-ary-2,7-carbazole)s were synthesized, characterized, and evaluated as a blue emitting material for OLED. Basically, poly(N-ary-2,7-carbazole)s were good emitting materials for blue photoluminescence in solution and films with good quantum efficiency. The HOMO level of the polymers could be controlled from $-5.3$ eV to $-5.8$ eV by modification of the N-aryl moiety. Several OLED devices emitting blue light could be made by using the poly(N-ary-2,7-carbazole)s as the emitting layer material. A problem was the irreversible change of the emitting color from blue to green during operation under applied voltages higher than a turning point. It is assumed that carriers’ injections from electrodes, transportsations, and recombination to form an exciton are in counterpoise
under operating voltages below the turning point, while undesired oxidations of the polymer or emissions from other excitons such as electroplex under supersaturated state of holes occur above the turning voltage. In order to increase EL efficiency and suppress the unfavorable emissions, balanced carriers’ injection and transport in the OLED were attempted by i) introduction of a buffering group for hole injection and transport, ii) copolymerization with electron accepting unit to stabilize against oxidation and to control balance of carriers’ injection and transport, and iii) protection of 3,5-positions of poly(2,7-carbazole)s to prevent from unfavorable electrooxidations. Figure 6 indicates CIE coordinates of typical blue light emitting poly(N-aryl-2,7-carbazole) based OLED devices, and Table 1 summarizes CIE \((x, y)\) results of these investigations.

Poly(N-(2-ethylhexyloxy-4-phenyl)-2,7-carbazole) \(P_1\), a standard polymer, emitted blue \((0.18, 0.15)\) below 7 V, but the change of color to green \(e.g., (0.24, 0.42)\) at 10 V was not a little under the higher voltages. Another standard polymer, \(P_3\), which have two 2-ethylhexyloxy substituents at \(m, p\) - positions of the \(N\)-phenyl also behaved as well as \(P_1\). \(P_2\) having a triphenylamine moiety at \(N\)-position kept to emit pure blue \((0.16, 0.17)\) by 10 V compared to the color of \(P_3\) \((0.20, 0.24)\) at 10 V. This result suggests that the triphenylamine moiety in \(P_2\) could function to buffer holes to suppress unfavorable oxidations. The copolymerization was also an effective manner to stabilize the emission color and heighten the EL efficiency. Practically, the initial emitting color of light blue \((0.21, 0.22)\) for \(P_4\) was kept under operating voltages below 7 V, furthermore, the efficiencies \(\eta_c\) were higher than those of respective homopolymers under these conditions. Nevertheless, the blue color gradually changed to bluish green \((0.23, 0.37)\) at 12 V and at last green \((0.27, 0.48)\) at 14 V. The protection of...
3,6-positions with fluorine was effective to keep color purity of deep blue emission (0.17, 0.09) by 8 V. The color change according to varying applied voltages from 0 to 15 V was within range of blue, that is, the purplish blue color gradually changed to greenish blue (0.19, 0.17) at 12 V. However, the luminance ($L_{\text{max}}=490 \text{ cd/m}^2$) and efficiency ($\eta_{\text{c, max}}=0.33$) were relatively low, which suggests that carriers’ injection and transport are unbalanced in the OLED device.

In conclusion, it is believed that further modifications with proper molecular design could develop the more stable and highly efficient blue light emitting poly(N-ary-2,7-carbazole)s for OLED.

Table 1. Summary of results on characteristics of blue light emitting and color change of poly(N-ary-2,7-carbazole)-based OLED devices.

| Polymer | Device$^a$ | CIE (x, y) | Emitting color | Reference |
|---------|------------|------------|----------------|-----------|
| P1      | A          | (0.19, 0.16) | blue (purplish) | 4         |
|         | B          | (0.18, 0.15) | blue           | 6         |
|         | B          | (0.24, 0.42) | light green    | 6         |
| P2      | B          | (0.18, 0.14) | blue (purplish)| 9         |
|         | B          | (0.19, 0.20) | blue           | 9         |
|         | C          | (0.16, 0.17) | blue           | 8         |
| P3      | B          | (0.17, 0.14) | blue           | 9         |
|         | B          | (0.22, 0.36) | light green (bluish) | 9         |
| P4      | B          | (0.21, 0.22) | pale blue (greenish) | 8         |
|         | B          | (0.23, 0.37) | light green (bluish) | 6         |
| P5      | B          | (0.17, 0.09) | deep blue (purplish) | 22         |

$^a$Configuration of OLED devices: ITO/PEDOT:PSS/polymer/cathode (A= Ca/Al , B= CsF/Al, C= Ba/Al).

$^b$Maximum luminance.

$^c$The CIE values were pointed in Figure 6.

Acknowledgement
The author thank Mr. T. Shinnai, Mr. K. Tsuchiya, Kanto Chemical Co. Inc. for device fabrication and evaluation of OLED, Prof. H. Goto, University of Tsukuba, for the measurement of GPC, and Chemical Analysis Division, Research Facility Center for Science and Technology, University of Tsukuba, for facilities of the NMR, elemental analysis, DSC, UV−vis, and PL measurements.

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