



# Synthesis of pure blue emissive poly(2,7-carbazole)s anchored by electron donor pendant

Takashi Inada,<sup>1</sup> Toshinobu Shinnai,<sup>2</sup> Masashi Kijima<sup>3</sup>

<sup>1</sup>Institute of Materials Science, Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

<sup>2</sup>Central Research Laboratory Technology and Development Division, Kanto Chemical Co., Inc., 1-7-1 Inari, Soka-City, Saitama 340-0003, Japan

<sup>3</sup>Department of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan

Correspondence to: M. Kijima (E-mail: kijima@ims.tsukuba.ac.jp)

Received 26 July 2019; Revised 25 September 2019; accepted 26 September 2019

DOI: 10.1002/pola.29523

**ABSTRACT:** Three novel poly(2,7-carbazole)s having hole injection and transporting pendant moieties of carbazole and triphenylamine at the *N*-position were synthesized for achieving pure blue electroluminescence. The *N*-pendants in the polymers correspond to *N*-phenylcarbazol-2-yl (**P1**), *N,N*-diphenylamino-*N*-phenylcarbazol-2-yl (**P2**), and 4-phenyl having a hydrocarbon chain with a triphenylamine terminal (**P3**), respectively. Electronic, optical, and electroluminescence properties of these polymers were compared with those of a poly(2,7-carbazole) directly connected with triphenylamine at the *N*-position (**P0**) having an aggregation-induced emissive property. The photoluminescence (PL) spectra suggested that they could emit in the region of blue light in the film state. Especially, **P2** that has the fixed and large diphenylaminocarbazolyl

pendant showed a deep-blue fluorescence with CIE(*x*, *y*) = (0.15, 0.07). The **P0**, **P2**, and **P3** based light emitting diode devices showed maximum electroluminescence wavelengths in the range of 430–450 nm. The **P2** device showed pure blue emission (CIE[*x*, *y*] = [0.18, 0.16]), high luminance (1130 cd/m<sup>2</sup>) and current density (628 mA/cm<sup>2</sup>) at 8 V, whereas low-energy emissions around 500–600 nm were emerged at higher than 9 V. The **P0** and **P3** devices also showed a blue electroluminescence in the range of 8–11 V, but their luminance and efficiency were low. © 2019 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* 2019

**KEYWORDS:** conjugated polymers; light-emitting diodes (LED); luminescence; polycarbazole; donor pendant

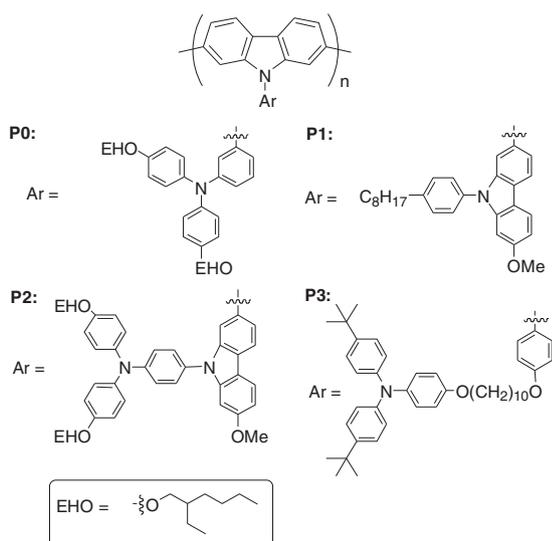
**INTRODUCTION** Polymer light-emitting diode (PLED) has much attracted attention because it has great potential to fabricate flexible and large area illuminating devices and replace the traditional liquid crystal display.<sup>1,2</sup> Polymers can simplify a process of fabricating large area organic light-emitting diodes (OLEDs) by solution-based processing such as gravure, inkjet, and screen.<sup>3–7</sup> To realize a full-color PLED display, development of a polymer emitting a pure blue color, the highest energy emission in RGB colors, is indispensable in addition to a good stability and high quantum efficiency of the PLED devices.

Polyfluorene-based conjugated polymer materials have been investigated for blue-light emitting materials<sup>8–10</sup> and could show blue emissions and good brightness on the OLED application, although they give rise to change of emitting color from blue to green due to the presence of a residual keto-defect at 9-position of fluorene.<sup>11,12</sup>

Additional supporting information may be found in the online version of this article.

© 2019 Wiley Periodicals, Inc.

Conjugated poly(2,7-carbazole)s are a structural analog of polyfluorenes whose carbon atom at 9-position is replaced with nitrogen to form a strained planer unit of an imino-bridged biphenylene. This structural difference extinguishes the keto-defect and realizes a pure blue color emission with high brightness on the OLED application. Thus, the polycarbazole has been considered as a candidate for blue light emitting materials as an alternative to polyfluorene for a long time.<sup>13,14</sup> Poly(2,7-carbazole)s having a phenyl group at the *N*-position showed a good solubility, high number-average molecular weight, and luminescent properties superior to *N*-alkyl derivatives in terms of blue emission and fluorescence quantum yields,<sup>15</sup> which is due to their rigid structures. It also has been reported that several types of poly(*N*-phenyl-2,7-carbazole)s have some good properties for application to PLEDs.<sup>15–21</sup> The poly(*N*-phenyl-2,7-carbazole) directly linked with a diphenylamino pendant (**P0** shown in Fig. 1) displayed a pure blue emission in Commission International de l'Éclairage (CIE) chromaticity diagram (*x*, *y* = 0.16,



**FIGURE 1** Chemical structures of poly(2,7-carbazole)s having hole injection and transporting moieties.

0.17) with the 1250  $\text{cd/m}^2$  luminance in the device configuration of ITO/PEDOT-PSS/polymer/Ba/Al.<sup>18</sup> A poly(*N*-phenyl-2,7-carbazole) with a long carbazolyl side chain at *p*-position of the *N*-phenyl group also showed a high efficiency of 2.05  $\text{cd/A}$  at 4 V.<sup>17</sup>

In the previous study, poly(2,7-carbazole)s having triarylamino at *N*-position showed small conformational change of the polymer backbone between solution and film states considering from little change of their absorption and fluorescence spectra. Their small Stokes shifts also suggest that these polymers have little structural difference between the ground and excited states.<sup>16</sup> In addition, the triarylamino group has good hole injection and transport properties, which is expected to work as an interlayer buffering moiety to protect the electron donor polycarbazole from peroxidation and maintain carrier balance of the electroluminescence (EL) device.<sup>10,17</sup> However, fluorescence quantum yields of several poly(*N*-triarylamino-2,7-carbazole)s in  $\text{CHCl}_3$  were quite low ( $\phi_f < 0.2$ ) compared to usual poly(*N*-phenylcarbazole)s ( $\phi_f \approx 0.7$ ),<sup>16</sup> which might be disadvantageous for applicative works in soft media such as light emitting electrochemical cells.<sup>22</sup> Introduction of a rigid carbazolyl group with electron-donor function might be substitute for superior role of the triarylamino pendent in the poly(*N*-triarylamino-2,7-carbazole)s and suppress quenching in solution.

In this article, we synthesized novel poly(*N*-aryl-2,7-carbazole)s in order to develop high-performance blue light emitting polymers for OLED application according to the synthetic strategy of direct connection of a rigid carbazolyl group (**P1**) and a sterically hindered *N*-triphenylaminated carbazolyl group (**P2**) with the 2,7-carbazolylene at the *N*-position as shown in Figure 1. To investigate the effect of the triarylamino group in the polymer, properties of **P0** and **P3** also constructed are compared with those of **P1** and **P2**.

## EXPERIMENTAL

### General Method Instrumentation

All synthetic manipulations were performed by a standard technique using a Schlenk tube under an argon atmosphere. Column chromatography was performed using silica gel (Kanto Chem., 60 N, 63–120  $\mu\text{m}$ ). NMR spectra were recorded on JEOL EX-270 spectrometer. H and C chemical shifts are given in units of  $\delta$  (ppm) relative to  $\delta$  (TMS) = 0.00 and  $\delta$  ( $\text{CHCl}_3$ ) = 77.0 ppm, respectively. Elemental analyses were carried out with a Perkin-Elmer type 2400. The number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of the polymers were estimated by gel permeation chromatography (GPC) equipped with a UV detector (Jasco) based on polystyrene standards using THF as the eluent. UV-vis and PL measurements of the polymer samples in  $\text{CHCl}_3$  and in a form of a thin film coating on quartz glass were performed using a U-3500 spectrophotometer (Hitachi) and an F-4500 fluorescence spectrophotometer (Hitachi). The measurement of the HOMO energy level of the polymer films on a Pt disk was performed at a scan rate of 50  $\text{mV}\cdot\text{s}^{-1}$  in acetonitrile (0.1 M  $\text{Et}_4\text{NBF}_4$ ) at room temperature under Ar using a saturated calomel electrode (SCE) as the reference and a platinum wire as the counter electrode. The electrochemical data (vs. SCE) obtained by cyclic voltammetry were corrected with the redox potential (4.8 eV) of ferrocene/ferrocenium<sup>+</sup>.<sup>23</sup>

### Device Fabrication

An ITO glass was cleaned by ultrasonication in a solution of detergent for 5 min. It was rinsed with flowing water, dried with a spin coater (3000 rpm for 60 s), and then treated with ultraviolet irradiation (Filgen Inc., UV253, Nagoya, Japan) for 20 min.

PEDOT-PSS aq (Baytoron PVP Al 4083) that had been filtered through a 0.45-mm pore filter was spin coated onto the cleaned ITO glass at 200 rpm for 5 s and 1000 rpm for 60 s. To remove water, it was dried on a hot plate for 15 min at 200 °C. A polymer solution (such as in toluene, chloroform, *o*-xylene, anisole, THF, and their mixture) that filtered out through a 0.5-mm pore filter was spin coated over the PEDOT-PSS-coated ITO glass at 500 rpm for 5 s and 2000 rpm for 60 s. To remove solvent, it was dried under a reduced pressure (ca. 40 Pa). Finally, CsF and Al were vacuum deposited on the substrate, respectively, under a high vacuum using an Ulvac VTR-350 M/ERH. The device configuration was ITO (150 nm)/PEDOT-PSS (90 nm)/polymer (**P0**: 100 nm, **P2**: 54 nm, **P3**: 70 nm)/CsF (2 nm)/Al (150 nm). The evaluation of the PLED devices that have an active surface area of 2 mm  $\times$  2 mm was carried out with a Hamamatsu C9920-12 system with a sweep rate of 1.25  $\text{V}\cdot\text{s}^{-1}$ .

### Materials

DMF,  $\text{CH}_2\text{Cl}_2$ , and toluene were distilled after drying with  $\text{CaH}_2$  under an argon atmosphere. THF and 1,4-dioxane were distilled after drying with sodium under an Ar atmosphere. The other solvents and all commercially available reagents were used without further purification. 2-Bromo-7-methoxy-9*H*-carbazole (**2**),<sup>24</sup> 2,7-dichloro-9*H*-carbazole (**4**),<sup>25</sup> and 1-(2-ethylhexylxy)-4-iodobenzene (**10**)<sup>26</sup> were prepared according to the literature procedures.



**2,7-Dichloro-*N*-[2-Methoxy-*N*-(4-Octylphenyl) Carbazol-7-yl]Carbazole (5)**

A mixture of **4** (135 mg, 0.57 mmol), CuI (4.6 mg, 0.024 mmol), potassium phosphate (306 mg, 1.44 mmol), 1,4-dioxane (2 mL), trans-1,2-cyclohexanediamine (11 mg, 0.096 mmol) and **3** (244 mg, 0.48 mmol) was stirred at 100 °C for 24 h. After the reaction was cooled to room temperature, the reaction mixture was subjected to column chromatography on silica gel eluted with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:4) to give **5** (251 mg, 84% yield) as a white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 8.12 (d, *J* = 8.1 Hz, 1H; 1), 7.98 (d, *J* = 8.6 Hz, 1H; 12), 7.87 (d, *J* = 8.4 Hz, 2H; a), 7.38–7.11 (10H; b, d, 2, 4, 14, 15), 6.88 (dd, *J* = 8.6, 2.3 Hz, 1H; 11), 6.81 (d, *J* = 2.2 Hz, 1H; 9), 3.78 (s, 3H; –OCH<sub>3</sub>), 2.58 (t, 2H; –Ar–CH<sub>2</sub>–), 1.61–1.53 (m, 2H; –Ar–CH<sub>2</sub>CH<sub>2</sub>–), 1.24–1.17 (10H; –CH<sub>2</sub>–), 0.80–0.75 (m, 3H; –CH<sub>3</sub>).; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 159.5 (10), 143.3 (3), 142.9 (5), 142.4 (e), 141.8 (8), 134.3 (13), 132.6 (16), 131.8 (c), 129.9 (15), 126.6 (14), 123.5 (7), 121.2 (1), 121.0 (12), 120.9 (a), 120.6 (b), 118.9 (f), 116.3 (6), 110.2 (d), 109.1 (2), 108.5 (4, 11), 94.1 (9), 55.7 (–OCH<sub>3</sub>), 48.1 (–Ar–CH<sub>2</sub>–), 38.6 (–CH<sub>2</sub>–), 35.8 (–CH<sub>2</sub>–), 31.9 (–CH<sub>2</sub>–), 31.4 (–CH<sub>2</sub>–), 29.5 (–CH<sub>2</sub>–), 29.3 (–CH<sub>2</sub>–), 23.2 (–CH<sub>2</sub>–), 22.7 (–CH<sub>2</sub>–), 14.2 (–CH<sub>3</sub>). IR (KBr): 3047, 1604, 1455, 1329, 1200, 1065, 961, 794 cm<sup>–1</sup>; Anal. Calcd for C<sub>39</sub>H<sub>36</sub>N<sub>2</sub>Cl<sub>2</sub>O: C, 75.60; H, 5.86; N, 4.52. Found: C, 75.18; H, 6.09; N, 4.22.

**2,7-Dichloro-*N*-[2-Methoxy-*N*-(4-(*N,N*-Bis(4-(2-Ethylhexyloxy)Phenyl)Amino)Phenyl)Carbazol-7-yl]Carbazole (11)**

A mixture of **9** (170 mg, 0.325 mmol), Pd(OAc)<sub>2</sub> (3.7 mg, 0.016 mmol), sodium *t*-butoxide (156 mg, 1.62 mmol), toluene (7 mL), P(*t*-Bu)<sub>3</sub> (10 wt % in hexane, 95 μL, 0.033 mmol), and **10** (541 mg, 1.63 mmol) was stirred at 110 °C for 24 h. After the reaction was cooled to the room temperature, CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction mixture and subjected to short path column chromatography on silica gel. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel eluted with hexane/CH<sub>2</sub>Cl<sub>2</sub> (2:1) to give **11** (148 mg, 88% yield) as a white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 8.12 (d, *J* = 8.2 Hz, 1H; 1), 7.98 (d, *J* = 8.6 Hz, 1H; 12), 7.90 (d, *J* = 8.2 Hz, 2H; a), 7.30 (d, *J* = 1.3 Hz, 1H; 4), 7.23–7.14 (7H; b, d, 9, 15), 7.04 (d, *J* = 9.0 Hz, 4H, 18), 6.94 (d, *J* = 8.9 Hz, 2H; 14), 6.88 (dd, *J* = 8.6, 2.3 Hz, 1H; 11), 6.81 (d, *J* = 8.7 Hz, 1H; 2), 6.76 (d, *J* = 9.0 Hz, 4H; 19), 3.81 (s, 3H; –OCH<sub>3</sub>), 3.72 (4H; –OCH<sub>2</sub>–), 1.67–1.58 (m, 2H; –OCH<sub>2</sub>CH<), 1.49–1.17 (16H; –CH<sub>2</sub>–), 0.87–0.81 (12H; –CH<sub>2</sub>CH<sub>3</sub>).; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 159.5 (10), 156.1 (20), 148.6 (3), 143.6 (e), 142.5 (17), 142.1 (5), 139.8 (8), 132.5 (13, 16), 131.8 (c), 127.9 (14), 127.4 (15), 127.1 (19), 123.3 (7), 121.2 (1), 120.9 (a, b), 120.5 (f), 119.7 (12), 118.8 (6), 116.2 (18), 115.3 (d), 110.2 (2), 108.9 (4), 108.6 (11), 94.2 (9), 70.6 (–OCH<sub>2</sub>–), 55.7 (–OCH<sub>3</sub>), 39.5 (–OCH<sub>2</sub>CH<), 30.6 (–CH<sub>2</sub>–), 29.1 (–CH<sub>2</sub>–), 23.9 (–CH<sub>2</sub>–), 23.1 (–CH<sub>2</sub>–), 14.2 (–CH<sub>3</sub>), 11.2 (–CH<sub>3</sub>). IR (KBr): 2926, 1603, 1505, 1457, 1320, 1238, 1065, 963, 827 cm<sup>–1</sup>; Anal. Calcd for

C<sub>59</sub>H<sub>61</sub>N<sub>3</sub>Cl<sub>2</sub>O<sub>3</sub>: C, 76.11; H, 6.60; N, 4.51. Found: C, 75.59; H, 6.68; N, 4.34.

**2,7-Dichloro-*N*-[4-[[10-(4-(*N,N*-Bis(4-*t*-Butylphenyl)-Aminophenoxy))Decyl]Oxy]Phenyl]Carbazole (17)**

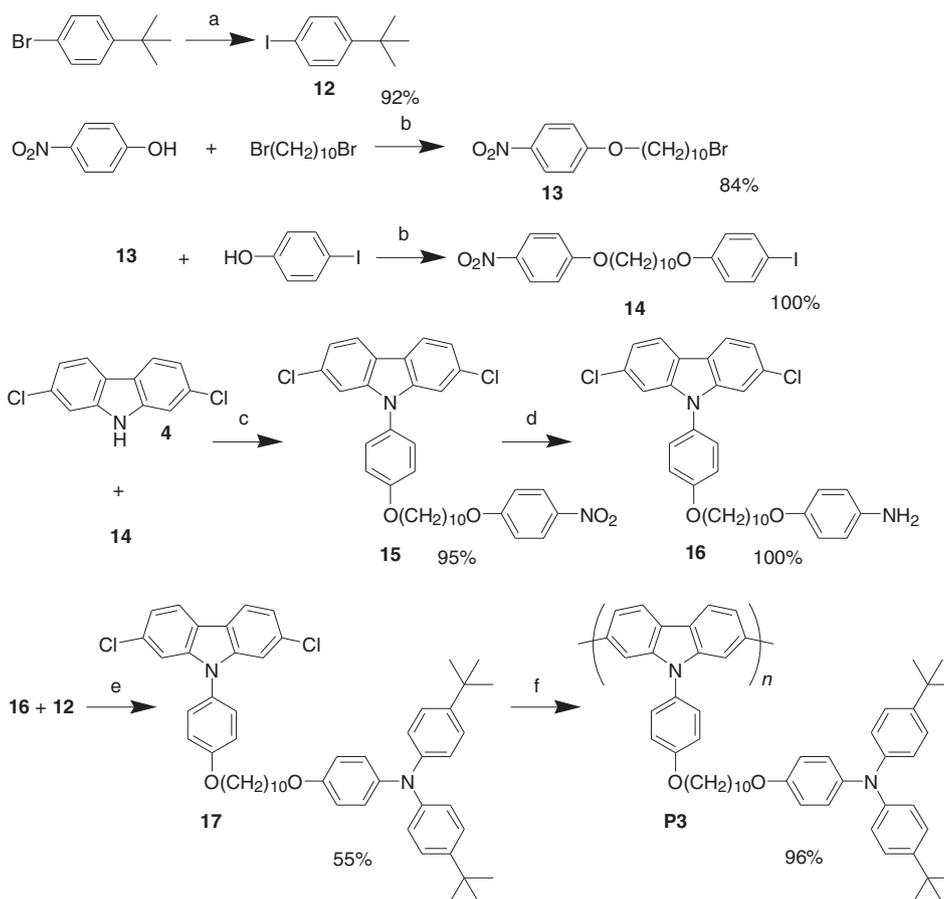
A mixture of **16** (200 mg, 0.35 mmol), Pd(OAc)<sub>2</sub> (3.93 mg, 0.018 mmol), sodium *t*-butoxide (168 mg, 1.75 mmol), toluene (5 mL), P(*t*-Bu)<sub>3</sub> (10 wt % in hexane [102 μL, 0.035 mmol]) and **12** (452 mg, 1.74 mmol) was stirred at 110 °C for 38 h. After the reaction was cooled to the room temperature, CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction mixture and subjected to short-path column chromatography on silica gel. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel eluted with hexane/CH<sub>2</sub>Cl<sub>2</sub> (4:1) to give **17** (162 mg, 55% yield) as a pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 7.97 (d, *J* = 8.6 Hz, 2H; a), 7.68–7.60 (6H; 7, 10), 7.36 (d, *J* = 8.9 Hz, 2H; 2), 7.38–7.33 (4H; 3, b), 7.22–7.16 (8H; 6, 11, d), 4.06 (4H; –OCH<sub>2</sub>–), 1.91–1.73 (4H; –OCH<sub>2</sub>CH<sub>2</sub>–), 1.66 (4H; –CH<sub>2</sub>–) 1.48–1.27 (26H; –CH<sub>3</sub>, –CH<sub>2</sub>–); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 158.9 (5), 155.3 (4), 146.1 (12), 144.5 (9), 142.3 (8), 141.1 (e), 132.2 (1), 129.0 (c), 128.7 (2), 127.2 (11), 125.8 (10), 122.3 (6), 121.0 (a), 120.9 (f), 120.5 (7), 116.3 (3), 115.8 (b), 110.2 (d), 68.4 (–OCH<sub>2</sub>–), 68.2 (–OCH<sub>2</sub>–), 34.2 (–C(CH<sub>3</sub>)<sub>3</sub>), 31.7 (–C(CH<sub>3</sub>)<sub>3</sub>), 29.6 (–CH<sub>2</sub>–), 29.4 (–CH<sub>2</sub>–), 26.1 (–CH<sub>2</sub>–). IR (KBr): 2930, 1592, 1512, 1455, 1237, 1066, 829, 795 cm<sup>–1</sup>; Anal. Calcd for C<sub>62</sub>H<sub>76</sub>N<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>: C, 77.21; H, 7.20; N, 3.34. Found: C, 77.23; H, 7.29; N, 3.34.

**A General Procedure for Homopolymerization**

Yamamoto polymerization<sup>27</sup> was carried out under modified conditions to obtain the polymer (**P1–P3**) in good yield with high-molecular weight. The GPC results are shown in Table 1. A mixture of bpy (91 mg, 0.58 mmol), Ni(COD)<sub>2</sub> (160 mg, 0.58 mmol), DMF (1.5 mL), and COD (62.9 mg, 0.58 mmol) was stirred at 55 °C for 10 min. To the mixture was added a solution of corresponding monomer (**5**, **11**, or **17**) (0.24 mmol) in THF (2 mL), and this was stirred at 65 °C for 48 h. The crude polymer was purified by reprecipitation from methanol. Polymer was dried under vacuum at 100 °C.

**RESULTS AND DISCUSSION****Synthetic Procedure**

Scheme 1 shows the synthetic route of a monomer with the carbazolyl group (**5**) and **P1**. To prepare the monomer **5** for **P1**, the carbazolyl moiety **3** was introduced to 2,7-dichlorocarbazole **4** at *N*-position by the CuI/trans-1,2-cyclohexanediamine (CHDA) catalyzed reaction. First, 4-Iodoctylbenzene **1** was prepared from 4-aminoctylbenzene by Sandmeyer reaction. To synthesize *N*-arylcarbazole **3**, *N*-arylation of 2-bromo-7-methoxycarbazole **2** with iodobenzene **1** was carried out by the CuI/CHDA catalyzed method.<sup>28</sup> An exchange reaction of bromo to iodo group on the carbazole moiety occurred during the *N*-arylation, forming a mixture of bromocarbazole and iodocarbazole. Thus, complete iodination of the halogenocarbazoles was carried out under the similar conditions but using NaI instead of K<sub>3</sub>PO<sub>4</sub>.<sup>29</sup>



**SCHEME 2** Syntheses of monomer **17** and **P3**. (a) CuI, NaI, CHDA, 1,4-dioxane, 100 °C; (b) K<sub>2</sub>CO<sub>3</sub>, acetone, 55 °C; (c) CuI, K<sub>3</sub>PO<sub>4</sub>, CHDA, 1,4-dioxane, 100 °C; (d) SnCl<sub>2</sub>•2H<sub>2</sub>O, EtOH, reflux; (e) Pd(OAc)<sub>2</sub>, P(*t*-Bu)<sub>3</sub>, *t*-BuONa, toluene, 110 °C; (f) Ni(COD)<sub>2</sub>, COD, bpy, DMF-THF, 70 °C.

Scheme 1 also illustrates the synthetic route of poly(*N*-carbazolyl-2,7-carbazole) with a triphenylamine moiety (**P2**). 2-Bromo-7-methoxycarbazole **2** was reacted with *p*-fluoronitrobenzene according to the reported procedure.<sup>30</sup> To improve reactivity of *N*-carbazoylation, iodination of bromocarbazole **6** was carried out under the Ni-catalyzed reaction (an alternate method for step c in Scheme 1) reported by Chang *et al.*,<sup>31</sup> giving 2-iodo-7-methoxy-*N*-(4-nitrophenyl)carbazole **7**. The *N*-carbazoylation of 2,7-dichlorocarbazole was carried out under the Pd-catalyzed reaction<sup>32</sup> to give 2,7-dichloro-*N*-[2-methoxy-*N*-(4-nitrophenyl)carbazol-7-yl]carbazole **8** in a good yield (84%). Using SnCl<sub>2</sub>, **8** was reduced to an amino compound, 2,7-dichloro-*N*-[2-methoxy-*N*-(4-aminophenyl)carbazol-7-yl]carbazole **9**. *N*-Arylation of 2,7-

dichloro-*N*-[2-methoxy-*N*-(4-aminophenyl)carbazol-7-yl]carbazole with 1-(2-ethylhexyloxy)-4-iodobenzene was carried out by the Pd-catalyzed reaction to give the monomer **9** for **P2**.

Scheme 2 illustrates the synthetic route of poly(*N*-aryl-2,7-carbazole) having a pendant side chain with a triphenylamine terminal (**P3**). Reaction of *p*-nitrophenol with excessive 1,10-dibromodecane gave **13**. Moreover, **14** was prepared from 4-iodophenol with **13**. *N*-arylation of 2,7-dichlorocarbazole with iodobenzene **14** was carried out by the CuI/CHDA catalyzed reaction, giving **15** in a high yield. After the terminal nitrobenzene moiety was reduced to amino, the monomer **17** for **P3** was prepared from **16** by the same method for *N*-arylation of **11** using **12**.

All the polymers were prepared by the Ni<sup>0</sup>-catalyzed dehalogenative polycondensation of the monomers **5**, **11**, and **17**, using the Yamamoto method, respectively.<sup>27</sup> All the polymers were soluble in the usual organic solvents such as THF and CHCl<sub>3</sub>, but **P1** had low solubility in toluene.

The results of number-average molecular weight ( $M_n$ ) and the weight average molecular weight ( $M_w$ ) of the polymers determined by gel permeation chromatography (GPC) are summarized

**TABLE 1** GPC Analysis Results of Polymers

Polymers	$M_n$ ( $\times 10^{-3}$ ) <sup>a</sup>	$M_w$ ( $\times 10^{-3}$ ) <sup>a</sup>	PDI	D.P.
<b>P1</b>	12.7	57.0	4.5	23.0
<b>P2</b>	16.4	108	6.6	19.0
<b>P3</b>	30.0	181	6.0	38.9

<sup>a</sup> Determined by GPC versus polystyrene standards in THF.

in Table 1. All the polymers showed a good degree of polymerization (DP) with large polydispersity indices (PDI). DP of **P2** was a little smaller than **P1**, which is due to the larger side pendant of the carbazolyl portion with the triaryl amino group, which hindered the polymerization a little.

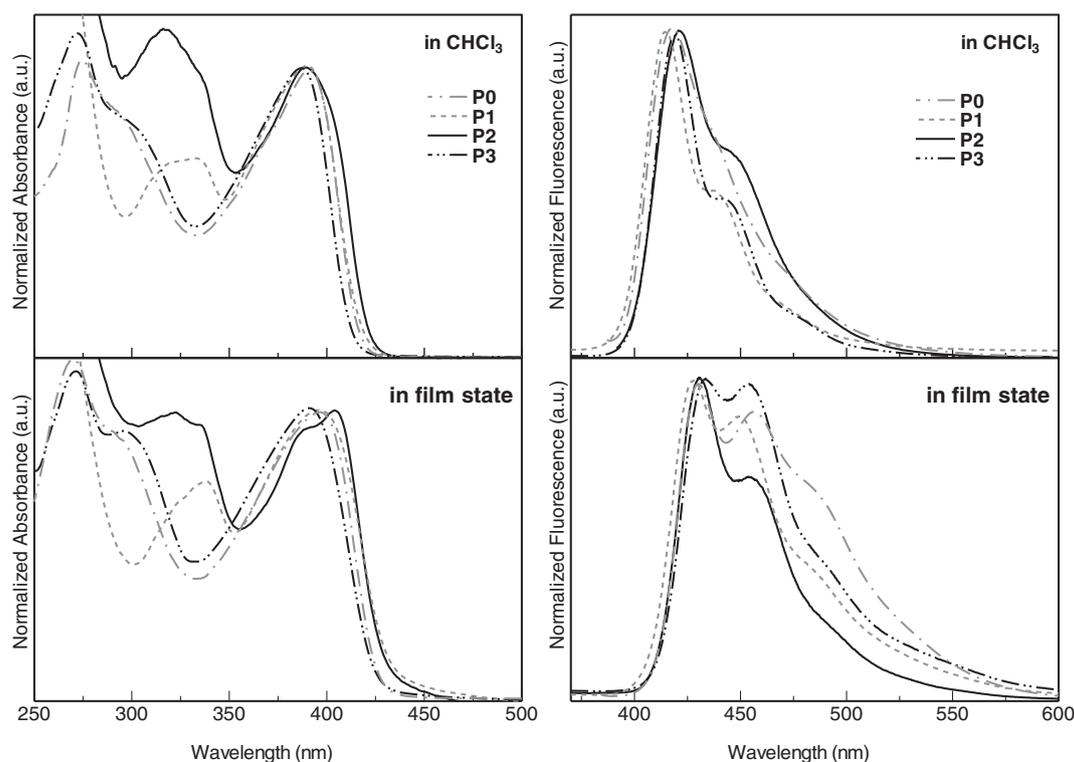
### Optical Properties

The UV-vis spectra of the polymers in  $\text{CHCl}_3$  and in the thin film state are depicted in Figure 2 and the spectral results are summarized in Table 2. All the polymers in chloroform had an absorption peak around 390 nm due to  $\pi$ - $\pi^*$  transition of the conjugated main chain. The bands around 330 nm of **P1** and **P2** are due to the carbazolyl side pendant.<sup>33</sup> Similarly, the absorption band around 300 nm of **P3** is attributed to the triphenylamino group.<sup>16</sup> **P2** also has the band due to the triphenylamino moiety, but it is involved in the carbazolyl band around 330 nm. These polymer films exhibit absorption spectra similar to those in solution except a red shift about 5 nm. The HOMO-LUMO energy gaps ( $E_g$ ) of the polymers estimated from the absorption edge of each thin film were around 2.85 eV in all cases.

PL spectra of the polymers in  $\text{CHCl}_3$  and films are also shown in Figure 2, and the results are summarized in Table 2. Their emission maximum wavelengths ( $\lambda_{\text{max}}[\text{em}]$ ) in  $\text{CHCl}_3$  are in the range from 418 to 421 nm. The spectral changes of fluorescence between the solution and film state are due to vibronic effect and  $\pi$ -aggregations, which were observed as shoulder emissions around 455 and 480 nm. The PL spectra of **P2** in  $\text{CHCl}_3$  and film state showed almost the same spectral

shape, and their difference of  $\text{Em } \lambda_{\text{max}}$  was a little about 10 nm, which was the smallest of all the polymers. This result suggests that the rigid and large steric hindered structure of **P2** is effective to suppress the concentration quenching of emissions from the main chain. The smaller spectral change for **P1** compared to **P0** suggests that the carbazolyl-carbazole skeleton in **P1** is more rigid than the triphenylamino-carbazole skeleton in **P0**. Interestingly, the spectral change of **P3** was similar to **P0**. This indicates that the rigidity of the emissive poly(2,7-carbazole) main chain of **P3** having the *N*-phenyl moiety with the enchaind triaryl amino group is similar to that of **P0**, which directly connected with the large triaryl amino group at the *N*-position. Nevertheless, all the polymers preserved blue emission. Note that **P2** showed a deep blue emission (CIE: 0.15, 0.06) (Table 2).

The fluorescence quantum yield of **P1** ( $\phi_f = 0.78$ ) in  $\text{CHCl}_3$  was satisfactorily high as well as those of general poly(*N*-phenyl-2,7-carbazole)s ( $\phi_f = 0.8$ ), while the quantum yields of **P2** ( $\phi_f = 0.22$ ) and **P3** ( $\phi_f = 0.26$ ) were lower than them. These results are similar to those of poly(*N*-phenyl-2,7-carbazole)s with diphenylamino group ( $\phi_f = 0.01$ – $0.19$ ) in our previous reports.<sup>16</sup> The result indicates that an exciton quenching might occur between the triaryl amino moiety and the main chain in the polymers, but the pendent carbazolyl moiety has no effect on the quenching. In order to investigate the quenching effect of the triaryl amino moiety in polycarbazoles, the emission behavior of **P0** was reinvestigated. As shown in Figure 2, the fluorescence spectrum of the **P0** film is rather broad with a slight red shift in wavelength compared to that



**FIGURE 2** Absorption (left) and PL spectra (right) of the polymers in  $\text{CHCl}_3$  (upper) and in film state (lower).

**TABLE 2** Absorption and Fluorescence Spectral Data of the Polymers

Polymers	In CHCl <sub>3</sub> <sup>a</sup>			In film state <sup>b</sup>					
	Abs λ <sub>max</sub> (nm)	Em λ <sub>max</sub> <sup>c</sup> (nm)	φ <sub>f</sub> <sup>d</sup>	Abs λ <sub>max</sub> (nm)	E <sub>g</sub> <sup>e</sup> (eV)	Em λ <sub>max</sub> <sup>f</sup> (nm)	HOMO <sup>g</sup> (eV)	LUMO <sup>h</sup> (eV)	CIE (x,y) <sup>i</sup>
<b>P1</b>	390	419	0.78	396	2.84	433, 454	-5.29	-2.45	(0.16, 0.11)
<b>P2</b>	389	421	0.22	404	2.85	431, 455	-5.22	-2.37	(0.15, 0.07)
<b>P3</b>	387	415	0.26	391	2.86	427, 450	-5.19	-2.33	(0.16, 0.12)
<b>P0</b>	391	418	0.19	397	2.90	430, 457	-5.27	-2.37	(0.15, 0.14)

<sup>a</sup> Absorption and fluorescence spectra at  $1.0 \times 10^{-5}$  M per unit, respectively, at room temperature.

<sup>b</sup> Cast film on a quartz glass plate from CHCl<sub>3</sub>.

<sup>c</sup> The excitation wavelength is almost the same as λ<sub>max</sub> absorption in each case because the excitation spectrum of each polymer almost matched at absorption spectrum.

<sup>d</sup> Determined using 9,10-diphenylanthracene (φ<sub>f</sub> = 0.97 in cyclohexane) as the standard.

<sup>e</sup> Band gaps estimated from the onset of the absorption band edge.

<sup>f</sup> Polymers were dissolved in chloroform and spin coated onto a quartz substrate and excited at 350 nm with a Xe lamp. Photon measurement range of PL was 400–700 nm.

<sup>g</sup> Determined by electrochemical analysis.

<sup>h</sup> Calculated based on the HOMO level and lowest energy absorption edge of the UV-spectrum (E<sub>g</sub>).

<sup>i</sup> Estimated from fluorescence spectrum.

in dilute CHCl<sub>3</sub> solution. The fluorescence quantum yield of **P0** in CHCl<sub>3</sub> was φ<sub>f</sub> = 0.19, which is comparable to **P2** and **P3**, but φ<sub>f</sub> of the thin film is reported being 0.32.<sup>18</sup> This phenomenon is considered being a kind of aggregation-induced emission<sup>34</sup> in the combination of triphenylamine and carbazole.

Analogous polymers with this combination have shown similar tendency; that is, φ<sub>f</sub> of thin film was higher than that in CHCl<sub>3</sub> while φ<sub>f</sub> in toluene was higher than that in CHCl<sub>3</sub>.<sup>15,18,21</sup>

### Electrochemical and EL Properties

The HOMO energy levels, the LUMO energy levels, and E<sub>g</sub> for all the polymers are summarized in Table 2. The HOMO energy levels were estimated from an onset potential of the oxidation waves.<sup>35,36</sup> The LUMO energy levels were estimated from the HOMO energy levels and E<sub>g</sub> values. The pendants of the *N*-phenylcarbazol-2-yl for **P1** (*N,N*-diphenyl-amino)-*N*-phenylcarbazol-2-yl for **P2** and triphenylamino for **P3** have similar donating ability to lower the ionization potential of the polymers as well as the triphenylamino pendant in **P0**. However, the pendent carbazolyl moiety does not stabilize EL in blue light region of poly(2,7-carbazole)s compared to the pendent triarylamine moiety in the OLED device having an ITO/PEDOT-PSS/polymer/CsF/Al structure in the previous report.<sup>17</sup> In addition, **P1** having no triphenylamine structure had low solubility in organic solvent to make uniform thin film device. Thus, EL performance of **P2** is investigated compared to those of **P3** and **P0** in the same device structure, ITO/PEDOT-PSS/polymer/CsF/Al, in this work to confirm the effect of the triphenyl amine pendant, and the results are summarized in Table 3 and Figure 3. Since usual polycarbazole LED devices in this configuration showed a blue EL at lower than 8 V operating voltages,<sup>17,19,20</sup> criterion performance (luminance, efficiency, and CIE value) of each device at 8 V is listed in Table 3 for evaluation of blue light emitting polymer materials.

The device embedded with **P2** which has the (*N,N*-diphenylamino)-*N*-phenylcarbazol-2-yl pendant showed purple-blue to blue emissions (Em λ<sub>max</sub> = 430 nm, CIE(x, y) = (0.17, 0.13) at 6 V– (0.20, 0.22) at 9 V), a modest current

efficiency (η<sub>c</sub> = 0.30 cd/A at 9 V), and an adequately high luminance (2902 cd/m<sup>2</sup> at 9 V). The turnon voltage was 4 V, which was the lowest of all. The EL spectra between 4 V and 9 V were similar to the PL spectrum in the film state (Figs. 2 and 3), and intensities of their similar figure were reversibly changed between these voltages. The steric hindrance of the rigid pendant with electron-donor ability might keep away from aggregation of the polymer main chains during the EL processes. The maximum luminance was 9870 cd/m<sup>2</sup> (η<sub>c</sub> = 0.60 cd/A) at an applied voltage of 11 V, although the emission color irreversibly changed from blue to bluish green. The higher the operating voltage is applied to the device, the more intense additional emission bands longer than 490 nm appear (Fig. 3) and the luminance decreases with time. These results suggest that the carrier injection/transport balance of the **P2** device is appropriately keeping during the operation voltages in the range of 4–9 V, but disruption of balance for the emission from an exciton originated from the polycarbazole main chains occurs in the range of high operating voltages, leading to low-energy emissions from oxidized species. The tendency of the EL spectral change was similar to those of poly-2,7-carbazoles having the *N*-aryl groups,<sup>19</sup> but the change was suppressed to some extent, probably due to presence of the triarylamine moiety. The irreversible spectral change might be due to hyperoxidation at 3,6-positions of the hole-injected 2,7-carbazol moieties and concentrated hole species near the interface of a reactive cathode under high applied voltages.<sup>17,37</sup> Thus, the triarylamine moiety should work as a buffer medium to prevent the hyperoxidation of polycarbazole in addition to the inherent hole injection and transporting functions under the operating conditions.

On the other hand, the **P0** device showed stable bluish emissions during the operation voltages thanks to the buffering effect of the directly linked triarylamine moiety, but its luminance was very low. This result suggests that there is limitation of hole injection to make exciton on the donor polycarbazole emitter in competition with the directly linked triarylamine moieties, although a **P0** device having different configuration (ITO/PEDOT-PSS/polymer/Ba/Al)<sup>18</sup> gave better results than in Table 3 in terms of luminance, efficiency, and purity of blue emission color.

**TABLE 3** EL Properties of the Polymers

Polymer	$V_{\text{on}}^{\text{a}}$ (V)	$L^{\text{b}}$ cd m $^{-2}$ (V)	$\eta^{\text{c}}$ cd A $^{-1}$ (V)	CIE $^{\text{d}}$ (x, y)
<b>P0</b>	8	5 (8)	0.29 (8)	(0.20, 0.19)
		272 (17)	0.37 (10)	(0.20, 0.24)
<b>P2</b>	4	1130 (8)	0.18 (8)	(0.18, 0.16)
		9870 (11)	0.60 (11)	(0.25, 0.41)
<b>P3</b>	5	28 (8)	0.03 (8)	(0.20, 0.18)
		1506 (13)	0.13 (13)	(0.21, 0.30)

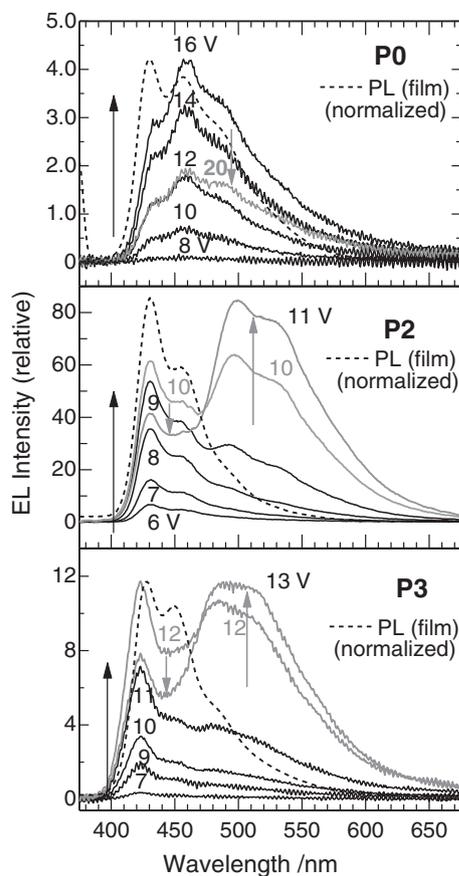
<sup>a</sup> Turn-on voltage.

<sup>b</sup> Upper is luminance at 8 V and lower is maximum luminance and the operating voltage.

<sup>c</sup> Upper is efficiency at 8 V and lower is maximum efficiency and the operating voltage.

<sup>d</sup> Upper is CIE index at 8 V and lower is data at voltage showing maximum luminance.

The **P3** device also showed stable bluish emissions during operation voltages as well as the **P0** device. The luminance was higher while the efficiency was lower compared to the results of the **P0** device (Table 3), which suggests that hole injection and transport in the **P3** device mainly proceed through the triarylamine moieties separated from the polycarbazole main chains by a hopping mechanism.



**FIGURE 3** EL spectral changes of the **P0**, **P2**, and **P3** devices at different applied voltages in the first sweep.

Comparison of the EL results of each polymer device at 8 V in Table 3 suggests that several factors determine the trade-off performance. To summarize of this point, the triphenylamine moiety is oxidized first at the anode to generate a hole. The hole is trapped at the triphenylamine moiety, but it can transfer to another triphenylamine moiety by a hopping mechanism or a donor carbazolyl moiety with a little energy gap toward the cathode under an applied voltage. As a result, the donor poly(2,7-carbazole) chain can undergo *p*-doping to generate a hole such as a polaron and a bipolaron. The more *p*-doping proceeds, the more conductivity along the polymer chain increases and the bandgap narrows. Thus, the directly linked triphenylamine moiety in **P0** traps a hole and stabilizes the polycarbazole luminophore against the hyperoxidation. On the other hand, the difficulty of the hole injection to the luminophore due to the stabilization and the subsequent low conductivity of the polymer chain at a low-level *p*-doping result in the very low luminance, but the good current efficiency probably due to keeping a balance of carriers' recombination. The *N*-carbazolyltriphenylamine moiety in **P2** might work more flexible in the hole trapping and hole transferring in association with a moderate *p*-doping, which brings about the highest luminance with an enough current flow among three polymers. The sterically hindered *N*-carbazolyl pendant might inhibit converting **P2** to a narrow band-gap quinoid structure with controlling the *p*-doping level, which results in high luminance with keeping blue emission at 8 V. The pendent triphenylamine moiety in **P3** mainly functions as the hole trapping and hopping with a little participating in the *p*-doping of the polycarbazole luminophore, which results in the low luminance and low efficiency.

## CONCLUSIONS

In summary, three poly(2,7-carbazole)s, **P1–P3**, which have hole injection and hole transfer functional moieties of carbazole and/or triphenylamine at *N*-position were synthesized and characterized to be applied in blue light emitting PLED.

The fluorescence quantum yield of **P1** having *N*-(2-carbazolyl) moiety in CHCl<sub>3</sub> was much higher than those of **P0**, **P2**, and **P3**; they all have a triphenylamino group bonded directly at the *N*-position, linked via the *N*-(2-carbazolyl) moiety, and connected as a flexible pendant, respectively. The low-emissive phenomenon in CHCl<sub>3</sub> for **P0**, **P2**, and **P3** is interpreted as an aggregate-induced emissive property, that is, combination of the polycarbazole and triarylamine give rise to self-quenching in dilute solution of a good solvent.

The shape of PL spectrum of **P2** in CHCl<sub>3</sub> was preserved that in a film state, realizing a deep blue emission in the film state (CIE: 0.15, 0.07), which is due to steric and electronic effects of the rigid and donor carbazolyl-triphenylamine moiety. Similar tendency was observed for **P1** that has the bulky and donor 2-carbazolyl moiety. On the other hand, the triphenylamine moieties in **P0** and **P3** were not very effective to preserve shapes of PL spectra between in CHCl<sub>3</sub> and film.

Introduction of the carbazolyl moiety lowered the ionization potential as well as the triaryl amino groups. As the result, all the obtained polymers had the shallow values of HOMO levels between  $-5.29$  and  $-5.13$  eV.

**P2** and **P3** which have good solubility in toluene and an aggregate-induced emissive property were used as emitting layer materials in PLEDs device with the configuration of ITO/PEDOT-PSS/polymer/CsF/Al for blue light emission in comparison with performance of **P0**. The **P2** device kept deep blue to pure blue EL, modest efficiency and luminance at 5–9 V with the aid of the rigid donor carbazolyltriaryl amino pendant and buffering effect of the triarylamine moiety, but the color turned to greenish blue similar to usual polycarbazoles over 9 V. The EL performance of the **P3** device showed similar tendency with that of **P0** except quite lower efficiency, which might be interpreted that hole injection and transport occur at the enchaind triphenylamine pendants with a hopping mechanism.

#### ACKNOWLEDGMENTS

The authors thank Dr. Norifumi Kobayashi, University of Tsukuba, for his valuable comments on the synthetic design. We also thank Chemical Analysis Division, Research Facility Center for Science and Technology, University of Tsukuba, for facilities of the NMR, elemental analysis, and PL measurements.

#### REFERENCES AND NOTES

- 1 D. D. C. Bradley, J. H. Burroughes, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, *347*, 539.
- 2 L. Akcelrud, *Prog. Polym. Sci.* **2003**, *28*, 875.
- 3 R. T. Hebner, C. C. Wu, D. Marcy, H. M. Lu, C. J. Sturm, *Appl. Phys. Lett.* **1998**, *72*, 519.
- 4 M. Suzuki, H. Fukagawa, Y. Nakajima, T. Tsuzuki, T. Takei, T. Yamamoto, S. Tokito, *J. Soc. Inf. Disp.* **2009**, *17*, 1037.
- 5 J. Birnstock, J. Blässing, A. Hunze, M. Scheffel, *Appl. Phys. Lett.* **2001**, *78*, 3905.
- 6 D.-Y. Chung, J. Huang, D. D. C. Bradley, A. J. Campbell, *Org. Electron.* **2010**, *11*, 1088.
- 7 A. Sandstrom, H. F. Dam, F. C. Krebs, L. Edman, *Nat. Commun.* **2012**, *3*, 1002.
- 8 K.-H. Weinfurter, H. Fujikawa, S. Tokito, Y. Taga, *Appl. Phys. Lett.* **2000**, *76*, 2502.
- 9 M. Gross, D. C. Müller, H.-G. Nothofer, U. Scherf, D. Neher, C. Braüchle, K. Meerholz, *Nature* **2000**, *405*, 661.
- 10 C.-W. Huang, C.-L. Tsai, C.-Y. Liu, T.-H. Jen, N.-J. Yang, S.-A. Chen, *Macromolecules* **2012**, *45*, 1281.
- 11 K. Becker, J. M. Lupton, J. Feldmann, B. S. Nehls, F. Galbrecht, D. Gao, U. Scherf, *Adv. Funct. Mater.* **2006**, *16*, 364.
- 12 M. R. Craig, M. M. de Kok, J. W. Hofstraat, A. P. H. J. Schenning, E. W. Meijer, *J. Mater. Chem.* **2003**, *13*, 2861.
- 13 N. Blouin, M. Leclerc, *Acc. Chem. Res.* **2008**, *41*, 1110.
- 14 J. -F. Morin, M. Leclerc, D. Adès, A. Siove, *Macromol. Rapid Commun.* **2005**, *26*, 761.
- 15 M. Kijima, R. Koguchi, S. Abe, *Chem. Lett.* **2005**, *34*, 900.
- 16 N. Kobayashi, R. Koguchi, M. Kijima, *Macromolecules* **2006**, *39*, 9102.
- 17 R. Koguchi, N. Kobayashi, T. Shinnai, K. Oikawa, K. Tsuchiya, M. Kijima, *Macromol. Chem. Phys.* **2008**, *209*, 439.
- 18 N. Kobayashi, M. Kijima, *Appl. Phys. Lett.* **2007**, *91*, 081113.
- 19 T. Mori, T. Shinnai, M. Kijima, *Polym. Chem.* **2011**, *2*, 2830.
- 20 T. Horii, T. Shinnai, K. Tsuchiya, T. Mori, M. Kijima, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 4557.
- 21 H. Yi, A. Iraqi, M. Stevenson, C. J. Elliott, D. G. Lidzey, *Macromol. Rapid Commun.* **2007**, *28*, 1155.
- 22 E. Fresta, R. D. Costa, *J. Mater. Chem. C* **2017**, *5*, 5643.
- 23 T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z. -H. Zhou, Y. Nakamura, T. Kanbara, *Macromolecules* **1992**, *25*, 1214.
- 24 D. A. Patrick, D. W. Boykin, W. D. Wilson, F. A. Tanious, J. Spychalaz, B. C. Bender, J. E. Hall, C. C. Dykstra, K. A. Ohemeng, R. R. Tidwell, *Eur. J. Med. Chem.* **1997**, *32*, 781.
- 25 J. -F. Morin, M. Leclerc, *Macromolecules* **2001**, *34*, 4680.
- 26 A. R. A. Palmans, M. Eglin, A. Montali, C. Weder, P. Smith, *Chem. Mater.* **2000**, *12*, 472.
- 27 D. Neher, *Macromol. Rapid Commun.* **2001**, *22*, 1365.
- 28 A. Klapars, J. C. Antilla, X. Huang, S. L. Buchwald, *J. Am. Chem. Soc.* **2001**, *123*, 7727.
- 29 A. Klapars, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 14844.
- 30 H. Jian, J. M. Tour, *J. Org. Chem.* **2003**, *68*, 5091.
- 31 S. H. Yang, C. S. Li, C. H. Cheng, *J. Org. Chem.* **1987**, *52*, 691.
- 32 Z. Suo, M. Drobizhev, C. W. Spangler, N. Christensson, A. Rebane, *Org. Lett.* **2005**, *7*, 4807.
- 33 Y. Fu, Y. Li, J. Li, S. Yan, Z. Bo, *Macromolecules* **2004**, *37*, 6395.
- 34 J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem. Commun.* **2001**, 1740. <https://doi.org/10.1039/B105159H>
- 35 J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch, J. Daub, *Adv. Mater.* **1995**, *7*, 551.
- 36 S. Gauvin, F. Santerre, J. P. Dodelet, Y. Ding, A. R. Hlil, H. -A. S. Hay, J. Anderson, N. R. Armstrong, T. C. Gorjanc, M. D'lorio, *Thin Solid Films* **1999**, *353*, 218.
- 37 G. Zotti, G. Schiavon, S. Zecchin, J. -F. Morin, M. Leclerc, *Macromolecules* **2002**, *35*, 2122.