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journal or publication title	Macromolecular chemistry and physics
volume	209
number	4
page range	439-449
year	2008-02-20
権利	(C) 2008 WILEY-VCH Verlag GmbH & Co.
URL	http://hdl.handle.net/2241/98526

doi: 10.1002/macp.200700448

Synthesis of poly (*N*-aryl-2,7-carbazole)s for efficient blue electroluminescence materials

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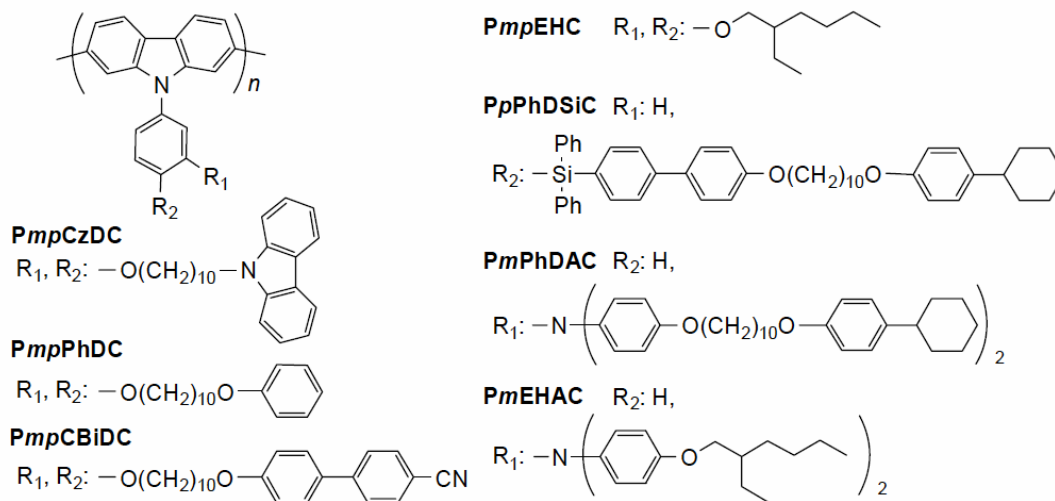
Keywords:

conjugated polymers; fluorescence; light-emitting diodes (LED); poly(carbazole)

Summary:

Several poly(*N*-phenyl-2,7-carbazole)s having dialkoxy groups at *m*- and *p*-positions (**PmpCzDC**, **PmpPhDC**, **PmpCbiDC**, **PmpEHC**), silyl group at *p*-position (**PpPhDSiC**) and diphenylamino group (**PmPhDAC**, **PmEHAC**) at *m*-position of the *N*-phenyl portion were synthesized, and their optical properties were characterized. These polymers were used as emitting layer materials of organic light emitting diode (OLED) devices having configuration of ITO/PEDOT(PSS)/polymer/CsF/Al. The OLED devices embedded with **PmpCzDC**, **PmpPhDC** and **PmpEHC** showed intense

luminance of about 15000 cd m^{-2} with efficiencies of about 1 cd A^{-1} , while the devices embedded with **PpPhDSiC**, **PmPhDAC** and **PmEHAC** showed less luminance but retained color purity of blue emission under wide range of applied voltages.



Introduction

Conjugated polymers are very important materials can be applied in electrical, optical and optoelectronic devices such as light-emitting diodes, field effect transistors, charge storage devices, photodiodes, and sensors, etc. In particular, the field of polymeric light-emitting diodes (PLEDs) had attracted large interest to develop full-color displays which could be a main display system in the near future.^[1] The full-color display system requires three basic emission colors of red, green and blue. A large number of blue-emitting materials have been investigated for application to PLED, because the blue emission is considered as the most important color and is difficult realizing when conjugated polymers are used as the emitting material. Conjugated polymers have an advantage to emit efficient even in the solid

thin-film state, which can simplify a process of fabricating organic light-emitting diodes (OLEDs) by appropriate manners such as spin coating and inkjet printing.

Recently, polycarbazoles have been considered as a candidate for blue light emitting materials alternative to polyfluorene-based materials. The carbazole unit can be linked in two different ways, leading to either poly(3,6-carbazole) or poly(2,7-carbazole). Interestingly, the latter has a longer extension of π -conjugation than the former due to having a conjugation structure like poly(*p*-phenylene). Effective conjugation along the polymer main chain is one of the most important reason to explain the superior luminescent properties of poly(2,7-carbazole) derivatives. Hence, some homopolymers and copolymers using the 2,7-linkage had been synthesized to understand their basic properties, but most of them investigated at that time were *N*-alkylcarbazole derivatives.^[2] Thus, we tried to synthesize poly(*N*-aryl-2,7-carbazole)s whose luminescent properties were expected to be superior to *N*-alkyl derivatives, because they had more rigid structures. Previously, we have reported that poly[*N*-[*p*-(2-ethylhexyloxy)phenyl]carbazol-2,7-ylene] had some good properties for application to PLED such as good solubility in organic solvents and quantitative fluorescence quantum efficiency in CHCl₃,^[3] but the number-average molecular weight ($M_n = 7700$) was not enough high to make homogeneous spin-coat films on a substrate. Nevertheless, the PLED device composed of ITO/PEDOT(PSS)/polymer/Ca/Al realized pure blue emission whose spectrum of electroluminescence (EL) was same to that of photoluminescence (PL) in the solid state, and it showed the good performance of maximum luminance of about 2000 cd m⁻² and efficiency higher than 0.2 cd A⁻¹ at 10 V. These results

suggested that poly (*N*-aryl-2,7-carbazole)s are potential materials for blue light emitters.

In this paper, we attempted to synthesize some novel poly(*N*-phenyl-2,7-carbazole)s having large dialkoxy side chains at *m*- and *p*-positions (**PmpXC**s: **PmpCzDC**, **PmpPhDC**, and **PmpCBiDC**), a large triarylsilyl substituent at *p*-position (**PpPhDSiC**) and a bulky diarylamino group at *m*-position (**PmPhDAC**) of the *N*-phenyl portion in order to develop high performance polymers for application to OLEDs in expectation of their high solubility, high molecular weights, intense luminance in a solid state^[4] and a good charge injection balance by modifying the energy level of HOMO. The chemical structures of these poly(*N*-aryl-2,7-carbazole)s are shown in Figure 1 together with **PmpEHC** and **PmEHAC** as comparison materials. The aromatic portions in the side chains are expected to assist carrier injection and carrier transport in solid films of the polymers, which should be important to apply the polymers to the devices. The molecular design and synthesis are based on the synthesis and properties of poly(*N*-phenyl-2,7-carbazole)s having dialkoxy groups and a diphenylamino group at the *N*-phenyl portion in our previous report.^[5] It is also presented initial evaluations of the PLED devices using these polymers.

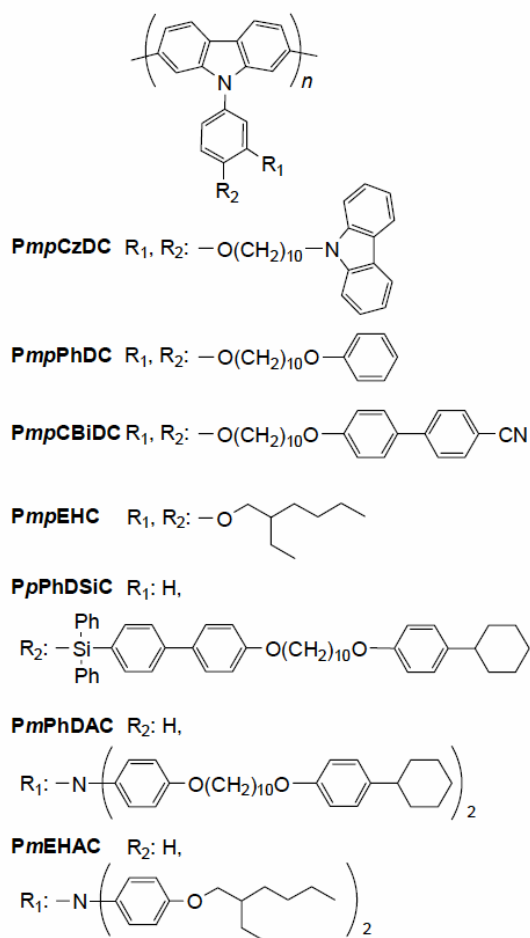


Figure 1. Chemical structures of poly(*N*-aryl-2,7-carbazole)s.

Experimental Part

Materials

N-(3,4-Dimethoxyphenyl)-2,7-dichlorocarbazole (**1**)

A mixture of 2,7-dichlorocarbazole^[6] (2.36 g, 10.0 mmol), 1-bromo-3,4-dimethoxybenzene (3.26 g, 15.0 mmol), CuI (63.0 mg, 0.331 mmol), potassium phosphate (2.97 g, 14.0 mmol), and *trans*-1,2-cyclohexanediamine (CHDA)^[7] (141 μ L, 1.30 mmol) in 1,4-dioxane (25 mL) was stirred at 110 °C for 5

days. After cooling to room temperature, CH₂Cl₂ was added to the reaction mixture. The organic layer was washed with H₂O and dried over Na₂SO₄. After evaporation, the residue was reprecipitated from a mixed solvent (CH₂Cl₂–methanol), affording **1** as a white solid (3.16 g, 85.0% yield).

¹H NMR (CDCl₃, 270 MHz): δ= 7.97 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 1.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.09–7.04 (m, 2H), 6.94 (d, *J* = 2.0 Hz, 1H), 4.00 (s, 3H), 3.94 (s, 3H).

¹³C-NMR (CDCl₃, 67.5 MHz): δ= 149.9, 149.0, 142.2, 135.0, 131.9, 129.0, 121.0, 120.6, 119.6, 111.8, 110.4, 110.0, 56.23, 56.21.

C₂₀H₁₅NCl₂O₂: Calcd. C 64.53, H 4.06, N 3.76; Found C 64.29, H 4.33, N 3.75.

N-(3,4-Dihydroxyphenyl)-2,7-dichlorocarbazole (**2**)

To a solution of **1** (2.97 g, 8.00 mmol) in CH₂Cl₂ 10.0 mL was added 1 M BBr₃ in CH₂Cl₂ (24.0 mL, 24.0 mmol) at –20 °C. The resulting mixture was stirred for 2 h at –20 °C. After stirring for 20 h at room temperature, NH₄Cl aq. was added to the reaction mixture, and then EtOAc was added to the reaction mixture. The organic layer was washed with H₂O and dried over Na₂SO₄. After evaporation, the residue was subjected to short pass column chromatography on silica gel with an eluent of CH₂Cl₂–EtOAc (10:1). After evaporation, the residue was reprecipitated from EtOAc–hexane, giving **2** (2.51 g, 91.8% yield) as a white solid.

¹H-NMR (DMSO-*d*₆, 270 MHz): δ= 9.47 (s, 2H), 8.24 (d, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.24 (d, *J* = 1.7 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 2.5 Hz, 1H), 6.84 (dd, *J* = 8.2, 2.5 Hz 1H).

^{13}C -NMR (DMSO- d_6 , 67.5 MHz): δ = 146.3, 145.6, 141.5, 130.8, 126.4, 122.0, 120.5, 120.2, 117.6, 116.3, 113.8, 109.4.

$\text{C}_{18}\text{H}_{11}\text{NCl}_2\text{O}_2$: Calcd C 62.81, H 3.22, N 4.07; Found C 62.58, H 3.55, N 4.02.

N-[3,4-Bis[10-(carbazol-9-yl)decyloxy]phenyl]-2,7-dichlorocarbazole (**3**)

A mixture of **2** (172 mg, 0.501 mmol), K_2CO_3 (276 mg, 2.00 mmol), and *N*-(10-bromodecyl)carbazole^[8] (456 mg, 1.64 mmol) in DMF (7 mL) was stirred at 130 °C for 24 h. After cooling to room temperature, CH_2Cl_2 was added to the reaction mixture. The organic layer was washed with H_2O , and successively dried over Na_2SO_4 . After evaporation, the residue was subjected to column chromatography on silica gel with an eluent of hexane- CH_2Cl_2 (3:2), affording **3** (442 mg, 92.3% yield) as a white solid.

^1H -NMR (CDCl_3 , 270 MHz): δ = 8.07 (m, 4H), 7.94 (d, J = 8.3 Hz, 2H), 7.45–7.34 (m, 8H), 7.27–7.17 (m, 8H), 7.02–6.92 (m, 3H), 4.29–4.21 (m, 4H), 4.05 (t, J = 6.6 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 1.87–1.76 (m, 8H), 1.52–1.25 (m, 24H).

^{13}C -NMR (CDCl_3 , 67.5 MHz): δ = 149.9, 149.0, 142.1, 140.3, 131.8, 128.8, 125.4, 122.7, 121.0, 120.9, 120.5, 120.2, 119.5, 118.6, 114.0, 112.5, 110.1, 108.5, 69.4, 43.1, 31.6, 29.8, 29.6, 29.5, 29.44, 29.39, 29.32, 29.28, 29.2, 29.0, 27.40, 27.36, 26.1, 25.9.

$\text{C}_{62}\text{H}_{65}\text{N}_3\text{Cl}_2\text{O}_2$: Calcd. C 77.97, H 6.86, N 4.40; Found C 77.78, H 7.19, N 4.21.

N-[3,4-Bis[10-(phenoxy)decyloxy]phenyl]-2,7-dichlorocarbazole (**4**)

In a similar way as the synthetic procedure for **3**, **2** was reacted with 1-bromo-4-(10-bromodecyloxy)benzene.^[9] After purification by silica gel column

chromatography with an eluent of hexane–CH₂Cl₂ (2:1), **4** was obtained as a white solid (389 mg, 96.5% yield).

¹H-NMR (CDCl₃, 270 MHz): δ= 7.94 (d, *J* = 8.2 Hz, 2H), 7.26–7.21 (m, 8H), 7.06–6.88 (m, 9H), 4.12–3.89 (m, 8H), 1.91–1.73 (m, 8H), 1.56–1.31 (m, 24H).

¹³C-NMR (CDCl₃, 67.5 MHz): δ= 158.9, 150.0, 149.1, 142.1, 131.8, 129.3, 128.8, 123.7, 120.9, 120.5, 120.33, 120.31, 119.5, 114.4, 114.0, 112.5, 110.0, 69.4, 67.8, 29.63, 29.61, 29.56, 29.55, 29.49, 29.46, 29.45, 29.43, 29.37, 29.35, 29.22, 29.21, 26.16, 26.1, 26.03, 26.02.

C₅₀H₅₉NCl₂O₄: Calcd. C 74.24, H 7.35, N 1.73; Found C 74.0, H 7.13, N 1.70.

N-[3,4-Bis[10-(4'-cyanobiphenyloxy)decyloxy]phenyl]-2,7-dichlorocarbazole (**5**)

In a similar way as the synthetic procedure for **3**, **2** was reacted with 4'-(10-bromodecyloxy)biphenyl-4-carbonitrile.^[10] The product was purified by silica gel column chromatography with an eluent of hexane–CH₂Cl₂ (4:1). After evaporation, the residue was reprecipitated from CH₂Cl₂–methanol, affording **5** (349 mg, 86.6% yield) as a white solid.

¹H-NMR (CDCl₃, 270 MHz): δ= 7.97 (d, *J* = 8.2 Hz, 2H), 7.69–7.60 (m, 6H), 7.52–7.48 (m, 4H), 7.28–7.04(m, 6H), 7.00–6.92 (m, 7H), 4.11–3.95 (m, 8H), 1.90–1.76 (m, 8H), 1.56–1.33 (m, 24H).

¹³C-NMR (CDCl₃, 67.5 MHz): δ= 159.6, 149.9, 149.2, 145.1, 142.1, 132.4, 131.8, 131.1, 128.8, 128.2, 126.9, 121.0, 120.9, 120.5, 119.5, 119.0, 114.9, 114.0, 112.5, 110.0, 109.9, 69.4, 68.1, 29.62, 29.58, 29.53, 29.47, 29.44, 29.40, 29.30, 29.26, 29.2, 26.12, 26.09, 26.0.

$C_{64}H_{65}N_3Cl_2O_4 \cdot 0.1 H_2O$: Calcd. C 75.89, H 6.49, N 4.15; Found C 75.66, H 6.54, N 3.99.

Poly[*N*-[3,4-bis[10-(carbazol-9-yl)decyloxy]phenyl]carbazol-2,7-ylene]

(PmpCzDC)

A mixture of 2,2'-bipyridine (bpy) (150 mg, 0.960 mmol), Ni(COD)₂ (264 mg, 0.959 mmol), DMF (2.0 mL), and COD (108 μ L, 0.880 mmol) was stirred at 50 °C for 40 min. To the mixture was added a solution of monomer **3** (318 mg, 0.334 mmol) in THF (2 mL), which was stirred at 70 °C for 2 days. The crude polymer was purified by reprecipitation from methanol, giving **PmpCzDC** (255 mg, 86.7% yield) as a yellow solid.

¹H-NMR (CDCl₃, 270 MHz): δ = 8.16–8.00 (br, 6H), 7.63–7.03 (br, 19H), 4.24–4.11 (br, 4H), 4.04 (br, 2H), 3.90 (br, 2H), 1.83–1.73 (br, 8H), 1.53–1.26 (br, 24H).

¹³C-NMR (CDCl₃, 67.5 MHz): δ = 149.7, 148.5, 142.4, 140.2, 140.0, 130.0, 125.4, 122.7, 122.6, 121.9, 120.21, 120.17, 119.8, 119.4, 118.6, 118.5, 113.9, 112.8, 108.5, 69.3, 43.0, 30.7, 29.8, 29.6, 29.5, 29.4, 29.3, 29.1, 29.0, 27.3, 26.1, 26.0.

(C₆₂H₆₅N₃O₂)_n: Calcd. C 84.22, H 7.41, N, 4.75; Found C 83.62, H 7.43, N 4.52.

Poly[*N*-[3,4-bis(10-phenoxydecyloxy)phenyl]carbazol-2,7-ylene] (**PmpPhDC**)

Similarly, **4** was polymerized using Ni(COD)₂, affording **PmpPhDC** (243 mg, 82.4% yield) as a yellow solid.

¹H-NMR (CDCl₃, 270 MHz): δ = 8.16 (br, 2H), 7.62–6.81 (br, 17H), 4.12–3.84 (br, 8H), 1.90–1.68 (br, 8H), 1.55–1.26 (br, 24H).

^{13}C -NMR (CDCl_3 , 67.5 MHz): δ = 158.9, 154.9, 149.8, 148.5, 148.3, 142.4, 140.4, 140.0, 130.0, 129.3, 121.9, 120.3, 119.8, 115.3, 114.4, 114.0, 112.8, 108.6, 69.3, 67.8, 29.6, 29.5, 29.4, 26.2, 26.1, 20.1.

$(\text{C}_{50}\text{H}_{59}\text{NO}_4)_n$: Calcd. C 81.37, H 8.06, N 1.90; Found C 79.82, H 7.87, N 2.17.

Poly[*N*-[3,4-bis[10-(4'-cyanobiphenyl)decyloxy]]phenyl]carbazol-2,7-ylene]
(PmpCBiDC)

Similarly, **5** was polymerized using $\text{Ni}(\text{COD})_2$, affording **PmpCBiDC** (236 mg, 92.9% yield) as a yellow solid.

^1H -NMR (CDCl_3 , 270 MHz): δ = 8.17 (br, 2H), 7.62–7.47 (br, 16H), 7.07–6.94 (br, 7H), 4.11–3.95 (br, 8H), 1.80 (br, 8H), 1.37–1.25 (br, 24H).

^{13}C -NMR (CDCl_3 , 67.5 MHz): δ = 159.6, 150.0, 149.8, 145.0, 138.4, 132.4, 131.1, 128.2, 126.9, 119.0, 114.9, 109.9, 108.5, 108.4, 69.4, 68.1, 29.63, 29.58, 29.54, 29.51, 29.4, 29.31, 29.26, 29.2, 26.2, 26.1.

$(\text{C}_{64}\text{H}_{65}\text{N}_3\text{O}_4)_n$: Calcd. C 81.76, H 6.97, N 4.47; Found C 81.23, H 6.96, N 4.41.

4-[(*p*-Bromophenyl)diphenylsilyl]-4'-methoxybiphenyl (**6**)

A mixture of bis(*p*-bromophenyl)diphenylsilane (1.48 g 3.00 mmol), 4-methoxyphenylboronic acid (304 mg 2.00 mmol), $\text{Pd}(\text{PPh}_3)_4$ (23 mg 0.020 mmol), THF (20 mL) and 1 M K_2CO_3 aq. (1.0 mL) was stirred at 70 °C for 2 days. After cooling to room temperature, CH_2Cl_2 was added to the reaction mixture. The organic layer was washed with H_2O and dried over Na_2SO_4 . After evaporation, the residue was subjected to column chromatography on silica gel with an eluent of hexane– CH_2Cl_2 (2:1), affording **6** (280 mg, 26.8 yield) as a white solid.

$^1\text{H-NMR}$ (CDCl_3 , 270 MHz): δ = 7.59–7.50 (m, 12H), 7.46–6.98 (m, 8H), 6.97 (dd, J = 6.8, 2.1 Hz, 2H), 3.83 (s, 3H).

$^{13}\text{C-NMR}$ (CDCl_3 , 67.5 MHz): δ = 159.2, 141.9, 137.8, 136.7, 136.2, 133.6, 133.2, 133.1, 131.3, 131.0, 129.7, 128.1, 127.9, 126.1, 124.6, 114.2, 55.3.

$\text{C}_{31}\text{H}_{25}\text{BrOSi}$: Calcd. C 71.39, H 4.83; Found C 71.89, H 5.25.

4-[(*p*-Bromophenyl)diphenylsilyl]-4'-hydroxybiphenyl (**7**)

In a similar way as the synthetic procedure for **2**, **6** was treated with BBr_3 . After purification by silica gel column chromatography with an eluent of CH_2Cl_2 , **7** was obtained as a white solid (313 mg, 78.1% yield).

$^1\text{H-NMR}$ (CDCl_3 , 270 MHz): δ = 7.57–7.24 (m, 20H), 6.89 (d, J = 8.4 Hz, 2H), 4.87 (s, 1H).

$^{13}\text{C-NMR}$ (CDCl_3 , 67.5 MHz): δ 155.2, 141.8, 137.8, 136.7, 136.2, 133.5, 133.4, 133.2, 131.5, 131.0, 129.7, 128.3, 127.9, 126.1, 124.6, 115.6.

$\text{C}_{30}\text{H}_{23}\text{BrOSi}$: Calcd. C 71.00, H 4.57; Found C 70.93, H, 4.57.

1-(10-bromodecyloxy)-4-cyclohexylbenzene (**8**)

According to the general procedure to synthesize ω -bromoalkyl arylether,^[10] 4-cyclohexylphenol was reacted with excess 1,10-dibromodecane in the presence of K_2CO_3 in DMF under stirring at 130 °C for 36 h. General procedures of ether extraction and successive silica gel column chromatography with an eluent of hexane– CH_2Cl_2 (5:1) afforded **8** as a white solid.

¹H-NMR (CDCl₃, 270 MHz): δ= 7.10 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 3.39 (t, *J* = 6.4 Hz, 2H), 2.43 (m, 1H), 1.87–1.70 (m, 8H), 1.41–1.29 (m, 18H).

¹³C-NMR (CDCl₃, 67.5 MHz): δ 157.0, 140.0, 127.4, 114.1, 67.9, 43.7, 34.8, 34.1, 32.9, 31.6, 29.8, 29.5, 29.4, 28.8, 28.2, 27.0, 26.3, 26.1.

C₂₂H₃₅BrO: Calcd. C 66.82, H 8.92; Found C 67.07, H 8.71.

4-[(*p*-Bromophenyl)diphenylsilyl]-4'-[10-(*p*-cyclohexyl-phenoxy)decyloxy]biphenyl
(**9**)

In a similar way as the synthetic procedure for **3**, **8** was reacted with **7**. The residue was reprecipitated from CH₂Cl₂–methanol, giving **9** (324 mg, 78.8% yield) as a white solid.

¹H-NMR (CDCl₃, 270 MHz): δ= 7.58–7.45 (m, 12H), 7.45–7.35 (m, 8H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.91 (t, *J* = 6.6 Hz, 2H), 2.43 (m, 1H), 1.85–1.71 (m, 8H), 1.44–1.25 (m, 18H).

¹³C-NMR (CDCl₃, 67.5 MHz): δ= 158.8, 157.0, 142.0, 140.0, 137.8, 136.4, 136.2, 133.6, 133.2, 132.8, 131.2, 131.0, 129.7, 128.0, 127.9, 127.5, 126.1, 124.6, 114.8, 114.2, 68.1, 67.9, 43.7, 34.8, 31.6, 29.6, 29.4, 27.4, 26.3, 26.3, 26.1.

C₅₂H₅₇BrO₂Si: Calcd. C 75.98, H 6.99; Found C 76.36, H 6.99.

N-[4-[4-[4'-[10-(4-Cyclohexylphenoxy)decyloxy]biphenyl]diphenylsilyl]phenyl]-2,7-dichlorocarbazole (**10**)

A mixture of dichlorocarbazole (71.0 mg, 0.301 mmol), **9** (271 mg, 0.330 mmol), Pd(OAc)₂ (3.0 mg, 0.015 mmol), *t*-BuONa (115 mg, 1.20 mmol), toluene (3 mL),

and P(*t*-Bu)₃ 10 wt% in hexane (880 μL, 0.0298 mmol) was stirred at 110 °C for 24 h. After cooling to room temperature, CH₂Cl₂ was added to the reaction mixture. The organic layer was washed with H₂O and dried over Na₂SO₄. After evaporation, **10** was obtained as a white solid (294 mg, 100% yield).

¹H-NMR (CDCl₃, 270 MHz): δ= 7.98 (d, *J* = 8.2 Hz, 2H), 7.86–7.80 (m, 2H), 7.77–7.39 (m, 20H), 7.27–7.24 (m, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 2.45–2.43 (m, 1H), 1.82–1.73 (m, 8H), 1.56–1.26 (m, 18H).

¹³C-NMR (CDCl₃, 67.5 MHz): δ 158.9, 157.0, 141.4, 140.0, 138.1, 137.9, 136.7, 136.3, 133.6, 132.0, 129.8, 128.04, 128.01, 127.98, 127.5, 126.2, 126.0, 125.9, 121.4, 121.03, 120.98, 120.5, 114.8, 114.2, 110.2, 107.1, 68.1, 67.9, 43.7, 34.8, 29.6, 29.44, 29.36, 27.0, 26.3, 26.1.

C₆₄H₆₃NCl₂O₂Si·0.3 toluene: Calcd. C 79.01, H 6.56, N 1.39; Found C 79.39, H 6.70, N, 1.65.

Poly[*N*-[4-[4-[4'-[10-(4-cyclohexylphenoxy)decyloxy]biphenyl]diphenylsilyl]phenyl]carbazol-2,7-ylene] (**PpPhDSiC**)

Similarly, **10** was polymerized using Ni(COD)₂, giving **PpPhDSiC** (185 mg, 82.0% yield) as a yellow solid.

¹H-NMR (CDCl₃, 270 MHz): δ= 8.09 (br, 2H), 7.76–7.33 (m, 24H), 7.00 (br, 2H), 6.86 (br, 2H), 6.75–6.71 (m, 2H), 3.86–3.81 (br, 4H), 2.36–2.30 (br, 1H), 1.74–1.71 (br, 8H), 1.35–1.25 (br, 18H).

^{13}C -NMR (CDCl_3 , 67.5 MHz): δ = 158.8, 157.0, 141.9, 140.0, 137.9, 136.7, 136.3, 133.8, 129.7, 127.9, 127.4, 126.1, 123.6, 120.2, 117.4, 114.7, 114.1, 109.0, 68.0, 67.9, 43.7, 34.8, 29.6, 29.4, 27.0, 26.3, 26.1.

$(\text{C}_{64}\text{H}_{63}\text{NO}_2\text{Si})_n$: Calcd. C 84.82, H 7.01, N 1.55; Found C 83.71, H 6.98, N 1.88.

1-[10-(cyclohexylphenoxy)decyloxy]-4-iodobenzene (**11**)

A mixture of *p*-iodophenol (220 mg, 1.00 mmol), K_2CO_3 (276 mg, 2.00 mmol), and **8** (396 mg, 1.00 mmol) in DMF (10 mL) was stirred at 130 °C for 36 h. After cooling to room temperature, CH_2Cl_2 was added to the reaction mixture. The organic layer was washed with H_2O , and successively dried over Na_2SO_4 . After evaporation, the residue was reprecipitated from CH_2Cl_2 –methanol, giving **11** (451 mg, 84.0% yield) as a white solid.

^1H -NMR (CDCl_3 , 270 MHz): δ = 7.53 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 8.7 Hz, 2H), 3.94–3.87 (m, 4H), 2.43 (br, 1H), 1.83–1.70 (m, 8H), 1.41–1.32 (m, 18H).

^{13}C -NMR (CDCl_3 , 67.5 MHz): δ = 158.8, 157.0, 140.0, 138.0, 127.5, 116.8, 114.1, 82.3, 68.1, 67.9, 43.7, 34.8, 33.6, 29.5, 29.42, 29.40, 29.2, 27.0, 26.3, 26.2, 26.1.

$\text{C}_{28}\text{H}_{39}\text{IO}_2 \cdot 0.2\text{H}_2\text{O}$: Calcd. C 62.50, H 7.38; Found C 63.23, H 7.26.

N-[3-[*N*-[10-(4-Cyclohexylphenoxy)decyloxyphenyl]amino]phenyl]-2,7-dichloro-carbazole (**12**)

A mixture of *N*-(3-aminophenyl)-2,7-dichlorocarbazole (133 mg, 0.250 mmol), **11** (402 mg, 0.776 mmol), $\text{Pd}(\text{OAc})_2$ (3.0 mg, 0.015 mmol), *t*-BuONa (96 mg, 1.0 mmol), toluene (3 mL), and $\text{P}(t\text{-Bu})_3$ 10 wt% in hexane (72 μL , 0.025 mmol) was

stirred at 110 °C for 4 days. After cooling to room temperature, CH₂Cl₂ was added to the reaction mixture. The organic layer was washed with H₂O and dried over Na₂SO₄. After evaporation, the residue was subjected to column chromatography on silica gel with an eluent of hexane–CH₂Cl₂ (5:1), giving **12** (100 mg, 55.0% yield) as a yellow solid.

¹H-NMR (CDCl₃, 270 MHz): δ= 7.95 (d, *J* = 8.2 Hz, 2H), 7.43–7.40 (m, 2H), 7.21–7.08 (m, 7H), 6.97–6.80 (m, 7H), 5.67 (s, 1H), 3.94–3.87 (m, 4H), 2.43 (m, 1H), 1.81–1.75 (m, 8H), 1.40–1.32 (m, 18H).

¹³C-NMR (CDCl₃, 67.5 MHz): δ= 157.1, 155.6, 147.4, 141.6, 140.0, 137.4, 134.0, 131.8, 130.8, 127.5, 123.6, 121.1, 120.9, 120.6, 117.0, 115.4, 114.5, 114.2, 112.8, 110.3, 68.4, 68.0, 43.7, 34.8, 28.6, 29.4, 27.0, 26.3, 26.15, 26.11.

C₄₆H₅₀Cl₂N₂O₂: Calcd. C 75.29, H 6.87, N, 3.82; Found C 74.98, H 7.01, N 3.82.

N-[3-[*N,N*-Bis[10-(4-cyclohexylphenoxy)decyloxyphenyl]amino]phenyl]-2,7-dichloro-*o*carbazole (**13**)

In a similar way as the synthetic procedure for **12**, **11** was reacted with **12**, giving **13** (145 mg, 93.0% yield) as a brown solid.

¹H-NMR (CDCl₃, 270 MHz): δ= 7.91 (d, *J* = 8.4 Hz, 2H), 7.39–7.08 (m, 13H), 7.00–6.80 (m, 11H), 3.94–3.89 (m, 8H), 2.45–2.41 (m, 2H), 1.82–1.70 (m, 16H), 1.44–1.20 (m, 36H).

¹³C-NMR (CDCl₃, 67.5 MHz): δ 157.0, 155.8, 150.6, 141.3, 140.0, 139.8, 136.9, 131.8,, 130.2, 127.4, 126.9, 121.2, 120.9, 120.6, 118.4, 117.3, 117.1, 115.4, 114.1, 110.3, 68.2, 67.9, 43.7, 34.8, 29.44, 29.38, 29.2, 27.0, 26.2, 26.1.

$C_{74}H_{88}N_2Cl_2O_4 \cdot 2.5 H_2O$: Calcd. C 74.98, H 7.91, N 2.36; Found C 74.89, H 7.68, N 2.04.

Poly[*N*-[3-[*N,N*-Bis[10-(4-cyclohexylphenoxy)decyloxyphenyl]amino]phenyl]-2,7-dichlorocarbazole] (**PmPhDAC**)

Similarly, **13** was polymerized using $Ni(COD)_2$, giving **PmPhDAC** (75.0 mg, 71.0% yield) as a yellow solid.

1H -NMR ($CDCl_3$, 270 MHz): δ = 8.13 (br, 2H), 7.73–7.54 (br, 3H), 7.37–7.29 (br, 2H), 7.00–6.93 (br, 11H), 6.73–6.59 (br, 8H), 3.83–3.50 (br, 8H), 2.43 (br, 2H), 1.74–1.62 (m, 16H), 1.27–1.16 (m, 36H).

^{13}C -NMR ($CDCl_3$, 67.5 MHz): δ = 157.0, 155.7, 141.6, 139.99, 139.96, 127.4, 126.9, 120.4, 115.3, 114.6, 114.1, 100.5, 67.92, 67.89, 43.7, 34.8, 29.6, 29.4, 29.3, 27.0, 26.3, 26.2, 26.1.

$(C_{74}H_{88}N_2O_4)_n$: Calcd. C 83.10, H 8.29, N 2.62; Found C 80.74, H 8.14, N 2.28.

General Method and Instrumentations

All synthetic manipulations were performed by a standard technique using a Schlenk tube under an argon atmosphere. Column chromatography was performed using a silica gel (Kanto Chem., 60 N, 63–120 μm). NMR spectrum was recorded on a JEOL EX-270 spectrometer. 1H and ^{13}C chemical shifts are given in units of δ (ppm) relative to δ (TMS) = 0.00 and δ ($CDCl_3$) = 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 CHCl_3 and in a form of coating thin film on quartz glass were performed using a U-3500 spectrophotometer (Hitachi) and an F-4500 fluorescence spectrophotometer (Hitachi). The measurement of HOMO energy level of the polymer films on a Pt disk was performed at a scan rate of 50 mV/s in acetonitrile containing 0.1 M Et_4NBF_4 at room temperature under Ar using a saturated calomel electrode (SCE) as the reference and platinum wire as the counter electrode. The electrochemical data (vs. SCE) obtained by cyclic voltammetry was made a correction with the redox potential (4.8 eV) of ferrocene/ferrocenium⁺.

Device fabrication

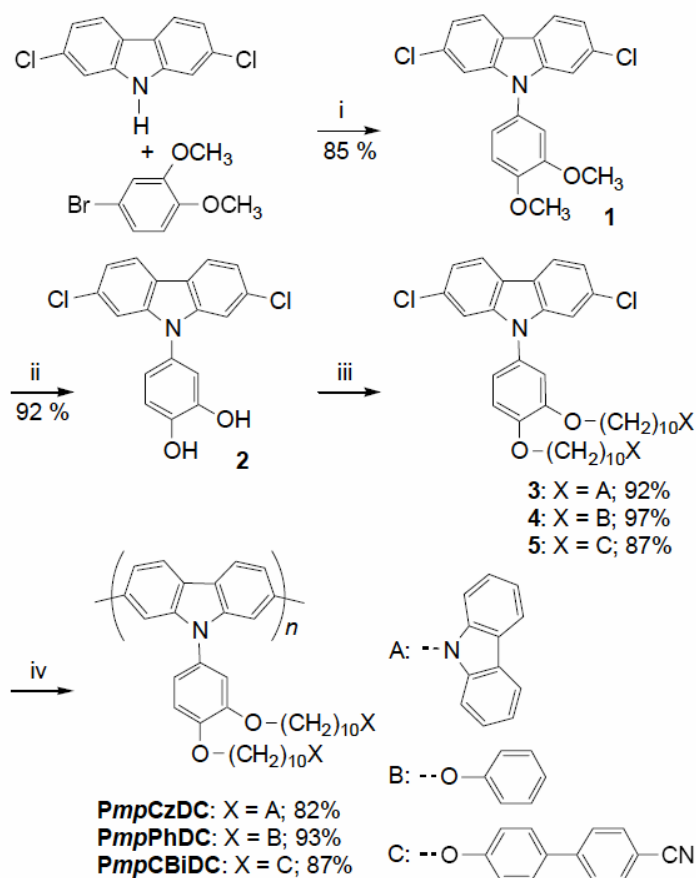
An ITO glass was cleaned by ultrasonication in a solution of detergent for 5 min. It was rinsed with flowing water, dried with spin coater (3000 rpm for 60 seconds) and then, treated with an ultraviolet irradiation (Filgen UV253) for 20 minutes. PEDOT(PSS) aq. (Baytoron PVP Al 4083) which filtered out through a 0.45 μm pore filter was spin-coated on the cleaned ITO glass with 200 rpm for 5 seconds and 1000 rpm for 60 seconds in order. To remove water, it was dried on a hot plate for 15 minutes at 200 °C. A polymer solution (in toluene) which filtered out through a 0.5 μm pore filter was spin-coated over the PEDOT(PSS)-coated ITO glass with 500 rpm for 5 seconds and 2000 rpm for 60 seconds in order. 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-350M/ERH. The device configuration was ITO (150 nm)/PEDOT(PSS) (90 nm)/polymer (70–90 nm)/CsF (2 nm)/Al (150 nm). The evaluation of the PLED devices having an active surface area of 2 mm × 2 mm was carried out with a Hamamatsu C9920-12 system.

Results and Discussions

Synthesis of Polymers.

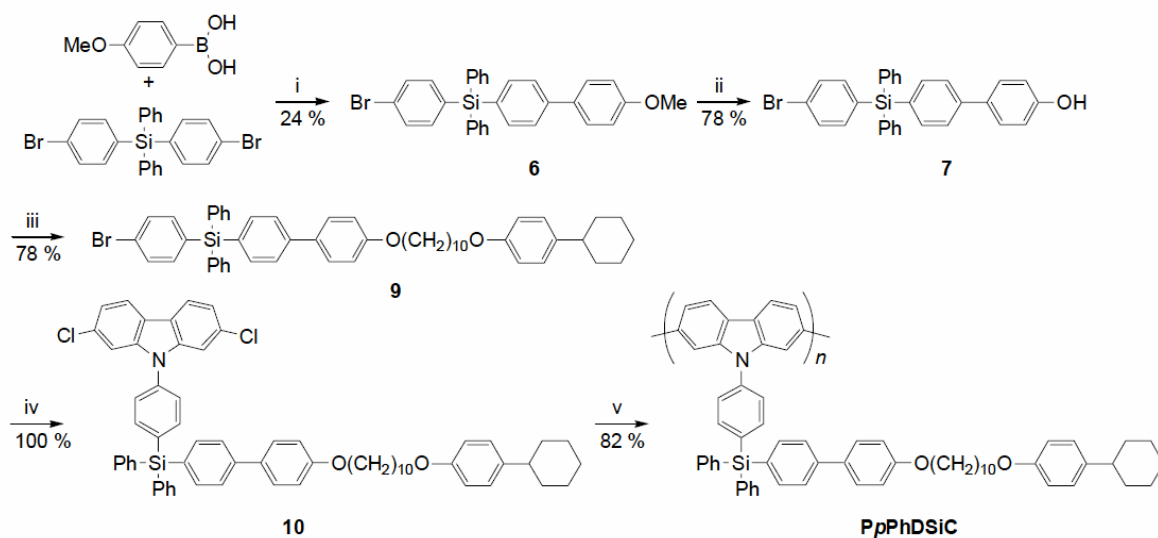
In our previous investigation,^[5] introduction of 2-ethylhexyloxy substituent at *m*- and *p*-positions of the *N*-phenyl portion of poly(*N*-phenyl-2,7-carbazole) was effective to show good blue luminescent properties, and the resulting polymer (**PmpEHC**) had an enough high molecular weight. Thus, it is attempted to synthesize some poly(*N*-aryl-2,7-carbazole)s having dialkoxy groups at *m*- and *p*-positions of the *N*-phenyl portion (**PmpCzDC**, **PmpPhDC**, **PmpCBiDC**), and Scheme 1 exhibits their synthetic route. The substituents introduced in this study are functional aromatic moieties bearing a decyloxy spacer. To facilitate the synthesis of the monomers (**3**, **4**, and **5**), we adopted a synthetic route involving etherification of **2** with the 10-bromodecyl derivatives. Polymerization of these monomers by Yamamoto method^[11] afforded the polymers **PmpXDCs** in good yield (**PmpCzDC**: 82%, **PmpPhDC**: 93%, **PmpCBiDC**: 87%), respectively.



Scheme 1. Synthetic route of **PmpCzDC**, **PmpPhDC** and **PmpCBiDC**: (i) CuI, K₃PO₄, CHDA, 1,4-dioxane, 110 °C; (ii) BBr₃, CH₂Cl₂, -20 °C to room temperature; (iii) Br(CH₂)₁₀X, K₂CO₃, DMF, 130 °C; (iv) Ni(COD)₂, COD, bpy, DMF–THF, 70 °C.

Next, the synthetic route of poly(*N*-aryl-2,7-carbazole)s having a silyl group at *p*-position of the *N*-phenyl portion (**PpPhDSiC**) is summarized in Scheme 2. The Si linkages make a bigger bone structure than corresponding carbon linkages do. Thus, **PpPhDSiC** is expected to avoid forming excimer due to having a large steric hindered substituent at the *N*-position. In fact, tetraphenylsilane effectively inhibited intermolecular interactions due to the rigid and noncoplanar structure.^[12]

Furthermore, polymers involving silane usually show good solubility in common organic solvents and frequently realize intense luminescence both in solution and solid states⁴ probably due to contribution of d- π interaction.

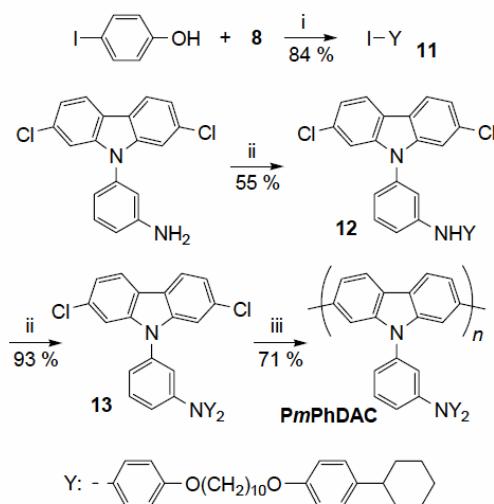


Scheme 2. Synthetic route of **PpPhDSiC**: (i) Pd(PPh₃)₄, K₂CO₃, THF–H₂O; (ii) BBr₃, CH₂Cl₂, –20 °C to room temperature; (iii) **8**, K₂CO₃, DMF; (iv) 2,7-dichlorocarbazole, Pd(OAc)₂, P(*t*-Bu)₃, *t*-BuONa, toluene, 110 °C; (v) Ni(COD)₂, COD, bpy, DMF–THF, 70 °C.

Suzuki coupling reaction^[13] of bis(*p*-bromophenyl)diphenylsilane^[14] with 4-methoxyphenylboronic acid in the presence of the Pd(PPh₃)₄ catalyst gave **6**. After cleavage of the methoxy group of **6** with BBr₃, **7** was etherified with 1-(10-bromodecyloxy)-4-cyclohexylbenzene (**8**) that was prepared in advance, affording **9**. In the case of *N*-arylation of 2,7-dichlorocarbazole with **9**, we tried first the same procedure as the preparation of **1**, but the reaction did not proceed. Hence,

we applied another method using the Pd(OAc)₂-P(*t*-Bu)₃-catalyst. In this case, the monomer **10** was obtained in an excellent yield (100%). Polymerization of the monomer gave **PpPhDSiC** in 82% yield.

Scheme 3 illustrates the synthetic route of the poly(*N*-aryl-2,7-carbazole)s having the diphenylamino group at the *m*-position of the *N*-phenyl portion (**PmPhDAC**). This polymer is expected to perform as an EL emitting material, because the polymer has small barrier of charge injection on account of the high HOMO energy level. In addition, optical properties of the *m*-substituted polymer (**PmEHAC**) were superior to those of *p*- and *o*-substituted ones.^[5] The stepwise *N*-arylation of *N*-(3-aminophenyl)-2,7-dichlorocarbazole with **11** was carried out, affording **12** and **13**, in order. Polymerization of **13** using Ni(COD)₂ gave **PmPhDAC** in 71% yield.



Scheme 3. Synthetic route of **PmPhDAC**: (i) K₂CO₃, DMF, 130 °C; (ii) **11**, Pd(OAc)₂, P(*t*-Bu)₃, *t*-BuONa, toluene, 110 °C; (iii) Ni(COD)₂, COD, bpy, DMF-THF, 70 °C.

All resulting polymers were obtained as a pale-yellow solid. They were well soluble in usual organic solvents such as THF, CHCl₃ and toluene, and were purified by reprecipitation from methanol. These polymers have good processability to make thin cast films. The GPC results are summarized in Table 1. In general, these polymers have moderate degrees of polymerizations (D. P.) and show low polydispersities (M_w/M_n). Exceptionally, the high polydispersity observed in **PmpCBiDC** might be due to a high aggregation property of the cyanobiphenyl portion in the side chain.

Table 1. GPC analysis results of the polymers.

Polymer	$M_n^a)$	$M_w^a)$	M_w/M_n	D. P. ^{b)}
	g mol ⁻¹	g mol ⁻¹		
PmpCzDC	13900	24400	1.8	16
PmpPhDC	17200	35300	2.1	23
PmpCBiDC	12000	53100	4.4	13
PmpEHC	29000	79900	2.8	58
PpPhDSiC	9900	17800	1.8	10
PmPhDAC	11100	16100	1.5	10

^{a)} GPC analysis was carried out in THF using polystyrene as the standard.

^{b)} The degree of polymerization was estimated from M_n .

Optical Properties

The optical properties of the poly(*N*-phenyl-2,7-carbazole) derivatives are summarized

in Table 2. The shapes of each absorption and PL spectra of these polymers in solution were almost same. Figure 2 and 3 show the absorption and PL spectra of the polymers in the thin film state, respectively. In dilute solutions and in the state of thin films, the polymers exhibited an absorption band around 350–400 nm due to π - π^* transition. In the case of **PmpCzDC**, two additional absorption bands are observed at 330 nm and 350 nm, which is attributed to the carbazole portions in the side chain.^[15] The HOMO–LUMO energy gaps (E_g) of the polymers estimated from absorption edge of the thin film samples are almost equivalent, being in the range from 2.87 to 2.94 eV. On the other hand, the HOMO energy levels estimated from the oxidation potentials^[16] are found in the range from –5.28 to –5.70 eV. **PmPhDAC** having the triphenylamino portion has the highest energy level of HOMO, while **PpPhDSiC** shows the lowest one. All the polymers exhibited two main fluorescence peaks at about 415 nm and 440 nm in CHCl_3 and at 435 nm and 450 nm in the solid state. The PL peaks observed around 415 nm in CHCl_3 and 435 nm in the thin film state are attributed to 0–0 emission. The other PL bands which appeared in the region of longer wavelength are mainly due to vibronic effect in solution and combined effects of vibronic and excimeric in the solid state. The vibronic fine structure is generally associated with a rigid and well-defined backbone in the excited state.^[17] Since a steric constraint of the polymers influences large intra- and intermolecular interactions in the solid state, PL spectra in the solid state were certainly different from those in the solution. Especially, the PL spectra of **PmpCzDC** and **PmpPhDC** bearing planar aromatic portions were broadened, decreasing color purity of the blue PL emission in the solid state.

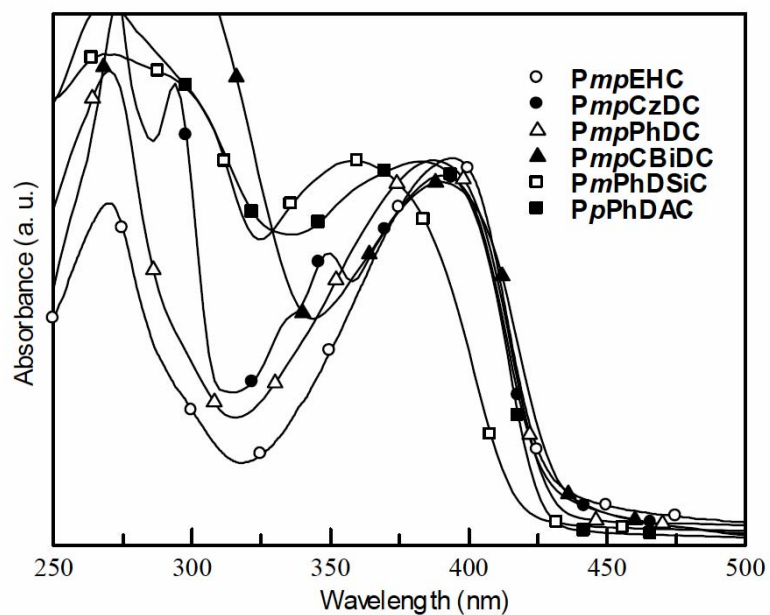


Figure 2. Absorption spectra of the polymers in the thin film state.

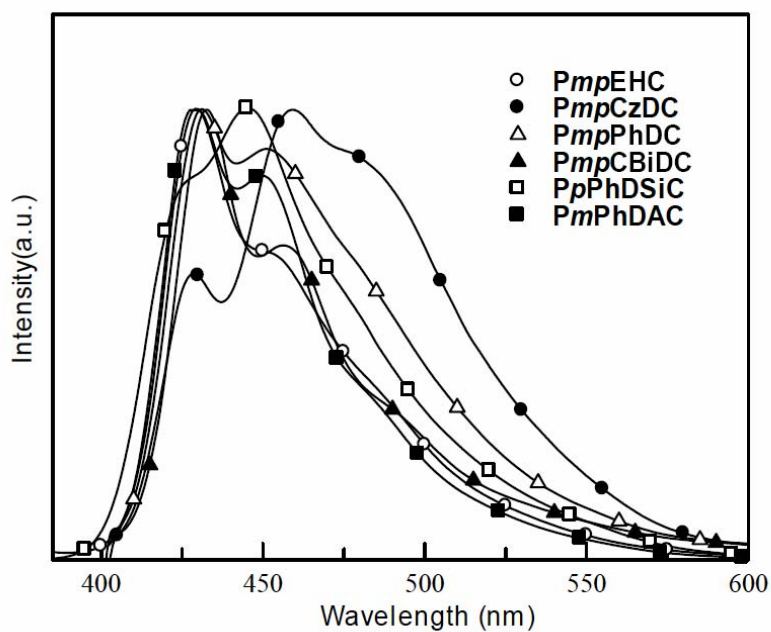


Figure 3. PL spectra of the polymers in the thin film state.

Table 2. Optical properties of the polymers.

Polymer	Abs. λ_{\max}		Em. λ_{\max}		HOMO ^{a)}	LUMO ^{b)}	E_g	ϕ_f ^{c)}
	nm		nm		eV	eV	eV	
	in CHCl ₃	Film	in CHCl ₃	Film				
PmpCzDC	384	390	411, 437	428, 459	-5.49	-2.60	2.89	0.96
PmpPhDC	384	388	414, 437	430, 450	-5.50	-2.62	2.88	0.96
PmpCBiDC	378	390	414, 438	432, 455	-5.60	-2.69	2.91	0.76
PmpEHC	389	394	417, 439	430	-5.62	-2.69	2.93	0.80
PpPhDSiC	356	358	411	445	-5.70	-2.76	2.94	0.87
PmPhDAC	376	382	410, 442	428, 450	-5.28	-2.41	2.87	0.07
PmEHAC	391	397	418	430	-5.27	-2.37	2.90	0.19

a) The HOMO energy levels vs. vacuum level were calculated from oxidation potentials according to the report in a literature.^[16]

b) The LUMO levels were determined from the optical band gap and the HOMO Level.

c) Referred to 9,10-diphenylanthracene ($\phi_f = 0.90$) in cyclohexane.

The fluorescence quantum yields of **PmpCzDC**, **PmpPhDC**, **PmpCBiDC** **PmpEHC** and **PpPhDSiC** in CHCl₃ were satisfactorily high. It is worth noticing that the

introduction of the large side substituents into the *N*-phenyl portion was effective to retain the excellent quantum efficiencies of polycarbazoles. On the other hand, the quantum yield of **PmPhDAC** was extremely low, which might be due to an exciton quenching through the triphenylamino portion directly linked to the conjugated main chain as well as **PmEHAC**.^[5] On the contrary, the thin solid films of these polymers were fluoresced intense in all cases.

Electroluminescence

Single layer PLEDs having the device structure of ITO/PEDOT(PSS)/polymer/CsF/Al were constructed using the polymers as the emitting layer material. Principal characteristics of these devices are summarized in Table 3. Figure 4 shows typical EL spectra of the polymers. These EL spectra were basically similar to corresponding PL spectra in the film state (Figure 3). Figure 5 and 6 show the changes of luminance and chromaticity vs. operating voltages, respectively. In most cases, voltages being confirmed luminance of these devices (turn-on voltages) were less than 5 V. These performances were generally superior to those of the device having a configuration of ITO/PEDOT(PSS)/**PmpEHC**/Ba/Al in our recent preliminary result.^[18]

Table 3. EL properties of the polymers.

Polymer	L_{\max} (voltage)	Current density at L_{\max}	Maximum efficiency (voltage)	Turn-on voltage	$\lambda_{\max}^{\text{EL}}$ at L_{\max}	CIE (x, y) at L_{\max}
	cd m^{-2} (V)	mA cm^{-2}	cd A^{-1} (V)		nm	
PmpCzDC	16540 (9)	1460	2.05 (4)	4	495	0.22, 0.38
PmpPhDC	14680 (11)	1671	0.88 (11)	4	502	0.25, 0.47
PmpCBiDC	489 (8)	1293	0.06 (5)	4	433	0.17, 0.16
PmpEHC	18800 (11)	1991	0.95 (11)	4	488	0.22, 0.36
PpPhDSiC	2557 (15)	848	0.41 (8)	7	483	0.21, 0.31
PmPhDAC	1170 (10)	541	0.22 (10)	5	426	0.19, 0.20
PmEHAC	272 (17)	114	0.37 (10)	8	461	0.20, 0.24

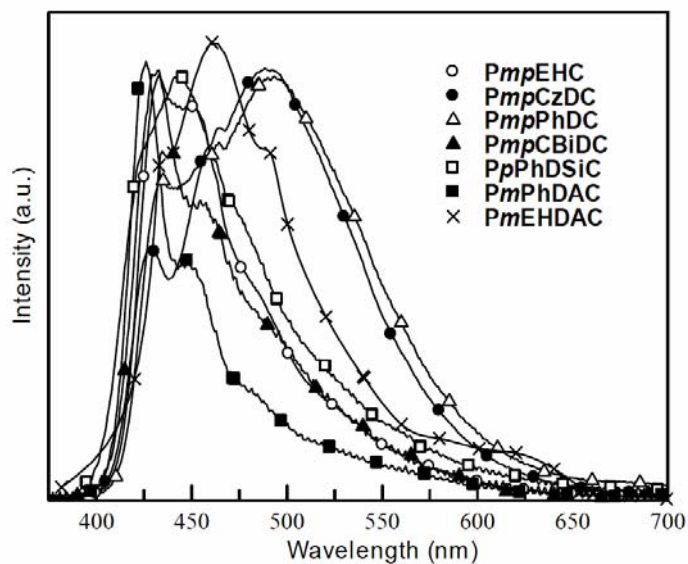


Figure 4. EL spectra of the polymers under the operating voltage at 8 V except for **PpPhDSiC** and **PmEHAC** at 12 V.

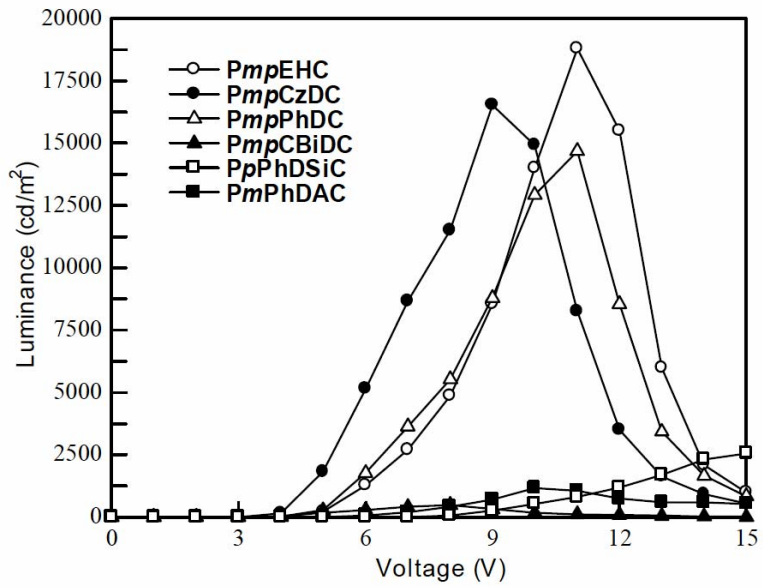


Figure 5. Luminance intensities vs. operating voltages.

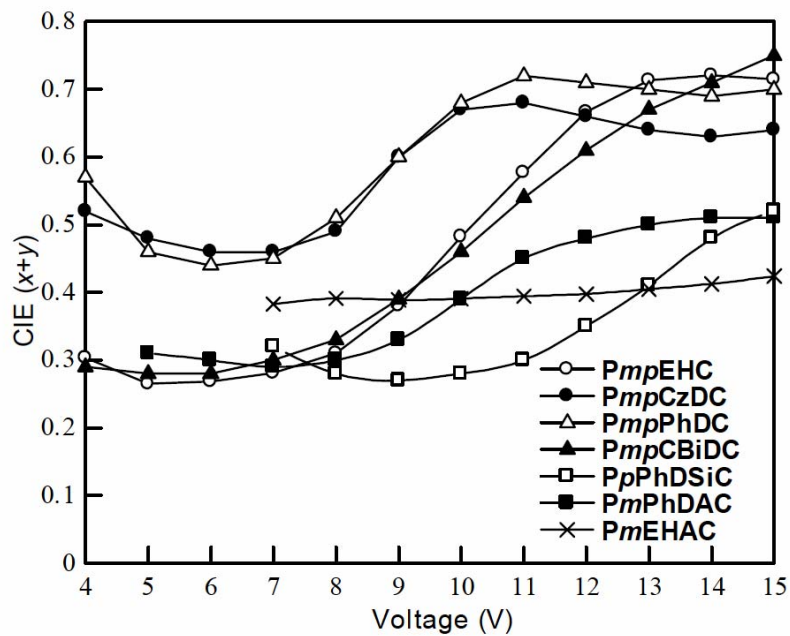


Figure 6. CIE (x + y) values vs. operating voltages.

The devices embedded with **PmpXC**s (**PmpCzDC**, **PmpPhDC**, and **PmpEHC**) which have dialkoxy groups at *m*- and *p*-positions of the *N*-phenyl portion showed high maximum luminance (L_{\max}) over 15000 cd m⁻² under applied voltages at about 10 V. In the case of the device embedded with **PmpCBiDC** that is also a type of **PmpXC**, the L_{\max} was unexpectedly low. The high aggregation property and poor solubility in toluene caused a rough interface of the emitting polymer layer in the device, which might bring about the poor performance. The current densities of these devices showed high values of over 1200 mA cm⁻² at L_{\max} . The large current densities which proportionally increased vs. applied voltages suggests that carrier mobility of these polymers in the devices are enough high but balance of carriers to form exciton is hardly adequate. Thus, modification of the device structure might improve the efficiencies, although the efficiency of the **PmpCzDC** device exceeded about 2 cd A⁻¹ at the initial stage. Color purity of the blue EL decreased as stepping up the applied voltages of these PLED devices. Since *x* and *y* values of CIE (*x*, *y*) indices range from minimum values (0.16, 0.11) to maximum values (0.29, 0.47) in these cases, CIE (*x* + *y*) values roughly indicate EL colors of the devices at each operating voltages (Figure 6). When the CIE (*x* + *y*) values are in the range of 0.27–0.4, 0.4–0.6, and 0.6–0.76, luminescence colors approximately correspond to blue, blue-green, and green, respectively. A blue EL color of the **PmpEHC** device (*x*, *y* = 0.16, 0.12) at 7 V changed to greenish blue (0.20, 0.28) at 10 V and, successively, green (0.24, 0.43) at 12 V. In the cases of the **PmpCzDC** and **PmpPhDC** devices, the EL colors at starting 4 V were already blue green, and the colors readily changed to green at 10 V. From these results, **PmpXC**s are concluded to be a family of intense luminescence materials for EL, but exciton generations under the unbalanced carrier

injection and transport conditions considerably decrease the color purity of blue EL. In addition, the planar aromatic moieties in the side substituents cause some exciplex interactions between the conjugated main chains, which resulted in decreasing the color purity of blue EL, although they might assist carrier transport in the solid state. In the case of the **PpPhDSiC** device, the turn-on voltage was 7 V, which was exceptionally high. A large injection barrier between the interfaces of the ITO coated with PEDOT(PSS) and **PpPhDSiC** whose HOMO level is low (-5.70 eV) might be a reason for the higher turn-on voltage than the others. The luminance proportionally increased vs. operating voltages, reaching to about 2500 cd m⁻² at 15 V, and the maximum current efficiency was 0.41 cd A⁻¹ at 8 V. Shapes of EL spectra until 12 V were similar each other showing a sharp emission peak at 441 nm with a shoulder around 423 nm, while a new emission band at about 480 nm developed under higher operating voltages than 12 V. The colors of EL fell in the range from purplish blue (0.17, 0.11) to bluish green (0.23, 0.38).

The EL spectrum of the device embedded with **PmPhDAC** was narrowest of all, and pure blue emissions whose CIE values are smaller than ($x, y = 0.19, 0.20$) were realized under operating voltages below 10V. The color purity of the blue EL almost retained in the range of the operating voltages (5–15 V) as well as the **PmEHAC** device. Although the L_{\max} was relatively low (1170 cd m⁻²) by comparison with the **PmpXC** devices, the initial performance admits of improvement by optimizing the device structure. It should be noted that **PmPhDAC** showed higher performances as the blue emitting material for the PLED device than **PmEHAC** in this work and poly[*N*-[*p*-(diarylamino)phenyl]carbazole] reported recently.^[19]

Conclusion

In this paper, we presented the syntheses and characterizations of some novel poly(*N*-phenyl-2,7-carbazole)s with the dialkoxy groups at *m*- and *p*-positions (**PmpCzDC**, **PmpPhDC**, **PmpCbiDC**), silyl group at *p*-position (**PpPhDSiC**) and diphenylamino group at *m*-positions (**PmPhDAC**) of the *N*-phenyl portion, and demonstrated that these polymers could be used as the blue emitting layer materials of the PLED device (ITO/PEDOT(PSS)/polymer/CsF/Al). That is, these polymers basically had the relatively high molecular weights (9900–17000 g mol⁻¹), good solubility in common organic solvents, acceptable shallow HOMO levels (5.28–5.70 eV), the conjugated backbone showing excellent fluorescence quantum efficiency, and proper band gaps (E_g) for blue emission.

A reason to introduce the large side substituents into the poly(*N*-phenyl-2,7-carbazole)s was to exclude interactions between the polymer chains for fear of emission of impure blue EL from excimeric species. At the same time, the large side substituents present in interchain of the polymers must disturb proper carrier transportations in the polymer thin films. This discrepancy might be resolved by assistance of aromatic portions in the side chain. As a result, the aromatic moieties in the side chain of **PmpXC**s might assist keeping the proper carrier mobility, which resulted in the high current densities of the PLED devices. In particular, the **PmpCzDC** device realized the highest EL efficiency. On the other hand, color purity of the blue EL of the **PmpXC**s devices seriously decreased during high operating voltages, which suggested occurrence of an undesired exciplex interaction between the polymer main chain and the planar aromatic portion in the side chain. However, introduction of the more sterically hindered aromatic portion,

the cyclohexylphenyl moiety into the side chain, could minimize the interaction. Hence **PmPhDAC** showed the higher performances in the PLED device than **PmEHAC**, i.e., exhibiting the narrower EL spectrum, purer blue emission, more intense L_{\max} , and higher luminous efficiency, which could demonstrate significance of the steric hindered aromatic side chains.

Lastly, we would like to describe limit values (CIE (x, y), L and η at the limit operating voltage (V_{lim})) of pure blue EL realized from the PLED devices embedded with poly(2,7-carbazole)s; **PmpEHC**: ((0.17, 0.14), 5000 cd m^{-2} , 0.57 cd A^{-1} , 8 V), **PmpCBiDC**: ((0.17, 0.16), 490 cd m^{-2} , 0.04 cd A^{-1} , 8 V), **PpPhDSiC**: ((0.19, 0.22), 1700 cd m^{-2} , 0.27 cd A^{-1} , 13 V), **PmPhDAC**: ((0.19, 0.20), 1200 cd m^{-2} , 0.22 cd A^{-1} , 10 V), and **PmEHAC**: ((0.19, 0.22), 220 cd m^{-2} , 0.26 cd A^{-1} , 15 V), respectively. In general, the blue colors observed under operating voltages below V_{lim} become deeper although their L intensities decrease.

Acknowledgement:

We thank to the Research Facility Center for Science and Technology, Chemical Analysis Division, University of Tsukuba, for NMR, PL, and elemental analysis data.

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Table of Contents

Several poly(*N*-phenyl-2,7-carbazole)s having large side chains at the *N*-phenyl portion were synthesized to be applied in blue emitting layer materials for polymer light emitting diodes (PLEDs). Intense and pure blue electroluminescence was realized from the PLED devices having configuration of ITO/PEDOT(PSS)/polymer/CsF/Al under moderate operating voltages.

