5946 *Macromolecules* **2009**, *42*, 5946–5952
DOI: 10.1021/ma900908b

Macromolecules
ARTICLE

Appropriately Conjugated Poly[oligo(*N*-phenyl-2,7-carbazolylene)-*alt*-diphenylsilylene]s

Ryohei Koguchi, Norifumi Kobayashi, and Masashi Kijima*

Institute of Materials Science, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Received April 28, 2009; Revised Manuscript Received June 11, 2009

ABSTRACT: A series of poly[oligo(2,7-carbazolylene)-*alt*-diphenylsilylene]s were synthesized by Suzuki couplings by combination of basic monomers, dibromo(oligocarbazole)s, bis(dioxaborolanyl)oligocarbazoles, bis(dioxaborolanylcarbazolyl)diphenylsilanes, and bis(dioxaborolanylphenyl)diphenylsilanes. The polymers consist of the conjugated units of the dimer, trimer, pentamer, heptamer, and nonamer of the *N*-[*p*-(2-ethylhexyloxy)phenyl]carbazole-2,7-diyl and the connecting diphenylsilylene portion between the oligomer units. All of the polymers had moderate number-average molecular weights of about 14 000 g/mol and good solubility in toluene. The absorption and emission maxima of these polymers in $CHCl_3$ were in the ranges of 339−381 and 409−413 nm, respectively. A red-shift was observed as the length of the oligocarbazole unit increased less than 6 (heptamer). Poly(pentamer) and poly(heptamer) showed quantitative fluorescence quantum yields in $CHCl_3$. The full width at half-maximum in photoluminescence spectra of these polymers in the solid state became narrower as the conjugation length got longer. The highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels of all of the polymers were located at about −5.6 and −2.6 eV, respectively. Investigations of polymeric light-emitting diodes having a configuration of ITO/PEDOT(PSS)/polymer/CsF/Al suggested that poly(pentamer) and poly(heptamer) had higher performances of $L_{\max}$ (> 8000 cd/m^2) and $\eta_{\max}$ (> 0.5 cd/A) than the other poly(oligomer)s.

Introduction

Conjugated polymers are very important materials and can be applied in electrical, optical, and optoelectronic devices such as light-emitting diodes, field-effect transistors, charge storage devices, photodiodes, sensors, and so on.[1] Polymeric light-emitting diodes (PLEDs) are very attractive by reason of their ability to be fabricated in devices by facile wet processes such as spin-coating and inkjet printing. Up to the present, a variety of electronic and photoactive materials such as poly(*p*-phenylene)s,[2] poly(*p*-phenylenevinylene)s,[3] polythiophenes,[4] polypyrroles,[5] polyanilines,[6] polyfluorenes,[7] and polycarbazoles[8] have been developed. In particular, as for the carbazole-based polymers, many studies were devoted to 3,6-linked carbazole derivatives because of the easy halogenation reaction of carbazoles at the 3,6 positions.[9] However, they exhibit poor luminescent properties, which is ascribed to poor extension of π-conjugation along the main chains. Accordingly, poly(2,7-carbazole) derivatives that have a poly(*p*-phenylene)-like conjugation have been developed as prospective luminescent materials.

Recently, we reported that poly(*N*-phenyl-2,7-carbazole)s are considered as candidates for blue-light-emitting materials alternatively to polyfluorene-based materials.[10] As an example, the PLED device composed of ITO/PEDOT(PSS)/polymer/Ba/Al using poly[*N*-(3,4-bis(2-ethylhexyloxy)phenyl)carbazol-2,7-ylene] as the emitting layer material realized good performance of blue emission (CIE(x,y) = 0.20, 0.24), a luminance of 1090 cd m^{-2}, and an efficiency of about 0.18 cd A^{-1} at 10 V.[10c] Improvement of this basic polymer is required to develop high-performance polycarbazoles. It is considered that various effective conjugations present in the polymer bring about broadening of the spectra and a lack of reproducibility of materials that have almost the same optical properties. Thus, we intend to synthesize poly(oligomer)s that have well-defined conjugated structures. Furthermore, utilization of characteristics of the oligomer unit in polymer architectures must be a reliable method to develop novel functional materials.

In this paper, in order to develop high-performance polymers, the *N*-[4-(2-ethylhexyloxy)phenyl]carbazole-2,7-ylene sequence that exhibited good performance for PLED applications[10] is used as the conjugated oligomer part, and diarylsilylene, which provides good solubility in organic solvents, high heat stability, and inhibition of intermolecular interactions for the rigid and noncoplanar structure,[11] is used as the connecting part between the oligomers. We synthesize these poly(oligocarbazole)s, investigate their optical and electronic properties in consideration of the length of the oligocarbazole unit, and evaluate the PLED devices embedded with them as the emitting layer material.

Experimental Section

General Method and Instrumentation. 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, 60N, 63−120 μm). IR and NMR spectra were recorded on a JASCO FT/IR 550 spectrophotometer and a JEOL FT-NMR (270 MHz) spectrometer, respectively. ^{1}H 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 apparatus. Molecular weights of the polymers were estimated using gel permeation chromatography (GPC) equipped with a UV detector (Jasco) based on polystyrene standards (eluent = THF). UV−vis and photoluminescence (PL) measurements of the polymer samples in $CHCl_3$ and in the form of a coating thin film on quartz glass were performed using a U-3500 spectrophotometer (Hitachi) and a FP-750 spectrofluometer (Jasco). The measurement of the highest occupied

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*To whom correspondence should be addressed. E-mail: kijima@ims.tsukuba.ac.jp.

molecular orbital (HOMO) energy level of the polymer films on a Pt disk was performed at a scan rate of 50 mV/s in an acetonitrile solution containing Et_4NBF_4 (0.1 M) at room temperature under Ar using a saturated calomel electrode (SCE) as the reference and a platinum plate as the counter electrode. The electrochemical data (vs SCE) obtained by cyclic voltammetry were corrected with the redox potential (4.8 eV) of ferrocene/ferricinium$^+$.[12]

Device Fabrication. An indium tin oxide (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 radiation (Filgen UV253) for 20 min. Aqueous poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) [PEDOT(PSS) aq.; Baytoron PVP Al 8043], which filtered out through a 0.45 μm pore filter, was spin-coated on the cleaned ITO glass at 200 rpm for 5 s and 1000 rpm for 60 s, in order. To remove water, the coated glass was dried on a hot plate for 15 min 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 at 500 rpm for 5 s and 1500 rpm, in order. To remove the solvent, the coated glass was dried under reduced pressure. Finally, CsF and Al were vacuum-deposited on the substrate under a high vacuum using an Ulvac VTR-350M/ERH. The device configuration was ITO (150 nm)/PEDOT(PSS) (90 nm)/polymer (34−84 nm)/CsF (2 nm)/Al (150 nm). An evaluation of the PLED devices having an active surface area of 2 mm × 2 mm was carried out with the Hamamatsu C9920-12 system.

Materials. DMF, CH_2Cl_2, and toluene were distilled after drying with CaH_2 under an argon atmosphere. THF and 1,4-dioxane were distilled after drying with sodium under an argon atmosphere. The other solvents and all commercially available reagents were used without further purification. 2,7-Dibromocarbazole,[13] 1-(2-ethylhexyloxy)-4-iodobenzene,[14] and bis(4-bromophenyl)diphenylsilane[15] were synthesized according to the procedures reported previously.

*2,7-Dibromo-N-[4-(2-ethylhexyloxy)phenyl]carbazole (**1**).* A mixture of 2,7-dibromocarbazole (6.14 g, 18.9 mmol), CuI (35.9 mg, 0.189 mmol), potassium phosphate (8.00 g, 37.8 mmol), THF (23.5 mL), 1-(2-ethylhexyloxy)-4-iodobenzene (30.7 g, 92.5 mmol), and *trans*-1,2-cyclohexanediamine (225 μL, 1.88 mmol) was stirred at 65 °C for 3 days. To the reaction mixture was added CH_2Cl_2, and the organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel eluted with hexane to give **1** (7.25 g, 72.5% yield) as a colorless oil. ^1H NMR (270 MHz, $CDCl_3$): δ 7.92 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2, 1.5 Hz, 2H), 7.34 (d, J = 1.9 Hz, 2H), 7.11 (d, J = 8.9 Hz, 2H), 3.95 (d, J = 5.8 Hz, 2H), 1.84−1.75 (m, 1H), 1.63−1.34 (m, 8H), 1.01−0.91 (m, 6H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 159.7, 142.2, 131.8, 128.5, 128.3, 122.6, 120.9, 120.5, 115.8, 110.0, 70.9, 39.5, 30.7, 29.3, 24.1, 23.3, 14.9, 11.4. IR (KBr): ν 2956, 2926, 2857, 1585, 1514, 1451, 1247, 1058, 833, 792 cm^{-1}. Anal. Calcd for $C_{26}H_{27}Br_2NO$: C, 59.00; H, 5.14; N, 2.65. Found: C, 58.71; H, 5.30; N, 2.65.

*N-[4-(2-Ethylhexyloxy)phenyl]-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)carbazole (**2**).* A mixture of **1** (1.06 g, 2.00 mmol), bis(pinacolato)diboron (1.12 g, 0.88 mmol), the [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) complex with CH_2Cl_2 (100 mg, 0.123 mmol), potassium acetate (1.18 g, 12.0 mmol), and DMF (65 mL) was stirred at 80 °C for 5 days. CH_2Cl_2 was added to the reaction mixture, and the organic layer was washed with H_2O and brine and dried over Na_2SO_4. After evaporation of the solvent, the residue was recrystallized from CH_2Cl_2−MeOH to give **2** (602 mg, 48.2%) as a white powder. ^1H NMR (270 MHz, $CDCl_3$): δ 8.15 (d, J = 7.7 Hz, 2H), 7.75−7.71 (m, 4H), 7.42 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 3.97 (d, J = 5.7 Hz, 2H), 1.90−1.75 (m, 1H), 1.40−1.03 (m, 32H), 1.01−0.95 (m, 6H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.6, 141.4, 134.6, 129.8, 128.9, 125.6, 125.2, 119.8, 116.1, 115.6, 83.7, 70.8, 39.6, 30.7, 29.2, 29.1, 24.9, 23.1, 14.2, 11.3. IR (KBr): ν 2929, 1518, 1481, 1437, 1350, 836, 787 cm^{-1}. Anal. Calcd for $C_{38}H_{51}NB_2O_5$: C, 73.21; H, 8.25; N, 2.25. Found: C, 73.13; H, 7.84; N, 2.20.

*2,7″-Dibromotris[N-[4-(2-ethylhexyloxy)phenyl]carbazole-2,7-diyl] (**3**), 2,7⁗-Dibromopentakis[N-[4-(2-ethylhexyloxy)-phenyl]carbazole-2,7-diyl] (**4**), 2,7⁗⁗-Dibromononakis[N-[4-(2-ethylhexyloxy)phenyl]carbazole-2,7-diyl] (**5**).* Condition 1. A mixture of $Pd(PPh_3)_4$ (5.2 mg, 0.0045 mmol), THF (15 mL), **1** (1.43 g, 2.70 mmol), **2** (281 mg, 0.451 mmol), and 1 M K_2CO_3 aq. (2.0 mL, 2.0 mmol) was stirred at 70 °C for 3 days. To the reaction mixture was added $CHCl_3$. The organic layer was washed with H_2O. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with hexane−CH_2Cl_2 (2.5:1) to elute **3** (200 mg, 35.0% yield) and **5** (60.0 mg, 13.3% yield), in order.

Condition 2. A mixture of $Pd(PPh_3)_4$ (5.2 mg, 0.0045 mmol), THF (17 mL), **1** (1.07 g, 2.05 mmol), **2** (281 mg, 0.451 mmol), and 1 M K_2CO_3 aq. (2.0 mL, 2.0 mmol) was stirred at 70 °C for 3 days. To the reaction mixture was added $CHCl_3$, and the organic layer was washed with H_2O. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with hexane−CH_2Cl_2 (2.5:1) and then hexane−CH_2Cl_2 (1:1) to elute **3** (white powder, 100 mg, 17.5% yield), **4** (white powder, 8.0 mg, 1.8% yield), and **5** (pale yellow powder, 32.0 mg, 8.2% yield), in order.

Compound **3**. ^1H NMR (270 MHz, $CDCl_3$): δ 8.11 (dd, J = 8.2 Hz, 2.3 Hz, 4H), 7.96 (d, J = 8.6 Hz, 2H), 7.34−7.54 (m, 18H), 7.10 (d, J = 8.7 Hz, 6H), 3.94 (d, J = 5.6 Hz, 6H), 1.84−1.75 (m, 3H), 1.60−1.35(m, 24H), 1.01−0.91 (m, 18H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.9, 158.6, 142.6, 142.3, 142.0, 140.6, 139.9, 129.6, 129.0, 128.5, 128.4, 122.8, 122.0, 121.7, 121.3, 120.3, 119.9, 119.3, 115.7, 115.6, 112.7, 108.8, 108.6, 70.8, 39.5, 30.6, 29.2, 24.0, 23.2, 14.2, 11.3. IR (KBr): ν 2926, 1596, 1514, 1451, 1331, 1245, 795 cm^{-1}. Anal. Calcd for $C_{78}H_{81}N_3Br_2O_3$: C, 73.87; H, 6.44; N, 3.31. Found: C, 73.77; H, 6.49; N, 3.19.

Compound **4**. ^1H NMR (270 MHz, $CDCl_3$): δ 8.12 (dd, J = 7.9, 4.6 Hz, 8H), 7.96 (d, J = 8.2 Hz, 2H), 7.56−7.34 (m, 30H), 7.11 (d, J = 8.9 Hz, 10H), 3.95 (d, J = 5.6 Hz, 10H), 1.85−1.75 (m, 5H), 1.61−1.33 (m, 40H), 1.01−0.91 (m, 30H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.8, 158.5, 142.5, 142.2, 141.9, 140.6, 140.1, 139.7, 129.5, 128.9, 128.4, 128.3, 122.7, 121.9, 121.8, 121.7, 121.6, 121.3, 121.2, 120.2, 119.8, 119.2, 115.6, 115.5, 112.9, 108.7, 108.5, 70.7, 39.4, 30.5, 29.1, 23.9, 23.0, 14.1, 11.2. IR (KBr): ν 2926, 1601, 1514, 1452, 1330, 1244, 1032, 797 cm^{-1}. Anal. Calcd for $C_{130}H_{135}N_5Br_2O_5$: C, 77.79; H, 6.78; N, 3.49. Found: C, 78.12; H, 6.83; N, 3.38.

Compound **5**. ^1H NMR (270 MHz, $CDCl_3$): δ 8.08−8.00 (m, 16H), 7.87 (m, 2H), 7.49−7.27 (m, 56H), 7.05−7.01 (m, 18H), 3.89−3.85 (m, 18H), 1.77−1.67 (m, 9H), 1.50−1.28 (m, 72H), 0.93−0.83 (m, 54H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.8, 158.5, 142.8, 142.2, 141.9, 140.5, 140.1, 140.0, 139.7, 129.6, 128.9, 128.4, 128.3, 121.9, 121.8, 121.6, 121.3, 120.2, 119.8, 119.2, 115.6, 115.5, 108.5, 70.7, 39.4, 30.5, 29.1, 23.9, 23.0, 14.1. IR (KBr): ν 2925, 1604, 1514, 1452, 1330, 1243, 1032, 797 cm^{-1}. Anal. Calcd for $C_{234}H_{243}N_9Br_2O_9$: C, 80.64; H, 7.03; N, 3.62. Found: C, 80.81; H, 7.21; N, 3.31.

*Bis[7-bromo-N-[4-(2-ethylhexyloxy)phenyl]carbazol-2-yl]diphenylsilane (**6**).* To a solution of **1** (1.02 g, 2.00 mmol) in Et_2O 10 mL was added a mixture of *n*-BuLi 2.6 M in hexane (770 μL, 2.00 mmol) and Et_2O (10 mL) dropwise for 2 h at −50 °C, and then diphenyldichlorosilane (237 μL, 1.13 mmol) was added dropwise for 1 h at −50 °C. The resulting mixture was warmed to room temperature and was stirred for 12 h. To the reaction mixture were added NH_4Cl aq. and ether. The organic layer was washed with H_2O. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel eluted with hexane to give **6** (363 mg, 42.0% yield) as a white powder. ^1H NMR (270 MHz, $CDCl_3$): δ 8.07 (d, J = 7.7 Hz, 2H), 7.97

(d, J = 8.2 Hz, 2H), 7.59−7.56 (m, 6H), 7.49−7.46 (m, 4H), 7.42−7.23 (m,12H), 6.92 (d, J = 8.9 Hz, 4H), 3.80 (d, J = 5.6 Hz, 4H), 1.73−1.68 (m, 2H), 1.54−1.33 (m, 20H), 0.96−0.89 (m, 12H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.5, 142.1,140.8, 136.3, 134.5, 132.0, 129.4, 128.9, 127.8, 127.7, 123.5, 122.8, 121.7, 121.6, 119.7, 119.5, 118.0, 115.5, 112.8, 70.8, 39.4, 30.6, 29.2, 23.9, 23.1, 14.2, 11.2. IR (KBr): ν 3049, 2926, 1619, 1589, 1513, 1454, 1419, 1327, 1244, 1178, 1106, 832, 797 cm^{-1}. Anal. Calcd for $C_{64}H_{64}Br_2N_2O_2Si$: C, 71.10; H, 5.97; N, 2.59. Found: C, 71.10; H, 6.08; N, 2.55.

*Poly[bis[N-[4-(2-ethylhexyloxy)phenyl]carbazole-2,7-diyl]]-alt-(diphenylsilylene)] (**P2**).* A mixture of bpy (56 mg, 0.36 mmol), Ni(COD)$_2$ (99 mg, 0.36 mmol), DMF (3 mL), and COD (44 μL, 0.33 mmol) was stirred at 50 °C for 10 min. To the mixture was added a solution of monomer **6** (162 mg, 0.150 mmol) in THF (3 mL), and this stirred at 70 °C for 2 days. The reaction mixture was poured into MeOH−conc. HCl (10:1) and stirred for 24 h. After filtration, the solid dissolved in THF was poured into a MeOH−NH_3 aq. (10:1) solution and was stirred for 12 h. After filtration, the solid was washed with MeOH to give **P2** (120 mg, 87% yield) as a pale yellow powder. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.17−8.14 (m, 4H), 7.64−7.61 (m, 6H), 7.54−7.51 (m, 4H), 7.39−7.32 (m, 12H), 6.95−6.91 (m, 4H), 3.82−3.80 (m, 4H), 1.75−1.66 (m, 2H), 1.55−1.29 (m, 16H), 0.93−0.88 (m, 12H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.2, 142.8, 141.2, 140.5, 136.4, 134.9, 131.4, 129.6, 129.3, 128.9, 127.6, 127.5, 123.9, 122.0, 120.6, 119.9, 119.6, 117.8, 115.4, 108.7, 70.7, 39.4, 30.6, 29.2, 23.9, 23.1, 14.2, 11.2. IR (KBr): ν 2926, 1623, 1513, 1453, 1427, 1325, 1294, 1234, 1106, 1031, 832, 801 cm^{-1}. Anal. Calcd for $(C_{64}H_{64}N_2O_2Si)_n$: C, 83.44; H, 7.00; N, 3.04. Found: C, 82.52 ; H, 6.86; N, 2.95.

Bis[7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-[4-(2-ethylhexyloxy)phenyl]carbazole-2-yl]diphenylsilane (7). A mixture of **6** (48.0 mg, 0.0444 mmol), bis(pinacolato)-diboron (50.7 mg, 0.200 mmol), 1,1′-bis(diphenylphosphino)-ferrocene (2.46 mg, 0.00444 mmol), the [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) complex with CH_2Cl_2 (3.63 mg, 0.00444 mmol), potassium acetate (39.2 mg, 0.400 mmol), and 1,4-dioxane (2.0 mL) was stirred at 90 °C for 13 h. To the reaction mixture was added CH_2Cl_2, and the organic layer was washed with H_2O and brine and was dried over Na_2SO_4. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel eluted with hexane−CH_2Cl_2 (1:2) to give **7** (21.5 mg, 41.2% yield) as a white powder. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.14 (dd, J = 7.7, 3.1 Hz, 4H), 7.81 (brs, 2H), 7.72 (d, J = 7.9 Hz, 2H), 7.61−7.57 (m, 6H), 7.47 (d, J = 7.7, 2H), 7.39−7.27 (m, 6H), 7.29 (d, J = 8.9, 4H), 6.92 (d, J = 8.9, 4H), 3.80 (d, J = 5.6, 4H), 1.77−1.68 (m, 2H), 1.54−1.26 (m, 16H), 1.35 (s, 24H), 0.96−0.90 (m, 12H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.2, 141.2, 140.8, 126.3, 134.8, 132.1, 129.6, 129.3, 128.0, 127.6, 127.2, 125.8, 123.8, 119.9, 119.7, 118.0, 116.2, 115.3, 83.7, 70.7, 39.4, 30.6, 29.2, 25.0, 23.9, 23.2, 14.2, 11.3. IR (KBr): ν 3466, 2927, 1621, 1561, 1513, 1438, 1346, 1238, 1145, 1074, 974, 833, 688 cm^{-1}. Anal. Calcd for $C_{76}H_{88}N_2B_2O_6Si\cdot 0.5\text{-}H_2O$: C, 77.08; H, 7.58; N, 2.37. Found: C, 77.08; H, 7.39; N, 2.37.

*General Procedure for the Preparation of **P3**, **P5**, **P7**, and **P9**: Poly[pentakis[N-[4-(2-ethylhexyloxy)phenyl]carbazole-2,7-diyl]]-alt-(diphenylsilylene)] (**P5**).* A mixture of **3** (12.3 mg, 0.00970 mmol), **7** (11.4 mg, 0.00970 mmol), tetrakis(triphenylphosphine)palladium(0) (0.45 mg, 0.00034 mmol), THF (2 mL), and potassium carbonate (33.6 mg, 0.242 mmol) in Ar-saturated H_2O (242 μL, 1.0 M) was stirred at 65 °C for 44 h. To the reaction mixture was added phenylboronic acid (1.42 mg, 0.0116 mmol), which was stirred at 65 °C for 2 h. Bromobenzene (1.53 μL, 0.0146 mmol) in THF (200 μL) was added to the reaction solution and further stirred at 65 °C for 2 h. After being cooled to room temperature, the reaction mixture was poured into 9:1 methanol/concentrated HCl (v/v). The precipitate was collected by filtration. The solid was washed with 5:1 MeOH/NH_3 aq. (v/v). The residue was reprecipitated from $CHCl_3$−hexane to give **P5** (12.6 mg, 64.0% yield) as a yellow powder. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.17−8.12 (m, 10H), 7.65−7.49 (m, 30H), 7.41−7.32 (m, 10H), 7.12 (d, J = 8.9, 6H), 6.93 (d, J = 8.7, 4H), 3.96 (d, J = 5.4, 6H), 3.82 (d, J = 5.4, 4H), 1.84−1.67 (m, 5H), 1.57−1.25 (m, 40H), 0.98 (t, J = 7.2, 15H), 0.94−0.91 (m, 15H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.5, 158.1, 142.2, 141.6, 141.0, 139.9, 136.2, 134.8, 131.2, 129.6, 129.5, 129.2, 128.4, 127.7, 127.5, 127.3, 123.8, 121.8, 120.4, 120.2, 119.8, 119.4, 117.7, 115.4, 115.2, 108.5, 70.7, 70.6, 39.4, 39.3, 30.52, 30.46, 29.1, 29.0, 23.9, 23.8, 23.03, 23.01, 14.10, 14.08, 11.2, 11.1. IR (KBr): ν 2926, 1604, 1514, 1453, 1427, 1328, 1243, 1106, 1032, 799 cm^{-1}. Anal. Calcd for $(C_{142}H_{145}N_5O_5Si)_n$: C, 84.02; H, 7.20; N, 3.45. Found: C, 82.14; H, 6.77; N, 3.34.

*Poly[tris[N-[4-(2-ethylhexyloxy)phenyl]carbazole-2,7-diyl]]-alt-(diphenylsilylene)] (**P3**).* A yellow powder was obtained (125 mg, 84.0% yield). ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.09−8.04 (m, 6H), 7.57−7.40 (m, 18H), 7.28−7.24 (m, 10H), 7.05−7.02 (m, 2H), 6.86−6.83 (m, 4H), 3.88−3.86 (m, 2H), 3.74−3.73 (m, 4H), 1.74−1.54 (m, 3H), 1.50−1.24 (m, 24H), 0.93−0.81 (m, 18H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.6, 158.2, 142.4, 141.8, 141.2, 140.5, 140.1, 136.4, 134.9, 129.7, 129.6, 129.3, 128.6, 127.9, 127.8, 127.6, 127.5, 127.4, 123.9, 121.9, 120.6, 120.3, 119.92, 119.87, 119.5, 117.8, 115.6, 115.4, 108.7, 108.6, 70.8, 70.7, 39.6, 39.4, 30.64, 30.58, 29.1, 24.0, 23.9, 23.1, 14.2, 11.3, 11.2. IR (KBr): ν 2926, 1622, 1513, 1453, 1427, 1326, 1294, 1241, 1106, 1030, 832, 800 cm^{-1}. Anal. Calcd for $(C_{90}H_{91}N_3O_3Si)_n$: C, 83.74; H, 7.11; N, 3.26. Found: C, 80.47; H,6.84; N, 3.52.

*Poly[heptakis[N-[4-(2-ethylhexyloxy)phenyl]carbazole-2,7-diyl]]-alt-(diphenylsilylene)] (**P7**).* A yellow powder was obtained (10.0 mg, 53.0% yield). ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.17−8.12 (m, 14H), 7.65−7.32 (m, 52H), 7.12 (d, J = 8.7, 10H), 6.93 (d, J = 8.9, 4H), 3.96 (d, J = 5.4, 10H), 3.82 (d, J = 5.6, 4H), 1.84−1.70 (m, 7H), 1.58−1.31 (m, 56H), 1.01−0.89 (m, 42H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.5, 158.1, 142.2, 141.6, 141.0, 140.4, 140.0, 139.9, 136.2, 134.8, 131.2, 129.6, 129.5, 129.2, 128.4, 127.7, 127.5, 127.3, 123.8, 121.8, 120.5, 120.2, 119.8, 119.4, 117.7, 115.5, 115.2, 108.5, 70.7, 70.6, 39.4, 39.3, 30.51, 30.46, 29.1, 29.0, 23.9, 23.8, 23.04, 23.01, 14.1, 11.2, 11.1. IR (KBr) ν 2925, 1603, 1514, 1452, 1329, 1242, 1105, 799 cm^{-1}. Anal. Calcd for $(C_{194}H_{199}N_7O_7Si)_n$: C, 84.16; H, 7.24; N, 3.44. Found: C, 81.02; H, 6.98; N, 3.37.

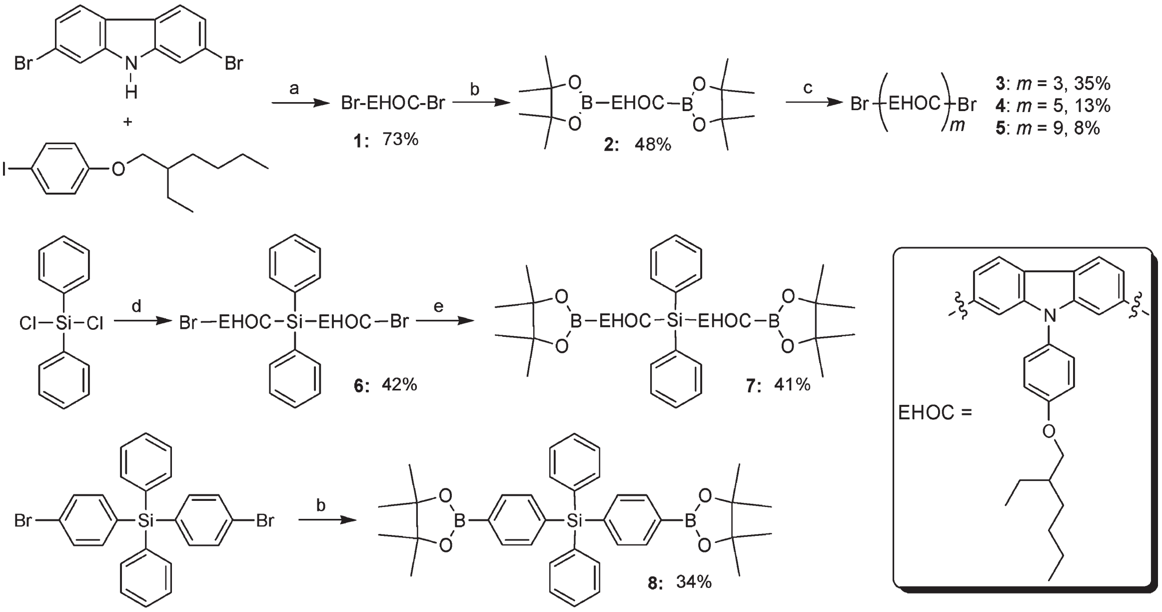
Diphenyl[4,4′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)diphenyl]silane (8). The same procedure was used as for the synthesis of **2**. A light gray powder was obtained (329 mg, 56.0% yield). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.79 (d, J = 7.9 Hz, 4H), 7.58−7.52 (m, 8H), 7.42−7.45 (m, 6H), 1.33 (s, 24H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 137.5, 136.3, 135.9, 135.6, 133.8, 129.5, 127.8, 83.8, 24.9. IR (KBr): ν 2929, 1518, 1481, 1437, 1350, 836, 787 cm^{-1}. Anal. Calcd for $(C_{36}H_{42}B_2O_4Si)_n$: C, 73.48; H, 7.19; N, 0.00. Found: C, 73.42; H, 7.07; N, 0.00.

*Poly[nonakis[N-[4-(2-ethylhexyloxy)phenyl]carbazole-2,7-diyl]]-alt-(diphenylsilylene)] (**P9**).* A yellow powder was obtained (18.9 mg, 73.8% yield). ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.15 (d, J = 7.9, 18H), 7.67−7.38 (m, 72H), 7.12 (d, J = 8.7, 18H), 3.96 (d, J = 5.3, 18H), 1.82−1.76 (m, 9H), 1.57−1.35 (m, 72H), 1.02−0.91 (m, 54H). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 158.5, 142.8, 142.2, 140.1, 140.0, 138.7, 136.6, 136.2, 134.0, 132.4, 129.6, 129.5, 128.4, 127.7, 127.3, 126.9, 116.7, 126.4, 122.1, 121.8, 120.2, 119.8, 119.2, 115.5, 108.5, 108.2, 70.7, 39.4, 30.5, 29.1, 23.9, 23.0, 14.1, 11.2. IR (KBr): ν 3066, 2978, 1603, 1504, 1361, 1145, 1075, 1022, 962, 859, 713 cm^{-1}. Anal. Calcd for $(C_{258}H_{261}N_9O_9Si)_n$: C, 84.91; H, 7.07; N, 3.39. Found: C, 82.69; H, 7.01; N, 3.31.

Results and Discussion

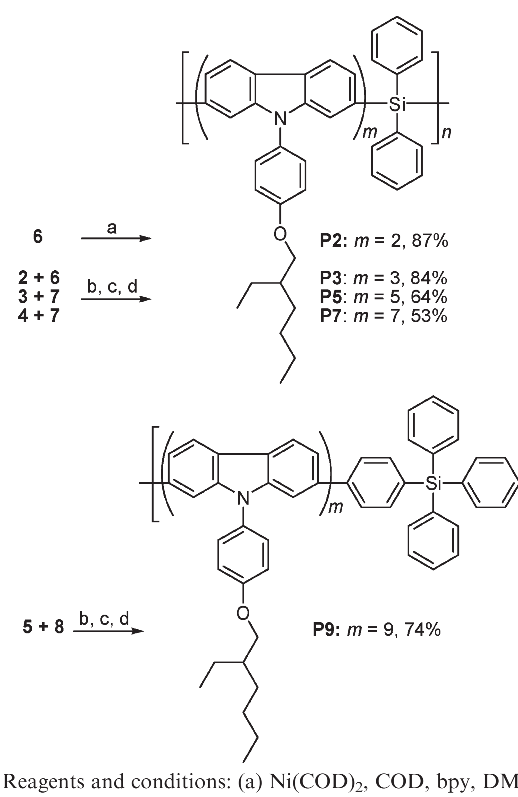
Syntheses of Basic Monomers. Scheme 1 illustrates the synthetic routes of the basic monomers for synthesis of

Scheme 1. Synthetic Route of Basic Monomers for the Synthesis of Poly[oligo(2,7-carbazolylene)-*alt*-diphenylsilylene]s[a]



[a] Reagents and conditions: (a) CuI, K_3PO_4, CHDA, THF, 65 °C; (b) bis(pinacolato)diboron, $PdCl_2(dppf)$ CH_2Cl_2, KOAc, DMF, 80 °C; (c) **1**, $Pd(PPh_3)_4$, K_2CO_3, THF−H_2O, 70 °C; (d) **1**, *n*-BuLi, Et_2O, −50 °C to rt; (e) bis(pinacolato)diboron, $PdCl_2(dppf)$ CH_2Cl_2, KOAc, 1,4-dioxane, 90 °C. Abbreviation: EHOC = *N*-[4-(2-ethylhexyloxy)phenyl]carbazole-2,7-ylene.

Scheme 2. Synthetic Courses of Polymers[a]



[a] Reagents and conditions: (a) $Ni(COD)_2$, COD, bpy, DMF−THF, 70 °C; (b) $Pd(PPh_3)_4$, K_2CO_3, THF−H_2O, 65 °C; (c) phenylboronic acid, 65 °C; (d) bromobenzene, THF, 65 °C.

poly[oligo(2,7-carbazolylene)-*alt*-diphenylsilylene]s. 2,7-Dibromo-*N*-[4-(2-ethylhexyloxy)phenyl]carbazole (**1**), which is used as a starting substance for the Suzuki coupling reactions,[16] was synthesized by the CuI-*trans*-1,2-cyclohexanediamine (CHDA)-catalyzed method.[17] The boronic ester **2**, which is another key starting material for copolymerization, was obtained from **1** with bis(pinacolato)diboron. A Suzuki coupling reaction of **1** with **2** resulted in three oligomers being afforded, a trimer (**3**, 35% yield), a pentamer (**4**, 13%), and a nonamer (**5**, 8%). We used different ratios of **1** and **2** in the synthesis of these oligomers (see the Experimental Section). By controlling the ratio, objective oligomers can be selectively formed in good yields and can be separated easily by silica gel column chromatography, but the heptamer was hard to isolate with enough purity. As for the silylene units, boronic esters **7** and **8** were synthesized from corresponding bis(bromoaryl)silylenes as well as the synthesis of **2**, respectively.

Syntheses and Characterization of Polymers. Synthetic courses of the polymers are illustrated in Scheme 2. Homopolymerization of **6** through the Yamamoto reaction[18] afforded poly[(dicarbazolylene)-*alt*-(diphenylsilylene)] (**P2**). Poly(trimer) (**P3**), poly(pentamer) (**P5**), poly(heptamer) (**P7**), and poly(nonamer) (**P9**) were synthesized from corresponding dibromo(oligomer)s (**3**, **4**, **5**, and **6**) and bis(dioxaborolanylaryl)diphenylsilanes (**2**, **7**, and **8**) through the Suzuki coupling reaction, respectively. All of the resulting polymers were obtained as a pale-yellow solid. They were soluble in the usual organic solvents such as toluene, THF, $CHCl_3$, and so forth and were purified by reprecipitation from THF−methanol or $CHCl_3$−hexane. All of the polymers have good processability to make thin cast films. The GPC results are summarized in Table 1. The number-average molecular weight (M_n) of the polymers was in the range of 9800−16700 g/mol, and the polydispersities (M_w/M_n) were about 2.

Optical Properties. The results of optical properties of the oligomers and polymers are summarized in Table 2. Figure 1 shows the absorption spectra of the polymers in $CHCl_3$. The maximum absorption wavelengths (λ_{max}) were red-shifted with an increase of the length of the oligocarbazole units (**P2** (λ_{max} = 339 nm) < **P3** (360 nm) < **P5** (371 nm) < **P7** (377 nm) < **P9** (381 nm)). Compared to the λ_{max} of the oligomers (**3** (λ_{max} = 354 nm) < **4** (370 nm) < **5** (379 nm), there are few differences of λ_{max} ($\Delta\lambda_{max}$) values between the polymers and corresponding oligomers (i.e., $\Delta\lambda_{max}$(**P3**−**3**) = 6 nm, $\Delta\lambda_{max}$(**P5**−**4**) = 1 nm, $\Delta\lambda_{max}$(**P9**−**5**) = 2 nm). This suggests that the optical properties of these polymers are reflected on the conjugation length of each oligomer unit. Therefore, the poly(oligomer)s are examined by fitting the relation $\lambda(m) = \lambda_\infty - (\lambda_\infty - \lambda_1)\ e^{-a(m-1)}$,[19] where m, λ_1, and λ_∞ represent the number of bonded carbazoles in each unit of the poly(oligomer)s, the $\lambda_{\max}$ of the monomer **1** (m = 1, 308 nm), and the limiting $\lambda_{\max}$ value ($m \rightarrow \infty$), respectively, in this case. By applying the data of $\lambda(m)$ in Table 2, we could obtain optimal values of λ_∞= 379 nm and a = 0.62 for the poly(oligomer)s (Figure 2). The λ_∞ value is comparable but slightly shorter than the $\lambda_{\max}$ = 384 nm (DP = 21) of poly[*N*-(*p*-(2-ethylhexyloxy)phenyl)carbazol-2,7-ylene (**P*p*EHOC**), that is, a homopolymer without silane units.[10a] UV−vis spectra of the polymers in the thin-film state were somewhat broader than those in $CHCl_3$, but they have almost the same $\lambda_{\max}$ values in $CHCl_3$ (see Figures S4−S8, Supporting Information). Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels (E_{HOMO} and E_{LUMO}) and their gaps (E_g) for the polymers were estimated from the absorption edge of the thin film samples and the oxidation potentials.[20] The E_g values became narrower as the conjugation length got longer (**P2** (3.15 eV), < **P3** (2.99 eV) < **P5** and **P7** (2.91 eV) < **P9** (2.86 eV)). Analogously, E_{HOMO} became lower to a limited value (−5.5 eV).

Figure 3 shows the PL spectra of the polymers in $CHCl_3$. The longer conjugation the polymer has, the longer the emission $\lambda_{\max}$ in wavelength the polymer shows (**P2** (386 nm, shoulder) < **P3** (403 nm) < **P5** (412 nm), **P7** (413 nm), **P9** (413 nm)). These values almost converge on a limiting value of emission, λ_∞, as well as the UV−vis results. Similarly, the fluorescence quantum efficiency (ϕ_f) in $CHCl_3$ basically increases as the conjugation length increases: (**P2** (ϕ_f = 0.48) < **P3** (ϕ_f = 0.71) < **P5**, **P7** ($\phi_f \approx 1.0$)). The silylene linker directly connected with the oligomeric sequences could stabilize the π-conjugation system effectively in **P2**−**P7** through the electronic effect with small steric hindrance, which brings about a higher ϕ_f for **P5** and **P7** than for **P9**. PL spectra of the polymers in the thin solid film state kept similar shapes to those in $CHCl_3$, but they all shifted to be longer by about 12 nm in wavelength (see Figures S4−S8, Supporting Information). It is noteworthy that full-width at half-maximum (fwhm) values of the PL spectra in the film state became narrower as the conjugation length got longer, as listed in Table 2 (fwhm: **P2** (64 nm) > **P3** (52 nm)

Table 1. GPC Analysis Results of the Polymers

Polymer	M_n,[a] g mol^{-1}	M_w,[a] g mol^{-1}	M_w/M_n	DP[b]
P2	14800	31200	2.1	16
P3	9800	18900	1.9	7.2
P5	16600	31800	1.9	8.2
P7	12000	22000	1.8	4.3
P9	16700	53900	3.2	4.5

[a] GPC analysis was carried out in THF using polystyrene as the standard. [b] The degree of polymerization (DP) was estimated from M_n.

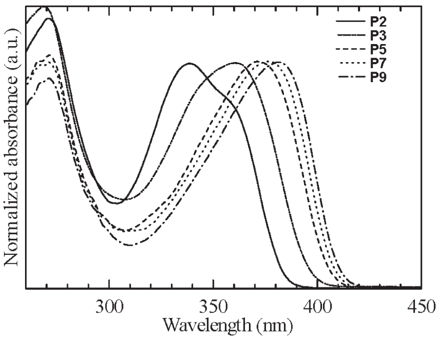


Figure 1. UV−vis absorption spectra of the polymers in $CHCl_3$.

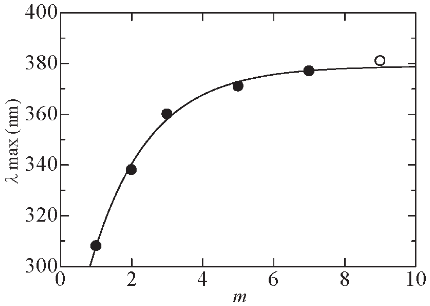


Figure 2. Plots of absorption $\lambda_{\max}$ of **P2**−**P7** (●) and **P9** (○) in $CHCl_3$ versus m and the analysis result fitting data into the equation, $\lambda(m) = \lambda_\infty - (\lambda_\infty - \lambda_1)\ e^{-a(m-1)}$, where m is equal to the number of bonded carbazoles in each unit of the poly(oligomer)s, λ_∞= 379 nm and a = 0.62.

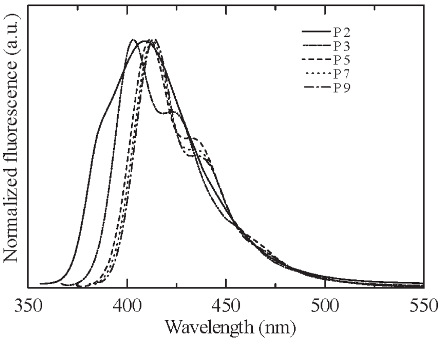


Figure 3. Photoluminescence spectra of the polymers in $CHCl_3$.

Table 2. Optical Properties of the Oligomers and Polymers

	abs.			em						
	in $CHCl_3$		film	in $CHCl_3$		film				
sample	$\lambda_{\max}$ /nm	log ε	$\lambda_{\max}$ /nm	$\lambda_{\max}$ /nm	ϕ_f[a]	$\lambda_{\max}$ /nm	fwhm	E_g, eV	E_{HOMO},[b] eV	E_{LUMO},[c] eV
3	354	4.9	364	399	0.30	431	56	2.97	−5.62	−2.66
4	370	5.2	374	411	0.78	448	52	2.87	−5.60	−2.73
5	379	5.4	387	414	0.67	429	49	2.87	−5.58	−2.71
P2	339, 364[d]	4.5[e]	338	386,[d] 409	0.48	416	64	3.15	−5.65	−2.50
P3	360	4.4[e]	362	403, 422[d]	0.71	415	52	2.99	−5.68	−2.68
P5	371	4.4[e]	370	412, 428[d]	1.00	425	49	2.91	−5.55	−2.64
P7	377	4.5[e]	379	413, 434[d]	0.99	427	48	2.91	−5.55	−2.64
P9	381	4.5[e]	383	413, 435[d]	0.85	425	44	2.86	−5.55	−2.69

[a] Optical quantum efficiencies in $CHCl_3$ were referred to 9,10-diphenylanthracene (ϕ_f = 0.90) in cyclohexane. [b] The HOMO energy levels vs vacuum level were calculated from oxidation potentials according to a report in the literature.[20] [c] The LUMO level was determined from the optical band gap and the HOMO level. [d] The shoulder peak value was determined by a Gaussian fitting. [e] Molar absorption coefficients were calculated from per carbazole units.

Table 3. Preliminary Results of PLEDs Embedded with Polyoligomers

polymer	turn-on voltage, V	L_{max} (voltage), cd m^{-2} (V)	η_{max} (voltage), cd A^{-1} (V)	L at 10 V, cd m^{-2}	η at 10 V, cd A^{-1}	EL λ_{max} at 10 V, nm	CIE (x, y) at 10 V
P2	6	3300 (12)	0.27 (12)	1900	0.22	434	0.19, 0.19
P3	9	490 (16)	0.05 (16)	14	0.03	435	0.24, 0.21
P5	6	8100 (13)	0.52 (13)	1500	0.19	485	0.21, 0.29
P7	5	9600 (12)	0.74 (12)	3600	0.44	491	0.23, 0.35
P9	5	5100 (12)	0.27 (12)	1500	0.12	494	0.23, 0.36

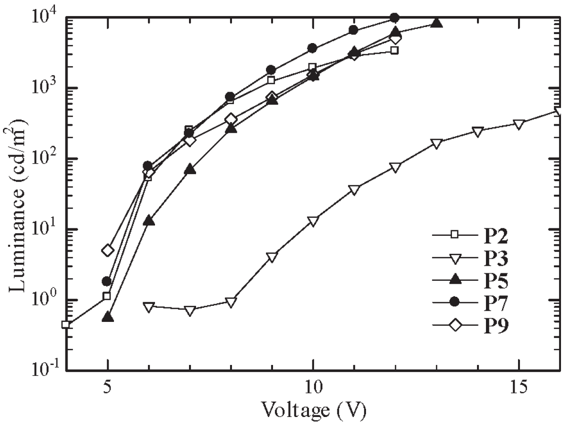


Figure 4. Brightness–voltage characteristics of the PLEDs.

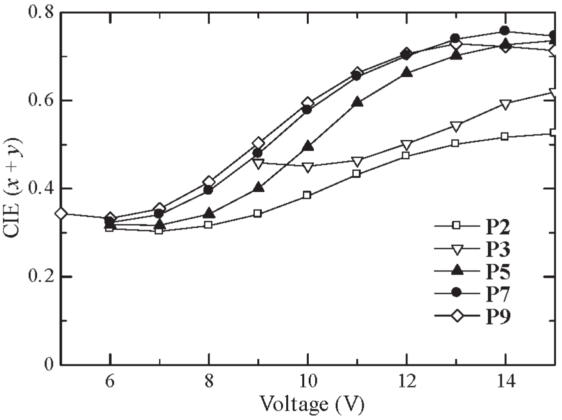


Figure 5. CIE (x + y)–voltage characteristics of the PLEDs.

> **P5** (49 nm) > **P7** (48 nm) > **P9** (44 nm)). The change of the fwhm values might relate to the relative intensity of emissions from the oligomeric unit and conjugated sequences engaged with Si in each polymer. Moreover, the fwhm values of **P5**–**P9** were narrower than that of **P*p*EHOC** (51 nm).[10a] It is thought that well-defined conjugated structures of polymers are reflected in the narrowing of the PL spectra. From these results, it is concluded that **P5** and **P7** have an appropriate conjugation length to fluoresce effectively.

Electroluminescence. Electroluminescence (EL) performances of these polymers were preliminarily investigated by constructing a PLED device that has the ITO (150 nm)/PEDOT(PSS) (90 nm)/polymer/CsF (2 nm)/Al (150 nm) structure. Inserting the thin layer of CsF between the emitting polymer and Al has been known to reduce the barrier of electron injection from the cathode.[21] The principal characteristics of these devices are summarized in Table 3.

Most of the devices started to emit around 5–6 V, and the EL spectra showed an EL λ_{max} at about 420 nm in the initial stages at low operating voltages and were similar but broader than the PL spectra in the thin film state (see Figures S11–S15, Supporting Information; Figure 4 shows brightness–voltage characteristics of the PLEDs). In analogy with the PLED devices using poly(N-phenylcarbazole)s that have the same device structure,[10d] the blue emitting color in the initial stage changed to bluish green as the operating voltages were heightened with a red-shift of EL λ_{max} toward 500 nm. Figure 5 shows the change of emission colors of the devices under various operating voltages using CIE indices, where CIE(x + y) values in the range of 0.27–0.4, 0.4–0.6, and 0.6–0.76 approximately correspond to blue, blue-green, and green, respectively. The tendency is more prominent in the cases of poly(oligocarbazole)s that have longer sequences (m). From that viewpoint, the device embedded with **P2** kept a color purity of blue under operating voltages compared to other devices, while luminance was moderate (Figure 5). Unexpectedly, the device embedded with **P3** showed low performances with an exceptionally high turn-on voltage, which might be due to the lowest M_n, to make a good-quality polymer layer on the substrate. As for **P5**, **P7**, and **P9**, they realized intense maximum luminance (L_{max}) higher than 5000 cd/m^2 and good current efficiency (η_{max}), though the EL color changed from blue to green as the operating voltages increased. The change of emitting color in EL might be due to irreversible chemical reactions near the interface between the cathode and the emitting layer, since polycarbazole has been known to be a good hole injection and transport material. As a result, **P5** and **P7** especially have an appropriate conjugation length to inject and transport holes and to emit efficiently, but the unbalanced carriers' injection and transportation in the device must be solved as well those of poly(N-phenylcarbazole)s for PLED applications.

Conclusions

It is thought that blue-emitting colors and the color purity of poly(N-aryl-2,7-carbazole)s can be tuned or improved by developing polymers that have well-defined conjugated structures. Therefore, we synthesized a series of poly[oligo(2,7-carbazolylene)-*alt*-diphenylsilylene]s that contains a dimer, trimer, pentamer, heptamer, and nonamer of N-[p-(2-ethylhexyloxy)phenyl]-carbazole-2,7-diyl through the Suzuki coupling of corresponding oligocarbazoles with bis(dioxaborolanylaryl)diphenylsilanes and investigated their properties. The diphenylsilylene portion is used as a connecting part between conjugated sequences of oligocarbazoles. It should be noted that key oligocarbazoles can be purified and isolated by a simple column chromatography on silica gel. Absorption and PL spectra of these polymers in solution and solid states suggest that effective π-conjugation is reflected in the λ_{max} values of absorption and PL. Furthermore, the well-defined conjugation of the poly(oligomer)s results in spectral narrowing of PL in the solid state. From the systematic observations on optical properties of these poly(oligomer)s, it is demonstrated that **P5** and **P7** have enough π-conjugation for exhibiting limiting optical values such as E_g (2.91 eV), E_{HOMO} (−5.5 eV), and ϕ_f (≈ 1.0), which are comparable to those of blue-emitting **P*p*EHOC** (E_g = 2.9 eV, E_{HOMO} = −5.4 eV, and $\phi_f \approx$ 1.0) and its analogues.[10] Although, these results are satisfactory for blue-emitting materials, the preliminary PLED examination of the poly(oligomer)s turned out to show moderate performances, of which **P7** showed the highest L_{max} and η_{max}. The unexpected spectral broadenings and considerable red-shift of the EL spectra under high operating voltages might be due to unbalanced carrier injection and transport in the emitting polymer as well as poly(*N*-aryl-2,7-carbazole)s, which are going to be improved by appropriate molecular design and modifications in consideration of the abilities of electron injection and transport. Nevertheless, it is believed that we will be able to properly modify the poly(oligomer)s by replacing the diarylsilylene portion with a crucial one, since we have already realized that **P5** and **P7** have appropriate conjugation to emit efficiently.

Acknowledgment. We thank Kanto Chemical Co., Inc. for making and evaluating the PLED devices and the Chemical Analysis Center, University of Tsukuba, for NMR spectroscopic and elemental analysis data.

Supporting Information Available: Figures of UV−vis, PL spectra, cyclic voltammograms, EL spectra, and NMR spectra of the oligomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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