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Synthesis and Properties of Conjugated Poly(1,8-carbazole)s

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ABSTRACT: During our search of novel conjugated carbazole polymers, we succeeded in the efficient synthesis of conjugated poly(1,8-carbazole) derivatives. The synthetic route to the 1,8-difunctionalized carbazole monomers and the polymerization methods under the Yamamoto, Sonogashira, and Hay conditions were established. The obtained poly(1,8-carbazole)s were comprehensively characterized by GPC, MALDI-TOF MS, ^{1}H NMR, and IR spectroscopies, and it was found that the alkyne spacer is an important factor in obtaining the high molecular weight polymers. Thermal analysis revealed that the alkyne-linked poly(1,8-carbazole)s possess a higher thermal stability than the directly linked poly(1,8-carbazole). The energy diagrams of a series of polycarbazoles were carefully estimated from the electrochemical and optical measurements. The alkyne-linked carbazole polymers were potent blue-light-emitting polymers due to their narrow band gaps. Furthermore, the remarkable decreased aggregation behavior of the butadiynylene-linked poly(1,8-carbazole) was demonstrated.

Introduction

The history of conjugated carbazole polymers started with poly(3,6-carbazole) derivatives, in which the highest electron density positions at the 3- and 6-positions of the carbazole are linked either directly or through π-spacers.[1] Recently, conjugated poly(2,7-carbazole)s and their copolymers have attracted more attention because the efficient synthetic routes for the 2,7-dihalogenocarbazole derivatives were established by Leclerc et al. and others.[2] Poly(2,7-carbazole)s generally have smaller band gaps than the corresponding poly(3,6-carbazole)s because of the linear conjugation of the 2,7-positions. Thus, the promising applications in optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), and organic photovoltaics, have been examined, and their excellent properties were indeed demonstrated.[3−6]

Among the many possibly applications, a blue-light-emitting polymer with good thermal and optical stabilities is always desired for OLED applications. Poly(2,7-fluorene) derivatives have been regarded as one of the most promising polymers for this purpose.[7] However, the excimer formation propensity in terms of intermolecular $\pi-\pi$ interactions and the contamination of fluorenone defects caused by photodegradation give rise to a different color emission and optical instability.[8] To overcome these problems, poly(2,7-carbazole) derivatives were anticipated to be good alternatives because of a structure similar to the fluorene unit and inertness toward the formation of the ketone defect at the 9-position. In fact, the initially synthesized poly(*N*-octyl-2,7-carbazole) did not show clear evidence for excimer formation even in the thin film state because of a lower crystalline state than the poly(9,9-dialkyl-2,7-fluorene)s.[2a]

Another important requirement for stable blue-light emissions in the solid state is based on the molecular design that prevents any strong aggregation propensity of the conjugated polymers. Previous successful examples include the incorporation of kinked moieties into the main chain, which interrupts the efficient organization of conjugated polymers in the aggregated states. For example, Advincula succeeded in the decreased aggregation of the poly(2,7-fluorene) copolymers by introduction of a small amount of the 3,6-carbazole unit in the main chain.[9] Other groups further extended this approach; they employed the 3,9-carbazole unit as a symmetry-breaking kink unit in the poly(2,7-fluorene) copolymers.[10] Very recently, the homopolymers of the 3,9-linked or 2,9-linked carbazole derivatives were also found to show a blue emission in solutions, although their solid-state emission behaviors were not reported.[11] Thus, the development of conjugated polycarbazole derivatives with new connectivities of the carbazole structure are highly interesting and, at least so far, very useful for improvement of blue-light emitting polymers.

In this study, we became interested in the new carbazole connectivity of the 1,8-linked carbazole and, for the first time, synthesized a new class of conjugated poly(1,8-carbazole)s with different numbers of alkyne spacers by the metal-catalyzed polycondensation methods.[12] The electronic properties were characterized by electrochemistry as well as optical absorption and emission spectroscopy. The decreased aggregation phenomena were also investigated by solvent-dependent spectroscopy. The data were analyzed in terms of the number of alkyne spaces and also compared with those of other conjugated carbazole homopolymers with different substitution patterns, namely, the poly(3,6-carbazole) and poly(2,7-carbazole) derivatives. The potent blue-light emission of the alkyne-linked poly(1,8-carbazole)s with a considerable optical stability against aggregation was demonstrated.

Experimental Section

Materials. All reagents were purchased from Kanto, Tokyo Kasei, and Wako and used as received. CH_2Cl_2 was distilled from P_2O_5. *N*-Hexadecylcarbazole (**1**) was synthesized from carbazole and 1-bromohexadecane.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL model AL400 spectrometer at 20 °C. Chemical shifts are reported in ppm downfield from $SiMe_4$, using the

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solvent's residual signal as an internal reference. Coupling constants (J) are given in hertz. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quintet), and m (multiplet). Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. MALDI-TOF-MS spectra were measured on an Applied Biosystems model Voyager-DE STR in reflector mode. UV−vis spectra were recorded on a JASCO V-550 spectrophotometer. The solution spectra were measured in a quartz cuvette of 1 cm. Fluorescence spectra were measured on a JASCO FP6500 spectrophotometer. Quantum yields were determined against quinine sulfate in 0.05 M aqueous H_2SO_4 (Φ_F = 0.546).[13] Gel permeation chromatography (GPC) was measured on a JASCO system equipped with polystyrene gel columns using THF as an eluent at a flow rate of 1.0 mL min^{-1} after calibration with standard polystyrene. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a Rigaku Thermoplus TG 8120 and DSC8230, respectively, under flowing nitrogen at a scanning rate of 10 °C min^{-1}. Electrochemistry measurements were carried out at 20 °C in a classical three-electrode cell. The working and auxiliary electrodes were a glassy carbon disk electrode (0.07 cm^2) and Pt, respectively. The reference electrode was Ag/Agt/CH_3CN/$(nC_4H_9)_4NClO_4$.

3,6-Di-*tert*-butyl-*N*-hexadecylcarbazole (2). To a suspension of *N*-hexadecylcarbazole, **1** (1.80 g, 4.60 mmol), and $AlCl_3$ (674 mg, 5.06 mmol) in CH_2Cl_2 (14 mL), 2-chloro-2-methylpropane (1.01 mL, 9.19 mmol) was added dropwise for > 20 min at 0 °C under nitrogen. After stirring at 20 °C for 16 h, CH_2Cl_2 was added and the organic phase was washed with 1 N aqueous HCl and brine. After drying over Na_2SO_4, the solution was filtered. Removal of the solvent in vacuo and column chromatography (SiO_2, hexane/CH_2Cl_2 2:1) afforded **2** (2.11 g, 91%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6 Hz, 3H), 1.24−1.30 (m, 26H), 1.45 (s, 18H), 1.84 (q, J = 8 Hz, 2H), 4.21 (t, J = 6 Hz, 2H), 7.30 (d, J = 8 Hz, 2H), 7.50 (dd, J = 4, 8 Hz, 2H), 8.10 (d, J = 8 Hz, 2H). IR (KBr): 3049, 2925, 2853, 1633, 1609, 1577, 1480, 1465, 1393, 1362, 1325, 1297, 1261, 1202, 1162, 1105, 1054, 1032, 878, 803, 742, 722, 693, 648, 611 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{36}H_{57}N^+$: 503.4 g mol^{-1}; found: 503.9 g mol^{-1} [M]$^+$.

1,8-Dibromo-3,6-di-*tert*-butyl-*N*-hexadecylcarbazole (3). To a solution of **2** (0.250 g, 0.496 mmol) in CH_3COOH (12.3 mL), *N*-bromosuccinimide (0.195 g, 1.09 mmol) was added and the mixture was stirred at 20 °C for 16 h. EtOAc was added and the organic phase was washed with aqueous NaOH and aqueous $NaHCO_3$. After drying over Na_2SO_4, the solution was filtered. Removal of the solvent in vacuo and column chromatography (hexane) afforded **3** (0.257 g, 78%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.91 (t, J = 6 Hz, 3H), 1.24 (s, 18H), 1.20−1.35 (m, 26H), 1.65−1.70 (m, 2H), 5.21 (t, J = 8 Hz, 2H), 8.14 (s, 2H), 8.20 (s, 2H).

3,6-Di-*tert*-butyl-1,8-diiodo-*N*-hexadecylcarbazole (4). To a solution of **2** (0.743 g, 1.47 mmol) in CH_2Cl_2 (5 mL) and CH_3COOH (5 mL), *N*-iodosuccinimide (0.682 g, 3.03 mmol) was added, and the mixture was stirred at 20 °C for 16 h. CH_2Cl_2 was added, and the organic phase was washed with aqueous $NaHCO_3$ and water. After drying over Na_2SO_4, the solution was filtered. Removal of the solvent in vacuo and column chromatography (hexane) afforded **4** (8.02 g, 72%) as a yellow oil. ^{1}H NMR (400 MHz, C_6D_6): δ 0.91 (t, J = 6 Hz, 3H), 1.24 (s, 18H), 1.27−1.32 (m, 26H), 1.65−1.70 (m, 2H), 5.21 (t, J = 8 Hz, 2H), 8.14 (s, 2H), 8.20 (s, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 14.36, 23.09, 26.09, 29.73, 29.80, 29.94, 29.99, 30.09, 30.11, 30.16, 31.12, 31.63, 32.31, 34.28, 43.49, 74.67, 116.25, 126.57, 138.17, 140.17, 145.11. IR (KBr): 2921, 2849, 1617, 1598, 1532, 1468, 1416, 1364, 1293, 1260, 1245, 1183, 1151, 1126, 1050, 926, 869, 864, 823, 786, 726, 660, 630 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{36}H_{55}I_2N^+$: 755.2 g mol^{-1}; found: 503.5 g mol^{-1} [M − 2I]$^+$.

3,6-Di-*tert*-butyl-1,8-bis[(trimethylsilyl)ethynyl]-*N*-hexadecylcarbazole (5). To a degassed solution of **4** (0.557 g, 0.735 mmol) in iPr$_2$NH (5.3 mL), (trimethylsilyl)acetylene (0.415 mL, 2.94 mmol), [PdCl$_2$(PPh$_3$)$_2$] (21.2 mg, 0.0302 mmol), and CuI (10.5 mg, 0.0551 mmol) were added, and the mixture was stirred for 24 h at 20 °C under nitrogen. CH_2Cl_2 was added, and the organic phase was washed with brine. After drying over Na_2SO_4, the solution was filtered. Removal of the solvent in vacuo and column chromatography (hexane/EtOAc 30:1) afforded **5** (0.466 g, 91%) as a yellow solid. ^{1}H NMR (400 MHz, C_6D_6): δ 0.35 (s, 18H), 0.89 (t, J = 6 Hz, 3H), 1.28 (s, 18H), 1.30−1.36 (m, 24H), 1.63−1.71 (m, 2H), 2.04−2.12 (m, 2H), 5.72 (t, J = 8 Hz, 2H), 7.99 (s, 2H), 8.24 (s, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 0.00, 14.25, 14.28, 22.94, 23.02, 26.46, 29.73, 30.02, 30.07, 30.32, 31.68, 31.83, 32.24, 34.37, 44.46, 97.82, 105.08, 105.54, 117.90, 124.57, 131.25, 138.79, 142.15. IR (KBr): 2955, 2920, 2851, 2146, 1594, 1578, 1485, 1470, 1424, 1387, 1376, 1364, 1329, 1314, 1247, 1228, 1208, 1151, 1104, 1085, 924, 841, 758, 745, 719, 701, 667, 641 cm^{-1}.

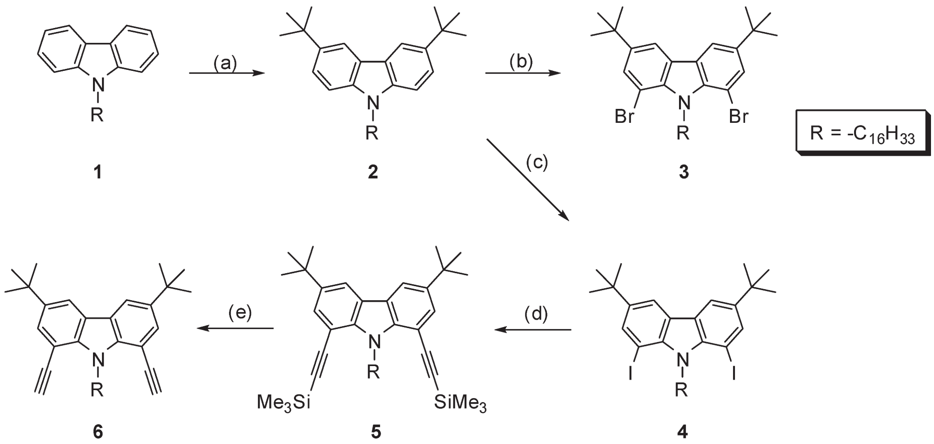
3,6-Di-*tert*-butyl-1,8-diethynyl-*N*-hexadecylcarbazole (6). K_2CO_3 (0.255 g, 1.85 mmol) was added to a solution of **5** (0.644 g, 0.925 mmol) in MeOH (22 mL) and THF (22 mL). After stirring for 2 h, CH_2Cl_2 was added. The organic phase was washed with water, dried over Na_2SO_4, and evaporated. Column chromatography (hexane/EtOAc 30:1) afforded **6** (0.419 g, 82%) as a yellow solid. ^{1}H NMR (400 MHz, C_6D_6): δ 0.91 (t, J = 6 Hz, 3H), 1.29 (s, 18H), 1.30−1.33 (m, 24H), 1.47−1.51 (m, 2H), 2.01−2.11 (m, 2H), 3.04 (s, 2H), 5.37 (t, J = 8 Hz, 2H), 7.92 (s, 2H), 8.22 (s, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 14.33, 14.37, 23.01, 23.09, 26.32, 29.80, 30.00, 30.07, 30.09, 30.11, 30.14, 30.16, 31.76, 31.92, 32.31, 34.42, 44.70, 80.81, 82.97, 104.25, 117.95, 124.42, 131.39, 138.94, 142.13. IR (KBr): 3309, 2957, 3925, 2853, 2100, 1485, 1469, 1428, 1393, 1375, 1364, 1322, 1310, 1269, 1229, 1202, 1099, 916, 874, 745, 643, 593, 509 cm^{-1}. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{40}H_{57}N^+$: 551.4 g mol^{-1}; found: 552.1 g mol^{-1} [MH]$^+$.

Poly(3,6-di-*tert*-butyl-*N*-hexadecyl-1,8-carbazolylene) (P1). To a solution of **4** (303 mg, 0.397 mmol) in dry DMF (1.4 mL), a solution of cyclooctadiene (cod, 48.5 μL, 0.395 mmol), Ni(cod)$_2$ (130 mg, 0.476 mmol), and 2,2′-bipyridyl (75 mg, 0.47 mmol) in dry DMF (4.1 mL) was added dropwise at 60 °C. After stirring at 60 °C for 24 h, the solvent was reduced in vacuo and poured into MeOH. The precipitate was collected, and the polymer was purified by reprecipitation in MeOH and then dried in vacuo (69.6 mg, 35%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.85−2.00 (m, 49nH), 5.20−5.40 (m, 2nH), 7.24 (d, J = 8 Hz), 7.56 (d, J = 8 Hz), 7.85 (m, 2nH), 8.11−8.37 (m, 2nH). IR (neat): 2958, 2924, 2852, 1732, 1599, 1541, 1478, 1466, 1416, 1376, 1363, 1295, 1261, 1211, 1178, 1048, 867, 820, 801, 724, 661 cm^{-1}.

Poly(3,6-di-*tert*-butyl-*N*-hexadecyl-1,8-carbazolylene) (P1′). To a solution of $FeCl_3$ (0.276 g, 1.70 mmol) in chlorobenzene (8.0 mL), a solution of **2** (0.257 g, 0.510 mmol) in chlorobenzene (1.8 mL) was added under nitrogen. After stirring at 50 °C for 24 h, the mixture was poured into MeOH. The precipitate was collected, and the polymer was purified by reprecipitation in MeOH and then dried in vacuo (65.9 mg, 26%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.90−1.53 (m, 49nH), 3.76−3.97 (m, 2nH), 3.76−3.97 (m, 2nH), 7.25−8.73 (m, 4nH).

Poly[(3,6-di-*tert*-butyl-*N*-hexadecyl-1,8-carbazolylene)ethynylene] (P2). To a degassed solution of **4** (72 mg, 0.095 mmol) and **6** (53 mg, 0.095 mmol) in iPr$_2$NH (0.64 mL) and toluene (1.92 mL), [PdCl$_2$(PPh$_3$)$_2$] (2.6 mg, 0.0038 mmol) and CuI (1.2 mg, 0.0038 mmol) were added, and the solution was stirred for 24 h at 80 °C under nitrogen. After cooling to 20 °C, the mixture was poured into MeOH (250 mL). The precipitate was collected, and the polymer was purified by reprecipitation into MeOH and then dried in vacuo (103 mg, 91%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.90 (3nH), 1.00−2.08 (m, 46nH), 5.58−5.88 (m, 2nH), 8.00−8.12 (m, 2nH), 8.18−8.32 (m, 2nH). IR (KBr): 3062, 2959, 2924, 2852, 2146, 1486, 1466, 1424, 1394, 1363, 1265, 1182, 1104, 1027, 871 cm^{-1}.

Scheme 1. Synthesis of the Carbazole Monomers[a]



[a] Conditions and reagents: (a) *t*BuCl, $AlCl_3$, CH_2Cl_2, 0 °C; (b) NBS, CH_2Cl_2/CH_3COOH; (c) NIS, CH_2Cl_2/CH_3COOH; (d) $Me_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, *i*Pr_2NH; (e) K_2CO_3, MeOH/THF.

Poly[(3,6-di-*tert*-butyl-*N*-hexadecyl-1,8-carbazolylene)butadiynylene] (P3). To a solution of **6** (88 mg, 0.16 mmol) in toluene (0.42 mL), CuCl (7.6 mg, 0.074 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (65.5 mL, 0.440 mmol) were added, and the solution was stirred for 7 h at 60 °C under air. After cooling to 20 °C, the mixture was poured into MeOH (300 mL). The precipitate was collected, and the polymer was purified by reprecipitation into MeOH and then dried in vacuo (75 mg, 86%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.80−2.42 (m, 51nH), 5.51 (s, 2nH), 8.02 (m, 2nH), 8.28 (m, 2n). IR (KBr): 3066, 2957, 2921, 2850, 2136, 1483, 1426, 1392, 1364, 1319, 1309, 1265, 1257, 1227, 1202, 1182, 869, 741, 669, 639.

Results and Discussion

Polymer Synthesis. The 1,8-dihalogeno- and 1,8-diethynylcarbazole derivatives were designed as a monomer for polymerization. Considering the electron density distribution of the carbazole, the highest electron density position of the 3,6-positions must first be protected.[14] Starting from *N*-hexadecylcarbazole (**1**), *tert*-butyl groups were introduced at the 3,6-positions of **1** under the modified Friedel−Crafts conditions using $AlCl_3$ as a catalyst, affording **2** in 91% yield (Scheme 1). The *tert*-butyl groups were stable in the following reactions. The second highest electron density positions of the carbazole are the 1,8-positions because of the *ortho* pattern relative to the carbazole nitrogen. The reaction of **2** with 2 equiv of *N*-bromosuccinimide or *N*-iodosuccinimide proceeded at room temperature to yield the corresponding 1,8-dibromo- or 1,8-diiodocarbazole derivatives **3** and **4** in moderate yields. These dihalogenated carbazoles could be used as a polymerization monomer by the palladiuim or nickel-catalyzed cross-coupling reactions, such as the Sonogashira reaction[15] and Yamamoto reaction.[16] The counter monomer of the Sonogashira reaction should possess the terminal alkyne groups. Therefore, the ethynyl groups were introduced at the 1,8-positions of the carbazole **4** by the Sonogashira reaction with trimethylsilylacetylene under standard conditions (CuI, [$PdCl_2(PPh_3)_2$], *i*Pr_2NH), followed by the deprotection of the silyl group with K_2CO_3. The obtained carbazole derivatives **5** and **6** were stable both in solutions and in the solid state under ambient conditions. The diethynyl-substituted carbazole **6** can also be employed as a monomer for the polymerization by the acetylenic oxidative coupling reactions, such as the Hay reaction.[17] It should be noted that the Sonogashira reaction of the dibromocarbazole derivative **3** with trimethylsilylacetylene did not give the desired product at all, probably because of the inferior bromide leaving group as compared to the iodine counterpart. This is also true for the nickel-catalyzed cross-coupling reaction (vide infra). Furthermore, to examine the polymerization possibility by the Suzuki coupling reaction,[18] synthesis of the carbazole derivative substituted by boronic acid groups at the 1,8 positions was tried. However, all trials were unsuccessful, and a small amount of the monosubstituted derivative was obtained from **4**, which was not sufficient for us to continue the subsequent reactions.

Table 1. Summary of the Polymerization Results and Thermal Properties

polymer	M_w[a]	M_n[a]	M_w/M_n[a]	$T_{5\%}$ (°C)[b]	T_g (°C)[c]
P1	1400	1400	1.0	234	[d]
P1′	1300	1100	1.2		
P2	6100	4000	1.5	320	80
P3	9400	4100	2.3	375	67

[a] Determined by GPC (THF eluent, calibrated by polystyrene standards). [b] Temperature at which 5% weight loss occurred upon heating. [c] Glass transition temperature determined by the second heating scan of DSC measurements. [d] No peak appeared.

Polymerization of the carbazole monomers **2**, **4**, and **6** was performed, and the resulting polymers were characterized by GPC, MALDI-TOF MS, ^{1}H NMR, and IR. First, the oxidative polymerization of **2** was examined using $FeCl_3$ to afford the directly linked poly(1,8-carbazole) **P1′** (Scheme 2). However, the molecular weight (M_w) determined by GPC was merely 1300, and the yield was disappointedly low (35%) (Table 1). Next, the same polymer was prepared from **3** or **4** under the conventional Yamamoto reaction conditions ([Ni(cod)], cod, bpy, DMF). The diiodocarbazole derivative gave a better result (yield 44%, M_w = 1400) than the dibromocarbazole derivative, although it is similar to the oxidative polymerization result. The ^{1}H NMR of the polymer showed multiplet peaks in the aromatic region, which includes the coupling of the *ortho* protons (Figure 1a). The MALDI-TOF MS spectrum of **P1** displayed the reasonable peaks of the oligomers (Figure 1, Supporting Information). These results suggest the presence of unstable intermediates in the catalytic cycle, leading to the hydro-dehalogenated oligomers. The steric hindrance with the long alkyl chain attached to the carbazole nitrogen would be another reason for the low molecular weight.

To obtain higher molecular weight poly(1,8-carbazole)s, polymerization of the diethynylcarbazole derivative **6** was tried. The Sonogashira polycondensation between **4** and **6** was performed in the presence of CuI and $PdCl_2(PPh_3)_2$ in a

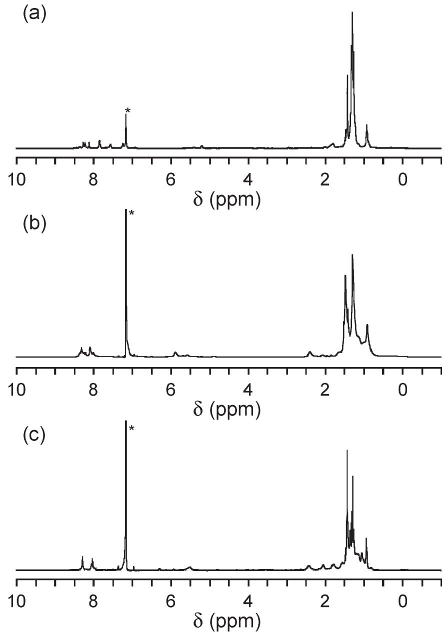
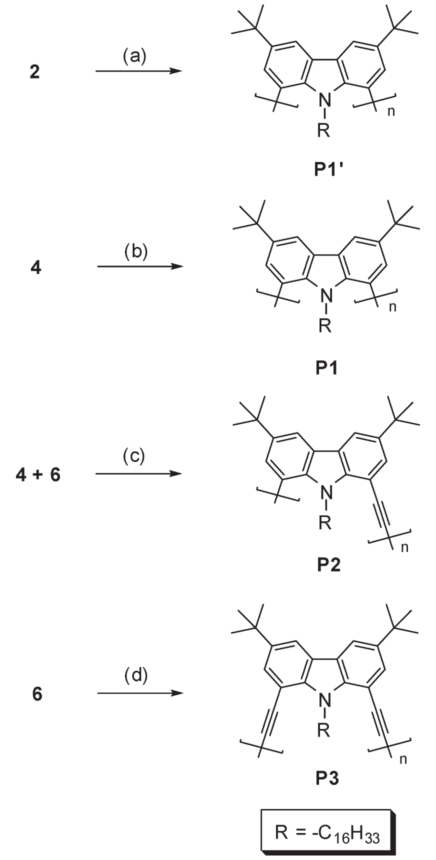


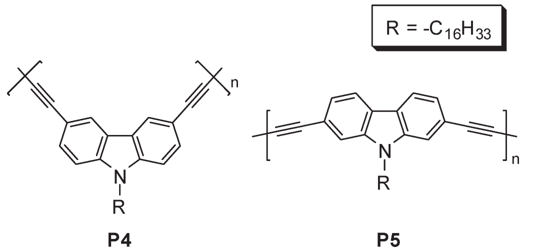
Figure 1. ^{1}H NMR spectra of (a) **P1**, (b) **P2**, and (c) **P3** in C_6D_6 at 20 °C. The residual solvent signal is marked.

Scheme 2. Synthesis of Conjugated Poly(1,8-carbazole)s[a]



[a] (a) $FeCl_3$, chlorobenzene; (b) Ni(cod)$_2$, cod, bpy, DMF; (c) $PdCl_2(PPh_3)_2$, CuI, *i*Pr_2NH, toluene, 80 °C; (d) O_2, CuCl, TMEDA, toluene, 60 °C.

Chart 1



mixture of toluene and *i*Pr_2NH (Scheme 2). The reaction generally proceeds at room temperature, but the reaction mixture was heated to 80 °C in order to obtain a preferably high molecular weight. The resulting ethynylene-linked poly(1,8-carbazole) **P2** was obtained as a yellow solid in a high yield and the M_w value of 6100 was much higher than those of **P1**. Furthermore, **6** was subjected to the oxidative polycondensation under the Hay conditions (O_2, CuCl, TMEDA, toluene) at 60 °C, affording the butadiynylene-linked poly(1,8-carbazole) **P3** as a yellow solid in a reasonable yield. The M_w value (9400) was further improved from that of **P2**. The MALDI-TOF MS also gave the well-defined peaks corresponding to the molecular weights determined by GPC (Figure 1, Supporting Information). Thus, the alkyne groups efficiently alleviate the steric hindrance, implying that both the Sonogashira reaction and Hay reaction are suitable polymerization methods for preparation of the conjugated poly(1,8-carbazole)s. The IR and NMR spectra substantiated the chemical structures of **P2** and **P3**. The IR peak at 3309 cm^{-1} of **6**, ascribed to the ethynyl C−H stretching vibration, completely disappeared for **P2** and **P3**. The ^{1}H NMR peak of the ethynyl protons of **6** was also absent in the spectra of these polymers, consistent with the IR spectra. Moreover, two well-defined single peaks were observed in the aromatic region, indicating the absence of any undesired side reactions (Figure 1b,c). Since the acetylenic oxidative polycondensation was proven to be the best method for producing the high molecular weight conjugated carbazole polymers, and diethynylcarbazole derivatives are readily accessible, we also prepared the butadiynylene-linked poly(3,6-carbazole) **P4** and poly(2,7-carbazole) **P5** from the corresponding *N*-hexadecyl-substituted diethynylcarbazole derivatives in a similar way to **P3** in order to compare the electrochemical and optical properties (Chart 1 and Supporting Information). The M_w values of **P4** and **P5** were 10 500 and 18 000, respectively. Comparison of the molecular weights between **P3**, **P4**, and **P5** suggests that a linear structure is superior to kinked structures for producing high molecular weight polymers.

Thermal Properties. Aromatic polymers containing multiple acetylene units are high-energy materials with thermally induced rearrangements or postpolymerization characteristics. To reveal the relationship between the alkyne content and the thermal stability, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of **P1**, **P2**, and **P3** were performed at the scanning rate of 10 °C min^{-1} under flowing nitrogen. Unexpectedly, the decomposition temperature increased with the increasing alkyne content. Thus, the 5% weight loss temperature ($T_{5\%}$) increased in the order of **P1** (234 °C) < **P2** (320 °C) < **P3** (375 °C) (Table 1). Decomposition of **P1** proceeded in two or three steps, whereas **P2** and **P3** showed single main decompositions (Figure 2). The DSC measurement of **P1** did not show any transitions in the range from −50 to 200 °C, whereas the glass transition temperature (T_g) of **P2** and **P3** clearly appeared at 80 and 67 °C, respectively (Table 1). Thus, it was demonstrated that alkyne spacers serve as an important component to improve the thermal properties of the poly(1,8-carbazole)s. For comparison, the TGAs of **P4**

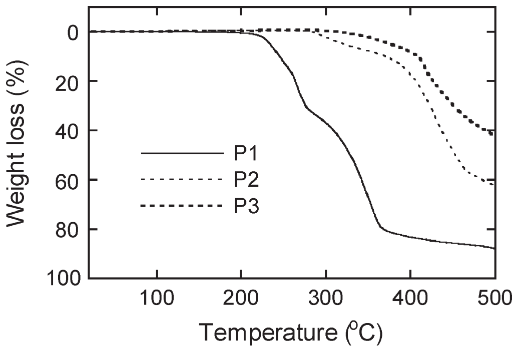


Figure 2. TGA curves of poly(1,8-carbazole)s at a heating rate of 10 °C $\min^{-1}$ under flowing nitrogen.

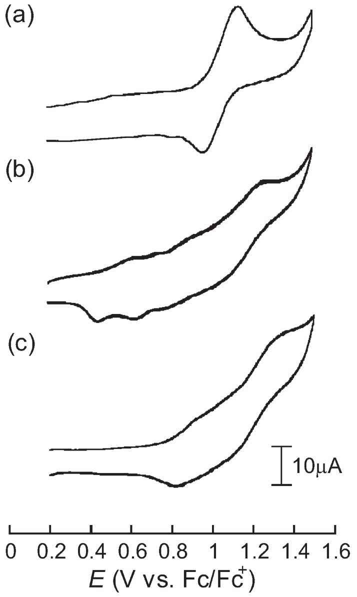


Figure 3. Cyclic voltammograms of (a) **P1**, (b) **P2**, and (c) **P3** in CH_2Cl_2 with 0.1 M $(nC_4H_9)_4NClO_4$ at the scanning rate of 0.1 V s^{-1} under flowing nitrogen.

and **P5** were also performed. The $T_{5\%}$ values of **P4** and **P5** were 335 and 445 °C, respectively. These results suggest that the high thermal stability of the alkyne-linked polycarbazole is a general phenomenon and that the thermal stability of the poly(1,8-carbazole)s lie between the poly(3,6-carbazole)s and poly(2,7-carbazole)s.

Electrochemistry. Since aromatic polyamines feature potent redox activities in the anodic direction because of their electron-rich nature,[19] cyclic voltammograms (CVs) of the polycarbazoles were measured both in solutions and in the solid film state. The obtained polymers were very soluble in the common organic solvents, such as $CHCl_3$, CH_2Cl_2, and THF. Therefore, the solution measurements were performed in CH_2Cl_2 with 0.1 M $(nC_4H_9)_4NClO_4$ at 20 °C.

Figure 3 shows the typical CV curves of the conjugated poly(1,8-carbazole)s in CH_2Cl_2. All poly(1,8-carbazole)s displayed reversible oxidations and the corresponding reduction steps on the CV time scale. **P1** had a well-defined single redox couple with a peak separation of 160 mV, whereas **P2** and **P3** showed much broader and multiple peaks. This difference probably reflects the effect of the electrostatic repulsion through the alkyne spacers as well as the difference in the molecular weight. The oligomeric **P1** behaved as a small molecule, in which each carbazole unit is electronically isolated, whereas the polymeric **P2** and **P3** tended to partially adsorb on the electrode surface during the voltage sweeps, resulting in the enhanced intra- and intermolecular interactions between the carbazole units. To investigate the CVs in the solid state, the polymer cast films were prepared on the Pt working electrode and subjected to measurements in CH_3CN with 0.1 M $(nC_4H_9)_4NClO_4$. In sharp contrast to the solution CVs, all the polymers exhibited irreversible oxidation peaks at 20 °C. The peak potential of **P1** was almost the same as that in solution, while the **P2** and **P3** polymers displayed much higher oxidation peak potentials than in the solutions. This result again highlights the difference in the molecular weight between the polymers. The observed peak potentials and formal redox potentials are summarized in Table 2.

Table 2. Summary of the Electrochemistry Data of Poly(1,8-carbazole)s[a]

	in CH_2Cl_2[b]				film[c]	
polymer	E_{onset} (V)	$E^{\circ\prime}$ (V)[d]	E_{pa} (V)[d]	E_{pc} (V)[d]	E_{onset} (V)	E_{pa} (V)
P1	0.98	1.06	1.14	0.98	0.88	1.17
P2	0.48	0.53	0.61	0.44	0.99	1.02
		0.69	0.74	0.63		1.13
		1.17	1.24	1.09		1.33
P3	0.80	0.85	0.87	0.83	0.96	1.10
		1.18	1.23	1.13		1.33

[a] Potentials vs Fc/Fc^+ couple. Working electrode: glassy carbon electrode; counter electrode: Pt wire; reference electrode: Ag/Ag^+. [b] Measured in CH_2Cl_2 with 0.1 M $(nC_4H_9)_4NClO_4$ at a scanning rate of 0.1 V s^{-1} under flowing nitrogen. [c] Measured in CH_3CN with 0.1 M $(nC_4H_9)_4NClO_4$ at a scanning rate of 0.1 V s^{-1} under flowing nitrogen. [d] $E^{\circ\prime} = (E_{pc} + E_{pa})/2$, in which E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.

To extract the important electrochemical characteristics of the poly(1,8-carbazole)s, the CVs of the butadiyne-linked poly(3,6-carbazole) **P4** and poly(2,7-carbazole) **P5** were also measured under the same conditions as **P3**. The electrochemical activity of **P4** was robust, although the second and third oxidations were irreversible (Figure 2SI and Table 1SI). On the other hand, **P5** was not as electrochemically active as **P3** and the reversibility of the CV was negligibly low. This is because the poly(1,8-carbazole)s can essentially be regarded as belonging to the same class of polymers as the poly(3,6-carbazole)s and not the poly(2,7-carbazole)s by taking into account the substitution pattern relative to the carbazole nitrogen.[3]

UV–vis and Fluorescence Spectroscopy. The spectroscopic properties of conjugated polymers offer a quick guide to the effective conjugation length and band gaps of the polymers. For example, the absorption maxima of the poly(2,7-carbazole)s usually appear at a longer wavelength than the corresponding poly(3,6-carbazole)s, suggesting a longer effective conjugation length and a smaller band gap of the poly(2,7-carbazole)s.[3]

Since all polymers in this study did not exhibit solvatochromic behaviors in homogeneous solutions, the normalized absorption and emission spectra measured in CH_2Cl_2 are shown in parts a and b of Figure 4, respectively, and the data are summarized in Table 3. The longest wavelength absorption maximum (λ_{max}) of **P1** was observed at 364 nm in CH_2Cl_2. As expected from the decrease in the band gap, the λ_{max} values bathochromically shifted with an increase in the alkyne spacer length. Accordingly, the λ_{max} of the ethynylene-linked polycarbazole **P2** was 389 nm, and that of the butadiynylene-linked polycarbazole **P3** was 420 nm. The solution fluorescence spectra of these polymers showed behavior similar to the absorption spectra. The most intense emission peak maxima (λ_{em}) in CH_2Cl_2 bathochromically shifted from 381 nm for **P1**, to 421 nm for **P2**, and further to

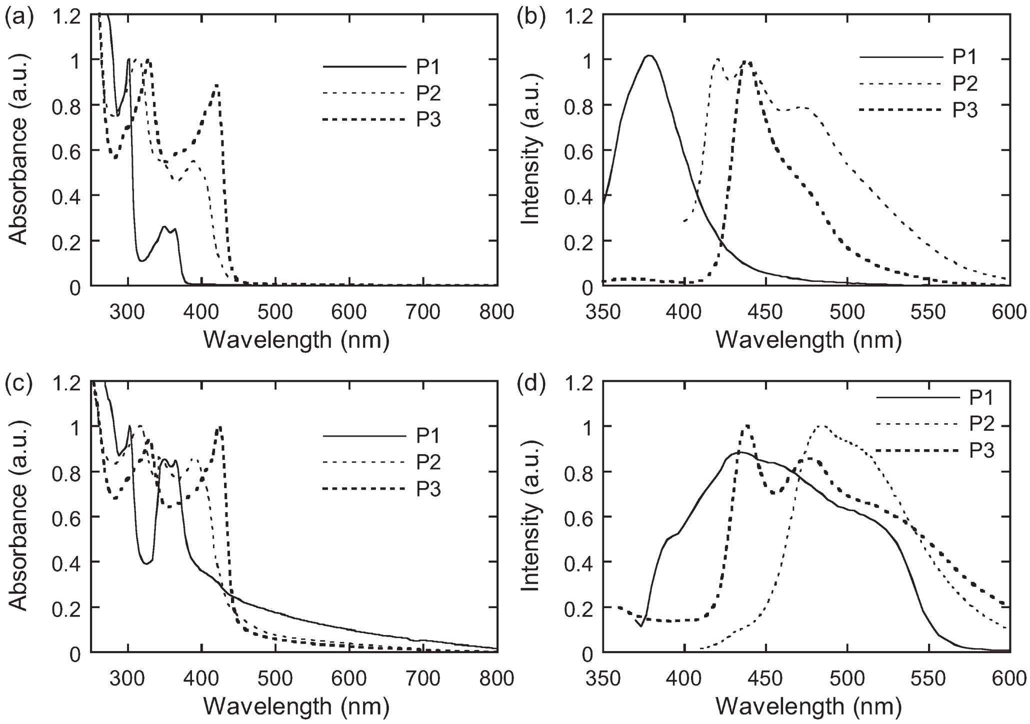


Figure 4. Normalized UV−vis absorption (a, in CH_2Cl_2; c, in film) and fluorescence spectra (b, in CH_2Cl_2; d, in film) of **P1**, **P2**, and **P3**.

Table 3. Summary of the Optical Properties of Poly(1,8-carbazole)s

	in CH_2Cl_2				film	
polymer	λ_{max} (nm)	λ_{em} (nm) [λ_{ex} (nm)]	Stokes shift (cm^{-1})	$\Phi_{f,sol}$[a]	λ_{max} (nm)	λ_{em} (nm) [λ_{ex} (nm)]
P1	364	381 [302]	1225	0.012	364	428 [350]
P2	389	421, 438, 473 [389]	1954	0.718	390	481, 512 [390]
P3	420	439 [328]	1030	0.308	423	439, 476, 525 [329]

[a] Determined against quinine sulfate in 0.05 M aqueous H_2SO_4 (Φ_f = 0.546) as a standard.

439 nm for **P3**. The quantum yield (Φ_f) of **P1** in CH_2Cl_2 was merely 0.012, but it was found that the incorporation of alkyne spacers into **P1** dramatically increased the fluorescence efficiency. Thus, **P2** and **P3** showed much higher Φ_f values of 0.718 and 0.308, respectively. Despite the general fact that a large Stokes shift generally leads to a lower quantum yield,[20] **P2** displayed the highest Φ_f among the three poly(1,8-carbazole)s. This is partly related to the broad emission peak with additional vibration peaks at 438 and 473 nm. In contrast, the emission peak of **P3** is composed of the main blue-light emission at 420 nm with a longer wavelength weak shoulder.

The optical properties of the butadiynylene-linked poly(1,8-carbazole) **P3** were compared with those of the poly(3,6-carbazole) **P4** and the poly(2,7-carbazole) **P5**. The λ_{max} of **P3** in CH_2Cl_2 was much greater than that of **P4** (385 nm)[21] and almost comparable to that of **P5** (419 nm) with an extended conjugation due to the rigid poly(*p*-phenylene) motif (Figure 3SI). This narrow band gap of **P3** could partially be attributed to the electron-donating *tert*-butyl groups at the 3,6-positions, but it is apparent that the effective conjugation length of the poly(1,8-carbazole)s is longer than that of the poly(3,6-carbazole) in this series. All the butadiynylene-linked polycarbazoles displayed a blue-light emission in CH_2Cl_2 at 20 °C, and the Stokes shift value of **P3** lies between **P4** and **P5** (Table 2SI). The Φ_f of **P3** was about 4 times greater than that of the same class of polymer **P4**.

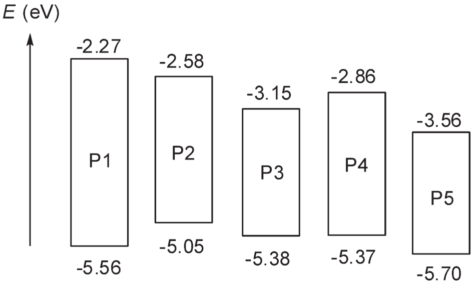


Figure 5. Schematic energy level diagrams of **P1**−**P5**.

The energy diagrams of **P1**−**P5** were determined by the onset oxidation potentials (E_{onset}) of the solution CVs and the optical band gaps in CH_2Cl_2 estimated from the end absorption (λ_{end}). The HOMO levels were calculated from the E_{onset} values based on the assumption of $Fc/Fc^+ = -4.80$ eV. Similarly, the LUMO levels were calculated from the HOMO levels and the optical band gaps (Figure 5 and Table 3SI). As shown in the diagram, the band gap decreases with the increasing amount of the alkyne spacer in poly(1,8-carbazole)s. In particular, the LUMO levels linearly decreased from **P1** to **P3**, which is consistent with a fact that the alkyne groups feature an electron-accepting ability and thereby affects the LUMO levels.[22] The energy level of **P3** was also compared to those of **P4** and **P5**. Because of the same class of substitution patterns, the HOMO levels of **P3** and **P4** were almost identical. Therefore, the LUMO levels reflect the difference in the band gaps between these polymers. On the other hand, the overall energy levels of **P5** were

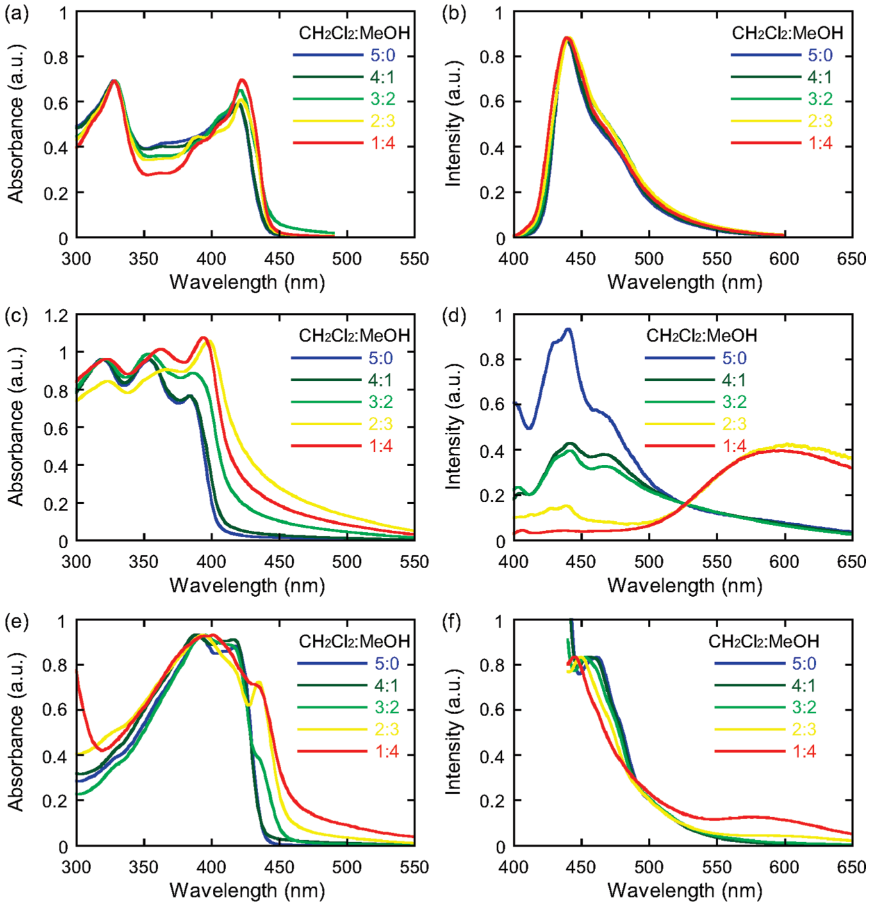


Figure 6. Solvatochromic behaviors of UV−vis absorption (a, **P3**; c, **P4**; e, **P5**) and fluorescence spectra (b, **P3**; d, **P4**; f, **P5**) in CH_2Cl_2/MeOH mixtures.

much lower than these two polymers, although the band gaps of **P3** and **P5** were comparable.

It was shown that most of the alkyne-linked carbazole polymers display a blue-light emission in solutions. However, the fluorescence spectra in the solid state or aggregated states become more important for practical OLED applications. To reveal the difference in the optical properties between in solutions and in the solid state, the absorption and fluorescence spectra in the solid state were measured. The polymer solutions in CH_2Cl_2 were cast on a quartz plate, and the solvent was allowed to evaporate. The absorption spectral shapes of **P1**−**P3** in the solid films were very similar to those in the solutions except for the broadened end absorptions reaching ∼800 nm (Figure 4c). It should be noted that the bathochromic shift in the $\lambda_{\max}$ values is negligible (Table 3). However, the fluorescence spectra in the solid films showed a significant change from the corresponding solution spectra. The spectra of the **P1**−**P3** solid films are shown in Figure 4d. The emission peaks of **P1** and **P2** in CH_2Cl_2 completely disappeared, and new broad peaks representing the excimers appeared at longer wavelengths. On the other hand, the solution emission peak of **P3** was retained even in the solid state. Thus, the butadiyne-linked poly(1,8-carbazole) **P3** displayed the three emission peaks in the solid state at 439 nm originating from single polymers as well as at 476 and 525 nm from the excimers. All these results suggest that the excited states upon light irradiation induce stronger intermolecular interactions in the solid states, whereas the interactions in the ground state are very weak. The observed absorption and fluorescence spectra in the solid state did not change even after annealing at 100 °C for 10 min, indicating the less crystalline feature of the conjugated poly(1,8-carbazole)s.

To shed light on this decreased aggregation propensity of **P3**, an additional solvatochromic analysis was performed for **P3**, **P4**, and **P5**. Previously, Leclerc et al. and Bunz et al. independently reported the continuous spectral changes upon the addition of a poor solvent into a good solvent of conjugated polymers, resulting in the aggregated states.[4d,4g,23] In this study, MeOH was employed as a poor solvent. The addition of MeOH to the homogeneous polymer solutions in CH_2Cl_2 lead to a gradual bathochromic shift in the absorption spectra (Figure 6). The shift of **P4** and **P5** was greater than that of **P3**. Remarkably, the difference between **P3** and **P4**/**P5** became more significant in the fluorescence spectra. With the increasing amount of MeOH, the initial single polymer-based emission peaks started to decrease and a new excimer peak appeared at 600 nm for **P4** and at 578 nm for **P5** when the MeOH content exceeded 60%. However, the poly(1,8-carbazole) derivative **P3** did not change the emission spectral shape up to the MeOH content of 80%, indicating efficient suppression of the excimer formation. This result was also supported by the fact that the spectroscopic behaviors of **P4** and **P5** in the solid film state were similar to those of **P1** and **P2** (Figure 3SI and Table 2SI). In other words, only **P3** displays an exceptionally stable blue-light emission. The low aggregation behavior of **P3** was also suggested by the preliminary OFET measurements of the conjugated carbazole polymers. The device containing **P3** did not work at all even after optimization of the measurement conditions.

Conclusion

A new class of conjugated carbazole polymers was synthesized from 1,8-difunctionalized carbazole derivatives. It was demonstrated that the alkyne spacer is an important component for the efficient synthesis of high molecular weight poly(1,8-carbazole)s, enhanced thermal stability, and high quantum yield of the blue-light emission. In particular, the butadiynylene-linked poly(1,8-carbazole) was found to show an excimer-insensitive blue-light emission, which offers a potential application in OLEDs. The device preparation and the evaluation are currently under way. Furthermore, in this study, we employed the *tert*-butyl substituent at the 3,6-positions of the carbazole because of the protecting stability and the easy synthesis. However, the effects of the bulky *tert*-butyl groups should be elucidated in detail. Therefore, we also plan to synthesize new conjugated poly(1,8-carbazole)s with other substituents at the 3,6-positions, such as long alkyl or alkyleneoxy chains.

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Supporting Information Available: MALDI-TOF MS spectra of **P1**−**P3** and experimental details on synthesis and measurements of **P4** and **P5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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