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STEPWISE SYNTHESES OF 3,6-CARBAZOLE-BASED CONJUGATED OLIGOMERS

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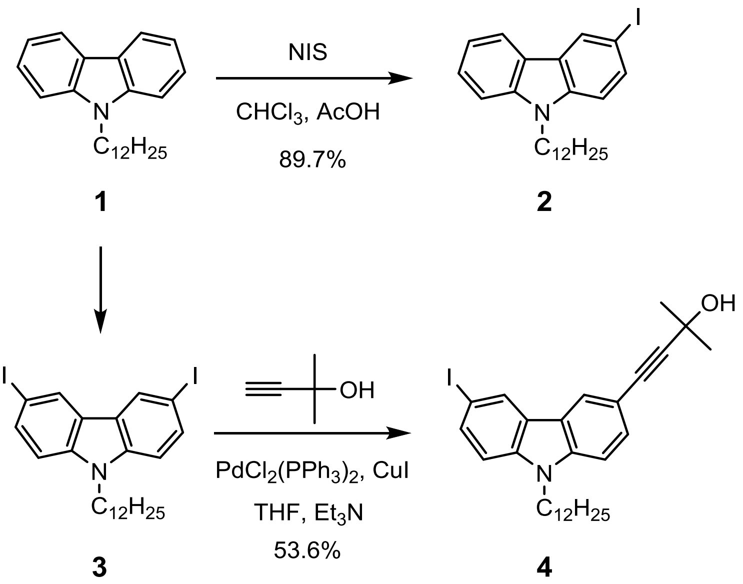
Abstract – A series of monodispersed ethynylene-linked 3,6-carbazole oligomers was synthesized by the Sonogashira coupling and deprotection protocol. The resulting conjugated carbazole oligomers were characterized by ^{1}H-, ^{13}C-NMR, and IR spectroscopies, and MALDI-TOF mass spectrometry. The effective conjugation length of the 3,6-carbazole structure was evaluated from the longest wavelength absorption maxima (λ_{max}) in CH_2Cl_2. The λ_{max} gradually red-shifted with the increasing carbazole unit, and this bathochromic shift saturated at the pentamer.

INTRODUCTION

Conjugated carbazole molecules and polymers have attracted considerable interest by both synthetic chemists and device physicists, because they show numerous optoelectronic properties, such as photorefractive, photoconducting, and hole-transporting properties, and their device performances can be tuned by chemical modification of the substituents and substitution patterns.[1] We have reported various conjugated carbazole molecules and polymers. For example, nitrogen-linked poly(2,7-carbazole)s were synthesized by the palladium-catalyzed amination reaction and applied to the hole-transporting layer of organic light-emitting diodes (OLEDs).[2] Conjugated poly(1,8-carbazole)s were also synthesized by the metal-catalyzed coupling reactions, and their white-light emitting and photovoltaic performances were recently evaluated.[3] Apart from the multistep synthetic routes of the 2,7-carbazole and 1,8-carbazole derivatives, the 3,6-positions of the carbazole are readily functionalized due to the highest electron density positions. Thus, conjugated poly(3,6-carbazole)s are also regarded as an important class of materials for organic device applications.[4] In order to obtain basic knowledge about the conjugated polymers, it is important to determine their structure-property relationship. To this end, the effective conjugation length, determined from the absorption maxima of the monodispersed conjugated oligomers, is a good guide to estimate the optical and electrical properties.[5] We now report the synthesis of 3,6-carbazole-based conjugated oligomers for the elucidation of their effective conjugation length. An ethynylene spacer was employed to connect the adjacent carbazole units, because it restricts the steric hindrance but retains the intramolecular electronic communication.[6]

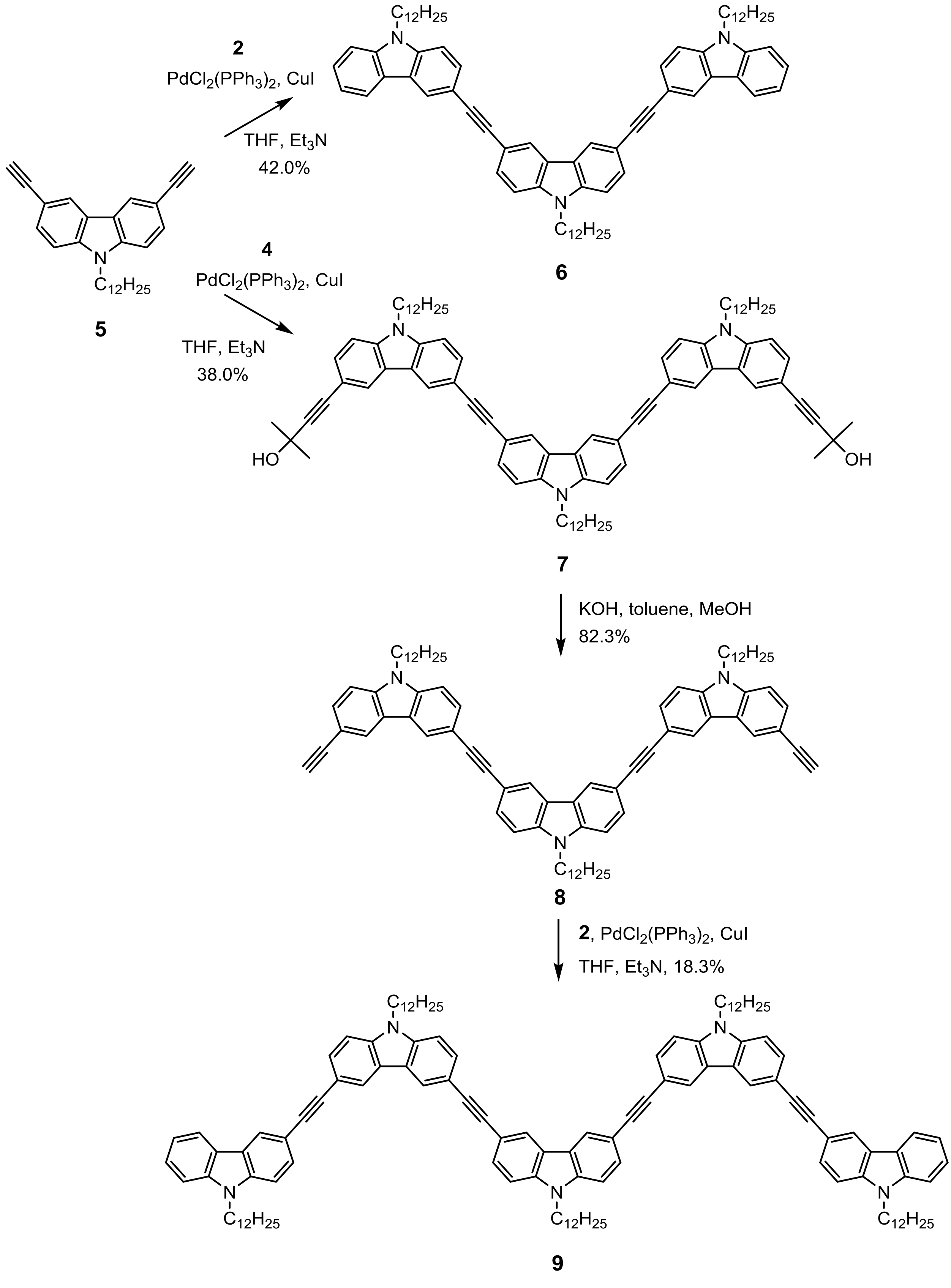
RESULTS AND DISCUSSION

The dodecyl chain was introduced at the 9-position of the carbazole in order to achieve sufficient solubilities in organic solvents even for the larger oligomers. Thus, starting from 9-dodecyl-9*H*-carbazole **1**,[7] treatment with 1 equiv. of *N*-iodosuccinimide (NIS) furnished 9-dodecyl-3-iodo-9*H*-carbazole **2** in 89.7% yield (Scheme 1). The 3-position of the carbazole was then selectively iodinated. Similar to this result, the addition of 2 equiv. of NIS furnished 9-dodecyl-3,6-diiodo-9*H*-carbazole **3**.[8] The ethynylene group was introduced into **3** by the Sonogashira cross-coupling ($PdCl_2(PPh_3)_2$, CuI, Et_3N, THF) with 1 equiv. of 2-methylbut-3-yn-2-ol, yielding **4** in 53.6% yield.



Scheme 1. Synthesis of carbazole derivatives

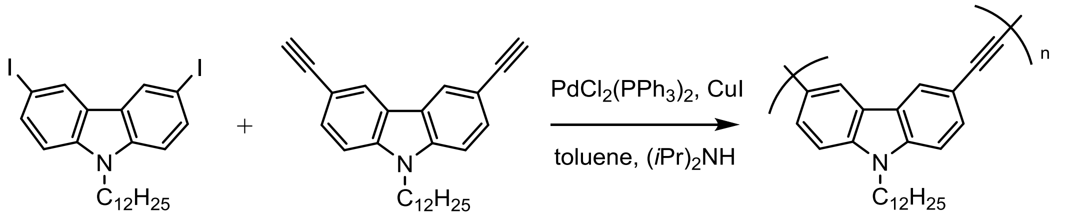
9-Dodecyl-3,6-diethynyl-9*H*-carbazole **5** was prepared from **3** by the Sonogashira coupling and deprotection protocol.[9] This carbazole molecule was further subjected to the Sonogashira coupling with 2.5 equiv. of **2** (Scheme 2). After chromatographic purification on SiO_2, the trimer **6** was isolated in 42.0% yield. Due to the electron-rich feature of the carbazole unit, the yield was moderate. The same protocol was applied to the synthesis of **7**. The Sonogashira cross-coupling of **5** with **4** (2.7 equiv.) afforded the desired product **7** in 38.0% yield. The protecting group of the alkyne was removed with KOH in a refluxing



Scheme 2. Synthesis of conjugated carbazole oligomers

toluene/THF mixture. The carbazole trimer **8** with two terminal alkynes was thus isolated in 82.3% yield. Finally, the Sonogashira coupling of **8** with an excess of **2** (4.0 equiv.) afforded the carbazole pentamer **9**. Since both purification methods using column chromatography on SiO_2 and a recycling high performance liquid chromatography (HPLC, Japan Analytical Industry Co., Ltd., column: JAIGEL-2.5H-40, eluent: $CHCl_3$) were required, the isolated yield was merely 18.3%. All compounds were fully characterized by their ^{1}H- and ^{13}C-NMR, FT-IR, and MALDI-TOF MS spectra. They were pure on the NMR detection level. In the NMR spectra of **6**-**9**, the expected peak patterns consistent with the symmetric structures were detected. Also, the presence of either terminal alkyne or internal alkynes was confirmed by the IR spectra. For example, carbazole oligomers **6**-**9** showed a weak peak ascribed to the alkyne (C≡C) vibration at 2204-2218 cm^{-1}. However, only **8** displayed an additional peak at 3309.3 cm^{-1} originating from the C-H vibration of the terminal alkyne. In the MALDI-TOF MS spectra, the desired molecular ion peaks and/or the protonated peaks were clearly detected.

In order to investigate the effective conjugation length of the alkyne-linked 3,6-carbazole structure, the corresponding linear polymer **10** was also synthesized. Sonogashira polycondensation was performed at the equimolar feed ratio of **3** and **5** in the presence of $PdCl_2(PPh_3)_2$ and CuI in a toluene/(iPr)$_2$NH mixture at 80 ^{o}C for 12 h (Scheme 3). The resulting polymer was purified by reprecipitation in MeOH, and the weight-average molecular weight (M_w) and number-average molecular weight (M_n), determined by gel permeation chromatography (GPC), were 8700 and 5200, respectively. The molecular weight (M_n) corresponds to the repeat unit (n) of 14.5. This polymer was also characterized by ^{1}H-NMR and IR.



3 **5** **10**

Scheme 3. Synthesis of conjugated carbazole polymer

The absorption spectra of **1** (monomer), **6** (trimer), **9** (pentamer), and **10** (polymer with n = 14.5) were measured in CH_2Cl_2. All the carbazole derivatives showed a well-defined unimodal absorption peak in the UV range. The longest wavelength absorption maximum (λ_{max}) of **1** was 347 nm. The λ_{max} bathochromically shifted when the repeat unit number (n) increased to **6** (356 nm) and **9** (365 nm). However, as shown in Figure 1, the λ_{max} (366 nm) of the polymer **10** was close to that of **9**. This result suggests that the effective conjugation length of the alkyne-linked 3,6-carbazole structure is approximately 5. This value is much lower than that estimated for the 2,7-carbazole-based oligomers (the effective conjugation length of 11 repeat units).[10] This discrepancy can be mainly explained by the different substitution patterns of the carbazole, although there is also a difference in the π-spacers (direct linkage for the 2,7-carbazole-based oligomers[10] vs. ethynylene linkage for the 3,6-carbazole-based oligomers in this work). The 2,7-linkage of the carbazole is classified as a linear conjugation pattern, whereas the 3,6-linkage of the carbazole is a cross-conjugated pattern. Thus, it is reasonable to conclude that the effective conjugation length of the 3,6-carbazole structure is less than that of the 2,7-carbazole one. It should be noted that there are similar reports on the alkyne-linked 3,6-carbazole oligomers, but the effective conjugation length was not described.[11] This work is the first study that has revealed the structure-property relationship of the alkyne-linked 3,6-carbazoles. The pentamer **9** is expected to possess optical and electronic properties similar to the corresponding polymer **10**.

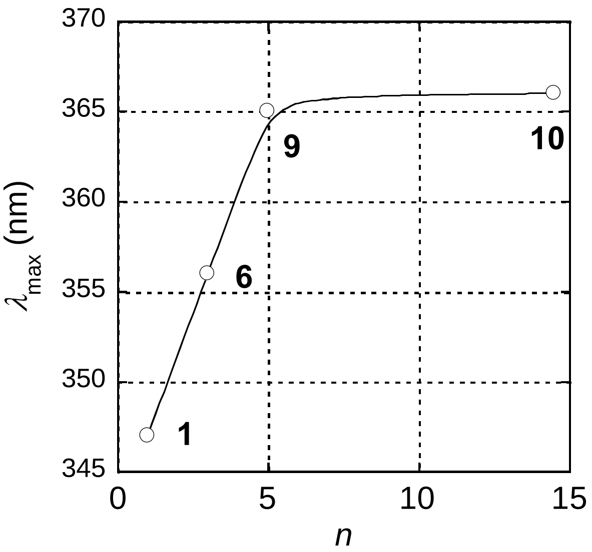


Figure 1. Relationship between the repeat unit number (n) and λ_{max} in CH_2Cl_2

EXPERIMENTAL

Materials

All reagents were purchased from Kanto, Tokyo Kasei, Wako, and Aldrich and used as received. 9-Dodecyl-9*H*-carbazole **1**[7], 9-dodecyl-3,6-diiodo-9*H*-carbazole **3**[8], and 9-dodecyl-3,6-diethynyl-9*H*-carbazole **5**[9] were prepared according to a literature method.

General Measurements

^1H NMR and ^{13}C NMR spectra were recorded on a JEOL model AL300 or AL400 spectrometer at 20 °C. Deuterated chloroform and benzene were used as a solvent. Chemical shifts are reported in ppm (parts per million) using either tetramethylsilane (TMS) or residual solvent signal as an internal reference. Coupling constants (*J*) are given in Hz. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), and m (multiplet). Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer in the range from 4000 to 400 cm^{-1}. MALDI-TOF MS spectra were measured on a Shimadzu/Kratos AXIMA-CFR mass spectrometer using dithranol as a matrix. Gel permeation chromatography (GPC) was measured on a JASCO system (PU-2080, CO-2065, RI-2031, AS-2055) equipped with polystyrene gel column (Shodex KF-804L) using tetrahydrofuran (THF) as an eluent at the flow rate of 1.0 mL min^{-1} after calibration with standard polystyrenes. UV spectra were recorded on a JASCO V-670 spectrophotomter.

9-Dodecyl-3-iodo-9*H*-carbazole (2): To a 300 mL round bottom flask, 9-dodecyl-9*H*-carbazole **1** (6.71 g, 20 mmol), $CHCl_3$ (140 mL), and AcOH (50 mL) were placed and the mixture was stirred at 20 °C. To this solution, *N*-iodosuccinimide (NIS, 4.73 g, 21.0 mmol) was added. After the mixture was stirred at 20 °C for 20 h, the organic phase was washed with saturated aq. $NaHCO_3$ (100 mL x 5) and H_2O (100 mL x 3) and dried over Na_2SO_4. After filtration, the solvent was evaporated and column chromatography (SiO_2, hexane/CH_2Cl_2 9:1) yielded the desired product (6.84 g, 89.7%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, *J* = 6.6 Hz, 3H), 1.22-1.48 (m, 20H), 3.62 (t, *J* = 7.1 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 1H), 7.08 (t, *J* = 8.1 Hz, 1H), 7.18 (m, 1H), 7.33-7.39 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 8.40 ppm (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.42, 23.15, 27.41, 29.00, 29.70, 29.82, 29.84, 30.00, 30.07, 30.08, 32.35, 42.87, 81.70, 109.07, 111.03, 119.67, 121.08, 122.09, 125.92, 126.56, 129.70, 134.13, 139.87, 140.77 ppm. IR (neat): ν 2919.7, 2847.4, 1591.0, 1489.7, 1472.4, 1464.7, 1454.1, 1444.4, 1348.0, 1328.7, 1313.3, 1274.7, 1242.9, 1224.6, 1148.4, 886.1, 786.8, 718.4 cm^{-1}. MALDI-TOF MS (dithranol) *m/z*: [M$^+$] calcd for $C_{24}H_{32}IN$: 461.16; found, 462.20.

4-(9-Dodecyl-6-iodo-9*H*-carbazol-3-yl)-2-methylbut-3-yn-2-ol (4): To a 30 mL flask, 9-dodecyl-3,6-diiodo-9*H*-carbazole **3** (5.87 g, 10.0 mmol), THF (25 mL), and Et_3N (15 mL) were placed. After bubbling with Ar for 1 h, 2-methylbut-3-yn-2-ol (0.858 mL, 10.0 mmol), $PdCl_2(PPh_3)_2$ (143 mg, 0.200 mmol), and CuI (32.7 mg, 0.171 mmol) were added, and the mixture was stirred at 20 °C for 5 h. After passing through Celite (CH_2Cl_2), the solvents were evaporated. The crude product was then dissolved into CH_2Cl_2 and dried over Na_2SO_4. Filtration and column chromatography (SiO_2, hexane/EtOAc 9:1→5:1) afforded the desired product (2.91 g, 53.6%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.92 (t, *J* = 8.8 Hz, 9H), 1.00-1.43 (m, 23H), 1,62 (s, 6H), 1.68 (s, 1H), 3.55 (t, *J* = 9.5 Hz, 2H), 6.67 (d, *J* = 11.6 Hz, 1H), 6.90 (d, *J* = 11.2 Hz, 1H), 7.62-7.67 (m, 2H), 8.04 (d, *J* = 2.0 Hz, 1H), 8.26 ppm (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 14.40, 23.13, 27.36, 28.95, 29.65, 29.80, 29.84, 29.98, 30.06, 32.04, 32.33, 42.97, 65.60, 82.20, 83.37, 93.32, 109.03, 111.12, 114.32, 121.94, 124.99, 125.36, 129.87, 130.12, 134.51, 140.13, 140.18 ppm. IR (neat): ν 3362.3, 2922.6, 2851.2, 2226.4, 1625.7, 1592.0, 1478.2, 1435.7, 1376.9, 1348.0, 1316.2, 1285.3, 1221.7, 1149.4, 1133.9, 1019.2, 963.3, 919.9, 871.7, 803.2, 793.6, 762.7, 720.3, 643.1, 613.3, 567.0, 556.4 cm^{-1}. MALDI-TOF MS (dithranol) *m/z*: [M$^+$] calcd for $C_{29}H_{38}INO$: 543.20; found, 544.15.

3,3'-((9-Dodecyl-9*H*-carbazole-3,6-diyl)bis(ethyne-2,1-diyl))bis(9-dodecyl-9*H*-carbazole) (6): To a 50 mL flask, 9-dodecyl-3,6-diethynyl-9*H*-carbazole **5** (200 mg, 0.521 mmol), **2** (602 mg, 1.30 mmol), THF (18.4 mL), and Et_3N (9.2 mL) were placed. After bubbling with Ar for 1 h, $PdCl_2(PPh_3)_2$ (18.7 mg, 0.0261 mmol) and CuI (8.02 mg, 0.0261 mmol) were added, and the mixture was stirred at 20 °C for 60 h. The solvents were concentrated under reduced pressure and the resulting solution was passed through a plug (SiO_2, CH_2Cl_2). Evaporation and column chromatography (SiO_2, hexane/CH_2Cl_2 2:1→0:1) afforded the desired product (230 mg 42.0%). ^{1}H NMR (300 MHz, C_6D_6): δ 0.92 (t, J = 6.6 Hz, 9H), 1.10-1.50 (m, 53H), 3.68-3.78 (m, 6H), 7.03 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.13-7.16 (m, 2H), 7.22 (t, J = 7.4 Hz, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.92 (dt, J = 1.2, 8.4 Hz, 4H), 8.06 (d, J = 7.5 Hz, 2H), 8.53 (d, J = 1.2 Hz, 2H), 8.58 ppm (d, J = 1.2 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6): δ 14.46, 23.19, 23.20, 27.54, 29.17, 29.79, 29.88, 29.90, 29.95, 29.99, 30.08, 30.11, 30.14, 30.17, 32.39, 32.42, 43.02, 89.71, 90.15, 109.22, 109.37, 114.93, 115.54, 119.75, 121.02, 123.13, 123.22, 123.57, 124.44, 124.66, 126.34, 129.72, 130.01, 140.30, 140.59, 141.29 ppm. IR (neat): ν 2921.6, 2851.2, 2206.2, 1865.8, 1628.6, 1598.7, 1489.7, 1465.6, 1381.8, 1349.9, 1283.4, 1216.9, 1147.4, 1125.3, 1061.6, 1022.1, 881.3, 802.2, 744.4, 725.1, 654.7, 635.4, 611.3, 592.0, 524.5 cm^{-1}. MALDI-TOF MS (dithranol) *m/z*: [M$^+$] calcd for $C_{76}H_{95}N_3$: 1049.75; found, 1049.50.

4,4'-(((9-Dodecyl-9*H*-carbazole-3,6-diyl)bis(ethyne-2,1-diyl))bis(9-dodecyl-9*H*-carbazole-6,3-diyl))-bis(2-methylbut-3-yn-2-ol) (7): To a 500 mL flask, 9-dodecyl-3,6-diethynyl-9*H*-carbazole **5** (0.863 g, 2.25 mmol, **4** (3.32 g, 6.10 mmol), THF (79 mL), and Et_3N (39.6 mL) were placed. After bubbling with Ar for 1 h, $PdCl_2(PPh_3)_2$ (32.2 mg, 0.045 mmol) and CuI (8.66 mg, 0.045 mmol) were added, and the mixture was stirred at 20 °C for 3 d. After filtration of the precipitated salts, the solvents were evaporated. Purification using a recycling HPLC afforded the desired product (1.04 g, 38.0%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.90 (t, J = 6.8 Hz, 9H), 1.06-1.50 (m, 60H), 1.75 (s, 12H), 2.86 (br s, 2H), 3.66 (br s, 4H), 3.73 (br s, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.98-7.06 (m, 4H), 7.65 (d, J = 11.6 Hz, 2H), 7.87 (t, J = 9.8 Hz, 4H), 8.29 (s, 2H), 8.40 (s, 2H), 8.52 ppm (s, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 14.47, 23.17, 27.80, 29.50, 29.86, 30.13, 32.14, 32.42, 43.10, 65.74, 83.61, 89.97, 93.35, 109.32, 114.34, 115.32, 115.39, 123.30, 124.58, 130.00, 140.49, 140.58, 140.62 ppm. IR (neat): ν 3371.9, 2922.6, 2851.2, 2217.7, 1600.0, 1487.8, 1465.6, 1380.8, 1350.9, 1283.4, 1219.8, 1148.4, 1131.1, 966.2, 935.3, 880.3, 803.2, 720.3, 652.8, 590.1 cm^{-1}. MALDI-TOF MS (dithranol) *m/z*: [M$^+$] calcd for $C_{86}H_{107}N_3O_2$: 1213.84; found, 1213.37.

6,6'-((9-Dodecyl-9*H*-carbazole-3,6-diyl)bis(ethyne-2,1-diyl))bis(9-dodecyl-3-ethynyl-9*H*-carbazole) (8): To a 50 mL flask, **7** (200 mg, 0.165 mmol), toluene (10 mL), and MeOH (1 mL) were placed. After KOH (307 mg, 4.71 mmol) was added, the mixture was refluxed for 3 h. After cooling to 20 °C, CH_2Cl_2 (100 mL) was added, and the organic phase was washed with water (100 mL x 3) and dried over Na_2SO_4. Filtration and column chromatography (SiO_2, hexane/EtOAc 9:1) afforded the desired product (149 mg, 82.3%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.90 (t, J = 7.2 Hz, 9H), 1.06-1.48 (m, 60H), 2.94 (s, 2H), 3.62 (t, J = 7.1 Hz, 4H), 3.72 (t, J = 6.7 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 7.64 (dd, J = 1.6, 8.4 Hz, 2H), 7.87 (dd, J = 1.6, 8.0 Hz, 2H), 7.91 (dd, J = 1.6, 8.0 Hz, 2H), 8.29 (d, J = 1.2 Hz, 2H), 8.36 (d, J = 1.6 Hz, 2H), 8.52 ppm (d, J = 1.6 Hz, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 14.46, 23.18, 27.45, 29.07, 29.73, 29.87, 29.93, 29.99, 30.06, 30.13, 32.39, 43.05, 43.16, 53.39, 76.12, 85.33, 89.84, 89.97, 109.17, 109.34, 109.39, 113.42, 115.39, 115.50, 122.92, 123.18, 124.60, 125.34, 130.02, 130.10, 130.28, 140.51, 140.60, 140.87 ppm. IR (neat): ν 3309.3, 2921.6, 2851.2, 2204.2, 1733.7, 1628.6, 1568.8, 1486.9, 1465.6, 1381.8, 1349.9, 1320.0, 1304.6, 1284.4, 1267.0, 1148.4, 1131.1, 1089.6, 1059.7, 944.0, 921.8, 880.3, 803.2, 754.0, 735.7, 679.8, 650.9 cm^{-1}. MALDI-TOF MS (dithranol) *m/z*: [M$^+$] calcd for $C_{80}H_{95}N_3$: 1097.75; found, 1097.02.

6,6'-((9-Dodecyl-9*H*-carbazole-3,6-diyl)bis(ethyne-2,1-diyl))bis(9-dodecyl-3-((9-dodecyl-9*H*-carbazol-3-yl)ethynyl)-9*H*-carbazole) (9): To a 20 mL flask, **8** (128 mg, 0.117 mmol), **2** (216 mg, 0.468 mmol), THF (4.1 mL), and Et_3N (2.0 mL) were placed. After bubbling with Ar for 1 h, $PdCl_2(PPh_3)_2$ (1.28 mg, 1.77 μmol) and CuI (0.40 mg, 2.10 μmol) were added, and the mixture was stirred at 20 °C for 60 h. After the solvents were evaporated, column chromatography (SiO_2, hexane/CH_2Cl_2 5:1→0:1) followed by the purification using a recycling HPLC afforded the desired product (37.8 mg, 18.3%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.92 (t, J = 7.0 Hz, 15H), 1.10-1.33 (m, 90H), 1.48 (br s, 10H), 3.71-3.76 (m, 10H), 7.02-7.08 (m, 8H), 7.14 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.94 (t, J = 8.0 Hz, 8H), 8.05 (d, J = 8.0 Hz, 2H), 8.54-8.55 (m, 6H), 8.59 ppm (d, J = 1.2 Hz, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 14.46, 23.19, 27.52, 29.15, 29.77, 29.88, 29.93, 29.97, 30.09, 30.13, 30.15, 32.39, 43.00, 43.14, 89.73, 89.97, 90.17, 109.16, 109.22, 109.38, 114.95, 115.51, 115.57, 119.76, 121.06, 123.16, 123.26, 123.58, 124.48, 124.70, 126.31, 129.72, 129.99, 130.09, 140.30, 140.59, 140.63, 141.28 ppm. IR (neat): ν 2921.6, 2851.2, 2204.2, 1627.6, 1600.0, 1568.8, 1489.7, 1465.6, 1382.7, 1349.9, 1283.4, 1215.9, 1147.4, 1131.1, 1060.7, 1022.1, 880.3, 833.1, 744.4, 726.1, 651.8, 590.1, 527.4 cm^{-1}. MALDI-TOF MS (dithranol) *m/z*: [M$^+$] calcd for $C_{128}H_{157}N_5$: 1764.24; found, 1764.52.

Poly((9-dodecyl-9*H*-carbazole3,6-diyl)ethynylene) (10): To a 30 mL flask, **3** (206 mg, 0.350 mmol), **5** (134 mg, 0.350 mmol), toluene (6.72 mL), and (iPr)$_2$NH (2.24 mL) were placed. After bubbling with Ar for 1 h, the flask was attached to a vacuum line. $PdCl_2(PPh_3)_2$ (12.3 mg, 17.5 μmol) and CuI (1.33 mg, 6.93 μmol) were added under positive pressure of N_2 gas. After the mixture was heated to 80 °C for 24 h, iodobenzene (39.0 μL, 0.35 mmol) was added as an end-cap reagent and the mixture was further stirred at 80 °C for 12 h. The mixture was cooled to 20 °C and poured into MeOH. The resulting precipitate was collected and purified by reprecipitation from CH_2Cl_2 into MeOH, yielding the desired product (250 mg). M_w (GPC) 8700, M_n (GPC) 5200. ^{1}H NMR (400 MHz, C_6D_6): δ 0.92 (br s, 3nH), 1.29 (br s, 20nH), 3.70 (br s, 2nH), 6.96-8.61 (m, 6nH). IR (neat): ν 2921.6, 2851.2, 2201.4, 1625.7, 1593.9, 1565.9, 1483.0, 1380.8, 1349.9, 1283.4, 1230.4, 1148.4, 1131.1, 880.3, 802.2 cm^{-1}.

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