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ORIGINAL ARTICLE

Synthesis and solid-state polymerization of diacetylene derivatives directly substituted with a phenylcarbazole moiety

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We synthesized five novel asymmetric carbamate diacetylene (DA) derivatives with a 9-phenyl-9*H*-carbazol-3-yl group as an aromatic donor moiety directly bound to the DA. Upon ultraviolet irradiation, three DA derivatives became greenish blue in color and exhibited characteristic excitonic absorption bands, indicating successful regular 1,4-addition polymerization in the solid state to afford polydiacetylenes (PDAs). Among the derivatives, the PDA with the highest conversion exhibited a small ionization potential of 5.2 eV. This value is appropriate for hole injection from general electrodes, and this PDA has the potential for application in low-operating voltage organic electronic devices.

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INTRODUCTION

Diacetylene (DA) derivatives are well known to polymerize topochemically in the solid state via ultraviolet (UV) irradiation[1,2] or thermal annealing[3,4] to afford polydiacetylenes (PDAs), as shown in Figure 1. This polymerization is greatly influenced by the DA packing in the solid state (that is, the translational distance (d) of the DA rod must be ~5 Å and the angle (ϕ) between the DA rod and the translational axis must be close to 45°).[5,6] These packing conditions can be achieved by appropriate design of the DA side groups. However, it is difficult to obtain polymerizable packing of DA with desired functions, and molecular designs for polymerizable DAs remain an interesting research area.[7]

The optical properties of PDAs, such as chromic[8] and nonlinear optical properties,[9] that are due to their unique one-dimensional π-conjugated PDA backbone have been previously investigated. In addition, PDAs are semiconducting polymer materials with ultrafast carrier mobility, which have been estimated to be ~10 000 cm^2 V^{-1} s^{-1} in a theoretical study.[10] To date, the highest experimental mobility of PDAs in field-effect transistors has been reported to be 3.8 cm^2 V^{-1} s^{-1}.[11]

To modify the optical and electronic properties of PDAs, direct connection of conjugated substituents, such as aromatic and heteroaromatic rings, to the PDA backbone may result in expansion of the conjugation. However, the direct introduction of rigid aromatic groups to both ends of DA typically hinders solid-state polymerization.[12] Therefore, asymmetric DA monomers that have a rigid heteroaromatic ring on one end and a flexible alkyl chain on the other end have been proposed to solve this problem, and the corresponding monomers have been studied.[13] Several types of asymmetric DA monomers have been synthesized for nonlinear optical materials,[14,15] charge-transfer complexes[16] and semiconducting PDAs.[17] In our previous study, we reported asymmetric DA monomers with a 4-(9*H*-carbazol-9-yl)phenyl (*N*-CzPh) group.[18] Among the four prepared derivatives, different solid-state polymerization behaviors were observed, and good hole conducting properties were expected for blue-colored PDAs due to the suitable energy level of the highest occupied molecular orbital (HOMO; ~ −5.4 eV).

In this study, we designed and synthesized five novel DA monomers with a 9-phenyl-9*H*-carbazol-3-yl (PhCz) group as a donor moiety. The *N*-CzPh and PhCz groups are structural isomers of each other. Electrophilic substitution reactions, such as bromination[19,20] of 9-phenyl-9*H*-carbazole, occur at the 3-position of carbazole due to the high electron density at this position. Therefore, the PhCz group has a stronger electron-donating ability than the *N*-CzPh group, and the electronic effects of the substituents were expected to modify the physical properties of the DA monomers and the corresponding PDAs. The synthesized DA monomers were characterized using spectroscopic studies, and their polymerization reactivity was investigated.

EXPERIMENTAL PROCEDURE

Reagents and materials

All chemicals, which were commercially available, were used as received. 3-(9-Phenyl)-9*H*-ethynylcarbazole **1** was synthesized from 3-bromo-9*H*-phenylcarbazole (Tokyo Chemical Industry, Tokyo, Japan) according to a previously reported protocol.[21] All DA monomers were synthesized using procedures similar to those described in our previous report.[18] The synthesis scheme is outlined in Figure 2. Asymmetric DA alcohol **2** was synthesized using

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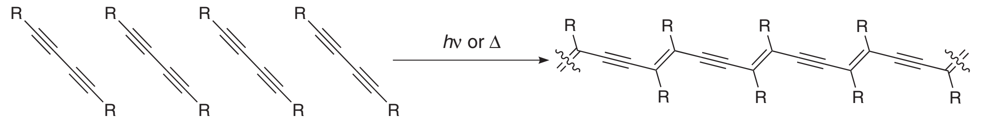

Figure 1 Solid-state polymerization scheme for diacetylene monomers.

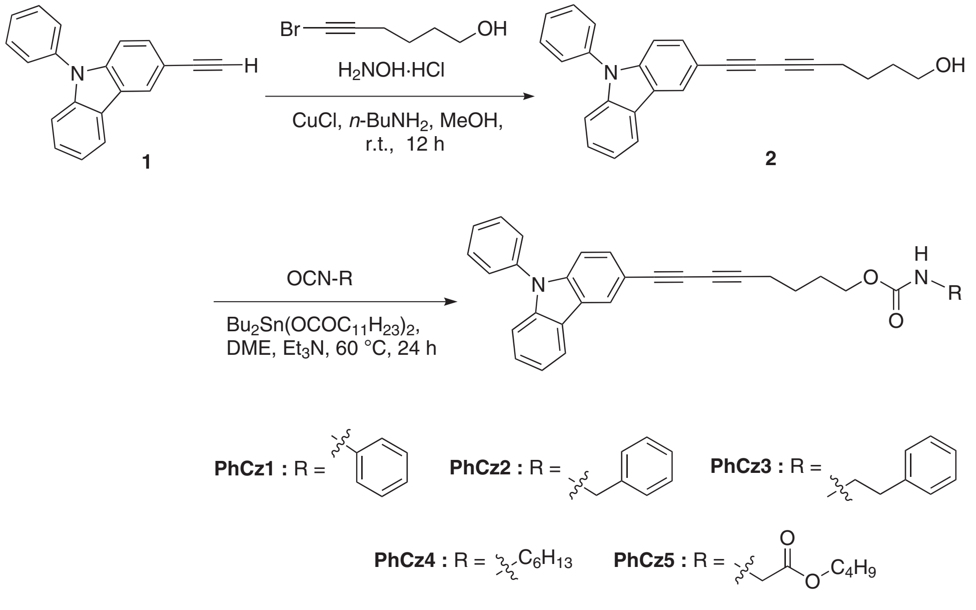

Figure 2 Synthesis scheme for diacetylene monomers **PhCz1**–**PhCz5**.

a Cadiot–Chodkiewicz coupling reaction[22] of **1** and 6-bromo-5-hexyn-1-ol. Five DA monomers with a carbamate group were obtained by reacting alcohol **2** and the corresponding isocyanates.

Characterization

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECX-500 instrument (Akishima, Japan, Supplementary Figure S1). The chemical shifts were calibrated by the Me_4Si peak at 0.000 p.p.m. for ^{1}H-NMR and the $CDCl_3$ peak at 77.160 p.p.m. for ^{13}C-NMR. The infrared (IR) spectra were recorded on a Horiba FT-720 spectrometer (Kyoto, Japan, Supplementary Figure S2). The elemental analyses were performed using a PerkinElmer 2400 series II CHNS/O elemental analyzer (Waltham, MA, USA). Differential scanning calorimetry was performed using a SII Nanotechnology DSC 6220 thermoanalyzer (Chiba, Japan) with a heating rate of 5 °C min^{-1} (Supplementary Figure S3). The UV–visible diffuse reflectance spectra were measured using a JASCO V-570 spectrophotometer (Hachioji, Japan) that was equipped with an integrated sphere. The HOMO energies of the DA monomers and the corresponding polymers were evaluated using photoelectron yield spectroscopy in air on a Riken Keiki AC-3 spectrometer (Tokyo, Japan).

Synthesis of 8-(3-[(9-phenyl)-9*H*-carbazolyl])octa-5,7-diyn-1-ol (2)

To a mixture of **1** (1.76 g, 6.60 mmol), *n*-butylamine (30 ml) and methanol (15 ml), copper(I) chloride (29.7 mg, 0.300 mmol) was added at room temperature under a nitrogen atmosphere. Although the solution immediately turned blue, the addition of a spatula tip's worth of hydroxylamine hydrochloride ($H_2NOH{\cdot}HCl$) to the mixture changed the solution color pale yellow. Then, 6-bromo-5-hexyn-1-ol (1.06 g, 6.00 mmol) in methanol (~1 ml) was added in one portion to the mixture, which was stirred vigorously at room temperature under a nitrogen atmosphere. Approximately every 2 min, a spatula tip's worth of $H_2NOH{\cdot}HCl$ was added for 2 h. After stirring for 12 h, a yellow color developed, and the reaction completion was confirmed by thin-layer chromatography. The reaction solution was concentrated *in vacuo*. The residual crude oil was purified by column chromatography (silica gel, dichloromethane) to afford compound **2** (1.16 g, 52%) as a yellow amorphous solid. T_g: 86 °C. ^{1}H-NMR: δ/p.p.m. (500 MHz, $CDCl_3$, Me_4Si) = 8.28 (d, 1H, J = 1.1 Hz); 8.09 (d, 1H, J = 7.9 Hz); 7.59 (dd, 2H, J = 8.5, 7.4 Hz); 7.52–7.49 (m, 3H); 7.49–7.45 (m, 1H); 7.43–7.39 (m, 1H); 7.37 (d, 1H, J = 8.5 Hz); 7.31–7.28 (m, 2H); 3.70 (t, 2H, J = 6.2 Hz), 2.44 (t, 2H, J = 6.8 Hz); 1.77–1.65 (m, 4H); and 1.48 (br, 1H). ^{13}C-NMR: δ/p.p.m. (125 MHz, $CDCl_3$, Me_4Si) = 141.46, 140.86, 137.18, 130.41, 130.09, 127.97, 127.16, 126.66, 125.19, 123.43, 122.79, 120.66, 120.57, 113.02, 110.13, 110.01, 83.60, 76.47, 72.89, 65.97, 62.44, 31.87, 24.78 and 19.56. IR: ν_{max}/cm^{-1} = 3400, 3057, 2933, 2862, 2235, 2142, 1597, 1500, 1475, 1455, 1363, 1335, 1261, 1228, 1178, 1058, 1026, 809, 744 and 698. Anal. calcd. For $C_{26}H_{21}NO$: C, 85.92; H, 5.82; and N, 3.85%. Found: C, 85.74; H, 5.69; and N, 3.79%.

Synthesis of 8-(3-[(9-phenyl)-9*H*-carbazolyl])octa-5,7-diyn-1-yl phenylcarbamate (PhCz1)

To a solution of **2** (290 mg, 0.800 mmol), triethylamine (three drops) and dibutyltin dilaurate (three drops) in 1,2-dimethoxyethane (20 ml), phenyl isocyanate (119 mg, 1.00 mmol) was added dropwise with vigorous stirring at 60 °C under a nitrogen atmosphere. After stirring for 24 h, the reaction solution was concentrated *in vacuo*. The resulting crude solid was purified by column chromatography (silica gel, dichloromethane) followed by recrystallization from hexane/acetone to afford **PhCz1** (290 mg, 75%) as a pale yellow solid. Mp: 114 °C. ^{1}H-NMR: δ/p.p.m. (500 MHz, $CDCl_3$, Me_4Si) = 8.29 (s, 1H); 8.10 (d, 1H, J = 7.4 Hz); 7.61 (dd, 2H, J = 7.9, 7.4 Hz); 7.55–7.46 (m, 4H); 7.44–7.36 (m, 4H); 7.33–7.28 (m, 4H); 7.06 (t, 1H, J = 7.1 Hz); 6.60 (br, 1H); 4.22 (t, 2H, J = 6.2 Hz); 2.46 (t, 2H, J = 7.1 Hz); 1.86 (tt, 2H, J = 7.7, 6.2 Hz); and 1.72 (tt, 2H, J = 7.7, 7.1 Hz). ^{13}C-NMR: δ/p.p.m. (125 MHz, $CDCl_3$, Me_4Si) = 153.69, 141.49, 140.91, 137.99, 137.20, 130.43, 130.11, 129.19, 127.99, 127.19, 126.69, 125.23, 123.55, 123.46, 122.80, 120.69, 120.59, 118.76, 112.98, 110.16, 110.04, 83.19, 76.61, 72.84, 66.19, 64.76, 28.22, 24.98 and 19.49. IR: ν_{max}/cm^{-1} = 3354, 3060, 2958, 2238, 2146, 1703, 1597, 1529, 1500, 1444, 1321, 1228, 1065, 896, 804, 748 and 702. Anal. calcd. For $C_{33}H_{26}N_2O_2$: C, 82.13; H, 5.43; and N, 5.81%. Found: C, 82.10; H, 5.42; and N, 5.75%,

Synthesis of 8-(3-[(9-phenyl)-9*H*-carbazolyl])octa-5,7-diyn-1-yl benzylcarbamate (PhCz2)

PhCz2 was synthesized (74% yield) using a method similar to that used for **PhCz1**. Mp: 110 °C. ^{1}H-NMR: δ/p.p.m. (500 MHz, $CDCl_3$, Me_4Si) = 8.29 (d, 1H, J = 1.1 Hz); 8.10 (d, 1H, J = 7.4 Hz); 7.61 (dd, 2H, J = 8.5, 7.4 Hz); 7.55–7.46 (m, 4H); 7.42 (dd, 1H, J = 7.9, 7.4 Hz); 7.39–7.26 (m, 8H); 4.98 (br, 1H); 4.38 (d, 2H, J = 5.7 Hz); 4.15 (t, 2H, J = 6.2 Hz); 2.43 (t, 2H, J = 6.5 Hz); 1.84–1.76 (m, 2H); and 1.72–1.62 (m, 2H). ^{13}C-NMR: δ/p.p.m. (125 MHz, $CDCl_3$, Me_4Si) = 156.77, 141.49, 140.90, 138.65, 137.21, 130.43, 130.11, 128.82, 127.99, 127.66, 127.20, 126.69, 125.22, 123.46, 122.81, 120.68, 120.59, 113.02, 110.16, 110.03, 83.31, 76.54, 72.87, 66.08, 64.56, 45.20, 28.34, 24.99 and 19.48. IR: ν_{max}/cm^{-1} = 3325, 3060, 2939, 2866, 2237, 2144, 1687, 1597, 1547, 1504, 1478, 1454, 1365, 1333, 1263, 1228, 1150, 806, 762, 739 and 702. Anal. calcd. For $C_{35}H_{28}N_2O_2$: C, 82.23; H, 5.68; and N, 5.64%. Found: C, 82.27; H, 5.78; and N, 5.61%.

Synthesis of 8-(3-[(9-phenyl)-9*H*-carbazolyl])octa-5,7-diyn-1-yl phenethylcarbamate (PhCz3)

PhCz3 was synthesized (62% yield) using a method similar to that used for **PhCz1**. Mp: 95 °C. ^{1}H-NMR: δ/p.p.m. (500 MHz, $CDCl_3$, Me_4Si) = 8.28 (d, 1H, J = 1.7 Hz); 8.10 (d, 1H, J = 7.4 Hz); 7.61 (dd, 2H, J = 7.4, 7.9 Hz); 7.55–7.46 (m, 4H); 7.42 (dd, 1H, J = 7.2, 7.2 Hz); 7.38 (d, 1H, J = 7.9 Hz); 7.35–7.28 (m, 4H); 7.24 (d, 1H, J = 7.4 Hz); 7.20 (d, 2H, J = 7.4 Hz); 4.68 (br, 1H); 4.10 (t, 2H, J = 6.2 Hz); 3.45 (td, 2H, J = 6.4, 6.4 Hz); 2.82 (t, 2H, J = 7.1 Hz); 2.42 (t, 2H, J = 6.8 Hz); 1.77 (m, 2H); and 1.66 (m, 2H). ^{13}C-NMR: δ/p.p.m. (125 MHz, $CDCl_3$, Me_4Si) = 156.67, 141.49, 140.90, 138.92, 137.21, 130.43, 130.11, 128.93, 128.77, 127.99, 127.21, 126.69, 126.63, 125.22, 123.46, 122.81, 120.68, 120.59, 113.02, 110.16, 110.04, 83.32, 76.54, 72.87, 66.07, 64.32, 42.26, 36.29, 28.34, 24.99 and 19.48. IR: ν_{max}/cm^{-1} = 3336, 3060, 3026, 2952, 2235, 2144, 1682, 1597, 1541, 1500, 1477, 1455, 1362, 1261, 1227, 1150, 1039, 806, 762, 742 and 700. Anal. calcd. For $C_{35}H_{30}N_2O_2$: C, 82.33; H, 5.92; and N, 5.49%. Found: C, 82.43; H, 5.77; and N, 5.47%.

Synthesis of 8-(3-(9-phenylcarbazolyl))-5,7-octadiyn-1-yl hexylcarbamate (PhCz4)

PhCz4 was synthesized (51% yield) using a method similar to that used for **PhCz1**. Mp: 78 °C. ^{1}H-NMR: δ/p.p.m. (500 MHz, $CDCl_3$, Me_4Si) = 8.29 (d, 1H, J = 1.7 Hz); 8.10 (d, 1H, J = 7.4 Hz); 7.60 (dd, 2H, J = 7.9, 7.9 Hz); 7.54–7.46 (m, 4H); 7.42 (dd, 1H, J = 7.4, 7.4 Hz); 7.37 (d, 1H, J = 7.9 Hz); 7.33–7.28 (m, 2H); 4.65 (br, 1H); 4.10 (t, 2H, J = 6.2 Hz); 3.17 (dt, 2H, J = 6.8, 6.2 Hz); 2.43 (t, 2H, J = 6.8 Hz); 1.78 (tt, 2H, J = 6.9, 6.9 Hz); 1.67 (tt, 2H, J = 6.9, 6.9 Hz); 1.49 (tt, 2H, J = 6.9, 6.9 Hz); 1.35–1.25 (m, 6H); and 0.88 (t, 3H, J = 6.8 Hz). ^{13}C-NMR: δ/p.p.m. (125 MHz, $CDCl_3$, Me_4Si) = 156.78, 141.50, 140.91, 137.21, 130.44, 130.12, 128.00, 127.21, 126.69, 125.22, 123.46, 122.81, 120.68, 120.59, 113.04, 110.17, 110.04, 83.36, 76.52, 72.87, 66.04, 64.22, 41.17, 31.61, 30.10, 28.39, 26.56, 25.02, 22.70, 19.50 and 14.16. IR: ν_{max}/cm^{-1} = 3327, 3060, 2952, 2927, 2856, 2237, 2146, 1691, 1597, 1537, 1504, 1478, 1455, 1365, 1332, 1263, 1227, 1136, 1052, 806, 763, 740 and 702. Anal. calcd. For $C_{33}H_{34}N_2O_2$: C, 80.78; H, 6.98; and N, 5.71%. Found: C, 80.95; H, 7.00; and N, 5.72%.

Synthesis of 8-(3-(9-phenylcarbazolyl))-5,7-octadiyn-1-yl) butoxycarbonylmethylcarbamate (PhCz5)

PhCz5 was synthesized (44% yield) using a method similar to that used for **PhCz1**. Mp: 72 °C. ^{1}H-NMR: δ/p.p.m. (500 MHz, $CDCl_3$, Me_4Si) = 8.29 (s, 1H); 8.10 (d, 1H, J = 7.4 Hz); 7.61 (dd, 2H, J = 7.7, 7.7 Hz); 7.55–7.46 (m, 4H); 7.43 (dd, 1H, J = 7.7, 7.7 Hz); 7.38 (d, 1H, J = 7.9 Hz); 7.33–7.29 (m, 2H); 5.16 (br, 1H); 4.17 (t, 2H, J = 5.8 Hz); 4.14 (t, 2H, J = 6.2 Hz); 3.97 (d, 2H, J = 5.1 Hz); 2.44 (t, 2H, J = 7.1 Hz); 1.84–1.77 (m, 2H); 1.71–1.59 (m, 4H); 1.38 (tq, 2H, J = 7.5, 7.4 Hz); and 0.94 (t, 3H, J = 7.4 Hz). ^{13}C-NMR: δ/p.p.m. (125 MHz, $CDCl_3$, Me_4Si) = 170.31, 156.61, 141.49, 140.90, 137.21, 130.44, 130.12, 127.99, 127.21, 126.68, 125.23, 123.46, 122.81, 120.68, 120.59, 113.04, 110.16, 110.03, 83.26, 76.53, 72.86, 66.10, 65.49, 64.85, 42.86, 30.66, 28.25, 24.92, 19.46, 19.16 and 13.80. IR: ν_{max}/cm^{-1} = 3319, 3062, 2964, 2933, 2869, 2239, 2144, 1763, 1689, 1597, 1541, 1504, 1477, 1456, 1362, 1292, 1227, 1198, 1057, 1026, 808, 764, 739 and 702. Anal. calcd. For $C_{33}H_{32}N_2O_4$: C, 76.13; H, 6.20; and N, 5.38%. Found: C, 76.19; H, 6.23; and N, 5.34%.

Solid-state polymerization

Solid-state polymerization was performed by UV irradiation at room temperature. The UV source was a 16 W low-pressure mercury lamp emitting at 254 nm (R-52G, UVP). Conversion to the corresponding polymers was determined using the gravimetric method. The conversion was defined as the ratio of the insoluble mass after extraction to the original mass before extraction. The solvent used for extraction was acetone, which is satisfactory for DA monomers. The insoluble portions were collected by suction filtration using Durapore (Darmstadt, Germany) membrane filters (VVHP with pore size of 1.0 μm).

RESULTS AND DISCUSSION

Five novel asymmetric DA carbamate monomers (that is, **PhCz1** with a phenyl group, **PhCz2** with a benzyl group, **PhCz3** with a phenethyl group, **PhCz4** with a hexyl group and **PhCz5** with a butoxycarbonylmethyl group) were successfully prepared according to the synthesis outlined in Figure 2. All compounds exhibited a phenyl-ring bending vibration peak at 701 ± 1 cm^{-1} in the IR spectra (Supplementary Figure S2). A weak C≡C stretching vibration for the DA framework was also observed at 2237 ± 2 and 2145 ± 1 cm^{-1} for all five monomers. Unfortunately, single crystals of the DA monomers that were suitable for X-ray crystallographic analysis could not be obtained after many trials. On the basis of differential scanning calorimetry measurements, sharp melting points for **PhCz1**, **PhCz2**, **PhCz3**, **PhCz4** and **PhCz5** were observed at 114, 110, 95, 78 and 72 °C, respectively (Supplementary Figure S3b–f). **PhCz4** and **PhCz5** bearing flexible alkyl end groups exhibited lower melting points than **PhCz1**, **PhCz2** and **PhCz3**, which possess rigid phenyl end groups. In addition, no exothermic peaks were observed for any of the monomer crystals during the heating process in a temperature range from 30 to 200 °C. Therefore, no polymerization occurred during this heating process. As in the present cases, DA monomers with carbamate groups are often thermally stable.[14] When these monomers were cooled to 30 °C from the molten state at 200 °C, no exothermic peaks were observed, indicating that no crystallization occurred from the molten states during the formation of amorphous solids.

Upon UV irradiation, all DA monomer solids changed to colored ones via solid-state polymerization. Introduction of a carbamate group to form intermolecular hydrogen bonding increases the probability of solid-state polymerization of DAs.[23] Figure 3 shows the UV–visible diffuse reflectance spectral changes of the DA monomers during the solid-state polymerization. All monomers exhibited an absorption increase in the visible region, indicating the formation of π-conjugated PDA backbones. In particular, the PDAs obtained from **PhCz2**, **PhCz4** and **PhCz5** exhibited clear excitonic absorption bands in a wavelength range from 600 to 650 nm, suggesting that regular 1,4-addition solid-state polymerization occurred. Therefore, the molecular packing of these three monomers must meet the previously mentioned DA monomer alignment rule for solid-state polymerization.[5,6] However, the PDA from **PhCz3** exhibited broad excitonic absorption, and the PDA from **PhCz1** exhibited no excitonic absorption peaks. These polymers may have disordered or irregular π-conjugated backbones compared with those in the PDAs from **PhCz2**, **PhCz4** and **PhCz5**. Interestingly, **PhCz2**, **PhCz4** and **PhCz5** yielded PDAs with clear

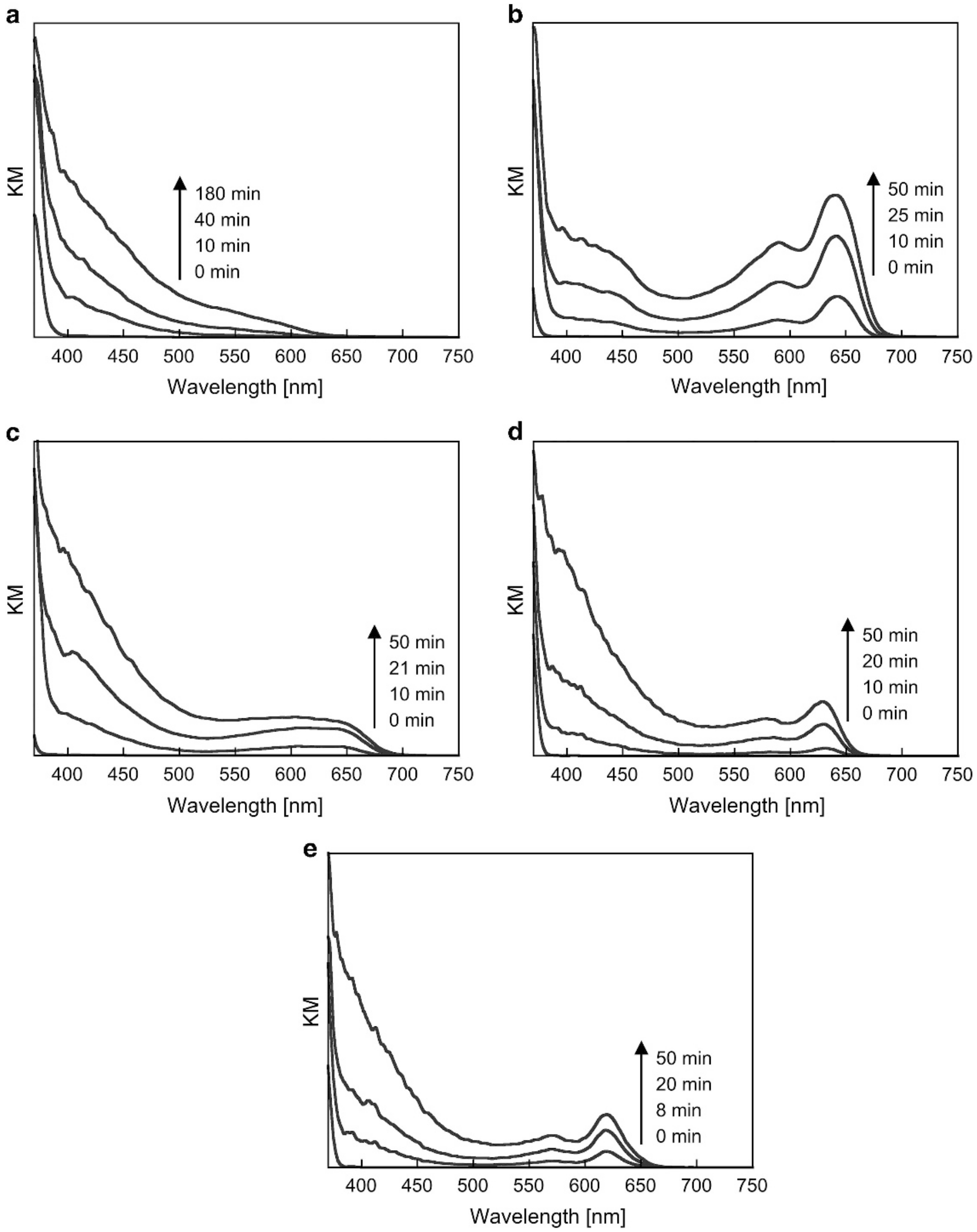

Figure 3 Diffuse reflectance spectra of 9-phenyl-9*H*-carbazol-3-yl (PhCz) derivatives as a function of the ultraviolet irradiation time: (**a**) **PhCz1**; (**b**) **PhCz2**; (**c**) **PhCz3**; (**d**) **PhCz4**; and (**e**) **PhCz5**.

excitonic bands that exhibited a N–H stretching vibration of the urethane groups at ~3320 cm^{-1}, and **PhCz1** and **PhCz3** yielded PDAs with relatively irregular main chains that exhibited a N–H stretching vibration at ~3345 cm^{-1}. Therefore, in this study, stronger intermolecular hydrogen bonding results in a DA monomer alignment that is suitable for the formation of regular PDA structures.

We estimated the initial solid-state polymerization rate from the increase in the excitonic peak intensity at its maximum. Figure 4 shows the variation in the normalized peak intensity at the maximum wavelength of each UV–visible diffuse reflectance spectrum for **PhCz2**, **PhCz4** and **PhCz5** as a function of the UV irradiation time. These three compounds exhibited a similar initial increase and subsequent saturation after ~50 min, suggesting similar polymerization rates. In contrast, the solid-state polymerization reactivity of the *N*-CzPh DA derivatives was strongly influenced by the end group attached to the carbamate group.[18] The conversions after the excitonic peak saturation were ~0% for **PhCz1**, 8% for **PhCz2**, 3% for **PhCz3** and 1% for **PhCz4** and **PhCz5**. The low conversions may be due to the UV irradiation not penetrating the entire powdered sample. Among the DA monomers in this study, the PDA obtained from **PhCz2** exhibited the highest conversion. This result is consistent with the relatively large excitonic peak of **PhCz2** compared with those of **PhCz4** and **PhCz5**.

To investigate their potentials as organic semiconducting materials, the ionization potentials (IPs) of the DA monomers and the corresponding PDAs were measured using photoelectron yield spectroscopy in air. Figure 5 shows the photoelectron yield spectra of **PhCz2** and the corresponding PDA. The IP values of the DA monomers, including **PhCz2** were ~5.8 eV due to the excitation

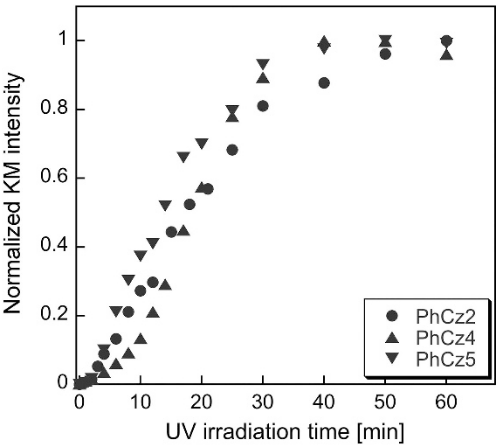

Figure 4 Normalized excitonic peak intensity of **PhCz2** (circle), **PhCz4** (up-pointing triangle) and **PhCz5** (down-pointing triangle) as a function of the ultraviolet (UV) irradiation time.

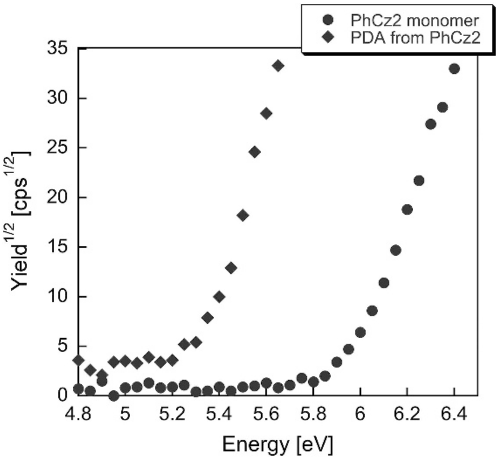

Figure 5 Photoelectron yield spectra of **PhCz2** (circle) and the corresponding polydiacetylene (PDA; tilted square).

energy from HOMO. To confirm these results, density functional theory calculations using the Gaussian 09 program[24] were carried out on **PhCz2** and three asymmetric model compounds. The molecular structure optimization and energy level calculation of the corresponding HOMO and lowest unoccupied molecular orbital (LUMO) were carried out at the B3LYP/6-31G(d) and B3LYP/6-311+G(d,p) levels of theory, respectively. In the model compounds, one of the substituents is a methyl group, and the other substituent is a 9*H*-carbazol-3-yl group in which the *N*-substituted groups are hydrogen for **HCz-DA**, methyl for **MeCz-DA** and phenyl for **PhCz-DA**. For all compounds, the electron distribution of the HOMO and LUMO was spread throughout DA and the conjugated carbazole ring (Figure 6). When the *N*-substituted group was changed from a hydrogen to a phenyl group, the LUMO levels were nearly the same but the HOMO level increased. However, when the *N*-substituted group was changed from a hydrogen to a methyl group, both the HOMO and LUMO levels increased. As a result, the HOMO–LUMO energy gap of **PhCz-DA** was the narrowest among the three model compounds. The results calculated for **PhCz2** were nearly the same as those calculated for **PhCz-DA**. The calculated HOMO energy of **PhCz2** was -5.56 eV, which was ~0.15 eV higher than that calculated for the *N*-CzPh DA derivatives[18] due to the stronger electron-donating ability of the 3-carbazolyl group. Therefore, the PhCz DA derivatives exhibited lower IP values than the *N*-CzPh DA derivatives. The IP value of PDA from **PhCz2** decreased to ~5.2 eV, as shown in Figure 5, due to effective π-conjugation between the polymer backbone and the PhCz moieties. This value allows for smooth hole injection into the PDA from typical electrodes, such as copper, gold and indium tin oxide. Insertion of polymer hole injection materials reduces the operating voltage of organic devices. For example, poly(3,4-ethylenedioxythiophene) and its derivatives have IPs of ~5.2 eV,[25] and poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(phenylimino)-[1,1′-biphenyl]-4,4′-diyl(phenylimino)-1,4-phenylene] and its derivatives have IPs of ~5.5 eV.[26] For PDAs from 10,12-pentacosadiynoic acid and its derivatives, Nishide *et al.*[27,28] reported IP values of 5.2–5.5 eV even though the substituents are simple alkyl groups, and the reason for these relatively low IPs remains unclear. However, as shown in the results in our previous study,[18] all PDAs do not possess such low IP

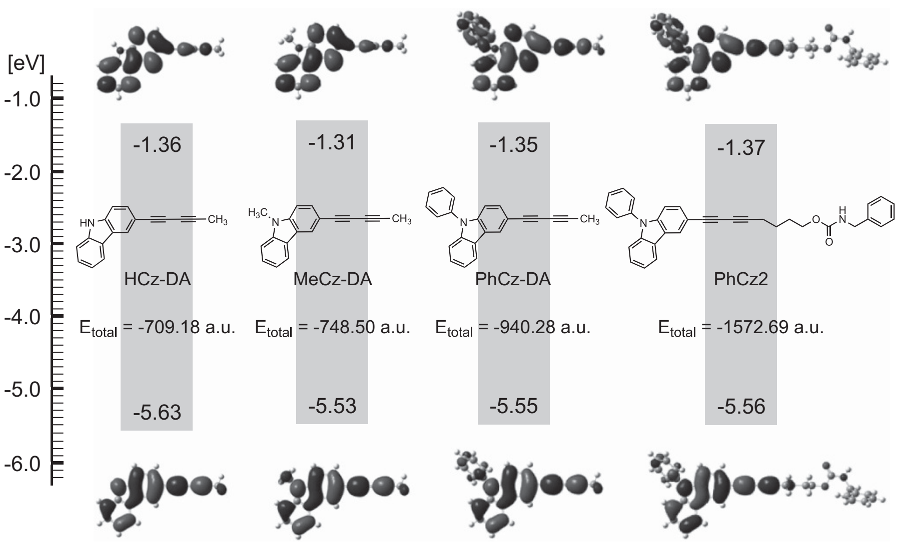

Figure 6 Calculated highest occupied molecular orbital and lowest unoccupied molecular orbital energies of **PhCz2** and model compounds. A full color version of this figure is available at *Polymer Journal* online.

values. Therefore, tailoring substituents is an important strategy for obtaining low IP PDAs. Owing to the satisfactorily small IP value as a hole injection material, the PDA from **PhCz2** can be used in various organic electronic device applications and is expected to exhibit good hole-conducting properties along both main chains and neighboring aromatic side chains.[29,30]

CONCLUSION

We synthesized five novel DA derivatives with a PhCz group as a stronger donor moiety than the *N*-CzPh group, which was previously studied. The results from density functional theory calculations confirmed the effective π-conjugation between the DA and the PhCz groups. The PhCz group is large and not mirror symmetric. However, DAs directly substituted by PhCz polymerized in the solid state via UV irradiation, with assistance from a carbamate group introduced in the other substituent. Among the DAs prepared, **PhCz2**, **PhCz4** and **PhCz5** exhibited characteristic excitonic absorption bands due to the PDAs that were obtained via regular 1,4-addition polymerization. The PDA from **PhCz2** possessed a small IP value of 5.2 eV, which is suitable for hole injection from typical electrodes. This result is due to PDA backbones with effective π-conjugation expansion of the PhCz group. We demonstrated that direct substitution of the DA framework by the PhCz group is a useful strategy for tuning the energy levels of PDAs as hole injection materials for application in low-operating-voltage organic electronic devices. The application of PDA from **PhCz2** to organic electronic devices is currently underway.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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