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Synthesis and Solid-State Polymerization of Diacetylene Derivatives with an *N*-Carbazolylphenyl Group

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Four diacetylene derivatives with an *N*-carbazolylphenyl group as a donor moiety have been synthesized and subsequently characterized. These diacetylene derivatives undergo solid-state polymerization via UV irradiation, although these compounds have relatively large π-conjugated aromatic groups. The polymerization behaviors of these derivatives were confirmed by distinct absorption bands for polydiacetylenes. The reactive process is strongly influenced by the slightly differing side groups. Single crystal growth of the two compounds was successful and their crystal structure analyses revealed large differences in the molecular conformations and intermolecular geometries caused by a methylene unit. The HOMO population of the monomers is predominantly expressed in the phenyl carbazole unit, while each polymer showed differing HOMO energies with some polymers exhibiting high-lying HOMO levels.

Polydiacetylenes (PDAs), which can be obtained through the topochemical solid-state polymerization of diacetylene (DA) monomers, have been studied extensively as materials for use in third-order nonlinear optics (NLO),[1,2] Langmuir–Blodgett (LB) films,[3] optical sensors,[4] and solid hole conductors.[5,6] Their extended π-systems along the polymer backbone explain their unique characteristics, such that the conduction paths through the polymer main chain have very fast charge transport properties. In fact, the charge carrier mobility of PDAs have been found to be ca. 10000 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in a theoretical study,[7] ca. 10 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ as estimated by the time-of-flight method,[8] and up to 3.8 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in field-effect transistors.[9] Such properties were achieved through single dimensional conjugation in the polymer chain because aliphatic side groups do not increase π-delocalization. Meanwhile, DA monomers with conjugated substituents, such as aromatic and heteroaromatic rings, can give PDAs with π-extension to the side groups in each repeating unit. In addition, the interactions between side groups may enhance the dimensionality of the charge transport paths. Moreover, this enables fine-tuning of the electronic properties of PDAs. Therefore, we designed new DA monomers with an *N*-carbazolylphenyl (*N*-CzPh) unit, which is an electron donor and has hole transport properties.[10,11] There have been several reports on PDAs with carbazole moieties such as 1,6-di-(*N*-carbazolyl)-2,4-hexadiyne (DCH),[12] 1-(9-carbazolyl)-6-iodohexa-2,4-diyne (CIHD),[13] 1-(*N*-carbazolyl)penta-1,3-diyn-5-ol (CPDO),[14] and 1-(*N*-carbazolyl)penta-1,3-diyn-5-acetoxy (CPDA).[15] However, PDAs from DCH and CIHD have no conjugation between the carbazole moieties and the PDA backbone. Although the carbazole moieties are directly bound to the PDA backbone in the PDAs from CPDO and CPDA, more extended π-conjugation in the side chains is expected for PDAs having direct conjugation with *N*-CzPh units. The structure of *N*-CzPh is more planar than triphenyl amine, where the molecules can show strong π-stacking, although its slightly twisted conformation may increase intermolecular interactions in two dimensions.[16] Moreover, carbazole derivatives are stable, easy to handle, and therefore widely used as side chains in conjugated polymers.[17] However, by directly introducing rigid aromatic groups to both sides creates the potential loss of the polymerization capability and solubility.[18,19] Thus, flexibility should be maintained in the other side group in order to provide for the appropriate orientation of DA monomers. We have chosen an alkyl chain with a carbamate (urethane) group, which proves to be effective in orientation through hydrogen bonding.[20] Here, we report the synthesis and solid-state polymerization behavior of asymmetric DA monomers substituted by *N*-CzPh and carbamate groups at each side (Figure 1). The DA monomers have been characterized by spectroscopic studies and some were further characterized with X-ray single crystal analysis. The relationship between their molecular packing and polymerization reactivity is also discussed.

Experimental

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL 500 MHz JNM-ECX instrument. Chemical shifts were calibrated by $\mathrm{Me_4Si}$ for ^{1}H NMR and by deuterated solvents for ^{13}C NMR. The elemental analyses were performed with a Perkin-Elmer 2400 series II CHNS/O elemental analyzer. Differential scanning calorimetry (DSC) was preformed using a TA Instruments DSC Q2000. UV–vis diffuse reflectance spectra were measured using a JASCO V-570 spectrophotometer with an integrated sphere. The highest occupied molecular orbital (HOMO) energies of DA monomers and the corresponding polymers were examined using photoelectron yield spectroscopy (PYS) in air obtained by a Riken Keiki AC-3 spectrometer. Thin films of the samples were prepared on glass substrates by drop-casting. For monomers, their 1,2-dichloroethane solutions

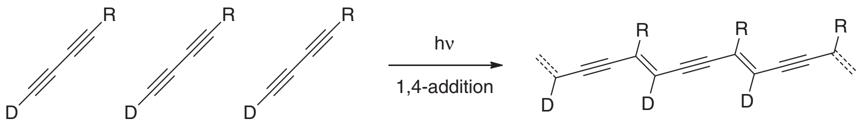


Figure 1. Solid-state polymerization of diacetylene (DA) with a donor moiety. D is *N*-CzPh as a donor and R contains a carbamate group.

were just cast and dried while dispersions of UV-irradiated samples in 1,2-dichloroethane were cast and dried for the polymer samples.

Materials and Reagents. All the commercially available chemicals were used as received. Compound **1** (9-(4-ethynylphenyl)-9*H*-carbazole) was synthesized from commercially available 9-(4-bromophenyl)-9*H*-carbazole according to the literature.[10]

Synthesis of 8-[4-(9*H*-Carbazol-9-yl)phenyl]octa-5,7-diyn-1-ol (2). Copper(I) chloride (39.6 mg, 0.400 mmol) was added to a solution of **1** (2.67 g, 10.0 mmol) and *n*-butylamine (30 ml) in methanol (10 ml) at room temperature under N_2 atmosphere. The solution immediately turned blue, but the solution was quenched by the addition of a spatula tip's worth of hydroxylamine hydrochloride ($H_2NOH{\cdot}HCl$) giving a pale yellow solution. 6-bromo-5-hexyn-1-ol (1.42 g, 8.00 mmol) was added in a single portion as a solution in methanol (ca. 1 mL). The reaction solution was stirred vigorously at room temperature under N_2 atmosphere. Approximately every 2 min a spatula tip's worth $H_2NOH{\cdot}HCl$ was added for 2 h. After stirring for 12 h, a yellow color developed and the reaction completion was confirmed by TLC. The reaction solution was concentrated in vacuo. The crude oil was purified by column chromatography on silica gel using dichloromethane to give compound **2** (1.91 g, 66%) as a yellow solid. Mp: 101.7–103.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.14 (d, 2H, $J = 7.7$ Hz), 7.70 (d, 2H, $J = 8.2$ Hz), 7.54 (d, 2H, $J = 8.2$ Hz), 7.44–7.39 (m, 4H), 7.30 (m, 2H), 3.72 (q, 2H, $J = 5.6$ Hz), 2.46 (t, 2H, $J = 6.6$ Hz), 1.79–1.68 (m, 4H), 1.28 (t, 1H, $J = 5.0$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si): δ 140.5, 138.3, 134.2, 126.9, 126.2, 123.7, 121.0, 120.5, 120.4, 109.8, 85.1, 75.3, 74.3, 65.6, 62.4, 31.9, 24.7, 19.6. Anal. Calcd. For $C_{26}H_{21}NO$: C, 85.92; H, 5.82; N, 3.85%. Found: C, 86.08; H, 5.96; N, 3.88%.

Synthesis of 8-[4-(9*H*-Carbazol-9-yl)phenyl]octa-5,7-diyn-1-yl Benzylcarbamate (DA1). To a solution of **2** (218 mg, 0.60 mmol), triethylamine (3 drops), and dibutyltin dilaurate (3 drops) in 1,2-dimethoxyethane (20 ml), benzyl isocyanate (107 mg, 0.800 mmol) was added dropwise with vigorous stirring at 50 °C under N_2 atmosphere. After stirring for 12 h, the reaction solution was concentrated in vacuo. The crude solid was purified by column chromatography on silica gel using dichloromethane followed by recrystallization from hexane/dichloromethane (10/1) to give **DA1** (240 mg, 80%) as a colorless solid. Mp: 120.4–122.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.14 (d, 2H, $J = 7.6$ Hz), 7.70 (d, 2H, $J = 8.3$ Hz), 7.54 (d, 2H, $J = 8.3$ Hz), 7.44–7.40 (m, 4H), 7.37–7.32 (m, 2H), 7.32–7.27 (m, 4H), 4.98 (br, 1H), 4.39 (d, 2H, $J = 5.8$ Hz), 4.16 (t, 2H, $J = 6.3$ Hz), 2.45 (t, 2H, $J = 6.7$ Hz), 1.84–1.78 (m, 2H), 1.72–1.66 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si): 156.8, 140.5, 138.6, 138.3, 134.2, 128.8, 127.7, 127.6, 126.9, 126.2, 123.7, 121.0, 120.5, 120.5, 109.8, 84.8, 75.3, 74.3, 65.7, 64.5, 45.2, 28.4, 24.9, 19.5. Anal. Calcd. For $C_{34}H_{28}N_2O_2$: C, 82.23; H, 5.68; N, 5.64%. Found: C, 82.23; H, 5.77; N, 5.67%.

Synthesis of 8-[4-(9*H*-Carbazol-9-yl)phenyl]octa-5,7-diyn-1-yl Phenethylcarbamate (DA2). **DA2** was synthesized (73% yield) by a similar method to that for **DA1**. Mp: 125.7–127.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.14 (d, 2H, $J = 7.8$ Hz), 7.70 (d, 2H, $J = 8.3$ Hz), 7.54 (d, 2H, $J = 8.3$ Hz), 7.32 (dd, 2H, $J = 7.4$ Hz, $J = 7.2$ Hz), 7.32–7.29 (m, 2H), 7.25 (t, 1H, $J = 7.4$ Hz), 7.21 (d, 2H, $J = 7.2$ Hz), 4.70 (br, 1H), 4.12 (t, 2H, $J = 6.2$ Hz), 3.47 (td, 2H, $J = 6.9$ Hz), 2.84 (t, 2H, $J = 6.9$ Hz), 2.44 (t, 2H, $J = 6.8$ Hz), 1.78 (m, 2H), 1.68 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si): δ 156.6, 140.5, 138.9, 138.3, 134.2, 128.9, 128.8, 126.9, 126.7, 126.2, 123.7, 121.0, 120.5, 120.5, 109.8, 84.8, 75.3, 74.3, 65.7, 64.3, 42.3, 36.3, 28.4, 24.9, 19.5. Anal. Calcd. For $C_{35}H_{30}N_2O_2$: C, 82.33; H, 5.92; N, 5.94%. Found: C, 82.44; H, 5.97; N, 5.59%.

Synthesis of 8-[4-(9*H*-Carbazol-9-yl)phenyl]octa-5,7-diyn-1-yl Hexylcarbamate (DA3). **DA3** was synthesized (86% yield) by a similar method to that for **DA1**. Mp: 102.5–104.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.14 (d, 2H, $J = 7.7$ Hz), 7.70 (d, 2H, $J = 8.3$ Hz), 7.54 (d, 2H, $J = 8.3$ Hz), 7.44–7.40 (m, 4H), 7.32–7.28 (m, 2H), δ 4.64 (br, 1H), 4.11 (t, 2H, $J = 6.2$ Hz), 3.18 (td, 2H, $J = 6.6$ Hz), 2.45 (t, 2H, $J = 6.9$ Hz), 1.81–1.76 (m, 2H), 1.71–1.66 (m, 2H), 1.52–1.48 (m, 2H), 1.34–1.30 (m, 6H), 0.89 (t, 3H, $J = 6.7$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si): δ 156.7, 140.5, 138.3, 134.1, 126.9, 126.2, 123.7, 121.0, 120.5, 120.4, 109.8, 84.8, 75.3, 74.3, 65.6, 64.1, 41.2, 31.6, 30.1, 28.4, 26.5, 24.9, 22.7, 19.5, 14.2. Anal. Calcd. For $C_{33}H_{34}N_2O_2$: C, 80.78; H, 6.98; N, 5.71%. Found: C, 80.95; H, 6.96; N, 5.70%.

Synthesis of Butyl 2-{[({8-[4-(9*H*-Carbazol-9-yl)phenyl]-octa-5,7-diyn-1-yl}oxy)carbonyl]amino}acetate (DA4). **DA4** was synthesized (80% yield) by a similar method to that for **DA1**. Mp: 82.3–85.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si): δ 8.14 (d, 2H, $J = 7.7$ Hz), 7.70 (d, 2H, $J = 8.5$ Hz), 7.54 (d, 2H, $J = 8.5$ Hz), 7.44–7.39 (m, 4H), 7.32–7.28 (m, 2H), 5.16 (br, 1H), 4.17 (t, 2H, $J = 6.6$ Hz), 4.15 (t, 2H, $J = 6.3$ Hz), 3.98 (d, 2H, $J = 5.5$ Hz), 2.45 (t, 2H, $J = 7.0$ Hz), 1.84–1.78 (m, 2H), 1.72–1.61 (m, 4H), 1.42–1.36 (m, 2H), 0.94 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si): δ 170.3, 156.6, 140.5, 138.3, 134.2, 126.9, 126.2, 123.7, 121.0, 120.5, 120.4, 109.8, 84.7, 75.3, 74.3, 65.7, 65.5, 64.8, 42.8, 30.7, 28.3, 24.8, 19.4, 19.2, 13.8. Anal. Calcd. For $C_{33}H_{32}N_2O_4$: C, 76.13; H, 6.20; N, 5.38%. Found: C, 76.18; H, 6.37; N, 5.38%.

X-ray Crystal Structure Analysis. X-ray diffraction data for **DA1** and **DA2** were collected on a Rigaku Saturn 724 CCD diffractometer with Mo Kα radiation ($\lambda = 0.71075$ Å) at 93 K. Data collection, cell refinement, and data reduction were carried out using the CrystalClear-SM software.[21] The structures were solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares methods on F^2 using SHELXL-97.[22] All non-hydrogen atoms were refined anisotropically. All materials for publication were prepared by Yadokari-XG 2009 software.[23]

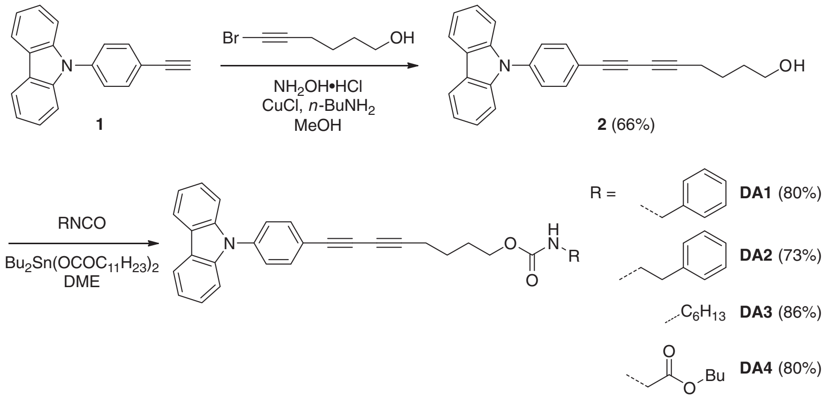
Solid-State Polymerization. Solid-state polymerization of **DA1–DA4** was performed by UV irradiation at room temperature. The UV source was a 16 W low-pressure mercury lamp emitting at 254 nm (R-52G, UVP). Conversion (%) to the corresponding polymer was determined by two methods. One is to calculate monomer ratio by DSC heat flow per unit mass during the monomer melting process before and after UV irradiation (DSC method). Since the monomers in this study are thermally inactive as mentioned later, no polymerization occurs during heating in the DSC measurement. In this method, reduction of heat flow is thought to originate from polymer production. The other is a gravimetric method, in which mass ratio of the insoluble portion after extraction to the original mass before extraction is considered to be the conversion. Solvent used for extraction was acetone, which is a good solvent for **DA1–DA4**. Collection of the insoluble portions was performed using Durapore® membrane filters (1.0 µm, VVHP).

Results and Discussion

The approach to the synthesis of these asymmetric DA monomers involves the use of Sonogashira coupling and Cadiot–Chodkiewicz coupling, which are often used to synthesize asymmetrical DA monomers,[24] and the formation of carbamates group from isocyanate. The synthetic routes are outlined in Scheme 1. Compounds **DA1** (benzyl group), **DA2** (phenethyl group), **DA3** (hexyl group), and **DA4** (buthoxycarbonylmethyl group) were readily and successfully synthesized in good yields and then characterized. All of the compounds showed good solubility in common organic solvents at room temperature. DSC measurements of **DA1–DA4** exhibited a sharp melting point at around 120 °C without mesophase transition and no exothermic peak at higher temperatures until decomposition had begun for all of the compounds, indicating potential difficulty in polymerization through heating. These results are consistent with previously reported DA monomers using carbamate groups, which also do not exhibit thermal polymerization.[2]

Single crystals suitable for X-ray analysis were grown by slow evaporation of 1,2-dimethoxyethane (DME) for **DA1** and ethyl acetate for **DA2**, for which the asymmetric unit is comprised of two independent molecules.[25] In order to clarify the reactivity of the polymerization process, the relative orientations of diacetylene moieties between the molecules are most important, whereby the stacking interval d and the inclination angle θ of the DA moiety to the stacking direction should be in the range of 4.2–5.7 Å and 40–60° (around 45° in most cases), respectively, according to the Baughmann criterion.[26] **DA1** has d of about 5.09 Å and θ of about 61.8° between the acetylene moieties along the direction of the a axis (Figure 2). The angle θ is large compared to the ideal orientation for polymerization. On the other hand, **DA2** has more preferable angles of about 50°, which better enables the polymerization process. Although the molecular structures for compounds **DA1** and **DA2** are quite similar with the exception of the end groups, they resulted in different packing motifs. Those two compounds **DA1** and **DA2** have similar π-stacking intermolecular interactions in the *N*-CzPh moiety, where the torsion angles between carbazole and phenyl rings are about 48° for both compounds. In the carbamate groups, conformation of the molecules is fixed by classical N—H···O hydrogen bonds (Table 1), which are nearly the same geometry for both compounds. However, the conformation of the butylene chain showed obvious differences, whereby **DA1** has trans–trans conformation and **DA2** has gauche–gauche conformation. This flexibility caused a difference of relative orientations of the acetylene units. These results indicate that the conformation of DAs is a relatively unpredictable and uncontrollable event. On the other hand, the rigid *N*-CzPh groups with strong π-interactions seem to be advantageous to aligning molecular orientations. Unfortunately, single crystals of **DA3** and **DA4** appropriate for X-ray crystallographic analysis could not be obtained after many trials so far. However, these compounds are likely to satisfy Baughmann's criterion due to higher flexibility of the side chains.

Upon irradiation by UV light, the colorless solids of the DA monomers turned to colored solids, suggesting solid-state polymerization. The color of the PDAs, which is caused by the linear π-conjugation of the polymer main chain, generally appears from absorption bands at around 500–700 nm.[27] Figure 3 (upper portion) shows the changes of UV–vis diffuse reflectance spectra vs. UV irradiation time for compounds **DA1–DA4**. The ordinate of these figures is for the values conducted from diffuse reflectance by using the Kubelka–Munk



Scheme 1. Synthesis of diacetylene (DA) monomer derivatives **DA1–DA4**.

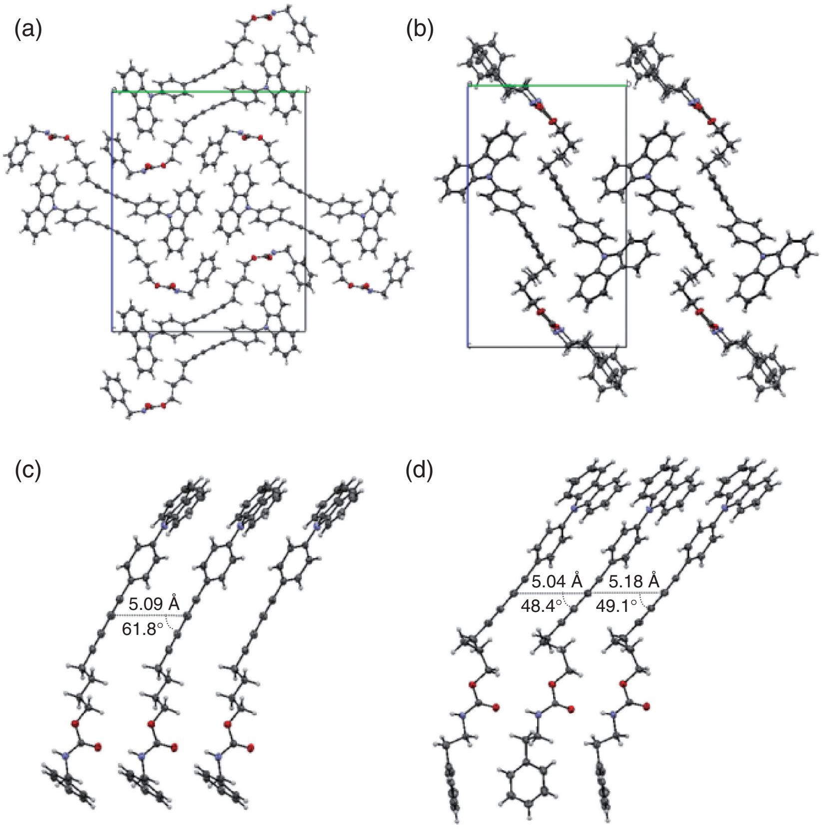


Figure 2. Molecular packing of (a) **DA1** and (b) **DA2** along with the *a* axis (thermal ellipsoids 50% probability). The geometry for monomers (c) **DA1** and (d) **DA2**.[22]

Table 1. Hydrogen-Bond Geometry (Å, °)

Compd.	D—H$\cdots A$[a)]	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
DA1	N2—H2A$\cdots$O2$^{\mathrm{i}}$	0.83	2.17	2.968(6)	163
DA2	N2—H2A$\cdots$O4$^{\mathrm{ii}}$	0.86	2.10	2.914(5)	159
	N4—H4A$\cdots$O2$^{\mathrm{iii}}$	0.78	2.19	2.959(5)	166

a) Symmetry codes: (i) $x - 1$, y, z; (ii) $-x$, $1 - y$, $1 - z$; (iii) $1 - x$, $1 - y$, $1 - z$.

function,[28] and the values are roughly proportional to the absorbance. The lower portions of each figure show the time dependence of absorbance near the absorption maxima of the polymers, i.e., 580 nm for **DA2**, 600 nm for **DA3** and 630 nm for **DA4**. From these figures, the order of time to reach the saturation of absorbance at the maximum is determined to be **DA4** < **DA3** < **DA2**, which should be related to the initial reaction rate. These results clearly show a different means of polymerization for DA monomers. Accordingly, each monomer showed different colors: yellow for **DA1**, red for **DA2**, red-violet for **DA3**, and blue for **DA4**.

The UV–vis diffuse reflectance spectra of compound **DA1** exhibited red-shift at the absorption edge without an increase in the absorption maxima for standard PDAs (Figure 3a). Therefore, compound **DA1** may react in distorted structure instead of via the regular 1,4-addition to form a fully conjugated backbone.[6] This is consistent with the result that the crystal structure of **DA1** does not meet Baughmann's criterion. On the other hand, **DA2** developed absorption bands around 540 and 580 nm with UV irradiation, which should be assigned to a less-ordered PDAs showing red color.[29] Some PDAs are known to exhibit thermochromism, where the color transforms from blue to red upon heating. The mechanism behind the chromatic transition has been discussed but is not fully understood. A possible explanation is the changing interplay between the conformation of the side groups and the backbone.[30] Compound **DA2** originally polymerized into a red color at room temperature, which means the relatively rigid side groups of **DA2** strongly constrain the conformation of the polymer backbone. In contrast, compounds **DA3** and **DA4** having more flexible side groups exhibited absorption bands at lower energies. The lowest energy absorption maximum of compounds **DA3** and **DA4** are 598 and 626 nm, respectively. The blue color of polymer **DA4** indicates the formation of conjugated backbone with an ordered structure, which may also be related to a faster conversion reaction in **DA4**. The violet color of polymer **DA3** may be the result of an intermediate state between the blue-colored and red-colored states. Interestingly, slight differences in the side groups, especially on the outside of the hydrogen bond, dramatically affect the conjugated polymer main chains, as well as the conformational changes of four methylene groups. As a result, the solid-state polymerization could be achieved despite the existence of a large π-conjugated *N*-CzPh group. Unfortunately, thermochromic transition behavior of polymers was not observed at heating temperatures below the melting points. However, the results provide valuable information for the design of DA monomers

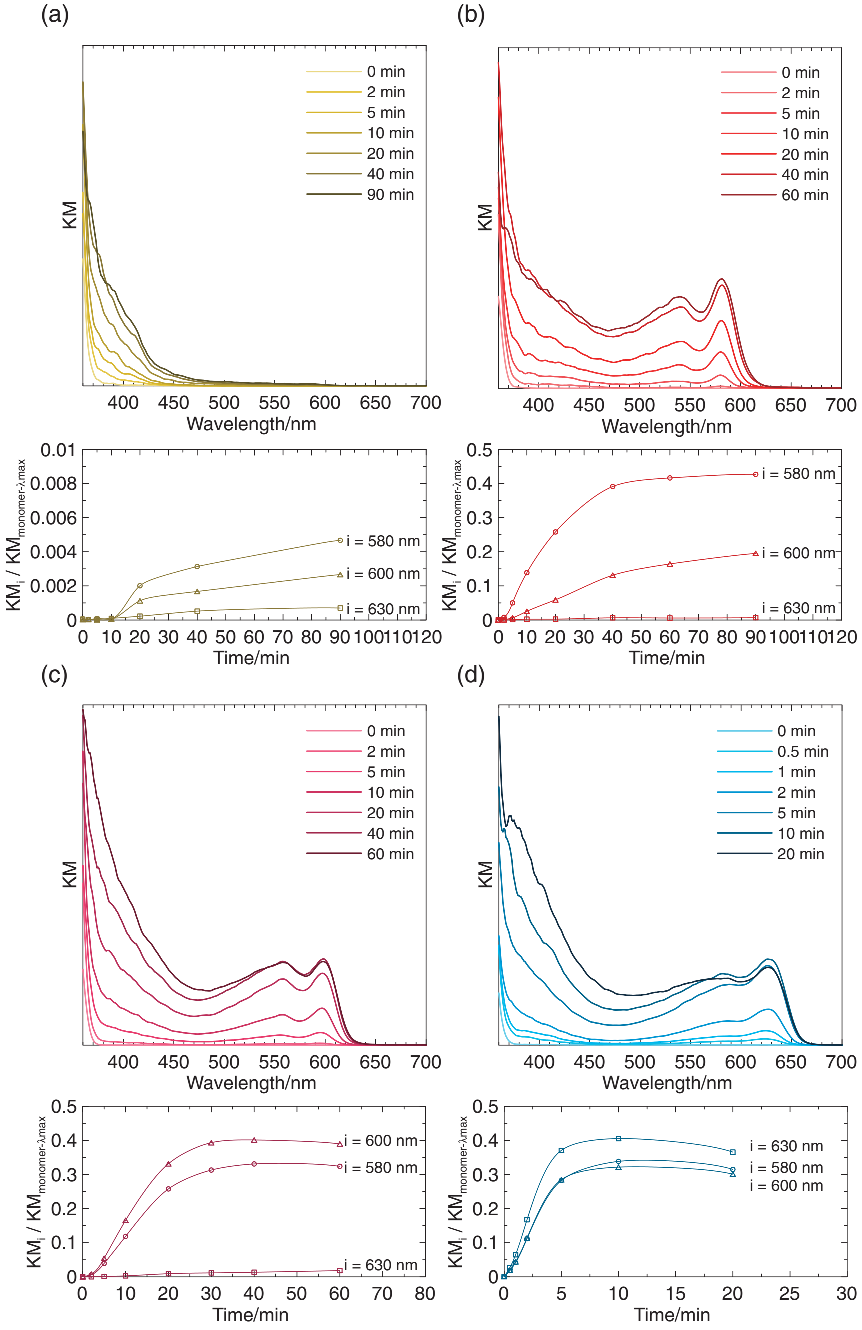


Figure 3. The diffuse reflectance spectra for each monomer: (a) **DA1**, (b) **DA2**, (c) **DA3**, and (d) **DA4**, as obtained from the diffuse reflection measurements; the lower portion shows KM in the range i from 580 to 630 nm, KM_i, normalized to that at absorption maximum wavelength of monomer ($KM_i/KM_{monomer\text{-}\lambda_{max}}$) plotted vs. UV irradiation time.

and the factors relating to the thermochromic properties of their PDA derivatives.

The heat flows for the UV-irradiated samples decreased with a decrease in the monomers. None of the monomers reached 100% conversion, even for the relatively reactive monomer **DA4**. The conversions obtained by the DSC method were 20% for **DA1**, 32% for **DA2**, 51% for **DA3**, and 68% for **DA4**, respectively. A percentage conversion level of 60% is not considered low level as compared to other reported polymers.[2,14] On the other hand, the conversions obtained by the gravimetric method were ca. 0% for **DA1**, 7% for **DA2**, 9% for **DA3**, and 12% for **DA4**, respectively. Generally, the former conversion becomes larger than the latter one because of the following reasons. The conversion by the DSC method may be overestimated when deterioration of crystallinity during polymerization and/or side reaction other than polymerization occur. In the gravimetric method, the conversion may be underestimated if the polymers disperse in the solvent for extraction and pass through the filter. Actually, after acetone extraction and filtration in the gravimetric method, yellow to orange filtrates were obtained for all the compounds. Especially for **DA1**, which did not show regular 1,4-addition polymerization, the

Table 2. Ionization Potentials of **DA1**–**DA4** before and after UV-Irradiation

	Ionization potential/eV			
	DA1	**DA2**	**DA3**	**DA4**
Monomer	5.96	6.04	6.01	5.85
After UV irradiation	6.01	6.02	5.68	5.39

insoluble polymers were hardly obtained. Thus, real conversions should be intermediate between the two values obtained by the two methods. It should be noted that the order of conversions is the same between two method, i.e., **DA1** < **DA2** < **DA3** < **DA4**. Thus, the photopolymerizability of the monomers must be in this order. Among the monomers in this study, the polymers showing lower energy absorption maxima tend to have higher levels of polymer conversion.

Preparation of thin films is an important step for electronic device fabrication. Therefore, we prepared thin films of the monomers and the UV-irradiated samples, whose structures may be different from the bulk crystals, and their electronic states were verified by PYS. PYS measurements showed nearly the same ionization potentials of around 6 eV for all monomers, as shown in Table 2. This is attributed to a localized-HOMO population on the *N*-CzPh moiety, whereby some simple *N*-CzPh derivatives have similar HOMO levels.[31] Slight differences among monomers are caused by variations in the solid state intermolecular interactions, which enable a shift in the HOMO–LUMO levels, rather than through intramolecular effects. In fact, the DFT calculations showed nearly the same HOMO energies for all monomers and an *N*-CzPh molecule (−5.7 eV), where the molecular geometries were optimized using the crystal structures as an initial geometry.[32] The polymerized **DA3** and **DA4** showed lower ionization potentials than monomers, which indicates formation of a π-conjugated chain. In addition, the polymer from **DA4** showed a large shift, suggesting a higher degree of conjugation. Interestingly, the ionization potentials of polymers from **DA1** and **DA2** remained nearly unchanged, nevertheless **DA2** turned reddish with a polymerization. These results indicate that less-ordered conformations in the red-colored state significantly prevent effective π-conjugations of the polymer backbone and the *N*-CzPh moieties. HOMO energies ranging from 5.0 to 5.5 eV are suitable as a hole conductor owing to their good contact with the work function of a gold electrode. Accordingly, these energy levels indicate potential for use of polymer **DA4** in organic electronic device applications.

Conclusion

We have developed four DA monomers, which possess aromatic donor moieties as side groups. Although aromatic groups such as *N*-CzPh were used, the monomers successfully underwent polymerizing reactions, which resulted in the formation of conjugated polymers. This result demonstrates that relatively large aromatic groups could be introduced into PDAs in combination with flexible side groups. This design strategy would be useful in tuning physical properties of PDAs. These compounds exhibited different polymerization modes, resulting in colors ranging from yellow to blue. It was found that small differences in molecular structure have a large impact on molecular conformation, which was validated by X-ray single crystal analysis, and are strongly related to the solid-state polymerization reactivity and the physical properties of the polymers. The blue-colored polymer is expected to have good hole conducting properties due to their suitable HOMO energy, which are being investigated.

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Supporting Information

Characterization, DFT calculations, and NMR spectra for all new compounds, and crystallographic information files (CIFs) for **DA1** and **DA2** are available free of charge on J-STAGE.

References

1 a) C. Sauteret, J.-P. Hermann, R. Frey, F. Pradère, J. Ducuing, R. H. Baughman, R. R. Chance, *Phys. Rev. Lett.* **1976**, *36*, 956. b) H. Matsuda, S. Shimada, H. Takeda, A. Masaki, E. Van Keuren, S. Yamada, K. Hayamizu, F. Nakanishi, S. Okada, H. Nakanishi, *Synth. Met.* **1997**, *84*, 909. c) A. Sarkar, S. Okada, H. Matsuzawa, H. Matsuda, H. Nakanishi, *J. Mater. Chem.* **2000**, *10*, 819.

2 A. Sarkar, S. Okada, H. Nakanishi, H. Matsuda, *Macromolecules* **1998**, *31*, 9174.

3 a) F. Kajzar, J. Messier, *Thin Solid Films* **1985**, *132*, 11. b) K. Kuriyama, H. Kikuchi, T. Kajiyama, *Langmuir* **1996**, *12*, 6468. c) H. Jiang, X.-J. Pan, Z.-Y. Lei, G. Zou, Q.-J. Zhang, K.-Y. Wang, *J. Mater. Chem.* **2011**, *21*, 4518.

4 a) W. Spevak, J. O. Nagy, D. H. Charych, *Adv. Mater.* **1995**, *7*, 85. b) X. Chen, G. Zhou, X. Peng, J. Yoon, *Chem. Soc. Rev.* **2012**, *41*, 4610. c) R. Jelinek, M. Ritenberg, *RSC Adv.* **2013**, *3*, 21192. d) O. Yarimaga, J. Jaworski, B. Yoon, J.-M. Kim, *Chem. Commun.* **2012**, *48*, 2469.

5 a) H. M. Barentsen, M. van Dijk, P. Kimkes, H. Zuilhof, E. J. R. Sudhölter, *Macromolecules* **1999**, *32*, 1753. b) J. Y. Lee, A. N. Aleshin, D. W. Kim, H. J. Lee, Y. S. Kim, G. Wegner, V. Enkelmann, S. Roth, Y. W. Park, *Synth. Met.* **2005**, *152*, 169. c) T. Koyanagi, M. Muratsubaki, Y. Hosoi, T. Shibata, K. Tsutsui, Y. Wada, Y. Furukawa, *Chem. Lett.* **2006**, *35*, 20. d) J. Nishide, T. Oyamada, S. Akiyama, H. Sasabe, C. Adachi, *Adv. Mater.* **2006**, *18*, 3120. e) H. Tabata, H. Tokoyama, H. Yamakado, T. Okuno, *J. Mater. Chem.* **2012**, *22*, 115.

6 Y. Tatewaki, S. Inayama, K. Watanabe, H. Shibata, S. Okada, *Mol. Cryst. Liq. Cryst.* **2012**, *568*, 87.

7 K. J. Donovan, E. G. Wilson, *Philos. Mag. B* **1981**, *44*, 9.

8 a) D. Moses, M. Sinclair, A. J. Heeger, *Phys. Rev. Lett.* **1987**, *58*, 2710. b) D. Moses, A. J. Heeger, *J. Phys.: Condens. Matter* **1989**, *1*, 7395.

9 T. Kato, M. Yasumatsu, C. Origuchi, K. Tsutsui, Y. Ueda, C. Adachi, *Appl. Phys. Express* **2011**, *4*, 091601.

10 K. Srinivas, C. R. Kumar, M. A. Reddy, K. Bhanuprakash, V. J. Rao, L. Giribabu, *Synth. Met.* **2011**, *161*, 96.

11 a) S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, F. Sato, *Appl. Phys. Lett.* **2003**, *83*, 569. b) R. J. Holmes, S. R. Forrest, Y.-J. Tung, R. C. Kwong, J. J. Brown, S. Garon, M. E. Thompson, *Appl. Phys. Lett.* **2003**, *82*, 2422. c) X. Cai, A. B. Padmaperuma, L. S. Sapochak, P. A. Vecchi, P. E. Burrows, *Appl. Phys. Lett.* **2008**, *92*, 083308.

12 K. C. Yee, R. R. Chance, *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 431.

13 S. M. Fomin, A. I. Stash, G. N. Gerasimov, I. V. Bulgarovskaya, V. M. Vozshennikov, N. V. Kozlova, E. N. Teleshov, *Polym. Sci. USSR* **1989**, *31*, 2003.

14 H. Matsuda, H. Nakanishi, T. Hosomi, M. Kato, *Macromolecules* **1988**, *21*, 1238.

15 G. Dellepiane, C. Cuniberti, G. F. Musso, D. Comoretto, A. Piaggi, A. Borghesi, S. De Silvestri, M. Nisoli, A. Cybo-Ottone, *Synth. Met.* **1993**, *57*, 5081.

16 F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380.

17 a) F. Sanda, T. Kawaguchi, T. Masuda, N. Kobayashi, *Macromolecules* **2003**, *36*, 2224. b) G.-S. Liou, H.-W. Chen, H.-J. Yen, *Macromol. Chem. Phys.* **2006**, *207*, 1589.

18 W. H. Kim, N. B. Kodali, J. Kumar, S. K. Tripathy, *Macromolecules* **1994**, *27*, 1819.

19 a) Y.-H. Chan, J.-T. Lin, I.-W. P. Chen, C. Chen, *J. Phys. Chem. B* **2005**, *109*, 19161. b) H. Liu, H. Li, T. Li, Y. Li, Y. Wu, S. Okada, H. Nakanishi, *J. Organomet. Chem.* **2014**, *767*, 144.

20 S. Spagnoli, J. Berréhar, C. Lapersonne-Meyer, M. Schott, A. Rameau, M. Rawiso, *Macromolecules* **1996**, *29*, 5615.

21 *CrystalClear*, Rigaku Corporation, Tokyo, Japan, **2008**.

22 Program for the Solution of Crystal Structures: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

23 a) Yadokari-XG: K. Wakita, *Software for Crystal Structure Analyses*, **2001**. b) Yadokari-XG 2009: C. Kabuto, S. Akine, T. Nemoto, E. Kwon, *Nippon Kessho Gakkaishi* **2009**, *51*, 218.

24 P. Cadiot, W. Chodkiewicz, in *Chemistry of Acetylenes*, ed. by H. G. Viehe, Marcel Dekker, New York, **1969**, pp. 597–647.

25 For crystallographic data of **DA1** and **DA2** in CIF, see the Supplementary data and the CCDC 1030996 and 1030997.

26 a) R. H. Baughman, *J. Appl. Phys.* **1972**, *43*, 4362. b) R. H. Baughman, *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1511. c) T. Okuno, A. Izuoka, T. Ito, S. Kuno, T. Sugawara, N. Sato, Y. Sugawara, *J. Chem. Soc., Perkin Trans. 2* **1998**, 889.

27 G. Wegner, *Z. Naturforsch., B* **1969**, *24*, 824.

28 P. Kubelka, F. Munk, *Z. Tech. Phys.* **1931**, *12*, 593.

29 a) R. R. Chance, R. H. Baughman, H. Müller, C. J. Eckhardt, *J. Chem. Phys.* **1977**, *67*, 3616. b) Y. Tokura, K. Ishikawa, T. Kanetake, T. Koda, *Phys. Rev. B* **1987**, *36*, 2913. c) D.-C. Lee, S. K. Sahoo, A. L. Cholli, D. J. Sandman, *Macromolecules* **2002**, *35*, 4347. d) S. Wacharasindhu, S. Montha, J. Boonyiseng, A. Potisatityuenyong, C. Phollookin, G. Tumcharern, M. Sukwattanasinitt, *Macromolecules* **2010**, *43*, 716.

30 a) R. A. Koevoets, S. Karthikeyan, P. C. M. M. Magusin, E. W. Meijer, R. P. Sijbesma, *Macromolecules* **2009**, *42*, 2609. b) S. Dei, T. Shimogaki, A. Matsumoto, *Macromolecules* **2008**, *41*, 6055. c) S. Dei, A. Matsumoto, A. Matsumoto, *Macromolecules* **2008**, *41*, 2467. d) R. W. Carpick, D. Y. Sasaki, M. S. Marcus, M. A. Eriksson, A. R. Burns, *J. Phys.: Condens. Matter* **2004**, *16*, R679. e) B. J. Orchard, S. K. Tripathy, *Macromolecules* **1986**, *19*, 1844. f) C. Tanioku, K. Matsukawa, A. Matsumoto, *ACS Appl. Mater. Interfaces* **2013**, *5*, 940.

31 a) M.-F. Wu, S.-J. Yeh, C.-T. Chen, H. Murayama, T. Tsuboi, W.-S. Li, I. Chao, S.-W. Liu, J.-K. Wang, *Adv. Funct. Mater.* **2007**, *17*, 1887. b) M.-S. Lin, L.-C. Chi, H.-W. Chang, Y.-H. Huang, K.-C. Tien, C.-C. Chen, C.-H. Chang, C.-C. Wu, A. Chaskar, S.-H. Chou, H.-C. Ting, K.-T. Wong, Y.-H. Liu, Y. Chi, *J. Mater. Chem.* **2012**, *22*, 870.

32 DFT calculations were carried out with the Gaussian 09 program package: M. J. Frisch, et al. *Gaussian 09 (Revision C.01)*, Gaussian, Inc., Wallingford, CT, **2010**; see the Supplementary data for full reference.