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Article

Synthesis and Solid-State Polymerization of 5-(Pyren-1-yl)penta-2,4-diyn-1-ol Derivatives with an *N*-Phenylurethane or *N*-Benzylurethane Group

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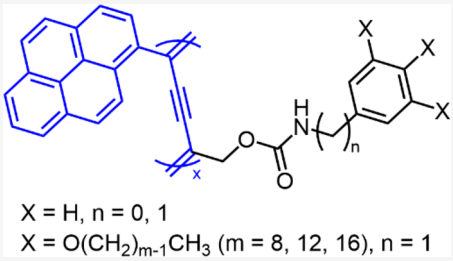
ABSTRACT: A series of 5-(pyren-1-yl)penta-2,4-diyn-1-yl *N*-phenylcarbamates and *N*-benzylcarbamates were synthesized. Phenyl groups in the *N*-phenyl and *N*-benzyl moieties were unsubstituted (**H-0** and **H-1**, respectively) and 3,4,5-trialkoxy substituted (**C_mO-0** and **C_mO-1**, respectively), in which the alkyl groups introduced were methyl (m = 1), octyl (m = 8), dodecyl (m = 12), and hexadecyl (m = 16) groups. Upon UV irradiation, a regular 1,4-addition polymerization to form polydiacetylene was confirmed for **H-0**, **H-1**, **C_8O-1**, **C_{12}O-1**, and **C_{16}O-1**. For **C_1O-0** and **C_1O-1**, the crystal structures were solved, and the reasons the regular polymerization did not occur were clarified. From the powder X-ray diffraction study, crystallinities of **C_mO-1** were found to be lower than those of **C_mO-0**, although **C_mO-1** regularly polymerized. This indicates that the total crystallinity is not directly related to local ordering around one-dimensional arrays for the polymerization direction. Polymerized **C_mO-1** species were soluble in chloroform. Their processability enabled us to fabricate cast films of polydiacetylene as well as the monomer. The conductivities of **C_{12}O-1** and the polymer (**PC_{12}O-1**) were evaluated in the pristine and iodine-doped states and in the charge-transfer-complexed states with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane. A conductivity of 1.2×10^{-2} S m^{-1} for iodine-doped **PC_{12}O-1** was achieved. In this case, pyrene moieties seemed to play an important role in realizing the appropriate electron transfer from pyrene moieties to iodine molecules and effective π conjugation between the pyrene moieties and the PDA backbone promoting charge transport.



INTRODUCTION

A variety of π-conjugated polymers have been investigated as materials for nonlinear optics,[1−3] electric conduction,[4−6] electrochromism,[7−9] light emission,[10−12] photovoltaics,[13−16] transistors,[17−19] sensors,[20−22] etc., and many of them have generally been synthesized via solution polymerization. However, polydiacetylene (PDA) is an exception. It is synthesized by the solid-state 1,4-addition polymerization of butadiyne monomers.[23] Since polymerization progresses topochemically, the resulting polymers can have quite regular stereostructures with high molecular weight. Although this is a kind of ideal polymerization, it also has challenges. First, the butadiyne monomers synthesized do not polymerize with a high probability because of narrow acceptable conditions for the solid-state polymerization. The monomers should satisfy the following conditions to react via regular 1,4-addition polymerization: the distance d between the adjacent monomers in the array with the translation relation is approximately 0.5 nm and angle θ between the translation axis and the butadiyne rod in the monomer is approximately 45°, as shown in Figure 1.[24,25] Second, the polymers obtained are generally insoluble and the processability is poor. However, since PDA has a π-conjugated backbone, a wide range of electronic and optical applications have been considered in general. Thus, the molecular design and the related properties

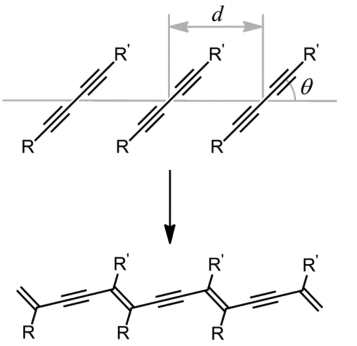


Figure 1. Topochemical polymerization scheme of butadiyne derivatives. Appropriate conditions for the regular 1,4-addition polymerization are a distance d of approximately 0.5 nm and an angle θ of approximately 45°.

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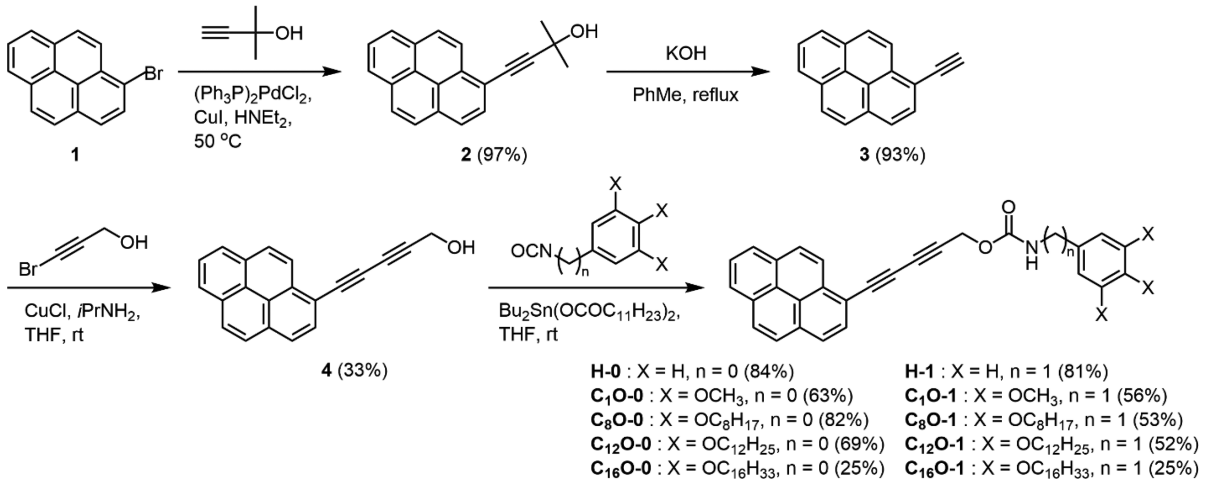

Figure 2. Synthesis scheme of pyrenylbutadiyne derivatives with an *N*-phenylurethane or *N*-benzylurethane moiety.

have been extensively investigated. The properties investigated are, for example, third-order nonlinear optical properties,[1,26−31] conductivities,[32−37] colorimetric properties,[38−41] etc.

From the viewpoint of the molecular design of PDA, PDAs with π conjugation between the backbone and substituents are interesting because of their improved electronic and optical properties.[42] However, the probability of solid-state polymerization of butadiyne monomers directly substituted by aromatic rings is lower than that of the monomers substituted by alkyl groups in general. Thus, strategies to align the monomers in polymerizable stacks are required. One of the strategies is to use a supramolecular host−guest system.[43,44] The other is modification by specific groups, which tend to align monomers in one-dimensional (1D) arrays. We have used the latter strategy to prepare butadiyne monomers with π conjugation between the backbone and substituents.[45,46] For example, butadiyne derivatives directly bound to electron-donating aromatics such as pyrene,[47,48] *N*-phenylcarbazole,[49,50] aniline,[51,52] and tetrathiafluvalene (TTF)[53] were recently synthesized, and some of them polymerized regularly to form PDAs with conjugated donors. Meanwhile, in order to improve the PDA processability, one of the potential approaches is its solubilization. Although some butadiyne derivatives with urethane groups have been found to dissolve in organic solvent,[54,55] we prepared those with 3,4,5-trialkoxyphenyl (TAOP) groups to impart self-organizing properties and solubilities of their polymers.[56,57]

In the present study, we focused on the preparation of soluble PDAs with donor substituents directly bound to the π-conjugated backbone. As a donor, we selected pyrene because of its relatively high photostability, and TAOP groups were introduced for solubilization. The alkyl chains in the TAOP groups were varied among octyloxy, dodecyloxy, and hexadecyloxy groups. For comparison, the derivatives with a simple phenyl group instead of the TAOP group or with the TAOP group containing methoxy groups were also synthesized. The photopolymerizability and crystallinity of the monomers and processability of the polymers were investigated. The electrical conductivities of the films of a monomer and the corresponding polymer were evaluated.

■ RESULTS AND DISCUSSION

Ten pyrenylbutadiyne derivatives with an *N*-phenylurethane or *N*-benzylurethane moiety were synthesized according to Figure 2. From 1-bromopyrene (**1**), 1-ethynylpyrene (**3**) was prepared via **2** as a product of Sonogashira coupling followed by acetone elimination using potassium hydroxide. A Cadiot−Chodkiewicz coupling reaction between **3** and 3-bromoprop-2-yn-1-ol afforded 5-(pyren-1-yl)penta-2,4-diyn-1-ol (**4**). Finally, addition reaction of isocyanates to **4** gave the desired compounds.

First, photopolymerization behaviors of the solid samples were investigated using visible diffuse reflectance spectra (see the Experimental Section for the sample preparation). Figure 3 shows the spectra obtained by UV irradiation of 254 nm. All pyrenylbutadiyne derivatives showed an absorption increase in the visible region, suggesting that polymerization occurred to form extended π-conjugated structures. The spectral patterns are roughly classified into two categories. Compounds in the first category (type I) showed spectra having absorption maxima in the wavelength range between 550 and 700 nm after UV irradiation. Compounds of type I are **H-0**, **H-1**, **C_8O-1**, **C_{12}O-1**, and **C_{16}O-1**, whose absorption maxima at the longest wavelengths were 646, 691, 668, 659, and 667 nm, respectively. These absorption bands are generally assigned to an excitonic absorption with its phonon sidebands originating from the regularly polymerized PDA structure. Other compounds in the second category (type II) showed an absorption increase in the visible region upon UV irradiation but no absorption maxima were observed in this region. In this case, the polymerization scheme seems to be not as regular as for the compounds of type I. Actually, in our previous study, we confirmed by single-crystal X-ray crystallographic analysis that the butadiyne derivatives showing the polymer absorption of type II aligned under the conditions with a large deviation from d = 0.5 nm and θ = 45° in Figure 1.[52]

Powder X-ray diffraction patterns of the monomers were obtained as shown in Figure 4. Sharp diffraction peaks were observed for the compounds with phenyl or trimethoxyphenyl groups: i.e., **H-0**, **H-1**, **C_1O-0**, and **C_1O-1**. Among these compounds, single crystals of **C_1O-0** and **C_1O-1** with large enough sizes for X-ray crystallography were obtained and analyzed. The crystal structures of **C_1O-0** and **C_1O-1** are shown in Figures 5 and 6, respectively, and their crystallographic data are summarized in Table 1. **C_1O-0** molecules

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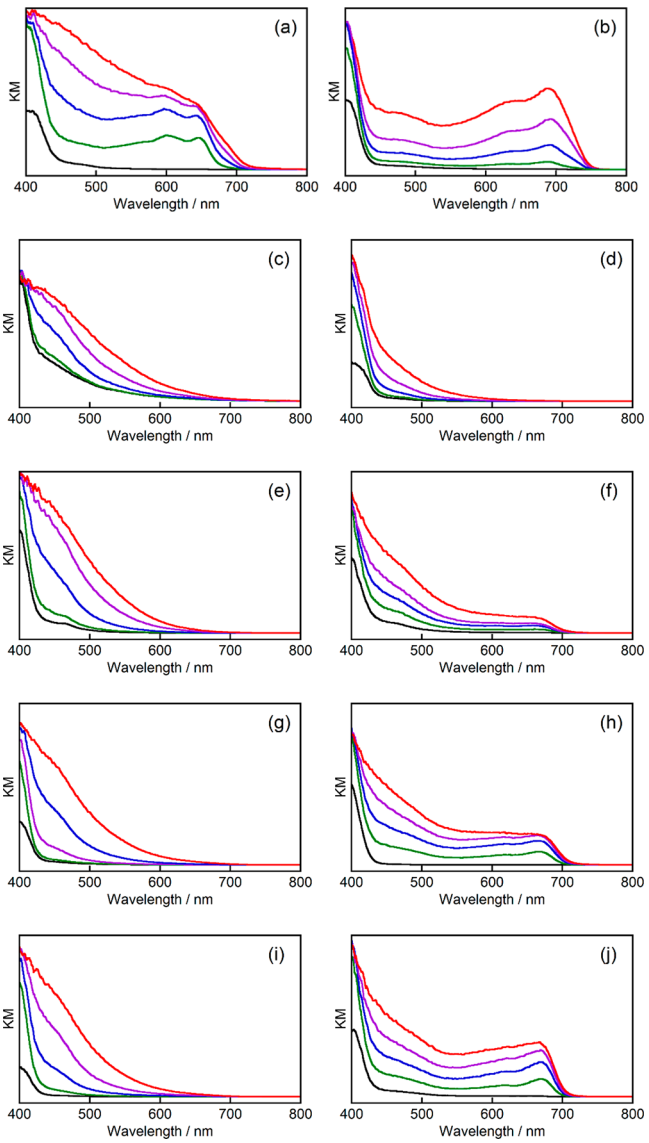

Figure 3. Visible diffuse reflectance spectra of (a) **H-0**, (b) **H-1**, (c) **C_1O-0**, (d) **C_1O-1**, (e) **C_8O-0**, (f) **C_8O-1**, (g) **C_{12}O-0**, (h) **C_{12}O-1**, (i) **C_{16}O-0**, and (j) **C_{16}O-1** in the course of UV irradiation at 254 nm. Black, green, blue, violet, and red lines correspond to the spectra after UV irradiation for 0, 5, 30, 120, and 480 min, respectively.

form 1D stacking along the *b* axis due to the intermolecular hydrogen bonding between urethane groups (green dashed lines in Figure 5b). The distance *d* and angle θ, defined in Figure 1, are 0.476 nm and 65.6°, respectively. In comparison with the polymerizable conditions, *d* is slightly shorter and θ is larger. The carbon−carbon (C−C) distances between adjacent molecules are 0.438, 0.443, and 0.470 nm for C1−C2, C3−C4, and C1−C4, respectively, whose carbon numbers are indicated in Figure 5b. Namely, C−C distances for 1,2-addition (C1−C2 and C3−C4) are shorter than those of 1,4-addition (C1−C4). This result is clear evidence that **C_1O-0** does not polymerize in the regular 1,4-addition manner, resulting in absorption spectra of **C_1O-0** without an excitonic peak after UV irradiation (Figure 3c). Unexpectedly for **C_1O-1**, there are no hydrogen bonds between urethane groups but the nitrogen atom of the urethane group forms an intermolecular hydrogen bond with the oxygen atom of a methoxy group (green dashed lines in Figure 6a). As a result, the carboxy group in the urethane bond

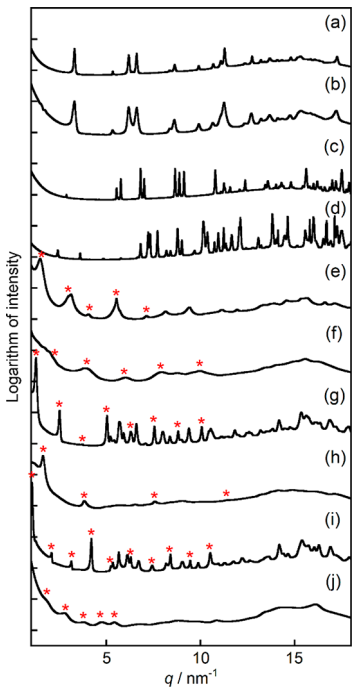

Figure 4. Powder X-ray diffraction patterns of (a) **H-0**, (b) **H-1**, (c) **C_1O-0**, (d) **C_1O-1**, (e) **C_8O-0**, (f) **C_8O-1**, (g) **C_{12}O-0**, (h) **C_{12}O-1**, (i) **C_{16}O-0**, and (j) **C_{16}O-1**. One scale of the vertical axis corresponds to 1 (=log 10), and the lowermost scale is 2 (=log 10^2) for each curve, which is shifted by 2 to avoid overlap. Red asterisks on the peak tops of the diffractograms (e)−(j) indicate that these peaks were used to calculate the interlayer spacings.

of **C_1O-1** does not form a hydrogen bond. This fact is also supported by the IR spectral data. Almost all urethane compounds in this study showed an absorption peak corresponding to a C═O stretching vibration in the range of 1693−1697 cm^{-1}, suggesting intermolecular hydrogen bonding of the urethane groups. However, **C_1O-1** exceptionally exhibited the peak at a higher wavenumber of 1722 cm^{-1}, indicating an isolated C═O bond without hydrogen bonding. As shown in Figure 6b, pyrene and butadiyne moieties of **C_1O-1** are alternately piled up. Thus, a regular 1,4-addition polymerization is impossible in this crystal. Among the powder X-ray diffractograms of the compounds with other trialkoxyphenyl groups, **C_{12}O-0** and **C_{16}O-0** showed clear progression of the peaks related to the layered structures, and the interlayer spacings were calculated to be 5.00 and 5.99 nm, respectively. In comparison with these, **C_8O-0** showed weaker and broad peaks, and the spacing was roughly estimated to be 4.4 nm. Namely, longer alkyl chains of the compound tend to give a larger spacing. **C_8O-1**, **C_{12}O-1**, and **C_{16}O-1** showed much weaker diffraction peaks, suggesting their lower crystallinity. However, **C_{12}O-1** showed a progression of the peaks corresponding to a spacing of about 3.3 nm. Although the peaks of **C_8O-1** and **C_{16}O-1** were broad, the spacings were roughly estimated to be 3.2 and 6.8 nm, respectively. The relationship between the alkyl chain length and the spacing of **C_mO-1** is similar to that of **C_mO-0**. However, the spacing of **C_{16}O-1** is slightly more than twice the spacing of **C_8O-1** or **C_{12}O-1**. This may suggest that the periodic structure of **C_{16}O-1** is the bilayer type but that of **C_8O-1** or **C_{12}O-1** is the monolayer type. The melting points of **C_mO-0** are higher than those of the corresponding **C_mO-1**, respectively, and these

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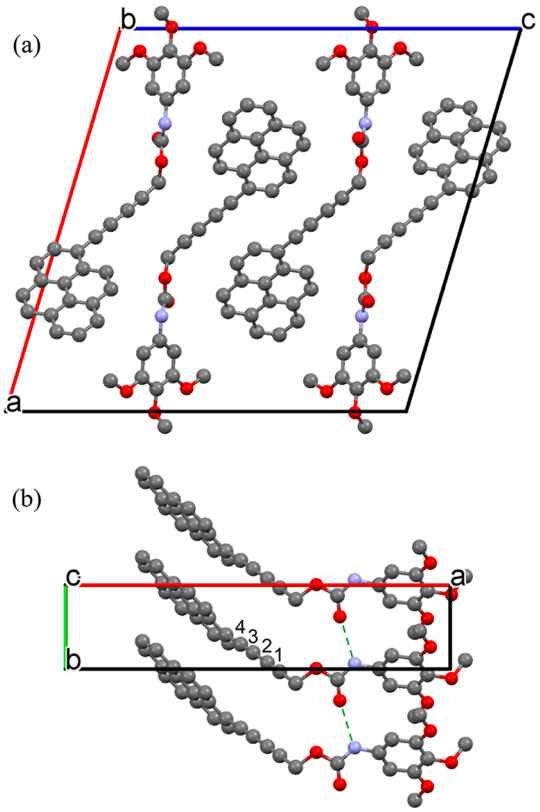

Figure 5. Crystal structure of $\mathbf{C_1O\text{-}0}$ viewed along (a) the *b* axis and (b) the *c* axis. Green dashed lines in (b) indicate intermolecular hydrogen bonds. Numbers labeling sp carbons in (b) are to enable an explanation of the carbon−carbon distance in the text. Atom color code: gray, blue, and red refer to carbon, nitrogen, and oxygen, respectively.

differences may originate from the crystallinity. As described above, $\mathbf{C_mO\text{-}1}$ with less crystallinity regularly polymerized and $\mathbf{C_mO\text{-}0}$ with more crystallinity did not. This fact seems contradictory. However, a similar situation, i.e., polymerizable butadiyne moieties in a less crystalline environment, can be found in segmented copolymers composed of polyurethane or polyamide with butadiyne moieties in the backbone.[58−60] In these polymers, the butadiyne moieties stacked regularly in the hard segment, which are surrounded by the amorphous soft segment, can polymerize in the 1,4-addition manner. In the less crystalline $\mathbf{C_mO\text{-}1}$, the butadiyne moieties are properly aligned but the methylene group in the benzyl urethane moiety may prevent an ordered assembling of the alkyl chains of TAOP groups. The contrast in crystallinity between $\mathbf{C_mO\text{-}0}$ and $\mathbf{C_mO\text{-}1}$ are interesting, although the more detailed structural differences were not able to be clarified. Regardless of polymerization in the regular manner or not, a close contact of the pyrene moieties was confirmed in the solid state of this series of compounds because a broad emission attributed to pyrene excimer formation was observed in the fluorescence spectra in the solid state (Figure S1).

$\mathbf{C_{12}O\text{-}1}$ after UV irradiation for 12 h was dissolved in chloroform, and the solution was added dropwise in methanol to reprecipitate. The yields of the polymer precipitated were 10−15%. The UV−vis spectrum of the resulting precipitate portion ($\mathbf{PC_{12}O\text{-}1}$) dissolved in chloroform is shown in Figure 7. The absorption maximum at 612 nm of the PDA structure was clearly observed even in chloroform, although the

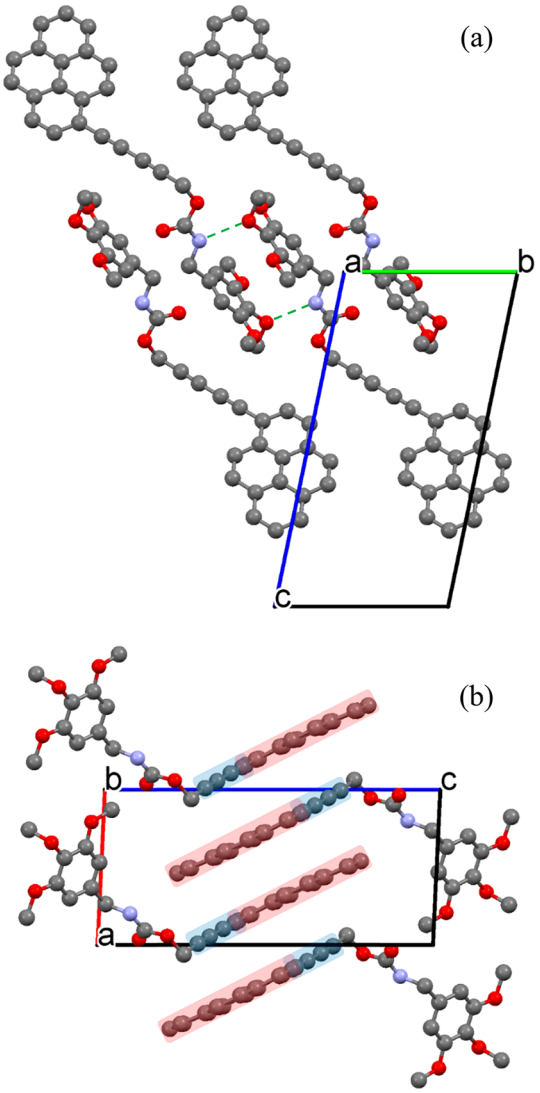

Figure 6. Crystal structure of $\mathbf{C_1O\text{-}1}$ viewed along (a) the *a* axis and (b) the *b* axis. Green dashed lines in (a) indicate intermolecular hydrogen bonds. In (b), red and blue rectangles indicate pyrene and butadiyne moieties, respectively. Atom color code: gray, blue, and red refer to carbon, nitrogen, and oxygen, respectively.

absorption maximum wavelength has been blue-shifted from that in the crystalline state at 659 nm. This blue shift may be due to less planarity of the π-conjugated backbone with the solvated side chains. Photopolymerized $\mathbf{C_8O\text{-}1}$ and $\mathbf{C_{16}O\text{-}1}$ were also soluble in chloroform. The chloroform solution of the polymerized sample of $\mathbf{C_{12}O\text{-}1}$ with 1 g L^{-1} concentration, which was filtered by a membrane filter with a pore size of 0.45 μm, was subjected to GPC, and the elution curve in Figure 8 was obtained. The molecular weight distribution was quite broad from the oligomer level to polymers with a molecular weight of more than 1×10^6, which is about the exclusion limit of the columns. A dip in the elution curve at a retention time of about 35 min corresponded to a molecular weight of about 6×10^3 of the standard polystyrene. If the components are divided at this molecular weight, the higher-molecular-weight components accounted for about 60% of the product, which is simply estimated by the area of the elution curve.

In order to investigate the function of the pyrenyl group introduced, experiments on chemical doping were performed.

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Table 1. Crystallographic Data of C_1O-0 and C_1O-1

	C_1O-0	C_1O-1
formula	$C_{31}H_{23}NO_5$	$C_{32}H_{25}NO_5$
formula wt	489.50	503.53
cryst syst	monoclinic	triclinic
space group	$P2_1/_C$	$P\bar{1}$
a/Å	22.7495(13)	8.030(13)
b/Å	4.7604(3)	8.963(16)
c/Å	22.7650(13)	17.65(4)
α/deg	90	101.61(8)
β/deg	106.637(4)	92.09(6)
γ/deg	90	92.97(6)
V/Å^3	2362.2(2)	1241(4)
Z	4	2
D_x/Mg m^{-3}	1.376	1.347
R	0.0483	0.0669
R_w	0.1102	0.1470
GOF	1.057	0.988
T/K	90(2)	100(2)

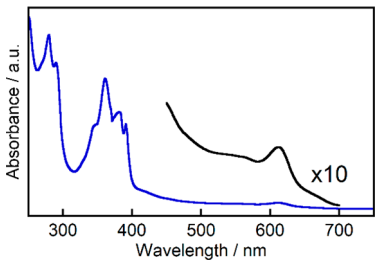

Figure 7. UV−vis absorption spectrum of the chloroform solution of **PC$_{12}$O-1** (blue curve). A magnified spectrum is shown between 450 and 750 nm using a black curve. The solution measured was prepared as follows: **C$_{12}$O-1** after irradiation of UV at 254 nm for 12 h was dissolved in chloroform, and the resulting solution was filtered by a membrane filter with a pore size of 0.45 μm.

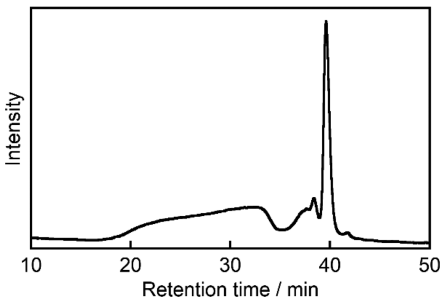

Figure 8. GPC elution curve of polymerized **C$_{12}$O-1**.

By using **C$_{12}$O-1** as a base compound, the four film samples, which were generally amorphous, were prepared on glass slides with gold electrodes, and their DC electrical conductivities were evaluated by the two-probe method (Table 2). Sample 1a was prepared by casting a **C$_{12}$O-1** chloroform solution. Iodine vapor treatment of sample 1a gave sample 1b, and sample 1c was obtained by keeping sample 1b in air for a prolonged time to remove iodine. Similar samples 3a−c were prepared for the corresponding PDA of **PC$_{12}$O-1**. Before iodine treatment and after removal of iodine, the conductivities of **C$_{12}$O-1** and **PC$_{12}$O-1** at room temperature were on the order of 10^{-8}−10^{-7} S m^{-1}. Since the conductivities of pristine PDAs are reported to be on the order of 10^{-14}−10^{-7} S m^{-1},[61−67] those of **C$_{12}$O-1** and **PC$_{12}$O-1** are within the range but are relatively high. During iodine doping, the conductivities of **C$_{12}$O-1** and **PC$_{12}$O-1** increased, and they were finally saturated at 8.4 × 10^{-5} and 1.2 × 10^{-2} S m^{-1}, respectively. Due to the conjugated backbone of **PC$_{12}$O-1**, about a 2 orders of magnitude conductivity enhancement was confirmed, in comparison with **C$_{12}$O-1**. Since pyrene is an electron donor and charge-transfer (CT) complexes of pyrene and 7,7,8,8-tetracyanoquinodimethane (TCNQ) derivatives have been known,[68−73] we prepared CT complexes of **C$_{12}$O-1** and **PC$_{12}$O-1** with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ). For the CT complex preparation, chloroform solutions of **C$_{12}$O-1** or **PC$_{12}$O-1** were mixed with F_4TCNQ acetone solution in a 1:1 molar ratio and the solvents were evaporated. Figure 9 shows UV−vis−NIR diffuse reflectance spectra of the complexes **C$_{12}$O-1**/F_4TCNQ and **PC$_{12}$O-1**/F_4TCNQ. In the spectrum of **C$_{12}$O-1**/F_4TCNQ, a broad CT band from around 1200 nm to the visible region was observed. Although **C$_{12}$O-1**/F_4TCNQ was irradiated at a UV wavelength of 254 nm, apparent spectral changes were not detected, indicating that the complex is photostable and not polymerizable. The spectrum of **PC$_{12}$O-1**/F_4TCNQ also showed a broad CT band from the NIR to visible region, but it seemed to be weaker than that of **C$_{12}$O-1**/F_4TCNQ. Since the peak at approximately 600 nm remained, the PDA backbone structure was considered to be maintained. The conductivities of **C$_{12}$O-1**/F_4TCNQ and **PC$_{12}$O-1**/F_4TCNQ were evaluated to be 1.4 × 10^{-5} and 1.3 × 10^{-4} S m^{-1}, respectively. When the conductivities were compared between iodine-doped and CT-complexed samples, higher conductivities were obtained for the former samples of both the monomer and polymer,

Table 2. Electric Conductivities (σ) of **C$_{12}$O-1**, **PC$_{12}$O-1**, and Their Charge-Transfer States

sample	donor	acceptor	σ/S m^{-1}	remark
1a	**C$_{12}$O-1**		2.3 × 10^{-7}	pristine
1b		I_2	8.4 × 10^{-5}	I_2 vapor treatment of sample 1a
1c			1.7 × 10^{-7}	sample 1b kept in air to remove I_2
2	**C$_{12}$O-1**	F_4TCNQ	1.4 × 10^{-5}	1:1 molar ratio
3a	**PC$_{12}$O-1**		1.9 × 10^{-8}	pristine
3b		I_2	1.2 × 10^{-2}	I_2 vapor treatment of sample 3a
3c			5.0 × 10^{-8}	sample 3b kept in air to remove I_2
4	**PC$_{12}$O-1**	F_4TCNQ	1.3 × 10^{-4}	1:1 molar ratio

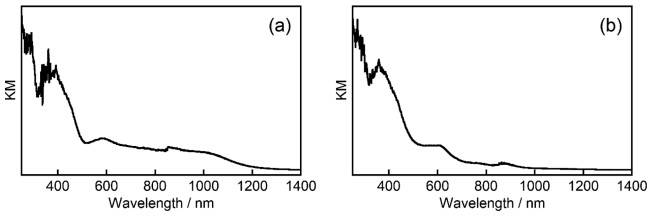

Figure 9. UV−vis−NIR diffuse reflectance spectra of CT complexes with F_4TCNQ: (a) **C$_{12}$O-1**/F_4TCNQ; (b) **PC$_{12}$O-1**/F_4TCNQ. The molar ratio of F_4TCNQ with respect to **C$_{12}$O-1** and the **PC$_{12}$O-1** monomer unit was 1:1.

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indicating that better CT states for electric conduction were achieved in iodine doping in these cases. For the iodine-doped PDAs in general, the conductivities have been reported to be on the order of 10^{-8}–10^{-4} S m^{-1}.[32−37,62] By using other dopants and polymerization under high pressure, the conductivities of PDA increased up to 10^{-3} S m^{-1}.[74] In the present study, the conductivity of the iodine-doped **PC$_{12}$O-1** was measured to be as high as 10^{-2} S m^{-1}, which may be due to an appropriate charge transfer from the pyrene moieties to iodine molecules and effective π conjugation between the pyrene moieties and the PDA backbone.

■ CONCLUSION

Ten pyrenyl-substituted PDAs with a urethane moiety were prepared. Regular 1,4-addition polymerization was confirmed for **H-0**, **H-1**, **C$_8$O-1**, **C$_{12}$O-1**, and **C$_{16}$O-1**, which showed characteristic excitonic absorption peaks between 646 and 691 nm. Although **C$_1$O-0** and **C$_1$O-1** were not polymerized in the regular manner, the crystal structures were able to be analyzed and the reasons they did not regularly polymerize were clarified. For **C$_1$O-0**, 1D monomer arrays due to the intermolecular hydrogen bonding between urethane groups were formed. However, d was shorter and θ was larger with respect to the regularly polymerizable conditions. For **C$_1$O-1**, intermolecular hydrogen bonding was not formed between urethane groups but formed between urethane and methoxy groups, which resulted in alternating stacking of pyrene and butadiyne moieties. Although the introduction of a urethane or amide group in butadiyne monomers promotes the formation of 1D arrays in the crystals in general, this principle is sometimes broken. For longer alkyl derivatives, crystallinities of **C$_m$O-1** were lower than those of **C$_m$O-0** despite the regular polymerization of **C$_m$O-1**. This fact indicates that local ordering around 1D arrays for the polymerization direction may not be reflected in the total crystallinity. Polymerized **C$_m$O-1** is soluble in chloroform and processable. Solution-cast films of **C$_{12}$O-1**, **PC$_{12}$O-1**, and their CT complexes with F$_4$TCNQ were prepared. For the **C$_{12}$O-1** and **PC$_{12}$O-1** films, iodine doping was performed and their conductivities were evaluated. The highest conductivity among the measured conditions was 1.2×10^{-2} S m^{-1} for iodine-doped **PC$_{12}$O-1**, in which appropriate charge transfer and effective π conjugation between the substituents and the PDA backbone seemed to be achieved.

■ EXPERIMENTAL SECTION

Materials. Commercially available reagents and solvents were used as received except for copper(I) chloride, which was washed with hydrochloric acid (2 mol/L) and vacuum-dried in an oven at 100 °C. The synthesis procedures of alkoxy-substituted phenyl isocyanates[55] **9a−d** and benzyl isocyanates **15a−d** are described in the Supporting Information.

2-Methyl-4-(pyren-1-yl)but-3-yn-2-ol (2). A mixture of 1-bromopyrene (**1**; 5.00 g, 17.8 mmol) and bis(triphenylphosphine)-palladium(II) dichloride (0.19 g, 0.27 mmol) in diethylamine (26 mL) was stirred at 50 °C until all compounds were dissolved. Then, 2-methyl-3-butyn-2-ol (1.85 mL, 18.9 mmol) and copper(I) iodide (51.4 mg, 0.27 mmol) were added, and the mixture was refluxed overnight. After the solvent was removed from the reaction mixture, chloroform was added and washed with water. The organic layer was dried over anhydrous sodium sulfate, and the solvent in the filtrate was removed under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform/ethyl acetate 9/1) to afford **2** (4.90 g, 17.2 mmol, 97%) as a dark orange solid: mp 116 °C; IR (KBr) 3305, 3035, 2978, 2931, 1162, 964, 845, 715 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.79 (6H, s), 2.77 (1H, br s), 7.80−8.03 (8H, m), 8.46 (1H, d, J = 8.8 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 31.67, 65.94, 81.15, 99.35, 116.93, 123.96, 124.08, 124.17, 125.07, 125.31, 125.36, 125.94, 126.93, 127.85, 128.07, 129.39, 130.73, 130.92, 130.95, 131.66.

1-Ethynylpyrene (3). A mixture of **2** (4.90 g, 17.2 mmol) and mashed potassium hydroxide (0.981g, 17.5 mmol) in toluene (100 mL) was refluxed for 30 min. After filtration, the solvent in the filtrate was removed under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform) to afford **3** (3.62 g, 16.0 mmol, 93%) as a brown solid: mp 115 °C; IR (KBr) 3296, 3033, 2094, 1600, 839, 714, 644, 593 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.56 (1H, s), 7.82−8.06 (8H, m), 8.46 (1H, d, J = 9.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 82.45, 82.75, 116.28, 123.93, 124.08, 124.19, 125.08, 125.49, 125.55, 126.06, 126.94, 128.18, 128.35, 129.96, 130.74, 130.93, 131.36, 132.29.

5-(Pyren-1-yl)penta-2,4-diyn-1-ol (4). A mixture of copper(I) chloride (43.8 mg, 0.442 mmol) and a spatulafull of hydroxylammonium chloride in isopropylamine (30 mL) was stirred under a nitrogen atmosphere. To this were added 3-bromoprop-2-yn-1-ol (2.20 g 16.3 mmol) and **3** (2.00 g 8.84 mmol) in 28 mL of anhydrous tetrahydrofuran (THF) dropwise for 30 min. When the mixture became dark during the addition, a small amount of hydroxyammonium chloride was added until the mixture turned yellow. This mixture was further stirred overnight. After the solvent in the reaction mixture was removed, chloroform was added and this solution was washed with water. The organic layer was dried over anhydrous sodium sulfate. After filtration, the solvent in the filtrate was removed under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform/ethyl acetate 9/1) and recrystallized from a mixture of chloroform and hexane to afford **4** (0.82 g, 2.93 mmol, 33%) as a pale orange powder: mp 123 °C dec; IR (KBr) 3367, 3035, 2917, 2852, 2227, 1600, 1596, 1392, 1007, 839, 713 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.92 (1H, br s), 4.52 (2H, s), 7.94−8.18 (8H, m), 8.47 (1H, d, J = 9.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 51.83, 70.86, 78.06, 78.41, 81.84, 115.42, 123.93, 124.14, 124.40, 125.03, 125.84, 125.90, 126.30, 127.03, 128.72, 128.81, 130.49, 130.80, 131.00, 131.83, 133.32.

5-(Pyren-1-yl)penta-2,4-diynyl *N*-Phenylcarbamate (H-0). A mixture of **4** (50.0 mg, 0.178 mmol), phenyl isocyanate (27.2 mg, 0.228 mmol), and a few drops of dibutyltin dilaurate in anhydrous THF (20 mL) was stirred overnight at ambient temperature. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel, chloroform/ethyl acetate 9/1) and recrystallized from a mixture of chloroform and hexane to afford **H-0** (60.0 mg, 0.150 mmol, 84%) as a pale yellow powder: mp 167 °C; IR (KBr) 3294, 3032, 2920, 2235, 1695, 1552, 1448, 1358, 1255, 1135, 1055, 978, 850, 754, 698 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.03 (2H, s), 6.77 (1H, br s), 7.11 (1H, t, J = 7.2 Hz), 7.34 (2H, t, J = 7.2 Hz), 7.43 (2H, d, J = 7.2 Hz), 8.00−8.23 (8H, m), 8.51 (1H, d, J = 9.0 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 53.54, 71.76, 77.72, 78.30, 78.40, 115.25, 118.76, 123.89, 124.00, 124.22, 124.42, 125.10, 125.95, 126.01, 126.40, 127.10, 128.88, 128.95, 129.14, 130.64, 130.87, 131.06, 132.01, 133.50, 137.31, 152.32. Anal. Found: C, 83.84; H, 4.07; N, 3.48. Calcd for C$_{28}$H$_{17}$NO$_2$: C, 84.19; H, 4.29; N, 3.51.

5-(Pyren-1-yl)penta-2,4-diynyl *N*-Benzylcarbamate (H-1). A mixture of **4** (320 mg, 1.14 mmol), benzyl isocyanate (197 mg, 1.47 mmol), and a few drops of dibutyltin dilaurate in anhydrous THF (20 mL) was stirred overnight at ambient temperature. After the solvent was removed, the residue was purified by column chromatography (silica gel, chloroform/ethyl acetate 9/1) and recrystallized from a mixture of chloroform and hexane to afford **H-1** (380 mg, 0.919 mmol, 81%) as an orange powder: mp 148 °C; IR (KBr) 3294, 3029, 2920, 2233, 1695, 1550, 1448, 1357, 1254, 1134, 1053, 976, 850, 756, 698 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.41 (2H, d, J = 5.9 Hz), 4.95 (2H, s), 5.22 (1H, br s), 7.26−7.36 (5H, m), 7.92−8.17 (8H, m), 8.44 (1H, d, J = 9.1 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 45.23, 53.39, 71.42, 78.17, 78.21, 78.39, 115.24, 123.88, 124.09, 124.32, 125.01, 125.84, 125.91, 126.29, 126.99, 127.52, 127.59, 128.70,

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128.74, 128.82, 130.53, 130.77, 130.97, 131.87, 133.36, 137.97, 155.42. Anal. Found: C, 84.16; H, 4.42; N, 3.39. Calcd for $C_{29}H_{19}NO_2$: C, 84.24; H, 4.63; N, 3.39.

5-(Pyren-1-yl)penta-2,4-diynyl *N*-(3,4,5-Trimethoxyphenyl)-carbamate (C_1O-0). A mixture of **4** (100 mg, 0.357 mmol), crude 3,4,5-trimethoxyphenyl isocyanate (**9a**; 1.64 g), and a few drops of dibutyltin dilaurate in anhydrous THF (30 mL) was stirred overnight at ambient temperature. After the solvent in the reaction mixture was removed, the residue was purified by column chromatography (silica gel, chloroform/ethyl acetate 9/1) and recrystallized from a mixture of chloroform and methanol to afford **C_1O-0** (110 mg, 0.225 mmol, 63%) as a pale orange powder: mp 193 °C; IR (KBr) 3294, 3051, 2937, 2835, 2231, 1695, 1601, 1545, 1510, 1454, 1415, 1352, 1304, 1236, 1169, 1134, 1080, 1005, 978, 843, 764, 714 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.82 (3H, s), 3.86 (6H, s), 5.02 (2H, s), 6.71 (2H, s), 6.72 (1H, s), 8.01−8.22 (8H, m), 8.50 (1H, d, J = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 53.53, 56.12, 60.98, 71.80, 77.68, 78.29, 78.48, 96.54, 115.22, 124.01, 124.24, 124.42, 125.07, 125.98, 126.03, 126.42, 127.10, 128.91, 128.97, 130.64, 130.88, 131.08, 132.06, 133.44, 133.51, 134.38, 152.45 153.48. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{31}H_{23}NO_5Na$ 512.1468; found 512.1486.

5-(Pyren-1-yl)penta-2,4-diynyl *N*-(3,4,5-Trioctyloxyphenyl)-carbamate (C_8O-0). A mixture of **4** (100 mg, 0.357 mmol), crude 3,4,5-trioctyloxyphenyl isocyanate (**9b**; 0.620 g), and a few drops of dibutyltin dilaurate in anhydrous THF (30 mL) was stirred overnight at ambient temperature. After the solvent in the reaction mixture was removed, the residue was purified by column chromatography (silica gel, chloroform) and recrystallized from a mixture of chloroform and methanol to afford **C_8O-0** (230 mg, 0.293 mmol, 82%) as a pale orange powder: mp 106 °C; IR (KBr) 3303, 3041, 2954, 2924, 2852, 2231, 1697, 1601, 1540, 1508, 1468, 1433, 1379, 1348, 1300, 1240, 1176, 1132, 1080, 1020, 989, 847, 820, 760, 714 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.85−0.91 (9H, m), 1.19−1.39 (24H, m), 1.44−1.50 (6H, m), 1.73 (2H, tt, J = 7.2 Hz, 7.2 Hz), 1.79 (4H, tt, J = 7.2 Hz, 7.2 Hz), 3.91 (2H, t, J = 7.2 Hz), 3.96 (6H, t, J = 7.2 Hz), 5.00 (2H, s), 6.64 (1H, s), 6.66 (2H, s), 8.02−8.25 (8H, m), 8.52 (1H, d, J = 9.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.10, 22.66, 22.69, 26.06, 26.12, 29.28*, 29.33*, 29.36*, 29.56*, 30.28, 31.82, 31.90, 53.45, 69.11, 71.72, 73.52, 77.78, 78.32, 78.40, 97.83, 115.28, 124.03, 124.27, 124.44, 125.11, 125.98, 126.03, 126.43, 127.11, 128.91, 128.98, 130.66, 130.91, 131.10, 132.06, 132.84, 133.53, 134.51, 152.44, 153.33. Asterisks indicate overlapped peaks. Anal. Found: C, 79.71; H, 8.55; N, 1.75. Calcd for $C_{52}H_{65}NO_5$: C, 79.66; H, 8.36; N, 1.79.

5-(Pyren-6-yl)penta-2,4-diynyl *N*-(3,4,5-Tridodecyloxyphenyl)carbamate (C_{12}O-0). A mixture of **4** (200 mg, 0.713 mmol), crude 3,4,5-tridodecyloxyphenyl isocyanate (**9c**; 0.961 g), and a few drops of dibutyltin dilaurate in anhydrous THF (30 mL) was stirred overnight at ambient temperature. After the solvent in the reaction mixture was removed, the residue was purified by column chromatography (silica gel, chloroform) and recrystallized from a mixture of chloroform and methanol to afford **C_{12}O-0** (470 mg, 0.493 mmol, 69%) as a pale orange powder: mp 104 °C; IR (KBr) 3288, 3045, 2917, 2850, 2231, 1693, 1601, 1539, 1465, 1431, 1382, 1346, 1298, 1230, 1178, 1120, 1080, 1020, 985, 843, 760, 715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (9H, t, J = 6.8 Hz), 1.16−1.37 (48H, m), 1.43−1.48 (6H, m), 1.71−1.80 (6H, m), 3.91 (2H, t, J = 6.4 Hz), 3.95 (6H, t, J = 6.6 Hz), 5.00 (2H, s), 6.66 (2H, s), 6.68 (1H, br s), 7.99−8.22 (8H, m), 8.50 (1H, d, J = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.12, 22.68, 26.07, 26.12, 29.32*, 29.36*, 29.38*, 29.40*, 29.63*, 29.69*, 29.75*, 30.27, 53.43, 69.05, 71.71, 73.49, 77.74, 78.30, 78.38, 97.74, 115.22, 123.98, 124.20, 124.40, 125.06, 125.93, 126.00, 126.38, 127.07, 128.87, 128.94, 130.60, 130.84, 131.04, 132.00, 132.85, 133.47, 134.40, 152.42, 153.30. Asterisks indicate overlapped peaks. Anal. Found: C, 80.50; H, 9.68; N, 1.41. Calcd for $C_{64}H_{89}NO_5$: C, 80.71; H, 9.42; N, 1.47.

5-(Pyren-1-yl)penta-2,4-diynyl *N*-(3,4,5-Trihexadecyloxyphenyl)carbamate (C_{16}O-0). A mixture of **4** (100 mg, 0.357 mmol), crude 3,4,5-trihexadecyloxyphenyl isocyanate (**9d**; 1.19 g), and a few drops of dibutyltin dilaurate in anhydrous THF (20 mL) was stirred overnight at ambient temperature. After the solvent in the reaction mixture was removed, the residue was purified by column chromatography (silica gel, chloroform) and recrystallized from a mixture of chloroform and methanol to afford **C_{16}O-0** (100 mg, 0.0892 mmol, 25%) as a pale orange solid: mp 109 °C; IR (KBr) 3290, 3045, 2916, 2848, 2231, 1693, 1599, 1537, 1466, 1431, 1383, 1344, 1298, 1227, 1120, 1081, 1016, 987, 843, 765, 715 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.85−0.90 (9H, m), 1.21−1.36 (72H, m), 1.42−1.50 (6H, m), 1.72−1.82 (6H, m), 3.91 (2H, t, J = 6.5 Hz), 3.97 (6H, t, J = 6.5 Hz), 5.00 (2H, s), 6.61 (1H, s), 6.66 (2H, s), 8.03−8.26 (8H, m), 8.53 (1H, d, J = 9.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.11, 22.68, 26.08, 26.14, 29.37*, 29.42*, 29.64*, 29.71*, 29.75*, 30.29, 31.92, 53.46, 69.14, 71.73, 73.52, 77.77, 78.33, 78.41, 97.84, 115.31, 124.06, 124.30, 124.45, 125.13, 125.99, 126.05, 126.44, 127.13, 128.92, 128.99, 130.67, 130.93, 131.13, 132.07, 132.83, 133.55, 134.57, 152.37, 153.34. Asterisks indicate overlapped peaks. Anal. Found: C, 81.44; H, 10.20; N, 1.23. Calcd for $C_{76}H_{113}NO_5$: C, 81.45; H, 10.16; N, 1.25.

5-(Pyren-1-yl)penta-2,4-diynyl *N*-[(3,4,5-Trimethoxyphenyl)methyl]carbamate (C_1O-1). A mixture of **4** (0.100 g, 0.357 mmol), crude (3,4,5-trimethoxyphenyl)methyl isocyanate (**15a**; 0.440 g), and a few drops of dibutyltin dilaurate in anhydrous THF (30 mL) was stirred overnight at ambient temperature. After the solvent in the reaction mixture was removed, the residue was purified by column chromatography (silica gel, chloroform/ethyl acetate 9/1) and recrystallized from a mixture of chloroform and methanol to afford **C_1O-1** (100 mg, 0.199 mmol, 56%) as an orange powder: mp 164 °C; IR (KBr) 3311, 3047, 2925, 2231, 1722, 1597, 1508, 1464, 1423, 1377, 1329, 1244, 1126, 1038, 993, 845, 777, 715 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.83 (3H, s), 3.87 (6H, s), 4.36 (2H, d, J = 6.0 Hz), 4.97 (2H, s), 5.23 (1H, s), 6.54 (2H, s), 8.01−8.23 (8H, m), 8.50 (1H, d, J = 9.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 45.55, 53.41, 56.13, 60.81, 71.38, 78.21, 78.35, 104.49, 115.27, 124.01, 124.25, 124.41, 125.04, 125.95, 126.00, 126.40, 127.09, 128.88, 128.95, 130.60, 130.88, 131.08, 132.03, 133.47, 133.77, 137.38, 153.44, 155.44. HRMS (ESI/Q-TOF) m/z: $[M + Na]^+$ calcd for $C_{32}H_{25}NO_5Na$ 526.1625; found 526.1631.

5-(Pyren-1-yl)penta-2,4-diynyl *N*-[(3,4,5-Trioctyloxyphenyl)-methyl]carbamate (C_8O-1). A mixture of **4** (80.0 mg, 0.285 mmol), crude (3,4,5-trioctyloxyphenyl)methyl isocyanate (**15b**; 0.270 g), and a few drops of dibutyltin dilaurate in anhydrous THF (30 mL) was stirred overnight at ambient temperature. After the solvent in the reaction mixture was removed, the residue was purified by column chromatography (silica gel, chloroform/ethyl acetate 9/1) and recrystallized from a mixture of chloroform and methanol to afford **C_8O-1** (120 mg, 0.150 mmol, 53%) as a yellowish green solid: mp 105 °C; IR (KBr) 3307, 3043, 2921, 2850, 2235, 1693, 1592, 1552, 1508, 1442, 1383, 1331, 1277, 1228, 1119, 1054, 978, 845, 754, 715 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.83−0.89 (9H, m), 1.17−1.35 (24H, m), 1.40−1.49 (6H, m), 1.69−1.81 (6H, m), 3.92 (2H, t, J = 6.6 Hz), 3.96 (4H, t, J = 6.6 Hz), 4.32 (2H, d, J = 6.0 Hz), 4.96 (2H, s), 5.14 (1H, t, J = 6.0 Hz), 6.49 (2H, s), 8.00−8.24 (8H, m), 8.50 (1H, d, J = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.07, 22.63, 22.66, 26.08, 29.26*, 29.35*, 29.39*, 29.53*, 30.29, 31.79, 31.87, 45.60, 53.37, 69.11, 71.36, 73.41, 78.16, 78.25, 78.38, 105.92, 115.31, 124.00, 124.23, 124.41, 125.08, 125.93, 125.99, 126.39, 127.09, 128.86, 128.93, 130.61, 130.88, 131.07, 132.00, 133.02, 133.47, 137.52, 153.32, 155.37. Asterisks indicate overlapped peaks. Anal. Found: C, 79.48; H, 8.70; N, 1.75. Calcd for $C_{53}H_{67}NO_5$: C, 79.76; H, 8.46; N, 1.75.

5-(Pyren-1-yl)penta-2,4-diynyl *N*-[(3,4,5-Tridodecyloxyphenyl)methyl]carbamate (C_{12}O-1). A mixture of **4** (300 mg, 1.07 mmol), crude (3,4,5-tridodecyloxyphenyl)methyl isocyanate (**15c**; 1.36 g), and a few drops of dibutyltin dilaurate in anhydrous THF (30 mL) was stirred overnight at ambient temperature. After the solvent in the reaction mixture was removed, the residue was purified by column chromatography (silica gel, chloroform/ethyl acetate 9/1) and recrystallized from a mixture of chloroform and methanol to afford **C_{12}O-1** (540 mg, 0.559 mmol, 52%) as a yellowish green solid: mp 97 °C; IR (KBr) 3309, 3009, 2920, 2850, 2237, 1693, 1593, 1552, 1508, 1468, 1439, 1387, 1331,

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1265, 1220, 1055, 973, 843, 714 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.85−0.89 (9H, m), 1.16−1.34 (48H, m), 1.41−1.48 (6H, m), 1.69−1.81 (6H, m), 3.92 (2H, t, J = 6.6 Hz), 3.97 (4H, t, J = 6.6 Hz), 4.32 (2H, d, J = 5.7 Hz), 4.96 (2H, s), 5.12 (1H, t, J = 5.7 Hz), 6.49 (2H, s), 8.02−8.25 (8H, m), 8.52 (1H, d, J = 9.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.10, 22.67, 26.10, 29.35*, 29.38*, 29.41*, 29.62*, 29.67*, 29.74*, 30.31, 31.90, 45.61, 53.38, 69.15, 71.37, 73.42, 78.18, 78.25, 78.41, 105.97, 115.36, 124.05, 124.28, 124.43, 125.12, 125.96, 126.02, 126.41, 127.11, 128.89, 128.96, 130.64, 130.92, 131.12, 132.04, 133.02, 133.52, 137.60, 153.35, 155.37. Asterisks indicate overlapped peaks. Anal. Found: C, 80.59; H, 9.55; N, 1.36. Calcd for $C_{65}H_{91}NO_5$: C, 80.78; H, 9.49; N, 1.45.

5-(Pyren-1-yl)penta-2,4-diynyl *N*-[(3,4,5-Trihexadecyloxyphenyl)methyl]carbamate (C_{16}O-1). A mixture of **4** (80.0 mg, 0.285 mmol), crude (3,4,5-trihexadecyloxyphenyl)-methyl isocyanate (**15d**; 0.500 g), and a few drops of dibutyltin dilaurate in anhydrous THF (30 mL) was stirred overnight at ambient temperature. After the solvent in the reaction mixture was removed, the residue was purified by column chromatography (silica gel, chloroform/ethyl acetate 9/1) and recrystallized from a mixture of chloroform and methanol to afford **C_{16}O-1** (80.0 mg, 0.0705 mmol, 25%) as a yellowish green solid: mp 78 °C; IR (KBr) 3307, 3043, 2918, 2848, 2237, 1693, 1592, 1554, 1508, 1468, 1439, 1385, 1331, 1267, 1230, 1122, 1055, 968, 842, 715 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.87 (9H, t, J = 6.9 Hz), 1.17−1.34 (72H, m), 1.40−1.48 (6H, m), 1.69−1.81 (6H, m), 3.92 (2H, t, J = 6.6 Hz), 3.97 (4H, t, J = 6.6 Hz), 4.32 (2H, d, J = 5.6 Hz), 4.96 (2H, s), 5.11 (1H, t, J = 5.6 Hz), 6.49 (2H, s), 8.02−8.25 (8H, m), 8.53 (1H, d, J = 9.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.10, 22.68, 26.11, 29.36*, 29.42*, 29.63*, 29.65*, 29.70*, 29.74*, 30.31, 31.91, 45.61, 53.38, 69.15, 71.37, 73.42, 78.18, 78.25, 78.40, 105.95, 115.36, 124.05, 124.28, 124.43, 125.12, 125.96, 126.02, 126.42, 127.11, 128.89, 128.96, 130.65, 130.92, 131.12, 132.04, 133.03, 133.52, 137.58, 153.34, 155.37. Asterisks indicate overlapped peaks. Anal. Found: C, 81.20; H, 10.89; N, 1.41%. Calcd for $C_{77}H_{115}NO_5$: C, 81.50; H, 10.21; N, 1.23.

Characterization Methods and Apparatus. UV−vis diffuse reflectance and absorption spectra were measured using a Jasco V-570 spectrophotometer, and an integrated sphere (ILN-472) was attached to obtain the diffuse reflectance spectra. The samples for the diffuse reflectance spectra were prepared by grinding solid compounds with potassium bromide, and the mixtures were placed in a sample cell with a quartz window for the measurements. FT-IR spectra were recorded on a Horiba FT-720 spectrometer. Melting points were measured using a SII TG/DTA 6200 calorimeter. ^1H and ^{13}C NMR spectra were measured using a JEOL ECX-400 or ECZ-600 spectrometer. Elemental analyses were performed on a PerkinElmer CHN/O 2400 II analyzer. High-resolution electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) was obtained by using a Bruker micrOTOF-Q II mass spectrometer in the positive ion mode.

Powder X-ray diffraction patterns were measured using a synchrotron radiation X-ray beam with a wavelength of 1.00 Å at the BL40B2 beamline at SPring-8 (Hyogo, Japan). Single crystals of **C_1O-0** and **C_1O-1** were obtained by the slow evaporation of a solution of a chloroform/methanol (1/1) mixture. X-ray crystallographic analyses of **C_1O-0** and **C_1O-1** were performed at the beamlines of BL40XU with an X-ray wavelength of 0.78192 Å and BL02B1 with that of 0.4249 Å, respectively, at SPring-8 (Hyogo, Japan). The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically.

Photopolymeriation was performed by UV irradiation at 254 nm using a 4 W lamp (UVP, UVG-11). GPC was performed using two serially connected Tosoh TSKgel G4000H_{HR} columns with a Jasco PU-980 pump and a UV-975 UV−vis detector. The eluent was chloroform, and polystyrene was used as a molecular weight standard. The electrical conductivity was evaluated for the cast films at room temperature from I−V curves measured using an apparatus based on a Keithley 2400 SourceMeter. On glass slides, gold electrodes with an electrode gap of 50 μm were prepared using VPC-060 vacuum deposition equipment (ULVAC Kiko), and chloroform solutions of the compounds were cast on the slides to form the films. The film thickness was measured using a Surfcoder ET200 microfigure measuring instrument (Kosaka Laboratory).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c00438.

Fluorescence spectra and synthesis of phenyl and benzyl isocyanates (PDF)

Accession Codes

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Notes

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