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ARTICLE

Synthesis of n-Type π-Conjugated Polymers with Pendant Crown Ether and Their Stability of n-Doping State against Air

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ABSTRACT: The n-type π-conjugated polymers with a 1,2,4-triazole ring substituted by a benzo-15-crown-5-ether (benzo15C5) subunit at the 4-position of the 1,2,4-triazole ring were synthesized by organometallic polycondensations. The UV−vis spectra of the polymers exhibited absorption maxima (λ_{max} values) at a longer wavelength than that exhibited by 4-benzo15C5-1,2,4-triazole (model-1), revealing that their π-conjugation system was expanded along the polymer chain. The electric conductivity measurements suggested that model-1 formed inclusion adducts with 1:1 and 2:1 molar ratios with Na^+ and K^+, respectively. Addition of $KClO_4$ to the DMSO solutions of the polymers with the benzo15C5 subunit caused the formation of the 2:1 inclusion between the 15C5 ring and K^+; this inclusion led to a bathochromic shift in λ_{max} of the polymers. In addition, photoluminescence intensity of the polymers decreased after the addition of $KClO_4$ to solution. The polymers with the benzo15C5 subunit underwent an electrochemical reduction (n-doping), and the corresponding oxidation (n-dedoping) occurred at an unusually high potential in an acetonitrile solution of $NaClO_4$; the factor responsible for the unusually high oxidation potential was the stabilized n-doping state that was attributed to the inclusion of Na^+ in the 15C5 ring. The electric conductivities of the polymers were increased by n-doping with sodium naphthalenide. The polymers with the benzo15C5 subunit exhibited a considerably higher stability of the n-doping state in air than did those without this subunit.

Introduction

π-Conjugated polymers have attracted considerable attention due to their interesting chemical properties and practical applications.[1] For example, they can undergo a reductive (n-type) or an oxidative (p-type) doping that effectively converts them into conducting materials.[1] However, reports on n-type conductive polymers are considerably less than those on p-type ones because of the difficulty associated with synthesizing n-type π-conjugated polymers and their low solubility in organic solvents.[2] Further, n-doping of π-conjugated polymers is carried out by treating them with alkaline metals such as sodium and potassium and subsequently applying them an adequate potential so as to cause their electrochemical reduction.[3,4] However, the n-doping state of π-conjugated polymers is usually unstable in air because the reduced polymer chain and countercations (usually alkaline metal ions) undergo oxidation with atmospheric O_2. These situations make it difficult to investigate the chemical properties of n-doped π-conjugated polymers and consequently restrict their utilization for industrial applications.

It was reported that polythiophene with a crown ethereal subunit (PTh-CE) exhibited a stable n-doping state in air when the polymer was doped with Na; this is in contrast to the fact that the n-doping state of PTh without a CE subunit is instable in air.[5,6] The stability of the n-doping state in PTh-CE is attributed to the fact that a dopant cation (Na^+) was captured in the CE subunit of PTh-CE during n-doping. In other words, the inclusion of Na^+ in the CE subunit prevents the disassociation of Na^+ from the reduced polymer chain and the consequent oxidation of the reduced polymer chain. In addition, p-type π-conjugated polymers with a CE subunit were applied for sensors that targeted alkaline metals, enzymes, and amino acids.[7] Further, it is expected that n-type π-conjugated polymers with a CE subunit will exhibit a stable n-doping state in air when they are doped with alkaline metals; this is because the dopant cation (alkaline metal ion) can be included in the CE subunit. This situation makes it easy to investigate the chemical and electrical properties of n-type π-conjugated polymers after n-doping. However, to the best of our knowledge, there has been no report on an n-type π-conjugated polymer with a CE subunit. In this study, the electrical and optical properties of n-type π-conjugated polymers with a CE subunit were investigated before and after n-doping with sodium naphthalenide in order to obtain fundamental information for the development of new conductive materials. π-Conjugated polymers with triazole rings should exhibit n-type electrical properties because 1,3,4-triazoles are π-electron-deficient compounds. In the present study, with the aim of obtaining the desired polymers, a new monomer, 3,5-bis(4-bromophenyl)-1,2,4-triazole with a benzo-15-crown-5-ether (benzo15C5) group at the 4-position of the triazole ring, was synthesized and polymerized using Ni(0)-complex-promoted dehalogenation, Pd-complex-catalyzed Suzuki-type reactions, or Sonogashira-type reactions.

Herein, we report the synthesis of n-type π-conjugated polymers with and without the benzo15C5 subunit and their optical, electrochemical, and electric properties before and after n-doping with sodium naphthalenide. In addition, a water-soluble model compound, 4-benzo15C5-1,2,4-triazole, was synthesized to investigate the inclusion behavior of alkaline metal ions and compare its chemical properties with those of the polymers.

Results and Discussion

Synthesis. Monomers with a 3,5-bis(4-bromophenyl)-1,2,4-triazole ring substituted by benzo15C5 or by 4-methoxyphenyl groups (monomer-1 and monomer-2) were synthesized

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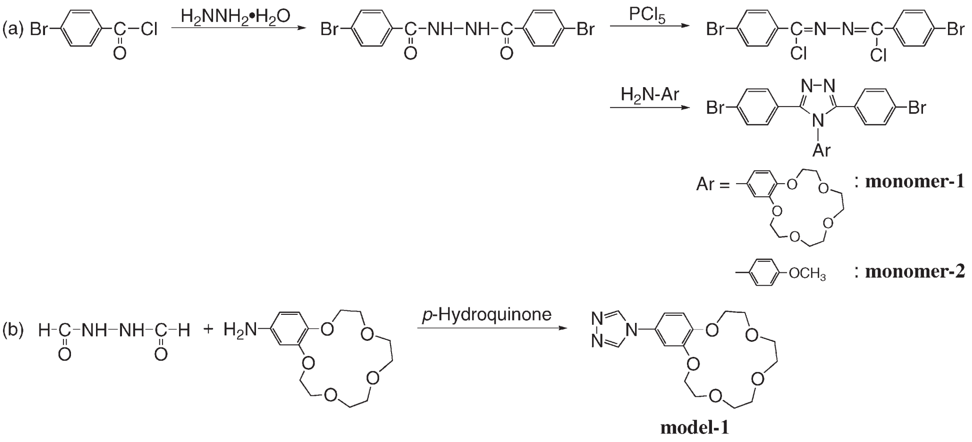
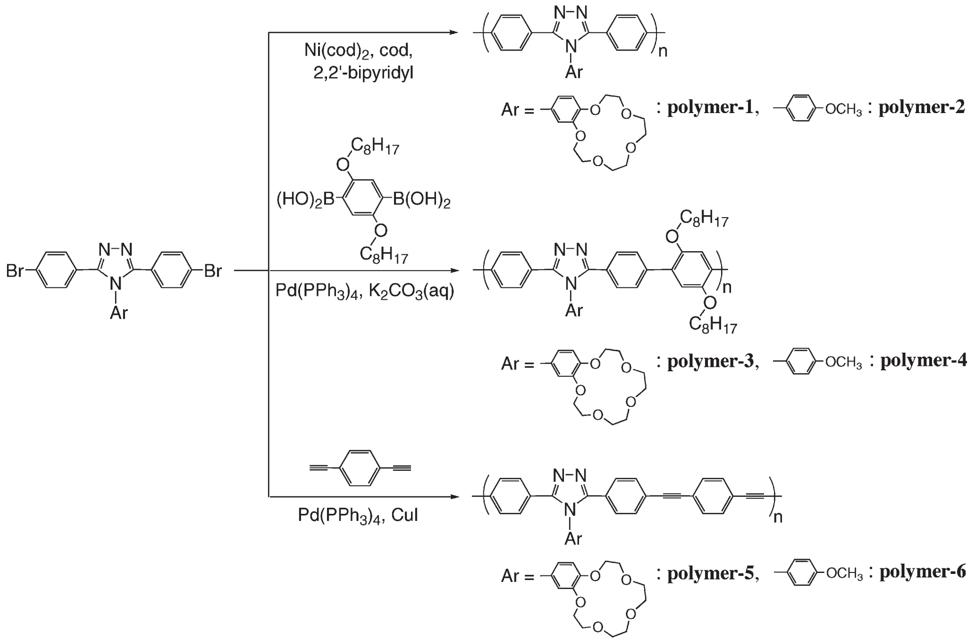


Scheme 1. Synthesis of Monomers and a Model Compound



Scheme 2. Synthesis of π-Conjugated Polymers with Pendant 15C5 Groups

through the 2:1 reaction of 4-bromobenzoyl chloride with hydrazine monohydrate and the following ring-closure reaction with 4′-aminobenzo-15-crown-5-ether or 4-aminoanisole, respectively (Scheme 1a). A model compound with the benzo15C5 group at the 4-position of a 1,2,4-triazole ring (model-1) was synthesized by the reaction of 1,2-diformylhydrazine with 4′-aminobenzo-15-crown-5-ether by using *p*-hydroquinone as a reduction agent (Scheme 1b).

π-Conjugated polymers with and without a pendant benzo15C5 subunit were synthesized by organometallic polycondensations, as shown in Scheme 2. Dehalogenation polycondensation of monomer-1 and monomer-2 carried out using Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) as a condensation reagent afforded polymer-1 and polymer-2 in 95% and 87% yields, respectively. Pd-complex-catalyzed polycondensation of monomer-1 and monomer-2 with 2,6-dioctyloxybenzene-1,4-diboronic acid or 1,4-diethynylbenzene resulted in 98%, 81%, 78%, and 99% yields for polymer-3, polymer-4, polymer-5, and polymer-6, respectively. The synthesis results are summarized in Table 1.

Polymer-1 was partly soluble in polar organic solvents such as *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) at 100 °C but was insoluble in polar organic solvents and nonpolar organic solvents such as chloroform and toluene at room temperature. On the other hand, polymer-2 was slightly soluble in DMSO at 120 °C. Polymer-3 was partly soluble in chloroform, but polymer-4 was slightly soluble in the solvent. The solubilities of polymer-1 and polymer-3 were higher than those of polymer-2 and polymer-4 because of the presence of the 15C5 rings in polymer-1 and polymer-3. However, polymer-5 and polymer-6 were insoluble in organic solvents, probably because of their stiff structures. Model-1 was soluble in water and organic solvents such as chloroform, DMF, and DMSO.

The M_n and M_w values of the obtained polymers, determined by GPC measurements, are summarized in Table 1. The M_n and M_w values of the DMF-soluble part of polymer-1 were 13 700 and 14 400, respectively, while those of the chloroform-soluble part of polymer-3 and polymer-4 were 5100 and 10 200 and 5100 and 12 200, respectively. The molecular weights of the other polymers could not be determined because of their insolubility.

IR and ^{1}H NMR Spectra. Figure 1 shows the IR spectra of monomer-1, polymer-1, polymer-3, and polymer-5. The peak

Table 1. Synthesis Results and Chemical Properties of the Obtained Polymers and Model Compound

	yield (%)	M_n[a]	M_w[a]	absorption/nm	λ_{em}/nm[f]	reduction potential/V[h] E_{pc}	reduction potential/V[h] E_{pc}	electric conductivity/S cm^{-1} nondoped	electric conductivity/S cm^{-1} Na-doped[i]
polymer-1	95	13700[b]	14400[b]	332[e]	391, 406 (0.35)[e]	−2.37	0.08	2.1×10^{-7}	5.0×10^{-4}
polymer-2	87	—[d]	—[d]	318[e]	404 (0.18)[e]	−2.27	−0.91	6.2×10^{-7}	6.1×10^{-4}
polymer-3	98	5100[c]	10200[c]	293, 347[c]	414 (0.20)[c]	−2.23	0.11	7.2×10^{-8}	5.6×10^{-4}
polymer-4	81	5100[c]	12200[c]	299, 346[c]	412 (0.27)[c]	−2.35	−0.84	1.1×10^{-7}	5.6×10^{-4}
polymer-5	78	—[d]	—[d]	—[d]	406, 424[g]	—[d]	—[d]	3.1×10^{-7}	6.1×10^{-4}
polymer-6	99	—[d]	—[d]	—[d]	406, 424[g]	—[d]	—[d]	5.7×10^{-7}	5.0×10^{-4}
model-1	23			241, 282[e]	355 (0.0034)[e]				

[a] Determined by GPC (vs polystyrene standards). [b] DMF-soluble part. [c] $CHCl_3$-soluble part. [d] Not measured due to insolubility in the eluent. [e] DMSO-soluble part. [f] Quantum yields of photoluminescence are shown in parentheses. [g] In solid state. [h] Measured by cyclic voltammetry in an acetonitrile solution of $NaClO_4$ (0.10 M). [i] Measured immediately after preparation of the sample under nitrogen.

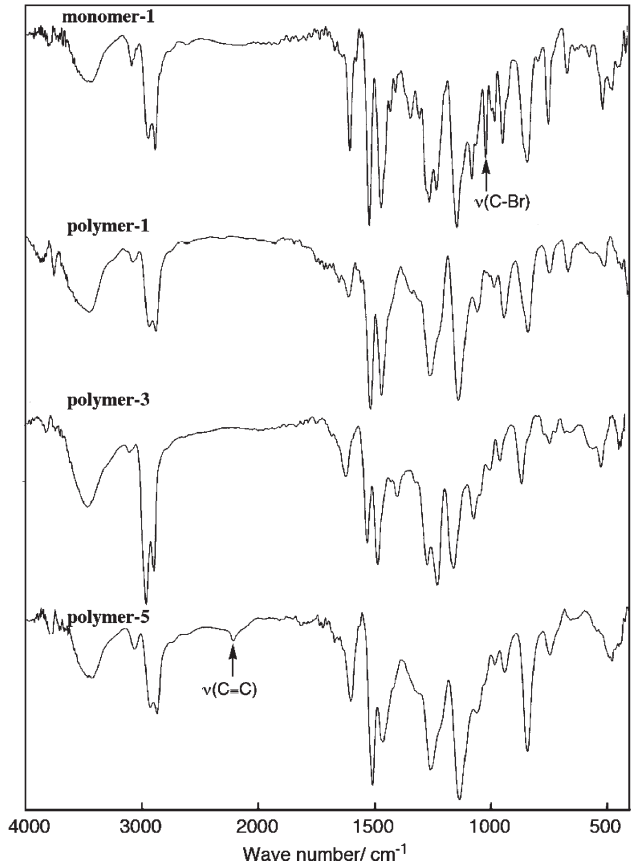


Figure 1. IR spectra of monomer-1, polymer-1, polymer-3, and polymer-5.

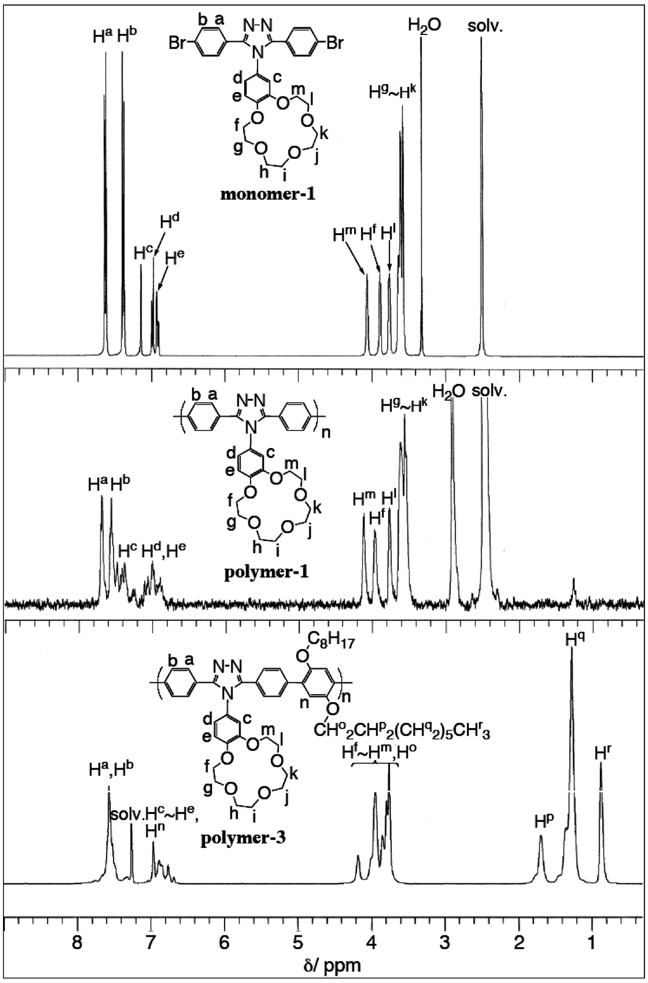


Figure 2. ^{1}H NMR spectra of monomer-1 and polymer-1 in DMSO-d_6 and that of polymer-3 in $CDCl_3$.

corresponding to the stretching vibrations of a C−Br bond is observed at 1071 cm^{-1} in the IR spectrum of monomer-1, whereas it disappeared in the IR spectra of polymer-1, polymer-3, and polymer-5. The disappearance suggests that the expected polycondensations occurred. Further, instead of the stretching vibrations of the C−Br and ≡C−H bonds, a new peak corresponding to the stretching vibrations of a disubstituted C≡C bond appears at 2207 cm^{-1} in the IR spectrum of polymer-5. These observations correspond to the fact that the peak corresponding to the terminal groups of polymer-5 disappears because of the high molecular weight of this polymer. The appearance of the absorption corresponding to ν(O−H) around 3500 cm^{-1} in the IR spectra of the polymers suggests that they contain hydrated water molecule(s). The analytical and TGA data of the polymers also support the hydration (see Figure S2).

Figure 2 shows the ^{1}H NMR spectra of monomer-1 and polymer-1 in DMSO-d_6 and that of polymer-3 in $CDCl_3$. The peak assignments are indicated in the figure. The signals corresponding to the aromatic (H^a−H^e) and crown ethereal (H^f−H^m) protons of polymer-1 are observed in the ranges δ 6.89−7.70 and δ 3.53−4.11, respectively, while those corresponding to the aromatic (H^a−H^e, H^n) protons, crown ethereal (H^f−H^m), and OCH^o_2 protons of octyloxy and octyloxy (H^p−H^r) protons of polymer-3 are observed in the ranges δ 6.77−7.57, δ 3.75−4.18, and δ 0.87−1.70, respectively. The relative peak integral ratio supports the structures shown in Scheme 2.

Inclusion of Alkaline Metals. In order to investigate the inclusion behavior of alkaline metals in the benzo15C5 ring of model-1, electric conductivity measurements of an aqueous solution of model-1 were carried out when limited amounts of

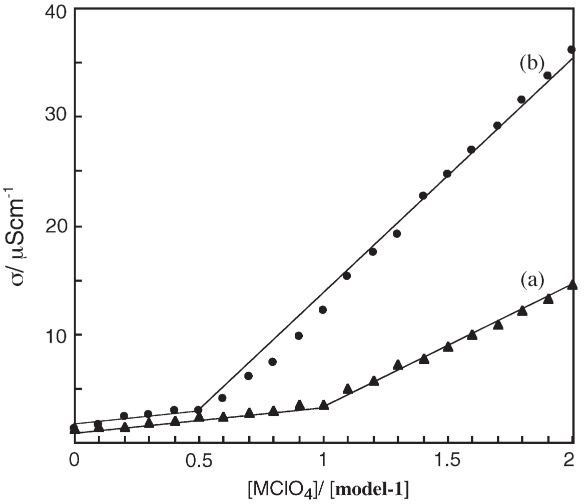


Figure 3. Conductivity changes of an aqueous solution of model-1 (2.0 mmol/L) by addition of NaClO$_4$ (a) and KClO$_4$ (b) in amounts of every 0.20 mmol.

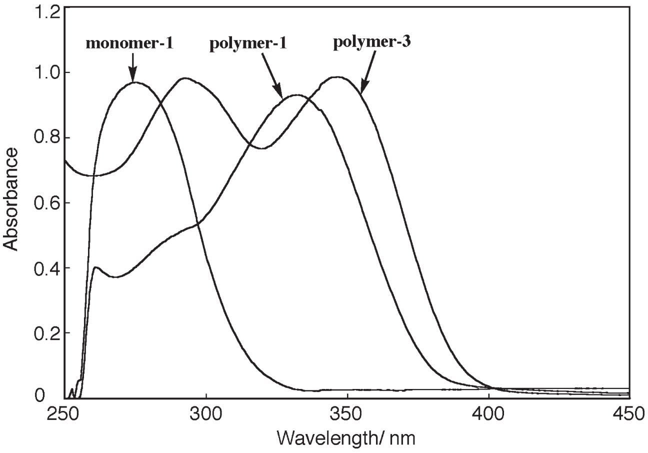


Figure 4. UV−vis spectra of monomer-1 in DMSO, polymer-1 in DMSO, and polymer-3 in chloroform.

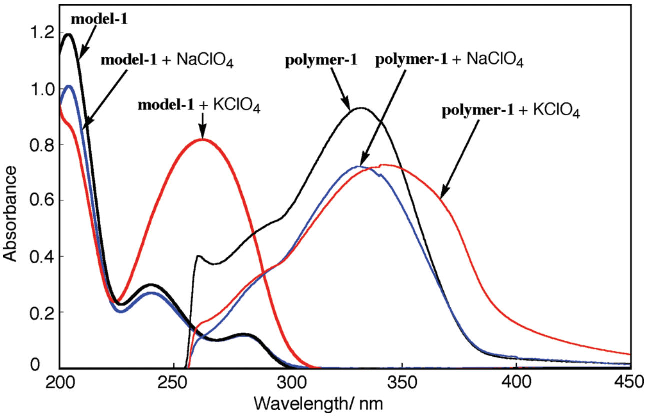


Figure 5. UV−vis spectra of model-1 in water and polymer-1 in DMSO before and after the addition of excess amounts of NaClO$_4$ or KClO$_4$.

aqueous solutions of NaClO$_4$ and KClO$_4$ were added to the solution. Figure 3 shows the measurement results. The conductivities of the model-1 solution slightly increase until the addition of an equimolar amount of NaClO$_4$ and then sharply increase after the equivalence point. On the other hand, the conductivities of the model-1 solution slightly increase until the addition of an half equimolar amount of KClO$_4$ and then sharply increase after the point corresponding to the half equimolar amount. These results suggest that model-1 formed 1:1 and 2:1 inclusion adducts with Na$^+$ and K$^+$, respectively. This suggestion seems valid considering that 15C5 can form 1:1 and 2:1 inclusion adducts with Na$^+$ and K$^+$, respectively.[8]

UV−vis and Photoluminescence Spectra. Optical data are summarized in Table 1. Figure 4 shows the UV−vis spectra of monomer-1 in DMSO, polymer-1 in DMSO, and polymer-3 in chloroform. The absorption maxima ($\lambda_{\max}$ values) of polymer-1 and polymer-3 were longer than that of monomer-1, suggesting that the π-conjugation system was expanded along the polymer chain. It has been reported that the two phenyl substituents at the 3- and 5-positions of a 1,2,4-triazole ring are twisted by approximately 90° toward the plane of the triazole ring.[9] This twisting angle is larger than that between the two *p*-phenylene rings in oligo(*p*-phenylene).[10] According to these reports, the fact that the $\lambda_{\max}$ value of polymer-3 is larger than that of polymer-1 is attributed to the presence of the dioctyloxybenzene spacing group between the two *p*-phenylene rings in polymer-3; this group reduces the twisting of the main chain of this polymer.

Figure 5 shows the UV−vis spectra of model-1 in water and polymer-1 in DMSO before and after the addition of excess amounts of NaClO$_4$ or KClO$_4$. The UV−vis spectra of the solutions of model-1 and polymer-1 were almost unchanged after the addition of NaClO$_4$. However, after the addition of KClO$_4$, the $\lambda_{\max}$ values of the solutions of model-1 and polymer-1 shifted to longer wavelengths by 22 and 10 nm, respectively. The bathochromic shift of model-1 and polymer-1 after the addition of KClO$_4$ is apparently due to the π-stacking in model-1 and polymer-1, which is attributed to the 1:2 inclusion between K$^+$ and the 15C5 ring in model-1 and polymer-1. The above-mentioned electric conductivity measurements of model-1 support the 1:2 inclusion between K$^+$ and the 15C5 ring. The fact that the bathochromic shift of polymer-1 was smaller than that of model-1 corresponds to the assumption that in polymer-1 the π-stacking caused by the inclusion between K$^+$ and the 15C5 ring occurred partly.

Monomer-1, model-1, and the polymers obtained in this study were photoluminescent in solution and in the solid state. The emission peak positions of polymer-1, polymer-2, polymer-3, and polymer-4 were longer than those of monomer-1 and model-1 in solution. These observations are consistent with the results that the $\lambda_{\max}$ values of polymer-1, polymer-2, polymer-3, and polymer-4 were larger than those of monomer-1 and model-1. The PL peaks of the polymers appear at the onset position of their absorption bands, as usually observed with photoluminescent aromatic compounds. The quantum yields (Φ values) of the PL of polymer-1, polymer-2, polymer-3, and polymer-4 were 0.35, 0.18, 0.20, and 0.18, respectively; these Φ values were considerably larger than that of monomer-1 (Φ = 0.003). Further, the PL peak intensity of polymer-1 in DMSO decreased after the addition of KClO$_4$ to the solution. This decrease in the PL was apparently attributed to the π-stacked structure of the polymer that was formed by the 1:2 inclusion between K$^+$ and the 15C5 ring in the polymer. This attribution is consistent with a reported result that the PL intensity of π-conjugated polymers decreased when they formed the π-stacking structures.[11] The PL measurements of polymer-5 and polymer-6 were carried out in the solid state because of their insolubility in organic solvents. Both polymer-5 and polymer-6 exhibited a PL peak at 406 nm. This wavelength was comparable to the PL peak wavelengths of polymer-1 and polymer-2.

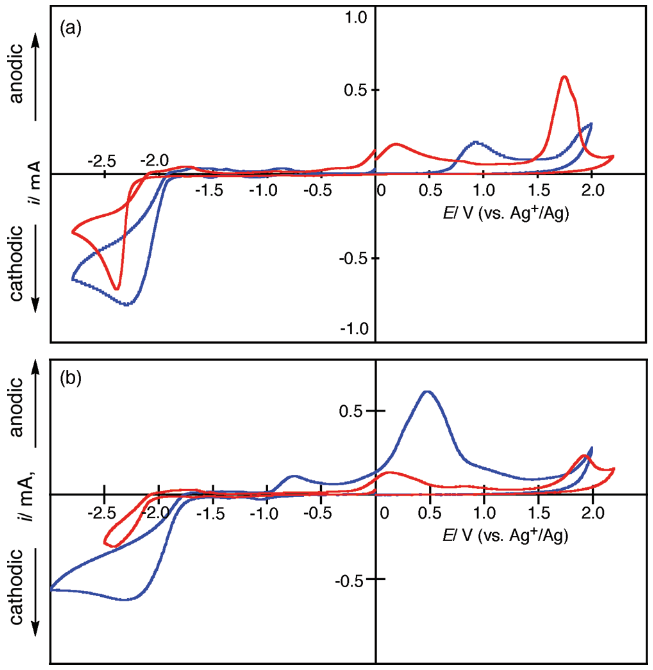


Figure 6. Cyclic voltammograms of cast films of polymer-1 (a) and polymer-3 (b) in an aqueous solution containing $NaClO_4$ (0.10 M) (red curve) and an acetonitrile solution containing $[Et_4N]BF_4$ (0.10 M) (blue curve).

Cyclic Voltammograms. Figure 6 shows the cyclic voltammograms of cast films of polymer-1 and polymer-3 in an aqueous solution containing $NaClO_4$ (0.10 M) and an acetonitrile solution containing $[Et_4N]BF_4$ (0.10 M). Polymer-1 and polymer-3 exhibited a peak at -2.37 V (vs Ag^+/Ag) and -2.23 V (vs Ag^+/Ag) corresponding to the electrochemical reduction of the triazole ring in the aqueous solution of $NaClO_4$, respectively. The observation that the reduction potential of polymer-3 is more positive than that of polymer-1 is consistent with the fact that the π-conjugation system of polymer-3 is larger than that of polymer-1. The corresponding oxidation (n-dedoping) peaks of polymer-1 and polymer-3 were observed at 0.14 V (vs Ag^+/Ag) and 0.11 V (vs Ag^+/Ag), respectively. The large difference between the reduction and oxidation potentials is attributed to the strong interaction of polymer-1 and polymer-3 with Na^+. That is, Na^+ was captured by the 15C5 ring of the reduced polymer-1 and polymer-3 at -2.37 V (vs Ag^+/Ag) and -2.23 V (vs Ag^+/Ag), respectively. The n-doped state thus formed is considered to be stabilized, and its oxidation (or n-dedoping) is considered to require a much higher potential than the n-doping potential. This assumption is supported by the result that the electrochemical reduction and the corresponding oxidation (n-dedoping) peaks of polymer-2 and polymer-4 in an acetonitrile solution of $NaClO_4$ were observed at -2.27 V (vs Ag^+/Ag) and -0.91 V (vs Ag^+/Ag) and -2.35 V (vs Ag^+/Ag) and -0.72 V (vs Ag^+/Ag), respectively. The above assumption is also supported by the result that the cyclic voltammogram of the cast film of polymer-1 in the aqueous solution containing $NaClO_4$ (0.10 M) obtained by scanning in a range of -1.5 V (vs Ag^+/Ag) to 2.2 V (vs Ag^+/Ag) did not exhibit both the n-doping and n-dedoping peaks. A similar exceptionally high potential for n-dedoping was observed in the case of PTh with a crown ethereal subunit: the polymer underwent electrochemical reduction (n-doping) at -2.2 V (vs Ag^+/Ag) and the corresponding oxidation (n-dedoping) at 0.2 V (vs Ag^+/Ag).[6c]

Electric Conductivity. n-Doping of the polymers was carried out by treating them with sodium naphthalenide in THF. Their electric conductivities are summarized in Table 1. The n-doped polymers exhibited electric conductivities that were $\sim 10^3$ times higher than those of the respective nondoped polymers. The electric conductivity of the n-doped polymers decreased with time when they were allowed to stand in air, as shown in Figure 7.

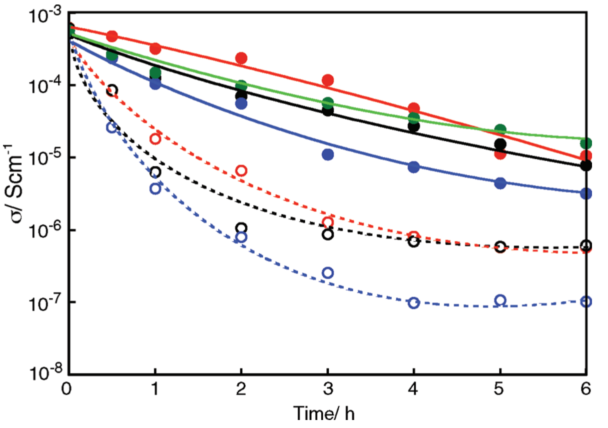


Figure 7. Changes of electric conductivity of the n-doped polymer-1 (black solid curve), polymer-1(Na^+) (green solid curve), polymer-2 (black dotted curve), polymer-3 (blue solid curve), polymer-4 (blue dotted curve), polymer-5 (red solid curve), and polymer-6 (red dotted curve) when they were allowed to stand in air.

This is because the reduced polymers are dedoped by oxidation in air. The electric conductivities of n-doped polymer-1, polymer-3, and polymer-5 with benzo15C5 groups decreased gradually and attained almost the 100 times higher values than those of the corresponding nondoped polymers after 6 h when the n-doped polymers were exposed to air. In contrast, the electric conductivities of n-doped polymer-2, polymer-4, and polymer-6 without benzo15C5 groups decreased rapidly and attained the same values as those of the corresponding nondoped polymers after 6 h when these n-doped polymers were exposed to air. The gradual decease in the electric conductivities of n-doped polymer-1, polymer-3, and polymer-4 in air corresponds to their stabilized n-doping state that originated from the inclusion of Na^+ in their 15C5 ring. This view is consistent with the above-mentioned CV results. However, the n-doped polymers may contain a site at which the inclusion of Na^+ in their 15C5 ring did not occur because the n-doping was carried out in the THF suspension of the polymers and sodium naphthalenide. Increasing the number of such sites in the n-doped polymers will lead to a further improvement in the stability of the polymer's n-doping state against exposure to air. In order to confirm this hypothesis, polymer-1 was treated with a DMSO solution of $NaClO_4$ to obtain polymer-1(Na^+) before n-doping, and changes in the electric conductivity of n-doped polymer-1(Na^+) were investigated when it was allowed to stand in air. As shown in Figure 7, n-doped polymer-1(Na^+) exhibited improved stability of the n-doping state against air, as expected; the electric conductivity of polymer-1(Na^+) when it was exposed to air for 6 h was 3 times higher than that of n-doped polymer-1 when the latter was allowed to stand in air for 6 h. These results confirmed that the inclusion of Na^+ in the pendant 15C5 rings of the polymers was responsible for the improved stability of the n-doped polymers against air.

Conclusion

π-Conjugated polymers with the benzo15C5 subunit at the 4-position of a 1,2,4-triazole ring were synthesized by Ni(0)-complex-promoted dehalogenation and Pd-complex-catalyzed

Suzuki- and Sonogashira-type polycondesations. Inclusion of alkaline metal ions in the 15C5 ring of the polymers affected their optical properties; the λ_{max} position of the polymers shifted to a longer wavelength, and the photoluminescence intensity of the polymers decreased when the 15C5 ring include K^+ in solution. The cast films of polymers underwent an electrochemical reduction (n-doping), and because of the stabilized n-doping state, they required an exceptionally high potential for n-dedoping. The polymers with the benzo15C5 subunits exhibited a higher stability of the n-doping state in air as compared to those without benzo15C5 subunits. From the results obtained in this study, it can be concluded that new air-stable n-type conductive materials can be developed on the basis of the ability of crown ether rings in n-type π-conjugated polymers to be an accepting site for a dopant alkaline metal ion.

Experimental Section

General. Solvents were dried, distilled, and stored under nitrogen. *N*,*N*′-Bis[chloro(*p*-bromophenyl)methylene]hydrazine and 2,5-dioctyloxy-1,4-benzenediboronic acid were synthesized according to the reported manner.[12,13] Other reagents were purchased and used without further purification. Reactions were carried out with standard Schlenk techniques under nitrogen.

IR and NMR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer with a KBr pellet and a JEOL AL-400 spectrometer, respectively. Elemental analysis was conducted on a Yanagimoto MT-5 CHN corder. GPC analyses were carried out by a Toso HLC 8020 with polystyrene gel columns (TSKgel G2000H_{HR} and TSKgel GMH_{HR}-M) using a DMF solution of LiBr (0.006 M) as an eluent with RI and UV detectors and a Jasco 830 refractometer with polystyrene gel columns (K-803 and K-804) using chloroform as an eluent with a RI detector. UV−vis and PL spectra were obtained by a JASCO V-560 spectrometer and a JASCO FP-6200, respectively. Quantum yields were calculated by using a diluted ethanol solution of 7-(dimethylamino)-4-methylcoumarin as the standard. Cyclic voltammetry was performed in a DMSO solution containing 0.10 M $[Et_4N]BF_4$ with a Hokuto Denko HSV-110. Electric conductivity measurements in aqueous solution and solid state were conducted by a Horiba Cond Meter ES-51 and an Advantest R8340A ultrahigh-resistance meter with a two-probe method, respectively.

Synthesis of Monomer-1. *N*,*N*′-Bis[chloro(*p*-bromophenyl)methylene]hydrazine (0.64 g, 1.5 mmol) and 4′-aminobenzo-15-crown-5-ether (0.50 g, 1.8 mmol) were dissolved in 12 mL of *N*,*N*-dimethyaniline under N_2. After the solution was stirred at 135 °C for 24 h, the reaction solution was cooled to room temperature and poured in hexane (200 mL). The resulting precipitate was washed with water dried under vacuum to give monomer-1 a light yellow powder (0.78 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.4 Hz, 4H), 7.33 (d, J = 8.4 Hz, 4H), 6.86 (d, J = 8.4 Hz, 1H), 6.70 (dd, J = 2.0 and 8.6 Hz, 1H), 6.59 (d, J = 2.4 Hz, 1H), 4.17 (m, 2H), 3.94 (m, 4H), 3.84 (m, 2H), 3.75−3.81 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 149.2, 148.6, 131.6, 130.2, 126.8, 126.2, 123.4, 120.5, 113.3, 113.1, 70.5, 69.5, 68.5, 68.4, 68.2, 68.1. Calcd for $C_{28}H_{19}Br_2N_3O_5$: C, 52.11; H, 4.22; N, 6.51. Found: C, 52.58; H, 4.14; N, 6.57. Mp = 259−261 °C.

Monomer-2 was synthesized by the reaction of *N*,*N*′-bis[chloro(*p*-bromophenyl)methylene]hydrazine with 4-aminoanisole in a similar manner.

Data of Monomer-2. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.60 (d, J = 6.8 Hz, 4H), 7.37 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 6.8 Hz, 4H), 7.02 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 153.8, 131.6, 130.3, 129.4, 126.2, 123.4, 115.0, 55.4. Calcd for $C_{21}H_{15}Br_2N_3O$: C, 51.99; H, 3.12; N, 8.66. Found: C, 52.04; H, 3.29; N, 8.78. Mp = 265−268 °C.

Synthesis of Model-1. A mixture of *N*,*N*′-diformylhydrazine (0.22 g, 2.4 mmol), 4′-aminobenzo-15-crown-5-ether (0.69 g, 2.4 mmol), and *p*-hydroquinone (0.11 g, 1.0 mmol) was melted at 170 °C and stirred at the temperature for 5 h. Afterward, the mixture was cooled to room temperature and washed with ether (100 mL). The ether-insoluble part was collected by filtration, dissolved in water, and extracted with chloroform. The solvent was removed under vacuum and dissolved in 3 mL of chloroform. The solution was poured in ether, and the resulting precipitate was collected by filtration and dried under vacuum to give model-1 as a light brown powder (0.19 g, 23%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.04 (s, 2H), 7.31 (d, J = 2.8 Hz, 1H), 7.19 (dd, J = 2.4 and 7.6 Hz, 1H), 7.40 (d, J = 8.8 Hz, 1H), 4.15 (m, 2H), 4.09 (m, 4H), 3.79 (m, 4H), 3.62 (s, 8H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.2, 148.1, 141.5, 127.4, 114.2, 113.4, 107.6, 70.5, 69.7, 68.7. Calcd for $C_{16}H_{21}N_3O_5 \cdot 0.1H_2O$: C, 57.00; H, 6.34; N, 12.46. Found: C, 56.80; H, 6.32; N, 12.13. Mp = 162−163 °C.

Synthesis of Polymer-1. $Ni(cod)_2$ (0.10 g, 0.37 mmol), 2,2-bipyridyl (0.058 g, 0.37 mmol), and cod (46 μL, 0.37 mmol) were dissolved in 7 mL of dry DMF under nitrogen. To the solution was added an DMF solution (3 mL) of monomer-1 (0.20 g, 0.31 mmol) at 60 °C. The reaction solution was stirred at 85 °C for 72 h. The precipitate was collected by filtration, washed with an aqueous solution of ammonia (three times), and dried under vacuum to give polymer-1 as a brown powder (0.14 g, 95%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.68 (4H), 7.55 (4H), 6.89−7.48 (3H), 4.11 (2H), 3.97 (2H), 3.77 (2H), 3.53−3.61 (10H). Calcd for $(C_{28}H_{21}N_3O_5 \cdot H_2O)_n$: C, 67.60; H, 4.66; N, 8.45. Found: C, 67.88; H, 4.90; N, 8.12.

Polymer-2 was synthesized analogously.

Data of Polymer-2. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.73 (2H), 7.41−7.48 (8H), 7.03 (2H), 3.79 (3H). Calcd for $(C_{21}H_{15}N_3O \cdot 2H_2O)_n$: C, 69.79; H, 5.30; N, 11.63. Found: C, 69.57; H, 5.02; N, 11.40.

Synthesis of Polymer-3. Monomer-1 (0.17 g, 0.26 mmol) and 2,5-dioctyloxy-1,4-benzenediboronic acid (0.11 g, 0.26 mmol) were dissolved in 10 mL of dry DMF under N_2. To the solution were added K_2CO_3(aq) (2.0 M, 2 mL; N_2 bubbled before use) and $Pd(PPh_3)_4$ (0.015 g, 0.013 mmol). After the mixture was stirred for 72 h at 80 °C, the mixture was poured in water. The precipitate was washed with water, methanol, and acetone. Polymer-3 was collected by filtration, dried under vacuum, and obtained as a black powder (0.21 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (8H), 6.77−6.97 (5H), 3.75−8.18 (20H), 1.70 (4H), 1.26−1.35 (20H), 0.87 (6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.8, 150.4, 149.9, 139.5, 132.2, 130.0, 129.6, 128.4, 128.0, 125.5, 120.8, 115.8, 114.8, 113.2, 112.9, 71.0, 70.1, 69.6, 68.9, 31.8, 29.3, 26.1, 22.7, 14.1. Calcd for $(C_{50}H_{63}N_3O_7)_n$: C, 73.41; H, 7.76; N, 5.14. Found: C, 73.15; H, 7.31; N, 5.29.

Polymer-4 was synthesized analogously.

Data of Polymer-4. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.57 (8H), 7.23 (2H), 7.00 (4H), 3.93 (3H), 3.87 (4H), 1.68 (4H), 1.28 (20H), 0.89 (6H). Calcd for $(C_{43}H_{51}N_3O_3)_n$: C, 78.50; H, 7.81; N, 6.39. Found: C, 78.30; H, 7.68; N, 6.74.

Synthesis of Polymer-5. Monomer-1 (0.20 g, 0.31 mmol), 1,4-diethynylbenzene (0.039 g, 0.31 mmol), and CuI (2.9 mg, 0.0016 mmol) were dissolved in 10 mL of dry toluene under N_2. To the solution were added $Pd(PPh_3)_4$ (0.018 g, 0.016 mmol) and triethylamine (1 mL). After the mixture was stirred for 72 h at 90 °C, the precipitate was collected by filtration, washed with methanol and chloroform, and dried under vacuum to give polymer-5 as a light brown powder (0.14 g, 78%). Calcd for $(C_{38}H_{31}N_3O_5)_n$: C, 73.86; H, 5.03; N, 6.43. Found: C, 73.69; H, 4.96; N, 5.93.

Polymer-6 was synthesized analogously. Data of polymer-6: Calcd for $(C_{31}H_{19}N_3O)_n$: C, 78.14; H, 4.09; N, 8.82. Found: C, 78.36; H, 4.10; N, 8.51.

Preparation of Polymer-1(Na^+). After a DMSO solution (15 mL) of polymer-1 (0.048 g, 0.10 mmol) and $NaClO_4$ (0.12 g, 1.0 mol) was stirred at 120 °C for 12 h, the solvent was removed under vacuum. The resulting solid was washed with water

(100 mL) and dried under vacuum to give polymer-1(Na^+) (0.046 g).

Electric Conductivity Measurements. The n-doping was carried out by using sodium naphthalenide according to the usual manner.[3]

Supporting Information Available: PL and TGA data. This material is available free of charge via the Internet at http://pubs.acs.org.

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