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New π-Conjugated Polymers Derived from a Benzimidazole Unit. Preparation, Solvatochromism, and Oxidation of Poly(aryleneethynlene)s Composed of 2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)benzimidazole Bearing a Hindered Phenolic Substituent

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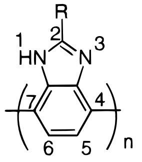
ABSTRACT: New π-conjugated polymers constituted of a benzimidazole unit have been prepared. Palladium-catalyzed polycondensation between 4,7-dibromobenzimidazole bearing a hindered phenolic substituent (3,5-di-*tert*-butyl-4-hydroxyphenyl) and four kinds of diethynylaromatic compounds HC≡C−Ar−C≡CH (e.g., Ar = *p*-phenylene (*p*-Ph), *m*-phenylene (*m*-Ph), and pyridine-2,5-diyl (2,5-Py)) gives the corresponding poly(aryleneethynylene) (PAE) type polymers in high yields. The polymers with the *p*-Ph, *m*-Ph, and 2,5-Py groups have molecular weights of $(0.4-3.3) \times 10^4$, as determined by GPC. The position of the $\pi-\pi^*$ absorption band as well as photoluminescence intensity of the polymers strongly depends on the kind of solvent. In general, the $\pi-\pi^*$ absorption peak of the PAE-type polymers with the *p*-Ph groups shifts to a shorter wavelength in acidic organic solvents, whereas that of the PAE-type polymers with the 2,5-Py unit shifts to a longer wavelength in the acidic solvent. Intensity of the photoluminescence increases in the acidic media. The polymers as well as a model compound are oxidized with PbO_2. The oxidized products give rise to an IR peak at about 1680 cm^{-1}, which is assigned to ν(C=O) originated from resonance structures of the oxidized species, and their ESR signals appear at about $g = 2.0$ with a peak-to-peak line width of 8−11 G.

Introduction

Preparation of π-conjugated polymers and revealing their chemical and physical properties are the subject of many papers.[1] Benzimidazole is an interesting building block for the π-conjugated polymer because of its attractive chemical properties (e.g., photoluminescence and acid−base behavior including solvatochromism),[2] and preparation of the following polymers, poly(benzimidazole-4,7-diyl)s (P(4,7-Bim)s), has been reported.[3] However, examples of such polymers with the 4,7-type bonding have still been limited, despite the presence of many examples of other types of poly(benzimidazole)s[4a−k] and polymers having the benzimidazole ring in their side chains.[4l]

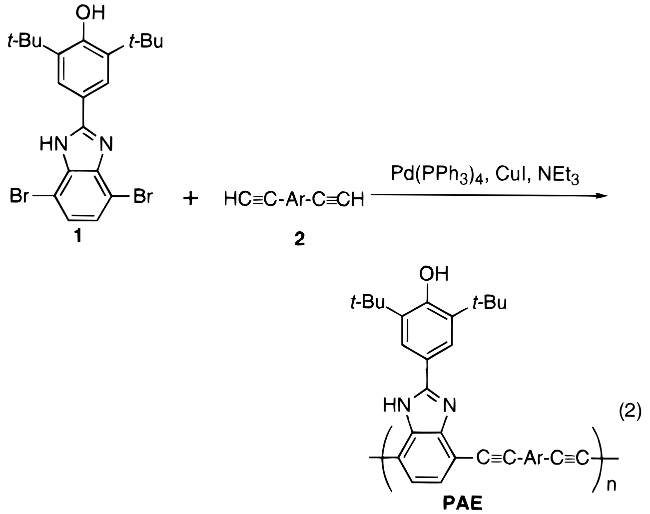


R= H[3a], n-C_7H_{15}[3b]
P(4,7-Bim)s

On the other hand, the following Pd-catalyzed polycondensation has contributed to the design of various π-conjugated poly(aryleneethynylene) (PAE) type polymers[5,6]

$$\text{X-Ar-X} + \text{HC≡C-Ar'-C≡CH} \xrightarrow{\text{Pd(PPh}_3)_4\text{, CuI, NEt}_3} \underset{\text{PAE}}{\left(\text{Ar-C≡C-Ar'-C≡C}\right)_n} \qquad (1)$$

In this paper, we report application of the Pd-catalyzed polycondensation to the preparation of the PAE-type polymer containing the benzimidazole-4,7-diyl unit. As the substituent R in the benzimidazole unit, a hindered phenolic group has been chosen since this group shows interesting chemical behaviors on its oxidation (e.g., generation of radical species).[7] Polymers having such a hindered phenolic group potentially are candidates that may show interesting magnetism like paramagnetism;[7,8] however, examples of such polymers have been limited. Many research groups have reported preparation of organic compounds and polymers having expanded π-conjugation system and bearing radical species, in their efforts to obtain organic ferromagnetic materials.



1
2
PAE
(2)

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Table 1. Results of the Polymerization[a]

run	monomer	polymer	reacn temp, °C	yield, %	10^{-3} M^{b}	[η], dL g^{-1}	ν(C≡C), cm^{-1}	ν(−OH), cm^{-1}
1	**2a**	PAE-**A**	100	96	15.1[c]		2186	3618
2	**2b**	PAE-**B**	100	82	3.9[c]		2188	3610
3	**2b**	PAE-**B**	60	70			2214	3618
4	**2b**	PAE-**B**	room temp	0				
5	**2c**	PAE-**C**	100	86	5.1[c]		2196	3612
6	**2d**	PAE-**D**	100	81	33	0.32[d]	2200	3616

[a] In DMF by using a 1:1 mixture of monomer **1** and monomer **2** and an excess amount of NEt_3 (cf. Experimental Section). [b] Determined by GPC (polystyrene standards, eluent = DMF containing LiCl (0.02 M)). [c] For a DMF-soluble part. [d] In DMF at 30 °C.

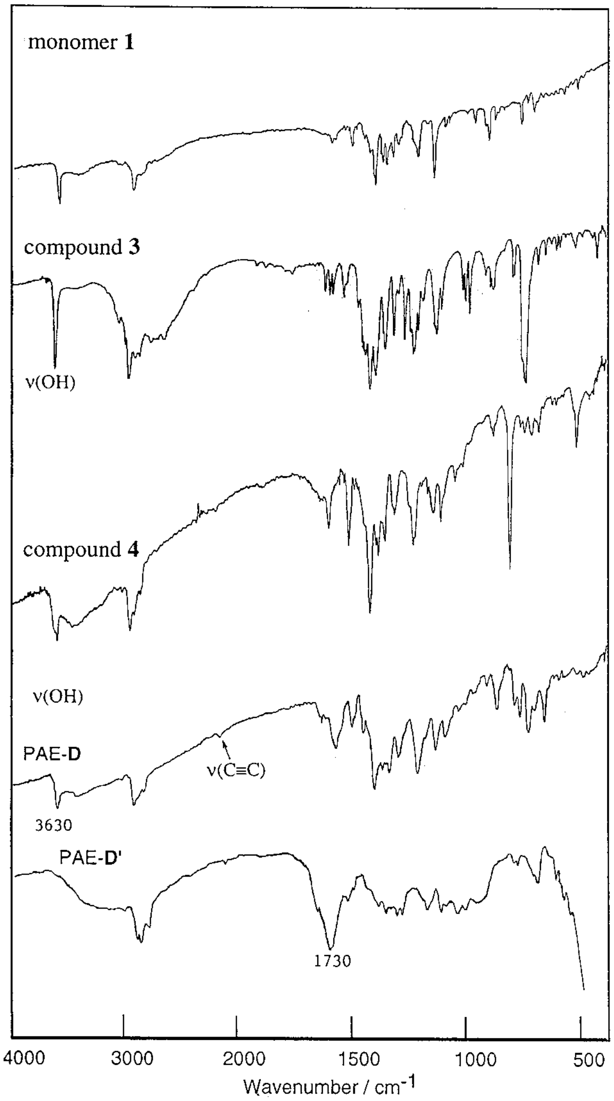


Figure 1. IR spectra of monomer **1**, compound **3**, compound **4**, PAE-**D**, and PAE-**D′** (oxidized PAE-**D**). **1**−PAE-**D**: in KBr disk. PAE-**D′**: sandwiched between two NaCl plates.

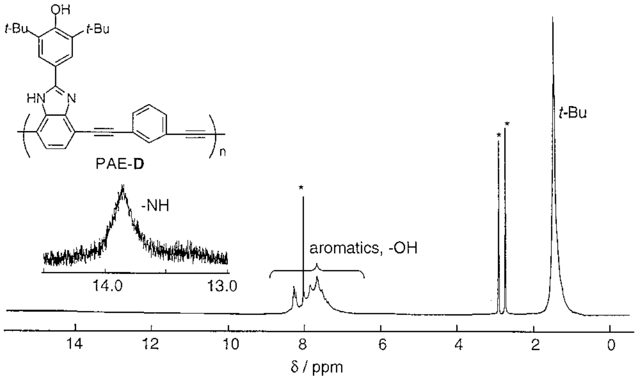


Figure 2. ^{1}H NMR spectrum of PAE-**D** at 28 °C in DMF-d_7. The peaks with the * mark are due to impurities of DMF-d_7.

Molecular models indicate that the PAE type polymer can take a coplanar structure due to the presence of the spacing −C≡C− group whereas the above shown P(4,7-Bim)s have a twisted structure due to the steric repulsion.

Experimental Section

Materials. 1,2-Diamino-3,6-dibromobenzene,[3] 1,4-didodecyloxy-2,5-diethynylbenzene **2b**,[9a] 2,5-diethynylpyridine **2c**,[6a] 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)benzimidazole compound **3**,[9b] and $Pd(PPh_3)_4$[9c] were synthesized by the respective literature methods. *o*-Phenylenediamine, *p*- and *m*-diethynylbenzene (**2a** and **2d**), *p*-ethynyltoluene, and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde were used as purchased.

Synthesis of Monomer 1. 4,7-Dibromo-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)benzimidazole, monomer **1**, was prepared by modifying a method reported for the preparation of compound **3**.[9b] Monomer **1** was synthesized as follows: 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (1.05 g, 3.95 mmol) was added to a mixture of 1,2-diamino-3,6-dibromobenzene (0.92 g, 3.93 mmol) in 10 mL of ethanol at room temperature, and this mixture was stirred for 2 days. The solvent was removed in vacuo and the resulting precipitate was washed with $CHCl_3$ and dried under vacuum to yield 0.96 g (51%) of **1**. ^{1}H NMR (DMSO-d_6, 90 MHz): δ 1.45 (s, 18H), 7.31 (d, 2H), 7.50 (s, 1H), 8.00 (s, 2H), 13.08 (s, 1H). Anal. Calcd for $C_{21}H_{24}Br_2N_2O$: C, 52.5; H, 5.0; N, 5.8; Br, 33.3. Found: C, 52.1; H, 5.1; N, 5.7; Br, 33.4.

Synthesis of Model Compound 4 for the Polymer. The preparation of 4,7-bis[2-(4-methylphenyl)ethynyl]-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)benzimidazole, compound **4**, was carried out as follows. Dry DMF (10 mL) was added to a mixture of **1** (240 mg, 0.5 mmol), *p*-ethynyltoluene (220 mg, 1 mmol), and triethylamine (1 mL) in a Schlenk tube under nitrogen. CuI (9.2 mg, 0.05 mmol) and $Pd(PPh_3)_4$ (56 mg, 0.05 mmol) were then added to the mixture, and the reaction mixture was stirred at 60 °C for 48 h to obtain a deep red solution. The solvent was removed by evaporation. The residue was dissolved in chloroform, and the chloroform solution was washed with water and brine. The product was purified by column chromatography on silica gel using chloroform as an eluent. Yield: 395 mg (66%). Mp: 270−273 °C. ^{1}H NMR (acetone-d_6, 400 MHz): 1.46 (s, 18H), 2.37 (s, 3H), 2.39 (s, 3H), 6.50 (s, 1H), 7.2−7.6 (m, 10H), 8.12 (s, 2H), 12.6 (s, 1H). Essentially the same spectrum was obtained at −30 °C, although the four peaks at δ 7.42−7.50 (cf. Figure 3) are shifted to a higher magnetic field and overlapped with other aromatic-H peaks at the higher magnetic field. Anal. Calcd for $C_{39}H_{38}N_2O{\cdot}H_2O$: C, 82.4; H, 7.1; N 4.9. Found: C, 82.4;

Table 2. Solubility of the Polymers[a]

polymer	DMF	DMSO	NMP	MeOH	$CHCl_3$	hexane	HCOOH	CF_3COOH
PAE-**A**	Δ	Δ	Δ	X	X	X	Δ	Δ
PAE-**B**	Δ	Δ	Δ	X	Δ	X	Δ	Δ
PAE-**C**	Δ	Δ	Δ	X	X	X	Δ	Δ
PAE-**D**	○	Δ	○	X	X	X	○	○

[a] ○: completely soluble. Δ: partially soluble. X: insoluble.

H, 7.2; N, 4.9. Mass: $m/e = 550.2955$: Calcd For $C_{39}H_{38}N_2O = 550.2984$. Its molecular structure determined by X-ray crystallography supports the monohydrated structure.[10] The model compound **4** was soluble in the usual organic solvents such as $CHCl_3$, DMF, and CF_3COOH.

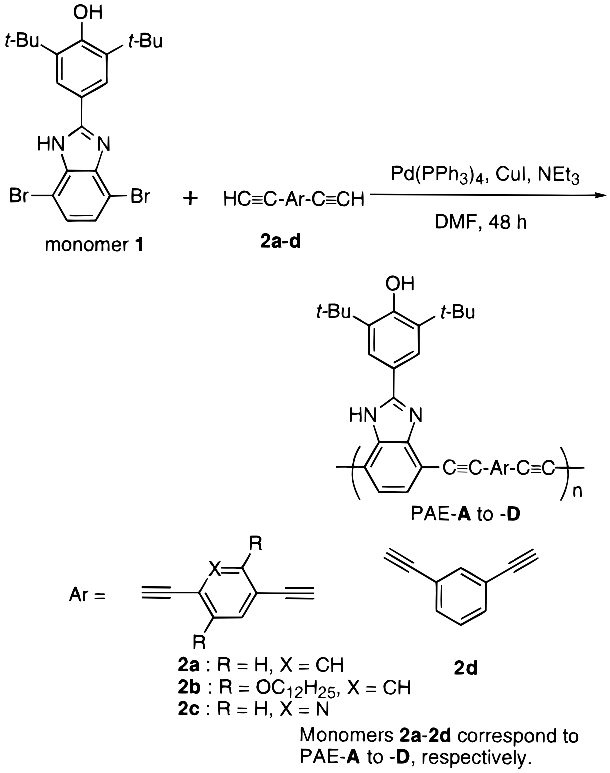
Polymerization. Polymerization was carried out in a manner similar to that previously reported by us and other research groups since 1981.[5] For example, the preparation of PAE-**A** was carried out as follows. Dry DMF (10 mL) was added to a mixture of the monomer **1** (240 mg, 0.5 mmol), **2a** (63 mg, 0.5 mmol), and triethylamine (1 mL) in a Schlenk tube under nitrogen. CuI (5 mg, 0.025 mmol) and $Pd(PPh_3)_4$ (27 mg, 0.025 mmol) were then added, and the reaction mixture was stirred at 100 °C for 48 h to obtain a deep black solution. The reaction mixture was poured into methanol to obtain an orange precipitate, which was collected by filtration, washed with methanol repeatedly, and dried under vacuum to obtain 212 mg (96%) of an orange powder of PAE-**A**. Anal. Calcd for $Br(C_{31}H_{28}N_2O{\cdot}0.7H_2O)_{11}Br$: C, 79.1; H, 6.3, N, 6.0; Br, 3.1. Found: C, 79.6; H, 6.1; N, 5.5; Br, 3.1. The polymer is considered to be hydrated, similar to the case of the model compound **4** (vide ante). The difference between the calculated and found values may partly be due to high thermal stability of the polymer. IR (KBr): 3618 (ν(OH)), 2186 cm^{-1} (ν(C≡C)). Other polymerizations were carried out analogously. (PAE-**B**) Anal. Calcd for $Br(C_{55}H_{76}N_2O_3{\cdot}0.8H_2O)_7Br$: C, 77.7; H, 9.2, N, 3.3; Br, 2.7. Found: C, 77.3; H, 8.9; N, 3.0, Br, 2.8. IR (KBr): 3612 (ν(OH)), 2196 cm^{-1} (ν(C≡C)). (PAE-**C**) Anal. Calcd for $Br(C_{30}H_{27}N_3O{\cdot}3.5H_2O)_{10}Br$: C, 68.7; H, 6.5; N, 8.0; Br, 3.0. Found: C, 68.5; H, 5.9; N, 8.0; Br, 2.6. The polymer containing the pyridine unit seems to absorb a larger amount of H_2O. IR(KBr): 3618 (ν(OH)), 2186 cm^{-1} (ν(C≡C)). (PAE-**D**) Anal. Calcd for $Br(C_{31}H_{28}N_2O{\cdot}1.6H_2O)_{24}Br$: C, 77.6; H, 6.5, N, 5.8; Br, 1.4. Found: C, 77.6; H, 6.3; N, 5.4; Br, 1.5. IR (KBr): 3612 (ν(OH)), 2196 cm^{-1} (ν(C≡C)). $[\eta] = 0.32$ dL g^{-1} (in DMF at 30 °C). For all the polymers, the M_n value estimated from GPC analysis is larger than that estimated from the elemental analytical data, probably due to a rigid structure of the polymer.

Oxidation of PAE Type Polymers. Under N_2, to a solution of PAE-**D** (22.6 mg, 0.08 mmol unit) in 20 mL of DMF was added 0.25 g of PbO_2. The mixture was stirred for 60 min at room temperature. The reaction mixture was filtered to remove PbO_2, and the solvent was taken off by evaporation from the filtrate. The obtained brown powder was dried under vacuum. Other oxidations, including oxidation of the model compound **4** with PbO_2, were carried out analogously. Analytical data of the oxidized product of **4**: Calcd for $C_{39}H_{37}N_2O{\cdot}H_2O$: C, 82.5; H, 6.9; N, 4.9. Found: C, 82.6; H, 7.3; N, 5.3. Recrystallization of the oxidized product of **4** was not possible.

Measurements. IR spectra were recorded on a JASCO IR-810 spectrometer. NMR spectra in solutions were taken using a JEOL JNM-GX-400 or JNM-EX-90 spectrometer. UV–visible spectra were recorded on a Shimadzu UV-3100PC spectrometer. Films of PAE-**B** and PAE-**D** were prepared from casting from a $CHCl_3$ solution of PAE-**B** ($CHCl_3$ soluble part) and a DMF solution of PAE-**D**, respectively. After natural evaporation of the solvent under air, the cast film on a glass substrate was dried under vacuum at room temperature. Photoluminescence spectra were measured with a Hitachi F-4010 spectrometer. The quantum yield of the photoluminescence in solutions was estimated by a literature method.[11a,b] ESR spectra were taken by using a JCS-RE3X ESR spectrometer at an X-band mode. Microanalysis of C, H, and N was carried out with Yanagimoto CHN Autocorder Type MT-2 by Mrs. Tanaka and Mrs. Hayashi of our research laboratory. Analysis of halogen was carried out with a Yazawa halogen analyzer or a Yanaco SX-Elements Micro analyzer by Mrs. Hayashi. GPC analysis was carried out on a Tosoh HLC-8020 gel permeation chromatograph (vs standard polystyrenes; eluent = a DMF solution of LiCl (0.02 M)). Viscosity was measured with an Ubbelohde viscometer using DMF for PAE-**D** at 30 °C.

Results and Discussion

Polymerization. The polycondensation expressed by eq 2 proceeds well between the monomer **1** and the following four diethynyl aromatic compounds, and the PAE-type polymers, PAE-**A** to PAE-**D**, are obtained in good yields.



(3)

Results of polymerization are summarized in Table 1. As shown in Table 1, the polymerization proceeds smoothly at 100 °C, and the polymer is obtained in 81–96% yield. The polymerization also proceeds at 60 °C to give somewhat lower yield (70% for PAE-**B**, run 3 in Table 1). At room temperature, the polymerization does not proceed smoothly, in accord with previous results reported for the preparation of other PAE-type polymers.[5]

Figure 1 depicts the IR spectra of the monomer **1**, PAE-**D** and oxidized product of PAE-**D** (PAE-**D′**, vide infra). By the polycondensation, a weak ν(C≡C) band of original HC≡C–Ar–C≡CH at 2120–2130 cm^{-1} is shifted to a higher frequency and appears in a range of about 2180–2210 cm^{-1}. It is known that disubstituted acetylenes RC≡CR give rise to the ν(C≡C) band at a higher frequency than monosubstituted acetylenes RC≡CH.[11c] The ν(C≡C) and ν(C–H) (at about 3150 cm^{-1}) bands of the terminal –C≡CH of the monomer **2** are not observable in the IR spectra of all the PAE type polymers. The polymers clearly show a sharp ν(OH) absorption band of the hindered phenolic group at about 3600 cm^{-1} (Table 1, the last column), similar to the case of the monomer **1**. Benzimidazoles (e.g., compound **3** described below) often show a broad absorption band in a region of 2500–2800 cm^{-1}, which is assigned to a hydrogen-bonded N–H vibration (e.g., Figure 1, the second top chart of compound **3**). However, such a band is not observed with the polymers as well as their model compound (compound **4**, vide infra), probably due to steric difficulty of forming such a hydrogen bonding in the polymer. The polycondensation expressed by eq 2

Table 3. UV–Visible Data of the Polymers[a]

		absorption λ_{max}/nm ($10^{-4}\epsilon$)[b]			
no.	compound	in nonacidic solvent	after addition of NaOH[d]	in acidic solvent	film
1	PAE-**A**[c]	363 (DMF)	408 (DMF)	330 (TFA)	
2	PAE-**B**[c]	410 ($CHCl_3$)		342 (TFA)	410
3	PAE-**C**[c]	383 (DMF)		397 (TFA)	
4	PAE-**D**	353 (DMF, 3.1)	397 (DMF)	341 (TFA, 4.4)	362
5	**3**	310 (MeOH) 314 (DMF)	363 (DMF)	320 (TFA)	
6	**4**	351 (DMF)	385, 485 (DMF)	342 (TFA)	

[a] Solvent: DMF = *N*,*N*-dimethylformamide, MeOH = methanol, TFA = trifluoroacetic acid. [b] The ϵ value (in M^{-1} cm^{-1}; molarity is based on the repeating unit) is given in parentheses. [c] Measured with the soluble part in the solvent. [d] Addition of NaOH alkaline methanol to the solution.

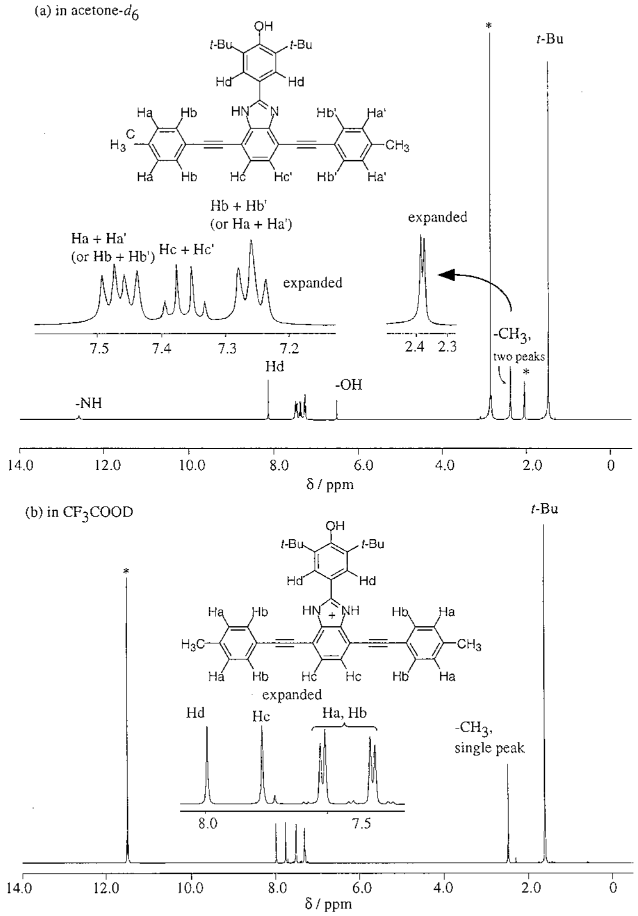


Figure 3. ^1H NMR spectrum of compound **4** in (a) acetone-d_6 and (b) CF_3COOD at 400 MHz. The peaks with the * mark are due to solvent impurities (C_3H_5DO, water, and CF_3COOH).

is considered to give Br-terminated polymers (cf. Experimental Section);[5f,6b,d] however, assignment of the ν(C–Br) absorption band of the polymer was not possible.

Table 2 summarizes solubility of the PAE-type polymers. The polymer with the *m*-Ph (*m*-phenylene) unit (PAE-**D**) has good solubility and is completely dissolved in DMF. On the other hand, the linear polymers with the *p*-Ph (*p*-phenylene) or 2,5-Py (pyridine-2,5-diyl) unit show considerably lower solubility even when the polymer has the long alkoxy chain (PAE-**B**). The linear type polymer is only partly soluble in organic solvents. For example, about 10% of PAE-**B** is soluble in $CHCl_3$. Since the IR spectrum of the soluble part is identical to that of the insoluble part, the portion with relatively low molecular weights is considered to be dissolved in the solvents. Molecular weights of DMF-soluble parts of the polymers are shown in Table 1. PAE-**D** has a molecular weight of 3.3×10^4, as determined by GPC (polystyrene standards), and gives an $[\eta]$ value of 0.32 dL g^{-1}. Some non π-conjugated polymers containing the benzimidazole unit (e.g., poly(arylene ether benzimidazole)) are soluble in NMP; however, PAE-**A** and PAE-**C** are soluble only partly (e.g., ca. 0.2 mg of PAE-**A** in 1 mL of NMP), presumably due to the stiffer main chain structure. PAE-**D** is soluble in NMP.

^1H NMR data of the polymers are also reasonable for the structure of the polymers. Figure 2 exhibits the ^1H NMR spectrum of PAE-**D**, which gives rise to the *t*-Bu, aromatic, and the NH hydrogen signals at δ 1.5, 7.2–8.4, and 13.8 ppm, respectively. The –OH signal of the hindered phenol group is considered to be overlapped with those of aromatic hydrogens. The peak area ratios agree with the structure of PAE-**D**. As shown in Figure 2, The two *t*-Bu groups give only one peak at δ 1.5 ppm, and this is attributed to perpendicular twisting or rapid rotation of the 3,5-di-*tert*-butyl-4-hydroxyphenyl group. The NH signal of the imidazole ring of PAE-**D** (δ 13.8) appears near the position of the NH signal of the model compound **4** described below. The signal of phenolic OH hydrogen usually apperas in a range of δ 5–8 (e.g., cf, Figure 3 described below) and seems to be overlapped with the aromatic H signals in the case of PAE-**D**.

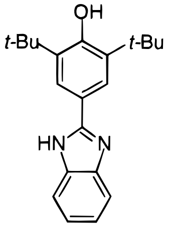
UV–Visible Spectrum. In Nonacidic Media. Table 3 summarizes UV–visible data of PAE type polymers. As shown in Figure 3, the π–π* absorption band of PAE-**A** in DMF is shifted to a wavelength longer than that of the following compound, compound **3**.

As shown in Chart 1, the π–π* absorption band of the compound **3** is shifted to a longer wavelength by introducing two *p*-tolylethynyl groups (compound **4**), However, PAE-**A** shows a larger shift compared with compound **4**, suggesting that the π-conjugation is expanded at least beyond the neighboring repeating unit of PAE-**A**. The position of the π–π* absorption band of the model compound **4** locates at a wavelength longer than that of 1,4-bis(2-phenylethynyl)benzene (321 nm).[12a] However, it locates at almost the same position as that of 1,4-bis(2-phenylethynyl)naphthalene (359 nm)[12b] with a larger π-electron system at the center of the molecule. The model compound **4** contains one H_2O as the solvent of crystallization.[10]

Previously reported π-conjugated PAE type polymers also show similar expansion of the π-conjugation system along the polymer chain.[5,6,13a] P(4,7-Bim)s show their absorption peaks at a somewhat shorter wavelength (e.g., 340 nm for R = H).[3a] The π–π* absorption band of compound **3** at 314 nm is very weakened or disappears in the UV–visible spectrum of PAE-**A**.

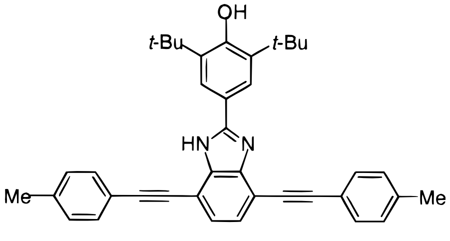
The *m*-Ph type polymer, PAE-**D** also shows a shift of the π–π* absorption band to 353 nm (no. 4 in Table 3), however, the degree of the bathochromic shift (3400 cm^{-1}) is smaller due to a weaker effect of the *m*-Ph unit for the expansion of the π-conjugation system. The absorption peak of PAE-**D** appears at the position almost the same as that of compound **4**, indicating that π-expansion essentially stops at the *m*-Ph unit. Films of PAE-**B** and PAE-**D** (nos. 2 and 4 in Table 3) give the absorption peak at the position essentially agreeing with that observed in the nonacidic solvent, indicating that π-stacking of the polymer[13b–f] does not take place due to the bulky hindered phenol side chain.

Chart 1. λ_{max} Positions of PAE-A (Soluble Part) and Its Related Compounds



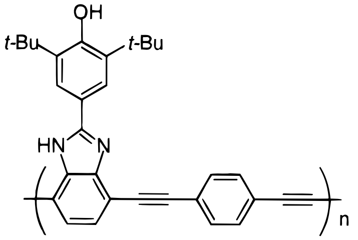
compound **3**

λmax = 314 (in DMF)
320 (in trifluoroacetic acid (TFA))
361 (in DMF after addition of NaOH)



compound **4**

λmax = 351 (in DMF) : shift from compound **3**
(Δλ) = 37 nm or 3400 cm^{-1}
342 (in TFA)



PAE-**A**

λmax = 363 (in DMF; for DMF soluble part) :
shift from compound **3** (Δλ) = 49 nm or
4300 cm^{-1}
330 (in TFA)

In CF_3COOH. In CF_3COOH (second last column in Table 3), PAE-**A**, -**B**, and -**D** with the *p*-Ph or *m*-Ph unit show their absorption peaks at a shorter wavelength near that of the compound **3**. These data suggest that protonation of the imidazole ring by CF_3COOH brings about a severe change in the electronic state of the polymer and the wave functions (e.g., HOMO and LUMO) are considered to be essentially confined in the unit of the compound **3**. The model compound **4** also gives analogous results in CF_3COOH (run 6).

For compound **4**, its ^1H NMR spectrum in CF_3COOH considerably differs from that in nonprotonic solvents, as depicted in Figure 3. In acetone-d_6 (part a in Figure 3), the CH_3 groups at the two ends give their peaks at different positions. Signals of the aromatic protons also support the unsymmetric structure of compound **4** originated from the difference between the −NH- and =N− units in the imidazole ring. In contrast to the NMR data in acetone-d_6, the two CH_3 groups appear as a sharp singlet at δ 2.48 ppm in CF_3COOD (part b in Figure 3) due to the symmetric structure of the protonated compound (cf. molecular structure depicted in Figure 3b). The aromatic signals are also consistent with the symmetrical structure, although the spectrum exhibits additional small peaks, which may originate from conformer(s) of the protonated compound **4** or diprotonated species.

As described above, the protonation of compound **4** by CF_3COOH leads to the shift of the $\pi-\pi^*$ absorption peak to a shorter wavelength, which suggests twisting of the *p*-tolyl group by the protonation. The NH groups in the protonated compound **4** are considered to be charged +, whereas the C−Hb (cf. Figure 3 for Hb) bond in the tolyl group will be polarized as $C^{\delta-}-Hb^{\delta+}$ due to the difference in the electronegativity between C and H. If such a polarization takes place, the steric repulsion between the NH unit and Hb will lead to the twisting of the *p*-tolyl group, and this accounts for the hypsochromic shift of compound **4** in CF_3COOH. Similar twisting of the Ar group in PAE-**A**, -**B**, and -**D** is also conceivable and accounts for the shift of λ_{max}. Control of the π-conjugation length of π-conjugated polymers by chemical reactions is the subject of recent interest.[14]

In contrast to these polymers, PAE-**C** with the 2,5-Py unit shows a bathochromic shift (no. 3 in Table 3) in CF_3COOH. Protonation of both nitrogen atoms of the imidazole ring and the 2,5-Py unit may constrain the positively charged imidazole ring and NH^+ of the protonated 2,5-Py unit to take a mutually trans conformation, thus giving the coplanar main chain.

In Alkaline Media. In alkaline media (the fourth column in Table 3), the UV−visible absorption peak of compound **3** is shifted to a longer wavelength, presumably due to deprotonation of the OH group to O^- or ONa; a similar shift in alkaline media has been reported with *p*-phenylphenol (from 260.5 to 291.5 nm).[7e] Deprotonation of the NH group[2] by NaOH also seems to take place partly. In the alkaline media, both compound **4** and PAE type polymers show similar bathochromic shifts. When treated with a DMF solution of NaOH, the polymer showed certain dc conductivity with an order of 10^{-6} S cm^{-1}, which may originate from the negative carrier formed by the deprotonation of the OH and NH groups.

Photoluminescence. Table 4 summarizes photoluminescence data of the PAE type polymers. Figure 4 shows the photoluminescence spectrum of PAE-**D**. As clearly seen from Figure 4, PAE-**D** gives a much stronger photoluminescence in CF_3COOH than in nona-

Table 4. Photoluminescence Data of the PAE-Type Polymers

		photoluminescence[b] λmax/nm (solvent, quantum yield)	
no.	compound	in CF_3COOH	in nonacidic solvent
1	PAE-**A**[a]	434 (6.5×10^{-2})	463 (DMF, 6.0×10^{-3})
2	PAE-**B**[a]	495 (8.6×10^{-2}, 0.14)[c]	511 ($CHCl_3$, 9.9×10^{-2}) 475 (DMF, 0.19)
3	PAE-**C**[a]	478 (1.5×10^{-2})	454 (DMF, 3.7×10^{-3})
4	PAE-**D**	421 (0.18)	463 (DMF, 6.0×10^{-3})
5	**3**	370 (0.46)	348 (MeOH)
6	**4**	456 (0.14)	412, 663 (DMF, 2.36×10^{-2})

[a] For solvent-soluble part. [b] Exited by light near λ_{max} listed in Table 3. [c] Excitation wavelength is 340 and 412 nm, respectively.

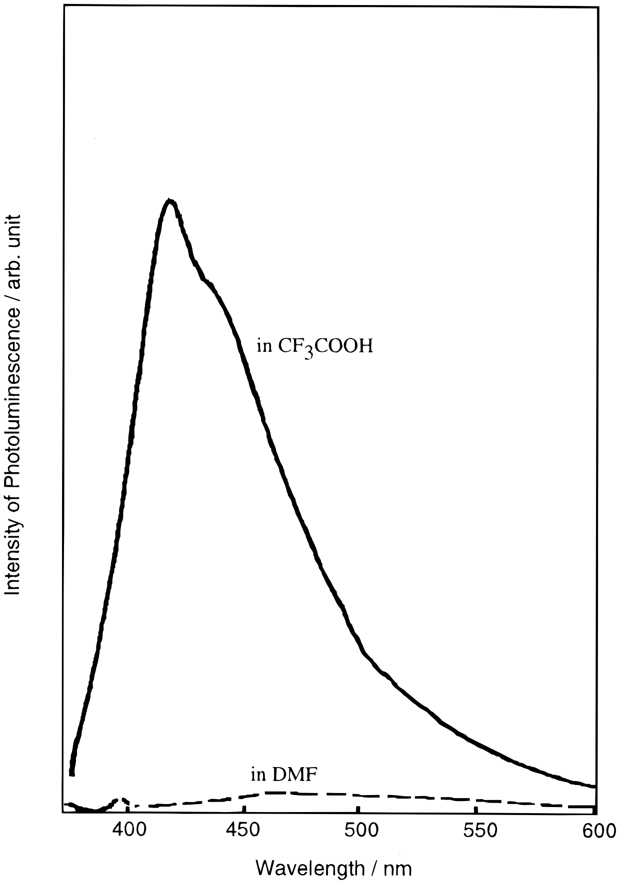


Figure 4. Photoluminescence spectra of PAE-**D** in CF_3COOH. (——) and DMF (– – –). Both the samples contain almost the same concentration of PAE-**D**.

cidic media like DMF, and a similar trend has also been observed with PAE-**A**. On the other hand, PAE-**B** and -**C** give similar quantum yields in both the acidic and nonacidic solvents. Since the quantum yield of the photoluminescence of 2-phenylbenzimidazole[2d] is reportedly virtually independent of the protonation, the above shown results indicate that delicate changes in the structure and electronic states of the polymers affect the quantum yield. The photoluminescence shown in Table 4 and Figure 4 occurs at the onset of the π–π* absorption bond, as usually observed with π-conjugated compounds and polymers.

Oxidation of the Polymers. The hindered phenolic group in the large π-conjugation system is expected to generate a stable radical protected by the bulky *t*-Bu groups. It is known that PbO_2 can oxidize such hindered phenols[7d] and application of the oxidation to PAE-**A** to -**D** (DMF-soluble part) gives a new polymer, PAE-**A′** to -**D′**.

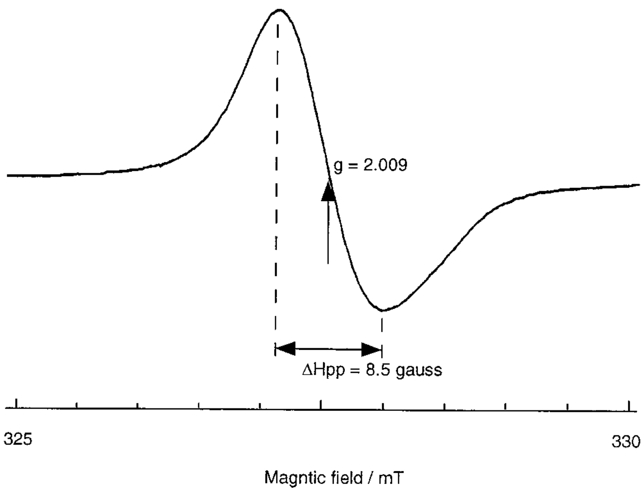
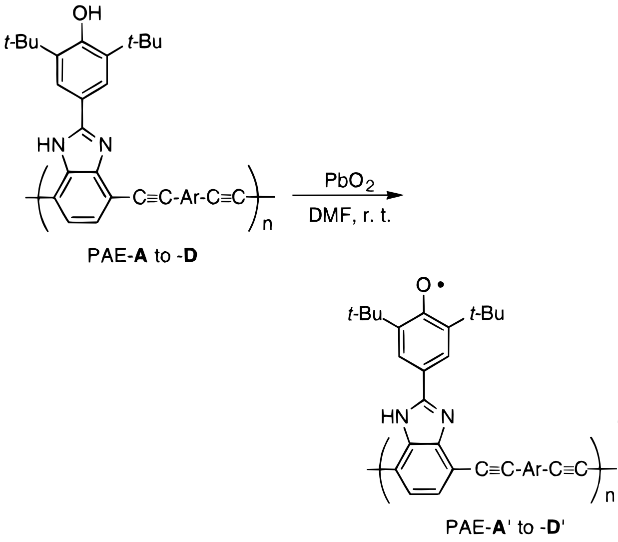


Figure 5. ESR spectrum of PAE-**D′** in the solid.



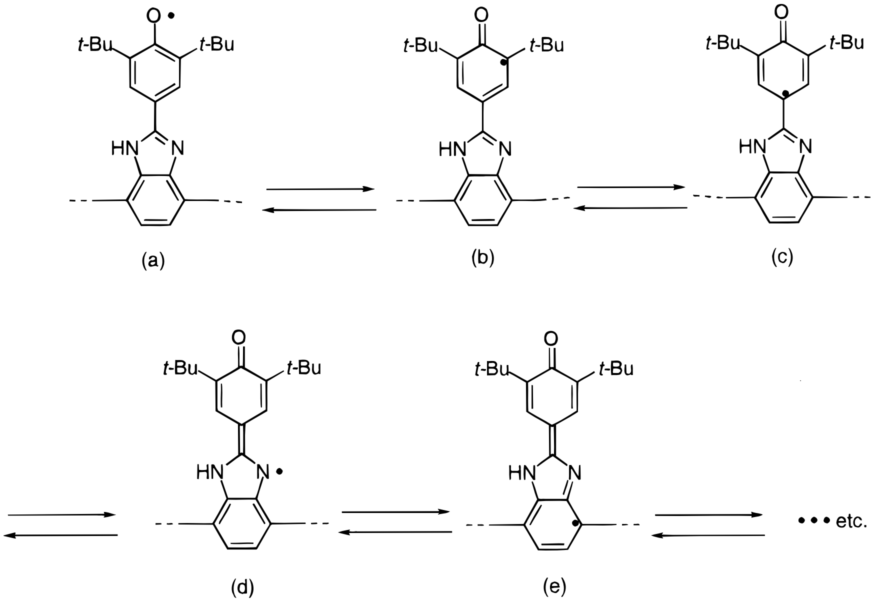
(4)

DMF solutions of PAE-**B′** and PAE-**D′** show new broad absorption bands at about 670 and 650 nm, respectively, characteristic of phenoxy radicals,[7d] although the intensity of absorption band is considerably smaller (ca. 30% for PAE-**B′** and 10% for PAE-**D′**) than that observed with the similar oxidation product of compound **3**.

As shown in Figure 1, the sharp ν(OH) absorption band of PAE-**D** at 3630 cm^{-1} completely disappears after the oxidation and a new strong absorption band at 1730 cm^{-1} emerges in the region of ν(C═O). Similar changes in the IR spectrum are observed on the PbO_2 oxidation of compound **3**; the oxidized product of compound **3** gives a new strong band at 1679 cm^{-1} and the ν(OH) band is not observed. Such phenoxy radical species in a large π-conjugation system[15] (including π-conjugated polymers[7e]) are often stabilized by taking various resonance forms including formation of a C═O bond (Chart 2).

ESR spectra of the oxidized polymers (e.g., PAE-**D′**: Figure 5) in the solid exhibit signals at about $g = 2.010$ with a peak-to-peak line width of 8–11 G. However, the intensity of the ESR signal is not so strong and corresponds to the presence of one spin per about 60 monomer units. Pairing of the radical species through the π-conjugation system or by interchain interaction

Chart 2. Possible Resonance Structures of the Oxidized Polymer



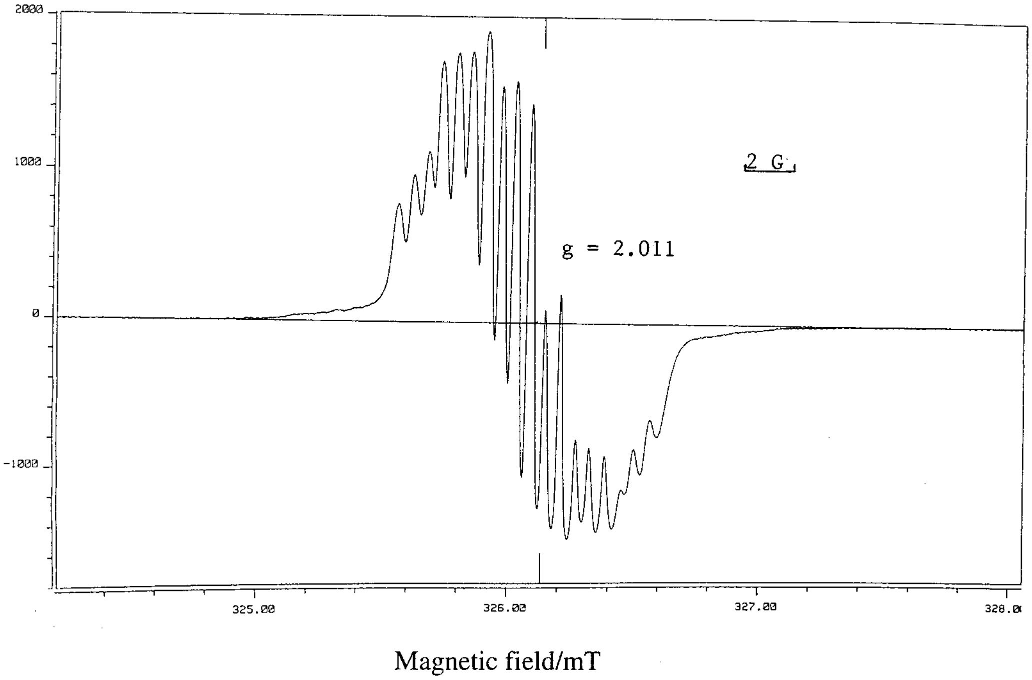


Figure 6. ESR spectrum of the oxidized model compound **4** (4.3 mM) in benzene at room temperature.

may take place with the present polymers to decrease the effective spin density of the oxidized polymer.

Nishide, Tsuchida, and Lahti reported ESR data of polyacetylenes bearing radical species in their side chains and found hyperfine structures.[16] For the present polymers (e.g., PAE-**D**′), attempts to measure their ESR spectra by using nonpolar solvents such as benzene in a usual ESR tube and by using polar solvents such as DMF in a capillary tube were not successful (the polymers are not soluble in nonpolar solvents; cf. Table 2). However, the ESR spectrum of the oxidized model compound **4** in benzene shown in Figure 6 exhibits a signal at $g = 2.011$ with the hyperfine structure, which reveals that the radical is delocalized in the large π-conjugation system to be coupled with many nuclei. This result supports the possibility for the pairing of the radical species through the π-conjugation system. In the solid state, the PbO_2-oxidized product of the model compound **4** also gives an ESR signal at $g = 2.010$ with a peak-to-peak width of 9.5 G, and the shape of the signal is similar to that of PAE-**D**′ shown in Figure 5. Magnetic measurements also indicate that the oxidized polymers are essentially diamagnetic or have a weak paramagnetism.

Conclusions

Palladium-catalyzed polycondensation between 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4,7-dibromobenzimidazole and four kinds of diethynyl aromatic compounds gives new poly(aryleneethynylene)s composed of the benzimidazole unit bearing the hindered phenolic substituent in high yields. In the π-conjugated polymers, the π–π^* absorption band of the corresponding monomeric compound is shifted to a longer wavelength by 4300 cm^{-1}. Optical properties of the polymers and their model compounds vary with the kind of the solvent, and intensity of the photoluminescence of PAE-**D** is strongly enhanced by protonation of the polymer with CF_3COOH. Oxidation of the polymers by PbO_2 proceeds at room temperature, and the oxidation products show a strong IR absorption band at about 1700 cm^{-1} originated from their resonance structures.

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(10) Monoclinic, $P2_1/c$ (No. 14); $a = 17.015$ (4) Å, $b = 12.637$ (2) Å, $c = 16.426$ (3) Å, $\beta = 106.48$ (1) °, $Z = 4$, $D_{\mathrm{calc}} = 1.115$ g cm^{-3}, $R = 0.116$, $R_{\mathrm{w}} = 0.070$.

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