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Synthesis and Chemical Properties of π-Conjugated Zinc Porphyrin Polymers with Arylene and Aryleneethynylene Groups between Zinc Porphyrin Units

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ABSTRACT: Organometallic polycondensation gave zinc porphyrin (Por) polymers (e.g., (−Ar−Por-Ar−)$_n$ and (−C≡C−Por-C≡C−Ar−)$_n$; Ar = arylene) having arylene or aryleneethynylene groups between the zinc porphyrin units. Polymers having long alkyl substituent(s) in the Ar unit were soluble in THF and chloroform, and gave M_n and M_w values of 4.6−37.9 × 10^3 and 6.3−49.1 × 10^3, respectively, in GPC analysis. Fully soluble polymers gave [η] values of 0.21−0.35 dL g^{-1}. All of the zinc porphyrin polymers showed absorption peaks in regions of the Soret and Q-bands, respectively, in chloroform solution and as cast films, and the shift and splitting of the absorption peaks depended on the Ar and −C≡C−Ar−C≡C− groups. They exhibited photoluminescence in chloroform. Powder X-ray diffraction patterns of the polymers indicated that the polymers bearing long alkyl chain(s) in the spacing Ar group formed an ordered structure in the solid state. Free-standing films were obtained by casting. Films of polymers on a Pt plate were electrochemically active and showed electrochromism. Comparison of the optical properties of the polymers with those of model compounds, Ar′-≡-Por-≡-Ar′ (Ar′ = phenyl or thiophene-2-yl), was also carried out.

Introduction

π-Conjugated metalloporphyrin macromolecules have attracted considerable attention due to their potential use in optical and electronics devices[1] and solar energy conversion.[2] Various types of metalloporphyrin macromolecules such as dendrimers,[3] linear oligomers,[2,4] and polymers[5] have been synthesized. Recently, the self-assembly of double-stranded porphyrin ladders was reported by Anderson.[6]

For practical use, obtaining polymers of metalloporphyrin with a high molecular weight and good solubility is desired to prepare films with good quality. However, metalloporphyrin polymers often show low solubility in organic solvents. When the metalloporphyrin units are directly bonded to form the polymer, another problem arises. Steric hindrance between the metalloporphyrin units often disturbs the formation of an extended π-conjugated system. Much effort has been devoted to the design of metalloporphyrin macromolecules with improved solubility and less steric hindrance. For example, the introduction of long alkyl chains in the porphyrin ring and the introduction of spacing groups such as a phenylene group or an oligo phenylenevinylene group between porphyrins have been attempted.[7]

We have investigated Ni- and Pd-promoted organometallic polycondensations of dihalo- and diethynylaromatic monomers to give π-conjugated polymers.[8,9]

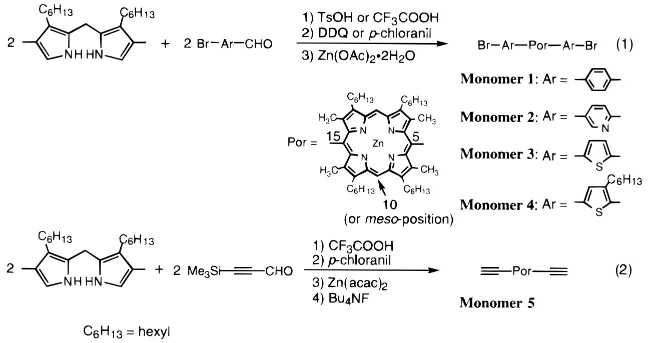
$$n\ \mathrm{X{-}Ar{-}X} + n\,\mathrm{M} \xrightarrow{\text{Ni-complex}} \left(\mathrm{Ar}\right)_n$$

$$n\ \mathrm{X{-}Ar{-}X} + n\,\mathrm{HC{\equiv}C{-}Ar''{-}C{\equiv}CH} \xrightarrow{\text{Pd-complex}} \left(\mathrm{Ar{-}C{\equiv}C{-}Ar''{-}C{\equiv}C}\right)_n$$

Application of these polycondensations to dihalo and diethynyl derivatives of porphyrins would give a series of linear porphyrin polymers. In this paper, we will report the synthesis of new porphyrin monomers having bromoaryl or ethynyl groups at positions 5 and 15 (or *meso*-positions) and hexyl groups at positions 2, 8, 12, and 18 of a zinc porphyrin ring. The monomers were useful in organometallic polycondensations, and the obtained polymers were, at least, partly soluble. Some of the polymers had good solubility in organic solvents and free-standing films were obtained by a casting method. Investigation of the soluble polymers and their films provided electrochemical and optical information on such metalloporphyrin macromolecules.

Results and Discussion

Preparation of Monomers and Model Compounds. Monomer. The following monomers were synthesized by the MacDonald coupling reaction of bispyrrole with aldehydes, followed by metalation with zinc (eqs 1 and 2).



IR spectra of monomers **1**−**5** show a ν(C=C) vibration peak characteristic of the porphyrin ring at about 1460 cm^{-1}. Absorptions due to ν(C≡*C*−*H*) and ν(C≡C) vibrations of monomer **5** were observed at 3308 and 2092 cm^{-1}, respectively.[10] Anderson and Bradley reported the preparation of a zinc porphyrin compound similar to

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Table 1. Results of the Polycondensation

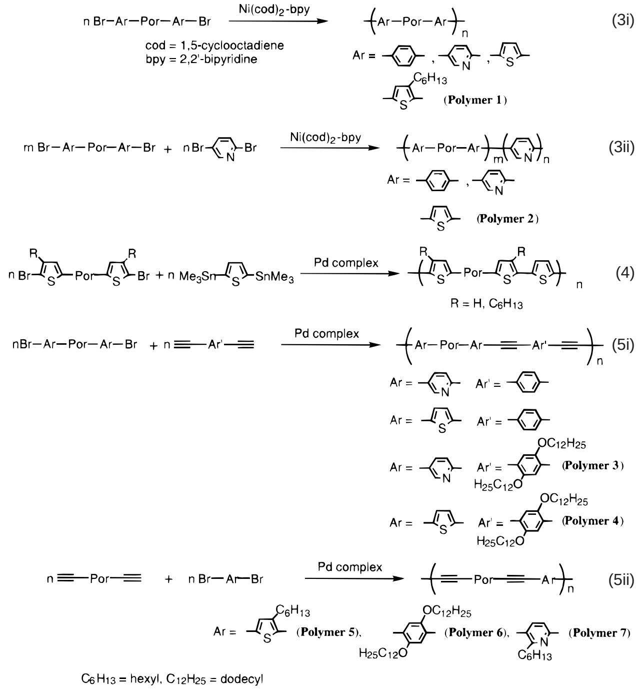
polymer	yield (%)	solubility[a] NMP	THF	$CHCl_3$	toluene	10^3M_n[b]	10^3M_w[b]	M_w/M_n	$[\eta]$/dL g^{-1} [d]
1	40	×	○	○	△	37.9	49.1	1.3	0.31
2	79	×	○	△	×				0.09
3	100	×	○	○	×				0.24
4	80	×	○	○	△	12.2	21.5	1.8	0.21
5	94	×	△	△	△	4.8[d]	5.8[d]	1.2	
6	57	△	△	△	△	4.6[d]	6.3[d]	1.4	
7	97	×	△	△	△	6.5[d]	9.3[d]	1.4	

[a] Key: ○, soluble (ca. 2 mg/mL^{-1}); △, partially soluble; ×, insoluble. [b] Determined by GPC (eluent = $CHCl_3$ (polymer **4**) or THF (polymers **1**, **5**, **6**, and **7**; polystyrene standards). [c] In $CHCl_3$ at 30 °C. [d] Data for soluble part.

monomer **5** and its oxidative coupling to give oligomers linked by a $-C{\equiv}C-C{\equiv}C-$ bond.[1c] ^1H NMR data of the monomers shown above agree with their structures and are given in the Experimental Section and Supporting Information. Peaks of *meso* hydrogens and α-CH_2 hydrogens of the hexyl group bonded to the porphyrin ring appear at higher magnetic field positions than those of zinc-free porphyrin by about 0.3 and 0.2 ppm, respectively. Similar shifts were observed for all of the monomers (cf. Experimental Section).

The molecular structure and the packing structure of monomer **3** were revealed by X-ray crystallography and are given in the Supporting Information. The thiophene ring and the porphyrin ring have a torsional angle of 86.9° in the crystal. The hexyl chains are positioned vertically with respect to the plane of the porphyrin ring. Two 5-bromothienyl groups take mutually trans positions in the isolated crystal, although thermal rotation of the 5-bromothienyl group may take place in solution. The porphyrin ring in monomer **3** is $\pi-\pi$ stacked in a slipped mode in the crystal, similar to other porphyrin derivatives.

Polymerization. We attemped to prepare π-conjugated zinc porphyrin polymers using the following three methods: (a) $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) promoted polycondensation (eqs 3i and 3ii);[8c,d] (b) Pd-complex-catalyzed polycondensation using Stille coupling[11] (eq 4); and (c) Pd-complex-catalyzed polycondensation using Sonogashira coupling (eqs 5i and 5ii). The polymerizations are shown above.



Among the above polymerizations, only about half of them gave polymers with M_n values higher than about 5000 in GPC analyses or $[\eta]$ values higher than about 0.1 dL g^{-1}. Other polymerizations gave oligomeric products in high yields.

Table 1 summarizes the yield, solubility, molecular weight determined by GPC (polystyrene standards), and $[\eta]$ of the obtained polymers. It is seen that use of Br−Ar−Br or HC≡C−Ar′-C≡CH with long alkyl chain(s) gives the polymers, whereas other monomers afford only oligomeric products. Polymers **1**−**4** were very soluble in organic solvents, and polymers **5**−**7** were partly soluble. These polymers prepared according to eq 6ii did not show high solubility, presumably due to a tendency to form a $\pi-\pi$ stacked structure between the zinc porphyrin units. For the partly soluble polymers, the GPC data are given only for the soluble part in Table 1.[12] The soluble and insoluble parts gave essentially the same IR spectrum.

Polymers **1** and **4** showed high M_n values of 37900 and 12200, respectively, from GPC analysis (Table 1). The M_n value of polymer **1** corresponds to a degree of polymerization of 34, which is high compared to those of already reported metalloporphyrin polymers,[13] and the polymer gives an $[\eta]$ value of 0.31 dL g^{-1} in chloroform. The polymers afforded films with smooth surfaces suitable for optical and electrochemical analyses, which were obtained by casting from the solutions.

IR and ^1H NMR data of the polymers are given in the Supporting Information. All the polymers show an IR absorption peak assigned to the ν(C=C) vibration of the porphyrin ring in the range of 1455−1465 cm^{-1}. The absence of peaks due to ν(C−Br) and terminal ν(C≡*C*−*H*) vibrations in the IR spectra of polymers indicates the occurrence of the desired polycondensation. Polymers obtained according to eqs 6i and 6ii show a ν(C≡C) peak of disubstituted acetylenes[10] at about 2200 cm^{-1}.

The ^1H NMR data of the polymers support the proposed structures. Peak area ratios for the polymers agree with the proposed structures. The ^1H NMR spectrum of polymer **4** exhibits two thiophene peaks at δ 7.8 and 7.5 with a peak area ratio of about 7:1. Since the thiophene-H of the terminal halogenated thiophene unit appears at a lower magnetic field,[9b] the peak at δ 7.5 is assigned to the terminal halogenated thiophene unit. The molecular weight of polymer **4** calculated from the peak area ratio of the two peaks is about 22000.

Optical Properties. UV−Vis Spectrum. Table 2 summarizes the optical properties of the monomers, the model compounds, and the polymers. The monomer shows a sharp Soret band with a half bandwidth of

Table 2. Optical Data of Monomers, Model Compounds, and Polymers

	absorption in $CHCl_3$/nm			absorption in $CHCl_3$ containing DABCO[a]/nm			absorption of film[b]/nm			photoluminescence in $CHCl_3$/nm	EX[c]
	B (Soret)	Q(1,0)	Q(0,0)	B (Soret)	Q(1,0)	Q(0,0)	B (Soret)	Q(1,0)	Q(0,0)		
monomer **1**	417	542	583							592, 644	416
2	418	548	583							590, 644	416
3	430	571	614							635, 691	432
4	417	547	584								
5	430	569	613								
polymer **1**	416, 430 ($\Delta = 780$ cm^{-1})[e]	543	582	426, 438	555	595	423[h]	552	556	590, 642	416
2	416	546	584							590, 639	416
3	415[f], 427	544	602							591, 643	
4	417, 431 (1370 cm^{-1})	547	585	418, 433	555	590	418[g], 433[h]	551	590	591, 646	422
5	454[h], 490[g] (1620 cm^{-1})	697[h]								724	455
6	448[h], 490[g] (1910 cm^{-1})	645[h]		455[h]	650[h]		434[h], 500[g]	670[h]		695	450
7	440[f,h]	645[f,h]		456[h]	657[h]		440[h]	655[h]		693	440

[a] DABCO: 1,4-Diazabicyclo[2.2.2]octane. An excess amount of DABCO to polymer was added. [b] Film formed on glass substrate by casting. [c] Peak position of the excitation spectrum monitored at the photoluminescence peak. [d] In formic acid. [e] Degree of the energy splitting. [f] In CH_2Cl_2. [g] Shoulder peak. [h] Broadened.

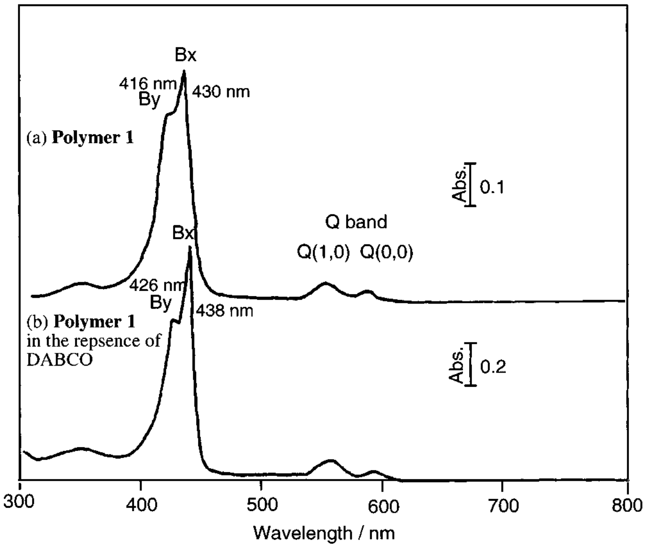
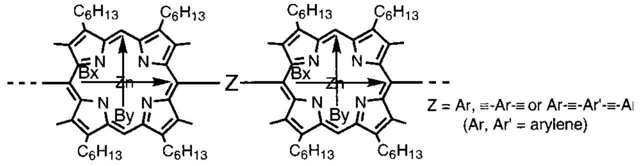


Figure 1. UV–visible spectra of $CHCl_3$ solutions of (a) polymer **1** and (b) polymer **1** in the presence of DABCO.

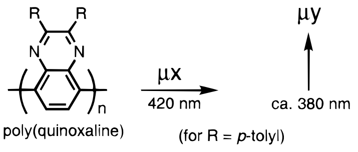
Chart 1. Soret Transition for Porphyrin Polymer



about 20 nm in organic solvents, although the peak position is shifted due to π-conjugation with $-$Ar$-$Br or $-C{\equiv}C-$Ar units.

All the polymers give peaks in the regions of the Soret band (B band) and the Q-band both in $CHCl_3$ solution and as films on a glass plate. Peak shape and intensity varied depending on the structure of the polymers. Clear peak splitting (with the degree of energy splitting of 780–1910 cm^{-1}; cf. the second column of Table 2) of the Soret band was observed in polymers **1**, **4**, **5**, and **6**. Figure 1a shows the UV–vis spectrum of polymer **1**. Zinc porphyrin itself and the monomeric compounds do not show such splitting, and the splitting of the Soret bands has been explained by the electronic coupling between the zinc porphyrin units.[4,14] As depicted in Chart 1, the Soret band of the porphyrin unit is considered to originate from two electronic transitions *Bx* and *By*, which are perpendicular to each other. *Bx* is due to the transition along the axis joining the porphyrin units and *By* is due to the transition perpendicular to *Bx*.

The peak due to *Bx* usually appears at a longer wavelength than that due to *By*.[15] The *By* peak is considered to be weakly affected by the π-conjugation system along the polymer chain, whereas the Bx peak seems to be sensitive to it. A similar situation has been observed in π-conjugated aromatic polymers such as the following poly(quinoxaline)s.[16] This polymer shows two main UV–vis absorption peaks, one at a longer wavelength and assigned to the transition along the π-conjugated main chain (μx) and the other at a shorter wavelength and assigned to a transition perpendicular to the π-conjugated main chain (μy).



The UV–vis peak assigned to the B*y* transition appears near the UV–vis peaks of monomeric quinoxalines, whereas the UV–vis peak assigned to the B*x* transition appears at a longer wavelength due to the expansion of the π-conjugation. In the cast film, the two Soret bands of polymers **1** and **4** are broadened; however, their positions seem unchanged. Among the oligomeric products prepared according to eq 3i, the one with the pyridine ring showed a large splitting (1370 cm^{-1}) of the Soret band.

When the $-C{\equiv}C-$ unit is directly bonded to the zinc porphyrin unit, as in the cases of polymers **5**–**7**, the Soret and Q-bands are shifted to a longer wavelength, suggesting the formation of a highly π-conjugated system along the main chain due to the lack of steric hindrance around the zinc porphyrin ring. Anderson reported that the UV–vis peaks of oligomeric zinc porphyrin linked by $-C{\equiv}C-C{\equiv}C-$ groups appeared at similar positions.[6] A linear and coplanar structure of compounds of the Ar$-C{\equiv}C-$Ar′ type was revealed by X-ray crystallography.[17] As shown in Figure 2, the UV–vis absorption bands of polymers **5-7** are broadened even in solution, and the shoulder peaks of polymers **5** and **6** at 490 nm suggest the splitting of the Soret band. The Q-bands are also broadened. The splitting of the Soret band in oligomeric zinc porphyrin compounds with $-C{\equiv}C-X-C{\equiv}C-$ spacing units has been reported.[4,6]

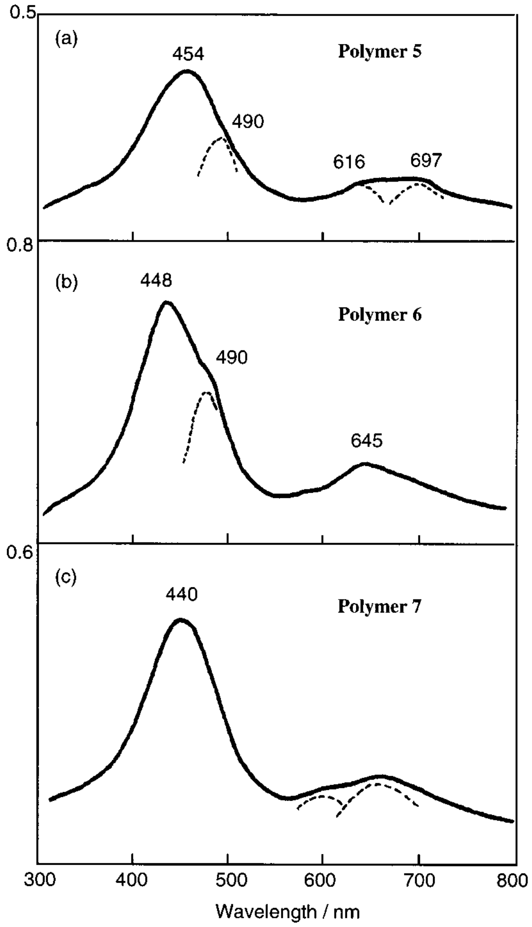
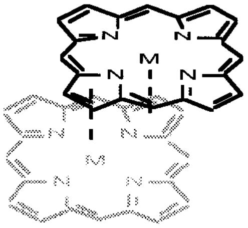


Figure 2. UV−visible spectra of $CHCl_3$ solutions of polymers (a) **5**, (b) **6**, and (c) **7**.

Chart 2. Self-Aggregation of Metalloporphyrin



Metalloporphyrins often aggregate via a direct π−π interaction, as shown in Chart 2[6,18] or by assistance from a bidentate ligand bridging two metal centers.

As shown in Table 2 and in Figure 1b, both the Soret and Q-bands of the zinc porphyrin polymers shift to a longer wavelength by about 10 nm upon the addition of 1,4-diazabicyclo[2,2,2]octane (DABCO), a typical bidentate ligand, to the chloroform solution of the polymers (fifth-seventh columns in Table 2). The formation of (a) a 1:1 complex of zinc porphyrin and DABCO and (b) a ladder-type complex of polymer **1** ligating DABCO onto the Zn metal in $CHCl_3$ is conceivable. A similar self-assembled ladder-type complex of a porphyrin dimer with DABCO was reported.[6] The formation of the ladder-type complex led to a shift of the ^1H NMR peak of *meso*-H to a higher magnetic field by about $\delta = 0.05$ ppm. A similar peak shift ($\delta = 0.08$ ppm) was observed in the ^1H NMR spectrum of polymer **1** in $CDCl_3$ containing DABCO. Thin films of the polymers were obtained by casting $CHCl_3$ solutions of polymers on glass plates, and the polymer films gave UV−vis data similar to those of polymers in chloroform.

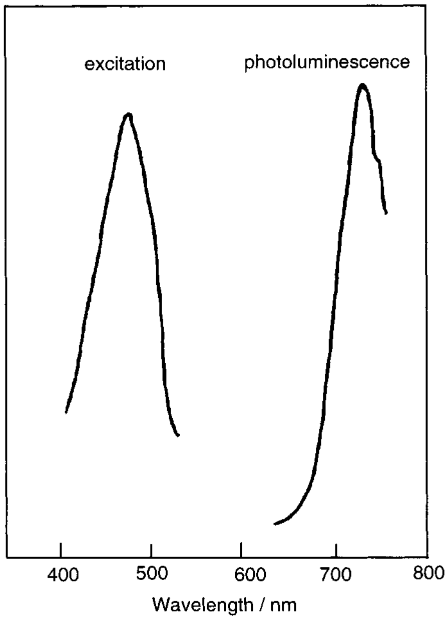


Figure 3. Phtoluminescence (right) and excitation (left) spectra of polymer **5**, in $CHCl_3$.

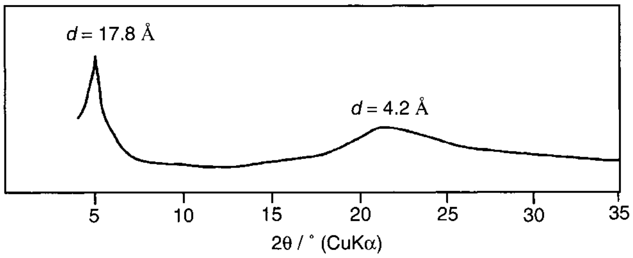


Figure 4. Powder X-ray diffraction pattern of polymer **1**.

Photoluminescence. Figure 3 shows the photoluminescence spectrum of polymer **5** in $CHCl_3$. Polymers **2**−**4**, which have the spacing arylene unit directly bonded to the zinc porphyrin unit, show two emission peaks at positions near the emission peaks of the corresponding monomers (cf. Table 2). The photoluminescence peaks of polymers **5**−**7** appear at a longer wavelength than those of other polymers, in accord with their UV−vis data (vide infra). Since internal conversion is rapid,[4] photoluminescence seems to occur at the onset position(s) of the Q-band(s); on the other hand, the excitation spectrum exhibits a peak at a position near the Soret band.

Powder X-ray Diffraction. As depicted in Figure 4, the powder X-ray diffraction pattern of polymer **1** shows two peaks at $d = 17.8$ and $d =$ about 4.2 Å, suggesting that the polymer takes an ordered structure assisted by the packing of long alkyl side chains, similar to the cases of regioregular poly(3-alkylthiophene-2,5-diyl)s.[19] The peak at $d = 17.8$ Å may correspond to the distance between core polymer chains separated by long alkyl side chains. Loose packing of alkyl chains often gives a broad peak at $d = 4.2$ Å, which corresponds to the distance between them.

Thermal Properties. TGA revealed that the 5% weight loss temperature for polymer **1** with a molecular weight of 37900 was 402 °C. TGA data of polymers **5**, **6**, and **7** are given in the Supporting Information.

Electronic Properties. Cyclic Voltammogram. Table 3 shows cyclic voltammogram (CV) data of cast films of the polymers. The film gives rise to an electro-

Table 3. Electrochemical Data for the Film of Polymers

	peak potential[a]/V					
polymer	E_{paI} (p-doping)	E_{paII}	E_{pcI} (p-undoping)	E_{pcII}	E_{pc} (n-doping)	E_{pa} (n-undoping)
1	0.46	0.68				
3	0.62	0.90	0.34	0.84	−0.60	−1.6
5	0.42	0.78	0.36	0.70	−1.8	−1.7
6	0.54	0.80	0.54			0.54

[a] Versus Ag^+/Ag. Measured in an acetonitrile solution of $[Et_4N]BF_4$ (0.1 M).

chemically active cycle in both oxidation and reduction regions. In the oxidation region, two couples of redox peaks were observed at E_{pa}'s of 0.62 and 0.90 V and E_{pc}'s of 0.34 and 0.84 V vs Ag^+/Ag, for polymer **3**. They are assigned to the first and second redox cycles of the zinc porphyrin (Por) unit, as shown in eqs 6i and 6ii. The

$$\text{Por} + BF_4^- \underset{+e,\ 0.34\ V}{\overset{-e,\ 0.62\ V}{\rightleftharpoons}} \underset{\text{Salt of radical cation}}{Por^{\bullet +}BF_4^-} \qquad (6i)$$

$$Por^{\bullet +}BF_4^- + BF_4^- \underset{+e,\ 0.84\ V}{\overset{-e,\ 0.90\ V}{\rightleftharpoons}} \underset{\text{Salt of dication}}{Por^{2+}2BF_4^-} \qquad (6ii)$$

reduction region also gives redox peaks with reduction (or n-doping) peaks at −1.8 V and the corresponding oxidation (or n-undoping) peaks at −1.7 V. These peaks are assigned to the following redox processes shown in eq 6iii.

$$\text{Por} + Et_4N^+ \underset{-e,\ -1.7\ V}{\overset{+e,\ -1.8\ V}{\rightleftharpoons}} Por^{\bullet -}Et_4N^+ \qquad (6iii)$$

The electrochemical processes are accompanied by color changes (electrochromism) of the film between black and yellowish green in the oxidation region and between red and yellowish green in the reduction region.

Poly(aryleneethynylene) type polymers are usually inactive toward electrochemical oxidation due to the presence of electron-withdrawing −C≡C− units.[20] However, polymers **3**−**7** were electrochemically active both in the oxidation and reduction regions, due to their having the electrochemically active large zinc porphyrin units (cf. Table 3).

Conclusion

Various π-conjugated zinc porphyrin polymers with the −Ar− or −C≡C−Ar−C≡C− spacing group were obtained by the organometallic polycondensation. Polymers with long side chains in the −Ar− group were fully soluble in organic solvents, and one of the polymers showed M_n of 37 900 and an $[\eta]$ value of 0.31 dL g^{-1}. The spacing groups lead to splitting of Soret band, similar to previously reported oligomeric zinc porphyrins.[4−6] Casting of solutions of the polymers gave free-standing films. Thin films of the polymers were electrochemically active in both the oxidation (p-doping) and reduction (n-doping) regions and show electrochromism. Because of the interesting properties, processability, and thermal stability of the polymers, these kinds of polymers may be useful materials to prepare electronic and optical devices.

Experimental Section

General Considerations, Materials, and Measurements. Solvents were dried over CaH_2 and distilled before use. Elemental analyses were carried out on a Yanaco MT-5 CHN autocorder. IR and NMR spectra were recorded on a JASCO−IR 810 spectrophotometer and JEOL EX-400 and EX-90 spectrometers, respectively. UV−vis spectra, photoluminescence spectra, and X-ray diffraction patterns were recorded on a Shimadzu UV-2100PC spectrometer, a Hitachi F-4010 spectrometer, and a Philips PS-1051 X-ray diffractometer, respectively. Polymer films were cast from chloroform solutions on a quartz glass plate or a Matsunami nonfluorescent glass plate. GPC analyses were carried out by a Toso HPLC 8120 equipped with polystyrene gel columns (TSK gel G2500, G4000, and G5000) (eluent = THF) and by a Shimadzu liquid chromatography system with a Shodex 80 M column (eluent = chloroform). TGA analyses were performed on a Shimadzu TGA-50 thermal analyzer under nitrogen at a heating rate of 10 °C min^{-1}. Cyclic voltammetry was carried out in an acetonitrile solution containing 0.1 M $[Et_4N]BF_4$ with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko KB-104 function generator. Polymer films were cast from chloroform solutions. 1,4-Diethynyl-2,5-didodecyloxybenzene,[21a] 2,5-didodecyloxybenzene,[21b] and 2,5-dibromo-6-hexylpyridine[21c] were prepared according to the literature.

Synthesis of Monomers 1−5. To a methanol (65 mL) solution of bis(3-hexyl-4-methyl-2-pyryl)methane (1.8 g, 5.3 mmol) and *p*-bromobenzaldehyde (0.97 g, 5.3 mmol) was added *p*-toluenesurfonic acid (0.26 g, 1.4 mmol). The mixture was stirred at 20 °C for 6 h and at 0 °C for 16 h to give a precipitate which was washed with methanol and recrystallized from ethyl acetate to afford bis(4-bromophenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphynogen (2.17 g, 81%) as a light yellow crystal.

To a THF (100 mL) solution of bis(4-bromophenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphynogen (2.2 g, 2.1 mmol) was added a THF (28 mL) solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.8 g, 7.7 mmol) by portions, and the mixture was stirred at 20 °C for 1.5 h. After the mixture was extracted with chloroform, the organic layer was washed with 10% NaOH(aq) and water, and dried over anhydrous magnesium sulfate. The solvent was removed by evaporation, and the resulting solid was recrystallized from chloroform and methanol to give 5,15-bis(4-bromophenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin (1.6 g, 88%) as purple crystals. ^1H NMR (400 MHz in $CDCl_3$): δ, 10.21 (s, 2H, hydrogens at *meso*-position), 7.85 (ABq, 8H, J = 6.4 and 19 Hz, hydrogen of benzene ring), 3.95 (t, 8H, J = 7.8 Hz, $CH_2(CH_2)_4CH_3$), 2.48 (s, 12H, CH_3 bonded to porphyrin), 2.21−2.13 (m, 8H, $CH_2CH_2(CH_2)_3CH_3$), 1.76−1.70 (m, 8H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.51−1.43 (m, 8H, $(CH_2)_3CH_2CH_2CH_3$), 1.40−1.31 (m, 8H, $(CH_2)_4CH_2CH_3$), 0.90 (t, 12H, J = 7.1 Hz, $(CH_2)_5CH_3$), −2.44 (br, 2H, NH). $^{13}C\{^1H\}$ NMR (100 MHz in $CDCl_3$): δ, 144.9, 143.6, 141.6, 141.3, 135.9, 134.5, 130.7, 122.6, 116.3, 97.2, 33.3, 32.0, 30.0, 26.8, 22.7, 15.0, 14.1. Mp: 215−216 °C (decomp.). Anal. Calcd for $C_{56}H_{72}Br_2N_4S_2$: C, 65.61; H, 7.08; N, 5.47. Found: C, 65.50; H, 7.34; N, 5.51.

After a THF (8.5 mL) solution containing 5,15-bis(2-bromophenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin (0.30 g, 0.30 mmol) and zinc acetate dihydrate (0.14 g, 0.62 mmol) was refluxed for 2 h, the solvent was removed by evaporation and the resulting solid was recrystallized from THF and methanol to give 5,15-bis(2-bromophenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin zinc (monomer **1**) as a red crystal (0.32 g, 100%). ^1H NMR (400 MHz in $CDCl_3$): δ, 10.02 (s, 2H, hydrogens at *meso*-position), 7.87 (s, 8H, hydrogens of benzen ring), 3.84 (br, 8H, $CH_2(CH_2)_4CH_3$), 2.41 (s, 12H, CH_3 bonded to porphyrin), 2.11 (br, 8H, $CH_2CH_2(CH_2)_3CH_3$), 1.71 (t, 8H, J = 8.3 Hz, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.32−1.08 (m, 16H, $(CH_2)_3(CH_2)_2CH_3$), 0.93 (t, 12H, J = 7.1 Hz, $(CH_2)_5CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz in $CDCl_3$): δ, 147.4, 146.3, 143.7, 142.7, 137.6, 134.8, 130.5, 122.3, 117.6, 97.6, 33.3, 31.9, 30.0, 26.6, 22.7, 15.5, 14.1. Anal. Calcd for $C_{60}H_{74}Br_2N_4Zn$: C, 66.95; H, 6.93; N, 5.20. Found: C, 66.45; H, 6.86; N, 5.13.

Monomers **2**−**5** were synthesized in a similar manner, and synthesis of monomer **3** was partly reported.[22]

Data for monomer **2**. ^1H NMR (400 MHz in $CDCl_3$): δ, 10.12 (s, 2H, hydrogens at *meso*-position), 7.76 and 7.29 (d, 4H, J =

7.3 Hz, 2 and 3-positions of pyridine ring), 6.90 (br, 2H, 5-position of pyridine ring), 3.90 (m, 8H, $CH_2(CH_2)_4CH_3$), 2.10 (t, 12H, $J = 7.8$ Hz, CH_3 bonded to porphyrin), 1.91 (br, 8H, $CH_2CH_2(CH_2)_3CH_3$), 1.71 (t, 8H, $J = 7.8$ Hz, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.50−1.33 (m, 16H, $(CH_2)_3(CH_2)_2CH_3$), 0.90 (t, 12H, $J = 7.3$ Hz, $(CH_2)_5CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz in $CDCl_3$): δ, 152.2, 147.6, 146.9, 144.2, 141.4, 138.7, 136.8, 126.2, 122.8, 98.1, 33.4, 32.0, 30.0, 26.8, 22.8, 16.2, 14.1. Anal. Calcd for $C_{58}H_{72}Br_2N_6Zn$: C, 64.60; H, 6.73; N, 7.79. Found: C, 64.50; H, 6.72; N, 7.79. The starting bromopyridiylaldehyde was prepared according to the literature.[23]

Data for monomer **3**. ^1H NMR (400 MHz in $CDCl_3$): δ, 9.94 (s, 2H, hydrogens at *meso*-position), 7.43 (d, 4H, $J = 3.9$ Hz, hydrogens of thiophene ring), 3.82 (t, 8H, $J = 7.8$ Hz, $CH_2(CH_2)_4CH_3$), 2.77 (s, 12H, CH_3 bonded to porphyrin), 2.12−2.09 (m, 8H, $CH_2CH_2(CH_2)_3CH_3$), 1.73−1.70 (m, 8H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.59−1.51 (m, 8H, $(CH_2)_3CH_2CH_2CH_3$), 1.50−1.24 (m, 8H, $(CH_2)_4CH_2CH_3$), 0.93 (t, 12H, $J = 7.1$ Hz, $(CH_2)_5CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz in $CDCl_3$): δ, 148.4, 147.3, 146.3, 143.8, 137.9, 132.6, 129.3, 112.9, 108.5, 98.1, 33.2, 32.0, 30.0, 26.5, 22.8, 14.3, 14.2. Mp: 236−238 °C. Anal. Calcd for $C_{56}H_{70}Br_2N_4S_2Zn$: C, 61.79; H, 6.48; N, 5.15. Found: C, 61.86; H, 6.55; N, 5.08. 2-Bromothiophene-5-carboxaldehyde was used as purchased.

Data for monomer **4**: ^1H NMR (400 MHz in $CDCl_3$): δ, 9.99 (s, 2H, hydrogens at *meso*-position), 7.44 (s, 4H, hydrogen of thiophene ring), 3.85 (t, 8H, $J = 7.5$ Hz, $CH_2(CH_2)_4CH_3$), 2.91 (t, 8H, $J = 7.5$ Hz, CH_2 bonded to thiophene ring), 2.80 (s, 12H, CH_3 bonded to porphyrin), 2.14−0.89 (m, 66H, $CH_2(CH_2)_4CH_3$). Anal. Calcd for $C_{68}H_{94}Br_2N_4S_2Zn$: C, 64.98; H, 7.54; N, 4.46. Found: C, 65.20; H, 7.69; N, 4.42.

2-Bromo-3-hexylthiophene-5-carbaldehyde was prepared from 2-bromo-3-hexylthiophene.[18b] Butyllithium (24.1 mmol) was added to a THF (112 mL) solution of diisopropylamine (24.1 mmol) at 0 °C and the mixture was stirred for 40 min at −40 °C. After cooling to −78 °C, 2-bromo-3-hexylthiophene (24 mmol) was added dropwise, and the mixture was stirred for 40 min at −40 °C. After cooling to −60 °C, DMF (36 mmol) was added and the reaction mixture was stirred for 12 h at room temperature. Workup including column chromatography on SiO_2 (eluent = ethyl acetate:hexane = 1:4) gave the aldehyde in 86% yield. ^1H NMR ($CDCl_3$): δ 9.8 (s, 1H), 7.5 (s, 1H), 2.6 (t, 2H), 1.6−0.9 (m, 11H).

Data for monomer **5**. ^1H NMR (90 MHz in $CDCl_3$): δ, 10.10 (s, 2H, hydrogens at *meso*-position), 4.47 (s, 2H, $HC\equiv C$), 4.00 (t, 8H, $J = 7.5$ Hz, $CH_2(CH_2)_4CH_3$), 3.68 (s, 12H, CH_3 bonded to porphyrin), 2.23−1.26 (br, 32H, $CH_2(CH_2)_4CH_3$), 0.91 (t, 12H, $J = 7.1$ Hz, $(CH_2)_5CH_3$). Anal. Calcd for $C_{52}H_{68}N_4Zn$: C, 76.68; H, 8.41; N, 6.88. Found: C, 76.92; H, 8.41; N, 6.81.

$Ni(cod)_2$-Promoted Polycondensation. Synthesis of Polymer 1. Monomer **4** (140 mg, 0.11 mmol) was added to a toluene (10 mL) solution of a mixture of $Ni(cod)_2$ (65 mg, 0.24 mmol), 1,5-cyclooctadiene (2 mL), and 2,2′-bipyridine (37 mg, 0.24 mmol). After being stirred for 48 h at 60 °C, the reaction mixture was poured into an excess amount of hexane to obtain a reddish purple precipitate, which was washed with NH_4OH, dilute aqueous HCl, an aqueous ammonia solution containing disodium ethylenediaminetetraacetate, NH_4OH(aq), and methanol in this order. The purple powder was collected by filtration and dried under vacuum to obtain polymer **1** as a reddish purple powder (98 mg, 79%). Anal. Calcd for $(C_{70}H_{98}N_4S_2Zn)_n$: C, 74.9; H, 8.8; N, 5.0. Found: C, 73.3; H, 8.2; N, 4.9. IR and ^1H NMR data are given in the Supporting Information. Polymer **2** was prepared analogously.

Pd Complex Catalyzed Sonogashira Type Polycondensation. Synthesis of Polymer 4. Monomer **3** (0.11 g, 0.10 mmol), $Pd(PPh_3)_4$ (6.3 mg, 5.4×10^{-3} mmol), and CuI (1 mg, 5.3×10^{-3} mmol) were added to a mixture of toluene (3 mL) and triethylamine (3 mL). After the mixture was stirred at room temperature for a few minutes, 1,4-diethynylbenzene (0.013 g, 0.10 mmol) was added to the mixture. After the reaction mixture was stirred at 60 °C for 24 h, the solvent was condensed by evaporation to a half volume. The solution was poured into methanol to give a precipitate, which was collected by filtration and washed with methanol two times and ethyl acetate to give polymer **4** as a purple solid (0.08 g, 57%).

Syntheses of polymers **10**, **11**, and **13**−**16** were carried out in similar manners. IR and ^1H NMR data are shown in Table 2.

X-ray Crystal Analysis of Monomer 3. Crystal data: $C_{56}H_{70}Br_2N_4S_2Zn$, $M_r = 1104.50$, triclinic, $P1$ (No. 2), $a = 15.90(1)$, $b = 17.08(1)$, $c = 10.531(6)$ Å, $V = 2711(3)$ Å^3, $\alpha = 101.84(6)$, $\beta = 90.99(5)$, $\gamma = 103.73(6)°$, $Z = 2$, $\mu = 20.49$ cm^{-1}, $F(000) = 1148$, $D_{calcd} = 1.352$ Mg m^{-3}, 2θ range = 6.0−45.0°, hkl ranges: $0 \leq h \leq 11$, $-13 \leq k \leq 13$, $-6 \leq l \leq 6$, no. of unique reflections = 3228, no. of used reflections ($I > 3\sigma(I)$) = 739, no. of variables = 589. The final $R(F_o)$ and $R_w(F_o)$ values were 0.026 and 0.021, respectively; $R = \Sigma||F_o|| - |F_c|/\Sigma|F_o|$; $R_w = [\Sigma w|F_o - F_c|^2/\Sigma w|F_o|^2]^{1/2}$; weighting scheme $w = [\{\sigma(F_o)^2]^{-1}$. The unit cell parameters were obtained by least-squares refinement of 2θ value of 25 reflections with $25° \leq 2\theta \leq 35°$.

Intensities were collected on a Rigaku AFC-5R automated four-cycle diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) and the $\omega-2\theta$ method. An empirical absorption correction (φ-scan method) of the collected data was applied. Calculations were carried out by using the program package teXsan on a VAX-II computer. Atomic scattering factors were taken from the literature.[24] A full-matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming ideal positions and were included in the structure calculation without further refinement of the parameters.

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Supporting Information Available: Figures showing NMR data and the X-ray crystal structure of monomer **3**. This material is available free of charge via the Internet at http// pubs.acs.org.

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(12) Since GPC analysis of monomer **3** with a molecular weight of 1089 under the same conditions gave a lower M_n of 640, real molecular weights of the polymers may be higher than those determined by the GPC analysis. The ^{1}H NMR spectrum of oligomer **1** (eq 3i) exhibits two thiophene-H peaks at δ 7.7 and 7.5. Since the thiophene-H of terminal halogenated thiophene unit appears at a lower magnetic field,[9b] the peak at δ 7.5 was assigned to the terminal bromothiophene unit. Relative peak area of the two peaks gave a M_n of 4700, whereas the GPC analysis of oligomer **1** gave M_n of 1500.

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