Poly(1,10-phenanthroline-3,8-diyl) and Its Derivatives. Preparation, Optical and Electrochemical Properties, Solid Structure, and Their Metal Complexes

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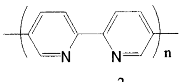
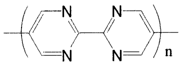
ABSTRACT: π-Conjugated poly(1,10-phenanthroline-3,8-diyl), PPhen, and its 5,6-dialkoxy derivatives, PPhen(5,6-OR)s, have been synthesized by using an organometallic polycondensation with a zerovalent nickel complex. They had average molecular weights of 4300−6800. PPhen had a stiff structure, as revealed by a light scattering method, and exhibited a strong dichroism in UV−vis absorption and photoluminescence. PPhen(5,6-OR)s formed an end-to-end packing assembly assisted by the side chain crystallization of the OR groups. PPhen and PPhen(5,6-OR)s were susceptible to chemical and electrochemical reduction, and the reduced state showed certain stability toward oxygen in air. The π-conjugated polymers underwent quantitative complex formation with $[\mathrm{Ru(bpy)_2}]^{2+}$. Introduction of two more imine nitrogens in the repeating unit of PPhen enhanced much the electron accepting property of PPhen, and n-doping of the obtained polymer took place at E_{pc} of −1.38 V vs $\mathrm{Ag^+/Ag}$.

Introduction

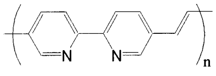
π-Conjugated polymers[1] constituted of chelating ligands such as 2,2′-bipyridyl (PBPy),[2] 2,2′-bipyrimidine (PBPym),[3] and 1,5-naphthyridine[4] are the subject of recent interest.[2−5] The chemical and optical properties of their metal complexes[2−6] have vigorously been investigated.[2−7] The chemical and physical properties of metal complexes of π-conjugated oligomeric ligands have also been investigated, for example, by Schanze.[8]



PBPy[2]



PBPym[3]

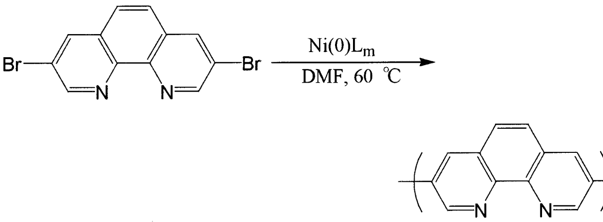


P(BPy-V)[5]

1,10-Phenanthroline is an attractive π-conjugated ligand, and its function to form molecular architectures[5a,9−14] (e.g. catenanes prepared by Sauvage[9]) has been pursued. However, π-conjugated polymers constituted of 1,10-phenanthroline have not received much attention. Herein we report the preparation, chemical properties, and functions of π-conjugated polymers consisting of the 1,10-phenanthroline unit. 1,10-Phenanthroline has considerably stronger (by 1 or 2 orders of magnitude) coordinating ability toward transition metals than 2,2′-bipyridyl,[15a,b] presumably due to its fixed cis-chelating structure in contrast to the case of 2,2′-bipyridyl, which takes a *s*-trans conformation.[15c,d]

Results and Discussion

Preparation. Organometallic dehalogenative polycondensation using a zerovalent nickel complex[1,16] gave the following π-conjugated poly(1,10-phenanthroline)s.

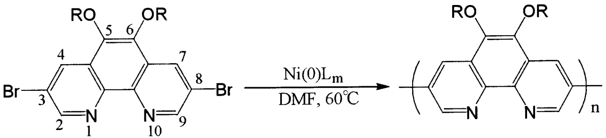


(1)

PPhen : M_w = 6800 ; 81% yield

[η] = 0.40 dLg^{-1}

Ni(0)Lm : a mixture of bis(1,5-cyclooctadiene) nickel(0), Ni(cod)$_2$, and 2,2'-bipyridyl, bpy



(2)

PPhen(5,6-OR) ; R = Pen (n-C_5H_{11})
Oct (n-C_8H_{17})
Dod (n-$C_{12}H_{25}$)
Hexd (n-$C_{16}H_{33}$)

The polycondensation proceeded smoothly, and good yields were attained.

Poly(1,10-phenanthroline-3,8-diyl), PPhen, was soluble in formic acid and partially soluble in sulfuric acid; however, it was not soluble in common organic solvents. PPhen had a weight average molecular weight, M_w, of 6800, as determined by light scattering analysis[17a−c] in formic acid, the M_w value corresponding to a degree of polymerization (n in eq 1) of 38. PPhen showed no content of Br in the elemental analysis, indicating that the formed polymer had a polymer−Ni terminal group and this terminal group was converted into a polymer−H group during workup, similar to the case of polypyridine.[2b]

PPhen gave an intrinsic viscosity, [η], of 0.40 dL g^{-1} in formic acid. This [η] value corresponds to a molecular

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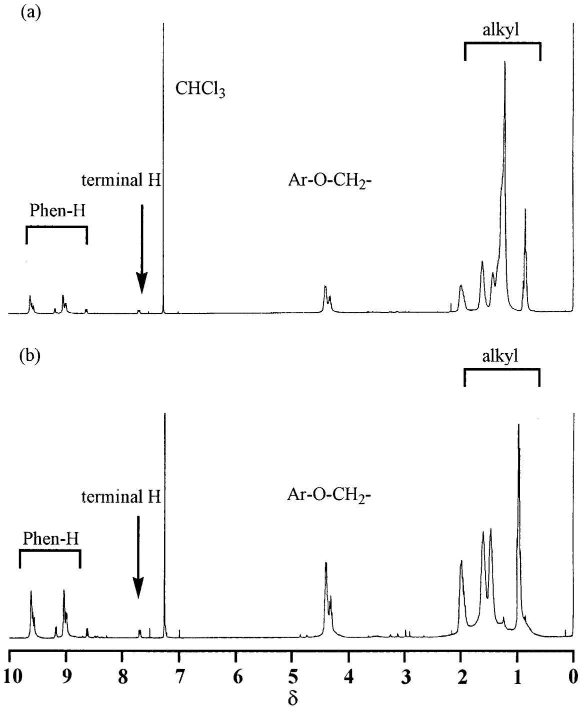


Figure 1. ^1H NMR spectra of (a) PPhen(5,6-ODod) and (b) PPhen(5,6-OPen) in $CDC1_3$.

weight of 79 000 for polystyrene.[17d] The light scattering analysis of PPhen gave a degree of depolarization, ρ_v, of 0.15. The ρ_v value can be taken as a measure for stiffness of polymers,[17a−c] and the obtained ρ_v value is comparable to that of a stiff all aromatic polyamide, poly(1,4-phenylene terephthalamide) or Kevlar, in sulfuric acid; poly(1,4-phenylene terephthalamide) shows ρ_v values of 0.175 and 0.11 at M_w values of 4500 and 35 000, respectively.[17c] The IR spectrum, ^1H NMR spectrum of PPhen in formic acid-d_2, and CP-MAS solid ^{13}C NMR spectrum of PPhen are given in the Supporting Information.

PPhen 5,6-dialkoxy derivative, PPhen(5,6-OR), type polymers were soluble in chloroform; however, they showed lower solubility in THF and DMF. Gel permeation chromatography (GPC) using chloroform as an eluent was not suited for determination of the molecular weight of the polymer due to strong interaction between the polymer and the column. One of the polymers, PPhen(5,6-OPen), was soluble in hexafluoroisopropanol, which had been used for GPC analysis of π-conjugated N-containing heteroaromatic polymers,[18] and the GPC analysis using the solvent gave a number average molecular weight, M_n, of 17 000 and M_w of 33 000 (vs poly(methyl methacrylate) standards), respectively. PPhen(5,6-OPen), PPhen(5,6-OOct), and PPhen(5,6-ODod) did not contain Br; on the other hand, PPhen(5,6-OHexd) contained Br in 0.5 wt % (cf. Experimental Section). This negligible or small content of Br supports a view that PPhen(5,6-OR)s have mainly an H-terminated Phen group. ^1H NMR spectra of PPhen(5,6-OR)s exhibited a small peak assigned to the 3-H proton in the terminal PPhen unit, as shown in Figure 1, and the peak area of the 3-H proton gave M_n of 6000, 4300, 5600, and 6100 for PPhen(5,6-OPen), PPhen(5,6-OOct), PPhen(5,6-ODod), and PPhen(5,6-OHexd), respectively. The larger M_n value of 17 000 estimated from the GPC analysis for PPhen(5,6-OPen) may be due to a stiff structure of PPhen(5,6-Pen), since a stiff polymer is considered to have a larger effective volume than that of the random-coil type poly(methyl methacrylate) used as the standard for the GPC analysis. The ^1H NMR peak area ratio between the aromatic-H and aliphatic-H agreed with the structure of PPhen(5,6-OR).

IR spectra of the polymers agreed with the structures shown in eqs 1 and 2. They showed peaks originated from the monomers, except for the ν(C−Br) peaks at about 1100 cm^{-1} (cf. the Supporting Information).

UV−vis Data. The UV−vis absorption peak of 1,10-phenanthroline at 277 nm in formic acid was shifted to 382 nm in PPhen due to the expansion of the π-conjugation system, the peak position being located near those of poly(pyridine-2,5-diyl) (374 nm) and poly(2,2′-bipyridine-5,5′-diyl) (373 nm).[2] For monomeric 1,10-phenanthroline itself, its UV−vis absorption peak was shifted from 265 nm in diethyl ether to 277 nm in formic acid. The absorption band of PPhen at 382 nm was sharp with a half-width of about 45 nm, and nonprotonated PPhen was considered to give the UV−vis band at somewhat shorter wavelength.

PPhen(5,6-OR)s also gave the UV−vis peak (λ_{max} = 353−359 nm ($\epsilon = (2.1-2.4) \times 10^4\ M^{-1}\ cm^{-1}$ on the basis of the repeating unit; cf. Table 1) near the λ_{max} position of PPhen; the λ_{max} position was shifted to a longer wavelength by 61−68 nm from that of the corresponding monomers. As shown in Table 1, the UV−vis absorption peak of PPhen(5,6-OR)s is shifted to a longer wavelength by 10−20 nm in the film, and this suggests the presence of intermolecular electronic interaction such as $\pi-\pi$ interaction due to formation of a π-stacked structure.[19−21]

Alignment of PPhen in a Stretched PVA Film. Due to the stiff structure of PPhen, it exhibited alignment in a stretched PVA (poly(vinyl alcohol)) film. Painting the PVA film with the formic acid solution of PPhen and drying up the film under vacuum gave the

Table 1. Synthetic and Optical Data of Polyphenanthrolines

			molecular weight[a]			UV−vis peak,[c] nm		PL peak,[c,d] nm	
no.	polymer	yield, %	M_n	M_w	$[\eta]$,[b] dL g^{-1}	in solution	film	in solution	film
1	PPhen	81		6800(L)	0.40	382(F)	380	413(F)	535
2	PPhen(5,6-OPen)	84	17000(G) 6000(N)	33000(G)		359(C)	369	504(C)	530
3	PPhen(5,6-OOct)	63	4300(N)			356(C)	368	485(C)	518
4	PPhen(5,6-ODod)	74	5600(N)			359(C)	380	478(C)	517
5	PPhen(5,6-OHexd)	86	6100(N)			353(C)	371	468(C)	520
6	PDPypd	70	3000(G)[f]			370(F)[e] 435(D)[e,f]	370	500(F) 500(D)	

[a] M_n = number average molecular weight. M_w = weight average molecular weight. L, determined by light scattering; G, determined by GPC; N, determined from ^1H NMR data. [b] Intrinsic viscosity. dL = 100 mL. [c] F, in formic acid; C, in chloroform; D, in N,N-dimethylformamide (DMF). [d] PL = photoluminescence. [e] An additional weak peak at about 440 nm is observed. [f] For a DMF soluble part.

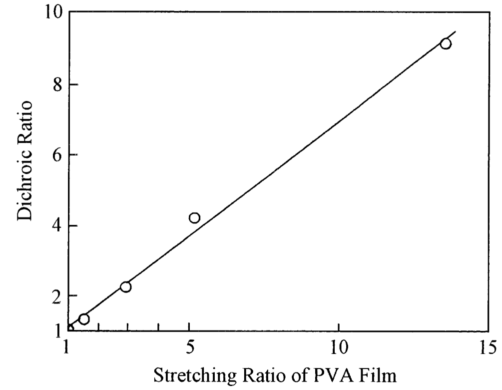


Figure 2. Dichroism of the stretched PVA film containing PPhen. At 385 nm. Dichroic ratio = Abs(||)/Abs(⊥); Abs(||) and Abs(⊥) are absorbances observed on irradiation with light with the oscillating electric field parallel and perpendicular, respectively, to the direction of the stretching of the PVA film. For the stretching ratio, cf. the Supporting Information.

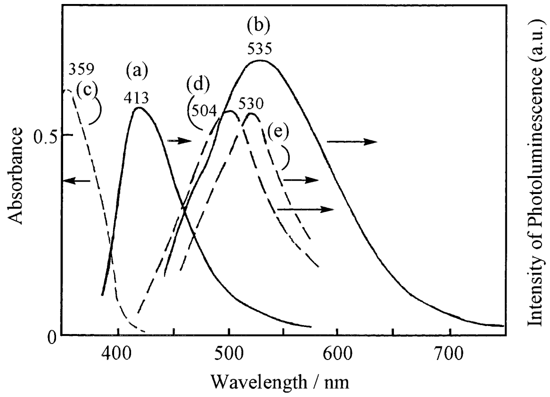


Figure 3. UV−vis and photoluminescence (PL) spectra of PPhen (—) and PPhen(5,6-OPen) (- - -): (a) PL of PPhen in formic acid at 10^{-6} M of the monomer units; (b) PL of a PPhen cast film; (c) UV−vis of PPhen(5,6-OPen) in chloroform; (d) PL of PPhen(5,6-OPen) in chloroform; (e) PL of a PPhen(5,6-OPen) cast film.

PVA film containing PPhen molecules in the surface region, and the film showed the UV−vis peak of PPhen at λ_{max} = 385 nm. Stretching of the PVA film caused alignment of the PPhen molecules along the direction of the stretching, which was seen from dichroism observed for the film. As shown in Figure 2, the dichroic ratio [=(absorbance at a parallel mode)/(absorbance at a perpendicular mode)] increases with increase in the stretching ratio of the PVA film. These results support the stiff linear structure of PPhen.

Photoluminescence. Figure 3 exhibits photoluminescence (PL) spectra of PPhen and PPhen(5,6-OPen). Other PPhen(5,6-OR)s gave essentially the same PL spectra as PPhen(5,6-OPen).

PPhen in formic acid shows a PL peak at 413 nm (curve a in Figure 3), which roughly agrees with the onset position of the UV−vis absorption band, as usually observed with aromatic compounds, including aromatic π-conjugated polymers.[1] However, in its cast film, the PL peak shifts to 535 nm, as exhibited by the curve b in Figure 3. A similar phenomenon was reported for stiff poly(pyridine-2,5-diyl),[2b] and this type of shift of the PL peak to a longer wavelength seems to be attributable to formation of a stabilized excimer-like adduct between photoactivated π-conjugated polymer and polymer in the ground state. In the solid, the distance between the neighboring PPhen molecules is short, and formation of the excimer-like adduct is considered to be enhanced.

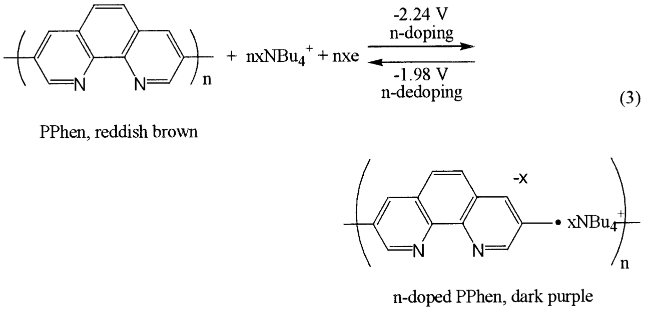
For PPhen(5,6-OPen), even the PL peak (504 nm) observed in the chloroform solution is deviated to a longer wavelength from the onset position (about 410 nm) of the UV−vis absorption band, as shown by curves c and d in Figure 3. These results indicate that PPhen(5,6-OPen) has a strong tendency to form the stabilized excimer-like adduct even in the chloroform solution at an order of 10^{-5}−10^{-4} M (molarity is based on the 1,10-phenanthroline unit). Assistance of the side OPen groups to form the excimer-like adduct is conceivable, since long alkyl side chains of π-conjugated polymers, as in head-to-tail type poly(3-alkylthiophene),[19−21] often assist self-assembly of the polymers. In the film, the PL peak of PPhen(5,6-OPen) shifts further to a longer wavelength, as depicted by curve e in Figure 3, presumably due to enhancement of the formation of the excimer-like adduct. PPhen(5,6-OR)s showed a quantum efficiency of about 4% for PL in the chloroform solution.

Photoluminescence of PPhen in the Stretched PVA Film. Since PPhen molecules were oriented along the direction of the stretching in the stretched PVA film, a unique PL response was observed with the stretched PVA film containing PPhen.

When nonpolarized light was used to irradiate the stretched (stretching ratio = 13.6) PVA film containing PPhen, PL light with a peak at 505 nm was emitted, and the emitted light was found to be polarized. The || (the direction of the oscillating electric field of the emitted light is parallel to the direction of the stretching of the film) component of the emitted light was about 6 times stronger than the ⊥ component. Irradiation with || polarized light of the film led to emission of || polarized light; however, irradiation with ⊥ polarized light caused a very weak emission of light. These results indicate that both absorption and emission of light take place along the direction of the main chain of the stiff PPhen molecule.

Electron-Accepting Properties. 1,10-Phenanthroline is a typical electron-accepting ligand and stabilizes low valent transition metal complexes.

The π-conjugated 1,10-phenanthroline polymers were inert against electrochemical oxidation. However, their cast films on a Pt electrode were susceptible to electrochemical reduction (or n-doping),[14] for example,



(3)

In eq 3, the peak cathode and anode potentials versus Ag$^+$/Ag evaluated from cyclic voltammetry (CV) are shown. The doping level, x in eq 3, was about 0.5, as estimated from the n-doping current. According to the reduction, the color of the film of PPhen changed from reddish brown to dark purple, as described in eq 3. UV−vis spectra of a cast film of PPhen on an ITO (indium−tin oxide) glass plate showed new broad absorption bands at 850 and 1360 nm at −1.9 V versus Ag$^+$/Ag and at 1100 and 1360 nm at −2.4 V versus Ag$^+$/Ag, respec-

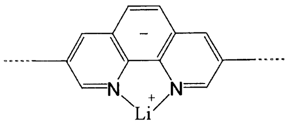
Table 2. Cyclic Voltammetry Data of the Polymer Films in a 0.10 M $[Bu_4N]PF_6$ CH_3CN Solution[a]

polymer	E_{pc}/V	E_{pa}/V	$E°$ [b]/V
PPhen	−2.24	−1.98	−2.11
PPhen(5,6-OPen)	−2.23	−1.93	−2.08
PPhen(5,6-OOct)	−2.15	−1.96	−2.06
PPhen(5,6-ODod)	−2.17	−1.95	−2.06
PPhen(5,6-OHexd)	−2.28	−1.97	−2.13
PDPypy	−1.38	−0.82	−1.10

[a] Voltage: vs Ag^+/Ag. [b] $E° = (E_{pc} + E_{pa})/2$. Obtained with cast films on a Pt electrode.

tively; such broad absorption bands in the near-infrared region were often observed with doped π-conjugated poly(heteroaromatic)s and assigned to polaron and/or bipolaron bands.[1] PPhen(5,6-OR)s also underwent analogous electrochemical reduction (n-doping) and the corresponding n-dedoping, and the CV data of the polymers are summarized in Table 2.

When $[NR_4]Y$ (Y = PF_6, BF_4) was used as the electrolyte, the polymer films afforded CV charts with good reproducibility in repeated scanning. However, when Li salts such as Li $[CF_3SO_3]$ were employed as the electrolyte, only the reduction peak was observed in the first scan, and its corresponding oxidation (n-dedoping) was not observed up to 1.5 V versus Ag^+/Ag. In the second scan, neither the reduction nor oxidation peaks were observed. These data suggest that a strong interaction[22a] of Li^+ with the 1,10-phenanthroline unit stabilizes the reduced state, for example,

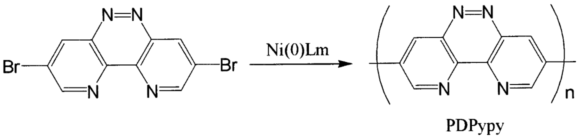


Similar stabilization of a reduced state was previously reported for a π-conjugated polythiophene with a crown ether subunit. In this case, trap of alkaline metal by the crown ether subunit seemed to bring about the stabilization of the reduced state,[22b] and the reduced polymer showed some stability even on exposure of the reduced polythiophene to air.

Analogously, PPhen reduced by sodium naphthalenide showed certain stability on exposure to air. In the case of Na-reduced poly(pyridine-2,5-diyl), its exposure to air caused instant color and IR changes;[2b] however, the changes in color and IR observed with the reduced PPhen were gradual. Potassium-doped PPhen gave a ultraviolet photoelectron spectrum similar to that of potassium-doped poly(2,2′-bipyridine-5,5-diyl),[23] and the ultraviolet photoelectron spectrum of PPhen indicated that PPhen had an ionization potential of about 6 eV. Changes of the IR spectrum of Na-doped PPhen on exposure to air and ultraviolet photoelectron spectra of PPhen and K-doped PPhen, which reveal formation of new electronic state(s), are shown in the Supporting Information. Due to the electron-accepting properties of PPhen, it is expected to serve as an electron-carrying material in electronic devices. For example, an electroluminescence device, ITO glass/vd-PTh (100 Å)/vd-PPhen (180 Å)/Mg:Ag (ITO = indium−tin oxide; vd-PTh = vacuum deposited poly(thiophene-2,5-diyl);[24] vd-PPhen[25] = vacuum deposited PPhen; Mg:Ag = Mg−Ag alloy (coevaporated)), showed electroluminescence at about 600 nm[24] from the vd-PTh layer. Electrons injected from the cathode seem to be able to move in the vd-PPhen layer, and they are considered to reach to the vd-PTh layer to meet holes in vd-PTh, which is considered to be a hole-carrying material,[24] to emit the light by the electron−hole coupling.

The IR spectrum of vd-PPhen was essentially identical to that of the original PPhen, showing main peaks at the same positions; however, PPhen molecules with a relatively small degree of polymerization were considered to be vacuum evaporated preferentially. The IR data and EL spectrum obtained at 9.0 V and 1.0 A cm^{-2} are shown in the Supporting Information.

The electron-accepting properties of PPhen are considered to originate from its containing electron-accepting −C=N− imine nitrogens.[1,26] To check the effect of the imine nitrogen and to enhance the electron-accepting properties of PPhen, we have prepared the following PDPypy, poly(dipyrido[3,2-*c*:2′,3′-*e*]pyridazine-3,8-diyl), using the zerovalent nickel complex.



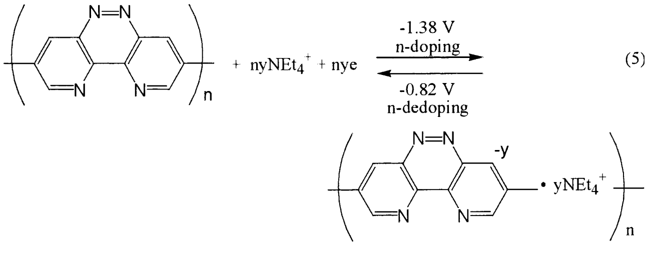
PDPypy

(4)

Assembled transition metal complexes of heteroaromatic ligand(s) with multi-N-coordinating sites are actively investigated, especially recently,[27] and transition metal complexes of dipyrido[3,2-*c*:2′,3′-*e*]pyridazine have been synthesized.[28a−c] Dipyrido[3,2-*c*:2′,3′-*e*]pyridazine is one of the strongest electron-accepting N-ligands, and MO calculation indicates that it has a LUMO with about 1 eV lower energy compared with that of 1,10-phenanthroline.[28c]

The obtained PDPypy had no Br, either, and was soluble in formic acid and partly (about 30%) soluble in DMSO and DMF. GPC analysis of the DMF-soluble part gave M_n of 3000 with a M_w/M_n value of 1.1. Since both the DMF-soluble and -insoluble parts showed the same IR spectrum, the polymer molecules with relatively low molecular weights were considered to be dissolved in DMF. PDPypy gave a UV−vis peak at 370 nm in formic acid. The PL spectrum of PDPypy showed a large Stokes shift from 370 to 500 nm. This large Stokes shift might be attributed to stabilization of protonated PDPypy by releasing a proton after the photoexcitation. Stabilization of photoexcited molecules by a shift of hydrogen or protons and ensuring molecular relaxation are subjects of recent interest.[28d−g]

CV data of a cast film of PDPypy in a 0.10 M $[NEt_4]BF_4$ solution of acetonitrile indicated that its electrochemical reduction took place more easily than that of PPhen, as expected.



(5)

The CV curve was reproducible on repeated scanning. The E_{pc} value indicates that PDPypy has the highest electron-accepting ability among various N-containing heteroaromatic π-conjugated polymers.[28h]

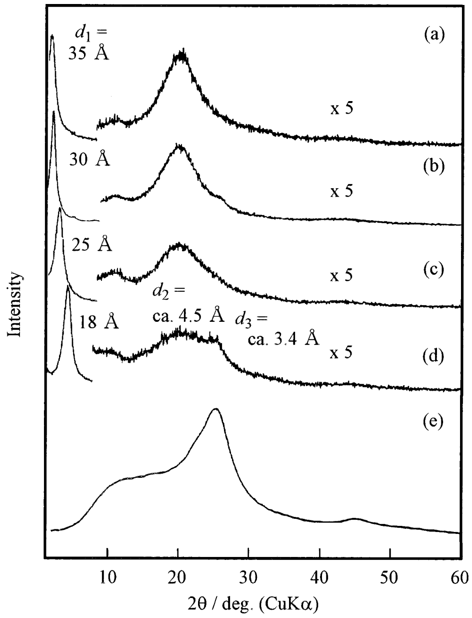


Figure 4. XRD patterns of (a) PPhen(5,6-OHexd), (b) PPhen-(5,6-ODod), (c) PPhen(5,6-OOct), (d) PPhen(5,6-OPen), and (e) PPhen.

Packing Structure of the Polymers. Figure 4 shows powder XRD patterns of PPhen and PPhen(5,6-OR)s. The XRD pattern of PPhen(5,6-OPen) gives three peaks at d_1 = 18 Å, d_2 = ~4.5 Å, and d_3 = ~3.4 Å. π-Conjugated heteroaromatic polymers with side chains and a regularly repeated structure often give an XRD peak at a low angle region (2θ(Cu Kα) < 5°), and the d_1 value of the peak at the low angle region has been assigned to the distance between the π-conjugated polymer chains separated by the side chains.[19−21,29] Plots of the d_1 values of PPhen(5,6-OR)s versus the number of carbons in the OR group give a linear line, as depicted in Figure 5. Since one $-CH_2-$ group has a height of 1.25 Å along the direction of the R chain,[30] the larger slope of the linear line, 1.51 Å/carbon, suggests that PPhen(5,6-OR) takes an end-to-end packing mode, as depicted in part b of Figure 5.

The XRD chart of PPhen(5,6-OPen) (curve d in Figure 4) shows two overlapped peaks at about d_2 = 4.5 Å and d_3 = 3.4 Å. The d_2 peak can be assigned to a side-to-side distance between the R chains,[30] and the d_3 distance of 3.4 Å is reasonable for the $\pi-\pi$ stacking distance of the 1,10-phenanthroline polymer sheets.[31] If this d_3 peak is assigned to the sheet-to-sheet $\pi-\pi$ stacking distance, it gives a calculated density of 1.23 g cm^{-3} for PPhen(5,6-OPen).[32] This calculated value agreed with the observed density of 1.23 g cm^{-3}. When the OR side chain gets longer, the d_2 peak becomes stronger and the d_3 peak becomes obscure (curves b and c in Figure 4). In the case of PPhen(5,6-OHexd), the d_3 peak seems to be hidden under the strong d_2 peak. As seen from the XRD data, PPhen(5,6-OR)s are considered to form a sheet depicted in Figure 5, and the sheets are considered to form a stacked structure. Although the CPK molecular model of PPhen(5,6-OR) indicates that there is some space between the OR groups along the PPhen(5,6-OR) main chain, penetration of the OR groups into the space in the neighboring PPhen(5,6-OR) molecules to form the interdigitation packing (cf. part b in Figure 5) does not seem possible; on this basis, PPhen(5,6-OR) is considered to take the end-to-end packing mode. PPhen (chart e in Figure 4) and PDPypy showed analogous broad XRD patterns.

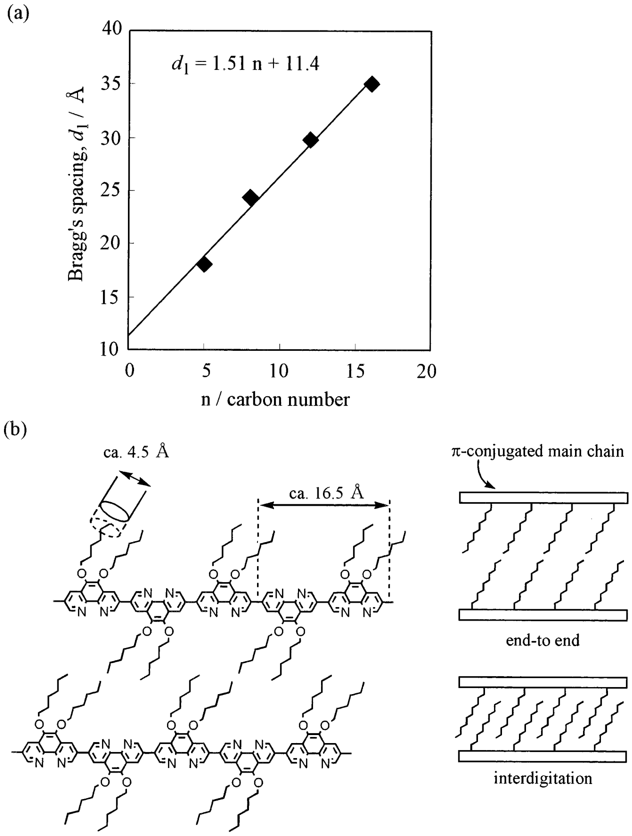
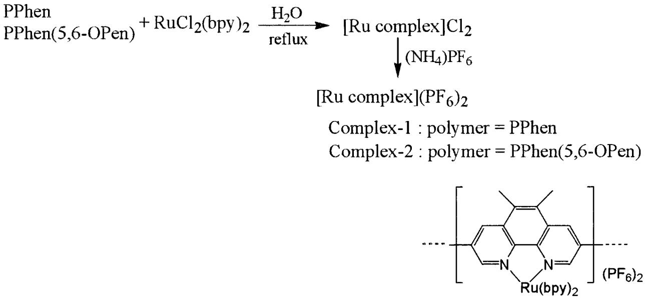


Figure 5. (a) Plots of the d_1 value vs number of carbons in the OR group of PPhen(5,6-OR). (b) Packing model of PPhen-(5,6-OR). Only one sheet is shown, and sheets are considered to form a stacked assembly; the OR groups in the lower layer are considered to come between the OR groups in the upper layer to form a well-stacked assembly.

PPhen and PPhen(5,6-OR) were thermally stable at 150 °C, as judged from their TGA and DSC curves (cf. the Supporting Information), although loss of the hydration water is observed with PPhen at the temperature. Annealing of the polymers afforded essentially the same XRD patterns for the polymers as those exhibited in the Supporting Information. PPhen and PPhen(OR) were stable under air, and no significant change in their IR spectra was observed after leaving the polymers for 7 and 1 year, respectively. PDPypy was also stable under air.

Ruthenium(II) Complexes. PPhen and PPhen(5,6-OPen) formed complexes in the reaction with $RuCl_2$-$(bpy)_2$ under reflux conditions in water. Data from elemental analysis and ^1H NMR spectroscopy indicated the occurrence of almost quantitative complexation of the 1,10-phenanthroline unit in 1:1 reactions with $RuCl_2(bpy)_2$. PPhen and PPhen(5,6-OPen) seemed to have higher reactivity toward Ru^{2+} than poly(2,2′-bipyridine-5,5′-diyl) (PBPy),[2] reflecting higher coordinating ability of 1,10-phenanthroline than 2,2′-bipyridyl, as discussed in the Introduction.

PPhen and PPhen(5,6-OPen) became soluble in CH_3CN by the complex formation, and the UV−vis chart of complex-1 is shown in Figure 6. It gives the $\pi-\pi^*$ transition bands originated from the bpy unit and PPhen at 287 and 353 nm, respectively. In addition, it gives an MLCT band[33,34] characteristic of the Ru^{2+} complex of electron-accepting N-ligands at about 440



nm. Complex-2 also gave analogous UV−vis peaks. The photochemistry of the $[Ru(bpy)_2(1,10\text{-phenanthroline})]^{2+}$ type complex,[33,34] especially that related to biochemistry, has actively been studied. In the cases of these complexes, they usually do not have absorption bands in the range 300−400 nm (cf. chart c in Figure 6). However, the UV−vis spectra of the $[Ru(bpy)_2]^{2+}$ complexes of PPhen and PPhen(5,6-OPen) have a $\pi-\pi^*$ absorption band covering the near-UV region, which may be advantageous for carrying out effective photochemical reactions. It was reported that photoenergy absorbed by the $\pi-\pi^*$ band of a π-conjugated polymer was transferred to metal centers such as $[Ru(bpy)_2]^{2+}$.[35] CV charts of complexes-1 and -2 in a CH_3CN solution of $[NBu_4]PF_6$ showed overlapped broadened peaks, suggesting the occurrence of electron exchange between Ru complexes in various oxidation states through the π-conjugated main chain.

Conclusion. π-Conjugated poly(1,10-phenanthroline)s have been synthesized and characterized. PPhen assumes a stiff structure, and PPhen(5,6-OR)s forms a molecular assembly, assisted by the side chain crystallization. Due to its stiff structure, PPhen exhibits unique dichroism in UV−vis absorption and photoluminescence. The polymers possess an expanded π-conjugated system and are susceptible to chemical and electrochemical reduction. The electron-accepting ability of PPhen is enhanced by increasing the number of the imine nitrogens, as in PDPypy. PPhen and PPhen(5,6-OPen) behave as good ligands and undergo quantitative complex formation with $[Ru(bpy)_2]^{2+}$, and the light absorption by the obtained complexes covers a wide range of the UV−vis region. These results are expected to contribute to understanding of 1,10-phenanthroline and related compounds and to design of future electronic and optical devices using 1,10-phenanthrolines.

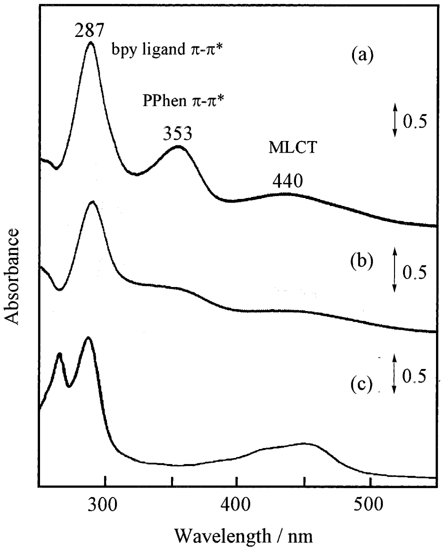


Figure 6. UV−vis spectra of (a) complex-1, (b) complex-2, and (c) $[Ru(bpy)_2(1,10\text{-phenanthroline})](PF_6)_2$ in CH_3CN.

Experimental Section

Materials. Solvents were dried, distilled, and stored under N_2. $RuCl_2(bpy)_2$,[36] $Ni(cod)_2$,[37] and 3,8-dibromo-1,10-phenanthroline[14] were prepared according to the literature. Chemicals were purchased from Aldrich Co. Ltd. and Tokyo Kasei Kogyo Co. Ltd. Salts used for the cyclic voltammetry were purified by recrystallization.

Measurements. The ultraviolet photoelectron spectra were measured with an angle-resolving UPS spectrometer at BL8B2 of the UVSOR Facility, Institute for Molecular Science. Monochromatized synchrotron radiation of $h\nu = 40$ eV obtained with a plane-grating monochromator was used as the light source. The spectra were measured at the normal emission with the incidence angle of the light of 45°. The total resolution of the UPS system was 0.3 eV, as estimated from the Fermi edge of gold. A thin film of PPhen used for UPS measurements was prepared on a gold coated Si(100) substrate by vacuum evaporation in the preparation chamber (base pressure 1×10^{-9} Torr) and was subsequently transferred to the measurement chamber with a base pressure of 5×10^{-10} Torr. Potassium doping of PPhen was carried out in situ using a SAES potassium-getter source in the preparation chamber. The getter was heated with a dc current of 5.8 Å for potassium evaporation. During the doping, the temperature of the film was kept at 125 ± 5 °C. The thickness of the deposited PPhen film was monitored with a quartz thickness monitor. The thickness of the PPhen film was 10 nm.

Electroluminescence data were obtained by Mr. T. Inoue in the R&D Center of TDK Corporation. PL spectra were recorded on a Hitachi F-4010 fluorescence spectrometer. PL spectra of solutions were measured under N_2. Vacuum evaporation of PTh and PPhen was carried out in a manner similar to that previously reported.[24] ^1H NMR spectra were obtained by using a JEOL EX-400 spectrometer. Cyclic voltammetry was performed with a Toyo Technica Solatoron SI 1287 electrochemical interface. XRD patterns were recorded on a Rigaku RINT 2100 diffractometer with Cu Kα radiation. For the determination of the degree of depolarization (ρ_v),[17a−c] it was used for the scattering geometry that the vertically polarized incident beam was irradiated, and the intensities of the vertically (V_v) and horizontally (H_v) scattered light were detected. To take account of the angular dependence of the scattered light intensity, the extrapolated values to zero scattering angle were used for the analysis of the optical anisotropy of PPhen, $\rho_v = H_v/V_v$.

Preparation of Monomers. 3,8-Dibromo-1,10-phenanthroline was prepared according to the literature.[14] Monomers for PPhen(5,6-OR)s were prepared according to the following procedure.

(1) 3,8-Dibromo-5,6-dialkoxy-1,10-phenanthroline. OR = OPen. A mixture of 3,8-dibromo-1,10-phenamthroline (5.0 g, 14.8 mmol), KBr (2.11 g, 17.8 mmol), and a mixed acid (18 mL of concentrated HNO_3 and 36 mL of concentrated H_2SO_4) was allowed to react for 3 h under reflux. The reaction mixture was poured on ice blocks and neutralized with NaOH(aq). The precipitate was separated by filtration, washed with water, and dried under vacuum to obtain 4.99 g (91.6%) of bright yellow 3,8-dibromo-1,10-phenanthroline-5,6-dione. ^1H NMR ($CDCl_3$) δ: 9.14 (d, 2.8 Hz, 2H), 8.61 (d, 2.8 Hz, 2H).

A mixture of 3,8-dibromo-1,10-phenanthroline-5,6-dione (2.21 g, 6.00 mmol) and dithiooxamide (0.864 g, 7.20 mmol) was allowed to react in anhydrous ethanol (40 mL) under reflux for 12 h under N_2. After the mixture was cooled to room temperature, the precipitate was separated by filtration, washed with anhydrous ethanol (3 times) and argon-bubbled chloroform (once), and dried under vacuum. Since the obtained yellow powder of 3,8-dibromo-5,6-dihydroxy-1,10-phenanthroline seemed unstable under air, the crude product was used directly for the next step.

To the above-described solid product were added NaH (346 mg, 14.4 mmol) and 40 mL of anhydrous DMSO under argon. After stirring at 60 °C for 12 h under argon, 1-iodopentane (1.88 mL, 14.4 mmol) was added to the red solution, and the mixture was stirred for 16 h at 60 °C. After the mixture was cooled to room temperature, an aqueous solution of sodium thiosulfate was added, and the reaction product was extracted with hexane (3 times). The combined hexane solution was washed with water (3 times) and a saturated aqueous solution of NaCl (once) and dried over $MgSO_4$. After removing hexane by evaporation, the product (light yellow needles) was isolated by column chromatography on silica (eluent = 7:3 mixture of hexane and ethyl acetate); yield = 46%; mp = 93−94 °C. ^{1}H NMR ($CDCl_3$) δ: 9.09 (d, 2.4 Hz, 2H), 8.68 (d, 2.4 Hz, 2H), 4.23 (t, 7.2 Hz, 4H), 1.90 (quin, 7.2 Hz, 4H), 1.52 (m, 4H), 1.45 (m, 4H), 0.98 (t, 7.2 Hz, 6H). Anal. Found: C, 51.68; H, 4.92; N, 5.49; Br, 31.46. Calcd for $C_{22}H_{26}Br_2N_2O_2$: C, 51.78; H, 5.14; N, 5.49; Br, 31.32.

Other monomers for PPhen(5,6-OR)s were prepared analogously, and their IR and ^{1}H NMR data agreed with their structures.

(2) OR = OOct. Light yellow needles (28%); mp = 53 °C. Anal. Found: C, 56.38; H, 6.31; N, 4.70; Br, 26.53. Calcd for $C_{28}H_{38}Br_2N_2O_2$: C, 56.58; H, 6.44; N, 4.71; Br, 26.88.

(3) OR = ODod. White powder (40%); mp = 71 °C. Anal. Found: C, 61.23; H, 7.85; N, 4.00; Br, 22.38. Calcd for $C_{36}H_{54}Br_2N_2O_2$: C, 61.19; H, 7.70; N, 3.96; Br, 22.62.

(4) OR = OHexd. White powder (39%); mp = 82 °C. Anal. Found: C, 64.84; H, 9.01; N, 3.48. Calcd for $C_{44}H_{70}Br_2N_2O_2$: C, 64.54; H, 8.62; N, 3.42.

3,8-Dibromodipyrido[3,2-*c*:2′,3′-*e*] pyridazine (the monomer for PDPypy) was synthesized as described below.

A mixture of dipyrido[3,2-*c*:2′,3′-*e*]pyridazine (1.57 g, 8.6 mmol),[38] concentrated HBr (70 mL), and Br_2 (41.4 g, 259 mmol) was stirred for 12 h at 100 °C. After the mixture was cooled to room temperature, the precipitate was separated by filtration and washed with water and ethanol. The precipitate was purified by column chromatography on silica gel (eluent = ethyl acetate). Evaporation of the solvent yielded a light yellow powder of 3,8-dibromodipyrido[3,2-*c*:2′,3′-*e*]pyridazine (2.7 g, 92% yield); dp = 250 °C (color change from yellow to black started at 250 °C without melting). Anal. Found: C, 35.42; H, 1.44; N, 16.31; Br, 47.27. Calcd for $C_{10}H_4Br_2N_4$: C, 35.33; H, 1.19; N, 16.48; Br, 47.01. ^{1}H NMR ($CDCl_3$) δ: 9.42 (d, 2.0 Hz, 2H), 9.27 (d, 2.0 Hz, 2H).

Preparation of Polymers. (1) PPhen. A mixture of 3,8-dibromo-1,10-phenanthroline (470 mg, 1.4 mmol), Ni (cod)$_2$, (610 mg, 2.2 mmol), bpy (220 mg, 1.4 mmol), and 1,5-cyclooctadiene (0.8 mL) in 50 mL of dry DMF was stirred at 60 °C for 2 days. The obtained yellow precipitate was separated by filtration, and workup of polymer, including washing with an aqueous solution of ethylenediaminetetraacetate, was carried out in a manner similar to those applied for workup of polypyridines.[2b] For IR and NMR data, see the Supporting Information. Anal. Found: C, 74.92; H, 3.56; N, 14.43; Br, O. Calcd for $(C_{12}H_6N_2{\cdot}0.75H_2O)_n$: C, 75.18; H, 3.94; N, 14.61. PPhen seemed to be hydrated similarly to 1,10-phenanthroline and polypyridines.[2b] It was difficult to remove hydrated water completely.

(2) PPhen(5,6-OPen). A DMF (20 mL) solution of 3,8-dibromo-5,6-dipentyloxy-1,10-phenanthroline (1.02 g, 2.0 mmol), Ni(cod)$_2$ (660 mg, 2.40 mmol), bpy (374 mg, 2.4 mmol), and 1,5-cyclooctadiene (1.2 mL) was stirred for 36 h at 60 °C. The light yellow precipitate was separated by filtration, and workup of the polymer was carried out similarly. However, PPhen(5,6-OR) seemed to have higher coordinating ability toward nickel compounds, and washing with an aqueous ammonium solution of dimethylglyoxime and ensuing washing with an HCl-acidic methanol were necessitated to obtain ash-free PPhen(5,6-OR). Examples of ^{1}H NMR spectra are shown in Figure 1. Anal. Found: C, 70.35; H, 7.72; N, 7.56; Br, O. Calcd for $(C_{22}H_{26}N_2O_2{\cdot}1.3H_2O)_n$: C, 70.68; H, 7.71; N, 7.49. Hydrated water of PPhen(5,6-OR) may exist in the space formed by the stacking of the polymer molecules; cf. the text.

Other PPhen(5,6-OR)s and PDPypy were prepared analogously.

(3) PPhen(5,6-OOct). Anal. Found: C, 74.29; H, 8.88; N, 6.51; Br, negligible (below the limit of detection). Calcd for $(C_{28}H_{38}N_2O_2{\cdot}H_2O)_n$: C, 74.30; H, 8.91; N, 6.18.

(4) PPhen(5,6-ODod). Anal. Found: C, 77.75; H, 9.71; N, 5.35; Br, 0. Calcd for $(C_{36}H_{54}N_2O_2{\cdot}0.5H_2O)_n$: C, 77.79; H, 9.97; N, 5.04.

(5) PPhen(5,6-OHexd). Anal. Found: C, 77.37; H, 10.13; N, 4.57; Br, 0.50. Calcd for $(C_{44}H_{70}N_2O_2{\cdot}H_2O)_n$: C, 78.06; H, 10.72; N, 4.14.

(6) PDPypy. Anal. Found: C, 52.23; H, 4.19; N, 24.37; Br, 0. Calcd for $(C_{10}H_4N_4{\cdot}2.8H_2O)_n$: C, 52.08; H, 4.20; N, 24.30.

Preparation of Ru Complexes. (1) Complex-1. A mixture of PPhen (53.4 mg, 0.25 mmol of the PPhen unit) and $RuCl_2(bpy)_2$ (121 mg, 0.25 mmol) in 50 mL of distilled water was stirred for 5 days under reflux. Oxygen in the water was removed by bubbling argon before use, and the reaction was carried out under argon using a Schlenk tube. The reaction gave a dark red and almost homogeneous solution. After removing a small amount of the remaining unreacted PPhen by centrifugation, NH_4PF_6 (97.8 mg, 0.60 mmol) was added to the dark red homogeneous solution to obtain a red precipitate. The precipitate was separated by filtration and washed with water repeatedly until the UV−vis spectrum of the filtrate did not show any sign of $RuCl_2(bpy)_2$ (monitored at 484 nm). After drying under vacuum, 146 mg (64%) of complex-1 was obtained. Anal. Found: C, 42.55; H, 3.26; N, 9.37. Calcd for $(C_{32}H_{22}F_{12}N_6P_2Ru{\cdot}1.7H_2O)_n$: C, 42.13; H, 2.81; N, 9.21.

(2) Complex-2 was prepared analogously. Anal. Found: C, 46.31; H, 3.93; N, 8.20. Calcd for $(C_{42}H_{42}F_{12}N_6P_2Ru{\cdot}H_2O)_n$: C, 47.01; H, 4.14; N, 7.84.

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Supporting Information Available: IR spectra of PPhen and related compounds, IR spectra of PPhen(5,6-OR)s, ^{1}H and ^{13}C NMR data of PPhen, comparison of ultraviolet photoelectron spectroscopic data of K-doped PPhen and K-doped poly(2,2′-bipyridine-5,5′-diyl), definition of the stretching ratio, IR data of vd-PPhen, EL spectrum, data (IR, CV, and XRD) of the Ru complex, and XRD patterns of annealed polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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