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Synthesis and Characterization of New Luminescent 1,10-Phenanthroline- and Pyridine-Containing π-Conjugated Polymers. Their Optical Response to Protic Acid, M^{n+}, and Solvents

Takuma Yasuda and Takakazu Yamamoto*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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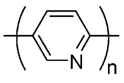
ABSTRACT: New π-conjugated polymers comprised of alternating 1,10-phenanthroline/1,4-didodecyloxybenzene, 1,10-phenanthroline/9,9-dioctylfluorene, or pyridine/1,4-dialkoxybenzene units were prepared by palladium(0)-catalyzed coupling reaction in 84−98% yields. The derived polymers gave M_n of 5400−8800 in GPC analysis, and they possessed good solubility in organic solvents and high thermal stability. Electrochemical reduction (or n-doping) of the polymers proceeded with peaks in the range −2.3 to −2.6 V vs Ag^+/Ag. The polymers were highly photoluminescent, and strong blue emission with the peak in the range 412−434 nm was observed in solutions. The emission peak as well as the UV−vis absorption peak of the polymer was influenced by the solvent polarity, protonation, and formation of metal complexes. When the polymers were protonated with trifluoroacetic acid, a large red-shift (ca. 40−60 nm) of the absorption peak was observed. The photoluminescent properties of the polymers were tuned by coordination of the polymer with metal ions. Polymers with long side chains formed an ordered structure in the solid state as judged from their XRD patterns.

Introduction

Control of optical and electrical properties of π-conjugated polymers is important for designing photonic and electronic devices using π-conjugated polymers.[1] Among the π-conjugated polymers, those with electron-withdrawing imine nitrogen(s) (C═N), for example, are attracting interest, because they not only have the electron-accepting ability but also are reactive for metal-complex-forming reactions, *N*-protonation, *N*-oxidation, and quaternization with RX, which can modify their optical and electrical properties.[2−4]



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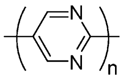
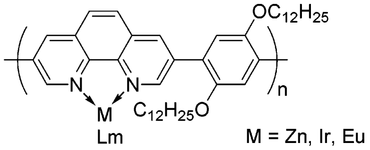


PPyrim

A variety of soluble π-conjugated copolymers consisting of *N*-containing heterocycles have also been developed.[3−7] Especially, luminescent properties of the copolymers have received significant attention, owing to their potential usability as electron-transporting emitters in polymer light-emitting diodes (LEDs)[6] and as luminescent chemosensors.[3,7] Wasielewski and coworkers demonstrated that the UV−vis absorption and emission behavior of a poly(*p*-phenylenevinylene) (PPV) type polymer containing the 2,2′-bipyridyl unit changed dramatically upon coordination with transition metal ions.[3a] Recently, we briefly reported preparation of a luminescent 1,10-phenanthroline-containing π-conjugated copolymer and its metal complexes with Zn(II), Ir(III), and Eu(III).[7] The color of emitted light from the polymer complex could be tuned from blue to red by the kind of metal ion coordinated to the polymer.



We have expanded the study, and herein we report the syntheses and chemical properties of a series of luminescent π-conjugated polymers containing the 1,10-phenanthroline or pyridine unit. The photophysical properties of the polymers are highly responsive to protonation and metal ion coordination. The polymers are expected to be unique candidates for polymer-based chemosensors.

Experimental Section

Materials and Syntheses. 2,7-Dibromo-9,9-dioctylfluorene was donated from Adchemco Co. Ltd. 1,4-Dibromo-2,5-dialkoxybenzene,[8a,b] 3,8-dibromo-1,10-phenanthroline (**7**),[9] $PdCl_2(dppb)$ (dppb = 1,4-bis(diphenylphosphino)butane),[8c] and $Pd(PPh_3)_4$[8d] were prepared according to the literature. Solvents were dried, distilled, and stored under N_2.

Synthetic procedures for the monomers and polymers and data for their characterization are given in the Supporting Information.

Measurements. NMR and FT-IR spectra were recorded on a JEOL EX-400 spectrometer and a JASCO FT/IR-460 Plus spectrometer, respectively. Elemental analyses were carried out with a Yanagimoto Type MT-2 CHN autocorder. GPC traces were obtained with a Toso HLC-8120 equipped with polystyrene gel columns using THF as an eluent. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50. Cyclic voltammetry of cast films of the polymers on Pt plates was performed in an acetonitrile solution of $[(C_2H_5)_4N]BF_4$ (0.10 M) with a Pt counter electrode and an Ag^+/Ag reference electrode by using a Toyo Technica Solartron SI 1287 electrochemical interface. The cast film was prepared from a dilute chloroform solution. UV−vis absorption and photoluminescence (PL) spectra were measured with a Shimadzu UV-3100 and a Hitachi F-4010 spectrometer, respectively. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT2100 diffractmeter with Cu Kα (1.54 Å) radiation.

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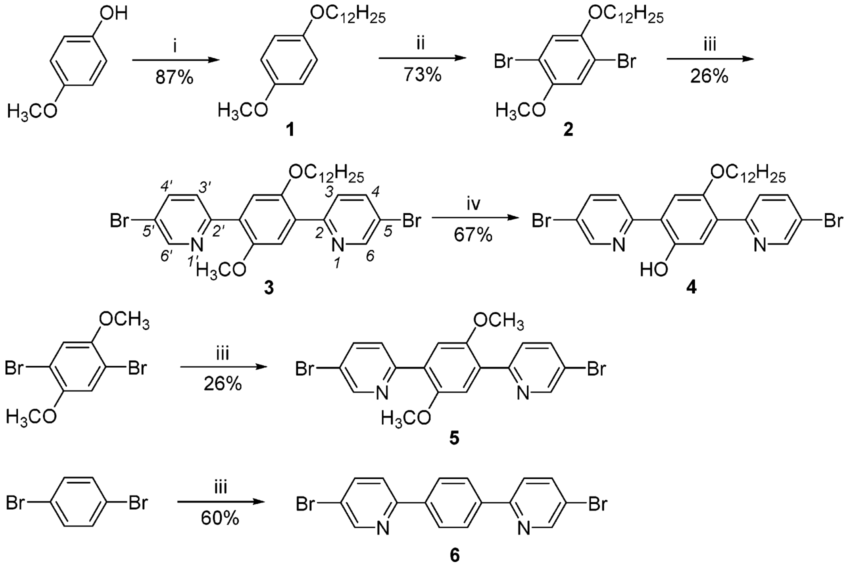
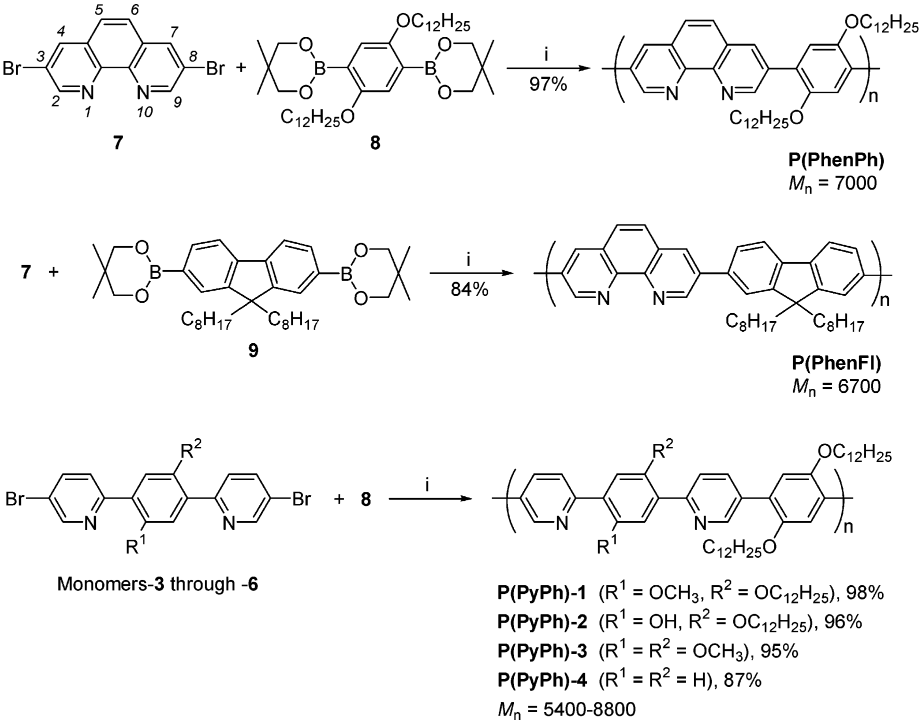
Scheme 1. Synthetic Routes of the Monomers[a]



[a] (i) $C_{12}H_{25}Br$, KOH, DMSO, 140 °C; (ii) Br_2, CCl_4, room temperature; (iii) (1) Mg, THF, reflux; (2) 2,5-dibromopyridine, $PdCl_2(dppb)$ (dppb = 1,4-bis(diphenylphosphino)butane), room temperature; (iv) LiI, 2,4,6-collidine, 150 °C.

Scheme 2. Synthesis of the Polymers[a]



[a] (i) $Pd(PPh_3)_4$, Na_2CO_3 or $NaHCO_3$, THF/H_2O, 60 °C.

Results and Discussion

Synthesis. The synthetic routes of the monomers are outlined in Scheme 1. 1,4-Dibromo-2-dodecyloxy-5-methoxybenzene (**2**) was readily prepared by the bromination of 1-dodecyloxy-4-methoxybenzene (**1**) with Br_2. 1,4-Bis[2-(5-bromopyridyl)]-2-dodecyloxy-5-methoxybenzene (**3**) was synthesized by a palladium(II)-catalyzed coupling reaction of the di-Grignard reagent of **2** with 2,5-dibromopyridine. This reaction occurred chemospecifically at the 2-position of 2,5-dibromopyridine. Subsequent treatment of **3** with LiI in 2,4,6-collidine gave the monomer **4** with a OH group. Synthesis of the pyridine-containing dibromo monomers **5** and **6** was carried out under conditions similar to those applied for the monomer **3**.

The new copolymers were prepared according to Scheme 2. The polymerizations in all cases are based on palladium(0)-catalyzed Suzuki-coupling reactions, which were carried out using monomers in a mixture of THF and aqueous Na_2CO_3 or $NaHCO_3$ containing 3 mol % $Pd(PPh_3)_4$ as the catalyst at 60 °C under N_2. After purification and vacuum-drying, all the polymers were obtained with satisfactory yields (84–98%).

Characterization of the Polymers. Results of the polymerization are summarized in Table 1. The obtained polymers showed good solubility in common organic solvents such as chloroform, THF, and toluene. As

Table 1. Preparation of the Polymers

polymer	yield, %	color	M_n[a]	M_w/M_n[a]	T_d,[b] °C
P(PhenPh)	97	yellow	7000	2.0	384
P(PhenFl)	84	yellow	6700	1.8	417
P(PyPh)-1	98	green	8800	1.2	412
P(PyPh)-2	96	orange	5900	1.9	389
P(PyPh)-3	95	yellow	8500	1.2	418
P(PyPh)-4	87	green	5400	1.3	419

[a] Estimated from GPC (eluent: THF, polystyrene standards). [b] 5% weight-loss temperature measured by TGA under N_2 with a heating rate of 10 °C min^{-1}.

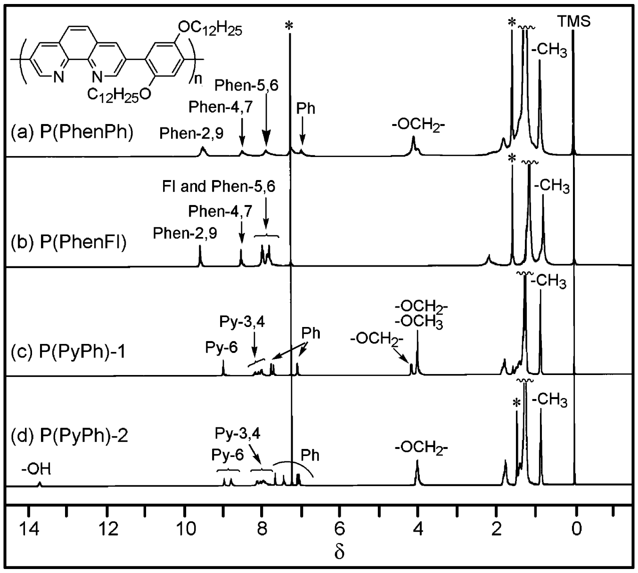


Figure 1. ^1H NMR spectra of (a) P(PhenPh), (b) P(PhenFl), (c) P(PyPh)-1, and (d) P(PyPh)-2 in $CDCl_3$. The peaks with the * are due to solvent impurities.

shown in Table 1, the number-average molecular weights (M_n) of the polymers are estimated to be 5400−8800 (polystyrene standards) with the polydispersity index (M_w/M_n) of 1.2−2.0 by GPC measurement (eluent = THF). The results agree with the data obtained from the elemental analysis.

Figure 1 depicts the ^1H NMR spectra of P(PhenPh), P(PhenFl), P(PyPh)-1, and -2 in $CDCl_3$; assignment of the peaks is made by comparing the ^1H NMR spectra with those of the corresponding monomers. The four peaks of P(PhenPh) at δ 9.50, 8.50, 7.87, and 7.00 are due to protons of 1,10-phenanthroline and phenylene rings, as assigned in Figure 1a. The peaks of the alkyl side chains are observed in the region of δ 4.09−0.87, and the peak areas agree with the structure of P(PhenPh).

^1H NMR spectra of P(PyPh)-1 and -2 (Figure 1c and d) show some difference due to the difference in the substituents. The $-OCH_3$ peak of P(PyPh)-1 appears at δ 4.01, which was overlapped with the $-OCH_2$ peak, whereas the peak due to the phenolic −OH group of P(PyPh)-2 is found at a considerably low magnetic field of δ 13.9. The peak position of the −OH group suggests the occurrence of an intramolecular hydrogen bonding to the neighboring pyridyl nitrogen; such hydrogen bonding to give the ^1H NMR peak near the position has been reported for compounds with a similar local structure.[10] IR spectra of the polymers resembled those of the monomers; however, the ν(C−Br) absorption peak of the dibromo monomers near 1100 cm^{-1} was not observable after the polymerization.

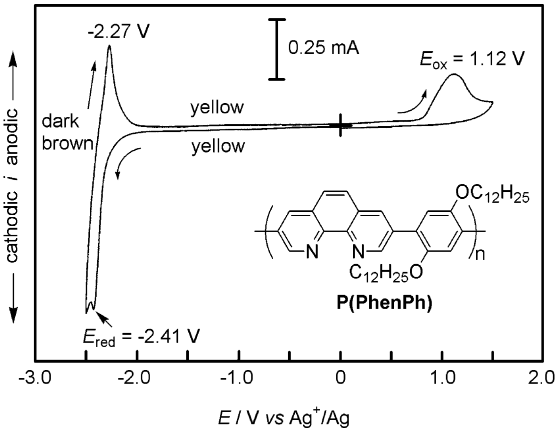


Figure 2. Cyclic voltammogram of a film of P(PhenPh) on a Pt plate in an acetonitrile solution of $[(C_2H_5)_4N]BF_4$ (0.10 M) under N_2. The sweep rate is 30 mV s^{-1}.

Table 2. Electrochemical and Optical Data of the Polymers

	redox potential[a] (V vs Ag^+/Ag)		optical data				
			THF solution			cast film	
polymer	E_{red}	E_{ox}	λ_{max} (nm)	λ_{EM} (nm)	Φ[c] (%)	λ_{max} (nm)	λ_{EM} (nm)
P(PhenPh)	−2.41	1.12	380	434	54	385	524
P(PhenFl)	−2.36	1.31	384	412, 435[d]	60	389	527
P(PyPh)-1	−2.60	1.09	380	428	91	388	434
P(PyPh)-2	*b*	1.17	401	581	<1	413	*b*
P(PyPh)-3	−2.59	1.06	380	425	87	385	508
P(PyPh)-4	−2.48	1.02	368	429	67	375	439

[a] Measured by cyclic voltammetry in an acetonitrile solution of $[(C_2H_5)_4N]BF_4$ (0.10 M). E_{red} and E_{ox} stand for reduction (n-doping) peak and oxidation (p-doping) peak potentials, respectively. [b] Not clearly observable. [c] PL quantum yield calculated by comparing with the standard of quinine sulfate (ca. 10^{-5} M solution in 0.5 M H_2SO_4, having a quantum yield of 54.6%).[19] [d] Subpeak.

The polymers had good thermal stability under N_2. The first major weight loss of the polymers started around 360−400 °C, and a residual weight of about 40−60% was observed at 900 °C. Data of the 5% weight-loss temperatures (T_d) of the polymers are included in Table 1.

Redox Behavior. Figure 2 shows the cyclic voltammogram (CV) for a cast film of P(PhenPh) on a Pt plate in an acetonitrile solution of $[(C_2H_5)_4N]BF_4$ (0.10 M). Electrochemical reduction (n-doping) starts at about −2.1 V with a peak at $E_{red} = -2.41$ V vs Ag^+/Ag, and the corresponding oxidation (n-dedoping) peak is observed at −2.27 V vs Ag^+/Ag. These types of n-doping and n-dedoping couples have been observed with π-conjugated polymers having electron-accepting units such as a pyridine unit.[2−6] The electrochemical process was accompanied by an obvious color change from yellow in the neutral state to dark brown in the n-doped state.

In the oxidative region, a peak is observed at E_{ox} = 1.12 V vs Ag^+/Ag, which is assigned to oxidation (p-doping) of the phenylene group; a similar oxidation potential of 1.0 V vs Ag^+/Ag has been reported for poly(*p*-phenylene).[11a] However, its reduction (p-dedoping) peak was not clearly observed. Presumably, the dopant BF_4^- seems to be trapped by coordination with the OR groups, and the strong interaction between the OR groups and the BF_4^- dopant may be the reason for the irreversibility of the p-doping. The electrochemical redox data of the polymers are summarized in Table 2.

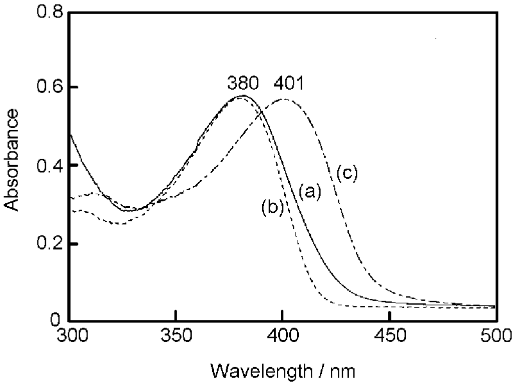


Figure 3. UV−vis absorption spectra of (a) P(PhenPh) (—), (b) P(PyPh)-1 (- - -), and (c) P(PyPh)-2 (— - —) in THF at room temperature.

UV−vis and Photoluminescence (PL) Data. Figure 3 depicts UV−vis absorption spectra of P(PhenPh), P(PyPh)-1, and -2 in THF. P(PhenPh) and P(PyPh)-1 exhibit the absorption peak (λ_{max}) at 380 nm, which is assigned to the $\pi-\pi^*$ absorption peak; the λ_{max} position is comparable to those of PPy,[2a] poly(1,10-phenanthroline),[2c] poly(*p*-phenylene),[11a,b] and poly(fluorene)s.[11c] The λ_{max} position of P(PyPh)-2 (Figure 3c) is shifted by about 20 nm to a longer wavelength, compared with that of P(PyPh)-1. This bathochromic shift may be due to formation of an intramolecular hydrogen bond between the OH group and the pyridyl nitrogen atom, which will assist the coplanarization of the polymer chain, as previously proposed for disk-shaped compounds.[10] The UV−vis absorption and photoluminescence (PL) data of the polymers in solution and in film are listed in Table 2. The λ_{max} of the polymers in film showed a small red-shift (by ca. 5−10 nm) from that in solution.

The polymers are highly photoluminescent both in solution and in film. The PL quantum yields (Φ in Table 2) of the polymers, except for P(PyPh)-2, in THF were found to be very high ($\Phi = 54-91\%$). The PL peak, λ_{EM}, position of the polymers in THF agreed with the onset position of the absorption band, as usually observed with π-conjugated polymers in solutions. However, the PL behavior of P(PhenPh), P(PhenFl), and P(PyPh)-3 in film was quite different from that in the solution. The λ_{EM} in film shifts by about 80−120 nm toward longer wavelength with broadening of the peak. This seems to be due to formation of the excimer-like adduct between the photoexcited polymer molecule and the polymer molecule in the ground state.

As presented in Table 2 and described above, the PL quantum yield of P(PyPh)-2 is very low ($\Phi < 1\%$). P(PyPh)-2 possesses the mobile-H in the OH group, and it may bring about excited-state intramolecular proton transfer (ESIPT)[12] from the acidic phenol to the basic imine nitrogen of the pyridine ring, thus providing nonradiative decay pathway(s) to decrease the quantum yield.

Effect of Solvent Polarity on the Optical Properties. Figure 4 shows the PL spectra of P(PhenPh) in various solvents. As seen in Figure 4, the λ_{EM} position of P(PhenPh) shifts by about 40 nm to a longer wavelength and the PL intensity gradually decreased with increase in polarity of the solvent, from less polar toluene to highly polar NMP (*N*-methyl-2-pyrrolidinone). In contrast, the λ_{max} position of P(PhenPh) was slightly influenced by polarity of solvent, indicating that the electronic state of P(PhenPh) in the ground state is not much affected by the solvent surrounding the polymer molecule.

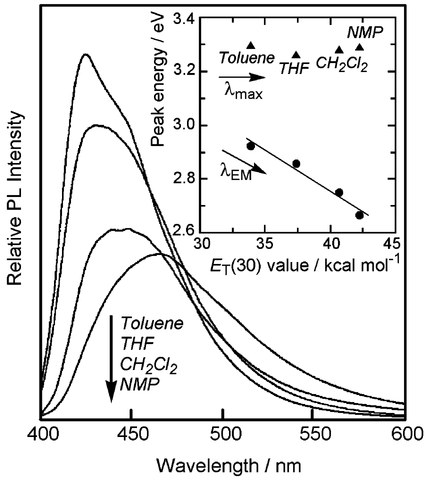


Figure 4. PL spectra of P(PhenPh) in various solvents. The inset shows plots of the energy of the UV−vis absorption (λ_{max}) and PL (λ_{EM}) against the $E_T(30)$ value of the solvent.

Plots of the emission energy versus the $E_T(30)$ value,[13] which is used as a measure of polarity of solvent, give a roughly straight line shown in the inset of Figure 4. This solvent effect on PL is considered to be due to stabilization of a polar excited state by solvation; the photoexcited polymer molecule seems to be stabilized by the interaction with the solvent molecules.[13,14] P(PhenPh) consists of an electron-accepting 1,10-phenanthroline unit and an electron-donating dialkoxybenzene unit, and it is considered to have an intramolecular alternating charge transfer (CT) structure. Photoexcitation will cause migration of an electron from the dialkoxybenzene unit to the 1,10-phenanthroline unit to increase the intramolecular polarization, and stabilization of this polar excited state by the polar solvent accounts for the larger Stokes shift in polar solvents. A similar solvent effect on PL was also observed for P(PhenFl); however, P(PyPh)-1 did not clearly show such a solvatochromism. The pyridine unit would have less electron-accepting property than the 1,10-phenanthroline unit.

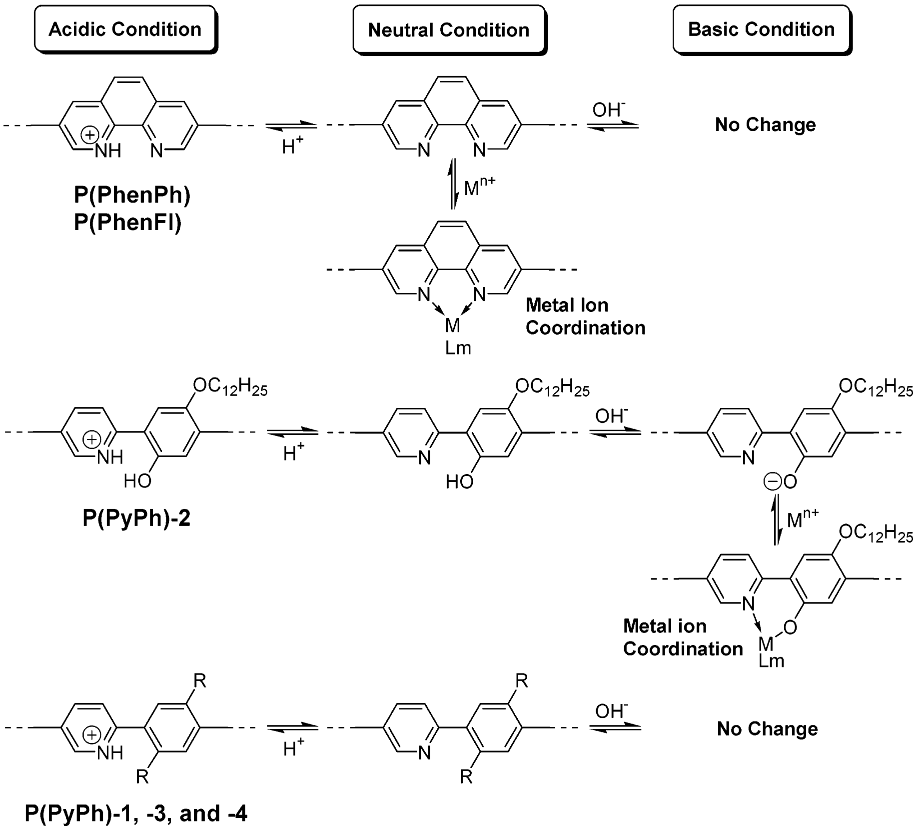
Response to Protic Acid and NaOH. The polymers are considered to react with protic acids and metal ions M^{n+}, and expected reactions under various conditions are illustrated in Scheme 3.

Actually, the polymers were effectively protonated with trifluoroacetic acid (TFA). As shown in Figure 5, addition of TFA (from 0 to 4.0×10^{-3} M) to a solution of P(PhenPh) (2.0×10^{-5} M) in chloroform leads to a considerably large red-shift of the λ_{max} position from 385 to 440 nm. The PL intensity is, on the other hand, strongly decreased due to the protonation of the imine nitrogen. Other polymers also gave similar changes (e.g., the data are shown in the Supporting Information).

In the case of P(PyPh)-2 having the acidic OH group, it responded to sodium hydroxide. As exhibited in Figure 6, the λ_{max} position of P(PyPh)-2 (2.0×10^{-5} M) in THF−methanol (25:1) shifts to a longer wavelength with increase in the concentration of NaOH, and the PL intensity is strongly enhanced (by greater than 10 times, compared with the neutral state). Similar optical changes of π-conjugated polymers having the phenolic OH group have been reported.[15]

Response to M^{n+}. P(PhenPh), P(PhenFl), and P(PyPh)-2 are expected to serve as metal ion receptors

Scheme 3. Reactions of the Polymers under Various Conditions



(cf. Scheme 3). Table 3 summarizes changes of the UV–vis and PL data for P(PhenPh), P(PhenFl), and P(PyPh)-2 observed upon addition of metal ions (20 mol per 1 mol of the repeating unit).[16] As seen in Table 3, Li^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Zn^{2+}, and La^{3+} cause only a small shift of the λ_{max} position. For these metal ions, PL was clearly observed with a shift of λ_{EM} position, which depends on the kind of metal ion.

Transition metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+}, and Pd^{2+}, on the other hand, led to a large red-shift of λ_{max} by about 20–50 nm and complete quenching of PL. This quenching effect of PL may be related to an energy transfer from the photoactivated π-conjugated polymer main chain to the metal complex part.[3a] Figure 7 is a photograph showing the emission of light from P(PhenFl) in solutions with and without metal ions under UV irradiation. It is found that the color of the emitted light can be tuned over a wide range of color by changing the kind of metal ion. P(PyPh)-1, -3, and -4, however, showed much less ionochromic effect by the addition of metal ions.

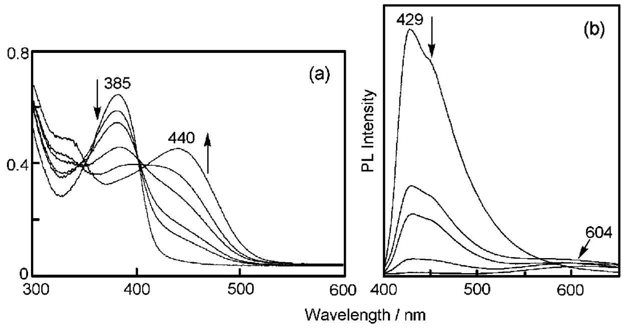


Figure 5. Changes in (a) UV–vis absorption and (b) PL spectra of P(PhenPh) (2.0×10^{-5} M (repeating unit)) in chloroform at various concentrations of TFA: [TFA] = 0, 2.0×10^{-5}, 4.0×10^{-5}, 2.0×10^{-4}, 5.0×10^{-4}, and 4.0×10^{-3} M.

It was reported that the 2,2′-bipyridyl-containing π-conjugated polymers serve as an excellent chemosensor of metal ions.[3a,b] These polymers, however, did not respond much to alkaline and alkaline earth metal ions. P(PhenPh), P(PhenFl), and P(PyPh)-2 indicated good response to a large variety of metal ions including alkaline and alkaline earth metal ions, presumably due to the high coordinating ability of the 1,10-phenanthroline and the pyridine-phenol blocks. 1,10-Phenanthroline possesses an exceptionally high selectivity and binding constant for Li^+ among alkaline metal ions,[17] and it forms complexes with divalent alkaline earth metal ions such as Mg^{2+} and Ca^{2+}.[17] To our knowledge, there is no precedent that 1,10-phenanthroline- and

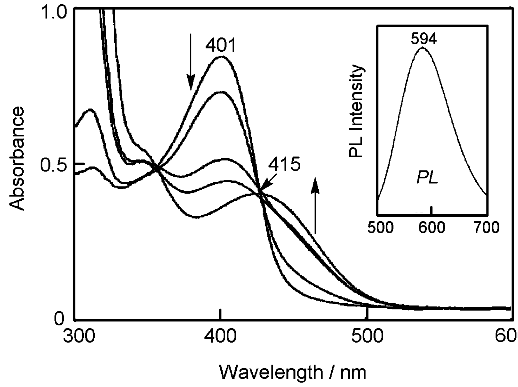


Figure 6. Changes in the absorption spectrum of P(PyPh)-2 (2.0×10^{-5} M (repeating unit)) in THF–methanol (25:1) at various concentrations of NaOH: [NaOH] = 0, 1.5×10^{-5}, 2.5×10^{-4}, 5.0×10^{-4}, and 2.0×10^{-3} M. The inset shows the PL spectrum of the polymer solution at [NaOH] = 2.0×10^{-3} M.

Table 3. UV–vis and PL Response of the Polymers to M^{n+} [a]

metal ion	P(PhenPh) λ_{max} (nm)	P(PhenPh) λ_{EM}[c] (nm)	P(PhenFl) λ_{max} (nm)	P(PhenFl) λ_{EM}[c] (nm)	P(PyPh)-2[b] λ_{max} (nm)	P(PyPh)-2[b] λ_{EM}[c] (nm)
ion-free	385	445 (s)	384	412, 434 (s)	415[d]	594 (w)[d]
Li$^+$	395	506 (s)	387	437 (s)	408	583 (w)
Mg^{2+}	395	519 (s)	399	468 (s)	410	545 (m)
Ca^{2+}	403	527 (s)	409	476 (s)	403	537 (m)
Al^{3+}	419	554 (m)	428	565 (s)	401	(q)
Zn^{2+}	418	540 (s)	417	480 (s)	403	570 (m)
Co^{2+}	411	(q)	415	(q)	*e*	(q)
Ni^{2+}	404	(q)	410	(q)	433	(q)
Cu^{2+}	420	(q)	411	(q)	431	(q)
Pd^{2+}	437	(q)	423	(q)	*e*	(q)
La^{3+}	411	521 (m)	413	471 (w)	398	537 (w)

[a] Conditions: polymer (2.0×10^{-5} M (repeating unit)) and metal ion (4.0×10^{-4} M) in THF–methanol (25:1). The following metal salts were used: LiCl, $MgCl_2$, $CaCl_2$, $Al_2(SO_4)_3$, $ZnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $PdCl_2$, and $LaCl_3$. [b] In the presence of NaOH (2.0×10^{-3} M) as a base. Without the base, no observable changes were detected on addition of M^{n+}. [c] Intensity of the emitted light given in parentheses: s, strong; m, medium; w, weak; q, very weak (quenched). [d] In THF without methanol, P(PyPh)-2 gave the λ_{max} at 401 nm as shown by curve c in Figure 3. [e] The absorption peak of the polymer was not clearly observed.

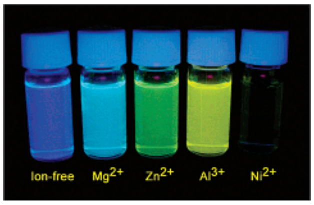


Figure 7. Emission of light from P(PhenFl) in the presence of metal ions in THF–methanol. This photograph was taken under irradiation with light at 365 nm.

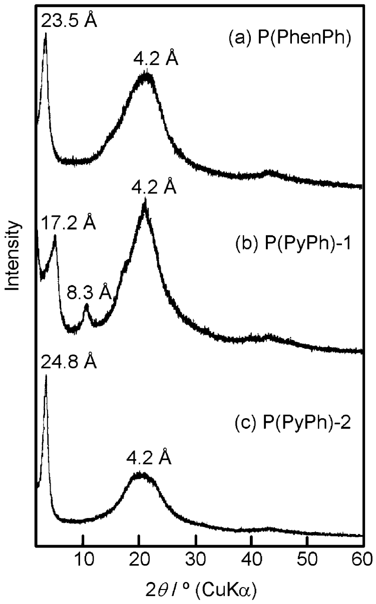


Figure 8. Powder X-ray diffraction patterns of (a) P(PhenPh), (b) P(PyPh)-1, and (c) P(PyPh)-2.

pyridine-containing π-conjugated polymers show such a highly sensitive ionochromic effect. The polymers are expected to serve as new polymer-based metal ion sensors.

X-ray Diffraction. Figure 8 exhibits powder X-ray diffraction (XRD) patterns of P(PhenPh), P(PyPh)-1, and P(PyPh)-2. The strong peaks in the low-angle region (d = 24.8–17.2 Å) seem to correspond to a distance between the polymer main chains separated by the long alkoxy side chains, as often observed with other π-conjugated polymers having such long side chains. The peak at d = 4.2 Å is considered to be originated from the side-to-side distance between loosely packed alkoxy chains. The alkyl group has a diameter of about 5 Å, and packing of alkyl groups often gives a peak in this region.[18] Thus, the polymers are considered to form an ordered structure in the solid state due to the crystallinity of the long alkoxy side chain.

As shown in Table 2, the UV–vis peaks of the three polymers in films are shifted by 5–12 nm to a longer wavelength from those in THF, and this may be due to intermolecular interaction between the polymer molecules in the ordered structure. However, the degree of the shift to a longer wavelength is much smaller than that observed with five-membered ring π-conjugated polymers such as regioregular head-to-tail type poly(3-alkylthiophene), which forms a π-stacked structure.[20] Formation of an ordered structure is considered to be disadvantageous in electroluminescence; however, it seems to be advantageous for higher mobility of carrier in the polymer film and large third-order optical nonlinear susceptibility.[21]

Conclusions

New luminescent π-conjugated polymers consisting of the 1,10-phenanthroline or pyridine unit have been synthesized. Cyclic voltammetry revealed electron-accepting properties of the polymers. The obtained polymers were soluble in organic solvents, and the solutions emitted intense blue PL. The polymers responded well to H$^+$ and M^{n+} with changes in UV–vis and PL spectra.

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Supporting Information Available: Synthetic procedures and spectroscopic and analytical data of the monomers and polymers; UV–vis and PL spectra of P(PyPh)-1 in chloroform at various concentrations of TFA; and UV–vis spectra of P(PhenPh) in THF–methanol (25:1) at various concentrations of $NiCl_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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