Preparation of Soluble π-Conjugated Poly(5,6-dialkoxy-1,10-phenanthroline-3,8-diyl)s. Their Stacking Behavior and Function as a π-Conjugated Polymer Ligand

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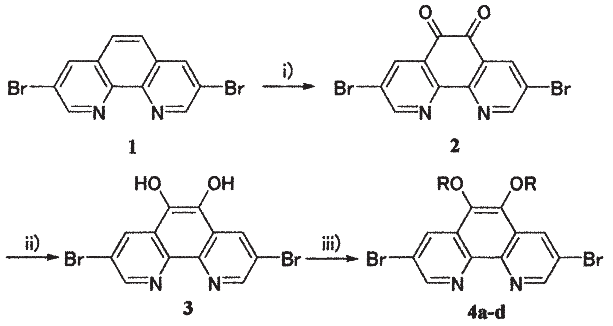
(Received April 22, 2002; CL-020346)

Soluble π-conjugated poly(dialkoxyphenanthroline)s were prepared by organometallic polycondensation using a Ni(0) complex. Stacking structure, optical and electrochemical properties, and Ru complex forming reactivity of the polymer have been revealed.

1,10-Phenanthroline (phen) is a typical chelating ligand for transition metals. Metal complexes of phen are useful as a photo sensitizer,[1a] electroluminescent material,[1b] and catalyst for organic synthesis.[1c,d] π-Conjugated polymers of phen are also expected to be useful and interesting materials. Preparation and some chemical properties of poly(1,10-phenanthroline-3,8-diyl) (PPhen) with a molecular weight of 6800 have already been reported.[2] However, its solubility in organic solvents is low showing complete insolubility in non-acidic solvents such as $CHCl_3$ and THF, and solubilization of the polymer by introducing appropriate substituent(s) is desired for further development of chemistry of poly(phenanthroline)s. We now report preparation of soluble π-conjugated poly(5,6-dialkoxy-1,10-phenanthroline-3,8-diyl)s and its basic chemical properties.

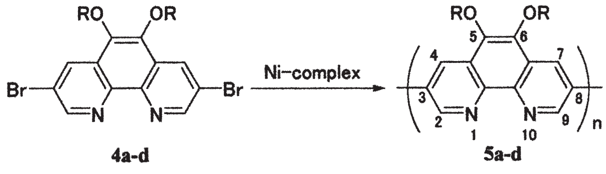
The starting monomers **4a–d** for new PPhens were prepared according to procedures shown in Scheme 1. Oxidation of 3,8-dibromo-phen (**1**)[2] in mixed acid in the presence of KBr afforded **2** as a bright yellow powder in 92% yield.[3] Reduction of **2** with dithiooxamide gave **3** as a dark yellow solid in a quantitative yield.[4] Sodium salt of **3** easily reacted with the corresponding alkyl iodide to afford **4a–d** as pale yellow crystals.[5] It was difficult to introduce alkyl group(s), instead of the alkoxy group, at the 5,6-positions.



a: R = n-C_5H_{11}; **b**: R = n-C_8H_{17}; **c**: R = n-$C_{12}H_{25}$; **d**: R = n-$C_{16}H_{33}$

Scheme 1. Reagent and conditions: i) conc. H_2SO_4 conc. HNO_3, KBr, 130 °C, 3 h (92%). ii) dithiooxamide, EtOH, 110 °C, 12 h. iii) a) NaH, DMSO, 60 °C, 12 h, b) RI, 60 °C, 16 h (46% for **4a**, 28% for **4b**, 40% for **4c**, 39% for **4d**).

Poly(5,6-dialkoxy-1,10-phenanthroline-3,8-diyl), **5a–d**, was prepared by dehalogenative polycondensation of **4a–d** (Scheme 2).[2,6] For example, dehalogenative polycondensation of **4a** (1.02 g, 2.0 mmol) with a mixture of $Ni(cod)_2$ (0.66 g, 2.4 mmol), bpy (0.37 g, 2.4 mmol), and cod (1.2 cm^3, 10 mmol) in DMF at 60 °C for 36 h gave a bright yellow powder of **5a** in 84% yield. **5a** was worked-up by washing with aqueous solutions (e.g., that of dimethylglyoxime) and methanol. Polymers **5b**, **5c**, and **5d** were obtained in similar ways.[7]



a: R = n-C_5H_{11}; **b**: R = n-C_8H_{17}; **c**: R = n-$C_{12}H_{25}$; **d**: R = n-$C_{16}H_{33}$

Scheme 2. Reagent and conditions: $Ni(cod)_2$ (cod = 1,5-cyclooctadiene), 2,2-bipyridyl, cod, DMF, 60 °C, 36 h (84% for **5a**, 63% for **5b**, 74% for **5c**, 86% for **5d**).

5a–d were soluble in organic solvents such as $CHCl_3$. **5a–d** showed only a minor content of Br below 0.5%. ^1H NMR and IR data of **5a–d** agreed with their structures. The ^1H NMR spectra gave two broad peaks at δ 9.6 and 9.0, which were assigned to aromatic 2,9-H and 4,7-H, respectively. Peaks of α-CH_2 and other alkyl protons appeared at δ 4.2–4.3 and 0.9–2.1, respectively. **5a** was soluble in hexafluoro-i-propanol, and GPC analysis of **5a** using this solvent gave a number average molecular weight (M_n) of 17000 (vs poly(methyl methacrylate) standards). **5b–d** were insoluble in the solvent, and GPC analysis of these polymers using chloroform and DMF as the eluent was not possible presumably due to interaction of the polymer with the GPC column. ^1H NMR spectra of these polymers showed a weak aromatic peak at δ 7.7 which seemed assignable to the terminal 3,8-H. From the area of this peak, M_n's of **5b–d** were estimated at 4300–6100. **5d** had solubility of 0.11 g cm^{-3} and 0.002 g cm^{-3} in $CHCl_3$ and THF, respectively.

UV-vis spectra of $CHCl_3$ solutions of the polymers exhibited the lowest energy π-π^* absorption peak in a range of 350–360 nm, which were shifted from those (ca. 290 nm) of the corresponding monomers **4a–d**. Films of the polymers showed UV-vis absorption peaks at a longer wavelength (e.g., 369 nm for **5a**) than the $CHCl_3$ solution, suggesting the presence of certain intermolecular interaction due to stacking[8] of the polymer in the solid. The polymers exhibited photoluminescence in $CHCl_3$ with a peak in a range of 468–504 nm. The photoluminescence peak in film is shifted by 30–60 nm to a longer wavelength, suggesting formation of an excimer-like adduct in the solid, similar to cases of poly(pyridine)[6] and PPhen.[2]

Cyclic voltammograms of cast polymer films in an CH_3CN solution containing $[Bu_4N]PF_6$ showed a redox cycle with cathodic and anodic peaks at about −2.2 V and −1.9 V vs Ag^+/Ag, respectively. However, the polymer film was inert in an oxidation region above 0 V vs Ag^+/Ag. These data reveal that the polymer is susceptible to reduction and inert to oxidation and behaves as an n-type conductor. Isolation of Na-doped polymer was not possible due to solubility of the polymer in THF, in which Na-doping is usually carried out.[6] Non-doped polymers did not show electrical conductivity.

XRD patterns of the polymers are shown in Figure 1. The peaks observed at a low angle region (e.g., the peak with $d = 18.3$ Å for **5a**) are related to a distance between polymer main chains separated by the long alkoxy groups. The *d* value increases with the length of the alkoxy group, and Figure 2 depicts plots of the *d* value vs number of carbons in the alkyl chain. The plots give a straight line with a slope of 1.43 Å/carbon, which is larger than the height of the CH_2 group (1.25 Å/carbon). Based on these results, the polymer is considered to take an end-to-end packing mode with a stacked π-conjugated main chain, similar to cases of poly(3-alkylthiophene-2,5-diyl)s, poly(4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl)s, and poly(5,8-dialkoxyanthraquinone-1,4-diyl).[8,9]

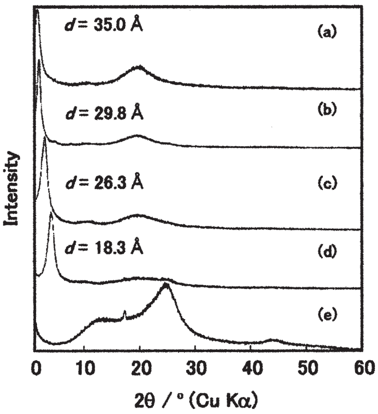


Figure 1. Powder XRD patterns of (a) **5d**, (b) **5c**, (c) **5b**, (d) **5a** and (e) PPhen.

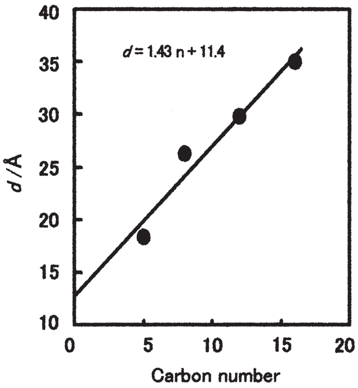


Figure 2. Plots of *d* value vs. number of carbons in the alkyl chain.

Reaction of **5a** with $RuCl_2(bpy)_2$ in an aqueous solution gave a water-soluble $[Ru(bpy)_2]^{2+}$-coordinated complex of **5a**, similar to the case of a reaction of poly(2,2′-bipyridine-5,5′-diyl) and $RuCl_2(bpy)_2$.[6,10] Addition of NH_4PF_6 gave a yellow precipitate of the polymer complex.[11] The Ru-complex forming reactivity of **5a** was considerably higher than that of unsubstituted PPhen. Examples of metal complexes of π-conjugated polymer ligands are still limited. ^{1}H-NMR analysis revealed quantative complex formation of the phen unit of **5a**. The Ru complex showed a broadened MLCT peak at 440 nm in $CHCl_3$ due to the presence of a wide π^* band[10] in **5a** and gave an electrochemical reduction peak at -2.1 V vs Ag^+/Ag.

References and Notes

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3 **2**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.14 (d, 2.8 Hz, 2H), 8.61 (d, 2.8 Hz, 2H). Anal. Found: C, 39.17; H, 1.10; N, 7.61; Br, 43.43%. Calcd for $C_{12}H_4Br_2N_2O_2$: C, 38.49; H, 0.89; N, 7.49; Br, 43.68%.

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5 **4a**: ^{1}H NMR ($CDCl_3$, 400 MHz) 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), 0.98 (t, 7.2 Hz, 6H). Anal. Found: C, 51.78; H, 5.14; N, 5.49; Br, 31.32%. Calcd for $C_{22}H_{26}Br_2N_2O_2$: C, 51.68; H, 4.92; N, 5.49; Br, 31.46%. **4b**: ^{1}H NMR δ: 9.09 (d, 2.4 Hz, 2H), 8.68 (d, 2.4 Hz, 2H), 4.23 (t, 7.2 Hz, 4H), 1.89 (quin., 7.2 Hz, 4H), 1.53 (m, 4H), 1.45–1.25 (m, 16H), 0.90 (t, 7.2 Hz, 6H). Anal. Found: C, 56.58; H, 6.44; N, 4.71; Br, 26.88%. Calcd for $C_{28}H_{38}Br_2N_2O_2$: C, 56.38; H, 6.31; N, 4.70; Br, 26.53%. **4c**: ^{1}H NMR δ: 9.09 (d, 2.4 Hz, 2H), 8.67 (d, 2.4 Hz, 2H), 4.23 (t, 7.2 Hz, 4H), 1.89 (quin., 7.2 Hz, 4H), 1.53 (m, 4H), 1.45-1.20 (m, 32H), 0.88 (t, 7.2 Hz, 6H). Anal. Found: C, 61.19; H, 7.70; N, 3.96; Br, 22.62%. Calcd for $C_{36}H_{54}Br_2N_2O_2$: C, 61.23; H, 7.85; N, 4.00; Br, 22.38%. **4d**: ^{1}H NMR δ: 9.09 (d, 2.4 Hz, 2H), 8.67 (d, 2.4 Hz, 2H), 4.23 (t, 7.2 Hz, 4H), 1.89 (quin., 7.2 Hz, 4H), 1.54 (m, 4H), 1.45-1.20 (m, 48H), 0.88 (t, 7.2 Hz, 6H). Anal. Found: C, 64.54; H, 8.62; N, 3.42; Br, 19.52%. Calcd for $C_{44}H_{70}Br_2N_2O_2$: C, 64.84; H, 9.01; N, 3.48; Br, 20.22%.

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7 **5a**: Anal. Found: C, 70.35; H, 7.72; N, 7.56; Br, 0%. Calcd for $C_{22}H_{26}N_2O_2 \cdot 1.3H_2O$: C, 70.68; H, 7.71; N, 7.49. 1,10-Phenanthroline forms hydrated products, and PPhen was also hydrated.[2a] **5b**: Anal. Found: C, 74.29; H, 8.88; N, 6.51; Br, 0.20%. Calcd for $C_{28}H_{38}N_2O_2 \cdot 0.8H_2O$: C, 74.90; H, 8.89; N, 6.24. **5c**: Anal. Found: C, 77.75; H, 9.71; N, 5.35; Br, 0%. Calcd for $C_{36}H_{54}N_2O_2 \cdot 0.5H_2O$: C, 77.79; H, 9.97; N, 5.04. **5d**: Anal. Found: C, 77.37; H, 10.13; N, 4.57; Br, 0.50%. Calcd for $C_{44}H_{70}N_2O_2 \cdot H_2O$: C, 78.06; H, 10.72; N, 4.14.

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11 Data from elemental analysis roughly agreed with a formation of $[C_{22}H_{26}N_2O_2 \cdot Ru(bpy)_2 \cdot 2PF_6 \cdot (H_2O)]_n$: C, 47.06; H, 4.14; N, 7.84; F, 21.27%. Found: C, 46.31; H, 3.93; N, 8.20; F, 20.61.