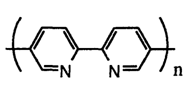
Preparation and Properties of π-Conjugated Poly(1,10-phenanthroline-3,8-diyl)

Yutaka Saitoh and Takakazu Yamamoto*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 226

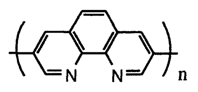
(Received June 5, 1995)

Poly(1,10-phenanthroline-3,8-diyl) has been synthesized by dehalogenation polycondensation of 3,8-dibromo-1,10-phenanthroline with a zerovalent nickel complex. The polymer has molecular weight of 6800 and is electrochemically reduced at $E_{pa} = 2.24$ V *vs* Ag/Ag$^+$.

π-Conjugated poly(arylene)s have been the subject of recent many papers.[1] On the other hand, chemisty of π-conjugated chelating ligands (e.g., 2,2'-bipyridine and 1,10-phenanthroline) and their metal complexes has been extensively explored. However, examples of π-conjugated chelating polymer ligands (e.g., poly(2,2'-bipyridine-5,5'-diyl) PBpy[2]) have been limited. We here report preparation and properties of new π-conjugated poly(arylene), poly(1,10-phenanthroline-3,8-diyl) PPhen, constituted of recurring 1,10-phenanthroline units.



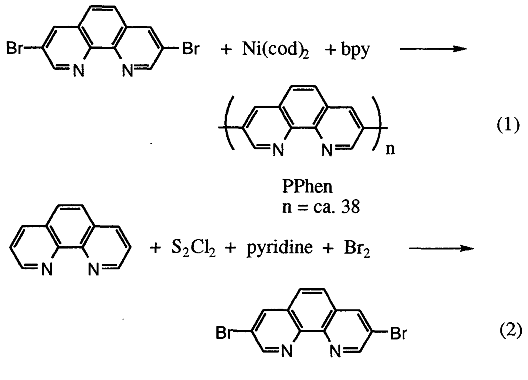
PBpy



PPhen

PBpy is considered to take an *s*-trans structure and rotation of the C-C bond is necessitated for the metal complex formation. In the case of PPhen, it has a more rigid chelating structure and recently interesting electrical and optical properties of metal complexes of 1,10-phenanthroline derivatives have been reported.[3]

PPhen has been prepared by Ni-promoted dehalogenation polycondensation[2] of 3,8-dibromo-1,10-phenanthroline, which is prepared by bromination of 1,10-phenanthroline.[4]



The dehalogenation polycondensation of the monomer (650 mg, 1.9 mmol) with a Ni(0) complex (a mixture of bis(1,5-cyclooctadiene)nickel(0) Ni(cod)$_2$ (650 mg, 2.4 mmol), 2,2'-bipyridine (310 mg, 2.0 mmol), and 1,5-cyclooctadiene (1.2 cm^3)) gave reddish brown PPhen, which was isolated in a manner similar to that applied to the isolation of PBpy :[2] yield = 80.7%.[5] PPhen is soluble in formic acid and partially soluble in sulfuric acid, however, it is not soluble in common organic solvents. PPhen has molecular weight of 6.8×10^3, which corresponds to the degree of polymerization of 38, as determined by a light-scattering method. The polymer shows intrinsic viscosity of 0.40 dlg^{-1} (dl = 100 cm^3) as measured in formic acid. Casting from a formic acid solution of PPhen gives a film free from formic acid and with good optical and mechanical quality.

The π-π^* absorption band of PPhen appears at a considerably longer wavelength ($\lambda_{max} = 382$ nm) in formic acid (Figure 1a) than that ($\lambda_{max} = 277$ nm) of 1,10-phenanthroline revealing the expansion of the π-conjugation system along the polymer chain. The casting film of PPhen exhibits the π-π^* absorption band at the same position. The formic acid solution of PPhen shows a strong fluorescence with a peak at 413 nm when excited by 384 nm light (Figure 1b). The fluorescence peak position agree with the onset position of the π-π^* absorption as usually observed with fluorescent π-conjugated compounds. On the other hand, a PPhen film prepared by casting from the formic acid solution gives a shifted fluorescence band with λ_{max} of 535 nm (Figure 1c), which lies apart from the onset position of the π-π^* absorption. A similar shift of fluorescence peak in film has also been observed with PBpy and the shift has been ascribed to formation of an excimer-like adduct between the rigidly linear PBpy molecules aligned in the film.[2]

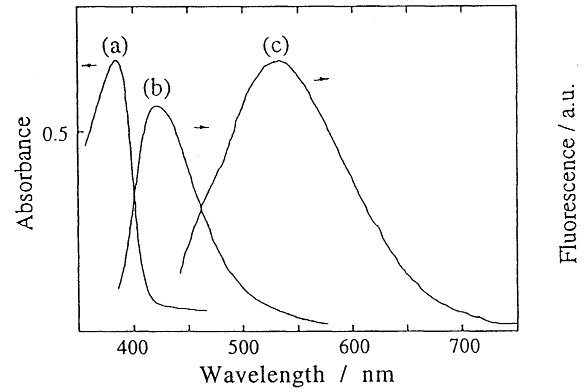
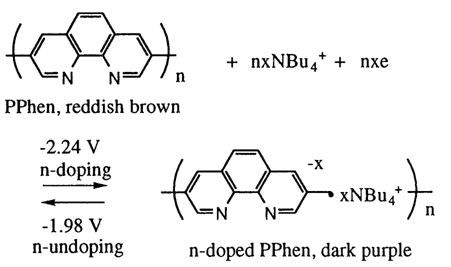


Figure 1. UV-visible spectrum of PPhen in formic acid (a), fluorescence spectrum of PPhen in formic acid (b), and fluorescence spectrum of PPhen film on a quartz glass plate (c); a.u = arbitrary unit.

Cyclic voltammogram (Figure 2) of the polymer film in a dry acetonitrile solution containing tetrabutylammonium tetrafluoroborate shows a redox cycle with cathodic and anodic peaks at -2.24 V, -1.98 V *vs* Ag/Ag$^+$, respectively, and the peaks are assigned to n-doping and n-undoping of PPhen .



(3)

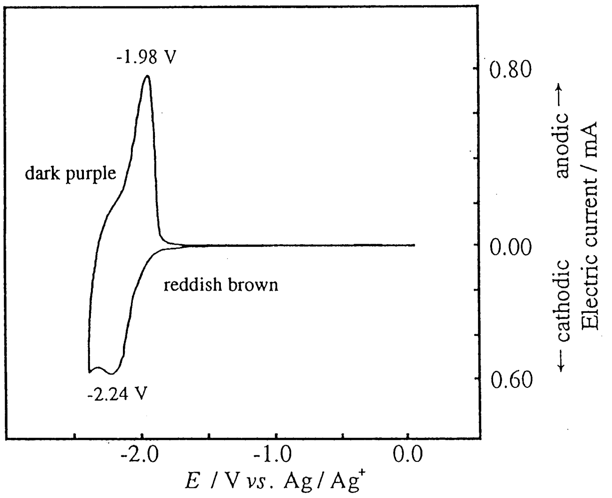


Figure 2. Cyclic voltammogram of a film of PPhen on a platinum plate in a CH_3CN solution of 0.1 M $[N(n\text{-}C_4H_9)_4][BF_4]$. Sweep rate = 5 mVs^{-1}.

The n-doping and n-undoping are accompanied by color change shown in Eq. 3 and repeated without change of the cyclic voltammogram. The doping level (x in Eq. 3) is about 0.5 as estimated from the n-doping current. In contrast to the facile n-doping, PPhen is inert against p-type doping (oxidation) up to 1.0 V vs Ag/Ag$^+$. These electrochemical properties agree with previously observed results that poly(arylene)s containing electron-withdrawing imine nitrogen(s) are active for the n-doping but inactive for p-doping. Treatment of PPhen with a THF solution of sodium naphthalide at room temperature gives dark purple product, which has electrical conductivity of about 10^{-5} S cm^{-1} as measured with compressed powder.

References and Notes

1 T. A. Skotheim, Ed. *Handbook of Conducting Polymers, Vols. I and II*, Marcel Dekker, New York (1986).

2 T. Yamamoto, T. Maruyama, Z. -H. Zhou, T. Ito, T.Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, and K.Kubota, *J. Am. Chem. Soc*, **116**, 4832 (1994).

3 T.Tsutsui, N.Takada, and S.Saito, and E.Ogino, *Appl. Phys. Lett*, **65**, 1868 (1994).

4 Preparation of 3,8-Dibromo-1,10-phenanthroline :
To 1,10-phenanthroline monohydrate (5.0 g, 28 mmol) dissolved in 200 cm^3 of 1-chlorobutane were added S_2Cl_2 (11.3 g, 83 mmol), pyridine (6.9 g, 87 mmol) and Br_2 (10 g, 63 mmol), and the reaction mixture was refluxed for 12 h. The precipitate formed was separated by decantation and dissolved in chloroform. After treatment with a SiO_2 short column, the $CHCl_3$ solution was condensed to about 60 cm^3, and Br_2 (3.0 g, 19 mmol) was added to the condensed solution to obtain an orange solid of a Phen-Br_2 complex. After 30 min, the solid was collected by filtration and purified by SiO_2 column chromatography and recrystallization from benzene to yeild white needles of PhenBr$_2$ (26% yeild). Anal. Found : C, 42.7; H, 1.8; N, 8.4; Br, 47.0%. Calcd for $C_{12}H_6N_2Br_2$: C, 42.6; H, 1.8; N, 8.3; Br, 47.3%. IR(KBr, cm^{-1}) : 3024, 1583, 1475, 1411, 1204, 1101, 906, 892, 776, 720; ^{1}H NMR($CDCl_3$) δ :7.73 (s, 2H), 8.39 (d, J = 2.2 Hz, 2H), 9.17 (d, J = 2.2 Hz, 2H).

5 Anal. Found : C, 74.9; H, 3.6; N, 14.4; Br, 0%. Calcd for $(C_{12}H_6N_2\cdot 0.8H_2O)_n$: C, 74.8; H, 4.0; N, 14.5%. IR (KBr, cm^{-1}) : 1419, 901, 730.