

Electrical and Magnetic Properties of Conjugated Schiff Base Polymers

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SYNOPSIS

Two new conjugated poly-Schiff bases (PPpP and PPmP) were synthesized by polycondensation of *p*-phenylene diamine or *m*-phenylene diamine with 2,6-pyridine dicarboxaldehyde. PPpP and PPmP can form charge transfer complexes with iodine. Maximum conductivity of PPpP-iodine complex at room temperature is 10^{-6} S/cm, which is 2 orders of magnitude higher than that of PPmP-iodine complex. Electronic spin resonance measurements discovered that there are stable radicals in both charge transfer complexes; and *g* value, line width, and spin concentration depend on doping degree. Magnetic susceptibility of charge transfer complexes of PPmP-iodine is composed of Curie magnetic susceptibility (χ_C) and Pauli magnetic susceptibility (χ_P). Its Curie constant (*C*), Curie spin concentration (N_C), and density of state at the Fermi level also depend on doping degree. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Interest has been focused on poly-Schiff bases because of their thermal stability,¹ electrical conduction,²⁻⁴ and photoconduction.⁵ Poly-Schiff bases can form coordinate complexes with metal ions by their nonbonded pair of electrons on nitrogen atoms, and charge-transfer complexes with an electron acceptor or electron donor by its nonbonded electrons or π electrons. It is expected that the physical properties, such as electrical, magnetic, and optical properties, of poly-Schiff bases and their derivatives could be modified by changing the molecular structure and molecular weight.

Poly-Schiff bases can be synthesized by polycondensation of aromatic or heterocyclic diamine with dialdehydes or diketones. Because there are delocalized π systems in the polymer chain, the conductivity of conjugated poly-Schiff bases is in the range of 10^{-10} – 10^{-15} S/cm, and the corresponding thermal active energies are about 0.9–1.5 eV or even higher⁶; but their conductivity can increase by several orders after doping. Most conjugated poly-Schiff bases can

be doped by oxidants, such as I_2 or Br_2 , to be semiconductors.⁷⁻¹¹ It is worth mentioning that poly-Schiff base prepared from 2,3-butanedione and hydrazine hydrate can be doped by iodine and reach a conductivity as high as 1.3 S/cm.⁹ In addition, the magnetic properties of poly-Schiff bases prepared by condensation of 2,6-diaminopyridine and glyoxal has also been reported.¹²

It has been discovered that polyaniline with a different chain structure shows different electrical and magnetic properties. Poly(*p*-aniline) is a nice electrical conductor with conductivity¹³ of about 10^1 S/cm and it is a paramagnet.¹⁴ However, poly(*m*-aniline) presents ferromagnetic interaction and very poor conductivity (10^{-5} – 10^{-6} S/cm).^{15,16} If Schiff base polymers resembling polyaniline could be prepared, electrical and magnetic properties similar to polyaniline would be expected.

In this study two new conjugated poly-Schiff bases similar to poly(*p*-aniline) and poly(*m*-aniline) and their charge transfer complexes with iodine were designed, synthesized, and characterized. The electrical and magnetic properties of their charge transfer complexes were investigated by measurements of conductivity, electronic spin resonance (ESR), and magnetic susceptibility.

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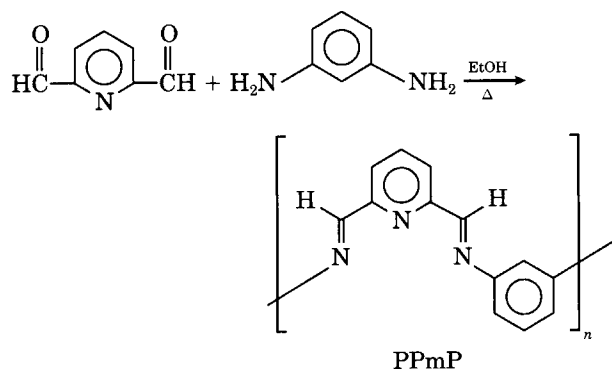
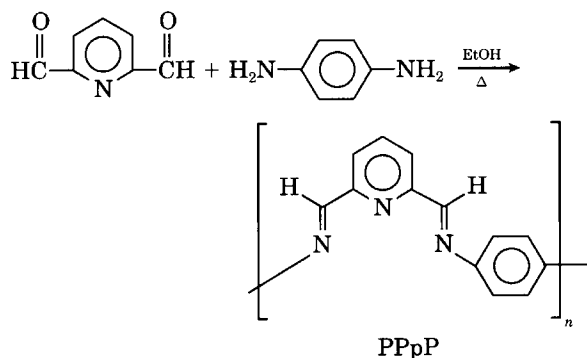
Table I Elemental Content of PPpP and Its Charge Transfer Complexes with Iodine

Ratio of I ₂ to PPpP in doping (mol/mol)	0	0.27	0.81	1.36	8.15	13.59
C%	73.51	53.10	37.64	28.69	25.61	24.72
H%	4.80	4.08	2.53	1.80	2.22	2.10
N%	20.31	14.24	9.25	6.35	5.43	4.97
I%*	0	28.6	50.6	63.2	66.7	68.2
Doping degree (x), (C ₁₃ H ₉ N ₃ I _x) _n	0	0.6	1.6	2.7	3.2	3.4
Color	Yellow	Brown	Brown	Black	Black	Black

* The content of iodine is calculated by the contents of C, H, and N: I% = 100% - C% - H% - N%.

EXPERIMENTAL

Two new conjugated poly-Schiff bases were prepared by polycondensation of 2,6-pyridine dicarboxaldehyde with *p*-phenylene diamine (PPpP) or *m*-phenylene diamine (PPmP) according to the following reaction equation:



PPpP Synthesis

In a 100-mL flask equipped with a condenser and stirrer, 3.0 g (22 mmol) 2,6-pyridine dicarboxaldehyde was dissolved in 20 mL absolute ethyl alcohol; 2.4 g (22 mmol) *p*-phenylene diamine dissolved in 20 mL absolute ethyl alcohol was added dropwise

within 30 min under protection of N₂. The mixture was heated to reflux for 1 h, then filtrated immediately. The resulting precipitate was washed with 20 mL ethyl alcohol 3 times, then dried in vacuum. Yellow powder (3.1 g, yield 75%) was obtained, which did not fuse or dissolve in common solvents.

ANAL. Calcd. for (C₁₃H₉N₃)_n: C, 75.3%; N, 20.3%; H, 4.4%. Found: C, 73.8%; N, N, 20.3%; H, 4.8%.

PPmP Synthesis

PPmP (yellow powder) was prepared by polycondensation of 2,6-pyridine dicarboxaldehyde with *m*-phenylene diamine instead of *p*-phenylene diamine. The preparation processes of PPmP are the same as PPpP. The yield of PPmP is 73%. PPmP also does not fuse or dissolve in common solvents.

ANAL. Calcd for (C₁₃H₉N₃)_n: C, 75.3%; N, 20.3%; H, 4.4%. Found: C, 73.7%; N, 19.4%; H, 5.9%.

Charge Transfer Complexes of PPpP and PPmP with Iodine

PPpP or PPmP was blended with iodine and ground into fine powder in an agate mortar. The powder was immersed in 20 mL absolute ethyl alcohol for 24 h, then the solvent was evaporated. The resulting sample was treated in vacuum at 60–70°C to remove the surplus iodine until the weight of the sample became stable. The color of charge transfer complexes was brown to black for the different contents of iodine used. The elemental analysis results of the doping experiment are given in Tables I and II, respectively. It seems that PPmP can be doped to a higher iodine level than PPpP.

Characterization and Measurements

PPpP, PPmP, and their charge transfer complexes with iodine were characterized with elemental anal-

Table II Elemental Content of PPMp and Its Charge Transfer Complexes with Iodine

Ratio of I ₂ to PPMp in doping (mol/mol)	0	0.20	0.61	1.01	2.04	4.12	8.17
C%	71.31	55.06	42.46	36.05	27.92	17.81	15.72
H%	7.90	2.72	2.53	2.30	1.46	1.18	0.88
N%	19.41	15.26	11.29	9.58	7.18	4.19	3.94
I%*	0	27.0	43.7	52.1	63.4	76.8	79.5
Doping degree (x), (C ₁₃ H ₉ N ₃ I _x) _n	0	0.6	1.3	1.8	2.8	5.3	6.2
Color	Yellow	Brown	Brown	Brown	Brown	Black	Black

* The content of iodine is calculated by the contents of C, H, and N: I% = 100% - C% - H% - N%.

ysis (Heraeus, CHN-Rapid), FTIR (Bruker, IFS-113V), UV-vis spectra (Hitachi, 340), and X-ray photoelectron spectroscopy (XPS; Kratos, ES-300). ESR was measured by a Bruker ER-200D. Magnetic measurement at 1.5–300 K was carried out by extracting sample magnetometer (Neel Lab. CF-1). Conductivity at room temperature was measured by the two probe method illustrated in Figure 1. The voltage applied at the sample was provided by a home-made DC source (0.1–200 V), and the current through the sample was measured by an electrometer (Takuriken, TR-8451).

RESULTS AND DISCUSSION

Characterization

The FTIR spectra of PPpP (pellet of KBr) [Fig. 2(a)] shows absorption at 3385, 1700, 1621, 1577, 1566, 1459, 1500, 1452, 1205, and 833 cm⁻¹. The absorption at 3385 cm⁻¹ is assigned to NH₂ at the end of the polymer chain. The weak peak at 1700 cm⁻¹ indicates that few aldehyde groups remain; the strong absorption at 1621 cm⁻¹ from C=N, which is due to stretching vibration, is the characteristic absorption of a Schiff base.⁹ Peaks at 1577, 1566, 1500, 1459, and 1452 cm⁻¹ are backbone vibration of the benzene or pyridine ring. Absorption at 833 cm⁻¹ suggests that there are *p*-phenylene structures in the polymer. The FTIR spectra of PPMp [Fig.

3(a)] show absorption at 3364, 1700, 1588, 1486, 1451, 737, and 691 cm⁻¹. The absorption at 3364 cm⁻¹ is attributed to NH₂ at the end of the polymer chain. The weak absorption at 1700 cm⁻¹ suggests that few aldehyde groups remain, and the strong peak at 1588 cm⁻¹ is the characteristic absorption of a Schiff base. Peaks at 1486 and 1451 cm⁻¹ are the backbone vibration of benzene and pyridine. Peaks at 737 and 691 cm⁻¹ are assigned to *m*-phenylene groups. As described above, the results of IR spectra are consistent with the structure of poly-Schiff bases proposed by us.

When PPpP is doped by iodine at the lower doping degree, the IR absorption of NH₂ at nearby 3300 cm⁻¹ disappears [see Fig. 2(b)]; and there are little changes in the peak positions of their IR spectra, except for the relative intensity of some peaks. This suggests that the charge transfer may occur between nonbonding electrons in the N atom of the poly-Schiff base and iodine; and the chain structure changes little, except for the oxidation of the end group (NH₂). At a high doping degree, most peaks become wide and some fine structure disappears. But the characteristic absorption of a Schiff base at nearly 1600 cm⁻¹ still can obviously be seen [see Fig. 2(c)]. This indicates that charge transfer may occur between the π electron in the poly-Schiff base and iodine, and the chain structure changes at a high doping degree. A similar effect of doping degree on the IR spectra of PPMp was observed as shown in Figure 3(b,c).

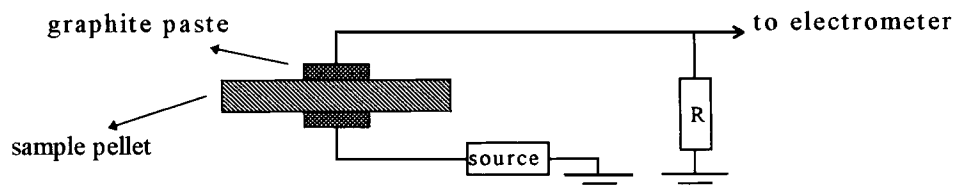


Figure 1 Illustration of the method for the measurement of conductivity of charge transfer complexes of Schiff base polymers.

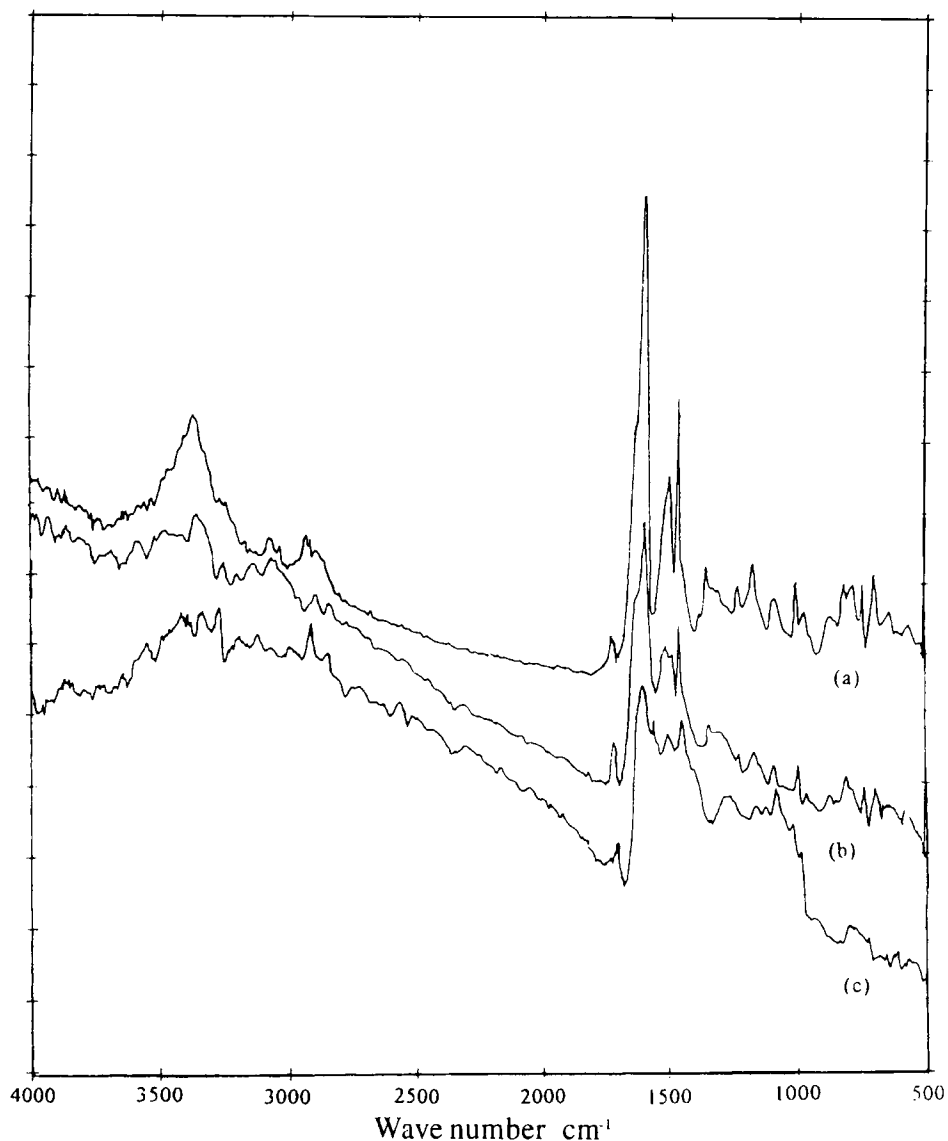


Figure 2 IR spectra of PpP and its charge transfer complexes with iodine. (a) PpP, (b) doping degree (x) = 0.6, and (c) doping degree (x) = 3.2.

There is a wide absorption band at 220–420 nm in UV-vis reflection spectra of both PpP and PpM. After PpP and PpM are doped by iodine, their UV-vis reflection spectra show a new absorption band at 400–550 nm with a long tail extending to about 850 nm, which is the charge transfer absorption. For PpP the charge transfer absorption is located at 400–540 nm, and appears at 400–640 nm in the high doping degree. For PpM the charge transfer absorption appears at 400–500 nm and shows a little bathochromic shift at the high doping degree. The changes in UV-vis spectra before and after doping prove that charge transfer between the poly-Schiff base and iodine occurred.

XPS shows that the binding energies of N_{1s} for PpM are 399.5 and 398.7 eV respectively, and the ratio of them is 92 : 8 (shown Table III). The peak at 399.5 eV is assigned to the N atom in the C=N group (including the N in pyridine), whereas the peak at 398.7 eV corresponds to the N in the end group (NH_2). The binding energies of N_{1s} turn to 399 and 401 eV after doping, and the intensity at the 401-eV peak increases with increasing doping degree. This indicates that charge transfer occurs at the C=N group, and increasing the doping degree leads to more charge transfer. The $I_{3d_{3/2}}$ of charge transfer complexes of PpM with iodine is made up of two peaks at

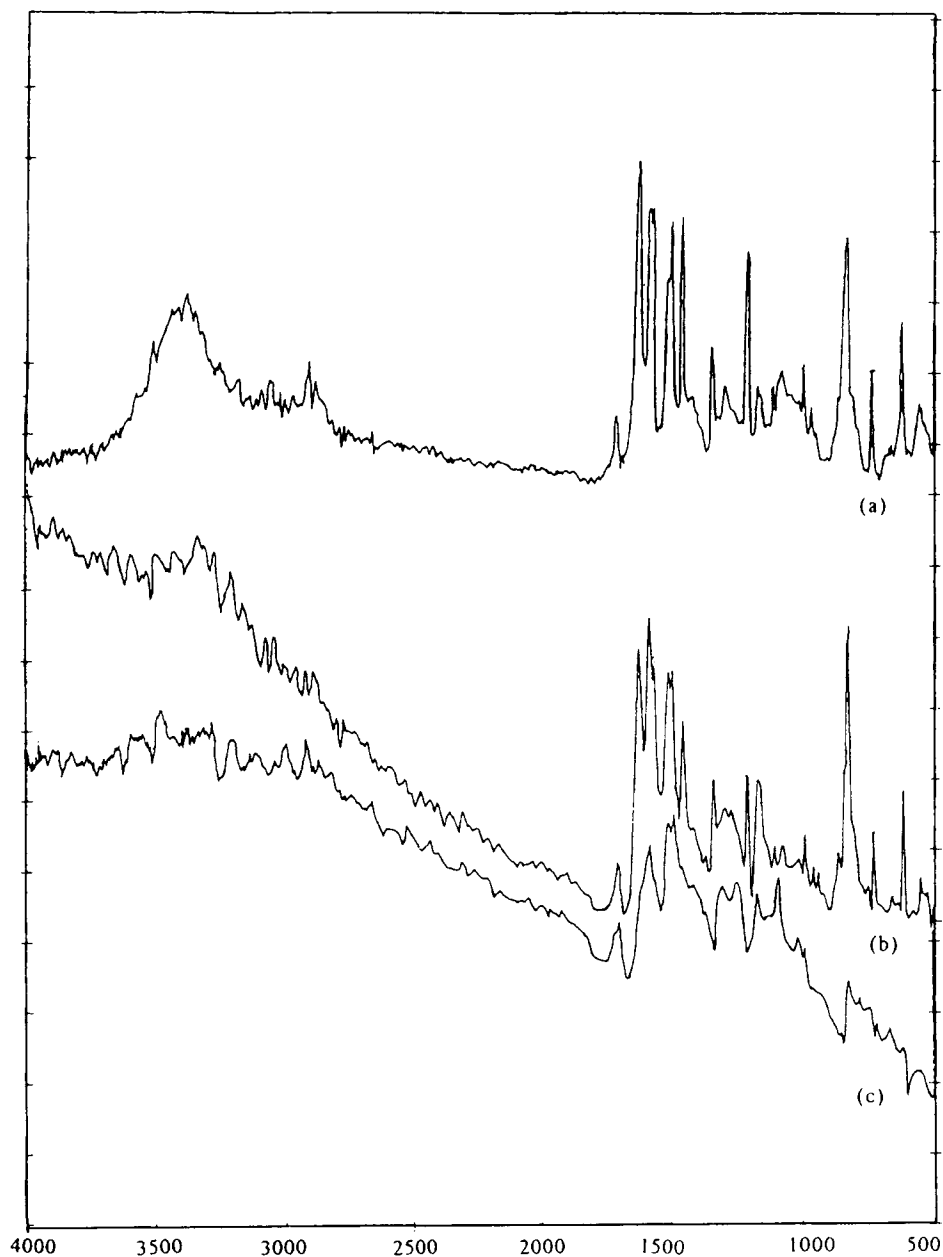


Figure 3 IR spectra of PPMp and its charge transfer complexes with iodine. (a) PPMp, (b) doping degree (x) = 0.6, and (c) doping degree (x) = 5.3.

about 620 and 619 eV. The relative intensity of the peak at about 619 eV is enhanced at the high doping degree. Therefore, I^- , I_3^- , or I_5^- may be the counterions in the charge transfer complex of PPMp.

The variation of binding energies of N_{1s} and $I_{3d3/2}$ for PPMp with the doping degree is similar to that of PPMp, and the related data are given in Table IV.

Electrical Properties of Charge Transfer Complexes of PPMp and PPMp with Iodine

Room-temperature conductivity of original PPMp and PPMp is about 10^{-10} – 10^{-11} S/cm and conductivity of PPMp is relatively higher. As shown in Figure 4, after PPMp and PPMp are doped by iodine, their conductivity is increased by 3–4 orders of magnitude, depending on the doping degree. Room-temperature

Table III Binding Energies of N_{1s} and $I_{2d3/2}$ of PpP and Its Charge Transfer Complexes with Iodine

	Doping Degree (x)					
	0		0.6		3.2	
	Binding Energy (eV)	Peak Area* (%)	Binding Energy (eV)	Peak Area (%)	Binding Energy (eV)	Peak Area (%)
N_{1s}	398.8	100	401.0	4.5	401.0	62.4
			398.6	95.5	399.2	37.6
$I_{2d3/2}$			620.5	24.1	620.5	7.8
			619.0	75.9	618.8	92.2

* Found via XPS.

conductivity of both PpP-I₂ and PmP-I₂ complexes increases with increasing doping degree. The maximum conductivity can reach about 10⁻⁸ S/cm for PmP and 10⁻⁶ S/cm for PpP. Apparently, conductivity of complexes of PpP is relatively higher than that of PmP at the same doping degree, because the *p*-phenylene structure in PpP favors electrical conduction. Compared with charge transfer complexes of other poly-Schiff bases, such as a poly-Schiff base from *p*-phenylene diamine and 1,3-phenylene dicarboxaldehyde,¹⁰ conductivity of PpP and PmP is lower. This may be due to the 2,6-pyridylidene structure, which is unfavorable to electrical conduction.

Magnetic Properties of Complexes of PpP and PmP with Iodine

Effect of Doping Degree on ESR Signal

The charge transfer complexes of PmP and PpP have strong ESR signals, which are symmetrical line shapes without fine structure. ESR signals measured repeatedly after 2 months change little, which indicates that stable radicals exist in the charge transfer complexes of PmP and PpP. Changes in *g* factor, line width data (ΔH), and the peak area of ESR signals with the doping degree for PpP and PmP are shown in Figure 5.

As shown in Figure 5(a) spin concentration, which is related to the area of ESR signals, of PmP increases with the increase of doping degree to reach the maximum value and then follows a decline, because the high concentration of iodine at the high doping degree dilutes the spin concentration. However, spin concentration for PpP increases with the increase of doping degree continuously to the maximum doping degree (about $x = 3$). Generally, for both PpP and PmP, spin concentration reaches its maximum value when doping degree (x) is about 3.

According to the theory of ESR, the *g* factor is determined by the following equation:

$$\vec{H}_e = \frac{1}{2}g \cdot \vec{H}, \quad (1)$$

where \vec{H}_e is the effective magnetic field applied on spins and \vec{H} is the applied magnetic field. Therefore, the *g* factor represents the difference between \vec{H} and \vec{H}_e . \vec{H}_e is affected by two factors: the diamagnetic shielding effect of saturated electronic structure, which decreases H_e , and the magnetic deshielding effect of unpaired electrons, which increases the \vec{H}_e . It was found that *g* factors of complexes of PmP and PpP increase with increasing doping degree. Furthermore, *g* factors of the two complexes change in the same range from 2.0035 to 2.0055 [shown in Fig. 5(b)]. Because the *g* factor presents the chemical environment of radicals, the radicals in two complexes may be alike. But it is difficult to determine the real nature of the spin center by such measurements. Along with the increase of doping degree, more radicals form on the polymer chain; magnetic deshielding effect is increased, in the meantime, because of the withdrawing electron effect of iodine. When iodine approaches radicals, diamagnetic shielding effect is decreased. All these cause the increase of \vec{H}_e , which results in a *g* factor increase with the increase of iodine content.⁸

Linewidth (ΔH) of the ESR signal represents the uncertainty of the spin resonance energy, and it is affected by spin relaxation time; spin-lattice relaxation time (t_1), and spin-spin relaxation time (t_2). For PmP, as shown in Figure 5(c), line width increases with increasing doping degree. The reason for this may be that concentration of radicals on the PmP chain at high doping degree increases, which enhances spin-spin interaction, and leads to enlarged line width. For PpP, line width shows a fast initial increase, then slightly increases. This indi-

Table IV Binding Energies of N_{1s} and $I_{2d3/2}$ of PPMp and Its Charge Transfer Complexes with Iodine

	Doping Degree (x)							
	0		0.6		1.8		5.3	
	Binding Energy* (eV)	Peak Area* (%)	Binding Energy (eV)	Peak Area (%)	Binding Energy (eV)	Peak Area (%)	Binding Energy (eV)	Peak Area (%)
N_{1s}	399.5	92	401.0	35	400.8	23	400.7	22
	398.7	8	399.4	65	399.1	77	399.2	78
$I_{3d3/2}$			621.0	71	620.0	47	620.4	40
			919.1	29	619.3	53	619.1	60

* Found via XPS.

cates that the interaction between spins or spin-lattice in the PPMp and PPpP may be different.

Magnetic Susceptibility Measurements

The magnetization of charge transfer complexes of PPMp with iodine vs. temperature is shown in Figure 6(a). It can be seen that magnetization of the two samples drops quickly with increasing temperature until 40 K; it becomes independent of temperature over 40 K. Therefore, magnetic susceptibility (χ) can be expressed in the following equation:

$$\chi = \chi_C + \chi_P = \frac{C}{T} + \chi_P \quad (2)$$

where $\chi_C = C/T$ is the Curie magnetic susceptibility, which is related to localized spins and depends on temperature, χ_P is the Pauli magnetic susceptibility, which represents delocalized spins, and can be expressed as

$$\chi_P = \mu_B^2 N(E_F) \left(1 - \frac{\pi^2}{12} k_B^2 T^2 E_0^2 \right), \quad (3)$$

where $N(E_F)$ is the density of the state at the Fermi level, μ_B is the Bohr magneton, and k_B is the Boltzmann constant. The second term can be omitted if T is not very high. Therefore, χ_P is independent of temperature at a lower temperature.

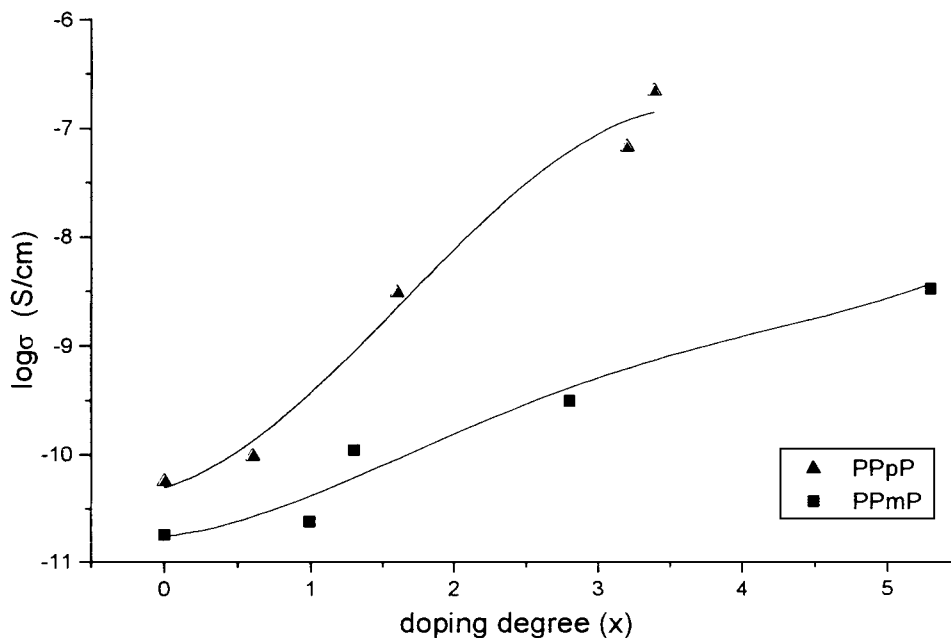


Figure 4 Effects of doping degree on room-temperature conductivity of (a) PPpP-iodine complex and (b) PPMp-iodine complex.

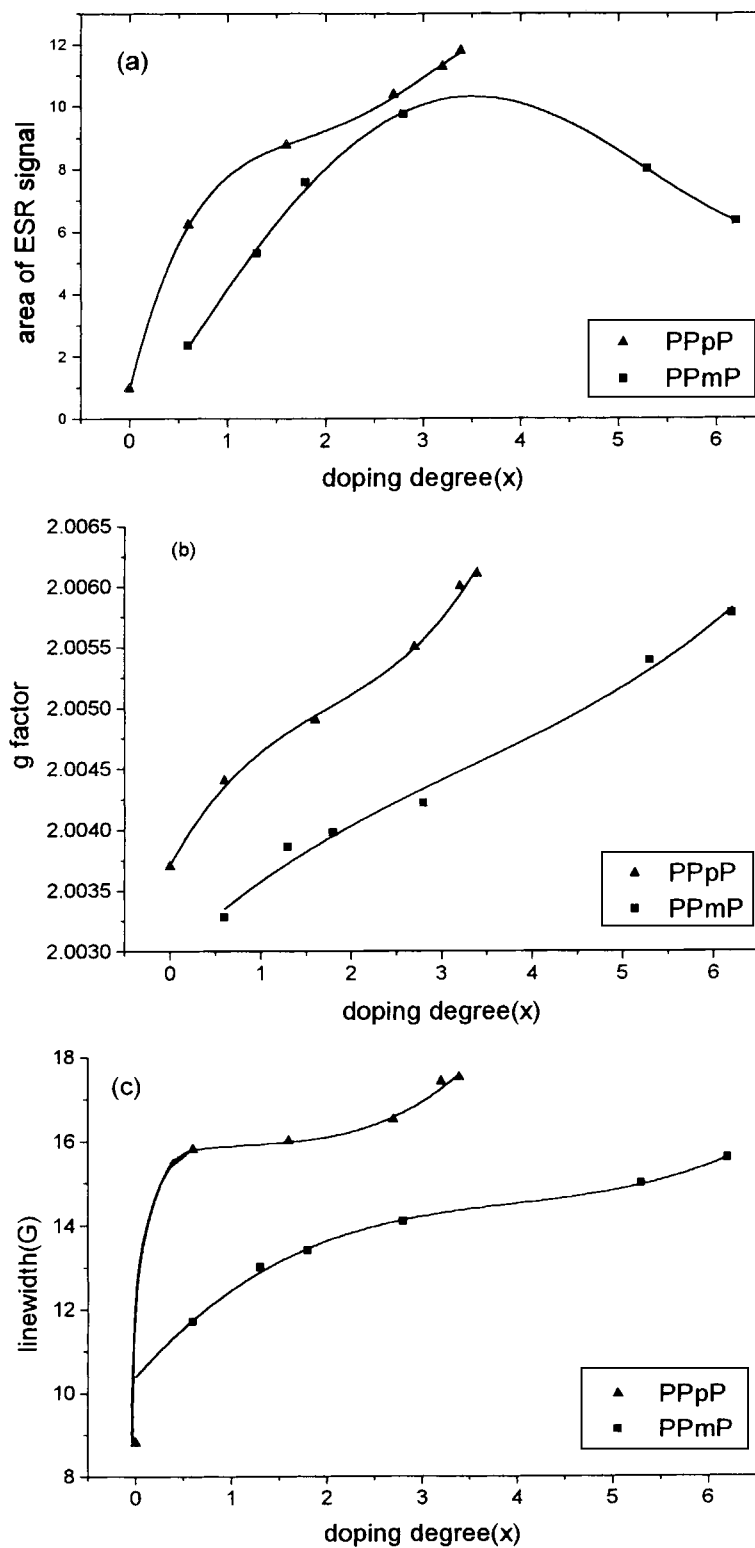


Figure 5 Effects of doping degree on ESR of PPpP-iodine and PPpP-iodine complexes. (a) Area of ESR signal, (b) line width, and (c) g factor.

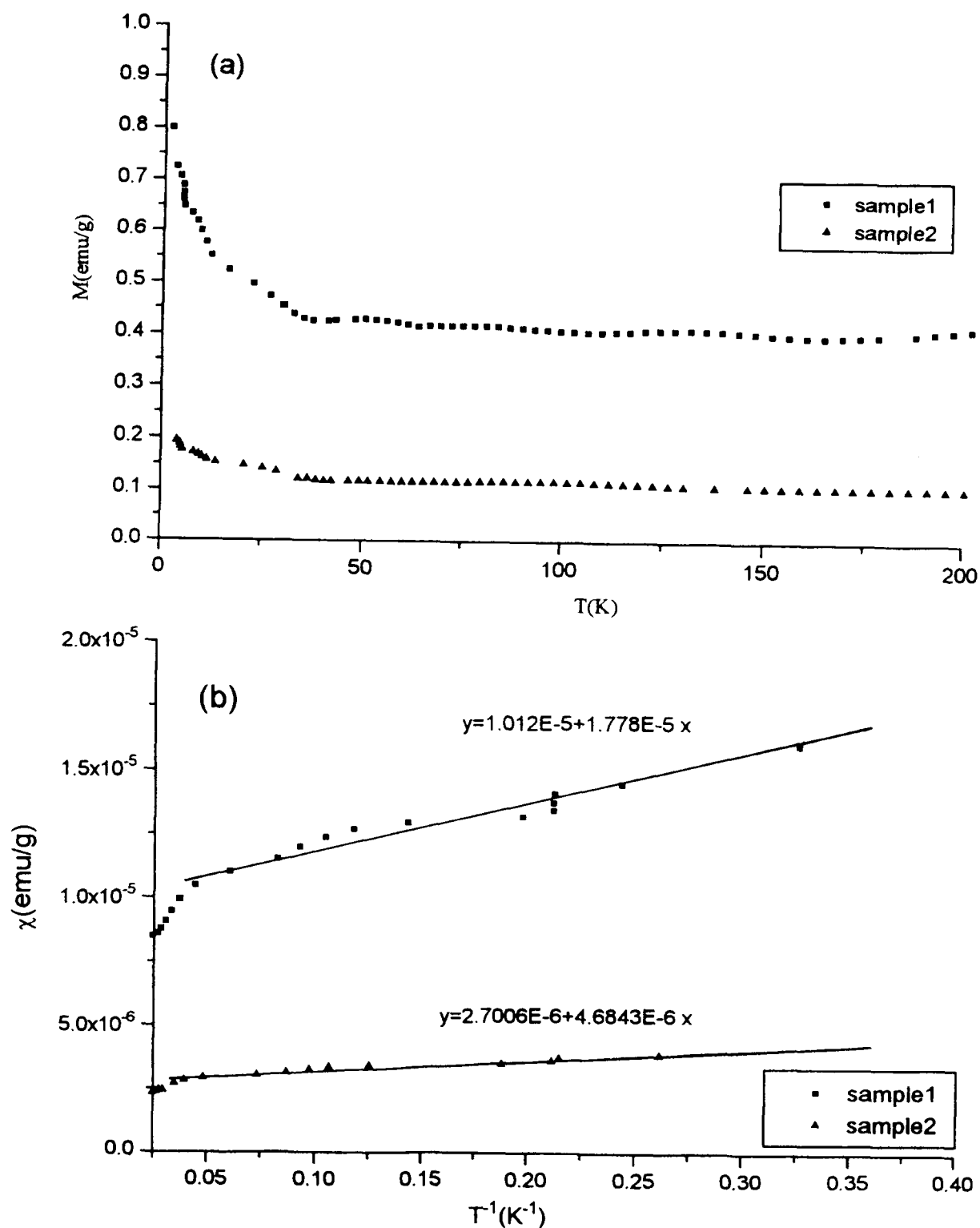


Figure 6 (a) Magnetization vs. temperature for PPMp-iodine complexes. (b) Magnetic susceptibility vs. reciprocal of temperature for PPMp-iodine complexes. Sample 1, doping degree (x) = 1.3 and sample 2, doping degree (x) = 5.3.

Table V Magnetic Measurement of Charge Transfer Complexes of PPmP with Iodine

Sample	Doping Degree (x)	C (emu · k/g)	χ_P (emu/g)	N_C (Spin/g)	$N(E_F)$ (State/eV)
1	1.3	1.78×10^{-5}	1.01×10^{-5}	8.58×10^{19}	3.01×10^{11}
2	5.3	4.68×10^{-6}	2.70×10^{-6}	2.26×10^{19}	8.04×10^{10}

$$\chi_P = \mu_B^2 N(E_F) \quad (4)$$

Curie constant (C) and Curie spin concentration (N_C) can be expressed as

$$C = \frac{N_C \mu_B^2}{3k_B} \quad (5)$$

As a result, Curie constant (C) and Pauli magnetic susceptibility (χ_P) can be determined by Figure 6(b), which is plotted by χ vs. $1/T$, density of state at Fermi level $N(E_F)$, and Curie spin concentration (N_C) can also be calculated from eqs. (4) and (5). As shown in Table V, it can be found that N_C , χ_P , and $N(E_F)$ decrease at a high doping degree.

CONCLUSIONS

1. Two new conjugated poly-Schiff bases (PPpP and PPmP) and their charge transfer complexes with iodine were synthesized and characterized with elemental analysis, IR, XPS, and UV-vis reflection spectra.
2. Room-temperature conductivity of charge transfer complexes of PPpP and PPmP with iodine increases with increasing doping degree. Maximum conductivity at room temperature can reach 10^{-6} S/cm for PPpP and 10^{-8} S/cm for PPmP. This indicates that the chain structure of PPpP favors electron conduction.
3. ESR measurements demonstrate that there are stable radicals in charge transfer complexes of PPmP and PPpP with iodine, and the g factor, line width, and area of the ESR signal depend on doping degree.
4. The magnetic susceptibility of charge transfer complexes of PPmP with iodine is composed of Curie magnetic susceptibility (χ_C) and Pauli magnetic susceptibility (χ_P). Curie constant (C), Curie spin concentration (N_C),

and density of state at Fermi level [$N(E_F)$] are found to be dependent on doping degree.

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