Synthesis, conductivity, and electromagnetic wave absorption properties of chiral poly Schiff bases and their silver complexes

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ABSTRACT: Four chiral poly Schiff bases were synthesized via polycondensation between L–lysine and p-benzoquinone, 1,4-naphthoquinone, dibenzoyl, and 2,3-butanedione, respectively. Subsequently, the silver coordination polymers of the chiral poly Schiff base were prepared upon silver ions coordinating with the chiral poly Schiff bases. The structures of the polymers were characterized with IR, UV-vis, GPC, elemental analysis, and optical activity analysis. The properties of polymers were studied through conductivity testing and electromagnetic parameter testing. The results show that they own good electrical conductvities, and the electrical conductivity of chiral poly-(L–lysine(2,3-butanedione)) Schiff base silver complex can reach 3.7×10^2 S/cm. The electromagnetic wave absorption properties of four silver complexes were calculated using transmission line theory, the maximum reflection loss of chiral poly-(L–lysine(p-benzoquinone)) Schiff base silver complex can reach -45.9 dB at a thickness of 5 mm, while that of achiral poly-(DL-lysine(p-benzoquinone)) Schiff base silver complex is -20.1 dB at a thickness of 5 mm. The enhanced microwave absorbing properties were attributed to the chiral feature. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42498.

INTRODUCTION

Stealth technology has received more and more attention in the military field since World War II. The electromagnetic (EM) wave absorption properties of materials are key in stealth technology.[1] In addition, EM radiation has become a serious environmental pollution problem, not only influencing the operation of electronic devices, but also being harmful to the health of human beings.[2,3] Therefore, the rapid development of EM wave absorption materials has occurred in recent years, which have been used in a wide range of military (such as aircraft, tanks, and ships) and civil (such as electronic devices) fields.[4]

In 1987, retinyl Schiff base salts were successfully used in a wave absorption coating, owing to their weight being only 1/10th that of ferrite and their attenuation of radar waves reaching more than 80%.[5,6] Positive and negative charges can easily move along the conjugated chain molecules through the restructuring of their double bonds, and have strong polarization characteristics, which make the complex permittivity and magnetic permeability change, to further affect EM wave absorption performance.[7,8] Wang *et al.*[9] reported the preparation of ethylenediamine and p-phenylenediamine retinyl Schiff base iron salts

with vitamin A acetate as a raw material, which showed that the reflection loss was below -9 dB in the frequency range of 8.4–10.72 GHz. Poly Schiff base complexes also have π-conjugated systems. The lone pair electron of nitrogen atoms in the poly Schiff base complexes is an electron donor, and the coordinated metal ion is an electron acceptor. When the EM wave rips into the poly Schiff base complexes, a charge transfer process will occur to consume the electronic energy of the EM waves. Therefore, poly Schiff base complexes have potential applications in EM wave absorption.[10]

Recent years, chiral EM wave absorption materials have become one of the hot spots in the stealth materials because their chiral features can make an EM field produce a cross polarization to offset incidental EM waves. In addition, it can reduce the sensitivity to frequency and realize broadband absorption.[11–16] Xu *et al.*[17] prepared a chiral polyaniline/barium hexaferrite composite by using L–camphorsulfonic acid as a chiral dopant, which exhibited a maximum absorption of -30.5 dB at the thickness of 0.9 mm.

In this article, the advantages of a poly Schiff base complex and chiral EM wave absorption material were combined; four chiral
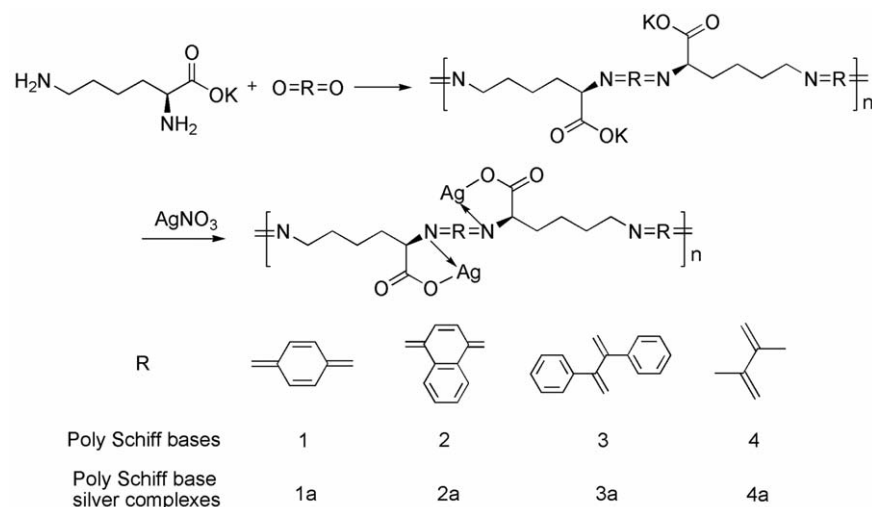
Figure 1. Synthesis of chiral poly Schiff bases and their silver complexes.

poly Schiff bases and their silver complexes using L–lysine as a chiral starting material were synthesized. The conductivity of the poly Schiff bases and their silver complexes were tested and analyzed. The wave absorption properties of the silver complexes were calculated by complex permittivity and permeability. The maximum reflection loss of chiral poly-(L–lysine(p-benzoquinone)) Schiff base silver complex could reach −45.9 dB, which has much better EM wave absorption properties than achiral poly-(DL-lysine(p-benzoquinone)) Schiff base silver complex.

EXPERIMENTAL

Materials

L–lysine (BR), DL-lysine (BR), and Tetrahydrofuran (HPLC) were provided by Sinopharm Chemical Reagent. P-benzoquinone (97%), 1, 4-naphthoquinone (95%), dibenzoyl (CP), 2,3-butanedione (95%) were purchased from Aladdin Industrial Corporation. Anhydrous ethanol, zinc chloride, potassium hydroxide, N,N-Dimethylformamide were all of analytical grade and supplied from Xilong Chemical. Silver nitrate (AR) was purchased from Foshan Chuangyi Nonferrous Metals.

Measurements

Melting points were measured by a SGWX-4 melting point apparatus. Elemental analysis was performed on a Flash EA1112 element analyzer (C, H, N) and JXA-8100 electron probe X-ray microanalyzer (Ag). Infrared spectra were recorded using a FTS-40 spectrometer with KBr pellets. UV-vis spectra of the poly Schiff base and complexes in methanol were recorded with a Cary300 spectrometer. Optical activity analyses were measured using a WZZ-2S automatic polarimeter, with Dimethylformamide (DMF) as the solvent. The molecular weights of all compounds were obtained by a Waters 515 type gel chromatography, with HPLC grade tetrahydrofuran (THF) as the solvent. Conductivity $(10^{-5}-10^4$ S/cm) was studied with a RTS-8x four-probe apparatus at room temperature, conductivity $(10^{-13}-10^{-6}$ S/cm) was studied by AS-31356 AC conductivity tester with copper as electrical contact at room temperature,

samples were prepared from the compounds in the form of tablets, their thickness was approximately 1 mm at a pressure of 15 MPa. The EM parameters of poly Schiff base complexes were determined with a HP8722ES vector network tester at a frequency of 1–18 GHz, the samples were prepared by uniformly mixing the poly Schiff base complexes in a paraffin matrix with a mass ratio of 7 : 3, and then by pressing the mixtures in a cylindrical (toroidal) shapes with outer diameter of 7.00 mm, inner diameter of 3.00 mm, and thickness of 2.00 mm.

Synthesis of the Chiral Poly Schiff Bases

Chiral poly Schiff bases have been synthesized by polycondensation of L-lysine with P-benzoquinone, 1,4-naphthoquinone, dibenzoyl and 2,3-butanedione, respectively (Figure 1). A solution of L–lysine (1.46 g; 10 mmol) and KOH (0.56 g; 10 mmol) in 40 mL of absolute ethanol was kept under continuous stirring in a 250 mL round-bottom flask. A solution of dicarbonyl compound (10 mmol) in 30 mL of absolute ethanol was then added slowly to the reaction flask. A few grains of zinc chloride were added as catalyst. The reaction mixture was vigorously stirred at 80°C for 12 hours under an atmosphere of nitrogen. The precipitate formed was collected by vacuum filtration, washed with absolute ethanol three times and dried in a vacuum desiccator (Figure 1).

Polymer **1**—yield 75%; color: gray; mp > 300°C; $[\alpha]_D^{20} = 1214$ cm^3 g^{-1} dm^{-1} ($c = 1.4 \times 10^{-5}$ g cm^{-3} in DMF); IR (KBr): $v = 2922$ (w; v_{as}(CH)), 2850 (w; v_s(CH)), 1577 (s; v(C=N)), 1393 (m; v(COO$^-$)), 1226 (m; v(C-N)), 729 cm^{-1}(w; ρ(CH)); Anal. calcd for (C$_{24}$H$_{26}$N$_4$O$_4$K$_2$)$_n$: C 56.25, H 5.07, N 10.94; found: C 55.88, H 5.26, N 10.65; molecular weight: Mn 2539, Mw 2762, PDI 1.09.

Polymer **2**—yield 89%; color: brown; mp > 300°C; $[\alpha]_D^{20} = 1500$ cm^3 g^{-1} dm^{-1} ($c = 1.4 \times 10^{-5}$ g cm^{-3} in DMF); IR (KBr): $v = 2921$ (w; v_{as}(CH)), 2860 (w; v_s(CH)), 1596 (s; v(C=N)), 1358 (m; v(COO$^-$)), 1259 (m; v(C-N)), 727 cm^{-1}(w; ρ(CH)); Anal. calcd for (C$_{32}$H$_{30}$N$_4$O$_4$K$_2$)$_n$: C 62.75, H 4.90, N 9.15; found: C 62.40, H 5.15, N 9.22; molecular weight: Mn 2823, Mw 3155, PDI 1.11.
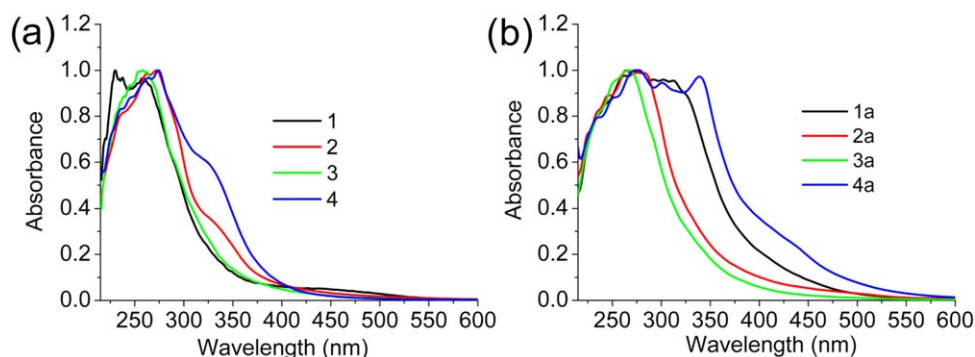
Figure 2. The UV-vis spectra of (a) chiral poly schiff bases and (b) their silver complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polymer **3**—yield 56%; color: buff; mp > 300°C; $[\alpha]_D^{20} = 1400$ cm^3 g^{-1} dm^{-1} ($c = 10^{-5}$ g cm^{-3} in DMF); IR (KBr): $v = 2941$ (w; v_{as}(CH)), 2887 (w; v_s(CH)), 1595 (s; v(C=N)), 1408 (m; v(COO$^-$)), 1099 (s; v(C-N)), 719 cm^{-1}(w; ρ(CH)); Anal. calcd for (C$_{40}$H$_{38}$N$_4$O$_4$K$_2$)$_n$: C 67.04, H 5.31, N 7.82; found: C 67.58, H 5.47, N 7.16; molecular weight: Mn 2650, Mw 2724, PDI 1.03.

Polymer **4**—yield 48%; color: gray; mp > 300°C; $[\alpha]_D^{20} = 1090$ cm^3 g^{-1} dm^{-1} ($c = 2.2 \times 10^{-5}$ g cm^{-3} in DMF); IR (KBr): $v = 2927$ (w; v_{as}(CH)), 2855 (w; v_s(CH)), 1596 (s; v(C=N)), 1381 (m; v(COO$^-$)), 1110 (w; v(C-N)), 730 cm^{-1}(w; ρ(CH)); Anal. calcd for (C$_{20}$H$_{30}$N$_4$O$_4$K$_2$)$_n$: C 51.28, H 6.41, N 11.97; found: C 50.66, H 6.92, N 12.18; molecular weight: Mn 5571, Mw 5933, PDI 1.06.

Synthesis of Chiral Poly Schiff Bases Silver Complexes

L–lysine (1.46 g; 10 mmol) and KOH (0.56 g; 10 mmol) in 40 mL of absolute ethanol was kept under continuous stirring in a 250 mL Round-bottom flask. A solution of dicarbonyl compound (10 mmol) in 30 mL of absolute ethanol was then added slowly to the reaction flask. A few grains of zinc chloride (0.05 g) were added as catalyst. The reaction mixture was vigorously stirred at 80°C for 6 hours under an atmosphere of nitrogen. AgNO$_3$ (2.04 g; 12 mmol) was added to the reaction mixture under consistent stirring within at 80°C for 6 hours during which the poly Schiff base silver complex appeared gradually. The precipitate formed was collected by vacuum filtration, washed with ethanol three times, and dried in a vacuum desiccator. The synthetic processes are shown in Figure 1. The same procedures were applied to prepare the achiral poly-(DL-lysine(p-benzoquinone)) Schiff base silver complex (complex **1b**, in short).

Complex **1a**—yield 51%; color: black; mp > 300°C; $[\alpha]_D^{20} = 722$ cm^3 g^{-1} dm^{-1} ($c = 1.8 \times 10^{-5}$ g cm^{-3} in DMF); IR (KBr): $v = 2927$ (w; v_{as}(CH)), 2855 (w; v_s(CH)), 1568 (s; v(C=N)), 1352 (m; v(COO$^-$)), 1219 (w; v(C-N)), 675 cm^{-1} (w; ρ(CH)); Anal. calcd for (C$_{24}$H$_{26}$N$_4$O$_4$Ag$_2$)$_n$: C 46.22, H 4.28, N 8.45, Ag 31.40; found: C 45.31, H 4.00, N 8.62, Ag 32.23; molecular weight: Mn 3147; Mw 3520; PDI 1.12.

Complex **1b**—yield 54%; color: black; mp > 300°C; $[\alpha]_D^{20} = 0$ ($c = 1.5 \times 10^{-5}$ g cm^{-3} in DMF); IR (KBr): $v = 2926$ (w; v_{as}(CH)), 2856 (w; v_s(CH)), 1568 (s; v(C=N)), 1354

(m; v(COO$^-$)), 1219 (w; v(C-N)), 678 cm^{-1} (w; ρ(CH)); Anal. calcd for (C$_{24}$H$_{26}$N$_4$O$_4$Ag$_2$)$_n$: C 46.22, H 4.28, N 8.45, Ag 31.40; found: C 45.44, H 4.73, N 8.17, Ag 32.31; molecular weight: Mn 3437; Mw 3677; PDI 1.07.

Complex **2a**—yield 61%; color: black; mp > 300°C; $[\alpha]_D^{20} = 666$ cm^3 g^{-1} dm^{-1} ($c = 1.8 \times 10^{-5}$ g cm^{-3} in DMF); IR (KBr): $v = 2922$ (w; v_{as}(CH)), 2853 (w; v_s(CH)), 1591 (s; v(C=N)), 1332 (m; v(COO$^-$)), 1257 (s; v(C-N)), 725 cm^{-1} (m; ρ(CH)); Anal. calcd for (C$_{32}$H$_{30}$N$_4$O$_4$Ag$_2$)$_n$: C 53.16, H 4.50, N 7.24, Ag 26.77; found: C 51.20, H 4.00, N 7.47, Ag 25.80; molecular weight: Mn 3512; Mw 3892; PDI 1.13.

Complex **3a**—yield 57%; color: brown; mp > 300°C; $[\alpha]_D^{20} = 1500$ cm^3 g^{-1} dm^{-1} ($c = 10^{-5}$ g cm^{-3} in DMF); IR (KBr): $v = 2923$ (w; v_{as}(CH)), 2854 (w; v_s(CH)), 1587 (s; v(C=N)), 1325 (m; v(COO$^-$)), 1210 (s; v(C-N)), 715 cm^{-1} (m; ρ(CH)); Anal. calcd for (C$_{40}$H$_{38}$N$_4$O$_4$Ag$_2$)$_n$: C 55.52, H 4.54, N 6.72, Ag 26.01; found: C 56.20, H 4.45, N 6.56, Ag 25.29; molecular weight: Mn 3410; Mw 3621; PDI 1.06.

Complex **4a**—yield 59%; color: black; mp > 300°C; $[\alpha]_D^{20} = 875$ cm^3 g^{-1} dm^{-1} ($c = 1.6 \times 10^{-5}$ g cm^{-3} in DMF); IR (KBr): $v = 2922$ (w; v_{as}(CH)), 2860 (w; v_s(CH)), 1585 (s; v(C=N)), 1350 (m; v(COO$^-$)), 1107 (w; v(C-N)), 682 cm^{-1} (w; ρ(CH)); Anal. calcd for (C$_{20}$H$_{30}$N$_4$O$_4$Ag$_2$)$_n$: C 38.86, H 5.56, N 9.45, Ag 35.48; found: C 39.60, H 4.95, N 9.24, Ag 35.64. molecular weight: Mn 7134; Mw 7633, PDI 1.07.

RESULTS AND DISCUSSION

Characterization Data of the Polymers

The melting point of the polymers is more than 300°C owing to the conjugation in the main chain of the polymers. The color of the poly Schiff base silver complexes are deeper than the free poly Schiff bases, which indicates that the poly Schiff bases reacted with the silver salts. The specific rotation $[\alpha]_D^{20}$ of the chiral polymers are from 666 to 1500, which are far more than the specific rotation of L–lysine ($[\alpha]_D^{20} = 14.6$ cm^3 g^{-1} dm^{-1}, $c = 0.065$ g cm^{-3} in H$_2$O), which indicate that the polymers have chiral characteristics. The specific rotation $[\alpha]_D^{20}$ of the complex **1b** is 0, which shows it is a achiral compound. The molecular weight of the polymers are slightly low, probably because the carboxyl of L–lysine has effect on the activity of amino which lead to a low degree of polymerization.
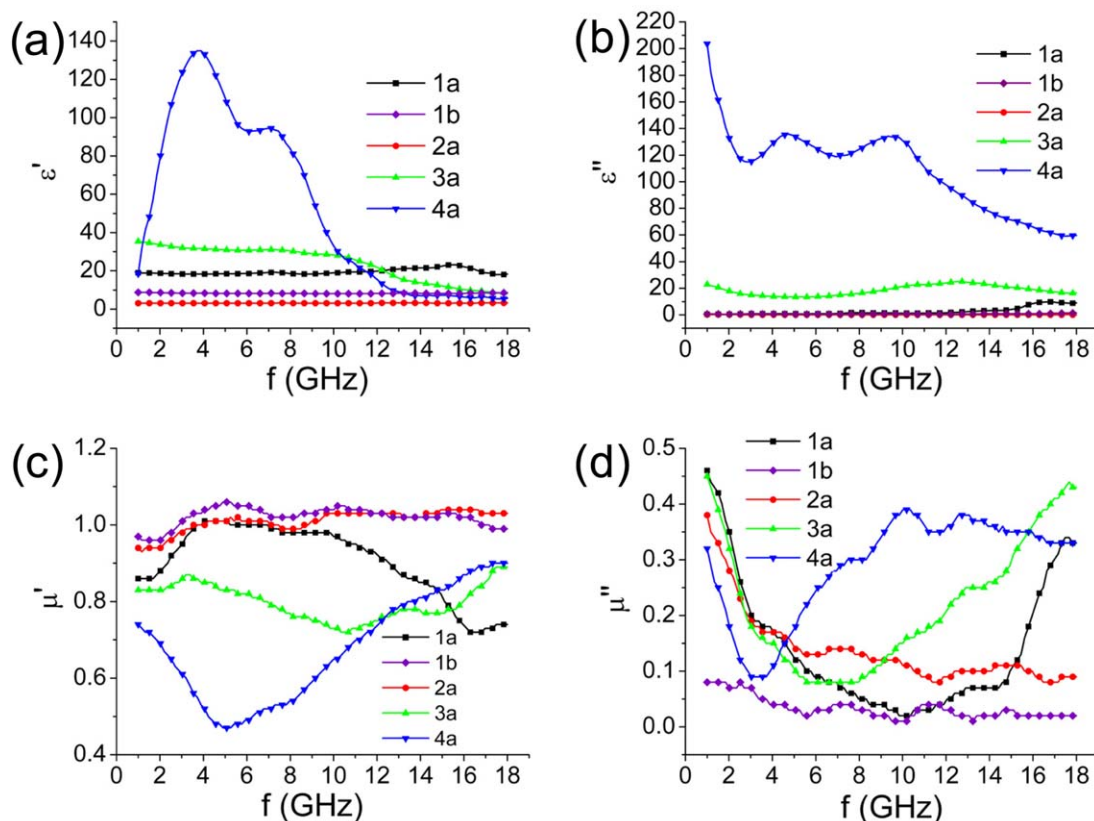
Figure 3. The relative complex dielectric permittivity and magnetic permeability of poly Schiff base silver complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Electrical Conductivities of the Chiral Poly Schiff Basesand Their Silver Complexes at Room Temperature

Poly Schiff bases	1		2		3		4
Conductivity (S/cm)	3.7×10^{-10}		8.0×10^{-11}		2.4×10^{-10}		3.9×10^{-10}
Poly Schiff basesilver complexes	1a	1b	2a		3a		4a
Conductivity (S/cm)	7.2×10^{-4}	2.4×10^{-4}	1.3×10^{-5}		11.7		3.7×10^{2}

Infrared Spectroscopy

The IR spectra provide valuable information regarding the nature of the functional groups present in the poly Schiff bases and their complexes. The appearances of strong peaks in the spectra of both poly Schiff bases and their complexes in the region of 1568–1596 cm^{-1} indicate the presence of C=N stretching bands.[18–20] These bands shift to a lower frequency in the spectra of corresponding silver complexes, which indicates that the nitrogen atom of imine group is coordinated to the silver ion.[18,20,21] The absorption peaks at 1325–1408 cm^{-1} are COO$^-$ symmetric stretching vibrations, which show that the carboxyl group of lysine is deprotonated to the carboxylic acid salt. The peaks at 2921–2941 cm^{-1}, 2850–2887 cm^{-1}, and 675–730 cm^{-1} belong to the asymmetric stretching vibration, symmetric stretching vibration, and rocking vibration of the methylene group present in the amino acid, respectively.[21] The peaks at 1099–1259 cm^{-1} were attributed to the C=N stretching vibrations.

UV-Vis Spectroscopy

Figure 2 shows the UV-vis spectral bands of four chiral polymers. Both chiral poly Schiff bases and their complexes display one prominent peak at around 257–281 nm. These are the characteristic peaks for π–$\pi^\star$ transitions of the imine (N=R=N) group.[22] The π–$\pi^\star$ transitions do not appear for the whole chain, because L–lysine is not a structure with alternating single and double bonds. There is a wide absorption band at 310–400 nm in the UV-vis spectra of chiral poly Schiff bases, while the UV-vis spectra of their complexes show a new absorption band at 350–475 nm with a little large bathochromic shift, which is the charge transfer absorption. When the oxygen and nitrogen atoms of ligands are coordinated to metal ions, the charge transfer of metal ions to polymers may increase electron delocalization and reduce the energy of electron transition, which leads to bathochromic shift compared to ligands.[23]
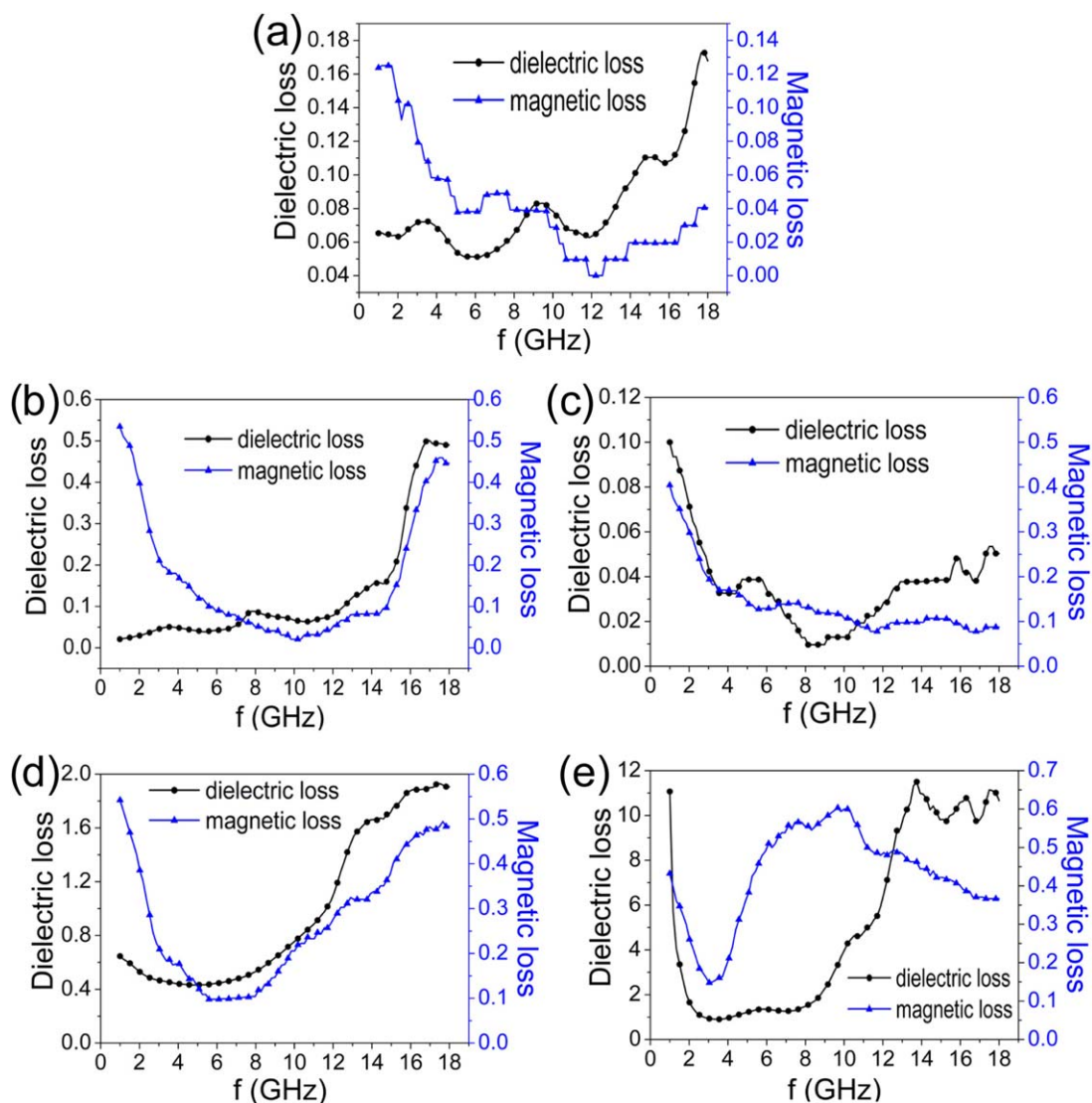
Figure 4. The dielectric and magnetic loss tangent of (a) complex **1b** and chiral poly Schiff base silver (b) complex **1a**, (c) complex **2a**, (d) complex **3a**, and (e) complex **4a**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conductivity Analysis

Table I shows the electrical conductivities of the poly Schiff bases and their complexes. The conductivities of the poly Schiff bases are around $10^{-11}-10^{-10}$ S/cm. The conductivities of the poly Schiff base silver complexes are significantly higher than corresponding free poly Schiff bases. Especially, the conductivity of complex **4a** can reach 3.72×10^2 S/cm and is a 12 orders of magnitude improvement compared with that of compound **4**. It indicates that the coordination of silver ions plays an important role in improving the conductivities of the poly Schiff bases, which can be attributed to the fact that the silver ions accelerate the charge transfer rate on the chains of the poly Schiff bases. The magnitude of the conductivities of four chiral complexes is different, which may be associated with the structures of the complexes. Four conjugated poly Schiff bases were prepared by Li *et al.* via the polycondensation of 1,4-diamino-benzene with glyoxal, 2,3-butanedione, 3,4-hexanedione, and 4,5-octanedione, then doped with iodine. Their conductivities

are 1.5×10^{-3}, 3.2×10^{-4}, $4.1 \times 10^{-}$, 2.2×10^{-4} S/cm, respectively. Li groups think that the conductivities of poly Schiff bases with side groups are lower by an order of magnitude than poly Schiff base without side groups, which may result from the decreasing intermolecular charge hopping because of the space barrier of side groups.[24] Shacklette *et al.* gave a comparison of chain length vs conductivity of potassium-complexed p-phenylenes. When the degrees of polymerization are 3, 4, 6, 16, the conductivities of potassium-complexed p-phenylenes are 4×10^{-5}, 2×10^{-5}, 0.5, 7 S/cm, respectively. It is satisfying to note that the conductivity increases with the degree of polymerization.[25] Baughman *et al.* reported the conductivities of AsF$_5$-doped poly(p-phenylene) and polyacetylene (ca. 500 and 1200 S/cm, respectively), and found that the planar backbone of polyacetylene was beneficial to obtain higher conducting complexes than the nonplanar backbone of poly(p-phenylene).[26] The conductivities of complexes **3a** and **4a** are higher than those of complexes **1a** and **2a**,
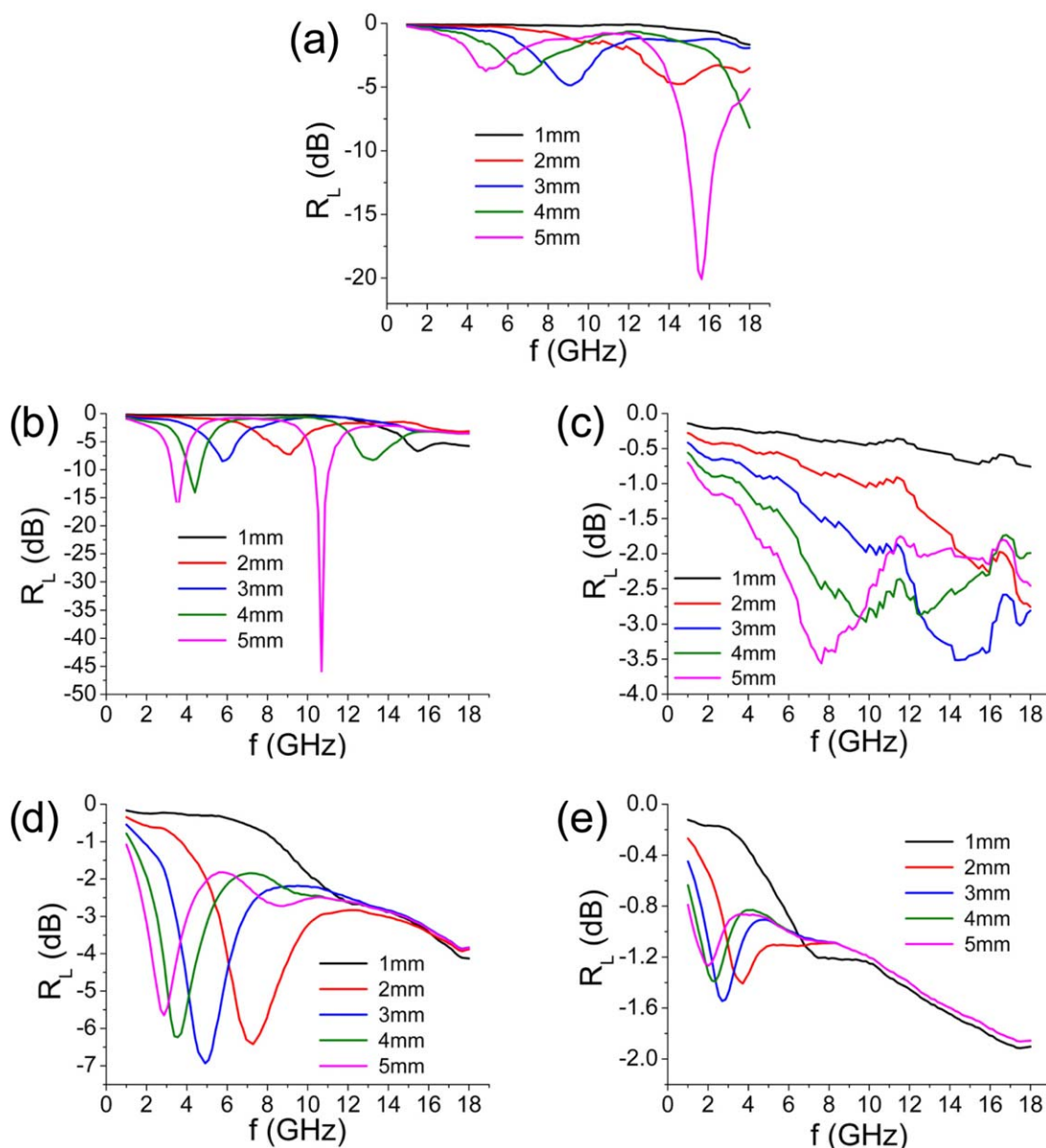
Figure 5. The reflection losses of (a) complex **1b** and chiral poly Schiff base silver, (b) complex **1a**, (c) complex **2a**, (d) complex **3a**, and (e) complex **4a** with the thickness of 1–5 mm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which may result from the planar backbone of complexes **3a**, **4a** and the nonplanar backbone of complexes **1a**, **2a**. The conductivities of complexes **4a** and **1a** is higher than that of complexes **3a** and **2a**, respectively, which result from the smaller space barrier of complexes **4a**, **1a** than that of complexes **3a**, **2a** respectively, and the higher degree of polymerization of complex **4a**. The conductivity of achiral complex **1b** is close to complex **1a**, which show chirality has no obvious effect on conductivity.

Electromagnetic Parameter Analysis

The complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) are two basic parameters influencing the EM absorption properties of materials.[27] Figure 3(a,b) show the real

part (ε') and imaginary part (ε'') of the complex permittivity of the poly Schiff base complexes in the frequency range of 1–18 GHz, respectively. The ε' of complex **1a** was steady around 20 and the ε'' of complex **1a** increases from 0.39 to 9.54, which is higher than that of complex **1b**, respectively, complex **1a** shows better dielectric loss across the frequency range of 1–18 GHz. The maximum ε' and ε'' of complex **2a** are only 3.18 and 0.31, respectively, which show that complex **2a** has a poor electric loss ability. The ε' and ε'' of complex **3a** are around 8.64–35.37 and 13.33–24.95, respectively, which shows complex **3a** has good electricity store and dielectric loss abilities. The maximum ε' and ε'' of complex **4a** are 134.96 and 203.63, respectively, which shows complex **4a** owns high electric polarization, but it is hard to match with its magnetic permeability

because of a high dielectric constant. The four types of complexes show different dielectric constants, and it can be found that the conductivity and dielectric constant have a positive relationship,[28] as via Figure 3 and Table I.

Figure 3(c,d) show the real part (μ') and imaginary part (μ'') of the complex permeability of complexes 1a–4a and 1b over the frequency range of 1–18 GHz, respectively. The μ'' of nonmagnetic material is approximately equal to 0,[29] while the μ'' of the four chiral complexes are 0.02–0.46 and higher than that of complex 1b. The results show that the chiral poly Schiff base silver complexes can obtain magnetic loss ability through cross polarization. The μ'' of complex 2a over the whole band decreases and has a maximum magnetic loss at 1.0 GHz, the μ'' of complexes 2a–4a firstly fall and then rise with the increase of frequency, indicating good magnetic loss ability in the low and high frequency regions.

The best effect of absorbing EM wave can be achieved when the dielectric loss tangent and magnetic loss tangent of the materials are equal.[30] Figure 4 shows the dielectric loss tangent ($\tan\delta_E = \varepsilon''/\varepsilon'$) and the magnetic loss tangent value ($\tan\delta_M = \mu''/\mu'$) of the poly Schiff base complexes over 1–18 GHz. The dielectric loss tangent of complex 1a starts to rise at 12.0 GHz, the maximum is 0.49 at 17.0 GHz. The magnetic loss tangent decreases from 0.53 and then rises to 0.46, the dielectric loss tangent and magnetic loss tangent is very close at 6–18 GHz. Both $\tan\delta_E$ and $\tan\delta_M$ of complex 1a are higher than complex 1b in the range 1–18 GHz. For general materials, electric polarization can only be induced by electric field while magnetic polarization can only be induced by magnetic field. However, in chiral materials both polarizations can be induced by electric and magnetic fields individually.[31] Thus, the values of dielectric loss and magnetic loss in complex 1a increase.

The magnetic loss tangent of complex 2a is higher than the dielectric loss tangent over the whole frequency range, the electromagnetic impedance matching effect is poor. The dielectric loss tangent of complex 3a increases and then decreases over the whole frequency range, its magnetic loss tangent has the same trend, the dielectric loss tangent is slightly higher than the magnetic loss tangent, and the absorption of EM wave is mainly from the dielectric loss. The dielectric loss tangent of complex 4a reaches 11.07 and 11.50 at 1.0 and 13.5 GHz, respectively, which are too high to match with the permeability.

Electromagnetic Wave Absorption Performance
To reveal the **EM** wave absorption properties of the complexes, the reflection loss (R_L) values were calculated according to the transmission line theory[32] as follows:

$$Z_{in} = \sqrt{\mu_r/\varepsilon_r}\tanh\left[j(2\pi f d/c)\sqrt{\mu_r\varepsilon_r}\right] \qquad (1)$$

$$R_L(dB) = 20\log\left|(Z_{in}-1)/(Z_{in}+1)\right| \qquad (2)$$

where Z_{in} is the input impedance of the absorbing material, c is the EM wave propagation speed in a vacuum, f is the frequency of the EM wave, d is the thickness of the absorbing material, μ_r and ε_r are the relative complex permeability and permittivity of the absorber medium, respectively.

Figure 5 reveals the obtained frequency dependence R_L of achiral complex 1b and four chiral poly Schiff base silver complexes with layer thickness ranging from 1 to 5 mm. As illustrated in Figure 5(b), a minimum R_L value of complex 1a reaches −45.9 dB at 10.7 GHz on a coating of 5 mm, while it is found that the minimum R_L value of complex 1b is −20.1 dB at 15.6 GHz with the same matching thickness in Figure 5(a). The reflection losses of complex 1a are much lower than those of complex 1b, indicating that the complex with chiral structure is beneficial to the absorption of electromagnetic wave. The chiral structure significantly affects the polarization characteristic of the electromagnetic wave. Both self-polarization and cross-polarization occur in complex 1a,[33] which may be the main reason for the increasing attenuation of EM wave.

The strongest reflection loss of complex 2a is only −3.6 dB at a thickness of 5.0 mm, as shown in Figure 5(c). The dielectric loss ability of complex 2a is low because of the low dielectric constant. Complex 3a [Figure 5(d)] has a reflection loss under −5 dB except at a thickness of 1 mm, the strongest reflection loss was −6.9 dB at a thickness of 3 mm and a frequency of 4.91 GHz. Complex 4a [Figure 5(f)] easily reflects the EM waves on the surface because of its high electrical conductivity,[34] the strongest reflection loss was only −1.9 dB at a thickness of 1.0 mm. The studies have shown that the complexes have a better microwave absorption performance when the conductivity was in the range of $10^{-4}-10^{0}$ S/cm.[35] Complex 1a shows better absorbing property than complexes 2a–4a likely because of its own appropriate conductivity.

CONCLUSIONS

Four types of chiral poly Schiff bases and their silver complexes were synthesized under a protective nitrogen atmosphere. The structures were confirmed by IR, UV-vis, GPC, and elemental analysis. The chiral characteristics of the polymers have been analyzed using specific optical rotation. The conductivity was significantly improved after the silver ions coordinated to the poly Schiff bases, the conductivity of chiral poly Schiff base complex 4a could reach 3.7×10^2 S/cm. The microwave absorption properties of chiral poly Schiff base complexes were calculated according to the transmission line theory, the reflection loss (R_L) of chiral poly Schiff base complex 1a could reach below −45.9 dB, which displayed better EM wave absorption effects than corresponding achiral complex 1b and three other chiral complexes 2a–4a. Experimental results indicated the enhanced microwave absorbing properties were attributed to the cross polarization of chiral structure and reasonable conductivity. Therefore, the chiral poly Schiff base silver complexes are expected to be good EM wave absorption materials by the regulation of electrical conductivity and matching with magnetic materials.

ACKNOWLEDGMENTS

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