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# Research on synthesis and conductivity of ferrocenyl Schiff base and its salt

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**Ferrocenyl Schiff base was synthesized through the condensation of ferrocenecarboxaldehyde and *p*-phenylenediamine under neutral conditions, and then a new interesting category of organometallic charge transfer complex was obtained by the doping of ferrocenyl Schiff base with $Fe^{3+}$, $Al^{3+}$ and $Ti^{3+}$ salts. The effects of the dosage of doping agent and doping temperature on the room-temperature electric conductivity of samples were discussed; in addition, the temperature dependence of the electric conductivity of samples was studied, their structures and compositions were characterized by $^1$H-NMR spectra, infrared spectra, ultraviolet spectra and an electron probe X-ray microanalyser. The results showed that the electric conductivity of sample can increase 4–5 orders of magnitude after doping with a metallic salt, and the electric conductivity has a positive temperature coefficient effect. The electrical activation energies of the complexes in the range 0.09–1.54 eV were calculated from Arrhenius plots, indicating their favourable semiconducting behaviour. Copyright © 2006 John Wiley & Sons, Ltd.**

**KEYWORDS:** ferrocenyl Schiff base; doping; conductivity; positive temperature coefficient

## INTRODUCTION

Organometallic complexes, especially some transition metals complexes of ferrocene and substituted ferrocenes, have attracted considerable interest in recent years because of their unique optical, electrical and magnetic properties. Potential applications of these complexes in semiconductivity,[1] nonlinear optics[2] and cooperative magnetics[3] have spurred research in this area. Many ferroconductive molecular materials have been synthesized and studied, for example, ferrocene–TCNQ,[4] ferrocene–silane,[5] ferrocene–alkene,[6] ferrocene–azo[7] and ferrocene–thiophene.[8] Interest has been focused on Schiff base functional group because of its thermal stability, electrical conduction and photoconduction.[9] Schiff base can form coordinate complexes with metal ions by its nonbonded pair of electrons on nitrogen atoms, and charge-transfer complexes with an electron acceptor or electron donor by its nonbonded electrons or $\pi$ electrons. It is expected that the physical properties, such as electrical, of its derivatives could be modified by changing the molecular structure.

In this paper, ferrocenyl Schiff base was synthesized by the condensation of ferrocenecarboxaldehyde with *p*-phenylenediamine under neutral conditions, and then doped with $Fe^{3+}$, $Al^{3+}$ and $Ti^{3+}$ salt by the existence of *p*-phenylenediamine ligand. The results showed that the values of conductivity for doping state are nearly 4–5 orders of magnitude larger than the value ($1.26 \times 10^{-9}$ S cm$^{-1}$) of conductivity for intrinsic state, and their electric conductivity has a positive temperature coefficient effect. The electrical activation energies of the complexes in the range 0.09–1.54 eV were calculated from Arrhenius plots, indicating their favourable semiconducting behaviour.

## EXPERIMENTAL

### Synthesis of ferrocenyl Schiff base

In a 100-ml flask equipped with a condenser and stirrer, 0.27 g (2.5 mmol) *p*-phenylenediamine was dissolved in 20 ml absolute ethyl alcohol; 1.07 g (5 mmol) ferrocenecarboxaldehyde dissolved in 40 ml absolute ethyl alcohol was added dropwise within 30 min under protection of $N_2$. The mixture was heated

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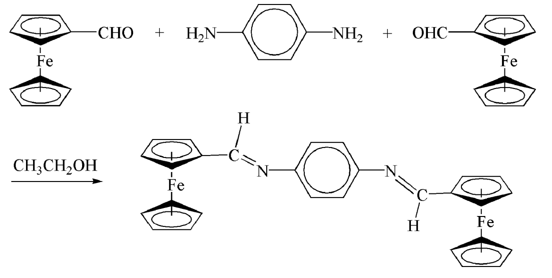


**Scheme 1.** Synthetic route to bi-ferrocenyl Schiff base.

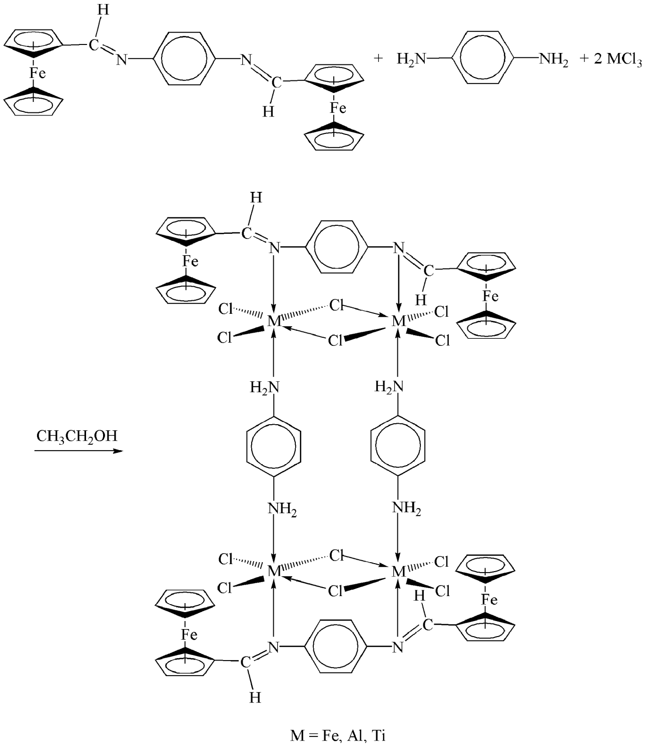
at 80 °C to reflux for 1 h, then cooled and filtered. The resulting precipitate was washed with ethyl alcohol three times, and then dried under vacuum. A golden fine powder was obtained, melting point 238–240 °C. The reaction equation is shown in Scheme 1.

## Synthesis of ferrocenyl Schiff base salt

In a 100 ml flask equipped with a condenser and stirrer, the equivalent molar masses of ferrocenecarboxaldehyde and *p*-phenylenediamine were dissolved in absolute ethyl alcohol; metal chloride dissolved in absolute ethyl alcohol was added dropwise slowly under nitrogen protection. The mixture was heated to reflux for 3 h, then filtered when the temperature of reaction mixture solution had cooled to room temperature naturally. The resulting precipitate was washed with ethyl alcohol and ethyl ether several times, and then dried in vacuum. Using many crystal growing methods, the resulting samples were still black powders but not crystals. The reaction equation is shown in Scheme 2 and it is notable that this ideal structure is proposed as a working hypothesis.

## Measurements

Melting points of ferrocenyl Schiff base were measured on an XT4A melting point apparatus. Elemental analysis was performed on a JXA-8100 electron probe X-ray microanalyser. Infrared spectra were recorded with an IMPACT-410 spectrometer by using KBr pellets. $^1$H-NMR spectra were recorded on a Bruker AV-400 spectrometer. UV spectra of complex solutions in *N*,*N*-dimethylformamide (DMF) were recorded on a TU-1810 spectrometer. Conductivity was measured using a two-probe apparatus. Samples were prepared from the complexes in the form of tablets; their thickness was approximately 5 mm at a pressure of $1 \times 10^6$ Pa. These tablets were made using the same tabletting methodology (the same quality, the same pressure and almost the same thickness, about 5 mm), so their densities were identical. At the same time, each result was repeated three times and the points in the graph were an average of three measurements (the experimental error of conductivity was within 1–2%). These tablets were placed between two copper electrodes with silver paste and contacts were tested to be ohmic. 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 using an electrometer. The conductivity was calculated using the general equation $\sigma = (I/V)(d/a)$, where $I$ is the current in ampere, $V$ the potential drop across the sample of cross-sectional area $a$ and thickness $d$.



**Scheme 2.** Synthetic route to complexes.

# RESULTS AND DISCUSSION

## Optimization of dosage of doping agent and doping temperature

To obtain good conductivity of complex, it is important to optimize the dosage of doping agent and doping temperature. According to the theoretical analysis, the fully complexes can be obtained on a mole ratio basis of 1 : 1:2 (Schiff base, ligand and metallic salt), but in reality, the coordination reaction can become very complex among the three reagents. If the mole ratio of regents was still 1 : 1:2, we could not obtain the full complexes with ideal molecule structure (see scheme 2); most complexes may have the ideal molecule structure, with a fraction having different co-ordination structures. For these complex reactions, we have no method to control their react mode according to one kind of molecular structure, and these side reactions have always gone with the reaction solution. We are unable to determine the solubility or insolubility of complexes with various molecule structures in reaction solution, but we wish to obtain the resulting precipitate or a majority of complexes

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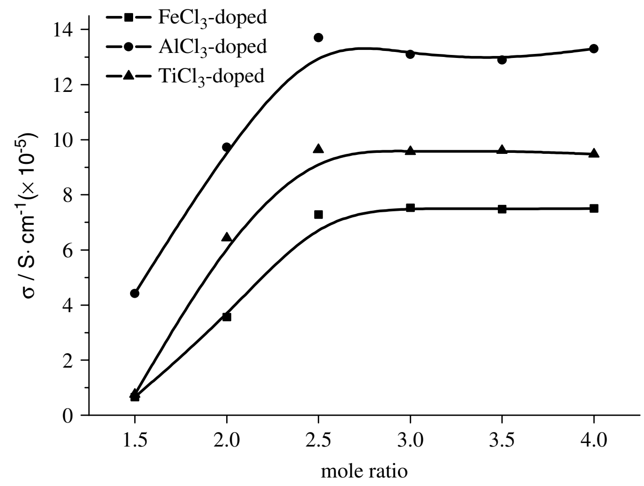

**Figure 1.** The relationship of conductivity versus doping mole ratio.

with ideal molecule structure and maximum conductivity via experiment condition optimization.

The effects of different doping agents and dosages on room-temperature conductivity of samples are shown in Fig. 1. The reaction conditions were: 1 : 1 (mole ratio of ferrocenyl Schiff base and *p*-phenylenediamine), 1 : 1.5–1 : 3.5 (mole ratio of ferrocenyl Schiff base and metal chloride), at 60 °C for 2 h under nitrogen. As can be seen from Fig. 1, after ferrocenyl the Schiff base is doped by metal chloride and its conductivity is increased by 4–5 orders of magnitude. Room-temperature conductivity of all complexes increases with increasing doping degree. The maximum conductivity can reach $7.53 \times 10^{-5}$, $1.37 \times 10^{-4}$ and $9.64 \times 10^{-5}$ S cm$^{-1}$ for $FeCl_3$-doped, $AlCl_3$-doped and $TiCl_3$-doped production, respectively.

## $^1$H-NMR spectra, IR spectra and elemental analysis

The $^1$H-NMR spectrum of the ferrocenyl Schiff base was recorded at room-temperature using $CDCl_3$ as solvent (Fig. 2). The spectrum of ferrocenyl Schiff base exhibited cyclopentadienyl ring proton signals at 4.50 and 4.82 ppm, benzene ring proton signal at 7.19 ppm and CH=N proton signal at 8.38 ppm. However, the spectra of complexes was not obtained due to the poor solubility in any solvent.

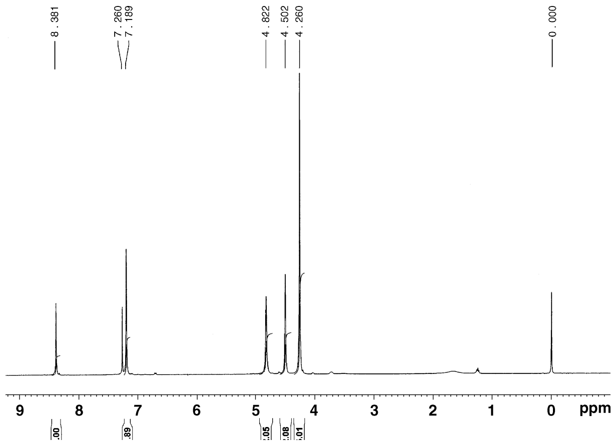

**Figure 2.** $^1$H-NMR spectrum of ferrocenyl Schiff base.

Complexes have different conductivity by doping with different doping agent and dosage; this phenomenon suggests that there may exist doping saturation in the doping process. When the doping degree reaches saturation, that is, the complexes have the structures of the reaction equation, and the complexes have a relatively higher conductivity. Figure 3(a–d) shows the IR spectra of complexes of undoped, $FeCl_3$-doped, $AlCl_3$-doped and $TiCl_3$-doped complexes (these doped complexes all have relatively higher conductivity). Before doping, the strong absorption at 1608.51 cm$^{-1}$ from C=N, which is due to stretching vibration, is the characteristic absorption of a Schiff base; peaks at 811 and 1080 cm$^{-1}$ are C–H perpendicular bend and C=C stretching vibration of the cyclopentyl ring; the absorption at 1520 and 1450 cm$^{-1}$ are attributed to C=C stretching vibration of the benzene ring. When Schiff base is doped by three kinds of metal chloride, these spectra of three complexes are similar, this suggests that three complexes have nearly identical structures, and that there are small changes in the peak positions and relative intensity of their IR spectra. This indicates that the charge transfer may occur between nonbonding electrons in the N atom of the Schiff base and metal ion. The elemental analysis results of the complexes are given in Table 1; this indicates the found according to their calculated.

## UV spectra analysis

UV spectra of complex solutions in *N*,*N*-dimethylformamide (DMF) are given in Fig. 4. The absorptions at 280, 274, 275 and

**Table 1.** Elemental content of ferrocenyl Schiff and its doping state

| | Found(calculated)/% | | | | | | |
|---|---|---|---|---|---|---|---|
| Compound | C | H | N | Fe | Al | Ti | Cl |
| Undoped | 67.20(67.22) | 4.80(4.81) | 5.60(5.59) | 22.40(22.39) | 0 | 0 | 0 |
| $FeCl_3$-doped | 43.73(42.24) | 3.43(3.52) | 6.00(6.16) | 24.00(24.64) | 0 | 0 | 22.83(23.43) |
| $AlCl_3$-doped | 46.63(45.12) | 3.66(3.76) | 6.40(6.58) | 12.80(13.16) | 6.17(6.35) | 0 | 24.34(25.03) |
| $TiCl_3$-doped | 44.50(43.00) | 3.49(3.58) | 6.11(6.27) | 12.21(12.54) | 0 | 10.47(10.75) | 23.20(23.85) |

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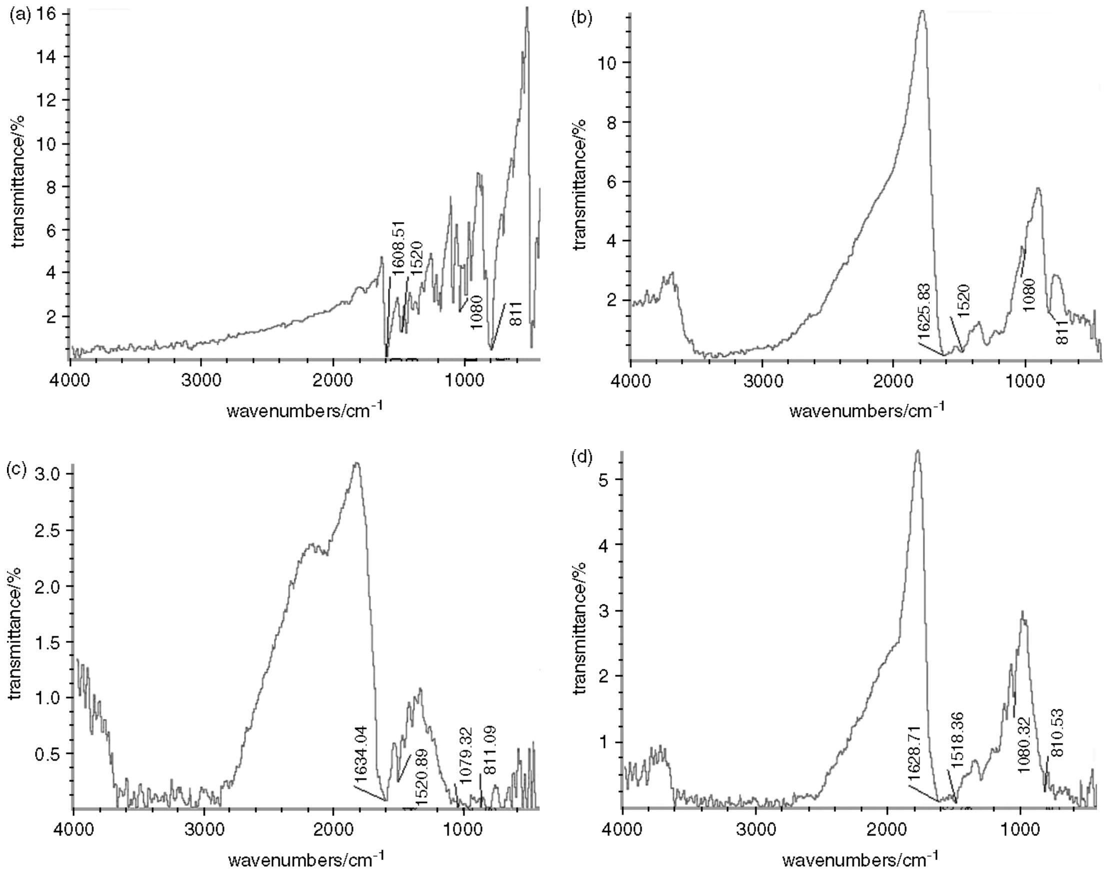

**Figure 3.** IR spectra of ferrocenyl Schiff base and its doping state: (a) undoped; (b) $FeCl_3$-doped; (c) $AlCl_3$-doped; (d) $TiCl_3$-doped.

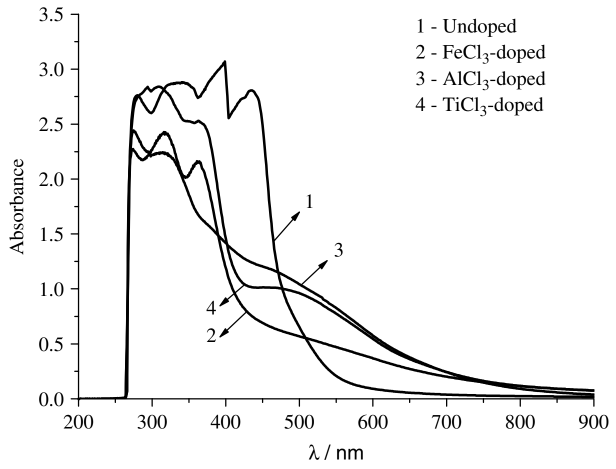

**Figure 4.** UV spectra of ferrocenyl Schiff base and its doping state.

294 nm are assigned to $\pi$–$\pi^*$ transition on the C=N of four complexes, respectively;[10] peaks at 342, 311, 311 and 308 nm are attributed to $\pi$–$\pi^*$ transition on the benzene ring. There is a wide absorption band at 410–550 nm in UV spectra of undoped complex. After doping by metal chloride, their UV spectra show a new absorption band at 420–700 nm with a long tail extending to 900 nm and show a small bathochromic shift, which is the charge transfer absorption. The change in UV spectra before and after doping proves that charge transfer between the Schiff base and metal ion occurred.

## Electrical conductivity

Electrical conductivities of the complexes were measured at the range of 313–373 K temperature. Figure 5(a–c) illustrates a typical temperature dependence of the electrical conductivity during the heat treatment. By analysing the shape of $\lg\sigma = f(10^3/T)$ graphs in Fig. 5(a–c), useful information regarding the processes occurring in investigated complexes during the heat treatment can be obtained. The DC conductivity of semiconductors has the general form, $\sigma = \sigma_0 \exp(E_a/kT)$, where $E_a$ is the thermal activation energy for the electrical conduction, and $k$ is the Boltzmann constant. A plot of $\lg\sigma$ vs $1000/T$ yields a straight line whose slope can be used to determine the thermal activation energies of the complexes.[11] As can be seen from Fig. 5(a–c), during the heating, the electrical conductivity may increase with the increasing in temperature, in the range 313–373 K. The curves are generally characterized by two portions with different slopes. The calculated activation energies may correspond to different levels. These two activation

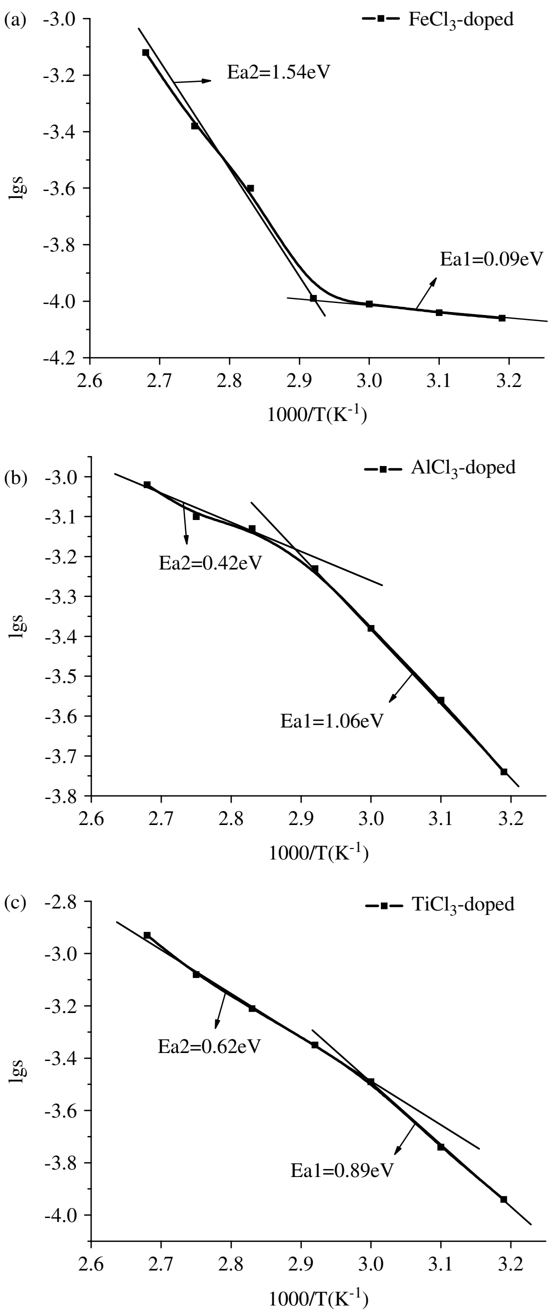

**Figure 5.** Temperature dependence of the conductivity of samples: (a) $FeCl_3$-doped; (b) $AlCl_3$-doped; (c) $TiCl_3$-doped.

energies are associated with the intramolecular and the intermolecular conductivity process. In these semiconduction complexes, there are two stages in the movement of carrier motion within the sample, which are the intramolecular and intermolecular transfer of the current carrier. In the intramolecular transfer of electrons, electrons can hop from one atomic site to another if orbitals exist at these sites with the same energy levels. In the case of intermolecular orbital overlap, electrons or holes can travel from one kind of molecule to another, $\pi$-electrons can also move from one type of molecule to another by hopping if orbitals with the same energy levels exist between the complex molecules. Because the excited carriers within the molecules are retarded by the barrier molecules, the activation energy of the intramolecular conduction process is higher. Therefore, the lower values of $E_a$ are associated with the intermolecular conduction process, while the higher values are related to the intramolecular conduction process. The intramolecular conduction process occurs between the metal atom and the ligands in the complex and the intermolecular conduction process between two molecular complexes. As shown in Fig. 5(a–c), the electrical conductivity of the complexes have a positive temperature coefficient, that is, with the increase in temperature, conductivity increases, and the electrical activation energies of the complexes are in the range 0.09–1.54 eV, calculated from Arrhenius plots, indicating their favourable semiconducting behaviour.[12] However the Fe complex behaves in an opposite way compared with the other two. This may be caused by the molecular structure: if we assume excited carriers within the molecules, the carriers are retarded by the barrier molecules and the activation energy of the intramolecular conduction process is higher. For the Fe complex, the intramolecular electrons transfer is easy in low temperature zone—when the temperature has reached certain range, the intramolecular electrons conduction occupy a leading role. Therefore, the first step of conduction starts between molecules corresponding to intermolecular transfer, and the second step of conduction mainly occurs in intramolecule corresponds to intramolecular transfer.

## CONCLUSIONS

Three new conjugated ferrocenyl Schiff base salts charge transfer complexes with metal chloride were synthesized and characterized with IR, electron probe X-ray microanalyser and UV spectra. Room-temperature conductivity of charge transfer complexes of $FeCl_3$-doped, $AlCl_3$-doped and $TiCl_3$-doped complexes can reach $7.53 \times 10^{-5}$, $1.37 \times 10^{-4}$ and $9.64 \times 10^{-5}$ S cm$^{-1}$, respectively. The electrical conductivity of the complexes has positive temperature coefficient, and the electrical activation energies of the complexes which were in the range 0.09–1.54 eV were calculated from Arrhenius plots, indicating their favourable semiconducting behaviour.

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