

# Magnetic and photoluminescent properties of three new organic radical cation salts



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## ABSTRACT

Three new organic radical cation salts were prepared by exchanging perchlorate anion of 2,3'-biimidazo[1,2-*a*]pyridin-2'-one radical perchlorate salt with metal coordination anions. These cation salts, [H (Hbipo<sup>•+</sup>)]<sup>+</sup>·[FeCl<sub>4</sub>]<sup>2-</sup>·H<sub>2</sub>O (**1**), [H (Hbipo<sup>•+</sup>)]<sup>+</sup>·[MnCl<sub>4</sub>]<sup>2-</sup> (**2**) and [H (Hbipo<sup>•+</sup>)]<sup>+</sup>·[Zn(SCN)<sub>3</sub>]<sup>-</sup>·H<sub>2</sub>O (**3**), were characterized by EPR and IR spectra, and their composition was demonstrated by the elemental analyses and TGA analyses. Salts **1** and **3** mainly exhibit antiferromagnetic properties, however, salts **2** and **3** reveal interesting magnetic phase transition at 243 K and 65 K, respectively. Compared to 2,3'-biimidazo[1,2-*a*]pyridin-2'-one radical itself (green emission), salts **1**, **2** and **3** display obviously blue shifted to blue emission, attributable to their low HOMO energy level caused by the protonation of N atom at imidazo[1,2-*a*]pyridine ring. Present work will provide new organic radical cation for the preparation of molecular materials with combination of different physical properties by using various metal coordination anions.

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## 1. Introduction

A lot of interest is currently devoted to the design and synthesis of new molecular materials with combination of different physical properties. The family of low dimensional organic radical cation salts based on organic  $\pi$ -donors with paramagnetic metal coordination anions is an important class of such materials [1]. The standard approach to design of such materials is to make two-network solids formed by alternating layers of  $\pi$ -electron donor radical cations based on derivatives of tetrathiafulvalene (TTF) which are responsible for electronic conduction, and layers of charge-compensating paramagnetic metal coordination anions. The introduction of magnetic moments due to transition metals in these anions could result in indirect exchange interaction between the  $\pi$ -electrons of radical cations and the localized magnetic anions. Organometallic chemistry provides a wide choice of metal complexes of various sizes and charges that can be used as charge-compensating counterions [2]. Up to date, there are a number of TTF-based conducting charge transfer salts with paramagnetic

metal coordination anions have been reported [3]. Moreover, other organic radical cation salts with paramagnetic metal coordination anions have also been synthesized and characterized [4]. Significant new results have been obtained by using the magnetic anions [MX<sub>4</sub>]<sup>n-</sup> (X = Cl, Br; M = transition metal), [MX(CN)<sub>5</sub>]<sup>3-</sup> (X = CN, NO), [M(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup>, and [M(II)M(III)(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>-</sup> as well as polyoxometalates, etc.

Our group has been interested in the physical properties of 2,3'-biimidazo[1,2-*a*]pyridin-2'-one (Hbipo<sup>•+</sup>) radical and its derivatives. These zwitterionic (neutral) 11 $\pi$ -electron radicals and their cation salts are of great interest due to their potential as magnetic, luminescent, or catalytic materials [5–8]. Zwitterionic radical and its derivative mainly exist as diamagnetic  $\pi$ -dimers in solid state, leading to low magnetic susceptibilities, however, they exhibit interesting spin-transition behavior [6,8]. On the other hand, zwitterionic radical cation salts adopt slipped columnar  $\pi$ -stacking chains. Such stacking structures result in near-room-temperature ferromagnetic to antiferromagnetic phase transition and high long-range ferromagnetic ordering temperature [5], or antiferromagnetic behavior [6]. As a part of our general research effort intending to extend the range of molecular materials combining two properties in the same solid, herein, we report the syntheses, magnetic and photoluminescent

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properties of three new organic radical cation salts based on 2,3'-biimidazo[1,2-*a*]pyridin-2'-yl one (Hbipo<sup>•+</sup>) radical: [H(Hbipo<sup>•+</sup>)]<sup>+</sup><sub>2</sub>·[FeCl<sub>4</sub>]<sup>2-</sup>·H<sub>2</sub>O (**1**), [H(Hbipo<sup>•+</sup>)]<sup>+</sup><sub>2</sub>·[MnCl<sub>4</sub>]<sup>2-</sup> (**2**) and [H(Hbipo<sup>•+</sup>)]<sup>+</sup><sub>2</sub>·[Zn(SCN)<sub>3</sub>]<sup>-</sup>·H<sub>2</sub>O (**3**).

## 2. Results and discussion

### 2.1. Syntheses and composition analyses

The synthesis of [H(Hbipo<sup>•+</sup>)](ClO<sub>4</sub>) was previously described [5]. (Et<sub>4</sub>N)[FeCl<sub>4</sub>] and (Et<sub>4</sub>N)[Zn(NCS)<sub>3</sub>] were synthesized first, however, [MnCl<sub>4</sub>] was *in situ* generated. Then, ClO<sub>4</sub> in [H(Hbipo<sup>•+</sup>)](ClO<sub>4</sub>) was exchanged with FeCl<sub>4</sub>, MnCl<sub>4</sub> and Zn(NCS)<sub>3</sub>, respectively (Scheme 1), giving rise to the formation of three new organic radical cation salts, [H(Hbipo<sup>•+</sup>)]<sup>+</sup><sub>2</sub>·[FeCl<sub>4</sub>]<sup>2-</sup>·H<sub>2</sub>O (**1**), [H(Hbipo<sup>•+</sup>)]<sup>+</sup><sub>2</sub>·[MnCl<sub>4</sub>]<sup>2-</sup> (**2**), and [H(Hbipo<sup>•+</sup>)]<sup>+</sup><sub>2</sub>·[Zn(SCN)<sub>3</sub>]<sup>-</sup>·H<sub>2</sub>O (**3**). Fig. 1 exhibits the solid-state EPR spectra of **1**, **2** and **3** recorded at room temperature. The EPR spectrum of **1** shows two lines with a characteristic signal of Fe(II) at low magnetic field (Fig. 1a), which demonstrates that radical cation salt **1** possesses paramagnetic anion FeCl<sub>4</sub>. It is apparent that there are two types of EPR signal in **2**: a sharp line in a higher magnetic field, and a broad anisotropic type of Mn(II) line at low field (Fig. 1b). We assume that such EPR spectra are caused by formation of an organic radical cation salt with paramagnetic anion MnCl<sub>4</sub>. The anisotropic EPR signal is ascribed to MnCl<sub>4</sub> form. The sharp EPR line should be attributed to a radical cation form. Salt **3** is found to give rise to a sharp isotropic EPR signal centered at *g* = 2.000 (Fig. 1c), attributable to the organic radical cation moiety. According that [Zn(II)(SCN)<sub>3</sub>] is a diamagnetic anion, as a result, EPR is active only due to the radical cation moiety. The [Zn(SCN)<sub>3</sub>] existed in **3** is further confirmed by the infrared (IR) spectral data: the SCN anion stretching vibration is observed at around 2086 cm<sup>-1</sup> (see Section 4), indicating the existence of SCN anion in salt **3**.

The composition of salts **1**, **2** and **3** is demonstrated by the elemental analysis results. The elemental analysis reveals that **1** is composed of C, 46.70 wt%; H, 3.57 wt% and N, 15.40 wt%. The optimum composition of salt **1** should be [H(Hbipo<sup>•+</sup>)]<sub>2</sub>·[FeCl<sub>4</sub>]·H<sub>2</sub>O (C<sub>28</sub>H<sub>24</sub>Cl<sub>4</sub>FeN<sub>8</sub>O<sub>3</sub>) with the calculated composition: C, 46.83 wt%; H, 3.37 wt% and N, 15.60 wt%. Therefore, such composition formula is more consistent with the elemental analysis data. It should be noted that because salt **1** consists of two [H(Hbipo<sup>•+</sup>)] cations which are supported by the elemental analysis result, FeCl<sub>4</sub> moiety should carry two negative charges in order to balance the positive charges of two [H(Hbipo<sup>•+</sup>)] cations.

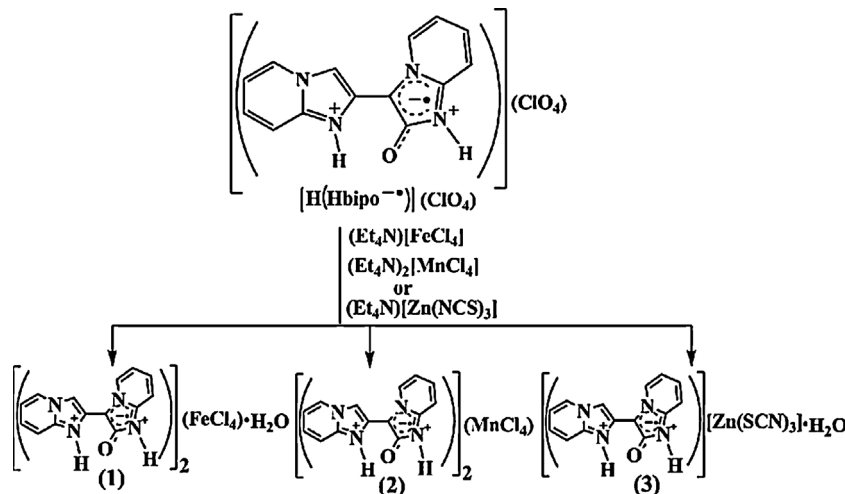
As a result, the paramagnetic anion should be [Fe(II)Cl<sub>4</sub>]<sup>2-</sup> form, implying [Fe(III)Cl<sub>4</sub>]<sup>-</sup> was *in situ* converted to [Fe(II)Cl<sub>4</sub>]<sup>2-</sup> during the anion exchange reaction process (see Section 4). X-ray photoelectron spectroscopy (XPS) further supports that [Fe(III)Cl<sub>4</sub>]<sup>-</sup> was *in situ* converted to [Fe(II)Cl<sub>4</sub>]<sup>2-</sup>. As shown in Fig. 2, salt **1** shows a Fe 2p<sub>3/2</sub> peak at 710.5 eV and a Fe 2p<sub>1/2</sub> peak at 724 eV, respectively. The spectrum of the salt **1** is in good agreement with Fe(II) ion [9]. From elemental analysis data of salt **2**: C, 50.67 wt%; H, 3.49 wt% and N, 16.74 wt%, the optimum composition of **2** should be [H(Hbipo<sup>•+</sup>)]<sub>2</sub>·[MnCl<sub>4</sub>] (C<sub>28</sub>H<sub>22</sub>Cl<sub>4</sub>MnN<sub>8</sub>O<sub>2</sub>) with the calculated composition: C, 48.09 wt%; H, 3.17 wt% and N, 16.02 wt%. Moreover, the optimum composition of salt **3** should be [H(Hbipo<sup>•+</sup>)]<sub>2</sub>·[Zn(SCN)<sub>3</sub>]·H<sub>2</sub>O (C<sub>17</sub>H<sub>13</sub>N<sub>7</sub>O<sub>2</sub>S<sub>3</sub>Zn): calcd. C, 40.12 wt%; H, 2.57 wt% and N, 19.27 wt%, such formula is more consistent with the elemental analysis data (C, 39.20 wt%; H, 2.31 wt% and N, 19.06 wt%).

Thermogravimetric analyses (TGA) further support the composition of three new organic radical cation salts. The TGA curve of salt **1** exhibits an initial weight loss (2.9%) from 89 to 175 °C (Fig. 3a), corresponding to the removal of one guest water molecule (calcd. 2.5%), demonstrating there exists one water molecule in **1** which is consistent with the elemental analysis result. No mass loss is observed from room-temperature to 361 °C for salt **2** (Fig. 3b), indicating it does not contain guest water molecule. The TGA curve of salt **3** shows an initial weight loss (4.3%) from 52 to 106 °C (Fig. 3c), corresponding to the removal of one guest water molecule (calcd. 3.5%), also supporting its composition as indicating by its elemental analysis data.

### 2.2. Magnetic properties

The magnetic susceptibility of **1**, **2** and **3** was measured on a solid-state sample from 4 to 300 K at an applied field of 1000 Oe. The temperature dependence of magnetic susceptibility for **1** is shown in Fig. 4. The  $\chi_M T$  value at 300 K is 1.982 emu K mol<sup>-1</sup>, which is lower than an isolated Fe(II) with *S* = 2, but in the same range of 1.876 emu K mol<sup>-1</sup> of *S* = 3/2. Upon cooling from 300 K, the  $\chi_M T$  gradually decreases, indicating an antiferromagnetic interaction for **1** (Fig. 4). The plot  $\chi_M^{-1}$  versus *T* (Fig. 4, the inset) for salt **1** can be fitted to the Curie–Weiss law with *C* = 2.04 emu mol<sup>-1</sup>,  $\theta$  = -9.47 K, and *R* = 8.4 × 10<sup>-5</sup>. The negative  $\theta$  value means the presence of an antiferromagnetic interaction in salt **1**.

Interestingly, although salt **2** reveals a dominant antiferromagnetic interaction, it exhibits different magnetic behavior from that **1**. As shown in Fig. 5, upon cooling from 300 K, the  $\chi_M T$  increases



Scheme 1. Syntheses of radical cation salts from [H(Hbipo<sup>•+</sup>)](ClO<sub>4</sub>).

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