



# Syntheses, crystal structures, electronic spectra and magnetic properties of two ion-pair charge transfer complexes based on $[\text{Ni}(\text{mnt})_2]^-$



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## ABSTRACT

Two new bimetallic ion-pair complexes **1** and **2** with general formula  $[\text{M}(\text{phen})_3][\text{Ni}(\text{mnt})_2]_2$  (phen = 1, 10-phenanthroline,  $\text{mnt}^{2-}$  = maleonitriledithiolate; M =  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$  for **1** and **2**), have been prepared and characterized by IR, elemental analysis, single crystal X-ray diffraction, UV-vis-NIR spectra and magnetic measurements. The structural determination reveals that the crystals of two ion-pair complexes, with monoclinic space group  $C2/c$ , have similar cell parameters and the  $[\text{M}(\text{phen})_3]^{2+}$  cations and the  $[\text{Ni}(\text{mnt})_2]^-$  anions are packed by forming alternate layers. Thermogravimetric (TG) analyses revealed that **1** and **2** are thermally stable up to  $\sim 170$  °C. UV-vis-NIR spectra disclose that two complexes exhibit sizable absorption in near-IR region because of ion-pair charge transfer (IPCT) transitions in **1** and **2**. Investigation of the magnetic properties **1** shows Curie-Weiss-type paramagnetic behavior in the temperature range 2–400 K. For **2**, the paramagnetic behavior above  $\sim 40$  K indicated the  $[\text{Fe}(\text{phen})_3]^{2+}$  ion has a low-spin state and the weak Curie-Weiss type tail below 40 K results from a trace amount of paramagnetic  $[\text{Ni}(\text{mnt})_2]^-$  species.

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## 1. Introduction

Dye-sensitized solar cells (DSSC) are currently attracting widespread interest for their use in the conversion of sunlight to electricity because of their low cost and high efficiency [1–8]. In such cells, dye is one of the key components for high conversion efficiencies, and ideally, the dye should have intensive absorption in the whole solar spectrum [9]. Therefore, the molecular photovoltaic devices with extended absorption in the near-IR spectrum region, are currently a hot topic in the solar cell area [10].

Charge-transfer salts formed between cations and anions (i.e., ion pair charge-transfer or IPCT complexes) are among an interesting subclass of the donor-acceptor system [11]. Charge-transfer

salts contain neutral donors and acceptors. The donor–acceptor-type salt could give rise to a charge transfer (CT) transition band in its electronic absorption spectrum, and the spectral property of the charge-transfer transition band is tunable via systematic modification of the acceptor/donor molecular structure [12]. For applications involving solar energy conversion, materials based on compositions such as CdS usually have low solar conversion efficiency, in part because of the low absorption in red and near-infrared (NIR) parts of the solar spectrum, the region in which the sun emits its maximum flux of photons. Efficiency could be improved by extending the range of the solar spectrum that semiconductor materials are capable of absorbing [13,14].

Bis(maleonitriledithiolato)metalate complexes  $([\text{M}(\text{mnt})_2]^{n-})$ ,  $n = 1$  or  $2$ ) have been one of the widely studied families of dithiolene complexes [15–17] due to their novel properties in the areas of conducting [18,19] and magnetic materials [20–22], dyes [23], non-linear optics [24], catalysis [25] and others. These unusual properties arise principally from the specially planar molecular geometry and delocalizing electron structure of  $[\text{M}(\text{mnt})_2]^{n-}$  anion.

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Near-infrared pigments based on ion-pair charge transfer salts of dicationic and dianionic metal–dithiolene  $[M(II) = Pd, Pt]$  complexes were obtained. The properties of these CT salts are related to the driving force of electron transfer from the donor (dianion) to the acceptor (dication), and that intramolecular interactions of different nature, in the present case contacts exchanged mainly through H-atoms, are suitable for mediating these interactions [26].

In our previous study, the electronic spectra for a series of ion-pair complexes,  $[RBz-1-Apy]_2[Ni(mnt)_2]$  ( $RBz-1-Apy^+$  represents the benzylidene-1-aminopyridinium derivatives), were investigated, which indicated that (1) there is a near-IR absorption band, arising from the ion-pair charge transfer (IPCT) between the HOMO of  $[Ni(mnt)_2]^{2-}$  and the LUMO of  $RBz-1-Apy^+$  for the ion-pair complexes and (2) the IPCT band position is almost independent on the substituent group features in the phenyl ring of the  $RBz-1-Apy^+$  cation since it has little contribution to the cationic LUMO, but sense to the structure of the pyridine moiety [27]. Besides, UV–vis–NIR spectra in acetonitrile solutions for three new ion-pair charge transfer (IPCT) complexes  $[1-Bz-4-NH_2-Py]_2[M(mnt)_2]$  ( $1-Bz-4-NH_2-Py^+ = 1$ -benzyl-4-aminopyridinium;  $M = Ni^{2+}, Pd^{2+}$  or  $Pt^{2+}$ ) were studied, which showed that the three complexes have novel M...H interactions in the solid state and exhibit an intense absorption band in the near-IR region [28].

Recently, two ion-pair complexes  $[M(phen)_3][Ni(mnt)_2]$  ( $phen = 1, 10$ -phenanthroline,  $M^{2+} = Ni^{2+}, Fe^{2+}$ ) were prepared and structural characterized; the UV-visible–NIR spectra and magnetic properties were investigated [29]. UV-vis–NIR spectra disclose that two complexes exhibit no sizable absorption in near-IR region. In this paper, the oxidized complexes of  $[M(phen)_3][Ni(mnt)_2]$  ( $[M(phen)_3][Ni(mnt)_2]_2$ ,  $M^{2+} = Ni^{2+}, Fe^{2+}$  for **1** and **2**) were prepared by the oxidation of iodine. The UV-visible–NIR spectra and magnetic properties were also investigated. UV-vis–NIR spectra disclose that two complexes exhibit sizable absorption in near-IR region because of ion-pair charge transfer (IPCT) transitions in  $[Ni(mnt)_2]^-$ .

## 2. Experimental

### 2.1. Materials and methods

All commercially available chemicals of AR or equivalent grades were used without further purification. Disodium maleonitriledithiolate ( $Na_2mnt$ ) [30],  $[(n-Bu)_4N]_2[Ni(mnt)_2]$  [30],  $[Ni(phen)_3]Cl_2 \cdot 2H_2O$  [31] and  $[Fe(phen)_3]Cl_2$  [32] were prepared according to the published method.

### 2.2. Preparation of $[Ni(phen)_3][Ni(mnt)_2]_2$ (**1**)

To a solution of  $[(n-Bu)_4N]_2[Ni(mnt)_2]$  (0.2 mmol, 0.1231 g) in acetonitrile (MeCN) (10 mL),  $[Ni(phen)_3]Cl_2 \cdot 2H_2O$  (0.2 mmol, 0.1561 g) in MeCN (20 mL) in a small amount of methanol (MeOH) (1 mL) was added slowly and the mixture was stirred at ambient temperature for 3 h, giving the reddish-brown precipitate, which was then filtered and dried. The solids were dissolved in N, N-dimethylformamide (DMF) and the insoluble residue was filtered off. The dark-red product  $[Ni(phen)_3]_2[Ni(mnt)_2]$  was obtained by adding methanol to the filtrate and recrystallized from DMF/MeOH ( $V_{DMF}:V_{MeOH} = 1:1$ ).

A MeOH solution (20 mL) of  $I_2$  (150 mg, 0.59 mmol) was slowly added to a MeCN solution (10 mL) of  $[Ni(phen)_3][Ni(mnt)_2]$  (572 mg, 1.0 mmol), the mixture was allowed standing overnight after stirred for 25 min. The black powdered sample formed were filtered off, washed with MeOH and dried in vacuum. Yield ca. 84% (based on  $[Ni(phen)_3][Ni(mnt)_2]$ ). Elemental Anal. (%). Calcd. for  $C_{52}H_{24}N_{14}Ni_3S_8$ : C, 48.89; N, 15.35; H, 1.89. Found: C, 48.76; N,

14.96; H, 1.63. IR spectrum (KBr disc,  $cm^{-1}$ ): 2203s ( $\nu_{C=N}$  of  $mnt^{2-}$  ligands) 1624w (phen) 1421s ( $\nu_{C=C}$  of  $mnt^{2-}$  ligands), 1580s, 1515s (phen), 1149 m ( $\nu_{C-C \equiv N}$  of  $mnt^{2-}$  ligands), 1100 m ( $\nu_{C-C \equiv N}, \nu_{C-S}$ ), 841s (phen), 722s (phen) and 504 m.

### 2.3. Preparation of $[Fe(phen)_3][Ni(mnt)_2]_2$ (**2**)

This was obtained in a similar way to that described in the preparation part of  $[Ni(phen)_3][Ni(mnt)_2]_2$ , except for the use of  $[Fe(phen)_3]Cl_2$  (0.2 mmol, 0.1437 g) instead of  $[Ni(phen)_3]Cl_2$ . The yield of the crude product was about 78%. Elemental Anal. (%). Calcd. for  $C_{52}H_{24}N_{14}FeNi_2S_8$ : C, 49.00; N, 15.38; H, 1.90. Found: C, 48.56; N, 15.36; H, 1.87. IR spectrum (KBr disc,  $cm^{-1}$ ): 2206s ( $\nu_{C=N}$  of  $mnt^{2-}$  ligands) 1629 m (phen), 1421s ( $\nu_{C=C}$  of  $mnt^{2-}$  ligands), 1510s (phen), 1149 m ( $\nu_{C-C \equiv N}$  of  $mnt^{2-}$  ligands), 1099 m ( $\nu_{C-C \equiv N}, \nu_{C-S}$ ), 839s (phen), 720s (phen) and 524w.

The columnar black crystals of **1** and **2**, being suitable size for X-ray diffraction, were obtained by dispersing methanol into DMF solution of the corresponding complexes for 7–10 days.

### 2.4. Physical measurements

Elemental analyses for C, H and N were carried out with an Elementar Vario EL III analytic instrument. IR spectra were recorded on a Bruker Vertex 80 Fourier Transform Infrared Spectrometer (KBr disc) in the range of 4000–400  $cm^{-1}$ . Thermogravimetric (TG) analyses were carried out on a NETZSCH STA 449F3 thermogravimetric analyzer under a nitrogen atmosphere (30–800 °C range) at a warming rate of 10 °C  $min^{-1}$  and the polycrystalline samples were placed in an  $Al_2O_3$  crucible. UV-visible–NIR spectra measurements in the solution were taken using a PerkinElmer Lambda 950 UV/VIS/NIR spectrometer. Magnetic susceptibilities of **1** and **2** were collected on microcrystalline samples from 2 to 400 K under a magnetic field of 10000 Oe, using a Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer.

### 2.5. X-ray crystallography

Single crystals of **1** and **2** were respectively selected to mount on a glass capillary, and the diffraction intensity data were collected at 296 K by a Bruker AXS SMART diffractometer equipped with CCD area detector and  $Mo K\alpha$  ( $\lambda = 0.71073$  Å) radiation [33]. The structures of **1** and **2** were solved using direct method and refined with the SHELX-97 [34] by the full-matrix least-squares procedure on  $F^2$ , respectively. All non-hydrogen atoms were anisotropically refined and the hydrogen atoms were introduced at calculated positions. The crystallographic details about data collection and structure refinements of **1** and **2** are summarized in Table S1.

## 3. Results and discussion

### 3.1. Synthesis and phase purity

In previous studies [29], we tried to obtain the target compounds  $[Ni(phen)_3][Ni(mnt)_2]_2$  and  $[Fe(phen)_3][Ni(mnt)_2]_2$  by mixing the acetonitrile solutions of  $[(n-Bu)_4N][Ni(mnt)_2]$  with the acetonitrile solutions of  $[Ni(phen)_3]Cl_2 \cdot 2H_2O$  or  $[Fe(phen)_3]Cl_3$ , but failed. Herein, the new method for preparing the target compounds **1** and **2** have been proposed through the oxidation of the reported compounds  $[Ni(phen)_3][Ni(mnt)_2]$  and  $[Fe(phen)_3][Ni(mnt)_2]$  with iodine. (Seeing the experimental section) The compounds **1** and **2** were distinguished from the  $[Ni(mnt)_2]^{2-}$  based compounds by the stretching vibration peak  $\nu_{C=N}$  of  $mnt^{2-}$  ligands in IR spectra. The stretching vibration peak  $\nu_{C=N}$  of  $mnt^{2-}$  ligands is greater than

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