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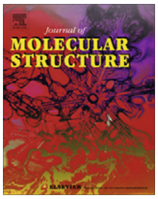

Two 2D metal–organic frameworks based on *N*-heterocyclic and polycarboxylates ligands: Syntheses, structures, and photoluminescent properties

Li Yan [a,*], Chuanbi Li [a], Dongsheng Zhu [b]

[a] *Department of Chemistry, Jilin Normal University, Siping 136000, PR China*
[b] *Department of Chemistry, Northeast Normal University, Changchun 130024, PR China*

HIGHLIGHTS

- Two complexes constructed from novel *N*-heterocyclic ligands have been synthesized and characterized.
- Weak interactions provide additional assembly forces.
- The fluorescence spectrum of the complexes and ligands are also investigated.

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ABSTRACT

Two novel complexes constructed from aromatic acid and *N*-heterocyclic ligands have been synthesized by hydrothermal reaction: {[Mn(dipt)(BDC)$_3$·H$_2$O]$_n$ (**1**) [dipt = 2-(2,4-dichlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline, BDC = terephthalic acid] and [Pb(dnpt)(BDC)$_2$]$_n$ (**2**) [dnpt = 2-(4-nitrophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline]. Complexes **1** and **2** were characterized by elemental analysis, IR, single crystal X-ray diffraction and thermogravimetric analysis (TGA). The results suggest that complexes **1**–**2** exhibit 1D chain structure. The intermolecular C–H···O and N–H···O interactions extend the complexes into 2D networks, and the existing H-bonds further stabilized the title complexes, which can be proved by TGA experiment. Furthermore, the solid-state fluorescence spectrum of complexes **1** and **2** were also investigated, as well as the ligands dipt and dnpt.

1. Introduction

Recently, rational design and synthesis of novel metal–organic frameworks (MOFs) have received intense interest and attentions for their potential applications as function materials as well as their structural diversity and intriguing variety of topologies [1–6]. In this regard, many complexes with various frameworks from one-dimensional (1D) to 3D have been designed and characterized. Selection of appropriate multidentate ligands to coordinate metal ions is a key strategy for building MOFs. *N*-heterocyclic ligands were found to reproduce the coordination behavior of peptides and their selectivity towards metal ions. Thus it is of great interest in using the *N*-heterocyclic ligand to synthesis of novel polymers. In this paper, we synthesized two novel *N*-heterocyclic ligands := 2-(2,4-dichlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (dipt) and 2-(4-nitrophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (dnpt) in view of their following characteristics: (1) they possess extended aromatic system, which potentially provide supramolecular interactions such as π–π interactions between the aryl rings to construct intriguing structures; (2) they have strong coordination with two nitrogen atoms; and (3) they possess rigidity of coordination to metal atoms [7]. The structures of ligands dipt and dnpt are shown in Scheme 1. Mn(II) ion plays an important role in biological system, and the Mn(II) carboxylate complexes are known to exist at the active sites of some metalloenzymes. Pb(II) is a heavy toxic metal, which commonly found in critical life cycles due to its widespread use in numerous industrial applications [8]. A good knowledge of the Pb(II) coordination properties, including the lone pair of electrons, coordination ability, coordination number, and coordination geometry, is important for the understanding of the toxicological properties of Pb(II) [9]. Therefore, in this paper, we synthesized two novel polymers containing Mn^{2+} and Pb^{2+} ions and reported the syntheses, crystal structures, thermogravimetric analysis (TGA), as well as photoluminescence properties of coordination polymers **1**–**2**.

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[*] Corresponding author. Tel.: +86 15844440698.
E-mail address: yanli820618@163.com (L. Yan).

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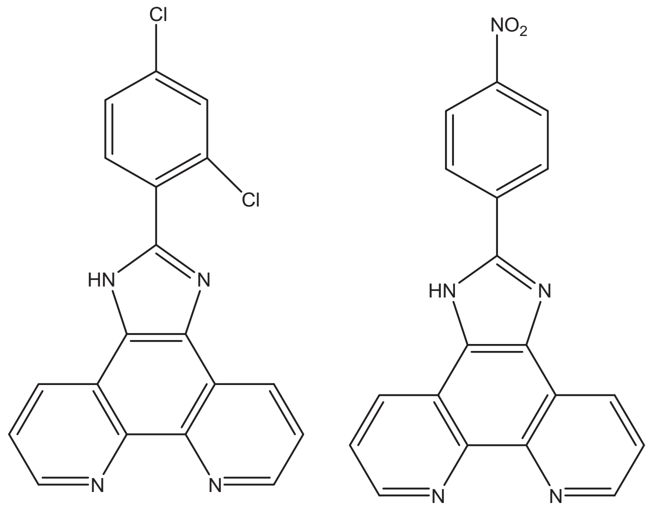

dipt dnpt

Scheme 1. The structures of dipt and dnpt.

2. Experimental section

2.1. Materials and physical measurements

The ligands dipt and dnpt were prepared according to the description in the literature procedures [10]. All the other chemicals from commercial sources were commercially available, and used without further purification. The FT-IR spectrum was measured with KBr pellets in the range of 4000–400 cm^{-1} on a Perkin–Elmer 240C spectrometer. TGA was performed using a Perkin–Elmer TG-7 analyzer at the rate of 10 °C/min rise of temperature in nitrogen atmosphere. Crystal structures were determined on a Bruker SMART APEX II CCD X-ray diffractometer. Carbon, hydrogen and nitrogen elemental analyses were performed with a PE-2400 elemental analyzer.

2.2. Syntheses

$[Mn(dipt)(BDC)_3 \cdot H_2O]_n$ (**1**): A mixture of dipt (0.109 g, 0.3 mmol), Mn $(SO_4)_2 \cdot H_2O$ (0.051 g, 0.3 mmol), 1,4-benzenedicarboxylate (BDC) (0.100 g, 0.6 mmol) in distilled H_2O (18 mL) was stirred at room temperature and adjusted the pH value to about 7.0 with NaOH. We put the cloudy solution into a 30-mL Teflon-lined stainless vessel at 170 °C for 3 days and afterwards cooled to room temperature at a rate of 5 °C/h. The yellow crystals of complex **1** were obtained in 80% yield based on Mn. $C_{31}H_{18}Cl_2MnN_4O_7$: calcd. C 54.40, H 2.65, N 8.18%; found: C 54.45, H 2.39, N 8.21%. IR (KBr, cm^{-1}): 3418(m), 3230(m), 2362(s), 1613(vs), 1378(vs), 1259(s), 745(m), 596(m).

$[Pb(dnpt)(BDC)_2]_n$ (**2**): A mixture of dnpt (0.102 g, 0.3 mmol), $Pb(Ac)_2 \cdot 3H_2O$ (0.114 g, 0.3 mmol), BDC (0.100 g, 0.6 mmol) in distilled H_2O (18 mL) was stirred at room temperature and adjusted the pH value to about 7.0 with NaOH. We put the cloudy solution into a 30-mL Teflon-lined stainless vessel at 180 °C for 3 days. The reaction was cooled to room temperature at a rate of 5 °C/h, and then small yellow crystals of complex **2** were collected in 76% yield based on Pb. $C_{27}H_{13}N_5O_6Pb$: calcd. C 45.63 H 1.84, N 9.85%; found: C 45.58, H 1.96, N 9.81%. IR (KBr, cm^{-1}): 3555(s), 3483(s), 3406(m), 2337(s), 1672(vs), 1500(vs), 1279(s), 1110(s), 731(m), 510(m).

2.3. X-ray crystallography

Single-crystal X-ray diffraction data for complexes **1** and **2** were collected at 293(2) K with a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) in the range of $1.79° \leqslant \theta \leqslant 26.02°$ for **1** and $1.55° \leqslant \theta \leqslant 26.11°$ for **2**. Absorption corrections were applied using multi-scan technique and all the structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using the programs SHELXS-97 [11] and SHELXTL-97 [12]. Non-hydrogen atoms were refined with anisotropic temperature parameters and all hydrogen atoms were refined isotropically. Experimental details for crystallographic data and structure refinement parameters for complexes **1** and **2** are listed in Table 1.

3. Results and discussion

3.1. Structural analysis of complex *1*

The molecular structure is shown in Fig. 1. The 1D chain structure is shown in Fig. 2, and 2D layer structure is shown in Fig. 3. Selected bond lengths and bond angles are given in Table 2.

Table 1
Crystal data and details of structure refinement parameters for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{31}H_{18}Cl_2MnN_4O_7$	$C_{27}H_{13}N_5O_6Pb$
Formula weight	684.33	710.62
Crystal system	Triclinic	Triclinic
Space group	$P-1$	$P-1$
a (nm)	1.14424(1)	0.94551(1)
b (nm)	1.19094(1)	1.0509(2)
c (nm)	1.25065(1)	1.3652(3)
β (°)	94.443(2)	76.522(3)
Volume (nm^3)	1.4274(4)	1.2735(4)
Z	2	2
Density (Mg/m^3) (calculated)	1.592	1.853
Absorption coefficient (mm^{-1})	0.708	6.676
F(000)	694	680
Crystal size (mm^3)	0.315 × 0.187 × 0.148	0.40 × 0.32 × 0.20
Theta range (°)	1.79–26.02	1.55–26.11
Reflections collected	7879	6937
Unique reflections [R_{int}]	5541 [0.0315]	4868 [0.0191]
Goodness-of-fit on F^2	1.025	1.068
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0625$, $wR2 = 0.1632$	$R1 = 0.0452$, $wR2 = 0.1327$
R indices (all data)	$R1 = 0.1057$, $wR2 = 0.1926$	$R1 = 0.0547$, $wR2 = 0.1391$
Largest difference peak and hole (*e*, Å^{-3})	1.268, −0.404	3.487, −0.621