Journal of Solid State Chemistry 258 (2018) 328–334

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Three coordination polymers based on a star-like geometry 4, 4', 4'' -nitrilotribenzoic acid ligand and their framework dependent luminescent properties

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ARTICLE INFO

Keywords:
Coordination polymers
Luminescence
Hydrothermal synthesis
4, 4', 4'' -nitrilotribenzoic acid

ABSTRACT

Three novel coordination polymers, $[Zn(\mu_2\text{-HTCA})(Phen)]_n$ (**1**), $\{[Cd(\mu_3\text{-HTCA})(Phen)]\cdot 2H_2O\}_n$ (**2**), $[Mn(\mu_2\text{-HTCA})(Phen)(H_2O)]_n$ (**3**) were prepared by hydrothermal synthesis from the 4, 4', 4''-nitrilotribenzoicacid (H_3TCA) and 1, 10-phenanthroline monohydrate (Phen) with different transition metal salts, which were characterized by elemental analysis, IR spectra, powder and single-crystal X-ray diffraction and thermogravimetric analysis. The photophysical properties of the complexes were investigated by solid-state diffuse reflectance spectra, photoluminescent properties, lifetime and quantum yield. For these complexes, it was found that the band gaps follow the order: **3** < **2** < **1** < 2.80 eV, fluorescence intensity order: **1** > H_3TCA > **2** > **3**; quantum yield order: H_3TCA > **1** > **2** > **3**; while the lifetime order: **1** > **2** > H_3TCA > **3**.

1. Introduction

Much progress has been achieved in the rational design and synthesis of coordination polymers (CPs) due to their potential applications in the areas of catalysis, gas storage, luminescence, magnetism, electrical conductivity, nonlinear optics, and molecular sensors [1–9]. Triphenylamine (TPA), which is a structural star-like geometry with a nitrogen atom in the center, is widely used in photoelectric materials and hole-transporting materials due to its unique free radicals, larger steric hindrance factors, superconjugate electronic effect and high hole mobility. Triphenylamine moiety, with obvious optical activity and easily modified property, can be connected with functional substituents at appropriate positions to form various function materials [10].

Carboxylic acid ligands not only have a variety of spatial configuration, but also the coordination of carboxyl with metal ions is also very rich in the construction of polymers [11]. The combination of three fold symmetry and carboxylic acid makes it to be an ideal building block in the field of crystal engineering. The multi-carboxylate ligands have exhibited potential applications in the generation of multi-dimensional porous CPs with new topologies [12].

Undoubtedly, the choice of suitably-tailored ligand is the key in order to get the desirable coordination polymers although the nature of coordination sites, conformation and flexibility of organic ligands as well as the geometric preference and potential properties of metal centers all affect the structure and property of the final CPs greatly [13–16]. Phen has a three-ring conjugate plane of the rigid structure as a commonly used ligand, it this is conducive to the effective transmission of electron energy between atoms, laying a foundation for its coordination with the metal [17–19].

It is very important that proper functional organic ligand as bridge was selected in constructing functional coordination polymers. Therefore, based on the consideration above, the present strategy using triphenylamine carboxylate and nitrogen donor of phen ligands should come into playing in the construction of photoluminescent CPs [20,21]. We selected three common metal salts, different coordination centers, $Zn^{II}(d^{10})$, $Cd^{II}(d^{10})$, $Mn^{II}(d^5)$ to tune their photoluminescent properties. Herein we report the syntheses, crystal structures, and characterizations and photophysical properties of the three novel coordination polymers, $[Zn(\mu_2\text{-HTCA})(Phen)]_n$ (**1**), $\{[Cd(\mu_3\text{-HTCA})(Phen)]\cdot 2H_2O\}_n$ (**2**), and $\{[Mn(\mu_2\text{-HTCA})(Phen)(H_2O)]\}_n$ (**3**).

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http://dx.doi.org/10.1016/j.jssc.2017.10.027
Received 8 May 2017; Received in revised form 2 October 2017; Accepted 20 October 2017

2. Experimental section

2.1. Materials and instruments

Ligand 4, 4', 4''-nitrilotribenzoic acid (H_3TCA) was prepared according to the literature method [22]. All the reagents and solvents were commercially available and used as received. The powder X-ray diffraction patterns (PXRD) were collected with a scan speed of 0.5 s/deg on a Bruker Advance D8 (40 kV, 40 mA) diffractometer with Cu radiation (λ= 1.54056 Å) at room temperature. FT-IR data were recorded on VERTEX 80 with KBr pellets in the 4000–400 cm^{-1} region. Elemental analyses (EA) for C, H and N were performed on Vario ELIII. TGA data were obtained on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 10 °C min^{-1} under N_2 atmosphere. Diffuse reflectance spectra were recorded on a U-41000 Spectrophotometer (Liquid) using $BaSO_4$ powder as a 100% reflectance reference. The solid state luminescence spectra were given by F-4500 FL spectrophotometer (EX Slit: 2.5 nm, EM Slit: 5.0 nm and PMT Voltage: 700 V).

2.2. Synthesis of $[Zn(\mu_2\text{-}HTCA)(Phen)]_n$ (1)

The mixture of $Zn(CH_3COO)_2·2H_2O$ (0.022 g, 0.100 mmol), H_3TCA (0.037 g, 0.100 mmol) and Phen (0.018 g, 0.100 mmol) in 1 mL of dimethylformamide (DMF) and 5 mL H_2O was sealed in a 15 mL vial, then transferred to the reaction of teflon reactor, heated to 140 °C for 3 days, and then cooled to room temperature. The colorless block crystals obtained were washed with ethanol, and dried at room temperature (yield: 62%). Anal. calcd for $C_{33}H_{21}N_3O_6Zn$(%): C, 63.83; H, 3.41; N, 6.77. Found: C, 63.78; H, 3.38; N, 6.76. IR (KBr, cm^{-1}): 3396.72 (m), 3072.80 (m), 2546.87 (m), 1676.28 (s), 1593.35 (s),1508.83 (s), 1431.13 (s), 1413.87 (s), 1383.40 (s), 1314.86 (s),1288.25 (s), 1173.35 (s), 1105.81 (m), 1016.61 (w), 943.53 (w),846.83 (s), 782.78 (s), 725.78 (m), 711.25 (m), 682.12 (w),664.99 (w), 644.00 (w), 549.24 (m), 514.10 (m), 445.79 (w).

2.3. Synthesis of $\{[Cd(\mu_3\text{-}HTCA)(Phen)]·2H_2O\}_n$ (2)

The mixture of $Cd(CH_3COO)_2·2H_2O$ (0.024 g, 0.100 mmol), H_3TCA (0.037 g,0.100 mmol) and Phen (0.018 g, 0.100 mmol) in 1 mL of dimethylformamide (DMF) and 5 mL H_2O was sealed in a 15 mL vial, then transferred to the reaction of teflon reactor, heated to 140 °C for 3 days, and then cooled to room temperature. The colorless block crystals obtained were washed with ethanol, and dried at room temperature (yield: 67%). Anal. calcd for $C_{33}H_{25}CdN_3O_6$(%): C, 58.98; H, 3.75; N, 6.25. Found: C, 58.92; H, 3.71; N, 6.34. IR (KBr,cm^{-1}): 3441.30 (m), 3063.00 (m), 1714.40 (m), 1592.50 (s), 1536.13 (s), 1510.85 (s), 1386.64 (s), 1315.19 (s), 1273.80 (s), 1171.53 (s), 1142.27 (m), 1101.84(m), 1013.95(w), 849.11 (m), 783.95 (m), 726.74 (m), 677.35 (w), 636.59 (w),517.72 (m).

2.4. Synthesis of $[Mn(\mu_2\text{-}HTCA)(Phen)(H_2O)]_n$ (3)

The mixture of $MnSO_4·H_2O$ (0.017 g, 0.100 mmol), H_3TCA (0.037 g, 0.100 mmol) and Phen (0.018 g, 0.100 mmol) in 1 mL of dimethylformamide (DMF) and 5 mL H_2O was sealed in a 15 mL vial, then transferred to the reaction of teflon reactor, heated to 140 °C for 3 days, and then cooled to room temperature. The light yellow crystals obtained were washed with ethanol, and dried at room temperature (yield: 51%). Anal. calcd for $C_{33}H_{23}MnN_3O_7$ (%): C, 63.06; H, 3.69; N, 6.69. Found: C, 63.01; H, 3.74; N, 6.73. IR (KBr, cm^{-1}): 2965.27 (m), 2539.56 (m), 1668.60 (s), 1592.87 (s), 1511.38 (m), 1385.00 (s), 1315.70 (s), 1280.90(s), 1173.90 (s), 1102.07 (m), 1013.61 (w), 968.08 (w), 845.37 (m), 775.32 (m), 726.84 (m), 710.11 (w), 668.79 (w), 638.68 (w), 554.28 (m), 508.84 (m), 441.46 (w).

2.5. X-ray crystallography

Single-crystal X-ray crystallographic studies: Data were collected on a Bruker Smart APEX II diffractometer with a CCD area detector. Raw data collection and reduction were done using APEX2 software [23]. Adsorption corrections were applied using the SADABS routine. The structures were solved by direct methods and refined by full-matrix least-squares on F2 using the SHELXTL software package [24]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. The diffuse electron densities resulting from these residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated [25]. The contents of the solvent region are not represented in the unit cell contents in crystal data. The final formula of complexes **1–3** were calculated from elemental analysis and TGA data, so the final formula and formula weight are different from those expected from the data set which is removed the diffractions of guest molecules.

2.6. Powder X-ray diffraction analysis

Powder X-ray diffraction experiments of complexes **1**–**3** were carried out to investigate the purity of the bulky crystalline samples, and the results closely match the simulated patterns generated from the single-crystal diffraction data by the mercury program (Figs. S1–S3).

3. Results and discussion

3.1. Crystal structure description

Complex 1: $[Zn(\mu_2\text{-}HTCA)(Phen)]_n$ (**1**) Single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the Monoclinic *P21/c* space group. As shown in Fig. 1, the asymmetric unit of **1** contains one Zn(II) ion, one $HTCA^{2-}$ unit and one Phen molecule. The Zn(II) ion occupies the center of a slightly distorted trigonal bipyramidal geometry and coordinates to three carboxylate oxygen donors from two separated $HTCA^{2-}$ ligands and two nitrogen donors from Phen ligand through chelating modes, respectively. In the structure of complex **1** (Fig. 2), the Zn-N and Zn-O bond lengths are in the range of 2.090(2)–2.111(2) and 1.949(2)–2.427(2)Å, respectively, and the coordination angles around Zn are in the range of 58.48(8)–156.80(8), which is comparable with literature reported [26]. In Fig. 3, the Zn(II) ions are interconnected through ligands $HTCA^{2-}$ and Phen alternately, generating an infinite 1D linear chain

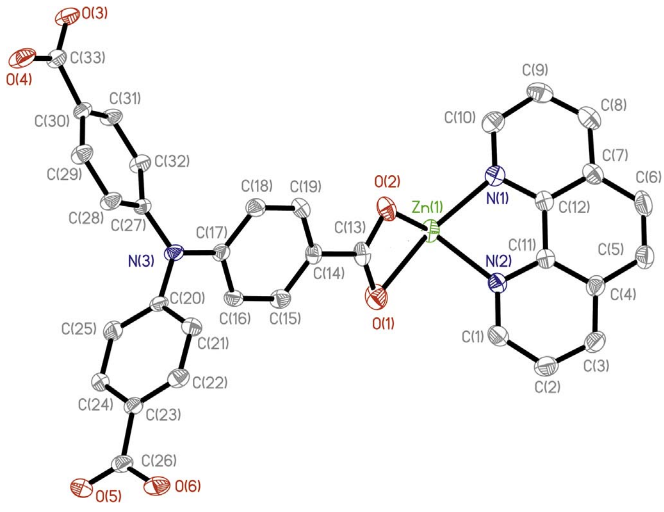

Fig. 1. The asymmetric unit of complex **1** with displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity.