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New in situ generated acylhydrazidate-coordinated complexes and acylhydrazide molecules: Synthesis, structural characterization and photoluminescence property

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ABSTRACT

By utilizing the hydrothermal in situ acylation of organic acids with N_2H_4, three acylhydrazidate-coordinated compounds $[Mn(L1)_2(H_2O)_2]$ (L1 = 2,3-quinolinedicarboxylhydrazidate; HL1 = 2,3-dihydropyridazino[4,5-*b*]quinoline-1,4-dione) **1**, $[Mn_2(ox)(L2)_2(H_2O)_6]\cdot 2H_2O$ (L2 = benzimidazolate-5,6-dicarboxylhydrazide; HL2 = 6,7-dihydro-1H-imidazo[4,5-g]phthalazine-5,8-dione; ox = oxalate) **2**, and [Cd(HL3)(bpy)] (L3 = 4,5-di(3′-carboxylphenyl)phthalhydrazidate; H_3L3 = 6,7-dihydro-1H-imidazo[4,5-g]phthalazine-5,8-dione; bpy = 2,2′-bipyridine) **3**, as well as two acylhydrazide molecules L4 (L4 = oxepino[2,3,4-*de*:7,6,5-*d′e′*]diphthalazine-4,10(5H,9H)-dione) **4** and L5 (L5 = 4,5-dibromophthalhydrazide; L5 = 6,7-dibromo-2,3-dihydrophthalazine-1,4-dione) **5** were obtained. X-ray single-crystal diffraction analysis reveals that (i) **1** only possesses a mononuclear structure, but it self-assembles into a 2-D supramolecular network via the $N_{hydrazine}$—H···$N_{hydrazine}$ and Ow—H···$O_{hydroxylimino}$ interactions; (ii) **2** exhibits a dinuclear structure. Ox acts as the linker, while L2 just serves as a terminal ligand; (iii) In **3**, L3 acts as a 3-connected node to propagate the 7-coordinated Cd^{2+} centers into a 1-D double-chain structure; (iv) **4** is a special acylhydrazide molecule. Two —OH groups for the intermediates 3,3′-biphthalhydrazide further lose one water molecule to form **4**; (v) **5** is a common monoacylhydrazide molecule. Via the $N_{hydrazine}$—H···$O_{hydrazine}$, $O_{hydroxylimino}$—H···$O_{acylamino}$ and the π···π interactions, it self-assembles into a 2-D supramolecular network. The photoluminescence analysis reveals that **4** emits light with the maxima at 510 nm.

1. Introduction

As an effective approach of preparation of new organic molecules and coordination compounds with potential functional properties, the ligand in situ synthesis has achieved a rapid development in the past eighteen years [1]. The ligand in situ synthesis approach not only simplifies the reactive procedure, but also creates a variety of new organic molecules and complexes. It is noteworthy that those in situ generated organic molecules or ligands are inaccessible through the routine synthetic methods [2]. A majority of ligand in situ reactions should originate from the chance discovery [3]. Now, the ligand in situ synthesis approach has entered a new stage. The researchers, on the one hand, have consciously designed the new ligand in situ reactions. On the other hand, those classical ligand in situ reactions as the cycloaddition of organic nitriles with azide [4], the *N*-alkylation of heterocyclic ligands with alcohols [5], and so on, have been extensively employed in the construction of novel supramolecular self-assemblies [6].

One of the investigations in our group is focused on the structural characterization of novel acylhydrazide molecules and acylhydrazidate-coordinated compounds, where the acylhydrazide moiety derives from the in situ acylation of phthalic acid moiety with N_2H_4 (see Scheme 1) [7]. Since the acylhydrazide moiety possesses the changeable character, it possesses a potential to form the diverse supramolecular aggregations with the metal ions. (i) Changeable oxidation. The H atom on the acylamino N atom maybe loses upon interaction with the metal ion, so the potential oxidation state for the phthalhydrazidate moiety is 0, −1 and −2. (ii) Changeable existing form. The acylamino group maybe isomerizes into the hydroxylimino group, so the phthalhydrazide moiety has three types of potential existing forms: diketo form, dihydroxyl form, and keto-hydroxyl form. (iii) Versatile coordination mode. It is noteworthy that once two O atoms or two acylamino groups act as the donors, the acylhydrazidate molecule can be viewed as a rode-like linker. (iv) Diverse synthon. Typically, two acylamino groups maybe form a kind of hydrogen-bonded synthon ($R_2^2(6)$), while two hydrazino groups maybe form another

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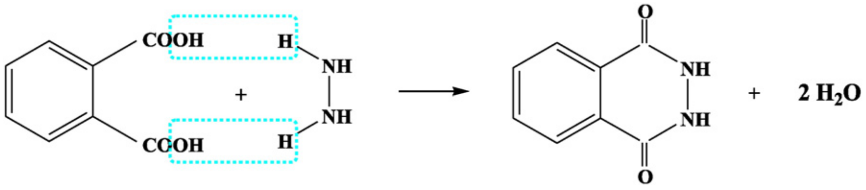


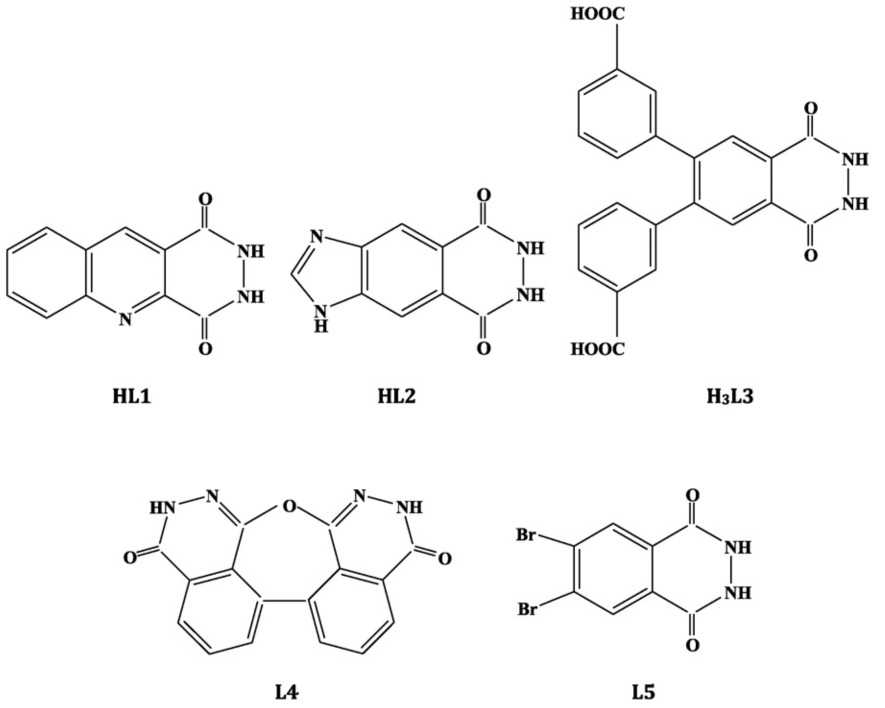
Scheme 1. Acylation of phthalic acid with N_2H_4.

kind of hydrogen-bonded synthon ($R_2^2(4)$). So far, some acylhydrazidate-containing compounds have been report including the 1-D [$Cd(mpdh)_2$] (mpdh = 6-methylpyridine-2,3-dicarboxylhydrazidate; Hmpdh = 2-methyl-6,7-dihydropyrido[2,3-*d*]pyridazine-5,8-dione) [8], [$Zn(npth)_2$] (npth = naphthalhydrazidate; Hnpth = 2,3-dihydrobenzo[g]phthalazine-1,4-dione) [9], 2-D [Cu(pth)] (pth = phthalhydrazidate; Hpth = 2,3-dihydrophthalazine-1,4-dione) [10], [$Mn(3\text{-}apth)_2(H_2O)$] (apth = 3-aminophthalhydrazidate; Hapth = 5-amino-2,3-dihydrophthalazine-1,4-dione) [11], and the 3-D [Ba(pmdh)] (pmdh = pyromellitdihydrazidate; Hpmdh = 2,3,7,8-tetrahydropyridazino[4,5-*g*]phthalazine-1,4,6,9-tetraone [12], [$Pb(3,4\text{-}pdh)_2$] (3,4-pdh = pyridine-3,4-dicarboxylhydrazidate; 3,4-Hpdh = 2,3-dihydropyrido[3,4-*d*]pyridazine-1,4-dione) [10]. Due to the existence of multiple electronic transferring paths, some of them display the interesting photoluminescence behaviors: red light for [Cu(pth)] [10], yellow light for [$Pb(mpdh)_2$] [11], green light for [$M(epdh)_3(H_2O)$] (M^{3+} = Dy^{3+}, Gd^{3+}, Y^{3+}, Lu^{3+}; epdh = 5-ethylpyridine-2,3-dicarboxylhydrazidate; Hepdh = 3-ethyl-6,7-dihydropyrido[2,3-*d*]pyridazine-5,8-dione) [13], and blue light for [$Zn_2(4\text{-}apth)(atez)_2$] (4-apth = 4-aminophthalhydrazidate; 4-H_2apth = 6-amino-2,3-dihydrophthalazine-1,4-dione; atez = 5-aminotetrazolate) [14]. Although some have been reported, the related investigation is actually still limited [15]. In order to further reveal the character of the acylhydrazidate molecule, and the relationship between the supramolecular structure and the photoluminescence property for the acylhydrazidate-containing compounds, in this article we will report the structural characterization and the photoluminescence property of three new acylhydrazidate-coordinated compounds [$Mn(L1)_2(H_2O)_2$] (L1 = 2,3-quinolinedicarboxylhydrazidate; HL1 = 2,3-dihydropyridazino[4,5-*b*]quinoline-1,4-dione) **1**, [$Mn_2(ox)(L2)_2(H_2O)_6$]·$2H_2O$ (L2 = benzimidazolate-5,6-dicarboxylhydrazide; HL2 = 6,7-dihydro-1H-imidazo [4,5-*g*] phthalazine-5,8-dione; ox = oxalate) **2**, and [Cd(HL3)(bpy)] (L3 = 4,5-di(3′-carboxylphenyl)phthalhydrazidate; H_3L3 = 3,3′-(1,4-dioxo-1,2,3,4-tetrahydrophthalazine-6,7-diyl)dibenzoic acid; bpy = 2,2′-bipyridine) **3**, as well as two acylhydrazide molecule L4 (L4 = oxepino[2,3,4-*de*:7,6,5-*d′e′*]diphthalazine-4,10(5H,9H)-dione) **4** and L5 (L5 = 4,5-dibromophthalhydrazide; L5 = 6,7-dibromo-2,3-dihydrophthalazine-1,4-dione) **5**. Scheme 2 illustrates the molecular structures of the acylhydrazide molecules in the title compounds.

2. Experimental section

2.1. General

All chemicals are of reagent grade quality, obtained from commercial sources without further purification. Elemental analysis (C, H and N) was performed on a Perkin-Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was recorded on a Perkin Elmer Spectrum 1 spectrophotometer in 4000–400 cm^{-1} region using a powdered sample on a KBr plate. Powder X-ray diffraction (XRD) data were collected on a Rigaku/max-2550 diffractometer with Cu-K_α radiation (λ = 1.5418 Å). Thermogravimetric (TG) behavior was investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of 10 °C min^{-1} in air. Fluorescence spectrum was obtained on a LS 55 florescence/phosphorescence spectrophotometer at room temperature with slit width



HL1 HL2 H_3L3

L4 L5

Scheme 2. Molecular structures of acylhydrazide molecules in title compounds.