

# Self assembly of two novel three-dimensional supramolecular networks with blue photoluminescence

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## Abstract

Two novel photoluminescent coordination polymers of the formula  $[\text{Cd}(\text{Haip})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Zn}(\text{aip})(\text{atz})] \cdot 3\text{H}_2\text{O}$  (**2**) ( $\text{H}_2\text{aip}$  = 5-aminoisophthalic acid;  $\text{atz}$  = 3-amino-1,2,4-triazole) have been synthesized through the self-assembly of metal(II) ions with  $\text{H}_2\text{aip}$  and *N*-containing ligands [2-amino-5-mercapto-1,3,4-thiadiazole for **1** and 3-amino-1,2,4-triazole for **2**, respectively] in the presence of NaOH. These complexes were characterized by FT-IR spectroscopy, thermogravimetric analysis (TG), elemental analysis and X-ray analysis. X-ray crystallographic studies of the complexes reveal that **1** is a first example where only one carboxylate group of the  $\text{H}_2\text{aip}$  ligand participates in coordination with the metal(II) ion and it exhibits a two-dimensional framework which further assembles into a three-dimensional supramolecular network *via* interlayer  $\pi$ - $\pi$  stacking interactions and strong hydrogen bonds, while **2** exhibits a two-dimensional porous architecture. The extensively strong hydrogen bonds and interlayer  $\pi$ - $\pi$  stacking interactions in **2** lead to the formation of a three-dimensional supramolecular network. Photoluminescence properties of the compounds **1** and **2** have been examined in the solid state at room temperature. These compounds have been found to exhibit blue photoluminescence and may be good candidates for photoactive materials.

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## 1. Introduction

In recent years the design and synthesis of supramolecular networks that provide new shapes, sizes and chemical environments as well as searches for new molecular-based functional materials has caused an increasing interest in supramolecular chemistry [1–11]. This is not only due to their abundant structural diversity, but also they are fundamental for the discovery and construction of various supramolecular devices or technologically useful materials [12–16]. The use of non-covalent interactions (such as hydrogen-bonding,  $\pi$ - $\pi$  interactions, etc.) to arrange molecular building blocks has evolved into one of the most useful and flexible strategies for the crystal engineering

design of extended supramolecular networks that have versatile functions [17–21]. The current interest is focused on the controlled assembly of donor and acceptor building blocks in order to generate high dimensional supramolecular polymers. In this context, the rational design of organic ligands and judicious selection of the coordination geometry of metal ions have great effect on the formation of desirable networks [10,22,23]. Among the current topic areas in supramolecular chemistry, there has been considerable interest in luminescent supramolecular assemblies due to their potential applications in light emitting molecular-based devices [24]. Luminescent metal-organic coordination compounds have attracted special interest due to their high thermal stability [25]. They can be synthesized by incorporating either organic ligands containing conjugated systems (such as aromatic rings) or inorganic emitting units [26,27]. In addition to metal ions and ligands, supramolecular interactions often play important role in fine tuning

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the luminescent properties of the supramolecular compounds [28,29]. The combination of organic emitting units with suitable metal ions and supramolecular interactions could fabricate a variety of luminescent materials.  $H_2aip$  is a good candidate for assembling such complexes due to its interesting structural characteristics. Compared with the ip ligand ( $H_2ip$  = isophthalic acid), the introduction of an amino group in  $H_2aip$  results in the following two effects at least: (i) a supramolecular effect, namely, providing more hydrogen-bonding donor or acceptor sites in the construction of supramolecular packing; (ii) a coordination effect, namely, adding a new coordination site to coordinate with more metal centers. To the best of our knowledge, only a few supramolecular complexes with  $H_2aip$  have been reported so far [30–35]. Furthermore, the introduction of *N*-containing ligands [such as atz or amtz (amtz = 2-amino-5-mercapto-1,3,4-thiadiazole)] may induce new structural evolution. The atz or amtz ligand is important in maintaining the desired low dimensional coordination polymer and may provide potential supramolecular recognition sites for hydrogen bonding and  $\pi$ – $\pi$  aromatic stacking interactions. We assumed that the  $H_2aip$  ligand could be useful in the formation of interesting supramolecular networks with some important features in the presence of atz or amtz ligand. So, we have started a systematic study on metal(II) coordination with the mixed  $H_2aip$  and atz or amtz ligands. One of the aims of this project is to analyze the influence that factors such as hydrogen bonding, rigidity and the possibility of specific attractive interactions between aromatic rings can exert on the structure and functional properties of aip containing metal(II) complexes. In the present paper, we report two novel three dimensional supramolecular coordination polymers  $[Cd(Haip)_2(H_2O)_2] \cdot 2H_2O$  (**1**) and  $[Zn(aip)(atz)] \cdot 3H_2O$  (**2**) based on mixed  $H_2aip$  and atz ligands. These complexes have been found to exhibit blue photoluminescence at room temperature.

## 2. Experimental

### 2.1. Materials and characterization

All reagents were purchased commercially and were used without further purification. Elemental analyses (C, H and N) were carried out on a 240C Elemental analyzer. FT-IR spectra (400–4000  $cm^{-1}$ ) were recorded from KBr pellets in a Magna 750 FT-IR spectrophotometer. Solid state emission spectra of the compounds were recorded using a 48000DSCF fluorescence spectrometer. Thermogravimetric analysis (TG) was taken on a NETZSCH STA 409 PG/PC instrument.

### 2.2. Synthesis

#### 2.2.1. $[Cd(Haip)_2(H_2O)_2] \cdot 2H_2O$ (**1**)

Amtz (2-amino-5-mercapto-1,3,4-thiadiazole) (0.0258 g, 0.165 mmol) was dissolved in water (3 ml) and then an

aqueous solution of  $CdCl_2 \cdot 2.5H_2O$  (0.0510 g, 0.165 mmol) in water–methanol (v:v = 1:1; 3 ml) was added whilst stirring. To this solution a mixture of  $H_2aip$  (0.0300 g, 0.165 mmol) and NaOH (0.0080 g, 0.200 mmol) in water–methanol (v:v = 1:1; 10 ml) was added and stirred for 10 min, and then filtered. The filtrate was kept at ambient temperature for several days and colorless crystals were formed. They were filtered and washed thoroughly with methanol and dried in a vacuum (41% based on  $H_2aip$ ). Anal. Calc. for  $C_{16}H_{20}CdN_2O_{12}$ : C, 27.13; H, 2.28; N, 12.66. Found: C, 26.85; H, 2.25; N, 12.10%.

#### 2.2.2. $[Zn(aip)(atz)] \cdot 3H_2O$ (**2**)

Atz (0.0140 g, 0.165 mmol) was dissolved in water (3 ml) and then an aqueous solution of  $Zn(NO_3)_2 \cdot 6H_2O$  (0.0492 g, 0.165 mmol) in water–methanol (v:v = 1:1; 3 ml) was added whilst stirring. To this solution a mixture of  $H_2aip$  (0.0300 g, 0.165 mmol) and NaOH (0.0132 g, 0.330 mmol) in water (8 ml) was added and stirred for 10 min, and then filtered. The solution was kept at ambient temperature for several days and brown crystals formed. They were filtered and washed thoroughly with methanol

Table 1  
Crystallographic data and structure refinement for the title complexes

Empirical formula	$C_{10}H_{15}N_5O_7Zn$	$C_{16}H_{20}CdN_2O_{12}$
Formula weight	382.64	544.74
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic,	monoclinic
Space group	$P2(1)/n$	$P2(1)/n$
<i>a</i> (Å)	12.0313(14)	12.7148(7)
<i>b</i> (Å)	8.2794(10)	11.3018(7)
<i>c</i> (Å)	15.5741(18)	14.6495(9)
$\alpha$ (°)	90	90
$\beta$ (°)	111.3070(10)	114.8950(10)
$\gamma$ (°)	90	90
Volume (Å <sup>3</sup> )	1445.3(3)	1909.5(2)
<i>Z</i>	4	4
Calculated density (Mg/m <sup>3</sup> )	1.758	1.895
Absorption coefficient (mm <sup>-1</sup> )	1.746	1.216
<i>F</i> (0 0 0)	784	1096
$\theta$ Range for data collection (°)	1.85–25.02	1.79–25.01
Limiting indices	$-14 \leq h \leq 14,$ $-9 \leq k \leq 8,$ $-18 \leq l \leq 18$	$-15 \leq h \leq 13,$ $-13 \leq k \leq 11,$ $-16 \leq l \leq 17$
Reflections collected/unique ( $R_{int}$ )	7604/2544 (0.0178)	10108/3366 (0.0192)
Completeness to $\theta = 25.02^\circ$	99.7%	( $\theta = 25.01^\circ$ ) 100%
Maximum and minimum transmission	1.00000 and 0.749005	1.00000 and 0.847411
Data/restraints/parameters	2544/9/209	3366/0/279
Goodness-of-fit on $F^2$	1.065	1.037
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0211,$ $wR_2 = 0.0570$	$R_1 = 0.0207,$ $wR_2 = 0.0574$
<i>R</i> indices (all data)	$R_1 = 0.0237,$ $wR_2 = 0.0580$	$R_1 = 0.0240,$ $wR_2 = 0.0592$
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.269 and –0.245	0.426 and –0.514

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