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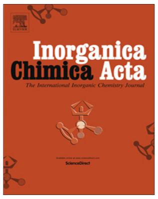

Modulated preparation and structural diversification of metal–organic frameworks based on 4,4′,4″-(1*H*-imidazole-2,4,5-triyl)tripyridine ligand

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ABSTRACT

Four metal–organic frameworks with 4,4′,4″-(1*H*-imidazole-2,4,5-triyl)tripyridine (Htpim), namely $\{[Cu_4(tpim)_4](DMAC)(H_2O)_3\}_\infty$ (**1**), $\{[Cu(H_2tpim)_2(H_2O)_2](NO_3)_4(H_2O)_2\}_\infty$ (**2**), $\{[Zn(Htpim)_2(H_2O)_2](NO_3)_2(H_2O)_5\}_\infty$ (**3**) and $\{[Zn(Htpim)(NO_3)(H_2O)](NO_3)\}_\infty$ (**4**) (DMAC = N,N-dimethylacetamide), have been prepared under solvothermal conditions. Single crystal X-ray diffraction analysis indicates that the ligand Htpim adopts ionized form in **1**, protonated form in **2**, and primary form both in **3** and **4**, respectively, with three types of binding modes including μ_2-N$_{py}$,N$_{py}$ mode in **2** and **3**, μ_3-N$_{py}$,N$_{py}$,N$_{im}$ mode in **1** and μ_3-N$_{py}$,N$_{py}$,N$_{py}$ mode in **4**. Different network structures, a 2D 3,4-connected $\{4.6^2\}_2\{4^2.6^2.8^2\}$ network of **1**, a 1D linear chain of **2** and **3**, and a 2D 6^3 framework of **4**, were observed and attributed to different synthetic conditions or metal ions. Nitric acid was used not only to adjust the pH value of reaction system, but also to act as a coordination component in **2**–**4**. Furthermore, luminescent properties have also been studied for these four complexes.

1. Introduction

The deliberate design of metal–organic crystalline materials has attracted considerable attention during the past two decades, for their interesting architectures and tailor-made applications in optics, magnetism, gas storage, ion exchange, and catalysis, etc [1,2]. As is widely known, the structural and functional information of such target materials significantly depends on used metal ions and organic ligands [1,2]. In this aspect, the design of new types of organic ligands is obviously important for constructing unusual complexes, and therefore a variety of organic building blocks containing various functional groups have been developed [1,2]. Pyridyl/imidazol-based organic ligands, with potential multi-donors of heterocyclic nitrogen [3], play an important role in the field of coordination chemistry. Very recently, increasing numbers of investigations have been focused on the coordination of such multidentate N-donor ligands with metal ions in different ways, which lead to the formation of either discrete polynuclear complexes or infinite coordination polymers [4,5], displaying intriguing luminescence properties and biological activities.

Considering all stated above, an interesting ligand 4,4′,4″-(1*H*-imidazole-2,4,5-triyl)tripyridine (Htpim) attracts our attention for achieving new coordination networks. Presumably, a variety of coordination modes may be anticipated for Htpim because of its changeable conformations and multiple interaction sites. To facilitate the generation and crystallization of complexes with Htpim, the solvothermal synthetic method is utilized [6]. Herein, four metal–organic frameworks based on Htpim, namely $\{[Cu_4(tpim)_4](DMAC)(H_2O)_3\}_\infty$ (**1**), $\{[Cu(H_2tpim)_2(H_2O)_2](NO_3)_4(H_2O)_2\}_\infty$ (**2**), $\{[Zn(Htpim)_2(H_2O)_2](NO_3)_2(H_2O)_5\}_\infty$ (**3**) and $\{[Zn(Htpim)(NO_3)(H_2O)](NO_3)\}_\infty$ (**4**) (DMAC = N,N-dimethylacetamide) were synthesized and characterized. Furthermore, the luminescent properties of the corresponding complexes have been studied.

2. Experimental

2.1. Materials and general methods

All the reagents and solvents for synthesis were commercially available and used as received or purified by standard methods prior to use. Htpim ligand was obtained commercially and used as received. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer. The IR spectra were recorded in the range of 4000–400 cm^{-1} on a Tensor 27 OPUS (Bruker) FT-IR

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spectrometer with KBr pellets. Thermogravimetric analysis (TGA) experiments were carried out on a NETZSCH STA 449F3 thermal analyzer from 40 to 850 °C under N2 at a heating rate of 10 °C/min. The solid UV–Vis spectra were measured on UV25500 UV–Vis–NIR Spectrophotometer (SHIMADZU Corp.). Emission spectra in solid state at room temperature were taken on a Cary Eclips fluorescence spectrophotometer.

*2.2. Synthesis of complexes **1–4***

*2.2.1. {[Cu$_4$(tpim)$_4$](DMAC)(H$_2$O)$_3$}$_\infty$ (**1**)*

A mixture of Htpim (32 mg) and $Cu(NO_3)_2{\cdot}6H_2O$ (50 mg) was dissolved in 2 mL DMAC and 4 mL aqueous solution in the presence of 0.10 mL 14 mol/L nitric acid. The resultant solution was sealed in a Teflon-lined stainless autoclave and heated to 160 °C. After keeping in these conditions for 3 days, red single crystals suitable for X-ray analysis were obtained after cooling to room temperature. Yield: 30% based on Htpim (13 mg). Elemental *Anal.* Calc. for $C_{76}H_{63}N_{21}O_4Cu_4$: C, 57.53; N, 18.55; H, 4.01. Found: C, 57.84; N, 18.32; H, 4.16%. IR (KBr pellet, cm^{-1}): 3378s(br), 1664m, 1609s, 1560s, 1462m, 1413s, 1364s, 1260w, 1223m, 1156w, 1113w, 1077w, 1027w, 971w, 838s, 789m, 752m, 685m, 624m, 579w, 532m, 440w, 397w.

*2.2.2. {[Cu(H$_2$tpim)$_2$(H$_2$O)$_2$](NO$_3$)$_4$(H$_2$O)$_2$}$_\infty$ (**2**)*

A mixture of Htpim (20 mg) and $Cu(NO_3)_2{\cdot}6H_2O$ (24 mg) was dissolved in 1 mL DMAC and 1 mL aqueous solution in the presence of 0.20 mL 14 mol/L nitric acid. The resultant solution was sealed in a glass autoclave and heated to 100 °C. After keeping in these conditions for 3 days, green single crystals suitable for X-ray analysis were obtained after cooling to room temperature. Yield: 50% based on Htpim (16 mg). Elemental *Anal.* Calc. for $C_{36}H_{36}N_{14}O_{16}Cu$: C, 43.94; N, 19.94; H, 3.69. Found: C, 43.61; N, 19.82; H, 3.57%. IR (KBr pellet, cm^{-1}): 3378s(br), 1689m, 1621s, 1572m, 1499m, 1389s, 1218m, 1137w, 1064m, 1027m, 991w, 966m, 844m, 752w, 709m, 623w, 543w, 513m, 471w, 422w, 397w.

*2.2.3. {[Zn(Htpim)$_2$(H$_2$O)$_2$](NO$_3$)$_2$(H$_2$O)$_5$}$_\infty$ (**3**)*

The same procedure as that for **2** was used for this complex except that $Cu(NO_3)_2{\cdot}6H_2O$ was replaced by $Zn(NO_3)_2{\cdot}6H_2O$. Light yellow single crystals suitable for X-ray analysis were obtained after cooling to room temperature. Yield: 40% based on Htpim (12 mg). Elemental *Anal.* Calc. for $C_{36}H_{40}N_{12}O_{13}Zn$: C, 47.36; N, 18.42; H, 4.42. Found: C, 47.51; N, 18.63; H, 4.25%. IR (KBr pellet, cm^{-1}): 3219s(br), 1683m, 1609s, 1566s, 1499m, 1413s, 1346m, 1283w, 1218m, 1138w, 1070w, 1015m, 960m, 838s, 758m, 691m, 654m, 617m, 544m, 513w, 455w, 415w, 397w.

*2.2.4. {[Zn(Htpim)(NO$_3$)(H$_2$O)](NO$_3$)}$_\infty$ (**4**)*

A mixture of Htpim (20 mg) and $Zn(NO_3)_2{\cdot}6H_2O$ (25 mg) was dissolved in 1 mL DMAC and 1 mL aqueous solution in the presence of 0.40 mL 14 mol/L nitric acid. The resultant solution was sealed in a glass autoclave and heated to 100 °C. After keeping in these conditions for 3 days, light yellow single crystals suitable for X-ray analysis were obtained after cooling to room temperature. Yield: 30% based on Htpim (10 mg). Elemental *Anal.* Calc. for $C_{18}H_{15}N_7O_7Zn$: C, 42.77; N, 19.41; H, 2.99. Found: C, 42.95; N, 19.63; H, 2.78%. IR (KBr pellet, cm^{-1}): 3108s(br), 1689m, 1621s, 1505m, 1438s, 1389s, 1303s, 1223m, 1138w, 1070m, 1040s, 966m, 838m, 752m, 697m, 617m, 524m, 476w, 415w, 397w

2.3. X-ray powder diffraction

The X-ray powder diffraction patterns (XRPD) of complexes **1–4** were recorded on a Rigaku D/Max-2500 diffractometer, operated at 40 kV and 100 mA, using a Cu-target tube and a graphite

Table 1
Crystallographic data and structure refinement parameters for **1–4**.

	1	**2**
Chemical formula	$C_{76}H_{63}N_{21}O_4Cu_4$	$C_{36}H_{36}N_{14}O_{16}Cu$
Formula weight	1588.63	984.33
Crystal system	monoclinic	monoclinic
Space group	*P*2(1)/*c*	*P*2/*c*
a (Å)	11.907(2)	14.660(3)
b (Å)	18.087(4)	9.965(2)
c (Å)	19.130(4)	14.652(3)
β (°)	106.44(3)	93.90(3)
V (Å^3)	3951.7(14)	2135.4(7)
Z	2	2
D (g cm^{-3})	1.335	1.531
μ (mm^{-1})	1.122	0.600
GOF	1.080	0.912
T (K)	293(2)	293(2)
R^a/wR^b [$I > 2\sigma(I)$]	0.0661/0.1902	0.0597/0.1614
	3	**4**
Chemical formula	$C_{36}H_{40}N_{12}O_{13}Zn$	$C_{18}H_{15}N_7O_7Zn$
Formula weight	914.17	506.74
Crystal system	monoclinic	triclinic
Space group	*P*2/*n*	$P\bar{1}$
a (Å)	11.624(2)	7.5515(15)
b (Å)	10.279(2)	10.679(2)
c (Å)	18.340(4)	13.612(3)
β (°)	100.32(3)	75.76(3)
V (Å^3)	2155.8(8)	982.4(3)
Z	1.408	1.713
μ (mm^{-1})	0.645	1.311
GOF	1.052	1.069
T (K)	293(2)	293(2)
R^a/wR^b [$I > 2\sigma(I)$]	0.0478/0.1473	0.0648/0.1716

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $^b wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)^2]^{1/2}$, where F_o = observed and F_c = calculated structure factors, respectively.

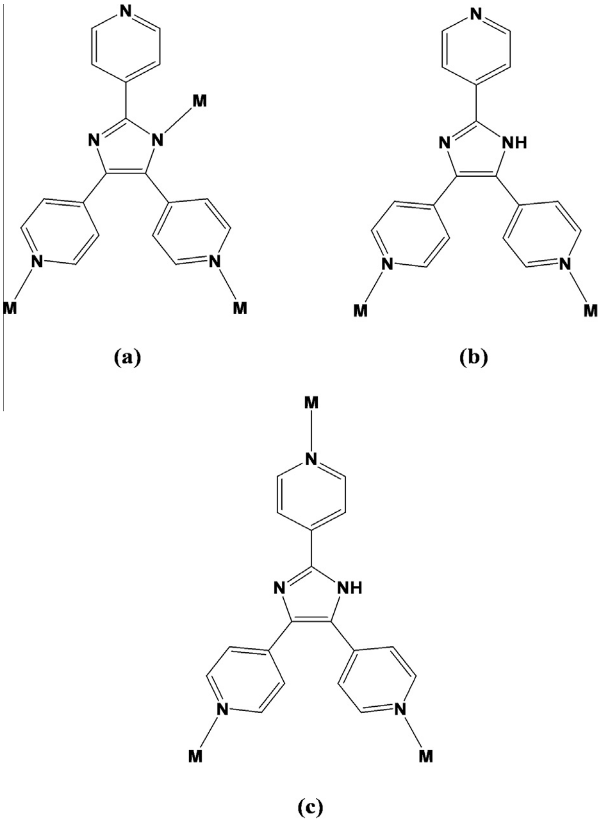

Fig. 1. Coordination modes of Htpim in **1–4**: (a) tridentate μ_3-N_{py},N_{py},N_{im}; (b) bidentate μ_2-N_{py},N_{py}; (c) tridentate μ_3-N_{py},N_{py},N_{py}.