

Syntheses and Structures of Two Zn-Pyrazole/carboxyl Coordination Frameworks^①

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ABSTRACT Two pyrazole-based zinc(II) metal-organic frameworks, $[(Zn_4(PDC)_2(BDC)(H_2O)_2)_n]$ (compound **1**, PDC = 1H-pyrazole-3,5-dicarboxylic acid, BDC = benzene-1,4,-dicarboxylic acid) and $[(Zn_3(PDC)_2(BPY)_3(H_2O)_2)_n]$ (compound **2**, BPY = 4,4-bipyridine), were synthesized and characterized by X-ray diffraction, elemental analysis, thermogravimetric analysis, infrared and fluorescence spectroscopy. Compound **1** crystallizes in space group $Pna2_1$ with $a = 14.325(3)$, $b = 10.004(2)$, $c = 16.454(3)$ Å, $V = 2357.8(8)$ Å³, $Z = 4$, $M_r = 821.83$, $D_c = 2.298$ g cm⁻³, $F(000) = 1608$, $GOOF = 1.163$, the final $R = 0.0218$ and $wR = 0.0686$ for 5150 observed reflections with $I > 2\sigma(I)$. Compound **2** crystallizes in monoclinic space group $C2/c$ with $a = 17.034(2)$, $b = 11.6313(9)$, $c = 11.7608(13)$ Å, $V = 2034.9(4)$ Å³, $Z = 2$, $M_r = 1006.91$, $D_c = 1.643$ g cm⁻³, $F(000) = 1020$, $GOOF = 1.084$, the final $R = 0.0320$ and $wR = 0.0768$ for 2435 observed reflections with $I > 2\sigma(I)$.

Keywords: pyrazole-carboxyl, X-ray crystallography, metal-organic frameworks, luminescence;

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1 INTRODUCTION

Metal-organic frameworks (MOFs) are microporous or even mesoporous crystalline materials constructed by the assembly of metal cations and organic linkers. As a new type of porous materials, MOFs have been at the cutting edge of research for the past few decades^[1]. Except for their captivating structures^[2], the enchanting properties of MOFs export diverse potential applications, including gas storage^[3], gas separation^[4], catalysis^[5], nonlinear optical devices^[6], magnetism^[7], chemical sensor^[8] and drug delivery^[9].

Pyrazole and its derivatives of heterocyclic molecules have been widely used in coordination chemistry, optical brighteners, ultraviolet stabilizers and photoinduced electron transfer systems^[10]. Among them, 1H-pyrazole-3,5-dicarboxylic acid (PDC) is a suitable ligand for constructing MOFs because of a large number of N or O coordination sites and rich coordination patterns. Complexes based on PDC with alkaline, transition and lanthanide metals have been reported^[11]. Lately, hybrid

ligands are used to build MOFs with novel structures and unique properties. Herein, we choose PDC and BDC (benzene-1,4,-dicarboxylic acid) or BPY (4,4-bipyridine) as ligands to fabricate two structures $[(Zn_4(PDC)_2(BDC)(H_2O)_2)_n]$ and $[(Zn_3(PDC)_2(BPY)_3(H_2O)_2)_n]$, which show interesting fluorescent performance.

2 EXPERIMENTAL

2.1 Materials and instruments

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses (EA) for C, H, and N were carried out on a German Elementary Vario EL III instrument. Infrared (IR) spectra (KBr pellets) were recorded on a Nicolet Magna 750 FT-IR spectrometer in the range of 500~4000 cm⁻¹. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku MiniFlex II using CuK α radiation and diffractometer at a scan speed of 5 °min⁻¹. Thermogravimetric analyses (TGA) data were investigated on

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a NETSCHZ STA-449C thermoanalyzer under N₂ (range, 0~1200 °C) at a heating rate of 10 °C min⁻¹.

2.2 Syntheses of **1** and **2**

1 (Zn-PDCBDC): A mixture of ZnSO₄·4H₂O (119 mg, 0.4 mmol), PDC (35 mg, 0.2 mmol), BDC (50 mg, 0.3 mmol) and KOH (16 mg, 0.4 mmol) was dissolved in water (10 mL), and then transferred into a 25 mL Teflon-lined stainless-steel vessel, followed by heating to 150 °C for 112 h. After cooling down to room temperature, colorless cylindrical crystals were harvested with the yield of 23% based on PDC. FT-IR (4000~450 cm⁻¹): 3385 (s), 1677 (s), 1595 (s), 1509 (m), 1425 (m), 1345 (s), 1287 (s), 1220 (w), 1136 (w), 1113 (w), 1019 (w), 940 (w), 841 (w), 782 (m), 773 (m). EA calcd. (C₁₈H₁₆N₄O₁₇Zn₄): C, 26.31; H, 1.96; N, 6.82%. Found: C, 26.33; H, 2.01; N, 6.80%. The slight discrepancy between measured and calculated EA values could be caused by the volatility of guest solvents.

2 (Zn-PDCBPY): A mixture of ZnSO₄·7H₂O (115 mg, 0.4 mmol), PDC (35 mg, 0.2 mmol), BPY (47 mg, 0.3 mmol) and NaOH (16 mg, 0.4 mmol) was dissolved in water (10 mL). Then the mixture was transferred into a 25 mL Teflon-lined stainless-steel vessel, heated to 160 °C in 3 h and kept at constant temperature for 72 h. After cooling down to room temperature, colorless cylindrical crystals were obtained with the yield of 70% based on PDC. FT-IR (4000~450 cm⁻¹): 3399 (s), 1606 (s), 1494 (w), 1455 (w), 1412 (w), 1357 (m), 1305 (m), 1224 (w), 1073 (w), 1053 (w), 835 (w), 808 (w), 777 (w). EA calcd. (C₄₀H₃₀N₁₀O₁₀Zn₃): C, 47.72; H, 3.00; N, 13.91%. Found: C, 47.76; H, 2.93; N, 13.93%. The slight discrepancy between measured and calculated EA values could be caused by the volatility of guest solvents.

2.3 Structure determination

Crystals of compounds **1** and **2** were selected and attached to a glass fiber. Single-crystal X-ray diffraction (SCXRD) data were collected on a MM007 CCD diffractometer equipped with graphite-monochromatic MoK α radiation ($\lambda = 0.71073$ Å) at 293 K. For compound **1**, a total of 17226 reflections were collected in the range of $2.38 \leq \theta \leq 27.48^\circ$ by using an ω -scan mode, of which 5150 were unique with $R_{\text{int}} = 0.0255$. The final $R = 0.0218$, $wR = 0.0686$ ($w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.0412P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.163$, $(\Delta/\sigma)_{\text{max}} = 0.001$, $(\Delta\rho)_{\text{max}} = 0.38$ and $(\Delta\rho)_{\text{min}} = -0.36 \text{ e} \cdot \text{Å}^{-3}$. For compound

2, a total of 7961 reflections were collected in the range of $2.22 \leq \theta \leq 27.48^\circ$ by using an ω -scan mode, of which 2450 were unique with $R_{\text{int}} = 0.0213$. The final $R = 0.0320$, $wR = 0.0768$ ($w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.0412P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.084$, $(\Delta/\sigma)_{\text{max}} = 0.000$, $(\Delta\rho)_{\text{max}} = 0.43$ and $(\Delta\rho)_{\text{min}} = -0.33 \text{ e} \cdot \text{Å}^{-3}$.

The structures were solved by direct methods with SHELXS and refined by full-matrix least-squares methods with SHELXL (embedded in OLEX2.0) program package^[12]. Non-hydrogen atoms were located with successive difference Fourier technique and refined anisotropically, while hydrogen atoms were added in the idealized positions. Selected bond lengths and bond angles of compounds **1** and **2** from SCXRD are listed in Tables 1 and 2.

3 RESULTS AND DISCUSSION

3.1 Crystal structure description

SCXRD studies demonstrate that compound **1** crystallizes in orthorhombic space group $Pna2_1$ and consists of BDC-pillared Zn-PDC layers (Fig. 1). The asymmetrical unit of the framework includes four Zn²⁺ ions, two water molecules, and two PDC³⁻ and one BDC²⁻ ligands. Two hexahedrally coordinated Zn²⁺ centers are ligated by a N-C-C-O moiety from a PDC³⁻ and further bonded with one carboxyl O-atom from another PDC³⁻, two carboxyl O-atoms from different BDC²⁻, and one H₂O molecule. Another two Zn²⁺ centers are in a distorted square pyramidal coordination geometry, surrounded by a N-C-C-O moiety from a PDC³⁻, two carboxyl O-atoms from another two different PDC³⁻, and one carboxyl O-atom from BDC²⁻. Four Zn²⁺ centers are linked by four μ_2 -O atoms from four different PDC³⁻ ligands to form a tetrameric ring {Zn₄O₄}, which are connected with each other by PDC³⁻ spacers to form a 2D layer. If serving the {Zn₄O₄} ring as a node, the {Zn-PDC} layer could be viewed as a (4,4) grid. Such 2D {Zn-PDC} layers are further pillared by the secondary ligand of BDC²⁻ to form a 3D structure, which adopts a 6-connected **rob** topology with its Schläfli symbol of {4[^]8;6[^]6;8}. All the Zn–O bond lengths fall in the range from 1.942(2) to 2.457(2) Å, and the lengths of Zn–N are between 1.970(3) and 2.069(3) Å.

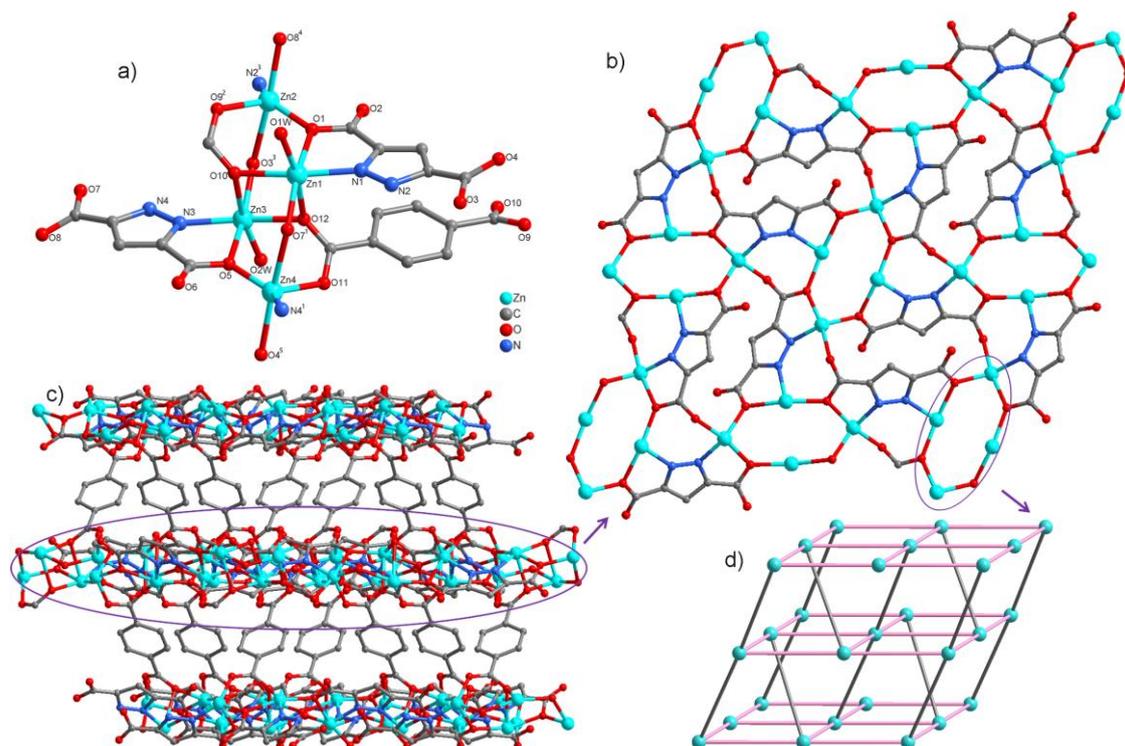


Fig. 1. a) Coordination environments of zinc atoms of compound 1, b) 2D {Zn-PDC} sheet, which is further linked by BDC to form c) 3D framework, and its d) topological net of compound 1

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) of Compound 1

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)–O(1)W	2.011(3)	Zn(1)–O(1)	2.142(2)	Zn(1)–O(7) ¹	2.047(2)
Zn(1)–O(10) ²	2.128(2)	Zn(2)–O(8) ⁴	2.111(2)	Zn(2)–O(9) ²	1.992(2)
Zn(2)–O(1)	1.942(2)	Zn(2)–O(3) ³	2.335(2)	Zn(2)–N(2) ³	1.974(3)
Angle	(°)	Angle	(°)	Angle	(°)
O(1)W–Zn(1)–O(1)	98.20(10)	O(7) ¹ –Zn(1)–O(10) ²	92.13(9)	N(1)–Zn(1)–O(10) ²	163.02(10)
O(1)W–Zn(1)–O(7) ¹	98.60(10)	O(7) ¹ –Zn(1)–O(12)	84.22(9)	N(1)–Zn(1)–O(12)	88.97(9)
O(1)W–Zn(1)–O(10) ²	88.45(11)	O(7) ¹ –Zn(1)–N(1)	100.58(9)	O(1)–Zn(2)–O(3) ³	89.63(9)
O(1)W–Zn(1)–N(1)	100.59(11)	O(10) ² –Zn(1)–O(1)	88.17(9)	O(1)–Zn(2)–O(8) ⁴	97.92(9)
O(1)–Zn(1)–O(12)	79.24(9)	O(10) ² –Zn(1)–O(12)	81.10(9)	O(1)–Zn(2)–O(9) ²	104.94(10)
O(7) ¹ –Zn(1)–O(1)	163.20(9)	N(1)–Zn(1)–O(1)	76.40(9)	O(1)–Zn(2)–N(2) ³	136.44(11)

Symmetry transformation: ¹: 1/2 + x, 1/2 – y, z; ²: 1/2 – x, –1/2 + y, –1/2 + z; ³: –1/2 + x, 3/2 – y, z; ⁴: x, 1 + y, z;

Based on SCXRD analysis, compound **2** crystallizes in the monoclinic space group $C2/c$. As shown in Fig. 2, **2** contains two crystallographically independent Zn^{2+} ions, of which one is equatorially ligated by two N-C-C-O moieties from two PDC^{3-} and axially bonded with two pyridine groups of BPY, and the other is coordinated by two carboxyl O-atoms from two different PDC^{3-} , one N-atom of PDC^{3-} , one H_2O molecule and two pyridyl groups from BPY. Ligands of PDC are fully-deprotonated during the self-assembly process. Two

six-coordinated Zn^{2+} centers are linked by two μ_2 -O atoms from two different PDC^{3-} ligands to form dimers which are connected with each other by PDC^{3-} spacers to form a 1D wave-like chain. Such chains are further linked by the neutral ligand of BPY to form a 2D structure packed in an ABAB fashion. All the Zn–O bond lengths fall in the range of 2.045(2)–2.201(19) Å, and the lengths of Zn–N are between 2.038(2) and 2.260(2) Å.

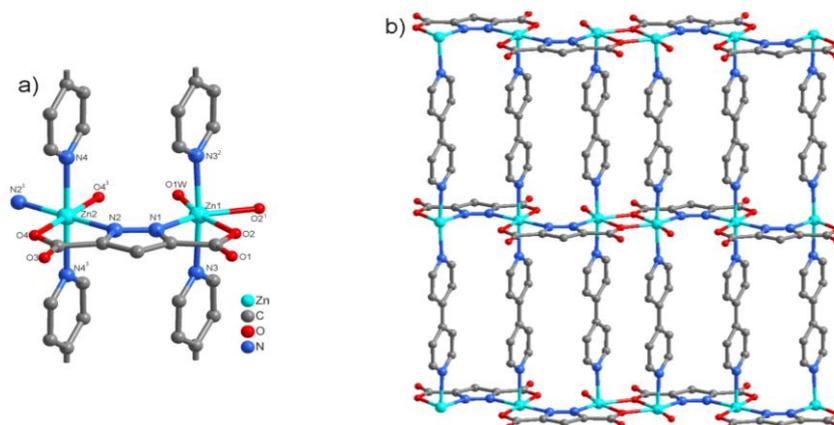


Fig. 2. a) Coordination environments of zinc atoms of compound 2, b) 2D layer built of 1D {Zn-PDC} chains and BPY pillars

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) of Compound 2

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)–O(1)W	2.045(2)	Zn(1)–N(3) ²	2.2572(19)	Zn(2)–N(2)	2.080(2)
Zn(1)–O(2) ¹	2.0477(19)	Zn(1)–N(3)	2.2572(19)	Zn(2)–N(2) ³	2.080(2)
Zn(1)–O(2)	2.2017(19)	Zn(2)–O(4) ³	2.1404(19)	Zn(2)–N(4) ³	2.260(2)
Zn(1)–N(1)	2.038(2)	Zn(2)–O(4)	2.1404(19)	Zn(2)–N(4)	2.260(2)
Angle	(°)	Angle	(°)	Angle	(°)
O(1)W–Zn(1)–O(2)	166.35(8)	O(2) ² –Zn(1)–O(2)	74.53(8)	N(1)–Zn(1)–O(1)W	118.30(9)
O(1)W–Zn(1)–N(3)	87.80(5)	O(2)–Zn(1)–N(3)	92.50(5)	N(1)–Zn(1)–O(2)	75.35(8)
O(1)W–Zn(1)–N(3) ¹	87.80(4)	O(2)–Zn(1)–N(3) ¹	92.50(5)	N(1)–Zn(1)–O(2) ²	149.88(8)
O(2) ² –Zn(1)–O(1)W	91.82(8)	O(2) ² –Zn(1)–N(3)	91.58(5)	N(1)–Zn(1)–N(3) ¹	89.72(4)
N(3) ¹ –Zn(1)–N(3)	174.66(9)	O(2) ² –Zn(1)–N(3) ¹	91.58(4)	N(1)–Zn(1)–N(3)	89.72(4)

Symmetry transformation: ¹: $x, 1-y, z$; ²: $1-x, 1-y, 2-z$; ³: $1-x, 1-y, 1-z$;

3.2 PXRD, TGA and IR

The phase purity of the crystalline products was determined by PXRD, which shows that the experimental PXRD patterns are nearly the same as the simulated ones from SCXRD data (Fig. 3), implying that compounds **1** and **2** are both pure. The TGA curves of **1** and **2** are quite similar, which show weight loss below 125 °C under N₂ atmosphere, suggesting that the

low-boiling water molecules could be evacuated at this temperature (Fig. 4). No obvious weight loss between 125 and 280 °C was observed, indicating the samples of **1** and **2** are fairly thermally stable. The two IR spectra are similar near the 1650 and 1350 cm⁻¹, which confirms the expectation that -COOH and C-N exist on the IR spectrum in this frequency range (Fig. 5).

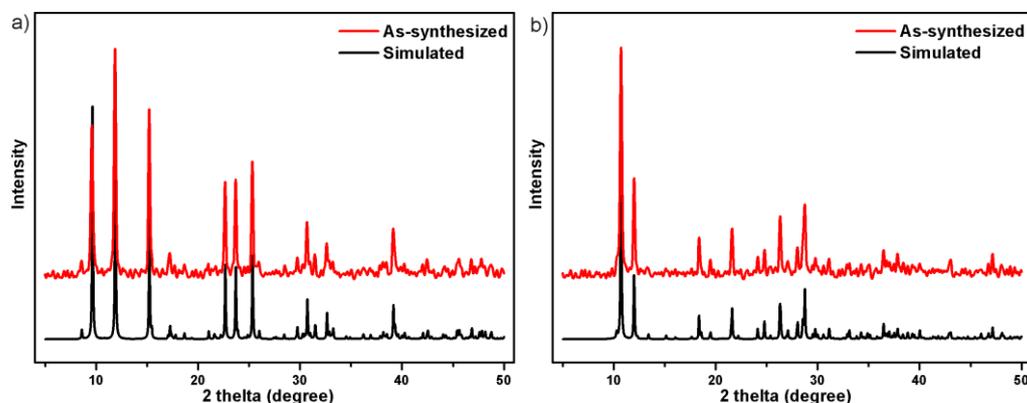


Fig. 3. PXRD patterns of compounds a) 1 and b) 2

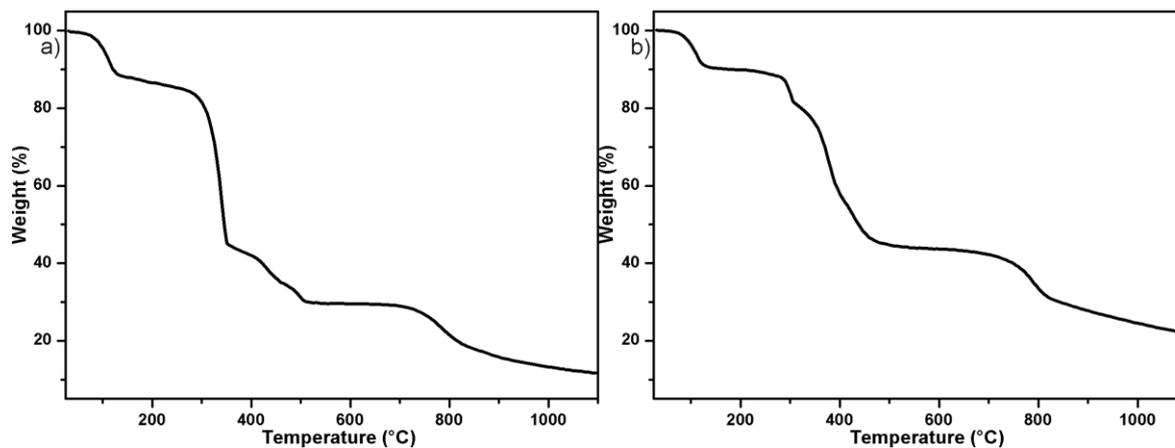


Fig. 4. TGA curves of compounds a) 1 and b) 2

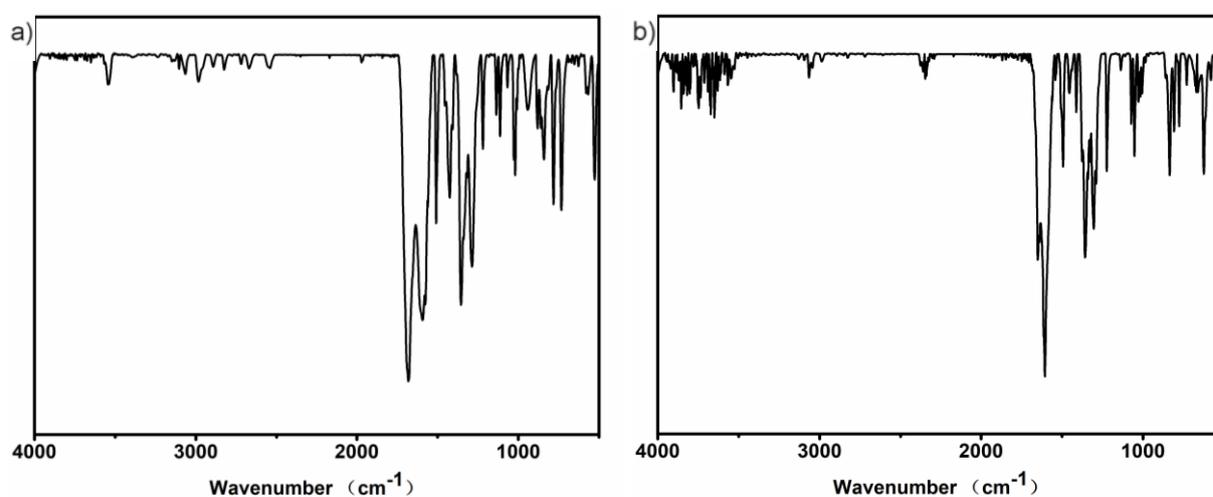


Fig. 5. IR spectra of compounds a) 1 and b) 2

3.3 Fluorescence studies

The fluorescence spectra of compounds **1** and **2** give the typical broad peaks mainly due to the π - π^* transition of the heterocyclic ligands of PDC (Fig. 6). According to the just published work^[13], the emission single peak of **1** at 414 nm is attributed to the ligand PDC. Differently, compound **2** displays bimodal excitation and emission features, which could be on account of the existence of double heterocyclic ligands (PDC

and BPY). The emission peak at 396 nm of **2** could be assigned to the ligand PDC (inset of Fig. 6). Because the pyridine of BPY has better charge transfer ability than the carboxyl group of BDC, compound **2** has another two emission peaks at 455 and 480 nm under excitation of 346 nm. Such fluorescence behavior is mainly caused by the synergistic effect of different ligands, which is of great significance for the study of fluorescent mixed-ligand MOFs.

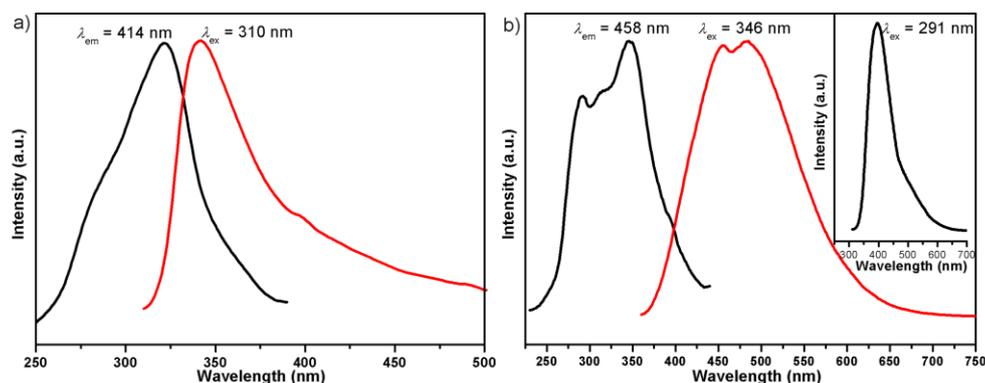


Fig. 6. Fluorescence excitation and emission spectra of compounds a) 1 and b) 2

4 CONCLUSION

In conclusion, two zinc MOFs of $[(Zn_4(PDC)_2(BDC)(H_2O)_2)_n]$ (**1**) and $[Zn_3(PDC)_2(BPY)_3(H_2O)_2]_n$ (**2**), prepared under hydrothermal conditions, were constructed by Zn^{2+} , pyrazole/carboxyl merged ligand of PDC, and a secondary

linker (BDC and BPY for **1** and **2**, respectively). The structures of compounds **1** and **2** were fully analyzed. Among them, compound **1** is a 3D 6-connected **rob**-type framework, while **2** is just a 2D structure. However, due to the different charge transfer capacity of the secondary ligands, two compounds showed significant differences in their fluorescence spectra.

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