Inorg. Chem. **2005**, *44*, 9279–9282

Inorganic Chemistry Article

Synthesis, Structure, and Luminescent Property of a Heterometallic Metal–Organic Framework Constructed from Rod-Shaped Secondary Building Blocks

Jianghua He, Jihong Yu,* Yuetao Zhang, Qinhe Pan, and Ruren Xu*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, China

Received July 11, 2005

A new heterometallic MOF compound, $[ZnNa(m\text{-}BDC)_2]\cdot NH_2(CH_3)_2$ (MOF-CJ2), has been solvothermally synthesized and characterized by single-crystal X-ray diffraction, X-ray powder diffraction, ICP, TGA, IR, and photoluminescence spectroscopy analyses. It crystallizes in monoclinic space group $C2/c$ (No. 15) with $a = 13.277(6)$ Å, $b = 14.323(7)$ Å, $c = 11.328(6)$ Å, and $\beta = 111.73(2)°$. Its framework is constructed from M–O–C (M = Na and Zn) rods composed of alternating six-coordinated Na(I) centers and four-coordinated Zn(II) centers. These rods are linked by *m*-BDC links to form primitive cubic (**pcu**) type rod packing. This framework exemplifies the first open-framework heterometallic MOF structure based on the assembly of infinite rod building units.

Introduction

The design and synthesis of porous metal−organic frameworks (MOFs) is currently an active research area because of their intriguing structural architectures as well as potential applications in catalysis, gas adsorption, and separation.[1] A versatile strategy for construction of porous MOFs is to assemble well-defined and rigid molecular building blocks into predetermined structures by decoration and expansion of the basic net topologies.[2] So far, many examples of MOFs have been reported.[3] The structures of the large majority of MOFs can be described as being constructed from discrete SBUs, including tetrahedral, square, triangular, octahedral, pentagonal bipyramidal, and trigonal prismatic building blocks.[4] More recently, we have successfully synthesized the first MOF structure with decorated body-centered cubic net topology constructed from cubic building units.[5] However, three-dimensional periodic MOF structures based on the assembly of infinite rod-shaped building units remain largely unexplored.[6,7] Rod-shaped metal−carboxylate SBUs may provide means for constructing the noninterpenetrating MOFs because of their intrinsic packing arrangement in the crystal structure.

Heterometallic coordination polymers have diverse, fascinating structures and potentially interesting physicochemical properties, such as catalytic, conductive, and magnetic ordering, that result from interactions between two distinct metal centers connected by a suitable linker.[8,9] However, to date, the synthesis of MOFs has been mainly focused on open-framework monometallic metal−organic frameworks,[1,3,4,6,7] whereas the chemistry, as well as the synthetic strategy toward open-framework heterometallic metal−

---

* To whom correspondence should be addressed. Email: jihong@mail.jlu.edu.cn.

(1) (a) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keefe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (b) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276−288. (c) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466−1496. (d) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334−2375.

(2) (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546−1554. (b) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705−714. (c) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217−225.

(3) (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276−279. (b) Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148−1150. (c) Sun, J.; Weng, L.; Zhou, Y.; Chen, J.; Chen, Z.; Liu, Z.; Zhao, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4471−4473. (d) Barea, E.; Navarro, J. A. R.; Salas, J. M.; Masciocchi, N.; Galli, S.; Sironi, A. *J. Am. Chem. Soc.* **2004**, *126*, 3014−3015. (e) Serre, C.; Millange, F.; Surblé, S.; Férey, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 6286−6289. (f) Xie, L.; Liu, S.; Gao, B.; Zhang, C.; Sun, C.; Li, D.; Su, Z.; *Chem. Commun.* **2005**, 2402−2404. (g) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040−2042.

(4) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176−182.

(5) He, J.; Yu, J.; Zhang, Y.; Pan, Q.; Xu, R. Submitted.

(6) (a) Rosi, N. L.; Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2002**, *39*, 284−287. (b) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504−1518.

(7) (a) Serre, C.; Millange, F.; Thouvenot, C.; Noguès, M.; Marsolier, G.; Loër, D.; Férey, G. *J. Am. Chem. Soc.* **2002**, *124*, 13519−13526. (b) Barthelet, K.; Marrot, J.; Férey, G.; Riou, D. *Chem. Commun.* **2004**, 520−521.

10.1021/ic051143v CCC: $30.25

organic framework, has received much less attention.[10,11] To the best of our knowledge, there is no open-framework heterometallic MOF structure constructed from rod-shaped building blocks reported. Here, we report the synthesis and characterization of a novel three-dimensional (3D) heterometallic metal−organic framework [ZnNa(*m*-BDC)$_2$]·NH$_2$(CH$_3$)$_2$ (*m*-BDC = 1,3-benzene-dicarboxylate), designated MOF-CJ2, whose framework is constructed from infinite M−O−C (M = Na and Zn) rod building units.

Experimental Section

Synthesis of MOF-CJ2. MOF-CJ2 was synthesized from the solvothermal reaction of Zn(NO$_3$)$_2$·6H$_2$O, *m*-H$_2$BDC, NaOH, and N,N′-dimethylformamide (DMF) with a molar ratio of 1.0:1.0:2.0:210. Typically, 0.084 g of *m*-H$_2$BDC was first dissolved into 8 mL of DMF with stirring, followed by addition of 0.040 g of NaOH. Next, 0.145 g of Zn(NO$_3$)$_2$·6H$_2$O was added to the above reaction mixture. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave, and heated at 170 °C for 2 days under static conditions. The final product, which consisted of colorless rod-shaped single crystals, was washed thoroughly with DMF, and dried at room temperature. The yield was 52% on the basis of Zn. The dimethylammonium cations in the product are believed to be a result of the decomposition of the DMF solvent under solvothermal conditions. This phenomenon has been commonly observed in the literature.[3f,12] When the reaction was carried out in different solvents, such as ethanol, tetrahydrofuran, and ethylene glycol, no MOF-CJ2 product was obtained. This fact implies the important role of the DMF decomposition in the formation of the product. When we chose dimethylamine (33 wt %) as the template and ethanol as the solvent, we could also obtain MOF-CJ2. This demonstrates that dimethylamine plays a templating role in the crystallization of this material.

Characterization. X-ray powder diffraction (XRPD) data were collected in the 2θ range of 4−40° on a Siemens D5005 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The step size used was 0.01°, and step time was 12 s. Inductively coupled plasma (ICP) analyses were carried out on a Perkin-Elmer Optima 3300Dv spectrometer. Elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer. The infrared (IR) spectrum was recorded (400−4000 cm^{-1} region) on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 thermogravimetric analyzer in the air with a heating rate of 10 °C/min. Fluorescence spectra were obtained with an LS55 fluorescence/phosphorescence spectrophotometer at room temperature.

Table 1. Crystal Data and Structure Refinement for MOF-CJ2

empirical formula	$C_{18}H_{16}NNaO_8Zn$
fw	462.68
T (K)	293(2)
λ (Å)	0.71073
cryst syst	monoclinic
space group	*C*2/*c*
a (Å)	13.277(6)
b (Å)	14.323(7)
c (Å)	11.328(6)
β (deg)	111.73(2)
V (Å^3)	2001.4(17)
Z	4
ρ calcd (g cm^{-3})	1.536
μ (mm^{-1})	1.294
F(000)	944
cryst size (mm^3)	0.32 × 0.29 × 0.25
θ range (deg)	3.30−27.48
limiting indices	$-16 \le h \le 17$, $-18 \le k \le 18$, $-14 \le l \le 14$
no. reflns collected/no. unique	9673/2286 [R(int) = 0.0360]
completeness to θ = 27.48°	99.5%
refinement method	full-matrix least-squares on F^2
data/restraints/params	2286/0/138
GOF on F^2	1.071
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0427$, $wR_2 = 0.1083$[a]
R (all data)	$R_1 = 0.0466$, $wR_2 = 0.1111$[a]
largest diff. peak and hole (e Å^{-3})	0.878 and −0.613

[a] $R_1 = \sum[\Delta F/\sum(F_o)]$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)]\}/\sum[w(F_o^2)^2]^{1/2}$, $w = (1/\sigma^2)F_o^2$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for MOF-CJ2[a]

Na(1)−O(4)#2	2.381(3)	Zn(1)−O(2)#1	1.982(2)
Na(1)−O(4)#1	2.381(3)	Zn(1)−O(2)	1.982(2)
Na(1)−O(1)#3	2.418(3)	Zn(1)−O(3)	2.038(3)
Na(1)−O(1)	2.418(3)	Zn(1)−O(3)#1	2.038(3)
Na(1)−O(2)#3	2.429(2)		
Na(1)−O(2)	2.429(2)		

O(2)1−Zn(1)−O(2)	108.38(14)	O(4)2−Na(1)−O(4)#1	180.000(1)
O(2)1−Zn(1)−O(3)	130.36(16)	O(4)2−Na(1)−O(1)#3	88.71(16)
O(2)−Zn(1)−O(3)	99.46(14)	O(4)1−Na(1)−O(1)#3	91.29(16)
O(2)1−Zn(1)−O(3)#1	99.46(14)	O(4)2−Na(1)−O(1)	91.29(16)
O(2)−Zn(1)−O(3)#1	130.36(16)	O(4)1−Na(1)−O(1)	88.71(16)
O(3)−Zn(1)−O(3)#1	92.1(2)	O(1)3−Na(1)−O(1)	180.0
O(2)#1−Zn(1)−Na(1)#1	47.58(6)	O(4)#2−Na(1)−O(2)#3	73.84(11)
O(2)−Zn(1)−Na(1)#1	94.96(7)	O(4)#1−Na(1)−O(2)#3	106.16(11)
O(3)−Zn(1)−Na(1)#1	90.72(14)	O(1)#3−Na(1)−O(2)#3	98.19(9)
O(3)#1−Zn(1)−Na(1)#1	133.24(15)	O(1)−Na(1)−O(2)#3	81.81(9)
O(2)#1−Zn(1)−Na(1)	94.96(7)	O(4)#2−Na(1)−O(2)	106.16(11)
O(2)−Zn(1)−Na(1)	47.58(6)	O(4)#1−Na(1)−O(2)	73.84(11)
O(3)−Zn(1)−Na(1)	133.24(15)	O(1)#3−Na(1)−O(2)	81.81(9)
O(3)#1−Zn(1)−Na(1)	90.72(14)	O(1)−Na(1)−O(2)	98.19(9)
Na(1)#1−Zn(1)−Na(1)	119.65(4)	O(2)#3−Na(1)−O(2)	180.0

[a] Symmetry transformations used to generate equivalent atoms: #1 −x, y, −z + 3/2; #2 x, −y, z + 1/2; #3 −x, −y, −z + 2.

Structure Determination. A suitable single crystal with dimensions of 0.32 × 0.29 × 0.25 mm^3 was selected for single-crystal XRD analysis. The intensity data were collected on a Rigaku R-AXIS RAPID IP diffractometer [λ(Mo Kα) = 0.71073 Å]. Cell refinement and data reduction were accomplished by the RAPID AUTO program. The structures were solved by direct methods, and refined on F^2 by full-matrix least-squares using the *SHELXTL97* software package.[13] All non-hydrogen atoms were easily found from the difference Fourier map. Hydrogen atoms associated with *m*-BDC molecules were placed geometrically, and refined in a riding model. H atoms on the disordered protonated dimethylamine (HDMA$^+$) cations were not added. All non-hydrogen atoms were refined anisotropically. Crystal data and details of the data collection are given in Table 1. The selected bond distances and angles of MOF-CJ2 are presented in Table 2.

Results and Discussion

The simulated and experimental X-ray powder diffraction (XRPD) patterns of MOF-CJ2 are shown in Figure 1. They

---

(8) (a) Ren, Y.; Long, L.; Mao, B.; Yuan, Y.; Huang, R.; Zheng, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 532−535. (b) Ma, B.; Gao, S.; Su, G.; Xu, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 434−437.

(9) Dong, Y.; Smith, M. D.; Loye, H.-C. *Angew. Chem., Int. Ed.* **2000**, *39*, 4271−4273.

(10) (a) Shorrock, C. J.; Jong, H.; Batchelor, R. J.; Leznoff, D. B. *Inorg. Chem.* **2003**, *42*, 3917−3924. (b) Li, D.; Zheng, L.; Wang, X.; Huang, J.; Gao, S.; Tang, W. *Chem. Mater.* **2003**, *15*, 2094−2098. (c) Colacio, E.; Domínguez-Vera, J. M.; Lloret, J. F.; Moreno Sánchez, J. M.; Kivekäs, R.; Rodríguez, A.; Sillanpää, R. *Inorg. Chem.* **2003**, *42*, 4209−4214. (d) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2005**, *44*, 3156−3161.

(11) (a) Pan, L.; Finkel, B. S.; Huang, X.; Li, J. *Chem. Commun.* **2001**, 105−106. (b) Chen, J.; Liu, S.; Gao, E. *Polyhedron* **2004**, *23*, 1877−1888.

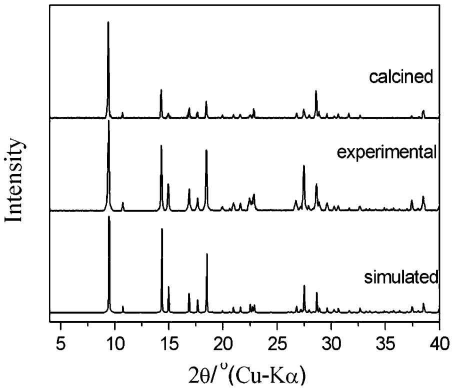


Figure 1. XRPD patterns of the simulated, experimental, and calcined MOF-CJ2.

are in good agreement with each other, which proves the phase purity of the as-synthesized product.

ICP analysis gives the contents of Zn and Na as 13.86 and 4.53 wt %, respectively (calcd: Zn, 14.13; Na, 4.97 wt %). Elemental analysis gives the contents of C, H, and N as 46.24, 3.21, and 2.59 wt %, respectively (calcd: C, 46.72; H, 3.49; N, 3.03 wt %). The compositional analysis results are in agreement with the empirical formula, $[\mathrm{ZnNa}(m\text{-BDC})_2]\cdot\mathrm{NH_2(CH_3)_2}$, given by single-crystal structure analysis.

The IR spectrum of MOF-CJ2 shows the characteristic bands of the organic ligand *m*-BDC at 1629−1564 cm^{-1} for the asymmetric vibration and at 1481−1355 cm^{-1} for the symmetric vibration. The absence of the characteristic bands attributed to the protonated carboxylic groups at around 1700 cm^{-1} indicates the complete deprotonation of the *m*-BDC ligand.[14] The broad band at ca. 3450 cm^{-1} is attributed to the vibrations of the N−H absorption vibration for DMA molecules.[12a]

The TG curve in Figure 2 shows two stages of weight loss occurring at ca. 330−425 and 550−600 °C. The weight loss, 74.52 wt % in total, is attributed to the loss of dimethylamine cations and the decomposition of the BDC ligands (calcd: 75.71%). The XRPD analysis reveals that the heterometallic MOF-CJ2 has a relatively high thermal stability compared to that of those isolated molecular complexes containing sodium cations. MOF-CJ2 maintains its crystallinity up to 250 °C (Figure 1c). However, it collapses above 300 °C with the loss of dimethylamine cations, and finally transforms to $\mathrm{Na_2Zn_2O_3}$ (JCPDS: 85-0235).

Single-crystal structure analysis reveals that MOF-CJ2 is a new 3D heterometallic MOF with the formula $[\mathrm{ZnNa}(m\text{-BDC})_2]\cdot\mathrm{NH_2(CH_3)_2}$. The coordination modes of the *m*-BDC ligand are illustrated in Scheme 1. The sodium atom is six-coordinated to six different carboxyl groups (two in mode A, two in mode B, and two in mode C) and exhibits an

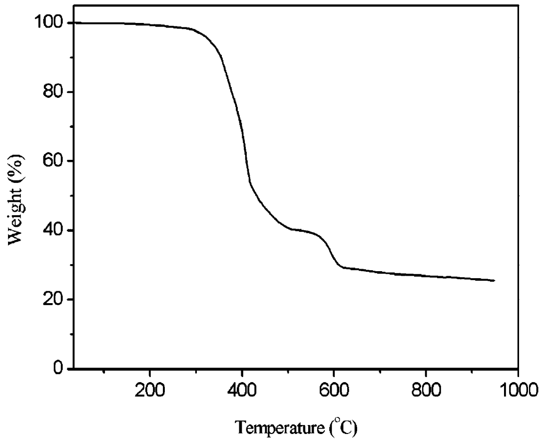


Figure 2. TG curve of MOF-CJ2.

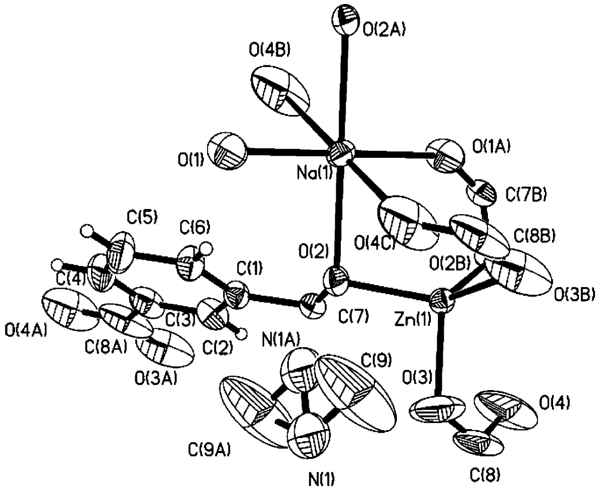
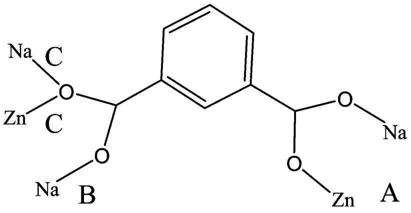


Figure 3. Thermal ellipsoid plot (50%) showing the asymmetric unit of MOF-CJ2.

Scheme 1. Coordination Modes of *m*-BDC in MOF-CJ2



octahedral geometry. The Zn atom is four-coordinated to four different carboxyl groups (two in mode A and two in mode C) and exhibits a tetrahedral geometry (Figure 3). Each Zn atom is corner-shared with two adjacent Na atoms through two carboxyl groups in mode C. This connectivity pattern leads to infinite M−O−C (M = Zn and Na) rods running along the [001] direction (Figure 4a,b). Each rod is linked to four neighboring rods by the benzene rings of the BDC units, resulting in a primitive cubic (**pcu**) type rod packing. To date, reports on heterometallic framework complexes containing $\mathrm{Zn^+}$ and $\mathrm{Na^+}$ ions are rare. Notable examples are a 3D framework formed by the hexagonal (**hex**) type packing arrangement of Zn−Na rods and a pillared 3D framework constructed by Zn−Na layers.[15] MOF-CJ2 represents the first open-framework heterometallic MOF structure formed by the **pcu** packing arrangement of infinite Zn−Na rods. The

---

(12) (a) Chen, W.; Wang, J.; Chen, C.; Yue, Q.; Yuan, H.; Chen, J.; Wang, S. *Inorg. Chem.* **2003**, *42*, 944−946. (b) Burrows, A. D.; Cassar, K.; Friend, R. M. W.; Mahon, M. F.; Rigby, S. P.; Warren, J. E. *CrystEngComm* **2005**, *7*, 548−550.

(13) (a) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; Göttingen University: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; Göttingen University: Göttingen, Germany, 1997.

(14) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986.

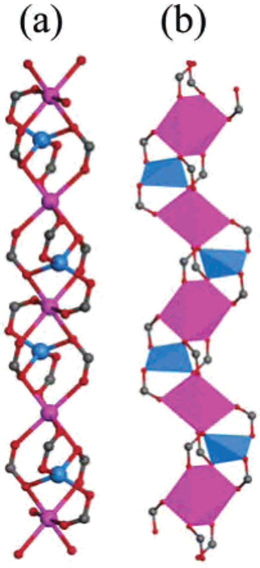


Figure 4. Infinite rod-shaped building blocks used to assemble MOF-CJ2: (a) ball-and-stick representation of SBU; (b) SBU shown as polyhedra (Zn, blue; Na, pink; O, red; C, gray).

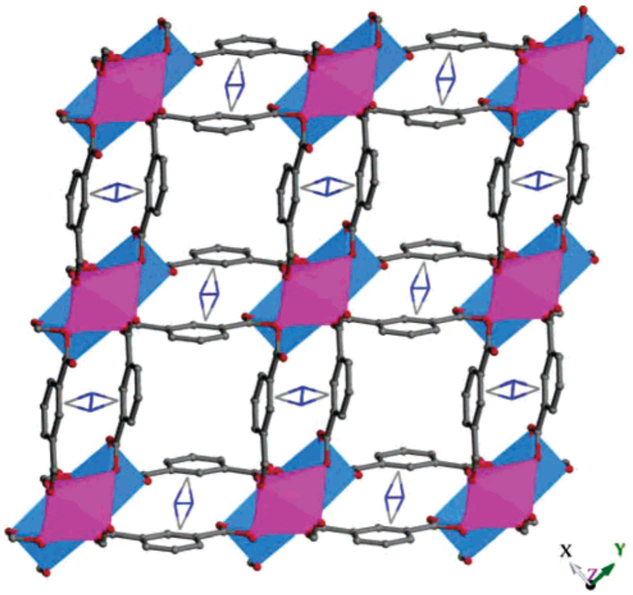


Figure 5. Framework of MOF-CJ2 with dimethylamine templating cations occupying the pores, viewed along the [001] direction (Zn, blue; Na, pink; O, red; C, gray). Hydrogen atoms have been omitted for clarity.

structure of MOF-CJ2 has channels of 3.1 × 3.1 Å^2 dimensions with void space running along the [001] direction (Figure 5), and channels of 3.1 × 5.7 Å^2 dimensions occupied by disordered protonated dimethylamine cations along the [110] direction. There exist N−H···O hydrogen bonds between the protonated dimethylamine cations and the oxygen atoms of carboxylate groups. The observed distances from the N atom to two carboxylate oxygen atoms are 3.041(5) and 3.118(5) Å.

The solid-state excitation−emission spectrum of the free *m*-BDC ligand shows the strongest emission peak at 380 nm with the excitation peak at 340 nm at room temperature. The emission band of the free ligand is attributed to the $\pi^* \rightarrow n$ transitions. Compared to the free ligands, the strongest excitation peak for MOF-CJ2 is at 318 nm, with an energy higher than that of the BDC ligand. The emission spectrum of MOF-CJ2 shows one strong peak at 421 nm (Figure 6), which can be assigned to the ligand-to-metal charge-transfer (LMCT) band.[16] The strong fluorescent emission of MOF-CJ2 may make it a potentially useful photoactive material.

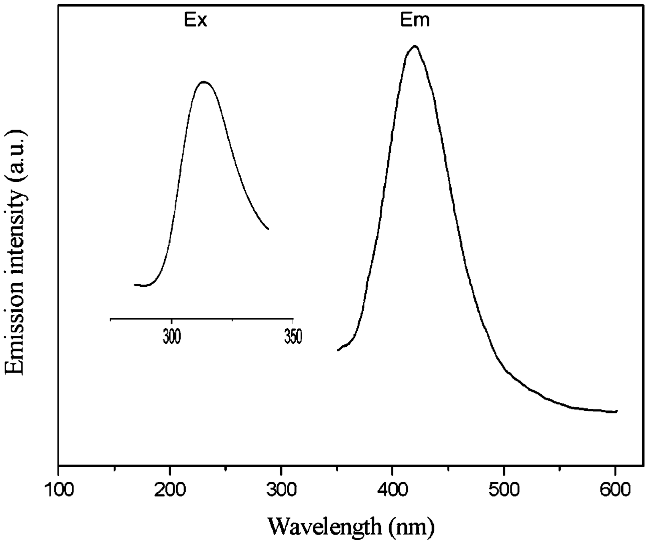


Figure 6. Photoluminescent spectrum of MOF-CJ2 in the solid state at room temperature. Ex = excitation, Em = emission.

Conclusions

A new heterometallic metal−organic framework has been synthesized from the solvothermal reaction of zinc nitrate hexahydrate, sodium hydroxide, and 1,3-benzene-dicarboxylic (*m*-BDC) acid. Its framework is constructed of infinite heterometallic M−O−C rods composed of alternating NaO_6 octahedra and ZnO_4 tetrahedra. The rods are linked together along the [001] direction by BDC connectors to give rod packing of **pcu** type. This framework exemplifies the first open-framework heterometallic MOF structure based on the assembly of infinite rod-shaped building blocks. Solvothermal reactions involving different transition metals and a wide variety of bridging ligands are currently under investigation with the aim of obtaining new heterometallic MOFs exhibiting interesting structures and properties.

Acknowledgment. This work is supported by the National Natural Science Foundation and the State Basic Research Project of China (G2000077507).

Supporting Information Available: Crystallographic data (CIF), atomic coordinates with isotropic temperature factors, and selected bond lengths and angles for MOF-CJ2. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051143V

---

(15) (a) Xu, H.; Wang, R.; Li, Y. *J. Mol. Struct.* **2004**, *688*, 1−3. (b) Wang, L.; Shi, Z.; Li, G.; Fan, Y.; Fu, W.; Feng, S. *Solid State Sci.* **2004**, *6*, 85−90.

(16) (a) Yersin, H., Vogler, A., Eds. *Photochemistry and Photophysics of Coordination Compounds*; Springer: Berlin, 1987. (b) Valeur, B. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH: Weinheim, Germany, 2002. (c) Dai, J.; Wu, X.; Fu, Z.; Hu, S.; Du, W.; Cui, C.; Wu, L.; Zhang, H.; Sun, R. *Chem. Commun.* **2002**, 12−13. (d) Tao, J.; Tong, M.; Shi, J.; Chen, X.; Ng, S. *Chem. Commun.* **2000**, 2043−2044.