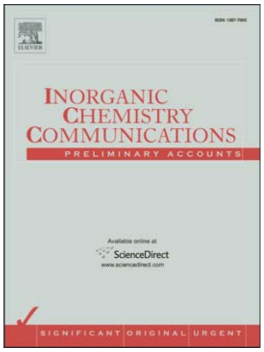

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A novel adenine-based zinc(II) metal-organic framework featuring the Lewis basic sites for heterogeneous catalysis

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Abstract

Metal-organic frameworks (MOFs), as a new sort of crystalline materials, have attracted lots of interest in many applications during the past decades. Recently, many efforts have been focused on the development of MOFs as heterogeneous catalysis. In this communication, we selected adenine (ad) and tetracarboxylic acid, namely 5,5’-(1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7-diyl)bis-1,3-benzenedicarboxylic acid (H_4L), as organic linkers to assemble with Zn(II) ions to construct a novel adenine-based porous MOF. There are three different inorganic clusters in the framework, including ZnO_2N_2, $Zn_2O_2N_6$, and ZnO_5N clusters. Interesting, the resultant porous MOF, namely $[H_2N(CH_3)_2]\bullet[Zn_4(L)_{1.5}(ad)_3(H_2O)_2]\bullet4DMF$, retains free amino groups in the framework, which can be served as Lewis basic sites to catalyse Knoevenagel condensation reaction. The catalytic study exhibits that the as-synthesized MOF with free amino groups can be used as heterogeneous catalysis with remarkable catalytic efforts and good recycle.

Keywords**:** metal-organic framework; adenine; amino group; catalysis; Knoevenagel reaction.

Metal-organic frameworks (MOFs),[1-3] as a burgeoning sort of crystalline materials, have attracted lots of interest in the past decades, not only due to their diverse structures, but also because of their widely potential applications, including magnetism,[4-6] gas sorption,[7-10] drug delivery,[11-15] chemical sensor,[16-20] optical device,[21-24] and heterogeneous catalysis[25-28] *etc*. To date, lots of structures have been successfully prepared through different ligands, metal ions, and synthetic conditions. From the previous investigations, most of organic ligands in MOFs are multicarboxylic acids. Nevertheless, more and more scientists pay attention to the aromatic N-heterocycles, such as adenine, imidazole, triazole, and tetrazolate, because they are able to generate lots of interesting structures and unique properties.[29-34] Particularly, adenine can be mixed with multicarboxylic acid ligands to prepare many available materials, such as bio-MOFs in Rosi’s group.[35-40]

However, only two previous researches have been reported to obtain adenine-based porous MOFs by mixing adenine and tetracarboxylic acid ligands.[39, 40] Therefore, it remains a significant challenge to develop and synthesize such adenine-based MOFs.

Inspired by the investigations on MOFs with basic functional groups, they always can be applied as catalysts for the basic catalytic reactions, such as Knoevenagel condensation reaction. Recently, some MOFs have been reported to catalyse Knoevenagel condensation reaction.[41-48] Adenine, as an aromatic N-heterocycles, not only has lots of nitrogen atoms to coordinate with metal ions, but also contains amino groups as Lewis basic sites. As we know, no previous investigations have been reported to explore adenine-based MOFs to catalyse the Knoevenagel condensation reaction. Evidently, it is a quite interesting and big challenge to form new adenine-based MOFs as basic catalysts for this reaction.

Herein, we selected a tetracarboxylic acid ligand as an organic ligand, namely 5,5’-(1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7-diyl)bis-1,3-benzenedicarboxylic acid (H_4L).[49] H_4L and adenine (ad) are both successfully connected with Zn(II) ions to obtain a novel adenine-based porous MOF, namely $[H_2N(CH_3)_2]\bullet[Zn_4(L)_{1.5}(ad)_3(H_2O)_2)]\bullet4DMF$ (denoted as JUC-188, DMF = *N*, *N*-dimethylformamide). As we expect, the resultant MOF retains free amino groups ($-NH_2$) as Lewis basic sites in the framework, which can be used as heterogeneous catalysis to catalyse Knoevenagel condensation reaction. In addition, there are three different inorganic clusters in JUC-188, including ZnO_2N_2, $Zn_2O_2N_6$, and ZnO_5N clusters. The yellow crystals of JUC-188 were successfully obtained *via* heating these organic ligands and $Zn(NO_3)_2\bullet6H_2O$ in a mixture of DMF and H_2O at 135 °C after 3 days.[50]

From the single-crystal X-ray diffraction analysis,[51] it exhibits that JUC-188 crystallizes in the triclinic space group *P*-1 and the asymmetric unit contains four Zn(II) ions, one and a half L^{4-} organic ligands, three adenine ligands and two terminal coordinated water molecules (Fig. S1). There are three different Zn(II) clusters in the structure. Zn1 is coordinated with three nitrogen atoms from three adenine ligands (Zn1-N = 1.980-2.031 Å), and one oxygen atom from a carboxylic acid group (Zn1-O = 1.943 Å). In addition, Zn2 has the same coordination environment with Zn1. Zn1 and Zn2 are further linked by adenine linkers to form a binuclear $Zn_2O_2N_6$ cluster (Fig. 1a). Meanwhile, Zn3 exhibits a distorted octahedral ZnO_5N geometry with five oxygen atoms (Zn3-O = 1.990-2.278 Å) from two carboxylic acids and two coordinated water molecules, and one nitrogen atom from an adenine molecule (Zn3-N = 2.059 Å) (Fig. 1b). As shown in Fig. 1c, the other Zn4 is bound with two oxygen atoms from two carboxylates (Zn4-O = 1.982-2.006 Å) and two nitrogen atoms from two different adenine molecules (Zn4-N = 2.030-2.037 Å). On the other hand, the L^{4-} ligand is linked with four different Zn(II) ions (Fig. 1d) and the adenine ligand is coordinated with three different Zn(II) ions (Fig. 1e). Therefore, the different Zn(II) clusters can be further linked with the bridging ligands to construct a three-dimensional (3D) porous coordination framework with widow sizes about 7.5 × 9 Å (Fig. 1f and Fig. 1g). The guest molecules can be determined from the TGA and elemental analyses (C, H and N). Interesting, the resultant porous MOF retains free amino groups as Lewis basic sites in the framework for heterogeneous catalysis (Fig. 1g).

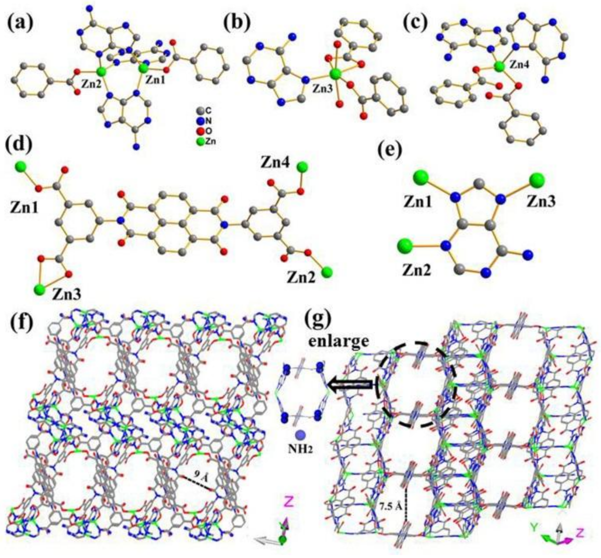


Fig. 1. (a, b, and c) The coordination environments of these Zn(II) ions; the coordination mode of

L^{4-} ligands (d) and adenine ligands (e); (f and g) viewing the 3D porous framework in different directions. (The hydrogen atoms are omitted for clarity, and C, gray; N, blue; O, red; Zn, green)

Powder X-ray diffraction (PXRD) pattern of JUC-188 was measured at room temperature. The characteristic peaks of the as-synthesized sample are closely matched well with those in the simulated patterns from the single crystal structure (Fig. 2a). The results confirmed the phase purity of the as-synthesized bulk crystalline materials. From the thermogravimetric analyses (TGA) results, the as-synthesized JUC-188 showed a gradual weight loss before 200 °C about 19.78%, corresponding to the loss of one $[H_2N(CH_3)_2]$ cation, two coordinated water and four DMF guest molecules (calculated 19.44%) (Fig. 2b). The main framework of JUC-188 began to collapse with the increasing of heating temperature. The as-synthesized samples were exchanged with MeOH about three days, and activated at room temperature to obtain the activated samples. However, the activated samples didn't have any N_2 adsorption, which was mainly ascribed to the collapse of the skeletal structure after removing the solvent molecules (Fig. S2). In addition, the PXRD pattern further indicated that the main framework of the activated samples was collapsed (Fig. S3). As shown in Fig. S4, the characteristic peaks of adenine and H_4L ligands were both found in the FT-IR spectrum of JUC-188, which undoubtedly exhibited that both organic ligands coexisted in JUC-188.

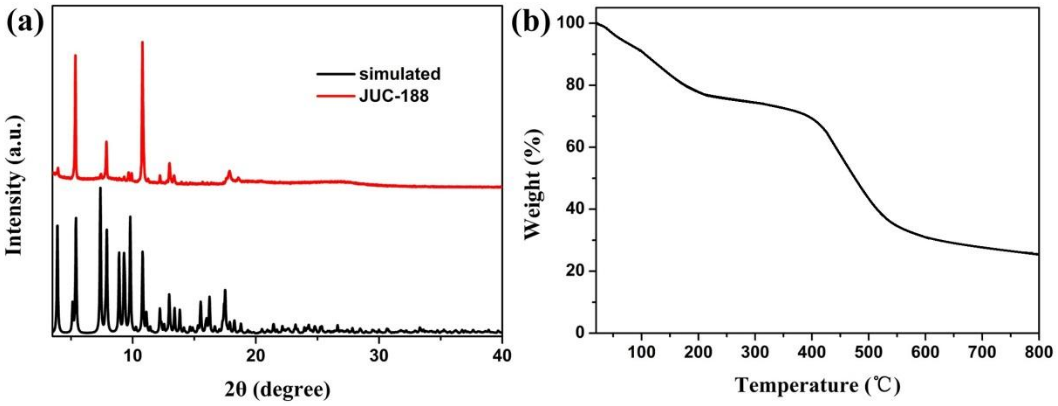
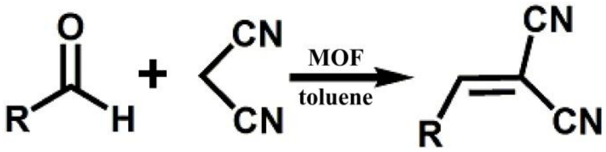


Fig. 2. (a) The simulated (black) and as-synthesized (red) PXRD patterns of JUC-188; (b) the TGA curve of as-synthesized JUC-188.

Furthermore, we have been systematically studied the catalytic properties of JUC-188 for the basic catalytic Knoevenagel condensation (Table 1), which is mainly ascribed to the free amino groups in JUC-188. Before the catalytic reaction, JUC-188 was soaked in toluene for one day to exchange the guest molecules. In a typical experiment, a mixture of substrate (0.1 mmol), malononitrile (0.11 mmol), and toluene (2.5 mL) with 10 mg of the catalyst (JUC-188) was putted into a 10 ml glass reactor, which was stirred at 80 °C. The corresponding products can be monitored by GC-MS. As shown in Table 1, it summarizes the results of Knoevenagel condensation of malononitrile with different substrates in the presence of JUC-188 as a solid catalyst. The results demonstrated that JUC-188 can effectively catalyse small aldehydes as substrates into their corresponding products (Table 1, entries 1-5). When 1-naphthyl or anthryl groups were introduced into the phenyl ring and prolonged the reaction time, the yields of the corresponding products were just about 43% (entry 6) and 21% (entry 7) under the similar reaction condition. Hence, the catalytic efficiency depends on the molecule interactions between the substrate and the catalytic sites. The low yields of large-sized substitute molecules may be mainly ascribed to the restricted diffusion of large molecules into the framework of JUC-188. The results clearly demonstrate that JUC-188 can serve as an efficient basic catalyst for the Knoevenagel condensation reaction with a size selective property. Compared with the other reported MOFs,[41-48] JUC-188 exhibits both high catalytic performance and size selective property. Furthermore, it also shows that adenine ligands can be applied to construct MOFs with the Lewis basic sites (-NH_2) as heterogeneous catalysis.

Table 1. Knoevenagel condensation of malononitrile with different substrates in the presence of JUC-188 as a solid catalyst.



Entry	R	Time (h)	Yield (%)

1	*Ph*	3	97
2	*4-MePh*	3	95
3	*4-NO_2Ph*	2.5	97
4	*4-FPh*	2.5	98
5	*4-OMePh*	2.5	97
6	*1-naphthyl*	6	43
7	*anthryl*	6	21

Meanwhile, it did not have any detectable leaching of Zn^{2+} ions in the reaction solution after removal of the catalyst by inductively coupled plasma (ICP) analysis. The results can confirm the essence of the heterogeneous catalysis of JUC-188. In addition, the recovered catalyst could be reused after filtration from the catalytic reaction, and washed several times with fresh toluene. As shown in Fig. 3a, the recovered catalyst can be reused at least four cycles almost without any loss of activity. In addition, the main framework of JUC-188 can be successfully reserved after the catalytic reactions, which can be confirmed by PXRD patterns (Fig. 3b).

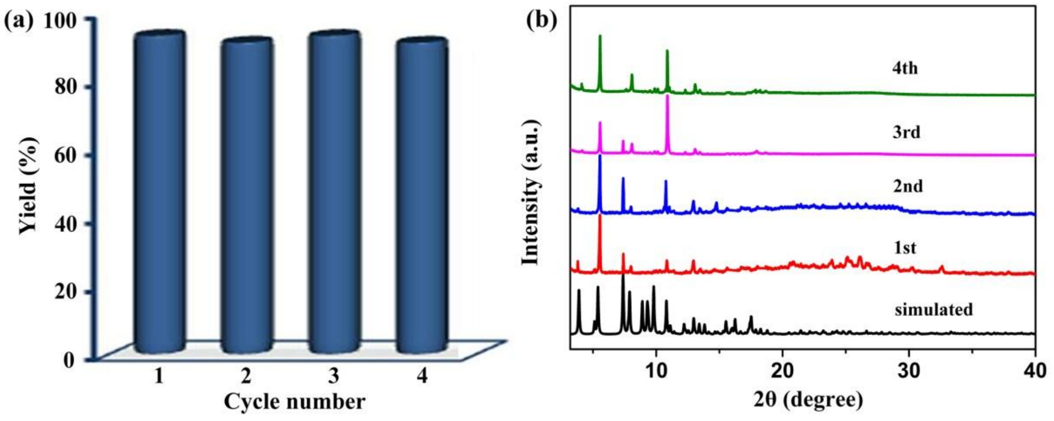


Fig. 3. The reproducibility (a) and the corresponding PXRD patterns (b) of JUC-188.

In summary, we successfully synthesized a novel adenine-based porous zinc(II) MOF featuring the Lewis basic sites (-NH_2) as heterogeneous catalysis for the basic catalytic Knoevenagel condensation reaction. Herein, we anticipate that it is able to provide a promising approach to obtain such adenine-based MOFs as basic catalysts.

Acknowledgments

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Appendix A. Supplementary data

The asymmetric unit, XRD, N_2 sorption and FT-IR spectra are listed in the supporting information. The CCDC reference numbers 1501692.

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[50] Preparation of $[H_2N(CH_3)_2]\cdot[Zn_4(L)_{1.5}(ad)_3(H_2O)_2]\cdot 4DMF$: A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (30 mg, 0.1 mmol), H_4L (15 mg, 0.025 mmol), adenine (8 mg, 0.06 mmol) was added in a mixture solution of DMF (4 mL) and H_2O (0.5 mL). Then 0.1 mL HNO_3 was added in the mixture. The obtain mixture was sealed into

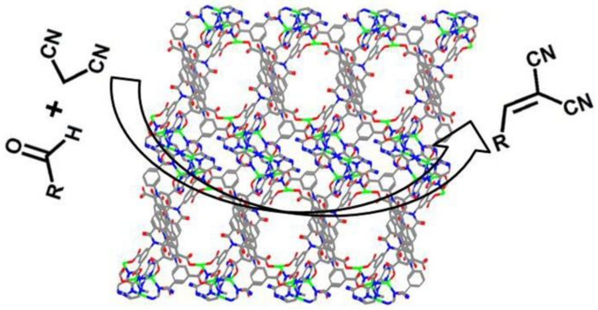
a 20 ml Teflon-lined autoclave and heated at 135 °C for three days. The as-synthesized samples can be obtained after filtration at room temperature. Finally, the yellow block-shaped crystals were washed with fresh DMF and dried in air. Yield: 52.9% (based on the H_4L). Element analysis (%) Calc. for C_{74} H_{67} O_{24} N_{23} Zn_4 (1921.9): C, 46.20; H, 3.49; N, 16.75. Found: C, 46.57; H, 3.44; N, 16.41. Selected FT-IR data (KBr pellet cm^{-1}): 3365 (br), 1714 (s), 1656 (s), 1572 (s), 1449 (s), 1344 (s), 1248 (s), 1157 (s), 1099 (s), 985 (s), 780 (s), 767 (s), 744 (s), 726 (s), 652 (s), 562 (s), 420 (s).

[51] Crystal data: C_{74} H_{67} O_{24} N_{23} Zn_4: F_w= 1921.9, Triclinic, space group *P*-1, a = 12.1467(4), b = 18.1091(7), c = 24.1338(9) Å, α = 107.541(2), β = 98.670(2), γ = 91.332(2), V = 4990.6(3) $Å^3$, Z = 2, Dc = 1.053 g cm^{-3}, μ = 1.594 mm^{-1}, R(int) = 0.0967, Nref = 17002, R_1 = 0.0500, wR_2 = 0.1148 [$I > 2\sigma(I)$], R_1 = 0.0763, wR_2 = 0.1232 [all data], GOF= 0.925. The crystal data of JUC-188 was collected on a Bruker SMART CCD diffractometer with Cu Kα (λ = 1.54178 Å) radiation at 100(2) K. The crystal structure was solved by direct methods, which can be further refined by the full-matrix least-squares on F^2 of the crystal data using the Shelxtl-97 program package.[52] All non-hydrogen atoms were also refined through anisotropic displacement parameters. However, the framework has lots of disordered solvent molecules, their corresponding peaks were successfully removed by using the PLATON/SQUEEZE.[53] In addition, the selected bond lengths and angles of JUC-188 are both listed in Table S1.

[52] G. M. Sheldrick, SHELXTL 97, Program for Crystal Structure Solution, Univ. of Göttingen, Göttingen (Germany) (1997).

[53] A. L. Spek, Single-crystal structure validation with the program PLATON, J. Appl. Cryst. 36 (2003) 7-13.

Graphical Abstract-Pictogram



A novel adenine-based zinc(II) MOF has been formed by mixing ligands, which can be used as base catalyst for the Knoevenagel condensation reaction.

Highlights

1. A novel adenine-based MOF has been obtained by mixing ligands.
2. The resultant MOF retains free amino groups in the framework,
3. It can be used as heterogeneous catalysis for the Knoevenagel condensation reaction.