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# A layered amino-functionalized zinc-terephthalate metal organic framework: Structure, characterization and catalytic performance for Knoevenagel condensation

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A new stable mixed-ligand metal organic framework $Zn_2(tpt)_2(2\text{-}atp)I_2$ **1** (tpt = tris (4-pyridyl) triazine, 2-atp = 2-aminoterephthalate) with split channels has been synthesized and characterized. The nitrogen containing ligands tpt and 2-atp are selected to create attractive basic sites for the catalyst. The Knoevenagel condensation between benzaldehyde and the active hydrogen compound (ethyl cyanoacetate or malononitrile) is carried out using compound **1** as solid basic catalytic support. The test results indicate that **1** is an efficient base catalyst with selective catalytic properties. It gives 37% and 99% yield respectively for the condensation products ethyl (E)-α-cyanocinnamate and 2-benzylidenemalononitrile. TG data show that the solid catalyst sample is fairly thermally stable. The compound does not show any signs of decomposition until 420 °C. PXRD data support that the catalyst remains its crystalline and framework stability after the catalysis process. These characters make it easily to be regenerated for the next cycle.

Porous zeolite materials have been widely used as commercial heterogeneous catalysts for the interconversion of hydrocarbons and the alkylation of aromatic compounds [1]. In the past decades, research interests to enrich the structural variety have shifted the exploration efforts to zeolite-like materials, such as metal phosphates [2,3] and metal organic frameworks [4–6]. Recently, the industrial requirements trigger an extensive research toward porous nitridated materials with basic properties [7–9]. By comparison with liquid bases, basic solid catalysts show high efficiency for basic catalysis reactions and they simplify the separation process for organic preparations [10]. Various strategies have been developed for the exploration of new families of basic porous materials [11]. Metal–organic frameworks (MOFs) are a class of complexes constructed by metal centers and organic linkers [12–16]. Many characteristic features make them a promising class of new heterogeneous catalysts. Structural motifs of MOF can be tailored by functionalized connection ligands and careful selection of metal ions. It is easy to decorate the channels with active sites via crystal engineering approach. The channel surfaces constructed by organic linkers provide more host–guest interactions. Organic guest reactants are included to the pores easily via π–π staking interactions or hydrogen bonds. These characters certainly benefit for the following catalytic process. The employment of different organic ligands with $NH_2$ or NH groups has gradually become a useful approach to produce the MOF solid base materials [17,18]. Size and distribution of the pores are important characters of the catalysts to determine the efficiency and selectivity of the catalytic process [19]. Numerous coordination networks with channel structures have been prepared and characterized in recent years [20–22]. The obtained data and synthesis strategy of them provide the possibility of a rational design of metal organic frameworks with new sizes, shapes, and chemical environments. In this report, a new stable metal organic framework $Zn_2(tpt)_2(2\text{-}atp)I_2$ **1** (tpt = tris (4-pyridyl) triazine, 2-atp = 2-aminoterephthalate) has been synthesized and characterized. Nitrogen containing ligands tpt and 2-atp are selected to construct the base sites of the framework. In the structure of compound **1**, a split channel is enclosed by the tpt and 2-atp ligands. There are nine free nitrogen sites that are decorated on the walls of the channel. Compound **1** is tested as solid catalytic support for the Knoevenagel condensation between benzaldehyde and the active hydrogen compound (ethyl cyanoacetate or malononitrile). The results show that it is an efficient base catalyst with an interesting size selectivity character. GC–MS data indicate that the yields of the condensation products ethyl (E)-α-cyanocinnamate and 2-benzylidenemalononitrile are 37% and 99% respectively. TG and PXRD data support that the catalyst is fairly stable. And it is easily to be regenerated for the next cycle.

Red crystals of compound **1** are obtained by a hydrothermal reaction of $ZnI_2$, tpt, 2-aminoterephthalic acid, N,N′-diethylethanamine, and water with a molar ratio of 2:1:1:2:5555 at 160 °C for 72 h [22]. X-ray single-crystal analysis reveals that the crystal structure of **1** is a 2D layer [23]. Its building unit is composed of a five-coordinated zinc center, an iodide ion, an atp ligand, and a tpt ligand. As depicted in Fig. 1a, the zinc center is in a little distorted pyramid coordination environment. It is coordinated with an iodide ion, a carboxylate group

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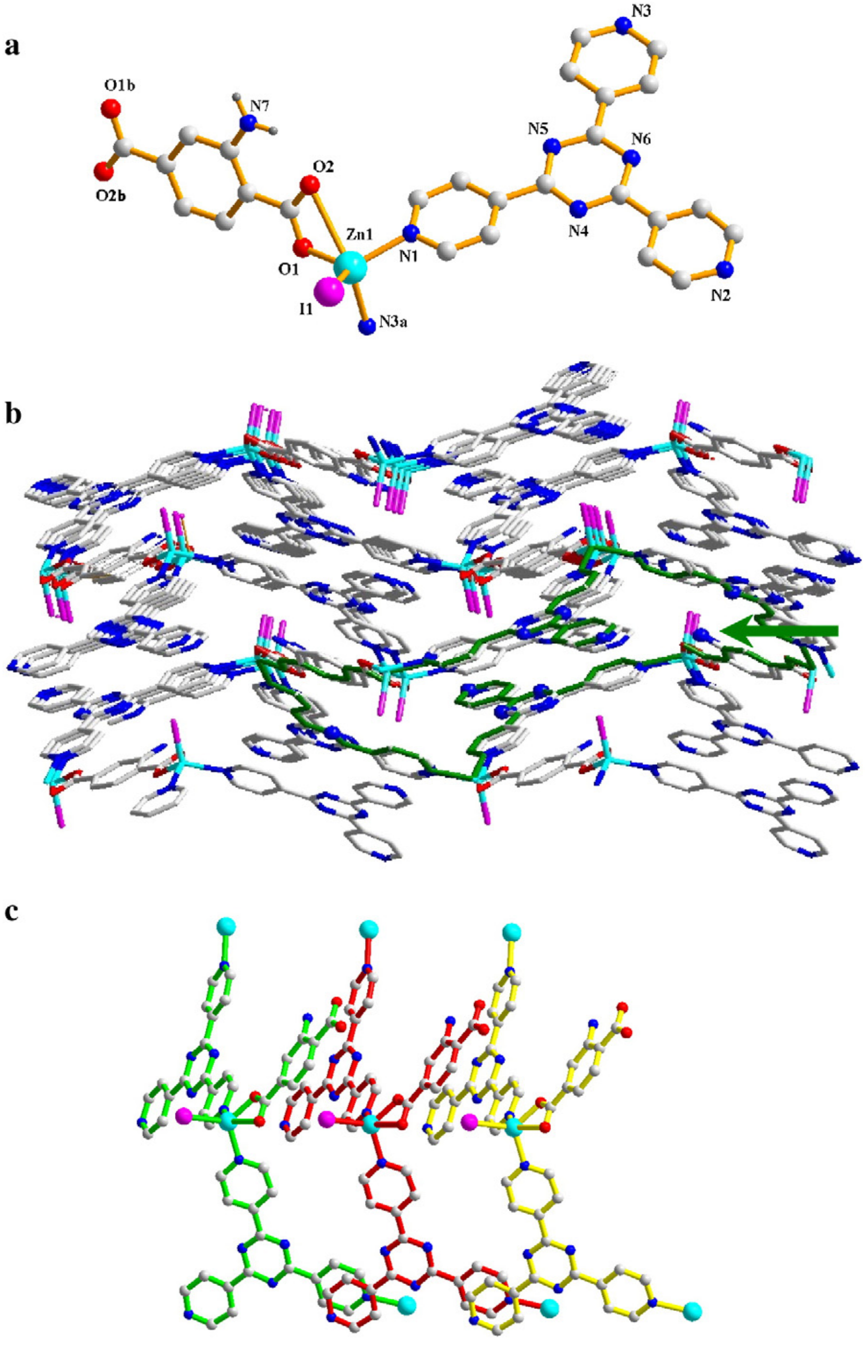
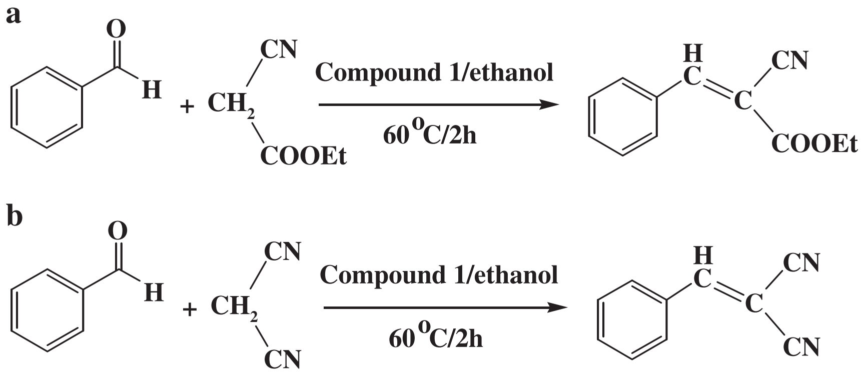


**Fig. 1.** a) The symmetric structural unit of compound **1**; b) view of the MOF layers with split channels along the *a* axis; and c) view of the stacking model of the layers along the *b* axis.



**Scheme 1.** Knoevenagel condensation of benzaldehyde and the active hydrogen compound (a: ethyl cyanoacetate; b: malononitrile) with compound **1** as solid catalytic support.

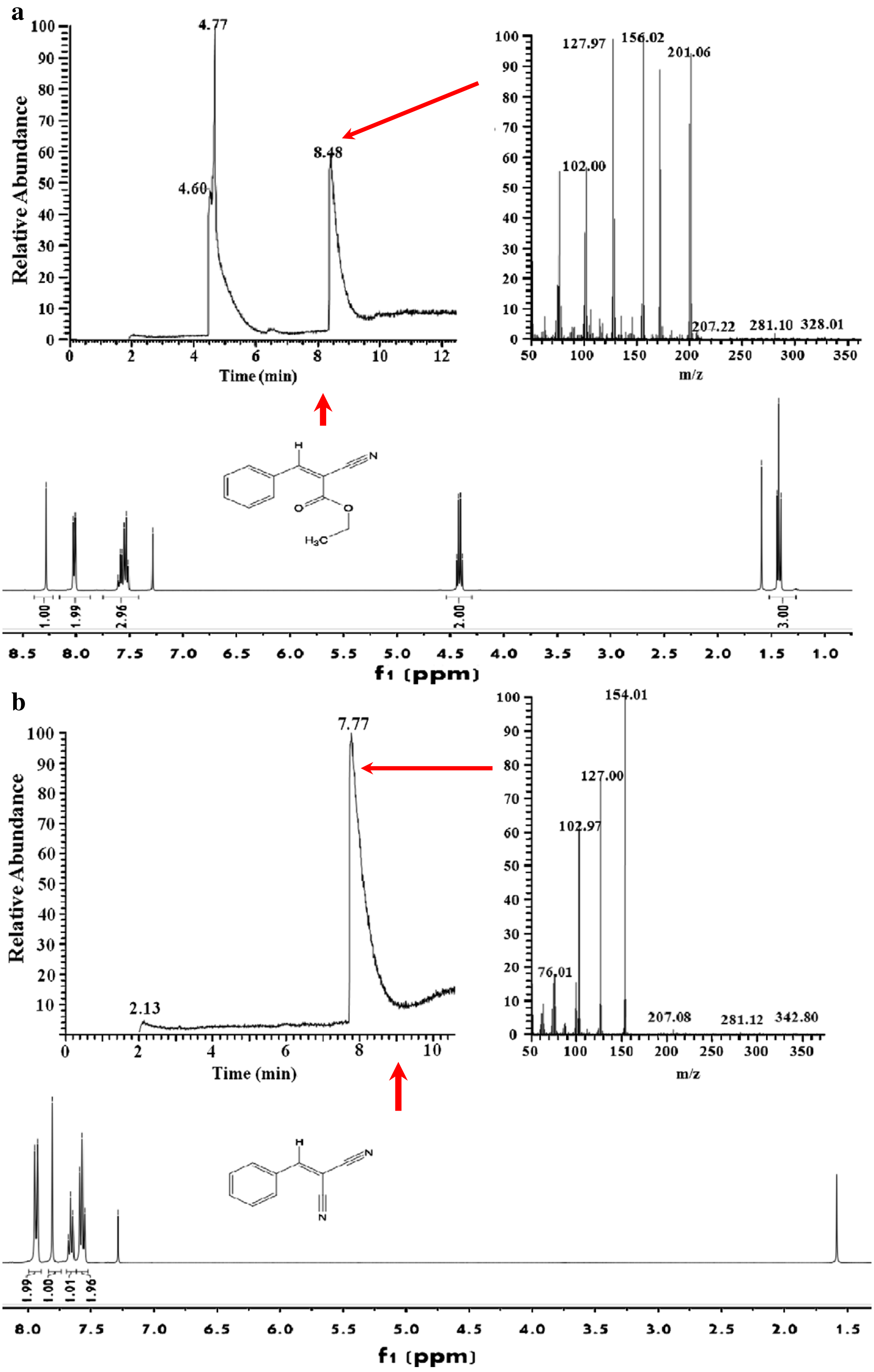


**Fig. 2.** GC–MS spectra and $^1$HNMR spectra of the condensation products: (a) ethyl (E)-α-cyanocinnamate; (b) 2-benzylidenemalononitrile.

of an atp ligand, and two nitrogen donors of a tpt ligand. The connections between the bridging ligand and the Zn ions generate a layer structural motif as reported [24] (Fig. 1b). The edges of the sheet are constructed by the linear 2-atp ligand, the two connected tpt ligands and the Zn centers. Nine uncoordinated nitrogen atoms from the bridging mixed-ligands are decorated on the wall of a spilt

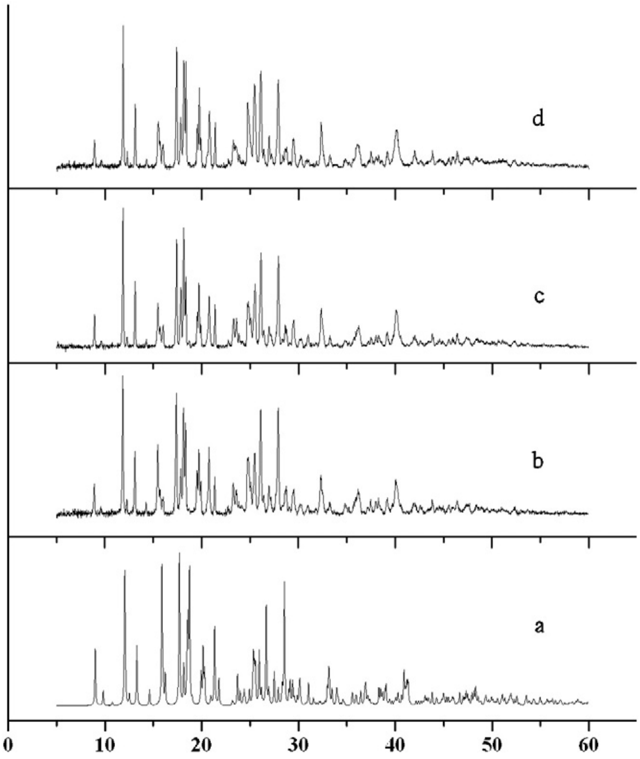


**Fig. 3.** PXRD patterns for compound **1**: (a) simulated; (b) sample before catalytic process; (c) sample after catalytic process of benzaldehyde with ethyl cyanoacetate; and (d) sample after catalytic process of benzaldehyde with malononitrile.

channel, providing the active base sites for the catalysis reaction. The iodide ion protrudes out from the layer acting as a terminal ligand. No guest molecule is included in the pores. This character prevents the structural collapse after the removal of small guest molecules. The stacks of layers along the *b* axis are interlocked to give a 3D supramolecular structural motif via π–π interactions (Fig. 1c). The π ring planes overlap in a parallel-displaced mode [25]. These weak interactions contribute to the stability of the framework of the structures.

The Knoevenagel condensation is important for the industrial syntheses of drugs. It is well known as a typical base-catalyzed model reaction [26]. The Knoevenagel condensation between benzaldehyde and the active hydrogen compound (ethyl cyanoacetate or malononitrile) is carried out to test the base catalytic ability of compound **1** (Scheme 1). In a typical experiment, 0.05 mmol of compound **1** was added to a solution of 10 mmol benzaldehyde and 10 mmol active hydrogen compound (ethyl cyanoacetate or malononitrile) in 3 ml of ethanol. The reaction mixture was then stirred vigorously at 333 K for 2 h. At the end of the reaction, the catalyst was removed by filtration. Ethanol was taken away by vacuum distillation. The amount of condensation product was determined using a gas chromatograph GC/MS Trance DSQ system (gas chromatograph coupled to a mass spectrometer; carrier gas—nitrogen; flow, 1 ml/min; oven, 80–280 °C; injector, 80 °C; detector, 280 °C). It is interesting to observe that 37% and 99% conversions are obtained for the condensation adducts ethyl (E)-α-cyanocinnamate and 2-benzylidenemalononitrile respectively (Fig. 2). The size of the reactive molecules is the reason for the different yields. Catalysis efficiency depends on the interactions between the reactant and the catalyst. The smaller molecule is easily to be accommodated into the channels and activated by the nitrogen base sites. These results support that compound **1** is an efficient base catalyst with a size selective property.

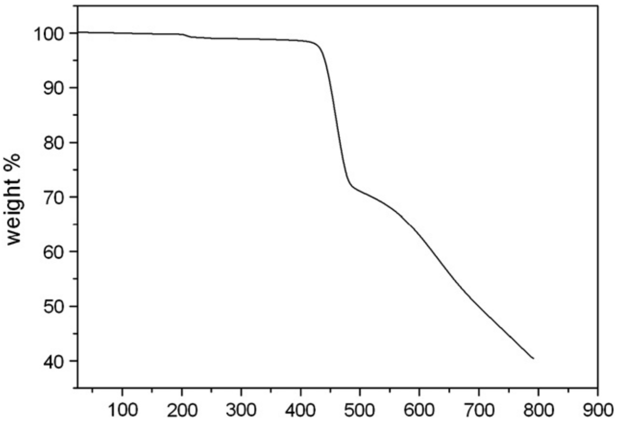


**Fig. 4.** The TGA diagram for compound **1**.

The stability of compound **1** is characterized by the X-ray powder diffraction (XRPD) data (Fig. 3) and thermo gravity analysis (TG) data (Fig. 4). Phase purity of the bulk sample is confirmed by comparison of the simulated and observed XRPD patterns. The same XRPD patterns indicate that the catalyst remains its crystalline and framework stability before and after the catalysis process. The TG data show that compound **1** begins to be decomposed at 420 °C. The stable catalyst is easily to be regenerated for the next cycle.

In conclusion, nitrogen containing ligands tpt and 2-atp are selected to construct the functional channel with base catalytic sites. The connections between the zinc centers and the mixed-ligands generate a new MOF based heterogeneous catalyst. The test of the Knoevenagel condensation was carried out with compound **1** as base catalyst. The experiment data show that it is a stable and efficient base catalyst with an interesting size selectivity character. It can be anticipated that more MOF based catalysts may be designed and prepared for basic heterogeneous catalytic process via crystal engineering approach.

## Appendix A. Supplementary materials

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.09.022.

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[22] Synthesis of **1**: a mixture of $ZnI_2$ (0.2 mmol, 64 mg), tpt (0.1 mmol, 31 mg), 2-aminoterephthalic acid (0.1 mmol, 18.1 mg), N,N′-diethylethanamine (28 μL), and $H_2O$ (10 mL) was heated at 160 °C in a Teflon-lined stainless steel autoclave for 72 h. When the autoclave was cooled to room temperature, red block crystals were obtained in about 59% yield (35 mg). Anal. Found (calcd) for $C_{44}H_{28}I_2N_{13}O_4Zn_2$ (%): C, 44.08 (44.51); H, 2.37 (2.38); N, 15.21 (15.34). IR (KBr): 3454 m, 3255 s, 3101 s, 2966 s, 2850 m, 1612 s, 1580 s, 1517 s, 1422 m, 1373 s,, 1312 m, 1252 m, 1216 m, 1057 m, 1024 m, 837 s, 800 m, 651 m, 512 m.

[23] Crystallographic data of **1** was collected on a Rigaku R-AXIS SPIDER IP diffractometer with graphite-Monochromated Mo-Kα radiation (wavelength 0.71073) at 298 K. Data were collected at 25 °C, using the ω and φ scans to a maximum θ value of 25.34°. The data were refined by full-matrix least-squares techniques on $F^2$ with SHELXTL-97. And the structure was solved by direct methods SHELXS-97. All non-hydrogen atoms were refined anisotropically. H atoms were positioned geometrically and refined using a riding model, with C−H = 0.93–0.97 Å. Crystal data for **1**: Monoclinic, $P2_1/c$, a = 9.809(2), b = 11.596(2), c = 20.754(6) Å, β = 111.44(3)°, V = 2197.3(9) $Å^3$, Z = 2, R1 = 0.0650, wR2 = 0.1450 (I>2σ(I)). CCDC reference number: 8378.

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