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Bifunctional Design of Stable Metal-Organic Framework Bearing Triazole–Carboxylate Mixed Ligand: Highly Efficient Heterogeneous Catalyst for Knoevenagel Condensation Reaction Under Mild Conditions[†]

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Abstract

A highly water stable zinc metal-organic fram work (ZnMOF), $\{[Zn(HL)_2]\}_n$, was synthesized using a triazole-carboxylate-base! mixed ligand (L= 5-(4H-1,2,4-triazol-4yl)isophthalic acid). A 2D MOF was formed by hydrothermal synthesis, and extended to a 3D supramolecular network through strong !vd* ogen bonding between two 2D sheets. This MOF was fully characterized by Fourier-transformation infrared spectroscopy, thermogravimetric analysis, single-crystal X-ray diffrac.ic. (ARD), powder XRD and elemental analysis. Owing to the d¹⁰ configuration of this ZnMOF, its luminescent properties were suitable for the sensing of the CN⁻ ions over ther anions, as inferred from the florescence result. However, regarding the catalytic mechanism, this ZnMOF showed a strong ability to react with CN⁻, which might be dne to the hydrogen bonding between the COOH groups without coordination. This interaction behavior with CN⁻ ions makes the ZnMOF a promising heterogeneous catalyst for Knoevenagel condensations using malononitrile and aldehyde derivatives as reactants under mild conditions. All reactions were conducted in water as a green solvent.

Keywords: MOF, Mixed ligand, Catalysis, Knoevenagel condensation, Luminescence Corresponding authors: renpeng@hit.edu.cn, <u>zhaolimin@gdpu.edu.cn</u>

Introduction

Metal-organic frameworks (MOFs) are a class of hybrid porous materials formed by the combination of metal ions/clusters and organic ligands/linkers.^{1,2} In the last few decades, MOFs have received research interest owing to their anticipated applications in different fields, including drug delivery,³ magnetism, catalysis,^{4,5} gas storage,⁶ separation,⁷ ion exchange,⁸ and sensing.^{9,10} MOFs can be constructed from metals and ligands through selfassembly to generate various topologies.¹¹ The ligands shapes and connectivity with the metal center play important roles in determining the dimensionality of the MOFs.¹² New developments in MOFs structure have led to the promising a covery of new materials for catalysis.¹³ Importantly, MOFs can be constructed by changing the metal or ligand to obtain the required functionality, which aids catalysis. Regarding catalytic activity, introducing functionality into the organic ligand that can interact with the incoming reactant and generate an unsaturated site at the metal center is very import. nt.¹¹ The incoming reactant can interact with the framework through weak interactions such as hydrogen bonding, $^{15} \pi - \pi$ interactions, and van der Waals forces. These weak interaction: help reactants interact with the active site, where product formation occurs.¹⁶ Fructional MOFs can be constructed using various approaches, such as using carboxylate ligands, which provide rigidity and organic pillars, to introduce functional sites through a three-component strategy.¹⁷ Mixed ligands can be designed using both pillars and certox, late ligands.

Herein, a mixed ligand has bee. synthesized by combining triazole and carboxylic groups.¹⁸ The triazole nitrogen acts a. a 3rønsted base, while the carboxylic group interacts with the reactant through hydrogen bonding. This hydrogen bonding provides extra support for catalysis. The Knoevena el condensation is the most significant for C-C bond formation reaction,¹⁹ and occurs between compounds bearing activated methylene groups, including malononitrile and carbonyl compounds such as aldehydes.²⁰ This reaction can be accelerated by Brønsted basic and Lewis acidic sites.²¹ Solid bases (such as metal oxides), amines, microwave, ionic liquids, and biotechnology-based approaches under homogeneous conditions have been applied to this reaction, which require high catalyst loadings. Furthermore, catalyst reuse in further transformations is difficult. Although there are numerous reports on this reaction, further exploration is still needed. In this study, we have constructed a 2D bifunctional zinc MOF (ZnMOF) through combination with a mixed ligand (5-(4H-1,2,4-triazol-4-yl)isophthalic acid). This MOF was constructed with the production of

both Brønsted basic and Lewis acidic functionalities in mind, allowing it to serve as an efficient heterogeneous catalyst for the Knoevenagel condensation.²² The luminescent nature of this MOF provided additional support to understanding the mechanism of this condensation reaction. The detection of CN^- ions over other anions using this MOF motivated us to perform the Knoevenagel condensation using malononitrile. This occurred through weak hydrogen bonding between the CN^- ions and free carboxylic acid groups present in the MOF, which accelerated the reaction.

Results and discussion

Herein, a new ZnMOF was prepared using a mixed triaze - carboxylate ligand (H₂L). Furthermore, this ZnMOF was employed as a sensor for CN ions and a heterogeneous catalyst for C-C bond formation. Crystals of this ZnMOI we grown using a hydrothermal reaction and used for single-crystal X-ray analysis.

Single-crystal structural analysis

Crystals of the ZnMOF suitable for single crystal analysis were grown using the hydrothermal technique and collected from the mother liquor.



Fig. 1. Coordination environment around the metal center (left) and the formation of a 2D coordination network in the ZnMOF (right).

A 2D coordination network was formed in the ZnMOF, which crystallized in the monoclinic C2/c space group. The asymmetric unit consisted of one metal center (Zn(II)) and two ligands (HL^{1–}). The geometry around the Zn(II) metal center was a distorted tetrahedron (butterfly shaped) surrounded by two nitrogen atoms of the triazole ring (Zn–N_{triazole} distances of 2.025 and 2.048 Å) and two oxygen atoms of the carboxylate group (distances of 1.948 and 1.945 Å) to form an N₂O₂ environment around the metal center (Figure 1). Interestingly,

the ligand contained two carboxylic groups, only one of which was deprotonated and bound with the metal center in a monodentate fashion, while the other remained in the carboxylic acid form and showed no binding with the metal center.

The ligand contained four binding sites, namely, two nitrogen atoms in the triazole ring and two carboxylic groups. However, only one triazole nitrogen and one carboxylic group participated in coordination bonds with the metal. In this case, the ligand acted as a bidentate ligand because only two atoms participated in coordination bond formation, while the Zn(II) metal was tetracoordinated and connected with the four other metal atoms, making it a four connected node. After combining these two nodes, a 4-c; unir odal net topology was formed (Figure S5, Supporting information). All crystallographic praneters, bond angles and distances are shown in Tables S1-S3 (Supporting information)

As discussed above, two types of carboxylic groups were present, namely, one bound with the metal (monodentate) and another that remained in the carboxylic acid form. Owing to the nature of this ligand, two different types of hydrogen bonding were observed (Table S4, Supporting information). The first type was between two carboxylic acid groups of two different ligands situated in different 2D sneets, while the second type was between the second carboxylic acid group and the oxygen of the bonded carboxylate group. Therefore, the asymmetric unit consisted of a metal with two ligands (HL⁻) in which both ligands behaved differently. The carboxylic acid group of one ligand generated a dimer with the other carboxylic acid group of another nublecule, while the other carboxylic acid did not show this type of dimeric behavior, but dal show hydrogen bonding with the bonded carboxylate group, as shown in Figure S6 Sup porting information). Owing to this hydrogen bonding, a three dimensional supramolecular network was formed from this 2D MOF. A 3D porous network was formed when packed three dimensionally (see Figure S7, Supporting information).

Luminescence properties of the ZnMOF

To study the photoluminescence properties of the ZnMOF, fluorescence spectra were recorded in suspension using a finely ground powder sample, exhibiting a strong and broad absorption with a λ_{max} of 310 nm corresponding to $\pi - \pi^*$ and $n - \pi^*$ transitions (Figure S9, Supporting information).²³ Based on the absorption data, of the **ZnMOF** emission spectra exhibited a strong emission band at 410 nm (excited at 310 nm), as shown in Figure S9, (Supporting information).



Fig. 2. (a) Change in luminescence intensity with respect to different anions and (b) bar diagram of the ZnMOF.

This emission was attributed to the strong ligand-metal interaction, because the ligand alone showed no fluorescence behavior.²⁴ The of ZnMO, emission was further studied in different solvents, including water, methanol, ethance, creconitrile, dimethylformamide, and dimethylacetamide, which were found to influe action the fluorescence intensity. The maximum ZnMOF emission intensity was observed in water, which was used as the solvent for further experiments accordingly (Figure S1C Supporting information). As water is also a green solvent, its use made this work environmentally friendly.

Detection of CN⁻ ions in water

For anion sensing, the ZnMOF (1 mg) was suspended in distilled water (2 mL) and fluorescence spectra were recorded by adding anion solution (40 mL, 5×10^{-3} M) prepared in distilled water. For anio: reasing, different anions, such as fluoride (F⁻), chloride (CI⁻), bromide (Br⁻), acetate (CH₃COO⁻), nitrate (NO₃⁻), dihydrogen phosphate (H₂PO₄⁻), hydrogen sulfate (HSO₄) and cyanide (CN⁻), were used. The results obtained illustrated that all anions enhanced the fluorescence intensity, but the maximum enhancement was observed with cyanide ions (Figure 2). This intensity enhancement might be due to the strong interaction of CN⁻ with the carboxylic acid groups. Accordingly, the transfer of energy between the metal center and ligand is increased, and enhanced fluorescence intensity is observed. As the MOF showed a good interaction with CN⁻ ions it was applied to C-C bond formation reaction.

Catalytic activity of ZnMOF for C-C bond formation reaction

The Knoevenagel condensation reaction proceeds owing to the Lewis acidic and Brønsted basic nature of the catalyst,^{25,26} and occurs between derivatives of benzaldehyde and malononitrile.²⁷ Brønsted basic site helps in activate the methylene group of malononitrile, while the Lewis acidic site enhances the reactivity of benzaldehyde. Therefore, to determine the potential of using both ZnMOF sites, the Knoevenagel condensation reaction was performed in the presence of this MOF.

To successfully perform this reaction, benzaldehyde (0.3 mmol) and malononitrile (0.33 mmol) were stirred with the catalyst (5 mol%) in solvent for 2 h. Dodecane (30 μ L, internal standard) was then added to the reaction mixture, followed by menching with water (10 mL) and extraction of the product using dichloromethane (10 mL). The organic layer was dried over anhydrous sodium sulfate and afforded the desired product. The conversion/yield and purity of the product were confirmed by GCMS analysis

Table 1. Knoevenagel reaction between benzalde.vd/ and malononitrile with ZnMOF at room temperature.

[СНО +		ZnA	1OF N	CN C
Entry	Time (h)	Solvei :	Temp. (°C)	Catalyst (mol%)	Yield ^a (%)
1	2	M. OH	25	5	66
2	2	FtOH	25	5	55
3	2	A · CM	25	5	17
4	2	CH₃CN	25	5	15
5	2	H ₂ O	25	5	100
6	0.5	H_2O	25	5	42
7	1	H_2O	25	5	66
8	2	H_2O	25	3	91
9	2	H_2O	25	1	67
10	2	H_2O	25	NA	30
11 ^b	2	H_2O	25	$Zn(ClO_4)_2$	31

^{*a*}Yield was calculated by GC using dodecane as standard, ^b5mol% catalyst was used.

The reaction conditions were optimized with respect to time and catalyst amount using the malononitrile and benzaldehyde system with the ZnMOF as catalyst (Table 1). As compared to no catalyst (30%) and Zn(ClO₄)₂ salt (31%), yield was improved significantly up to 100% with this ZnMOF (Entry 5, Table 1). From solvent screening, the maximum conversion was obtained in water (100%) compared with other common solvents, such as DCM (17%),

MeOH (66%), EtOH (55%), and acetonitrile (15%) when using the catalyst (5 mol%) at room temperature.

 Table 2. Knoevenagel reaction between benzaldehyde derivatives and malononitrile

 with ZnMOF at room temperature.



Entry	-R	Product	Yield ^{<i>a</i>} (%)
1	Н		100
2	4-F	F C N	100
3	4-NO ₂		100
4	4-OMe		70
5	4-Cl		100
6	Pent.		100
7	Hex.		50
8	4-CH ₃		58
9	Nepth.		24 74*
10	Anth.		17 13*
11	Phen.		0 20*

aYield was calculated by GC using dodecane as standard, *in MeOH.

Furthermore, different catalyst amounts 1 mol% (67%), 3 mol% (91%) were tested, but a catalyst loading of 5 mol% gave the best conversion (100%) at room temperature in water.

Other than catalyst amount, the reaction time was screened, with only 43% yield observed after 30 min, while 66% and 100% yield were achieved after 1 and 2h, respectively. Furthermore, we extended the substrate scope of the ZnMOF as heterogeneous catalyst using different aldehyde derivatives (Table 2), including both aliphatic and aromatic aldehydes. As a 2D MOF was employed for catalysis, aldehydes of different sizes behaved differently.

Larger aldehydes showed lower conversions, while smaller aldehydes gave excellent conversions under the optimized conditions in water. From the evidence, we have proposed a mechanism for the Knoevenagel condensation reaction catalyzed by the ZnMOF, as shown in Scheme 1.



Scheme 1. Proposed methanism of the Knoevenagel condensation reaction using ZnMOF as catalyst.

The florescence spectra showed that CN^- anions had a stronger interaction with the framework compared with those of other ions. Therefore, in the proposed mechanism, the cyanide group of malonitrile interacts with the deprotonated carboxylic acid group, which moves malononitrile closer to the Brønsted base (triazole nitrogen) and, removes hydrogen from the activated carbon center (methylenic group of malononitrile) as shown by intermediate A (Scheme 1). After deprotonation, the malononitrile acts as a nucleophile.

In the second step (intermediate B), the aldehyde group interacts with the Lewis acidic site present at the metal center (unsaturated metal) and becomes polarized, increasing the electrophilicity of the aldehyde. This polarization enhances nucleophilic attack by

malononitrile at the polarized carbonyl group of the aldehyde to form a C–C bond. After the C-C bond formation, dehydration occurs. The third step (intermediate C) then involves charge neutralization while, the final step (intermediate D), shows the removal of water as a side product and formation of the final product.

Conclusions

In summary, we have constructed a 2D Metal-Organic Framework (MOF) with bifunctional catalytic sites. Although this MOF is highly stable in water, all catalytic reactions were conducted in water as a green solvent. Furthermore, the use of both functionalities (Lewis acid and Brønsted base) has been demonstrated in $\mathbb{C} \cdot \mathbb{C}$ bond formation reaction. Interestingly, of the two carboxylic groups, only one is depro ona ed and binds with the metal center, while the other is not deprotonated and remains in he carboxylic acid form. This deprotonated carboxylic acid group expand the 2D \mathbb{E}^{OF} sheet to a 3D supramolecular network through strong hydrogen bonding. Owing \mathbb{C} its florescent nature, the ZnMOF was used to screen anions, with \mathbb{CN}^- ions shown to have a high affinity for interaction with the framework through hydrogen bonding with the catboxylic acid group.

Additionally, the high affinity of the CN is no for interacting with the framework allowed the Knoevenagel condensation, a C-C cond formation reaction between benzaldehyde and malononitrile, to be performed. As this reaction used both the Lewis acid and Brønsted base natures of the catalyst, the ZnMCF showed high efficiency toward this conversion. Furthermore, hydrogen bonding interactions with the cyanide group of malononitrile, which brought malononitrile close to the catalytic site, enhanced the conversion. This research is particularly relevant to the drign of 2D metal organic framework bearing bi-functional sites, which act as heterogeneous catalysts for the C-C bond formation reactions.

Acknowledgments

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[†] Electronic supplementary information (ESI) available: Details of the synthesis and characterization; experimental section; crystallographic information table; packing digram of

ZnMOF; crystallographic information files (CIF); ¹H NMR, ¹³C NMR, GC, GCMS and PL spectra. Crystallographic data: CCDC-1985716 for ZnMOF. For ESI and crystallographic data in CIF or other electronic format see DOI: xxx.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical abstract



A bi-functional MOF formed by the combination of Zn(II) and mixted triazole-carboxylate based ligands for the detection of CN^- over other ions and an efficient heterogenous catalyst for the Knovengal Condensation Reaction

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Highlights

- Design of bifunctional zinc MOF, bearing triazole-carboxylate mixed ligand
- Heterogeneous catalyst for C-C bond forming reactions such as Knoevenagel condensation
- Highly efficient catalysis under mild conditions, water as solvent at room temperature
- Selective sensing of CN⁻ ion over other anions by **ZnMOF**, using florescence technique
- Detection of CN⁻ ion supports the proposed mechanism of Knoevenagel condensation