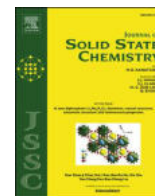




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# A 2D-layered Cd(II) MOF as an efficient heterogeneous catalyst for the Knoevenagel reaction

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## ABSTRACT

A Cd(II) coordination polymer based on a polytopic compartmental ligand was synthesized, and used as an efficient heterogeneous catalyst for the Knoevenagel reaction between benzaldehyde and malononitrile under mild reaction conditions. The solid catalyst was characterized using single crystal XRD, X-ray powder diffraction, SEM, TGA, UV diffuse reflectance, infrared spectroscopy and elemental analysis. The compound is a two-dimensional (2D) MOF with a grid structure. Topological analysis of the framework revealed that it is a 2,4-connected binodal net. The catalytic activity was tested between various benzaldehydes containing different substituents with malononitrile. The effect of reaction parameters such as solvent, time, reactant ratio and catalyst amount was investigated. Furthermore, the catalyst stability was examined through reusability experiments and it is observed that the catalyst can be recycled at least five times without significant drop in its activity.

## 1. Introduction

Porous coordination polymers or metal organic frameworks (MOFs) are built from multi-functionalized organic molecules that are bound together by inorganic units. The advantageous features of these materials has caught increasing attention in recent years and turns out to be one of the fastest growing areas in synthetic chemistry and materials science. Compared to conventionally used porous inorganic materials, these metal-organic structures exhibit the potential for more flexible rational design, by controlling the size and the functionalization of the organic linkers and nodes [1,2]. Because of their unparalleled structural diversities, highly-ordered porous structure, high specific surface area and great structural designability, they have wide range of applications in the growing fields of molecular storage, drug delivery, sensing and catalysis [3–9].

The design and synthesis of MOFs with desired properties are of immense interest in heterogeneous catalysis [10]. As is known, the architectural diversities and pore surface properties of MOFs greatly depend on reactivity and flexibility of linkers and coordination modes of metal nodes, the designing of ligands with suitable functional groups is a key strategy for the construction of MOFs with required catalytic properties. The presence of multiple catalytic sites with appropriate coordination environments for metal ions also play a significant role in

enhancing the catalytic activities [11]. Compared to ditopic linkers based MOFs the polytopic compartmental linkers-based MOFs can more functionalize as heterogeneous catalysts due to the presence of multiple catalytic centers. Double hydrazone ligands, due to their specific geometry, including the different relative orientation of N-donors and the zigzag conformation of the spacer moiety ( $-\text{CR}=\text{N}-\text{N}=\text{CR}-$ ) between the two terminal coordination groups, favors polymerization with novel network patterns not achievable by other rigid linking ligands, such as bipyridine and dicarboxylate ligands. All the known MOF linkers bind metal ion in a monodentate or bidentate coordination mode and a tetradentate spacer is never involved in metal coordination environment. The terminal nitrogens of these polytopic linkers have been shown to bind exodentate to metal nodes and the compartmental atoms lock by endodentate binding (Fig. 1).

As one of the most promising inorganic-organic hybrid materials for catalysis, MOFs function as solid catalysts or catalyst supports for several organic transformations such as Knoevenagel reaction, aldol condensation, oxidation, hydrogenation, Paal–Knorr reactions Suzuki cross-coupling, transesterification reaction, Friedel–Crafts alkylation, and epoxide ring-opening reaction [12–24]. Knoevenagel reaction is one of the most versatile reaction in organic chemistry and is widely employed for the condensation of aldehydes with active methylene compounds with numerous applications in the synthesis of useful chemicals as well as

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