

Three-dimensional cobalt(II) and cadmium(II) MOFs containing 1,4-naphthalenedicarboxylate: Catalytic activity of Cd-MOF

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ARTICLE INFO

Article history:

Received 10 November 2015

Accepted 11 December 2015

Available online 17 December 2015

Keywords:

Metal-organic framework

1,4-Naphthalenedicarboxylate

MOF catalysis

Cyanosilylation

Shape selectivity

ABSTRACT

Three-dimensional (3D) cobalt(II) and cadmium(II) metal-organic frameworks (MOFs) bearing rigid 1,4-naphthalenedicarboxylate (1,4-NDC) linkers were prepared and their solid-state structures were characterized by X-ray crystallography. Both Co-MOF and Cd-MOF exhibited isostructural frameworks. 1,4-NDC ligands bridge the metal ions in chelating/bridging and simple bridging modes to form a 1D chains, and these 1D chains are interconnected by 1,4-NDC to form 3D frameworks with the formula of $[M_2(1,4-NDC)_2(DMF)_2]$ ($M = Co^{II}$ or Cd^{II}). The as-prepared Cd-MOF was found to be catalytically active for the cyanosilylation reaction of aromatic aldehydes with nitro substituent in varying positions in the presence of trimethylsilyl cyanide to afford cyanohydrin trimethylsilyl ethers in a shape and size selective manner. The catalytic reaction is thought to have mainly occurred inside the Cd-MOF micropores which were generated through the partial dissociation of DMF ligands near the surfaces of Cd-MOF, where openly accessible coordination sites are available once the labile DMF ligands dissociate from Cd^{II} ions. The as-prepared Co-MOF did not exhibit catalytic activities for the same reaction.

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1. Introduction

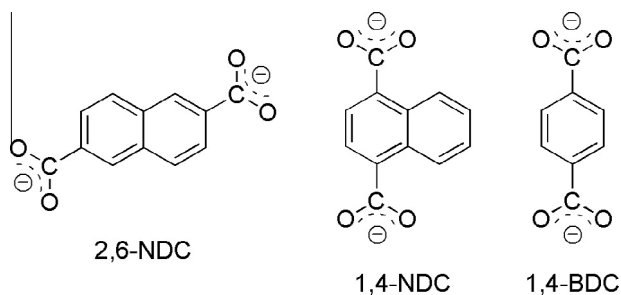
Since the first report of MOF-5 by Yaghi and coworkers [1], a large number of metal-organic frameworks have been disclosed. The chemical functionalities of the interior surfaces of MOFs are often strongly dependent on the type and nature of the polytopic organic bridging linkers which effectively interconnect different metal ion-based nodes [2]. The geometry and symmetry of these organic bridging linkers also influence the final topological networks of the resultant MOFs. Among the known ditopic organic bridging linkers, 2,6-naphthalenedicarboxylate (2,6-NDC) has often been employed as the bridging linker because it is commercially available and its geometry and molecular dimension are adequate for the production of novel MOF structures: In-MOF [3] with an anionic framework, Zn-MOFs (IRMOF-8 [4]), Cr-MOF [5] with MIL-101 topology, $[M_3(2,6-NDC)_3(DMF)_4]_n$ ($DMF = N,N$ -dimethylformamide) [6] type of MOFs with Mn^{II} , Fe^{II} , and Co^{II} ions, Mg-MOF (TUDMOF-2 and TUDMOF-3) [7], Cd-MOF with an additional 4-pyridinecarboxylate linker [8], Al-MOF (MIL-69) [9], and MOFs containing lanthanide ions such as Ce^{III} , Eu^{III} , and Tb^{III} [10].

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In contrast, the commercially available geometrical isomer, 1,4-naphthalenedicarboxylate (1,4-NDC), was less explored for the preparation of MOFs, presumably because 1,4-NDC has a much shorter dimension of two carboxylate groups than 2,6-NDC (Scheme 1). Despite its smaller dimension of two carboxylate groups which will bind two different metal ion centers, the perfectly linear angle between these two carboxylate groups compared to 2,6-NDC will benefit the generation of new topologically interesting MOF systems. The backbone structure of 1,4-NDC is exactly the same as that of the more commonly used 1,4-benzenedicarboxylate (1,4-BDC), which is a bridging linker found in MOF-5. Nevertheless, the extra phenyl ring in 1,4-NDC usually leads to different secondary building units (SBUs) and framework structures compared to the MOFs prepared from 1,4-BDC. A few examples of MOF contain 1,4-NDC without other ditopic N-donor co-ligands: $Zn_6(1,4-NDC)_5(OH)_2(DMF)_2 \cdot 4DMF$ containing hexanuclear SBU (MOF-48) [11], $Al(OH)(1,4-NDC)$ of MIL-53 topology [12], $In(OH)(1,4-NDC) \cdot 2H_2O$ and $HIn(1,4-NDC)_2 \cdot 2H_2O \cdot 1.5DMF$ [13]. Therefore, we predicted that new functional MOFs based on 1,4-NDC linkers with various metal ions would be possible.

MOFs can be utilized as efficient heterogeneous catalytic systems when either Lewis acidic metal centers or Lewis acidic/basic functional ligands act as catalytic sites for organic transformations. Generally, the Lewis acidic metal centers are available due to the



Scheme 1. Structural comparison of 2,6-NDC, 1,4-NDC, and 1,4-BDC anionic ditopic linkers.

Table 1
Crystallographic data for Co-MOF and Cd-MOF.

	Co-MOF	Cd-MOF
Empirical formula	C ₃₀ H ₂₆ Co ₂ N ₂ O ₁₀	C ₃₀ H ₂₆ Cd ₂ N ₂ O ₁₀
Formula weight	692.39	799.33
T (K)	100(2)	170(2)
Wavelength (Å)	1.54178	0.71073
Space group	P2 ₁ /c	P2 ₁ /c
a (Å)	7.0771(2)	7.2030(14)
b (Å)	19.3930(7)	19.888(4)
c (Å)	19.6397(6)	19.968(4)
α (°)	90.00	90.00
β (°)	97.168(2)	94.94(3)
γ (°)	90.00	90.00
V (Å ³)	2674.41(15)	2849.9(10)
Z	4	4
D _{calc} (Mg/m ³)	1.720	1.863
Absorption coefficient (mm ⁻¹)	10.305	1.556
Crystal size (mm)	0.10 × 0.03 × 0.02	0.15 × 0.08 × 0.02
Reflections collected	16,209	16,490
Independent reflections (R _{int})	2062 (0.0745)	6272 (0.1488)
Data/restraints/parameters	2062/7/401	1272/15/363
Goodness-of-fit (GOF) on F ²	1.043	0.996
Final R indices [I > 2σ(I)]	R ₁ = 0.0401, wR ₂ = 0.0935	R ₁ = 0.1307, wR ₂ = 0.3200
R indices (all data)	R ₁ = 0.0508, wR ₂ = 0.0994	R ₁ = 0.2101, wR ₂ = 0.3519
Largest difference peak and hole (e Å ⁻³)	0.796 and -0.536	3.944 and -1.869

Table 2
Selected Bond Distances for Co-MOF and Cd-MOF.

	Co-MOF	Cd-MOF
M–O _{carboxylate}	2.008(4)–2.279(4)	2.232(14)–2.379(10)
M–O _{DMF}	2.105(5), 2.2112(7)	2.248(13), 2.262(17)
M···M	3.845, 3.876	3.925, 4.024

presence of openly accessible metal sites or defects in the frameworks [14]. There are several excellent review articles summarizing recent MOF-based catalytic systems for various organic transformations [15–17]. One of the most valuable MOF-based catalytic systems may be the cyanosilylation reaction between aldehydes and trimethylsilyl cyanide because the resulting products, cyanohydrins, are very useful intermediate compounds for fine chemicals and pharmaceuticals [18,19].

In this report, we present two isostructural 1,4-NDC-based three-dimensional (3D) MOFs: Co-MOF and Cd-MOF. Co-MOF was obtained as very small single crystals while Cd-MOF was hierarchically grown as single crystals. The crystal structures of both 3D MOFs and the shape-selective catalysis of Cd-MOF for cyanosilylation reaction of aromatic aldehydes are also reported.

2. Experimental

2.1. General methods

1,4-Napthalenedicarboxylic acid (1,4-H₂NDC) was purchased from TCI. All other commercially available starting materials and solvents were purchased from Sigma–Aldrich and TCI and were used without further purification.

2.2. Preparation of [Co₂(1,4-NDC)₂(DMF)₂]

A mixture of Co(NO₃)₂·6H₂O (0.145 g, 0.5 mmol) 1,4-H₂NDC (0.216 g, 1.0 mmol) dissolved in 10 mL of DMF was sealed in a Teflon-lined high pressure bomb and stored at 130 °C for 48 h. The mixture was cooled to room temperature and the violet colored crystals were retrieved by filtration and washed with DMF.

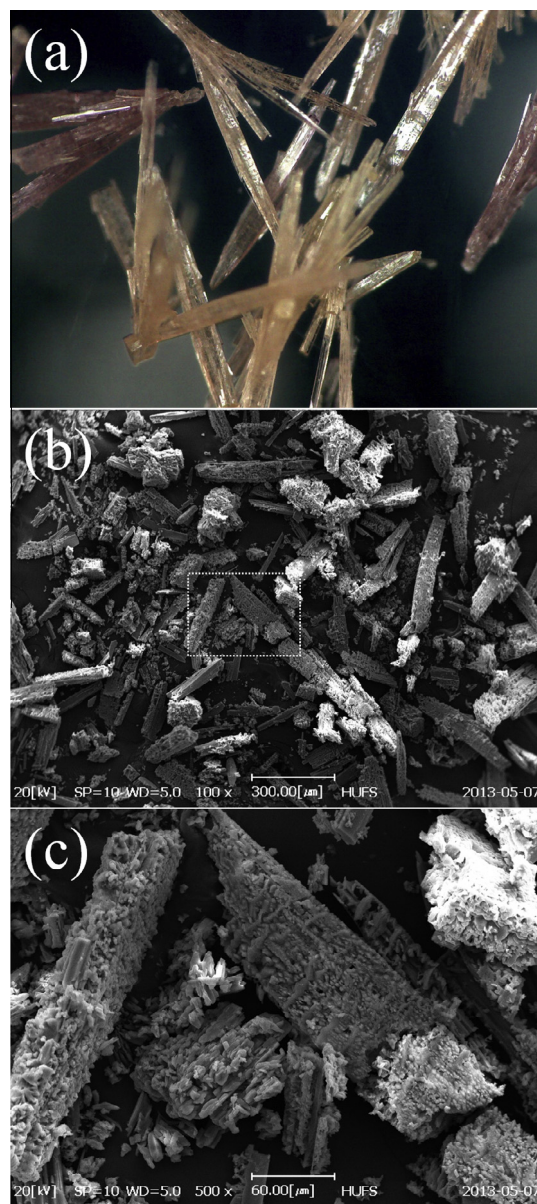


Fig. 1. Optical microscopy image of Cd-MOF (a). SEM images of hierarchical Cd-MOF crystals at different magnifications. Image (c) is the enlarged view of the square outlined area of (b).

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