New Bifunctional Metal–Organic Frameworks and Their Utilization in One-Pot Tandem Catalytic Reactions

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Supporting Information

ABSTRACT: Two new metal–organic framework (MOF) compounds were synthesized by a room temperature slow diffusion reaction. The compounds, $[\text{Cd}_3(\text{C}_8\text{H}_3\text{SO}_7)_2(\text{C}_{10}\text{H}_8\text{N}_4)_3(\text{C}_3\text{H}_7\text{NO})_2](\text{CH}_3\text{OH})_4$, **I**, and $[\text{Cd}_3(\text{C}_8\text{H}_3\text{SO}_7)_2(\text{C}_{12}\text{H}_{10}\text{N}_4)_3(\text{C}_3\text{H}_7\text{NO})_2](\text{C}_{12}\text{H}_{10}\text{N}_4)(\text{C}_3\text{H}_7\text{NO})_2$, **II**, have comparable structures formed by Cd-sulfoisophthalate layers cross-linked by bipyridyl linkers forming three-dimensional structures. The compounds have both Lewis acidic (Cd metal centers) as well as basic (azine, free pyridine, and uncoordinated sulfo oxygens) sites, and they exhibited good catalytic activity for one-pot tandem deacetalization–Knoevenagel condensation reactions. The compounds exhibit catalytic activity both in the presence of a solvent as well as in solvent-free conditions. Compound **I** also exhibits good proton conductivity at room temperature.

INTRODUCTION

Metal–organic frameworks (MOF) or coordination polymers (CP) have occupied a central stage during the last two decades.^{1–4} The aesthetic structures, large functional pores, which are often flexible and tunable in nature,^{5–8} make this class of compounds attractive and have found applications in storage,^{9–12} separation,^{13–16} catalysis,^{17–22} drug delivery,^{23–25} sensing,^{26,27} etc.

MOFs with their extra-large pore openings and channels could be candidates for exploring heterogeneous catalytic studies and can provide good activity as well as selectivity.²⁸ Thus, there is considerable interest to investigate MOFs as a heterogeneous catalyst in many catalytic reactions. One of the important developments over the years in organic reactions/transformations is to generate processes that are environmentally benign and with good atom economy. One such process is one-pot tandem reactions. In a tandem or cascade reaction, two or more reactions proceed successively within the same reaction pot, which reduces energy consumption, waste of chemicals, and the reaction time.²⁹

One-pot reaction types include, but are not limited to, cascade (domino) process,^{30,31} tandem catalysis (catalysis performed sequentially),³² multifunctional catalysts having more than one active site,³³ and reactions involving two distinct catalysts.³⁴ The one-pot catalytic reactions present certain difficulties (i) controlling and optimizing selectivity and (ii) competing interactions (usually detrimental) between multiple catalytic sites and catalysts, which presents opportunities to explore newer catalysts.³⁵ The attractive side of these one-pot reactions, on the other hand, is the possibility of

isolating energetically unfavorable products. We have been interested in these one-pot tandem reactions as the MOFs provide a suitable platform to investigate multifunctional catalysts that would help in different types of transformations under similar reaction conditions.

In the present study, we have employed two organic ligands, sodium salt of 5-sulfoisophthalic acid ($\text{Na}-\text{C}_8\text{H}_3\text{SO}_7$ - NaSIPA) and two pyridine based organic linkers 4,4'-azopyridine ($\text{C}_{10}\text{H}_8\text{N}_4$ - ABPY) and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene ($\text{C}_{12}\text{H}_{10}\text{N}_4$ - BPDB) along with the cadmium salts to prepare two new three-dimensional (3D) MOFs $[\text{Cd}_3(\text{C}_8\text{H}_3\text{SO}_7)_2(\text{C}_{10}\text{H}_8\text{N}_4)_3(\text{C}_3\text{H}_7\text{NO})_2](\text{CH}_3\text{OH})_4$ (**I**) and $[\text{Cd}_3(\text{C}_8\text{H}_3\text{SO}_7)_2(\text{C}_{12}\text{H}_{10}\text{N}_4)_3(\text{C}_3\text{H}_7\text{NO})_2](\text{C}_{12}\text{H}_{10}\text{N}_4)(\text{C}_3\text{H}_7\text{NO})_2$ (**II**).

The hexa-coordinated Cd metal centers have been known to act as Lewis acidic centers and have been exploited for several applications that include heterogeneous catalysis.^{36,37} In addition, the presence of the sulfo group (uncoordinated sulfo oxygens with lone pairs) as well as azine and uncoordinated pyridine sites can potentially act as Lewis base centers.^{38–41} The possibility of combining the Lewis acidic and basic properties in single MOFs provides an attractive option for exploring catalytic reactions. One reaction that would combine the Lewis acidity and basicity would be the deacetalization–Knoevenagel (DK) reaction. There have been studies in the literature exploring such a tandem catalytic

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reaction.^{42–45} In the present study, the isolated compounds possess some of the desirable properties to carry out the tandem catalysis that would involve both the Lewis acidic as well as basic reaction centers. We have explored such a reaction as part of the present investigations and found the present compounds to be active as good heterogeneous catalysts. In addition, we have also discussed the proton conductivity behavior of compound **I**. In this paper, we present the synthesis, structure, tandem catalytic behavior, and proton conductivity studies on the two compounds, **I** and **II**.

EXPERIMENTAL SECTION

Synthesis of Compounds **I and **II**.** All the chemicals were obtained from commercially available sources. The ligand BPDB was synthesized following the established procedure.⁴⁶ All the syntheses of the MOFs were carried out at room temperature employing slow diffusion of the reactants separated by immiscible layers. Typically, 0.04 mmol of NaSIPA salt (10.7 mg) and 0.04 mmol of bipyridine linkers [ABPY for **I** (7.4 mg) and BPDB for **II** (8.4 mg)] were dissolved in 2 mL of methanol and were transferred to a 5 mL culture tube (capped) and carefully layered over a 2 mL of dimethylformamide (DMF) solution containing 0.04 mmol of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (12.3 mg). After 2–3 days, reddish orange (**I**) and yellow (**II**) colored crystals started to form on the wall of the tubes. The reaction was allowed to continue for 1 week, and then the crystals were separated from the mother liquor and washed with a 1:1 mixture of DMF and methanol solution under vacuum filtration and dried at ambient conditions. Yields: 89% (**I**) and 82% (**II**); based on the metal salts (Table S1).

Initial Characterization. All the compounds were characterized by elemental analysis (C, H, N, S; Thermo Finnigan EA Flash 1112), powder X-ray diffraction (PXRD; PANalytical, Empyrean), IR (Perkin-Elmer Spectrum 1000), thermogravimetric analysis (TGA; Mettler-Toledo), and UV/vis absorption studies (Perkin-Elmer, Lambda-35). Elemental analysis results are presented in Table S2. The PXRD patterns of the samples were recorded at room temperature ($\text{CuK}\alpha$), and the observed PXRD patterns were consistent with the simulated PXRD patterns generated from the structures determined by the single-crystal XRD studies (Supporting Information, Figure S1).

Room temperature IR spectroscopic studies were carried out in the mid-IR region using KBr pellets, which exhibited characteristic bands (Figure S2). A sharp band at $\sim 1735\text{ cm}^{-1}$ could be assigned to the presence of the $-\text{COO}$ group of the SIPA ligand in compounds **I** and **II**. The bands at 1230 cm^{-1} (**I**) and 1160 cm^{-1} (**II**) could be due to the asymmetric and symmetric stretching band of the $\text{S}=\text{O}$ group of the ligand. The strong sharp band at $\sim 1040\text{ cm}^{-1}$ could be due to the $\text{S}-\text{O}$ stretching.⁴⁷ The strong band near $\sim 1610\text{ cm}^{-1}$ in **II** could be assigned to the presence of the azine group ($-\text{C}=\text{N}-$) of the BPDB ligand.^{48,49} A sharp band at $\sim 1646\text{ cm}^{-1}$ (**I**) and 1640 cm^{-1} (**II**) is for the $\text{C}=\text{O}$ stretch of DMF⁵⁰ and a band at around 3540^{-1} (**I**) could be for the OH stretch of MeOH.

UV–vis spectra of compounds **I** and **II** recorded at room temperature exhibit broad absorption bands in the visible region (Figure S3). For **I**, two maxima centered at $\sim 350\text{ nm}$ and $\sim 480\text{ nm}$ were observed, and for **II** one maximum at $\sim 380\text{ nm}$ with a shoulder at $\sim 330\text{ nm}$ was noted. The absorption bands arise due to the intraligand charge transfer ($n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$). The observed UV–vis spectra for **I** and **II** are similar to those observed before.⁵¹

The solid-state photoluminescence (PL) studies of compounds **I** and **II** were carried out at room temperature on the powdered sample (Figure S4). The compounds **I** and **II** were excited using a wavelength of 350 and 380 nm, respectively. An emission band at $\sim 395\text{ nm}$ with two shoulders at ca. 490 and 530 nm was observed for compound **I** (Figure S4a). For **II**, a maximum at $\sim 450\text{ nm}$ with two shoulders at ~ 485 and 525 nm was observed (Figure S4b). The observed emissions are due to intraligand emissions. Similar observations have been made before.^{51,52}

Single-Crystal Structure Determination. Suitable single crystals of compounds **I** and **II** were selected and mounted with a fiber loop. The single-crystal data were collected at 100(2) K on an Oxford Xcalibur (Nova) diffractometer equipped with an EOS CCD detector. The X-ray was generated by operating at 50 kV and 0.8 mA by using $\text{MoK}\alpha$ ($\lambda = 0.71073\text{ \AA}$) radiation. The refinement of the cell and the data reduction were carried out using CrysAlis RED.⁵³ The structures were solved using direct method, and refinement was accomplished by employing SHELX-2014 present in WINGX suite of programs (version 1.63.04a).⁵⁴ The hydrogens could be assigned from the difference Fourier map, and for the final refinement the hydrogens were fixed at the geometrically ideal position and refined using the riding mode. The full-matrix least-squares refinement against $|F_o|^2$ was executed on the WinGX package of programs.⁵⁵ The final refinements were carried out including atomic positions of all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. All the details of structural parameters and refinement details are listed in Table 1. Important bond lengths and bond angles are presented in

Table 1. Crystal Data and Structure Refinement Parameters for All the Compounds^a

structural parameter	I	II
empirical formula	$\text{C}_{62}\text{H}_{58}\text{N}_{16}\text{O}_{22}\text{S}_2\text{Cd}_3$	$\text{C}_{76}\text{H}_{74}\text{N}_{20}\text{O}_{18}\text{S}_2\text{Cd}_3$
crystal system	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
<i>a</i> (Å)	10.1392(5)	10.2282(14)
<i>b</i> (Å)	13.6080(6)	13.5641(19)
<i>c</i> (Å)	13.6470(6)	15.9140(2)
α (deg)	73.330(10)	108.464(3)
β (deg)	82.470(10)	98.421(4)
γ (deg)	81.922(10)	97.469(4)
<i>V</i> (Å ³)	1777.71(14)	2034.70(5)
<i>Z</i>	1	1
<i>T</i> /K	100(2)	100(2)
ρ (calc/g cm ^{−3})	1.663	1.597
μ (mm ^{−1})	1.034	0.909
λ (Mo $\text{K}\alpha$ /Å)	0.71073	0.71073
θ range (deg)	3.095 to 25.998	3.042 to 26.000
<i>R</i> _{int}	0.0509	0.0333
<i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0483; <i>wR</i> ₂ = 0.1306	<i>R</i> ₁ = 0.0617; <i>wR</i> ₂ = 0.1714
<i>R</i> indexes (all data)	<i>R</i> ₁ = 0.0498; <i>wR</i> ₂ = 0.1317	<i>R</i> ₁ = 0.0665; <i>wR</i> ₂ = 0.1746

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)] \}^{1/2}$, $w = 1 / [\rho^2(F_o)^2 + (aP)^2 + bP]$. $P = [\max(F_o, O) + 2(F_c)^{-2}] / 3$ where $a = 0.0699$ and $b = 11.4708$ for **I** and $a = 0.0959$ and $b = 12.9591$ for **II**.

Tables S3 and S4. The supplementary crystallographic data for this paper can be found in CCDC 1838396–1838397. The Cambridge Crystallographic Data Centre (CCDC) provides free access to the single crystal data.

Catalytic Studies. To perform the tandem catalytic reactions, an optimization of the catalytic conditions was investigated. Thus the deacetalization and Knoevenagel condensation reactions were carried out independently with the MOFs as catalyst in different solvents such as EtOH, MeOH, toluene, MeCN, DMA, and DMF. The investigations reveal that catalytic performance was optimal when DMF was employed as the solvent. Thus we have chosen DMF as the solvent for the tandem one-pot DK reactions. The next step is to perform the catalytic reactions at different temperatures. We observed that the deacetalization was slow at lower temperatures. Our studies indicate that optimum products were observed when the reactions were carried out at 353 K.

Figure 1. (a) View of [Cd₂(CO₂)₄] unit in I ($\mu_1\text{-}\eta^1\text{:}\eta^1$ and $\mu_2\text{-}\eta^1\text{:}\eta^1$ bridgings can be observed); (b) view of 1D double chain formed by SIPA and Cd metal; (c) view of 2D layer of Cd and SIPA ligand in the *abc* plane; (d) view of 2D layer from the *a* axis; (e) view of the 3D structure of I (lattice solvents and hydrogens are omitted for clarity; Cd atoms are shown in green colored polyhedral).

To optimize the amount of the catalysts that may be required, we have taken the catalyst (compound I) in three different amounts [5 mg (0.28 mol %), 10 mg (0.56 mol %), and 25 mg (1.4 mol %)] to carry out the tandem DK reactions. The yields were better when the catalytic studies were carried out using 10 mg of the sample. Higher quantity of the catalyst did not result in improved yields for the product.

The independent deacetalization and Knoevenagel condensation reactions were carried out by taking 1 mmol of the reactants and 10 mg of catalysts in 2 mL of DMF. For the tandem one-pot DK reaction also we have taken similar quantities of the reactant: benzaldehyde

dimethyl acetal (BA) (1 mmol) and malononitrile (MN) (1 mmol) along with the catalyst (10 mg; 0.56 mol %) in 2 mL of DMF as the solvent in a round-bottom (RB) flask under nitrogen atmosphere. The catalysts were activated at 373 K overnight before being employed for the catalytic studies. The mixture was first stirred for 3 min at room temperature, and the catalytic reaction was carried out at 353 K. The progress of the reaction was monitored by thin-layer chromatography (TLC) at a regular interval of time. After 5 h of reaction, the mixture was filtered and washed with 1 mL of DMF along with CH₂Cl₂. The organic product was extracted with CH₂Cl₂ and water. At the end, the

crude product was purified using silica gel column chromatography (hexane/ethyl acetate) and characterized by ^1H NMR spectroscopy.

RESULTS AND DISCUSSION

Structure of $[\text{Cd}_3(\text{C}_8\text{H}_3\text{SO}_7)_2(\text{C}_{10}\text{H}_8\text{N}_4)_3(\text{C}_3\text{H}_7\text{NO})_2] \cdot \text{C}_3\text{H}_7\text{NO} \cdot (\text{CH}_3\text{OH})_4$ (I). Compound I crystallizes in the triclinic ($P\bar{1}$) space group and has 53 non-hydrogen atoms present in the asymmetric unit (Figure S5). The asymmetric unit contains one and a half Cd^{2+} ions, one SIPA ligand, one and a half ABPY ligands, one coordinated DMF molecule, and one lattice DMF molecule along with two methanol molecules. One of the Cd atoms, Cd(2), occupies a special position (1a) with a site multiplicity of 0.5. Both the Cd atoms have a distorted octahedral geometry formed by four oxygen and two nitrogen atoms. Cd(1) is bonded with four oxygen atoms of SIPA carboxylates and two ABPY ligands, whereas Cd(2) is bonded with two sulfo groups of SIPA ligand, two ABPY ligands, and two DMF molecules. The Cd–O/N bond lengths are in the range 2.275(1)–2.385(3) Å (Table S3).

The carboxylate groups of the SIPA ligand have different bonding with the cadmium centers. Thus, one carboxylate forms a $\mu_1\text{-}\eta^1\text{:}\eta^1$ -chelating coordination and the other forms a $\mu_2\text{-}\eta^1\text{:}\eta^1$ -bridging coordination modes to form a $[\text{Cd}_2(\text{CO}_2)_4]$ unit (Figure 1a). This connectivity gives rise to a one-dimensional (1D) double chain along the a axis (Figure 1b). The 1D double chains are bonded with the Cd(2) atom via a $\mu_1\text{-}\eta^1\text{:}\eta^0$ monodentate coordination mode through the sulfonate group forming a two-dimensional (2D) layer (Figure 1c–d). The 2D layers are connected to each other through the ABPY ligands giving rise to the 3D structure (Figure 1e). This connectivity results in a 1D pore with a diameter of $\sim 5.0 \text{ \AA} \times \sim 8.0 \text{ \AA}$ (atom–atom contact distance not including the van der Waals radii) along the a axis (Figure S6). The extra-framework DMF and methanol molecules are located inside the 1D channels in the structure (Figure S7). The solvent molecules are stabilized by a number of noncovalent interactions with the pore surface. The prominent C–H $\cdots$ O interactions and their distances are shown (Figure S8).

Structure of $[\text{Cd}_3(\text{C}_8\text{H}_3\text{SO}_7)_2(\text{C}_{12}\text{H}_{10}\text{N}_4)_3(\text{C}_3\text{H}_7\text{NO})_2] \cdot (\text{C}_{12}\text{H}_{10}\text{N}_4) \cdot (\text{C}_3\text{H}_7\text{NO})_2$ (II). The structure of II is similar to that of I. Compound II has 60 non-hydrogen atoms, which contains one and a half Cd^{2+} ions, one SIPA ligand, one and a half coordinated BPDB ligands, and half noncoordinated BPDB ligand, one bonded DMF molecule along with a half nonbonded DMF molecule (Figure S9). One of the cadmium atoms, Cd(2), occupies a special position (1a) with site multiplicity of 0.5. Both Cd(1) and Cd(2) have octahedral geometry with Cd(1) connected with four carboxylate oxygens and two nitrogens of BPDB ligands, and Cd(2) is bonded with two sulfo oxygens of SIPA, two DMF oxygens, and two nitrogens of BPDB ligand. The Cd–O/N bond length is in the range 2.271(6)–2.400(4) Å (Table S3).

The structure of II has connectivities that are similar to that observed in I. Thus, a 1D double chain formed by the connectivities between the Cd^{2+} centers and sulphonate oxygens are further bonded through the sulfonate oxygen involving Cd(2) forms a 2D layer. The 2D layers are further connected by the BPDB linkers to form the 3D structure (Figure 2). This connectivity gives rise to a 1D channel ($\sim 7.0 \text{ \AA} \times \sim 9.0 \text{ \AA}$) along the a axis (Figure S10). In structure II, we observed that one unbounded BPDB molecule along with DMF molecules resides inside the channels (Figure S11), which nearly fills the channel.

Figure 2. View of 3D structure of II (lattice solvent, ligands, and hydrogens are removed for clarity; Cd atoms are shown in green colored polyhedral). Benzaldehyde dimethyl acetal (BA), benzaldehyde (BD), benzyldene malononitrile (BM).

Thermal Stability and Gas Adsorption Studies.

Thermogravimetric analysis (TGA) (Mettler-Toledo) of the compounds was carried out in the temperature range of 30–850 °C (heating rate = 5 °C/min) in oxygen atmosphere (flow rate = 50 mL/min) (Figure S12). Both the compounds exhibited similar behavior. For compound I, a continuous weight loss up to 175 °C, followed by a sharp weight loss in the temperature range of 315–500 °C was noted. The total observed weight loss was 79.2%, which would correspond to the loss of all the organic moieties (81.1%) present in the compound. A similar behavior was also noted for compound II with the total observed weight loss of 80.9% (calculated for the loss of organic moieties 82.8%). The final calcined product in both cases was found to be CdO (ICSD - 24802) (Figure S13).

The thermal stability of the compounds was also examined by employing variable temperature in situ (up to 483 K) powder X-ray diffraction (HTPXRD) studies (Figure S14) (Rigaku, SmartLab rotating anode diffractometer (CuK_α radiation) employing an alumina (Al_2O_3) sample holder. The in situ PXRD studies suggest that both I and II appear to be stable up to 483 K. The broad peak observed near $2\theta = 6^\circ$ was from the sample holder. The HTPXRD studies also confirm that the gradual weight loss observed in the TGA is mainly due to the loss of the solvent molecules from the framework, and the collapse of the framework starts only after $\sim 300^\circ\text{C}$. It may be noted that the overall crystallinity of the compounds was slightly reduced at higher temperatures (Figure S14). The calcined sample (483 K) was examined employing proton NMR as well as elemental analysis to verify the removal of the solvent molecules (DMF) from the framework (Figure S15 and Table S2). The studies indicate that at 483 K, most of the DMF molecules have been removed.

Catalysis. The present compounds appear to possess more than one functional group. Thus, we have explored both the compounds, I and II, as a heterogeneous catalyst in a one-pot tandem deacetalization–Knoevenagel condensation reaction. The deacetalization reaction, generally, is acid-catalyzed and produces aldehydes or ketones. The base-catalyzed Knoevenagel condensation reaction can form nitriles. The catalytic conditions were optimized by carrying out the reaction by changing the temperature, solvent, and catalyst amount (Table S5). As mentioned in the Experimental Section, the optimal conditions are $T = 353 \text{ K}$, solvent = DMF, and catalyst = 0.56 mol % (10 mg for I and 11 mg for II). In the present study, the deacetalization reaction produces benzaldehyde (BD) from

benzaldehyde dimethyl acetal (BA) as a reactant, which is acid-catalyzed. The base-catalyzed Knoevenagel condensation reaction produces benzylidene malononitrile (BM) in the presence of the reactants BD and malononitrile (MN).

Initially, we have carried out the two reactions separately to monitor which one is the rate determining step. The first step, the deacetalization reaction, was found to be slow with conversion of $\sim 15\%$ after 5 h of reaction at 353 K. The formation of aldehyde did not improve much even when the reaction was carried out for 12 h. The Knoevenagel reaction, on the other hand, was found to be fast under the same reaction conditions. Typically the reaction was observed to be complete within ~ 3.5 h for **I** and ~ 3 h for **II**. The superior conversion in the Knoevenagel reaction inspired us to carry out a tandem DK reaction by keeping the amounts of the reactants and the other experimental conditions constant (Scheme 1).

Scheme 1. Scheme for the One-Pot Tandem Deacetalization-Knoevenagel Reaction

The tandem reaction was found to be successful with yields of $\sim 84\%$ (**I**) and $\sim 95\%$ (**II**) after 5 h of reaction at 353 K. The higher yields of the product in the tandem reaction are the result of the aldehyde formed by the Lewis acid catalyzed reaction being consumed immediately by the Lewis base catalyzed reaction. As observed in the separate experiments, the Lewis base catalyzed reaction was much faster, which helped convert the acetal immediately to the nitrile. This would facilitate the first reaction to proceed in the forward direction in a facile manner due to Le Chatelier's principle. The recyclability of the catalysts in this tandem reaction was tested up to three cycles, which does not indicate any major drop in the catalytic activity (Figure S16). The PXRD pattern of the catalysts also did not reveal any appreciable changes in the crystallinity after the third cycle of the catalytic studies (Figure S17). The success of the tandem catalysis prompted us to investigate the DK catalytic reactions employing other substituted BA, and the results are listed in Table 2 (Figure S18). From the studies it appears that the yields of the para-substituted methoxy ($-\text{OCH}_3$) and bromo ($-\text{Br}$) groups are comparable to the nonsubstituted BA under the same reaction conditions. On the other hand, the reaction does not proceed well when phenylacetaldehyde dimethyl acetal was employed. Similar behavior has been noted earlier.⁵⁶ It is likely that the

Table 2. One-Pot Tandem Catalysis Yield with the Heterogeneous Catalysts Compounds **I and **II**^a**

Substrate	Product	% of Yield	
		I	II
		84	95
		81	92
		76	85
		Trace	Trace

^aReaction conditions: Benzaldehyde dimethyl acetal (1 mmol), malononitrile (1 mmol), DMF (2 mL), and catalyst (0.56 mol %; 10 mg of compound **I**/11 mg of compound **II**). The yields were determined by employing silica gel column chromatography after 5 h of reaction.

substitution at the α position does not provide the needed delocalization energy. We have also attempted to carry out the tandem reactions in a solvent-free condition at 353 K. Solvent-free reactions provide an opportunity to achieve a greener and more sustainable route of chemical transformations.^{57–60} Our studies indicate that the reactions do proceed to near completion albeit taking longer time (~ 15 h). The catalysts also retain their crystallinity under the solvent-free catalytic reactions as well (Figure S19). An IR spectroscopic investigation on the catalysts after both solvent free as well as with DMF as the solvent catalytic reactions did not reveal any observable changes (Figure S20). The elemental analysis after the catalytic studies also did not reveal any changes (Table S2).

The catalytic studies indicate that **II** is more active compared to **I**. Structurally, compound **I** has more open pores compared to **II**. It is likely that the presence of free BPDB in **II** enhances the overall basicity in **II** and favors the aldehyde to nitrile reaction. In order to get a better insight into this reaction, we sought to carry out time dependent catalytic studies. For this reaction, we collected small quantities of the reaction mixture at regular intervals and analyzed employing NMR spectroscopy.

In a typical solvent-free tandem reaction, 25 mmol of BA and MN along with 250 mg of **I** and 275 mg of **II** were reacted at 353 K. Dimethyl terephthalate (0.077 mmol) was used as an internal standard for the NMR study. A small aliquot (0.064 mL) was removed from the reaction mixture using a syringe starting from $t = 0$ (beginning of the reaction) followed by every 3 h. The mixture was transferred to the NMR tube along with the internal standard and CDCl_3 as the NMR solvent (Figures S21–22). The distributions of the products from the experiments are shown in Figure 3. The distribution of the reactants and the products employing **I** and **II** appears to be showing similar trends. Initially the conversion is slow, and it becomes maximum in between 9 and 12 h for **I** and it is in between 6 and 9 h for **II** and then the saturation occurs. In addition, the product formation appears to be faster when **II** was employed as the catalyst. It was found that after 15 h the amount of reactants was negligible in the case of **II**. A similar observation was also noted employing DMF as the solvent. It is clear that the catalytic activity of **II** is superior to that of **I**. We have also carried out a hot filtration test to prove the heterogeneity of the reaction.

The deacetalization-Knoevenagel catalytic reactions have been carried out by employing MOFs (Table 3). As can be seen, the present compounds are active and exhibit catalytic activity that is comparable to those reported earlier.^{42–45,66–69} It may be noted that in the present study no postsynthetic modifications or nanoparticle incorporation have been carried out, and the compounds were used as synthesized. In addition, the Cd-MOFs exhibit catalytic activity with minimal quantity of solvent, which would be desirable for environmental reasons and a green process.

Proton Conductivity. The TGA investigations along with in situ PXRD and IR studies suggest that the solvent molecules may be removed without collapse of the framework. We wanted to explore the water absorption capability of the preheated samples of the compounds **I** and **II** (BELSORB aqua). The water sorption isotherm studies indicate a gradual water uptake, which reaches a value of 157 mL/g at $p/p_0 = 0.9$ and 104 mL/g at $p/p_0 = 0.9$ for compounds **I** and **II**, respectively (Figure S23). The adsorbed water would

Figure 3. Kinetic study for the one-pot tandem deacetalization-Knoevenagel reaction with **I** (a) and **II** (b) as a heterogeneous catalysts (solvent-free condition).

correspond to 12.5 mol of H_2O /mol of **I** and 9.1 mol of H_2O /mol of **II**. Compound **I** exhibits a higher water uptake compared to **II** due to the presence of more open channels. The adsorption isotherm for both the compounds exhibits a hysteresis, which does not close at lower partial pressures. This suggests that the pores could be hydrophilic in nature and can absorb water irreversibly. The PXRD pattern of the water absorbed sample does not show any observable changes, which suggests that the compounds retain their structures (Figure S24).

The water adsorption studies indicated that the compound **I** uptakes a considerable amount of water. Structurally **I** contains pores that are decorated by sulfonate moieties, which opens up the possibility of accommodating the lattice water molecules either as clusters or chains along the 1D channel. There have been reports of proton mobility in compounds having sulfonate functionality along with the solvent molecules. This prompted us to investigate the possible proton conductivity in **I**. A pellet of compound **I** was prepared and kept at 98% humidity chamber at room temperature for 24 h. The measurement was carried out in the frequency range of 0.1– 10^6 Hz with the signal amplitude of 0.12 V (Alpha, Novocontrol). A proton conductivity value of $0.86 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ was observed from the Nyquist plots for compound **I** at 30 °C (Figure 4). The proton conductivity behavior of **I** found to be temperature dependent as the value was found to

Table 3. Table Summarizing the Various MOF Catalysts Employed in the Tandem Deacetalization-Knoevenagel Condensation Reaction^a

name of catalyst	catalyst amount	solvent	temp (°C)	reaction time	yield (%)	ref
Cu-PCN-126	0.5 mol %	DMSO	50	12 h	99	42
Cr-MIL-101-AB-x	4 mol %	DMF	90	2 h	>91	43
Yb-BDC-NH ₂	2 mol %	DMSO	50	24 h	97	44
MIL-101(Al)-NH ₂	100 mg	1,4-dioxane	90	3 h	94	45
Fe ₃ O ₄ @Cu-HKUST-1	50 mg	1,4-dioxane	90	5 h	99	66
Cu-HNUST-8	0.5 mol %	DMSO	50	48 h	99	67
Cu-HNUST-6	0.5 mol %	DMSO	50	48 h	99	68
PBSA/Cr-MIL-101 + PMAP/Cr-MIL-101	5 mol %	DMSO/H ₂ O	70	12 h	89	69
Compound I	0.56 mol %	DMF	90	5 h	84	this work
Compound II	0.56 mol %	DMF	90	5 h	95	this work

^aPCN-126 = C₂₃H₁₁Cu₂N₃O₁₁, HNUST-8 = [Cu₂(PDBAD)]_n·xGuest, HNUST-6 = [Cu₂(MOPBD⁴⁻)(H₂O)₂]_n·xGuest, HNUST-1 = Cu₃(BTC)₂, Cr-MIL-101 = [Cr₃(O)X(bdc)₃(H₂O)₂], MIL-101(Al)-NH₂ = Al₃O(DMF)[(COO)C₆H₃NH₂(COO)]₃·nH₂O.

Figure 4. Proton conductivity study for I: Nyquist plots at different temperatures are shown (relative humidity of 98% was maintained).

increase with the increase of temperature (Figure 4). The observed proton conductivity value at RT was found to be comparable with those reported elsewhere. The activation energy was calculated from the Arrhenius plot, which gave a value of 0.3 eV, suggesting a possible Grotthuss mechanism in this compound (Figure S25).^{61–65}

CONCLUSION

Two new 3D MOFs [Cd₃(C₈H₃SO₇)₂(C₁₀H₈N₄)₃·(C₃H₇NO)₂](C₃H₇NO)₂·(CH₃OH)₄ (I) and [Cd₃(C₈H₃SO₇)₂(C₁₂H₁₀N₄)₃(C₃H₇NO)₂](C₁₂H₁₀N₄)·(C₃H₇NO)₂ (II) have been prepared and their structures were determined. The compounds have 3D structures with I having 1D open channels. The compounds exhibit both Lewis acidic (from Cd center) as well as Lewis basic (from the sulfo oxygens and azine/free pyridyl group) functionality. The dual functionality was exploited for the one-pot tandem deacetalization-Knoevenagel reaction both under the solvent as well as solvent-free conditions. Our studies reveal that compound II is more active for the tandem catalysis compared to compound I, possibly due to the presence of azine functionality and uncoordinated BPDB linkers. Proton conductivity studies on I indicate moderate proton conductivity behavior at room temperature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.8b01327.

Synthesis composition table, elemental analysis results, selected bond distances and angles of the compounds, PXRD patterns, IR spectra, PL spectra, space filled views, views of lattice solvent molecules, TGA plots, ¹H NMR results, optimization of reaction condition for the deacetalization-Knoevenagel catalytic reaction, recyclability of the catalysts, adsorption–desorption isotherms, activation energy (PDF)

Accession Codes

CCDC 1838396–1838397 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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