

# A Carboxylate-Rich Metalloligand and Its Heterometallic Coordination Polymers: Syntheses, Structures, Topologies, and Heterogeneous Catalysis

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**Supporting Information** 

**ABSTRACT:** This work reports three heterometallic coordination polymers (HCPs), namely,  $[\{(1')_2 Zn_8 Na_2(H_2 O)_{21}\}$ ,  $20H_2O]_n$  (2),  $[\{(1')(1'')Cd_8(H_2O)_{21}\}$ ,  $32H_2O]_n$  (3), and  $[\{(1')_2Mn_8Na_2(H_2O)_{27}\}$ ,  $3H_2O]_n$  (4), originated from a common Co<sup>3+</sup> based metalloligand 1 offering eight arylcarboxylic acid groups where 1' and 1" respectively contribute eight and six anionic carboxylate groups. The crystal structure analyses display three-dimensional nature of all three HCPs wherein metalloligands are connected through secondary metals. Detailed topological analyses illustrate that the metalloligands function as the nodes that are connected to secondary building units (SBLIs) composed of  $Zn^{2+}$   $Cd^{2+}$  and



secondary building units (SBUs) composed of  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Mn^{2+}$  ions coordinated by the arylcarboxylate groups. All three HCPs effectively function as the heterogeneous catalysts for the Lewis acid assisted Knoevenagel condensation reactions of assorted aldehydes with three different active methylene compounds.

## INTRODUCTION

Crystalline coordination polymers constitute an important class of materials due to their interesting  $\operatorname{architectures}^{1-10}$  and significant structure-based applications in sorption,<sup>11,12</sup> sepra-tion,<sup>13,14</sup> sensing,<sup>15–17</sup> ion-exchange and transport,<sup>18,19</sup> proton conduction,<sup>20–22</sup> optics,<sup>23–27</sup> magnetic materials,<sup>28,29</sup> devi-ces,<sup>30,31</sup> and catalysis.<sup>32–36</sup> In particular, their utilization as the heterogeneous catalysts in assorted organic transformation reactions has often resulted due to their crystalline nature and therefore orderly arrangement of the catalytic centers and their unique ability to support the facile diffusion of substrates and reagents, a feature reminiscent of zeolites.<sup>32-40</sup> While the literature presents numerous homometallic coordination polymers, heterometallic coordination polymers incorporating two different metals are comparatively fewer.<sup>41-44</sup> Such a stark difference between two categories is due to the synthetic difficulty in placing two different metals in close proximity. Although judiciously selected ligands, offering two different coordination environments suitable to satisfy the geometrical and/or electronic requirement of two different metals, have been successfully used for the construction of heterometallic coordination polymers (HCPs), $^{45-53}_{49,50,53}$  such examples are limited due to cumbersome syntheses.<sup>49,50,53</sup> In this context, a welldefined metalloligand,<sup>1</sup> already having a primary metal ion but offering additional coordination-sensitive functional groups to potentially ligate a secondary metal ion, offers much better prospects for the construction of HCPs.

Our research group has reported various metalloligands offering assorted appended functional groups ranging from hydrogen bonding (H-bonding) sensitive groups<sup>54–56</sup> to

coordination-bonding sensitive groups.<sup>57–72</sup> We have illustrated the effect of number, position, and orientation of such appended functional groups, being offered from a metalloligand, on the material design. Using diversified metalloligands, we have been able to showcase examples of hydrogen bonded assemblies,<sup>54–56</sup> discrete trimetallic complexes,<sup>57–61</sup> and two- (2D) and three-dimensional (3D) heterobimetallic coordination polymers.<sup>62–72</sup> These examples adequately illustrate the significance of the metalloligand concept for the construction of ordered architectures.

Out of assorted metalloligands, the ones offering appended arylcarboxylic acid groups ( $ML^1$  and  $ML^2$ ) were successfully utilized for the synthesis of moderately porous crystalline HCPs with noteworthy heterogeneous catalytic applications (Scheme 1).<sup>69–72</sup> As a logical extension, we became interested to incorporate aryldicarboxylic acid functional groups and evaluate

Scheme 1. Our Earlier Metalloligands (ML<sup>1</sup> and ML<sup>2</sup>) and the Carboxylate-Rich Metalloligand 1 Used in the Present Work



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the role of such a carboxylate-rich metalloligand (1) in the construction of various HCPs. Herein, we present the syntheses, structures, topological analyses, and heterogeneous catalytic properties of  $\{Co^{3+}-Zn^{2+}\}, \{Co^{3+}-Cd^{2+}\}, \text{ and } \{Co^{3+}-Mn^{2+}\}$  HCPs using a common  $Co^{3+}$ -based metalloligand (1) offering eight appended carboxylic acid groups. The resultant HCPs display interesting structures and unprecedented topologies and function as the heterogeneous catalysts for the Knoevenagel condensation reactions.

## EXPERIMENTAL SECTION

**Materials and Methods.** Reagents of analytical grade were procured from Sigma-Aldrich, Alfa-Aesar, and Spectrochem and were used without further purification. The solvents were purified using standard literature methods.<sup>73,74</sup>

Synthesis of 2,6-(3,5-Methylbenzoatecarbamoyl)pyridine (H<sub>2</sub>L<sup>3,5-COOMe</sup>). Pyridine-2,6-dicarboxylic acid (1.0 g, 6.0 mmol) was added as a solid in one portion to a suspension of dimethyl 5aminoisophthalate (2.5 g, 12.00 mmol) in pyridine (10 mL), and the mixture was stirred at 40 °C for 40 min. Triphenyl phosphite (4.0 g, 13.2 mmol) was added dropwise over 10 min to the aforementioned mixture, and the temperature was increased to 90 °C. The reaction mixture was stirred for 4 h at 90 °C. On cooling to room temperature, a colorless precipitate was obtained, which was filtered, washed with water, and dried. The crude product was purified by recrystallization from aqueous CH<sub>3</sub>OH. Yield: 3.2 g, 97%. Anal. Calcd for C27H23N3O10·4H2O: C, 52.17%; H, 5.03%; N, 6.76%. Found: C, 52.02%; H, 4.78%; N, 6.34%. FTIR spectrum (Zn-Se (ATR), selected peaks): 3247 (N-H), 1726 (COO), 1665 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 3.9 (s, 6H, H6), 7.24–7.26 (m, 3H, H1/H5), 8.56-8.54 (d, 2H, H2), 9.07 (s, 4H, H4), 11.05 (s, 2H, H3). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 52.23 (C10), 125.2 (C2/ C6), 125.59 (C8), 126.3(C7), 131.28 (C5), 138.27 (C1), 148.35

(C3), 161.3 (C4), 166.3 (C9). Synthesis of 1<sup>P</sup>. The ligand H<sub>2</sub>L<sup>3,5-COOMe</sup> (0.50 g, 0.909 mmol) was dissolved in dinitrogen-flushed DMF and treated with solid NaH (0.048 g, 1.99 mmol). The resulting mixture was then stirred for 30 min at room temperature, and solid  $[Co(H_2O)_6](ClO_4)_2]$  (0.166 g, 0.45 mmol) was added to the aforementioned mixture. After another 30 min of stirring, dry O2 was purged to the solution for 2 min. The solution was finally stirred for 1 h at room temperature. The reaction mixture was filtered, followed by the removal of the solvent under reduced pressure. The product thus obtained was isolated after washing with diethyl ether. The crude product was dissolved in DMF and subjected to vapor diffusion of diethyl ether, which afforded a crystalline material within 2 days. Yield: 0.58 g, 88%. Anal. Calcd for  $C_{54}H_{42}N_6O_{20}CoNa \cdot 4C_3H_7NO: C, 53.95\%; H, 4.80\%; N, 9.53\%.$ Found: C, 53.46%; H, 4.46%; N, 9.55%. FTIR spectrum (Zn-Se (ATR), selected peaks): 3424 (OH), 1712 (COO), 1608, 1581 (C= O) cm<sup>-1</sup>. Absorption spectra ( $\lambda_{max}$ , nm, DMF ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 650 (95), 475 (sh). Conductivity (~1 mM, DMF, 298 K):  $\Lambda_{\rm M} = 85 \ \Omega^{-1}$ cm<sup>2</sup> mol<sup>-1</sup> (the range for 1:1 electrolyte in DMF is 65–160). <sup>1</sup>H NMR spectrum (DMSO-d<sub>6</sub>,400 MHz): 3.78 (s, 24H, H1/H1'), 7.95 (s, 4H, H2/H2'), 7.48 (s, 8H, H3/H3'), 7.69 (d, 4H, H4/H4'), 8.00 (t, 2H, H5/H5').  $^{13}\mathrm{C}$  NMR spectrum (DMSO- $d_{6\prime}$  100 MHz):  $\delta$  = 51.91 (OMe), 166.24 (C1), 162.48 (C6), 155.58 (C7), 146.33 (C5), 139.74 (C2), 131.13 (C9/C8), 125.23 (C4), 124.31 (C3).

Synthesis of 1. The compound  $1^{p}$  (1 g, 1 mmol) was dissolved in a mixture of THF/H<sub>2</sub>O (3:1, v/v; 25 mL) and treated with 8 equiv of NaOH. The reaction mixture was stirred for 12 h at room temperature. The resulting solution was neutralized using 3 N HCl. Removal of THF under reduced pressure resulted in the precipitation of the product, which was isolated and dried under vacuum. The crude product was recrystallized from DMF after diffusing vapors of diethyl ether, which produced a highly crystalline product within 2–3 days. Yield: 0.35 g, 78%. Anal. Calcd for C<sub>110</sub>H<sub>94</sub>CO<sub>2</sub>N<sub>18</sub>Na<sub>2</sub>O<sub>46</sub>·8C<sub>3</sub>H<sub>7</sub>NO: C, 51.05%; H, 4.80%; N, 11.55%. Found: C, 51.49%; H, 4.33%; N, 11.73%. FTIR spectrum (Zn-Se (ATR), selected peaks): 1714 (COO),

1568 (C=O) cm<sup>-1</sup>. Absorption spectra (λ, nm, DMF (ε, M<sup>-1</sup> cm<sup>-1</sup>): 650 (100), 475 (sh), 300 (sh). Conductivity (~1 mM, DMF, 298 K):  $\Lambda_{\rm M}$  = 80 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> (the range for 1:1 electrolyte in CH<sub>3</sub>OH is 65–160). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>, 400 MHz): 7.93 (t, 2H, H10), 7.90 (s, 4H, H4), 7.57 (d, 4H, H9), 7.43 (s, 8H, H5). <sup>13</sup>C NMR spectrum (DMSO-*d*<sub>6</sub>, 100 MHz): δ = 167.07 (C2, COOH), 166.61 (C7, amide), 155.92 (C8), 146.84 (C6), 131.70 (C3), 131.43 (C10/ C9), 125.68 (C5), 124.79(C4).

**Synthesis of HCPs.**  $[{(1')_2 Zn_8 Na_2(H_2O)_{21}] \cdot 20H_2O]_n$  (2). HCP 2 was synthesized by treating a solution of  $Zn(OAc)_2 \cdot 2H_2O$  (0.75 g, 0.34 mmol) in CH<sub>3</sub>OH (3 mL) with a solution of metalloligand 1 (0.1 g, 0.08 mmol) in CH<sub>3</sub>OH (10 mL). The reaction mixture was stirred at room temperature for 2 h. Subsequently, a yellowish-green product was collected, washed several times with CH<sub>3</sub>OH, and dried under vacuum at ambient temperature. The crude product thus obtained was redissolved in water and layered with isopropyl alcohol at room temperature. After a period of three to four days, green colored crystals suitable for diffraction analysis were collected. Yield: 0.11 g (84%). Anal. Calcd for  $C_{92}H_{78}Co_2N_{12}Na_2O_{61}Zn_8 \cdot 20H_2O$ : C, 32.74%; H, 3.52%; N, 4.98%. Found: C, 32.60%; H, 3.80%; N, 4.90% . FTIR spectrum (Zn-Se attenuated total reflectance (ATR), selected peaks): 3347 (OH), 1565 (COO, C=O) cm<sup>-1</sup>. Diffused reflectance absorption spectra ( $\lambda_{max}$ , nm): 616, 450.

[{(1')(1")Cd<sub>8</sub>(H<sub>2</sub>O)<sub>21</sub>·32H<sub>2</sub>O]<sub>n</sub> (**3**). HCP **3** was prepared in a similar fashion with an identical scale as that of HCP **2**; however, Cd(OAc)<sub>2</sub>· 2H<sub>2</sub>O was used instead of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O. Green colored crystals of **3** were obtained after a period of three to four days. Yield: 0.15 g (90%). Anal. Calcd for C<sub>92</sub>H<sub>80</sub>Co<sub>2</sub>N<sub>12</sub>O<sub>61</sub>Cd<sub>8</sub>·32H<sub>2</sub>O: C, 28.16%; H, 3.70%; N, 4.28%. Found: C, 28.66%; H, 3.39%; N, 4.16%. FTIR spectrum (Zn-Se ATR, selected peaks): 3337 (OH), 1569 (COO, C= O) cm<sup>-1</sup>. Diffused reflectance absorption spectra ( $\lambda_{max}$  nm): 620, 470.

[{(1')<sub>2</sub>Mn<sub>8</sub>(Na)2(H<sub>2</sub>O)<sub>27</sub>]·3H<sub>2</sub>O]<sub>n</sub> (**4**). HCP 4 was also synthesized in a similar manner with an identical scale as mentioned for HCP **2**, however, using Mn(OAc)<sub>2</sub>·2H<sub>2</sub>O instead of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O. Green colored crystals of HCP **4** were obtained after a period of four to five days. Yield: 0.12 g (86%). Anal. Calcd for C<sub>92</sub>H<sub>90</sub>Co<sub>2</sub>N<sub>12</sub>Na<sub>2</sub>Mn<sub>8</sub>O<sub>67</sub>· 3H<sub>2</sub>O: C, 35.72%; H, 3.13%; N, 5.43%. Found: C, 35.96%; H, 3.39%; N, 5.16%. FTIR spectrum (Zn-Se ATR, selected peaks): 3345 (OH), 1562 (COO, C=O) cm<sup>-1</sup>. Diffused reflectance absorption spectra ( $\lambda_{max}$  nm): 630, 470.

General Procedure for the Knoevenagel Condensation Reaction. The respective aldehyde and active methylene substrates were dissolved in ethanol. The solid catalyst (1 mol %, 2, 3, and 4; based on the repeating unit of the polymer) was then added, and the reaction mixture was stirred at 50 °C for 1-3 h. The progress of the reaction was monitored by TLC (5% EtOAc/hexane) and/or GC. The solvent was removed under the reduced pressure, and the residue was triturated with ethyl acetate. The catalyst thus separated was collected by filtration, and the filtrate was concentrated to afford the crude organic product. This product was purified by column chromatography with 100-200 mesh silica using 1:1 EtOAc/hexanes as the eluent. The products were identified by GC, GC-MS, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopy when required. The isolated yield as well as characterization data for a few representative products is provided below whereas their <sup>1</sup>H and <sup>13</sup>C NMR spectra are included in Figures S14-S25.

**Characterization Data for a Few Representative Products.** (*E*)-*Ethyl 2-Cyano-3-(4-nitrophenyl)acrylate.* Yield: 95%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.35–8.33 (d, *J* = 8.8 Hz, 2H), 8.29 (s, 1H), 8.11–8.14 (d, *J* = 8.8 Hz, 2H), 4.44–4.39 (q, *J*<sub>1</sub> = 7.2 Hz, *J*<sub>2</sub> = 14.4, 2H), 1.39–1.43 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 161.451 151.86, 149.79, 136.97, 131.61, 124.43, 114.64, 107.43, 63.47, 14.20. ESI-MS spectrum (EtOAc): *m/z* = 246.

(E)-Ethyl 2-Cyano-3-(thiophen-2-yl)acrylate. Yield: 80%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.34 (s, 1H), 7.82–7.80 (d, *J* = 7.8, 1H), 7.79–7.77 (d, *J* = 7.8, 1H), 7.25–7.23 (m, *J* = 7.23, 1H), 4.38–4.33 (q, *J* = 0.36, 2H), 1.39–1.36 (t, 3H). <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 162.80, 148.83, 137.30, 136.09, 135.28, 128.71, 115.84, 99.36, 62.67, 14.30. ESI-MS spectrum (EtOAc): *m*/*z* = 207.

Table 1. Cryst	allographic Data	Collection and	l Structure I	Refinement	Parameters	for HCPs	2 - 4
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	HCP 2	HCP 3	HCP 4
mol formula	$C_{92}H_{78}Co_2N_{12}O_{61}Na_2Zn_8{\cdot}20H_2O$	$C_{92}H_{80}Co_2N_{12}O_{61}Cd_8{\cdot}32H_2O$	$C_{92}H_{90}Co_2N_{12}O_{67}Na2Mn_8\cdot 3H_2O$
fw	3164.29	3736.40	2984.69
<i>T</i> (K)	293(2)	293(2)	293(2)
cryst syst	monoclinic	triclinic	triclinic
space group	C2/m	$P\overline{1}$	$P\overline{1}$
a (Å)	19.108(5)	16.413(5)	16.280(5)
b (Å)	28.704(5)	18.430(5)	18.430(5)
c (Å)	13.646(5)	24.700(5)	23.550(4)
$\alpha$ (deg)	90	87.900(5)	89.061(5)
$\beta$ (deg)	99.582(5)	85.395(5)	89.688(5)
γ (deg)	90	75.058(5)	77.706(5)
V (Å <sup>3</sup> )	1380(4)	7195(3)	6903(3)
Z	2	2	2
$ ho~({ m g~cm^{-3}})$	1.424	1.725	1.436
F (000)	3144.0	3632	2968
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	1.594	1.491	1.040
collected reflns	48728	98875	79829
unique reflns	6652(0.0653)	25307(0.0894)	37922(0.0497)
no. of obs	5423	17973	21111
goodness of fit $(F^2)$	1.148	1.012	1.117
$R1^{a}$ , $wR2^{b}$ $[I > 2\sigma(I)]$	0.0796, 0.2697	0.0901, 0.2232	0.0775, 0.2130
R1 <sup>a</sup> , wR2 <sup>b</sup> [all data]	0.0944, 0.2843	0.1212, 0.2416	0.1055, 0.2292
${}^{a}R1 = \sum   F_{a}  -  F_{a}   / \sum  F_{a} , {}^{b}v$	$wR2 = \{\sum [w( F_{c} ^{2} -  F_{c} ^{2})^{2}] / \sum [wF_{c}^{4}]\}^{1}$	/2	

2-(Phenylmethylene)malononitrile. Yield: 95%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.91–7.88 (d, *J* = 7.9 Hz, 2H), 7.77 (s, 1H), 7.64–7.60 (t, *J* = 7.3 Hz, 1H), 7.55–7.51 (t, *J* = 7.9 Hz, 2H). <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.02, 134.74, 130.83, 130.28, 129.87, 114.12, 112.65, 82.92. ESI-MS spectrum (EtOAc): *m*/*z* = 154.

2-((Thiophen-2-yl)methylene)malononitrile. Yield: 90%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.87 (s, 2H), 7.80–7.79 (d, *J* = 3.6 Hz, 1H), 7.27–7.25 (dd, *J* = 4.8 Hz, 1H). <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.30, 138.41, 137.09, 135.48, 129.15, 113.92, 113.08, 78.31. ESI-MS spectrum (EtOAc): *m*/*z* = 160.

2-((Furan-2-yl)methylene)malononitrile. Yield: 80%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.78–7.7 (d, *J* = 1.83 Hz, 1H), 7.51 (s, 1H), 7.32–7.24 (d, *J* = 3.6 Hz, 1H), 6.69–6.68 (dd, *J* = 1.8 Hz, 1H). <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 149.81, 148.51, 143.29, 123.91, 114.59, 113.99, 112.77. ESI-MS spectrum (EtOAc): m/z = 144.

2-(3-Methoxybenzylidine)malononitrile. Yield: 95%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.73 (s, 1H), 7.48 (s, 1H), 7.45–7.39 (m, 2H), 7.17–7.15 (m, 1H), 3.85 (s, 3H). <sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 162.21, 160.03, 132.12, 130.69, 124.04, 121.48, 114.13, 113.76, 112.71, 83.03, 55.63. ESI-MS spectrum (EtOAc): m/z = 184.

Physical Methods. The FTIR spectra (Zn-Se ATR, 4000-600 cm<sup>-1</sup>) were recorded with a PerkinElmer Spectrum-Two spectrometer. The NMR spectroscopic measurements were carried out with a Jeol 400 MHz spectrometer. The absorption spectra were recorded with either PerkinElmer Lambda 25 or Lambda 35 spectrophotometers. The elemental analysis data were obtained with an Elementar Analysen Systeme GmbH Vario EL-III instrument. Gas chromatographic analyses were done with a PerkinElmer Clarus-580 instrument having an Elite-5 column. GC-MS studies were performed with a Shimadzu instrument (QP 2010) with an RTX-5SIL-MS column. Thermal gravimetric analysis (TGA) was performed with a DTG 60 Shimadzu at 5 °C min<sup>-1</sup> heating rate under a nitrogen atmosphere. The X-ray powder diffraction (XRPD) studies were performed with either an X'Pert Pro from Panalytical or a Bruker AXS D8 Discover instrument (Cu K $\alpha$  radiation,  $\lambda = 1.54184$  Å). The samples were ground and subjected to the range of  $\theta$  = 5–30 °C with a scan rate of 1–0.72

 $^{\circ}$ /min at room temperature. SEM measurements were performed with a Jeol SM 6610 LV instrument.

Single-Crystal Structure Determination. The intensity data for HCPs 2-4 were collected at 298 K with an Oxford XCalibur CCD diffractometer equipped with graphite monochromated Mo K $\alpha$ radiation ( $\lambda = 0.71073$  Å).<sup>75</sup> An empirical absorption correction was applied using spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm.<sup>75</sup> The structures were solved by direct methods using SIR-92<sup>76</sup> and refined by full-matrix least-squares refinement techniques on  $F^2$  using the program SHELXL-97 for HCP 2 and SHELXH-97 for HCPs 3 and 4 in the WinGX module.<sup>77,78</sup> The hydrogen atoms were fixed at the calculated positions with isotropic thermal parameters whereas all non-hydrogen atoms were refined anisotropically. In all cases, hydrogen atoms of the coordinated and lattice water molecules could not be located from the difference Fourier map; however, their numbers have been included in the empirical formulas. In addition, a few highly disordered water molecules were removed by using the SQUEEZE procedure implemented in PLATON,<sup>79</sup> which considerably improved the structure convergence; however, their numbers have been added to the empirical formulas of all HCPs. For HCP 4, some unassigned electron density was noted very close to Mn atoms (<1 Å) due to absorption artifacts. Details of the crystallographic data collection and structural solution parameters are provided in Table 1.

## RESULT AND DISCUSSION

**Synthesis and Characterization.** The metalloligand Na[Co(L<sup>3,5-COOH</sup>)<sub>2</sub>] (1) offers eight uncoordinated arylcarboxylic acid groups. This metalloligand on reaction with M(OAc)<sub>2</sub>. 2H<sub>2</sub>O salts produced the desired HCPs **2**–**4** (Scheme 2). It is important to note that the metalloligand **1** was found to exist in either its 9-form (1') or its 7-form (1'') in the resultant HCPs (Scheme 2). Reaction of **1** with secondary metal salt resulted in a distinct color change from deep green to pale green followed by the precipitation of compound. All three HCPs were recrystallized from H<sub>2</sub>O. The three HCPs exhibit strong bands between 1555 and 1570 cm<sup>-1</sup> due to  $\nu_{COO}$  as well as  $\nu_{C=O}$  stretches in their FTIR spectra. In addition, broad features

Scheme 2. Metalloligand 1 and Its Two Observed Anionic Forms 1' and 1" and the Resultant Heterometallic Coordination Polymers 2–4



between 3300 and 3400 cm<sup>-1</sup> are indicative of the presence of coordinated as well as lattice water molecules (Figure S1). HCPs 2-4 displayed the absorption maxima in the range of 615-630 nm in their diffused reflectance absorption spectra (Figure S2). Such a band is tentatively assigned to the d-dtransition in the  $Co^{3+}$  ion of the metalloligand core. The three HCPs were also characterized by measuring their XRPD patterns. The XRPD patterns of the as-synthesized HCPs 2-4 were found to be in great agreement to those simulated from the single-crystal structural data. Such a fact indicates phase purity of the bulk crystalline sample (Figures \$3-\$5). Thermogravimetric analysis (TGA) and differential scanning colorimetry (DSC) studies of HCPs 2-4 reveal a weight loss between 25 and 180 °C assigned to the loss of water molecules (Figures S6 and S7). For HCP 2, observed and calculated weight losses were 7.56 and 7.38% for the loss of 41 (21 coordinated and 20 uncoordinated) water molecules. Similarly, for HCP 3, observed and calculated weight changes were 10.37 and 9.54% for the loss of 21 coordinated and 32 uncoordinated water molecules. For HCP 4, thermal weight loss corresponds to the loss of 9 coordinated and 28 uncoordinated water molecules (obsd/calcd, 5.44/5.40). Importantly, TGA and DSC studies were adequately supported by the microanalysis results and crystallographic data for all three HCPs 2-4. Thermal studies further suggested that all three HCPs are thermally stable close to 400 °C.

**Crystal Structures and Topological Analysis.** All three HCPs **2–4** were characterized by single crystal X-ray diffraction analysis and then simplified by the topological analysis to understand the network generation via the mediation of metalloligands. For all three HCPs, Table 2 provides selected bond distances whereas Tables S1–S3 contain detailed bonding

Table 2. Selected Bond Distances and Ranges (Å) for HCPs 2-4

parameters. Metalloligand 1 has four aryldicarboxylic acid functional groups and as a consequence offers eight free carboxylic acid groups. HCPs 2-4 are constituted from metalloligand 1 offering arylcarboxylic acid groups that coordinate to  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Mn^{2+}$  ions, respectively. Notably, metalloligand 1 was found to coordinate the secondary metals either through all eight carboxylate groups (1' form) or via six  $-COO^{-}$  and two -COOH groups (1" form; cf. Scheme 2). The molecular structures of HCPs 2, 3, and 4 are quite different; however, the central metalloligand core is nearly identical, in which two tridentate ligands create an N<sub>6</sub> coordination environment around the Co<sup>3+</sup> ion. Two ligands coordinate the Co3+ ion via five-membered chelate rings between  $N_{amide}$  and  $N_{pyridine}$  atoms. The Co $-N_{pyridine}$  bond distances (1.853–1.867 Å) are much shorter than Co $-N_{amide}$ bond distances (1.938–1.974 Å).<sup>57,58</sup> Further, all diagonal angles are close to linear, ranging from 174.8° to 179.6°, suggesting a symmetrical arrangement of donors around the cobalt ion. Notably, two tridentate ligands enforce a compressed octahedral geometry around the Co3+ ion.57,

HCP 2 was crystallized in the monoclinic cell with C2/mspace group. The unit cell of HCP 2 contains 2 metalloligands, 8  $Zn^{2+}$  ions, 2  $Na^+$  ions, and 21 coordinated and 20 uncoordinated water molecules. A thermal ellipsoidal representation of asymmetric unit without lattice water molecules is shown in Figure 1a. The crystal structure of HCP 2 shows that the Co<sup>3+</sup>-based metalloligands are connected through the secondary Zn<sup>2+</sup> ions. Every metalloligand offers four appended aryldicarboxylic acid groups, and as a result, a total eight carboxylate groups are available. Out of eight O<sub>carboxylate</sub> atoms, O3 and O4 coordinate to Zn1 atom, O<sub>carboxylate</sub> atoms O5 and O6 bridge Zn2 and Zn3 atoms, O7 ligates to Zn1 while O8 remains free, and the remaining two, O9 and O10, coordinate to Na<sup>+</sup> and Zn2 ions, respectively (Figure 1b). The sixcoordinated Zn1 is ligated by three  $O_{\text{carboxylate}}$  atoms (O3 and O4 from one metalloligand and O7 from another metalloligand) while the remaining three sites are occupied by the water molecules (O1W, O2W, and O3W) (Figure 1c). The sixcoordinated Zn2 ion is coordinated by four  $O_{\text{carboxylate}}$  atoms (O5, O5<sup>#</sup>, O9, and O9<sup>#</sup>) from different metalloligands and two axial water molecules (O5W and O4W) (Figure 1c). The seven-coordinated Zn3 is ligated by two O<sub>carboxylate</sub> atoms (O6 and O6<sup>#</sup>) from two different metalloligands and five water molecules (O5W, O6W, O8W, O6W, and O8W) (Figure 1c). The four-coordinated  $Na^+$  ion is ligated by two  $O_{carboxylate}$  (O10 and O10<sup>#</sup>) from two different metalloligands and two water molecules (O5W and O7W). The secondary  $Zn^{2+}$  ions coordinated by carboxylate groups constitute the secondary building units (SBUs) that are connected to different

bon	nd	HCP 2	HCP 3	HCP 4
Co1-N	1	1.962	1.946(8)	1.952(4)
Co1-N2	2	1.859	1.853(8)	1.856(3)
Co1-N	3	1.958	1.974(8)	1.948(5)
Co1-N-	4		1.960(7)	1.955(4)
Co1-N	5		1.867(8)	1.858(4)
Co1-N	6		1.963(7)	1.938(4)
$M^{a}-O_{ca}$	arboxylate	1.949(6)-2.361(6)	2.173(8)-2.581(9)	2.099(5)-2.379(9)
$M^a - O_w$	ater	2.052(8)-2.290	2.24 (1)-2.515(9)	2.01(2) - 2.441(7)

 ${}^{a}M = Zn^{2+}$  (for HCP 2),  $Cd^{2+}$  (for HCP 3),  $Mn^{2+}$  (for HCP 4).



Figure 1. (a) Asymmetric unit of HCP 2; thermal ellipsoids are drawn at the 30% probability level, whereas hydrogen atoms and lattice water molecules are omitted for clarity. Color code: light green, Co; yellow, Zn; blue, N; green,  $O_{carboxylate}$ ; purple,  $O_{water}$ ; red,  $O_{amide}$ ; gray, C; pink, Na. (b) Wire and stick representation of a selected part of HCP 2 which shows the coordination of metalloligand 1 with secondary Zn<sup>2+</sup> and Na<sup>+</sup> ions. (c) Polyhedron representations of the coordination spheres of Zn(II) ions (Zn1–Zn3). (d) Space-filling mode of the extended structure of HCP 2 along the *a*-axis. Color code: selected part of HCP in red; yellow, Zn; blue, Na. (e) Topological representation of HCP 2. Color code: green, dimer of metalloligand 1; yellow, Zn.

metalloligands generating a 3D architecture (Figure 1d). HCP 2 offers solvent-accessible voids (SAVs) of 1935.5 Å<sup>3</sup>, corresponding to 26.2% of the unit cell volume (7380.0 Å<sup>3</sup>), which are filled by the lattice water molecules.

HCP 2 was simplified by the ToposPro software<sup>80–83</sup> using the standard simplification method. HCP 2 contains different types of SBUs<sup>69–72,84,85</sup> that are composed of Zn atom coordinated by a certain number of arylcarboxylate groups, such as Zn1(COO)<sub>2</sub>, Zn2(COO)<sub>4</sub>, and Zn3(COO)<sub>2</sub>. Such SBUs function as the SBU nodes in the resultant network.<sup>86–91</sup> Further, Co<sup>3+</sup>-based metalloligands also act as the multitopic nodes (defined as the ML nodes) that are connected with different SBUs to generate a network with a unique topology.<sup>69–72</sup> In the present case, a dimer of metalloligands acting as a ML node was connected to a total of 20 different Zn(II) ions (8Zn1, 6Zn2 and 6Zn3 ions). Herein, Zn1, Zn2, and Zn3 atoms were found to respectively connect to 2, 3, and 3 ML nodes. Such an arrangement generates a network with an overall point symbol of  $\{4\land3\}4\{4\land42.6\land24.8\land108.12\land16\}$ {4}4 where the individual contribution of Zn1, Zn2, and Zn3 was {4}, {4\land3}, and {4\land3}, respectively, whereas metalloligand contributed {4\land42.6\land24.8\land108.12\land16} (Figure 1e).

HCP 3 was crystallized in triclinic cell with  $P\overline{1}$  space group. The unit cell of HCP 3 contains 2 metalloligands, 8 Cd<sup>2+</sup> ions, and 21 coordinated and 32 lattice water molecules. Figure 2a displays the asymmetric unit of HCP 3, however, without the lattice water molecules. In this case, two metalloligands are connected with 8 symmetrically unique Cd<sup>2+</sup> ions (Figure 2b). Two metalloligands offer 16 carboxylic acid groups; however, only 14 exist in the anionic carboxylate form and coordinate to



**Figure 2.** (a) Asymmetric unit of HCP 3; thermal ellipsoids are drawn at the 30% probability level, whereas hydrogen atoms and lattice water molecules are omitted for clarity. Color code: light green, Co; yellow, Cd; blue, N; green,  $O_{carboxylate}$ ; purple,  $O_{water}$ ; red,  $O_{amide}$ ; gray, C. (b) Wire and stick representation of a selected part of HCP 3 which shows the coordination of metalloligand 1 with secondary Cd<sup>2+</sup> ions. (c) Wire and stick representations of the appended aryldicarboxylic acid groups and their coordination with Cd<sup>2+</sup> ions (Cd1–Cd8).

 $Cd^{2+}$  ions whereas two groups remain as the carboxylic acid and participate in intermolecular H-bonding with the lattice water molecules. Figure 2c displays different coordination modes of the carboxylate groups as well as carboxylic acid synthons. HCP 3 displayed SAVs of volume 595.5 Å<sup>3</sup> that corresponded to 8.3% (7195.0 Å<sup>3</sup>) of its cell volume.

The coordination environments of eight different  $Cd^{2+}$  ions, described by polyhedra, are shown in Figure 3a. Importantly, out of eight Cd<sup>2+</sup> ions, three are six-coordinated (Cd1, Cd3, and Cd7) whereas the remaining five are seven-coordinated (Cd2, Cd4, Cd5, Cd6, and Cd8). The coordination environment around various  $Cd^{2+}$  ions changes drastically. For example, six-coordinated Cd1 ion is ligated only to Ocarboxylate atoms (O3, O4, O8, O13, O23, and O32) whereas sixcoordinated Cd7 atom is ligated with one  $\mathrm{O27}_{\mathrm{carboxylate}}$  atom and five water molecules (O17W, O18W, O19W, O20W, and O21W). The Cd(COO)<sub>n</sub> based SBUs  $[Cd1(COO)_4, Cd2-$ (COO)<sub>3</sub>, Cd3(COO)<sub>3</sub>, Cd4(COO)<sub>2</sub>, Cd5(COO)<sub>2</sub>, Cd6- $(COO)_3$ , Cd7(COO), and Cd8(COO)\_2] are connected with different metalloligands to generate a 3D structure (Figure 3b). Topological analysis of HCP 3 shows that different SBU nodes are connected to ML nodes;<sup>69-72,84,85</sup> however, topological contribution of SBU Cd7(COO) was not considered as it was not involved in extending the network. Notably, there were two

types of multitopic metalloligand-based nodes, ML-1 and ML-2 (shown in red and blue, respectively), which were connected to 12 and 6 Cd ions, respectively. The network topological analysis revealed an overall point symbol of  $\{4.6.8\}$   $\{4\land15.6\land19.8\land27.10\land5\}$  $\{4\land3.6\land3.8\land9\}$  $\{4\land3\}$  $\{4\land4.6\land2\}$  $\{4\}2$ {8}2 (Figure 3c) where metalloligand-based nodes, ML-1 and ML-2, contributed  $\{4\land15.6\land19.8\land27.10\land5\}$  and  $\{4\land3.6\land3.8\land9\}$ , respectively.<sup>84,85</sup> On the other hand, SBUs based on Cd1, Cd2, Cd3, Cd4, Cd5, Cd6, and Cd8 respectively provided  $\{4\land4.6\land2\}$ ,  $\{4.6.8\}$ ,  $\{4\}$ ,  $\{8\}$ ,  $\{8\}$ ,  $\{4\land3\}$ , and  $\{4\}$  point symbols.

HCP 4 was crystallized in triclinic cell with  $P\overline{1}$  space group. The unit cell of HCP 4 contains 2 metalloligands, 8 Mn<sup>2+</sup> ions, 2 Na<sup>+</sup> ions, and 27 coordinated and 3 uncoordinated water molecules. The asymmetric unit of HCP 4 is presented in Figure 4a, however, without lattice water molecules. In this case also, a dimer composed of two metalloligands is involved in generating the network via Mn(COO)<sub>n</sub>-based SBUs (Figure 4b). Out of 16 carboxylate groups from a dimer of two metalloligands, 15 -COO<sup>-</sup> groups coordinate to 8 Mn<sup>2+</sup> and 2 Na<sup>+</sup> ions whereas one carboxylate group (with O7 and O8 atoms) does not participate in bonding (Figure 4c).

The local coordination environment of all SBUs, described by the polyhedron representation, is shown in Figure 5a. **Crystal Growth & Design** 



**Figure 3.** (a) Polyhedron representations of the coordination spheres of  $Cd^{2+}$  ions (Cd1–Cd8) in HCP 3. Color code: yellow, Mn; green,  $O_{carboxylate}$ , purple,  $O_{water}$ ; gray, C. (b) Extended structure of HCP 3 along the *a*-axis. Color code: selected part of HCP in red; light green, Co; yellow, Cd. (c) Topological representation of HCP 3. Color code: red and blue, two different types of metalloligands Co1 and Co2; yellow, Cd.

Interestingly, out of eight  $Mn^{2+}$  ions, four are six-coordinated (Mn4, Mn6, Mn7, and Mn8) whereas the remaining four are seven-coordinated (Mn1, Mn2, Mn3, and Mn5). Various  $Mn^{2+}$  ions receive coordination from a combination of  $O_{carboxylate}$  and  $O_{water}$  ranging from all six  $O_{carboxylate}$  ligation in Mn4 to one  $O_{carboxylate}$  and five  $O_{water}$  in Mn8. A combination of bonding between metalloligands and secondary  $Mn^{2+}$  ions generates a 3D network (Figure 5b). HCP 4 offered large SAVs of 1476.7 Å<sup>3</sup> correlating to 21.4% of cell volume (6903.0 Å<sup>3</sup>). Such voids were noted to be filled by the lattice water molecules.

In topological simplification,  $^{80-85}$  SBUs Mn1(COO)<sub>2</sub>, Mn2-(COO)<sub>2</sub>, Mn3(COO)<sub>2</sub>, Mn4(COO)<sub>4</sub>, Mn5(COO)<sub>2</sub>, Mn6-(COO)<sub>5</sub>, and Mn7(COO)<sub>3</sub> were found to contribute point symbols {4}, {4}, {4, {4^3}, {4^3}, {4^3}, {4^3}, {4}, and {4}, respectively. The SBU based on Mn8(COO) did not contribute to the point symbol as it was not involved in extending the network. Similarly, the point symbol of metalloligand-based node was {4^30.6^27.8^68.10^11} whereas the overall point symbol of HCP 4 was found to be {4^30.6^27.8^68.10^11}{4^3}{4^3} (Figure 5c).

Heterogeneous Catalysis. As a new class of crystalline porous materials, coordination polymers have attracted a great deal of interest; and a number of such architectures have been utilized as the heterogeneous catalysts for various organic transformations.<sup>32–36</sup> The possibilities to carry out the catalysis heterogeneously and perform structure-specific reactions have been the major advantages of coordination polymers.<sup>92,93</sup> The crystal structures of three HCPs show several important features that suggested their potential applications in catalysis. For example, (i) all three HCPs contain Lewis acidic secondary metal ions, Zn(II), Cd(II), and Mn(II), arranged in an orderly manner; (ii) such secondary metals are coordinated by the labile water molecules that are likely to be replaced by the substrates and/or reagents; (iii) all three HCPs are thermally stable close to 400 °C; and (iv) all three HCPs are insoluble in common organic solvents therefore suggesting their probable roles as the heterogeneous catalysts. We selected Knoevenagel condensation reaction of aromatic aldehydes with substrates having active methylene groups to provide benzylidene derivatives.<sup>94,95</sup> This reaction has been a favorite test reaction to assess the strength of solid and heterogeneous catalysts.

Knoevenagel Condensation Reactions. Knoevenagel condensations (KCs) are significant for their role in C–C double bond formation and are frequently used in organic synthesis.<sup>94,95</sup> KCs can be catalyzed by various reagents, acids, and bases, as well as assorted Lewis acids.<sup>94,104</sup> In this context,



Figure 4. (a) Asymmetric unit of HCP 4; thermal ellipsoids are drawn at the 30% probability level, whereas hydrogen atoms and lattice water molecules are omitted for clarity. Color code: light green, Co; yellow, Mn; blue, N; green,  $O_{carboxylate}$ ; purple,  $O_{water}$ ; red,  $O_{amide}$ ; gray, C. (b) Wire and stick representation of a selected part of network which shows the coordination of metalloligand 1 with secondary  $Mn^{2+}$  and  $Na^+$  ions. (c) Wire and stick representations of the appended aryldicarboxylic acid groups and their coordination to  $Mn^{2+}$  (Mn1-Mn8) and  $Na^+$  ions (Na1 and Na2). Color code: yellow, Mn; blue, N; green,  $O_{carboxylate}$ ; gray, C.

Lewis acid based heterogeneous catalysts, particularly reusable ones, are important due to their high efficiency and ease in product separation.<sup>94,95</sup> HCPs **2–4** were tested as the potential heterogeneous catalysts for KCs using assorted aromatic and heterocyclic aldehydes with three active methylene compounds, ethyl cyanoacetate, 1,3-diketocyclohexane, and malononitrile.

To optimize the best reaction conditions, several control experiments were performed using HCP 2 as a model catalyst in a reaction of benzaldehyde with ethyl cyanoacetate (Table 3). It was noted that the catalyst was essential, as no product was obtained without it (entry 1). Entry 2 shows that only 1 mol % HCP 2 was able to catalyze the reaction and produces the product in 40% at 25 °C; however, a mild elevated temperature of 50 °C led to nearly quantitative reaction (entry 3). The presence of solvent plays an important role which probably allows better mixing and thus a facile reaction between the reagents (entry 4). The quantitative product yield was noted at 4 h, although 98% transformation had already taken place within 3 h (entry 5). Ethanol was adjudged to be the best solvent for the condensation reaction, as other solvents such as MeOH, MeCN, EtOAc, and toluene resulted in considerably lower conversion (entry 6). Notably, use of water as the solvent led to nearly 50% yield (data not shown); however, it also caused partial dissolution of HCPs and therefore was not used.  $^{105}$  Entry 7 displays that only 1 mol %catalyst loading was sufficient for the complete reaction. Finally, use of  $M(OAc)_2 \cdot 2H_2O$  salts (M = Zn, Cd, and Mn) as the

catalysts resulted in negligible product formation (entry 8). Such a fact suggests that catalytically active M(II) ions have not leached out from the HCPs.

These optimized reaction conditions were employed to explore the scope of catalysis for all three HCPs, and the results are summarized in Table 4. Three different types of reagents having active methylene groups, ethyl cyanoacetate, 1,3cyclohexanedione, and malononitrile, were used with assorted aldehydes (Table 4). Thus, when benzaldehyde was treated with ethyl cyanoacetate in the presence of only 1 mol % of any of the HCPs, a smooth reaction took place that produced ethyl 2-cyano-3-phenylacrylate in high yield (entry 1).<sup>106</sup> Subsequently, a variety of substituted aldehydes were treated with ethyl cyanoacetate (entries 1-6), 1,3-cyclohexanedione (entries 7-12), and malononitrile (entries 13-18) in the presence of catalysts, and such reactions afforded the desirable products in high yield (Table 4).<sup>107</sup> Importantly, assorted electronic substituents present on a substrate did not result in considerable effect on the yield. For example, substituted benzaldehydes having p-NO2, p-Cl, or m-OMe substituents produced the corresponding products in yield as good as noted for benzaldehyde. Such an observation suggests that the catalytic reactions are not driven by the electronic factors. Further, heterocyclic aldehydes such as furan-2-carbaldehyde as well as thiophene-2-carbaldehyde all provided high yield of the respective products. Importantly, malononitrile resulted in nearly quantitative transformation with most of the substrates



Figure 5. (a) Polyhedron representations of the coordination sphere of  $Mn^{2+}$  (Mn1–Mn8). Color code: yellow, Mn; green,  $O_{carboxylate}$ ; purple,  $O_{water}$ ; gray, C. (b) Extended structure of HCP 4 along the *a*-axis. Color code: selected part of HCP in red; green, Co; yellow, Mn; blue, Na. (b) Topological representation of HCP 4. Color code: green; dimer of metalloligands Co1 and Co2; yellow, Mn.

Table 3. Con	trol Experiments fo	or the Knoevenagel	Condensation	of Benzaldehyde	with Ethyl	Cyanoacetate	Using HCP	' 2 as a
Model Cataly	/st	C C						

	CHO + CN COO	DEt Catalyst COOEt			
entry	catalyst [mol %]	solvent	time (h)	temp (°C)	yield <sup>a</sup> (%)
1		EtOH	4	25	0
2	2 [1]	EtOH	4	25	40
3	2 [1]	EtOH	4	50	>99
4	2 [1]		4	25, 50	22, 55
5	2 [1]	EtOH	1, 2, 3, 4	50	40, 72, 98, >99
6	2 [1]	MeOH, CH <sub>3</sub> CN, EtOAc, Toluene	4	50	45, 18, 22, 35
7	2 [0.5, 1, 2]	EtOH	4	50	70, 99, 99
8	$Zn(OAc)_2.2H_2O, Cd(OAc)_2.2H_2O, Mn(OAc)_2.2H_2O$	EtOH	4	50	2, 2, 4
a					

<sup>a</sup>Yield was calculated using gas chromatography.

Table 4. Knoevenagel Condensations of Assorted Aldehydes with Ethyl Cyanoacetate (A), 1,3-Cyclohexanedione (B), and Malononitrile (C) Using HCPs  $2-4^a$ 



			yield <sup>®</sup> (%)		
R	reagents	time (h)	HCP 2	HCP 3	HCP 4
C <sub>6</sub> H <sub>5</sub>	Α	3	98 (10) <sup>c</sup>	92	95
$4-NO_2C_6H_4$	Α	3	99	94	96
4-ClC <sub>6</sub> H <sub>4</sub>	Α	3	86	83	86
3-MeOC <sub>6</sub> H <sub>4</sub>	Α	3	83	87	80
furan-2-yl	Α	3	83	90	83
thiophen-2-yl	Α	3	86	91	77
C <sub>6</sub> H <sub>5</sub>	В	3	80 (8) <sup>c</sup>	75	78
$4-NO_2C_6H_4$	В	3	85	83	82
4-ClC <sub>6</sub> H <sub>4</sub>	В	3	80	82	80
$3-MeOC_6H_4$	В	3	81	85	80
furan-2-yl	В	3	75	80	75
thiophen-2-yl	В	3	79	82	65
C <sub>6</sub> H <sub>5</sub>	С	1	98 $(28)^c$	96	95
$4-NO_2C_6H_4$	С	1	99	99	99
4-ClC <sub>6</sub> H <sub>4</sub>	С	1	99	>99	>99
3-MeOC <sub>6</sub> H <sub>4</sub>	С	1	99	>99	>99
furan-2-yl	С	1	85	89	80
thiophen-2-yl	С	1	95	90	90
	R $C_{6}H_{5}$ $4-NO_{2}C_{6}H_{4}$ $4-ClC_{6}H_{4}$ $3-MeOC_{6}H_{4}$ furan-2-yl           thiophen-2-yl $C_{6}H_{5}$ $4-NO_{2}C_{6}H_{4}$ $4-ClC_{6}H_{4}$ $3-MeOC_{6}H_{4}$ $4-ClC_{6}H_{4}$ $4-NO_{2}C_{6}H_{4}$ $4-NO_{2}C_{6}H_{4}$ $4-NO_{2}C_{6}H_{4}$ $4-NO_{2}C_{6}H_{4}$ $4-ClC_{6}H_{4}$ $3-MeOC_{6}H_{4}$ $6-R_{5}$ $4-NO_{2}C_{6}H_{4}$ $4-ClC_{6}H_{4}$ $3-MeOC_{6}H_{4}$ $6-R_{1}-2-yl$ thiophen-2-yl	R         reagents $C_6H_5$ A $4\cdotNO_2C_6H_4$ A $4\cdotClC_6H_4$ A $3\cdotMeOC_6H_4$ A           furan-2.vl         A           thiophen-2.vl         A $C_6H_5$ B $4\cdotOlC_6H_4$ B $4\cdotOlC_6H_4$ B $4\cdotOlC_6H_4$ C $4\cdotOlC_6H_4$ C $6_6H_5$ C $4\cdotOlC_6H_4$ C	R         reagents         time (h)           C <sub>6</sub> H <sub>5</sub> A         3           4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> A         3           4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> A         3           4-ClC <sub>6</sub> H <sub>4</sub> A         3           3-MeOC <sub>6</sub> H <sub>4</sub> A         3           furan-2-yl         A         3           thiophen-2-yl         A         3           C <sub>6</sub> H <sub>5</sub> B         3           4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> B         3           4-ClC <sub>6</sub> H <sub>4</sub> B         3           furan-2-yl         B         3           6 <sub>c</sub> H <sub>5</sub> C         1           furan-2-yl         B         3           c <sub>6</sub> H <sub>5</sub> C         1           Hiophen-2-yl         B         3           c <sub>6</sub> H <sub>5</sub> C         1           +NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> C         1           4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> C         1           4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> C         1           4-ClC <sub>6</sub> H <sub>4</sub> C         1           3-MeOC <sub>6</sub> H <sub>4</sub> C         1           6         1         1 <tr tboppen-2-yl<="" td="">         C  <!--</td--><td>Rreagentstime (h)HCP 2<math>C_{c}H_{5}</math>A398 (10)^{c}<math>4 \cdot NO_{2}C_{6}H_{4}</math>A399<math>4 \cdot ClC_{6}H_{4}</math>A386<math>3 \cdot MeOC_{6}H_{4}</math>A383furan-2-ylA386<math>C_{c}H_{5}</math>B380 (8)^{c}<math>4 \cdot NO_{2}C_{6}H_{4}</math>B385<math>4 \cdot ClC_{6}H_{4}</math>B381furan-2-ylB375thiophen-2-ylB379<math>C_{c}H_{5}</math>C198 (28)^{c}<math>4 \cdot NO_{2}C_{6}H_{4}</math>C199<math>4 \cdot ClC_{6}H_{4}</math>C199<math>4 \cdot ClC_{6}H_{4}</math>C199<math>5 \cdot MeOC_{6}H_{4}</math>C199furan-2-ylC185thiophen-2-ylC185</td><td>Network intermediation intermediatintermediation intermediation int</td></tr>	Rreagentstime (h)HCP 2 $C_{c}H_{5}$ A398 (10)^{c} $4 \cdot NO_{2}C_{6}H_{4}$ A399 $4 \cdot ClC_{6}H_{4}$ A386 $3 \cdot MeOC_{6}H_{4}$ A383furan-2-ylA386 $C_{c}H_{5}$ B380 (8)^{c} $4 \cdot NO_{2}C_{6}H_{4}$ B385 $4 \cdot ClC_{6}H_{4}$ B381furan-2-ylB375thiophen-2-ylB379 $C_{c}H_{5}$ C198 (28)^{c} $4 \cdot NO_{2}C_{6}H_{4}$ C199 $4 \cdot ClC_{6}H_{4}$ C199 $4 \cdot ClC_{6}H_{4}$ C199 $5 \cdot MeOC_{6}H_{4}$ C199furan-2-ylC185thiophen-2-ylC185	Network intermediation intermediatintermediation intermediation int
Rreagentstime (h)HCP 2 $C_{c}H_{5}$ A398 (10)^{c} $4 \cdot NO_{2}C_{6}H_{4}$ A399 $4 \cdot ClC_{6}H_{4}$ A386 $3 \cdot MeOC_{6}H_{4}$ A383furan-2-ylA386 $C_{c}H_{5}$ B380 (8)^{c} $4 \cdot NO_{2}C_{6}H_{4}$ B385 $4 \cdot ClC_{6}H_{4}$ B381furan-2-ylB375thiophen-2-ylB379 $C_{c}H_{5}$ C198 (28)^{c} $4 \cdot NO_{2}C_{6}H_{4}$ C199 $4 \cdot ClC_{6}H_{4}$ C199 $4 \cdot ClC_{6}H_{4}$ C199 $5 \cdot MeOC_{6}H_{4}$ C199furan-2-ylC185thiophen-2-ylC185	Network intermediation intermediatintermediation intermediation int				

<sup>*a*</sup>Conditions: catalyst, 1 mol %; solvent, EtOH; temperature, 50 °C. <sup>*b*</sup>Yield was calculated using gas chromatography. <sup>*c*</sup>The values in parentheses are the GC yield of the product without any catalyst under the otherwise identical conditions.

within 1 h (entries 13-18). Such a fact suggests the importance of an activated substrate in catalysis.

We then focused on plausible size-selective KC reactions<sup>108</sup> and selected sterically taxing substrates such as 1-naphthaldehvde and 2-naphthaldehvde as well as 9-anthraldehvde (Table 5). For these sterically hindered substrates, the results of KCs are compared to that of benzaldehyde. In general, product yields for the bulkier substrates were quite on the lower side when compared with benzaldehyde. We believe that, while benzaldehyde (molecular size:  $4.2 \times 6.03 \times 1.4$  Å<sup>3</sup>) could freely diffuse through the pores and channels offered by all three HCPs, 1-naphthaldehyde (molecular size:  $6.03 \times 6.64 \times 1.4$ Å<sup>3</sup>), 2-naphthaldehyde (molecular size: 5.66  $\times$  7.21  $\times$  1.4 Å<sup>3</sup>), and particularly 9-anthraldehyde (molecular size:  $6.22 \times 9.28 \times$ 1.4  $\overline{A}^3$ ) were too much bulkier to have favorable accessibility. Therefore, for these bulkier substrates, catalytic reaction primarily occurred on the surface rather than within the interior of the three HCPs. It is worth to note that yields were always on the higher side whenever malononitrile was used. Such a point suggests that an activated substrate could still result in higher product yield despite catalysis primarily occurring on the surface. Nevertheless, KC results depict that substrate size accessibility plays an important role in heterogeneous catalysis.

and crystallinity to delineate possible structural change(s) during the catalysis. In addition, such studies would also allow exploring their recyclability. For such studies, HCP 2 was selected as a model catalyst in the reaction of benzaldehyde with ethyl cyanoacetate. HCP 2 could be successfully used for five consecutive cycles without appreciable change in the catalytic performance (Figure S8). The HCP 2 was recovered after every catalytic cycle and characterized by the FTIR spectra and powder XRD studies. In addition, scanning electron micrograph (SEM) was recorded and compared to that of pristine sample to evaluate the morphological changes to the crystalline sample. The powder XRD pattern of the recovered HCP 2 shows that it maintained its crystallinity as well as structural integrity in the form of nearly superimposable peaks as compared to pristine sample (Figure S9). A similar conclusion can be drawn from the superimposable FTIR spectrum of the recovered catalysts to that of as-synthesized sample (Figure S10). These studies together with the reusability of HCP 2 (cf. Figure S8) adequately support the stable nature of HCPs in KCs. The SEM image of a single crystal of recovered HCP 2 illustrates only minor changes to the crystal surface, therefore further suggesting stable nature of HCPs (Figure S11).

Mechanistic Insights. The present catalysis results rely on two important assumptions: First, that the coordinated water molecules present on the Lewis acidic metals are labile and therefore are easily replaceable. Such a critical step allows a substrate to interact with the Lewis acidic metal before its activation followed by reaction with the active methylene compound. Second, that a substrate is freely able to diffuse through the pores and channels of HCPs. In order to support both suggested points, additional experiments were performed using HCP 2 as a representative case. To investigate that the coordinated water molecules are indeed labile in nature and a substrate is able to replace them, D<sub>2</sub>O exchange was performed. For such an experiment, powdered sample of HCP 2 was first heated at 150 °C under vacuum to remove lattice as well as coordinated water molecules followed by allowing the sample to equilibrate in a sealed environment of D<sub>2</sub>O vapors. Such an experiment resulted in nearly complete exchange of H<sub>2</sub>O by  $D_2O_1$  and the  $\nu_{O-D}$  stretches were observed at ca. 2500 cm<sup>-1</sup> with a shift of ca. 950 cm<sup>-1</sup> from  $\nu_{O-H}$  stretches (Figure S12).

To illustrate possible inclusion of a substrate within the pores and channels of HCPs, FTIR spectra were recorded. Thus, when a powdered sample of HCP 2 was impregnated with a CH<sub>2</sub>Cl<sub>2</sub> solution containing benzaldehyde, the FTIR spectrum displayed red-shifted  $\nu_{\rm C=O}$  stretches for the impregnated benzaldehyde by ca. 15 cm<sup>-1</sup> when compared to neat benzaldehyde (Figure S13). Further, inclusion of benzaldehyde resulted in considerable perturbation to the  $\nu_{\rm O-H}$  stretches of the coordinated/lattice water molecules. Both these features point toward inclusion of benzaldehyde within the pores of HCP. More importantly, red-shifted  $\nu_{C=O}$  stretches of the impregnated benzaldehyde strongly infer its activation by coordination to the Lewis acidic metal ion. We therefore conclude that an aldehydic substrate first replaces the coordinated water molecule(s) followed by its activation by the Lewis acidic metal before its reaction with the active methylene compound to produce the desired benzylidene derivatives.

Table 5. Knoevenagel Condensations of a Few Bulkier Aldehydes with Ethyl Cyanoacetate (A), 1,3-Cyclohexanedione (B), and Malononitrile (C) Using HCPs  $2-4^{a}$ 



<sup>a</sup>Conditions: catalyst, 1 mol %; solvent, EtOH; temperature, 50 °C. <sup>b</sup>Yield was calculated using gas chromatography.

## CONCLUSION

We have utilized a carboxylate-rich  $Co^{3+}$ -based metalloligand for the construction of  $\{Co^{3+}-M^{2+}\}$  (M = Zn, Cd, and Mn) heterometallic coordination polymers. The structure analyses exhibited 3D nature of three HCPs wherein metalloligands are connected through the secondary metals. The topological analyses illustrated that the metalloligands function as the nodes that are connected to SBUs composed of  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Mn^{2+}$  ions coordinated by the arylcarboxylate groups. All three HCPs acted as the heterogeneous catalysts for the Knoevenagel condensation reactions of assorted aldehydes. While the recyclability experiments substantiated the reusable nature of HCPs, the mechanistic studies suggested the potential activation of a substrate by the secondary Lewis acidic metal ion.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.6b00176.

FTIR spectra, diffuse reflectance absorption spectra, TGA and DSC plots, powder XRD patterns, SEM images, <sup>1</sup>H and <sup>13</sup>C NMR spectra, and tables of bond distances and bond angles (PDF)

## **Accession Codes**

CCDC 1451491–1451493 contains 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

The authors declare no competing financial interest.

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## REFERENCES

- (1) Kumar, G.; Gupta, R. Chem. Soc. Rev. 2013, 42, 9403.
- (2) Sessoli, R.; Powell, A. K. Coord. Chem. Rev. 2009, 253, 2328.
- (3) Kurmoo, M. Chem. Soc. Rev. 2009, 38, 1353.
- (4) Kuppler, R. J.; Timmons, D. J.; Fang, Q.-R.; Li, J.-R.; Makal, T. A.; Young, M. D.; Yuan, D.; Zhao, D.; Zhuang, W.; Zhou, H.-C. *Coord. Chem. Rev.* **2009**, 253, 3042.
- (5) Rasappan, R.; Laventine, D.; Reiser, O. Coord. Chem. Rev. 2008, 252, 702.

(6) Maspoch, D.; Ruiz-Molina, D.; Veciana, J. Chem. Soc. Rev. 2007, 36, 770.

(7) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. Chem. Rev. 2011, 111, 6810.

- (8) Cook, T. R.; Stang, P. J. Chem. Rev. 2015, 115, 7001.
- (9) Farha, O. K.; Hupp, J. T. Acc. Chem. Res. 2010, 43, 1166.
- (10) Chen, B.; Xiang, S.; Qian, G. Acc. Chem. Res. 2010, 43, 1115.

(11) Pan, L.; Olson, D. H.; Ciemnolonski, L. R.; Heddy, R.; Li, J. Angew. Chem., Int. Ed. 2006, 45, 616.

(12) Li, J. R.; Kuppler, R. J.; Zhou, H. C. Chem. Soc. Rev. 2009, 38, 1477.

(13) O'Keeffe, M.; Yaghi, O. M. Chem. Rev. 2012, 112, 675.

## **Crystal Growth & Design**

- (14) Tranchemontagne, D. J.; Mendoza-Cortés, J. L.; O'Keeffe, M.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1257.
- (15) Hu, Z.; Deibert, B. J.; Li, J. Chem. Soc. Rev. 2014, 43, 5815.
- (16) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. *Chem. Rev.* **2012**, *112*, 1105.
- (17) Potyrailo, R. A.; Surman, C.; Nagraj, N.; Burns, A. Chem. Rev. **2011**, 111, 7315.
- (18) Brozek, C. K.; Dinca, M. Chem. Soc. Rev. 2014, 43, 5456.
- (19) Ramaswamy, P.; Wong, N. E.; Shimizu, G. K. H. Chem. Soc. Rev. 2014, 43, 5913.
- (20) Sen, S.; Nair, N. N.; Yamada, T.; Kitagawa, H.; Bharadwaj, P. K. J. Am. Chem. Soc. **2012**, 134, 19432.
- (21) Sadakiyo, M.; Yamada, T.; Kitagawa, H. J. Am. Chem. Soc. 2014, 136, 13166.
- (22) Sadakiyo, M.; Yamada, T.; Kitagawa, H. J. Am. Chem. Soc. 2009, 131, 9906.
- (23) Hu, Z.; Deibert, B. J.; Li, J. Chem. Soc. Rev. 2014, 43, 5815.
- (24) Stavila, V.; Talin, A. A.; Allendorf, M. D. Chem. Soc. Rev. 2014, 43, 5994.
- (25) Wang, C.; Zhang, T.; Lin, W. Chem. Rev. 2012, 112, 1084.
- (26) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. Chem. Soc. Rev. 2009, 38, 1330.
- (27) Bunzli, J. C. G.; Piguet, C. Chem. Rev. 2002, 102, 1897.
- (28) Cheng, X. N.; Zhang, W. X.; Lin, Y. Y.; Zheng, Y. Z.; Chen, X. M. Adv. Mater. 2007, 19, 1494.
- (29) Wang, X. Y.; Wang, Z. M.; Gao, S. Chem. Commun. 2008, 281.
  (30) Deng, J. H.; Yuan, X. L.; Mei, G. Q. Inorg. Chem. Commun. 2010, 13, 1585.
- (31) Yang, Q. Y.; Li, K.; Luo, J.; Pan, M.; Su, C. Y. Chem. Commun. 2011, 47, 4234.
- (32) Ma, L. Q.; Abney, C.; Lin, W. Chem. Soc. Rev. 2009, 38, 1248.
  (33) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C.-Y. Chem. Soc. Rev. 2014, 43, 6011.
- (34) Dhakshinamoorthy, A.; Garcia, H. Chem. Soc. Rev. 2014, 43, 5750.
- (35) Corma, A.; Garcia, H.; Llabrés i Xamena, F. X. *Chem. Rev.* 2010, 110, 4606.
- (36) Lee, J. Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. B. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450.
- (37) Zhao, M.; Ou, S.; Wu, C.-D. Acc. Chem. Res. 2014, 47, 1199.
- (38) Horike, S.; Dinca, M.; Tamaki, K.; Long, J. R. J. Am. Chem. Soc. 2008, 130, 5854.
- (39) Roberts, J. M.; Fini, B. M.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T.; Scheidt, K. A. J. Am. Chem. Soc. **2012**, 134, 3334.
- (40) Wang, C.; Zheng, M.; Lin, W. J. Phys. Chem. Lett. 2011, 2, 1701.
  (41) Gu, X.; Xue, D. Inorg. Chem. 2006, 45, 9257.
- (42) Zhang, S.; Li, H.; Duan, E.; Han, Z.; Li, L.; Tang, J.; Shi, W.; Cheng, P. *Inorg. Chem.* **2016**, *55*, 1202.
- (43) Gasnier, A. E.; Barbe, J. M.; Bucher, C.; Duboc, C.; Moutet, J. C.; Saint-Aman, E.; Terech, P.; Royal, G. *Inorg. Chem.* **2010**, *49*, 2592.
- (44) Kilduff, B.; Pogozhev, D.; Baudron, S. E. A.; Hosseini, M. W. Inorg. Chem. 2010, 49, 11231.
- (45) Wei, Q.-H.; Argent, S. P.; Adams, H.; Ward, M. D. New J. Chem. 2008, 32, 73.
- (46) Argent, S. P.; Adams, H.; Harding, L. P.; Riis-Johannessen, T.; Jeffery, J. C.; Ward, M. D. New J. Chem. **2005**, *29*, 904.
- (47) Constable, E. C.; Housecroft, C. E.; Poleschak, I. Inorg. Chem. Commun. 1999, 2, 565.
- (48) Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schaffner, S.; Scherer, L. J. Dalton Trans. 2004, 2635.
- (49) Constable, E. C.; Handel, R. W.; Housecroft, C. E.; Farràn Morales, A.; Ventura, B.; Flamigni, L.; Barigelletti, F. *Chem.–Eur. J.* **2005**, *11*, 4024.
- (50) Constable, E. C.; Thompson, A. M. W. C.; Harveson, P.; Macko, L.; Zehnder, M. *Chem.-Eur. J.* **1995**, *1*, 360.
- (51) Tor, Y. Synlett 2002, 2002, 1043.
- (52) Connors, P. J.; Tzalis, D.; Dunnick, A. L.; Tor, Y. Z. Inorg. Chem. 1998, 37, 1121.
- (53) Tzalis, D.; Tor, Y. Angew. Chem., Int. Ed. Engl. 1997, 36, 2666.

- (54) Ali, A.; Hundal, G.; Gupta, R. *Cryst. Growth Des.* **2012**, *12*, 1308. (55) Kumar, G.; Aggarwal, H.; Gupta, R. *Cryst. Growth Des.* **2013**, *13*,
- 74.
- (56) Ali, A.; Bansal, D.; Gupta, R. J. J. Chem. Sci. 2014, 126, 1535.
- (57) Mishra, A.; Ali, A.; Upreti, S.; Gupta, R. Inorg. Chem. 2008, 47, 154.
- (58) Mishra, A.; Ali, A.; Upreti, S.; Whittingham, M. S.; Gupta, R. Inorg. Chem. 2009, 48, 5234.
- (59) Singh, A. P.; Gupta, R. Eur. J. Inorg. Chem. 2010, 2010, 4546.
- (60) Srivastava, S.; Ali, A.; Tyagi, A.; Gupta, R. Eur. J. Inorg. Chem. 2014, 2014, 2113.
- (61) Srivastava, S.; Dagur, M. S.; Ali, A.; Gupta. Dalton Trans. 2015, 44, 17453.
- (62) Singh, A. P.; Ali, A.; Gupta, R. Dalton Trans. 2010, 39, 8135.
- (63) Singh, A. P.; Kumar, G.; Gupta, R. Dalton Trans. 2011, 40,
- 12454. (64) Srivastava, S.; Dagur, M. S.; Gupta, R. Eur. J. Inorg. Chem. 2014,
- 2014, 4966. (65) Kumar, G.; Gupta, R. Inorg. Chem. Commun. 2012, 23, 103.
- (66) Kuman, G., Gupta, R. Inorg. Chem. Commun. 2012, 25, 105.
- (66) Kumar, G.; Kumar, G.; Gupta, R. Inorg. Chim. Acta 2015, 425, 260.
- (67) Bansal, D.; Hundal, G.; Gupta, R. Eur. J. Inorg. Chem. 2015, 2015, 1022.
- (68) Bansal, D.; Pandey, S.; Hundal, G.; Gupta, R. New J. Chem. 2015, 39, 9772.
- (69) Kumar, G.; Gupta, R. Inorg. Chem. 2012, 51, 5497.
- (70) Kumar, G.; Gupta, R. Inorg. Chem. 2013, 52, 10773.
- (71) Kumar, G.; Kumar, G.; Gupta, R. Inorg. Chem. 2015, 54, 2603.
- (72) Srivastava, S.; Aggarwal, H.; Gupta, R. Cryst. Growth Des. 2015, 15, 4110.
- (73) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. Purification of Laboratory Chemicals; Pergamon Press: Oxford, 1980.
- (74) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics **1996**, *15*, 1518.
- (75) CrysAlisPro, version 1.171.33.49b; Oxford Diffraction Ltd.: 2009.
  (76) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. J. Appl. Crystallogr. 1993, 26, 343.
- (77) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112.
- (78) Farrugia, L. J. WinGX version 1.70, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-Crystal X-ray Diffraction Data; Department of Chemistry, University of Glasgow: 2003.
- (79) Spek, A. L.; PLATON, A. *Multipurpose Crystallographic Tool*; Utrecht University: The Netherlands, 2002.
- (80) Blatov, V. A.; Shevchenko, A. P.; Serezhkin, V. N. J. Appl. Crystallogr. 2000, 33, 1193.
- (81) Blatov, V. A.; Shevchenko, A. P.; Proserpio, D. M. Cryst. Growth Des. 2014, 14, 3576.
- (82) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Mitina, T. G.; Blatov, V. A. Chem. Rev. 2014, 114, 7557.
- (83) Blatov, V. A.; O'Keeffe, M.; Proserpio, D. M. CrystEngComm 2010, 12, 44.
- (84) Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler,
- D. B.; O'Keeffe, M.; Yaghi, O. M. J. Am. Chem. Soc. 2001, 123, 8239. (85) Tranchemontagne, D. J.; Mendoza-Cortés, J. L.; O'Keeffe, M.;
- Yaghi, O. M. Chem. Soc. Rev. 2009, 38, 1257.
   (86) Shin, J. W.; Bae, J. M.; Kim, C.; Min, K. S. Inorg. Chem. 2013,
- (67) Setti, F., Baliza, A., Frontera, A., Massera, C., Gamez, F., Ghosh, A. CrystEngComm **2013**, 15, 3031.
- (88) Husain, A.; Ellwart, M.; Bourne, S. A.; Ohrstrom, L.; Oliver, C. L. *Cryst. Growth Des.* **2013**, *13*, 1526.
- (89) Gong, Y.; Hao, Z.; Sun, J. L.; Shi, H.-F.; Jiang, P.-G.; Lin, J.-H. Dalton Trans. 2013, 42, 13241.
- (90) Nasani, R.; Saha, M.; Mobin, S. M.; Martins, L. M. D. R. S.; Pombeiro, A. J. L.; Kirillov, A. M.; Mukhopadhyay, S. *Dalton Trans.* **2014**, *43*, 9944.

(91) D'Vries, R. F.; Iglesias, M.; Snejko, N.; Gutierrez-Puebla, E.; Monge, M. A. *Inorg. Chem.* **2012**, *51*, 11349.

(92) Roberts, J. M.; Fini, B. M.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T.; Scheidt, K. A. J. Am. Chem. Soc. **2012**, 134, 3334.

(93) Park, J.; Li, J. R.; Chen, Y. P.; Yu, J.; Yakovenko, A. A.; Wang, Z. U.; Sun, L. B.; Balbuena, P. B.; Zhou, H. C. *Chem. Commun.* **2012**, *48*,

9995.

(94) Freeman, F. Chem. Rev. 1980, 80, 329.

(95) Tietze, L. F. Chem. Rev. 1996, 96, 115.

(96) Lee, A.; Michrowska, A.; Sulzer-Mosse, S.; List, B. T. Angew. Chem., Int. Ed. 2011, 50, 1707.

(97) Wei, Y. D.; Zhang, S. G.; Yin, S. F.; Zhao, C.; Luo, S. L.; Au, C. T. Catal. Commun. **2011**, *12*, 1333.

(98) Ikeue, K.; Miyoshi, N.; Tanaka, T.; Machida, M. Catal. Lett. 2011, 141, 877.

(99) Brooks, A. C.; France, L.; Gayot, C.; Li, J.; Pui, H.; Sault, R.; Stafford, A.; Wallis, J. D.; Stockenhuber, M. J. Catal. **2012**, 285, 10.

(100) Peng, Y.; Wang, J. Y.; Long, J.; Liu, G. H. Catal. Commun. 2011, 15, 10.

(101) Postole, G.; Chowdhury, B.; Karmakar, B.; Pinki, K.; Banerji, J.; Auroux, A. J. Catal. **2010**, *269*, 110.

(102) Xu, D. Z.; Shi, S.; Wang, Y. RSC Adv. 2013, 3, 23075.

(103) Kalbasi, R. J.; Mosaddegh, N. Catal. Commun. 2011, 12, 1231.

(104) Merino, E.; Verde-Sesto, E.; Maya, E. M.; Iglesias, M.; Sanchez, F.; Corma, A. *Chem. Mater.* **2013**, *25*, 981.

(105) For a recent report of heterogeneous catalysis in water, see: Howlader, P.; Das, P.; Zangrando, E.; Mukherjee, P. S. J. Am. Chem. Soc. 2016, 138, 1668.

(106) With ethyl cyanoacetate, both "E" and "Z" isomers are possible. However, in our case, only "E" isomer was observed as frequently noted in the literature. See: Xu, D. Z.; Shi, S.; Wang, Y. RSC Adv. **2013**, *3*, 23075.

(107) Water as the solvent in a reaction of benzaldehyde with ethyl cyanoacetate, 1,3-cyclohexanedione, and malononitrile led to ca. 50, 45, and 70% of the respective product, respectively.

(108) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki, K.; Kinoshita, Y.; Kitagawa, S. J. Am. Chem. Soc. 2007, 129, 2607.